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X-ray Diffraction and Nuclear Magnetic Resonance Studies of Nylon 6/I_2/KI Complexes and Their Transformation into the γ Crystalline Phase

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ABSTRACT: Solid-state ^{13}C and ^{15}N NMR results relevant to the structure of iodinated Nylon 6 (N6) and its conversion into the γ phase are presented. The polymer chain-axis repeat in KI/I_2-treated N6 is 15.7 Å. This is shorter than that for the α (17.2 Å) and γ (16.8 Å) structures. This new structure gives rise to a carbonyl NMR peak at 176.5 ppm, compared to 173.4 and 173.1 ppm in the α and γ structures, respectively. Some NMR evidence is presented that suggests that the interchain hydrogen bonds in the complex are weak or absent. Additionally, there are likely to be conformational changes in the methylene carbons adjacent to the amide moiety. Such changes may provide a mechanism by which the chain-axis shortens and is capable of forming a commensurate structure with I_5^- ions as postulated by XRD studies. Experimental evidence is also presented that indicate that γ crystalline phase is formed during initial KI/I_2 desorption even while the amorphous chain segments remain complexed. This suggests that the γ phase evolves from the complex without going through an identifiable, intermediate, native amorphous phase.

Introduction

The most thermodynamically stable crystalline structure of Nylon 6 (N6) is known as the α form. In this structure the molecules are in an extended-chain conformation with hydrogen bonds between antiparallel chains.[1] The other crystalline form of Nylon 6 is known as γ. Here, the hydrogen bonds are between parallel chains and the molecules form pleated hydrogen-bonded sheets.[2]

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The γ form is obtained either during high-speed melt spinning or by desorption of I_2/KI from a N6/I_2/KI complex. The structure of this "iodinated" Nylon 6 has been previously studied by X-ray diffraction,[3-5] infrared,[6-10] and Raman[11] spectroscopies. However, questions still remain concerning the structure of the iodinated Nylon 6 and its transformation into the γ phase. Solid-state NMR has been recently applied to Nylon 6[12-19] and is providing new insights into its structure and morphology. In this report, we present the first ^{13}C and ^{15}N nuclear magnetic resonance (NMR) study of the iodinated Nylon 6 and its conversion into the γ phase.

Experimental Section

Samples. Nylon 6 films (CAPRAN 77A, thickness ~1 mil) with a crystalline (mixtures of α and γ) content of roughly 20% were soaked in an aqueous solution of 0.15 M I_2/KI for between 5 min and 16 h. In these thin films the KI/I_2 distribution is expected to be uniform across the thickness of the film. Excess I_2 and KI was removed from the films by rinsing with water. The remaining I_2/KI was then gradually removed by soaking the films in an aqueous solution of 0.1 M $Na_2S_2O_3$ for between 1 min and 24 h, depending upon the degree of iodine content desired in the films. For the purposes of carrying out ^{15}N NMR experiments, samples of ^{15}N-enriched Nylon 6 were prepared[20] and subjected to the preparation scheme described above.

X-ray Diffraction. X-ray diffraction (XRD) patterns were obtained in transmission mode on a Huber two-circle goniometer using nickel-filtered Cu Kα radiation and either a Nicolet area detector or by step-scanning with a scintillation detector. Diffractometer scans in the parafocus geometry were obtained on a Philips APD3600 diffractometer with Cu Kα radiation and a graphite monochromator in the diffracted beam. Measurements were carried out under ambient conditions. Unlike the starting (native) and the final iodine-desorbed films (the γ form), the fully and partially iodinated films had a significant amount of moisture during the data collection.

Nuclear Magnetic Resonance. Solid-state ^{13}C and ^{15}N NMR spectra were acquired at 75.3 and 30.3 MHz, respectively, on a Chemagnetics CMX300 NMR spectrometer. Data were obtained under magic angle spinning (MAS) conditions using standard cross-polarization (CP) and single-pulse (BD, "Bloch decay") techniques.[21-23] The application of these approaches to Nylon 6 have been described elsewhere.[12,13] The magic angle was adjusted to within 0.1° using the ^{79}Br spectrum of KBr.[24] CP/MAS spectra were acquired using a 0.8-ms contact time and a 2-s pulse decay. BD/MAS spectra were acquired using a 1-s pulse delay. All of the ^{13}C spectra presented in the text were taken from wet samples. Saturation with water has been shown to induce ^{13}C shifts in the spectra of Nylon 6.[25] Measurements were carried out on both ambient and wet KI/I_2 treated films to ensure that the changes induced by KI/I_2 treatment were not due solely to hydration effects. All spectra were externally referenced relative to tetramethylsilane (^{13}C, 0 ppm) or ammonia (^{15}N, 0 ppm).

Results

Figure 1 shows a typical sequence of XRD patterns (parafocus geometry) of Nylon 6 at various stages of I_2/KI treatment. These scans, except the one in Figure 1a which is from an unoriented film, correspond to meridional scans. It has been previously shown that, although the initial film may be unoriented, the polymer chains in the I_2/KI/N6 complex become oriented perpendicular to the plane of the film.[4,26] The scan in Figure 1a can be interpreted as due to Nylon 6 with a crystalline index of ~20%, the crystalline fraction being a mixture of γ (major fraction) and α. The freshly iodinated sample (Figure 1b) has an intense peak at ~4.0 Å due to Nylon 6 and intense peaks at ~4.75 and ~3.1 Å due to iodide ion arrays. A weak reflection at ~8 Å is also visible in this pattern. The peaks due to iodide ion arrays are asymmetric due to lack of register between iodide ion columns.[27] The Nylon 6 peaks, on the other hand, are symmetric. The Nylon 6 reflection at ~8 Å is the second order of a chain-axis repeat of 15–17 Å, and the reflection at ~4 Å has contributions from the fourth order of the chain-axis repeat. These two peaks are present in both the α and γ crystalline forms of Nylon 6, as well as in the I_2/KI/N6 complex. However, the position and relative intensity of each peak varies from one crystalline form to another. The 8-Å peak is intense in the γ form but is weak in the freshly iodinated complex and the α form. As I_2/KI is desorbed from the film, the intensity of this 8-Å peak increases and the peak appears to shift toward 8.4 Å (Figure 1c,d). The changes in the iodide ion peaks that accompany the desorption of iodide ions have been discussed earlier.[5] The changes observed in the reflection from Nylon 6 at 8 Å (corresponding to half the chain-axis repeat) in Figure 1 show that the chain-axis repeat increases from 15.7 Å in the freshly iodinated sample to 16.6 Å in the uncomplexed γ form. Upon more extensive desorption of iodine and aging, the chain-axis repeat in the γ form eventually reaches 16.8 Å.

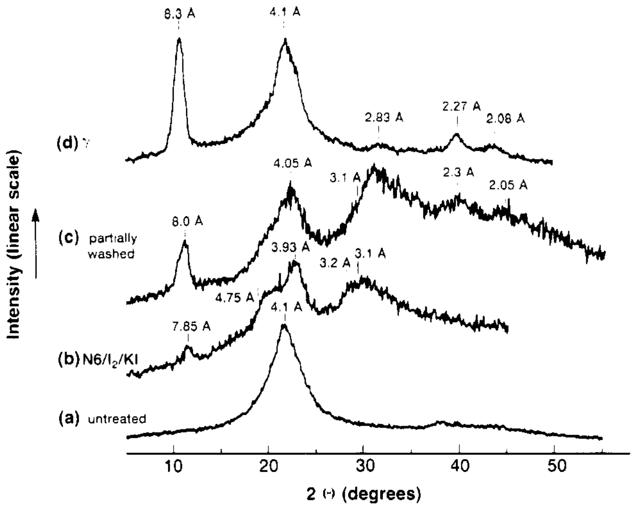


Figure 1. X-ray diffractometer scans of Nylon 6 at various stages of iodination. (a) Starting film (crystalline index ~20%) with α and γ crystalline forms, γ being the major fraction. (b) Freshly iodinated film. (c) Partially desorbed film. (d) γ Nylon 6 obtained from the iodinated film. The 3.1-, 3.2-, and 4.75-Å reflections are marked on the low-angle side of the peak maximum to take into account the lack of register between the adjacent iodine columns.[27]

The transmission scan (equatorial pattern) shown in Figure 2 was obtained from the freshly iodinated film used to obtain the meridional scan in Figure 1b. This can shows at least 4 orders of a crystallographic repeat of 15.6 Å perpendicular to the fiber (chain) axis. This repeat period is due to the intercalation of iodide ion layers between sheets of Nylon 6 chains.[4,5] Also seen in this figure is a 4.3-Å reflection due to the packing of Nylon 6 chains. The 15.6-Å repeat seen in this equatorial scan is different from the 16-Å repeat in the meridional scans (Figure 1b–d). The former corresponds to the intercalated layers and the latter to the chain-axis repeat. The absence of any significant amorphous halo in the scan in Figure 2 suggests that the complex is highly crystalline.

Representative NMR spectra of a starting Nylon 6 film, a freshly iodinated Nylon 6 complex, a partially KI/I_2 desorbed film, and the final γ form are given in Figure 3. The spectral details of the α, γ, and amorphous forms have been presented elsewhere[12] and will not be repeated here. The most obvious difference between the iodi-

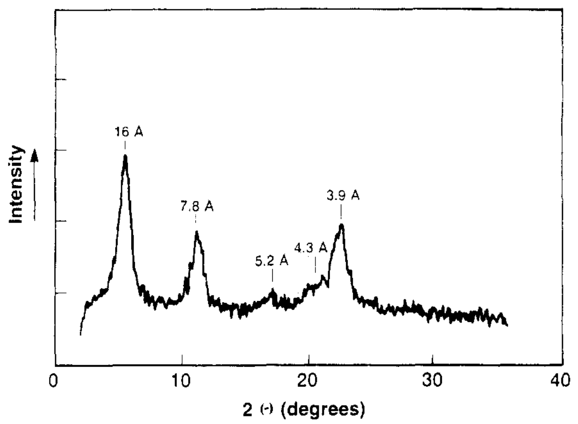


Figure 2. Transmission scan of the film used in Figure 1b to show that the film is highly crystalline.

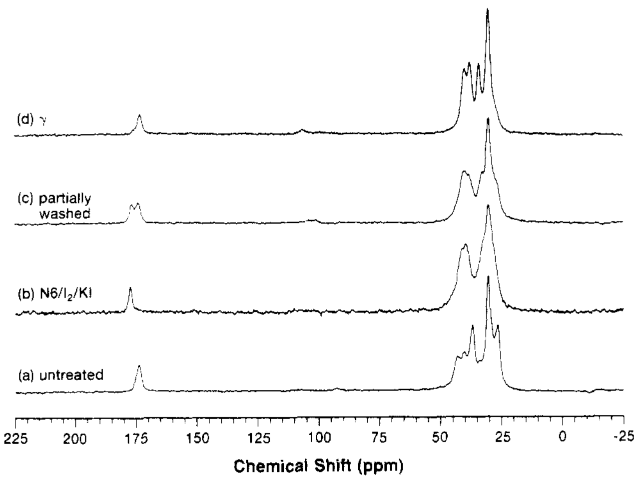
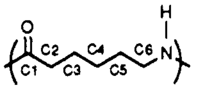


Figure 3. ^{13}C CP/MAS NMR spectra of Nylon 6 at various stages of iodination. (a) Nylon 6 film before iodination (20% crystalline, mixtures of α and γ, γ being the major fraction). (b) Freshly iodinated film. (c) Partially desorbed film. (d) γ Nylon 6.

Table I
^{13}C and ^{15}N Chemical Shifts (ppm) for the Amide Moiety in Nylon 6



structure	^{13}CO	^{15}NH
α[a]	173.4	116.5
γ[a]	173.1	121.8
amorphous—ambient[a]	174.5	119.1
amorphous—wet[b]	175.7	122.9
KI/I$_2$/N6	176.5	123.2
solution[c]	177.8	122.7

[a] Taken from ref 12. [b] See ref 25. [c] Dilute trifluoroethanol solution.

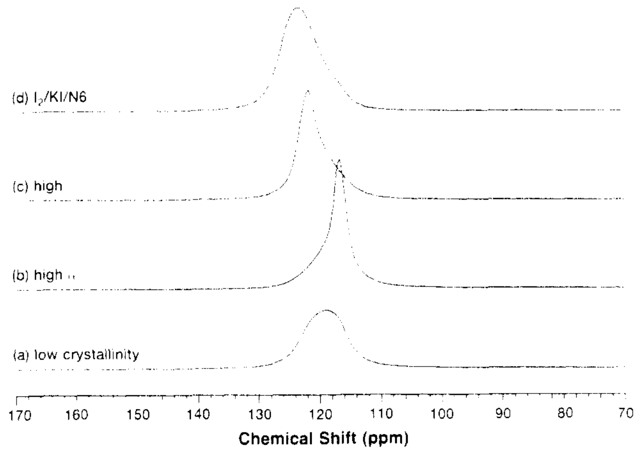


Figure 4. ^{15}N CP/MAS NMR spectra of (a) mostly amorphous, (b) mostly α, (c) mostly γ, and (d) I$_2$/KI complexed forms of Nylon 6.

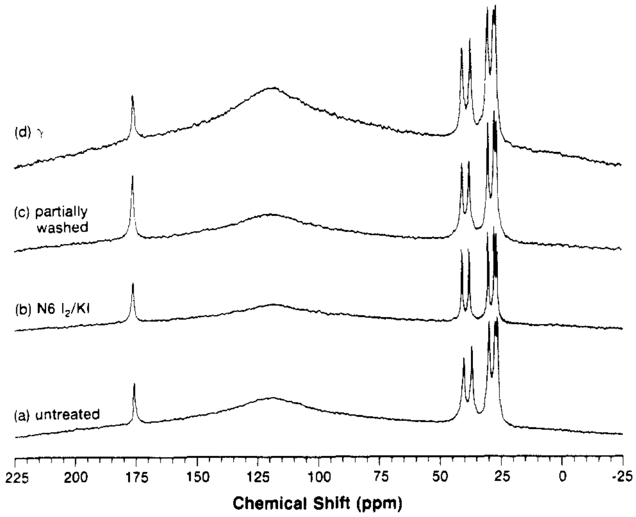


Figure 5. ^{13}C BD/MAS NMR spectra of Nylon 6 films corresponding to those in Figure 3.

nated Nylon 6 and these phases is the chemical shift corresponding to the carbonyl (176.5 ± 0.4 ppm). This peak is downfield of that for the analogous carbon in the α, γ, and amorphous Nylon 6 structures. The shifts for this peak in each phase are given in Table I. We examined 12 iodinated Nylon 6 films, and most were observed to have two carbonyl peaks at ~176.5 and 173.6 ppm. It is interesting to note that the ^{13}CO peak in the N6/KI/I$_2$ complex appeared to have a large range of chemical shifts (±0.4 ppm). Reasons for this have not yet been established. As illustrated in Figure 3, the intensity of the 173.6 ppm peak increases during iodine desorption while the 176.5 ppm peak decreases. Significant changes in the NMR spectra of the aliphatic region are also observed. However, this region is complicated by overlapping signals from the α, γ, amorphous, crystalline complex, and amorphous complex structures. Thus, we will not attempt to interpret this region. In addition to a new carbonyl peak, a new amide nitrogen peak is also observed in the ^{15}N spectrum of the complex. This is illustrated in Figure 4. The chemical shift of the amide nitrogen is also downfield of that for the α, γ, and amorphous Nylon 6 structures, as detailed in Table I.

Bloch decay (BD) experiments, in which one can observe only the most mobile carbons, were also carried out. It has been previously shown that this approach observes the amorphous fraction in Nylon 6.[12,13] Representative spectra, corresponding to those in Figure 3, are given in Figures 5 and 6. Tentative peak assignments for the iodinated and native amorphous phases of Nylon 6 are given in Table II. The differences in the chemical shift are largest for those carbons of, or adjacent to, the amide moiety.

Discussion

New peaks for the carbonyl at 176.5 ppm and the nitrogen at 123.2 ppm in I$_2$/KI treated Nylon 6 suggest a significant change in the amide moiety of the complex. These shifts in the complex are downfield of (deshielded rela-

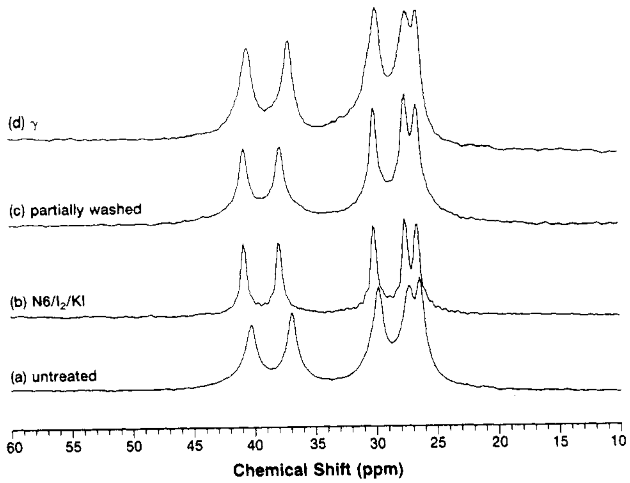
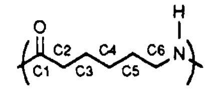


Figure 6. Expanded aliphatic regions of Figure 5.

Table II
Chemical Shifts (ppm) of Native and I_2/KI Complexed Amorphous Phases of Nylon 6[a]



amorphous structure	C1	C2	C3	C4	C5	C6
native	175.7	36.9	26.5	27.3	29.8	40.2
complexed	176.1	37.9	26.5	27.5	30.1	40.8

[a] Results taken from BD/MAS experiments (see text).

tive to) those for α, γ, and amorphous Nylon 6. One possible explanation for the ^{13}CO and ^{15}NH shifts is that changes are introduced in the hydrogen-bonding network upon complexation. Hydrogen bonding to either the NH or CO sites creates a delocalization of electronic charge in the amide group, which results in a net decrease in electron density at both the carbon and nitrogen sites. This is expected to deshield each nucleus. Both the ^{13}CO and ^{15}NH shifts in the complex are downfield of that for the other solid phases of Nylon 6 and are similar to that found for Nylon 6 dissolved in trifluoroethanol (TFE). It has been previously shown[28,29] that, for amides in solution, ^{15}N shifts move downfield as the strength of the hydrogen-bonding solvent increases. TFE is a stronger hydrogen donor than an amide, and it is possible for more than one TFE molecule to solvate the carbonyl group. This would effectively withdraw electron density from the amide moiety, producing the observed downfield ^{15}N and ^{13}C shift. Similarly, the ^{13}CO and ^{15}NH chemical shifts have been shown to move downfield upon hydration.[25] When a similar argument is extended to the N6/I_2/KI complex, it is reasonable to assert that the carbonyl carbon and the amide nitrogen interact preferentially with solvent-type molecules rather than being hydrogen bonded to each other. In other words, it is possible that the carbonyl in iodinated Nylon 6 is no longer hydrogen bonded to an NH group on a neighboring chain. It has been previously suggested by XRD and IR measurements that the carbonyl exists as CO^-H^+ or CO^-K^+ [5,10] and that the nitrogen coordinates with iodide ions.[5,8] Thus, hydrogen bonding between Nylon 6 chains in the crystalline complex is apparently absent. Associated with such changes in the amide region, other conformational changes in the polymer chain are expected. We have earlier reported that the Nylon 6 chain in the complex has a shorter pitch (15.7 Å) than even the γ form (16.8 Å) of Nylon 6.[5] These conformational changes are also reflected in the differences in the ^{13}C spectra of the methylene regions, especially in the C_2 and C_6 carbons next to the amide moiety (Figure 3). We have shown earlier[11] that two iodide ion species (I_3^- and I_5^-) are present in N6/KI/I_2 complexes. I_3^- arrays are oriented perpendicular to the chain axis, and I_5^- columns are oriented parallel to the chain axis. The conformational changes in the ^{13}C spectra upon iodination may be associated with the short chain-axis length required for the postulated lattice match between the Nylon 6 chains in the complex and the I_5^- ions.[5]

As the iodine is desorbed from the complex, the intensity of the ~8 Å peak in the XRD pattern increases, indicating the conversion of the complex into γ crystallites (Figure 1). This ~8 Å peak has contributions from 020 reflections from two distinct lattices, one with a repeat of 15.7 Å from the complex and the other with 16.8 Å from the γ form in the native, uncomplexed form.[5] As the iodine is desorbed, the intensity of the 8.4-Å peak increases while that of the 7.9-Å peak decreases, and at the same time the intensity of the 173 ppm peak in the NMR spectra increases while that of the 176 ppm peak decreases. The peak at 173 ppm can be ascribed to only the carbonyls in the γ phase since no α phase is present. However, the peak at 176 ppm is potentially a composite of carbonyls in the native amorphous, amorphous complex, and crystalline complex. Since the amount of native amorphous is expected to be negligible due to the high concentration of KI/I_2, the 176 ppm shift is probably due to the carbonyls in the crystalline and the amorphous complexes. The 176 ppm shift in the crystalline regions can thus be associated with the 15.7-Å repeat observed in the XRD patterns.

As discussed above, by using the BD/MAS NMR experiment it is possible to examine only the amorphous phase. The results of this experiment are given in Figure 5 with expansions in Figure 6. Note that the two iodinated samples (Figure 6b,c) give rise to chemical shifts that are different from those of native amorphous and crystalline γ (Figure 6a,d). These differences, summarized in Table II, indicate that the amorphous chains remain complexed during the desorption process. In contrast, as shown in Figures 1 and 3, the desorption is accompanied by the formation of γ crystallites. It is difficult, at this juncture, to determine whether this γ phase results from the transformation of the crystalline or the amorphous regions in the complex. However, previous small-angle X-ray scattering data[5] have suggested that KI/I_2 is first desorbed from the crystalline lamellae. By combining these results with the NMR data just discussed, we speculate that the crystalline complex transforms directly into the γ crystalline form. This would not be surprising since the Nylon 6 chains in the crystalline complex are strained relative to that in the α and γ forms. Future experiments designed to confirm this hypothesis are underway.

Conclusions

The changes observed in the NMR spectra of the amide ^{13}CO and ^{15}NH in KI/I_2 treated Nylon 6 are consistent with the presence of chains that do not participate in interchain hydrogen bonding in the complex. Associated with this, there are conformational changes in the methylene carbons adjacent to the CONH group. These changes may account for the X-ray diffraction observation that the chains form a structure whose axial length is equal to that of the I_5^- ions. During iodine desorption, the γ crystalline form is observed even when the chains in the amorphous region still remain complexed, leading us to speculate that the crystalline complex transforms into the γ form without going through an identifiable, intermediate, native amorphous phase.

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