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Effect of Local Heterogeneity on Dielectric Relaxation Spectra in Concentrated Solutions of Poly(vinyl acetate) and Poly(vinyl octanoate)

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ABSTRACT: The effect of local heterogeneity on the distribution of dielectric relaxation times was studied for concentrated solutions of poly(vinyl acetate) (PVAc) in 1-methylnaphthalene (MN) and those of poly(vinyl octanoate) (PVOc) in toluene (Tol). The half-widths Λ of the dielectric loss curves for the primary processes of those systems are compared with those of the PVAc/Tol system reported previously. The data indicate that Λ decreases in order of PVAc/Tol, PVAc/MN, and PVOc/Tol systems if compared at the same temperature T/T_g where T_g denotes the glass transition temperature of solutions. The half-width of each solution increases with decreasing temperature. The loss curve is calculated by assuming a Gaussian distribution of the local concentration ϕ which results in the distribution of relaxation times $g(\tau)$. The calculated loss curves agree fairly well with the observed ones. The broadening behavior is also explained by assuming that Λ is proportional to the amplitude of the local concentration fluctuation $\Delta\phi$ times the slope of the ϕ dependence curve of the average relaxation time τ. This assumption leads to a linear relationship between Λ and $\Delta\phi/(T - T_0)^2$ where T_0 is the Vogel critical temperature. Using this relation, we have attempted to estimate $\Delta\phi$. Small-angle X-ray scattering was also measured on PVAc/MN solutions and found that the scattering intensity was lower than that for PVAc/Tol. This is consistent with the fact that Λ of PVAc/MN solutions is narrower than PVAc/Tol solutions.

Introduction

Understanding of nonexponential correlation functions for segmental motions of flexible chains is a long-lasting problem. For both isolated chains and chains in condensed states, a variety of theories predict nonexponential correlation functions on the time domain and corresponding broad relaxation spectra on the frequency domain.[1−10] Such spectra are due to the intrinsic mechanisms of polymer chain dynamics. An additional mechanism due to local heterogeneity causes distribution of relaxation times. Ediger and co-workers found that local heterogeneity affects chain dynamics even in single-component systems.[11,12] In multicomponent systems, the latter effect is enhanced due to local concentration fluctuation. Yada et al.[13] reported the effect of concentration fluctuation on the distribution of dielectric relaxation times for concentrated solutions of poly(vinyl acetate) (PVAc) in toluene (Tol). They found that the half-width (Λ) of the loss curves, which is a measure of the distribution of relaxation times, depended strongly on concentration and that Λ for concentrated solutions was much broader than those in dilute solution and in the bulk state. They also found that Λ increased with decreasing temperature. The data of small-angle X-ray scattering (SAXS) for a 30 wt % PVAc/Tol solution indicated that the correlation length in this solution was of the order of 1 nm. This means that there exist very local irregularities in configuration of the segments and the solvent molecules. Assuming a Gaussian distribution of local concentration as proposed by Zetsche and Fischer[14] for polymer blends, Yada et al.[13] explained the anomalously broad distribution of relaxation times. The correlation length in PVAc/Tol concentrated solutions was much shorter than that for a polymer blend reported by Katana et al.,[15] who explained the distribution of dielectric relaxation times by assuming a Gaussian distribution of the local concentration with the correlation length of 6−10 nm. A different approach was reported for polymer blends by Roland and Ngai, who used a Gaussian distribution of the coupling parameter n to take into account the effect of heterogeneity.[16,17]

A natural question arises whether the dielectric behavior observed in PVAc/Tol solutions (ref 13) can be generally observed in concentrated solutions of flexible polymers. To test this issue, we have carried out dielectric measurements on two systems: PVAc/1-methylnaphthalene (MN) and poly(vinyl octanoate) (PVOc)/Tol solutions. The former was used to clarify the effect of solvent and the latter the effect of chemical structure of repeat units. PVAc and PVOc have a common chemical formula $-(CH_2-CHR)_n-$, and the formulas of R for the former and the latter are given by $-O-CO-CH_3$ and $-O-CO-(CH_2)_6-CH_3$, respectively. With regard to the solvent effect, MN has a chemical structure similar to Tol. As described later, the solvent quality of MN against PVAc is also similar to Tol. Thus, we expect that the effect of the size of solvent on the local heterogeneity may be clarified. To examine the heterogeneity, we carried out measurements of small-angle X-ray scattering (SAXS) on PVAc/MN solutions and compared with the previous results for PVAc/Tol.

Experimental Section

Materials. Poly(vinyl acetate) was purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan) and was purified by conventional reprecipitation from methanol solution in water. The weight-average molecular weight M_w was determined to be 2.0×10^5 by GPC equipped with a light scattering detector. The polydispersity M_w/M_n was 1.8. The PVAc was dried under vacuum at 40 °C for 72 h. The intrinsic viscosity of the PVAc was measured with a Ubbelohde capillary viscometer to be 52 mL/g in toluene and 62 mL/g in methylnaphthalene at 25 °C. The similarity of those intrinsic viscosities indicates that the solvent quality of Tol is similar to that of MN. The viscosity-average molecular weight was calculated

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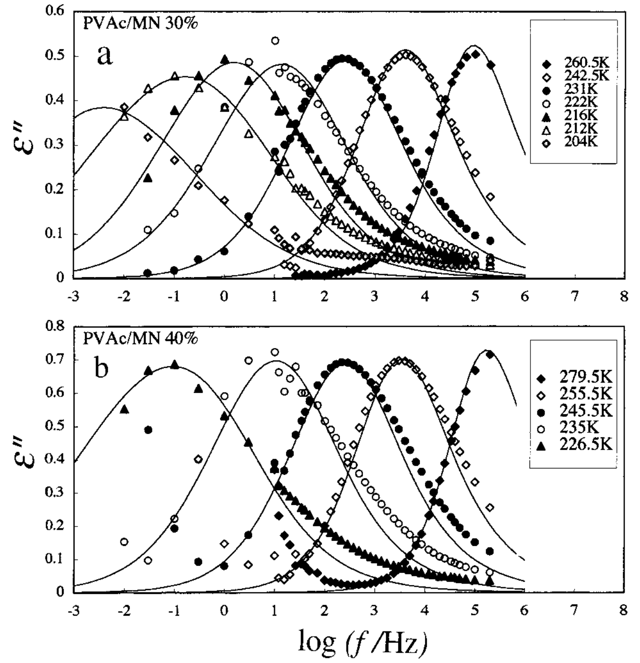

Figure 1. Frequency f dependencies of dielectric loss factor ϵ'' for 30 wt % (a) and 40 wt % (b) solutions of PVAc in methylnaphthalene. The solid lines indicate the calculated ϵ'' curves with eq 9.

to be 1.2×10^5 with the parameters of the Mark–Houwink–Sakurada equation for toluene solution reported by Moore and Murphy.[18,19]

PVOc was synthesized as follows. Vinyl octanoate monomer purchased from Wako Pure Chemical Industries Ltd. was purified by conventional distillation. Then 13 g of dehydrated benzene and 0.11 g of azobis(isobutyronitrile) (AIBN) were added to 40 g of purified monomer and allowed to polymerize at 60 °C for 48 h. The PVOc was characterized by GPC as for PVAc: $M_w = 7.3 \times 10^5$ and $M_w/M_n = 4.3$.

Solvents Tol and MN used for preparation of the sample solutions were 99.9% pure grade and purchased from Dojin Chemicals Industries Ltd. (Kumamoto, Japan). They were used as received.

Methods. Dielectric measurements were carried out in the frequency range from 0.001 to 10^8 Hz. The dielectric cell was specially designed for measurements on viscous liquids. The cross section of the cell and cryostats were reported previously.[20] Details of dielectric measurements have been described previously.[13] Measurements of small-angle X-ray scattering (SAXS) were performed by using the BL-10C beam line at the Synchrotron Radiation Facilities in the National Laboratory for High Energy Physics, Tsukuba, Japan. The q range was from 0.01 to 0.2 Å^{-1}.

Results and Discussion

Dielectric Relaxation in PVAc/MN and PVOc/Tol Solutions. Parts a and b of Figure 1 show the frequency dependencies of the dielectric loss factor ϵ'' at varying temperatures for 30 and 40 wt % solutions of PVAc in MN, respectively. Figure 2 shows the normalized plots for the data shown in Figure 1. As is seen in these figures, the half-widths Λ of the ϵ'' curves are 2.5–4 decades and are slightly narrower than Λ of PVAc/Tol solutions where Λ changed from 3 to 5 decades with decreasing temperature. For both Tol and MN solutions we see that the ϵ'' curves become broad with decreasing temperature.

Figures 3 and 4 show the ϵ'' curves of PVOc solutions in Tol with concentration ranging from 30 wt % to the undiluted state. For 5 and 10 wt % solutions the ϵ'' curves are narrow, and the shapes of the curve were similar to that for bulk PVOc (Figure 4b). As seen in those figures, the ϵ'' curves of the PVOc/Tol system do not exhibit anomalously broad distribution as observed in PVAc/Tol solutions. Figures 5 and 6 show the normalized ϵ'' curves for 30, 50, and 70 wt % solutions and undiluted PVOc. Although the ϵ'' curves of the

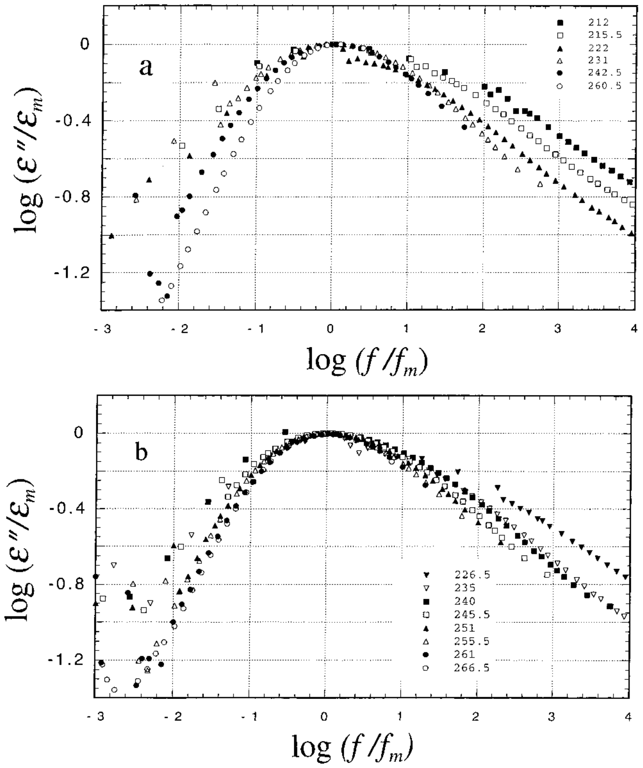

Figure 2. Normalized ϵ'' curves for 30 wt % (a) and 40 wt % (b) solutions of PVAc in methylnaphthalene. Here ϵ_m and f_m denote the maximum value of ϵ'' and the frequency at which ϵ'' becomes maximum.

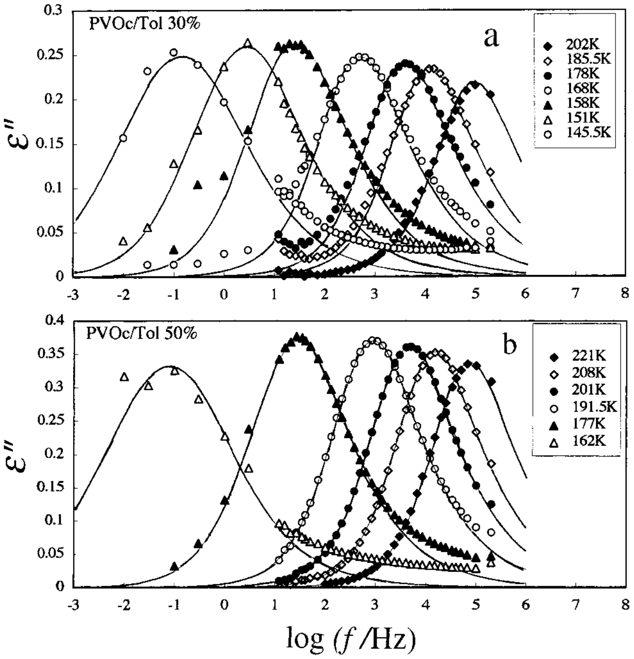

Figure 3. Dielectric loss ϵ'' curves for 30 wt % (a) and 50 wt % (b) solutions of PVOc in toluene. The solid lines indicate the calculated ϵ'' curves with eq 9.

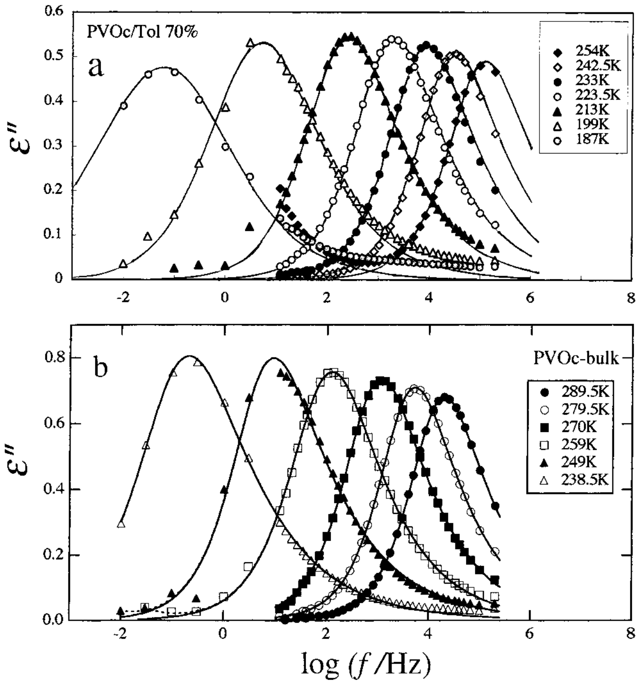

Figure 4. Dielectric loss ϵ'' curves for 70 wt % solitions of PVOc in toluene (a) and those of undiluted PVOc (b). The solid lines for 70 wt % solutions (a) indicate the calculated ϵ'' curves with eq 9. The solid lines for bulk PVOc (b) indicate the Havriliak–Negami equation calculated with $\alpha = 0.841$ and $\beta = 0.549$.

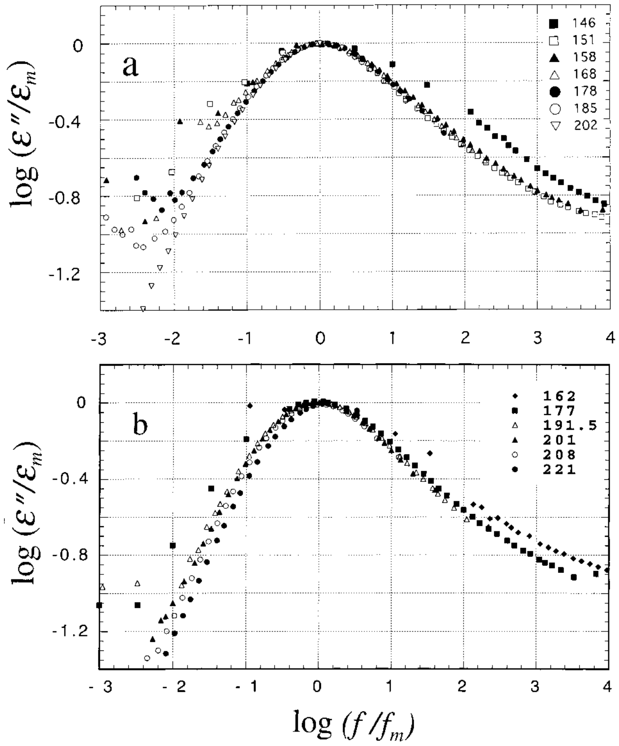

Figure 5. Normalized ϵ'' curves for 30 wt % (a) and 50 wt % (b) solutions of PVOc in toluene.

PVOc/Tol system are narrower than those of the PVAc/Tol system, the ϵ'' curves of PVOc solutions tend to broaden with decreasing temperature as seen in PVAc solutions. Thus, the broadness of the distribution of relaxation times depends on the chemical structures of the polymer and solvent, but those systems exhibit a similar temperature dependence for the broadness.

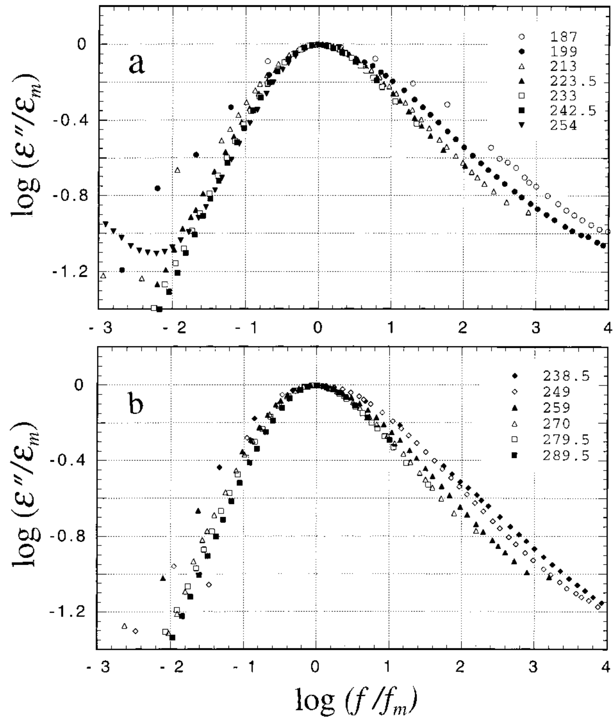

Figure 6. Normalized ϵ'' curves for 50 wt % solutions of PVOc in toluene (a) and those of undiluted PVOc.

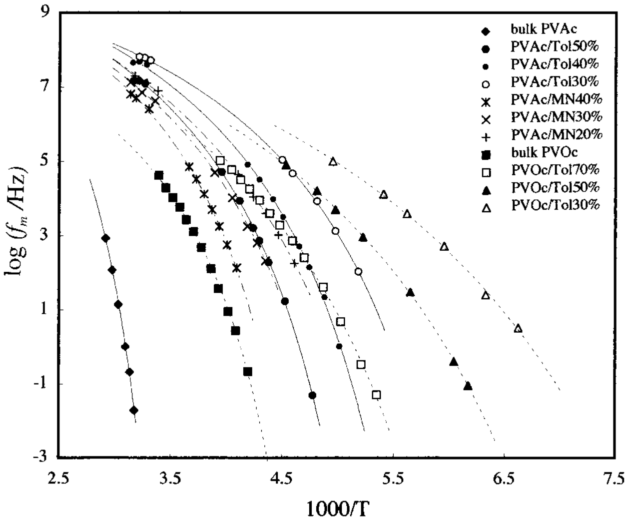

Figure 7. Arrhenius plots of the loss maximum frequency f_m for solutions and bulk PVAc and PVOc. The curves indicate eq 1 calculated with the parameters given in Table 1.

The relaxation frequencies f_m defined as the frequency at maximum loss are plotted in Figure 7. Those data are fitted to the Vogel–Fulcher equation:[21,22]

$$\log f_m = A - B/[T - T_0] \qquad (1)$$

where A, B, and T_0 are parameters. The parameters for the PVAc/MN and PVOc/Tol systems are listed in Table 1 together with those for the PVAc/Tol system which were reported previously.[13]

SAXS of PVAc Solutions. To assess the magnitude of local concentration fluctuation $\Delta\phi$, we measured small-angle X-ray scattering SAXS. Measurements were made on 30 and 40 wt % PVAc/MN solutions in the temperature range from 295 to 330 K. It was found that the intensity $I(q)$ did not change appreciably with

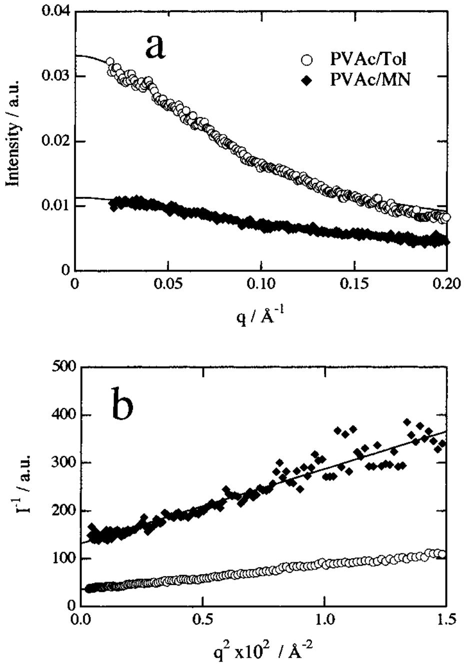

Figure 8. Comparison of the SAXS profiles between 30 wt % solutions of PVAc in methylnaphthalene and toluene at 295 K (a) and plots of the inverse of the SAXS intensity against the square of scattering vector q for 30 wt % solutions of PVAc in methylnaphthalene and toluene (b).

Table 1. Parameters of Vogel–Fulcher Equation and Glass Transition Temperatures for PVAc/1-Methylnaphthalene (MN), PVAc/Toluene (Tol), and PVOc/Tol

solution	C/wt %	C/g mL^{-1}	A	B	T_0/K	T_g/K
PVAc/MN	20	0.21	11.0	645	140	196
	30	0.32	11.0	637	154	200
	40	0.43	11.0	606	173	216
PVAc/Tol	30	0.28	12.1	840	104	160
	40	0.39	12.1	755	131	181
	50	0.50	12.1	707	154	201
PVOc/Tol	30		10.2	594	82	127
	50		10.2	631	98	146
	70		10.2	663	124	174
	100		10.2	704	171	224

temperature. The representative SAXS profile for a 30 wt % PVAc/MN solution is shown in Figure 8a and compared with that for a 30 wt % PVAc/Tol solution reported previously.[13] To determine the correlation length, we used the Ornstein–Zernike equation[23] as shown in Figure 8b where the inverse of $I(q)$ is plotted against q^2 for 30 wt % solution. As is seen in this figure, the intensity of scattering for MN solutions is lower than that for Tol solutions. The forward scattering at $q = 0$ is proportional to the number of scattering body or the amplitude of concentration fluctuation. Thus, the SAXS data indicate that the amplitude of concentration fluctuation $\Delta\phi$ in Tol solution is higher than that in MN solution. The correlation length ξ is listed in Table 2 together with the data for PVAc/Tol solutions reported previously.[13] The correlation length for MN solution is ca. 1.0 nm and is the order of the size of the monomeric unit and the solvent molecule as observed for PVAc/Tol solutions.

Comparison of the Half-Widths of PVAc and PVOc Solutions. In this section we discuss the temperature dependence of the half-width Λ. First we test whether Λ is a universal function of T/T_g where T_g is defined as the temperature at which the relaxation frequency f_m becomes 0.001 and is listed in Table 1. As shown in Figure 9, the Λ versus T/T_g curves have a similar shape and suggest that the broadening of Λ is closely related to the glass transition. However, it appears that T/T_g at which the half-width increases steeply changes from sample to sample, and therefore Λ of concentrated solutions cannot be expressed by a common function of T/T_g.

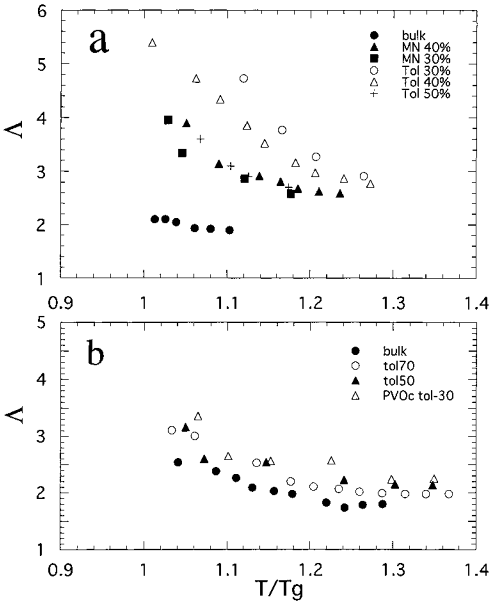

Figure 9. Half-width Λ versus T/T_g plots for PVAc solutions (a) and those for PVOc solutions (b).

Table 2. Correlation Length ξ and the Forward Scattering $I(0)$

solution	C/wt %	T/K	$I(0)$	ξ/nm
PVAc/Tol	30	297	0.0282	1.20
	30	333	0.0272	1.09
	40	297	0.0241	0.83
	40	333	0.0212	0.78
PVAc/MN	30	297	0.0076	1.09
	30	333	0.0071	1.10
	40	313	0.0071	0.98
	40	333	0.0075	1.07

Katana et al.[15] explained the temperature dependence of the broadness of the dielectric loss curve of a polymer blend assuming that the distribution of relaxation times is proportional to the amplitude of concentration fluctuation $\Delta\phi$. Using this idea, Yada et al. also explained the distribution of relaxation times in PVAc/Tol solutions:[13] As proposed by Zetsche and Fischer,[14] Yada et al.[13] indicated that the concentration fluctuation in PVAc/Tol solutions can be approximately represented by a Gaussian distribution:

$$P(\phi) \sim P_0 \exp[-(\phi - \phi_0)^2/(2\sigma)] \qquad (2)$$

where $P(\phi)$ is the distribution function and ϕ_0 the average local concentration. The parameter σ is equal to the mean-square fluctuation of local concentration $\langle(\phi - \phi_0)^2\rangle$ in a volume of the size of the correlation length ξ^3. Since relaxation times vary with concentration, the distribution of local concentration ϕ causes the distribution of relaxation times $g(\tau)$. Here, we may assume that the dependence of τ on ϕ is the same as the dependence on macroscopic concentration C. Yada et al.[13] reported the C dependence curve of log f_m for PVAc/Tol solutions. Their data indicate that, in a relatively narrow range

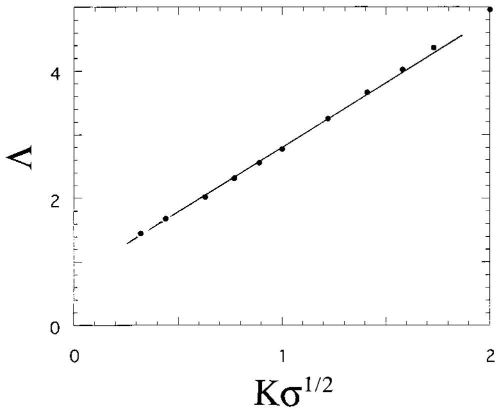

Figure 10. Plots of Λ agaist $K\sigma^{1/2}$ for loss curves given by eqs 4 and 5.

of concentration, the logarithm of τ is linear with respect to ϕ:

$$\log \tau = \log \tau_0 + K(\phi - \phi_0) \tag{3}$$

where K (= d log τ/dϕ) is the constant depending on temperature and τ_0 is the average relaxation time at concentration ϕ_0. From eqs 2 and 3, we can express $g(\tau)$ as

$$g(\tau) \propto \exp\left(-\frac{(\log \tau - \log \tau_0)^2}{2\sigma K^2}\right) \tag{4}$$

Then the dielectric loss curve is given by

$$\epsilon'' = \int_0^\infty g(\tau)\,\frac{\omega\tau}{1 + \omega^2\tau^2}\,\mathrm{d}\tau \tag{5}$$

Unfortunately, this integral cannot be solved analytically. Therefore, we calculated eq 5 numerically and examined the relation between the effect of concentration fluctuation ($\sigma = \langle(\phi - \phi_0)^2\rangle$) on Λ. As is shown in Figure 10, the calculated Λ is approximately linear to $K\sigma^{1/2}$ with the slope of unity. Therefore, if $\Delta\phi$ is defined by $\Delta\phi = \sigma^{1/2} = \langle(\phi - \phi_0)^2\rangle^{1/2}$, the half-width Λ can be written as

$$\Lambda \approx \Delta\phi\,\frac{\mathrm{d}\log \tau}{\mathrm{d}\phi} + \Lambda_0 \tag{6}$$

where Λ_0 is the intrinsic half-width. Assuming that the dependence of τ on ϕ is the same as the dependence on macroscopic concentration C, we calculate eq 6 with the aid of the Vogel−Fulcher equation:[21,22]

$$\log \tau(T,\phi) = B/[T - T_0] - A - \log(2\pi) \tag{7}$$

As is seen in Table 1, the parameters A and B depend weakly on concentration C, but T_0 depends strongly on C. Therefore, we approximate that A and B are independent of ϕ. From the relation $T_g \sim 1.3T_0$,[24] T_0 of a concentrated solution of polymer 1 and solvent 2 is a function of ϕ and may be given by mixing laws similar to T_g.[25] Then eq 6 is written as

$$\Lambda \cong B\Delta\phi\left(\frac{\partial T_0(\phi)}{\partial\phi}\right)\frac{1}{[T - T_0(\phi)]^2} + \Lambda_0 \tag{8}$$

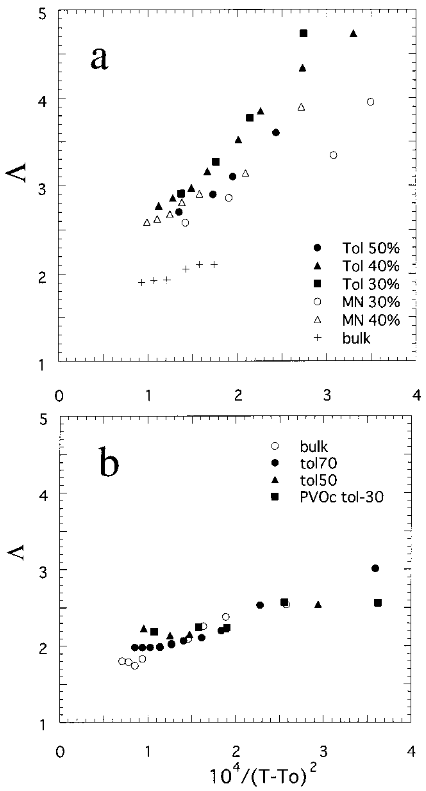

Figure 11. Plots of Λ agaist $1/(T - T_o)^2$ for solutions of PVAc (a) and those of PVOc (b). Tol and MN denote toluene and methylnaphthalene, respectively.

This equation predicts that the half-width Λ due to local heterogeneity is proportional to $1/(T - T_0)^2$. Figure 11a tests eq 8 for the PVAc/MN and PVAc/Tol systems by plotting the values of Λ against $1/(T - T_0)^2$ with T_0 given in Table 1. As is seen, the plots conform approximately to straight lines. However, we recognize that those lines tend to deviate upward at higher $1/(T - T_0)^2$. Figure 11b shows Λ versus $1/(T - T_0)^2$ plots for the PVOc/Tol system. For this system the concentration dependence is weak, and all plots for different concentration conform approximately to a common straight line. As is seen in Figure 11a,b, the extrapolation of the plots to $1/(T - T_0)^2 = 0$ results in nearly the same Λ_0 equal to 1.7 ± 0.2. This limiting Λ_0 is larger than Λ of the Debye curve for a single relaxation time (=1.15) and may correspond to Λ due to the intramolecular interactions at high temperatures.

In eq 8 we note that Λ is proportional not only to $\Delta\phi$ but also to $B(\partial T_0/\partial\phi)$. The narrow Λ of PVOc solutions compared with that of PVAc solutions can be partly attributed to the difference in this factor. Thus, $\Lambda - \Lambda_0$ divided by $B(\partial T_0/\partial\phi)$ is replotted in Figure 12 in which Λ_0 (=1.7) was determined above and $B(\partial T_0/\partial\phi)$ was estimated from the data listed in Table 1. It is seen that the slopes of the plots for PVAc and PVOc solutions become similar order, indicating that the amplitudes of concentration fluctuation in both solutions are similar in order although the observed Λ for PVAc/Tol is much wider than that of PVOc/Tol. From the slopes of the plots, the values of $\Delta\phi$ are determined and listed in Table 3 together with Λ_0 and $\partial T_0/\partial\phi$. Comparing PVAc/Tol and PVAc/MN solutions, we see that $\Delta\phi$ for the former is higher than the latter. This is consistent with the SAXS data.

According to Zetsche and Fischer,[14] the concentration fluctuation in polymer blends can be represented by a Gaussian distribution. Replacing the Debye function

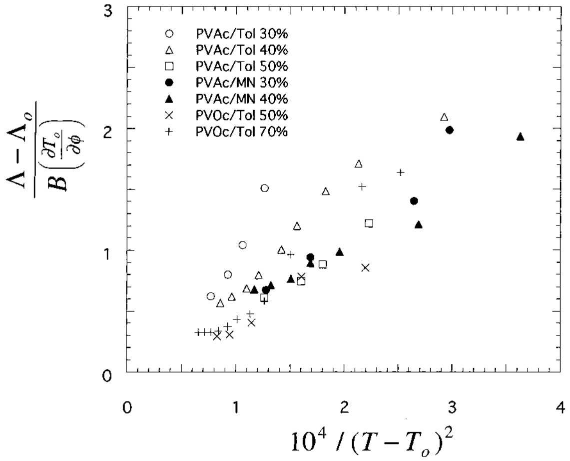

Figure 12. Replots of Figure 11 based on eq 5. Here T_0 and B are the parameters of Vogel equation and are listed in Table 1.

Table 3. Value of Limiting Half-Width Λ_0, Concentration Dependence of T_0, Amplitude of Concentration Fluctuation $\Delta\phi = [(\phi - \phi_0)^2]^{1/2}$ Determined with Eq 8, and σ Determined by Curve Fitting of Eqs 4 and 9

solution	C/wt %	Λ_0	$\partial T_0/\partial\phi$	$\Delta\phi$/(g/cm^3)	$\sigma^{0.5}$/(g/cm^3)
PVAc/Tol	30	1.63	245	0.10 ± 0.02	0.057
	40	1.80	227	0.073 ± 0.01	0.041
	50	1.80	209	0.049	0.032
PVAc/MN	30	1.75	150	0.054	0.045
	40	1.88	172	0.050	0.034
PVOc/Tol	50	1.90	130	0.036	0.031
	70	1.70	130	0.045	0.026

appearing in eq 5 by an intrinsic function Ψ, eq 5 is rewritten as[18]

$$\epsilon''(\omega) = \int_0^\infty g(\tau)\, \Psi(\omega,\tau)\, d\tau \tag{9}$$

We used the Havriliak–Negami equation[26] for bulk PVAc and PVOc as the intrinsic Ψ. The parameters of the Havriliak–Negami equation Ψ were taken as follows: $\alpha = 0.882$ and $\beta = 0.527$ for PVAc solutions; for PVOc solutions $\alpha = 0.841$ and $\beta = 0.549$. Details of the method of calculation were reported in our previous paper.[13] The best fit ϵ'' curves for PVAc/MN and PVOc/Tol solutions are shown in Figures 1, 3, and 4. The values of the parameter $\sigma^{0.5}$ ($=\Delta\phi$) of eq 2 used for fitting are listed in Table 3. It is seen that the values of $\Delta\phi$ determined by the curve fitting is slightly smaller than those determined from the plots based on eq 8. Here it is noted that in eq 3 we assumed that log τ is linear against ϕ, but in calculation of eq 9, we used the experimental log τ vs ϕ curves being curved slightly. As is seen in Figures 1, 3, and 4, eq 9 reproduces the experimental loss curves approximately. One of the origins for the deviation of the experimental curves in the high-frequency tails may be ascribed to the β relaxation due to motions of the side group.

Relation between Heterogeneity and Cooperative Motions. In condensed systems the polymer segments are believed to reorient cooperatively. Two mechanisms of cooperative rotational motions may be expected. One is the model in which there exists a correlation in angular momentum between a test segment and the neighboring segments. Another model is the model where an assembly of segments reorients as a whole. In both models, the local heterogeneity of concentration may affect the cooperative mobility. However, the correlation length of spatial heterogeneity is not always equal to the average size of cooperative regions, i.e., dynamical correlation length. The probability of coupling of neighboring segments is induced by an irregular shape of the segments as modeled in the gear model[6] and also by anisotropic intermolecular force such as dipole–dipole interactions. In the present system the correlation length ξ determined by SAXS is of the order of 1 nm. We expect that dynamical correlation length is longer than 1 nm. The relationship between the local heterogeneity and the dynamic correlation length remains as an important problem.

Conclusions

Effects of concentration fluctuation on the dielectric relaxation spectra have been studied for concentrated solutions of poly(vinyl acetate) (PVAc)/1-methylnaphthalene (MN) and poly(vinyl octanoate) (PVOc)/toluene (Tol), and the results have been compared with those in PVAc/Tol solutions reported previously. Two features have been elucidated. The first finding is that the half-width Λ of the dielectric loss curve for solutions of PVAc/MN is anomalously broad and is slightly narrower than that for solutions of PVAc/Tol while the width of PVOc/Tol is much narrower than PVAc solutions. This indicates that Λ of concentrated solutions depends strongly on the chemical structures of the components. On the basis of small-angle X-ray scattering, the broad relaxation spectra have been attributed to heterogeneity in local concentration ϕ. The correlation length ξ is of the order of 1 nm. The second finding is that although the magnitude of Λ depends on the chemical structures, the widths Λ for all these solutions exhibit the same temperature dependence: Λ increases with decreasing temperature T. It has been found that Λ is proportional to $B\Delta\phi/(T - T_0)^2$ where B and T_0 are the parameter of the Vogel–Fulcher equation (eq 1) and $\Delta\phi$ the amplitude of concentration fluctuation in a volume of ξ^3. From the plots of Λ reduced by $B(\partial T_0/\partial\phi)$ against $1/(T - T_0)^2$, we have assessed $\Delta\phi$ to be 3–10%. The shapes of the loss curves can be approximately represented by assuming a Gaussian distribution of concentration fluctuation. Present results pose future problems. With regard to the effect of chemical structures on the relaxation spectra, it is needed to clarify the effect of the thermodynamic properties of solutions such as the solvent quality. The relationship between dynamic correlation length for cooperative segmental motions and the correlation length of concentration fluctuation is an interesting issue, and this may be clarified theoretically and also by computer simulations.

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