Co[Poly(Ethylene Terephthalate-p-Oxybenzoate)] Thermotropic Copolyester. II. X-Ray Diffraction Analysis

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SYNOPSIS

A series of co[poly(ethylene terephthalate-p-oxybenzoate)] thermotropic copolyester with different compositions were prepared by the copolymerization of either poly(ethylene terephthalate) (PET) polymer or its oligomer with p-acetoxy-benzoic acid. The polymeric products were subjected to solid-state polymerization for various time intervals. Effects of composition ratio and solid-state polymerization time on X-ray diffraction behavior were investigated. It is found that the effect of transesterification induced by solid-state polymerization causes an increase in crystallinity with the copolyesters having high mol % of p-oxybenzoic acid (POB) moiety and causes a decrease in crystallinity with the copolyesters having high mol % of PET moiety. In general, the crystallinity of copolyesters is first increased and then decreased as solid-state polymerization time proceeds. However, the crystallinity of copolyester having POB/PET = 80/20 composition is increased generally at 4-h solid-state polymerization. It is also found that the crystallinity of copolyesters is decreased by quenching. The copolyester based upon either PET oligomer with 4-h solid-state polymerization or PET polymer with 8-h solid-state polymerization shows the most similar X-ray diffraction pattern with that of 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 that received a great attention from both industry and academia.[1] For practical purposes, there is a need for nematic mesophases at relatively low temperature. One way to lower the melting temperature of products is to copolymerize substances having a relatively high degree of crystalline with a low melting point. The later development by Tennessee Eastman of p-hydroxybenzoic acid (PHB) modified by poly(ethylene terephthalate) (PET),[2-4] both of which have excellent mechanical properties, is a good example of these thermotropic crystalline polyesters. It has been proposed that the copolyesters obtained are random copolymers of p-oxybenzoic acid (POB) units served

as mesogen units and PET units[4] served as flexible spacers:

(I) POB

(II) PET
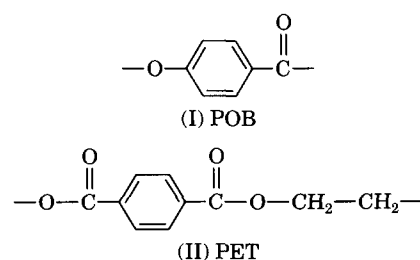
The structure of this type of copolyester with 80 mol % POB was investigated by optical and electron microscopy, wide-angle X-ray, and thermal analysis by Zachariades et al. of IBM Research Laboratory.[5] A series of co[poly(ethylene terephthalate-p-oxybenzoate)] copolyesters with POB content of 0–100 mol % were prepared by melt polycondensations of p-acetoxybenzoic acid with either PET or its oligomer according to the procedure reported in our previous article,[6] where the thermal stability of this

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type of copolyester was studied. It is the purpose of this article to report the results of wide-angle X-ray diffraction analysis on these samples.

EXPERIMENTAL

p-acetoxybenzoic acid (PAB) was Aldrich reagent grade with the purity of 98%. PET was the product of Far East Textile Co. (Taiwan) having IV value of 0.62, equivalent to the molecular weight of ca. 20,000.

The PET oligomer having molecular weight of ca. 2000 was obtained by the glycolysis of PET resin. This procedure of glycolysis of PET was reported already in our previous article.[6]

The copolyesters before solid-state polymerization were prepared by melt polycondensation of PAB with either PET polymer or PET oligomer according to the procedure as reported in our previous article.[7] Poly(p-oxybenzoate), labeled PPOB, was also prepared from PAB according to the procedure as reported.[7] A commercial copolyester, Eastman 10109, labeled EAS, was supplied by the Eastman Company. The codes for each samples studied are listed in Table I. Solid-state polymerizations were then performed for various time intervals.

The polymeric product was ground to form a powder sample. The X-ray diffraction pattern was determined by a wide-angle X-ray diffraction system (Siemens D5000) by using Cu Kα radiation of the wavelength of 1.54 Å. The crystallinities of samples were calculated the same as reported in the literature[8] using the following proposed by Kasai and Kakudo[9]:

$$\% \text{ crystallinity} = \frac{100 \ I_c}{I_a + I_c}$$

where I_c is the intensity of the crystalline component and I_a is the intensity of the amorphous component.

All intensities obtained in this study were the in-

Table I Codes of Copolyesters Characterized

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

tegrations between $2\theta = 10°$ and $2\theta = 30°$ as a measure of the degree of crystallinity of samples using wide-angle X-ray spectrometry (WAXS). Figure 1(a) shows the WAXS of the diffractogram for PET resin with an amorphous background line. The percent of two regions were calculated by taking the area under the background line as amorphous and above as crystalline by the aid of the Siemens computer. A background line is drawn that should connect the minima between the crystalline peaks.

According to our measurements, the degrees of crystallinity of PET and OET samples were 17 and 25, respectively. These values were much smaller than the values for the oriented fiber of PET measured by Johnson and Popoola[10] because our samples were nonoriented resins of PET that indicate smaller densities as well as crystallinities.

RESULTS AND DISCUSSION

X-Ray Diffraction Patterns

Two different sources of PET moiety have been employed to synthesize copolyesters. One is from PET having molecular weight of about 20,000 (PET) and one from its oligomer having molecular weight of about 2000 (OET). The PET moieties act as the flexible spacers in the thermotropic copolyester synthesized. These two different types of copolyester may consist of structures shown in Figure 1(b), which shows the X-ray diffraction patterns of POB/PET copolyesters synthesized by modification of either PET or OET with PAB before the solid state polymerization, as well as a commercial product, Eastman 10109, PET polymer (PET) and its oligomer (OET), PAB monomer, and PPOB polymer. It is seen that the X-ray patterns are quite different in the relative intensities between the cases of PET and OET [see Fig. 2(a)]. Also, it is seen that the pattern of PAB monomer is quite different from that of PPOB polymer [see Fig. 2(b)]. In contrast, they are almost the same in the relative intensities in the cases of all copolyesters regardless of the source of PET moiety: whether they are based upon OET or PET. In O28 and P28, for instance, both have the peaks at $2\theta = 26.0, 22.6, 17.6$, and $16.3°$ with almost the same intensities. As the mol % of POB moiety is increased, the sharp peaks tend to confine to a broad peak at around $20.0°$ (see O64 and P64). However, if the POB content continues to increase the new sharp peaks distinguish at around 21, 23, and $29°$ along with $19.9°$ characteristic peaks of PPOB as seen in O82, P82, O91 and P91 as well as PPOB. However, the pattern of PPOB/PET = 80/20 mixture [see Fig. 2(b)] remains with both char-
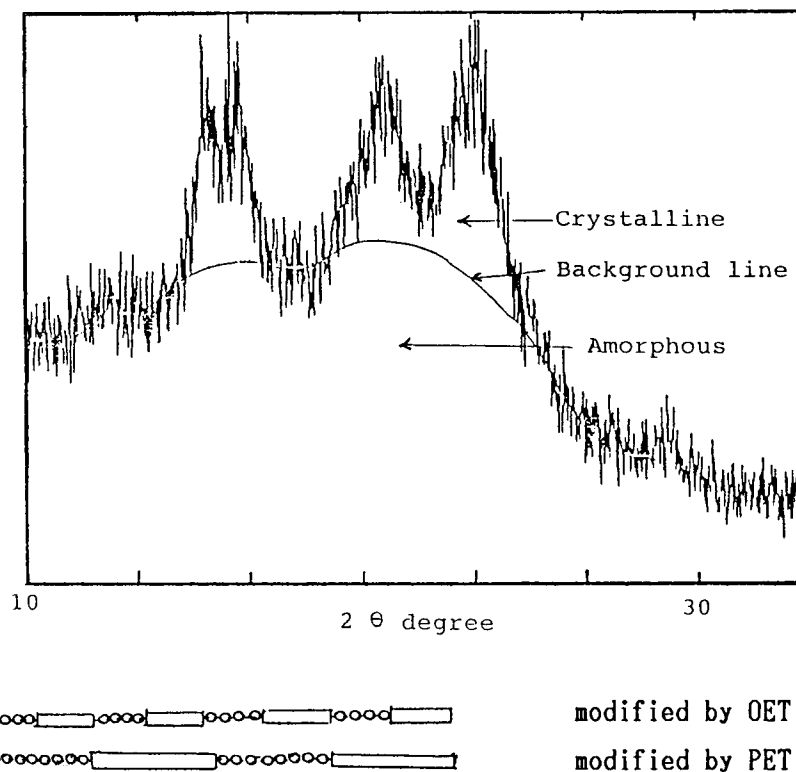
Figure 1   (a) WAXS diffractogram for PET resin with a background line superimposed. (b) Schematic model of two different types of copolyesters.

acteristic peaks of PPOB at 19.8, 21.0, 23.2, and 29.3° and characteristic peaks of PET at 17.7 and 26.9°, whereas peaks in the pattern of POB/PET = 80/20 copolyester (O82 or P82) are confined to a broad peak at around 20.0°. It is clear that the patterns shown in rich PET composition, which is not anisotropic, are contributed mainly from PET moiety. While the patterns shown in rich POB composition, which is anisotropic, are contributed mainly from POB moiety. Figure 3 shows the X-ray diffraction patterns after 4-h solid-state polymerization. If these are compared with ones before the solid-state polymerization as shown in Figure 2, the corresponding peaks in the same composition will slightly shift to the larger angle sides. This is distinguished especially in the case of PET-rich formulation, indicating the changes in interplanar spaces. Table II shows the shift of a maximum peak for the corresponding copolymers before and after 4-h solid-state polymerization. It is shown that co-polyesters having the PET-rich composition normally show the shifts from 0.1 to 0.4° of angle of incidence, indicating the tendency toward a smaller interplanar spacing of the crystal planes. However, this trend is quite minor in the cases of POB-rich composition. It is believed that solid-state polymer-

ization corresponds to an effect of the annealing of polyester main chains, causing a decrease in the interplanar spacing of the crystal planes and the reorientation of macromolecules. This annealing effect on the decrement of the interplanar spacing is distinguished only in the cases of PET-rich formulation. Figure 4 shows the changes in pattern as a function of solid-state polymerization time in the cases of O82 and P82. In O82 and P82, it is seen that the peaks of pattern merely shift even after solid-state polymerization. However, the sharpness of peaks will be changed by solid-state polymerization, indicating the changes in crystallinity due to the reorientation of macromolecules, probably by the effect of transesterification.

Degree of Crystallinity

Table III shows the crystallinities of the corresponding copolyesters before and after 4-h solid-state polymerization. It is worth noting that crystallinity of OET (25%) is larger than that of PET (17%), while that of PPOB attains the highest crystallinity (42%). In general, the cooperation of PET moiety with POB moiety causes the dramatic decrease in crystallinity of PPOB. Moreover, the
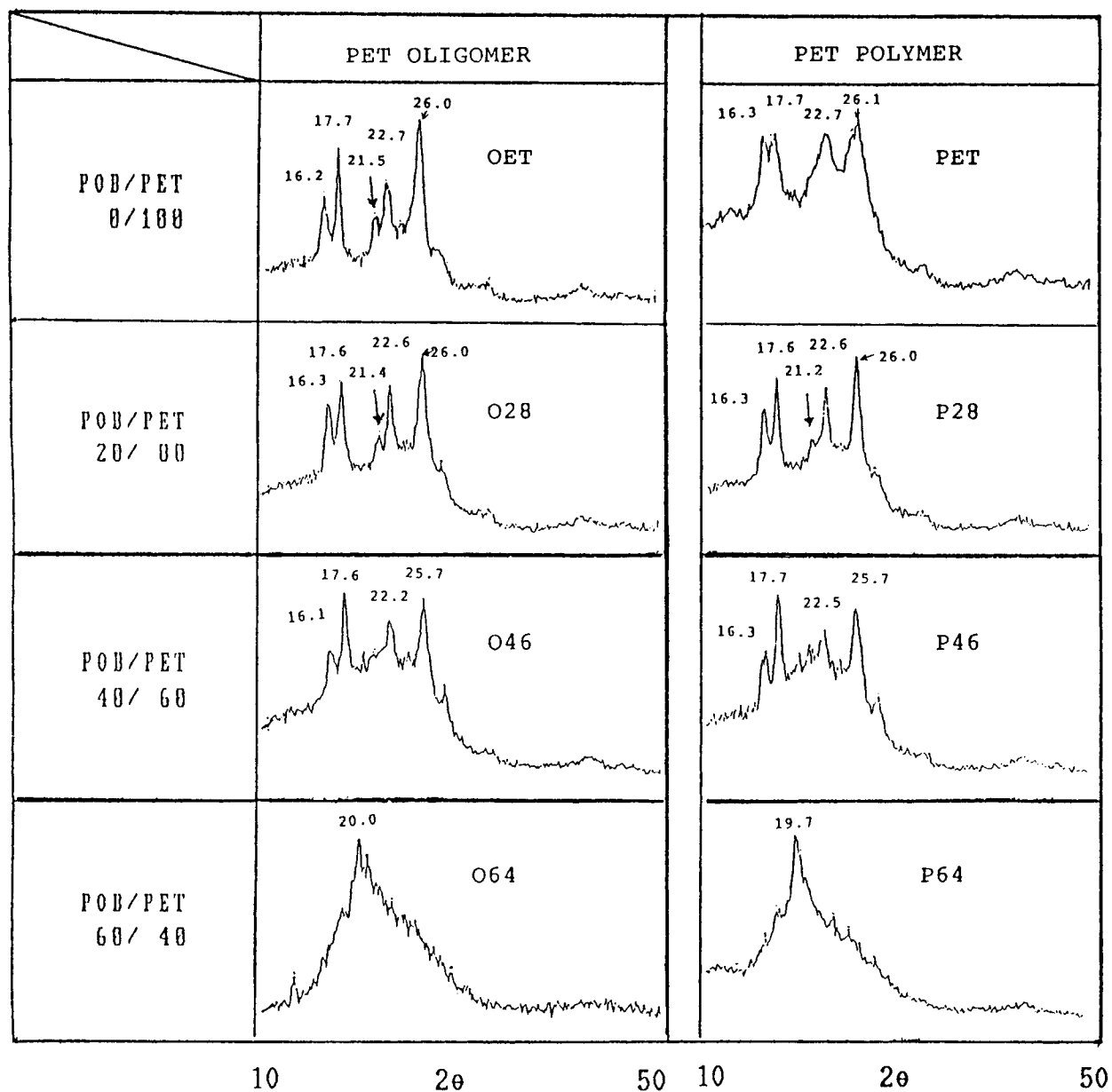
Figure 2 (a) Intensity of X-ray scattering vs. 2θ of powdered copolyesters at different POB/PET compositions before solid-state polymerization. (b) Intensity of X-ray scattering vs. 2θ of powdered copolyesters at different POB/PET compositions before solid-state polymerization. Pure PPOB, Eastman; PAB, mixture of PPOB/PET cited as references.

composition with POB/PET = 80/20 based upon PET has a higher crystallinity (21%) than that based upon OET (18%) before solid-state polymerization. In contrast, the composition with POB/PET = 20/80 based upon OET has a higher crystallinity (23%) than that based upon PET (21%). Furthermore, the crystallinities of copolyesters with high POB composition, e.g., in the cases of O64, P64, O82, and P82, which are highly anisotropic, tend to increase the crystallinity by the annealing effect during 4-h solid-state polymerization, whereas the

crystallinities of the copolyesters with high PET composition, e.g., in the cases of O46, P46, O28, and P28, which are not highly anisotropic, tend to decrease in the crystallinities by the annealing effect during 4-h solid-state polymerization. It is believed that the annealing effect damages the crystallinity of copolyesters in the cases of PET-rich composition during 4-h solid-state polymerization, because the PET segment is flexible and isotropic, while the annealing effect would improve the crystallinity of copolyester significantly in the cases of POB-rich
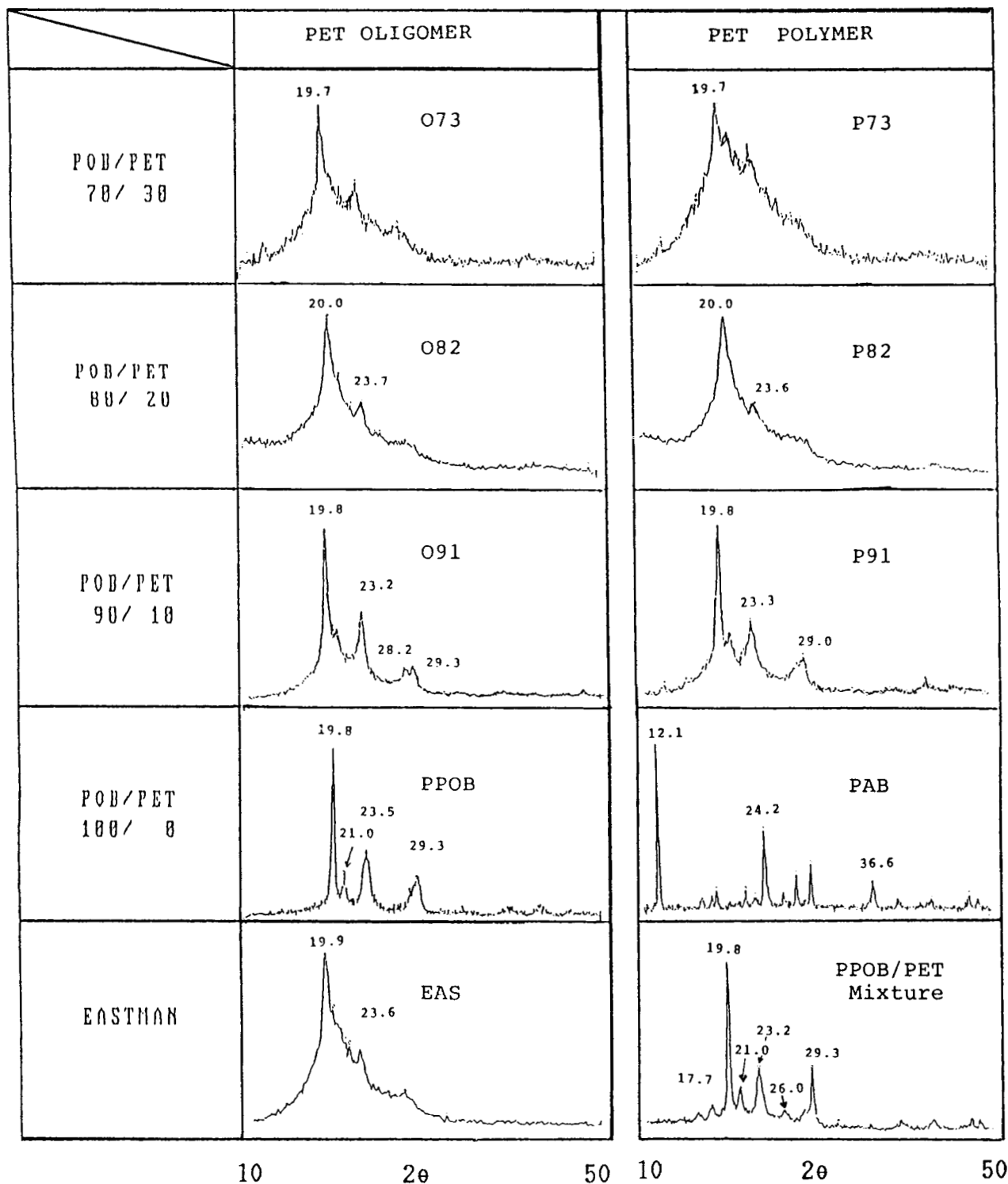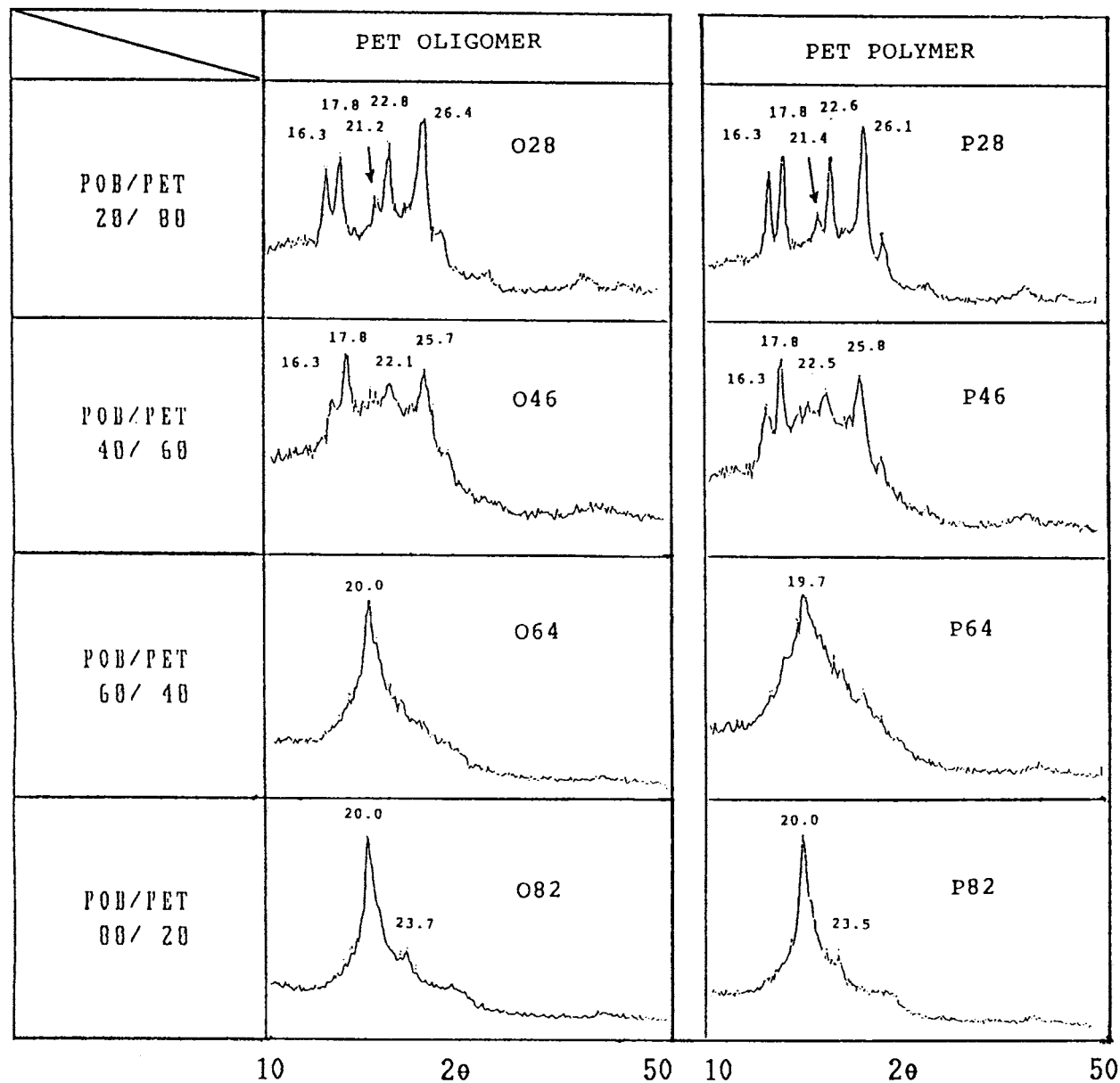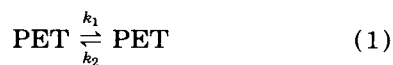
Figure 2 (b)

composition during 4-h solid-state polymerization because the POB segment is rigid and anisotropic. Table IV shows the effect of solid-state polymerization time on the crystallinity of copolyesters of O82 and P82, both of which are highly anisotropic. In

O82, the crystallinity is increased at 1-h, decreased at 2-h, and increased again at 4-h solid-state polymerization. In P82, the crystallinity is also increased at 1 h, decreased at 2 h, and increased again at 4 h, but for a longer time, i.e., 8 h, it is decreased again.

Figure 3   Intensity of X-ray scattering vs. 2θ of powdered copolyesters at different POB/ PET compositions after 4-h solid-state polymerization.

It is interesting to note that the crystallinities for O82 and P82 before solid-state polymerization are 18 and 21, respectively. However, after 8-h solid-state polymerization O82 finally exhibits higher crystallinity (22%) than P82 (20%). It is believed that the copolyester subject to solid-state polymerization is followed by the two competitive reactions:

$$\text{PET} \overset{k_1}{\underset{k_2}{\rightleftharpoons}} \text{PET} \tag{1}$$

$$\text{POB} \overset{k_3}{\underset{k_4}{\rightleftharpoons}} \text{POB} \tag{2}$$

Table II   Shift of a Maximum Peak in 2θ of Corresponding Copolyester Before and After 4-h Solid-State Polymerization

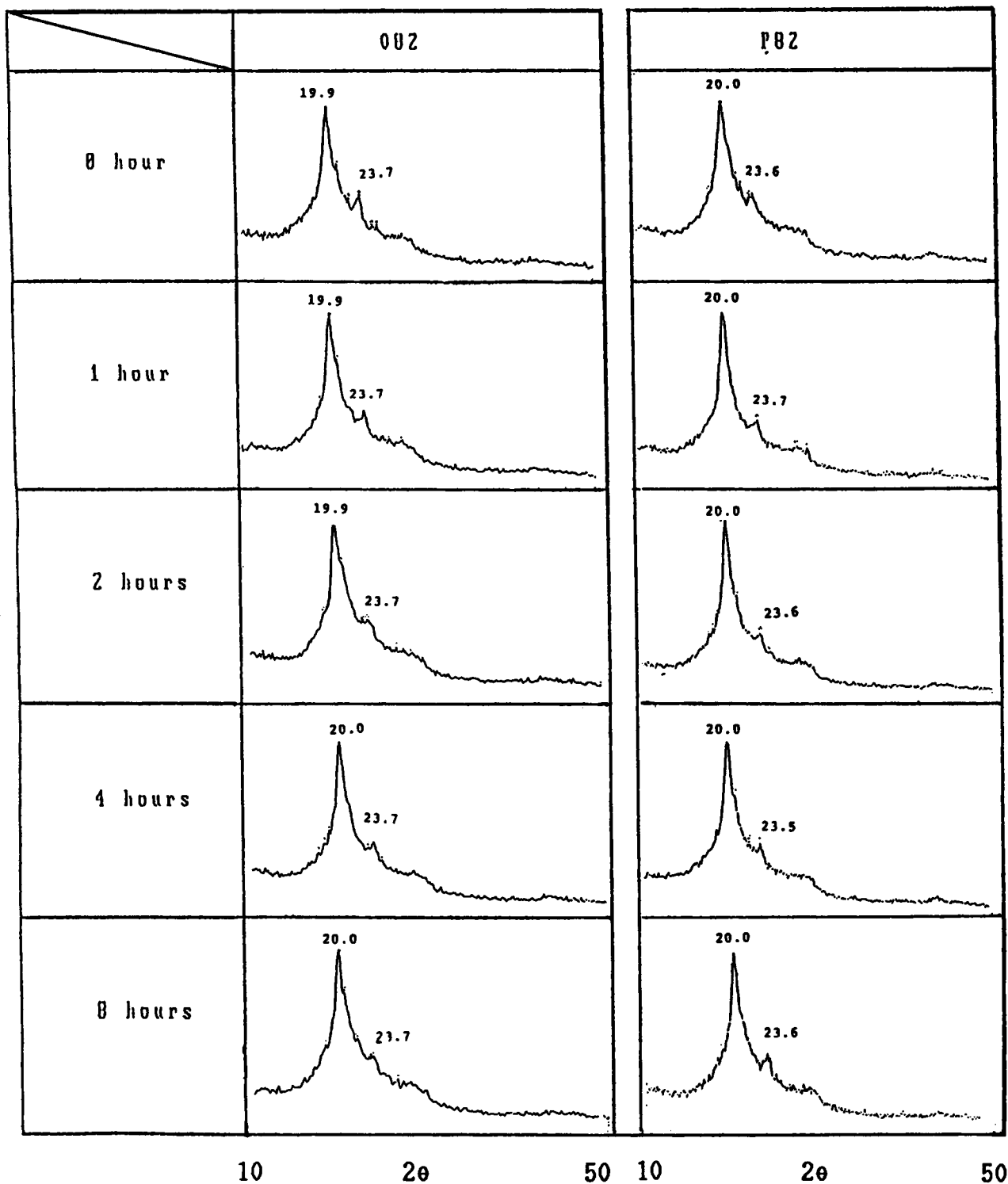| POB/PET	OET Moiety (°) Before → After		PET Moiety (°) Before → After
0/100	26.0		26.1
20/80	26.0 → 26.4		26.0 → 26.1
40/60	17.6 → 17.8		17.7 → 17.8
60/40	20.0 → 20.0		19.7 → 19.7
80/20	20.0 → 20.0		20.0 → 20.0
100/0		19.8	
Eastman		19.9	

Figure 4   Intensity of X-ray scattering vs. 2θ of powdered copolyesters of POB/PET = 80/20 at different solid-state polymerization times.

where k_1 and k_3 are the rate constants of polymerization and k_2 and k_4 are the rate constants of decomposition.

The crystallinity of a copolyester depends upon the segmental orientation and length of PET spacer, as well as POB mesogen moiety. Both PET and POB

Table III   Change in Crystallinities of Corresponding Copolymers Before and After 4-h Solid-State Polymerization

POB/PET	OET Moiety (% crystallinity) Before → After	PET Moiety (% crystallinity) Before → After
0/100	25	17
20/80	23 → 21	21 → 21
40/60	14 → 13	14 → 12
60/40	15 → 16	14 → 17
80/20	18 → 21	21 → 21
100/0	42	
Eastman	20	

have originally excellent crystallinities. The competitive reactions will go through a series of changes in the values of k_1, k_2, k_3, and k_4 during solid-state polymerization. If $k_1 > k_2$, the crystallinity will be decreased due to the growth of molecular weight of spacer units of PET moiety. And, if $k_3 > k_4$ the crystallinity will be increased due to the growth of mesogen units of POB moiety. In the early stage of solid-state polymerization within 0.5 h, it is $k_3 > k_4$ in reaction (2) and $k_2 > k_1$ in reaction (1), causing the growth of POB segments and cleavage of PET segments in copolyester main chain. Until 2-h polymerization, the system might become $k_4 > k_3$, showing a decrease in the crystallinity due to the cleavages of POB segments. At 4-h polymerization, the reaction keeps $k_2 > k_1$ in reaction (1) and $k_3 \approx k_4$ in reaction (2); in turn, the effect of transesterification becomes predominant and the crystallinity increases again in both O82 and P82. For a longer polymerization time, say 8-h polymerization, O82 continues to increase in its crystallinity because it keeps $k_2 > k_1$ and $k_3 \approx k_4$. But, P82 tends to decrease in its crystallinity because it becomes $k_1 \approx k_2$ and $k_4 > k_3$ at this stage, indicating more cleavages of POB segment due to its higher molecular weight. In solid-state polymerization, these two reactions of eqs. (1) and (2) might induce the transesterifications that cause the randomization of the copolymer sequences. It should be pointed out that the crystallinities of O82 at 4-h solid-state polymerization and at P82 for 8-h solid-state polymerization have finally the most similar values of crystallinity with that of Eastman 10109 (20%).

Effect of Quenching

The samples were heated as quickly as possible to 320°C in a test-tube that could be sealed and then quenched by plunging the tube into a dry ice/isopropanol mixture. It is worth observing that the relative intensities of peaks in the X-ray diffraction diagram were slightly affected by the quenching and the positions shift in the order of $2\theta = 0.1–0.3°$ ($\Delta d = 0.02$ and 0.06 Å) to the smaller angles of incidence.

The effect of quenching on the crystallinities calculated from patterns of samples O82 and P82 with 4- and 8-h solid-state polymerizations is shown in Table V. The OET and PET samples are also quenched and the results are cited for comparison. It is seen that the crystallinities are decreased after quenching. It is interesting to note that the decrements of OET and PET are much larger than those of O82 and P82. Moreover, the decrement of O82 is larger than that of P82 at 4-h solid-state polymerization. However, the decrement of P82 is now only slightly larger than that of O82 at 8-h solid-state polymerization. Also, the decrement of PET is always larger than that of OET.

When a sample is quenched, much of the structural deformation of the polymeric chain is stored in the solid polymer in the form of dislocations and other imperfections of crystalline. Thus, an anisotropic copolyester (i.e., P82 and O82) might exhibit less imperfection than that of PET or OET. As a result, the decrement is larger in the case of O82 than that of P82 at 4-h solid-state polymerization. The same reason explains why the decrement of O82 by quenching at 8-h solid-state polymerization is only slightly larger than that of P82: because the segments of spacer PET moiety become shorter due to the cleavages of PET segments during long solid-state polymerization time.

CONCLUSION

It is found that the peaks in the copolyester having high PET moiety content shift to higher incident

Table IV   Effect of Solid-State Polymerization Time on the Crystallinity for O82 and P82

Time (h)	Sample O82 (% crystallinity)	P82 (% crystallinity)
0	18	21
0.5	24	23
1	24	25
2	21	21
4	21	21
8	22	20

Table V   Change in Crystallinity with and without Quenching

	Sample			
	O82 (% crystallinity)		P82 (% crystallinity)	
Time	Without	With	Without	With
4-h solid-state polymerization (decrement)	21 → (−Δ4)	17	21 → (−Δ1)	20
8-h solid-state polymerization (decrement)	22 → (−Δ4)	18	20 → (−Δ3)	17

For comparison

	Sample			
	OET (% crystallinity)		PET (% crystallinity)	
Time	Without	With	Without	With
(decrement)	25 → (−Δ8)	17	17 → (−Δ12)	5

angles during solid-state polymerization, indicating that the interplanar spacings become smaller due to the increase of randomness of the structure. However, the peaks in copolyesters having high POB moiety content are virtually not affected by solid-state polymerization because of the rigidity of POB moiety, which is difficult to affect by the effect of annealing during solid-state polymerization. The crystallinity of copolyesters is decreased as POB content is increased until the composition with POB/PET = 40/60. When the POB content is over 40 mol %, in which the system now becomes anisotropic, the crystallinity of copolyester is raised again because of the contribution of mesogen units of POB moiety.

The composition effect on the crystallinity of the copolyester, however, is not quite similar between copolyesters based upon PET oligomer and PET polymer acted as flexible spacers.

In general, solid-state polymerization of a copolyester results first in an increase and then a decrease in crystallinity within 2-h solid-state polymerization. For a longer solid-state polymerization, however, it causes an increase in crystallinity due to the effect of transesterification. The X-ray diffraction data of Eastman 10109 is found to be similar to those of O82 and P82 after 4- and 8-h solid-state polymerization, respectively. The quenching process could only slightly affect the shift of the peaks of the X-ray pattern but causes decreases in crystal-

linity of copolyesters of O82 and P82, as well as PET resin of OET and PET.

A decrement of crystallinity by quenching can be best interpreted as a storage of imperfection of crystalline domains caused mainly by the flexible spacers of PET moiety at melt state.

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