Studies on Co[poly(ethylene terephthalate-*p*-oxybenzoate)] Thermotropic Copolyester (I): Synthesis and Thermogravimetric Behavior

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SYNOPSIS

A series of co[poly(ethylene terephthalate-*p*-oxybenzoate)] thermotropic copolyester was synthesized from various ratios of two different moieties of either poly(ethylene terephthalate) (PET) or its oligomer as moiety (II) with *p*-acetoxybenzoic acid as moiety (I) through the polycondensation process. The polymeric products obtained were then ground and subjected to solid-state polymerization under vacuum for various polymerization times. Thermogravimetric analysis (TGA) and the derivative thermogravimetric analysis (DTG) were performed with these samples obtained. Also, a commercial product, Eastman 10109, was analyzed in comparison with these samples. It was found that the copolyesters made of PET and of its oligomer in a *p*-oxybenzoate (POB):PET = 80 : 20 composition ratio and subjected to 8 and 4 h solid-state polymerization times, respectively, showed the most similar thermogravimetric behavior with Eastman 10109. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In the last two decades, a new class of thermotropic polymeric materials known as liquid crystalline polymers (LCPs) has been developed, which has received great attention from both industry and academia.[1] Many of the stiff-chain aromatic polymers that are used as high-strength–high-modulus materials exhibit liquid crystalline behavior. For practical purposes, there is a need for nematic mesophases at relatively low temperature in regard of processing. A thermotropic aromatic aliphatic copolyester by the reaction of *p*-acetoxybenzoic acid (PAB) and poly(ethylene terephthalate) (PET) has been produced by the Tennessee Eastman Co.[2-4] The chemical structure of *p*-oxybenzoate (POB)/PET copolyesters consists of the following two moieties:
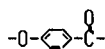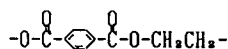
(I) POB   (II) PET

POB/PET copolyesters with POB unit content from 40 to 90 mol % were found to be highly anisotropic.[2] Lader and Krigbaum studied the thermal behavior of a copolyester of the same type of co[poly(ethylene terephthalate-*p*-oxybenzoate)].[5] In this paper, POB/PET copolyesters with POB content from 0 to 100 mol % were prepared by melt polycondensations of PAB modified by either PET polymer or its oligomer. The effects of moiety composition as well as two sources of PET moiety (II) on the thermogravimetric behavior of products were investigated. The effect of solid-state polymerization time on the thermogravimetric behavior was also discussed. Moreover, a commercial product, Eastman 10109, was characterized in comparison with the samples synthesized in this paper.

EXPERIMENTAL

A. Materials

PAB as comonomer for the POB moiety (I) was Aldrich reagent grade with purity of 98%. PET for moiety (II) was from the Far East Textile Co., having an I.V. value of 0.62, corresponding to molecular

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Table I   Codes of Copolyesters Synthesized

| POB/ PET	PET Moiety from Polymer	PET Moiety from Oligomer
100/0	PPOB	
80/20	P82	O82
60/40	P64	O64
40/60	P46	O46
20/80	P28	O28
0/100	PET	OET
Eastman	EAS	

weight of about 20,000. The PET oligomer as another source for moiety (II) was obtained by the glycolysis of PET resin. The PET resin in a 1 : 4 ratio of the EG/PET mixture was depolymerized under 2 atm pressure at 190°C for 4 h in a laboratory-stirred reactor having a bomb cylinder of 2000 mL (Parr Instrument). The PET oligomer (OET) thus obtained has a molecular weight of about 2000 with degree of polymerization of 10. The procedure of glycolysis of PET mentioned above was already reported in our previous paper.[6]

B. Synthesis

The copolyesters before solid-state polymerization were prepared by the modification of PET with POB moieties in the main chain. 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 and 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 vacuum. The reactants were melted under nitrogen atmosphere. The reactants were then 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. The polymer product obtained was then ground and dried.

C. Solid-state Polymerization

The dry ground sample obtained was charged into a glass tube equipped with vacuum line for the solid-state polymerization. After vacuum was applied, the tube was heated to 220–260°C and held for various
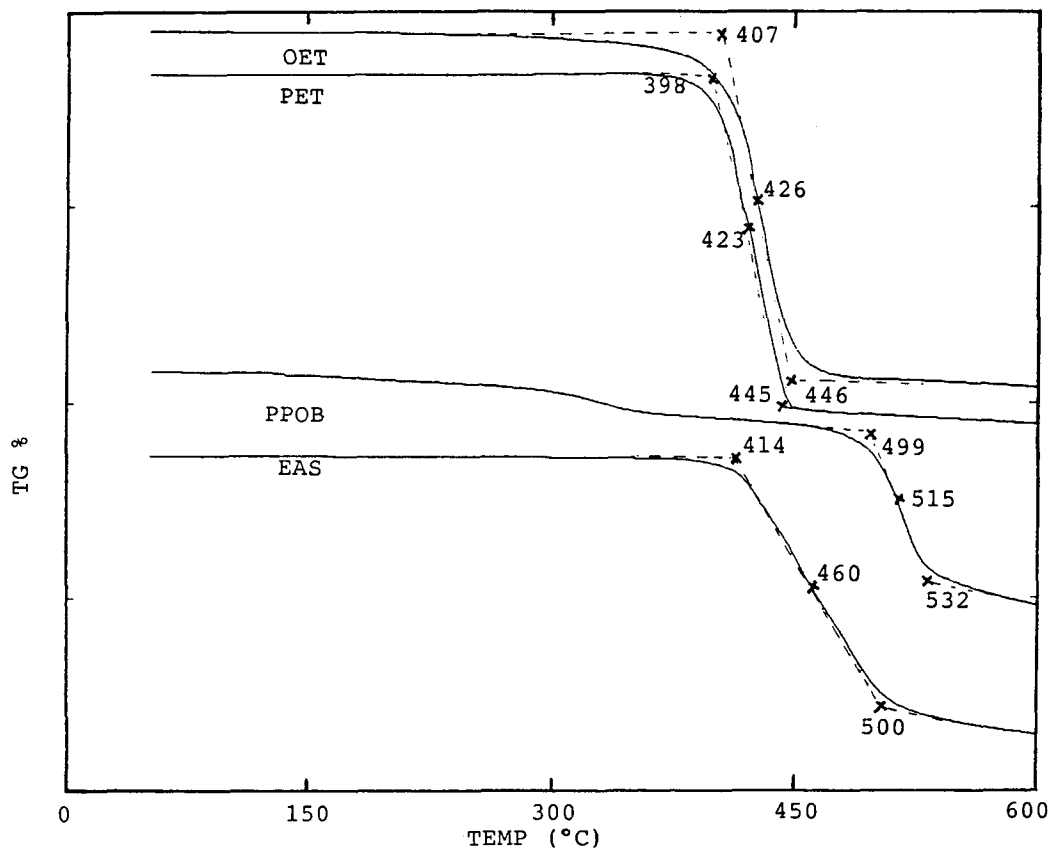
Figure 1   Thermogravimetric curves for OET, PET, PPOB, and EAS.

time intervals. The codes for each samples synthesized are listed in Table I.

D. Thermogravimetric Analysis

The thermogravimetric analysis (TGA) for all samples was performed by a TGA system (Seiko Instrument SSC-5200). The TGA measured weight change of a material was a function of temperature at a heating rate of 10°C/min, whereas the derivative thermogravimetric analysis (DTG) indicated the decomposition rate of samples at a definite heating temperature.

E. Eastman Copolyester

Eastman 10109 examined in this study was a commercial thermotropic liquid crystalline copolyester obtained from the market. This product is surmised to be a copolyester synthesized from 20 mol % of PET and 80 mol % of p-hydroxybenzoic acid.

F. Poly(p-oxybenzoate)

Poly(p-oxybenzoate) was prepared by the polycondensation of p-acetoxybenzoic acid (PAB) using the

same reaction conditions as with the copolyester. The product is labeled PPOB.

RESULTS AND DISCUSSION

The thermal stability of a polymeric material is primally characterized by the decomposition temperature in TGA. Above the decomposition temperature, the rate of degradation is rapid and there appears a sharp peak in DTG. In general, we can categorize degradation as having an effect on the backbone of the polymer chain.

A. Thermogravimetric Analysis

Figure 1 shows the thermogravimetric curves of samples for PET oligomer (OET) and PET polymer (PET), poly(p-oxybenzoate) homopolymer (PPOB), and Eastman 10109 copolyester, respectively. The category of a thermogravimetric curve in TGA is determined by the average decomposition temperature (T_d) as well as the lower decomposition temperature (T_1) and the upper decomposition temperature (T_2). It is seen in Figure
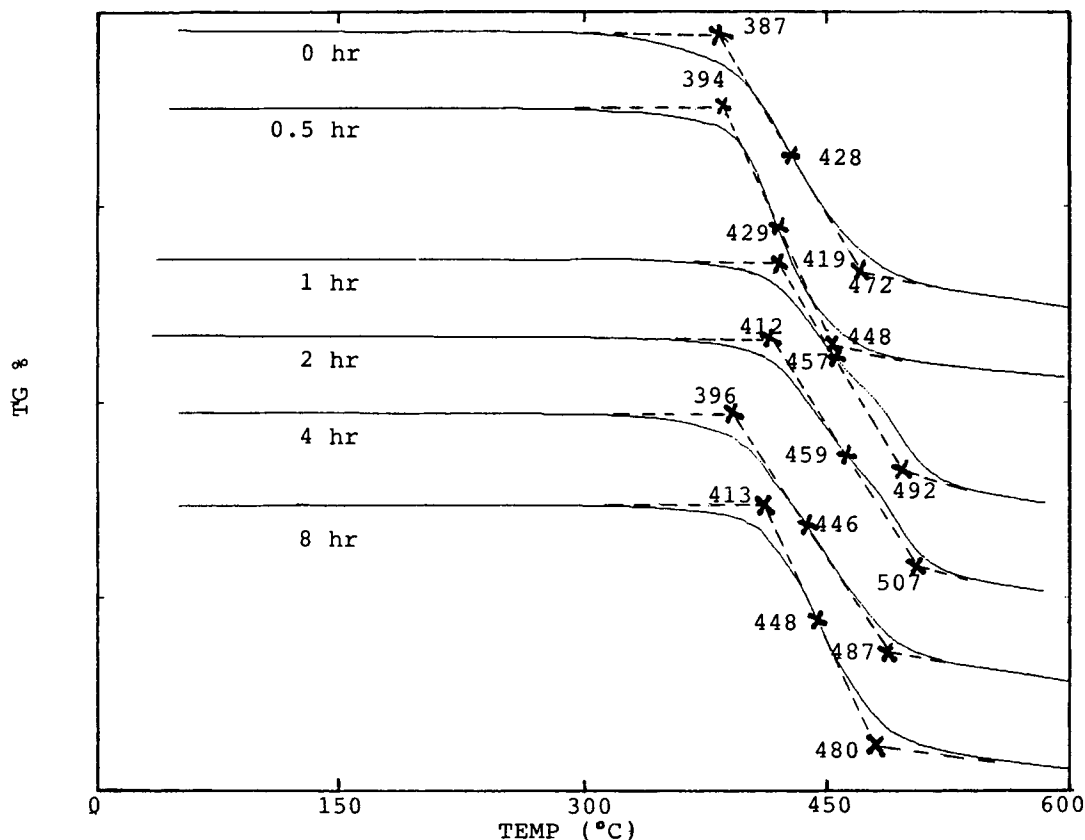

Figure 2   TGA of O82 as a function of solid-state polymerization time.

Table II Decomposition Temperature vs. Solid-state Polymerization Times for O82 and P82

Polymerization Time (h)	O82	P82
0	428	420
0.5	429	460
1	457	453
2	459	452
4	446	448
8	448	455

1 that PPOB has a high decomposition temperature at 515°C, whereas those of PET and OET have lower average decomposition temperatures at 423 and 426°C, respectively. OET having a low molecular weight indicates a slightly higher decomposition temperature than that of PET having a high molecular weight. This means that the higher degree of polymerization of the same chemical segment may be less stable under the thermal decomposition temperature. Moreover, the difference between upper

and lower decomposition temperatures (ΔT) of POB/PET copolyester is larger than those of the homopolymer consisting itself of pure moiety (**I**) or (**II**) (i.e., PPOB or PET). This means that a copolyester has more uniform thermal characteristics over the broad heating temperature interval.

Figure 2 shows the TGA of O82 as a function of the solid-state polymerization time, from where the values of T_1, T_2, and T_d for each curve are measurable, as shown in Figure 1. Decomposition temperature vs. solid-state polymerization time for O82 and P82 are listed in Table II. It is shown that the decomposition temperature is increased first and then decreased as the solid-state polymerization proceeds within a 4 h solid-state polymerization in the case of O82.

However, for a longer solid-state polymerization, e.g., for 8 h, the decomposition temperature tends to increase again. A similar trend is observed in the TGA of P82 (see Fig. 3 and Table II). It is clear that the lower decomposition temperature is related to the PET moiety, whereas the upper decomposition temperature is related to the POB moiety. To compare the temperature changes in lower and upper
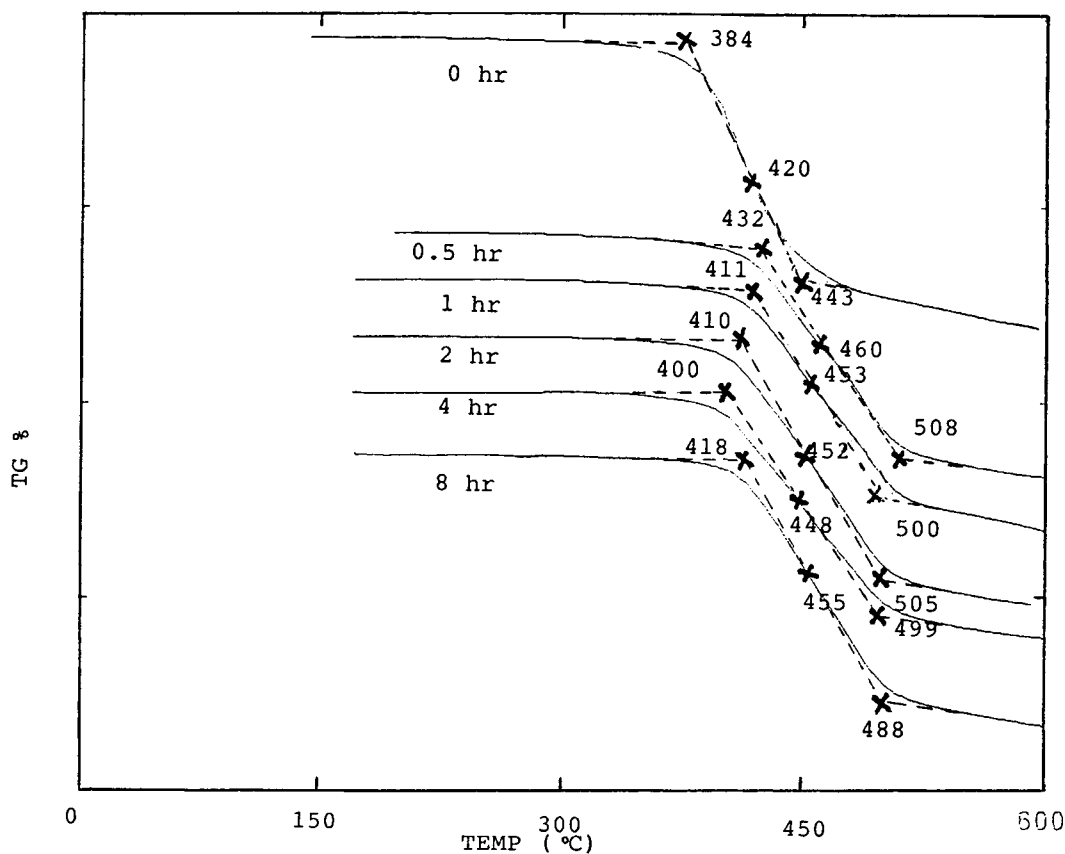

Figure 3 TGA of P82 as a function of solid-state polymerization time.

Table III   Effect of 4-H Solid-State Polymerization on Changes in Lower (T_1) and Upper (T_2) Temperatures and the Difference of Lower and Upper Temperatures

	T_1 $T_b \to T_a$	ΔT_1	T_2 $T_b \to T_a$	ΔT_2	$\Delta T_b \to \Delta T_a$	ΔT Change	T_d T_{db}	T_{da}
O28	406 → 409	(+)	450 → 448	(−)	Δ44 → Δ39	(−)	425	428
P28	406 → 407	(+)	445 → 449	(+)	Δ39 → Δ42	(+)	426	429
O46	407 → 405	(−)	453 → 455	(+)	Δ46 → Δ50	(+)	430	430
P46	407 → 406	(−)	460 → 456	(−)	Δ53 → Δ50	(+)	431	431
O64	383 → 406	(+)	459 → 476	(+)	Δ76 → Δ70	(−)	420	439
P64	406 → 412	(+)	479 → 464	(−)	Δ73 → Δ52	(−)	436	442
O82	387 → 396	(+)	472 → 487	(+)	Δ85 → Δ91	(+)	428	446
P82	384 → 400	(+)	443 → 499	(+)	Δ59 → Δ99	(+)	420	448

		For Comparison		
	T_1	T_2	ΔT	T_d
PET	398	428	Δ30	423
OET	407	446	Δ39	426
EAS	413	500	Δ87	460
PAB	499	532	Δ33	515

(+) increased, $\Delta T = T_2 - T_1$; (−) decreased, ΔT change $= \Delta T_a - \Delta T_b$; T_1: lower temperature, ΔT_1 : T_1 change; T_2: upper temperature, ΔT_2 : T_2 change; ΔT_b: ΔT before solid-state polymerization; ΔT_a: ΔT after solid-state polymerization; T_d: average decomposition temperature; T_{db}: average decomposition temperature before solid-state polymerization; T_{da}: average decomposition temperature after solid-state polymerization.
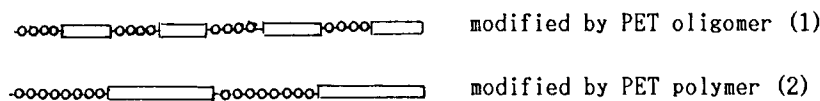
temperatures after 4 h solid-state polymerization for polyesters modified by both OET and PET, the experimental data obtained in Figures 2 and 3 are summarized in Table III.

From Table III, it is observed that the lower temperature (T_1) of O28 is slightly increased, but the upper temperature (T_2) is slightly decreased after 4 h solid-state polymerization. In contrast, in the case of P28, the upper temperature is slightly increased and the lower temperature is also increased. On the other hand, in the case of O82 and P82, it is observed that both lower and upper temperatures are increased for both PET sources of copolyesters after 4 h solid-state polymerization. It is believed that the influence of two moieties in copolyester on the thermogravimetric behavior depends on the PET moiety whether its starting source stems from PET polymer or PET oligomer. The composition structures of polyesters stemmed from two different starting PET sources are sketched in Figure 4.

The copolyester subjected to the solid-state polymerization is followed by two competitive reactions:

$$\text{PET} \underset{k_2 \text{ (degradation)}}{\overset{k_1 \text{ (polymerization)}}{\rightleftharpoons}} \text{PET} \qquad (3)$$

$$\text{POB} \underset{k_4 \text{ (degradation)}}{\overset{k_3 \text{ (polymerization)}}{\rightleftharpoons}} \text{POB} \qquad (4)$$
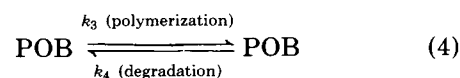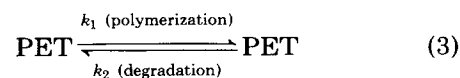
If the reactants are taken to a sufficiently high temperature, the competitive reactions will go through a series of changes in the values of k_1, k_2, k_3, and k_4. In general, copolyester having structure (2) has larger values of k_2 and k_4 than those of a copolymer having structure (1), because a segment having a higher degree of polymerization is less thermal-resistant. In the case of a PET-rich formulation for a copolyester modified by PET oligomer (e.g., O28), eq. (3) for eq. (1) is dominant, where $k_2 > k_1$ and $k_3 > k_4$, but the chain-cleavage of PET will less often

modified by PET oligomer (1)

modified by PET polymer (2)

Figure 4   Schematic model of composition structures for copolyesters.

occur. As a result, the lower temperature is increased, but the upper temperature is decreased after a 4 h solid-state polymerization, because the structure composition of the product tends toward shorter PET units and longer POB units due to PAB polymerization. In the case of the PET-rich formulation for a copolyester modified by PET polymer (e.g., P28), eq. (3) for eq. (2) is now dominant, where $k_2 > k_1$, and $k_4 > k_3$, but the chain cleavage of PET more often occurred. As a result, both lower and upper temperatures are increased after 4 h solid-state polymerization, because the composition structure of the product tends toward both shorter PET and shorter POB units due to both PET and PPOB degradations. It is recognized that the shorter the degree of polymerization of the units is, the more thermal stable the sample is.

In contrast, in the case of the POB-rich formulation, the copolyesters modified by both PET oligomer and PET polymer (e.g., O82 and P82) are increased in both lower and upper temperatures after 4 h solid-state polymerization (see Table II). Here, eq. (4) is dominant, and if $k_4 > k_3$ and $k_2 > k_1$, the lower and upper temperatures are both increased

regardless of the copolyester modified by PET oligomer or PET polymer, because the influence of eq. (3) is now minor in this formulation. The composition structures now consist of shorter PET units and shorter POB units as well. It is also seen that the decomposition temperatures of copolyester modified by PET polymer are always slightly higher than those modified by PET oligomer in each pair of the same composition. Also, the change in ΔT is decreased in O28, whereas it is increased in P28 after 4 h solid-state polymerization. In contrast, the change in ΔT is increased in both O82 and P82. In general, the change in ΔT is enlarged during solid-state polymerization. As shown in Table II, the ΔT after the solid-state polymerization for O82 and P82 are 91 and 99, respectively, whereas ΔT for Eastman (EAS) is 87.

B. Derivative Thermogravimetric Analysis

Figure 5 shows the derivative thermogravimetric analysis (DTG) for OET, PET, PAB, and EAS. OET and PET have peaks near 420 and 430°C, whereas PAB has a peak at 521°C. Eastman 10109,
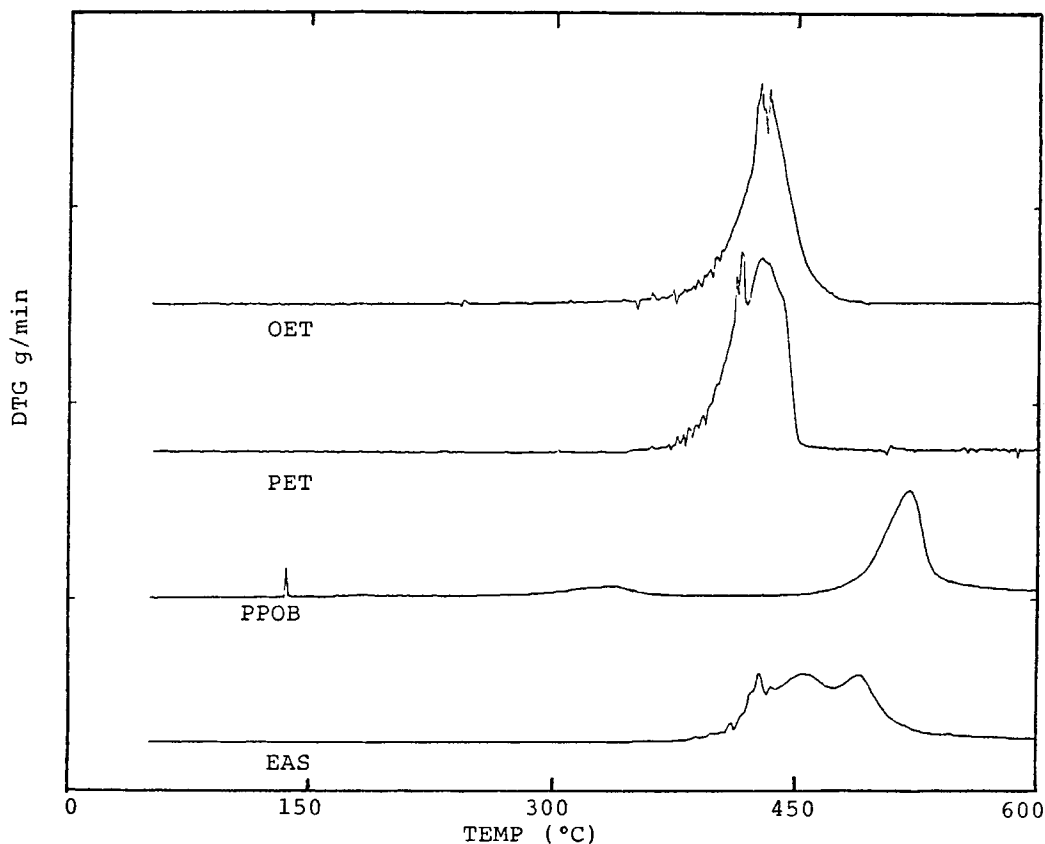
Figure 5   Derivative thermogravimetric analysis for OET, PET, PPOB, and EAS.

a commercial copolyester, has three split broad peaks at 428, 457, and 489°C, respectively. Figure 6 examines the DTG of O82 as a function of the solid-state polymerization time. It is seen that a new peak at a higher temperature range near 490°C has appeared during the first 1 h solid-state polymerization. After 4 h polymerization, it tends to be combined together by these two peaks and becomes a broad peak with three major high points, which is very similar to the DTG of Eastman 10109 (see Figs. 5 and 6).

A new peak at a higher-temperature range does not appear even after 4 h solid-state polymerization in the case of a rich PET moiety formulation, such as of O28 and P28. Furthermore, peaks of DTG for higher PET moiety copolyesters merely shift their peaks to a higher-temperature range even after 4 h solid-state polymerization, such as 028, P28, and even 064. For P64, however, the peak will only slightly shift to a higher-temperature range.

Figure 7 examines the DTG for P82 as a function of the solid-state polymerization time, which is very similar to that of O82 shown in Figure 6. However, the appearance of a second peak at a higher tem-

perature seems to be quicker in the solid-state polymerization than in the case of O82. The second peak at the higher-temperature range is attributable to the growth of the POB moiety in the copolyester main-chain backbone according to the reaction of eq. (4), where $k_3 > k_4$ at the early stage of the solid-state polymerization.

C. Decomposition Temperature

The decomposition temperature depends primary on the ratio of POB moiety (II) in the main chain. It is indicated that the decomposition temperature is increased as the ratio of POB moiety (II) is increased (see Table II).

It is believed that a copolyester having uniform thermal characteristics can be obtained by the modification of smaller molecular weight of PET oligomer moiety as in O82, where the chain cleavage of PET less often occurred during the solid-state polymerization process. On the other hand, this also can be prepared by the modification of larger molecular weight of PET polymer moiety as in P82 where the chain cleavage of PET more often oc-
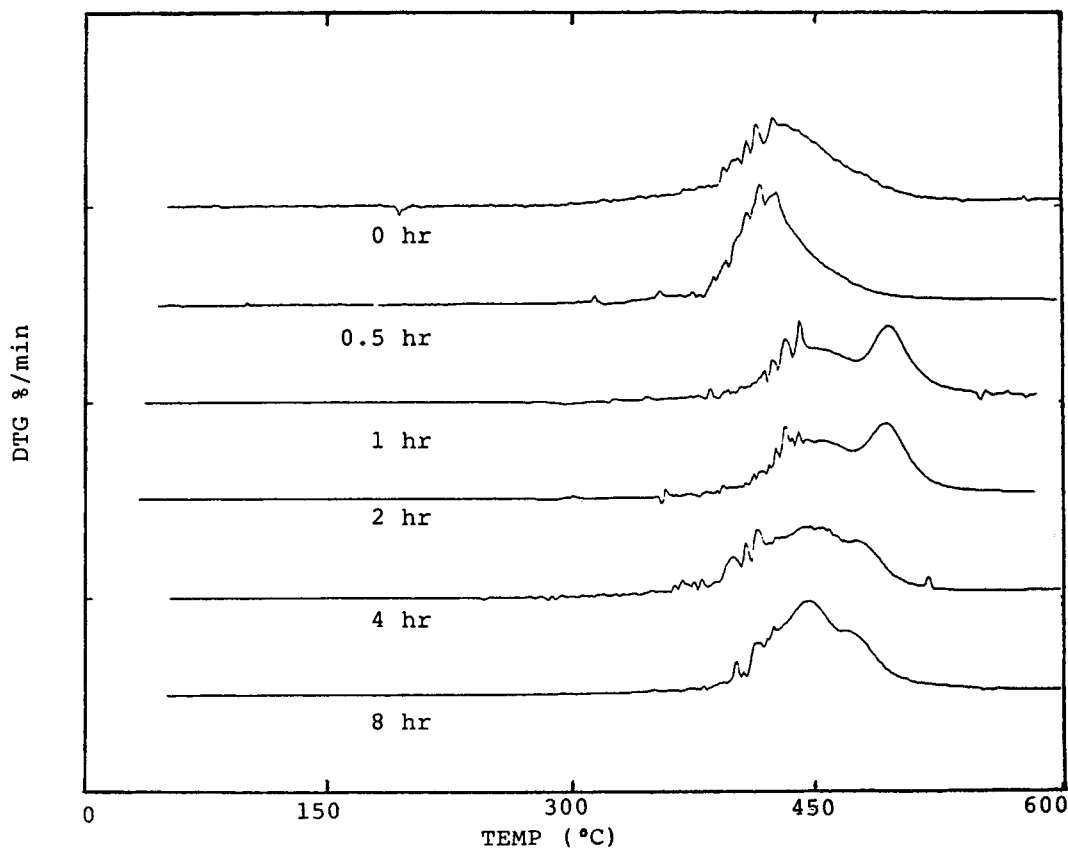

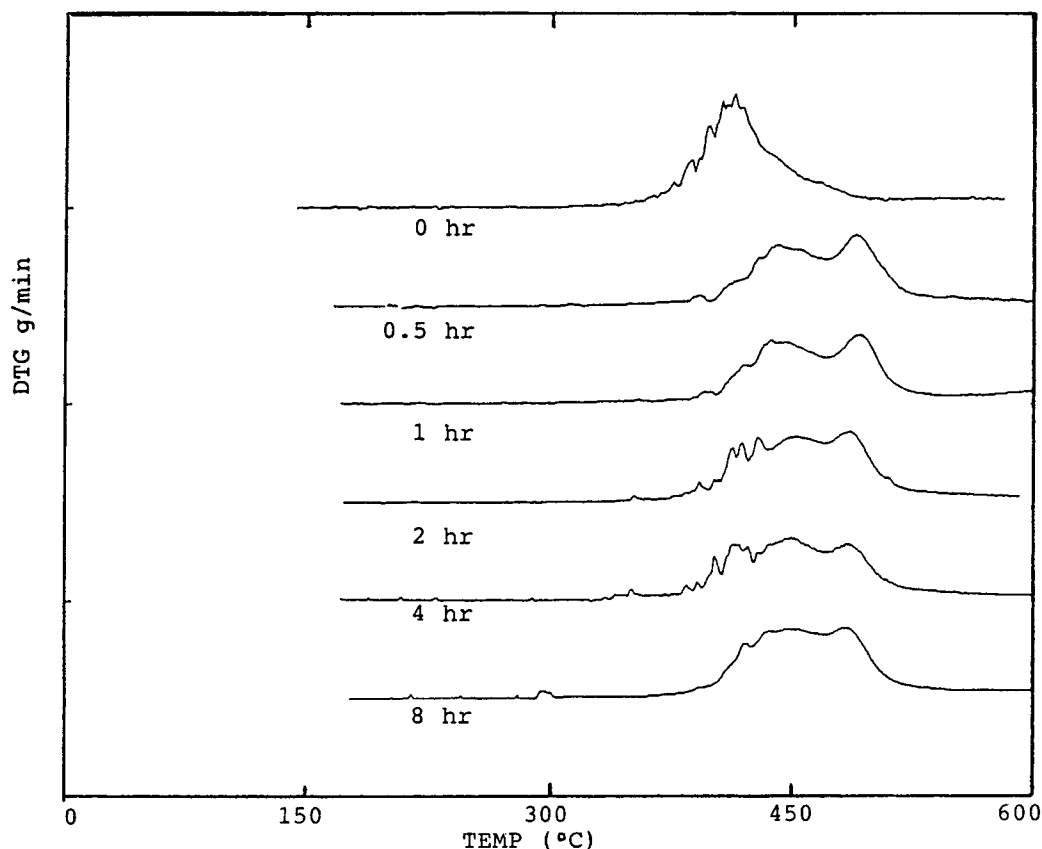**Figure 6** DTG of O82 as a function of solid-state polymerization time.

Figure 7 DTG of P82 as a function of solid-state polymerization time.

curred during the solid-state polymerization process. At an early stage of the solid-state polymerization, $k_3 > k_4$ of eq. (4) is preferred in the POB-rich formulation. At the long solid-state polymerization stage for over 4 h, however, $k_4 > k_3$ of eq. (4) is to be assumed. Finally, k_1, k_2 and k_4, k_3 approach in an equilibrium state for a longer polymerization time. Therefore, the competitive reactions of eqs. (3) and (4) could effect the decomposition temperature of the polyester produced. In fact, the decomposition temperature of a copolyester will first increase, then decrease, as the solid-state polymerization proceeds. Finally, this will be increased again for a longer polymerization time. It is indicated that this trend is quicker to occur in P82 than in O82 (see Table III).

CONCLUSION

A series of copolyesters have been made by several composition ratios of p-oxybenzoate as moiety (**I**) and poly(ethylene terephthalate) as moiety (**II**). Moiety (**II**) can stem from either PET polymer or

PET oligomer. The copolyesters can be synthesized to have a thermal behavior in a desirable range by introducing of the chain flexibility of moiety (**II**). The introduction of moiety (**II**) into the structure composition causes the decrease in the upper decomposition temperature, but the increase in the lower decomposition temperature of copolyester in TGA curves. The decomposition temperature of a copolyester depends on the composition of these two moieties (**I**) and (**II**) in the structure as well as the sources of PET moiety of different molecular weights.

The function of the solid-state polymerization is to make originally separated two peaks to a combined peak in a balanced and uniform manner over a broader heating temperature range in DTG curves. Furthermore, the change in $\Delta T (= \Delta T_a - \Delta T_b)$ will be enlarged after solid-state polymerization in the case of the POB-rich formulation in the TGA curves.

It is found that the copolyester synthesized from p-acetoxybenzoic acid and either PET oligomer or PET oligomer in the composition ratio of 80 : 20 and performed for a 4 and 8 h solid-state polymerization times, respectively, under sufficient vacuum

and temperature showed the most similar thermo-gravimetric behaviors with Eastman 10109 scanned in the TGA and DTG curves.

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