Macromolecules 1985, *18*, 1486-1491

Effects of Excluded Volume and Solvent Polarity on the Dielectric Normal Mode Process in Dilute Solutions of Poly(2,6-dichloro-1,4-phenylene oxide)

Keiichiro Adachi,* Hiroshi Okazaki, and Tadao Kotaka

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received October 2, 1984*

ABSTRACT: The excluded volume effect and the influence of solvent polarity on the relaxation strength of the "dielectric normal mode process" originating from fluctuation of the end-to-end distance were investigated on dilute solutions of poly(2,6-dichloro-1,4-phenylene oxide) (PDCPO) in various solvents. In mixed solvents of a good solvent, chlorobenzene, and a nonsolvent, *n*-bromohexane, both the dielectric relaxation strength and the intrinsic viscosity decreased with increasing content of the nonsolvent. This result indicates qualitatively the proportionality between the relaxation strength for the normal mode process and the mean square end-to-end distance $\langle r^2 \rangle$. For quantitative analysis of the relaxation strength, it was necessary to establish the dependence of the ratio F of the internal and external electric fields on the dielectric constant of the solvents, ϵ_s. For this purpose, the dielectric constants of PDCPO solutions in chlorobenzene (ClBz), *o*-dichlorobenzene (DClBz), and carbon disulfide (CS_2) were compared at 2 kHz, well below the relaxation region. The ratios of the values of F in these solvents were approximately unity despite the difference in their ϵ_s, indicating that F itself should be close to unity. The values of $\langle r^2 \rangle F$ in poor solvents determined from the dielectric data were 1.5 ± 0.4 times greater than $\langle r^2 \rangle_0$ calculated for unperturbed chains by postulating free rotation of the repeat units around the ether bond.

Introduction

Linear flexible polymers in which the dipole moments are aligned in the direction parallel to the chain contour exhibit a dielectric relaxation termed the "dielectric normal mode process" due to fluctuation of the end-to-end vector.[1,2] Stockmayer classified such a polymer as a type-A polymer and that having the moment perpendicular to the chain contour as a type-B polymer, which exhibits the "segmental mode process".[1]

Using a "bead-spring model", Zimm[3] and Stockmayer and Baur[4] showed that the polarization of a type-A polymer molecule is proportional to its mean square end-to-end distance $\langle r^2 \rangle$. As will be described later, it is easily shown that this proportionality holds also for non-Gaussian chains. Thus, the dielectric relaxation strength, $\Delta\epsilon = \epsilon_0 - \epsilon_u$, for the normal mode process is given by

$$\frac{\Delta\epsilon}{C} = \frac{4\pi N_A \mu^2 \langle r^2 \rangle F}{3 k_B T M} \tag{1}$$

where ϵ_0 and ϵ_u are the relaxed (static) and unrelaxed dielectric constants, respectively, C is the concentration in g cm^{-3}, μ is the dipole moment per unit contour length, F is the factor of the enhancement of the internal electric field over the external field dependent only on the dielectric constant of the solvent, and N_A, k_B, T, and M have the usual meanings.

Most studies on the dielectric normal mode process reported to date[5-11] were concerned with dynamic properties of the normal mode process, and the static properties given by eq 1 have not been fully investigated. Recently, Mattice and Carpenter[12] demonstrated by computer simulation that the mean-square dipole moment $\langle \mu^2 \rangle$ of a model polymer having parallel dipoles is proportional to $\langle r^2 \rangle$. Thus, we expect that the dielectric data on the normal mode process provide a convenient method for determining $\langle r^2 \rangle$ of type-A polymer chains not only in dilute solutions but also in condensed and bulk systems, for which determination of the coil dimension is usually very difficult.

There are three objectives in this study: the first is to test the validity of eq 1 qualitatively, the second to examine the dependence of F on solvent polarity, and the third to compare $\langle r^2 \rangle$ determined from dielectric data with $\langle r^2 \rangle$ calculated on the basis of statistical mechanics. We used poly(2,6-dichloro-1,4-phenylene oxide) (PDCPO) as a model polymer. The reason was twofold: first, the PDCPO molecule does not possess the moment perpendicular to the chain contour so that the dielectric relaxation is not obscured by the segmental mode, and second, the dielectric behavior in dilute solutions was examined previously.[5] The dielectric relaxation time for PDCPO with molecular weight below 2×10^4 was in agreement with the Rouse[13] and Zimm[3] theory, but that for samples with $M > 2 \times 10^4$ was shorter than the theoretical value on account of long-chain branchings.[5] Although the effect of excluded volume on the dimensions of branched polymers is complex, we used both linear and branched PDCPO samples, since the highest limit of the molecular weight, 2×10^4, below which the PDCPO molecule is linear seemed to be too small to manifest the excluded volume effect. For solvents, we employed three good solvents, chlorobenzene (ClBz), *o*-dichlorobenzene (DClBz), and carbon disulfide (CS_2), and two mixed solvents, ClBz/*n*-bromohexane (BrHx) and ClBz/*n*-hexane (Hx). Since BrHx and Hx are nonsolvents for PDCPO, we could change the quality of the solvents by changing their composition. To examine the variation in the dimension of the PDCPO molecules, we also determined the intrinsic viscosity, $[\eta]$, in the mixed solvents.

For quantitative analysis of the relaxation strength, it is necessary to know the effect of the dielectric constant, ϵ_s, of the solvent on the magnitude of F given in eq 1. According to Stockmayer and Baur,[4] F for the normal mode process in nonpolar solvents is given by

$$F = (\epsilon_s + 2)^2/9 \tag{2}$$

However, the validity of this equation has not been tested experimentally.

For solutions of simple molecules, several equations for F have been proposed. Among them, the Lorentz field being valid for nonpolar solvents is most familiar as the basis of the Clausius-Mosotti and Debye equations:

$$F = (\epsilon_s + 2)/3 \tag{3}$$

For solutions of a simple molecule in polar solvents, Onsager's approximation[14] is more appropriate to express the internal field (see, for example, eq 5-65 in ref 15).[16] Onsager expressed polarization of solutions as a sum of the enhanced electronic and orientational polarizations. As shown in Appendix A, F is approximately equal to the enhancement factor for the orientational polarization of the solute molecule. Thus, F in a polar solvent is given by

$$F = \frac{\epsilon(n_1^2 + 2)^2(2\epsilon + 1)}{3(2\epsilon + n_1^2)^2} \tag{4}$$

where ϵ and n_1^2 are the dielectric constant of the solution and the refractive index of the solute, respectively. For the present dilute solutions, we may assume $\epsilon = \epsilon_s$ and that n_1^2 is approximately equal to the dielectric constant, ϵ_g, of PDCPO in the glassy state. Thus, eq 4 may be rewritten as

$$F = \epsilon_s(\epsilon_g + 2)^2(2\epsilon_s + 1)/[3(2\epsilon_s + \epsilon_g)^2] \tag{5}$$

Although eq 3 and 4 represent the enhancement of the internal field for simple molecules, their validity for the normal mode process of a type-A polymer has not yet been tested experimentally. Since these equations were derived by assuming a spherical cavity field, their applicability to the polarization of a whole random coil may be doubtful. In this study, we examined the ϵ_s dependence of F by comparing the increment of the static dielectric constants of solutions of PDCPO in different solvent systems: DClBz (ϵ_s = 10.1 at 298 K), ClBz (ϵ_s = 5.6 at 298 K), and CS_2 (ϵ_s = 2.6 at 298 K). The ratios of F in these solvents were determined in terms of eq 14 given later and compared with the theoretical values expected from eq 2, 3, and 5.

Theory

Average Polarization of a Model Chain. First, we show that the relaxation strength, $\Delta\epsilon$ ($=\epsilon_0 - \epsilon_u$), for the normal mode process is proportional to $\langle r^2\rangle$ irrespective of the shape of the distribution function of the end-to-end distance r. We consider a model chain having the parallel dipole moment μ per unit contour length. One end having the negative charge is fixed at the origin of a Cartesian coordinate system, and the other end at a coordinate (x, y, z) is distributed around the origin with a spherically symmetrical distribution function $\Phi(r)$. When an external electric field of strength E is applied in the z direction, the molecule is subjected to an effective internal field EF. Since the dipolar vector of the whole molecule is μr, the electric energy for the molecule is $-\mu zEF$. Therefore, the distribution function $\Phi(r)$ in the absence of an electric field may be modified into $\exp(\mu zEF/k_BT)\Phi(r)$. Thus, the average polarization p of the model chain may be written as

$$p = \int\int\int \mu z \exp(\mu zEF/k_BT)\Phi(r) \sin\theta \, r^2 \, d\theta \, d\phi \, dr \tag{6}$$

where θ and ϕ denote the angles in a polar coordinate system, e.g., $z = r\cos\theta$. Under the condition of $\mu zFE \ll k_BT$, p is reduced to

$$p = (\mu^2EF/3k_BT)\int 4\pi r^4\Phi(r)\, dr \tag{7}$$

Since the integral in eq 7 represents $\langle r^2\rangle$, eq 1 holds irrespective of the shape of the distribution function. Obviously, eq 1 is valid even for an extreme case of a rodlike conformation.

Relaxation Strength for a Branched Chain. Since branched samples were used in the present study, we need to analyze the relaxation strength of branched polymers. We regard the main chain as one of the branches and consider the polarization p of a branched molecule composed of n branches having a dipole moment directed from the branch point to the end. They are numbered as 1, 2, ..., n. It may be assumed that the polarization of any particular branch is independent of any other branch, and hence eq 7 can be applied. Thus, p is given by

$$p = \sum_{i=1}^{n} \frac{\mu^2\langle r_{bi}^2\rangle FE}{3k_BT} \tag{8}$$

where r_{bi} denotes the end-to-end distance of the ith branch. From this equation, $\Delta\epsilon$ for solutions of a branched polymer with the concentration C (in g cm^{-3}) is given by

$$\Delta\epsilon/C = (4\pi\mu^2N_AF/3k_BTM)\sum_{i=1}^{n}\langle r_{bi}^2\rangle \tag{9}$$

$$= (4\pi\mu^2N_AF/3k_BT)\langle r_b^2\rangle/M_b \tag{10}$$

where M_b and $\langle r_b^2\rangle$ denote, respectively, the number averages of the molecular weight of the branches and the mean square distance between the branch point and the end of the branch.

Internal Field for the Normal Mode Process. Finally, we propose a method to determine F from the concentration dependence of the dielectric constant ϵ at a sufficiently low frequency satisfying that ϵ is equal to ϵ_0. The unrelaxed dielectric constant, ϵ_u, in eq 1 is composed of two terms: the polarization of the solvent molecules, p_s, and that of the monomer units, p_m. Since the relaxation frequency for polar solvents is usually much higher than that for the normal mode process, p_s is due to both the orientational and electronic polarizations of the solvent molecules, but p_m is due only to the atomic and electronic polarization of the polymer. Under a given external field E, ϵ_u is given by

$$(\epsilon_u - 1)E/4\pi = N_sp_s + N_mp_m \tag{11}$$

where N_s and N_m denote the number of solvent molecules and repeat units in a unit volume, respectively. Hereafter, the suffixes s and m denote the quantities referred to the solvent and the monomer, respectively. By using Onsager's approximation,[14] p_s and p_m are expressed in terms of ϵ_s and ϵ_g as shown in Appendix B. It should be noted that p_m was calculated by assuming that the monomer unit has a spherical shape. Thus, ϵ_u is given by

$$\epsilon_u - 1 = (\rho/\rho_s)[(1 - w)(\epsilon_s - 1) + w\epsilon_s\xi + 3\epsilon_g\rho_sw(\epsilon_g - 1)/(2\epsilon_s + \epsilon_g)] \tag{12}$$

where w is the weight fraction of the polymer, and ρ and ρ_s are the densities of the solution and the pure solvent, respectively. As indicated in Appendix B, ξ is a small correction factor for the change in the reaction field and is given by

$$\xi = \frac{(2\epsilon_s^2 + \epsilon_sn_s^4 + n_s^4 - 4\epsilon_s^2n_s^2)(\epsilon_s - \epsilon_g)}{\epsilon_s^2(2\epsilon_s + n_s^2)^2} \tag{13}$$

where n_s is the solvent refractive index. For nonpolar solvents, ϵ_s equals n_s^2, and hence $\xi = (1 - \epsilon_s)(\epsilon_s - \epsilon_g)/(3\epsilon_s^2)$. By differentiating eq 1 and 12 with respect to w, we finally obtain

$$C_1\langle r^2\rangle\rho_sF = d\epsilon/dw + (\epsilon_s - C_2) \tag{14}$$

where C_1 is a factor independent of the solvent, and C_2 is independent of the molecular weight of the solute, as defined in Appendix B. In eq 14, we assumed that ρ is equal to ρ_s for very dilute solutions. Equation 14 enables us to determine the ratio of F determined in different solvents, provided the ratio of $\langle r^2\rangle$ in these solvents is known in advance.

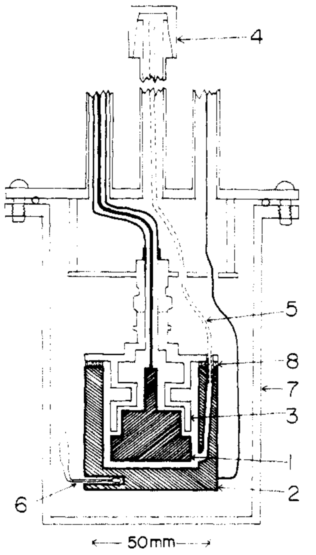

Figure 1. Cross section of the condenser cell: (1) guarded electrode; (2) unguarded electrode; (3) guard; (4) inlet for sample solutions; (5) a tube made of poly(tetrafluoroethylene); (6) thermistor; (7) jacket; (8) insulator (PTFE).

Table I
Characteristics of the Samples

code	$10^{-3}M_w$	M_w/M_n
P7	1380	1.36
P8	933	1.45
P9	16.6	1.26
P12	15.0	1.30

Experimental Section

Materials. Four PDCPO samples, coded P7, P8, P9, and P12, were used. The methods of preparation and characterization were described previously.[5] Their weight-average molecular weights M_w and M_w/M_n ratios are given in Table I. Samples P9 and P12 are linear, but P7 and P8 are branched. All solvents for dielectric measurements were distilled together with calcium hydride under reduced pressure.

Methods. The method of dielectric measurements was the same as described previously[5] except that we used a condenser cell specially designed for precise dielectric measurements on dilute solutions in the range below 100 kHz. The cross section of the cell is shown in Figure 1. Before measurements, the container (7) was evacuated thoroughly and then filled with argon. When a temperature equilibrium was attained, the capacitance of the empty cell (ca. 10 pF) was measured. Then a sample solution was introduced into the cell from the inlet (4) through a PTFE tube (5) without dismantling the cell. In this way, the dielectric constant was measured to a precision of 10^{-5}. Temperature was measured with a thermistor (6) to an accuracy of ±0.01 K.

Density and intrinsic viscosity of solutions were determined with a Lipkin–Davison type pycnometer (of 5.9-cm^3 volume) and with a Ubbelohde-type viscometer, respectively.

Results and Discussion

Effect of Excluded Volume. Dielectric measurements in the relaxation frequency region were made on solutions of P8 and P9 in ClBz/BrHx and ClBz/Hx at 300 K. Figure 2 shows the frequency dependence of the normalized dielectric loss factor of P9, i.e., the difference of the loss factor ϵ'' of a solution minus that of the solvent ϵ_s divided by concentration C (in g cm^{-3}). As seen in this figure, the height of the loss maximum ϵ''_{max} and hence the relaxation strength $\Delta\epsilon$ decreased with increasing content of BrHx. Similar behavior was observed for solutions of P8 in the same mixed solvent and for solutions of P9 in ClBz/Hx. The values of $\Delta\epsilon/C$ determined from the area under the loss curves for these solutions are listed in Table II. We reported previously[5] that $\Delta\epsilon/C$ for P9 in ClBz was 6.7. Careful measurement indicated $\Delta\epsilon/C = 5.9$ as given in Table II.

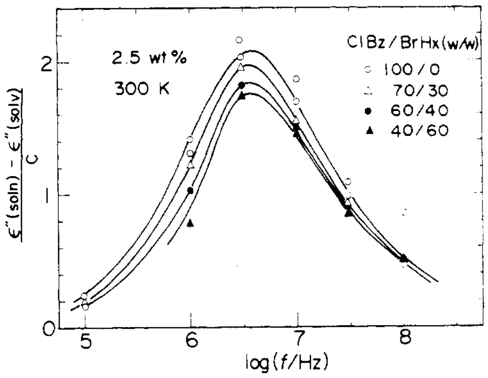

Figure 2. Frequency dependence of $[\epsilon''(\text{soln}) - \epsilon''(\text{solv})]/C$ for solutions of P9 dissolved in mixed solvents of chlorobenzene (ClBz) and *n*-bromohexane (BrHx), where ϵ''(soln) and ϵ''(solv) represent the loss factors of the solution and solvent, respectively, and C denotes concentration in g/cm^3. Compositions of the solvent are given in this figure.

Table II
$\Delta\epsilon/C$, $[\eta]$, and $F\langle r^2\rangle$ for Solutions of P8 and P9 in Mixed Solvents

sample code	solvent[a]	solvent comp, wt/wt	$\Delta\epsilon/c$, g^{-1} cm^3	$[\eta]$, g^{-1} cm^3	$10^{12}\langle r^2\rangle F$, cm^2
P9	ClBz/BrHx	100/0	5.9	12.5	1.97
		70/30	5.62	12.1	1.88
		60/40	5.22	11.8	1.74
		40/60	5.00	(13.1)	1.67
P9	ClBz/Hx	90/10	5.65		1.88
		85/15	5.48		1.83
P8	ClBz/BrHx	100/0	6.5	42.7	122[b]
		80/20	6.07	38.0	114
		60/40	5.71	34.9	107

[a] ClBz, BrHx, and Hx represent chlorobenzene, *n*-bromohexane, and *n*-hexane, respectively. [b] $\langle r^2\rangle$ for P8 represents $\sum\langle r_{bi}{}^2\rangle$ as shown by eq 9.

For interpretation of this result, it is necessary to check the effect of ϵ_s on F, because F might vary as the composition of the mixed solvent is changed. The dielectric constant of the ClBz/BrHx system increased slightly from 5.61 for pure ClBz to 5.71 for BrHx with increasing BrHx content. On the other hand, ϵ_s for the ClBz/Hx system decreased with Hx content: $\epsilon_s = 4.70$ for 15 wt % Hx content. If we assume that F for the normal mode process increases monotonously with ϵ_s as is given by eq 2–5, we expect that the effect of the internal field causes a slight increase in $\Delta\epsilon$ for the normal mode process in ClBz/BrHx with increasing BrHx content. Since the experimental data given in Table II show a tendency opposite to this expectation, the decrease in $\Delta\epsilon$ with increasing content of the nonsolvent BrHx should be attributed to the excluded volume effect.

To confirm this, we measured the intrinsic viscosity $[\eta]$ of P8 and P9 in ClBz/BrHx mixtures. As shown in Table II, $[\eta]$ also decreased with BrHx content, reflecting a decrease in chain dimensions. Figure 3 shows the double-logarithmic plot of $\Delta\epsilon/C$ vs. $[\eta]$. According to the Flory–Fox theory,[17] $[\eta]$ is proportional to $\langle s^2\rangle^{3/2}$ in the unperturbed state, where $\langle s^2\rangle$ is the mean-square radius of gyration. This relation is expected to hold roughly even for a good solvent system, and hence we expect that the logarithm of $\Delta\epsilon/C$ is approximately proportional to (2/3) log $[\eta]$.

In Figure 3, the dashed line represents the slope of $^2/_3$. The slope for P8 is in agreement with this expectation but that for P9 is not. Since the molecular weight of P9 is low,

Table III
Parameters[a] in Eq 14 and B.8

code	solvent	T	$d\epsilon/dw$	ϵ_s	ρ_s	$d\epsilon/dw$	ξ	C_2	$C_1\langle r^2\rangle F$
P7	CS_2	298	10.98	2.63	1.26	0.332	−0.052	3.27	8.09
	ClBz	298	7.33	5.62	1.10	0.387	−0.078	4.06	8.02
	DClBz	298	3.17	10.05	1.30	0.269	−0.092	4.40	6.68
P12	CS_2	298	9.52					3.27	6.93
	ClBz	298	6.53					4.06	7.30
	DClBz	298	3.58					4.44	7.00
P7	ClBz	293	7.40	5.70				4.08	8.15
	DClBz	293	4.00	10.27				4.47	7.44

[a] C_2 for P12 at 298 K and P7 at 293 K were calculated with the values of ρ_s, $d\epsilon/dw$, and ξ for P7 at 298 K since the slight change in ρ was negligible. Units of T, ρ_s, and $C_1\langle r^2\rangle F$ are K, g cm^{-3}, and g^{-1} cm^3, respectively. Other parameters are dimensionless.

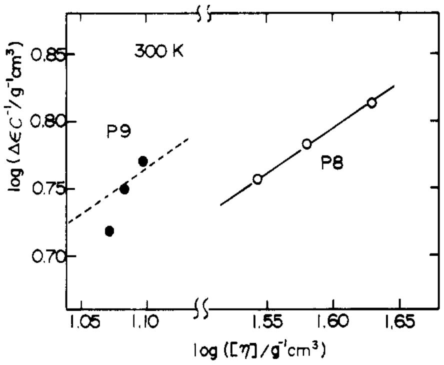

Figure 3. Double-logarithmic plot of relaxation strength $\Delta\epsilon$ and intrinsic viscosity $[\eta]$ for solutions of P8 and P9 in a mixed solvent of chlorobenzene and *n*-bromohexane.

the excluded volume effect is not effective for this polymer. The result on P9 suggests that for polymers with relatively low molecular weight, $\langle r^2\rangle$ is more sensitive to the excluded volume effect than $\langle s^2\rangle$. In contrast to P9, the branched sample P8 exhibited a slope close to $^2/_3$. As indicated by eq 7, $\Delta\epsilon$ for P8 is linear to the sum of $\langle r_{bi}^2\rangle$. Since the calculation of the excluded volume effect on $\langle s^2\rangle$ for branched polymers is complex, it is difficult to describe theoretically the relation between $\langle r_b^2\rangle$ and $\langle s^2\rangle$.[18] The present result indicates that the expansion factor for $\langle s^2\rangle$ of a branched molecule is approximately equal to that for $\langle r_b^2\rangle$.

In Table II, we note that values of $\Delta\epsilon/C$ for P8/ClBz solutions are greater than those for P9/ClBz solutions. This result may be attributed to the difference in the average chain length between P8 and P9. From the relaxation time for P8 solutions reported previously,[5] the average molecular weight, M_b, of the branch for P8 is estimated to be 5.6×10^4, which is greater than the molecular weight of P9. Generally, the excluded volume effect causes an increase in $\langle r^2\rangle/M$ with increasing molecular weight. Hence, $\langle r_b^2\rangle/M_b$ for P8 is greater than $\langle r^2\rangle/M$ for P9 in the good solvent ClBz.

Concentration Dependence of Static Dielectric Constant. Plots of ϵ at 2 kHz vs. the weight fraction w for solutions of P7 and P12 in ClBz, DClBz, and CS_2 are shown in Figures 4, 5, and 6, respectively. Since the relaxation frequency for PDCPO solutions was located in the range from 100 kHz to 10 MHz,[5] ϵ at 2 kHz can be regarded as the static dielectric constant. On the basis of these data, we examined the dependence of F on ϵ_s using eq 12. The values of $d\epsilon/dw$ determined from the slope of these plots are listed in Table III. The intrinsic viscosities for P7 in CS_2, ClBz, and DClBz determined at 298 K were 59.7, 51.4, and 50.9 cm^3/g, respectively. From these data with the assumption of linearity between $\langle r^2\rangle$ and $[\eta]^{2/3}$, $\langle r^2\rangle$ in CS_2 was estimated to be 1.10 times greater than that in ClBz, but those in ClBz and DClBz are approximately the same. The parameters in eq 14 and eq B.8 were calculated in this way with ϵ_g (=3.29) and ρ_g (=1.56)[19] and are listed in Table III.

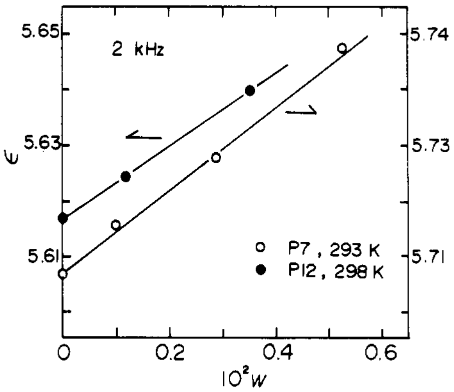

Figure 4. Weight fraction dependence of the dielectric constant at 2 kHz for P7 and P12 solutions in chlorobenzene (ClBz).

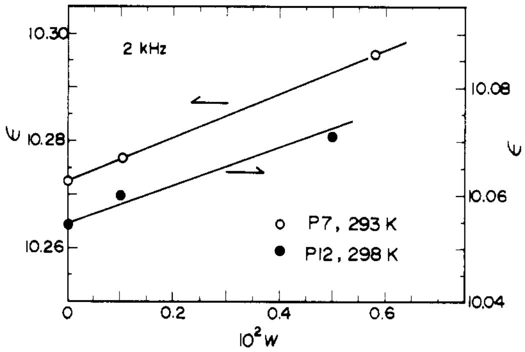

Figure 5. Weight fraction dependence of the dielectric constant at 2 kHz for P7 and P12 solutions in *o*-dichlorobenzene (DClBz).

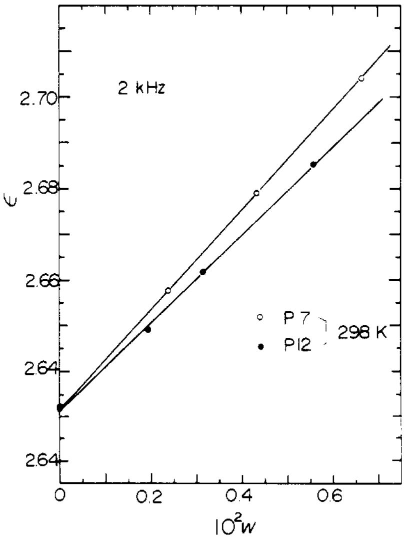

Figure 6. Weight fraction dependence of the dielectric constant at 2 kHz for P7 and P12 solutions in carbon disulfide (CS_2).

Table IV
Ratio of F for Solutions of PDCPO in DClBz, ClBz, and CS_2 at 298 K and Ratios of F Calculated Based on Eq 2, 3, and 5[a]

	exptl values		theor values		
	P7	P12	a	b	c
F(ClBz)/F(CS_2)	1.09	1.16	5.25	3.40	
F(DClBz)/F(CS_2)	0.91	1.11	7.22	4.67	
F(DClBz)/F(ClBz)	0.83	0.96			1.19

[a] The values in columns a, b, and c were those calculated with the combinations of eq 5/eq 3, eq 5/eq 2, and eq 5/eq 5, respectively.

From the values of $C_1\langle r^2\rangle F$ listed in Table III, we calculated the ratios of F in different solvents, taking into account that $\langle r^2\rangle$ in CS_2 is 1.10 times greater than those in the other solvents. These ratios are listed in Table IV and compared with the theoretical values calculated with eq 2–5. Since ClBz and DClBz are polar solvents, eq 5 was used to estimate F for solutions in these solvents, but eq 2 and 3 were used for nonpolar CS_2 solutions. As shown in Table IV, the experimental values of the ratio of F is close to unity, while the theoretical ratio is several times greater than unity. This fact indicates strongly that F is independent of the value of ϵ_s and hence F itself should be unity because $F = 1$ in a vacuum ($\epsilon_s = 1$). Therefore, eq 2–5 are not applicable to the normal mode process.

This result can be explained as follows. It is known that when the strength of an electric field is measured over a relatively long distance, say 10 nm, or over the entire range between electrodes, it is always the same as that in a vacuum, regardless of whether a dielectric material is inserted or not. Since the normal mode process is accompanied by fluctuations of the end-to-end vector, the effective electric field for the normal mode process could be a field averaged, at least, over the order of the end-to-end distance r. Hence F can be close to unity.

However, one may also assume that the polarization of a polymer having parallel dipoles is a consequence of the accumulation of the polarization vector of each repeat unit. The torque for the dipole of the repeat unit should be governed by the local electric field given by any of the equations in eq 2–5. The effective dipole moment due to the influence of the reaction field may be greater than the moment in a vacuum. However, the experimental data are not in harmony with any of these equations. It should be noted that the solvent molecules cannot be placed at the positions where neighboring repeat units are located. Therefore, the internal field for the parallel dipoles of the repeat units should be much weaker than the field for the free dipole placed in a random arrangement of other dipoles.

Calculation of Mean Square End-to-End Distance. In the previous section, we considered that F is close to unity from the ratio of F for solutions of PDCPO in different solvents. To confirm this, we compared $\langle r^2\rangle F$ determned from the dielectric data with the value of $\langle r^2\rangle$ calculated in terms of the statistical mechanics of chain molecules.[20] In our previous paper,[5] we estimated μ for the PDCPO molecule to be 2.85×10^{-11} (in cgs esu) from the bond moments. Using this value, we calculated $\langle r^2\rangle F$ by eq 1 for solutions of P8 and P9, and the results are listed in Table II.

The mean square end-to-end distance in the unperturbed state $\langle r^2\rangle_0$ is given by

$$\langle r^2\rangle_0 = C_X X b^2 \qquad (15)$$

where C_X is the characteristic ratio, X is the number of repeat units in the molecule, and b is the length of the repeat unit (=0.548 nm). Tonelli[21] calculated conformational energies for derivatives of poly(phenylene oxide) substituted with methyl and phenyl groups. He reported that the statistical average of cos ψ is nearly zero, where ψ represents the angle for rotation of the repeat unit around the C–O bond. Since the van der Waals radius of a chlorine atom is similar to that of the methyl group, we may assume that $\langle\cos\psi\rangle$ for the PDCPO molecule also vanishes. Thus, we calculated C_X by assuming free rotation of the repeat unit with respect to the C–O bond:

$$C_X = (1+\alpha)/(1-\alpha) - (2\alpha/X)(1-\alpha^X)(1-\alpha)^{-2} \qquad (16)$$

where α is the cosine of the supplement θ of the C–O–C angle. θ is reported to be 61° from the dimensions in dilute solutions[22] and 53° from crystallographic data on poly(2,6-diphenyl-1,4-phenylene oxide).[23] For $\theta = 61°$ and $\theta = 53°$, C_X amounts to 2.88 and 4.02, and $\langle r^2\rangle_0$ amounts to 8.9×10^{-13} and 1.40×10^{-12} cm^2 for P9 ($X = 103$), respectively. $\langle r^2\rangle_0$ values thus calculated are 1.9–1.2 times smaller than $\langle r^2\rangle F$ determined for solutions of P9 in a mixed solvent of ClBz/BrHx containing 60% BrHx, which is expected to have a quality similar to a Θ solvent. If the assumptions used in this calculation are valid, we should take $F = 1.2$–1.9. These values are still smaller than the values of $F = 6.5$, 2.5, and 3.0 expected from eq 2, 3, and 5, respectively, indicating that F is close to unity. It is noted that if $\langle\cos\psi\rangle$ (=β) for the PDCPO molecule does not vanish, C_X increases by a factor of $(1+\beta)/(1-\beta)$. If we assume a relatively small value of β of ca. 0.2, the statistically calculated $\langle r^2\rangle_0$ coincides with the observed $\langle r^2\rangle F$, resulting in $F = 1$. At present, $F = 1$ appears to be a better approximation than those given by eq 2, 3, and 5.

Conclusions

(1) The dielectric relaxation strength for the normal mode process is proportional to the mean square end-to-end distance irrespective of the excluded volume effect. It was confirmed that the relaxation strength decreases in poor solvents.

(2) The factor of the enhancement F of the internal over external electric fields for the normal mode process is close to unity. The vacuum field approximation appears to be most appropriate over either the Lorentz or the Onsager field approximations.

Acknowledgment. This work was supported in part by The Institute of Polymer Research, Osaka University.

Appendix A

From the Onsager equation,[14] the static dielectric constant, ϵ_0, of a solution in a polar solvent is given by

$$\frac{\epsilon_0 - 1}{4\pi} = \frac{N_1\epsilon_0(n_1^2+2)}{2\epsilon_0+n_1^2}\left[\alpha_1 + \frac{(n_1^2+2)(2\epsilon_0+1)}{3(2\epsilon_0+n_1^2)}\left(\frac{\mu_1^2}{3k_BT}\right)\right] + N_2p_2(0) \qquad (A.1)$$

where suffixes 1 and 2 denote the solute and the solvent, respectively, n is the refractive index, $p(0)$ is the polarization per molecule under unit static field, N is the number of molecules, α is the polarizability, and μ_1 is the dipole moment of the solute. Similarly, the unrelaxed dielectric constant $\epsilon(f)$ of the solution at a frequency f satisfying $f_{c1} < f < f_{c2}$ is given by

$$\frac{\epsilon(f) - 1}{4\pi} = \left[\frac{N_1\epsilon(f)(n_1^2+2)}{(2\epsilon(f)+n_1^2)^2}\right]\alpha_1 + N_2p_2(f) \qquad (A.2)$$

where f_{c1} and f_{c2} denote the relaxation frequencies for the solute and the solvent, respectively, and $p_2(f)$ is the polarization of the solvent molecule at the frequency. In very dilute solutions, the front factor for the first term of eq A.1 is approximately equal to that for eq A.2, and $p_2(0)$ is equal to $p_2(f)$. From these equations we obtain

$$\frac{\epsilon_0 - \epsilon(f)}{4\pi} = \frac{N_1\epsilon_0(n_1{}^2 + 2)^2(2\epsilon_0 + 1)}{3(2\epsilon_0 + n_1{}^2)^2}\left(\frac{\mu_1{}^2}{3k_BT}\right) \tag{A.3}$$

Therefore, F in a polar solvent is given by eq 4.

Appendix B

From the Onsager approximation, p_s in eq 11 is given by

$$p_s/E = N_s\frac{\epsilon_u(n_s{}^2 + 2)}{2\epsilon_s + n_s{}^2}\alpha_s + \frac{(n_s{}^2 + 2)^2(2\epsilon_u + 1)\epsilon_u}{(2\epsilon_u + n_s{}^2)^2}\left(\frac{N_s\mu_s{}^2}{9k_BT}\right) \tag{B.1}$$

where ϵ_u is the high-frequency dielectric constant of the solution, N_s is the number of solvent molecules, n_s is the refractive index, α_s is the polarizability, and μ_s is the dipole moment of the solvent. For dilute solution, eq B.1 may be written by using a parameter $x = \epsilon_s - \epsilon_u$:

$$p_s/E = \frac{\rho(1 - w)N_{s0}}{\rho_s}\left[\left(\frac{\epsilon_s(n_s{}^2 + 2)\alpha_s}{2\epsilon_s + n_s{}^2}\right)\left(1 + \frac{2x}{2\epsilon_s + n_s{}^2} - \frac{x}{\epsilon_s}\right) + \left(\frac{(n_s{}^2 + 2)^2(2\epsilon_s + 1)\epsilon_s\mu_s{}^2}{9k_BT(2\epsilon_s + n_s{}^2)^2}\right)\left(1 + \frac{4x}{2\epsilon_s + n_s{}^2} - \frac{2x}{2\epsilon_s + 1}\right)\right] \tag{B.2}$$

where ρ is the density of the solution, w is the weight fraction of the polymer, and ρ_s and N_{s0} are the density and the number of molecules of pure solvent, respectively. The terms appearing in this equation are divided into two groups, one not including x and the other including x. The former is proportional to the polarization of the pure solvent multiplied by the number of solvent molecules, while the latter is the calibration term representing the change in the polarization of the solvent due to the variation of the reaction field. Therefore, eq B.2 may be cast into the following form:

$$p_s/E = \frac{\rho(1 - w)}{\rho_s}\left(\frac{\epsilon_s - 1}{4\pi}\right) + \frac{\rho w\epsilon_s}{\rho_s}\left(\frac{\xi}{4\pi}\right) \tag{B.3}$$

where the second term is the correction term and ξ is the a parameter. In order to evaluate ξ, we assume additivity of the dielectric constant of the solute and the solvent: x is given by $x = w(\epsilon_s - \epsilon_g)$. By substituting this in eq B.2 and neglecting the terms of order higher than w^2, we calculate ξ as given by eq 13.

On the other hand, p_m in eq 11 is given by

$$p_m/E = N_m(\epsilon_g + 2)\epsilon_u\alpha_m/(2\epsilon_u + \epsilon_g) \tag{B.4}$$

where N_m is the number of monomer units in 1 cm^3, ϵ_g is the dielectric constant in the glassy state, and α_m is the polarizability of the monomer unit. α_m may be given by

$$(\epsilon_g - 1)/(\epsilon_g + 1) = (4\pi/3)N_{mg}\alpha_m \tag{B.5}$$

where N_{mg} is the number of monomer units in a unit volume of the glassy sample. Thus, p_m is finally given approximately by

$$p_m/E = \frac{\rho w}{\rho_g}\left(\frac{3\epsilon_g}{2\epsilon_s + \epsilon_g}\right)\left(\frac{\epsilon_g - 1}{4\pi}\right) \tag{B.6}$$

By using eq B.3 and B.6, we obtain eq 12. By differentiating eq 1 (in which $\epsilon_0 = \epsilon$) and eq 12 with respect to w, we obtain eq 14. The parameters C_1 and C_2 in eq 14 are given by

$$C_1 = 4\pi N_A\mu^2/(3k_BTM) \tag{B.7}$$

$$C_2 = 1 + \left(\frac{\epsilon_s - 1}{\rho_s}\right)\left(\frac{d\rho}{dw}\right) + \epsilon_s\xi + \frac{3\epsilon_s(\epsilon_g - 1)\rho_s}{(2\epsilon_s + \epsilon_g)\rho_g} \tag{B.8}$$

Registry No. PDCPO (SRU), 26023-26-7; 2,6-dichlorophenol homopolymer, 25511-62-0.

References and Notes

(1) Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539.
(2) North, A. M. *Chem. Soc. Rev.* **1972**, *1*, 49.
(3) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(4) Stockmayer, W. H.; Baur, M. E. *J. Am. Chem. Soc.* **1964**, *86*, 3485.
(5) Adachi, K.; Kotaka, T. *Macromolecules* **1983**, *16*, 1936.
(6) Baur, M. E.; Stockmayer, W. H. *J. Chem. Phys.* **1965**, *43*, 4319.
(7) Stockmayer, W. H.; Burke, J. J. *Macromolecules* **1969**, *2*, 647.
(8) Jones, A. A.; Stockmayer, W. H.; Molinari, R. J. *J. Polym. Sci., Polym. Symp.* **1976**, *No. 54*, 227.
(9) Hirose, M.; Yamakawa, N.; Araki, K.; Imamura, Y. *Rep. Prog. Polym. Phys. Jpn.* **1977**, *20*, 117.
(10) Adachi, K.; Kotaka, T. *Macromolecules* **1984**, *17*, 120.
(11) Mashimo, S.; Yagihara, S.; Chiba, A. *Macromolecules* **1984**, *17*, 630.
(12) Mattice, W. L.; Carpenter, D. K. *Macromolecules* **1984**, *17*, 625.
(13) Rouse, P. E. *J. Chem. Phys.* **1956**, *24*, 269.
(14) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.
(15) Bottcher, C. J. F. "Theory of Electric Polarization"; Elsevier: Amsterdam, 1973; Vol. I.
(16) F should be calculated by considering both the electric and orientational polarization. However, in eq 4 and 5, only the enhancement of the orientational polarization was taken into account for the sake of simplicity.
(17) Flory, P. J.; Fox, T. G. *J. Am. Chem. Soc.* **1951**, *73*, 1907, 1909, 1915.
(18) Berry, G. C.; Orofino, T. A. *J. Chem. Phys.* **1964**, *40*, 1614.
(19) Adachi, K.; Ohta, K.; Kotaka, T. *Polymer* **1984**, *25*, 625.
(20) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience Publishers: New York, 1969.
(21) Tonelli, A. E. *Macromolecules* **1973**, *6*, 503.
(22) Shultz, A. R. *J. Polym. Sci., Part A-2* **1970**, *8*, 883.
(23) Boon, J.; Magre, E. P. *Makromol. Chem.* **1969**, *126*, 130; **1970**, *136*, 267.