Microenvironments at Specific Chain Sites in Atactic Polystyrene Gels Studied by Photoisomerization

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ABSTRACT: Microenvironments in atactic polystyrene solutions of a wide range of viscosities in either toluene or tetrohydrofuran (THF) are investigated as a function of temperature from −60 to 25 °C by the studies of the photoisomerization of azobenzene, attached to specific sites on a polystyrene (PS) chain. The sites investigated are the chain center (CPS), the chain end (EPS), and the side chain (SPS). A free probe, 4−(phenylazo)aniline, is studied for comparison. The photoisomerization behavior is explained by a biphasic process, involving fast and slow processes. The fraction of the fast process is used as a useful indicator of the microenvironments. Also, the fast fraction is correlated with the macroscopic viscosity of the solution to incorporate the temperature and concentration effects. The site dependencies both in dilute solution and near the gel temperature were observed and interpreted to shed light on the gelation mechanism of atactic polystyrene.

Introduction

A physical gel is a three-dimensional network of flexible chains cross-linked by physical bonds between certain sites on different chains. A comprehensive understanding about the nature and the structure of junction points is still elusive because a large variety of systems exhibit physical gelation with their own characteristics. Only semicrystalline or at least stereoregular polymers were believed capable of physical gelation except for poly(vinyl chloride). The discovery by Wellinghoff et al.[1] for atactic polystyrene (aPS) gels triggered reconsideration about the gelation mechanism.

The studies[2,3] of the atactic polystyrene gelation in several solvents suggested that the chain overlap is a necessary condition for network formation with the chain entanglement enhancing gel stability. On the basis of the solubility parameter, Boyer et al.[3] concluded that the physical gelation was related to a segment−segment interaction which was hindered in a good solvent such as toluene or tetrahydrofuran (THF) but promoted in a poor solvent such as CS_2.

However, Gan et al.[4] correlated the physical gelation of atactic polystyrene with the enhanced low-angle scattering (ELAS) observed in a good solvent, a puzzling phenomenon because atactic polystyrene forms aggregates in good solvents rather than in poor solvents. Moreover, the phase diagram of the aPS/CS_2 system determined by measuring a gel-formation exotherm and a gel-melting endotherm with differential scanning calorimetry (DSC)[5] meant the physical gelation is a first-order transition, rather than a second-order transition[3] due to a segment−segment interaction. Francois et al.[5] suggested that the junction points of aPS/CS_2 gel consist of a polymer−solvent stoichiometric compound, based on the occurrence of the maximum in the phase diagram as well as in the enthalpy variation with concentration at the same concentration. In other words, the solvent is viewed as intercalated between the polymer chains, resembling a ladder structure, as confirmed by a neutron diffraction study.[6]

Although the ladderlike model was supported by several experimental evidences, a recent NMR study[7] cast doubt on this model. Perez et al.[7] could not observe any evidence for rigid or even anisotropically mobile solvent molecules, thereby proposing a model where both ends of the polymer chains are fixed in junction points while most polymer segments remain in solution. Even though this result was obtained from isotactic polystyrene systems, it may be applied to atactic polystyrene systems because of its similarity in the gelation mechanism.

Performing swelling tests and small-angle neutron scattering, Klein et al.[8] investigated this issue further to discriminate between these contradictory models and came to support the ladderlike model. Recently, they modified the ladderlike model to allow the intercalated solvent to have a higher mobility.[9] Only a model in which solvent has liquid-like mobility with an ability to stabilize the polymer−solvent complex may reconcile NMR findings with other results.

As demonstrated in our previous study,[10] the behavior of photoisomerization of azobenzene attached to the specific sites of a polystyrene chain strongly depends on the microenvironments in polymer solutions. Further, the site dependency of chain mobility provides detailed information on the change of segment density due to chain overlap, chain interpenetration, or chain contraction. In this study, we investigated the site dependency of the microenvironments as a function of temperature, especially when atactic polystyrene solution undergoes sol−gel transition.

Experimental Procedures

1. Materials and Sample Preparation. The three site-specifically labeled polystyrenes, whose chemical structures and some properties are shown in Table 1, were used as in the previous study.[10] Azobenzene chromophore was attached to the specific chain sites of polystyrene, such as the chain center (CPS) in the chain backbone, the chain end (EPS), or randomly distributed (1 mol %) in side chain (SPS). A free probe molecule (FP), 4-(phenylazo)aniline purchased from Aldrich Chemical Co., was recrystallized from toluene and acetone. Monodisperse polystyrene (MW = 90 000) was purchased from Pressure Chemical Co. Toluene and THF were purchased from Fischer. All the solvents were used without further purification. For dilute solutions, a certain amount of each labeled polymer or free probe was dissolved in toluene to obtain an initial optical density of the trans isomer peak in the range of 0.7-1.2. The concentration (by weight) in dilute solution for the CPS, EPS, SPS, or free probe was 0.46, 0.23, 0.69, or 1.15×10^{-3}%, respectively. These dilute solutions did

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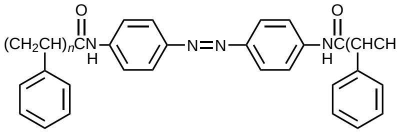
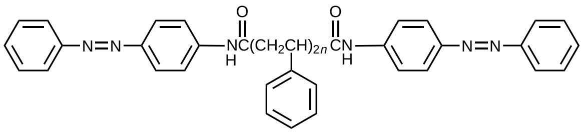
Table 1. Chemical Structures and Characteristics of Three Azobenzene-Labeled Polystyrenes and Free Probe

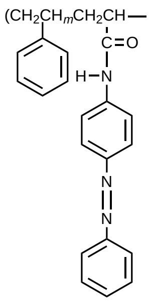
(1) center-labeled PS (CPS)



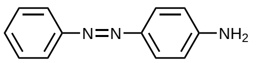
(2) end-labeled PS (EPS)



(3) side-labeled PS (SPS)



(4) free probe



samples	MW	M_n	T_g (°C)
CPS	84 000	80 000	100
EPS	92 000	79 000	100
SPS	39 000	26 000	100

not contain any unlabeled PS. For the concentrated solutions (50% by weight), a certain amount of monodisperse polystyrene (MW = 90 000) was added into the respective dilute solution and dissolved in an ultrasonic bath for several hours. Toluene or THF was used as solvent for concentrated solutions.

A physical gel was prepared by cooling the solution temperature below −60 °C, using a Multicool temperature bath (FTS Systems, Inc.) with methanol as a refrigerant. The temperature range studied was from −60 to +25 °C. In this range, only a PS/toluene solution (50%) experienced physical gelation.

2. Determination of Sol−Gel Transiton. Two methods were used: a ball-drop method and differential scanning calorimetry (DSC). In the first method, a steel ball (54 mg) was placed on the top of the prepared gel. Then the temperature was allowed to rise at 0.5 °C/min and the height of the steel ball recorded as a function of temperature. In DSC experiment, a Perkin-Elmer 7 series thermal analysis system was used with a heating rate of 5 °C/min.

3. Photoisomerization Studies. The photoisomerization studies of dilute and concentrated solutions were carried out as a function of temperature using a specially designed sample holder, which was placed inside a tightly sealed Plexiglass box to eliminate any condensation. This box was purged with dry argon gas, and silica gel was placed within the box to absorb moisture. The samples were sealed tightly in a fluorescence cuvette prior to photoisomerization studies. As the sample reached the desired temperature, the outsides of the windows for the analyzing beam were dried with an air gun before UV−visible spectra were taken. UV−visible spectra were taken with a Spectronic 3000 Array (Milton Roy) spectrometer, immediately following a certain number of flashes.

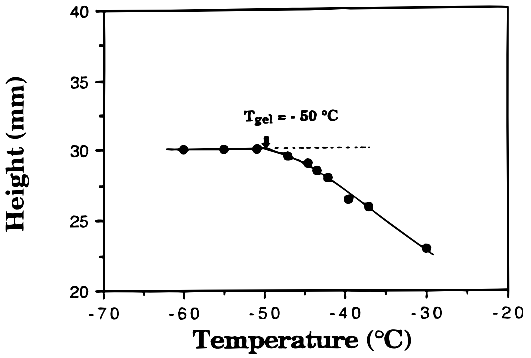


Figure 1. Illustration of the ball-drop method to measure the gel temperature (T_{gel}) of the aPS/toluene (50% by weight, MW = 90 000) system.

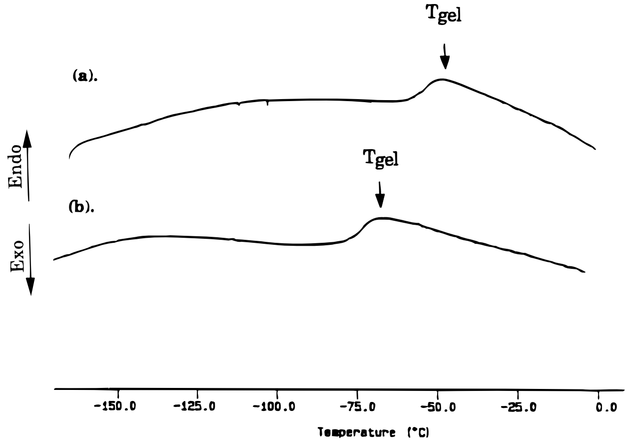


Figure 2. DSC thermograms for aPS solutions (50% by weight): (a) in toluene; (b) in THF.

4. Viscosity Measurement. Viscosity of polystyrene solutions in toluene was measured as a function of polymer concentration (0.5−50% by weight)) and temperature (−70 to +25 °C). For the polymer solutions (0.5−50%), a cone/plate viscometer (Brookfield, Model DV-II, cone no.: CP-40 and -51) was employed, using a 0.5 mL sample at 35 °C. For viscosites of dilute solution from +5 to +35 °C, a cone/plate viscometer was also used. The viscosity at lower temperature was extrapolated from the following Andrade's equation since it takes care of the temperature effect on the viscosity, η, of solvents: $\eta = B \exp(E_\eta/RT)$, where B is a constant, R is the gas constant, and E_η is an activation energy. The measurements for the concentrated solution (50%) were made using a Rheometrics System IV with a parallel plate geometry, using a fluid motor for the range of +25 to −20 °C and a dynamic motor for the range of −30 to −70 °C. The details of these experiments are found elsewhere.[11] In the measurements with a fluid motor, complex viscosity (η^*) was recorded as a function of temperature at a frequency of 1 rad/s with a strain of 1%. When using a dynamic motor, the complex viscosity (η^*), the dynamic storage modulus (G'), and the loss modulus (G'') were monitored as a function of temperature at frequencies from 0.1 to 1 rad/s with a strain of 1%.

Results and Discussion

1. General Features of PS Gels. Polystyrene gels in toluene or THF in 50% solution were investigated. From the ball-drop method, the gelation temperature (T_{gel}) of the PS/toluene system was obtained as the deviating point from the horizontal line in the plot of the height versus temperature, as shown in Figure 1. The T_{gel} of the PS/toluene system was −50 °C, while the PS/THF system was still in the sol state even at −65 °C. In DSC studies, as shown in Figure 2, a gel melting point was observed in both PS/toluene and PS/THF at −50 and −70 °C, respectively. The observation

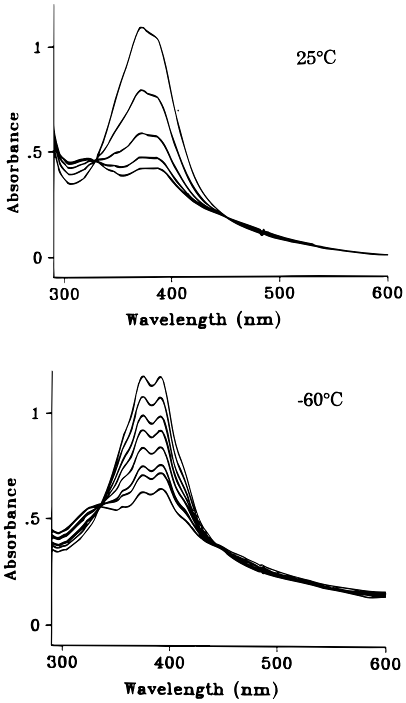


Figure 3. Change of UV−visible spectra of the dilute CPS/toluene (0.46% by weight) as a function of photoisomerization at two different temperatures. (from top to bottom curves, the number of flashes corresponds to 0, 20, 40, 60, 100, 150, 200, 300).

of the lower T_{gel} in PS/THF is consistent with other studies.[2] The gelation temperature of the PS/toluene system obtained from two different methods was identical. The enthalpy associated with the sol−gel transition was calculated from the endotherm of each solution to be around 2−3 J/g, which is comparable to the result of Tan et al.[2] The glass transition was not observed clearly in either solution. On the basis of the theoretical treatment of the plasticizer effect developed by Bueche,[12] the glass transition temperature (T_g) of the aPS/toluene or aPS/THF solution (50%) is estimated to be about −100 °C.

2. Photoisomerization Studies. In Dilute Solutions. The temperature dependence in photoisomerization was first studied in dilute solutions in which physical gelation does not occur. Figure 3 shows UV−visible spectra of CPS in toluene with photoisomerization at two different temperatures (+25 and −60 °C) for comparison. In general, UV spectra at −60 °C show fine structures, due to the reduced rotational and collisional energy transfer processes, resulting in an UV band corresponding to pure electronic−vibrational transitions.[13] This observation is most pronounced in the CPS solution. Also, the base line of UV spectra at −60 °C was raised to 0.1 because of condensation on the windows, requiring base line correction for the data analysis.

Kinetic plots of photoisomerization of the three labeled polystyrenes and the free probe were obtained by using the following equations.[14]

$$I(\delta) = \left(1 + \frac{D_\infty}{2} + \frac{D_\infty^{\,2}}{12}\right)\ln|\delta| - \left(\frac{1}{2} + \frac{D_\infty}{6}\right)\delta + \frac{\delta^2}{24} = -At + \text{constant} \qquad (1)$$

$$I'(\delta) = \text{constant} - I(\delta) = At \qquad (2)$$

Here, $\delta = D_\infty - D$, D_∞ and D are the optical densities in the photostationary state and after t flashes, respectively, and A is equal to $I_0\phi_t\epsilon_t/y_\infty$, where I_0 is the irradiation intensity, ϕ_t is the quantum yield of photoisomerization, ϵ_t is the molar extinction coefficient of the trans isomer, and y_∞ is the fraction of the cis isomer at the photostationary state. Among these parameters, only the cis content at the photostationary state where no further photoisomerization occurs was determined to be 90% by subtraction of the cis peak. Therefore, D_∞ was assumed to equal $0.1D_0$, where D_0 is the optical density for the trans isomer before irradiation. Figure 4 illustrates the kinetic plots of the CPS solution as a function of temperature, showing the slowing down as well as deviation from linear behavior at low temperatures. Such a deviation is most severe in the CPS solution. However, the free probe shows no deviation even at −60 °C.

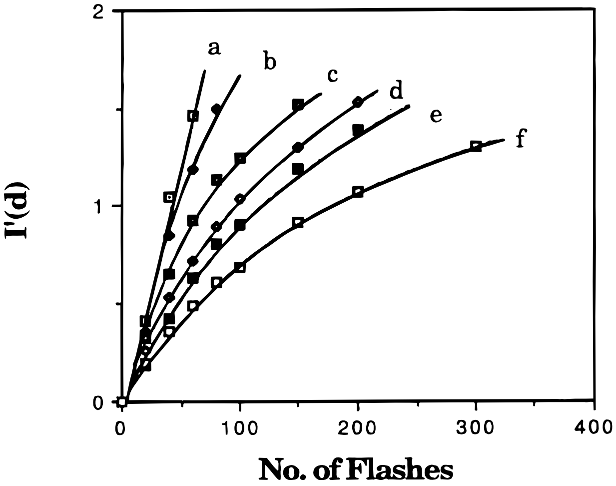


Figure 4. Kinetic plots of photoisomerization of dilute CPS/toluene at different temperatures: (a) +25, (b) 0, (c) −25, (d) −40, (e) −53, and (f) −60 °C.

Table 2. Kinetic Parameters of the Dilute Solution of the CPS in Toluene as a Function of Temperature

temp (°C)	α	10^2A_1 (s^{-1})	10^5A_2 (s^{-1})
25	1	2.0	1.0
0	0.94	2.0	1.0
−25	0.81	2.2	8.0
−40	0.79	1.8	8.0
−53	0.72	1.2	8.0
−60	0.69	1.5	8.0

For analysis of such nonlinear behavior, a biphasic process consisting of fast and slow processes was fitted with the following equation[15]

$$e^{-I'(\delta)} = \alpha e^{-A_1 t} + (1 - \alpha)e^{-A_2 t} \qquad (3)$$

where t is the number of flashes, A_1 and A_2 are the rate constants for the fast and slow processes, respectively, and α is the fraction of the fast species. When this equation is applied to dilute solutions in a good solvent, α = 1 except for the SPS case, where α = 0.86. Therefore, the value for the SPS was normalized by the α value found in the dilute solution in toluene as described in the previous paper.[10] Table 2 summarizes the kinetic parameters for the center label as a function of temperature. The relative rate constant for the fast process (A_1) remains almost constant with decreasing temperature within experimental error. The relative rate constant for the slow process (A_2) differs from A_1 by approximately 3 orders of magnitude. The values of A_1 and A_2 were about the same order of magnitude for the three labeled polymers.

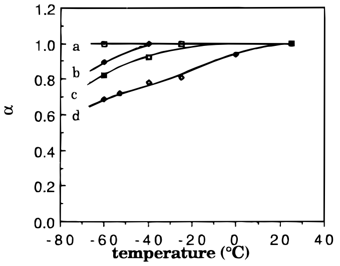


Figure 5. Change in the fraction of the fast photoisomerization, α, as a function of temperature for the dilute solutions: (a) free probe, (b) EPS, (c) SPS, and (d) CPS.

Figure 5 shows the plot of α values as a function of temperature for dilute solutions of the three labeled polystyrenes as well as those for the free probe. Almost all of the free probe can quickly photoisomerize down to −60 °C, while some fractions of the three labeled polymers exhibit difficulty in fast photoisomerization whose extent depends on the label's site. The chain center has the most pronounced temperature effect, followed by side chains and chain ends. The decrease in the α value means that the slow process is becoming more and more important,[16] mainly due to the increasingly congested environment near the label.[10] Richard et al.[17] found that the radius of gyration of polystyrene in a dilute cyclohexane solution decreases when the temperature decreases from +65 to +32 °C. Since the *θ* temperature for the PS/toluene system is known to be −113 °C,[18] some contraction in the chain dimension occurs when the temperature goes down to −60 °C, leading to the increase in segment density. This increase in the segment density seems to make the contribution of the slow process greater, as observed in silute solutions of the CPS and SPS in the *θ* condition (cyclohexane at +34.8 °C).[10]

Another factor which affects the result of photoisomerization as a function of temperature is the temperature effect on the chain mobility. With decreasing temperature, higher energy is required to overcome the activation energy to move a segment of the polymer. As described in the previous study,[10] a combination of chain motions allowed the photoisomerization reaction of the labeled dye to occur in polymers as fast as in the free probe at +25 °C. However, this combined motion becomes more difficult with decreasing temperature. Among the three labeled polymers, the center labeled PS experienced the greatest decrease in the α value at lower temperatures since it is connected at both sides, probably requiring a higher energy barrier than SPS or EPS which is connected at only one side.

In Concentrated Solutions. Photoisomerization reactions in 50% PS/toluene and PS/THF solutions were studied as a function of temperature. In the temperature range of −60 to +25 °C, only the PS/toluene system experienced physical gelation. Thus, the PS/THF solution could be a good reference for discrimination of the gelation effect on the microenvironments from the other effects such as temperature and chain contraction since it has similar viscosity and T_g as the PS/toluene solution.

The UV−visible spectra of the PS/THF solution were almost identical with those of the PS/toluene solution. Parts a and b of Figure 6 show kinetic plots of center-labeled polystyrene in toluene and THF, respectively. In these concentrated solutions, center-labeled PS experiences some deviation from linearity at +25 °C which becomes more prominent with decreasing temperature.

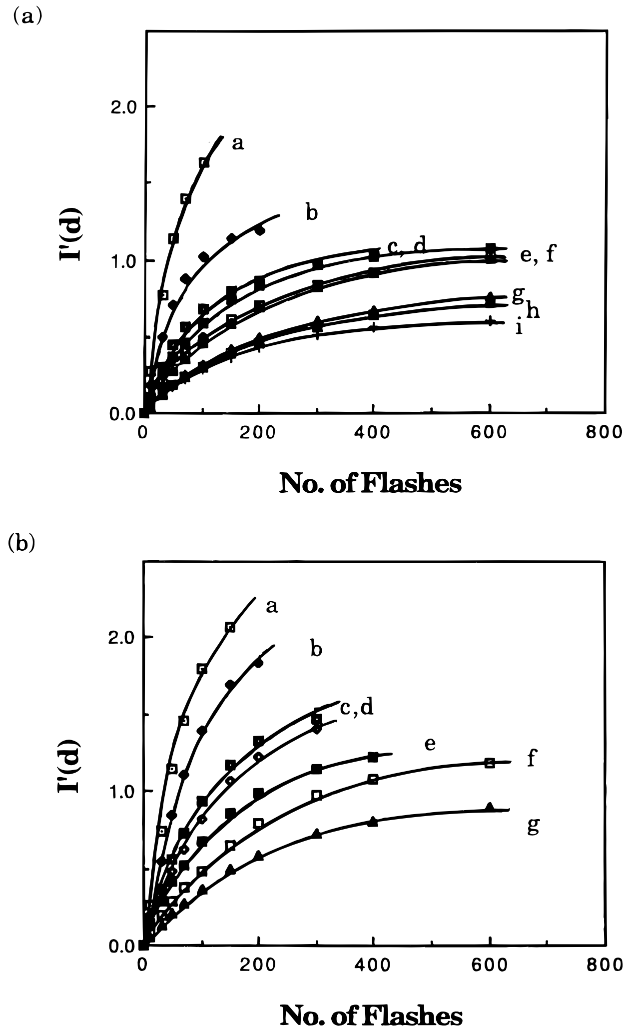


Figure 6. (Plot a) Kinetic plots of photoisomerization of aPS/toluene (50% by weight) laced with the CPS at different temperatures: (curve a) +25, (curve b) 0, (curve c) −25, (curve d) −35, (curve e) −40, (curve f) −48, (curve g) −51, (curve h) −55, and (curve i) −60 °C. (Plot b) Kinetic plots of photoisomerization of aPS/THF (50% by weight) laced with the CPS at different temperatures: (curve a) 25, (curve b) 0, (curve c) −24, (curve d) −35, (curve e) −48, (curve f) −52, (curve g) −60 °C.

Parts a−d Figure 7 show the plots of α values as a function of temperature for the free probe, SPS, EPS, and CPS in both solvents, respectively. The free probe shows little change in the fast fraction as a function of temperature in either solvent, while three labeled polystyrenes show significant changes in the fast fraction with decreasing temperature. Based on the results of the free probe, the assumption that the aPS/toluene solution has similar properties to the aPS/THF solution is found to be sound microscopically as well as macroscopically for this particular label. The SPS in Figure 7b shows gradual decreases in α values in toluene, with values lower than those in THF. It does not show any significant change around the T_{gel} in toluene. The EPS in Figure 7c shows similar trends but with larger α values than SPS. However, the CPS shows a noticeable change near the T_{gel} in toluene, as shown in Figure 7d.

Although the photoisomerization results reveal no direct information on the mobility of the solvent, our results may be explained by the ladderlike model.[5] According to this model, the cross-link points are composed of syndiotactic sequences of atactic polystyrene.[19] All three labels in the polymers and the free

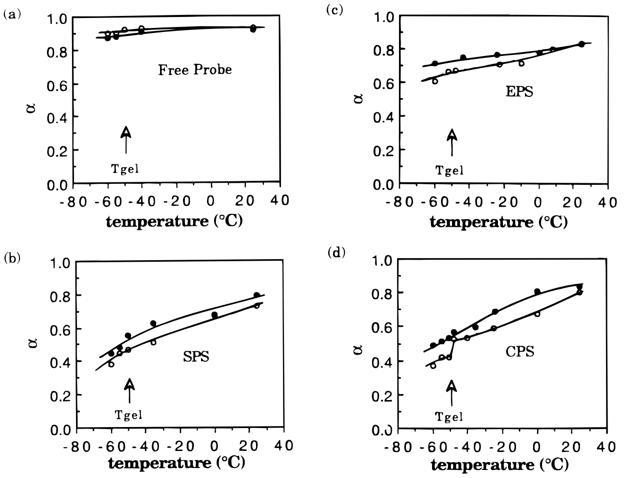


Figure 7. Change in the fraction of the fast photoisomerization, α, of the 50% aPS solutions in two different solvents ((○) in toluene; (●) in THF) as a function of temperature laced with different labels.

probe may be excluded from junction points because it is too bulky to form a ladder structure. If so, the photoisomerization reaction of each chromophore may not be affected by physical gelation except for the CPS case. The CPS is expected to show some decrease in the fast fraction of photoisomerization if the junction points are close enough not to allow isomerization through many small oscillations of the internal angle of rotation.[20] Since CPS is affected by gelation, we may conclude that the junction points are formed closely to the chain center. Even though the EPS is not influenced appreciably by physical gelation, we still cannot exclude the possibility that the chain ends participate in junction points as Perez et al.[7] suggested for isotactic polystyrene. However, if junction points are formed only near chain ends, it would not explain the observed effect on the CPS label.

3. Correlations of α Values with Viscosities. When the temperature and the concentration are changed in polystyrene solutions, their viscosity varies in a wide range. It was of interest to see whether the fast fractions (α values) of photoisomerization of each labeled polystyrene and the free probe might be correlated with such macroscopic viscosity. As shown in Figure 8a–d, the effects of concentration and temperature on the chain mobility are incorporated in the same figure in terms of viscosity. The free probe experiences little change in the α value in a wide range of viscosity, as shown in Figure 8a. This is not surprising since 90% of the free probe is able to isomerize even in the glassy state.[21] However, three labeled polymers showed a gradual decrease in the α value with increasing viscosity. Among three labeled polystyrenes, the CPS experiences the greatest decrease in the fast fraction with decreasing temperature, as shown in Figure 8d. It is interesting to note that the temperature effect on the microenvironments in a dilute solution, as indicated by + type data points, does not follow the general trend. This trend was observed in other labeled polymers as well. The deviation was most severe in the CPS, followed by SPS and EPS, indicating an activation energy for the CPS greater than that of others.

Conclusion

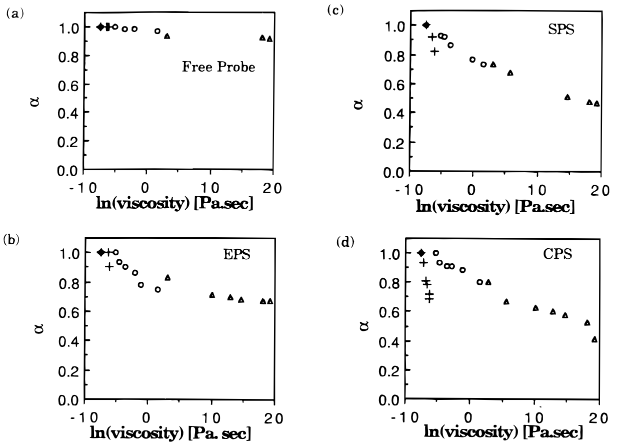


Figure 8. Viscosity effect of the fast fraction of photoisomerization, α, of atactic polystyrene solutions: (○) polymer concentration effect in the concentration of 0.5–50%; (+) temperature effect in the dilute solution; (△) temperature effect on the 50% aPS/toluene solution).

The photoisomerization behavior of azobenzene attached to specific sites on a polystyrene chain were characterized in atactic polystyrene solutions of a wide range of viscosities in either toluene or THF. The behavior of specific sites such as the chain center, the chain end, and the side chain were compared with that of a free probe.

While almost all of the free probe could quickly isomerize down to −60 °C, some fractions of the three labeled polystyrenes exhibited difficulty in fast photoisomerization in dilute solution with decreasing temperature, with the CPS experiencing the most effect. In concentrated solutions, the free probe showed little change down to −60 °C in either solvent. The SPS and the EPS showed a gradual decrease in the fast fraction of photoisomerization without any abrupt change around T_{gel}. However, the CPS showed a noticeable change near T_{gel}. This result suggests that the junction points of physical gels may be close to the chain center. Also, there was a general correlation between the fast fraction and the macroscopic viscosity of the solution, except for the dilute solution cases.

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