Polyaryletherketone polymers and copolymers by a Friedel Crafts dispersion polymerisation

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Abstract

A range of particulate polyaryletherketone polymers and copolymers, incorporating ether-imide, sulfone, naphthalene, and aliphatic functionalities, along with branching monomers, may be successfully produced by a dispersion polymerisation process, provided that the reaction parameters are optimised. This significantly expands the range of monomers suitable for application in the Friedel Crafts dispersion polymerisation process.

Introduction

A large variety of polyaryletherketone (PAEK) copolymers can be produced reliably using a Friedel-Crafts gel process[1,2] using different monomers with a range of functionalities. Once integrated into the polymer backbone, these groups alter the Glass Transition Temperature (T_g), Melting Point (T_m), and Crystallisation Temperature (T_c) values along with the degree and rates of crystallisation of the polymer. As long as the capacity for Friedel-Crafts polymerisation is maintained, with any substituent groups being stable to the reaction conditions, either of the "EKKE type" dinucleophilic monomer or the diacid chloride monomer may be modified.[3] Dinucleophilic monomers suitable for the gel or dispersion processes are either in the "standard-X" form or "EXE" form (Figure 1) where X represents a variable functional group.

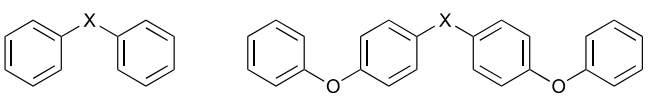


Figure 1 : "Standard-X" and "EXE" dinucleophilic monomers

When selecting possible X groups, both their reactivity and directing effect must be considered; thus, the monomers used in the gel process require electron releasing, *ortho*-/*para*- directing X

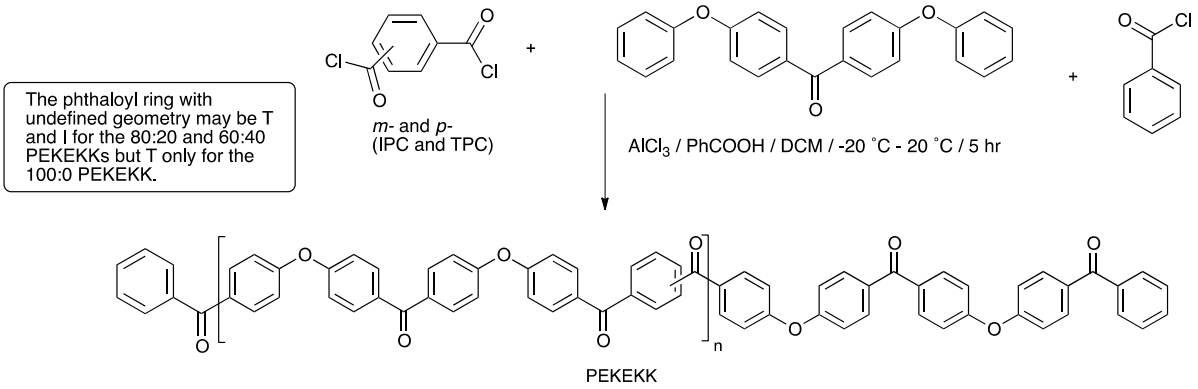
groups to avoid cyclisation reactions and to result in stable all 1,4- substituted linear polymers. These effects are most pronounced for the "standard-X" monomers, but have less effect on the "EXE" monomers due to the greater distance of the X group from the terminal phenyl ring. Suitable groups for the standard-X monomers which produce high molecular weight polymer by the gel process are ether (X = O) and aliphatic (X = CH_2CH_2) groups. Suitable groups for the EXE monomers on the other hand are more varied, and include ether, ketone, sulfone, imide, amide, naphthalene, ester, azo, phenylquinoxaline, benzamidazole, benzoazole, benzothiazole and aliphatic groups.[1,2] The carbonyl functionality in EKE or EKKE (K = ketone) monomers deactivates the terminal ring to a great enough extent to prevent *ortho*- substitution. The development and optimisation of a dispersion process which permits the reliable production of capped poly(ether ketone ketone) (PEKK)[4,5] has opened the design window for the similar production by a dispersion process of particulate polyaryletherketone (PAEK) copolymers and this is important because the aromatic ether ketone units are responsible for providing high performance properties, including temperature resistance and oxidative stability. A key question was whether monomers which were suitable for the gel process would be transferable to the dispersion, and we report here the successful production of a range of PAEK copolymers using a dispersion process, permitting the synthesis of PEKEKK, PEKEKK-imide and PEKEKK-sulfone copolymers, along with some more unusual copolymers. This is important because the incorporation of a wide variety of functional groups into the monomer system allows the design and synthesis of materials to address a wider range of polymer properties and therefore possible applications.

Results and Discussion

We have recently published details of a aluminium chloride catalysed dispersion process which provides access to PAEK polymers and amino-terminated versions,[5,4] and have found that 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 could be synthesised successfully; removal of the aluminium(II) catalyst is achieved by careful acid washing at the end of the reaction. The goal in the work reported here was to generate novel PAEK co-polymers using appropriate monomer mixtures by appropriately adapting this dispersion process.

This dispersion approach was initially extended to PEK-type systems, and the first system which was examined was poly(ether ketone ether ketone ketone) (PEKEKK) (Figure 1, X = C=O). This is an alternative material to PEKK, having a lower T_g of 161 °C (compared to 165 °C for PEKK) and lower T_m of 377 °C (compared to 386 °C) for the fully 1,4- versions.[6] This outcome results in a lower processing temperature combined with a marginally lower use temperature; it is thought that this offers greater thermal stability. Previous studies had demonstrated the feasibility

of the production of PEKEKK by the dispersion process[7] but it was noted that this synthesis was not as reliable as the gel process, most often producing a gel and only occasionally giving a dispersion. Particulate PEKEKK has also been synthesised at low reactor loading without a dispersant.[8] In our case, PEKEKK was easily synthesised by the reaction of bis(4-phenoxyphenyl)methanone (EKE) with terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC), using the standard dispersion process (Scheme 1),[9] and over a terephthaloyl (T): isophthaloyl (I) ratio range; the phthaloyl 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. The effect of added benzoic acid, shown previously to be excellent for the generation of controlled dispersion,[4] and its concentration, on the particle size of the product was also investigated. The structures of the PEKEKK products were confirmed by NMR spectroscopy, and the overlaid spectra for EKE, 100:0 PEKEKK and 90:10 PEKEKK are shown in Figure 1 (ESI). The ^{1}H and ^{13}C spectra are in agreement with the previously reported spectrum of 100:0 PEKEKK obtained by a similar process.[8]



Scheme 1

PEKEKKs were synthesised using 100:0, 90:10 and 80:20 T:I ratios, along with increasing benzoic acid concentration from 4 to 6 stoichiometric equivalents per acid chloride, and all at 3% out-of-balance. All of the product PEKEKKs were produced reliably as dispersions, although the products were obtained as granular material with diameter of approximately 1 mm, which is much larger than PEKK dispersions.[5,4] Both altering the T:I ratio and increasing the concentration of benzoic acid resulted in little effect on the particle size, as shown by visual inspection. Almost identical thermal properties were observed for all of the synthesised PEKEKKs with the same T:I ratios with 4, 5 and 6 benzoic acid equivalents (Table 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. In the case of 90:10 PEKEKK, increasing the I content decreased the thermal points to approximately T_g 163 °C, T_m 363 °C and T_c 305 °C, along with the degree of crystallinity, due to the disruptive geometry of the additional IPC.

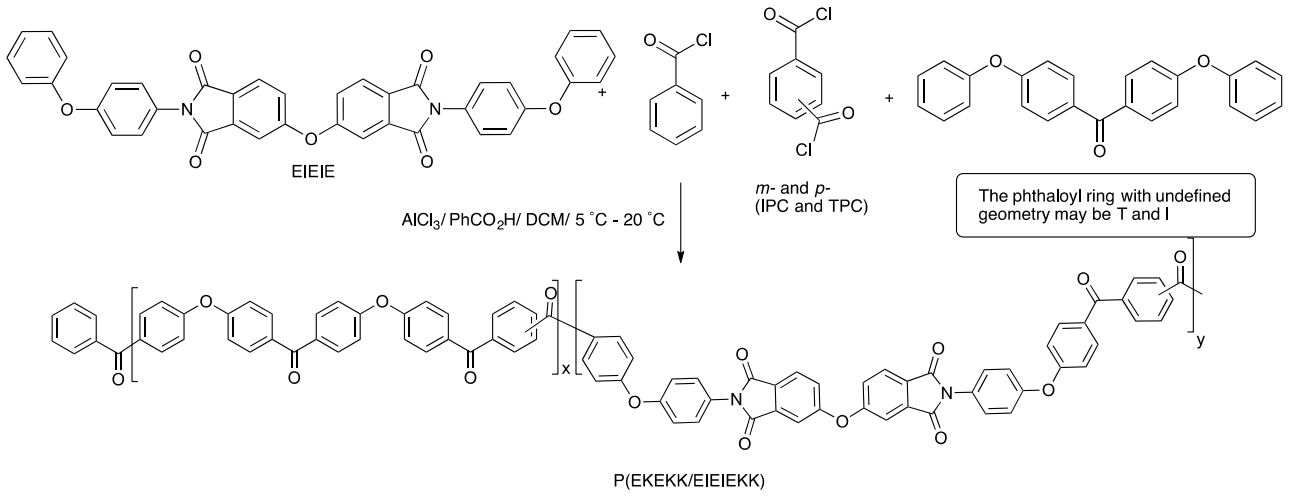
Table 1. Thermal data by DSC for the range of PEKEKKs produced by the dispersion process, with two cycles of heating 90 – 400 °C at 20 °C.min^{-1} and cooling 400 – 90 °C at 10 °C.min^{-1}, initially for amorphous polymers.

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

Preliminary melt rheology data indicated that these PEKEKKs had extremely high melt viscosities, although for the 100:0 PEKEKK, for example, the inherent viscosity (IV) was 0.73 dLg^{-1}. Since all of the polymerisations were carried out at 3% out-of-balance, this can be assumed to be representative of all materials. This outcome was not expected, as PEKEKK has a very similar structure to PEKK, for which at 3% out-of-balance, the same stoichiomeric ratio had a melt viscosity of around 500 – 1000 Pa.[5,4] On increasing the number of benzoic acid equivalents in the polymerisation system from 2 to 4,[7] dispersion PEKEKK can be successfully produced over a range of T:I ratios, for which bulk properties are maintained but the particle size is larger than that of PEKK produced by the same process. This outcome clearly demonstrated that polymerisation had been successfully achieved.

The second system to be examined for group X was an imide function; this has been successfully incorporated into PAEKs by the gel process,[10,1] and the aromatic imide functionality imparts increased T_g due to its rigidity, accompanied by decreased T_m due to its steric bulk and poor packing ability.[11] For the dispersion polymerisation, this was achieved by incorporation of the imide monomer 5,5'-oxybis(2-(4-phenoxyphenyl)isoindoline-1,3-dione) (EIEIE, Scheme 2) into the monomer feed. Such PEKEKK-EIEIE copolymers were synthesised over a range of imide contents and T:I ratios as above, and again the phthaloyl 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. It has been reported that the relative reactivity of monomers used in a co-polymerisation can be assessed by a consideration of δ_C of the reacting carbon; this results from the strong correlation of δC values to the Hammet-Brown constant for the relevant functional group.[12,13] Similar chemical shift values suggest a similar level of electron density and therefore similar reactivity for Friedel-Crafts

polymerization, and provided there is no encumbering steric effect, a random monomer homologation at chain ends can be expected. In the NMR spectrum, the δ_C of the EIEIE *para*-carbon, δ_C 124.41 ppm, is slightly different to the δ_C of the EKE *para*- carbon, δC 124.56, suggesting that a partial block character with several consecutive EIEIE units is likely.



Scheme 2

The structures of these PEKEKK-EIEIE copolymers were confirmed by NMR spectroscopic analysis, and the overlaid spectra for EIEIE, 100:0 PEKEKK, 100:0 PEKEKK-EIEIE 30 and 80:20 PEKEKK-EIEIE 10 are shown in Figure 2 (ESI). On polymerisation, the peaks associated with the terminal sections of EIEIE shift as a result of the change in electron density, and overlap with those of the 100:0 PEKEKK. Inclusion of IPC into the polymer results in the expected new peaks in the spectra. This dispersion process produced particulate PEKEKK-EIEIE copolymers, with the particle size generally smaller than that of PEKEKK polymers produced earlier (Scheme 1). Fine dispersions were formed with increasing EIEIE content from 10, 20 and 30 % and increasing T:I ratio to from 100:0 to 80:20 (Table 2). Altering both the T:I ratio and increasing the concentration of benzoic acid had little effect on the particle size as seen by visual inspection. While with 4 benzoic acid equivalents, the 40 % EIEIE copolymer formed a gel, increasing the number of benzoic acid equivalents to 6 led to a fine dispersion being formed. This suggests that the benzoic acid concentration does have an effect on the morphology of the copolymer product, which becomes more pronounced as the copolymer becomes more amorphous. It is possible that the aluminium benzoate seeding species[4] is a more efficient nucleating agent for the polymerisation of semi-crystalline polymers, whereas a larger quantity of seeding crystals is required to produce an amorphous polymer in particulate form.

Table 2. The combined effect of variable imide content, benzoic acid concentration and T:I ratio on the size of the copolymer dispersion

	Imide content/ %

		0	10	20	30	40
Benzoic acid equivalents	4					
	5					
	6					

		Imide content/ %				
		0	10	20	30	40
T:I ratio	100:0					
	90:10	*				
	80:20					

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

Fine particulate Granular Gel

Table 3. 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

Sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Benzoic acid equivalents	4	4	4	4	5	6	6	4	4	4
EIEIE %	10	20	30	40	30	30	40	10	20	10
T:I ratio	100:0	100:0	100:0	100:0	100:0	100:0	100:0	90:10	90:10	80:20
Heating 1										
T_g/ °C	-	-	-	-	-	-	-	-	-	-
ΔCp*/ Jg^{-1}K^{-1}	-	-	-	-	-	-	-	-	-	-
T_m/ °C	369.2	366.2	350.3	339.5, 369.2	343.8	346.7	335.8	349.1	342.8	330.6
ΔH/ Jg^{-1}	-32.2	-37.71	-24.23	-12.99	-9.147	-13.72	-18.93	-36.02	-19.83	-29.03
Heating 2										
T_g/ °C	178.7	170.7	183.0	190.7	184.0	186.0	179.2	174.1	176.7	168.0
ΔCp*/ Jg^{-1}K^{-1}	0.091	0.027	0.121	0.142	0.212	0.200	0.130	0.098	0.118	0.151
T_m/ °C	367.7	361.0	348.5	360.3	348.0	344.5	327.6	349.6	338.3	326.0
ΔH/ Jg^{-1}	-29.36	-32.58	-14.43	-8.177	-4.400	-5.459	-6.237	-27.04	-19.83	-20.79
Cooling 1								-	-	-
T_g/ °C	-	313.5	180.7	169.1	179.1	179.6	175.7	-	-	-
ΔCp*/ Jg^{-1}K^{-1}	-	44.6	0.070	0.029	0.133	0.111	0.058			
T_c/ °C	310.2	-	-	-	-	-	-			
ΔH/ Jg^{-1}	36.42	-	-	-	-	-	-	275.9	241.6	236.0
								31.77	15.74	26.65
Cooling 2								-	-	-
T_g/ °C	-	310.6	182.8	182.9	180.7	179.5	169.0	-	-	-
ΔCp*/ Jg^{-1}K^{-1}	-	42.45	0.065	0.114	0.141	0.124	0.069			
T_c/ °C	306.4	-	-	-	-	-	-			
ΔH/ Jg^{-1}	36.43	-	-	-	-	-	-	273.5	241.6	235.3
								31.86	15.74	26.47

Almost identical thermal properties were observed for the same PEKEKK-EIEIE copolymers synthesised with 4, 5 and 6 benzoic acid equivalents (Table 3) indicating that the benzoic acid concentration did not have an effect on the bulk polymer properties. Increasing the EIEIE content increased T_g and decreased T_m and the 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 which disrupts crystallisation. These effects may be used in combination to achieve a range of thermal properties from the same polymer system. As with PEKEKK, preliminary melt rheology data indicated that the PEKEKK-EIEIE copolymers had extremely high melt viscosities. In this

case, the copolymers have a different structure to PEKK, so this significant difference in melt viscosity may be expected. Overall, 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. However, the amorphous PEKEKK-EIEIE copolymer containing 40 % imide formed a gel. This outcome is of interest, because while other imide-containing monomers proved to be successful in the gel process, including those with ketone and trifluoromethyl groups (Figure 2),[14,10] these polymers do not exhibit good thermal stability.

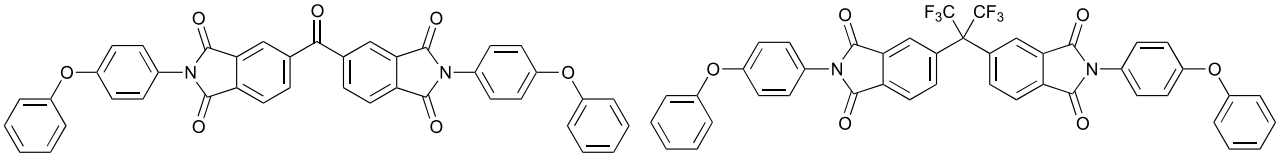
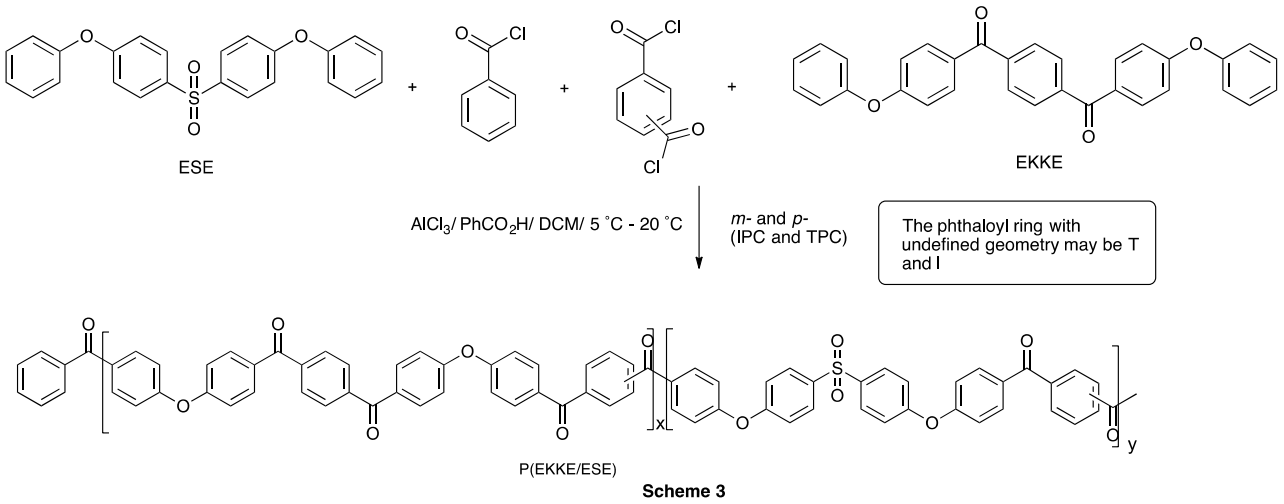


Figure 2

The third system to be examined was sulfone functionality (X = SO_2), which is commonly incorporated into PAEKs; this usually 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 greater steric bulk and particularly poor packing capability. PAEK-sulfone copolymers can be made easily from the gel process either by the incorporation of 1,1'-sulfonylbis(4-phenoxybenzene) (ESE)[1] or by a modification of the gel process[15,16] which polymerises ESE with diacid chlorides, using N-methylpyrrolidone as the dispersant in 1,2-dichloroethane. By analogy to the earlier cases, 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, but all polymerisations were carried out with 4 benzoic acid equivalents (Scheme 3). Again, the reactivity ratio reasoning used for the formation of PEKKs can be applied to the polymerisation of PEKEKK-ESE copolymers, and it was 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 imply partial block character on the structure.



Scheme 3

The structure of the PEKEKK-ESE product was confirmed by NMR spectroscopy, and the overlaid spectra for ESE, 100:0 PEKK-ESE 40 and 70:30 PEKK-ESE 30 are shown in Figure 3 (ESI). On polymerisation, the peaks associated with the terminal sections of ESE shift as expected from the change in electron density, and incorporation of IPC into the polymer results in the corresponding new peaks in the spectrum.

Fine particulate PEKK-ESE copolymers, with varying ESE and T:I ratios (Table 4) were produced which were 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. Altering the degree of ESE incorporation affected the thermal properties of the copolymers (Table 4 and Figures 3 and 4). Increasing the % ESE decreased the T_m, T_c and degree of crystallinity, but increased the T_g, for the reasons discussed above. Increasing the % I decreased T_g, T_m, T_c and degree of crystallinity due to the geometry of the IPC.

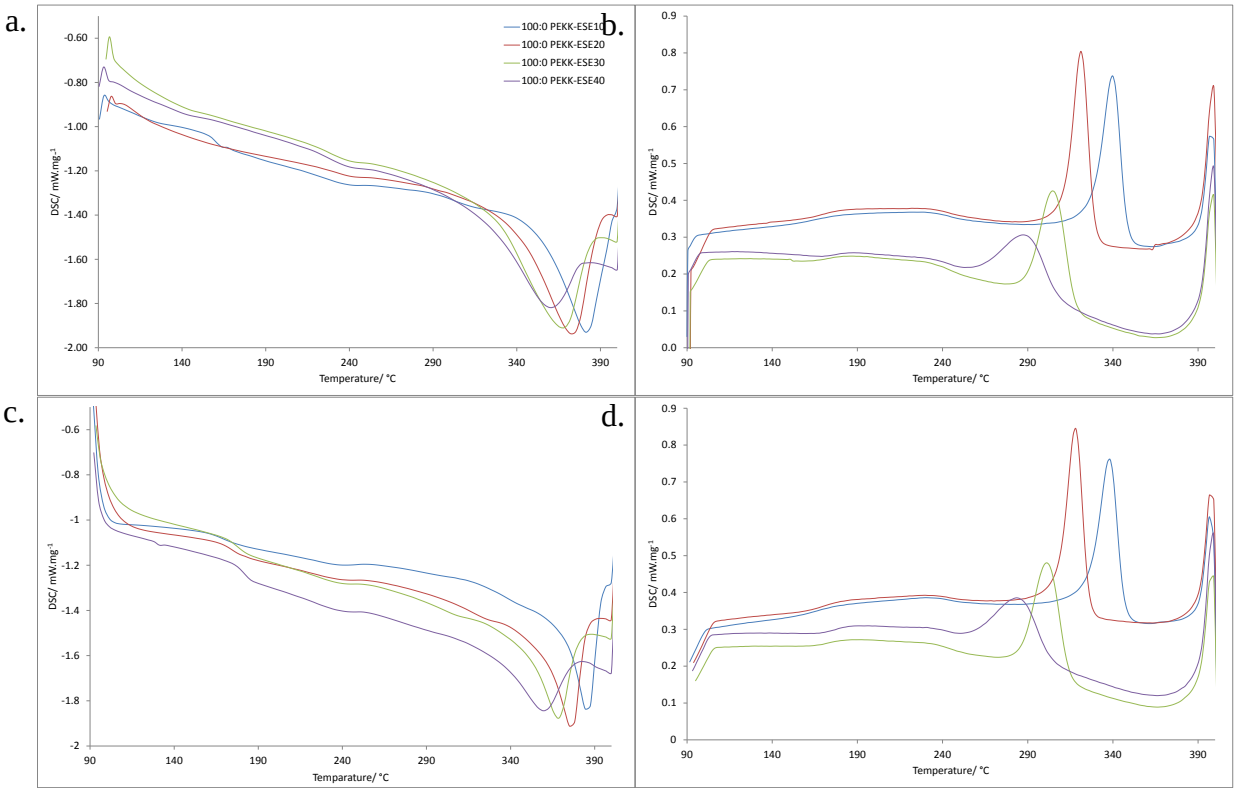


Figure 3: Stacked DSC traces for PEKK-ESE copolymers with increasing ESE content a. heating 90 – 400 °C at 20 °C.min^{-1}, b. cooling 400 – 90 °C at 10 °C.min^{-1}, c. heating 90 – 400 °C at 20 °C.min^{-1}, d. cooling 400 – 90 °C at 10 °C.min^{-1}

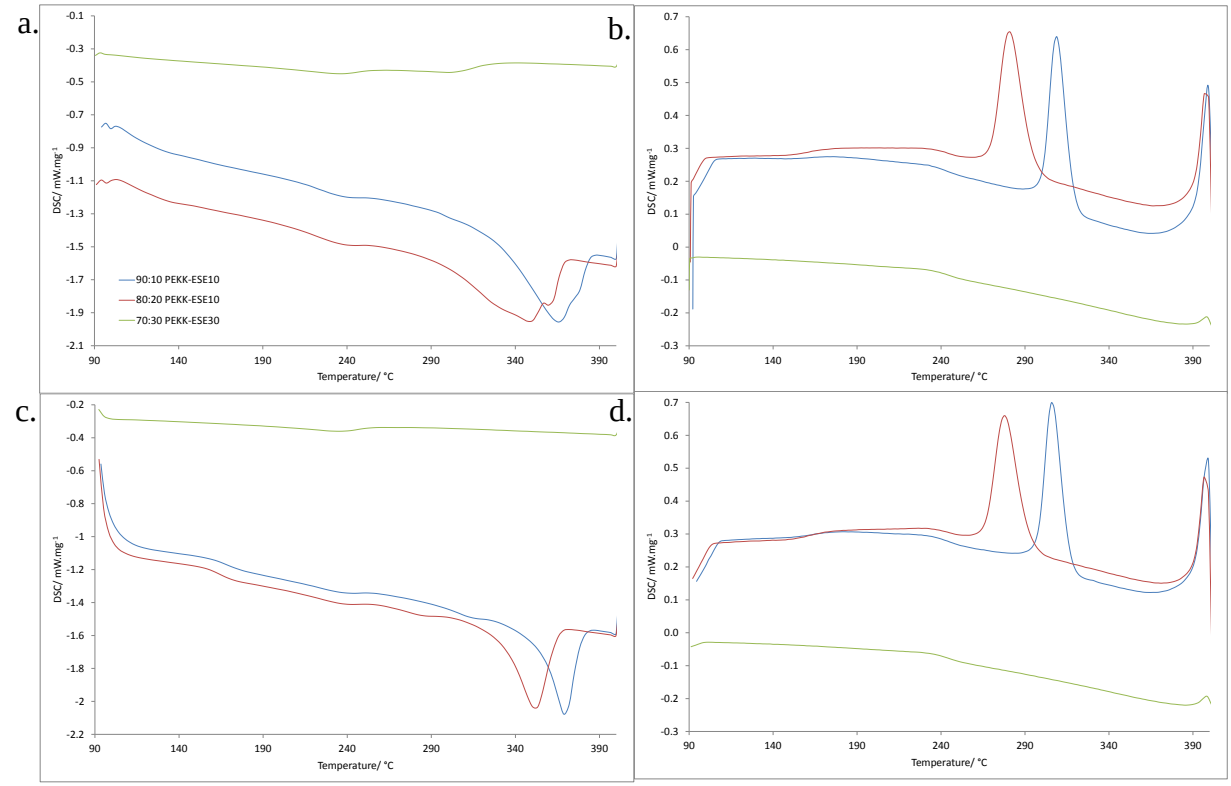


Figure 4: Stacked DSC traces PEKK-ESE20 copolymers with increasing T:I ratio a. heating 90 – 400 °C at 20 °C.min^{-1}, b. cooling 400 – 90 °C at 10 °C.min^{-1}, c. heating 90 – 400 °C at 20 °C.min^{-1}, d. cooling 400 – 90 °C at 10 °C.min^{-1}

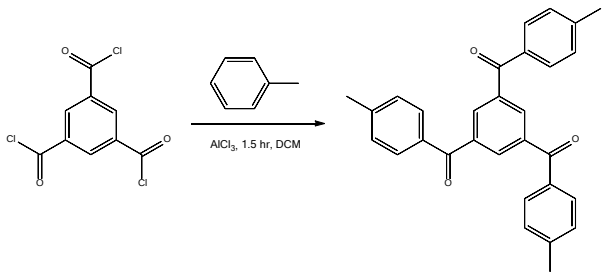
Table 4: Thermal data from DSC for the range of PEKEKK-ESE copolymers produced by the dispersion process, with two cycles of heating 90 – 400 °C at 20 °C.min^{-1} and cooling 400 – 90 °C at 10 °C.min^{-1}

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

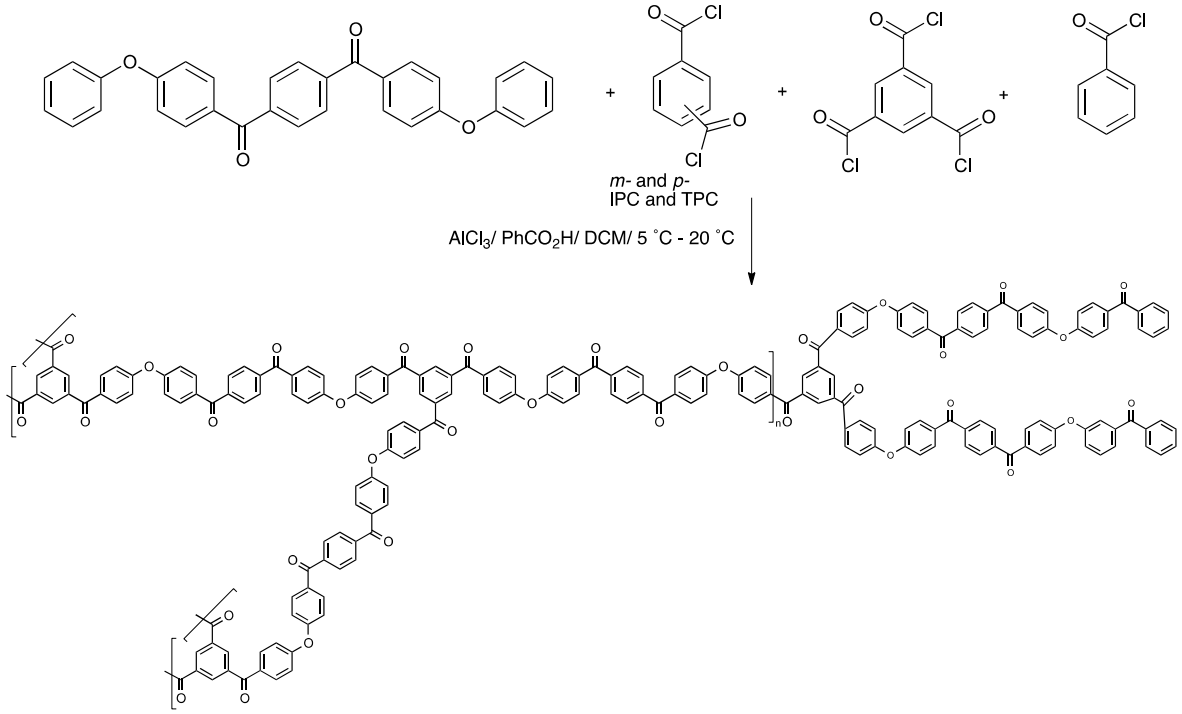
Preliminary rheological analysis demonstrated a wide range of melt viscosities of the PEKK-ESE copolymers, and the IV measurements for 100:0 PEKK-ESE10 and 100:0 PEKK-ESE40 were 0.62 and 0.90 dL.g^{-1} respectively. Overall, particulate PEKEKK-ESE copolymers were produced over a range of sulfone contents and T:I ratios. Bulk properties were maintained and the particle size was comparable to that of PEKK for all of the samples.

To achieve a branched PEKK structure, the trifunctional monomer 1,3,5-benzenetricarbonyl chloride (TRI) was introduced into the monomer feed; the use of this monomer had been reported earlier in the one-pot synthesis of branched PAEKs, by the electrophilic polycondensation of DPE and acid chloride co-monomers.[17] To confirm its reactivity in the present 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 solvent (Scheme 4); the product was fully characterised, and since it was readily formed, it was assumed that TRI would be compatible with the polymerisation system.[18]



Scheme 4. 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 (Scheme 5).



Scheme 5

The incorporation of TRI into the PEKK structure was confirmed by NMR spectroscopy, and the overlaid spectra for the 10% TRI PEKK and 80:20 PEKK are shown in Figure 4 (ESI). Most notable is the additional peak in the carbonyl region of the ^{13}C NMR spectrum, around 198 ppm, which can be attributed to the presence of the TRI unit.

The incorporation of a greater % of TRI decreased the IV of the resulting PEKKs (Table 5) which most likely results from the main chain branching, rather than a reduction of molecular weight.[19] Visually, the fine particulate PEKKs are similar in particle size and are comparable to the particle size of PEKK dispersions.

Table 5: Viscosity and thermal properties of linear PEKK and 1%, 5% and 10% branched PEKK by DSC using a 20 °C.min^{-1} heating rate and a 10 °C.min^{-1} cooling rate, for two cycles.

		Linear	**1% Tri**	**5% Tri**	**10% Tri**
IV/ dL.g^{-1}		1.38	1.10	0.87	0.72
Heating 1	T_m/ °C	337.7	340.5	341.7	344.3
	ΔH/ J.g^{-1}	-50.01	-47.02	-52.76	-50.19
Cooling 1	T_c/ °C	267.3	265.5	273.7	274.9
	ΔH/ J.g^{-1}	29.5	29.58	35.66	36.28
Heating 2	T_g/ °C	163.6	155.3	153.7	151.3
	ΔCp^*/ J.g^{-1}.K^{-1}	0.123	0.102	0.112	0.101
	T_m/ °C	344.7	344.4	347.2	347.3
	ΔH/ J.g^{-1}	-24.61	-27.54	-31.52	-30.76
Cooling 2	T_c/ °C	266.7	264.2	275.0	276.4
	ΔH/ J.g^{-1}	29.45	29.4	35.84	35.93

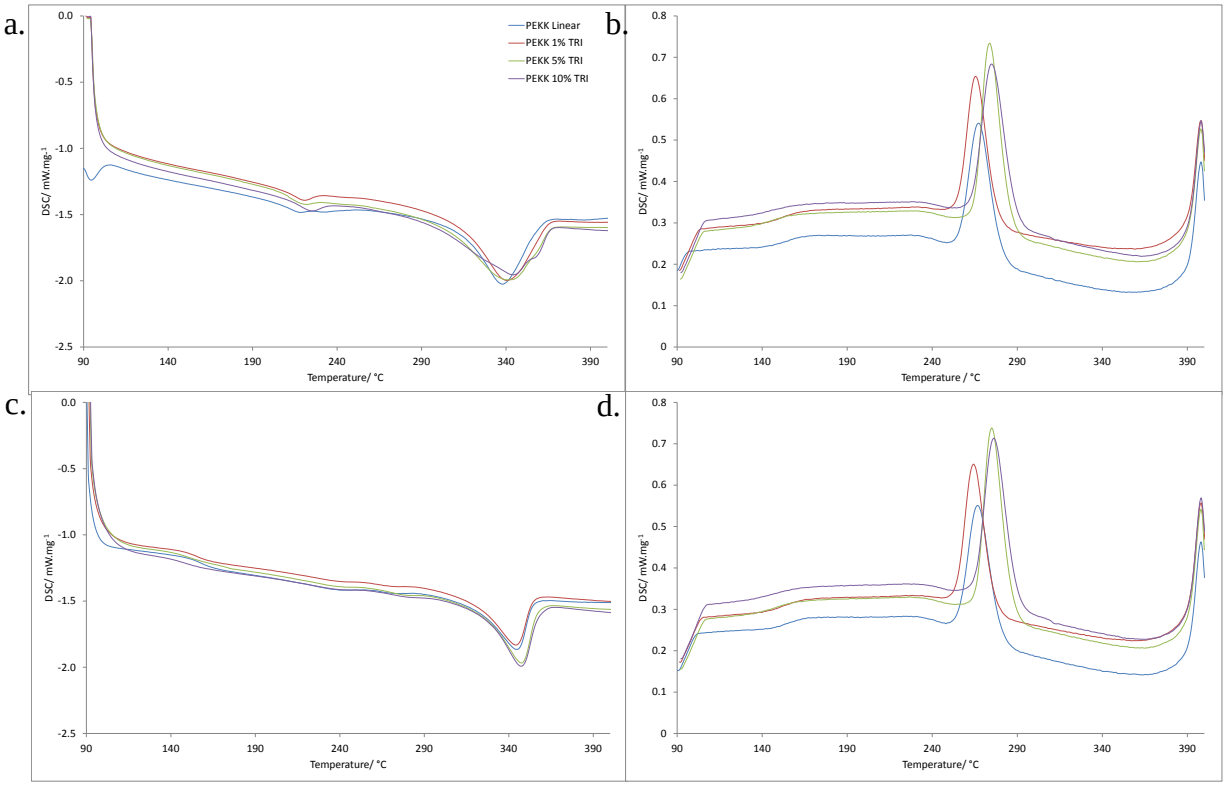
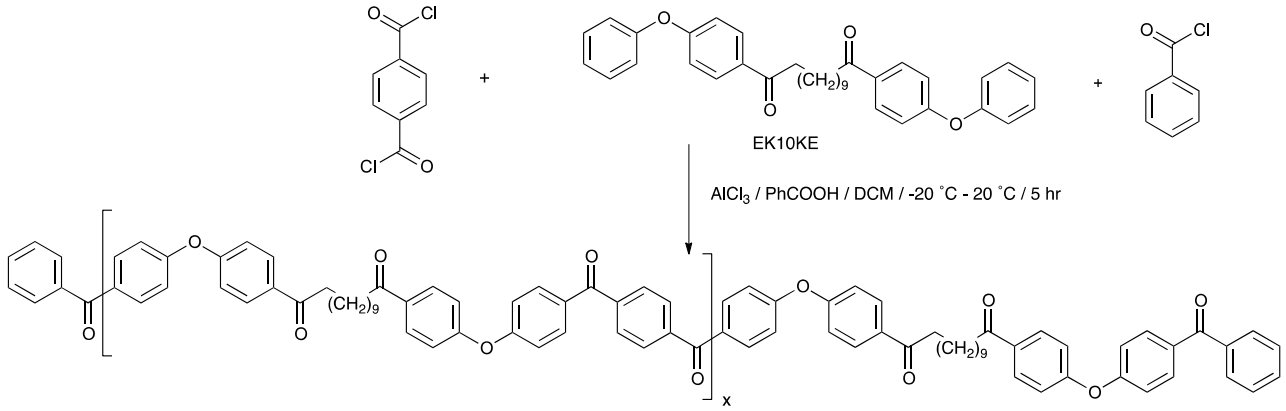


Figure 5: Stacked DSC traces for the linear PEKK and 1%, 5% and 10% TRI PEKKs, a. heating 90 – 400 °C at 20 °C.min^{-1}, b. cooling 400 – 90 °C at 10 °C.min^{-1}, c. heating 90 – 400 °C at 20 °C.min^{-1}, d. cooling 400 – 90 °C at 10 °C.min^{-1}

Thermal data is listed in Table 5, with stacked plots of DSC traces in Figure 5. A marginally decreased T_g was observed with increased % TRI content, while an increase in T_m and T_c is observed on increasing the % TRI content. Overall, the T_m and T_c values on the 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. Fine particulate, branched PEKKs were produced over a range TRI contents, and their particle size was visually comparable to those of unbranched PEKK. Unlike unbranched PEKKs which completely dissolve in concentrated sulphuric acid, branched PAEKs did not dissolve fully in concentrated sulfuric acid.

It was of interest to extend this approach to aliphatic linking systems. Aliphatic-aromatic PAEKs are not as common as the wholly aromatic versions, with the first aromatic-aliphatic PEK polymer being reported in 1962, synthesised by the electrophilic reaction of diphenyl ether and decanedioyl dichloride ($ClCO(CH_2)_8COCl$)[20] which had a melting point of 184 – 185 °C. In 1989, a nucleophilic route using silylated alkylenebiphenol and aromatic difluoroketones produced aromatic aliphatic PEKs[21]. This study reported the phase separation of the aliphatic and aromatic regions to form a well-defined supermolecular structure, and these polymers exhibited double melting peaks

and crystallisation peaks, attributable 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 were also reported by the gel process.[1] 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 TPC[22] (Scheme 6) 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 was confirmed by NMR spectroscopy (Figure 5 (ESI)); 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 ^{13}C NMR spectrum in the 25 – 40 ppm region.



Scheme 6

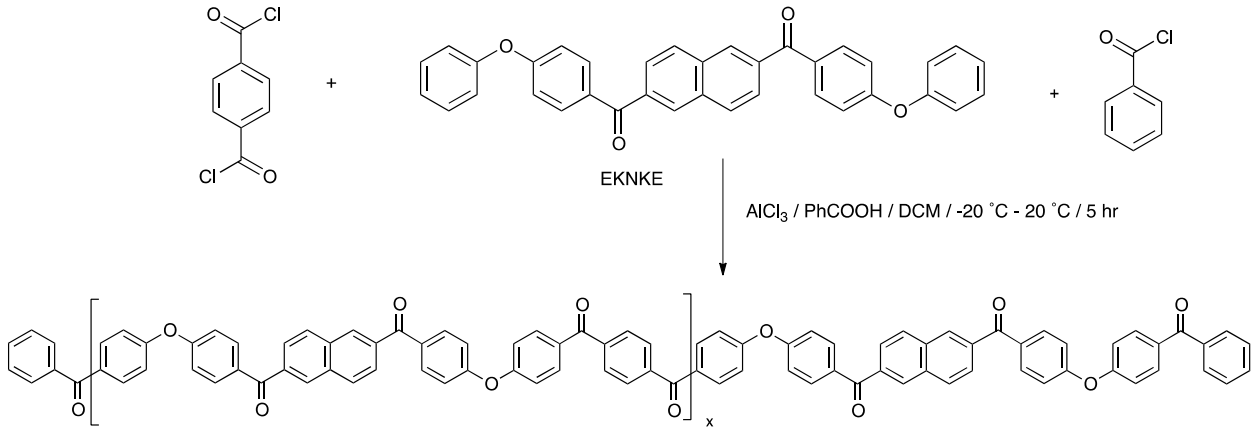
Table 6: Thermal data from DSC for the PEK10KE polymer produced by the dispersion process, with two cycles of heating 90 – 300 °C at 20 °C.min^{-1} and cooling 300 – 90 °C at 10 °C.min^{-1}

Heating 1	T_m/ °C	275.9
	ΔH/ J.g^{-1}	-48.93
Cooling 1	T_c/ °C	232.5
	ΔH/ J.g^{-1}	42.77
Heating 2	T_g/ °C	-
	ΔCp^*/ J.g^{-1}.K^{-1}	-
	T_m/ °C	274.7
	ΔH/ J.g^{-1}	-35.5
Cooling 2	T_c/ °C	228.6
	ΔH/ J.g^{-1}	38.92

DSC analysis (Table 6) confirmed that the aliphatic region of the EK10KE acts to decrease the T_g compared to PEKK due to the 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 °C.

This material may find application in selective laser sintering (SLS) since its thermal properties are very similar to that of nylon-12, which is commonly used.

The synthesis of naphthalene containing PAEKs have been reported, including by a precipitation method,[23] and a gel process,[24] so modification of the aromatic monomer alone was attempted with the dispersion process. A dispersion polymerisation was carried out with a monomer feed containing naphthalene-2,6-diylbis((4-phenoxyphenyl)methanone) (EKNKE) and TPC (Scheme 7), and this produced particulate polymer, visually comparable in size to PEKK dispersions, with 0.99 $dL.g^{-1}$. The polymer structure was confirmed by NMR spectroscopy (Figure 6, ESI) and was in agreement with reported data.[23]



Scheme 7

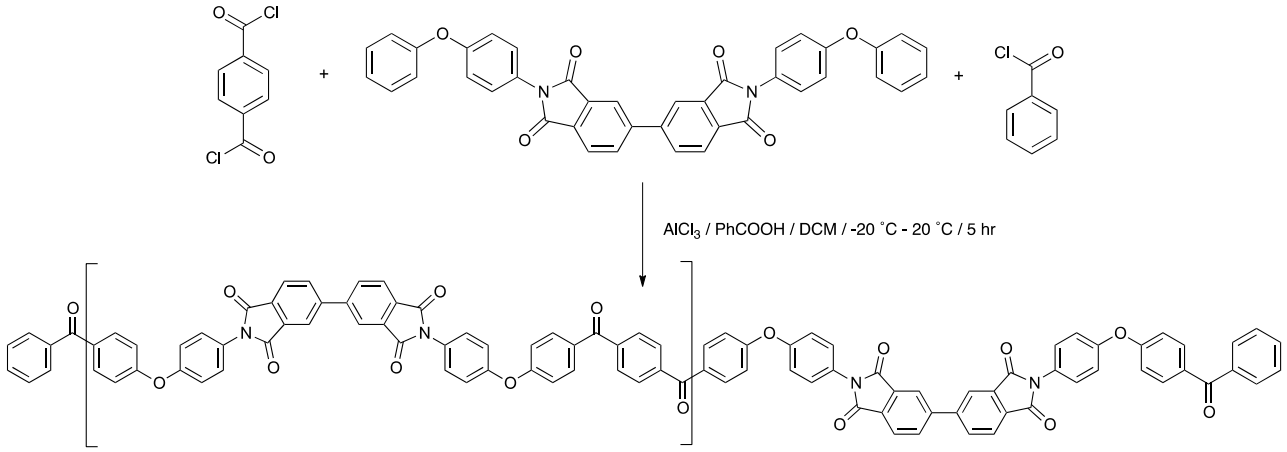
Table 7: Thermal data by DSC for the polymer formed from EKNKE and TPC for two cycles of heating 90 – 400 °C at 20 $C.min^{-1}$ and cooling 400 – 90 °Cat 10 °$C.min^{-1}$

Heating 1	T_m/ °C	390.8, 339.4
	ΔH/ $J.g^{-1}$	-18.59 -3.239
Cooling 1	T_c/ °C	306.6
	ΔH/ $J.g^{-1}$	19.16
Heating 2	T_g/ °C	186.0
	ΔCp^*/ $J.g^{-1}.K^{-1}$	0.113
	T_m/ °C	371.0
	ΔH/ $J.g^{-1}$	-23.29
Cooling 2	T_c/ °C	297.5
	ΔH/ $J.g^{-1}$	20.62

DSC analysis (Table 7) 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. The melt viscosity of the PEKNKE polymer was too high to carry out rheological analysis.

The incorporation of imide monomers into the polymerisation system was extended to include the imide monomer 2,2'-bis(4-phenoxyphenyl)-[5,5'-biisoindoline]-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. This EI-IE monomer has been successfully used in the gel process.



Scheme 8

The polymerisation was successful but did not produce product with the required morphology. The 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 (Scheme 8). The polymer was produced in the form of a yellow gel, rather than a dispersion, which required blending. 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. However, the polymer structure was broadly confirmed by NMR spectroscopy (Figure 7, ESI). IE/TPC polymerisation was carried out at a greater (5%) stoichiometric 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.

Conclusion

It has been shown that a range of particulate PAEK copolymers incorporating ether-imide, sulfone, naphthalene, and aliphatic functionalities may be successfully produced by the dispersion process, provided that the reaction parameters are optimised. The incorporation of PEKEKK and branching agents has also been successful. The selection of copolymer variants accessible by the dispersion process has been increased. The dispersion process now offers a range of particulate PAEK

copolymers[27] with easily tailored properties. An advantage over the gel process is that the dispersion process is procedurally simpler than the gel process, and this 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, suitable for a range of new applications.[11,25]

Acknowledgements

KJS gratefully acknowledges the award of an 1851 Royal Commission Industrial Fellowship.

Experimental

Analytical techniques

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 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. 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). ^{1}H 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. ^{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

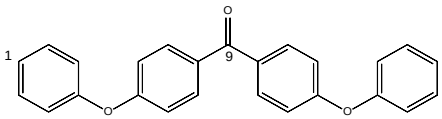
parts per million (ppm) and are referenced to the residual protonated solvent peak. Assignment was aided by the use of DEPT editing and edited HSQC, performed on either AVN400 or DRX500 spectrometers.

Reagents and solvents

1,4-Bis(4-phenoxybenzoyl)benzene) (polymerisation grade) (EKKE) may be obtained by the literature procedure.[26] Terephthaloyl chloride (99+ %) (TPC), isophthaloyl chloride (98 %) (IPC), benzoic acid (99 %, extra pure), aluminium chloride (99 %, extra pure, anhydrous) and benzoyl chloride (98+ %) were obtained from Acros Organics. Dichloromethane (DCM) (99.5 %) was obtained from APC Pure. All reagents and solvents were used as received.

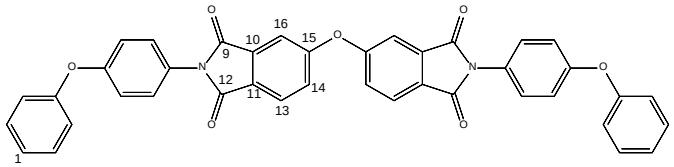
Monomer synthesis

Bis(4-phenoxyphenyl)methanone (EKE)



White solid; mp 148.4 °C (2 °C/min) (lit. [27] 142 – 145 °C); purity 99.85 mol% (DSC); ν_{max}/cm^{-1} 3062 (CH), 3039 (CH), 2493-1685 (Ar CH), 1643 (CO), 1585 (ring stretch), 1487 (ring stretch), 1265 (COC); δ_H (400 MHz, $CDCl_3$ (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, $CDCl_3$ (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, $CDCl_3$) 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, $CDCl_3$) 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^+) $C_{25}H_{18}O_3^+$ ($[M]^+$) requires 366.1256 found 366.1260.

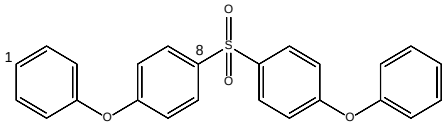
5,5'-oxybis(2-(4-phenoxyphenyl)isoindoline-1,3-dione) (EIEIE)



White solid; mp 293.4 °C (2°C/min) (lit.[1] 292.2 – 293.8 °C); purity 99.35 mol% (DSC); ν_{max}/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, $CDCl_3$ (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,

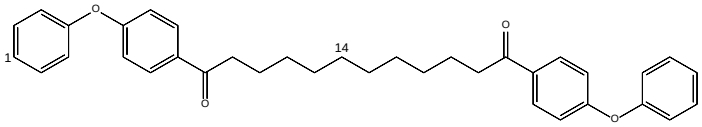
C(2)*H*), 7.58 (2H, dd, *J* 8.07, 2.20, C(14)*H*), 7.65 (2H, d, *J* 2.20, C(16)*H*), 8.10 (2H, d, *J* 8.31, C(13)*H*); δ_C (100 MHz, $CDCl_3$ (TFA)) 114.65 (*C*(16)H), 118.79 (*C*(6)H), 119.85 (*C*(3)H), 124.41 (*C*(1)H), 124.75 (*C*(11)), 125.53 (*C*(14)H), 126.75 (*C*(8)), 126.95 (*C*(13)H), 128.42 (*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^+) $C_{40}H_{24}N_2O_7^+$ ($[M]^+$) requires 644.1583 found 644.1472.

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



White solid; mp 143.6 °C (2°C/min) (lit.[1] 142.4 – 143.5 °C); purity 99.89 mol% (DSC); ν_{max}/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, $CDCl_3$ (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, $CDCl_3$ (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^+) $C_{24}H_{18}O_4S^+$ ($[M]^+$) requires 402.0926 found 402.0930.

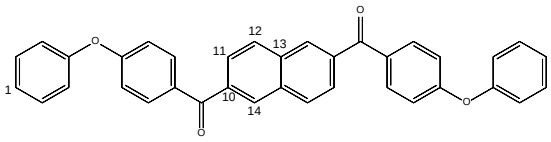
1,12-Bis(4-phenoxyphenyl)dodecane-1,12-dione (EK10KE)



White solid; mp 105.8 °C (2°C/min); purity 99.51 mol% (DSC); ν_{max}/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))

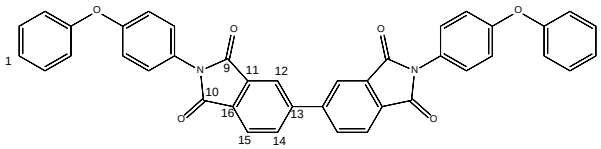
24.54 (*C*(11)H), 29.45 (*C*(12/13/14)H), 38.44 (*C*(10)), 117.34 (*C*(6)H), 120.13 (*C*(3)), 124.55 (*C*(1)H), 130.04 (*C*(2)H), 130.33 (*C*(7)H), 131.83 (*C*(8)), 155.59 (*C*(4)), 161.77 (*C*(5)), 199.22 (*C*(9)); HRMS (TOF EI$^+$) $C_{36}H_{38}O_4^+$ ([M]$^+$) requires 534.2770 found 534.2784.

Naphthalene-2,6-diylbis((4-phenoxyphenyl)methanone) (EKNKE) [28]



White solid; mp 218.4 °C (2 °C/min); purity 99.17 mol% (DSC); ν_{max}/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$^+$) $C_{36}H_{24}O_4^+$ ([M]$^+$) requires 520.1675 found 520.1677.

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



White solid; mp 273.6 °C (2°C/min) (lit.[1] 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)); ν_{max}/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$^+$) $C_{40}H_{24}N_2O_6^+$ ([M]$^+$) requires 628.1634 found 628.1625.

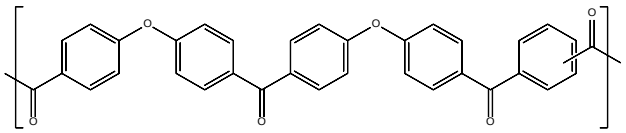
Yellow needles; mp 273.7 °C (2°C/min) (lit.[1] 272.8 – 273.9 °C); purity 99.79 mol% (DSC); δ_H (400 MHz, $CDCl_3$ (TFA)) 7.13 (4H, d, *J* 7.58, C(3)*H*), 7.16 (4H, d, *J* 9.05, C(6)*H*), 7.23 (2H, t, *J* 7.46, C(1)*H*), 7.37 (4H, d, *J* 9.05, C(7)*H*), 7.44 (4H, t, *J* 8.60, C(2)*H*), 8.17-8.20 (4H, m, C(14)*H*, C(15)*H*), 8.34 (2H, s, C(12)*H*); δ_C (100 MHz, $CDCl_3$ (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^+) $C_{40}H_{24}N_2O_6^+$ ($[M]^+$) requires 628.1634 found 628.1635.

General polymer synthesis

A representative PEKK polymerisation with 80:20 T:I ratio is as follows. To a one litre reaction flask equipped with a mechanical stirrer, having been purged with dry nitrogen, was added aluminium chloride (105.18 g, 788.81 mmol) along with dichloromethane (250 ml). Stirring was maintained at 200 rpm. Having cooled the slurry to -20 °C, benzoic acid (39.304 g, 321.61 mmol) was slowly added so as not to raise the temperature of the slurry above -10°C and to minimise any splashing up the walls of the reactor. After cooling back to -20 °C, the combined isophthaloyl chloride (9.9448 g, 48.984 mmol) and terephthaloyl chloride (6.3780 g, 31.416 mmol) was added to the slurry along with a further 100 ml of dichloromethane. Also at -20 °C, l,4-bis(4-phenoxybenzoyl)benzene (EKKE) (39.000 g, 82.887 mmol) was added with a further 100 ml of dichloromethane, which was accompanied by a colour change from yellow to orange. 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. During this heating, the benzoyl chloride (0.73690 g, 5.2422 mmol), diluted in the remaining DCM, was added. The formation of particles was observed after approximately 15 minutes. The vessel was stirred at a constant rate of 500 rpm and maintained at 20 °C for four hours. The orange complexed polymer was filtered and was added to iced water in portions with stirring, causing it to decomplex and turn white. 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. Having transferred the polymer to a suitable vessel, the vessel was heated and the dichloromethane distilled off. The polymer was subsequently subjected to a workup procedure of sequential washings, consisting of hot water, aqueous acid and base stages. Polymers were dried at 80 °C for 48 hours, then at 200 °C (up to 250 ºC) under vacuum overnight, and then characterised as indicated in the main text.

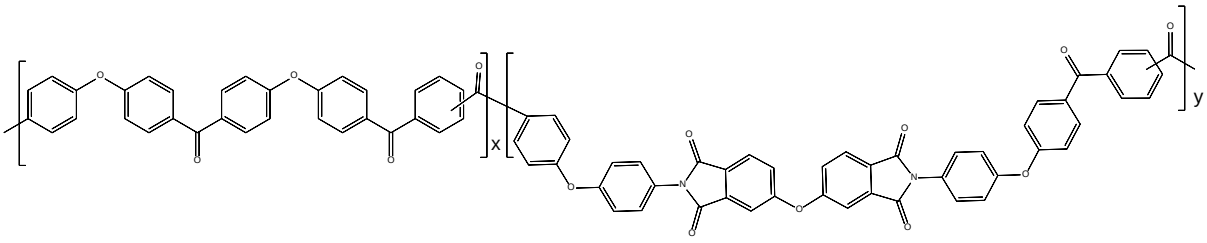
PEKEKK



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/g	36.0005	35.9998	35.9999	36.9995	36.9999
TPC/g	19.3477	19.3476	19.3475	15.8467	15.8468
IPC/g	-	-	-	4.0387	4.0382
Benzoic acid/g	46.5862	58.2328	69.8790	47.8810	59.8505
$AlCl_3$/g	108.66	123.56	142.09	128.14	143.73
Benzoyl chloride/g	0.8468	0.8366	0.8356	0.8667	0.8657
DCM/mL	500	500	500	500	500
Polymer mass/g	42.64	42.76	44.37	46.97	43.32
Polymer morphology	Granular	Granular	Granular	Fine particulate	Granular

Imide copolymers, P(EKE-EIEIE)



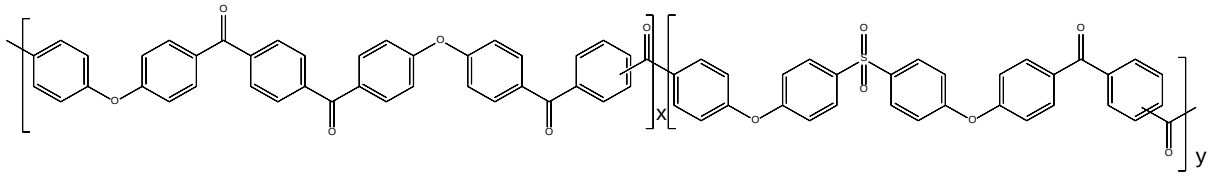
All of the copolymers were synthesised in a one litre reactor according to the general polymerisation method, using the monomer feeds as listed below. Each were synthesised with a 10% reactor loading, at 3% out of balance.

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/g	17.9996	31.0001	25.9998	21.9996	21.9995
EIEIE/g	21.1112	6.0599	11.4354	16.5872	16.5877

TPC/g	16.1232	18.5117	17.4667	16.8905	16.8905
IPC/g	-	-	-	-	-
Benzoic acid/g	38.8222	44.5751	42.0584	40.6710	50.8375
$AlCl_3$/g	115.41	123.26	119.74	116.77	129.54
Benzoyl chloride/g	0.6985	0.8014	0.7825	0.7724	0.7347
DCM	500	500	500	500	500
Polymer mass/g	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/g	21.9997	17.9998	31.4995	26.5002	31.5005
EIEIE/g	16.5872	21.1117	6.1578	11.5002	18.8109
TPC/g	16.8905	16.1229	15.1843	14.5547	11.5582
IPC/g	-	-	3.6263	3.2482	7.2727
Benzoic acid/g	61.0060	58.2327	45.2923	42.8657	45.2919
$AlCl_3$/g	143.41	139.28	124.86	119.54	123.20
Benzoyl chloride/g	0.7988	0.7256	0.8152	0.7676	0.8041
DCM/mL	500	500	500	500	500
Polymer mass/g	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/g	35.5002	31.9996	28.4998	24.5002	34.4998
ESE/g	3.0362	6.8432	10.4480	13.9705	3.3742
TPC/g	16.3433	16.7419	17.0403	17.0899	13.3267
IPC/g	0	0	0	0	3.1822
Benzoic acid/g	39.3513	40.3104	41.0300	41.1504	39.7507
$AlCl_3$/g	104.04	107.28	110.46	110.44	107.67
Benzoyl chloride/g	0.6984	0.7161	0.7315	0.7329	0.7081
DCM/mL	500	500	500	500	500
Polymer mass/g	40.48	39.15	40.88	41.47	39.02
Polymer morphology	Fine particulate	Fine particulate	Fine particulate	Fine particulate	Fine particulate

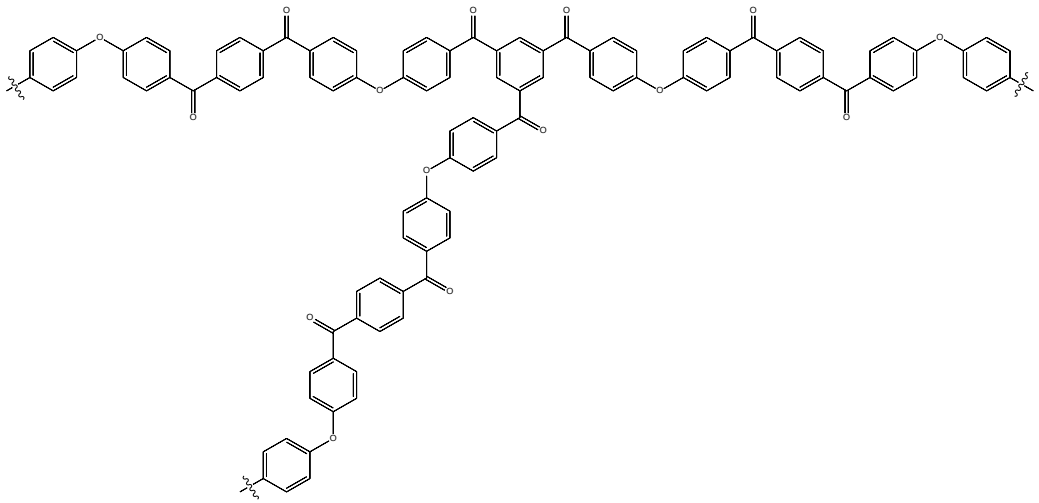
Sulphone %	10	30
T:I	80:20	70:30
Benzoic acid equivalents	4	4
EKKE/g	35.4997	28.4999
ESE/g	3.3737	10.4479
TPC/g	10.1435	8.2391
IPC/g	6.3652	8.8017
Benzoic acid/g	39.7513	41.0308
$AlCl_3$/g	105.63	108.96
Benzoyl chloride/g	0.7080	0.7304
DCM	500	500
Polymer mass/g	39.49	43.25
Polymer morphology	Fine particulate	Fine particulate

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); ν_{max}/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, C*H*$_3$), 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 (*C*H_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^+) $C_{30}H_{24}O_3^+$ ($[M]^+$) requires 432.1725 found 432.1727.

Branched PEKKs

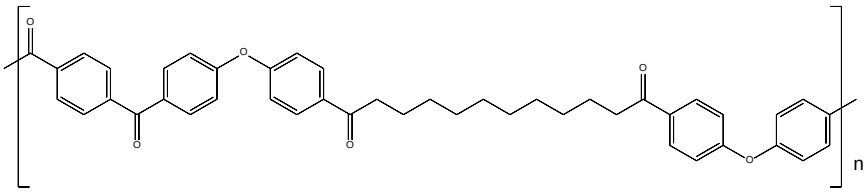


The 80:20 PEKK copolymers were synthesised on a one litre scale according to the general polymerisation method, using the monomer feed as listed below. The polymers were synthesised with a 10% reactor loading, at 5% out of balance. No benzoyl chloride was used.

% TRI	**0%**	**1%**	**5%**	**10%**
EKKE/g	8.0002	8.0006	8.0008	8.0005

TPC/g	1.9345	1.9174	1.8080	1.6774
IPC/g	1.3540	1.3420	1.3169	1.2836
TRI/g	-	0.0293	0.1439	0.2875
Benzoic acid/g	7.9256	7.8948	7.9247	7.9296
$AlCl_3$/g	23.37	22.84	22.58	22.24
DCM/mL	125	125	125	125
Polymer mass/g	7.93	8.00	7.23	7.34
Polymer morphology	Fine particulate	Fine particulate	Fine particulate	Fine particulate

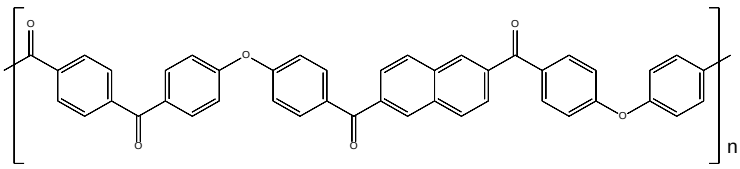
Aliphatic copolymer P(EK10KE-TPC)



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/g	40.0001
TPC/g	14.7317
Benzoic acid/g	35.4725
$AlCl_3$/g	94.26
Benzoyl chloride/g	0.6312
DCM/mL	500
Polymer Mass/g	48.87
Polymer morphology	Fine particulate, irregular

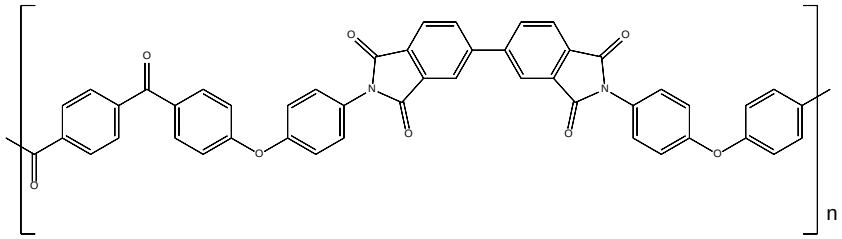
Naphthalene copolymer P(EKNKE-TPC)



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/g	40.0003
TPC/g	15.1312
Benzoic acid /g	36.4348
$AlCl_3$/g	96.71
Benzoyl chloride /g	0.6471
DCM/mL	500
Polymer mass/g	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/g	41.5001
TPC/g	12.7321
Benzoic acid/g	102.86
$AlCl_3$/g	30.6578
Benzoyl chloride/g	0.9288
DCM/mL	500
Polymer mass/g	26.32
Polymer morphology	Gel (yellow)

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