

Effect of Linear Comonomers on the Rate of Crystallization of Copolyesters

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ABSTRACT: Small amounts of dimethyl-4,4'-biphenyldicarboxylate, 2,7-dimethyl-4,5,9,10-tetrahydropyrenedicarboxylate, and dimethyl-2,7-pyrenedicarboxylate have been copolymerized into poly(ethylene) terephthalate (PET). The thermal transitions of the copolymers have been characterized, and the crystallization rates have been measured isothermally. Avrami analysis indicates that all the copolymers crystallized at a slower rate than that of the PET homopolymer. Addition of perylene to the copolymers containing pyrene enhanced the rate of crystallization, which could be the consequence of stacked arene assemblies serving as templates for crystal formation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2696–2704, 2001

INTRODUCTION

Poly(ethylene terephthalate) (PET) enjoys a position of dominance in the thermoplastic polyester market because of its relatively low cost and its balance of mechanical, thermal, and chemical properties. The relatively slow rate of crystallization of PET leads to variable crystallinities (and therefore variable mold shrinkages, clarity, chemical stability, and mechanical stresses) and presents a significant limitation to its use in some applications.¹ Because of its higher rate of crystallization, poly(*butylene* terephthalate) (PBT) is often used in injection molded applications, despite its higher cost.

In an effort to enhance the rate of crystallization of PET, various additives and strategies have

been employed. Orientation, heterogeneous plate-like nucleating agents, plasticizers, and chemical chain-end modifiers have all been used to modify the crystallization rate.² The addition of inorganic nucleants, such as talc, titania, silica, and clays, to PET has been reviewed³ and is practiced commercially to shorten PET mold cycling times. These nucleated PET products crystallize rapidly, with optimum nucleant loadings of 0.2–0.4 wt %. Modifiers such as sodium benzoate or sodium bicarbonate,⁴ which convert the acid chain ends of PET to carboxylate salts, also exhibit their maximum effect with approximately 0.3 wt %. The use of chain-slip agents, such as polyethylene wax or low-molecular-weight ester lubricants, also enhances PET crystallization rates.⁵

Instead of using large platelike heterogeneous nucleating agents such as talc, we set out to incorporate comonomer units that act as molecular seeds for crystallization. Flat, rigid, linear, aromatic comonomers⁶ with a high aspect ratio could induce ordering in the isotropic melt and form a template for crystallization. For example,

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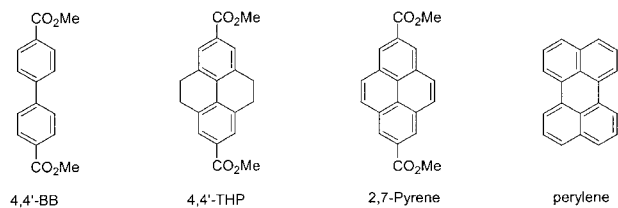


Figure 1 Structures of comonomers.

phenanthrene has been used to nucleate crystallization in PET.⁷ In addition to the effects of rigidity and geometry, π -stacking of aromatic units introduces the possibility of association of chains in the isotropic melt before crystallization. For example, stacking between the naphthalene structural units in poly(ethylene terephthalate-co-naphthalate) copolymers has been demonstrated at concentrations as low as 1% naphthalate.⁸ Other arenes, such as perylene, pyrene, anthracene, naphthalene, and benzene, form a variety array of assemblies through π -stacking, quadrupolar interactions, charge transfer, and dipolar interactions, as well as excimers.^{9,10} Of these complexes, those involving larger fused arenes (perylene and pyrene) are generally more stable. In particular, both perylene and pyrene form complexes with benzene.^{10,11} Perylene¹² and pyrene¹³ assemblies are formed in polymers containing these arenes. Aggregates of these units and complexes between these units and terephthalate units could nucleate crystallization. To assess the effect of incorporating fused arene comonomers on the rate of crystallization of PET, pyrene diacids were copolymerized at various concentrations.

Dimethyl 2,7-pyrenedicarboxylate (2,7-pyrene), dimethyl 4,5,9,10-tetrahydropyrenedicarboxylate (THP), and dimethyl 4,4'-biphenyldicarboxylate (4,4'-BB) were chosen as comonomers for this study (Fig. 1). The 2,7-pyrene-based copolymers were selected for copolymerization with PET because of their rigid planar structure, thermal stability, ability to form π -stacked assemblies, and synthetic accessibility. The THP comonomer has a size and shape similar to that of the 2,7-pyrene, but it is nonplanar by virtue of the saturated two-carbon (C_2) bridges between the phenylene units. The THP unit is less conjugated than pyrene and does not form stable π -complexes. The 4,4'-BB comonomer has been incorporated into a variety of polyesters. It has the same length and linearity as the 2,7-pyrene and THP, but it is narrower and has greater torsional mobility. High concentration PET copoly-

mers with 4,4'-BB exhibit a high degree of ordering and possess some liquid crystalline properties.¹⁴

Measurement of the rates of crystallization of PET and its copolymers is complicated by many factors. These include molecular weight,^{15,16} orientation,¹⁷ reaction side products (e.g., diethylene glycol),¹⁸ catalysts,¹⁶ nucleating agents,¹ water content,¹⁹ and comonomers.²⁰ By preparing samples under identical conditions, we sought to separate the effect of comonomers on the crystallization rate of PET.

The kinetics of crystallization can be evaluated both isothermally¹⁵ and nonisothermally^{21,22} using infrared (IR) absorption,²³ density methods,^{16,24} microscopy,^{17,20} calorimetry,^{15,18,25,26} and many other methods.²⁷ The interpretation of data from isothermal crystallization kinetics is simpler, but isothermal crystallization studies can only be performed when the thermal response time of the technique is significantly less than the thermal response time of the crystallization process being measured.²¹ If this condition is not met, the crystallization process begins before the onset of data collection.

Most studies of polymer crystallization rely on the Avrami expression (eq 1) for treatment of data²⁸:

$$\theta_a = e^{-kt^n} \quad (1)$$

In the Avrami expression, θ_a is the fraction of uncrystallized sample at time t , and k is the crystallization kinetic rate constant. The Avrami exponent n provides an indication of the mechanism for nucleation and growth of crystallites. Interpretations of the various values of n (normally ranging between 1 and 4) can be found in many sources.²⁸

A qualitative method of evaluating rates of crystallization from the melt entails examining the difference in temperature between the melting peak on heating and the crystallization peak on cooling (ΔT) in a differential scanning calorimetry (DSC) experiment. Although, in essence, this measures only the degree of supercooling, and is susceptible to many biases, including variation in the melt viscosity, it is a qualitative assessment of the crystallization rate and should correlate with processes that occur during extrusion and injection molding. We use both isothermal DSC crystallization measurements with Avrami analysis and assessment of ΔT values to compare the effect of a series of linear comonomers on the crystallization rate of PET.

Table I Synthesis of Copolymers

Sample Comonomer (mol %)	Monomers			Catalysts		
	DMT/g (mol)	EG/g (mol)	Comonomer/g (mol)	Mn(OAc) ₂ (g)	Sb ₂ O ₃ (g)	PPA (g)
Control PET	777.0	558.0	—	0.282	0.289	1.72
2.5% 4,4'-BB	757.4	558.0	27.0	0.282	0.289	1.72
5% 4,4'-BB	738.0	558.0	54.1	0.282	0.289	1.72
2.5% THP	236.8	174.7	10.076	0.089	0.091	0.054
5% THP	230.6	174.7	20.154	0.089	0.091	0.054
2.5% 2,7-Pyrene	236.7	174.7	9.954	0.089	0.091	0.054
5% 2,7-Pyrene	230.6	174.7	19.892	0.089	0.091	0.054

DMT, dimethyl terephthalate; EG, ethylene glycol; PPA, polyphosphoric acid.

EXPERIMENTAL

Dimethyl 4,4'-biphenyldicarboxylate, perylene, and trifluoroacetic acid (TFA) were obtained from Aldrich. Dimethyl terephthalate and ethylene glycol were obtained from KoSa. DSC was performed using a Perkin–Elmer Series 7 DSC operating under N₂ and equipped with an Intercooler 2. All samples were dried under vacuum overnight at 80°C.

Samples of polyester were dissolved in *o*-chlorophenol at room temperature, and the solutions were filtered before dilute solution viscometry. Viscometry was performed at 25°C, using a 4% polymer solution in *o*-chlorophenol. Run times were measured for five trials and averaged. Intrinsic viscosities were extrapolated from the infinite dilution curve of PET homopolymer.

Dimethyl 4,5,9,10-Tetrahydropyrene-2,7-Dicarboxylate

The title compound was prepared by a previously reported method²⁹: mp 209–212°C. ¹H-NMR (500 MHz, CDCl₃) δ 2.93 (s, 8H, CH₂), 3.91 (s, 6H, methyl), 7.76 (s, 4H, Ar-H). IR (KBr) 2956, 1720, 1429, 1290, 1206, 768 cm⁻¹.

Dimethyl 2,7-Pyrenedicarboxylate

The title compound was prepared by a previously reported method²⁹: mp 287–289°C. ¹H-NMR (500 MHz, CDCl₃) δ 4.08 (s, 6H, methyl), 8.16 (s, 4H, Ar-H_{4,5,9,10}), 8.85 (s, 4H, Ar-H_{1,3,6,8}). IR (KBr) 2953, 1723, 1302, 1235 cm⁻¹.

Synthesis of PET Copolymers

A standard melt polymerization method was used. Dimethyl terephthalate, ethylene glycol, Mn(OAc)₂, and Sb₂O₅, were added to either a 0.5- or 2-L 316 stainless-steel reaction vessel equipped with a mechanical stirrer, distillation head, and condenser. For the copolymers, various mole percentages of the dimethyl terephthalate were replaced with comonomer (Table I). The reaction mixtures were heated for 2 h at 180–210°C, during which methanol was removed by distillation. Polyphosphoric acid (10% w/w in ethylene glycol) was added to deactivate the manganese ester interchange catalyst, and the reactor pressure was slowly reduced over 40 min to ≤1 Torr. The reaction mixtures were heated to 285–290°C, during which ethylene glycol was removed by distillation. The progress of the reaction was monitored by the current required to maintain the mechanical stirrer at a rate of 10 rpm. The polymer was extruded from the vessel under a positive pressure of N₂.

Perylene Blends With PET Copolymers

A solution of perylene (32.8 mg, 0.130 mmol) in CHCl₃ (100 mL) was added to a solution of 2.5 mol % copolymer (1.00 g, i.e., equimolar comonomer and perylene) in TFA (25 mL). The solutions were mixed, the solvent was removed under reduced pressure, and the sample was dried overnight under reduced pressure. The resulting polymers were crystallized by annealing for 2 h at 150°C under vacuum. Blends of the 5 mol % (65.6 mg, 0.260 mmol of perylene) copolymers and control samples (see Fig. 4) were prepared in the same manner.

Table II Characterization of Copolymers

Copolymer	IV ^a	$M_v^{b/}$ 1000 g/mol	First Thermal Cycle			Second Heating		
			$T_{cc}^c/^\circ\text{C}$ ($\Delta H_{cc}^d/\text{J g}^{-1}$)	$T_m^e/^\circ\text{C}$ ($\Delta H_m^f/\text{J g}^{-1}$)	$T_c^g/^\circ\text{C}$ ($\Delta H_c^h/\text{J g}^{-1}$)	$T_g^i/^\circ\text{C}$	$T_{cc}^c/^\circ\text{C}$ ($\Delta H_c^h/\text{J g}^{-1}$)	$T_m^e/^\circ\text{C}$ [$T_{\text{onset}}^j/^\circ\text{C}$] ($\Delta H_m^f/\text{J g}^{-1}$)
Control PET	0.609	19.2	132 (-27)	260 (41)	200 (-34)	83	155 (-1)	258 [247] (37)
2.5% 2,7-Pyrene	0.683	22.0	148 (-32)	246 (40)	155 (-5)	82	168 (-27)	244 [231] (36)
5% 2,7-Pyrene	0.579	18.0	163 (-28)	245 (32)	156 (-5)	86	175 (-20)	242 [227] (26)
2.5% THP	0.558	17.2	147 (-23)	240 (29)	153 (-7)	77	152 (-15)	238 [224] (29)
5% THP	0.695	22.5	172 (-28)	242 (29)	156 (-5)	85	170 (-12)	240 [226] (21)
2.5% 4,4'-BB	0.545	16.8	140 (-28)	252 (36)	175 (-36)	85	—	250 [237] (32)
5% 4,4'-BB	0.571	17.7	144 (-27)	248 (34)	175 (-24)	84	161 (-6)	245 [232] (32)

^a Intrinsic viscosity.

^b Viscosity average molecular weight.

^c Temperature of cold crystallization.

^d Enthalpy of cold crystallization.

^e Melting point.

^f Enthalpy of melting.

^g Temperature of crystallization on cooling.

^h Enthalpy of crystallization on cooling.

ⁱ Glass transition temperature.

Dynamic DSC Evaluation of Copolymers

Polymer samples (10–20 mg) were heated from 50°C to 294°C and held for 10 min at 294°C to remove thermal history.²⁴ The samples were then cooled to 50°C and reheated to 294°C. All samples were heated and cooled at 10°C/min. Samples were analyzed for T_g , T_c , and T_m , as appropriate. T_g and T_m (peak and onset values) were recorded during the second heating scan. The value of ΔT is defined as the difference in peak temperatures of melting and crystallization on heating and cooling scans, respectively.

Isothermal DSC Crystallization of Copolymers

Polymer samples (6–8 mg) were heated to 294°C, held for 10 min, and then cooled at 200°C/min to 20°C above the upper limit of which isothermal crystallization was observed and held for 12 s. Samples were then cooled at 150°C/min to the isothermal crystallization temperature and held until crystallization was complete, as indicated by a flat baseline. The first half of the crystallization isotherm peak was integrated, and the data were treated by the standard Avrami analysis. Data from samples that crystallized too fast (causing

significant loss of the first part of the crystallization exotherm) were discarded.

RESULTS AND DISCUSSION

All the copolymers were prepared using the same conditions and catalysts, and all were processed to similar molecular weights. The molecular weights of the copolymers were high enough to prevent small differences in molecular weights from significantly affecting crystallization rates. The intrinsic viscosities and thermal characterization data of the copolymers used in this study are given in Table II. All the copolymers had similar glass transition temperatures but lower melting points than those of the PET homopolymer.

From the ΔT values of the dynamic DSC experiments, all the copolymers crystallize at a slower rate than that of the PET homopolymer (Table III). The order of crystallization rate is PET homopolymer > 2.5% 4,4'-BB \approx 5% 4,4'-BB > 2.5% THP \approx 5% THP > 2.5% 2,7-pyrene \approx 5% 2,7-pyrene. Only small differences are seen in the ΔT values of the 2.5% and 5% copolymers, but the

Table III ΔT Values for Copolymers

Copolymer	$\Delta T/^\circ\text{C}$
Control PET	58
2.5% BB	75
5% BB	73
2.5% THP	85
5% THP	84
2.5% 2,7-Pyrene	89
5% 2,7-Pyrene	90

5% copolymers crystallize to a lesser extent than do the 2.5% copolymers (Table II). Significant differences are seen in the ΔT values between copolymers containing different comonomer structures. The incorporation of comonomers also increases the width of the melting endotherms (Table IV): the samples with lower crystallinity give rise to broader melting transitions.

For a more quantitative study of crystallization kinetics, crystallization isotherms were constructed by plotting θ_a versus $\ln(t)$ according to the Avrami treatment [Fig. 2(A)]. In general, the isotherms are offset from one another along the temperature axis, indicating that crystallization takes place by a similar mechanism.¹⁵ Qualitative assessment of the curves indicates that, as expected, the fastest crystallization takes place at intermediate temperatures (i.e., the fastest crystallization takes place at 170°C for the 2.5 mol % 2,7-pyrene copolymer shown in Fig. 2).

By rearranging the Avrami expression (eq. 1) into eq. 2 and plotting $\ln[-\ln(\theta_a)]$ versus $\ln(t)$, the independent kinetic parameters n and k can be obtained:

$$\ln[-\ln(\theta_a)] = \ln(k) + n \ln(t) \quad (2)$$

The slope of the straight line obtained gives n , whereas the intercept gives $\ln(k)$. An example of an Avrami plot for the 2.5% 2,7-pyrene copolymer

Table IV ΔT Values for Copolymers Containing Equimolar Amounts of Perylene

Copolymer	$\Delta T/^\circ\text{C}$
PET + 2.5% perylene	72
2.5% 2,7-Pyrene + 2.5% perylene	79
5% 2,7-Pyrene + 5% perylene	92
5% THP + 5% perylene	91

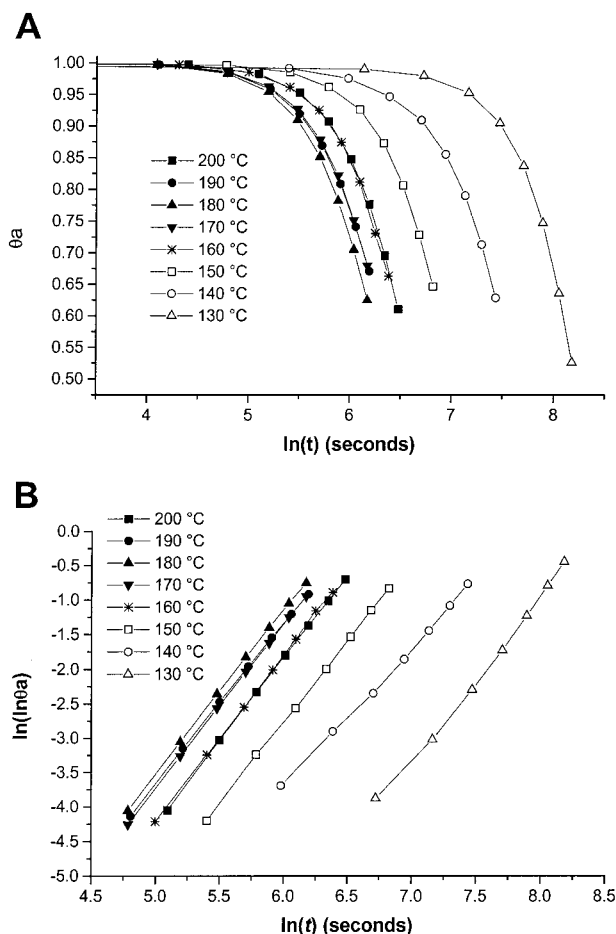


Figure 2 Avrami treatment of isothermal crystallization data for 2.5 mol % 2,7-pyrene copolymer. (A) Crystallization isotherms. (B) Avrami plot.

is shown in Figure 2(B). The linearity of the plots over the time and temperature ranges shown indicates a common mechanism for crystallization and the absence of secondary crystallization. Outside of this temperature range, and at lower values of θ_a (i.e., longer times), there is significant curvature to these isotherms. This is indicative of the presence of other crystallization pathways. It is particularly important to study the initial rates to compare data for processes that are not limited by slow diffusion. The values for the Avrami exponent n for all the polymers studied within the range of 220–120°C are 2.4 ± 0.3 . Deviations from this value were observed at the highest and lowest temperatures of crystallization. An n value of 2 indicates a crystallization mechanism of either one-dimensional (1D) growth (rodlike) from sporadic nuclei or two-dimensional (2D) growth (disklike) from instantaneous nuclei. An n value of 3 indicates a crystallization mechanism of ei-

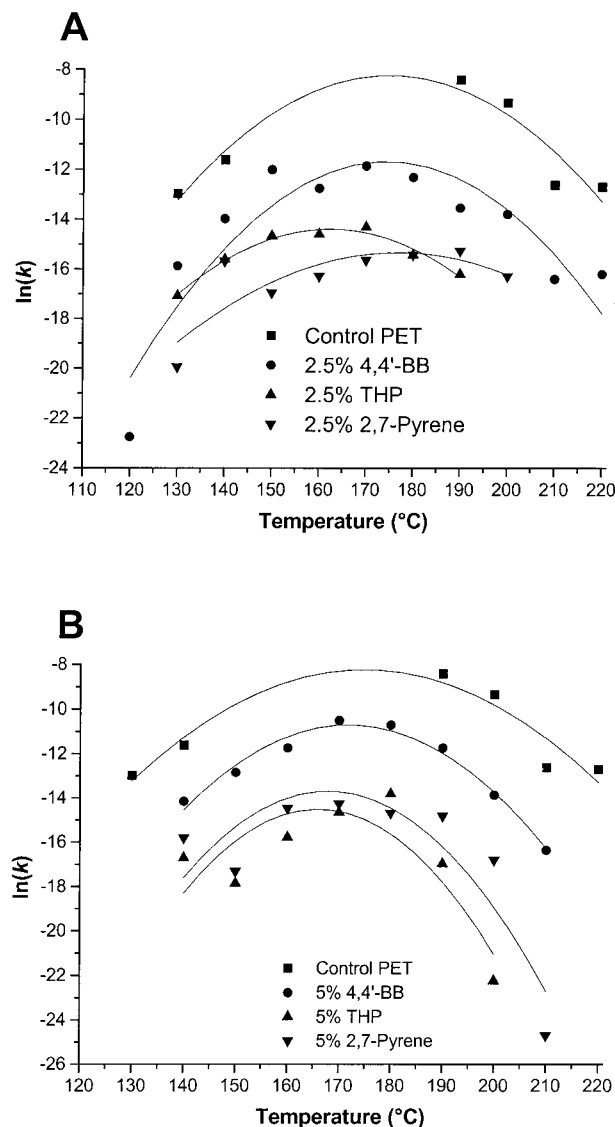


Figure 3 Crystallization rate versus temperature. (A) 2.5 mol % copolymers. (B) 5 mol % copolymers.

ther 2D growth from sporadic nuclei or 3-dimensional (3D) growth (spherulitic) from instantaneous nuclei.¹⁵ The fact that we find a n value of 2–3 indicates a combination of crystallization mechanisms. Noninteger n values are common for PET.³⁰

Because the polymers crystallize by the same mechanism, as indicated by the constant value of n , we can extrapolate the Avrami plots to obtain the isothermal crystallization rate constant, k . The intercept of the Avrami plots was obtained from a least-squares fit, and $\ln(k)$ was plotted as a function of temperature [Fig. 3(A,B)]. The curves were fit with a second-order polynomial.²⁰

Measurement of rate constants at temperatures below the temperature at which the rate of crystallization is maximum is prone to error. Because the melt viscosity of the polymer increases with decreasing temperature, the crystallization rate is diffusion controlled at lower temperatures and therefore is not described adequately by the Avrami equation. Given the errors inherent in this method, we make only qualitative arguments regarding the relative rates of crystallization in the classes of copolymers studied.

Figure 3(A,B) shows an optimal temperature for maximum crystallization rate that is different for each copolymer. All the copolymers crystallize slower at any given temperature than the PET homopolymer by a factor of 10^2 – 10^{10} . Among the 2.5 mol % copolymers, the 2.5% THP and 2,7-pyrene copolymers crystallize at approximately the same rate, although they have different temperatures of maximum crystallization rate [Fig. 3(A)]. The 2.5% 4,4'-BB copolymer crystallizes at a slower rate than does the PET homopolymer, but faster than the THP or 2,7-pyrene. This is qualitatively similar to the order of crystallization determined by dynamic DSC measurements. The crystallization rate decreases as the comonomer becomes more planar and conformationally restricted. Thus, copolymers containing the biphenyl unit, which is free to rotate around the aryl–aryl bond, have the fastest crystallization rate. Restricting this rotation with ethylene bridges (i.e., THP), or even to a greater extent by fusing the arenes (i.e., the 2,7-pyrene), decreases the crystallization rate further. The effect of comonomer rotational rigidity on crystallization rate could be due to an increase in the melt viscosity as the comonomers become more conformationally constrained. In addition, inclusion of comonomers also imparts an element that is incommensurate with the crystal structure of PET, thus further slowing crystallization. The same trends can be seen with the 5% copolymers.

In an effort to accelerate the crystallization of pyrene-containing copolyesters, we investigated the effect of adding small amounts of perylene to the polymer melts. If the pyrene units in the backbone complex the perylene, this association could provide a seed for crystal growth, and we reasoned that we should see an increase in the crystallization rate. The diester functionalized 2,7-pyrene comonomer is electron deficient due to the electron-withdrawing nature of the ester groups. Perylene is an excellent electron donor.

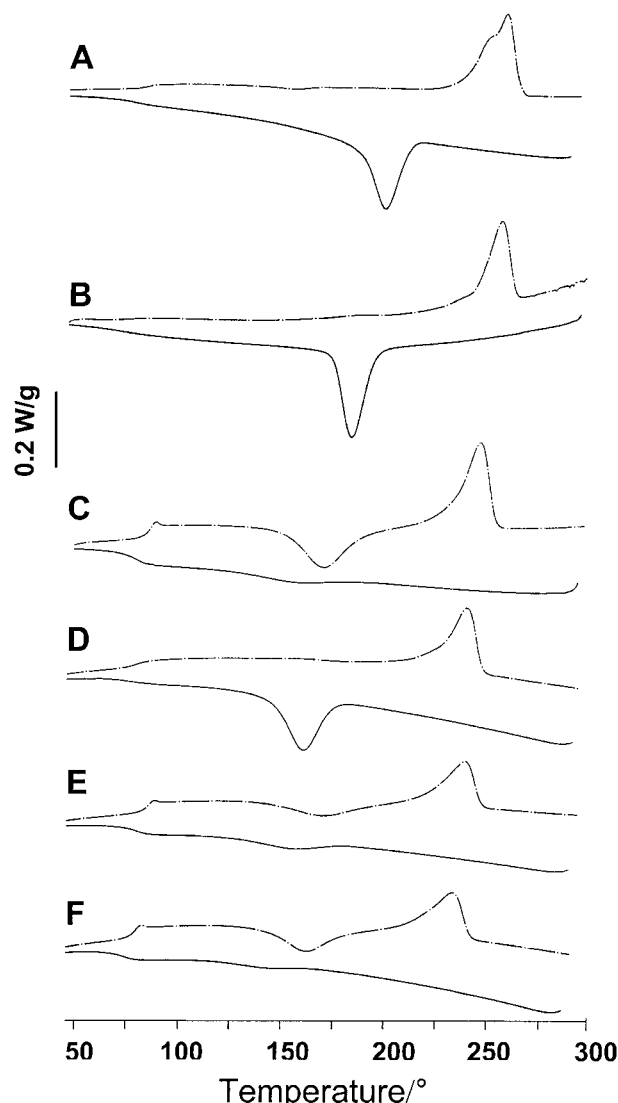


Figure 4 Effect of perylene on copolymer crystallization. Differential scanning calorimetry (DSC) thermograms showing first cooling and second heating. (A) Control PET. (B) PET + 2.5 mol % perylene. (C) 2.5 mol % 2,7-pyrene. (D) 2.5 mol % 2,7-pyrene + 2.5 mol % perylene. (E) 5 mol % THP. (F) 5 mol % THP + 5 mol % perylene.

Adding 2.5 mol % perylene to the PET homopolymer retards crystallization and shifts T_c to lower temperatures [Fig. 4(B)], consistent with a decrease in the rate of crystallization upon addition of a small impurity. Both the control PET [Fig. 4(A)] and the PET with 2.5 mol % perylene crystallize completely on cooling, as indicated by the absence of cold crystallization on heating. The DSC thermogram of the 2.5 mol % 2,7-pyrene copolymer shows very little crystallization on cooling at 10°C/min (5 J/g) [Fig. 4(C)]. On second

heating, the sample crystallizes (27 J/g) and then melts (36 J/g). However, adding 2.5 mol % perylene to this copolymer induces significant crystallization (25 J/g) on cooling [Fig. 4(D)]. Since the sample crystallizes completely on cooling, no crystallization peak is seen on second heating, unlike the 2,7-pyrene copolymer without perylene. A similar trend is observed upon the addition of 5 mol % perylene to the 5 mol % 2,7-pyrene copolymer. To assess whether the induction of crystallization, upon addition of perylene, occurs only because the 2,7-pyrene-containing copolymers crystallize at such a slow rate compared with the PET homopolymer, 5 mol % perylene was added to the copolymer containing 5 mol % THP copolymer, which also crystallizes slowly. Tetrahydropyrene does not form strong π -complexes and has less propensity to stack with perylene than do the fully aromatic pyrene units.

The 5 mol % THP copolymer itself shows a small crystallization exotherm on cooling (5 J/g) [Fig. 4(E)]. Upon second heating, the sample crystallizes further (12 J/g), followed by melting (21 J/g). Adding 5 mol % perylene simply further inhibits the crystallization on cooling (1 J/g) [Fig. 4(F)]. The smaller amount of crystallization on cooling is further demonstrated by the larger cold crystallization peak (16 J/g) on second heating compared with the sample without perylene.

The acceleration of the crystallization of 2,7-pyrene-containing copolyesters by the addition of perylene clearly relies on the presence of the pyrene structural units. The addition of perylene to the PET homopolymer or THP-containing copolymers retards crystallization. This acceleration is consistent with the formation of π -stacked assemblies of perylene with the pyrene structural units and the formation of aggregates that serve as seeds for crystallization. This hypothesis is consistent with earlier work that found that some derivatives of perylene and pyrene associate in solid polymers.^{12,13} The possibility of associations of perylene and pyrene in polyester copolymers is further supported by the finding that naphthalene units (which have a weaker attraction for each other than perylene and pyrene⁹) form assemblies in PET/PEN copolymers at low concentrations of naphthalene units.⁸

Another possible explanation for the enhancement of the crystallization rate by the addition of perylene could be that the perylene is acting as a phase-separated nucleating agent. Perylene melts at 277°C and thus could crystallize on cooling and provide very small and effective nucle-

ation sites. However, if this were the mechanism, the effect would be expected in the PET homopolymer and in the THP-containing copolymer, which crystallize more slowly in the presence of added perylene. The inhibitory effect of perylene with these two control samples constitutes evidence against heterogeneous nucleation for the pyrene-containing copolymer.

The PET homopolymer and the 5% THP copolymer display a greater degree of supercooling upon the addition of perylene (Table IV). However, adding perylene to the polymer containing 2.5% 2,7-pyrene reduces the ΔT by 10°C indicating significantly faster crystallization. Thus, the crystallization enhancement of adding perylene to 2,7-pyrene-containing copolymers can be observed from the ΔT data as well.

CONCLUSIONS

Incorporation of low levels of dimethyl-2,7-pyrenedicarboxylate, 2,7-dimethyl-4,5,9,10-tetrahydropyrenedicarboxylate, and dimethyl-4,4'-biphenyldicarboxylate units into PET slows the crystallization rate relative to that of the homopolymer. The smaller, more rotationally mobile, 4,4'-BB monomer inhibits crystallization to a lesser degree than the larger fused aromatic comonomers. These trends are observed in both the isothermal calorimetric data and the effect of comonomers on the extent of supercooling (ΔT). Addition of equimolar amounts of perylene into the copolymers containing the 2,7-pyrene copolymer enhances the crystallization rate. The specificity of this enhancement to the pyrene-containing copolymers suggests the possibility that complexation and aggregates of polymer chains are seeding crystallization. Preliminary spectroscopic analysis has not yielded further information on such aggregates and is the subject of further studies.

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REFERENCES

1. Sperling, L. H.; Barrett, L. W. US Pat 5,356,972 (Oct. 18, 1994).
2. Dege, G. J.; Akkapeddi, M. K.; Tuller, H. W.; Vanderkooi, N. US Pat 5389710 (Feb. 14, 1995).
3. Groeninckx, G.; Berghmans, H.; Overbergh, N.; Smets, G. *J Polym Sci Part B: Polym Phys* 1974, 12, 303.
4. Legras, R.; Mercier, J. P.; Nield, E. *Nature (London)* 1983, 304, 432.
5. Vanderkooi, N.; Haylock, J. C.; Schulze, S. R.; Tuller, H. W. US Pat 4357268 (Nov. 2, 1982).
6. Jones, J. R.; Liotta, C. L.; Collard, D. M.; Schiraldi, D. A. *Macromolecules* 2000, 33, 1640. Connor, D. M.; Krieger, R. M.; Collard, D. M.; Liotta, C. L.; Schiraldi, D. A. *J Polym Sci A: Polym Chem* 2000, 38, 1291. Jones, J. R.; Liotta, C. L.; Collard, D. M.; Schiraldi, D. A. *Macromolecules* 1999, 32, 5786.
7. Bu, H.; Pang, Y.; Hu, W. *Fudan Xuebao Ziran Kexueban* 1991, 30, 1. *Chem Abstr* 1992, 116, 215217.
8. Allan, J. S.; Dickson, T. J.; Wilson, B. E.; Duhamel, J. *Macromolecules* 1999, 32, 2956.
9. (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970. (b) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic Press: New York, 1971. (c) Kaziska, A. J.; Wittmeyer, S. A.; Topp, M. R. *J Phys Chem* 1991, 95, 3663. (d) Stratton, J. R.; Troxler, T.; Pryor, B. A.; Smith, P. G.; Topp, M. R. *J Phys Chem* 1995, 99, 1424. (e) Price, S. L.; Stone, A. J. *J Chem Phys* 1987, 86, 2859. (f) Sadvovskii, N.; Shirov, P.; Kuzmin, M. *Thin Solid Films* 1991, 204, 441. (g) Motyka, A. L.; Wittmeyer, S. A.; Babbit, R. J.; Topp, M. R. *J Chem Phys* 1988, 89, 4586.
10. Doxtader, M. M.; Mangle, E. A.; Bhattacharya, A. K.; Cohen, S. M.; Topp, M. R. *Chem Phys* 1986, 101, 413.
11. (a) Doxtader, M. M.; Topp, M. R. *Chem Phys Lett* 1986, 124, 39. (b) Joireman, P. W.; Connell, L. L.; Ohline, S. M.; Felker, P. M. *Chem Phys Lett* 1991, 182, 385.
12. Rohr, U.; Schlichting, P.; Böhm, A.; Gross, M.; Meerholz, K.; Bräuchle, C.; Müllen, K. *Angew Chem Int Ed Engl* 1998, 37, 1434.
13. Jao, T. C.; Mishra, M. K.; Rubin, I. D.; Duhamel, J.; Winnik, M. A. *J Polym Sci Part B: Polym Phys* 1995, 33, 1173.
14. Carr, P. L.; Nicholson, T. M.; Ward, I. M. *Polym Adv Technol* 1997, 8, 592.
15. Jabarin, S. A. *J Appl Polym Sci* 1987, 34, 86.
16. Gümther, B.; Zachmann, H. G. *Polymer* 1983, 24, 1008.
17. Jabarin, S. A. *Polym Eng Sci* 1992, 32, 1341.
18. Patkar, M.; Jabarin, S. A. *J Appl Polym Sci* 1993, 47, 1749.
19. Bianchi, R.; Chiavacci, P.; Vosa, R.; Guerra, G. *J Appl Polym Sci* 1991, 43, 1087.

20. Jackson, J. B.; Longman, G. W. *Polymer* 1969, 10, 873.
21. Ozawa, T. *Polymer* 1971, 12, 150.
22. Jabarin, S. A. *J Appl Polym Sci* 1987, 34, 97.
23. Cobbs, W. H.; Burton, R. L. *J Polym Sci* 1953, 12, 275.
24. Keller, A.; Lester, G. R.; Morgan, C. B. *Philos Trans R Soc London* 1954, A247, 1.
25. Varma, P.; Logfren, E. A.; Jabarin, S. A. *Polym Eng Sci* 1998, 38, 237.
26. Martins, J. C. A.; Novack, K. M.; Gommès, A. S. *Polymer* 1998, 39, 6941.
27. *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons: New York, 1968; Vol 8, p 63.
28. *Encyclopedia of Polymer Science and Engineering*; John Wiley & Sons: New York, 1989; 231.
29. Connor, D. M.; Allen, S. D.; Collard, D. M.; Liotta, C. L.; Schiralid, D. A. *J Org Chem* 1999, 64, 6888.
30. Mandelkern, L. *Crystallization of Polymers*; McGraw-Hill: New York, 1964.