Effect of Comonomers on the Rate of Crystallization of PET: U-Turn Comonomers

DANIEL M. CONNOR,[1] SCOTT D. ALLEN,[1] DAVID M. COLLARD,[1] CHARLES L. LIOTTA,[1] DAVID A. SCHIRALDI[2]

[1] School of Chemistry and Biochemistry, Molecular Design Institute and Polymer Education and Research Center, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

[2] KoSa, P.O. Box 5750, Spartanburg, South Carolina 29304-5750

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ABSTRACT: The effect of incorporating phthalate, 1,8-naphthalenedicarboxylate, and 1,8-anthracenedicarboxylate structural units on the crystallization rate of PET are evaluated by isothermal and dynamic calorimetry. Although all of the comonomers retard crystallization, the 1,8-naphthalene unit shows no concentration dependence between 2.5 and 10% incorporation, in contrast to the smaller phthalate and larger anthracene units. The greater rate at which the 1,8-naphthalene copolymer crystallizes, relative to that of the other copolymers, is consistent with the notion that the U-turn geometry induces chain folding and nucleates crystallization. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1675–1682, 2001

INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the dominant materials in the thermoplastics market because of its relatively low cost and its balance of mechanical, thermal, and chemical properties. However, PET is limited in some applications such as injection molding because of its relatively low crystallization rate compared to that of other polyesters.[1] Because of its higher rate of crystallization, poly(butylene terephthalate) (PBT) is often used in injection-molded applications, despite its higher cost.

Many attempts have been made to enhance the rate of crystallization of PET. Strategies such as orientation, heterogeneous platelike nucleating agents, plasticizers, chain-end modifiers, and chain-slip agents have all been used to modify the crystallization rate with some success.[2–4] Most of these approaches reach maximum utility with between 0.2 and 0.4 wt % incorporation of the modifier.

We set out to investigate a new approach to enhance the crystallization rate of PET. Instead of using heterogeneous nucleating agents such as talc, we incorporated comonomer units into PET that might act as molecular seeds for crystallization.

Dimethyl 1,8-anthracenedicarboxylate (1,8-anthracene), dimethyl 1,8-naphthalenedicarboxylate (1,8-naphthalene), and phthalic anhydride (phthalate) were chosen as comonomers for this study (Fig. 1). These comonomers were selected for copolymerization with PET for their rigid planar structure, thermal stability, and the U-turn geometry that they enforce on the polymer chain (Fig. 2). The 1,8-anthracene and the 1,8-naphthalene units fold the polymer chains parallel to each other, whereas the phthalate unit imparts a wider angle. These folds could serve as a template to induce the parallel alignment of polymer chains for some distance from the comonomer unit in the same fashion as they would align in the crystal lattice. This association of chains

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Correspondence to: D. Collard.

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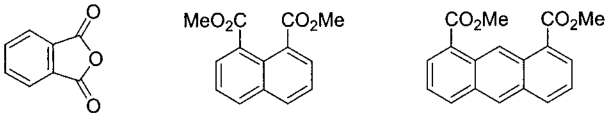


Figure 1 Structures of comonomers.

could form a seed for crystallization and thus enhance the crystallization rate. The distance between parallel chains can be controlled by the size of the comonomer unit. The 1,8-anthracene, 1,8-naphthalene, and phthalate units differ in the spacing, and allow the evaluation of the effect of spacing on crystallization rate.

Precedence for the concept of template-based chain folding is found in biological systems. For example, folding of peptides into β sheets has been nucleated by the incorporation of 4,6-dibenzofuran units.[5] This U-turn unit has a similar size and shape to that of the 1,8-anthracene and 1,8-naphthalene comonomers used in this study. It was previously shown that this template reverses the polypeptide chain direction, facilitates strand–strand interactions, and nucleates folding of attached chains into β sheets in aqueous media.

In general, incorporation of low levels of comonomers into PET significantly retards the rate and extent of crystallization from the melt.[6] The comonomers retard crystallization by acting as impurities in the crystal lattice. In addition, large rigid structural units might increase melt viscosity and thereby slow crystallization.

The measurement of crystallization rate in PET and its copolymers is complicated by many issues, including molecular weight,[7,8] orientation,[9] presence of by-products (e.g., diethylene glycol),[10] catalysts,[8] nucleating agents,[1] water content,[11] and comonomers.[12] By preparing samples under identical conditions, we sought to separate the effect of comonomers on the crystallization rate of PET.

Kinetics of crystallization can be evaluated both isothermally and nonisothermally using a number of techniques.[13] Most studies of polymer crystallization rely on the Avrami expression for treatment of data.[14]

$$\theta a = e^{-kt^n} \tag{1}$$

In the Avrami expression, θa 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.[14]

A qualitative evaluation of crystallization rates can be made by measuring the difference in temperature (ΔT) between the melting peak on heating and the crystallization peak on cooling in a dynamic differential scanning calorimetry (DSC) experiment. Although this is in essence only measuring the degree of supercooling and prone to many biases including variation in the melt viscosity, it is a qualitative assessment of the crystallization rate and should correlate with processes occurring 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 U-turn comonomers on the crystallization rate of PET.

EXPERIMENTAL

Materials

Dimethyl formamide and methyl iodide were obtained from Fisher Scientific (Springfield, NJ). Dimethyl terephthalate and ethylene glycol were obtained from KoSa (Spartanburg, SC). All other materials were obtained from Aldrich Chemical (Milwaukee, WI). All materials were used without further purification.

Characterization

Nuclear magnetic resonance (NMR) spectra were obtained on either a 500-MHz Bruker DRX spectrometer (Bruker Instruments, Billerica, MA) or a 300-MHz Varian Gemini 2000 instrument (Varian Associates, Palo Alto, CA). Samples were dissolved in $CDCl_3$ or DMSO-d_6. Infrared spectra were obtained on a Nicolet 520 FTIR spectrophotometer (Nicolet Instruments, Madison, WI). Melting points were collected using a Thomas–

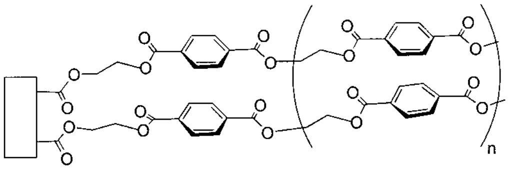


Figure 2 Proposed U-turn in PET.

Hoover melting point apparatus and are uncorrected.

DSC was performed using a Perkin–Elmer Series 7 differential scanning calorimeter (Perkin–Elmer Cetus Instruments, Norwalk, CT) operating under N_2 and equipped with an Intracooler 2. All samples were dried under vacuum overnight at 80°C.

Dilute solution viscometry was performed at 25°C using a 4% (w/w) polymer solution in *o*-chlorophenol. Run times were measured for five trials and averaged. Intrinsic viscosities were extrapolated from the infinite dilution curves for PET homopolymer.

Dimethyl 1,8-Naphthalenedicarboxylate

A mixture of naphthalic anhydride (150 g, 0.757 mol), PCl_5 (225 g, 1.08 mol), and $POCl_3$ (300 mL) was heated to reflux for 48 h. The $POCl_3$ was removed under reduced pressure and the resulting liquid was carefully added to dry MeOH (750 mL) at 0°C. The volume of methanol was reduced to about 400 mL under reduced pressure, and the white precipitate was collected by vacuum filtration and washed with cold MeOH (100 mL). The solid was recrystallized from MeOH (~ 400 mL) to give dimethyl 1,8-naphthalenedicarboxylate (130.0 g, 70%). mp = 100–103°C (Carpino[15]: 99–101°C).

^{1}H–NMR (500 MHz, $CDCl_3$): δ 8.00 (d, J = 7.0 Hz, 2H, Ar–$H_{2,7}$); 7.99 (d, J = 8.2 Hz, 2H, Ar–$H_{4,5}$); 7.53 (dd, J = 7.0, 8.2 Hz, 2H, Ar–$H_{3,6}$). IR (neat): 2954, 1723, 1289, 1196, 1144, 752 cm^{-1}.

1,8-Dicyanoanthraquinone

A slurry of copper(I) cyanide (97.0 g, 1.08 mol), 1,8-dichloroanthraquinone (100 g, 361 mmol), and dimethylacetamide (600 mL) was heated at reflux under N_2 for 3 h. The resulting hot brown solution was poured onto ice and the brown/green precipitate was collected by vacuum filtration and washed with H_2O (100 mL). The filtrate was added to 3 L of 4*N* HNO_3 and the mixture was stirred at 60°C for 4 h. After cooling, the solid was collected by vacuum filtration, washed with H_2O (100 mL), and dried overnight under reduced pressure at 80°C to yield crude 1,8-dicyanoanthraquinone (~ 90 g) as a crude yellow/brown solid, which was used without further purification.

^{1}H–NMR (300 MHz, DMSO-d_6): δ 8.49 (dd, J = 1.2, 7.8 Hz, 2H, Ar–$H_{2,7}$); 8.41 (dd, J = 1.2, 7.8 Hz, 2H, Ar–$H_{4,5}$); 8.09 (t, J = 7.8 Hz, 2H, Ar–$H_{3,6}$).

Anthraquinone-1,8-dicarboxylic Acid

A mixture of the crude 1,8-dicyanoanthraquinone (50 g, 0.19 mol) and 70% H_2SO_4 (3 L) was heated to reflux for 3 h. After cooling to 100°C, the mixture was poured onto ice (600 g). The precipitate was filtered and dissolved in 5% NaOH (aq) (1 L). Insoluble material was removed by filtration and the filtrate was acidified with conc. HCl. The precipitate was collected by filtration and dried to give anthraquinone-1,8-dicarboxylic acid (~ 40 g), which was used without further purification.

^{1}H–NMR (300 MHz, DMSO-d_6): δ 8.27 (dd, 2H, J = 1.0, 7.8 Hz, Ar–$H_{2,7}$); 7.96 (dd, 2H, J = 7.5, 7.8 Hz, 2H, Ar–$H_{3,6}$); 7.84 (dd, 2H, J = 1.0, 7.5 Hz, 2H, Ar–$H_{4,5}$). IR (KBr): 3467, 1697, 1282 cm^{-1}.

1,8-Anthracenedicarboxylic Acid

A mixture of crude anthraquinone-1,8-dicarboxylic acid (30.0 g, 0.101 mol) and Zn dust (113 g, 1.72 mol) in 20% NH_4OH (1.3 L) was heated at reflux for 4.5 h. The color of the mixture changed from deep red to yellow. The mixture was cooled to room temperature and filtered. H_2O (1 L) was added to the filtrate, the mixture was cooled to 0°C, and the solution was acidified with conc. HCl. The yellow precipitate was collected by vacuum filtration and dried in a vacuum oven overnight to afford crude 1,8-anthracenedicarboxylic acid (25 g), which was used without further purification.

^{1}H–NMR (500 MHz DMSO-d_6): δ 10.45 (s, 1H, Ar–H_9); 8.77 (s, 1H, Ar–H_{10}); 8.33 (d, J = 8.5 Hz, 2H, Ar–$H_{2,7}$); 8.18 (d, J = 6.8 Hz, 2H, Ar–$H_{4,5}$); 8.18 (d, J = 6.8 Hz, 2H, Ar–$H_{4,5}$); 7.60 (dd, J = 6.8, 8.5 Hz, 2H, Ar–$H_{3,6}$).

Dimethyl 1,8-Anthracenedicarboxylate

A solution of crude anthracene-1,8-dicarboxylic acid (74.25 g, 0.279 mol), lithium carbonate (165 g, 2.23 mol), and methyl iodide (150 mL, 2.41 mol) in *N*,*N*-dimethylformamide (1.5 L) was stirred under N_2 for 24 h. The mixture was acidified with 2*M* HCl (1.5 L) and the precipitate was collected by vacuum filtration. The solid was dissolved in CH_2Cl_2 (1 L) and filtered. The filtrate was washed with 5% $NaHCO_3$ (500 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure. Recrystallization from 1 : 1 dioxane : ethanol (~ 1 L) gave dimethyl 1,8-anthracenedicarboxylate (39.9 g, 30% from 1,8-dichloroanthraquinone). mp = 102–104°C (Rogers and Averill[16]: 101–103°C).

Table I Synthesis of Copolymers

Sample (mol % Comonomer)	Mass of Monomer/g (mol)			Mass of Catalyst/g		
	DMT	EG	Comonomer	$Mn(OAC)_2$	Sb_2O_3	PPA
Control PET	242.8	174.7	—	0.089	0.091	0.0539
Phthalate						
2.5%	757.4	558.0	19.4	0.282	0.289	1.72
5%	738.0	558.0	38.8	0.282	0.289	1.72
10%	699.1	558.0	77.7	0.282	0.289	1.72
1,8-Naphthalene						
2.5%[a]	757.4	558.0	19.8	0.282	0.289	1.72
5%	230.6	174.7	15.28	0.089	0.091	0.0539
10%	218.5	174.7	34.04	0.089	0.091	0.0539
1,8-Anthracene						
2.5%	236.8	174.7	9.19	0.089	0.091	0.0539
5%	230.6	174.7	18.40	0.089	0.091	0.0539

[a] Made from 1,8-naphthalic anhydride instead of dimethyl 1,8-naphthalenedicarboxylate.

^{1}H–NMR (500 MHz $CDCl_3$): δ 10.68 (s, 1H, Ar–H_9); 8.49 (s, 1H, Ar–H_{10}); 8.26 (d, J = 6.8 Hz, 2H, Ar–$H_{2,7}$); 8.17 (d, J = 8.4 Hz, 2H, Ar–$H_{4,5}$); 7.50 (dd, J = 6.8, 8.4 Hz, 2H, Ar–$H_{3,6}$); 3.96 (s, 6H, OCH_3). IR (KBr): 2960, 2848, 1721, 1269, 1032, 894, 749 cm^{-1}.

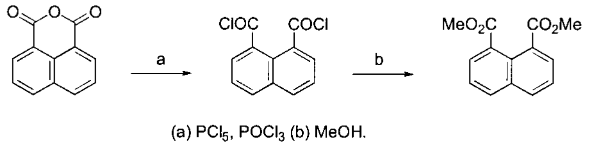
Synthesis of PET Copolymers

A standard melt polymerization method was used. Dimethyl terephthalate, ethylene glycol, $Mn(OAc)_2$, and Sb_2O_3 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 or the ethylene glycol were replaced with comonomers (see Table I). The reaction mixtures were heated for 2 h at 180–210°C, during which time 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 $\leq$133.3 Pa. The reaction mixtures were heated to 285–290°C, during which time ethylene glycol was removed by distillation. The progress of the reaction was monitored by the current draw required to maintain the mechanical stirrer at a rate of 10 rpm. The polymer was extruded from the vessel under a positive pressure of N_2.

RESULTS AND DISCUSSION

The dimethyl 1,8-naphthalenedicarboxyate was prepared in high yield from naphthalic anhydride by converting the anhydride to the acid chloride and quenching with anhydrous methanol (Fig. 3).[15] Attempts to convert the anhydride directly to the dimethyl ester with H_2SO_4 and MeOH were unsuccessful. The dimethyl 1,8-anthracenedicarboxylate was prepared from the commercially available 1,8-dichloroanthraquinone (Fig. 4).[16] The dichloro compound was treated with CuCN to make the dicyanoanthraquinone. After decomposition of the copper complex with HNO_3, the dicyanoanthraquinone was converted to anthraquinone-1,8-dicarboxylic acid in aqueous H_2SO_4. Hydrolysis under basic conditions was also successful, although yields were lower. Reduction of the anthraquinone with zinc in NH_4OH gave 1,8-anthracenedicarboxylic acid. Conversion to the dimethyl ester was carried out by treating the diacid with Li_2CO_3 and methyl iodide in DMF. This procedure is particularly useful because it is amendable for the preparation of 100-g quantities of material and purification is often not needed until the final step.

All the copolymers were polymerized to the same molecular weight using the same conditions and catalysts. The molecular weights of the copol-



(a) PCl_5, $POCl_3$ (b) MeOH.

Figure 3 Synthesis of dimethyl 1,8-naphthalenedicarboxylate.

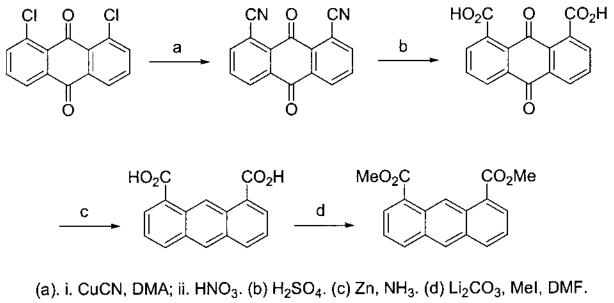


Figure 4 Synthesis of dimethyl 1,8-anthracenedicarboxylate.

ymers were high enough so that small differences did not significantly affect crystallization properties.[8] The intrinsic viscosity and thermal characterization data of the copolymers used in this study are given in Table II. All of the copolymers had similar values of T_g but lower melting points than that of PET homopolymer. The most significant difference between the copolymers is found in the temperature and enthalpy of crystallization on cooling from the isotropic melt (T_c and ΔH_c, respectively). All of the copolymers exhibit a greater degree of supercooling than that of PET homopolymer, as indicated by the lower temperature of the crystallization exotherm on cooling. Most of the copolymers crystallize completely on cooling at 10°C/min, with the exception of the 5% 1,8-anthracene, which crystallizes only slightly.

From the ΔT values of the dynamic DSC experiments, all the copolymers crystallize at a rate slower than that of PET homopolymer (Table III). The order of crystallization rate is PET homopolymer > 5% 1,8-naphthalene ≈ 2.5% phthalate > 10% 1,8-naphthalene ≈ 2.5% 1,8-anthracene > 2.5% 1,8-naphthalene ≈ 5% phthalate ≈ 10% phthalate > 5% 1,8-anthracene. The most interesting result from the supercooling data is that, unlike most comonomers, incorporating higher concentrations (5 or 10%) of the 1,8-naphthalene monomer does not inhibit crystallization any more than does the 2.5% copolymer. The incorporation of the large 1,8-anthracene unit into the polymer backbone significantly retards crystallization. This might be the result of the increase in melt viscosity brought about by the incorporation of such a large rigid unit into the polymer backbone.

For a more quantitative study of crystallization kinetics, crystallization isotherms were constructed by plotting θa versus $\ln(t)$ according to the Avrami treatment [e.g., Fig. 5(A)]. In general, the isotherms are offset from one another along the temperature axis, indicating that crystallization takes place by a similar mechanism.[7] 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 5 mol % 1,8-naphthalene copolymer shown in Fig. 5(A)].

Table II Characterization of Copolymers

Copolymer	IV[a]	M_v[b] (1000 g/mol)	T_g[c] (°C)	T_{cc}[d] (°C) [ΔH_c[e] (J/g)]	T_m[f] (°C) [ΔH_m[g] (J/g)]	T_c[h] (°C) [ΔH_c[i] (J/g)]
Control PET	0.608	19.1	83	155 (−1)	258 (37)	200 (−34)
Phthalate						
2.5%	0.583	18.2	81	—	251 (38)	182 (−40)
5%	0.571	17.7	77	—	247 (33)	171 (−36)
10%	0.588	18.4	79	—	240 (31)	163 (−30)
1,8-Naphthalene						
2.5%	0.555	17.1	82	158 (−3)	254 (36)	177 (−32)
5%	0.594	18.6	79	—	254 (37)	186 (−38)
10%	0.647	20.6	80	—	253 (33)	180 (−37)
1,8-Anthracene						
2.5%	0.637	20.2	83	150 (−1)	249 (34)	176 (−32)
5%	0.534	16.4	81	168 (−27)	241 (31)	157 (−2)

[a] Intrinsic viscosity.
[b] Viscosity average molecular weight.
[c] Glass-transition temperature.
[d] Temperature of cold crystallization.
[e] Enthalpy of cold crystallization.
[f] Melting point.
[g] Enthalpy of melting.
[h] Temperature of crystallization on cooling.
[i] Enthalpy of crystallization on cooling.

Table III **ΔT Values for Copolymers**

Copolymer	ΔT (°C)
Control PET	58
Phthalate	
2.5%	69
5%	76
10%	77
1,8-Naphthalate	
2.5%	77
5%	68
10%	73
1,8-Anthracenate	
2.5%	73
5%	84

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

$$\ln[-\ln(\theta a)] = \ln(k) + n \ln(t) \tag{2}$$

The slope of the straight line obtained gives n and the intercept gives $\ln(k)$. An example of an Avrami plot for the 5% 1,8-naphthalene copolymer is shown in Figure 5(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 θa (i.e., longer times), there is significant curvature to these isotherms, which is indicative of the presence of other crystallization pathways under these conditions. It is particularly important to study the initial rates so that we are comparing data for processes that are not limited by slow diffusion. The values for the Avrami exponent n for all of the polymers studied in 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 growth (rodlike) from sporadic nuclei or two-dimensional growth (disklike) from instantaneous nuclei. An n value of 3 indicates a crystallization mechanism of either two-dimensional growth from sporadic nuclei or three-dimensional growth (spherulitic) from instantaneous nuclei.[7] The fact that we find an n value between 2 and 3 indicates a combination of crystallization mechanisms. Noninteger n values are common for PET.[17]

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 constants 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. 6(A), (B)]. The curves were fitted with a second-order polynomial.[12] 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 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.

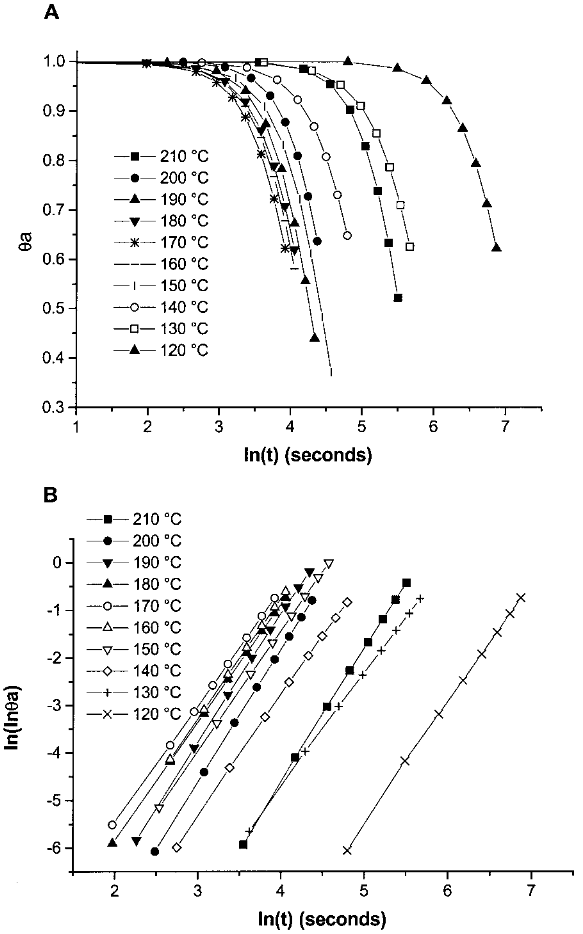


Figure 5 Example of Avrami treatment of isothermal crystallization data for the 5 mol % 1,8-naphthalene copolymer: (A) Crystallization isotherms; (B) Avrami plot.

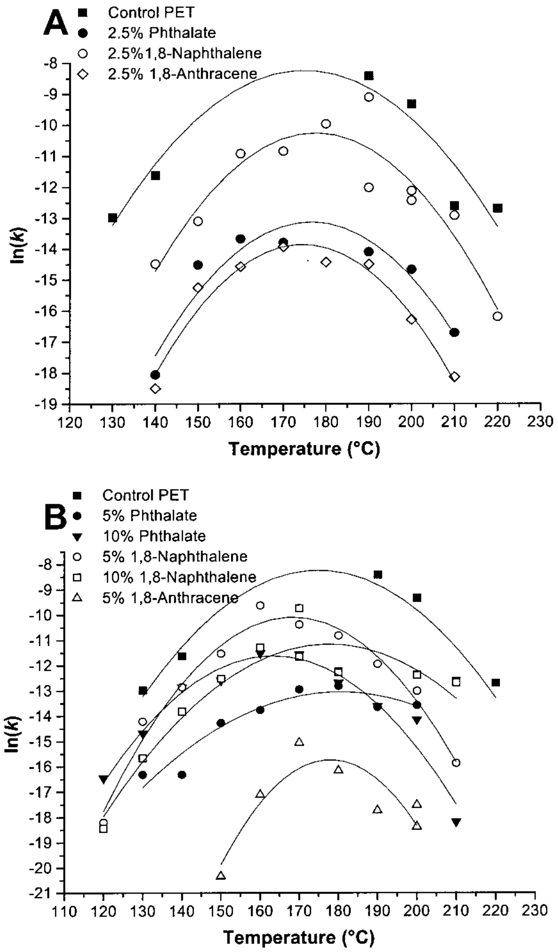


Figure 6 Crystallization rate versus temperature: (A) 2.5 mol % copolymers; (B) 5 and 10 mol % copolymers.

Figure 6(A), (B) shows that the optimal temperature for maximum crystallization rate is different for each copolymer. All of the copolymers crystallize at a slower rate, at a given temperature, than that of the PET homopolymer by a factor of 10^2–10^{10}. Among the 2.5 mol % copolymers, the 2.5% 1,8-naphthalene copolymer crystallizes at a faster rate than that of the other copolymers by a factor of 10^2 [Fig. 6(A)]. The 2.5% phthalate and 1,8-anthracene copolymers crystallize at essentially the same rate. If the comonomers are simply acting as impurities, they should inhibit crystallization to a greater extent as the size of the comonomer increases and becomes incommensurate with the crystal lattice. The fact that the 1,8-naphthalene copolymer crystallizes at a significantly faster rate than that of either phthalate or anthracene copolymers, at the same level of incorporation, is consistent with an additional nucleating effect with the naphthalene unit.

Among the 5 and 10% copolymers [Fig. 6(B)], the 5 and 10% 1,8-naphthalene copolymers crystallize the fastest, although still at a slower rate than that of the PET control. The 5% 1,8-anthracene crystallizes at a significantly slower rate than that of all the other copolymers, which is consistent for the incorporation of a large rigid unit into the polymer backbone. The copolymers containing 1,8-naphthalene crystallize at essentially the same rate with 2.5, 5, and 10% incorporation. This is surprising. The crystallization rate is usually slowed further by increasing the concentration of comonomer, as we have seen previously with linear comonomers.[6] The fact that the rate is unaffected at up to 10% incorporation is consistent with the nucleating effect brought about by the U-turn 1,8-naphthalene units.

In our effort to increase the crystallization rate by incorporating comonomers with specific geometries, any benefit to the crystallization rate brought about by nucleation is likely being counteracted by the inhibitory effects of putting impurities in the crystal structure plus the effect of increasing the melt viscosity by the incorporation of large rigid units. It is possible that the anthracene units place the polymer chains too far apart to bring them together for crystallization. Moreover, the size of the anthracene units could exert significant deleterious effects on the melt viscosity and also disrupt the crystal structure. Thus, we suggest that the 1,8-naphthalene units space the polymer chains at an optimum distance, while not incorporating too large a unit into the polymer backbone. Further studies are needed to fully explain why the 1,8-naphthalene does not inhibit crystallization more at 10% than at 2.5%. The 1,8-naphthalene copolymers crystallize faster than any of the other copolymers studied. A comparison of the crystallization rates of six other 2.5 mol % copolymers we have studied is shown in Figure 7.[6]

CONCLUSIONS

In general, incorporation of low levels of phthalic anhydride, dimethyl 1,8-naphthalenedicarboxylate, and 1,8-anthracenedicarboxylate units into PET slows the crystallization rate relative to that of the homopolymer. The copolymers containing the 1,8-naphthalene unit crystallize the fastest at all concentrations. Little concentration depen-

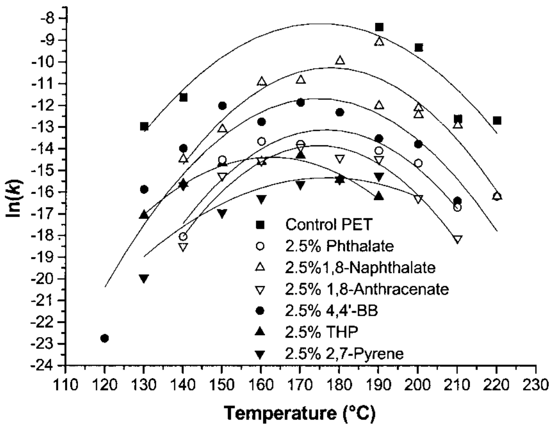


Figure 7 Crystallization rate versus temperature for 2.5 mol % copolymers. Comparison of linear and U-turn copolymers.

dence on crystallization rate is seen for the 1,8-naphthalene copolymers. These trends are seen in both the isothermal calorimetric and supercooling (Δ*T*) data. The greater rate at which the 1,8-naphthalene copolymer crystallizes, relative to that of the other copolymers, is consistent with the notion that the U-turn geometry induces chain folding and nucleates crystallization.

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