

# Type-A dipole moment and segmental dynamics of poly(styrene oxide)

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## Abstract

We report the dielectric properties of poly(styrene oxide)s (PSO) in bulk and concentrated solution states. Since the structure of PSO is asymmetric along the backbone, the repeat unit of PSO is expected to possess the non-zero component of the dipole moment  $p_A$  parallel to the chain contour as well as the perpendicular component  $p_B$ . The former and latter cause the dielectric normal mode and segmental mode relaxations, respectively. Contrary to the above mentioned expectation the temperature dependence of  $\epsilon''$  exhibits only the primary ( $\alpha$ ) relaxation and weak secondary relaxation ( $\beta$ ) in the glassy state. No loss peak due to the normal mode relaxation was observed in the frequency region expected from the viscoelastic terminal relaxation in bulk and toluene solutions. The dielectric behaviours of the  $\alpha$  relaxation in the bulk state were analyzed in detail and the parameters of the Vogel–Fulcher and the Havriliak–Negami equations were determined. The Kirkwood correlation factor was determined to be 0.36. The  $^{13}\text{C}$  NMR spectra indicate that the present PSO samples contain about 2% head-to-head linkages. This cannot be the origin of the disappearance of the normal mode. We conclude that  $p_A$  of PSO is too small to be detected. The  $p_A$  calculated with molecular orbital methods supports this conclusion.

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**Keywords:** Poly(styrene oxide); Dielectric relaxation; Segmental mode

## 1. Introduction

Dielectric properties of amorphous polymers have been studied extensively by many scientists and dielectric data of most polymers are available in literature [1]. However, the dielectric properties of type-A polymers having the dipole moment aligned parallel to the chain contour have not been completely investigated [2,3]. The dielectric normal mode relaxation of type-A chains reflects fluctuation of the end-to-end vector and consequently global motions of the chains prevailing in viscoelastic terminal relaxation [4,5]. On the other hand, polymer molecules having the perpendicular component of the monomeric dipole moment (type-B) exhibit the dielectric primary relaxation due to local segmental motions [1,3] and have been studied extensively by many scientists [1]. Polyethers ( $-\text{CH}_2-\text{CHR}-\text{O}-$ ) $_n$  with  $\text{R} \neq \text{H}$  possess the type-A dipole, and are expected to exhibit dielectric normal mode relaxation. So far the dielectric normal mode relaxations of poly(propylene

glycol) (PPG) ( $\text{R} = -\text{CH}_3$ ) [6–9] and poly(butylene oxide) (PBO) ( $\text{R} = -\text{CH}_2\text{CH}_3$ ) [10,11] were reported. However, no systematic data of normal mode relaxations of polyethers having R greater than the ethyl group have been reported.

Matsuo et al. [12] studied the dielectric relaxation in dilute solution of poly(styrene oxide) (PSO) having the phenyl ( $\text{C}_6\text{H}_5$ ) group as the side group R, but they could not observe the normal mode relaxation [12]. Since the dielectric relaxation strength is low in dilute solutions, weak relaxation processes cannot be detected. In this study we carried out dielectric measurements on bulk and concentrated solutions of PSO expecting that the normal mode can be observed by increasing concentration. As far as we know the dielectric data of bulk or concentrated solutions of PSO are not available in literature. There are two objectives in this study. The first is to examine whether the normal mode can be observed for bulk and concentrated solutions of PSO. The second is to clarify the overall dielectric behaviour of bulk and concentrated solutions of PSO since the dielectric data of PSO in condensed states are not available. We will provide the fundamental dielectric data of PSO through routine analyses.

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## 2. Experimental section

### 2.1. Materials

Samples of PSO were prepared by polymerization of 1,2-epoxyethylbenzene in tetrahydrofuran with potassium hydride as the initiator and 18-crown-6 as the catalyst [13]. Temperature of polymerization was changed from 0 to 50 °C to control molecular weight. It was found that the molecular weight increased with decreasing temperature of polymerization. Weight-average molecular weight ( $M_w$ ) and polydispersity index ( $M_w/M_n$ ) were determined by a gel permeation chromatograph, GPC, equipped with a light scattering detector (Tosoh LS 8000). Sample characteristics are shown in Table 1. The contents of irregular microstructures such as the head-to-head linkage were determined by  $^{13}\text{C}$  NMR. The density  $\rho$  of bulk PSO at 300 K was measured to be  $1.14 \times 10^3 \text{ kg m}^{-3}$  with a buoyancy method.

### 2.2. Methods

Glass transition temperature  $T_g$  was determined by a differential scanning calorimeter (Seiko Instruments and Electronics Ltd, DSC-20, Japan) at a heating rate of 10 K/min.  $T_g$  was determined as the middle point of the stepwise change of the DSC curve. For dielectric measurements, RLC meters (QuadTech, models 1693 and 7600, USA) were used. The capacitance cell for measurements of viscous liquids was reported previously [14]. Complex shear moduli  $G'$  and  $G''$  were measured with a stress rheometer (Rheometric SR-200, USA). The steady state viscosity of toluene solutions of PSO was measured with a Ubbelohde capillary viscometer.

## 3. Results and discussion

### 3.1. Glass transition and dielectric relaxation of bulk PSO

Fig. 1(a) shows the dependence of  $T_g$  of bulk PSO on the weight average molecular weight  $M_w$ . It is seen that  $T_g$  increases with  $M_w$  as is observed commonly for amorphous polymers. This is due to the effects of chain ends creating free volume. Fox and Loshaek firstly proposed the well known equation [15]:

$$T_g = T_g(\infty) - K/M_n \quad (1)$$

Table 1  
Characteristics of PSO samples

Code	$10^{-3} M_w$	$M_w/M_n$
PSO-2	1.6	1.23
PSO-3	3.1	1.21
PSO-6	5.6	1.14
PSO-9	8.7	1.27
PSO-12	12.1	1.19

where  $T_g(\infty)$ ,  $K$  and  $M_n$  are the  $T_g$  of the homologous polymer with infinitely high molecular weight, the constant, and the number average molecular weight, respectively. Fig. 1(b) shows the plot of  $T_g$  of PSO against  $1/M_n$ . The plot conforms to a straight line within the experimental error and  $T_g(\infty)$  is determined to be 312 K. The constant  $K$  becomes  $1.2 \times 10^4$ . This value is one order smaller than polystyrene having similar structure to PSO [16]. Eq. (1) was also derived from theoretical models by Bueche [17] and Gibbs and DiMarzio [18]. However, the discussion on Eq. (1) is out of the scope of this paper.

Figs. 2(a) and (b) show the temperature dependences of the dielectric constant  $\epsilon'$  and the logarithm of the loss factor  $\log \epsilon''$  for bulk PSO-12, respectively. We see a main peak at about 330 K at 1 kHz. Since  $T_g$  of PSO-12 is 312 K, the main peak can be assigned to the primary  $\alpha$  relaxation. A weak and broad loss peak at about 170 K is assigned to the secondary ( $\beta$ ) relaxation. The loss peak due to the normal mode relaxation is expected to be observed above 330 K. Unfortunately  $\epsilon''$  increases steeply with temperature on account of ionic conduction above 360 K and therefore the normal mode relaxation cannot be seen in Fig. 2(b).

The frequency  $f$  dependence of  $\epsilon''$  in the  $\alpha$  relaxation region is shown in Fig. 3. It is seen that the maximum values of  $\epsilon''$  are almost independent of temperature. Since the relaxation strength is proportional to  $1/T$ , the intensity increases with decreasing temperature if the relaxation spectrum is independent of temperature. The present data indicate that the  $\epsilon''$  curve broadens slightly with decreasing temperature. However, the extent of the broadening is small

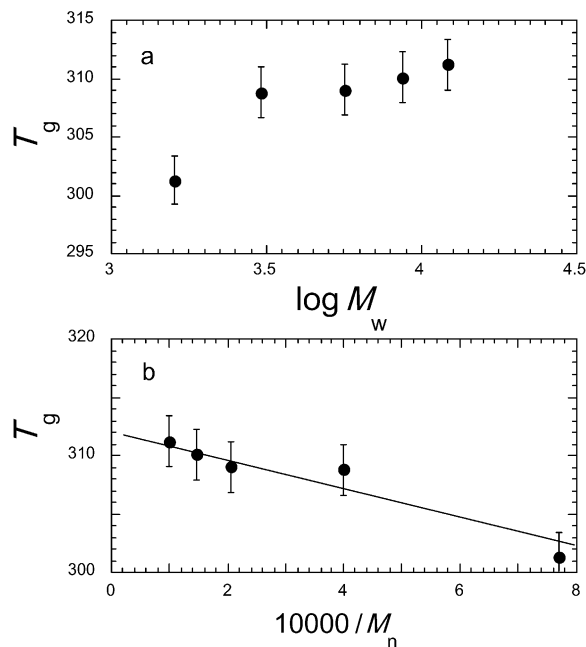


Fig. 1. Molecular weight dependence of glass transition temperature  $T_g$  (a) and plot of  $T_g$  against the inverse of number average molecular weight  $M_n$  (b).

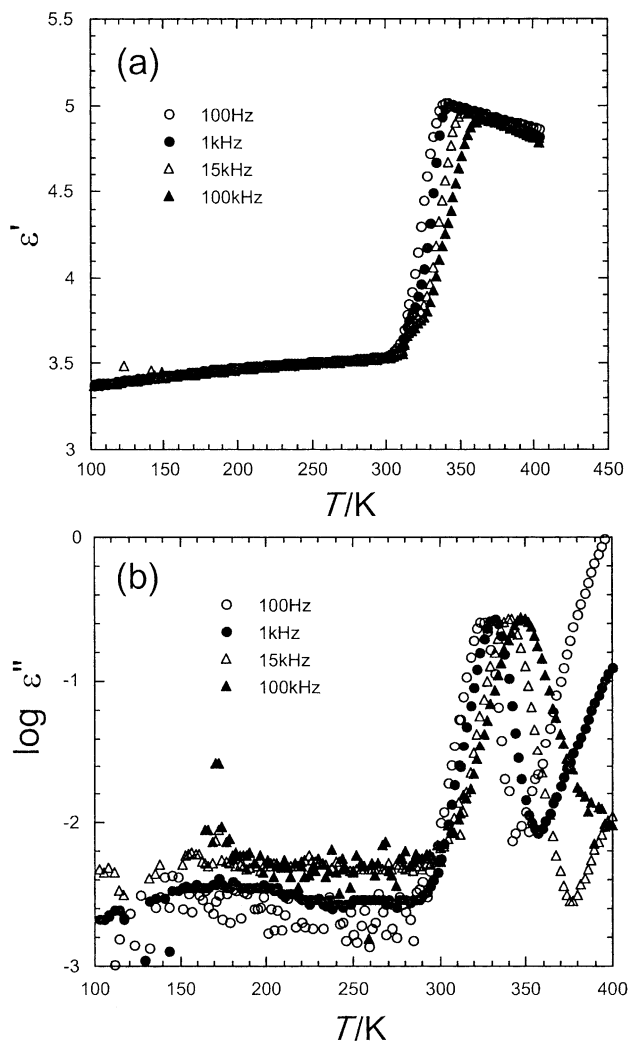


Fig. 2. Temperature dependences of  $\epsilon'$  (a) and  $\epsilon''$  (b) of PSO-12.

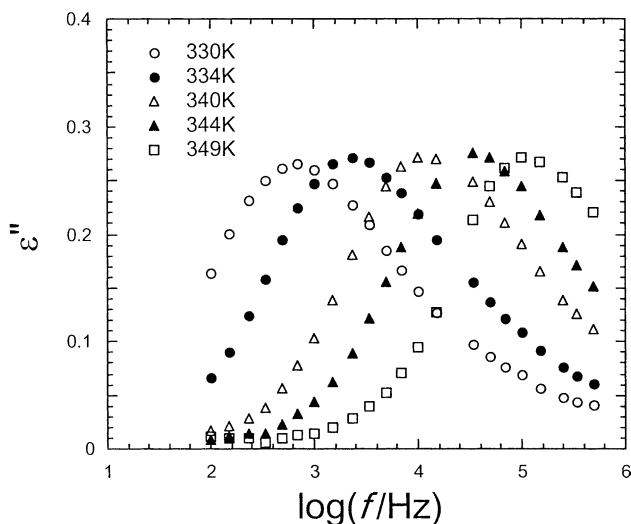


Fig. 3. Frequency dependence of  $\epsilon''$  of bulk PSO-12.

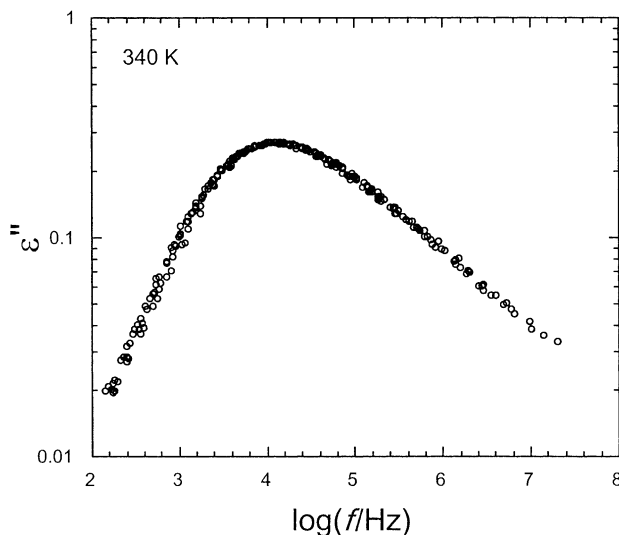


Fig. 4. Master curve of  $\epsilon''$  of bulk PSO-12 in the segmental relaxation region at 340 K.

and the curves are almost superposable as indicated in Fig. 4.

The phenomenological parameters for the  $\alpha$  process have been determined through the routine methods as follows. The frequency dependences of the  $\epsilon''$  have been fitted to the Havriliak–Negami equation [19]. The exponents of the inner  $\alpha_{HN}$  and outer bracket  $\beta_{HN}$  are determined to be 0.85 and 0.41, respectively. Those values are slightly smaller than  $\alpha_{HN}$  and  $\beta_{HN}$  of typical amorphous polymers [1] indicating broader relaxation spectrum of PSO. The loss maximum frequencies for the  $\alpha$  process are fitted to the Vogel–Fulcher equation [20,21]. The parameters  $A$ ,  $B$ , and  $T_0$  have been determined to be 14.9, 1010, and 246.4 K, respectively. Although segmental motions of polymers have been studied long from 1940s [1], the theory of segmental relaxations has not been established and therefore the relationship between the molecular structure of PSO and those parameters cannot be explained at the present stage. The activation energy for the  $\beta$  process was not determined due to scattering of data points.

Fig. 5 shows the Cole–Cole plots of PSO-12 at 329.7 K. As shown in this figure the relaxed  $\epsilon_R$  and unrelaxed  $\epsilon_U$  dielectric constants are 4.93 and 3.85, respectively and the relaxation strength  $\Delta\epsilon$  becomes 1.08. The type B dipole moment  $p_B$  of the monomer unit of PSO has been calculated

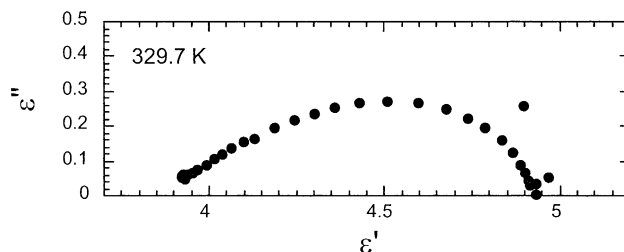


Fig. 5. Cole–Cole plot of PSO-12 at 329.7 K.

on the basis of the Onsager–Kirkwood equation [22–24]:

$$\Delta\varepsilon = \frac{4\pi N g p_B^2}{3k_B T} \frac{(\varepsilon_U + 2)^2 \varepsilon_R}{3(2\varepsilon_R + \varepsilon_U)} \quad (2)$$

where  $N$  is the number of the monomer unit in unit volume and  $g$  the Kirkwood correlation factor. It is noted that Eq. (2) is the expression in the cgs-esu unit. From the data given above, the value of  $g^{1/2} p_B$  is determined to be  $2.39 \times 10^{-30}$  C m (=0.72 D) where D is the Debye unit ( $10^{-18}$  cgs esu). The dominant dipole moment of the monomer unit of PSO is the ether group and is reported to be 1.2 D [25], and hence  $g$  of PSO becomes 0.36. The effects of the odd–even numbers of the methylene groups of polyethers on their dielectric properties were studied by Read [26]. In PSO, the number of the methylene groups is two and in this case  $g$  is given by

$$g = \frac{(1 - \eta^2)(1 - \cos \theta)}{3\eta + (1 - \eta^2)(1 - \cos \theta + \cos^2 \theta)} \quad (3)$$

where  $\eta = \langle \cos \phi \rangle$  with  $\phi = 0$  for the trans conformation and  $\theta$  is the bond angle. When the chain has the trans (planer zigzag) conformation, the type B dipole moments of the neighboring monomers cancel each other and  $g$  becomes zero. If  $q$  for C–C–O and C–O–C linkages are assumed to be  $109^\circ$ ,  $\eta$  becomes 0.535 and  $\phi = 58^\circ$  for  $g = 0.36$ . The result indicates that PSO takes a trans-rich local conformation. The value of  $g = 0.36$  is smaller than those of poly(ethylene oxide) ( $g = 0.60$ – $0.69$ ) and poly(propylene oxide) ( $g = 0.49$ – $0.54$ ) [27]. The value of  $g = 0.36$  is also smaller than  $g$  of vinyl polymers ( $g = 0.6 \pm 0.2$ ) [27,28].

### 3.2. Dielectric behaviour of concentrated toluene solutions

Fig. 6 shows the temperature dependences of  $\varepsilon'$  and  $\varepsilon''$  at 1 kHz for 40% toluene solutions of PSO with various molecular weight. The main objective of measurements on toluene solutions of PSO samples with various  $M_w$  is to search for the normal mode relaxation.

The reason for the use of concentrated solutions is as follows. Usually dielectric relaxations shift to low temperature by addition of a diluent and hence the effect of the conductivity is expected to be suppressed. The second reason is the technical one. In order to obtain accurate dielectric data, the perfect contact of the sample and electrodes is required. This can be achieved easily for concentrated solution rather than the bulk samples.

We carried out dielectric measurements on solutions of PSO with different  $M_w$ . We expected to be able to observe a loss peak (due to the normal mode) which shifts to high temperature with increasing  $M_w$ . In Fig. 6(b), three loss peaks are seen. The behaviour is similar to toluene solutions of polystyrene [29,30], and those loss peaks at 100, 145, and 200 K can be assigned to the local secondary relaxation in the glassy state, rotation of the toluene molecules, and the  $\alpha$  relaxation of PSO, respectively. The normal mode

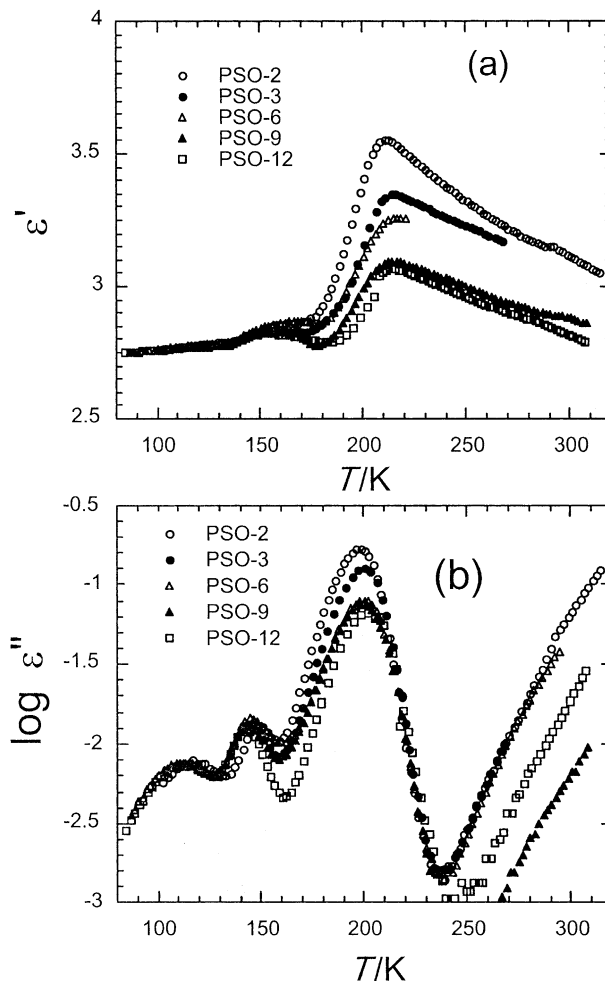


Fig. 6. Temperature dependences of  $\varepsilon'$  (a) and  $\varepsilon''$  (b) at 1 kHz for 40 wt% solutions of PSO in toluene. The molecular weights are indicated in the figure.

relaxation is expected to appear above the  $\alpha$  relaxation region and shifts to high temperature with increasing  $M_w$  if it has enough intensity. However, no loss peaks exhibiting such a behaviour are seen in Fig. 6.

The other characteristic feature seen in Fig. 6 is that the relaxation strength of PSO increases with decreasing molecular weight. This suggests that the relaxation strength increases due to a polar group attached at the ends of the PSO chains. If this is the case, the relaxation strength  $\Delta\varepsilon$  of 40 wt% PSO solutions is given by:

$$\Delta\varepsilon = \Delta\varepsilon_0 + \frac{8\pi\rho N_A \mu^2}{3k_B T M_n} \frac{(\varepsilon_U + 2)^2 \varepsilon_R}{3(2\varepsilon_R + \varepsilon_U)} \quad (4)$$

where  $\Delta\varepsilon_0$  is the relaxation strength for PSO with infinite molecular weight,  $\rho$  the concentration,  $\mu$  the dipole moment of the polar groups at the chain ends, and  $M_n$  the number average molecular weight. Here, the internal field factor given by Onsager has been used. Using Eq. (4), we attempted to estimate  $\mu$  as follows. The experimental values of  $\Delta\varepsilon$ ,  $\varepsilon_R$  and  $\varepsilon_U$  for various  $M_n$  have been determined from

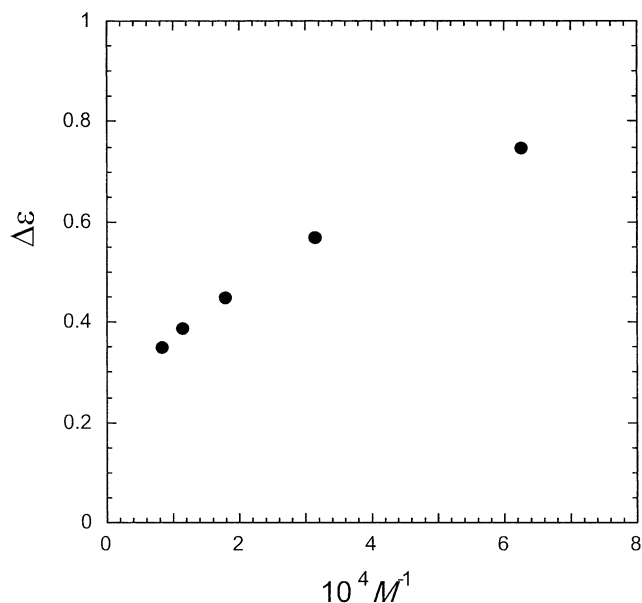


Fig. 7. Dependence of the relaxation strength  $\Delta\epsilon$  on the inverse of molecular weight for 40 wt% solution of PSO-12.

the jump of  $\epsilon'$  shown in Fig. 6(a). Thus determined values of  $\Delta\epsilon$  are plotted against  $1/M_n$  in Fig. 7. It is seen that the plots conform approximately to a straight line. The slope of this plot is determined to be  $910\text{--}650\text{ g mol}^{-1}$  and  $\mu$  of Eq. (4) becomes  $7.0 \times 10^{-30}$  to  $6.0 \times 10^{-30}\text{ C m}$  (2.1–1.8 D). We speculate that probably the hydroxyl groups are attached at the chain ends. The value of  $\Delta\epsilon_0$  of Eq. (4) becomes  $0.32 \pm 0.05$ . If this value is normalized into 100% concentration the relaxation strength becomes 0.80 which is slightly lower than the relaxation strength of the bulk state ( $\Delta\epsilon = 1.08$ ). This may be ascribed to the effect of the change of  $g$  of Eq. (2) caused by interactions with the solvent. Finally, it is noted that in the analysis of the dipole moment of bulk PSO, Eq. (2) has been applied to PSO-12 having the highest molecular weight among the samples. The effect of the end group for PSO-12 is negligibly small.

### 3.3. Estimation of the normal mode relaxation time from zero shear viscosity

Although PSO has a structure belonging to type-A chains, we have not been able to observe the normal mode relaxation in both the bulk and solution states. Two origins for this behaviour can be raised. Firstly, the type-A dipole moment is too small to be detected and secondly the PSO samples used in this study contains many head-to-head linkages which result in the decrease of the normal mode relaxation time to the order of the segmental mode. In order to test the first possibility, it is needed to examine  $\epsilon'$  and  $\epsilon''$  more carefully in the frequency region where the normal mode relaxation is expected to appear. This frequency region corresponds to the region where the terminal viscoelastic relaxation is observed.

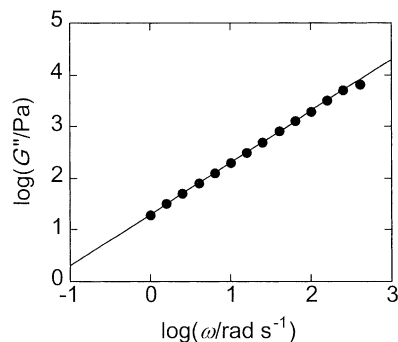


Fig. 8. Angular frequency dependence of the loss shear modulus at 373 K for bulk PSO-12.

For bulk PSO-12, we estimated the dielectric longest relaxation time  $\tau_1$  ( $=1/2\pi f_m$ ) from the zero shear viscosity  $\eta_0$  [3,4,31]. Fig. 8 shows the dependence of the loss modulus  $G''$  of PSO-12 at 373 K on the angular frequency  $\omega$ . In this frequency region,  $G''$  is linear with respect to  $\omega$  indicating that PSO-12 is in the flow region. From the relation  $G'' = \eta_0 \omega$ ,  $\eta_0$  is determined to be  $10^{1.31}\text{ Pa s}$ . According to the Rouse theory [31,32],  $\tau_1$  is given by

$$\tau_1 = \frac{12\eta_0 M}{\pi^2 \rho RT} \quad (5)$$

Thus, we determined  $\tau_1$  to be  $8.4 \times 10^{-5}\text{ s}$  using  $\eta_0$  determined above. Here density  $\rho$  is  $1.14 \times 10^3\text{ kg m}^{-3}$ . From this result  $f_m$  ( $=1/2\pi\tau_1$ ) for the normal mode relaxation of PSO-12 is expected to be  $10^{3.3}\text{ Hz}$  at 373 K.

Fig. 9(a) shows the frequency dependence of  $\epsilon''$  of PSO-12 at 373 K. The dashed line indicates the expected peak frequency of the normal mode. The increase of  $\epsilon''$  with decreasing  $f$  is the contribution of ionic conduction which is given by  $\epsilon'' = \sigma/\epsilon_0 \omega$  where  $\sigma$  and  $\epsilon_0$  are the ionic conductivity and the absolute dielectric constant of vacuum, respectively. The  $\epsilon''$  curve from which the contribution of  $\sigma$  has been subtracted is also plotted in Figs. 9(a) and (b). In Fig. 9(b), a small loss peak and the corresponding small dispersion in the  $\epsilon'$  curve are seen. However, it is a subtle problem whether these behaviours can be assigned to the normal mode relaxation since the experimental error for  $\epsilon''$  is similar to the height of the bump of the  $\epsilon''$  curve as is seen in Fig. 9(b). As to the small dispersion in the  $\epsilon'$  curve, we suspect that the dispersion is due to a weak electrode dispersion. Therefore, we conclude at the present stage that the intensity of the normal mode of  $\epsilon''$  is less than 0.001 if it could be observed.

Similar analysis has been also made for 40 wt% toluene solutions of PSO-12 on which the shear viscosity was measured with a capillary viscometer at 273 and 298 K. Thus, determined viscosities are converted into the relaxation frequency  $f_m$  and plotted against  $1/T$  in Fig. 10 where  $f_m$  for the dielectric segmental relaxation are also plotted. Then the plot for the normal mode is extrapolated to the low frequency side with the aid of the Vogel–Fulcher

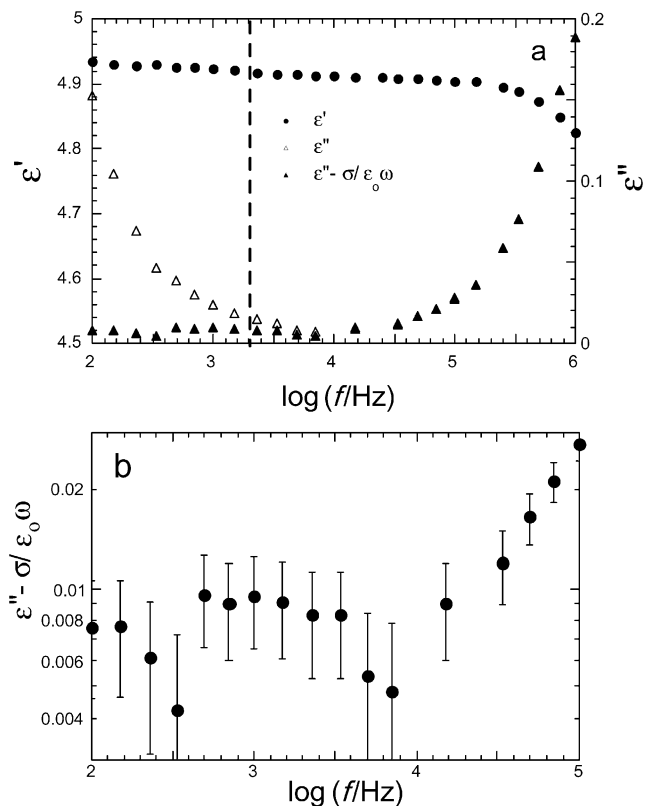


Fig. 9. Dielectric constant  $\epsilon'$  and loss factor  $\epsilon''$  at 373 K for bulk PSO-12 (a). The dashed line indicates the frequency at which the normal mode relaxation is expected from the viscoelastic behaviour. The plots by filled triangle indicates the loss curve after subtraction of the contribution of dc conduction. Logarithm of these values are plotted in (b).

equation [20,21] by using the same values of the parameters as those for the segmental mode. This is rationalized since it has been demonstrated for polyisoprene that the ratio of  $\tau_n/\tau_s$  is independent of temperature in the region above  $T_g + 30$  K where the segmental mode is observed in the audio frequency region [33]. The segmental mode can be regarded

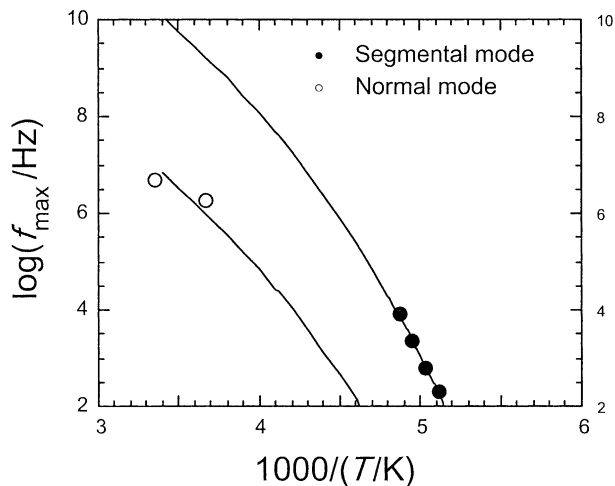


Fig. 10. Arrhenius plots for the segmental and normal modes for the 40 wt% solution of PSO-12.

as the elementary process for the normal mode and the constancy of  $\tau_n/\tau_s$  holds generally. Therefore, error in this extrapolation is estimated to be less than 0.1 decade. In this way the relative location of the normal and segmental modes has been estimated. Frequency dependences of  $\epsilon'$  and  $\epsilon''$  in 40 wt% toluene solution of PSO-12 at 226 K are shown in Fig. 11(a). From Fig. 10, the normal mode peak is expected to locate at  $f = 10^{3.04}$  Hz (indicated by the dashed line). Fig. 11(b) shows the double logarithmic plot of  $\epsilon''$  versus  $f$ . The solid line with the slope = 1 is also drawn. Since the  $\log \epsilon''$  conforms to the straight line in this region, we conclude that the normal mode does not exhibit detectable intensity.

### 3.4. Effect of microstructure on dielectric relaxation strength

As mentioned above, the second possible origin for the disappearance of the normal mode is the irregular microstructures of the PSO chains. Fig. 12 shows the  $^{13}\text{C}$  NMR spectrum of PSO-12. According to Sepulchre et al. [34], the resonance lines are assigned as shown in the figure. From the intensities of those lines, we calculated the contents of the head-to-head and tail-to-tail linkages of PSO-16 and PSO-12 as shown in Table 2. It is seen that the intensity of the T–T linkage is higher than that of the H–H linkage. This is due to the overlapping of the unknown resonance lines as pointed out by Sepulchre et al. [34]. Thus, we conclude that PSO-12 contains about 2% H–H and T–T linkages.

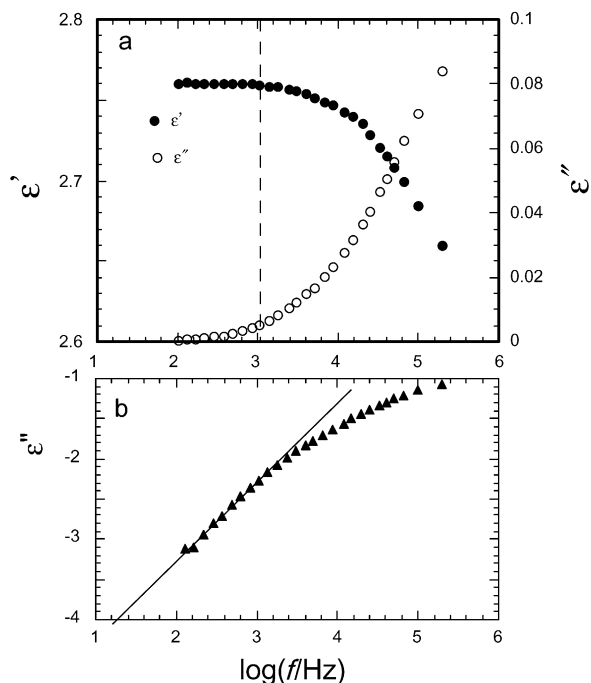


Fig. 11. Dielectric constant  $\epsilon'$  and loss factor  $\epsilon''$  at 226 K for 40 wt% toluene solutions of PSO-12 (a) and double logarithmic plot of  $\epsilon''$  (b). The dashed line indicates the frequency at which the normal mode relaxation is expected.

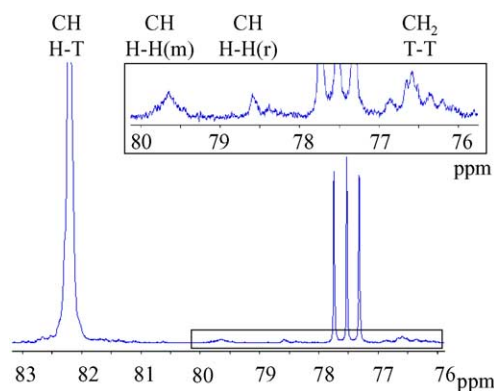


Fig. 12.  $^{13}\text{C}$  NMR spectra of PSO. The resonance lines at 82.3, 79.7, 78.6, and 76.6 ppm are assigned to the head-to-tail (H–T), head-to-head (H–H), and tail-to-tail (T–T) linkages, respectively.

It is speculated that a propagation reaction of polymerization occurs so that the monomer unit (TH) reacts with the active site  $\text{TH}^*$  taking a certain preferential orientation ( $\text{TH}^*-\text{TH}$ ) against the active site. If the H–H linkage is accidentally formed ( $\text{TH}^*-\text{HT}$ ), the next monomeric unit reacts in the regular direction and the T–T linkage is formed ( $\text{THHT}^*-\text{TH}$ ) resulting in the recovery of the regular alignment. Therefore, it is likely that the PSO chains possess the type-A dipoles aligned uniaxially in the direction of the chain contour. Small numbers of the HHTT linkages do not affect the normal mode relaxation. Therefore, the second possibility may be ruled out.

### 3.5. Theoretical dipole moment

In order to confirm the above conclusion that  $p_A$  is too small to be observed, we have estimated the parallel ( $p_A$ ) and perpendicular ( $p_B$ ) components of the monomer dipole using the molecular orbital methods, i.e. the Austin model-1 (AM1) [35] and the parametalized model revision 3 (PM3) [36] for a model molecule  $\text{CH}_3-\text{CH}(\text{C}_6\text{H}_5)-\text{O}-\text{CH}_2-\text{CH}_3$  taking the planer zigzag conformation. The parallel and perpendicular components with the AM1 method become  $p_A=0.04$  and  $p_B=1.32$  D (Debye unit), respectively. On the other hand the PM3 method gives  $p_A=-0.025$  and  $p_B=1.24$  D. We see that  $p_A$  is very small and the sign changes by the method indicating the absolute values given here are not reliable. It is noted that  $p_A$  of *cis*-polyisoprene is 0.2 D and the intensity of the  $\epsilon''$  curve is

0.03 [14]. Since the dielectric relaxation strength is proportional to square of the dipole moment, we expect that the peak value of  $\epsilon''$  for the normal mode of PSO is of the order of  $10^{-4}$ . This explains well the present results.

## 4. Conclusion

We have carried out dielectric measurements on the bulk state and 40% toluene solution of PSO. Bulk PSO exhibits the dielectric primary ( $\alpha$ ) relaxation at about 330 K and the weak secondary loss peak at about 170 K at 1 kHz. In 40% solutions, the  $\alpha$  process is seen at 200 K at 1 kHz. Although PSO has an asymmetrical structure of the backbone, the normal mode relaxation due to the dipole moment aligned parallel to the chain contour has not been observed in the frequency region where the normal mode is expected to occur from the terminal viscoelastic relaxation. This is supported by the small type-A dipole moment calculated with the molecular orbital methods. The other possible origin for the disappearance of the normal mode is the irregular microstructure. However, the  $^{13}\text{C}$  NMR spectrum of PSO-12 indicates that the present samples of PSO contain about 2% head-to-head linkages and rules out this possibility.

We have also analyzed the segmental mode process ( $\alpha$  process) and determined the parameters of the phenomenological equations characterizing the  $\alpha$  process. The exponents of the inner and outer bracket of the Havriliak–Negami equation are determined to be 0.85 and 0.41, respectively. Those values are slightly smaller than typical amorphous polymers indicating broader relaxation spectrum of PSO. The parameters  $A$ ,  $B$ , and  $T_0$  of the Vogel–Fulcher equation are 14.9, 1010, and 246.4 K, respectively. The effective dipole moment of the monomer unit of PSO is determined to be  $2.39 \times 10^{-30}$  C m ( $=0.72$  D). The Kirkwood correlation factor becomes 0.36 indicating the trans rich local conformation. The relaxation strength of PSO increases with decreasing molecular weight due to a polar group attached at the two ends of the PSO chains. The dipole moment of the polar group is estimated to be ca.  $6.5 \times 10^{-30}$  cm (2.0 D).

To summarize PSO is a very unusual polymer in the sense that in spite of the asymmetrical structure of the repeat unit, PSO possesses a very weak type-A dipole moment and exhibits only the segmental mode relaxation.

Table 2  
Percentages of linkages of PSO determined by  $^{13}\text{C}$  NMR

Code	Linkages/%			
	H–T	H–H (meso)	H–H (racemo)	T–T
PSO-16	86.7	2.6	1.0	9.7
PSO-12	93.5	1.6	0.7	4.2

## References

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