

Blends of Polyethylene Terephthalate with Co[poly(ethylene terephthalate-*p*-oxybenzoate)]

I. Crystallization Kinetics by DSC Study

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SYNOPSIS

The dynamic and isothermal crystallization behaviors of polyethylene terephthalate (PET) blended with two types of co[poly(ethylene terephthalate-*p*-oxybenzoate)] copolyesters with different compositions, i.e., POB/PET = 20/80 (P28) and POB/PET = 80/20 (P82), has been studied by using differential scanning calorimetry (DSC). Both of these copolyesters in 10 wt % increase crystallization rate of PET in a manner similar to that of a nucleating agent. It is found that sample P28, which is an isotropic copolyester, accelerates the crystallization rate more significantly than that of P82, which is a thermotropic copolyester. The Avrami exponents n and rate constants k of these samples based on DSC studies were obtained in order to discuss the crystallization kinetics of PET accelerated by these copolyesters. The crystallization rate of the blends is also increased by 8 min blending due to the increased uniformity of the copolyester dispersed in the PET matrix.

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INTRODUCTION

Polyethylene terephthalate (PET) is widely used in the manufacture of beverage bottle, textile fiber, and packaging film. Historically, it has not been considered for application involving high-speed processing because it crystallizes or solidifies very slowly from melt. However, crystallization can be increased by the addition of polymeric nucleating agents. These include linear low-density polyethylene (LLDPE)¹ and poly(methyl methacrylate).² Differential scanning calorimetry (DSC) can be utilized for following crystallization.^{3,4} In fact, crystallization kinetics of PET have been investigated by many investigators by using DSC.^{5,6} Studies on the blend of liquid crystalline polymer (LCP) with PET have been also reported by Bairds and co-workers.^{7,8} They covered a large range of compositions with relatively high amounts of LCP and showed significant effect of liquid crystalline polyester on the properties of PET. Tendokar et al.^{9,10} have studied low-level LCP and

considered LCP as a modifier for PET due to its significant effect on the morphology and properties of PET. In the present work, we report the crystallization and thermal behavior of the commercial PET resin blended with two types of co[poly(ethylene terephthalate-*p*-oxybenzoate)] copolyesters (POB-PET). POB-PET copolyester with POB unit content from 40 to 90 mol % is a well-known thermotropic copolyester developed by Tennessee Eastman Co.¹¹⁻¹³

EXPERIMENTAL

Materials

Two co[poly(ethylene terephthalate-*p*-oxybenzoate)] copolyesters, designated as [POB-PET], were synthesized according to the procedure as reported in our previous study.¹⁴ Copolyester P28 having a composition [POB]/[PET] = 20/80 mole ratio is an isotropic copolyester. On the contrary, copolyester P82 having a composition of [POB]/[PET] = 80/20 is a thermotropic copolyester (i.e., liquid crystalline polymer). PET was the commer-

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cial product from the Far East Textile Co. (Taiwan) having an Intrinsic Viscosity (IV) value of 0.62, corresponding to molecular weight of about 20,000. PET and nucleating copolyesters were dried at 70°C for 48 h in a vacuum oven prior to blend.

Blending Method

All samples were blended at a ratio of PET/[POB-PET] = 90/10 by weight by using a Brabender Plasticorder. The dry polymer pellets in the desired weight ratio were transferred to the mixing bowl of the Brabender, which had been preheated to 300°C. The speed of the mixing blades was 30 rpm. After different blending times of 8, 30, and 50 min, the sample was taken from the bowl and thrown immediately into liquid nitrogen. The quenched samples were dried at 70°C for 48 h in a vacuum oven prior to DSC measurements.

DSC Measurement

The dry blend samples were milled to grain size of about 0.05 mm in diameter using a cutting mill. The weight of all samples was kept between 10 and 11 mg in DSC measurement by using Seiko SSC-5200.

The isothermal crystallization data were obtained by heating the sample to 305°C at the rate of 10°C/

Table I Codes of Blends for Different Blending Times

Composition	Blend Time (min)	Code
PET/P28	0	P2800
PET/P28	8	P2808
PET/P28	30	P2830
PET/P28	50	P2850
PET/P82	0	P8200
PET/P82	8	P8208
PET/P82	30	P8230
PET/P82	50	P8250

min under N₂ atmosphere, holding there for 5 min in order to destroy anisotropy, and then cooling down at the rate of 90°C/min until the crystallization temperature (T_c) was reached. The corresponding crystallization exotherm was scanned as a function of time until no change was observed.

The sample was heated up to 305°C at the rate of 10°C/min to obtain a heating scan. The sample was held there for 5 min under N₂ atmosphere; then it was cooled down at the rate of 10°C/min until 20°C to obtain a cooling scan. From these heating and cooling scans, one can obtain the dynamic crystallization data.

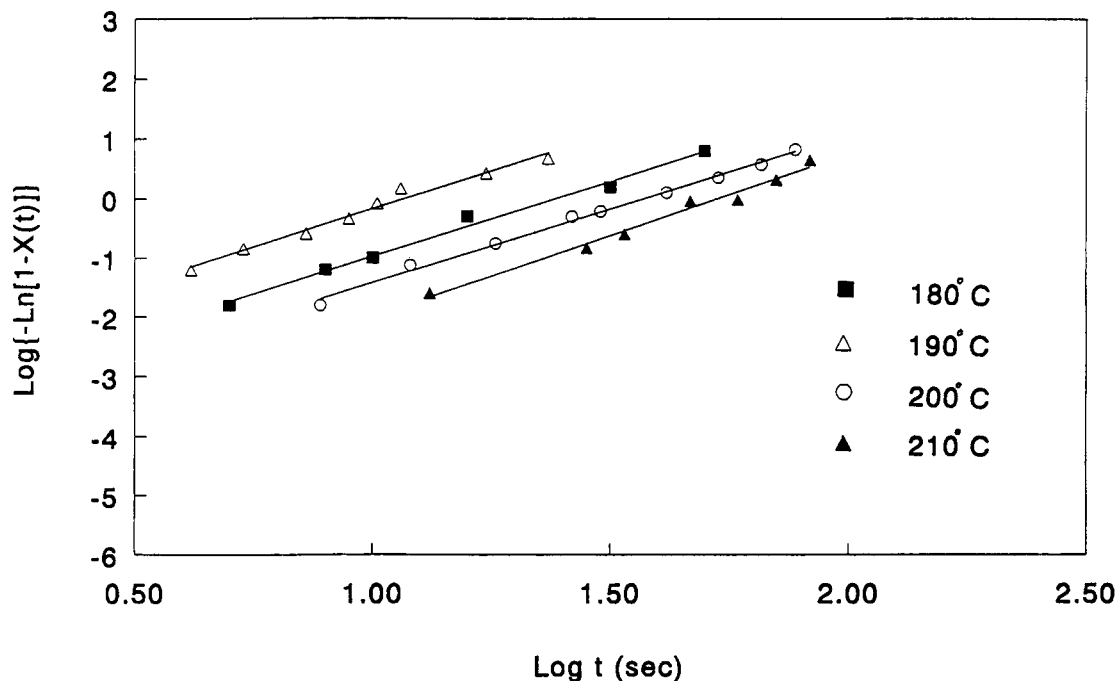


Figure 1 Avrami plots of PET at various temperatures.

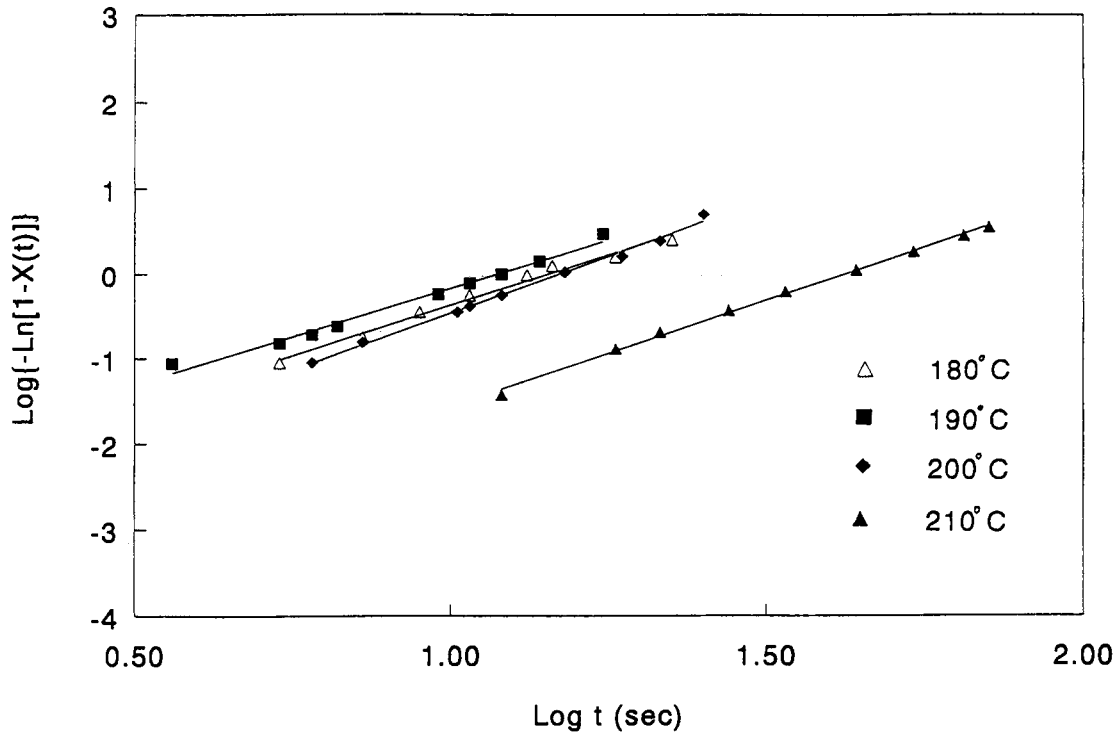


Figure 2 Avrami plots of PET/P28(90/10) blends at various temperatures.

Code

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

THEORETICAL CONSIDERATION

The kinetic data of PET crystallization have been interpreted on the basis of Avrami analysis. The

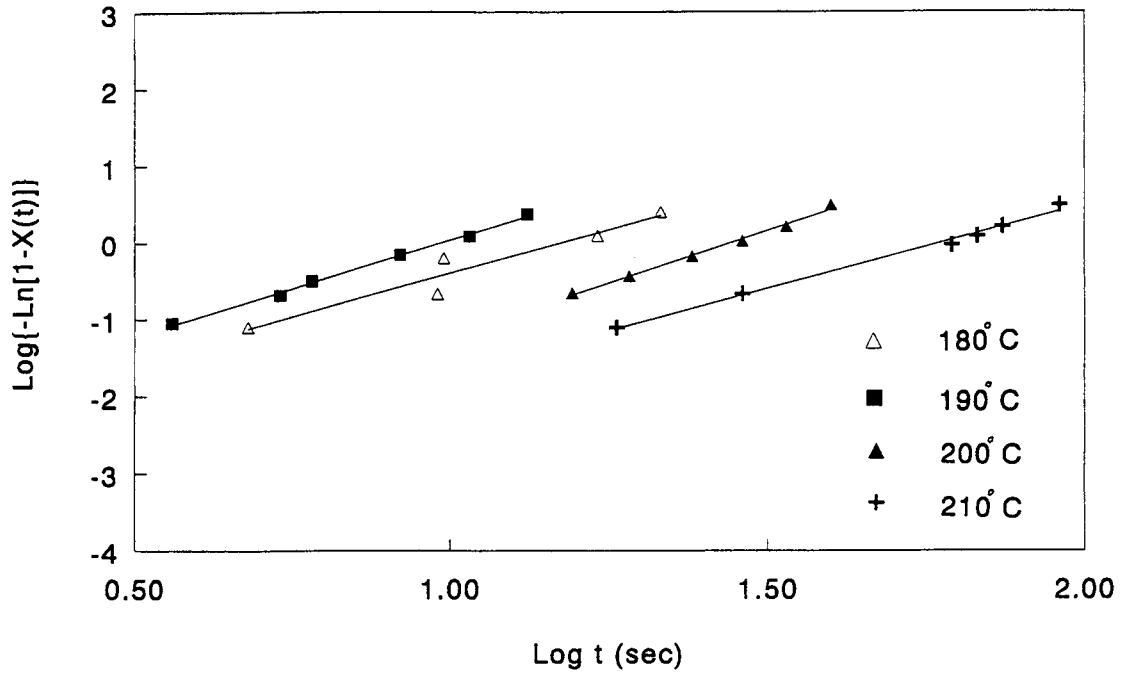


Figure 3 Avrami plots of PET/P82(90/10) blends at various temperatures.

Table II Isothermal Crystallization Parameters of PET

<i>T</i> (°C)	PET		
	<i>k</i> (s ^{-<i>n</i>})	<i>n</i>	<i>n</i> _{ave}
210	7.91 × 10 ⁻⁵	2.48	2.48
200	1.44 × 10 ⁻⁴	2.55	
190	3.38 × 10 ⁻³	2.49	
180	2.16 × 10 ⁻³	2.39	

weight fraction of crystalline material, $X(t)$, at time t has been calculated according to the following equation^{5,15}:

$$X(t) = \frac{\int_0^t \frac{dH}{dt} dt}{\int_0^\infty \frac{dH}{dt} dt} \quad (1)$$

where dH/dt is the rate of evolution of heat and t is the time. According to the Avrami equation¹⁶:

$$X(t) = 1 - \exp(-kt^n) \quad (2a)$$

or

$$\log\{-\ln[1 - X(t)]\} = n \log t + \log k \quad (2b)$$

where k is the rate constant and n is a constant that depends both on the nucleation and growth of the polymer.

The plot of $\log\{-\ln[1 - X(t)]\}$ vs. $\log t$ should yield a straight line with slope n .

According to the relationship⁵ among t_{\max} , n and k is

$$t_{\max} = \left(\frac{n-1}{nk}\right)^{1/n} \quad (3)$$

where t_{\max} denotes the time to attain a maximum rate of crystallization. One can calculate the rate constant k from this equation.

RESULTS AND DISCUSSION

Isothermal Crystallization Behavior

Figures 1, 2, and 3 illustrate the plots of Eq. (2b) for quenched PET, blends of PET/P28, and PET/P82 after 50 min blending, respectively, under the different crystallization temperatures ranging from 180 to 210°C. The values of k and n under the different crystallization temperatures are summarized in Table II for pure PET and Table III for the blends, respectively.

The rate constant k , which controls the crystallization of sample and is extremely sensitive to temperature, determines both the rate of nucleation and the growth processes. The value of k is dependent on the molecular weight and structure of the polymer, molecular weight distribution, degree of tacticity, and presence of impurities.

As shown in Tables II and III, the changes in the value of n were in the order of 10² for PET, in the order of 10¹ for the blends of PET/P28, and in the order of 10² for the blends of PET/P82, respectively, by changing crystallization temperature in the range from 180 to 210°C. It is seen that maximum values of k for PET itself, PET/P28 blend, and PET/P82 blend all appear at 190°C. In general, the value of k for the PET/P28 system is larger than that of the PET/P82 system at the same corresponding crystallization temperature except at 190°C. Moreover, note that the value of k for PET itself is the smallest in comparison with those of the blends at the same corresponding temperature. This suggests that both copolyesters can be considered to act as nucleating agent during crystallization of PET. But the crystallization process is more accelerated by copolyester

Table III Isothermal Crystallization Parameters of the Blends of PET/Copolyester after 50-min Blending

<i>T</i> (°C)	PET/P28			PET/P82		
	<i>k</i> (s ^{-<i>n</i>})	<i>n</i>	<i>n</i> _{ave}	<i>k</i> (s ^{-<i>n</i>})	<i>n</i>	<i>n</i> _{ave}
210	3.34 × 10 ⁻⁴	2.25	2.35	8.60 × 10 ⁻⁵	2.36	
200	1.86 × 10 ⁻³	2.56		1.45 × 10 ⁻⁴	2.63	2.43
190	5.57 × 10 ⁻³	2.31		6.80 × 10 ⁻³	2.50	
180	5.07 × 10 ⁻³	2.26		2.26 × 10 ⁻³	2.21	

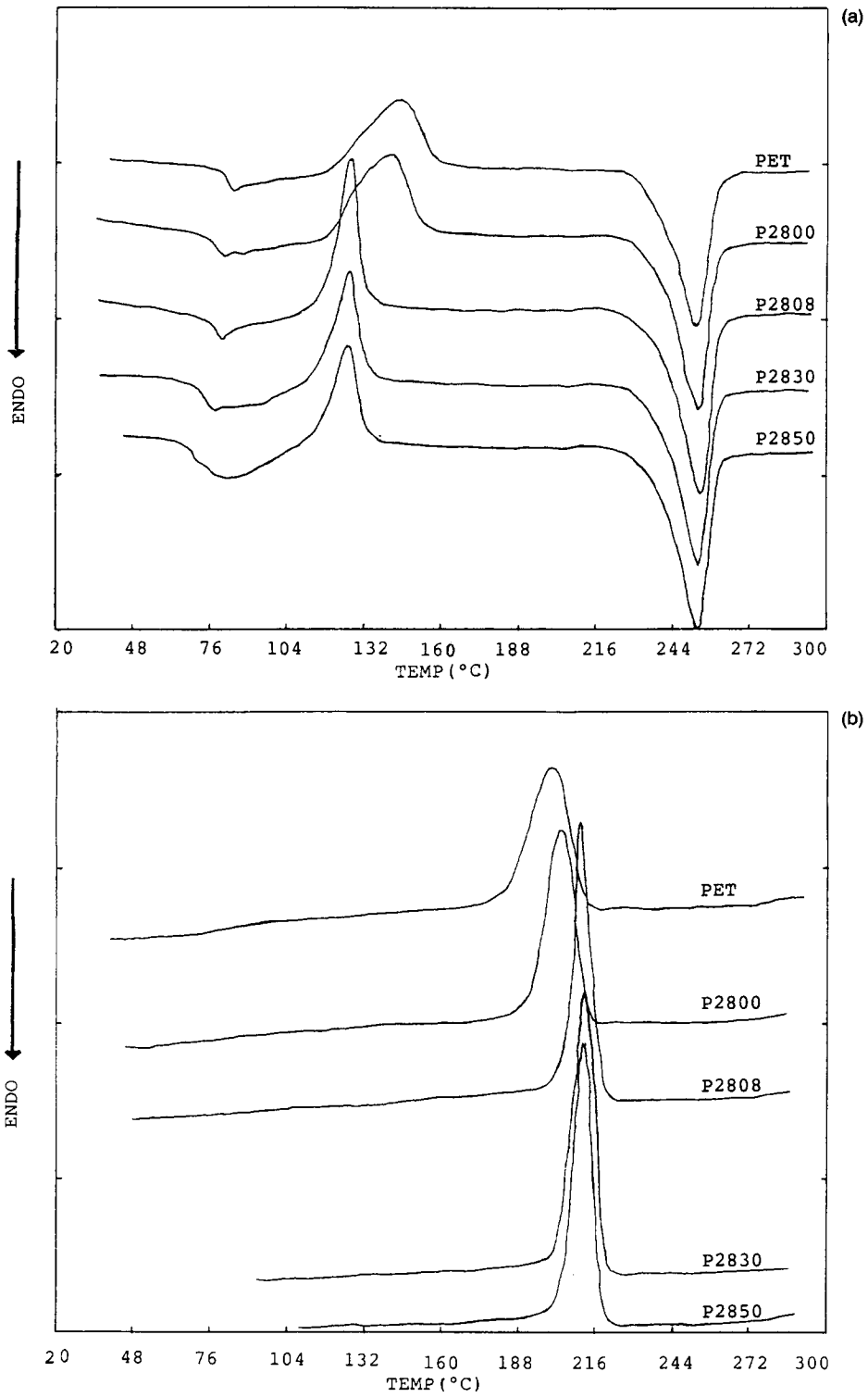


Figure 4 (a) DSC thermograms of PET/P28 blends (heating scans). (b) DSC thermograms of PET/P28 blends (cooling scans).

Table IVa DSC Data of PET/P28 Blends for Different Blending Times from Heating Scans

Sample	Recrystallization					Melting				Difference
	T_g (°C)	Onset (°C)	T_{rc} (°C)	ΔT_{rc}^a (°C)	ΔH_{rc} (J/g)	Onset (°C)	T_m (°C)	ΔT_m^b (°C)	ΔH_f (J/g)	$\Delta H_f - \Delta H_{rc}$ (J/g)
PET	82	115	145	50	26.5	223	253	48	38.7	12.2
P2800	78	112	141	46	28.6	224	253	44	41.6	13.0
P2808	78	109	127	34	23.8	219	253	48	47.0	23.2
P2830	76	109	126	34	18.0	220	253	48	46.1	28.1
P2850	74	109	126	33	19.2	220	253	48	48.1	28.9

^a ΔT_{rc} : recrystallization temperature range.

^b ΔT_m : melting temperature range.

P28 than by copolyester P82 in terms of rate constant. For instance, P82 accelerates 1.09 times only, whereas P28 accelerates 4.2 times of PET crystallization rate at 210°C (see Tables II and III).

The value of the exponent n does not vary significantly with temperature for all of the samples. However, as shown in Tables II and III, the average value of n at the temperature ranging from 180 to 210°C is 2.48 for PET, 2.35 for PET/P28, and 2.43 for PET/P82, respectively. Namely, all of the values lie between 2 and 3. The deviation of n could be attributed to factors such as time-dependent nucleation, variant growth rate constant, combination of homogeneous and heterogeneous nucleation. However, it is difficult to elucidate the growth geometry and type of nucleation solely from the value of the exponent n . On the basis of Mandelkern's analysis,¹⁷ the crystallization of pure PET itself may involve homogeneous nucleation. On the other hand, the blends of PET/P28 and PET/P82 might involve heterogeneous nucleation with two directional diffusion controlled growths.

Table IVb DSC Data of PET/P28 Blends for Different Blending Times from Cooling Scans

Sample	Crystallization			
	Onset (°C)	T_c (°C)	ΔT_c^a (°C)	ΔH_c (J/g)
PET	216	200	42	40.7
P2800	218	204	34	41.5
P2808	222	211	30	44.8
P2830	222	211	30	45.4
P2850	222	211	31	46.0

^a ΔT_c : crystallization temperature range.

Dynamic Crystallization Behavior

The results of the DSC heating and cooling scans for PET/P28 blends are illustrated in Figures 4(a) for heating scans and 4(b) for cooling scans, respectively. The various parameters determined from these scans are tabulated in Table IVa for heating scans and IVb for cooling scans, respectively. It is evident that there is a distinct glass transition temperature, T_g , a recrystallization exothermic peak, and a melting endothermic peak in all of the heating scans. On the other hand, there is a distinct crystallization exothermic peak in all of the cooling scans. It is known that the total crystallinity (ΔH_f) of PET resins is the sum of primary crystallinity and secondary crystallinity. Although the extent of primary crystallinity cannot be directly monitored at rapid cooling rate, it can be estimated from the heating curves as the difference between the area under the induced secondary crystallinity peak (ΔH_{rc}) and the area of the total crystallinity melting peak (ΔH_f) [endotherms on right end of curves in Fig. 4(a) for PET/P28 blends and Fig. 5(a) for PET/P82 blends]. It is seen that from the heating scans (Table IVa), the recrystallization temperatures (T_{rc}) or secondary crystallization temperature of the blends are appreciably lower than that of quenched PET itself after at least 8-min blending process. The heating scans [Fig. 4(a)] show that the melting temperature (T_m) of PET/P28 blend is the same as that of PET itself at 253°C. The heat of fusion (ΔH_f) or the total crystallinity and the value of primary crystallinity ($\Delta H_f - \Delta H_{rc}$) are increased after 8-min blending time. The larger the value of primary crystallinity, the higher crystallization is the rate in the primary crystallization. The crystallization temperature (T_c) of PET/P28 blends is about 11°C higher than that of PET itself. The

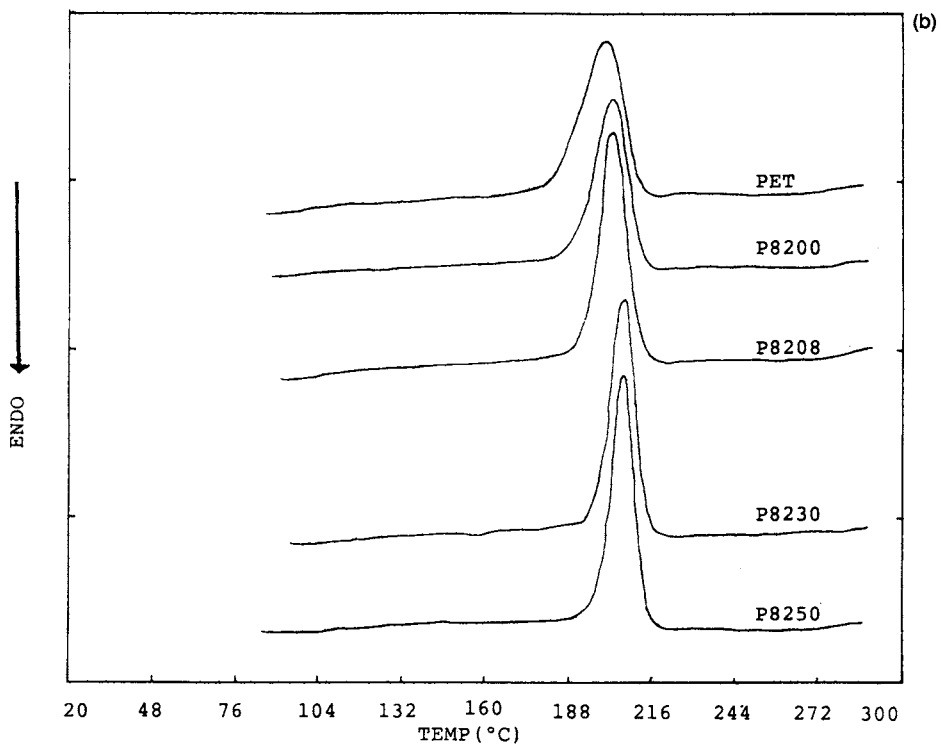
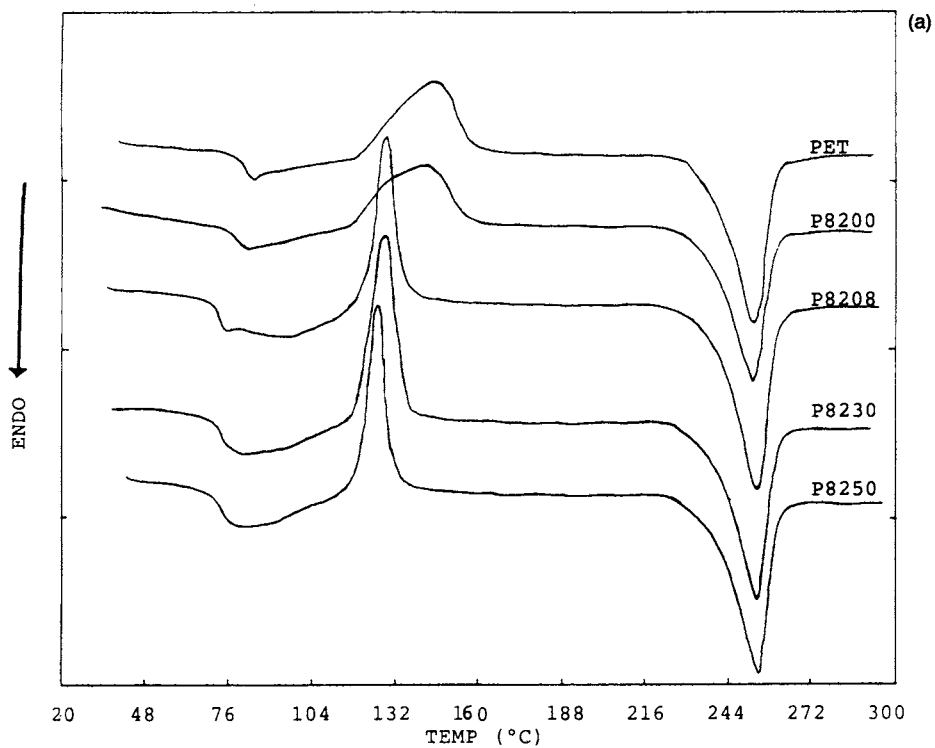


Figure 5 (a) DSC thermograms of PET/P82 blends (heating scans). (b) DSC thermograms of PET/P82 blends (cooling scans).

Table Va DSC Data of PET/P82 Blends for Different Blending Times from Heating Scans

Sample	T_g (°C)	Recrystalliation				Melting				Difference $\Delta H_f - \Delta H_{rc}$ (J/g)
		Onset (°C)	T_{rc} (°C)	ΔT_{rc} (°C)	ΔH_{rc} (J/g)	Onset (°C)	T_m (°C)	ΔT_m (°C)	ΔH_f (J/g)	
PET	82	115	145	50	26.5	223	253	48	38.7	12.2
P8200	80	111	142	53	25.8	220	253	52	37.3	11.5
P8208	74	110	129	36	20.4	219	253	48	37.5	17.1
P8230	75	110	128	36	18.9	220	253	48	37.1	18.2
P8250	74	108	126	35	22.8	220	253	49	41.3	18.5

sample prior to blending (i.e., P2800) is only 4°C higher than that of PET itself (see Table IVb).

This result suggests that P28 copolyester acts like a nucleating agent for the crystallization of PET if it is blended at a level of 10 wt %. Blending can increase crystallization temperature due to the more uniformity of the nucleating agent dispersed in the PET matrix. Because the values of T_{rc} , ΔH_{rc} , ΔH_f , $\Delta H_f - \Delta H_{rc}$, T_c , ΔH_c , ΔT_c , and ΔT_{rc} keep almost constant over 8-min blending for PET/P28 blends, it is believed that the 8-min blending is enough for the uniformity of copolyester in the PET matrix. It is consistent with the result reported by Baird et al.,⁸ indicating a residence time in the extruder of the order 4.5 to 6 min was necessary before any transesterification reaction of the blends could be observed based on DSC studies. It is concluded that the copolyester domains might have good distribution in the PET matrix after 8-min blending.

The results of the DSC heating and cooling scans for PET/P82 blends are illustrated in Figures 5(a) for heating scans and 5(b) for cooling scans, respectively. The various parameters determined from these scans are tabulated in Table Va for heating scans and Vb for cooling scans, respectively. It is evident that there is a distinct glass transition in

Figure 5(a) in all of the heating scans. The value of T_{rc} obtained from heating scans seems to decrease with increasing blending time. The value of T_{rc} of blends is always lower than that of PET itself. The value of T_m of the PET/P82 blends even after blending are kept the same as that of PET itself at 253°C. The primary crystallinity ($\Delta H_f - H_{rc}$) is significantly higher as compared to that of PET after blending. These results suggest that the crystallization of PET is also accelerated by the blending of 10 wt % of P82 copolyester. But the effect on PET is not as significant as on P28.

Comparing Tables IVa with Va the values of $\Delta H_f - \Delta H_{rc}$ and ΔH_f of PET/P28 blend are larger than those of PET/P82 blend under the same blending times. From Tables IVb and Vb, it is seen that the value of T_c of PET/P28 blend is higher than that of PET/P82 blend, and the value of ΔT_c of PET/P28 blend is smaller than that of PET/P82 blend under the same blending times. The higher the value of T_c is, the higher the crystallization rate. The larger the value of ΔT_c is, the lower crystallization rate. These results reveal that crystallization rate of PET is accelerated more significantly by P28 copolyester than by P82 copolyester. This result is consistent with that obtained in the preceding isothermal DSC data.

CONCLUSION

When POB/PET copolyesters are blended in small quantities (10 wt %) to polyethylene terephthalate melts, these copolyesters act as nucleating agents, speeding up PET crystallization and in turn, permitting high-speed processing. Sample P28 accelerates the crystallization rate more significantly than P82 sample based on the isothermal crystallization and dynamic crystallization behaviors. Moreover, the crystallization rate of the blends is increased as the blending time exceeds at least 8 min, due to the increased uniformity of the copo-

Table Vb DSC Data of PET/P82 Blends for Different Blending Times from Cooling Scans

Sample	Crystallization			
	Onset (°C)	T_c (°C)	ΔT_c (°C)	ΔH_c (J/g)
PET	216	200	42	40.7
P8200	218	202	39	38.2
P8208	218	203	36	37.8
P8230	222	205	37	38.9
P8250	222	205	37	39.8

lyester nucleating agent dispersed in the PET matrix.

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REFERENCES

1. L. Bourland, *Plastics Eng.*, July, 39 (1987).
2. V. M. Nadkarni and J. P. Jog, *Polym. Eng. Sci.*, **27**, 451 (1987).
3. B. Miller, *J. Appl. Polym. Sci.*, **11**, 2343 (1967).
4. A. Booth and J. N. Hay, *Polymer*, **10**, 95 (1969).
5. C. C. Lin, *Polym. Eng. Sci.*, **23**, 113 (1983).
6. S. A. Jabarin, *J. Appl. Polym. Sci.*, **34**, 85 (1987).
7. E. G. Joseph, G. L. Wilkes, and D. G. Baird, *Prep. Am. Chem. Soc., Div. Polym. Chem.*, **24**, 304 (1983).
8. A. M. Sukhadia, D. Done, and D. G. Baird, *Polym. Eng. Sci.*, **30**(9), 519 (1990).
9. S. K. Battacharya, A. Tendokar, and A. Misra, *Mol. Cryst. Liq. Cryst.*, **153**, 501 (1987).
10. S. K. Sharma, A. Tendokar, and A. Misra, *Mol. Cryst. Liq. Cryst.*, **157**, 597 (1988).
11. W. R. Jackson and H. F. Kuhfuss, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2043 (1976).
12. W. R. Jackson and H. F. Kuhfuss, *J. Appl. Polym. Sci.*, **25**, 1685 (1980).
13. W. R. Jackson, *Macromolecules*, **16**, 1027 (1983).
14. T. H. Shinn, J. Y. Chen, and C. C. Lin, *J. Appl. Polym. Sci.*, **47**, 1233 (1993).
15. C. Mancarella and E. Martucelli, *Polymer*, **13**, 407 (1977).
16. M. Avrami, *J. Chem. Phys.*, **7**, 1103 (1939); **8**, 212 (1940); **9**, 177 (1941).
17. L. Mandelkern, *Crystallization of Polymer*, McGraw-Hill, New York, (1964).

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