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Dielectric study on dynamics and conformation of poly(D,L-lactic acid) in dilute and semi-dilute solutions

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Abstract

Fractionated samples of D,L-poly(lactic acid) (PLA) were prepared and the dielectric normal mode relaxation was studied for dilute and semi-dilute solutions of the PLA in a good solvent benzene. Results indicate that in the dilute regime the normal mode relaxation time is proportional to $[\eta]M_w$ in agreement with the Rouse–Zimm theory, where $[\eta]$ and M_w denote the intrinsic viscosity and weight average molecular weight, respectively. The dielectric relaxation strength which is proportional to the mean square end-to-end distance $\langle r^2\rangle$ increases with increasing M_w with the power of 2ν, where ν is the excluded volume parameter determined from $[\eta]$. The relaxation time in the semi-dilute regime increases with increasing concentration C due to increases of the entanglement density and the friction coefficient. The relaxation time corrected to the iso-friction state agrees approximately with the dynamic scaling theories. The relaxation strength decreases with increasing concentration indicating that $\langle r^2\rangle$ decreases on account of the screening of the excluded volume effect. The concentration dependence of $\langle r^2\rangle$ agrees approximately with the scaling theory proposed by Daoud and Jannink.

Keywords: Poly(D,L-lactic acid); Solution; Dielectric normal mode relaxation

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1. Introduction

Aliphatic polyesters having the structure of $(R_m{-}COO)_n{-}$ is one of type-A polymers [1–3] and exhibit the dielectric normal mode relaxation due to fluctuation of the end-to-end vector since the overall dipole moment of the chain is proportional to the end-to-end distance. Here R_m represents an aliphatic hydrocarbon composed of m backbone atoms. Jone et al. [4] first reported the dielectric normal mode relaxation in dilute solutions of poly(ε-caprolactone) ($m = 5$). Later Urakawa et al. [5] reported the dielectric normal mode relaxations in solutions of poly(ε-caprolactone) and poly(varelolactone) ($m = 4$) with a narrow distribution of molecular weight. Poly(lactic acid) (PLA) is an aliphatic polyester of $m = 1$ as shown in Fig. 1(a). Due to the resonance effect, the $C_2{-}O_3$ bond has a character of double bond and hence the internal rotation around $C_2{-}O_3$ is forbidden [6]. Thus the backbone atoms C_1, C_2, O_3, and C_4 are on a same plane and the whole repeat unit can be regarded as a virtual bond (dashed line in Fig. 1(a)). The virtual bond possesses the parallel (type-A) and perpendicular (type-B) components of the dipole moment p_A and p_B (Fig. 1(a)).

There are two kinds of type-A polymers termed as types-A1 and -A2. In type-A1 polymers, the parallel dipoles are connected directly but in type-A2 polymers the dipoles are connected with non-polar groups as shown in Fig. 1(b). In dynamical processes of a type-A1 chain, its overall dipole vector $\mathbf{M}_A$ $(=\sum p_A)$ is exactly proportional to the end-to-end vector $\mathbf{r}$ in all instants:

$$\mathbf{M}_A = \mu\mathbf{r} \tag{1}$$

where μ is the parallel dipole moment per unit contour length. In type-A2 polymers μ changes with time because the conformation of the non-polar bonds is irrelevant to the dipole moment. Thus the mean square average of $\mathbf{M}_A$ is proportional to the mean square end-to-end vector $\langle r^2\rangle$. In this view the difference in structure between PLA ($m = 1$) and poly(ε-caprolactone) ($m = 5$) is significant. As mentioned above, the whole monomeric unit of PLA can be regarded as a virtual bond and hence PLA is a type-A1 polymer. On the other hand poly(ε-caprolactone) is a typical type-A2 polymer since the polar COO group is connected

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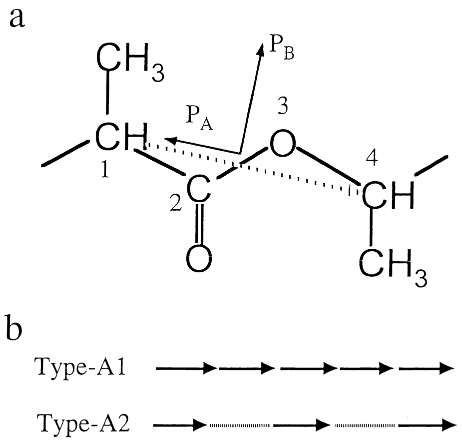

Fig. 1. (a) Structure of the monomeric unit of PLA. p_A and p_B denote the type-A and -B dipoles, respectively. The dashed line indicates the virtual bond. (b) Schematic representations of type-A1 (top) and type-A2 (bottom) polymers.

with non-polar methylene groups. A few type-A1 polymers are known, i.e. poly(2,6-dichlorophenylene oxide) [7], poly(butyl acetylene) [8] and poly(phenoxy phosphazene) [9]. However, those polymers have not been studied fully due to difficulties in sample preparation.

Among various type-A polymers polyisoprene was studied most extensively since narrow distribution samples can be prepared by anionic polymerization [10–15]. Polyisoprene has a structure $-C^1H_2-C^2(CH_3)=C^3H-C^4H_2-$ and the line connecting C^1 and C^4 atoms can be regarded as the virtual bond having the parallel dipole moment but the bond connecting C^4 and C^1 of the next monomeric unit is non-polar. Therefore, polyisoprene is a type-A2 polymer. It was found that the relaxation time in dilute theta solutions of polyisoprene conforms to the Zimm model [10,16]. In good solvent, the relaxation times are proportional to $M[\eta]$, where $[\eta]$ denotes the intrinsic viscosity as predicted by the Rouse–Zimm theory [16,17]. We also pointed out that this relation holds quite well for various polymer–solvent systems [3,5].

Besides the dynamic properties, the dielectric spectroscopy provides us an important information of the mean square end-to-end distance $\langle r^2 \rangle$ [2,18]. It was found for dilute solutions of polyisoprene that the value of $\langle r^2 \rangle/M$ is independent of the molecular weight M in a theta solvent but $\langle r^2 \rangle$ is proportional to $M^{1.2}$ in a good solvent [10]. In semi-dilute solutions of polyisoprene, $\langle r^2 \rangle$ decreases with increasing concentration due to screening of the excluded volume effect [11,12,14,19].

In this paper we have carried out dielectric measurements on dilute and semi-dilute solutions of PLA. The objective is to examine whether the characteristic behaviours mentioned above are also seen in dilute and semi-dilute solutions of PLA. We will compare the dielectric behaviour of PLA with those of poly(ε-caprolactone) and polyisoprene.

2. Experimental

2.1. Materials

Samples of poly(D,L-lactic acid) (PLA) were prepared by co-polymerization of a 1:1 mixture of L- and D,L-dilactides with a small amount (0.01 wt%) of $Sn(C_8H_{15}O_2)_2$ as a catalyst and dodecanol as a co-catalyst as described by Ajioka and co-workers [20]. The monomers L-dilactide and D,L-dilactide were purchased from Aldrich (San Francisco, USA) and used without further purification. The catalysts were obtained from Wako Chemicals (Tokyo, Japan) and were used as received. The mixture was dried in vacuum of 0.1 Pa over night and then heated up to 170–200 °C under atmosphere of dry helium. Above the melting point of the dilactides, the mixture was stirred. The reaction products were dissolved in chloroform and then precipitated by addition of excess amount of methanol. Those samples were fractionated with dioxane as a good solvent and methanol or *n*-hexane as non-solvents. The molecular weights of those fractions were measured with size exclusion chromatography by using an apparatus equipped with a low-angle laser-light scattering detector (Tosoh, Tokyo, Japan). Results are summarized in Table 1. The sample code indicates the weight average molecular weight in kg/mol. Benzene used as the solvent of sample solutions for dielectric measurements was 99.9% pure grade and obtained from Dojin Chemicals (Kumamoto, Japan). The density of the undiluted D,L-PLA was measured to be 1.246 g/ml (298 K) by a buoyancy method. We calculated concentration C in g/ml assuming the additivity of the densities of benzene (0.874 g cm^{-3}) and PLA.

2.2. Methods

Dielectric measurements were carried out at 298 K with a capacitance bridge (General Radio 1615A) and an RLC digibridge (QuadTech 7600, Maynard, USA) over the frequency ranges from 10 Hz to 2 MHz. A guarded capacitance cell for measurements on liquids was reported previously [21]. Intrinsic viscosity was determined at 298 K in benzene with a Ubbelohde type viscometer.

Table 1
Sample characteristics

Code	M_w ($\times 10^{-3}$)	M_w/M_n	$[\eta]$	C^* ($\times 10^2$)
PLA119	119	1.19	145.6	0.69
PLA75	75.3	1.17	101.1	0.99
PLA55	55.4	1.19	79.2	1.26
PLA38	37.9	1.22	58.6	1.71
PLA29	28.5	1.17	46.7	2.14
PLA20	20.7	1.21	36.2	2.76

M_w: weight average molecular weight, M_n: number average molecular weight, $[\eta]$: intrinsic viscosity in ml/g, C^*: overlapping concentration in g/ml.

3. Results and discussion

3.1. Intrinsic viscosity

Fig. 2 shows the dependence of the intrinsic viscosities $[\eta]$ on the weight average molecular weight M_w in benzene. The result can be cast into the Mark–Houwink–Sakurada equation

$$[\eta] = KM_w^{\alpha} \tag{2}$$

with $K = 1.10 \times 10^{-2}$ ml/g and $\alpha = 0.806$. Since this α value is slightly higher than the upper limit of 0.8 for flexible polymers, one may consider that PLA is a semi-flexible worm-like chain. However, according to our recent study, the characteristic ratio $C_\infty = \langle r^2 \rangle / N b_v^2$ was determined to be 3.15, indicating PLA is a typical flexible polymer, where N is the degree of polymerization and b_v the length of the virtual bond [22]. Thus, the present viscosity data indicate that benzene is a good solvent. The excluded volume parameter ν is determined to be 0.60 from the relation $\alpha = 3\nu - 1$. We determined the overlapping concentration C^* by using the relation $C^* \approx 1/[\eta]$ and listed in Table 1 together with $[\eta]$.

3.2. Overview of dielectric relaxation of PLA solutions

The representative frequency f dependence curves of the dielectric loss factor ε'' for PLA119 and PLA38 solutions are shown in Fig. 3(a) and (b), respectively. Solutions of the other PLA samples exhibited similar behaviour but the loss maximum frequency depended strongly on the molecular weight indicating that the observed dielectric relaxation is due to the normal mode process. In Fig. 3(a), we see that in the range of $C < 0.02$ the loss maximum frequency of the normal mode relaxation for PLA119 is almost independent of concentration and stays at $\log f = 4.3$. This regime is defined as the dynamically dilute regime and the dynamic crossover concentration C_τ^* is defined as the concentration above which the relaxation time increases with concentration [12]. We will discuss C_τ^* in Section 3.4.

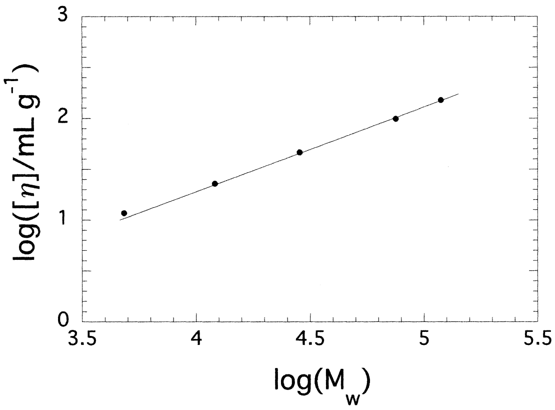

Fig. 2. Double logarithmic plots of intrinsic viscosity $[\eta]$ against weight average molecular weight M_w. $T = 298$ K.

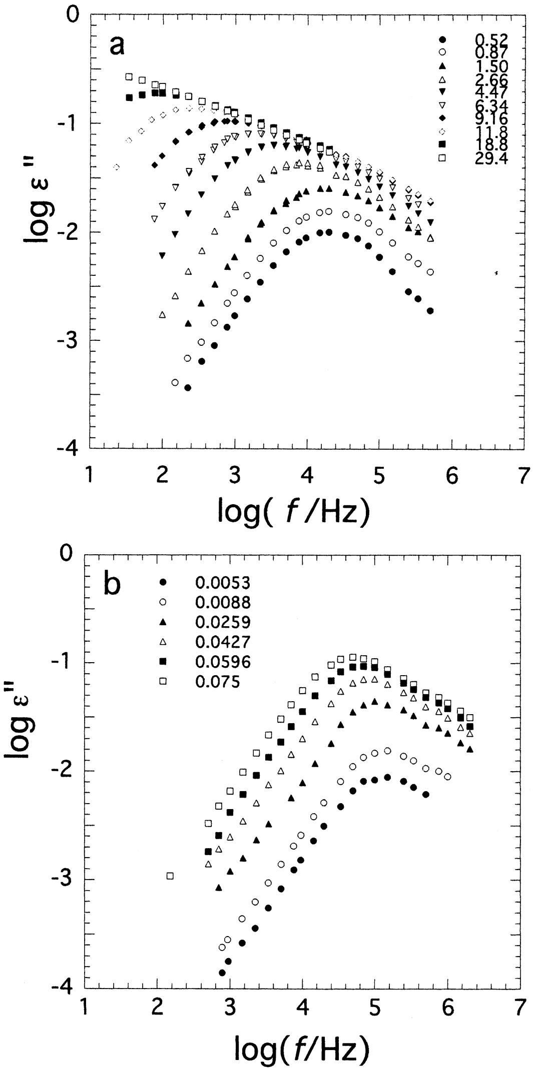

Fig. 3. Double logarithmic plots of the loss factor ε'' vs frequency f for (a) solutions of PLA119 and (b) solutions of PLA38 at 298 K. The values of 100 C in g/ml are listed in the figure (a), but those of C in figure (b).

The intensity increases with increasing concentration as expected. In the semi-dilute regime of $C > 0.027$, the ε'' peak shifts to lower frequency with increasing concentration and at the same time the peak becomes broader. The origin of this behaviour must be ascribed to the onset of entanglement, i.e. the PLA chains begin to overlap each other and the mobility of the chains slows down. In the whole concentration region, the slope of low frequency side of the $\log \varepsilon''$ vs $\log f$ curves is unity. On the other hand, the slope in the high frequency side of the peak changes from 0.62 in the very dilute regime to 0.25 in the semi-dilute regime indicating the broadening of the relaxation spectra with concentration. The behaviour observed for PLA solutions is very similar to those of solutions of poly-isoprene [10–15] and poly(ε-caprolactone) [5].

In Fig. 3(b) we see that the intensity and the loss maximum frequency for PLA38 change with concentration in a similar manner to PLA119 solutions. However, the width of the loss curve does not increase with concentration in contrast to PLA119 solutions. Thus the broadening of the loss curves in semi-dilute solutions is enhanced with increasing molecular weight and can be attributed to the entanglement effect.

3.3. Dilute solutions

The ε'' curves for dilute solutions of PLA having varying molecular weights are compared in Fig. 4, where ε'' divided by concentration C has been plotted. We see that the loss maximum frequency f_m shifts to low-frequency side with increasing molecular weight as observed commonly for type-A polymers [1–3]. For type-A polymers, the complex dielectric constant $\varepsilon^*(=\varepsilon' - i\varepsilon'')$ is given by the Fourier–Laplace transform of the autocorrelation function of the end-to-end vector $\langle \mathbf{r}(0)\cdot\mathbf{r}(t)\rangle$. According to the Zimm model [16], $\langle \mathbf{r}(0)\cdot\mathbf{r}(t)\rangle$ is expressed as

$$\langle \mathbf{r}(0)\cdot\mathbf{r}(t)\rangle = \frac{8\langle r^2\rangle}{\pi^2}\sum_{p:\mathrm{odd}}\frac{1}{p^2}\exp(-t/\tau_p) \tag{3}$$

$$\tau_p = \frac{\pi^{3/2}\eta_s N^{3/2} b^2}{12^{1/2} k_B T \lambda_p} \tag{4}$$

where τ_p is the relaxation time for the pth normal mode; η_s the solvent viscosity; b, the average distance between beads; $k_B T$, the thermal energy; and λ_p, the pth eigenvalue tabulated by Zimm et al. [23]. The non-draining Zimm model predicts $\tau_1 \propto M^{1.5}$.

The experimental relaxation time τ_n is determined from the loss maximum frequency f_m as $\tau_n = 1/(2\pi f_m)$. Fig. 5 shows the double logarithmic plot of τ_n vs weight average molecular weight M_w. The slope of this plot is determined to be 1.82 which is larger than 1.5 given by Eq. (4). Strictly speaking the Zimm theory is applicable only to θ solutions since the bead-spring model assumes a Gaussian chain. On the other hand, the PLA chains in benzene assume non-Gaussian conformation since benzene is a good solvent. The excluded volume effect is approximately accommodated in the theory by modifying Eq. (4) as

$$\tau_1 = K\frac{M\eta_s[\eta]}{RT} \tag{5}$$

where K is the constant and η_s the solvent viscosity [16,17]. The Rouse and Zimm models predict K to be 1.22 and 0.85, respectively. The exponent α of Eq. (2) has been determined to be 0.81 and hence Eq. (5) predicts $\tau_n \propto M^{1.81}$. Thus Eq. (5) explains well the M_w dependence of the normal mode relaxation in dilute PLA solutions.

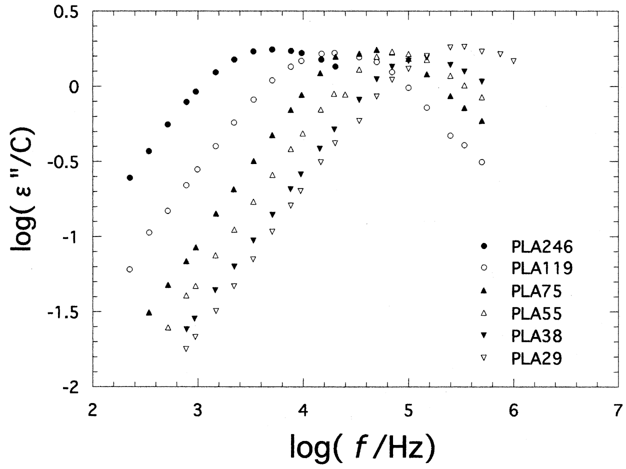

Fig. 4. Comparison of the ε''/C vs frequency curves of dilute PLA solutions at 298 K.

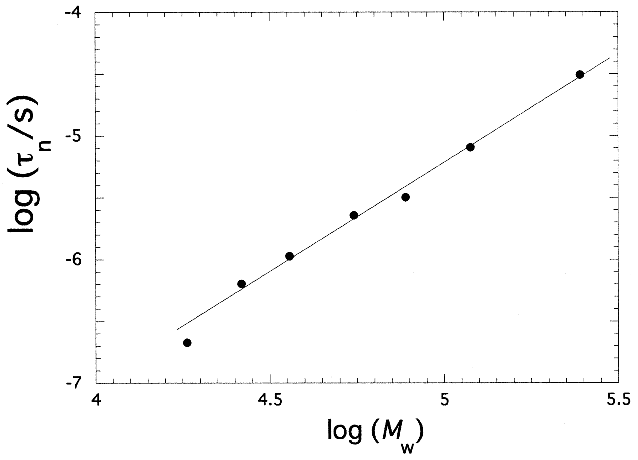

Fig. 5. Double logarithmic plot of molecular weight vs relaxation time τ_n in dilute solution at 298 K.

Fig. 6 shows double logarithmic plots of τ_n against

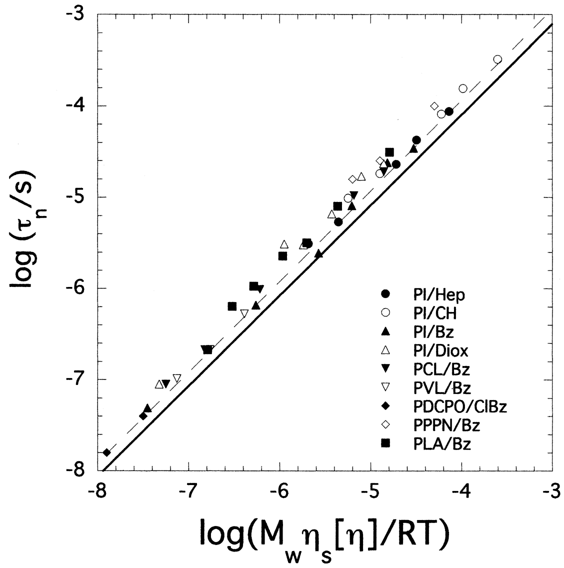

Fig. 6. Test of the Rouse–Zimm theory (Eq. (5)) for solutions of various type-A polymers including benzene solutions of PLA. PI, polyisoprene; PCL, poly(ε-caprolactone); PVA, poly(varelolactone); PDCPO, poly(dicholorophenylene oxide); PPPN, poly(phenoxy phosphazene); Hep, heptane; CH, cyclohexane; Bz, benzene; Diox, dioxane, and ClBz, chlorobenzene. The dashed line and solid line represent the Rouse and Zimm theories, respectively.

$M\eta_s[\eta]/RT$ for dilute solutions of various type-A polymers including the present benzene solutions of PLA [3]. We see that all plots conform approximately to a universal straight line of the slope of unity. The front factor K for the PLA/Bz system becomes 1.78. This value is slightly larger than the theoretical value of K for the Rouse theory and also larger than the average of the experimental K values ($= 1.4$) for the other solutions.

3.4. Longest relaxation time in semi-dilute solutions

As pointed out above for Fig. 3, f_m decreases with increasing concentration in the semi-dilute regime. The concentration dependence of the normal mode relaxation time τ_n is shown in Fig. 7(a). We see that all curves are similar and there exists a dynamical crossover concentration C_τ^* below which τ_n is independent of concentration but above which τ_n increases with concentration. In Fig. 7(a), C_τ^* is defined as the break point (the cross point of the extrapolated two straight lines). Previously, we found that $C_\tau^* \approx C^*$ for solutions of polyisoprene in a good solvent and moderately good solvents [12]. In the present PLA solutions, we see that C^* tends to decrease with increasing molecular weight as indicated by arrows in Fig. 7(a) but C_τ^* for solutions of low molecular weight PLAs is almost independent of molecular weight. We conclude that the ratio of C_τ^*/C^* increases with increasing molecular weight.

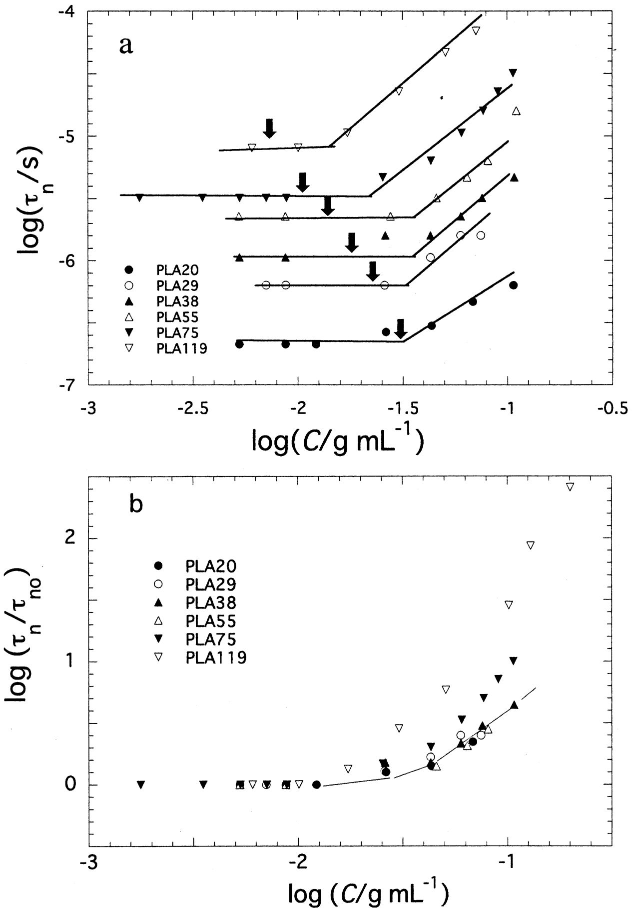

Fig. 7. (a) Double logarithmic plots of τ_n at 298 K against concentration C. (b) Double logarithmic plots of τ_n/τ_{n0} against concentration C, where τ_{n0} denotes the relaxation time in dilute regime.

It is known that molecular weight between entanglement M_e in concentrated solutions of a polymer increases with decreasing concentration as M_e^0/C, where M_e^0 denotes the M_e of the undiluted polymer [24]. Recently we determined M_e^0 of D,L-PLA to be 7700 from the plateau modulus of undiluted PLAs [25]. In the semi-dilute regime M_e is proportional to $(C/C^*)^{\nu/(1-3\nu)}$ if the correlation length ξ is assumed to be equal to the end-to-end distance of the PLA chain of $M = M_e$ [19]. For good solvent systems of $\nu = 3/5$, $M_e \propto C^{-0.75}$. The crossover concentration C^+ between the semi-dilute and concentrated regimes is estimated to be 0.25 g ml^{-1}. Then M_e becomes ca. 80,000 at $C = 0.1$. Therefore solutions of PLA55, PLA38, PLA29, and PLA20 with concentration less than 0.1 are in a non-entangled state. Nevertheless τ_n of those solutions increases with increasing concentration. Thus the increase of τ_n in those four solutions is attributed to increase of the friction coefficient ζ on account of intermolecular hydrodynamic interactions. On the other hand, the concentration dependencies of τ_n in solutions of PLA119 and PLA75 are due to both friction and entanglements. Fig. 7(b) shows the plots of log τ_n/τ_{n0} against log C, where τ_{n0} denotes the relaxation time in the dilute regime. As is seen in this figure, the plots for PLA20, PLA29, PLA38, and PLA55 can be superposed indicating that τ_n depends only on the segment density. This confirms the above conclusion that the concentration dependencies of τ_n in solutions of PLA20, PLA29, PLA38, and PLA55 are due to the friction effect.

3.5. Longest relaxation time in crossover regime

In Section 3.4, the phenomenological analysis has been made and the concentration dependencies of τ_n has been attributed to the friction and the entanglement effect. However, in the molecular view point, both the friction and entanglement effects result from intermolecular interactions. Both the effects are interrelated. Muthukumar and Freed [26,27] proposed a theory to describe the concentration dependence of relaxation time in the crossover region by considering the inter-chain hydrodynamic interactions. They did not use the concepts of friction and entanglement. We test whether this theory explains the concentration dependencies of τ_n in the crossover regime.

In dilute regime $\langle \mathbf{r}(0)\cdot\mathbf{r}(t)\rangle$ is expressed by the Zimm model (Eq. (4)) but around the crossover region the pth relaxation time τ_p is written as

$$\tau_p = \tau_{p0}[1 + CAp^{-\kappa} - 2^{0.5}(CAp^{-\kappa})^{1.5} + 2(CAp^{-\kappa})^{2.0} + \cdots] \qquad (6)$$

where τ_{p0} is the pth relaxation time at infinite dilution; A, the constant proportional to $[\eta]$ and κ is equal to $3n-1$. Since Eq. (6) resembles to the expansion of an exponential equation, the longest relaxation time τ_l can be rewritten approximately as [4,28,29]

$$\tau_l = \tau_{l0}\exp(CA'[\eta]) \tag{7}$$

where A' is the constant. This equation indicates that the logarithm of dielectric relaxation time is proportional to concentration in semi-dilute solutions. Fig. 8 tests this prediction. We see that plots are approximately straight line and conform to Eq. (7). From the slope, A' is determined to be 0.24 for PLA119 and 0.32 for PLA29. There is a tendency that A' increases with decreasing molecular weight. Previously we found for semi-dilute PI solutions that A' was found to be 0.29, irrespective of M_w and solvent quality [15]. We also reported that A' for semi-dilute poly(ε-caprolactone) (PCL) and poly(varelo lactone) solutions in benzene were 0.26 and 0.21 ± 0.06 [5]. Jone et al. [4] reported $A' = 0.21$ for dioxane solutions of PCL. Baysal and Stockmayer [29] reported for ternary solutions of PCL/polychlorostyrene/dioxane that $A' = 0.35$. The value of A' for PLA solutions agree approximately with those of the other polymers. We conclude that A' takes a universal value of 0.2–0.35 irrespective of the chemical structure of polymers.

3.6. Reptation theory in semi-dilute regime

In this section, we apply the reptation theory proposed by De Gennes [30] and examine whether the theory successfully explains our results compared with the Muthukumar–Freed theory. He developed the theory assuming that the correlation length of the segment density is equal to the diameter of the tube in which chains are constrained. The longest relaxation time τ_d (tube disengagement time) is given by

$$\tau_d \propto \zeta N^3 (C/C^*)^{(3-3\nu)/(3\nu-1)} \tag{8}$$

where ζ is the friction coefficient, N the number of beads, and ν the excluded volume exponent. Eq. (8) has a form in which the effects of the friction and entanglements are independent and is similar to the following equation known well in rheology [31]

$$\tau = \zeta(T,C)F(N_e,C) \tag{9}$$

where ζ(T,C) is the friction factor depending only on temperature T and concentration C. $F(N_e)$ is the structural factor depending on the architecture of the chains and on the number of entanglements $N_e(= M/M_e)$. It is assumed that the friction acting on beads is proportional to the solvent viscosity η_s and does not change with concentration. As mentioned above this condition is not satisfied in the present systems. In order to examine the effect of entanglement on the concentration dependence of τ_n, we need to correct the effect of friction.

As mentioned above, plots of log τ_n/τ_{n0} (Fig. 7(b)) for PLA20, PLA29, PLA38, and PLA55 almost superpose. The smoothed common line for these four solutions has been drawn as shown in Fig. 7(b). This smoothed curve is proportional to $\zeta(T,C)$ of Eq. (9). Then for PLA119 and PLA75 solutions, we obtain the relaxation time $\tau_{n\zeta}$ corrected to the iso-friction state by subtracting the values of the smoothed curve (logarithmic scale) from log τ_n/τ_{n0} of PLA119 and PLA75 solutions. It is noted that ζ corresponds to that in the dilute regime. Thus determined log $\tau_{n\zeta}/\tau_{n0}$ is plotted against $C[\eta]$ $(= C/C^*)$ in Fig. 9.

Eq. (9) indicates that the log $\tau_{n\zeta}$ vs log $C[\eta]$ plot has the slope of $(3-3\nu)/(3\nu-1)$. For good solvent systems of $\nu = 3/5$, the slope becomes 1.5. In Fig. 9 we see that the plot is not straight line and does not agree with the theory quantitatively. However, the theory explains the present result approximately if a line of slope 1.5 is drawn as shown in Fig. 9.

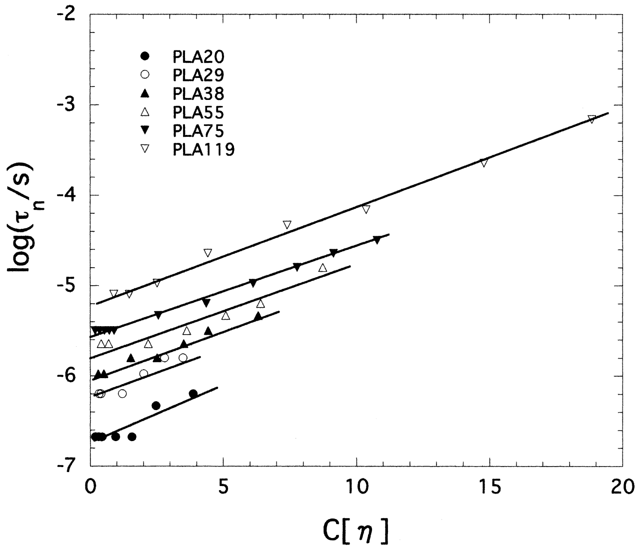

Fig. 8. Plots of log τ_n against $C[\eta]$ for PLA solutions for the test of Eq. (8).

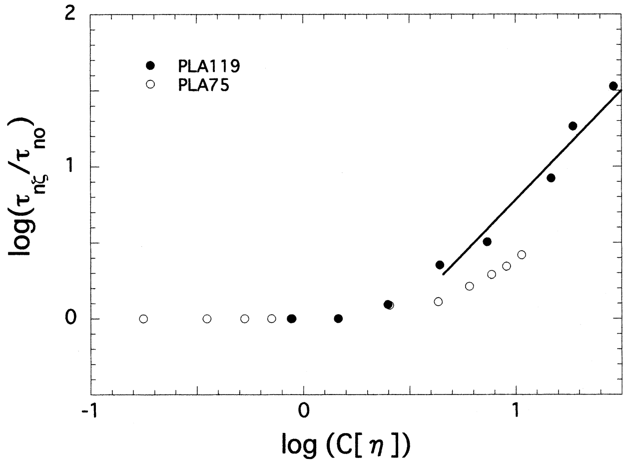

Fig. 9. Double logarithmic plots of $\tau_{n\zeta}/\tau_{n0}$ against concentration $C[\eta]$ for solutions of PLA75 and PLA119. The solid line indicates Eq. (9).

3.7. Relaxation spectra in semi-dilute regime

Fig. 10 shows the normalized ε'' curves for PLA119/benzene solution with various concentration. For the sake of comparison, the loss curve predicted by the Zimm model is plotted by the dashed line. The loss curves in the dilute regime are slightly broader than that predicted by the Zimm theory. We consider that this is due to the distribution of molecular weight since the PLA samples used here have a little broader molecular weight distribution ($M_w/M_n = 1.19$) than the samples of polyisoprene and poly(ε-caprolactone) used previously ($M_w/M_n < 1.08$) [5,10–15]. The slope of the loss curve in the low frequency side is unity in agreement with the theory.

For semi-dilute solutions, we see that the high-frequency side of the peak broadens with increasing concentration. The broadness of the spectra can be assessed from the negative slope in the high frequency side which changes from -0.73 in the dilute regime to -0.25 in the semi-dilute regime. The same behaviour was reported for solutions of polyisoprene and poly(ε-caprolactone) [5,10–12,14,15]. Thus, the broadening of the dielectric spectra is a universal phenomenon and does not depend on the type of the configuration of dipoles A1 and A2.

The reptation model [32] proposed by De Gennes predicts the same spectrum as the Rouse model and does not explain the effect of entanglement on the broadening of the dielectric spectra. The Muthukumar–Freed theory (Eq. (6)) predicts the change in the spectra. In Eq. (6), the relaxation times for the odd modes are calculated assuming $A = A'[\eta]$ for PLA119 solution with $C = 0.1$. The intensity for each mode is proportional to $1/p^2$ and the sum of the Debye functions are calculated. As shown in Fig. 10, this model does not explain the experimental ε'' curve quantitatively.

Ngai [33] also proposed a general theory of the relaxation spectra. The theory does not explain the broadening of the dielectric spectra since the theory predicts the broadening in both the low and high frequency sides of the ε'' curves. This is not the case i.e. the slope of the ε'' curve in the low frequency side is unity irrespective of concentration. Thus at present no theory satisfactorily explains the broadening of the spectra in the semi-dilute regime.

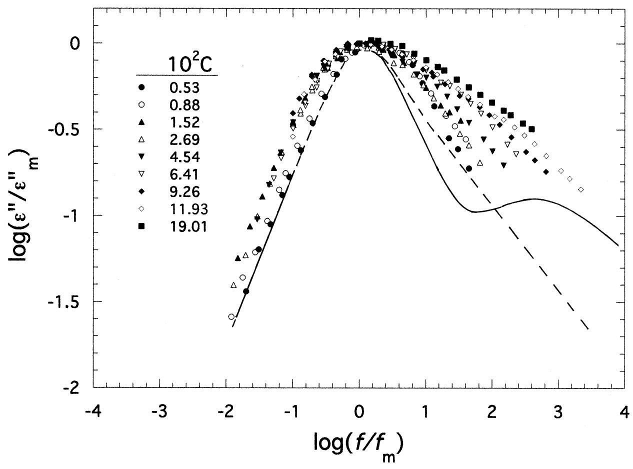

Fig. 10. Double logarithmic plots of $\varepsilon''/\varepsilon''_m$ against f/f_m for examination of the concentration dependence of the shape of the loss curve. Here suffix m indicates the maximum of loss. The dashed line indicate the Zimm theory and the solid line, the Muthukumar–Freed theory.

3.8. Relaxation strength

For type A polymers, the relation between the dielectric relaxation strength $\Delta\varepsilon$ and the mean square end-to-end distance $\langle r^2\rangle$ is given by

$$\frac{\Delta\varepsilon}{C} = \frac{4\pi N_A \mu^2 \langle r^2\rangle F}{3k_B TM} \qquad \text{(in cgs esu unit)} \qquad (10)$$

where μ is the dipole moment per unit contour length, N_A, Avogadro's constant, F, the ratio of the internal and external electric fields. Stockmayer and Baur [18] proposed that F is given by

$$F = \frac{(\varepsilon + 2)^2}{9} \qquad (11)$$

where ε is the dielectric constant of the solvent. We expect that F for the normal mode relaxation is close to unity since the local inhomogeneity of electric field smeared out in the scale of the end-to-end distance of the polymers chains. This was experimentally tested [34]. Recently we calculated μ of PLA to be $1.37 \pm 0.01 \times 10^{-11}$ esu based on the semi-empirical molecular orbital theories [24]. From this value and the assumption of $F = 1$, the average end-to-end distance $\langle r^2\rangle^{0.5}$ of PLA119 in dilute solution becomes 102 nm at 298 K. If Eq. (11) is used, $\langle r^2\rangle^{0.5}$ of PLA119 becomes 51 nm.

In the dilute solution, flexible polymer chains expand owing to the excluded volume effect: $\langle r^2\rangle \propto M^{2\nu}$. Thus, we obtain:

$$\frac{\Delta\varepsilon}{C} \propto N^{2\nu-1} \qquad (12)$$

The relaxation strength of PLA solutions increases in proportion to $M_w^{0.2}$. Because of limited frequency range of our dielectric measurement, especially for dilute solutions having a weak dielectric relaxation strength, relatively high error is accompanied in determination of $\Delta\varepsilon$. We determined $\Delta\varepsilon$ from the Cole–Cole plot. We estimate that the error in the determination of $\Delta\varepsilon$ is $\pm 10\%$.

From Eq. (2), the exponent of $(2\nu - 1)$ for PLA/benzene dilute solution was determined to be 0.19. Fig. 11(a) shows the M_w dependence of $(\Delta\varepsilon/C)$ for PLA/benzene dilute solutions. The solid line indicates the theoretical prediction from Eq. (12) with the slope of 0.12. We can see that within the error, our result agrees with the theory.

Fig. 11(b) shows the concentration dependence of $\Delta\varepsilon$ for PLA75/benzene solutions. With increasing concentration, $\Delta\varepsilon$ decreases in the semi-dilute regime, where the chains

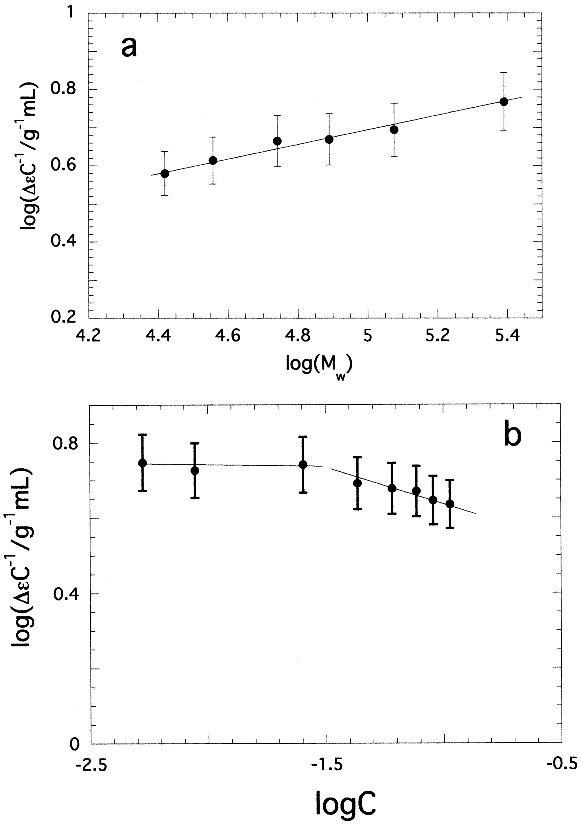

Fig. 11. (a) Double logarithmic plots of $\Delta\varepsilon/C$ against M_w for dilute solutions of PLA at 298 K. (b) Double logarithmic plots of $\Delta\varepsilon/C$ against C for semi-dilute solutions of PLA at 298 K.

overlap each other, and hence the excluded volume effect is partially screened. According to Daoud and Jannink [35], the M_w and concentration dependence of $\langle r^2 \rangle$ in semi-dilute regime is given by

$$\langle r^2 \rangle \propto C^{(2\nu-1)/(1-3\nu)} \tag{13}$$

From this equation ($\langle r^2 \rangle/M_w$) is expressed as a function of only the concentration C. This means that for semi-dilute solutions of PLA in benzene, we expect that the slope of the $\log(\Delta\varepsilon/C)$ vs $\log C$ is equal to $(2\nu-1)/(1-3\nu) = -0.185$. The slope of the plot shown in Fig. 11(b) is -0.185. We see that in spite of experimental errors, our data conform to the theory.

4. Conclusions

We have examined the dielectric normal mode relaxation of benzene solutions of PLA focusing our attention on the influences of the type-A1 dipole moment. The excluded volume parameter ν is determined to be 0.60 from the molecular weight dependence of the intrinsic viscosity. In dilute solutions, the dielectric relaxation time τ_n is found to be proportional to $M^{1.82}$ ($\propto [\eta]M$) in agreement with the Rouse–Zimm theory. With increasing concentration the slope in the high frequency side of the $\log \varepsilon''$ vs $\log f$ curve changes from -0.62 to -0.25 but that in the low frequency side does not change keeping the slope of unity. This behaviour is very similar to solutions of polyisoprene and poly(ε-caprolactone) which are type-A2 polymers. At present, no theories explain successfully the broadening of the spectra. The normal mode relaxation time τ_n increases with concentration and there exists a dynamical crossover concentration C_τ^* below which τ_n is independent of concentration but above which τ_n increases with concentration. The concentration dependence of τ_n in solutions of PLA with high molecular weight is ascribed to both the intermolecular hydrodynamic interactions and entanglements. It is found that the $\log \tau_n$ is linear to concentration C in agreement with the Muthukumar–Freed theory. The relaxation time is corrected to the iso-friction state $\tau_{n\zeta}$ and the concentration dependence of $\tau_{n\zeta}$ agrees approximately with the dynamic scaling theory proposed by De Gennes. The mean square end-to-end distance $\langle r^2 \rangle$ is determined from the relaxation strength. In dilute solution, $\langle r^2 \rangle$ increases with M_w with the power of 0.2 in agreement with the theory. The concentration dependence of $\Delta\varepsilon$ for PLA75/benzene solutions. With increasing concentration, $\Delta\varepsilon$ decreases in the semi-dilute solution regime. We conclude that the behaviour agrees with the scaling theory proposed by Daoud and Jannink.

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References

[1] Stockmayer WH. Pure Appl Chem 1967;15:539.
[2] Adachi K, Kotaka T. Prog Polym Sci 1993;18:585.
[3] Adachi K. In: Runt JP, Fitzgerald JJ, editors. Dielectric spectroscopy of polymeric materials. Washington, DC: American Chemical Society; 1997. Chapter 9.
[4] Jones AA, Stockmayer WH, Molinari RJ. J Polym Sci, Polym Symp 1976;54:227.
[5] Urakawa O, Adachi K, Kotaka T, Takemoto Y, Yasuda H. Macromolecules 1994;27:7410.
[6] Flory PJ, Williams AD. J Polym Sci, A2 1967;5:399.
[7] Adachi K, Kotaka T. Macromolecules 1983;16:1936.
[8] North AM, Phillips PJ. Trans Faraday Soc 1968;64:3235.
[9] Uzaki S, Adachi K, Kotaka T. Macromolecules 1988;21:153.
[10] Adachi K, Kotaka T. Macromolecules 1987;20:2018.
[11] Adachi K, Kotaka T. Macromolecules 1988;21:157.
[12] Adachi K, Imanishi Y, Shinkako T, Kotaka T. Macromolecules 1989;22:2391.
[13] Adachi K, Imanishi Y, Kotaka T. J Chem Soc, Faraday Trans 1 1989;85:1065.
[14] Urakawa O, Adachi K, Kotaka T. Macromolecules 1994;27:7410.
[15] Adachi K, Kotaka T. Macromolecules 1988;21:157.
[16] Zimm BH. J Chem Phys 1956;24:269.
[17] Rouse PE. J Chem Phys 1953;21:1272.
[18] Stockmayer WH, Baur ME. J Am Chem Soc 1964;86:3485.

[19] De Gennes PG. Scaling concepts in polymer physics. London: Cornell University Press; 1979. Chapter 8.
[20] Ajioka M, Enomoto K, Suzuki K, Yamaguchi A. Bull Chem Soc Jpn 1995;68:2125.
[21] Imanishi Y, Adachi K, Kotaka T. J Chem Phys 1988;89:7585.
[22] Ren J, Urakawa O, Adachi K. in preparation.
[23] Zimm BH, Roe GL, Epstein LF. J Chem Phys 1956;24:279.
[24] Ferry JD. Viscoelastic properties of polymers. New York: Wiley; 1961. Chapter 10.
[25] Ren J, Urakawa O, Adachi K. Macromolecules, in press.
[26] Muthukumar M, Freed KF. Macromolecules 1978;11:843.
[27] Muthukumar M. Macromolecules 1984;17:971.
[28] Patel SS, Takahashi KM. Macromolecules 1992;25:4382.
[29] Baysal B, Stockmayer WH. J Mol Liq 1993;56:175.
[30] De Gennes PG. Macromolecules 1976;9:594.
[31] Berry GC, Fox TG. Adv Polym Sci 1974;16:1.
[32] De Gennes PG. J Chem Phys 1971;55:572.
[33] Ngai KL, Rajagopal AK, Teitler SJ. Chem Phys 1988;88:6088.
[34] Adachi K, Okazaki H, Kotaka T. Macromolecules 1985;18:1486.
[35] Daoud M, Jannink G. J Phys (Paris) 1976;37:973.