Crystallization Behavior and Mechanical Properties of a Nylon-6, -6/6, and -12 Terpolyamide

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SYNOPSIS

Composition, tacticity, and processing history can affect the morphology of semicrystalline polymers. Although homopolyamides are a family of polymers well known for semicrystalline character, through copolymerization or multicomponent copolymerization significant changes in materials' crystalline and thermal properties can occur. Due to chain irregularities introduced by terpolymerization, differential scanning calorimetry shows RDG 114T, a commercial polyamide of nylon-6, -6/6, and 12, to have an atypically low T_m and exhibit interesting recrystallization behavior. Specifically, the polyamide is wholly amorphous upon cooling from the melt, and since its T_g is about 20°C (due to the presence of plasticizers), chain ordering is found to occur over time at room temperature. Since the polyamide's morphology is time-dependent, the tensile properties of the polymer are also found to vary with ambient aging. For instance, Young's moduli for an amorphous and 7-day room temperature-annealed sample are 1.3×10^2 and 2.8×10^2 MPa, respectively. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Depending on a polymer's composition, tacticity, and processing history, its resulting morphology may be entirely amorphous or exhibit a wide range of order, i.e., semicrystalline nature.[1] One family of important polymers that is well known for its semicrystalline character is polyamides. Common methods for synthesizing homo-polyamides include the reaction of diacids and diamines, e.g., adipic acid and hexamethylene diamine, giving nylon-6/6. The repeat unit for these polyamides is generically shown as

$$-(CO-R-CONH-R'-NH)_n$$

Self-reaction of cyclic amides (lactams), such as ε-caprolactam, giving nylon-6, also result in polyamides whose repeat unit can be shown as

$$-(NH-R-CO)_m$$
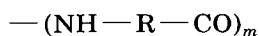
The high level of crystallinity, e.g., about 50%, attainable for some homo-polyamides[2] is a result of these polymers' structural regularity and high amide-functionality frequency providing intermolecular forces, i.e., hydrogen bonding, that promote ordering. However, through copolymerization or multicomponent copolymerization, the crystallization characteristics and thermomechanical properties of polyamides can be affected. For instance, by random copolymerizing nylon-6/6 with different amounts of nylon-6/10, the former's T_m, originally at about 265°C, can be drastically reduced.[3] Changes in polyamide properties as a result of copolymerization can be attributed to the disruption of the original polymer's structural-unit regularity and decreasing amide-functionality frequency. Such structural changes also lead to a reduction of overall degree of crystallinity. By using DSC and standard tensile testing methodologies, the crystalline characteristics of a ter-polyamide whose composition consists of nylon-6, -6/6, and -12 and how the polymer's thermal and mechanical properties are dependent upon morphology and volatile components will be discussed in this paper.
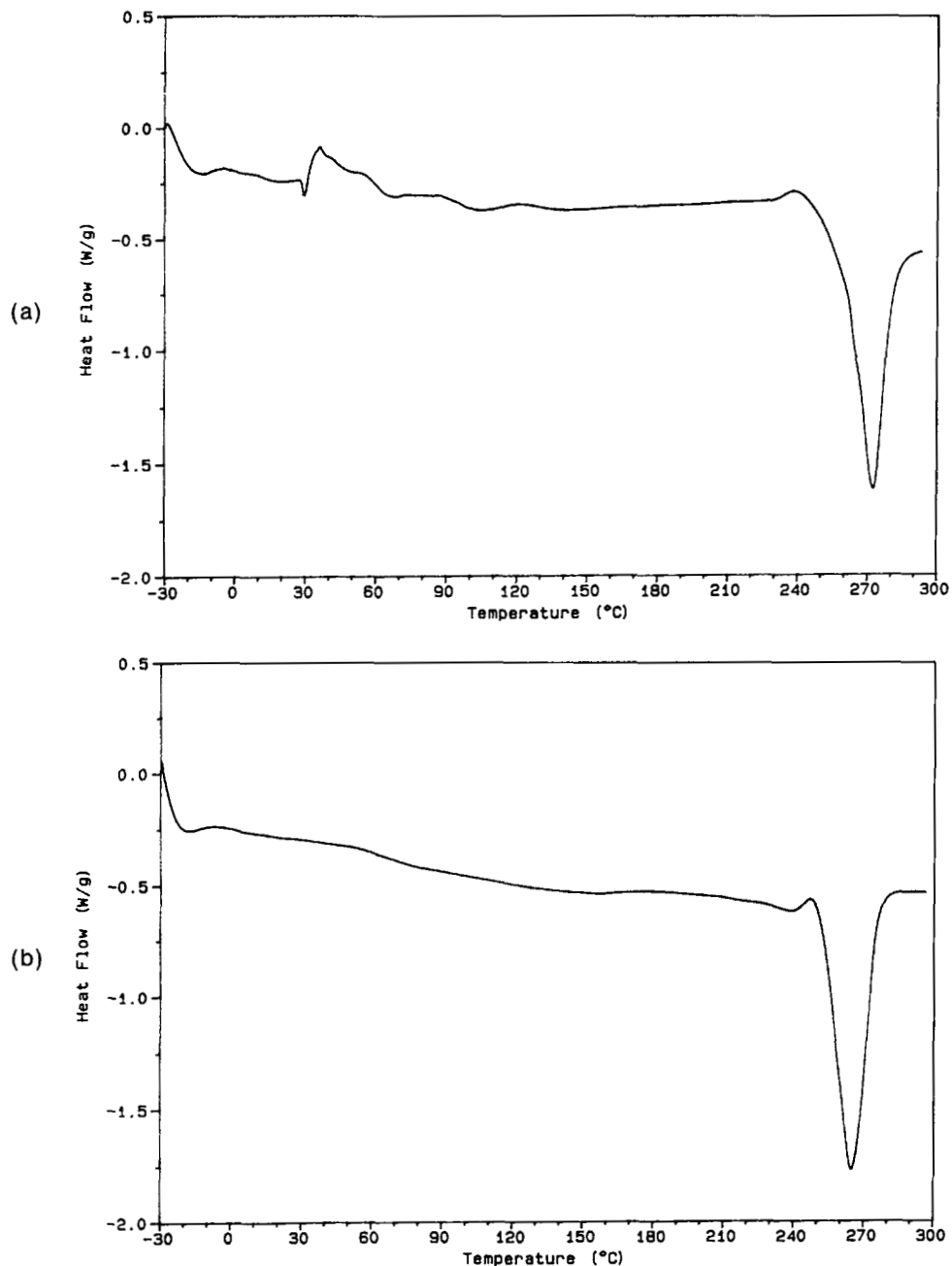
Figure 1   DSC scans of Zytel 101: (a) as received; (b) immediately upon cooling from the melt.

EXPERIMENTAL

Zytel 101, a nylon-6/6, and RDG 114T, a terpolymer of nylon-6, nylon-6/6, and nylon-12, were obtained in pellet form from E.I. Du Pont de Nemours and Elf Atochem North America, respectively, and used as received. The ratio of the three polyamides comprising RDG 114T was not available. A TA Instrument's Thermal Analyst 2100 station having a DSC module (model 2910) was used to evaluate polymer thermal transitions and gross morphology. Samples were sealed in aluminum pans and the DSC was operated at a heating rate of 10°C/min with a N_2 purge. For rescanned samples, cooling from the melt was accomplished *in situ,* at about 40°C/min, with a dewar attachment that holds liquid N_2. The dewar resides over the DSC head. T_m values were based on minima of melting endotherms, whereas T_g values
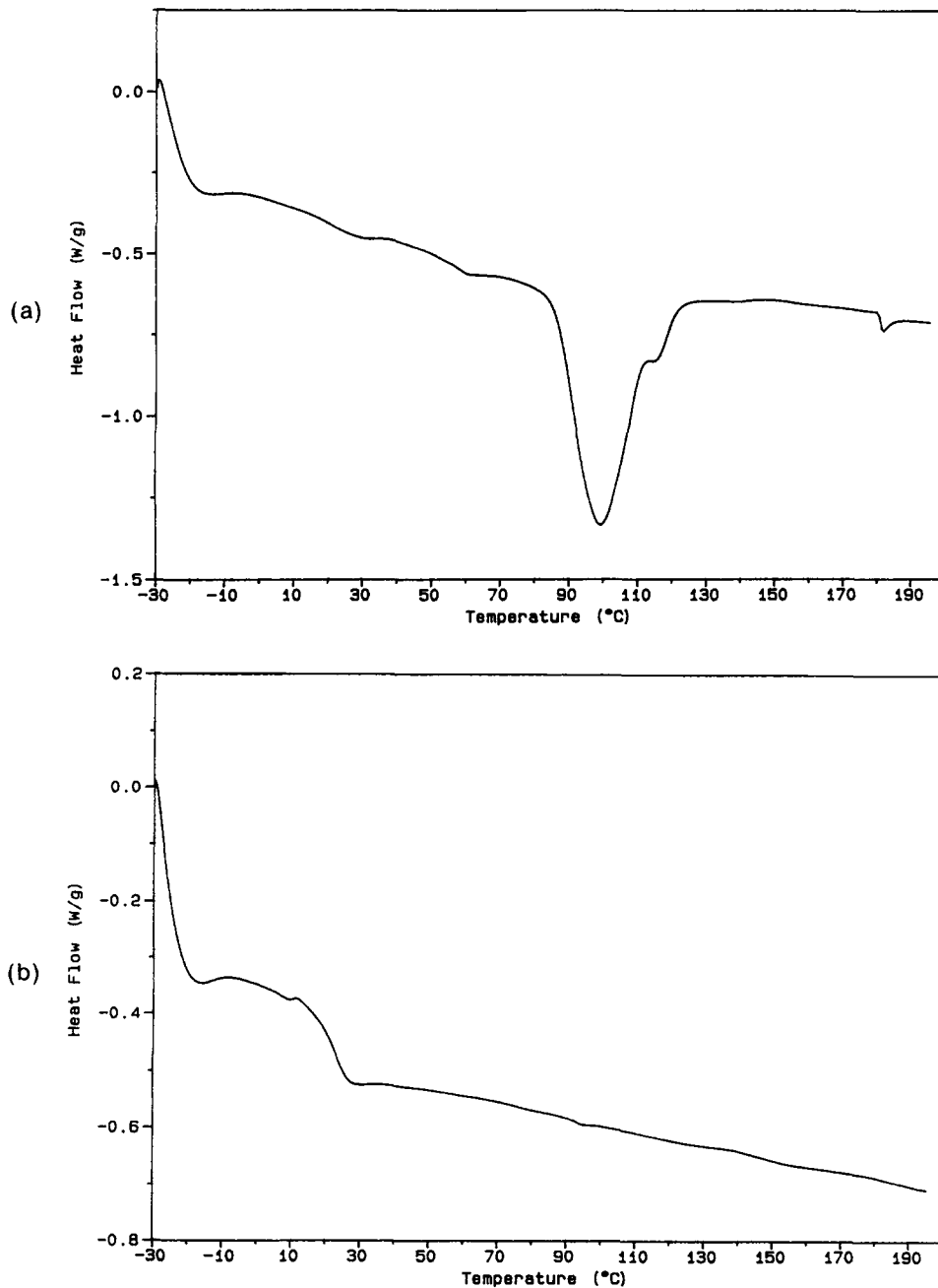
Figure 2 DSC scans of RDG 114T: (a) as received; (b) immediately upon cooling from the melt.

were determined from the intercept resulting from trace discontinuities in the DSC scan.

The tensile properties of RDG 114T were investigated using an Instron and ASTM D638 testing methodology. All reported values are an average of five samples evaluated at room temperature using a crosshead speed of about 5.0 cm/min.

Volatile analyses of RDG 114T were performed using headspace and thermal desorption gas chro-

matography/mass spectroscopy (GC/MS). For headspace studies a 20 ml vial was filled with 1.2 g of sample and heated for 4 h at about 200°C. The headspace was then injected into the gas chromatograph/mass spectrometer for analysis using the following equipment and conditions: a) 12 meter HP-1 column; b) isothermal hold at 40°C for 4 min followed by a 25°C/min ramp to 240°C; and c) an injection port temperature of 325°C. For thermal
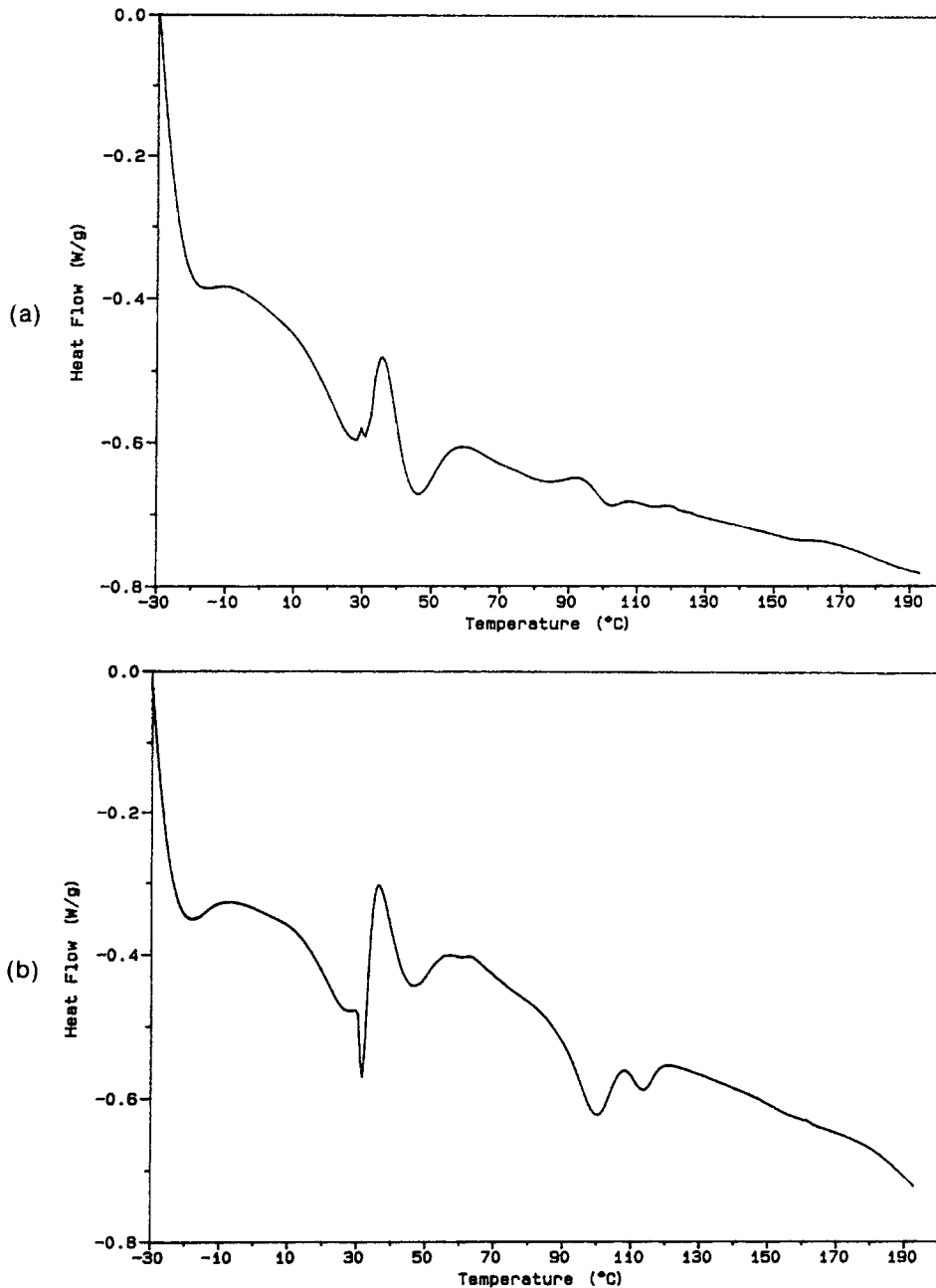
Figure 3 DSC scans of RDG 114T following: (a) 2.5, (b) 6, (c) 24, (d) 92, and (e) 173 h anneal at room temperature.

desorption analysis, a 0.11 g sample was rapidly heated to about 200°C and held for 15 min. Using He as a carrier gas, volatiles produced from the thermal exposure were directly deposited onto the GC column that was cooled to −10°C. The GC oven containing the column was heated at 25°C/min to 325°C and the volatiles analyzed via the mass spectrometer. For both techniques, analyses occurred using a Hewlett Packard GC-5890/MS-5988A system.

DISCUSSION

Figures 1(a) and 1(b) are the as-received and immediate rescan following a rapid cool from the melt, respectively, of nylon-6/6. The primary thermal event associated with both DSC scans is a melting endotherm. The endotherms occur at about 270 and 265°C for the as-received and melted polyamide, respectively. Although recrystallization conditions can have significant effects on the resulting morphology
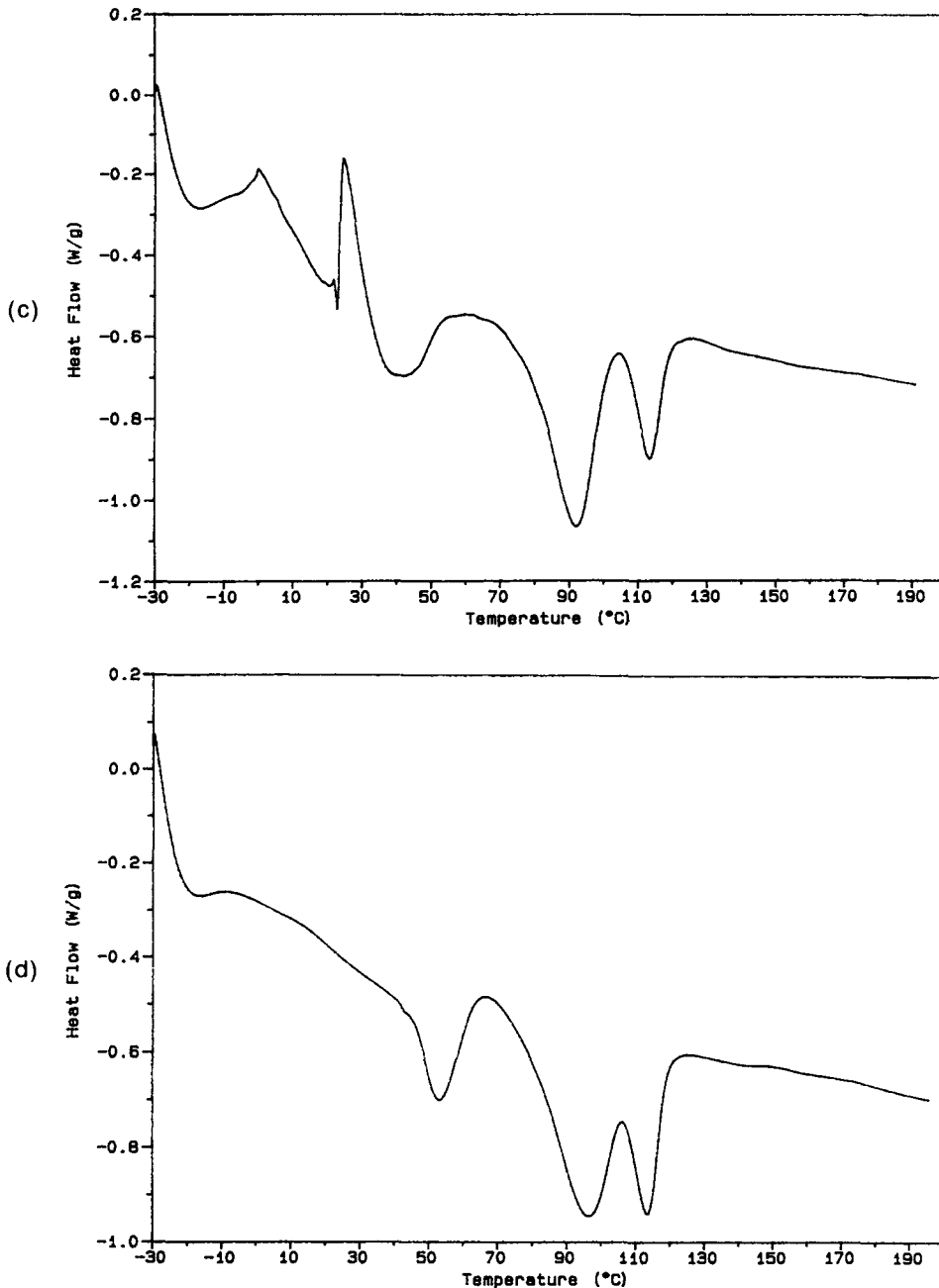
Figure 3   *(Continued from the previous page.)*

for a given polymer system, the observed behavior for nylon-6/6 indicates that its chemical structure is sufficiently regular, and with the presence of hydrogen bonding (high amide frequency) the wholly amorphous state cannot be attained using the identified cooling rate. In addition, using the method discussed in greater detail below, the estimated level of crystallinity for both samples is similar, about 26%.

In comparison, Figures 2(a) and 2(b) are the as-received scan and immediate rescan following a rapid

cool from the melt, respectively, of RDG 114T. The dominant thermal event in the as-received sample is a broad and uncharacteristically low-temperature endotherm. The melting is bimodal, having a major portion at about 100°C and a small shoulder at about 115°C. Immediate rescan, Figure 2(b), of RDG 114T following rapid cooling from the melt shows contrasting behavior to that observed for its nylon-6/ 6 homopolymer counter-part. That is, upon immediate rescanning there is no indication of any crys-
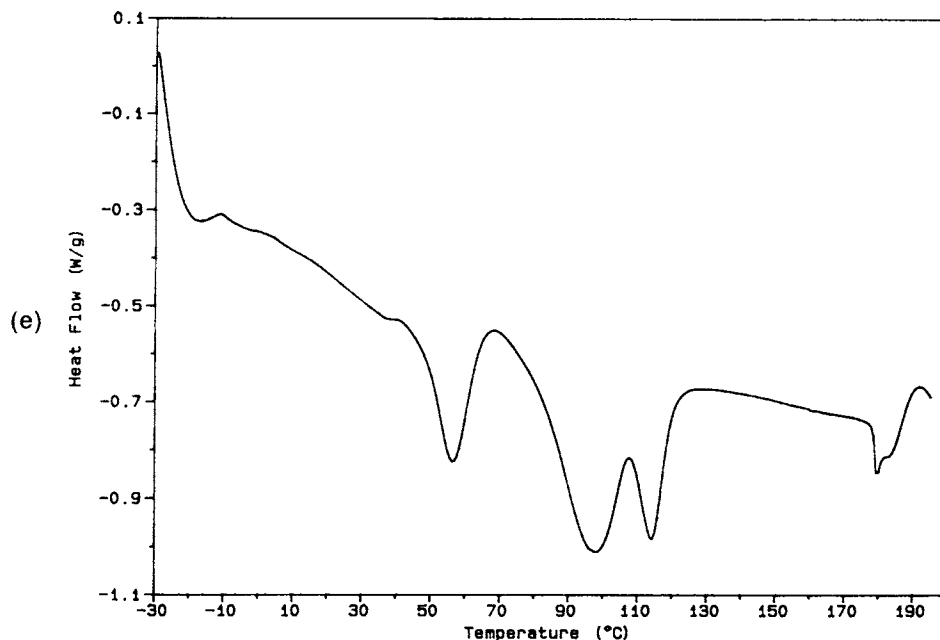
Figure 3 *(Continued from the previous page.)*

talline phases (as detected by DSC) due to the absence of melt endotherms. The sole thermal transition present is a T_g at about 20°C. Therefore, RDG 114T has been quenched to the wholly amorphous state.

Although quenching of semicrystalline polymers from the melt to the amorphous state isn't new,[4] the fact that the polymer has a T_g slightly below room temperature provides interesting behavior. Specifically, room temperature allows sufficient chain mobility to permit crystallization to occur over time. This is clearly illustrated on subsequent scans of RDG 114T samples (Fig. 3(a–e)) that were cooled from the melt and permitted to anneal at room temperature for the following identified times: Figure 3(a) (2.5 h); Figure 3(b) (6 h); Figure 3(c) (24 h); Figure 3(d) (92 h); and Figure 3(e) (173 h, about 7 days). Viewing Figures 3(a–e) in sequence, a

Table I Extent of Crystallization for RDG 114T as Received and Following Several Anneal Times at Room Temperature

RDG 114T Sample	% Crystallinity	$\Delta H_f'$ (J/g)
As Received	21	42
0 h anneal	0	0
24 h anneal	9	18
92 h anneal	20	40
173 h anneal	21	41

gradual and distinctive morphology change is observed over time, i.e., the polymer transforms from a wholly amorphous state to semicrystalline in nature. Figure 2(b) shows the wholly amorphous polymer with a T_g being the sole thermal transition. Figure 3(a) again shows the T_g of the polymer's amorphous region. However, a crystallization exotherm at about 35°C and two small melts, at about 100 and 115°C, are visible. Figures 3(b) and 3(c) are similar to 3(a) except the crystalline melts become more developed. Figures 3(d) and 3(e) show a continued growth in crystallinity of the two originally identified types, but in contrast to the previous samples an additional crystalline region, identified by the presence of a melt at about 55°C, becomes visible. Thus, three distinctive events are apparent in a collective review of the figures from time = 0 to time = 173 h: 1) a T_g at about 20°C; 2) a crystallization exotherm at about 35°C; and 3) broad, multicrystalline melts of potentially different morphologies and/or like-crystalline phases having different degrees of perfection,[4b,5] most dramatically seen at the end of the 7 day anneal.

The relative degree of crystallinity for the as-received and room temperature-annealed samples are investigated. Since the heat of fusion for a perfect RDG 114T crystal is not known, for comparative purposes ΔH_f for nylon-6/6 (196 J/g)[6] was used to calculate relative crystallinities for the as-received and annealed samples via the simple equation

Table II   Tensile Properties of RDG 114T: a) as Received; and b) Following a 7 Day Anneal at Room Temperature

Sample	Tensile Yield Strength (MPa)	Elongation (%)	Young's Modulus (MPa)
time = 0	1.4×10^1	565	1.3×10^2
	+/−0.2	+/−17	+/−4.9
time = 7 Days	2.8×10^1	365	2.8×10^2
	+/−2.4	+/−68	+/−2.4

$$w_c = \Delta H'_f / \Delta H_f \times 100 \quad (1)$$

w_c = % crystallinity
$\Delta H'_f$ = heat of fusion for the semicrystalline sample
ΔH_f = heat of fusion for 100% crystalline sample

By subtracting ΔH_f(formation), occurring at about 35°C, from ΔH_f(melting), the data indicate that there are no crystalline phases in the terpolyamide until about 24 h following cooling from the melt. Table I compares the relative percent crystallinity of the as-received and 0, 24, 96, and 173 h room temperature annealed samples. From the data, RDG 114T's crystallinity increases with anneal time. Also, the as-received and room temperature-annealed samples clearly have different morphologies.

It is well known that the level of crystallinity and its morphology can have profound effects on the mechanical properties of a given polymer around

and above T_g.[7] RDG 114T follows the expected trend. Hand manipulation of tensile test specimens immediately after cooling from the melt show the polyamide to be soft and ductile. However, following an anneal, e.g., 7 days at room temperature, the polymer is rigid. Tensile-property testing methodology was used to evaluate RDG 114T immediately upon cooling to room temperature from the melt and after a 7 day room temperature anneal. The observations of stiffness variation between annealed and unannealed samples are quantified in Table II. Table II shows that the material's percent elongation decreases about 2X and tensile strength and modulus increase about 2X upon permitting the test specimens to anneal, i.e., crystallize. Crystalline regions can act as rigid fillers and temporary crosslink sites, resulting in the observed reduction in elongation, and increase in modulus and tensile strength at the investigated temperature.[7]
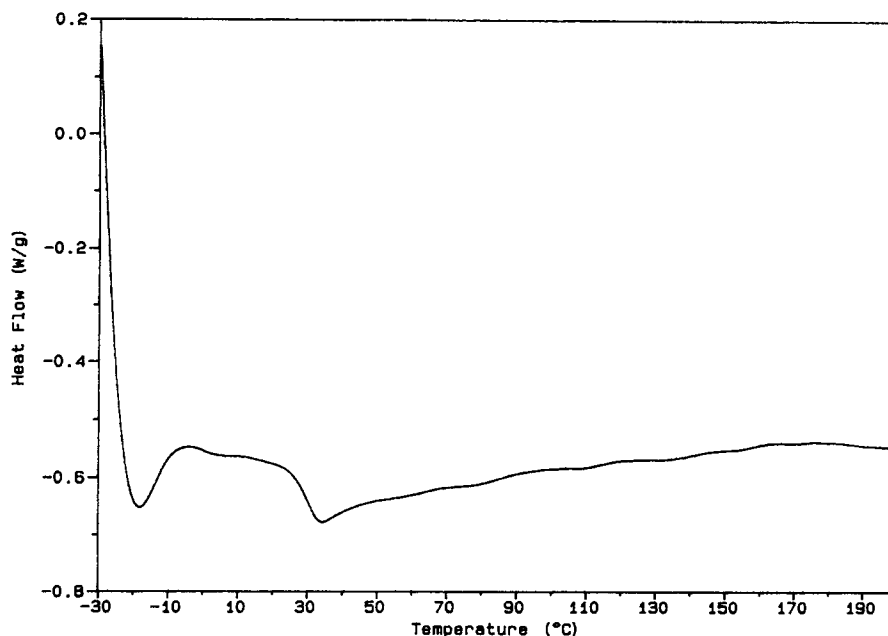
Figure 4   DSC scan of treated RDG 114T immediately upon cooling from the melt.
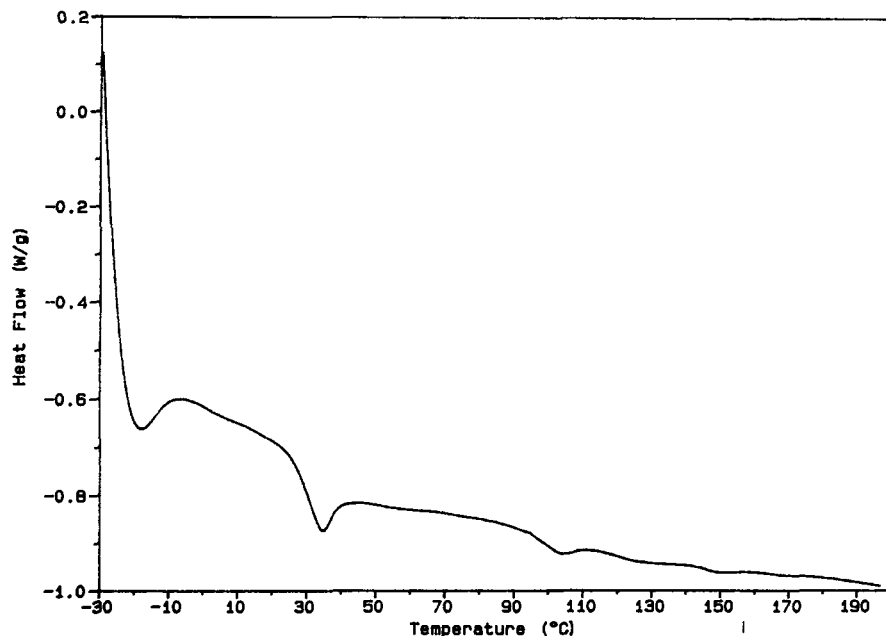
Figure 5 DSC scan of treated RDG 114T following a 72 h room temperature anneal.

Finally, the T_g of polyamides is known to be dramatically affected, through plasticization, by the presence of water.[8] Headspace and thermal desorption GC/MS of RDG 114T were used to investigate the presence of any plasticizers. The analytical technique identifies three volatiles present in the polymer, specifically water, ϵ-caprolactam, and laurolactam, all of which are potential plasticizers (the latter two are monomers for the synthesis of nylon-6 and nylon-12, respectively, and their presence is not surprising). Although the actual amount of each volatile was not quantified, peak area comparisons identify that laurolactam is the dominant species.

The effect of the collective volatiles on RDG 114T's properties was investigated by removing water and residual monomers (confirmed via GC/MS
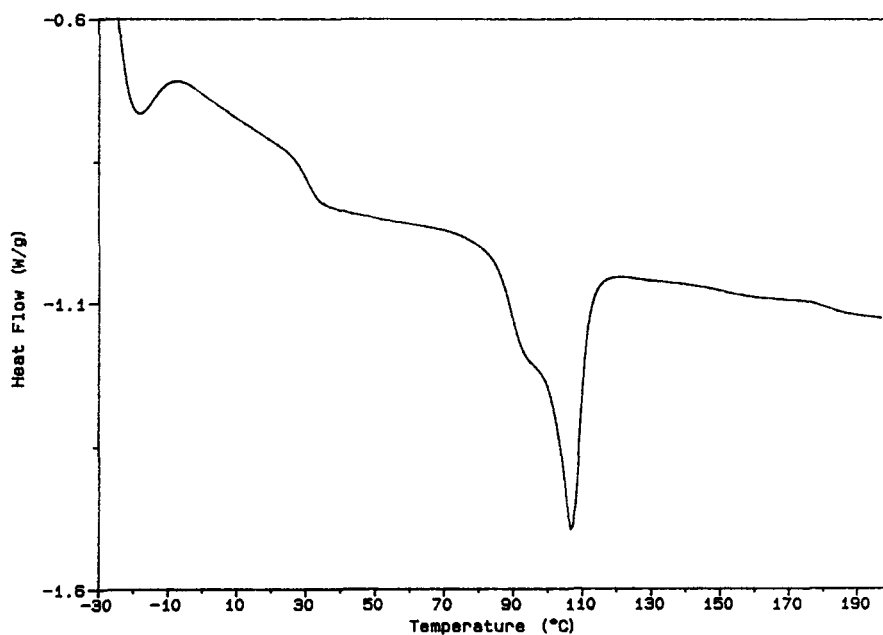

Figure 6 DSC scan of treated RDG 114T following a 15 min anneal at 75°C.

analysis) through vacuum baking at 200°C for 24 h. Once cooled to room temperature it is immediately evident that the properties of treated (vacuum baked) polymers are different than those that received no thermal treatment. Specifically, the treated material is rigid and not ductile. DSC quantifies the effect. Comparing the immediate scan of a treated sample cooled from the melt, Figure 4, with that of an untreated sample, Figure 2(b), shows the T_g has increased to about 30°C from about 20°C, respectively. In addition, unlike the untreated sample, it is only after a 72 h anneal at room temperature (Fig. 5), that there is some evidence of semicrystalline nature (an endotherm at about 100°C), albeit small, in the polymer. This is in contrast to the semicrystalline nature (about 10%) of the untreated sample following a 24 h room temperature anneal, Figure 3(c). However, upon annealing a treated sample above its T_g, e.g., 75°C for 15 min, considerable crystallinity generation occurs (about 10%) (Fig. 6).

SUMMARY

Polyamide structure, composition, amide-frequency, and plasticizers are shown to affect crystalline melt temperatures, degree of crystallinity, and recrystallization behavior. For instance, a homopolyamide such as nylon-6/6 that is structurally regular and has a high amide frequency shows a high melt temperature and readily recrystallizes when rapidly cooled from the melt. In contrast, RDG 114T, a terpolyamide of nylon-6, -6/6, and -12 is structurally irregular and has a reduced amide frequency, resulting in a lower melt temperature, and does not immediately recrystallize upon cooling from the melt, i.e., it is readily quenched to the wholly amorphous state. However, since the terpolyamide has a T_g at about 20°C, due to water and residual mono-mers (ϵ-caprolactam and laurolactam) acting as plasticizers, crystallization occurs over time at room temperature. As a result of crystallinity level variation, the polymer's mechanical properties also change. For example, crystalline phases can act as temporary crosslinks and rigid fillers, resulting in the polymer's tensile modulus increasing from about 1.3×10^2 MPa immediately upon cooling from the melt to about 2.8×10^2 MPa following a 7 day room temperature anneal.

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