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### Determination of Average Sequence Length in Poly(Butylene Terephthalate)-Poly(Ethylene Terephthalate-co-Isophthalate-co-Sebacate) Segmented Copolyesters

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## Determination of Average Sequence Length in Poly(Butylene Terephthalate)-Poly(Ethylene Terephthalate-co-Isophthalate-co-Sebacate) Segmented Copolyesters

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### ABSTRACT

Copolyesters, namely, poly(butylene terephthalate)-poly(ethylene terephthalate-co-isophthalate-co-sebacate) (PBT-PETIS) were synthesized by means of melting transesterification. In the five-component copolycondensates system, average sequence length was calculated based on the analysis of <sup>1</sup>H-NMR spectra and the equal probability of interchange reaction for three kinds of polyester units in PETIS with PBT. The results reveal that the average sequence length of both PBT and PETIS segments vary almost linearly with reaction time. The determination of degree of randomness that lies within the range of 0.1749–0.5282 suggests the formation of segmented copolyesters.

*Key Words:* Segmented copolyesters; Poly(butylene terephthalate) (PBT); Poly(ethylene terephthalate-co-isophthalate-co-sebacate) (PETIS); Sequence length; Degree of randomness.

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## INTRODUCTION

In past decades, transesterification reaction has been found occurring in blends and polycondensates synthesized by melting processing. The reaction itself, therefore, is available to obtain new polyester materials. Essentially, transesterification reaction time is of importance, since variation of reaction time induces more sensitive changes in sequence length of polyesters, and thus influences properties of copolyesters.

Yamadera<sup>[1]</sup> is the person who studied sequence distribution of copolyesters involving transesterification reaction between poly(ethylene terephthalate) (PET) and poly(ethylene sebacate) (PES). Montaudo<sup>[2]</sup> investigated the transesterification kinetics of three-component polycondensates of PET and poly(ethylene adipate) (PEA). Other investigations on the three-component copolyester system of PET and poly(ethylene 2,6-naphthalate) (PEN) blends were undertaken by many researchers.<sup>[3–6]</sup> More detailed descriptions of the kinetics of the reaction and sequence distribution in four-component blends of polycarbonate (PC)-PBT and PC-PET were reported by Devaux's research group.<sup>[7–10]</sup> With respect to copolycondensates with five components, Wei<sup>[11,12]</sup> examined the mechanism and kinetics of transesterification reaction in blends of copoly(oxybenzoate-ethylene terephthalate) (POB-PET) and PC. In the case of transesterification which occurred between PBT and binary copolyester-poly(butylene adipate-co-succinate) or ternary copolyesters-poly(butylene glutarate-co-adipate-co-succinate), Park and Kang<sup>[13,14]</sup> have solved the problem to determine the sequence for copolyesters with a single diol.

In order to obtain copolyesters with moderate elasticity, we have synthesized a series of segmented copolyesters by melting transesterification employing PBT and ternary random copolyester-poly(ethylene terephthalate-co-isophthalate-co-sebacate) (PETIS). As for segmented copolyesters, the use of uniform crystallisable units has several advantages.<sup>[15]</sup> By transesterification reaction, PETIS amorphous segments with aliphatic polyester units were introduced to a PBT chain, and the elasticity is expected to be greatly improved.

We report here the use of <sup>1</sup>H-NMR on segmented copolyesters of PBT-PETIS. To determine the average sequence length, we did some initial studies with this five-component copolyester system that consisted of two kinds of diols and three different kinds of diacids. Since PETIS is random copolyester, the probability of interchange reaction for each polyester unit in PETIS with PBT can be assumed to be equal. From the assignments of resonance of the NMR, we have calculated the average sequence length for both PBT and PETIS in copolyesters, and the degree of randomness is also determined.

## EXPERIMENTAL

### Materials

PBT chips were kindly supplied by the Yi Zheng Chemical Fiber Co., China. Dimethyl terephthalate (DMT), ethylene glycol (EG), isophthalate acid (IPA), sebacate acid (SA), magnesium acetate (Mg(OAC)<sub>2</sub>), manganese acetate (Mn(OAC)<sub>2</sub>), and tetrabutyl orthotitanate (TBT) were all reagent grade and used as received.

### Synthesis of PETIS Random Copolyesters

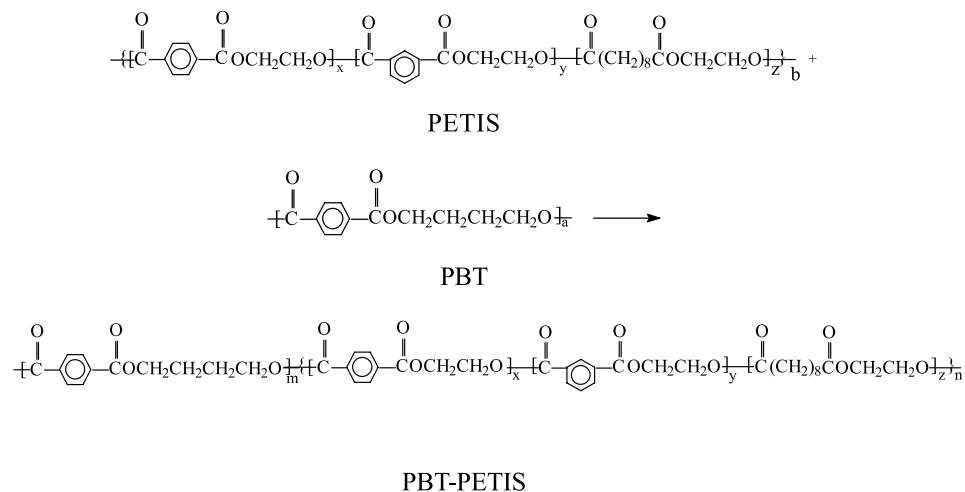
The synthesis of ternary amorphous random copolyesters PETIS can be divided into two steps. The first involves the transesterification of DMT and EG with magnesium acetate and manganese acetate as catalyst, and also involves the esterification of IPA, SA and EG, yielding bis(hydroxyethyl) terephthalate (BHET), bis(hydroxyethyl) isophthalate (BHEI), and bis(hydroxyethyl) sebacate (BHES). The second one is the principal reaction leading to the formation of PETIS copolyester by means of polycondensation in the presence of tetrabutyl orthotitanate (TBT) as a catalyst. In the latter step, BHET, BHEI, and BHES (with the feed ratio of 40:20:40(wt%)) were put in a four-neck flask equipped with a mechanically sealed stirrer and condenser under nitrogen atmosphere and vacuum condition less than 133 Pa. The melting processing was proceeded isothermally at  $255 \pm 2^\circ\text{C}$ .

### Synthesis of PBT–PETIS Segmented Copolyesters

Melting transesterification between PBT and PETIS was conducted in a four-neck flask just as described before under nitrogen atmosphere and vacuum conditions less than 133 Pa at  $255 \pm 2^\circ\text{C}$ . The synthesis process is given in Sch. 1.

### Measurement of Intrinsic Viscosity and Density

The intrinsic viscosity was determined at  $25.0 \pm 0.1^\circ\text{C}$  in a phenol/1,1,2,2-tetrachloroethane (50/50, w/w) solution with a concentration of 0.5 g/100 ml by an Ubbelohde viscometer, and the density was measured with a gradient density tube



Scheme 1.

prepared according to the ASTM-D1505 method in a thermostat at  $25.0 \pm 0.1^\circ\text{C}$  using an aqueous solution of sodium bromide.

### Sample Preparation

PBT–PETIS copolyester was dissolved in a mixed solvent of phenol and 1,1,2,2-tetrachloroethane (50/50, w/w). Having been completely dissolved, the solution was precipitated in a large excess of anhydrous methanol. After filtration and washing, each precipitated polymer was Soxhlet extracted for at least 24 h with anhydrous ethanol. The polymers were then dried overnight in a vacuum oven at about  $80^\circ\text{C}$ .

### Analysis of Sequence Length

Quantitative  $^1\text{H-NMR}$  spectra were obtained on a Varian UNITY-plus 400 MHz spectrometer at ambient temperature by dissolving each sample in deuteriated chloroform ( $\text{CDCl}_3$ ).

## RESULTS AND DISCUSSION

For the purpose of quantitative comparison among the different copolyesters with the same composition, on PBT–PETIS copolyesters with 20% PBT (wt%) the influence of reaction time was studied. The reaction has been carried out by the interval time 20 min, 40 min, and 60 min in order to check the variation of sequence length with reaction time. Table 1 summarizes the designated samples with intrinsic viscosity and density.

### Analysis of Transesterification Reaction

Figure 1 shows the  $^1\text{H-NMR}$  spectra of PBT(a), PETIS(b), and copolyesters with different reaction time-20PBT-20(c), 20PBT-40(d), and 20PBT-60(e). Table 2 describes

**Table 1.** Designated samples with their intrinsic viscosity and density.

Samples	Feed ratio (wt%) (PET/PEI/PES) = 40/20/40		Reaction time (min)	Intrinsic viscosity ( $\text{dL g}^{-1}$ )	Density ( $\text{g cm}^{-3}$ )
	PBT	PBT/(PET/PEI/PES)			
PETIS	0	0/(40/20/40)	150	0.4866	1.2476
20PBT-20	20	20/(32/16/32)	20	0.5860	1.2591
20PBT-40	20	20/(32/16/32)	40	0.6231	1.2596
20PBT-60	20	20/(32/16/32)	60	0.6350	1.2601
PBT	100	100/(0/0/0)	—	0.8000	1.2795

## Average Sequence Length of PBT and PETIS Segments

465

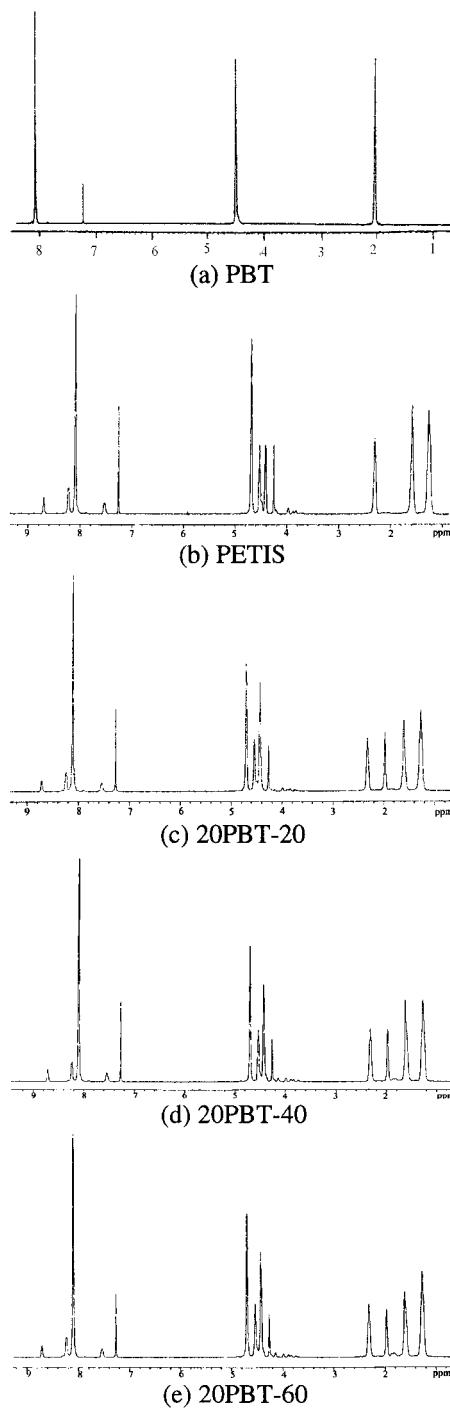


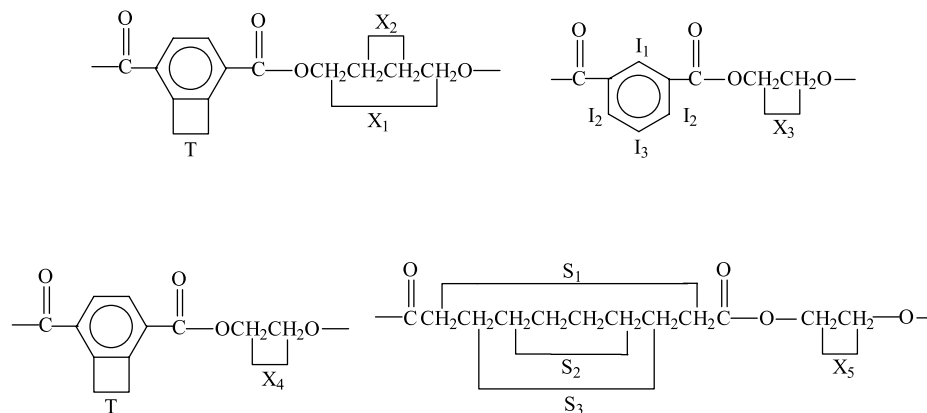
Figure 1.  $^1\text{H-NMR}$  spectra of PBT, PETIS, and copolyesters.

**Table 2.** Assignments of proton signal and their chemical shift in the  $^1\text{H-NMR}$  spectra.

	PBT $\delta$ (ppm)	PETIS $\delta$ (ppm)	Copolyester $\delta$ (ppm)
I <sub>1</sub>	—	8.697	8.709
I <sub>2</sub>	—	8.231	8.229
I <sub>3</sub>	—	7.534	7.544
T	8.091	8.094	8.100
S <sub>1</sub>	—	2.309	2.320
S <sub>2</sub>	—	1.261	1.269
S <sub>3</sub>	—	1.584	1.621
X <sub>1</sub>	4.432	—	4.431
X <sub>2</sub>	1.974	—	1.976
X <sub>3</sub> –X <sub>5</sub>	—	4.687	4.701
	—	5.529	4.539
	—	4.415	4.431
	—	4.253	4.265

the proton signals and their chemical shift in  $^1\text{H-NMR}$ . The protons are labeled according to Sch. 2.

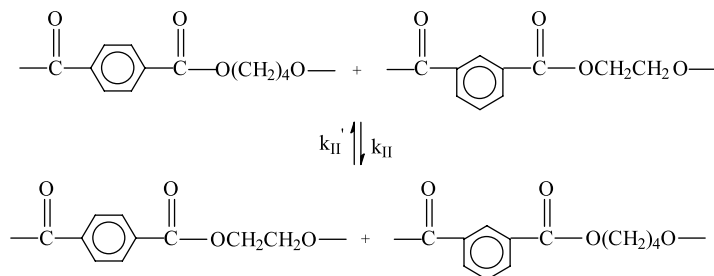
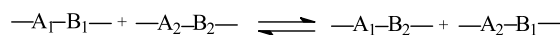
The absorbance attributed to glycol residue can be unambiguously located in Fig. 1(b) as a set of peaks at 4.253–4.687 ppm. The strong resonance of proton attached to benzene nucleus is visible at 8.091 ppm in Fig. 1(a). The resonances ascribed to aliphatic chain usually show up in 1.269, 2.320, and 1.621 ppm. Spectra, which can discriminate in 8.709, 8.229, and 7.544 ppm, are used to assign proton in isophthalate. The resonances at 4.431 and 1.976 ppm, seen in all spectra of copolyesters in Fig. 1(c–e), indicate the presence of PBT segments in the polymers, which is important evidence of transesterification in the reactions.

**Scheme 2.**

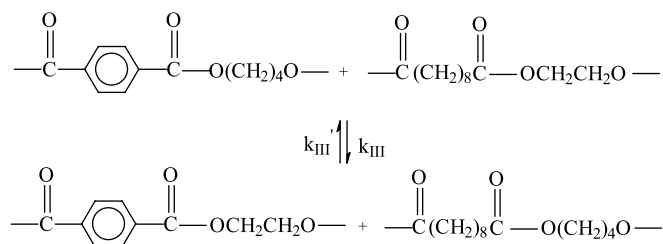
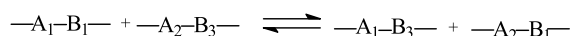




## II. Reaction between PBT and PEI unit in PETIS:



## III. Reaction between PBT and PES unit in PETIS:



## Determination of Average Sequence Length

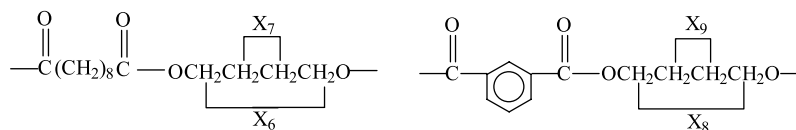
Figure 1(c-e) compare the  $^1\text{H-NMR}$  spectra of copolyesters with the same composition. A new peak appears at 4.133 ppm whose relative intensity increases as reaction time is prolonged. The relative intensity of peak at 1.976 ppm, which is assigned to be the protons in butyl in PBT gradually decreases with the increasing reaction time (Table 3). If degradation is negligible, both the rise and drop in relative intensity of corresponding peaks are mainly attributed to the fact that protons generated from

**Table 3.** Comparison of relative intensity at proton signals for samples with various reaction time.

Sample	Relative intensity (arbitrary unit) at								
	8.100	4.701	4.539	4.431	4.265	4.133	2.320	1.976	1.621
20PBT-20	15.52	10.09	5.89	9.65	2.23	0.233	7.11	5.19	9.80
20PBT-40	15.23	10.09	5.42	9.27	2.13	0.332	6.86	4.68	11.48
20PBT-60	15.48	10.39	5.24	8.91	1.98	0.380	6.80	4.29	9.20

## Average Sequence Length of PBT and PETIS Segments

469



Scheme 3.

transesterification reaction corresponds to the 1,4-butanediol lying along the main chain and bonded to sebacate or isophthalate (labeled  $X_7$  and  $X_9$  in Sch. 3).

Subtracting the mole of PBT calculated from the protons at 1.976 ppm in copolyesters spectra from the mole of PBT ( $N_{\text{PBT}}$ ) may result in mole amount of reaction **II** and **III** ( $N_{\text{II+III}}$ ).

One technical problem associated with is that interchange reaction **I** may bring out no creation of hetero-unit. Properly comparing the results obtained for mole of reaction **I** ( $N_I$ ) requires that reasonable assumption be made. If we assume that the three kinds of polyester units in PETIS has the equal probability to take part in interchange reaction with PBT, the value of mole of reaction **I** ( $N_I$ ) is achieved according to the ratio of PET:PEI:PES in PETIS detected by  $^1\text{H-NMR}$  (2.25:1:1.69).  $N_{\text{PBT}}$ ,  $N_I$ , and  $N_{\text{II+III}}$  as well as the mole of total hetero-unit  $N_{\text{BE}}$  (sum of  $N_I$  and  $N_{\text{II+III}}$ ) are collected in Table 4.

Detailed analysis of PBT and PETIS homo-units in copolyesters has accomplished the consideration of complexity in NMR spectra. To obtain the most reliable mole of homo-unit of PBT in copolyesters ( $N_B$ ), we detract the mole of reaction **I** ( $N_I$ ) from the mole of PBT corresponding to the intensity at 1.976 ppm. Included in the set of peaks from 4.133 to 4.701 ppm, as well as the reiteration of PBT at 4.431 ppm and the overlapped mole of hetero-unit ( $N_{\text{BE}}$  and  $N_{\text{EB}}$ ). Taking both the factors mentioned above into account, the value of  $N_E$  is obtained. On the basis of Eqs (1)–(4) proposed by Yamadera,<sup>[1]</sup> mole fraction  $F_B$ ,  $F_E$ , and  $F_{\text{BE}}$  of PBT, PETIS and hetero-linkage dyads are used instead as listed in Table 5. The values of transesterification ratio ( $Tr$ ) are also included.

$$F_B = \frac{N_B}{N_B + N_{\text{BE}} + N_{\text{EB}} + N_E} \quad (1)$$

$$F_E = \frac{N_E}{N_B + N_{\text{BE}} + N_{\text{EB}} + N_E} \quad (2)$$

$$F_{\text{BE}} = F_{\text{EB}} = \frac{N_{\text{BE}}}{N_B + N_{\text{BE}} + N_{\text{EB}} + N_E} = \frac{N_{\text{EB}}}{N_B + N_{\text{BE}} + N_{\text{EB}} + N_E} \quad (3)$$

Table 4. Mole of PBT and hetero-linkage.

Sample	$N_{\text{PBT}}$	$N_{\text{II+III}}$	$N_I$	$N_{\text{BE}}$
20PBT-20	1.4057	0.1075	0.0899	0.1974
20PBT-40	1.3325	0.1625	0.1359	0.2984
20PBT-60	1.3950	0.3225	0.2697	0.5922

**Table 5.** Mole of homo- and hetero-unit and mole fraction of dyads.

Sample	Relative intensity			Fraction of dyads			Tr (%)
	$N_B$	$N_{BE} + N_{EB}$	$N_E$	$F_B$	$F_{BE} + F_{EB}$	$F_E$	
PETIS	0	0	1.00	0	0	1.0000	0
20PBT-20	1.2076	0.3948	5.5480	0.1689	0.05522	0.7759	5.52
20PBT-40	1.0341	0.5968	5.3785	0.1475	0.08514	0.7673	8.51
20PBT-60	0.8028	1.1844	5.1279	0.1128	0.16640	0.7207	16.64
PBT	1.00	0	0	1.0000	0	0	0

$$Tr = \frac{N_{BE} + N_{EB}}{N_B + N_{BE} + N_{EB} + N_E} \quad (4)$$

Moreover, using the fraction of dyads, we obtain the mole fractions  $P_B$  and  $P_E$ , of PBT and PETIS, the probabilities,  $P_{BE}$  and  $P_{EB}$ , of finding unit of hetero-linkage. The average sequence length of PBT and PETIS ( $\overline{Ln_B}$  and  $\overline{Ln_E}$ ) and degree of randomness ( $R$ ) can also be calculated through brief manipulation of expressions given by Yamadera<sup>[1]</sup>:

$$P_B = \frac{1}{2}(F_{BE} + F_{EB}) + F_B = F_{BE} + F_B \quad (5)$$

$$P_E = \frac{1}{2}(F_{EB} + F_{BE}) + F_E = F_{EB} + F_E \quad (6)$$

$$P_{BE} = \frac{F_{BE} + F_{EB}}{2P_B} = \frac{F_{BE}}{P_B} \quad (7)$$

$$P_{EB} = \frac{F_{EB} + F_{BE}}{2P_E} = \frac{F_{EB}}{P_E} \quad (8)$$

$$\overline{Ln_B} = \frac{2P_B}{F_{BE} + F_{EB}} = \frac{F_{BE} + F_B}{F_{BE}} = \frac{1}{P_{BE}} \quad (9)$$

$$\overline{Ln_E} = \frac{2P_E}{F_{EB} + F_{BE}} = \frac{F_{EB} + F_E}{F_{EB}} = \frac{1}{P_{EB}} \quad (10)$$

$$R = P_{BE} + P_{EB} \quad (11)$$

The typical data set shown in Table 6 account not only for the dependence of average sequence length on reaction time, but also for variation in the degree of randomness from copolyester to copolyester.

It seems that transesterification reaction yields copolyesters with average sequence lengths that vary almost linearly with reaction time within the time scale studied (Fig. 2). The value of degree of randomness ( $R$ ) ranging from 0.1749–0.5282 provides an indication that segmented copolyesters are produced by melting transesterification reaction.

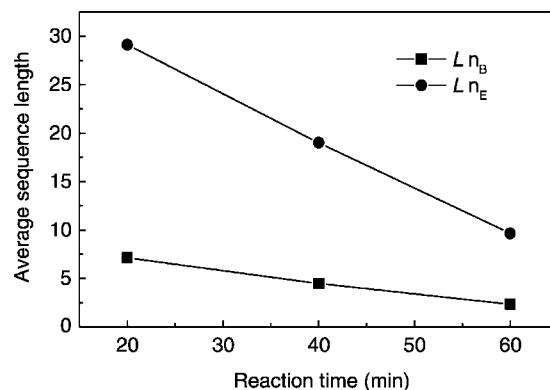
**Table 6.** Average sequence length and degree of randomness.

Sample	Mole fraction of diesters		Probability of finding unit		Average sequence length		$R$
	$P_B$	$P_E$	$P_{BE}$	$P_{EB}$	$\overline{Ln}_B$	$\overline{Ln}_E$	
PETIS	0	1.000	0	0	0	—	0
20PBT-20	0.1951	0.8035	0.1405	0.03436	7.12	29.10	0.1749
20PBT-40	0.1901	0.8099	0.2240	0.05256	4.46	19.02	0.2740
20PBT-60	0.1960	0.8039	0.4245	0.10350	2.36	9.66	0.5282
PBT	1.000	0	0	0	—	0	0

Figure 3 depicts the relationship of degree of randomness and reaction time, and result obtained for copolyesters of transesterification ratio ( $Tr$ ) is also included for comparison. It turns out that transesterification reaction proceeds at the cost of an increase in degree of randomness. This observation emphasizes that segmented copolyesters tend to be random ones in the proceeding of transesterification reaction.

### CONCLUSION

$^1\text{H}$  nuclear magnetic resonance spectroscopy measurements were performed in the five-component copolyesters (PBT-PETIS). Proton NMR spectra corroborate the structural information, and also allow one to observe the interchange reaction so important to average sequence length. Analysis was done on the basis of our suggestion to the special system and with the equations proposed by Yamadera. A decrease in average sequence length with reaction time was found for both PBT and PETIS in copolyesters.

**Figure 2.** Variation of average sequence length with reaction time.

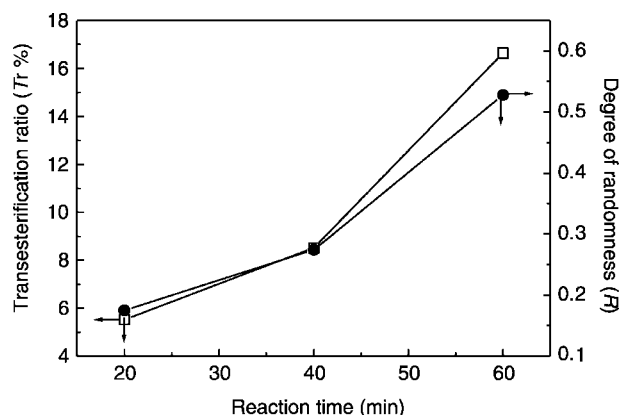


Figure 3. Dependence of degree of randomness and transesterification ratio on time.

The value of degree of randomness ( $R$ ) ranges from 0.1749–0.5282, which is an indication of segmented copolyesters.

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