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Dielectric Study of Miscibility in Weakly Segregated Polymer Blends

Kazunori Se* and Osamu Takayanagi

Department of Materials Science and Engineering, Faculty of Engineering,
Fukui University, Bunkyo, Fukui 910, Japan

Keiichiro Adachi*

Department of Macromolecular Science, Graduate School of Science, Osaka University,
Toyonaka, Osaka 560, Japan

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ABSTRACT: Miscibility of polymer blends around the critical solution temperatures was studied by using a dielectric method for the system composed of low molecular weight *cis*-polyisoprene (*cis*-PIp) and polystyrene (PSt) and the system of *cis*-PIp and vinylpolyisoprene (vinyl-PIp). All these polymers exhibit the dielectric relaxation due to the segmental mode and *cis*-PIp also exhibits the normal mode relaxation. In the *cis*-PIp/PSt blend, the normal mode relaxation conformed to the blending law, indicating that the blend is homogeneous over a length scale of the end-to-end distance. On the other hand the *cis*-PIp/vinyl-PIp system exhibited a complex loss curve mainly due to the segmental mode of vinyl-PIp. The shape of the loss curve varied with temperature, indicating that the blend is weakly segregated and that the degree of inhomogeneity of the length scale of the monomeric unit varies with temperature.

Introduction

When two polymers are miscible, their blend exhibits a single glass transition temperature T_g at an intermediate temperature between the T_g's of the components.[1−3] Since the glass transition is the temperature at which the relaxation time of the segmental mode becomes of the order of 1 min, the segmental relaxation times of both components in a miscible blend become the same. Thus, a single dielectric α relaxation can be observed for the blend. In contrast, if polymers 1 and 2 are immiscible, the α relaxations of 1 and 2 are observed in separate frequency ranges. Thus dielectric spectroscopy is expected to provide fruitful information on the local fluctuation of concentration and the local miscibility.[1] If a blend is composed of polymers having type-A and type-B dipoles, the dielectric normal mode and the segmental mode can be observed.[4,5] The former is due to the fluctuation of the end-to-end vector, and hence the behavior of the normal mode reflects the concentration fluctuation of the order of the end-to-end distance. On the other hand the segmental mode reflects the local inhomogeneity of the order of the size of the monomeric unit. Thus we may obtain information of the fluctuation of different length scales, i.e., scales of the sizes for the monomeric unit and the overall polymer molecule. As far as we know, few dielectric studies of polymer blends based on this view have been reported.[6]

cis-polyisoprene (*cis*-PIp) is one of type-AB polymers and hence exhibits the normal mode relaxation as well as the segmental mode process.[7−9] On the other hand, polystyrene (PSt) and vinylpolyisoprene (vinyl-PIp) do not have the component of the type-A dipole moment since all the vinyl polymers possess symmetries of mirror image or inversion.[5] Therefore, we chose the blends of these polymers for the present study. It is known that PSt and PIp are immiscible at high molecular weight.[2] In order to increase the miscibility, we used low molecular weight samples of PIp and PSt. We also studied the phase diagram to examine the dielectric behavior below and above the critical solution temperature.

Table 1. Sample Characteristics

sample code	$10^{-3}M_n$	$10^{-3}M_w$	M_w/M_n	T_g
cis-PIp22	2.20	2.38	1.08	200
cis-PIp32	3.10	3.22	1.04	
vinyl-PIp27	2.66	2.76	1.04	258
PSt8	0.77	0.87	1.13	260
PSt22	2.20	2.33	1.06	
PSt25	2.56	2.66	1.04	

Experimental Section

Polymer Samples. Samples of *cis*-PIp were prepared by anionic polymerization with *sec*-butyllithium in pentane.[10] The so-called seeding method was employed to prepare samples with narrow distributions of molecular weight.[11] Vinyl-PIp and PSt were prepared with *n*-butyllithium in tetrahydrofuran and benzene, respectively. The microstructures of *cis*-PIp and vinyl-PIp samples were determined by proton NMR to be 93 and 30%, respectively.[12] The molecular weight and the distribution of *cis*-PIp, vinyl-PIp, and PSt were determined by using gel permeation chromatography (GPC), vapor phase osmometry, end group analyses with NMR, and viscometry. Details of the characterization were reported previously.[10] Their characteristics are listed in Table 1. The number in the codes indicates the weight average molecular weight, M_w, divided by 100.

The blends were prepared by mixing prescribed amounts of component polymers in a sample bottle by stirring for 40 h with a magnetic stirrer. The miscibility was judged by observation of turbidity.

Method. The dielectric loss factor ϵ'' was measured with a transformer capacitance bridge (Showa Denki) in the frequency range from about 100 Hz to 1 MHz. The capacitance cell was reported previously.[9] The capacitance of the empty cell was adjusted in the range from 15 to 35 pF by using glass spacers.

The phase diagram of the *cis*-PIp22/PSt8 blend was constructed from the turbidity in the range above room temperature by using a He−Ne laser.[13,14]

Glass transition temperatures were determined from the middle point of the jump of the heat capacity by a differential scanning calorimeter (Seiko Model SSC-580). The heating rate was 10 °C/min.

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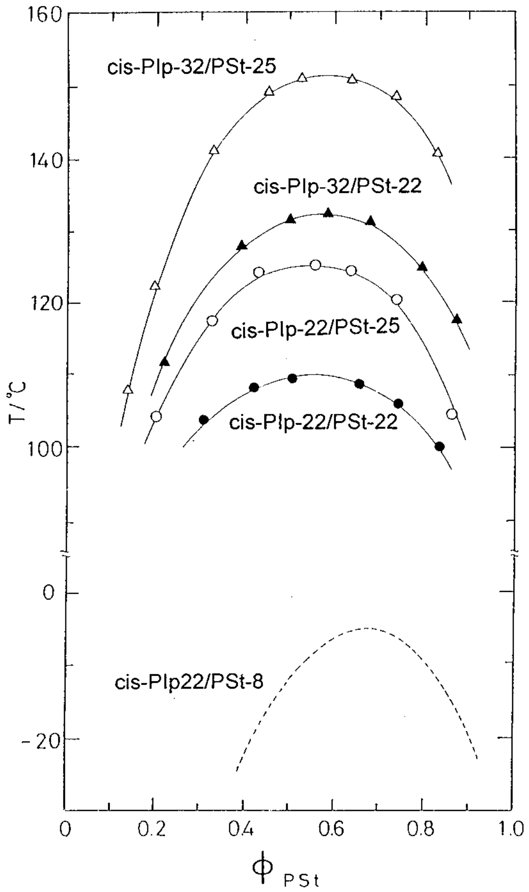

Figure 1. Phase diagrams of the *cis*-PIp/PSt blends. The dashed line indicates the binodal curve of the *cis*-PIp22/PSt8 system estimated from the χ parameter determined from the other data.

Results and Discussion

1. Phase Behavior. Before dielectric measurements, we examined the phase separation behavior by observing the turbidity. Since the temperature control below room temperature was difficult, we measured the cloud points only above room temperature. Figure 1 shows the phase diagrams of four combinations of *cis*-PIp and PSt with different molecular weights. The *cis*-PIp22/PSt8 blend was transparent at room temperature and hence it is in a mixed state at +15 °C.

The phase diagram of the *cis*-PI22/PSt8 blend was estimated as follows. First the interaction parameter χ between the *cis*-isoprene and styrene units was determined from the critical solution temperature T_c and the composition ϕ_c.[15−17] According to the Flory−Huggins−Scott equation,[17] ϕ_c and T_c of a blend composed of polymers 1 and 2 are given by

$$\phi_c = 1/[1 + (m_2/m_1)^{1/2}]$$

$$1/T_c = (1/2\beta)[(1/m_1)^{1/2} + (1/m_2)^{1/2}] + \alpha/\beta \qquad (1)$$

where m is the degree of polymerization and α and β are the constants appearing in the expression of the interaction parameter χ:

$$\chi = \alpha + \frac{\beta}{T} \qquad (2)$$

From the plot of $1/T_c$ versus $(1/m_1)^{1/2} + (1/m_2)^{1/2}$ for the four PSt/*cis*-PIp blends, we determined the parameters α and β to be −0.087 and +63, respectively. Then we estimated T_c and ϕ_c for the PSt8/*cis*-PIp22 blend with eq 1. The cloud point thus estimated for the PSt8/*cis*-PIp22 blend is shown in Figure 1 by the dashed line. The details of the phase behavior of the PSt/PIs systems are reported elsewhere.[13,14]

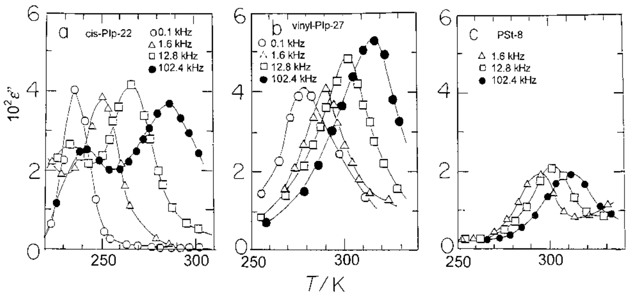

Figure 2. Temperature dependence of dielectric loss factor ϵ'' of (a) *cis*-PIp22, (b) vinyl-PIp27, and (c) PSt8. Frequencies of the measurements are given in the figures.

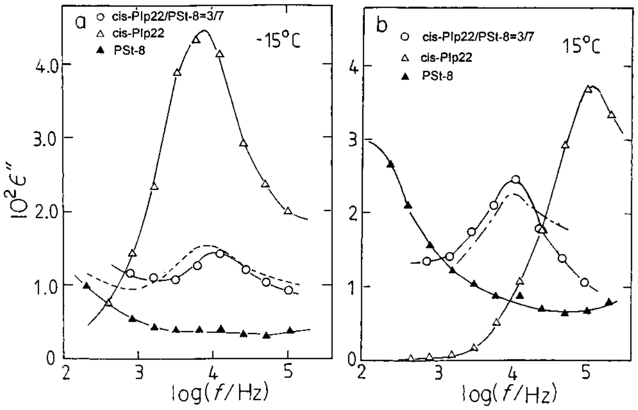

Figure 3. Dielectric loss ϵ'' versus frequency f curves of *cis*-PIp22/PSt8(3/7) at −15 °C (a) and 15 °C (b). The ϵ'' curves of pure *cis*-PIp22 and PSt8 are also shown for comparison. The dashed and dash−dot lines indicate the ϵ'' curves calculated with eqs 3 and 4, respectively.

The *cis*-PIp/vinyl-PIp system was transparent above room temperature. Therefore, we could not construct the phase diagram.

2. Dielectric Behavior of Homopolymers. Parts a−c of Figure 2 show the temperature dependences of the dielectric loss factor ϵ'' of *cis*-PIp22, PSt8, and vinyl-PIp27, respectively. In Figure 2a it is seen that *cis*-PIp22 exhibits two loss maxima around 240 and 290 K at 12.6 kHz. The low-temperature peak is assigned to the segmental mode relaxation due to the type-B component of the dipole moment. The high-temperature peak is assigned to the normal mode relaxation due to the type-A dipole moment. This behavior agrees well with that reported previously.[7−9] On the other hand, PSt and vinyl-PIp exhibit a single peak as shown in Figure 2b,c. Since these loss peaks locate near T_g, they are assigned to the segmental mode relaxations. It is expected that vinyl-PIp also exhibits the normal mode relaxation because it contains ca. 30% cis-linkages. However, we could not observe the normal mode since the loss due to the ionic conduction overcame the ϵ'' signal of the normal mode occurring in the low-frequency region.

3. *cis*-PIp22/PSt8 System. Dielectric Behavior and Blending Law. Parts a and b of Figure 3 show the ϵ'' curves of the blend of *cis*-PIp22 and PSt8 at −15 and +15 °C, respectively. The blending ratio was 0.297/0.703 by weight, and this blend is coded as *cis*-PIp22/PSt8(3/7). In these figures we also plotted the ϵ'' curves

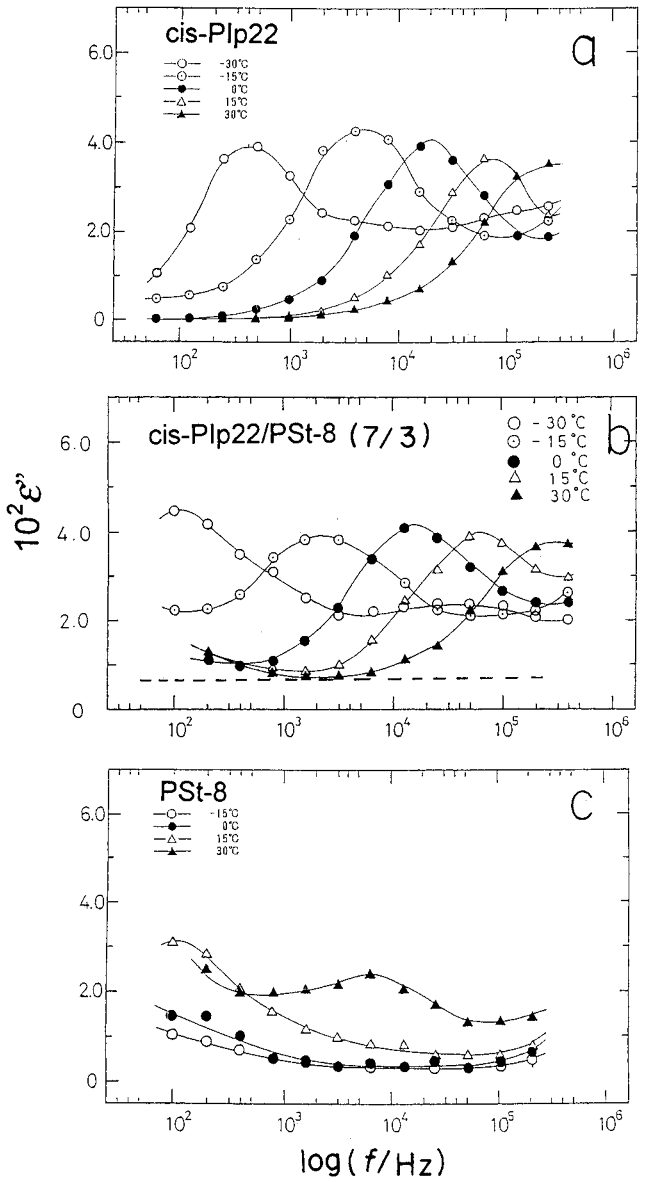

Figure 4. Dielectric loss factor ϵ'' versus logarithm of frequency f in the range −30 to +30 °C: (a) *cis*-PIp22; (b) blend of *cis*-PIp22/PSt8(7/3); (c) PSt8.

of pure *cis*-PIp22 and PSt8. From the phase diagram we see that this blend is in a phase-separated state at −15 °C but is in a mixed state at 15 °C.

Figure 4 compares the frequency (f) dependence of ϵ'' of the blend of *cis*-PIp22 and PSt8 in which the content of PIp is 74.2% by weight. This blend is coded as *cis*-PIp22/PSt8(7/3). The ϵ'' curves of pure *cis*-PIp22 and PSt8 are also shown. From the phase diagram shown in Figure 1, the blend is in a mixed state in the range −30 to +30 °C in which dielectric measurements were performed. As is seen in the figure, the ϵ'' curve at −30 °C exhibits two maxima around 0.1 and 50 kHz. The curve is similar to the ϵ'' curve of pure *cis*-PIp22 shown in Figure 4a, and hence, the low- and high-frequency peaks of the blend are assigned to the normal and segmental modes, respectively. Comparing the ϵ'' curves of the blend and pure *cis*-PIp at the same temperature, we note that the loss maximum frequencies of the blend are lower than those of pure *cis*-PIp22. The friction coefficient ζ for the *cis*-PIp chains in the blend is higher than ζ in pure *cis*-PIp due to the PSt chains having a lower mobility than PIp.

We consider the dielectric behavior of a blend composed of components 1 and 2. In the case of a completely segregated state, the ϵ'' curve is simply given by the weighted sum of the ϵ'' curves of each component:

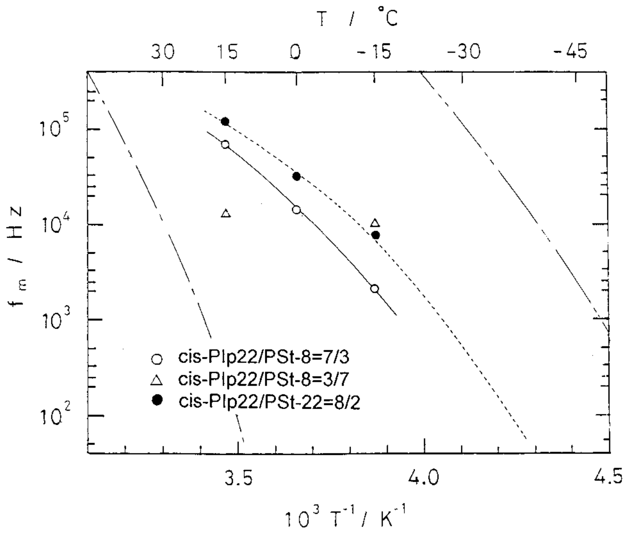

Figure 5. Loss maximum frequency f_m for the normal and segmental modes plotted against $1/T$ for the *cis*-PIp/PSt systems: (dash−dot line) pure PSt8; (dotted line), the normal mode of pure *cis*-PIp22; (dash−dot−dot line) the segmental mode of PIp22.

$$\epsilon_b''(\omega) = w_1\epsilon_1''(\omega) + w_2\epsilon_2''(\omega) \qquad (3)$$

where w denotes the weight of the component in unit volume. The ϵ'' curve calculated for segregated *cis*-PIp22/PSt8(3/7) is plotted by the dashed line in Figure 3a. It is seen that the calculated ϵ'' agrees approximately with the observed one. In a real system, phase separation results in two phases with 1-rich and 2-rich phases. In that case the above equation must be modified by taking into account the composition of the two phases. In eq 3 we also neglected the interfacial polarization that occurs at the interface of the two phases. The agreement of the calculated and experimental ϵ'' curves in Figure 3a indicates the interfacial polarization is negligible in the present system.

In the completely mixed state, the intensity is proportional to the weight fraction w of the components as in the segregated state. But the relaxation times vary due to the change of the friction in the blend; i.e., components 1 and 2 move under the frictional drag ζ_b in the blend. Then the relaxation time τ_j of the component j changes from τ_j in the pure state to $\tau_j\zeta_b/\zeta_j$, and hence, the ϵ'' curve shifts along the frequency axis by a shift factor $a_T = \zeta_j/\zeta_b$. Thus the ϵ'' of the blend is given by

$$\epsilon_b''(\omega) = w_1\epsilon_1''(\omega\zeta_1/\zeta_b) + w_2\epsilon_2''(\omega\zeta_2/\zeta_b) \qquad (4)$$

where the subscripts b, 1, and 2 denote the mixed blend, component 1, and component 2, respectively.

It is expected that even in a completely mixed state the friction for component 1 differs from that for 2 when the barriers of the internal rotation of the component polymers are different.[18] Then the concept of common friction ζ_b cannot be rationalized. However, many experiments on the miscibility of polymers indicated that the effect of internal rotation is not dominant compared with the effect of intermolecular interactions.[1,2] Therefore we may approximately apply eq 4 to blends of miscible polymers.

Figure 5 shows the Arrhenius plots of the loss maximum frequency f_m for the blends of *cis*-PIp22/

PSt8(7/3), *cis*-PIp22/PSt8(3/7), and *cis*-PIp22/PSt22(8/2). In the same figure, the f_m of pure PSt8 and those of the segmental and normal modes of *cis*-PIp22 are plotted. From the phase diagram shown in Figure 1 we see that *cis*-PIp22/PSt22(8/2) is in the segregated state. The f_m's for the normal mode in the segregated states of *cis*-PIp22/PSt8 and *cis*/PIp22/PSt22 coincide with those of pure *cis*-PIp22.

In the case of the mixed blends, the Arrhenius plots of f_m locate in the lower side of f_m for the normal mode of pure *cis*-PIp22. The ratio of the f_m of pure *cis*-PIp22 and that of the blend of *cis*-PIp/PS(7/3) is equal to the shift factor $a_T = \zeta_1/\zeta_b$, where the subscript 1 indicates *cis*-PIp22, as predicted by eq 4. The value of $\log(a_T)$ becomes 0.5 and decreases with increasing temperature. We attempted to calculate a_T on the basis of the free volume theory proposed by Doolittle,[19] assuming the additivity of the free volume fraction. It was found that the calculated a_T is larger than the experimental a_T.

The WLF coefficients for the dielectric relaxation time of *cis*-PIp in the miscible blend should be the same as those of the blends instead of those of the pure homopolymer. There is no basic reason that the coefficients in the blend and those in the pure state are the same.

Application of Blending Law to Mixed Systems. First we analyze the loss peak of *cis*-PIp22/PSt8(3/7) at 15 °C shown in Figure 3b. There are two possibilities that the observed loss peak for the blend is due to the segmental modes of PSt8 and PIp22 or the peak is due to the normal mode of *cis*-PIp in the blend. It is noted that since the segmental motions are governed by the common friction ζ_b for both components, the loss maximum frequencies of PIp and PSt coincide in the mixed state. From the sharpness of the loss peak, we may assign the peak to the normal mode of *cis*-PIp22. The calculated ϵ'' curve is shown by the dash–dot line with $\log \zeta_1/\zeta_b = 1.1$. We see that the agreement between the calculated and observed ϵ'' is fairly good.

Next we analyze the data shown in Figure 4b. In this figure we see that the base line is relatively high due to impurity ions, as indicated by the dashed line. The peak height from this base line is ca. 0.7 times the peak height of pure *cis*-PI, as predicted by eq 4. We note that the shape of the ϵ'' curves of pure *cis*-PIp and the blend (7/3) are similar. Thus the blend is homogeneous for the normal mode of *cis*-PIp as in the pure state.

For nonentangled *cis*-PIp with molecular weight M below the characteristic molecular weight M_c (=10 000), the relaxation time τ_n for the normal mode conforms to the Rouse theory:[20]

$$\tau_n = \frac{\zeta N \langle R^2 \rangle}{3\pi^2 k_B T} \tag{5}$$

where ζ is the monomeric friction coefficient, N is the degree of polymerization, and $\langle R^2 \rangle$ is the mean square end-to-end distance. This equation indicates that τ_n reflects the motion of the size of the dimension of the chains. Thus we conclude that PSt8 and PIp22 are miscible in the length scale of $\langle R^2 \rangle$ of the PIp22 molecule.

4. *cis*-PIp22/Vinyl-PIp27 System. Phase Separation. As mentioned in the section on the phase diagram, the *cis*/vinyl-PIp blends were transparent at room temperature at any composition. Therefore the blend is in a mixed state at room temperature.

In order to see the phase behavior below room temperature, we measured the glass transition temperature T_g by means of differential scanning calorimetry (DSC). Figure 6 shows the DSC diagrams for pure *cis*-PIp, pure vinyl-PIp, and the blend *cis*/vinyl-PIp(5/5). In pure *cis*-PIp or vinyl-PIp, a clear jump of the heat capacity is seen at 200 and 258 K, respectively. On the other hand, no clear jump of the diagram is seen for the blend, indicating that the broad glass transition occurs over a wide temperature range. If *cis*- and vinyl-PIp are mixed completely in the order of the segments, one clear T_g would be observed, but if completely phase separated, two T_g's corresponding to the T_g of the components would be seen.[1,2] Therefore, the DSC diagram indicates that the blend is in a weakly segregated state in the range below room temperature.

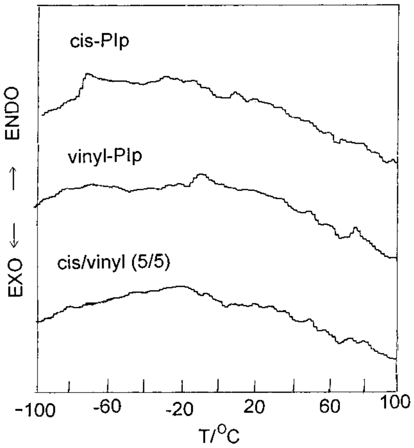

Figure 6. DSC curves of *cis*-PIp, vinyl-PIp, and blends of *cis*-PIp22/vinyl-PIp27(5/5).

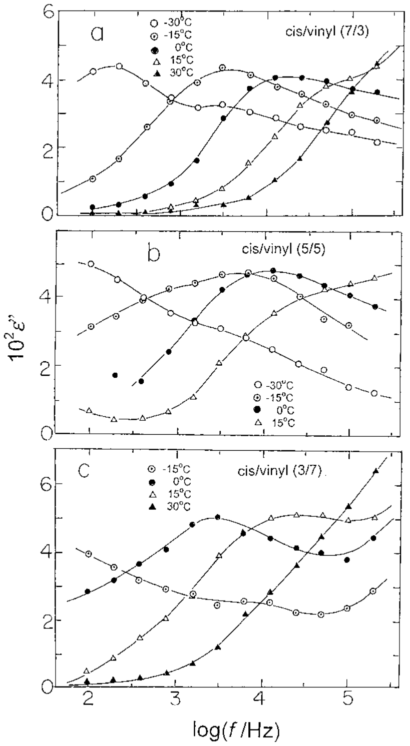

Figure 7. Dielectric loss factor ϵ'' versus logarithm of frequency f for blends of (a) *cis*-PIp22/vinyl-PIp27(7/3), (b) *cis*/vinyl(5/5), and (c) *cis*/vinyl(3/7) in the range −30 to +30 °C.

Dielectric Relaxation. Figure 7 shows the ϵ'' curves of *cis*-PIp22/vinyl-PIp27 blends with mixing ratios of 0.709/0.291, 0.520/0.480, and 0.278/0.722, which are coded as *cis*/vinyl(7/3), (5/5), and (3/7), respectively. In Figure 7, the shape of the ϵ'' curve changes with temperature. For example the ϵ'' curve of the *cis*/vinyl(7/3) blend is bimodal at −30 °C but at 0 °C it has a single peak. Above 15 °C the loss in the

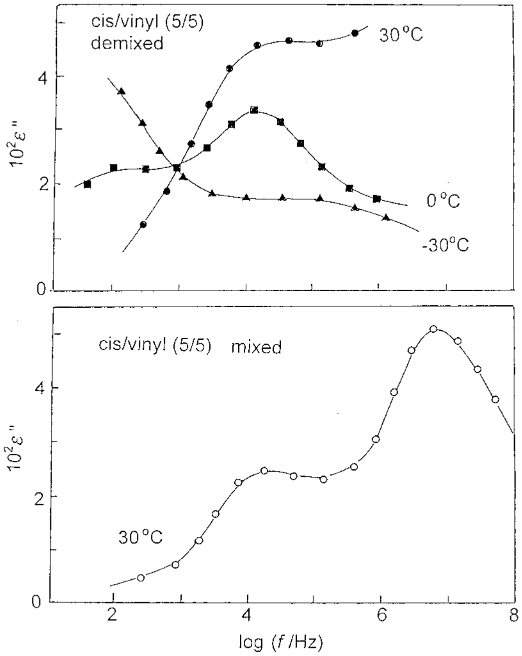

Figure 8. Dielectric loss factor ϵ'' of PIp22/vinyl-PIp27(5/5) calculated with eqs 3 and 4 for the segregated state (a) and the completely mixed state (b).

high-frequency region increases steeply and the peak around 10 KHz appears only as a shoulder.

This behavior indicates strongly that the degree of the segregation varies with temperature. As for the *cis*-PIp/PSt system, we assume that in the completely mixed state the loss curve of the blend is given by eq 4 while in the completely segregated state, the loss curve is given by eq 3. The ϵ'' curves at 5/5 blending ratio are calculated with eqs 3 and 4 and shown schematically in Figure 8. It is noted that in the completely mixed state, the relaxation times of the segmental modes of *cis*- and vinyl-PIp become the same and hence the loss maxima for the segmental modes of the components appear in the same frequency range. Since the intensity of the segmental mode of vinyl-PIp is strong, the relative intensity of the segmental mode with respect to the normal mode in the completely mixed state becomes much higher than the segregated system.

Returning to Figure 7, we see that in the high-temperature range above 280 K, ϵ'' increases steeply in the high-frequency region. This behavior is close to the behavior of the calculated ϵ'' curve in the mixed state shown in Figure 8. On the other hand in the range below 258 K, the ϵ'' curve resembles that of vinyl-PIp. In the segregated state the ϵ'' curve is expected to exhibit three loss maxima, i.e., the loss peaks due to the normal and segmental modes of *cis*-PIp and the segmental mode of vinyl-PIp. The broad and complex ϵ'' curves of *cis*/vinyl(7/3) in the low-temperature region can be regarded as the ϵ'' curve in the intermediate state between the segregated and mixed states.

Figure 9 shows the Arrhenius plot of the loss maximum frequency of the *cis*-PIp22/vinyl-PIp27 system. It is seen that the plots are not smooth as in the case of pure PIp. Therefore, the observed loss maxima are assigned to either the normal mode of *cis*-PIp22 or the segmental mode of the mixed blend of *cis*- and vinyl-PIp that appears depending on the degree of segregation. From the intensity of ϵ'' the loss peak observed is due to the segmental mode of vinyl-PIp. The change of the shape of the ϵ'' curve with temperature indicates that the miscibility of the length scale of the monomeric unit varies with temperature. In order to interpret the complicated behavior of the blends of *cis*- and vinyl-PIp, we are planning more systematic measurements on this system.

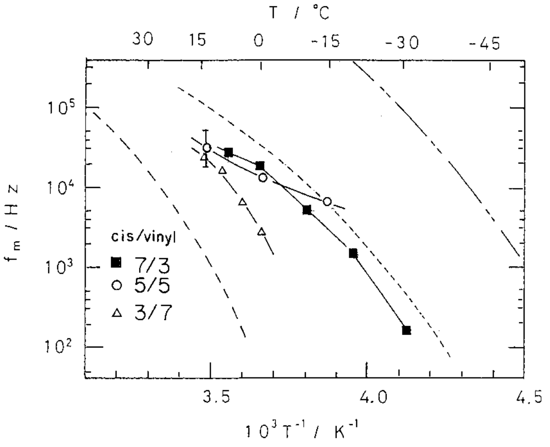

Figure 9. Plot of log(f_m) versus 1/*T* for blends of *cis*-PIp22/vinyl-PIp27(7/3), -(5/5), and -(3/7): (dashed line) f_m of vinyl-PIp27; (dotted line) normal mode of *cis*-PIp22; (dash–dot line) segmental mode of *cis*PIp*22*.

Conclusion

1. The dielectric normal mode of the *cis*-PIp molecule in mixed blends of *cis*-PIp/PSt conforms approximately to the blend law given by eq 4. The blends are homogeneous in the length scale of the order of the end-to-end distance of the *cis*-PIp chains.

2. The loss curves of *cis*-PIp/vinyl-PIp are broad and the shape of the loss curve broadens with decreasing temperature. The blend is weakly segregated in the length scale of the monomeric unit.

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