Inclusion Compound Formed between Poly(L-lactic acid) and Urea

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ABSTRACT: We have successfully incorporated poly(L-lactic acid) (PLLA) into the narrow channels of its inclusion compound (IC) with urea (U). PLLA-U-IC was obtained by cocrystallization following the addition of a warm, saturated solution of urea in methanol to a warm, dilute chloroform solution of PLLA. Calorimetric observations (DSC) revealed that PLLA-U-IC melted at 137 °C with an approximate enthalpy of 41 cal/g. Wide-angle X-ray diffractograms of PLLA-U-IC powders and FTIR spectra of their KBr pellets both strongly point to the formation of a hexagonal PLLA-U-IC structure very similar to that observed for the U-IC's formed with *n*-alkanes and polyethylene. High-resolution solid-state ^{13}C NMR observations of pure PLLA and PLLA-U-IC reflect the differences between the PLLA conformations and packing environments found in the ordered, solid bulk and U-IC samples.

Introduction

The behavior of conformationally ordered polymer chains in solid and liquid-crystalline environments is determined not only by the structure of the individual polymer chains but also by cooperative interactions between neighboring chains. The study of crystalline inclusion compounds (IC's) provides a means to decouple these contributions so that single-chain properties can be observed in isolated, well-defined environments. An IC is formed when a small molecule "host" crystallizes into a matrix which encapsulates and squeezes individual polymer chains into separate, well-characterized channels. As a consequence, each chain is forced into an extended conformation by the confines of the channel and is completely isolated from neighboring chains. By studying[1] the conformations and mobility of a single chain, it is possible to more fully understand the contribution each chain makes to the behavior of bulk ordered systems.

Urea has been shown[2–4] to form crystalline IC's with polymer guests by crystallizing into an extensively hydrogen-bonded hexagonal matrix, isolating each guest molecule into parallel channels as shown in Figure 1. Polymeric guests successfully isolated in urea inclusion compounds include linear polymers such as polyethylene[5] (PE), poly(ethylene oxide),[6] poly(tetrahydrofuran),[7] and poly(ϵ-caprolactone) (PEC).[8] Since the host channels are well defined (5.5 Å diameter)[2] in urea-based IC's, only those molecules capable of conforming to this limiting cross-sectional dimension can be successfully included.

In a recent communication we reported[9] the successful formation of urea–poly(L-lactic acid) (PLLA) inclusion compounds. PLLA IC's with urea provide an interesting system to study because of the diverse crystalline forms in which PLLA is known to exist.[10–13] In the bulk, PLLA has been shown to crystallize in an α or β form. The orthorhombic α form (the more stable of the two) consists of a unit cell composed of two molecules each in a 10_3 helical conformation. By contrast, the β form

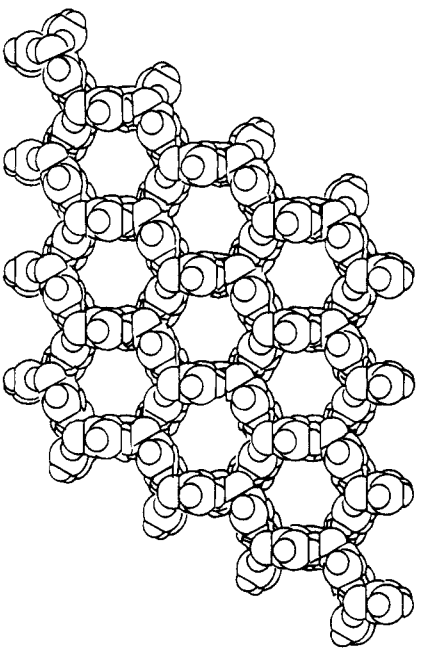

Figure 1. Cross-section of the hexagonal channel matrix formed by urea in the presence of *n*-alkane guest.

(obtained during fiber draw) is known to be a hexagonal crystal which has a unit cell of 4 molecules existing in a 3_1 helical conformation. A third crystalline form is observed in the 1:1 stereocomplex[14–17] formed when PLLA and poly(D-lactic acid) (PDLA) are cocrystallized. A triclinic crystal results with a unit cell consisting of paired L and D chains packed in parallel 3_1 helices.

Molecular modeling[18] has shown that PLLA chains must adopt a nearly all-*trans*, planar zigzag conformation to fit into the channels formed by urea IC's, even though it is not the lowest energy conformation of PLLA. On a more practical level, fiber-forming polymers are of particular interest since extended conformations have been retained after collapse of IC structure.[5,21,22] Therefore, it may be possible to spin highly elongated, high-modulus fibers from polymer IC's using conventional spinning techniques.

In our initial study,[9] results from solid-state ^{13}C NMR were provided as evidence for successful IC formation.

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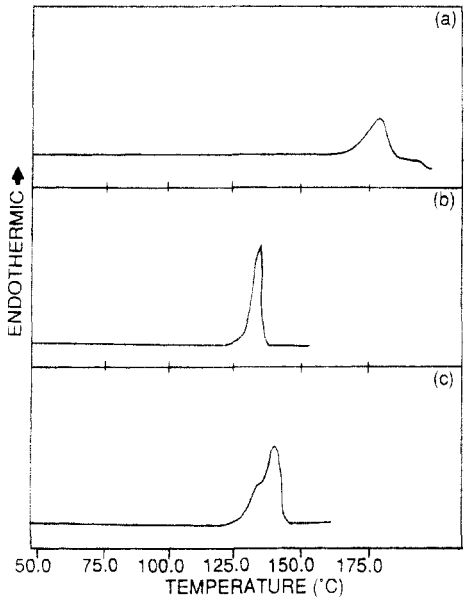

Figure 2. DSC thermograms recorded during first heat (10 °C/min) of (a) PLLA, (b) urea, and (c) PLLA-U-IC.

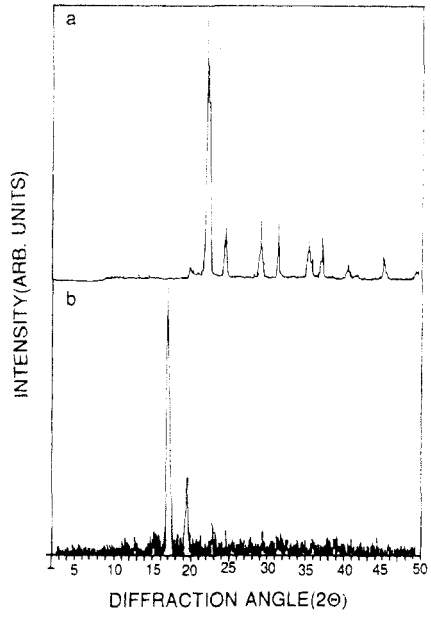

Figure 3. X-ray diffractograms of (a) urea and (b) PLLA (α form) recorded at room temperature.

Here we provide the details of a more complete evaluation of PLLA-U-IC using several techniques, including FTIR, DSC, X-ray diffraction, and solid-state ^{13}C NMR.

Materials

The PLLA used in this work was obtained from Research Triangle Institute. Intrinsic viscosity measurements recorded at 25 °C in chloroform indicate the PLLA sample has a molecular weight of 285 000. Urea was purchased in pellet form from Fisher Scientific and used without further purification. Certified ACS grade methanol and chloroform were obtained from Fisher Scientific.

Experimental Procedures

PLLA-U-IC was prepared by slowly adding 10 mL of a heated (ca. 50 °C) saturated methanol solution of urea (1.2 g) to a solution (also held at ca. 50 °C) of 0.28 g of PLLA in 40 mL of chloroform. After 2 h of stirring and application of mild heat, the covered flask was removed from the hot plate and left undisturbed overnight. A white precipitate has collected by filtration and air-dried for several days.

Thermal transitions were recorded on a Perkin-Elmer DSC-7. The compounds were evaluated under a nitrogen purge by two or more heat/cool cycles (heating rate of 10 °C/min and cooling rate of 200 °C/min) after calibration with indium under the same conditions.

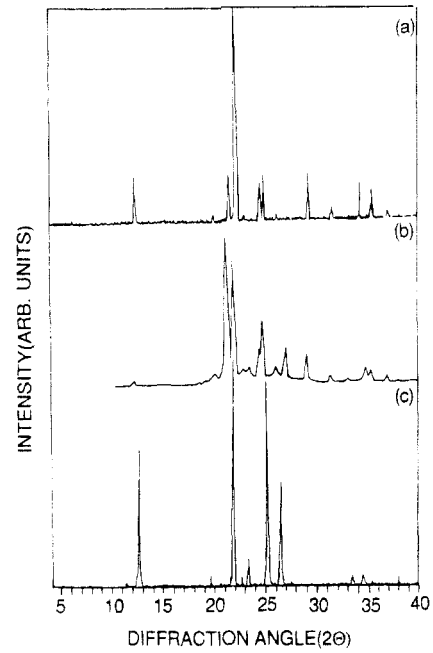

Figure 4. Presence of hexagonal IC as evidenced by the structure in the X-ray diffractograms of (a) PLLA-U-IC, (b) PEC-U-IC, and (c) *n*-hexadecane-U-IC taken at room temperature.

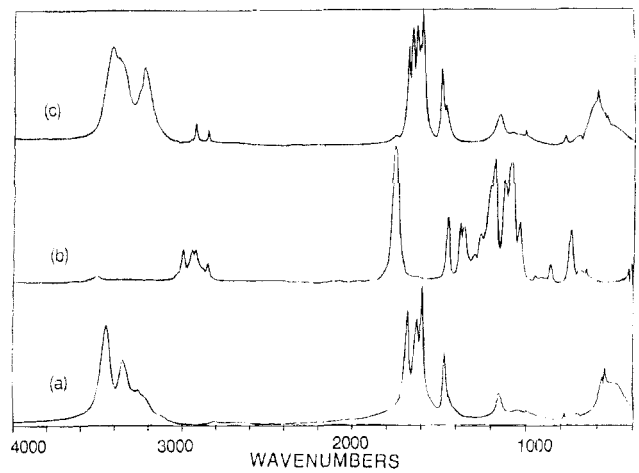

Figure 5. IR spectra of (a) urea, (b) PLLA, and (c) PLLA-U-IC.

Wide-angle X-ray diffractograms of powder samples were obtained at ambient conditions on a Scintag 2000 XDS using Ni-filtered Cu Kα radiation. The supplied voltage and current were set to 45 kV and 40 mA, respectively. Samples were run at a scan rate of 5° 2θ/min between $2\theta = 0$ and 50°.

Infrared spectra in the region of 400–4000 cm^{-1} were recorded for KBr pellets on a Nicolet 510P FTIR spectrometer using a resolution of 2 cm^{-1}. The sample chamber was purged with desiccated air.

Solid-state ^{13}C NMR spectra were obtained at 50.14 MHz on a Chemagnetics CMC 200S NMR spectrometer equipped with a CP/MAS probe. The rotating radio frequency field strengths for both carbons and protons were approximately 50 kHz. Approximately 1000 transients were collected over a spectral width of 15 kHz using 2000 data points and a 5 μs 90° pulse at a sample spinning rate of 4 kHz. The spectra were obtained with a 2 ms contact time and a pulse delay of 3 s. The signal-to-noise ratio for both spectra were improved by apodization which introduced 10 Hz line broadening. A sample of *p*-di-*tert*-butylbenzene was used to calibrate the chemical shifts (31.0 ppm vs TMS).

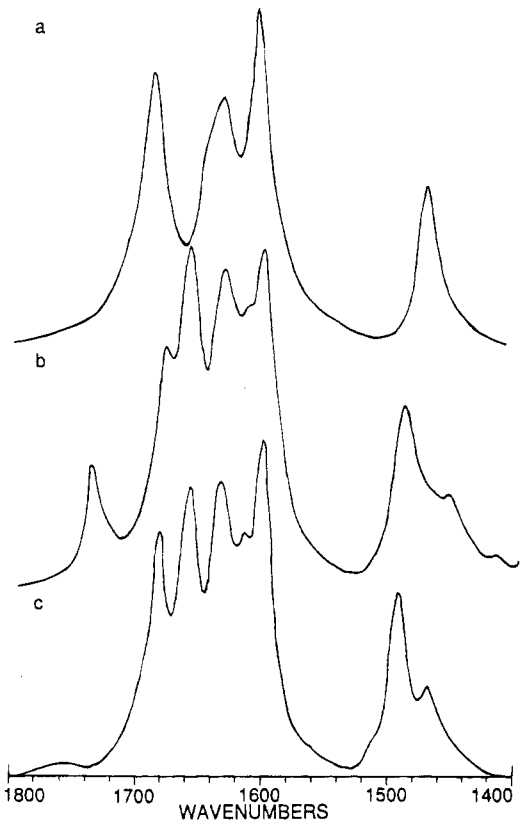

Figure 6. FTIR spectra of (a) urea, (b) PEC-U-IC, and (c) PLLA-U-IC.

Results and Discussion

To determine whether a true IC was successfully formed, we compared thermal, crystallographic, and spectroscopic properties of the pure components—PLLA and urea—and a physical mix of urea and PLLA to those of the suspected IC. To eliminate solvent and temperature effects, urea and PLLA were individually subjected to the exact conditions of IC formation. For example, urea was dissolved in hot methanol, added to hot chloroform, stirred, and mildly heated for 2 h. DSC analysis of treated base components suggests that no change in materials can be attributed to the solution process.

Four analytical tools were used in this study. DSC was used to screen all suspected IC's and to determine their thermal behavior. Wide-angle X-ray diffraction, the technique most often cited in the literature for identifying hexagonal urea, was then used to confirm IC crystal structure. FTIR provided additional evidence of hexagonal urea geometry and polymer inclusion as well as information regarding the chemical environment of the polymer. Solid-state ^{13}C NMR, due to its sensitivity to local chemical environments, was utilized for additional information on the conformation of the PLLA chains in the bulk and in the urea IC.

The DSC curve of PLLA presented in Figure 2a shows a melting endotherm at 180 °C with an associated enthalpy of 14 cal/g. Using an enthalpy of melting value of 22 cal/g for 100% crystalline PLLA,[11] our bulk sample was calculated to be 68% crystalline. We have recorded a melting temperature of 135 °C and corresponding ΔH_m of 54 cal/g for pure tetragonal urea as shown in Figure 2b. In contrast, Figure 2c shows thermograms of PLLA-U-IC which exhibit a large endothermic peak at 137 °C with a well-defined shoulder at 133 °C. The shoulder, assigned to free urea, exhibits a ΔH_m of 15.41 cal/g. The peak at 137 °C is associated with the melting endotherm of PLLA-U-IC and reflects an enthalpy of 40.95 cal/g. Comparing the enthalpy values of free urea for the initial and final heat cycles, we estimate 68% of the urea is in the hexagonal IC form in our original sample.

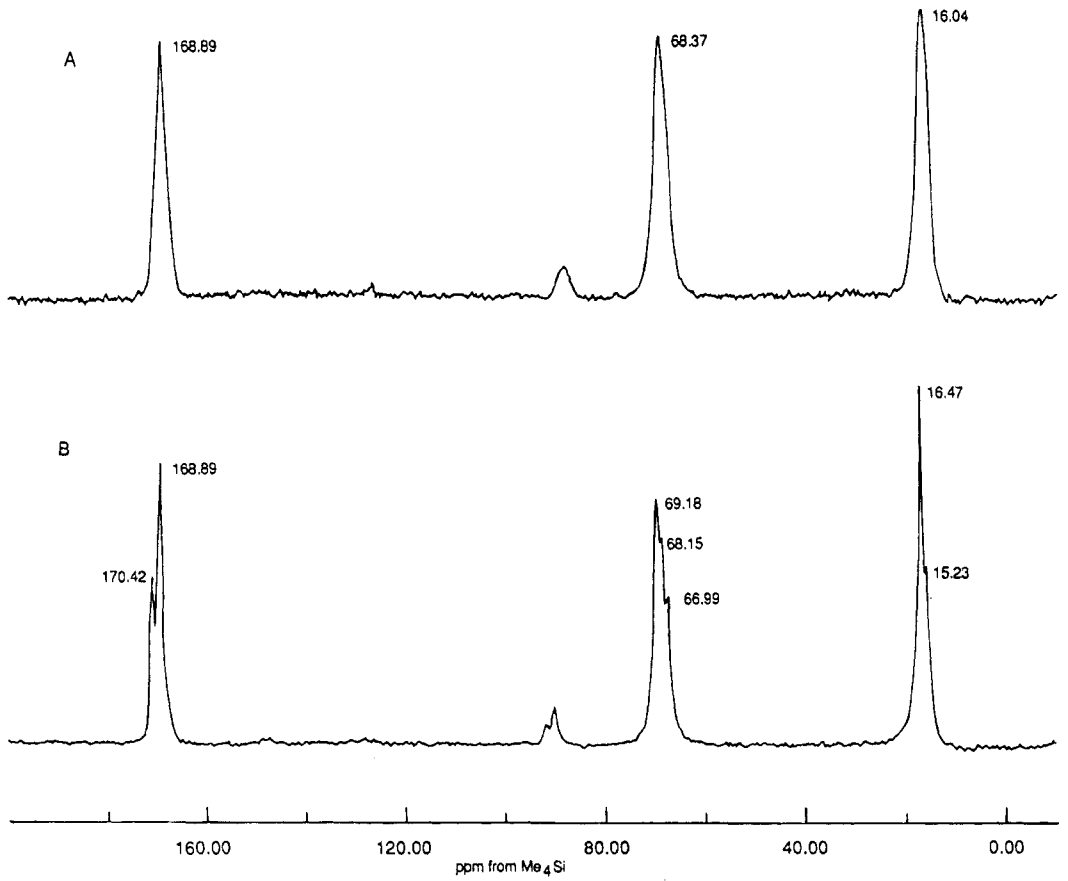

Figure 7. CP/MAS/DD ^{13}C NMR spectra for (A) PLLA-U-IC and (B) pure PLLA.

Degradation of urea at 165 °C prevents any evaluation of polymer endotherms in the presence of urea. As a consequence, an estimate of IC stoichiometry determined by comparison of the changes in the amount of uncomplexed urea and polymer as the IC is melted and converted to pure components[8] could not be achieved with calorimetry. Under these limitations, the DSC was primarily used as a screening tool to verify the presence of two peaks in the region between 130 and 140 °C. Samples passing this requirement were further evaluated using wide-angle X-ray diffraction.

X-ray diffractograms recorded for powder samples of pure urea show major peaks at 2θ = 22.5, 29.5, and 31.5° as shown in Figure 3a. Figure 3b shows prominent peaks at 2θ = 17.3, 19.5, and 22.8° for pure PLLA (α form). As expected, the 3:1 physical mix of urea:PLLA shows a simple combination of these peaks (not shown). The diffractogram of PLLA-U-IC shown in Figure 4a indicates several unique peaks, the most notable being 2θ = 12.6°. This peak has also been reported for PE-U-IC[5] and PEC-U-IC[8] and can be attributed to the hexagonal structure of the urea inclusion compound. In fact, the diffractograms for PLLA-U-IC[5] (Figure 4a), PEC-U-IC[5] (Figure 4b), and *n*-hexadecane-U-IC (Figure 4c) are very similar, again offering substantial proof of the formation of a PLLA-U-IC. It was concluded from the presence of peaks at 22.5 and 31.5° that the IC sample contains some free urea. The lack of a 17° peak suggests all PLLA is incorporated in the urea IC. Unfortunately, we were unsuccessful in obtaining single crystals of PLLA-U-IC, which prevented the calculation of unit cell characteristics.

The IR spectrum of pure tetragonal urea is shown in Figure 5a. The presence of three main vibrational regions is indicated and assigned as follows: NH_2 stretch = 3447 and 3347 cm^{-1}, NH bend = 1628 and 1599 cm^{-1}, and C=O stretch = 1682 cm^{-1}. Figure 5b shows the IR spectrum obtained for bulk PLLA. The band assignments were not made previously. Normal coordinate analysis of PLLA is currently underway in an attempt to assign the vibrational bands for PLLA. Figure 5c shows the IR spectrum obtained for PLLA-U-IC.[23] The most notable difference between the two spectra is the shifting of the NH_2 and C=O bands to lower frequencies in the IC. This is as expected for the hexagonal lattice since this form has stronger hydrogen bond associations within the urea matrix.[2] The IR spectrum of PEC-U-IC was studied previously. Similar shifts were observed for NH_2 and C=O absorption bands, further supporting the presence of the hexagonal form. The region between 1400 and 1800 cm^{-1} for urea, PEC-U-IC, and PLLA-U-IC is shown in Figure 6a–c. New bands due to hexagonal urea are clearly seen at 1658 and 1491 cm^{-1}. The absorption bands at 1467 and 1682 cm^{-1} indicate some uncomplexed urea was also present in the PLLA-U-IC sample. This is consistent with our DSC and X-ray findings.

CP/MAS/DD ^{13}C NMR spectra recorded for PLLA-U-IC and PLLA are presented in Figure 7. Bulk PLLA shows multiple resonances for each carbon type: methine = 68 ppm, methyl = 16 ppm, and carbonyl = 168 ppm. This splitting is not surprising since PLLA in the bulk may contain both α and β crystalline modifications resulting in different conformations and packing arrangements. In addition, recording spectra at room temperature, approximately 25 °C below the T_g, would also be expected to evidence resonances from the relatively rigid amorphous carbons as well. In contrast to the pure polymer, PLLA in the IC shows single resonances for each carbon type, suggesting the presence of a uniform environment. Similar behavior has been reported previously for PE when included in urea-based IC's. Under the geometrical constraints of the urea channel, both polymers are required to adopt an all-*trans* conformation resulting in a homogeneous local conformational environment as indicated by the single observed resonance for each carbon type and also suggests a homogeneous channel packing environment, at least on the NMR time scale of MHz.

An alternative explanation for the multiple resonances observed for each carbon type in the bulk PLLA sample may be the presence of a single crystalline polymorph (α form) which possesses multiple packing environments for the PLLA chains, a situation reminiscent of the α-form crystals of isotactic polypropylene.[24] Our X-ray diffractogram of the bulk PLLA samples (see Figure 3b) is consistent[14] with the presence of only α-form crystals.

It should be noted that, although the urea C=O resonance expected at 163 ppm was not observed in either pure tetragonal urea or PLLA-U-IC, its presence was verified by DSC, X-ray, and solution ^{13}C NMR analyses. The absence of the urea carbonyl resonance has previously been accounted for.[9]

Further analyses of the structure, stoichiometry, and stability of PLLA-U-IC's are in progress.

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