

# Studies on Co[Poly(Ethylene Terephthalate-*p*-Oxybenzoate)] Thermotropic Copolyester (IV) Thermal History by Differential Scanning Calorimetry

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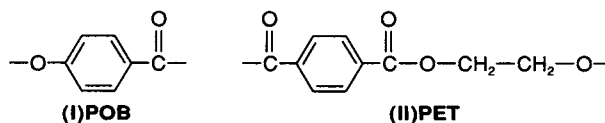
## SYNOPSIS

A series of co[poly(ethylene terephthalate-*p*-oxybenzoate)] thermotropic copolyesters with various compositions were prepared by the copolymerization of either poly(ethylene terephthalate) polymer (PET) or its oligomer (OET) as moiety (II) and *p*-acetoxy-benzoic acid (POB) as moiety (I). The polymeric products obtained were then subjected to solid-state polymerization. The glass and melting transitions of the copolyesters obtained have been studied by differential scanning calorimetry (DSC). Effects of composition and solid-state polymerization on DSC are discussed. The melting point of copolyesters possesses a higher value if the PET polymer is used as PET moiety in the copolyesters. In the DSC scan of the POB rich composition, the endothermic peak shows obscurely and enthalpy of fusion becomes small due to the change in the crystalline morphology from isotropic to anisotropic. In general, the melting point of copolyesters is increased by the solid-state polymerization reaction. It is also found that both the melting temperature and enthalpy of fusion of the copolyesters can be increased simultaneously by the solid-state polymerization reaction only when the composition of POB/PET is 80/20. This phenomenon at this composition may be attributed to the annealing effect caused by the randomness of two moiety units on the backbone chain of copolyesters and the increased molecular weight as well. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

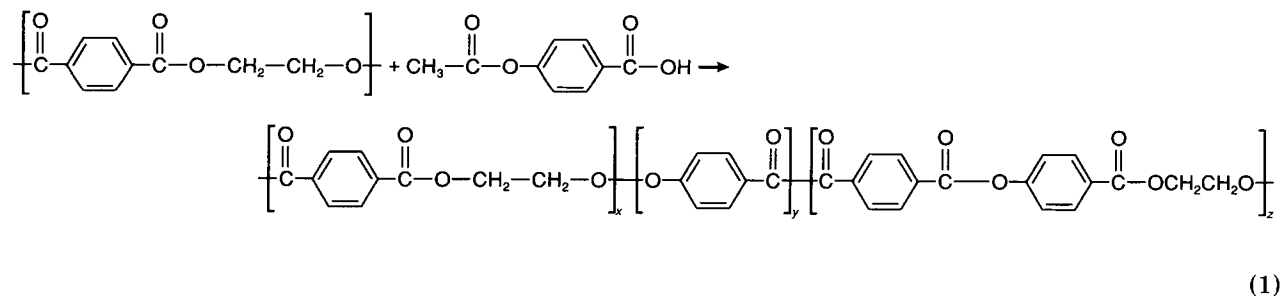
Liquid crystalline polymers (LCPs) have been developed and represent a rapidly expanding field of research both in industry and academia.<sup>1</sup> The principal reason for the effort was that these materials might exhibit ultrahigh strength and ultrahigh modulus due to the rigid and semirigid polymeric backbone. For practical purposes, there is a need for nematic mesophases at relatively low temperature in regard to processing.

Thermotropic aromatic aliphatic copolyesters by the polycondensation of *p*-acetoxybenzoic acid (PAB) and poly(ethylene terephthalate) (PET) were first developed by the Tennessee Eastman Co.<sup>2-4</sup> The chemical structure of the kind of *p*-acetoxy-benzoic acid (POB)/PET copolyesters consists of the following two moieties:



This modification by reacting PET with POB may proceed according to the following equation:

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These POB/PET copolyesters with POB unit content from 40 to 90 mol % were highly anisotropic.<sup>2</sup> The phase transition of these compositions has become the subject of many investigations.<sup>5-9</sup> The effects of moiety composition and solid-state polymerization time as well as two different sources of PET moiety (II) on the thermogravimetric, X-ray diffraction pattern, and morphology observation were intensively discussed in our previous articles.<sup>10-12</sup> We investigated the effects of solid-state polymerization reaction and two different molecular weights of PET moiety (II) on the differential scanning calorimetry (DSC) of POB/PET copolyesters having various compositions. Moreover, a commercial product, Eastman 10109 is characterized in comparison with the samples synthesized.

## EXPERIMENTAL

### Materials

The copolyesters having various POB/PET compositions have been synthesized according to the procedure as reported in previous articles.<sup>10-12</sup>

Eastman 10109 examined as reference in this study was a commercial thermotropic liquid crystalline copolyester produced by Tennessee Eastman Co.

### Method

The thermal behavior analysis for all samples was performed by a DSC system (Seiko Instrument SSC-5200). Specimens controlled at appropriate weight 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 ( $\Delta H$ ) was calculated by the area of the peak near the melting temperature.

### Code

The codes for each sample examined in this paper are listed in Table I.

## RESULTS AND DISCUSSION

### Composition Effect

Figure 1 shows the DSC scans during the first heating of PET oligomer (OET), PET polymer (PET), poly(*p*-oxybenzoate) homopolymer (PPOB), and Eastman 10109 copolyester (EAS), respectively. As OET and PET are both isotropic, they both exhibit the crystal-isotropic melt transition with a large value of enthalpy of fusion. It is well known that  $\Delta H$  is referred to as the enthalpy of melting. It is seen that the values of temperature phase transition

**Table I** Codes of Copolyesters Synthesized

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

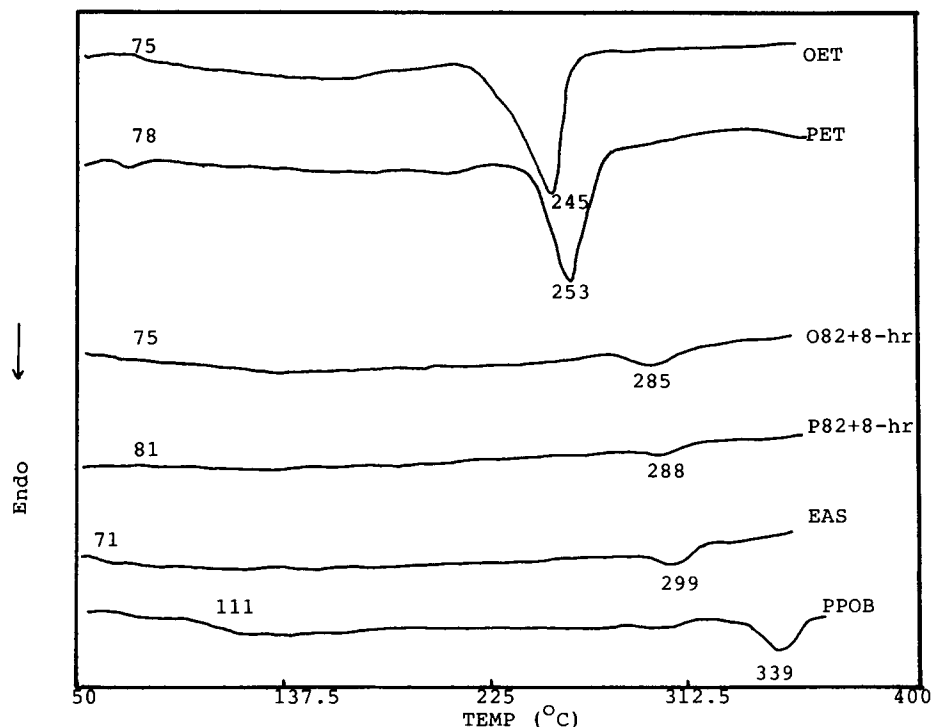


Figure 1 DSC scans of OET, PET, O82 + 8 h, P82 + 8 h, EAS, and PPOB.

( $T_m$ ) and glass transition ( $T_g$ ) for PET indicate slightly higher values at  $T_m = 253^\circ\text{C}$  ( $\Delta H = 51.9$  mJ/mg) and  $T_g = 78^\circ\text{C}$  than those of OET at  $T_m = 245^\circ\text{C}$  ( $\Delta H = 51.9$  mJ/mg) and  $T_g = 75^\circ\text{C}$ , respectively, due to the higher molecular weight of 20,000 for PET compared with of 2,000 for OET (see Table II). It is also noteworthy that  $\Delta H$  of OET is slightly higher than that of PET. This data is also consistent with the data for the degree of crystallinity as measured in previously.<sup>11</sup> On the other hand, PPOB, which has long segments of mesogenic units without flexible spacers in its structure, has a highest peak temperature at  $340^\circ\text{C}$  ( $\Delta H = 5.8$  mJ/mg) with much less value of enthalpy of fusion due to its crystal-nematic mesophase transition. EAS is the co-

polyester that has a composition of POB/PET of 80/20. EAS  $T_m$  at  $299^\circ\text{C}$  with a small enthalpy of fusion (6.7 mJ/mg), and two values of  $T_g$  at  $71^\circ\text{C}$  and  $152^\circ\text{C}$  were identified. This DSC of EAS describes the typical thermal behavior of a main-chain liquid crystalline polymer modified by a flexible chain.

In Table III the  $T_m$  and  $T_g$  temperatures of O28 are lower than those of P28. The thermal behavior of this composition of copolyesters depends mainly on the  $M_w$  of the source of PET moiety used (e.g., PET polymer or PET oligomer), which possesses flexible segments and exhibits isotropic melting phenomena. In general, after the solid-state polymerization, the DSC curves of copolyesters were flatter. In other words, the anisotropic phase tends to be more precise and dispersed among the matrix.<sup>12</sup> After the solid-state polymerization, the endothermic peak of fusion ( $\Delta H$ ) decreases and shifts to the higher temperature stage both for O28 and P28. In this composition, the higher value of  $T_m$  is attributable to the increasing molecular weight mainly in the result of the transesterification reaction. A depression in the enthalpy of fusion is attributable to the destruction of the isotropic crystal domain by the incorporation of POB moiety.

Table II Differential Scanning Calorimetric Results of OET, PET, EAS, and PPOB

|      | $T_g$ ( $^\circ\text{C}$ ) | $T_g$ ( $^\circ\text{C}$ ) | $T_m$ ( $^\circ\text{C}$ ) | $\Delta H$ (mJ/mg) |
|------|----------------------------|----------------------------|----------------------------|--------------------|
| OET  | 75                         | —                          | 245                        | 59.2               |
| PET  | 78                         | —                          | 253                        | 51.9               |
| EAS  | 71                         | 152                        | 299                        | 6.7                |
| PPOB | —                          | 111                        | 339                        | 5.8                |

In O46 and P46, these curves appeared with two distinct  $T_g$ s. And the  $T_m$ s were lower than those of O28 and P28. The appearance of two points of  $T_g$  resulted from the existence of two chemidomains with diverse mobilities in this composition of copolyesters. The shapes of the crystalline in this composition still exhibited the similar type of PET spherulite as reported.<sup>11,12</sup> In fact, the lower  $T_m$ s of O46 and P46 compared with those of O28 and P28 are attributed to a diluent effect by the incorporation of POB moiety.

The curves of DSC of O64 and P64 showed the typical anisotropic exotherm as discussed by many researchers.<sup>5-9</sup> In this study, we also observe two  $T_g$ s at ca. 75 and 145°C and two melting endotherms at ca. 170°C with a broad peak and at 270°C with a distinct peak. Moreover, the  $T_g$ s of the copolyesters became less pronounced than those for O46 and P46. In the composition of POB/PET at 40/60, it began to exhibit the general mesophase, resulting in a distinct peak during the thermal process. In the composition of POB/PET at 60/40, in contrast the mesophase became the continuous phase resulting in a broad peak during the thermal process because the heating process dealt with a rigid-chain softening process of the liquid crystalline polymer. The solid-state polymerization reaction elevated the melting temperature of copolymers and resulted in a flat curve because of the increase in  $M_w$  and the randomness of the two chemical domains.

The curves of DSC for O82 and P82 are plotted as a function of the solid-state polymerization time in Figures 2 and 3, respectively. As the solid-state polymerization time of copolyesters elapsed, the

curves of DSC became smoother and the melting temperature shifted to a higher point and became more pronounced (also see Table IV). As described previously,<sup>10</sup> the solid-state polymerization reaction caused more randomness of the two moieties of the copolyesters as well as the higher molecular weight due to the transesterification reactions. In Figure 4, the melting temperature versus the POB content before and after solid-state polymerization reaction is plotted. The melting temperature of the copolyesters decreased as the POB content increased in the ranges from 0 to 40 mol %, then it increased as the POB content increased in the ranges from 60 to 100 mol %. In Figure 5, the melting temperatures of O82 and P82 versus solid-state polymerization time are plotted. The melting temperature of the copolyesters increased as the solid-state polymerization time elapsed. The transesterification reaction as a result of the solid-state polymerization process plays an important role in the growth of the degree of polymerization.

#### Crystallinity Analysis

From thermal methods (DTA-DSC), the degree of crystallinity ( $\chi_c$ ) can be determined by using enthalpies of fusion:

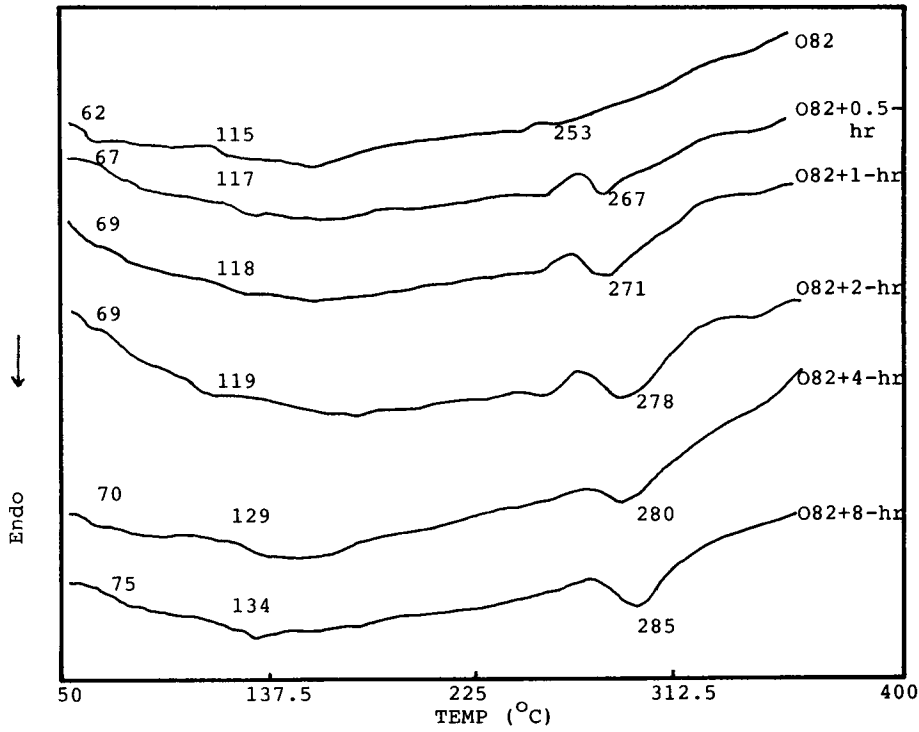
$$\chi_c = \frac{\Delta H_a - \Delta H}{\Delta H_a - \Delta H_c}$$

where  $\Delta H$  is the enthalpy of fusion of the unknown specimen,  $\Delta H_a$  and  $\Delta H_c$  are the enthalpies of fusion of the amorphous and crystalline standards, respec-

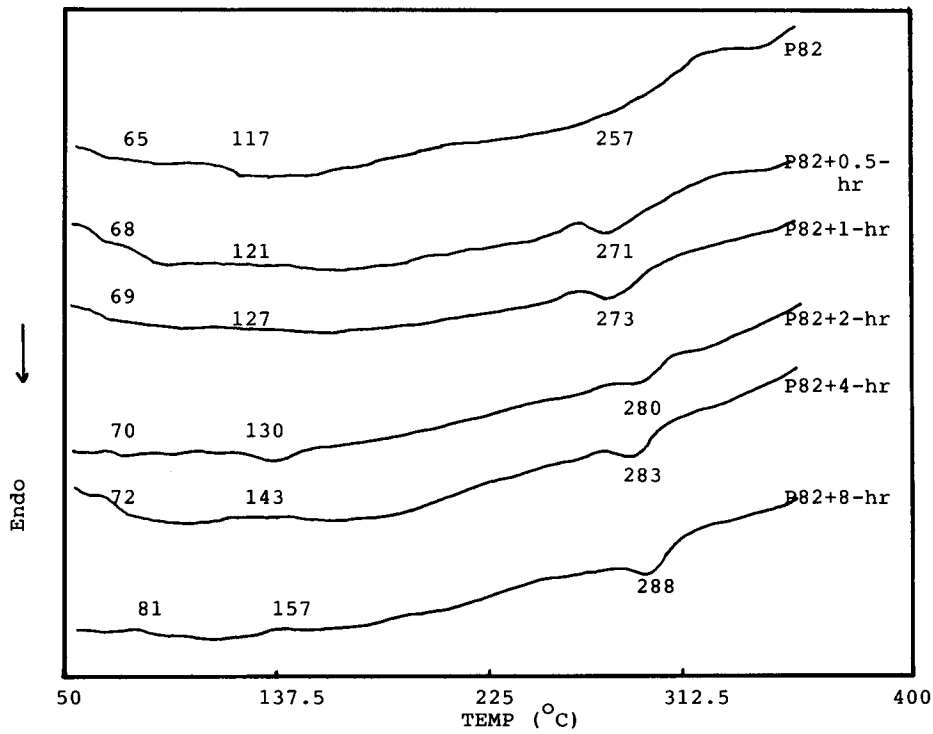
**Table III** Effect of 4-h Solid-State Polymerization on Change in Differential Scanning Calorimetric Results

|               | $T_g$ (°C) | $T_g$ (°C) | $T_m$ (°C) | $\Delta H$ (mJ/mg) |
|---------------|------------|------------|------------|--------------------|
| O28           | 75         | —          | 208        | 33.3               |
| O28 + 4-h SSP | 76         | —          | 232        | 12.8               |
| P28           | 76         | —          | 219        | 38.4               |
| P28 + 4-h SSP | 78         | —          | 236        | 28.9               |
| O46           | 79         | 154        | 180        | 28.6               |
| O46 + 4-h SSP | 82         | 157        | 187        | 25.3               |
| P46           | 86         | 158        | 198        | 31.4               |
| P46 + 4-h SSP | 84         | 161        | 201        | 31.1               |
| O64           | 77         | 143        | 250        | 2.9                |
| O64 + 4-h SSP | 73         | 145        | 259        | 0.3                |
| P64           | 70         | 150        | 253        | 1.8                |
| P64 + 4-h SSP | 76         | 153        | 270        | 0.1                |

SSP, solid-state polymerization.



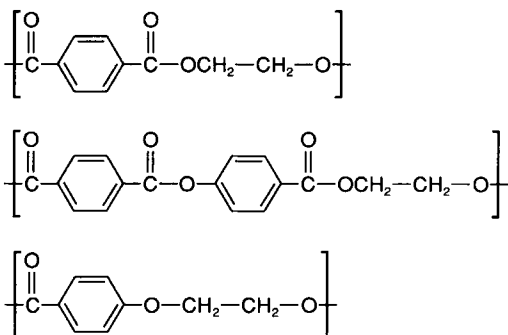
**Figure 2** DSC of O82 as a function of solid-state polymerization time.



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

tively. In this study, we found that the isotropic crystalline indicated a higher value of enthalpy of fusion, while liquid crystalline gives a small value of enthalpy of fusion.

The resultant copolyesters may contain sequences of the form shown below as reported by Viney and Windle.<sup>6</sup>



The peaks at the phase transition temperature may be, therefore, concerned as the sequences illustrated above. Table III and IV shows the values of  $T_g$ ,  $T_m$ , and the enthalpy of fusion ( $\Delta H$ ) in the melting stage for the copolyester having POB content from 0 to 100%.

In principle, the PET-rich copolyester exhibited higher melting temperature but less enthalpies of fusion after the solid-state polymerization (see Table III). As mentioned in our previous articles,<sup>10,11</sup> in PET-rich compositions, the PET-rich domain consists of a continuous phase, but the POB-rich domain is a dispersed phase in the PET matrix. Less

enthalpy of fusion after the solid-state polymerization is due to the destruction of the isotropic crystalline in the continuous phase of the copolyester.

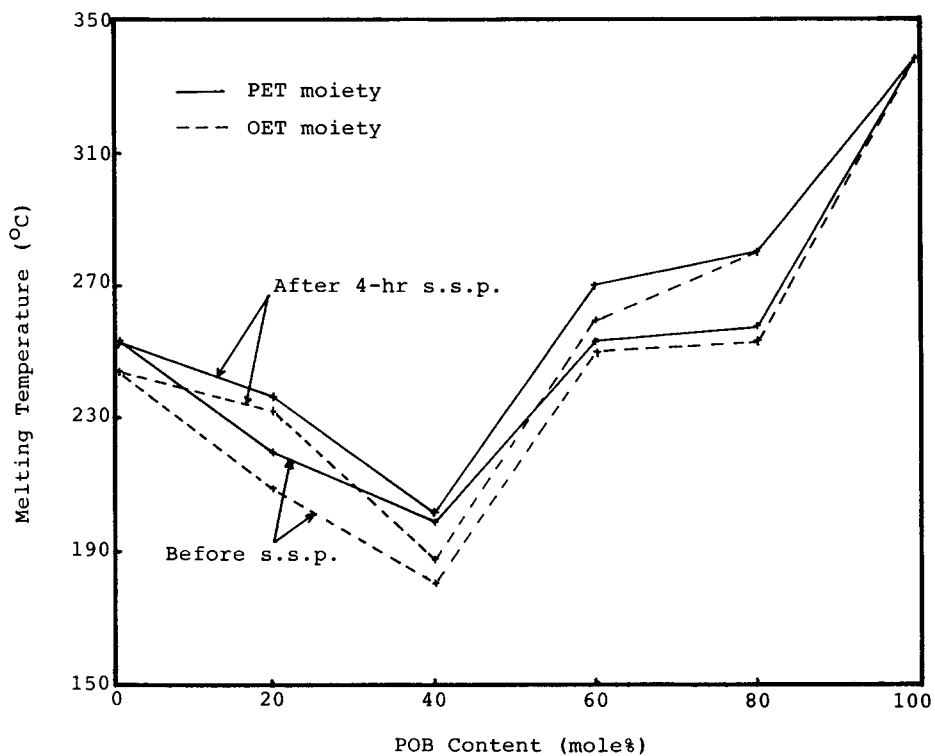
In the case of the POB/PET 80/20 formulation, the copolyesters modified by both PET oligomer and PET polymer as moiety (II) (Table IV) exhibit higher melting temperature as well as the enthalpy of fusion after the solid-state polymerization. The transesterification and annealing happened during the solid-state polymerization only in the case of the copolyesters having POB content > 60%. This effect contributes the increased enthalpy of fusion in both O82 and P82 during the solid-state polymerization reaction.

The degrees of crystallinity of the copolyesters could have resulted from either the spherulite-like isotropic crystalline of PET moiety or the liquid crystalline mesogen unit of POB moiety. The evaluation of the total degrees of crystallinity of these copolyesters, however, cannot be based on the energy absorbed near the melting temperature because the values of the enthalpy of fusion exhibited differently by these two moieties. In the case of the POB/PET 80/20 composition (i.e., O82 and P82), the comparative enthalpy of fusion increased as the solid-state polymerization time elapsed due to the growth of the liquid crystalline (see Table IV). In contrast, in the cases of O28, P28, O46, and P46, the comparative enthalpy of fusion is depressed as the solid-state polymerization time elapses (Table III). These phenomena and explications are consistent with the data on the degrees of crystallinity obtained by WAXS study.<sup>11</sup>

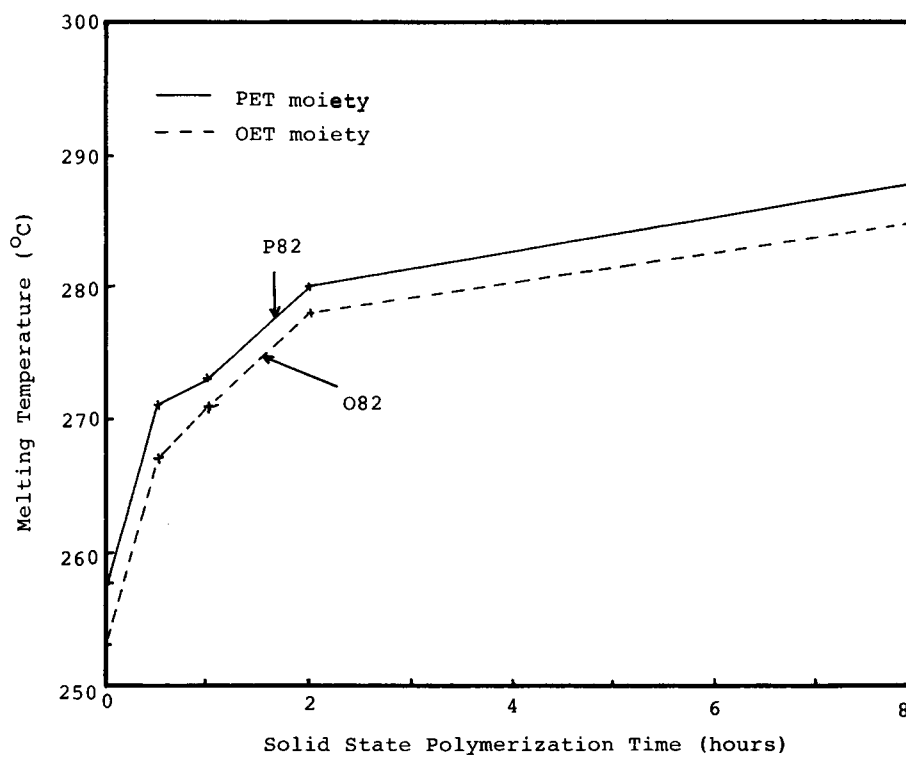
**Table IV** Effect of Solid-State Polymerization Time on Change in Differential Scanning Calorimetric Results of O82 and P82

|                 | $T_g$ (°C) | $T_g$ (°C) | $T_m$ (°C) | $\Delta H$ (mJ/mg) |
|-----------------|------------|------------|------------|--------------------|
| O82 + 0-h SSP   | 62         | 115        | 253        | 0.4                |
| O82 + 0.5-h SSP | 67         | 117        | 267        | 1.3                |
| O82 + 1-h SSP   | 69         | 118        | 271        | 3.7                |
| O82 + 2-h SSP   | 69         | 119        | 278        | 3.8                |
| O82 + 4-h SSP   | 70         | 129        | 280        | 3.9                |
| O82 + 8-h SSP   | 75         | 134        | 285        | 5.9                |
| P82 + 0-h SSP   | 65         | 117        | 257        | 1.1                |
| P82 + 0.5-h SSP | 68         | 121        | 271        | 1.4                |
| P82 + 1-h SSP   | 69         | 127        | 273        | 1.8                |
| P82 + 2-h SSP   | 70         | 130        | 280        | 2.0                |
| P82 + 4-h SSP   | 72         | 143        | 283        | 2.3                |
| P82 + 8-h SSP   | 81         | 157        | 288        | 4.4                |

SSP, solid-state polymerization.



**Figure 4** Melting temperature of OET and PET modified with POB before and after solid-state polymerization.



**Figure 5** Melting temperature of O82 and P82 with different solid-state polymerization time.

## CONCLUSION

This study on the relationships between the compositions and the phase transition temperature of a series of copolyesters has led to the following conclusions:

1. The PET polymer indicates a crystal–isotropic melt transition with a large value of enthalpy of fusion of around 50–60 mJ/mg at 250–260°C. The liquid crystal polymer indicates a crystal–nematic mesophase transition with a small value of enthalpy of fusion of around 5–7 mJ/mg at 290–340°C.
2. The melting temperature of copolyester can be controlled by using different molecular weights of PET moiety [e.g., by selecting either PET polymer having larger molecular weight or PET oligomer having smaller molecular weight as moiety (II)]. In general, values of  $T_g$  and  $T_m$  of copolyesters are higher if PET polymer is used as PET moiety (II).
3. The function of the solid-state polymerization may bring about more randomness of two moiety units and the increasing degree of polymerization of copolyesters with a higher melting temperature due to the transesterification reactions. These effects contribute to the higher enthalpy of fusion ( $\Delta H$ ) at the

same time in the case of copolyester in the composition of POB/PET 80/20.

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