

Studies on Co[poly(ethylene terephthalate-*p*-oxybenzoate)] Thermotropic Copolyester: Thermomechanical and Thermodynamic Properties

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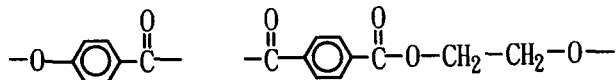
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SYNOPSIS

A series of co[poly(ethylene terephthalate-*p*-oxybenzoate)] thermotropic copolyesters were prepared by the copolymerization of poly(ethylene terephthalate) (PET) as moiety (II) and *p*-acetoxybenzoic acid (POB) as moiety (I). The polymeric products obtained were subjected to solid-state polymerization. Characterization of the copolyesters by thermomechanical analysis shows that properties such as the coefficient of thermal expansion, transition temperature, and maximum softening rate temperature varied directly as a function of composition as well as did solid-state polymerization time. All thermomechanical data were found to increase with the solid-state polymerization time due to the increase in the degree of polymerization and the effect of annealing. The coefficient of thermal expansion behaves in a manner that is interpretable by the crystalline state of the copolyester. The relationship between the free-volume fraction and thermodynamic properties is further correlated for a more comprehensive discussion on its molecular arrangements. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

A series of copolyesters based upon poly(ethylene terephthalate) (PET) that has been copolymerized with *p*-acetoxybenzoic acid has been the subject of several investigations into their structure and properties.¹⁻³ The chemical structure of this kind of *p*-acetoxybenzoic acid (POB)/PET copolyester consists of the following two moieties:



(1) POB

(2) PET

POB/PET copolyesters that contain at least 40 mol % POB are highly anisotropic.³ The relationships between properties and compositions for POB/PET copolyesters have been intensively investigated.⁴⁻⁹ In this article, we present a comprehensive study of the microdomain structure and microphase

mixing in segmented POB/PET copolyesters as provided by thermomechanical analysis.

THEORETICAL CONSIDERATION

When the temperature of a material changes from T_1 to T_2 , it will bring about a change in volume from V_1 to V_2 , and the mean thermal coefficient of volumetric expansion β_M is now defined by

$$\beta_M = \frac{V_2 - V_1}{V_1(T_2 - T_1)} \quad (1)$$

When the temperature changes by δT , a limiting value of this ratio becomes the true thermal coefficient of volume expansion:¹⁰

$$\beta = \frac{1}{V} \left(\frac{dV}{dT} \right) \quad (2)$$

The corresponding definition of the mean thermal coefficient of linear expansion is

$$\alpha_M = \frac{L_2 - L_1}{L_1(T_2 - T_1)} \quad (3)$$

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and the true thermal coefficient of linear expansion is

$$\alpha = \frac{1}{L} \left(\frac{dL}{dT} \right) \quad (4)$$

When the specimen is isotropic, then

$$\alpha = \frac{\beta}{3} \quad (5)$$

From eq. (4), the value of α becomes

$$\alpha = \frac{d \ln L}{dT} = 2.303 \frac{d \log L}{dT} \quad (6)$$

The thermal coefficient of linear expansion is commonly defined by

$$\alpha_l = \frac{L_2 - L_1}{L_0(T_2 - T_1)} \quad (7)$$

where L_0 is the specimen length at room temperature. If $L_1 \approx L_0$ and $\delta T \rightarrow 0$, only then does α_l approach the true value of α , as defined by eqs. (4) and (6). Equation (4) can be integrated to give

$$\frac{L - L_0}{L_0(T - T_0)} = \alpha \left[1 + \frac{\alpha}{2!} (T - T_0) + \frac{\alpha^2}{3!} (T - T_0)^2 + \dots \right] \quad (8)$$

It is thus shown that eq. (3) is the first term in an expansion of eq. (8). To study the molecular motion in a polymer molecular structure promoted by its thermal energy, the first coefficient of linear expansion (α_g), which is defined as the coefficient determined below the glass transition temperature, and the second coefficient of linear expansion (α_r), which is defined as the coefficient above the glass transition temperature, were measured experimentally.

The values of α change abruptly at the glass transition temperature. One of the most useful approaches to analyze the glass transition is to use the concept of free volume. Fox and Flory¹¹ defined free volume, V_f , as the difference between the total sample volume, V , and the volume occupied by molecules, V_0 , such that

$$V = V_0 + V_f \quad (9)$$

The free-volume fraction, f , is defined as

$$f = V_f/V \quad (10)$$

At and below T_g , f_g is given by $f_g = V_{f,g}/V$, where $V_{f,g}$ is the free volume at and below T_g . Above T_g , the free-volume fraction is then given by

$$f = f_g + (T - T_g)\beta_f \quad (11)$$

where β_f is the coefficient of thermal expansion of the free volume which will be given by the difference between the coefficients of thermal expansion of rubbery and glassy polymers. Simha and Boyer¹² suggested an alternative method for calculating the free-volume fraction f_g :

$$f_g = T_g(\beta_r - \beta_g) \quad (12)$$

where β_r and β_g represent the coefficients of thermal expansion above and below T_g , respectively. Therefore, $\alpha_g = \beta_g/3$ and $\alpha_r = \beta_r/3$.

EXPERIMENTAL

Materials

The copolyesters having various POB/PET compositions (Table I) were synthesized and subjected to solid-state polymerization according to the procedures reported previously.⁴⁻⁹ A typical procedure of preparation is as follows: A mixture of PAB (20–80 mol %) and PET pellets was placed in a 500 mL flask with a short head with an inlet and outlet for nitrogen. The nitrogen outlet was connected to a glass tube (distillation column), which led to a receiver with a provision for applying a vacuum. The reactants were melted under nitrogen atmosphere and heated at 275°C for 30 min. Acetic acid was distilled out at this stage. The reaction mixture was now heated to 275–320°C, then vacuum was applied slowly to about 0.5 mmHg and held for 4 h. *p*-Acetoxybenzoic acid as a comonomer for the POB moiety (I) was Aldrich reagent grade with purity of 98%. Poly(ethylene terephthalate) for moiety (II)

Table I Codes of Copolyesters Synthesized

POB/PET (mol %)	Code
0/100	PET
20/80	P28
40/60	P46
60/40	P64
80/20	P82
Eastman	EAS

was from Far Eastern Textile Co. having an IV value of 0.62, corresponding to the molecular weight of about 20,000. The copolyesters were prepared by the modification of PET with POB moieties in the main chain. The copolymer product obtained was ground and dried, then charged into a glass tube equipped with a vacuum line for the solid-state polymerization. Eastman 10109, which was examined as reference in this study, is a commercial thermotropic liquid crystalline copolyester produced by Tennessee Eastman Co.

Differential Scanning Calorimetry (DSC)

The thermal behavior analysis for all samples was performed by a DSC system (Seiko Instrument SSC-5200).⁷ Specimens controlled at an appropriate weight (7.5 mg) were heated in an atmosphere of dry nitrogen at a rate of 10°C/min to obtain the first heating curves. The enthalpy of fusion (ΔH) was then calculated by the area of the peak near the melting temperature.

Thermomechanical Analysis (TMA)

The thermomechanical behavior analysis for all samples was performed with a standard expansion-type probe with a 10 g load by a TMA system (DuPont TMA 2940). Samples were dried prior to compression molding at the melting temperature

and cooled down slowly to room temperature. Specimens controlled at an appropriate thickness (1.5 mm) were heated in an atmosphere of dry nitrogen at a rate of 10°C/min, mounted on a quartz cantilever platform, and scanned over the temperature range between 30 and 400°C to obtain a continuous curve of dimension change. All measurements are repeated for several times in order for the differences to be statistically significant. The observed transition temperature in the TMA is the intersection of tangents drawn to the probe position vs. the temperature curve before and during deflections. The first linear expansion coefficient (α_g) was calculated by the slope of the range between 35 and 50°C, while the second linear expansion coefficient (α_r) was calculated between 100 and 150°C.

RESULTS AND DISCUSSION

Above the onset penetration temperature, the rate of penetration is rapid and a sharp peak appears in the derivative TMA (designated as DTMA). In general, we can categorize penetration as having an effect on softening the backbone of the polymer chain. Discontinuities observed in the coefficient of thermal expansion below a transition point can be attributed to the onset of restricted motions of both POB and PET segments in the POB/PET copolyester.

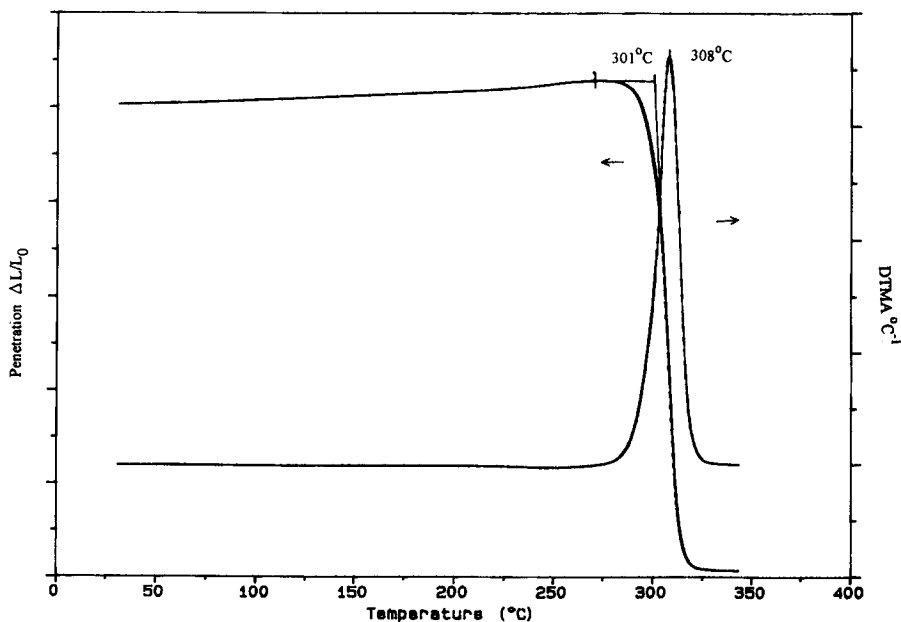


Figure 1 TMA and DTMA curves of the EAS sample.

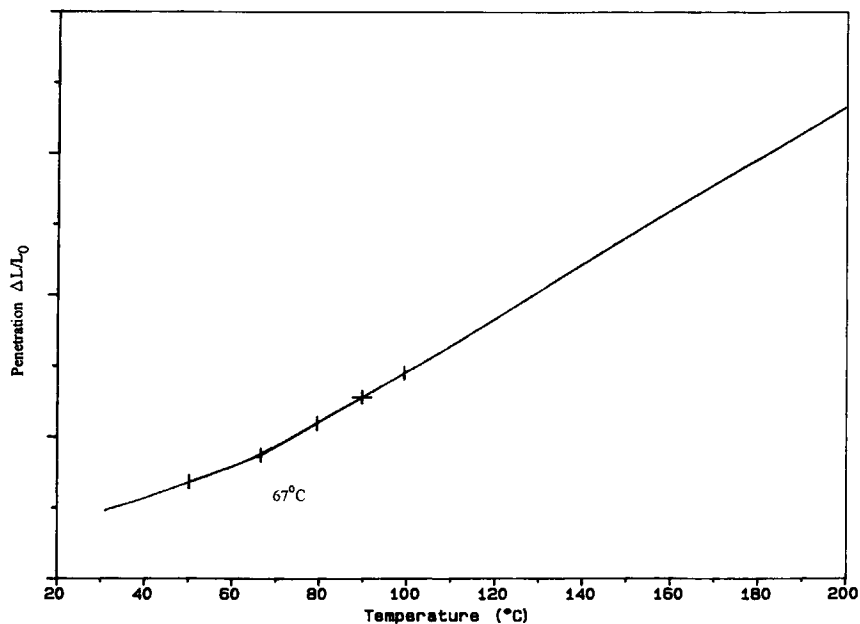


Figure 2 Amplified TMA curves of EAS in the temperature range 30–200°C.

Composition Effect

Figure 1 shows TMA and DTMA curves of the Eastman 10109 (EAS) sample. EAS is a commercialized product and its trade name is X7H. The onset and maximum rate of penetration temperature of the EAS sample were 301 and 307°C, respectively. The temperature range between 30 and 200°C of the TMA of the EAS sample was carefully reviewed

by amplifying the scale of dimensional change, as shown in Figure 2. It is observed that there is a distinct change in slope at 79°C which can be compared to its glass transition temperature in the DSC.⁷ First (α_g) and second (α_r) linear coefficients of thermal expansion are then determined in the range of 30–50°C and 100–150°C, respectively. The values of α_g and α_r of the EAS sample, for instance, are observed as 0.0091 and 0.0134 C⁻¹, respectively.

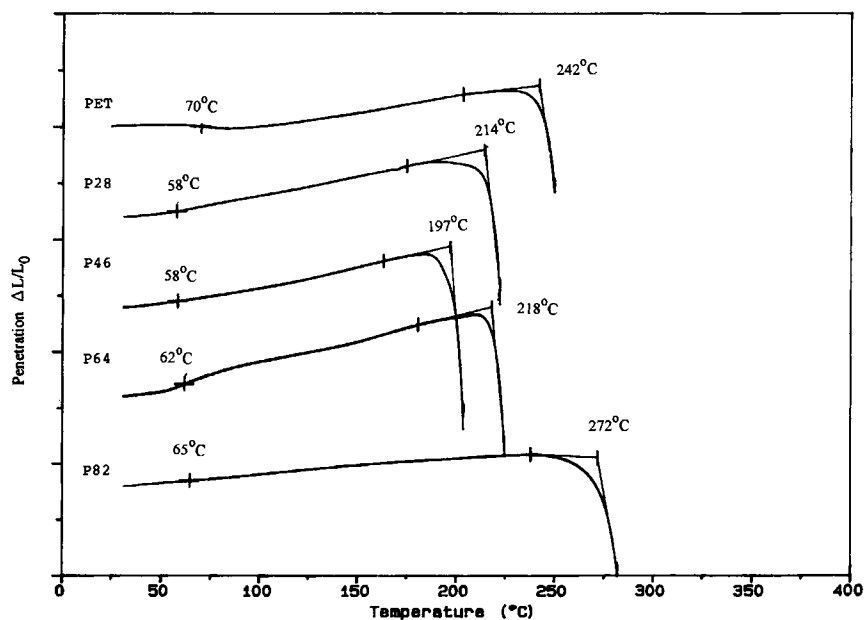


Figure 3 TMA curves as a function of composition.

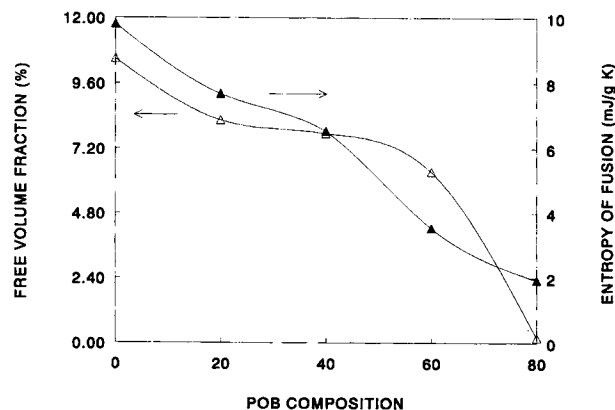
Table II Thermomechanical Properties and Correlation of Free-Volume Fraction with Thermodynamic Data of the Copolyesters

Code	α_g ($\times 10^5 \text{ C}^{-1}$)	T_g ($^{\circ}\text{C}$)	α_r ($\times 10^5 \text{ C}^{-1}$)	Penetration Temperature	
				Onset ($^{\circ}\text{C}$)	Maximum Rate ($^{\circ}\text{C}$)
PET	1.8	70	12.0	242	256
P28	8.7	58	17.0	214	227
P46	10.2	58	18.0	197	207
P64	10.7	62	17.0	218	235
P82	8.7	65	8.9	272	298

Code	T_f ($^{\circ}\text{C}$)	ΔH_f (J/g)	ΔS_f (J/g k)	f_g (%)
PET	253	51.9	0.0987	10.50
P28	219	38.4	0.0780	8.25
P46	198	31.4	0.0667	7.75
P64	253	1.8	0.0034	6.33
P82	257	1.1	0.0021	0.20

Figure 3 shows the TMA of the samples with various POB compositions. As the POB composition varies from 0 to 60%, the transition temperature, which is controlled by the PET composition, detected by the TMA remains almost the same (i.e., around 67–70°C) except for the P82, which is evaluated to be at 75°C, a little bit higher than the others. If the composition of the POB moiety is increased, the hindrance potential becomes large, resulting in a stiff chain and affecting the transition temperature associated to the PET segments in polymer chain. The onset penetration temperature is decreased as the POB composition varies from 0 to 40 mol % and then increased again from 40 to 80 mol % (see Fig. 3). This phenomenon is very similar to the values of T_m determined by the DSC as reported in our previous article.⁷ The phenomenon may be due to the heterogeneous combination of two different moieties in the polymer structure. It is well known that random copolymers have glass transitions at a temperature intermediate between those of the two homopolymers. It is believed that the transition and penetration behaviors are dependent on the composition of copolyester under consideration in a similar manner as for a random copolymer. All thermomechanical properties of various compositions are summarized in Table II. Both linear coefficients of thermal expansion (i.e., α_g , α_r) increase monotonously from 0 to 60 mol % POB. However, the P82 (80 mol % POB) shows smaller values (e.g., $8.7 \times 10^{-5} \text{ C}^{-1}$ for α_g and $8.9 \times 10^{-5} \text{ C}^{-1}$

for α_r) than those of the P64 (60 mol % POB) (e.g., $1.07 \times 10^{-4} \text{ C}^{-1}$ for α_g and $1.17 \times 10^{-4} \text{ C}^{-1}$ for α_r). The reason is that the thermal expansion behavior of P28, P46, and P64 is dominated mainly by the properties of the PET crystalline structure (in a folded chain state), whereas the thermal expansion behavior of the P82 is described by the properties of the POB crystalline structure (in liquid crystalline state). In our morphological observation by a polarizing microscopy,⁶ P28 and P46 show the conventional spherulite crystalline texture. In contrast, P64 and P82 indicate a typical liquid crystal pattern of a colored streak texture that is consistent with the anisotropic mesomorphic

**Figure 4** Plots of free-volume fraction and entropy of fusion as a function of POB composition.

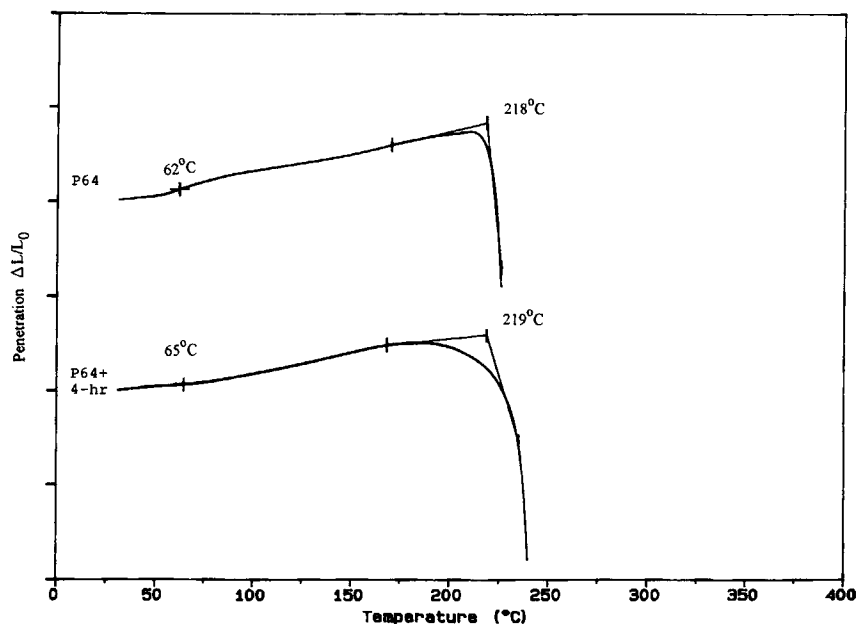


Figure 5 Effect of solid-state polymerization on TMA curves of P64.

phases. Therefore, the smaller values of α_g and α_r for the P82 than those for the P64 are due to the liquid crystalline state in which the polymeric molecules fit together (see Fig. 8).

The correlation of the free-volume fraction with the thermodynamic data of the copolyesters is shown in Table II. The free-volume fraction is calculated from eq. (12), and the DSC data are taken from our previous article.⁷ The entropy of fusion is calculated from the relation of $\Delta S_f = \Delta H_f/T_f$. The plots of the free-volume fraction and the entropy of fusion against the POB composition are shown in Figure 4. The values of the free-volume fraction decrease as the POB composition increases. Similarly, the entropy of fusion also decreases as the POB com-

position increases. The phenomena may be due to the incorporation of the rigid rodlike chain of the POB unit which consists of less mobile domain. It is worthwhile to note that both values of ΔH_f and ΔS_f decreased abruptly at the composition where the transition of the crystalline state takes place normally because there is still some confinement in the liquid crystalline state. It is believed that the crystalline state of the copolyester is responsible for this phenomenon.

Solid-state Polymerization Effect

TMA curves of the P64 with and without 4 h solid-state polymerization are shown in Figure 5. Tran-

Table III Thermomechanical Properties and Correlation of Free-Volume Fraction with Thermodynamic Data of P64 Before and After 4-hr Solid-state Polymerization.

Run	α_g ($\times 10^5 \text{ C}^{-1}$)	T_g ($^{\circ}\text{C}$)	α_r ($\times 10^5 \text{ C}^{-1}$)	Penetration Temperature	
				Onset ($^{\circ}\text{C}$)	Maximum Rate ($^{\circ}\text{C}$)
Before	10.7	62	17.0	218	235
After	11.7	65	22.0	219	249

Run	T_f ($^{\circ}\text{C}$)	ΔH_f (J/g)	ΔS_f (J/g k)	fg (%)
Before	253	1.8	0.0034	6.33
After	270	0.1	0.0002	10.45

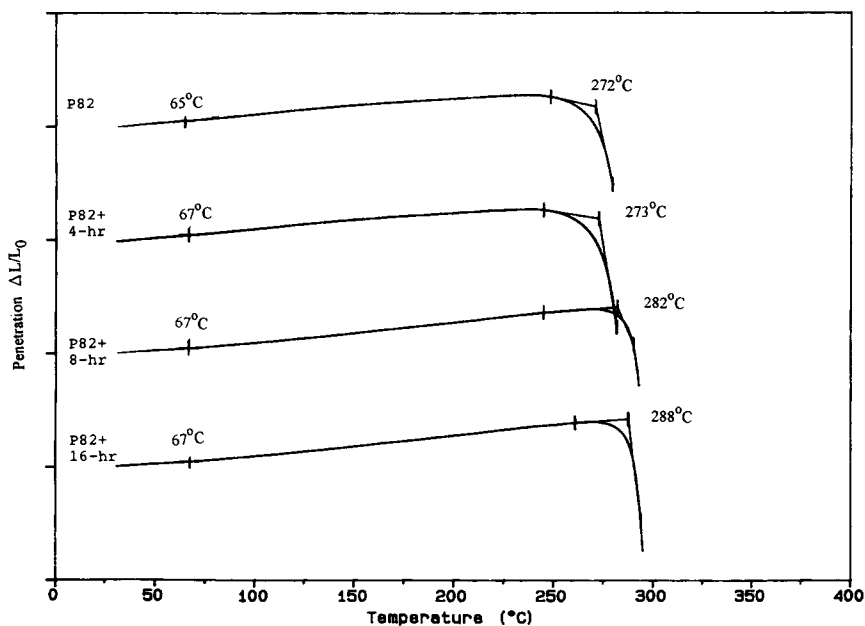


Figure 6 Effect of solid-state polymerization times on TMA curves of P82.

sition temperature, onset, and maximum rate penetration temperatures all increase after the solid-state polymerization. They indicate better heat-resistant properties due to a higher degree of polymerization. All thermomechanical properties of the P64 before and after 4 h solid-state polymerization are shown in Table III. Both linear coefficients of

thermal expansion become higher after solid-state polymerization (i.e., $1.07 \times 10^{-4} \text{ C}^{-1}$ to $1.17 \times 10^{-4} \text{ C}^{-1}$ for α_g and $1.17 \times 10^{-4} \text{ C}^{-1}$ to $2.2 \times 10^{-4} \text{ C}^{-1}$ for α_r). This implies that the linear coefficient of the thermal expansion of a sample under a certain composition is dependent on the degree of polymerization and the molecular orientation. Table III also

Table IV Thermomechanical Properties and Correlation of Free-Volume Fraction with Thermodynamic Data of P82 with Various Solid-state Polymerization Time

SSP ^a Time	α_g ($\times 10^5 \text{ C}^{-1}$)	T_g (°C)	α_r ($\times 10^5 \text{ C}^{-1}$)	Penetration Temperature	
				Onset (°C)	Maximum Rate (°C)
0 h	8.7	65	8.9	272	298
4 h	8.8	67	9.1	273	299
8 h	8.9	67	10.1	282	296
16 h	8.9	67	13.1	288	302
EAS ^b	9.1	67	13.4	301	308

SSP ^a Time	T_f (°C)	ΔH_f (J/g)	ΔS_f (J/g k)	f_g (%)
0 h	257	1.1	0.0021	0.0020
4 h	283	2.3	0.0041	0.0031
8 h	288	4.4	0.0078	0.0122
16 h	292	5.1	0.0090	0.0429
EAS ^b	299	6.7	0.0117	0.0439

^a SSP: solid-state polymerization.

^b EAS: Eastman 10109 cited for reference.

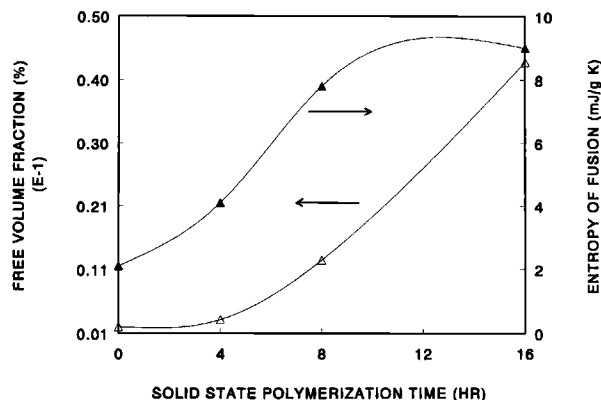


Figure 7 Free-volume fraction and entropy of fusion as a function of solid-state polymerization times.

shows the correlation of the free-volume fraction with the thermodynamic data of the P64 before and after 4 h solid-state polymerization. The free-volume fraction is always increased after 4 h solid-state polymerization.

Similar phenomena are observed in the P82. Figure 6 shows the TMA results of the P82 with various solid-state polymerization times. The transition temperature, onset, and maximum penetration temperature of copolyesters increase monotonously with the solid-state polymerization time. All thermomechanical properties of the P82 with various solid-state polymerization times are listed in Table IV, where data of the EAS sample are also cited as a reference. It is seen that the thermomechanical properties of the P82 after 8 and 16 h solid-state polymerizations approach more and more similar values as those of the EAS sample. The correlation of the free-volume fraction with various solid-state polymerization times is also shown in Table IV. The relation between free-volume fraction and entropy

of fusion with various solid-state polymerization times are shown in Figure 7. The free-volume fraction and entropy of fusion are increased as the solid-state polymerization time proceeds due to increasing in the randomness caused by transesterification. The changes in molecular arrangements due to composition and solid-state polymerization can be illustrated as in Figure 8, which are in accordance with the thermomechanical and thermodynamic data measured.

CONCLUSION

The copolyesters having a composition of *p*-oxybenzoate as moiety (I) and poly(ethylene terephthalate) as moiety (II) can be formed to have a thermomechanical behavior in a desirable range. Moreover, thermomechanical properties can be modified by means of the solid-state polymerization process. This study led to the following conclusions.

1. Transition temperature, onset, and maximum rate penetration temperature are decreased monotonously as the POB composition increases from 0 to 40 mol %, and then increased as the POB composition increases from 40 to 80 mol % in the general manner as a random copolymer.
2. Transition temperature, onset, and maximum rate penetration temperatures are always increased after solid-state polymerization. This implies a higher degree of polymerization and a better molecular orientation and is in accordance with the thermodynamic data measured by DSC.
3. In general, the linear coefficient of thermal

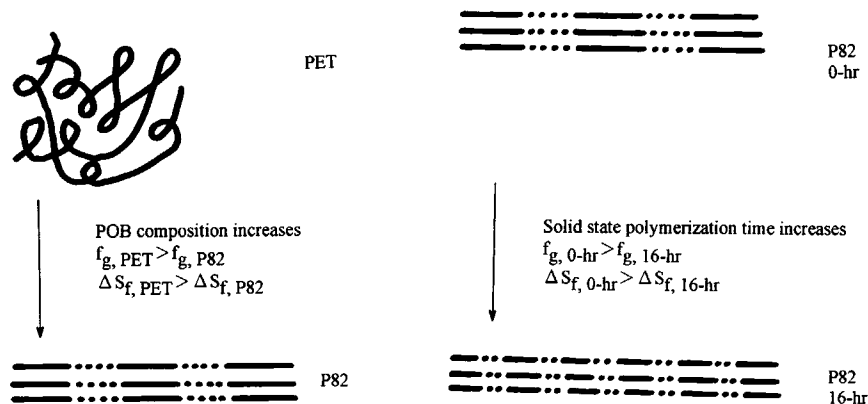


Figure 8 Illustration of molecular arrangement changes by composition and solid-state polymerization.

expansion (i.e., α_g and α_r) is increased monotonously from 0 to 60 mol % as the POB composition is increased. However, values of α_g and α_r for the P82 showed smaller values than for the P64. It is believed that the thermal expansion behavior is also affected by the state of the crystalline structure when the composition is over P64 where the transition of the crystalline state normally takes place.

4. The behavior of the free-volume fraction has the same tendency as that of the entropy of fusion. As the POB composition increases, the free-volume fraction and, therefore, the entropy of fusion decrease. In contrast, as the solid-state polymerization time increases, the free-volume fraction and, therefore, the entropy of fusion increase.

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