Dielectric Normal Mode Relaxation of Poly(lactone)s in Solution

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ABSTRACT: We studied the dielectric normal mode relaxation in dilute and semidilute solutions of poly(ϵ-caprolactone) (PCL) and poly(δ-valerolactone) (PVL) in benzene using narrow distribution samples prepared with an initiator of a lanthanoid complex. The effect of long nonpolar groups separating the polar ester groups on the dielectric behavior was investigated by comparing the present results with those for *cis*-polyisoprene (PI) solutions reported previously. In dilute solutions, the longest relaxation time τ for both PCL and PVL increased in proportion to $M^{1.63\pm0.03}$. The double-logarithmic plots of τ *vs* $[\eta]\eta_s M/RT$ for the dilute solutions as well as those of PI fell on the same universal straight line irrespective of the solvent quality. Here $[\eta]$ and η_s are the intrinsic viscosity and the solvent viscosity, respectively. The dielectric loss factor ϵ'' *vs* frequency f curves for the dilute PCL and PVL solutions agreed with the Zimm theory. In the semidilute solutions, log τ increased linearly with respect to C as predicted by the Muthukumar−Freed theory. The ϵ'' curve broadened with C as observed previously for PI semidilute solutions. The dynamical behavior is independent of the local structure. The dielectric relaxation strength $\Delta\epsilon$, which is proportional to the mean square end-to-end distance $\langle r^2\rangle$, increased with M in dilute solution but decreased with C above the overlap concentration.

I. Introduction

Since the pioneering work by Stockmayer and coworkers[1−4] on dielectric normal mode relaxations of poly(propylene oxide)[2,3] and poly(ϵ-caprolactone) (PCL),[4] the dielectric behavior of several other *type-A* polymers possessing monomeric dipoles aligned in the same direction parallel along the chain contour have been reported.[5] They are polychloroprene,[6] poly(dichloro-1,4-phenylene oxide),[7−9] *cis*-polyisoprene (PI),[10−13] poly(phenoxyphosphazene),[14] and poly(phenylacetylene).[15] Among these polymers, we have extensively studied narrow molecular weight distribution (MWD) PI chains in bulk and in solution over wide ranges of concentration and molecular weight (MW) as well as those in blends with PI and polybutadiene (PB) and block copolymers with PB and polystyrene (PS).[5,10−12]

Examining the chemical structure of these type-A polymers, we notice that the type-A polymers can be further classified into three subtypes, as schematically shown in Figure 1,[16] according to the configuration of the dipole vectors on the backbone. Here the arrows indicate polar bonds and the dashed lines nonpolar bonds. Type-A1 polymers (intrinsic type-A polymers) belong to an ideal type-A polymer in which all bonds are equivalent carrying the same dipole moment. Thus the end-to-end vector $\mathbf{r}$ is always proportional to the vector sum of the monomer dipoles, $\sum\mathbf{m}_A$, which is in turn equal to the overall type-A dipole vector $\mathbf{P}_A$:

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

with the moment per unit contour length μ being a constant.

Type-A2 polymers (type-A/non-type-A alternating polymers) include aliphatic polyesters having the structure $[-OCO(CH_2)_n-]$. Poly(ϵ-caprolactone) (PCL) ($n = 5$) and poly(valerolactone) (PVL) ($n = 4$) are typical polyesters and have relatively long methylene bonds between the polar ester groups. In such polymers, the end-to-end vector $\mathbf{r}$ is not always proportional to $\sum\mathbf{m}_A = \mathbf{P}_A$. In other words, the directions of two vectors do not coincide and μ is thus not a constant but might be configuration dependent. Nevertheless, PCL exhibits normal mode relaxation as reported by Jones, Stockmayer, and Molinari.[4] This fact implies that the time averages of $\mathbf{P}_A$ and $\mathbf{r}$ taken over a period much longer than that of the segmental motion but much shorter than the time scale of the reorientation of the end-to-end vector $\mathbf{r}$ are correlated with each other.

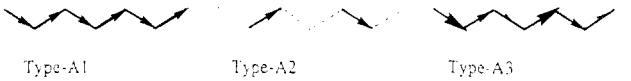

Figure 1. Schematic representation of three types of type-A chains. The arrows indicate dipole vectors and the dashed lines the nonpolar bonds.

How does the local chemical structure affect the normal mode relaxation? The behavior of these other type-A polymers has not been fully investigated due mainly to the difficulty in synthesizing narrow MWD samples. In fact, comparison among the dielectric data of type-A2 polymers of broad MWD samples is somewhat ambiguous. For example, the dielectric loss ϵ'' curve of PCL reported by Jones *et al.* is much broader than that reported for narrow MWD PI. Is this totally due to the difference in MWD or due to the difference in the local structure? Recently, one of us (H.Y.) found a novel lanthanoid catalyst with which narrow MWD samples of polymethacrylates and polyesters can be prepared.[17−19] In this study we thus reexamined the dielectric relaxation of dilute and semidilute solutions of PCL and PVL using these narrow MWD samples. Our objective is to clarify the MW and concentration dependences of the longest relaxation time and the distribution of relaxation times.

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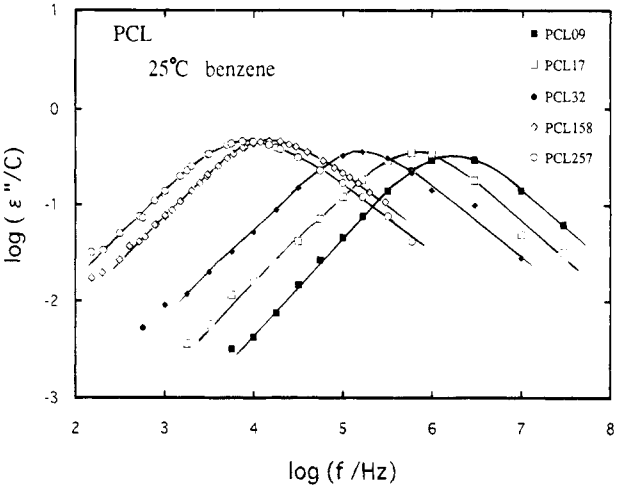

Figure 2. Double-logarithmic plots of dielectric loss ϵ'' divided by concentration C *vs* frequency f for dilute solutions of PCL in benzene at 298 K. The sample code indicates M_w in kg/mol.

Table 1. Characteristics of PCL and PVL

code	$10^{-3}M_w$	M_w/M_n	$[\eta]$/(g mL^{-1})
PCL09	9.12	1.07	25.4
PCL17	16.6	1.09	37.4
PCL38	38.0	1.09	(65.7)
PCL158	158	1.09	170
PCL257	257	1.10	223
PVL14	13.9	1.08	22.0
PVL24	23.8	1.07	29.8
PVL38	38.0	1.07	44.2

II. Experimental Section

PCL and PVL samples with narrow MWD were prepared by using a lanthanoid catalyst as described previously.[17-19] The weight- and number-average molecular weights, M_w and M_n, were determined on a gel permeation chromatograph equipped with a low-angle light scattering detector. Intrinsic viscosities $[\eta]$ were determined at 298 K in benzene with a Ubbelohde type viscometer. The results were cast into the Mark–Houwink–Sakurada equation:[20]

$$[\eta] = 6.4 \times 10^{-2} M_w^{0.66} \quad \text{for PCL/benzene} \qquad (2)$$

$$[\eta] = 3.0 \times 10^{-2} M_w^{0.69} \quad \text{for PVL/benzene} \qquad (3)$$

where the unit of $[\eta]$ is mL/g. For the benzene solution of PCL, Jones *et al.*[4] reported the M dependence of $[\eta]$, which agrees with eq 2 within 15%. The characteristics of the PCL and PVL samples are listed in Table 1, in which the code number indicates M_w in kg/mol.

Dielectric measurements were carried out with a capacitance bridge (General Radio 1615A), an LCR meter (Hewlett-Packard 4284A), and a twin-T type bridge (Fujisoku DLB 1101D), covering the frequency ranges of 20 Hz to 20 kHz, 10–300 kHz, and 1–100 MHz, respectively. The details were described previously.[10,21,22]

1. Relaxation Time in Dilute Solutions. Figure 2 shows double-logarithmic plots of the dielectric loss factor ϵ'' divided by mass concentration C (g/mL) *vs* frequency f for dilute solutions of five PCL samples in benzene at 25 °C. The concentration was regulated to be less than the overlap concentration $C^* \simeq 1/[\eta]$. Similar plots for dilute solutions of three PVL samples are shown in Figure 3. In both figures we see the typical behavior of the normal mode process: The loss maximum frequency f_m shifts to the low-frequency side with increasing MW.

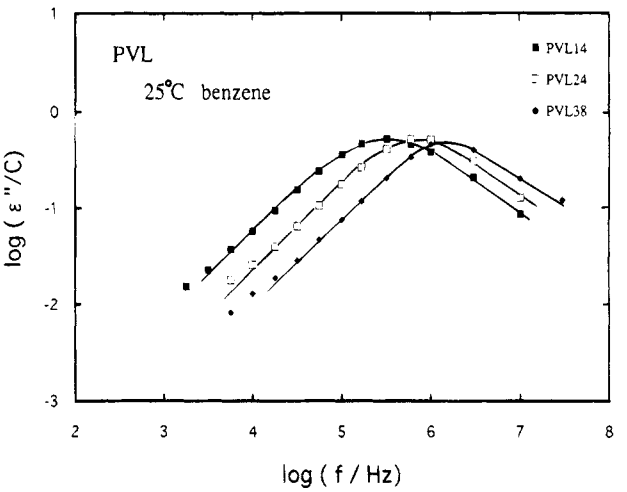

Figure 3. Double-logarithmic plot of ϵ''/C vs f for dilute solutions of PVL in benzene at 298 K.

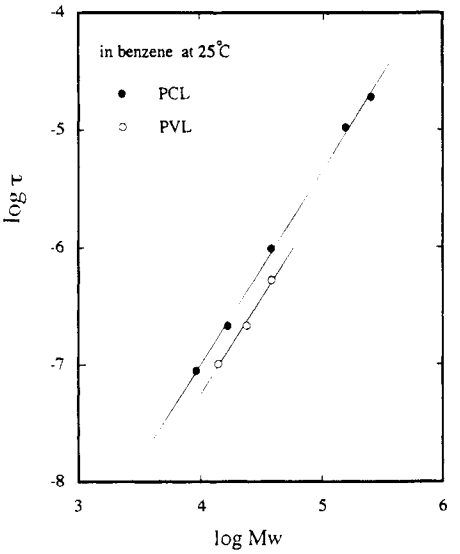

Figure 4. Molecular weight M_w dependence of the longest relaxation times τ in dilute solutions of PCL and PVL.

As has been frequently pointed out,[4,22] the nominal relaxation time τ determined as $\tau = 1/(2\pi f_m)$ for the normal mode of narrow MWD samples is close to the longest relaxation time τ_1, because for the dielectric normal modes only the odd-numbered (p = 1, 3, 5, ...) modes are active, with their intensity decreasing roughly in proportional to p^{-2}. As long as $C \ll C^*$, τ thus determined is independent of C. Figure 4 shows a double-logarithmic plot of τ against M_w. The slopes of the straight lines for PCL and PVL solutions are 1.63 ± 0.03.

According to the nondraining bead–spring model proposed by Zimm, the theoretical τ for the pth normal mode is given by[23]

$$\tau_p = \pi^{3/2}\eta_s b^3 N^{3/2}/(12^{1/2}k_B T\lambda_p) \quad (p \text{ odd}) \qquad (4)$$

where η_s is the solvent viscosity; b, the average distance between beads; N, the number of beads; and λ_p, the pth eigenvalue tabulated by Zimm *et al.*[24] The Zimm model predicts $\tau_1 \propto M^{1.5}$. On the other hand, the free-draining Rouse model[25] predicts M^2. It is noted that eq 4 is derived for a Gaussian chain and hence, strictly speaking, eq 4 is applicable only to a Θ solvent system. From the exponents of the Mark–Houwink–Sakurada equation, the Flory exponents ν are estimated to be 0.55 and

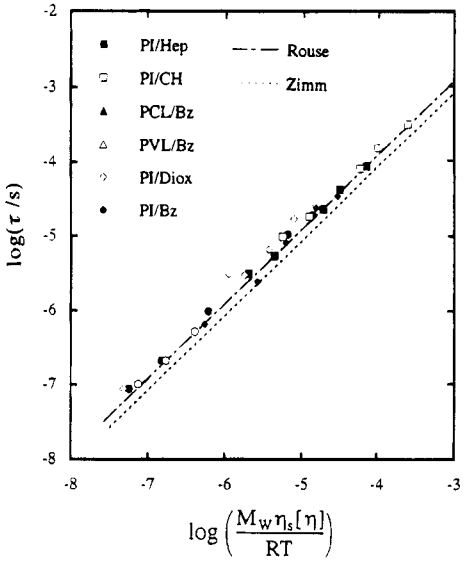

Figure 5. Double-logarithmic plots of τ *vs* $M\eta_s[\eta]/RT$ for dilute solutions of PCL/Bz, PVL/Bz, PI/Bz, PI/CH, PI/Hep, PI/Diox, poly(phenoxyphosphazene)/Bz, and poly(propylene oxide)/Bz.

0.56, respectively, for PCL and PVL solutions. Benzene is thus a marginal solvent for PCL and PVL. However, for such systems plausible models of polymer dynamics are not yet available.

To include the excluded volume effect empirically, we rewrite eq 4 as

$$\tau_1 = KM[\eta]\eta_s/RT \tag{5}$$

where K is a constant and RT is the thermal energy. This equation has been used to understand the viscoelastic behavior of dilute solutions[26-28] and also the dielectric behavior of PCL by Jones *et al.*[4] The front factor K is equal to $12/\pi^2$ (=1.22) for the free-draining Rouse model[25] and 0.85 for the nondraining Zimm model.[23] It is noted that K for the viscoelastic relaxation time becomes half of these values. In Figure 5, the observed τ are replotted against $M_w[\eta]\eta_s/RT$. For comparison, this figure also includes the data for dilute solutions of PI in benzene (Bz; good solvent),[11] cyclohexane (CH; good),[10] heptane (Hep; marginal),[10] and dioxane (Diox; Θ solvent).[11] Interestingly all data points fall approximately on the same straight line of the slope of unity and $K = 1.4 \pm 0.3$. This value agrees with K for dioxane solutions of PCL reported by Jones *et al.*[4] This result is also consistent with that of the viscoelastic relaxation of infinitely dilute polymer solutions:[26-28] Sakanishi[26] and Osaki *et al.*[27,28] indicated that the bead–spring model explains well the reduced shear moduli *vs* $\omega[\eta]\eta_sM/RT$ curve.

2. Semidilute Solutions: Relaxation Time. Figure 6 shows ϵ'' curves of semidilute PCL158/benzene solutions in the regime of $C > C^*$. The loss maximum frequency f_m shifts to the low-frequency side and the peak value ϵ''_{max} increases with increasing C as observed for PI solutions.[10,11] Furthermore, we note that the shape of the ϵ'' curve broadens on the high-frequency side of the loss peak with increasing C.

Figure 7 shows the log τ *vs* C plot for PCL158 solutions. We see that the plot conforms well to a straight line. This behavior agrees with the previous results reported by Jones *et al.*,[4] Patel and Takahashi,[29] and ourselves,[10,11] who reported that the C dependence

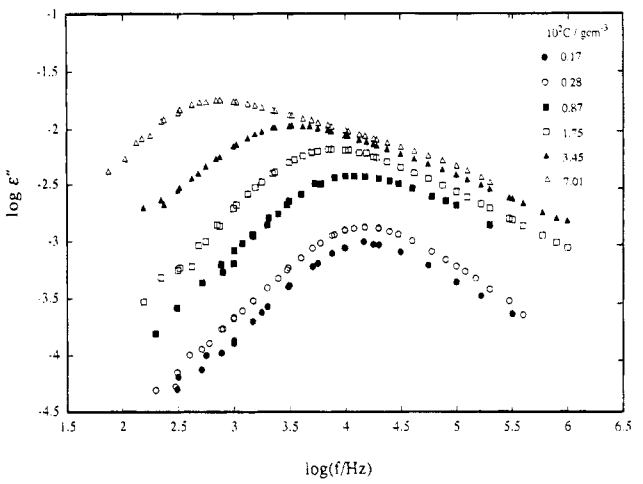

Figure 6. Concentration C dependence of ϵ'' curves for benzene solutions of PCL158 at 298 K.

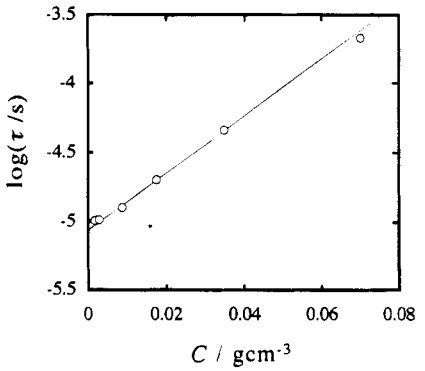

Figure 7. log τ *vs* C plot for PCL158/benzene solutions.

of τ for PI solution can be cast into

$$\tau = \tau_1^\circ \exp(A'C[\eta]) \tag{6}$$

where τ_1° is the relaxation time for the first mode at infinite dilution and A' is a constant independent of M_w. Muthukumar and Freed[30,31] proposed a C dependence of the relaxation time τ_p for the pth mode, considering intermolecular hydrodynamic interactions:

$$\tau_p = \tau_p^\circ[1 + CAp^{-k} - 2^{1/2}(CAp^{-k})^{1.5} + 2(CAp^{-k})^{2.0} + ...] \tag{7}$$

where A is another constant proportional to $[\eta]$ and $k = 3\nu - 1$. For the first mode, this equation reduces to eq 6 with $A = A'[\eta]$, when C is sufficiently low. In semidilute PI solutions, A' was found to be 0.29, irrespective of MW and solvent quality.[10,26]

For the present PCL/benzene solutions, A' was determined to be 0.26. Jones *et al.* reported previously that A' for dioxane solutions of PCL is 0.21 ± 0.06.[4] Baysal and Stockmayer[32] carried out dielectric measurements on a PCL/poly(4-chlorostyrene) (PCST)/dioxane ternary system in which PCL was used as a dielectric probe. They found the C dependence of τ as

$$\log \tau = \log \tau_0 + B(C_1[\eta]_1 + C_2[\eta]_2) \tag{8}$$

where the subscripts 1 and 2 denote PCL and PCST, respectively. The factor B was determined to be 0.35, which is slightly larger than A' for the binary systems.

3. Distribution of Relaxation Times. In this section we discuss the distribution of relaxation times of the dilute and semidilute benzene solutions. Figure

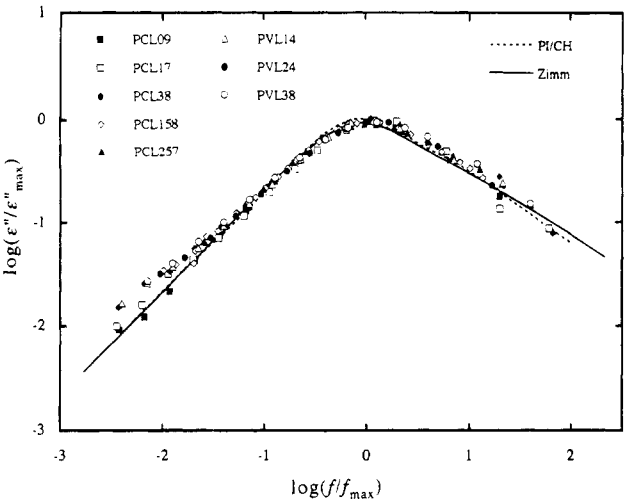

Figure 8. Normalized ϵ'' curves for dilute solutions of PCL and PVL in benzene. The dashed line indicates the data for cyclohexane solutions of polyisoprene and the solid line Zimm theory.[23]

8 is a replot of the dilute solution data shown in Figures 2 and 3 in the double-logarithmic form of $\epsilon''/\epsilon''_{max}$ *vs* f/f_m. Here ϵ''_{max} indicates the peak value of ϵ''. The dashed line indicates the data for dilute cyclohexane solutions of PI, and the solid line, the theoretical curve calculated from the Zimm theory.[23] The data points for the samples with various MW fall approximately on a single curve, indicating that the distribution of relaxation times in dilute solution does not depend either on MW or on the chemical structure of the polymer.

As pointed out previously, the ϵ'' curve of dilute solutions of PI conforms well to the Zimm theory.[10,11] We thus conclude that the ϵ'' curve of dilute solution agrees with the Zimm theory irrespective of the chemical structure of the monomeric unit for flexible polymers.

To see the broadening of the ϵ'' curve with increasing C, we produced in Figure 9 the normalized ϵ'' curves for the PCL158 solutions shown in Figure 6. It is seen that the slope κ on the high-frequency side decreases with increasing C and approaches the bulk PI data. This behavior is the same as that for PI solutions, for which we demonstrated that κ is given by a universal function of $C[\eta]$ regardless of the sample MW. From the data shown in Figure 9, κ at $C[\eta] = 11.9$ ($C = 0.07$) is -0.28, which agrees with $\kappa = -0.29$ in PI/heptane solutions with $C[\eta] = 12$.[10] This indicates again that the shape of the ϵ'' curves that reflects the mode distribution for the global motions is not affected by the local chemical structure.

The origin of the broadening must be ascribed to the onset of some kind of intermolecular interactions. The Muthukumar theory (eq 7) explains qualitatively the broadening of the ϵ'' curve. The theory predicts the ratio of τ_1/τ_p increases in proportion to $(1 + CA + ...)/(1 + CAp^{-k} + ...)$ and hence the separation between τ_1 and τ_p increases with increasing C.

In Figure 9, we compare quantitatively the ϵ'' curves with the Muthukumar theory. Here we took into account the distribution of MW assuming the Zimm–Schultz distribution function.[33] As shown in this figure the observed curve at $C[\eta] = 3$ agrees fairly well with the theoretical prediction (dashed line). However, in the range of $C[\eta] > 6$ the observed ϵ'' curves become broader than the theoretical ones as C is increased. The calculation of the Muthukumar–Freed theory was performed for the relaxation modes related to the viscosity, and therefore the theory may be insufficient in the explanation of the distribution of dielectric relaxation times. The mode–mode coupling effect as proposed by de Gennes[34] might be the other source of the disagreement between the theory and experiments.

4. Relaxation Strength. Now we turn our attention to the problem of the relaxation strength $\Delta\epsilon$, which is proportional to the mean square end-to-end distance $\langle r^2\rangle$. We have proposed the possibility that through measurements of $\Delta\epsilon$ of a type-A chain, $\langle r^2\rangle$ can be determined by

$$\frac{\Delta\epsilon}{C} = \frac{4\pi N_A \mu^2 \langle r^2\rangle}{3Mk_B T} F \tag{9}$$

where N_A is Avogadro's constant; and F, the ratio of the internal to external electric field being equal to one.

We determined $\Delta\epsilon/C$ from the area under the ϵ'' curve:[35]

$$\Delta\epsilon = (2/\pi)\int_{-\infty}^{\infty} \epsilon'' \, d \ln \omega \tag{10}$$

For calculation of eq 10, we need the ϵ'' data over the full range of frequency. Due to the limitation of the experimental window of frequency, we used a linear extrapolation of the log ϵ'' *vs* log f curve using the slope κ of the high-frequency tail discussed in the previous section. Figure 10 shows the MW dependence of $\Delta\epsilon/C$ for dilute PCL/benzene solutions. The slope of the $\langle r^2\rangle/M$ *vs* M plot is 0.11. The weak MW dependence of $\Delta\epsilon/C$ reflects the MW dependence of $\langle r^2\rangle$. On the other hand, from the MW dependence of $[\eta]$ for PCL ($\propto M_w^{0.66}$) and for PVL ($\propto M_w^{0.69}$), we expect that the Flory excluded volume exponent $\nu = 0.55$ and 0.56 for PCL and PVL,

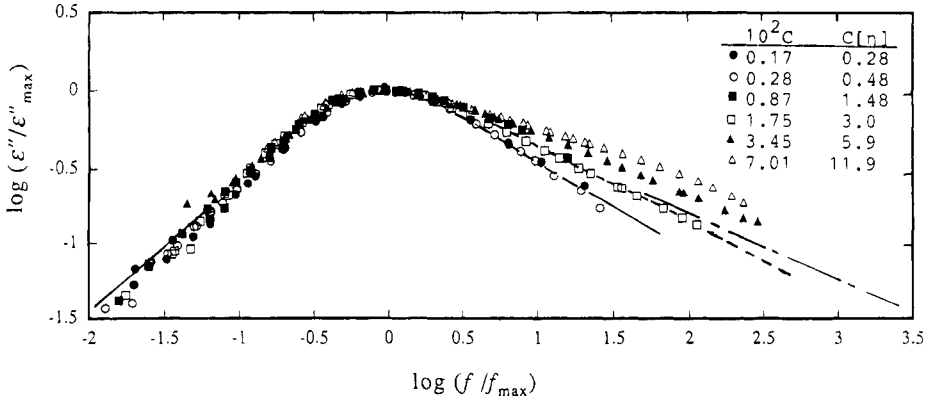

Figure 9. Normalized ϵ'' curves for PCL/benzene solutions. The concentrations C and the values of $C[\eta]$ are indicated in the figure. The solid, dashed, and dash–dot lines represent the Muthukumar theory for $C[\eta] = 0$, 3, and 6, respectively.

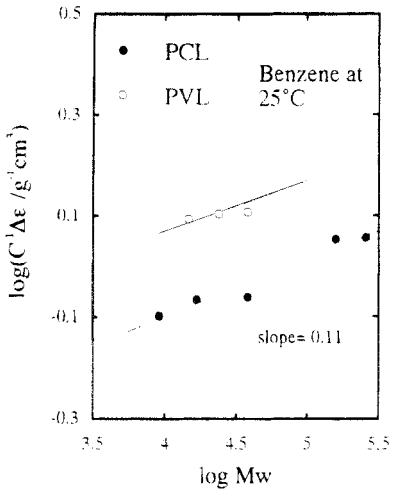

Figure 10. M_w dependence of $\Delta\epsilon/C$ for benzene solutions of PCL and PVL.

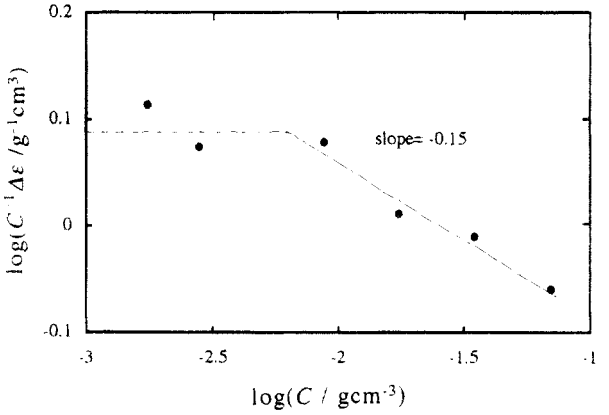

Figure 11. Concentration dependence of $\Delta\epsilon/C$ for the PVL158/benzene system.

respectively. Thus the slopes of $\log\langle s^2\rangle/M$ *vs* $\log M_w$ for PCL and PVL solutions are expected to be 0.13 and 0.14, respectively, consistent with the observation.

Figure 11 shows the C dependence of $\Delta\epsilon/C$ for PCL158/benzene solutions. We see $\Delta\epsilon/C$ decreases with increasing C. For semidilute solutions the increase in C results in the shielding of the excluded volumes. According to the scaling theory of Daoud and Jannink,[35] the C dependence of $\langle r^2\rangle$ can be expressed by

$$\langle r^2\rangle = \langle r^2\rangle_0[C/C^*]^{-(2\nu-1)/(3\nu-1)} \qquad (11)$$

In Figure 11, we see that the slope of the straight line for $C > C^*$ is -0.15, which corresponds to $\nu = 0.55$. This value of ν agrees with that determined from $[\eta]$. The same behavior was observed in semidilute solutions of PI. Therefore we may conclude that the nonpolar bonds of the PCL chain do not influence the relaxation strength.

Conclusion

1. Dielectric normal mode relaxation times τ of poly(ϵ-caprolactone) (PCL) and poly(δ-valerolactone) (PVL) in dilute benzene solution increase with molecular weight M_w with the power of 1.63 ± 0.3.

2. With increasing concentration C, $\log\tau$ increases linearly with respect to $C[\eta]$. The slope is 0.26 for benzene solutions of PCL.

3. In dilute solution, the dielectric loss curve conforms to the Zimm theory but it broadens with increasing C. The shape of the loss curve is explained with the Muthukumar theory for $C < 3C^*$ but fails beyond this concentration.

4. The relaxation strength $\Delta\epsilon$ increases with M_w in dilute solution due to the excluded volume effect. In semidilute solutions of PCL with $M_w = 158 \times 10^3$, $\Delta\epsilon$ decreases with increasing C.

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References and Notes

(1) Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539.
(2) Baur, M. E.; Stockmayer, W. H. *J. Chem. Phys.* **1965**, *43*, 4319.
(3) Burke, J. J.; Stockmayer, W. H. *Macromolecules* **1969**, *2*, 647.
(4) Jones, A. A.; Stockmayer, W. H.; Molinari, R. J. *J. Polym. Sci., Polym. Symp.* **1976**, *No. 54*, 227.
(5) Adachi, K.; Kotaka, T. *Prog. Polym. Sci.* **1993**, *18*, 585.
(6) Adachi, K.; Kotaka, T. *Macromolecules* **1985**, *18*, 294.
(7) Adachi, K.; Kotaka, T. *Macromolecules* **1983**, *16*, 1936.
(8) Adachi, K.; Kotaka, T. *Polym. J.* **1986**, *18*, 315.
(9) Adachi, K.; Kotaka, T. *Polym. J.* **1986**, *18*, 371.
(10) Urakawa, O.; Adachi, K.; Kotaka, T. *Macromolecules* **1993**, *26*, 2036, 2042.
(11) Adachi, K.; Kotaka, T. *Macromolecules* **1988**, *21*, 157.
(12) Adachi, K.; Imanishi, Y.; Shinkado, T.; Kotaka, T. *Macromolecules* **1989**, *22*, 2391.
(13) Adachi, K.; Imanishi, Y.; Kotaka, T. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1065.
(14) Uzaki, S.; Adachi, K.; Kotaka, T. *Macromolecules* **1988**, *21*, 153.
(15) North, A. M.; Phillips, P. J. *Trans. Faraday Soc.* **1968**, *64*, 3235.
(16) Urakawa, O.; Adachi, K.; Kotaka, T. *Rep. Prog. Polym. Phys. Jpn.* **1993**, *36*, 113.
(17) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908.
(18) Yasuda, H.; Yamamoto, H.; Yamashita, M.; Yokota, K.; Nakamura, A.; Miyake, S.; Kai, Y.; Kanehisa, N. *Macromolecules* **1993**, *26*, 7134.
(19) Yasuda, H.; Tamai, H. *Prog. Polym. Sci.* **1993**, *18*, 1097.
(20) Kurata, M.; Stockmayer, W. H. *Adv. High Polym. Phys.* **1963**, *3*, 196.
(21) Adachi, K.; Okazaki, H.; Kotaka, T. *Macromolecules* **1985**, *18*, 1486.
(22) Imanishi, Y.; Adachi, K.; Kotaka, T. *J. Chem. Phys.* **1988**, *89*, 7585.
(23) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(24) Zimm, B. H.; Roe, G. R.; Epstein, L. F. *J. Chem. Phys.* **1956**, *24*, 279.
(25) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(26) Sakanishi, A. *J. Chem. Phys.* **1968**, *48*, 3850.
(27) Osaki, K.; Schrag, J. L.; Ferry, J. D. *Macromolecules* **1972**, *5*, 144.
(28) Osaki, K.; Mitsuda, Y.; Johnson, R. M.; Schrag, J. L.; Ferry, J. D. *Macromolecules* **1972**, *5*, 17.
(29) Patel, S. S.; Takahashi, K. M. *Macromolecules* **1992**, *25*, 4382.
(30) Muthukumar, M.; Freed, K. F. *Macromolecules* **1978**, *11*, 843.
(31) Muthukumar, M. *Macromolecules* **1984**, *17*, 971.
(32) Baysal, B.; Stockmayer, W. H. *J. Mol. Liquids* **1993**, *56*, 175.
(33) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099.
(34) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(35) See for example: Hill, N. E.; Vaugham, W. E.; Price, A. H.; Davies, M. *Dielectric Properties and Molecular Behavior*; Van Nostrand Reinhold: London, 1969.
(36) Daoud, M.; Jannink, G. *J. Phys. (Paris)* **1976**, *37*, 973.