

Type of manuscript

Article

Manuscript title

Synthesis of statistical PET/PEN random block copolymers and their crystallizability in the bulk and at the surface.

Abstract

A series of PET/PEN copolyesters were synthesized by molten transesterification. The degree of randomness and the sequence length of the copolymers were determined by ^1H NMR spectroscopy, and the changes in the bulk glass transition temperature (T_{gB}), bulk crystallization temperature (T_{cB}), and bulk melting temperature (T_{mB}) were observed by DSC. A clear relationship was obtained between the observed enthalpy of melting (ΔH_m) and degree of randomness (B), and T_{mB} was suppressed for the mid-compositions. As with their homopolymer counterparts, there was significant depression in crystallization temperature at the surface (T_{cS}) of the random/block copolymers compared with the bulk, and so surface-localised crystallization could be induced in spin-coated thick films (thickness ranging from ca. 400 to 700 nm) by annealing at a temperature in which the surface region is mobile, but the bulk is not. The formation of these clear surface crystals allows the morphology to be directly imaged by AFM, and we observed that the crystallizability and the lamellar morphology of the surface crystals deviated from those of the original homopolymers, depending on the mixing ratio of PET/PEN and degree of randomness.

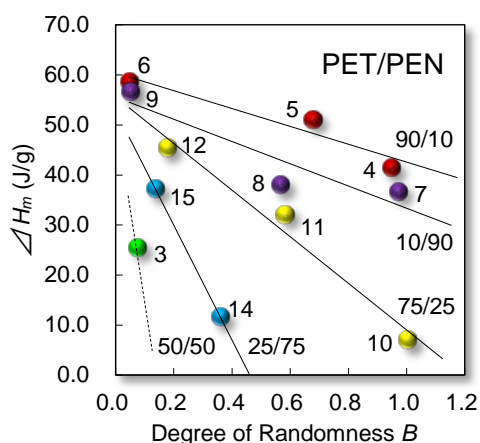
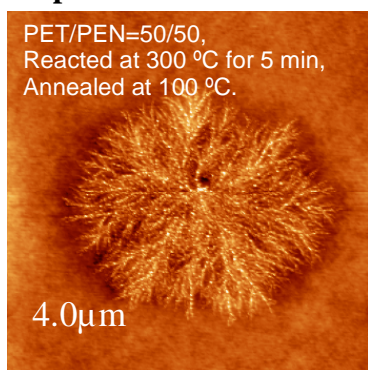
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1. Introduction

Crystallization of polymers is important in controlling structural and functional characteristics, and in random copolymers it is often suppressed to a greater or lesser degree as the different monomer units cannot pack randomly into a regular crystal structure. In random copolymers, crystallization depends either on rejection of one component into the interlamellar amorphous regions, or incorporation of both components within the crystal structure, for example by the matching of crystallizable sites on the molecular chains. Where only one of the monomers is crystallizable, such as in a study of poly(butylene terephthalate) (PBT) / poly(tetramethylene ether glycol), the other component may be rejected from crystals for small (in this case up to 17%) mol fraction, after which crystallization is suppressed [1]. Other copolymer systems have shown crystallization by rejection of one component from the crystalline phase e.g. [2, 3]. However, in some cases of two, similar, crystallizing monomers, such as poly(ethylene terephthalate) (PET) / poly(ethylene 2,6-naphthalate) (PEN) copolymers, crystallization involving both monomers may occur. On the basis of diffraction studies, Windle *et al.* [4, 5] concluded that random/blocky copolyesters were able to crystallize under strained conditions by lateral matching of similar monomer sequences. [6], An analogous idea had been proposed by Gutierrez *et al.* [7] based on three dimensional ordering generated by parallel arrangement of multiple random sequences, and similar crystallization behaviour has been observed in PBT/poly(butylene 2,6-naphthalate) (PBN) [8]. In contrast to this, in quiescently crystallized PET/PEN copolymers, only the major component was observed to crystallize [9], without the progressive change in the unit cell lattice parameters observed in the co-crystallization case. The degree of crystallinity is observed to decrease in the central compositions. A study of PET/PEN random/blocky copolymers with a range of block lengths established that a critical sequence length is needed for components to crystallize [10]. In this study, a series of PET/PEN random/blocky copolymers are synthesized by transesterification reaction, and their thermal transition behaviour in the bulk and near-surface crystalline morphologies are investigated. As we reported previously [11], there is a surface layer with ca. 13 nm in thickness at the near-surface region of PET films, in which enhanced molecular mobility results in the reduction of T_{gS} and T_{cS} , and characteristic two-dimensional surface crystals appear in the temperature range between T_{cS} and T_{cB} . The direct observation of the surface crystals by AFM shows detailed lamellar crystalline morphologies, and can be utilized as a very powerful tool to probe the crystallizability of polymeric materials, as the crystals can be very clearly discerned and directly imaged from a cold-crystallized sample. In this study, the crystallizability in the PET/PEN copolymer system is investigated as functions of PET/PEN mixing ratio, degree of randomness, as well as sequence length, by observation of both the bulk and the surface crystallization behaviour, aiming to understand the influence of degree of randomness and sequence length to the crystallizability of the copolymer system, and to understand the differences in the characteristic lamellar growth habit across the composition sequence.

There are few previous reports regarding the microscopic crystalline morphology of random/blocky copolymers e.g. [2, 3, 12] and no previous direct study of the near-surface crystallization behaviour in such a system. The co-crystallizable copolyester series has been investigated intensely by Windle's [4, 5, 6, 13, 14, 15, 16, 17] and by Jabarin's [9, 18, 19]

groups, but their observation mainly depended on diffractometry, hence a clear microscopic crystalline morphology has not previously been reported.

2. Experimental

2-1. Copolymer synthesis

Molecular level mixtures of PET (Sigma Aldrich) and PEN (kindly provided from Teijin Chemical Co., Ltd) at various ratios were prepared by dissolving the homopolymers in a mixed solvent of 70 wt% 2-chlorophenol (Fisher Scientific) and 30 wt% 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, Sigma Aldrich). Solutions were filtrated with 0.2 μm pore sized PTFE syringe filters (Gelman), and coprecipitated by pouring the solution into acetone [20]. The precipitation was thoroughly washed with acetone by Soxhlet extractor for 48 hours, and dried in a vacuum oven at 120 °C for 24 hours.

A series of PET/PEN copolymers (Table 1) with different mixing ratio and reaction periods was synthesized by transesterification reaction in the molten state in a differential scanning calorimeter (DSC) (Perkin Elmer DSC-7) [20, 21, 22] at 300 °C for 5, 20, and 60 minutes in an argon gas atmosphere. The transesterification reactions in a DSC pan were carried out repeatedly under the same thermal conditions over more than 10 samples to provide sufficient copolymer material for all the experiments in this study. Viscosity average molecular weight for the resulting copolymers was measured with an Ostwald viscometer at 25 °C.

2-2. DSC

The bulk thermal behaviour of PET, PEN and their copolymers was measured by DSC (Perkin Elmer DSC-7) at a heating rate of 10 °C/min in an argon gas atmosphere. All the starting samples for the DSC measurements were once melted and crash-quenched to preserve the amorphous state and to ensure good sample-pan contact. The DSC scans were carried out by the heating process to induce cold crystallization from the amorphous material.

2-3. ^1H NMR spectroscopy

The series of synthesized copolymers were dissolved in deuteride 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP- d_2 , Sigma Aldrich) at 1.0 wt%, and ^1H NMR spectroscopy was carried out at 27 °C with high resolution 500 MHz NMR (Bruker DRX 500, TBI probe, 16 scans, recycle delay = 1.0 sec, acquisition time = 3.2 sec) to determine the statistical sequence length and the degree of randomness of the copolymers (calculations will be described in detail in the section 3-2).

2-4. *In-situ* AFM observation

All the copolymers and homopolymers were dissolved in a mixed solvent of 70 wt% 2-chlorophenol and 30 wt% 1,1,1,3,3,3-hexafluoro-2-propanol, and the solutions were filtrated with 0.2 μm pore sized PTFE filters before casting. Amorphous polymer films were deposited on single crystal silicon substrates (Compart Technology, orientation (100) plane) by spin coating of the solutions at 3000 rpm, and dried in a vacuum oven at 40 °C for 6 hr in order to remove residual solvent. The film thicknesses were measured by ellipsometry (Rudolph Research / Auto EL).

The developing crystalline morphology was observed at a range of temperatures, using an AFM (Auto-probe CP microscope, Park Scientific Instruments) operated at 0.5 Hz. Each sample cast on a Si substrate was set on a specially designed *in-situ* heating stage placed on

an AFM scanner, and annealed at elevated temperatures ranging from 50 to 140 °C to induce cold crystallization while remaining at a temperature range well below the 300 °C i.e. the melt phase required for further transesterification. Indeed, the annealing temperature range in this study is much lower than T_{mB} of any of the copolymer or homopolymer samples. The heating was performed stepwise and samples were kept at each increasingly elevated temperature for two hours before the morphology was recorded.

3. Results and discussion

3-1. Molecular weight

Of the 15 synthesized copolymers, eight representative specimens were chosen, and their viscosity average molecular weights were determined by viscometry with application of the Mark-Houwink-Sakurada equation [23], summarised in Table 1. The observed decrease in molecular weight on transesterification has been reported previously for PET/d-PET [24] and PET/PEN [25], although an increase in the molecular weight in PET/PEN [20] has also been reported due to end group reactions. The resultant molecular weights in Table 1 mean that the degree of polymerization of the products are from ca. 51 to 68, large enough for the statistical calculations in the following section.

3-2 ¹H NMR interpretation

Fig. 1 shows a representative ¹H NMR spectrum obtained for Copolymer 1 (PET/PEN = 50/50, reaction time = 60 min). The spectra indicate three independent resonances for NEN (4.879 ppm), NET (4.828 ppm), and TET (4.776 ppm), which are very close to those in a ¹H NMR study of PET/PEN copolymers [18], where NEN indicates the ethylene groups between two naphthalene dicarboxylate groups, NET the ethylene groups between one naphthalene and one terephthalate groups, and TET the ethylene groups between two terephthalates. The possible different combinations of the two aromatic groups adjacent to an ethylene glycol residue are illustrated in Fig. 1. As shown in Table 2, a clear increase in the proportion of NET groups was observed as transesterification progresses by reaction time.

In this study, the degree of randomness and sequence length of the product PET/PEN random/block copolymers are determined by statistical calculation using the ¹H NMR peak area ratios [26]. This quantitative approach has been applied in many studies by ¹H NMR e.g. [10, 18, 19, 23, 27, 28, 29, 30, 31, 32, 33, 34, 35]. The mole fractions of PET (F_T) and PEN (F_N) units in the PET/PEN copolymers are calculated by the ratio of the three ethylene glycol residues obtained by three ¹H NMR peak areas (A_{TET} , A_{NET} , and A_{NEN}) and the total peak area A ($= A_{TET} + A_{NET} + A_{NEN}$) as,

$$F_T = \frac{0.5A_{NET} + A_{TET}}{A}, \quad F_N = \frac{0.5A_{NET} + A_{NEN}}{A} \quad (eq.1)$$

When the units along a PET/PEN copolymer chain are examined from one end to the other, the probability of finding a naphthalate unit next to a terephthalate unit, and the finding a terephthalate unit next to a naphthalate unit would be,

$$P_{TN} = \frac{A_{NET}}{2AF_T}, \quad P_{NT} = \frac{A_{NET}}{2AF_N} \quad (eq.2)$$

The degree of randomness (degree of transesterification) (B), and the number average sequence length of ethylene terephthalate blocks (L_T) and ethylene naphthalate blocks (L_N) can be defined by:

$$B = P_{TN} + P_{NT}, \quad (eq.3)$$

$$L_T = \frac{1}{P_{TN}}, \quad L_N = \frac{1}{P_{NT}}. \quad (eq.4)$$

Therefore, when the degree of randomness $B = 1$, the PET and PEN units take a totally

random distribution, which means the product is a random copolymer. When $B < 1$, the PET and PEN units form certain long sequence length of the same repeating units that is random block copolymer. When $B = 0$, the system consist of homopolymer PET or PEN.

The number average sequence lengths L_T and L_N should be in between 1 and infinity. When the sequence length is 1, the product is a strict alternating copolymer. When the numeric value is 2, it means the minority component units are randomly distributed over all the monomer units in the copolymer. When it is infinity, the system is homopolymer.

The results for our copolymers are summarised in Table 2. The relationship between calculated sequence length and degree of randomness is summarized in Fig. 2. As the reaction progresses, the sequence length L_T and L_N gradually decreases and the degree of randomness B increases, depending on the ester exchange reaction rate.

Fig. 2 indicates several points as follows:

1. The PET/PEN mixing ratio decides the position of the sequence length curve, e.g., for a given randomness, any copolymers which have a larger PET composition exhibited larger sequence length L_T than those of smaller PET composition. Thus, any combination of sequence length and randomness is attainable by altering PET/PEN composition and reaction time.
2. Just 5 minutes reaction rapidly decreases the sequence length of both the major and minor component. Even in the case of PET/PEN=90/10 or 10/90, the ester exchange reaction swiftly shortens the sequence length of the major component.
3. The degree of randomness for any PET/PEN composition approaches 1.0 within 60 minutes reaction, which means the system achieves a fully random distribution of the component monomer units.

The observed behaviour of the sequence length and the degree of randomness in this study are consistent with previous reports of the copolymerization of PET/PEN [18, 31, 33, 34, 35] and PET/PBT [22].

3-3 Thermal behaviour of the bulk products

Thermal transition temperatures, obtained by DSC, of PET, PEN and their copolymers are shown in Table 3 (The DSC traces are shown in Appendix Fig. A1). After just 5 minutes reaction at 300°C, the melting (T_{mB}) and crystallization (T_{cB}) temperatures had changed depending on the PET/PEN ratio, as a result of transesterification. As the reaction time increases, the crystallinity decreases and the DSC peaks became indistinct, and after 60 minutes isothermal reaction, there is little endothermal or exothermal behaviour for PET/PEN = 75/25, 50/50, and 25/75 specimens. In all samples only single T_{gB} and T_{mB} transitions were observed, suggesting single phase systems in all cases.

Our measured T_g agrees closely (Fig. 3a), independent of the reaction time, with the Fox equation [36], which describes the relationship between T_g of the homopolymers and either copolymer or miscible blend systems:

$$\frac{1}{T_g} = \frac{w_{PET}}{T_{gPET}} + \frac{w_{PEN}}{T_{gPEN}} \quad (eq.5)$$

where w_{PET} and w_{PEN} are the weight fractions of the PET and PEN components.

Similarly, the crystallization temperature, T_{cB} of the copolymers is only mildly affected by

reaction time (Fig. 3b), i.e. the degree of randomness. As a function of the PET/PEN composition ratio, however, the crystallization temperature remains close to that of PEN up until about the 50/50 composition, before decreasing more rapidly to that of PET, likely as a result of low crystallizability in the central compositions. A similar behaviour has been reported previously [29].

In the particular case of Copolymer 9 (PET/PEN = 10/90), T_{cB} showed a clear decrease compared to the homopolymer, even having had just 5 minutes transesterification. Becker *et al.* reported that the slightly transesterified PET/PEN copolymer chains resulted in poor packing in the melt, showing substantial reduction of the intrinsic viscosity and T_m [25]. Their observation implies that heterogeneous units in the slightly transesterified copolymer may decrease the packing of the entire system including all the rest of the crystallizable homogeneous units. The results in this study might be compared with their observations, as the degree of randomness of Copolymer 9 is quite close to their transesterification percentage. In the case of Copolymer 6 (PET/PEN = 90/10), however, there is no such a phenomenon observed regardless the small degree of transesterification.

The magnitude of the enthalpy of crystallization in the bulk, $|\Delta H_c|$, decreases as the mixing ratio approaches PET/PEN=50/50 (Fig. 3c). It also decreases as the reaction time increases. If the mixing ratio becomes closer to PET/PEN=50/50 or reaction time becomes longer, the degree of randomness enlarges and sequence length is shortened, resulting in the decrease in the crystallinity which is reflected in the ΔH_c . Thus, although T_{cB} is basically not influenced by reaction time, ΔH_c reflects the decrease of the crystallizability depending on the degree of transesterification. In the case of Copolymers 1, 2 and 13, ΔH_c was not detected due to their negligible crystallizability.

Similarly, the enthalpy of melting in the bulk (ΔH_m) of the copolymers (Fig. 3d) decreases as the PET/PEN component approaches 50/50, and as the reaction period increases. These changes are also associated with the decrease in sequence length, and consistent with the decrease in crystallinity associated with the increase of randomness [30]. For Copolymers 1, 2 and 13 it is expected that ΔH_m would be nearly zero in accordance with the ΔH_c results above, and indeed these samples did not show a melting peak in the DSC trace. Jun *et al.* observed, from bulk thermal analysis [10], that a minimum sequence length of ca. 2.7 – 4.0 was required for quiescent crystallization. The sequence lengths for copolymers 1, 2 and 13, in which no bulk crystallization is observed, is at most 4.40. All the other copolymers are observed to crystallize, and the shortest sequence length of either of the components in each of the materials is 5.10 (Copolymer 10). From this observation, the shortest sequence length for bulk crystallization in PET/PEN copolymer system is thought to be between 4.40 and 5.10.

The bulk melting point (T_{mB}) of the copolymers in this study exhibited an obvious decrease as the PET/PEN ratio becomes close to 50/50 (Fig. 3e), which might be associated with smaller crystallites and/or changes in disorder in the crystalline or amorphous phases across the reaction sequence. This suppression in T_{mB} becomes more exaggerated with reaction time. Experimental studies have previously shown that substantial T_m depression is observed in the copolyesters of PET/PEN [6, 10, 29, 31, 34], PET/PBT [22], PBT/PBS [32], PBT/PBN [8], and PBN/poly(butylene adipate) [30]. Lu *et al.* [6] observed the same trend in T_{mB} independent of whether the samples had been quiescently or strain-crystallized. The T_{mB}

results in this study are consistent with the results of the change in sequence length and degree of randomness (see Fig. 2), i.e. the shorter sequence length, L_T and L_N , and higher randomness B give lower T_{mB} . Both Lu [6] and Jun [10] associated this depression of T_{mB} with shorter crystallizable sequence lengths leading to thinner crystals, even though Lu [6] and Patchek [9] concluded from scattering studies that the crystallite thickness was constant. We must note that the observed decrease in molecular weight as a result of the transesterification reaction will also influence the thermal parameters such as T_{mB} , as would any constraint on the configuration of the amorphous material surrounding the crystal e.g. due to rejection of non-crystallizable material.

Fig.3f shows the relationship between ΔH_m and degree of randomness, B . The gradient of ΔH_m with B depends on the mixing ratio. From this plot, it is obvious that as the reaction progresses, B increases and ΔH_m decreases, reflecting the suppression of crystallinity with increasing randomness. The PET-rich copolymers always show shallower slopes than the PEN-rich copolymers (i.e. PET/PEN = 10/90 < 90/10 and PET/PEN = 25/75 < 75/25), as it is expected that the PET-rich copolymers are more capable than PEN-rich copolymers to arrange crystallizable sequences due to their greater molecular flexibility.

As the PET/PEN ratio approaches 50/50 the magnitude of gradient increases, as finding an arrangement of crystallizable sequences becomes much less probable. Thus, the steep lines (PET/PEN = 50/50 and 25/75) pass $\Delta H_m = 0$ before B reaches 1.0, which implies that as the reaction progresses the PET/PEN = 50/50 and 25/75 systems lose crystallizability before statistical randomness reaches ‘totally random’. On the other hand, it was shown that PET/PEN = 90/10, 10/90, and 75/25 systems still maintain crystallizability even at $B = 1.0$. The gradient observed for each composition is a measure of the intrinsic potential crystallizability of PET/PEN copolymers, with PET being more crystallizable than PEN, and with the more extreme composition ratios being more crystallizable than the central compositions, because of the greater sequence lengths (Table 2).

3-4 Crystallization morphology

In this study, crystallization morphology is observed directly by AFM imaging of crystals at the near-surface of the sample. It has previously been reported that the glass transition temperature at the polymer surface (T_{gs}) is depressed to some degree [37, 38, 39, 40, 41] compared with that in the bulk. In the case of the cold crystallization, the enhanced local molecular mobility at the surface plays an important role for the primary crystal nucleation and subsequent crystal growth. As a result, the observed crystallization temperature at the polymer surface (T_{cs}) is decreased, resulting in preferential crystallization at the surface [42, 43, 44] under suitable process conditions. As we reported previously [11, 45, 46], the surface molecules of PET and PEN films crystallize at lower temperatures than the bulk, exhibiting characteristic lamellar crystalline morphologies with, for films this thick, typically an edge-on morphology.

It is intriguing to examine how the surface crystallization behaviour of the PET/PEN random/blocky copolymers changes from the original homopolymers, PET and PEN. As we were not able to take suitable diffraction measurements, we have no direct evidence for the presence, or otherwise, of co-crystallization in the surface crystals. Table 4 shows that, for

all compositions, the surface crystallization temperature T_{cS} , determined by AFM observation of relatively thick (436–680 nm) copolymer films, is ca. 60–90 °C below of the bulk crystallization temperature T_{cB} measured by DSC, meaning that the enhanced local molecular mobility at the surface is observed in PET/PEN copolymers, showing the same trend of crystallizability with composition. The heating rates to induce the cold crystallization in this study were different between the DSC and AFM measurements, however, previous studies [37, 38, 39, 40, 41, 46] on various polymers, including our previous papers on PET and PEN, have shown that the T_{gS} is lower than the T_{gB} , and that there are distinct morphological differences observed at the onset of surface crystallization, and the subsequent crystallization that occurs at T_{cB} , hence it is reasonable to infer that the crystallization temperature differences between T_{cB} by DSC and T_{cS} by AFM in these copolymer materials are also as a result of the depressed T_{gS} .

For the most random copolymer, Copolymer 1 (PET/PEN = 50/50, 60 min reaction, larger sequence length $L_T = 2.11$), crystallization was totally inhibited and there were no surface crystals observed. The crystallizability can be enhanced at the surface, however, as in the case of Copolymer 13 (PET/PEN = 25/75, 60 min reaction, larger sequence length, L_N is 4.40) for instance, in which surface crystals appeared at 135 °C, even though there is no T_{cB} observed by DSC. This selective crystallization might be attributed to the enhanced molecular mobility at the surface, which enables polymer crystallization only at the surface in this degree of randomness. This suggests that surface crystallization not only allows for crystallization at lower temperatures, but also at a shorter sequence length in the copolymer.

The lamellar crystalline morphology of the copolymer films depends upon the composition and reaction time (Fig. 4). After only 5 mins transesterification reaction time, the sequence lengths of PET and PEN units are still long (Table 2), and so the crystalline morphology is quite similar to that of the homopolymers. Down the sequence of composition, the morphology changes gradually from PET-like to PEN-like; it had been observed previously [46] that PEN surface crystals are more finely branched than PET. The crystalline morphology of Copolymer 3 (PET/PEN = 50/50, 5 min reaction) exhibits an intermediate crystalline morphology including both PET-like and PEN-like features (Fig. 4). This gradual trend in morphology would be consistent with there being both monomers present within the crystalline morphology, either by co-crystallization or nucleation (primary and secondary) of both types of crystal in the system, and indeed the rather flat profile of the ΔH_m vs composition curve (Fig 3d) in the central compositions is consistent with this e.g. if the crystallinity of copolymer 3 were entirely due to one component, say PEN, we would expect a lower value, with the trend in crystallinity due to pure PEN crystals tending to zero as the figure is traversed from left (pure PEN) to right (pure PET).

For 60 minute transesterification reaction times, with the greater degree of randomness, at compositions towards the centre of the series, Copolymer 10 and 13 (PET/PEN = 75/25 and 25/75, 60 min reaction), the surface crystals appeared only at elevated temperatures, higher than that of the nearest homopolymers by 15 and 20 °C (Table 4), and at the 50/50 composition, no crystallinity was observed at all. The surface morphologies also differ from the shorter transesterification times. For these more random copolymers the sequence lengths are much shorter (Table 2), and the copolymer lamellae appear finer. Towards the centre of the composition series the radiating lamellae become difficult to resolve, giving

rise to a crystalline morphology that is rather closer to spherulites, such as those reported for polylactide films of 500-600 nm thickness [47].

When the random copolymers start to crystallize, it is possible that particular monomer sequences might be incorporated into the crystal, or that the minor component will be rejected from inclusion in the crystal, limiting crystallization. In either case, the randomness of the chains will give rise to a greater exclusion of material from particular lamellae, and a lowering of the overall crystallization, as observed. In the poly(L-lactide-co-D-lactide) system, SAXS and melting point analysis both suggested that the lamellar thickness decreased as the concentration of D-isomers increased and the authors concluded that the D-isomers were rejected from crystallization [48], limiting the crystal lamellar thickness to the statistical length of a sequence of L-isomers. A later study with AFM directly imaged the lamella thicknesses, in good agreement with the SAXS measurements [49]. In contrast, a study of linear aliphatic polyesters consisting of ϵ -caprolactone (CL) and ω -pentadecalactone (PDL) [50] indicated that, up to 80% CL units could be incorporated within the PDL lattice without loss of crystallinity and with constant lamellar thickness. Contrary to the PET/PEN system however, the authors considered that in the CL/PDL system the CL units are incorporated within the PDL crystal structure without the need for sequence matching. Other systems lie somewhere between. A study of a poly(butylene succinate-*ran*-butylene azelate) showed, by SAXS, an increase in lamellar thickness, as well as an increase in interlamellar amorphous thickness, which they associated with some degree of comonomer inclusion in the crystals, which they could adjust with suitable thermal treatments [51]. This *greater* lamellar thickness at central compositions (for a given undercooling) might be associated with a smaller free energy change on crystallization than for the homopolymers due to the more random nature of the crystal structure. Rather than a random incorporation of non-matching monomers into the crystal structure, the PET/PEN system is thought, under suitable crystallization conditions, to co-crystallize by sequence matching with the local rejection of non-matching sequences, as postulated by Lu & Windle [5]. This rejection of material was thought to be responsible for the increase in long period observed by SAXS in the central compositions, despite no increase in lamellar thickness being suggested from WAXS peak widths i.e. the rejected material increased the spacing between the crystals. A SAXS study for PET/PEN copolymer reported by Jabarin's group [9] showed that the quiescently crystallized material, that they conclude has independent homopolymer crystallization, also exhibits an increase in interlamellar amorphous thickness and long period towards the central composition, whereas the lamellar thickness stays constant over the whole composition range.

In this study, we can directly observe the surface crystallized lamellae microscopically and comparisons, for example of Copolymers 6, 3, and 9 suggest, consistent with the previous diffraction study of these materials, that the crystal lamellae are not thicker, and are even perhaps thinner, in the central compositions, but that there are wider gaps between the lamellae.

The rejection of material from the crystals can affect other aspects of the morphology. It was reported that poly(trimethylene terephthalate) (PTT as hard segment)/poly(ethylene oxide terephthalate) (PEOT as soft segment) block copolymers changed crystalline morphology from banded spherulites to seaweed-like morphology with increasing PEOT

content [52]. The authors associated this with the soft segment, being rejected from the crystals, modifying the interfacial energy and local chain diffusivity. In the case of PBN/poly(butylene adipate) copolymer system, similar crystalline morphology caused by limited incorporation of the minor comonomer in the crystals was reported [30]. PET/PEI copolymers were reported [2] to show loosely organized crystals with a vague boundary, and in the case of PTT/PEOT [52], AFM imaging was not possible because of the rejected soft component surrounding the crystals. In the case of the PET/PEN system in this study, the two monomers both crystallize, whether by sequence matching, or by sequences of both monomer types nucleating, however, for longer sequence length samples (short reaction times or outer compositions) there is no large-scale rejection of a heterogeneous minor component into the interlamellar amorphous, meaning that we do observe a clear outline to the crystals. Decreasing the sequence length does lead to more locally rejected material, with the shortest sequence length samples (Copolymer 10 and 13) giving rise to the spherulitic morphologies with unresolved lamellae.

4. Conclusions

1. A series of PET/PEN random/block copolymers were synthesized by molten transesterification at 300 °C. The degree of randomness for any PET/PEN composition reaches to around 1.0 after 60 minutes reaction.
2. T_{gB} showed clear dependence on PET/PEN composition which is consistent with the Fox equation. T_{cB} was maintained close to that of PEN for much of the composition range before dropping towards that of PET. On the other hand, T_{mB} , $|\Delta H_c|$, and ΔH_m were lower in the highly reacted copolymers compared with that expected for a rule of mixtures. This would be consistent with the reduced crystallinity reported previously.
3. Even though the degree of randomness became nearly 1.0, some copolymers still exhibited distinct T_{mB} , ΔH_c , and ΔH_m , indicating remaining crystallizability in the bulk. Thus, randomness is not the decisive factor for the crystallizability but the sequence length of the major component is influential.
4. Crystallization at the surface of thick films was observed in the copolymers. T_{cS} decreased from T_{cB} by 60-90 °C, due to the enhanced molecular mobility at the surface. In particular, Copolymer 13 (PET/PEN = 25/75, 60 min reaction) produced surface crystals despite there being no evidence of bulk crystallization in DSC.
5. For copolymers with long sequence lengths, i.e. after only 5 min transesterification reaction time, there is a progressive transition in surface crystal morphology across the composition sequence from a morphology similar to PET, to the more branched morphology observed for PEN. For longer transesterification times, the mid-range compositions show a more spherulitic structure with individual lamellae barely resolvable, likely due to material rejected from the crystallites during formation. In all cases, we are able to observe directly how the shorter sequence lengths lead to crystalline morphology which differs from the original homopolymers.

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6. Acknowledgements

The authors acknowledge for the financial support for this study by Oji Paper Co., Ltd. We thank Mr. Kimihiro Ogawa in Teijin Chemical Co., Ltd. for kind offer of PEN pellets and its instructions.

7. Figures and Tables

Table 1 PET/PEN copolymers with different mixing ratio and reaction time with viscosity average molecular weights shown below

		Composition PET/PEN						
		100/0	90/10	75/25	50/50	25/75	10/90	0/100
Reaction time (min)	0	PET 25928						PEN 14543
	5	Copoly 6 13416		Copoly 12	Copoly 3 12802	Copoly 15	Copoly 9 12923	
	20	Copoly 5		Copoly 11	Copoly 2	Copoly 14	Copoly 8	
	60	Copoly 4 13047		Copoly 10 12309	Copoly 1 14858	Copoly 13 16400	Copoly 7 12151	

Reaction Temperature: 300°C

The composition fractions are weight ratios

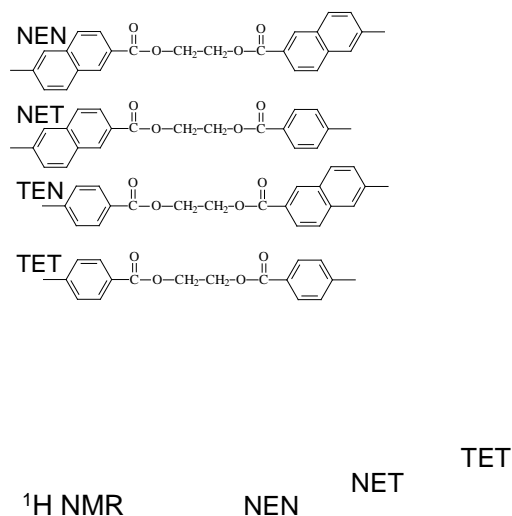


Fig. 1 An example of a ¹H NMR spectrum (Copolymer 1, PET/PEN = 50/50, reaction time = 60 min). The three types of electrostatic shielding for the ethylene glycol residue produce three independent resonances which show the existing ratio of NEN, NET, and TET. Due to the same chemical environment, NET and TEN show identical chemical shift. The sharp peak at 4.75 ppm signifies the remaining proton in deuteride HFIP.

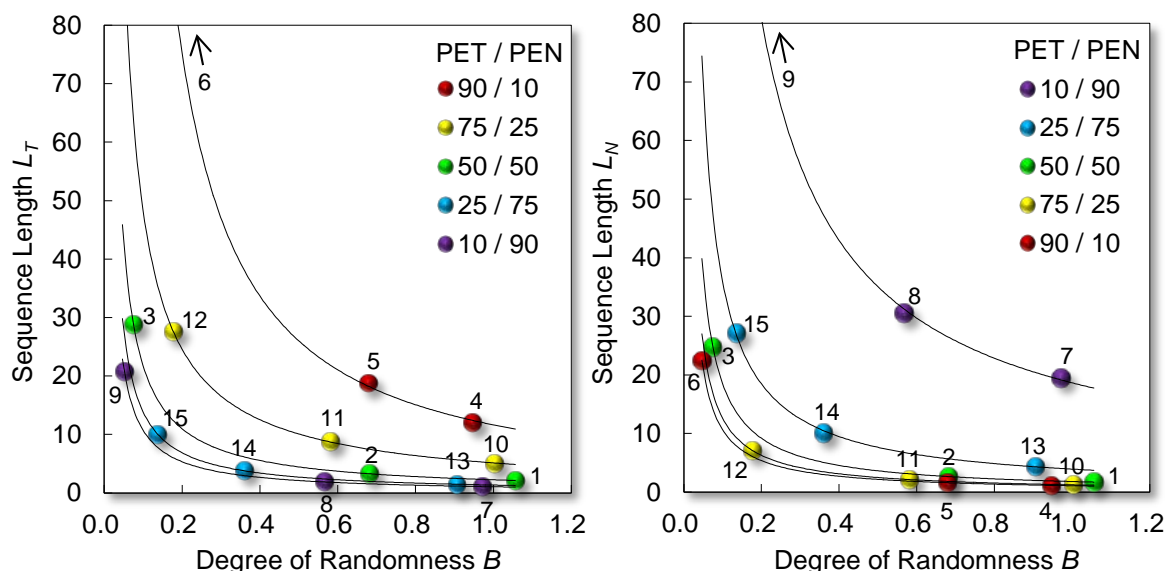


Fig. 2 Relationship between sequence length and degree of randomness. The labelled numbers correspond to the copolymer names. As the reaction proceeds, the sequence length L_T and L_N decrease and degree of randomness B increases. All the lines are power approximation.

Table 2 ^1H NMR peak area ratio and the calculated degree of randomness and sequence lengths

	Composition	Reaction		1H NMR Peak Area			Finding		Degree of	Sequence	
	PET/PEN	Time (min)	Temp. ($^{\circ}\text{C}$)	TET	NET	NEN	P_{TN}	P_{NT}	Randomness B	L_T	L_N
Copolymer 1	50/50	60	300	1.000	1.796	0.642	0.473	0.583	1.056	2.11	1.72
Copolymer 2	50/50	20	300	1.000	0.870	0.715	0.303	0.378	0.682	3.30	2.64
Copolymer 3	50/50	5	300	1.000	0.072	0.855	0.035	0.040	0.075	28.81	24.78
Copolymer 4	90/10	60	300	1.000	0.181	0.014	0.083	0.864	0.947	12.07	1.16
Copolymer 5	90/10	20	300	1.000	0.112	0.034	0.053	0.626	0.679	18.81	1.60
Copolymer 6	90/10	5	300	1.000	0.005	0.054	0.002	0.044	0.047	402.84	22.51
Copolymer 7	10/90	60	300	0.005	0.108	1.000	0.920	0.051	0.971	1.09	19.52
Copolymer 8	10/90	20	300	0.030	0.068	1.000	0.534	0.033	0.567	1.87	30.55
Copolymer 9	10/90	5	300	0.071	0.007	1.000	0.048	0.004	0.052	20.82	278.25
Copolymer 10	75/25	60	300	1.000	0.488	0.058	0.196	0.807	1.003	5.10	1.24
Copolymer 11	75/25	20	300	1.000	0.259	0.147	0.114	0.468	0.582	8.74	2.14
Copolymer 12	75/25	5	300	1.000	0.075	0.229	0.036	0.141	0.177	27.60	7.09
Copolymer 13	25/75	60	300	0.139	0.588	1.000	0.679	0.227	0.906	1.47	4.40
Copolymer 14	25/75	20	300	0.311	0.220	1.000	0.261	0.099	0.360	3.83	10.09
Copolymer 15	25/75	5	300	0.346	0.076	1.000	0.100	0.037	0.136	10.04	27.16

Table 3 T_{gB} , T_{cB} , and T_{mB} obtained by DSC

Reaction (min)		Composition PET/PEN					
		100/0	90/10	75/25	50/50	25/75	0/100
		PET					
0	Bulk T_g	71.1					112.0
	Bulk T_c	130.0					201.0
	Bulk T_m	255.8					262.8
5			Copoly 6	Copoly 12	Copoly 3	Copoly 15	Copoly 9
	Bulk T_g		77.8	82.3	87.3	104.3	108.1
	Bulk T_c		140.9	159.3	182.8	195.4	177.9
20			Copoly 5	Copoly 11	Copoly 2	Copoly 14	Copoly 8
	Bulk T_g		74.4	76.8	88.5	103.2	108.0
	Bulk T_c		141.0	147.4	-	200.0	191.5
60			Copoly 4	Copoly 10	Copoly 1	Copoly 13	Copoly 7
	Bulk T_g		72.9	80.4	88.9	105.0	108.3
	Bulk T_c		137.6	176.9	-	-	191.5
			Copoly 4	Copoly 10	Copoly 1	Copoly 13	Copoly 7
	Bulk T_m		239.8	213.6	-	-	247.5

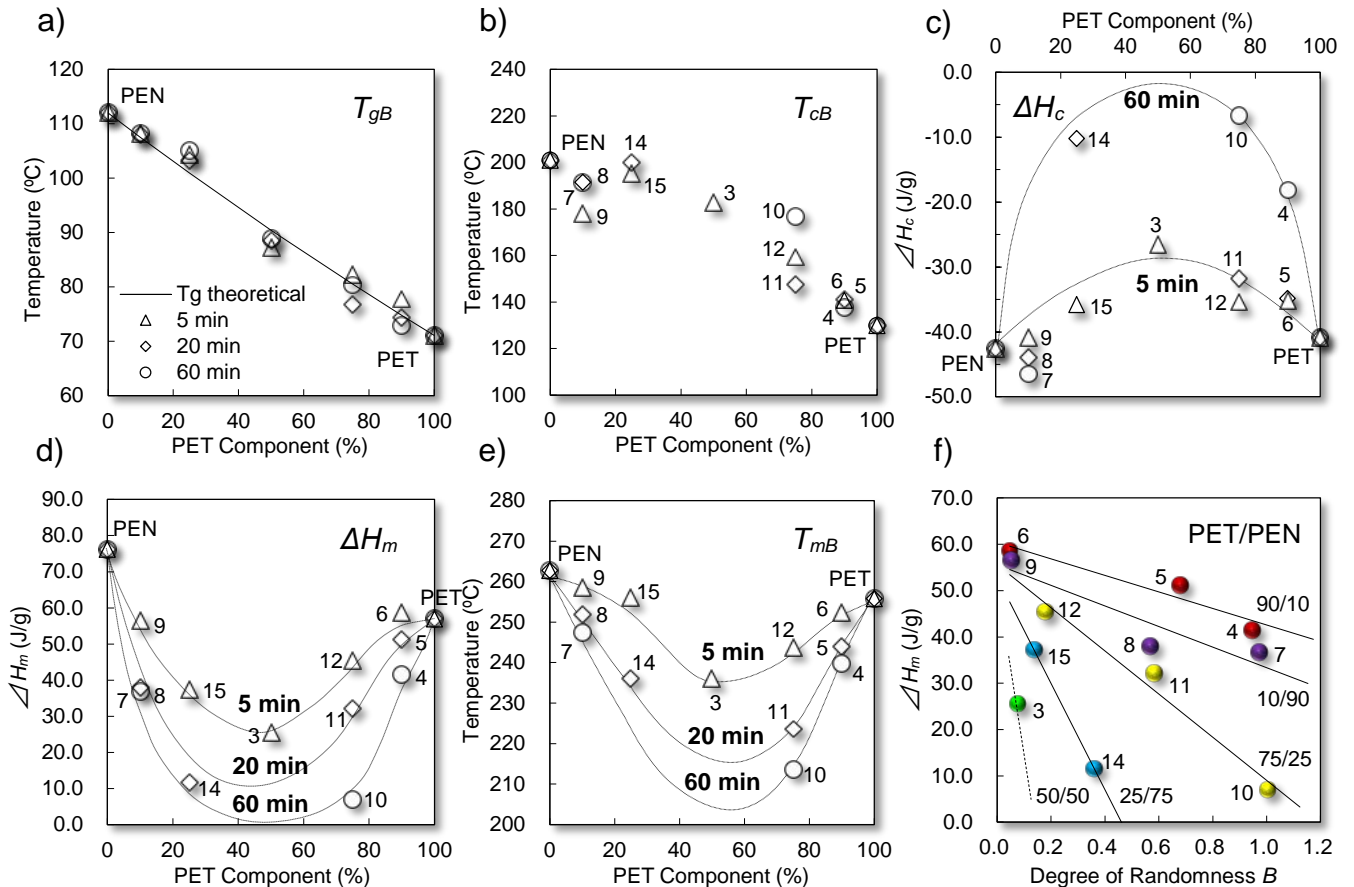


Fig. 3 a) T_{gB} of the copolymers obtained experimentally compared with theoretical value calculated by Fox equation. b) T_{cB} of the copolymers. c) ΔH_c of the copolymers. d) ΔH_m of the copolymers. These changes are associated with the decrease in crystallinity in the copolymers. In the case of Copolymer 1 and 13, ΔH_m was not detected. e) T_{mB} of the copolymers. Copolymer 1, 2, and 13 did not show any melting behaviour. f) ΔH_m as a function of degree of randomness B shows linear relationships with slope dependent on composition. PEN-rich copolymers always show smaller slopes (10/90 < 90/10 as well as 25/75 < 75/25).

Table 4 Surface and bulk T_c of the PET/PEN copolymers

	Composition	Reaction time	T_{cs} by AFM	T_{gb} by DSC	T_{cb} by DSC
	(PET/PEN)	(min)	($^{\circ}\text{C}$)	($^{\circ}\text{C}$)	($^{\circ}\text{C}$)
PET	100/0	0	70	71.1	130.0
Copoly 6	90/10	5	70	77.8	140.9
Copoly 4	90/10	60	70	72.9	137.6
Copoly 10	75/25	60	95	80.4	176.9
Copoly 3	50/50	5	90	87.3	182.8
Copoly 1	50/50	60	-	88.9	-
Copoly 13	25/75	60	135	105.0	-
Copoly 7	10/90	60	115	108.3	191.5
Copoly 9	10/90	5	100	108.1	177.9
PEN	0/100	0	115	112.0	201.0

The T_{cs} data are for the thick films

The T_{cb} data are the maxima of the exotherm by DSC

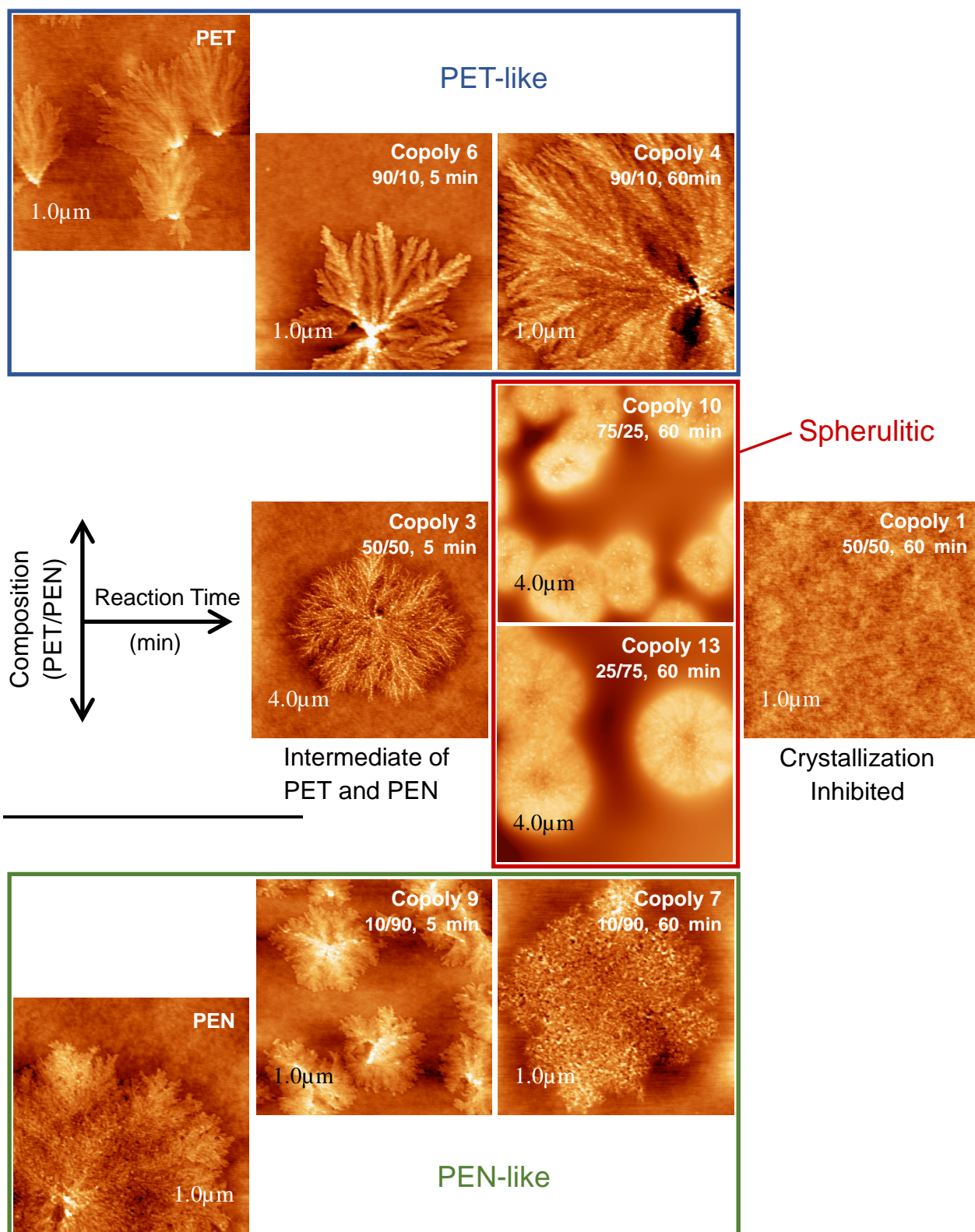


Fig.4 AFM images of surface crystals of PET, PEN and PET/PEN random/block copolymers at the surface of thick films. PET: thickness 680 nm, annealed 75°C, Copolymer 6: PET/PEN=90/10, 5 min reaction, thickness 501 nm, annealed 75 °C, Copolymer 4: PET/PEN=90/10, 60 min reaction, thickness 532 nm, annealed 80 °C, Copolymer 10: PET/PEN=75/25, 60 min reaction, thickness 477 nm, annealed 110 °C, Copolymer 3: PET/PEN=50/50, 5 min reaction, thickness 436 nm, annealed 100 °C, Copolymer 1: PET/PEN=50/50, 60 min reaction, thickness 562 nm, annealed up to 180 °C, Copolymer 13: PET/PEN=25/75, 60 min reaction, thickness 613 nm, annealed 155 °C, Copolymer 9: PET/PEN=10/90, 5 min reaction, thickness 566 nm, annealed 110 °C, Copolymer 7: PET/PEN=10/90, 60 min reaction, thickness 493 nm, annealed 120 °C, PEN: thickness 680 nm, annealed 120°C.

8. Appendix

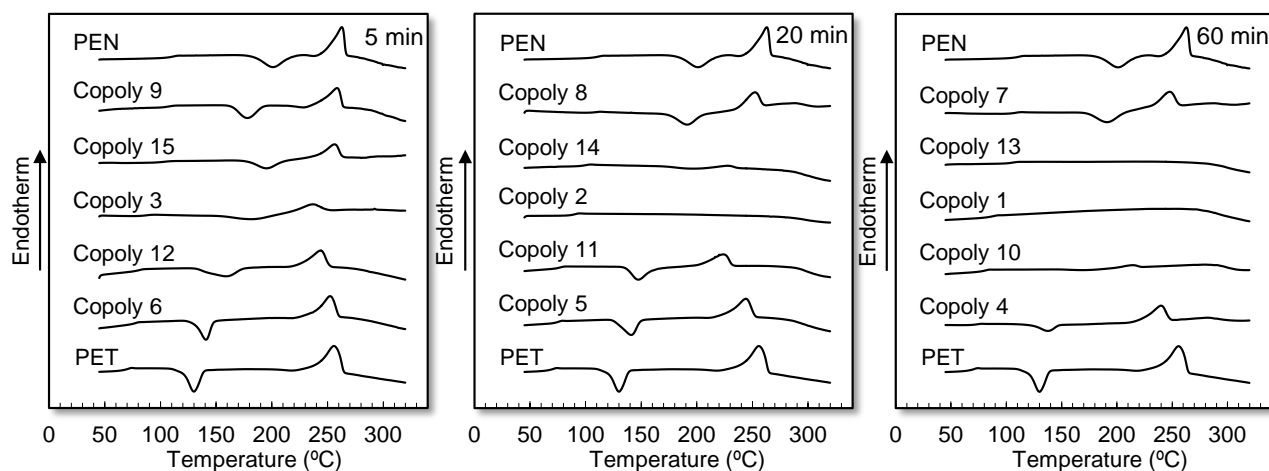


Fig. A1 DSC traces of PET, PEN, and their copolymers for 5, 20, and 60 minutes reaction time. After just 5 minutes reaction time, the crystallization and melting temperature changed depending on the PET/PEN mixing ratio. As the reaction time increases, the crystallinity decreases and the peaks became indistinct. After 60 minutes reaction, there is little indication of thermal transitions for PET/PEN = 75/25, 50/50, and 25/75 specimens.