A SLOW RELAXATION MODE OF POLYMER CHAINS IN A SEMIDILUTE SOLUTION[*]

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Abstract Dust-free semidilute and concentrated polystyrene (PS) solutions in different solvents were prepared by slow evaporation and *in situ* anionic polymerization, which removes the effects of troublesome artifacts such as dust contamination and concentration gradient. The dynamics was reexamined by a combination of static and dynamic laser light scattering. In benzene and toluene (good solvents for PS), only one fast diffusive mode of polymer chains can be observed when the concentration (c) is up to 20%, which is attributed to thermally agitated fluctuation of "blobs" or chain segments. Static and dynamic correlation lengths (ξ_S and ξ_D) are scaled with c as ξ_S (or ξ_D) $\sim c^{-0.72 \pm 0.02}$. In cyclohexane, whose quality decreases with temperature in the range 32–50°C, an additional slow mode of polymer chains can be observed. Such a slow mode is viewed more obviously at a large scattering angle even in a concentrated solution with high chain entanglement. The present study indicates that the slow mode is due to the solvent quality.

Keywords: Semidilute; Anionic polymerization; Laser light scattering; Blob; Correlation length; Slow mode.

INTRODUCTION

It is well known that polymer chains start to touch each other and the solution enters the semidilute regime at the overlap concentration (c^*). c^* is usually estimated by $c^* = 3M/(4\pi N_A R_g^3)$, $c^* = M/(2^{3/2} N_A R_g^3)$ or $c^* = [\eta]^{-1}$, where M, R_g, N_A, and $[\eta]$ are the molar mass, radius of gyration, Avogadro number and intrinsic viscosity, respectively[1, 2]. Using the concept of "blob", which was defined as the segments between two neighboring cross-linking points, de Gennes and his co-workers[3–5] developed scaling laws to predict the properties of semidilute solutions. If the solvent is thermodynamically good or athermal, only one characteristic length or one dynamic process in semidilute solutions is expected. Experimentally, the static and dynamic correlation lengths (ξ_S and ξ_D) can be measured respectively from the angular dependence of the average scattering intensity and the cooperative diffusion coefficient (D_C) by light scattering. At a distance longer than ξ, the segment-segment interaction is completely counteracted in a good solvent[4, 6, 7]. It reveals that the scaling relations are $\xi_S \sim c^{-0.72 \pm 0.01}$ and $\xi_D \sim c^{-0.70 \pm 0.01}$, which slightly deviate from $\xi \sim c^{-0.75}$ predicted by theories[1, 8], where ξ is the correlation length.

On the other hand, some light scattering studies showed one additional slow relaxation mode of polymer chains in a semidilute solution by the intensity-intensity time correlation function[9–28]. It has been attributed to the chain reptation inside a "tube" made of the surrounding chains[3, 5], the scattering vector (q) independent relaxation of a transient network[10, 15, 16], the q^2-dependent translational diffusion of large aggregates or dust particles[1, 13, 14, 16, 17–20] and internal motions of large transient chain clusters[8, 9]. However, because of the

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... ren ... h b... refrig nsid ... R... nitiate on ... as imm ly c ... benze eede... ng ch e ter... he h vacuum stopcock. Each solution was kept at 50°C for ... ek efore ... e m cu ar weight and the polydispersity were determined by

a combination of gel permeation chromatograph (a Waters-1515) and light scattering (Wyatt MALLS) and tetrahydrofuran (THF) as the eluent with a flow rate of 1.0 mL/min.

LLS Measurements

A commercial LLS spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-τ digital time correlation (ALV5000) and a cylindrical 22 mW UNIPHASE He-Ne laser ($\lambda_0 = 632.8$ nm) as the light source was used. The details of LLS instrumentation and theory can be found elsewhere[29–31]. In static LLS, the excess absolute time-averaged scattered light intensity, known as the excess Rayleigh ratio $R_{vv}(q)$, of a dilute polymer solution at concentration c (g/mL) is related to the weight average molar mass M_w, the root-mean square z-average radius of gyration $<R_g^2>_z^{1/2}$ (or written as $<R_g>$), and the scattering vector q as:

$$\frac{KC}{R_{vv}(q)} \approx \frac{1}{M_w}(1 + \frac{1}{3}<R_g^2>q^2) + 2A_2C \tag{1}$$

where $K = 4\pi^2 n^2 (dn/dc)^2/(N_A\lambda_0^4)$ and $q = (4\pi n/\lambda_0)\sin(\theta/2)$ with N_A, dn/dc, n and λ_0 being the Avogadro number, the specific refractive index increment, the solvent refractive index and the wavelength of the light in vacuum, respectively, and A_2 is the second virial coefficient. The plots of $[KC/R_{vv}(q)]_{c\to0}$ versus q^2 and $[KC/R_{vv}(q)]_{q\to0}$ versus c respectively lead to $<R_g^2>$ and A_2. In semidilute solutions, Eq. (1) is not applicable because what we observe by LLS are not the properties of individual chains. Therefore, we have to use $<R_g>$ obtained in dilute solutions to estimate c^*.

In dynamic LLS, the intensity-intensity time auto-correlation function $G^{(2)}(q, t)$, defined as $<I(q,0)I(q,t)>/<I(q)>^2$, in the self-beating mode was measured, where t is the delay time and $<I(q)>$ is the time-average scattering intensity, *i.e.*, the measured baseline. $G^{(2)}(q, t)$ is related to the normalized electric field-field time auto-correlation function $|g^{(1)}(t, q)|$, defined as $<E(0, q)E^*(t, q)>/<E(0)E^*(0)>$, by the Siegert relation as[32]

$$G^{(2)}(q, t) = A[1 + \beta|g^{(1)}(t, q)|^2] \tag{2}$$

where A is the measured baseline and β is the coherent factor, depending on the detection optics. For a broadly distributed relaxation, $|g^{(1)}(t, q)|$ is related to a characteristic relaxation time distribution $(G(\tau))$ as

$$|g^{(1)}(t, q)| = \int_0^\infty G(\tau)e^{-t/\tau}d\tau \tag{3}$$

The Laplace inversion of measured $G^{(2)}(q, t)$ can lead to $G(\tau)$ on the basis of Eqs. (2) and (3). In this study, we used CONTIN program to analyze the data[33].

RESULTS AND DISCUSSION

Preparation of dust-free solution is critical for LLS experiments, especially for viscous semidilute solutions. To test whether the previously observed slow mode is due to artifacts, we reexamined PS solutions in toluene[6, 17–19, 34]. We first clarified a dilute solution by filtration. The solution was kept at 25°C to allow a gradual removal of solvent so that the solution changed from dilute to semidilute. In our experiments, the evaporation was so slow that the whole process had lasted for about one year. In this way, we managed to avoid any possible concentration gradient, especially at the late stage of evaporation.

Figure 1 shows the typical intensity-intensity time correlation functions of four PS samples in toluene at the highest concentrations. Clearly, only one fast relaxation mode is observed over the entire concentration range. This is consistent with some previous results[1, 4]. In a semidilute solution with good solvent, linear polymer chains entangle with each other to form a transient network, and the segment-segment interaction is shielded by the solvent-segment interaction. Therefore, thermally agitated motions of the segments inside different blobs are independent of each other, and as such, the light scattered from them is not correlated. The intensity-intensity time correlation function only reflects diffusive motions of the segments inside each blob, arrested around their gravity center in a short time scale.
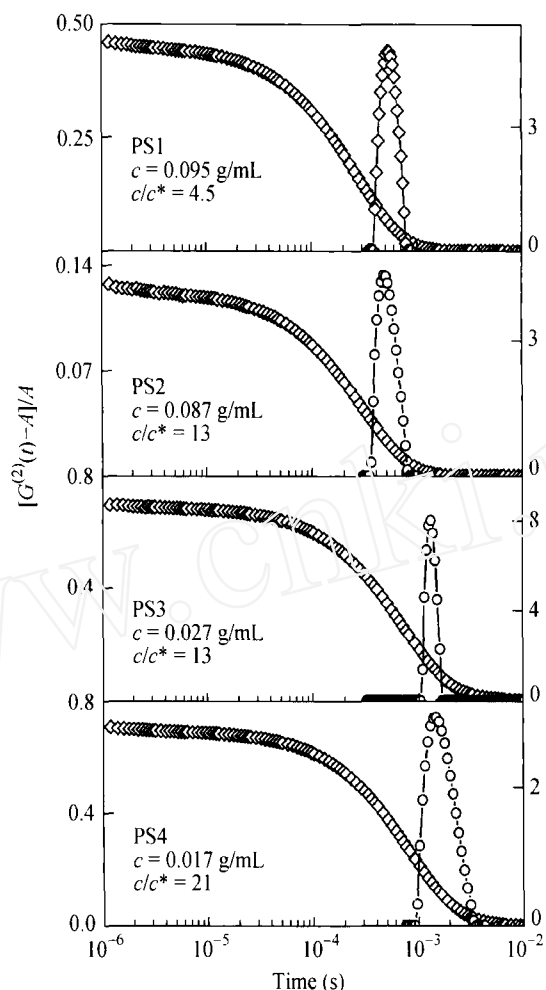
Fig. 1 Intensity-intensity time correlation functions and characteristic relaxation time (τ) distributions of polystyrenes in toluene at 25°C

Figure 2 shows that the average line-width ($<\Gamma>_f = 1/<\tau>_f$) is not only a linear function of q^2, but also passing through the origin as $q \to 0$. This is a characteristic of diffusive relaxation. Each slope of $<\Gamma>_f$ versus q^2 leads to a cooperative diffusion coefficient (D_C) or the dynamic correlation length (ξ_D) defined by the Stokes-Einstein equation, $\xi_D = k_B T/6\pi\eta_0 D_C$. On the other hand, we can obtain the static correlation length (ξ_S) of a semidilute solution from the angular dependence of $<I(q)>$ by using the Ornstein-Zernike equation[7, 35, 36],

$$\frac{1}{<I>_q} = \frac{1}{<I>_{q\to0}}(1+\xi_s^2 q^2)$$

(4)

Figure 3 shows the concentration dependence of $\xi_{D,fast}$ and $\xi_{S,fast}$. Either $\xi_{D,fast}$ or $\xi_{S,fast}$ is scaled to c as $\xi_{fast} \sim c^{-0.72 \pm 0.02}$. This agrees with the previous results[1, 8, 9]. Note that the scaling exponent is slightly lower than 0.75 predicted by the scaling theory[3–5]. So far, we have not presented anything new except that we have confirmed some of previous results in an athermal solvent and shown that we are able to prepare homogeneous dust-free semidilute solutions by slow evaporation. Using the same procedure, we have studied PS semidilute solutions in cyclohexane at 50°C.

Figure 4 shows that such a slow relaxation mode in cyclohexane appears only when $c > c^*$. Note that cyclohexane with the Θ-temperature (T_Θ) of *ca.* 34.5°C is no longer a good solvent for PS at 50°C. The slight shift of the fast mode to the left (even fast) as c increases is reasonable because the related dynamic correlation length (ξ_{blob}) decreases as c increases. Similarly, the intercept at $t \to 0$ (β_{app}) also becomes smaller in the semidilute solution because $<I>_{blob}$ decreases with ξ_{blob}.
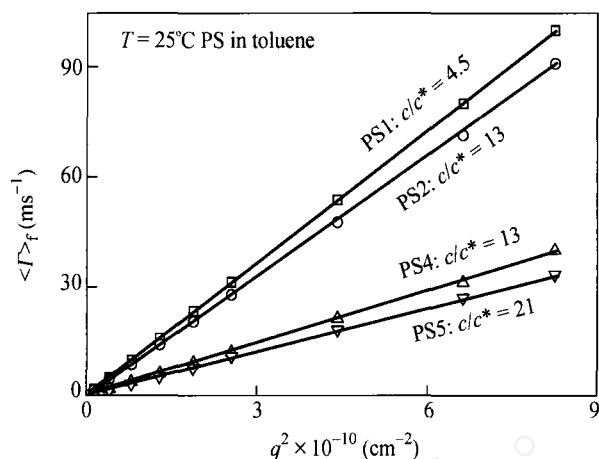
Fig. 2 Scattering vector (q) dependence of average characteristic line-width ($<\Gamma>_f$) of fast diffusive mode of polystyrenes in toluene at 25°C
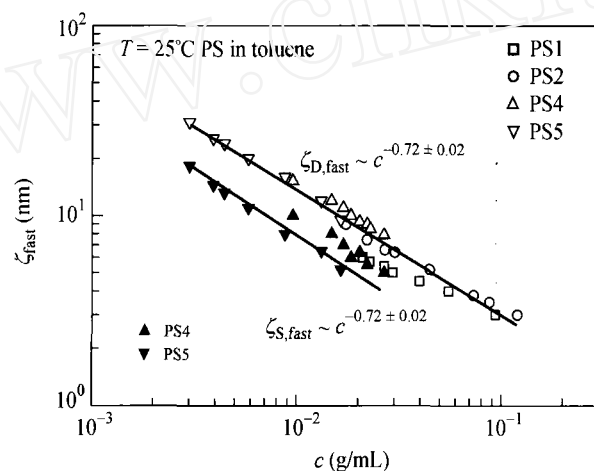
Fig. 3 Concentration dependence of dynamic and static correlation lengths ($\zeta_{D,fast}$ and $\zeta_{S,fast}$) of fast diffusive mode of polystyrenes in toluene at 25°C
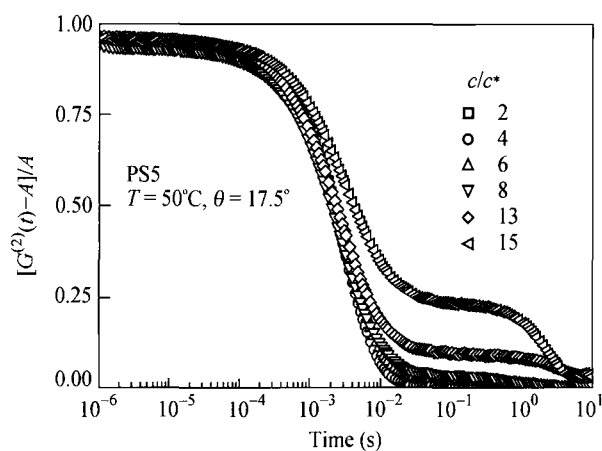
Fig. 4 Concentration dependence of the intensity-intensity time correlation function of PS5 in cyclohexane at 50°C
The scattering angle is 15°.

Furthermore, we have monitored $<I>_{q\to0}$ during one cooling-and-heating cycle as shown in Fig. 5. The sharp increase of $<I>_{q\to0}$ at *ca.* 33°C indicates interchain aggregation or micro-phase separation. In the temperature

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range 36–55°C, the slight decrease of $<I>_{q\to0}$ reflects the decrease of ζ_{blob} because the chain extends as the temperature increases. The temperature dependence of $<I>_{q\to0}$ further shows that the observed slow mode is not due to the artifacts introduced in the sample prepartion[15–19, 23, 37–39].

Figure 6 shows the temperature dependence of the intensity-intensity time correlation function of PS3 solutions in cyclohexane. As temperature decreases, c/c^* decreases from 4.0 to 1.0 and the slow mode gradually disappears, indicating that the effect of the chain contraction dominates here. To make sure that such prepared semidilute solutions are free from dust particles or insoluble chain aggregates or a possible concentration gradient, we have measured the sample position dependence of time-average scattering intensities $<I>$ by randomly lifting and rotating the scattering cell so that the incident laser beam stroke any positions in the solution. Figure 7 shows that $<I>$ randomly fluctuates around an average value without a speckle, indicating a "homogeneous" solution.
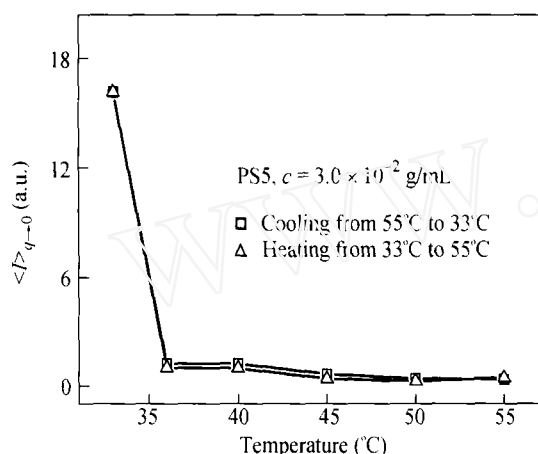
Fig. 5 Temperature dependence of time-average scattering intensity $(<I>_{q\to0})$ of polystyrene in cyclohexane in one cooling-and-heating cycle
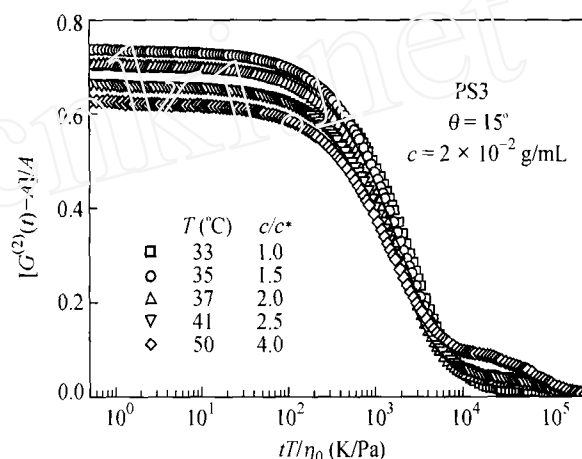
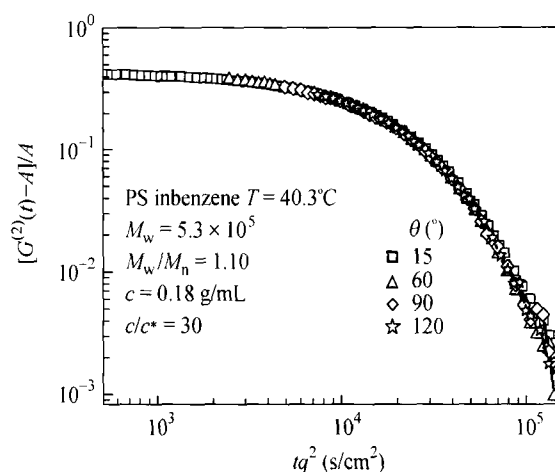**Fig. 6** Temperature (T) and solvent viscosity (η_0) normalized intensity-intensity time correlation function of PS3 in cyclohexane at 15°
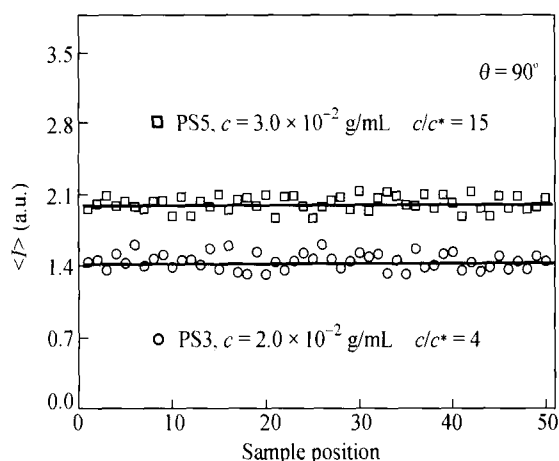
Fig. 7 Sample position dependence of time-average scattering intensity ($<I>$) of polystyrenes in cyclohexane at 50°C
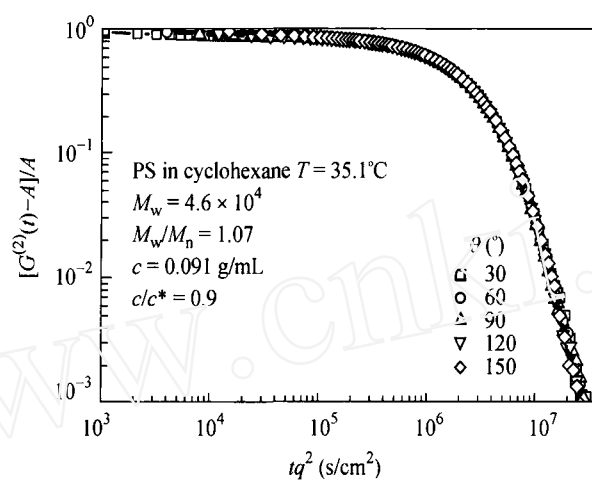The position of the light-scattering cell was changed by randomly rotating and lifting.

Fig. 8 Scattering vector (q) dependence of intensity-intensity time correlation functions of polystyrene in benzene

To examine the slow mode of PS chains in cyclohexane in the temperature range 34–55°C, we have prepared dust-free semidilute solutions directly inside the specially setup LLS cell with high vacuum stopcock via

living anionic polymerization, starting from a dust-free monomer solution. Figure 8 shows only one fast relaxation mode in the measured intensity-intensity time correlation function for PS semidilute solution (c/c^* ca. 30) in benzene. Moreover, such a fast relaxation mode is q^2 dependent. The investigations on other three PS samples ($M_w = 4.83 \times 10^4$, $M_w/M_n = 1.05$ and $c = 0.091$; $M_w = 1.14 \times 10^5$, $M_w/M_n = 1.07$ and $c = 0.11$ g/mL; $M_w = 2.86 \times 10^4$, $M_w/M_n = 1.17$ and $c = 0.18$ g/mL) also show only one fast relaxation mode (not shown). Thus, it can be attributed to the diffusive motion of the segments inside each blob, arrested around their gravity center in a short time scale.
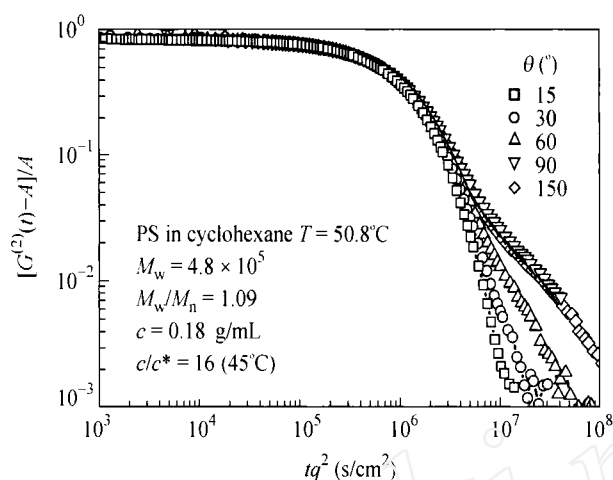

Fig. 9 Scattering vector (q) dependence of intensity-intensity time correlation functions of polystyrene dilute solution in cyclohexane

Using the same procedure, we have also prepared PS dilute and semidilute solutions in cyclohexane. Figure 9 shows only one fast mode in the dilute solution reflected in the intensity-intensity time correlation functions in the whole angular range. As the concentration or molar mass of PS increases, the solution enters into semidilute region. As shown in Figs. 10–12, the intensity-intensity time correlation function reveals an additional slow mode. Particularly, in the concentrated solution, a more obvious slow mode can be observed at a large angle. Note that large objects are more visible at smaller scattering angles, so the slow mode can not be attributed to dust. Our experiments convincingly demonstrate that the slow mode is due to the solvent quality instead of artifacts.
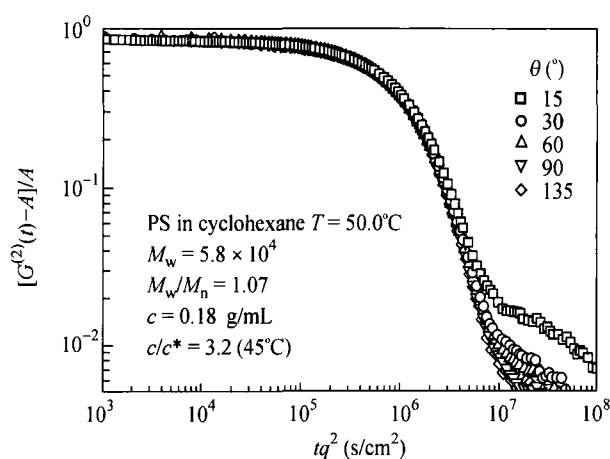
Fig. 10 Scattering vector dependence (q) of intensity-intensity time correlation functions of polystyrene in cyclohexane as $c/c^* = 3.2$

Fig. 11   Scattering vector dependence (*q*) of intensity-intensity time correlation functions of polystyrene in cyclohexane (*c/c** = 16)
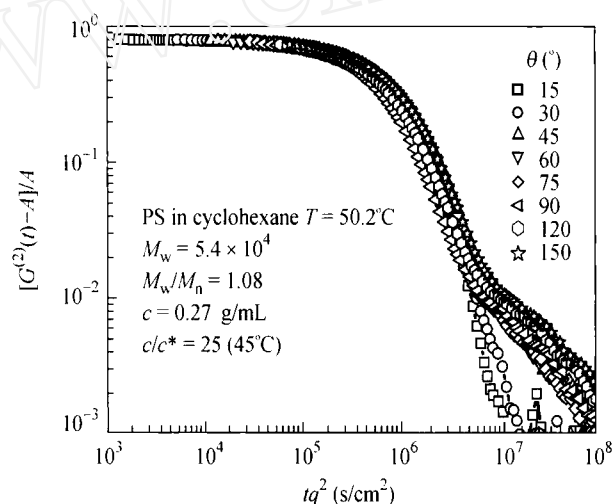
Fig. 12 Scattering vector dependence (*q*) of intensity-intensity time correlation functions of polystyrene in cyclohexane (*c/c** = 25)

CONCLUSIONS

The current study on polystyrene solutions leads to the following conclusions. There is only one fast diffusive relaxation mode of polymer chains in good solvent at a concentration (*c*) 30 times higher than the overlapping concentration (*c**). In cyclohexane, whose quality decreases with the temperature in the range 32–50°C, there exists an additional slow mode of polymer chains in semidilute region. It is not due to artifacts but the solvent quality.

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