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Structural Characterization of Nylon 7 By Solid-State NMR, DSC, and ATR-FTIR

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ABSTRACT

Samples of commercial nylon 7 were given different thermal or precipitation histories. Structure and crystallinity were followed by DSC, solid-state NMR, and attenuated total reflectance FTIR (ATR-FTIR). ΔH and T_m values ranged from 52 to 93 J/g and 228 to 242 °C, respectively. Surprisingly, annealing did not give material with the greatest ΔH *although it possessed the highest melting point. Solid-state* ^{13}C *and* ^{15}N NMR methods were used to observe the amorphous and crystalline fractions. For example, the amide nitrogens show resonances near 86.5 ppm in amorphous domains, near 84 ppm in α-crystals, and near 89 ppm in γ-crystals. ^{15}N CP/MAS spectra of solution cast samples contained peaks consistent with all three domains in various intensity ratios but with the γ-peak being the most intense for most samples. Solid-state ^{13}C spectra contained peaks which supported the presence of these phases but with the α-phase peaks predominating. Treatment of solution-cast thin films with aqueous KI/I_2 gave materials whose NMR spectra contained peaks consistent with these three phases in different ratios than for the initial solution-cast samples. Spectra of the melt crystallized samples contained peaks for amorphous and α-domains only. ^{13}C T_1 magnetization decays could be fit to two or three exponentials (T_1's of hundreds of milliseconds, a few seconds, and hundreds of seconds) consistent with semicrystalline polymer behavior. T_1 values for the long-relaxing component ranged from 350 s to 23 s for the annealed and precipitated samples, respectively. Amide V bands near 682 cm^{-1}, assigned previously to the α-phase, were present in the ATR FTIR spectra of all the samples. However, the chemically treated and solution cast samples contained additional bands at 690 and 620 cm^{-1} due to the γ-phase. Spectra of quenched samples contained bands not seen in the other spectra.

INTRODUCTION

Nylon 7, while structurally and physically similar to nylon 6, possesses piezoelectric properties which nylon 6 does not possess.[1] Nylon 7 is reported to crystallize into the triclinic unit cell while nylon 6 adopts the monoclinic unit cell with both having chains in an anti-parallel arrangement.[2,3] In these crystallites, the amide unit and the polymethylene chains are coplanar in the thermodynamically preferred α-crystal phase (seen for nylon 6 and odd nylons such as nylons 7 and 11). The odd number of carbons between amide groups in nylon 6 force the carbonyls to align in alternating directions along the polymer chains. However, the even number of carbons between the amide units in nylon 7 allows the carbonyl groups to align in the same direction parallel to the planar, extended methylene chains of the backbone. This makes the unit cell polar and noncentrosymmetric. Strong macroscopic polarization (through an external field) gives rise to piezoelectric behavior resulting from microscopic alignment of the carbonyl dipoles of the extended chain α-crystallites.

Thermal[1] and solution[2] crystallization of nylon 7 both give the more stable α-modification. There has been no report[3] on the γ-modification for nylon 7 in which the amide unit and the zig-zag polymethylene planes are twisted ca. 60° from each other.[4] This is the stable crystal form for most even A-B type nylons such as nylon 8[3] and nylon 12.[5] The γ-form can be induced in nylon 6 samples through thermal or chemical treatment.

To date, no solid-state ^{13}C and ^{15}N NMR characterization of nylon 7 appears in the literature although wide-line solid-state ^{1}H NMR was reported.[6] Solid-state NMR is sensitive to crystal packing environments[7] and has been used to characterize amide conformations of nylon 6,[8] nylon 6,6,[9] nylon 11,[10] and nylon 12[11] polymorphs. For example, in nylon crystallites, the chemical shift of the carbon attached to the nitrogen side of the amide unit is near 39 ppm for the γ-crystal form in which the amide unit is rotated out of the polymethylene plane by about 60°. The same carbon in α-crystallites, in which the amide and polymethylenes are coplanar, appears near 43 ppm. This difference in chemical shift is caused mainly by conformationally induced interactions[12] although possible intermolecular effects in different unit cells may also contribute as is the case for alkanes.[7]

The α- and γ-polymorphs represent extremes of stable conformations available for polyamide chains in crystalline domains. For conformations intermediate to these extremes (amorphous regions), the chemical shift of the carbon on the nitrogen side of the amide unit falls between these values (near 40.5 ppm) and can be seen separately from the crystalline resonances as a broad peak or shoulder in the CP/MAS spectrum.

An intermediate chemical shift may also arise due to segmental motions that occur in the mobile amorphous domains (observed by direct-polarization) that can lead to a time-average conformation around the amide group that lies between the trans coplanar and the twisted conformation.

Along with the changes in carbon chemical shifts, the solid-state nitrogen NMR data shows similar chemical shift changes with respect to amide conformation and packing. ^{15}N analysis offers advantages of simplified spectra (usually a single or a few chemically distinct groups) and larger spectral range (leading to better peak separation). This more than offsets the disadvantages of low natural abundance and low magnetic susceptibility. Moreover, the increased availability of high-field NMR spectrometers partially diminishes the latter disadvantages. In this paper, we describe the use of solid-state ^{13}C and ^{15}N NMR techniques to selectively observe and evaluate the amorphous and crystalline phases of nylon 7 in conjunction with attenuated total reflectance (ATR) FTIR to confirm the presence of different phases. We present evidence for the existence of the γ-form of nylon 7 which has not previously been reported.

EXPERIMENTAL

The nylon 7 sample used here was a gift from Dr. Miller at DuPont Chemical Company. Solvents were reagent grade and used without further purification. Differential scanning calorimetry (DSC) measurements were made using a Perkin-Elmer DSC-7 equipped with an IBM personal computer. The DSC instrument was calibrated immediately prior to use with tin and indium standards with data collected at 10 °C/min.

Attenuated total reflectance FTIR measurements were made using a Bruker IFS 88 instrument equipped with a Spectra-Tech Model 300 ATR cell using a KRS-5 crystal and a 45° angle of incidence. Approximately 256 scans were taken per sample.

Solution NMR spectra were gathered using a Bruker AC-300 operating at 75.469 MHz for ^{13}C. A mixture of 2,2,2-trifluoroethanol and methylene chloride (3:2 by volume) was used as the solvent along with a sealed capillary containing D_2O as the lock solvent. Peaks were referenced to methylene chloride at 53.8 ppm. Solid-state ^{13}C NMR measurements were collected using a Bruker MSL-400 operating at 100.614 MHz, while the ^{15}N NMR measurements were obtained on a Bruker MSL-200 operating at 20.287 MHz. Approximately 2000 to 4000 transients were collected for carbon experiments, while 15,000 to 25,000 were needed for nitrogen. A standard Bruker MAS 7-mm probe was used with the MSL-200 and a 4-mm probe with the MSL-400. Samples were placed in fused zirconia rotors and spun with dry air at 5 kHz during ^{13}C acquisition and at 3 kHz during ^{15}N acquisition. ^{13}C spectra were referenced to the methine resonance of solid adamantane at 29.5 ppm, while ^{15}N spectra were referenced to solid glycine at 0 ppm.

Data were collected under magic-angle spinning conditions with high-power proton decoupling. The magic-angle was set to within 0.1° using the spinning-sidebands of ^{79}Br of powdered KBr. A 1-ms mixing pulse, 5-s recycle delay, and 50-ms acquisition time were used during both carbon and nitrogen experiments. A ^{1}H 90°-pulse of a 4.0 to 4.5 μs pulse was used for both carbon and nitrogen acquisition. Ring-down delays of 30 and 40 μs were used for ^{13}C and ^{15}N, respectively. A ^{13}C 90°-pulse of 4.3 to 4.4 μs was used for magic-angle spinning experiments without cross-polarization and during relaxation experiments. A 3-s recycle delay was used for direct polarization experiments (referred to as HP/MAS experiments). Spin-lattice data were collected using the method developed by Torchia.[13] The CPT1 experiment used here is a modification of the Torchia experiment using a single pulse delay between carbon pulses instead of a collection of delays. The single delay is based on the determined T_{1C} values in which the delay was chosen to be about five times the intermediate relaxing component in order to selectively observe the most rigid fractions of the polymer samples. On the other hand, the short recycle used in the HP/MAS experiments is not long enough to allow the rigid components to relax back to thermal equilibrium leaving only the fast relaxing components to be observed.

Solid-state and solution NMR, ATR FTIR, and DSC data were processed off-line using *SpectraCalc*[14] and *SC_NMR* an array basic program written in-house to process NMR data. The T_{1C} data were analyzed using **SIMFIT** from Bruker, which was run on an Aspect-3000 computer.

The nylon 7 flakes were processed as follows; samples with different histories were given names according to treatments. The flakes were melt-pressed at about 25 kpsi at 280 °C (above the T_m = 233 °C[15]) and either annealed under vacuum at 200 °C for 2 days in a sealed tube (**AF** = annealed film), quenched from the melt (280 °C) in ice-water (**QF** = quenched film), or cast from 2,2,2-trifluoroethanol and methylene chloride (3:2 by volume) under ambient conditions in a glass dish (**CF** = cast film). Additionally, the glass surface was treated with 3 N hydrochloric acid, dried and another sample cast on the surface (**CFH** = acid-treated cast film). A separate sample cast onto the untreated glass was annealed 2 days in a sealed tube under vacuum at 160 °C (**CA** = cast, annealed film). Another sample of the polymer dope in TFE:CH_2Cl_2 was precipitated into rapidly stirring diethyl ether and dried under high vacuum at ambient temperature for several days (**PF** = precipitated flakes). A sample of the solution-cast film was treated with a solution of potassium iodide (17.6 g) and iodine (15.2 g) in 120 mL of water for 2 days at ambient temperature. The resulting black film was then treated with aqueous sodium thiosulfate (7.2 g in 120 mL of water) for 2 days which gave a colorless film that was dried for 2 days under high vacuum at ambient temperature (**IF** = KI/I_2 treated film).

RESULTS AND DISCUSSION

The methods described above to prepare the different polymer sample do not appear to have caused degradation. The resulting films were all creasable and were not discolored. The precipitated flakes also did not discolor upon thermal treatment. The 2,2,2-trifluoroethanol:methylene chloride mixture is an excellent solvent system for dissolution of semicrystalline nylons for solution NMR characterization and has been used successfully to prepare nylon blends.[16]

Solid-state NMR

Several methods of observing solid-state NMR spectra of semicrystalline polymers can be used to selectively view rigid or mobile phases, or both together. Spectra obtained using magic-angle spinning, cross-polarization, and high-power proton decoupling during acquisition (CP/MAS) contain contributions from both rigid and mobile components. This method is the one most commonly used for polymer characterization.

A slightly different method, in which the carbon magnetization is allowed to decay in the laboratory frame after cross-polarization followed by high-power proton decoupling and acquisition (CPT1 pulse sequence[13]), allows observation of rigid or crystalline components using the appropriate value of tau, the variable delay used between the carbon 90° pulses. Values used for the CPT1 acquisitions were based on the results from the carbon T_1 experiments such that they were at least 5-times the carbon T_1 values for the fast-relaxing component. Finally, magic-angle spinning combined with high-power proton decoupling during acquisition (HP/MAS), but without CP, allows observation of the more mobile components and is most like solution NMR in terms of behavior observed.

The ^{13}C solution and HP/MAS spectra of nylon 7 (QF) are shown in Figure 1. The HP/MAS spectra of the other polymer samples were virtually identical to that shown. The similarity of all of the HP/MAS spectra suggests that the behavior of the mobile amorphous fraction of the samples is essentially independent of sample history. The peaks in the upper trace correspond well with those in the lower trace, with the downfield shift of the carbonyl peak in the solution spectrum probably due to strong solvent interaction (strong hydrogen bonding) not present in the bulk polymer. Peak broadening in the HP/MAS spectrum is due to a distribution of conformational environments present in the amorphous regions. It is clear that the peaks of the carbons on either side of the amide group (C-1 and C-6) are cleanly separated from the remaining peaks, and provide a sensitive measure of local environment involving crystallinity and amorphous packing.

For comparison, the ^{13}C CPT1 and ^{15}N CP/MAS spectra of α-nylon 6,[8] and the α- and γ-forms of nylon 8[17] are shown in Figures 2 and 3, respectively, along with the spectra for the cast film (CF) of nylon 7 prepared here. Only the crystalline resonances are shown in the carbon spectra while the nitrogen spectra contain peaks for crystalline and amorphous domains. Similarities can clearly be seen for the top three CPT1 spectra, all of which are for samples possessing the α-crystalline form. The most downfield peak belongs to the carbon immediately adjacent to the amide nitrogen appearing near 43 ppm. The next most downfield peak of similar intensity belongs to the carbon adjacent to the carbonyl (near 36 ppm). The highest field peak is for the carbon β to the carbonyl carbon (28 ppm for nylon 7 and 25-26 for nylons 6 and 8). The position of these three peaks is characteristic of the α-polymorph. The bottom CPT1 spectrum is for γ-nylon 8 and the peak positions are consistent with those observed for γ-nylon 6.[8] The crystalline resonances for the carbons immediately surrounding the amide unit of γ-nylon 6 appear at 40 and 38 ppm while the carbon β to the carbonyl carbon does not appear as a separate peak.

The ^{15}N spectra reflect large chemical shift differences in the nylon phases. The α-phase appears near 84 ppm, while the γ-phase appears near 89 ppm. The amorphous fraction is observed between these two values as a broad peak with a maximum between 86 and 87 ppm. Trace A shows only α-crystal form while both traces B and C show peaks for both types of crystalline domains. The small peak at 89 ppm in trace C is consistent with weak peaks for the γ-phase seen in the ^{13}C spectrum. Surprisingly, the intense ^{15}N peak for the γ-phase in trace B does not have a correspondingly intense set of carbon peaks (Figure 2). The nylon 8 sample, however, shows peaks only for γ-crystal domains by both ^{13}C and ^{15}N NMR. Solid-state ^{15}N spectroscopy offers greater sensitivity for qualitative observation of the γ-form crystallites, although both methods should be used to obtain a more complete picture of molecular level packing and behavior.

The ^{13}C CP/MAS and CPT1 NMR spectra (high-field region between 5 and 65 ppm) of the various nylon 7 samples are shown in Figure 4, while the chemical shift values (from the CPT1 spectra) are contained in Table 1. All of the CP/MAS spectra contain similar major peaks near 28, 32, 36, 40 and 43 ppm, with the peak at 32 being the most intense. In fact, the traces look similar for the pairs **AF-CA** and **PF-QF** and their resemblance to the α-phase spectra in Figure 2 indicates that the crystalline domains of these samples are predominantly in this crystal form also. The traces for **CF** and **IF** are dissimilar from the rest and have additional peaks which correspond to γ-phase components. Casting of a nylon 7 TFE-CH_2Cl_2 solution onto glass followed by evaporation of the solvent induces the formation of the γ-phase, although the main phase is α. All other sample treatments gave the thermodynamically stable α-phase.

Samples **CF** and **CA** were cut from the same original cast film and initially contained the same fractions of crystalline polymorphs. **CA** was annealed at 160 °C for 2 days under vacuum and the resulting CPT1 spectrum shows no traces of the peaks corresponding to the γ-phase that was once present in the sample. This indicates that the γ-phase can be thermally converted to the α-phase. This behavior is similar to that of nylon 6 α- and γ-phases.[3] γ-Nylon 6 can be annealed into the α-phase at temperatures below the melting point at ambient pressures. Although the two polymorphic nylons (6 and 7) appear to behave in a similar manner, nylon 7 may not be as easy to convert from the α- to the γ-form due to the extra methylene unit. In support of this, treatment of nylon

7 **IF** (which already contains some γ-phase) with KI/I_2 in water does not fully convert all of the α-crystallites into γ-crystallites even after soaking for 2 days, while a thin film of α-nylon 6 is quickly converted to γ-nylon 6 in a few minutes.[18]

Additionally, the nylon 7 α-crystallites formed upon crystallization during solution casting may be somewhat smaller and less ordered than those of the α-crystallites present in the annealed sample based on T_{1C} measurements, ^{13}C chemical shifts, and DSC results. The α-phase can be partially converted to the γ-phase by treatment with aqueous potassium iodide/iodine, in direct opposition to an earlier report[19] of the interaction of KI/I_2 solutions with polyamides. In that study, the crystal phases of several types of polyamides (A-B and AA-BB) were monitored by IR spectroscopy both before and after treatment. Nylon 7 showed virtually identical spectra, implying that γ-nylon 7 did not form. However, treatment of nylon 7 here is slightly different than that reported earlier: the sample already contained some γ-polymorph and the chemical treatment converted some of the α-phase to the γ-phase as shown by differences in both the NMR and IR spectra.

The chemical shift of C-1 for the series of nylon 7 samples studied here appears to follow a trend; the longer the annealing time and the more order induced by annealing below the melting transition, the further downfield the C-1 peak. **AF** C-1 appears at 43.7 ppm which is the most downfield of any of the C-1 resonances. The next most downfield C-1 resonance is for **CA** at 43.3 ppm, followed by **CF** at 43.1 ppm, **PF** at 43.0 ppm, and **QF** at 42.9 ppm. This order of decreasing chemical shift may be related to the amount of crystallite imperfections that are present. The more perfect the crystals, the narrower the distribution of conformational environments of the amide unit. The more conformations present (more crystal disorder) the more the average chemical shift of C-1 approaches the resonance of C-1 in the amorphous phase (near 40.5 ppm). Thus, going from ordered to less ordered α-crystallites should cause an upfield shift in C-1.

Carbon-13 spin-lattice values are listed in Table 2 as obtained using **SIMFIT**, a simplex algorhythm for calculating T_1 values. It was found that most of the magnetization decays could be best fit using two or three exponential components. A multi-component decay is common for semicrystalline polymers.[11,20,21,22] The longest values (T_1's of hundreds of seconds) correspond to rigid, crystalline components, while intermediate values (T_1's of tens of seconds) are for constrained amorphous fractions (interphase). The fastest relaxing component (T_1's of hundreds of milliseconds) is the mobile amorphous material for which very little short range order and no long range order exists. The two annealed samples (**AF** and **CA**) have the highest degrees of order and the most well formed crystallites as suggested by their long T_1 component (>150 s). The estimated intensities of the signals for this slow-relaxing component were 42% and 32%, respectively, as calculated using the **SIMFIT** program.

The solid-state ^{15}N CP/MAS NMR spectra of the various nylon 7 samples (Figure 5) contain one or two resonances, with some of the spectra showing similarities to each other. The α-modification of nylon 7 appears near 84 ppm with a broad peak near 86 to 87 ppm for the amorphous fraction (**AF** and **CA**). Broad, featureless peaks centered near 86 ppm (**PF** and **QF**) indicate low levels of crystallinity. The polycrystalline samples (**CF** and **IF**) have three peaks, with the crystalline peaks near 89 and 84 ppm (γ and α, respectively) and a broad amorphous peak overlapping the two, centered near 86 ppm. These chemical shifts agree very well for those of similar modifications for nylon 6,[8] nylon 11,[10] and nylon 12.[11]

Figure 6 contains spectra of **CF**, **QF**, and the subtraction spectrum (**CF** - **QF**). This corresponds to the removal of the amorphous contribution to the **CF** spectrum. Two crystalline peaks in the same sample were also seen for nylon 12 cast from phenol:ethanol (84:16 by weight).[11] While the spectral subtraction method used here is not quantitatively valid and leads to artificially narrow peaks, it is qualitatively useful in confirming peak multiplicities and chemical shifts. In fact, the peak widths at half height for the difference spectrum (trace C in Figure 6) are only a little narrower (2-2.5 ppm) than those seen in the CPT1 spectra of ^{15}N-labeled nylons (2-3.5 ppm). The presence of these two peaks clearly confirms the presence of the two crystal polymorphs which we believe exist as highly ordered and separate domains based on T_1 data obtained for labeled samples of other nylons exhibiting similar behavio. It is possible, however, that the two conformations are contained in the same crystalline domains.

ATTENUATED TOTAL REFLECTANCE FTIR

The FTIR band positions and relative intensities are given in Table 3 along with the tentative assignments.[19,23] The spectra shown in Figure 7 focus on the regions 1500 to 900 cm^{-1} and 800 to 400 cm^{-1}. The ΔA-values represent the difference in absorption values from the lowest to the highest point in the spectra and indicate comparable spectral ranges in absorption values. In general, all the spectra are similar across the range from 4000 to 400 cm^{-1}. In fact, the spectra for **AF** and **CA** are almost indistinguishable.

Observable differences appear in the region near 1400 cm^{-1} for methylene scissoring. Several bands common to all the spectra are seen near 1476, 1466, 1438 and 1419 cm^{-1}. However, the relative intensity ratio of the 1466 and 1419 cm^{-1} bands changes depending on sample treatment. For the low-crystallinity samples (**PF** and **QF**), the band at 1419 cm^{-1} is much lower in intensity while both bands appear to be more pronounced in the sample rich in α-crystallites.

Differences also appear in the amide III and methylene twisting/wagging region (1300-1225 cm^{-1}) although no pattern is discernable. **AF**, **CA**, **PF**, and **QF** have bands at 1279, 1266, 1250, and 1225 cm^{-1} with the 1250 band having the greatest intensity of the four bands for all but the quenched sample. The 1225 band is the most intense for **QF**. The remaining two samples do not have the 1279 and 1266 bands, but two new peaks appear at 1301 and 1287 cm^{-1}.

Bands near 1197, 1165, and 1125 cm^{-1} appear in the spectra of all of the samples except for **QF**, in which the two higher frequency bands disappear and new ones appear at 1206 and 1153 cm^{-1}. Additionally, the spectra of the samples containing the γ-phase have a high frequency shoulder on the 1197 band occurring near 1205 cm^{-1}. In the **QF** sample, this band is the most intense in the region near 1200 and it has a higher frequency shoulder at ca. 1197 cm^{-1}. The 1205 band in the other spectra are of low intensity with respect to other bands in this region which are sharp with no observable shoulders.

Several low intensity bands appear in the region from 1100 to 900 cm^{-1}, which have been assigned to the -CONH- skeletal deformations.[18] Low crystallinity samples and α-rich samples show bands near 1079, 1063, 1044, and 1018 cm^{-1}, although the 1063 band is hardly seen in **QF**. Other bands appear at 1086 and 1006 cm^{-1} in the sample containing the γ-polymorph. All of the spectra contain a band at 939 cm^{-1}.

The region between 900 and 400 cm^{-1} is assigned to the amide V, amide VI and fundamental CH_2 rocking modes.[24] Several bands in this region are of diagnostic importance. All of the spectra have bands near 875, 790, and 725 cm^{-1}, while the γ-phase samples have extra peaks. The amide V peak appears near 685 cm^{-1} for the α-phase and moves progressively to higher frequency upon annealing: 681 for **AF**; 684 for **CA**; 687 for **QF**; and 689 for **PF**. This correlates with increases in solid-state NMR T_1 values, and may be related to increased crystallite perfection. This band is split into two peaks for the samples that also contain the γ-polymorph, one near 705 cm^{-1} and the other near 690 cm^{-1}. A band is also observed at 620 cm^{-1} for these samples (**CF** and **IF**) which is low or absent from the remaining spectra. The **QF** spectrum, however, contains two peaks at 640 and 626 cm^{-1} plus a third at 554 cm^{-1} which are absent from all the remaining spectra. These low frequency bands may be related to a rigid amorphous phase locked in by quenching from the melt.

The amide VI mode is seen in all spectra near 578 cm^{-1} and moves to higher frequencies on annealing. In the region below 520 cm^{-1}, unassigned bands are observed near 520 and 435 cm^{-1}, with the higher of the two appearing to sharpen on annealing and skew to higher frequencies for the polymorphic samples. The lowest frequency band behaves very similarly, although it is very low in intensity for **QF** and **PF**.

Thermal Analysis

The DSC data for the nylon 7 samples is summarized in Table 4. No clear correlation exists between either T_m and ΔH and the main crystal form in a given sample. Clearly, the annealed sample (**AF**) has the highest melting point and shows the most order as suggested by the narrowness of the melting peak (ΔT, see Table 4). However, the cast and annealed film (**CA**) has the highest heat of fusion at 93 J/g while its melting temperature is 13 °C lower than **AF**. The **CF** sample, which has a high γ content, shows melting behavior more like **CA** than **AF**, seeming to indicate that transformation of the unstable γ-crystals to stable α-crystals is fast on the time scale of dynamic temperature increase in the DSC experiment. In contrast, the more amorphous samples (**PF** and **IF**) do <u>not</u> rapidly form highly ordered domains during DSC analysis as indicated by lower temperature and broader T_m's and by the significantly reduced values of ΔH. It appears as if the thermally induced γ-to-α transformation is facilitated by the presence of the γ-domains and not by amorphous content. This would be reasonable if this process involved direct transformation of one crystal form to the other and did not involve intermediate formation of a totally amorphous or melted phase. Variable temperature NMR and x-ray analysis of the crystal-crystal and amorphous-crystal transformations would help answer these questions. We conclude that the reason that the unstable γ-form has not been previously observed for nylon 7 is that thermal analysis data gave no indication of its presence, and the x-ray studies were therefore not carried out.

Interestingly, **CF** has a heat of fusion that is greater than that of **AF**, but an NMR

T_1 value that is about one-third that of the **AF** sample. It is possible to have many small, imperfect crystallites that give rise to a large total ΔH value (DSC measurement) but have small T_1's (NMR data). A possible crystal defect that may account for this was suggested by Ruland.[25] In predominantly anti-parallel nylon 7 crystallites, a few chains may in fact run parallel to each other but *maintain the all-planar amide-polymethylene* conformation. This would cause the crystallites to be less perfect than a wholly anti-parallel crystallite without perturbing the hydrogen-bonding or the average chemical shifts of C-1, C-6, and the nitrogen. The parallel chains (in the anti-parallel network) would loosen up the interior of the crystallites leading to reduced spin-lattice values independent of the crystallite size.

The precipitated flakes (**PF**) and quenched sample (**QF**) have the broadest melting peak and the lowest heats of fusion. The breadth of the endotherm suggests that a large distribution of relatively small crystallites is present. This is consistent with broad peaks seen in the ^{13}C and ^{15}N solid-state NMR spectra of these two samples and with their very short ^{13}C T_1 values.

CONCLUSIONS

Nylon 7 cast from 2,2,2-trifluoroethanol:methylene chloride (3:2 by volume) crystallizes into a mixture of the thermodynamically preferred α-modification and the kinetically formed γ-modification. The sample cast onto acid-treated glass was virtually identical to the sample cast onto untreated glass (identical carbon and nitrogen chemical shifts, FTIR band positions, and DSC behavior). Both forms (α and γ) can be observed in the same sample using solid-state ^{13}C and ^{15}N NMR methods and ATR FTIR. While peak separation in the carbon spectrum is not as clean, the peaks in the nitrogen spectrum are clearly observable and can be emphasized by spectral subtraction of the non-crystalline contribution from the ^{13}C and ^{15}N spectra containing both polymorphs. Annealing causes peak sharpness and T_1 values to increase while the chemical shift of C-1, the carbon immediately adjacent to the nitrogen of the amide unit, moves slightly to lower field (more ordered α-form).

Several IR-bands have been tentatively assigned to γ-phase nylon 7 at 1301, 1205, 1085, 1006, 762, 706, 692, and 620 cm^{-1}. These bands are not present in the spectra of samples containing only α-phase and amorphous material. The appearance of new peaks can be rationalized in terms of conformational differences between chains in α-crystallites and γ-crystallites. The two nylon 7 polymorphs are not expected to have identical unit cells, based on the polymorphism of other A-B type nylons such as nylon 6, nylon 11, and nylon 12. However, the ordered chain packing of the γ-form crystals appears to allow much more rapid thermal transformation to the α-form crystals than from the more amorphous samples, and this process may not require melting of the less stable form but could involve direct crystal-crystal transformation.

Finally, despite the fact that the quenched sample (containing the most amorphous material) and the α-rich samples both possess three components (according to the solid-state NMR T_1 relaxation times and chemical shifts), unique IR bands are observed at 1206, 1153, 640, 626, and 554 cm^{-1}. This suggests that the quenched, frozen-in amorphous fraction is different than either crystalline form and the typical amorphous fraction present in the semicrystalline samples, and this difference in molecular level packing and motion may inhibit the thermal transformation to the stable α-form crystals.

Acknowledgements

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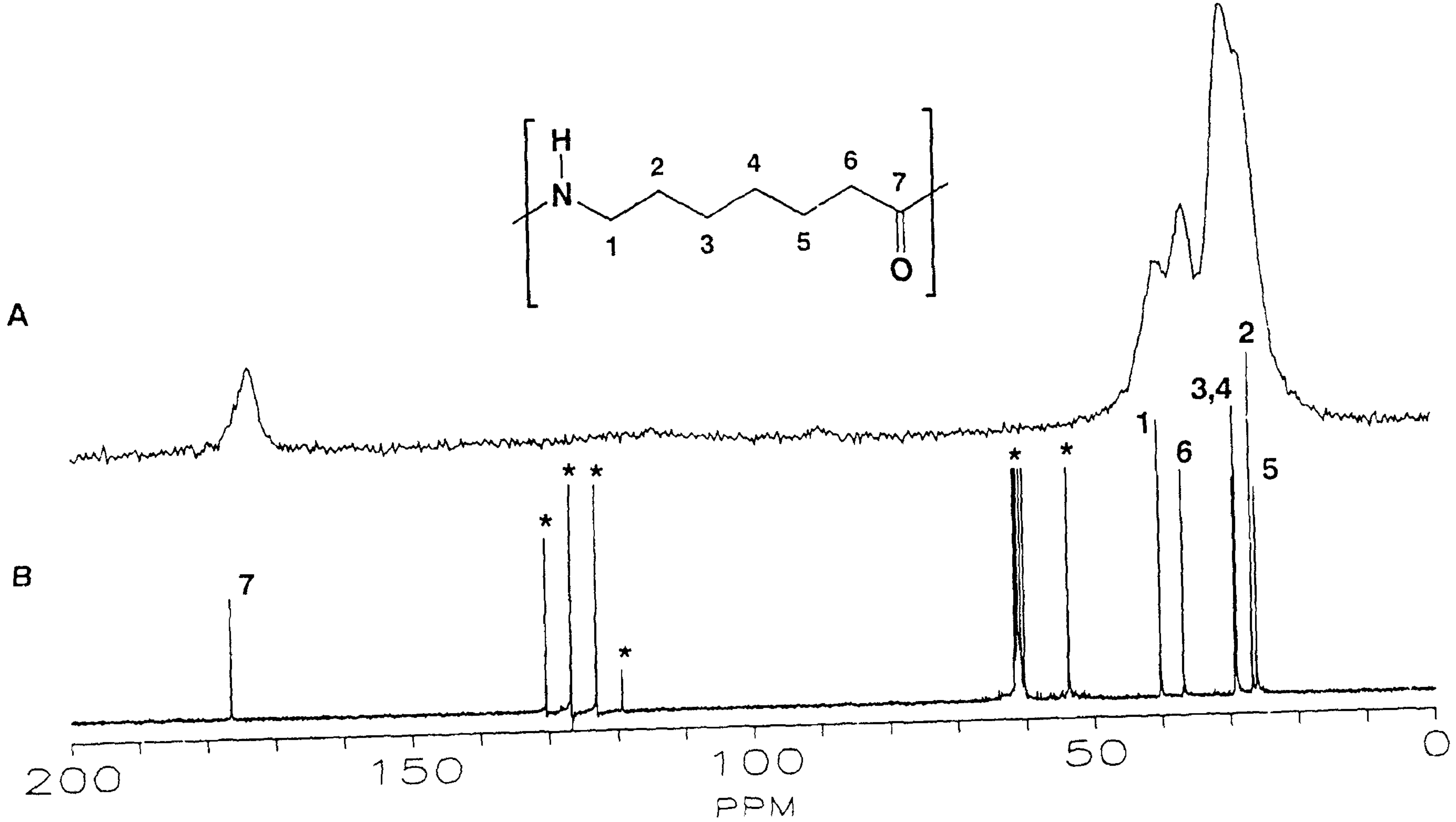
List of Figures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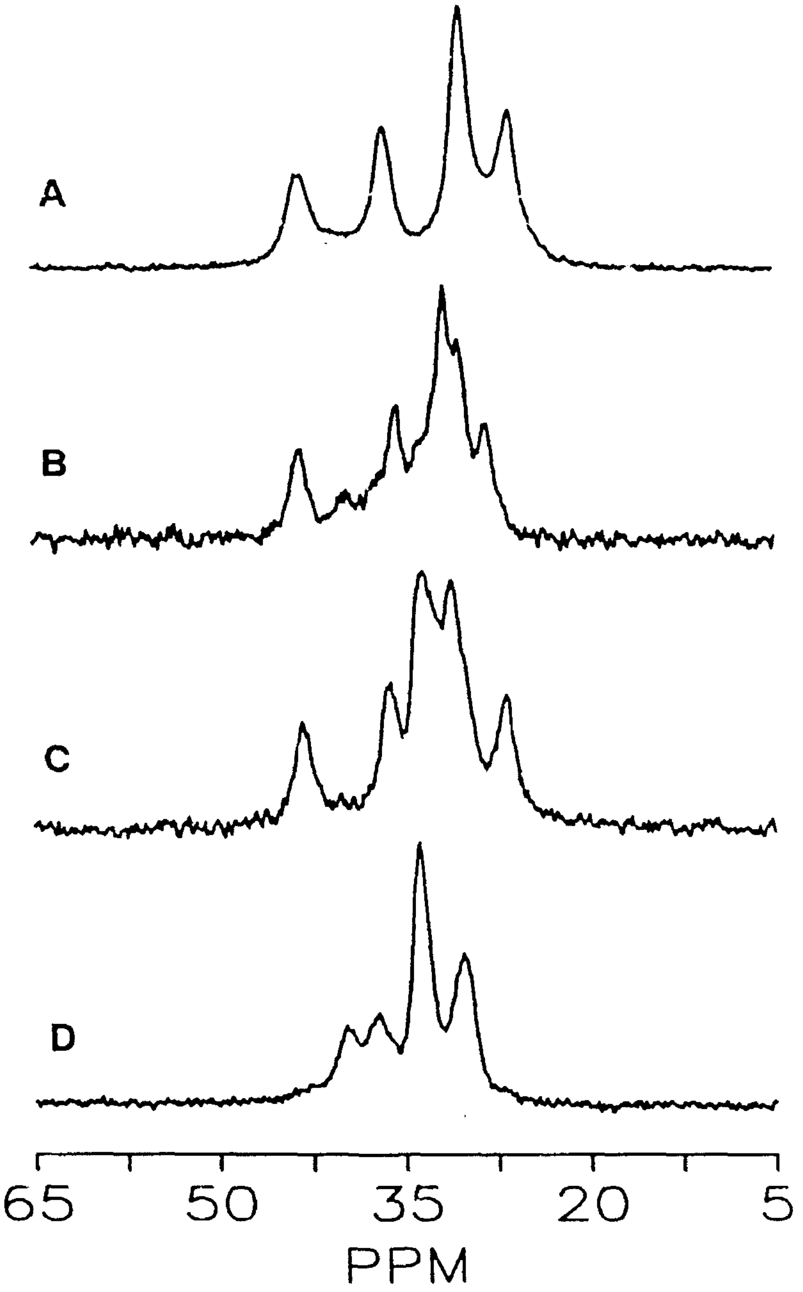
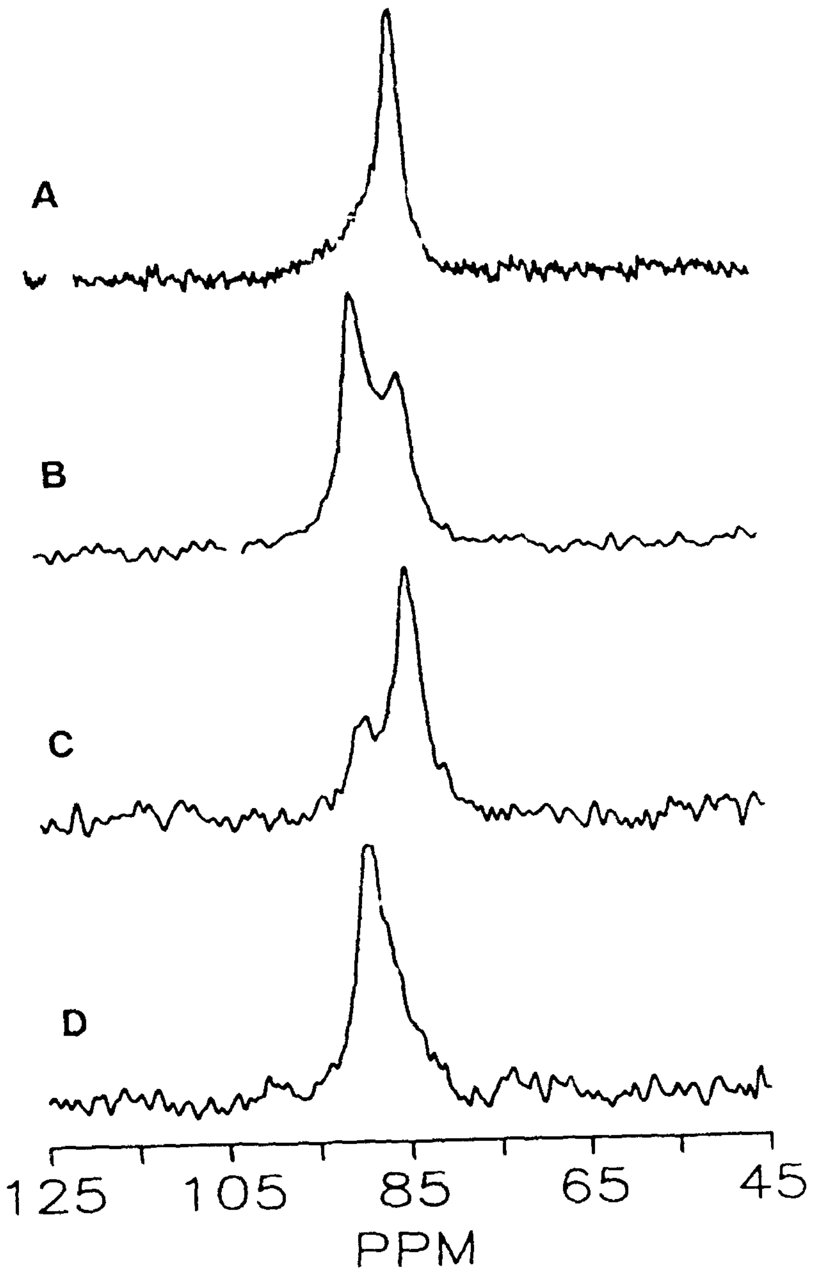


Fig 2



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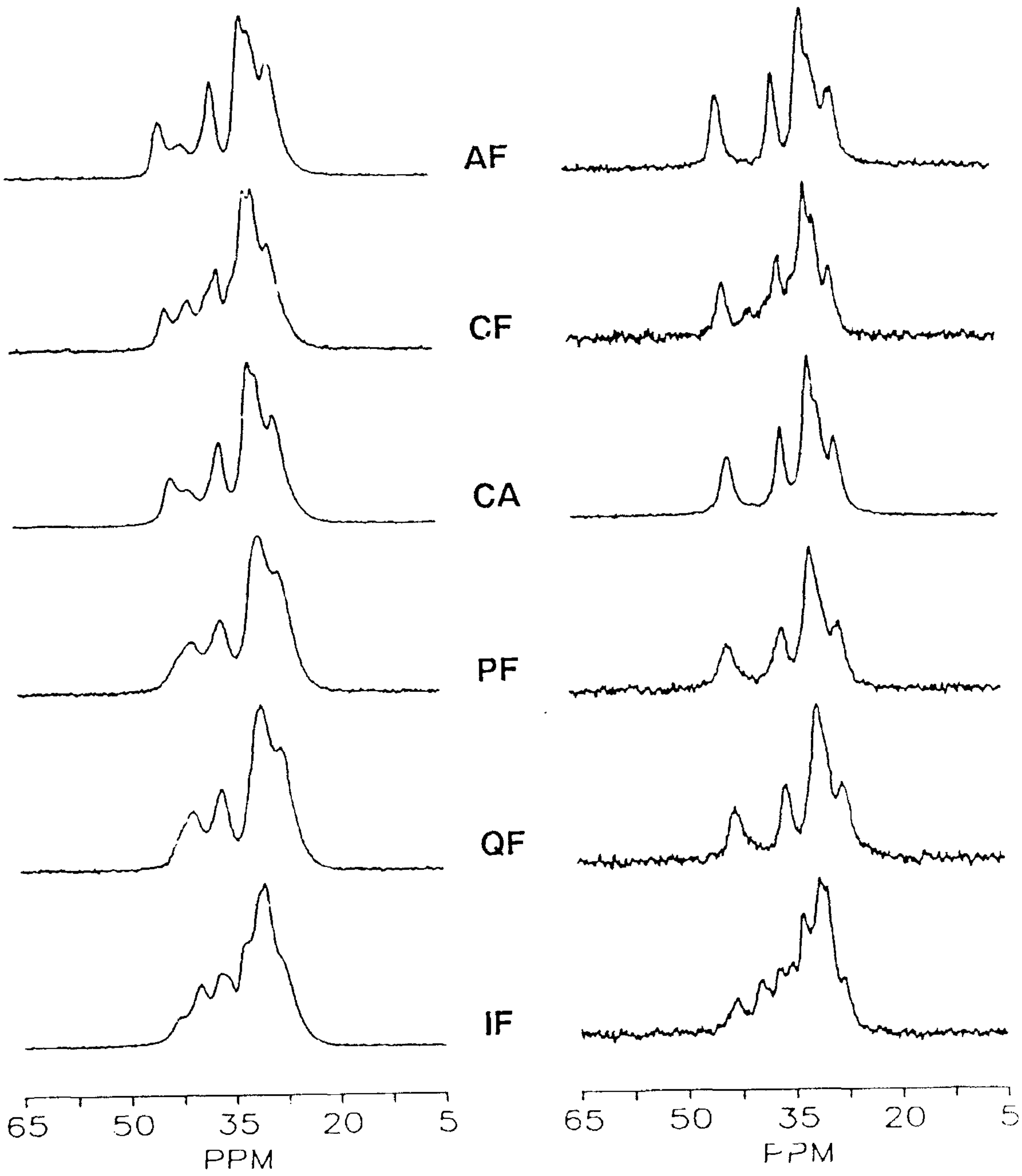


Fig 4

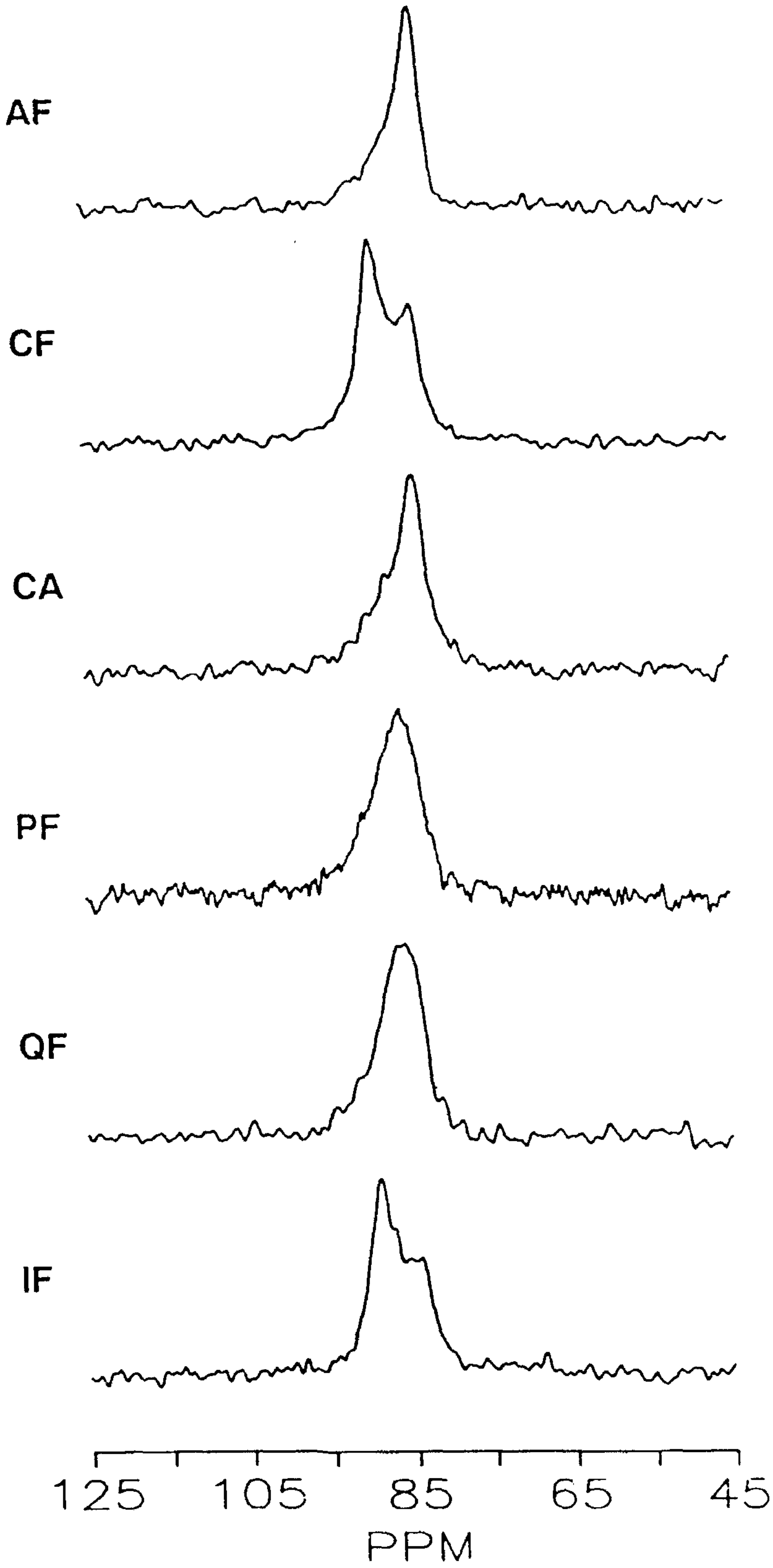
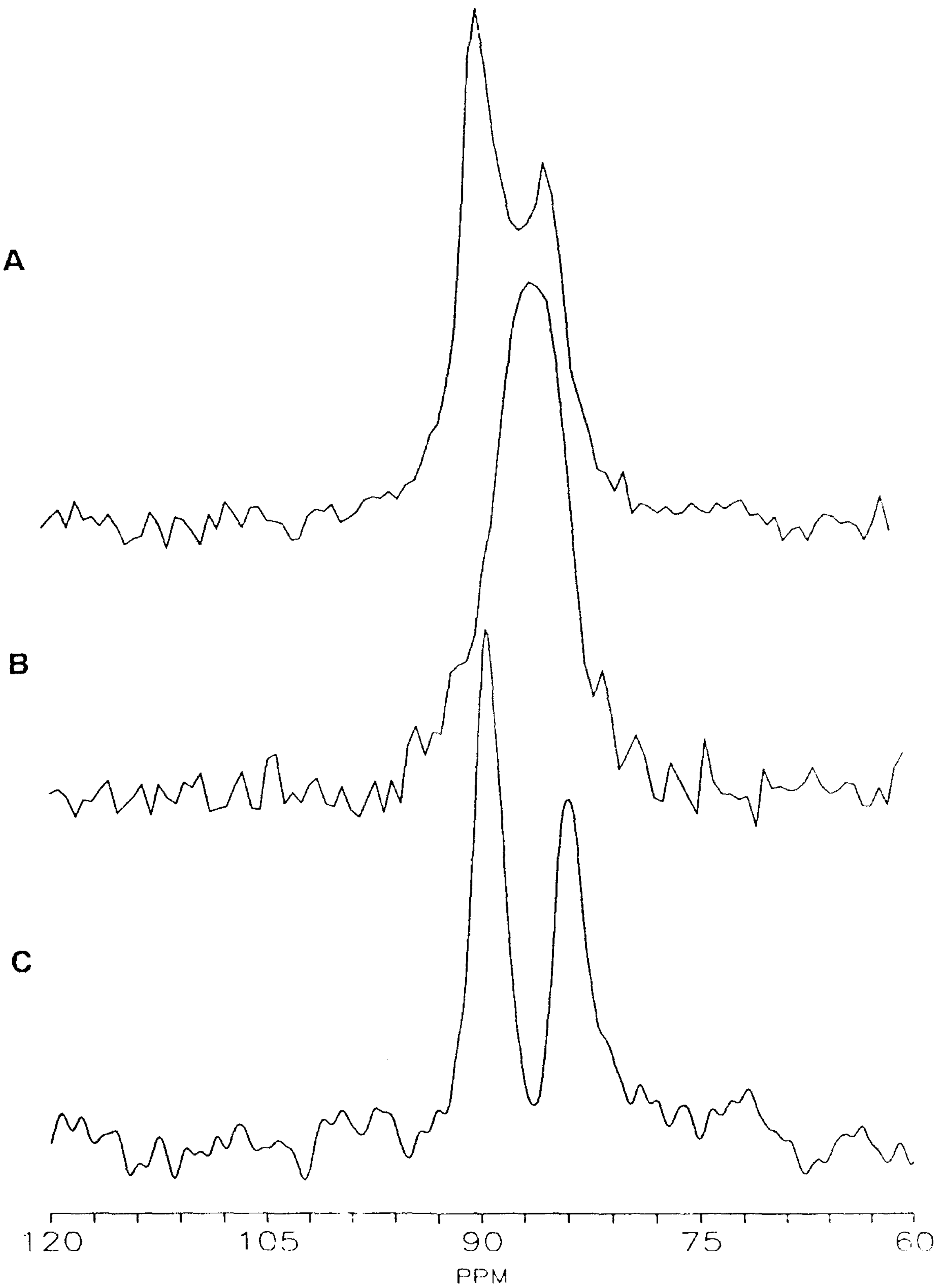


Fig 5



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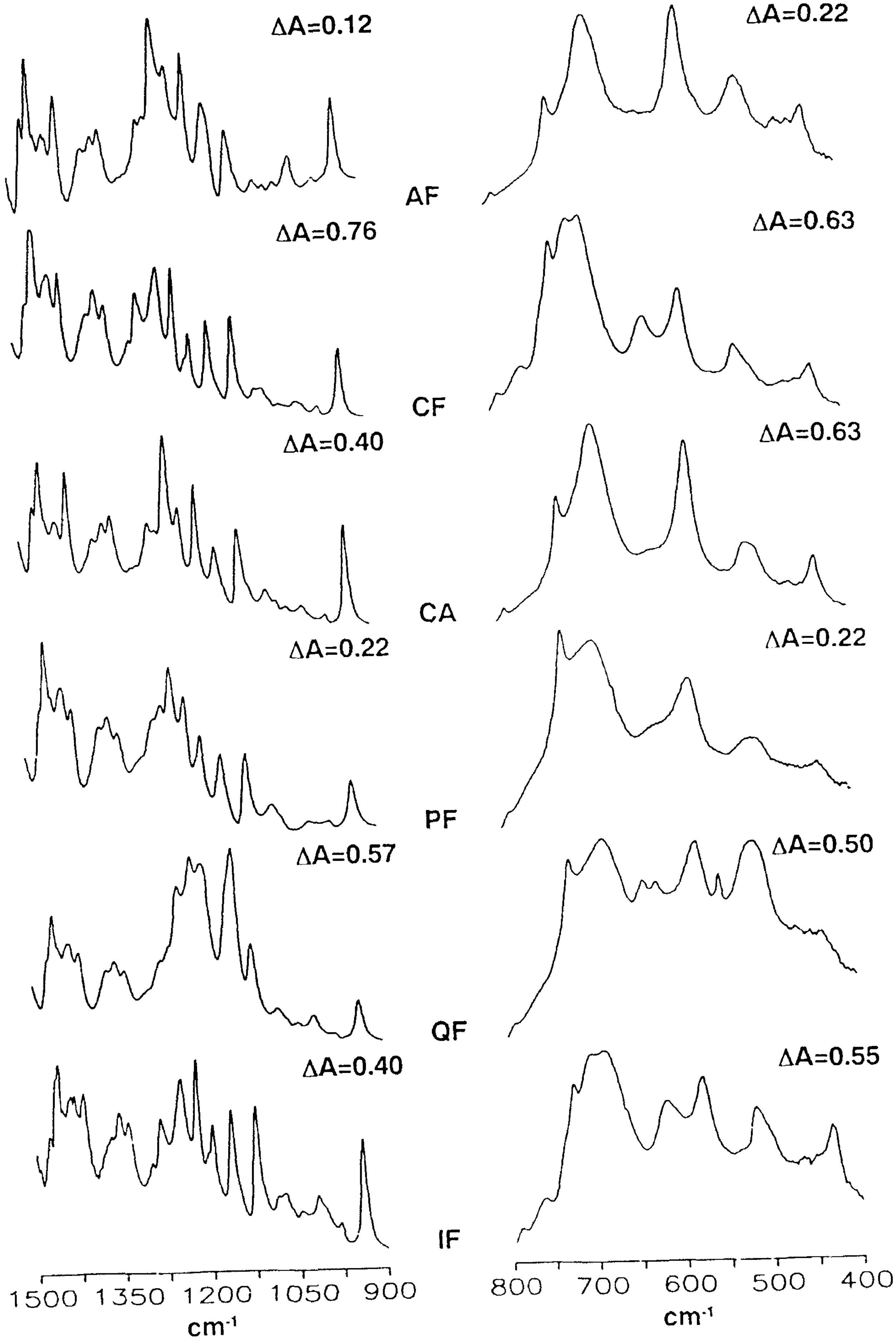
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QF
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IF
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1050
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cm⁻¹
800
700
600
500
400
cm⁻¹

Table 1. ^{13}C Chemical shift data (from CPT1 experiment) in PPM for nylon 7 taken at 100.6 MHz

Sample	C-7	C-1	C-6	C-2,3,4	C-5	NH[a]
AF	173.3	43.7	35.8	31.7	28.7	84.1
CF	173.3	43.1 (α-form) 39.6 (γ-form)	35.6	31.7	28.4 (α-form)	84.5 (α-form) 89.3 (γ-form)
CA	173.8	43.3	35.7	31.7	28.2	84.6
PF	173.2	43.0	35.6	31.5	27.8	86.3
QF	173.5	42.9	35.8	31.4	27.9	85.9
IF	172.8	43.2 (α-form) 39.7 (γ-form)	35.4 (α-form) 37.0 (γ-form)	31.4 (α-form) 33.7 (γ-form)	28.3 (α-form)	84.3 (α-form) 89.0 (γ-form)
amorphous[b]	173.8	40.5	36.6	30.2	28.1	
solution[c]	176.6	40.3	36.9	29.3/29.1/26.1	26.0	

a - data collected at 20.287 MHz under CP/MAS conditions

b - data taken from HP/MAS experiment

c - 5% (w/v) solution in 2,2,2-trifluoroethanol:methylene chloride 3:2 by volume, 75.469 MHz

Table 2. ^{13}C Solid-state spin-lattice relaxation data[a] (T_1 in seconds) for various nylon 7 samples

Sample	C-7	C-1	C-6	C-2,3,4	C-5
AF	4.8 42.6 352.4	0.8 37.8 303.9	0.9 15.5 245.7	0.7 12.0 236.1	0.5 15.2 275.4
CF[b]	3.5 99.5	1.3 7.2 80.3	0.4 4.5 69.4	0.5 5.6 69.8	0.5 5.8 59.1
CA	10.1 65.6 257.0	1.3 26.0 201.4	0.9 15.8 171.3	0.8 13.8 169.4	0.6 10.2 164.3
PF	3.8 23.3	0.60 9.5	0.80 16.2	0.57 9.5	0.50 7.7
QF	8.0 48.7	0.4 3.4 23.9	0.1 1.0 6.6	0.1 1.2 12.9	0.4 3.5 30.6

a - data taken at 100.6 MHz, not collected for IF sample

b - T_{1C}'s for C-[illegible] (39.6 ppm) of the γ form are 0.4, 8.3, and 105.0 s

Table 3. FT-IR data[a] for Nylon 7 samples collected using an ATR cell

AF	CF	CA	PF	QF	IF	assignment
3297 (0.29)	3293 (1.20)	3297 (0.45)	3298 (0.39)	3297 (0.57)	3289 (0.47)	hydrogen-bonded N-H
3064 (0.18)	3091 (0.31)	3069 (0.22)	3080 (0.17)	3080 (0.29)	3088 (0.32)	amide B
2928 (0.30)	2925 (1.07)	2925 (0.44)	2929 (0.41)	2927 (0.62)	2920 (0.48)	CH_2 stretching
2853 (0.30)	2853 (0.83)	2852 (0.39)	2857 (0.31)	2854 (0.52)	2851 (0.46)	
	1638 (3.24)				1637 (1.00)	amide I, CO stretching
1632 (0.58)	1634 (3.16)	1632 (1.24)	1636 (1.30)	1632 (1.38)	1632 (1.03)	
	1558 (1.70)				1561 (0.78)	amide II, CN stretching plus N-H in plane vibr.
1536 (0.53)	1538 (2.10)	1536 (1.09)	1544 (0.84)	1537 (1.19)	1536 (0.93)	
1476 (0.32)	1476 (0.65)	1474 (0.51)	1475 (0.30)	1474 (0.55)	1477 (0.56)	CH_2 scissoring
1464 (0.36)	1464 (0.94)	1466 (0.60)	1466 (0.39)	1464 (0.68)	1461 (0.69)	
1438 (0.31)	1438 (0.76)	1438 (0.48)	1438 (0.33)	1437 (0.59)	1439 (0.64)	
1417 (0.34)	1419 (0.75)	1417 (0.58)	1420 (0.32)	1419 (0.57)	1417 (0.64)	
1372 (0.30)	1372 (0.60)	1372 (0.44)	1373 (0.28)	1372 (0.51)	1371 (0.56)	CH_2 twisting
1357 (0.31)	1359 (0.69)	1358 (0.47)	1359 (0.29)	1358 (0.54)	1357 (0.61)	
1343 (0.32)	1342 (0.63)	1343 (0.49)	1341 (0.27)	1341 (0.51)	1341 (0.59)	
	1300 (0.49)				1301 (0.51)	amide III
1278 (0.32)	1278 (0.67)	1278 (0.47)	1279 (0.29)	1279 (0.54)	1285 (0.59)	

1266 (0.32)		1267 (0.46)	1265 (0.30)	1264 (0.58)		CH_2 twisting and wagging
1249 (0.39)	1251 (0.76)	1249 (0.65)	1250 (0.35)	1248 (0.76)	1250 (0.64)	
1226 (0.36)	1225 (0.77)	1226 (0.50)	1227 (0.31)	1225 (0.84)	1223 (0.70)	
	1205 (0.41)			1206 (0.82)	1204 (0.53)	amide III splitting
1197 (0.37)	1198 (0.51)	1197 (0.55)	1200 (0.27)		1197 (0.58)	
1162 (0.33)	1166 (0.56)	1165 (0.42)	1165 (0.25)		1164 (0.60)	CONH skeletal motion
				1153 (0.86)		
1125 (0.31)	1124 (0.57)	1125 (0.45)	1122 (0.25)	1123 (0.58)	1122 (0.61)	C-C stretching
	1085 (0.29)				1085 (0.45)	CONH skeletal motions
1079 (0.28)	1075 (0.30)	1079 (0.33)	1078 (0.19)	1079 (0.39)	1074 (0.45)	
1062 (0.27)		1064 (0.31)	1065 (0.18)			
1044 (0.28)	1045 (0.23)	1045 (0.29)		1045 (0.35)	1046 (0.42)	
1018 (0.29)	1016 (0.24)	1019 (0.29)	1016 (0.17)	1018 (0.37)	1017 (0.45)	
	1006 (0.23)				1006 (0.43)	
978 (0.28)	980 (0.22)	978 (0.28)	980 (0.17)	981 (0.31)	980 (0.40)	
939 (0.33)	940 (0.43)	940 (0.46)	939 (0.21)	939 (0.41)	939 (0.55)	
875 (0.28)	876 (0.19)	877 (0.26)	875 (0.17)	877 (0.30)	872 (0.38)	fundamental CH_2 rocking
	858 (0.20)				860 (0.36)	
791 (0.31)	791 (0.32)	791 (0.32)	792 (0.21)	791 (0.40)	790 (0.46)	
	762 (0.40)				761 (0.55)	

725 (0.41)	726 (0.80)	726 (0.67)	726 (0.41)	725 (0.78)	725 (0.87)	
	706 (0.87)				704 (0.95)	amide V
	692 (0.88)				690 (0.96)	
681 (0.50)		684 (0.90)	684 (0.40)	686 (0.83)		
				640 (0.73)		unassigned
				626 (0.72)		
	622 (0.55)				620 (0.82)	amide VI
577 (0.51)	580 (0.64)	578 (0.84)	583 (0.36)	580 (0.82)	578 (0.88)	
				554 (0.74)		unassigned
509 (0.43)	519 (0.46)	512 (0.52)	510 (0.29)	515 (0.82)	518 (0.79)	
435 (0.40)	433 (0.39)	435 (0.47)	439 (0.26)	438 (0.67)	432 (0.74)	

a - values in paranthesis are relative intensities for a given sample

Table 4. DSC data for nylon 7 taken at 10 °C/minute

Sample	Onset T_m, (°C)	Peak T_m, (°C)	ΔH, (J/g)	ΔT[a]
AF	239	242	73	3
CF[b]	223	229	85	6
CA	225	229	93	4
PF	219	230	63	11
QF	220	228	52	8
IF	226	230	82	4

a - ΔT = peak T_m - onset T_m

b - entry values are for sample cast onto untreated glass, acid-treated values are: onset T_m = 222 °C, peak T_m = 229 °C, ΔH = 87 J/g, and ΔT = 7