

Intrinsic Viscosity and Unperturbed Dimension of Poly(DL-lactic acid) Solution

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Abstract: The intrinsic viscosities were determined for poly(DL-lactic acid) (PDLLA) solutions in 1,2-dialkyl phthalate at temperatures ranging from 30 to 60 °C. A series of dialkyl phthalate, in which the alkyl group was changed from methyl to propyl, was used as the solvent to control the solvent quality systematically. The intrinsic viscosity of the PDLLA solution was higher in the better quality solvent, with a higher molecular weight of PDLLA, and at lower temperatures. The unperturbed dimensions of the PDLLA molecule and polymer-solvent interaction parameter of PDLLA in dialkyl phthalate were deduced using extrapolation methods based on the temperature-dependent intrinsic viscosities. Slight shrinkage in the unperturbed chain dimension was observed, which resulted from a change in polymer conformation with temperature. It was also observed that the polymer-solvent interaction became more favorable with the dialkyl phthalate containing a shorter alkyl chain.

Keywords: poly(lactic acid), polymer solution, intrinsic viscosity, unperturbed dimension.

Introduction

Investigation of viscoelastic properties on polymer molecule has drawn great interest as a serviceable method for polymer characterization. Specifically, intrinsic viscosity reflecting the capability of a polymer chain to increase the viscosity of the solution, provides a reliable yardstick for physical insight on the molecular weight and hydrodynamic property of the polymer as well as the interaction between the polymer chain and surrounding solvent.

The dimension of polymer chain in solvent depends partly on the choice of solvent, polymer concentration and temperature. The viscoelastic property of polymer molecule is strongly affected by the chain dimension, and this dependence becomes more apparent in dilute solution where the intrinsic viscosity relies directly on chain dimension. Especially, unperturbed chain dimension determined when intermolecular interaction between polymer and solvent vanishes, has been an issue. Several indirect techniques have been designed to estimate the unperturbed dimensions by simple measurements of intrinsic viscosity in non-ideal solvents, since the theta condition cannot be achieved readily. These approaches using the extrapolation method are available for the polymer solution no matter whether the solvent is ther-

modynamically favorable or not.

Biocompatible and biodegradable poly(lactic acid)¹ (PLA) has been extensively studied as a versatile material in biomedical and tissue engineering fields,²⁻⁸ where it has been utilized in a variety of shapes such as porous cell-supporting scaffolds,³⁻⁶ nano/micro-sized drug delivery carriers,⁷ fracture fixation devices⁸ and so on. Understanding of thermodynamic property of the polymer solution should be a critical factor in tailoring poly(DL-lactic acid) (PDLLA) material into desired morphology on demand. In our previous study,^{9,10} the thermally induced phase separation and the thermodynamic parameters for the systems of PDLLA/dialkyl phthalate mixtures were explored. In the present paper, the intrinsic viscosities of PDLLA solution in dialkyl phthalate were determined experimentally and the unperturbed chain dimensions and polymer-solvent interactions were deduced using different extrapolation methods.

Experimental

Materials. Amorphous PDLLAs of different molecular weight were used and listed in Table I. The solvents were dimethyl phthalate, diethyl phthalate, and dipropyl phthalate, each of which was designated as C1, C2, and C3, respectively. Molecular characteristics of the solvents were summarized in Table II. The solvents were used as received

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Table I. Number Average Molecular Weight (M_n), Weight Average Molecular Weight (M_w) and Polydispersity (M_w/M_n) of PDLLA

	M_n	M_w	Polydispersity
	10,000	12,000	1.20
PDLLA	26,000	46,000	1.77
	42,000	94,000	2.23

Table II. Symbol, Molecular Weight, Boiling Point and Supplier of Solvents

Solvent	Symbol	Molecular Weight	Boiling Point (°C)	Supplier
Dimethyl phthalate	C1	194.19	282.0	TCI
Diethyl phthalate	C2	222.24	298.0	Aldrich
Dipropyl phthalate	C3	250.29	317.5	Aldrich

without further purification.

Determination of Intrinsic Viscosity. The viscometric measurements of PDLLA solutions were carried out using a Cannon-Fenske viscometer. The concentration of the PLLA solution covered 1.0-4.5 g/dL. The outflow times of the pure solvent and PDLLA solutions ranging from 50 to 500 sec, were determined at 30, 45 and 60 °C. Temperature was controlled by thermostat within ± 1 °C. The concentration-dependent viscosities were extrapolated to zero concentration to deduce intrinsic viscosity.

Results and Discussion

Intrinsic Viscosity. The value of the intrinsic viscosity provides a measure of the ability of an isolated polymer single chain to increase the viscosity of the solvent in the absence of intermolecular interactions between polymer molecules. The intrinsic viscosity, $[\eta]$, could be calculated from the extrapolation of reduced viscosity (η_{sp}/c) to zero concentration.

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = \lim_{c \rightarrow 0} \left(\frac{\eta_{rel} - 1}{c} \right) = \lim_{c \rightarrow 0} \left(\frac{t/t_0 - 1}{c} \right) \quad (1)$$

where η_{sp} and η_{rel} represent the specific viscosity and relative viscosity; t and t_0 denote the efflux time of the solution and solvent in the Cannon-Fenske viscometer, respectively.

The typical plots of reduced viscosities as a function of polymer concentration for PDLLA solutions in dialkyl phthalate are presented in Figure 1, which shows the effects of temperature, polymer molecular weight, and the type of dialkyl phthalate. It seems to be a linear relationship between η_{sp}/c and c in the experimental range of polymer concentration (i.e., 1.0-4.5 g/dL). While the slope of extrapolated line is hardly affected by the temperature of polymer solution, it is under a definite influence of the polymer molecular weight and the number of carbon atoms in the alkyl chain of

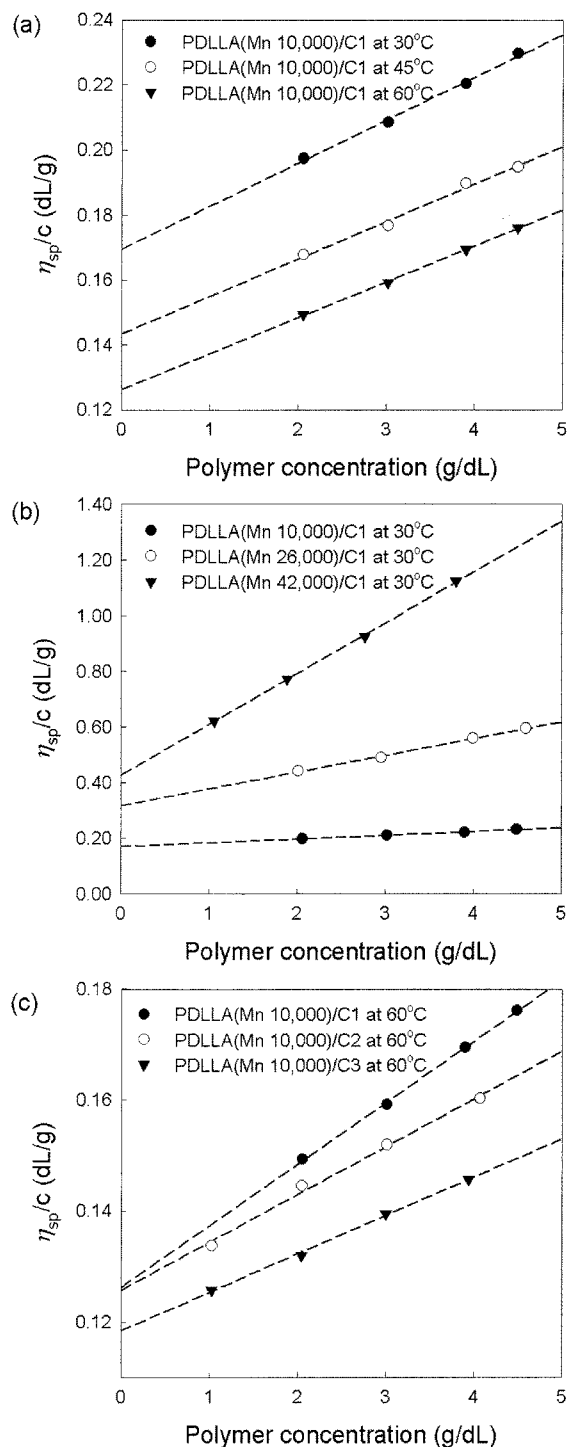


Figure 1. Plots of the reduced viscosity (η_{sp}/c) as a function of polymer concentration for PDLLA solutions in dialkyl phthalate to show the effects of temperature (a), PDLLA molecular weight (b), and the kind of dialkyl phthalate (c).

phthalate. It was reported in the previous works that a phthalate containing shorter alkyl chains has stronger interaction with PDLLA, that is, the solvent power of dialkyl phthalate decreases in the order of C1, C2, and C3.^{9,10} The

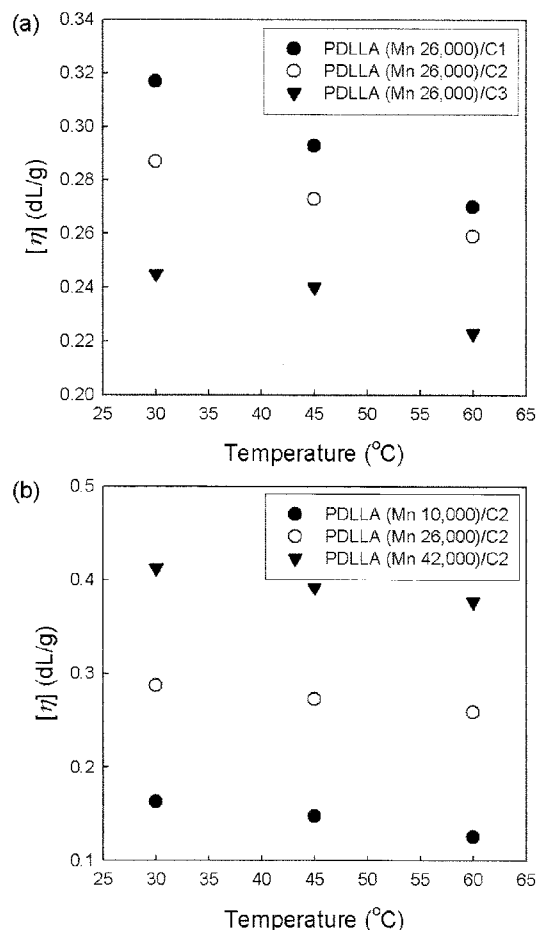
Table III. Intrinsic Viscosities for PDLLA Solution in a Series of Dialkyl Phthalate

Polymer	Temp. (°C)	[η] (dL/g)		
		C1	C2	C3
PDLLA (M_n 10,000)	30	0.170	0.163	0.140
	45	0.144	0.148	0.126
	60	0.126	0.126	0.118
PDLLA (M_n 26,000)	30	0.317	0.287	0.245
	45	0.293	0.273	0.240
	60	0.270	0.259	0.223
PDLLA (M_n 42,000)	30	0.427	0.412	0.325
	45	0.403	0.392	0.309
	60	0.373	0.377	0.297

extrapolated lines become steeper with higher molecular weight of PDLLA and with more favorable solvent. These trends were observed in all pairs of PDLLA and dialkyl phthalate at the experimental temperatures, and the extrapolated lines did not intersect one another.

Intrinsic viscosities of PDLLA solution in a series of dialkyl phthalate are summarized in Table III. The intrinsic viscosity of PDLLA solution decreases when the solvent is changed from C1 to C3, indicating that the hydrodynamic volume of the polymer chain shrinks with the unfavorable interaction between polymer and solvent. The intrinsic viscosity measurements manifest that the polymer-solvent interaction becomes gradually favorable with a dialkyl phthalate containing smaller number of carbon atoms in the alkyl chain, which is consistent with the results of the quantitative analysis by light scattering measurement.¹⁰ PDLLA of higher molecular weight causes higher intrinsic viscosity in a given solvent at the same temperature in Table III as expected. The effects of the type of dialkyl phthalate and molecular weight of PDLLA on intrinsic viscosities of PDLLA solutions as a function of temperature are shown in Figure 2. The intrinsic viscosity becomes smaller at higher temperature, which suggests that PDLLA coils tend to shrink at higher temperature. This phenomenon was also demonstrated by the works of Flory.^{11,12} Flory and his coworkers carried out the experimental and theoretical studies on the conformation of poly(lactic acid). They found that the unperturbed dimension of poly(lactic acid) molecule decrease with the temperature rise, which could be explained from the calculation of conformation energy. Conformation estimation revealed the poly(lactic acid) chain has the two states of lowest energy, approximately g^+t and g^-g^+ conformations, and this result rationalizes dimension shrinkage at higher temperature.

Polymer-Solvent Interaction and Unperturbed Dimension. In the infinitely dilute solution, the intermolecular


Figure 2. Effects of temperature on intrinsic viscosities of PDLLA (M_n 26,000) solutions in a series of dialkyl phthalate (a) and PDLLA with different molecular weight in diethyl phthalate (b).

interaction between the polymer chains vanishes and the excluded volume effect caused by the segments in the same polymer chain should be considered in the determination of polymer chain dimension.¹³ In this study, the information on the unperturbed dimension and polymer-solvent interaction was derived from the extrapolation method using Kurata-Stockmayer-Fixman equation,^{14,15} Berry equation¹⁶ and Inagaki-Suzuki-Kurata equation,¹⁷ which were abbreviated KSF, Berry and ISK hereafter. These semi-empirical equations are originated from an excluded volume equation correlating the intrinsic viscosity with molecular weight of the polymer. We employed them to deduce polymer-solvent interaction parameter and unperturbed dimension parameter from polymer molecular weight and intrinsic viscosity determined experimentally.

(i) Kurata-Stockmayer-Fixman equation (KSF)

$$[\eta]M^{-1/2} = K_o + 0.51B\Phi_oM^{1/2} \quad (2)$$

(ii) Berry equation (Berry)

$$[\eta]^{1/2}M^{1/4} = K_o^{1/2} + 0.42K_o^{1/2}\Phi_oBM[\eta]^{-1} \quad (3)$$

(iii) Inagaki-Suzuki-Kurata equation (ISK)

$$[\eta]^{4/5} M^{2/5} = 0.786K_o^{4/5} + 0.454K_o^{2/5} \Phi_o^{2/3} B^{2/3} M^{1/3} \quad (4)$$

where M is the number-average molecular weight of the polymer, and K_o and B denote the unperturbed dimension parameter and the parameter for the polymer-solvent interactions, respectively. And Φ_o is Flory's universal constant, $2.5 \times 10^{21} \text{ mol}^{-1}$. When KSF equation ($[\eta]M_n^{-1/2}$ vs. $M_n^{1/2}$),

Berry equation ($[\eta]^{1/2}M_n^{-1/4}$ vs. $M_n[\eta]^{-1}$) and ISK equation ($[\eta]^{4/5}M_n^{-2/5}$ vs. $M_n^{1/3}$) were plotted, one can readily determine K_o and B from the slope and the intercept of them.

KSF plot, Berry plot and ISK plot for PDLLA solutions are shown in Figure 3 to Figure 5, respectively. All the points of each were extrapolated to yield the straight lines to obtain K_o and B , and the resultant values are summarized in Table IV. The unperturbed dimension parameters, K_o , calculated from KSF, Berry and ISK equation were in good

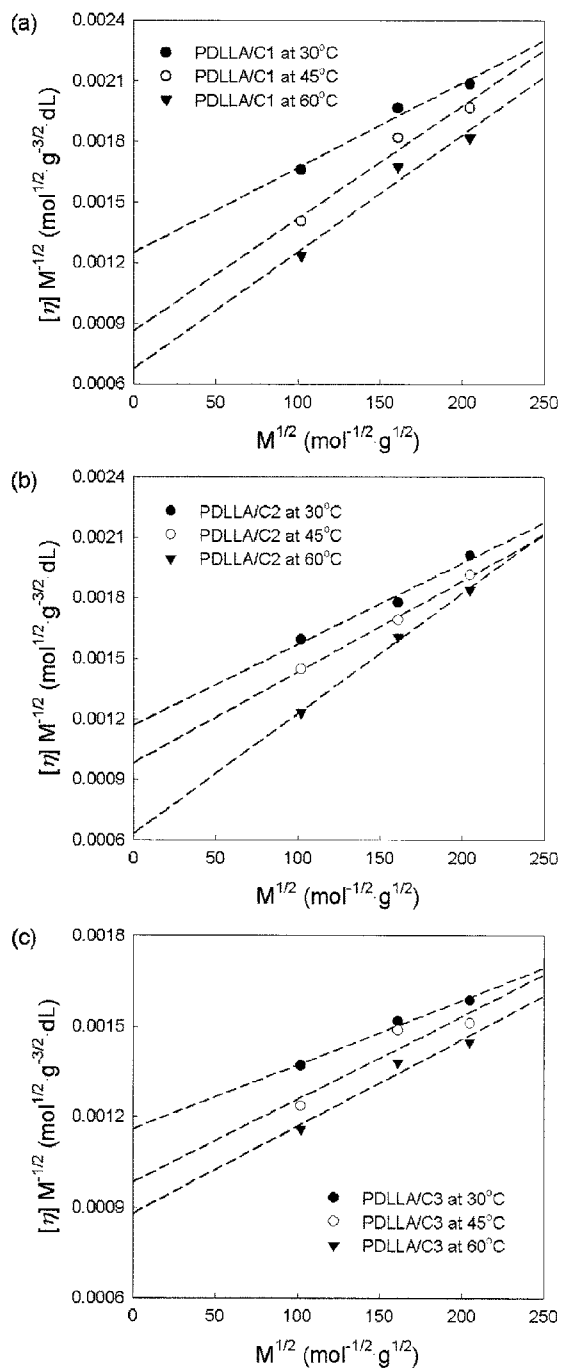


Figure 3. Kurata-Stockmayer-Fixman plot for PDLLA/C1 (a), PDLLA/C2 (b), and PDLLA/C3 (c).

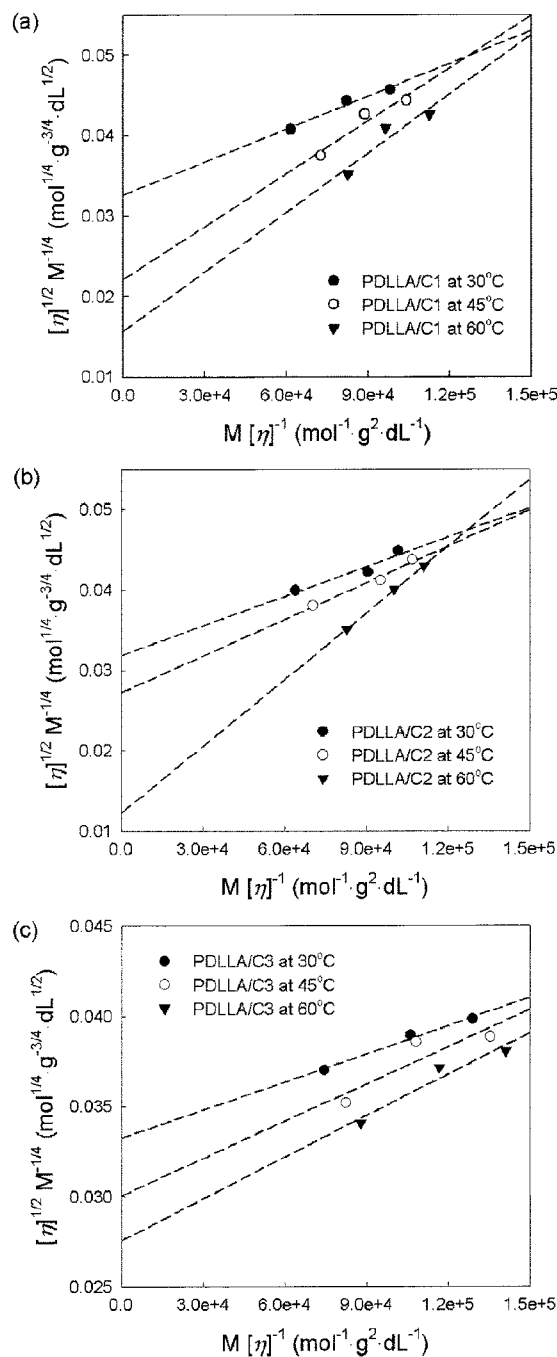


Figure 4. Berry plot for PDLLA/C1 (a), PDLLA/C2 (b), and PDLLA/C3 (c).

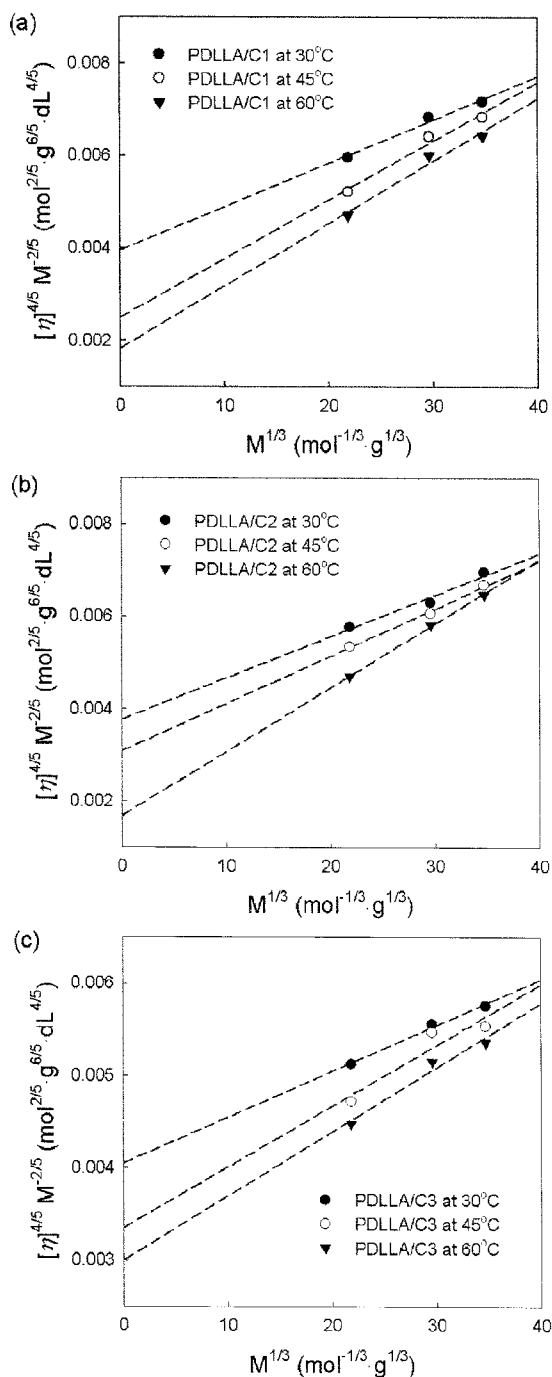


Figure 5. Inagaki-Suzuki-Kurata plot for PDLLA/C1 (a), PDLLA/C2 (b), and PDLLA/C3 (c).

agreement. The unperturbed dimension parameter of the PDLLA in dialkyl phthalate decreased with increasing temperature. It could be interpreted on the basis of the conformation change of the polymer chain. From the viewpoint of conformation of polymer chain, the PDLLA polymer chain prefers g^+t and g^+g^+ conformation for the more stable energy state, which triggers the shrinkage of the unperturbed molecular chain at the higher temperature.¹² The parameter

for polymer-solvent interaction, B , increased with temperature rise and with a solvent having shorter alkyl chain. It demonstrates that the polymer-solvent interaction became favorable at higher temperature and with a dialkyl phthalate having shorter alkyl chain, which is similar tendency to the second virial coefficient obtained from light scattering experiment.¹⁰

The unperturbed dimension parameter, K_o can be converted to the unperturbed end-to-end distance by the Flory's equation given as below.^{13,18}

$$K_o = [\eta]_o M^{-1/2} = \Phi_o (\langle r^2 \rangle_o / M)^{3/2} \quad (5)$$

where $[\eta]_o$ is the intrinsic viscosity at theta temperature and $\langle r^2 \rangle_o^{1/2}$ represents the root-mean-square end-to-end distance of unperturbed polymer chain.

The unperturbed root-mean-square end-to-end distance was calculated according to eq. (5) and the result is summarized in Table V. The unperturbed dimension is defined as the dimension of a polymer coil in dilute solution at theta temperature. Under these conditions the interaction between segments of the polymer chains, causing the chain contraction, are just balanced by the solvation forces. The polymer chain conformation is then solely determined by short-range forces through bond angles, bond distances and bond rotations. As can be seen in Table V, the temperature and molecular weight of the polymer affected the unperturbed chain dimension of the PDLLA significantly whereas the unperturbed chain dimension was hardly influenced by the solvent quality. Considering the fact that unperturbed state excludes solvent effect, this result looks quite reasonable. The unperturbed dimension decreased as the temperature was increased and the molecular weight of polymer was decreased. With regard to the temperature effect, the chain shrinkage was explained by thermodynamic equilibrium ratio of gauche and trans conformations of the chain segments as described before.

Conclusions

The intrinsic viscosities for PDLLA solutions in dialkyl phthalate were evaluated. The different length of the alkyl chain in dialkyl phthalate from methyl to propyl was adopted to control the solvent quality systematically. Intrinsic viscosity of PDLLA solution increased with the phthalate having shorter alkyl chain, with higher molecular weight of PDLLA, and at lower temperature. Several extrapolation methods were employed to deduce the unperturbed end-to-end distance and polymer-solvent interaction parameter. Higher temperature caused a slight shrinkage of the unperturbed chain dimension, which can be explained by the conformation change of PDLLA chain. The actual chain dimension decreased upon temperature rise and when the phthalate of longer alkyl chain was used. When considering

Table IV. Calculated Thermodynamic Parameters for PDLLA/Dialkyl Phthalate

	Temp. (°C)	$K_o \times 10^4$ (mol ^{1/2} ·g ^{-3/2} ·dL)			$B \times 10^{27}$ (mol ² ·g ⁻² ·dL)		
		KSF	Berry	ISK	KSF	Berry	ISK
PDLLA/C1	30	12.5	10.7	13.4	3.30	3.97	63.2
	45	8.63	4.90	7.56	4.36	9.42	140
	60	6.75	2.47	5.13	5.30	14.9	194
PDLLA/C2	30	11.7	10.2	12.6	3.15	3.64	61.0
	45	9.82	7.43	9.84	3.54	5.27	86.6
	60	6.31	1.49	4.61	4.67	21.6	214
PDLLA/C3	30	11.6	11.1	13.8	1.67	1.49	23.9
	45	9.84	9.03	10.9	2.16	2.18	42.0
	60	8.81	7.61	9.49	2.26	2.65	49.4

Table V. Calculated Unperturbed End-to-End Distance of PDLLA in Dialkyl Phthalate

Polymer	Temp. (°C)	Unperturbed End-to-End Distance, $\langle r^2 \rangle_o^{1/2}$ (nm)								
		KSF			Berry			ISK		
		C1	C2	C3	C1	C2	C3	C1	C2	C3
PDLLA (M_n 10,000)	30	8.1	7.9	7.9	7.7	7.6	7.8	8.3	8.1	8.4
	45	7.2	7.5	7.5	5.9	6.8	7.3	6.9	7.5	7.7
	60	6.6	6.5	7.2	4.7	4.0	6.9	6.0	5.8	7.4
PDLLA (M_n 26,000)	30	12.8	12.5	12.5	12.1	11.9	12.3	13.1	12.8	13.2
	45	11.3	11.8	11.8	9.4	10.8	11.5	10.8	11.8	12.2
	60	10.4	10.2	11.4	7.4	6.3	10.8	9.5	9.2	11.7
PDLLA (M_n 42,000)	30	16.3	15.9	15.9	15.4	15.2	15.6	16.6	16.3	16.8
	45	14.4	15.0	15.0	11.9	13.7	14.6	13.7	15.0	15.5
	60	13.2	12.9	14.5	9.5	8.0	13.8	12.1	11.7	14.8

favorable polymer-solvent interaction at higher temperature, these results demonstrate that the effects of the polymer conformation are dominant over those of the interaction between polymer and solvent. The polymer-solvent interaction parameter indicates that the solvent power reduces as the length of alkyl chain in phthalate become large.

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