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SOLID STATE NMR INVESTIGATION OF NYLON 7

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Nylon 7 obtained from Du Pont was treated to give samples with very different histories. As-obtained flakes were melt-pressed above the T_m into films, quenched in ice-water or annealed at 220 °C. Polymer flakes were dissolved in 2,2,2-trifluoroethanol:methylene chloride (3:2 by volume) to give a 3 w/v % dope which was cast onto glass or precipitated into diethyl ether. A sample of the cast film was annealed at 160 °C. Differences were observed in both the ^{13}C and ^{15}N solid state NMR spectra of the samples. Most strikingly, the ^{13}C spectrum of the sample cast onto glass showed multiple peaks consistent with the presence of both α ($\delta^{15}N$ = 84.2 ppm) and γ ($\delta^{15}N$ = 89.4 ppm) crystallites, while the DSC thermogram showed a single melting endotherm. Annealing this film at 160 °C converted the γ crystallites into α crystallites without sample melting or degradation. ^{13}C T_1 values increase with annealing. That is, the annealed sample (220 °C) had the longest T_1's followed by the cast-annealed film (160 °C), cast film, quenched film and precipitated sample. The ^{13}C chemical shift of the carbon immediately adjacent to the nitrogen atom consistently move downfield in the same order as the T_1's increase. Crystallite size and perfection can account for these trends.

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Solid State NMR Investigation of Nylon 7

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INTRODUCTION

Nylon 7 is an important AB-nylon because of its piezoelectric, pyroelectric, and ferroelectric response when thin films are melted, quenched, elongated, and poled above the glass transition temperature in a strong electric field.[1] Nylon 7 and nylon 6 are structurally similar differing by a single methylene. This difference allows all of the carbonyl carbons of nylon 7 extended chains to be aligned in the same direction. Crystallization of these extended chains results in a polar unit cell with piezoelectric properties.[1]

Both nylon 6 and nylon 7 crystallize into the α polymorph from the melt. The γ polymorph for nylon 6 can be achieved by treating thin films with KI/I_2 in water.[2] To the best of our knowledge, the γ crystal form of nylon 7 has not been reported to date.

All of the crystal forms of nylon 6 have been characterized thoroughly by solid state NMR,[3,4] thermal methods,[5,6] FT-IR,[7,8,9] and X-ray methods.[10] Much has been done to characterize nylon 7's electrical responses as mentioned above, although, little structural characterization of nylon 7 has been reported. Structural data does exist for nylon 7 crystallized from solution[11] and from wide-line solid state ^1H NMR used to characterize nylon 7 fibers.[12]

We report here the solid state ^{13}C and ^{15}N NMR characterization of various nylon 7 crystal forms including the first report on the γ-form of nylon 7. The resulting opaque films cast from solution onto glass contain not only γ crystallites and amorphous material but also α crystallites. Included is a discussion regarding the relative size of nylon 7 crystallites based on ^{13}C T_1 results and the relative chemical shift of the carbon immediately adjacent to the nitrogen of the amide group (C_N).

EXPERIMENTAL

The nylon 7 used here was a gift from Dr. Miller at duPont. Solvents were reagent grade and used without further purification. Nylon 7 flakes were melt-pressed at 280 °C (T_m = 233 °C)[13] under 25 kpsi pressure. Samples were then processed and named as follows: qf - a melt-pressed film immediately quenched in ice-water; af - a sample of the melt-pressed film placed in a glass tube, sealed under vacuum, and annealed at 220 °C for 2 days; cf - polymer flakes dissolved in a solution of 3:2 2,2,2-trifluoroethanol:methylene chloride by volume cast onto a glass substrate, solvent evaporated under ambient conditions, and the film dried at room temperature for several days; pf - a sample of the polymer dope precipitated into diethyl ether, collected and dried at room temperature for several days; and caf - a sample of the cast film placed in a glass tube, sealed under vacuum, and annealed at 160 °C for 2 days.

Solid state ^{13}C NMR measurements were made using a Bruker MSL-400 operating at 100.62 MHZ, while ^{15}N NMR measurements were made using a Bruker MSL-200 operating at 20.287 MHz. Standard magic-angle spinning probes were used with both MSL's with samples spun using dry air at 5 kHz for carbon experiments and 3 kHz for nitrogen experiments. Peaks in the carbon spectra are referenced to the upfield peak of solid adamantane at 29.5 ppm, while peaks in the nitrogen spectra are referenced to solid glycine at 0 ppm.

Data was collected under magic-angle spinning conditions with high-power proton decoupling used during acquisition. A 1-ms mixing time, 5-s recycle delay, and 50-ms acquisition time were used during both carbon and nitrogen experiments. A ^1H 90°-pulse of 4.5 to 5.0 μs was used for both carbon and nitrogen experiments. Spin-lattice relaxation data was collected using the method developed Torchia.[14]

RESULTS AND DISCUSSION

The DSC thermograms for the polymer samples are shown in Figure 1, while the T_m's and estimated % crystallinities are listed in Table 1. The Figure shows that the melt annealed sample has the highest T_m (= 242 °C) of the samples presented here. This is consistent with a literature report of a highly crystalline sample with well formed crystallites.[13] The samples quenched from the melt and precipitated into a non-solvent show the broadest melting peaks and the lowest percent crystallinities. This is expected for ill-formed or small crystallites. What is important to note is that the sample cast onto glass shows a single melting peak but, as will be argued in a moment, there are two types of crystallites present in this sample.

Table 1. DSC data[a] for nylon 7 taken at 10° C/minute

sample	Onset T_m (°C)	Peak T_m (°C)	ΔH (J/g)	est. % cryst.
cf	223	229	77	33
af	239	242	77	33
qf	220	228	49	21
pf	219	230	65	28
caf	225	229	88	38

a - data averaged over three runs with est. % crystallinity based on ΔH = 230 J/g for pure crystalline nylon 6, collected using a Perkin-Elmer DSC-7.

The ^{13}C solid state NMR spectra of the polymer samples are shown in Figure 2 with the CPT1 chemical shifts summarized in Table 2.

Table 2. ^{13}C CPT1 Chemical shifts in PPM (100.61 MHz) for nylon 7

sample	CO (C-7)	C_N (C-1)	C_α (C-6)	C-2,3,4	C_β (C-5)	NH[a]
cf	173.3	43.1 (α) 39.6 (γ)	35.6	31.7	28.6	84.5 (α) 89.3 (γ)
af	173.3	43.7	35.8	31.7	28.7	84.1
qf	173.5	42.9	35.8	31.4	27.9	85.9
pf[b]	173.2			31.7	27.3	86.3
caf	173.8	43.3	35.7	31.7	28.2	84.6
amor.[c]	173.8	40.5	36.6	30.2	28.1	
solut.[d]	176.6	40.3	36.9	29.3/29.1 /26.1	26.0	

a - nitrogen frequency = 20.287 MHz
b - peak assignments tentative due to poor S/N, except for CO
c - data from HP/MAS experiment
d - 5% (w/v) in 2,2,2-trifluoroethanol:methylene chloride 3:2 by volume at 75.5 MHz

The CPT1 method favors rigid, crystalline fractions under acquisition conditions specific for slow relaxing material. The subtle differences in conformation of the carbons directly attached to the amide unit exist for the α and γ polymorphs. This results in differences in shielding of these carbons giving them different chemical shifts. This also extends to the nitrogen atom of the amide group. The carbonyl carbon (CO) of α and γ crystallites and the amorphous region appear at ca. 173 ppm and therefore is of little diagnostic value. However, the carbon immediately adjacent to the nitrogen atom (C_N), which is the most downfield in the aliphatic region, appears at ca. 43 ppm for α crystallites, ca. 39 ppm for γ crystallites, and ca. 40.5 ppm for the amorphous fraction. The carbon immediately adjacent to the CO (C_α) appears at ca. 36 ppm for α crystallites of nylon 7, while the carbon beta to CO (C_β) appears ca. 28 ppm. These assignments are consistent with those observed for the respective polymorphs of nylon 6.[15]

The fact that the peak at ca. 40.5 ppm in the spectra of the annealed film, quenched film, and cast annealed film disappears in the CPT1 spectra confirms it as belonging to the fast relaxing amorphous fraction. The peak present in the CPT1 spectrum at ca. 39 ppm of the cast sample is indicative of the presence of γ crystallites as are the shoulders on other peaks.

The solid state ^{15}N NMR spectra of the nylon 7 samples are shown in Figure 3. Clearly, there are two peaks present in the upper trace of the sample cast onto glass which are consistent with the two known crystal forms (α at 84.5 ppm and γ at 89.3 ppm) of nylons. These peaks much more clearly confirm the presence of two crystal polymorphs in the same sample. The peak at 84.1 ppm in trace B is for well-formed α crystallites which overlaps a broad envelope of resonances centered ca. 86 ppm

belonging to the amorphous fraction. Traces C and D are similar in position (ca. 86 ppm) and width indicating a broad distribution of amorphous conformational environments. Trace E contains a single crystalline peak at 84.6 ppm consistent with α crystallites which again overlaps the amorphous region peak. This single sharp peak indicates that the once-present γ crystallites have been converted into α crystallites by annealing above T_g but below T_m. This too is consistent with the conversion of the less thermodynamically stable crystal form into the preferred form.

Table 3. Spin-lattice relaxation data[a] for the nylon 7 samples

sample	CO	C_N	C_α	C-2,3,4	C_β
cf[b]	3.5 99.5	1.3 7.2 80.3	0.4 4.5 69.5	0.5 5.6 69.8	0.5 5.8 59.1
af	4.8 42.3 352.4	0.8 37.8 303.9	0.9 15.5 245.7	0.7 12.0 236.1	0.5 15.2 275.4
qf	8.0 48.7	0.6 3.4 23.9	0.8 6.6	0.1 1.2 12.9	0.4 3.5 30.6
pf	3.8 23.3	0.6 9.5	0.8 16.2	0.8 9.5	0.5 7.7
caf	10.1 65.6 257.0	1.3 26.0 201.4	0.9 15.8 171.3	0.8 13.8 169	0.6 10.2 164.3

a - data taken at 100.61 MHz
b - carbon T_1's for C_N (39.6 ppm) of the γ-form are 0.4, 8.3, and 105.0 s

Table 3 summarizes the carbon T_1 values for these samples. The multicomponent relaxation behavior is consistent with that of a semi-crystalline polymer (like polyethylene[16]) in that a liquid-like phase is present with a T_1 of fractions of seconds along with a more rigid, constrained fraction with a T_1 of several seconds, and a highly rigid (crystalline) domain with a T_1 of hundreds of seconds. Polyethylene[17] shows an increase in carbon T_1 values with crystallite thickness which may also be reflected in the behavior of the nylon 7 carbon T_1 values. That is, the annealed film has the highest T_1 value, followed by the cast-annealed sample, then the cast-film, the quenched-film, and finally the precipitated flakes. Also, the chemical shift of the C_N moves consistently downfield with increase in carbon T_1. The nitrogen chemical shifts reflect a similar trend in that they move upfield with increasing carbon T_1 values. An increase in crystallite perfection and size may be the cause of this downfield trend for C_N chemical shifts and the upfield trend for the amide nitrogen chemical shifts, while it is certainly the cause of the increase in carbon T_1 values.

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