



PEK Homo and Copolymers via Dispersion Polymerisation

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Linacre College
University of Oxford
2015

A thesis submitted for the degree of
Doctor of Philosophy

Declaration

The work described in this thesis is entirely my own, except where I have either acknowledged help from a named source or given a reference to a published source or thesis. Text taken from another source will be enclosed in quotation marks and a reference given.

ABSTRACT

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This thesis is concerned with the development of the Ketonex dispersion process in order to reliably and reproducibly produce PEKK dispersions with controlled properties, together with the modification of pre-existing process parameters to achieve a range of particulate PAEK copolymers. Specific emphasis was placed on industrial considerations, pre-commercial scale-up and addressing potential materials applications.

Chapter 1 explores well established methods for the production of PAEKs by both nucleophilic and electrophilic routes. General materials properties are described, and structure-property relationships are discussed.

Chapter 2 describes in detail the process parameters associated with the Ketonex dispersion process. Parameters are discussed on a laboratory scale and are related to scale-up, industrial and commercial considerations.

Chapter 3 evaluates the production of PEKKs with a range of T:I ratios by the dispersion process. The PEKKs are analysed using a range of techniques and are compared to literature data for process evaluation.

Chapter 4 discusses the theory behind the action of the benzoic acid dispersant used in the dispersion process, which results in the production of fine particulate PEKK. A hypothesis involving the nucleation of polymerisation by aluminium benzoate is proposed.

Chapter 5 demonstrates how the dispersion process can be modified to produce a range of PAEK copolymers. The incorporation of imide and sulfone co-monomers are evaluated in detail, while a selection of alternative monomers undergo preliminary evaluation.

Chapter 6 addresses an epoxy toughening application. Amine end-capped PAEKs are produced by the dispersion process by *in situ* functionalisation. A protected end-capper is devised, its attachment and deprotection confirmed through a model compound approach and is successfully applied to the polymerisation system.

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Even if you lose sight of your Carrot, you must not give in. The memory of that Carrot will spur you on, to do what is right for you, what means the most to you, to excel.

CONTENTS

CONTENTS	i
ABBREVIATIONS	vii
NOMENCLATURE	xi
CHAPTER 1 : INTRODUCTION	1
1.1 Context of the project	1
1.2 Engineering polymers	2
1.3 The comparison of thermoplastic and thermoset polymers	3
1.4 General structures of and nomenclature for PAEKs	4
1.5 General properties of PAESs and PAEKs	5
1.6 Synthetic routes to PAESs and PAEKs	7
1.6.1 Nucleophilic synthetic routes	7
1.6.2 Electrophilic synthetic routes	9
1.6.2.1 Friedel-Crafts acylation	9
1.6.2.2 Friedel-Crafts polymerisation	10
1.6.2.3 Reported electrophilic synthetic routes	11
1.6.2.4 Modified Friedel-Crafts synthesis	15
1.7 Modifications to PAES and PAEK structures	19
1.8 Alternative routes to PAEKs	19
1.8.1 Ring-opening polymerisation	19
1.8.2 Soluble precursor approach	20
1.9 Project aims	21
1.10 References	21
CHAPTER 2 : EVALUATION OF DISPERSION PROCESS PARAMETERS	24
2.1 Background to the dispersion process	24

2.2	The dispersion polymerisation of PEKK.....	24
2.3	Process parameters	25
2.3.1	Evolution of molecular weight	26
2.3.2	Monomer purity	28
2.3.3	Order of addition of reactants	30
2.3.4	Reaction temperature	32
2.3.5	Solvent	33
2.3.6	Benzoic acid concentration.....	34
2.3.7	Reactor loading.....	37
2.3.7.1	Reactor loading study.....	39
2.3.8	Polymer workup	41
2.3.9	Drying of the polymer	43
2.3.10	Scale-up	44
2.3.10.1	Reactor and stirrer design.....	44
2.3.10.2	Scale-up study	49
2.3.10.3	Commercial scale-up considerations.....	52
2.3.11	Recycling of reagents	53
2.3.11.1	Mass balance calculation.....	56
2.4	Additional parameters.....	57
2.5	Industrial implications of the dispersion process parameters	57
2.6	References	59
CHAPTER 3 : PEKK SYNTHESIS EVALUATION		60
3.1	Synthetic evaluation requirements.....	60
3.2	PEKK polymer synthesis.....	60
3.3	Polymer structure confirmation	61
3.3.1	DPE synthesis vs EKKE synthesis	61

3.3.2	Monomer reactivity ratios	62
3.3.3	Determination of polymer structure by NMR spectroscopy	64
3.4	Thermal properties.....	67
3.5	Polymer processability	71
3.5.1	Molecular weight determination by inherent viscosity measurements	71
3.5.2	Polymer melt rheology and thermal stability	72
3.6	Polymer morphology	75
3.6.1	Particle size.....	75
3.6.2	Particle shape.....	76
3.7	Crystallinity and mechanical strength	79
3.8	Summary.....	80
3.9	References	81
CHAPTER 4 : THE ROLE OF BENZOIC ACID IN THE DISPERSION PROCESS		82
4.1	Benzoic acid in the dispersion process	82
4.2	Controlling agents.....	83
4.2.1	Known controlling agents.....	83
4.2.2	Screening of alternative dispersants	88
4.3	Aluminium chloride morphology	89
4.4	Observation of crystal formation.....	90
4.4.1	Isolation of the aluminium complex.....	91
4.4.2	Anhydrous isolation of the aluminium complex	93
4.5	Order of addition of reactants	97
4.6	Introduction of additives.....	100
4.7	Overall theory of the action of benzoic acid.....	104
4.8	References	113
CHAPTER 5 : PAEK COPOLYMERS.....		115

5.1 PAEK copolymers	115
5.2 Functional group incorporation	115
5.3 Poly(ether ketone ether ketone ketone) (PEKEKK)	119
5.4 Imide copolymers	122
5.5 Sulfone copolymers	127
5.6 Branched PEKK	132
5.7 Incorporation of additional functionality.....	137
5.7.1 Aliphatic copolymers.....	137
5.7.2 Naphthalene copolymers	140
5.7.3 Biphenyl imide copolymers.....	142
5.8 Summary.....	145
5.9 References	146
CHAPTER 6 : SYNTHESIS OF AMINE FUNCTIONALISED PAEKs	147
6.1 Background.....	147
6.2 Model compound approach	150
6.2.1 Direct end-capping	150
6.2.2 Synthesis of acetyl and trifluoroacetyl end-cappers	152
6.2.3 Hydrolysis of acetyl and fluoroacetyl end-cappers	153
6.2.4 Synthesis of linear model compounds	154
6.2.5 Deprotection of linear model compounds	155
6.2.6 Trifunctional model compounds.....	156
6.3 Amine end-capped PAEKs	158
6.3.1 Trial synthesis of amine end-capped PEKK.....	158
6.3.2 Large scale synthesis of amine end-capped PAEKs.....	159
6.3.2.1 Confirmation of amine end-capping	159
6.3.2.2 Bulk polymer properties.....	161

6.4	Fracture toughness and mechanical strength	165
6.5	Summary.....	166
6.6	References	167
CHAPTER 7 : SUMMARY AND FUTURE WORK.....		168
7.1	Summary.....	168
7.2	Future work.....	170
CHAPTER 8 : EXPERIMENTAL		172
8.1	Analytical techniques	172
8.2	Materials	175
8.3	General procedures	178
8.3.1	Calculations	179
8.3.2	General small scale polymerisation procedure	179
8.3.3	General polymerisation procedure for one litre reactor.....	180
8.3.4	General polymerisation procedure for five litre reactor	183
8.3.5	General decomplexation procedure	183
8.3.6	General decomplexation procedure for the dispersion process	183
8.3.7	General decomplexation procedure for the gel process.....	184
8.3.8	General workup procedure	184
8.3.9	General drying procedure	185
8.4	Experimental for Chapter 2	185
8.4.1	Reactor loading.....	185
8.4.2	Benzoic acid concentration.....	186
8.4.3	Scale-up	187
8.4.4	Recycling of reagents	187
8.5	Experimental for Chapter 3	188
8.5.1	Monomer characterisation	188

8.5.2	PEKK polymerisation.....	189
8.6	Experimental for Chapter 4	189
8.6.1	Controlling agents.....	189
8.6.2	Aluminium chloride morphology	191
8.6.3	Observation of crystal formation.....	192
8.6.4	Anhydrous isolation of the aluminium benzoate complex	192
8.6.5	Order of addition of reactants	193
8.6.6	Introduction of additives.....	196
8.7	Experimental for Chapter 5	198
8.7.1	Monomer characterisation	198
8.7.2	Copolymer synthesis.....	202
8.8	Experimental for Chapter 6	209
8.8.1	Attempted direct end-capping	209
8.8.2	End-capper synthesis	210
8.8.3	End-capper deprotection.....	213
8.8.4	Linear model compound synthesis	214
8.8.5	Linear model compound deprotection.....	216
8.8.6	Trifunctional model compound synthesis.....	217
8.8.7	Trifunctional model deprotection	219
8.8.8	Small scale polymer synthesis	219
8.8.9	Large scale polymer synthesis	220
8.9	References	220
APPENDIX : X-RAY CRYSTAL STRUCTURE DATA		a

ABBREVIATIONS

ALM	additive layer manufacturing
Ar	aryl
BzO	benzoate
COSY	2D ¹ H correlation spectroscopy
D(0.1)	particle diameter where 10 % of the distribution is below this value
D(0.5)	particle diameter where 50 % of the distribution is below this value
D(0.9)	particle diameter where 90 % of the distribution is below this value
DCM	dichloromethane
DEPT	distortionless enhancement by polarisation transfer
DSC	differential scanning calorimetry
EC-A	<i>N</i> -(4-phenoxyphenyl)acetamide
EC-F	2,2,2-trifluoro- <i>N</i> -(4-phenoxyphenyl)acetamide
EI	electron impact ionisation
EI-IE	2,2'-bis(4-phenoxyphenyl)-[5,5'-biisoindoline]-1,1',3,3'-tetraone
EIEIE	5,5'-oxybis(2-(4-phenoxyphenyl)isoindoline-1,3-dione)
EK10KE	1,12-bis(4-phenoxyphenyl)dodecane-1,12-dione
EKE	bis(4-phenoxyphenyl)methanone
1,3- EKKE	1,3-bis(4-phenoxybenzoyl)benzene
1,4- EKKE	1,4-bis(4-phenoxybenzoyl)benzene
EKNKE	naphthalene-2,6-diylbis((4-phenoxyphenyl)methanone)
eq.	equivalents
ESE	1,1'-sulfonylbis(4-phenoxybenzene)
ESI	electrospray ionisation
FDM	fused deposition modelling

FI	field ionisation
FT-IR	Fourier transform-infra red spectrometry
G'	storage modulus (elastic modulus)
G''	loss modulus (viscous modulus)
G_{IIC}	fracture toughness
HRMS	high resolution mass spectroscopy
HSQC	heteronuclear single quantum correlation
IPA	isopropyl alcohol
IPC	isophthaloyl dichloride
IPC-EC	<i>N,N'</i> -(((isophthaloylbis(3,1-phenylene))bis(oxy)bis(4,1-phenylene)) bis(2,2,2-trifluoroacetamide)
IPC-EC-D	1,3-phenylenebis((3-(4-aminophenoxy)phenyl)methanone
IR	infra red
IV	inherent viscosity
J	coupling constant
L	litres
Lit.	literature
M_n	number average molecular weight
mol	moles
mp	melting point
M_v	viscosity average molecular weight
m/z	mass/charge ratio
NMR	nuclear magnetic resonance
PAEK	polyaryletherketone
PAES	polyarylethersulfone
PEEK	poly(ether ether ketone)

PEEKK	poly(ether ether ketone ketone)
PEK	poly(ether ketone)
PEKEKK	poly(ether ketone ether ketone ketone)
PEKK	poly(ether ketone ketone)
PES	poly(ether sulfone)
Ph	phenyl
ppm	parts per million
rpm	rotations per minute
SEM	scanning electron microscopy
SLS	selective laser sintering
$\tan \delta$	phase angle
T_c	crystallisation temperature
TFA	trifluoroacetic acid
T_g	glass transition temperature
T_m	melting temperature
TPC	terephthaloyl dichloride
TPC-EC	2,2,2-trifluoro- <i>N</i> -(4-(3-(4-(4-(4-(2,2,2-trifluoroacetamido)phenoxy)benzoyl)benzoyl) phenoxy)phenyl)acetamide
TPC-EC-D	(4-(3-(4-aminophenoxy)benzoyl)phenyl)(4-(4-aminophenoxy)phenyl) methanone
TRI	1,3,5- benzenetricarbonyl chloride
TRI-EC	<i>N,N',N''</i> -(((benzene-1,3,5-tricarbonyl)tris(benzene-4,1-diyl))tris(oxy)) tris(benzene-4,1-diyl))tris(2,2,2-trifluoroacetamide)
TRI-EC-D	benzene-1,3,5-triyltris((4-(4-aminophenoxy)phenyl)methanone)
TRI-TOL	benzene-1,3,5-triyltris(<i>p</i> -tolylmethanone)
UV-vis	ultraviolet- visible

\bar{X}_n	number average degree of polymerisation
XPS	x-ray photoelectron spectroscopy
XRD	x-ray diffraction
δ_{Al}	^{27}Al chemical shift
δ_C	^{13}C chemical shift
δ_F	^{19}F chemical shift
δ_H	1H chemical shift
η^*	complex viscosity
λ_{max}	wavelength of maximum absorbance
ν_{max}	absorption maximum

NOMENCLATURE

The following nomenclature has been used throughout this thesis.

Monomer and polymer nomenclature

Monomers and polymers are referred to by their constituent functionalities, where E represents ether, K ketone, S sulfone, I imide and N naphthalene. Each of these groups are alternated with phenylene. A hyphen indicates a direct C-C bond, *e.g.* in EI-IE, and no phenylene groups are present between the imide and the direct C-C bond. A number indicates the length of an aliphatic chain, *e.g.* a 10 carbon chain in EK10KE. No phenylene groups are present between the ketone and the aliphatic chain.

Polymers are prefixed by P, and use the same nomenclature as the monomers.

Aromatic ring substitution

The introduction of terephthaloyl dichloride into the polymer results in *1,4-* links, referred to as T links. The introduction of isophthaloyl dichloride into the polymer results in *1,3-* links, referred to as I links.

1,4- or *para-* aromatic substitution is referred to as T (*tere-*).

1,3- or *meta-* aromatic substitution is referred to as I (*iso-*).

T:I ratios

T:I ratios are the ratios of TPC:IPC in the monomer feed or T:I links in the polymer backbone.

Out-of-balance

Out-of-balance is used to refer to the stoichiometric imbalance of arene to diacid chloride monomers in a monomer feed. For example, a 3 % stoichiometric imbalance is referred to as 3 % out of balance. Unless otherwise stated, the arene monomer is in excess.

Benzoic acid equivalents

The number of benzoic acid equivalents is the number of stoichiometric equivalents of benzoic acid which is added to a dispersion polymerisation compared to that of the total acid chloride.

CHAPTER 1 : INTRODUCTION

1.1 Context of the project

This project was carried out under an Industrial Fellowship of the Royal Commission for the Exhibition of 1851. This Fellowship is intended to promote and develop British industry, and requires that doctoral research is carried out at the facilities of, and to the benefit of, a company in collaboration with a university. This project was carried out at Ketonex Ltd, a micro-SME (small and medium sized enterprise) which specialises in the custom design and synthesis of high performance engineering thermoplastics, in conjunction with the University of Oxford. The project was designed to enhance foundation knowledge and to facilitate research into areas which would not otherwise have been financially viable, thereby providing maximum intellectual property benefit to Ketonex. This arrangement resulted in a doctoral project with heavy industrial focus.

The research was based on the patented Ketonex dispersion polymerisation process, to produce high performance engineering thermoplastics in the form of a fine, particulate dispersion rather than the normal flake. All of the materials were based on the polyaryletherketone platform.

From an applied point of view, the aims of the project were to verify the critical synthetic parameters, and to increase the scope of the materials which could be produced. This would result in materials to address a wider range of applications and sectors. The additional contribution was aimed to study the fundamental intricacies of the mechanism behind the process and to strengthen the intellectual property position of Ketonex. This would not have been possible with work done solely internally within Ketonex.

The research has generated a large amount of intellectual property, together with a selection of published outputs. These include,

- 5 patent applications
- 3 academic papers, in production
- A chapter in “Encyclopaedia of Polymeric Nanomaterials”, Springer
- A poster presented at MACRO2014 which received a poster prize.

The publication of journal papers has been delayed due to patent filing restrictions, but they are currently in production. In addition, the project has resulted in an evaluation licence agreement with a major global PAEK producer, and the generation of significant revenues.

1.2 Engineering polymers

The evolution of polymer chemistry has allowed new materials to replace traditional materials and to be integrated into emerging applications. One of these areas is high performance engineering, where more common engineering polymers such as polycarbonate have been thermally and mechanically outperformed by polymers such as polyaryletherketones (PAEKs), polyarylethersulfones (PAESs) and polyetherimides. These specialist polymers are produced on a comparatively small scale and at higher cost compared to commodity polymers such as polyethylene and polypropylene. However, their significant advantages and attractive properties outweigh the expense for certain applications.

The polymer performance pyramid¹, Figure 1.1, highlights these trends for a range of both amorphous and semi-crystalline polymers. The bottom of the pyramid represents low cost, commodity polymers which are produced in large quantities. Moving up the pyramid, the production quantity decreases and the cost increases. The peak of the pyramid represents high cost, high performance polymers which are produced in small quantities.

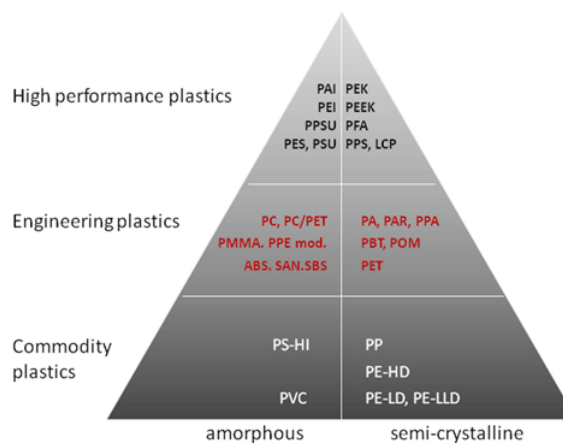


Figure 1.1 The polymer performance pyramid divided into commodity polymers, engineering polymers, and high - performance polymers with prominent examples: PS (HI): polystyrene (high -impact); PVC: polyvinyl chloride; PE (LD, LLD, HD): polyethylene (low- density, linear low density, high -density); ABS: acrylonitrile-butadiene-styrene copolymer; PP: polypropylene; PMMA: poly(methyl methacrylate); SAN: styrene-acrylonitrile copolymer; POM: poly(oxymethylene); PA: polyamide; PC: polycarbonate; PPE: poly(phenylene ether); PBT: poly(butylene terephthalate) ; PET: poly(ethylene terephthalate) ; SBS styrene-butadiene-styrene block copolymer; PAR: polyaramide ; PPA: polyphthalamide; PES: poly(ether sulfone) ; PSU: polysulfone; PPS: poly(phenylene sulfide); PPSU: polyphenyl sulfone; PFA: perfluoroalkoxy copolymer; LCP: liquid crystalline polymer; PEI: polyether imide ; PEEK: poly(ether ether ketone); PAI: poly(amide imide); PEK: poly(ether ketone). Image reproduced from ¹

High performance engineering polymers exhibit a range of attractive properties such as mechanical strength, high use temperature, thermal, chemical and radiation resistance, fire retardancy and low smoke emission. They are therefore suitable for advanced applications involving extreme environments, in fields such as medical devices, aerospace engineering and industrial manufacturing². PAEKs and PAESs are related classes of high performance polymers. Poly(ether ether ketone) (PEEK) is the most well-known polymer in this family and has a tensile strength of 98 MPa and a tensile modulus of 4 GPa³. Thermal properties of PAEKs are discussed later in this chapter. A variety of other related high performance materials are also commercially available from a range of suppliers.

1.3 The comparison of thermoplastic and thermoset polymers

PAEKs and PAESs are examples of high performance thermoplastic polymers which offer advantages over the other family of commonly used polymers, thermosets⁴. Thermoset products are generated by the moulding of branched oligomeric material into the desired

shape, which is then cured using heat or a catalyst to create a chemically crosslinked polymeric structure, for example, the thermal curing of epoxy resins. This type of curing is discussed further in Chapter 6. Alternatively, a linear polymeric material with functional groups along the chains is moulded as required. The chains are then chemically crosslinked by the direct reaction between functional groups on neighbouring chains, or by the addition of a linking molecule between functional groups, for example in the vulcanisation of rubber. Thermosets have the advantage of having very robust structures, however, the main disadvantage is that once cured, they cannot be remoulded or recycled.

In comparison, thermoplastic polymers are linear, long chain molecules whose conformations are set at low temperature by intermolecular interactions. However, at higher temperatures approximately the melting temperature (T_m) for semi-crystalline polymers, the polymer chains can reorientate and the polymer can flow. Cooling then sets the polymer in the desired shape. No T_m is observed for amorphous polymers but they may be processed in the same manner. This allows the polymer to be heated, moulded and cooled to produce the desired shape by, for example, injection moulding or extrusion. Since no chemical reaction takes place and the polymer chains are never entirely fixed, theoretically these cycles may be repeated multiple times without affecting the overall properties of the material. In practice, some degree of degradation is likely to occur. This characteristic makes thermoplastics of great interest due to waste reduction and recycling capability. PAEKs and PAESs are focused on in the following discussion.

1.4 General structures of and nomenclature for PAEKs

PAEKs and PAESs are formed of aromatic subunits linked by ether and ketone groups or ether and sulfone groups respectively. Most commonly, the aromatic portions comprise phenylene groups but other substituted or unsubstituted aromatic moieties may be

incorporated. The aromatic units in one chain may be all the same or different, for example, phenylene only or a mixture of phenylene and biphenylene. The typical nomenclature for PAESs and PAEKs is to refer to a phenylene-ether unit as “E”, a phenylene-ketone unit as “K” and a phenylene-sulfone unit as “S”. In this way, the polymer is represented by the constituents of the repeat unit. For example, poly(ether ether ketone) or “PEEK” has a repeat unit of $-\text{[Ph} - \underline{\text{E}}\text{ther} - \text{Ph} - \underline{\text{E}}\text{ther} - \text{Ph} - \underline{\text{K}}\text{etone]} -$, where Ph represents phenylene.

1.5 General properties of PAESs and PAEKs

PAESs are aromatic polymers which exhibit high glass transition temperatures (T_g). Poly(ether sulfone) (PES) has a T_g of 224 °C, Table 1.1. Electronegativity of the oxygen atoms in the sulfone group promotes delocalisation across the group^{5,6}. The associated resonance structures, Figure 1.2, increase S-C chain rigidity due to the double bond character, increasing T_g . The 1,3- version exhibits a lower T_g than the 1,4- version since only two resonance structures are possible which results in a greater chain flexibility.

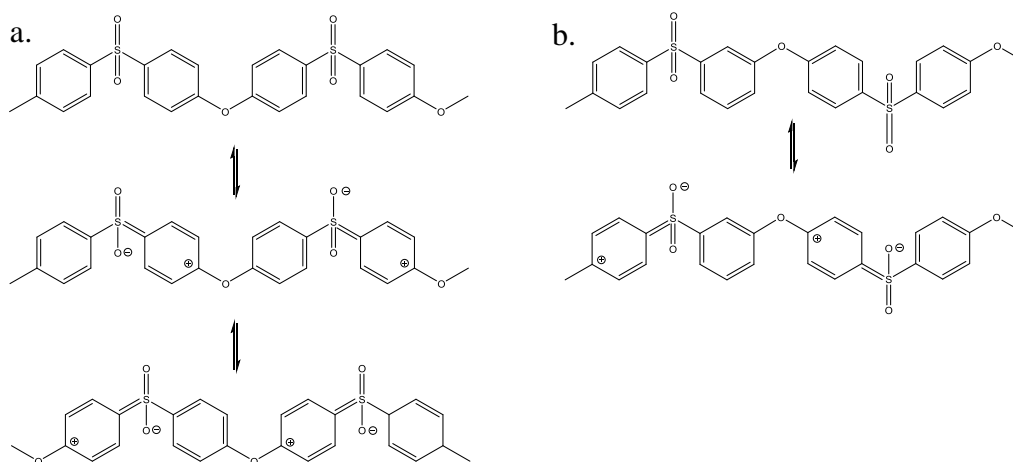


Figure 1.2 Resonance structures of PES a. 1,4- version b. 1,3- version⁵

Flexible ether linkages are incorporated to decrease the chain rigidity and maintain processability. This property is in contrast to poly(phenylene sulfone) which is so rigid that it does not exhibit a T_g before its decomposition temperature⁴. The steric arrangement of the

bulky tetrahedral sulfone group restricts the packing ability of the polymer chain, reducing the degree of crystallinity and therefore decreasing the T_m . Due to this effect, PAESs are often amorphous, although semi-crystalline PES is induced by some solvents such as dichloromethane, and by copolymerisation with crystallising co-monomers. Unlike PAEKs which may be semi-crystalline, this amorphous character excludes PAESs from applications requiring solvent resistance. PAESs are prone to stress crazing in the presence of solvents, which is a precursor to stress cracking and material failure. PES can be produced by both nucleophilic and electrophilic routes.

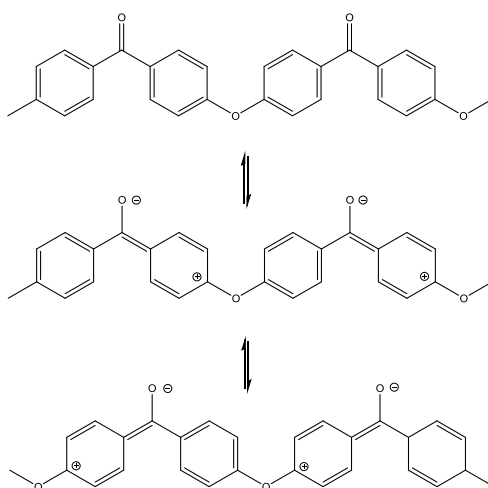


Figure 1.3 Resonance structures of PEK

PAEKs are similar in structure to PAESs but instead have ether and ketone functionality between the aromatic subunits. As with PAESs, in addition to the high performance properties, the attraction of the PAEK family is the combination of high T_g s combined with comparatively low T_m s. This combination allows the polymers to be easily processed whilst maintaining high use temperatures. As Table 1.1 demonstrates, increasing the ratio of ketone groups compared to ether groups acts to increase both the T_g and T_m values^{2,7}. Similar to PES, the incorporation of ketones increases the rigidity of the polymer chain due to the possible resonance structures along the chain, Figure 1.3. However, unlike PAESs, the geometry of the ketone allows the successful formation of crystalline domains. Whilst the Ph-SO₂-Ph bond

angle is 105° ⁸, both Ph-O-Ph bond angle and the Ph-CO-Ph bond angles are 124° ⁹, resulting in efficient packing. The greater percentage crystallinity (of a maximum of 30 - 35% for PAEKs⁷) increases the T_m and imparts solvent resistance, widening the market for potential applications. As with PAESs, PAEKs can also be produced by both nucleophilic and electrophilic routes.

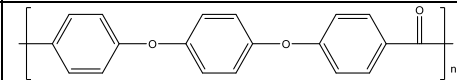
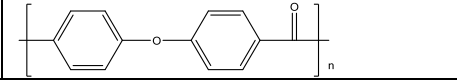
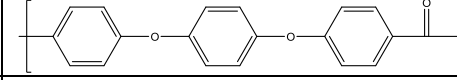
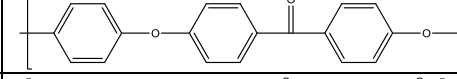
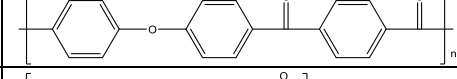
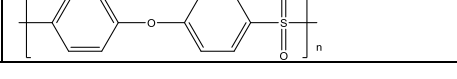
Polymer	Structure	$T_g/^\circ\text{C}$	$T_m/^\circ\text{C}$
PEEK ¹⁰		143	334
PEK ⁸		154	367
PEEKK ¹⁰		158	363
PEKEKK ¹⁰		161	377
PEKK ¹⁰		165	386
PES ²		224	-

Table 1.1 Structures, crystalline glass transition temperatures (T_g) and melting temperatures (T_m) for common poly(aryl ether ketone)s and poly(ether sulfone) each with all 1,4- conformation, adapted from^{2,7}

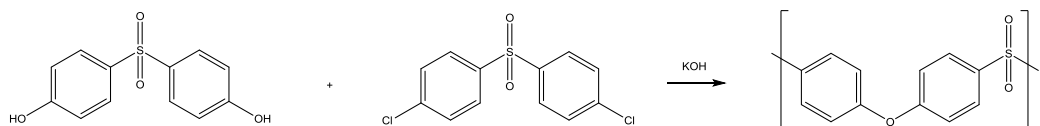
1.6 Synthetic routes to PAESs and PAEKs

There are a wide variety of accepted methods for the synthesis of PAESs and PAEKs, many being developed by the several industrial contenders in the development of PES and PAEKs during the 1960s – 1980s. Generally, they may be split into nucleophilic and electrophilic routes, each having their own advantages and limitations.

1.6.1 Nucleophilic synthetic routes

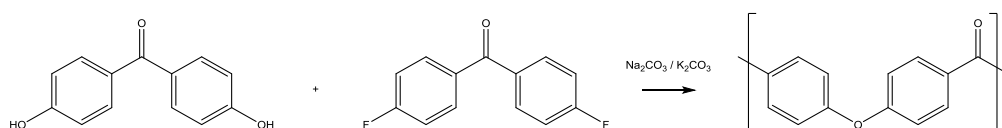
The nucleophilic synthetic route to PAESs and PAEKs proceeds by forming the ether link. For the formation of PAESs, this usually requires the use of dihydroxy- and di-halogenated sulfone-containing monomers¹¹, exemplified in Scheme 1.1. The dihydroxy- monomer is converted to the bis-phenolate in the presence of alkali metal salts such as potassium

hydroxide prior to polymerisation. Due to the electronegativity of the sulfone, the ring is activated and the chloride is easily displaced. Based on this system, a range of other monomers may be used to produce polymers with modified properties⁵. For example, the incorporation of a diphenyl moiety increases the T_g substantially. A self-polymerisation route is achieved using the difunctional monomer 4-hydroxy-4'-chlorophenyl sulfone.



Scheme 1.1 The nucleophilic synthesis of poly(ether sulfone)

The PAES nucleophilic synthetic technology is partially transferable to PAEKs. However, under the same reaction conditions, high molecular weight PAEKs are unachievable. Reactions using the 4,4'-dichlorobenzophenone monomer are unsuccessful⁵, therefore requiring the use of fluorine-containing monomers, such as 4,4'-difluorobenzophenone⁸, which have greater reactivity on the adjacent carbon due to the higher electronegativity of the fluorine. The use of an alkali metal carbonate or dicarbonate promotes the reaction between hydroquinone and 4,4'-difluorobenzophenone¹², Scheme 1.2. A mixture of sodium carbonate and potassium carbonate at 320 °C in diphenyl sulfone yielded high molecular weight, tough and thermally stable PEK. The alkali metal carbonates were used in place of potassium hydroxide as they are more stable and are not hygroscopic. The carbonates decompose to the hydroxide at high temperature, and so have the same action.



Scheme 1.2 The nucleophilic synthesis of poly(ether ketone)

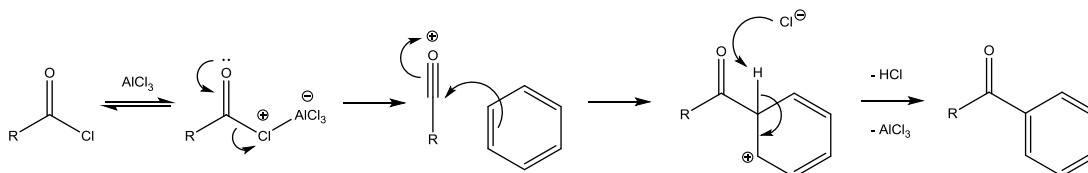
Whilst the nucleophilic process can be used to produce high quality product, a major disadvantage is the requirement for a metal salt to deprotonate the monomers. Residual metal

salts are extremely detrimental to the polymer melt stability¹³ and so a very efficient post-polymerisation removal procedure is required. In addition, the high reaction temperature can lead to side reactions and crosslinking.

1.6.2 Electrophilic synthetic routes

1.6.2.1 Friedel-Crafts acylation

The basis behind the electrophilic routes for the production of PAESs and PAEKs is the Friedel-Crafts acylation reaction^{14,15}. Friedel-Crafts acylation is an electrophilic aromatic substitution (S_{EAr}) reaction, typically between an alkyl halide and an electron rich arene, resulting in the formation of an aromatic ketone. The reaction is catalysed by a Lewis acid, often aluminium chloride. The S_{EAr} reaction mechanism¹⁴ is illustrated in Scheme 1.3.



Scheme 1.3 A reaction scheme for the Friedel-Crafts acylation of an arene, adapted from¹⁴

The aluminium chloride complexes to the chlorine atom on the acid chloride, abstracts the chloride and results in the formation of a stable acylium ion. The acylium ion undergoes nucleophilic attack by the benzene ring to produce an aromatic ketone, eliminating a molecule of HCl. The benzene molecule or other arene must be activated to electrophilic attack to ensure successful reaction. Although the aluminium chloride catalyst is regenerated, it is also consumed by complexation with both reactant and product carbonyl groups. Therefore, the catalytic aluminium chloride must be supplemented by a stoichiometric quantity equal to that of the total carbonyl content in order to achieve a successful reaction. The R group may comprise many possible functionalities, providing that an acylium ion can be formed. Monosubstitution sufficiently deactivates the aromatic ring to further substitution due to the

electron withdrawing capabilities of the acyl group. This mechanism is adapted to form a sulfone by the reaction of a sulfonyl chloride *via* a sulfonylium ion.

1.6.2.2 Friedel-Crafts polymerisation

The small molecule Friedel-Crafts acylation reaction may be adapted to a Friedel-Crafts condensation polymerisation¹⁶⁻¹⁸. In this case, difunctional monomers are required for the reaction between a sulfonyl chloride or a carboxylic acid chloride and an arene, resulting in the formation of an aromatic sulfone or an aromatic ketone respectively. The reaction is catalysed by a Lewis acid, commonly AlCl_3 for PAEKs, or FeCl_3 for PAESs.

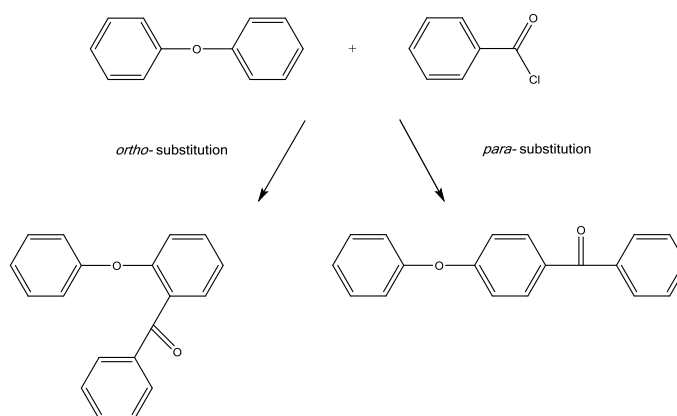


Figure 1.4 *Ortho*- and *para*- substitution occurring during Friedel-Crafts acylation reactions to produce an aromatic “EK” entity, illustrated by the reaction between diphenyl ether and benzoyl chloride in equal stoichiometry

A model for Friedel-Crafts polymerisation is the acylation reaction between diphenyl ether and benzoyl chloride, Figure 1.4. During this reaction, both the *ortho*- and the *para*-positions of the diphenyl ether aromatic ring are activated to substitution due to the electron donating oxygen atom attached to the ring. Activation is less pronounced for the *ortho*- position compared to the *para*- position, but some *ortho*- substitution does occur. The ratio of products formed depends on the temperature of reaction¹⁴, but there is little control. When this principle is extended to a polymerisation by the substitution of benzoyl chloride with a diacyl chloride for example TPC, both substitutions are still viable. The orientation of the product

molecule caused by *ortho*- substitution increases the likelihood of cyclisation and gelation reactions, as discussed in Chapter 2. In this case, the terminal phenylene groups are in much closer proximity, increasing the likelihood of intramolecular reactions. Even in small quantities, this is detrimental to the melt stability of the product. *Para*- substitution resulting in a straight chain product is desired. In the case of polymerisations, *ortho*- substitution is disfavoured due to steric hindrance.

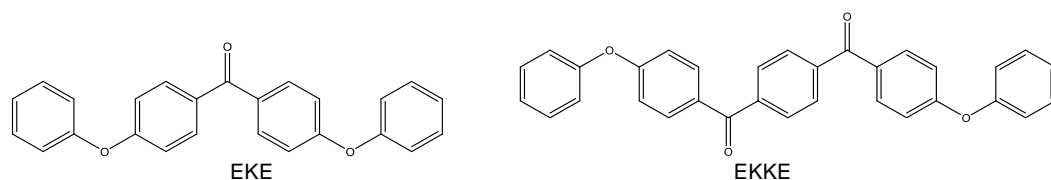
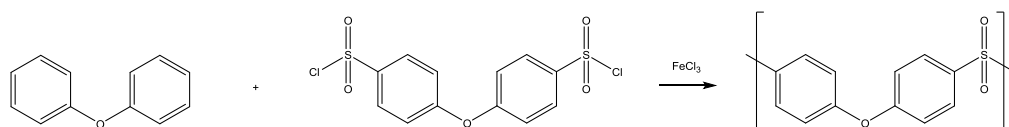


Figure 1.5 The structures of EKE (1,4'-diphenoxybenzophenone) and EKKE (1,4'-bis(4-phenoxybenzoyl)benzene)

Replacing the diphenyl ether with a ketone-containing monomer such as 1,4'-diphenoxybenzophenone (EKE) or 1,4'-bis(4-phenoxybenzoyl)benzene (EKKE)¹⁹ decreases the overall reactivity of the monomer and increases the selectivity of substitution. The ketone is close enough to have an electron withdrawing effect on the terminal arene. The ketones deactivate both the *ortho*- and *para*- positions of the terminal aromatic rings to electrophilic attack, but do not entirely inhibit the reaction. The *ortho*- deactivation virtually eliminates substitution, but *para*- activation is maintained. This effect may be achieved if the ketone is replaced by other electron withdrawing groups, for example sulfone.

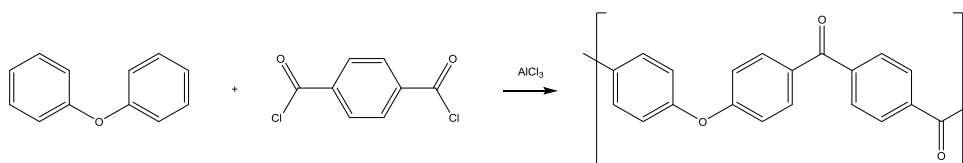
1.6.2.3 Reported electrophilic synthetic routes

The electrophilic synthesis of PAESs offers a route using cheaper monomers and lower reaction temperatures than the nucleophilic route. The polymerisation requires the use of phenoxyaroyl and phenoxyarenesulfonyl halide monomers, together with a Friedel-Crafts catalyst such as FeCl_3 ²⁰, exemplified in Scheme 1.4.



Scheme 1.4 The electrophilic synthesis of poly(ether sulfone)

In the early 1960s it became apparent that PAEKs had potential commercial interest. Industrial research emerged, with patents registered by DuPont and ICI. In 1962, Bonner²¹ at DuPont reported a Friedel-Crafts synthesis to produce PAEKs. PEKK was produced by the condensation of diphenyl ether and isophthaloyl chloride (IPC) at 65 °C in nitrobenzene, in the presence of an aluminium chloride catalyst, Scheme 1.5. Despite producing predominantly linear PEK using a relatively cheap and simple process, the low molecular weight polymers, with inherent viscosities (IVs) of approximately 0.15 dL.g⁻¹, were unstable and unsuitable for industrial processing. A competing process was reported by Goodman²² of ICI in 1964, which for the first time produced PEKs of higher molecular weight and increased viscosity. For example, PEKK with an IV of 1.6 dL.g⁻¹ was produced using the same monomers in dichloromethane at room temperature which could be processed into high strength fibres and films.



Scheme 1.5 The electrophilic synthesis of poly(ether ketone ketone)

Since the PAEK produced is semi-crystalline unlike PES, it can be problematic to maintain the oligomers in solution long enough to produce high molecular weight polymer. A wide variety of methods have been attempted to combat this issue. In 1969, Marks²⁰ of DuPont reported a process to produce PAEKs and PAESs using a mixed HF/BF₃ Friedel-Crafts mixture, where HF was the solvent and BF₃ the catalyst. Suitable monomers for the condensation reaction were aromatic acyl chlorides including *p*-phenoxybenzoyl chloride.

The monomers were added at low temperature and the reaction increased 50 °C. The polymers produced had high molecular weight, yet were melt processable since they had low melt viscosity. They also had excellent thermal, oxidation and hydrolytic stability. Dahl of Raychem also disclosed process based on the HF/BF₃ system to produce PEK²³ and PAEKs containing biphenyl units²⁴. These polymers were formed by the reaction of 1,4-diphenoxybenzene and TPC with a 4-phenoxybenzophenone capping agent and of *p*-(biphenyloxybenzoyl chloride) with a biphenyl capping agent respectively. The monomers were added to anhydrous hydrogen fluoride at subzero temperatures. The vessel was charged with boron trifluoride gas to 50 psi, then allowed to warm to room temperature whilst stirring for 6 hours. The PEKs produced were thermally stable and stable to compression moulding. Despite these advantages in product quality, these polymerisation systems used particularly corrosive reagents and required a pressure vessel and expensive monomers rendering it not viable for an industrial process.

In 1983, Rose²⁵ of ICI reported a process to produce PEKK and PEKEKK in trifluoromethanesulfonic acid with phosphorous pentachloride. Condensation reactions occurred between dicarboxylic acid and activated aromatic monomers at moderate temperatures, 50 – 150 °C. It is thought that the reaction proceeds via the *in situ* formation of diacyl chlorides. This process was developed to avoid the need for a pressurised system and expensive starting materials. However, at the time trifluoromethanesulfonic acid was extremely expensive and the acidic system produced polymers which were too viscous to be easily processable.

Another potential solution to avoid intractability was proposed by Reamey²⁶ of Raychem. The introduction of pressurised HCl into the system which condenses into the reaction mixture causes the formation of a polymer in the form of a liquid or tractable gel. It was suggested that

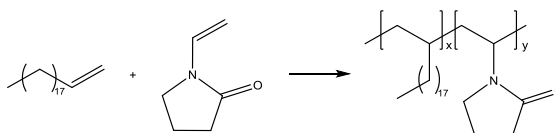
the HCl disrupts any complex formation that occurs between the aluminium chloride and the ketone groups on different chains. If HCl is introduced at the start, the product is a viscous liquid. However, if it is introduced once gelation has occurred, the gel becomes more tractable. Overall, this allows easier removal of the product from the reaction vessel and more efficient purification. However, expensive pressurised equipment is required.

Solution polymerisations are often favoured over bulk polymerisations for industrial processes as they allow greater control over the synthetic parameters¹⁸. Dissipation of the heat of polymerisation by the solvent allows better control of the process. Also, more efficient stirring due to the reduced viscosity of the mixture by the solvent gives a better distribution and disrupts heat spots. This cannot easily be achieved with bulk polymerisations due to the large viscosity increase on polymerisation. A solution process allows for easier removal of the product from the reaction vessel. However, it must be ensured that the solvent of choice does not participate in the polymerisation reaction. For these reasons, several options for the solution synthesis of PAEKs have been considered.

Gander et al.²⁷ disclosed a process to produce PEKK in a granular form, achieved by pouring the polymerisation mixture, pre-gelation, into an excess of heated, higher boiling point and vigorously stirred solvent. The patent suggests that the fluid maintains separation of the polymer particles in the initial mixture whilst the high temperature ends the reaction quickly. The resultant dispersion can be decomplexed and purified more efficiently which gives better melt stability. However, the high temperature of the fluid increases the likelihood of undesirable side reactions.

In 1998, Daniels²⁸ of Victrex reported a dispersion process using polymeric dispersants to produce PAEKs. PEKK is produced by a high temperature electrophilic process in the

presence of aluminium chloride in 1,2-dichlorobenzene. It is suggested that the polymeric dispersant must only be added in small quantities to ensure a dispersion. The polymeric dispersants have aliphatic backbones with two types of pendant groups; one which is compatible with the solvent but incompatible with the polymer, and one which contains the Lewis base. This combination maintains the polymer in solution long enough to give a high molecular weight. Such a polymer may be produced by the copolymerisation of 1-eicosene ($\text{CH}_3(\text{CH}_2)_{17}\text{CH}=\text{CH}_2$) and *N*-vinyl pyrrolidone, Scheme 1.6. The major disadvantage of this route is the difficulty in removing the polymeric dispersant from the polymer product which could prove costly in an industrial process. If not removed efficiently, the aliphatic residues decrease the thermal stability of the bulk PAEK since they are inherently less thermally stable.



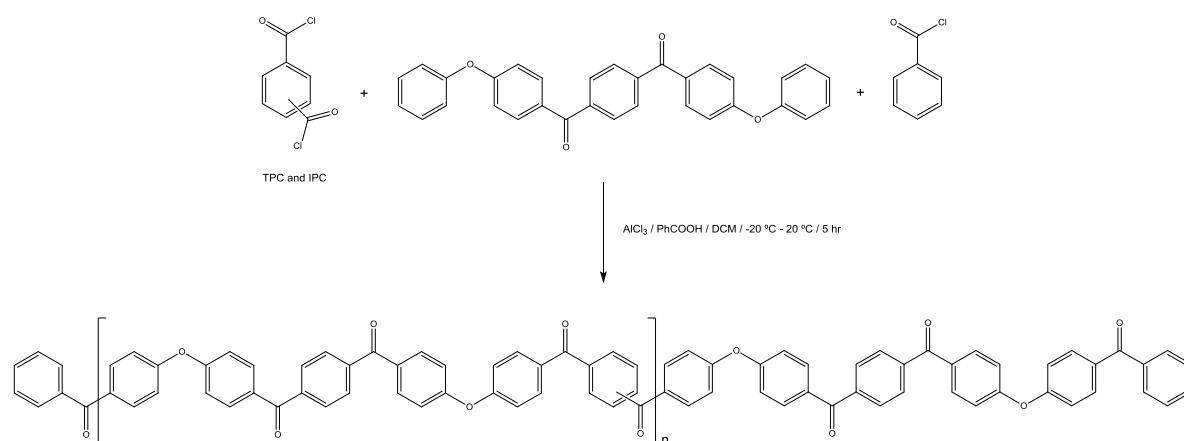
Scheme 1.6 Polymerisation of 1-eicosene and *N*-vinyl pyrrolidone

Zolotukhin²⁹ reported the successful production of PAEKs by low temperature, electrophilic precipitation polymerisations. These polymerisations are catalysed by AlCl_3 in 1,2-dichloroethane. Suitable monomers are a combination of a diacid chloride and an aromatic monomer such as 1,4'-bis(4-phenoxybenzoyl)benzene. Although high molecular weight polymers are produced, these precipitation polymerisations are carried out at a low reactor loading of approximately 3%, which is too low to be scaled up industrially.

1.6.2.4 Modified Friedel-Crafts synthesis

A room temperature, modified Friedel-Crafts method, the “gel process”, Scheme 1.7, avoids side reactions and produces high molecular weight polymer¹⁹. Suitable monomers include the combination of a diacid dihalide with a polynuclear aromatic compound with two active

carbon atoms, catalysed by AlCl_3 . The use of a Lewis base controlling agent, such as dimethyl sulfone, results in a tractable gel product of high molecular weight polymer. The mode of action is unclear, although one explanation is that the Lewis acid:Lewis base complex alters the solubility parameter of the reaction system such that the complexed polymer either remains in solution or is highly swollen, allowing further increase in molecular weight. Largely linear PAEKs with high molecular weight, high melt stability and that are largely free from defects caused by side reactions are produced at a high reaction rate at room temperature. An aprotic solvent such as dichloromethane is employed, and capping agents such as benzoyl chloride in stoichiometric quantities successfully control the molecular weight of the polymer.



Scheme 1.7 The modified Friedel-Crafts synthesis of poly(ether ketone ketone)

After removal from the reaction vessel, the polymer- Lewis acid complex is decomplexed³⁰ by a base with greater than pK_a 4.5, often water. The decomplexing base must be in a molar excess compared to the aluminium chloride to ensure complete decomplexation. The polymer gel is blended in iced water using an industrial blender, or a hammer mill for industrial scale, before the polymer flake is isolated by filtration.

This general method was also reported in both patents^{19,31} and journal literature^{32,33,34} to successfully produce a variety of related copolymers. These included the incorporation of

imide, amide, sulfone, ester, azo, phenylquinoxaline, benzimidazole, bezazole and benzothiazole groups into the polymer backbone by the copolymerisation of specialist dinucleophilic monomers with TPC and/or IPC. The success in terms of thermal and mechanical properties was varied. The synthesis of copolymers will be discussed in detail in Chapter 5.

The laboratory scale gel process was modified to an industrial-sized process capable of producing 15 kg batch sizes³⁵. A schematic diagram of the reactor is shown in Figure 1.6.

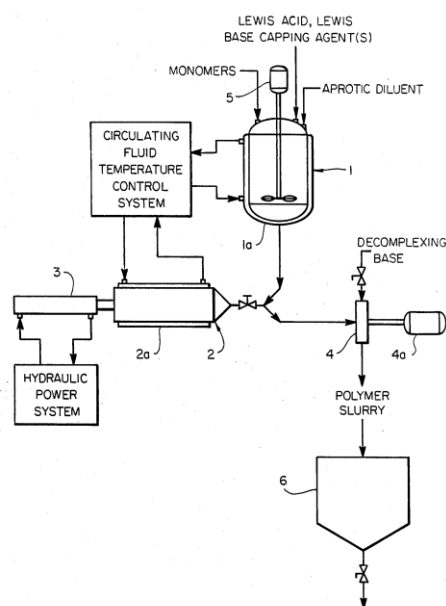


Figure 1.6 A schematic diagram of the tube plant used by Raychem as disclosed in patent US 4,843,131

All of the reactants are first mixed in a jacketed (1a) Hastelloy B2 reactor (1), equipped with a motorised stirrer (5). This specialised material is necessary to withstand the harsh reaction conditions. Subzero temperatures are initially maintained as previously discussed. The mixture is stirred until a viscosity increase is observed. At this point, before gelation, the partially polymerised mixture is transferred to a jacketed (2a) and cooled PTFE lined tube reactor (2). The mixture resides in the tube at 25 °C for four hours until polymerisation is complete. The gelled polymer is pushed out of the tube through a nozzle using a PTFE tipped

hydraulic piston (3). This process can be likened to a large syringe. The gel is cut into small pieces using a motorised (4a) hammer mill (4) whilst being decomplexed with a flood of water. The resulting polymer flake is collected in a filtered vessel (6) for workup.

Unlike the laboratory scale process, the industrial scale process requires a second tubular reactor. At this scale, substantial force is needed to remove the gelled polymer from the reaction vessel so it would be impossible to remove it from a mixing vessel with motorised stirrer. The tubular reactor allows convenient removal of the polymer. The hammer mill is further required to manage the large scale decomplexation. An industrial benefit of this process is that one mixing vessel may feed several reactor tubes due to the difference in residence times in the mixing vessel and the tube reactor.

A further modification of the “gel process” to the “dispersion process” uses a controlling agent that promotes the production of the polymer in the form of a fine dispersion of largely spherical and uniform shaped particles³⁶. Despite this change in morphology, all of the desired polymer properties such as high molecular weight, thermal stability and mechanical properties are maintained. It cannot be reliably predicted whether a controlling agent will produce a polymer in the form of a gel or a dispersion. Benzoic acid, benzenesulfonic acid and trifluoroacetic acid are reported to be dispersants³⁶.

A continuation patent filed in 2011 for Ketonex³⁷ focuses on the industrial benefits of dispersion PEKK, produced using a benzoic acid dispersant. The benefits include the recycling of benzoic acid due to the large difference in its solubility in hot water compared to cold water, the recycling of dichloromethane due to its low boiling point, the control of molecular weight by end-capping and its impact on processability, and the control of particle

size by methods commonly used in conventional dispersion polymerisations. The work carried out in this project is based on the dispersion process.

1.7 Modifications to PAES and PAEK structures

PAESs and PAEKs have been modified to address a range of applications. This includes in-chain and pendant modification. A wide range of functional groups may be built into the main chain by the incorporation of a range of monomers. Other than ether, ketone and sulfone groups, possible functionality includes imide, amide, naphthalene, ester, azo, phenylquinoxaline, benzamidazole, bezoazole, benzothiazole and aliphatic groups^{32,38}. These monomers alter the T_g and T_m due to chain rigidity and crystallinity. A wide range of methods exists for the sulfonation of PEEK and other materials for use in fuel cell membranes³⁹. Amine termination of PAEKs⁴⁰ has been explored for use in composites, which will be discussed in Chapter 6.

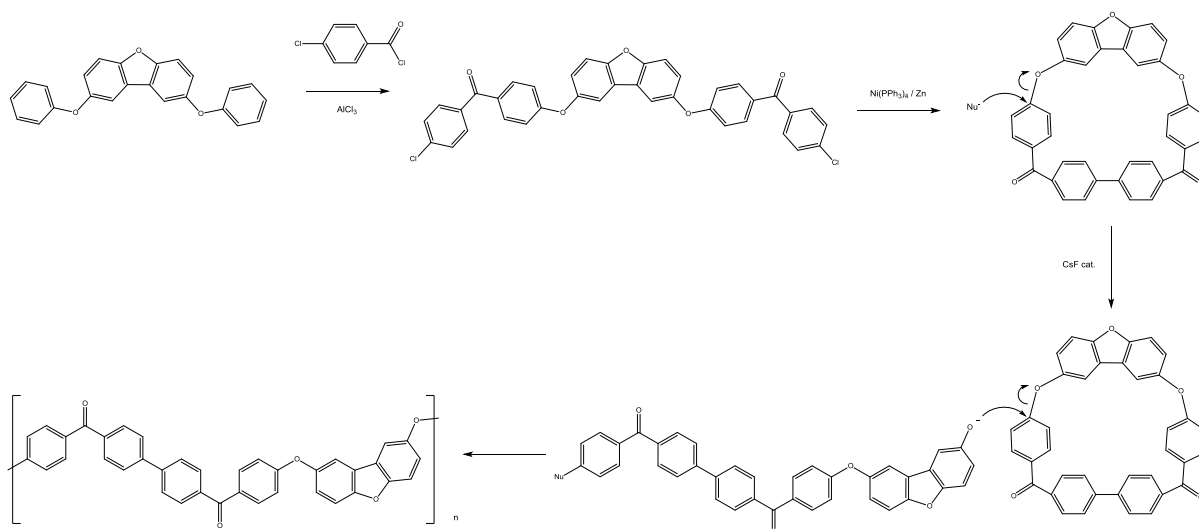
1.8 Alternative routes to PAEKs

Less conventional routes to PAEKs also exist. Rather than being classed simply as nucleophilic and electrophilic polycondensations, these routes exploit structural variations in the monomers to achieve the PAEKs.

1.8.1 Ring-opening polymerisation

Colquhoun^{41, 42} used ring opening polymerisation to produce PAEKs, Scheme 1.8. Monodisperse, fully aromatic, ether ketone based macrocycles were produced by the intramolecular nickel-promoted coupling of bis(4-chlorobenzoyl) terminated oligomers. On the addition of a caesium fluoride or 4-benzoylphenolate catalyst at the melting point of the oligomer, the highly strained macrocycles undergo nucleophilic cleavage at the activated ethers. The resultant ionic ether ketone oligomer promotes the ring opening polymerisation of

further stained macrocycles to produce amorphous PAEK. A sulfone-containing version was also synthesised.



Scheme 1.8 The formation of the macrocycle which undergoes ring-opening polymerisation to produce PAEK

1.8.2 Soluble precursor approach

The synthesis of low molecular weight PAEKs due to the poor solubility of the highly crystalline material has been addressed by several routes using soluble precursors. These routes involve using monomers modified with large, bulky pendent groups but which remain suitable for nucleophilic reaction. These bulky groups increase the solubility of the polymer during polymerisation, and are removed post polymerisation to result in PAEKs with standard structures and of high molecular weight. Pendent groups which have been incorporated include *t*-butyl⁴³, cyclic ketal⁴⁴, and ketimine⁴⁵, Figure 1.7.

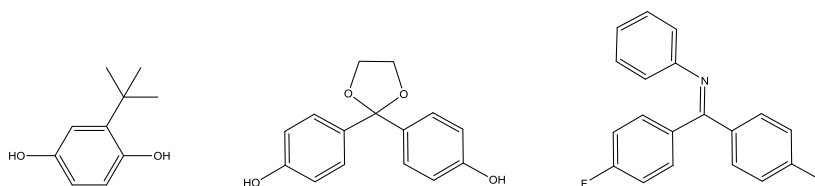


Figure 1.7 Structures of the monomers which include pendent groups of *t*-butyl, cyclic ketal and ketimine

1.9 Project aims

The first aim of this project was the evaluation, modification and optimisation of the existing Ketonex dispersion process, with focus on the production of PEKK polymer. PEKK is known to be a suitable material for this process evaluation, and will be compared to reported PEKK materials. The parameters required to transform the dispersion process into an industrially viable option, including limited scale-up, will be discussed with reference to preliminary evaluation. The second aim was to develop the underlying chemistry behind the dispersion process, and to investigate the action of the benzoic acid dispersant. The production of PAEKs in particulate form is unusual but offers attractive advantages. The third aim was to extend the boundaries of the range of products which can be produced by the dispersion process. This was carried out by the incorporation of a range of alternative monomers and the modification of process parameters accordingly. Finally, a method was devised for the *in situ* amine functionalisation of a range of PAEKs in order to increase the application scope of the polymer product.

Extracts of this chapter have been taken from the following reference with the prior knowledge and consent of the publisher.

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CHAPTER 2 : EVALUATION OF DISPERSION PROCESS PARAMETERS

2.1 Background to the dispersion process

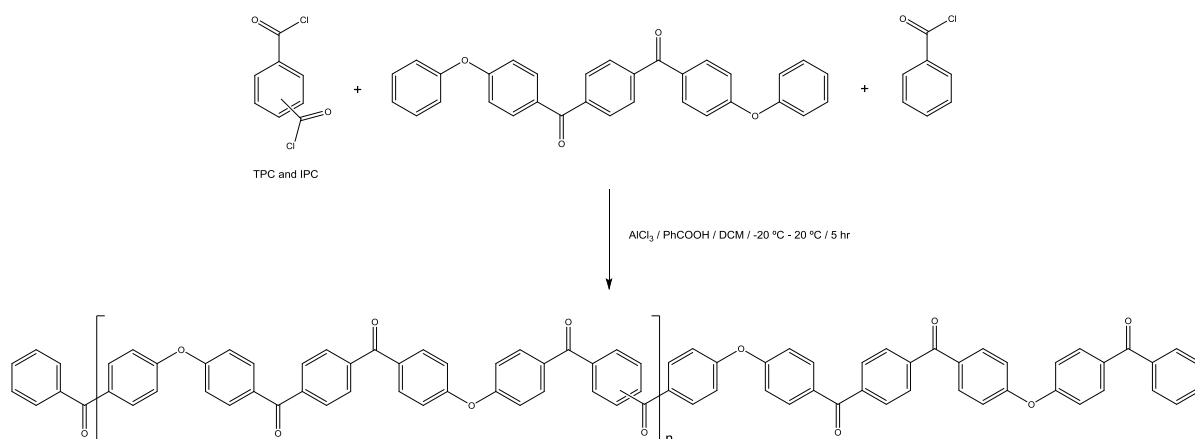
In 1987, Raychem disclosed a modified Friedel-Crafts polymerisation process¹ to produce a range of PAEKs, referred to as the “gel process”. It was later found that by modification of one component of the system, some product types could be produced in the form of a fine powder² rather than flake, *via* the “dispersion process”. This route was not investigated in detail and was never commercially exploited. Since commercial opportunities for PAEK fine powders had become apparent, in 2011 Ketonex filed an extension patent application³ for the use of the dispersion process to produce PEKK alone. Whereas the gel process was known to be reliable, robust and to produce a wide range of PAEK materials^{1, 4-7}, the dispersion process was limited to the reliable production of PEKK alone. It was not known to what extent the dispersion process could be adapted to suit the production of other PAEK based materials, nor which process parameters were most influential on the product.

Due to the emerging commercial opportunities for PAEK powders, this project was designed to extend the boundaries of the capabilities of the dispersion process. The intention was to gain a better understanding of the process parameters, to apply this knowledge to increase Ketonex’s materials portfolio and to scale-up and develop the dispersion process to a potentially industrially viable process, limited to a laboratory scale. This chapter discusses the process parameters for the production of PEKK, chosen as a model due to its synthetic reliability. This knowledge base is transferred to the production of a range of other PAEK materials in Chapters 5 and 6.

2.2 The dispersion polymerisation of PEKK

PEKK is produced *via* a modified Friedel-Crafts dispersion polymerisation^{2, 3} in DCM of

EKKE with TPC and IPC acid chloride monomers, with an end-capper of benzoyl chloride, Scheme 2.1. The AlCl_3 Lewis acid catalyst is added to the reaction mixture in a quantity equal in stoichiometry to that of all the constituent carbonyl groups *i.e.* totalled in the EKKE, TPC, IPC and benzoic acid, with 20% excess. The Lewis base dispersant is benzoic acid which historically was added in 2 molar equivalents compared to the total acid chloride content⁸. Reactant addition is carried out at a temperature of $-15 - -20\text{ }^\circ\text{C}$, before the reaction mixture is heated to room temperature (in practice $20\text{ }^\circ\text{C}$) and the temperature maintained for the duration of the reaction time of 4 - 5 hours. The AlCl_3 is decomplexed from the polymer, usually with iced water, before a workup process is carried out to remove the benzoic acid and aluminium salts. The workup procedure ordinarily involves multiple aqueous and acidic aqueous washes at approximately $80 - 90\text{ }^\circ\text{C}$.



Note: the phenyl ring with undefined geometry is a mixture of T and I linkages in a ratio determined by the ratio of TPC to IPC in the monomer feed.

Scheme 2.1 The modified Friedel-Crafts dispersion polymerisation of PEKK

2.3 Process parameters

The process parameters associated with the dispersion process were examined to evaluate their influence on the dispersion process methodology and of the polymer product. Although only carried out on a laboratory scale, the data obtained gave a good approximation of the

suitability of the dispersion process on a moderate industrial scale. The parameters are all discussed in relation to the production of PEKK.

2.3.1 Evolution of molecular weight

Many of the physical properties of a polymer are influenced by its molecular weight. In general, the higher the molecular weight, the better the mechanical properties of the polymer *i.e.* higher strength and toughness. However, a balance must be struck, since if the molecular weight is too high, melt processing becomes impossible. It is extremely attractive to be able to easily and accurately control the molecular weight of a polymer product during polymerisation.

It is commonly known that the molecular weight of a condensation polymerisation may be controlled by the “out-of-balance” *i.e.* the stoichiometric ratio, of the constituent monomers⁹. The molecular weight is also dependent on the extent of reaction, which is often presumed to be 100%. The Friedel-Crafts polymerisation used in the dispersion process is an example of such a polymerisation, to which the following theory applies.

For an “in-balance” condensation polymerisation *i.e.* one with a 1:1 stoichiometric ratio of monomers, the Carothers equation applies,

$$\bar{X}_n = \frac{1}{1-p}$$

where \bar{X}_n is the number average degree of polymerisation, and p is the extent of reaction. The average degree of polymerisation is defined as the average number of monomer units in a polymer chain. On calculation of the theoretical \bar{X}_n from 99 – 100% complete reaction, Figure 2.1, the \bar{X}_n trends from 100 towards ∞ .

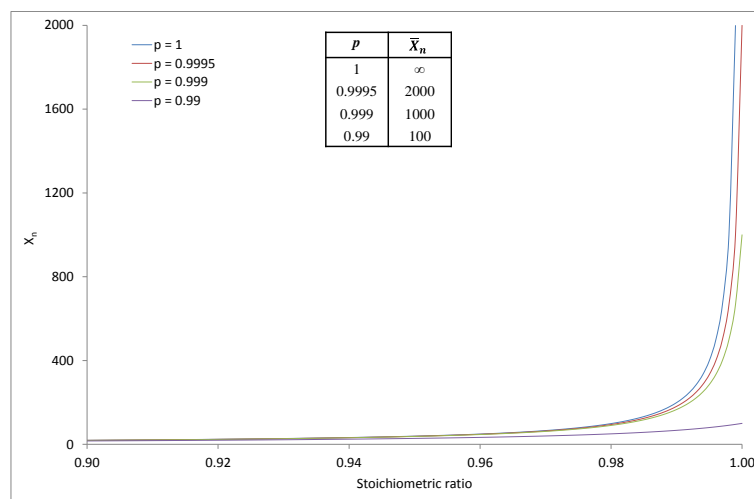


Figure 2.1 The effect of the extent of reaction, p , on the average degree of polymerisation, \bar{X}_n

The molecular weight is also controlled by the stoichiometric imbalance of the monomers, referred to as the “out-of-balance”, and is calculated using a modified Carothers equation,

$$\bar{X}_n = \frac{1 + r}{1 + r - 2rp}$$

where \bar{X}_n is the average degree of polymerisation, p is the extent of reaction and r is the stoichiometric ratio of monomers. On calculation of the theoretical \bar{X}_n from 5% out-of-balance to in-balance, Figure 2.2, the \bar{X}_n increases from 39 trending towards ∞ , assuming 100% extent of reaction. The number average molecular weight \bar{M}_n is calculated using the mass of the repeat unit in the polymer backbone, exemplified by 600 for PEKK. \bar{M}_n is defined as the average mass of a polymer chain and its values follow the same trend as \bar{X}_n .

The large change in \bar{X}_n and \bar{M}_n seen over a small range of extent of reaction and stoichiometric imbalance highlights the importance of a tightly controlled reaction system, and what might commonly considered to be unimportant matters in fact become critical. For example, it must be ensured that the standard reaction time is long enough to allow for complete reaction of the monomer system. The weighing of monomers must be accurate, all monomer must be transferred to the reaction vessel including washings, and it must be

ensured that no monomer is lost around the sides of the vessel, in order to ensure the correct stoichiometric imbalance. It is also imperative to use a very high purity monomer as impurities effectively create stoichiometric imbalance.

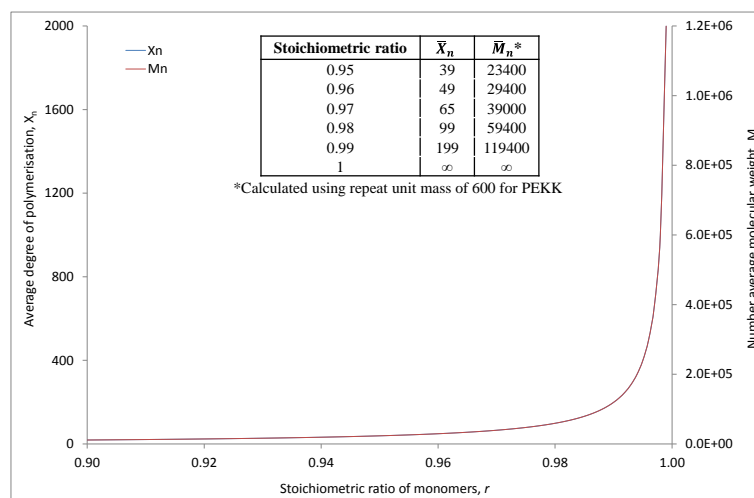


Figure 2.2 The effect of the stoichiometric ratio of monomers on the average degree of polymerisation, \bar{X}_n , and the number average molecular weight \bar{M}_n

The relationship between out-of-balance and IV, and therefore molecular weight, is specific to each monomer system. This relationship is used to determine the out-of-balance required for a target IV or molecular weight. An experimental relationship for 80:20 PEKK⁸ is exemplified in Figure 2.3.

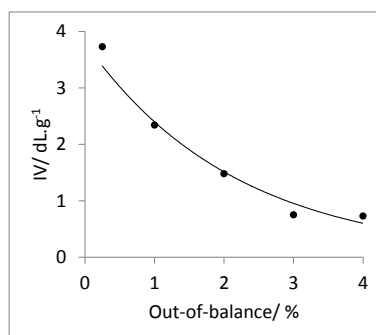


Figure 2.3 Experimental relationship of out-of-balance to inherent viscosity, IV, as determined in concentrated sulfuric acid at 25 °C

2.3.2 Monomer purity

As explained mathematically in the previous section, very high purity monomers are required to produce high molecular weight polymers. Monomer purity is generally calculated by DSC,

using the purity analysis software as described in Chapter 7. Monomers are expected to have a purity of above 99.80%, and preferably above 99.90%.

It has been suggested that PEKK instability is related to the presence of 9-phenylxanthrydrol end groups, Figure 2.4, produced by cyclisation reactions during monomer synthesis¹⁰. It was also reported that the polymer stability may be increased by the conversion of 9-phenoxyxanthrydrol to xanthene. UV-vis spectra of several samples of EKKE monomer in DCM with five drops of TFA were recorded. λ_{\max} for xanthrydrol is 455 nm.

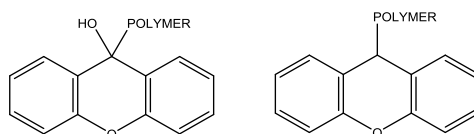


Figure 2.4 9-Phenoxyxanthrydrol and xanthene end groups

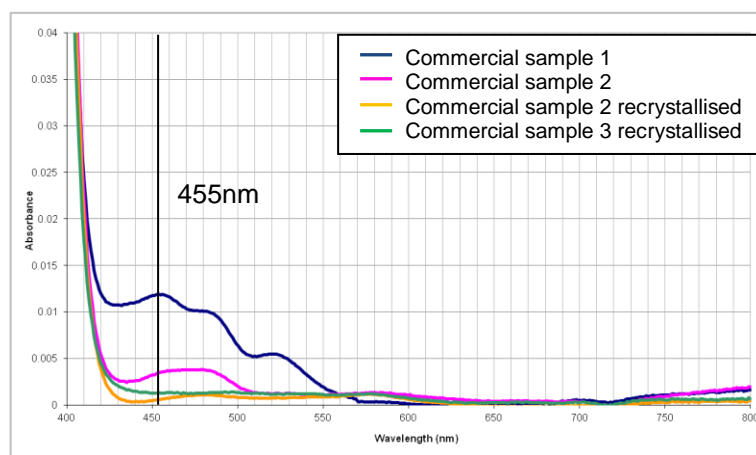


Figure 2.5 UV-vis absorption spectra of EKKE from several sources, measured in a solution of DCM with five drops of TFA

Preliminary UV-vis spectra of three commercial samples of EKKE were obtained, Figure 2.5. There is a clear spectroscopic difference between the samples. Commercial sample 1 had the highest absorbance at 455 nm, followed by commercial sample two. Recrystallised commercial samples 2 and 3 had extremely low absorbances at this wavelength. This data suggests that recrystallisation removes an impurity, which could be 9-phenylxanthrydrol.

Further analysis would be required to confirm this observation and the resultant effect on polymer stability.

2.3.3 Order of addition of reactants

In addition to the monomers, the dispersion polymerisation system also includes AlCl_3 and benzoic acid. It would be expected that the order of addition of reactants would affect the polymer product. There are two points to consider when determining the optimum order of addition of reactants. The first is the chemistry of the Friedel-Crafts reaction, including catalyst complexation. The second is the production and management of exotherms produced on addition of the reaction components, which vary in magnitude between reactants.

Firstly, the DCM alone is cooled to a temperature of -5 – -10 °C. The AlCl_3 Lewis acid is then added, with the generation of a small exotherm, and cooled to within the desired range of addition temperature. It is essential that this is the first addition, as the AlCl_3 complexes with any water present in the solvent. The water would otherwise act as a nucleophile and react with the acid chloride monomers, yielding carboxylic acids and terminating the polymerisation. The reaction mixture is cooled to -15 – -20 °C. The benzoic acid Lewis base is next added, also complexing with the AlCl_3 to form aluminium benzoate, as discussed in detail in Chapter 4, accompanied by the evolution of hydrogen chloride. The temperature of the reaction mixture may reach up to -10 °C due to the accompanying moderate exotherm. However, this must be quenched before the addition of the monomers to avoid side reactions.

The next steps are the monomer additions. It is essential that the temperature of the reaction mixture is kept low, -15 – -20 °C, during these additions in order to minimise *ortho*-substitution. The addition of the TPC and IPC is accompanied by a small exotherm, followed by the addition of the EKKE which is accompanied by the largest exotherm of all the

additions. This large exotherm can be used to help to raise the temperature of the reaction mixture to the polymerisation temperature of room temperature (in practice 20 °C). Although it is possible to reverse the order of the monomer additions, it would be necessary to eliminate the large exotherm generated from the addition of the EKKE before the addition of the TPC and IPC. This does not pose a problem on a small scale but has important cost implications on an industrial scale where heating and cooling processes are expensive and time consuming. The benzoyl chloride end-capper is added as the reaction temperature is increasing to room temperature. The addition of the end capper may be delayed if required, as this impacts on the polydispersity of the product.

If the end-capper is added early in the reaction, chain termination occurs on short chain polymers whilst longer chains undergo further growth, resulting in double peaks of molecular weight and a large polydispersity. However, if the end-capper is added later in the reaction, the polymer chains have undergone unhindered growth to achieve similar molecular weights before chain termination occurs. This results in a single peak in molecular weight and a smaller polydispersity.

Although there are several potential variations to this order of addition, the method described is the optimum order to ensure a successful polymerisation and whilst being more industrially compatible. In summary, the optimum order of addition is:

DCM – AlCl₃ – benzoic acid – TPC/IPC – EKKE – benzoyl chloride

A representative temperature profile for the polymerisation of PEKK, including the set point, cooler temperature and reactor temperature, is shown in Figure 2.6a. This illustrates the overall temperature changes in the system. The set point temperature is increased up to 20 °C in steps to have better control of the heating rate. From the initiation of the set point, both the

cooler temperature and reactor temperature have time lags. An example of a temperature profile for the reactant additions for a typical PEKK polymerisation is shown in Figure 2.6b. The individual exotherms are labelled with the corresponding reactants. The exotherm for the addition of the end-capper is obscured by that of the EKKE.

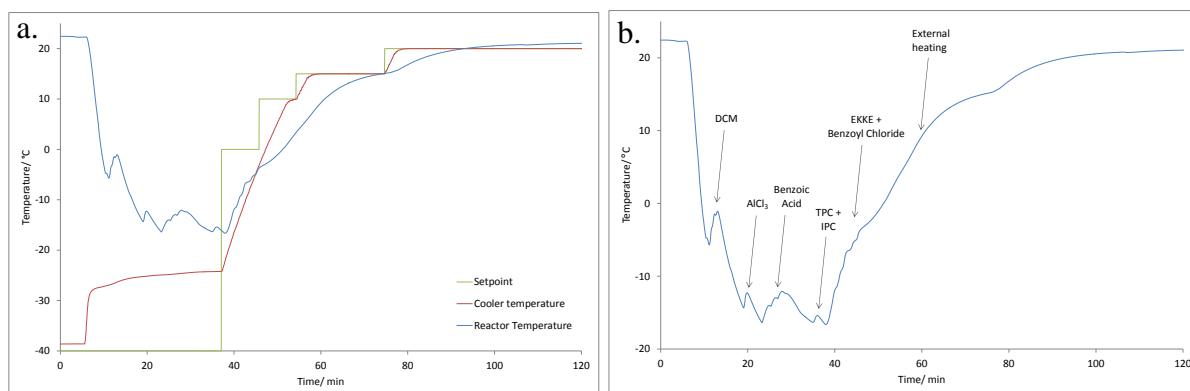


Figure 2.6 A representative temperature profile for a PEKK polymerisation detailing a. the set point, cooler and reactor temperatures and b. the reactor temperature only, with exotherms assigned to reactant additions

2.3.4 Reaction temperature

As discussed in the previous section, the reactants are added at low temperature to avoid side reactions during the preliminary monomer additions, before being warmed to the final reaction temperature of 20 °C which is maintained over the whole reaction time. The low reaction temperature is employed to minimise alkylation of the polymer chain by DCM which would occur at higher temperatures. It also has the benefit of being approximately room temperature which minimises the energy requirement for heating or cooling. At this reaction temperature, 5 hours is required for complete reaction. On decreasing the reaction temperature to 10 °C, the initial rate of reaction approximately doubles. This is demonstrated by the graphs of IV in relation to reaction time of PEKK polymerisation at 10 and 20 °C, Figure 2.7. The reaction times used for these studies were increased substantially compared to the usual reaction time of five hours. It would be expected that the rate of reaction would tend to zero at this point. However, the increased IV could be attributed to cyclisation reactions which would not occur if the polymerisation had been quenched.

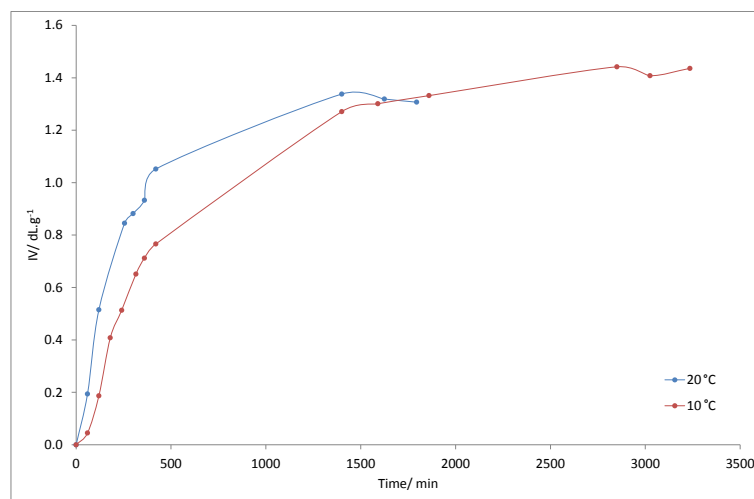


Figure 2.7 The relationship of IV and reaction time for a PEKK polymerisation at 10 °C and 20 °C

2.3.5 Solvent

Solvents which have been reported to be suitable for electrophilic PEKK polymerisations include DCM² and 1,2-dichloroethane¹¹ and *ortho*-dichlorobenzene¹². DCM is preferred due to its suitability to the process, its low cost and the ease of removal from the polymer due to its low boiling point. However, it must be noted that chlorinated solvents have health implications. In addition, it is preferred if the solvent for a new process fits into the waste stream for an existing plant.

Ortho-dichlorobenzene is commonly used as a solvent for nucleophilic PEKK polymerisations¹², which must be carried out at 160 - 180 °C. At lower temperature, the PEKK precipitates out as a dense mass which cannot be penetrated by the monomers and oligomers in solution, restricting the molecular weight. Heating the reaction mixture softens the polymer mass and allows monomer and oligomer diffusion to increase the molecular weight of the resultant polymer.

PEKK polymerisation by the dispersion process using *ortho*-dichlorobenzene as a solvent was attempted on a small scale⁸, carried out at 3 % out of balance. Reactions at 40 °C and 60 °C

produced PEKK with IVs of 0.27 and 0.60 dL.g⁻¹ respectively. Compared to the product of an identical reaction in dichloromethane which would be expected to have an IV of approximately 0.9 dL.g⁻¹, these values are extremely low. One theory to explain the low molecular weight is that at the elevated polymerisation temperatures, some of the benzoic acid is chlorinated by the excess aluminium chloride to form benzoyl chloride which terminates polymer growth on reaction with the PEKK oligomers.

From these results, it appears that *ortho*-dichlorobenzene is not a suitable alternative solvent for this dispersion polymerisation system. No further modification of the polymerisation solvent was carried out, and DCM was used throughout.

2.3.6 Benzoic acid concentration

Benzoic acid is used in the dispersion process as a Lewis base and dispersant. It is known that the addition of benzoic acid to the polymerisation system promotes the formation of PEKK particles of small diameter. The benzoic acid concentration is defined in terms of the number of benzoic acid equivalents, which is calculated as the number of stoichiometric equivalents compared to that of the acid chloride monomers. It was hypothesised that decreasing the benzoic acid concentration would result in increased particle size. Industrially, the aim was to use as little benzoic acid as possible, to reduce the raw material cost and for ease of removal post polymerisation, whilst maintaining the desired particle size and bulk material properties.

70:30 PEKKs were synthesised using 4, 3, 2, 1.5, 1, 0.5 and 0 benzoic acid equivalents to assess the effect of benzoic acid concentration on product morphology. Decreasing the number of benzoic acid equivalents increased the particle size and decreased the density, Table 2.1. The threshold level for powder morphology is 1.5 benzoic acid equivalents, where the product was granular. Above this concentration, the products were fine powders, and

below this concentration the products were large masses of polymer ranging between 0.5 – 3 centimetres in diameter.

Benzoic acid equivalents	IV/ dL.g ⁻¹	Free- flow density/ gcm ⁻³	Tapped density/ gcm ⁻³	Morphology
4	1.04	0.35	0.40	Fine particulate
3	0.82	0.32	0.37	Fine particulate
2	0.85	0.29	0.34	Fine particulate
1.5	0.76	0.19	0.21	Granular
1	0.61	0.14	0.15	Large masses
0.5	0.43	0.11	0.12	Large masses
0	0.63	0.16	0.17	Large masses

Table 2.1 Data for PEKK produced using 4, 3, 2, 1.5, 1, 0.5 and 0 benzoic acid equivalents to include IV measured in conc. sulphuric acid at 25 °C, free-flow and tapped densities, and appearance

All IVs were in the region of 0.4 - 1.0 dL.g⁻¹, Table 2.1. In general, decreasing the benzoic acid concentration decreased the IV. Assuming that the benzoic acid does not take part in the polymerisation itself, this could be attributed to inefficient workup. During workup, the water cannot penetrate the centre of the larger particles to remove the residues. The aluminium chloride and/or benzoic acid residues in the particles add to the mass used for the IV sample preparation and so act to reduce the polymer concentration. The residues themselves would not affect the IV of the solution since small molecules do not affect solution viscosity.

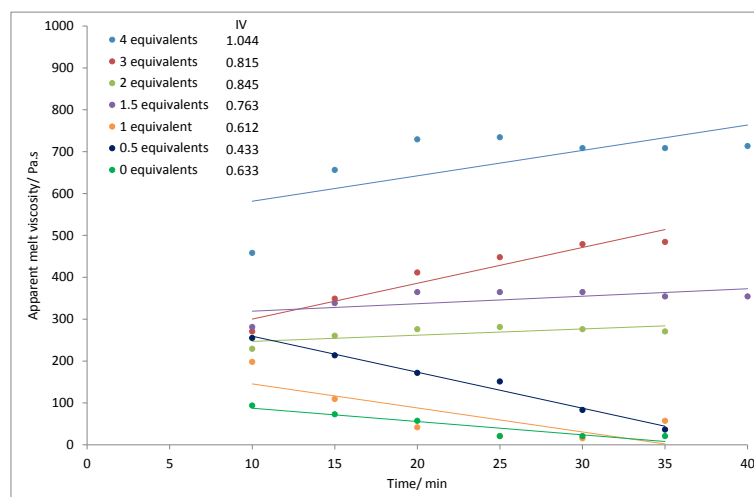


Figure 2.8 Melt viscosity data comparing PEKK produced using 4, 3, 2, 1.5, 1, 0.5 and 0 benzoic acid equivalents, recorded at a shear rate of 30 s⁻¹ at 400 °C

Above and including 1.5 benzoic acid equivalents, the melt viscosities of the polymers increased over time and exhibited good melt stability at 400 °C, Figure 2.8. However, below 1.5 benzoic acid equivalents, the melt viscosities decreased over time and the polymers were less melt stable *i.e.* they demonstrated an increased rate of viscosity change. It appears that the PEKKs produced as large masses undergo inefficient workup since the outer edges of the larger particles were white, whereas the centres of the particles were beige, likely to be due to impurities. It is known that impurities greatly affect melt viscosity¹³. In addition, when the larger particles were loaded into the barrel of the capillary rheometer, benzoic acid sublimation was observed. A threshold level of particle size and the relating workup efficiency is indicated.

Benzoic acid equivalents	T _g (1)/ °C	T _g (2)/ °C	T _c (1)/ °C	T _c (2)/ °C	T _m (1)/ °C	T _m (2)/ °C
4	160.5	164.8	237.7	-	332.2	332.4
3	157.9	160.3	232.0	-	333.3	333.2
2	159.2	159.9	226.8	-	334.2	334.8
1.5	163.6	165.9	240.0	-	333.0	331.1
1	167.3	166.8	234.4	-	334.5	332.9
0.5	167.3	166.8	234.4	-	334.5	332.9
0	159.3	164.7	227.9	-	340.9	339.8

Benzoic acid equivalents	ΔCp* (T _g (1))/ Jg ⁻¹ K ⁻¹	ΔCp* (T _g (2))/ Jg ⁻¹ K ⁻¹	ΔH (T _c (1))/ Jg ⁻¹	ΔH (T _c (2))/ Jg ⁻¹	ΔH (T _m (1))/ Jg ⁻¹	ΔH (T _m (2))/ Jg ⁻¹
4	0.260	0.152	27.04	-	-28.77	-28.10
3	0.282	0.129	27.98	-	-30.98	-29.23
2	0.269	0.077	28.76	-	-35.67	-30.16
1.5	0.183	0.217	14.21	-	-21.54	-15.57
1	0.228	0.171	11.70	-	-22.72	-17.77
0.5	0.166	0.074	17.85	-	-27.71	-24.80
0	0.212	0.078	28.53	-	-42.58	-32.37

Table 2.2 DSC data for PEKK produced using 4, 3, 2, 1.5, 1, 0.5 and 0 benzoic acid equivalents from two cycles of 90 - 380 °C heating at 20 °C.min⁻¹ and cooling at 10 °C.min⁻¹

Small variation in thermal properties was observed on decreasing the number of benzoic acid equivalents, Table 2.2, with thermal properties of approximately T_g 160 °C , T_m 330 °C, and

T_c 230 °C. Variation in T_m is commonly a function of molecular weight. At low molecular weight, melting temperatures can be higher than those associated with high molecular weight polymers since the chains can easily rotate to form crystalline domains. However, at high molecular weight, a high melt viscosity inhibits movement of the polymer chains and therefore inhibits the formation of crystalline domains. This limits the time available for the chains to order and crystallise before the temperature change in the DSC moves the sample temperature outside the range where crystallisation is fastest. In extreme cases, a certain polymer of high molecular weight may be amorphous but a low molecular weight version of the same polymer may be crystalline. On analysis of this data, there is a correlation between molecular weight (IV), melting temperature and the enthalpy change for melting, with all parameters increasing simultaneously.

The benzoic acid concentration in the polymerisation system affected polymer morphology, with lower concentrations resulting in larger masses. Polymer morphology affected the workup efficiency, with lower efficiency for larger polymer masses. This study suggests that 2 benzoic acid equivalents balances the need for a low benzoic acid concentration with the requirement for small particles with desirable bulk properties. The value of 2 benzoic acid equivalents is carried to the reactor loading study, but 4 benzoic acid equivalents is commonly used in subsequent chapters. The role of benzoic acid in the dispersion process is discussed in detail in Chapter 4.

2.3.7 Reactor loading

Three calculations can be used when considering the reactor loading for a synthetic process,

$$\text{Initial loading} = \frac{\text{total mass of all the reactants}}{\text{solvent volume (mass)}}$$

$$\text{Solid content} = \frac{\text{mass of PEKK with 100\% theoretical yield} + \text{mass AlCl}_3 + \text{mass benzoic acid}}{\text{solvent volume (mass)}}$$

$$\text{Polymer loading} = \frac{\text{mass of PEKK with 100\% theoretical yield}}{\text{solvent volume (mass)}}$$

Initial loading and solid content are used at the start and end of the process respectively to give an indication of the stirring requirement. The higher the initial loading or solid content, the greater the torque required by the stirring system. Polymer loading gives the mass of polymer produced per unit volume.

Calculated using solvent volume			Calculated using solvent mass		
Polymer loading/ %	Solid content/ %	Initial loading/ %	Polymer loading/ %	Solid content/ %	Initial loading/ %
10.0	29.7	30.9	7.6	22.4	25.8
15.0	44.9	46.7	11.3	33.9	39.0
17.0	50.2	52.3	12.8	37.9	43.7
20.0	59.1	61.6	15.1	44.6	51.4

Table 2.3 Calculated values of reactor loading to include polymer loading, solid content and initial loading, using both solvent mass and solvent volume, for a PEKK polymerisation at 3 % out-of-balance and 2 benzoic acid equivalents

Each of the equations may be used to calculate loading, using either solvent volume or solvent mass, although using solvent volume is most common. All of the methods are comparable within the same system, however, only polymer loading is comparable between systems as it does not take into account other components. The polymer loading, solid content and initial loading for a PEKK polymerisation at 3% out-of-balance with two benzoic acid equivalents, calculated using both solvent volume and solvent mass, are listed in Table 2.3 for comparison. Throughout this project, only polymer loading, calculated using solvent volume, was used as a measure of reactor loading.

As high reactor loadings as possible are targeted for industrial syntheses in order to maximise economic viability. Polymerisations carried out in this project were routinely run at a reactor loading of 10%, with some being carried out at higher reactor loadings. It is understood that this is a higher loading than the loading used by some commercial plants⁸, and is significantly

higher than the 3% loading reported by laboratory scale polymerisations to produce particulate PAEKs¹⁴.

2.3.7.1 Reactor loading study

In the benzoic acid concentration study, it was found that two benzoic acid equivalents was the lowest concentration to exhibit good high IV, good melt stability and high density. At this concentration, fine particulate PEKK was produced. On the assumption that particle size would increase to a granular product with reactor loading, the concentration of two equivalents was chosen to continue on to the reactor loading study. 70:30 PEKKs were synthesised with reactor loadings of 10, 15, 17 and 20%, with two benzoic acid equivalents.

Loading	Inherent viscosity/ dL.g ⁻¹	Free- flow density/ g.cm ⁻³	Tapped density/ g.cm ⁻³	Morphology
10%	0.85	0.29	0.34	Powder
15%	0.81	0.28	0.30	Granules
17%	0.86	0.29	0.31	Granules
20%	0.83	0.32	0.32	Granules

Table 2.4 Data for PEKK produced at 10, 15, 17 and 20% reactor loadings with two benzoic acid equivalents to include IV measured in conc. sulphuric acid at 25 °C, free-flow and tapped densities, and appearance

A large difference in particle size was observed between the PEKK with 10% and 15% reactor loadings, with the particle size increasing from powder to granules, with associated decrease in tapped density, 0.34 to 0.30 g.cm⁻¹. Above 15% reactor loading, PEKK granules were produced and increasing the reactor loading did not significantly affect the size nor the density of the products. The IVs remained in the region of 0.81 – 0.86 dL.g⁻¹, indicating that the molecular weight was unaffected by loading, demonstrating the consistency of the process.

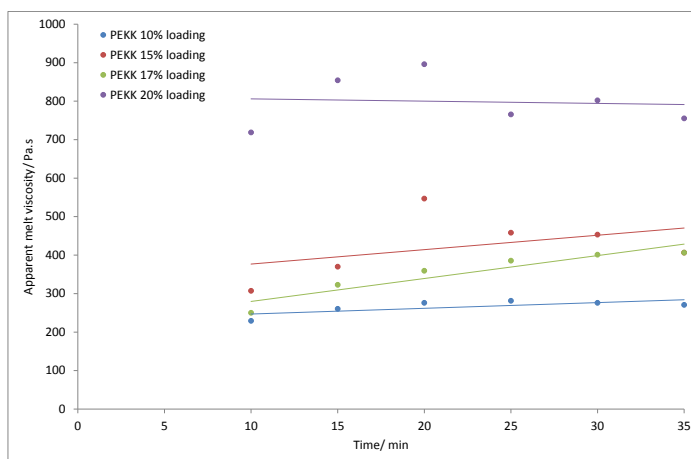


Figure 2.9 Melt viscosity data comparing PEKK produced at 10, 15, 17 and 20% reactor loadings, recorded at a shear rate of 30 s^{-1} at $400 \text{ }^\circ\text{C}$ by capillary rheometry

The PEKKs produced with 10, 15 and 17% reactor loadings exhibited little variation in melt viscosity at $400 \text{ }^\circ\text{C}$, Figure 2.9, with approximately equal values of between 200 – 450 Pa.s, demonstrating good thermal stability. The data point at 20 minutes for the 15% loading PEKK was discounted from the trend line. At this point, dust was extruded through the capillary which increased the pressure together with the observed viscosity. The data for the 20% loading PEKK showed large variation in melt viscosity, despite exhibiting good melt stability *via* the trend line. It is likely that reliance on this trend line is not suitable to achieve a realistic indication of melt viscosity for this data set. The overall viscosity is also approximately twice as high, approximately 800 Pa.s, as those of the other PEKKs. Whilst loading the barrel of the melt rheometer, it was noted that benzoic acid sublimed onto the instrument. Whilst the particle size was no different from the other loadings, this suggested inefficient workup. If this were the case, then the polymer would also have high residual aluminium content which would increase melt viscosity. On increasing the reactor loading from 10 - 17%, the rate of viscosity change also increased, but retained its agreement with the trend line. It is possible that small quantities of residual benzoic acid were present at higher loadings which decreased the melt stability. This data suggested that a threshold level for workup efficiency existed at a reactor loading of 17%.

Reactor loading/ %	T _g (1)/ °C	T _g (2)/ °C	T _c (1)/ °C	T _c (2)/ °C	T _m (1)/ °C	T _m (2)/ °C
10	159.2	159.9	226.8	-	334.2	334.8
15	160.9	161.1	231.9	-	334.2	334.2
17	160.7	162.1	233.9	-	333.0	332.7
20	166.1	165.8	234.9	-	333.4	333.5

Reactor loading/ %	ΔC_p^* (T _g (1))/ J.g ⁻¹ .K ⁻¹	ΔC_p^* (T _g (2))/ J.g ⁻¹ .K ⁻¹	ΔH (T _c (1))/ J.g ⁻¹	ΔH (T _c (2))/ J.g ⁻¹	ΔH (T _m (1))/ J.g ⁻¹	ΔH (T _m (2))/ J.g ⁻¹
10	0.269	0.077	28.76	-	-35.67	-30.16
15	0.243	0.129	29.15	-	-32.56	-29.45
17	0.268	0.129	25.00	-	-32.26	-28.27
20	0.298	0.152	29.22	-	-31.32	-29.91

Table 2.5 DSC data for PEKK produced at 10, 15, 17 and 20% reactor loadings, from two cycles of heating 90 - 380 °C cycles at 20 °C.min⁻¹ and cooling at 10 °C.min⁻¹

Little variation in thermal properties was observed between samples, Table 2.5, with T_g approximately 160 °C, T_c 226.8 – 234.9 °C and T_m 332.7 – 334.8 °C, indicating that increasing the loading had little effect of the thermal properties of the PEKK product.

A 17% reactor loading, combined with two benzoic acid equivalents, was the highest loading for PEKK to exhibit a high IV, good melt stability and high density. A 20% loading produced PEKK with residual benzoic acid which was detrimental to melt stability. Although these are optimised conditions for the Ketonex one litre reactor, both parameters will be affected by reactor and stirrer design. In subsequent chapters, 4 benzoic acid equivalents and 10% reactor loading are used to ensure the reliable formation of fine particulate product.

2.3.8 Polymer workup

Aluminium chloride is required as a Friedel-Crafts catalyst for polymerisation. A stoichiometric quantity equal to that of the total carbonyl content of the monomers is required, since the aluminium chloride will complex to the carbonyl groups. This is indicated by the generation of orange colour on addition of aluminium chloride to the monomers, with an

associated exotherm, due to extended conjugation. A 20% excess of aluminium chloride then acts as the catalyst species. The orange colour remains throughout the polymerisation until workup. An efficient polymer workup is essential to remove aluminium ions and to produce good quality polymer. Initial decomplexation is carried out using iced water, which removes the complexed aluminium chloride from the ketones on the polymer backbone. At this point, the polymer turns from orange to white as the extended conjugation caused by the complexation is disrupted.

The polymer then undergoes a workup sequence including multiple aqueous washes to remove the residual aluminium ions and benzoic acid. After the removal of the residual DCM by distillation, an aqueous acid (HCl) wash is required as the first stage for polymers produced by the dispersion process. The reason for the requirement for this acid wash is discussed in Chapter 4. If an acid wash is not carried out, a large quantity of residual benzoic acid remains in the polymer. Although no residual aluminium levels in the polymers were measured during this project, the target is to achieve an aluminium content of below 100 ppm.

Several alternative methods have been suggested for the more efficient removal of aluminium ions. A commonly used method is the decomplexation in methanol or a methanol wash¹⁵. Washes in other media such as dilute aqueous acid or acetone have been reported to be successful. All of these methods are thought to remove a greater proportion of aluminium ions as these solvents wet the polymer more efficiently. An alternative is the use of chelating agents such as dicarbonyl compounds such as 2,4-pentanedione¹⁶ or aliphatic alpha-hydroxycarboxylic acids such as lactic acid¹⁷ in solution at 60 – 120 °C, which claim to reduce the aluminium residue by one order of magnitude to approximately 400 ppm.

2.3.9 Drying of the polymer

After workup, the polymers are dried in an air oven at 80 – 90 °C for 48 hours, at which point they visually appear to be dry. However, it has been observed that the PEKKs must undergo further drying at 250 °C to ensure melt stability. The polymers are melt unstable if the second drying is not carried out, indicated by the wide variation in melt viscosity, Figure 2.10. This effect is observed by PEKKs produced using both the gel and dispersion processes.

It is hypothesised that since 250 °C is well above the polymer T_g , the flexibility of the polymer chains increases and a volatile is released which would otherwise cause melt instability. It is reasonable to suggest that this volatile may be hydrogen chloride, since this is evolved during the polymerisation. However, neither hydrogen chloride, nor indeed any other species, can be detected by preliminary analysis by mass spectroscopy when the polymer is heated to 250 °C. This analysis does not rule out the presence of hydrogen chloride or another volatile species, as the instrument may not have been optimised for their detection during preliminary analysis. Further optimisation of experimental parameters would be required for a definitive conclusion.

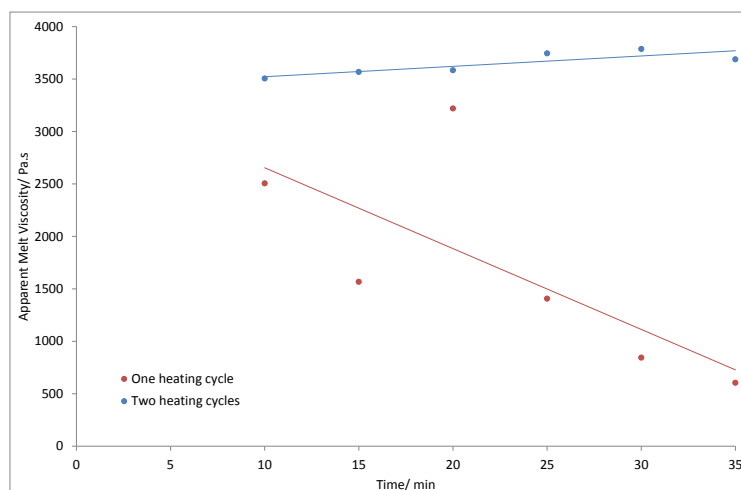


Figure 2.10 The variation in melt viscosity PEKK after drying at 90 °C and with an additional drying at 250 °C, measured at a shear rate of 30 s^{-1} at 400 °C by capillary rheometry

2.3.10 Scale-up

Process scale-up capability is the largest hurdle to overcome in the industrialisation of any synthetic process. A multidisciplinary approach relies on the close collaboration between R&D chemists, industrial chemists, chemical engineers, process engineers together with finance and business development personnel to achieve full commercial success.

A degree of scale-up was planned in this project, but restricted to laboratory scale equipment. The aim was to reliably and reproducibly replicate the dispersion process in a one litre reactor on a larger scale to produce comparable polymer product. The larger the reactor, the more comparable to an industrial process which may be an indication of issues to be encountered with further scale-up.

2.3.10.1 Reactor and stirrer design

Ideally, a reactor would be designed specifically for the dispersion process but this project was restricted to the reactors available at Ketonex. The one litre reactor is a standard round bottomed, cylindrical, jacketed vessel with a multi-neck lid. The vessel temperature is controlled by a circulating cooler. An overhead motor operates either an anchor or propeller stirrer, both made from PTFE.

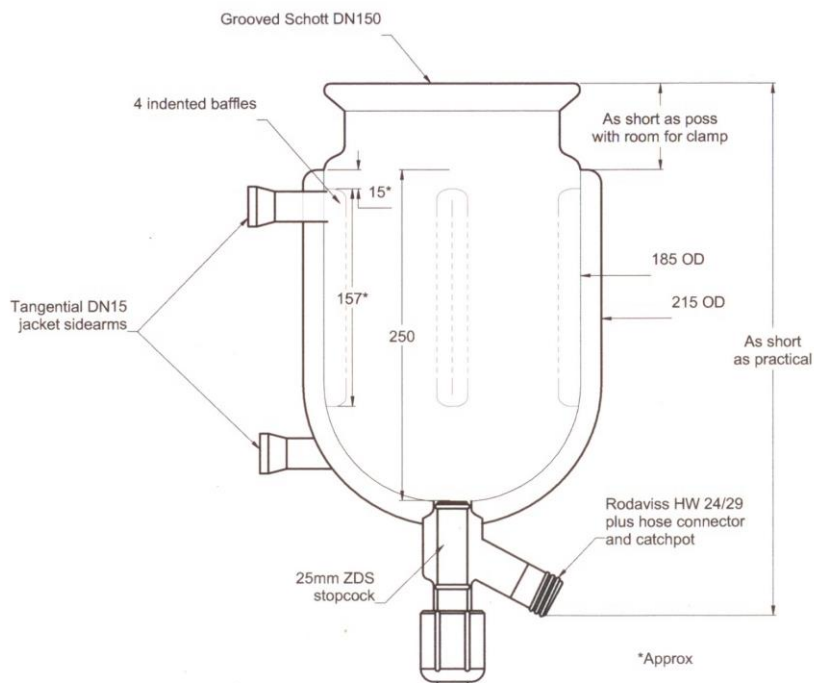


Figure 2.11 Dimensions of the Ketonex five litre reactor, with measurement units of mm

The five litre reactor is custom made and is more similar to an industrial reactor. The glass jacketed reactor, Figure 2.11, has four built-in internal baffles and a bottom outlet. The temperature of the vessel is controlled by a Julabo heater/ cooler bath via a thermocouple inside the vessel. The vessel has a glass multi-necked lid to house the thermocouple, stirrer gland and nitrogen inlet/ water pump and a solids input, Figure 2.12. All of the stirrer components are PTFE. A propeller shaft is commonly used with the addition of two adjustable rotors, Figure 2.13.

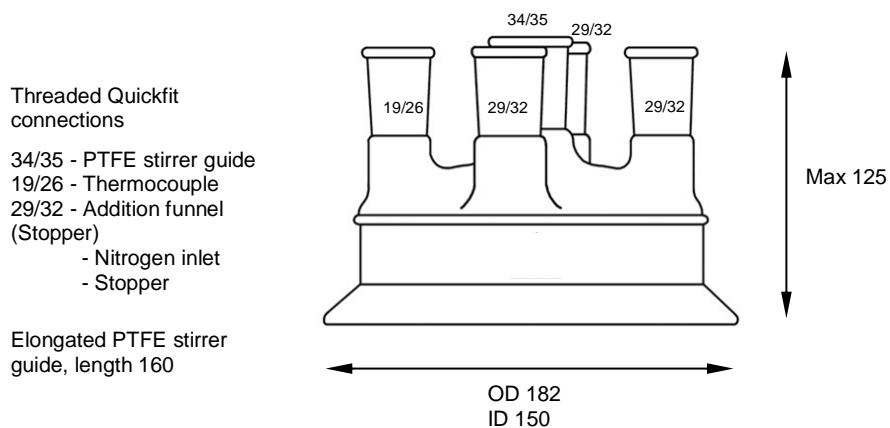


Figure 2.12 Dimensions of the lid for the Ketonex five litre reactor, with measurement units of mm

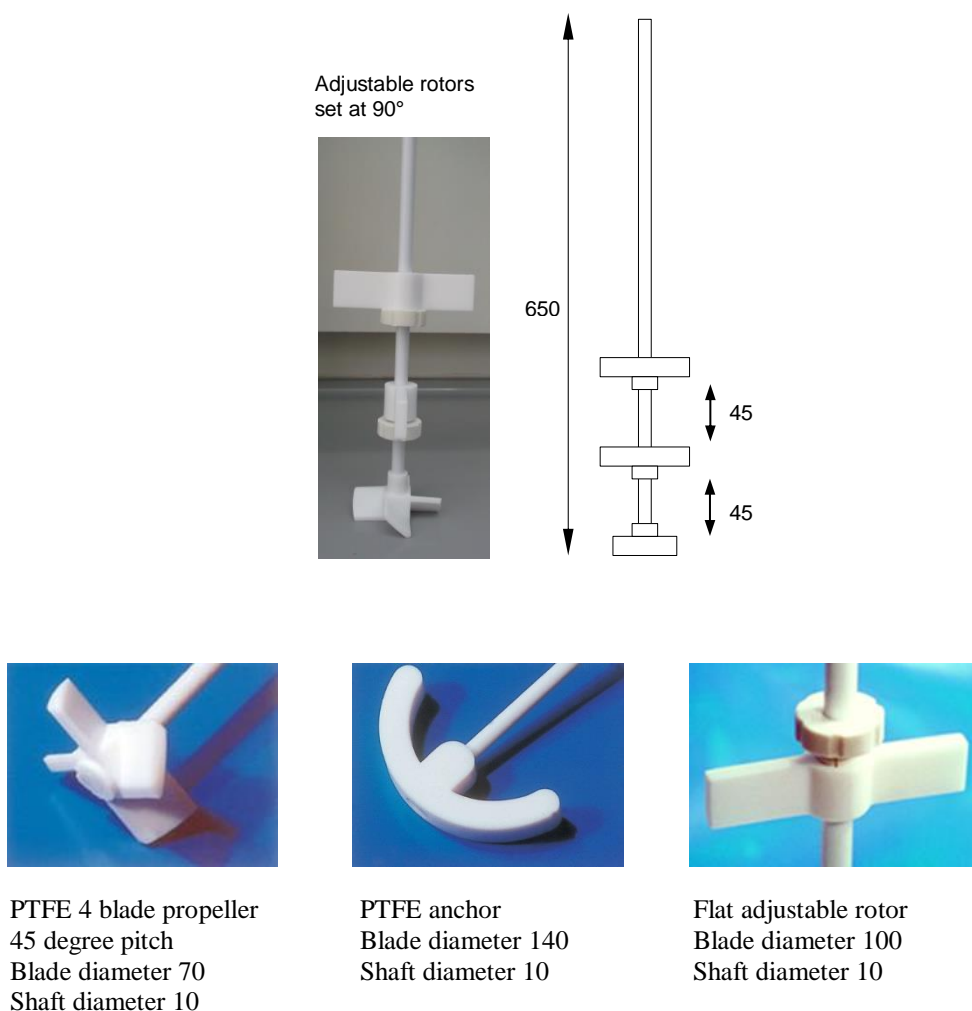















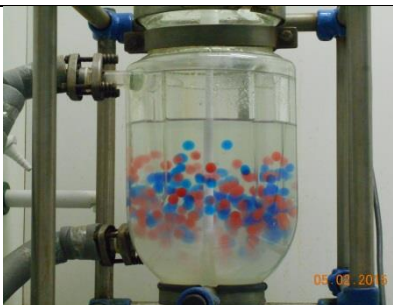

Figure 2.13 Dimensions of the stirrer geometries used in the Ketonex five litre reactor, with measurement units of mm

Each stirrer and reactor setup has a different effect on the turbulence of the reaction mixture and the flow patterns. The flow patterns inside the one litre and five litre reactors are

illustrated in Table 2.6 by the use of coloured beads in water. The anchor stirrer in the one litre reactor exerts high shear, illustrated by the large vortex at higher stirrer speeds and the distribution of red and blue beads, with a maximum of 400 rpm. The propeller is of lower shear and does not distribute the beads as effectively. A vortex is not as apparent and the stirrer speed can be increased up to 700 rpm. No vortices are observed in the five litre reactor with an anchor stirrer with or without rotors, as this is disrupted by the baffles. The rotors increase the distribution of beads vertically through the reaction vessel.

a. One litre reactor		
Speed/ rpm	Anchor	Propeller
50		
100		
200		
300		

400		
500	-	
600	-	
700	-	

b. Five litre reactor		
Speed/ rpm	Anchor	Anchor with rotors
60		

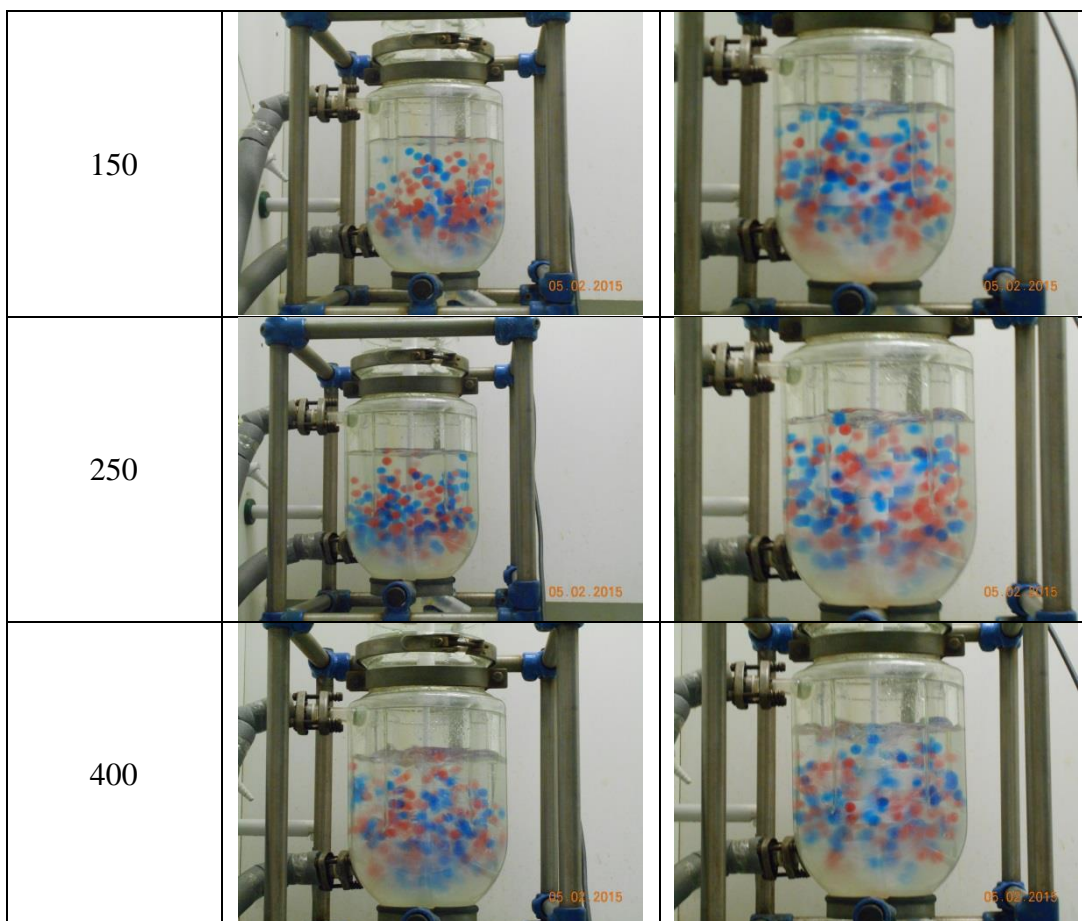


Table 2.6 Reactor flow mapping for the a. one litre reactor and the b. five litre reactor

2.3.10.2 Scale-up study

PEKKs were synthesised at 3% out of balance, with 4 benzoic acid equivalents, a 12% loading and at a stirrer speed of 500 rpm in the five litre reactor. 60:40 PEKK was produced using a stirrer configuration of a propeller with two adjustable rotors and 80:20 PEKK was produced using an anchor, Table 2.7.

Sample	TPC:IPC	Stirrer geometry	Inherent viscosity/ dL.g^{-1}	Av melt viscosity/ Pa.s
60:40T	60:40	Turbine and two rotors	0.90	575
80:20T	80:20	Turbine and two rotors	0.80	347
80:20A	80:20	Anchor	0.76	-

Table 2.7 Preparation conditions including inherent viscosity data for the PEKK samples, measured in concentrated sulphuric acid at 25°C, and average melt viscosity values measured at a shear rate of 30 s^{-1} by capillary rheometry at 400 °C

	60:40T	80:20T	80:20A
Volume weighted mean/ μm	85.7		331.2
Surface weighted mean/ μm	26.0	Large	37.7
D(0.1)	24.3	needles	27.0
D(0.5)	81.1		269.1
D(0.9)	146.9		734.1
Free-flow density/ gcm^{-3}	0.31	0.18	0.34
Tapped density/ gcm^{-3}	0.34	0.20	0.39

Table 2.8 Particle sizing data for the PEKK samples to include the surface weighted and volume weighted means, and particle size distributions, recorded in 50:50 vol% water:IPA diluent

The particle size data demonstrate the difference in the surface weighted mean and the volume weighted mean. Overall, the former has the larger value. In each of the samples, a small particle diameter tail is apparent which affects the calculation of the mean particle diameters. This is characteristic of the synthetic method. Sample 80:20A has a much higher average diameter and a wider distribution. This sample was prepared using an anchor stirrer rather than a propeller, which appears to have an effect on particle size. The density data indicates that the samples with small particle diameter have higher density due to more efficient packing. The sample with larger, irregular particles had significantly lower density.

There is variation in the IV which is not expected to be due to T:I ratio. It is more likely to be attributed the incomplete removal of benzoic acid in the polymers which would act as to artificially reduce the calculated IV.

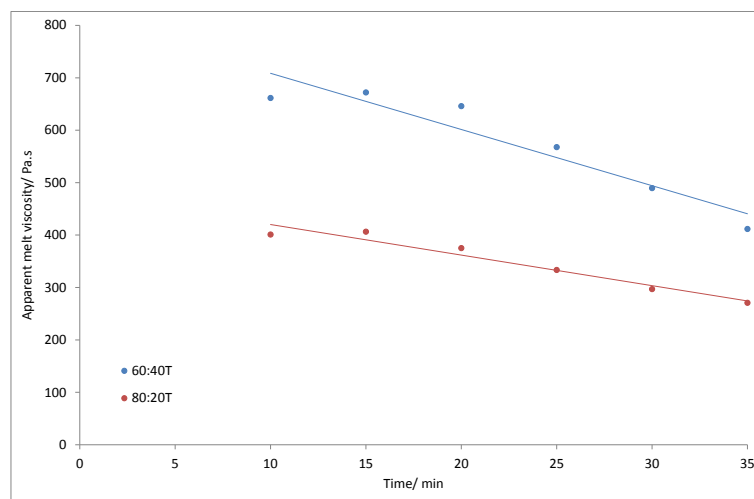


Figure 2.14 Melt viscosity data for the PEKK samples, recorded at a shear rate of 30 s^{-1} at $400 \text{ }^\circ\text{C}$

Samples 60:40T and 80:20T had average melt viscosities of 575 and 347 Pa.s respectively, Figure 2.14. The large amount of residual benzoic acid remaining in sample 80:20A, which could be seen to sublime on entering the capillary rheometer, caused the PEKK to become extremely viscous. Its melt viscosity could not be recorded.

Sample	$T_g(1)/$ $^\circ\text{C}$	$T_g(2)/$ $^\circ\text{C}$	$T_c(1)/$ $^\circ\text{C}$	$T_c(2)/$ $^\circ\text{C}$	$T_m(1)/$ $^\circ\text{C}$	$T_m(2)/$ $^\circ\text{C}$
60:40T	-	162.1	-	-	275.1 301.2	-
80:20T	-	-	-	-	353.3	358.8
80:20A	-	160.6	-	-	364.4	344.6

Sample	ΔC_p^* ($T_g(1)$)/ $\text{Jg}^{-1}\text{K}^{-1}$	ΔC_p^* ($T_g(1)$)/ $\text{Jg}^{-1}\text{K}^{-1}$	ΔH ($T_c(1)$)/ Jg^{-1}	ΔH ($T_c(2)$)/ Jg^{-1}	ΔH ($T_m(1)$)/ Jg^{-1}	ΔH ($T_m(2)$)/ Jg^{-1}
60:40T	-	0.306	-	-	-43.27	-
80:20T	-	-	-	-	-61.73	-30.34
80:20A	-	0.098	-	-	-103.3	-17.69

Table 2.9 DSC data for the PEKK samples from two cycles of $90 - 380 \text{ }^\circ\text{C}$ heating at $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and cooling at $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$

Since the DSCs were run without a hot film press step, double melting points were seen on one of the samples during the first heating cycle. Single melting peaks were seen on the second heating cycles, with the peaks between $345 - 360 \text{ }^\circ\text{C}$. None of the polymers show T_g s

during the first heating cycle, but two do during the second around 160 °C. None of the polymers showed crystallisation peaks on either the first or second heating cycles.

Overall it was found that the dispersion process was reliable and robust, and could be scaled-up successfully to the five litre scale for the production of PEKK with desirable bulk properties. The reactor and agitator design has a large effect on the morphology of the product, but may be altered to achieve the required particle size. This is ultimately dependent on the equipment available.

2.3.10.3 Commercial scale-up considerations

If the dispersion process was to be evaluated for commercial suitability, a range of points would be considered which are not possible to explore in a laboratory environment. A large scale pre-commercial setup would be used for evaluation before a full scale commercial plant could be considered. The process would become fully automated in a closed system, requiring a large shift in the style of equipment used. Related Health and Safety and Waste Management procedures would be implemented. Further cost analysis would account for economies of scale in monomer and reactant sources, together with the practicalities of reagent recycling. The management of exotherms and the required cooling capacity is equipment dependent. Cooling is more energy and cost intensive than heating. Flow modelling would need to be undertaken with respect to reactor and agitator design to aid the design and building of a commercial reactor.

For this process specifically, two problematic areas may be the removal of aluminium salts from the polymers to an acceptable level during workup, and the filtering of the polymer during workup which often resemble thick silts. On a laboratory scale, this gravity filtration

can be alleviated the use of steel mesh as a filter material. However, on an industrial scale, filtration with applied vacuum, pressure or a combination of both would be required.

2.3.11 Recycling of reagents

The recycling of reagents has both cost and environmental implications. The overall recycling potential of DCM and benzoic acid were investigated, to include the likelihood of recovery and to quantify the potential recycling capacity. In addition, quality of the PEKK produced using recycled reagents was investigated. 70:30 PEKKs were produced using recycled DCM and benzoic acid.

DCM was recovered by distillation from both the initial filtrate on isolation of the polymer and from the polymer itself. The wet DCM was dried over molecular sieves with a nominal pore size of 3 Å. The benzoic acid was recovered from the decomplexed initial filtrate on isolation of the polymer and from the cooled filtrate after the first acid wash. The crystallised benzoic acid was washed with iced water and was dried in an air oven.

Reactants	IV/ dL.g ⁻¹	Free-flow density/ g.cm ⁻³	Tapped density/ g.cm ⁻³	Morphology
As received	0.86	0.29	0.31	Fine particulate
Recycled DCM	0.86	0.28	0.29	Fine particulate
Recycled benzoic acid	0.91	0.30	0.31	Fine particulate

Table 2.10 IV, free-flow and tapped density data for the PEKKs produced using recycled DCM and benzoic acid compared to PEKK produced using materials as received

The use of the recycled DCM and benzoic acid had little effect on the IVs of the PEKKs, Table 2.10, with values of 0.86 and 0.91 dL.g⁻¹, compared to the IV of 0.86 dL.g⁻¹ of the PEKK produced using reagents as received. It also had no effect on the free flow and tapped

densities of the PEKKs densities of the fine particulate polymers, with values of 0.28 – 0.30 and 0.29 – 0.31 g.cm⁻³ respectively.

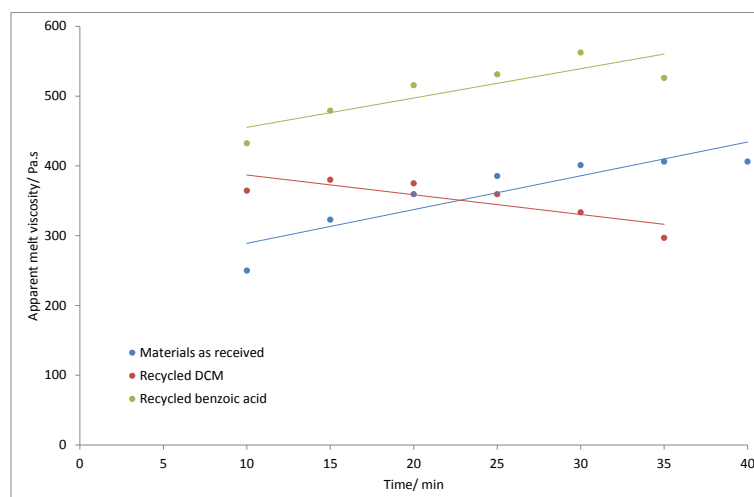


Figure 2.15 Melt viscosity data comparing PEKK produced using supplied and recycled dichloromethane, and from materials as supplied, recorded at a shear rate of 30s⁻¹ at 400°C

The PEKK produced using recycled benzoic acid showed good melt stability and melt viscosities similar to those of the polymer produced using supplied benzoic acid, with an approximate average of 500 and 350 Pa.s respectively, Figure 2.15. The polymer produced using recycled DCM was melt stable and had an average melt viscosity similar to that of the polymer produced using supplied DCM, approximately 350 Pa.s. However, instead of showing a melt viscosity increase as before, it instead showed a melt viscosity decrease. The supplied DCM is stabilised with 0.005% amylene (1-pentene) and is of 99% purity. On distillation, both the amylene and any impurities would be removed from the DCM. It is possible that the amylene may react in the polymerisation system in a Friedel-Crafts manner, to result in aliphatic impurities in the polymer. These aliphatic regions would be less thermally stable than the aromatic regions, and so would decrease the melt stability of the bulk polymer. This effect may account for the difference in observed melt viscosity between the PEKK produced using supplied and recycled DCM, although repeat experiments would be required to verify the observation.

	$T_g(1)/$ $^{\circ}\text{C}$	$T_g(2)/$ $^{\circ}\text{C}$	$T_c(1)/$ $^{\circ}\text{C}$	$T_c(2)/$ $^{\circ}\text{C}$	$T_m(1)/$ $^{\circ}\text{C}$	$T_m(2)/$ $^{\circ}\text{C}$
As received	160.7	162.1	233.9	-	333.0	332.7
Recycled DCM	162.6	165.8	235.2	-	337.7	333.3
Recycled benzoic acid	160.7	164.9	235.8	-	332.5	332.1

	ΔC_p^* ($T_g(1)$)/ $\text{Jg}^{-1}\text{K}^{-1}$	ΔC_p^* ($T_g(2)$)/ $\text{Jg}^{-1}\text{K}^{-1}$	ΔH ($T_c(1)$)/ Jg^{-1}	ΔH ($T_c(2)$)/ Jg^{-1}	ΔH ($T_m(1)$)/ Jg^{-1}	ΔH ($T_m(2)$)/ Jg^{-1}
As received	0.268	0.129	25.00	-	-32.26	-28.27
Recycled DCM	0.279	0.164	19.75	-	-27.5	-21.84
Recycled benzoic acid	0.282	0.153	26.85	-	-30.35	-27.48

Table 2.11 DSC data comparing PEKK produced using supplied and recycled dichloromethane and benzoic acid and materials as received, with two cycles of 90 – 380 °C heating at 20 °C.min⁻¹ and cooling at 10 °C.min⁻¹

Little effect on the thermal properties of the PEKKs was observed when using supplied and recycled DCM and benzoic acid, Table 2.11.

From this preliminary data, PEKK with extremely similar properties was produced using recycled reagents, indicating successful DCM and benzoic acid recycling. It is presumed that the combination of both recycled DCM and benzoic acid would be successful also, although further analysis would be required for confirmation.

A continuation of this topic would be to investigate the possibility of recycling the “active mixture” rather than isolating the DCM and benzoic acid entirely. The active mixture would be isolated from the product by filtration prior to decomplexation. It contains DCM, benzoic acid, aluminium chloride and low molecular weight oligomers. Recycling in this manner avoids isolation and purification steps. It is possible that this solution could be put straight back into another batch reactor and the concentrations of reactants adjusted by the addition of new reactants before a new polymerisation. A potential issue with this theory is the

calculation of the concentration of remaining reactants in the active mixture. By this route, the batch-based dispersion process could be converted to a continuous process.

2.3.11.1 Mass balance calculation

A mass balance calculation is a vital tool in the development of an industrial process. It is a technique which calculates the inputs, outputs and losses of a synthetic process and therefore is used to determine whether it could potentially be cost effective. For a process to be commercially viable, any recyclable reactants and products must be recovered at a level of at least 90 %. A mass balance was carried out using the five litre reactor, Table 2.12.

Component	Reactants & Solvent/ g	Product & Recovery/ g	Recovery/ %
EKKE	331.89	-	-
TPC	54.32	-	-
IPC	84.60	-	-
Benzoyl chloride	6.04	-	-
Aluminium chloride	668.61	-	-
Benzoic acid	167.20	39.61	24 (85)
Dichloromethane	3000ml	2500ml	83
PEKK	-	368.31	87

Table 2.12 Mass balance data for the production of PEKK using the 5 litre reactor

An efficient recovery of 87% PEKK was achieved. A small quantity was lost on transfer from the reactor to the workup vessel and there was a small amount of fouling around the neck of the reactor, indicating that the yield was higher. There is the potential to increase the recovery with specialist filtering equipment. Furthermore, a high recovery of 83% DCM was achieved. Again, a small quantity was lost on transfer from the reactor to the workup vessel. Due to its low boiling point of 41 °C, some DCM evaporated. With optimisation it is believed that recovery could reach over 90%. A suggested improvement is the use of chilled water in the condenser to avoid further evaporation. In the first instance, a low recovery of 24% of benzoic acid was achieved. It is thought that the large volume of water necessary to remove the aluminium chloride has a detrimental effect on the benzoic acid recovery. In cold water, the

solubility of benzoic acid is approximately 3 g.L⁻¹, increasing markedly to approximately 70 g.L⁻¹ in hot water. Although benzoic acid does crystallise from the filtrate when it is cooled, a large quantity may still be lost to the water. A second method of concentrating the aqueous filtrates was attempted in the hope of improving the benzoic acid recovery. Although this method was very time and power consuming and so is not suitable for a large scale, a much improved 85% recovery was achieved. Although this mass balance is based on a single polymerisation, it gives a positive impression that the necessary 90% recovery can be achieved with optimisation.

2.4 Additional parameters

Although many parameters are discussed in relation to PEKK, they are all transferable to the production of other PAEK copolymers. The effect of T:I ratio in relation to PEKK is discussed in Chapter 3, the role of the benzoic acid dispersant is discussed in Chapter 4, and the adaptation of the process to produce PAEK copolymers is discussed in Chapters 5 and 6.

2.5 Industrial implications of the dispersion process parameters

Although the major driving force behind the industrialisation of a synthetic process is the production of a material with properties capable of filling a gap in the market, the economics of the process often determine its success. A high quality product must be made reliably by a financially accessible route. The parameters described have great influence on the overall economic assessment of the dispersion process.

The production of high purity monomers removes the requirement for costly purification steps whilst ensuring high purity and consistency of the product. The economies of scale must also be considered from a laboratory to an industrial setup. The dispersion process is a batch process, yet the reaction time is short enough to maximise the number of possible runs whilst

minimising down time. Heating and maintaining the temperature of an industrial scale reactor is expensive, and cooling is even more so. The dispersion process has the benefit of a 20 °C reaction temperature, eliminating the need for intensive heating power. The cooling required during reactant addition is more problematic, but is a requirement to ensure a high quality product. The workup requires heating steps but at manageable temperature of 80 - 90 °C. DCM is a low cost solvent which could potentially fit into existing purchasing, health and safety management and waste streams, depending on the current output of the plant and other company activities. As high a reactor loading as possible is necessary to maximise product output per reactor volume. The dispersion process has a high loading for a solution polymerisation whilst maintaining control over the product. Reagent and solvent recycling is essential to reduce the cost of both purchased reagents and of waste disposal. DCM and benzoic acid can be recovered in approximately 85% which should be increased with more specialised equipment. It is possible that the energy required for recycling may be harvested from other “waste” energy generated in the plant. The dispersion process does not require the bespoke design of any particularly costly or specialised equipment. The process can be managed under standard chemical engineering methods, and can potentially be adapted to existing equipment.

Overall, the dispersion process for the production of PEKK has demonstrated to be robust and reliable, yielding consistent product. Theoretically, all of the process parameters described should be able to be further optimised in an industrial plant with a wealth of chemical engineering knowledge and specialised equipment. The dispersion process for the production of PEKK has the potential to be transformed into a streamlined industrial polymerisation process.

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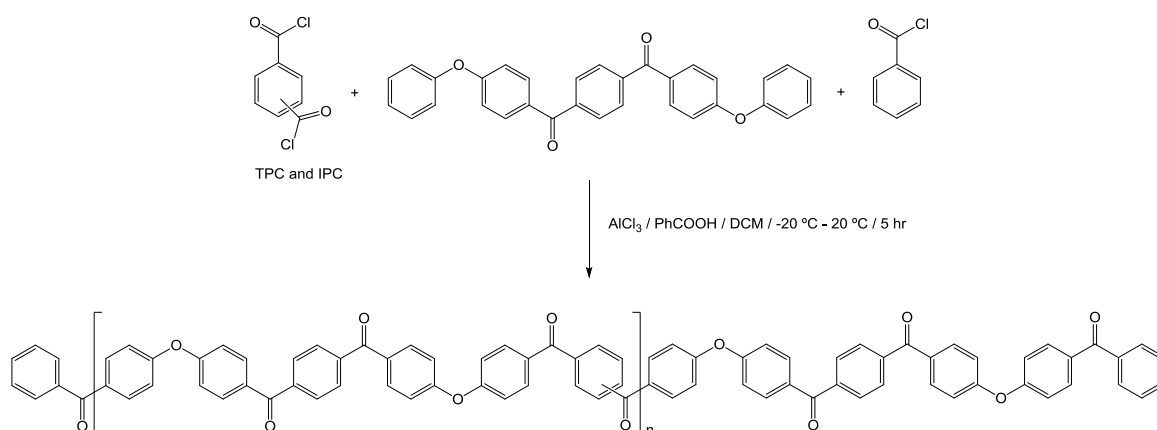
CHAPTER 3 : PEKK SYNTHESIS EVALUATION

3.1 Synthetic evaluation requirements

Following the detailed evaluation of process parameters in Chapter 2, a standard method for the production of PEKK by the dispersion process was proposed. As in Chapter 2, PEKK was selected for evaluation due to its synthetic reliability, together with the availability of comparative data. Importantly, the ratio of TPC:IPC in the monomer feed, and therefore in the polymer, can be altered easily to adapt the thermal properties, together with the degree of crystallinity and crystallisation rate of the PEKK. It was confirmed that the dispersion process produced material identical to that reported by other sources, by the synthesis of a set of PEKKs with a range of TPC:IPC ratios in the monomer feed. The polymer products were evaluated using a range of methods, which will be discussed in detail in this chapter.

3.2 PEKK polymer synthesis

PEKKs were prepared according to the general dispersion¹, decomplexation and workup methods on a one litre scale, as described in Chapter 8, Scheme 3.1. PEKKs were synthesised with TPC:IPC ratios of 100:0, 90:10, 80:20, 70:30 and 60:40 in the monomer feed.



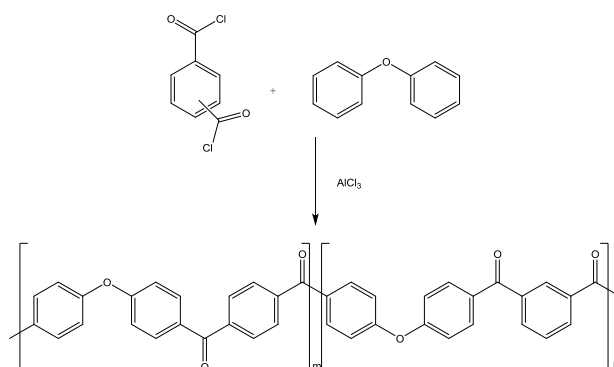
Note: the phenyl ring with undefined geometry is a mixture of T and I linkages in a ratio determined by the ratio of TPC to IPC in the monomer feed.

Scheme 3.1 Reaction scheme for the synthesis of PEKK by the aluminium chloride catalysed polymerisation of EKK with TPC and IPC in DCM at -20 to $+20$ °C for 5 hours

3.3 Polymer structure confirmation

3.3.1 DPE synthesis vs EKKE synthesis

The synthesis of PEKK was first patented in 1962 by the electrophilic reaction of diphenylether (DPE) with TPC and IPC², Scheme 3.2. The reaction was conducted in nitrobenzene for 14 hours at 65 °C, in the presence of an aluminium chloride catalyst, resulting in low molecular weight oligomers.



Scheme 3.2 The synthesis of PEKK by the aluminium chloride catalysed polymerisation of DPE with TPC and IPC in nitrobenzene at 65 °C for 14 hours.

1,4-bis(4-phenoxybenzoyl)benzene (EKKE) was first introduced as an alternative monomer to DPE by Jansons *et al.*³. The ketones deactivate the terminal phenyl ring to *ortho*-substitution, so that *para*-substitution is favoured, resulting in a more stable polymer. This effect is discussed in detail in Chapter 1. This monomer system was transferred to the dispersion process^{1,4}.

The PEKK produced using EKKE has subtle structural differences to the PEKK produced from DPE⁵, Figure 3.1. By the DPE process a., the polymer chain is comprised of alternating DPE units and acid chloride (either TPC, T or IPC, I) units which results in a repeat unit of [EKK] where the adjacent acid chlorides *i.e.* in adjacent repeat units, may be T-T, T-I or I-I. This is a truly random structure. However, using the EKKE process b., the polymer chain is comprised of alternating EKKE and acid chloride (either TPC, T or IPC, I) units which results

in a repeat unit of [EKKEKK] where one T always originates from the EKKE. Therefore, adjacent acid chlorides can either be T-T or T-I. I-I links can only be achieved by this route with the introduction of 1,3-EKKE.

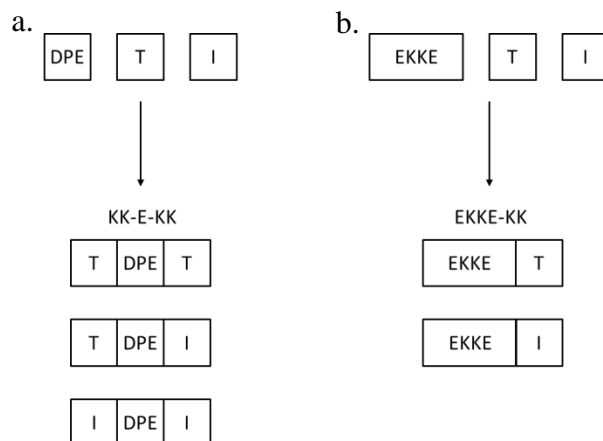


Figure 3.1 Schematic representation of a. the synthesis of PEKK using DPE, TPC and IPC demonstrating the three possible structural variations b. the synthesis of PEKK using EKKE, TPC and IPC demonstrating the two possible structural variations.

There are several drawbacks to the DPE process. The phenyl rings are activated by the ether, resulting in *ortho*-substitution, aided by the moderate reaction temperature. This is disfavoured, as the now possible cyclisations⁶, discussed in detail in Chapter 2, result in polymer instability. Polymers produced by this method are of low molecular weight, due to the early precipitation of the polymer in the polymerisation system, and so do not possess the target bulk properties. DPE cannot be used as supplied and must be distilled under reduced pressure which adds extra cost to the process on an industrial scale.

3.3.2 Monomer reactivity ratios

Monomer reactivity ratios can be used to determine the likely progression of polymerisation, and therefore the likely backbone structure, of a polymer. In the dispersion process, although the sequence of monomer addition to the polymer chain must alternate between EKKE and acid chloride to comply with Friedel-Crafts polymerisation requirements, two situations are possible. Firstly, that the TPC and IPC are equally reactive and so react randomly to form a

backbone with random structure. Alternatively, that one of either TPC or IPC is significantly more reactive and so all of that monomer reacts first, followed by all of the other, forming a more backbone with block character. An intermediate scale spans the two extremes. 1,4-EKKE is used as the sole co-monomer in this study.

Using the model compounds 1,3- and 1,4-EKKE, which are in fact monomers, the polymer phenyl chain ends can be simulated. The terminal *para*- carbon of 1,3-EKKE has δ_C 124.9 ppm, and the terminal *para*- carbon of 1,4-EKKE has δ_C 125.1 ppm from ^{13}C NMR in CDCl_3 ⁷. The similar chemical shift values suggest a similar level of electron density and therefore similar reactivity for Friedel-Crafts polymerisation. There is not a large enough difference in structure for reactivity to be dominated by a steric effect, as the modification is at the centre of the molecule, not at the reactive ends, and does not significantly alter the geometry of the EKKE molecule itself. Therefore, the random addition of acid chloride monomers at chain ends can be expected. This approach can be extended to the carbonyl chemical shift values of the acid chlorides, which simulate the polymer acid chloride chain ends. Using the same argument, similar reactivity is expected due to chemical shift and steric considerations.

Due to the little difference in δ_C at the reaction points of both of the monomers, together with the one-step synthetic method where all of the monomers are present for the whole of the reaction time, it can be presumed that the PEKKs have a random structure with regards to the location of TPC and IPC. The EKKE monomer alternates with a random selection of either TPC or IPC. A truly random structure can only be achieved with a 50:50 TPC:IPC ratio, which removes any concentration effect. In this particular case, the polymer may have I or T acid chloride reactive ends, but only T EKKE reactive ends. An I EKKE reactive end may

only be achieved using 1,3-EKKE. The PEKKs synthesised in this chapter are polymerised at 3% out-of balance, with EKKE excess, resulting in EKKE ends only before end-capping.

3.3.3 Determination of polymer structure by NMR spectroscopy

Solution NMR spectroscopy studies of PEKK and other PEK-based polymers are only possible in a CDCl_3 /trifluoroacetic acid (TFA) solvent, or another strong acid combination. It is thought that the TFA protonates the carbonyl groups on the polymer backbone, introducing short range steric and electrostatic interactions, expanding the polymer chain to force conformational mobility and rendering it soluble⁸. Several drops of TFA are added to the solid polymer sample, and CDCl_3 is added after five minutes with stirring to achieve solubilisation. This approach is required for all of PAEKs. Quartets centred at 164 ppm and 116 ppm are due to TFA which arise from the carbon-fluorine coupling.

The most distinct signals observed in the ^{13}C NMR spectra which can be used for stoichiometric analysis are those which originate from the carbonyl groups, observed at a distance from the other carbon signals at 198 – 199 ppm. In order to determine accurate stoichiometric information, ^{13}C NMR spectra must be recorded with pulse delays of 20 seconds to ensure that the carbonyl carbon atoms relax fully between pulses, resulting in stoichiometric peak heights. The large pulse delays are required to allow for the long relaxation times of the carbonyl carbon atoms due to the Nuclear Overhauser Effect⁹.

The structures of the PEKKs with variable T:I ratios, Figure 3.2, were confirmed by ^{13}C and ^1H NMR analysis, Figure 3.3, with chemical shift values detailed in Table 3.1.

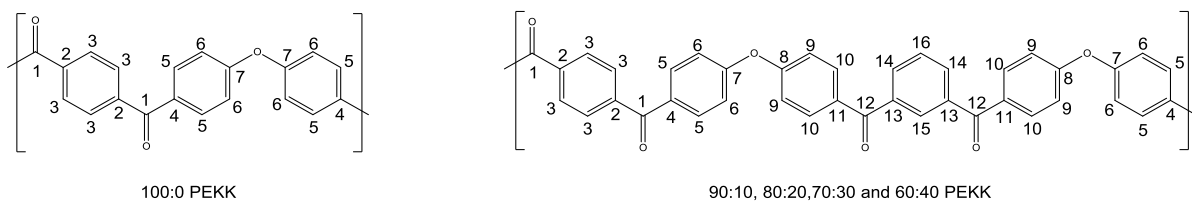


Figure 3.2 Annotated structures of 100:0 PEKK and the 90:10, 80:20, 70:30 and 60:40 PEKKs

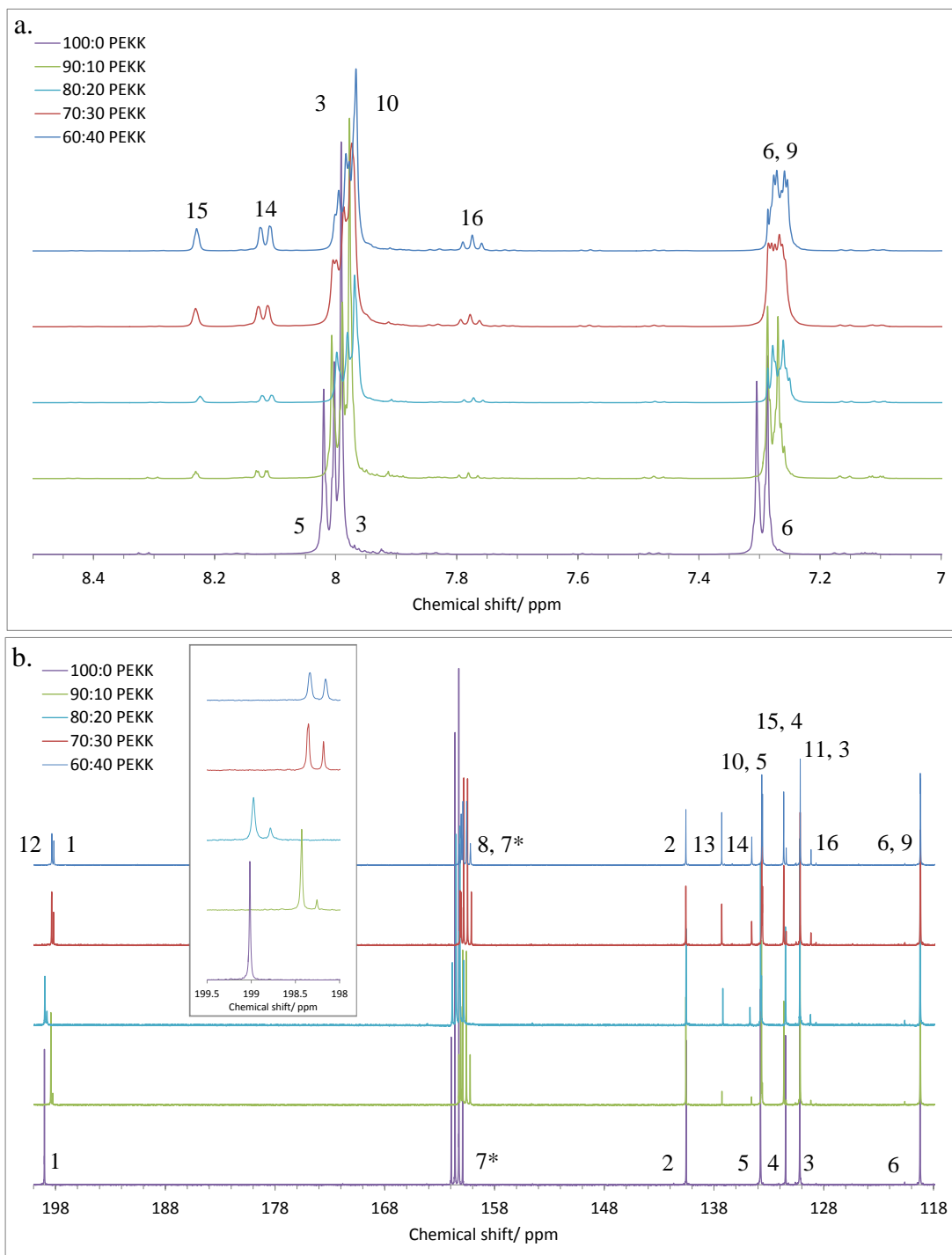


Figure 3.3 Stacked a. ^1H and b. ^{13}C NMR spectra for the 100:0, 90:10, 80:20, 70:30 and 60:40 PEKK structures, demonstrating the growing in of the peaks associated with the IPC on increasing the quantity of IPC in the monomer feed and polymer. Expansion of δ 198–199.5 ppm, demonstrating the growing in of the isophthaloyl carbonyl peak on increasing the isophthaloyl content of the PEKK

Atom	δ_H		δ_C	
	100:0	60:40	100:0	60:40
1	-	-	161.26**	161.01
2	-	-	119.22	119.21
3	7.98 (m)	7.98 (m)	133.77	133.65
4	-	-	131.48	131.65
5	7.98 (m)	-	199.02	198.33
6	7.27 (d)	7.27 (m)	140.54	140.56
7	-	-	130.19	130.14*
8	-	-	-	164.04
9	-	7.27 (m)	-	119.17
10	-	7.98 (m)	-	133.58
11	-	-	-	130.14*
12	-	-	-	198.16
13	-	-	-	137.30
14	-	8.12 (d)	-	131.42
15	-	8.23 (s)	-	134.56
16	-	7.77 (t)	-	129.16

*Peaks are overlaid

**Peak is overlaid with TFA

Table 3.1 ^1H and ^{13}C NMR chemical shift data for the 100:0 and 60:40 PEKK structures, with atoms assigned as detailed in Figure 3.2, and splitting patterns for ^1H NMR spectra

The overlaid ^1H NMR spectra show peaks associated with the IPC links, most notably at 8.12, 8.23 and 7.77 ppm, which grow into the spectrum for the 100:0 PEKK. Similarly, the overlaid ^{13}C NMR spectra show peaks associated with the IPC links growing into the spectrum of 100:0 PEKK. Exact values of chemical shift are detailed in Table 3.1. This structural analysis is identical to that of Zolotukhin⁶. The incorporation of IPC in the monomer feed into the polymer is confirmed. Increasing the IPC quantity in the monomer feed increases the intensity of the peaks associated with the IPC in both the ^1H and ^{13}C fully relaxed spectra. Under these conditions, the chain ends are in too low concentrations to be detected and analysed successfully. This may be resolved by increasing the number of scans.

Monomer feed T:I	Polymer T:I
100:0	100:0
90:10	91:9
80:20	79:21
70:30	72:28
60:40	61:39

Table 3.2 Comparison of the TPC:IPC ratio in the monomer feeds compared to that of the resultant PEKKs, as determined by a deconvolution analysis of the ^{13}C NMR spectra in the carbonyl region at δ_C 198 – 199.5 ppm

The two distinct carbonyl peaks associated with the T and I units, occurring at δ_C 198-199 ppm, Figure 3.3 expansion, were used to determine if the stoichiometric ratio of TPC:IPC in the monomer feed was transferred to the polymer. Rather than using simple integration of the two peaks, a deconvolution simulated a Lorentzian peak which instead fitted first to peak-width-at-half-height, and then to the area. This method allowed more accurate determination of area, and therefore a more accurate stoichiometric ratio. By this method, it was demonstrated that the monomer feed stoichiometry was successfully translated to the polymers over the range of TPC:IPC ratios, to within 2% accuracy, Table 3.2, indicating a very controlled synthesis.

3.4 Thermal properties

The PEKKs were subject to DSC analysis to determine the effect of the T:I ratio on the thermal properties of the bulk material. The PEKKs were subject to two heating cycles of 90-400 °C at 20 °C.min⁻¹ followed by cooling from 400-90 °C at 10 °C.min⁻¹ *i.e.* one examining the particulate polymer and one examining the consolidated film. DSC data is given in Table 3.3 and Figure 3.4, and trends in thermal properties are illustrated in Figure 3.5.

During the first heating cycle carried out on the particulate PEKKs Figure 3.4a, all of the PEKKs except the 100:0 PEKK exhibited double melting peaks, indicating two crystalline states. These peaks converged and increased in temperature on decreasing the I content, until a single melting peak was observed for the 100:0 PEKK. The double melting peaks are likely to be due to the different crystal structures of the T-T and T-I sections of the polymer^{5, 10}. T_g and T_m both decreased with increased I content. The enthalpy change associated with T_m also decreased with increased I content, indicating a lower degree of crystallinity. During the first cooling cycle, Figure 3.4b, single T_c s were observed which decreased and broadened,

accompanied by a decreased enthalpy change, with increased I content. The 60:40 PEKK did not demonstrate a T_c indicating that it was amorphous at this point.

1st heat-cool cycle

Polymer	Heating					Cooling			
	$T_g/ J.g^{-1}.K^{-1}$		T_{m1}	T_{m2}	$J.g^{-1}$	$T_g/ J.g^{-1}.K^{-1}$		$T_c/ J.g^{-1}$	
60:40	193.7	0.081	274.7	301.5	-43.31	153.5	0.162	-	-
70:30	197.3	0.046	312.8	332.0	-39.80	146.7	0.012	245.2	32.34
80:20	218.1	0.084	355.6	365.9	-36.49	157.1	0.009	295.8	42.64
90:10	227.0	0.058	372.7	383.6	-56.18	-	-	331.7	44.70
100:0 *	215.7	0.088	388.7	-	-61.38	154.8	0.013	335.5	44.14

2nd heat-cool cycle

Polymer	Heating				Cooling			
	$T_g/ J.g^{-1}.K^{-1}$		$T_m/ J.g^{-1}$		$T_c/ J.g^{-1}$		$T_g/ J.g^{-1}.K^{-1}$	
60:40	162.0	0.297	-	-	-	-	154.7	0.205
70:30	160.9	0.104	331.2	-29.1	245.5	31.28	145.4	0.004
80:20	161.6	0.001	358.1	-34.94	297.6	42.85	134.5	0.001
90:10	150.6	0.025	379.5	-43.88	329.4	47.62	-	-
100:0 *	175.8	0.059	389.8	-45.23	328.3	43.80	171.6	0.078

*maximum temperature of 420 °C

Table 3.3 DSC data for two heating and cooling cycles: the first of the PEKK powder heating from 90 °C to 400 °C at 20 °C.min⁻¹ followed by cooling from 400 °C to 90 °C at 10 °C.min⁻¹, the second of the resultant consolidated PEKK heating from 90 °C to 400 °C at 20 °C.min⁻¹ followed by cooling from 400 °C to 90 °C at 10 °C.min⁻¹.

60:40 PEKK is ordinarily considered to be amorphous. However, the particulate 60:40 PEKK directly from the reactor was highly crystalline and exhibited two melting peaks. It is known that PEKK films may undergo solvent-induced crystallisation in DCM⁵. It is likely that the DCM in the polymerisation system induced crystallinity in the PEKKs during the polymerisation. In comparison, the PEKK was amorphous during the second heating cycle since the solvent induced crystallinity had been destroyed during the first heating cycle.

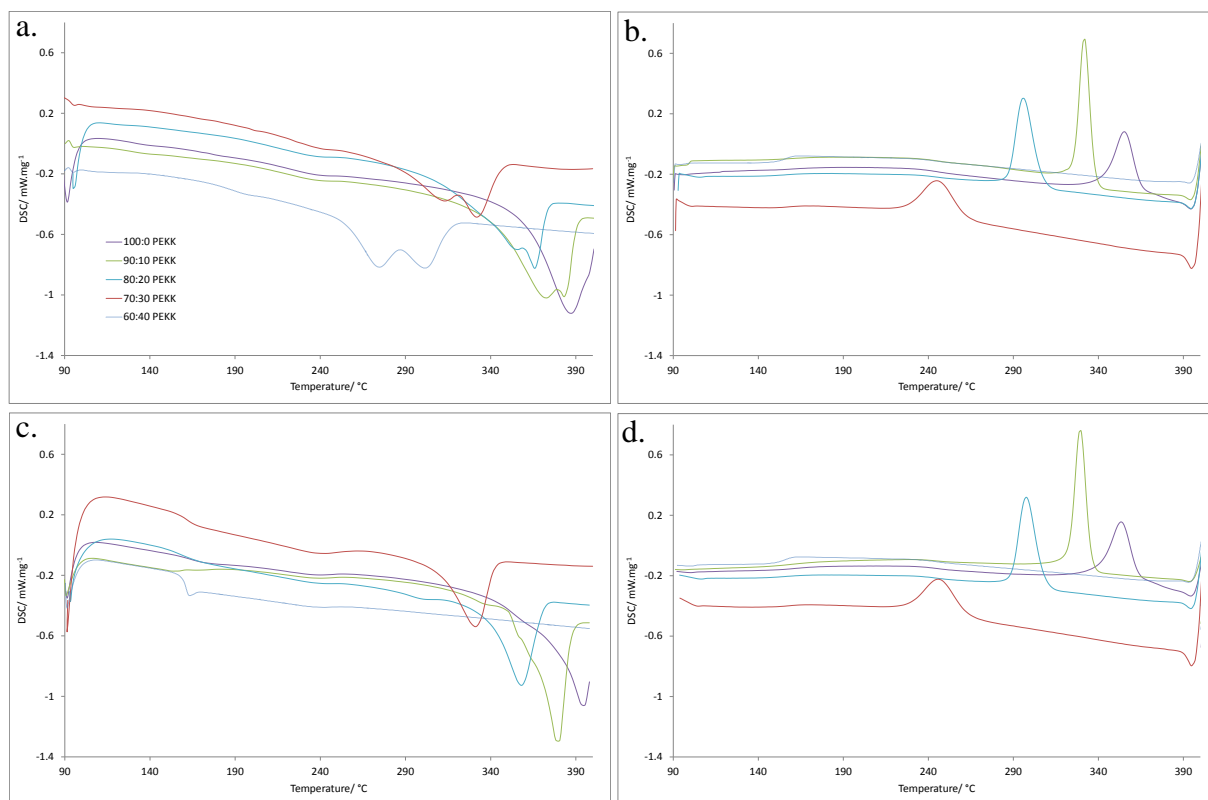


Figure 3.4 DSC traces for two continuous heating ($20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) and cooling cycles ($10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) of 100:0, 90:10, 80:20, 70:30 and 60:40 PEKKs, a. The first heating cycle of the particulate polymer from $90\text{ }^{\circ}\text{C}$ to $400\text{ }^{\circ}\text{C}$, b. The first cooling cycle of the sample from $400\text{ }^{\circ}\text{C}$ to $90\text{ }^{\circ}\text{C}$, c. The second heating cycle of the now consolidated sample from $90\text{ }^{\circ}\text{C}$ to $400\text{ }^{\circ}\text{C}$, d. The second cooling cycle of the sample from $400\text{ }^{\circ}\text{C}$ to $90\text{ }^{\circ}\text{C}$

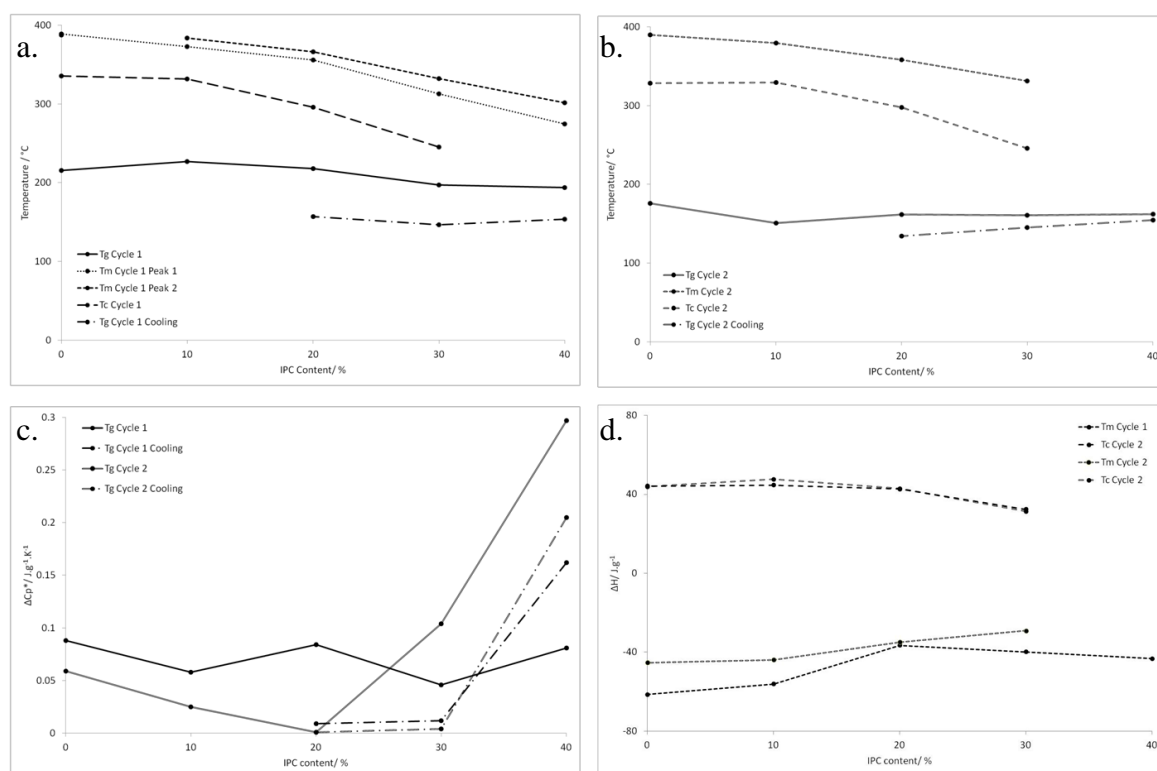


Figure 3.5 The trends in glass transition, crystallisation and melting temperatures and associated energy transitions of 100:0, 90:10, 80:20, 70:30 and 60:40 PEKKs over two heating ($20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) and cooling ($10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) cycles

$^{\circ}\text{C}\cdot\text{min}^{-1}$) cycles of 90°C to 400°C , as determined by DSC, a. The trends in glass transition, crystallisation and melting temperatures for the first heating and cooling cycle of the particulate polymer from 90°C to 400°C and the polymer melt from 400°C to 90°C , b. The associated energy transitions for the glass transition, crystallisation and melting temperatures for the first heating cycle of the particulate polymer from 90°C to 400°C and the polymer melt from 400°C to 90°C , c. The trends in glass transition, crystallisation and melting temperatures for the second heating and cooling cycle of the now consolidated polymer from 90°C to 400°C and the polymer melt from 400°C to 90°C , d. The associated energy transitions for the glass transition, crystallisation and melting temperatures for the first heating cycle of the particulate polymer from 90°C to 400°C and the polymer melt from 400°C to 90°C .

The DSC trace for the second heating cycle is shown in Figure 3.4c. On increasing the I content, the T_g decreases from 175.8 to 162.0°C . The introduction of the IPC has little effect on the mobility of the predominantly T polymer backbone. The effect of increasing the I content on the T_m is more pronounced, decreasing the T_m of the 100:0 PEKK from 389.8°C to 331.2°C of the 70:30 PEKK. Since T_m s are dependent on the presence and extent of crystallite formation in a polymer, a T_m is not observed for the 60:40 PEKK after initial melting, indicating that it is amorphous. 100:0 PEKK is highly crystalline due to the effective packing of the T units in the crystal lattice. X-ray studies¹¹ demonstrated that the average bond angle between both ether and ketone groups, linked by a phenylene, was 124° , with a 10 \AA distance between every second group. This highly ordered, planar “zig-zag” configuration, is conducive to crystallisation¹². The I units have a different geometry, do not pack as efficiently and disrupt the formation of crystal lattices. The lower degree of crystallinity results in a lower T_m . Increasing the I content continually decreases the T_m until the amorphous 60:40 PEKK is observed.

During the cooling cycle, Figure 3.4d, increasing the I content decreases the crystallisation temperature, for the reasons detailed above. It is also expected that polymers with higher degrees of crystallinity will have narrower crystallisation peaks since there is lower barrier to the ease of crystallisation, and this effect is partially demonstrated.

3.5 Polymer processability

3.5.1 Molecular weight determination by inherent viscosity measurements

Molecular weights of PAEKs are determined using IV measurements in concentrated sulfuric acid rather than the more common method of gel permeation chromatography, due to their poor solubility in common solvents. A target molecular weight is determined by the end application but in general must be high enough to impart mechanical properties on the bulk material but low enough to be easily processable.

The PEKKs with variable T:I ratio should have the same molecular weight since they were all polymerised at 3% out-of-balance. For this polymerisation system, a 3% out-of-balance should result in a PEKK with IV $0.8 - 0.9 \text{ dL.g}^{-1}$ ¹³. However, considering that these reactions were carried out on a one litre scale, a small amount of monomer loss will have a large effect on the resultant molecular weight of the polymer, as discussed in Chapter 2. It is inevitable that a small degree of monomer loss will occur which could be avoided by the use of a closed reaction system or by converting the monomers to high density tablet or flake form. Therefore, small variation in molecular weight was anticipated.

Inherent viscosities were calculated using a 0.1 wt% polymer solution in concentrated sulfuric acid at 25 °C. The measurements were carried out by hand using a glass Ostwald viscometer, and take into account the time it takes for the polymer solution to run through the viscometer compared to the solvent. Inherent viscosity is calculated in dL.g^{-1} using,

$$\text{inherent viscosity} = \ln(t_{\text{sample}}/t_{\text{solvent}}) / C$$

where t_{sample} is the time taken in seconds for the polymer solution to run through the viscometer, t_{solvent} is the time taken in seconds for the solvent to run through the viscometer and C is the concentration of the polymer solution in g.dL^{-1} .

The viscosity average molecular weight (M_v) is then calculated from the inherent viscosity value using the Mark-Houwink equation,

$$[\eta]_{25^\circ\text{C}} = k (M_v)^a \text{ (dL.g}^{-1}\text{)}$$

where $[\eta]_{25^\circ\text{C}}$ is the inherent viscosity in dL.g^{-1} at 25°C and k and a are the polymer specific Mark-Houwink constants.

Literature values of k and a for PEKK were not available, so those for PEEK were used as an approximation according to

$$[\eta]_{25^\circ\text{C}} = 6.195 \times 10^{-5} (M_v)^{0.94} \text{ (dL.g}^{-1}\text{) (PEEK)}^{14}$$

to calculate the M_v for each of the PEKKs, Table 3.4.

Polymer T:I	Inherent viscosity/ dL.g^{-1}	Molecular weight (M_v)
100:0	0.88	26,100
90:10	0.80	23,600
80:20	0.78	23,000
70:30	0.77	22,700
60:40	0.90	26,800

Table 3.4 Inherent viscosity measurements for the PEKKs, as determined in concentrated sulfuric acid at 25°C , together with the corresponding M_v values

Little variation and no trend in the inherent viscosity values of the PEKKs was observed, with the average being 0.83 dL.g^{-1} , corresponding to an average M_v of 24,440. Since there is little difference in the IV values over the range of T:I ratios, this variation is likely to be due to monomer loss rather than the effect of variable T:I ratio.

3.5.2 Polymer melt rheology and thermal stability

Melt viscosity and thermal stability are vital for the processing of thermoplastics since processing is carried out at $15 - 20^\circ\text{C}$ above T_m , by for example, extrusion or injection moulding. In both cases, the polymer is molten and must reside in the equipment for an amount of time, during which it must not decompose or crosslink. The melt viscosity must be

balanced so that the molten polymer flows into the moulds efficiently, but does not flow out uncontrollably. The melt viscosity of a polymer will decrease if it decomposes due to chain scission, resulting in decreased molecular weight. Conversely, melt viscosity will increase if the polymer crosslinks, resulting in increased molecular weight. A change in molecular weight of the molten polymer during processing is often accompanied by a darkening in colour due to oxidation. Figure 3.6 shows the colour of extruded PEKKs of a. good melt stability, b. poor melt stability and c. very poor melt stability.

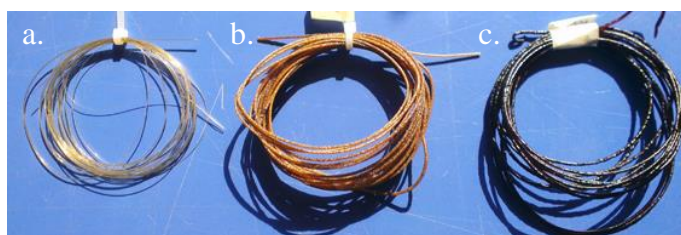


Figure 3.6 Extruded PEKKs with a. good melt stability, b. poor melt stability, and c. very poor melt stability

Thermal stability can be measured by parallel plate rheometry, which measures the viscosity of the molten polymer at constant temperature and shear rate over time. Melt viscosity (η^*) measurements and processing require temperatures of approximately 15 °C above the melting temperature. For PAEKs with $T_{m,s}$ of 365 °C or less, these parameters are usually 380 °C over 30 minutes. The temperature may be increased up to 390 °C if required, although this may result in polymer degradation. For this study, a polymer was deemed stable if its viscosity did not change by 50% over 30 minutes. This is based on the fact that it takes approximately 30 minutes to change a die on an industrial extruder without the barrel being emptied¹³.

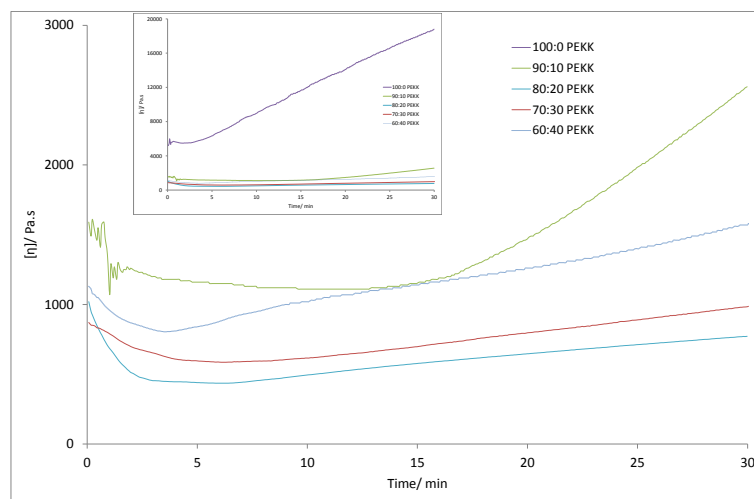


Figure 3.7 Melt viscosity of 100:0, 90:10, 80:20, 70:30 and 60:40 PEKKs at 380 °C (100:0 PEKK at 400 °C) and a shear rate of 1 s^{-1} over 30 minutes by parallel plate rheometry

It would be expected that the T:I ratio would not affect the melt viscosity since melt viscosity is generally affected by molecular weight, as described in Chapter 2. The PEKKs are too similar for a structural influence to be apparent. The 70:30 and 80:20 PEKKs had approximately equal melt viscosities, of 800 – 900 Pa.s, expected due to their similar molecular weights. The 60:40 PEKK has a higher melt viscosity, most likely associated to its higher molecular weight rather than to the influence of T:I ratio. The 90:10 PEKK initially maintains a similar melt viscosity to the 80:20 PEKK which then increases over the final 15 minutes, probably as the analysis temperature is not high enough to maintain a melt of the high T_m material. The 100:0 PEKK has a much higher initial melt viscosity of 5,000 Pa.s at 400 °C, as this temperature is unlikely to fully melt the 100:0 PEKK with a melting point of 390 °C. The viscosity of the polymer rose rapidly to 18,000 Pa.s after 30 minutes due to a high level of thermal degradation.

The melt viscosity of the 60:40, 70:30, 80:20 and 90:10 PEKKs were recorded at 380 °C, and demonstrate little change in melt viscosity over 30 minutes. However, the melting temperature of 100:0 PEKK is 389.8 °C, requiring a processing temperature of over 400 °C.

This is not desirable, as at this temperature the polymer degrades, causing a rapid increase in viscosity. For this reason, 100:0 PEKK is not suitable for industrial applications.

3.6 Polymer morphology

3.6.1 Particle size

The most attractive attribute of the dispersion process is the ability to produce near-spherical, particulate PEKK at high reactor loading without post-polymerisation processing such as cryogenic grinding. It is most common that PEKK is produced in the form of flake. Competing processes that produce particulate PAEKs have been reported, but at much lower reactor loading of 2 – 3% ¹⁵, which is not economically viable for an industrial synthetic process.

Mastersizer light scattering was used to examine the effect of the T:I ratio on the PEKK particle size. A continuous phase of 50:50 vol% IPA:water was required to sufficiently wet the particles and to avoid agglomeration. The particle size distributions are shown in Figure 3.8. The volume-weighted mean increased from 71.1 μm for 100:0 PEKK to 166.1 μm for 60:40 PEKK. Increasing the IPC content of the PEKKs increased both the mean particle diameter and the range of particle diameter, indicated by the greater difference between the D(0.1) and D(0.9) values, whilst decreasing the uniformity of shape, Table 3.5. It is hypothesised that a high % crystallinity *i.e.* for the 100:0 PEKK, causes overall contraction of the polymer, resulting in smaller particles. Conversely, a greater incorporation of IPC results in a more amorphous and less compact structure, resulting in larger particles. An alternative explanation is that the polymer becomes more soluble in DCM with increased IPC content, resulting in a swollen structure and larger particles. The porous nature of the particles maintains the larger particle size on drying.

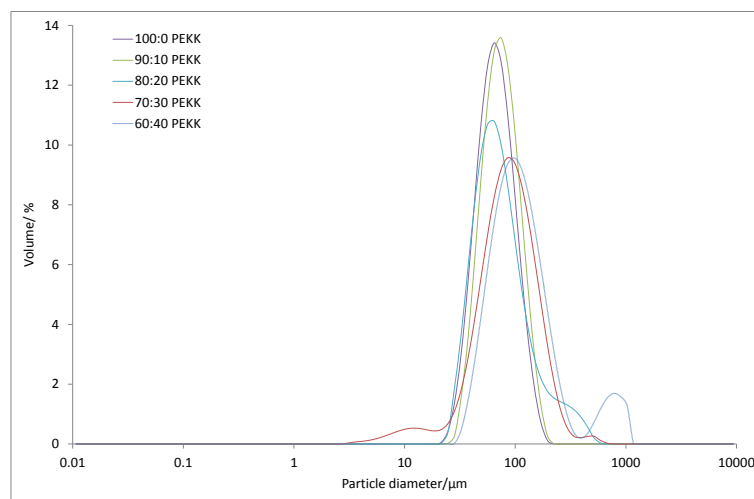


Figure 3.8 Particle sizing distributions for 100:0, 90:10, 80:20, 70:30 and 60:40 PEKKs, as recorded by Mastersizer light scattering in 50:50 IPA:water solvent.

Polymer	Mean particle diameter/ μm		D (0.1)	D (0.5)	D (0.9)
	Volume weighted	Surface weighted			
100:0	71.1	61.1	39.6	65.7	110.1
90:10	78.5	68.1	44.5	72.9	120.4
80:20	91.7	64.6	38.4	68.5	171.6
70:30	98.3	58.1	37.8	85.0	172.5
60:40	166.1	96.1	54.1	105.2	352.6

Table 3.5 Mean particle diameter data and distribution percentiles for 100:0, 90:10, 80:20, 70:30 and 60:40 PEKKs, as determined by Mastersizer light scattering in 50:50 IPA:water solvent.

A small particle size tail was observed for 70:30 PEKK, whilst large particle size tails were observed for 80:20, 70:30 and 60:40 PEKKs. Larger particle size tails may be attributed to the agglomeration of smaller particles, caused either by physical agglomeration of the particles or by poor wetting and distribution of the particles by the solvent. It is suspected that all of the polymers would initially demonstrate small particle size tails but most small particles are washed through the 40 μm mesh during workup. This cannot be avoided whilst maintaining efficient filtering procedures on a laboratory scale.

3.6.2 Particle shape

SEM was used to investigate the effect of T:I ratio on the shape of the particulate PEKKs, Table 3.6. The aim was to produce spherical PEKK consistently. It was found that T:I ratio

does have an effect on the shape of the polymer particles which are produced. Particles of 100:0 PEKK are near-spherical and have a relatively smooth surface. As the I content and particle size increases, the particles also become more irregular in shape. It appears that many of the particles were hollow and have imploded, possibly during drying stages under vacuum. However, the 70:30 PEKK particles were more irregular, with the appearance of agglomerates.

White flecks were observed on the SEM images of the PEKK samples in Table 3.6, which were confirmed to be calcium salts by *in situ* EDS analysis. The workup of the PEKKs was carried out in tap water, with the final wash being conducted in deionised water. Calcium salts were deposited into the particulate PEKK from the tap water. Later workup procedures were carried out entirely in deionised water to avoid this complication.

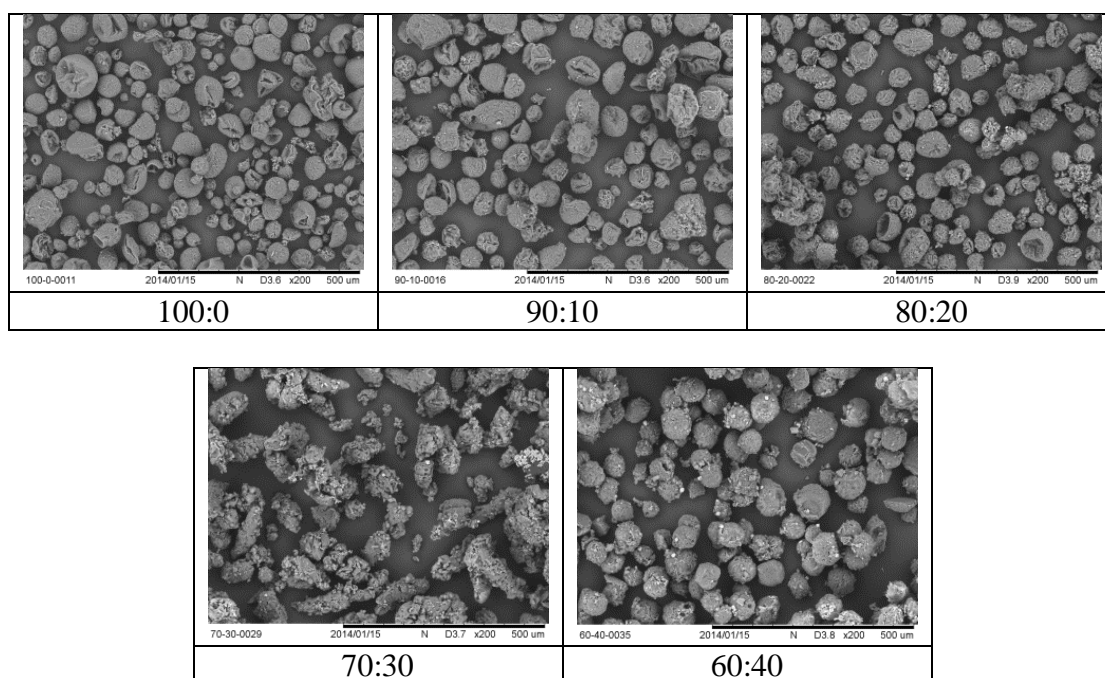


Table 3.6 SEM images of particulate PEKK with 100:0, 90:10, 80:20, 70:30 and 60:40 T:I ratios

100:0 PEKK particles¹³ synthesised under the same conditions were “potted and polished” in epoxy resin to examine the interior of the particles, Figure 3.9. The particles were found to

have a porous centre with a skin on the outside. It must be noted that some of the particles were flattened during polishing, so this internal structure cannot be seen on all samples. It is suspected that the HCl gas evolved during the polymerisation causes the formation of pores within the particles. The more dense skin forms on the outside where the HCl can escape efficiently. It is likely that the particles produced in this study have the same internal porous structure, although further analysis would be required for confirmation.

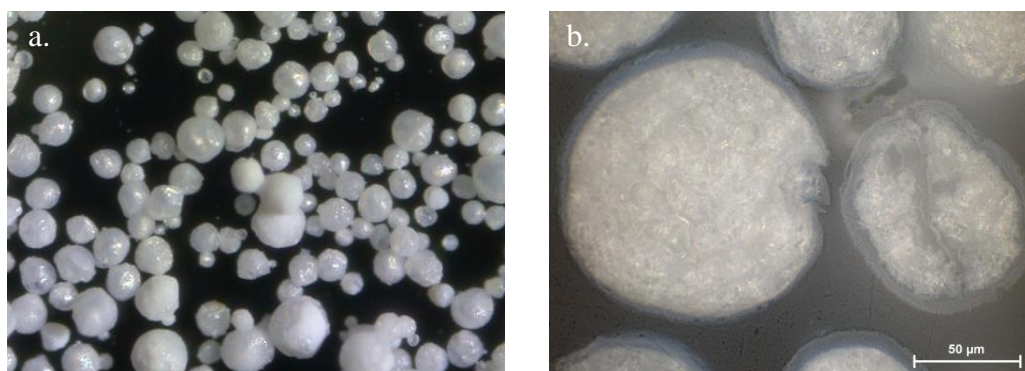


Figure 3.9 Optical microscopy images of a. largely spherical PEKK particles, b. “potted and polished” PEKK particles

The syntheses of PAEKs in particulate form have been reported by electrophilic precipitation polycondensation^{16, 17}. A concentration dependence was apparent as at a monomer concentration of 0.20 mol.L^{-1} , PEKEKK was produced in the form of smooth elliptical particles in the range of $0.4 - 0.7 \text{ mm}$. However, at 0.15 mol.L^{-1} , aggregates of smooth spherical particles of 0.1 mm were produced, and at 0.083 mol.L^{-1} a mixture of needles and rough elongated particles of $0.4 - 0.7 \text{ mm}$ were produced. Visually, these appear more similar to the 70:30 particles in this study. Morphology was also dependent on the TPC:IPC ratio, where a mixture of smooth spherical particles and needles were produced with all T PEKEKK, and on addition of IPC, ribbons joined at a central point were produced. Structural characterisation of the products was later carried out¹⁸ and it was discovered that the spherical particles were formed of polymer, whilst the needles were formed of dimer macrocycles due to ultra high dilution.

An alternative to achieve fine particulate PAEKs was proposed by a rapid quenching method¹⁹, where heated PEEK solution is rapidly cooled to induce nucleation and precipitation. This method produced PEEK particles of 0.6 μm in diameter.

There is no report of an alternative synthetic route to produce fine particulate PAEKs at high reactor loading.

3.7 Crystallinity and mechanical strength

PAEKs are semi-crystalline, which imparts solvent resistance and mechanical strength. The determination of the maximum degree of crystallinity and the rate of crystallisation are required processing parameters. For example, during injection moulding, the maximum degree of crystallinity must be reached in the mould as further external crystallisation may cause contraction of the moulded part. Overall, this allows tightening of the design parameters.

The degree of crystallinity of a polymer can be determined by DSC, by the comparison of the enthalpy change associated with the melting peak with the enthalpy of fusion of a 100% crystalline sample. For PEKK, the value of 130 KJ.mol^{-1} ²⁰ is commonly used. This is a theoretical value since PEKK has a relatively low maximum degree of crystallinity of 30 - 35%²¹.

Polymer T:I	Degree of crystallinity/ %
100:0	35
90:10	34
80:20	27
70:30	23
60:40	-

Table 3.7 The % crystallinity of PEKK with 100:0, 90:10, 80:20, 70:30 and 60:40 T:I ratios as determined by DSC

The 100:0 PEKK was calculated as having 35% degree of crystallinity, Table 3.7, which is similar to that of the maximum known value. On increasing the I content, crystallite formation is disrupted by the geometry of the I monomer segments, decreasing the overall degree of crystallinity until for the 60:40 PEKK, no crystallites form and the PEKK is amorphous.

A continuation from the determination of the effect of T:I ratio on the degree of crystallinity would be to quantify the effect of the T:I ratio on the rate of crystallisation. This could be studied by isothermal crystallisation methods.

3.8 Summary

PEKKs with 100:0, 90:10, 80:20, 70:30 and 60:40 T:I ratios were synthesised with a large degree of control by the dispersion process. The PEKKs were shown to have comparable properties to identical materials produced by different processes. The structures of the PEKKs were confirmed by NMR analysis, which also established that the stoichiometry of the monomer feed was translated to the polymer backbone with high success. Thermal (DSC) analysis demonstrated the presence of solvent induced crystallinity in the particulate samples which was erased once molten. Increased I content caused the decrease in T_g , T_m and T_c , together with the degree of crystallinity. Each of the PEKKs had comparable molecular weights and had good melt stability. The T_{ms} of the 100:0 PEKK and to an extent the 90:10 PEKK are too high to be considered for successful processing since they would require a temperature of over 400 °C. The most attractive attribute of the dispersion process is the ability to produce near-spherical, particulate PEKK at high reactor loading without post-polymerisation processing. This was achieved over the range of PEKKs and indicated that larger particles were produced at higher I contents. Overall, the work described in this chapter demonstrates that excellent control is achieved over the dispersion process to produce highly desirable particulate PEKK.

3.9 References

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CHAPTER 4 : THE ROLE OF BENZOIC ACID IN THE DISPERSION PROCESS

4.1 Benzoic acid in the dispersion process

It has been demonstrated in Chapter 3 that high molecular weight, fine particulate PEKK can be produced reliably by the dispersion process. The clear difference between the dispersion process and other reported processes to produce PAEKs is the use of benzoic acid which acts to maintain a fine particulate product at higher reactor loadings.

A Lewis base is used as a controlling agent in both the gel process and the dispersion process to modify the strength of the AlCl_3 Lewis acid. This Lewis acid:Lewis base complex does not participate in the polymerisation itself, but promotes the formation of high molecular weight polymer, largely free from side reactions by reversible complexation with the growing polymer chain. It is clear that the Lewis bases used for the gel process and the dispersion process have different actions as this is the only modification to the system, and result in different product morphologies. While the major aim of the Lewis base was to modify the reactivity of the Lewis acid catalyst, the overall mode of action was unclear. One explanation is that in the gel process, the aprotic dimethyl sulfone Lewis base: Lewis acid complex modifies the solubility parameter of the reaction system such that the polymer remains in solution or highly swollen over a longer time, allowing the propagation of a high molecular weight polymer¹. Likewise, the benzoic acid protic Lewis base used in the dispersion process could have this effect, but evidently also plays a vital role in the determination of polymer morphology.

The action of the benzoic acid is discussed in this chapter. Initial observations were supplemented by experiments devised to extend the understanding of the role of the benzoic

acid. Finally, an overall theory of the action of benzoic acid in the dispersion process is proposed.

4.2 Controlling agents

4.2.1 Known controlling agents

A different range of controlling agents can be used for the gel and dispersion processes respectively. Jansons¹ reported a large number of polar, aprotic controlling agents suitable for the gel process which span a wide variety of structures, although dimethyl sulfone is preferred since it produces polymer with the greatest stability. These compounds promote the production of polymer in the form of a gel. However, only three suitable controlling agents for the dispersion process, benzoic acid, benzenesulfonic acid and trifluoroacetic acid, have been reported², Figure 4.1. In comparison, these compounds are all polar and protic. Controlling agents for the dispersion process are referred to as dispersants.

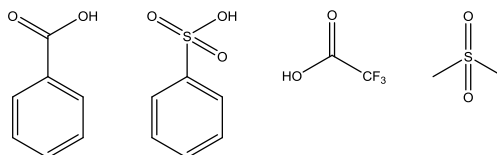


Figure 4.1 Structures of the known dispersants, benzoic acid, benzenesulfonic acid and trifluoroacetic acid, and the preferred controlling agent for the gel process, dimethyl sulfone

Initial investigations focused on these known dispersants with the intention of replicating the reported results. PEKKs were produced on a small scale using two of the dispersants, benzoic acid and benzenesulfonic acid, and two substances reported to promote the formation of gels, acetic acid and dimethyl sulfone. The morphology and colour of the PEKK products are detailed in Table 4.1.





Controlling agent	Final colour of worked up polymer	PEKK morphology	Image
Benzoic acid	Pale yellow	Fine particulate	
Benzenesulfonic acid	Pink	Large, cuboidal particulate	
Acetic acid	Pink/ brown	Coarse particulate	
Dimethyl sulfone	White	Flake	

Table 4.1 The effect of the dispersant on the colour and morphology of the PEKK products (1 mm scale)

The polymerisations using benzoic acid and the dimethyl sulfone produced PEKK in the form of fine particulate and gel respectively, in agreement with the reported observations^{1, 2}. However, the benzenesulfonic acid produced PEKK in the form of a large cuboidal dispersion where a fine dispersion was anticipated, and the acetic acid produced PEKK in the form of a coarse dispersion where a gel was anticipated, according to reported observations. These experiments were carried out on a small scale with relatively unregulated stirring. Although these may not be results obtained using optimum reaction conditions, this set of experiments suggested that benzoic acid and dimethyl sulfone have successful and predictable action, but benzenesulfonic acid and acetic acid have unpredictable action.

Under standard reaction conditions, PEKK is white after workup, which is not the case at longer reaction times. It has been advised³ that coloured PEKKs are unstable and are likely to be crosslinked.

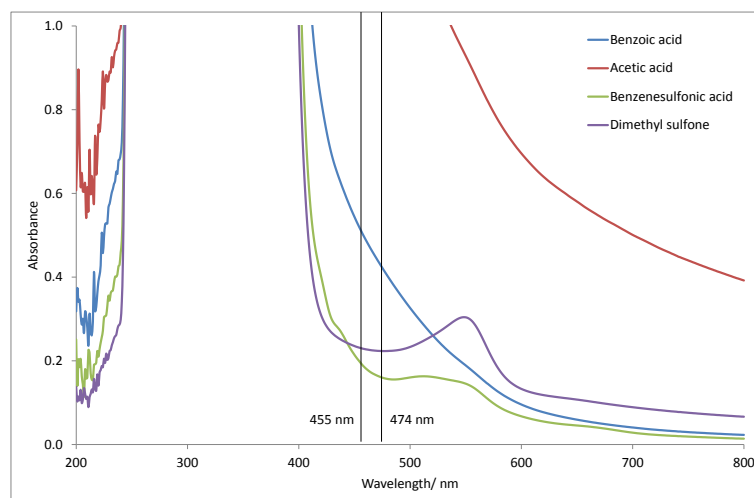


Figure 4.2 UV-vis absorption spectra of the PEKK produced by a range of dispersants, measured in a solution of DCM/TFA



Figure 4.3 Solutions of each of the PEKKs in DCM/TFA; from left to right PEKK by the use of acetic acid, benzenesulfonic acid, dimethyl sulfone, benzoic acid, reference (DCM)

It has been suggested that PEKK instability is related to the presence of 9-phenoxyxanthrol end groups⁴, as described in Chapter 2. UV-vis spectra of the PEKKs, Figure 4.2, were recorded of the PEKKs in DCM/TFA solution, Figure 4.3. λ_{\max} for 9-phenoxyxanthrol is 455nm⁴. While distinct peaks are not observed at this wavelength, the polymer solutions have variable absorbance at this wavelength. PEKKs produced with dimethylsulfone and benzenesulfonic acid had the lowest absorbances, PEKK produced using benzoic acid had a

higher absorbance, and PEKK produced with acetic acid had the highest absorbance, suggesting increasing 9-phenoxyxanthidrol content in this order.

Another proposed method of determining the stability of PEKKs is by calculating the quantity of defects in the polymer *via* its absorbancy index, A_s ⁵.

$$A_s = [\log(1/T)]bc$$

where b is the light path length in cm, c is the sample concentration in g.cm⁻¹ and T is the transmittance at the wavelength of measurement.

Dispersant	$A_s(474)$
Benzenesulfonic acid	4.8
Benzoic acid	16.1
Dimethyl sulfone	7.3
Acetic acid	off scale

Table 4.2 Absorbancy index values measured at 474 nm of PEKK produced by a range of dispersants

Often $A_s(474)$ is reported, the wavelength of measurement being 474nm. An A_s value of less than 15 is deemed to represent a stable polymer with few defects, and a value of more than 15 an unstable polymer with many defects. The A_s values, Table 4.2, for the PEKKs produced using different controlling agents suggested a range of levels of defects and stabilities. By this method, the PEKKs produced with benzoic acid and acetic acid were unstable, whilst the PEKKs produced with benzenesulfonic acid and dimethyl sulfone were stable. The two methods of stability determination were in approximate agreement.

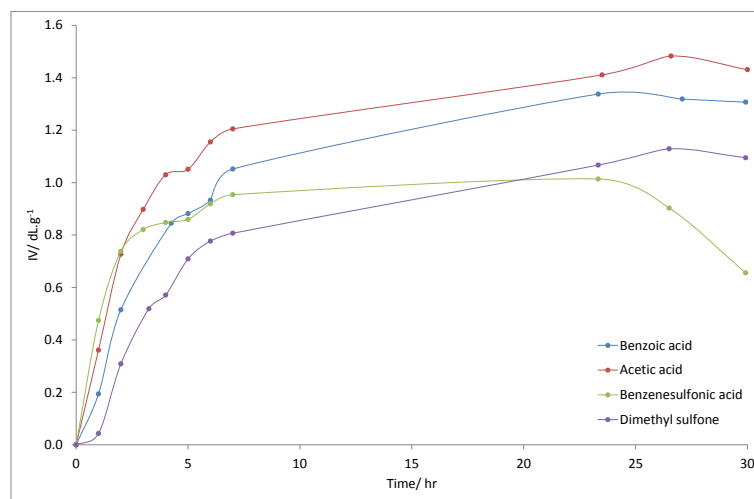


Figure 4.4 The evolution of inherent viscosity, and therefore molecular weight, over reaction time of PEKKs produced using a range of dispersants

The evolution of molecular weight for the range of PEKKs with reaction time was investigated by the relation of molecular weight to IV, Figure 4.4, by continuous sampling. A high initial rate of reaction was observed for all of the PEKKs, followed by a decrease in rate.

All of the PEKKs exhibited an inflexion in IV at about 5 hours. It is possible that this is the point at which linear polymerisation was completed and side reactions, such as crosslinking, began to occur. This theory is supported by the sustained increase in molecular weight beyond this point and the development of colour. The IV of the the PEKK produced using benzenesulfonic acid decreased at extended reaction times. This may be explained by the observation of insoluble gels in concentrated sulfuric acid which contribute to the mass of the sample used for the IV measurement. In this way, the gels act to artificially reduce the observed IV.

Overall, this is conflicting analysis but does suggest a range of stabilities of the PEKKs produced using a range of controlling agents. This data would need to be compared to that of

PEKK produced under standard reaction conditions, at a reaction time of 5 hours for a more conclusive result.

4.2.2 Screening of alternative dispersants

A continuation of the study on known dispersants was intended to discover an alternative successful dispersant to benzoic acid. Small scale PEKK polymerisations were carried out using a range of potential dispersants, Table 4.3, selected for their structural and chemical similarity to either benzoic acid or TFA, another of the reported dispersants.

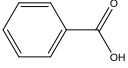

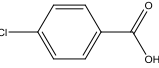





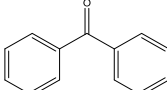

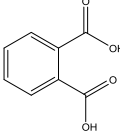

Dispersant	Structure	Polymer morphology	Image
Benzoic acid		Fine particulate (regular)	
4-Chlorobenzoic acid		Fine particulate (irregular)	
Chloroacetic acid		Coarse particulate	
Trichloroacetic acid		Coarse particulate	
Benzophenone		Coarse particulate	
Phthalic acid		Gel (blended)	

Table 4.3 The range of potential dispersants screened with their structures, together with the morphology of the PEKK produced and images of the polymer products (1 mm scale)

A range of PEKK morphologies were produced. Benzoic acid produced a fine, regular dispersion and 4-chlorobenzoic acid produced a fine irregular dispersion. Chloroacetic acid, trichloroacetic acid and benzophenone produced coarse particulate dispersions. Phthalic acid produced a gel which was blended on workup. Chloroacetic acid, trichloroacetic acid and benzophenone produced PEKK which was pink in colour, the PEKK produced using

chloroacetic acid being the darkest in colour, probably indicating a range of stabilities. However, the primary objective of these experiments was morphological analysis, and no further analysis was carried out.

Despite the production of PEKK dispersions using alternative potential dispersants, the PEKK dispersions were not as fine or as regular as those produced using benzoic acid. From this analysis alone, it would appear that the optimum Lewis base for the polymerisation of PEKK is benzoic acid. The screening of dispersants in this manner was inconclusive, and so a further screening approach was not carried forward. Further investigations focused on benzoic acid alone.

If an alternative dispersant had been discovered to produce a fine particulate, regular PEKK, other factors would need to be considered to determine if it would be a realistic alternative. Benzoic acid has the advantages of being inexpensive, easily handled, easily removed from the polymer, and recyclable.

4.3 Aluminium chloride morphology

An unsystematic experimental observation involved the morphology of the aluminium chloride used in the dispersion process. Aluminium chloride in the form of both granules and powder can be used as the Lewis acid catalyst for polymerisation in both the gel and dispersion processes. Aluminium chloride powder had previously been favoured for the gel process to avoid “hot spots” in the forming polymer gel by complexation, which could form due to the poor solubility of aluminium chloride in DCM. The disadvantage of the powder version is that its hygroscopicity is more pronounced due to its high surface area. Overall, aluminium chloride morphology was not deemed to be crucial. Aluminium chloride granules were used for all polymerisations unless otherwise stated.

AlCl₃ morphology	Reactor loading/ %	Polymer morphology
Granules	10	Fine particulate
Granules	15	Gel
Powder	10	Fine particulate
Powder	15	Fine particulate

Table 4.4 The combined effect of the aluminium chloride morphology and the reactor loading on the morphology of the PEKK product

A series of small-scale PEKK polymerisations were carried out using both aluminium chloride granules and powder, combined with both high and low reactor loadings, Table 4.4. It was observed that particulate PEKK could be produced at higher reactor loadings, of 15% compared to 10%, when using aluminium chloride powder than when using granules.

Zolotukhin reported the Friedel-Crafts dispersion polymerisation of PAEKs^{6, 7}. The components of the polymerisation are 1,2-dichloroethane solvent, monomers compatible with Friedel-Crafts polymerisation and aluminium chloride. The low reactor loading of approximately 3% produces PAEKs in the form of fine particulates. The morphology of the product is attributed to template polymerisation centred around the aluminium chloride particles⁸. This explanation could account for the experimental observations described, although it does not account for the action of benzoic acid.

4.4 Observation of crystal formation

An additional unsystematic experimental observation involved the formation of white crystals during the sequence of reactant addition. Previously, the importance of the order of addition of reactants had been largely overlooked, focusing solely on the monomer addition rather than the additional components. The standard order of addition was: half of the DCM – aluminium chloride – benzoic acid – TPC/IPC – EKKE – benzoyl chloride – any remaining DCM after washings. The overall intention was to add the aluminium chloride first to allow complexation to the other components as they were added, to more easily manage the resulting exotherms,

and to add the EKKE last to use the largest exotherm efficiently to increase the reaction temperature to 20 °C. Otherwise, it was thought that the order of the additions were essentially interchangeable.

It was previously observed that the addition of EKKE caused a colour change of the reaction mixture from yellow to orange due to the delocalisation across the EKKE monomer. The preceding additions caused no colour change, remaining pale yellow from the aluminium chloride slurry. Focusing purely on colour, it appeared that the notable point was the EKKE addition. At the point of addition of benzoic acid, no colour change was noted and the benzoic acid dissolved. On cooling to -20 °C after the addition, the mixture became opaque. This observation was previously attributed the precipitation of what was assumed to be benzoic acid on cooling. However, on inspection it was discovered that the opacity was in fact due to the precipitation of fine white crystals which were not benzoic acid.

4.4.1 Isolation of the aluminium complex

The next step was to isolate the crystals from the reaction mixture for analysis. Small scale reactions between aluminium chloride and benzoic acid in DCM were carried out to simulate the initial stages of a polymerisation sequence, using the same reactant stoichiometry as for a complete PEKK polymerisation at 3% out-of-balance and 10% loading, with 4 benzoic acid equivalents. Two approaches were investigated and are described further.

The first reaction was the exact replication of the first stages of polymerisation, where the white solid was isolated from the complete reaction mixture with a mass of 3.43 g. In the second reaction, the aluminium chloride slurry was left to settle, the liquor decanted and used for the next step of the reaction. Benzoic acid was added to the liquor, resulting in the precipitation of a fine white solid, in much smaller quantity than the first reaction, 0.016 g.

Aluminium chloride has poor solubility in DCM, *c.f.* 0.0072 g/100ml (chloroform)⁹, and so a very small quantity is in solution alone. These results suggested that the white precipitate was formed from both the dissolved and the solid aluminium chloride. It is possible that some aluminium chloride remained in the isolated sample or that not all of the sample was isolated. However, it can be seen that the reactions proceeded in approximately stoichiometric quantities.

The isolated product was subjected to preliminary analysis. White crystals are characteristic of pure aluminium complexes¹⁰. Pure aluminium chloride is white but in practice is often yellow due to an iron trichloride contaminant. It was therefore hypothesised that the white crystals could be ultrapure aluminium chloride. Many overlapping signals were observed in the aromatic regions of the solution ¹H and ¹³C NMR spectra which could not be resolved. This indicated that aluminium trichloride was not the product, and instead confirmed the presence of an aromatic component. Considering that aluminium chloride and benzoic acid were the only reactants, it was supposed that the product would be a straightforward single-centred aluminium benzoate or aluminium chlorobenzoate, Figure 4.5.

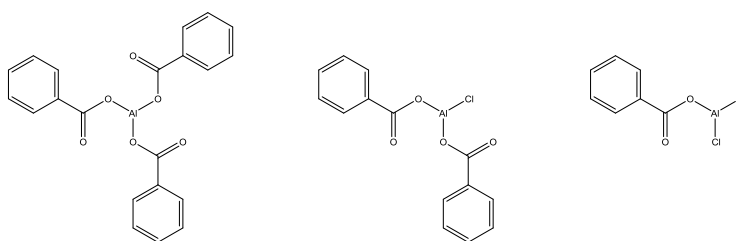


Figure 4.5 Structures of single centred aluminium tribenzoate and aluminium chlorobenzoates

Mass spectroscopy indicated a molecular ion of (m/z) 401, whilst aluminium tribenzoate has a molecular ion of (m/z) 390. Additionally, several fragments might be attributed to a form of aluminium chlorobenzoate, but others could not be assigned. It is possible that the aluminium complex could equilibrate between species *via* ligand exchange. Overall, this initial chemical

analysis was inconclusive. However, optical microscopy indicated that the compound was highly hygroscopic, absorbing water within seconds of exposure to air. Since the compound was not handled in a dry atmosphere, the discovery of the hygroscopicity and potential associated ligand exchange was a possible explanation for the inconclusive structural analysis.

Focusing on the fact that the molecular ion had (m/z) 401 and that the compound was hygroscopic, there were several suggested structures, Figure 4.6. Each of these structures have two aluminium centres and assume some ligand exchange with water on exposure to atmospheric moisture. An anhydrous initial product before isolation is likely, since any dissolved water in the DCM would complex to the aluminium chloride and effectively be removed from the reaction system.

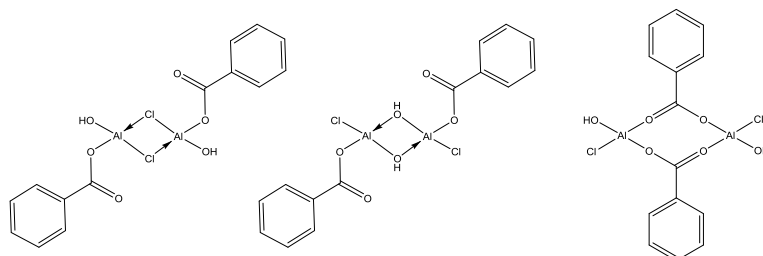


Figure 4.6 Possible structures of aluminium benzoate complexes to satisfy (m/z) 401

The analytical data obtained from the preliminary experiments was inconclusive, and further analysis in an anhydrous environment was necessary to obtain representative chemical and structural characterisation.

4.4.2 Anhydrous isolation of the aluminium complex

In the knowledge that the complex was highly hygroscopic, the methodology for the isolation of the crystals was repeated in an argon-filled glove box, which allowed a much more accurate and detailed characterisation. An accurate product mass still could not be obtained

due to the crude separation method, although again, the reaction proceeded in approximately stoichiometric quantity. A range of analytical techniques were employed.

X-ray photoelectron spectroscopy (XPS) was carried out, although the equipment required for anhydrous analysis was not available. XPS analysis confirmed the presence of carbon 68.20%, oxygen 22.04%, aluminium 6.40%, and chlorine 2.90%, Table 4.5, which broadly confirmed the molecular formula of aluminium tribenzoate, $\text{Al}(\text{BzO})_3$, where BzO represents benzoate.

Atom %	$\text{Al}(\text{BzO})_3$		AlCl_3 trace	$\text{AlCl}_2(\text{BzO})$ trace	$\text{AlCl}(\text{BzO})_2$ trace
	Actual	XPS			
C	75.00	68.20	71.29	70.67	66.44
O	21.43	22.04	23.04	23.30	25.13
Cl	0	2.90	0	0	0
Al	3.57	6.40	5.68	6.03	8.43

Table 4.5 Elemental composition of aluminium tribenzoate calculated theoretically and by XPS analysis, compared to the corrected elemental composition calculated with an impurity of AlCl_3 , $\text{AlCl}_2(\text{BzO})$ or $\text{AlCl}(\text{BzO})_2$

The XPS results were used to calculate a more accurate determination of the % components of the system. Considering the presence of chlorine in the analysis, it can be assumed that the major component is $\text{Al}(\text{BzO})_3$ with a trace quantity of either AlCl_3 , $\text{AlCl}_2(\text{BzO})$ or $\text{AlCl}(\text{BzO})_2$. Presuming that all of the Cl detected is attributed to one of the trace impurities, it can be subtracted from the % composition, together with the associated % Al (*i.e.* for AlCl_3 , % Al subtracted is % Cl/3). The total percentage compositions were then reassigned for the remaining quantities. The final % for the aluminium tribenzoate, taking into account each of the possible impurities, is detailed in Table 4.5. The closest match to both the XPS data and the theoretical value is if the impurity is AlCl_3 , resulting in a composition of 71.29% C, 23.04% O and 5.68% Al. The data is less in agreement with increased Cl composition. The % O is higher than the theoretical value, whereas the % C and Al are lower. Since this complex was not handled in an inert atmosphere, ligand exchange with water would increase the O

content whilst effectively decreasing the overall % C and Al. However, the presence of other chlorinated species was not ruled out.

Solution ^{27}Al NMR spectroscopy showed a large peak at 78.0007 ppm, with a minor peak at 89.8062 ppm, which is partially obscured by the reference. This indicated one major aluminium environment together with another minor aluminium environment. Solution ^{13}C NMR spectroscopy demonstrated peaks at 174.1981 (CO), 138.3226 (ArC), 133.2575 (ArC), 129.5763 (ArC), and 126.4665 (ArC) ppm, consistent with the presence of benzoate¹¹. Minor aromatic peaks were also visible, which could not be assigned.

The solid state ^{27}Al NMR spectrum showed two peaks at 29.8488 and -26.6183 ppm, indicating two aluminium environments. From their intensities, the species attributed to the peak at 29.8488 ppm is in significant excess to the one at -26.6183 ppm. It is possible that the weaker ^{27}Al signal is associated with the weaker ^{13}C signal. The solid state ^{13}C NMR spectrum demonstrated peaks at 170.6704, 170.187 (CO) 135.2632 (ArC), 134.1608 (ArC), 130.4434 (ArC), 129.2874 (ArC) ppm, again consistent with the presence of benzoate¹¹. The presence of two peaks which may be attributed to carbonyl is unexpected, although a single peak may be split. A seventh, much less intense, 124.1555 (ArC) peak is visible, but others may be present in the close and overlapping spectrum of peaks. This could be evidence for non-symmetry of the structure. However, it remained possible that the compound could be chemically symmetrical but geometrically non-symmetrical.

Mass spectroscopy confirmed the presence of $\text{Al}(\text{BzO})_3$ at m/z 390, together with a range of chlorinated fragments. Aluminium chloride was not detected, but its presence was not ruled out. This analysis was consistent with the presence of $\text{Al}(\text{BzO})_3$, in addition to a small quantity of chlorinated species.

FT-IR spectroscopy was carried out in both a solution cell in DCM and on KBr discs. The appearance of the carbonyl region was consistent with the presence of carboxylate anion by the peak at $1650\text{-}1550\text{ cm}^{-1}$ attributed to asymmetrical stretching, and another at approximately 1400 cm^{-1} attributed to symmetrical stretching. This is in agreement with reported assignment¹². It also confirmed that no water, $\text{Al}(\text{OH})_3$ nor hydroxyl groups were present due to the lack of a broad OH peak.

DSC analysis was attempted using both standard pierced aluminium pans in air, and high pressure steel pans prepared in an inert atmosphere. The success of sealing the steel pans was uncertain. Both methods produced DSC traces which contained a range of exothermic and endothermic peaks which could not be assigned. The traces differed between methods and the DSC analysis was inconclusive.

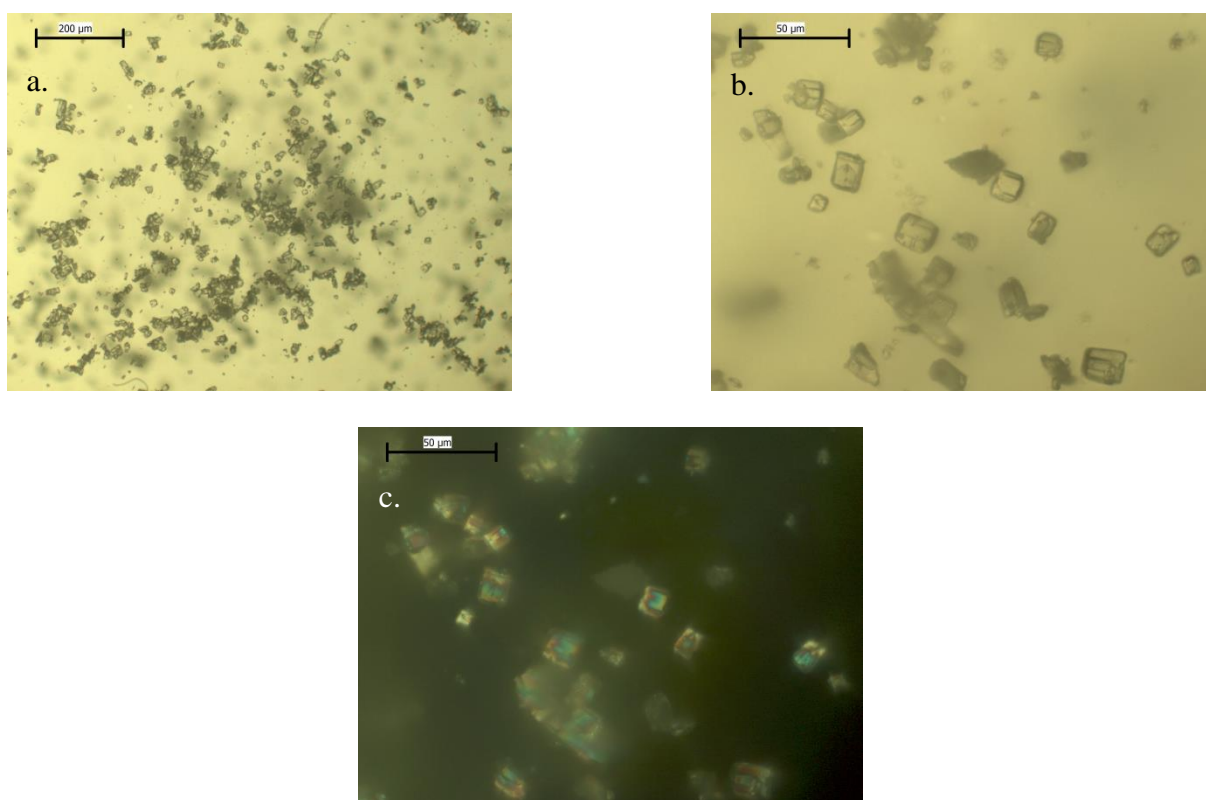


Figure 4.7 Optical microscopy images of the aluminium benzoate crystals, a. and b. transmission and c. birefringence

Optical microscopy demonstrated that the complex was crystalline. The crystals ranged in size, all below 25 μm in diameter, Figure 4.7.

Powder XRD spectroscopy was attempted using a capillary filled and sealed in an inert atmosphere. On analysis, no scattering was detected which was unexpected since the complex was crystalline.

Overall, the structural and chemical analysis suggested a major product $\text{Al}(\text{BzO})_3$ with minor chlorinated species. Definitive determination could be achieved by x-ray crystallography. Ideally, the aluminium benzoate would be isolated and reintroduced into the polymerisation system without benzoic acid to test its action. However, it is soluble in excess DCM and so this approach was not possible.

4.5 Order of addition of reactants

On isolation of the crystals, it was hypothesised that the crystals were acting as nucleants for particle formation. PEKK polymerisations were carried out, altering the order of addition of reactants to determine whether this affected either the crystal formation or the morphology of the polymer product. It might have been expected that the crystals would need to be formed pre-polymerisation to achieve successful nucleation. The order of addition of reactants for each polymerisation is detailed in Table 4.6.

Experiments 1 and 2 took the standard order of addition of reactants. Experiment 1 was the standard procedure, where the crystals form before monomer addition, but in experiment 2 all of the monomers were added quickly, before crystal formation. In experiments 3 and 4, the benzoic acid was added later in the process, and no benzoic acid was added in the experiment 5. Experiments using both 100:0 PEKK and 80:20 PEKK were carried out. The following

observations for experiments 1-4 applied to both polymers. The observations for experiment 5 are discussed in more detail.

PEKK	Order of addition of reactants					
	—————→					
1*	AlCl ₃	BzOH	crystal formation	TPC/IPC	EKKE	BzCl
2**	AlCl ₃	BzOH	TPC/IPC	EKKE	crystal formation	BzCl
3	AlCl ₃	TPC/IPC	BzOH	EKKE	BzCl	
4	AlCl ₃	TPC/IPC	EKKE	BzOH	BzCl	
5	AlCl ₃	TPC/IPC	EKKE	BzCl		

*Crystals formed before monomer addition

BzCl - benzoyl chloride

**All reactants added before crystals form

Table 4.6 Order of addition of reactants for each of the PEKK polymerisations, indicating the point of crystal formation.

Standard observations were seen for experiment 1. This comprised the production of a yellow slurry on the addition of aluminium chloride, the dissolution of the benzoic acid with no further colour change, the precipitation of white crystals as the mixture turned opaque, the dissolution of TPC and IPC with no colour change, the colour change from yellow to orange on the addition of EKKE, and no further colour change on the addition of benzoyl chloride.

The reactants were added before the formation of crystals in experiment 2. The same colour changes were observed during the additions, but the mixture remained transparent throughout. The orange mixture turned opaque approximately five minutes after the final addition, when a fine precipitate formed rapidly. By inspection, there appeared to be a greater quantity of aluminium chloride remaining as a slurry than in experiment 1. 100:0 PEKK and 80:20 PEKK were produced in the form of fine dispersions.

In experiment 3, the yellow slurry from the addition of aluminium chloride underwent no colour change on the dissolution of TPC and IPC nor benzoic acid. A transparent orange solution with aluminium chloride slurry was formed on the addition of EKKE. The orange mixture turned opaque approximately five minutes after the final addition, when a fine precipitate formed rapidly. 100:0 PEKK and 80:20 PEKK were produced in the form of fine dispersions.

In experiment 4, the yellow slurry from the addition of aluminium chloride underwent no colour change on the dissolution of TPC and IPC. A transparent orange solution with aluminium chloride slurry was formed on the addition of EKKE. No colour change was observed on the dissolution of benzoic acid. The orange mixture turned opaque approximately five minutes after the final addition, when a fine precipitate formed rapidly. 100:0 PEKK and 80:20 PEKK were produced in the form of fine dispersions.

In experiment 5, the yellow slurry from the addition of aluminium chloride underwent no colour change on the dissolution of TPC and IPC. A transparent orange solution with aluminium chloride slurry was formed on the addition of EKKE. The orange mixture did not turn opaque after five minutes, and remained in solution for approximately 20 minutes before it turned opaque and a phase separation occurred. The reaction mixture was darker orange than experiments 1-5 which were approximately the same shade. The 100:0 PEKK was formed as a coarse dispersion and the 80:20 PEKK was formed as a dense gel. A plaque of solid polymer gel formed on the bottom of the vessel, in comparison to experiments 1-5 which formed thin films only.













All of the polymerisations which included benzoic acid formed fine particulate PEKK, regardless of the order of addition of reactants, or if the crystals had formed prior to monomer

addition. This suggested an extremely robust process which is a huge benefit if scaled to a commercial process. Without benzoic acid, the 100:0 PEKK was particulate, possibly influenced by the high degree of crystallinity, and the 80:20 PEKK was a dense gel. Polymerisation still occurred without benzoic acid but the product morphology was uncontrolled. These experiments demonstrated that the aluminium benzoate crystals achieved the controlled synthesis of particulate PEKK, but it is not clear whether it was specifically aluminium benzoate that is required.

4.6 Introduction of additives

The aluminium benzoate crystals promoted the controlled synthesis of particulate PEKK. It was not known if it was the chemical composition of the crystals that was the important factor, or if any solid particles introduced into the reaction system would have the same effect. A range of additives were introduced into small scale PEKK polymerisations to explore their effect.

PEKK polymerisations were carried out on a small scale to include standard dispersion polymerisation conditions, a polymerisation without benzoic acid, and polymerisations with one and two molar equivalent of silica, alumina, sodium benzoate and graphite additives replacing the benzoic acid, compared to the theoretical quantity of aluminium benzoate produced from 4 benzoic acid equivalents at 10% loading.

Dispersant	One molar equivalent of additive	Two molar equivalents of additive
Benzoic acid		
None		
Silica		
Alumina		
Sodium benzoate		
Graphite		

*Graphite particles

- Larger particles 1 – 3 mm made up of agglomerated small particles < 1mm. No graphite
- Larger particles 1 – 3 mm mass. Graphite in interior seen through cracked surface.

Table 4.7 The morphology and size scale (1mm) of the PEKK s produced under standard dispersion process conditions, with no benzoic acid and with one and two molar equivalents of silica, alumina, sodium benzoate and graphite additives replacing the benzoic acid, compared to the theoretical quantity of aluminium benzoate (Polymers were white in colour)

The morphology of the PEKKs produced using each additive at one and two molar equivalents are detailed in Table 4.7. The standard dispersion process produced PEKK in the form of a fine dispersion, as anticipated. The incorporation of the additives produced PEKKs with a range of morphologies and sizes. PEKK produced with an alumina additive was in the form of large masses. Graphite additive produced a range of particle sizes but predominantly a coarse dispersion. Large masses were produced which encapsulated the graphite, Figure 4.8, and small elongated particles without encapsulated graphite agglomerated to form similar sized masses.



Figure 4.8 The two types of polymer morphology produced with a graphite additive, a. agglomerations on small elongated particles not containing graphite, b. large masses with encapsulated graphite visible through the surface cracks

It was hypothesised that each of the additive particles was acting as a locus for polymerisation, with the PEKK forming around the additive particles. It was also hypothesised that the addition of two molar equivalents of additive compared to the theoretical quantity of aluminium benzoate, would decrease the resultant polymer particle size. The polymer formation would be divided across a larger number of polymerisation loci, *i.e.* divided across a larger number of additive particles. Small scale PEKK polymerisations were carried out using the same range of additives as the previous study, but with double the quantity.

The standard dispersion process produced PEKK in the form of a fine dispersion, as anticipated. Hard gels were formed without benzoic acid and with the addition of silica and alumina. Graphite additive produced a range of particle sizes but predominantly a coarse

dispersion. As with the previous section, large masses were produced which encapsulated the graphite, and small elongated particles without encapsulated graphite agglomerated to form similar sized masses. Sodium benzoate additive produced a fine but irregular shaped dispersion.

Overall, the standard dispersion process produced PEKK in a controlled manner, despite being on the small scale. Without benzoic acid, the morphology of the product was unpredictable, ranging from a coarse dispersion to a gel. This could be accounted for by the unregulated stirring on the small scale. On increasing the molar equivalents from one to two, both of the PEKKs produced using silica and alumina increased in the size of the mass produced. It appears that these additives promote the agglomeration of polymer rather than to promote the discrete formation of particles. This can be likened to the polymer films which adhere to the inside of the glass reaction vessels. The addition of graphite caused the formation of two distinct types of masses. The graphite was encapsulated in large polymer particles which were single masses. In addition, a second type of mass comprised the agglomeration of small elongated particles which had not incorporated graphite. The addition of a larger quantity of graphite did not substantially alter the morphology.

The most successful additive, *i.e.* the additive which resulted in the smallest dispersion most similar to that produced by benzoic acid, was sodium benzoate. This produced a granular dispersion with one molar equivalent of sodium benzoate, and a fine but irregular dispersion with two molar equivalents. Sodium benzoate has most similar chemical structure and composition to aluminium benzoate, although it is pre-formed rather than formed *in situ*. While it is not definitively known if the chemical structure or composition of the additive is critical for the morphology of polymer formation, it may be supposed that the most similar compounds would have the most similar action. In this system, sodium benzoate could

provide the benzoate for ligand exchange to form aluminium benzoate, and so may not be the active species itself.

From this preliminary investigation it was found that additives can either increase or decrease the size of the polymer mass produced. This suggests that the chemical composition of the nucleating particle is critical. The additives were not all the same size, but it is possible that polymer particle size may be related to dispersant size. This effect could be investigated by the incorporation of a range of particle sizes of the same additive. In addition, the experiments only investigated the morphological effect of the additives, and further work would be required to determine if they had any effect on the bulk polymer properties.

If any of these dispersants were to be used further, a complication would be the post polymerisation removal of the additive. It is likely that the sodium benzoate could be removed by the standard workup procedure. However, silica, for example, could not be removed in this manner. This could have its own application as a toughening agent which would usually be blended into a polymer matrix. It is possible that this *in situ* addition could offer better dispersion of the toughening material in the matrix, and that a range of functional additives, *e.g.* graphene for conductivity and strength, could be incorporated. It is not known whether the additives are chemically bonded to the polymer. Also, the effect of using both benzoic acid and an additive in the polymerisation system is not known.

4.7 Overall theory of the action of benzoic acid

The overall theory for the action of the benzoic acid in the dispersion process encapsulates all of the concepts discussed in this chapter. As previously stated, the primary action of the benzoic acid is dependent on its Lewis base character. The benzoic acid complexes with the aluminium chloride catalyst to modify the strength of the aluminium chloride Lewis acid and

therefore to limit side reactions during polymerisation. However, the benzoic acid has additional actions in the polymerisation system, promoting the production of a particulate PAEK product.

It is well known that solid additives can be introduced into polymer melts to promote crystallisation. A range of sources have reported the use of aluminium benzoate, basic aluminium benzoate and sodium benzoate as nucleating agents for polyolefins, specifically polypropylene¹³⁻¹⁵. These additives cause the crystallisation of smaller and more numerous spherulites on cooling the melt. It was agreed that the addition of monocarboxylic, benzoic acid-type compounds were most successful, but there was debate whether aluminium salts¹³ or sodium salts¹⁵ were most effective. It was also reported that aromatic carboxylic acids were more effective than aliphatic carboxylic acids, and the effectiveness was altered with ring substituents. Generally, ring substituents decreased the efficiency of nucleation, although the most symmetrical compounds crystallised the fastest. On the addition of both sodium benzoate and aluminium benzoate to polypropylene, electron probe microanalysis confirmed the presence of aluminium and sodium respectively at spherulitic centres only¹⁶, suggesting heterogeneous catalysis. It was also confirmed that the aluminium benzoate caused a greater abundance of smaller spherulites than sodium benzoate, which caused a higher T_c than sodium benzoate.

Polymer nucleation theory was extended to PAEKs. However, instead of the use of a solid additive, the fluorine end groups of PEEK produced by a nucleophilic reaction were modified by further nucleophilic reaction with a phenate salt, $\text{NaOPhSO}_3\text{Na}$, to have $-\text{SO}_3\text{Na}$ chain ends¹⁷. The ionic association of the chain ends resulted in “chemical nucleation”¹⁸ which increased crystallisation rate and crystallisation density compared to the unmodified PEEK.

Solid additives of talc and glass bubbles have been reported for PEEK¹⁹, but to act as tougheners rather than nucleating agents.

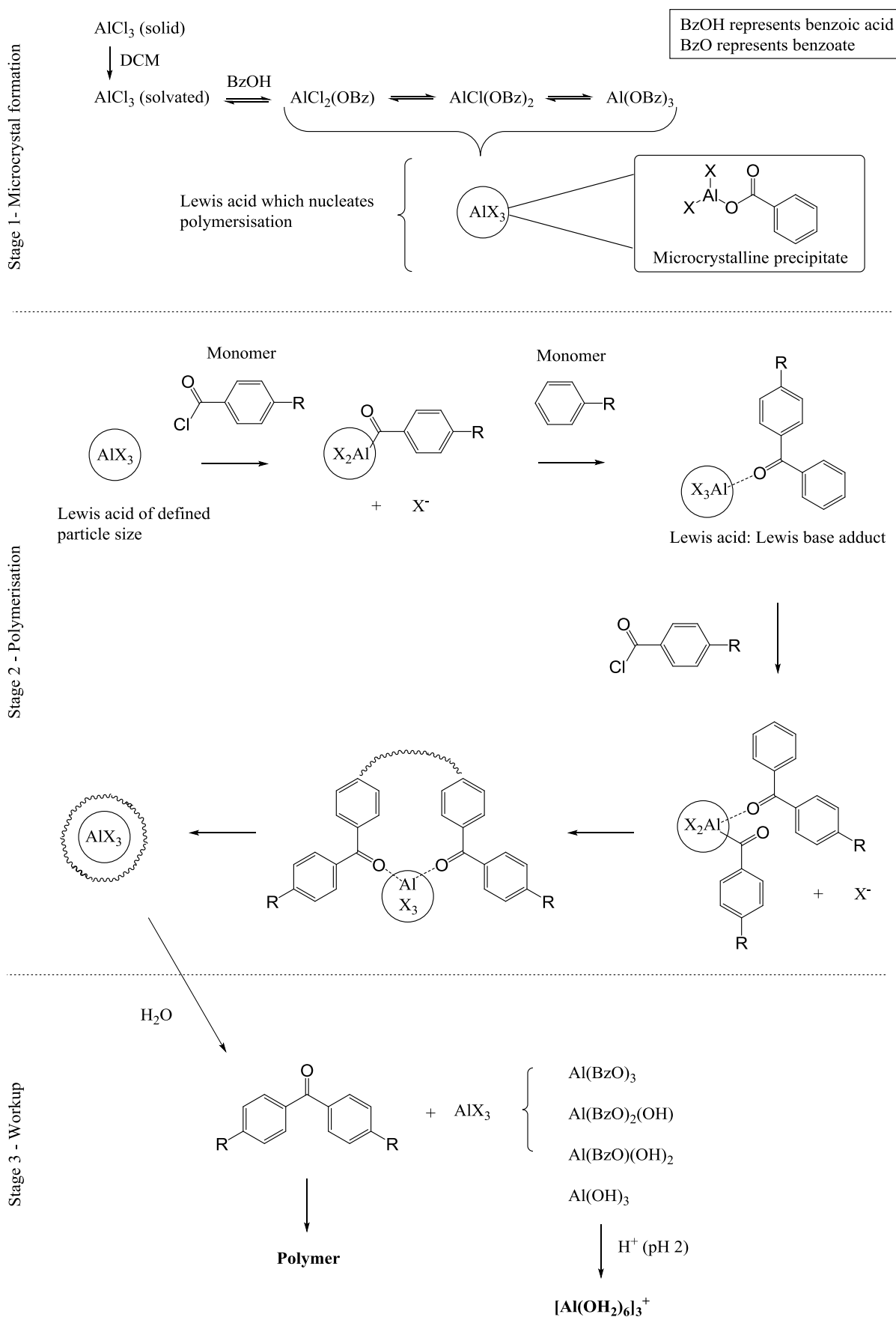
This nucleation approach was extended to the *in situ* formation of aluminium carboxylates as nucleating agents for polypropylene²⁰. A solution of an aromatic carboxylate and a solution of an aluminium salt were added to a slurry of polypropylene powder. On extraction of the solvent, a mixture of polypropylene powder and a finely divided aluminium aromatic carboxylate remained. This mixture was then melted and solidified by cooling to promote crystallisation.

A successful nucleant should be wetted by, but be insoluble in, the polymer at or below the T_m ²¹. It should have a T_m higher than that of the polymer, should be non-volatile and should not react in the polymer system. Ideally, it should also have a crystal structure similar to that of the polymer. These parameters are applicable to a nucleant added to a polymer melt. However, if a nucleant was to be used in the dispersion process, this would be nucleating during polymerisation itself, not in the polymer melt. Therefore, these parameters would need to be applicable in the polymerisation system. Applying this theory to the dispersion polymerisation system, the aluminium benzoate is stable in the system, however it is not known if the crystal structures of the aluminium benzoate and PEKK are similar. This could be confirmed by x-ray crystal structure determination.

If the aluminium benzoate was acting as a nucleant for particle formation, and potentially simultaneous crystallisation, during polymerisation in the dispersion process, it may have been expected that the nucleating species would need to be present prior to monomer addition. However, it was demonstrated by the order of addition of reactants study that the process was robust, forming particulate PEKK during all sequences, regardless of at which point the

benzoic acid was introduced. This suggested that the benzoic acid reacted with the aluminium chloride only, and that the large excess of AlCl_3 remained available after monomer addition.

The action of the nucleant can be accounted for by encapsulation interfacial polymerisation, where a polymer forms around an inorganic substance to produce a shell²², which can be applied to the dispersion process. This type of heterophase system is classified as a dispersion²³ polymerisation since initially all of the reactants are dissolved in a homogeneous solution. When the polymer precipitates, the DCM is a poor solvent for the polymer and swells the structure. The polymer forms around the inorganic particle to form a shell, which is followed by monomer migration to thicken the polymer layer. The polymerisation occurs at the polymer – DCM interface. In addition, it is probable that the aluminium benzoate also acts as a heterogeneous catalyst for Friedel-Crafts polymerisation.



Scheme 4.1 The suggested role of benzoic acid in the dispersion process

The following description is a plausible explanation for the action of benzoic acid in the dispersion polymerisation system, which would need further experimental verification. A schematic representation to accompany the explanation is detailed in Scheme 4.1.

Stage 1 – Microcrystal formation

Solid AlCl_3 dissolves in DCM with poor solubility. On the addition of benzoic acid, which is soluble, an equilibrium is established between AlCl_3 , AlCl_2BzO , $\text{AlCl}(\text{BzO})_2$, and $\text{Al}(\text{BzO})_3$ by ligand exchange. These complexes would be expected to increase in solubility with the number of benzoate ligands, and their formation draws further solid AlCl_3 into solution according to Le Chatelier's principle. A central core crystal structure develops, involving Al^{3+} and benzoate bound using chelation of the bidentate benzoate ligand and dative bonding of O to Al^{3+} . At this point, the complex is soluble. At a critical point where little free benzoic acid remains, complete ligand exchange can no longer occur, and the equilibrium shifts at the crystal surface towards $\text{AlCl}(\text{BzO})_2$. As the complexed structure increases in size, it reaches the solubility limit and formation of a microcrystalline precipitate occurs. The microcrystals have similar size since they grow at the same rate, but critically they all possess an Al-Cl bond at the surface capable of reaction as a Friedel-Crafts catalyst.

A structure for AlX_3 which would satisfy these criteria is shown in Figure 4.9, which assumes octahedral aluminium centres and involves both bidentate and bridging benzoate ligands. These two aluminium environments would explain the two NMR spectroscopic analysis. In this case, the minor peaks would not be attributed to AlCl_3 impurity but instead to the surface complexes. It may also explain why AlCl_3 was not detected by mass spectroscopy. Definitive structural characterisation could be achieved by the x-ray crystallography.

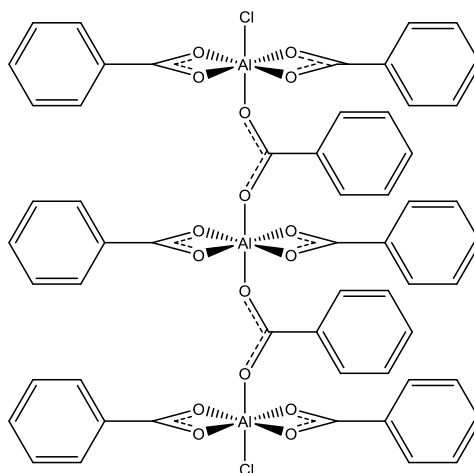


Figure 4.9 A proposed structure for AlX_3

Stage 2 - Polymerisation

The microcrystals have two actions; firstly to template the polymerisation and secondly to act as a Lewis acid for Friedel-Crafts polymerisation. The microcrystals of AlX_3 *i.e.* central $Al(BzO)_3$ with exterior chlorinated complexes, act as a Friedel-Crafts catalyst by complexation with an acid chloride monomer. Addition of an arene monomer subsequently occurs. The dimer remains associated with AlX_3 *via* the carbonyl lone pair, to form a Lewis acid:Lewis base adduct. The next acid chloride monomer complexes with AlX_3 at a location further around the microcrystal. This monomer can then undergo Friedel-Crafts acylation with the dimer of the Lewis acid:Lewis base adduct. Repetition of this process and the movement of the site of complex formation results in polymerisation around the microcrystal to form a polymer shell. Growth occurs around each crystal until completion, resulting in uniform polymer particle size. It is likely that this highly regulated template polymerisation results in a crystalline polymer since the microcrystal tethers the incoming monomers and resultant polymer in a defined conformation *via* the Lewis acid:Lewis base interaction.

This model is in agreement with the observations from the benzoic acid concentration study. The same mass of polymer is produced for each example, and only the benzoic acid concentration (and associated aluminium chloride concentration) is altered. Aluminium

benzoate crystals, assumed to be in a tight size range and with high surface area, are formed *in situ*. At a high concentration of benzoic acid, a large number of aluminium benzoate crystals form, rather than larger crystals. The overall polymer mass is spread between a large number of nucleating crystals, only a small amount of polymer forms around each nucleus, resulting in small particles of controlled size, Figure 4.10. If the number of benzoic acid equivalents is decreased from four, a smaller number of nucleating crystals are present. The overall polymer mass is spread between a smaller number of crystals, the polymer mass per crystal is higher, resulting in larger particles. If no benzoic acid is used, then the polymerisation does still occur but the particle size is solely dependent on the turbulence generated by the stirrer setup, often resulting in centimetre sized masses of polymer.

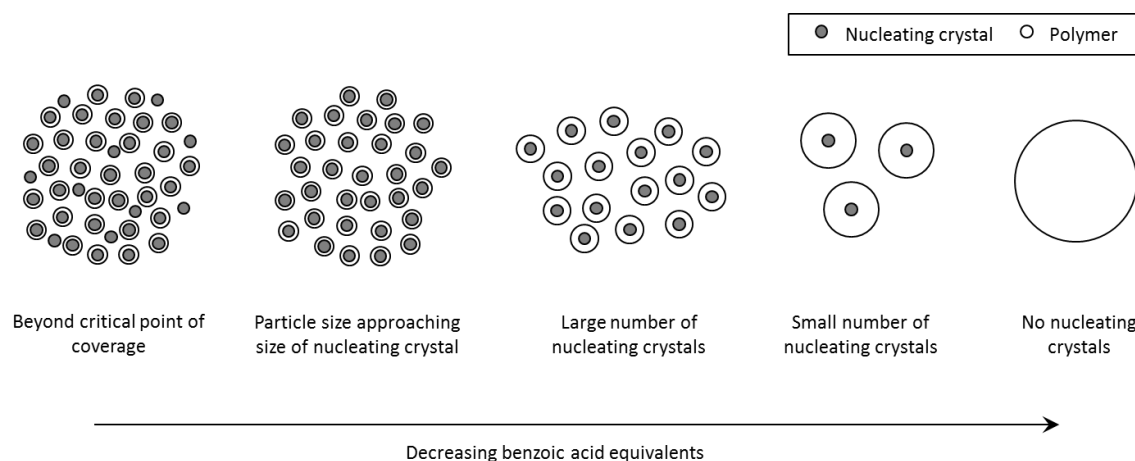


Figure 4.10 Illustration of the theory of polymer nucleation by aluminium benzoate crystals on decreasing the number of benzoic acid equivalents, and therefore the number of nucleating crystals, in the polymerisation system.

Conversely, on increasing the number of benzoic acid equivalents from four, little change in particle size is observed. A greater number of nucleating crystals are present, the overall polymer mass is spread between a larger number of crystals and the polymer mass per crystal is lower. It may be expected that this would result in smaller particles, however, the size of the nucleating crystal is the limiting factor for particle size. Only a very thin polymer layer forms on the crystal. It may also be assumed that a critical point exists where complete

coverage of the nucleating particles cannot be achieved. This could be an explanation as to why the dispersion process required fast stirring in the initial stages to avoid agglomeration of the polymer particles. When some whole crystals or sections of crystals remain exposed, these areas are able to interact with the polymer shell forming on other crystals due to the Lewis acid:Lewis base interaction, to result in the agglomeration of particles. Only when the polymer shell has fully formed around the crystal do the particles no longer agglomerate. The assumption is that one crystal is in the centre of each polymer particle.

Stage 3 - Decomplexation

Decomplexation in iced water removes the AlCl_3 which was initially complexed to the monomers, to result in $\text{Al}(\text{OH})_3$. $\text{Al}(\text{OH})_3$ is an insoluble “gelatinous” precipitate in water, which is observed experimentally. Conversely, water alone does not break down the highly ordered AlX_3 crystal structure. The acid wash is required for two reasons; firstly to convert the insoluble $\text{Al}(\text{OH})_3$ to soluble $[\text{Al}(\text{OH}_2)_6]^{3+}$, and secondly to break down the AlX_3 crystal structure to $\text{Al}(\text{BzO})_3$, $\text{Al}(\text{BzO})_2\text{OH}$, $\text{Al}(\text{BzO})(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ which are subsequently converted to $[\text{Al}(\text{OH}_2)_6]^{3+}$. $[\text{Al}(\text{OH}_2)_6]^{3+}$ is water soluble and can be extracted from the polymer during the workup procedure.

It would be thought that larger polymer particles would have more residual benzoic acid than smaller polymer particles. In this case, the overriding factor for benzoic acid removal would be structural *i.e.* pores, wettability and transport, rather than the hydrolysis of the aluminium benzoate complex.

In summary, a series of characteristics appear to have been coincidentally combined to result in an extremely successful dispersant in the form of benzoic acid. The benzoic acid is an effective Lewis base for the polymerisation reaction which maintains the polymer in solution

for long enough to produce high molecular weight polymer. The benzoic acid reacts with the aluminium chloride to form small aluminium benzoate crystals which act as nucleating centres for the polymerisation, resulting in a PAEK dispersion. The aluminium benzoate complex is broken down by water during the workup procedure, the benzoic acid removed from the polymer in acidic solution, and the resultant ions removed from the polymer during subsequent workup steps through the porous structure of the particles. While it was discussed in Chapter 3 that the porous nature of the particles was likely to be due to the evolution of HCl during the polymerisation, it is also possible that the aluminium benzoate crystals are a source of porosity. When the crystals are broken down during the workup procedure, it is likely that pores remain inside the polymer particles in their place.

In later chapters it is demonstrated that a range of copolymers can be produced by the dispersion process. Although many polymerisations are successful, the sizes of the dispersions are variable. It may be possible that while aluminium benzoate is a suitable nucleating agent for PEKK, it may not be the optimum selection for other copolymers. Further work would be required to fully optimise the dispersion process for a wide range of copolymers, either by modification of the existing parameters or by the use of an alternative dispersant.

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CHAPTER 5 : PAEK COPOLYMERS

5.1 PAEK copolymers

Previous chapters have focused on the development and optimisation of the dispersion process and the associated parameters, specifically for the reliable production of PEKK. This process optimisation has resulted in a vast increase in the available design window for the production of particulate PAEK copolymers. This chapter discusses the production of a range of PAEK copolymers by the dispersion process. The production of dispersion PEKEKK, PEKEKK-imide and PEKEKK-sulfone polymers were studied and evaluated in depth, while the success of the dispersion process to produce a selection of more unusual copolymers underwent preliminary evaluation.

5.2 Functional group incorporation

A large variety of copolymers can be produced reliably by the gel process^{1,2} by the incorporation of monomers containing a wide range of functionalities. Once integrated into the polymer backbone, these groups alter the T_g , T_m , T_c and degree and rate of crystallinity of the polymer. Each functional group has a different effect on the polymer properties, dependent on its flexibility and ability to form crystalline domains. As long as the potential for Friedel-Crafts polymerisation is maintained, either the “EKKE type” dinucleophilic monomer or the diacid chloride monomer may be modified³. Self-polymerising monomers may also be used, although are not discussed further in this study. In addition, the incorporated groups must be stable in the polymerisation system. Some example structures of monomers known to produce polymer successfully by the gel process include those in Figure 5.1, where X represents a variable functional group.

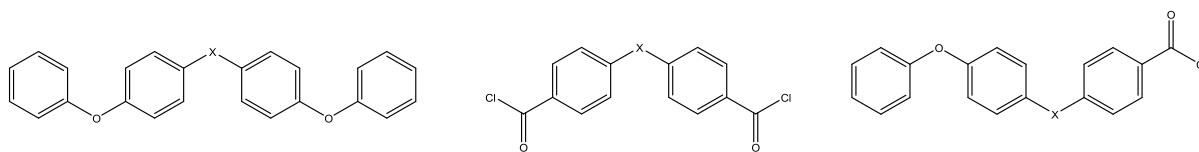


Figure 5.1 Example structures of dinucleophilic, diacid chloride and self-polymerising monomers for the gel process, where X represents a variable functional group

Dinucleophilic monomers suitable for the gel or dispersion processes are either in the “standard-X” form or “EXE” form, Figure 5.2, where X represents a variable functional group. The standard-X monomers have a central functional group with terminal phenylene groups, and the EXE monomers have a central functional group with terminal phenoxybenzene groups.

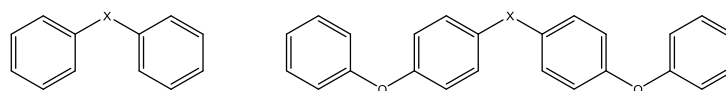


Figure 5.2 “Standard-X” and “EXE” dinucleophilic monomers

When selecting possible X groups, the reactivity of the group must be considered. In a small molecule context, the reactivity of these monomers depends on the functional groups incorporated into them. A substituent on a benzene ring can either be *ortho*-/*para*- directing or *meta*- directing to electrophilic attack depending on whether the substituent is electron donating or electron withdrawing respectively⁴. Functional groups such as $^+NR_3$ and CF_3 are electron withdrawing by induction, deactivate the ring and result in *meta*- substitution. Functional groups such as NO_2 , CN , COR and SO_3R are electron withdrawing by conjugation, deactivate the ring and result in *meta*- substitution. Functional groups such as alkyl and phenyl are electron donating by induction, activate the ring and are *ortho*-/*para*-directing. Functional groups such as $OCOR$, $NHCOR$, OR , OH , NH_2 and NR_2 have an electron withdrawing effect by induction, due to their electronegativity, which deactivates the ring. However, they also have a lone pair of electrons which is electron donating by conjugation. This dominant effect results in an overall activation of the ring which is *ortho*-

/para- directing. Halides have a similar effect as they are both electronegative and have a lone pair. Cl, Br, I and F are electron withdrawing by induction but electron donating by conjugation, and overall are *ortho-/para-* directing.

This principle may be applied to monomer design. The monomers used in the gel process require the electron withdrawing, *ortho-/para-* directing X groups to avoid cyclisation reactions and to result in stable all 1,4- substituted linear polymers⁵. These effects are most pronounced for the standard-X monomers, but have less effect on the EXE monomers due to the greater distance of the X group from the terminal phenyl ring. Realisable groups for the standard-X monomers which produce high molecular weight polymer by the gel process are ether and aliphatic (CH₂CH₂). Realisable groups for the EXE monomers are more varied, to include ether, ketone, sulfone, imide, amide, naphthalene, ester, azo, phenylquinoxaline, benzimidazole, benzoazole, benzothiazole and aliphatic^{1,2}. The carbonyl functionality in EKE or EKKE deactivates the terminal ring to a great enough extent to prevent *ortho-* substitution, as discussed in Chapter 2.

The relative reactivity of monomers can be predicted by the relationship of δ_C of the *para*-carbon on the terminal phenyl ring to the Hammett-Brown constant for the functional group⁵⁻⁷, since there is a strong correlation between the two parameters. This effect is illustrated in Figure 5.3 by the correlation between δ_C of the *para*- carbon on the terminal phenyl ring to the Hammett-Brown constant for the functional group of a range of mono substituted benzenes. However, the effect of the addition of AlCl₃ into the reaction system must be considered also, as the complexation will affect the chemical shift and therefore the reactivity of the monomer.

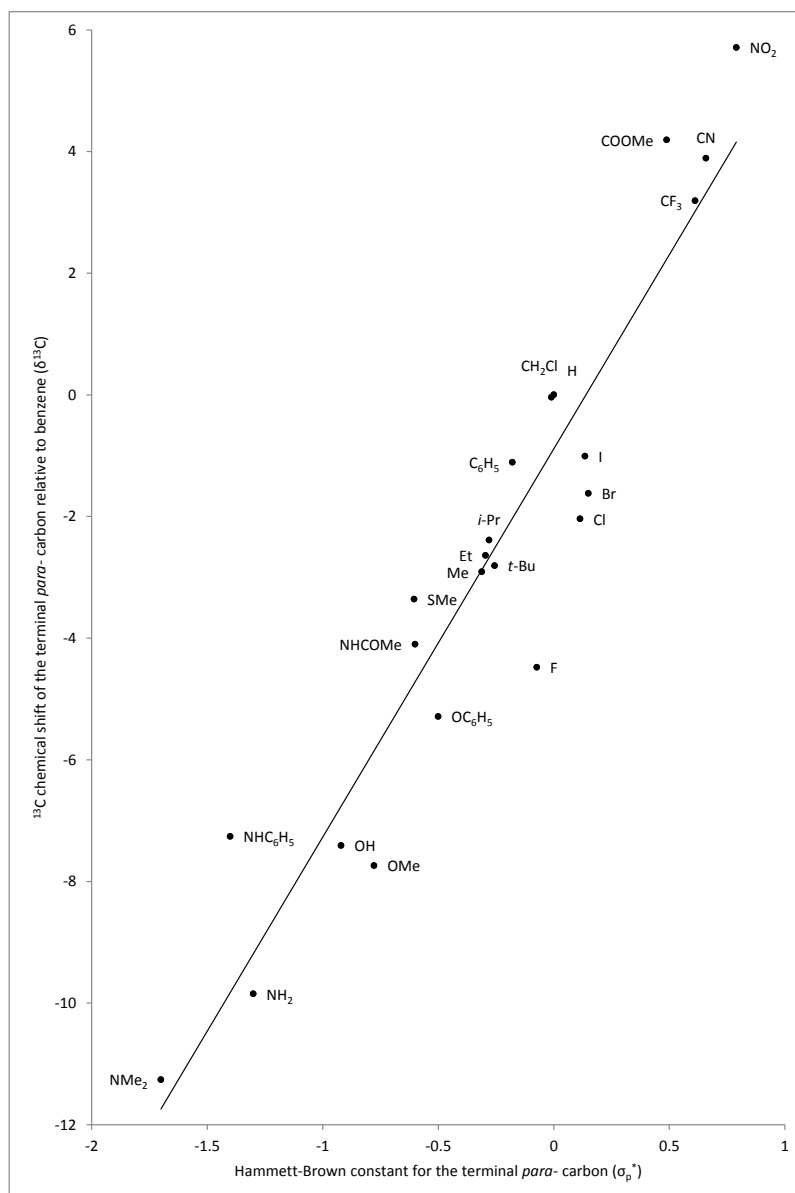


Figure 5.3 The relationship between the Hammett-Brown constant for the terminal *para*- carbon (σ_p^*) and the ^{13}C chemical shift of the terminal *para*- carbon relative to benzene ($\delta_{\text{C}^{13}}$) for a series of monosubstituted benzenes with the functional groups as listed⁵⁻⁸

The incorporation of a wide variety of functional groups into the monomer system allows the design and synthesis of materials to address specific applications. The high performance properties of the PAEKs, including temperature resistance and oxidative stability, are maintained by the aromatic ether ketone sections. When it was first discovered, the dispersion process was thought to be inconsistent and unpredictable, and monomers which are suitable for the gel process were not guaranteed to be transferable to the dispersion process. This observation was in relation to polymer morphology rather than to bulk polymer properties,

which remained comparable to those produced by the gel process. It was thought that the range of possible particulate polymer products was very limited. However, by modification of the dispersion process parameters, most notably by increasing the benzoic acid concentration in the polymerisation system, a range of fine particulate PAEK copolymers were synthesised successfully by the dispersion process. These copolymers underwent structural and thermal analysis.

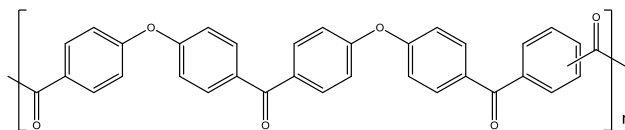
5.3 Poly(ether ketone ether ketone ketone) (PEKEKK)

PEKEKK is an alternative material to PEKK with lower T_g , 161 °C compared to 165 °C, and lower T_m , 377 °C compared to 386 °C, for the fully 1,4- versions⁹. This results in a lower processing temperature combined with a marginally lower use temperature. PEKEKK is thought to offer greater thermal stability⁵, which is important during composites manufacture, where multiple heating cycles are carried out. T_c is another important parameter as the degree of crystallinity at T_c regulates the size of the part *i.e.* a greater degree of crystallinity results in greater contraction of the part. If a material is not stable, the contraction must be designed into the specification. The stabilisation of the materials properties allows tightening of the design window.

Previous studies¹⁰ demonstrated the production of PEKEKK by the dispersion process but it was noted⁵ that its synthesis was not reliable over the gel process, most often producing a gel but producing a dispersion on occasion. Particulate PEKEKK has also been synthesised at low reactor loading without a dispersant¹¹.

Poly(ether ketone ether ketone ketone) (PEKEKK) was synthesised by the reaction of bis(4-phenoxyphenyl)methanone (EKE) with TPC and IPC, using the standard dispersion process¹². A range of PEKEKKs were synthesised over a T:I range in order to evaluate and adapt the

standard dispersion methodology to produce particulate PEKEKK reliably. The effect of benzoic acid concentration on the particle size of the product was also investigated.



Note: the phenyl ring with undefined geometry is a mixture of T and I linkages in a ratio determined by the ratio of TPC to IPC in the monomer feed

Figure 5.4 Structure of PEKEKK with variable T:I ratio

The structures of the PEKEKK products, Figure 5.4, were confirmed by NMR spectroscopy. The overlaid spectra for EKE, 100:0 PEKEKK and 90:10 PEKEKK are shown in Figure 5.5. The ^1H and ^{13}C spectra are in agreement with the reported spectrum of 100:0 PEKEKK¹¹. On polymerisation, the peaks associated with the terminal sections of EKE shift to account for the change in electron density. On incorporation of IPC into the polymer, new peaks grow into the spectrum. More detailed analysis would be required for full structural assignment.

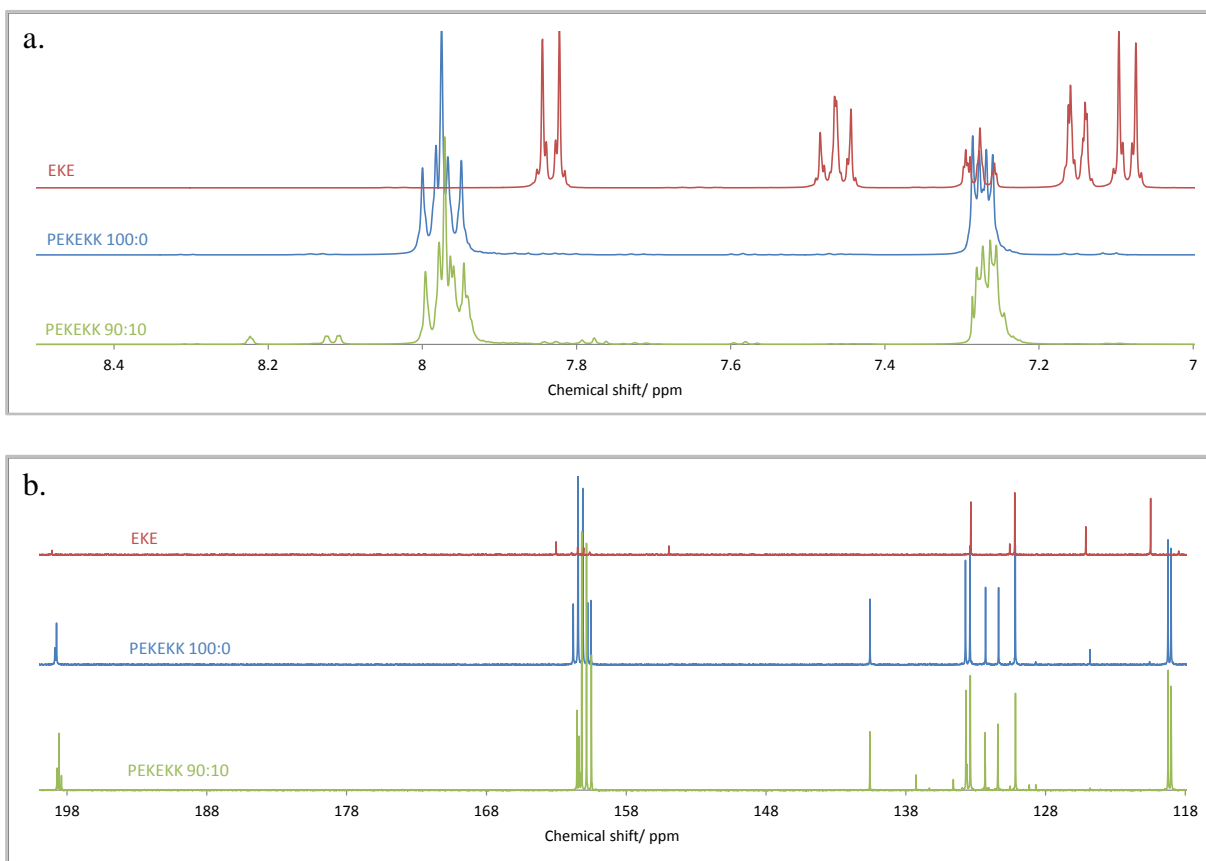


Figure 5.5 ^1H and b. ^{13}C NMR spectra of EKE, 100:0 PEKEKK and 90:10 PEKEKK

PEKEKKs were synthesised using 100:0, 90:10 and 80:20 T:I ratios, together with increased benzoic acid concentration from 4 to 6 stoichiometric equivalents per acid chloride, and all at 3% out-of-balance. All of the PEKEKKs were produced in the form of dispersions, although the products were granular, with diameter of approximately 1 mm, and much larger than PEKK dispersions. Both altering the T:I ratio and increasing the concentration of benzoic acid visually demonstrated little effect on the particle size.

T:I	100:0	100:0	100:0	90:10	90:10
Benzoic acid eq	4	5	6	4	5
Heating 1					
$T_g/ ^\circ\text{C}$	-	-	-	-	-
$\Delta C_p^*/ \text{Jg}^{-1}\text{K}^{-1}$	-	-	-	-	-
$T_m/ ^\circ\text{C}$	380.0	380.6	379.6	363.5	364.9
$\Delta H/ \text{Jg}^{-1}$	-49.23	-49.78	-45.83	-45.45	-44.8
Heating 2					
$T_g/ ^\circ\text{C}$	166.2	166.2	164.7	161.6	166.3
$\Delta C_p^*/ \text{Jg}^{-1}\text{K}^{-1}$	0.582	0.070	0.069	0.058	0.065
$T_m/ ^\circ\text{C}$	381.2	381.4	380.6	361.0	363.1
$\Delta H/ \text{Jg}^{-1}$	-31.62	-31.44	-29.48	-31.67	-32.67
Cooling 1					
$T_c/ ^\circ\text{C}$	337.4	334.8	333.0	304.6	305.3
$\Delta H/ \text{Jg}^{-1}$	42.82	42.33	39.91	45.43	45.19
Cooling 2					
$T_c/ ^\circ\text{C}$	337.5	334.5	333.4	304.6	305.7
$\Delta H/ \text{Jg}^{-1}$	42.18	42.23	39.91	44.75	44.84

Table 5.1 Thermal data by DSC for the range of PEKEKKs produced by the dispersion process, with two cycles of heating 90 – 400 °C at 20 °C.min⁻¹ and cooling 400 – 90 °C at 10 °C.min⁻¹, initially for amorphous polymers

Almost identical thermal properties were observed for PEKEKKs synthesised with the same T:I ratios with 4, 5 and 6 benzoic acid equivalents, Table 5.1, with approximate values of T_g 166 °C, T_m 380 °C, and T_c 335 °C for the 100:0 PEKEKK. This indicates that the benzoic acid concentration did not have an effect on the bulk polymer properties. Increasing the I content decreased the thermal points to approximately T_g 163 °C, T_m 363 °C and T_c 305 °C, together with the degree of crystallinity for the 90:10 PEKEKK due to the geometry of the IPC.

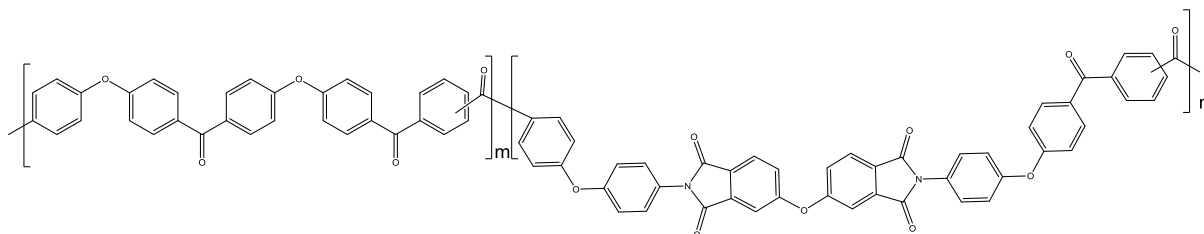
Since all of the polymerisations were carried out at 3% out-of-balance, the IV of 0.73 dLg^{-1} for the 100:0 PEKEKK can be presumed to be representative. Preliminary melt rheology data indicated that the PEKEKKs had extremely high melt viscosities, which were too high to be suitable for this type of analysis. This is not expected, as PEKEKK has a very similar structure to PEKK, which at 3% out-of-balance had a melt viscosity of around 500 – 1000 Pa.s, Chapter 3. The out-of-balance would need to be reduced to produce a polymer with lower viscosity capable of more detailed analysis. An alternative possibility is that inefficient workup has resulted in a high level of residual aluminium ions, which has increased the melt viscosity. The polymerisations would need to be repeated, and the workup procedures reassessed.

On increasing the number of benzoic acid equivalents in the polymerisation system from 2^{10} to 4, dispersion PEKEKK can be successfully produced over a range of T:I ratios. Bulk properties are maintained but the particle size is larger than that of PEKK by the same process. Modification of the reactor design may result in a finer dispersion. Adjustment of the monomer feed would result in lower molecular weight, and hence lower viscosity, PEKEKK which could undergo more detailed analysis.

5.4 Imide copolymers

Imide functionality can be incorporated into PAEKs by the gel process^{2, 13, 14}. Aromatic imide functionality imparts increased T_g s on the polymers due to the rigidity of the group, accompanied by decreased T_m s due to its steric bulk and poor packing ability. The PEKEKK study was extended by the incorporation of the imide monomer 5,5'-oxybis(2-(4-phenoxyphenyl)isoindoline-1,3-dione) (EIEIE) into the monomer feed. PEKEKK-EIEIE copolymers were synthesised over a range of imide contents and T:I ratios.

The same reactivity ratio reasoning used in Chapter 3 for the formation of PEKKs can be applied to the polymerisation of PEKEKK-EIEIE copolymers. However, in this case it has been found that the δ_C of the EIEIE *para*- carbon, δ_C 124.41 ppm, is sufficiently different to the δ_C of the EKE *para*- carbon, δ_C 124.56, to impart partial block character on the structure⁵, *i.e.* sections of the polymer backbone have several consecutive EIEIE units.



Note: the phenyl ring with undefined geometry is a mixture of T and I linkages in a ratio determined by the ratio of TPC to IPC in the monomer feed.

Figure 5.6 Structure of the copolymer synthesised from EKE and EIEIE with a mixture of TPC and IPC

The structures of the PEKEKK-EIEIE copolymers, Figure 5.6, were largely confirmed by NMR spectroscopy. The overlaid spectra for EIEIEE, 100:0 PEKEKK, 100:0 PEKEKK-EIEIE 30 and 80:20 PEKEKK-EIEIE 10 are shown in Figure 5.7. On polymerisation, the peaks associated with the terminal sections of EIEIE shift to account for the change in electron density, and combine with those of the 100:0 PEKEKK to achieve the spectrum of 100:0 PEKEKK-EIEIE 30. On incorporation of IPC into the polymer, new peaks grow into these spectra. More detailed analysis would be required for full structural assignment.

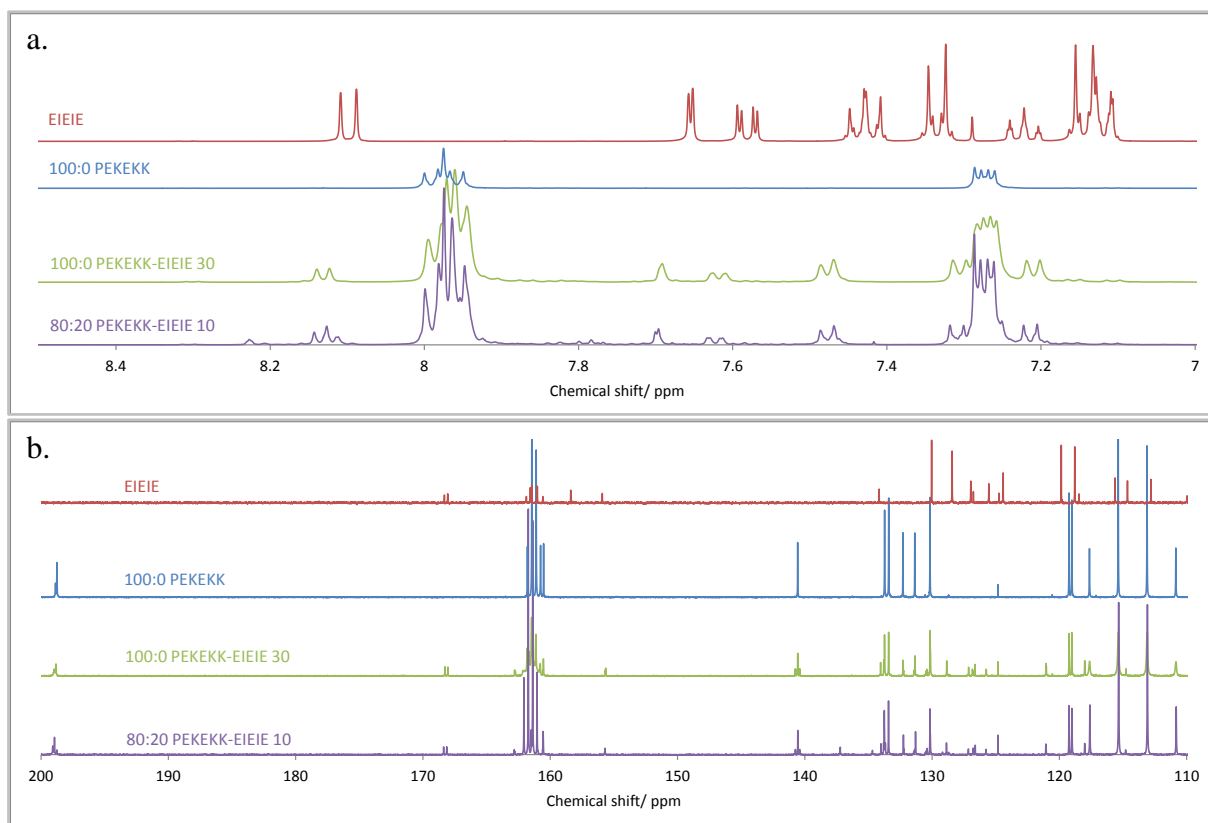


Figure 5.7 ^1H and b. ^{13}C NMR spectra of EIEIE, 100:0 PEKEKK, 100:0 PEKEKK 30 and 80:20PEKEKK 10

Particulate PEKEKK-EIEIE copolymers were produced by the dispersion process. The particle size of the copolymers was generally smaller than that of the PEKEKK polymers. Fine dispersions were formed with 10, 20 and 30 % EIEIE content and increasing T:I ratio to from 100:0 to 80:20, Table 5.2. Both altering the T:I ratio and increasing the concentration of benzoic acid visually demonstrated little effect on the particle size. With 4 benzoic acid equivalents, the 40 % EIEIE copolymer formed a gel. However, on increasing the number of benzoic acid equivalents to 6, a fine dispersion was formed. This suggests that the benzoic acid concentration does have an effect on the morphology of the copolymer product, which is more pronounced as the copolymer tends to being amorphous. It is possible that the aluminium benzoate seeding species is a more efficient nucleant for the polymerisation of semi-crystalline polymers, whereas a larger quantity of seeding crystals is required to produce an amorphous polymer in particulate form.

	Imide content/ %						Imide content/ %						
		0	10	20	30		40		0	10	20	30	40
Benzoic acid equivalents	4						T:I ratio	100:0					
	5							90:10	*				
	6							80:20					

*90:10 PEKEKK produced with 5 benzoic acid equivalents yielded a smaller dispersion than with 4 equivalents

Fine particulate
 Granular
 Gel

Table 5.2 The combined effect of variable imide content, benzoic acid concentration and T:I ratio on the size of the copolymer dispersion

Sample	Benzoic acid equivalents	EIEIE %	T:I
1	4	10	100:0
2	4	20	100:0
3	4	30	100:0
4	4	40	100:0
5	5	30	100:0
6	6	30	100:0
7	6	40	100:0
8	4	10	90:10
9	4	20	90:10
10	4	10	80:20

Table 5.3 Composition of the copolymers and number of benzoic acid equivalents used in the polymerisations

	1	2	3	4	5	6	7
Heating 1							
$T_g/^\circ\text{C}$	-	-	-	-	-	-	-
$\Delta C_p^*/\text{Jg}^{-1}\text{K}^{-1}$	-	-	-	-	-	-	-
$T_m/^\circ\text{C}$	369.2	366.2	350.3	339.5, 369.2	343.8	346.7	335.8
$\Delta H/\text{Jg}^{-1}$	-32.2	-37.71	-24.23	-12.99	-9.147	-13.72	-18.93
Heating 2							
$T_g/^\circ\text{C}$	178.7	170.7	183.0	190.7	184.0	186.0	179.2
$\Delta C_p^*/\text{Jg}^{-1}\text{K}^{-1}$	0.091	0.027	0.121	0.142	0.212	0.200	0.130
$T_m/^\circ\text{C}$	367.7	361.0	348.5	360.3	348.0	344.5	327.6
$\Delta H/\text{Jg}^{-1}$	-29.36	-32.58	-14.43	-8.177	-4.400	-5.459	-6.237
Cooling 1							
$T_g/^\circ\text{C}$	-	313.5	180.7	169.1	179.1	179.6	175.7
$\Delta C_p^*/\text{Jg}^{-1}\text{K}^{-1}$	-	44.6	0.070	0.029	0.133	0.111	0.058
$T_c/^\circ\text{C}$	310.2	-	-	-	-	-	-
$\Delta H/\text{Jg}^{-1}$	36.42	-	-	-	-	-	-
Cooling 2							
$T_g/^\circ\text{C}$	-	310.6	182.8	182.9	180.7	179.5	169.0
$\Delta C_p^*/\text{Jg}^{-1}\text{K}^{-1}$	-	42.45	0.065	0.114	0.141	0.124	0.069
$T_c/^\circ\text{C}$	306.4	-	-	-	-	-	-
$\Delta H/\text{Jg}^{-1}$	36.43	-	-	-	-	-	-

	8	9	10
Heating 1			
$T_g/^\circ\text{C}$	-	-	-
$\Delta C_p^*/\text{Jg}^{-1}\text{K}^{-1}$	-	-	-
$T_m/^\circ\text{C}$	349.1	342.8	330.6
$\Delta H/\text{Jg}^{-1}$	-36.02	-19.83	-29.03
Heating 2			
$T_g/^\circ\text{C}$	174.1	176.7	168.0
$\Delta C_p^*/\text{Jg}^{-1}\text{K}^{-1}$	0.098	0.118	0.151
$T_m/^\circ\text{C}$	349.6	338.3	326.0
$\Delta H/\text{Jg}^{-1}$	-27.04	-19.83	-20.79
Heating 3			
$T_g/^\circ\text{C}$	-	-	-
$\Delta C_p^*/\text{Jg}^{-1}\text{K}^{-1}$	-	-	-
$T_c/^\circ\text{C}$	275.9	241.6	236.0
$\Delta H/\text{Jg}^{-1}$	31.77	15.74	26.65
Heating 4			
$T_g/^\circ\text{C}$	-	-	-
$\Delta C_p^*/\text{Jg}^{-1}\text{K}^{-1}$	-	-	-
$T_c/^\circ\text{C}$	273.5	241.6	235.3
$\Delta H/\text{Jg}^{-1}$	31.86	15.74	26.47

Table 5.4 Thermal data by DSC for the range of PEKEKK-EIEIE copolymers produced by the dispersion process, with two cycles of heating 90 – 400 °C at 20 °C.min⁻¹ and cooling 400 – 90 °C at 10 °C.min⁻¹, initially for amorphous polymers

Almost identical thermal properties were observed for the same PEKEKK-EIEIE copolymers synthesised with 4, 5 and 6 benzoic acid equivalents, Table 5.4, indicating that the benzoic acid concentration did not have an effect on the bulk polymer properties. Increasing the EIEIE content increased the T_g and decreased the T_m and degree of crystallinity. Increasing the % I decreased the T_g , T_m and degree of crystallinity from 100:0 PEKEKK due to the geometry of TPC. These effects were used in combination to achieve a range of thermal properties.

As with PEKEKK, preliminary melt rheology data indicated that the PEKEKK-EIEIE copolymers had extremely high melt viscosities, which were too high to be suitable for this type of analysis. In this case, the copolymers have a different structure to PEKK, so a significant difference in melt viscosity may be expected. The out-of-balance would need to be reduced substantially to produce a polymer with lower viscosity capable of more detailed analysis. As with PEKEKK, an alternative possibility is that inefficient workup has resulted in a high level of residual aluminium ions, which has increased the melt viscosity. The

polymerisations would need to be repeated using a larger out-of-balance, and the workup procedures reassessed.

Fine particulate PEKEKK-EIEIE copolymers were produced over a range of imide contents and T:I ratios by the dispersion process. Bulk polymer properties were maintained and the particle size is comparable to that of PEKK for the majority of samples. The amorphous PEKEKK-EIEIE copolymer with 40 % imide formed a gel, although it may be possible to form a dispersion on further modification of the dispersion process.

Alternative imide-containing monomers proved to be successful in the gel process include those with ketone and trifluoromethyl groups^{13, 14}, Figure 5.8. However, the polymers produced using these monomers do not exhibit good thermal stability.

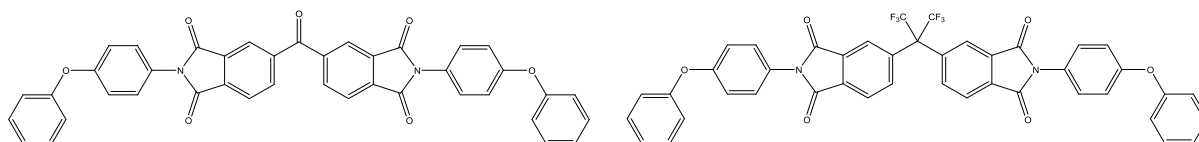


Figure 5.8 Alternative imide-containing monomers

5.5 Sulfone copolymers

In addition to imide functionality, sulfone functionality is commonly incorporated into PAEKs. The incorporation of sulfone functionality results in an increased T_g due to the poor rotation of the sulfone and associated decrease in flexibility, accompanied by a dramatic decrease in T_m often to an amorphous state due to the steric bulk and particularly poor packing capability. This effect is discussed in more detail in Chapter 1.

The syntheses of PAESs have been reported by both nucleophilic and electrophilic routes. While PAESs are commonly known, PAEK-sulfone copolymers are less so. PAEK-sulfone

copolymers can be made easily by the gel process by the incorporation of 1,1'-sulfonylbis(4-phenoxybenzene) (ESE)². PAEK-sulfone copolymers were also produced by a version of the gel process^{15,16}, polymerising ESE with diacid chlorides, using NMP as the dispersant in 1,2-dichloroethane.

The sulfone monomer ESE was incorporated into the monomer feed for PEKK polymerisation by the dispersion process. PEKK-ESE copolymers were synthesised over a range of sulfone contents and T:I ratios. All polymerisations were carried out with 4 benzoic acid equivalents.

As with the imide copolymers, the reactivity ratio reasoning used in Chapter 3 for the formation of PEKKs can be applied to the polymerisation of PEKEKK-ESE copolymers. It has been found that δ_C of the ESE *para*- carbon, δ_C 125.38 ppm, is sufficiently different to the δ_C of the EKKE *para*- carbon, δ_C 125.30, to impart partial block character on the structure⁵.

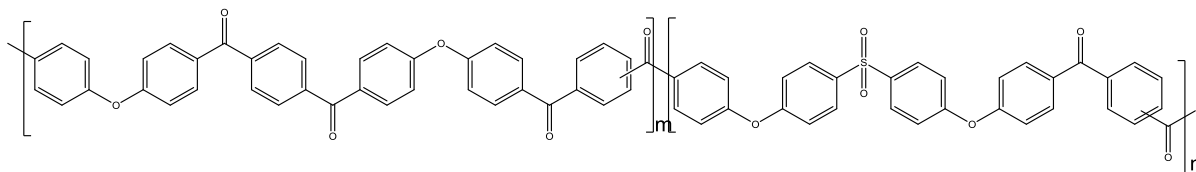


Figure 5.9 Structure of the copolymer synthesised from EKKE and ESE with a mixture of TPC and IPC

The structure of the PEKEKK-ESE product, Figure 5.9, was confirmed by NMR spectroscopy. The overlaid spectra for ESE, 100:0 PEKK-ESE 40 and 70:30 PEKK-ESE 30 are shown in Figure 5.10. On polymerisation, the peaks associated with the terminal sections of ESE shift to account for the change in electron density. On incorporation of IPC into the polymer, new peaks grow into the spectrum. More detailed analysis would be required for full structural assignment.

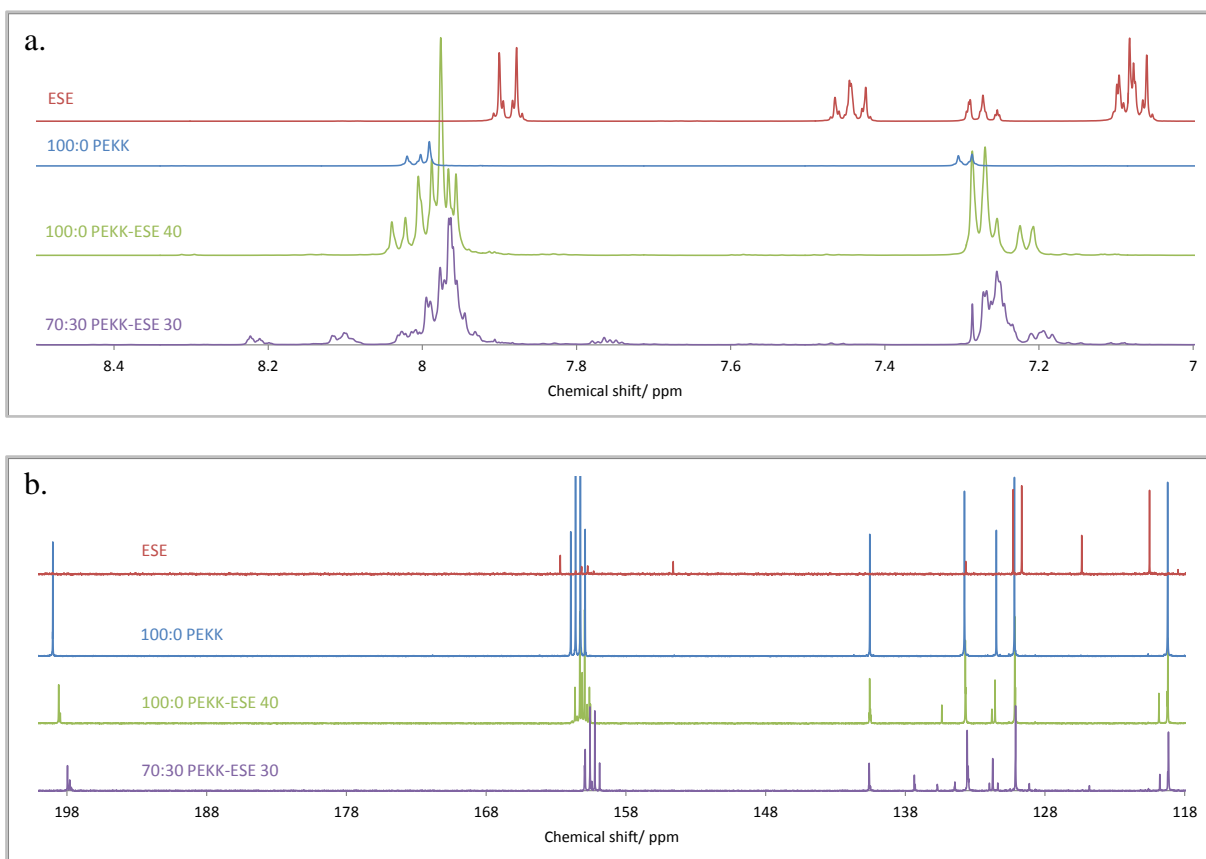


Figure 5.10 a. ^1H and b. ^{13}C NMR spectra of ESE, 100:0 PEKK, 100:0 PEKK-ESE 40 and 70:30PEKK-ESE 30

Fine particulate PEKK-ESE copolymers, detailed in Table 5.5, were produced with all samples visually comparable in size to particulate PEKK. The number of benzoic acid equivalents was limited to 4 since increasing both the ESE and IPC content did not result in increased particle size. In contrast to the PEKEKK-EIEIE with 40% imide content which was amorphous and formed a gel, the amorphous PEKK-ESE polymers remained as dispersions.

Sample	ESE/ %	T:I ratio
1	10	100:0
2	20	100:0
3	30	100:0
4	40	100:0
5	10	90:10
6	20	90:10
7	30	70:30

Table 5.5 The composition of the PEKK-ESE copolymers to include ESE composition and T:I ratio

Altering the degree of ESE incorporation affected the thermal properties of the copolymers. Data is listed in Table 5.5, with overlaid traces in Figure 5.11 and Figure 5.12. Increasing the % ESE decreased the T_m , T_c and degree of crystallinity, but increased the T_g , for the reasons discussed in Chapter 1. Increasing the % I decreased T_g , T_m , T_c and degree of crystallinity due to the geometry of the IPC.

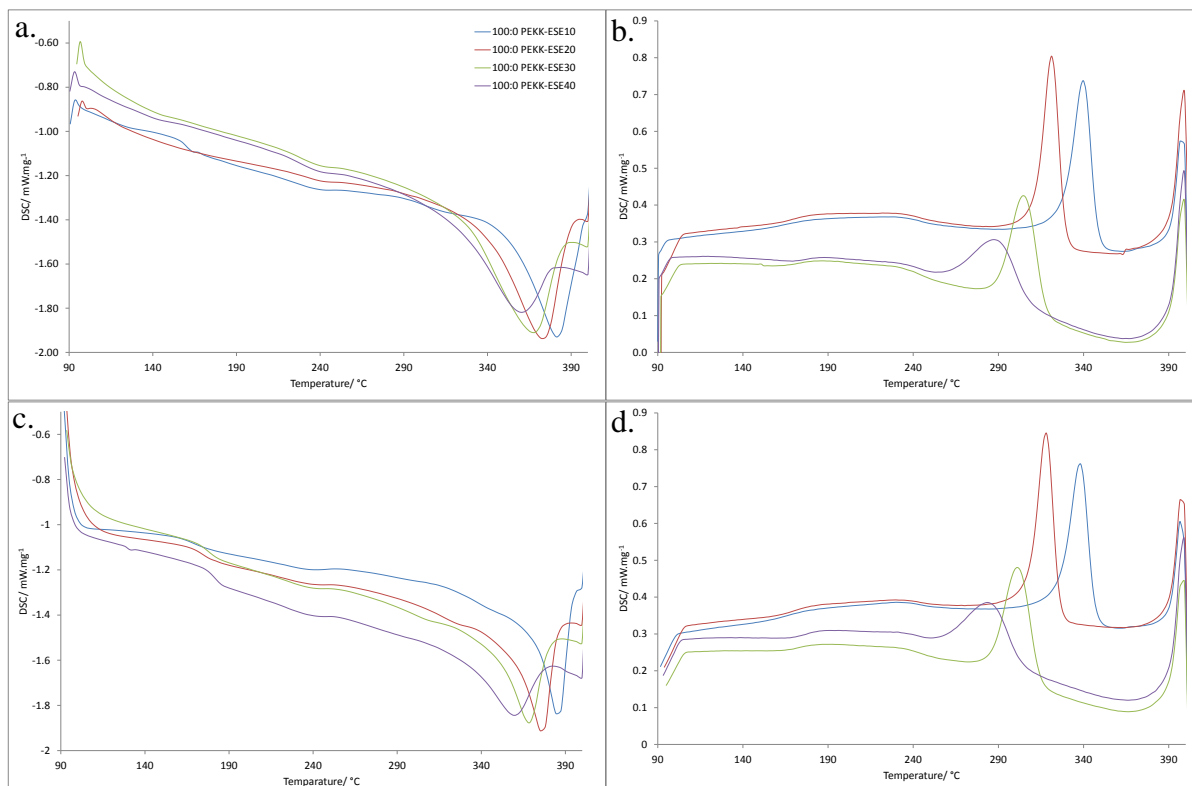


Figure 5.11 Stacked DSC traces for PEKK-ESE copolymers with increasing ESE content a. heating 90 – 400 °C at 20 °C.min⁻¹, b. cooling 400 – 90 °C at 10 °C.min⁻¹, c. heating 90 – 400 °C at 20 °C.min⁻¹, d. cooling 400 – 90 °C at 10 °C.min⁻¹

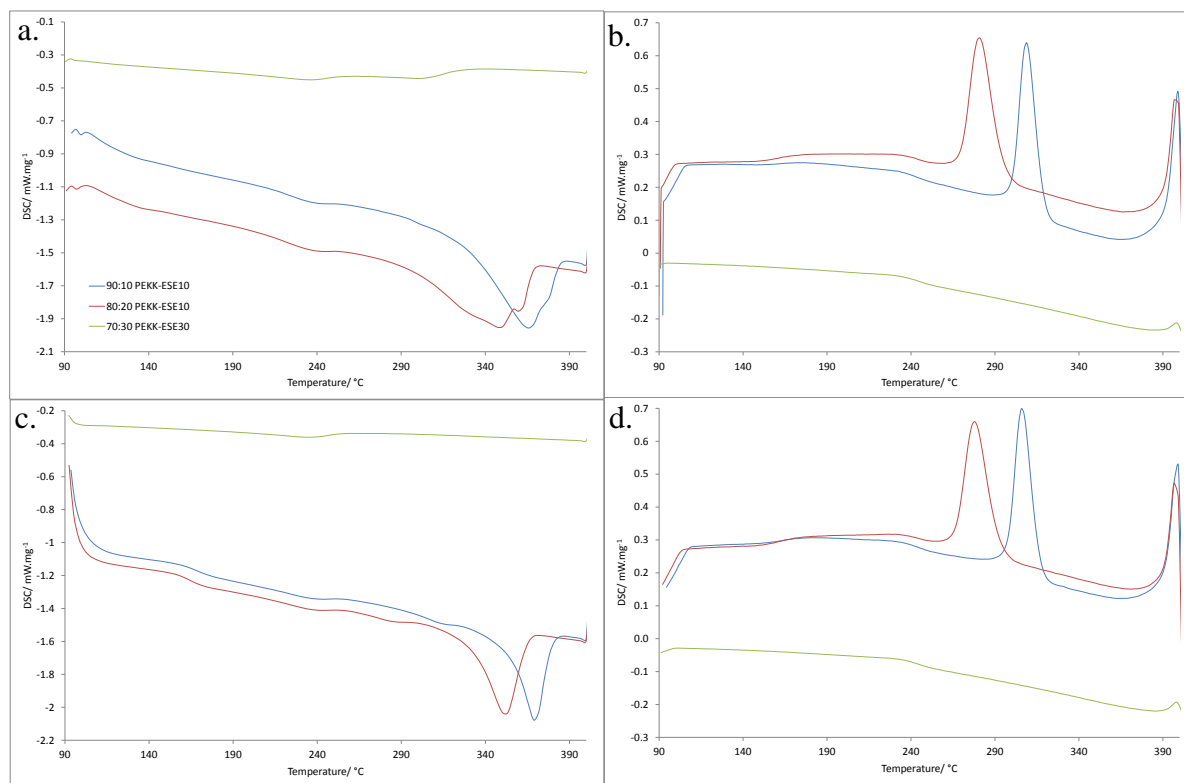


Figure 5.12 Stacked DSC traces PEKK-ESE20 copolymers with increasing T:I ratio a. heating 90 – 400 °C at 20 °C.min⁻¹, b. cooling 400 – 90 °C at 10 °C.min⁻¹, c. heating 90 – 400 °C at 20 °C.min⁻¹, d. cooling 400 – 90 °C at 10 °C.min⁻¹

	1	2	3	4	5	6	7
Heating 1							
T _g /°C	164.1	-	-	-	-	-	*
ΔCp*/ Jg ⁻¹ K ⁻¹	0.098	-	-	-	-	-	
T _m /°C	381.9	373.2	367.6	360.5	366.0	348.4, 360.8	
ΔH/ Jg ⁻¹	-47.84	-53.42	-48.01	-24.02	-43.06	-42.81	
Heating 2							
T _g /°C	172.7	181.8	178.3	182.8	168.1	161.7	
ΔCp*/ Jg ⁻¹ K ⁻¹	0.076	0.096	0.103	0.140	0.096	0.105	
T _m /°C	386.0	376.5	368.5	359.6	369.6	351.7	
ΔH/ Jg ⁻¹	-30.34	-26.31	-22.43	-17.33	-25.66	-29.65	
Cooling 1							
T _c /°C	339.6	321.1	304.9	287.2	308.6	280.7	
ΔH/ Jg ⁻¹	36.91	36.14	32.8	23.24	35.74	39.50	
Cooling 2							
T _c /°C	337.9	317.8	300.8	283.2	306.1	277.9	
ΔH/ Jg ⁻¹	38.02	35.78	32.99	22.73	36.15	38.13	

*Amorphous. DSC unclear

Table 5.6 Thermal data from DSC for the range of PEKEKK-ESE copolymers produced by the dispersion process, with two cycles of heating 90 – 400 °C at 20 °C.min⁻¹ and cooling 400 – 90 °C at 10 °C.min⁻¹

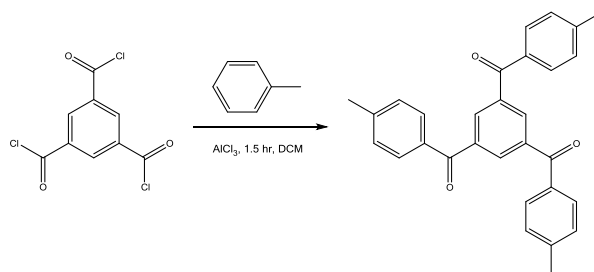
The IV measurements of 0.62 and 0.90 dL.g⁻¹ for 100:0 PEKK-ESE10 and 100:0 PEKK-ESE40 respectively span a wide range. Additional IV measurements would be required to determine if a correlation between IV and ESE composition is apparent.

Preliminary rheological analysis demonstrated a wide range of melt viscosities of the PEKK-ESE copolymers. Further rheological analysis would be required to determine if there is a correlation between melt viscosity and the % ESE content. It is also possible that modification of the workup procedure is required to accommodate the sulfone functionality in the polymer structure.

Particulate PEKEKK-ESE copolymers were produced over a range of sulfone contents and T:I ratios. Bulk properties are maintained and the particle size is comparable to that of PEKK for all of the samples.

5.6 Branched PEKK

A variant of linear PAEKs are branched PAEKs. To achieve a branched PEKK structure, it was thought that a trifunctional monomer 1,3,5-benzenetricarbonyl chloride (TRI) could be introduced into the monomer feed. The use of this monomer had been reported in the one-pot synthesis of PAEKs, by the electrophilic polycondensation of DPE and acid chloride comonomers, for the synthesis of branched PAEKs¹⁷. To confirm its reactivity in the system, a model compound TRI-TOL was synthesised by the reaction of TRI with toluene, under dispersion process conditions, in comparison to the synthesis reported in a toluene solvent¹⁸. Toluene was used rather than EKKE as it only reacted at one end, resulting in discrete structures. TRI-TOL was fully characterised. It was therefore presumed that TRI would be compatible with the polymerisation system.



Scheme 5.1 The synthesis of TRI-TOL

Small-scale polymerisations were carried out to examine the effect of the trifunctional monomer on the properties of the resulting polymers. 80:20 PEKKs containing 1, 5 and 10% TRI compared to the total carbonyl functionality in the calculated acid chloride content, were synthesised.

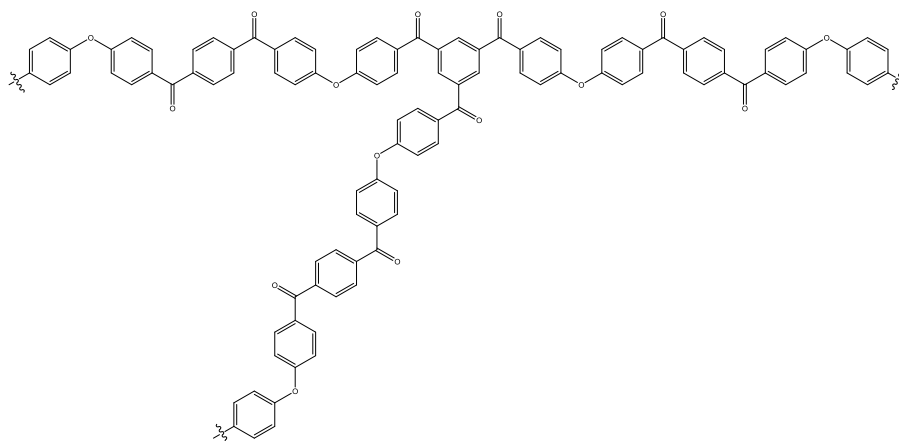


Figure 5.13 Structure of the branched PEKK polymer

The incorporation of TRI into the PEKK structure, Figure 5.13, was confirmed by NMR spectroscopy. The overlaid spectra for the 10% TRI PEKK and 80:20 PEKK are shown in Figure 5.14. Most notable is the additional peak in the carbonyl region of the ^{13}C NMR spectrum, around 198 ppm, which can be attributed to TRI. More detailed analysis would be required for full structural assignment.

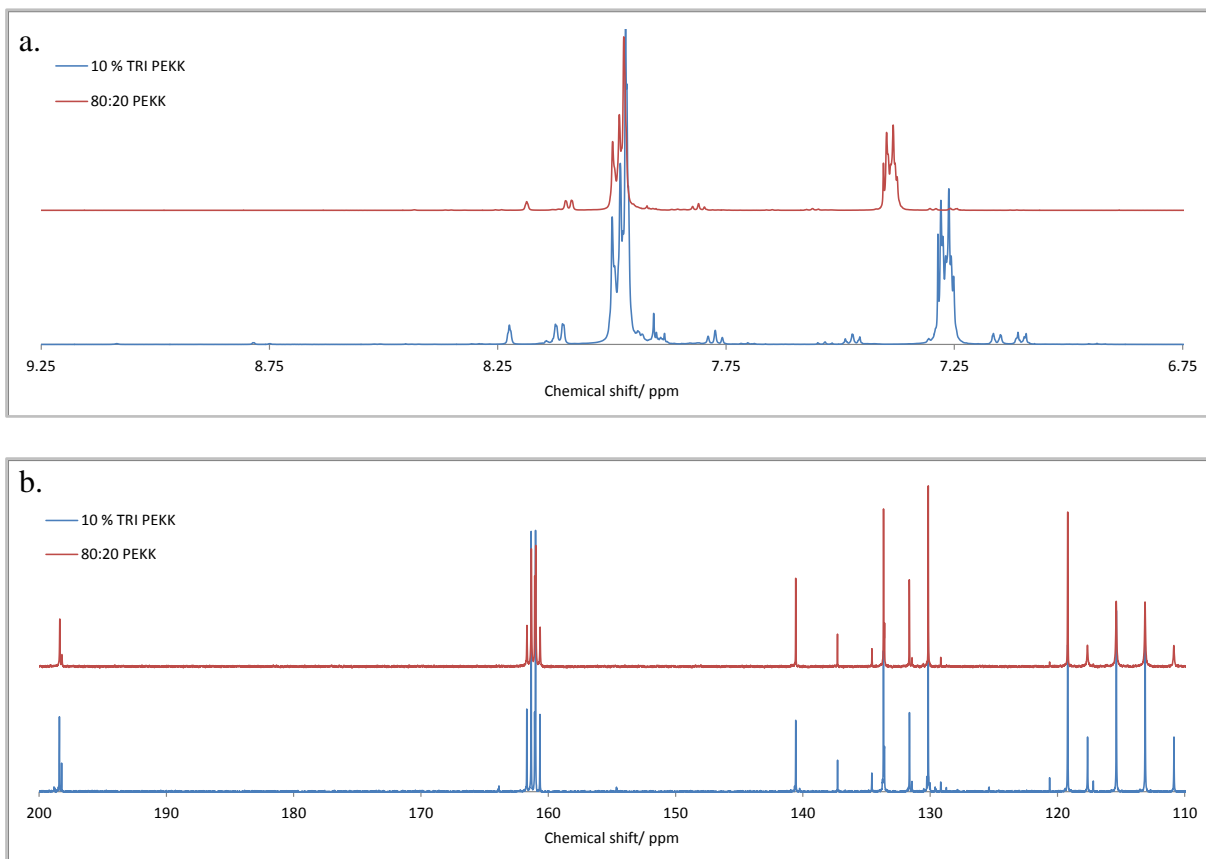


Figure 5.14 ^1H and b. ^{13}C NMR spectra of 80:20 PEKK and 10% TRI PEKK

% TRI	IV/ $\text{dL}\cdot\text{g}^{-1}$
0	1.38
1	1.10
5	0.87
10	0.72

Table 5.7 IV data for the branched PEKKs carried out in concentrated sulphuric acid at 25 °C

The incorporation of a greater % of TRI decreased the IV of the PEKKs, Table 5.7, which does not necessarily indicate a decrease in molecular weight. Instead, main chain branching often decreases the solution viscosity of polymers. The increased branching results in a more conformationally restricted structure, and therefore fewer inter-chain entanglements¹⁹. Ordinarily, these entanglements cause increased viscosity. Visually, the fine particulate PEKKs are equal in particle size and are comparable to the particle size of PEKK dispersions.

		Linear	1% Tri	5% Tri	10% Tri
Heating 1	$T_m/ ^\circ\text{C}$	337.7	340.5	341.7	344.3
	$\Delta H/ \text{J.g}^{-1}$	-50.01	-47.02	-52.76	-50.19
Cooling 1	$T_c/ ^\circ\text{C}$	267.3	265.5	273.7	274.9
	$\Delta H/ \text{J.g}^{-1}$	29.5	29.58	35.66	36.28
Heating 2	$T_g/ ^\circ\text{C}$	163.6	155.3	153.7	151.3
	$\Delta C_p^*/ \text{J.g}^{-1}.\text{K}^{-1}$	0.123	0.102	0.112	0.101
	$T_m/ ^\circ\text{C}$	344.7	344.4	347.2	347.3
	$\Delta H/ \text{J.g}^{-1}$	-24.61	-27.54	-31.52	-30.76
Cooling 2	$T_c/ ^\circ\text{C}$	266.7	264.2	275.0	276.4
	$\Delta H/ \text{J.g}^{-1}$	29.45	29.4	35.84	35.93

Table 5.8 Thermal properties of linear PEKK and 1%, 5% and 10% branched PEKK by DSC using a $20\text{ }^\circ\text{C}.\text{min}^{-1}$ heating rate and a $10\text{ }^\circ\text{C}.\text{min}^{-1}$ cooling rate, for two cycles.

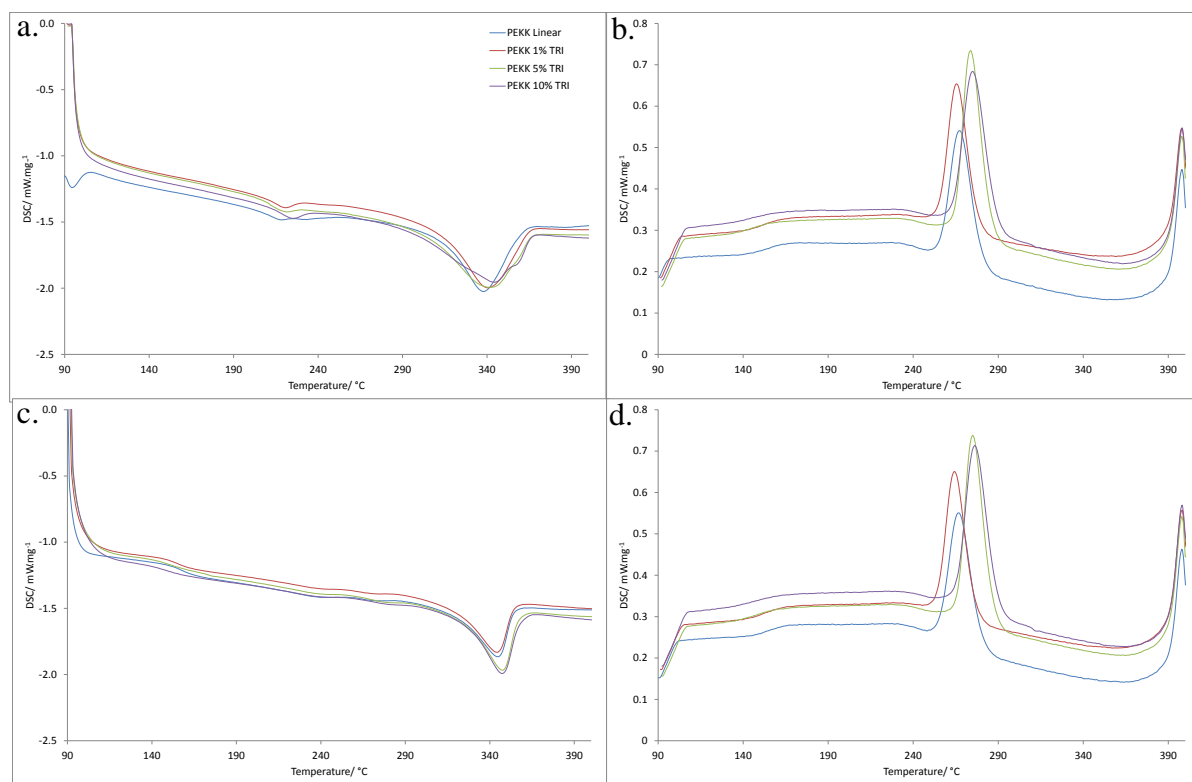


Figure 5.15 Stacked DSC traces for the linear PEKK and 1%, 5% and 10% TRI PEKKs, a, heating $90 - 400\text{ }^\circ\text{C}$ at $20\text{ }^\circ\text{C}.\text{min}^{-1}$, b, cooling $400 - 90\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}.\text{min}^{-1}$, c, heating $90 - 400\text{ }^\circ\text{C}$ at $20\text{ }^\circ\text{C}.\text{min}^{-1}$, d, cooling $400 - 90\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}.\text{min}^{-1}$

Thermal data listed in Table 5.8, with stacked plots of DSC traces in Figure 5.15. A marginally decreased T_g was observed with increased % TRI content. An increase in T_m and T_c is observed on increasing the % TRI content. Overall, the T_m and T_c on second cycle are higher than those observed during the first cycle.

Preliminary melt rheological analysis was carried out over a shear rate frequency sweep. G' and G'' for the PEKKs containing TRI cross at increasing frequency with increasing % TRI, which suggests higher degrees of branching in the polymer structure. However, this was over a very small frequency range. While the major aim of this set of experiments was to assess the compatibility of TRI in the polymerisation system, optimisation of the molecular weight, and therefore the viscosity, of the polymers would be necessary to achieve conclusive analysis.

Fine particulate, branched PEKKs were produced over a range TRI contents. The particle size of all of the PEKKs was visually comparable to those of PEKK. All of the PEKKs completely dissolved in concentrated sulphuric acid, indicating that the PEKKs were branched rather than crosslinked. Crosslinked PAEKs do not dissolve fully in concentrated sulfuric acid.

The TRI monomer was added in addition to the TPC and IPC to maintain the original order of addition, resulting in a randomly branched polymer. For an extra element of control, it could be possible to react the TRI with EKKE initially, before the addition of TPC and IPC, to ensure that TRI was fully functionalised. However, high dilution conditions would be required to avoid bridging reactions between TRI molecules.

A development to the production of branched PAEKs would be to investigate the production of hyperbranched or dendritic PAEKs by the dispersion process. Hyperbranched polymers offer advantages such as lower solution viscosities than linear analogues and easily adapted properties by modification of the high density of end groups¹⁹. Hyperbranched PAEKs have been reported by both nucleophilic²⁰ and electrophilic²¹ processes and require the synthesis of suitable AB_2 monomers. Hyperbranched PAEKs are amorphous, despite the semi-crystalline nature of linear analogues.

5.7 Incorporation of additional functionality

The additional functionalities already discussed in this chapter are well known in the field of PAEKs and engineering thermoplastics. Although incorporation of each of the functionalities were shown to be successful in the dispersion process, a wider variety of functionalities which are able to be incorporated into PAEKs allows a further increase in scope of the materials to address wider applications and requirements. A selection of more unusual monomers were employed undergo preliminary evaluation as to the success of their incorporation into the dispersion polymerisation system. Each gave a large difference in thermal properties once incorporated into the polymer, which will be discussed in further detail. All of the appropriate monomers were fully characterised prior to use.

5.7.1 Aliphatic copolymers

Aliphatic-aromatic PAEKs are not as common as the wholly aromatic versions. In 1962, the first aromatic-aliphatic PEK polymer was reported, synthesised by the electrophilic reaction of diphenyl ether and decandioyl dichloride ($\text{ClCO}(\text{CH}_2)_8\text{COCl}$)²², which had a melting point of 184 – 185 °C. In 1989, a nucleophilic route using silylated alkylenebiphenol and aromatic difluoroketones²³ produced aromatic aliphatic PEKs which were fully analysed. This study reported the phase separation of the aliphatic and aromatic regions to form a well-defined supermolecular structure. These polymers exhibit double melting peaks and crystallisation peaks, attributed to the two structures. The incorporation of aliphatic functionality into PAEKs results in a large decrease in T_g and T_m , whilst maintaining the high performance properties of the aromatic EK sections. Polymers with aliphatic–amide functionality was also reported by the gel process².

A dispersion polymerisation was carried out with a monomer feed containing the aliphatic monomer 1,12-bis(4-phenoxyphenyl)dodecane-1,12-dione (EK10KE) and TPC²⁴, which

successfully produced particulate polymer with IV 1.11 dL.g⁻¹. The polymer particles were visually larger and more irregular than PEKK particles, but nevertheless, produced a fine dispersion. The polymer structure, Figure 5.16, was broadly confirmed by NMR spectroscopy, Figure 5.17. Unlike other copolymers studied in this project which were entirely aromatic, the resonances attributed to the aliphatic sections are clearly visible in the ¹H NMR spectrum in the 1 – 3.5 ppm region, and in the ¹³C NMR spectrum in the 25 – 40 ppm region. Further analysis is required for full structural characterisation.

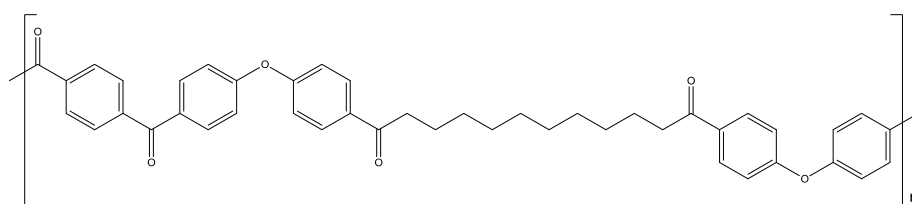


Figure 5.16 Structure of polymer produced from EK10KE and TPC

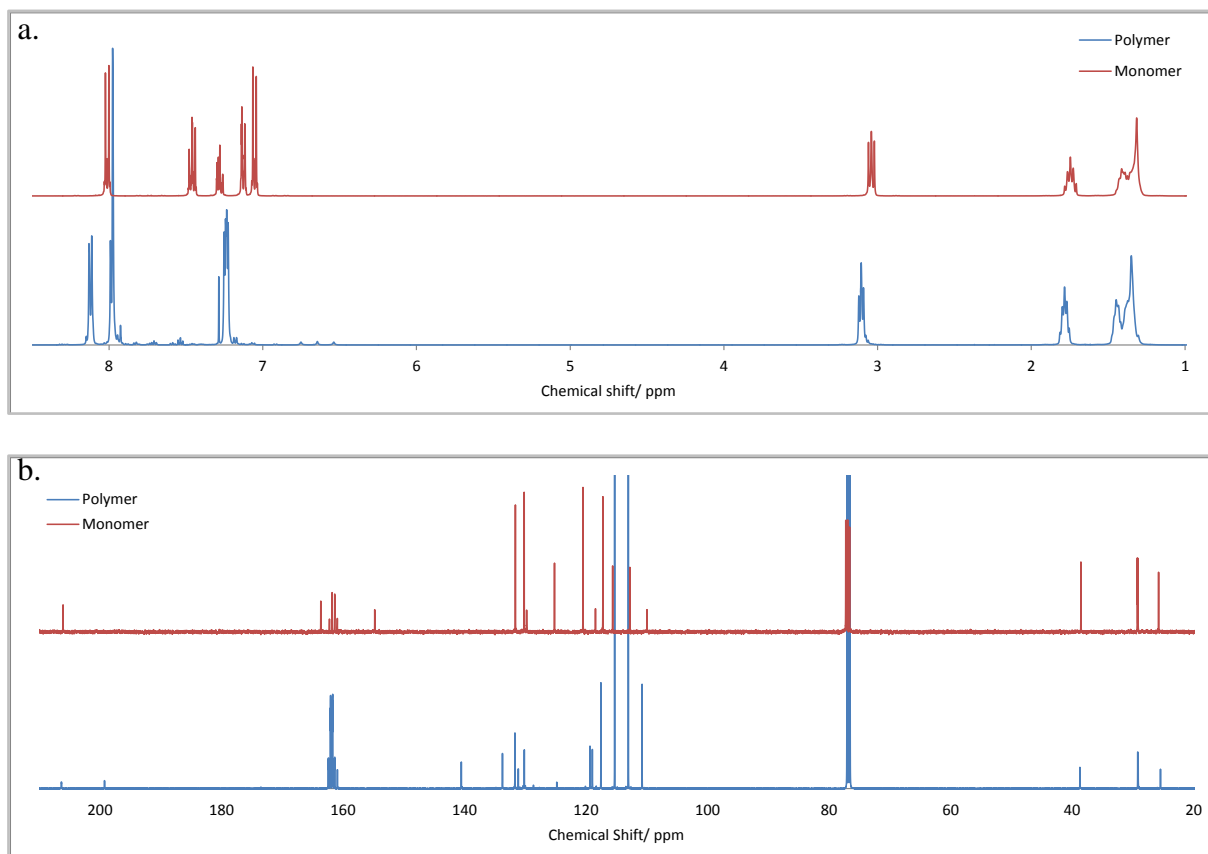


Figure 5.17 a. ¹H and b. ¹³C NMR spectra of the EK10KE monomer and the polymer formed from EK10KE and TPC

Heating 1	$T_m/ ^\circ\text{C}$	275.9
	$\Delta H/ \text{J.g}^{-1}$	-48.93
Cooling 1	$T_c/ ^\circ\text{C}$	232.5
	$\Delta H/ \text{J.g}^{-1}$	42.77
Heating 2	$T_g/ ^\circ\text{C}$	-
	$\Delta C_p^*/ \text{J.g}^{-1}.\text{K}^{-1}$	-
	$T_m/ ^\circ\text{C}$	274.7
	$\Delta H/ \text{J.g}^{-1}$	-35.5
Cooling 2	$T_c/ ^\circ\text{C}$	228.6
	$\Delta H/ \text{J.g}^{-1}$	38.92

Table 5.9 Thermal data from DSC for the PEK10KE polymer produced by the dispersion process, with two cycles of heating 90 – 300 °C at 20 °C.min⁻¹ and cooling 300 – 90 °C at 10 °C.min⁻¹

DSC analysis, Table 5.9, confirmed that the aliphatic region of the EK10KE acts to decrease the T_g compared to PEKK due to its increased flexibility of the aliphatic component. The T_g is expected to be around 70 °C, which was not in the range of DSC analysis. It also acts to decrease the T_m and its associated enthalpy change, as crystallisation is disfavoured.

In comparison to this polymer version containing TPC only, the version containing all IPC has T_g 76 °C and T_m 197 °C⁵. This material finds a potential application in selective laser sintering (SLS) since its thermal properties are very similar to that of nylon-12, commonly used for SLS. The advantages of the aliphatic PAEK over nylon-12 are that it maintains approximately 70% of the mechanical properties of the solely aromatic PEKs so can be used in structural applications, it is much more melt and oxidatively stable and it is resistant to hydrolysis. Produced by the dispersion process, the aliphatic PAEK may be produced in the optimum size range for SLS without cryogenic grinding. A range of particle sizes is required to optimise packing in the bed of the instrument and to form well sintered parts.

Although only the EK10KE monomer has been used in this example, it is possible to produce a range of monomers with variable chain length which will be compatible with the dispersion process to allow further modification of the polymer properties.

5.7.2 Naphthalene copolymers

Naphthalene containing PAEKs have been reported in both journal and patent literature. Particularly, a precipitation method was reported²⁵, and although it was carried out at similar reactor loading, the reaction time was vastly increased to 20 hours. The gel process successfully produces PEK naphthalene copolymers²⁶ by the incorporation of naphthalene functionality into both the aromatic and the acid chloride monomer. The modification of the aromatic monomer alone is trialled in this section.

A dispersion polymerisation was carried out with a monomer feed containing naphthalene-2,6-diylbis((4-phenoxyphenyl)methanone) (EKNKE) and TPC which produced particulate polymer, visually comparable in size to PEKK dispersions, with 0.99 dL.g⁻¹. The polymer structure, Figure 5.18, was confirmed by NMR spectroscopy, Figure 5.19, and was in agreement with reported data²⁵. Further analysis is required for full structural characterisation.

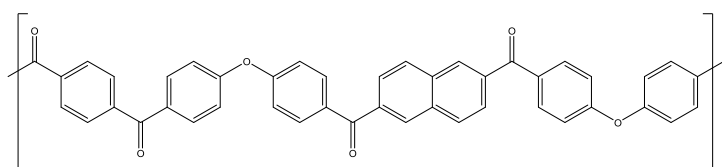
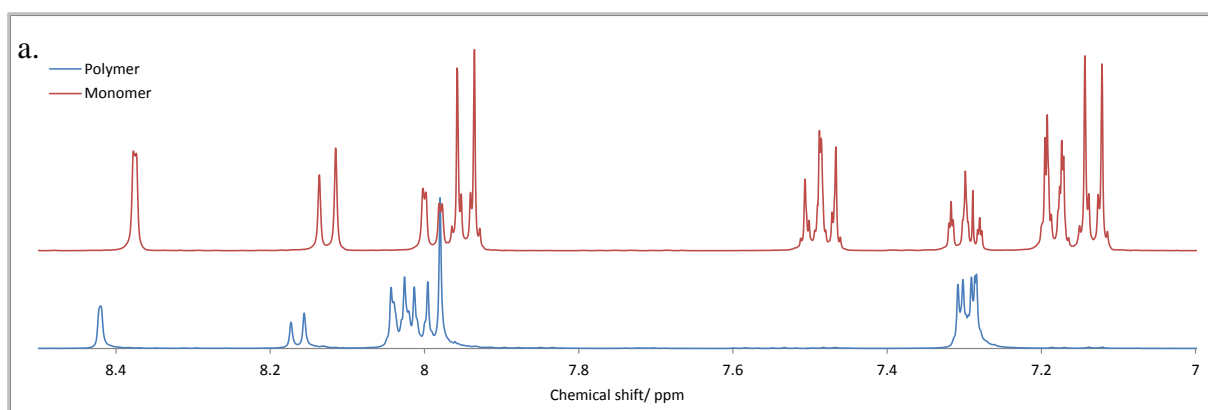


Figure 5.18 Structure of polymer produced from EKNKE and TPC



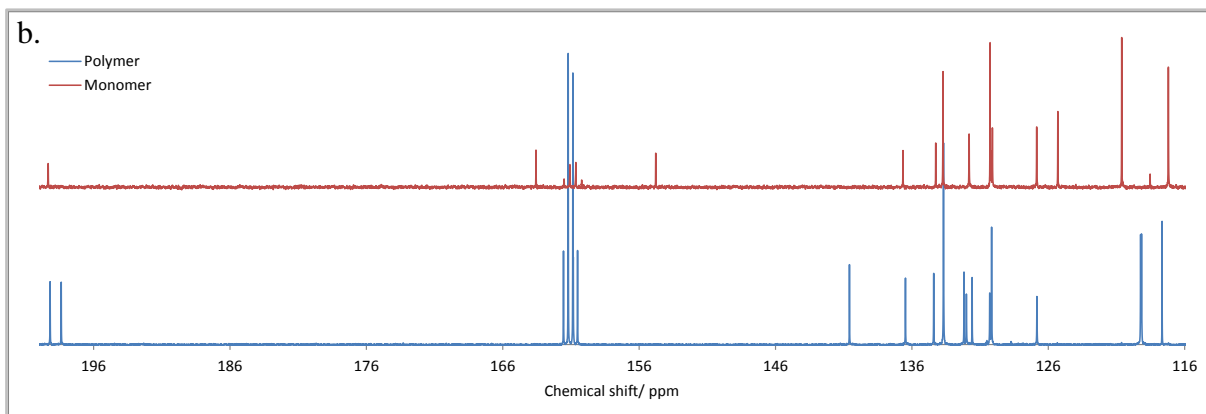


Figure 5.19 a. ^1H and b. ^{13}C NMR spectra of the EKNKE monomer and the polymer formed from EKNKE and TPC

Heating 1	$T_m/ ^\circ\text{C}$	390.8, 339.4
	$\Delta H/ \text{J.g}^{-1}$	-18.59 -3.239
Cooling 1	$T_c/ ^\circ\text{C}$	306.6
	$\Delta H/ \text{J.g}^{-1}$	19.16
Heating 2	$T_g/ ^\circ\text{C}$	186.0
	$\Delta C_p^*/ \text{J.g}^{-1}\text{.K}^{-1}$	0.113
	$T_m/ ^\circ\text{C}$	371.0
	$\Delta H/ \text{J.g}^{-1}$	-23.29
Cooling 2	$T_c/ ^\circ\text{C}$	297.5
	$\Delta H/ \text{J.g}^{-1}$	20.62

Table 5.10 Thermal data by DSC for the polymer formed from EKNKE and TPC for two cycles of heating 90 – 400 $^\circ\text{C}$ at 20 C.min^{-1} and cooling 400 – 90 $^\circ\text{C}$ at 10 $^\circ\text{C.min}^{-1}$

DSC analysis, Table 5.10, confirmed that EKNKE acts to increase the T_g compared to EKKE due to its increased rigidity of the naphthalene component. It also acts to decrease the T_m and its associated enthalpy change, as crystallisation is disfavoured. If π -stacking had been dominant on a macroscopic scale, it might have been expected that an increased T_m would be observed but the required conformational arrangement is not accessible.

The melt viscosity of the PEKNKE polymer was too high to carry out rheological analysis. Modification of the out-of-balance would achieve the lower molecular weight polymer required for effective processing.

5.7.3 Biphenyl imide copolymers

The previously discussed incorporation of imide monomers into the polymerisation system was extended to include the imide monomer 2,2'-bis(4-phenoxyphenyl)-[5,5'-biisindoline]-1,1',3,3'-tetraone (EI-IE). In comparison to EIEIE, the lack of central ether functionality further decreases the flexibility and therefore further increases the T_g of the polymer chain into which it is incorporated. The EI-IE monomer was reported to be successful in the gel process^{2,13}.

The EI-IE monomer was found to take two forms on recrystallization, unlike previous data² which reported a single melting point. On recrystallisation in dimethylacetamide, the monomer took the form of white, approximately spherical crystals, Figure 5.20. However, on recrystallisation in chlorobenzene, the monomer took the form of yellow needles. The two products were fully characterised and were found to be identical in chemical composition.

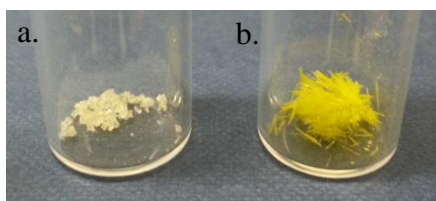


Figure 5.20 EI-IE monomer recrystallised from a. dimethylacetamide and from b. chlorobenzene

Single crystal x-ray structures were obtained to unambiguously determine the conformation of the molecules. It was determined that the difference in appearance of the products was dependent on the orientation of the central biphenyl section. The biphenyl section of the white crystals had a twisted orientation, Figure 5.21 a, which did not allow for delocalisation across the molecule as the π orbitals do not align. However, the biphenyl section of the yellow crystals had a flat structure, Figure 5.21 b, which aligns the π orbitals, promotes delocalisation across the molecule and results in the yellow colour. Crystal structure data is included in the Appendix. It was therefore confirmed that the EI-IE monomer was dimorphic.

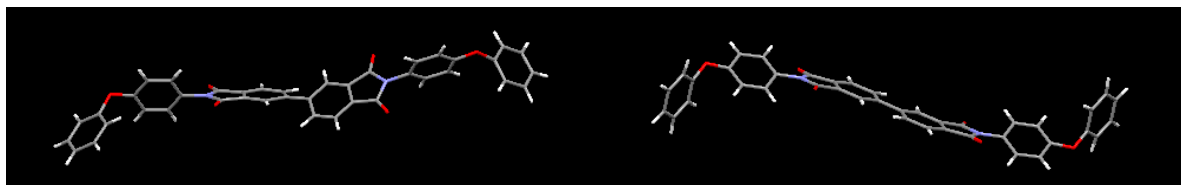


Figure 5.21 Crystal structure of the EI-IE monomer in the a. twisted (white) form and b. flat (yellow) form

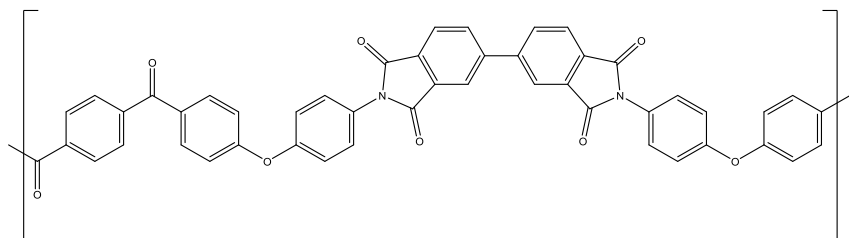


Figure 5.22 Structure of polymer produced from EI-IE and TPC

EI-IE acts to increase the T_g compared to EKKE due to its increased rigidity. It also acts to decrease the T_m and its associated enthalpy change, as crystallisation of the bulky imide groups is strongly disfavoured.

The white form of the EI-IE monomer was used to synthesise copolymer with EI-IE and TPC. The polymer was produced in the form of a yellow gel which required blending, rather than a dispersion. The gel was very solid and was difficult to blend, indicating a very high molecular weight. However, an IV of 0.39 dL.g^{-1} suggested that it was of low molecular weight. A successful DSC trace could not be obtained as the T_m was over 400°C . It was not possible to carry out rheological analysis due to the combination of high molecular weight and high T_m .

However, the polymer structure, Figure 5.22, was broadly confirmed by NMR spectroscopy, Figure 5.23. Further analysis is required for full structural characterisation.

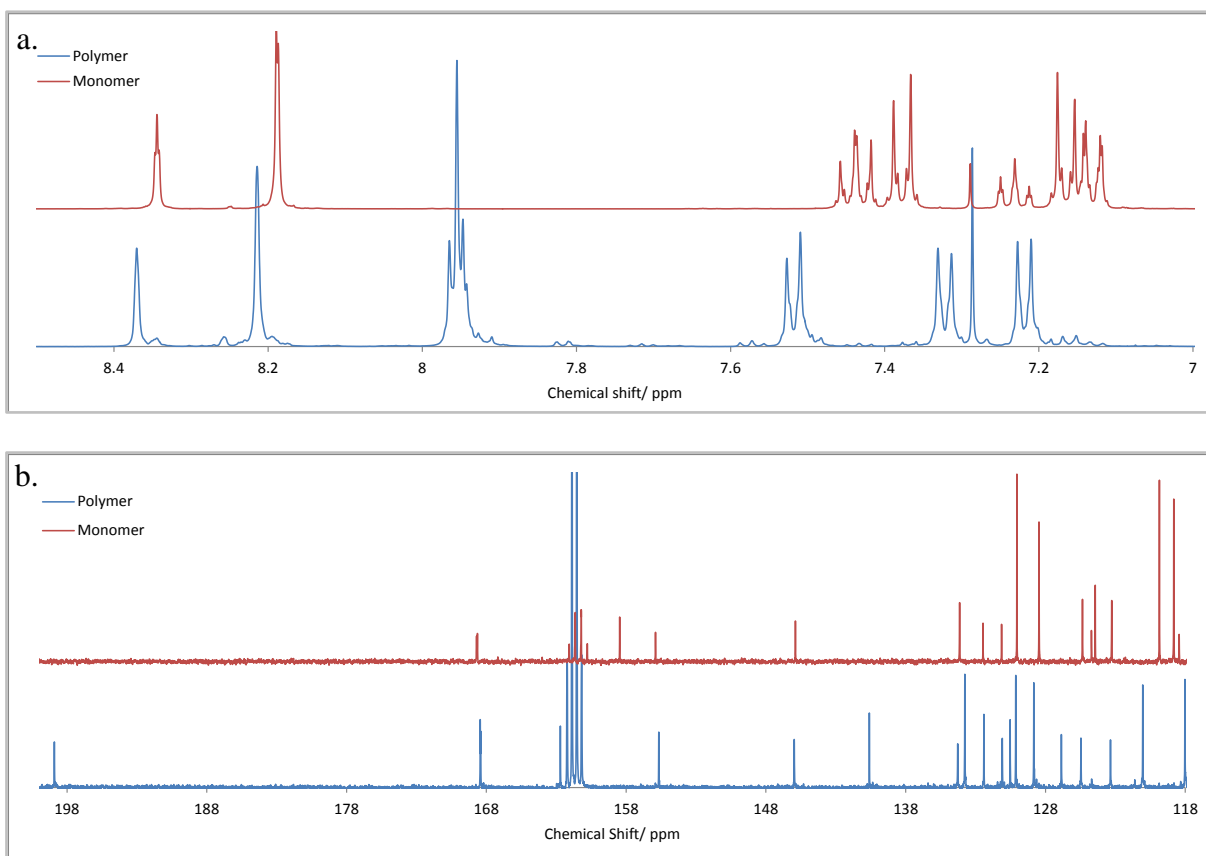


Figure 5.23 a. ^1H and b. ^{13}C NMR spectra of the EI-IE monomer and the polymer formed from EI-IE and TPC

The polymerisation was successful but did not produce product in the required morphology. The EI-IE/TPC polymerisation was carried out at 5% out-of-balance, compared to 3% for other polymerisations, as it was known that a high molecular weight polymer was produced under gel conditions. The 5% out-of-balance monomer feed contains less acid chloride than the 3%. Considering that benzoic acid concentration in the dispersion process is directly related to the quantity of acid chloride in the monomer feed, there is a lower % of benzoic acid in the system. This may result in the production of a smaller quantity of seeding particles which cannot maintain the product as a dispersion, and instead produces a gel. It is possible that a dispersion would result if a greater quantity of benzoic acid was used.

5.8 Summary

At the start of the project, it was known that a large range of polymers could be produced by the gel process, incorporating a large range of functionalities and resulting in an enormous property design window. It was thought that the dispersion process was limited to the reliable production of PEKK, and it was not anticipated that the product range would be extended broadly. Many attempts of copolymer production had been unsuccessful under previous dispersion conditions.

During this project, it has been determined that a range of particulate copolymers incorporating ether-imide, sulfone, naphthalene, and aliphatic functionalities may be successfully produced by the dispersion process on modification of the reaction parameters. The incorporation of PEKEKK and branching agents have also been successful. The selection of copolymer variants accessible by the dispersion process has been vastly increased. It is anticipated that the range of monomers which can be incorporated may be further increased by further modification of the reaction conditions to include many, if not all, of the possible monomers for the dispersion process.

The dispersion process now offers a range of particulate PAEK copolymers²⁷ which have easily tailored properties. An advantage over the gel process is that the dispersion process uses standard equipment. The product may be compounded for bulk properties, or more likely in powder form for additive layer manufacturing. This combination means that it is now a viable alternative production method for PAEK copolymers. The modifications to and the greater control over the dispersion process may also lead to the design and production of with more advanced morphologies such as block copolymers, hyperbranched polymers, dendrimers or core-shell particles. These new morphologies could access a range of new applications.

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CHAPTER 6 : SYNTHESIS OF AMINE FUNCTIONALISED PAEKs

6.1 Background

Epoxy resins are one of the thermoset frameworks commonly used as the matrices in high performance composites for engineering applications. The starting materials for the epoxy resins are linear, epoxide rich “prepreg” oligomers. A wide variety of these oligomers are available which vary in structure including backbone structure, functional groups, epoxide density and molecular weight, depending on the application of the material¹. Curing of the oligomers results in a chemically crosslinked structure via ring-opening reactions at the epoxides by a range of Lewis acids and bases, commonly amines. The major disadvantage of epoxy resins is that they are usually brittle, and therefore methods of improving their toughness have been researched widely¹⁻³. Many methods of toughening have been attempted, the most common being the incorporation of fibrous fillers such as carbon fibre and glass fibre. Another route is to disperse toughening particles through the epoxy resin. Successful toughening has been achieved by a range of inclusions such as rubbers⁴, silica⁵, and microvoids⁶, together with thermoplastics, which will be discussed further.

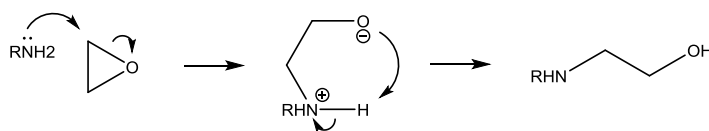
Significant commercial interest exists in the composites sector for the production of high performance thermoplastic particles to act as toughening agents in thermoset resins, specifically PEIs⁷, PAEKs, and PAESs⁸. It is known that the dispersion of thermoplastic particles in thermoset resins acts to maintain the modulus of the material whilst increasing fracture toughness^{8, 9}. It is thought that each thermoplastic particle acts as an energy absorption point which impedes fracture propagation through the thermoset matrix¹⁰.

Attempts have been made to toughen epoxy resins with PES by the exploitation of solubility parameters¹¹. PES is soluble in uncured epoxy resin but precipitates as fine droplets and forms

solid particles when the epoxy is cured, producing the particles *in situ*. Although this system does impart toughness, PES is often amorphous and does not exhibit the required solvent resistance in application. In comparison, whilst PAEKs are semi-crystalline which imparts solvent resistance, they are insoluble in uncured epoxy resin and therefore this phase separation approach is not possible.

The alternative to the phase separation method is the dispersion of non epoxy soluble thermoplastic particulates into the resin. These particulates are commonly produced by the cryogenic grinding of pellets, which is an extremely expensive process due to the energy cost of cooling which significantly adds to the cost of composites manufacture. In addition, the particles produced are irregular in shape and size, whereas ideally the particles should be as close to spherical as possible and have particle diameters in the range of 10 – 50 μm to obtain the optimum mechanical properties¹². A further issue is that many thermoplastics do not withstand the high temperatures of around 150 °C required for the curing of thermoset resins. Thus, the production of thermally resistant, largely spherical PEKK particles directly by the dispersion process avoids all of these issues and is a very attractive synthetic process for applications requiring such particles.

An extension of this concept is that the fracture toughness of the composite increases further if the thermoplastic particles are chemically bound to the epoxy matrix. Since amines are commonly used as curing agents for epoxy resins, it was hypothesised that the amine end groups would chemically bind to epoxy resin during curing, forming a covalent bond, fusing the interface and increasing toughness⁹.



Scheme 6.1 Mechanism for an S_N2 reaction of an amine with an epoxide¹³

The reaction between an amine and an epoxide proceeds *via* a ring opening S_N2 reaction¹³, where the epoxide undergoes nucleophilic attack by the amine, opening the strained ring and resulting in the formation of a hydroxyl group by proton transfer, Scheme 6.1. This small molecule mechanism can be applied to the polymer system, where R represents the PAEK chain and the epoxide is a constituent of the oligomer present in the pre-impregnated (pre-preg) matrix. The terminal amines on the PAEK particles react with the epoxides in the thermoset resin to form a chemical bond between the two constituents at their interface, Figure 6.1. These chemical bonds tether the PAEK particles in the epoxy matrix.

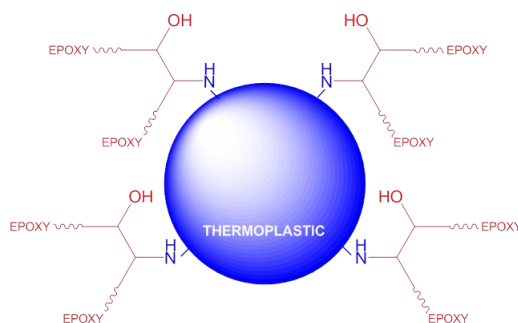


Figure 6.1 Representation of the bond formation between an amine end-capped PEK toughening particle in an epoxy matrix

The syntheses of amine end-capped PAEK oligomers and polymers for epoxy toughening have been reported. Bennett¹⁴ reported a one-pot synthesis of amine end-capped oligomers by the nucleophilic reaction of 4,4'-difluorobenzophenone with a substituted hydroquinone, with aminophenol. Low molecular weight oligomers were produced with poor amine termination efficiency due to competitive ketimine formation. A comparative two-step synthesis where the aminophenol was added during the second step was more successful and less susceptible to ketimine formation. Another one pot synthesis using the same monomer system¹⁵ also

reported ketimine formation, which could be promoted by heat curing. In attempts to avoid ketimine formation, amine end-capping was achieved by the nucleophilic reaction of a hydroxy-terminated PEK oligomer with a halo nitro aromatic end-capper¹⁶, which underwent subsequent reduction to achieve amine functionality. In addition, halogen terminated oligomers were reacted with ammonia with a copper (I) chloride catalyst to achieve amine functionality.

This chapter discusses the synthesis of amine end-capped, near spherical, particulate PEKK by the dispersion process. A range of PEKKs were successfully amine functionalised, including linear PEKKs, branched PEKKs and PEKK-EIEIE copolymers.

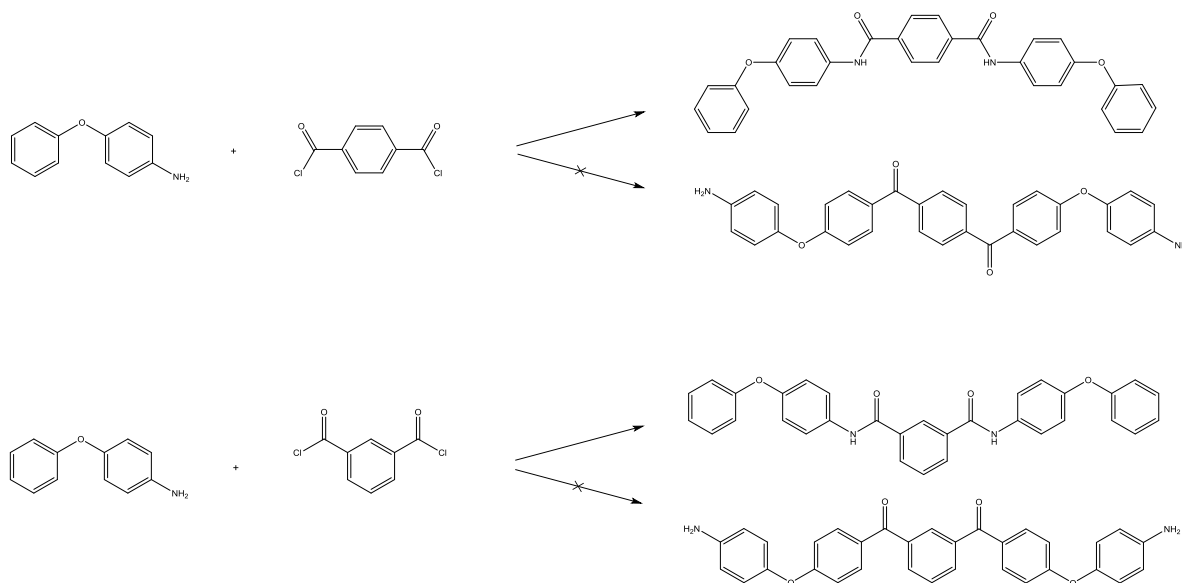
6.2 Model compound approach

Two methods were examined for the production of a range of PAEKs by the dispersion process with terminal amine functionality. The first was the direct end-capping of the polymers with 4-phenoxyaniline *i.e.* an unprotected amine. The second was to end-cap with a molecule designed to react in a Friedel-Crafts manner with the growing polymer chain, with an incorporated protected amine. The end-capping molecules which were trialled were the acetyl end capper *N*-(4-phenoxyphenyl)acetamide (EC-A) and the trifluoroacetyl end capper 2,2,2-trifluoro-*N*-(4-phenoxyphenyl)acetamide (EC-F), Scheme 6.3. A model compound approach was initially required to assess the compatibility of the end-cappers in the polymerisation system, the feasibility of end-capper attachment, and the deprotection strategy.

6.2.1 Direct end-capping

The simplest method to achieve amine functionalisation would be by the addition of a species to the end of a polymer chain which incorporates amine functionality. 4-Phenoxyaniline has the required terminal amine group, combined with an activated phenyl ring which can react in

a Friedel-Crafts manner. It was intended that this phenyl ring would react with the acid chloride end of a polymer chain. The reaction of 4-phenoxyaniline with TPC or IPC in a 2:1 stoichiometric ratio was used to investigate the potential success of direct end-capper attachment in the polymerisation system. The intended products had a central TPC or IPC with terminal amines from the addition of 4-phenoxyaniline, Scheme 6.2.



Scheme 6.2 The formation of products by the reaction of 4-phenoxyaniline with TPC and IPC

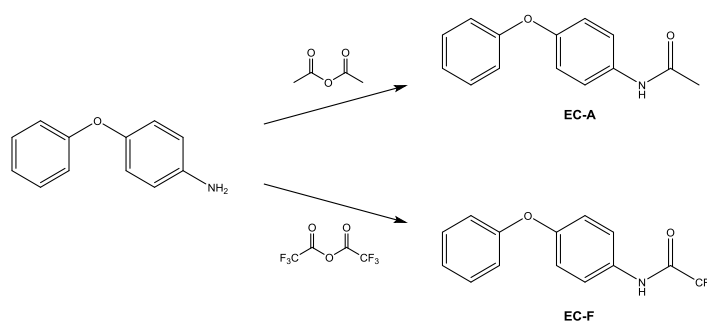
The dark brown products were of poor purity by DSC and had double melting points of 261.8 and 332.5 °C for the TPC analogue, and 208.7 and 274.3 °C for the IPC analogue. Literature values for the intended products of 226.0 – 230.0 °C for the TPC analogue and 161.5 – 164.0 °C¹⁷ for the IPC analogue indicate that these were not the products. Literature values of 328.4 – 329.5 °C and 268.5 – 269.7 °C¹⁸ suggested that the products were instead poor purity *N1,N4*-bis(4-phenoxyphenyl)terephthalamide and *N1,N3*-bis(4-phenoxyphenyl)isophthalamide respectively, Scheme 6.2.

4-Phenoxyaniline has two possible points of reaction in this system, the terminal phenyl ring and the amine. From this result, the reaction between the amine and the acid chloride was preferential to the reaction at the phenyl ring with the acid chloride. The nitrogen lone pair of

electrons is more accessible than the delocalised π -electrons in the phenyl ring *i.e.* the amine is the better nucleophile for the reaction with the acid chloride. This observation is in agreement with the previously mentioned methods for amine functionalisation using aminophenol as an end-capper, which often reacted with ketones on the polymer chain to form ketimines¹⁵. This data suggested that a protecting group for the amine would be necessary to ensure reaction at the phenyl ring and therefore to achieve the desired terminal amine functionalisation. No further analysis was carried out and the direct end-capping route was discounted.

6.2.2 Synthesis of acetyl and trifluoroacetyl end-cappers

Following the unsuccessful direct end-capping attempt, a protected end-capper approach was investigated. Two related end-capping molecules were devised which were compatible with the reaction system. The amine of the 4-phenoxyaniline was protected with acetyl and fluoroacetyl groups.



Scheme 6.3 The synthesis of the acetyl end capper (EC-A) and the fluoroacetyl end capper (EC-F)

EC-A and EC-F were synthesised according to Scheme 6.3, both resulting in high purity product, by DSC, in good yield. The compounds were fully characterised by NMR spectroscopy, mass spectroscopy, FT-IR and DSC. These potential end-cappers were evaluated for suitability using a model compound approach.

6.2.3 Hydrolysis of acetyl and fluoroacetyl end-cappers

Post-polymerisation deprotection of both end-capping molecules would be required following successful addition to the polymer chain to result in terminal amine end functionality. From the literature, the removal of the acetamide protecting group occurs by treatment in aqueous solution at $\text{pH} > 12$ or $\text{pH} < 1$, at $100\text{ }^\circ\text{C}$ ¹⁹. Since the trifluoroacetamide protecting group is more sensitive to base, hydrolysis occurs by treatment in aqueous solution at $\text{pH} > 10$ or $\text{pH} < 1$, at $100\text{ }^\circ\text{C}$ ¹⁹. Theoretically, the base hydrolysis of EC-F required less harsh conditions than the hydrolysis of EC-A, to result in 4-phenoxyaniline.

End capper	Condition	Result
EC-A	HCl	Negative
	NaOH	Negative
	NaOH reflux	Positive
EC-F	HCl	Negative
	NaOH	Positive
	NaOH reflux	Positive

Table 6.1 The outcome of deprotection attempts of the acetyl end-capper (EC-A) and fluoroacetyl end-capper (EC-F), where a positive result is the isolation of 4-phenoxyaniline and a negative result is the isolation of starting material.

The acid and base deprotection of EC-A and EC-F were tested experimentally, Table 6.1. The deprotection was deemed to be successful if the melting point of the product decreased from that of the end-capper, $131.2\text{ }^\circ\text{C}$ for EC-A and $114.2\text{ }^\circ\text{C}$ for EC-F, to that of 4-phenoxyaniline {lit.²⁰ $85 - 86\text{ }^\circ\text{C}$ } by DSC. Unsuccessful hydrolysis was indicated by recovery of the starting material and therefore no change in melting point. Experimentally, hydrolysis of EC-A using aqueous base, sodium hydroxide at $\text{pH} 13$, was unsuccessful when the mixture was simply boiled, and the compound remained in suspension. However, hydrolysis was successful using aqueous base by reflux for 1.5 hours. The formation of 4-phenoxyaniline product confirmed successful hydrolysis. However, acid hydrolysis by the addition of HCl at $\text{pH} 1$ was unsuccessful. Base hydrolysis of EC-F was successful on heating the compound in water at 80

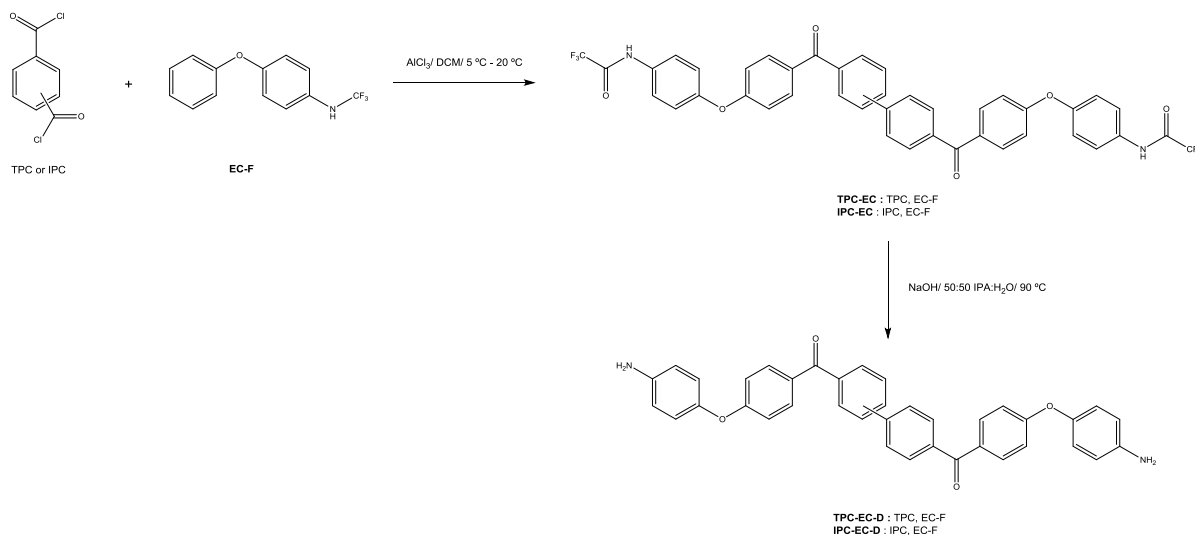
°C, and on reflux. The 4-phenoxyaniline product confirmed successful hydrolysis. Acid hydrolysis was unsuccessful.

From an industrial perspective, EC-F is less favourable than EC-A since the raw materials for its synthesis are more expensive. In addition, the handling and disposal of the trifluoroacetic acid by-product is more complex than that of the acetic acid by-product. The expense of raw materials and the disposal of by-products may be managed. However, the conditions required for its deprotection only require small modification of the standard polymer workup procedure *i.e.* a washing step using sodium hydroxide rather than ammonia. This is the most important factor and is of the greatest benefit. However, one concern relating to the use of sodium hydroxide for the deprotection step is the risk of introducing sodium ions into the polymer. If not removed successfully during workup, the sodium ions will greatly decrease melt stability of the polymer²¹. For these reasons, the EC-F was selected for further model compound studies.

6.2.4 Synthesis of linear model compounds

Conclusive analysis could not be achieved directly from amine end-capped PEKK polymer *via* a trial polymerisation due to the extremely low concentration of chain ends in comparison to the bulk polymer. A model compound approach was required to predict the feasibility of end-capper attachment in the polymer system.

Linear model compounds were produced by the AlCl₃ catalysed Friedel-Crafts acylation reaction of a diacyl chloride and EC-F in a 1:2 stoichiometric ratio, in DCM, Scheme 6.4. The success of reaction of EC-F when combined with both TPC and IPC was investigated. This method was intended to simulate the polymerisation system as far as possible.



Scheme 6.4 The synthesis of linear model compounds TPC-EC and IPC-EC by reaction of the fluoroacetyl end-capper (EC-F) with TPC and IPC respectively, with deprotection to form TPC-EC-D and IPC-EC-D respectively

Addition of EC-F to both TPC and IPC produced grey compounds, TPC-EC and IPC-EC respectively, which were fully characterised. NMR spectroscopy indicated additional minor products for both of the model compounds. Minor peaks were observed in similar positions to the peaks associated with the major product which could be attributed to the mono- addition product for each model compound. No literature data was available for the protected model compounds suggesting that they were novel structures.

Confirmation that the model compounds could be deprotected in the same manner as EC-F alone was then required.

6.2.5 Deprotection of linear model compounds

The deprotection method for the model compounds by base hydrolysis, Scheme 6.4, simulated the base wash stage in the polymer workup procedure, with as little modification as possible. The use of ammonia solution was replaced with sodium hydroxide solution. The attempted deprotection method for the model compounds required a mixed solvent system of

2:1 volume ratio water : isopropyl alcohol due to the hydrophobic nature of the compounds. Subsequent polymer workup was carried out in water only.

The deprotection of TPC-EC to TPC-EC-D by base hydrolysis (sodium hydroxide, pH 13) was suggested by the reduced melting point of 221.1 °C {lit.¹⁷ 226.0 – 230.0 °C} from 325.9°C by DSC. Although not within the literature range, the large reduction in melting point indicates a definite change in structure.

IPC-EC was deprotected in the same manner to result in IPC-EC-D, with a reduced melting point of 165.2 °C {lit.¹⁷ 161.5 – 164 °C} from 231.2 °C. Both compounds were subsequently fully characterised. NMR spectroscopy indicated a small proportion of protected species remaining in the deprotected samples. The compounds could be fully deprotected by increasing the reaction time.

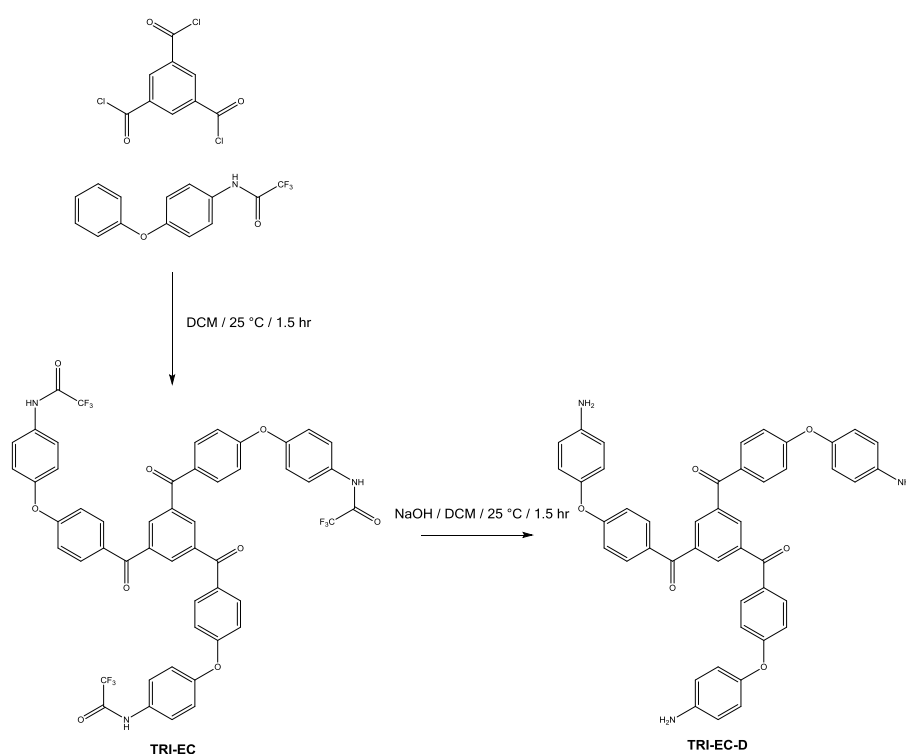
Based on the results of the model compound approach, it was likely that the use of EC-F would be a successful route to achieve terminal amine functionality in the polymerisation system. It was anticipated that post polymerisation deprotection of the amines would be achievable during polymer workup with a sodium hydroxide washing step replacing the ammonia washing step.

6.2.6 Trifunctional model compounds

An alternative to amine end-capped linear PEKK was branched PEKK. This was produced by the incorporation of the trifunctional monomer 1,3,5-benzenetricarbonyl chloride (TRI) into the monomer feed, also used in Chapter 5. With the incorporation of this monomer, there was a statistical probability that EC-F would react with the trifunctional acid chloride rather than

TPC or IPC. Thus, trifunctional model compounds were synthesised to investigate the compatibility of EC-F with TRI.

TRI was reacted with EC-F in 1:3 stoichiometric ratio to form the trifunctionalised molecule TRI-EC, Scheme 6.5. TRI-EC underwent base deprotection by NaOH at pH 13, in the same manner as the linear model compounds, to form TRI-EC-D. The structure of TRI-EC was confirmed by NMR spectroscopy and was fully characterised. The structure of TRI-EC-D was partially confirmed by DSC, mass spectroscopy and FT-IR spectroscopy.

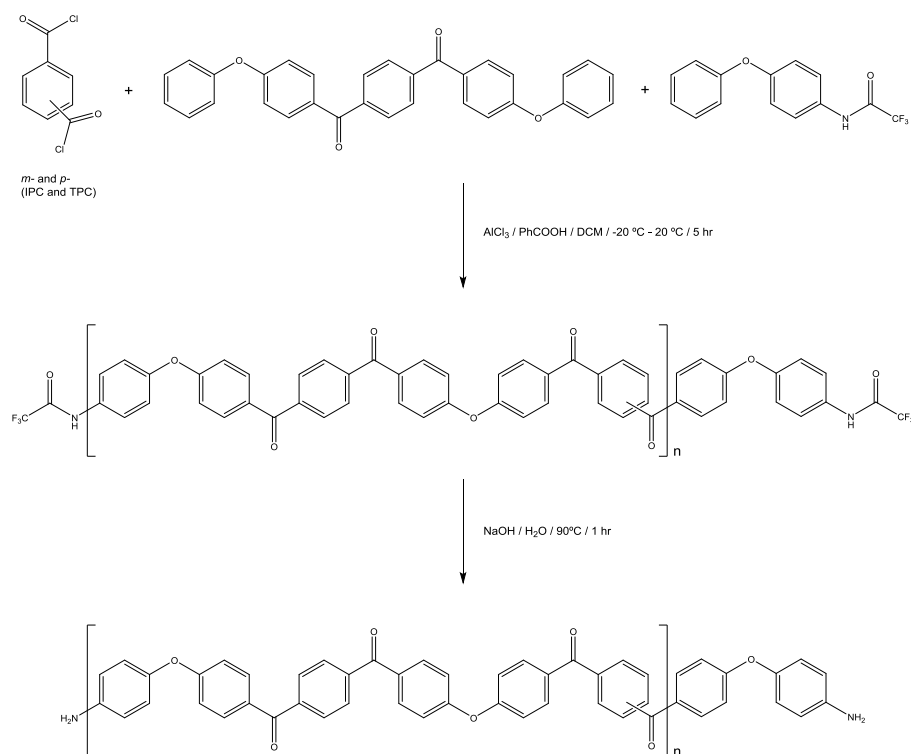


Scheme 6.5 The synthesis of TRI-EC and its base deprotection to form TRI-EC-D

Since the end-capper addition was successful by small molecule reaction, it was presumed that end-capping by EC-F would be compatible with the polymerisation system by incorporation of TRI into the monomer feed. It was also presumed that post-polymerisation deprotection would be successful by the same sodium hydroxide washing step to achieve terminal amine functionality.

6.3 Amine end-capped PAEKs

The protected end-capper method for amine functionalisation was extended to the dispersion polymerisation system. Amine end-capped PEKK was produced by the standard dispersion process²², replacing the usual benzoyl chloride end-capper in the monomer feed with EC-F²³,²⁴, Scheme 6.6. The use of EC-F requires that the out-of-balance is calculated with the acid chloride in excess to ensure terminal attachment.



Scheme 6.6 Synthesis of the amine end capped PEKK. The ring with undefined geometry may be T and I for the 80:20 and 60:40 PEKKs and T only for the 100:0 PEKK.

6.3.1 Trial synthesis of amine end-capped PEKK

A small scale polymerisation of 100:0 PEKK was carried out at 10% out-of-balance with EC-F replacing the benzoyl chloride in the monomer feed to confirm the addition of the end-cappers in the polymerisation system and the subsequent deprotection during basic workup. The high out-of-balance resulted in the production of oligomers with a large proportion of amine end groups. The presence of amines was confirmed by the presence of a characteristic broad peak at 9.52 ppm in the ¹H NMR spectrum.

6.3.2 Large scale synthesis of amine end-capped PAEKs

The protected end-capping method was used to produce a range of PAEKs, scaled up to a five litre reactor with batch size 300 g of polymer, to include linear PEKKs (100:0, 80:20, 60:40), branched PEKK and PEKK-imide copolymer by modification of the monomer feed. The polymerisations were carried out at 5% out-of-balance to result in a large end group concentration whilst maintaining a high enough molecular weight to impart desirable mechanical properties.

6.3.2.1 Confirmation of amine end-capping

Quantitative combustion analysis was carried out on amine end-capped 100:0 PEKK. The theoretical composition of the PEKK was C 75.93%, H 4.03% and N 0.23%. Whilst the analysis confirmed the presence of nitrogen, a large discrepancy between the theoretical and calculated values was apparent, Table 6.2. Analysis of the neat sample was initially carried out, with no nitrogen detected in the first sample and 0.44% in the second. Subsequently, tungsten oxide was added to the samples to ensure complete combustion, as PAEKs are known to have good fire resistance, low combustion and a high char residue^{25,26}. The theoretical % N of between 0.62 and 0.67% is above, but close to, the detection limit of 0.1%. Theoretically, the higher % N would require a much lower molecular weight polymer, which is not the case, as demonstrated by the IV, Table 6.4. It is likely that incomplete combustion has occurred despite the addition of tungsten oxide. Combustion analysis was deemed not to be a suitable technique to analyse the nitrogen content of PAEKs with low flammability.

FT-IR spectroscopy was carried out on the solid 100:0 PEKK which confirmed two weak absorption bands at 3500-3300 cm^{-1} which are characteristic of primary amines²⁷, and have been observed for amine terminated PEEK oligomers¹⁵.

%	C	H	N
Theoretical	75.93	4.03	0.23
100:0 (1)	77.97	3.93	0.44
100:0 (2)	78.27	4.01	-
100:0 (3)*	77.80	3.92	0.67
100:0 (4)*	77.69	3.93	0.67
100:0 (5)*	78.14	3.91	0.67
100:0 (6)*	78.00	3.95	0.62

*Tungsten oxide catalyst to ensure complete combustion

Table 6.2 Theoretical and calculated values for % C, H, N combustion analysis for 100:0 PEKK with and without tungsten oxide catalyst

Qualitative analysis using ninhydrin was used to confirm the presence of amine groups, a positive result being the generation of purple colour. The use of ninhydrin for the confirmation of surface amine functionalisation of polymers has been reported²⁸. A purple colour was observed for each of the amine end-capped PAEKs, whereas the non amine end-capped samples remained white, Table 6.3.

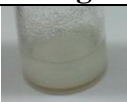






Polymer	Image	Colour	Result
PEKK 100:0		White	Negative
PEKK 90:10		White	Negative
PEKK-NH ₂ 100:0		Pink	Positive
PEKK-NH ₂ 80:20		Purple	Positive
PEKK-NH ₂ 60:40		Purple	Positive
PEKK-NH ₂ 100:0, branched 5%		Dark purple	Positive
PEKK-EIEIE-NH ₂		Dark purple	Positive

Table 6.3 Results of ninhydrin tests for the presence of amine end-capping on the PAEKs

The test was carried out in DCM to swell the polymer particles, rendering the amine groups accessible. The colour developed over several hours as the ninhydrin was required to diffuse into the polymer particles before reacting with the amine groups. A further consideration is the location of amine functionalisation on the polymer particles. It would be thought that since the end-capper was added at the beginning of the reaction, then amines would be dispersed through the particles as the polymerisation progressed. Evidence for this theory is that as the ninhydrin test is not instant, taking time for the solution to diffuse in to the particles to promote a colour change. An instant colour change on the addition of ninhydrin was not observed visually, but it would be presumed that a proportion of amines would be on the exterior of the particles. It may be possible that an instant colour change could be observed by colourimetric analysis. On the assumption that the amine groups do not affect the thermal properties of the bulk PAEK, the distribution of the amines through the particles should not prove problematic. The optimum degree of amine functionalisation of the PAEK particles is not known, and can only be determined by mechanical testing. It is possible that a higher degree of external functionalisation may be achieved by the addition of the end-capper at a later stage in the polymerisation, as the end-capping reaction would occur on the exterior of the already formed particles.

6.3.2.2 Bulk polymer properties

Although the main aim was to incorporate terminal amine functionality, it was also necessary to determine if the functionalisation affected the bulk polymer properties. The IVs of the linear and branched PEKK polymers were in the region of 0.46 – 0.63 dL.g⁻¹, Table 6.4, in the expected range of a PEKK polymerisation run at 5% out-of-balance. However, the IV of the PEKK-EIEIE copolymer was significantly lower than the other polymers, 0.24 dL.g⁻¹, and lower than what would be expected from an imide copolymer at this out-of-balance.

Polymer	IV/ dL.g ⁻¹
PEKK 100:0	0.63
PEKK 80:20	0.50
PEKK 60:40	0.46
PEKK branched	0.50
PEKK-EIEIE	0.24

Table 6.4 Inherent viscosity measurements of amine end-capped PEKKs, carried out in concentrated sulphuric acid at 25 °C

	100:0 PEKK	80:20 PEKK	60:40 PEKK	Branched PEKK	PEKK- EIEIE
Heating 1					
T _g / °C	-	-	-	-	*
ΔCp*/ Jg ⁻¹ K ⁻¹	-	-	-	-	
T _m / °C	380.1	351.7, 362.5	272.7, 306.2	345.2, 358.6	
ΔH/ Jg ⁻¹	-47.98	-49.52	-17.18	-40.32	
Heating 2					
T _g / °C	177.7	160.4	164.8	168.1	
ΔCp*/ Jg ⁻¹ K ⁻¹	0.078	0.067	0.219	0.121	
T _m / °C	354.4	347.3	-	328.9	
ΔH/ Jg ⁻¹	-15.13	-23.74	-	-17.57	
Cooling 1					
T _g / °C	-	-	151.2	-	
ΔCp*/ Jg ⁻¹ K ⁻¹	-	-	0.021	-	
T _c / °C	289.9	274.2	-	234.9	
ΔH/ Jg ⁻¹	17.42	29.15	-	21.89	
Cooling 2					
T _g / °C	165.1	-	152.9	164.2	
ΔCp*/ Jg ⁻¹ K ⁻¹	0.020	-	0.001	0.105	
T _c / °C	288.8	259.8	-	261.4	
ΔH/ Jg ⁻¹	8.057	25.11	-	9.315	

*The DSC trace for the imide copolymer is unclear and thermal transitions cannot be assigned

Table 6.5 DSC data for the amine end-capped PEKK based polymers, including two heating and cooling cycles 90 - 400 °C at 20 °C.min⁻¹ and 400 - 90 °C at 10 °C.min⁻¹

The thermal properties of the bulk amine end-capped polymers differ from the non amine end-capped versions, Table 6.5, indicating that the addition of amine end-capping has an effect on the thermal properties of the bulk polymer. The T_g, T_m and T_c values for all of the amine end-capped polymers are lower than those of the non end-capped versions, described in

Chapters 3 and 5, although each of these parameters still remain in the region expected from PAEK copolymers. The DSC trace for the imide copolymer is unclear and thermal transitions could not be assigned.

Parallel plate rheology was not carried out on the amine end-capped PAEKs as the particles are a solid phase additive in application. Although they would be subject to heating cycles during composites processing, the degradation temperature of the epoxy matrix is much lower than that of the melting points of the PAEK additives. Therefore, they would not be melted and their melt rheology is not a critical factor.

SEM analysis¹² confirmed the size and morphology of the particles, Figure 6.2. The particle diameter increased in the order of 100:0 PEKK, 80:20 PEKK and branched PEKK from approximately 40 – 90 μm . These particles were substantially spherical, with grooves in the comparatively smooth exteriors. The particle diameter of the PEKK-imide copolymer ranged from 60 – 90 μm , and the particles had an irregular, porous appearance, possibly suggesting agglomerates of smaller particles. The 60:40 PEKK was in the form of elongated particles of around 500 μm in length and 100 μm in width, with a porous interior. All of the samples contained a proportion of particles outside the size ranges stated.

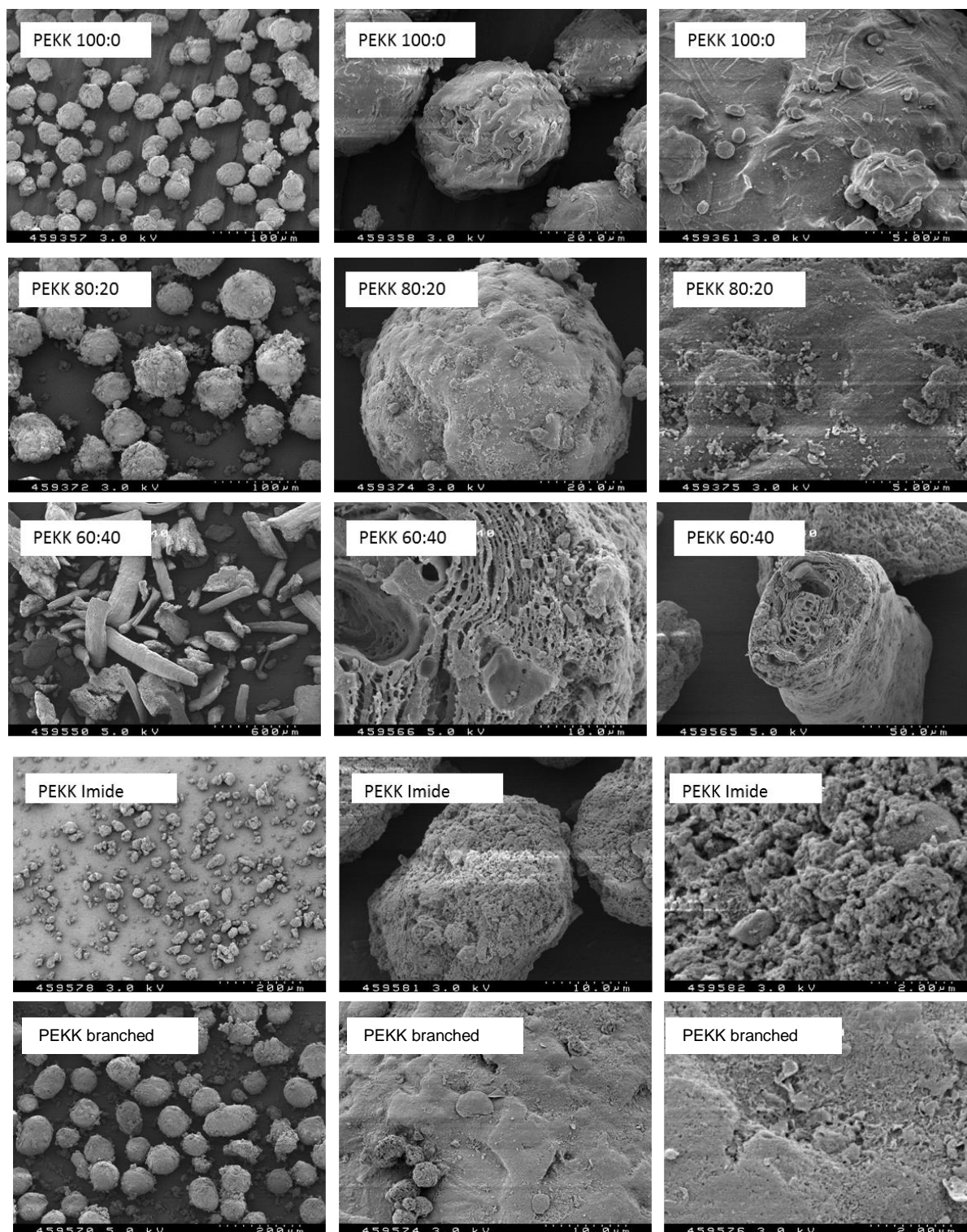


Figure 6.2 SEM images of the amine end-capped 100:0 PEKK, 80:20 PEKK, 60:40 PEKK, PEKK-imide and branched PEKK, reproduced from¹²

6.4 Fracture toughness and mechanical strength

The amine functionalised PAEK particles were incorporated into composite laminates to evaluate their toughening potential¹². The particles were dispersed in the resin-rich, inter-laminar region between the carbon fibre toughened epoxy resin layers, Figure 6.3.

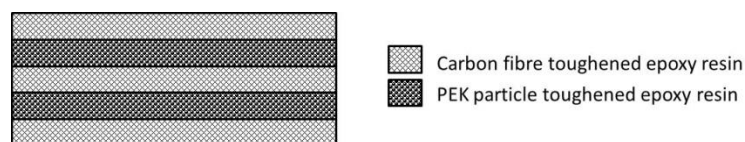


Figure 6.3 Representation of the structure of a composite laminate to include the carbon fibre toughened epoxy resin layers and the inter-laminar PAEK particle toughened epoxy resin layers

PEKK	$G_{IIC}/KJ.m^{-2}$	
	Sample 1	Sample 2
Unfunctionalised	1.331	1.347
Functionalised	2.634	2.314

Table 6.6 Fracture toughness (G_{IIC}) data for cured epoxy resin test panels with incorporated non-functionalised and functionalised PEKK particles¹²

The incorporation of functionalised PEKK particles into epoxy resin test panels showed approximate doubling of fracture toughness, G_{IIC} , compared to those prepared with non-functionalised PEKK particles from 1.3 – 2.6 $KJ.m^{-2}$ for sample 1, Table 6.6.

SEM analysis was carried out on the fracture surface of an epoxy resin test panel incorporated with functionalised PEKK particles. It demonstrated that the fracture propagation caused both a. particle pull-out which leaves a crater in the surface and b. particle fracture-through where part of the particle remains attached to the surface, Figure 6.4. The evidence of particle fracture-through indicated that the particles were chemically bonded to the epoxy resin. The fracture had propagated through the particle rather than around the particle-epoxy interface, indicating that the chemical bond could withstand fracture propagation better than the bulk particle. Particle pull-out dominates with the incorporation of non-functionalised particles, as

no chemical bonds are present at the interface and fractures will propagate around the particles.

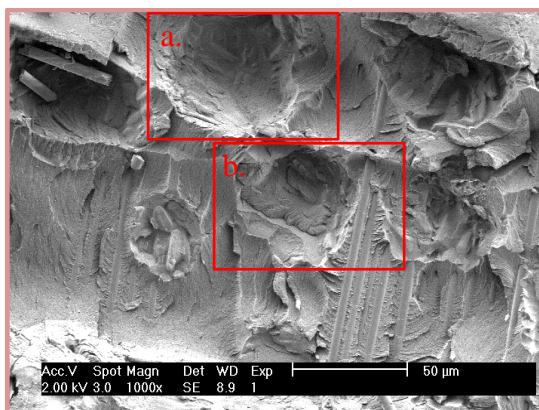


Figure 6.4 SEM image of a fracture surface of an epoxy resin text panel with incorporated functionalised PEKK particles, to show a. particle pull-out and b. particle fracture-through, reproduced from¹²

Since the thermoplastic toughening particles increase the fracture toughness and damage tolerance of the composite laminate, these materials are suitable for applications which require load bearing and impact resistant structures.

6.5 Summary

Amine end-capped PAEKs were synthesised *via* minor modification of the dispersion process. An end-capping aromatic derivative was designed to incorporate terminal amine functionality onto the PAEKs *in situ* using a protection-deprotection strategy which added no further steps to the original dispersion polymerisation and workup methods. A model compound approach was employed to ensure successful attachment to the polymer and subsequent deprotection, together with its compatibility and suitability within the polymer system. This was successful for linear and trifunctional versions. Scale-up of the PAEK dispersion synthesis was achieved to 300 g batches, with amine functionalisation confirmed qualitatively. Amine end-capped PEKK with 100:0, 80:20, 60:40 T:I ratios, branched PEKK and PEKK-imide copolymers were synthesised. Mechanical analysis confirmed a substantial increase in fracture toughness

on incorporation of the functionalised PEKK particles in an epoxy resin laminate compared to non-functionalised PEKK particles.

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CHAPTER 7 : SUMMARY AND FUTURE WORK

7.1 Summary

Over the course of this project, a significantly greater understanding of the dispersion process to produce PAEKs was achieved. Initially, the process parameters were evaluated and it was determined that comparable PEKK to reported materials could be produced, and that the process was scalable. The effect of benzoic acid in the polymerisation was investigated, and a seeding mechanism was proposed. The polymerisation process was then greatly extended to successfully incorporate a range of monomers with alternative functionality, together with the design of an end-capper molecule to achieve terminal amine functionalisation.

A detailed study of the process parameters of the dispersion process was carried out. It was noted that high monomer purity is essential to achieve a high molecular weight polymer product, that sub-zero reactant addition temperatures are necessary to avoid side reactions and that DCM is a suitable solvent for the dispersion process whereas *ortho*-dichlorobenzene is less favourable. Reactor loading was determined to have an effect on the resultant particle size, with higher loadings producing larger polymer particles. A 200 °C drying cycle is required to achieve melt stable polymer. Recycling of the DCM benzoic acid is possible with an efficiency of over 80%, which is industrially significant. Critical observations include that particulate polymer formation is not dependent on the order of addition of reactants, indicating a very robust process. The concentration of benzoic acid used has a large effect on the size of the polymer particle produced, with a higher concentration producing smaller polymer particles. Unlike the gel process, the use of an aqueous acid wash is essential to remove all residual benzoic acid. The dispersion process was shown to be scalable, with a 300 g batch size achieved.

It was determined that PEKK with a range of T:I ratios, which were identical to reported materials, could be produced by the dispersion process with a high degree of control. The T:I ratio allowed adaptation of the thermal properties and the degree of crystallinity of the PEKKs. The PEKKs were of high molecular weight and demonstrated good thermal stability. The particles produced were in the region of 50 - 100 μm in diameter, with particle size dependent on T:I ratio. The particles were semi-crystalline, largely spherical, and likely to be porous with an exterior skin. The polymerisations were carried out at a 10% reactor loading, significantly higher than other reported systems to produce PEKK particles.

It was determined that benzoic acid has a more involved role in the dispersion polymerisation process than initially thought. Through a set of experiments and observations, a seeding mechanism was proposed. Aluminium benzoate crystals are formed which act both as a Lewis acid Friedel-Crafts catalyst and as a template for polymerisation. PAEK polymerises around the crystals to result in a polymer dispersion at high reactor loading. The aluminium benzoate complex is broken down and the resultant ions removed from the particles during aqueous acidic workup.

The dispersion process was used to produce a range of particulate PAEK copolymers by modification of the process parameters. PEKEKK, sulfone and ether-imide copolymers were successfully synthesised by the incorporation of co-monomers and were analysed in detail. A range of additional copolymers were trialled to include aliphatic, naphthalene, biphenyl imide and branching functionalities. Each co-monomer affected the thermal properties and degree of crystallisation of the resultant polymer, dependent of their structure. This study vastly increased the range of materials which can be produced by the dispersion process, and has indicated that it will be possible to incorporate additional functionalities.

Amine end-capped PAEKs were produced by the dispersion process. A protected end-capper was devised to incorporate terminal amine functionality, which was trialled in a model compound approach. The protected amine end-capper was successfully added to PAEKs, with deprotection achieved by minor modification of the workup procedure. Polymer amine functionality was confirmed by colourimetric tests. The amine functionalised particles were incorporated into epoxy panels, which resulted in the doubling of the fracture toughness.

Overall, this project has determined that the dispersion process is robust and reliable in the production of a range of PAEKs in particulate form. It has indicated that the dispersion process has advantages over existing processes and has the potential to be a viable industrial alternative for the production of PAEKs.

7.2 Future work

Three main areas for future work have been highlighted over the course of the project, which are discussed here in more detail.

Despite there being a major advancement in the knowledge of the chemical mechanism behind the dispersion process, and a mechanism proposed, this is not definitively known. Additional information in this area has the potential to further widen the scope of materials production and to increase control of the process and products. This could be achieved by the definitive determination of the structure of the seeding species by x-ray diffraction studies. In addition, the formation of the complex could be monitored, for example by react-IR spectroscopy or by *in situ* NMR spectroscopy. In this case, a method to handle the HCl evolved during analysis would need to be overcome. It may also be possible to use a particle sizing probe in the reactor to study the evolution of particle size, from crystals to polymer particles, which may clarify the mechanism.

Another opportunity for future work concerns PAEK copolymers, with two potential routes to explore. Firstly, increasing the range of materials by the incorporation of alternative monomers is of interest. This is likely to require the modification of synthetic parameters, such as the concentration of benzoic acid, to achieve a fine dispersion. The second option is the optimisation of existing materials. The focus of the copolymer work was to discover if the materials were compatible with the dispersion process. Optimisation of, for example, the melt viscosity, would allow these materials to be analysed more thoroughly and to assess their suitability for applications.

The third area for future work is the optimisation of the workup procedure to minimise aluminium residues which are known to affect the melt stability and viscosity of the polymers. Aluminium analysis would be required to determine the level of aluminium residues, and then to devise a method for more efficient extraction. Whereas the current workup procedure is carried out in aqueous media, it is possible that a solvent which would swell the polymer would result in more efficient extraction. This approach may be used in combination with a Soxhlet thimble.

CHAPTER 8 : EXPERIMENTAL

8.1 Analytical techniques

UV-visible spectra were recorded on an Agilent Cary 5000 spectrometer capable of analysing from 175 to 3300 nm. Polymer solutions in mixed DCM/ TFA solvent were analysed by transmission.

Inherent viscosity (IV) measurements were carried out using Poulten Selfe & Lee glass Ostwald viscometers, size D, in a Townson and Mercer E270 viscometer bath. Measurements were carried out using 0.1 wt% polymer solutions in concentrated sulfuric acid at 25 °C.

Melt viscosities were recorded on a Malvern Instruments Rosand RH7 capillary rheometer at 400 °C and at a shear rate of 30 s⁻¹, unless otherwise stated. A barrel with length 290 mm and bore diameter 15 mm was used. A tungsten carbide die with length 16 mm and a bore diameter of 1 mm was used, with a 90 ° die entrance.

Melt viscosities were measured using a Thermo Scientific Haake Mars III parallel plate rheometer with a controlled test chamber. Steel plates of 25 mm diameter were used, and measurements were carried out at 400 °C and a shear rate of 1 s⁻¹, unless otherwise stated.

Differential scanning calorimetry (DSC) data were recorded on a Netzsch DSC 200 F3 *Maia*[®] instrument. Data was recorded using pierced lid aluminium crucibles in a nitrogen atmosphere. Cooling was achieved via a forced air system above 20 °C, or by liquid nitrogen cooling for lower temperatures and fast cooling rates. Data was analysed using *Proteus*[®] software. Melting point and mol% purity were calculated using the standard protocol in *Proteus*[®] software.

Particle size analysis was recorded on a Malvern Instruments Mastersizer 2000 instrument, coupled with a Hydro 2000MU large volume manual wet dispersion accessory. Analysis was carried out in a dispersant of 50:50 vol% IPA:water, unless otherwise stated. The parameters used were particle refractive index 1.5, particle absorption index 0.1 and dispersant refractive index 1.33.

Fourier transform infrared (FT-IR) spectra were recorded on an Agilent Digilab Excalibur bench, fitted with a permanently aligned diamond window attenuated totally internal reflecting (ATR) sampling attachment, Spectra Tech Goldengate. The spectrometer is also fitted with an imaging FTIR UMA 600 microscope with single point MCT detector and imaging solid state detector, and a Micro Ge ATR sampling accessory. Absorption maxima (ν_{\max}) are reported in wavenumbers (cm^{-1}) and only selected peaks are reported.

Low resolution mass spectra were recorded on a Fisons Platform spectrometer using electrospray ionisation (ESI) or a Fisons AutoSpec-oaTof spectrometer using electron impact ionisation (EI) or field ionisation (FI). The m/z values of major peaks are reported in Daltons. High resolution mass spectra (HRMS) were recorded on a Bruker microTof spectrometer (ESI).

^1H NMR spectra were recorded on Bruker AVN400 (400 MHz), and DRX500 (500 MHz) spectrometers. Chemical shifts (δ_{H}) are reported in parts per million (ppm) and are referenced to the residual protonated solvent peak. The abbreviations used to describe multiplicities are as follows: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), m (multiplet) and br (broad). In most cases, first order multiplicities are reported only. Coupling constants (J) are given in Hertz (Hz). Two dimensional COSY (correlation spectroscopy) were obtained on a Bruker AVN400 or DRX500 spectrometer.

^{13}C NMR spectra were recorded on a Bruker AVN400 spectrometer at 100.6 MHz or a Bruker DRX500 spectrometer at 125.8 MHz with proton decoupling. Chemical shifts (δ_{C}) are reported in parts per million (ppm) and are referenced to the residual protonated solvent peak. Assignment was aided by the use of DEPT editing and edited HSQC, performed on either AVN400 or DRX500 spectrometers.

^{19}F NMR spectra were recorded on a Bruker AVN400 spectrometer at 376.6 MHz. Chemical shifts (δ_{F}) are reported in parts per million (ppm) and are referenced to CFCl_3 .

^{27}Al NMR spectra were recorded on a Bruker AVN400 spectrometer at 15 kHz. Chemical shifts (δ_{Al}) are reported in parts per million (ppm).

^{27}Al DPMAS and ^{13}C CPMAS solid state NMR spectra were obtained at 104.2 and 100.5 MHz respectively (9.4 T) on a Bruker Avance IIIHD spectrometer, using 4mm O.D. zirconia rotors and MAS rate of 15 and 10 kHz. For ^{27}Al in order to obtain quantitative MAS spectra, a single pulse excitation was applied using a short pulse length (0.23 μs). 2400 scans were acquired with a 0.1 s delay and a MAS rate of 15 kHz. The ^{27}Al chemical shift was referenced to an aqueous solution of $\text{Al}(\text{NO}_3)_3$ (0 ppm). ^{13}C CPMAS NMR spectra were acquired using cross-polarization sequence with a variable X-amplitude spin-lock pulse and spinal64 proton decoupling at MAS rates of 8 and 10 kHz. 1500 transients were acquired using a contact time of 2.5 ms, an acquisition time of 25 ms (2048 data points zero filled to 16 K) and a recycle delay of 120 s. All ^{13}C spectra were referenced to adamantane (the upfield methine resonance was taken to be at $\delta = 29.5$ ppm on a scale where $\delta(\text{TMS}) = 0$) as a secondary reference.

Scanning electron microscopy (SEM) was carried out using a Hitachi HT3000 Tabletop SEM. Samples were sputter coated with platinum prior to analysis. Elemental analysis was achieved using built-in energy dispersive x-ray spectroscopy (EDS).

X-ray photoelectron spectroscopy (XPS) was carried out using a VG – Escalab X-Ray Photoelectron Spectrometer VGX900 using Aluminium $K\alpha$ radiation with an energy of 1486 eV. The operating pressure was $<1 \times 10^{-8}$ mbar. Samples were attached to the sample stub using double sided tape. The Pass Energy was set at 50 eV for the wide scan of the sample, and 20 eV for the more intense scans of specific areas. The resulting spectra were then analysed using CasaXPS peak fitting software, and sample charging corrected using C 1s as a reference setting at 285.0 eV.

Optical microscopy was carried out using a Reichert Polyvar Met Microscope which operates with bright field, dark field and polarisation modules. Images were analysed with digital integration.

8.2 Materials

Due to the dependence of the chemistry described on the starting material purity and to its commercial relevance, the sources of all materials used are detailed below.

Acetic acid	99.5%	Acros Organic
Acetic anhydride	98+%	Acros Organic
Acetone	99.5%	APC Pure
Activated carbon	Decolourising	Sigma Aldrich
Alumina	99.5%, $\leq 10 \mu\text{m}$ average	Sigma Aldrich

Aluminium chloride	99% extra pure, anhydrous Powder and granules	Acros Organics
Ammonia solution	35%	SpeciFied
Benzenesulfonic acid	90%	Acros Organics
1,3,5-benzenetricarbonyl chloride	98+%	Alfa Aesar
Benzoic acid	99% extra pure	Acros Organics
Benzophenone	99%	Alfa Aesar
Benzoyl chloride	98+%	Acros Organics
Chloroacetic acid	99%	Alfa Aesar
Chlorobenzene	99+%	Acros Organics
4-Chlorobenzoic acid	98+%	Alfa Aesar
DCM	99.5%	APC Pure
<i>N,N</i> -Dimethylacetamide	99%	Acros Organics
Dimethyl sulfone	98%	Acros Organic
EKKE	Standard grade	Commercial
Graphite	Microfine powder	Kasp Security
Hexane	99%, mixture of isomers	Acros Organics
Hydrochloric acid	32%	Fisher Scientific
IPC	98%	Acros Organic
IPA	99.9%	APC Pure
Magnesium sulfate	97%, anhydrous	Acros Organics
Methanol	99.9%	APC Pure
Methylcyclohexane	99%	Acros Organics
Ninhydrin	99%	Alfa Aesar
4-Phenoxyaniline	97%	Acros Organics
Phthalic acid	99%	Alfa Aesar

Silica gel	High purity, pore size 60 Å, 200 – 425 mesh	Sigma Aldrich
Sodium benzoate	99+%, extra pure	Acros Organics
Sodium hydrogen carbonate	99+%	SpeciFied
Sodium hydroxide	97+%, pellets	SpeciFied
Sulfuric acid	95+%	SpeciFied
Toluene	99+%, extra pure	SpeciFied
TPC	99+%	Acros Organics
Trichloroacetic acid	99%	Alfa Aesar
Trifluoroacetic anhydride	99+%	Acros Organics

All reactants and reagents were used as supplied unless otherwise stated.

Custom synthesised monomers

1,4-bis(4-phenoxybenzoyl)benzene (EKKE)

Bis(4-phenoxyphenyl)methanone (EKE)

5,5'-oxybis(2-(4-phenoxyphenyl)isoindoline-1,3-dione) (EIEIE)

1,1'-sulfonylbis(4-phenoxybenzene) (ESE)

Monomers synthesised at Ketonex

2,2'-bis(4-phenoxyphenyl)-[5,5'-biisoindoline]-1,1',3,3'-tetraone (EI-IE)

1,12-Bis(4-phenoxyphenyl)dodecane-1,12-dione (EK10KE)

Naphthalene-2,6-diylbis((4-phenoxyphenyl)methanone) (EKNKE)

Monomer recrystallisation

EKKE may be recrystallised from chlorobenzene.

TPC and IPC may be recrystallised from hexane.

8.3 General procedures

All of the homopolymers and copolymers were synthesised using the same conditions as stated in the general sections, but altering the composition of the monomer feeds. Monomer feeds and reactants are stated for individual experiments and are listed in g, apart from DCM which is listed in ml. Additional parameters are listed in individual experimental sections to include % out-of-balance, T:I ratios, the number of benzoic acid equivalents and reactor loading. The general procedures can be scaled to accommodate a range of reactor sizes, and a range of monomers can be incorporated into the monomer feed to produce copolymers. All polymers were subject to the general decomplexation, workup and drying procedures unless otherwise stated. Polymer masses are listed in g.

All monomers were weighed to ± 0.5 mg. Benzoic acid was weighed to ± 1 mg. Benzoyl chloride was weighed to ± 0.1 mg. Aluminium chloride was weighed to ± 1 g. All of the reactants were stored in sealed vessels until they were used to prevent water uptake and/or reactant loss.

If stirrer failure occurred within one hour of the final reactant addition, the newly formed polymer particles were “sticky” and agglomerated at the bottom of the vessel. This agglomeration did not re-disperse if stirring was resumed. After this one hour period, the particles were no longer “sticky” and did not agglomerate on stirrer failure. Stirring was resumed successfully to re-disperse the polymer particles.

The polymer film on the inside of the reactors was removed by soaking in water. The polymer film was decomplexed, turned white and detached from the sides of the reactor. On isolation

of the complexed polymer, the filtrate was decomplexed with an excess of water which turned white.

8.3.1 Calculations

The out-of-balance was calculated with the EKKE, and/or other aromatic monomer, in excess to the acid chloride monomer. The benzoyl chloride end-capper was added in corresponding quantity. In the case of the amine end-capped polymer in Chapter 6, the acid chloride monomer was in excess to accommodate the aromatic end-capper.

The benzoic acid dispersant was used at four (or other) molar equivalents relative to acid chloride. The aluminium chloride was used at a total 1:2:2 molar equivalents of benzoic acid: EKKE: acid chloride respectively *i.e.* corresponding to carbonyl equivalents, with an overall excess of 20%. The polymer loading *i.e.* the mass of polymer produced per volume of dichloromethane, was 10% unless otherwise stated.

8.3.2 General small scale polymerisation procedure

Small scale polymerisations were carried out in 250 ml glass jars with PTFE lined lids, and were stirred using a magnetic stirrer bar. A representative polymerisation of 80:20 PEKK is described for reference.

A Julabo HP40-FP refrigerated-heating circulator was set to -30 °C. Once the set temperature was reached, dichloromethane (~75 ml) was added to a 250 ml glass jar with PTFE lid, containing a magnetic stirrer bar, and the lid sealed. The dichloromethane was cooled in the bath of the cooler with swirling to -15 °C. The following sequence of additions was carried out. The mixture was stirred at a rate of approximately 200 rpm with the lid of the jar partially undone. The mixture was cooled to -15 °C between each of the additions in the sealed jar.

Aluminium chloride (23.37 g, 175.3 mmol) was added, followed by benzoic acid (7.9256 g, 64.85 mmol), not allowing the mixture to rise above -10°C due to the exotherms. The dichloromethane developed a yellow colour due to the aluminium chloride, the majority of it remained at the bottom of the jar. No colour change occurred on initial addition of the benzoic acid, but a white precipitate formed after approximately five minutes. The reaction mixture was then allowed to cool back to -15°C . Terephthaloyl chloride (1.9345g, 9.5286 mmol) and isophthaloyl chloride (1.3540 g, 6.6692 mmol) were carefully added at a rate so as not to allow the mixture to rise above -10°C . The remaining acid chlorides were transferred by washing with approximately 50 ml dichloromethane in three portions. EKKE (8.0002 g, 17.003 mmol) was carefully added at a rate so as not to allow the mixture to rise above -10°C . At this point the mixture turned bright opaque orange. The remaining monomer was transferred by washing with approximately 50 ml dichloromethane in three portions. Lastly, benzoyl chloride (0.2262 g, 1.610 mmol) was added with its washings, together with the remaining dichloromethane. The stirrer speed was increased to approximately 300 rpm and maintained over the reaction time. The lid of the jar was not sealed over the reaction time to allow the release of HCl gas. The reaction mixture was naturally warmed to room temperature. After approximately 30 minutes, dispersed polymer particles began to form in the orange solution. The reaction mixture was stirred rapidly for 4.5 hours. The resultant polymer was decomplexed, according to Section 8.3.5.

8.3.3 General polymerisation procedure for one litre reactor

A representative PEKK polymerisation with 70:30 T:I ratio, run at 3% out of balance and 10% reactor loading in a one litre reactor is stated.

The temperature of the reaction vessel was controlled by a Julabo HP40-FP refrigerated-heating circulator which was set to its maximum cooling temperature of -30°C , not

circulating through the reactor vessel jacket. The glass, one litre reaction vessel, manufactured by Labglass was set up. The round-bottomed vessel had a multi-neck lid to house a thermometer, a nitrogen inlet and a PTFE stirrer gland to regulate the PTFE anchor stirrer rod, powered by an overhead motor, and a stopper. All glassware was dry and the anchor rested on the bottom of the vessel.

The reaction vessel was purged with a high flow of nitrogen for 2 minutes. Once the cooler had reached at least $-25\text{ }^{\circ}\text{C}$, half of the DCM (250 ml) was added to the vessel and was stirred at 200 rpm. The nitrogen purge was used throughout the addition sequence to prevent the condensation atmospheric moisture onto the glassware. The inlet stopper was kept in position but not fully inserted when the inlet was not in use. The DCM was allowed to cool to $-20\text{ }^{\circ}\text{C}$.

The mixture in the reaction vessel was stirred constantly at a medium rate of approximately 200 rpm during the additions. The reactant additions were made via a long stem funnel so that the reactants did not adhere to the inside of the vessel above the solvent level. The nitrogen purge was removed during additions to prevent the loss of fine solid reactant to the atmosphere, and was replaced for cooling periods between additions. HCl gas was evolved throughout the reaction from the point of benzoic acid addition. The funnel was removed and the stopper was partially replaced between additions to prevent the condensation of evolved HCl or atmospheric moisture on the funnel. The additions were made at a suitable rate so as not to allow the mixture to rise above $-15\text{ }^{\circ}\text{C}$. The mixture was allowed to return to at least $-18\text{ }^{\circ}\text{C}$ after each addition.

Aluminium chloride (105.18 g, 788.81 mmol) was added rapidly, not requiring the washings, to form a pale yellow solution and aluminium chloride slurry. The mixture was not allowed to rise above -10°C due to the exotherm. The addition funnel was washed and dried. Benzoic

acid (39.304 g, 321.61 mmol) was added slowly, in two portions, without the washings. No colour change was initially observed and an exotherm was evolved. The temperature was allowed to decrease in between each addition. After approximately five minutes, the transparent yellow solution became opaque. The combined TPC (6.3780 g, 31.416 mmol) and IPC (9.9448 g, 48.984 mmol) was added in one portion, with washings of approximately 50 ml DCM in three portions, at a rate so as not to allow the mixture to rise above -10 °C. No colour change was observed and a small exotherm was evolved. EKKE (39.000 g, 82.887 mmol) was added over approximately 5 minutes, so as not to allow the temperature to increase above -10 °C. The remaining EKKE was transferred by washing with approximately 50ml dichloromethane in three portions. The yellow solution immediately turned orange on addition of EKKE and a large exotherm was evolved.

The nitrogen purge was removed and replaced with a water pump with an air bleed to remove the HCl gas evolved during the polymerisation. The remaining DCM was added, retaining a small amount (15-20 ml) for the addition of the benzoyl chloride. The stirrer speed was increased to 500 rpm and the cooler set to -5°C to raise the temperature of the reaction mixture. During this heating, the benzoyl chloride (0.73690 g, 5.2422 mmol) was diluted in a small amount of DCM and pipetted in to the vessel, with the washings. Once the temperature of the reaction mixture had reached -5 °C, the cooler temperature was increased to 5 °C. This incremental increase was to ensure that the temperature did not increase too quickly. The reaction mixture remained at a temperature of 5 °C for 30 minutes to avoid evaporation of DCM. The formation of particles was observed after approximately 15 minutes. The cooler was set to 20 °C, and the reaction mixture took approximately 10 – 15 minutes to reach this temperature. The vessel was stirred at a constant rate of 500 rpm and maintained at 20 °C for four hours, during which time the mixture turned deeper orange. . The resultant polymer was decomplexed as described in Section 8.3.5.

8.3.4 General polymerisation procedure for five litre reactor

The same general method was carried out as for the one litre reactor, but instead using a five litre reaction vessel. The glass jacketed vessel had five litre capacity and had built-in glass baffles, according to the specification described in Chapter 2. The temperature of the vessel was controlled by a Julabo HP40-FP refrigerated-heating circulator via a thermocouple in in the multi neck lid. An overhead motor powered an anchor stirrer with two extra paddles further up the shaft. Initial stirring was carried out at 200 rpm, with a polymerisation stirring rate of 500 rpm. The vessel was evacuated through a bottom outlet.

8.3.5 General decomplexation procedure

Polymers produced using both the dispersion and gel processes are decomplexed in iced deionised water. The ice was produced using tap water. The methods for decomplexation of both gel and dispersion polymer are different. After decomplexation, white PEKK is produced but copolymers may be cream or yellow in colour.

8.3.6 General decomplexation procedure for the dispersion process

A 5 litre beaker was filled with four litres of iced deionised water. The stirrer was stopped, the cooler was disconnected from the vessel and all of the ancillary parts removed together with the lid. The contents of the vessel were poured in to a beaker, and any remaining polymer was removed with a spatula. A thin film of polymer remained inside the vessel. The orange complexed polymer was filtered through a dry 40 μm stainless steel mesh (of minimum size for the quantity of polymer) and was compressed to remove as much of the DCM as possible. The orange filtered polymer was added to the iced water in portions with stirring, causing it to decomplex and turn white. Any polymer remaining on the filter was washed into the vessel with iced water. During decomplexation, the mixture did not exceed 5 °C. The beaker was stirred occasionally over approximately ten minutes until the majority of the polymer had

turned white, with some orange parts remaining. The beaker was left to stand overnight and until workup to achieve full decomplexation. Prior to workup, the polymer particles were entirely white, with no orange regions remaining. The polymer underwent workup as described in Section 8.3.8.

8.3.7 General decomplexation procedure for the gel process

The orange complexed polymer gel was removed from the vessel by hand, to leave the orange solution remaining. The polymer gel was decomplexed in a Waring blender in three litres of iced water. Blending for approximately two minutes resulted in a white polymer flake of low density. High molecular weight polymer results in a more coarse polymer flake than low molecular weight polymer, and may require blending for longer. During decomplexation, the mixture did not exceed 5 °C. The blended mixture was transferred to a five litre beaker and the polymer remained in deionised water over night and until workup. Prior to workup, the polymer flake was entirely white, with no orange regions remaining. The polymer underwent workup as described in Section 8.3.8.

8.3.8 General workup procedure

This workup procedure is suitable for the product of a one litre reactor. The polymer had remained in water overnight and was fully decomplexed.

The polymers were worked up using the following procedure, carried out in a five litre beaker on a stirrer-hotplate with constant stirring achieved at a moderate rate by a large magnetic stirrer bar. The polymer was isolated by filtration through a 40 µm steel mesh, and the residual DCM removed by slowly adding it to two litres of stirred deionised water at 80 – 90 °C. The foam filled the majority of the beaker. The polymer was then exposed to a series of solutions for one hour each at 80 – 90 °C with constant stirring. Between each step the

polymer was filtered through steel mesh, washed in the filter with deionised water (250 ml), pressed and washed back into the beaker with deionised water. The sequence was: concentrated HCl (40 ml) was added after the removal of residual DCM, deionised water (three litres) with ammonia (30 ml, pH 13), deionised water (three litres), deionised water (three litres), deionised water (three litres).

Polymers were subsequently subject to the drying procedure as detailed in Section 8.3.9.

8.3.9 General drying procedure

Polymers were dried in a shallow ceramic dish in an air oven at 80 °C for 48 hours. If the polymer was to be used for melt viscosity measurements, it was subject to a second heating cycle of 200 °C (up to 250 °C) under vacuum overnight.

8.4 Experimental for Chapter 2

All of the following polymerisations were carried out in accordance with the general polymerisation method, general decomplexation method, general workup method and general drying method. In addition, specific details corresponding to individual polymerisations are listed in each section.

8.4.1 Reactor loading

70:30 PEKKs were synthesised on a one litre scale at 3% out-of-balance and with two benzoic acid equivalents, with variable reactor loading.

Reactor loading	10%	15%	17%	20%
EKKE	39.04	58.61	66.33	78.14
TPC	6.3943	9.5904	10.8552	12.7879
IPC	9.9457	14.9403	16.9061	19.9182
Benzoic acid	19.6498	29.41	33.39	39.25
AlCl ₃	78.56	119.91	132.75	156.21
Benzoyl chloride	0.7635	1.0504	1.1939	1.5094
DCM	500	500	500	500
Polymer mass	42.47	70.45	74.95	89.98
Polymer morphology	Fine particulate	Granular	Granular	Granular (larger)

8.4.2 Benzoic acid concentration

70:30 PEKKs were synthesised on a one litre scale at 3 % out-of balance and 10 % reactor loading, with a variable number of benzoic acid equivalents.

No. benzoic acid equivalents	4	3	2	1.5
EKKE	39.16	39.08	39.04	39.05
TPC	6.4068	6.3916	6.3943	6.3872
IPC	9.9834	9.9655	9.9457	9.9571
Benzoic acid	39.18	29.50	19.6498	14.71
AlCl ₃	105.01	91.32	78.56	72.59
Benzoyl chloride	0.7386	0.7239	0.7635	0.7270
DCM	500	500	500	500
Polymer mass	45.11	44.61	42.47	31.94
Polymer morphology	Fine particulate	Fine particulate	Fine particulate	Granular

No. benzoic acid equivalents	1	0.5	0
EKKE	39.63	39.05	39.02
TPC	6.4839	6.3871	6.3823
IPC	10.1034	9.9573	9.9498
Benzoic acid	9.91	4.90	0
AlCl ₃	66.65	59.28	52.49
Benzoyl chloride	0.7825	0.7014	0.7441
DCM	500	500	500
Polymer Mass	37.97	40.37	42.29
Polymer morphology	Large masses	Large masses	Large masses

8.4.3 Scale-up

PEKKs were synthesised on a five litre scale at 3% out-of-balance and 8% reactor loading, with 4 benzoic acid equivalents. Stirring was carried out at 500 rpm with either a turbine (T) or an anchor (A) stirring rod.

	60:40T	80:20T	80:20A
T:I	60:40	80:20	80:20
Stirrer	Turbine	Turbine	Anchor
EKKE	300.02	300.06	300.56
TPC	23.66	74.63	74.64
IPC	101.92	50.95	51.02
Benzoic acid	301.98	302.05	302.76
AlCl ₃	802.43	802.41	797.76
Benzoyl chloride	5.46	5.35	5.41
DCM	3500	3500	3500
Polymer mass	338.68	246.90	406.19
Polymer morphology	Fine particulate	Large needles	Fine particulate

8.4.4 Recycling of reagents

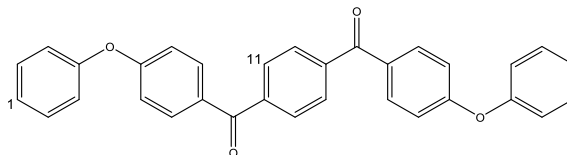
70:30 PEKKs were synthesised on a one litre scale at 3% out-of-balance and 17% reactor loading, with two benzoic acid equivalents. One polymerisation used recycled benzoic acid, and the other used recycled DCM.

	Recycled benzoic acid	Recycled DCM
EKKE	66.52	66.40
TPC	10.8855	10.8650
IPC	16.9563	16.9253
Benzoic acid	33.42	33.41
AlCl ₃	134.31	133.26
Benzoyl chloride	1.2353	1.2323
DCM	500	500
Polymer mass	78.70	51.03
Polymer morphology	Granular	Granular

8.5 Experimental for Chapter 3

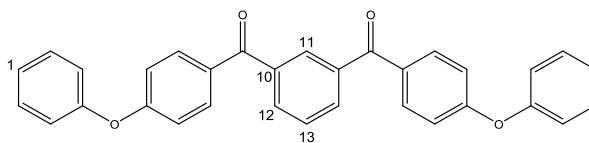
8.5.1 Monomer characterisation

1,4-phenylenebis((4-phenoxyphenyl)methanone) (1,4-EKKE)



White solid; mp 216.9 °C (2 °C/min) {lit.¹ 211 – 217 °C}; purity 99.71 mol% (DSC); $\nu_{\max}/\text{cm}^{-1}$ 3067 (CH), 3040 (CH), 2490 – 1685 (aromatic CH), 1643 (CO), 1587 (ring stretch), 1489 (ring stretch), 1400, 1306, 1287, 1254 (COC), 1198, 1153, 1109, 1072, 1017; δ_{H} (400 MHz, $\text{CDCl}_3(\text{TFA})$) 7.10 (4H, d, J 8.80, C(6) H), 7.16 (4H, d, J 7.58, C(3) H), 7.29 (2H, t, J 8.10, C(1) H), 7.47 (4H, t, J 7.82, C(2) H), 7.91 - 7.89 (8H, m, C(7) H , C(11) H); 7.09 (6H, d, J 8.80, C(6) H), 7.17 (6H, d, J 9.05, C(9) H), 7.64 (6H, d, J 9.05, C(10) H), 7.88 (6H, d, J 8.80, C(5) H), 8.35 (3H, s, C(1) H); δ_{C} (100 MHz, $\text{CDCl}_3(\text{TFA})$) 117.19 (C(6) H), 120.59 (C(3) H), 125.30 (C(1) H), 129.83 (C(8)), 129.96 (C(11) H), 130.26 (C(2) H), 133.60 (C(7) H), 140.69 (C(10)), 154.75 (C(4)), 163.63 (C(5)), 198.28 (C(9)); HRMS (TOF FI⁺) $\text{C}_{32}\text{H}_{22}\text{O}_4^+$ ($[\text{M}]^+$) requires 470.1518 found 470.1522.

1,3-phenylenebis((4-phenoxyphenyl)methanone) (1,3-EKKE)



White solid; mp 119.2 °C (2 °C/min); purity 99.81 mol% (DSC); $\nu_{\max}/\text{cm}^{-1}$ 3053 (CH), 2490 – 1870 (aromatic CH), 1651 (CO), 1601, 1584 (ring stretch), 1487 (ring stretch), 1418, 1321, 1300, 1231 (COC), 1157; δ_{H} (400 MHz, $\text{CDCl}_3(\text{TFA})$) 6.96 (4H, d, J 9.05, C(6) H), 7.03 (4H, d, J 7.58, C(3) H), 7.15 (2H, t, J 7.30, C(1) H), 7.34 (4H, t, J 8.30, C(2) H), 7.57 (1H, t, J 7.70, C(13) H), 7.76 (4H, d, J 8.80, C(7) H), 7.93 (2H, dd, J 7.83, 1.71, C(12) H), 8.03 (1H, s, C(11) H); δ_{C} (100 MHz, CDCl_3) 117.19 (C(6) H), 120.43 (C(3) H), 124.99 (C(1) H), 128.73

(C(13)H), 130.18 (C(2)H), 130.65 (C(8)), 131.07 (C(11)H), 132.96 (C(7)H), 133.51 (C(12)H), 137.86 (C(10)), 155.09 (C(4)), 162.70 (C(5)), 196.10 (C(9)); HRMS (TOF FI⁺) C₃₂H₂₂O₄⁺ ([M]⁺) requires 470.1518 found 470.1538.

8.5.2 PEKK polymerisation

70:30 PEKKs were synthesised on a one litre scale at 3% out-of balance with 10% reactor loading and 4 benzoic acid equivalents, with variable T:I ratio. The general workup method was modified to used tap water in place of deionised water, except the final stage.

T:I ratio	100:0	90:10	80:20	70:30	60:40
EKKE	39.0990	39.0748	38.9996	39.0001	38.9997
TPC	16.3642	13.0354	9.6928	6.3780	3.0636
IPC	0	3.3194	6.6302	9.9448	13.2596
Benzoic acid	39.18	39.26	39.3021	39.3039	39.3024
AlCl ₃	105.00	104.53	107.41	105.18	105.87
Benzoyl chloride	0.8253	0.8007	0.7050	0.7369	0.7055
DCM	500	500	500	500	500
Polymer mass	43.92	42.38	43.76	46.01	42.95
Polymer morphology	Fine particulate	Fine particulate	Fine particulate	Fine particulate	Fine particulate

8.6 Experimental for Chapter 4

8.6.1 Controlling agents

Known controlling agents

70:30 PEKKs were synthesised on a one litre scale at 3% out-of-balance with 10% reactor loading. The benzoic acid was replaced with a range of dispersants, in either 2 or 4 equivalents compared to total acid chloride content.

	Benzoic acid 20 °C	Benzoic acid 10 °C	Benzenesulfonic acid	Acetic acid	Dimethyl sulfone
No. equivalents	4	4	4	2	2
Controlling agent	39.46	39.20	50.00	9.64	15.01
	4	4		2	2
EKKE	39.23	39.10	34.41	39.30	39.07
TPC	6.4164	6.3999	5.6376	6.4279	6.3939
IPC	10.0038	9.9648	8.7665	10.0211	9.9627
AlCl ₃	106.06	104.75	148.23	79.23	78.81
BzCl	0.7146	0.6999	0.6174	0.7155	0.7136
DCM	500	500	500	500	500
Polymer morphology	Fine particulate	Fine particulate	Large cuboidal	Granular	Gel

Alternative dispersants

80:20 PEKKs were synthesised on a small scale at 3% out-of balance with 10% reactor loading. The benzoic acid was replaced with a range of dispersants, in 4 equivalents compared to total acid chloride content.

	Chloroacetic acid	Trichloroacetic acid	4-chlorobenzoic acid	Phthalic acid*
Controlling agent	6.24	10.78	10.35	10.96
EKKE	7.99	7.99	8.00	7.99
TPC	2.01	2.00	2.00	2.01
IPC	1.34	1.35	1.36	1.33
AlCl ₃	22.02	22.08	22.13	32.33
BzCl	-	-	-	-
DCM	125	125	125	125
Polymer Mass	9.05	9.52	9.46	8.33
Polymer morphology	Granular	Granular	Fine particulate, irregular	Gel
Polymer colour	Orange	Cream	Cream	Pale pink

*4 molar equivalents of phthalic acid, but both carbonyl groups taken into account for AlCl₃

	Benzophenone	Benzoic acid
Controlling agent	12.04	8.06
EKKE	8.00	8.00
TPC	1.98	2.00
IPC	1.37	1.36
AlCl ₃	23.43	22.51
Benzoyl chloride	-	-
DCM	125	125
Polymer Mass	9.38	8.47
Polymer morphology	Granular	Fine particulate
Polymer colour	Pink	White

8.6.2 Aluminium chloride morphology

60:40 PEKKs were synthesised on the small scale at 3% out-of balance and with 2 benzoic acid equivalents. Both aluminium chloride granules and powder used in combination with 10% and 15% reactor loadings.

AlCl₃ morphology	Granules	Granules	Powder	Powder
Loading	10%	15%	10%	15%
EKKE	9.76	14.64	9.72	14.61
TPC	1.60	2.40	1.59	2.38
IPC	2.49	3.73	2.47	3.73
Benzoic acid	4.90	7.36	4.89	7.34
AlCl ₃	20.09	29.84	19.50	29.33
Benzoyl chloride	-	-	-	-
DCM	125	125	125	125
Polymer morphology	Fine particulate	Gel	Fine particulate	Fine particulate

8.6.3 Observation of crystal formation

Initial isolation of the aluminium benzoate complex

Aluminium chloride (10.02g, 75.14 mmol) was added to DCM (100 ml) at ≤ 0 °C, with stirring. Benzoic acid (3.78 g, 3.09 mmol) was added to the slurry which initially remained in suspension then slowly dissolved over approximately five minutes. After a further five minutes, a fine white solid quickly precipitated. After five minutes, the suspension was decanted from the remaining aluminium chloride granules, and the precipitate was left to settle. The solvent was decanted and the resultant white solid was dried under vacuum, 3.43 g.

Aluminium chloride (10.01 g, 75.07 mmol) was added to DCM (100 ml) at ≤ 0 °C with stirring for ten minutes, then left to settle before the liquor was decanted. Benzoic acid (3.79 g, 3.10 mmol) was added to the liquor which initially remained in suspension then slowly dissolved over approximately five minutes. After a further five minutes, a fine white solid quickly precipitated. After a further five minutes, the precipitate was left to settle, the solvent decanted and the resultant white solid was dried under vacuum, 0.016 g.

Analytical data for the composition of the products could not be obtained from these experiments due to its hygroscopic nature.

8.6.4 Anhydrous isolation of the aluminium benzoate complex

The reaction was carried out in a thick walled, glass screw top bottle with 100 ml capacity to withstand the vacuum applied in the inlet port of the glove box. The bottle was placed in an ice/acetone bath and a magnetic stirrer bar and thermometer added. Between the additions, the lid of the bottle was screwed on loosely to allow evolved HCl to vent but to prevent the condensation of atmospheric moisture in the vessel. DCM (8 ml) was added and cooled with stirring to < 0 °C. Aluminium chloride (1.46 g, 0.0109 mol) was added with its washings

(3ml) with stirring and cooled to $< 0\text{ }^{\circ}\text{C}$, for approximately five minutes. A large proportion of the aluminium chloride remained undissolved in the pale yellow solution. Benzoic acid (0.55 g, 0.00450 mol) was added with its washings (4 ml) with stirring and cooled to $< 0\text{ }^{\circ}\text{C}$, for approximately 10 minutes, during which time a fine white solid precipitated. After approximately 10 minutes, a nitrogen blanket was added to the headspace of the bottle, and the lid screwed on tightly. At this point, the reaction was relocated to an argon-filled glove box. The suspension, now yellow in colour, was decanted into an oven-dried, glass fibre filter paper, to leave the excess aluminium chloride. A white precipitate was isolated on the filter paper, and the yellow filtrate collected and stored in a sealed vessel for disposal. The precipitate was not washed with DCM aliquots to prevent its dissolution. The precipitate was dried under vacuum using the inlet port of the glove box. The product mass could not be determined due to the crude separation method. Samples for analysis were prepared in an argon-filled glove box using dry solvents.

8.6.5 Order of addition of reactants

100:0 and 80:20 PEKKs were synthesised on the small scale at 3% out-of balance and 10% loading, with 4 benzoic acid equivalents. The order of addition of reactants was altered as shown in Table 8.1.

Sample	Order of addition of reactants					
	→					
1*	AlCl ₃	BzOH	crystal formation	TPC/IPC	EKKE	BzCl
2**	AlCl ₃	BzOH	TPC/IPC	EKKE	crystal formation	BzCl
3	AlCl ₃	TPC/IPC	BzOH	EKKE	BzCl	
4	AlCl ₃	TPC/IPC	EKKE	BzOH	BzCl	
5	AlCl ₃	TPC/IPC	EKKE	BzCl		

*Crystals formed before monomer addition

**All reactants added before crystals form

Table 8.1 Order of addition of reactants for each of the PEKK polymerisations, indicating the point of crystal formation, where benzoic acid is represented by BzOH and benzoyl chloride is represented by BzCl

100:0 PEKK

	1	2	3	4	5
EKKE	7.9999	8.0004	7.9998	8.0001	8.0005
TPC	3.3483	3.3477	3.3481	3.3475	3.3474
Benzoic acid	8.0611	8.0613	8.0605	8.0607	-
AlCl ₃	21.77	21.66	21.85	21.61	11.11
Benzoyl chloride	0.1442	0.1448	0.1446	0.1449	0.1442
DCM	125	125	125	125	125
Polymer mass	8.6881	9.7263	8.6531	8.6072	8.9885
Polymer morphology	Fine particulate	Fine particulate	Fine particulate	Fine particulate	Particulate

80:20 PEKK

	1	2	3	4	5
EKKE	8.0001	7.9998	7.9995	8.0005	7.9995
TPC	2.6787	2.6783	2.6780	2.6782	2.6780
IPC	0.6686	0.6698	0.6699	0.6698	0.6702
Benzoic acid	8.0608	8.0608	8.0613	8.0604	-
AlCl ₃	22.17	22.44	22.46	22.54	11.33
Benzoyl chloride	0.1438	0.1441	0.1449	0.1433	0.1437
DCM	125	125	125	125	125
Polymer Mass	9.0384	9.5016	9.3232	9.2114	5.7146 *
Polymer morphology	Fine particulate	Fine particulate	Fine particulate	Fine particulate	Gel

* Much fouling on sides and bottom of vessel

The same observations apply to the 80:20 PEKKs as the 100:0 PEKKs, apart from that the 80:20 experiment 5 formed a polymer gel.

Experiment 1 gave the standard observations for the dispersion process. A yellow slurry was produced on the addition of aluminium chloride to DCM. The benzoic acid dissolved with no accompanying colour change, followed by the production of a white precipitate which caused the mixture to turn opaque. The TPC and IPC dissolved with no accompanying colour change. The EKKE dissolved with a colour change of yellow to orange. No further colour change was observed on the addition of benzoyl chloride.

The same colour changes were observed during the additions, but the mixture remained transparent throughout. The orange mixture turned opaque approximately five minutes after the final addition, when a fine precipitate formed rapidly. A fine particulate product was formed.

In experiment 3, the yellow slurry from the addition of aluminium chloride underwent no colour change on the dissolution of TPC and IPC nor benzoic acid. A transparent orange solution with aluminium chloride slurry was formed on the addition of EKKE. The orange mixture turned opaque approximately five minutes after the final addition, when a fine precipitate formed rapidly. A fine particulate product was formed.

In experiment 4, the yellow slurry from the addition of aluminium chloride underwent no colour change on the dissolution of TPC and IPC. A transparent orange solution with aluminium chloride slurry was formed on the addition of EKKE. No colour change was observed on the dissolution of benzoic acid. The orange mixture turned opaque approximately five minutes after the final addition, when a fine precipitate formed rapidly. A fine particulate product was formed.

In experiment 5, the yellow slurry from the addition of aluminium chloride underwent no colour change on the dissolution of TPC and IPC. A transparent orange solution with aluminium chloride slurry was formed on the addition of EKKE. The orange mixture did not turn opaque after five minutes, and remained in solution for approximately 20 minutes before it turned opaque and a phase separation occurred. The reaction mixture was darker orange than experiments 1-5 which were approximately the same shade. The 100:0 PEKK was formed as a coarse dispersion and the 80:20 PEKK was formed as a dense gel. A plaque of

solid polymer gel formed on the bottom of the vessel, in comparison to experiments 1-5 which formed thin films only.

8.6.6 Introduction of additives

Low concentration of additive

70:30 PEKKs were synthesised on the small scale at 3% out-of balance and 10% loading. Additives were incorporated into the monomer feed to replace the benzoic acid. Additive quantities were calculated using a theoretical molar value of aluminium benzoate produced from 4 benzoic acid equivalents. Additives were incorporated in a molar equivalent quantity to the theoretical quantity of aluminium benzoate.

	Standard	No benzoic acid	Silica
EKKE	8.0000	8.0000	8.0003
T+I	3.3483	3.3480	3.3482
TPC	1.9885	1.9883	1.9887
IPC	1.3598	1.3597	1.3595
AlCl ₃	22.21	11.79	11.22
Benzoic acid	7.9950	-	-
Additive	-	-	1.9810
Benzoyl chloride	0.1433	0.1432	0.1434
DCM	125	125	125
Polymer mass	8.53	9.48	8.01
Polymer morphology	Fine particulate	Small agglomerates	Granular

	Alumina	Sodium benzoate	Graphite
EKKE	7.9997	8.0002	8.0001
T+I	3.3481	3.3484	3.3485
TPC	1.9884	1.9888	1.9890
IPC	1.3597	1.3596	1.3595
AlCl ₃	11.23	21.52	11.64
Benzoic acid	-	-	-
Additive	3.3610	4.7510	0.3965
Benzoyl chloride	0.1429	0.1432	0.1431
DCM	125	125	125
Polymer mass	9.67	6.90	7.12
Polymer morphology	Large masses	Granular	Granular, 2 types**

* Note 2 molar equivalents of AlCl₃ per sodium benzoate

**Two types of polymer particles

1. Larger particles 1 – 3 mm made up of agglomerated small particles < 1 mm. No graphite.
2. Larger particles 1 – 3 mm with graphite in interior seen through cracked surface.

High concentration of additive

70:30 PEKKs were synthesised on the small scale at 3% out-of balance and 10% loading. Additives were incorporated into the monomer feed to replace the benzoic acid. Additive quantities were calculated using a theoretical molar value of aluminium benzoate produced from 4 benzoic acid equivalents. Additives were incorporated in a two molar equivalent quantity to the theoretical quantity of aluminium benzoate.

	Standard	No benzoic acid	Silica
EKKE	8.0001	8.0003	7.9996
T+I	3.3475	3.3485	3.3489
TPC	1.9887	1.9885	1.9890
IPC	1.3588	1.3600	1.3599
AlCl ₃	21.59	10.99	11.08
Benzoic acid	7.9965	-	-
Additive	-	-	3.9619
Benzoyl chloride	0.1428	0.1431	0.1427
DCM	125	125	125
Polymer mass	8.90	9.75	9.93
Polymer morphology	Fine particulate	Large mass	Large mass

	Alumina	Sodium benzoate	Graphite
EKKE	8.0005	8.0009	7.9996
T+I	3.3485	3.3482	3.3490
TPC	1.9889		1.9901
IPC	1.3596	1.3596	1.3589
AlCl ₃	11.11	32.28	11.07
BzOH	-	-	-
Additive	6.7271	9.5020	0.7950
BzCl	0.1430	0.1432	0.1426
DCM	125	125	125
Polymer mass	11.97	8.83	8.13
Polymer morphology	Large mass	Fine particulate	Coarse particulate, large mass

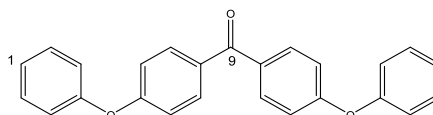
*Graphite particles

1. Larger particles 1 – 3 mm made up of agglomerated small particles < 1 mm. No graphite.
2. Large mass with graphite in interior seen through cracked surface.

8.7 Experimental for Chapter 5

8.7.1 Monomer characterisation

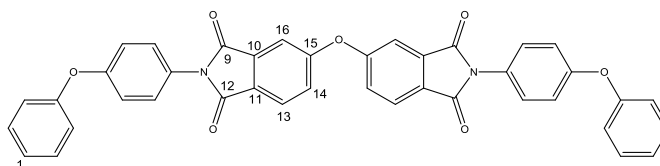
Bis(4-phenoxyphenyl)methanone (EKE)



White solid; mp 148.4 °C (2 °C/min) {lit.² 142 – 145 °C}; purity 99.85 mol% (DSC); $\nu_{\max}/\text{cm}^{-1}$ 3062 (CH), 3039 (CH), 2493-1685 (Ar CH), 1643 (CO), 1585 (ring stretch), 1487 (ring stretch), 1265 (COC); δ_{H} (400 MHz, CDCl₃ (TFA)) 7.09 (4H, d, *J* 8.80, C(6)*H*), 7.15 (4H, d, *J* 7.58, C(3)*H*), 7.28 (2H, t, *J* 7.34, C(1)*H*), 7.46 (4H, t, *J* 8.31, C(2)*H*), 7.83 (4H, d, *J* 8.80, C(7)*H*); δ_{C} (100 MHz, CDCl₃ (TFA)) 117.11 (C(6)*H*), 120.48 (C(3)*H*), 125.11 (C(1)*H*), 130.20 (C(2)*H*), 130.56 (C(8)), 133.34 (C(7)*H*), 154.95 (C(4)), 163.01 (C(5)), 199.07 (C(9)); δ_{H} (400 MHz, CDCl₃) 7.06 (4H, d, *J* 8.80, C(6)*H*), 7.13 (4H, d, *J* 7.58, C(3)*H*), 7.23 (2H, t, *J* 7.58, C(1)*H*), 7.43 (4H, t, *J* 8.60, C(2)*H*), 7.83 (4H, d, *J* 8.80, C(7)*H*); δ_{C} (100 MHz, CDCl₃) 117.22 (C(6)*H*), 120.14 (C(3)*H*), 124.56 (C(1)*H*), 130.07 (C(2)*H*), 132.25 (C(7)*H*), 155.63

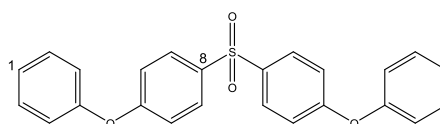
(C(4)), 161.42 (C(5)), 194.31 (C(9)); HRMS (TOF FI⁺) C₂₅H₁₈O₃⁺ ([M]⁺) requires 366.1256 found 366.1260.

5,5'-oxybis(2-(4-phenoxyphenyl)isoindoline-1,3-dione) (EIEIE)



White solid; mp 293.4 °C (2°C/min) {lit.³ 292.2 – 293.8 °C}; purity 99.35 mol% (DSC); $\nu_{\max}/\text{cm}^{-1}$ 3062 (CH), 3034 (CH), 2374-1703 (Ar CH), 1604 (CO), 1589 (ring stretch), 1485 (ring stretch), 1267 (COC), 1234 (CN), 1024 (CN); δ_{H} (400 MHz, CDCl₃ (TFA)) 7.12 (4H, d, *J* 7.58, C(3)*H*), 7.14 (4H, d, *J* 9.05, C(6)*H*), 7.22 (2H, t, *J* 7.58, C(1)*H*), 7.33 (4H, d, *J* 9.05, C(7)*H*), 7.43 (4H, t, *J* 7.58, C(2)*H*), 7.58 (2H, dd, *J* 8.07, 2.20, C(14)*H*), 7.65 (2H, d, *J* 2.20, C(16)*H*), 8.10 (2H, d, *J* 8.31, C(13)*H*); δ_{C} (100 MHz, CDCl₃ (TFA)) 114.65 (C(16)*H*), 118.79 (C(6)*H*), 119.85 (C(3)*H*), 124.41 (C(1)*H*), 124.75 (C(11)), 125.53 (C(14)*H*), 126.75 (C(8)), 126.95 (C(13)*H*), 128.42 (C(7)*H*), 130.03 (C(2)*H*), 134.16 (C(10)), 155.90 (C(5)), 158.39 (C(4)), 161.57 (C(15)), 168.05 (C(9)), 168.31 (C(12)); HRMS (TOF EI⁺) C₄₀H₂₄N₂O₇⁺ ([M]⁺) requires 644.1583 found 644.1472.

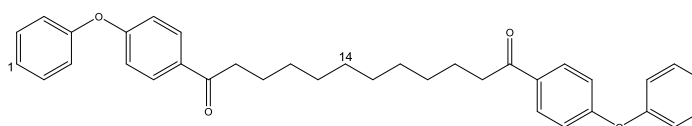
1,1'-sulfonylbis(4-phenoxybenzene) (ESE)



White solid; mp 143.6 °C (2°C/min) {lit.³ 142.4 – 143.5 °C}; purity 99.89 mol% (DSC); $\nu_{\max}/\text{cm}^{-1}$ 3067 3064 (CH), 2357-1645 (Ar CH), 1645 (CO), 1579 (ring stretch), 1485 (ring stretch), 1317 (SO), 1249 (COC), 1143 (SO); δ_{H} (400 MHz, CDCl₃ (TFA)) 7.07 (4H, d, *J* 6.85, C(6)*H*), 7.09 (4H, d, *J* 5.62, C(3)*H*), 7.27 (2H, t, *J* 7.60, C(1)*H*), 7.45 (4H, t, *J* 7.58, C(2)*H*), 7.89 (4H, d, *J* 9.05, C(7)*H*); δ_{C} (100 MHz, CDCl₃ (TFA)) 117.80 (C(6)*H*), 120.52 (C(3)*H*),

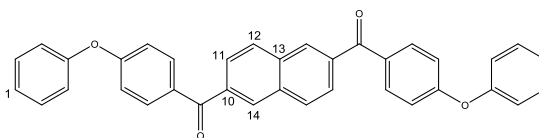
125.38 (C(1)H), 129.67 (C(7)H), 130.28 (C(2)H), 133.67 (C(8)), 154.62 (C(5)), 162.69 (C(4)); δ_{H} (400 MHz, CDCl_3) 7.04 (4H, d, J 8.80, C(6)H), 7.07 (4H, d, J 8.56, C(3)H), 7.25 (2H, t, J 7.50, C(1)H), 7.43 (4H, t, J 7.58, C(2)H), 7.90 (4H, d, J 9.05, C(7)H); δ_{C} (100 MHz, CDCl_3) 117.73 (C(6)H), 120.38 (C(3)H), 125.08 (C(1)H), 129.76 (C(7)H), 130.21 (C(2)H), 135.48 (C(8)), 154.97 (C(5)), 161.98 (C(4)); HRMS (TOF FI^+) $\text{C}_{24}\text{H}_{18}\text{O}_4\text{S}^+$ ($[\text{M}]^+$) requires 402.0926 found 402.0930.

1,12-Bis(4-phenoxyphenyl)dodecane-1,12-dione (EK10KE)



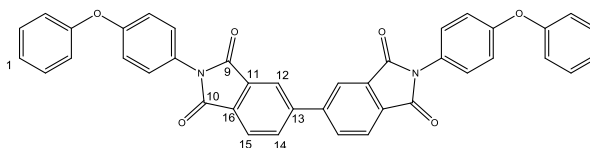
EK10KE was synthesised at Ketonex⁴.

White solid; mp 105.8 °C (2°C/min); purity 99.51 mol% (DSC); $\nu_{\text{max}}/\text{cm}^{-1}$ 3064 (CH), 3039 (CH), 2908 (CH_2), 2845 (CH_2), 2358-1772 (Aromatic CH), 1645 (CO), 1587 (ring stretch), 1487 (ring stretch), 1373 (CH_2), 1269 (CH_2), 1234 (COC); δ_{H} (400 MHz, CDCl_3 (TFA)) 1.25 – 1.47 (12H, m, C(12/13/14)H), 1.75 (4H, q, J 7.52, C(11)H), 3.04 (4H, t, J 7.58, C(10)H), 7.05 (4H, d, J 8.80, C(6)H), 7.13 (4H, d, J 7.58, C(3)H), 7.28 (2H, t, J 7.34, C(1)H), 7.46 (4H, t, J 8.60, C(2)H), 8.01 (4H, d, J 9.05, C(7)H); δ_{C} (100 MHz, CDCl_3 (TFA)) 25.76 (C(11)H), 29.14 (C(12/13/14)H), 29.23 (C(12/13/14)H), 29.26 (C(12/13/14)H), 38.55 (C(10)), 117.23 (C(6)H), 120.50 (C(3)), 125.19 (C(1)H), 129.78 (C(2)H), 130.18 (C(7)H), 131.63 (C(8)), 154.79 (C(4)), 163.67 (C(5)), 206.09 (C(9)); δ_{H} (400 MHz, CDCl_3) 1.27 – 1.47 (12H, m, C(12/13/14)H), 1.75 (4H, q, J 7.34, C(11)H), 2.94 (4H, t, J 7.34, C(10)H), 7.02 (4H, d, J 9.05, C(6)H), 7.10 (4H, d, J 7.58, C(3)H), 7.22 (2H, t, J 7.58, C(1)H), 7.42 (4H, t, J 8.40, C(2)H), 7.97 (4H, d, J 9.05, C(7)H); δ_{C} (100 MHz, CDCl_3 (TFA)) 24.54 (C(11)H), 29.45 (C(12/13/14)H), 38.44 (C(10)), 117.34 (C(6)H), 120.13 (C(3)), 124.55 (C(1)H), 130.04 (C(2)H), 130.33 (C(7)H), 131.83 (C(8)), 155.59 (C(4)), 161.77 (C(5)), 199.22 (C(9)); HRMS (TOF EI^+) $\text{C}_{36}\text{H}_{38}\text{O}_4^+$ ($[\text{M}]^+$) requires 534.2770 found 534.2784.

Naphthalene-2,6-diylbis((4-phenoxyphenyl)methanone) (EKNKE)

EKNKE was synthesised at Ketonex^{4,5}.

White solid; mp 218.4 °C (2 °C/min); purity 99.17 mol% (DSC); $\nu_{\max}/\text{cm}^{-1}$ 3062 (CH), 3035 (CH), 2358-1772 (Ar CH), 1641 (CO), 1585 (ring stretch), 1487 (ring stretch), 1234 (COC); δ_{H} (400 MHz, CDCl_3 (TFA)) 7.13 (4H, d, J 8.80, C(6)*H*), 7.18 (4H, d, J 7.58, C(3)*H*), 7.30 (2H, t, J 7.34, C(1)*H*), 7.49 (4H, t, J 8.60, C(2)*H*), 7.95 (4H, d, J 9.05, C(7)*H*), 7.99 (2H, dd, J 8.31, 1.47, C(11)*H*), 8.13 (2H, d, J 8.31, C(12)*H*), 8.38 (2H, s, C(14)*H*); δ_{C} (100 MHz, CDCl_3 (TFA)) 117.19 (C(6)*H*), 120.61 (C(3)*H*), 125.30 (C(1)*H*), 126.84 (C(11)*H*), 130.10 (C(12)), 130.19 (C(8)), 130.26 (C(2)*H*), 131.80 (C(14)*H*), 133.71 (C(7)*H*), 134.25 (C(13)), 136.65 (C(10)), 154.78 (C(4)), 163.56 (C(5)), 199.33 (C(9)); HRMS (TOF EI^+) $\text{C}_{36}\text{H}_{24}\text{O}_4^+$ ($[\text{M}]^+$) requires 520.1675 found 520.1677.

2,2'-bis(4-phenoxyphenyl)-[5,5'-biisindoline]-1,1',3,3'-tetraone (EI-IE)

EI-IE was synthesised at Ketonex^{3,4}

White solid; mp 273.6 °C (2°C/min) {lit.³ 272.8 – 273.9 °C}; purity 98.71 mol% (DSC); δ_{H} (400 MHz, CDCl_3 (TFA)) 7.13 (4H, d, J 7.58, C(3)*H*), 7.16 (4H, d, J 9.05, C(6)*H*), 7.23 (2H, t, J 7.34, C(1)*H*), 7.38 (4H, d, J 8.80, C(7)*H*), 7.44 (4H, t, J 8.60, C(2)*H*), 8.18-8.20 (4H, m, C(14)*H*, C(15)*H*), 8.34 (2H, s, C(12)*H*); δ_{C} (100 MHz, CDCl_3 (TFA)) 118.82 (C(6)*H*), 119.85 (C(3)*H*), 123.26 (C(12)*H*), 124.44 (C(1)*H*), 124.71 (C(8)), 125.35 (C(15)*H*), 128.46 (C(7)*H*), 130.04 (C(2)*H*), 131.14 (C(16)), 132.47 (C(11)), 134.14 (C(14)*H*), 145.89 (C(13)), 155.90 (C(5)), 158.46 (C(4)), 168.63 (C(9/10)), 168.70 (C(9/10)); $\nu_{\max}/\text{cm}^{-1}$ 3062 (CH), 2358-1770

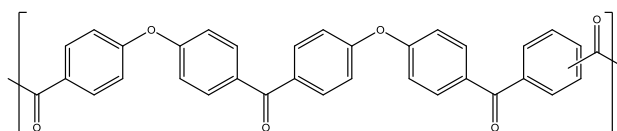
(Ar CH), 1604 (CO), 1589 (ring stretch), 1485 (ring stretch), 1267 (COC), 1238 (CN), 1018 (CN); HRMS (TOF EI⁺) C₄₀H₂₄N₂O₆⁺ ([M]⁺) requires 628.1634 found 628.1625.

Yellow needles; mp 273.7 °C (2°C/min) {lit.³ 272.8 – 273.9 °C}; purity 99.79 mol% (DSC); δ_H (400 MHz, CDCl₃ (TFA)) 7.13 (4H, d, *J* 7.58, C(3)*H*), 7.16 (4H, d, *J* 9.05, C(6)*H*), 7.23 (2H, t, *J* 7.46, C(1)*H*), 7.37 (4H, d, *J* 9.05, C(7)*H*), 7.44 (4H, t, *J* 8.60, C(2)*H*), 8.17-8.20 (4H, m, C(14)*H*, C(15)*H*), 8.34 (2H, s, C(12)*H*); δ_C (100 MHz, CDCl₃ (TFA)) 118.82 (C(6)*H*), 119.85 (C(3)*H*), 123.25 (C(12)*H*), 124.44 (C(1)*H*), 124.72 (C(8)), 125.34 (C(15)*H*), 128.45 (C(7)*H*), 130.04 (C(2)*H*), 131.15 (C(16)), 132.47 (C(11)), 134.13 (C(14)*H*), 145.88 (C(13)), 155.90 (C(5)), 158.45 (C(4)), 168.61 (C(9/10)), 168.66 (C(9/10)); ν_{max}/cm⁻¹ 3068 (CH), 2358-1772 (Aromatic CH), 1618 (CO), 1587 (ring stretch), 1485 (ring stretch), 1286 (COC), 1226 (CN), 1018 (CN); HRMS (TOF EI⁺) C₄₀H₂₄N₂O₆⁺ ([M]⁺) requires 628.1634 found 628.1635.

8.7.2 Copolymer synthesis

Copolymers were synthesised on a one litre scale at 3% out of balance and 10% reactor loading. Individual monomer feeds are detailed for each set, together with specific parameters applying to each polymerisation.

PEKEKK

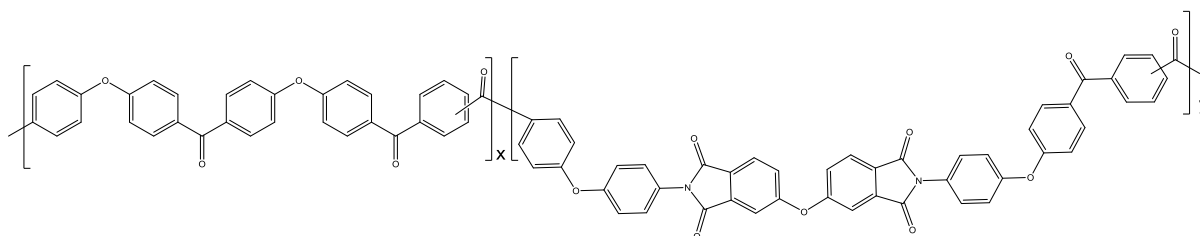


Note: the phenyl ring with undefined geometry is a mixture of T and I linkages in a ratio determined by the ratio of TPC to IPC in the monomer feed

All of the copolymers were synthesised in a one litre reactor according to the general polymerisation method, using the monomer feeds as listed below. Each were synthesised with a 10% reactor loading, at 3% out of balance.

EIEIE %	0	0	0	0	0
T:I	100:0	100:0	100:0	90:10	90:10
Benzoic acid equivalents	4	5	6	4	5
EKE	36.0005	35.9998	35.9999	36.9995	36.9999
TPC	19.3477	19.3476	19.3475	15.8467	15.8468
IPC	-	-	-	4.0387	4.0382
Benzoic acid	46.5862	58.2328	69.8790	47.8810	59.8505
AlCl ₃	108.66	123.56	142.09	128.14	143.73
Benzoyl chloride	0.8468	0.8366	0.8356	0.8667	0.8657
DCM	500	500	500	500	500
Polymer mass	42.64	42.76	44.37	46.97	43.32
Polymer morphology	Granular	Granular	Granular	Fine particulate	Granular

Imide copolymers, P(EKE-EIEIE)



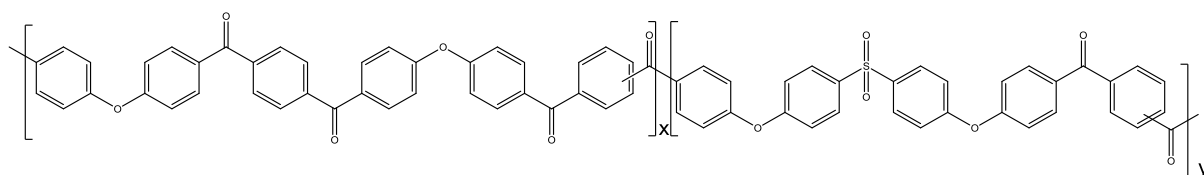
Note: the phenyl ring with undefined geometry is a mixture of T and I linkages in a ratio determined by the ratio of TPC to IPC in the monomer feed.

All of the copolymers were synthesised in a one litre reactor according to the general polymerisation method, using the monomer feeds as listed below. Each were synthesised with a 10% reactor loading, at 3% out of balance.

Imide %	40	10	20	30	30
T:I	100:0	100:0	100:0	100:0	100:0
Benzoic acid equivalents	4	4	4	4	5
EKE	17.9996	31.0001	25.9998	21.9996	21.9995
EIEIE	21.1112	6.0599	11.4354	16.5872	16.5877
TPC	16.1232	18.5117	17.4667	16.8905	16.8905
IPC	-	-	-	-	-
Benzoic acid	38.8222	44.5751	42.0584	40.6710	50.8375
AlCl ₃	115.41	123.26	119.74	116.77	129.54
Benzoyl chloride	0.6985	0.8014	0.7825	0.7724	0.7347
DCM	500	500	500	500	500
Polymer mass	39.91	40.45	30.06	37.37	42.81
Polymer morphology	Fouling, masses blended	Fine particulate	Fine particulate	Fine particulate	Fine particulate

Imide %	30	40	10	20	10
T:I	100:0	100:0	90:10	90:10	80:20
Benzoic acid equivalents	6	6	4	4	4
EKE	21.9997	17.9998	31.4995	26.5002	31.5005
EIEIE	16.5872	21.1117	6.1578	11.5002	18.8109
TPC	16.8905	16.1229	15.1843	14.5547	11.5582
IPC	-	-	3.6263	3.2482	7.2727
Benzoic acid	61.0060	58.2327	45.2923	42.8657	45.2919
AlCl ₃	143.41	139.28	124.86	119.54	123.20
Benzoyl chloride	0.7988	0.7256	0.8152	0.7676	0.8041
DCM	500	500	500	500	500
Polymer mass	44.68	33.14	40.17	43.87	43.85
Polymer morphology	Fine particulate	Fine particulate	Fine particulate	Fine particulate	Fine particulate

Sulfone copolymers, P(EKKE-ESE)

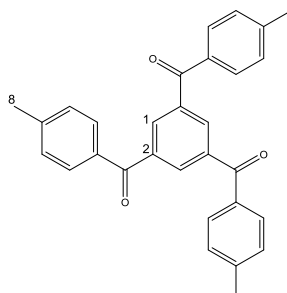


All of the copolymers were synthesised in a one litre reactor according to the general

polymerisation method, using the monomer feeds as listed below. Each were synthesised with a 10% reactor loading, at 3% out of balance.

Sulphone %	10	20	30	40	10
T:I	100:0	100:0	100:0	100:0	90:10
Benzoic acid equivalents	4	4	4	4	4
EKKE	35.5002	31.9996	28.4998	24.5002	34.4998
ESE	3.0362	6.8432	10.4480	13.9705	3.3742
TPC	16.3433	16.7419	17.0403	17.0899	13.3267
IPC	0	0	0	0	3.1822
Benzoic acid	39.3513	40.3104	41.0300	41.1504	39.7507
AlCl ₃	104.04	107.28	110.46	110.44	107.67
Benzoyl chloride	0.6984	0.7161	0.7315	0.7329	0.7081
DCM	500	500	500	500	500
Polymer mass	40.48	39.15	40.88	41.47	39.02
Polymer morphology	Fine particulate	Fine particulate	Fine particulate	Fine particulate	Fine particulate

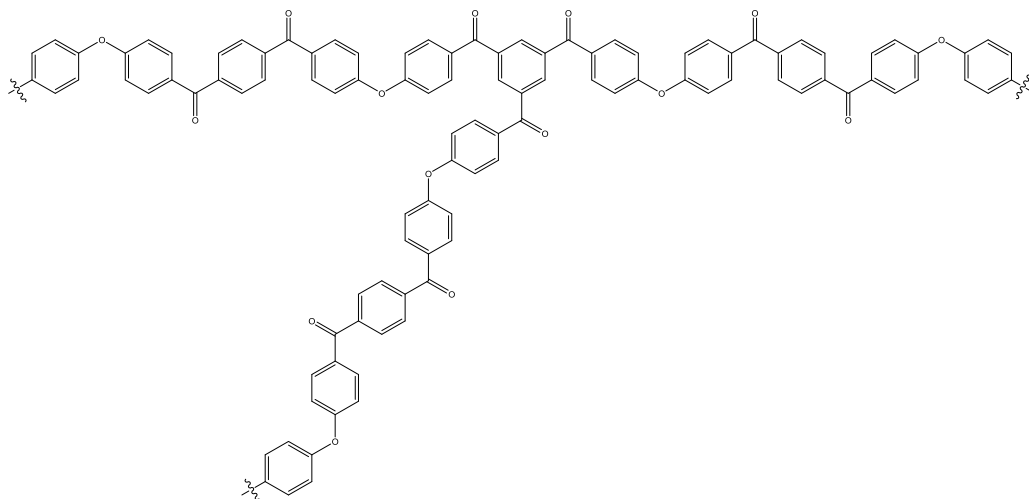
Sulphone %	10	30
T:I	80:20	70:30
Benzoic acid equivalents	4	4
EKKE	35.4997	28.4999
ESE	3.3737	10.4479
TPC	10.1435	8.2391
IPC	6.3652	8.8017
Benzoic acid	39.7513	41.0308
AlCl ₃	105.63	108.96
Benzoyl chloride	0.7080	0.7304
DCM	500	500
Polymer mass	39.49	43.25
Polymer morphology	Fine particulate	Fine particulate

Branched PEKK**Benzene-1,3,5-triyltris(*p*-tolylmethanone) (TRI-TOL)**

DCM (100 ml) was added to a conical flask with a magnetic stirrer and cooled in ice to 5 °C. Aluminium chloride (2.86 g, 21.4 mmol) was added, with swirling, together with the DCM washings. Between each of the subsequent additions and washings, the mixture was cooled in ice to below room temperature with swirling. Next, 1,3,5- benzenetricarbonyl chloride (1.50 g, 5.65 mmol) was added, followed by toluene (3.13g, 34.0 mmol), including the DCM washings (100 ml total). The mixture was stirred at room temperature for 6 hours. After 15 minutes the yellow solution became orange, then after a further 5 minutes became green-brown. The resulting brown solution was poured into iced water, and was stirred at a moderate speed overnight, causing the organic layer to turn from yellow to orange. This mixture was heated on a hotplate to remove the DCM. An orange sticky solid was isolated by decanting the aqueous layer. This solid was dissolved in acetone (100 ml) and decolourising charcoal added (~1 g). After stirring for 10 minutes, the solution was filtered, yielding a pale yellow solution. On evaporation of the acetone, a yellow sticky solid remained. This solid was stirred in methanol (100 ml), causing the precipitation of a cream solid. The solid was isolated by filtration and dried in an air oven, yielding TRI-TOL as a pale yellow solid (0.78g, 32%); mp 118.5 °C; purity 98.00 mol% (DSC); $\nu_{\max}/\text{cm}^{-1}$ 2385 - 1900 (aromatic CH), 1659 (CO), 1605 (central ring stretch), 1248, 1180, 1013; δ_{H} (400 MHz, CDCl_3) 2.47 (9H, s, CH_3), 7.33 (6H, d, J 7.83, C(6)H), 7.78 (6H, d, J 8.31, C(5)H), 8.37 (3H, s, C(1)H); δ_{C} (100 MHz, CDCl_3) 21.75 (CH_3), 129.37 (C(6)H), 130.37 (C(5)H), 133.72 (C(1)H), 133.87 (C(4)), 138.47

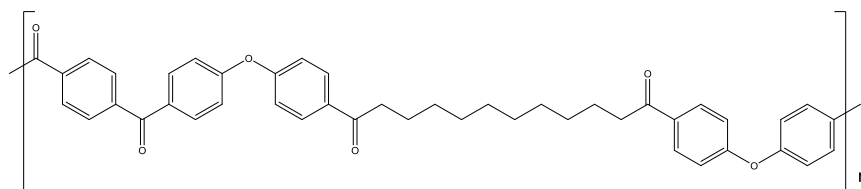
(C(2)), 144.26 (C(7)), 194.79 (C(3)); HRMS (TOF FI⁺) C₃₀H₂₄O₃⁺ ([M]⁺) requires 432.1725 found 432.1727.

Branched PEKKs



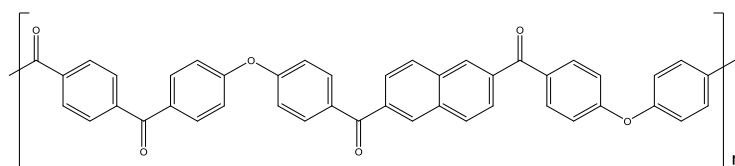
The 80:20 PEKK copolymers were synthesised on a one litre scale according to the general polymerisation method, using the monomer feed as listed below. The polymers were synthesised with a 10% reactor loading, at 5% out of balance. No benzoyl chloride was used.

% TRI	0%	1%	5%	10%
EKKE	8.0002	8.0006	8.0008	8.0005
TPC	1.9345	1.9174	1.8080	1.6774
IPC	1.3540	1.3420	1.3169	1.2836
TRI	-	0.0293	0.1439	0.2875
Benzoic acid	7.9256	7.8948	7.9247	7.9296
AlCl ₃	23.37	22.84	22.58	22.24
DCM	125	125	125	125
Polymer mass	7.93	8.00	7.23	7.34
Polymer morphology	Fine particulate	Fine particulate	Fine particulate	Fine particulate

Aliphatic copolymer P(EK10KE-TPC)

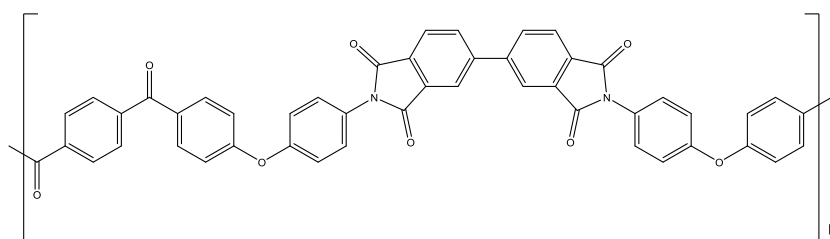
The copolymer was synthesised in a one litre reactor according to the general polymerisation method, using the monomer feed as listed below. It was synthesised with a 10% reactor loading, at 3% out of balance.

EK10KE	40.0001
TPC	14.7317
Benzoic acid	35.4725
AlCl ₃	94.26
Benzoyl chloride	0.6312
DCM	500
Polymer Mass	48.87
Polymer morphology	Fine particulate, irregular

Naphthalene copolymer P(EKNKE-TPC)

The copolymer was synthesised in a one litre reactor according to the general polymerisation method, using the monomer feed as listed below. It was synthesised with a 10% reactor loading, at 3% out of balance.

EKNKE	40.0003
TPC	15.1312
BzOH	36.4348
AlCl ₃	96.71
BzCl	0.6471
DCM	500
Polymer mass	44.07
Polymer morphology	Fine particulate

Biphenyl imide copolymer P(EI-IE - TPC)

The copolymer was synthesised in a one litre reactor according to the general polymerisation method, using the monomer feed as listed below. It was synthesised with a 10% reactor loading, at 5% out of balance.

EI-IE	41.5001
TPC	12.7321
Benzoic acid	102.86
AlCl ₃	30.6578
Benzoyl chloride	0.9288
DCM	500
Polymer mass	26.32
Polymer morphology	Gel (yellow)

8.8 Experimental for Chapter 6**8.8.1 Attempted direct end-capping****Attempted synthesis of TPC-P**

DCM (50 ml) was added to a conical flask with a magnetic stirrer, and cooled in ice to 5 °C. Aluminium chloride (5.03 g, 37.7 mmol) was added, with swirling, together with the DCM washings. Between each of the subsequent additions and washings, the mixture was cooled in ice to below room temperature with swirling. Next, 4-phenoxyaniline (2.74 g, 14.8 mmol) was added, followed by TPC (1.50 g, 7.39 mmol), including the DCM washings (100 ml total). The dark green mixture was stirred at room temperature for 1.5 hours. The reaction mixture was poured into stirring iced water, yielding a beige precipitate in the DCM layer. This mixture was heated on a hotplate to remove the DCM. The beige precipitate was isolated

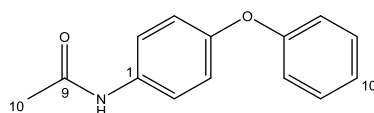
by filtration, was washed with deionised water (3 x 50ml) and dried in an air oven. The beige product was recrystallised in dimethylacetamide, washed with acetone and dried in an air oven, yielding TCP-P as a grey solid (2.87 g).

Attempted synthesis of IPC-P

DCM (50 ml) was added to a conical flask with a magnetic stirrer, and cooled in ice to 5 °C. Aluminium chloride (5.04 g, 37.7 mmol) was added, with swirling, together with the DCM washings. Between each of the subsequent additions and washings, the mixture was cooled in ice to below room temperature with swirling. Next, 4-phenoxyaniline (2.73 g, 14.7 mmol) was added, followed by TPC (1.50 g, 7.39 mmol), including the DCM washings (100 ml total). The dark purple mixture was stirred at room temperature for 1.5 hours. The reaction mixture was poured into stirring iced water, yielding a beige precipitate in the DCM layer. This mixture was heated on a hotplate to remove the DCM. The beige precipitate was isolated by filtration, was washed with deionised water (3 x 50ml) and dried in an air oven. The beige product was recrystallised in dimethylacetamide, washed with acetone and dried in an air oven, yielding IPC-P as a grey solid (2.93 g).

8.8.2 End-capper synthesis

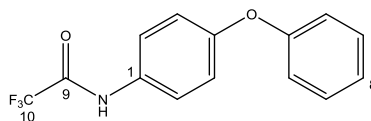
N-(4-phenoxyphenyl)acetamide (EC-A)



4-Phenoxyaniline (20.4 g, 0.110 mol) was dissolved in DCM (200 ml) with stirring. To the very dark brown solution was added decolourising charcoal (3 g) and the resulting suspension stirred for 15 minutes. The suspension was filtered through a Soxhlet thimble into a conical flask. On drainage of the thimble, further DCM (200 ml) was filtered into the conical flask via the thimble. After cooling the conical flask in an ice bath to 5 °C, acetic anhydride (11.1

cm³, 0.109 mol) was added to the aniline solution. An exothermic reaction occurred, raising the temperature to 30 °C. After stirring for 30 minutes the solution was poured into water (1000 ml) and stirred for 10 minutes. Stirring was stopped before decanting the majority of the aqueous layer. Water (500 ml) was replaced. A saturated solution of sodium hydrogen carbonate was added to the water/ DCM mixture, accompanied by effervescence. Addition was continued until the pH of the mixture was below pH 7. At this point, the organic layer was extracted using a separating funnel. This layer was dried by the addition of anhydrous magnesium sulphate (5 g). Decolourising charcoal (3 g) was added and, after stirring for 15 minutes, the suspension was filtered through a fresh Soxhlet thimble, washed through with DCM, resulting in a transparent pale red-brown solution. Methylcyclohexane (300 ml) was added to the solution with heating, removing the DCM and reducing the overall volume to approximately 75 ml and resulting in the production of pale pink crystals. The solid was recrystallised from methylcyclohexane, was washed with methanol and EC-A was isolated as a pink crystalline solid (21.0 g, 85%); purity 99.99 mol% (DSC); mp 131.2 °C {lit.⁶ 130-131 °C}; $\nu_{\max}/\text{cm}^{-1}$ 3286 (NH), 2240-1760 (aromatic CH), 1699 (CO), 1659 (NH), 1545, 1842; δ_{H} (400 MHz, CDCl₃) 2.19 (3H, s, CH₃), 6.97-7.01 (4H, m, C(6)H, C(3)H), 7.11 (1H, t, *J* 7.58, C(8)H), 7.34 (2H, t, *J* 7.95, C(7)H), 7.48 (2H, d, *J* 9.05, C(2)H), 7.57 (1H, br. s, NH); δ_{C} (100 MHz, CDCl₃) 24.40 (C(10)H₃), 118.47 (C(3)), 119.56 (C(6)), 121.81 (C(8)), 123.12 (C(2)), 129.75 (C(7)), 133.38 (C(1)), 153.53 (C(4)), 157.50 (C(5)), 168.47 (C(9)O); *m/z* (ESI⁺) 250 ([M+H]⁺); HRMS (ESI⁺) C₁₄H₁₃NNaO₂⁺, ([M+Na]⁺) requires 250.0838 found 250.0827.

2,2,2-Trifluoro-N-(4-phenoxyphenyl)acetamide (EC-F)

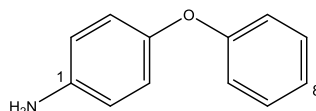


4-Phenoxyaniline (15.0 g, 81.1 mmol) was dissolved in DCM (200 ml) with stirring. To the very dark brown solution was added decolourising charcoal (3 g) and the resulting suspension

stirred for 15 minutes. The suspension was filtered through a Soxhlet thimble into a conical flask. On drainage of the thimble, further DCM (200 ml) was filtered into the conical flask via the thimble. After cooling the conical flask in an ice bath to 5 °C, trifluoroacetic anhydride (16.1 g, 76.5 mmol) was added to the aniline solution. An exothermic reaction occurred, raising the temperature to 35 °C. After stirring for 30 minutes, the solution was poured into water (1000 ml) and stirred for 10 minutes. Stirring was stopped before decanting the majority of the aqueous layer. Water (500 ml) was replaced. A saturated solution of sodium hydrogen carbonate was added to the water/ DCM mixture, accompanied by effervescence. Addition was continued until the pH of the mixture was below pH 7. At this point, the organic layer was extracted using a separating funnel. This layer was dried by the addition of anhydrous magnesium sulphate (5 g). Decolourising charcoal (3 g) was added and, after stirring for 15 minutes, the suspension was filtered through a fresh Soxhlet thimble, washed through with DCM, resulting in a transparent pale red-brown solution. Methylcyclohexane (300 ml) was added to the solution with heating, removing the DCM and reducing the overall volume to approximately 75 ml and resulting in the production of pale pink crystals. The solid was recrystallised from methylcyclohexane, was washed with methanol and EC-F was isolated as a pale pink crystalline solid (19.9 g, 88%); purity 99.99 mol% (DSC); mp 114.2 °C; $\nu_{\max}/\text{cm}^{-1}$ 3284 (NH), 2260-1770 (aromatic CH), 1702 (CO), 1540 (NH), 1148; δ_{H} (400 MHz, CDCl_3) 6.91-6.96 (4H, m, C(6)H, C(3)H), 7.27 (2H, t, J 8.07, C(7)H), 7.44 (2H, d, J 9.05, C(2)H), 7.58 (1H, t, J 7.05, C(8)H), 7.91 (1H, br. s, NH); δ_{C} (100 MHz, CDCl_3) 115.79 (q, CF_3), 119.05 (C(6)), 119.36 (C(3)), 122.36 (C(2)), 123.75 (C(8)), 129.92 (C(1)), 130.10 (C(7)), 154.64 (C(4)), 155.52 (C(9)O), 156.77 (C(4)); δ_{F} (376 MHz, CDCl_3) -75.63 (CF_3); m/z (ESI⁺) 304 ([M+Na]⁺); HRMS (ESI⁺) $\text{C}_{14}\text{H}_{10}\text{F}_3\text{NNaO}_2^+$, ([M+Na]⁺) requires 304.0556 found 304.0550.

8.8.3 End-capper deprotection

4-Phenoxyaniline by the hydrolysis of EC-F



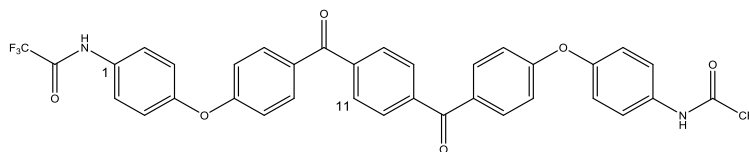
A portion of EC-F (100 mg, 0.36 mmol), was placed in a beaker with deionised water (25 ml) and isopropyl alcohol (25 ml), and made up to pH 13 with a single sodium hydroxide pellet, which caused EC-F to dissolve. The mixture was heated at 85 °C for 1.5 hours, during which time a white suspension was produced. The solid was isolated by filtration and, washed with deionised water and dried in an air oven to yield 4-phenoxyaniline as a white crystalline solid (47 mg, 71%), mp 85.1 °C {lit.⁷ 85-86 °C}; purity 99.95 mol% (DSC); $\nu_{\max}/\text{cm}^{-1}$ 3386 and 3309 (NH), 3224, 2250-1740 (aromatic CH), 1585 (NH), 1482, 1221; δ_{H} (400 MHz, CDCl₃) 3.45 (2H, br. s, NH₂), 6.60 (2H, d, *J* 8.80, C(2)H), 6.80 (2H, d, *J* 8.56, C(3)H), 6.85 (2H, d, *J* 7.58, C(26)H), 6.93 (1H, t, *J* 7.34, C(8)H), 7.17-7.22 (2H, t, *J* 8.0 C(7)H); δ_{C} (100 MHz, CDCl₃) 116.29 (C(2)), 117.25 (C(6)), 121.15 (C(3)), 122.09 (C(8)), 129.55 (C(7)), 142.64 (C(1)), 148.64 (C(4)), 158.91 (C(5)); *m/z* (ESI⁺) 186 ([M+H]⁺); HRMS (ESI⁺) C₁₂H₁₂NO⁺, ([M+H]⁺) requires 186.0913 found 186.0906.

Attempted hydrolysis of EC-A

A portion of EC-A (100 mg, 0.37 mmol), was placed in a beaker with deionised water (25 ml) and IPA (25 ml), and made up to pH 13 with a single sodium hydroxide pellet, which caused EC-A to dissolve. The mixture was heated at 85 °C for 1.5 hours, during which time a white suspension was produced. The solid was isolated by filtration and, washed with deionised water and dried in an air oven to yield unreacted starting material (80 mg, 82%).

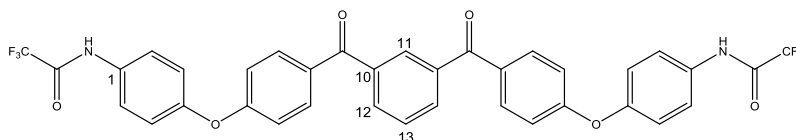
8.8.4 Linear model compound synthesis

2,2,2-Trifluoro-N-(4-(3-(4-(4-(4-(2,2,2-trifluoroacetamido)phenoxy)benzoyl)benzoyl)phenoxy)phenyl)acetamide (TPC-EC)



DCM (50 ml) was added to a conical flask with a magnetic stirrer, and cooled in ice to 5 °C. Aluminium chloride (5.03 g, 37.7 mmol) was added, with swirling, together with the DCM washings. Between each of the subsequent additions and washings, the mixture was cooled in ice to below room temperature with swirling. Next, EC-F (4.17 g, 14.8 mmol) was added, followed by TPC (1.51 g, 7.44 mmol), including the DCM washings (100 ml total). The mixture was stirred at room temperature for 1.5 hours, during which time the orange-brown solution became yellow. The reaction mixture was poured into stirring iced water, yielding a white precipitate in the DCM layer. This mixture was heated on a hotplate to remove the DCM. The cream precipitate TPC-EC was isolated by filtration, was washed with deionised water (3 x 50ml) and dried in an air oven. The cream product was recrystallised in dimethylacetamide, washed with acetone and dried in an air oven, yielding TPC-EC as a grey solid (4.72 g, 92%); mp 325.9 °C; purity 98.85 mol% (DSC); $\nu_{\max}/\text{cm}^{-1}$ 3275 (NH), 2250-1800 (aromatic CH), 1705 (CO), 1645 (amide CO), 1517 (aromatic C=C), 1543 (NH), 1234 (CF), 1150 (PhOPh); δ_{H} (500 MHz, $\text{CDCl}_3(\text{TFA})$) 7.13 (4H, d, J 8.83, C(6)H), 7.22 (4H, d, J 8.51, C(2)H), 7.63 (4H, d, J 8.51, C(3)H), 7.91-7.93 (8H, m, C(7)H, C(11)H), 8.56 (2H, s, NH); δ_{C} (125 MHz, $\text{CDCl}_3(\text{TFA})$) 114.86 (CF₃, q), 119.79 (C(6)H), 121.71 (C(2)H), 124.12 (C(3)H), 130.35 (C(8)), 130.49 (C(11)H), 134.24 (C(7)H), 140.99 (C(1)), 142.21 (C(10)), 154.32 (C(4)), 157.56 (CF₃, q), 163.69 (C(5)), 200.03 (C(9)O); HRMS (TOF EI⁺) $\text{C}_{36}\text{H}_{22}\text{N}_2\text{O}_6\text{F}_6^+$, ([M]⁺) requires 692.1382 found 692.1423.

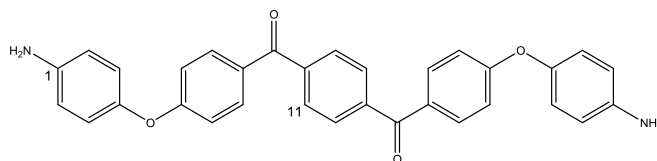
***N,N'*-(((Isophthaloylbis(3,1-phenylene))bis(oxy)bis(4,1-phenylene))bis(2,2,2-trifluoroacetamide) (IPC-EC)**



DCM (50 ml) was added to a conical flask with a magnetic stirrer and cooled in ice to 5 °C. Aluminium chloride (4.84 g, 36.3 mmol) was added, with swirling, together with the DCM washings. Between each of the subsequent additions and washings, the mixture was cooled in ice to below room temperature with swirling. Next, EC-F (4.16 g, 14.8 mmol) was added, followed by TPC (1.51 g, 7.44 mmol), including the DCM washings (100 ml total). The mixture was stirred at room temperature for 1.5 hours, during which time the orange-brown solution became bright orange. The reaction mixture was poured into stirring iced water, yielding a white precipitate in the DCM layer. This mixture was heated on a hotplate to remove the DCM. The cream precipitate IPC-EC was isolated by filtration, was washed with deionised water (3 x 50 ml) and dried in an air oven. The cream product was recrystallised in dimethylacetamide, washed with acetone and dried in an air oven, yielding IPC-EC as a grey solid (4.76 g, 92%); mp 231.2 °C; purity 97.42 mol% (DSC); $\nu_{\max}/\text{cm}^{-1}$ 3277 (NH), 2200-1850 (aromatic CH), 1705 (CO), 1651 (amide CO), 1595 (aromatic C=C), 1543 (NH), 1494, 1228 (CF), 1150 (PhOPh); δ_{H} (500 MHz, $\text{CDCl}_3(\text{TFA})$) 7.08 (4H, d, J 8.83, C(3)*H*), 7.17 (4H, d, J 8.83, C(2)*H*), 7.62 (4H, d, J 9.14, C(7)*H*), 7.73 (1H, t, C(13)*H*), 7.87 (4H, d, J 8.83, C(2)*H*) 8.06 (2H, dd, C(12)*H*), 8.11 (1H, s, C(11)*H*), 8.50 (2H, s, NH); δ_{C} (125 MHz, $\text{CDCl}_3(\text{TFA})$) 114.90 (CF₃, q), 117.94 (C(6)*H*), 121.67 (C(2)*H*), 123.89 (C(3)*H*), 124.60 (C(1)), 129.57 (C(13)*H*), 130.71 (C(8)), 131.32 (C(11)*H*), 134.02 (C(7)*H*), 134.85 (C(12)*H*), 137.69 (C(10)), 154.06 (C(4)), 156.95 (CF₃, q), 163.33 (C(5)), 198.83 (C(9)O); HRMS (TOF EI⁺) C₃₆H₂₂N₂O₆F₆⁺, ([M]⁺) requires 692.1382 found 692.1420.

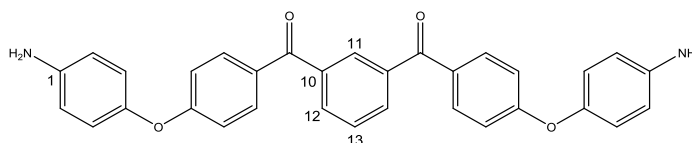
8.8.5 Linear model compound deprotection

(4-(3-(4-Aminophenoxy)benzoyl)phenyl)(4-(4-aminophenoxy)phenyl)methanone (TPC-EC-D) by the deprotection of (TPC-EC)



A portion of TPC-EC (130 mg, 0.188 mmol), was placed in a beaker with deionised water (25 ml) and IPA (25 ml), and made up to pH 13 with a single sodium hydroxide pellet, which caused TPC-EC to dissolve. The mixture was heated at 85 °C for 1.5 hours, during which time a cream suspension was produced. The solid was isolated by filtration, washed with deionised water and dried in an air oven to yield TPC-EC-D as a beige crystalline solid (76 mg, 85%); mp 199.5 °C {lit.⁸ 226 – 230 °C}; purity 97.63mol% (DSC); $\nu_{\max}/\text{cm}^{-1}$ 3377 and 3310 (NH), 2150-1760 (aromatic CH), 1643 (CO), 1595 (aromatic C=C), 1506, 1306 (NH₂), 1328 (PhOPh), 1153; δ_{H} (500 MHz, CDCl₃) δ_{H} (500 MHz, CDCl₃) 7.14 (4H, d, *J* 8.83, C(6)*H*), 7.26 (4H, d, *J* 8.51, C(2)*H*), 7.48 (4H, d, *J* 8.83, C(3)*H*), 7.90-7.93 (8H, m, C(7)*H*, C(11)*H*); δ_{C} (125 MHz, CDCl₃(TFA)) 118.13 (C(6)H), 121.60 (C(2)H), 124.56 (C(3)H), 130.05 (C(11)H), 130.78 (C(8)), 133.74 (C(7)H), 140.46 (C(1)), 153.86 (C(10)), 156.81 (C(4)), 168.20 (C(5)), 199.42 (C(9)O); HRMS (TOF EI⁺) C₃₂H₂₄N₂O₄⁺, ([M]⁺) requires 500.1736 found 500.1734.

1,3-Phenylenebis((3-(4-aminophenoxy)phenyl)methanone (IPC-EC-D) by the deprotection of (IPC-EC)

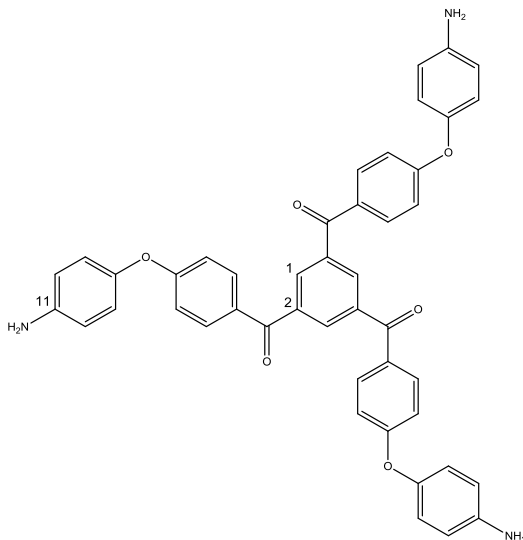


A portion of IPC-EC (113 mg, 0.164 mmol), was placed in a beaker with deionised water (25 ml) and IPA (25 ml), and made up to pH 13 with a single sodium hydroxide pellet, which

washings. Between each of the subsequent additions and washings, the mixture was cooled in ice to below room temperature with swirling. Next, 1, 3, 5- benzenetricarbonyl chloride (TRI) (1.52 g, 5.73 mmol) was added, followed by EC-F (6.00 g, 21.3 mmol), including the DCM washings (100 ml total). The addition of EC-F caused the solution to turn green. The mixture was stirred at room temperature for 1.5 hours. After 5 minutes the solution became orange, then after a further 15 minutes a dark viscous liquid formed at the bottom of the flask. The resulting orange solution and dark orange viscous solid was poured into iced water, and was stirred at a moderate speed for 1 hour, resulting in a small amount of a white precipitate in the aqueous layer and an orange organic layer. This mixture was heated on a hotplate to remove the DCM. A green sticky solid was isolated by decanting the aqueous layer. This solid was dissolved in acetone (100 ml) and decolourising charcoal added (~1 g). After stirring for 10 minutes, the solution was filtered, yielding a pale brown solution. On evaporation of the acetone, a brown sticky solid remained. This solid was stirred in methanol (100 ml), causing the precipitation of a white solid. The solid was isolated by filtration and dried in an air oven, yielding TRI-EC as a pale grey solid (4.24 g, 74%); mp 172.3 °C; purity 97.82 mol% (DSC); $\nu_{\max}/\text{cm}^{-1}$ 3442 and 3302 (NH), 2395 - 1925 (aromatic CH), 1702 (amide CO), 1655 (CO), 1591 (central ring stretch), 1559 (NH), 1497 (central ring stretch), 1292 (NH), 1227 (COC), 1157, 1003; δ_{H} (400 MHz, CDCl_3 (TFA)) 7.09 (6H, d, J 8.80, C(6)H), 7.17 (6H, d, J 9.05, C(9)H), 7.64 (6H, d, J 9.05, C(10)H), 7.88 (6H, d, J 8.80, C(5)H), 8.35 (3H, s, C(1)H); δ_{C} (100 MHz, CDCl_3 (TFA)) 114.23 and 117.08 (quartet partially visible) (CF_3), 117.54 (C(6)), 121.26 (C(9)), 123.13 (C(10)), 130.21 (C(11)), 131.31 (C(4)), 133.26 (C(5)), 134.27 (C(1)), 138.21 (C(2)), 153.29 (C(8)), 157 quartet (CF_3), 162.80 (C(7)), 195.80 (C(3)); δ_{F} (376 MHz, CDCl_3 (TFA)) -75.66 (CF_3); HRMS (TOF EI⁺) $\text{C}_{51}\text{H}_{30}\text{F}_9\text{N}_3\text{O}_9^+$ ($[\text{M}]^+$) requires 999.1838 found 999.1856.

8.8.7 Trifunctional model deprotection

Benzene-1,3,5-triyltris((4-(4-aminophenoxy)phenyl)methanone) (TRI-EC-D)



A portion of TRI-EC (153 mg, 0.153 mmol), was placed in a beaker with deionised water (25 ml) and IPA (25 ml), and made up to pH 13 with a single sodium hydroxide pellet, which caused TRI-EC to dissolve. The mixture was heated at 85 °C for 1.5 hours, during which time a yellow suspension was produced. The solid was isolated by filtration, washed with deionised water and dried in an air oven to yield TRI-EC-D as a pale yellow solid (0.0771 g, 71 %); mp 167.4 °C; purity 97.72 mol% (DSC); $\nu_{\max}/\text{cm}^{-1}$ 3456 and 3366 (NH), 2150 - 1820 (aromatic CH), 1702 (amide CO), 1651 (CO), 1593 and 1499 (central ring stretch), 1312 (CN), 1236 (COC), 1197, 1159 (COC), 1157, 1005; HRMS (TOF EI⁺) C₃₀H₂₄O₃⁺ ([M]⁺) requires 711.2369 found 711.2212.

8.8.8 Small scale polymer synthesis

A small scale polymerisation was carried out for the production of 100:0 PEKK at 10 % out-of-balance and with 4 benzoic acid equivalents, with EC-F replacing the benzoyl chloride in the monomer feed. A modified workup procedure was carried out, where the ammonia step was replaced by a wash using sodium hydroxide at pH 13.

EKKE	9.75
TPC	4.63
Benzoic acid	11.11
Aluminium chloride	30.42
EC-F	1.12
DCM	125
Polymer mass	11.49
Polymer morphology	Fine particulate

8.8.9 Large scale polymer synthesis

All polymerisations were carried out on a five litre scale, with EC-F replacing the benzoyl chloride in the monomer feed. Polymerisations were carried out at 5% out-of-balance with respect to the EKKE and acid chlorides in the monomer feed, and with four benzoic acid equivalents. A modified workup procedure was carried out, where the ammonia step was replaced by a wash using sodium hydroxide at pH 13.

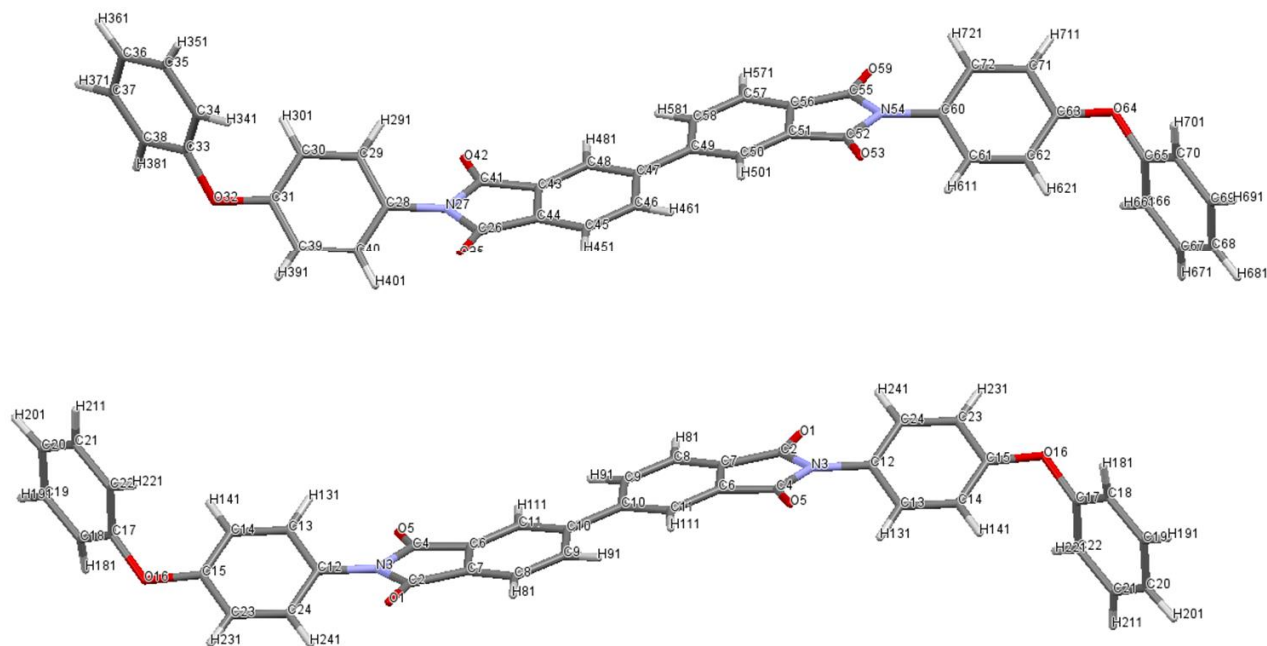
	100:0 PEKK	80:20 PEKK	60:40 PEKK	Imide	Branched
EKKE	266.00	265.99	265.98	140.02	265.04
TPC	120.83	73.71	26.66	90.60	68.37
IPC	-	47.10	94.17	-	45.68
Benzoic acid	292.99	293.09	293.02	218.25	289.10
AlCl ₃	766.17	764.80	767.87	609.16	751.37
EC-F	16.67	16.69	16.68	11.94	15.89
EIEIE	-	-	-	82.21	-
TRI	-	-	-	-	5.22
DCM	3500	3500	3500	3500	3500

8.9 References

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APPENDIX : X-RAY CRYSTAL STRUCTURE DATA

Flat EI-IE monomer



Atom number	Label	Xfrac + ESD	Yfrac + ESD	Zfrac + ESD
1	O1	0.25168(3)	1.0601(3)	0.39129(3)
2	C2	0.23717(4)	1.1127(3)	0.41284(4)
3	N3	0.20601(3)	1.0077(3)	0.41743(3)
4	C4	0.19573(4)	1.1178(4)	0.44425(4)
5	O5	0.17092(3)	1.0604(3)	0.45494(3)
6	C6	0.22156(4)	1.3112(3)	0.45665(4)
7	C7	0.24701(4)	1.2993(3)	0.43876(4)
8	C8	0.27441(4)	1.4595(4)	0.44510(4)
9	C9	0.27516(4)	1.6332(4)	0.46946(4)
10	C10	0.24916(4)	1.6522(3)	0.48739(4)
11	C11	0.22193(4)	1.4832(3)	0.48076(4)
12	C12	0.18663(4)	0.8292(3)	0.39640(4)
13	C13	0.15117(4)	0.8365(4)	0.39022(4)
14	C14	0.13233(5)	0.6625(4)	0.36977(4)
15	C15	0.14893(5)	0.4870(4)	0.35475(5)
16	O16	0.13227(3)	0.3060(3)	0.33439(4)
17	C17	0.09773(5)	0.3385(4)	0.32059(4)
18	C18	0.07484(6)	0.1709(4)	0.32787(5)
19	C19	0.04090(6)	0.1882(5)	0.31305(6)
20	C20	0.02987(6)	0.3741(5)	0.29155(5)
21	C21	0.05288(7)	0.5448(5)	0.28462(6)

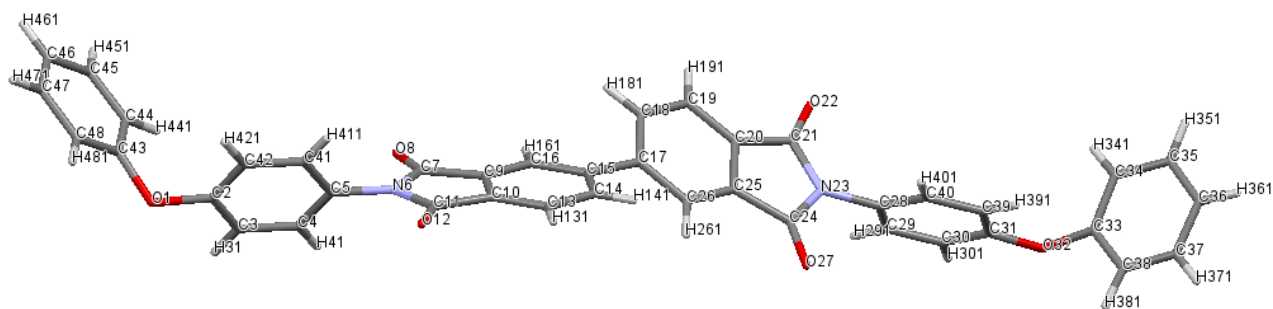
22	C22	0.08710(7)	0.5273(5)	0.29916(6)
23	C23	0.18430(5)	0.4802(4)	0.36057(5)
24	C24	0.20308(5)	0.6491(4)	0.38147(4)
25	H81	0.2930(5)	1.447(4)	0.4324(5)
26	H91	0.2936(5)	1.753(4)	0.4739(5)
27	H111	0.2038(5)	1.490(4)	0.4917(4)
28	H131	0.1395(5)	0.968(4)	0.3998(5)
29	H141	0.1063(5)	0.664(4)	0.3660(5)
30	H181	0.0825(6)	0.057(5)	0.3439(6)
31	H191	0.0233(6)	0.066(5)	0.3184(6)
32	H201	0.0050(6)	0.381(5)	0.2802(6)
33	H211	0.0462(7)	0.686(6)	0.2701(7)
34	H221	0.1032(7)	0.641(5)	0.2952(6)
35	H231	0.1952(5)	0.360(4)	0.3500(5)
36	H241	0.2294(5)	0.645(4)	0.3864(5)
37	O1	0.24832(3)	2.4399(3)	0.60871(3)
38	C2	0.26283(4)	2.3873(3)	0.58716(4)
39	N3	0.29399(3)	2.4923(3)	0.58257(3)
40	C4	0.30427(4)	2.3822(4)	0.55575(4)
41	O5	0.32908(3)	2.4396(3)	0.54506(3)
42	C6	0.27844(4)	2.1888(3)	0.54335(4)
43	C7	0.25299(4)	2.2007(3)	0.56124(4)
44	C8	0.22559(4)	2.0405(4)	0.55490(4)
45	C9	0.22484(4)	1.8668(4)	0.53054(4)
46	C10	0.25084(4)	1.8478(3)	0.51261(4)
47	C11	0.27807(4)	2.0168(3)	0.51924(4)
48	C12	0.31337(4)	2.6708(3)	0.60360(4)
49	C13	0.34883(4)	2.6635(4)	0.60978(4)
50	C14	0.36767(5)	2.8375(4)	0.63023(4)
51	C15	0.35107(5)	3.0130(4)	0.64525(5)
52	O16	0.36773(3)	3.1940(3)	0.66561(4)
53	C17	0.40227(5)	3.1615(4)	0.67941(4)
54	C18	0.42516(6)	3.3291(4)	0.67213(5)
55	C19	0.45910(6)	3.3118(5)	0.68695(6)
56	C20	0.47013(6)	3.1259(5)	0.70845(5)
57	C21	0.44712(7)	2.9552(5)	0.71538(6)
58	C22	0.41290(7)	2.9727(5)	0.70084(6)
59	C23	0.31570(5)	3.0198(4)	0.63943(5)
60	C24	0.29692(5)	2.8509(4)	0.61853(4)
61	H81	0.2070(5)	2.053(4)	0.5676(5)
62	H91	0.2064(5)	1.747(4)	0.5261(5)
63	H111	0.2962(5)	2.010(4)	0.5083(4)
64	H131	0.3605(5)	2.532(4)	0.6002(5)
65	H141	0.3937(5)	2.836(4)	0.6340(5)
66	H181	0.4175(6)	3.443(5)	0.6561(6)
67	H191	0.4767(6)	3.434(5)	0.6816(6)

68	H201	0.4950(6)	3.119(5)	0.7198(6)
69	H211	0.4538(7)	2.814(6)	0.7299(7)
70	H221	0.3968(7)	2.859(5)	0.7048(6)
71	H231	0.3048(5)	3.140(4)	0.6500(5)
72	H241	0.2706(5)	2.855(4)	0.6136(5)
73	O25	0.40727(3)	1.2876(3)	0.59298(3)
74	C26	0.42352(4)	1.2166(3)	0.57356(4)
75	N27	0.45705(3)	1.2935(3)	0.57240(3)
76	C28	0.47696(4)	1.4521(3)	0.59624(4)
77	C29	0.51034(4)	1.3878(4)	0.61009(4)
78	C30	0.52904(5)	1.5346(4)	0.63439(4)
79	C31	0.51410(4)	1.7417(3)	0.64503(4)
80	O32	0.53092(3)	1.8979(3)	0.66892(3)
81	C33	0.55961(5)	1.8095(4)	0.69024(5)
82	C34	0.55810(8)	1.6042(5)	0.70890(6)
83	C35	0.58765(14)	1.5346(7)	0.73087(7)
84	C36	0.61702(11)	1.6738(10)	0.73359(9)
85	C37	0.61756(7)	1.8790(10)	0.71485(8)
86	C38	0.58882(6)	1.9477(6)	0.69298(6)
87	C39	0.48087(5)	1.8064(4)	0.63113(4)
88	C40	0.46234(5)	1.6628(4)	0.60676(4)
89	C41	0.46930(4)	1.1681(4)	0.54795(4)
90	O42	0.49710(3)	1.1976(3)	0.54125(3)
91	C43	0.44172(4)	0.9954(3)	0.53282(4)
92	C44	0.41417(4)	1.0295(3)	0.54764(4)
93	C45	0.38529(4)	0.8851(4)	0.53927(4)
94	C46	0.38507(4)	0.7050(4)	0.51576(4)
95	C47	0.41292(4)	0.6648(3)	0.50068(4)
96	C48	0.44186(4)	0.8174(4)	0.50944(4)
97	C49	0.41159(4)	0.4644(3)	0.47615(4)
98	C50	0.38330(4)	0.3049(4)	0.46858(4)
99	C51	0.38293(4)	0.1288(3)	0.44505(4)
100	C52	0.35590(4)	-0.0533(4)	0.43152(4)
101	O53	0.32967(3)	-0.0950(3)	0.44052(3)
102	N54	0.36701(3)	-0.1725(3)	0.40583(3)
103	C55	0.39949(4)	-0.0848(3)	0.40291(4)
104	C56	0.40951(4)	0.1012(3)	0.42871(4)
105	C57	0.43796(4)	0.2507(4)	0.43613(4)
106	C58	0.43858(4)	0.4308(4)	0.45974(4)
107	O59	0.41495(3)	-0.1486(3)	0.38238(3)
108	C60	0.34679(4)	-0.3430(3)	0.38377(4)
109	C61	0.31186(4)	-0.3066(4)	0.37427(4)
110	C62	0.29243(5)	-0.4692(4)	0.35268(4)
111	C63	0.30789(4)	-0.6647(3)	0.33994(4)
112	O64	0.29076(3)	-0.8336(3)	0.31800(4)
113	C65	0.25668(5)	-0.7890(4)	0.30377(4)

114	C66	0.24785(6)	-0.6003(4)	0.28169(5)
115	C67	0.21379(6)	-0.5723(5)	0.26694(6)
116	C68	0.18951(6)	-0.7309(5)	0.27399(5)
117	C69	0.19872(6)	-0.9200(4)	0.29583(6)
118	C70	0.23253(5)	-0.9490(4)	0.31099(5)
119	C71	0.34276(5)	-0.7014(4)	0.34948(5)
120	C72	0.36220(5)	-0.5410(4)	0.37124(5)
121	H291	0.5206(5)	1.239(4)	0.6027(5)
122	H301	0.5523(5)	1.490(4)	0.6434(5)
123	H341	0.5372(7)	1.510(6)	0.7061(7)
124	H351	0.5829(10)	1.395(8)	0.7413(9)
125	H361	0.6393(10)	1.634(7)	0.7482(10)
126	H371	0.6411(9)	1.984(7)	0.7175(8)
127	H381	0.5892(7)	2.094(5)	0.6794(6)
128	H391	0.4710(5)	1.946(4)	0.6387(5)
129	H401	0.4376(5)	1.709(4)	0.5978(5)
130	H451	0.3655(5)	0.911(4)	0.5501(5)
131	H461	0.3644(5)	0.598(4)	0.5096(5)
132	H481	0.4619(5)	0.799(4)	0.4991(4)
133	H501	0.3640(5)	0.319(4)	0.4785(5)
134	H571	0.4576(5)	0.235(4)	0.4248(5)
135	H581	0.4586(5)	0.537(4)	0.4664(5)
136	H611	0.3015(5)	-0.168(4)	0.3829(5)
137	H621	0.2673(5)	-0.445(4)	0.3462(5)
138	H661	0.2647(6)	-0.489(5)	0.2773(5)
139	H671	0.2077(6)	-0.444(5)	0.2515(6)
140	H681	0.1648(6)	-0.709(5)	0.2623(6)
141	H691	0.1813(6)	-1.036(5)	0.3019(6)
142	H701	0.2394(5)	-1.076(4)	0.3270(5)
143	H711	0.3532(5)	-0.838(4)	0.3401(5)
144	H721	0.3866(5)	-0.567(4)	0.3776(5)

Estimated standard deviation (ESD)/ %

Twisted EI-IE monomer



Atom number	Label	Xfrac	Yfrac	Zfrac
1	O1	1.1438	0.2002	0.7245
2	C2	1.046	0.2183	0.7144
3	C3	1.0092	0.3586	0.7134
4	C4	0.9129	0.3768	0.706
5	C5	0.8549	0.2533	0.7003
6	N6	0.7547	0.2747	0.6921
7	C7	0.6971	0.3568	0.6463
8	O8	0.7233	0.4166	0.6083
9	C9	0.6001	0.3502	0.6555
10	C10	0.6035	0.2682	0.7047
11	C11	0.7029	0.2176	0.7291
12	O12	0.7355	0.1432	0.7715
13	C13	0.523	0.2447	0.724
14	C14	0.4392	0.3074	0.6916
15	C15	0.4349	0.3921	0.6424
16	C16	0.517	0.4138	0.6236
17	C17	0.3436	0.4622	0.6106
18	C18	0.3185	0.4694	0.5504
19	C19	0.2348	0.5341	0.5197
20	C20	0.1753	0.5919	0.5508
21	C21	0.0814	0.6651	0.5307
22	O22	0.0347	0.6866	0.4822
23	N23	0.0547	0.7037	0.5809
24	C24	0.1219	0.6594	0.6308
25	C25	0.1999	0.5877	0.6105
26	C26	0.2835	0.524	0.6413
27	O27	0.1151	0.6774	0.6794
28	C28	-0.0332	0.7763	0.5808
29	C29	-0.0453	0.926	0.5669
30	C30	-0.1305	0.9942	0.5652
31	C31	-0.2025	0.9126	0.5776
32	O32	-0.2845	0.9916	0.5756
33	C33	-0.3671	0.9137	0.5756
34	C34	-0.4221	0.8569	0.5255
35	C35	-0.5103	0.794	0.5264
36	C36	-0.5366	0.7911	0.5771
37	C37	-0.4798	0.8443	0.6255
38	C38	-0.3947	0.9061	0.6254
39	C39	-0.1912	0.7641	0.5922
40	C40	-0.1053	0.6955	0.5938
41	C41	0.8922	0.1127	0.7016
42	C42	0.9886	0.0949	0.7086
43	C43	1.1763	0.1403	0.6792
44	C44	1.146	0.1948	0.624
45	C45	1.1843	0.1391	0.5817

46	C46	1.2513	0.026	0.5943
47	C47	1.2799	-0.0285	0.6495
48	C48	1.2429	0.0276	0.6925
49	H31	1.0514	0.4401	0.7189
50	H41	0.886	0.4735	0.704
51	H131	0.5256	0.1862	0.7585
52	H141	0.3829	0.2936	0.704
53	H161	0.5156	0.4738	0.5906
54	H181	0.3618	0.428	0.5298
55	H191	0.2187	0.5404	0.479
56	H261	0.3	0.5227	0.683
57	H291	0.006	0.9822	0.5592
58	H301	-0.1395	1.0988	0.5556
59	H341	-0.4014	0.8624	0.4911
60	H351	-0.5482	0.7524	0.4923
61	H361	-0.5967	0.7528	0.5782
62	H371	-0.4996	0.8372	0.6606
63	H381	-0.3525	0.9442	0.6597
64	H391	-0.2412	0.7095	0.6011
65	H401	-0.0964	0.5937	0.6041
66	H411	0.8525	0.028	0.6981
67	H421	1.0156	-0.0004	0.7081
68	H441	1.0985	0.2717	0.6169
69	H451	1.1655	0.181	0.5435
70	H461	1.2769	-0.0152	0.5652
71	H471	1.3251	-0.1072	0.6587
72	H481	1.2634	-0.0083	0.7311
