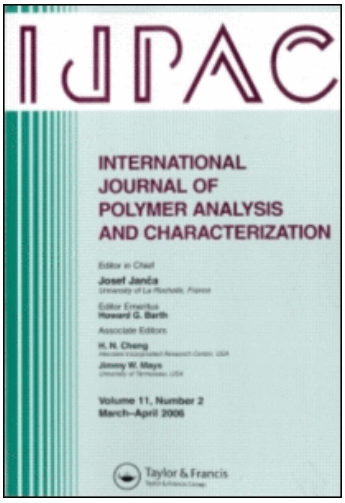

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^{1}H NMR Spectroscopy in the Analysis and Characterization of Poly(lactide)*

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High resolution 500 MHz ^{1}H NMR spectroscopy is a powerful tool for the analysis and characterization of poly(lactide) (PLA). It accurately provides information about the distribution of a few stereosequences in the polymer whose resonances are well-resolved in the NMR spectrum. Here, the splitting of the methine resonance due to coupling to the methyl protons in the polymer is removed by homonuclear decoupling. ^{13}C NMR provides complementary stereosequence information, but due to the poor signal-to-noise ratio its accuracy is not comparable to that of ^{1}H NMR. Through the analysis of the stereosequence distribution in a number of PLA spectra, it was determined that there is a preference for *syndiotactic* addition during lactide stereo copolymerization. It was shown that the normalized intensity of a few well-resolved resonances in the ^{1}H spectrum of PLA can be used to quantitatively determine the lactide stereoisomer composition incorporated in the polymer. The change in stereosequence distribution with polymerization can also be conveniently monitored by ^{1}H NMR. By following the reversible polymerization of D,L-lactide (*racemic* lactide) in this manner, it was found that the stereospecificity (or reactivity ratio) for *syndiotactic* addition reduced with increasing polymerization. This increasingly random polymerization is due to the interplay of kinetic and thermodynamic effects. Kinetic effects control the stereochemistry during the early stages of polymerization while equilibrium effects dominate at later stages. The viscosity changes during the melt polymerization additionally influence the stereochemistry.

Keywords: ^{1}H NMR; PLA; Lactide; Lactic acid; Reversible polymerization; Kinetics; Stereospecificity

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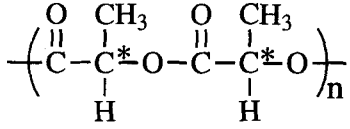
INTRODUCTION

Lactic acid based aliphatic polyesters are increasingly being explored for use in several applications including biodegradable packaging materials, food containers, bioresorbable medical implants and sutures, and drug delivery systems.[1–6] Cargill Incorporated has been developing poly(lactide) (PLA) products like yard-waste bags, food containers, and agricultural mulch films to replace non-degradable polymer products. The non-degradable polymer products produced from non-renewable resources, e.g., crude oil and natural gas, are increasingly becoming a source of ecological problems. High-molecular-weight PLA, however, is prepared by ring-opening polymerization of lactide acid dimers which in turn are produced using L-lactic acid derived from natural renewable sources (e.g., corn) or recycled waste products (e.g., agricultural starch waste[2]). Furthermore, PLA decomposes rapidly and completely in a typical compost environment and its degradation products have been shown to promote plant growth.[7]



Poly(lactide)

Lactic acid possesses one asymmetric carbon and exists in two configurations, *R* and *S*. The lactic acid with *S* configuration is referred to as L-lactic acid in comparison with L-glyceraldehyde. Lactic acid cyclic dimers (lactides) are diastereoisomers which exist in either the *RR*, *SS* or *RS* configuration. The *RR* configuration of the cyclic dimer is referred to as D-lactide while *SS* configuration is referred to as L-lactide. An equimolar ratio of *RR*- and *SS*-lactide is referred to as *racemic* or D,L-lactide, and the *RS*-lactide is referred to as *meso*-lactide. High purity *RR*- and *SS*-lactide are each known to polymerize into stereoregular (*isotactic*) poly(D-lactide) and poly(L-lactide) respectively, while poly(D,L-lactide) and poly(*meso*-lactide) are *atactic* polymers.[8–11]

A number of physical properties of PLA are linked to its stereosequence distribution.[3,12–14] The stereosequence distribution is influenced by a number of factors including the starting lactide feed

composition, polymerization kinetics, and extent of conversion.[15] The polymerization kinetics in turn are influenced by the catalyst, temperature, impurities, batch vs. continuous process, and other factors. A number of studies have used NMR spectroscopy to identify the stereosequence distribution in PLA.[15–22]

Depending on the magnetic field strength used, the NMR chemical shifts of ^{13}C and ^{1}H nuclei in PLA are affected by the stereoconfiguration of 1-3 adjacent stereogenic centers on either side. In the NMR spectra of PLA, the observed resonances can be assigned to various stereosequence combinations in the polymer.[15] The assignments are designated as various combinations of "*i*" *isotactic* pairwise relationships (*–RR–* and *–SS–*) and "*s*" *syndiotactic* pairwise relationships (*–RS–* and *–SR–*). In the NMR spectra, the diads *–RR–* and *–SS–* are indistinguishable and would have identical chemical shifts, as would *–RS–* and *–SR–*. Furthermore, since the chemical shifts of the lactide are different from those of the polymer, it is not necessary to separate the residual lactide in order to determine the stereosequence distribution in the polymer. The chemical shifts of the end groups in PLA are also well-resolved from that of the polymer.[23,24] In the methyl decoupled ^{1}H NMR spectra of PLA containing predominantly either L-lactide or D-lactide, methine hexad resonances of *isisi*, *iiisi*, and *iiiss* are well resolved.[22] In the ^{13}C NMR spectra of PLA, the methine resonances are also assigned to hexad resonaces, but the well-resolved regions correspond to the tetrad sequences of *sss*, *iss*, *ssi*, and *isi*.

The stereosequence distribution in the polymer for any particular composition of lactide stereoisomers is strongly dependent on the kinetics of polymerization. If the lactide polymerization process is truly random, the stereosequence distribution should match the distribution predicted by pairwise Bernoullian statistics. If there is a preference for either *isotactic* or *syndiotactic* addition, Markovian statistics apply. Using ^{13}C NMR, Kasperczyk[21] has shown that during the polymerization of D,L-lactide catalyzed by lithium *tert*-butoxide, there is preference for *syndiotactic* addition (*syndiotactic* stereospecificity). More recently, analyses of ^{1}H and ^{13}C NMR have shown that the lactide polymerization process using Sn(II) octoate as a catalyst proceeds with *syndiotactic* stereospecificity.[15,25] In this report, we hope to show that ^{1}H NMR is a convenient tool to accurately investigate the

stereosequence distribution in PLA and hence can be used in its analysis and characterization.

EXPERIMENTAL SECTION

Polymerization

Each of the lactide mixtures was sealed in a number of glass vials and simultaneously placed in an oil bath at 180°C. Sn(II) *bis*-2-ethylhexanoate (Sn(II) octoate) or butyl Sn(IV) *tris*-2-ethylhexanoate was used in a 1 : 10,000 catalyst : monomer ratio to catalyze the ring-opening polymerization of the lactides. The hydroxyl impurities in the catalyst and lactide are expected to act as initiators since additional initiators were not added. At various time intervals, glass vials were pulled out from the oil bath and placed in water at room temperature to quench the polymerization.

NMR Spectroscopy

The ^{1}H solution NMR spectra were acquired on a Varian 500 MHz NMR spectrometer. Unless specifically stated, the spectra were acquired on $\sim$1% solution in $CDCl_3$ with the methyl protons decoupled from the methine protons (homo-nuclear decoupled) during the acquisition time. A total of 64 scans were acquired, each with 40,000 data points at a spectral width of 10 kHz corresponding to an acquisition time of 4 s. A delay of 1 s was used between transients.

Monte Carlo Calculation of Lactide Polymerization

In order to predict the stereosequence distribution for the reversible lactide stereo copolymerization in a batch process such as in a vial, Monte Carlo (MC) calculations were utilized. Analytical equations to represent the observed kinetics and predict stereosequence distributions were not available. Details of the calculations have been reported elsewhere.[22,26] The reaction efficiencies (r) for *isotactic* addition (k_i/k_s) and removal (k_{xi}/k_{xs}) were set at 0.60. The probability of lactide removal was set at 0.035, i.e., 3.5%.

RESULTS AND DISCUSSION

The physical properties of poly(lactide) are strongly influenced by its stereosequence distribution. For any given lactide stereoisomer composition, the choice of catalyst influences the stereo copolymerization kinetics, and hence determines the stereosequence distribution in the polymer. For example, a catalyst which provides a preference for *isotactic* addition is likely to create a polymer with longer *isotactic* chain length distribution. Hence, it is necessary to determine the kinetics of stereo copolymerization for any given catalyst system. It was determined that during the lactide copolymerization using Sn(II) octoate in a 1 : 10,000 catalyst : monomer ratio at 180°C there is a preference for *syndiotactic* addition.[15] The value of the rate constant for *isotactic* addition (k_i), defined in Scheme 1, was shown to be lower than the value of the rate constant for *syndiotactic* addition (k_s).

$$-S^* + SS \underset{k_{xi}}{\overset{k_i}{\rightleftharpoons}} -SSS^*$$

$$-S^* + RR \underset{k_{xs}}{\overset{k_s}{\rightleftharpoons}} -SRR^*$$

$$-R^* + SS \underset{k_{xs}}{\overset{k_s}{\rightleftharpoons}} -RSS^*$$

$$-R^* + RR \underset{k_{xi}}{\overset{k_i}{\rightleftharpoons}} -RRR^*$$

SCHEME 1 Proposed kinetic scheme.

A preference for *syndiotactic* addition during the copolymerization of D-lactide and L-lactide will cause the minor component to be depleted with a higher pseudo rate constant than the major component.[15]

For example, during copolymerization of 80% L-lactide and 20% D-lactide, the D-lactide will be depleted with a higher apparent rate constant. Since the active growing site will often be $-SS^*$ due to the excess of L-lactide, the D-lactide (RR) will be preferentially polymerized. At low conversions, the polymer will be enriched with D-lactide and asymptotically reach the feed stock composition in the limit of 100% conversion. As long as the stereospecificity stays constant, two exceptions to this behavior would be D,L-lactide (viz. 50% L-lactide + 50% D-lactide) and *meso*-lactide since the Sn(II) catalyst is achiral and does not preferentially polymerize either S or R stereoconfigurations of the lactide. In an irreversible polymerization, the stereosequence distribution in poly(D,L-lactide) and poly(*meso*-lactide) would be expected to be independent of its conversion (or extent of polymerization).

In order to accurately determine the kinetics of the reversible lactide stereo copolymerization catalyzed by Sn(II) *bis*-2-ethylhexanoate, the stereosequence distribution in partially polymerized poly(D,L-lactide) quenched at various time intervals was investigated by ^{1}H NMR spectroscopy. The normalized intensities of the two well-resolved stereosequence resonances of *isisi* and *iiisi* were measured. A typical spectrum of poly(D,L-lactide) is shown in Figure 1. Here, the splitting

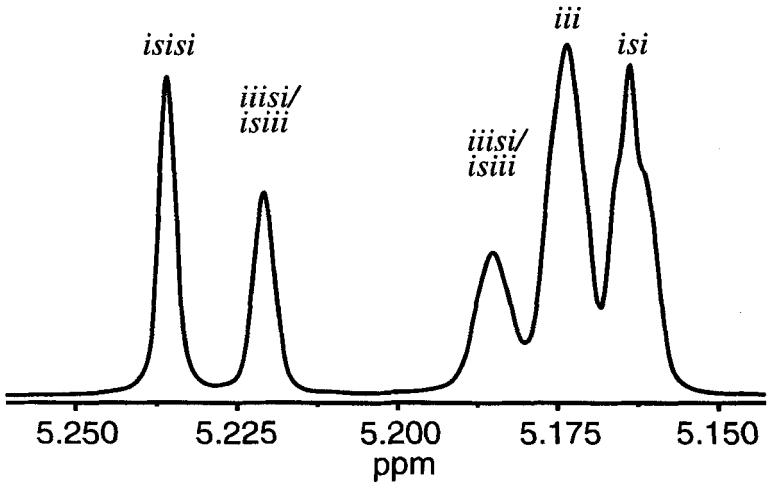


FIGURE 1 The methine region in the homonuclear decoupled ^{1}H NMR spectrum of poly(D,L-lactide) with the well-resolved stereosequence resonances of *isisi* and *iiisi* identified.

of the methine resonance due to coupling to the methyl protons in the polymer was removed by homonuclear decoupling.[15] For a totally random polymerization, the probability of both these stereosequences is 0.125. The normalized intensity of *isisi*, which represents sequences of *–RRSSRR–* and *–SSRRSS–* formed by two *syndiotactic* additions, is dependent on the stereospecificity during the polymerization. A value greater than 0.125 represents preference for *syndiotactic* addition, while a value lower than 0.125 represents preference for *isotactic* addition. The *iiisi*, which represents sequences such as *–SSSSRR–* and *–RRRRSS–*, is a result of one *isotactic* and one *syndiotactic* addition. Hence its normalized intensity is less sensitive to stereospecificity and can be used to determine if the catalyst is stereoselective. Since the *iiisi* is dependent on the stereoisomer composition of the poly(D,L-lactide), preference for either D-lactide or L-lactide polymerization by the catalyst would significantly reduce its intensity.

The normalized intensities of *isisi* and *iiisi* resonances observed for poly(D,L-lactide) quenched at various polymerization time intervals are shown in Figure 2. The *isisi* intensity reduces with extent of conversion while the *iiisi* intensity gradually increases by a tiny fraction. The almost constant value for the *iiisi* resonance indicates that the relative fractions of L-lactide and D-lactide in the polymer are independent of the extent of polymerization. This is also evidence for the catalyst being non-stereoselective; i.e., it does not preferentially polymerize either L-lactide or D-lactide. A value greater than 0.125 for normalized intensity of the *isisi* resonance implies that during the polymerization alternation of the two lactides is preferred. In other words, there is a preference for *syndiotactic* addition. The reduction in this *isisi* value with the extent of polymerization represents (cumulative) lowering of the preference for *syndiotactic* addition. This changing value for the *syndiotactic* preference is due to the reversible nature of lactide polymerization[26] (*vide infra*).

In Figure 2, the lines are the normalized probability values predicted by MC calculations using reaction efficiency ratios for *isotactic* addition ($=k_i/k_s$) and removal ($=k_{xi}/k_{xs}$) of 0.60. The x-axis values in the simulation were adjusted to match the time (120 min) at approximately the conversion of the last experimental data point. Possible transesterification and racemization events were ignored.

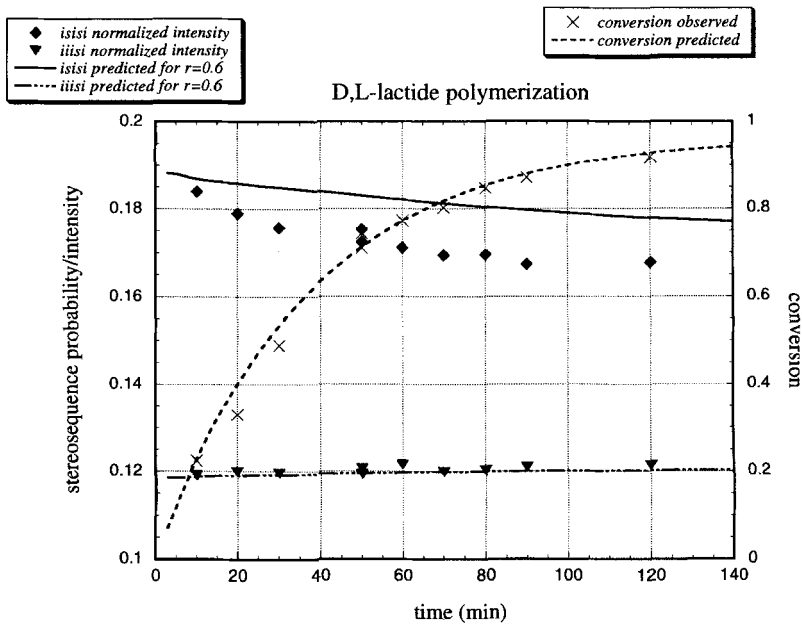


FIGURE 2 The normalized integrated intensities of *isisi* and *iiisi* stereosequence resonances in Sn(II) octoate catalyzed, partially polymerized poly(D,L-lactide) and the corresponding extents of conversion are plotted against the time intervals at which the polymerization was quenched. The line is the stereosequence probability predicted by MC calculations for a reaction efficiency ratio of 0.6. See the text for details.

The preference for *syndiotactic* addition can result from steric hindrance at the polymer growing active site. Kricheldorf *et al.*[24] have proposed that the polymerization proceeds by lactide insertion at the growing active site with the catalyst either covalently bound to the polymer or co-ordinatively complexed to the hydroxyl end of the polymer. It is conceivable that due to the limited space available around the Sn(II) catalyst, there is less steric hindrance for *syndiotactic* addition as compared to *isotactic* addition.

As mentioned earlier, the decreasing *syndiotactic* stereospecificity, which represents increasingly random addition during the lactide stereo copolymerization process, is due to the reversible nature of the polymerization. As a result of the increasing residence time of the lactide at the active site, where it is coming on and off the polymer, the relative probability of *isotactic* addition increases due to increased opportunities for addition. Alternatively, this may be thought of as an

interplay of the kinetics (activation energy difference) and the thermodynamics (equilibrium energy difference) of stereo copolymerization. A possible schematic relationship among various states involved during *isotactic* and *syndiotactic* lactide addition is shown in Figure 3. The enthalpy changes for *isotactic* addition and *syndiotactic* addition (ΔH_i and ΔH_s, respectively) are likely to be similar (~ 23 kJ/mol)[27–30] since L-lactide and D-lactide are energetically identical and only marginal energy difference may be expected between an *isotactic* bond (*S–S* or *R–R*) and a *syndiotactic* bond (*S–R*). The activation energy values for the two processes ($\Delta H_i^{\ddagger}$ and $\Delta H_s^{\ddagger}$, respectively) are expected to be different. The activation energy for L-lactide polymerization, which is $\Delta H_i^{\ddagger}$, has been reported to be ~ 71 kJ/mol.[27,28] Using the value of 0.6 for k_i/k_s at 180°C, the activation energy for *syndiotactic* addition is calculated to be ~ 69 kJ/mol.

This influence of reversibility of the polymerization process on the stereospecificity may be explained by examining the following equations:

From Scheme 1, the rates of *syndiotactic* addition (ds/dt) and *isotactic* addition (di/dt) are:

$$ds/dt = k_s \cdot [S^*] \cdot [RR] - k_{xs} \cdot [SRR^*] + k_s \cdot [R^*] \cdot [SS] - k_{xs} \cdot [RSS^*], \tag{1}$$

$$di/dt = k_i \cdot [S^*] \cdot [SS] - k_{xi} \cdot [SSS^*] + k_i \cdot [R^*] \cdot [RR] - k_{xi} \cdot [RRR^*]. \tag{2}$$

For the special case of D,L-lactide polymerization, at any given instant of time,

$$\begin{aligned}
&[SS] = [RR] = [lac]_t/2,\\
&[S^*] = [R^*] = [end]/2,\\
&[SRR^*] = [RSS^*] = [end_s]_t/2,\\
&[SSS^*] = [RRR^*] = [end_i]_t/2,\\
&[end_s]_t + [end_i]_t = [end],
\end{aligned}$$

where $[lac]_t$ is the concentration of the residual lactide at time t, and $[end_s]_t$ and $[end_i]_t$ are the concentrations of end groups formed by

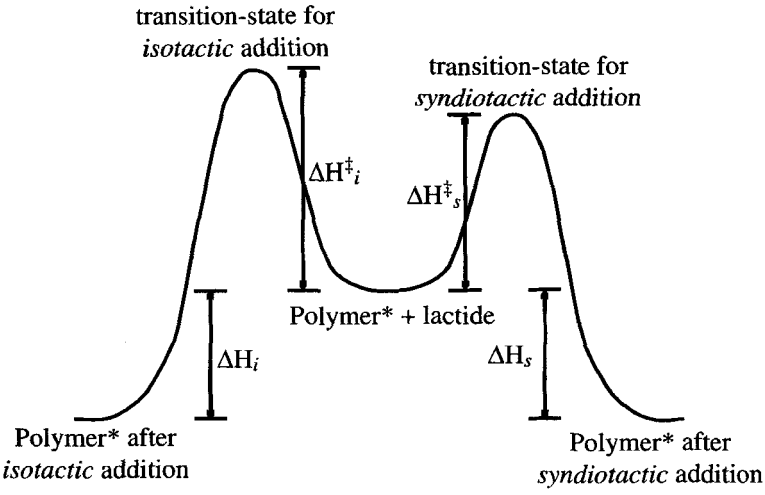


FIGURE 3 A schematic diagram of the relative energy values for the various states defined for *isotactic* and *syndiotactic* lactide polymerization. $\Delta H_i^{\ddagger}$ and $\Delta H_s^{\ddagger}$ represent activation energies for *isotactic* and *syndiotactic* lactide addition of ~ 71 and ~ 69 kJ/mol, respectively. ΔH_i and ΔH_s, respectively represent the change in enthalpy for the two reactions and are expected to be equal at ~ 23 kJ/mol.

syndiotactic and *isotactic* additions, respectively. [*end*] is the total concentration of end groups which is invariant with time.

The relative values of $[end_s]_t$ and $[end_i]_t$ are dependent on the relative rates for *syndiotactic* and *isotactic* addition at any given instant. The relative rates of *isotactic* vs. *syndiotactic* polymerization are,

$$\left(\frac{di}{ds}\right)_t = \frac{k_i}{k_s}\left\{\frac{[end]\cdot([lac]_t/2) - \left((k_{xi}/k_i)\cdot[end_i]_t\right)}{[end]\cdot([lac]_t/2) - \left((k_{xs}/k_s)\cdot[end_s]_t\right)}\right\} = \frac{k_i}{k_s}\cdot X(t),$$

where $X(t)$, defined by the terms in the curly brackets, is a measure of the deviation of the ratio of rates for *isotactic* and *syndiotactic* addition from the ratio of rate constants. For an irreversible polymerization, $di/ds = k_i/k_s = \text{constant}$, since $X(t) = 1.0 = \text{constant}$. From Figure 3, $k_{xi}/k_i = k_{xs}/k_s = 1/K_{eq} = \text{constant}\cdot\exp(-\Delta H_i/RT)$ since $\Delta H_i = \Delta H_s = -23$ kJ/mol. However, for a reversible polymerization with $k_i < k_s$, the concentration of *isotactic* ends is less than the concentration of *syndiotactic* ends; i.e., $[end_i]_t < [end_s]_t$. Therefore, $(di/ds)_t > k_i/k_s$, since the numerator in $X(t)$ is larger than the denominator. As the residual

lactide concentration decreases, the relative contribution from equilibrium effects increases and $X(t)$ grows larger (than 1.0), in effect reducing the preference for *syndiotactic* addition. Approaching equilibrium, the rates of *isotactic* and *syndiotactic* addition are nearly equal ($di/ds = 1$).[26] The *isisi* normalized intensity in Figure 2 represents the cumulative change in stereospecificity, and hence does not reduce to the 0.125 probability expected for a totally random polymerization.

The observed cumulative change in stereospecificity is larger than this predicted change (see Figure 2) as expected from MC calculations. This discrepancy is the result of viscosity changes during the polymerization. The increasing viscosity of the melt with increasing polymer size reduces the mobility and diffusion of the residual lactide and increases the lactide residence time at the active site. Even though these two effects of reduced diffusion rate and increased residence time counteract each other in their influence on the overall polymerization rate, they both reduce the stereospecificity in this reversible polymerization process.

^{1}H NMR can also be used to determine the D-lactide and *meso*-lactide stereoisomer impurities in PLA containing predominantly L-lactide.[22] The D-lactide and *meso*-lactide impurities lead to *–RR–* and *–R–* stereogenic defects respectively, in the mostly *–SSSSS–* PLA. The three well-resolved resonances in the ^{1}H NMR spectrum represent sequences of *isisi*, *iiisi*, and *iiiss*. The *isisi* and *iiisi* represent stereosequences of *–SSRRSS–* and *–SSSSRR–* respectively, and reflect the presence of D-lactide in the polymer. The *iiiss* represents stereosequences of *–SSSSRS–* which can only be formed by the presence of *meso*-lactide in the PLA. The correlation of the *isisi* and *iiisi* resonances with the D-lactide content in the polymer and the correlation of *iiiss* resonance with the *meso*-lactide content is shown in Figure 4. As a result of the complicated kinetics of lactide stereo copolymerization, analytical equations relating the stereosequence probabilities and the lactide stereoisomer composition of the polymer are not available.[26] Hence, MC calculations were used to simulate the kinetics of polymerization and empirical correlations were determined from their predictions of the stereosequence probabilities for a number of copolymerizations.[22] The details of this method for determining the lactide stereoisomer composition of PLA are published elsewhere.[22]

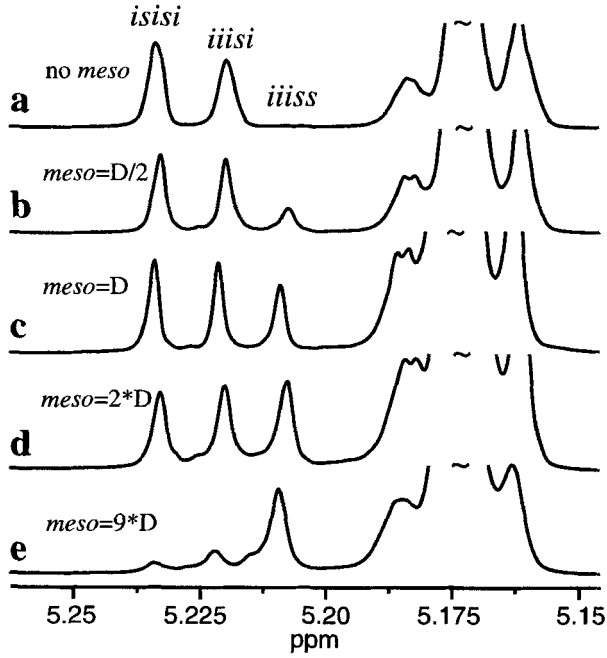


FIGURE 4 The methine region in the homonuclear decoupled ^{1}H NMR spectra of (a) 80% L + 20% D; (b) 85% L + 10% D + 5% *meso*; (c) 90% L + 5% D + 5% *meso*; (d) 85% L + 5% D + 10% *meso*; and (e) 81% L + 1% D + 18% *meso*; with the region expanded where the *isisi*, *iiisi*, and *iiiss* resonances are well-resolved. L, D, and *meso* refer to L-lactide, D-lactide, and *meso*-lactide, respectively.

CONCLUSIONS

Partial stereosequence distribution values from a few well-resolved resonances in the ^{1}H NMR spectra of poly(lactide) have been successfully used in the analysis and characterization of the polymer. From the NMR spectrum of poly(D,L-lactide) it was determined that there is a preference for *syndiotactic* addition during the reversible lactide polymerization catalyzed by Sn(II) *bis*-2-ethylhexanoate. By comparing the NMR spectra of a few partially polymerized poly(D,L-lactide) it was clear that this preference decreased with increasing extent of polymerization. Furthermore, ^{1}H NMR can also be used to determine the lactide stereoisomer composition of PLA.

Acknowledgments

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