

Sol-Gel Transition of PBLG Solutions Observed by Dynamic Light Scattering

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Thermoreversible sol-gel transition of PBLG-toluene solution, which concentration was in the vicinity of the critical crossover concentration, has been investigated by dynamic light scattering. The obtained intensity time correlation functions were converted into the distribution functions of correlation time τ by means of CONTIN software. The τ -distribution above gel threshold temperature T_{gel} exhibited the characteristic bimodal peaks, *i.e.*, the fast and the slow modes. From the scattering vector dependence, both the modes were found to be a diffusion mode, and were assigned to the relaxation of concentration fluctuation without and with the changes of alignment, respectively. The much broad τ -distribution at T_{gel} was shown over five to six decades. With further decreasing temperature, the slow mode disappeared thoroughly below T_{gel} , and then the only single decay mode, which τ -value was nearly the same as that of the fast mode, still remained. In addition, the dynamics on sol-gel transition was discussed.

Key words: lyotropic liquid crystal polymer, poly(γ -benzyl- α , L-glutamate), sol-gel transition, dynamic light scattering, correlation time

1. INTRODUCTION

Poly(γ -benzyl- α , L-glutamate) (PBLG) is a typical lyotropic liquid crystal polymer (LCP) [1], whose properties are closely associated with the rigidity and rod-like α -helical conformation along PBLG chain dissolved in some helicogenic solvents such as dimethylformamide (DMF), toluene, benzene, benzyl alcohol etc. As predicted theoretically by the Flory's lattice model [2], the thermodynamic phase diagram of a lyotropic LCP displays the characteristic chimney structure, and is usually divided into three regions: isotropic (I) phase, liquid crystal (LC) phase, and the mixed or coexistence region of isotropic and liquid crystal (I + LC) phase, so-called biphasic phase, over a wide concentration range at relatively low temperature. These general features were found experimentally, *e.g.*, in PBLG-DMF solution [1-3], but actual behaviors seem to be much more complex as discussed later [1,3]. In fact, a number of thermodynamic and hydrodynamic properties of PBLG solutions in the (I) phase have been extensively investigated so far [1-3]. In addition, some applications by mainly utilizing the (LC) phase have been recently reported for nonlinear optical devices and functional gels [4-6].

On the other hand, PBLG solutions lose their fluidity and apparently gel, when cooled or quenched from the (I) phase to the (I + LC) phase [1,7]. Thermoreversible gelation of rod-like polymers such as PBLG is said to occur by the competitive process between connectivity of rod-to-rod interactions and liquid-to-liquid phase separation, and to be one of the most poorly understood aspects in polymer science [7]. The gelation process is affected significantly by temperature, thermal history, average molecular weight, concentration, and so on. We

have already measured the intensity time correlation function $g^{(2)}(\tau)$ of scattered light fluctuation, where τ is correlation time, for highly concentrated PBLG-toluene solution, but being still in a semi-dilute regime, using dynamic light scattering (DLS) technique [8]. All the decay curves of $g^{(2)}(\tau)$ was double-exponential above gelation threshold temperature T_{gel} , *i.e.*, the fast and the slow modes. The decay constants of the fast mode were proportional to q^2 with a downward curvature, where q is scattering vector. This mode was attributed to the cooperative diffusive mode, due to entanglement effect and hydrodynamic excluded volume interactions in a transient PBLG network [9]. On the contrary, it was likely that the slow mode was a relaxation mode [10], because of less dependence on q^2 . In addition, $g^{(2)}(\tau)$ could not be detected below T_{gel} , which described that PBLG gel structure was so rigid that the concentration fluctuation was almost frozen [11].

In the present article, our attention was focused mainly on $g^{(2)}(\tau)$ and its τ -distribution for PBLG-toluene solution in the vicinity of the critical crossover concentration to understand further thermoreversible gelation process of rod-like polymers, and the dynamics of sol-gel transition will be discussed in detail. This is not only of scientific interest but also a matter of practical significance to fabricate polymer thin films for porous membrane filters [7].

2. EXPERIMENTAL SECTION

2.1 Material and Sample Preparation

PBLG used in the present was purchased from Sigma Co., Ltd. The weight-average molecular weight M_w is 1.0×10^5 , which value was determined using low-angle laser light scattering instrument, and the

polydispersity, *i.e.*, the distribution of molecular weight, was evaluated to be less than *ca.* 2.0 from the measurement with GPC. A given amount of PBLG was dissolved completely in toluene at 353 K, cooled slowly at the rate of *ca.* 0.5 deg/min, and then kept in the equilibrium state at a given temperature for more than 24 hours before DLS measurements. Dust-free toluene was prepared previously using a 0.2 μm Millipore filter (25HP020AN). All operations were carried out in a clean bench to avoid dust in the air. According to Doi and Edwards discussion on a semi-dilute region of stiff rod-like polymer solution [12], the critical crossover volume fraction of polymer ϕ_2^* is approximately given by $\phi_2^* = (\pi/4) (d/L)^2 = 1.48 \times 10^{-3}$ with a contour length $L (= 70 \text{ nm})$ and a diameter $d (= 1.6 \text{ nm})$ in the present case. The volume fraction ϕ_2 of PBLG-toluene solution prepared was 7.0×10^{-3} in the vicinity of ϕ_2^* .

2.2 DLS measurements and Analysis

The DLS instrument used was ALV-5000 Spectrogoniometer system of homodyne spectroscopy (ALV, Langen, Germany), and the incident laser light was vertically polarized He-Ne laser (20 mW, $\lambda = 632.8 \text{ nm}$). The temperature inside the sample cell housing was maintained to be within ± 0.1 deg in the range of 300 K to 320 K, and scattering angles θ were varied from 30° to 120° . Although the present PBLG sample was optically clear at T_{gel} or below, the sample holder was rotated at random amount more than 50 runs to make sure of overcoming non-ergodic problem and to obtain the ensemble-average $g^{(2)}(\tau)$ [13]. The τ -distribution was estimated from the measured $g^{(2)}(\tau)$ in terms of the constrained regularization method [14] (CONTIN software) provided by ALV. To smooth the decay curve of $g^{(2)}(\tau)$ over a wide range of τ , the solutions generated by CONTIN were chosen with the Fisher static F-test under the assumption that the factor of the regularization term was 0.5, which is considered generally to be the best compromise between too little regularization and too strong biasing due to the regularizer [14].

3. RESULTS AND DISCUSSION

Fig. 1 indicates the typical decay curves of $g^{(2)}(\tau)$ measured at $\theta = 60^\circ$ through the sol-gel transition of PBLG-toluene. $T_{\text{gel}} = 308.6 \text{ K}$ was determined by the upside-down method [8]. The initial amplitude, which corresponds to the so-called β -value in the Siegert relation [14], decreased sigmoidally before and after T_{gel} . There was no decaying portion in $g^{(2)}(\tau)$ measured below 300 K. In addition, $g^{(2)}(\tau)$ at T_{gel} did not satisfy the power-law decay function [15]. It was reported that $g^{(2)}(\tau)$ for the similar PBLG ($M_w = 9.1 \times 10^4$)-toluene solution ($\phi_2 = \text{ca. } 4.0 \times 10^{-3}$) nearly obeyed the power-law type decay with ripples over about five decades at T_{gel} on the "melting" process, but the power-law type decay was not seen at T_{gel} on the "cooling" process [7], likewise the present case. Two reasons were mainly speculated: (1) a temperature step that was too large around T_{gel} , and (2) kinetic (or supercooling) effect in spite of more than 24 hours waited before DLS measurements. In fact, the non

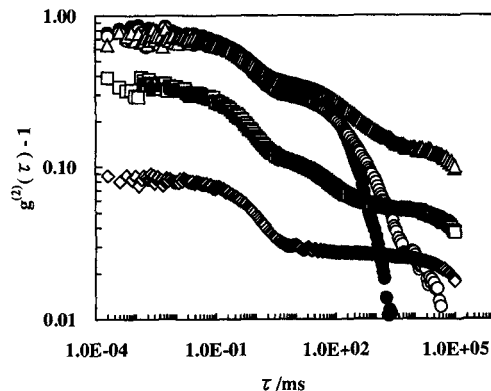


Fig. 1 Intensity time correlation functions $g^{(2)}(\tau) - 1$ measured at scattering angle $\theta = 60^\circ$: ●, 313.6 K; ○, 310.8 K; △, 310.1 K; □, 308.6 K; ◇, 303.5 K. τ indicates the correlation time.

power-law type decay of $g^{(2)}(\tau)$ was also found in the case of poly(*N*-isopropylacryamide) chemically crosslinked by redox polymerization from a monomer solution [16]. The complex competitive process between connectivity of PBLG chains and phase separations on thermoreversible gelation is probably responsible for the non power-law type decay of $g^{(2)}(\tau)$ measured at T_{gel} in the present study.

Anyway, it should be emphasized that the decay curves of $g^{(2)}(\tau)$ became obviously non-exponential in any case as shown in Fig. 1. So, it would be more convenient and advantageous to evaluate directly the τ -distribution, since there was no arbitrary room to choose and fit a suitable decay function among some theoretically proposed functions to the measured $g^{(2)}(\tau)$. The τ -distribution was evaluated successfully at each temperature as shown in Fig. 2, which was displayed by the equal-area representation plots of $\tau A(\tau)$ vs. $\log \tau$, where $A(\tau)$ is the distribution function of τ [14]. The two decay modes appeared clearly above T_{gel} , *i.e.*, the fast and the slow modes: τ_{Fast} was *ca.* 1.0 ms, whereas τ_{Slow} was nearly 150 ms. In the previous sample of highly concentrated PBLG-toluene solution ($\phi_2 = 3.6 \times 10^{-2}$) [8], the value of τ_{Fast} was *ca.* 10 ms and obviously longer than the present τ_{Fast} . On the other hand, τ_{Slow} was not so influenced by changing concentration, and the previous

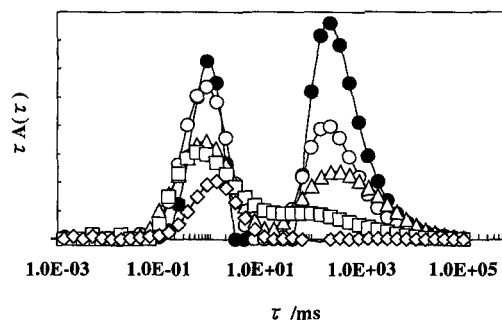


Fig. 2 Distribution functions of correlation time $A(\tau)$, which were evaluated from $g^{(2)}(\tau)$ using CONTIN and were displayed by the equal-area representation plots of $\tau A(\tau)$ vs. τ . Symbols as in Fig. 1.

τ_{Slow} value was roughly 200 ms. The τ -distribution near T_{gel} became broad remarkably over five to six decades. With further decreasing temperature, the slow mode disappeared evidently below T_{gel} , and the single decay mode, *i.e.*, gel mode, was only observed at *ca.* $\tau = 1.0$ ms, which value was almost the same as that of the present fast mode.

Let us further consider the assignment of the fast and the slow modes above T_{gel} . Fig. 3 indicates the plots of the decay constants, $\Gamma_{\text{Fast}} (= \tau_{\text{Fast}}^{-1})$ and $\Gamma_{\text{Slow}} (= \tau_{\text{Slow}}^{-1})$, vs. q^2 at various temperatures. In any case, the straight lines through the original point could be drawn well by the least-squares method within the experimental error, which implies that both the modes were confirmed to be a diffusion mode, not being a relaxation mode [10]. This fact was distinctly different from the dependence of Γ_{Fast} and Γ_{Slow} on q^2 in the previous case of highly concentrated PBLG-toluene solution as described in INTRODUCTION [8]. So far, the fast and the slow modes were investigated extensively in PBLG-DMF solution [1-3], in comparison with the so-called DSO theory [17]. In the original DSO theory [9,18,19], the ratio of $\Gamma_{\text{Fast}}/\Gamma_{\text{Slow}}$ and the amplitude ratio of the fast and the slow modes $A_{\text{Fast}}/A_{\text{Slow}}$ increase rapidly with concentration up to the critical concentration v^* at which the (I) phase becomes thermodynamically unstable and turns into the (LC) phase [3,17]. Instead of increasing concentration, the sol-gel transition with decreasing temperature may also induce and enhance markedly nematic-like interactions between PBLG chains [1]. Thus, as a first approximation, the lowering of temperature would be equivalent

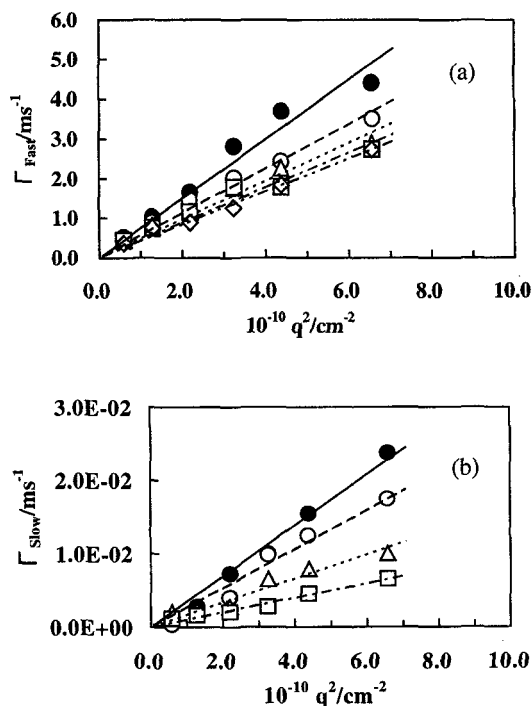


Fig. 3 Dependence of decay constants Γ on square of scattering vector q^2 : (a), Γ_{Fast} for the fast mode, and (b), Γ_{Slow} for the slow mode. Symbols as in Fig. 1.

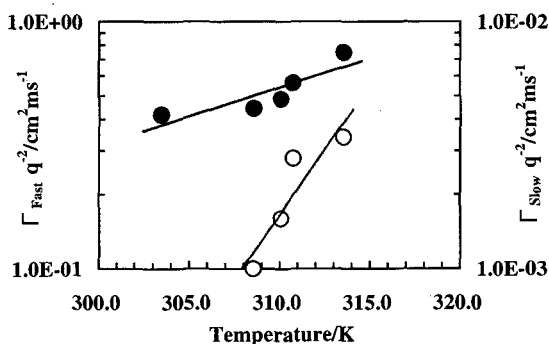


Fig. 4 Plots of diffusion coefficients vs. temperature: ●, Γ_{Fast}/q^2 for the fast mode; ○, Γ_{Slow}/q^2 for the slow mode.

phenomenologically to the increase in concentration in the (I) phase from the viewpoint of an isotropic-to-nematic transition. Fig. 4 suggests that the ratio of $\Gamma_{\text{Fast}}/\Gamma_{\text{Slow}}$ at a given q would be enlarged monotonically with a decrease in the temperature, except at the gel state. In addition, A_{Fast} also exceeded A_{Slow} as shown in Fig. 2. On the assumption that the above-mentioned approximation may be reasonable, the fast and the slow modes are considered to be assigned to the relaxation of concentration fluctuation without and with the changes of alignment by reference to the DSO theory, respectively [17,19].

From Fig. 4, the following relations were empirically derived:

$$\Gamma_{\text{Fast}}/q^2 \approx \xi_{\text{Fast}}^{-1} \approx \epsilon^{0.37} \quad (1)$$

$$\Gamma_{\text{Slow}}/q^2 \approx \xi_{\text{Slow}}^{-1} \approx \epsilon^{0.60} \quad (2)$$

Where, ξ is the hydrodynamic correlation length calculated from the diffusive constant Γ/q^2 using Einstein-Stokes' equation [10], and ϵ indicates the reduced temperature normalized by T_{gel} : $\epsilon = |T - T_{\text{gel}}| / T_{\text{gel}}$.

As shown in Fig. 5, ξ_{Fast} , which may reflect a local concentration fluctuation without changes of alignment, did not so much vary with the sol-gel transition (*ca.* 75 nm to *ca.* 97 nm), relative to ξ_{Slow} based upon long range of concentration fluctuation with changes of alignment.

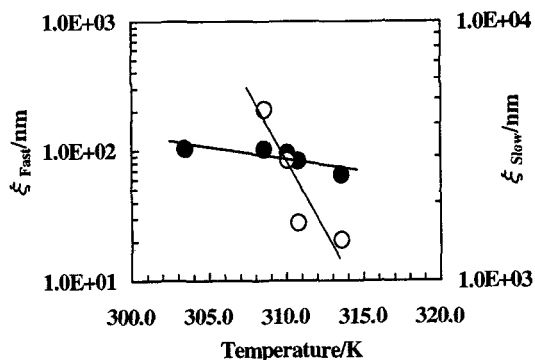


Fig. 5 Relationship between dynamic correlation length ξ and temperatures: ●, ξ_{Fast} for the fast mode; ○, ξ_{Slow} for the slow mode.

As the temperature approached T_{gel} , ξ_{Slow} was multiplied and became of order of about several micro-meter (ca. 1.3 μm to ca. 4.75 μm). In a word, the behavior of the slow mode is said to be essentially important and correlated with thermoreversible gelation process. The disappearance of the slow mode at T_{gel} , which may be attributable to convergence of either Γ_{Slow} or A_{Slow} to zero, suggests clearly the divergence of ξ_{Slow} and/or the freezing of concentration fluctuation with ξ_{Slow} . The value of ξ_{Slow} may give a mesh size or a porous size in PBLG gel structure [11]. However, the present thermoreversible gel structure of PBLG formed was not likely so rigid, in comparison with the previous PBLG gel sample, because the concentration still fluctuated locally below T_{gel} as shown in Fig. 2, even when the slow mode disappeared.

Now, the reduced conversion factor ϵ_0 in the sol-gel transition is expressed by $\epsilon_0 = |p - p_c|/p_c$, where p is the conversion factor, and p_c is the critical p at gelation threshold. Thus, an infinite cluster of pre-gel starts to appear at p_c . The correlation length is proportional theoretically to ϵ_0 to the power of the critical exponent ν [20]:

$$\xi \approx \epsilon_0^{-\nu} \quad (3)$$

When ϵ in Eqs. (1) and (2) is assumed to be analogous to ϵ_0 in Eq. (3), the exponent in Eq. (2) is numerically close to 0.63 proposed by the correlated percolation model based upon three-dimensional Ising-magnet (or lattice-gas model) theory in thermal phase transition [20], rather than three-dimensional random bond percolation model ($\nu = 0.88$) and classical mean field theory ($\nu = 0.5$) [20]. The value of p in the correlated percolation model is necessarily dependent on two real variables: "temperature" and "concentration" in a thermoreversible gelation. The monomer units for connectivity between rod-like polymer chains, which are distributed in the thermal equilibrium, may interact *via* an attractive nearest-neighbor force. This connectivity may induce the alignments of rod-like polymers and is also responsible for the onset of liquid-to-liquid phase separation on gelation process [21]. Alternatively, the connectivity between rod-like polymer chains through the sol-gel transition is similar to a kind of order-disorder transition, which exists between liquid phases [7]. Probably, these may predominantly specify the behavior of the slow mode. Recently, the related theories try to deal with the connectivity and the kinetic effect on thermoreversible gelation [22,23].

As described previously, T_{gel} was determined macroscopically by the upside-down method [8], since the obtained $g^{(2)}(\tau)$ did not all obey the power-law decay function [15]. T_{gel} evaluated microscopically by means of the light scattering techniques and the thermal analysis is often higher than the macroscopic T_{gel} to some extent [20]. In the present study, if the microscopic T_{gel} is assumed to be the temperature at which the β -value of $g^{(2)}(\tau)$ started to decrease with lowering temperature, the microscopic T_{gel} is ca. 1.5 degrees higher than the present $T_{gel} = 308.6$ K, and then the

exponents in Eqs. (1) and (2) are at most about 5 % lower than the present values. It follows that the above-mentioned discussion on the exponent for the slow mode may be qualitatively valid.

4. CONCLUDING REMARKS

The sol-gel transition of PBLG-toluene solution in the vicinity of ϕ_2^* has been investigated from the τ -distribution, which was the bimodal one above T_{gel} : the fast and the slow modes. These two modes were found to be a diffusion mode from their q -dependence, and were assigned in accordance to the DSO theory. The fast mode induced by a local concentration fluctuation was not so changed with the sol-gel transition. The τ -distribution at T_{gel} became much broad over five to six decades, and then the slow mode based upon the relaxation of concentration fluctuation with the changes of alignment disappeared below T_{gel} . Especially, it seems likely that the present slow mode at T_{gel} was not the relaxation mode, as is distinct from the previous case of the more concentrated PBLG-toluene solution [8]. The dynamics of sol-gel transition, *i.e.*, the dependence of ξ_{Slow} on temperature, was semi-quantitatively explained by the correlated percolation theory. It would be expected that there exists the high potential usefulness for novel materials produced by three-dimensional networks or porous structure made up of rigid rod-like polymers.

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