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Dynamics of thermoresponsive PNIPAM-*g*-PEO copolymer chains in semi-dilute solution

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Abstract

The effects of concentration and temperature on dynamics of poly(*N*-isopropylacrylamide)-*graft*-poly(ethylene oxide) (PNIPAM-*g*-PEO) chains in semi-dilute aqueous solution were studied by static and dynamic laser light scattering. The intensity–intensity time correlation function shows a fast and a slow relaxation mode, with line widths Γ_f and Γ_s, respectively. Γ_f is scaled to the scattering vector (q) as $\Gamma_f \propto q^2$, revealing that it is due to the cooperative diffusion of the subchains between two neighboring entangled points. As the concentration increases, the slow relaxation becomes slower and contributes more to the total scattered light intensity, indicating that the slow relaxation is related to the chain entanglement. On the other hand, when the solution temperature increases, the PNIPAM chain backbone shrinks, but the fast relaxation remains and the slow mode slows down with a minimum rate at ~33 °C. It indicates that the slow mode arises from inter-chain clustering, which is gradually suppressed by the intra-chain shrinking. The sample position independence of the time-averaged scattered light intensity $\langle I \rangle_T$ reveals that the solution is homogeneous and the clustering is transient.

Keywords: Semi-dilute solution; Light scattering; Thermoresponsive polymers

1. Introduction

The cooperative diffusive relaxation in semi-dilute solution of linear flexible chains in a good solvent has long been predicted by scaling theory [1]. Such a relaxation characterized by the diffusion coefficient (D_c) of the subchains or blobs between two neighboring entangled points can be measured by dynamic laser light scattering (DLS). However, the interpretation of the results is not straightforward because some other dynamics were also observed, leading to the intensity–intensity time correlation function $g^{(2)}(q,\tau)$ to deviate. In a theta or poor solvent, such a deviation would be more pronounced [2–5]. Generally, two relaxation modes can be observed, namely, the fast mode related to the cooperative diffusion and the so-called slow mode which is attributed to the dynamics of the entangled chains. The former has been experimentally confirmed, but the latter remains largely unknown.

Brown et al. showed that for polystyrene semi-dilute solutions in good and theta solvents, the characteristic line width (Γ_f) of the fast mode was scaled to the scattering vector (q) as $\Gamma_f \propto q^2$, while the slow mode had q-independence [6]. Koch et al. found that the slow relaxation of short polyisoprene and polystyrene chains in semi-dilute solutions was diffusive [7], i.e., $\Gamma_s \propto q^2$, which was attributed to translational motion of the inhomogeneous network-like structure or transient clusters formed by the overlapping of polymer chains [8,9]. Brown et al. attributed the transient clusters to the incomplete dissolution of the polymer chains because only one relaxation mode was observed after a long-time dissolution [6], whereas Heckmeier et al. thought the transient clusters were due to physical association [10]. Ngai et al. examined the concentration, crosslinking density, solvent quality on the dynamics of photo-cross-linkable poly(methylmethacrylate-*co*-7-methacryloyloxy-4-methylcoumarin) [poly(MMA-*co*-AMC)] chains,

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and they observed two distinct relaxation modes [11–14]. The slow relaxation was attributed to the thermally agitated density fluctuation. Yu et al. investigated PNIPAM semi-dilute solutions in H_2O, D_2O, and tetrahydrofuran (THF) by using dynamic light scattering. They observed a slow mode interchain association in H_2O and D_2O, but such a slow mode was absent in THF. Thus, the hydrogen bonding of PNIPAM with H_2O and D_2O was thought to be responsible for the behavior [15]. Recently, Yuan et al. investigated the slow modes in semi-dilute aqueous solutions of PNIPAM and poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO-*b*-PPO-*b*-PEO), and they attributed the slow modes to the long-range correlated concentration fluctuation [16].

Poly(*N*-isopropylacrylamide)-*g*-poly(ethylene oxide) (PNIPAM-*g*-PEO) copolymer chains are known to form stable individual single-chain globules or multi-chain aggregates (mesoglobules) in dilute aqueous solutions at a temperature above the lower critical solution temperature (LCST) [17–19]. Accordingly, the so-called slow relaxation in PNIPAM-*g*-PEO semi-dilute solution can be examined by adjusting the solvent quality via temperature. In the present work, using laser light scattering, we have investigated the concentration and temperature dependences of the slow relaxation.

2. Experimental section

2.1. Materials and preparation

N-Isopropylacrylamide (NIPAM) was purified by recrystallization in a benzene/*n*-hexane ($v/v = 35/65$) mixture. Narrowly distributed monohydroxyl poly(ethylene oxide) (PEO) ($M_w = 5000$ g/mol, $M_w/M_n = 1.14$) from Fluka was used as received. Potassium persulfate (KPS) was purified by recrystallization in water. Other chemicals were used without further purification. The synthesis of PEO macromonomers end-capped with methacrylate can be found elsewhere [18]. PNIPAM-*g*-PEO was prepared by free radical copolymerization in water with KPS/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) redox as the initiator at 29 °C. Typically, 19 mmol of NIPAM and 0.12 mmol of PEO macromonomer in 180 mL of deionized water was introduced into a 250 mL two-neck flask equipped with a nitrogen inlet tube and a magnetic stirrer. The molar ratio of KPS/TEMED was 1:1. After 5 mL of KPS (15.2 mM) solution was added, the solution was repeatedly degassed at 20 °C and then purged with nitrogen for 30 min. Then, the reaction mixture was heated to 29 °C, and 1.0 mL TEMED (76 mM) solution was introduced. The reaction was further carried out at the temperature for 60 min. The PNIPAM-*g*-PEO copolymer was purified by dialysis using a semi-permeable membrane with cut-off molar mass of 8000 g/mol for a week. The final product was dried under reduced pressure at 40 °C.

^{1}H NMR (Bruker DPX-400 spectrometer) and laser light scattering (LLS) were used to characterize the resultant copolymer. By using the area ratio of the two peaks located at 3.63 and 4.00 ppm, the weight percentage of PEO in the copolymer was estimated to be 20 wt%. The weight-average molar mass (M_w) and the *z*-average root-mean-square radius of gyration ($\langle R_g\rangle$) of the copolymer measured in dilute solution (2×10^{-5} g/mL) are 4.0×10^6 g/mol and 106 nm, respectively. The overlap concentration (C^*) was evaluated to be 0.14 wt% [11].

2.2. Laser light scattering

A commercial LLS spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-τ digital time correlation (ALV5000) and a cylindrical 22 mW He–Ne laser ($\lambda_0 = 632$ nm, UNIPHASE) as a light source was used. In static LLS [20], we can obtain the weight-average molar mass (M_w) and the *z*-average root-mean-square radius of gyration ($\langle R_g^2\rangle^{1/2}$ or written as $\langle R_g\rangle$) of scattering objects in a dilute solution or dispersion from the angular dependence of the excess scattering intensity, known as Rayleigh ratio $R_{vv}(q)$. In dynamic LLS [21], the Laplace inversion of each measured intensity–intensity time correlation function $g^{(2)}(q,\tau)$ in the self-beating mode can lead to a line-width distribution $G(\Gamma)$. For a diffusive relaxation, Γ is related to the translational diffusion coefficient D by $(\Gamma/q^2)_{C\to 0, q\to 0} \to D$, so that $G(\Gamma)$ can be converted into a transitional diffusion coefficient distribution $G(D)$ or further a hydrodynamic radius distribution $f(R_h)$ via the Stokes–Einstein equation, $R_h = (k_BT/6\pi\eta)/D$, where k_B, T and η are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively. In the present study, copolymer chains used were first characterized in dilute solutions. It is helpful to note that in the semi-dilute solutions where the concentration was higher than the overlap concentration C^*, molecular characteristic properties of individual chains were often masked by inter-chain interaction.

For an ergodic system, $\langle I_s\rangle = 0$, and $g^{(2)}(q,\tau)$ can be related to the normalized electric field–electric field time correlation function $|g^{(1)}(q,\tau)| (\equiv [\langle E(q,0)E^*(q,\tau)\rangle / \langle E(q,0)E^*(q,0)\rangle])$ via the Siegert relation [21]

$$g^{(2)}(q,\tau) \equiv \frac{\langle I(q,0)I(q,\tau)\rangle}{\langle I(q,0)\rangle^2} - 1 = \beta\left|g^{(1)}(q,\tau)\right|^2 \tag{1}$$

where β (≈ 0.95) is a constant related to the coherence of the detection optics. For a polydisperse system [20,21], $g^{(1)}(q,\tau)$ is related to the distribution of the characteristic line width $G(\Gamma)$ by

$$\left|g^{(1)}(q,\tau)\right| = \int_0^\infty G(\Gamma)e^{-\Gamma t}d\Gamma \tag{2}$$

For a diffusive relaxation, Γ is related to the translational diffusion coefficient D or the collective diffusion coefficient D_c by $\Gamma = Dq^2$ or D_cq^2, depending on whether the solution is in a dilute ($C < C^*$) or a semi-dilute ($C > C^*$) regime. For a semi-dilute solution, $g^{(1)}(q,\tau)$ can often be described by a combination of a single-exponential function and a stretched exponential function [22–25], namely

$$\left|g^{(1)}(q,t)\right| = A_{\mathrm{f}}\exp\left(-\frac{\tau}{\langle\tau_{\mathrm{c}}\rangle_{\mathrm{f}}}\right) + A_{\mathrm{s}}\exp\left[-\left(\frac{\tau}{\langle\tau_{\mathrm{c}}\rangle_{\mathrm{s}}}\right)^{b}\right] \qquad (3)$$

where A and $\langle\tau_c\rangle$ are the intensity weighting and characteristic decay time, respectively; subscripts "f" and "s" denote the fast and slow modes, respectively; and $0 < b < 1$, a constant related to the distribution width of the slow relaxation mode.

3. Results and discussion

Fig. 1 shows a typical intensity–intensity time correlation function $g^{(2)}(q,\tau)$ of a dilute solution of PNIPAM-*g*-PEO in water at $\theta = 15°$ and $T = 25$ °C. The inset shows its corresponding hydrodynamic radius distribution ($f(R_h)$) calculated from $g^{(2)}(q,\tau)$ on the basis of Eqs. (1) and (2) by using a CONTIN program. It shows only one relaxation with hydrodynamic radius $\langle R_h\rangle$ = 81 nm at room temperature. From static laser light scattering measurements, we can know the corresponding $\langle R_g\rangle$ = 106 nm. It is known that for flexible random coil chains, the ratio $\langle R_g\rangle/\langle R_h\rangle$ is ~1.5 in a good solvent. Here, $\langle R_g\rangle/\langle R_h\rangle \sim 1.3$ indicates the branching structure of the copolymer chains.

Fig. 2 shows the concentration dependence of intensity–intensity time correlation function $g^{(2)}(q,\tau)$ of a semi-dilute solution of PNIPAM-*g*-PEO at 25 °C. The correlation function shows a fast and a slow relaxation mode. As expected, the fast relaxation is almost independent of the concentration. It is reasonably attributed to the cooperative diffusion of the subchains between two entangled points. However, as the concentration increases, the slow relaxation becomes slower with more contribution to the total scattered light intensity. The facts clearly indicate that the slow relaxation is related to the entanglement of the chains. Note that the fast and slow relaxations in the semi-dilute solution cannot be attributed to the motions of PNIPAM backbones and PEO side chains, respectively. Otherwise, such a slow relaxation should be observed in the dilute solution.

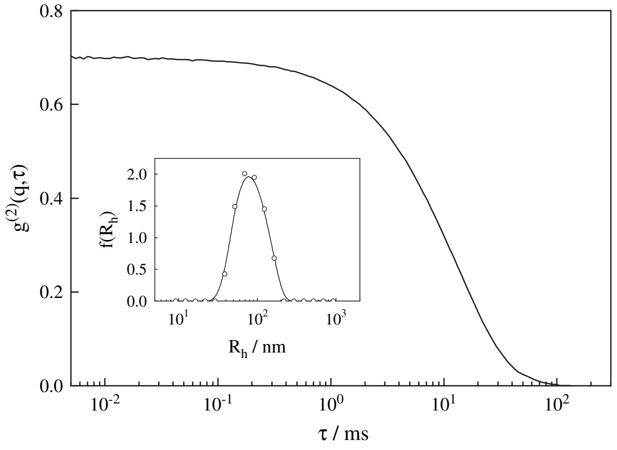

Fig. 1. Normalized intensity–intensity time correlation function $g^{(2)}(q,\tau)$ of dilute solution of PNIPAM-*g*-PEO copolymer in water at 24.9 °C, where $\theta = 15°$ and $C = 2 \times 10^{-5}$ g/mL. The inset shows its corresponding hydrodynamic radius distribution $f(R_h)$.

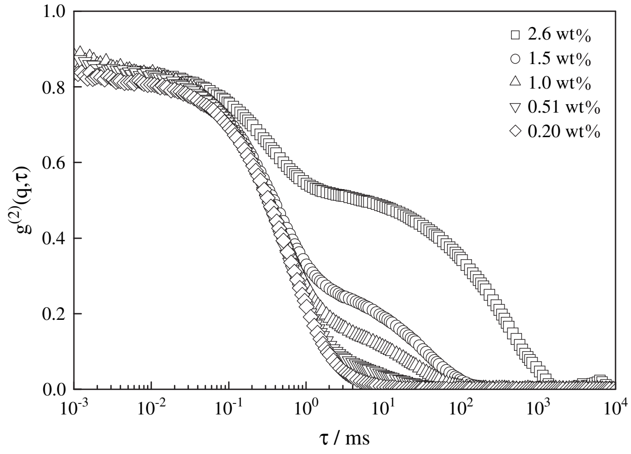

Fig. 2. Concentration dependence of normalized intensity–intensity time correlation functions $g^{(2)}(q,\tau)$ at $\theta = 45°$ and $T = 25$ °C.

Fig. 3 shows that the line width of the fast relaxation mode (Γ_f) is linearly dependent on q^2, and the extrapolation of Γ_f to $q \to 0$ passes the origin, clearly indicating that the fast relaxation is related to the chain diffusion. The slope of $\Gamma_f \propto q^2$ leads to the cooperative diffusion coefficient (D_c). Obviously, as the concentration increases, D_c becomes large, and the length of the subchain between two entanglement points becomes short. Fig. 4 shows that the line width of the slow relaxation mode (Γ_s) is scaled to q as $\Gamma_s \propto q^{\alpha_s}$ with $\alpha_s > 3.0$. It has been reported that Γ_s has the q-independence and the q^2-dependence in some systems [26–28]. Higher values of α_s were also reported for copolymer chains in a selective solvent [29,30] and for gels [31,32], which was attributed to the formation of transient clusters. Here, $\alpha_s > 3.0$ suggests that the slow relaxation is related to the formation of inter-chain clusters.

Fig. 5 shows the concentration dependence of normalized intensity–intensity time correlation functions $g^{(2)}(q,\tau)$ at

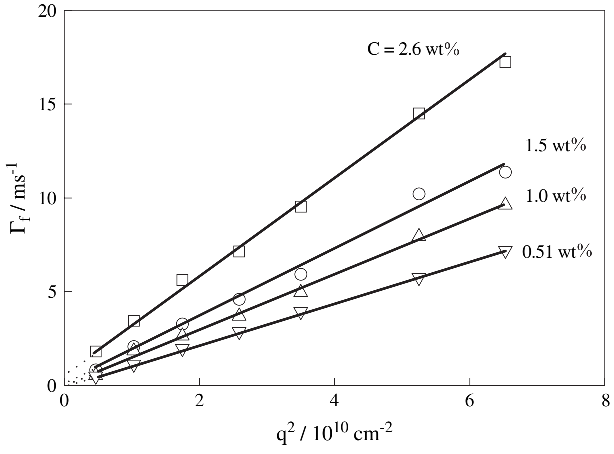

Fig. 3. Scattering vector (q) dependence of characteristic line width of the fast relaxation (Γ_f) of semi-dilute solutions of PNIPAM-*g*-PEO copolymer in water at 25 °C.

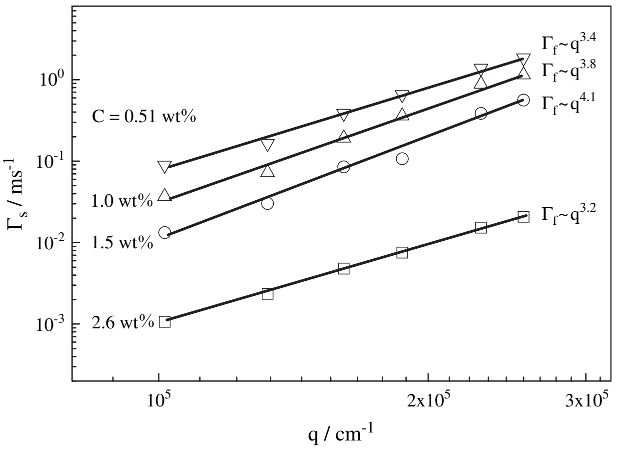

Fig. 4. Scattering vector (q) dependence of characteristic line width of the slow relaxation (Γ_s) of semi-dilute solutions of PNIPAM-*g*-PEO copolymer in water at 25 °C.

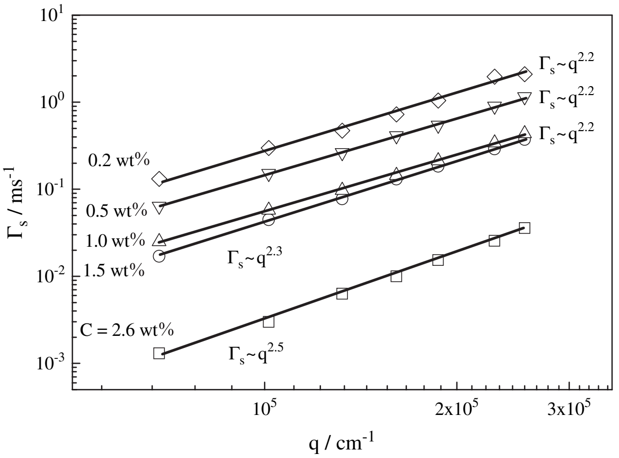

Fig. 6. Scattering vector (q) dependence of characteristic line width of the slow relaxation (Γ_s) of semi-dilute solutions of PNIPAM-*g*-PEO copolymer in water at 34.5 °C.

$\theta = 90°$ and $T = 34.5$ °C. At the temperatures above the LCST of PNIPAM, the correlation functions show almost only one relaxation whose relaxation time is comparable to the slow relaxation in Fig. 2. This is due to the inter-chain aggregates since PNIPAM-*g*-PEO chains form stable inter-chain aggregates even in dilute solution at such high temperatures [17–19]. Clearly, this indicates that the slow relaxations in good and poor solvents have the same source, namely, they are due to the inter-chain clustering. However, the clusters formed at the temperatures below the LCST are transient and via entanglement, whereas those formed at temperatures above the LCST are via the aggregation of collapsed chains. Fig. 6 shows $\alpha_s = 2.2$ when concentration is below 1.0 wt%, indicating that the relaxation is not pure one, but a mixture of the diffusive relaxation and the internal motions of inter-chain clusters. As the concentration increases from 0.2 to 2.6 wt%, α_s increases from 2.2 to 2.5. This is because larger clusters lead Γ_s to be more dependent on q.

Fig. 7 shows the temperature dependence of the normalized intensity–intensity time correlation functions $g^{(2)}(q,\tau)$ of PNIPAM-*g*-PEO solution at $\theta = 90°$, where the concentration is 2.6 wt%. In the range of 25–33 °C, as the temperature increases, the slow relaxation becomes faster, and its contribution to the total light scattering intensity decreases reflecting in the decline in the amplitudes. Since the concentration is much higher than the overlapping concentration ($C^* = 0.14$ wt%), PNIPAM-*g*-PEO chains are highly overlapped at 25 °C. As the temperature increases, PNIPAM backbones undergo

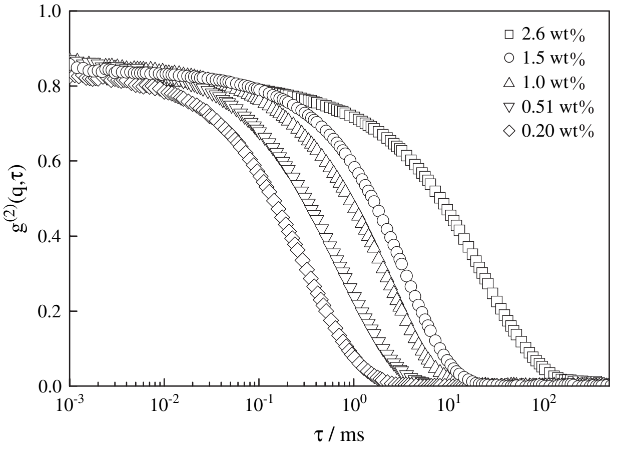

Fig. 5. Concentration dependence of normalized intensity–intensity time correlation functions $g^{(2)}(q,\tau)$ at $\theta = 90°$ and $T = 34.5$ °C.

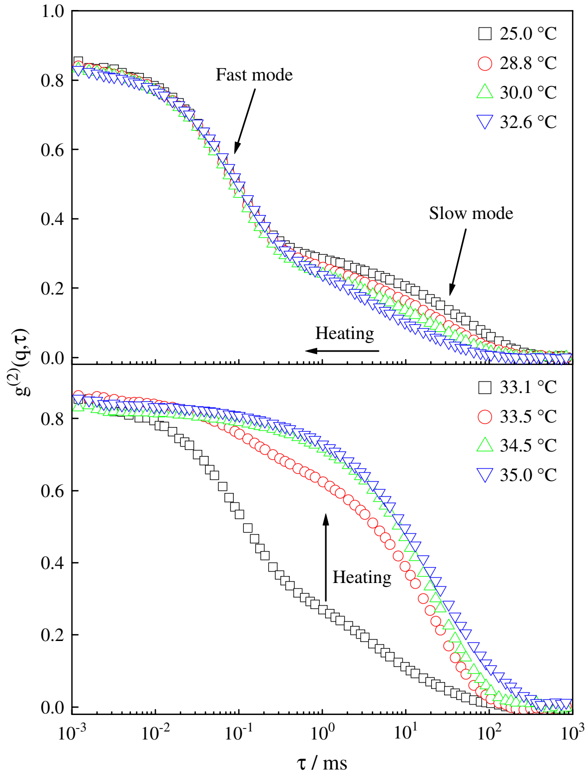

Fig. 7. Temperature dependence of normalized intensity–intensity time correlation functions $g^{(2)}(q,\tau)$ of PNIPAM-*g*-PEO solutions in water, where $\theta = 90°$ and $C = 2.6$ wt%.

intra-chain shrinking [18]. Note that PNIPAM backbones do not aggregate at temperatures below its LCST. Accordingly, the faster slow relaxation in the range of 25–33 °C comes from the intra-chain shrinking. It also demonstrates that the intra-chain shrinking reduces the number of the inter-chain entanglement points. The slow relaxation turns slow at ~33 °C, and its contribution to the total scattering light intensity increases. This is because PNIPAM backbones collapse and aggregate at the critical temperature, leading to more inter-chain clustering. Further increasing the temperature in the range ~34–35 °C leads to one relaxation. This is because the subchain between the entanglement points has been collapsed and is no longer in motion. Note that $g^{(2)}(q,\tau)$ can still completely relax to zero even when the relaxation is fairly slow, indicating no static frozen-in component in the system, namely, the solution is homogeneous. This can be further confirmed by sample position dependence testing in Fig. 8.

Fig. 8 shows the position dependence of time-averaged scattered light intensity $\langle I\rangle_T$ of PNIPAM-*g*-PEO solution with concentration of 2.6 wt% at temperatures below, near, and above the LCST of PNIPAM. The sampling positions were randomly chosen. Obviously, $\langle I\rangle_T$ does not have position dependence at any temperature, indicating that the system is ergodic in the range we investigated. The system becomes opaque or nonergodic above 37 °C. When the concentration is lower than 1.5 wt%, the system is ergodic even at 50 °C.

To qualitatively extract the information about the two relaxation modes, the exponential decay for the fast mode and a stretched exponential decay for the slow mode were combined, which is normally used for semi-dilute ergodic solution [22–25]. Fig. 9 shows temperature dependence of fast and slow characteristic decay ($\langle\tau_c\rangle_f$ and $\langle\tau_c\rangle_s$) calculated on the basis of Eq. (3) for PNIPAM-*g*-PEO solution with $C = 2.6$ wt%. It shows $\langle\tau_c\rangle_s$ with 130 ms which is about 10^3 times of $\langle\tau_c\rangle_f$ at 25 °C and $\theta = 90°$. Fig. 9 also shows that $\langle\tau_c\rangle_f$ almost does not have temperature dependence, whereas $\langle\tau_c\rangle_s$ is quite dependent on temperature. In the range of 25 to ~33 °C, $\langle\tau_c\rangle_s$ decreases from 130 to 20 ms. As discussed above, when the temperature increases from 25 to ~33 °C, PNIPAM backbones undergo intra-chain shrinking, leading some of the entangled polymer chains to disentangle, namely, the transient cluster formed becomes smaller, so that the slow relaxation becomes faster. The abrupt increase of $\langle\tau_c\rangle_s$ at the temperatures above ~33 °C reveals the formation of larger clusters.

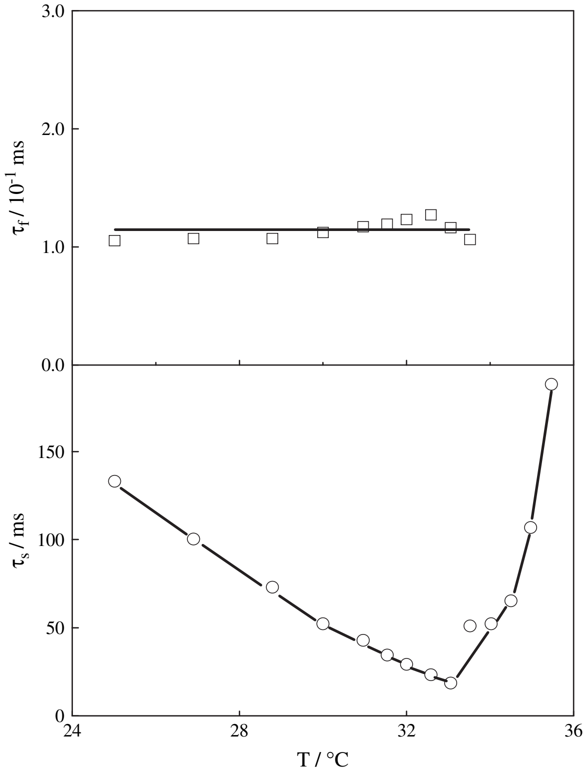

Fig. 9. Temperature dependence characteristic decay of the fast relaxation ($\langle\tau_c\rangle_f$) and slow relaxation ($\langle\tau_c\rangle_s$), where $\theta = 90°$ and $C = 2.6$ wt%.

Fig. 10 shows the temperature dependence of slow characteristic decay time ($\langle\tau_c\rangle_s$) at different concentrations. In the range of 25–33 °C, $\langle\tau_c\rangle_s$ decreases with temperature. Moreover, the higher the concentration, the more the decrease is.

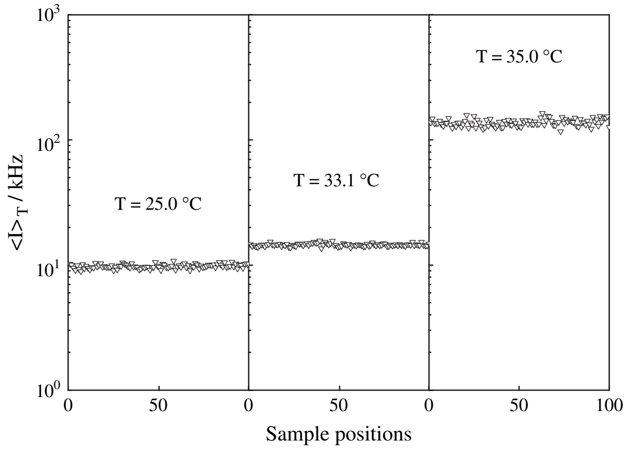

Fig. 8. Sample positions dependence of time-averaged scattered light intensity $\langle I\rangle_T$ at $\theta = 90°$.

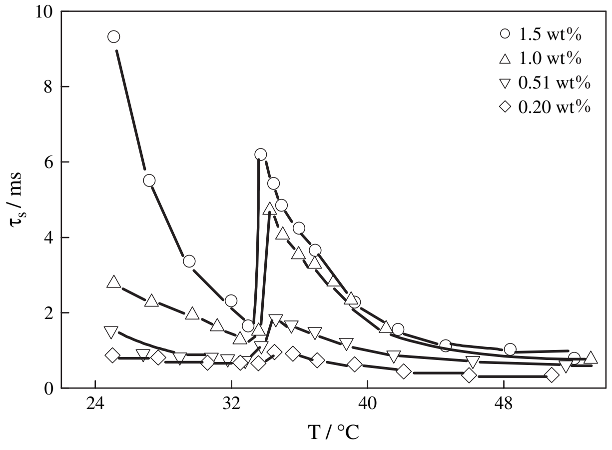

Fig. 10. Temperature and concentration dependences of the characteristic decay time of the slow relaxation at $\theta = 90°$.

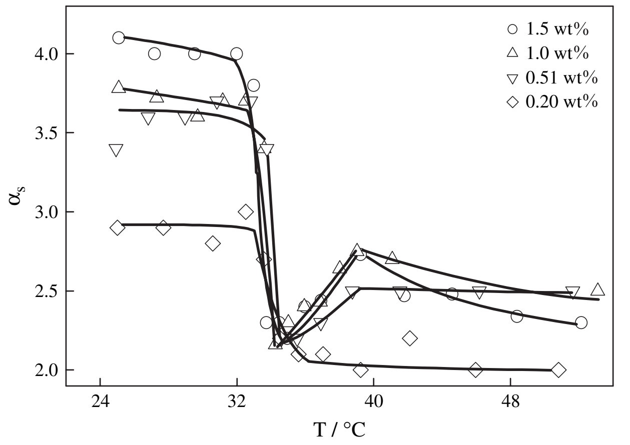

Fig. 11. Temperature and concentration dependences of α_s.

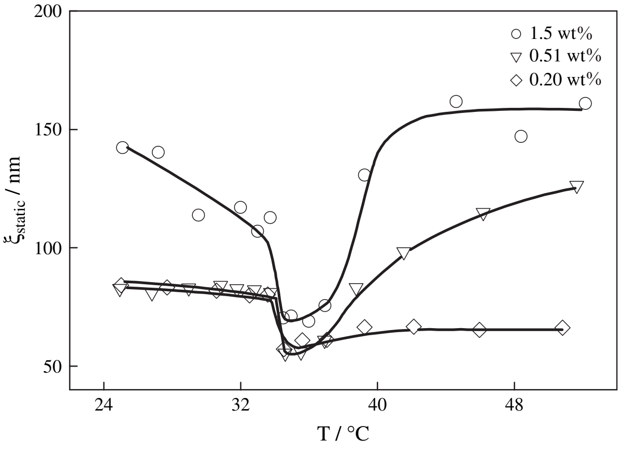

Fig. 12. Typical plot of temperature and concentration dependences of static correlation length ξ_{static}.

This is understandable because more inter-chain entanglements are expected in a more concentrated solution, which exhibits more marked decrease as the temperature increases. In the range ~33–34.5 °C, $\langle\tau_c\rangle_s$ increases with temperature, further indicating the formation of the clusters or aggregates of the chains. When temperature is higher than 34.5 °C, $\langle\tau_c\rangle_s$ gradually decreases due to the further collapse of the aggregates.

Fig. 11 shows the temperature dependence of α_s at different concentrations, where α_s was obtained from $\Gamma_s(=1/\langle\tau\rangle_s)\propto q^{\alpha_s}$. At lower temperatures, $\alpha_s > 3$ when concentration is higher than 0.51 wt%. As mentioned above, the value of α_s may be related to the formation of transient clusters. The sharp decrease of the α_s at ~33 °C is attributed to the intra-chain collapse of the entangled PNIPAM chains, which reduces the entanglement of the chains. The collapsed aggregates exhibit only the diffusive relaxation with $\alpha_s \sim 2$. The subsequent increase of the α_s indicates that collapsed aggregates further correlate or aggregate. Note that when the concentration is slightly higher than the overlap concentration ($C = 0.2$ wt%), α_s preserves about 2 at the temperatures above ~34 °C, indicating the formation of independent mesoglobules. The facts clearly indicate that the value of α_s is related to the formation of transient clusters.

It has been known that the static correlation length (ξ_{static}) inside a semi-dilute solution or a gel network can be related to the scattering light intensity ($I(q)$) and the scattering vector (q) by the Ornstein–Zernike equation [33]:

$$I(q) = \frac{I(q\to 0)}{1+q^2\xi_{static}^2} \qquad (4)$$

Fig. 12 shows the temperature dependence of ξ_{static}, where ξ_{static} was calculated from the slope-to-intercept ratio by typical Ornstein–Zernike plots of $1/I(q)$ versus q^2. The gradual decrease of ξ_{static} during ~25–33 °C indicates that the density fluctuation of entangled polymer chains becomes faster, i.e., the inter-chain clustering becomes less correlated. At temperatures above ~33 °C, ξ_{static} sharply decreases, further indicating the collapse of the PNIPAM chains backbones, which remarkably reduces the inter-chain entanglement. The quick increase in ξ_{static} at temperatures above ~35 °C indicates the inter-chain aggregation. When temperature is higher than ~41 °C, ξ_{static} slightly increases because the aggregation almost stops.

4. Conclusions

Using a combination of static and dynamic laser light scattering (LLS), we have investigated the effects of concentration and temperature on the dynamics of PNIPAM-*g*-PEO in the semi-dilute aqueous solution. The intensity–intensity time correlation function shows two relaxations at room temperature. As the concentration decreases, the slow relaxation becomes faster with less contribution to total scattering light intensity and tends to mix with the fast relaxation. As the temperature increases, the slow relaxation first becomes faster due to the shrinking and collapse of PNIPAM backbones and then slows down because of the inter-chain aggregation. Our results indicate that the slow relaxations in good and poor solvents origin from the inter-chain clustering. However, the clusters formed at the temperatures below the LCST of PNIPAM are transient and via entanglement, whereas those formed at temperatures above the LCST are via the aggregation of collapsed chains.

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