Macromolecules **2003,** *36,* 2349−2354

Dielectric Study of Concentration Fluctuation in Solutions of Polystyrene

Kazuyuki Yoshizaki, Osamu Urakawa, and Keiichiro Adachi*

Department of Macromolecular Science, Graduate School of Science, Osaka University,
Toyonaka, Osaka 560-0043, Japan

Received November 19, 2002

ABSTRACT: The effect of the solvent quality on local concentration fluctuation was studied for concentrated solutions of polystyrene (PS) in toluene (Tol), ethylbenzene (EtBz), *n*-propylbenzene (PrBz), and *n*-butylbenzene (BuBz) by using dielectric spectroscopy. The exponents of the Mark−Houwink−Sakurada equation of those solutions indicate that the solvent quality deteriorates in the order of Tol, EtBz, PrBz, and BuBz. Three dielectric relaxations designated as α, β, and γ are observed in the temperature dependence curves of the dielectric loss in the order of decreasing temperature. According to our previous study on PS/Tol solution, the α, β, and γ relaxations have been assigned to local segmental motions of PS, rotation of the solvent molecules, and the secondary relaxation in the glassy state, respectively. The half-width of the dielectric loss curve Λ_α for the α relaxation of PS/Tol solutions is independent of temperature, but the values of Λ_α for solutions in EtBz, PrBz, and BuBz increase with decreasing temperature in proportion to $(T - T_0)^{-2}$ as observed previously for solutions of poly(vinyl acetate) in toluene where T_0 is the critical temperature of the Vogel−Fulcher equation. The slope of the Λ_α vs $(T - T_0)^{-2}$ plots which is a measure of the amplitude of concentration fluctuation increases with the deterioration of the solvent quality, and hence it increases with increasing interaction parameters between the PS chains and the solvent molecules.

Introduction

Recently, Yada et al.[1] and Nakazawa et al.[2] studied the dielectric relaxation spectra for concentrated solutions of poly(vinyl acetate) (PVAc) and poly(vinyl octanoate) (PVOc) dissolved in toluene and methylnaphthalene.[1,2] It was found that the half-width (Λ) of the dielectric loss curves of those solutions, which is a measure of the distribution of relaxation times, depends strongly on concentration, and Λ's for concentrated solutions are much broader than those in dilute solution and in the bulk state. It was also found that Λ increases with decreasing temperature. The behavior was explained by assuming the Gaussian distribution of local concentration as proposed by Zetsche and Fischer[3] for polymer blends.[3−7] Although the behavior was commonly observed for those solutions, the value of Λ depended on a combination of the polymer and solvent. This suggests that the concentration fluctuation in solutions depends on interactions between the polymer and solvent molecules.

The present study is an extension of the above-mentioned studies and aims to examine the effect of polymer/solvent interactions on the dielectric relaxation spectra in concentrated solutions. For this purpose we have chosen polystyrene (PS) since the solution properties of PS have been studied extensively.[8,9] Alkylbenzenes, i.e., toluene (Tol), ethylbenzene (EtBz), *n*-propylbenzene (PrBz), and *n*-butylbenzene (BuBz), have been chosen as the solvents. Toluene is a good solvent for PS, and the exponent *a* of the Mark−Houwink−Sakurada equation is 0.75.[10] On the other hand, *a* of PS/EtBz solution is 0.68.[11] Although the data of *a* for PS solutions in PrBz and BuBz have not been reported, we expect that the solvent quality deteriorates with increasing carbon number of the alkyl group of the solvent since linear alkanes are nonsolvent for PS. For PS/Tol solutions, Adachi et al.[12] studied the mechanisms of the dielectric relaxation processes using broad-line NMR. They also determined the parameters of the Vogel−Fulcher equation[13,14] for PS/Tol solutions. We will utilize those previous results for elucidation of the relationship between the interaction parameter and the distribution of dielectric relaxation times in solutions of PS.

Table 1. Characteristics of PS Samples

code	M_w	M_w/M_n
PS-5	5 250	1.05
PS-13	12 900	1.05
PS-17	16 800	1.05

Experimental Section

Materials. Samples of polystyrene (PS) were prepared by anionic polymerization with *sec*-butyllithium in benzene. The weight-average molecular weight M_w was determined by gel permeation chromatography by using standard PS samples purchased from Tosoh (Tokyo, Japan). The molecular weights are listed in Table 1. The solvents Tol, EtBz, PrBz, and BuBz used for preparation of the sample solutions were purchased from Aldrich (San Francisco, CA) and used as received. In dielectric measurements on toluene solutions of PS with concentration above 50 wt %, we used a mixed solvent of toluene/*p*-chlorotoluene (PCT) of the composition of 95/5. PCT was purchased from Wako Chemicals (Tokyo, Japan).

Methods. Dielectric measurements were carried out in the frequency range from 10 to 10^6 Hz with a capacitance bridge (General Radio 1615A) and an RLC meter (QuadTech 7600, Maynard, NJ). The dielectric cell used in this study was specially designed for measurements on viscous liquids and was reported previously.[15] In the present study, a relatively large cell with the empty capacitance of ca. 100 pF was used since the relaxation strength of PS is very low. It is noted that despite this effort, the data still contained a relatively large error. The intrinsic viscosity was measured with a Ubbelohde capillary viscometer at 298 K.

---

* Corresponding author: phone/fax +81 66850 5464; e-mail adachi@chem.sci.osaka-u.ac.jp.

10.1021/ma021696e CCC: $25.00

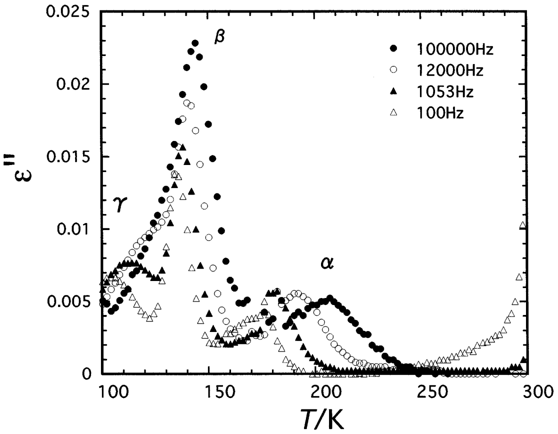

Figure 1. Temperature dependencies of dielectric loss factor ϵ'' for 30 wt % solutions of PS-5 in toluene at frequencies indicated in the figure.

Results and Discussion

Dielectric Relaxation Behavior in PS Solutions. Figure 1 shows the temperature dependence of the dielectric loss factor ϵ'' for 30 wt % solution of PS-5 in toluene. Three loss peaks designated as α, β, and γ are seen at about 180, 140, and 110 K, respectively, at 1 kHz. This behavior was already reported previously.[12] With increasing concentration of PS, the α peak shifted to higher temperature and the intensity increased. On the other hand, the intensity of the β relaxation decreased with concentration. Thus, the α and β relaxations can be assigned to segmental motions of PS and rotation of the toluene molecules, respectively. The intensity of the γ relaxation was not proportional to the PS content in solutions and exhibited a maximum around 30 wt %. Therefore, the γ relaxation can be assigned to motions of both the PS segments and the toluene molecules.[12] This conclusion was confirmed previously from the temperature dependencies of the second moments of proton NMR for solutions of PS dissolved in ordinary toluene (C_8H_8) and fully dueterated toluene (C_8D_8).[12] In the former system the motional narrowing of the NMR line is due to motions of both PS and toluene, but in the latter, only motions of PS chains are detected. The NMR second moment in the γ relaxation region decreased gradually in both C_8H_8 and C_8D_8 solutions, supporting the conclusion drawn above.[12] They also indicated that the glass transition temperature T_g of PS/Tol solution measured by thermal analyses coincides with the temperature at which the loss maximum frequency f_m for the α relaxation becomes 10^{-3} Hz.[12] This relationship will be used for estimation of T_g's of the solutions used in the present study.

In toluene solutions of PS with concentration above 50 wt % the intensity of the β relaxation becomes very weak. To observe the β relaxation process clearly, we used a mixed solvent of toluene/*p*-chlorotoluene (PCT) of the composition of 95/5. Figure 2 shows the temperature dependencies of ϵ'' at 1 kHz for 50−70 wt % solutions of PS in the Tol/PCT mixed solvent. We see the α, β, and γ peaks similar to the 30 wt % solution. The behavior is essentially the same as that of the 30 wt % solution, but the loss peaks shift to higher temperatures.

Figure 3 shows the temperature dependence of the dielectric loss factor ϵ'' for 30 wt % solution of PS-5 in *n*-propylbenzene (PrBz). Two relaxations designated as α and β can be seen as observed for PS/Tol solutions.

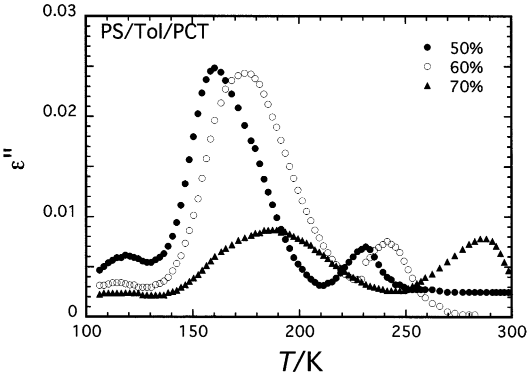

Figure 2. Temperature dependencies of dielectric loss factor ϵ'' at 1 kHz for solutions of PS in a mixed solvent of toluene/*p*-chlorotoluene (PCT) of mixing ratio of 95/5. Here PS-17, PS-13, and PS-13 were used for 50, 60, and 70 wt % solutions, respectively.

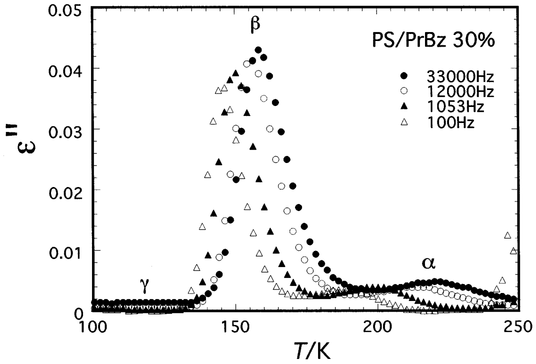

Figure 3. Temperature dependencies of dielectric loss factor ϵ'' for 30 wt % solutions of PS-5 in propylbenzene (PrBz) at frequencies indicated in the figure.

However, the γ peak is not seen clearly. For the PS/EtBz and PS/BuBz systems, similar behaviors were observed. This indicates that the mobilities of the PS chains and the solvent molecules in the glassy state depend on the size of the solvent molecules, and only the toluene molecules having the smallest size exhibit the secondary relaxation at a relatively high intensity.

Comparing Figures 1 and 3, we see that the amplitude of the β peak for 30% PrBz solution is about 2 times higher than that for Tol solution of the same concentration. The dipole moments of Tol, EtBz, and isopropylbenzene were reported to be 0.37, 0.58, and 0.65 D, respectively.[16] Although the dipole moment of PrBz is not available, these data indicate that the dipole moment of PrBz is higher than that of Tol. Thus, the higher intensity of the β peak of PrBz solutions than Tol solutions can be ascribed to the dipole moment of the PrBz molecules. Because of this effect, the β relaxations in solutions of PS in EtBz, PrBz, and BuBz with high concentration were observed without addition of *p*-chlorotoluene.

The loss maximum frequencies f_m for the α relaxations of PS/Tol solutions are plotted against the inverse of temperature in Figure 4. Previously, the Arrhenius plots for PS/Tol solutions were investigated in detail[12] and were cast into the Vogel−Fulcher equation:[13,14]

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

where A, B, and T_0 are the parameters. It was reported that A (=10.65) and B (=569) of PS/Tol solutions are almost independent of concentration.[12] The solid curves

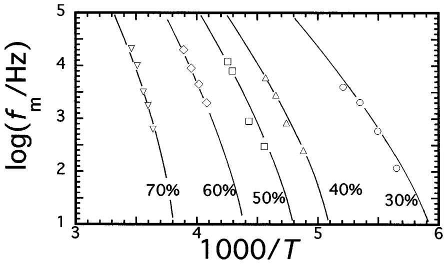

Figure 4. Arrhenius plots of the loss maximum frequency f_m for solutions of PS-5 in Tol with varying concentration. The solid lines indicate eq 1 calculated with the parameters given in ref 12.

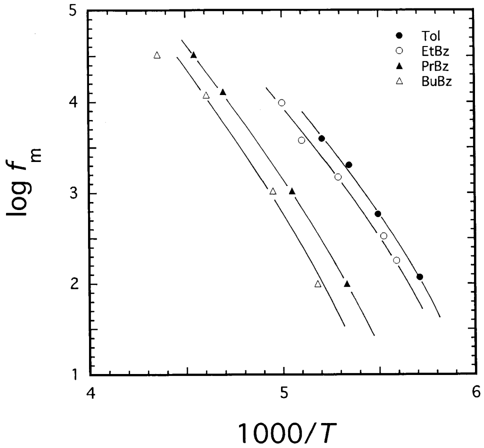

Figure 5. Arrhenius plots of the loss maximum frequency f_m for 30 wt % solutions of PS-5 in Tol, EtBz, PrBz, and BuBz.

Table 2. Parameters of Vogel–Flucher Equation and Glass Transition Temperatures for PS Solutions

solution	wt %	C (wt/vol)	T_0	T_g
PS/Tol	30	0.27	106	148
	40	0.37	123	164
	50	0.47	162	206
	60	0.57	185	229
	70	0.68	210	254
PS/EtBz	30	0.27	110	150
	40	0.37	118	161
PS/PrBz	30	0.27	116	160
	40	0.37	129	173
PS/BuBz	30	0.27	120	164
	40	0.37	135	179

indicate eq 1 with the parameters determined previously for PS solutions. Here T_0 has been determined by interpolation of the previous results.[12] The values of T_0 thus determined are listed in Table 2. The glass transition temperature T_g was defined as the temperature at which log f_m becomes −3 as reported previously for PS/Tol solutions.[12] The results are also listed in Table 2.

Figure 5 compares the Arrhenius plots for the α relaxations of 30% solutions in Tol, EtBz, PrBz, and BuBz. It is seen that the plots are almost parallel and shift to the high-temperature side with increasing carbon number of the alkyl group of the solvents. For 40% solutions similar data were obtained. In the present study the frequency range of measurements was ca. 2 decades, and the values of T_0 and T_g for solutions of PS in EtBz, PrBz, and BuBz were determined by assuming the same values of A and B as those of Tol solutions. The curves shown by the solid lines indicate eq 1. The results are listed in Table 2. The error due to this assumption in the estimation of T_0 and T_g is estimated as follows. Our previous data[1,2,12] indicated that A and B were almost independent of the chemical structures of the components and concentration of a polymer solution. For example, the value of A for solutions of poly(vinyl acetate) and poly(vinyl octanoate) in toluene and methylnaphthalene ranges from 10.2 to 12.1 and the value of B from 600 to 840.[2] By changing the values of A and B from 10 to 12 and from 600 to 900, respectively, the errors in the determination of T_0 and T_g are less than ±15 and ±10 K, respectively, and are typically ±5 K.

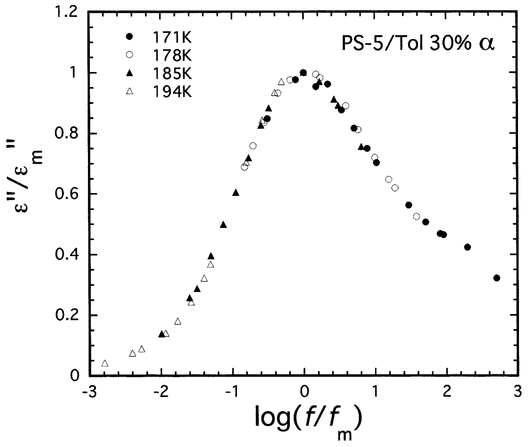

Figure 6. Normalized ϵ'' curves for the α relaxation of 30 wt % solutions of PS-5 in toluene.

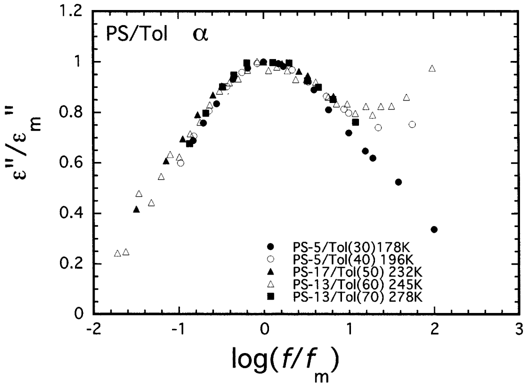

Figure 7. Comparison of the normalized ϵ'' curves for the α relaxation of PS solutions in toluene with varying concentration at approximately the same T/T_g. The PS samples used are indicated in this figure.

Shape of Loss Curves of the α Relaxation. Figure 6 shows the normalized ϵ'' for the α relaxation of 30 wt % toluene solutions; i.e., the value of ϵ'' divided by the maximum value ϵ_m'' is plotted against logarithm of frequency f divided by the loss maximum frequency f_m. It is seen that the shape of the ϵ'' curves does not change with temperature. This behavior is also seen for PS/Tol solutions with concentration higher than 30 wt % and is quite different from that of poly(vinyl acetate)/Tol solutions reported previously,[1,2] in which the ϵ'' curves broaden with decreasing temperature. This suggests that broadening of the ϵ'' curves depends on the quality of solvent since the PS/Tol system is special among the systems examined so far in the sense that toluene is almost perfectly good solvent for PS.[17]

Figure 7 compares the normalized ϵ'' curves for solutions of PS/Tol with varying concentration at approximately the same T/T_g. Here the glass transition temperature T_g has been defined above. It is seen that ϵ'' tends to increase in the high-frequency region. This

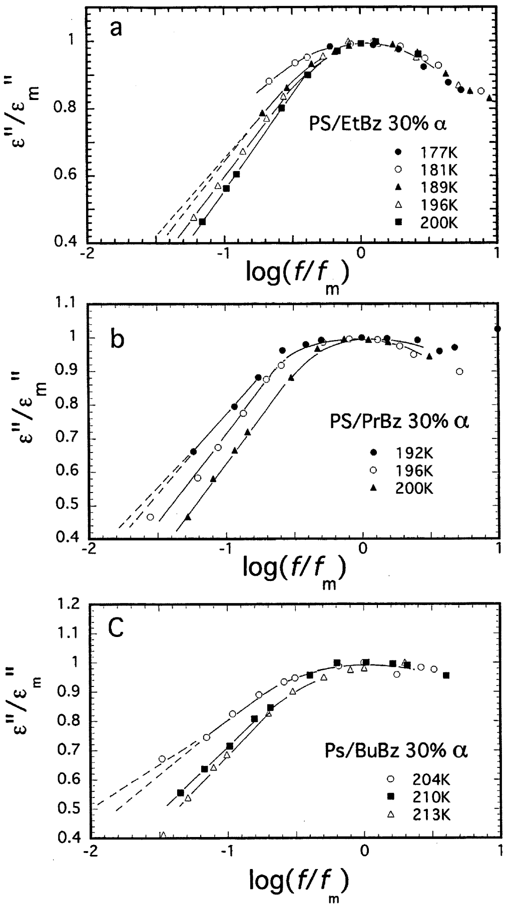

Figure 8. Normalized ϵ'' curves for the α relaxation of 30 wt % solutions. (a) PS-5/EtBz, (b) PS-5/ PrBz, and (c) PS-5/BuBz solutions.

is due to overlapping of the β relaxation process. Within experimental error the curves coincide with each other. Thus, we conclude that the half-width Λ_α of the loss curve for the α relaxation in PS/Tol solutions is independent of temperature and concentration.

Parts a, b, and c of Figure 8 show the normalized ϵ'' curves for the α relaxation in 30 wt % solutions of PS in EtBz, PrBz, and BuBz, respectively. In contrast to PS/Tol solutions, the loss curves become broad with decreasing temperature in the low-frequency side of the loss peaks. Unfortunately, the broadening in the high-frequency side cannot be determined quantitatively due to the overlapping of the β process. Therefore, we have determined the half-width $\Lambda_\alpha/2$ in the low-frequency side of the loss peak.

Here one may doubt that the broadening in the low-frequency side of the loss curve is due to direct current (dc) conductivity and is not due to broadening of the relaxation spectra. This is ruled out for two reasons. First, we note that the width of the ϵ'' curves shown in Figure 8 increases with decreasing temperature. If the broadening is due to the additional contribution of dc conduction to ϵ'', the contribution of the dc conduction should decrease with decreasing temperature, and hence ϵ'' curves should become narrower with decreasing temperature. Second, the dc conductivity σ_{dc} is estimated for PS/PrBz solutions as follows. In Figure 3, ϵ'' at 100 Hz and at 220 K is almost zero and is as low as 0.0005. Thus, the alternating current (ac) conductivity σ_{ac} ($=\omega\epsilon_0\epsilon''$) at 220 K becomes 3×10^{-13} S m^{-2} where ω is the angular frequency and ϵ_0 the absolute dielectric constant of vacuum. Since σ_{ac} is equal to the sum of σ_{dc} and the contribution of the dipolar relaxation, σ_{dc} is less than 3×10^{-13} S m^{-2} in the temperature range 192−200 K where the frequency dependence was measured (Figure 8). The upper limit of σ_{dc} thus estimated is negligibly small.

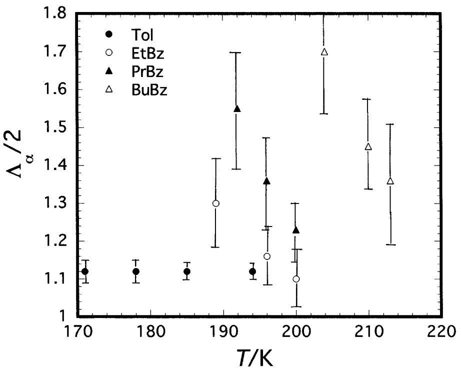

Figure 9. Temperature dependence of $\Lambda_\alpha/2$ for the α relaxations of PS solutions in Tol, EtBz, PrBz, and BuBz. Here $\Lambda_\alpha/2$ indicates the half-width in the low-frequency side of the loss peak and is equal to $\log f_m - \log f_{1/2}$, where $f_{1/2}$ is the frequency at which ϵ'' becomes $\epsilon''_m/2$. Thus, the unit of $\Lambda_\alpha/2$ is log(Hz).

The smoothed curves were drawn as shown in Figure 8, and the values of $\Lambda_\alpha/2$ in the low-frequency side of the α loss peaks were determined. For some curves it is necessary to extrapolate the data to $\epsilon''/\epsilon''_m = 0.5$. This accompanies the error in determination of $\Lambda_\alpha/2$. The dashed line indicates the ambiguity in the extrapolation. We also note that the ϵ'' curves are flat around the loss peak. This also results in the error in determination of $\Lambda_\alpha/2$, and the error is estimated to be ±0.05, ±0.1, and ±0.1 decades for the curves show in parts a, b, and c of Figure 8, respectively. Figure 9 shows the temperature dependence of Λ_α /2 thus determined. Although the error is relatively large, the results indicate clearly that Λ_α /2 increases in the order of Tol, EtBz, PrBz, and BuBz.

Shape of Loss Curves of the β Relaxation. Parts a and b of Figure 10 show the normalized ϵ'' curves for the β relaxations in PS/Tol/PCT systems of 30 and 40 wt % concentrations, respectively. The increase of ϵ'' in the high-frequency side of the loss curves is due to overlapping with the γ process. We see that the shape of the curves does not change with temperature as observed for the loss curves of α relaxation. Parts a and b of Figure 11 show the representative ϵ'' curves for the β relaxations of PS/EtBz and PS/BuBz solutions, respectively. For PS/PrBz solutions similar behavior was observed. In those solutions the ϵ'' curves broaden slightly with decreasing temperature. If this broadening is due to overlapping of the α process, the broadening should be also seen in Figure 10 for PS/Tol solutions. Therefore, we consider that the broadening observed in Figure 11 is not due to the effect of overlapping. The effect of the solvent quality on the broadening for the β relaxation is similar to that of the α relaxation. This result indicates that the concentration fluctuation also affects the mobilty of the solvents and becomes stronger with decreasing solvent quality. However, comparing Figures 8 and 10, we see that the extent of broadening for the β relaxation is relatively small compared with the α relaxation.

Half-Width of Loss Curves of the α Relaxation. In this section the relationship between Λ_α /2 and the solvent quality is discussed. Zetsche and Fischer[3]

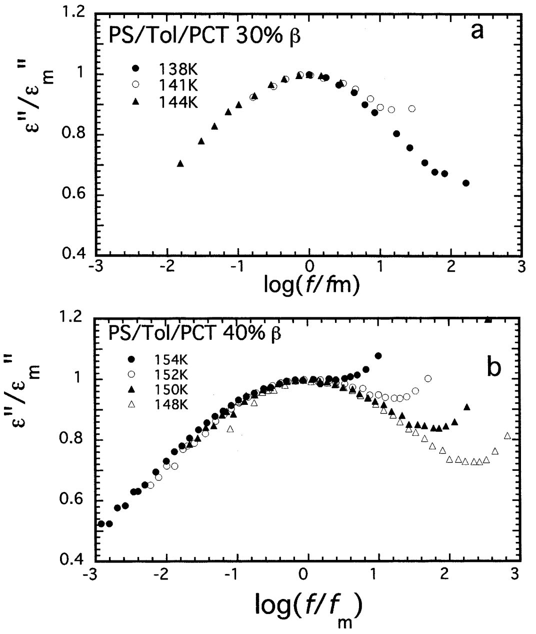

Figure 10. Normalized ϵ'' curves for the β relaxation of 30 wt % PS solutions in mixed solvent of Tol/PCT (95/5): (a) 30 wt % and (b) 40 wt % solutions.

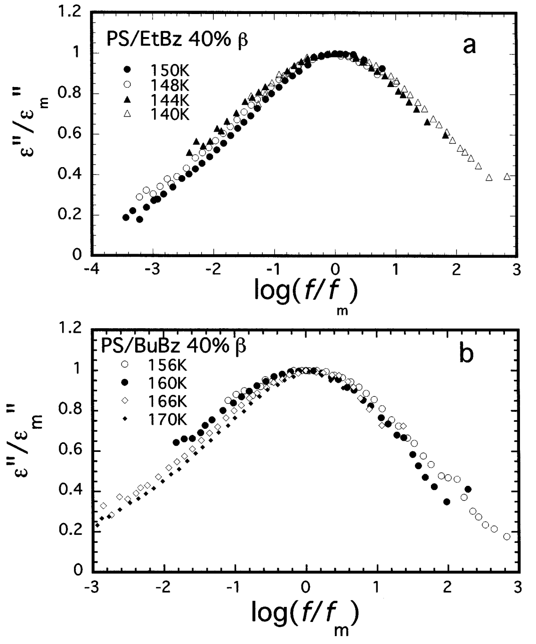

Figure 11. Normalized ϵ'' curves for the β relaxation of 40 wt % PS solutions in (a) EtBz and (b) BuBz.

proposed the Gaussian distribution of local concentration for interpretation of the distribution of dielectric relaxation spectra of polymer blends. On the basis of this idea, Nakazawa et al.[2] defined the distribution of relaxation times $g(\tau)$ by

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

where τ_0 is the average relaxation time, σ $(= \langle(\phi - \phi_0)^2\rangle)$ the mean-square fluctuation of local polymer concentration ϕ, and K the constant. Here ϕ_0 is the average concentration. We define the amplitude of concentration fluctuation $\Delta\phi$ by $\Delta\phi = \langle(\phi - \phi_0)^2\rangle^{1/2}$. Then the dielectric loss curve is given by

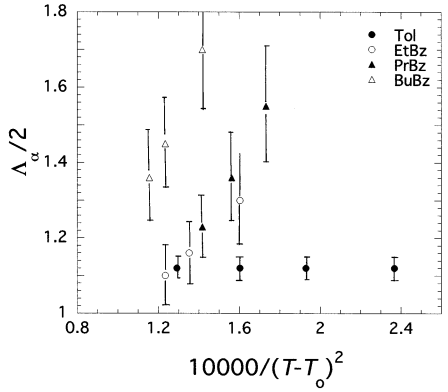

Figure 12. Plots of $\Lambda_\alpha/2$ against $1/(T - T_0)^2$ for solutions of PS. The unit of $\Lambda_\alpha/2$ is log(Hz).

$$\epsilon'' = \int_0^\infty g(\tau)\,\frac{\omega\tau}{1 + \omega^2\tau^2}\,\mathrm{d}\tau \tag{3}$$

Since the half-width Λ is approximately linear to $K\sigma^{1/2}$, Λ can be written as

$$\Lambda \approx \Delta\phi\,\frac{\mathrm{d}\log\tau}{\mathrm{d}\phi} + \Lambda_0 \tag{4}$$

where Λ_0 is the constant. Assuming that the dependence of τ on ϕ is the same as the dependence on macroscopic concentration C, Nakazawa et al.[2] have calculated eq 4 with the aid of the Vogel–Fulcher equation:[13,14]

$$\log\tau(T,\phi) = B/[T - T_0] - A - \log(2\pi) \tag{5}$$

where A, B, and T_0 are the parameters. Among these parameters, A and B depend weakly on concentration C, but T_0 depends strongly on C. Therefore, we assume that A and B are independent of ϕ. Then eq 4 is rewritten as

$$\Lambda \cong B\Delta\phi\left(\frac{\partial T_0(\phi)}{\partial\phi}\right)\frac{1}{[T - T_0(\phi)]^2} + \Lambda_0 \tag{6}$$

This equation predicts that the half-width Λ due to local heterogeneity is proportional to $1/(T - T_0)^2$. It is known generally that $T_g/T_0 \approx 1.3$,[18] and hence $\partial T_0/\partial\phi$ is proportional to $\partial T_g/\partial\phi$. The concentration dependence of T_g is given by various empirical equations such as the Fox equation and the Gordon–Tayler equation.[19,20] To the first approximation, T_g is linear to the composition. Therefore, $\partial T_0/\partial\phi$ depends weakly on ϕ. As mentioned above, B also depends weakly on ϕ. Thus, the slope ξ of the Λ vs $1/(T - T_0)^2$ plot is approximately proportional to $\Delta\phi$.

Figure 12 shows the plot of $\Lambda_\alpha/2$ against $1/(T - T_0)^2$ for 30 wt % solutions. Here we have used T_0 given in Table 2. As is seen, the plots conform approximately to straight lines. The slope and hence the amplitude of concentration fluctuation increase with increasing the carbon number of the alkylbenzene.

As described in the introductory section, the solvent quality is expected to be a key factor for the broadening of the loss curves. The solvent quality can be assessed from the exponent a of the Mark–Houwink–Sakurada equation, $[\eta] = KM^a$, where K is the constant and M

Table 3. Comparison of ξ and Polymer−Solvent Interaction Parameters χ_{exp} and χ_m Defined in the Text

solvent	T/K	$10^4\xi$	χ_{exp}	χ_m
toluene	170	0.00 ± 0.05	−1.32	−0.98
ethylbenzene	190	0.53 ± 0.3	−0.99	−0.70
n-propylbenzene	200	0.98 ± 0.4	−0.85	−0.57
n-butylbenzene	210	1.25 ± 0.5	−0.81	−0.61

the molecular weight. The values of a for toluene and ethylbenzene solutions were reported to be 0.75 and 0.68, respectively.[10,11] Unfortunately, the data of a for PrBz and BuBz solutions are not available. Therefore, we measured the intrinsic viscosity of PS in BuBz and obtained $K = 0.0454$ mL g^{-1} and $a = 0.60$. Thus, the solvent quality decreases in the order of Tol, EtBz, and BuBz. We speculate that the solvent quality of PrBz is intermediate of EtBz and BuBz.

The interaction parameters χ for PS solutions were reported by many authors. However, the values of χ reported in the literature differ greatly depending on the methods.[21] Therefore, we need the data of χ obtained by means of the same method for the solvents used here. One method is to calculate χ from the solubility parameters of PS and the solvents.[22] However, the heat of mixing calculated from the solubility parameter often includes relatively large error. Bianchi et al. measured the heat of solution ΔH_{exp} of PS in Tol, EtBz, PrBz, and BuBz.[23] They reported that ΔH_{exp} is different from the heat of mixing ΔH_m calculated with the solubility parameters and the volume change of mixing. The difference ($\Delta H_{exp} - \Delta H_m$) was attributed to the change in the conformational energy of the PS chains. We have calculated $\chi_{exp} = \Delta H_{exp}/RT$ and $\chi_m = \Delta H_m/RT$ from ΔH_{exp} and ΔH_m reported by Bianchi et al., where R is the gas constant and T is temperature. Those values are compared with the slope ξ of the $\Lambda_\alpha/2$ vs $1/(T - T_0)^2$ plot in Table 3. From those results we conclude that the amplitude of concentration fluctuation increases with deteriorating solvent quality.

Conclusion

We have reported the dielectric relaxations in concentrated solutions of polystyrene (PS) in toluene (Tol), ethylbenzene (EtBz), *n*-propylbenzene (PrBz), and *n*-butylbenzene (BuBz). The normalized ϵ'' curves for the α relaxation of Tol solutions do not exhibit broadening with temperature, in contrast to the behavior of poly(vinyl acetate)/Tol solutions reported previously. On the other hand, the normalized ϵ'' curves for the α relaxations in 30 wt % solutions of PS in EtBz, PrBz, and BuBz exhibit broadening with decreasing temperature in the low-frequency side of the loss peaks. The half-width $\Lambda_\alpha/2$ in the low-frequency side of the loss peaks is found to be approximately proportional to $1/(T - T_0)^2$, and the slope of the plots increases with the deterioration of the solvent quality assessed from the intrinsic viscosity and the interaction parameter. The result indicates that the amplitude of local concentration fluctuation increases with deterioration of the solvent quality. For the β relaxations, we have also observed that the ϵ'' curves broaden with decreasing temperature. Interestingly, the behavior becomes prominent with the deterioration of solvent quality as for the α relaxation.

References and Notes

(1) Yada, M.; Nakazawa, M.; Urakawa, O.; Morishima, Y.; Adachi, K. *Macromolecules* **2000**, *33*, 3368.
(2) Nakazawa, M.; Urakawa, O.; Adachi, K. *Macromolecules* **2000**, *33*, 7898.
(3) Zetsche, A.; Fischer, E. W. *Acta Polym.* **1994**, *45*, 168.
(4) Katana, G.; Fischer, E. W.; Hack, Th.; Abetz, V.; Kremer, F. *Macromolecules* **1995**, *28*, 2714.
(5) Roland, C. M.; Ngai, K. L. *Macromolecules* **1991**, *24*, 2261.
(6) Roland, C. M.; Ngai, K. L. *Macromolecules* **1992**, *25*, 363.
(7) Kumar, S. K.; Colby, R. H.; Anastasiadis, S. H.; Fytas, G. *J. Chem. Phys.* **1996**, *105*, 3777.
(8) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(9) Kurata, M. *Thermodynamics of Polymer Solutions*; Harwood: New York, 1982.
(10) Papazian, L. A. *Polymer* **1969**, *10*, 399.
(11) Bawn, C. E. H.; Freeman, C.; Kamaliddin, A. *Trans Faraday Soc.* **1950**, *46*, 1107.
(12) Adachi, K.; Fujihara, I. Ishida, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 2155.
(13) Vogel, H. *Phys. Z.* **1921**, *22*, 645.
(14) Fulcher, G. A. *J. Am. Ceram. Soc.* **1925**, *8*, 339.
(15) Imanishi, Y.; Adachi, K.; Kotaka, T. *J. Chem. Phys.* **1988**, *89*, 7585.
(16) Smyth, C. P. *Dielectric Behavior and Structure*; McGraw-Hill: New York, 1955; Chapter 10.
(17) Bawn, C. E.; Freeman, R. F. J.; Kamaliddin, A. R. *Trans. Faraday Soc.* **1950**, *46*, 677.
(18) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139.
(19) Fox, T. G. *Bull. Am. Chem. Soc.* **1956**, *1*, 123.
(20) Gordon, M.; Tayler, J. S. *J. Appl. Chem.* **1952**, *2*, 495.
(21) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; John-Wiley: New York, 1989.
(22) Hildebrand, J. H.; Scott, R. L. *Solubility of Nonelectrolytes*; Reinhold: New York, 1950.
(23) Bianchi, U.; Cuniberti, C.; Pedemonye, E.; Rossi, C. *J. Polym. Sci., Part A2* **1969**, *7*, 855.

MA021696E