

Blends of Poly(ethylene terephthalate) with Co[poly(ethylene terephthalate-*p*-oxybenzoate)]. III. Crystallization Behavior Observed by Polarized Light Microscopy

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SYNOPSIS

Poly(ethylene terephthalate) (PET) has been melt-mixed at 293°C with two types of co[poly(ethylene terephthalate-*p*-oxybenzoate)] (POB-PET) copolyester, designated as P28 and P82, at the level of 10 wt %. The different *p*-acetoxybenzoic acid/PET mole ratios are 20/80 in P28 and 80/20 in P82. The blends were heated to 305°C and then cooled to 25°C at rate of 10°C/min. The crystalline morphology of these blends in the range from 25°C to 305°C is monitored by polarized light microscopy. Morphologic observations revealed a quicker appearance of crystalline in the blends upon the addition of 10 wt % copolyester as a nucleating agent. It is found that P28, which contains fewer POB units, is much more advantageous to the nucleation process than P82, which contains more POB units. According to the optical photomicrographs, sufficient uniformity of distribution of copolyester domains in the PET matrix is reached after 8 min blending. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene terephthalate) (PET) has not been considered for applications involving high-speed processing because it crystallizes or solidifies very slowly from melt. It is known that the PET crystallization involves a slower homogeneous nucleation step followed by the growth process. PET crystallization can be increased by the addition of polymeric nucleating agents such as linear low density polyethylene,¹ poly(methyl methacrylate),² poly(phenylene sulfide),³ high-density polyethylene,³ and liquid crystalline polymer (LCP).⁴⁻⁷ PET/LCP blends of PET/VLC (trade name Vectra A900) and PET/KLC (poly[*p*-hydroxybenzoate] (PHB)/PET = 80/20 mole ratio) were studied by Misra and colleagues.⁶⁻⁷ According to the investigations, VLC and KLC act as nucleating agents for PET crystallization; this effect probably reaches a maximum at an

LCP level between 0 and 5 wt %. In the range from 10 to 15 wt %, VLC and KLC possibly destroy the symmetry of PET.

Co[poly(ethylene terephthalate-*p*-oxybenzoate)] (POB-PET) copolyesters were first developed by Tennessee Eastman Co.⁸⁻¹⁰ The properties of these copolyesters have been widely studied.⁸⁻¹² The copolyester with POB contents from 40% to 90% is known as thermotropic LCP. A thorough understanding of the transition and phase behavior is thus desired for comprehending structure-property relationships and processabilities for these copolyesters and their blends with other polymers.

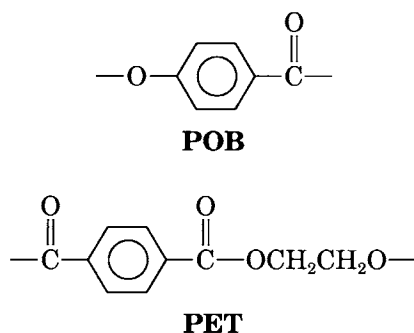
Morphologic studies have been performed by many researchers¹³⁻¹⁶ on the POB-PET copolyesters by using polarized light microscopy (PLM). In our previous papers, we have reported the thermal and crystallization behavior of the blends composed of PET and POB-PET copolyesters by using differential scanning calorimetry (DSC)¹⁷⁻¹⁸ and the transesterification between PET and POB-PET copolyesters by proton nuclear magnetic resonance analysis.¹⁹

The objectives of this present investigation are

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to reveal the crystalline morphology of crystallines of PET blends with 10 wt % copolyester as a function of temperature observed by PLM and to clarify the fact that the addition of 10 wt % copolyester can accelerate the PET crystallization.

The chemical structure of POB–PET copolyester consists of the following two moieties:



EXPERIMENTAL

Materials

POB–PET copolyesters of P28 and P82 were synthesized according to the procedure reported in our previous paper.²⁰ The PET resin was kindly supplied by Far East Textile Co (Taiwan) having an intrinsic viscosity of 0.62 (dL/g) in 60/40 (w/w) phenol/tetrachloroethane at 30°C.

Blending Method

PET and copolyesters were dried *in vacuo* at 105°C for 48 h before blending to avoid degradation caused by moisture. The weight ratio of PET to the copolyester was 90/10. The blends were prepared by melt-mixing in a Brabender Plasticorder at 293°C and at a mixing-blade speed of 30 rpm. Samples were taken at various times from the mixing bowl and immediately quenched in liquid nitrogen.

Polarized Optical Microscopy

Specimens were observed microscopically as a function of temperature using a Zeiss polarizing microscope (III) equipped with a programmable Mettler FP82HT hot stage. The specimens held between two thin microscope cover slips were prepared on the hot stage preheated to 280°C. When the blends melted they were pressed on the upper cover slip and then immediately quenched by liquid nitrogen. The sequence of heating, pressing, and quenching was always accomplished in under 20 s. The pho-

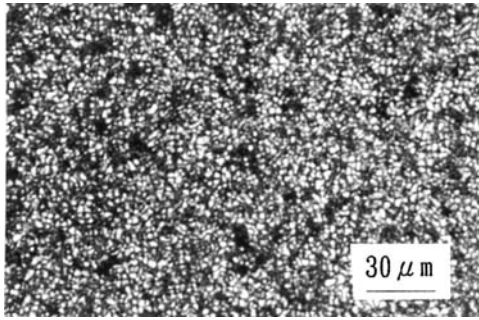
tomicrographs were obtained as a function of temperature ranging from 25 to 305°C.

RESULTS AND DISCUSSION

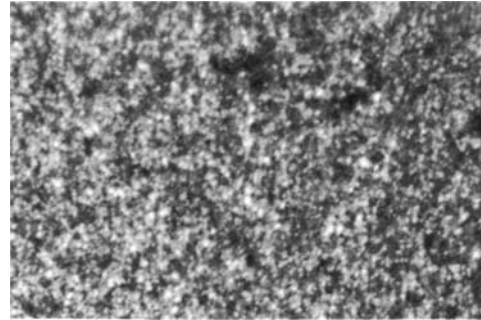
Effects of Heating and Cooling

Optical micrographs obtained on a melt-cast film of neat PET are presented in Figures 1 and 2 for heating and cooling cycles, respectively. These figures are temperature sequences of optical micrographs using crossed polarizers. It is seen that the texture of PET crystalline at 25°C is the typical spherulites [Fig. 1(a)]. When heated to 225°C at the rate of 10°C/min, the crystal grain boundary becomes obscure and indicates that the crystals of PET have melted partly [Fig. 1(b)]. At 250°C, the texture becomes more obscure than that at 225°C, [Fig. 1(c)]. At 270°C, the spherulites melted completely. On further heating to 305°C, only the isotropic liquid phase was found. After holding there for 5 min, the PET melt was then cooled down from 305 to 25°C at the rate of 10°C/min. The optical micrographs are shown in Figure 2. The melt remained isotropic at 220°C. The crystals began to form at 210°C [Fig. 2(a)] and their population increased at around 200°C [Fig. 2(c)]. It can be concluded from these observations that neat PET crystallites melt between 225 and 270°C in the heating cycle and the crystallites form between 210 and 200°C in the cooling cycle.

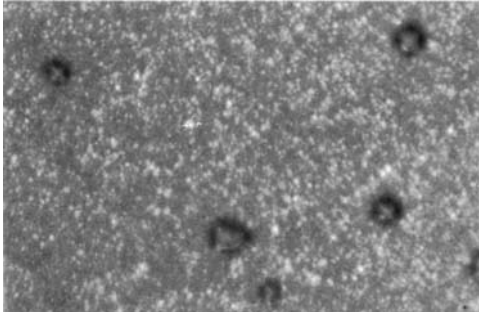
The morphologic observations of the crystalline P28 copolyester as a function of temperature are presented in Figures 3 and 4 for heating and cooling cycles, respectively. It is seen that the texture of P28 crystalline at 25°C remains in the character of spherulites [Fig. 3(a)]. The crystals have melted partly at 195°C [Fig. 3(b)]. A few bright spots which represent the POB-rich domains of the anisotropic phase still exist even at 225°C [Fig. 3(d)]. In the cooling cycle, on the other hand, the P28 crystallites have already formed at 180°C [Fig. 4(a)] and their population increased at around 155°C [Fig. 4(d)]. Disappearance of the dark amorphous areas between 180°C and 170°C [compare Fig. 4(a) with 4(b)] is large, whereas that between 170°C and 160°C [compare Fig. 4(b) with 4(c)] is less. This observation suggested that P28 crystallizes much more quickly between 180 and 170°C than between 170 and 160°C in the cooling process. The optical micrograph of the copolyester P82, which is a liquid crystalline polymer, displayed a well-defined nematic texture. The result is consistent with the previous investigation.^{8–10}



(a)

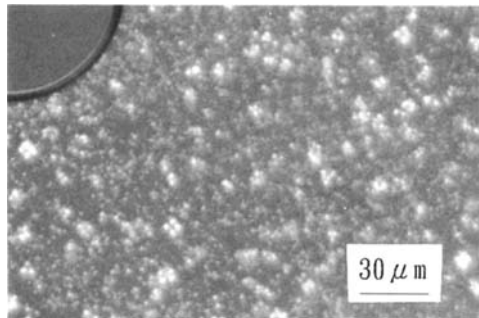


(b)

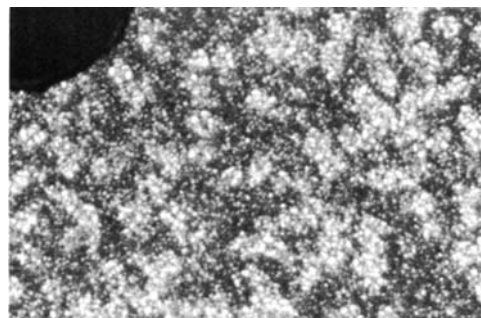


(c)

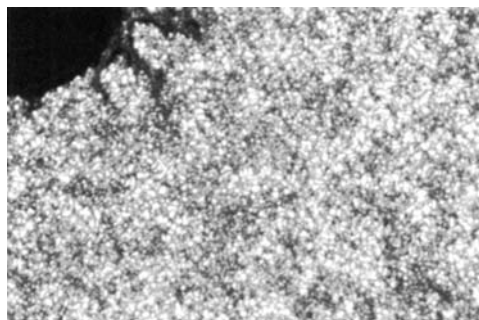
Figure 1 Optical micrographs of PET under crossed polarizers as a function of temperature in the heating cycle: (a) 25°C, (b) 225°C, and (c) 250°C ($\times 320$).



(a)

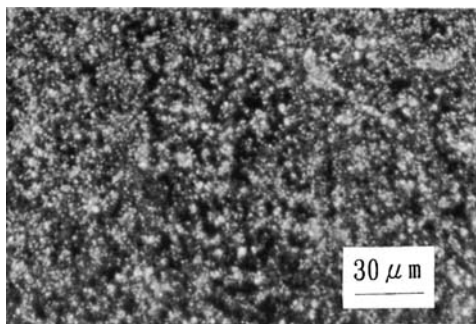


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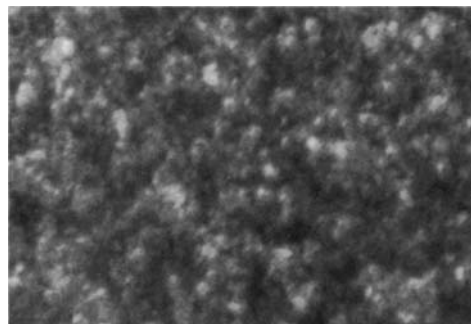


(c)

Figure 2 Optical micrographs of PET under crossed polarizers as a function of temperature in the cooling cycle: (a) 210°C, (b) 207°C, and (c) 200°C ($\times 320$).



(a)

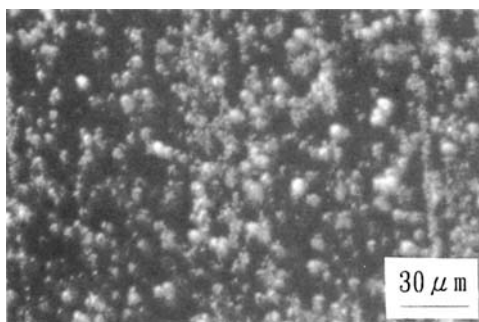


(b)

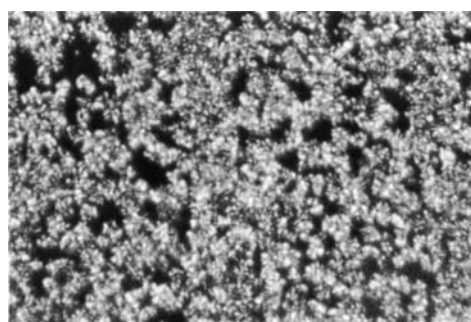


(c)

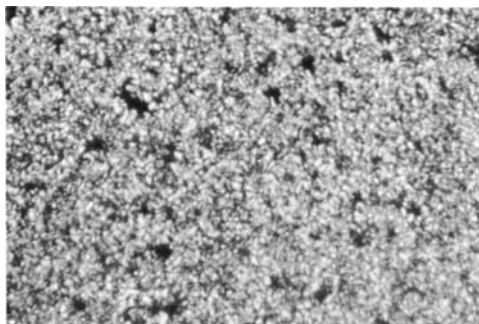
Figure 3 Optical micrographs of P28 under crossed polarizers as a function of temperature in the heating cycle: (a) 25°C, (b) 195°C, and (c) 225°C ($\times 320$).



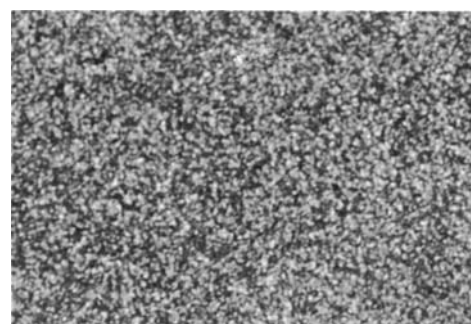
(a)



(b)



(c)



(d)

Figure 4 Optical micrographs of P28 under crossed polarizers as a function of temperature in the cooling cycle: (a) 180°C, (b) 170°C, (c) 160°C, and (d) 155°C ($\times 320$).

The optical micrographs of the 90/10 PET/P28 blend as a function of temperature are presented in Figures 5 and 6. At 25°C, the texture of crystalline is isotropic [Fig. 5(a)]. When the blend was heated from 25°C to 305°C, the crystal melted between 220°C [Fig. 5(b)] and 265°C [Fig. 5(d)]. The blend became fluid around 265°C, and the bright spots which represent the POB-rich domains of anisotropic phase were observed [Fig. 5(d)]. In the cooling cycle [Fig. 6(a)–(d)], the onset temperature of crystallization of the 90/10 PET/P28 blend around 220°C [Fig. 6(a)] is higher than that of neat PET (210°C). Moreover, the onset temperature of crystallization of copolyester P28 (around 180°C) is lower than that of PET. These results reveal that the PET crystallization is accelerated by the addition of P28 in 10 wt % as a nucleating agent.

The optical micrographs of the 90/10 PET/P82 blend as a function of temperature are presented in Figures 7 and 8. At 25°C, the texture of crystalline consists of isotropic and anisotropic phases, which can be characterized as a liquid crystalline of POB rich in brown color based on the high birefringence

under cross polarizers [Fig. 7(a)]. The anisotropic phase is scattered among the isotropic matrix phase. The crystals of the isotropic phase begin to melt at about 220°C [Fig. 7(b)] and vanish between 250°C [Fig. 7(c)] and 270°C in the heating cycle. This transition is considered to be the upper melting limit of the PET crystallites. The anisotropic phase still exists even at 300°C [Fig. 7(d)]. In the cooling cycle, the crystals form at around 217°C [Fig. 8(a)] and the completion temperature of crystallization is around 180°C [Fig. 8(d)]. These observations reveal that the PET crystallization is accelerated by the addition of P82 in 10 wt % as a nucleating agent. On the other hand, the anisotropic phase becomes deep brown between 215°C [Fig. 8(b)] and 210°C [Fig. 8(c)] in the cooling cycle. The disappearance of the anisotropic phase can be interpreted as a transition from the liquid crystalline phase to part of the domains of the POB-rich semicrystalline phase.

Comparing the crystallization behavior of the 90/10 PET/P28 blend with the 90/10 PET/P82 blend based on PLM observations, the onset temperature

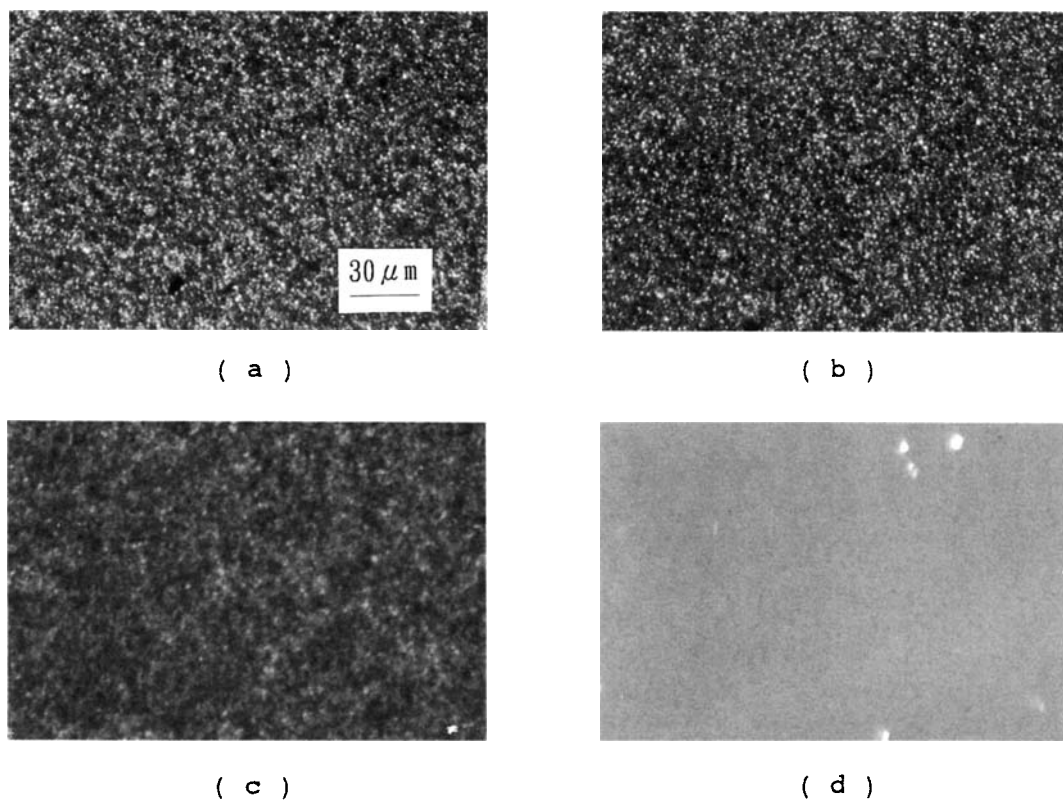


Figure 5 Optical micrographs of 90/10 PET/P28 blend under crossed polarizers as a function of temperature in the heating cycle: (a) 25°C, (b) 220°C, (c) 240°C, and (d) 265°C ($\times 320$).

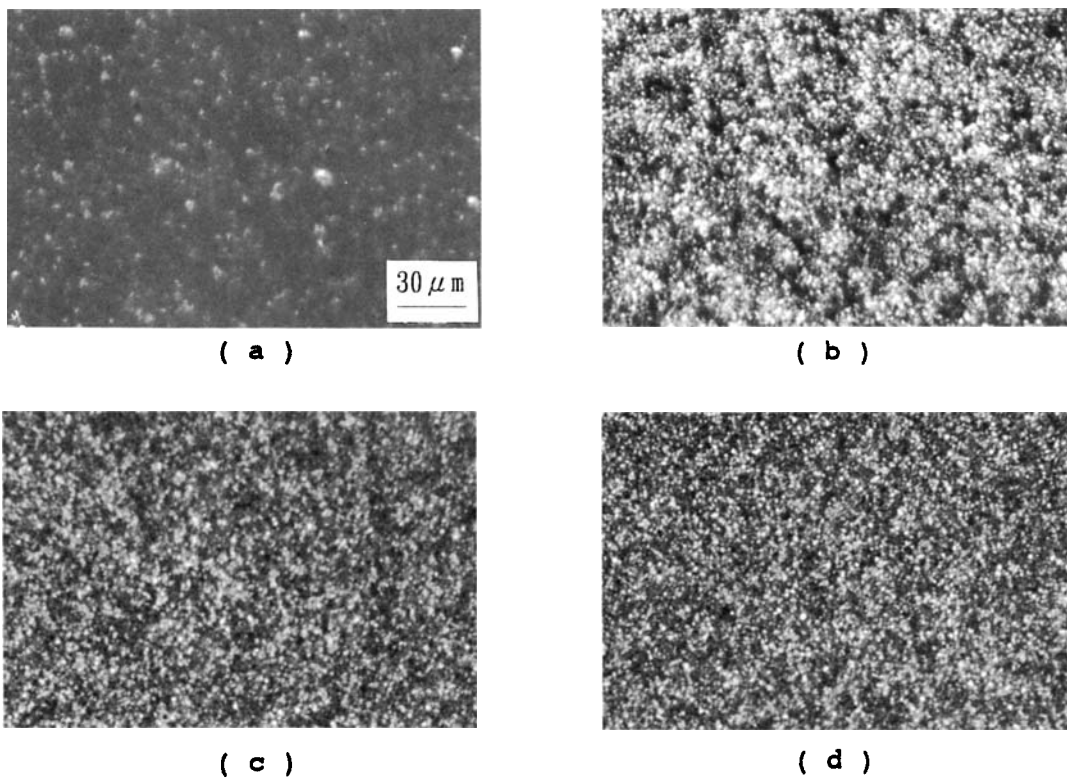


Figure 6 Optical micrographs of 90/10 PET/P28 blend under crossed polarizers as a function of temperature in the cooling cycle: (a) 220°C, (b) 210°C, (c) 200°C, and (d) 170°C ($\times 320$).

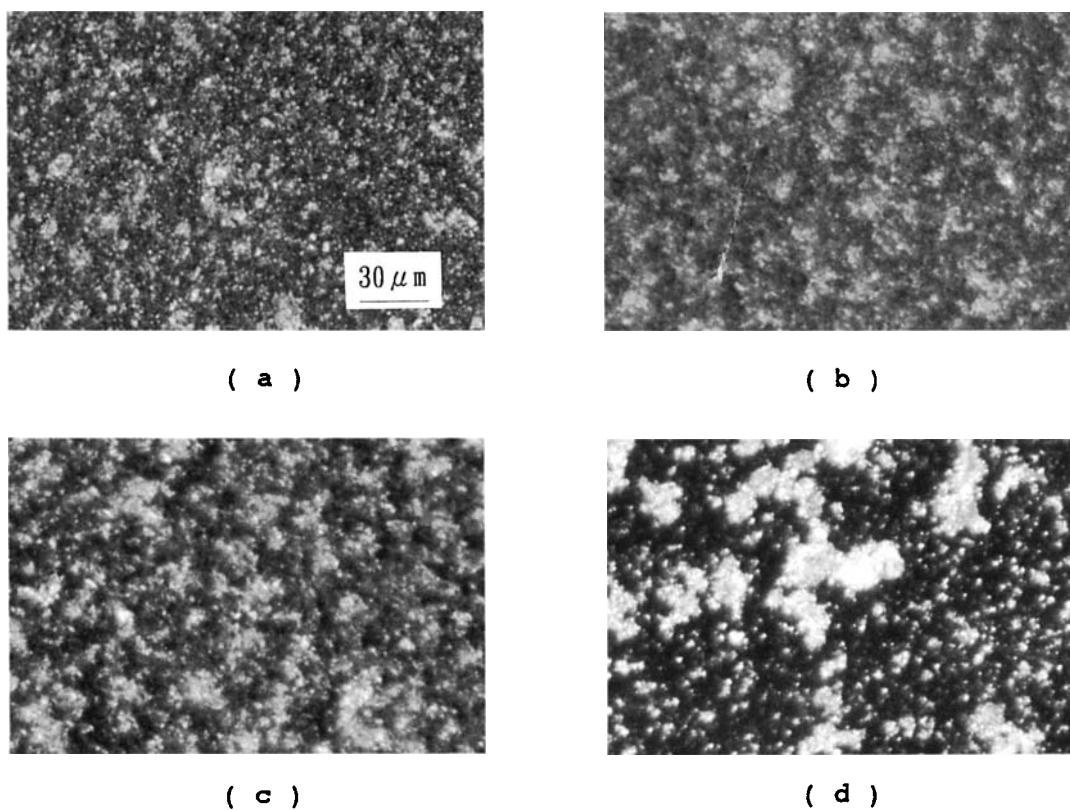
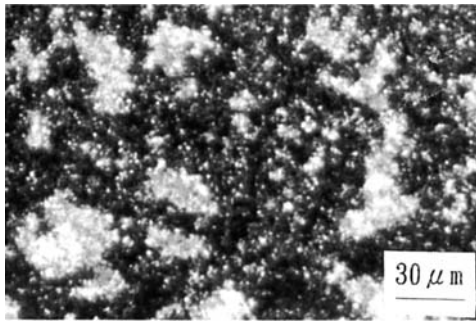
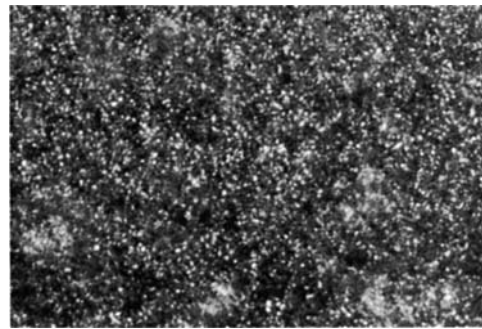


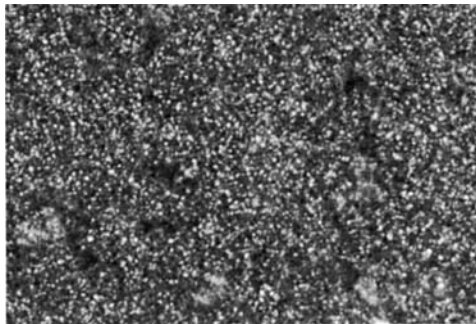
Figure 7 Optical micrographs of 90/10 PET/P82 blend under crossed polarizers as a function of temperature in the heating cycle: (a) 25°C, (b) 220°C, (c) 250°C, and (d) 300°C ($\times 320$).



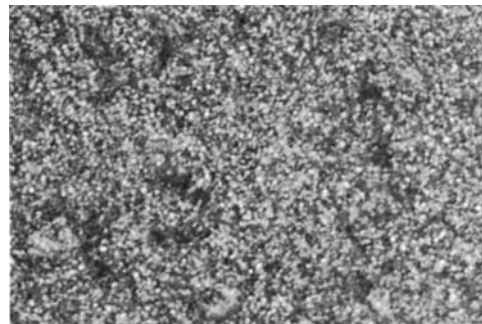
(a)



(b)

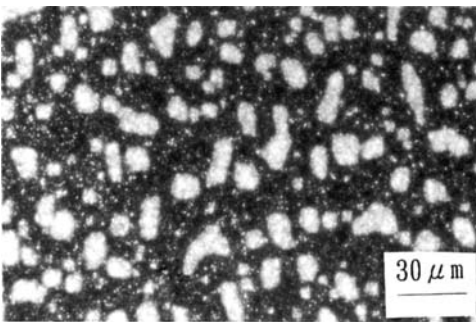


(c)

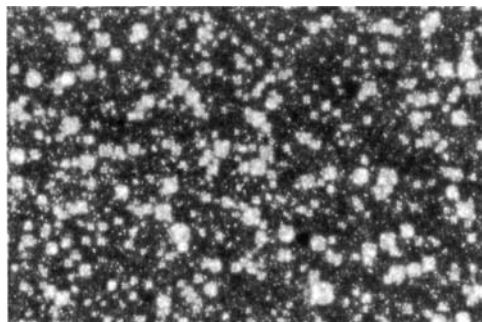


(d)

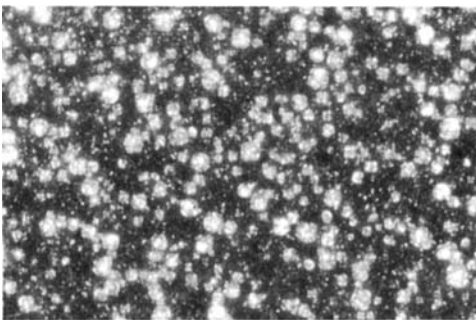
Figure 8 Optical micrographs of 90/10 PET/P82 blend under crossed polarizers as a function of temperature in the cooling cycle: (a) 217°C, (b) 215°C, (c) 210°C, and (d) 180°C ($\times 320$).



(a)



(b)



(c)

Figure 9 Optical micrographs of 50/50 PET/P64 blend under crossed polarizers as a function of blending time: (a) 3 min, (b) 8 min, and (c) 60 min ($\times 320$).

of crystallization for the 90/10 PET/P28 blend (220°C) is higher than that of the 90/10 PET/P82 blend (217°C). The result confirms that PET crystallization is accelerated more significantly by copolyester P28 than by copolyester P82, consistent with our previous study by DSC.¹⁷⁻¹⁸

Blending Effect

From our previous report,¹⁷ the distribution of copolyester in the PET matrix would affect the acceleration of PET crystallization. To verify the relation between distribution of copolyester and blending times, the 50/50 PET/P64 blend was blended for 3, 8, and 60 min. The distribution of the copolyester P64 scattered among the PET matrix after different blending times is shown in Figure 9. There are many large aggregates of the copolyester P64 dispersed among the PET matrix after 3 min blending [Fig. 9(a)]. The anisotropic phase of P64 copolyester becomes finer and dispersed among the PET matrix after 8 min blending [Fig. 9(b)]. On further blending for 60 min, the distribution of P64 is almost the same as that of after 8 min blending [compare (c) with (b) in Fig. 9]. It is concluded that the copolyester domains might have good distribution in the PET matrix after 8 min blending. The good distribution of the nucleating agent is responsible for the crystallization rate of matrix due to the uniformity of the nucleating spots of crystallization.

CONCLUSIONS

As can be seen in the optical micrographs, the fractions of the optically isotropic phase (i.e., PET-rich domains) in the blends turn completely dark under crossed polarizers at elevated temperatures, indicating the disappearance of PET crystallites. On the other hand, the fractions of the optically anisotropic phase in the blends (i.e., POB-rich domains) remain brown spots even at 300°C, indicating the anisotropic phase in the liquid crystalline state. It is detected that the PET crystallization is accelerated more significantly by copolyester P28 than by copolyester P82 in 10 wt %. The copolyesters act as

nucleating agents for PET. The distribution of copolyester among the PET matrix is significantly improved after 8 min blending.

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