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Manipulation of Nylon-6 Crystal Structures with Its α-Cyclodextrin Inclusion Complex

Min Wei,[†] Walter Davis,[†] Brad Urban,[†] Yanqiu Song,[†] Francis E. Porbeni,[†] Xingwu Wang,[§] Jeffery L. White,[§] C. Maurice Balik,[‡] Cristian C. Rusa,[†] Justin Fox,[†] and Alan E. Tonelli*[,†]

Fiber and Polymer Science Program, Campus Box 8301, North Carolina State University, Raleigh, North Carolina 27695-8301; Materials Science and Engineering, Campus Box 7907, North Carolina State University, Raleigh, North Carolina 27695-7907; and Department of Chemistry, Campus Box 8204, North Carolina State University, Raleigh, North Carolina 27695-8204

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ABSTRACT: We successfully formed an inclusion complex between nylon-6 and α-cyclodextrin and attempted to use the formation and subsequent disassociation of the nylon-6/α-cyclodextrin inclusion complex to manipulate the polymorphic crystal structures, crystallinity, and orientation of nylon-6. Formation of the inclusion complex was verified by Fourier transform infrared (FTIR) spectroscopy, wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and CP/MAS ^{13}C NMR. After obtaining the inclusion complex of nylon-6 and α-cyclodextrin, the sample was treated in an acid environment to remove the host α-cyclodextrin and coalesce the nylon-6 guest polymer. Examination of as-received and IC coalesced nylon-6 samples showed that the α-form crystalline phase of nylon-6 is the dominant component in the coalesced sample. X-ray diffraction patterns demonstrate that the γ-form is significantly suppressed in the coalesced sample. Along with the change in crystal form, an increase in crystallinity of ∼80% was revealed by DSC, and elevated melting and crystallization temperatures were also observed for the coalesced nylon-6 sample. FTIR spectroscopy revealed a significant degree of orientaion for the nylon-6 chains coalesced from their α-cyclodextrin inclusion complex crystals. Thermogravimetric analysis indicated that nylon-6 has an ∼30 °C higher thermal degradation temperature after modification by threading into and being extracted from its α-cyclodextrin inclusion complex.

Introduction

Nylon polymers consist of methylene segments $(CH_2)_n$ separated by amide units (−CO−NH−) and are packed either parallel or antiparallel in their crystal lattices. These amide units provide hydrogen bonding between polymer chains, giving nylon some of its unique properties. In contrast to other highly crystalline polymers, like polyethylene, nylons can have their degree of crystallinity controlled over a wide range. Also, by changing the crystal structures, one can modify such properties as the melting point, modulus, low-temperature impact strength, moisture absorption, and chemical resistance to metal salts and acids.[1]

Nylon-6 [poly(ϵ-caprolactam)] is a member of the nylon family and is a versatile polymer. Nylon-6 exhibits polymorphic structures that contain two types of stable crystal forms: monoclinic α-form and pseudohexagonal (or monoclinic) γ-form, whose populations are sensitive to the method of sample preparation. The γ-form crystal of nylon-6 can be transformed into the α-form by annealing nylon-6 or by drawing.[2,3] Conversely, the α-form of nylon-6 can be transformed to the γ-form by treating nylon-6 with iodine.[4] The change in polymorphic structures of nylon-6 results from the spatial rearrangement of the hydrogen bonding between the oxygens in the carbonyl groups of one polyamide molecular chain and the hydrogens attached to the nitrogens in the neighboring polyamide molecular chains. The γ-form nylon-6 crystal is constituted by nonplanar polyamide molecules adopting the parallel-chain arrangement of hydrogen bonding, whereas the polyamide molecules in the monoclinic α-form crystal are fully extended and planar and are packed in the more stable antiparallel-chain arrangement of hydrogen bonds. The α-form is more stable than the γ-form presumably because of shorter, stronger hydrogen bonds.[5]

In the past decade, many studies have shown that cyclodextrins (CDs) can form molecularily assembled inclusion complexes (ICs) with various high molecular weight polymer guests.[6−9] In these tubular inclusion complexes, the guest polymer chains occupy narrow cylindrical channels (diameter ∼ 0.5−1.0 nm) created by the stacking of cyclodextrins in the crystalline lattice. As a consequence, the included guest polymer chains are constrained to assume highly extended conformations and are generally segregated from neighboring included polymer chains by the channel walls of the host crystalline lattice. When these complex crystals are treated to remove the host, but without damaging or dissolving the guest polymers, they are forced to coalesce into a bulk polymer solid. We have recently demonstrated that crystallizable polymer samples coalesced from their cyclodextrin inclusion complexes often reveal melting temperatures that are elevated from those measured on samples crystallized from their completely disordered solutions and melts and likely with an extended chain crystalline morphology.[10] Because α-form nylon-6 has a more extended chain conformation (larger unit cell *C*-axis value, which is along the chain direction) than the γ-form, we attempted to induce the nylon-6 to crystallize in the α-form polymorph by forming and disassociating the nylon-6/α-CD inclusion complex. The overall crystallinity, hydrogen-bonding density, and possibly chain orientation are expected to increase as a

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[†] Fiber and Polymer Science Program.

[‡] Materials Science and Engineering.

[§] Department of Chemistry.

* To whom correspondence should be addressed: Tel +1-919-515-6588; FAX +1-919-515-6532; e-mail atonelli@tx.ncsu.edu.

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result of this processing method, since parallel, nonplanar (γ) or antiparallel, planar, and extended (α) polymer chains are necessary to achieve interchain hydrogen bonding and nylon-6 crystallization.

Experimental Section

Sample Preparation. To prepare the polymer cyclodextrin inclusion complex, nylon-6 (Aldrich) (0.15 g) was dissolved in 3 mL of formic acid (Aldrich, 90%), and then 12 mL of acetic acid (Aldrich) was added to the solution. Eight grams of α-cyclodextrin (Cerestar Co.) was dissolved in 40 mL of dimethyl sulfoxide (Aldrich), which corresponds to more than a 2-fold molar excess of α-cyclodextrin, and added to the nylon-6 solution. The mixed solutions were stirred on a hot plate for 2 h at 50 °C and then cooled to room temperature, while stirring, for another 6 h. The vacuum-filtered, solid precipitate was washed with cool water to remove free cyclodextrin and filtered and dried under a heating lamp and in a vacuum oven at 40 °C to obtain dry nylon-6/α-cyclodextrin inclusion complex as a white powder. To disassociate the inclusion complex, the sample was placed into aqueous HCl solution (pH = 1.0) with heating at 80 °C. The mixture was stirred for 10 min, and then the coalesced polymer was removed by filtration and was washed several times with cool water and dried in a vacuum oven at room temperature. The physical blend in this study is made by mechanical milling α-cyclodextrin and nylon-6 together ($w_{\text{nylon}}/w_{\text{CD}} = 1{:}20$) into a fine powder.

Characterization Measurements. FTIR spectral studies on samples in the form of KBr pellets were carried out with a Nicolet 510P FTIR spectrometer in the range between 4000 and 400 cm^{-1}, with a resolution of 2 cm^{-1}. To study IR bands directly related to crystalline vibrations, the powder form IC coalesced nylon-6 was also studied by single reflection ATR−FTIR (Nicolet 510P), after mounting on a KBr pellet, and compared with as-received nylon-6.

Wide-angle X-ray diffraction (WAXD) patterns of samples were obtained with a Siemens type-F X-ray diffractometer. The X-ray source was Ni-filtered Cu Kα radiation (1.54 Å), with voltage and current set to 30 kV and 20 mA. The specimens were mounted on aluminum frames, scanned from 5° to 40° = 2θ at a rate of ($2\theta = 1.2°$)/min, and the scattering data were recorded in the reflection geometry.

Differential scanning calorimetric (DSC) thermal scans were performed with a Perkin-Elmer DSC-7 instrument. The measurements were run in the range of 30−280 °C at heating and cooling rates of ±20 °C/min. The thermal decomposition behaviors of samples were measured with a Perkin-Elmer Pyris 1 thermogravimetric analyzer (TGA) between 40 and 600 °C at a heating rate of 20 °C/min. Nitrogen was used as the purge gas.

Solid-state ^{13}C NMR data were collected at 75 MHz, using a Bruker DSX wide-bore system with MAS speeds of 4−5 kHz and a CP contact time of 1 ms.

Results and Discussion

Demonstration of Inclusion Complex Formation. To observe the presence of both host and guests in the ICs, FTIR was employed. The FTIR spectra of pure α-CD, as-received nylon-6, and nylon-6/α-CD IC are presented in Figure 1. The presence of absorption frequencies characteristic of the guests in the IC spectrum indicates IC formation. For α-CD, the bands at 1026 and 1079 cm^{-1} are contributed by coupled C−C/C−O stretching vibrations, and the band at 1158 cm^{-1} is attributed to the antisymmetric stretching vibration of the C−O−C glycosidic bridge.[11,12] By contrast, a new band at around 1540 cm^{-1},which is assigned to the N−H in-plane bending deformation of nylon-6,[13] is found in nylon-6/α-CD IC, but not in α-CD, indicating the presence of nylon-6 in the α-CD IC sample. Moreover, this N−H deformation band moves toward higher wavenumber in the nylon-6/α-CD IC spectrum, verifying that the nylon-6 chains are threaded into the α-cyclodextrin channels and are close enough to the host α-CD to experience some molecular-level interaction.

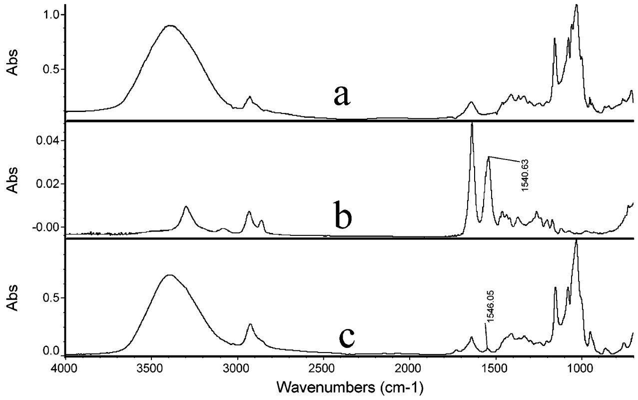

Figure 1. FTIR spectra of (a) α-CD, (b) as-received nylon-6, and (c) nylon-6/α-CD IC.

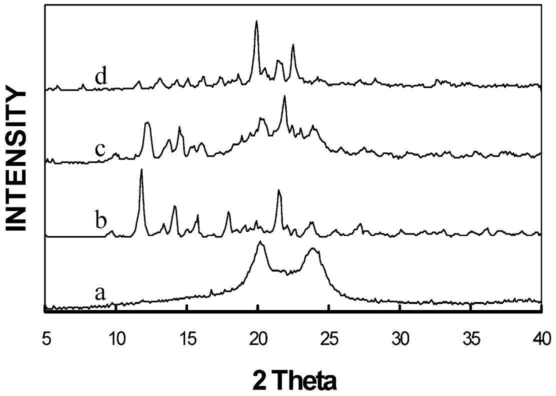

Figure 2. Wide-angle X-ray diffraction patterns of (a) as-received nylon-6, (b) α-CD, (c) α-CD/nylon-6 physical blend, and (d) nylon-6/α-CD IC.

For nylon-6/α-CD IC, two prominent X-ray diffraction peaks were observed at 20° and 22.6° (2θ), which are well-known to be characteristic of α-CD-based IC crystals adopting a channel structure (see Figure 2).[14] This diffraction pattern is markedly different from the semicrystalline, as-received nylon-6, pure α-CD, and their physical blend. The distinct differences between the patterns for the inclusion complex and the two starting materials, as well as their physical blend, are strong evidence that the α-CD is hosting guest nylon-6 polymer chains in a channel structure inclusion complex.

The solid-state CP/MAS ^{13}C NMR spectra of as-received nylon-6, α-CD, and nylon-6/α-CD IC are shown in Figure 3. The spectrum of α-CD in the uncomplexed state shows strong splitting for all C_{1-6} resonances, indicating that α-CD molecules are in a rigid, less symmetric cyclic conformation. On the contrary, for the nylon-6/α-CD IC prepared here, all ^{13}C resonances of α-CD showed much less splitting. This indicates that α-CD in the IC has adopted a more symmetric cyclic conformation. Similar observations, which are believed to support the formation of ICs between CDs and polymers, have been observed in the solid-state CP/MAS ^{13}C NMR spectra of ICs containing various guest polymers and formed with different CDs.[15−17]

When the nylon-6 methylene carbon region of the NMR spectra is examined (see Figure 4), it is found that the methylene carbon connected to the N−H group

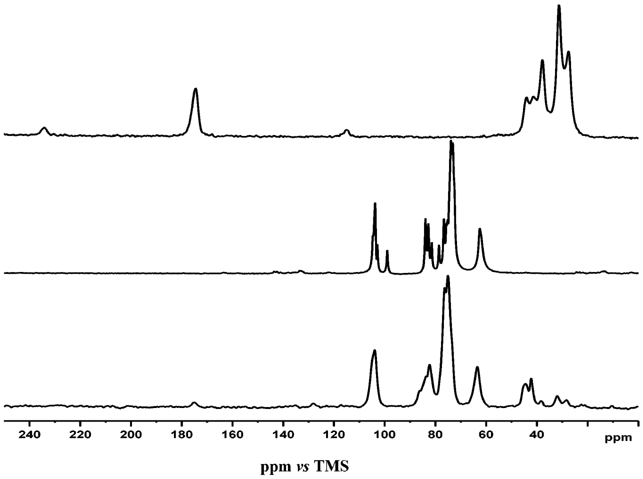

Figure 3. From top to bottom, the CP-MAS ^{13}C NMR spectra of as-received nylon-6, α-CD, and nylon-6/α-CD IC.

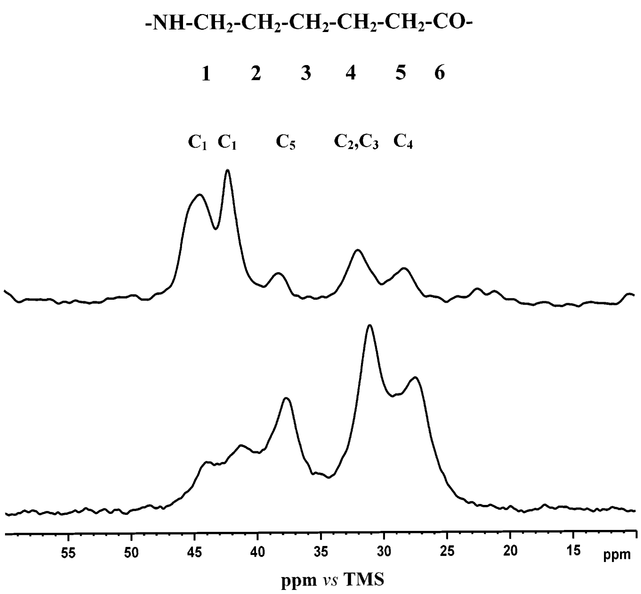

Figure 4. CP-MAS ^{13}C NMR spectra of nylon-6/α-CD IC (top) and as-received nylon-6 (bottom).

shows a higher intensity than the other methylene carbons in the nylon-6/α-CD IC, although there is not any change in resonance frequencies relative to the as-received nylon-6. This interesting observation is consistent with that found by FTIR and mentioned in the previous discussion and serves to further indicate a molecular-level interaction taking place between α-cyclodextin and nylon-6 molecules in the inclusion complex.

The DSC heating scan of nylon-6/α-CD IC is presented in Figure 5. No thermal transition can be found for the IC sample in the experimental temperature range. However, the physical blend of the same composition shows a melting peak at around 220 °C, which is produced by the thermal fusion of semicrystalline nylon-6. Since cyclodextrin does not have any thermal transitions in the range 25−300 °C, the straight DSC line for the IC demonstrates that all the potentially crystallizable nylon-6 chains are included as guests, where they are covered by the cyclic α-cyclodextrin host and isolated in the molecular IC channels.[18]

Manipulation of Crystal Structures. After removing the host α-cyclodextrin from the nylon-6 inclusion complex, we first examined the coalesced sample by ATR−FTIR. Figure 6 compares the ATR−FTIR spectrum of the coalesced sample to that of the as-received nylon-6. It is found that the two infrared spectra look broadly similar, and no vibrational bands characteristic of cyclodextrin (1026, 1079, and 1158 cm^{-1}) remain, indicating the nylon-6 polymer chains have been completely extracted from the α-cyclodextrin channels. However, it is also evident that the bands in the region between 1300 and 800 cm^{-1} show clear differences between the two nylon-6 samples. FTIR band assignments for both α- and γ-crystal forms of nylon-6 have been reported in the literature.[19−21] The bands at 928, 959, and 1200 cm^{-1} were attributed to the α-crystalline phase, whereas the band at 973 cm^{-1} was attributed to the γ-crystalline phase. In Figure 7, for the as-received nylon-6 chips, there is a strong band at 973 cm^{-1}, showing that these samples contain a considerable

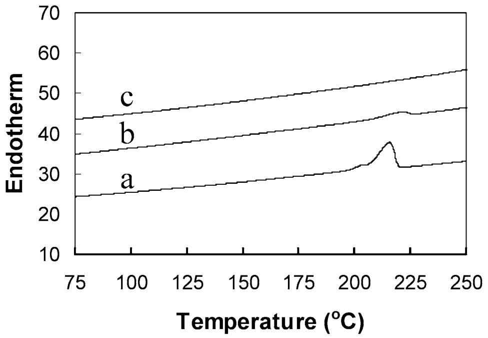

Figure 5. DSC heating scans of (a) as-received nylon-6, (b) α-CD/nylon-6 physical blend, and (c) nylon-6/α-CD IC.

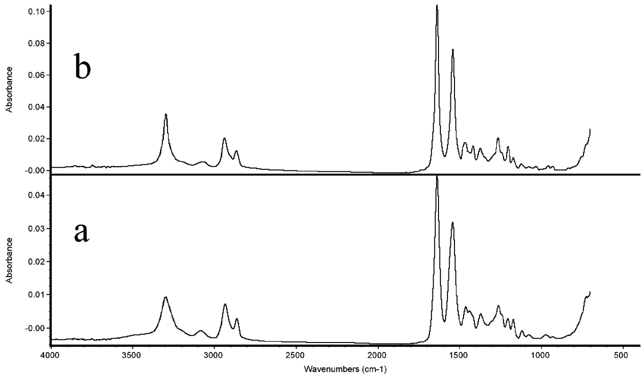

Figure 6. FTIR spectra of (a) as-received nylon-6 and (b) coalesced nylon-6.

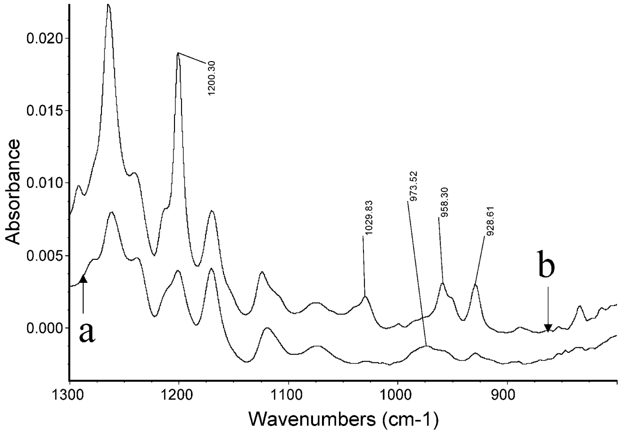

Figure 7. FTIR spectra of (a) as-received nylon-6 and (b) coalesced nylon-6.

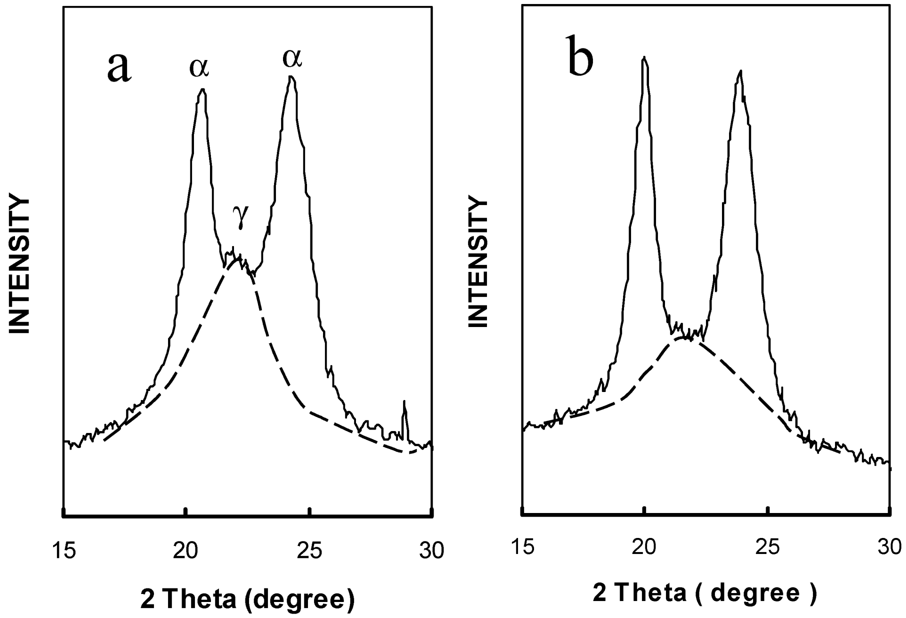

Figure 8. Wide-angle X-ray diffraction patterns of (a) as-received nylon-6 and (b) coalesced nylon-6.

Table 1. Comparison of As-Received and IC Coalesced Nylon-6 Hydrogen Bonding Related FTIR Bands

	bandwidth at half-maximum (cm^{-1})	
sample	3297 cm^{-1}	1637 cm^{-1}
as-received nylon-6	76	33
nylon-6 coalesced from its α-CD IC	36	24

amount of the γ-crystal form, with only a small amount of the α-crystal form indicated by the weak bands at 928, 959, and 1200 cm^{-1}. In contrast, the FTIR spectrum of nylon-6 coalesced from its α-cyclodextrin inclusion complex does not show the band at 973 cm^{-1}, but strong bands at 930, 959, and 1200 cm^{-1}, indicating a much higher fraction of α-form crystals.

Another interesting result is suggested by the absorption peak at 1030 cm^{-1}. According to FTIR studies of nylon-6 yarns, it is clear that the intensity of this peak increases with increasing yarn draw ratio and presumeably reflects the increased orientation of the constituent nylon-6 chains.[22] In the FTIR spectrum of the sample coalesced from its inclusion complex, there is a very strong peak at 1030 cm^{-1} compared to as-received nylon. This may demonstrate that the extended, planar conformation adopted by nylon-6 in the cyclodextrin inclusion complex is substantially retained after coalescence, leading to an improved orientation of the extended nylon-6 chains.

The amide units provide hydrogen bonding between polymer chains, giving nylon hydrogen-bonding-dependent crystalline behavior. The crystalline N−H····O=C hydrogen bond density in nylon can be estimated by measuring the widths of peaks for N−H and O=C stretching at 3297 and 1637 cm^{-1}.[13] The sharper the peaks, the more crystalline are the N−H····O=C hydrogen bonds, because of the greater homogeniety of their structural environment in comparison to the N−H····O=C hydrogen bonds in the heterogeneous environments characteristic of the amorphous portions of the nylon-6 sample. The normalized peak widths at half-maximum observed for these two characteristic bands in the nylon-6 samples are tabulated in Table 1. Compared to the as-received sample, the modified nylon-6 has much narrower hydrogen bond related peaks than the as-received nylon sample, thereby indicating a higher overall crystallinity.

Wide-angle X-ray diffraction is often used to determine the total crystallinity and the ratio of α and γ-crystalline phases for nylon-6.[23,24] In the X-ray diffraction patterns of nylon-6, the diffraction peak at $2\theta = 21.8°$ is contributed by the γ-form crystal of nylon and a pair of peaks, $2\theta = 20°$ and 24°, are distinctive features of the α-form crystal of nylon-6. The single diffraction peak of γ-form nylon-6 is contributed by the {200} plane, and the two well-separated diffraction peaks for the α-form come from {200} and {002} planes, respectively. Figure 8 shows the WAXD patterns for as-received and coalesced nylon-6. In the pattern of as-received nylon-6, it is apparent that there is a substantial amount of γ-form crystal, although the peak at 21.8° is overlapped. However, the 21.8° diffraction peak almost disappears in the X-ray pattern of the α-cyclodextrin inclusion complex treated nylon. For the coalesced nylon-6, the two strong diffraction peaks characteristic of the α-form crystal, with much less scattering from the unstable γ-form crystals and amorphous material, can be observed.

Solid-state NMR is one of the more powerful and versatile tools to study polymer structure, morphology, and dynamics. The ^{13}C resonances of CH$_2$ groups in nylon-6 occur in the range of 15−50 ppm vs TMS and overlap strongly. This frequency range includes resonances from the amorphous, γ- and α-crystalline phases. Resonances of the amorphous phase, which are much broader than the crystalline resonances, are not separately visible. However, the narrower line widths of resonances from the crystalline fraction cause them to dominate the CP/MAS spectrum, and the lines assigned here are therefore essentially due to the crystalline fraction. Some methylene carbons have a chemical shift which is sensitive to the crystalline modification, and therefore, a distinction between the different crystalline phases is possible.[25,26] The peak at 43.9 ppm is assigned to C1 in the α-polymorph and the peak at 41.3 ppm to C1 in the γ-form. The CP/MAS ^{13}C NMR spectra of as-received nylon-6 and nylon-6 coalesced from its α-cy-

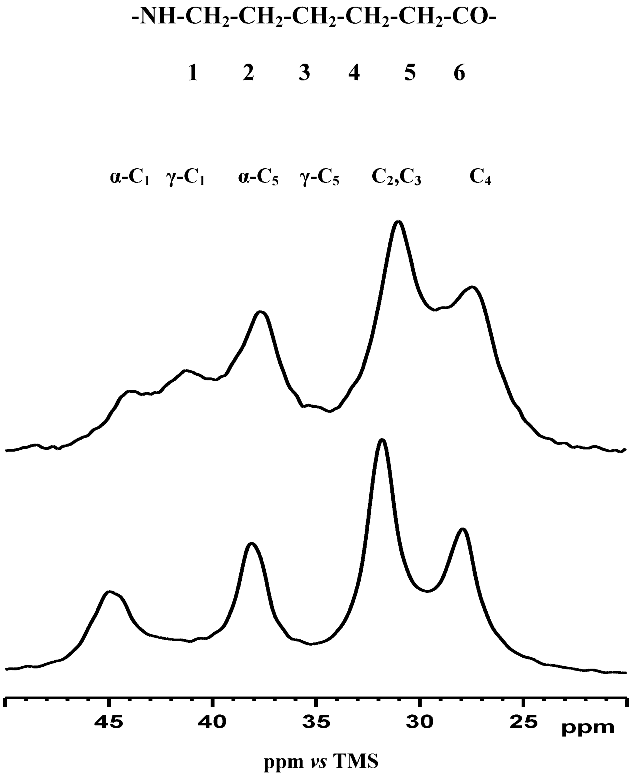

Figure 9. CP-MAS ^{13}C NMR spectra of as-received nylon-6 (top) and coalesced nylon-6 (bottom).

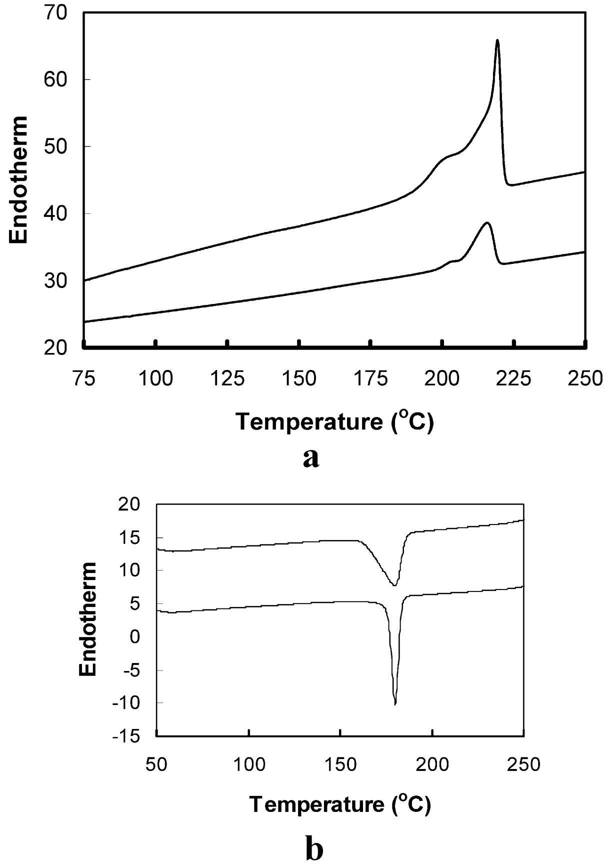

Figure 10. (a) DSC heating scans of coalesced (top) and as-received (bottom) nylon-6 samples and (b) DSC cooling scans of as-received (top) and coalesced (bottom) nylon-6 samples.

Table 2. Thermal Properties Obtained from DSC for As-Received and IC Coalesced Nylon-6

thermal properties	as-received nylon-6	coalesced nylon-6
T_m (°C)	215.6	219.3
ΔH_f (J/g)	55.8	100.4
crystallinity (%)[a]	29.4	52.8
T_{cc} (°C)	179.9	180.0
ΔH_{cc} (J/g)	60.2	66.2
temp range of crystallization (°C)	190.7−156.8	188. 6−161.8

[a] The ΔH_f of 100% crystalline nylon-6 is taken[27] as 190 J/g.

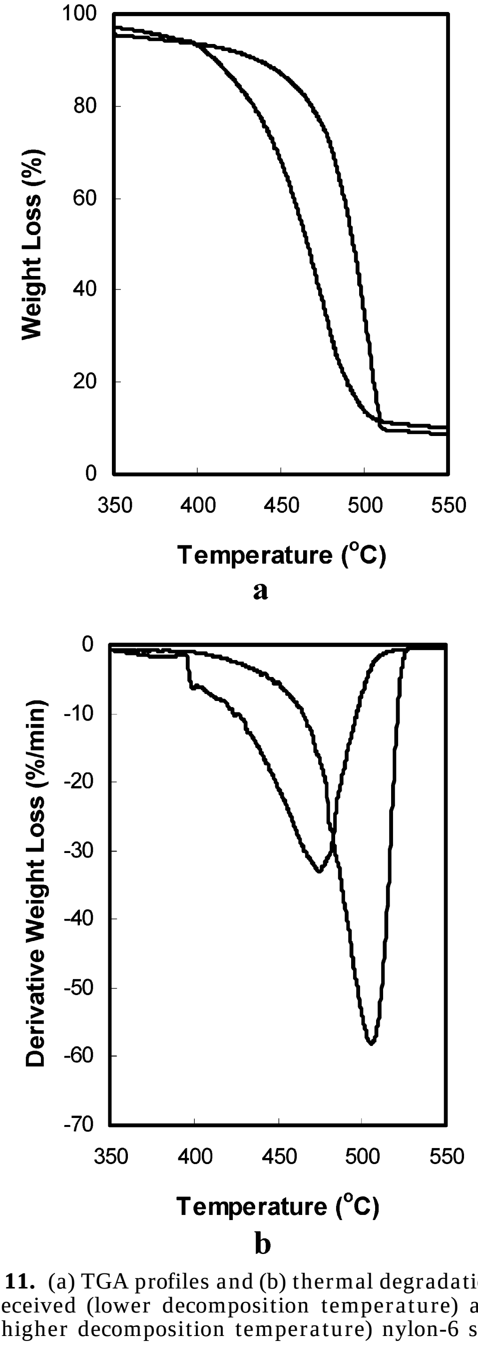

Figure 11. (a) TGA profiles and (b) thermal degradation rates for as-received (lower decomposition temperature) and coalesced (higher decomposition temperature) nylon-6 samples.

clodextrin inclusion complex are given in Figure 9. From this figure, it can be seen that α-form crystals dominates the crystalline regions of nylon-6 coalesced from its α-cyclodextrin inclusion complex.

DSC was carried out to obtain the melting and crystallization behaviors of nylon-6 as-received and coalesced from its α-cyclodextrin inclusion complex, although this is not an unambiguous way to distinguish between the two crystal forms of nylon-6. Figure 10 shows the DSC heating and cooling scans, and Table 2 lists the melting temperatures (T_m), the crystallization temperatures observed upon cooling (T_{cc}), and the crystallinity of both nylon-6 samples. Compared to the as-received sample, elevated T_m and T_{cc} and an almost doubled crystallinity were found for the sample coalesced from its α-cyclodextrin inclusion complex. It is known that α-form nylon-6 crystals have a higher T_m than the γ-form.[28] Therefore, the DSC results, again, reveal that α-form crystals are the dominant component in the coalesced material.

For the purpose of comparison, as-received nylon-6 was treated in the same manner as the coalesced nylon-6 except that α-CD was not dissolved in dimethyl sulfoxide, thereby avoiding the formation of nylon-6/α-CD inclusion complex. This control sample of nylon-6 exhibited a crystallinity of 33%, as determined by DSC, compared with crystallinities of 29.4% and 52.8% for as-received and coalesced nylon-6 samples, respectively (see Table 1). The FTIR spectrum of the control nylon-6 sample, though not identical, was more similar to that of the FTIR spectrum of as-received nylon-6 than to that of the coalesced sample (see Figure 7). These results confirm that the formation of and coalescence from its α-CD inclusion complex is the primary cause of the alteration in the structure and morphology of the coalesced nylon-6 relative to the as-received sample.

Finally, Figure 11 shows the TGA profiles for as-received and coalesced nylon-6 samples. The coalesced nylon-6 is observed to have an ~30 °C higher thermal degradation temperature than the as-received nylon-6. Once again, this likely demonstrates a different organization of nylon-6 chains in the coalesced sample compared to the normal morphology found in the as-received bulk polymer.

Conclusions

In summary, threading into and extraction from cyclodextrin inclusion complexes is an effective way to transform nylon-6 from its γ- to its α-polymorph, to obtain a much higher level of crystallinity, and substantially improve the orientation of the extended nylon-6 chains. The capability of cyclodextrin inclusion complexation for manipulation of the crystal structures of nylons is likely due to the confining channel environment for the included polyamide chains, which requires them to assume highly extended conformations with narrow cross sections in order to fit into the stacked α-cyclodextrin host crystalline channels.

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