Formation and Characterization of Polypropylene−Urea Inclusion Compounds

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ABSTRACT: Isotactic (i) and syndiotactic (s) polypropylenes (PP) have been successfully incorporated into the channels of their inclusion compounds (IC) with urea (U). The IC's were obtained by cocrystallization following the addition of a warm toluene solution of polymer to a warm solution of urea in methanol. The white crystalline precipitates formed upon cooling were filtered and analyzed using X-ray diffraction, differential scanning calorimetry (DSC), and Fourier transform infrared (FTIR) and ^{13}C NMR spectroscopies. The results were compared with the components (urea and polypropylene) in their pure crystalline forms, the known hexagonal poly(ϵ-caprolactone)−urea IC, and the known trigonal poly(ethylene oxide)−urea IC. X-ray diffraction data indicated that no free polymer was present in either sample, while FTIR showed that the i-PP−U and s-PP−U IC's were not the hexagonal and trigonal structures commonly observed. Instead the structure appears similar to a "large tetragonal" structure observed for the poly(ethylene glycol)−urea IC. DSC indicated a melting point for the i-PP−U IC at 138 °C, while ^{13}C NMR showed that the i-PP and s-PP polymer chains are included in their respective 3_1 and 2_1 helical, crystalline conformations. Previous modeling has indicated that the crystalline conformations are unable to fit in an IC channel with a diameter less than 7 Å. This again confirms the nonhexagonal and nontrigonal structure of the IC, because the channel diameters for these structures are ca. 5.5 Å. Similarities have been found with the partially characterized "large tetragonal" structure of the low molecular weight poly(ethylene glycol)−urea IC, whose channel diameter is not yet known.

Introduction

The ability of inclusion compounds to isolate polymer chains based upon their conformations is very important in the field of polymers. A polymer chain in the narrow, cylindrical IC channels usually exists in an extended state and is isolated from the effects of other polymer chains. In this isolated environment, it is possible to study the conformational and motional behavior of a single polymer chain in the solid state. This information can be used to improve the understanding of the behavior of polymer chains in their ordered, bulk states where they are closely packed and cooperative interchain interactions are prevalent.[1]

Extensive literature exists concerning urea's ability to form crystalline IC's with polymer guests, by crystallizing into an extensively hydrogen-bonded matrix.[2−4] Each polymeric guest is isolated into the parallel channels formed by the matrix. Usually the urea crystallizes into a matrix composed of a hexagonal crystal structure, with the diameter of the channels in the matrix approximately 5.5 Å. Perturbations in the matrix have also resulted in matrices with trigonal and orthorhombic crystal structures, but the diameter of the channel is still approximately 5.5 Å. A "large tetragonal" crystal structure has also been reported, and partially characterized, for a low molecular weight poly(ethylene glycol) (PEG)−urea IC.[5] The complex itself was not thermally stable at room temperature, but we were successful in isolating a single crystal of the IC for FTIR analysis. Previous X-ray diffraction (XRD) studies indicate a tetragonal unit cell ($I4_1/amd-D_{4h}$ space group) with dimensions $a = b = 9.30$ Å and $c = 19.51$ Å.

The following report will discuss the formation of a nonhexagonal, nontrigonal inclusion compound between urea and isotactic polypropylene. A similar complex was also formed with urea and syndiotactic polypropylene. The attempt at forming an IC with polypropylene was made after looking at the modeling results of polypropylene with perhydrotriphenylene (PHTP), which forms a channel with a diameter similar to that of hexagonal urea IC's.[6] It was found that the isotactic polypropylene polymer chains would have to assume high-energy elipsed conformations in order to fit in the channel, while the syndiotactic polypropylene chains could fit in an all-trans conformation that is energetically similar to its bulk, crystalline 2_1 helical conformation.

Recently, we have focused on FTIR's ability to differentiate between polymer−urea IC crystal structures by looking at the shifts in the vibrational bands of the functional groups in urea, as a result of the change in hydrogen bonding. Comparisons were made with known hexagonal and trigonal polymer−urea IC's. DSC, XRD, and ^{13}C NMR were also used to provide a better understanding of the i-PP−U and s-PP−U IC's.

Experimental Section

Materials. The isotactic polypropylene used in the experiments was supplied by Aristech Chemical Co. The sample was used as received in its bulk pellet form. FTIR was used to determine if any additives were present. The sample was determined to be pure. The sample had a melt flow index of 34, corresponding to a molecular weight of 150 000. The sample was also highly isotactic with >97% meso diads.

The syndiotactic polypropylene sample was obtained from Dr. Sozzani. The sample was prepared using the new metallocene catalyst system and contained nearly all (>99%) racemic diads. GPC analysis had indicated a weight-average molecular weight of 164 000.

Urea was purchased from Fisher Scientific and was ground to a fine powder using a mortar and pestle. It was also used in pellet form, dissolved in methanol, and precipitated at low temperature. The solvents used in this experiment, methanol and toluene, were certified ACS grade and obtained from Fisher Scientific.

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IC Preparation. The polymer solution consisted of 0.1 g of i-PP dissolved in 50 mL of toluene at 100 °C. The solution was cooled to 60 °C and added dropwise to a solution of 0.5 g of urea in 50 mL of methanol, also at 60 °C. This solution was stirred at this temperature for 1 h and then allowed to cool slowly, while still stirring. The solution was then allowed to stir overnight and was filtered. The resulting precipitate was a fine white crystalline powder. Attempts were made at making a single crystal, but they were not successful. The s-PP IC was made by the same method, but the concentrations of the solutions were different. In this case, 0.5 g of s-PP was dissolved in 50 mL of toluene, and 2.0 g of urea was dissolved in 50 mL of methanol. A white powder precipitate was also the final result. In both cases, it was determined that by adding the polymer solution to the urea solution, there was an increase in likelihood that the product formed would be an IC.

FTIR Spectroscopy. The first technique used for characterization of the IC's was Fourier transform infrared analysis. Absorbance spectra were recorded from 400 to 4000 cm^{-1}. The samples were thoroughly mixed with KBr and pressed into pellet form. The spectra were taken on a Nicolet 510P FTIR spectrometer under the following conditions: resolution = 2 cm^{-1}, gain = 1, scans = 32. Due to the hygroscopic behavior of KBr, the sample cell was purged with dry, or desiccated, air.

NMR Spectroscopy. High-resolution ^{13}C NMR spectra were recorded using a Chemagnetics CMC 200S NMR spectrometer at 50.1 MHz, under cross-polarization, magic angle spinning (CP/MAS), and high-power ^{1}H dipolar decoupling (DD). The optimum conditions were calibrated using *p*-di-*tert*-butylbenzene (PDTBB, 31.0 ppm vs TMS). The spinning speed ranged from 4−4.3 kHz. During acquisition, DD was applied at 47 kHz. The spectral width was 15 kHz in 2K data points, which were zero-filled to 8K before Fourier transformation. The T_1's, or spin−lattice relaxation times, were obtained using the CP-T_1 exponential decay function using different, τ values.[7] Contact times were varied from 0.2 to 2.0 ms, but the pulse delay was held at 3.0 s. For the bulk i-PP sample, few transients (500) were necessary to get a good spectrum. For the i-PP IC, clean spectra were obtained with 1000−3000 transients. In the case of the s-PP bulk sample, clean spectra were obtained with 1000 transients. The s-PP IC spectrum was more difficult to resolve and was still noisy after accumulating 10 000 transients.

X-ray Diffraction and DSC Measurements. X-ray diffraction data were collected from powdered samples on a Scintag 2000 XDS in a wide-angle setup. Samples were mounted on a solid circular sample holder, and the proportional counter detector was set to collect data at a rate of 2θ = 5°/min over the range of 2θ = 0−50°. The X-ray radiation used was Ni-filtered Cu Kα with a wavelength of 1.54 Å. The voltage was set at 45 kV and the current was set at 40 mA. The computer recorded the most intense 2θ peaks and calculated the corresponding *d*-spacings.

Thermal characteristics of the samples were determined using a Perkin-Elmer differential scanning calorimeter, Model 7. A sample of 4−10 mg in weight was placed in a volatile aluminum sample pan and pressed shut. The samples were scanned from 60 to 155 °C for the urea and IC samples and from 60 to 175 °C for the bulk polymer samples, with a heating rate of 10 °C/min. The urea was not scanned at a higher temperature due to its propensity to degrade above 160 °C. The melting points were consistently taken as the maximum peak height. Due to the similar melting points for the IC and pure urea, this technique was only used to get a qualitative answer concerning the melting behavior of the IC. The higher melting temperature of the polymer made it difficult to determine whether the polymer was free or included as a guest.

Results and Discussion

The resulting spectroscopic, crystallographic, and thermal data were difficult to interpret at first. They did not correspond to anything that had been observed previously, except for the formation of a low molecular weight poly(ethylene glycol)−urea (PEG−U) IC.[5] The data were compared to the pure reaction components, physical mixes of the two reactants, and the control samples. The control samples were studied to make sure that the reaction conditions did not cause the two reactants to alter their crystallographic structures. The urea crystallized into its normal tetragonal structure, and the PP's crystallized into their normal bulk crystal structures. The physical mixes were completed to confirm the additive behavior of the mixing data.

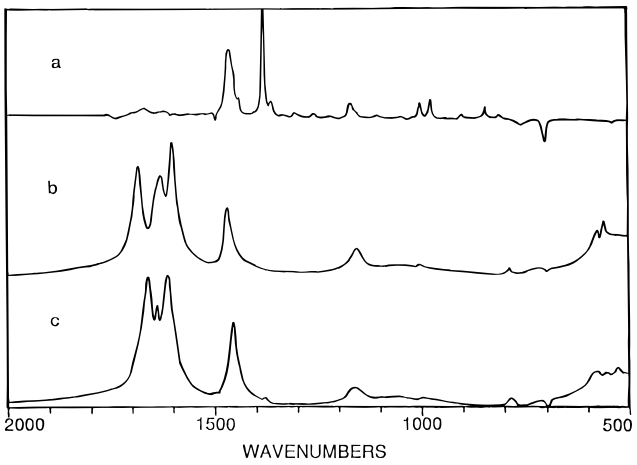

Figure 1. Comparison of the infrared spectra of i-PP (a), bulk urea (b), and i-PP−U IC (c) from 500 to 2000 cm^{-1}.

Four analytical techniques were used in order to characterize the resulting IC's. FTIR and XRD were used in order to determine the crystal structure, and the latter technique was also useful in determining if free polymer was present in the sample. Due to its sensitivity to the local chemical environment, ^{13}C NMR was used to determine the conformation of the included polymer. DSC was used to study the melting behavior of the IC. Most IC melting points are only slightly higher than that of pure urea and can be observed as a shoulder on the free urea melting endotherm peak.

For the i-PP−U IC, FTIR has become an invaluable tool in verifying the change from the bulk tetragonal cyrstal structure to a new nonhexagonal, nontrigonal crystal structure for urea. Figure 1 shows a comparison of i-PP (a), bulk tetragonal urea (b), and the i-PP−U IC (c) over the range of 500−2000 cm^{-1}.

The most noticeable shifts occur in the 1600−1700 cm^{-1} range (see Figure 1b,c). Fortunately, the i-PP has no stretching or bending vibrations in this range, so additive effects are much easier to detect. The urea C═O stretching vibration has shifted from 1682 to 1663 cm^{-1}. The NH bending vibrations at 1628 and 1599 cm^{-1} have shifted to 1638 and 1614 cm^{-1}, respectively. The other noticeable change has occurred at 1377 cm^{-1}, the CH_3 symmetric deformation vibration in i-PP. There is no corresponding peak in urea and the IC only shows a small absorption peak, due to the polymer. The low intensity of this absorption peak is the result of the low concentration of polymer in the IC. Comparison of parts b and c of Figure 1 also make clear that free, bulk, tetragonal urea is present in the i-PP−U IC sample.

More subtle shifts in the vibrational bands occur where free urea and i-PP have some small overlaps. The polymer has a weak absorption at 1455 cm^{-1} and a stronger absorption at 1460 cm^{-1}. The N−C−N vibrational stretching in pure urea has a strong absorption band at 1467 cm^{-1}. The IC shows an absorption band

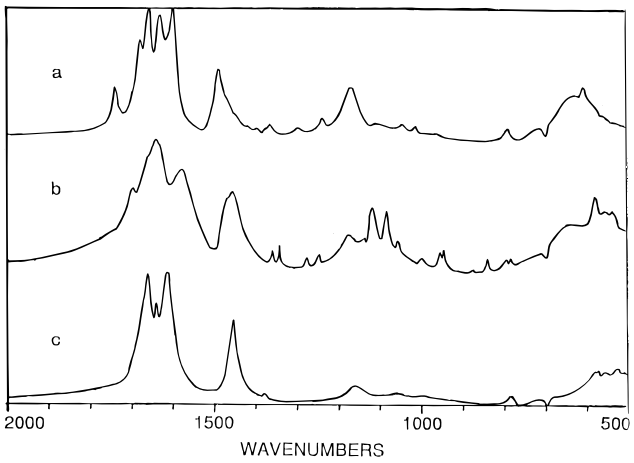

Figure 2. Comparison of the spectra of the hexagonal PEC−U IC (a), the trigonal PEO−U IC (b), and the i-PP−U IC (c) from 500 to 2000 cm^{-1}.

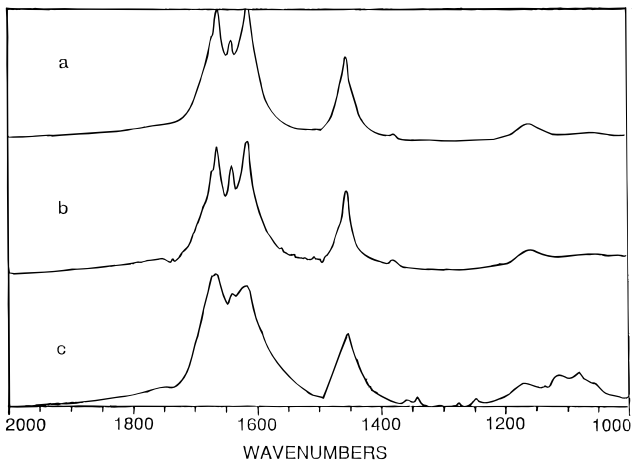

Figure 3. Infrared spectra of i-PP−U IC (a), s-PP−U IC (b), and PEG−U IC (c) from 500 to 2000 cm^{-1}.

Table 1. Compilation of the Important Vibrational Frequencies of Urea in Their Different IC Crystal Structures

vib freq for bulk urea (cm^{-1})	PEC−U IC (cm^{-1})	PEO−U IC (cm^{-1})	I-PP−U IC (cm^{-1})
1154	N/A	N/A	1161
1467	1491	1457	1454
1599	no change	1577	1614
1628	no change	1639	1638
1682	1658	1694	1663
		1659	

at 1454 cm^{-1}. Since there is a low concentration of polymer in the IC sample, it is believed that the absorption contributed by the polymer in this region would be very little if any. This is deduced from the fact that in the bulk i-PP spectrum, the peak at 1377 cm^{-1} is more intense than either the 1455 or 1460 cm^{-1} peaks. If the 1377 cm^{-1} band is greatly reduced in the IC spectrum, then the other peaks must also be reduced by the same relative amount. Therefore the absorption peak at 1454 cm^{-1} must be due to the urea forming the IC matrix. It is then possible to assign the N−C−N stretching vibration to this absorption peak. Another subtle shift occurred with the peak at 1161 cm^{-1} in the IC spectrum. The i-PP spectrum has a C−C axial stretching vibration that occurs at 1168 cm^{-1}, while free urea has an absorption at 1154 cm^{-1} for the NH rock. Using the same reasoning as before, we believe that the peak at 1161 cm^{-1} represents the NH rocking vibration in the IC spectrum.

Most recently, the structure determination of poly(L-lactic acid)−urea (PLLA−U) and poly(ϵ-caprolactone)−urea (PEC−U) IC's have been accomplished using FTIR, by confirming the presence of absorption bands due to urea in its complexed hexagonal state versus the bands due to urea in its bulk tetragonal form.[8,9] The same analysis has also resulted in the interpretation of the poly(ethylene oxide)−urea (PEO−U) IC spectrum, in which urea assumes a trigonal crystal structure.[10] In the hexagonal crystal form, the C═O stretching vibration shifted from 1682 to 1658 cm^{-1}, while in the trigonal form two peaks were observed at 1694 and 1659 cm^{-1}. This is due to the two types of urea present in the PEO−U IC, that which is in the channel and that which forms the host matrix. The N−C−N stretching vibration shifted from 1467 to 1491 cm^{-1} in the hexagonal crystal and to 1457 cm^{-1} in the trigonal crystal form. It was also observed that the two NH bending peaks at 1628 and 1599 cm^{-1} shifted to 1639 and 1577 cm^{-1}, respectively, in the trigonal crystal. These shifts in the vibrational bands demonstrate the sensitivity of FTIR to the change in hydrogen bonding that occurs when urea converts from the bulk tetragonal to the hexagonal and trigonal IC crystal forms. Figure 2 shows a comparison of the FTIR spectra for PEC−U IC (a) PEO−U IC (b), and i-PP−U IC (c). Table 1 contains the vibrational band assignments for the three different crystal structures and makes clear that the urea lattice in i-PP−U IC is distinct from the hexagonal PEC−U IC and trigonal PEO−U IC structures.

The experiments performed by Suehiro et al. have allowed us to suggest a possible structure for the nonhexagonal, nontrigonal i-PP−U IC[5]. The PEG(400 MW)−U IC was reproduced and studied by using infrared techniques on a single crystal that must be refrigerated due to the instability of the crystal at room temperature.[10] The PEG−U IC spectrum is compared to the i-PP−U IC spectrum in Figure 3. The shifts in the vibrational bands are very similar to that seen in the i-PP−U IC spectrum, though ther are slight differences in the position of some peaks. In the PEG−U IC spectrum, the C═O vibration shifts to 1665 cm^{-1} (1663 cm^{-1} for i-PP−U IC), and the NH bending vibrations shift to 1631 and 1617 cm^{-1} (1638 and 1614 cm^{-1}, respectively, for the i-PP−U IC). In both IC spectra, the N−C−N stretching vibration occurs at 1454 cm^{-1}. Considering the instrumental resolution of 2 cm^{-1}, it is possible to say that FTIR indicates that the two IC's have a similar structure and that both structures are definitely not hexagonal nor trigonal.

The experiment with the s-PP was performed in an attempt to include the all-trans conformation in the hexagonal urea matrix. The result has been the formation of an s-PP−U IC in which urea, according to FTIR, is in a complexed crystalline lattice identical to the urea in the i-PP−U IC. The urea matrix vibrational frequencies are identical: 1663, 1638, 1614, 1454, and 1161 cm^{-1}. This is an indicator that the two crystal structures are closely similar, because the hydrogen bonding of the matrix is producing the same shifts in the vibrational bending and stretching behavior of the functional groups of the urea molecules in both urea IC's compared with tetragonal free urea. The FTIR spectra of the two PP−U IC's are compared to the PEG−U IC in Figure 3.

X-ray diffractograms recorded for the pure components (urea, i-PP, and s-PP) and their IC's (i-PP−U IC and s-PP−U IC) are presented in Figures 4 and 5,

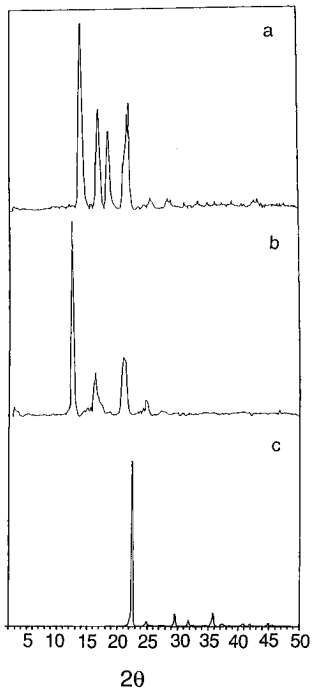

Figure 4. X-ray diffraction patterns for i-PP (a), s-PP (b), and urea (c).

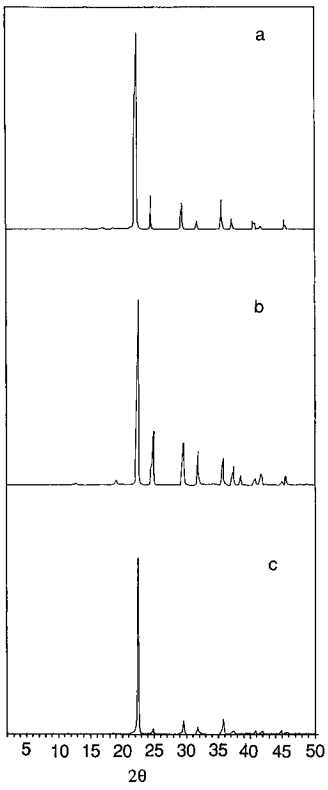

Figure 5. X-ray diffraction patterns for i-PP−U IC (a), s-PP−U IC (b), and urea (c).

respectively, and the scattering angles (2θ) and distances (d-spacing) between scattering planes are summarized in Table 2. The diffraction patterns of the IC's were very similar to that of pure tetragonal urea, but are notable for the absence of diffraction peaks attributable to the pure, bulk, semicrystalline phases of either polypropylene. Since both the FTIR spectra and ^{13}C NMR spectra to be discussed subsequently show clear evidence for the presence of both polypropylenes, we must conclude that i-PP and s-PP chains are not present

Table 2. Crystallographic Data of the Pure Components (Urea, i-PP, and s-PP) and Their IC's (i-PP−U IC and s-PP−U IC)

component	2θ (deg)	d-spacing (Å)
urea	22.5	4.02
	24.8	3.58
	29.5	3.02
	31.7	2.81
	35.5	2.52
	37.1	2.41
	40.8	2.21
	41.8	2.15
	44.9	2.02
i-PP	14.0	6.28
	16.9	5.20
	18.6	4.78
	21.1	4.19
	21.7	4.08
s-PP	12.4	7.12
	16.2	5.48
	20.9	4.23
	24.7	3.60
i-PP−U IC	22.2	3.99
	22.5	3.96
	24.7	3.60
	29.5	3.03
	31.8	2.81
	35.6	2.52
	37.2	2.42
	40.5	2.22
	40.8	2.21
	41.6	2.17
	45.4	2.00
	45.6	1.99
s-PP−U IC	19.2	4.61
	22.4	3.97
	22.6	3.93
	25.0	3.56
	29.6	3.01
	31.9	2.80
	35.8	2.50
	37.3	2.40
	38.6	2.33
	40.9	2.21
	41.7	2.16
	45.1	2.00

in phase-separated, bulk forms, but rather included in the channels of their IC's formed with urea.

The concentration of free urea in these PP−U IC's makes separation of pure tetragonal and IC diffraction peaks difficult. Work is continuing on the formation of a single crystal of the PEG−U IC, in order to completely elucidate its structure (even though previous work has indicated a large tetragonal structure). Due to the similarity of the PP−U IC and PEG−U IC FTIR spectra, a similar comparison will be made between their powder diffraction patterns. Attempts have been made to grow single crystals of the PP−U ICs, but to no avail.

The melting behavior of the i-PP−U IC has been studied, and the thermograms are compared in Figure 6. As stated earlier, most IC melting points are slightly higher than that of pure urea. The melting points of the pure components are very well separated, with the melting point of i-PP being greater than the degradation temperature of urea. A shoulder is apparent in the IC thermogram. The melting point of the IC is 138 °C, which is 2−3 °C higher than the melting point of pure urea. The size of the shoulder and the proximity of the melting temperatures indicate that the concentrations of free urea and IC are comparable. The same experiment has not been completed for the s-PP−U IC sample, due to the small amount of sample that is available.

The ^{13}C NMR CP/MAS/DD spectra obtained for i-PP and its IC with urea are presented in parts a and b of

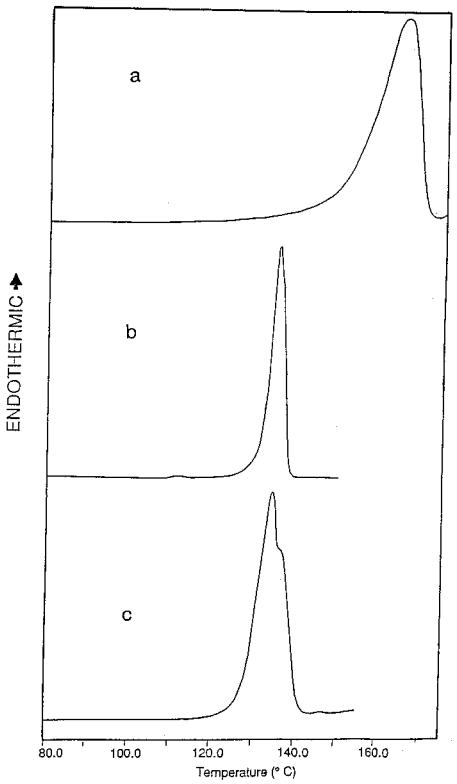

Figure 6. DSC thermograms of i-PP (a), urea (b), and i-PP−U IC (c).

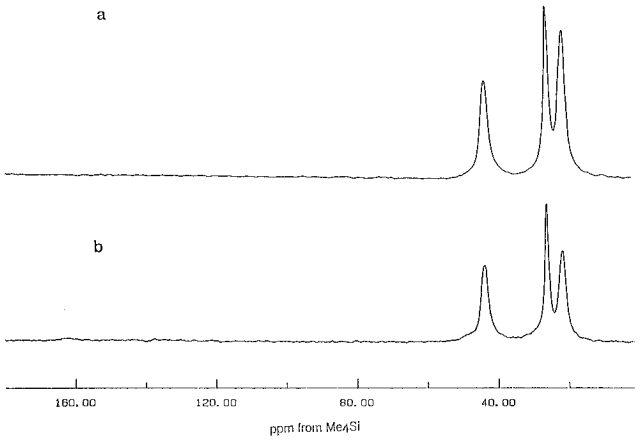

Figure 7. ^{13}C NMR CP/MAS/DD spectra for bulk i-PP (a) and i-PP−U IC (b).

Figure 7, respectively. The spectrum of the bulk sample was collected with 500 transients, a contact time of 1 ms, a τ of 200 μs, and a pulse delay of 3.00 s. This spectrum was compared with those found in the literature, and it was observed that the CH_3 chemical shift at 21.07 ppm and the CH_2 chemical shift at 43.26 ppm were not split into two peaks, as found in the literature.[11,12] It was noted in the literature that those samples were annealed at 160 °C for 1 h. This was repeated for our i-PP sample, and a splitting of the methyl and methylene peaks was observed. This confirmed that our i-PP sample was indeed in the 3_1 helical, α crystalline form. The spectrum of the IC sample required 3000 transients, a contact time of 200 μs, a τ of 108 μs, and a pulse delay of 3.00 s. The chemical shifts of the methyl peak at 21.26 ppm, the methine peak at 25.73 ppm, and the methylene peak at 43.37 ppm were virtually identical to the chemical shifts observed for the bulk i-PP sample. This indicates that the polymer is included in either its bulk crystalline conformation or the partially eclipsed conformations modeled by Tonelli.[6] If the urea was in a hexagonal IC crystal form, the eclipsed conformations are the only ones that would fit into the channel created by urea. It is interesting to note that a resonance peak was not observed for the C=O in the urea comprising the matrix. Sometimes this peak has been observed in the hexagonal IC's. The i-PP−U IC has been proven not to be the hexagonal or trigonal IC's previously recorded but instead a new type of IC. We believe that since no free polymer is present, the polymer present in the sample must be included in the IC matrix.

Table 3. The Spin−Lattice Relaxation Times (T_1's), for Bulk i-PP, i-PP−U IC, and Bulk s-PP

	T_1 (s)		
type	CH_3	CH	CH_2
i-PP	0.35	7.38	9.88
i-PP−U IC	0.46	7.16	10.27
s-PP	0.33	8.44	14.26 (38.69 ppm) 10.84 (47.40 ppm)

In a preliminary study, Schilling et al.[13] formed and observed by solid-state ^{13}C NMR the IC between i-PP and PHTP. They observed that both the resonance chemical shifts and spin−lattice relaxation times of i-PP−PHTP IC were very similar to those of bulk i-PP. Because the PHTP lattice formed in its IC's creates hexagonal channels 5.5 Å in diameter,[14] it seems likely that the partially eclipsed conformation(s) found by modeling i-PP in 5.5 Å cylinders[6] occurs in the PHTP IC channels, rather than the 3_1 helical, bulk crystalline conformation which requires a channel ca. 7 Å in diameter but which is apparently the case as described here for the i-PP chains included in i-PP−U IC.

A comparison of the mobility of the carbon nuclei in the bulk samples with those in the IC's has produced some insight into the effect of cooperative interchain interactions. The T_1's, or spin−lattice relaxation times, for some polymers have been compared to their IC counterparts.[15,16] For the polymers in the IC channels, there is usually a significant drop in the T_1 values, indicating an increase in the motional behavior of the polymer. It is believed that the mobility increases because the polymer chains are isolated from other polymer chains, and cooperative interchain interactions are no longer possible.

For crystalline polymers, such as polyethylene, the T_1 recorded for the methylene carbon is very long, ca. 300 s.[16,17] A long relaxation time is characteristic of polymers with a rigid crystalline structure. As Table 3 indicates, the T_1's for i-PP in the bulk and in the urea IC are relatively small. The methylene carbon in the bulk and IC samples has $T_1 = 10$ s. This is not typical of a rigid crystalline polymer. We believe that the T_1's of the methylene and methine carbons in the bulk and IC samples are being influenced by the motional behavior of the methyl side group. The methyl side group is free to spin and its rotating protons may increase the relaxation rates of the other two carbons, thereby reducing their spin−lattice relaxation times.

Parts a and b of Figure 8 show the ^{13}C NMR CP/MAS/DD spectra recorded for s-PP and the s-PP−U IC, respectively. For the bulk s-PP spectrum, 1000 transients were recorded, with a contact time of 2.00 ms, a τ of 108 μs, and a pulse delay of 3.00 s. The IC spectrum was still noisy even after 10 000 transients were recorded, at a contact time of 200 μs, a τ of 108 ms, and a pulse delay of 3.00 s. For the bulk s-PP sample, the methyl resonance peak at 20.46 ppm, the methine

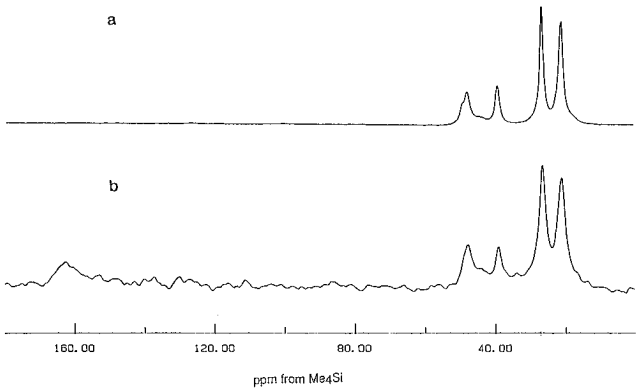

Figure 8. ^{13}C NMR CP/MAS/DD spectra for bulk s-PP (a) and s-PP−U IC (b).

resonance peak at 25.95 ppm, and the two methylene resonances at 38.69 and 47.40 ppm agree with the chemical shifts reported in the literature.[18] The 8.7 ppm splitting of the methylene ^{13}C resonance is present and is believed to arise from the two inequivalent sites for the methylene carbons. This is inherent in the 2_1 helical conformation, *...ttggttgg...*, where half of the methylene carbons are gauche to their γ-CH substituents and the other half are trans to their γ-CH substituents.[6,18,19] This shifts the methylene carbons with the γ-gauche substituents 8.7 ppm upfield.

The spectrum for the s-PP−U IC, like the i-PP counterpart, is nearly identical to that of its bulk sample. The methyl, methine, and methylene groups have very similar chemical shifts: 20.68, 26.09, 38.91, and 47.55 ppm, respectively. This indicates that the polymer is present in its urea-IC in the 2_1 helical conformation. The methylene carbons are still inequivalent and the resonance peaks are still split by 8.7 ppm. In order for the polymer to fit into a hexagonal urea IC channel, it would have to adopt the all-trans conformation, in which all of the methylene carbons are trans to their γ-CH's.[6] Therefore the methylene resonance would exist as a single peak. In the all-trans conformer, the methyl resonance peak would also be shifted one γ-gauche effect upfield because the methyl carbon is gauche to both of its γ-CH's, instead of to one CH for the *...ttggttgg...* conformation.[6] The other resonance peak of interest is the possible urea C=O peak at 162.42 ppm. This peak has a low intensity and is barely visible above the baseline noise, and it appears in the s-PP−U IC spectrum, but not in the i-PP−U IC spectrum. This is believed to be due to the concentration of the IC in the sample. There is obviously more free urea present in the i-PP−U IC than in the s-PP−U IC sample. Even in samples with a higher concentration of IC, the C=O resonance is very weak relative to the other resonance peaks.

Due to the difficulty in obtaining a good spectrum of the s-PP−U IC, the T_1's have only been recorded for the bulk s-PP sample. They are included in Table 3. Initial attempts at getting T_1 values for the s-PP−U IC have resulted in values similar to that of the bulk s-PP sample. The same trend observed in the bulk i-PP is observed in the bulk s-PP spectrum. The methylene carbons have a longer spin−lattice relaxation time than the methine carbons, which is longer than the methyl carbon. Again the methyl carbon has a T_1 less than a second. It is believed that the spinning of this group is again influencing the motional behavior of the other local carbons.

Because the T_1's observed for i-PP, s-PP, and i-PP−U and i-PP-PHTP-IC's are very similar, because of the different crystal structures of i-PP (3_1 helical) and s-PP (2_1 helical), and because of the generally more mobile natures of polymer backbones included in urea IC's compared to their bulk crystals,[15,16] the T_1's of solid PP's must be dominated by the facile rotational motions of their methyl groups, which are apparently not affected by these different solid-state environments.

Further analyses of the PP−U IC structure and its stability are in progress. The discovery of a new urea IC crystal form with large inclusion channels could have many uses, including the study of polymers with rings in their backbone. The traditional hexagonal urea IC has a channel diameter that is too small for many of these types of polymers.[20]

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