

Quantitative Description of Aggregation and Dissociation of Polystyrene Chains in Cyclohexane Solutions by Resonance Light Scattering Technique

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The resonance light scattering (RLS) technique based on a conventional fluorescence spectrophotometer was used to quantitatively describe the aggregation and dissociation of polystyrene (PS) in cyclohexane solution during cyclic heating and cooling. Transitions in conformation of PS molecules and aggregation of PS chains in the course of phase separation were revealed. The results indicated that PS chains changed from random coils to collapsed globules and then aggregated when temperature decreased. In contrast, when the system is heated, the chain aggregates were initially swelled and followed by gradual dissociation. Subsequently, the conformation of PS chains returned to the original state. Kinetics of phase separation of the PS solution was analyzed, which allowed estimation of the apparent activation energy.

Introduction

In a polymer solution, when temperature is lower than its upper θ -temperature (or exceeds the lower θ -temperature), intramolecular interactions become more prominent, leading to contraction of the polymer coils.¹ Similarly, conformation of a flexible polymer chain in poor solvent would transform from random coil to collapsed globule at the θ -temperature.² With further decreasing or increasing temperature, polymer chains form compact globules and aggregates, and phase separation occurs. So far, collapse of a single polymer chain, or coil-to-globule phase transition, has been investigated, both theoretically and experimentally.³ However, few attempts have been made to study kinetics of aggregation and dissociation processes and phase separation of dilute polymer solution during cyclic heating and cooling. Considering that the investigation in this aspect would provide useful information about intermolecular interactions of polymer chains, the temperature dependence of conformation of polystyrene (PS) in cyclohexane solution was studied in this work.

It is well-known that PS/cyclohexane solution possesses the upper critical solution temperature (UCST), which is soluble at elevated temperatures, but cooling below the critical temperature would result in phase separation (i.e., aggregation of macromolecular chains in solution). A series of techniques have been applied to study phase separation of PS/cyclohexane solution, such as differential scanning calorimetry (DSC),⁴ capillary viscometer,^{5–7} thermo-optical analysis (TOA),⁸ differential refractometer,⁹ laser light scattering,^{10–14} small-angle X-ray scattering,¹⁵ and small-angle neutron scattering.^{16,17} In general, thermal analyses represented by DSC are able to measure the amount of the heat absorbed in the whole sample during phase transition but can not provide the information about molecular aggregation. Although the structural variation on a molecular scale can be monitored by laser light scattering and small-angle X-ray or neutron scattering, expensive equipment and complicated testing processes are needed.

Recently, resonance light scattering (RLS) has been the focus of many studies owing to its high sensitivity, convenience in performance, simplicity, and rapidity. We have shown that RLS is a promising technique to follow temperature-induced phase transition^{18,19} and macromolecular aggregation.²⁰ In addition, it helps to reveal the interactions between biopolymers and their probes.²¹ RLS spectra are collected by simultaneously scanning the excitation and emission monochromators of a conventional spectrofluorimeter with $\Delta\lambda = 0$ nm.^{22,23} According to the literature,²⁴ the scattering acquired with the same procedure as that of RLS in this study is ascribed to elastic light scattering, which is able to describe the aggregation process in polymer solution in terms of a single parameter: RLS intensity (I_{RLS}), which is factually an index of the degree of aggregation. Accordingly, I_{RLS} can be correlated to the changes in macromolecular phase behavior.

In the present work, RLS is employed to investigate the transition of molecular conformation and aggregation of macromolecular chains during the phase separation process in PS/cyclohexane solution. Since RLS can provide morphological information about the aggregates' size and shape,^{25–27} a quantitative characterization of the aggregation and dissociation of macromolecular chains during one heating and cooling cycle is conducted by monitoring the change in geometric size of aggregates from the RLS intensity variances.

Experimental Section

Materials and Sample Preparation. Atactic PS (general purpose grade PG-33) from Chi Mei Co. Ltd. (Taiwan) was purified by precipitating the toluene solution into methanol three times. Its average molecular weight characterized by gel permeation chromatography (GPC) is 267 900 g/mol (M_w) and 90 400 g/mol (M_n), respectively. Cyclohexane (analytical reagent) purchased from Guangzhou Chemical Reagent Factory (China) was used as supplied without additional purification. The standard solutions of different concentrations (0.05, 0.07, and 0.10 w/v %) were prepared in series by dissolving a definite quantity of PS in a 10 mL volumetric flask filled with cyclohexane. Prior to the experiments, PS/cyclohexane solutions were incubated for one day above the UCST for equilibration.

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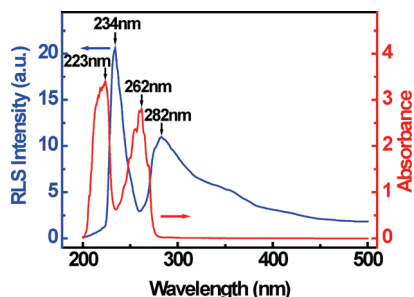


Figure 1. RLS and absorption spectra of PS/cyclohexane solution ($C = 0.05$ w/v %) at 34.5 °C.

Apparatus. RLS measurements were performed on a Cary Eclipse fluorescence spectrophotometer (Varian, Inc., America) equipped with a Xenon flash lamp, R928 photomultiplier detector, dual monochromators, and a single-cell Peltier holder. The latter is an electronically controlled thermostating single cell accessory capable of controlling temperature within ± 0.1 °C. By using this unit, variable-temperature measurements within 0–100 °C were carried out. RLS spectra were recorded from 260 to 700 nm with synchronous scanning at $\lambda_{\text{ex}} = \lambda_{\text{em}}$ (i.e., $\Delta\lambda = 0$ nm). The RLS spectra given in the context are the spectra after correction.

UV–vis absorption spectra of PS/cyclohexane solutions were collected by a UV-3150 spectrophotometer (Shimadzu Corporation, Japan). The slit width was 1 nm during the measurements.

Fluorescence spectra of PS/cyclohexane solutions were recorded with the aforesaid fluorescence spectrophotometer using 262 nm as the excitation wavelength. The slit (ex/em) width of the measurements was 1.5 nm/2.5 nm.

Procedures. The sample solution was put into the single-cell Peltier holder where the temperature was set at 34.5 °C. After 20 min, resonance light scattering spectra were measured by synchronous scanning at $\Delta\lambda = 0$ nm. Then, the sample was cooled from 34.5 to 8 °C at a cooling rate of 0.5 °C/min, in which there was a time interval of 10 s for each decrease of 0.5 °C. The subsequent heating was also conducted at a rate of 0.5 °C/min. The slit (ex/em) width of the measurements was 1.5 nm/2.5 nm.

Results and Discussion

RLS and Absorption Spectra of PS/Cyclohexane Solution.

Figure 1 shows RLS and absorption spectra of PS/cyclohexane solution ($C = 0.05$ w/v %) at 34.5 °C. It can be seen that PS exhibits two absorption peaks at 223 and 262 nm, and the absorbance approaches zero in the range over 279 nm. Moreover, the absorption peak at 223 nm is stronger than that at 262 nm, and the absorbance sharply decreases from 262 to 279 nm. Likewise, the PS/cyclohexane solution shows two scattering peaks, a strong one at 234 nm and a weak one at 282 nm.

It is found that the two scattering peaks are all located at the red side of the absorption peaks where the absorbance is weak, manifesting that the enhanced scattering peaks appear within the absorption band. In this context, we can deduce that these peaks are RLS peaks.²⁴ In the following, only the changes in the strong RLS peak (at 234 nm) during phase separation are of interest.

Temperature Dependence of RLS Spectra of PS/Cyclohexane Solution. It is known that the aggregation state of molecular chains in polymer solutions changes with their concentrations. According to the characteristics of segment density,²⁸ polymer solutions can be classified into three categories: dilute, semidilute, and concentrated. For the transitions from

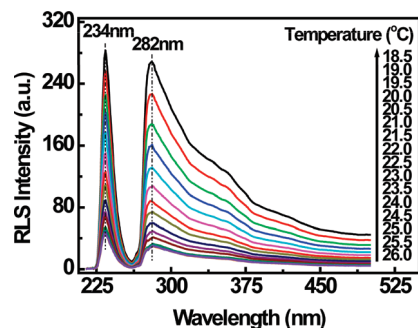


Figure 2. RLS spectra of PS/cyclohexane solution ($C = 0.10$ w/v %) recorded during cooling.

dilute to semidilute to concentrated regimes, there exist two critical concentrations, denoted as C^* and C^+ , respectively. At very low concentration ($C < C^*$), polymer chains exist as isolated coils that are far apart, and intermolecular interaction is very weak. Thereinto, the critical concentration C^* is called overlap concentration. With a rise in concentration ($C > C^*$), in semidilute solution, linear chains begin to overlap and interpenetrate each other. The overlap concentration C^* in a θ -solvent is given by $C^* \approx \rho N^{-1/2} \times 100\%$,²⁹ where ρ is the density of the polymer and N is the degree of polymerization. In this work, C^* of PS/cyclohexane solution at 34.5 °C is 1.9 w/v %. At the θ -temperature, polymer chains have nearly ideal conformations. PS in cyclohexane at about 34.5 °C is a polymer–solvent pair at the θ -temperature.²⁹ Herein, we only investigate the aggregation and dissociation process of PS macromolecular chains in the dilute solution during one heating and cooling cycle; i.e., the concentration of PS/cyclohexane solution is lower than the overlap concentration C^* (1.9 w/v %).

Figure 2 shows RLS spectra of PS/cyclohexane solution ($C = 0.10$ w/v %) recorded during cooling. There are two scattering peaks on the curves at 234 and 282 nm, respectively. Their intensities increase with decreasing temperature, and the maximum scattering wavelength (λ_{max}) appears at 234 nm. The increase in I_{RLS} results from the fact that the segment–segment attractions begin to gradually dominate the segment–solvent attractions, and the polymer phase separates to form aggregates during cooling.^{10,30} In this process, interaction between aromatic rings and solvent is weakened, and the π – π conjugation interaction between aromatic rings of PS becomes stronger.³¹ Finally, the aromatic rings closely stack, forming microsegregating or interlocking structure.³² This change of the interaction between aromatic rings and solvent results in the aggregation of PS chains. Considering the sensitivity of detection, the maximum scattering wavelength at 234 nm is selected for the subsequent work.³³

To highlight the phase separation behavior, temperature dependences of the normalized RLS intensities (at the maximum scattering wavelength of 234 nm) of PS/cyclohexane solutions are plotted in Figure 3. With increasing PS concentration, I_N is greatly enhanced due to the rise in molecular number of PS per unit volume. Accordingly, the onset temperatures of phase separation, T_p , can be determined at 22.3, 23.2, and 23.8 °C, respectively. They well agree with those reported in the literature.^{8,34–36} It can be seen from Figure 3 that T_p increases with a rise in solution concentration. This can be attributed to the increase of probability of diffusion and collision of molecular chains under high concentration. As a result of the increased molecular number of PS per unit volume, aggregation of PS chains is favored at higher temperature.

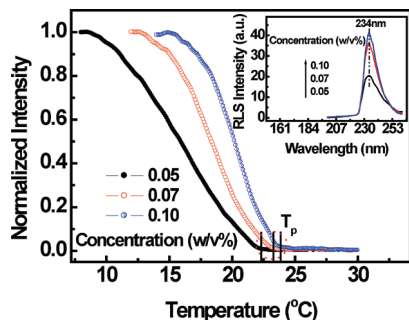


Figure 3. Temperature dependences of normalized RLS intensities (at the maximum scattering wavelength of 234 nm) of PS/cyclohexane solutions during cooling. The normalized intensity, I_N , is obtained from $I_N = (I - I_{\min}) / (I_{\max} - I_{\min})$, where I_{\min} and I_{\max} are the minimum and maximum values of RLS intensities at 234 nm. The inset gives the RLS spectra of PS/cyclohexane solutions at 34.5 °C.

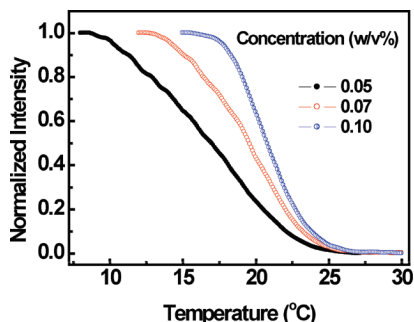


Figure 4. Plots of the normalized intensities of RLS (at 234 nm) of PS/cyclohexane solutions against temperature during heating.

Moreover, we can see that I_N is almost constant at the initial stage of cooling and then presents a sharp increase in the lower-temperature regime, corresponding to a drastic change in polymer concentration in the polymer-rich phase by the aggregation process of chains.³⁷ The transition of conformation and the aggregation of chains of PS make the I_{234} begin to gradually increase, which can be considered as the signal of the onset of phase separation. Subsequently, the molecular chains further aggregate, leading to the sharp increase of the aggregate size. According to the coalescence-induced coalescence mechanism of phase separation,^{38–40} any process of domains coalescence that induces hydrodynamic flow would push other domains toward each other and result in further coalescence events. Such a “chain-reaction process” is not self-sustained and finally stops.⁴¹ Therefore, we conclude that diffusion and aggregation of PS chains account for the drastic increase in I_{234} . Eventually, I_N reaches a plateau, suggesting that phase separation comes into the last stage. In such a manner, the normalized RLS intensity at 234 nm exhibits its feasibility in serving as an indication of phase separation extent of PS/cyclohexane solution. The higher the extent of phase separation, the stronger the RLS.

To have knowledge of dissociation of PS chains in cyclohexane, RLS spectra of the dilute solution during heating were recorded. Again, S-shaped plots of the normalized intensities of RLS (at 234 nm) against temperature are observed (Figure 4). Compared with the curves in Figure 3 that were collected during cooling, those in Figure 4 shift to a higher-temperature regime in the case of identical concentration. This should originate from the formation of interlocking structure when the aromatic rings closely stack, which is caused by the increase of the π – π conjugation interaction between the aromatic rings of PS during cooling.³² The interlocking structure can only be

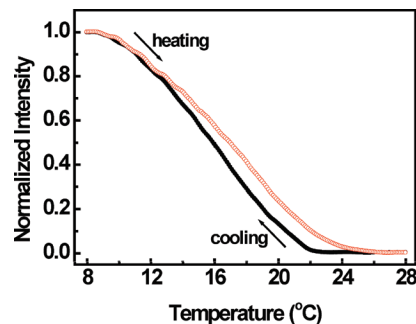


Figure 5. Temperature dependence of normalized RLS intensities (at 234 nm) of PS/cyclohexane solution ($C = 0.05$ w/v %) collected during one heating and cooling cycle.

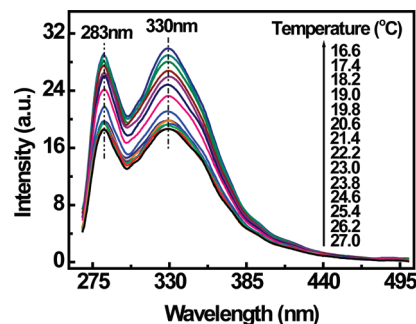


Figure 6. Fluorescence spectra of PS/cyclohexane solution ($C = 0.05$ w/v %) upon excitation at 262 nm during cooling.

gradually removed in the course of heating, leading to the shift of the curves in Figure 4 to higher temperature. In addition, the interchain entanglement within the aggregates of chains formed during cooling can also induce the shift of the inflection temperatures on the curves.

When the curves of $C = 0.05$ w/v % in Figure 3 and Figure 4 are plotted together in Figure 5, the variation in normalized RLS intensities during cyclic heating and cooling can be perceived. At the beginning of heating, no obvious hysteresis appears, when the chain aggregates are swelled and partially dissociated. Subsequently, a distinct hysteresis is observed. This may be caused by two factors: (i) establishment of π – π conjugation interaction in the aggregated state at lower temperature and (ii) the rate of disengagement of polymer chains from the swollen phase–liquid interface.^{42–44}

To confirm the above analysis and to gain an in-depth understanding of the collapse and aggregation of PS chains in the process of phase separation, fluorescence spectra of PS/cyclohexane solution were studied. In dilute solutions of vinyl polymers containing aromatic groups, an intramolecular excimer can be formed. The excimer formation occurs by the rotation of bonds to bring two adjacent chromophores into a coplanar arrangement.⁴⁵ By comparison with model bibenzyl compounds, Vala et al.⁴⁶ concluded that the PS fluorescence peak at 335 nm is due to excimer emission, while the peak at 280–285 nm is due to monomer emission.⁴⁵ Figure 6 shows the fluorescence spectra of PS/cyclohexane solution ($C = 0.05$ w/v %) during cooling upon excitation at 262 nm. Two emission peaks appear at 283 and 330 nm, respectively. The fluorescence intensities increase with decreasing temperature. For the purposes of investigation, the two peaks were used to monitor the monomer and excimer emission intensities, respectively.⁴⁷

Accordingly, the temperature dependences of fluorescence intensities at 283 and 330 nm (after peak fitting) of PS/cyclohexane solution ($C = 0.05$ w/v %) during cooling are

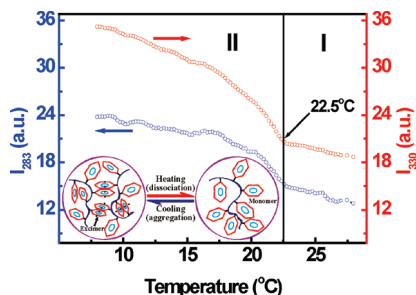


Figure 7. Temperature dependences of fluorescence intensities (at 283 and 330 nm, after peak fitting) of PS/cyclohexane solution ($C = 0.05$ w/v %) during cooling. The inset gives the schematic representation of the change in conformation of PS molecular chains in dilute cyclohexane solution during one heating and cooling cycle.

presented in Figure 7. It is seen that I_{283} and I_{330} are almost invariant at the beginning of cooling and then increase slowly and smoothly above 22.5 °C. In stage I, the increase of I_{330} is due to the fact that the number of formed excimers increases when the chains collapse and their conformation changes. The decrease in coil dimensions can affect vicinal excimer formation through changes in local conformation, which would raise I_{330} by facilitating the diffusional formation of excimer.⁴⁷ Additionally, the decrease of temperature may also induce the increase of I_{330} ,⁴⁸ as the amount of excimer formation strictly depends on a temperature region in which chromophores may possess the so-called sandwich geometry.⁴⁹

In stage II, I_{283} and I_{330} present a drastic increase when temperature is lower than 22.5 °C, and finally I_{330} increases continuously with a reduced slope, while I_{283} increases very slowly. In fact, the chains begin to aggregate in stage II, which facilitates formation of excimers. The excimer emission is a diffusion-controlled process and depends on the translational diffusion of molecules.⁵⁰ The aggregation of PS chains promotes the translational diffusion of molecules, thus increasing the amount of excimer formation. So, the increase of I_{330} is caused by the continuous diffusion and aggregation of the molecular chains. Moreover, the increase in I_{283} originates from (i) reduced probability of collisional quenching between monomer and solvent molecules as a result of the increased viscosity of medium or the change of chain conformation and the collapse and aggregation of chains⁴⁸ and (ii) weakened action of internal energy transform of molecules. In the factor (ii), the excited molecules can not receive the extra heat energy, which makes it possible that the excited energy is transformed into vibrational energy of the ground state, and the vibrational energy is lost by the vibrational relaxation.⁴⁸

Figure 7 indicates that the onset temperature of phase separation measured by the fluorescence method is about 22.5 °C, which is very close to the value (22.3 °C) determined by RLS. This demonstrates that the results obtained by RLS are accurate and reliable.

Kinetics of Phase Separation in PS/Cyclohexane Solution.

In the above sections, temperature-dependent aggregation and dissociation of PS chains in cyclohexane solutions have been clarified. However, how the aggregation of chains progresses to the final state is determined by its kinetics.⁵¹ On this basis, the dynamic process of the phase separation is inspected by investigating the time dependence of RLS intensities. It will reveal kinetics information about molecular aggregation in the solution.

To conduct the measurement, the sample cell was put into the single cell Peltier holder at a fixed temperature (19.0, 19.5,

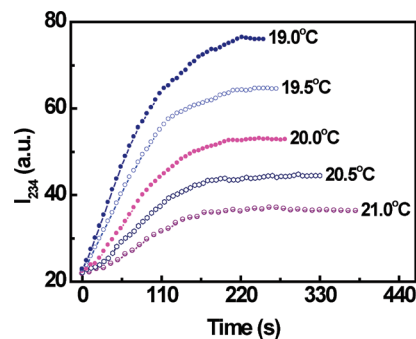


Figure 8. Time dependence of I_{234} of PS/cyclohexane solution ($C = 0.05$ w/v %) at the constant temperatures.

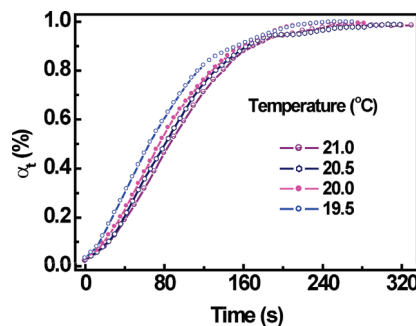


Figure 9. Time dependences of relative extent of phase separation of PS/cyclohexane solution ($C = 0.05$ w/v %) at different temperatures.

20.0, 20.5, and 21.0 °C) and kept for 15 s. Afterward, RLS spectra of PS/cyclohexane solution ($C = 0.05$ w/v %) were measured. Figure 8 shows the time dependence of I_{234} of the solution at constant temperatures. All the time dependences of I_{234} have a similar profile. With a drop in temperature, the curve slope gradually increases due to a rise in the rate of phase separation. In such a case, the rates of diffusion and aggregation of molecular chains are enhanced at lower temperature, so that phase separation is accelerated.

Hereinafter, the relative extent of phase separation at a constant temperature is calculated⁵² to perform a quantitative analysis of the dynamics of this system.

$$\alpha_t = (R_t - R_0)/(R_\infty - R_0) \quad (1)$$

where α_t is the relative extent of phase separation at time t ; R_0 and R_t are relative RLS intensities at time 0 and t , respectively; and R_∞ is the maximum relative intensity during the phase separation. The relative intensity is calculated from $R = I_t/I_\infty$, where I_t and I_∞ are RLS intensities at 234 nm for PS/cyclohexane solution in which the phase separation is performed at time t and ∞ , respectively. I_t/I_∞ of the samples with the same degree of phase separation are identical, regardless of the ways of formation of phase separation.

By means of eq 1 and the experimental data in Figure 8, time dependences of the relative extent of phase separation of PS/cyclohexane solution are yielded (Figure 9). It is known that the common approach for describing the isothermal crystallization kinetics is the Avrami model.⁵³ When the relative crystallinity in the Avrami equation is replaced by the relative extent of phase separation at time t , the kinetics of phase separation would be depicted^{54,55}

$$\ln[-\ln(1 - \alpha_t)] = \ln k_p + n \ln t \quad (2)$$

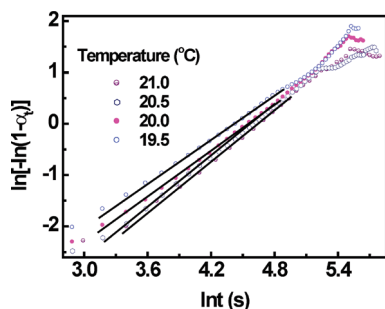


Figure 10. Avrami plots of isothermally phase-separated PS/cyclohexane solution ($C = 0.05$ w/v %) measured by the RLS method.

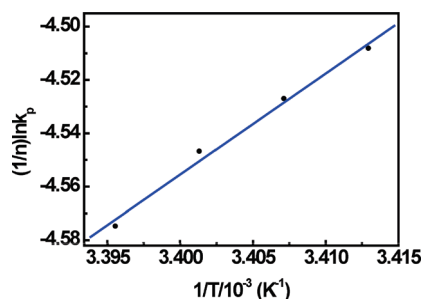


Figure 11. Plot of $(1/n)\ln k_p$ of PS/cyclohexane solution ($C = 0.05$ w/v %) against the reciprocal temperature.

where k_p and n are rate constant and the Avrami exponent, respectively. Both k_p and n can be obtained from the linear regression curve of $\ln[-\ln(1 - \alpha_t)] \sim \ln t$.

According to refs 4, 8, 35, 36, and 56, the upper temperature limit of the metastable region of PS/cyclohexane solution is about 22 °C, and the lower limit is lower than 19 °C. It implies that phase separation of PS/cyclohexane solution ($C = 0.05$ w/v %) under different testing temperatures (19.5, 20.0, 20.5, and 21.0 °C) occurs in the metastable region of the phase diagram, the region between binodal and spinodal curves. Therefore, the mechanism of nucleation and growth should take the responsibility. During the phase separation, chain–chain aggregation starts in the course of the knotting process of the individual chains and is accompanied by the formation of interchain entanglements.³ In this process, chain aggregates are formed, and the individual chains further collapse by intrachain knotting.³ Figure 10 shows the Avrami plots of isothermally phase-separated PS/cyclohexane solution ($C = 0.05$ w/v %) at different temperatures measured by RLS. The plots are able to distinguish the primary phase separation from the late stage of phase separation. That is, the phase separation at the linear portion represents the primary phase separation, while the late stage of phase separation occurs at the nonlinear portion. As only the kinetics of the primary phase separation is focused, the best-fit lines are drawn except the initial points in phase separation and the points (deviating from the linearity) of the late stage as well.

Figure 11 presents the plot of $(1/n)\ln k_p$ of PS/cyclohexane solution ($C = 0.05$ w/v %) against the reciprocal temperature. According to the equation $k_p^{1/n} = A \exp(-E_a/R'T)$,⁵⁷ where A refers to the preexponential factor related to collision frequency of molecules, R' is the universal gas constant, and T is the temperature, the apparent activation energy of phase separation can be obtained from the slope of the straight line in the chart. Meanwhile, the preexponential factor is calculated from the intercept. Table 1 lists all the kinetic parameters of phase separation of this solution together with the effective collision fraction, Q .⁵⁸ $Q = \exp(-E_a/R'T)$ and is correlated with k_p through $k_p^{1/n} = AQ$. It is seen that the values of Q and k_p increase

TABLE 1: Kinetics Parameters of Phase Separation in PS/Cyclohexane Solution Determined by RLS

C (w/v %)	T (°C)	k_p (s ⁻ⁿ)	n	A (s ⁻¹)	Q	E_a (kJ/mol)
0.05	19.5	1.72×10^{-3}	1.41	2.67×10^{-8}	4.22×10^5	-31.5
	20.0	1.16×10^{-3}	1.49		4.13×10^5	
	20.5	4.94×10^{-4}	1.67		4.04×10^5	
	21.0	4.39×10^{-4}	1.69		3.95×10^5	

with decreasing temperature. However, n decreases with decreasing temperature. So, it may be concluded that Q plays an important role in the increase of k_p when the system stays at lower temperature.

Conclusions

In this work, the RLS technique was used to quantitatively characterize the aggregation and dissociation of PS chains in cyclohexane solutions. The onset temperature of phase separation of PS/cyclohexane solution was identified, and its apparent activation energy was evaluated by kinetics analysis. In addition, both fluorescence and RLS spectra provided information about aggregation and dissociation of PS chains in dilute cyclohexane solution (refer to the inset of Figure 7).

It was found that cooling resulted in coil-to-globule transition and aggregation of PS chains. When the solution was cooled below the UCST, PS chains underwent interchain association/entanglement, forming large and dense aggregates.⁵⁹ The amount of excimer formation because of the aggregation of chains increased.

On the other hand, heating led to swelling and dissociation of the aggregates. At the initial stage of heating, the chain aggregates were swelled and began to dissociate. Subsequently, distinct hysteresis occurred, which can be explained by the fact that the strong π – π conjugation interaction between aromatic rings of PS formed in the aggregated state and the rate at which the polymer chains disengaged themselves from the swollen phase–liquid interface affected the dissolution rate. As the solution temperature was further increased, the aggregated chains were dissociated, and the hysteresis gradually disappeared. The amount of excimer formation because of dissolution of chains decreased. Eventually, the conformation of PS chains returned to the original state at higher temperature.

Owing to the convenience in performance and rapidity of the RLS technique based on a conventional fluorescence spectrophotometer, it might be widely applied to the study of phase separation in polymer solutions or polymer blends.

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