polymer communications

Nylon 13,13 analysis by X-ray and solid state n.m.r.: treatment-dependent crystal forms

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Nylon 13,13 samples were prepared by various solvent-casting and thermal-treatment methods. Melt-quenched material showed broad, amorphous-like peaks in the X-ray powder pattern (at $2\theta = 21°$, 4.2 Å) and both the ^{13}C and ^{15}N solid-state n.m.r. spectra. Two different crystal forms of this polymer could be generated using different methods: a type A form was obtained by extended annealing just below the melting temperature and by film casting from 1,1,1,3,3,3-hexafluoroisopropanol, while a type B form developed on precipitating from m-cresol into methanol or film casting from m-cresol. The X-ray pattern for type A was similar to those of other nylons possessing an α-crystal form, although the n.m.r. data, especially the strong, sharp ^{15}N peak at 88.7 ppm, was more consistent with a γ-phase. The type B crystals gave an X-ray pattern similar to those of other γ-form nylons and to the pseudohexagonal phase observed in some homo- and copolyamides. The n.m.r. data for the type B form (especially the sharp ^{15}N peak at 87.3 ppm) seemed to indicate an amide conformation of c. 30° with respect to the planes of the attached all-*trans* methylene chains; this value is half-way between those of the α and γ-crystal forms of most nylons (^{15}N chemical shifts of c. 84 and 89 ppm, respectively). We believe these crystal forms are unique to nylon 13,13 but have insufficient data to further describe the molecular conformations and crystalline packings that correspond to each.

Introduction

Only a few examples exist of commodity polymers made mainly from natural, renewable sources. Nylon 11 is one of these, with its monomer synthesized from castor oil and then polymerized using conventional thermal dehydration[1]. The synthesis of nylon 13,13, based on erucic acid obtained from crambe and rapeseed oil, has also been described[2]. While conversions are excellent and polymer molecular weights high, commercialization has not occurred. One reason may be the lack of detailed understanding of the physical properties of this novel nylon and the associated molecular-level behaviour that can allow control and optimization of these properties. In this communication, we describe preliminary solid-state n.m.r. and X-ray findings on nylon 13,13. (The nylon 13,13 sample was obtained from Professor R. S. Porter, University of Massachusetts, who received it from the USDA, Peoria Station; it had an estimated molecular weight of 41 000 based on viscosity measurement.) The samples had undergone various treatments that induced unique crystal forms. (Sample treatments included: annealing as-obtained material at 160°C for 12 h (AN); rapid quenching of molten sample in liquid nitrogen (QF); casting a film onto glass from m-cresol solution (CFM); precipitating an m-cresol solution into methanol, filtering and drying *in vacuo* for 12 h (PF); and casting a thin film onto glass from 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) (CFH).)

We have been exploring the use of solid-state n.m.r. for the molecular-level observation of various polymers such as nylons[3,4], especially for selected ^{15}N-enriched

samples[5,6]. A wide range of nylons has also been examined at natural abundance levels[7], including nylons 6, 7, 8, 11 and 12. General chemical shift trends were found for virtually all samples: the α-crystal form peak appears at c. 84 ppm (with respect to glycine at 0 ppm) while the γ-form crystals show up at c. 89 ppm and the amorphous domains appear as a broad peak centred at c. 86–87 ppm[8,9]. Crystalline peaks give long T_{1N} values (100–300 s) while amorphous peaks give short values (<1 s to tens of seconds). However, the high temperature δ-form of nylon 11 (above the Brill transition) gives a sharp peak at 87 ppm but with a long T_1 (110 s). Solid-state [13]C n.m.r. results show chemical shift effects and relaxation time values confirming the ^{15}N observations. Based on the findings with homopolymers, we have extended analysis to the packing of various copolymers, including nylon 6-*co*-7[10,11] and 11-*co*-12[12,13], for which thermodynamically stable pseudohexagonal phases were observed for some samples (86–87 ppm).

The ^{13}C CPT1 spectra of the various nylon 13,13 samples in *Figure 1* represent the more ordered, rigid domains in the samples, while the ^{15}N CP/MAS spectra in *Figure 2* are composites of peaks from all regions in the samples, although rigid or crystalline domains tend to be emphasized with this method for nylons. Chemical shift data are given in *Table 1*. (The CPT1 method uses a typical T_1 pulse train with a single delay selected to allow relaxation of the mobile components; in this case, delays of 2.5–15 s were used. The CP/MAS method employs normal cross-polarization and high power decoupling with magic angle spinning.) The quenched melt sample (QF) shows broad peaks in both spectra,

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Table 1 ^{13}C and ^{15}N chemical shifts (ppm) for solid-state and solution samples; data for nylon 11 (N11) and nylon 12 (N12) samples are taken from refs 6, 9 and 13

Sample	CPT1					CP/MAS NH
	CO	C_N	C_α	C_{AT}	C_β	
AN	172.9	39.5	37.3	34.1	31/29.4	88.7
QF	173.6	40.5	36.4	33.4	31/27.5	87.0
CFM	173.7	38.6	36.1	33.1	30/29	87.3
PF	173.6	38.7	36.1	33.1	30/29	87.3
CFH	172.8	39.2	37.2	34.0	31/29.2	88.5
solution				27.8		
in	176.9	39.1	35.3	27.6	25.1	–
HFIP				27.3	24.1	
αN12	172.9	43.1	36.0	34.3	31/27.2	84.2
γN12	172.9	39.3	37.1	33.6	30.1	89.3
γ'N12	173.1	40.3	37.0	33.1	31/27	88.8
αN11	173.7	42.5	35.8	33.4	27.5	85.2

indicating a low degree of crystallinity. In fact, the X-ray powder pattern for this sample (*Figure 3*) shows a broad peak corresponding to amorphous domains or perhaps a disordered pseudohexagonal phase. Measured T_{1C} data for the methylene carbons were computer-fitted with a biexponential decay to give longer (of the fit) values centred around 2–8 s, which indicate high mobility and poor packing. In contrast, the T_{1C} data for the other four samples examined were fitted with a three-component decay, with the shortest values being less than 1 s, intermediate values clustering around 20 s and the longest values being greater than 200 s. These last are some of the highest T_{1C} values we have observed for any nylon, and indicate very rigid domains.

The crystalline samples exhibit two different types of crystalline packing, neither of which are similar to any other nylon examined to date. Comparison of the two sets of similar spectra in *Figures 1* and *2* illustrate this: the film cast from HFIP (CFH) and the annealed sample
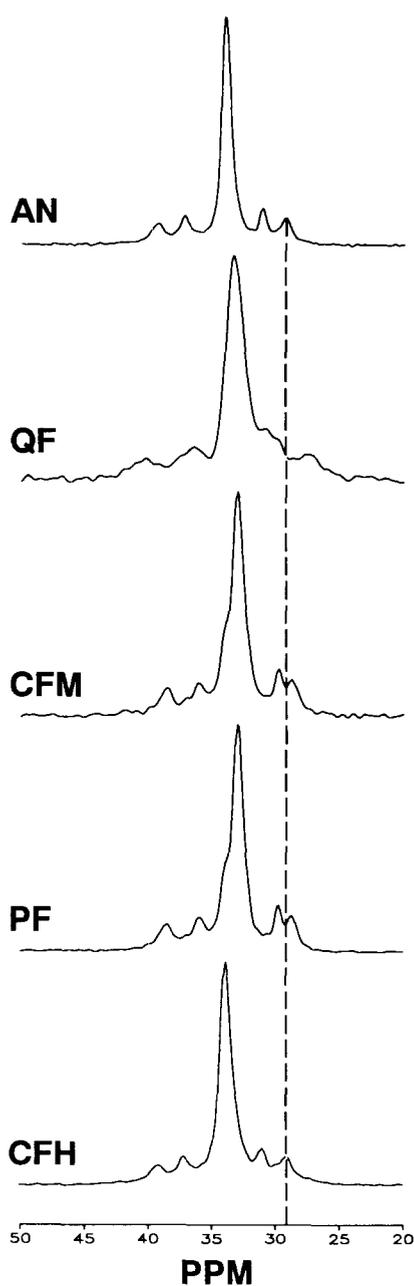

Figure 1 CPT1 ^{13}C n.m.r. spectra of the variously treated nylon 13,13 samples referenced to the adamantane methine peak at 29.5 ppm
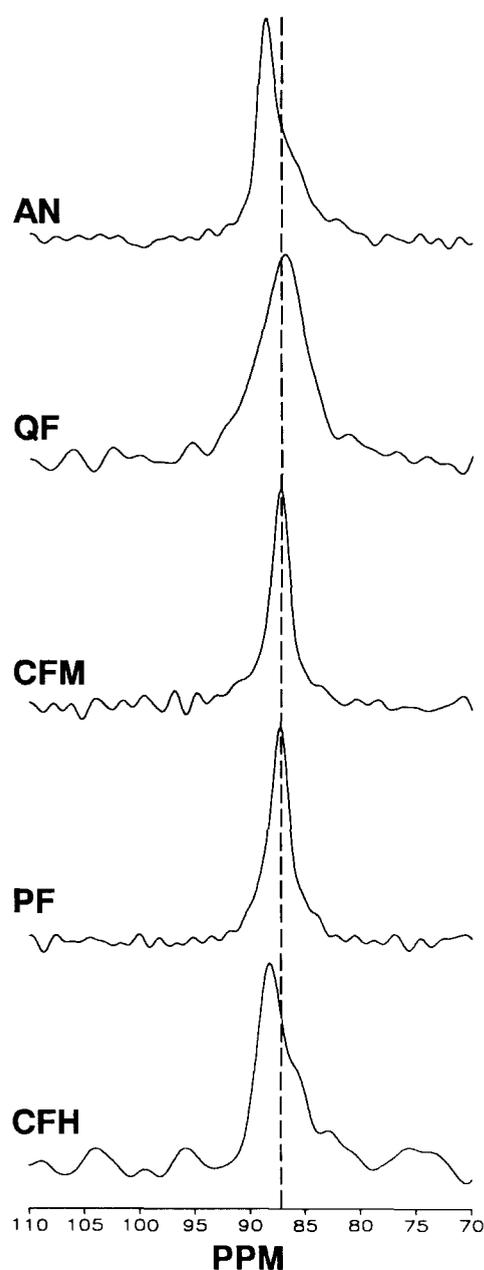

Figure 2 CP/MAS ^{15}N n.m.r. spectra of the nylon 13,13 samples referenced to glycine at 0 ppm
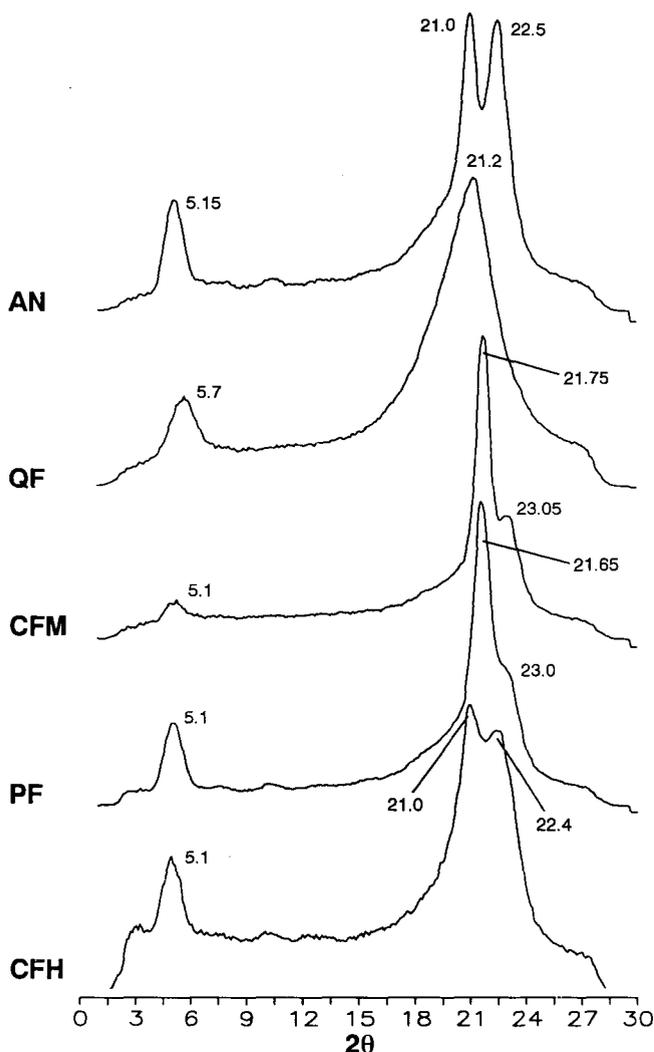
Figure 3 X-ray powder diffraction patterns for the nylon 13,13 samples obtained using a Siemens XPD-700P system

(AN) represent one form (type A) while those of the film cast from *m*-cresol (CFM) and the precipitated flakes (PF) represent the other (type B). The X-ray powder patterns for these two pairs of samples clearly confirm the differences (*Figure 3*).

First, consider the type A structure which gives a pair of intense X-ray peaks at $2\theta = 21$ and $22.5°$ (4.23 and 3.95 Å) plus a weaker peak at $5.15°$ (17.1 Å). These are very similar in relative peak height and shape to the pair of peaks observed for α-crystals of various nylons; we have measured values for α-form nylon 6 (20.3, 23.7°), nylon 7 (20.3, 23.3°), nylon 11 (20.2, 22.8°) and nylon 12 (19.7, 23.4°). In contrast, the nylon 13,13 ^{15}N peaks at 88.5 and 88.7 ppm are very close to that of γ-nylon 12 at 89.3 ppm and other γ-form nylons. The ^{13}C peaks for C_N and C_α are also very similar to those of γ-nylon 12. The two C_β peaks, however, are more like those of the α-forms of nylon 12 and nylon 11, while the main methylene peak (C_{AT} where AT stands for all-*trans*) is very near that of α-nylon 12 (but not α-nylon 11). In fact, the value for this peak implies a very different degree or type of packing for the all-*trans* methylene chain, similar to what is seen for linear alkanes and polyethylene. For the latter, the ^{13}C crystal peak moves downfield by about 1.3 ppm in going from the thermodynamically stable orthorhombic form (chains packed perpendicular to each other) to the less stable monoclinic modification (chains

packed parallel)^{14}. A similar change in packing is indicated here, although we have insufficient data to draw firm conclusions on the conformation and packing in the type A crystal modification of nylon 13,13.

Let us now consider the type B data. The X-ray pattern consists of a very sharp and intense main peak at $2\theta = 21.7°$ (4.1 Å) with a weak shoulder at 23° (3.8 Å) and a weak peak at 5.1° (17.3 Å). Peak positions and overall shape are virtually identical to those seen for annealed nylon 12 (γ-form). In fact, the main peak in this pattern is one of the sharpest, most well-defined that we have observed for highly crystalline nylons. The peak for pseudohexagonal phases also appears at this scattering angle although peak widths are usually much greater. While the X-ray data thus seems to indicate γ-form crystals, the n.m.r. data are contradictory or inconclusive. The ^{15}N peak is very sharp (indicating highly ordered crystals) but is almost exactly half-way between the values for the α and γ crystals, corresponding to both the high-temperature δ-form and the mesomorphic pseudohexagonal phase observed for nylon 11 above 95°C (86.6 ppm^6). This may imply a conformation of the amide plane with respect to those of the all-*trans* methylene segments that is intermediate to those of the α and γ forms, i.e. at a dihedral angle of *c.* 30°. The ^{13}C value for C_N is clearly different from those observed for α-forms of nylons 11 and 12 (38.7 ppm compared to 43.1 and 42.5 ppm, respectively) and more in line with the γ-form values (39.3 ppm for nylon 12). The other ^{13}C peaks show no dramatic correlations or differences that are obviously useful. Again, we have insufficient data to fully describe the molecular and crystalline order existing in this thermodynamically stable phase of nylon 13,13.

Overall, we conclude that the combination of well-defined X-ray powder patterns coupled with the sharp, well-resolved peaks in the ^{15}N and ^{13}C solid-state n.m.r. spectra correspond to two completely different crystal forms of nylon 13,13. This is not surprising, since virtually all nylons can be treated in some manner to induce more than one type of crystallinity. What is surprising about both nylon 13,13 crystal modifications is that they do not correspond to those of any other nylon we have examined to date. This unusual behaviour may result from the extended methylene segments in this polyamide playing a significant role in determining the orientation and packing of both the all-*trans* hydrocarbon chains and amide units with respect to each other and to adjacent chains. Once understood, this unique behaviour may offer insight into the molecular features controlling solid-state properties of other nylons, and of polymers in general. In fact, unique molecular-level behaviour might be expected to generate unusual physical properties and processing opportunities.

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