

Crystallization, Melting, and Rheology of Reactive Polyamide Blends

Wendell B. Lake, Sumod Kalakkunnath, Douglass S. Kalika

Department of Chemical and Materials Engineering and Center for Manufacturing, University of Kentucky, Lexington, Kentucky 40506-0046

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ABSTRACT: The crystallization and melting characteristics of a series of polyamide blends based on PA 4,6 and PA 6I were investigated by calorimetric methods; preparation of the samples was conducted so as to control the extent of transamidation occurring in the melt before crystallization. Blend samples with minimal prior thermal history displayed a modest degree of melting point depression compared to the equilibrium melting temperature of PA 4,6 ($T_m^0 = 309.5^\circ\text{C}$). Application of the Nishi–Wang equation indicated a value of $\chi = -0.25$ for the blends. PA 4,6 and the blends followed Avrami crystallization kinetics with exponents in the range 2.0 to 2.5; no systematic variation of n with blend composition was observed. The influence of transamidation was investigated for samples exposed to varying melt temperatures and melt times with the extent of transreaction

quantified using ^{13}C -NMR. Increasing extents of transreaction led to a decrease in both the rate of crystallization and the overall bulk crystallinity of the blends owing to a reduction in the length and number of crystallizable blocks present along the polymer chains. Capillary rheometry studies indicated a strong sensitivity to time in the melt for the PA 4,6 homopolymer, and the mechanism responsible for the observed decrease in apparent viscosity was also operative in the blend samples. As such, it was not possible to independently assess the influence of transreaction on the rheology of the blends. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1245–1252, 2004

Key words: polyamides; crystallization; blends; transamidation; rheology

INTRODUCTION

The crystallization and morphology of melt-miscible binary polymer blends containing a single crystallizable component have been the subject of numerous studies.¹ The investigations have focused on the influence of the noncrystallizable “diluent” on crystal structure and kinetics, and the ultimate disposition of this component in the resulting semicrystalline morphology. Systems of interest have included pairs composed of relatively flexible polymers [e.g., poly(vinylidene fluoride)/poly(methyl methacrylate)]^{2–4}; poly(ethylene oxide)/poly(methyl methacrylate)^{5–7} and blends based on less-flexible polymers [e.g., poly(butylene terephthalate)/bisphenol A polyarylate^{8–13}; poly(ether ether ketone)/poly(etherimide)^{14–19}]. An overview of such blends and their corresponding morphological behavior has been provided by Debier et al.²⁰

One route by which to tailor the bulk morphology of heterogeneous polymer blend systems is reactive compatibilization.²¹ In the case of crystalline–amorphous

blends based on polyesters or polyamides, the occurrence of interchain exchange reactions in the melt results in the formation of initially blocky copolymers that become increasingly random at elevated melt temperatures and/or extended melt residence times.²² The formation of copolymers has a potentially dramatic influence on the crystallization behavior of the blends because the insertion of noncrystallizable (i.e., diluent) segments into the otherwise crystallizable polymer chains leads to a reduction in the length of the crystallizable blocks and a corresponding decrease in both crystallization rate and bulk crystallinity. Although the *in situ* formation of copolymers provides a possible method by which to enhance the properties of these materials during the blending/processing step, careful specification of processing parameters is essential to control the extent of transreaction and the characteristics of the blend.

A reactive crystalline–amorphous system that has been the subject of detailed investigation is the blend of polyamide 4,6 (PA 4,6) and polyamide 6I (PA 6I). PA 4,6 is an aliphatic polyamide that crystallizes rapidly from the melt state, whereas PA 6I is an aromatic polyamide that remains wholly amorphous due to the inclusion of a 1,3-connected isophthalate linkage in the chain backbone repeat unit. Binary melt blends of PA 4,6/PA 6I are reported to be miscible at all compositions.²³ Eersels and coworkers characterized the

Correspondence to: D. Kalika (kalika@engr.uky.edu).

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exchange reactions that occur in this blend system using ^{13}C -NMR.^{24,25} The investigators reported on the sensitivity of transamidation rate and extent of reaction to blend process conditions, as well as the impact of chain interchange on the dynamic crystallization characteristics of the blends.^{26–28} A comprehensive review of these studies has also been published.²⁹

In a previous article, the morphological characteristics of a series of blends based on PA 4,6 and PA 6I were investigated by dynamic mechanical and dielectric methods.³⁰ The morphology was similar to that observed for blends such as PEEK/PEI, in that two amorphous phase glass–rubber relaxations were observed, corresponding to the coexistence of two distinct amorphous phase populations in the crystallized sample (i.e., interlamellar mixed phase, and interfibrillar/interspherulitic PA 6I-rich phase). The work presented in the current article focuses on the characterization of crystallization and melting in PA 4,6/PA 6I blends prepared with carefully controlled thermal histories. Specifically, calorimetric methods were used to determine the equilibrium melting temperatures of PA 4,6 and the blends, and to determine the extent of melting point depression in samples with minimal prior transreaction. Crystallization kinetics were examined within the context of the Avrami relation, and the impact of transreaction on bulk crystallinity and crystallization rate was assessed. In addition, capillary rheometry measurements were undertaken to elucidate the influence of composition and time in the melt on the apparent viscosity of the blends.

EXPERIMENTAL

Materials and methods

Polyamide 4,6 was obtained in pellet form from DSM Engineering Plastics (Stanyl TW341; Evansville, IN). Polyamide 6I pellets were obtained from Bayer Polymers Division (Durethan T40; Pittsburgh, PA). Samples for calorimetric studies were prepared by blending the appropriate weight ratio of pellets in 90% formic acid (1–2 wt % polymer, total) with precipitation in excess deionized water. The resulting powder was filtered, washed with hot water, and dried under vacuum for a minimum of 48 h (80°C; 0.1 Torr). Samples for rheological study were prepared by melt-mixing the pellets in a Custom Scientific Instruments (CSI, Newark, NJ) model 194 mixing extruder at 305°C under nitrogen blanketing with pelletization of the extruded strands; the residence time in the extruder was about 2–3 min. All blend samples were dried under vacuum at 80°C before measurement.

Calorimetric studies were performed using a Perkin–Elmer DSC-7 differential scanning calorimeter (Perkin Elmer Instruments, Shelton, CT). Measured

transition temperatures and corresponding enthalpies were calibrated using indium and zinc standards, and all experiments were performed under an inert atmosphere. Isothermally crystallized samples were prepared by heating each sample rapidly to 305°C and holding at that temperature for 2 min. The samples were then quenched in the DSC to crystallization temperatures in the range of 235 to 270°C, where they were allowed to isothermally crystallize for a period of 20 min. The samples were cooled to room temperature, with subsequent heating sweeps recorded at a rate of 20°C min⁻¹.

The extent of transreaction in a series of 50/50 PA 4,6/PA 6I blends exposed to varying times in the melt (305°C) was assessed by ^{13}C -NMR according to the method of Aerdts et al.²⁴ A 400-MHz Varian spectrometer (Varian Inc., Palo Alto, CA) was used with spectra recorded at 60°C. Samples were prepared at a concentration of 14% (w/v) in 98% D₂SO₄; D₂SO₄ was used as the locking agent. The recorded spectra corresponded to a total of 10,000 scans. The percentage transamidation was determined by following the emergence of adipic acid–diaminohexane (ADI–DAH) and isophthalic acid–diaminobutane (IA–DAB) dyad sequences in the NMR spectrum at about 177.6 and 171.7 ppm, respectively (i.e., carbonyl resonances).²⁹

Rheological measurements were performed using a Dynisco LCR 6000 capillary rheometer (Dynisco Instruments, Franklin, MA) with a capillary diameter of 1 mm ($L/D = 40$); the instrument was operated using a 9 kN load cell mounted on the crosshead. Apparent viscosity (η_A) was measured as a function of apparent shear rate ($4Q/\pi R^3$) over a range of rates from 50 to 4000 s⁻¹; no end corrections were applied. In addition, viscosity–time studies were conducted at a fixed rate of 1000 s⁻¹. All measurements were performed on previously vacuum-dried samples under nitrogen blanketing at a melt temperature of 305°C.

RESULTS AND DISCUSSION

Melting characteristics of PA 4,6 and blends

The melting characteristics of PA 4,6 and the blends were assessed for samples melted at 305°C (2 min) and then rapidly quenched to isothermal crystallization temperatures in the range of 235 to 270°C. All blend samples were prepared by solvent blending (i.e., physical blends), and the time in the melt was kept short to minimize potential transamidation reactions.

Representative melting curves for a series of isothermally crystallized 60/40 PA 4,6/PA 6I blend samples are shown in Figure 1. The samples display a single, broad melting endotherm that shifts to lower temperatures with decreasing crystallization temperature. The measured peak melting temperature for each sample is plotted versus isothermal crystallization

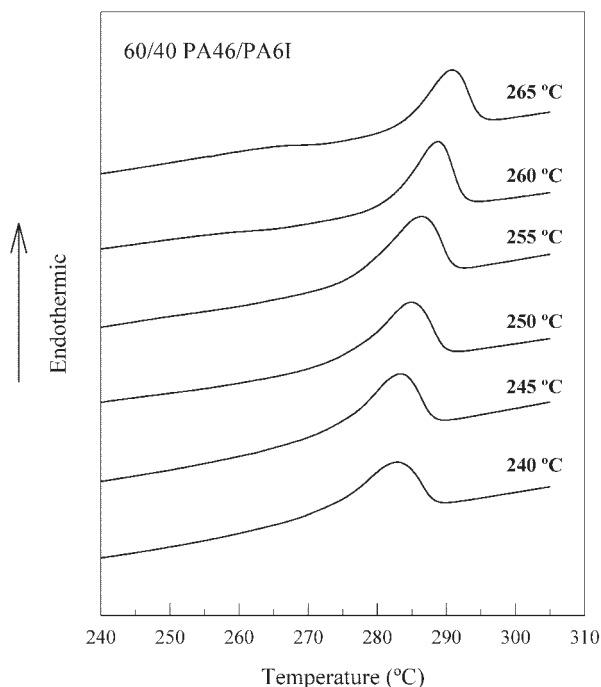


Figure 1 DSC heating sweeps for solvent-prepared 60/40 PA 4,6/PA 6I blend samples with varying isothermal crystallization temperature; heating rate = 20°C min⁻¹.

temperature in Figure 2 (Hoffman–Weeks plot³¹); linear extrapolation of each data set to the $T_m = T_c$ line provides the equilibrium melting temperature T_m^o . The equilibrium melting temperature for PA 4,6 is 309.5°C, which is close to the value reported previously by Zhang et al.³² The T_m^o values for the blends, reported in Table I, reveal a modest melting point depression for this blend system. For a binary (crystalline–amorphous) blend of high molecular weight polymers, the Nishi–Wang equation can be used to estimate the polymer–polymer interaction parameter χ ³³:

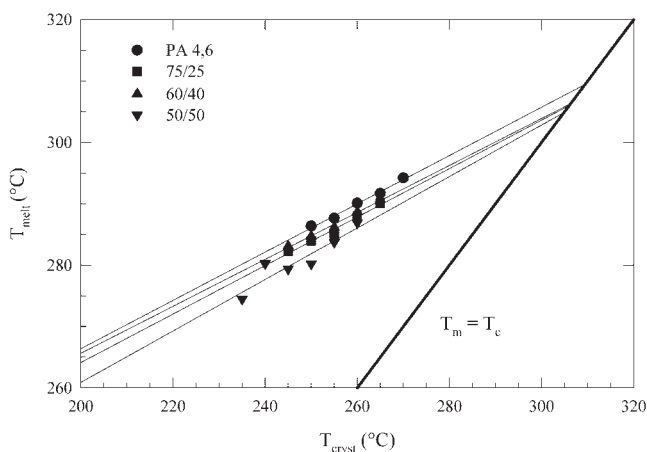


Figure 2 Hoffman–Weeks³¹ plot of T_m (°C) versus T_c (°C) for PA 4,6 and PA 4,6/PA 6I blends.

TABLE I
Equilibrium Melting Temperatures for PA 4,6 and Blends Based on PA 4,6 and PA 6I

PA 4,6/PA 6I Composition	T_m^o (°C)
100/0	309.5
75/25	306.0
60/40	306.3
50/50	304.9

$$\frac{1}{T_m} - \frac{1}{T_m^o} = - \left(\frac{R \bar{V}_C}{\Delta H_f^o \bar{V}_A} \right) \chi \phi_A^2 \quad (1)$$

where T_m is the equilibrium melting temperature of the blend, T_m^o is the equilibrium melting temperature of PA 4,6, \bar{V}_C and \bar{V}_A are the respective molar volumes for the crystalline and amorphous components, ΔH_f^o is the 100% crystalline heat of fusion for the crystallizable polymer, and ϕ_A is the volume fraction of the amorphous component. The molar volumes can be determined from density values reported previously (PA 4,6: $\rho_C^{100\%} = 1.24 \text{ g cm}^{-3}$,³⁴ $\rho_A = 1.10 \text{ g cm}^{-3}$; PA 6I: $\rho = 1.18 \text{ g cm}^{-3}$,²⁸), and ΔH_f^o is taken as 149 J g⁻¹.³⁰ For the 60/40 and 50/50 blends, $\chi = -0.25$, which is comparable to values reported for other crystalline–amorphous systems (see discussion in Runt¹).

Crystallization kinetics of PA 4,6 and blends

The kinetics of isothermal melt crystallization for PA 4,6 and the (solvent-prepared) blends were investigated for samples initially melted at 305°C (2 min) and rapidly quenched to the desired crystallization temperature; upon thermal stabilization, heat flow was recorded as a function of crystallization time. Representative heat flow curves for PA 4,6 and 75/25, 60/40, and 50/50 blend compositions are shown in Figure 3 ($T_c = 260^\circ\text{C}$), with the presence of the PA 6I diluent leading to a substantial reduction in both the crystallization rate and overall degree of crystallinity obtained. The crystallization rate for each isotherm can be quantified using the crystallization half-time ($t_{1/2}$), which is defined as the time at which crystallization is 50% complete (i.e., $X_t = 0.5$; see Avrami equation, below). The crystallization half-time for PA 4,6 and the blends is plotted versus isothermal crystallization temperature in Figure 4. Because of the rapid crystallization of PA 4,6, only crystallization temperatures on the high-temperature side of the rate–temperature curves were accessible. The data suggest a maximum crystallization rate for PA 4,6 and the blends at about 255°C.

The isothermal crystallization curves were analyzed according to the Avrami equation,^{35–37} as follows:

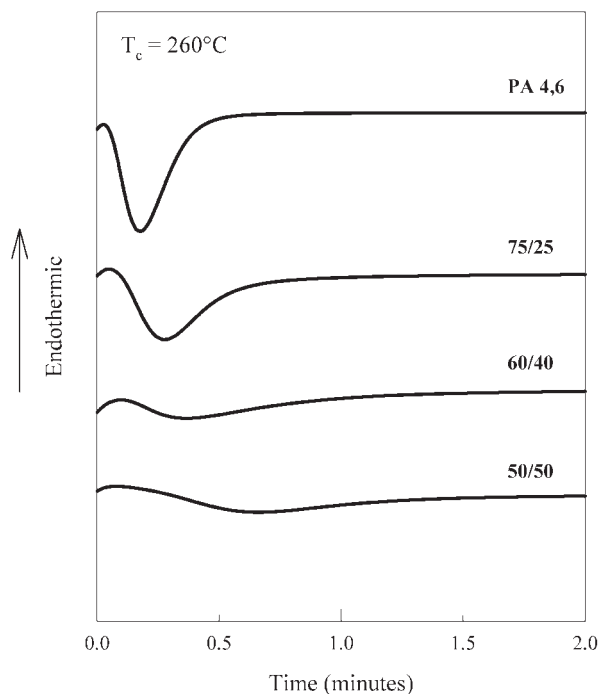


Figure 3 Crystallization isotherms for PA 4,6 and PA 4,6/PA 6I blends; isothermal crystallization at 260°C.

$$1 - X_t = \exp(-kt^n) \quad (2)$$

where $X_t = X_c/X_\infty$ is the extent of crystallinity at time t , and k and n are the Avrami rate constant and exponent, respectively. Avrami plots of $\log[-\ln(1 - X_t)]$ versus $\log(t)$ for PA 4,6 and the 50/50 blend are provided in Figure 5(a) and (b), respectively. A linear result is obtained over the region of primary crystallization, with the slope corresponding to the Avrami exponent n . For the materials examined (i.e., PA 4,6 and each blend), n was determined to be essentially independent of crystallization temperature. Table II contains the Avrami exponents for the various samples. In each case, nonintegral values of n were obtained in an overall range from 2.0 to 2.5; there was no clear dependence of Avrami exponent on blend composition. According to the classical Avrami treatment, values of $n = 3$ are consistent with athermal nucleation and spherulitic crystal growth, whereas values of $n = 2$ indicate disclike crystal growth.³⁸ The values obtained here suggest possibly mixed nucleation and/or crystal growth mechanisms. The relative consistency of the exponent values determined for the PA 4,6 homopolymer compared to those of the blends seems to indicate that the presence of the PA 6I diluent does not alter the crystallization mechanism over the linear Avrami range. As noted in Wunderlich,³⁸ additional information on the nucleation and morphology de-

velopment in these materials would be required to definitively interpret the value of n .

Influence of time in the melt

The influence of prior time in the melt on the isothermal and nonisothermal crystallization of the PA 4,6/PA 6I blends was also investigated. DSC heating sweeps for solvent-prepared 75/25 blend samples held in the melt at 305°C for varying times are shown in Figure 6; these samples were rapidly heated to 305°C in the calorimeter, held at that temperature for 2 to 20 min, and then quenched to an isothermal crystallization temperature of 250°C (20 min crystallization time). The specimens were then cooled to room temperature, and the thermogram recorded at a heating rate of 20°C min⁻¹. The melting endotherms reflect the impact of the transamidation reactions with increasing time in the melt. At longer melt times, higher degrees of transamidation are achieved, with a corresponding reduction in the number and length of PA 4,6 blocks capable of crystallization. This is manifested in a decrease in both the overall degree of crystallinity in the blends, as well as their corresponding melting temperature (see Fig. 6).

The overall fraction crystallinity in the isothermally crystallized 75/25 blends was calculated based on a 100% crystalline heat of fusion of 149 J g⁻¹; these results are plotted as a function of time in the melt in

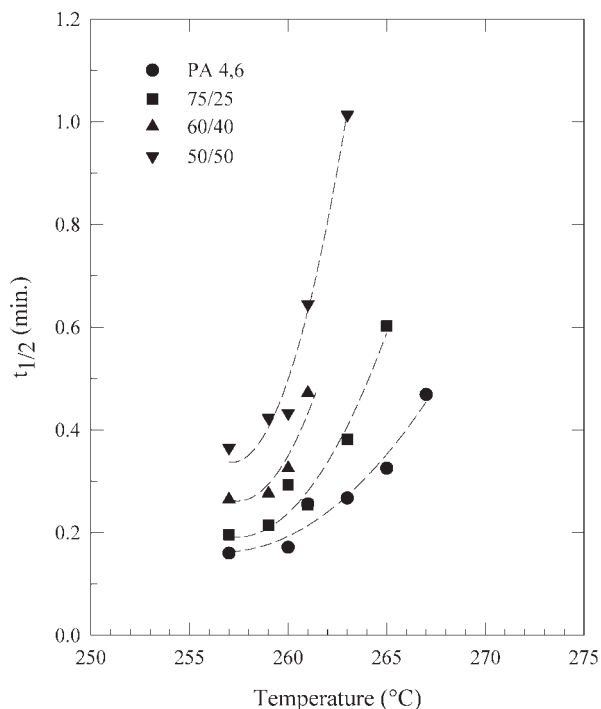


Figure 4 Crystallization half-time ($t_{1/2}$, min) versus isothermal crystallization temperature (°C) for PA 4,6 and PA 4,6/PA 6I blends.

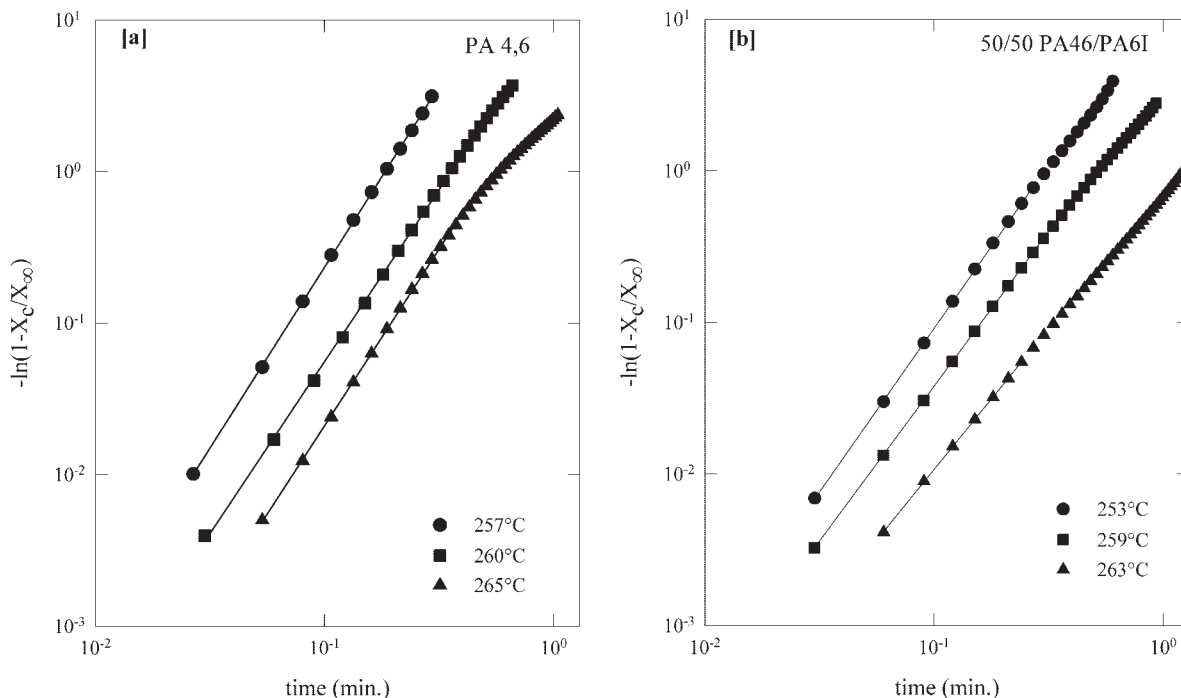


Figure 5 Avrami plots of $\log [-\ln(1 - X_c)]$ versus $\log(t)$ for selected isothermal crystallization temperatures. (a) PA 4,6; (b) 50/50 PA 4,6/PA 6I.

Figure 7 (melt temperatures of 305, 310, and 320°C). For each temperature investigated, there is a strong initial decrease in the overall fraction crystallinity with melt time as a result of the formation and increasing randomization of the transreacted copolymer chains. At the higher temperatures studied, it appears that the degree of transreaction approaches a maximum, as evidenced by a discontinuity in the crystallinity–time data for the 310 and 320°C melt temperatures. This behavior is consistent with ¹³C-NMR results reported by Eersels and coworkers²⁵ that show the percentage transamidation in 50/50 blends approaching a plateau value after about 30 min of melt time (315°C). In each case, the extent of randomization achieved in the polymer chains was not sufficient to fully suppress crystallization.

Nonisothermal crystallization studies were conducted by rapidly heating melt-prepared blend samples to 305°C, holding in the melt for times ranging from 2 to 60 min, and then cooling at $-20^\circ\text{C min}^{-1}$.

TABLE II
Range of Avrami Exponents (*n*) for PA 4,6 and Blends Based on PA 4,6 and PA 6I

PA 4,6/PA 6I Composition	<i>n</i>
100/0	2.3–2.4
75/25	2.1–2.2
60/40	2.3–2.5
50/50	2.0–2.2

The exothermic peak temperature associated with the nonisothermal crystallization of each sample is plotted as a function of melt time in Figure 8. The negative

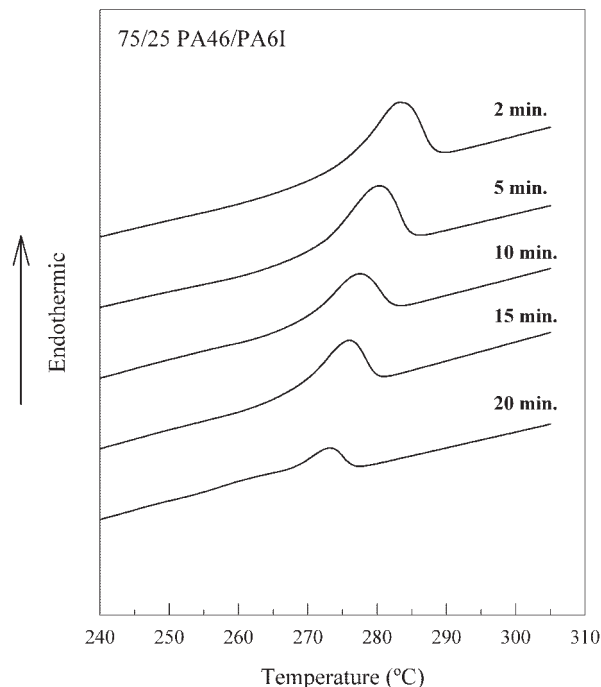


Figure 6 DSC heating sweeps for 75/25 PA 4,6/PA 6I blends conditioned in the melt at 305°C for varying times, with subsequent isothermal crystallization at 250°C; heating rate = $20^\circ\text{C min}^{-1}$.

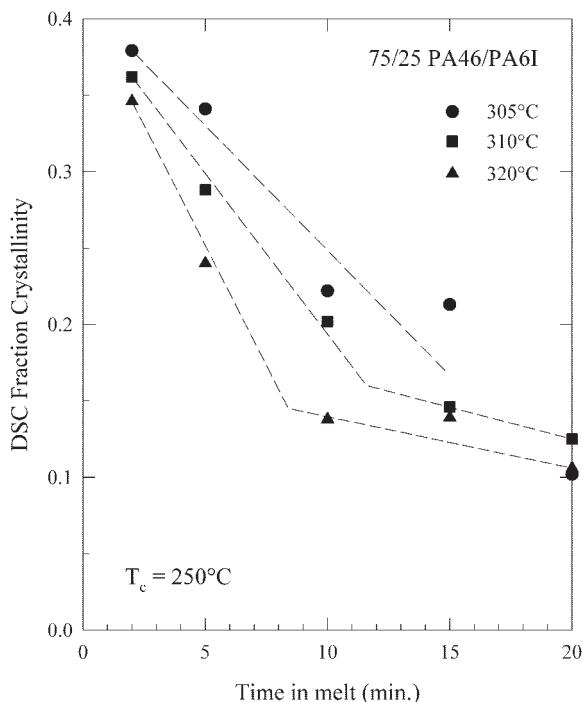


Figure 7 DSC fraction crystallinity versus time in the melt for 75/25 PA 4,6/PA 6I blend samples conditioned at 305, 310, or 320°C with subsequent isothermal crystallization at 250°C.

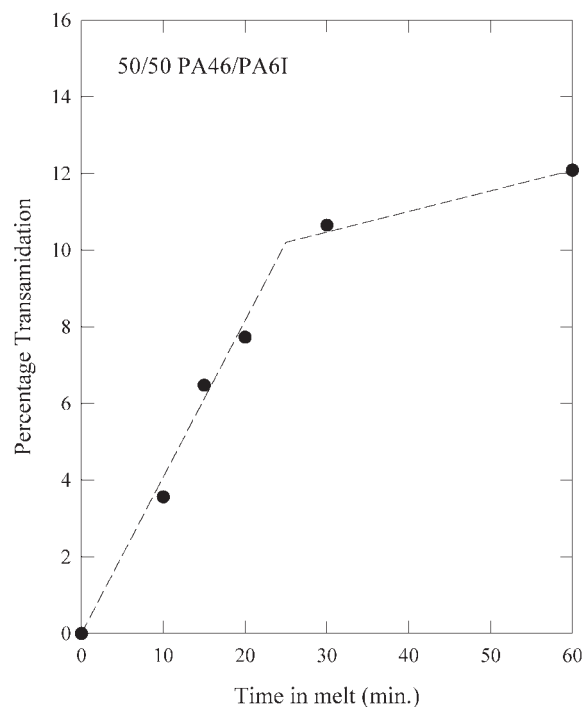


Figure 9 Percentage transamidation versus time in the melt (305°C) for 50/50 PA 4,6/PA 6I blend specimens as determined by ^{13}C -NMR.

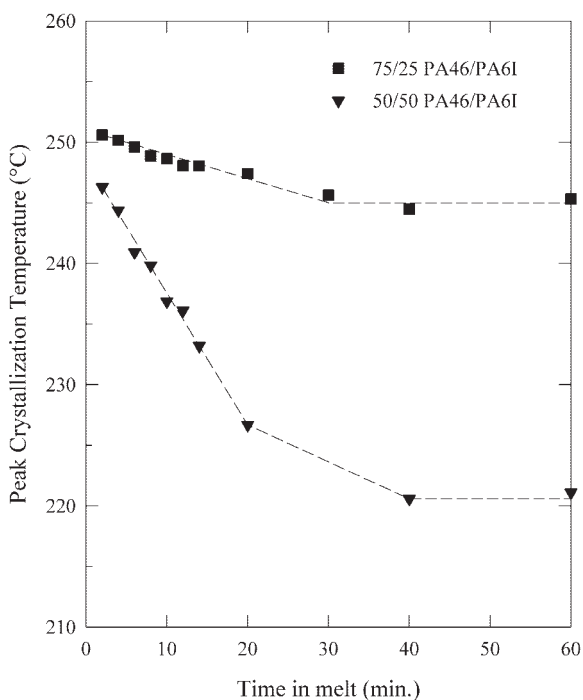


Figure 8 DSC peak crystallization temperature versus time in the melt for PA 4,6/PA 6I blends conditioned at 305°C for varying times; cooling scan rate = $-20^\circ\text{C min}^{-1}$.

offset in crystallization peak temperature with increasing time in the melt reflects both a decrease in the crystallization rate, and morphological (i.e., crystal thickness) effects attributed to an overall reduction in the crystallizable block length. At longer times, the crystallization peak temperature appears to approach a plateau value, again suggesting a maximum in the extent of transreaction that can be achieved in the blends. These data are in good agreement with previously reported nonisothermal crystallization studies.²⁹

Rheological measurements

In addition to the calorimetric studies reported above, capillary flow measurements were undertaken to determine the viscosity characteristics of the blends and the influence of time in the melt on the apparent viscosity of both the constituent homopolymers and the blends. Because of the quantities of sample required, the rheological measurements were performed using pellets prepared by melt blending in the CSI extruder at 305°C. To assess the extent of transreaction in these samples, 50/50 blends were conditioned in the rheometer reservoir at 305°C for times ranging from 10 to 60 min. These samples were then characterized using ^{13}C -NMR, and the percentage transamidation was determined by integration of the carbonyl peak areas associated with the various dyad sequences. The percentage transamidation as a function

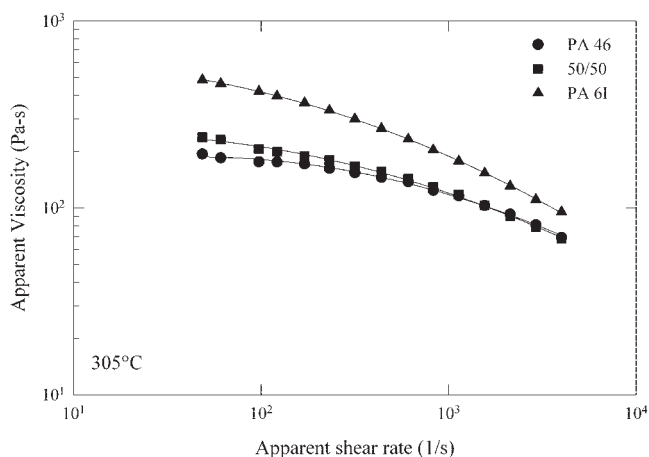


Figure 10 Apparent viscosity (Pa s) versus apparent shear rate (s^{-1}) for PA 4,6, PA 6I, and 50/50 blend sample; 305°C, $L/D = 40$.

of time in the melt is plotted in Figure 9. The data indicate a rapid increase in the percentage transamidation over the first 30 min in the melt, with only a modest increase beyond that time. A percentage transamidation of 12% was determined after 60 min in the melt at 305°C; a value of 50% transamidation would correspond to the formation of a completely random copolymer. These data are in good agreement with the original results reported by Eersels et al.,^{25,29} and confirm that, even at long melt times, the copolymers retain a significant degree of blocky character.

Viscosity–rate results for PA 4,6, PA 6I, and a 50/50 blend at 305°C are shown in Figure 10. All specimens were exposed to the minimum practical melt time during the rheometer loading process, which corresponded to approximately 6 min. The curves presented represent the average of at least five replicate runs for each material; the sample-to-sample variability in the measurements was about 5%. Both homopolymers show typical shear-thinning behavior over the range of accessible shear rates, with PA 6I displaying a substantially higher apparent viscosity compared to that of PA 4,6 at the lowest rates examined. The viscosity of the 50/50 blend is only slightly higher than that measured for the PA 4,6 homopolymer, with data for the two materials coincident at higher apparent shear rates.

Viscosity–time studies were performed for both homopolymers and the 50/50 blend at an apparent shear rate of 1000 s^{-1} . Plots of apparent viscosity versus time in the melt (305°C) are provided in Figure 11. The PA 4,6 displays a strong decrease in apparent viscosity with time in the melt, with η_A decreasing by a factor of nearly 40 over a period of 30 min. Capillary studies reported by Shah³⁹ demonstrated the sensitivity of PA 4,6 viscosity to time in the melt, with especially severe polymer degradation effects encountered at rheometer

temperatures at or above 307°C. By comparison, PA 6I shows a much smaller decrease in apparent viscosity over the 30 min rheometer dwell time (see Fig. 11).

The apparent viscosity–time results for the 50/50 blend sample are similar to the data for the PA 4,6 homopolymer. Although η_A for the blend is initially about 20% higher than that of PA 4,6, the blend displays a comparable decrease in viscosity with melt time, such that the data for PA 4,6 and the blend overlap at times greater than 20 min. This result indicates that the same degradation mechanism that is pervasive in the PA 4,6 is operative in the 50/50 blend. That is, the apparent degradation of the PA 4,6 segments in the blend copolymers dictates the overall viscosity of the blend material. Unfortunately, because of the large magnitude of the degradation effect, it is not possible to carry out an independent study of the influence of transamidation reactions on the viscosity of the blends.

CONCLUSIONS

The crystallization, melting, and rheological characteristics of a series of reactive polyamide blends were investigated for samples with carefully controlled thermal histories. Hoffman–Weeks analysis was used to determine the equilibrium melting temperatures of PA 4,6 and blends based on PA 4,6 and PA 6I. Melting point depression of 3 to 4°C was observed, consistent

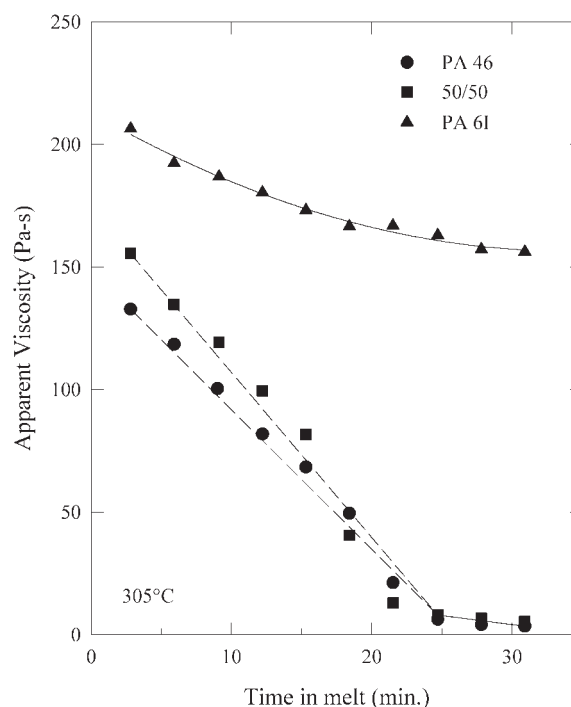


Figure 11 Apparent viscosity (Pa s) versus time in the melt (min.) for PA 4,6, PA 6I, and 50/50 blend sample; 305°C, $L/D = 40$. Apparent rate = 1000 s^{-1} .

with a value of the polymer-polymer interaction parameter, $\chi = -0.25$. The primary crystallization of PA 4,6 and the blends followed Avrami kinetics, with the corresponding Avrami exponent in the range from 2.0 to 2.5. The introduction of the noncrystallizable PA 6I diluent led to a significant decrease in crystallization rate as quantified by $t_{1/2}$; the maximum crystallization rate for PA 4,6 and the blends occurred at a temperature of approximately 255°C. ^{13}C -NMR was used to quantify the extent of transreaction in 50/50 blends, as a function of time in the melt, according to the method of Aerdts et al.²⁴ A maximum extent of transreaction (12%) was approached at melt times greater than 30 min ($T_{\text{melt}} = 305^\circ\text{C}$), and the crystallization and melting characteristics of the transreacted blends reflected this result. Capillary rheometry studies on PA 4,6, PA 6I and the blends showed a high sensitivity of PA 4,6 viscosity to time in the melt, suggesting an underlying degradation mechanism for the PA 4,6 homopolymer. Comparable viscosity-time behavior was observed for the 50/50 blend, indicating that the same mechanism was operative in the blend samples.

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