Crystalline Homopolyimides and Copolyimides Derived from 3,3′,4,4′-Biphenyltetracarboxylic Dianhydride/ 1,3-Bis(4-aminophenoxy)benzene/1,12-Dodecanediamine. 1. Materials, Preparation, and Characterization

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ABSTRACT: Crystalline homopolyimides are shown to occur by DSC from 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) and either 1,3-bis(4-aminophenoxy)benzene (134APB) or 1,12-dodecanediamine (C12). Additionally, copolyimides synthesized from these monomers are crystalline in all compositions studied. Each composition was found to have a singular glass transition temperature, which is rectilinearly dependent on the percent of 134APB/C12. A similar relationship is found for the crystallization temperature but not for the apparent melting temperature. Upon heating, a triple-melting behavior was observed when materials were crystallized at large degrees of supercooling. Otherwise, a conventional double-melting behavior was seen. The equilibrium melting temperature ($T_m°$) was estimated using the Hoffman–Weeks method. Results indicate that compositions with 134APB composition ≥40% are dominated by the 134APB/BPDA polyimide phase, and below it by the C12/BPDA polyimide phase. The value of $T_m°$ for the 134APB/BPDA polyimide is about 410 °C and for the C12/BPDA polyimide is about 243 °C.

Introduction

The electrical insulating and mechanical properties of aromatic polyimides for long duration at high temperatures are well documented.[1–3] Coincident with this performance is the fact that most polyimides are only amenable to fabrication by solution casting into the shaped article (e.g. a film or a fiber), followed by drying and heating to convert to the intractable polyimide.

A less expensive and more environmentally compatible process is perceived to be melt extrusion of the polyimide at a temperature that is beyond the use temperature, but yet not excessive in terms of equipment capability. Ideally, if the polyimide were crystallizable, then it might be possible to utilize the polyimide at temperatures considerably higher than the glass transition temperature without mechanical distortion. As a result, many laboratories have pursued the study of crystalline thermoplastic polyimides[4–8] and one commercial grade polyimide has become available.[9–10]

In this work, a model copolyimide system exhibiting thermoplastic behavior is examined. It is based on combinations of 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) and either 1,3-bis(4-aminophenoxy)benzene (134APB) or 1,12-dodecanediamine (C12). In consideration of each of the homopolyimides, the crystalline behavior of 134APB/BPDA has been reported.[11] Also, C12/BPDA might be suspected to be crystalline by analogy to earlier work with C12/PMDA,[12,13] and that is shown to be true by this work. The presence of C12, however, either in the homopolyimide or in the copolyimides would detract from long term thermal oxidative stability in most end use applications. Nevertheless, this model system provides a means of controlling polymer glass transition temperature (T_g), crystallization temperature (T_c), and crystalline melting temperature (T_m). The preparation and thermal characterization of this unique copolyimide family is presented in this paper, the first in a series. Additional publications will cover the detailed thermal analysis, morphology, and X-ray structural studies.

Experimental Section

Monomers and Solvent. The 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) was obtained from Mitsubishi Chemical Co. and was used after heat treating 50 g portions at 250 °C for 1 h under vacuum (25 mmHg) with a sweep of nitrogen. The 1,3-bis(4-aminophenoxy)benzene (134APB) and 1,12-dodecanediamine (C12) were obtained from DuPont and were used as received without further purification. The solvent, *N,N*-dimethylacetamide (DMAC), was Burdick & Jackson reagent grade; it was stored over 4 Å molecular sieves for at least 24 h before use to further dry the solvent.

Polymerization. The protocol for polymerization was to use a nitrogen-filled glovebox containing a mechanical stirrer and baked-out glassware. The BPDA was always slurried first in the DMAC and to this was added the diamine(s), with C12 being added first, except for the homopolymer containing 134APB alone. All poly(amic acids) were made with 98 mol % of the theoretical amount of BPDA. Two hours after all materials had dissolved, the 2 mol % imbalance of diamine was end-capped with 4 mol % of phthalic anhydride. Another 2 h of stirring ensued before storing the (co)poly(amic acids) at 5 °C. Additional small samples (ca. 2 g) were stored over dry ice until they were analyzed for inherent viscosities and size exclusion chromatographic (SEC) molecular weights.

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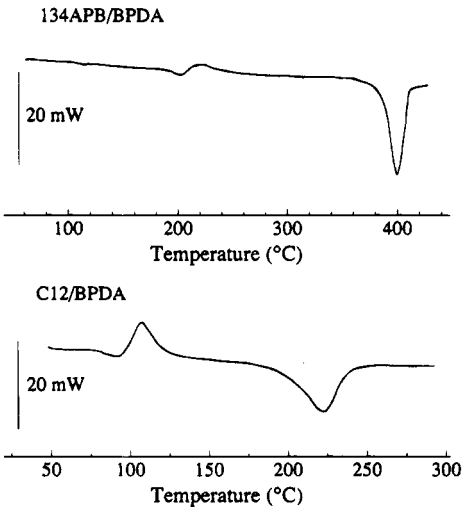
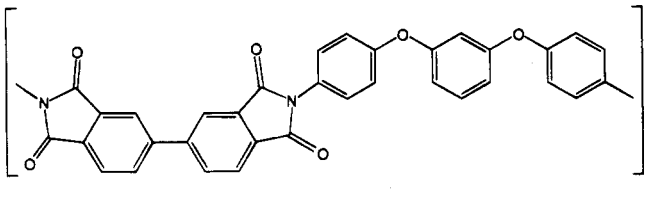


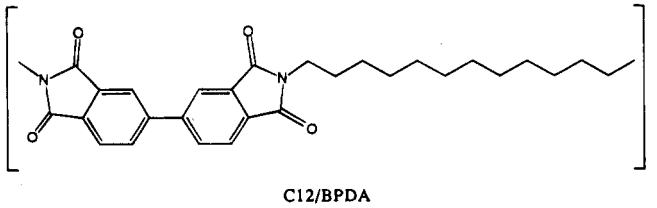
Figure 1. DSC traces of the two rapidly quenched (by dry ice) homopolyimides: 134APB/BPDA, C12/BPDA.

Viscosities and Molecular Weights. Inherent viscosities were determined from relative viscosity values using an Ubbelohde viscometer at 30 °C in a constant temperature bath at 0.5% concentration (g/dL). The solvent was DMAC (same as above).

Molecular weights were measured using the SEC method of Walker.[14] The calibration standards were referenced to absolute molecular weights of poly(amic acids) derived from pyromellitic dianhydride and 4,4′-oxydianiline. Molecular weights are, therefore, approximate and not absolute.

Polyimide Preparations. All conversions to the homo- and copolyimides were carried out by chemical dehydration. The theoretical amount of triethylamine was mixed with the polymer solution on the basis of carboxylic acid groups present, along with twice the theoretical amount of acetic anhydride. The reaction mixture was then allowed to stand for 24 h under nitrogen at 30 °C. The homo- and copolyimides were isolated in a Waring blender in methanol, washed 2× in methanol, and dried to constant weight at 150 °C under vacuum and 25 mmHg with a nitrogen sweep. The chemical structures of the two homopolyimides 134APB/BPDA and C12/BPDA are listed below.





Thermal Characterizations. Differential scanning calorimetry (DSC) was done under nitrogen at a heating and cooling rate of 10 °C/min using a TA DSC-990 station, unless otherwise stated. For the T_g measurement, results were taken after the second heating pass which followed rapid quenching of the molten sample in dry ice. For the equilibrium melting temperature ($T_m°$) measurement, samples were first melt crystallized at varying temperatures for at least 1 h (longer time for higher crystallization temperature) and then quenched rapidly by liquid nitrogen. The value of $T_m°$ was estimated by the Hoffman–Weeks method.[15]

Table 1. Sequenced Copolymers (Copoly(amic acids)) of 134APB/C12 and BPDA Molecular Weight Data at 98% Stoichiometry)[a]

134APB/C12	η_v[b] 0.5%; 30 °C	M_w	M_n	n[c]
100/0	0.86	39 500	11500	3.43
80/20	0.59	18 900	7500	2.52
60/40	0.73	27 100	9400	2.88
40/60	0.70	25 500	9100	2.80
20/80	0.69	20 400	7800	2.62
0/100	0.50	18 300	7200	2.54

[a] Phthalic anhydride end-capped. [b] Inherent viscosity in DMAC. [c] Polydispersity.

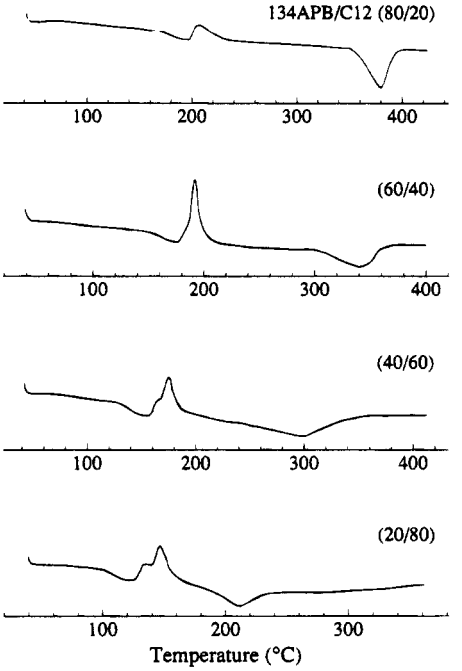


Figure 2. DSC traces of the rapidly quenched (by dry ice) copolyimides with four 134APB/C12 compositions: 80/20, 60/40, 40/60, and 20/80.

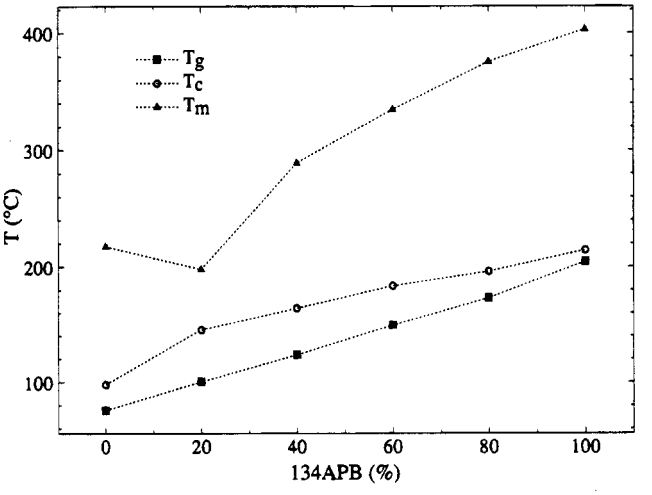


Figure 3. Apparent thermal transition temperatures of copolyimides based on 134APB/C12 and BPDA (data determined from Figures 1 and 2).

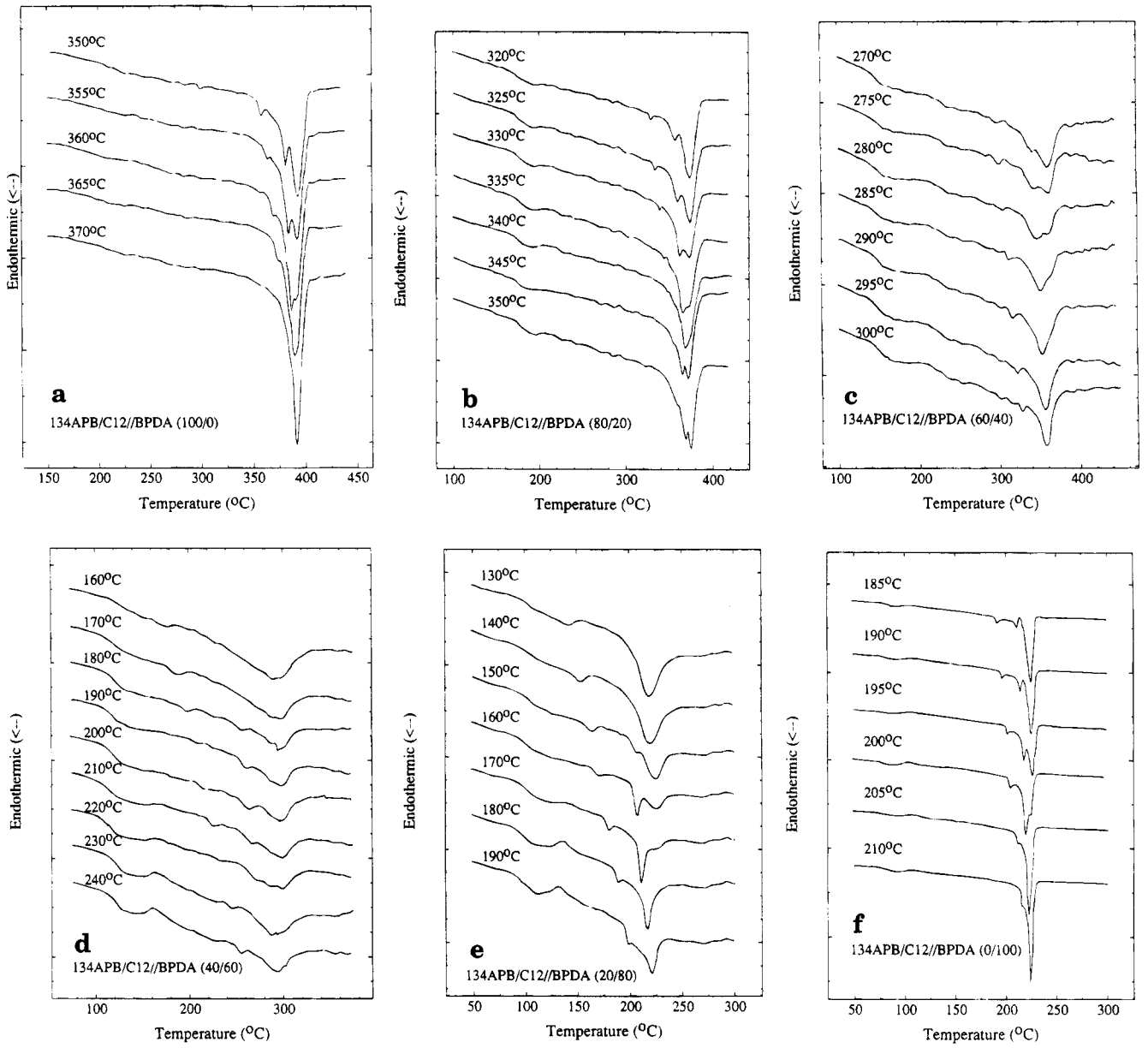


Figure 4. DSC heating scans of polymers crystallized at different temperatures with the 134APB/C12 compositions of (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80, and (f) 0/100. The heating rate was 10 °C/min.

Results and Discussion

Copolyimides from 134APB/C12 and BPDA. For reasons stated above, it became of interest to study a copolymer system, wherein the T_g's and T_m's of each homopolyimide component were separated from each other by perhaps 100 deg. Through a number of exploratory syntheses of various potential thermoplastic polyimides, it was found that the two homopolyimides, comprising 134APB/BPDA, and C12/BPDA met the criteria. They were indeed crystalline by examination with differential scanning calorimetry (Figure 1), and they also had separations in T_g and T_m of 130 deg (C12/BPDA) and 200 deg (134APB/BPDA), respectively. Although there was no a priori reason to assume that the corresponding copolymides would necessarily be crystalline, syntheses were carried out and initial characterizations of the copolyimides were done by DSC.

Syntheses of all pol(amic acids), except the homopoly(amic acid) from 134APB alone, were complicated by the fact that the strongly basic aliphatic diamine, C12, would gel severely during addition of dianhydride to diamine forming cross-linked salts of oligomeric poly(amic acid) and unreacted diamine. The gels required several days to disperse and react. To obviate this problem, BPDA was slurried in the solvent and C12 was slowly added to allow the dianhydride to always be in excess. Following complete solution and reaction of C12, the 134APB was added next. Finally, the unreacted amino functions, 2% in excess in all cases, were end-capped with phthalic anhydride. The polymerization procedure tended to produce copolymers that were sequenced, but due to the fact that no attempt was made to study the rates of equilibration, there is no assurance that the final copoly(amic acids) were indeed sequenced. Molecular weight data on the homopoly(amic acids) and copoly(amic acids) is summarized in Table 1.

Conversion to the copolyimides was accomplished with acetic anhydride/triethylamine. The homopolyimides and copolyimides were isolated as powders in methanol and dried to constant weight at 150 °C. The molecular weights of the copolyimides should be the same as the corresponding values in Table 1.

Figure 2 is a summary of DSC scans of the copolymer compositions that were synthesized. Again, all the samples have been quenched in dry ice from the melt to minimize the crystallinity. Detailed analysis of Figures 1 and 2 indicates that the complete amorphous state cannot be obtained in several 134APB/C12 compositions: 100/0, 80/20, and 0/100 (in these compositions, the enthalpy change of exotherm is always smaller than that of endotherm). This suggests that, in these compositions, the crystallization rates are too fast to allow the total elimination of crystallinity through a rapid quenching. It is further noticed that both 60/40 and 80/20 compositions exhibit two exothermic peaks rather than one, which may be indicative of phase separation between the two homopolyimide crystals. The detailed crystallization study will be carried out in a later paper.

In Figures 1 and 2, for each copolyimide system studied, a single T_g was clearly evident, indicating a homogeneous copolymer system. All of the copolyimides were crystalline, and major peaks were found for the exotherms of the T_c's and the endotherms of the T_m's. Figure 3 is a graphical summary of the apparent transition temperatures (T_g, T_c, T_m) determined by DSC in these quenched copolyimides. Rectilinear relationships of T_g (but not T_c and T_m) relative to the mole percent composition of the diamines were found. In the case of T_m, a minimum value was found in the composition of 20% 134APB.

Separate evidence supporting the generation of single copolymers was obtained by synthesizing a 50/50 134APB/C12 copolyimide with BPDA and comparing the thermal transitions of this to a 50/50 homopolyimide mixture of 134APB/BPDA and C12/BPDA. The copolyimide showed a single T_g at 145 °C, as well as primary peaks for T_c and T_m. The physical mixture, however, showed multiple T_g's at 81 and 210 °C as well as multiple melting endotherms, evidence that was clearly consistent with the physical mixture and different from the copolyimide.

Equilibrium Melting Temperature. In Figure 3, the apparent melting temperature is not a thermodynamic variable and thus may not fully reflect the crystalline properties. One of the thermodynamic variables accessible by DSC is the equilibrium melting temperature, which can be estimated by using the Hoffman–Weeks method.[15] In this method, all the samples are first isothermally crystallized at different temperatures prior to the thermal analysis.

DSC heating scans of different polymers (100/0 to 0/100 134APB/C12) annealed at varying temperatures are shown in Figure 4a–f, respectively. A consistent melting pattern is seen in all compositions: at lower crystallization temperatures, the samples exhibit a triple-melting behavior; at higher crystallization temperatures, the samples show a conventional double-melting behavior. In both cases, the lowest endotherm can be attributed to the annealing process since it always occurs at approximately 10 deg above the annealing temperature. In the triple-melting behavior, the middle endotherm is found to increase its peak position as well as its mass fraction (thus more thermodynamically stable) with increasing crystallization temperature, whereas the highest endotherm is found to decrease its fraction but remains at about the same position. It further appears that the higher endotherm in the double-melting behavior is directly associated with the middle endotherm in the triple-melting behavior. We have investigated the triple-melting behavior by changing the DSC heating rate as well as examining the annealed samples through X-ray (results to be shown later) and concluded that this behavior is not due to the polymorphism of different crystal forms. Some possibilities for the triple-melting behavior are due to the premelting–recrystallization–melting processes or the melting of different morphologies.

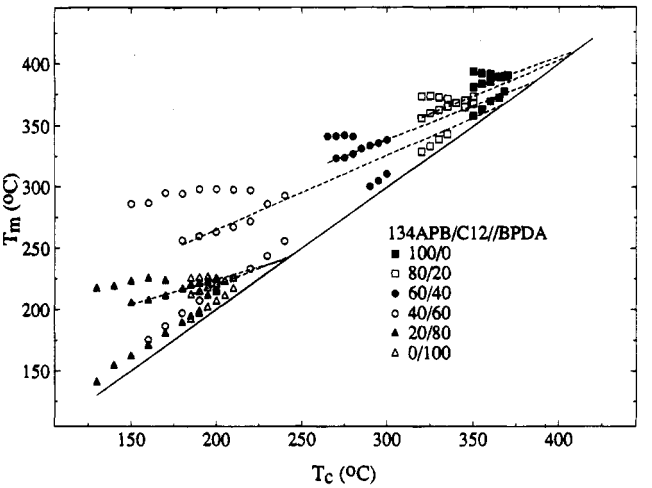


Figure 5. Hoffman–Weeks plot (T_m *vs* T_c) using data from Figure 4 to extrapolate the equilibrium melting temperature ($T_m°$).

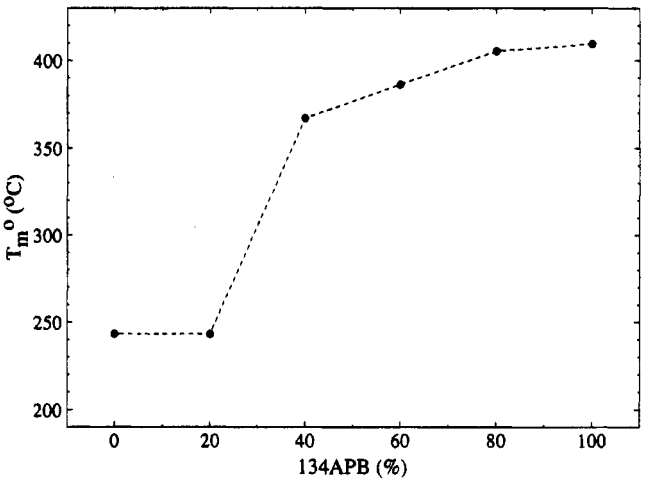


Figure 6. Equilibrium melting temperature plotted as a function of the 134APB composition.

The Hoffman–Weeks plot (T_m *vs* T_c) of this copolyimide family is shown in Figure 5. For the reasons stated before, we have chosen the middle endotherm position in the triple-melting behavior and the final endotherm position in the double-melting behavior to represent the nominal melting temperature. The equilibrium melting temperature ($T_m°$) was extrapolated at the intercept of the linear correlation between the nominal melting temperature and T_c (the dotted line) and the $T_m = T_c$ line. It is seen that the value of $T_m°$ decreases with increasing C12 composition, as expected. The relationship between $T_m°$ and the percentage of 134APB is shown in Figure 6, which is similar to that found in Figure 3. Although the apparent melting points of the copolyimides in Figure 3 were significantly decreased by increasing C12 composition, this decrease was somewhat smaller in $T_m°$. As a result, at the 134APB composition between 20% and 40%, $T_m°$ showed a near step-change behavior. When the 134APB composition is 40% or greater, the depression in $T_m°$ is low

(ca. 40 °C) which indicates that the crystalline properties are dominated by the 134APB/BPDA polyimide phase. When the 134APB composition is below 20%, no $T_m°$ depression is seen which indicates that the properties are dominated by the C12/BPDA polyimide phase.

Conclusion

We have demonstrated that crystalline copolyimides can be derived from 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) and either 1,3-bis(4-aminophenoxy)benzene (134APB) or 1,12-dodecanediamine (C12). All compositions were found to have a singular glass transition temperature, which is rectilinearly dependent on the mole percent of 134APB/C12. This indicates the chosen preparation method has not produced a phase separation in the amorphous state. A detailed study of the equilibrium melting temperature ($T_m°$) using the Hoffman–Weeks method reveals that the crystal properties do not obey the rule of mixing. At compositions of 134APB/C12 above 40/60, the crystals are dominated by the 134APB/BPDA polyimide phase, whereas below it by the C12/BPDA polyimide phase. Clearly, the 134APB/BPDA polyimide crystal is a more dominant one, for it consists of a faster crystallization rate than its C12/BPDA counterpart.

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