Preparation and Characterization of Selectively Isotopically Labeled Nylon 66 Polymers[†]

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ABSTRACT: A series of isotopically labeled high molecular weight nylon 66 (poly(hexamethylene adipamide)) polymers have been synthesized and characterized. Six polymers have been prepared, each of which is labeled at only one chemically distinct site of the repeat unit. The polymers have been labeled at either the 1,1,6,6, the 2,2,5,5 or the 3,3,4,4 positions of the hexamethylenediamine moiety or the 2,2,5,5 or the 3,3,4,4 positions of the adipoyl moiety with deuterium or at the 1,6 positions of the adipoyl moiety with carbon-13. The molecular weight distributions of the as-polymerized materials, prepared by interfacial polymerization, exhibited low molecular weight tails and were transformed to the most probable distributions by melt equilibration. The physical properties of these polymers have been extensively characterized by a variety of methods: the isotopic and chemical compositions have been established by solution NMR and FT-Raman spectroscopic methods, the crystal modification has been characterized by X-ray diffraction, and the percent crystallinity has been characterized by X-ray diffraction and DSC and is compared to results obtained from solid-state ^{2}H NMR.

Introduction

Many modern methods of polymer physics require the preparation and use of labeled materials. Examples of such experiments are forced Rayleigh scattering, which requires polymer chains labeled with a fluorescent label at a well-defined position in the chain; neutron scattering, where in most cases the entire chain is labeled with deuterium to provide maximum contrast with the protonated matrix; and solid-state ^{2}H NMR spectroscopy, which requires polymers that have been selectivley labeled at one chemically distinct site within each repeat unit. There exists a large body of literature which purports to use labeled *polymers*, but the labeled material is of such dubious pedigree that the veracity of the conclusions drawn from the experiments is not certain.[1] We report here the syntheses of six selectively labeled nylon 66 *polymers* (poly(hexamethylene adipamides)) that are of high isotopic purity and of similar molecular weights and molecular weight distributions to that found in commercial materials. These selectively labeled polymers will be subsequently used to characterize the molecular dynamics of nylon 66 via solid-state NMR methods[2] and to obtain a detailed vibrational assignment.[3]

Solid-state NMR methods have been of use in characterizing the segmental dynamics of macromolecules, with great molecular specificity[4] in terms of the rates and amplitudes of motion, for both completely amorphous[5,6] and semicrystalline[7,8] polymers. Systems containing segments composed of methylene chains are of particular interest because of the considerable number of models of motion[9] that may be tested by comparison with experimental results; however, in these cases it is experimentally difficult to differentiate the different types of motion that each methylene group and its adjacent neighbors undergo. This difficulty may be overcome by labeling sequential positions in the polymer chain. Furthermore, these methods are of use in estimating the number of chain segments which are in crystalline and noncrystalline environments. In this paper we also compare values of crystallinity obtained for these polymers from solid-state ^{2}H NMR experiments to those we report here from X-ray diffraction and DSC methods.

A detailed vibrational assignment for nylon 66 has not been possible due to the near degeneracy of some of the vibrational modes associated with the 10 methylene groups in each repeat unit and the lack of Raman data due to fluorescence of the polymer when exposed to visible light. The as-polymerized polymers reported on here have a sufficiently small fluorescent background when irradiated in the visible to allow[3] the collection of Raman spectra. More importantly, the specifically isotopically substituted polymers allow the vibrational modes predominately associated with an individual methylene group to be analyzed without spectral overlap from modes that are predominantly associated with other methylene groups.

Experimental Section

Selectively isotopically labeled diamines and diacid chlorides were obtained from MSD Isotopes, Division of Merck Frosst Canada, Inc., Montreal, Canada. The monomers were reported to be of very high isotopic and chemical purity and thus were used as received without further purification. The monomers used (reported isotopic purity) were hexamethylene-*1,1,6,6*-d_4-diamine (97–99%), hexamethylene-*2,2,5,5*-d_4-diamine (97–99%), hexamethylene-*3,3,4,4*-d_4-diamine (97–99%), adipoyl-*2,2,5,5*-d_4 chloride (98.7%), adipoyl-*3,3,4,4*-d_4 chloride (99%), and adipoyl-*1,6*-$^{13}C_2$ chloride (99%). Unlabeled monomers (nominal purity 98%) were obtained from Aldrich Chemical Co. and were used without further purification. Each monomer was confirmed by solution 80-MHz ^{1}H NMR spectroscopy (1% solutions of the diamines in D_2O and 1% solutions of the dichlorides in $CDCl_3$) to be both chemically and isotopically pure with an uncertainty of less than 2%. Spectroscopic grade methylene chloride was used as a polymerization solvent without further purification.

Polymers were prepared on a nominal scale of 50 mmol via the following procedure. A solution of 5.81 g (0.050 mol) of hexamethylenediamine and 10.60 g (0.100 mol) of sodium carbonate in 300 mL of water was cooled in an ice bath for 15 min before addition as the water phase to a 1 L Waring blender. With the blender initially operating at moderate speed, a solution of 9.15 g (0.050 mol) of adipoyl chloride in 200 mL of methylene chloride (which had been previously cooled in an ice bath for 15 min) was added to the blender as the organic phase during a period of 30–60 s. During addition of the organic phase the speed of the blender was progressively increased to its maximum to avoid excessive agglomeration of the polymer. Immediately after addition of the organic phase an additional 20 mL of methylene chloride was used to rinse the original acid chloride container. The polymerization medium was stirred at maximum speed for an additional 3 min. The resulting white fluffy polymer was collected on a fritted glass filter. This product was then vigorously washed with water in the blender and recollected on a fritted glass filter a minimum of 3 times, until the filtrate was neutral. This product was then washed with acetone and recollected on a fritted glass filter; this acetone wash was repeated twice. The product was vacuum-dried at 80 °C overnight to yield 6–8 g of white, fluffy, fibrous polymer with an inherent viscosity in the range 0.9–1.9 dL/g. The reference

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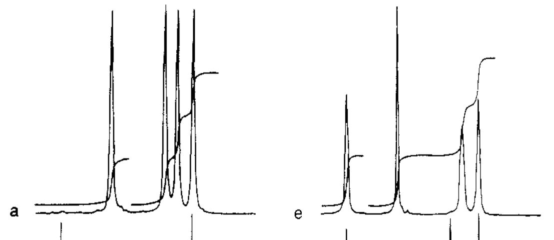

Figure 1. 300-MHz ^1H solution NMR spectra of isotopically labeled as-polymerized nylon 66 polymers as 1% solutions in trifluoroacetic acid-d_1/D_2O/TMS (99/1/0.1): a, NY16NH; b, NY25NH; c, NY34NH; d, NY25CO; e, NY34CO; f, NY16C13; g, control; h, reference commercial nylon.

commercial nylon used as a comparative standard is Zytel 101.

Room temperature solution NMR spectra were obtained on IBM FT80A, Varian XL200, and Nicolet QE300 spectrometers. Differential scanning calorimetry was carried out on a Mettler TA-3000 instrument. Gel permeation chromatographs were obtained on a Waters 150 HPLC instrument (Shodex AD-80M/S columns) using *m*-cresol containing 1% trihexylamine at 110 °C.

Wide-angle X-ray diffraction scans were obtained by using a Philips X-ray diffractometer (symmetrical transmission mode, curved crystal monochrometer, pulse height analyzer, divergence and receiving slits of 1°, and Cu Kα radiation). For these experiments the powdered sample was sandwiched between 0.1-mil Mylar films to give a sample approximately 0.3 mm thick. Typically, data were collected in a fixed time mode with a step size of 0.02° in 2θ and run from 3° to 60° in 2θ. Background scattering was fitted with a cubic spline function and removed. The remaining pattern was fit with a series of Gaussian peaks that were defined by the refinable parameters of height, position, and breadth. Instrumental broadening was measured (using NBS-640A) and found to be 0.19°. The crystalline persistence lengths in various crystallographic directions were estimated by using the breadths of the 001 and 100 reflections (after correction for instrumental broadening) using the Scherrer equation. Crystallinity was estimated by ratioing the areas of the fitted peaks attributable to crystalline scattering to the total scattering after the background was removed.

FT-Raman spectra of samples contained in 1-mm glass capillaries were acquired by using 300 mW of 1.064-μm radiation from a Spectron SL50 Nd/YAG laser. The scattered radiation was analyzed by using a Bomem DA3.02 interferometer equipped to operate in the near-infrared.[10] Two thousand scans were averaged resulting in a total measurement time of 1 h. The intensities were corrected for the instrument response function. Spectra obtained after extensive irradiation established that no detectable polymer degradation took place during the collection of the Raman spectra.

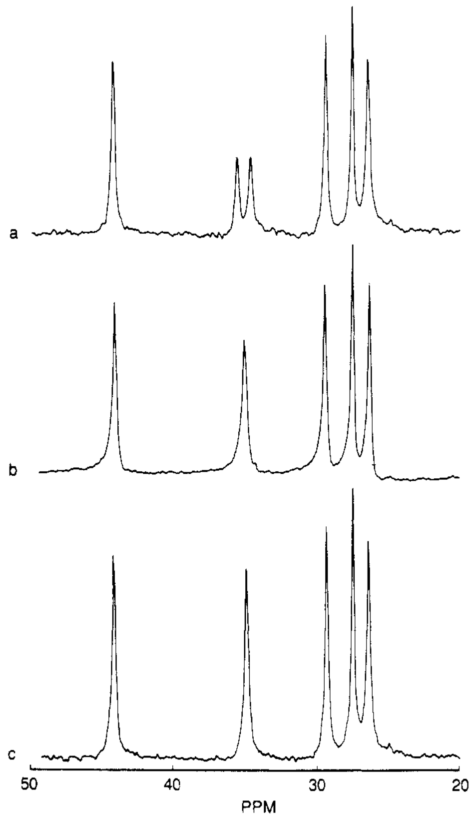

Figure 2. 50-MHz $^{13}C\{^1H\}$ solution NMR spectra of isotopically labeled as-polymerized nylon 66 polymers as 3% solutions in trifluoroacetic acid-d_1: a, NY16C13; b, control; c, reference commercial nylon. Only the methylene region of the spectrum is shown.

Table I
Isotopically Labeled Nylon 66 Synthetic Yields

polymer	code	yield, %
poly(hexamethylene-*1,1,6,6*-d_4 adipamide)	NY16NH	53
poly(hexamethylene-*2,2,5,5*-d_4 adipamide)	NY25NH	50
poly(hexamethylene-*3,3,4,4*-d_4 adipamide)	NY34NH	51
poly(hexamethylene adipamide-*2,2,5,5*-d_4)	NY25CO	53
poly(hexamethylene adipamide-*3,3,4,4*-d_4)	NY34CO	55
poly(hexamethylene adipamide-*1,6*-$^{13}C_2$)	NY16C13	57
poly(hexamethylene adipamide)	control	57

Results

Six specifically isotopically labeled nylon 66 polymers were prepared by low-temperature (5 °C) interfacial condensation polymerization[11-14] of either labeled hexamethylenediamine or labeled adipoyl chloride with the nonlabeled counterpart. The polymers were labeled in symmetrical positions with either deuterium or carbon-13. The polymers were prepared via the procedure described in the Experimental section. Yields of as-prepared polymers are given for each of the six labeled polymers and a nonlabeled control polymer in Table I.

The isotopic purity of each of the six polymers was examined by ^1H NMR spectroscopy at a nominal frequency of 300 MHz (1% solutions in trifluoroacetic acid-d_1/D_2O/TMS 99/1/0.1) and/or by ^{13}C NMR spectroscopy at a nominal frequency of 50 MHz (3% solutions in trifluoroacetic acid-d_1). These results illustrate (Figures 1 and 2) that there was no detectable isotopic scrambling during the interfacial polymerization procedure. Chemical shift information for the polymers is collected in Table II. The isotopically labeled as-polymerized polymers are

Table II
^{1}H and ^{13}C{^{1}H} NMR Chemical Shifts of As-Polymerized Nylon 66 Polymers

	diamine			adipoyl		
site[a]	α	β	γ	α	β	carbonyl
$\delta(^1H)$[b]	3.58	1.75	1.50	2.80	1.95	
$\delta(^{13}C)$[c]	44.2	29.6	27.7	35.2	26.5	180.4

[a] The nomenclature used for each site refers to the protons or carbons located at the α, β, γ, or carbonyl positions within the respective moieties. [b] ^{1}H NMR data acquired at 300 MHz as 1% solutions in trifluoroacetic acid-d_1/D_2O/TMS (99/1/0.1). Chemical shifts are in ppm with respect to an internal TMS standard. [c] ^{13}C{^{1}H} NMR data acquired at 50 MHz as 3% solutions in trifluoroacetic acid-d_1. Chemical shifts are in ppm with respect to TMS, taking the chemical shift of the trifluoromethyl group of trifluoroacetic acid-d_1 to be 116.6 ppm. The ^{13}C spin–spin coupling constant between the carbonyl site and the adjacent methylene group is 47 Hz.

Table III
Inherent Viscosities, Intrinsic Viscosities, and GPC Values of M_w and M_n for As-Polymerized Nylon 66 Polymers[a]

polymer	η_{inh}	$[\eta]$	M_n	M_w	M_w/M_n
NY16NH	0.82	0.90	4.5	23	5.1
NY25NH	0.92	1.01	3.7	25	6.8
NY34NH	1.49	1.63	5.0	44	8.8
NY25CO	1.88	2.05	5.7	42	7.4
NY34CO	1.68	1.88	5.8	40	6.9
NY16C13	1.54	1.68	5.6	38	6.8
control	1.45	1.57	4.0	39	9.8
commercial	1.17	1.25	19	36	1.9

[a] η_{inh} and $[\eta]$ in dL/g; M_n and M_w in kg/mol.

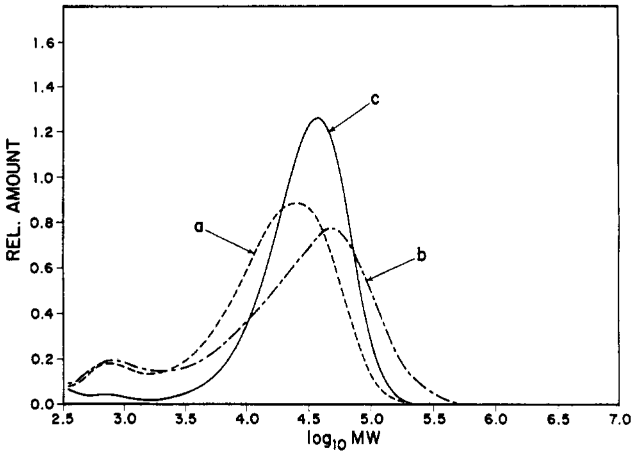

Figure 3. GPC-derived molecular weight distribution curves of a, NY16NH; b, control nylon 66; c, commercial melt-polymerized nylon 66.

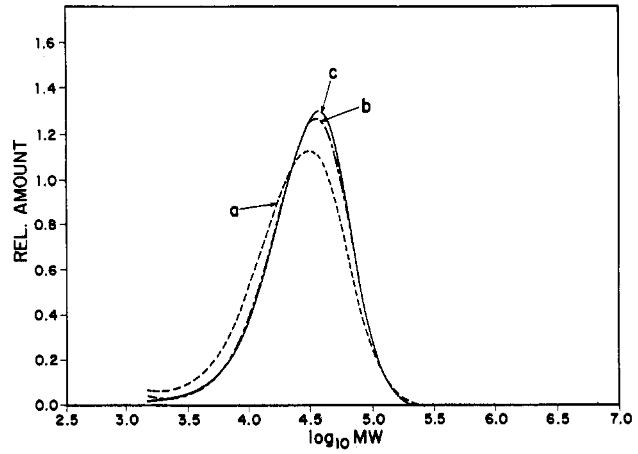

Figure 4. GPC-derived molecular weight distribution curves of a, NY16NHME; b, melt-equilibrated control nylon 66; c, commercial melt-polymerized nylon 66.

Table IV
GPC Values of M_w and M_n for Melt-Equilibrated Nylon 66 Polymers[a]

polymer	M_n	M_w	M_w/M_n
NY16NHME	15.2	32.6	2.1
NY25NHME	19.6	55.9	2.9
NY34NHME	21.1	48.9	2.3
NY25COMe	23.9	45.0	1.9
NY34COMe	20.9	43.3	2.1
NY16C13ME	22.3	45.2	2.0
control (ME)	18.8	35.6	1.9
commercial	19.0	36.0	1.9

[a] M_n and M_w in kg/mol.

designated by the following nomenclature (labeled monomer): NY16NH (hexamethylene-1,1,6,6-d_4-diamine), NY25NH (hexamethylene-2,2,5,5-d_4-diamine), NY34NH (hexamethylene-3,3,4,4-d_4-diamine), NY25CO (adipoyl-2,2,5,5-d_4 chloride), NY34CO (adipoyl-3,3,4,4-d_4 chloride), and NY16C13 (adipoyl-1,6-$^{13}C_2$ chloride).

Table III lists values of the inherent viscosities (η_{inh}) determined at 0.5% concentration in *m*-cresol at 30 °C, intrinsic viscosities $[\eta]$ determined in *m*-cresol at 25 °C, and molecular weight distributions obtained from gel permeation chromatography in *m*-cresol at 110 °C for each of the as-polymerized polymers and a reference commercial material. Figure 3 illustrates representative GPC results for the control, one of the labeled as-polymerized polymers, and the reference commercial material. These results illustrate that while the weight average molecular weights of the as-polymerized polymers are high, the interfacially polymerized polymers contain low molecular weight tails as compared to the reference commercial material, which is prepared from the melt and has a most probable molecular weight distribution.

Linear and cyclic oligomers[15-20] have been previously reported as low molecular weight products produced during interfacial polymerization.[14] Extraction experiments (using either water, 10% HCl in water, ethanol, methanol, ethyl acetate, or dimethyl acetamide) with the control as-polymerized polymer confirmed the presence of 6–14% low molecular weight linear and cyclic oligomers. A 2-day Soxhlet extraction with dimethyl acetamide yielded the best results (14% extraction) and yielded a product with a molecular weight distribution quite similar to the reference commercial material. However, this method was quite tedious, and an alternative method of melt equilibration proved to be simpler and more effective at producing polymer with a molecular weight distribution which closely resembled that of the reference commercial material. The as-polymerized polymers were first carefully dried in a vacuum oven for 24–36 h at 100 °C, and then each was placed in a 10-mm glass tube under vacuum (<5 Torr) for 1 h. The tube was heated under vacuum to 300 °C for a period of 15 min and was then allowed to cool to ambient temperature in a period of 3–5 min. The resulting polymers could, with great difficulty, be removed from the glass tubes and were then subsequently ground by hand with a mortar and pestle under liquid nitrogen to produce powders. Figure 4 illustrates that the molecular weight distributions of the interfacially polymerized materials after melt equilibration are very similar to that found for the reference commercial material. Table IV lists values of M_w, M_n, and polydispersity ratios for the melt-equilibrated polymers (now designated as before, but with the appendage of ME to signfy melt equilibration; e.g., NY16NHME is the polymer obtained from melt equili-

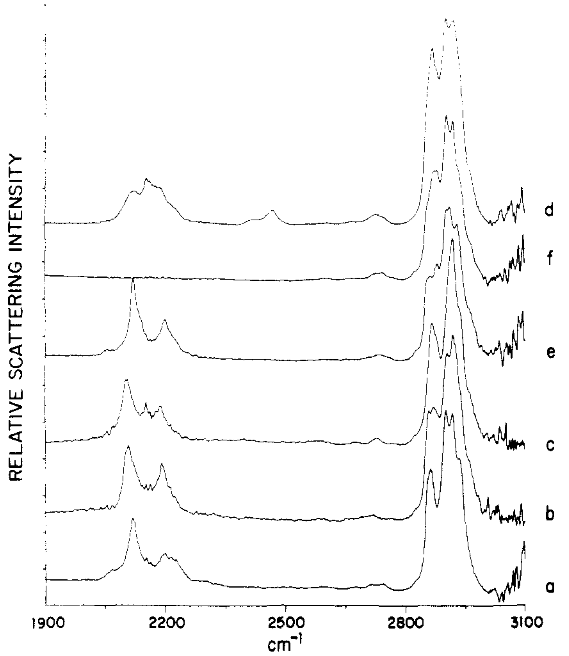

Figure 5. FT-Raman spectra of a, NY16NHME; b, NY25NHME; c, NY34NHME; d, NY25COME; e, NY34COME, f, control nylon.

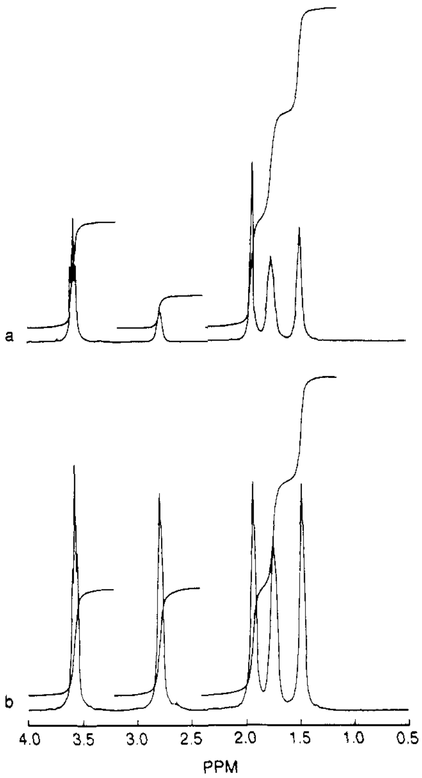

Figure 6. 300-MHz ^{1}H soluton NMR spectra of isotopically labeled melt-equilibrated nylon 66 polymers as 1% solutions in trifluoroacetic acid-d_1/D_2O/TMS (99/1/0.1): a, NY25COME; b, control.

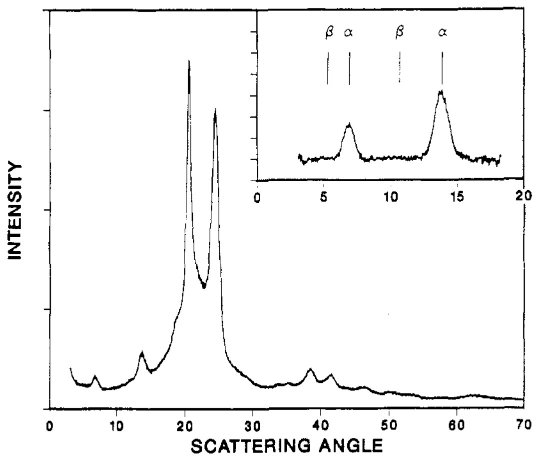

Figure 7. X-ray diffraction curve for melt-equilibrated interfacially polymerized nylon 66 control polymer. The reflections for the α and the β crystal modifications are indicated in the figure.

bration of the as-polymerized polymer derived from hexamethylene-*1,1,6,6*-d_4-diamine).

Subsequent to the melt equilibration procedure, we obtained FT-Raman spectra of each of these polymers in an effort to ascertain whether any isotopic exchange between the labeled C-D positions and the amide N-H had taken place during this procedure. These results illustrate (Figure 5) that there is detectable isotopic scrambling from the C-D sites (2050–2300-cm^{-1} region) to the amide N-D site (2400–2500-cm^{-1} region) only for NY25COME. Figure 6 illustrates ^{1}H NMR spectra of this melt-equilibrated polymer where it is evident that the α-methylenes are only deuteriated to a level equal to two-thirds of the value predicted by the level of labeling present in the starting monomer and previously found prior to melt equilibration for the as-polymerized polymer (Figure 1).

The melt-equilibrated polymers were transferred to individual 5-mm NMR tubes and after 1 h under vacuum were sealed and then annealed at 238 °C for 20 min in a silicon oil bath. X-ray diffractometry scans for the melt-equilibrated control polymer prepared in such a fashion are illustrated in Figure 7. A DSC scan (heating rate of 10 °C/min over the range −50 to 330 °C) of this same polymer found a peak melting temperature of 261.1 °C and a melting endotherm of 74.65 J/g.

Discussion

An interfacial polymerization method was chosen to synthesize the selectively isotopically labeled nylon 66 polymers reported upon here rather than a melt polymerization method for a variety of reasons.[14] The principle factors favoring the low-temperature technique included the following: the stoichiometry and purity of the monomers are less critical, the mild reaction conditions minimize potential isotopic scrambling, the reactions are very rapid, and the method is easily adaptable to the requisite laboratory scale. This method does produce polymers with molecular weight distributions substantially different from that obtained with the melt condensation method. From the inherent viscosities measured for these polymers and the reference commercial material (Table III) it is evident that these polymers are of comparable viscosity average molecular weight (M_v). From the intrinsic viscosity data (Table III) an estimate of M_v can be obtained from the Mark–Houwink relationship for nylon 66.[21]

$$[\eta]_{m\text{-cresol},25^\circ\mathrm{C}} = 0.015 + 35.3 \times 10^{-5} M_v^{0.792}$$

The intrinsic viscosity of the control polymer is 1.57 dL/g, which corresponds to a M_v of 40 000 g/mol.

The molecular weights determined by this method may be compared to the GPC data (Table III), which indicate that the weight average molecular weights of these polymers are quite close to that of the reference commercial material but that the number average molecular weights are substantially lower. As is obvious from Figure 3, the reason for this difference is the presence of low molecular weight tails in each of the molecular weight distribution curves of the interfacially polymerized materials. As detailed in the previous section of this paper, several methods of removing and/or modifying the molecular weight distributions have been evaluated, and melt equilibration was chosen as the most expeditious path. This phraseology is meant to describe a procedure whereby the polymers are simply heated to the melt under vacuum for a short period of time to allow the molecular weight distributions to attain their most probable form and thus more closely resemble the molecular weight distribution (Figure 4) of the reference commercial polymer, which was made through a melt condensation process.

During the process of melt equilibration, not only are condensation and depolymerization processes operative, but for at least one of the polymers (NY25CO) it is evident from the ^{1}H NMR results (Figure 6) that there is some isotopic scrambling taking place. The loss of deuteriation at the methylene group α to the carbonyl group upon melt equilibration is 30% of the total amount that was present prior to melt equilibration. Additional evidence as to the process responsible for this loss of deuteriation is obtained from the solid-state ^{2}H NMR line shape of NY25COME,[22] where it is evident that some secondary species (which can not be an aliphatic carbon) is deuteriated in addition to the expected methylene site. Additionally, nylon 66 polymer deuteriated at the amide nitrogen has been prepared, and the solid-state ^{2}H NMR line shape is consistent with the secondary species observed in the NY25COME line shape. Thus it is evident that during melt equilibration all of the nylon polymers are subject to a keto/enol tautomeric exchange reaction involving the hydrogens bonded to the nitrogen and the carbon α to the carbonyl. This process is unimportant for all of the polymers except NY25CO, where the presence of deuterium on one of the sites involved in this exchange reaction allows the reaction to be detected. At equilibrium in the melt, the deuterons and protons will be statistically distributed over the N–H and CD_2 sites which are α to the carbonyl. It is then expected that the amount of deuteration at the α-methylene groups will decrease by one-third, which is consistent with the results from high-resolution ^{1}H NMR analysis (Figure 6). The solution ^{1}H NMR analysis cannot detect the amide hydrogens due to exchange with the acidic solvent, trifluoroacetic acid-d_1; however, the FT-Raman spectra (Figure 5) clearly indicate that the amide nitrogen of only the NY25CO polymer has been partially deuteriated during the melt equilibration process.

A wide-angle X-ray diffractometry scan for the melt-equilibrated nylon 66 control polymer that had been annealed at 238 °C is given in Figure 7. The sample is semicrystalline, with the crystalline component in the α form[23] (see insert in Figure 7). The crystalline persistence lengths parallel to the *a* and *c* (chain) axes are 16.5 and 8.6 nm, respectively. By X-ray analysis, this polymer is estimated to be approximately 35% crystalline. This value of crystallinity may be compared to that found from two other methods. From a DSC measurement of the control melt-equilibrated nylon 66, the heat of fusion is 74.65 J/g, which corresponds to 39.2% crystallinity, with 190 J/g being used as the heat of fusion of the crystal.[24] Lastly, these values may be compared to a value determined from solid-state ^{2}H NMR spin–lattice relaxation experiments. This method finds[22] an average value of 40 ± 2.5% crystallinity for the five melt-equilibrated deuteriated nylons described here. It is evident that these three methods of characterizing the crystallinity of these polymers are in reasonable agreement.

Conclusions

Six isotopically labeled high molecular weight nylon 66 (poly(hexamethylene adipamide)) polymers have been prepared by low-temperature interfacial polymerization and extensively characterized. The polymers have been selectively and symmetrically labeled at either the 1,1,6,6, the 2,2,5,5, or the 3,3,4,4 positions of the hexamethylenediamine moiety or the 2,2,5,5 or the 3,3,4,4 positions of the adipoyl moiety with deuterium or at the 1,6 positions of the adipoyl moiety with ^{13}C. The molecular weight distributions of the as-polymerized materials exhibited low molecular weight tails. Most probable molecular weight distributions were obtained by melt equilibration; however, in the case of the polymer labeled with deuterium on the methylene groups α to the carbonyl group isotopic scrambling with the amide N–H was evident. The polymers possess the α crystalline modification and are characterized as being 39% crystalline by DSC, 40% crystalline by solid-state ^{2}H NMR methods, and 35% crystalline by X-ray diffractometry. These isotopically labeled materials are essentially identical with a reference commercial polymer in molecular weight and molecular weight distribution and thus should be representative of the structure and dynamics of unlabeled nylon 66 polymers.

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Registry No. NY16NH (copolymer), 115797-50-7; NY16NH (SRU), 115797-45-0; NY25NH (copolymer), 115797-52-9; NY25NH (SRU), 115797-46-1; NY34NH (copolymer), 115797-54-1; NY34NH (SRU), 115797-47-2; NY25CO (copolymer), 115797-56-3; NY25CO (SRU), 115797-48-3; NY34CO (copolymer), 115797-58-5; NY34CO (SRU), 115825-95-1; NY16C13 (copolymer), 115797-60-9; NY16C13 (SRU), 115826-85-2; poly(hexamethyleneadipamide), 32131-17-2.

References and Notes

(1) English, A. D.; Smith, P.; Axelson, D. E. *Polymer* **1985**, *26*, 1523.

(2) Miura, H.; English, A. D. *Macromolecules* **1988**, *21*, 1543.

(3) Zimba, C. G.; Rabolt, J. F.; English, A. D., to be submitted for publication.

(4) Spiess, H. W. *Colloid Polym. Sci.* **1983**, *261*, 193.

(5) Jones, A. A. *Molecular Dynamics in Restricted Geometries*; Klaster, J., Drake, J. M., Eds.; Wiley: New York, in press.

(6) English, A. D. *Macromolecules* **1985**, *18*, 178.

(7) Hentschel, D.; Sillescu, H.; Spiess, H. W. *Polymer* **1984**, *25*, 1078.

(8) Vega, A. J.; English, A. D. *Macromolecules* **1980**, *13*, 1635.

(9) (a) Stockmayer, W. H. *Pure Appl. Chem. Suppl. Macromol. Chem.* **1973**, *8*, 379. (b) Helfand, E. *Science (Washington, D.C.)* **1984**, *226*, 647.

(10) Chase, D. B. *Microchim. Acta* **1987**, *3*, 81.

(11) Wittbecker, E. L.; Morgan, P. W. *J. Polym. Sci.* **1959**, *40*, 289.

(12) Morgan, P. W.; Kwolek, S. L. *J. Polym. Sci.* **1959**, *40*, 299.

(13) Morgan, P. W.; Kwolek, S. L. *J. Polym. Sci.* **1962**, *62*, 33.

(14) Morgan, P. W. *Condensation Polymers: By Interfacial and Solution Methods*; Interscience: New York, 1965.

(15) Zahn, H.; Gleitsman, G. B. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 410.

(16) Zahn, H.; Schmidt, F. *Chem. Ber.* **1959**, *92*, 1381.

(17) Zahn, H.; Miro, P.; Schmidt, F. *Chem. Ber.* **1957**, *90*, 1411.

(18) Zahn, H., Lauer, W. *Makromol. Chem.* **1957**, *23*, 85.

(19) Setter, H.; Marx, J. *Liebigs Ann. Chem.* **1957**, *607*, 59.

(20) Rothe, I.; Rothe, M. *Makromol. Chem.* **1963**, *68*, 206.

(21) Elias, H.-G.; Schumacher, R. *Makromol. Chem.* **1964**, *76*, 23.

(22) Miura, H.; English, A. D., in preparation.

(23) Bunn, C. W.; Garner, E. V. *Proc. R. Soc. London, A* **1947**, *189*, 39.

(24) Starkweather, H. W.; Zoller, P.; Jones, G. A. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *22*, 1615.