^{13}C n.m.r. observation of poly(L-lactide) in the narrow channels of its inclusion compound with urea

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The high resolution CP/MAS/DD ^{13}C n.m.r. spectra of bulk, semicrystalline poly(L-lactide) (PLLA) and PLLA confined to the narrow channels of its urea clathrate (PLLA-U) are compared and contrasted to the recently reported CP/MAS/DD spectrum of the crystalline 1:1 stereocomplex (PLLA*PDLA) formed by mixing dilute solutions of PLLA and poly(D-lactide) (PDLA) followed by their cocrystallization. Single resonances are observed for all three carbon types in PLLA-U, while the carbonyl carbons in PLLA*PDLA and all three carbon types in bulk PLLA evidence multiple resonances. Differences in the conformations and packing of PLLA chains in these distinct, ordered solid-state environments are the likely sources of their very different high resolution, solid-state ^{13}C n.m.r. spectra.

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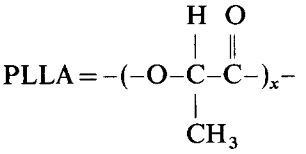
The simple, high-melting (~180°C) poly(L-lactide) (PLLA)



$$\mathrm{PLLA} = -(-\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-)_x-$$

can be crystallized in several unique solid-state polymorphs. Pure PLLA is known[1–4] to crystallize in both a pseudo-orthorhombic α-form and a hexagonal β-form with 10_3- and 3_1-helical chain conformations, respectively. Mixing separate solutions of PLLA and poly(D-lactide) (PDLA) followed by their cocrystallization has recently been shown[4–8] to lead to a 1:1 stereocomplex PLLA*PDLA with a triclinic unit cell, where 3_1-helical PLLA and PDLA chains are packed side by side.

In addition, we[9] have recently formed the crystalline inclusion compound (IC) between PLLA and urea (PLLA-U-IC), where the PLLA chains are separated and individually confined to occupy the narrow urea clathrate channels. PLLA-U-IC was formed by mixing a saturated solution of urea in methanol with a solution of PLLA in chloroform, followed by cocrystallization upon cooling. Based on the intrinsic viscosity measured at 25°C in chloroform, our sample of PLLA has a molecular weight of ~285 000. Also, the melting temperature and melting endotherm observed[9] for our PLLA sample indicate that it is highly stereoregular with very small content of D-lactide residues.

Molecular modelling[10] of PLLA chains in narrow cylinders ($D = 5.5$ Å), which mimic the constraining environment found[11,12] in polymer–urea ICs, indicates that only PLLA chains adopting a nearly planar zigzag, all-*trans* conformation are slim enough to reside in the urea IC channels. As a consequence, PLLA and/or PDLA chains may be observed in four unique ordered, solid-state environments, two bulk crystalline states (α- and β-forms) composed of either stereoisomer, the PLLA*PDLA stereocomplex crystals, and the crystalline PLLA-U-IC. PLLA chains adopt at least three distinct conformations (3_1- and 10_3-helical and planar zigzag) and experience at least four different organized packing environments.

Because high resolution, solid state ^{13}C n.m.r. spectroscopy has shown[13] a sensitivity to the chain conformations and packing environments in polymer crystals, it seems worthwhile to record and compare the CP/MAS/DD ^{13}C n.m.r. spectra of PLLA in these four distinct crystalline structures. Here we report preliminary ^{13}C n.m.r. observations of the recently obtained[9] PLLA-U-IC and contrast them with those observed for bulk PLLA and the 1:1 PLLA*PDLA stereocomplex[14] crystals.

The 50 MHz CP/MAS/DD ^{13}C n.m.r. spectra observed for (A) PLLA-U-IC and (B) PLLA are presented in *Figure 1*. Tsuji *et al.*[14] report a very similar spectrum for PDLA. Under the conditions employed in recording these spectra (see *Figure 1*), the C=O resonance of urea in PLLA-U-IC, which is observed[15,16] at around 165 ppm, is not visible, probably because of quadrupolar broadening caused by the directly bonded ^{14}N nuclei and/or molecular motion in the kilohertz regime, which can render either or both high power decoupling of proton spins (DD) and cross-polarization (CP) of ^{1}H and ^{13}C magnetization ineffective. In fact, under the same conditions employed in recording the spectra in *Figure 1*, the C=O resonance in pure tetragonal crystalline urea is also not detected. However, d.s.c., X-ray diffraction, and solution ^{13}C n.m.r. observations[9] of PLLA-U-IC confirm the presence of urea clathrate.

The most striking difference between the spectra is the multiple resonances observed for each carbon type in PLLA compared with the single resonances for PLLA-U-IC. The bulk PLLA sample contains crystalline carbons, possibly both α- and β-form crystals, and relatively rigid amorphous carbons, because T_g is about

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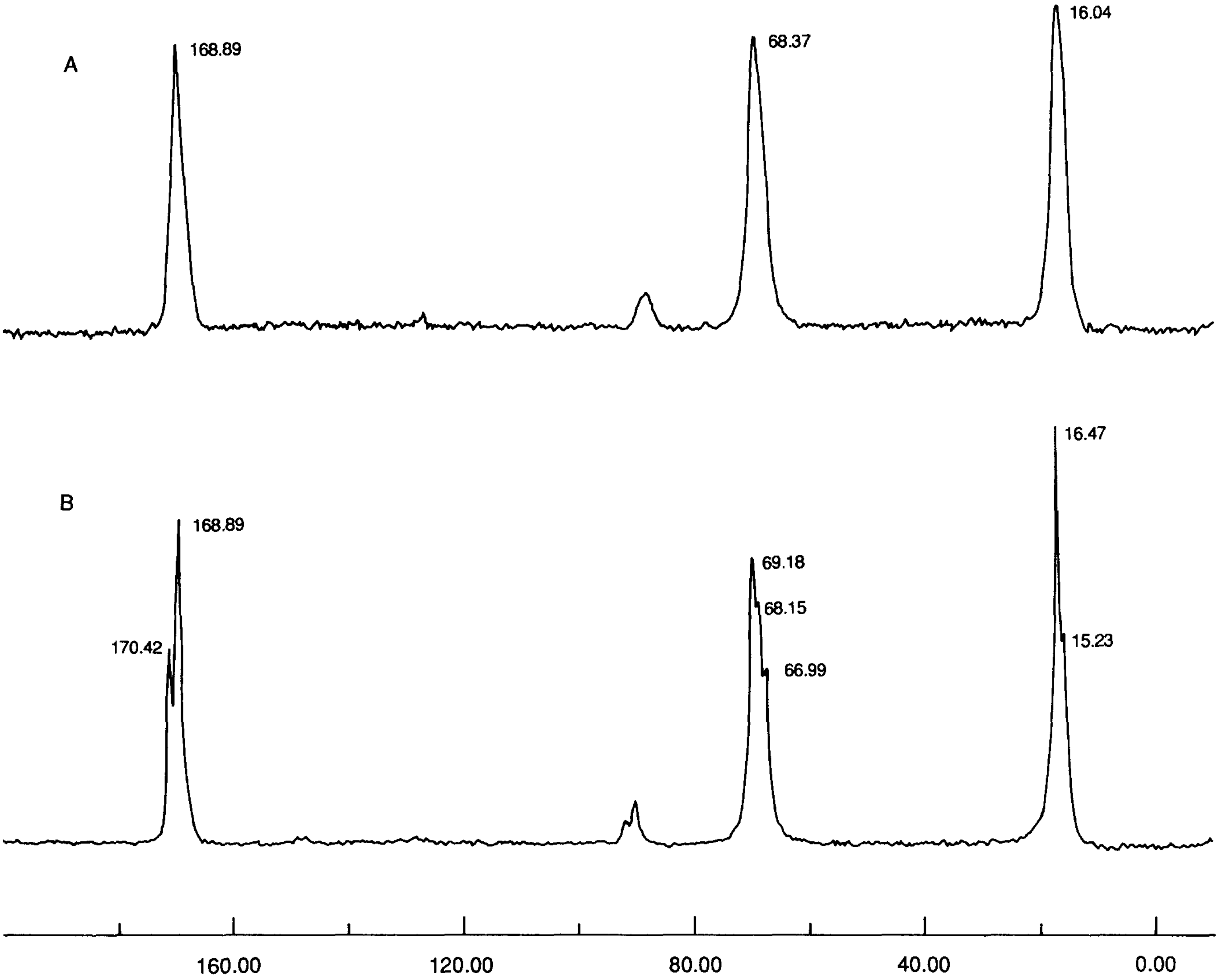

Figure 1 CP/MAS/DD ^{13}C n.m.r. spectra for PLLA-U-IC (A) and bulk, semicrystalline PLLA (B). Both solid-state ^{13}C n.m.r. spectra were obtained at 50.14 MHz on a Chemagnetics CMC 200S n.m.r. spectrometer equipped with a CP/MAS probe. The rotating radio frequency field strengths for both carbons and 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 was improved by apodization which introduced 10 Hz line broadening. A sample of *para*-ditertiarybutylbenzene (PDTBB) was used to calibrate the chemical shifts

60°C for PLLA[14]. Thus the observation of two or more resonances for each carbon type in bulk PLLA is not unexpected. Observation of single resonances for each carbon type in PLLA when complexed with urea implies a single homogeneous environment (homogeneous on the n.m.r. time scale) for the PLLA chains confined in their narrow clathrate channels. This behaviour has also been observed[16] for the poly(ε-caprolactone)-U-IC[15], and is consistent with the single, nearly planar zigzag conformation suggested[17] for included aliphatic polyester chains when modelling their conformational behaviour in narrow urea-IC-like cylinders ($D = 5.5$ Å).

Tsuji *et al.*[14] have aiso reported the CP/MAS/DD ^{13}C n.m.r. spectra of the 1:1 PLLA*PDLA stereocomplex crystals and observe three carbonyl resonances, but only single resonances for the methine and methyl carbons. They assign the three carbonyl resonances to the PLLA*PDLA stereocomplex crystals, to incidental pure PLLA and PDLA crystals, and to amorphous PLLA and PDLA portions of their sample. However, they offer no explanation for the single methine and methyl carbon resonances observed in the same sample. As seen in *Figure 1B*, bulk PLLA shows at least two resonances for each carbon type.

Until the structural insensitivity of the methine and methyl carbon resonances observed by Tsuji *et al.*[14] for the 1:1 PLLA*PDLA crystalline stereocomplex is understood, conclusions drawn from their analysis of the carbonyl region of the spectrum would seem to be uncertain. Continuation of our studies[9,18] on the PLLA-U-IC may aid our understanding of the connections between the solid structural environments and CP/MAS/DD ^{13}C n.m.r. spectra of PLLA.

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