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Dielectric Properties of Polymer—Solvent Systems

Akio NOJIRI and Shigeharu OKAMOTO

Department of Applied Physics, Waseda University,
Nishiokubo, Shinjuku-ku, Tokyo, Japan.

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ABSTRACT: Measurements of the dielectric absorption of solutions, poly(vinyl acetate)—toluene and poly(vinyl chloride)—dioxane systems were carried out. Based on the effects of temperature, frequency, and concentration of the polymer in the dielectric absorption, the mechanism of this absorption is discussed. The frequency at which the maximum loss occurs depends largely upon the concentration of the polymer. This dependence is described successfully in terms of the free volume model. The activation enthalpy and entropy of this dielectric relaxation process were obtained as functions of the volume fraction of the polymer. These values increase with the volume fraction of the polymer and approach those for the α-relaxation process observed in pure polymers. The variation of free energy with volume fraction in this process can be explained by the change of free volume. Observed relaxation times show apparent molecular weight dependence and this effect can also be explained in terms of the free volume variation.

KEY WORDS Dielectrics / Polymer Solution / Poly(vinyl acetate) / Poly(vinyl chloride) / Concentration / Molecular Weight / Free Volume / Free Energy of Activation / α-Process /

Dielectric properties have been studied extensively by many investigators both experimentally and thoretically. A theoretical analysis of the dielectric relaxation process of polymer solutions has been given by Rouse,[1] Bueche,[2] and Zimm[3] (R—B—Z theory). Their calculations treated the molecular motion of polymer for a very simplified model in which only the motion of the subchain was considered. In the actual cases, however, it sometimes occurs that other motions such as small scale or local motions in the subchain play an important role in dielectric behavior. Recently, Work, *et al.*,[4] have reported that some of the dielectric relaxation process of polymer solutions should be ascribed to the local motion of polymer chains. Their study was made on polymers with dipoles attached rigidly to the chain backbone. It is said that the observed dielectric behavior for polymers[5] whose dipoles are parallel to the chain direction can be explained by the R—B—Z theory. Further extensive study indicates, however, that this model does not hold for the dielectric behavior of poly(propylene oxide)[6] solutions.

In the present work, dielectric measurements on polymer—solvent systems, poly(vinyl acetate) (PVAc)—toluene, and poly(vinyl chloride) (PVC)—dioxane for various polymer concentrations have been carried out. Those polymers have flexible main chains with one component of the dipole vector perpendicular to the chain direction. The mechanism of the dielectric relaxation process of those polymer solutions is discussed by using the free volume model or the rate process theory.

EXPERIMENTAL APPARATUS AND PROCEDURE

Dielectric measurements of PVAc solutions and PVC solutions were carried out over the frequency range from 30 Hz to 150 MHz by using a conventional transformer bridge and a twin T bridge. In these measurements, cylindrical and parallel plate electrodes were used.

Polymer species used were pure PVAc and PVC which do not contain antioxidants and plasticizers. Careful purification of these samples was made before use. The former was purified by a method described previously[7] and the toluene solution of PVAc was kept at room temperature for 24hr before the measurement.

Purification of PVC was carried out by dissolving it in dioxane at 80°C for 12hr, and then by reprecipitating it in methanol. Measurements were carried out after leaving the solution at 80°C for 12hr. Frequency dependence of the dielectric constant and the loss factor of these systems was measured at several fixed temperatures in the range of -70 to 45°C.

EXPERIMENTAL RESULTS

Frequency dependence of the dielectric loss factor, ε'', of PVAc—toluene was measured at various temperatures and as example, the results for various volume fractions, ϕ, of PVAc at -31°C are shown in Figure 1. The polymerization degree of PVAc used was 500. Figure 1 indicates that a dielectric loss peak appears in each solution and that the frequency at which the loss maximum occurs, f_m shifts to lower frequency with increasing volume fraction of PVAc. Maximum value of ε'' in each curve, which is expressed as ε_m'', increases with the volume fraction.

Frequency dependence of the dielectric constant, ε' and ε'' measured at various temperatures is given in Figure 2. The value of P of PVAc was 500. Although the measurement was made for various concentrations, only the results for $\phi=0.25$ and $\phi=0.56$ are given. The

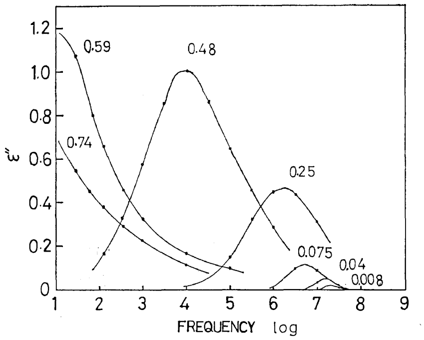

Figure 1. Frequency dependence of ε'' at -31°C for PVAc—toluene. The volume fraction of polymer is shown for each curve.

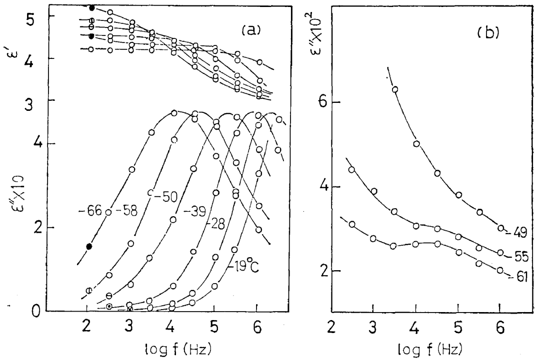

Figure 2. (a) Frequency dependence of ε' and ε'' for PVAc—toluene ($\phi=0.25$) and (b) frequency dependence of ε'' for PVAc—toluene ($\phi=0.56$) at low temperatures.

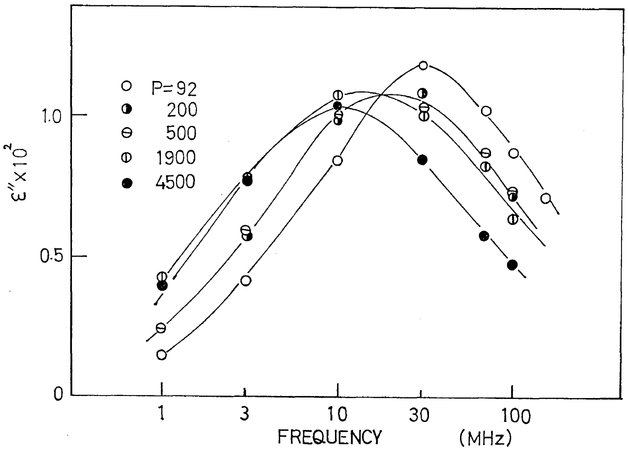

Figure 3. Frequency dependence of PVAc—toluene ($\phi=0.008$) at -31°C for PVAc of varying degrees of polymerization.

asymmetric shape of the ε'' curve is observed, that is, ε'' varies more abruptly on the lower frequency side. This shape is similar to that of undiluted PVAc.

Figure 3 shows the relation between ε'' and the frequency for various degrees of polymerization P, when $\phi=0.008$. Figure 3 was used to get the relation between f_m and P shown in Figure 4.

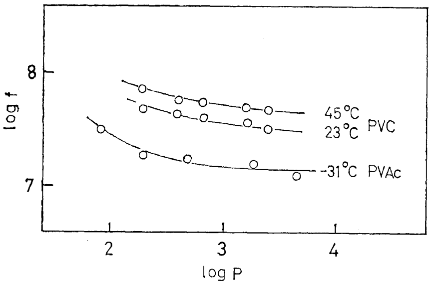

Figure 4. The relationship between f_m and P for PVAc—toluene ($\phi=0.008$) at −31°C and PVC—dioxane ($\phi=0.006$) at 23°C and 45°C.

Frequency dependence of ε'' for the PVC—dioxane system was also measured and the loss peak was also observed in each solution. In this case, too, f_m was found to shift to a lower frequency as the volume fraction ϕ increases. The Polymerization degree of PVC used for these measurements was 400. The change of f_m as a function of P is shown in Figure 4, when $\phi=0.006$.

DISCUSSION

From the observed results given in Figure 1, *i.e.*, the frequency dependence of ε' and ε'' for PVAc—toluene at −31°C, we can obtain the concentration dependence of f_m and the magnitude of the absorption, $\Delta\varepsilon$. The results are shown in Figure 5. This graph suggests that $\Delta\varepsilon$ increases and f_m decreases as the concentration ϕ increases. Extrapolating the curve to $\phi=1$, the values of 10^{-16}Hz for f_m and 12.0 for $\Delta\varepsilon$ were obtained. Those values may correspond to those of the α-relaxation process in pure PVAc already reported by several authors.[8,9]

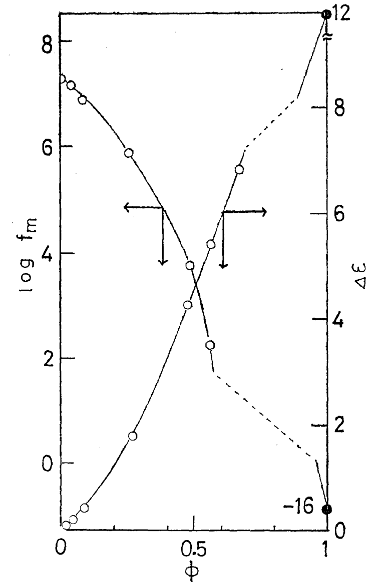

Figure 5. Concentration dependence of f_m and $\Delta\varepsilon$ for PVAc—toluene at −31°C. The extrapolated value is shown by closed circle.

It has been reported[10] that the dielectric relaxation of dilute polymer solutions is due to local mode molecular motion of the dipoles in the polymer chain. It is not, however, clear how such relaxation processes are related to

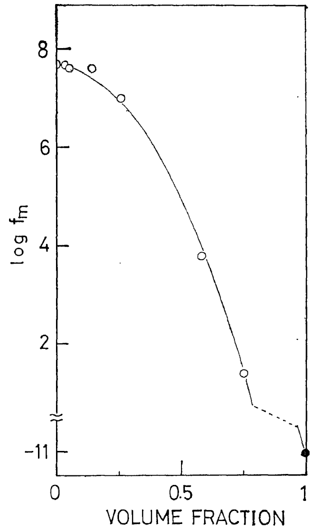

Figure 6. Concentration dependence of f_m for PVC—dioxane at 23°C. The extrapolated value is shown by closed circle.

those of undiluted polymers. Judging from the concentration dependence of f_m and $\Delta\varepsilon$ in PVAc—toluene systems, we may conclude that they correspond to the so-called α-relaxation process due to segmental motion of the main chain. The shape of the absorption curve is slightly non-symmetrical, being broader on the higher frequency side. We found that a small and broad absorption exists as seen for $\phi=0.56$ in Figure 2.

In the PVC—dioxane system, the variation of f_m with ϕ is obtained from the frequency dependence of ε''. Only the results at 23°C are shown in Figure 6. As the extrapolated value for $\phi=1$, $f_m=10^{-11}$Hz is obtained. This frequency agrees well with that of the α-relaxation process[11,12] observed in pure polymer. This result indicates that the dielectric absorption in this system too may be due to the segmental motion of the main chain. It has been reported that the frequency at which maximum loss occurs, f_m, in polymer solutions, such as poly(ethylene oxide)[13] and poly(propylene oxide)[6] solutions is independent of the concentration ϕ. The origin of the dielectric relaxation process of these solutions, therefore, may be different from that of the present samples.

According to Stockmayer[10] and other investigators,[14] the relationship between f_m and ϕ in poly(p-chlorostylene)—toluene can be described as

$$f_m=f_0\exp(-B/v_f)\,; \qquad v_f=v_0-c\phi \qquad (1)$$

where v_f may be denoted as the free volume,[15,16] which is obtained from the difference between the volume of the polymer molecule sphere in the solution and the van der Waals volume of the polymer molecule, and f_0, v_0, B, and C are constant. We can see in this equation that $1/\ln(f_0/f_m)$ varies linearly with ϕ. The plot of $1/\ln(f_0/f_m)$ $vs.$ ϕ obtained from Figure 5 is given in Figure 7 together with the plots for different temperatures. The linear relation is satisfied in those plots, showing that eq 1 can be applied to the PVAc—toluene system. The constants of eq 1 are chosen to fit the observed curves. The fractional free volume of the polymer of 0.05 was assumed at any temperature for the sake of simplicity. Constants obtained thus are tabulated in Table I. The constant f_0 in this equation is regarded as f_m in a monomer unit or in a segment, because f_0 becomes equal to f_m when v_f increases to infinity, which can be attained by extending the polymer chain and by assuming the radius of this molecular sphere to be infinity. The value obtained is of reasonable magnitude, compared with the value for f_m of

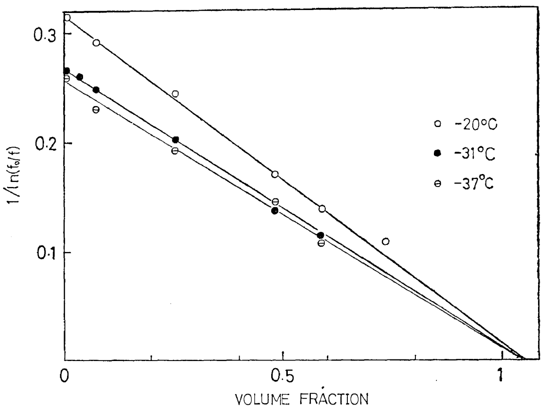

Figure 7. The relationship between $1/\ln(f_0/f)$ and ϕ for PVAc—toluene at fixed temperatures. Temperature is shown for each line.

Table I. The parameters applied to eq 1

Polymer	Temp	f_0	C/B	v_0/B
PVAc	−20°C	50×10^9	0.131	0.138
	−31°C	100×10^9	0.110	0.116
	−37°C	50×10^9	0.106	0.111
PVC	23°C	25×10^9	0.169	0.169

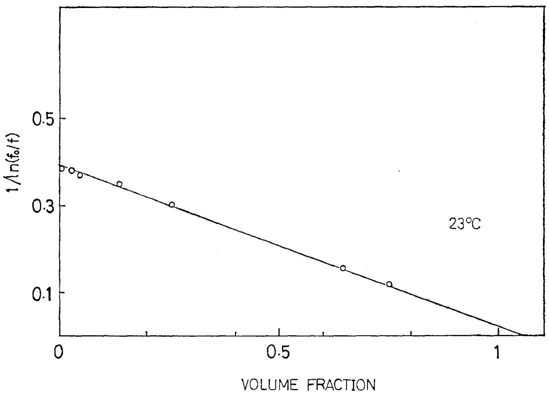

Figure 8. The relationship between $1/\ln(f_0/f)$ and ϕ for PVC—dioxane at 23°C.

small molecules. In the diluted solution, interaction and long range intramolecular interaction can be neglected, because each polymer molecule is isolated and extended well in the solution.

From the concentration dependence of f_{m} given in Figure 6, we find that the dielectric behavior in the PVC—dioxane system can also be described by eq 1 as seen in Figure 8. Decrease of the value of f_{m} with the concentration seen in Figures 5 and 6 may thus be ascribed to the decrease of the free volume, which occurs with increasing polymer concentration.

As regards the temperature dependence of f_{m}, the analysis by means of the rate theory was tried. Some information on the dielectric relaxation process can be obtained from such treatment. According to the theory of rate process by Eyring,[17] f_m is expressed by

$$f_{\mathrm{m}}=(kT/2\pi h)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \qquad (2)$$

where T, ΔS^*, and ΔH^* are temperature, the entropy, and the heat of activation, respectively, and h, k and R are Planck's constant, Boltzmann's constant, and the gas constant, respectively. This equation shows that ΔH^* can be calculated from the slope of the plot of $\ln f_m$ *vs.* $1/T$. The result obtained as a function of ϕ is shown in Figure 9. The value of ΔH^* obtained for $\phi=0.008$ is 5.0 kcal/mol. The value of ΔH^* increases linearly with ϕ up to $\phi=0.6$, and above 0.6 it increases more rapidly with ϕ. It reaches the value observed for the pure polymer, *i.e.*, 60 kcal/mol.[8] The entropy of activation, ΔS^* is also obtained from eq 2. The value thus obtained of $T\Delta S^*$ at -20°C, is also shown in this figure. It is clearly seen that $T\Delta S^*$ is approximately zero at $\phi=0.01$ or less. The value increases linearly with increasing ϕ in the range of $0<\phi<0.7$, while it increases more rapidly and deviates from the linear relation above 0.7.

It is noted that the increase of ΔH^* with ϕ is due mainly to term of inter-segmental interaction, and the increase of $T\Delta S^*$ can be ascribed to that of the motional units which cooperate in a movement[18,19] as reported by Bueche[18] in the glass transition process. As a consequence, it is reasonable that $T\Delta S^*$ is much smaller at lower ϕ, that is, in the dilute solution and increases with increasing ϕ.

As is well known, free energy of activation, ΔF^* is defined by $\Delta H^*-T\Delta S^*$. Value of ΔF^* which was obtained by using observed values of ΔH^* and $T\Delta S^*$ is given as a function of ϕ in Figure 9. From eq 1 and 2, we obtain the relation

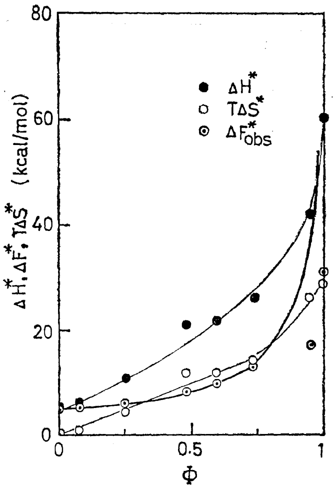

Figure 9. Concentration dependence of ΔH^*, $T\Delta S^*$, and $\Delta F^*_{\mathrm{obs}}$ -20°C for relaxation process of PVAc—toluene. $\Delta F^*_{\mathrm{calc}}$ is obtained by eq 3 and shown by solid line.

$$\begin{aligned}\Delta F^* &= H^*-T\Delta S^* \\ &= BRT/(v_0-C\phi)+RT\ln(kT/2\pi hf_0) \qquad (3)\end{aligned}$$

ΔF^* can be calculated from this equation if parameters, v_0, f_0, C, and B are known. We used here the parameters shown in Table I and the result of the calculation is shown by the solid line in Figure 9. The observed free energy $\Delta F^*_{\mathrm{obs}}$ agrees well with ΔF^* in the range of $0<\phi<0.7$ but $\phi>0.7$, $\Delta F^*_{\mathrm{obs}}$ deviates from the calculated curve. This discrepancy may be due to the fact that at $\phi>0.7$, ΔH^* and ΔS^* have been measured at temperatures much higher than -20°C. In fact, it has been reported that ΔH^* in the dielectric relaxation process of pure PVAc increases when the temperature is lowered. Eq 3 indicates that the change of the free energy of activation with concentration may be due mainly to the change of free volume of the polymer—solvent system. If we put $f_m=f_0$ in eq 2, it can be found that the term $RT\ln(kT/2\pi hf_0)$ in eq 3 is equal to the free energy of the monomer unit or the segment, $\Delta F_0{}^*$, when inter-molecular and long

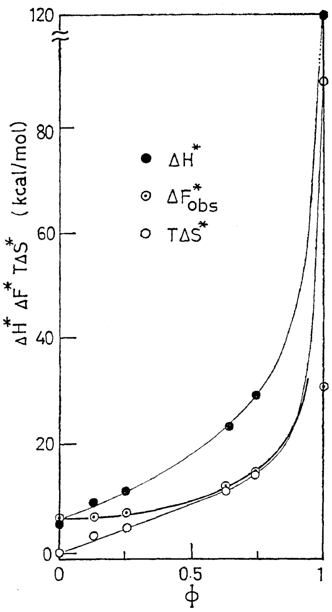

Figure 10. Concentration dependence of ΔH^*, $T\Delta S^*$, and $\Delta F^*_{\mathrm{obs}}$ at 23°C for PVC—dioxane. $\Delta F^{**}_{\mathrm{calc}}$ is shown by sclid line.

range intra-molecular interaction is negligibly small, while the term $BRT/(v_0-C\phi)$ may be due to the relaxation process in a random coil state at where long range interaction is dominant. The value of $\Delta F_0{}^*$ for PVAc at −20°C is calculated from observed data as 1.4 kcal/mol. Substituting $\phi=0$ in eq 3, the intrinsic free energy of activation, $F^*(\phi=0)$ of 5.0 kcal/mol can be obtained. As the value is an extrapolated one, it is not

Table II. ΔF^* and ΔH^* (kcal/mol)

Polymer—solvent	$\Delta F_0{}^*$	$\Delta F^*(\phi=0)$	ΔH^*
PVAc—toluene	1.4	5.0	5.0($\phi=0.008$)
PVC—dioxane	2.2	5.8	4.9($\phi=0.006$)

dependent on polymer concentration. This free energy of activation may be a useful parameter in comparison with other energy values which depend on the polymer concentration.

Values of ΔH^*, $T\Delta S^*$, and ΔF^* for the PVC—dioxane system were also obtained in a similar way and the results are given in Figure 10. The variation of these values with ϕ is similar to those in the PVAc—toluene system described above. There are some non-agreements between observed and calculated free energy in the range of $\phi>0.7$. As the values ΔH^* at $\phi=0.006$ and $\Delta F_0{}^*$, we obtain 4.9 kcal/mol and 2.2 kcal/mol, respectively. The value for such a dilute solution is in good agreement with the intrinsic free energy of activation of 5.8 kcal/mol obtained at 23°C.

It was reported by Brouckère, *et al.*,[20] some years ago, that the relaxation time in PVAc—toluene is independent of molecular weight of the polymer. However, their measurement was made only for the sample with molecular weight larger than 2.2×10^5. In the present investigation, measurements were extended to lower molecular weight samples. The present result as seen in Figure 4, shows that the relaxation time is considerably affected by the polymeriza-

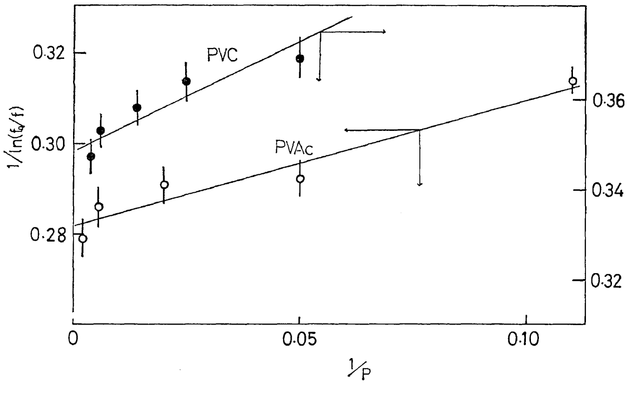

Figure 11. The relationship between $1/\ln(f_0/f)$ and $1/P$ for PVAc—toluene ($\phi=0.008$) and PVC—dioxane ($\phi=0.006$).

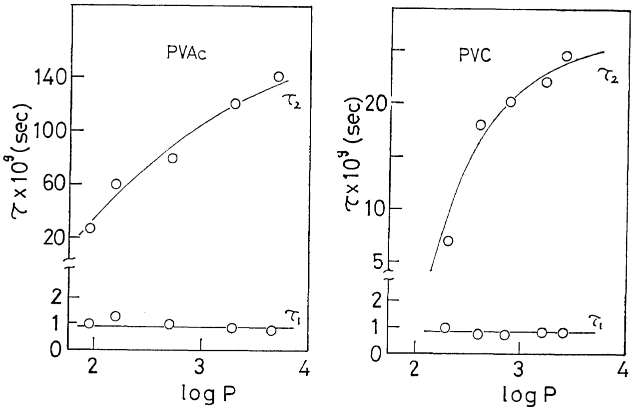

Figure 12. Molecular weight dependence of τ_1 and τ_2 defined by eq 5.

tion degree of the samples. This tendency is more evident in the low molecular weight range. The molecular weight dependence of f_m observed here is also expressed by the free volume type equation by considering the molecular weight dependence of v_f.[21] If v_0 in eq 1 is replaced by v_0+D/M:

$$f_m=f_0 \exp\{B/(v_0+D/M)\} \qquad (4)$$

where M is the molecular weight and D is a constant. From the obtained results given in Figure 4, plots of $1/\ln(f_0/f_m)$ *vs.* $1/P$ are obtained as given in Figure 11, where 50×10^9 and 25×10^9 are used as the value of f_0 for PVAc—toluene and PVC—dioxane, respectively.

In discussing this relaxation process, we assume a distribution function $f(\tau)$ of relaxation time τ, already proposed by Fröhlich:[22]

$$f(\tau)=1/A\tau \qquad (5)$$

for $\tau_1 \leqq \tau \leqq \tau_2$, and

$$f(\tau)=0 \qquad (6)$$

for $\tau<\tau_1$ or $\tau>\tau_2$, where τ_1 and τ_2 are constants.

It has been shown by Bergmann[23] that for materials obeying eq 5, the absorption curve plotted against frequency in the log scale is symmetrical and very close to that for substances which obey the Cole—Cole[24] relation when the parameter A is smaller than 4. Values of A, and τ_1 and τ_2 in eq 5 can be determined from Cole—Cole's parameter β and the average relaxation time, $\tau_{av}=1/2\pi f_m$, by a procedure proposed by Higasi, *et al.*[23] From the frequency dependence of ε', τ_1, and τ_2 were obtained for the PVAc—toluene system when $\phi=0.008$ and for PVC—dioxane system when $\phi=0.006$. The results are shown in Figure 12. The absorption curve for the PVAc—toluene system is somewhat asymmetrical, that is, broad at the high frequency side as shown in Figure 3. The shape of the absorption curve for the PVC—dioxane system is not clear owing to lack of measurements at higher frequencies. Normalized loss factor $\varepsilon''/\varepsilon_m''$ plotted against $\log(f/f_m)$ for the PVC—dioxane system is shown in Figure 13. Curves, in the same figure are Cole—Cole-type absorption curves. When eq 5 is applied to the present absorption curves, we can obtain an approximate but quantitave distribution of the dielectric relaxation times. Figure 12 shows τ_1 and τ_2 obtained in this way. This figure

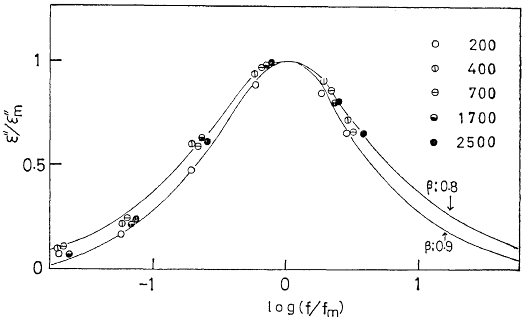

Figure 13. Normalized loss factor, $\varepsilon''/\varepsilon_m''$ *vs.* log (f/f_m) for PVC—dioxane ($\phi=0.006$). Cole—Cole-type absorption curves of $\beta=0.8$ and $\beta=0.9$ are shown.

indicates that the relaxation time τ_1, which may be the relaxation time of the segmental motion of the most mobile units, is independent of the molecular weight, and that the relaxation time τ_2 increases with the increase of the degree of polymerization, P, in the low P region and approaches a constant value as P increases. The molecular weight dependence of τ_2 is similar to that of the average relaxation time, $\tau_{av}=1/2\pi f_m$.

The molecular weight dependence of the distribution of relaxation times described above is consistent with the fact that the absorption curves are broadened as P increases, as is seen in Figures 3 and 13, and also that the parameter β decreases with increasing P; the value of β changes from 0.8 to 0.65 in the PVAc—toluene system and from 0.9 to 0.8 in the PVC—dioxane system with increasing P if the Cole—Cole relation is assumed. The broadening of the distribution of τ with P indicates, when the free volume model is adopted, that the free volume of the segment in a random coil gets a broader distribution with increasing P. This distribution of free volume should be taken into account in discussing dielectric behavior, especially the distribution of relaxation times and the shape of absorption curves in polymer—solvent systems.

CONCLUSIONS

The following conclusions were obtained as a result of these dielectric measurements:

(1) The frequency at which the maximum loss occurs, the magnitude of the absorption and the heat of activation in the PVAc—toluene and PVC—dioxane systems change monotonously with increasing concentration of polymers in the solution. These values approach the values for the α-relaxation process in undiluted polymers with increasing concentration of polymer. This suggests that the dielectric relaxation process observed may correspond to the segmental motion of polymer chains.

(2) The frequency at which the maximum loss occurs shifts with increasing concentration of the polymer segment. This concentration dependence can be described in terms of the free volume model.

(3) The heat of activation of this dielectric relaxation process is 5.0 kcal/mol for PVAc—toluene ($\phi=0.008$) and 4.9 kcal/mol for PVC—dioxane ($\phi=0.006$). This value increases with increasing concentration of the polymers. The entropy of activation is negligibly small at low concentration, and increases with the concentration. The change of the free energy of activation with concentration can be explained only by considering the change of free volume. From this relation, the intrinsic free energy of activation which is independent of polymer concentrations is evaluated to be 5.0 kcal/mol for the PVAc—toluene system and 5.8 kcal/mol for the PVC—dioxane system.

(4) Molecular weight dependence of the frequency at which maximum loss occurs for the PVAc—toluene and PVC—dioxane systems can be described by the free volume model.

(5) Molecular weight dependence of the distribution of dielectric relaxation times is observed for PVAc—toluene ($\phi=0.008$) and PVC—dioxane ($\phi=0.006$).

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