Direct Observation of Stereodefect Sites in Semicrystalline Poly(lactide) Using ^{13}C Solid-State NMR

Mark T. Zell,[†] Brian E. Padden,[†] Amanda J. Paterick,[†]
Marc A. Hillmyer,[†] Robert T. Kean,[‡]
Khalid A. M. Thakur,[‡,§] and Eric J. Munson*,[†]

Department of Chemistry, University of Minnesota 207 Pleasant Street SE, Minneapolis, Minnesota 55455, and Cargill Incorporated, Central Research P.O. Box 5699, Minneapolis, Minnesota 55440

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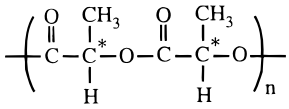
Stereoregular polymers such as isotactic polypropylene compose a significant fraction of the bulk polymer market. The number and distribution of stereoirregularities, or defects, in this type of polymer have a direct influence on its final crystallinity. The local environment of the defect site can be investigated using solid-state NMR spectroscopy if the peaks corresponding to the defect sites can be identified in the NMR spectrum, especially at very low concentrations (<5%).[1−3] Isotopic labeling is one method that can be used to identify defect resonances. In polyolefins such as isotactic polypropylene, defect sites are generated during the polymerization process, making it impossible to specify which monomer unit will become a defect site. For this reason, most studies of defect sites in polymers have used copolymers, in which the minor component in the copolymer corresponds to a defect site that can readily be identified in the NMR spectrum.[4−7] However, defect sites in copolymers are constitutional defects, not configurational defects as found in stereoregular polymers.[8] Another approach to study defect sites is to predict their chemical shifts based upon ab initio calculations and compare the simulated NMR spectrum to the experimental spectrum.[9,10] The presence of stereodefects is inferred by their effect on the line shape, but this method requires extensive deconvolution of the line shape into multiple peaks.

In this communication, ^{13}C CP/MAS NMR was used to determine whether defect sites of a poly(D-lactide) that contained 3% L-lactide as a stereodefect were incorporated into the crystalline region or forced into the amorphous region of the polymer. We found that the L-lactide was equally divided between the crystalline and amorphous regions of the polymer. We also found that the L-lactide defects were located in multiple sites in the crystalline region and that the chemical shifts suggest that the enviroment of this site is very different from that of the D-lactide units.

Poly(lactide) (PLA) is prepared from lactide, which is a cyclic dimer of lactic acid.[11]



Lactic acid contains one asymmetric carbon and therefore has two absolute configurations, *R* and *S*. The *RR* configuration of lactide is referred to as D-lactide, and the *SS* configuration as L-lactide. Quiescently crystallized poly(L-lactide) or poly(D-lactide) is semicrystalline, with spherulites composed of crystalline lamellae and amorphous regions located between lamellae and between spherulites.[12−14] Within the lamellae, the polymer adopts a 10_3 helical structure.[15−17] The degree of crystallinity and melting point of PLA are affected by the stereoregularity of the polymer.[18,19] For example, as the L-lactide content in a polymer composed of primarily D-lactide increases, both the degree of crystallinity and the spherulite size decrease.[18] At concentrations greater than 12−15% L-lactide, the polymer does not crystallize.

Two different polymer samples were prepared.[20] Sample **1** was polymerized from 97% D-lactide and 3% L-lactide. The L-lactide was ^{13}C-labeled in the carbonyl carbon. Sample **2** was polymerized and annealed under conditions identical to that for **1**, except that unlabeled L-lactide was used.

Parts a and b of Figure 1 show the ^{13}C CP/MAS NMR spectra of **1** and **2**, respectively. We have previously shown that it is possible to accurately determine the crystallinity of PLA by spectral deconvolution of the carbonyl region of the ^{13}C CP/MAS NMR spectrum.[18] The degree of crystallinity for these samples as determined from Figure 1b is 57 ± 5%. The carbonyl carbon signal in Figure 1a contains both a natural-abundance (i.e., 1.1% ^{13}C) signal (Figure 1b) and a more intense signal from the 98% ^{13}C-labeled L-lactide. The spectrum of the 3% L-lactide component in the carbonyl region is obtained by subtracting the two spectra, as shown in Figure 1c. There is very little residual peak intensity left for the methyl and methine peaks, confirming that the morphologies of **1** and **2** are identical. The remaining peak intensity in the carbonyl region is due exclusively to the 3% L-lactide stereodefects in the polymer.

Figure 2a shows the spectral region corresponding to the carbonyl carbon after spectral subtraction (same as spectrum shown in Figure 1c). There are two possible contributions to this peak, one due to the L-lactide located in the amorphous region of the polymer and the other due to L-lactide in the crystalline region

† University of Minnesota.
‡ Cargill Inc.
§ Present address: 3M Center, Building 201-B5-05, St. Paul, MN 55144.

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(20) [^{13}C]Lactide was prepared from [^{13}C]lactic acid (Isotec) by standard procedures. Lactide was polymerized using tin octanoate as an initiator in toluene at 70 °C for 18 h. ^{13}C solution NMR showed that >98% of the L-lactide units had neighboring D-lactide units, indicating that the L-lactide units correspond to isolated defect sites in the polymer. All samples were annealed at 200 °C for 35 min, 150 °C for 17 h, 135 °C for 24 h, 120 °C for 24 h, 105 °C for 24 h, and finally 90 °C for 4 h to create a highly crystalline polymer. ^{13}C CP/MAS NMR spectra were acquired using a Chemagnetics CMX-300 spectrometer operating at 75.58 MHz for ^{13}C and using a 7.5-mm spinning system equipped with zirconia rotors. Samples were spun at the magic angle at rates between 4 and 5 kHz. All spectra were acquired with a contact time of 5 ms, decoupling power of 62 kHz, repetition delay between pulses of 3 s, and 2048 acquisitions. Spectral deconvolution was performed using Spinsight software provided with the spectrometer.

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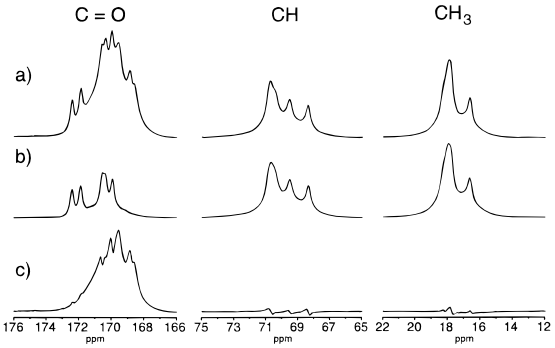

Figure 1. ^{13}C CP/MAS NMR spectra of samples **1** and **2**: (a) sample **1**; (b) sample **2**; and (c) spectral subtraction of (b) from (a). The remaining intensity in (c) is due only to ^{13}C-labeled L-lactide. Residual peak intensity in the methine and methyl regions likely represents slight differences in the morphology of the two samples.

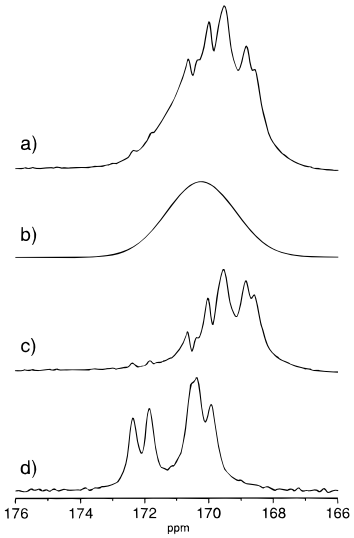

Figure 2. ^{13}C CP/MAS NMR spectra of the ^{13}C-labeled carbonyl region of sample **1**: (a) same spectrum as shown in Figure 1c; (b) amorphous component obtained by deconvolution of the peak in (a); (c) crystalline component of the peak shown in (a), obtained by subtracting (b) from (a); (d) spectrum of highly crystalline poly(L-lactide), with a (*R*)-lactic acid content of <0.3%.

of the polymer. The amorphous region of PLA has been shown experimentally to have a Gaussian line shape that can easily be simulated.[19] Parts b and c of Figure 2 show the resulting spectral deconvolutions of the amorphous and crystalline components, respectively, of the spectrum shown in Figure 2a, assuming that only these components are represented in the spectrum. The spectrum in Figure 2c was obtained by subtracting the amorphous component of the peak until a relatively flat baseline is found for the downfield region of the spectrum. Using this method, the integrated area of the amorphous peak is ~50%, with the remaining area in the crystalline peak. We estimate the error in determining these values to be less than 10%. Figure 2d shows the spectrum of poly(L-lactide) (<0.3% (*R*)-lactic acid content, ~90% crystalline). The spectra in Figure 2c and d are very different, suggesting that the local environment of the defect sites is very different from the local environment of the crystalline polymer.

We have also investigated the source of multiple peaks for the L-lactide defect sites in the crystalline regions of the polymer. The two-dimensional exchange NMR spectrum shown in Figure 3 contains broad cross-peaks from the amorphous polymer and distinct cross-peaks between the peaks in the crystalline defect sites. These cross-peaks can only arise from pairs of ^{13}C-labeled lactic acid units, as experiments on polymers containing isolated

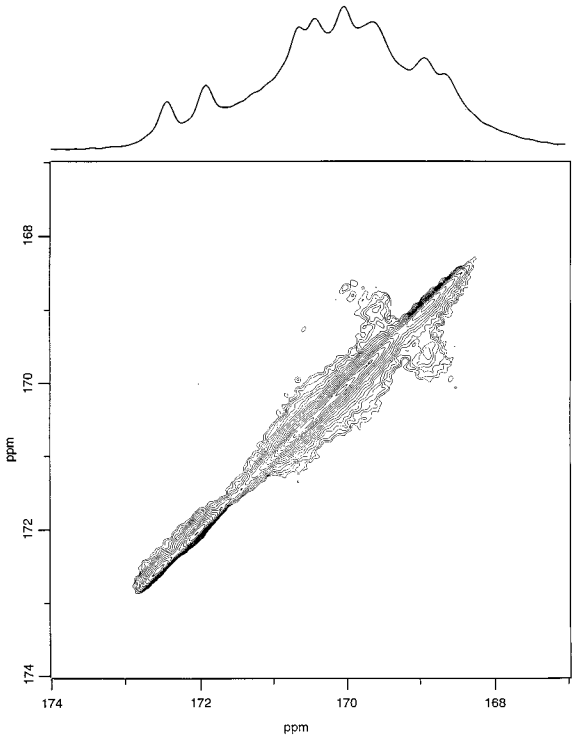

Figure 3. Two-dimensional exchange ^{13}C CP/MAS NMR spectrum of **1**. The spectrum was acquired as a hypercomplex data set with 128 points in each dimension, a spectral width of 1.3 kHz, 96 acquisitions per t_1 increment, and a 1-s mixing time. The data were zero filled to 1024 × 1024 prior to transformation. No apodization was applied to the data.

^{13}C-labeled lactic acid units produced no cross-peaks in a spectrum acquired using similar acquisition parameters.

There are several conclusions that can be drawn from the above data. First, ~50% of the L-lactide is incorporated into the crystalline lattice of the polymer. This is somewhat suprising, because this value is almost the same as the percent crystallinity determined for this polymer. This means that defect sites can readily be incorporated into the crystalline region of the polymer. Second, the environment of the crystalline defect sites is well-defined, as shown by the well resolved peaks in Figure 2c. The two-dimensional NMR experiment showed that the two neighboring lactic acid units in the polymer are located in slightly different environments in the crystalline lattice and have different chemical shifts. The presence of at least five peaks in the spectrum means that there is more than one type of local environment for the defect sites in the crystalline region of the polymer, corresponding to two or more crystallographically inequivalent sites for the defect sites. There are at least five peaks in the carbonyl region of 90% crystalline PLA (Figure 2d), indicating the presence of at least five crystallographically inequivalent sites for the homopolymer. Third, the average chemical shift for the defect sites is upfield from the chemical shift of amorphous PLA, and the average chemical shift of the peaks for highly crystalline PLA (Figure 2c) is downfield from amorphous PLA. We propose that when stereodefects are incorporated into the crystalline lattice, the helical nature of PLA is maintained. The methyl groups in the defect sites occupying positions where the hydrogen atoms are normally located, induce steric repulsions that produce a distortion of the helical chain in the neighborhood of a defect site. This disturbs the local environment of the carbonyl groups and causes the subsequent change in chemical shift. Future work includes molecular modeling of the structure that might result from this type of distortion.

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