Investigation of Melting Behaviors and Crystallinity of Linear Polyamide with High-Aliphatic Content

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ABSTRACT: The melting behaviors and crystal structures of a long alkyl chain polyamide and nylon 18 18, were investigated under annealing and isothermal crystallization conditions. Nylon 18 18 showed multiple melting peaks in differential scanning calorimetry (DSC) thermograms depending on thermal history of the samples. The origin of the multiple melting peaks may be a result of a melting and recrystallization mechanism during DSC scans. Wide-angle X-ray diffraction patterns showed two new diffraction peaks, which appeared at 0.44 and 0.37 nm, and are characteristic peaks of α-form (triclinic structure) of even–even nylons with increasing annealing temperature. The intensities of these peaks increased, and they split further apart, with elevated annealing temperatures. The solid-state ^{15}N CP/MAS NMR spectra of the nylon 18 18 samples that had been quenched and annealed also confirmed the α-crystalline form. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 92–98, 2012

Key words: annealing; crystallization; crystal structures; polyamides; thermal properties

INTRODUCTION

Nylons have excellent mechanical properties resulting from backbone symmetry and total amide density combined with processing induced morphology. The backbone symmetry determines if the polymer can be crystalline or amorphous while the processing controls the orientation of the polymer chains and the degree of crystallinity. Amide density affects T_m and, to some extent, T_g. In the recent years, there have been several reports on nylons with low-amide unit density.[1–4] This is desirable to improve certain properties such as hydrophophobicity, solvent resistance, and processing conditions. These nylons may be thought of as backbone-functionalized polyethylene. They possess the hydrophobic character of polyethylene along with improved thermal properties due to the hydrogen-bonding amide units. These long alkyl chain nylons have also been considered as compatibilizers between polyamides and polyolefins.[5] Previous work by our group and others has emphasized synthesis and crystal structures of nylons with long alkyl chains.[1,6,7] However, there have been no reports on the affect of crystallization conditions on melting behavior of long alkyl chain nylons.

Multiple melting peaks have been reported for many semicrystalline polymers such as poly(ethylene terepthalate),[8–10] poly(butylene terepthalate),[11,12] poly(ether ether ketone)[13-15], and traditional nylons.[16,17] There have been several interpretations proposed for these multiple endotherms based on three hypotheses. First, the two melting endotherms may result from two different crystal morphologies (polymorphism).[18,19] For instance, nylon 12[19] was shown to have two separate peaks depending on the history of the samples. These two peaks were attributed to α and γ-crystal forms of the polymer. The melting point of α nylon 12 was given as 173°C, while the γ form of nylon 12 melted at around 200°C. The multiple peaks seen during differential scanning calorimetry (DSC) scans were explained by recyrstallization to γ form after melting of α form.

The second hypothesis was associated with crystal structures having different lamellar thicknesses, and, therefore, different thermodynamic stabilities.[20] For this scenario, the main crystal population, grown first during isothermal crystallization, is overlaid by a smaller population of crystallites formed in intermediate spaces, perhaps nucleated at the surfaces of the primary crystals. The third interpretation for multiple endotherms during DSC scans is related to melting and recyrstallization of one initial morphology as a result of prior thermal history of the samples.[21] According to this explanation, the lower endotherm involves the onset of melting of the characteristic crystals, which formed rapidly during initial cooling and are less perfect. These crystals experience continuous melting and recyrstallization during the DSC

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analysis to give a trace in which the peak shape observed is the combination of continuously overlapping melting and recrystallization processes.

In this work, the change in melting behavior and crystal morphology of nylon 18 18 was investigated with various annealing and isothermal crystallization conditions. The synthesis and characterization of nylon 18 18 are given elsewhere.[22] Unlike the other long alkyl chain nylons described in literature, nylon 18 18 possesses relatively even distribution of amide units along the polymer chains. Melting behaviors of this long alkyl chain nylon were studied on samples crystallized from either the glassy state or the melt. The samples later were either quenched from melt and annealed at certain temperature or cooled to a certain temperature and isothermally crystallized for a given time. The multiple endotherms are discussed with respect to changes in crystal morphology as seen by wide-angle X-ray diffraction (WAXD), FTIR, CP/MAS solid-state ^{15}N, and ^{13}C-NMR.

Synthesis of nylon samples

Nylon 18 18 was produced here by a melt polycondensation technique. 1,18-Octadecanediamine and 1,18-octadecanedioic acid were supplied by Cognis Corp. and used as received. The monomers were mixed together in equimolar amounts (approximate total 4–5 g) and heated under nitrogen purge using a silicon oil bath at 170–180°C for 4 h, then at 220–230°C for 4 h. At this point, no bubbling was visible in the melt, and a vacuum was applied for 0.5 h. The sample was cooled under vacuum. The resulting material was opaque and white in color. The intrinsic viscosity was determined to be 0.54 dL/g in dichloroacetic acid.

Instrumentation and techniques

Dilute solution viscometry was performed using a Cannon-Ubbelohde 1C C628 viscometer, with dichloroacetic acid as the solvent. Efflux times were recorded at a temperature of 35°C ± 0.2°C.

Nylon 18 18 was melted at 190°C for 3 min and quenched between two cold metal plates. For DSC experiment, all thermal treatment was performed in TA Instruments 2920 using aluminum pans. For all other experiments, the samples were annealed in a conventional oven with an automated temperature controller. The samples were placed in aluminum holder, which was purged with argon for 10 min and sealed after purging to minimize oxidation of the samples. For consistency, the samples annealed using the conventional oven were analyzed by DSC, and the data was compared to those annealed in the DSC.

Transmission FTIR spectroscopy was carried out on a Mattson Galaxy Series FTIR 5000 and 256 transients. DSC experiments were performed on a TA Instruments 2920 using pierced-lid crimped aluminum pans. The temperature and heat capacity were calibrated with indium and sapphire standards, respectively. Unless otherwise stated, DSC analyses were recorded at a ramp rate of 10.0°C/min for both heating and cooling. For a typical DSC analyses, small pieces (~ 6 mg) were cut and placed in an aluminum DSC pan. The samples were heated at 10°C/min to a given temperature and annealed at that temperature for 2 h. They were cooled down to 20°C at a cooling rate of 10°C/min and heated again with a heating rate of 10°C/min trough complete melting. Each sequence of thermal scans was recorded at least three times for reproducibility. The melting temperature was taken as the endotherm maximum, and the crystallization temperature was taken as the exotherm maximum. The overlapped peaks of thermograms were separated by fitting with multiple Gaussian functions using Origin 7.0 data analysis and plotting software.

WAXD measurements were obtained with a Rigaku Ultima III diffractometer operated at 40 kV and 44 mA. Melt-pressed samples were quenched and run with a scan speed of 0.5° per minute from 2° to 45°. The thermal treatments of these samples were as similar as possible to those analyzed by other methods.

CP/MAS solid-state ^{15}N and ^{13}C-NMR experiments were performed on a Bruker MSL 400 MHz spectrometer, and peaks were referenced to the amide nitrogen of ^{15}N labeled glycine at $\delta = 0.0$ ppm and adamantane methane at 29.5 ppm, respectively, as external standards.

RESULTS AND DISCUSSION

The melting behaviors and crystal structures of various nylon 18 18 samples were considered to be the result of both amide group content and the spacing of polymethylene segments between these amide units. Unlike other nylons with shorter alkyl chains, the comformational and librational motions of the polymethylene chains enhance the mobility of the hydrogen bonding amides, enhancing the reordering process during annealing. This may be the reason for the broad melting endotherm seen between 120 and 140°C, most likely associated with melting of ordered domains of less perfect crystallinity then that of the main crystalline regions. This peak occurs in each trace at roughly 5°C above the annealing temperature, consistent with gradual increase in the size and/or perfection of these domains, which is followed by a cold crystallization exotherm around 140°C. Based on this observation and experimental

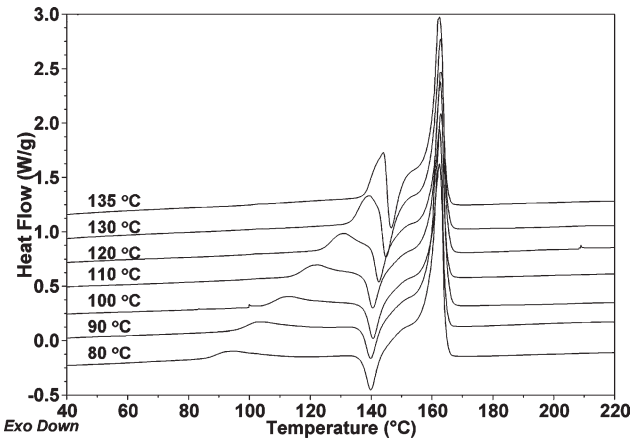

Figure 1 DSC thermograms of nylon18 18 annealed at (a) 80°C, (b) 90°C, (c) 100°C, (d) 110°C, (e) 120°C, (f) 130°C, and (g) 135°C for 2 h (samples annealed in DSC).

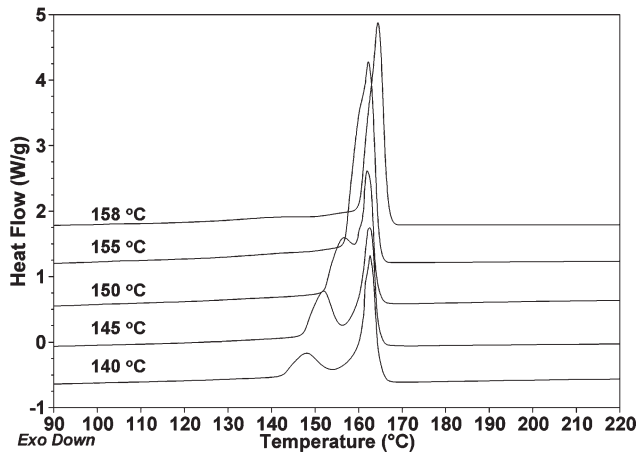

Figure 2 DSC thermograms of nylon18 18 annealed at (a) 140°C, (b) 145°C, (c) 150°C, (d) 155°C, and (e) 158°C for 2 h (samples annealed in DSC).

data given in this work, the DSC results for annealed nylon 18 18 samples were divided into two sections.

Figure 1 shows the DSC scans of nylon 18 18 samples annealed at different temperatures in the range of 80–135°C. The samples were first quenched between two cold metal plates from the molten state before DSC analysis. All curves have a sharp endothermic peak resulting from melting of the main crystal population at around 163°C. They also posses another wide endotherm as a result of smaller crystal population found ~ 12°C above the annealing temperature. The lower melting peak becomes stronger and sharper with increasing annealing temperature, while the higher melting peak area slightly decreases.

Overall, crystallinity is not affected with increasing annealing temperature for given time periods. The percent crystallinity (X%) was calculated using a procedure based on group additivity values from Van Krevelen[23] to give the theoretical ΔH_f. The equilibrium heat of fusion, ΔH_f, was calculated by adding two amide groups (67.4 J/g each) and 34 methylene groups (at 270.8 J/g each) to give a total of 338.2 J/g. The calculated percent crystallinity is lower than for typical commercial polyamides, which may be a result of high-conformational mobility of the polymethylene chains kinetically inhibiting crystallization. Samples annealed up to 135°C showed the same percent crystallinity (Table 1), which meant even at 135°C, the temperature was not high enough for the extensive molecular motion required to form proper register of amide groups into a lamella structure. However, imperfections such as gauche conformations in the polymethylene chains can be excluded under this low-temperature annealing conditions. In addition, the perfection and narrower distribution of the crystals may occur as a result of the fact that the temperature in this region was high enough to give polymer chains enough mobility to form high-ordered crystals.

DSC scans of nylon 18 18 that had been annealed for 2 h at higher temperatures are shown in Figure 2. Two distinct peaks are observed for those samples annealed in the range of 140–158°C. The lower endothermic peak was 5–7°C higher than the annealing temperature and increased linearly with annealing temperature until it merged with the higher peaks at an annealing temperature 158°C.

TABLE I
DSC Parameters of Nylon 18 18 Samples Annealed Between 80 and 135°C

T_a[a] (°C)	T_m1[b] (°C)	T_m2[b] (°C)	ΔH_m1[c] (J/g)	ΔH_m2[c] (J/g)	X_{DSC} (%)[d]
80	94	162.5	4.7	66.96	19.8
90	102.4	162.5	5.6	65.11	19.2
100	112	162.9	7.1	63.05	18.6
110	122.4	162.6	10	61.45	18.2
120	131.2	162.9	11.4	59.65	17.6
130	139.3	162.8	12.2	59.87	17.7
135	143.9	162.4	12.6	59.66	17.6

[a] Annealing temperature.
[b] Melting point of lower and higher endotherms.
[c] Heat of fusion of lower and higher endotherms.
[d] Percent crystallinity based on only ΔH_m2.

TABLE II
DSC Parameters of Nylon 18 18 Samples Annealed Between 140 and 158°C

T_a[a] (°C)	T_m1[b] (°C)	T_m2[b] (°C)	ΔH_m1[c] (J/g)	ΔH_m2[c] (J/g)	H_m[d] (J/g)	X_{DSC} (%)[e]
140	147.9	162.6	16.4	47.6	77.7	23
145	151.9	162.5	24.3	43.1	87.8	26
150	156.6	162	36.1	34.3	93.1	27
155	160.7	162.2	52.3	28.5	115.8	34
158	163.1	164.4	29.6	36.6	95.7	28

The low-temperature endotherm also increased continuously in size with increasing annealing temperature, while the heat of fusion of the high-temperature endotherm decreased. These changes are more pronounced compared to the results obtained for low-temperature annealing. The heat of fusion for each endotherm, the melting points, and total crystallinity is given in Table II. Overlapped peaks were separated by fitting with a multiple Gaussian function. The heat of fusion of the higher melting domains is almost independent of the annealing temperature below 135°C but decreased with higher annealing temperatures. This result cannot be explained by the increased heat of fusion of the lower endotherm at the expense of the higher endotherm, because the transformation of the higher melting crystals to lower melting crystals is prohibited by thermodynamics. However, it clearly shows that two endotherms are somehow associated, and the melting/recrystallization hypothesis may be well suited to explain this result.

It is noteworthy that, unlike the low-temperature annealing, the total percent cystallinity also increases as the annealing temperature increased. The minimum temperature required for the polymer chains to overcome the energy barrier to form larger crystalline domains of nylon 18 18 may be around 140°C. Once the annealing temperature reaches 158°C, only one endotherm is observed, and the melting point was increased to 164°C. This may be due to the fact that at this temperature, defects can be excluded, and the chains can be reorganized to form thicker crystals with a higher melting point.

Figure 3 shows the DSC traces of nylon 18 18 annealed at 145°C for different periods of time. The upper endothermic peak was nearly constant at 163°C, while the lower temperature melting peak gradually shifted from 151 to 154°C with increasing annealing time. The heat of fusion for the lower endotherm also increased with the annealing time from 18 to 27 J/g. By contrast, the heat of fusion of the upper endothermic peak decreases with time from 30 to 20 J/g. These changes may be attributed to the perfection and/or thickening of the thinner lamellar crystals produced by annealing the sample. The total crystallinity, on the other hand, is almost invariant with annealing time in range of 22–25%. This result may indicate that at this specific temperature melting/recrystalization is in equilibrium.

The DSC heating curves of Nylon 18 18 samples, isothermally crystallized from the melt, are given in Figure 4. The samples were heated to 190°C with a heating rate of 10°C/min and held at this temperature for 5 min to erase thermal history of the samples. Then, they were cooled to a given temperature with a cooling rate of 60°C/min and held at that temperature for 2 h. After being isothermally

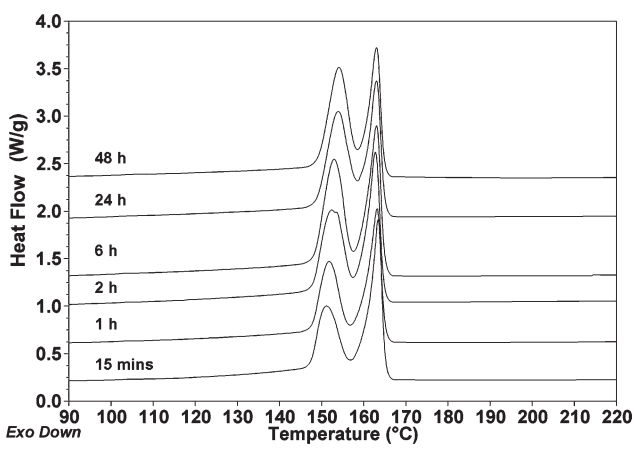

Figure 3 DSC thermograms of nylon18 18 annealed at 145°C for different times from bottom to top 15 min, 1, 2, 6, 24, and 48 h.

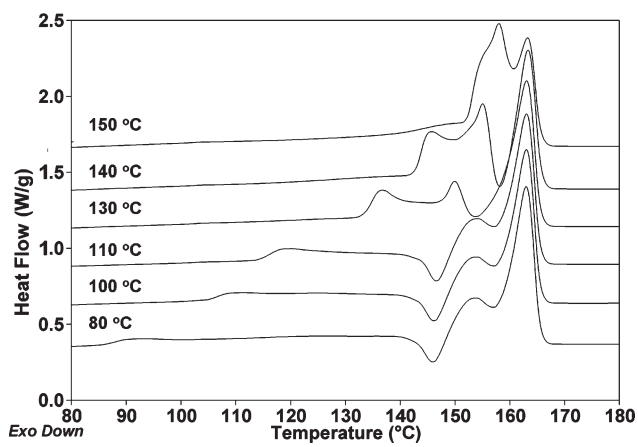

Figure 4 DSC heating thermograms of nylon18 18 isothermally crystallized from melt at (a) 80°C, (b) 100°C, (c) 110°C, (d) 130°C, (e) 140°C, and (f) 150°C for 2 h (cooling rate is 60°/min).

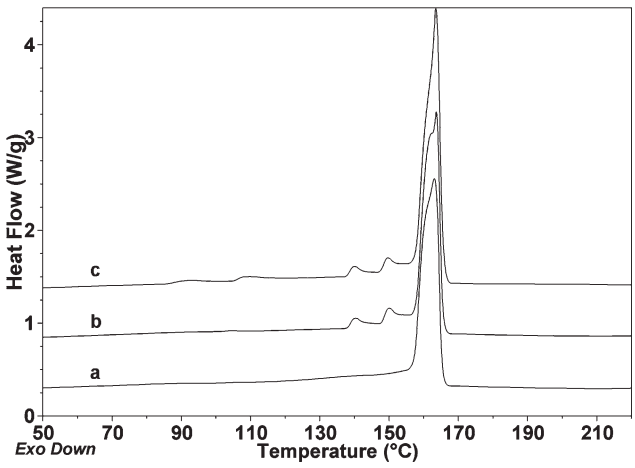

Figure 5 DSC thermograms of nylon18 18 annealed at (a) first at 80, 100, 135, 145, and finally 155°C for 2 h; (b) first 155°C then 145°C, and 135°C for 6 h; (c) first 155°C then 145, 135, 100, and 80°C for 2 h.

crystallized at the specified temperature for 2 h, the samples were cooled with a rate of 60°C/min to 20°C and then heated up to 190°C with a heating rate of 10°C/min. Thermograms obtained from isothermal crystallization of nylon 18 18 from the melt are totally different from those obtained by annealing from the glassy state. Unlike the quenched samples that shows slight variations in DSC traces even at lower temperatures, the samples isothermally crystallized up to 110°C gave almost the same thermograms with a higher cold crystallization peak. A higher cold crystallization peak is not surprising considering crystallization during cooling was not as fast as for the quenched sample, this leads to more organized chains melted and recrystallized at a higher temperature. Once the isothermal crystallization temperature reaches 130°C, there are three distinct peaks and no crystallization peak.

The two lower endotherms may be attributed to different sizes of crystals. The lower peaks are at the same position as the lower peak resulting from annealing from the glassy state. This endotherm may result from annealing at a given temperature. The middle peak, on the other hand, must be a result of both melting of the crystals formed during the cooling process and recrystallization of smaller, imperfect crystals into more stable and thicker lamellae. The same observation was given for nylon 10 14.[24] When nylon 10 14 was isothermally crystallized from the glassy state, three distinct peaks were observed. Two lower endotherms were attributed to different thicknesses, and perfection of the crystals formed during isothermal crystallization. The position of the main melting endotherm was constant regardless of the isothermal crystallization temperature.

Figure 5 shows the DSC curves for the stepwise annealed samples of nylon 18 18. The top thermogram is of the sample first annealed at 155°C for 2 h and then progressively annealed at 145, 135, 100, and 80°C for another 2 h at each annealing temperature. The sample annealed first at 155°C for 2 h and then progressively annealed at 145 and 135°C for 6 h gave the middle thermogram. After the stepwise annealing of the sample at lower temperatures, multiple melting endotherms were observed, and the number of melting endotherms was dependent on the number of annealing steps with the number of endothermic peaks increasing with the number of annealing steps. The bottom thermogram was of the sample annealed progressively at 80, 100, 135, 145, and 155°C for 2 h. It showed only a main endothermic peak due to the fact that the crystals formed during lower annealing steps transformed to thicker lamellae with each step. It is noteworthy to mention that the main melting peak was almost invariant for both annealing process, and the heat of fusion for the thinner lamella was much lower compared to those samples annealed at specific temperatures.

A series of WAXD patterns, recorded at room temperature, of the annealed nylon 1818 at various temperatures for 2 h is shown in Figure 6. The sample quenched from the molten state without further thermal treatment is also presented for comparison. The quenched sample shows only an amorphous halo. The samples annealed up to 130°C show partially ordered structures but still are mostly amorphous. Once the annealing temperature reaches 140°C, two new diffraction peaks appeared at 0.44 and 0.37 nm, which are characteristic peaks of

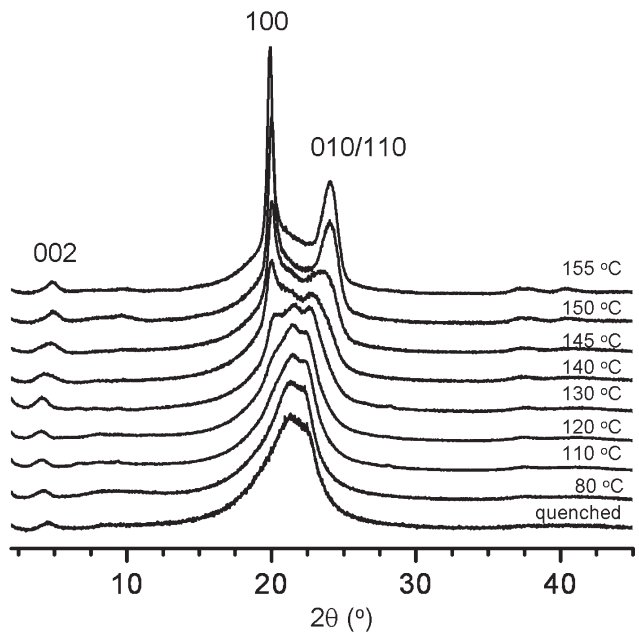

Figure 6 The WAXD patterns of the nylon 18 18 annealed at various temperatures for 2 h from bottom to top: quenched, 80, 110, 120, 130, 140, 145, 150, and 155°C.

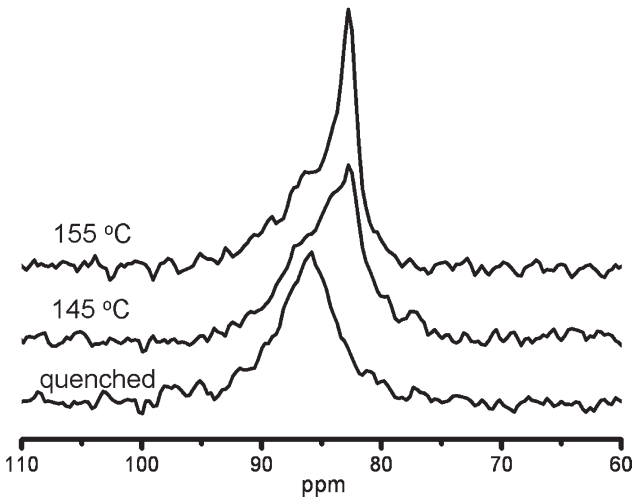

Figure 7 The solid state ^{15}N CP/MAS NMR spectrum of the nylon 18 18 (a) quenched samples, (b) annealed at 145°C, and (c) 155°C for 2 h.

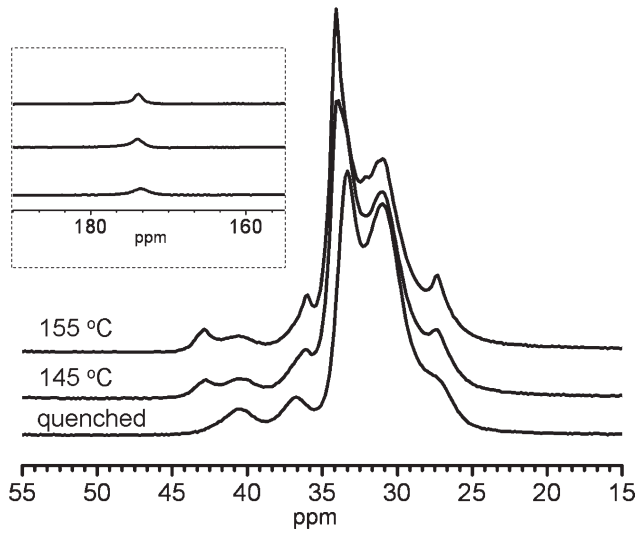

Figure 8 The solid-state ^{13}C CP/MAS NMR spectrum of the nylon 18 18 (a) quenched samples, (b) annealed at 145°C, and (c) 155°C for 2 h.

the α-form (triclinic structure) of even–even nylons. The (100) and (010) planes (which represent the interchain spacing within the hydrogen-bonded sheets and intersheet spacing, respectively) continuously separate as the annealing temperature increases. The intensity of the diffraction peaks also increases with increasing annealing temperature. This suggests that the crystals become more perfect as the degree of crystallinity increases.

Nylons can show different crystalline forms and can exhibit crystal–crystal transitions.[25–27] The WAXD patterns of nylon 11,[26] for instance, show α to δ and again to α transition with prolonged annealing time. Nylon 12 12[27] was reported to give a strong diffraction peak at 0.42 nm, characteristic of a pseudohexagonal structure (or γ form), but once crystallized at 90°C from the melt, the γ form was transformed to the α form. No X-ray polymorphism was observed for nylon 18 18 during annealing, which suggests only one type of crystalline form develops for this polymer. Therefore, the multiple melting endotherms are not related to different crystalline structures but are a result of the melting of α-form crystallites of different size and perfection. Finally, hydrogen bonding is still the most important factor controlling the crystal morphology of this nylon even with its low-amide density.

Previous works by our group on various A-B and AA-BB nylons have shown that the chemical shift of the amide nitrogen is determined by crystalline form.[28–31] The α form gives a chemical shift at ~ 84 ppm, whereas the γ form gives a chemical shift around ~ 89 ppm. Most other nylon X 18 where X is even possess α-form crystallinity, the thermodynamically stable form for even–even nylons. However, the even–even nylons *X* 18 previously reported show a trend toward higher amorphous content as the aliphatic content increases. Quenched nylon 18 18 gives a broad peak resulting from a highly amorphous system, with a peak value at 86 ppm (Fig. 7). Once the sample is annealed at 145°C for 2 h, a new peak appears at 84 ppm associated with the α structure. The peak intensity increases while the amorphous peak decreases when the sample is annealed at 155°C for 2 h. This result is consistent with the WAXD patterns of Figure 6.

The solid-state ^{13}C CP/MAS NMR spectrum of the nylon 18 18 samples, neat, annealed at 145°C, and at 155°C are shown in Figure 8. The peak at 173.5 ppm of carbonyl group is shifted to 173.9 ppm on annealing. The aliphatic regions, on the other

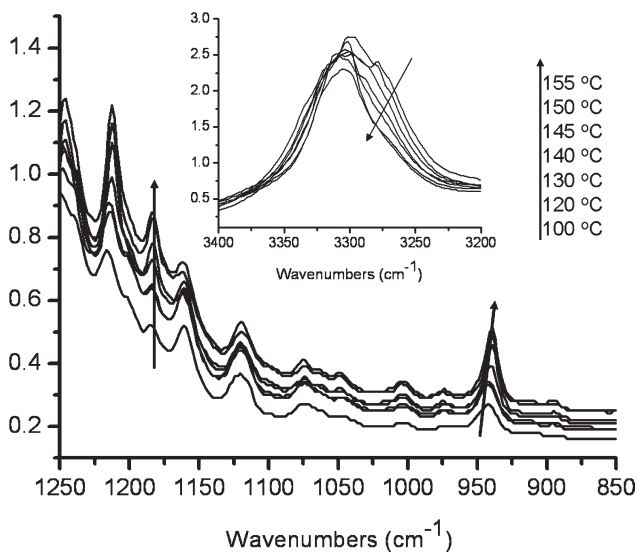

Figure 9 Partial FTIR spectrum of annealed nylon 18 18 with increasing annealing temperature (arrows indicate direction of increasing temperature).

hand, showed significant changes, especially for those carbons α to the amide nitrogen. There is one broad peak at 40.5 ppm for quenched nylon 18 18. After annealing at 145°C, a new peak is seen at 42.9 ppm for highly crystalline regions, which shifted even further and became more distinct once the sample is annealed at 155°C. The peak at 40.5 ppm can be still observed, but the intensity of this peak is much smaller compared to the quenched sample. Similar sharpening is seen for the all-trans polymethylene peak at 33–35 ppm and the β-CH_2 to carbonyl peak at 25–26 ppm. The peaks are narrower for the annealed samples due to the fact that increasing crystallinity leads to less conformational disorder and narrower peaks.

FTIR spectra of annealed nylon 18 18 are given in Figure 9. For comparison, the same sample was used throughout the annealing process. The band at 942 cm^{-1} (amide IV and C—CO stretching mode)[26] is related to the crystalline region of the polymer. On annealing, this peak shifts to 939 cm^{-1} and becomes more narrow as a result of restricted conformational motions of the amide group in the crystalline regions. The band at 1184 cm^{-1} is due to stretching vibration mode of C—C bonds.[26] There is no significant change on this band up to 130°C. Once the annealing temperature reaches 140°C, the intensity of this band is much higher and narrower. The band around 3305 cm^{-1} is due to the stretching vibration of NH groups (amide A),[32] and can be related to hydrogen bonding.[27] Enhanced vibration as a result of conformational disorder leads to a broader band, while an ordered structure will result in narrowing of this band. For nylon 18 18 samples, the annealing process lead to narrowing of this band as well as giving a more defined peak.

CONCLUSIONS

The melting behaviors and crystal structures of a long alkyl chain polyamide, nylon 18 18, were investigated under annealing and isothermal crystallization conditions. Nylon 18 18 showed multiple melting peaks in DSC thermograms depending on the thermal history of the samples. The annealed samples posses only α-form crystals, which was confirmed by WAXD patterns and solid-state ^{15}N CP/MAS NMR spectrum of the nylon 18 18. The multiple endotherms can be explained by the hypothesis that the origin of the multiple melting peaks may be as a result of the melting and recrystallization mechanism during DSC scans. Finally, hydrogen bonding is still the most important factor controlling the crystal morphology of this nylon even with its low-amide density.

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