polymer

Relationship between sequence distribution and transesterification of PEN/PET random/block copolyesters

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Abstract

The random and block copolyesters of poly(ethylene 2,6 naphthalate) (PEN) and poly(ethylene terephthalate) (PET) are synthesized and studied by ^1H-n.m.r., DSC, X-ray. The block length decreases and the degree of transesterification increases at a similar composition ratio. The melting point depressions occur with increasing the content of the other component, and melting peaks disappear at a similar composition ratio. The results of X-ray diffractograms match well with those of dyads fraction, block length, and DSC. It can be seen that a critical block length is needed for components in order to crystallize. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: PEN/PET random/block copolyesters; Sequence distribution; Transesterification

1. Introduction

The industrial use of polymer blends was growing rapidly. This growth is largely caused by the unique combination of properties which is sometimes achieved by blending two or more polymers. The polyesters have also been used for many commercial blends.

The occurrence of transesterification reaction in polyesters was known for many years [1]. However, it is only recently that more detailed descriptions of the kinetics of the transesterification and the sequence length distribution in the resulting copolymer were obtained [2–4]. In addition, extensive investigations relating to the transesterification and crystallization behaviour were performed mainly in blends of polycarbonate and poly(ethylene terephthalate)(PET) [5–7] or poly(butylene terephthalate)(PBT) [8,9].

The transesterification plays an important role in the formation of block or random copolyesters. The majority of studies in the literature have qualitatively monitored transesterification through phase changes as measured by DSC, WAXD [10,11]. These indirect analyses cannot provide quantitative information in regard to the transesterification in the polyester blends. Yamadera and Murano [12] investigated the sequence distribution and randomness of copolyesters using direct measurement and some other studies [13,14] have employed direct measurements, such as i.r. and n.m.r. to identify the transesterification between two polyesters.

Accordingly, we try to find the relationship between sequence distribution and transesterification of PEN/PET random/block copolyesters including crystallization and thermal behaviour. The degree of transesterification is also confirmed by the observation of the melting point and the crystal pattern.

2. Experimental

2.1. Synthesis of PEN/PET random copolyesters

PEN/PET cooligomers were synthesized from dimethyl 2,6 naphthalate (DMN), dimethyl terephthalate (DMT) and ethylene glycol (EG) with zinc acetate as a catalyst. The starting materials were of commercial grade and were used without further purification. The synthesis of the cooligomers was carried out with agitating at 230°C for 2 h. The polycondensation reaction was continued at 285°C for 2 h under vacuum using antimony trioxide as a catalyst and trimethylphosphate as a stabilizer. The obtained PEN/PET random copolyesters were quenched into cold water and dried in vacuo.

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Table 1
Annealing condition, inherent viscosity and density of PEN/PET random copolyesters

Random copolymer	DMT unit (mol%)	Inherent viscosity (dl g^{-1})	Annealing condition		Density(g cm^{-3})	
			Temp(°C)	Time(h)	Quenched	Annealed
PEN	0.0	0.80	220	3	1.335	1.356
NT1	18.3	0.85	200	3	1.334	1.335
NT2	43.2	0.75	120	12	1.335	1.335
NT3	54.4	0.63	70	12	1.335	1.335
NT4	64.1	0.77	120	12	1.336	1.335
NT5	84.0	0.78	200	3	1.341	1.376
PET	100	0.62	210	3	1.345	1.395

Table 2
Annealing condition, inherent viscosity and density of PEN/PET random copolyesters

Block copolymer		DMT unit (mol%)	Inherent viscosity (dl g^{-1})	Annealing condition		Density(g cm^{-3})	
				Temp(°C)	Time(h)	Quenched	Annealed
PEN		0.0	0.48	220	3	1.327	1.333
NTB1	60	14.5	0.50	220	3	1.323	1.356
	90	14.5	0.45	220	3	1.327	1.359
	120	14.5	0.41	220	3	1.327	1.359
NTB2-60		25.3	0.44	200	6	1.329	1.346
NTB3-60		48.4	0.35	120	6	1.332	1.333
NTB4-60		66.9	0.46	120	6	1.332	1.333
NTB5-60		84.5	0.68	200	3	1.334	1.369
PET		100.0	0.63	210	3	1.346	1.399

2.2. Synthesis of PEN/PET block copolyesters

PEN and PET chips were supplied by courtesy of SKI Korea. PEN and PET chips were dried in vacuo at 100°C to minimize possible hydrolysis during melting process. PEN/PET block copolyesters, from 90:10 to 20:80 (wt:wt), were synthesized in a reaction tube during various reaction times at 300°C in vacuo. Under vacuum conditions of 0.5–0.9 torr, the polymers were premelted for 30 min

with agitating and then the reaction was continued for 60, 90 and 120 min. The obtained samples were quenched in cold water and dried in vacuo.

3. Measurements

The inherent viscosity of PEN/PET copolyesters was measured in *o*-chlorophenol with an Ubbelohde viscometer
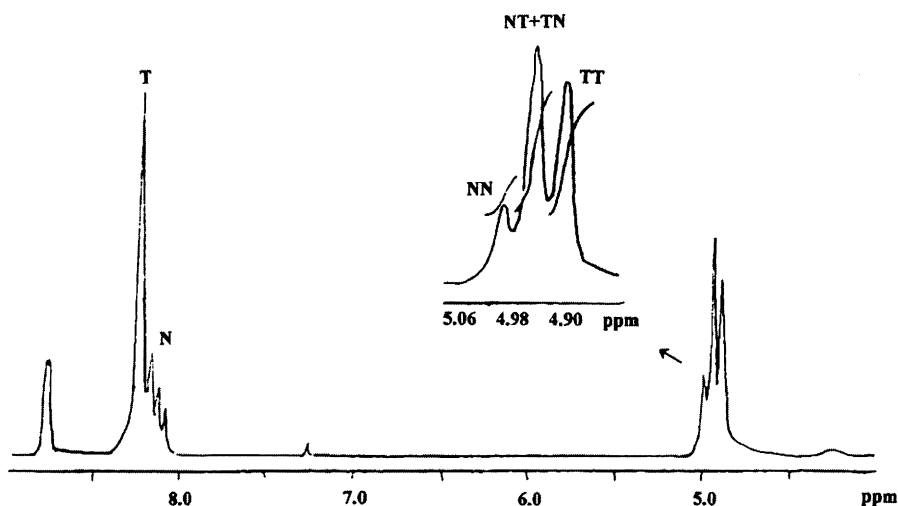

Fig. 1. ^1H-n.m.r. spectrum of NT4 (DMT 64.1 mol%) random copolyester.

at 25°C ± 0.1°C (dl g^{-1}). The density was measured with a gradient density column at 25°C ± 0.1°C using a mixture of *n*-heptane and carbon tetrachloride.

The composition determination and the sequence distribution analysis of the copolyesters were conducted on ^{1}H-n.m.r. spectra recorded using a Bruker 500 MHz *FT*-n.m.r. spectrometer. Samples were dissolved in deuterated trifluoacetic acid.

Thermal analysis was carried out from 30°C to 300°C at a heating rate of 10°C min^{-1} using a Perkin–Elmer DSC 7. Wide angle X-ray diffraction (WAXD) patterns were recorded on a Rigaku Denki diffractometer with Ni-filtered CuKα radiation.

4. Results and discussion

4.1. Analysis of sequence distribution

The PEN/PET random and block copolyesters were almost amorphous. Therefore the PEN/PET copolyesters were isothermally annealed and crystallized at 30°C below melting point (T_m) to attain a high degree of crystallinity. Tables 1 and 2 show the annealing condition of quenched PEN/PET random and block copolyesters.

The inherent viscosity and the density decrease at a similar composition ratio of PEN and PET in both random and block copolyesters. In the block copolyester, the inherent viscosity also decreases with blending time. These results will be explained afterwards in detail.

Fig. 1 shows the ethylene proton peak splitting of PEN/PET random copolyester containing 64.1 mol% DMT with using a 500MHz ^{1}H-n.m.r. spectrometer. All the ethylene proton resonances (4.8–5.2 ppm) of the
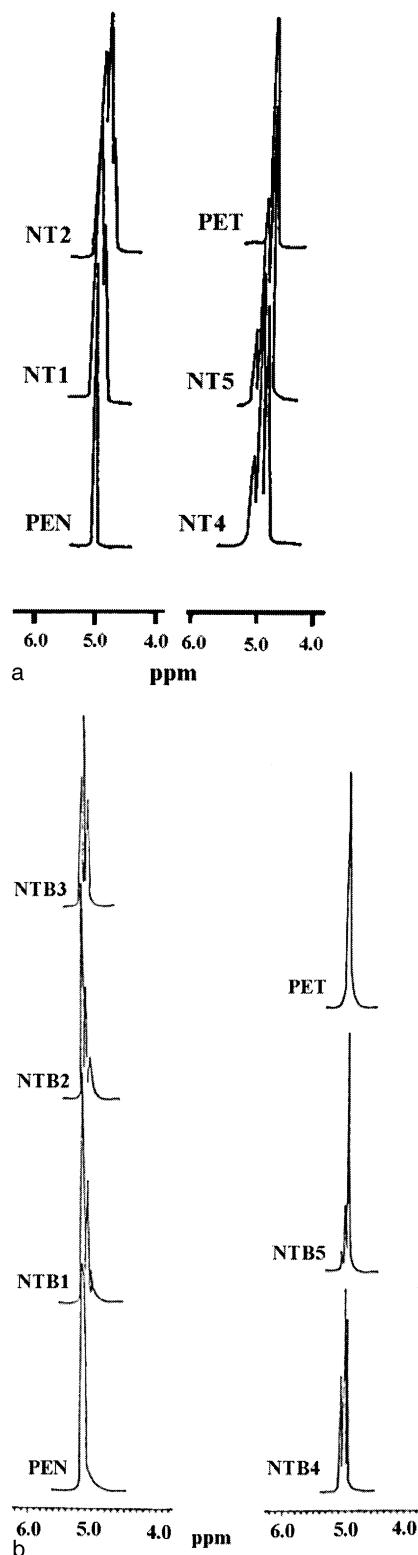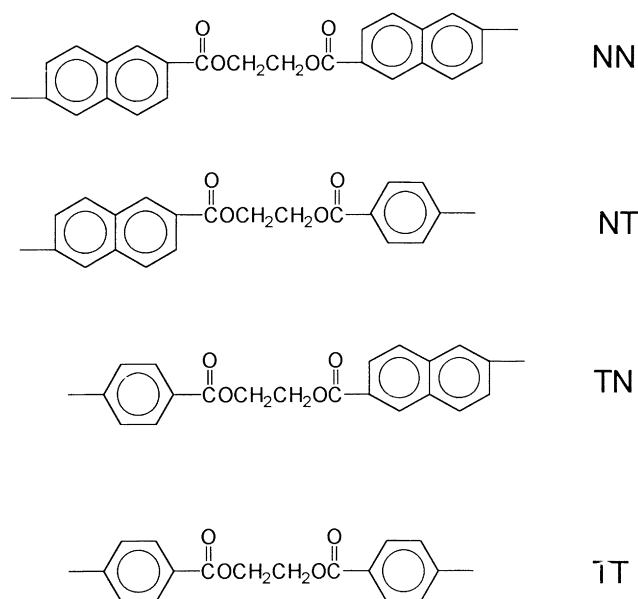

Fig. 2. Ethylene peak splitting of ^{1}H-n.m.r. spectra in PEN/PET copolyesters: (a) random; and (b) block (blending time is 60 min).

Scheme 1. Four possible environments for ethylene unit.

Table 3
Sequence distribution of PEN/PET random copolyesters

Random copolymer	DMT unit (mol%)	f_{NN}	$f_{NT} + f_{TN}$	f_{TT}	B	L_{nN}	L_{nT}
NT1	18.3	0.640	0.321	0.039	1.000	4.988	1.243
NT2	43.2	0.317	0.481	0.202	0.975	2.318	1.840
NT4	64.1	0.179	0.464	0.357	0.958	1.772	2.539
NT5	84.0	0.075	0.340	0.585	0.919	1.441	4.441

PEN/PET copolyesters are split into multiplets owing to four possible environments for ethylene unit: NN, TT, NT, and TN where N and T represent naphthalate and terephthalate units respectively, as shown in Scheme 1. The proton resolution peak at 4.95 ppm representing the amount of heterogenity, shows that NT and TN peaks of ethylene chain were overlapping each other. As shown in Fig. 2, it can be seen that the new ethylene proton signals such as NT and TN, are caused by the substitution of a naphthalate unit by a terephthalate unit. The dyads fraction (f_{NN}) corresponding to PEN decreases progressively, while the dyads fraction (f_{TT}) corresponding to PET increases in both random and block copolyesters.

According to Yamadera and Murano [12] the block length of the naphthalate (L_{nN}) and terephthalate unit (L_{nT}) as well as the probability (P_{NT} and P_{TN}) of finding a N (or T) unit next to a T(or N) unit, can be calculated from the integral intensities of the corresponding dyad fraction (f_{NN}, f_{NT} and f_{TN}) as shown in Tables 3 and 4.

$$P_{NT} = \frac{f_{NT}}{2P_N} = \frac{f_{NT}}{f_{NT} + 2f_{NN}} = \frac{1}{L_{nN}} \qquad (1)$$

$$P_{TN} = \frac{f_{TN}}{2P_T} = \frac{f_{TN}}{f_{TN} + 2f_{TT}} = \frac{1}{L_{nT}} \qquad (2)$$

Fig. 3 shows the changes of the dyads fraction for PEN/PET random and block copolyesters with DMT mole fraction and blending time. As shown in Fig. 3a and b, the values of ($f_{NT} + f_{TN}$) increase at a similar composition ratio in the random and block copolyesters, respectively.

In the block copolyesters, these results mean that the amount of hetero units in the copolyesters increases. Therefore we can define the value of $f_{NT} + f_{TN}$ as the degree of transesterification (DT) [15] in both cases:

$$DT = \frac{f_{NT} + f_{TN}}{f_{NN} + f_{NT} + f_{TN} + f_{TT}} = f_{NT} + f_{TN} \qquad (3)$$

Especially in the case of block copolyesters, the dyads fraction of PEN/PET block copolyesters of which DMT mole fraction is 14.5% increases with blending time as shown in Fig. 3c. It can be seen that the degree of transesterification increases with blending time.

The degree of randomness (B) can also be defined as the summation of two probabilities ($P_{NT} + P_{TN}$). For random copolyesters, B is unity. If B is less than unity, the units tend to cluster in blocks of each unit, and the value of B becomes zero in a mixture of homopolymer. If the value of B becomes 2, it means an alternating distribution.

Fig. 4 shows the randomness of PEN/PET random and block copolyesters. As shown in Fig. 4a, the randomness is independent of the DMT mole fraction in the random copolyesters which almost have a random distribution, but in block copolyesters, the randomness increases at a similar composition ratio of PEN and PET. The randomness of block copolyesters (NTB1) with blending time is shown in Fig. 4b. The tandomness of samples increases with blending time, and finally becomes close to unity which means random distribution.

It can be seen that the more the degree of transesterification increases, the more the randomness increases at a similar composition ratio and with blending time. The block length of PEN/PET random and block copolyesters is shown in Fig. 5. The block length of PEN/PET random and block copolyesters decreases at a similar composition ratio as shown in Fig. 5a and b.

It can be seen that the variation of block length in each

Table 4
Sequence distribution of PEN/PET random copolyesters

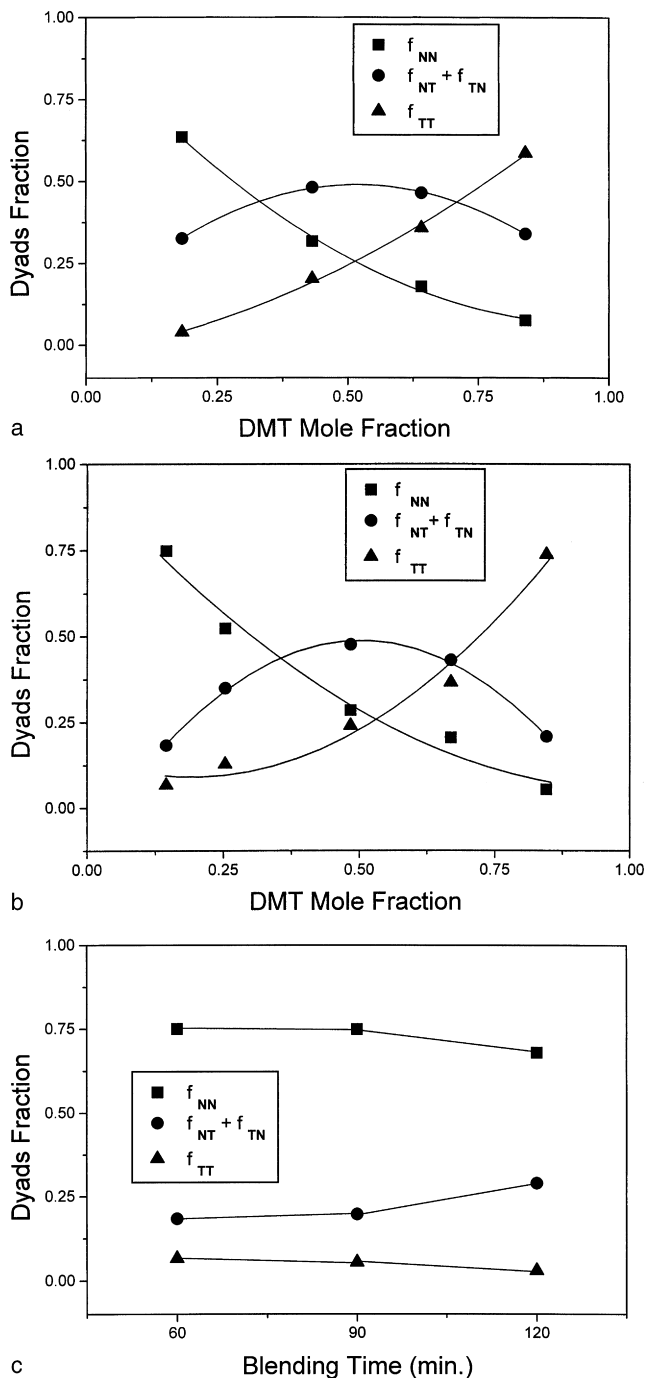| Block copolymer		DMT unit (mol%)	f_{NN}	$f_{NT} + f_{TN}$	f_{TT}	B	L_{nN}	L_{nT}
NTB1	60	14.5	0.750	0.184	0.066	0.692	9.152	1.717
	90	14.5	0.749	0.197	0.054	0.762	8.604	1.548
	120	14.5	0.680	0.290	0.030	1.000	5.670	1.207
NTB2-60		25.3	0.522	0.350	0.128	0.829	3.983	1.731
NTB3-60		48.4	0.285	0.475	0.240	0.952	2.200	2.011
NTB4-60		66.9	0.205	0.430	0.365	0.883	1.953	2.698
NTB5-60		84.5	0.054	0.209	0.737	0.783	1.517	8.053

a

b

c

Fig. 3. Dyads fraction of PEN/PET copolyesters: (a) random; (b) block (blending time is 60 min); and (c) NTB1 with blending time.
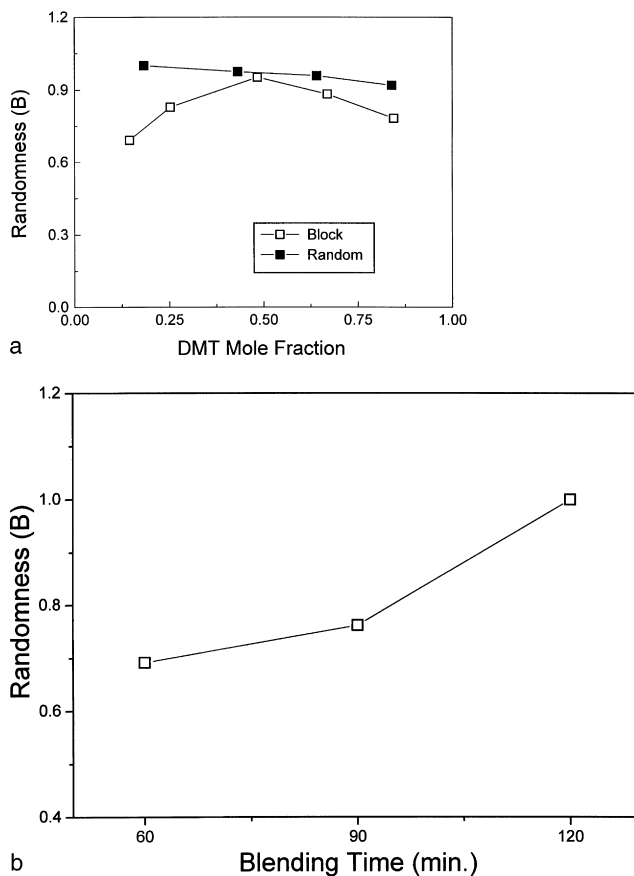

a

b

Fig. 4. Randomness of PEN/PET copolyesters: (a) random and block (blending time is 60 min); and (b) NTB1 with blending time.

4.2. Thermal property

DSC thermograms of the PEN/PET random and block copolyesters are shown in Fig. 6. In both the random and block copolyesters, melting point depressions occur with increasing content of the other component, and melting peaks disappear at a similar composition ratio as shown in Fig. 6a and b. Fig. 6c shows that the melting peaks decrease with blending time, and only the melting peak of PEN is observed. These results match well with those obtained for the block lengths.

On the basis of 3, if the value of block length is larger than 3, a melting peak is observed, but in the case of less than 3, no melting peak is observed.

Hence, we correlated the sequence length of each PEN/PET copolyester with Flory's equation to explain the above phenomena. If so, when N (or T) sequence units in the random copolyesters crystallize but T (or N) sequence units are exactly excluded from crystal formation, the melting point can be expressed as a function of composition.

Flory [16] proposed that the melting temperature depression can be expressed by

unit has a close relation to the change of chemical structure, especially intermolecular chain reactions which means a transesterification reaction between two polymers. In Fig. 5c, the values obtained for the block length of PEN/PET block copolyesters show that L_{nN} decreases clearly with blending time, but L_{nT} decreases slightly from the initial blending time. It seems that the block length of the rich component is more affected than that of the poor component by the transesterification reaction.

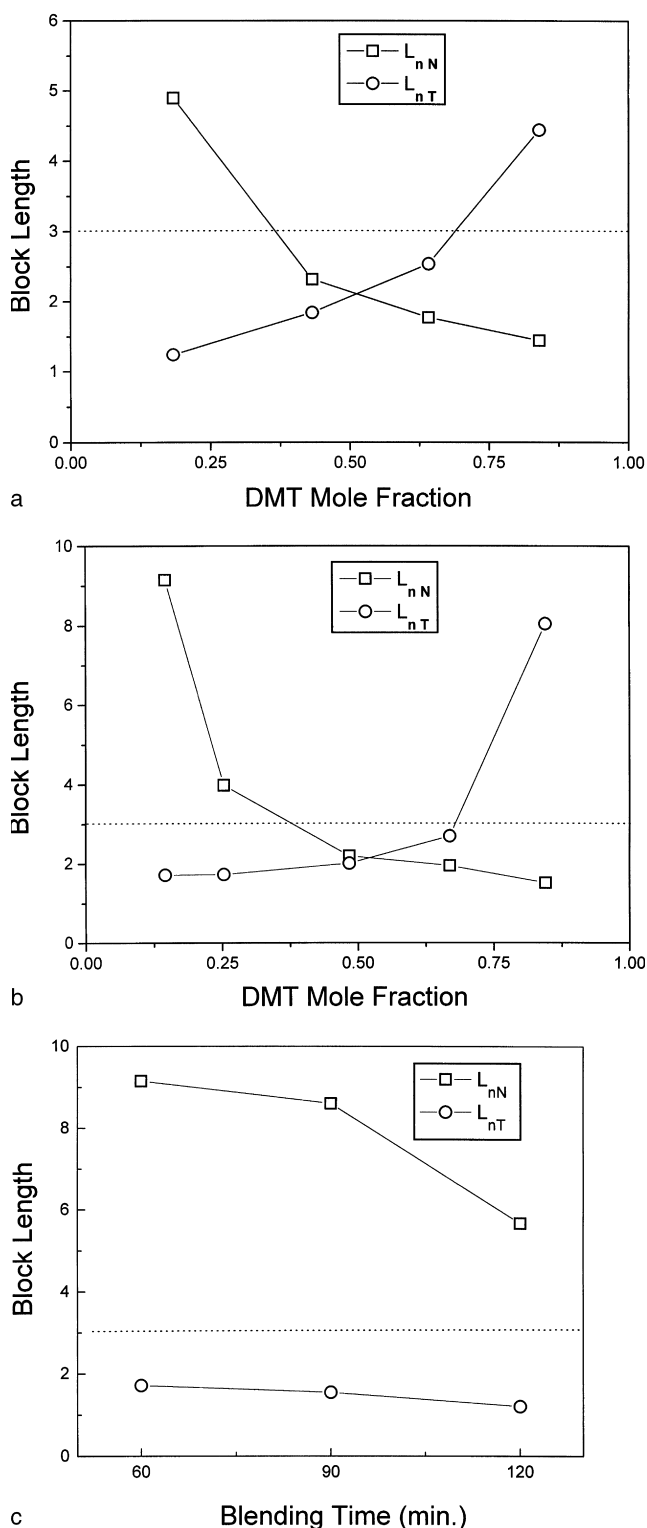$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\left(\frac{R}{\Delta H_f}\right) In P(= X_a) \tag{4}$$

Fig. 5. Block length of PEN/PET copolyesters: (a) random; (b) block (blending time is 60 min); and (c) NTB1 with blending time.

where T_m and T_m^0 are the melting temperature at the mole fraction (X_a) corresponding to random copolyesters and homopolymers respectively, R is the gas constant (8.314 J mol^{-1}) and H_f is the enthalpy of fusion per repeating unit. Here, H_f is taken as 25 kJ mol^{-1} for PEN and PET. The sequence propagation probability (P) can also be substituted by mole fractions (X_a).

If $P \gg X_a$, block copolyester is formed, $P \ll X_a$ in alternating copolymers and $P = X_a$ in random copolyesters [17]. If two sequence units could be crystallized independently and simultaneously in each crystal formation or be cocrystallized together, P could also be represented as $f_{NN} + f_{TT}$. However, when only the N or T sequence unit is crystallized, P can also be represented by f_{NN} or f_{TT}. Fig. 7 shows the melting temperatures of PEN/PET random copolyesters at various compositions. Because these results correspond to the P values representing lone crystallization of one component excluding the other component, it can be seen that only one component in the PEN/PET random copolyesters is crystallized.

Considering the relatively good fit of experimental values that mean $P = f_{NN}$ or f_{TT}, it can be seen that the melting point depression is a result of reduction of block length and the minimum points in the melting temperature correspond to the points having the short average sequence length in the copolyesters.

4.3. Crystallization behaviour

WAXD diffractograms for the PEN/PET random and block copolyesters are shown in Fig. 8. For the PEN homopolymer, the peak at the diffraction angle of 15.5° is assigned to (010) plane while those at diffraction angles of 23.4° and 26.8° correspond to (100) and ($\bar{1}$10) planes[18]. These peaks are also observed in the NT1 for random copolyesters as well as in NTB1 and NTB2 for block copolyesters. In the case of both random and block, only the rich component can be crystallized.

The crystal lattice transitions occur exactly in between NT2 and NT4 for the random copolyesters as well as between NTB3 and NTB4 for the block copolyesters

Briber and Thomas [19] insisted that the whole sequence lengths participate in crystal formation. In contrast, Zhu and Wegner [20] asserted that only the longer sequence length excluding the shorter sequence length was crystallized.

The peaks of crystallinity disappear at a similar composition ratio of PEN/PET in the both random and block copolyesters. These results match well with those of dyads, fraction, block length, and DSC.

Our study has found that the critical sequence length is needed for components in order to crystallize. It is well accepted that the crystal formation in PEN/PET copolyesters is related to the sequence length.

5. Conclusion

The relationship, between sequence distribution and transesterification of PEN/PET random/block copolyesters including crystallization and thermal behaviour was
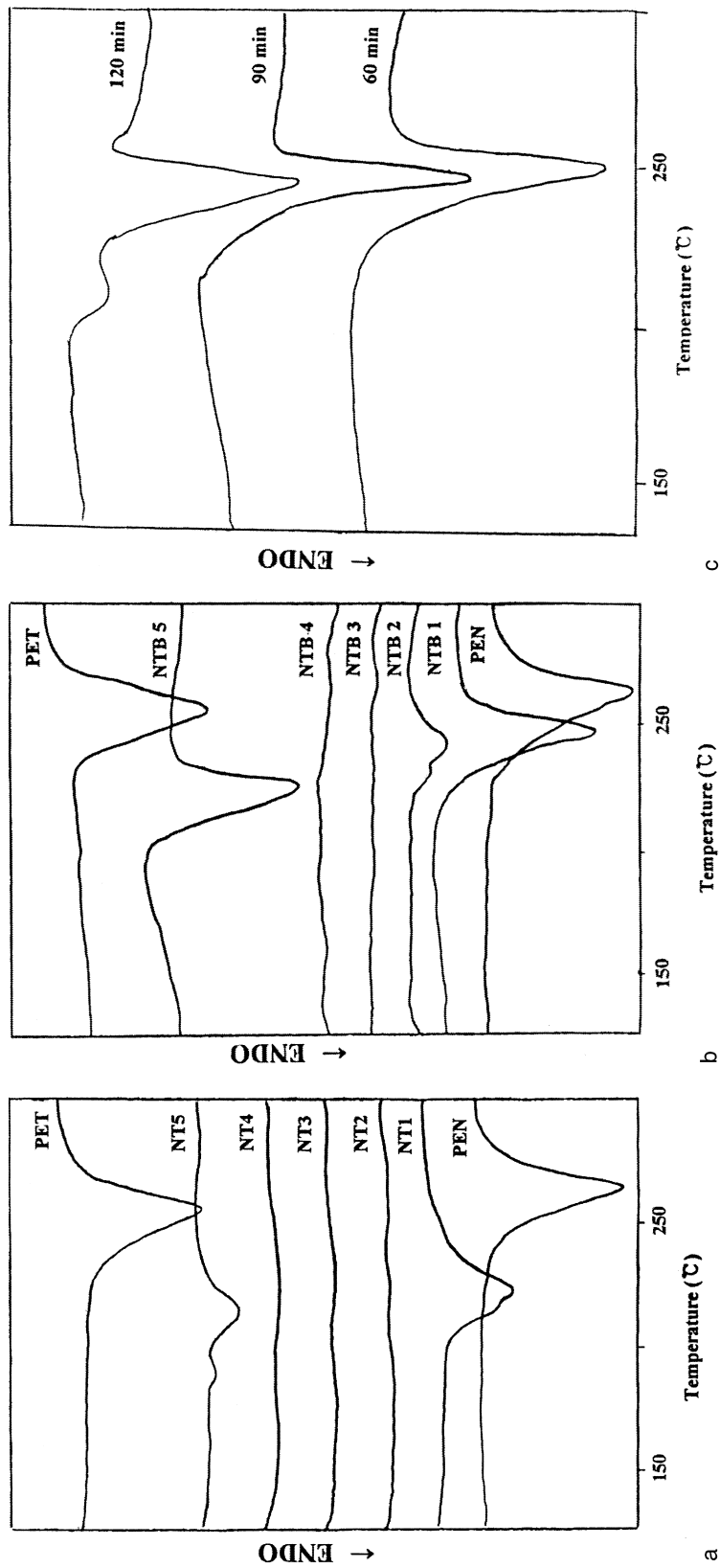
Fig. 6. DSC thermogram of PEN/PET copolyesters: (a) random; and (b) block (blending time is 60 min); and (c) NTB1 with blending time.
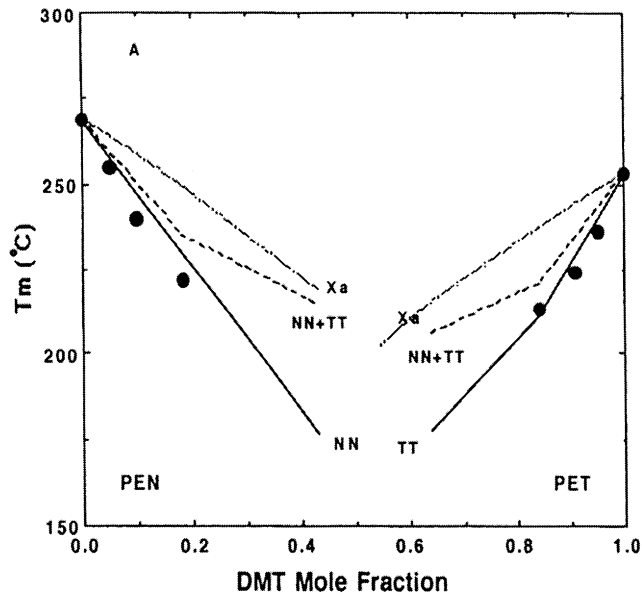
Fig. 7. Melting temperature (T_m) of PEN/PET random copolyesters.

investigated. At a similar composition ratio and with blending time, the degree of transesterification increases but the block length decreases. The melting peak depressions occur with increasing content of the other component and the melting peaks disappear at a similar composition ratio. Because the crystal peaks of PEN/PET random and block copolyesters disappear at a similar composition ratio, it can be seen that a critical block length is needed for components in order to crystallize.

Acknowledgements

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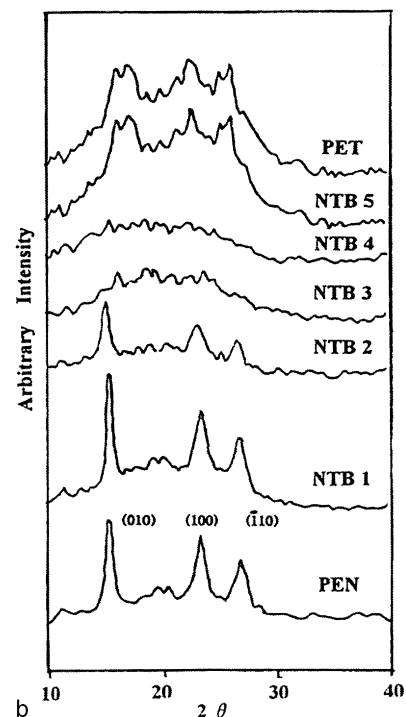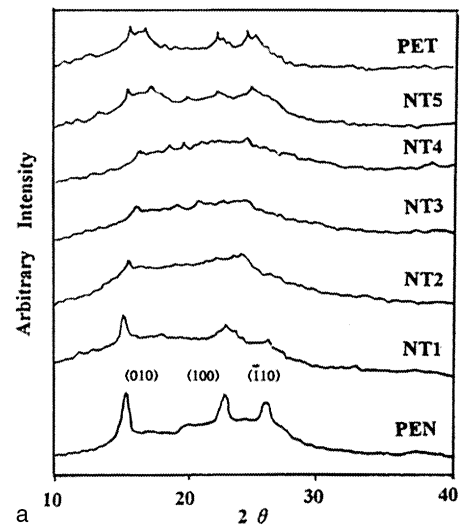[12] Yamadera R, Murano N. J Polym Sci 1967;5:2259.

Fig. 8. X-ray diffraction pattern of PEN/PET copolyesters: (a) random; and (b) block (blending time is 60 min).

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