NOTES

Dielectric Relaxation in Solutions of Poly(2,6-dimethyl-1,4-phenylene oxide)

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Flexible polymers having the dipole moment parallel to the chain contour exhibit the dielectric normal mode process due to fluctuation of the end-to-end vector. Stockmayer classified such polymers as type-A polymers.¹ Recently, we reported a series of studies on the dielectric normal mode process for solutions of poly(2,6-dichloro-1,4-phenylene oxide) (PDCPO),²⁻⁴ cis-polyisoprene,⁵⁻⁷ and polychloroprene⁸ over a wide concentration range including the bulk state. Resemblance of the chemical structure of poly(2,6-dimethyl-1,4-phenylene oxide) (PDMPO) to PDCPO ensures that PDMPO should also exhibit a normal mode process. The symmetrical structure of the repeat unit of the PDMPO molecule obviously indicates that this molecule has only the component of dipole moment parallel to the chain contour. Therefore, if the dielectric relaxation can be observed, it must be assigned to the normal mode process, provided that the sample does not contain impurities and irregular linkages.

To date, no data have been reported indicating clearly that PDMPO shows the molecular-weight-dependent dielectric relaxation which is characteristic of the normal mode process. Karasz *et al.*⁹ reported that undiluted PDMPO exhibits a clear loss peak at about 500 K in the temperature dependence curve of the loss

factor observed at 1 kHz. However, they did not examine the molecular weight dependence of the relaxation time or the loss peak temperature. In this study, we investigated the dielectric behavior of benzene solutions of PDMPO with varying molecular weight to clarify whether PDMPO is a type-A polymer.

EXPERIMENTAL

The PDMPO samples used were prepared by the oxidative-coupling method of Hay¹⁰ from 2,6-dimethylphenol at 303 K in a mixture of nitrobenzene and pyridine of 20/7 (vol/vol) ratio using CuCl₂ catalyst. We prepared a few samples with different average molecular weights by controlling the amount of catalyst. The as-synthesized samples were fractionated from chloroform or benzene solutions using methanol as the precipitant. However, gel permeation chromatograms of the fractionated samples were almost as broad as those unfractionated. It was found that only low molecular weight species were removed by this procedure. Probably crystallization of PDMPO in the polymer rich phase may be the cause of this unsuccessful fractionation.¹¹ The fractionated samples were further purified by repeating (more than twice) precipitation and

Table I. Sample characteristics

Code	$10^{-3} M_w$	$[\eta]^a$	$10^{-3} M_v$
PDMPO-34	34	15.5	32
PDMPO-330	326	62.8	290

^a In toluene at 300 K.

dissolution using benzene and methanol.

The weight-average molecular weight M_w was determined by low-angle light scattering. Viscosity average molecular weight M_v was determined from intrinsic viscosity $[\eta]$ at 300 K in toluene using the Mark-Houwink-Sakurada equation reported by Barrales-Rienda and Pepper.¹² The characteristics of the purified samples used in this study are given in Table I.

Dielectric measurements were carried out in the frequency range between 100 Hz to 100 MHz as reported previously.² High purity grade benzene was distilled after drying with calcium hydride, and used as the solvent.

RESULTS AND DISCUSSION

Frequency dependence of the dielectric constant ϵ' and the loss factor ϵ'' for solutions of PDMPO-34 and PDMPO-330 with concentration from 9 to 25 wt% are shown in Figures 1 and 2, respectively. Measurements on dilute solutions were unsatisfactory because of high ionic conductivity. The increase in ϵ'' with decreasing frequency below 10 kHz is due to this ionic conduction. The relaxation time τ and relaxation strength $\Delta\epsilon$ were determined from the loss maximum frequency f_m and the area under the loss curve, respectively. The values of τ and $\Delta\epsilon$ divided by concentration C (in g cm^{-3}) for the loss peak around 10 MHz are listed in Table II. Here, C was estimated by assuming additivity of the densities between the bulk (1.06) and solvent (0.875). We note that the loss maximum frequencies f_m for the 9% solutions of PDMPO-34 and PDMPO-330 are almost the same in spite of the difference in

Figure 1. Frequency f dependence of ϵ' and $\log \epsilon''$ in benzene solutions of PDMPO-34. Arrows indicate the loss maximum frequency. **Figure 2.** Frequency f dependence of ϵ' and $\log \epsilon''$ in benzene solutions of PDMPO-330. Arrows indicates loss maximum frequency.**Table II.** Relaxation time τ and relaxation strength $\Delta\epsilon$ divided by concentration C at 300 K for benzene solutions of PDMPO

Sample	Concn/wt%	$10^8 \tau/\text{s}^a$	$\Delta\epsilon/C^b$
PDMPO-34	8.7	1.3	0.17
	14.4	1.3	0.18
PDMPO-330	8.9	1.0	0.18
	14.4	2.5	0.21
	25.4	2.5	0.20

^a τ was determined from the loss maximum frequency f_m using a relation $\tau = 1/(2\pi f_m)$.^b Unit of C is g cm^{-3} .

molecular weight by a factor of about 10. This does not conform to the usual behavior of the normal mode process. In the following, we

compare τ and $\Delta\epsilon$ more quantitatively with the theories.

Relaxation Time

If chains are not entangled each other, the dielectric relaxation time for the normal mode process is given to a good approximation by the relaxation time τ_1 for the first normal mode in the Rouse-Zimm theory.^{13,14} For dilute solutions, the nondraining model¹⁴ predicts that τ_1 is given by

$$\tau_1 = 2M\eta_s[\eta]/(0.586RT\lambda_1') \quad (1)$$

where η_s and λ_1' denote the solvent viscosity and the first eigenvalue, respectively. Other quantities have the usual meanings. Using the data of $[\eta]$ ¹⁵ and η_s ¹⁶, we calculated τ_1 to be 2.4×10^{-7} and 1.11×10^{-5} s for the solutions of PDMPO-34 and PDMPO-330, respectively. As discussed previously on *cis*-polyisoprene solutions,⁷ the relaxation time for dilute to semi-dilute solutions should be longer than the theoretical values predicted for infinitely dilute solutions. This is obviously due to the effect of entanglement and the increase in the local frictional constant ζ with increasing C . Contrary to this expectation, we recognize in Table II that the observed relaxation times for the present PDMPO solutions are shorter than τ_1 by a factor of 10^{-1} to 10^{-3} .

Relaxation Strength

Generally, the relaxation strength $\Delta\epsilon$ for the normal mode process of a solution with concentration C (in g cm^{-3}) is given by³

$$\Delta\epsilon/C = (4\pi N_A \mu^2 \langle r^2 \rangle) / (3k_B T M) \quad (2)$$

where μ and $\langle r^2 \rangle$ denote the dipole moment per unit contour length and the mean square end-to-end distance of the polymer, respectively. It is noted that $\Delta\epsilon/C$ is proportional to $\langle r^2 \rangle/M$, and hence varies only slightly with M depending on the solvent quality. As indicated by Karasz *et al.*⁹ we may expect that the two C–O bonds of the monomer have bond moment of the same magnitude but aligning in the

opposite direction and hence they cancel each other out. Therefore, the dipole moment μ_{PDMPO} of the monomer unit is equal to that of *m*-xylene, which was reported to be $0.37 D$.¹⁷ From the bond length data, the length b (O–O distance) of the repeat unit was estimated to be 0.550 nm .² Therefore, μ in eq 2 is estimated to be 6.73×10^{-12} cgs esu. Since we used semi-dilute and concentrated solutions, $\langle r^2 \rangle$ may be close to the value in the θ state rather than that in a good solvent. Therefore, we approximated $\langle r^2 \rangle/M$ by $C_\infty b^2/M_0$, where M_0 and C_∞ denote the molecular weight and the characteristic ratio of the repeat unit, respectively. As discussed previously,³ we estimated C_∞ to be 2.9, assuming free rotation about the C–O bond¹⁸ and the C–O–C bond angle 119° .¹⁹ Thus, $\Delta\epsilon/C$ for the PDMPO solutions becomes 0.177. This value is roughly in agreement with the observed $\Delta\epsilon/C$ shown in Table II.

Assignment of the Relaxation Process

As described above, we found a controversy that the observed relaxation strength is in agreement with the theoretically estimated value (eq 2) but the molecular weight dependence and the absolute value of the relaxation time are not (eq 1). Although there is a possibility that the observed loss maximum in PDMPO solutions are not due to the normal mode process, we tentatively interpret the results as follows. We notice that this behavior are quite similar to that observed in solutions of polychloroprene⁸ in which the dipole persistent number is much smaller than the average degree of polymerization, presumably due to the frequent occurrence of head-to-head linkages. In such a case, the k th normal mode becomes dielectrically active rather than the first mode given by eq 1. According to the Zimm and Rouse theories,^{13,20} the relaxation time τ_k for the k th normal mode is proportional to $k^{-1.5}$ and $k^{-2.0}$, respectively. The value of k can be determined from the observed relaxation time for the normal mode process.⁸ On the other hand, $\Delta\epsilon/C$ is

almost independent of the dipole persistent number as pointed out for eq 2. Although there is no direct evidence indicating the presence of the head-to-head linkages in the PDMPO molecule, it is likely that this polymer contains such irregular linkages. From the relaxation time data, we estimate that the direction of the dipole moments changes every 45 to 73 degrees of polymerization from the $k^{-1.5}$ to $k^{-2.0}$ dependence of τ_k .

That the observed relaxation time is shorter than the theoretical τ_1 may possibly be due to the branches in the PDMPO molecule. However, the $[\eta]$ data of PDMPO^{12,15} indicate that this polymer has a linear structure and thus branching is unlikely.

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