Macromolecules **2001,** *34,* 5037−5041

A Spectroscopic Analysis of Chain Flexibility of Poly(lactic acid)

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Received November 17, 2000; Revised Manuscript Received April 23, 2001

ABSTRACT: A Raman analysis was conducted to examine the disordered structures of poly(lactic acid). Simulated spectra were obtained for an ensemble of chains generated by several rotational isomeric state models. Analysis of the differences between simulated and experimental spectra showed that the rotational isomeric state reported in earlier work leads to a chain that is much more flexible than the experimental data suggest. The Raman analysis suggests a chain dominated by tgt conformations in a 3_1 helix with a characteristic ratio of 12, consistent with other experimental data.

Introduction

Poly(lactic acid) as an environmentally friendly biodegradable polymer with the potential for large volume applications has recently attracted a great deal of attention in the polymer community. Applications include prosthetic devices and sutures,[1] as a matrix material in bioresorbable composites,[2] and in controlled release of drugs and agricultural chemicals.[3] High volume applications in food packaging are being considered since recently poly(lactic acid) is approved for this use.[4]

For poly(lactic acid), the definition of processing conditions and evaluation of ultimate achievable properties are hampered by uncertainties in the structures which develops as a function of deformations. As shown in Figure 1, poly(lactic acid) has a chiral atom in the repeat unit. Both poly(L-lactic acid) (PLLA) and the enantiomer poly(D-lactic acid) (PDLA) have been synthesized and are semicrystalline.[5] The crystalline chain conformation is generally considered to be a 10_3 helix.[6] In certain crystallization conditions a distorted 3_1 helix has been postulated.[7] Recent studies also suggest the presence of frustrated structures.[8]

Raman spectroscopy has proven to be useful for investigating the chain conformation of both crystalline and disordered chains in melt, solution, or other condensed states. Raman scattering has been used to follow the deformation behavior of poly(lactic acid)[9] and to characterize the various chain conformations[10] in the processed material. Experimental studies supported by normal-coordinate analysis have differentiated the various possible chain conformations in the crystalline state and suggested that an intermediate between the 3_1 and 10_3 helix structures exists in neat poly(L-lactic acid).[11]

To evaluate the efficiency of mechanical deformation and thermal annealing to produce films or fibers with desired properties, it is necessary to characterize the initial amorphous state.[9] Raman spectroscopy is a useful technique for this work[12] and, by comparison with synthetic spectra computed using Snyder's ensemble-based approach,[13] facilitates studies of polymer structures lacking in long-range order.[14] Recent work in these laboratories analyzed features that are associated with ensembles numbering 2000−5000 of different but relatively probable chain conformations generated using the conformational probabilities based on a postulated rotational isomeric states model.

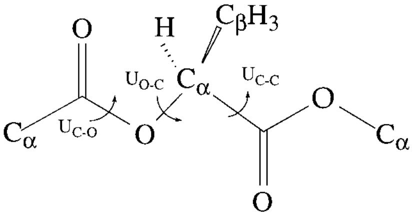

Figure 1. Schematic drawing of poly(L-lactic acid) structure.

The rotational isomeric states governing the chain conformation distribution of poly(lactic acid) are not well-defined. Assuming a planar ester group, Brant developed a rotational isomeric state model to analyze the poly(lactic acid) chain conformation.[15] Based on the Brant model, a low characteristic ratio of 4.5 was estimated for poly(L-lactic acid) when the characteristic ratio is defined as $\langle r^2 \rangle_0 / x(l_{CC}^2 + l_{CO}^2 + l_{OC}^2)$. Here $\langle r^2 \rangle_0$ is the mean-square end-to-end distance, x is the degree of polymerization, and the term in parentheses is the sum of the squares of the lengths of the three covalent bonds contributed to the chain contour by each repeat unit. This result was consistent with light scattering and intrinsic viscosity measurements at 85 °C in bromobenzene solutions and would imply that poly(L-lactic acid) is extremely flexible, since even polyethylene has a characteristic value of $C_\infty = 7$.[16] The brittle nature of both poly(L-lactic acid) and poly(D-lactic acid) seems inconsistent with a polymer possessing such a flexible backbone.[17−19] More recent light scattering measurements of poly(L-lactic acid) in acetonitrile solution suggest a much higher characteristic value of 11.8.[17]

In the previous study, structural parameters and force fields transferred from other polyesters were used to

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10.1021/ma001969a CCC: $20.00

simulate vibrational spectra of crystalline poly(lactic acid).[11] Once intensity parameters were included, it was possible to reproduce experimental data accurately. This analysis strongly suggested that some of the chain conformations described in the literature are inconsistent with the experimental data.[11] It was also shown that only one of the four 3_1 helical structures predicted by conformational analysis has a synthetic spectrum that agrees well with experiment. The analysis provided a new understanding of the relative probability of occurrence of a 10_3 or 3_1 helix for poly(lactic acid). By convoluting the synthetic spectrum expected for an ensemble of chains calculated for various rotational isomeric states models, it is possible to assess the applicability of each model. Specific conformationally sensitive spectroscopic features of the backbone bond stretching vibrations located in the range 1000−200 cm^{-1} indicate that improvement in the rotational isomeric states model is needed. In the present study, it is found that poly(lactic acid) chains are not flexible as previous studies suggest. The probabilities of finding various conformers need to be reevaluated.

Experimental Section

Poly(lactic acid) pellets of molecular weight 85 000−100 000 with less than 1% D impurity were purchased from Aldrich. A transparent and isotropic film sample with 1.4% D impurity was provided by the Cargill-Dow Co. Based on the Δ*H* of 93 J/g,[20] the DSC scan revealed a very low degree of crystallinity (2%). Highly crystalline samples (73%) were obtained by dissolving the polymer in *p*-xylene at 130 °C and growing crystals in 0.05% solution at 80 °C. The melting temperature was determined to be 168 °C. After filtration, the translucent layered single-crystal mat was annealed at 130 °C for 24 h and dried for 3 days in a vacuum oven at room temperature. No degradation of polymer was observed after annealing. The conditions employed did not lead to degradation.[21] In addition, consistent with previous studies, we did not observe any evidence of structural transformation at room temperature.[22]

Raman spectra were obtained using a Bruker Fourier transform Raman spectrometer (model FRA 106) excited by the 1.064 μm line of a Nd:YAG laser operated to deliver 200 mW at the sample. The resolution was 4 cm^{-1}, and 256 scans were collected in backscattering geometry. Polarized Raman spectra were obtained by installing a polarization analyzer followed by a scrambler in the path of the scattered beam with the sample facing the incident beam. The polarized component was obtained by setting the analyzer polarization parallel to the polarization direction of the incident beam while the depolarized component was obtained by setting the analyzer perpendicular to that direction. Isotropic Raman spectra were calculated from eq 1:

$$I_{\mathrm{iso}} = I_{\parallel} - \frac{4}{3}I_{\perp} \qquad (1)$$

The Raman spectrum of a highly crystalline sample is shown in Figure 2. Isotropic Raman spectra for the film sample are shown in Figure 3.

Normal-Coordinate Analysis

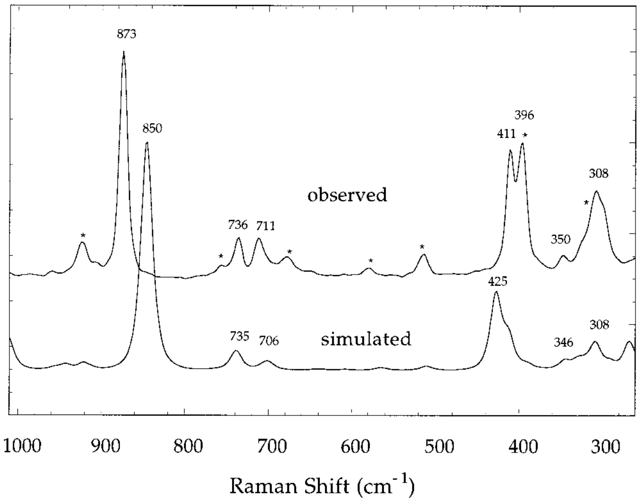

Figure 2. Simulated isotropic Raman spectrum of poly(L-lactic acid) 3_1 helix compared with observed Raman spectrum obtained from crystalline poly(L-lactic acid). Only amodes are simulated E modes.

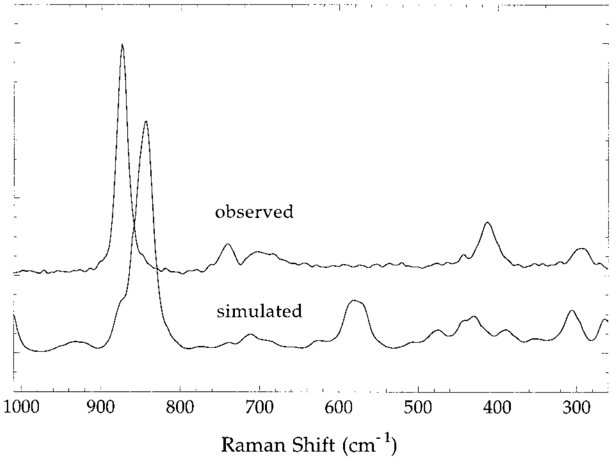

Figure 3. Simulated and observed isotropic Raman spectrum of disordered poly(L-lactic acid). Chain statistics are based on ref 15 (see text).

The molecular structures (bond lengths, bond and torsion angles) used in our studies were transferred from previous structural analysis. Since only limited studies have been conducted that characterize the interaction energies, the force constants used in this work are transferred from past polyester studies.[23,24] The transferred force field gave frequencies and relative intensities that compared surprisingly well with the observed values.[11] Two types of vibrational analyses, one for specific chain conformations associated with the crystalline phase and one for disordered structures, were carried out. For ordered structures of well-defined chain conformation, the normal-coordinate analysis performed by using Wilson's GF matrix method was adapted from computer programs first developed at University of Michigan and UC Berkeley.[25] In these modified programs, band intensities can be simulated using polarizability changes associated with backbone bond stretching and valence angle bending coordinates.[14]

The computational algorithm used for analyzing disordered chains was adapted from the program first developed by Snyder to analyze disordered structures of polyolefins.[26,27] The isotropic Raman spectrum of polymers in the disordered state is the weighted sum of spectra calculated for an ensemble of individual chains according to their occurrence probability, derived from a postulated rotational isomeric states (RIS) model.

Three skeletal bonds occur along the molecular chain in poly(lactic acid): C−O(ester), O−C, and C−C. The C−O(ester) bond is assumed to be always trans due to conjugation with the C=O double bond.[6] The O−C bond has two energy minima around −160° and −48°, and the C−C bond has two energy minima around 160° and −73°.[15] Since ±160° is close to 180°, the 160° angles are termed trans (t). In the same way, −48° and −73° are close to −60° and are termed gauche (g^+). The rotational isomeric states model can then be expressed as statistical weight matrices with two states.[28]

$$U_{C-O} = \begin{array}{ccc} & t & g^+ \\ t & 1 & 0 \\ g^+ & 1 & 0 \end{array} \qquad U_{O-C} = \begin{array}{ccc} & t & g^+ \\ t & 1 & 1 \\ g^+ & 0 & 0 \end{array}$$

$$U_{C-C} = \begin{array}{ccc} & t & g^+ \\ t & \sigma_{tt} & \sigma_{tg} \\ g^+ & \sigma_{gt} & \sigma_{gg} \end{array}$$

The t and g^+ at top of the matrices refer to the conformation states of the present bond being considered while those at left side are for the previous bonds according to Flory's standard notation.[16]

For a chain with n repeat units, the partition function Z can be calculated by[16]

$$Z = [1 \quad 0][U_{C-O}U_{O-C}U_{C-C}]^n \begin{bmatrix} 1 \\ 1 \end{bmatrix} \tag{2}$$

Hence, the probability of a given chain conformation with m bonds is

$$p_{\{\phi\}} = Z^{-1}\prod_{i=2}^{m-1}\sigma_{\zeta\eta,i} \tag{3}$$

where $\sigma_{\zeta\eta,i}$ is the statistical weight matrix element for bond i whose present state is η and its preceding bond is in state ζ. Here, the η and ζ only take values t and g^+. In Brant's rotational isomeric states model, $\sigma_{tt} = 0.042$, $\sigma_{tg} = 0.040$, $\sigma_{gt} = 0.550$, and $\sigma_{gg} = 0.368$ for a C−C bond which gives rise to four minimum energy states: III′(tt), I′(tg), III(gt), and I(gg).[15]

When additivity in bond polarizability is assumed, only a few parameters are needed to calculate the isotropic Raman scattering intensities below ~1000 cm^{-1}.[26,27] We have adopted this procedure and extended this type of analysis to other polymers with nonequivalent atoms along the backbone.[29−31] It was found that reasonable values (as compared to experimental data) for the relative polarizability tensor elements are 1.0, 1.0, 0.5, 0.2, 0.1, 0.2, 0.01, 0.01, 0.02, 0.6, and 0.3 for C−O, C−C$_\alpha$, O−C$_\alpha$, O−C$_\alpha$−C, O−C−C$_\alpha$, C−O−C$_\alpha$, O−C$_\alpha$−C$_\beta$, C−C$_\alpha$−C$_\beta$, C$_\alpha$−C=O, and C$_\alpha$−C$_\beta$, C=O, respectively.

A linear octomer of L-lactic acid units was used in the present study as the model compound. To remove end effects, only the bands from the middle six repeats were used. The band shape function used was a mixture of Lorentzian and Gaussian functions in a ratio of 9 to 1, and the bandwidth was fixed at 8 cm^{-1}. An ensemble of 2000 chains was generated.

Results and Discussion

If the chain conformation is fixed, the isotropic Raman spectrum can be simulated accurately for ordered structures associated with the crystalline phase. Figure 2 shows a comparison of the observed spectra to the one simulated for a 3_1 helix. Evidently, the calculated and observed 873, 700, 400, and 300 cm^{-1} bands all agree well, which indicates that the structural and intensity parameters and the force constants used in the analysis are all acceptable. A comparison of observed and simulated isotropic Raman spectra for a disordered structure based on earlier rotational isomeric states model is shown in Figure 3. It was shown in an earlier work that the skeletal band at 410 cm^{-1} is important for structural characterization.[11] However, the simulated features do not agree well with the experimental data of disordered structure in either intensity or shape (Figure 3). On the other hand, an intense band appears around 570 cm^{-1}, which is not observed in experiment. Given the fact that we have reproduced the poly(L-lactic acid) crystalline features accurately, this lack of agreement for the amorphous structure is the first clue that the model used to deduce conformational distribution may not be correct. To fit the simulated disordered spectra to experimental data, some modification of the chain statistical weight matrices appears to be needed.

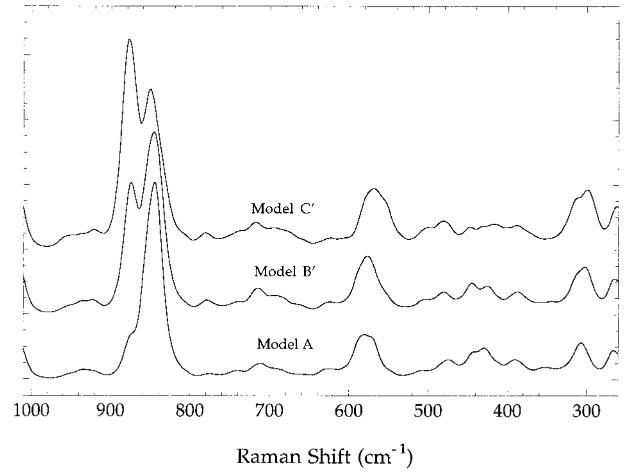

Figure 4. Simulated isotropic Raman spectra obtained by varying the relative ratio of unfavorable conformation I′ and III′ to favorable conformation I and III: model A (Brant's model), R = 1:9; model B′, R = 3:7; model C′, R = 5:5.

Table 1. Statistical Weight Matrix Elements for Skeletal C−C Bond Corresponding to Different Ratios of Unfavorable to Favorable States

	ratio	σ_{tt}	σ_{tg}	σ_{gt}	σ_{gg}
model A (Brant)	1:9	0.05	0.05	0.54	0.36
model B′	3:7	0.15	0.15	0.42	0.28
model C′	5:5	0.25	0.25	0.30	0.20

According to proposed model,[15] the states I′(tg) and III′(tt) are unfavorable conformations while states I(gg) and III(gt) are favorable ones. Thus, the first approach is to change the relative ratio of unfavorable to favorable states but keep the other ratios the same. The statistical weight matrix elements used are listed in Table 1 and the three simulated spectra shown in Figure 4. It can be seen that the situation is worsened by increasing the ratio of unfavorable states I′(tg) and III′(tt) since the desired band at 410 cm^{-1} decreases while the undesired band 570 cm^{-1} increases in intensity and the strongest band at 870 cm^{-1} splits unexpectedly.

A second approach is to change the relative ratio of two favorable states I(gg) and III(gt) while fixing the ratio of unfavorable to favorable states. The corresponding statistical weight matrix elements are listed in Table 2, and the simulated spectra are shown in Figure 5. It can be seen that the agreement between the simulated spectra and experiment improves consistently by decreasing this ratio.

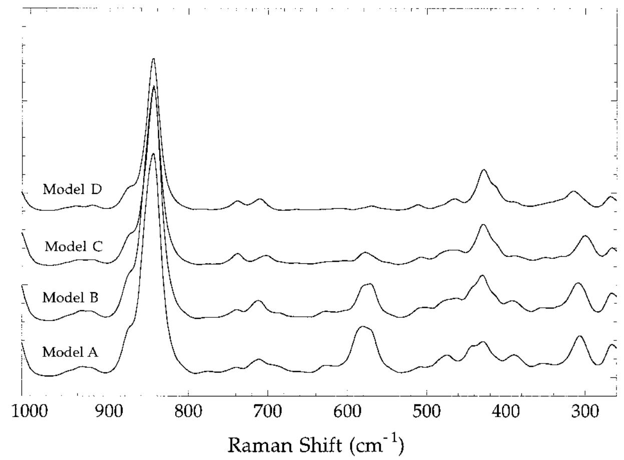

Figure 5. Simulated isotropic Raman spectra obtained by varying the relative ratio of two favorable conformations I and III: model A (Brandt's model), $R = 4{:}6$; model B, $R = 3{:}7$; model C, $R = 2{:}8$; model D, $R = 1{:}9$.

Table 2. Statistical Weight Matrix Elements for Skeletal C−C Bond Corresponding to Different Ratios of Two Favorable States I(gg) and III(gt)

	ratio (gg to gt)	σ_{tt}	σ_{tg}	σ_{gt}	σ_{gg}	$E_I - E_{III}$ (kcal/mol)
model A (Brant)	4:6	0.05	0.05	0.54	0.36	0.083
model B	3:7	0.05	0.05	0.63	0.27	0.264
model C	2:8	0.05	0.05	0.72	0.18	0.667
model D	1:9	0.05	0.05	0.81	0.09	1.148

On the basis of this result, we would conclude that a distribution containing 70% of conformation III(gt) would be appropriate in describing the amorphous state. The conformation I(gg) should be less than 20%. The other two chain conformations I′(tg) and III′(tt) are approximately 5% each. The conformational energy differences between state I(gg) and III(gt) can be obtained from the relative probabilities.[15]

$$w_I/w_{III} = A \exp[-(E_I - E_{III})/RT] \qquad (4)$$

where w_I and w_{III} are the statistical weight matrix elements σ_{gg} and σ_{gt}. The preexponential factor A is a constant that reflects the relative population degeneracies of these domains and is independent of temperature. Here, A is equal to 0.77. The energy difference between these two states can be calculated on the basis of eq 4. The results are listed in Table 2.

Simulated spectra based on models C and D are quite close to experimental data. The $\Delta E = E_I - E_{III}$ values are calculated to be 0.667 kcal/mol for model C and 1.148 kcal/mol for model D. Using the relative energies found empirically in our simulation experiments. The characteristic values for different model chains can be calculated using a program previously published.[32] The value of ΔE's requires the characteristic ratio[15] to fall into the range 7−12, which is very close to the values postulated in more recent publications.[18,33,34] Apparently, the poly(L-lactic acid) chain is much stiffer than the original model suggested. It should be noted that the original study revealed that incorporation of electrostatic interactions can potentially significantly change the chain dimension.[15]

It is necessary then to consider the reason for the substantial difference between the relative probability of the various rotational isomeric states deduced from light scattering results and Raman analysis. The light scattering results are based on the chain dimension of dilute solutions. In contrast, our Raman analysis is based on samples quenched from the molten phase. The conformational distribution of a polymer, even in a Θ-solution, is not always the same as that in the bulk. It has been reported previously that the chain dimensional changes measured using small-angle neutron scattering for bulk polyethylene are consistent with the data from a Θ-solution of polyethylene, but small-angle neutron scattering data for atactic bulk polypropylene is quite different from that from a Θ-solution.[35] In an earlier publication,[29] Raman analysis showed that poly(ethylene oxide) conformational distribution in Θ-solution differs from the distribution in its molten state. The results in the current study raise the same question. Poly(L-lactic acid) conformational distributions may be quite different in different solvents. The low value of $C_\infty = 2.0$ measured in C_6H_5Br and the high value of $C_\infty = 11.8$ in acetonitrile may be special cases. In the present study, evidence is provided that in the bulk poly(L-lactic acid) the chain is stiff with $C_\infty = 7{-}12$.

Acknowledgment. The financial support of Cargill-Dow and Materials Research Science and Engineering Center is greatly appreciated. X.Y. thanks the Chinese Natural Science Foundation and Special funds for Major State Basic Research Project (G1999064800).

References and Notes

(1) Kulkarni, R. K.; Moore, E. G.; Hegyeli, A. F.; Leonard, F. J. *J. Biomed. Mater. Res.* **1971**, *5*, 169.
(2) St. John, K. R. *Biocompatible Polymers, Metals, and Composites*; Technomic Publishing Co.: Lancaster, PA, 1983; p 861.
(3) Wood, D. A. *Int. J. Pharm.* **1980**, *7*, 1.
(4) Sinclair, R. G. *Pure Appl. Chem.* **1996**, *A33*, 585.
(5) Kleine, J.; Kleine, H. H. *Makromol. Chem.* **1959**, *30*, 23.
(6) De Santis, P.; Kovacs, A. J. *Biopolymers* **1968**, *6*, 299.
(7) Brizzolara, D.; Cantow, H.-J.; Diederichs, K.; Keller, E.; Domb, A. J. *Macromolecules* **1996**, *29*, 191.
(8) Lotz, B.; Cartier, L.; Okihara, T.; Puiggali, J. *Polym. Mater. Sci. Eng.* **1999**, *218*, 228.
(9) Smith, P. B.; Leugers, A.; Kang, S.; Yang, X.; Hsu, S. L. *J. Appl. Polym. Sci.*, in press.
(10) Kister, G.; Cassanas, G.; Vert, M. *Polymer* **1998**, *39*, 267.
(11) Kang, S.; Yang, X.; Hsu, S. L.; Stidham, H.; Smith, P. B.; Leugers, A. *Macromolecules*, in press.
(12) Hahn, T. D. Ph D. Thesis, University of Massachusetts, 1998.
(13) Snyder, R. G. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1823.
(14) Hahn, T.; Suen, W.; Kang, S.; Hsu, S. L.; Stidham, H. D.; Siedle, A. R. *Polymer*, in press.
(15) Brant, D. A.; Tonelli, A. E.; Flory, P. J. *Macromolecules* **1969**, *2*, 228.
(16) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience Publishers: New York, 1969.
(17) Joziasse, C. A.; Veenstra, H.; Grijpma, D. W.; Pennings, A. J. *Macromol. Chem. Phys.* **1996**, *197*, 2219.
(18) Grijpma, D. W.; Penning, J. P.; Pennings, A. J. *Colloid Polym. Sci.* **1994**, *272*, 1068.
(19) Wu, S. *Polym. Int.* **1992**, *29*, 229.
(20) Fisher, E. W.; Sterzel, H. J.; Wegner, G. *Kolloid Z. Z. Polym.* **1973**, *251*, 980.
(21) Jamshidi, K.; Hyon, S.-H.; Ikada, Y. *Polymer* **1988**, *29*, 2229.
(22) Cai, H.; Dave, V.; Gross, R. A.; McCarthy, S. P. *J. Polym. Sci, Part B*: *Polym. Phys.* **1996**, *34*, 2701.
(23) Boerio, F. J.; Bahl, S. K. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1029.
(24) Bahl, S. K. Ph.D Dissertation, University of Cincinnati, 1974.
(25) Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular Vibrations*: *The Theory of Infrared and Raman Vibrational Spectra*; Dover Publications: New York, 1955.

(26) Cates, D. A.; Strauss, H. L.; Snyder, R. G. *J. Phys. Chem.* **1994**, *98*, 4482.

(27) Hallmark, V. M.; Bohan, S. P.; Strauss, H. L.; Snyder, R. G. *Macromolecules* **1991**, *24*, 4025.

(28) Tonelli, A. E. *Macromolecules* **1992**, *25*, 3581.

(29) Yang, X.; Su, Z.; Wu, D.; Hsu, S. L.; Stidham, H. D. *Macromolecules* **1997**, *30*, 3796.

(30) Hsu, S. L. In *Raman Scattering in Materials Science*; Weber, W. H., Merlin, R., Eds.; Springer: Heidelberg, Germany, 2000.

(31) Tao, H. J.; MacKnight, W. J.; Gagnon, K. D.; Lenz, R. W.; Hsu, S. L. *Macromolecules* **1995**, *28*, 2016.

(32) Mattice, W. L.; Suter, U. W. *Conformational Theory of Large Molecules. The Rotational Isomeric State Model in Macromolecular Systems*; John Wiley and Sons: New York, 1994; p 449.

(33) Dorgan, J. R.; Williams, J. S.; Lewis, D. N. *J. Rheol.* **1999**, *43*, 1141.

(34) Cooper-White, J. J.; Mackay, M. E. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 1803.

(35) Fetters, L. J.; Thomas, E. L. *Structure and Properties of Polymer*; VCH Publishers: New York, 1993; Vol. 12, p 22.

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