Synthesis of Copolyamides Containing Octadecanedioic Acid: An Investigation of Nylon 6/6,18 in Various Ratios

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ABSTRACT: A series of copolyamides of various compositions of nylon 6 and nylon 6,18 were produced. Increased resistance to organic solvents resulted from greater incorporation of nylon 6,18, as shown by decreasing solubility. High-resolution solution NMR indicated there were four amide carbonyls that corresponded to the four possible pairs of comonomer units, allowing detailed composition determination. The melting points of the comonomers decreased as the ratio of hydrogen bonding amide units to methylene groups increased, going from nylon 6 to copolymers with an increasing number of nylon 6,18 repeat units. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2062–2067, 2006

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INTRODUCTION

Copolyamides are of commercial interest because copolymerization allows tailoring of physical properties and processability, mainly from decreased crystallinity compared to that with homopolyamides.[1] Typical nylon homopolymers are made with either AB- or AABB-type repeat units, allowing several combinations: AB monomers with other AB monomers, AABB monomers with other AABB pairs, or AB with AABB systems. The most widely reported nylon copolymers involve two AB monomers (typically lactams[2–6]) or lactams with diamines and diacids in order to combine the properties of AB- and AABB-type polymeric systems. Widely used copolymers are made up of nylon 6 units with nylon 6,6 monomers in various ratios. Comonomers may be entirely aliphatic[7–13] or may incorporate some aromatic content.[14,15] However, even in copolymer samples with reduced crystallinity, virtually all the amide linkages are fully hydrogen-bonded, leading to a material with good mechanical properties.[9] A key design parameter of nylons is hydrocarbon content, as reflected in the ratio of amide to methylene units, and equilibrium water content is generally reduced by the incorporation of higher aliphatic monomers, that is, nylon 6/6,9 compared to nylon 6 or 6,6.

We recently reported the synthesis and characterization data for a series of high-aliphatic-content homopolyamides incorporating octadecanedioic acid with a variety of aliphatic diamines.[16] These nylons showed decreased moisture uptake and increased resistance to organic solvents compared with nylons with higher amide density. Similar behavior may develop in nylon 6 by incorporating nylon 6,18, and this report details the syntheses, solvent resistance, thermal properties, and both solution and solid-state nuclear magnetic resonance (NMR) spectroscopy of such copolymers.

EXPERIMENTAL

Synthesis

All materials were used as received. Octadecanedioic acid was supplied by Cognis Corp (Cincinnati, OH). All diamines and solvents were purchased from Aldrich (Milwaukee, WI).

The polymers were produced by melt polycondensation at temperatures in excess of 230°C. Varying amounts of ε-caprolactam, combined with equimolar amounts of hexamethylenediamine and octadecanedioic acid, were charged to a test tube, which was then flushed with nitrogen for approximately 1 h. The scale of each reaction was on the order of 4–5 g of total material. The test tube was then heated in a high-temperature wax bath (>230°C) while maintaining a positive nitrogen atmosphere for 3–4 h. At this point, high vacuum was applied for an additional 3–4 h. The test tube was then allowed to cool to room temperature and was carefully broken while wrapped in a

paper towel. The resulting solid product varied in color from light brown to white.

Larger-scale synthesis of nylon 6/6,18 copolymers in molar ratios from 20 : 80 to 80 : 20 was performed to produce about 150 g of the final product. Polycondensation reactions were performed in 1-L glass kettle reactors heated by an appropriately sized heating mantle. For these reactions, stirring was achieved with a mechanical stirring rod inserted through a Teflon sleeve capable of maintaining a vacuum. The reaction was stirred in the melt under a nitrogen purge for several hours; then vacuum was pulled for several more hours until extremely high viscosity was attained and stirring became difficult. At this point, the contents of the kettle were poured into a beaker of ice water. The polymer was broken up, washed with methanol, and dried in a vacuum oven.

Figure 1 Nylon 6/6,18 copolymers in an 80 : 20 mixture by weight of 2,2,2-trifluoroethanol : $CHCl_3$.

Characterization

Dilute solution viscometry (DSV) was carried out using a Cannon-Ubbelohde 1B E847 viscometer. The samples were dissolved in m-cresol, with efflux times recorded at 30°C ± 0.2°C. Fourier transform infrared (FTIR) measurements were recorded using a Mattson Galaxy Series FTIR 5000.

Thermogravimetric analysis (TGA) was performed on a TA Instruments 2960, controlled by a Thermal Analyst 2100. In each case, the temperature was ramped at a heating rate of 20°C/min under nitrogen to well above the degradation temperature (>500°C). Analysis of each trace gave the temperature at which 5% weight loss occurred, which was recorded as the decomposition onset temperature. In addition, the peak maximum of the derivative of the weight loss curve was recorded as the peak decomposition temperature. Differential scanning calorimetry (DSC) experiments were performed on a TA Instruments 2920, controlled by a Thermal Analyst 2100. The samples were heated to above the melt and held isothermally for 5 min, then cooled to room temperature at 10°C/min to determine the crystallization temperature, taken as the peak of the crystallization exotherm. The samples were again ramped to above the melt at a rate of 10°C/min, and the melting temperature recorded was as the endotherm maximum.

All solution ^{13}C-NMR experiments were performed on a Varian $^{UNITY}INOVA$ 500 MHz spectrometer operating at 125.7 MHz. Routine solution ^{13}C-NMR experiments used a pulse width of 7.8 μs, an acquisition time of 1.3 ms, and a relaxation delay of 1 s. A minimum of 5000 scans were taken for each sample. All samples were prepared at a concentration of approximately 10 wt % in an 80 : 20 weight mixture of trifluoroacetic acid in $CDCl_3$, and referenced to the center peak of the deuterated solvent triplet at δ = 77.23 ppm. {^{1}H}^{13}C-gated decoupling (DECGATE)

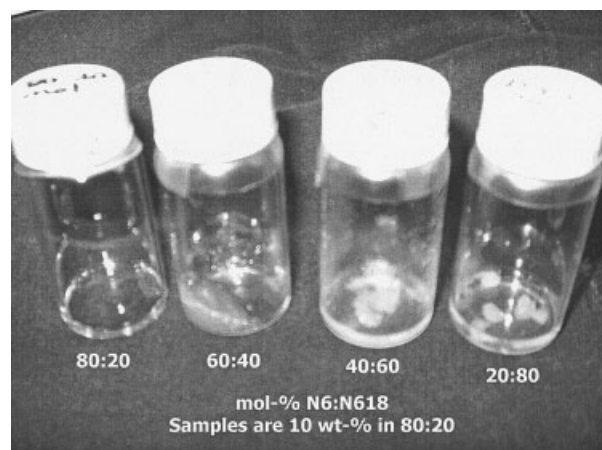experiments were performed using a relaxation delay of 10 s, a pulse width of 11.5 μs, and an acquisition time of 0.5 s. Decoupling was employed during the pulse and acquisition times only.

Cross-polarization magic angle spinning (CP/MAS) solid-state ^{15}N-NMR experiments were performed on a Bruker MSL 200-MHz spectrometer operating at 20.28 MHz with a 7.5-mm Chemagnetics double-resonance probe, with a sample spinning speed of 2.2 kHz. Cross-polarization was conducted using a 3.5-μs ^{1}H 90° pulse followed by a mixing time of 2 ms. An acquisition time of 42 ms using high-powered decoupling was used, with a relaxation delay of 3 s between scans. No fewer than 20,000 scans were acquired for each sample. Peaks were referenced to the amide nitrogen of ^{15}N-labeled glycine at δ = 0.0 ppm as an external standard.

Fiber spinning was carried out on homopolymer and copolymer samples that had been dried in an oven at 75°C under vacuum for 48 h. Fibers were spun at a temperature of 270°C from a 500-μm spinneret at an extrusion speed of 3 mm/min, with a take-up speed of 70 m/min. All fiber-spinning experiments were performed under a nitrogen atmosphere. The fibers were then drawn at a ratio of approximately 4.6 to 1, at a temperature of 80°C. Further heat treatment was conducted at 120°C at constant length for 10 min.

RESULTS AND DISCUSSION

The incorporation of high-aliphatic-content monomers into nylons increases their resistance to selected organic solvents. For example, a mixture of 80 wt % 2,2,2-trifluoroethanol (TFE) and 20 wt % chloroform-d has been used for NMR characterization of a wide range of nylons with varying aliphatic content, for example, nylon 6, nylon 12, and nylon 6,12.[17–19] However, this solvent mixture does not dissolve nylons
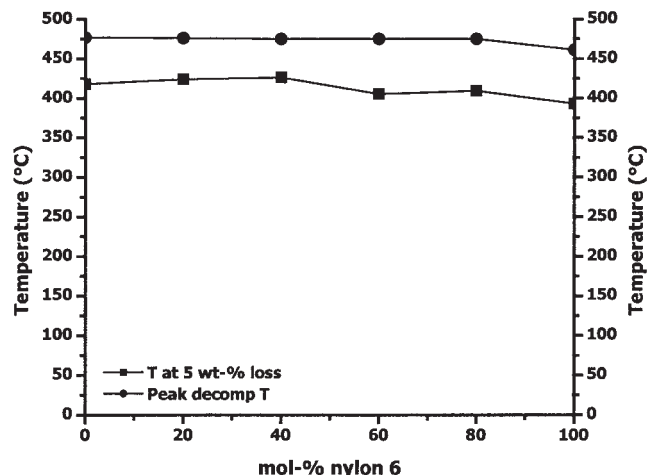
Figure 2 TGA data for nylon 6/6,18, recorded at 20°C/min.

TABLE I
Thermal Data for Nylons 6/6,18, Taken at a Scan Rate of 10°C/min.

N6 mol %	T_d (°C)	T_p (°C)	T_c (°C)	ΔH_c (J/g)	ΔH_m (J/g)	T_m (°C)
0	418	477	178	50	58	197
20	424	476	153	39	28	187
40	426	475	121	32	23	164
60	405	475	113	32	26	155
80	409	475	—	—	—	—
100	393	461	181	74	48	221

No crystallization or melting was observed for the 80 : 20 N6 : N6,18 sample.

incorporating octadecanedioic acid. It can be seen in Figure 1 that this mixture dissolved only the copolymer containing 80 mol % nylon 6, gave a swollen gel for the 60 mol % nylon 6 sample, and only swelled the 40 mol % nylon 6 sample. The 20 mol % nylon 6 sample showed no signs of dissolving at all, nor did the nylon 6,18 homopolymer. All copolymers were soluble in *m*-cresol, and use of this solvent gave intrinsic viscosities of 1.29 dL/g for the 20 mol % nylon 6 sample, 1.53 dL/g for the 40 mol % nylon 6 sample, 1.62 dL/g for the 60 mol % nylon 6 sample, and 1.51 dL/g for the 80 mol % nylon 6 sample. Despite variation in viscosity with nylon 6 content, all polymers were easily processed by melt-pressing films or extruding fibers.

The infrared spectra of the copolymers contained the characteristic peaks of amide groups and methylene groups. However, the spectra were more complex for the copolymers than for the homopolymers because of the differences in the proximity of the intrachain amide units, which affects crystallinity and packing in the amorphous domains. The randomness of the copolymer resulted in a variety hydrogen bonds of differing strength, leading to groups of peaks in each of the signature regions that could be attributed to polyamides. Specifically, broad or overlapping peaks were observed at 3360–3214 cm^{-1} (amide A, H-bonded N—H stretching), 3091–3081 cm^{-1} (amide B, overtone of N—H in-plane bending), 2961–2891 cm^{-1} (C—H stretching), 1659–1630 cm^{-1} (amide I, C—O stretch), 1571–1530 cm^{-1} (amide II, C—N stretch and CO—N—H bend), 1283–1281 cm^{-1} (amide III), 981–938 cm^{-1} (amide IV, C—CO stretch), 722–720 cm^{-1} (CH$_2$ rocking), 689 cm^{-1} (amide V, N—H out-of-plane bend), and 591–584 cm^{-1} (amide VI, C—O out-of-plane bend).

A graph of the temperature at 5 wt % loss and the peak decomposition temperature versus nylon 6 con-

tent for the copolymer series are shown in Figure 2. The peak decomposition temperature plot shows little deviation, and the temperature at 5 wt % loss decreased only slightly with increasing nylon 6 content. A possible explanation for the latter is that, as nylon 6 content increased, there were more nylon 6 units at the chain ends, increasing the possibility of a backbiting depolymerization reaction that would generate volatile ε-caprolactam. This process decreased with increased nylon 6,18 content, leading to a larger number of nylon 6,18 chain ends. A limit to the depolymerization process was reflected by the peak decomposition temperature results, which were relatively constant in excess of 460°C for all samples studied (Table I).

Cooling traces for these copolyamides are shown in Figure 3. The T_c decreased with increasing incorporation of nylon 6 until at 80 mol % nylon 6, no crystallization exotherm was observed at all. The crystallization temperature and enthalpy of crystallization both decreased with increasing nylon 6 content, as shown
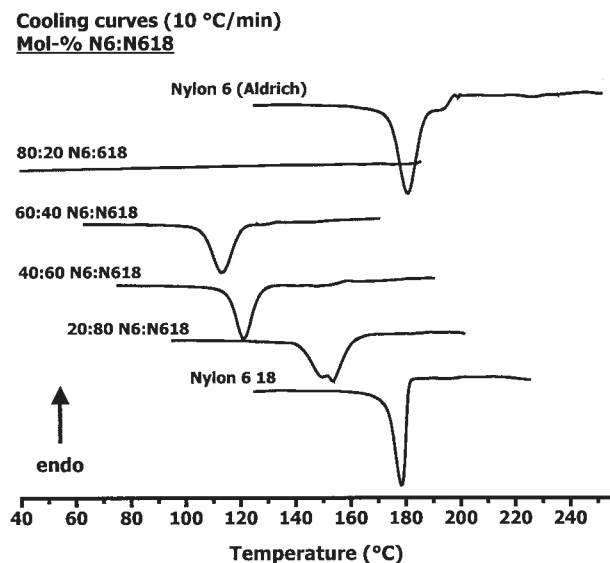

Figure 3 DSC crystallization traces for nylon 6/6,18, recorded at a cooling rate of 10°C/min.
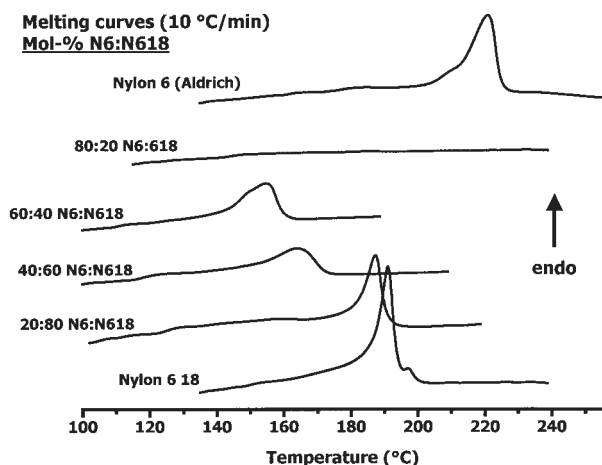
Figure 4 DSC melting traces for nylon 6/6,18, recorded at a heating rate of 10°C/min.

in Table I. The ability of the copolymer to crystallize was disrupted to a larger degree when nylon 6 was the larger fraction of the copolymer, consistent with formation of a random copolymer.

It must also be noted that copolymerization of AB- and AABB-type nylons statistically led to AB units that were antiparallel to each other on either side of an AA or BB monomer unit. Nylon 6 is inherently a polymorphic material, displaying two crystal forms, with the chains hydrogen bonded in a parallel or antiparallel manner, and this is an additional factor to consider when looking at the crystallization of nylon copolymers of this type. The nylon 6,18 repeat unit had no chain directionality, so that random incorporation of a nylon 6 unit was not as detrimental to the ability of the polymer to crystallize. When considering aliphatic chain length, 2–3 nylon 6 monomer units possibly could be incorporated into the nylon 6,18 crystalline domain without disrupting the overall hydrogen bonding and packing scheme of nylon 6,18. The opposite case— random incorporation of a C6 diamine or C18 diacid into nylon 6—entirely disrupted the crystalline structure of nylon 6, in effect acting as a plasticizer directly incorporated into the polymer backbone.

The DSC heating traces are shown in Figure 4 for comparison. As nylon 6 incorporation increased, a significant broadening of the melting endotherm resulted. This can be attributed to crystal size both decreasing on average and having a broader distribution. Even at relatively low incorporation of nylon 6 into nylon 6,18 (i.e., 20 mol %), the distribution of crystallite sizes in the sample increased and the melting peak broadened significantly. However, the overall peak remained relatively well defined. In contrast, when a small amount of nylon 6,18 was incorporated into nylon 6, the melting peaks were not well defined. Indeed, there was no observable crystalline melting

for the 80:20 mol % sample and no peak in the crystallization trace. Because of the difference in melting points of nylon 6 (221°C) and nylon 6,18 (197°C), there should have been two distinct melting endotherms if blocky homopolymer segments were present. The single melting points for all copolymers, lower and broader than the respective homopolymers, were consistent with completely random structures.

The solution ^{13}C-NMR results showed a carbonyl peak at 185 ppm, indicating the presence of residual ε-caprolactam. Residual monomer is typically found in commercial samples of nylon 6.[18] Qualitative analysis of the routine solution ^{13}C-NMR spectra showed that as the copolymer ratio changed, there was a change in peak intensity in the aliphatic region for specific peaks attributed to either nylon 6 or nylon 6,18. Quantitative NMR studies were done in the manner outlined below.

To do quantitative solution {^{1}H}^{13}C-NMR experiments, a solution ^{13}C-NMR T_1 study was performed on one of the copolymer samples to determine the longest T_1 value for the carbonyl carbons that possessed the longest spin-lattice relaxation times, with a t_{null} of 0.4 s. From this a T_1 of 0.6 s ($T_1 = 1.44 \times t_{null}$) was calculated. For the subsequent DECGATE experiments, a relaxation delay of 4 s was used, which is about 5 times the longest T_1 of the sample. The carbonyl and aliphatic regions (most notably the carbons α to the amide linkages, at about 43 and 34.5 ppm), shown in Figure 5, clearly reflected the changing ratio
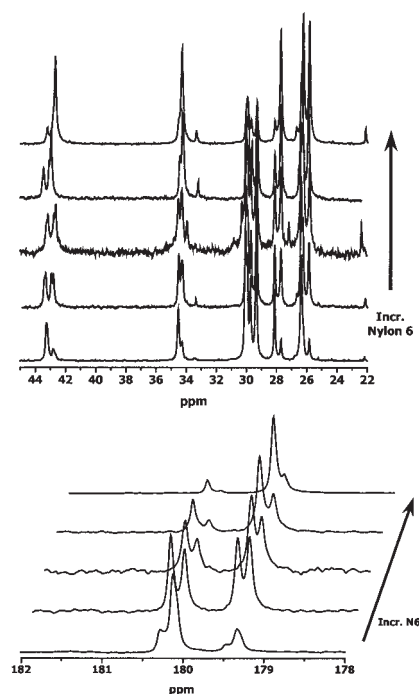

Figure 5 Aliphatic and carbonyl regions of the DECGATE solution {^{1}H}^{13}C-NMR of nylon 6/6,18. Samples were dissolved in a mixture of HFIP : CDCl$_3$
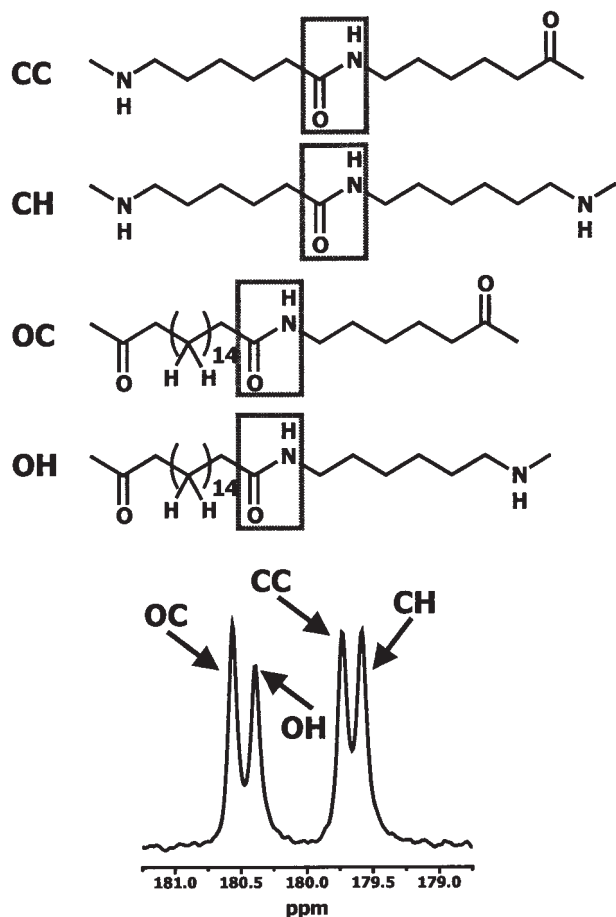
Figure 6 Solution ^{13}C-NMR carbonyl peak assignments according to adjacent monomer unit.

of nylon 6 to nylon 6,18. In addition, sufficient resolution of the carbonyl peaks was obtained in order to identify all combinations of comonomer repeat units possible based on two different carbonyls each bonded to a different amine group, as shown in Figure 6. The nylon 6 unit carbonyl could be bonded either to the amine group of another nylon 6 unit (CC) or to a hexamethylenediamine amine group (CH). The octadecanedioic acid carbonyl could be bonded either to the amine group of a nylon 6 unit (OC) or to a hexa-

TABLE II
Integrated Values of Carbonyl Peaks from DECGATE Solution {^{1}H}^{13}C NMR of Nylons 6/6,18

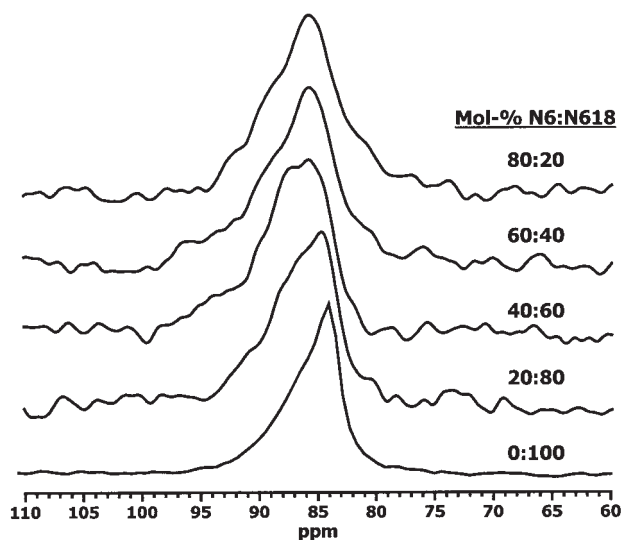| Molar ratio N6 : N6,18	Carbonyl integration values			
	CC	CH	OC	OH
24 : 76	1.3	8.0	13.6	77.1
43 : 57	3.2	18.2	16.4	62.3
72 : 28	25.1	28.7	24.7	21.5
79 : 21	36.3	27.5	21.9	14.4
85 : 15	51.2	25.9	18.0	4.9
93 : 7	73	15.9	9.9	1.2

Figure 7 Solid-state CP/MAS ^{15}N-NMR of nylon 6/6,18.

methylenediamine amine group (OH). Table II shows the integrated values for each of these combinations compared to monomer feed ratios. At a copolymer mole ratio of 72 : 28 N6 : N6,18, the values for each combination are nearly equal. As the comonomer incorporation approached that of either homopolymer, the polymers remained random. That is, there was a significant peak intensity for the nylon 6 units bonded to hexamethylenediamine units (CH) even when there was mostly nylon 6 present, and conversely, there were significant peaks for the octadecanedioic acid bonded to a nylon 6 unit (OC) when there were mostly nylon 6,18 segments.

Crystallinity in nylons is complex, and it has been shown that the thermodynamically stable α-form for AB and AABB nylons produces a nitrogen NMR peak at ~84 ppm, whereas the γ-form is observed at ~89 ppm; the amorphous phase is usually a broad peak between and under either or both these two crystalline peaks.[20–22] Solid-state ^{15}N-NMR results, shown in Figure 7, support the DSC results, with the 80 mol % nylon 6 copolymer showing a peak indicative of an entirely amorphous sample. In going from nylon 6,18 homopolymer to 20 mol % nylon 6 incorporation, the peak at ~δ = 84 ppm shifted slightly downfield, and a significant amorphous shoulder could be seen. For the 40 mol % nylon 6 sample, the effect was more pronounced and appeared to be mostly amorphous. This increase in amorphous content continued as nylon 6 content increased.

The physical properties and enthalpy of melting for the nylon copolymer fibers are given in Table III. Enthalpy of melting was generally greater than that of the unprocessed samples, indicating enhanced crystallinity from the extrusion process. Indeed, the results showed that the extrusion process induced some crys-

TABLE III
Physical Properties and Enthalpy of Melting of Nylons 6/6,18

Nylon 6 (mol %)	Draw ratio	Initial modulus (GPa)	Tensile strength (GPa)	Elongation at break (%)	Enthalpy of melting (J/g)
0	6.2	4.3 ± 0.7	0.44 ± 0.08	10 ± 2	64
20	5.8	4.0 ± 0.8	0.50 ± 0.08	14 ± 6	60
40	5.2	2.9 ± 0.5	0.41 ± 0.10	15 ± 4	54
60	4.2	3.3 ± 0.5	0.44 ± 0.09	15 ± 2	32
80	5.3	2.8 ± 0.3	0.44 ± 0.08	19 ± 2	38
100	5.8	6.6 ± 1.0	0.73 ± 0.07	15 ± 4	66

tallinity even in the 80 mol % nylon 6 copolymer, which showed no crystallinity in the unprocessed sample. The enthalpy decreased with increasing nylon 6 content, similar to the unprocessed samples. The initial modulus generally decreased with increasing nylon 6 content to a minimum value of 80 mol % nylon 6 and increased again with the nylon 6 homopolymer. The tensile strength values of the copolymers and the nylon 6,18 homopolymer were virtually identical, within experimental error, although that of the nylon 6 homopolymer is higher. Last, the elongation at break increased slightly with increasing nylon 6 content (and a decrease in crystallinity).

CONCLUSIONS

Copolymers of nylon 6 and nylon 6,18 were synthesized and characterized. The solubility of the copolymers in a trifluoroethanol:chloroform mixture decreased with increasing nylon 6,18 content. The thermal behavior of this series of copolymers suggests that when nylon 6,18 is the minor component, there is a significant decrease in the crystalline content, and when nylon 6 is the minor component, the endotherms and exotherms are broadened but still consistent with being crystalline materials. Solution ^{13}C-NMR spectra showed distinct carbonyl and aliphatic peaks for statistically random polymer repeat units. Solid-state ^{15}N-NMR data indicated that crystallinity was disrupted and reduced by comonomer incorporation, but less for nylon 6 incorporation into nylon 6,18-rich samples than for the converse. The sharp peak in the nylon 6,18 sample, indicative of the α form, broadened with nylon 6 incorporation of 20 mol %, and this trend continued as more nylon 6 units were added. At a copolymer composition of 80 mol % nylon 6 to 20 mol % nylon 6,18, a completely amorphous sample was obtained, as confirmed by formation of a transparent, nonhazy melt-pressed film. Fiber tensile properties were high and generally similar for the nylon 6,18 homopolymer and the copolymers, although all displayed values significantly lower than those of the nylon 6 homopolymer. With increasing nylon 6 content, the elongation at break generally increased, whereas the initial modulus decreased. The

heat of melting was significantly lower for the 60 and 80 mol % nylon 6 copolymers compared to both homopolymers and the other two copolymers. Surprisingly, the highly drawn fiber of the 80 mol % nylon 6 copolymer displayed a crystalline melting point not seen in the undrawn sample.

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