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Melt Chain Dimensions of Polylactide

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ABSTRACT: Melt chain dimensions of two polylactide samples were measured using small-angle neutron scattering. Three polylactides were synthesized: a deuterated polylactide containing 26% R-stereocenters (d-PLA-26), a hydrogenous polylactide with an R-content similar to the deuterated polylactide (PLA-28), and a hydrogenous polylactide that contained no R-stereocenters (PLA-0). The hydrogenous polylactides were each solution blended with the d-PLA-26 at a volume fraction of 0.2 for the deuterated polymer, and the melt chain dimensions of these polymers were determined. Small-angle neutron scattering experiments were performed at 30 °C for the d-PLA-26/PLA-28 blend and at 200 °C for both the d-PLA-26/PLA-28 and d-PLA-26/PLA-0 blends. Using three analysis methods, the average values for the statistical segment lengths, based on a C_6 repeat unit, were found to be 10.0 ± 0.2 Å for the PLA-28 at 30 °C, 8.9 ± 0.2 Å for the PLA-28 at 200 °C, and 9.9 ± 0.4 Å for the PLA-0 at 200 °C.

Introduction

Polylactide is arguably the most important plastic derived from renewable resources given its omnipresent status in the biomedical field[1] and recent commercial production as a commodity material.[2] The foundation of current and future applications of polylactide will depend strongly on the use of reliable physical and chemical property data. As such, the determination of inherent material properties of polylactide has been and will continue to be an imperative endeavor. Of these characteristics, the unperturbed dimensions of a polymer chain in the melt are certainly one of the most fundamental properties of any macromolecule.[3] In addition to rheological properties relevant for polymer processing and product manufacturing, the chain dimensions are intimately tied to mechanical properties such as toughness, impact resistance, and tensile strength.[4] Furthermore, differences in chain dimensions have been implicated in polymer−polymer miscibility,[5,6] are important for the self-assembly of conformationally asymmetric block copolymers,[7,8] and play an important role in interfacial adhesion and polymer welding.[9,10] Many studies aimed at the careful determination of the unperturbed polylactide chain dimensions have appeared.[11−13] However, these literature values are not in agreement. In examination of this literature, we realized that the determination of the melt chain dimensions for polylactide by small-angle neutron scattering analysis of H/D isotopic blends, debatably the most direct measurement of melt chain dimensions, had not been carried out. In this study we report the unperturbed chain dimensions of polylactide in the melt using small-angle neutron scattering.

Experimental Section

Materials. L-Lactic-*3,3,3-d*$_3$ acid (methyl deuterated) was obtained from Isotec as an 85% aqueous solution with a minimum D atom content of 98% according to the manufacturer. L-Lactide (Aldrich), DL-lactide (Aldrich), and deuterated lactide (prepared as described below) were recrystallized from ethyl acetate and subsequently dried in a vacuum oven at room temperature for 48 h. Diethylaluminum ethoxide (Et_2AlOEt) (Aldrich, 1.6 M solution in toluene) and tin(II) 2-ethylhexanoate (Aldrich) were used as received. Toluene used for the ring-opening polymerization of lactide was purified by passage through an activated alumina column and a supported copper catalyst on a home-built system.[14] All other solvents were used without further purification.

Synthesis of d_6-Lactide (Deuterated Lactide). L-Lactic-*3,3,3-d*$_3$ acid (6.22 g, 0.0668 mol) was heated to 175 °C under nitrogen for 24 h, giving low molecular weight polylactic acid (3.20 g). Tin(II) 2-ethylhexanoate (0.098 g, 0.242 mmol) was then added to the flask, and the low molecular weight polylactic acid was heated to 230 °C under reduced pressure (50 Torr). The pressure was lowered to 12 Torr over a period of 1 h, during which time d_6-lactide was distilled into a collection flask (2.65 g, 83% yield). The crude d_6-lactide was purified by recrystallization in ethyl acetate. After three successive recrystallizations, the d_6-lactide crystals were collected and dried in the vacuum oven at room temperature for 48 h (0.985 g, 31% purified yield). The synthesized d_6-lactide was found to contain 26% of the R-stereocenters from both D-lactide and *meso*-lactide based on polarimetry (see the equipment/general procedures section for further details on the polarimetry measurements). The fact that pure d_6-L-lactide (S,S) was not obtained from the deuterated L-lactic acid was surprising, since pure hydrogenous L-lactide (S,S) was obtained when the above procedure was performed with hydrogenous L-lactic acid. The reason for the significant amount of R-stereocenters in the d_6-lactide is not known, but epimerization of the S-stereocenter during ring closure (at high temperature) is the most likely cause.

Synthesis of Polylactide. The following is a general procedure for the synthesis of polylactide with a targeted molecular weight of 60 kg mol^{-1} (assuming 60% conversion of lactide). In a glovebox, a Teflon-coated stir bar, 2.0 g of lactide (0.013 88 mol), 14 mL of toluene, and 12.5 μL of Et_2AlOEt (1.6 M in toluene, 0.02 mmol) were placed into a 38 mL Chemglass high-pressure vessel. The mixture was stirred in an oil bath at 80 °C for ∼ 24 h. Acetic anhydride (3 mL) was then added to the reaction vessel to end-cap the polylactide. The high-pressure vessel was placed back in the 80 °C oil bath for 24 h. The polylactide was then precipitated into methanol and dried in a vacuum oven for 48 h at 65 °C (1.4 g, 68% conversion of lactide). The deuterated polymer (d-PLA) and hydrogenous polymers with varying amounts of R-stereocenters were synthesized using this method. The end-capping of the polymers was verified using ^{1}H NMR spectroscopy, and the percentage of the R-stereocenters in the polymers was determined using polarimetry. The molecular characteristics of the polylactides

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Table 1. Characterization of Polylactide Homopolymers

polymer	$M_n{}^a$ (kg mol^{-1})	PDI^a	$M_n{}^b$ (kg mol^{-1})	$M_w/M_n{}^b$	% R^c
PLA-0	57.8	1.20	34.8	1.08	0
PLA-28	56.2	1.24	44.0	1.15	28
d-PLA-26	70.4	1.30	48.6	1.31	26

[a] Determined by SEC vs polystyrene standards (RI detector). [b] Determined by SEC with multiangle light scattering detection. See Supporting Information for SEC chromatographs. [c] Determined by polarimetry.

are given in Table 1. (The nomenclature that will be used in this study for referring to the polylactides is PLA-*x*, where *x* is the percentage of R-stereocenters in the polymer.) The polydispersity of d-PLA-26 is slightly higher than either of the hydrogenous polymers. The reason for the broadening of the polydispersity is unknown but is likely due to the slightly higher conversion of monomer for the d-PLA-26 polymer. The well-controlled nature of this type of polymerization has been demonstrated with narrow polydispersities being obtained at low conversions while broadening occurs as the conversion increases.[15] Decoupled ^{1}H NMR spectroscopy was also performed in order to examine the stereosequence distribution in the hydrogenous polymers.[16] Using this technique, the stereosequence distribution of the hydrogenous PLA-28 was found to be similar to that of the d-PLA-26.

Equipment and General Procedures. The molecular weights and the molecular weight distributions of the polymers were determined on a Hewlett-Packard 1100 series liquid chromatograph equipped with a Hewlett-Packard 1047A refractive index detector and three Jordi poly(divinylbenzene) columns with 10^4, 10^3, and 500 Å pore sizes. The mobile phase was tetrahydrofuran (40 °C and 1 mL min^{-1}). The columns were calibrated using polystyrene standards from Polymer Laboratories. In addition, SEC analysis was done using a liquid chromatograph equipped with three Phenomenex Phenogel columns with pore sizes of 10^5, 10^4, and 10^3 Å and a Wyatt DAWN multiangle light scattering detector. The eluent was tetrahydrofuran, and the d*n*/d*c* for polylactide in THF was found to be 0.0576.[17]

The ^{1}H NMR spectra were recorded using $CDCl_3$ on an INOVA 500 MHz NMR spectrometer. The following ^{1}H NMR resonances are representative of the polylactide synthesized in this study: 5.1 (m, $-C(O)-C(\mathbf{H})(CH_3)-O-$), 1.6 (m, $-C(O)-C(H)(C\mathbf{H}_3)-O-$), 4.2 (q, $CH_3-C\mathbf{H}_2-O-$), 2.1 (s, $-O-C(O)-C\mathbf{H}_3$). For the d-PLA-26 there was a small resonance at 1.6 ppm due to a small amount (7 mol %) of nondeuterated methyl groups. The amount of nondeuterated material found in the d-PLA-26 is inconsistent with the manufacturers' claim of 98% D atom content in the deuterated lactic acid. The reason for this is unknown. The homonuclear decoupled ^{1}H NMR spectra of the hydrogenous polylactides were obtained by decoupling using the methyl resonance at 1.57 ppm. The molecular weights of the polylactides were also determined from the ^{1}H NMR spectra (PLA-0 = 55.3 kg/mol; PLA-28 = 69.3 kg/mol; d-PLA-26 = 79.7 kg/mol); however, this analysis gave anomalously high values for the molecular weights when compared to the absolute molecular weights determined by SEC with the multiangle light scattering detector given in Table 1. These large molecular weight values are believed to be due to the significant error associated with the integration of the end-group peak owing to its low concentration in the sample.

Specific optical rotation measurements, [α], were determined for the lactide and polylactide samples using a Jasco DIP-370 digital polarimeter with a Na lamp at a wavelength of 589 nm. Solutions of 10 mg/mL in chloroform were analyzed at room temperature in a 100 mm cell. The optical purity (OP) was determined using eq 1:

$$\mathrm{OP} = \frac{[\alpha]}{[\alpha]_0} \times 100 \tag{1}$$

where [α] and $[\alpha]_0$ are the optical rotations of the sample and an optically pure sample, respectively. The optically pure sample was taken to be either the L-lactide obtained from Aldrich or the PLLA that was synthesized from L-lactide, which was found to contain no stereodefects based on methine decoupled ^{1}H NMR spectroscopy. The percentage of the R-enantiomer in the lactide or polylactide was then determined from

$$\%\,\{\mathrm{R}\} = \frac{100 - \mathrm{OP}}{2} \tag{2}$$

Neutron Scattering Measurements. To prepare the small-angle neutron scattering samples, each of the hydrogenous polymers was codissolved with the d-PLA-26 in chloroform (5 wt % solution). The blends were then precipitated into methanol and dried in a vacuum oven at 65 °C for 24 h. All blends were prepared with a volume fraction of d-PLA-26 of 0.2 (verified by ^{1}H NMR spectroscopy). The polymer blends were then pressed into aluminum disks (1 mm × 16 mm i.d.) using a hot press at 200 °C. The samples were kept under pressure at 200 °C for 5 min after which they were quenched to ca. 30 °C using circulating water over a period of 3 min. (Some of the polymer blends needed to be pressed several times before a bubble-free sample was obtained; however, the molecular weights of all of the polymer blends were determined by SEC with refractive index detector after pressing, and no obvious degradation was evident.) The pressed samples contained in the aluminum disks were then sandwiched between quartz disks and sealed using a high-temperature silicone sealant. Blank samples containing only hydrogenous PLA-28 and d-PLA-26 were also prepared for incoherent scattering measurements (see Supporting Information).

The neutron scattering experiments were performed on the NIST/Exxon/ University of Minnesota 30 m SANS instrument at NIST in Gaithersburg, MD. A wavelength of 6 Å was used with a sample-to-detector distance of 7 m, which gave a *q* range of $0.006 < q = 4\pi\lambda^{-1}\sin(\Theta/2) < 0.10$ Å^{-1} where Θ is the scattering angle. Data were collected at 30 °C for the as-prepared (pressed) amorphous blend and at 200 °C for both polymer blends. Sample transmissions were measured for both blends at 30 °C. In addition, data were corrected for background radiation (blocked beam and empty cell scattering), sample thickness, detector sensitivity, and incoherent scattering. The data were then converted to an absolute scale based on the open beam intensity. Excess scattering was observed at $q < 0.01$ Å^{-1} for all of the polymer blends as well as the incoherent blank samples. Although we have no direct evidence, we believe this is due to foreign matter or voids in the samples. Therefore, all data below $q = 0.01$ Å^{-1} were discarded when performing analysis of the scattering data. This type of excess scattering has been reported in the literature previously, resulting in similar treatment to the low *q* data.[18,19]

Results

We prepared deuterated polylactide by first synthesizing deuterated lactide from *S*-d_3-lactic acid (deuterated in the methyl position). Formation of the d_6-lactide led to some epimerization of the chiral centers; thus, the deuterated lactide obtained contained appreciable amounts of R stereocenters (presumably in *R*,*S*-*meso*-lactide, *R*,*R*-D-lactide). As a result, the polylactide prepared from this stereochemically impure lactide gave an amorphous, atactic microstructure with a slight isotactic tendency, confirmed using ^{1}H NMR spectroscopy.[16] This is the only deuterated polylactide we prepared, so to make a matched hydrogenous material we polymerized a D,L mixture of hydrogenous lactide with approximately the same level of R stereocenters and overall molecular weight as the deuterated sample. By ^{1}H NMR spectroscopy, this hydrogeneous

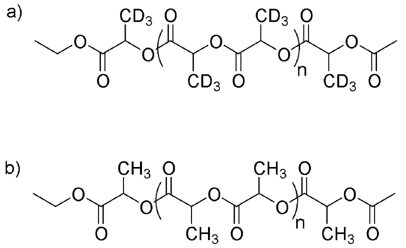

Figure 1. Chemical structures of the polymers used in this study: (a) deuterated polylactide (d-PLA-26). (b) hydrogenous polylactides (PLA-28 and PLA-0).

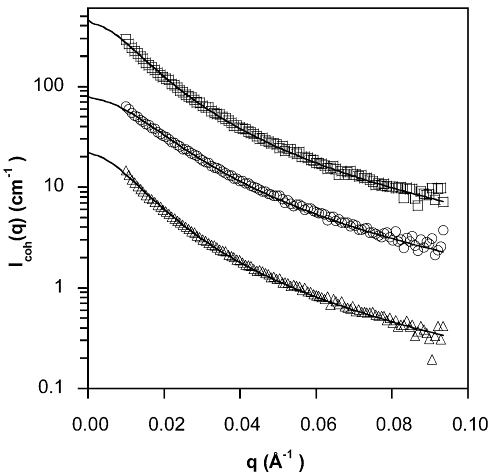

Figure 2. Nonlinear least-squares best fits of coherent scattering using eq 3 for d-PLA-26/PLA-0 at 200 °C (squares) (data shifted up by 20× for clarity), d-PLA-26/PLA-28 at 200 °C (circles) (data shifted up by 5× for clarity), and d-PLA-26/PLA-28 at 30 °C (triangles).

polymer had a similar stereosequence distribution as the deuterated polymer (see Supporting Information). In addition, we prepared a purely isotactic polylactide sample from L-lactide. To avoid transesterification reactions of the deuterated and hydrogenous polymers in the blends used for SANS, the polylactide chains were end-capped with an acetate group using acetic anhydride.[20]

Figure 1 shows the structures of both the hydrogenous and deuterated polymers used in this study, and Table 1 gives the molecular characteristics of these polymers. For the SANS experiment, the deuterated polymer (d-PLA-26) was separately blended with the hydrogenous polymer of similar stereosequence distribution (PLA-28) and the hydrogenous polymer containing no R-stereocenters (PLA-0). Both blends contained d-PLA-26 at a volume fraction of 0.2. Although the SANS scattering intensity is attenuated using such an asymmetric blend, this volume fraction was chosen in an effort to prevent macrophase separation of the H/D blends (deuterium isotope effect).[21] The blends were pressed at 200 °C and subsequently quenched. The scattering experiments on the d-PLA-26/PLA-28 amorphous polymer blend were performed at 30 and 200 °C. The d-PLA-26/PLA-0 blend was examined at 200 °C only. The molecular characteristics of the polymer blends were determined after the scattering experiment, and some degradation in the molecular weight of the polymers was noted; however, the level of degradation in these samples did not significantly impact the SANS results for these blends (see Supporting Information).

To determine the statistical segment lengths of the hydrogenous polylactides in the polymer blends, three different analysis methods were used. In the first method, the coherent small-angle scattering from the single phase polymer blend was modeled on the basis of de Gennes' random phase approximation for polydisperse components given by[19,22,23]

$$I_{\mathrm{coh}}(q) = \left(\frac{\sum_i b}{v_i} - \frac{\sum_j b}{v_j}\right)^2 S(q)$$

$$\frac{1}{S(q)} = \frac{1}{N_i \phi_i g_{pi}(x_{ni})} + \frac{1}{N_j \phi_j g_{pj}(x_{nj})} - 2\chi_{ij}$$

$$g_{pi}(x_{ni}) = \left(\frac{2}{x_{ni}}\right)^2 \left[x_{ni} - 1 + \left(1 + \frac{x_{ni}}{k_i}\right)^{-k_i}\right]$$

$$x_{ni} = q^2 R_{\mathrm{g},ni}{}^2 \qquad k_i = \left(\frac{N_{wi}}{N_{ni}} - 1\right)^{-1}$$

$$R_{\mathrm{g},ni}{}^2 = \frac{N_{ni} a^2}{6} \tag{3}$$

where $\sum_i b$ is the sum of the coherent scattering lengths per C_6 unit for the hydrogenous or deuterated polymers, v_i are the molar volumes per C_6 unit at the temperature of the experiment, ϕ_i is the volume fraction of hydrogenous or deuterated polymer, g_{pi} is the polydisperse Debye function, χ_{ij} is the Flory−Huggins interaction parameter between the hydrogenous and deuterated polymers, N_{ni} and N_{wi} are the number- and weight-average degrees of polymerization, respectively, $R_{\mathrm{g},ni}$ is the number-average radius of gyration, and a is the statistical segment length. For this anlaysis, the repeating unit molar volumes for the hydrogenous and deuterated polylactides were assumed to be equal (v = 115.5 cm^3 mol^{-1} at 30 °C; v = 130.6 cm^3 mol^{-1} at 200 °C).[24] The molecular weights determined from SEC with the multiangle light scattering detector were used when analyzing the SANS results (Table 1).

The statistical segment length of the hydrogenous polylactide in the blends was found by performing a simultaneous fit of the scattering data using the functions given in eq 3 and floating both the statistical segment length and χ (see Supporting Information for details on the fitting procedures and relevant calculations). The nonlinear least-squares regressions are shown in Figure 2. When performing the fit for the d-PLA-26/PLA-28 blend, the statistical segment lengths of the deuterated and hydrogenous polylactides were assumed to be equal given that they contain essentially the same number of R-stereocenters and consequently should have the same chain dimensions. This value of the statistical segment length was then fixed for d-PLA-26 when fitting the d-PLA-26/PLA-0 blend data, and the statistical segment length of PLA-0 and χ were floated. The statistical segment lengths determined from the fit of the data are given in Table 2.

The second analysis method makes use of the intermediate q range approximation to eq 3. In this case, the slope of $S(q)^{-1}$ vs q^2 yields the statistical segment length (see Supporting Information for details). In addition, the Flory−Huggins interaction parameter can also be determined from the y-intercept. These plots are shown in Figure 3. To calculate the statistical segment length of the hydrogenous polymers from the slope, the following relationships were used:[25]

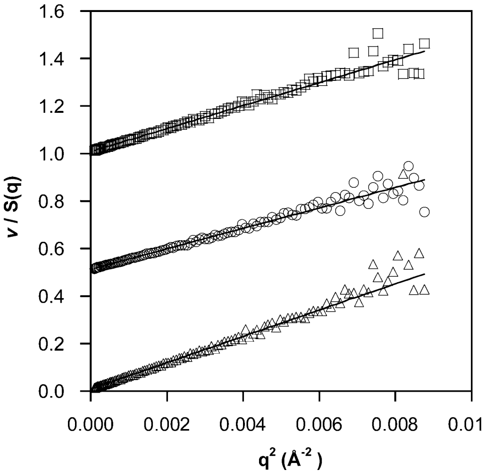

Figure 3. Plots of v/S(q) vs q^2 from scattering data for d-PLA-26/PLA-0 blend at 200 °C (squares) (data shifted up by +1.0 for clarity), d-PLA-26/PLA-28 blend at 200 °C (circles) (data shifted up by +0.5 for clarity), and d-PLA-26/PLA-28 blend at 30 °C (triangles).

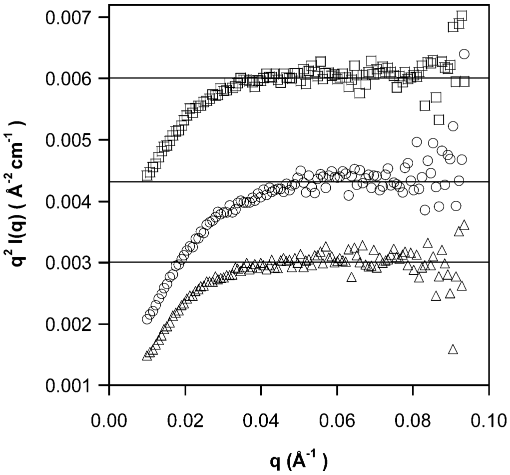

Figure 4. Kratky plots for scattering data of d-PLA-26/PLA-0 blend at 200 °C (squares) (data shifted up by +0.003 for clarity, plateau value = 0.0030), d-PLA-26/PLA-28 blend at 200 °C (circles) (data shifted up by +0.001 for clarity, plateau value = 0.0033), and d-PLA-26/PLA-28 blend at 30 °C (triangles) (plateau value = 0.0030).

$$S(q)^{-1} = \frac{1}{N_{nd}\phi_{\mathrm{d}}} + \frac{1}{N_{nh}\phi_{\mathrm{h}}} - 2\chi_{ij} + \frac{q^2a^2}{12}\frac{1}{\phi_{\mathrm{d}}\phi_{\mathrm{h}}} \qquad (4)$$

$$a^2 = \frac{{a_{\mathrm{h}}}^2}{v_{\mathrm{h}}\phi_{\mathrm{h}}} + \frac{{a_{\mathrm{d}}}^2}{v_{\mathrm{d}}\phi_{\mathrm{d}}} \qquad (5)$$

In the case of the d-PLA-26/PLA-28 blend the statistical segment lengths of the deuterated and hydrogenous polymers were assumed to be equal when performing the analysis, so the statistical segment length was calculated directly from the slope. For the d-PLA-26/PLA-0 blend, to determine the statistical segment length of the hydrogenous polymer, PLA-0, eq 5 was used. The value for the statistical segment length of the deuterated polymer, a_{d}, was taken as the statistical segment length determined for the d-PLA-26/PLA-28 blend. The statistical segment lengths of the hydrogenous polymers from this analysis method are given in Table 2.

Finally, the statistical segment lengths were determined from the Kratky plateau. In the limit that the q^2 term in eq 4 dominates, a plot of $q^2I(q)$ vs q comes to a constant value. The statistical segment length is then determined from the following relationship:[25]

$$a^2 = \frac{12\phi_{\mathrm{h}}\phi_{\mathrm{d}}\left(\frac{\sum_i b}{v_i} - \frac{\sum_j b}{v_j}\right)^2}{(q^2I(q))_{\mathrm{plateau}}} \qquad (6)$$

Kratky plots for the polylactide blends at 30 and at 200 °C are given in Figure 4 (see Supporting Information for details on Kratky plateau determination). The value for the statistical segment length of the hydrogenous polymer in the d-PLA-26/PLA-28 blend was found using eq 6, since we assumed that the statistical segment lengths of the hydrogenous and deuterated polymer were equal. The statistical segment length of the hydrogenous polylactide in the d-PLA-26/PLA-0 blend was then determined using eq 5 and the statistical segment length of d-PLA-26 from the d-PLA-26/PLA-28 blend. The statistical segment length values from this analysis are given in Table 2.

Discussion

All three analysis methods gave values for the statistical segment lengths of the hydrogenous polymers that were in agreement with each other (Table 2). For the matched H/D blend, d-PLA-26/PLA-28, the statistical segment length at 30 °C is 10.0 ± 0.2 Å and at 200 °C it is 8.9 ± 0.2 Å. For the d-PLA-26/PLA-0 blend, where the hydrogenous polymer contains no stereodefects, the statistical segment length of the PLA-0 is 9.9 ± 0.4 Å at 200 °C. In addition, the average values and standard deviations for the Flory−Huggins interaction parameter between the hydrogenous and deuterated polymer in the two different blends are given in Table 2.

The ratio of the unperturbed chain dimensions to the molecular weight was calculated for both PLA-28 and PLA-0 using the following relationship:[26]

$$\frac{\langle R^2\rangle_0}{M} = \frac{6\langle {R_{\mathrm{g}}}^2\rangle_0}{M} = \frac{a^2N}{m_0N} = \frac{a^2}{m_0} \qquad (7)$$

where m_0 is the molecular weight of the C_6 repeat unit (144.217 g/mol). These values are also given in Table 2. By directly comparing the value of $\langle R^2\rangle_0/M$ from this study to other values reported in the literature for polylactide, we see some interesting differences. A $\langle R^2\rangle_0/M$

Table 2. PLA Statistical Segment Lengths and Flory−Huggins Interaction Parameters[a]

	a (Å)				$\langle R^2\rangle_0/M$ (Å^2 mol g^{-1})	χ (10^{-3})
polymer	RPA (eq 3)	intermediate q (eq 4)	Kratky (eq 6)	average[b]	average[b]	average[b]
PLA-0 (200 °C)	10.3	9.6	9.8	9.9 ± 0.4	0.681 ± 0.050	7.1 ± 2.0
PLA-28 (30 °C)	10.2	9.8	10.1	10.0 ± 0.2	0.699 ± 0.029	5.7 ± 2.0
PLA-28 (200 °C)	9.0	8.7	9.1	8.9 ± 0.2	0.554 ± 0.026	3.7 ± 1.9

[a] Flory−Huggins interaction parameters between hydrogenous polymer and d-PLA-26. [b] ±1 standard deviation.

of 0.380 Å^2 mol g^{-1} was reported for a stereoregular poly(L-lactide) by Fetters et al.[27] based on experiments performed by Flory et al.[28] This value for $\langle R^2\rangle_0/M$ is significantly lower than the value determined for the PLA-0 at 200 °C (0.685 Å^2 mol g^{-1}). The light scattering experiments by Flory et al. were performed at 85 °C rather than 200 °C; however, on the basis of the trend for PLA-28, the $\langle R^2\rangle_0/M$ for PLA-0 should be larger at lower temperatures. The most likely reason for the large discrepancy between the values is that the experiments of Flory were done in bromobenzene, and the quality of this solvent for light scattering measurements of polylactide has been brought into question.[12] More recently, a value of 0.77 Å^2 mol g^{-1} was reported by Adachi et al. for polylactide with a D/L ratio of 1/3 (ca. PLA-25).[29] This value agrees quite well with the value determined for PLA-28 at 30 °C (0.699 Å^2 mol g^{-1}). In the case of Adachi et al., light scattering measurements were taken at room temperature, and benzene was used as the solvent, which is a good solvent for polylactide. This could account for their slightly larger chain dimensions than those that we determined in the melt.

To determine whether the value we found for the statistical segment length of polylactide was reasonable compared to other common polymers, we calculated the statistical segment lengths based on a commonly used polyolefin reference volume ($v_{\text{ref}} = (1.084 \times 10^{-22})$ exp[$6.85 \times 10^{-4}(T - 296)$], with v_{ref} in cm^3 and T in absolute temperature).[19,30] The statistical segment length of polylactide was determined by first calculating the effective repeat unit molecular weight for polylactide using the polyolefin reference volume and the density of polylactide. With this value the statistical segment length based on the polyolefin reference volume was found by means of eq 7 and the $\langle R^2\rangle_0/M$ value in Table 2. At 30 °C the statistical segment length for PLA-28 (7.6 Å)[31] is in the range of the statistical segment lengths for other common polymers (based on the previously defined polyolefin reference volume). For instance, the statistical segment length of polyethylene at 25 °C is 8.9 Å,[27] for 1,4-polybutadiene it is 7.2 Å,[3] for polystyrene it is 5.5 Å,[3,32] and for poly(cyclohexylethylene) it is 4.6 Å.[33] Furthermore, the ratio of the unperturbed chain dimensions to the molecular weight, $\langle R^2\rangle_0/M = 0.699$ Å^2 mol g^{-1}, is also intermediate when compared to the values reported for these polymers (PE = 1.42,[27] PBD = 0.876,[3] PS = 0.434,[3,32] PCHE = 0.337 Å^2 mol g^{-1} [33]).

Using the experimentally determined statistical segment length, the characteristic ratio, C_∞, of polylactide was also calculated. This parameter is of interest because it gives an indication as to the intrinsic flexibility of the polylactide chain. The characteristic ratio was determined using the following equation:[34]

$$C_\infty = \frac{\langle R^2\rangle_0}{nl^2} \tag{8}$$

where $\langle R^2\rangle_0$ is the mean-square end-to-end distance of a polymer coil and n is the number of statistical skeletal units of length l in the polymer chain. Since $n = Nn_v$, where n_v is the number of real or virtual bonds per repeat unit, and making use of relationships given in eq 7, this equation can then be reduced to

$$C_\infty = \frac{a^2}{n_v l^2} \tag{9}$$

In this analysis, we have chosen $n_v = 6$ and $l = 1.41$ Å for polylactide.[11]

For PLA-28 the average value of the characteristic ratio at 30 °C is 8.4 ± 0.3 and at 200 °C it is 6.7 ± 0.3. For PLA-0 the average value is 8.2 ± 0.6 at 200 °C. In comparison, Pennings et al. found the characteristic ratio of a polylactide containing 29 mol % D-lactide to be 9.4 at 25 °C.[11] In addition, Hsu et al. found the characteristic ratio at 25 °C to be 8.5 for a polylactide containing 20% D-stereocenters.[13] These values are in general agreement with the characteristic ratio of 8.4 determined in this study for the PLA-28 at 30 °C. To be able to compare the characteristic ratio of PLA-0 to other values found in the literature, we also estimated the temperature dependence of the unperturbed chain dimensions for PLA-28 by calculating the temperature coefficient, $\kappa = \text{d} \ln R_g^2/\text{d}T$. Using the statistical segment lengths at 30 and 200 °C, κ was found to be -0.00141 K^{-1}. If we assume that the PLA-0 has the same temperature dependence as PLA-28, the radius of gyration and hence the statistical segment length of PLA-0 at 30 °C can be determined. Using this assumption, the statistical segment length of PLA-0 at 30 °C was calculated to be 11.2 Å. From eq 9, the characteristic ratio at room temperature for PLA-0 is 10.5. In comparison, a characteristic ratio of 12.4 was reported for a PLA-0 at 25 °C by Hsu et al., and a value of 11.8 was reported by Pennings et al. Our value is significantly lower, indicating that the assumption of similar temperature dependence for PLA-28 and PLA-0 may not be valid. However, in the case of Pennings et al., rather than making a direct measurement they extrapolated to zero D content, and Hsu et al. used a solvent mixture in their light scattering experiment that may have caused a larger coil dimension than would be determined in the melt. Nevertheless, both Pennings et al. and Hsu et al. found that the characteristic ratio of polylactide decreased as the R-content increased, which is consistent with our results at 200 °C.

Finally, we used our value of the statistical segment length to reevaluate the conformational asymmetry parameter, ϵ, which we previously reported for the poly(ethylene-*alt*-propylene)-*b*-polylactide (PEP−PLA) system.[35] The conformational asymmetry parameter is calculated from the following equation:[36]

$$\epsilon = (\nu_A^{-1} a_A^{\,2}/\nu_B^{-1} a_B^{\,2}) \tag{10}$$

This parameter accounts for the differences in the molar volumes and statistical segment lengths between the two polymers. Using the characteristic ratio reported by Pennings et al.,[11] a statistical segment length was determined, and the ϵ value between PLA and PEP was calculated to be 1.39. However, on the basis of the experimentally determined morphology diagram for these block copolymers, we expected the ϵ value to be closer to 1.0, since the phase diagram appears symmetric around $f_{\text{PLA}} = 0.5$. We can now recalculate this parameter on the basis of our experimental data for the polylactide statistical segment length. Using the polyolefin reference volume previously defined and making use of κ to determine the chain dimensions of PLA-28 at 140 °C, the statistical segment length of PLA-28 is 7.0 Å and for PEP the statistical segment length is 6.8

Å.[3] From these values the conformational asymmetry parameter between PLA and PEP is now 1.06. This value is in good agreement with the symmetric phase diagram that was observed.

We also experimentally obtained the morphology diagram for PS−PLA block copolymers.[37] Polystyrene and polylactide apparently have a higher degree of asymmetry, resulting in a shift of the experimental morphology diagram from the idealized symmetric case. The statistical segment length for PLA-28 at 110 °C (using κ) is 7.1 Å, and for PS it is 5.5 Å based on the polyolefin reference volume at this temperature. From these statistical segment lengths, the asymmetry parameter is 1.67. Fortuitously, Whitmore et al. calculated what the position of the cylinder to lamellar phase boundary would be for a block copolymer with a χN value of 80 and an asymmetry parameter of 1.67.[36] They predict that the boundary will shift from 0.33 to 0.40. Experimentally, we determined that the cylinder to lamellar phase boundary in the intermediate to strong segregation limit is between 0.43 and 0.44, which is in qualitative agreement with their prediction.

Conclusions

The melt chain dimensions of two polylactide samples were investigated using small-angle neutron scattering. The statistical segment lengths were determined to be 10.0 ± 0.2 Å for PLA-28 at 30 °C, 8.9 ± 0.2 Å for PLA-28 at 200 °C, and 9.9 ± 0.4 Å for PLA-0 at 200 °C based on a C_6 repeating unit. The chain dimensions were found to decrease with both increasing temperature and increasing D content. On the basis of its statistical segment length, the characteristic ratio of PLA-28 at 30 °C was calculated to be 8.4, which is in general agreement with other values reported in the literature for polylactides with similar D contents. However, the characteristic ratio of PLA-0 at 30 °C was found to be somewhat smaller than other reported values for isotactic PLLA. Finally, we calculated the conformational asymmetry parameters for both PEP−PLA and PS−PLA block copolymer systems based on the experimentally determined chain dimensions for polylactide and found them to be in agreement with the experimentally determined morphology diagrams.

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Supporting Information Available: Size exclusion chromatographs of all polymers used, coherent scattering data, intermediate q-range analysis, Kratky plateau determination, effect of sample degradation on data analysis, and comparison of stereosequence distribution in polylactide. This material is available free of charge via the Internet at http://pubs.acs.org.

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