

Studies on *co*[poly(ethylene terephthalate–*p*-oxybenzoate)] thermotropic copolyester: sequence distribution evaluated from TSC measurements

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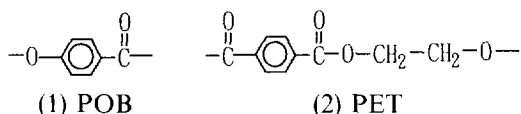
(Received 18 April 1994; revised 15 July 1994)

Relaxation/transition behaviours for copolyesters made from poly(ethylene terephthalate) (PET) and *p*-acetoxybenzoic acid (POB) have been characterized by thermally stimulated current (TSC) measurement. The sequence distribution, in terms of the degree of blockiness, in dual chemidomains of POB/PET copolyester is simulated from a model developed by us to predict the probability between block sequence and random sequence under a given composition and measuring condition. It is found that the degree of blockiness, a measure of sequence distribution, under the same polarization temperature generally increases with increasing POB content in the POB/PET copolyester. For copolyesters of the same composition, the degree of blockiness shows a large decrease after solid-state polymerization when high molecular weight PET is used, whereas it shows only a small decrease or an increase after solid-state polymerization when PET of lower molecular weight is used. It is concluded that the change in the degree of blockiness caused by the solid-state polymerization of copolyesters is dependent on the molecular weight of sequences of the PET moiety in the structure.

(Keywords: *co*[poly(ethylene terephthalate–*p*-oxybenzoate)]; thermally stimulated current; sequence distribution)

INTRODUCTION

A series of copolyesters based upon poly(ethylene terephthalate) (PET) copolymerized with *p*-acetoxybenzoic acid (POB) has been the subject of several investigations into their structure and properties^{1–4}. The chemical structure of this kind of POB/PET copolyester consists of the following two moieties:



It was described that POB/PET copolyesters containing 40–90 mol% POB units were highly anisotropic. The relationships between properties and compositions for POB/PET copolyesters have been intensively investigated by us in the past^{5–8}. Very recently, we have measured the relaxation/transition for these copolyesters by the thermally stimulated current (TSC) technique, a method that can provide information on phase separation and segmental motions of dual chemidomains of these copolyesters⁹.

The approach used involves finding the possible sequences distribution of such a copolymer under given conditions of preparation. The possible sequence could be either blocked sequence (i.e. –AAAAAA–, –BBBBBB–) or random sequence (i.e. –ABBABAA–). Although the copolyesters have been reported to be random copolyesters based upon ¹³C n.m.r. spectra¹, their phase separation and morphology have been interpreted as showing evidence for a blocked sequence distribution^{10–14}. From this prospective, we suggest in this paper that POB/PET copolyester may best be viewed as a dual chemidomain system, both in the solid and in the ‘liquid’ states. Further, TSC measurements have been extended to predict the sequence distributions of the POB and PET moieties in the two chemidomains of the copolyesters synthesized.

EXPERIMENTAL

Materials

Copolyesters having various compositions have been synthesized and subjected to solid-state polymerization according to the procedure reported in our previous papers^{5–9}. Two different molecular weights of PET were used for preparation of copolyesters. The copolyesters

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synthesized from low molecular weight (=2000) PET are denoted as the OET series, while the copolyesters synthesized from high molecular weight (=20000) PET are denoted as the PET series. Eastman 10109, examined as a reference in this study, is a commercial thermotropic liquid crystalline copolyester produced by Tennessee Eastman Co.

Principle

The principle of the TSC technique is basically as follows¹⁵⁻¹⁷. The sample is polarized by a static electric field E at temperature T_p . For a given chemical structure, the magnitudes of E and T_p determine the extent of orientation of dipoles in the materials. Free charges drift toward the electrodes during this time.

The polarization by orientation is due to permanent dipoles within the materials. The model of this type of polarization uses the classic Debye assumption. The orientation polarization P for a giving relaxing mode increases with a rate which is proportional to the distance to equilibrium as:

$$\frac{dP}{dt} = -\frac{P}{\tau} \tag{1}$$

where P is the polarization of the dielectric, t is time and τ is the relaxation time. The temperature dependence of the relaxation frequency, $\alpha(T)$, can be calculated by an exponential law from:

$$\alpha(T) = \exp\left(-\frac{\Delta H}{kT}\right) \tag{2}$$

where ΔH denotes the activation energy of relaxation, k is Boltzmann's constant and T is the thermodynamic temperature. In polymers, the polarization P is the residual polarization at time t . The temperature dependence of τ is often represented by an Arrhenius-type equation as:

$$\tau = \tau_0 \exp\left(\frac{\Delta H}{kT}\right) \tag{3}$$

where τ_0 is a relaxation time constant. The current is equal to the rate of change of the polarization, given by the Debye equation as:

$$J(T) = \frac{dP(t)}{dt} = -\alpha(T)P(t) \tag{4}$$

where $J(T)$ is the current measured at temperature T . The relation between time t and temperature T is:

$$s_2 dt = dT \tag{5}$$

where s_2 is the heating rate in $K s^{-1}$. The activation energy of relaxation can be calculated using the method of Perlman¹⁸:

$$\ln J(T) = C - \frac{\Delta H}{kT} \tag{6}$$

where C is a constant. Activation energy of relaxation (ΔH) can be found by multiplying the slope of the straight line obtained from the plot of $\ln J(T)$ against $1/T$ by the Boltzmann constant (k). Once ΔH is known, the relaxation time constant τ_0 can be evaluated from:

$$\tau_0 = \frac{\exp(-\Delta H/RT_m)}{s_2(\Delta H/RT_m^2)} \tag{7}$$

where R is the gas constant, T_m is the maximum peak temperature and s_2 is again the heating rate in $K s^{-1}$. Hence, the value of τ_0 can be calculated from the activation energy of relaxation ΔH using the relationship:

$$\ln \tau_0 = -\frac{\Delta H}{RT_m} - \left(\ln s_2 + \ln \frac{\Delta H}{RT_m^2} \right) \tag{8}$$

Simulation model

In order to develop a simulation model of relaxation behaviours of the copolymers by TSC measurements, let us consider the existence of two domains – A, a PET-rich domain (mol%) and B, a POB-rich domain (mol%) – in the structure of the POB/PET copolyester. These domains display their own relaxation/transition behaviour around their respective glass transition temperature (T_g). Suppose that there is x mol% of PET segment in domain A, then $1-x$ mol% of POB segment will also be in domain A. The total activation energy of relaxation of domain A should be the sum of $x\Delta H_1$ and $(1-x)\Delta H_2$, where ΔH_1 and ΔH_2 are activation energies of relaxation of pure PET and POB, respectively. The Arrhenius-type equation for the first peak in the TSC spectrum might be rewritten as:

$$\tau = \tau_0 \exp\left(\frac{\Delta H}{kT}\right) = \tau_1 \exp\left(\frac{x\Delta H_1}{kT}\right) + \tau_2 \exp\left(\frac{(1-x)\Delta H_2}{kT}\right) \tag{9}$$

where τ_0 , τ_1 and τ_2 are relaxation time constants of copolymer, pure PET and pure POB, respectively, and ΔH is the activation energy of relaxation of the copolymer. Similarly, the Arrhenius-type equation for the second peak in TSC spectrum might be rewritten as:

$$\tau' = \tau'_0 \exp\left(\frac{\Delta H}{kT}\right) = \tau_1 \exp\left(\frac{y\Delta H_1}{kT}\right) + \tau_2 \exp\left(\frac{(1-y)\Delta H_2}{kT}\right) \tag{10}$$

where τ'_0 is the relaxation time constant of the second peak of the copolyester. The symbol y now represents the mol% of PET segment and $1-y$ represents the mol% of POB segment, respectively, in B domain. Considering the mass balance of PET and POB segments in the structure of the copolyester, it is shown that:

$$Ax + (1-A)y = M \tag{11}$$

$$A(1-x) + (1-A)(1-y) = N \tag{12}$$

where A is the fraction of domain A (mol%), M and N are the mole fractions of PET and POB segments of the copolyester, respectively, and the following relation stands:

$$M + N = 1 \tag{13}$$

If the chains consist of sequences of A for the PET-rich domain and sequences of B for the POB-rich domain, the ratio of probabilities¹³ in the copolyester chain, R_p , which may be used to describe the degree of blockiness, is:

$$R_p = \frac{P_{AA} + P_{BB}}{P_{AB} + P_{BA}} \tag{14}$$

where P_{ij} is the probability of unit i following unit j along the chain. If heterogeneous polycondensation occurs in this system, the PET composition in PET-rich domain

A is represented by P_{AA} and the POB composition in PET-rich domain A is represented by P_{AB} . Similarly, the POB composition in POB-rich domain B is represented by P_{BB} and the PET composition in POB-rich domain B is represented by P_{BA} . Finally, equation (13) might be rewritten in terms of mol% of the two moieties, PET and POB:

$$R_p = \frac{Ax + (1-A)(1-y)}{A(1-x) + (1-A)y} \quad (15)$$

where A is again the amount of PET-rich domain in mol%, and R_p is the degree of blockiness, a measure of the sequence distribution of PET and POB segments.

TSC measurement

The thermally stimulated current measurement for all samples was performed using a TSC/RMA (Solomat Instrument) at 3M Company. The thickness and area of the test samples were 0.05 mm and 38 mm², respectively; samples were annealed at 200°C for 0.1 min. The magnitude of the polarization field (E_p) was 10 000 V mm⁻¹. The polarization time was 5 min and the polarization temperature varied from 80 to 200°C. The test sample is quenched into -100°C for 2 min. After that, the sample is heated at a rate of 7°C min⁻¹. By way of example, the depolarization currents as a function of temperature for Eastman 10109 (EAS) and POB/PET 80/20 (P82) are shown in Figure 1 and 2, respectively.

RESULTS AND DISCUSSION

The codes for each sample examined in this paper are listed in Table 1. All the maximum peak temperatures

Table 1 Codes of copolyesters synthesized

	OET moiety	PET moiety
POB/PET = 0/100	OET	PET
POB/PET = 20/80	O28	P28
POB/PET = 40/60	O46	P46
POB/PET = 60/40	O64	P64
POB/PET = 80/20	O82	P82
POB/PET = 100/0		PPOB
Eastman product		EAS

(T_{max}) of the copolyesters stimulated at various temperatures (e.g. 80, 100, 150 and 200°C) and the activation energies of relaxation of the copolyesters calculated from TSC spectra using equation (6) have been already reported in our previous paper⁹. The relaxation time constants τ_0 of Arrhenius-type relaxation times calculated from obtained ΔH data by using equation (8) are listed in Table 2. It is seen that, as the polarization temperature increases, the relaxation time constant generally decreases in both first and second peaks because of the higher thermal energy needed at the elevated maximum peak temperature.

Relaxation time constants of POB/OET 60/40 (code O64) and POB/PET 60/40 (code P64) before and after 4 h solid-state polymerization are shown in Table 3. There are two main factors that influence the relaxation constant during the solid-state polymerization reaction: the molecular weight of the spacer segment and transesterification-induced randomization. The relaxation time constants τ_1 and τ_2 of O64 at any of the polarization

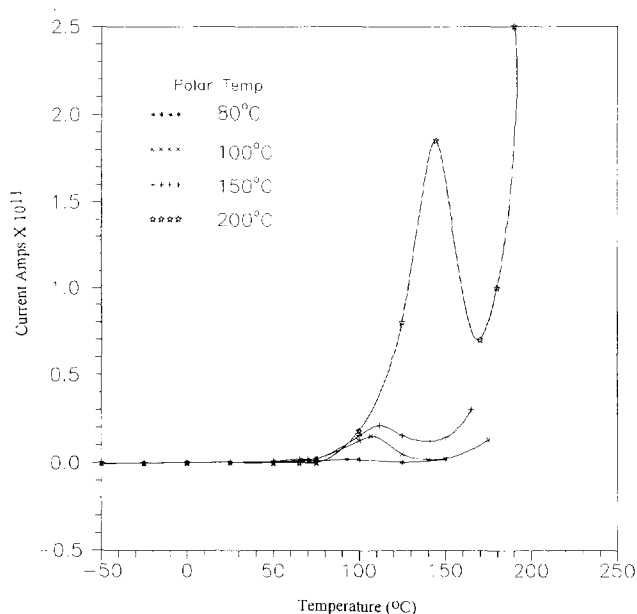


Figure 1 TSC spectra of EAS as a function of polarization temperature

Table 2 Relaxation time constants of the copolyesters, calculated from the TSC spectra using equation (8), as a function of polarization temperature (T_p)

	$T_p = 80^\circ\text{C}$		$T_p = 100^\circ\text{C}$		$T_p = 150^\circ\text{C}$		$T_p = 200^\circ\text{C}$	
	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2
OET	4.96×10^{-5}		3.67×10^{-5}		1.16×10^{-6}		3.96×10^{-8}	
O28	4.27×10^{-7}	5.3×10^{-4}	1.21×10^{-7}	1.88×10^{-4}	2.22×10^{-8}	2.92×10^{-4}	2.06×10^{-8}	7.32×10^{-4}
O46	4.32×10^{-7}	8.23×10^{-8}	2.25×10^{-9}	7.68×10^{-9}	3.05×10^{-10}	3.52×10^{-8}	5.87×10^{-12}	2.99×10^{-8}
O64	2.09×10^{-7}	2.96×10^{-7}	5.8×10^{-8}	1.17×10^{-9}	2.10×10^{-10}	9.83×10^{-10}	2.58×10^{-11}	1.3×10^{-9}
O82	1.04×10^{-5}	3.53×10^{-6}	7.07×10^{-6}	1.12×10^{-6}	2.60×10^{-6}	8.09×10^{-9}	7.35×10^{-7}	7.05×10^{-10}
PET	5.49×10^{-8}		3.66×10^{-8}		2.18×10^{-2}	6.80×10^{-5}	3.74×10^{-2}	7.42×10^{-6}
P28	3.84×10^{-3}	9.45×10^{-4}	9.36×10^{-5}	1.22×10^{-4}	7.29×10^{-7}	4.87×10^{-6}	6.21×10^{-7}	4.00×10^{-6}
P46	2.81×10^{-4}	2.63×10^{-5}	1.76×10^{-5}	4.54×10^{-6}	8.06×10^{-7}	3.95×10^{-7}	1.27×10^{-7}	7.41×10^{-8}
P64	4.52×10^{-4}	3.82×10^{-5}	3.56×10^{-7}	6.52×10^{-6}	4.24×10^{-10}	2.97×10^{-7}	1.41×10^{-12}	1.12×10^{-8}
P82	1.47×10^{-3}	5.95×10^{-6}	1.45×10^{-4}	3.14×10^{-6}	3.89×10^{-7}	2.03×10^{-7}	1.62×10^{-7}	4.36×10^{-12}
PPOB	1.48×10^{-4}		1.84×10^{-5}		2.44×10^{-5}		5.22×10^{-6}	
EAS	2.83×10^{-2}	8.06×10^{-3}	5.21×10^{-4}	5.32×10^{-7}	9.45×10^{-6}	2.12×10^{-7}	1.22×10^{-5}	1.79×10^{-11}

Table 3 Relaxation time constants of O64 and P64, calculated from TSC spectra using equation (8) before and after 4 h solid-state polymerizations, as a function of polarization temperature (T_p)

	$T_p=80^\circ\text{C}$		$T_p=100^\circ\text{C}$		$T_p=150^\circ\text{C}$		$T_p=200^\circ\text{C}$	
	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2
O64	2.09×10^{-7}	2.96×10^{-7}	5.8×10^{-8}	1.17×10^{-9}	2.10×10^{-10}	9.83×10^{-10}	2.58×10^{-11}	1.3×10^{-9}
O64+4	7.44×10^{-8}	3.42×10^{-8}	3.87×10^{-8}	6.64×10^{-10}	4.46×10^{-10}	1.1×10^{-9}	1.35×10^{-11}	4.2×10^{-10}
P64	4.52×10^{-4}	3.82×10^{-5}	3.56×10^{-7}	6.52×10^{-6}	4.24×10^{-10}	2.97×10^{-7}	1.41×10^{-12}	1.12×10^{-8}
P64+4	2.61×10^{-5}	2.13×10^{-5}	1.73×10^{-8}	2.29×10^{-7}	2.11×10^{-9}	3.42×10^{-7}	1.81×10^{-10}	2.23×10^{-11}

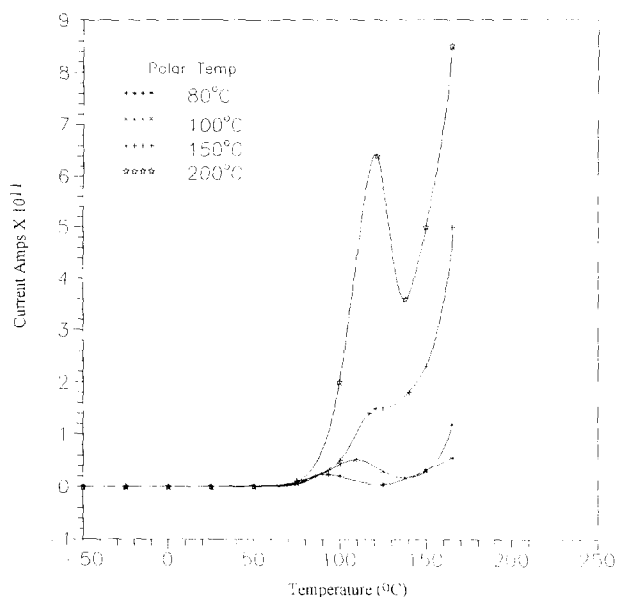


Figure 2 TSC spectra of P82 as a function of polarization temperature

temperatures, in general, decrease after solid-state polymerization. However, at elevated temperature (150 or 200°C), τ_1 remains almost unchanged after the solid-state polymerization due to the reduced effect of transesterification on the spacer OET segment. For P64, on the other hand, τ_1 increases after solid-state polymerization (e.g. $4.24 \times 10^{-10} \rightarrow 2.11 \times 10^{-9}$ at 150°C, $1.41 \times 10^{-12} \rightarrow 1.81 \times 10^{-10}$ at 200°C) due to the greater transesterification effect on the PET segment.

The mole fraction of chemidomains and sequence distribution of the copolyesters of different compositions, calculated using equations (9) to (13) and the relaxation time data in Table 3, are presented in Tables 4 to 9. In Table 4, the data for POB/OET 20/80 (code O28) and POB/PET 20/80 (code P28) are shown under different polarization temperatures. It is seen that there is a greater mole fraction of PET-rich domain than of POB-rich domain (e.g. 99 mol% PET-rich domain and 1 mol% POB-rich domain for O28 at $T_p=80^\circ\text{C}$) in these copolyesters. The reason is that PET is the main component of the copolyester; therefore the PET-rich domain determines the main behaviour of the copolyester.

In POB/OET 40/60 (code O46) and POB/PET 40/60 (code P46) systems, Table 5, the domain sizes tend to be closer to each other than those in O28 and P28, Table 4 (e.g. 68.4 mol% in PET-rich domain and 31.6 mol% in POB-rich domain for O46 at $T_p=80^\circ\text{C}$). The competition between the two moieties for which is to be the continuous phase becomes obvious in these copolyesters.

Table 4 Mole fractions of chemidomains and sequence distributions for O28 and P28

Polarization temperature, T_p ($^\circ\text{C}$)	Domain	Mol%	Moiety	Content (%)
<i>For O28 series</i>				
80	PET rich	99.0	PET	80.5
			POB	19.5
	POB rich	1.0	PET	0.0
			POB	100.0
100	PET rich	99.0	PET	79.2
			POB	20.8
	POB rich	1.0	PET	4.4
			POB	95.6
150	PET rich	99.0	PET	80.6
			POB	19.4
	POB rich	1.0	PET	12.4
			POB	87.6
200	PET rich	99.0	PET	80.5
			POB	19.5
	POB rich	1.0	PET	7.2
			POB	92.8
<i>For P28 series</i>				
80	PET rich	80.1	PET	98.5
			POB	1.5
	POB rich	19.9	PET	0.5
			POB	99.5
100	PET rich	81.3	PET	97.8
			POB	2.2
	POB rich	18.7	PET	2.8
			POB	97.2
150	PET rich	100.0	PET	68.0
			POB	32.0
	POB rich	0.0	PET	12.5
			POB	87.5
200	PET rich	100.0	PET	66.0
			POB	34.0
	POB rich	0.0	PET	3.7
			POB	96.3

The moiety contents of the two segments in the two chemidomains tend to be closer at an elevated polarization temperature (e.g. 85% PET segment and 15% POB segment in PET-rich domain for O46 at $T_p=80^\circ\text{C}$, and 77.5% PET segment and 22.5% POB segment in PET-rich domain for O46 at $T_p=200^\circ\text{C}$), probably due to the annealing effect.

Data for POB/OET 60/40 (O64) and POB/PET 60/40 (P64) are listed in Table 6. The mole fraction of POB-rich domain is always larger than that of the PET-rich domain in the O64 series (e.g. 56.8 mol% POB-rich domain and 43.2 mol% PET-rich domain at $T_p=80^\circ\text{C}$). The P64 series shows a more blockwise sequence distribution than the O64 series. For instance, the PET-rich domain of O64 consists of 86 mol% of PET moiety and 14 mol% of POB moiety at 80°C polarization temperature, while the

Table 5 Mole fractions of chemidomains and sequence distributions for O46 and P46

Polarization temperature, T_p (°C)	Domain	Mol%	Moiety	Content (%)
<i>For O46 series</i>				
80	PET rich	68.4	PET	85.0
			POB	15.0
	POB rich	31.6	PET	6.0
			POB	94.0
100	PET rich	75.2	PET	77.1
			POB	22.9
	POB rich	24.8	PET	8.5
			POB	91.5
150	PET rich	69.9	PET	79.5
			POB	20.5
	POB rich	30.1	PET	14.8
			POB	85.2
200	PET rich	73.2	PET	77.5
			POB	22.5
	POB rich	26.8	PET	12.3
			POB	87.7
<i>For P46 series</i>				
80	PET rich	59.0	PET	98.5
			POB	1.5
	POB rich	41.0	PET	4.6
			POB	95.4
100	PET rich	60.7	PET	93.0
			POB	7.0
	POB rich	39.3	PET	9.1
			POB	90.9
150	PET rich	92.1	PET	64.5
			POB	35.5
	POB rich	7.9	PET	7.5
			POB	92.5
200	PET rich	100	PET	59.5
			POB	40.5
	POB rich	0	PET	3.6
			POB	96.4

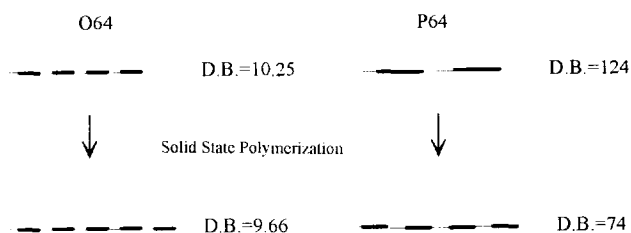
Table 6 Mole fractions of chemidomains and sequence distributions for O64 and P64

Polarization temperature, T_p (°C)	Domain	Mol%	Moiety	Content (%)
<i>For O64 series</i>				
80	PET rich	43.2	PET	86.0
			POB	14.0
	POB rich	56.8	PET	5.0
			POB	95.0
100	PET rich	41.3	PET	82.0
			POB	18.0
	POB rich	58.7	PET	10.5
			POB	89.5
150	PET rich	35.0	PET	80.0
			POB	20.0
	POB rich	65.0	PET	18.0
			POB	82.0
200	PET rich	38.8	PET	79.5
			POB	20.5
	POB rich	61.2	PET	15.0
			POB	85.0
<i>For P64 series</i>				
80	PET rich	40.0	PET	98.0
			POB	2.0
	POB rich	60.0	PET	0.0
			POB	100.0
100	PET rich	40.0	PET	98.0
			POB	2.0
	POB rich	60.0	PET	0.0
			POB	100.0
150	PET rich	65.1	PET	58.5
			POB	31.2
	POB rich	34.9	PET	5.4
			POB	94.6
200	PET rich	100.0	PET	40.0
			POB	60.0
	POB rich	0.0	PET	3.0
			POB	97.0

PET-rich domain of P64 consists of 98% of PET moiety and 2% of POB moiety at the same polarization temperature. This means that the O64 series contains a more random sequence whereas the P64 series contains a more blockwise sequence in its chemidomains. Therefore, the solid-state polymerization reaction is necessary for the P64 series to improve the degree of blockiness in order to attain the uniform role of spacer in a thermotropic liquid crystalline polymer.

Tables 7 and 8 present the mole fractions of chemidomains and sequence distributions for POB/OET 80/20 (O82), POB/PET 80/20 (P82) and the commercial product, Eastman 10109 (EAS). As the POB moiety is more heat-resistant than the PET moiety, variations in the sequence distributions of chemidomains by means of polarization temperature are not distinct (e.g. the results show ~19–21 mol% of PET-rich domain for O82 and P82 at all polarization temperatures) due to the reduced effect of annealing. The TSC data indicate that the mole fractions of chemidomains in EAS are closer to those in P82 than to those in O82.

Data for O64 and P64 after solid-state polymerization are given in Table 9. As reported by Nicely *et al.*¹⁹, at 280°C two phases were found in the 'liquid' state of POB/PET 60/40, containing 35 and 80 mol% POB residue respectively, on the basis of n.m.r. investigation, dynamic mechanical loss and thermo-transmittance


Figure 3 Schematic illustration of changes in structure during solid-state polymerization: —, PET-rich segment; —, POB-rich segment; D. B. = degree of blockiness

analyses. The results obtained in this paper for O64 and P64 before and after 4 h solid-state polymerization reaction, Tables 6 and 9, indicate a similar, but more random sequence distribution for the copolyesters because of the occurrence of the transesterification reaction during the solid-state polymerization.

The degree of blockiness (R_p) calculated from equation (15) is listed in Table 10. The degree of blockiness can be regarded as a measure of randomness of the two sequences POB and PET. The smaller the degree of blockiness, the more random the two sequences in the physical sense. At low polarization temperatures (80 and 100°C) the degree of blockiness of the OET-based copolyester is always smaller than that of PET-based copolyester. This means that the OET series contains

Table 7 Mole fractions of chemidomains and sequence distributions for O82 and P82

Polarization temperature, T_p (°C)	Domain	Mol%	Moiety	Content (%)
<i>For O82 series</i>				
80	PET rich	20.1	PET	92.2
			POB	7.8
	POB rich	79.9	PET	1.8
			POB	98.2
100	PET rich	21.6	PET	89.5
			POB	10.5
	POB rich	78.4	PET	0.9
			POB	99.1
150	PET rich	12.5	PET	89.2
			POB	10.8
	POB rich	87.5	PET	10.1
			POB	89.9
200	PET rich	18.8	PET	87.0
			POB	13.0
	POB rich	81.2	PET	4.5
			POB	95.5
<i>For P82 series</i>				
80	PET rich	19.2	PET	100.0
			POB	0
	POB rich	81.8	PET	1.0
			POB	99.0
100	PET rich	19.4	PET	99.4
			POB	0.6
	POB rich	80.6	PET	0.9
			POB	99.1
150	PET rich	17.3	PET	77.0
			POB	23.0
	POB rich	82.7	PET	8.1
			POB	91.9
200	PET rich	21.9	PET	72.0
			POB	28.0
	POB rich	78.2	PET	5.4
			POB	94.6

Table 8 Mole fractions of chemidomains and sequence distributions for EAS (Eastman 10109)

Polarization temperature, T_p (°C)	Domain	Mol%	Moiety	Content (%)
80	PET rich	20.0	PET	100.0
			POB	0.0
	POB rich	80.0	PET	0.0
			POB	100.0
100	PET rich	38.9	PET	100.0
			POB	0.0
	POB rich	61.1	PET	1.8
			POB	98.2
150	PET rich	41.8	PET	80.5
			POB	19.5
	POB rich	58.2	PET	10.9
			POB	89.1
200	PET rich	25.2	PET	79.5
			POB	20.5
	POB rich	74.8	PET	0.0
			POB	100.0

shorter and more random sequences of both PET and POB moieties in its domains. At high polarization temperatures (150 and 200°C), however, the value of R_p decreases for each copolyester composition and shows a more random distribution, probably due to the effect of annealing in both OET and PET moieties. In Figure 3, the changes in structure that occur during solid-

Table 9 Mole fractions of chemidomains and sequence distributions for O64 and P64 after 4 h solid-state polymerization

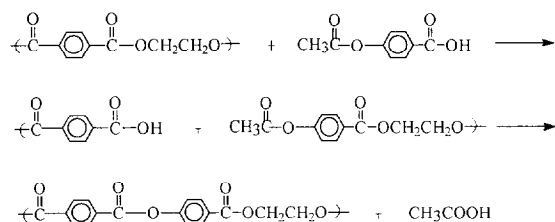
Polarization temperature, T_p (°C)	Domain	Mol%	Moiety	Content (%)
<i>For O64 + 4 series</i>				
80	PET rich	43.8	PET	85.0
			POB	15.0
	POB rich	56.2	PET	5.0
			POB	95.0
100	PET rich	43.2	PET	82.0
			POB	18.0
	POB rich	56.8	PET	8.0
			POB	92.0
150	PET rich	41.3	PET	80.5
			POB	19.5
	POB rich	58.7	PET	11.5
			POB	88.5
200	PET rich	18.4	PET	79.1
			POB	20.9
	POB rich	81.6	PET	6.7
			POB	93.3
<i>For P64 + 4 series</i>				
80	PET rich	41.3	PET	96.8
			POB	3.2
	POB rich	58.7	PET	0.0
			POB	100.0
100	PET rich	39.9	PET	92.0
			POB	8.0
	POB rich	60.1	PET	5.5
			POB	94.5
150	PET rich	54.5	PET	64.0
			POB	36.0
	POB rich	45.5	PET	11.2
			POB	88.8
200	PET rich	67.0	PET	57.5
			POB	42.5
	POB rich	33.0	PET	4.4
			POB	95.6

Table 10 Degree of blockiness of the copolyesters as a function of polarization temperature (T_p)

	$T_p = 80^\circ\text{C}$	$T_p = 100^\circ\text{C}$	$T_p = 150^\circ\text{C}$	$T_p = 200^\circ\text{C}$
O28	4.18	3.85	4.17	4.16
O46	7.23	4.17	4.32	4.06
O64	10.25	6.35	4.48	4.84
O82	31.60	32.63	8.82	15.4
P28	75.86	42.25	2.13	1.94
P46	35.09	11.78	2.00	1.47
P64	124	124	3.20	0.67
P82	122.47	117.79	8.36	8.67
O64 + 4	9.66	7.12	5.75	9.74
P64 + 4	74.67	14.39	3.05	2.34

state polymerization for O64 and P64 are illustrated schematically. The solid-state polymerization has less influence on R_p for O64 than for P64, because the transesterification reaction is probably less significant in O64 than in P64. In other words, a copolyester having a larger molecular weight of segment undergoes transesterification more readily than a copolymer having a smaller molecular weight of segment. Thus it might be suggested that P64 has a higher degree of polymerization of segments but a less random sequence distribution before the solid-state polymerization, which causes the

transesterification reaction to insert the rigid-rod like POB moiety into the PET-rich domain by reducing the degree of blockiness according to the following mechanism:



This transesterification mechanism has been confirmed already by many investigators^{4,7,19,20}.

CONCLUSIONS

The phenomenon of dual chemidomains and sequence distribution is one of the most interesting aspects of this thermotropic copolyester. Based on the experimental work on the sequence distribution and composition of the two chemidomains by the simulation from relaxation/transition data of TSC, the following conclusions appear to be warranted:

1. the sequence distribution of the two chemidomains in the copolyesters can be predicted by TSC and simulated from their relaxation/transition data through a model proposed in this paper;
2. the OET-based copolyester has more significant randomness than the PET-based copolyester at the same composition as indicated by the degree of blockiness, R_p ; and
3. owing to the transesterification reaction, solid-state polymerization has a more significant effect on the sequence distribution for PET-based copolyesters, which are originally less random, than for OET-based copolyesters, which are originally more random.

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