

Dielectric normal mode relaxation of tethered polyisoprene chains in styrene-isoprene block copolymers

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Abstract: Polyisoprene (PI) possesses type-A dipole moment aligned in the direction parallel to the chain contour and exhibits the dielectric normal mode relaxation due to the fluctuation of the end-to-end vector. Using this property of PI, we have studied the dynamics of the PI block chains of styrene-isoprene diblock copolymers (SI) and styrene-isoprene-styrene triblock copolymers (SIS). The results indicate that the distribution of relaxation times in SI having the lamella morphology is broadest and the distribution becomes narrow in order of cylinder and sphere morphologies. In SIS the dielectric normal modes are observed in the temperature range above the glass transition temperature of the styrene domain indicating that the styrene block chains can jump from one domain to the other.

Introduction

The dielectric relaxation spectroscopy has been a powerful tool for studying conformation and dynamics of polar macromolecules. Obviously information obtained from the dielectric spectroscopy depends on the orientation of dipole vectors with respect to the chain contour of a polymer chain. Stockmayer(1) classified the dipoles of polymers into three types: Those aligned in the same direction parallel to the chain contour were classified as type-A; those aligned perpendicular to the contour as type-B; and those located on mobile side groups as type-C. The dipole moment of a totally type-A chain is proportional to the end-to-end vector of the chain so that the dielectric relaxation reflects fluctuation of the end-to-end vector prevailing in the viscoelastic terminal relaxation.(2,3) We designated such a relaxation *normal mode relaxation*.(2) On the other hand, the relaxation of type-B dipoles reflects the local segmental motion relevant to the glass transition, while that of type-C dipoles reflects the motion within the side group and is responsible to a high frequency local relaxation mode. For example, cis-polyisoprene(PI) possesses both type-A and -B dipoles, while polystyrene (PS) possesses only type B dipole.

Diblock copolymers composed of immiscible polymers A and B exhibit microphase separation(4,5). When the glass transition temperature T_g of the A block is above ambient temperature but that of the B block is below ambient temperature, only the B block chain moves under a constraint that one end is anchored at the interface of the A and B domains. Such a chain is called a tethered chain. In the case of ABA triblock copolymer, the both ends of the B block chain are fixed and hence the fluctuation of the end-to-end vector of the B block is frozen. However, by increasing temperature above the T_g or by adding a diluent, the A domain becomes no longer a rigid constraint. In the case that the A and B blocks are PS and PI, respectively the dynamics of the tethered PI chains can be observed in terms of the dielectric normal mode spectroscopy. In our previous papers(6-8), we reported such a dielectric measurement on SI with the lamella morphology. We observed that the distribution of relaxation times in SI was anomalously broad compared with homo PI. In this paper we describe the study of the normal mode relaxation of the PI block of SI with spherical and cylindrical morphologies as well as lamella in order to see the influence of the morphology on the dynamics of tethered PI chains. We also aim to study the motion of the PI block of styrene-isoprene-styrene triblock copolymers SIS in which the both chain ends are tethered. Besides the dielectric measurement, we also carried out viscoelastic measurements and thermo stimulating current (TSC) to observe the slow dynamics in SIS.

Experimental

The samples of SI and SIS were prepared by anionic polymerization in benzene with sec-buthyllithium as an initiator and have the polydispersity of $M_w/M_n = 1.07$. The contents of cis-, trans-, and 3,4-vinyl-linkages were determined to be 68.1, 26.4, and 5.5 %, respectively, by using ^{13}C NMR. The molecular weights were determined by using an apparatus of gel permeation chromatography equipped with a detector of low angle light scattering. The sample code indicates the molecular weight of the blocks in kg/mol. For example SIS(4-27-5) represents that the weight average molecular weights of the styrene-1, isoprene and styrene-2 blocks are 4, 27, and 5 kg/mol, respectively. The characteristics of SI and SIS samples are listed in TABLE 1.

TABLE 1 Characteristics of SI and SIS

Code	$10^{-3}M_w(\text{S1})$	$10^{-3}M_w(\text{I})$	$10^{-3}M_w(\text{S2})$	$10^{-3}M_w(\text{total})$	PS content
SI(4-27)	4.4	26.9	-	31.3	14.0 %
SI(8-16)	7.6	15.6	-	23.2	32.6
SI(8-8)	7.6	8.3	-	15.9	47.8
SIS(4-27-5)	4.4	26.9	5.5	36.9	26.9
SIS(8-16-7)	7.6	15.6	6.8	30.0	48.0
SIS(8-8-11)	7.6	8.3	11.3	27.2	69.6

Results and Discussion

SI diblock copolymer

Two dielectric relaxation processes were observed for the SIs around 230 K and 330-400 K. The low temperature process was almost independent of the molecular weight of the PI and PS blocks and can be assigned to the segmental mode process due to the type-B dipoles of PI. On the other hand, the high temperature process depended strongly on the molecular weight and the composition of the block copolymer. The relaxation process can be assigned to the normal mode process of the PI block.(2) Hereafter we focus our attention on the normal mode relaxation.

Fig.1 shows the normalized loss curves for the normal modes, i.e., $\log(\epsilon''/\epsilon''_{\max})$ versus $\log(f/f_m)$ where ϵ'' , ϵ''_{\max} , f , and f_m denote the dielectric loss factor, the maximum value of ϵ'' , the frequency, and the frequency of maximum loss, respectively.

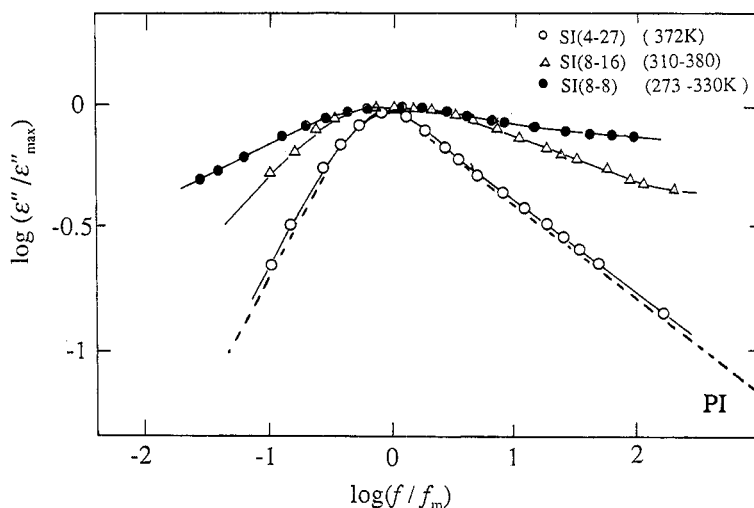


Fig.1 Normalized loss curves for SI(4-27), SI(8-16), and SI(8-8). The dashed line shows the curve for homo-PI.

Molau(5) first pointed out that the morphologies of block copolymers are governed by the volume fraction of the component. When the styrene content ϕ is less than ca.20% in an SI or SIS, the styrene domain takes the spherical morphology. With increasing the PS content the morphology of the PS domain changes to cylinder and then to lamella(4,5). The PI block chain of an SI reorients in a narrow PI domain under a constraint that one end is fixed at the interface of the domains. From the PS content shown in Table I, the morphologies of the PS domain of SI(4-27), SI(8-16), and SI(8-8) are expected to be sphere, cylinder, and lamella, respectively. Figure 2 shows the morphologies schematically.

In Fig.1 we see clearly the effect of the morphology on the shape of the ϵ'' curve. The slope of the $\log \epsilon''$ versus $\log f$ curve in the low frequency side of the loss maximum α_l and that in high frequency side α_h are measures of the broadness of the distribution of relaxation times. They are listed in TABLE 2.

TABLE 2 Slope of $\log \epsilon''$ vs $\log f$ curve α_l (low frequency side), α_h (high frequency side), and ratio of relaxation times $\log [\tau(\text{SI})/\tau(\text{PI})]$

Code	α_l	α_h	$\log [\tau(\text{SI})/4\tau(\text{PI})]$
SI(8-8)	0.34	-0.10	0.5
SI(8-16)	0.53	-0.18	0.8
SI(4-27)	0.91	-0.38	1.6

As is seen in the table, the distribution of relaxation times for SI(8-8) having lamella morphology is broadest and decreases in the order of lamella, cylinder and sphere. The nominal relaxation τ is defined by $\tau = 1/(2\pi f_m)$. The nominal relaxation time $\tau(\text{SI})$ of SI is affected by various factors as well as the constraint in the microphase. Assuming that the factors other than the constraint in the microphase are the same as those in homo-PI, $\tau(\text{SI})$ is normalized with $\tau(\text{PI})$ of homo PI with the same molecular weight as SI at the same temperature. Since the Rouse model(9,10) predicts that the relaxation time for a chain with one end tethered is four times longer than that of the non-tethered free chain, $\tau(\text{SI})$ is divided by $4\tau(\text{PI})$. The values of $\log [\tau(\text{SI})/4\tau(\text{PI})]$ are listed in TABLE 2. It is seen that the relaxation time of SI is much retarded in SI(4-27) but not so much in SI(8-8). In our previous paper by Yao et al.(6-8) we reported that the normal mode relaxation of SI diblock copolymers having lamella morphologies and found that the ϵ'' curve of SI was much broader than PI homopolymer in agreement with the present result.

Three factors may cause the increase of the nominal relaxation time and the broadening of the distribution of relaxation times, i.e., (i) the spatial confinement of the hard polystyrene domain, (ii) the thermodynamic constraints due to the requirement that the chains must move keeping the homogeneous density, and (iii) the effect of the concentration gradient in the interphase of PI and PS domains.

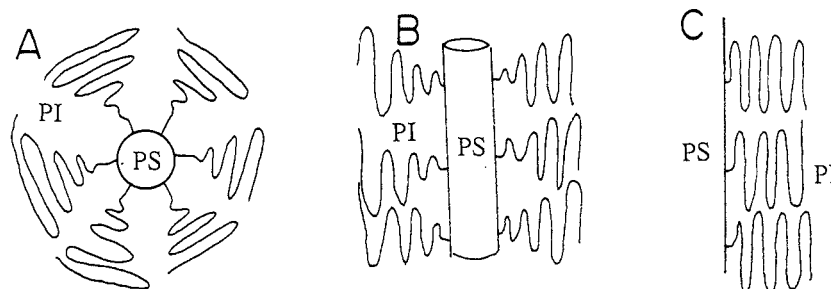


Fig.2 Schematic illustration of morphologies of SI: (A) sphere, (B) cylinder, and (C) lamella. Note that the PI chain near the junction point is stretched.

In TABLE 2, we see that the distribution of relaxation times and the increment of the nominal relaxation times have the reverse tendency on the morphology: In SI(4-27) having the morphology of the PI corona on the spherical PS domain, τ is prolonged but the distribution of relaxation times is almost similar to homo PI but in SI(8-8) and SI(8-16) τ is similar to homo PI but the distribution is much broader than free PI. What is implication of this result?

To keep uniform density, the PI chain near the anchor point is stretched. This degree of the stretching decreases in order of cylinder to lamella as illustrated in Fig. 2. Thus the probability that a part of chain locates in the interphase region becomes high in the order of the lamella, cylinder and sphere morphologies as shown in Fig. 2. In the interphase the friction coefficient is much higher than the PI phase. Thus depending on the configuration of the chain the mobility of the chain changes and hence the contact of the chain to the interphase results in a broad distribution of the relaxation time. Helfand(11) reported a theoretical calculation of the width of the interphase. For block copolymers with $\chi Z = 10$ have a relatively broad interphase where χ is the interaction parameter and Z the degree of polymerization. Since $\chi = 0.14$ for polystyrene and polyisoprene, low molecular weight SI has χZ of the order of 10.

As to the effect of the spatial confinement and the thermodynamic effects on the dynamics of a tethered chain, there is no theory available at present. We note that these effects cause a requirement that the chains must move cooperatively. Computer simulations of the dynamics of tethered chains may clarify these contributions.

SIS triblock copolymer

In the dielectric measurements on the SISs, two relaxations were also observed. In low temperature region around 230 K, the segmental mode was observed and around 400 K the normal mode was observed. Fig. 3A, 3B, and 3C show the loss curves of SIS(4-27-5), SIS(8-8-11), and SIS(8-16-7), respectively in the normal mode region. The occurrence of the dielectric normal mode relaxation indicates that in a temperature above T_g of the PS domain, the junction of the PI and PS blocks is not fixed but can fluctuate. It is seen that the ϵ'' curve of SIS(8-8-11) is extremely broad but the broadness of the SIS(4-27-5) and SIS(8-16-7) are similar. In Fig. 3A, we see that the width of the ϵ'' curve for SIS(4-27-5) tends to increase slightly with decreasing temperature and hence the time-temperature superposition principle fails. This indicates that with temperature the structure of SIS also changes.

In order to examine the morphology, we measured small angle X-ray scattering for SIS(4-27-5).(12) We observed that the intensity of the scattering decreased suddenly in the temperature interval between 80 and 100 °C indicative of the order-disorder transition(ODT). However, above the ODT a small but well defined peak was still observed. Therefore the PS domain still exists above the ODT although the

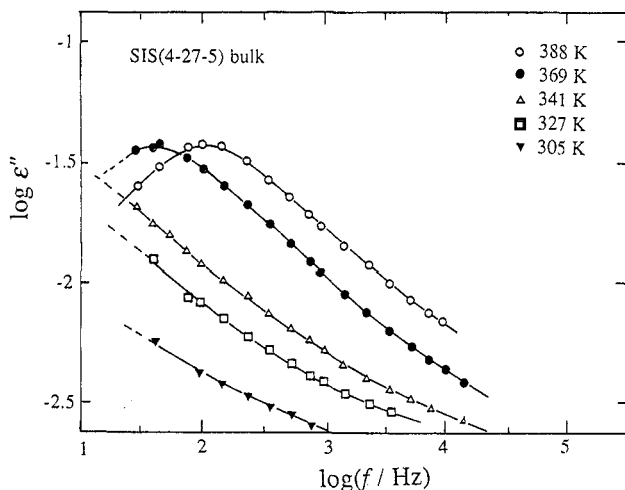


Fig.3A Double logarithmic plot of dielectric loss factor ϵ'' versus frequency f for SIS(4-27-5).

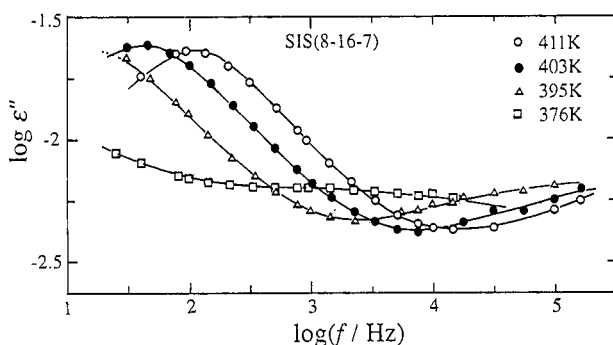


Fig.3B Double logarithmic plot of dielectric loss factor ϵ'' versus frequency f for SIS(8-16-7).

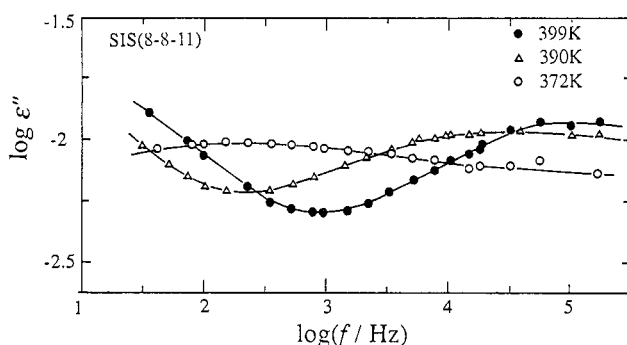


Fig.3C Double logarithmic plot of dielectric loss factor ϵ'' versus frequency f for SIS(8-8-11).

long range order has been lost above the ODT. In Fig. 3A, we see that the ODT does not cause a drastic change in the shape of the ϵ'' curve as well as the frequency region of the relaxation process.

The morphologies of the PS domain in SIS(4-27-5) and SIS(8-16-7) are cylinder and lamella, respectively. In these SIS the dielectric relaxation can occur through either the fluctuation of the junction point in the interphase or the jump of the PS block from one domain to the other as illustrated in Fig. 4A and B. If the former mechanism is the case the relaxation strength $\Delta\epsilon$ should be much smaller than that expected from the motion of a free PI chain. The observed $\Delta\epsilon$ divided by the volume fraction of PI for SIS(4-27-5) is 0.07 which is close to $\Delta\epsilon$ of the homo PI (0.082 at 320K). Therefore we conclude that the jump of the PS blocks between the PS domains is the major origin of the normal mode relaxation of the PI block chain. If this is the case, the activation energy E should be proportional to the molecular weight M of the PS block times the interaction parameter χ between PS and PI. The observed E 's for SIS(8-16-7) and SIS(4-27-5) are 110 and 67 kJ/mol, respectively, and are roughly proportional to M of the PS block.

In SIS(8-8-11), the PS phase forms a continuous phase and the PI phase forms cylindrical domain. In this case the reorientation of the end-to-end vector of the PI block can be achieved without the two mechanisms mentioned above, i.e., the diffusion of the PS block chains in the PS domain as schematically shown in Fig. 4C. As is seen in Fig. 3C, the loss curve is extremely broad and its mode distribution is different from the other two SISs. These complex mechanisms may contribute and result in the broad loss curve.

With decreasing temperature, the relaxation time prolongs and the loss peak goes out of our experimental window. Such the slow dynamics was studied by measurements of viscoelastic relaxation and the thermo-stimulating current (TSC) method for SIS(4-27-5). The frequency dependence of the storage moduli of SIS(4-27-5) were measured in the frequency range from 0.01 to 10Hz in the temperature range from 280K to 380 K. Below 300 K, the SIS was rubbery indicating that the PS domains work as a cross-link but above 300 K, it was viscoelastic and the PS domains do not work as a permanent cross-link.

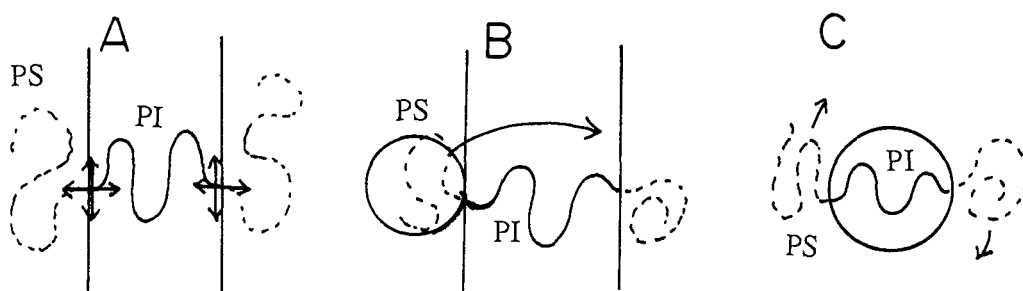


Fig.4 Three possible mechanisms of the reorientation of the end-to-end vector of PI block chain in SIS. A: Oscillation of the junction point in the interphase, B: Jumping of the PS block chain from one domain to the other, C: Diffusion of the PS block chains in the PS continuous phase.

Another evidence indicating that the PS block of SIS(4-27-5) can jump from one domain to the other even around 300 K is obtained from the TSC measurement. When the SIS was subjected to the electric field of 9 kV/cm for a poling time t_p at 303K and then cooled, the TSC peak due to the normal mode was observed. From the dependence of the height of the TSC peak on t_p the relaxation time was estimated to be ca. 300s at 303 K.

Conclusion

- (1) Distribution of relaxation times for the normal mode relaxation of SI depends strongly on the morphology of the PS domain. The broadness is highest for the lamella morphology and decreases in the order of the cylinder and sphere morphologies.
- (2) The dielectric normal mode relaxation of the PI block chain in SIS is observed around 400K although the both ends of PI are tethered.
- (3) The relaxation strength for SIS is similar to free PI indicating that the reorientation of the end-to-end vector of the PI block chain in SIS is mainly due to diffusion of the PS block chains across the PI domain.
- (4) The activation energy for the normal mode in SIS is proportional to the molecular weight of PS block.
- (5) Measurements of viscoelastic relaxation and thermo-stimulating current on SIS(4-27-5) provide another evidence of the jumping motion of the PS from one domain to the other.
- (6) In SIS(8-8-11) in which the PS domain forms a continuous phase and the PI domain has the morphology of cylinder, the shape of the loss curve is much different from that in SIS in which the PI phase is continuous.

References

1. W. H. Stockmayer, *Pure Appl. Chem.* **15**, 539 (1967).
2. K. Adachi and T. Kotaka, *Progr. Polym. Sci.*, **18**, 585 (1993).
3. T. Kotaka and K. Adachi, *Macromol. Chem., Macromol. Symp.* **79**, 125 (1994).
4. J. J. Burke and V. Weiss Ed. *Block and Graft Copolymers*, Syracuse Univ. Press, Syracuse, New York, 1973.
5. G. E. Molau, in *Block Copolymers*, S. L. Aggarwal ed., Plenum, New York, 1970.
6. M.-L. Yao, H. Watanabe, K. Adachi, and T. Kotaka, *Macromolecules*, **24**, 2955 (1991).
7. M.-L. Yao, H. Watanabe, K. Adachi, and T. Kotaka, *Macromolecules*, **24**, 6175 (1991).
8. M.-L. Yao, H. Watanabe, K. Adachi, and T. Kotaka, *Macromolecules*, **25**, 1699 (1992).
9. P. E. Rouse, *J. Chem. Phys.*, **21**, 1272 (1953).
10. See, for example, M. Doi and S. L. Edwards, *The Theory of Polymer Dynamics*, Clarendon Press; Oxford, 1986.
11. E. Helfand, *Macromolecules*, **8**, 552 (1975).
12. K. Tashiro et al., in preparation.