Mobility Measurement and Computer Simulation at Specific Sites in Polystyrene Solutions and Gels

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Trans--> cis photoisomerization of azobenzene chromophore labeled at the chain center, the chain end, or as a side chain of polystyrene as well as free probe was studied to investigate the mobility at specific chain sites in polymer solutions and gels. The site dependency of the chain mobility indicated that the chain center was least affected by increasing concentration, followed by the chain end and the side chain. Computer simulation to predict segmental density near the chromophore supports the experimental trends. Also photoisomerization of 50% atactic polystyrene (aPS) solutions in toluene and tetrahydrofuran was studied as a function of temperature from 25°C to -60°C. In aPS / toluene gel, the chain mobilities of the chain center and the chain end showed significant changes near the T_gel, while side chain and free probe exhibited little change. Effects of concentration and temperature were characterized by bulk viscosity measurement to see how chain mobility is influenced at specific sites.
Mobility Measurements and Computer Simulation at Specific Sites in Polystyrene Solutions and Gels

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INTRODUCTION

The development of a molecular probe which senses the microscopic environment of polymer solutions has been the subject of many recent studies. Using the fluorescence energy transfer phenomenon\(^1\), the extent of chain interpenetration was characterized as a function of polymer concentration and the nature of solvent. On the other hand, the twisted intramolecular charge-transfer (TICT) phenomenon was applied for the study of microenvironment of polymer solution such as local polarity or segmental density.\(^2\)

In this study, photosomerization technique was explored in order to study the chain mobility in polymer solution. This method has been previously applied mainly in polymer films.\(^3,4\) It was found that the dominant factor in the photochemistry of labeled in polymer films is the local free volume in the vicinity of the label.

One major concern of this work was the site dependency of the change of chain mobility as a function of concentration, solvent polarity, and temperature, especially when solution undergoes sol-gel transition. This result was compared with computer simulation result and correlated with macroscopic viscosity. It is hoped that the site dependency of chain mobility due to the process of physical gelation can shed light on the gelation mechanism.

EXPERIMENTAL

Azobenzeno chromophore was attached to the specific chain sites of polystyrene such as the chain center (CPS), the chain end (EPS), or the side chain (SPS) as described in a previous paper from our laboratory.\(^6\) A free probe molecule, 4-phenylazoaniline, was also employed for comparison. Concentration range studied were 0.4 - 50% by weight for the PS / toluene system and 0.4 - 30% for the PS / cyclohexane system. Temperature was maintained at 34.8°C which is the \(\Omega\) temperature for the polystyrene solution in cyclohexane. For the study of physical gelation of azatrac polymer (aPS) / toluene system, a concentrated solution (50%) was chosen. Also, aPS solution (50%) in tetrahydrofuran (THF) was studied for comparison. Temperature range studied was from 25°C to 60°C which covers \(T_g\) for the aPS / toluene system, but not for the aPS / THF system. The gel temperatures for these systems were determined by the ball-drop method and differential scanning calorimetry (DSC). In order to study the temperature effect, a dilute solution (0.4%) in toluene was also studied.

A PRA flash light source (Model 6100A) was used to irradiate the sample to induce trans \(\rightarrow\) cis photosomerization. UV-visible spectra of the sample were taken with a Perkin-Elmer diode-array system (Model 7500 data station).

Computer simulation was performed using molecular dynamics with a spring-bead model. Two types of interaction were considered: spring type interaction between the segments along the chain backbone and Lennard-Jones potential for other interactions. The specific segment density distribution and radial distribution functions of polymer chain were calculated as a function of concentration.

In order to measure the macroscopic viscosity, Cone / Plate viscometer and Rheometric System 4 were employed.

RESULTS AND DISCUSSION

Figure 1 illustrates UV-visible spectra of the dilute solution of CPS as a function of photosomerization at 34.8°C. The absorption peak at 533 nm which is due to the \(\pi\rightarrow\pi^+\) transition of the trans isomer is decreasing with irradiation while the absorption at 445 nm is increasing. Using an appropriate equation\(^5\), kinetic plots of photosomerization were obtained as shown in Figure 2. It is obvious that non-linear behavior was observed in higher concentrations than 10%. Based on the assumption that photosomerization reaction occurs with a combination of two processes: fast and slow processes, these non-linear behaviors in concentrated solutions were characterized by the following equation.

\[
\frac{1}{1 - f(t)} = a e^{-A_f t} + (1 - a) e^{-A_s t}
\]

where \(t\) is the number of flashes. \(A_f\) and \(A_s\) are the rate constants for the fast and slow processes, respectively. And \(a\) stands for the fraction of the fast process. The concentration dependency of the fast fraction, \(a\), in the case of PS in toluene was shown in Figure 3. Although free probe had little difficulty in photosomerization up to 50% solution, three labeled PS showed significant site dependency after 10% when the chain overlapping concentration (C*) except the SPS case. For the SPS, C* is 17.02% by weight. SPS experienced most difficulty, followed by the EPS and the CPS. This result implies that the local environment near the chain center doesn't change as much as near the chain ends and the side chain with increasing concentration. In the case of PS in cyclohexane (CPS), photosomerization reactions were retarded even in the dilute solutions of the CPS and the SPS. Although the general trend was about the same as in the good solvent case, the fast fraction, \(a\), was smaller and decreased slower with increasing concentration in cyclohexane.

In order to understand this result better, computer simulation was used. The results from the ladderlike model (Figure 4) suggests that the chain end in the \(\Theta\) condition. However, the segmental density near the chain center was higher than the chain end by the \(\Theta\) condition. Therefore, it is quite clear that the major factor affecting the photosomerization behavior of azobenzene in polymer solution is the site dependency in the vicinity of the chromophore.

Since Wellnhoef et al.\(^7\) found that aPS can undergo physical gelation in several solvents, several groups have investigated this phenomenon further with a special emphasis on the mechanism and the nature of the junction points. Although the ladderlike model developed by Guenet et al.\(^8\) was supported by several experimental evidences, a recent NMR study\(^9\) made this model questionable. They could not observe any evidence for rigid or even anisotropically mobile solvent molecules. Even though this result was obtained from isotactic PS system, it may be applied to atactic PS system since the mechanism of gelation is quite similar. They proposed a model that both chain ends of the polymer are fixed in junction points while the rest of the chains remain in solution.

Therefore, a change of the chain mobility at specific sites due to sol-gel transition may provide a clue to understanding a real mechanism.

The gel temperatures of aPS / toluene and aPS / THF systems were -50°C and -70°C, respectively. Before the measurement of physical gelation, photosomerization reactions of dilute solutions were studied as a function of temperature. Although free probe didn't show any difficulty up to -60°C, three labeled PS showed significant retardation at lower temperatures. It was found that the CPS experienced most difficulty, followed by the EPS and the THF. This result could be due to the increase in segmental density caused by chain contraction and/or the greatest activation energy for photosomerization reaction in the CPS. In concentrated solutions, fast and slow processes of the chain mobility in photosomerization up to -60°C either in toluene or in THF. The chain mobility of the SPS decreases gradually with decreasing temperature in both solutions with little difference. However, it didn't show any significant change around the gel temperature of the aPS / toluene system.

In the case of the CPS, the fast fraction, \(a\), showed a significant change when approaching the gel temperature as shown in Figure 5. This trend was observed also in the EPS case, but with a lesser extent. In other words, the chain mobilities of the chain center and the chain end were influenced by the gelation process while the side chain and the free probe exhibited little change.

Effects of concentration and temperature on the chain mobility were characterized by the measurement of macroscopic viscosity to see how the chain mobility at specific sites is influenced. Free probe showed little retardation in a wide range of viscosity. In other cases, chain mobility decreased gradually with increasing viscosity except the region of...
the temperature effect in dilute solutions. The chain mobility of the CPS was significantly reduced with a little change in macroscopic viscosity as shown in Figure 6. This trend was observed in other cases except the free probe.

REFERENCES