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^{13}C and ^{15}N Solid-State NMR of Copolymers of Nylons 6 and 7: Observation of a Stable Pseudohexagonal Phase

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ABSTRACT: A series of nylon copolymers were synthesized and characterized based on the even–odd A–B monomer combination caprolactam and enantholactam. The nylon 6-*co*-nylon 7 samples displayed physical properties which directly correlate with copolymer composition. The degrees and types of crystallinity for these materials were examined using a combination of thermal, NMR, and X-ray measurements. The homopolymers each displayed highly ordered α-crystallites while the copolymers possessed less-ordered domains that decreased in α-like characteristics down to the 1:1 copolymer, which possessed a thermodynamically stable pseudohexgonal ordered phase. The ^{13}C T_1 values determined for the annealed 1:1 copolymer were shorter than those of crystalline regions of annealed homopolymers. In fact, they were comparable to values observed for amorphous domains in melt-quenched nylon 6 and nylon 7 homopolymers but significantly longer than the values for a precipitated and annealed 1:1 nylon 11-*co*-nylon 12 sample. Annealing at temperatures ca. 10 °C below the DSC T_m increased the perfection of the copolymer ordered domains based on both NMR and X-ray measurements but did not convert the pseudohexagonal phase to α-crystallites.

Introduction

Nylons possess excellent physical properties that promote their use in applications ranging from fibers to composites and reaction injection molded parts. One potential application of nylons is in piezoelectric materials, which possess the unique ability to interconvert mechanical and electrical energy.[1] The piezoelectric properties of odd A–B nylons (e.g., nylon 7 and nylon 11) have been under study for only a few years.[2,3] The relationship between molecular and microscopic order and the macroscopic behavior of the odd nylons is only now beginning to become clear. Especially important are recent results indicating *increased* piezoelectricity with increasing temperature, significantly past the T_g and even up to the melt.[4] This can be compared to a large reduction in electrical properties for poly(vinylidene fluoride) when heated much above its T_g and suggests that extended crystalline order is maintained at elevated temperatures. Early work on the crystal forms and transformations of nylon 11 illustrates the lack of molecular-level understanding that has existed for nylons until recently: for years it was thought that the α–δ (or Brill) transition[5] that occurs at ca. 95 °C involved formation of a pseudohexagonal phase in which rapid amide group rotation around the chain axis occurred via 60° jumps.[6] We used variable-temperature solid-state NMR techniques, including ^{13}C and ^{15}N cross polarization/magic angle spinning (CP/MAS) and high-power decoupling/magic angle spinning (HP/MAS) observation,[7] along with wide-line ^{2}H analysis of ^{2}H–N labeled samples,[8] to prove that rapid amide bond reorganization did *not* occur in the nylon 11 δ-phase. These results confirmed that the rigid hydrogen-bonded network that exists in the crystalline domains of nylons is maintained even at temperatures close to the crystalline melting point, a conclusion consistent with high-temperature piezoelectric behavior.[4] The question still remains, however, of the nature of the pseudohexagonal phase that has been observed for a variety of nylons; i.e., how is it different from the high-temperature crystal phase which (by X-ray) appears so similar?

We hypothesized that it might be possible to study the pseudohexagonal phase by a combination of synthetic and spectroscopic methods focused on random nylon copolymers of A–B monomers. While several AA–BB systems have been examined in the past, the A–B copolymers are just beginning to be intensively investigated. In fact, it is surprising that ring-opening copolymerizations of lactams have been rarely studied despite the fact that high molecular weight homopolymers are obtained rapidly and efficiently. Recent studies of A–B copolymers involved ring-opening polymerization of caprolactam with laurolactam to give nylon 6-*co*-nylon 12 samples[9] and reaction of the lactam for nylon 8 with laurolactam to give the corresponding nylon 8-*co*-nylon 12 polymers.[10] Condensation polymerization of activated amino esters to give odd terpolyamides has also been reported.[11] We recently described initial results with nylon 11-*co*-nylon 12 polymers obtained by thermal polycondensation of the corresponding amino acids.[12]

The present report describes the copolymerization of caprolactam with enantholactam to give a series of nylon 6-*co*-nylon 7 samples. Our interest in these materials concerns, specifically, the role disruption of the polar piezoelectric α-nylon 7 crystallites by the nylon 6 units might have on both processability and electrical properties. Figure 1 gives a probable packing arrangement for each polymer in its most stable crystal form; notice the nonadditive and additive orientations of amide dipoles in nylons 6 and 7, respectively. The latter accounts for nylon 7's ability to be oriented to give a permanent net dipole across a thin film, a necessary requirement for piezoelectric behavior. In a more general sense, it was hoped that these copolymers would serve as useful examples of materials displaying deliberately induced, thermodynamically stable pseudohexagonal packing at ambient temperatures. Comparison of the spectral and X-ray scattering data from these copolymers would then help in observation and understanding of other nylons displaying both stable and metastable pseudohexagonal phases and high-temper-

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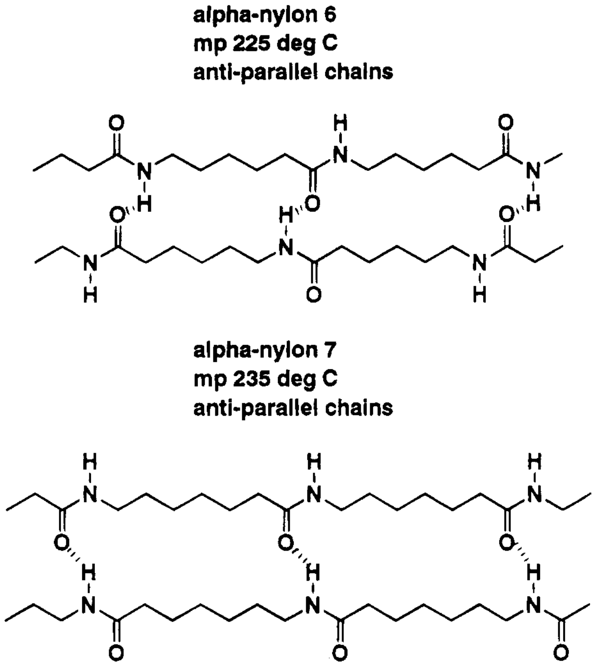

Figure 1. α-Crystal forms for nylon 6 (top) and nylon 7 (bottom).

ature crystalline forms that resemble the pseudohexagonal phase.

Experimental Section

Anionic ring-opening polymerizations of lactams by themselves and in various mixtures were initiated with NaH using *N*-acetylcaprolactam as coinitiator. Polymerizations were carried out in small test tubes under a N_2 atmosphere with rapid conversion at temperatures ranging from 80 to 150 °C. Small amounts of residual lactam monomers (observed in all cases) were removed by reprecipitation or methanol extraction. For comparison purposes, mixtures of the appropriate six- and seven-carbon amino acids were subjected to thermal polycondensation under nitrogen purge to give nylon 6-*co*-nylon 7 copolymers of similar compositions and identical physical properties.

Characterization involved inherent viscosity measurements in 3:2 mixtures of trifluoroethanol (TFE) with CH_2Cl_2 and differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7. Solution NMR (^1H and ^{13}C) spectra were obtained using ca. 10 wt % solutions of nylons (same TFE–CH_2Cl_2 solvent) on a Bruker AC-300 spectrometer. Annealed samples were prepared by heating overnight at ca. 10 °C below the DSC T_m endotherm in glass tubes sealed under vacuum. Solid-state ^{13}C and ^{15}N NMR spectra were obtained on Bruker MSL-200 and MSL-400 spectrometers using conditions described previously, with spectra referenced respectively to the adamantane methine peak at 29.5 ppm and the glycine ^{15}N peak at 0 ppm.[7,12,13]

Results

Ring-opening polymerizations of these two lactams to give copolymers was fast and clean and occurred in high yields. Removal of residual monomer by extraction or precipitation from TFE–CH_2Cl_2 mixtures into acetone gave pure polymers. Viscosities were obtained in this same solvent mixture, and films could also be cast if appropriate care was taken to eliminate water and allow slow solvent evaporation during the casting process. Inherent viscosities ranged from 2 to 4 dL/g (at 0.5 g/dL), confirming formation of high molecular weight polymers. This solvent system is an excellent one also for high-resolution NMR in that it gives relatively low-viscosity, high-concentration solutions.[14]

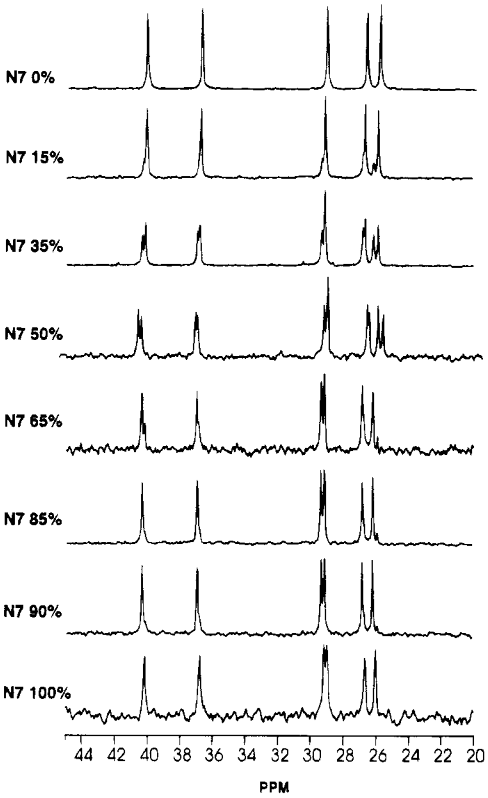

Figure 2. Solution NMR of copolymers (compositions shown).

Solution NMR characterization of the copolymers was used to confirm overall compositions. Figure 2 gives representative ^{13}C spectra illustrating separation of peaks for the two repeat units which allowed approximate determination of repeat unit ratios. No indication is apparent of additional sequence information such as diad or triad peaks. Good correlation of composition to feed ratio was observed (based on peak heights), although there appeared to be a slightly higher incorporation of the nylon 7 monomer unit in all copolymers studied. This is surprising given the high conversions; i.e., if preferential incorporation of one of the monomers occurred early in the reaction, the drift in monomer ratio would lead to higher incorporation of the less reactive species near the end. In fact, the 8-membered ring lactam has been reported to possess a higher reactivity compared to the 7-membered homolog, a difference which has been discussed in terms of enthalpy and entropy considerations.[15] Based on the high heats of polymerization (which allow rapid transamidation) and the fact that amino acid condensation polymers gave very similar compositions and identical properties to those of the lactam polymers (results not reported here), we believe random copolymerization occurred and that the qualitative and quantitative observations below reflect correlations with random compositions.

Figure 3 gives the values determined by DSC (second heating run) of apparent melting points (T_m) and heats of fusion (ΔH_f) for the series of copolymers and the homopolymers synthesized under the same conditions. Good correlation is seen with respect to composition, similar to what was reported previously for nylon 8-*co*-nylon 12 and nylon 11-*co*-nylon 12 polymers. That is, gradual decrease in T_m and ΔH_f values to a minimum at ca. 1:1 composition was observed. This is consistent with disruption of crystal packing and crystallinity due to mismatch of the number of CH_2 units in the two

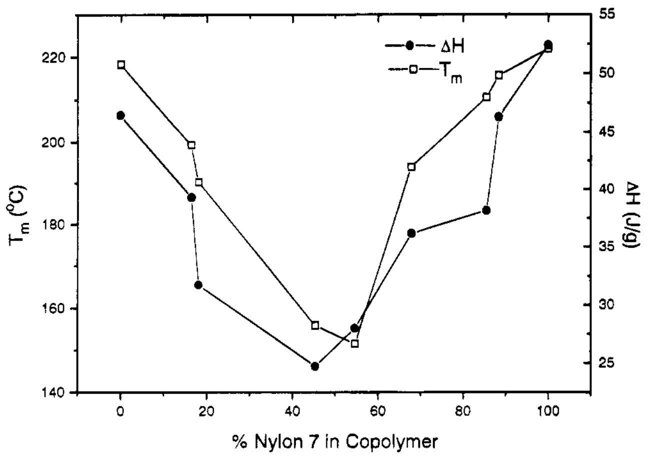

Figure 3. Plots of T_m and ΔH versus nylon 7 content in copolymer (from second DSC heating run).

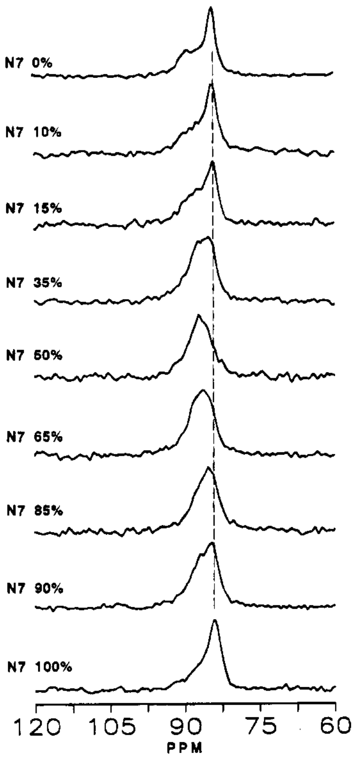

Figure 4. ^{15}N CP/MAS spectra of precipitated nylon 6-*co*-nylon 7 samples after annealing.

repeat unit structures within the overall hydrogen-bonded framework. In fact, it should be noted that the copolymers ranging from 30:70 to 70:30 compositions could all be solvent cast into transparent, colorless films. This indicates a lower degree of crystallinity and/or very small crystallites as would be expected for mostly amorphous materials or those not forming spherulites. However, the observation of melting enthalpies measured by DSC argue for the existence of ordered domains. NMR and X-ray data given below indicate that the copolymers do, in fact, form ordered arrays which do not possess the same type of crystallinity existing in the α- and γ-forms common to most nylons.

Solid-state NMR analysis of these samples allowed identification of the type and relative content of typical crystalline forms seen in nylons plus rigid and mobile amorphous regions. Figure 4 gives the ^{15}N spectra of precipitated, dried, and then annealed samples. Sample history was found to have a large effect on the type and degree of crystallinity. For example, annealing pure nylon 7 homopolymer greatly increased the relative height and sharpness of the α-form crystal peak (at 84 ppm). The precipitated nylon 6 sample showed peaks for both α- and γ-crystals (84 and 89 ppm, respectively), and annealing greatly increased the former at the expense of the latter. The intense α-form NMR peaks for the homopolymers are consistent with previous reports of α-crystalline contents of 30–40% for annealed samples of these polymers.[15]

It should be noted that nylon 7 readily adopts the α-crystal form[16] preferred for odd A–B nylons as seen for higher members of the homologous series including nylon 11,[7] while nylon 6 adopts the α-form *in contrast* to higher even-numbered polyamides, such as nylons 8, 10, and 12, which prefer the γ-form thermodynamically.[17] Nylon 6 is, therefore, at the borderline between higher members of the homologous series (γ-form preferred) and the lower members (nylons 2–5), all of which prefer the α-form. This should allow the copolymers to adopt the same thermodynamically stable α-crystalline form, if possible. If not, the pseudohexagonal form expected should represent as mildly a disrupted ordered form as it is possible to get for nylon copolymers.

In fact, the intermediate compositions show decreasing α-form peak intensity with an increase in the broad peak located at ca. 87 ppm until it becomes the major or only peak. The latter has been observed for the amorphous regions of all nylons examined by us to date by solid-state ^{15}N NMR[13] and corresponds to random methylene unit conformations around the plane of the amide group. Sharp peaks at this same chemical shift have been observed for the δ-form of nylon 11 (generated from the α-crystallites at temperatures above the Brill transition at 95 °C) and for a metastable form of nylon 11 obtained by melt quenching. Both forms of nylon 11 generate X-ray patterns consistent with pseudohexagonal packing of chain segments,[18,19] although they differ fundamentally in registry of adjacent amide hydrogen bond orientations (see Discussion).

The ^{15}N solid-state NMR observations were based on results obtained using CP/MAS, which does not discriminate among crystalline, amorphous, or intermediate regions; it would be desirable to use other solid-state methods but they are too time-consuming with natural-abundance ^{15}N samples.[20] These spectra are thus composites (although not quantitative ones) of all domains present in the sample but with apparent emphasis on the crystalline peaks, which are sharper and therefore more easily seen over the broader amorphous peak. With ^{13}C NMR analysis, higher natural abundance and better NMR response of ^{13}C over ^{15}N allow selective observation of the more rigid (ordered) domains with pulse programs,[21] for example, that select for longer T_1 relaxation times (CPT1 editing method).[22] The spectra in Figure 5 are of annealed samples obtained with the CPT1 pulse train although they are similar to spectra obtained with the normal CP/MAS method. The α-crystal forms of the two homopolymers give the C_N peak at 43.4 ppm, but there are clear differences for the tallest peak (at 30.1 ppm for nylon 6 and 31.6 ppm for nylon 7) and for the C_β peak (β to the carbonyl carbon) at 26.3 and 28.3 ppm, respectively. The ordered domain peaks for the copolymers are not averages of these but instead show a combination of two peaks that are roughly equivalent in relative intensities to the repeat unit contents in the copolymers; similar behavior is seen in solution (Figure 2). For example,

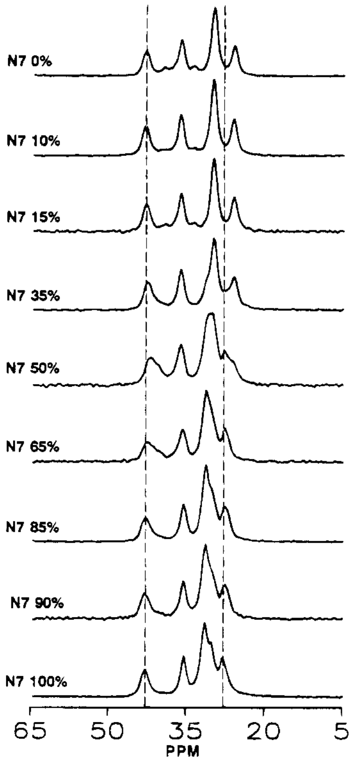

Figure 5. ^{13}C CPT1 spectra of the annealed copolymers.

the C_β peak for nylon 6 units decreases while a peak for the nylon 7 units increases with increasing nylon 7 content. Similarly, two peaks are seen in the intermediate compositions at ca. 30 and 31.5 ppm for the most intense CH_2 peaks of the nylon 6 and 7 repeat units, respectively. The C_N peak for the 1:1 copolymer (and to a lesser extent, the 35:65 and 65:35 samples) shows only a slight upfield movement consistent with contributions to the peak from additional conformations approaching the nonplanar or 60° twisted form of γ-crystallites of nylons. This indicates that the intermediate copolymers possess relatively ordered domains (since CPT1 observation was effective) with conformations around the amide groups ranging from α- to γ-like, exactly as expected for pseudohexagonal packing as described above. A referee has pointed out the γ-gauche interactions along the chain in the various conformations available should also affect the peak positions. This effect will be minimized here to a large extent due to preferred conformations of the backbone segments predominating even in the amorphous regions. This effect therefore manifests itself as a broadening of individual peaks, evident especially in the intermediate copolymers, and is consistent with the observations above.

The ^{13}C T_1 relaxation times determined for the CH_2 carbons of the annealed 1:1 copolymer were all in the range 6−8 s. These are shorter than those of crystalline regions of the homopolymers, which range from tens to hundreds of seconds, but are comparable to those observed for poorly ordered domains in melt-quenched nylon 6 and nylon 7 homopolymers.[12,16] However, they are significantly longer than the values observed for a precipitated and annealed 1:1 nylon 11-*co*-nylon 12 sample.[23]

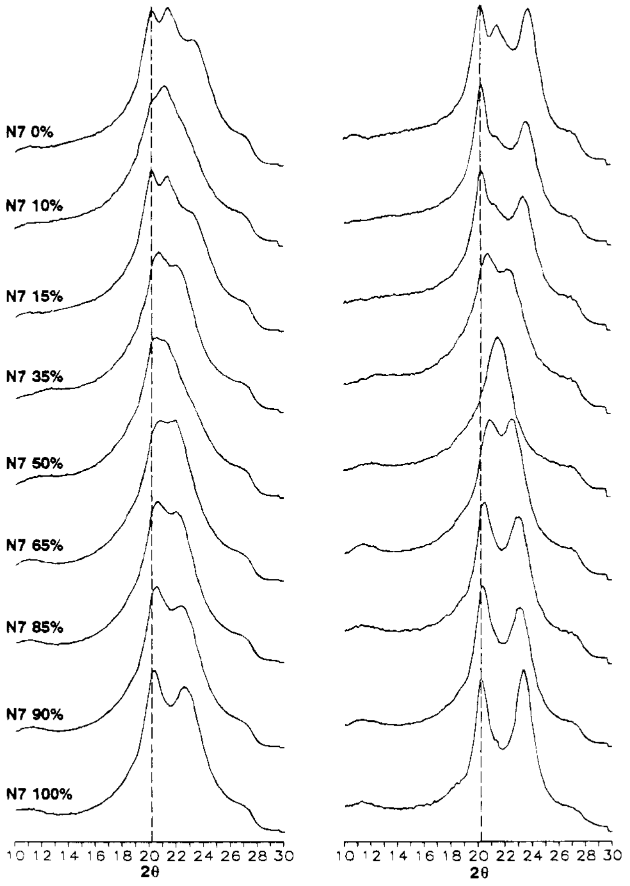

Figure 6. X-ray powder patterns of the as-precipitated (left column) and annealed copolymers (right column).

The X-ray results confirm microscopic-level behavior implied by the NMR and DSC results. Figure 6 shows powder patterns for the as-precipitated and annealed samples (left and right columns, respectively), with the latter showing sharper and more defined peaks consistent with increased order. The characteristic pair of α-form peaks for the homopolymers (at 2θ values of 20.3 and 23.7° for nylon 6 and 20.3 and 23.3° for nylon 7) gradually merge into a single peak at the 1:1 copolymer (21.5). A similar peak (in terms of 2θ value and peak shape) was observed for the 1:1 nylon 11-*co*-nylon 12 polymer[23] as well as nylon 6-*co*-nylon 66 polymer,[24] both of which exhibited characteristics of the pseudohexagonal phase. Three additional points should be made. First, the patterns for the as-precipitated samples were sometimes markedly different from those of the annealed samples; see especially that of the 10% nylon 7 sample, which looks essentially amorphous or perhaps pseudohexagonal before annealing but strongly α-like after. This behavior is certainly kinetic in origin. Second, all the as-precipitated patterns show a peak or shoulder at ca. $2\theta = 20.3°$ which moved to larger values for the 35:65 to 85:15 samples. Third, the top three patterns show a shoulder at 21.5° which corresponds to the γ-crystallites in these samples as confirmed by the 89 ppm shoulder in the ^{15}N spectra (Figure 4); this peak is even stronger in the ^{15}N spectra of the as-precipitated samples (spectra not shown).

Discussion

The behavior observed here is completely consistent with the observations of others and with previous results from our work. The complicating factors are how adjacent hydrogen bonds are arrayed (in planes or random intermolecular hydrogen bonds) along polymer chains in pseudohexagonal structures, and this is determined by both inherent potential for ordered packing and sample history and/or analysis temperature.

It is therefore important to discuss the pseudohexagonal phase in nylons with respect to whether the room temperature form is stable or metastable and whether that occurring at elevated temperatures is stable there but reverts rapidly to a low-temperature crystalline form. The former is usually labeled the pseudohexagonal phase and has been observed, for example, in nylon 6-*co*-nylon 66 and nylon 6-*co*-nylon 68 copolymers.[24] The latter behavior involves the well-established Brill transition of nylons 6 and 66,[25] and while it is often called a pseudohexagonal phase, we prefer to call it a high-temperature crystalline phase to differentiate it from the former.

The high-temperature crystalline phase has been observed and studied in detail for nylons 6 and 66 and nylon 11. The sharpness and breadth of the thermally induced transitions for each polymer differ significantly. For nylon 11, the transition is readily observed as a first-order DSC endotherm. Variable-temperature solid-state NMR[7] clearly elucidated the molecular and crystalline packing changes involved in the transformation. At the molecular level, crystal lattice expansion is observed as changes in chemical shifts for both carbons and nitrogens of the backbone units in the low-temperature form on going to the higher temperature form.

Nylon 66 has been extensively studied by English[26] and co-workers at DuPont. Based on ^{2}H and X-ray evaluations, a high-temperature crystalline phase was gradually formed with increasing temperature, but over a ca. 50 °C range. X-ray results showed a gradual coalescence of the two characteristic peaks to a single peak between 130 and 180 °C. The intermediate temperature range was suggested to be a composite of low- and high-temperature forms that coexist to account for broad scattering. Most important was the NMR evidence that clearly confirmed maintenance of the rigid hydrogen bond array up to the melting point; i.e., no observable random organization of H-bonds was observed as exists in the "true" pseudohexagonal phase observed for the various copolymers (below).

Nylon 6 was also shown to have a metastable crystalline phase on going through the Brill transition, but again over a broad temperature range, 80−170 °C.[27,28] X-ray analysis demonstrated expansion of the crystal lattice, again with coalescence of the two crystalline peaks at ca. $2\theta = 20.8$ and 24.3° to a new peak at $2\theta = 21.5°$. The formation of the single peak may seem to imply that the H-bond sheets are replaced at higher temperatures by a random distribution of H-bonds around the chain axis, but, in fact, careful analysis again confirmed retention of the integrity of the planar arrays of hydrogen bonds.

In contrast to the above, ambient temperature X-ray data of melt-crystallized samples of nylon 6-*co*-nylon 66 copolymers demonstrated the presence of a relatively stable pseudohexagonal phase over a composition range of 16−40 mol % nylon 66 by the coalescence of two crystalline peaks (seen for each of the homopolymer crystalline phases) to a single broad peak positioned between them. In the case of the nylon 6-*co*-nylon 68 copolymers, less coalescence was observed, suggesting a more defined H-bonding array in these copolymers with less distortion of the crystal lattice on incorporation of nylon 68 units. A similar trend to that of the 6-*co*-66 series was observed for the annealed copolymers studied in this paper. This implies the presence of room temperature, thermodynamically stable hexagonal-ordered arrays of polymer backbones with randomly oriented hydrogen bonds.

The "true", low-temperature (and sometimes metastable) pseudohexagonal form possesses arrays of chains ordered with respect to chain alignment along the polymer axes, but with no all-trans arrangement of the methylene segments and with random directional distribution of the amide groups down the chain. The hydrogen bonds are thus randomly arranged at 60° angles with respect to each other, with no sequential order and no driving force to align themselves. The higher temperature crystalline phase (δ-phase for nylon 11) is clearly *not* the same as this pseudohexagonal phase. While there is an apparent hexagonal array of chain backbones oriented parallel to each other, the hydrogen bonds more or less maintain the planar array structure of the low-temperature crystalline phase. On cooling, the low-temperature crystalline phase is almost immediately regenerated. It should be noted that it is possible to generate a low-temperature pseudohexagonal phase for many nylon homo- and copolymers but this phase is only kinetically stable. On standing or mild heating, it quickly transforms into the thermodynamically stable crystal form for the particular nylon being examined.

Conclusions

The similarity of both local packing and motion (as evidenced by NMR chemical shifts) and extended arrangements of polymer backbones (as indicated by X-ray data) has made differentiation of the high-temperature crystalline and pseudohexagonal phases difficult, especially considering the effects of sample history and the kinetics of molecular reorganization and crystallization, which is inhibited by the strong hydrogen bonding in these materials. The facile synthesis of the random copolymers of nylon 6 and nylon 7 by ring-opening lactam polymerization has made available a unique series of ordered materials that display a stable pseudohexagonal phase at ambient conditions. DSC indicated strong enthalpic interactions and a pronounced first-order transition, which appears to be a melting endotherm, although glass transitions were not observed. X-ray analysis showed gradual merging of the characteristic α-form peaks into a single, broad peak characteristic of both an amorphous and a somewhat disordered mesomorphic state possessing pseudohexagonal chain packing. The solid-state NMR results indicate that the copolymers gradually decreased in α-crystal content with increasing comonomer incorporation until, at the 50:50 mixture, only the pseudohexagonal phase was observed. This is evident from the shift of the main ^{15}N peak from ca. 84 to ca. 87 ppm and by the combined changes of several of the ^{13}C peaks for the rigid-selective CPT1 experiment. The solid-state NMR results, which probe molecular-level conformation as well as crystalline packing, are consistent with the DSC and X-ray results. Measuring both macroscopic and microscopic organization clearly shows the copolymers to be less crystalline overall, able to accommodate both the α- and γ-forms near the two compositional extremes, but with the thermodynamically stable pseudohexagonal form developing around the 1:1 composition. While this phase is not "crystalline" in the same way that the α- and γ-crystal forms are in the pure homopolymers, it represents a degree of order between those of crystallites and the amorphous region. Overall, these copolymers show that it is possible to synthetically generate a stable pseudohexagonal phase.

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