

Sequence Distribution and Crystallization Behavior on Block Copolyesters of Poly(butylene glutarate-co-adipate-co-succinate) Ternary Random Copolyester and Poly(butylene terephthalate)

Sang Soon PARK and Hye Jung KANG[†]

Organic Chemistry Division, National Institute of Technology and Quality, 2, Joongang-dong, Kwachen, Kyunggi-do 427-010, Republic of Korea

(Received July 21, 1998)

ABSTRACT: PB(GAS)/PBT block copolyesters of poly(butylene glutarate-co-adipate-co-succinate), PB(GAS), and poly(butylene terephthalate), PBT, were prepared by molten-state processing for different times. The degree of randomness, melting temperature, and crystallization behavior for these copolyesters were studied by means of ¹H NMR spectroscopy, DSC, and wide angles X-ray diffraction. Average block length, \overline{Ln}_{Al} and \overline{Ln}_{Ar} , of aliphatic and aromatic sequences obviously decreased with mixing time. Melting points also moved to lower temperature with mixing time. PB(GAS) sequences in copolyesters were completely excluded from the crystal formation of block copolyesters.

KEY WORDS Poly(butylene terephthalate) / Poly(butylene glutarate-co-adipate-co-succinate) / Block Copolyester / Sequence Distribution / Transesterification / Crystallization Behavior /

A group of polyesters, that are biodegradable, has recently become of remarkable interest as they provide an alternative to conventional waste management. Among different naturally occurring and synthetic polymeric materials, supposed to be potentially biodegradable, synthetic polyesters have been widely investigated.¹ One successfully developed material is aliphatic polyester.

The determination of the sequence distribution of block and/or random copolymers² is important in relation to the basic properties such as melting temperature and mechanical properties and so on. Although many measurements,³⁻¹⁰ such as those by ¹H or ¹³C NMR, have been carried out on the sequence distribution of binary copolyesters, there are only a few reports on ternary copolyesters owing to the difficulty in spectral assignments.¹¹

While aliphatic ternary random copolyesters such as poly(butylene glutarate-co-adipate-co-succinate), PB(GAS), exhibit good biodegradability, these materials

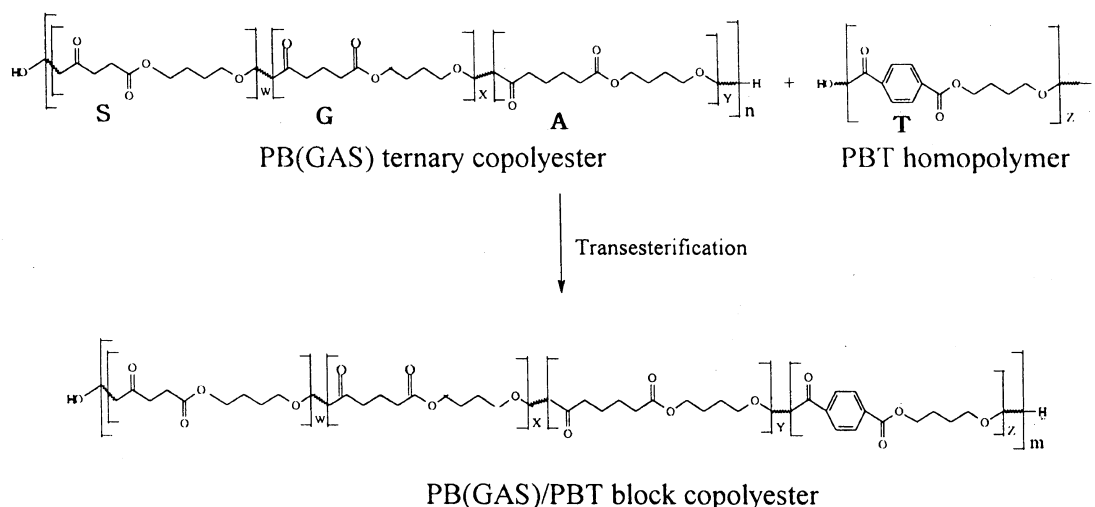
usually lack suitable properties, e.g., melting point or mechanical properties. For improving material characteristics, aromatic polyesters such as poly(butylene terephthalate), PBT, can be introduced into aliphatic-based ternary copolyesters, although biodegradability changes somewhat depending on the aromatic unit.

In the present study, PB(GAS)/PBT block copolyesters of PB(GAS) ternary random copolyester and PBT, were prepared by melt processing for different times and investigated at different sequence distributions, thermal properties, and crystallization behavior.

EXPERIMENTAL

Synthesis of PB(GAS) Copolyester

Dimethyl glutarate (DMG, Aldrich), dimethyl adipate (DMA, Aldrich), dimethyl succinate (DMS, Aldrich), and 1,4-butane diol (BD, Aldrich) as starting materials were of commercial grade, and titanium tetrabutoxide (2×10^{-3} mol mol⁻¹ diesters, Aldrich) and zinc acetate



Scheme 1. Structural formula of PB(GAS)/PBT block copolyester.

[†] To whom correspondence should be addressed.

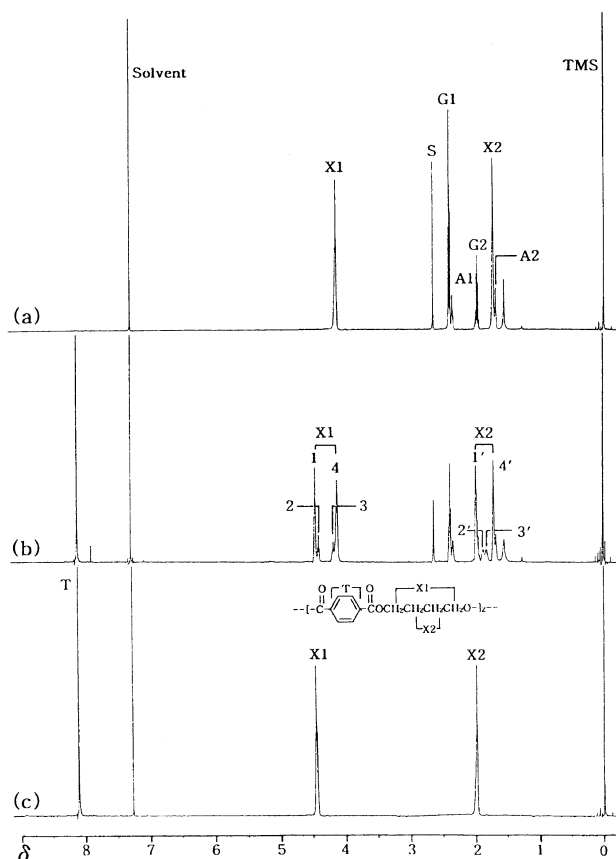


Figure 1. 500 MHz ^1H NMR spectra: (a) PB(GAS), (b) T50-40 (PBT 44.2 mol%, mixing time 40 min), and (c) PBT homopolymer.

dihydrate (6×10^{-4} mol mol $^{-1}$ diesters, Junsei) as catalysts were used without further purification. An appropriate mixture (DMG 0.62 mol, DMA 0.15 mol, and DMS 0.23 mol) of dibasic ester (DBE, Du Pont), BD (1.70 mol), and two catalysts were also introduced into the reaction vessel in order to obtain bishydroxybutyl-(glutarate-*co*-adipate-*co*-succinate), BHB(GAS), and it is cooligoester.

The transesterification of dibasic ester and BD was carried out with agitation at 200°C for 2 h. After 2 h, methanol evolution ceased and BHB(GAS), and cooligoesters were obtained. In the second step, BHB(GAS) cooligoesters (200 g), antimony trioxide (1.5×10^{-6} mol g $^{-1}$ cooligoesters), as a catalyst, trimethyl phosphate (1.0×10^{-6} mol mol $^{-1}$ cooligoesters), as a thermal stabilizer, and cobalt acetate dihydrate (2.0×10^{-7} mol g $^{-1}$ diesters), as a control agent, were introduced into a 500 mL polymerization tube and the polycondensation was carried out at 250°C for 3 h. The vacuum was lowered from 760 mmHg to 1 mmHg over 30 min. PB(GAS) ternary random copolyesters formed were quenched into cold water and dried in vacuum.

Preparation of PB(GAS)/PBT Block Copolyesters

All PB(GAS)/PBT block copolyesters used in this study were prepared by molten-state mixing under vacuum from PB(GAS) and PBT without catalyst, as shown in Scheme 1. Two polyesters were preheated for 10 min. Agitation started with increasing speed from 10 to 120 rpm gradually for 10 min and then the reaction was finished by interval time, 20, 40, and 60 min.

Table I. Proton signal assignments of PBG, PBA, PBS, PBT, PB(GAS), and PB(GAS)/PBT block copolyesters

Symbol	Chemical shifts (ppm) from TMS					
	PBG ^a	PBA ^b	PBS ^c	PBT ^d	PB(GAS) ^e	T50-40 ^f
G1	2.37	—	—	—	2.37	2.37
G2	1.94	—	—	—	1.94	1.94
A1	—	2.32	—	—	2.33	2.33
A2	—	1.66	—	—	1.66	1.66
S	—	—	2.62	—	2.64	2.64
T	—	—	—	8.09	—	8.09
X1	4.10	4.11	4.10	4.43	4.11	4.10–4.43
X2	1.70	1.70	1.71	1.97	1.70	1.70–1.97

^a Poly(butylene glutarate). ^b Poly(butylene adipate). ^c Poly(butylene succinate). ^d Poly(butylene terephthalate). ^e Poly(butylene glutarate-*co*-adipate-*co*-succinate). ^f Block copolymer of PB(GAS) and PBT.

Byproducts, such as 1,4-butane diol, tetrahydrofuran, and water, can be removed by applying vacuum.

PB(GAS)/PBT block copolyesters formed were quenched into cold water and dried in vacuum. Block copolymers were isothermally annealed at 45°C for 180 min to get the highest degree of crystallinity.

Analysis of Block Copolyesters

Inherent viscosity was measured in dichloroacetic acid with a Ubelohde viscometer at $25 \pm 0.1^\circ\text{C}$ (1 g dL $^{-1}$). Data of 500 MHz ^1H NMR spectrum were obtained by dissolving each sample in CDCl $_3$. Differential scanning calorimetry (DSC) studies on the thermal property were performed by an updated computer-interfaced Rheometric Scientific Co. The samples were scanned from 30 to 300°C with heating rate of 10°C min $^{-1}$. The wide angle X-ray diffraction (WAXD) observation of the samples was carried out by a Rigaku X-ray generator with a 12 kW rotating anode as the source of the incident X-ray beam.

RESULTS AND DISCUSSION

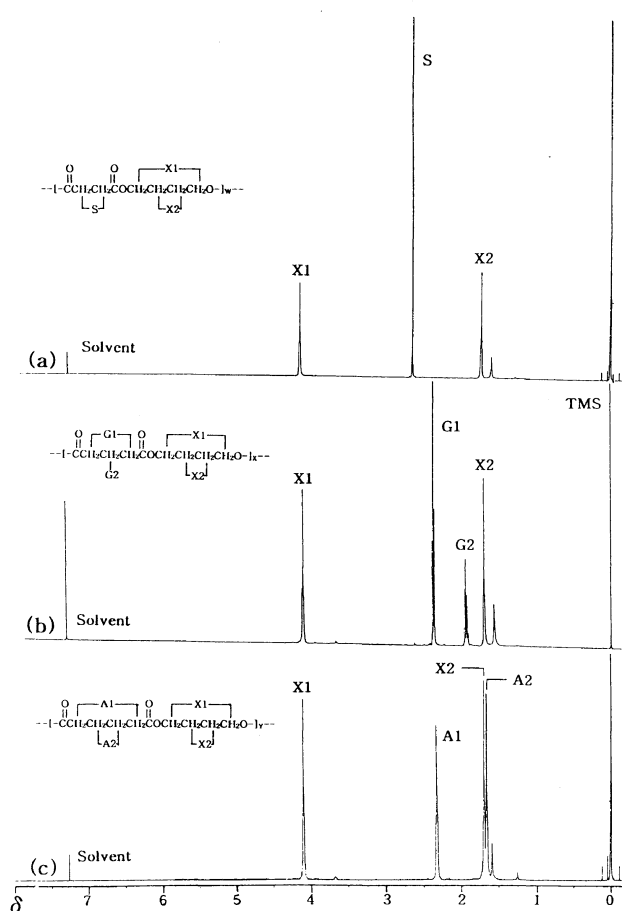
Copolymer Composition and Its Sequence Distribution^{5–10}

Figure 1 shows the 500 MHz ^1H NMR spectra of PB(GAS) ternary random copolyester, T50-40 as a blend of PB(GAS)/PBT (PBT 44.2 mol%, mixing time 40 min), and PBT. Assignments of proton signals obtained from the NMR spectra are listed in Table I together with chemical shifts of aliphatic homopolymers, poly(butylene succinate) (PBS), poly(butylene glutarate) (PBG), and poly(butylene adipate) (PBA) (see Figure 2). Peaks at 2.37, 1.94, 2.33, 1.66, 2.64, 4.11, and 1.70 ppm were assigned to proton signal of PB(GAS) ternary random copolyester. Peaks at 8.09, 4.43, and 1.97 ppm were assigned to proton signal of PBT. The diester compositions of PB(GAS)/PBT block copolyesters with mixing time were determined by NMR spectroscopy, as listed in Table II.

Figure 2 represents the ^1H NMR spectra of PBS, PBG, and PBA as fundamental materials of PB(GAS) ternary random copolyesters. The positions of methylene proton signals are at 2.37 and 1.94 ppm for glutarate, adipate at 2.32 and 1.66 ppm for adipate, and at 2.62 ppm for succinate. Figure 1(a) shows two characteristic peaks,

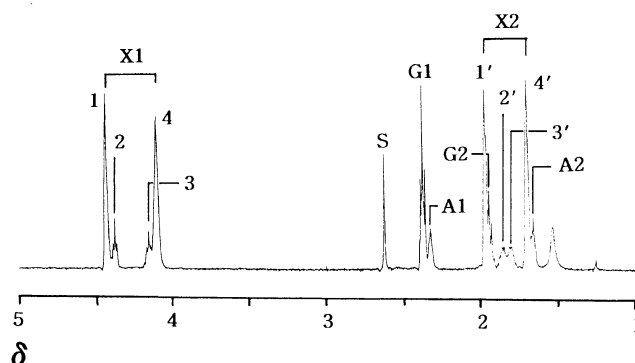
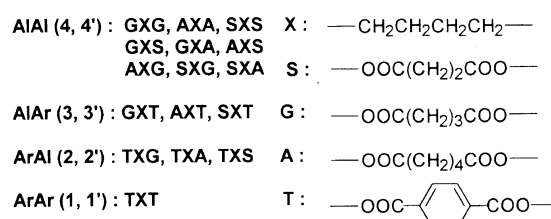
Table II. Mixing conditions, composition, and inherent viscosity of PB(GAS)/PBT block copolyesters

Copolymer	Mixing time min	Polymer feed composition/wt%		Diester compositions in block copolyesters/mol%				Inherent viscosity dL g ⁻¹
		PB(GAS)	PBT	Succinate	Glutarate	Adipate	Terephthalate	
PB(GAS)	—	100	0	21.0	61.5	17.5	0.0	0.673
T20-20	20	80	20	16.1	49.2	15.3	19.5	0.548
T20-40	40	80	20	15.8	48.6	14.2	21.3	0.565
T20-60	60	80	20	15.0	46.9	17.7	20.4	0.563
T40-20	20	60	40	11.9	35.4	10.4	41.3	0.556
T40-40	40	60	40	12.3	37.2	11.3	39.2	0.559
T40-60	60	60	40	11.9	36.6	10.2	41.4	0.529
T50-20	20	50	50	12.3	36.4	13.0	38.4	0.473
T50-40	40	50	50	11.2	33.7	10.8	44.2	0.494
T50-60	60	50	50	9.8	30.8	9.3	50.0	0.444
T60-20	20	40	60	8.7	28.6	9.6	53.1	0.464
T60-40	40	40	60	8.4	26.3	8.4	56.9	0.520
T60-60	60	40	60	8.2	27.0	8.2	56.6	0.435
PBT	—	0	100	0	0	0	100.0	0.748

**Figure 2.** 500 MHz ¹H NMR spectra: (a) PBS homopolymer, (b) PBG homopolymer, and (c) PBA homopolymer.

X1 and X2, related to butylene unit in PB(GAS) ternary random copolyester. Unfortunately the butylene proton position of PB(GAS) ternary random copolyester is very similar to that of aliphatic homopolymers because of the overlap of butylene proton signal in PBG, PBA, and PBS, as shown in Figure 2.

The butylene proton signals located at 4.10–4.43 ppm as well as 1.70–1.97 ppm are split into multiples owing to four possible environments for the butylene unit; homo-unit, A1A1 and ArAr, and hetero-unit, A1Ar and ArA1.

**Figure 3.** Butylene proton peak splitting of ¹H NMR spectrum in T50-40, a blend of PB(GAS) and PBT.

In truth, the transesterification between PB(GAS) ternary random copolyester and PBT will generate sixteen types of butylene units (-X-), including 10 homolinkage and 6 heterolinkage, as shown in Figure 3. Nine homolinkages are GXG, AXA, SXS, GXS, GXA, AXG, AXS, SXG, and SXA, adjacent to aliphatic unit at both side, one is TXT, adjacent to aromatic unit at both side. Six heterolinkages are GXT, AXT, SXT, TXG, TXA, and TXS, adjacent to aliphatic and aromatic units.

No splitting was observed in the proton signals (GXG, AXA, SXS, GXS, GXA, AXG, AXS, SXG, and SXA) of the butylene units in PB(GAS) ternary random copolyester because of the reiteration of chemical shifts in PBG, PBA, and PBS.

We thus suggest 4 groups of sequence again and put an abbreviated mark, A1A1, A1Ar, ArA1, and ArAr, on the signals due to homolinkages and heterolinkages, as listed in Figure 3.

Several papers on sequence distribution analysis in copolymers studied by NMR spectroscopy have already been described in the literature. These investigations showed that such determinations are possible when chemical shifts of the homolinkages and heterolinkage are sufficiently different.

Figure 4 shows the ^1H NMR spectra of the butylene proton signals, X1, splitting around 4.10–4.43 ppm with melt processing time in T50 as a blend of PB(GAS) and PBT. The two new proton signals at 4.15 and 4.38 ppm are due to the substitution of an aliphatic diester unit for a terephthalate unit and *vice versa*, respectively as discussed above. This reveals how much transesterification between PB(GAS) ternary random copolyester, as aliphatic diesters, and PBT occurred. With increasing mixing time, the degree of transesterification increased

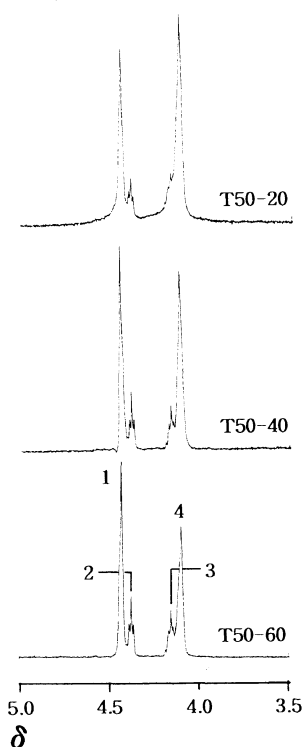


Figure 4. Butylene proton peak splitting of ^1H NMR spectra for T50 with mixing time.

considerably.

Figure 5 shows the NMR spectra of the butylene proton signals, X1, with change of the PBT composition ratios in PB(GAS)/PBT copolyesters. With increasing PBT in copolymers, the relative intensity of the butylene proton signal due to aromatic diesters at 4.43 ppm increased more than that of the butylene proton signal at 4.10 ppm due to aliphatic dibasic esters. Of course, two proton signals are bonded to the different dibasic esters at both sides of butylene unit were observed at 4.38 and 4.10 ppm.

From the results of PB(GAS)/PBT including the above data of Figures 4 and 5, the fractions of dyads, f_{AlAl} , f_{AlAr} , f_{ArAl} , and f_{ArAr} , centered on butylene unit were calculated from the relative integrated intensities, A_{AlAl} , A_{AlAr} , A_{ArAl} , and A_{ArAr} , on the basis of the proton signals mentioned above, as listed in Table III.

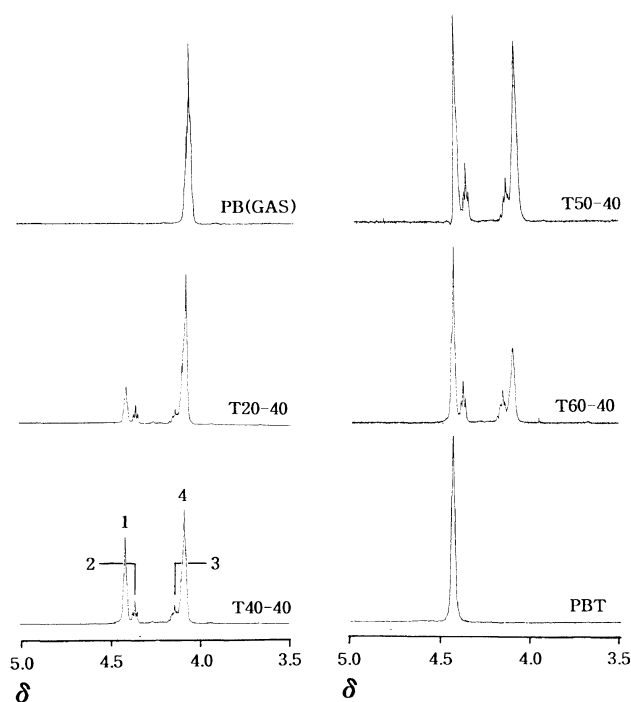


Figure 5. Butylene proton peak splitting of ^1H NMR spectra with PBT composition ratios in PB(GAS)/PBT block copolyesters.

Table III. Relative intensity at butylene proton signals and fractions of dyads of PB(GAS)/PBT block copolyesters

Copolymer	Relative intensity (arbitrary unit) at butylene proton (X1) signals/ppm				Fractions of dyads centered on butylene proton (X1)		
	A_{AlAl} at 4.11	A_{AlAr} at 4.15	A_{ArAl} at 4.38	A_{ArAr} at 4.43	f_{AlAl}	$f_{\text{AlAr}} + f_{\text{ArAl}}$	f_{ArAr}
PB(GAS)	3.423	—	—	—	1.000	—	—
T20-20	3.728	0.234	0.232	0.770	0.751	0.094	0.155
T20-40	4.998	0.419	0.417	1.000	0.731	0.122	0.146
T20-60	6.044	0.683	0.683	1.000	0.719	0.162	0.119
T40-20	1.566	0.203	0.199	1.070	0.515	0.132	0.352
T40-40	1.731	0.264	0.266	1.050	0.523	0.160	0.317
T40-60	1.567	0.365	0.361	1.000	0.476	0.220	0.304
T50-20	1.371	0.237	0.231	0.852	0.509	0.174	0.317
T50-40	1.045	0.230	0.228	0.823	0.449	0.197	0.354
T50-60	0.784	0.245	0.245	0.792	0.379	0.237	0.383
T60-20	0.900	0.172	0.168	1.150	0.377	0.142	0.481
T60-40	0.740	0.275	0.265	1.10	0.522	0.227	0.462
T60-60	0.559	0.204	0.202	0.80	0.317	0.230	0.453
PBT	—	—	—	4.38	—	—	1.000

Table IV. Parameters calculated from Table III

Copolymer	PBT content	Mole fractions of diesters		Probability of finding unit		Average block length		Randomness
	mol%	P_{Al}	P_{Ar}	P_{AlAr}	P_{ArAl}	Ln_{Al}	Ln_{Ar}	R
PB(GAS)	0.0	1.000	0.000	—	—	—	—	—
T20-20	19.5	0.798	0.202	0.06	0.23	17.00	4.30	0.29
T20-40	21.3	0.793	0.207	0.08	0.30	12.96	3.39	0.38
T20-60	20.4	0.800	0.200	0.10	0.41	9.85	2.46	0.51
T40-20	41.3	0.582	0.418	0.11	0.16	8.79	6.32	0.27
T40-40	39.2	0.603	0.397	0.13	0.20	7.53	4.96	0.33
T40-60	41.4	0.586	0.414	0.19	0.27	5.32	3.75	0.46
T50-20	38.4	0.596	0.404	0.15	0.22	6.86	4.64	0.37
T50-40	44.2	0.548	0.452	0.18	0.22	5.56	4.59	0.40
T50-60	50.0	0.498	0.502	0.24	0.24	4.20	4.23	0.48
T60-20	53.1	0.448	0.552	0.16	0.13	6.29	7.76	0.29
T60-40	56.9	0.424	0.576	0.18	0.20	5.60	5.07	0.38
T60-60	56.6	0.432	0.568	0.27	0.20	3.75	4.94	0.47
PBT	100.0	0.000	1.000	—	—	—	—	—

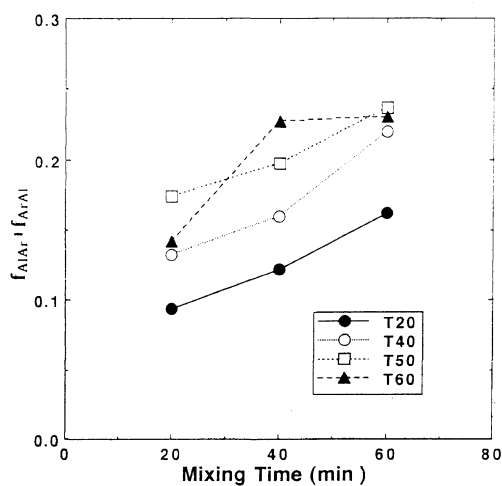


Figure 6. Relationship between fractions of dyads, $f_{AlAr} + f_{ArAl}$, and mixing time of PB(GAS)/PBT block copolyesters.

Using the fractions of dyads, we calculated the mole fractions, P_{Al} and P_{Ar} , of aliphatic and aromatic dibasic esters, the probability, P_{AlAr} and P_{ArAl} , of finding an aliphatic (or aromatic) unit next to an aromatic (or aliphatic) unit, the average block length, Ln_{Al} and Ln_{Ar} , of aliphatic and aromatic sequences, and the degree of randomness, R , calculated by eq 1–3 suggested by Yamadera and Murano.¹⁰

$$P_{Al} = \frac{1}{2} (f_{AlAr} + f_{ArAl}) + f_{AlAl},$$

$$P_{Ar} = \frac{1}{2} (f_{AlAr} + f_{ArAl}) + f_{ArAr} \quad (1)$$

$$\overline{Ln}_{Al} = \frac{2P_{Al}}{f_{AlAr} + f_{ArAl}} = \frac{1}{P_{AlAr}},$$

$$\overline{Ln}_{Ar} = \frac{2P_{Ar}}{f_{AlAr} + f_{ArAl}} = \frac{1}{P_{ArAl}} \quad (2)$$

$$R = P_{AlAr} + P_{ArAl} \quad (3)$$

The characteristic parameters obtained from above eq 1–3 are shown in Table IV. Figure 6 shows the relationships between the fractions of dyads and mixing

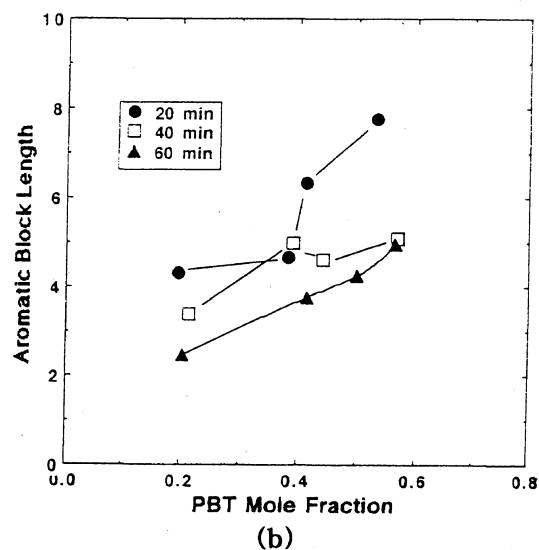
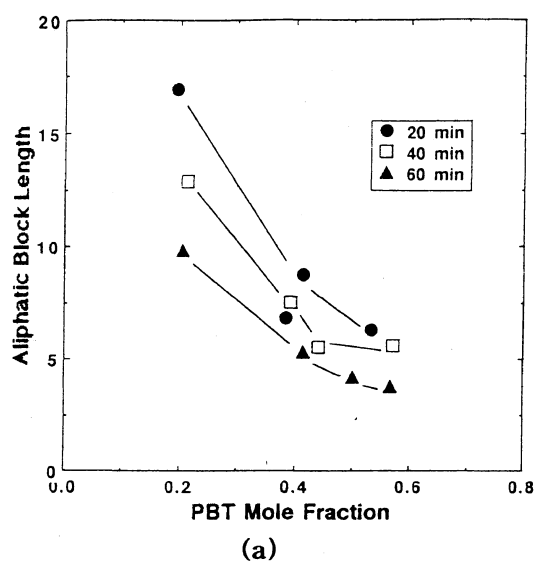


Figure 7. Relationship between average block length and PBT composition ratio in PB(GAS)/PBT block copolyesters with mixing time.

time with change of PBT composition ratios in block copolyesters. The values of the fractions of dyads increased with mixing time and PBT ratio in copolyesters.

Figure 7 shows the average block length, including aliphatic and aromatic unit, with PBT composition ratios in PB(GAS)/PBT block copolyesters. The average block length of aliphatic sequence diminished remarkably as mixing time and PBT content in copolyester increased. The average block length of aromatic sequence decreased with mixing time whereas average block length of aromatic sequence seems to increase generally with PBT content in copolyester.

Figure 8 shows changes of the degree of randomness with mixing time for PB(GAS)/PBT block copolyesters. Randomness increased with mixing time, regardless of variation of PBT content in copolymers. The velocity of transesterification reaction between PB(GAS) and PBT depends on mixing time and PBT composition ratio in copolyesters.

Thermal Properties

Using DSC, the thermal properties of PB(GAS)/PBT

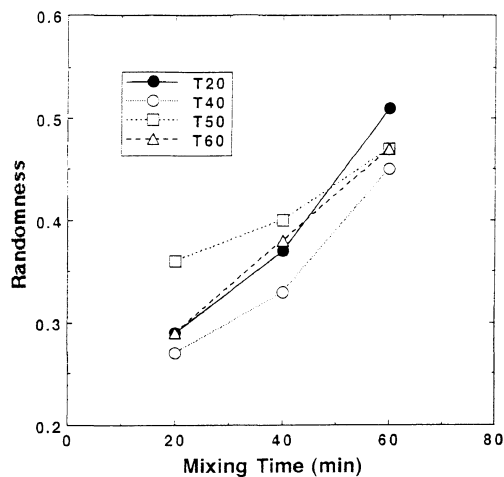
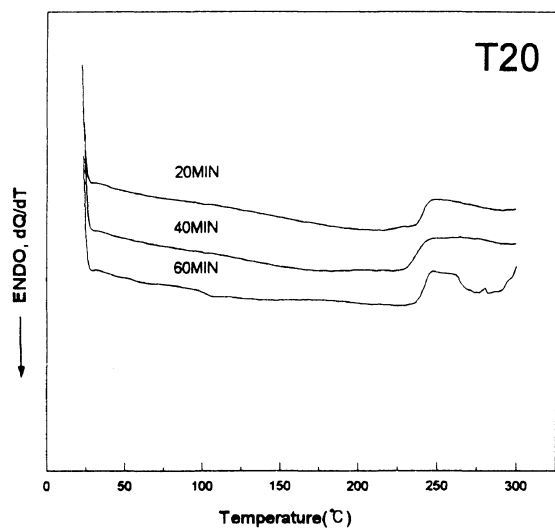
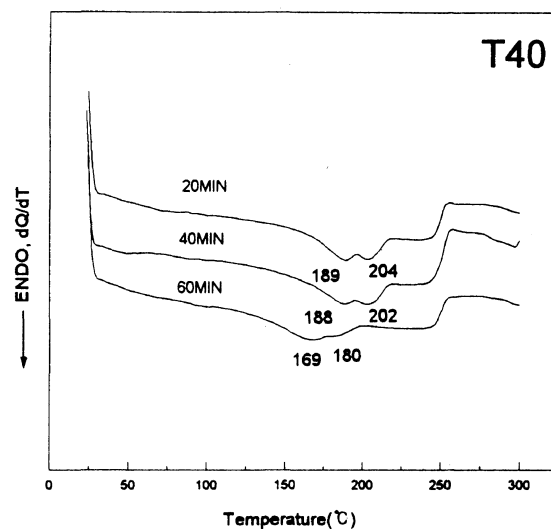


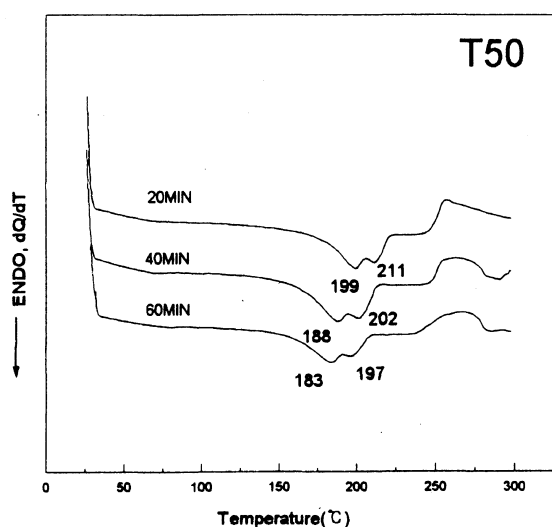
Figure 8. Relationship between randomness and mixing time of PB(GAS)/PBT block copolyesters.



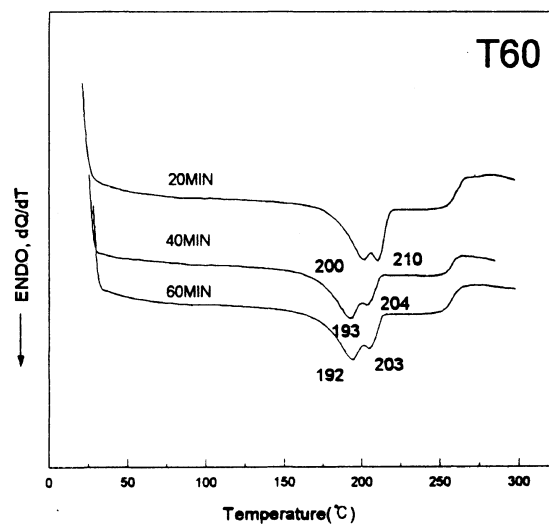
(a)



(b)



(c)



(d)

Figure 9. DSC curves of PB(GAS)/PBT block copolyesters with mixing time.

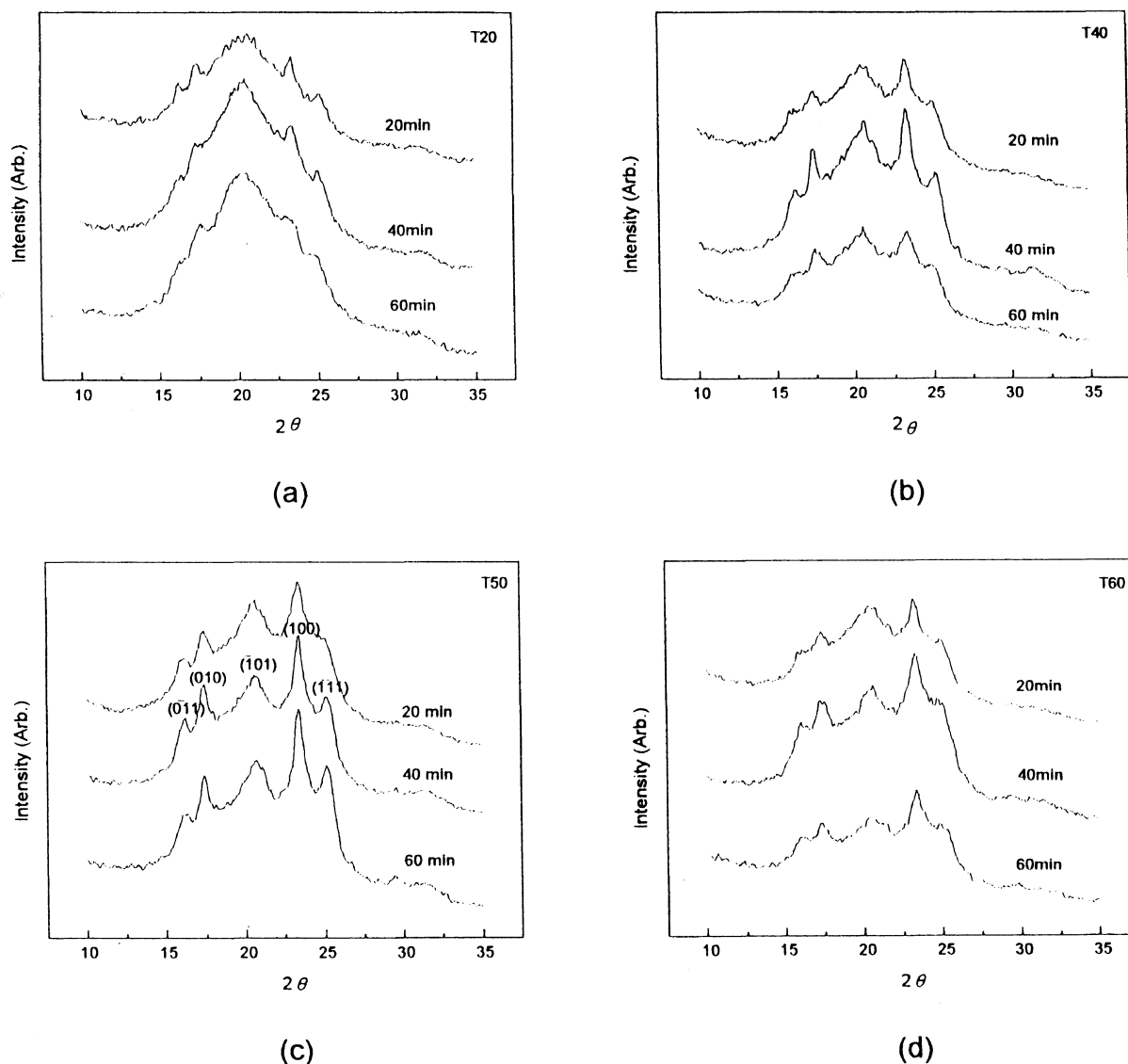


Figure 10. WAXD curves of PB(GAS)/PBT block copolyesters with mixing time.

block copolyesters were measured. The block copolyesters were annealed at 45°C for 180 min. Figure 9 shows DSC curves of PB(GAS)/PBT copolyesters with mixing time. PB(GAS) ternary random copolyester is an amorphous random copolyester. In the case of T20, no melting peak was observed for different mixing times, as shown in Figure 9(a). T40-20, molten for 20 min, shows two endothermic peaks at the temperatures of 189 and 204°C, as shown in Figure 9(b). With increasing mixing time, the melting peak gradually moves to lower temperature. The lower one can be attributed to the melting of PBT crystal related to PB(GAS) ternary random copolyester, and the other to that of pure PBT crystal. For these phenomena, Yoo *et al.*⁴ suggest that the lower one may be associated with crystals formed during the cooling process after isothermal crystallization but the other, to crystals formed by isothermal crystallization.

Similar results were obtained for T50 and T60 copolyesters, as shown in Figure 9(c) and (d). Accordingly, the decrease of melting peak with mixing time can be explained by assuming an intermolecular chain reaction, so called transesterification, between PB(GAS)

and PBT leads to a random copolyester. PB(GAS)/PBT block copolyesters except T20, molten for 60 min, show two endothermic peaks including a shoulder, as shown in Figure 9. With increasing the composition ratio of PBT unit in copolyester, the melting peak gradually moves to a high temperature, and the heat of fusion becomes more intense.

Changes in Crystal Pattern by X-Ray Diffraction

Further information on the crystallization behavior was obtained by wide angle X-ray diffraction (WAXD) measurements. Figure 10 shows WAXD of PB(GAS)/PBT block copolyester for all compositions and mixing time. No diffraction peaks of PB(GAS) in T20 were observed regardless of mixing time, as shown in Figure 10(a). But the crystal pattern of PBT in T20 appeared weakly.

PB(GAS) ternary random copolyester is an amorphous polymer in spite of the PBA and PBS sequences in PB(GAS). From Figure 10(a) PB(GAS) sequence is excluded from the crystal formation when the PBT sequence is crystallized in the block copolyester.

The crystal patterns of PBT sequences are clearly

shown for T40, T50, and T60 in Figure 10(b), (c), and (d). In PB(GAS)/PBT block copolyesters, the peaks at diffraction angles of 16.2° , 17.4° , 20.7° , 23.4° , and 25.1° are assigned for (0 $\bar{1}$ 1), (010), ($\bar{1}$ 01), (100), and ($\bar{1}\bar{1}$) planes, respectively. Mencik *et al.*¹² suggest that the crystal system of PBT sequence is triclinic with parameters $a=0.596$ nm, $b=0.483$ nm, c (fiber axis)=1.162 nm, and $\alpha=115.2^\circ$, $\beta=99.9^\circ$, $\gamma=111.3^\circ$. The results of X-ray curves in Figure 10 are not clear, since a block type changed into a random type by ester interchange reaction between PB(GAS) ternary random copolyester and PBT.

The transesterification between PB(GAS) and PBT was sufficiently confirmed from increase in randomness and melting point depression with mixing time.

CONCLUDING REMARKS

From sequence distribution and crystallization behavior of PB(GAS)/PBT block copolyesters, the following conclusions were obtained. Increase in transesterification between PB(GAS) ternary random copolymer and PBT with mixing time was confirmed by the fractions of dyads of NMR spectra, melting point depression in DSC

curves, and crystal patterns of X-ray diffractograms. Randomness indicated that, with increasing mixing time, PB(GAS)/PBT block copolyesters are at least partially miscible.

REFERENCES

1. Y. Tokiwa and T. Suzuki, *J. Appli. Polym. Sci.*, **26**, 441 (1981).
2. N. Kamiya, Y. Yamamoto, Y. Inoue, R. Chûjô, and Y. Doi, *Macromolecules*, **22**, 1676 (1989).
3. S. Bloombergen, D. A. Holden, T. L. Bluhm, G. K. Hamer, and R. H. Marchessault, *Macromolecules*, **22**, 1663 (1989).
4. H. Y. Yoo, S. Umamoto, T. Kikutani, and N. Okuii, *Polymer*, **35**, 117 (1994).
5. J. Devaux, P. Godard, and J. P. Mercier, *Polym. Eng. Sci.*, **22**, 229 (1982).
6. M. Guo, *Polym. Mater. Sci. Eng.*, **75**, 12 (1996).
7. M. Guo and H. G. Zachman, *Polymer*, **34**, 2503 (1993).
8. E. Andresen and H. G. Zachman, *Colloid Polym. Sci.*, **272**, 1352 (1994).
9. J. Devaux, P. Godard, and J. P. Mercier, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 1881 (1982).
10. R. Yamadera and M. Murano, *J. Polym. Sci.*, **5**, 2259 (1967).
11. V. S. Shah, J. D. Keitz, D. R. Paul, and W. Barlow, *J. Appli. Polym. Sci.*, **32**, 3863 (1986).
12. Z. Mencik, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 2173 (1975).