Cornell and Koenig[6] for a PTBD rubber containing 89% trans units and the vibration assignments of Hsu, Moore, and Krimm.[7]

Discussion

In the paper of Hsu, Moore, and Krimm[7] the higher-frequency part of the 529-cm^{-1} band was given a noncrystalline assignment; this assignment was partially based on a sharpening of this band upon annealing at an unspecified temperature. In the present work annealing at 80°C is not found to sharpen this band nor do crystal mats with two- to threefold differences in amorphous content show significant variations in this band. A second indication of increased crystallinity cited by Hsu et al.[7] was an increase in the 1331/1311 height ratio. However, in the present work this ratio is not found to be sensitive only to crystallinity changes.

The transformation of form I to II taking place at 71°C brings about significant changes in the =CH–CH$_2$– torsion angle.[2] This change is expected to cause a shift in some of the Raman bands, particularly those at low frequencies. The analysis of Hsu et al.[7] correctly predicts the direction of this frequency shift of the bands at 1018, 762, 529, and 238 cm^{-1} found experimentally, as given in Table I. The lattice vibration bands at 90–120 cm^{-1} are expected to shift to lower frequencies with an increase in temperature, as observed in this work in the 25°C to 69°C range and by Hsu et al.[7] with measurements at −160°C and room temperature. The disappearance of the bands at 967 and 1152 cm^{-1} at higher temperatures appears to be consistent with the chain analysis.[7] X-ray diffraction results[2] and energy calculations[3] for form II suggest that rotation about C–C bonds is taking place and this should lead to the disappearance of such bands as well as the disappearance of the band at 238 cm^{-1}, due principally to C–C torsion, and the lattice vibration bands at 90–120 cm^{-1}. An increase in Raman scattering intensity, observed in the 20–200-cm^{-1} frequency region at temperatures above 60°C, accompanies the form I to II transition. This apparently is a manifestation of the various conformations made available to the PTBD chain molecules in form II. The changes taking place in the CH$_2$ stretching, overtone, and combination band region at higher frequencies (see Table I) are probably due to shifts in one or more of the lower-frequency bands which contribute to this region. A similar effect was observed in these laboratories earlier for the infrared bands in the –CH and –CH$_2$ stretching region.

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Dielectric Study of Chain Motion of Poly(*p*-chlorostyrene) in Dilute Solution

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ABSTRACT: Dielectric relaxation measurements were carried out on dilute solutions of poly(*p*-chlorostyrene) in benzene, toluene, ethyl benzene, and dioxane in the frequency range of 1–150 MHz. An asymmetrical loss curve was observed for each solution. The relaxation time τ_m could be described by $\tau_m = 8.0 \times 10^{-9}\eta_0 \exp(E/RT)$ (sec), where η_0 is solvent viscosity in units of poise and E has a value of 2.9 kcal/mol. The dielectric loss could be attributed to a local conformational transition in the chain backbone. If the transition is assumed to be that of the crankshaft, a reasonable value of the number of monomer units between the two collinear bonds, which turned out to be 1–4, was obtained by employing the Kramers rate constant for the transition and the three-state model.

Dielectric behavior of polymers having dipoles rigidly and perpendicularly attached to the chain backbone in dilute solution is a subject of considerable interest, since the relaxation phenomenon of such dipoles is directly connected with the backbone motion.

It was previously reported that such polymers in dilute solution generally exhibit a dielectric dispersion in a rather high-frequency region (10^6–10^{10} Hz) and have relaxation times which do not depend on the molecular weight of the polymer.[1-5] Although the dispersion is undoubtedly attributable to the backbone motion associated with a conformational transition,[3,7] it is still unclear what kind of conformational transition gives rise to the dispersion; an understanding of the magnitude of the relaxation time is not established. The relaxation time is of particular interest in connection with the rate constant for the conformational transition.

In our previous paper[5] it was reported that (1) the relaxation time of some vinyl polymers in dilute solution is approximately proportional to solvent viscosity and (2) the apparent activation energy for the relaxation process, ΔH_A, is related to that for the solvent viscosity, ΔH_η, by the ex-

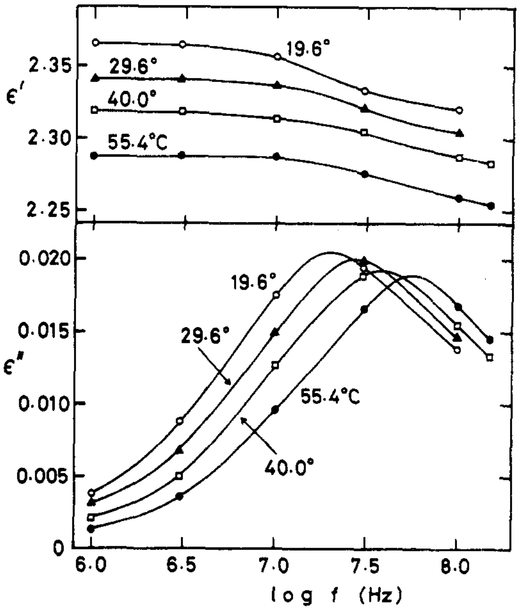

Figure 1. Frequency dependence of dielectric constant and loss at various temperatures for 3.99% PpCS ($\bar{M}_v$ = 6.4 × 10^5) in benzene.

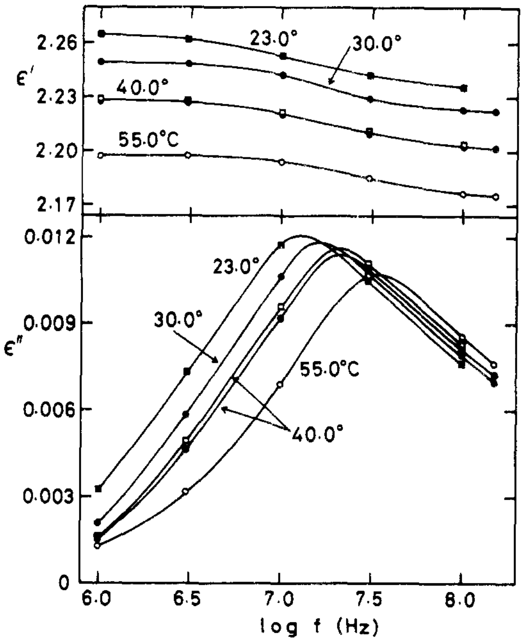

Figure 2. Frequency dependence of dielectric constant and loss at various temperatures for PpCS in dioxane: (□, ■) $\bar{M}_v$ = 6.4 × 10^5, 2.14%; (○, ⊙, ●) $\bar{M}_v$ = 8.6 × 10^4, 2.09%.

pression $\Delta H_A = \Delta H_\eta + E$, where E is a constant. It has been suggested that the Kramers theory of the rate constant[3,6,7] is applicable to the relaxation time and that the value of E represents a height of the potential barrier for a local conformational transition in the chain backbone.

In the present investigation dielectric relaxation measurements were carried out on poly(*p*-chlorostyrene) (PpCS), which is a typical polymer having the dipoles rigidly and perpendicularly attached to the chain backbone, in four nonpolar solvents (benzene, toluene, ethyl benzene, and dioxane) in the frequency range of 1-150 MHz at temperatures between −23 and 61°C. An expression is obtained experimentally for the relaxation time in which only the solvent viscosity enters as a property of the solvent. The expression is the same as that predicted by the Kramers theory in its dependence on solvent viscosity and temperature. Some conformational transitions are discussed in relation to this expression. Assuming the transition to be that of the crankshaft, a reasonable value of the number of monomer units between two collinear bonds was obtained by employing the Kramers expression for the rate constant of the transition.

Experimental Section

Three samples of PpCS were prepared by isothermal polymerization from purified monomers in a bulk under vacuum in order to avoid complications of catalyst fragments and other impurities. The viscosity-average molecular weights of the samples polymerized at temperatures of 200, 100, and 80°C, for 10–20 hr were 8.6 × 10^4, 4.7 × 10^5, and 6.4 × 10^5, respectively.[8] The purification of monomers was carried out using a conventional distillation apparatus in order to remove inhibitors and other impurities. In order to remove monomers and low molecular weight materials the polymer samples were dissolved in benzene and reprecipitated by adding methanol. After a few repetitions of this procedure, the samples were dissolved again in benzene and then freeze dried in order to remove any trace of the solvent remaining. The polymers obtained from this polymerization are atactic.[9]

Solvents used were dehydrated and distilled before use. Concentration of the solution is expressed by weight percent of PpCS.

Dielectric constant and loss were measured with a 1101D Twin-T bridge manufactured by Fujisoku Electric Co., Ltd.[5,10,11] The bridge was first balanced with the solvent in the sample cell so that the current was zero at the detector; it was balanced again after replacing the solvent by the solution in the cell. The dielectric constant and loss for the solution can be evaluated from the difference between these two balance points of the bridge. The loss employed in the present investigation is the difference between that of the solution and that of the solvent.

Results

The frequency dependence of dielectric constant ε' and loss ε'' of 3.99% PpCS ($\bar{M}_v$ = 6.4 × 10^5) in benzene and of 2.14% PpCS ($\bar{M}_v$ = 6.4 × 10^5) and 2.09% PpCS ($\bar{M}_v$ = 8.6 × 10^4) in dioxane is shown in Figures 1 and 2. Each dispersion curve exhibits a single inflection and each loss curve a single maximum.

Some results of the dielectric measurements are listed in Table I. The frequency corresponding to the maximum dielectric loss $\epsilon''_{\max}$, f_m, does not depend on the molecular weight of the polymer. Furthermore, f_m does not depend on the concentration below 5%, as is shown in the cases of toluene and benzene solutions.

In order to investigate the shape of the loss curve, master plots, i.e., plots of $\epsilon''/\epsilon_{\max}''$ against log (f/f_m), constructed for all solutions used, are shown in Figure 3. All plots lie on the same curve irrespective of the molecular weight of the polymer, the concentration, the solvent, or the temperature. The curve is asymmetric, broader on the high-frequency side.

Cole–Cole plots are shown in Figure 4. From this plot, the distribution of relaxation time can be obtained quantitatively by employing Kirkwood's distribution parameter[12] $H_m = \epsilon_{\max}''/(\epsilon_0' - \epsilon_\infty')$, where ϵ_0' and ϵ_∞' are the low- and high-frequency dielectric constants obtained as the intercepts on the abscissa of the Cole–Cole plot. The value of H_m thus obtained is 0.32 ± 0.01.

An effective dipole moment for the monomeric unit $(\mu^2/z)^{1/2}$ can be calculated from the observed value of $\epsilon_0' - \epsilon_\infty'$ by employing the Onsager equation,[13] where z is the degree of polymerization. The dipole moment of PpCS of $\bar{M}_v$ = 6.4 × 10^5 in benzene and toluene solutions, calculated by extrapolating the quantities appearing in the Onsager equation to zero concentration, are 1.4 D both for benzene and toluene solutions at 40°C. The dipole moments in dioxane and ethyl benzene solutions are 1.4 D at 40 and 45.3°C. In these calculations 2.14% dioxane solutions and 3.39% ethyl

Table I
Examples of Results of Dielectric Measurements on PpCS in Solution

Solvent	$\bar{M}_v \times 10^5$	Concn, %	Temp, °C	ϵ_{max}''/concn	log f_m, Hz	ΔH_A, kcal/mol
Benzene	6.4	5.01	14.5	0.531	7.23	5.4 ± 0.1
			25.5	0.511	7.38	
			39.5	0.484	7.57	
			55.0	0.464	7.74	
		3.99	19.6	0.514	7.30	
			29.6	0.501	7.44	
			40.0	0.482	7.58	
			55.4	0.462	7.74	
		3.00	40.0	0.470	7.58	
		2.00	40.0	0.470	7.58	
Toluene	6.4	5.06	40.0	0.484	7.60	4.9 ± 0.1
		1.85	40.0	0.481	7.60	
	4.7	4.95	23.0	0.498	7.38	
			40.0	0.489	7.60	
			60.0	0.464	7.80	
	0.86	5.00	−22.5	0.598	6.76	
			0.4	0.550	7.10	
			23.0	0.497	7.40	
			40.0	0.485	7.60	
			60.0	0.464	7.80	
Ethylbenzene	6.4	3.39	15.5	0.514	7.24	5.0 ± 0.1
			30.2	0.497	7.42	
			45.3	0.482	7.60	
			60.8	0.460	7.75	
Dioxane	6.4	2.14	23.0	0.567	7.09	5.9 ± 0.1
			40.0	0.543	7.31	
	0.86	2.09	30.0	0.565	7.19	
			40.0	0.543	7.32	
			55.0	0.514	7.52	

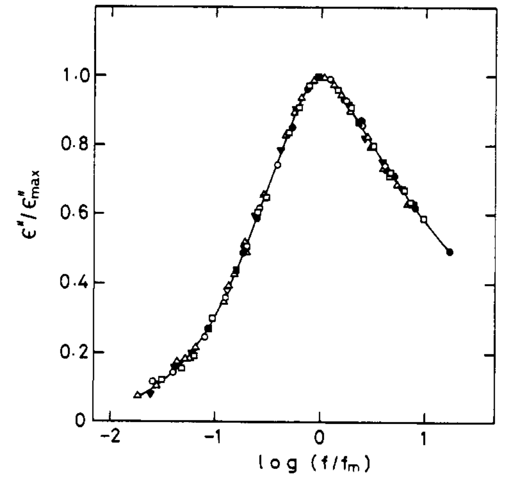

Figure 3. Master plots of $\epsilon''/\epsilon_{max}''$ against log (f/f_m): (△) $\bar{M}_v = 6.4 \times 10^5$, 3.99 and 5.01% in benzene; (○) $\bar{M}_v = 4.7 \times 10^5$, 4.95% in toluene; (●) $\bar{M}_v = 8.6 \times 10^4$, 5.00% in toluene; (▼) $\bar{M}_v = 6.4 \times 10^5$, 3.39% in ethyl benzene; (■) $\bar{M}_v = 6.4 \times 10^5$, 2.14% in dioxane; (□) $\bar{M}_v = 8.6 \times 10^4$, 2.09% in dioxane.

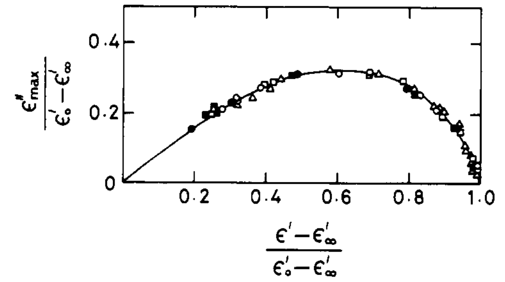

Figure 4. Cole–Cole plot: (△) $\bar{M}_v = 6.4 \times 10^5$, 3.99% in benzene; (○) $\bar{M}_v = 4.7 \times 10^5$, 4.95% in toluene; (●) $\bar{M}_v = 8.6 \times 10^4$, 5.00% in toluene; (□) $\bar{M}_v = 8.6 \times 10^4$, 2.09% in dioxane; (■) $\bar{M}_v = 6.4 \times 10^5$, 2.14% in dioxane.

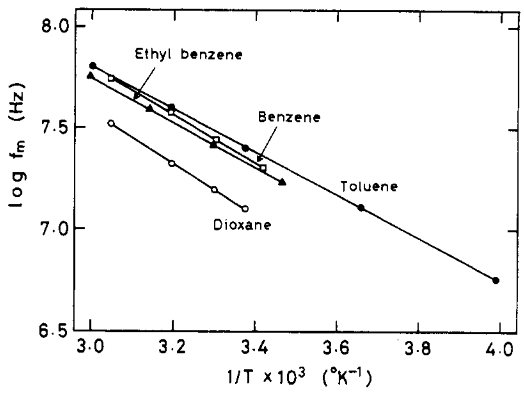

Figure 5. Plot of log f_m against $1/T$.

benzene solutions were employed and the density of the solution was replaced by that of the solvent because the solutions are dilute. It may be concluded that the value of the dipole moment is not much affected by the solvent used.

In order to determine apparent activation energy for the dielectric relaxation process, ΔH_A, the value of log f_m is plotted against the reciprocal of the absolute temperature $1/T$ in Figure 5. The plot gives a straight line for each solution. The activation energy can be obtained from the slope of this line; values thus obtained are listed in Table I. In order to investigate the effect of solvent on the relaxation process, the activation energy ΔH_A is plotted against the apparent activation energy for the solvent viscosity ΔH_η in Figure 6. The plot lies on a straight line described by

$$\Delta H_A = \Delta H_\eta + E \qquad (1)$$

where E takes a value of 2.9 kcal/mol. The activation energy ΔH_η in this figure was determined from the plot of log η_0 against $1/T$, where η_0 is the solvent viscosity.[14,15]

In order to investigate further the effect of the solvent on the relaxation process, the mean relaxation time τ_m (= 1/

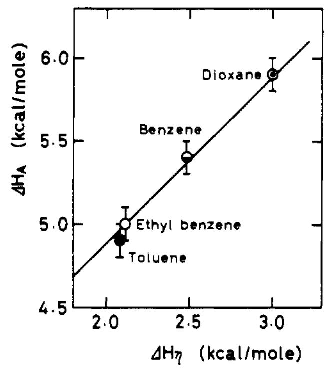

Figure 6. Plot of ΔH_A against ΔH_η.

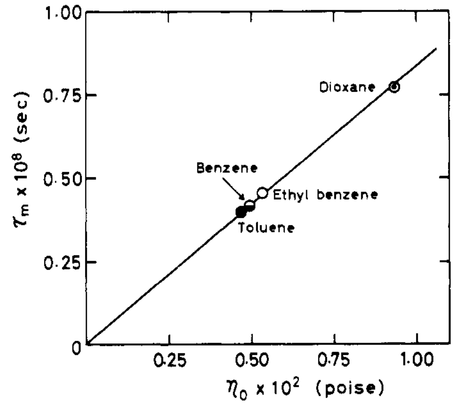

Figure 7. Relationship between relaxation time τ_m and solvent viscosity η_0 at 40°C. The value of τ_m for ethyl benzene solution at 40°C was estimated from the plot of log f_m against $1/T$ in Figure 5.

$(2\pi f_m))$ is plotted against the solvent viscosity η_0 in Figure 7. The plot gives a straight line described by

$$\tau_m = 8.4 \times 10^{-7}\eta_0 \text{ sec} \qquad (\text{at } 40°\text{C}) \qquad (2)$$

where the viscosity is in units of poise. Combining eq 1 and 2, we obtain an experimental equation for the relaxation time

$$\tau_m = 8.0 \times 10^{-9}\eta_0 \exp(E/RT) \text{ sec} \qquad (3)$$

where R is the gas constant. In order to ascertain whether eq 3 is adequate to describe all of the relaxation times observed experimentally, the observed value of log (τ_m/η_0) is plotted against $1/T$ for all solutions in Figure 8 and comparison is made between the observed value and that evaluated from eq 3. The plot lies fairly well on the straight line derived from eq 3 and confirms the adequacy of the equation. Equation 3 is quite independent of the molecular weight of the polymer.

Discussion

The value observed of the effective dipole moment for the monomer unit is in agreement with the value of the dipole moment obtained by Kotera from the low-frequency measurement of dielectric constant.[16] The sample of PpCS employed by Kotera was prepared by the same method of polymerization as ours, so that our value of the dipole moment should naturally turn out to be the same as that of his sample. Furthermore, our value is not much different from other experimental values previously reported.[17-19] This result may be taken to indicate that dielectric dispersions other than the present one do not exist.

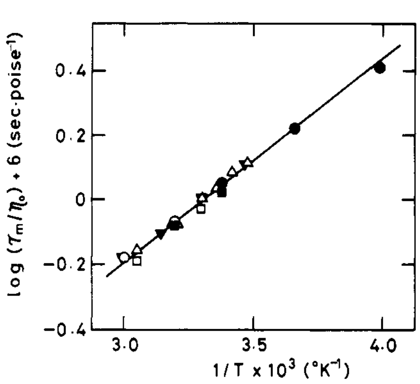

Figure 8. Plot of log (τ_m/η_0) against $1/T$. Symbols are the same as in Figure 3. Line calculated from eq 3.

The observed relaxation time and the observed shape of the loss curve, which are quite independent of the molecular weight of the polymer, indicate that the dielectric dispersion of PpCS in dilute solution can be attributed to a local conformational transition of the chain backbone.

The observed values of the frequency f_m for PpCS in toluene and benzene are in good accord with the results by Stockmayer et al.,[1-3,20] North et al.,[4] and Mikhailov et al.[21] The agreement of the present results for PpCS in toluene with the results of Baysal et al.[20] is perfect.

1. Effect of Solvent on Relaxation Process. None of the solvents studied influenced either the experimental dipole moment or the shape of the loss curve. Only the relaxation times were affected. Experimental relaxation times are proportional to solvent viscosity. Recently Baysal et al.[20] reported that the dielectric relaxation time of poly(*p*-fluorostyrene) in binary solvent mixtures such as toluene–*p*-cymene (1:1) and toluene–*trans*-decaline (2:1) at 25°C are about 50% longer than that in pure toluene, very nearly in the same ratio as the solvent viscosities. In our previous paper,[5] the ratio of the relaxation time of poly(*p*-bromostyrene) in toluene to that in dioxane was reported to be in good agreement with the ratio of the solvent viscosities.

It may be concluded that the relaxation time of poly(*p*-halostyrene) in dilute solution is proportional to the solvent viscosity.

2. Crankshaft Transition. It is well known that isotactic polystyrene in the crystalline state has a three-fold screw axis and three monomer units between two collinear bonds.[22] Some isotactic substituted polystyrenes, such as *p*-fluoro, *o*-fluoro, *o*-methyl, and *m*-methylstyrene, have four-, three-, four-, and eleven-fold screw axes, respectively.[23,24] The crankshaft transition in such polymers occurs as a result of a rotation of a few monomer units around the two collinear bonds.[3,7,25]

It was reported that isotactic polymers such as isotactic polystyrene and isotactic polypropylene in solution have the same helical conformations as those in the crystalline state.[26,27] Moreover, Kobayashi et al.[27] report that isotactic PpCS in a gel solution has a partially helical conformation similar to that of isotactic polystyrene.

Previously Pohl and Zabusky[28] measured dielectric relaxation properties of isotactic and atactic PpCS in benzene, and reported that the mean relaxation time, the relaxation time distribution, and the dipole moment are not seriously influenced by stereoregularity. If the conformational transition in the isotactic PpCS, which gives rise to the dielectric dispersion, is the crankshaft transition, their result indicates that the same transition exist in the atactic PpCS, too.

It is evident, however, that the component of resultant dipole moment of monomer units between the two collinear bonds perpendicular to the crankshaft is zero in the helical conformation of isotactic polymers such as polystyrene and some substituted polystyrenes in the crystalline state. The crankshaft rotation is, then, inactive in dielectric relaxation. Nevertheless, the crankshaft transition is undoubtedly the simplest type of transition giving the molecular weight independent rate constant for conformational transition. Therefore, we will extend the definition of crankshaft transition and call a rotational transition of a few monomer units between two collinear bonds undergoing rotation in general a generalized crankshaft transition. According to this definition, the monomer units between the two bonds do not necessarily form the helical structure of isotactic polymer, but the units must be rigid and no increase of the distance between the two bonds should be involved in this transition. The resultant dipole moment is not necessarily zero.

If the transition observed in the present investigation is assumed to be the crankshaft transition, the number of monomer units between the two collinear bonds has been calculated by employing a three-state model and the Kramers expression for the rate constant.[3,7]

When the potential energy for the conformational transition has the form illustrated in Figure 9 in which upper states are degenerate, two relaxation times

$$\tau_1 = 1/k_1$$

and (4)

$$\tau_2 = 1/(k_1 + 2k_2) = \tau_1/(1 + 2\exp(-\Delta H_0/k_BT))$$

are obtained according to the site theory of relaxation,[29] where k_1 is the rate constant for transition from state 1 to 2, k_2 that from state 2 to 1, and k_B is the Boltzmann constant. The two constants are related by

$$k_2 = k_1 \exp(-\Delta H_0/k_BT) \tag{5}$$

This three-state model was employed in studies of ultrasonic relaxation of polystyrene solution[25,30] because the observed ultrasonic relaxation is of a single type and rotational isomers around a C–C bond have generally three states. The absorption due to τ_1 is inactive in the ultrasonic relaxation.[25,30,31]

Although the three-state model presents two dielectric relaxation times τ_1 and τ_2, the two relaxation times are not very different. When ΔH_0 takes a value between zero and infinity, τ_2 takes a value between τ_1 and $\tau_1/3$. Furthermore, their temperature dependences are nearly the same, since the change in the value of $1/(1 + 2\exp(-\Delta H_0/k_BT))$ with change of temperature is only slight, and its contribution to the apparent activation energy of τ_2 can be neglected in comparison with the observed value of ΔH_A. The largest contribution is that when $\Delta H_0/k_BT = 1.463$, which is only 0.3 kcal/mol in the temperature range employed here. On the other hand, the value of ΔH_A is 4.9–5.9 kcal/mol. It is therefore evident that the loss curve does not show two peaks clearly and the curve does not change distinctly as the temperature changes in conformity with the experimental results. In the present investigation, therefore, the three-state model is assumed to be applicable for an approximate estimation of the relaxation time. The mean relaxation time τ_m, then, takes a value between τ_1 and τ_2:

$$\tau_1/3 \leq \tau_2 \leq \tau_m \leq \tau_1 \tag{6}$$

Experimental eq 3 suggests that the Kramers theory is applicable to the relaxation process.[3,5,7] According to the theory,[7] the rate constant for the crankshaft rotation of a few monomer units over a potential barrier from a position A to C in a viscous medium in the case of large friction, i.e., when $\Sigma_i m_i r_i^2 \gamma_B/(\Sigma_i \xi_i r_i^2)^2 < 1$, is given by

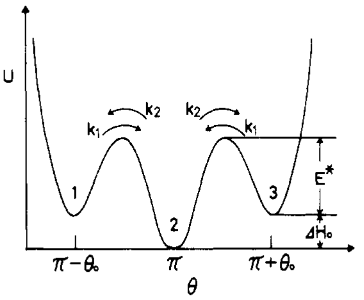

Figure 9. Schematic potential energy for rotational isomers.

$$k = \left[(\gamma_A\gamma_B)^{1/2} \Big/ \left(2\pi \sum_i \xi_i r_i^2\right)\right] \exp(-E^*/k_BT) \tag{7}$$

where γ_A is the curvature of the potential for the rotation at A and the potential has a form $U = \frac{1}{2}\gamma_A(\theta - \theta_A)^2$ near A, γ_B is that at B, the top of the potential, where the potential is given by $U = E^* - \frac{1}{2}\gamma_B(\theta - \theta_B)^2$, ξ_i is the frictional coefficient of ith moving unit, m_i is the mass of the unit, and r_i is the distance of the unit from the shaft.

The Kramers rate constant was employed hitherto by only a few authors for the calculation of the rate of conformational transition in the polymer chain.[3,7,32,33] Recently Paul and Mazo[32] calculated the rate of conformational transition taking account of three states which are similar to ours.

When the monomer unit is treated as a sphere of radius a and Stokes law is employed, the frictional coefficient ξ_i is given by $\xi_i = 6\pi a \eta_0$. If the Kramers rate constant given in eq 7 is used as the constant k_1 in eq 4, the relaxation time τ_1 is given by

$$\tau_1 = \left[\left(12\pi^2 a \sum_i r_i^2\right) \Big/ (\gamma_A\gamma_B)^{1/2}\right] \eta_0 \exp(E^*/k_BT) \tag{8}$$

This equation is the same as eq 3 obtained experimentally in its dependences on solvent viscosity and temperature. The value of E appearing in eq 3 is, therefore, suggested to represent a height of the potential barrier for the crankshaft transition in the chain backbone.

A few monomer units must displace the surrounding solvent molecules in order to rotate around the two collinear bonds in the crankshaft rotation. Stokes law will then be applicable to the frictional coefficient as was pointed out previously by Clark.[34] That this is the case is suggested experimentally as is indicated by eq 2 and 3.

In order to obtain the number of monomer units between the two collinear bonds, we employ a value of 3 Å as the radius a which gives a volume of the sphere equivalent to the van der Waals volume of the monomer unit, and a value of 2.9 kcal/mol for E^* which is the value observed for E in eq 1. The value of γ $(=(\gamma_A\gamma_B)^{1/2})$ employed is 0.91×10^{-12} erg/(radian)^2, which is determined by assuming the form of the potential to be

$$U = \tfrac{1}{2}E^*(1 - \cos 3\theta) \tag{9}$$

Using these values in the inequality 6 and eq 7, and also using eq 3, we obtain

$$2 \times 10 \leq \sum_i r_i^2 \leq 6 \times 10 \text{ Å}^2 \tag{10}$$

Taking the mean value of r_i to be 4 Å, which was assumed to be a reasonable value, judging from the conformation of isotactic polystyrene [22] or isotactic poly(*p*-fluorostyrene),[24] a value of 1–4 was obtained as the number of monomer units between the two collinear bonds. This value is in good agreement with the model of the crankshaft transition mentioned above. If the value of γ_B is taken to be 0.91×10^{-12} erg/(radian)^2 which is the value of γ, the condition of large friction, $\Sigma_i m_i r_i^2 \gamma_B/(\Sigma_i \xi_i r_i^2)^2 = 10^{-3}$–$10^{-2} \ll 1$, is sufficiently satisfied.

A very similar value of the number of the monomer units can also be obtained, even if the frictional coefficient in eq 7, $\Sigma_i \xi_i r_i^2$, is replaced by the frictional coefficient for rotational diffusion of the whole moving unit, $\xi = 8\pi R^3 \eta_0$, where R is the radius of the unit when the unit is treated as a sphere. The volume of the unit is found from the inequality 6 and eq 3 to be

$$1.9 \times 10^2 \leq \tfrac{4}{3}\pi R^3 \leq 5.8 \times 10^2 \text{ Å}^3 \quad (11)$$

The value of 1.9×10^2 Å^3 is nearly the same as the volume of the monomer unit and the value of 5.8×10^2 Å^3 is about four times of that of the unit.

The number of monomer units for several other polymers can also be calculated by using the data previously reported and by employing the inequality 6 and eq 7. The number for poly(p-fluorostyrene) obtained is 2–5, which is in good agreement with that required for the crankshaft transition in isotactic poly(p-fluorostyrene). The number for poly(p-bromostyrene) is 8–20, that for poly(vinyl acetate) is 2–5, and that for poly(vinyl chloride) is 1–3. In these calculations, a value of 3 Å was employed for the radius a and that of 4 Å for the mean value of r_i. The value of E^* employed, in the cases of poly(p-bromostyrene), poly(vinyl acetate), and poly(vinyl chloride), was that observed for E and was reported previously,[5] and in the case of poly(p-fluorostyrene) it was that determined from eq 1 using the data of Baysal et al.[20] The value of γ was determined from eq 9. All of the values of the number of monomer units thus obtained are very small and do not differ much from each other, and their magnitudes are of the order expected for local conformational transition in the chain backbone.

The observed value of E in eq 1 seems rather too small for the rotation of a few monomer units around two skeletal bonds to take place simultaneously. The value of 1–3 kcal/mol found for other polymers also seems too small for such rotation. These small values seem at first sight to suggest a transition which involves only a rotation around a single bond rather than the crankshaft transition which involves a simultaneous rotation around two bonds. However, if the transition involves only a rotation around a single bond, a large part of the chain has to swing through the solvent. Such a transition cannot occur within a local part of the chain, and should be rejected.[35] Very recently Boyd and Breitling[36] performed conformational energy calculations on polyethylene and showed the existence of the low barrier heights, which turned out to be 2.7–4.2 kcal/mol, for a crankshaft transition which involves a simultaneous rotation of two monomer units around two bonds which are parallel but only approximately collinear in this case. Further, Nomura et al.[25] measured ultrasonic relaxation for polystyrene in toluene and suggested the existence of the low barrier of only 1.1 kcal/mol for a crankshaft transition. Their simple calculation of the barrier height also indicates a low barrier height of 0.8 kcal/mol. Therefore, the observed low value of E for PpCS or those for other polymers mentioned above may not be unreasonable.

Reasonable values of the number of monomer units required for the crankshaft transition for some polymers can thus be obtained by employing the three-state model and the Kramers rate constant and by assigning reasonable values to several parameters. This result may support the existence of the crankshaft transition even in atactic polymers in solution.

3. Another Transition. It is thus shown that the dielectric behavior observed in this experiment can be explained fairly well by assuming a crankshaft transition. It seems, however, necessary to consider some other transition too, which may also explain the experimental results. There exists some doubt as to whether the crankshaft transition in a rigorous sense, especially an undistorted rotation of the crankshaft, is occurring in real polymers, since the process involves a simultaneous surmounting of two potential barriers. Some distorted chain motion was also thought worth consideration.

Recently Helfand[7] extended the Kramers theory to the polymer problem and derived an expression for the rate constant of a conformational transition which is a rotational transition somewhat similar to the crankshaft one. The transition involves rotation of a few monomer units between two simultaneously rotating bonds which do not necessarily form a crankshaft in this case. When one of the two bonds translates slightly relative to the other and small displacements of atoms in the chains next to the two bonds occur in the vicinity of a harmonic potential in such a way that the chain may be constructed with harmonic springs bearing the atoms, the rate constant derived does not depend on the chain length and is not affected much by the springs. Moreover, the constant is not much different from that of the crankshaft transition. Therefore, a similar value can be obtained for the number of monomer units between the two bonds undergoing rotation, when this transition is assumed to be that observed in the present investigation. The resultant dipole moment of the monomer units is not necessarily zero in this case either.

4. Shape of Loss Curve. The observed shape of the loss curve is just the same as that observed previously for vinyl polymers such as poly(vinyl chloride), poly(vinyl acetate), and poly(p-bromostyrene) in dilute solution.[5] It may, therefore, be concluded that the observed curve presents a characteristic feature of the dielectric property of the main chain motion of vinyl polymers in dilute solution. It is evident that this characteristic feature of the loss curve cannot be explained by the three-state model employed above, since the loss curve obtained from the model is not necessarily asymmetric.

Several attempts to explain the loss curve were previously presented. Perhaps the most important attempt is to introduce a certain kind of correlation among dipoles.[34,37–41] Some calculations which take such correlation into account were carried out by using the time-dependent Ising model.[37–39] For example, Work and Fujita[37] derived an asymmetrical loss curve and a bimodal curve. The loss curve obtained was, however, very different from the observed one. Anderson[38] calculated the autocorrelation function of a dipole element in an infinite chain and derived an asymmetrical curve, which accords with the Davidson–Cole curve in the limiting case of strong coupling between chain elements. The Davidson–Cole curve is very similar to our observed curve, and the value of H_m obtained by Anderson was 0.35, which is very close to our value of 0.32. It is, however, dangerous to compare the calculated results with experimental data quantitatively, as was pointed out by Anderson, since it was necessary to adopt a model which departs from the real polymer in some respects in order to carry out the calculation.

Williams et al.[40] proposed an empirical equation for the correlation function and succeeded in fitting the calculated curve to the observed one by using appropriate parameters. It is possible to obtain a curve very similar to the present one by employing the equation of Williams et al., though the physical meaning of the equation and the parameter is not sufficiently clear.

It is expected that the observed shape of the loss curve will be explained by taking account of an appropriate correlation among dipoles in the near future.

Conclusion

Dielectric dispersion of poly(*p*-chlorostyrene) in dilute solution can be attributed to a local conformational transition of the chain backbone, which is either a crankshaft transition or a transition in which rotation of a few monomer units between two simultaneously rotating bonds is accompanied by a slight translation of one of the two bonds relative to the other. The relaxation process can be interpreted by the Kramers theory of the rate constant for the transition and evidence is presented which shows that Stokes law is applicable to the friction for the chain motion. The theory gives an adequate explanation not only to the dependence of the relaxation time observed on solvent viscosity and temperature, but also to the magnitude of the relaxation time.

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Frictional Properties of Dilute Block-Copolymer Solutions and Homopolymer Solutions. Application to Molecular Weight Determination

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ABSTRACT: An equation for the translational diffusion coefficient of block copolymers in dilute solution has been obtained by modifying Zimm's equation for homopolymers to take into account the existence of dissimilar segments in block copolymers. Illustrative calculations for homopolymers and block copolymers have been made and the results for homopolymers have been compared with experiments and with the calculations of Yamakawa and Fujii. A procedure has been proposed to determine the molecular weight of a block copolymer from measurements of its limiting viscosity number and its sedimentation coefficient or translational diffusion coefficient.

I. Introduction

There has been much interest in the dynamics of block copolymers. For example, Hall and DeWames,[1] Shen and Hansen,[2] Stockmayer and Kennedy,[3] and Wang and DiMarzio[4] have all discussed the dynamics of free-draining block copolymers. In a previous paper[5] hereafter referred to as paper I, we have discussed the viscoelasticity of block copolymers in dilute solution. In this work, we generalize the bead-spring model theory of Zimm[6] to obtain an equation for the translational diffusion coefficient of block copolymers in dilute solution. Applications of the equation thus obtained to homopolymers and block copolymers in dilute solution are then presented. Finally, we discuss the