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A COMPARATIVE STUDY OF CHAIN DYNAMICS OF DI- AND TRI-BLOCK COPOLYMERS IN SEMIDILUTE SOLUTION IN A NON-SELECTIVE SOLVENT*

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Abstract The chain dynamics of a pair of diblock poly(styrene-b-butadiene) (PS_{210}-b-PB_{960}) and triblock poly(styrene-b-butadiene-b-styrene) (PS_{200}-b-PB_{1815}-b-PS_{200}) copolymers in both dilute and semidilute toluene solutions has been comparatively studied by dynamic laser light scattering. As expected, the mutual diffusion of individual chain changes into a fast cooperative diffusion of the chain segments ("blobs") between two neighboring entanglement points for both the copolymers as the solution changes from dilute to semidilute. Further increases of the concentration lead to a second slow relaxation mode. For the triblock chains, there exists an additional middle relaxation between the fast and the slow modes. The concentration (c) dependent study of the average characteristic decay time of the fast mode ($<\tau_f>$) reveals that $1/<\tau_f> \sim c^{-\alpha}$ with $0.33 < \alpha < 0.44$, much smaller than 0.75 predicted or 0.72 observed for linear homopolymer chains in good solvent. It implies that the solvent quality of toluene for PB might not be as good as that for PS. Due to such a difference in solubility, it is reasonable to speculate that the PB and PS blocks are transiently segregated in semidilute solution. The relaxation of these transient PB and PS richer domains leads to the observed slow relaxation. Such a speculation is supported by the appearance of an additional slow relaxation mode in the study of polyisoprene-b-polystyrene-b-polyisoprene in semidilute solution in cyclohexane, a non-selective solvent, in which we alternated the solubility difference by a variation of the solution temperature.

Keywords Semidilute, Solutions, Chain dynamics, Block copolymers

INTRODUCTION

Block copolymers normally consist of a few chemically distinct short chains joined by covalent bonds. In a solvent selectively good only for one block, they can display more complicated structures and morphology, such as polymeric core-shell and cylindrical micelles, than homopolymers even in dilute solution. In semidilute solution, the chain dynamics of block copolymers become even more complicated due to chain overlapping[1-3]. A better understanding of the dynamics of block chains in semidilute solution is not only conceptually important, but also has some implications in the formation of thin films as well as in the solution-spinning of polymer fibers[4]. The dilute and semidilute solutions are distinguished by the so-called overlap concentration (c*) defined as $3M/(4\pi N_A Rg^3)$ or $M/(2^{3/2}N_A R_g^3)$, or $[\eta]^{-1}$, where M and R_g are the molar mass and the radius of gyration of polymer chains, N_A is the Avogadro constant, and $[\eta]$ is the intrinsic viscosity, respectively[5]. It is helpful to note that $R_g \propto M^v$ with $0.5 < v < 0.6$, depending on the quality of a good solvent[6,7]. Therefore, $c^* \sim M^{1-3v}$; namely, a

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long chain leads to a lower c^*.

In the study of semidilute solutions, two important parameters are static and dynamic correlation lengths (ξ_s and ξ_D). They can be scaled to polymer concentration (c)[8-10]. ξ_s is directly measurable from the angular dependence of the time-averaged scattering intensity[11], while ξ_D is related to the characteristic decay time (τ) measured in dynamic laser light scattering (LLS) by $\xi_D = q^2 \tau k_B T/6\pi\eta_0$, where T, k_B and η_0 are the absolute temperature, the Boltzmann constant and the solvent viscosity, respectively[12]. For homopolymers in semidilute solution in good solvent, there exits a fast relaxation elegantly described by the "blob" concept; namely, such a relaxation is related to the cooperative diffusion of the chain segments (blobs) between two neighboring entanglement points. The concentration dependence (τ_f or $\xi_D \propto c^\alpha$) of such fast cooperative relaxation has been well predicted by the scaling theory[6] and also experimentally confirmed[8,10] where the observed scaling exponent α is only slightly smaller than the predicted value of 0.75. For example, Browan and Nicolai[13] have summarized some results of homopolymers in good solvent and found that ξ_s and ξ_D could be scaled to c as $\xi_s \sim c^{-0.72 \pm 0.06}$ and $\xi_D \sim c^{-0.70 \pm 0.04}$. In marginal solvents[14,15], α is generally smaller in the range 0.4-0.7. Unexpected from the scaling theory, some past studies of linear homopolymer chains in semidilute solution showed an additional slow relaxation mode which was attributed to transient clusters or incomplete dissolution[13,16,17]. Our recent study revealed that this slow relaxation could be related to large spatial density fluctuation, not necessarily to real clusters[8]. In comparison, the results of block copolymer chains in semidilute solution were more controversial and diversified.

For diblock chains in a selective solvent, at least two distinct relaxation modes are normally observed; namely, one fast mode, similar to that of homopolymers in good solvent, and another expected slow mode, related to the association-induced polymeric clusters[8,18-21]. However, two relaxation modes were also observed in the study of symmetric diblock copolymers, *i.e.,* the two blocks have a similar length in good solvent. In this case, the slow mode was attributed to the relative internal motion of the two blocks on a single chain[22-25]. Pan *et al.*[25] and Liu *et al.*[26] even found three relaxation modes in the study of symmetric diblock polystyrene-polyisoprene chains in good solvent using a combination of dynamic LLS and pulsed-field-gradient NMR. They attributed the additional relaxation to the hetergeneity-related translatable diffusion, which was supported by theoretical analysis and experimental observations[1,27-29]. They found that for the fast cooperation diffusion as well as the heterogeneity relaxation, $1/\tau \propto q^2$ and $\langle I \rangle$ is independent of q; but for the internal motion, $1/\tau$ is independent of q and $\langle I \rangle \propto q^2$, where q is defined as $q = (4\pi n/\lambda_0) \sin(\theta/2)$, with n and λ_0 being the solvent refractive index and the wavelength of the light in vacuum, respectively.

As for triblock copolymers in a selective solvent, the result becomes even more complicated because triblock chains can form flower-like micelles or inter-connected clusters or even a gel network, depending on whether the solvent is selectively good for the middle or the two end blocks. To our knowledge, only a limited number of studies related to the chain dynamics of triblock copolymers in selective solvent have been published so far[30]. Nystrom and Kjoniksen[31] observed two relaxation modes for triblock PEO-PPO-PEO copolymers in semidilute solution in a certain range of concentration and temperature. They found that the fast mode was diffusive, while the slow mode was strongly dependent on the scattering vector *(q), **i.e.***, $1/\tau_s \propto q^3$. Using both dynamic LLS and pulsed-field gradient NMR, Konak *et al.*[30,32] studied triblock PS-PEB-PS and PS-PHB-PS copolymers in n-heptane, a solvent selectively good for the middle PEB and PHB block and found three relaxation modes. They attributed the fast mode to the collective diffusion of physically interconnected nodes and the middle mode to local motions of nodes trapped in a physical gel network; but no satisfactory interpretation of the slow mode was given. Using a combination of LLS, small-angle neutron scattering (SNAS) and viscometry, Raspaud *et al.*[33] studied triblock PS-PI-PS copolymer in n-heptane, a solvent selectively good for the middle PI block and also found three relaxation modes. They attributed the middle mode to the node jumping from one cage to another; and the slow mode to the cutoff in the distribution of the number of polystyrene blocks. Table 1 summarizes some of the past studies of polymers in different semidilute solutions. It is clear that in semidilute solution, especially for block copolymers, there is still no clear understanding of the middle and the slow relaxation modes.

Table 1. Summary of literature values of scaling exponent α_s between characteristic decay time ($<\tau>$) and scattering vector *(q)* in $1/\langle\tau_s\rangle \sim q^{\alpha_s}$

Literature	Balsara; Stepamck; Lodge; Tirell Macromolecules, 1991, 24: 6227	Konak; Helmstedt and Bansil Macromolecules, 1997, 30: 4342	Konak; Helmstedt and Bansil Macromolecules, 1996, 26: 6158
Polymer	Poly(styrene-isoprene)	Poly(St-b-MMA)	PMMA, Poly(MMA-co-EDMA)
Solvent	Toluene	Acetone	4-Heptanone
M_w (g/mol)	3.1×10^4	1.7×10^6 9.1×10^5 5.9×10^5 4.9×10^5	1.3×10^6
α_s	3.0	4.5 3.0 3.0 2.5	2.6
Literature	Esquent; Buhler Macromolecules, 2002, 35: 3708	Kjoniksen; Nystrom Macromolecules, 1996, 29: 7116	Koike; Nemoto; Inoue Macromolecules, 1995, 28: 2339
Polymer	Polysaccharide	PVA	PVA
Solvent	Water	Water	Water
M_w (g/mol)	9.0×10^5	5.3×10^4	0.26×10^5-1.1×10^5
α_s	3.0	2.0-2.4	2.0-3.0
Literature	Koch; Strobl; Stuhn, Polymer, 1993, 34: 1988	Stepanek; Brownm. Macromolecules, 1998, 31: 1889	Faraone; Magazu; Ponterio; Villar. Macromolecules, 1999,32: 1128
Polymer	Polyisoprenes, Polystyrene	Polystyrene	PMMA
Solvent	Toluene	Benzene	Acetone
M_w(g/mol)	1400 and 430	2×10^3-20×10^6, (Γ_{s1},Γ_{s2}, Γ_{s3})	1×10^4-8×10^5
α_s	2.0	$\alpha_{s1}\sim2$, $\alpha_{s2}\sim0$, $\alpha_{s3}\sim2$	0
Literature	Heckmeier; Mix; Strobl Macromolecules, 1997, 30: 4454	Ngai; Wu Macromolecules, 2003, 36: 848	Nystrom; Kjoniksen Langmuir, 1997, 13:4520
Polymer	Polystyrene	Poly(MMA-co-coumarin)	PEO-PPO-PEO
Solvent	Toluene	Chloroform	Water
M_w (g/mol)	8×10^4	2.12×10^5	1.04×10^4
α_s	2.0	3.0	3.0

Recently, Huang *et al.*[3a] found an unexpected inverted micelle phase in a thin film cast from a dilute solution of PS_{210}-b-PB_{960} in toluene, *i.e.*, the major component PB becomes the dispersed phase, if the solvent is quickly removed by evaporation. Note that toluene is a good solvent for both PS and PB in dilute solution. Following this strange finding, they discovered that triblock PS_{200}-b-PB_{1815}-b-PS_{200} copolymer (containing almost two PS_{210}-b-PB_{960} chains) also had such a strange phase behavior[3b]. It is not difficult to visualize that during the evaporation, the solution first changes into semidilute and then becomes concentrated before the formation of a bulk thin film. We suspected that even toluene is a good solvent for both PS and PB in dilute solution, but in semidilute solution, it might become a relatively less good solvent for PB. Therefore, the PB and PS blocks might tend to segregate to form transient PB and PS richer domains. However, the driving force for the segregation is very weak because toluene is still a good solvent for both PB and PS. When the solvent is slowly evaporated, thermodynamics has time to play a determining role so that the minor component PS forms the expected disperse phase. On the other hand, the fast removal of toluene could kinetically freeze transient PB and PS richer domains to form the unexpected inverted micellar morphology. In order to support such a speculation, we designed the present study of the chain dynamics of a pair of diblock PS_{210}-b-PB_{960} and triblock PS_{200}-b-PB_{181}-b-PS_{200} chains during the solvent evaporation. There were two objectives in our minds. One is to conduct a comparative study of the concentration dependence of the chain dynamics of diblock and triblock copolymers in good solvent. Another is to find whether there exist transient PB and PS richer domains during the solvent evaporation, which should be reflected in a different chain dynamics between PS_{210}-b-PB_{960} and PS_{200}-b-PB_{1815}-

b-PS_{200}.

EXPERIMENTAL

Sample Preparation

Poly(styrene-b-butadiene) (PS_{210}-b-PB_{960}) and poly(styrene-b-butadiene-b-styrene) (PS_{200}-b-PB_{1815}-b-PS_{200}) were purchased from Aldrich Chemical Co. (Milwaukee, WI). The weight average molar masses (and polydispersity index M_w/M_n) of PS_{210}-b-PB_{960} and PS_{200}-b-PB_{1815}-b-PS_{200} are 7.4×10^4 g/mol (and ~1.1) and 1.4×10^5 g/mol (and ~1.2), respectively. The weight content of polystyrene is ~30%. The overlap concentrations (c*) estimated from $3M/(4\pi N_A R_g^3) < c^* < M/(2^{3/2} N_A R_g^3)$ are in the range 1.2×10^{-2}-1.8×10^{-2}g/mL for PS_{210}-b-PB_{960} and 0.96×10^{-2}-1.4×10^{-2} g/mL for PS_{200}-b-PB_{1815}-b-PS_{200}, respectively. For LLS measurement, dilute solutions with $c < c^*$ were first prepared in toluene. The solution was clarified by a 0.2 μm Millipore filter to remove dust. The solvent was gradually removed under vacuum from a LLS cell. The concentrations at different stages were determined by weighing.

Laser Light Scattering (LLs)

The details of LLS instrumentation and theory can be found elsewhere[34,35]. All the measurements were done at (25.0 ± 0.1)°C. In dynamic LLS, the intensity-intensity time correlation function $G^2(t, q)$ in the self-beating mode was measured, where t is the delay time. $G^{(2)}(t, q)$ can be related to the normalized first-order electric field-electric field time correlation function $|g^{(1)}(\tau, \theta)| = [<E(0,q)E^*(t,q)>]$ as[36]

$$G^{(2)}(t, q) = \langle I(0, q)\, I(t, q)\rangle = A[1 + \beta |g^{(1)}(t,q)|^2] \quad (1)$$

where A [≡ $<I(0)>^2$] is the measured baseline and β is the coherent factor, depending on the detection optics. For broadly distributed relaxation, $|g^{(1)}(t, q)|$ is related to a characteristic relaxation (decay) time distribution G(τ) as

$$|g^{(1)}(t, q)| = \int_0^\infty G(\tau) e^{-t/\tau} d\tau \quad (2)$$

G(τ) can be calculated from the Laplace inversion of the measured $G^{(2)}(t,q)$ on the basis of Eqs. (1) and (2). In this study, the CONTIN program in the correlator was used[37].

RESULTS AND DISCUSSION

Figure 1 shows typical double logarithmic plots of intensity-intensity time correlation functions of PS_{210}-b-PB_{960} and PS_{200}-b-PB_{1815}-b-PS_{200} in both dilute and semidilute solutions, respectively. When $c < c^*$, there is only one decay, which can be attributed to the mutual diffusion of individual copolymer chains. As the concentration increases, another slow relaxation appears in the tail of $G^{(2)}(t, q)$. Such a slow relaxation mode was previously related to large spatial density fluctuation in the study of homopolymer[8] or to the formation of polymer clusters in the study of copolymers in selective solvent[11]. The Laplace analysis of each measured $G^{(2)}(t, q)$ resulted in a characteristic decay time distribution G(τ), as shown in Fig. 2. It clearly shows that the appearance of the slow relaxation (second peak) with a longer τ appears as the concentration increases. The first fast relaxation peak slightly shifts to the lower τ direction, indicating that the fast relaxation becomes faster. This is understandable because the average length of the chain segments between two neighboring entanglement points decreases with increasing concentration.

Figure 2 shows that in the semidilute regime ($c < c^*$), there is a difference between the two block copolymers; namely, tri-block chains have an additional relaxation mode. It is helpful to note that the Laplace analysis is an ill-condition problem. Therefore, we are not so sure whether the additional middle mode is real or is due to the split of a broadly distributed slow relaxation in the analysis. However, it at least shows that the slow relaxation is more broadly distributed for the triblock chains. Note that each tri-block chain is twice as long as its counterpart, the diblock chain, so that PS_{200}-b-PB_{1815}-b-PS_{200} has a lower c than PS_{210}-b-PB_{960} because $c^* \propto M^{1-3v}$ as discussed before. In Fig. 2, the PS_{210}-b-PB_{960} concentrations used are much higher than the corresponding c^*

(~ 1.5 × 10 ^{2}g/mL). In comparison, PS$_{200}$-b-PB$_{1815}$-b-PS$_{200}$ concentrations are relatively close to its c*(~ 1.0 × 10 ^{2}g/mL). Therefore, the appearance of the additional middle relaxation or a broad slow relaxation mode can not be attributed to the effect of concentration. We will come back to this point after examining the scattering vector *(q)* dependence of the chain dynamics.

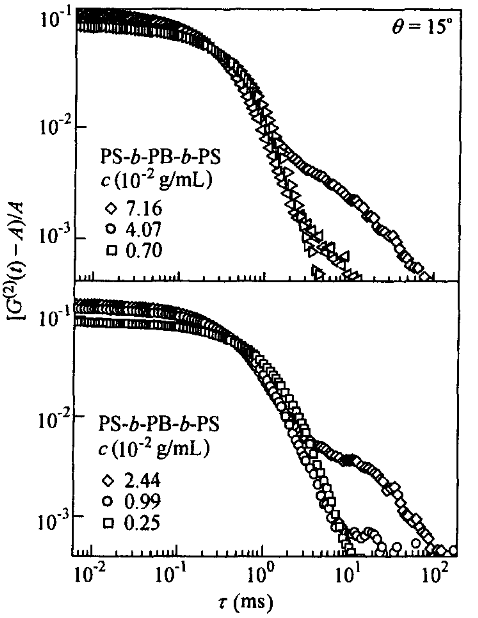

Fig. 1 Concentration dependence of intensity-intensity time correlation functions of diblock and triblock copolymers in toluene, where the scattering angle is 15°

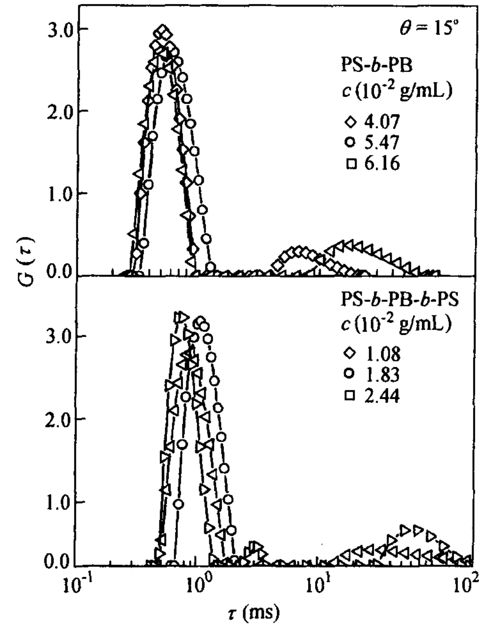

Fig. 2 Concentration dependence of characteristic decay time distribution G(τ) of diblock and triblock copolymers in toluene

Figure 3 shows that for a given concentration in the semidilute regime (c > *c**), the peak position related to the fast relaxation at different scattering angles remains unchanged after τ is scaled by q^2, indicating that the plot of $1/\langle\tau_f\rangle$ ($\equiv\langle\Gamma_f\rangle$) versus q^2 should be a straight line passing through the origin. Figure 4 shows such plots for different concentrations. It clearly reveals that the fast relaxation is diffusive for both PS$_{210}$-b-PB$_{960}$ and PS$_{200}$-b-PB$_{1815}$-b-PS$_{200}$ in semidilute solutions. As for the slow relaxation mode, Fig. 5 shows that $1/\langle\tau_s\rangle$ ($\equiv\langle\Gamma_s\rangle$) can be scaled to q as $1/\langle\tau_f\rangle \sim q^{\alpha_s}$ with α_s in the range 2.0-2.4 and 2.3-2.4 for diblock chains and triblock chains, respectively, in different concentrations. Previously, we found that such a deviation of α_s from 2 could be attributed to an insufficient observation length scale *(1/q)* used in LLS[8]. The disappearance of the slow relaxation mode at a higher scattering angle (a smaller observation length $1/q$) suggests that the slow relaxation corresponds to larger scale fluctuation. Similarly, the middle relaxation mode also disappears at high scattering angles.

As discussed before, $<\tau_f>$ can be related to the average cooperative diffusion coefficient $<D_c>$ by $1/<\tau_c> = <D_c>q^2$ and $<D_c>$ can be further related to the dynamic correlation length ξ_D by $\xi_D = k_BT/(6\pi\eta D_c)$. Note that D_c can be scaled to the c as $D_c = D_0(c/c^*)^\alpha$, where D_0 is the translational diffusion coefficient of the chain at infinite dilution and $\alpha = v/(3v - 1)$ defined before[15]. Figure 6 shows that ξ_D deduced from $<\tau_f>$ decreases with increasing concentration (c) with $\alpha_s = 0.46 \pm 0.04$ for PS$_{210}$-WB$_{960}$ and 0.37 ± 0.03 for PS$_{200}$-b-PB$_{1815}$-b-PS$_{200}$-However, it has to be noted that the concentration range used in this study is very limited and one should not be too serious about the exact values of α. The only conclusion that could be obtained from Fig. 6 is that α for the two block copolymer semidilute solutions is much smaller than 0.75 predicted by the scaling theory[6] or (0.70 ± 0.02) observed for linear homopolymer chains in semidilute solutions under a good solvent condition[13]. It is worth noting that Amis and Han[15] and Chu[11] also observed lower values of α, which was attributed to the marginal solvent quality.

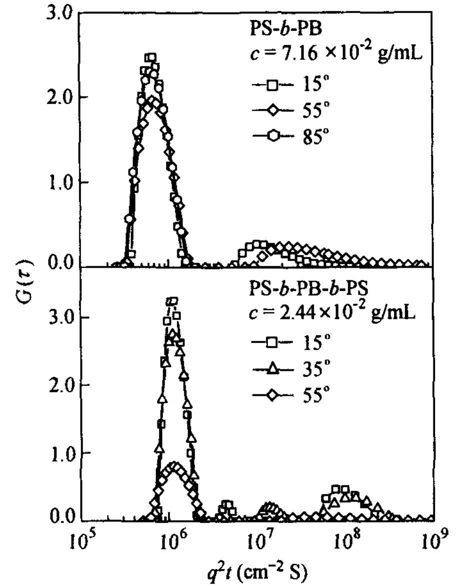

Fig. 3 Scattering angle dependence of characteristic decay time distribution $G(\tau)$ of diblock and triblock chains in toluene for a given concentration well above the overlap concentration ($c^* \sim 1.5 \times 10^{-2}$g/mL for PS$_{210}$-b-PB$_{960}$ or~ 1.2×10^{-2}g/mL for PS$_{200}$-b-PB$_{1815}$-b-PS$_{200}$)

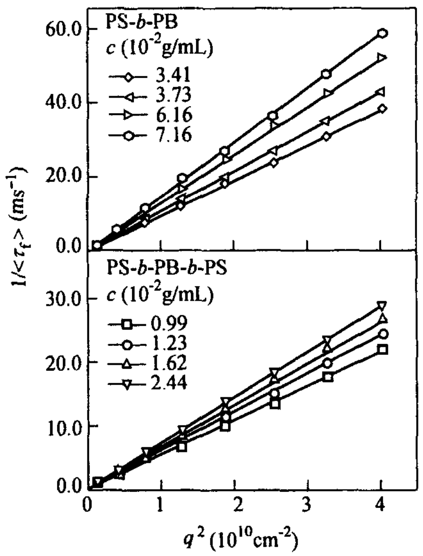

Fig. 4 Scattering vector (q) dependence of average characteristic decay time ($\langle\tau_f\rangle$) of fast relaxation for diblock and triblock chains in semidilute toluene solution

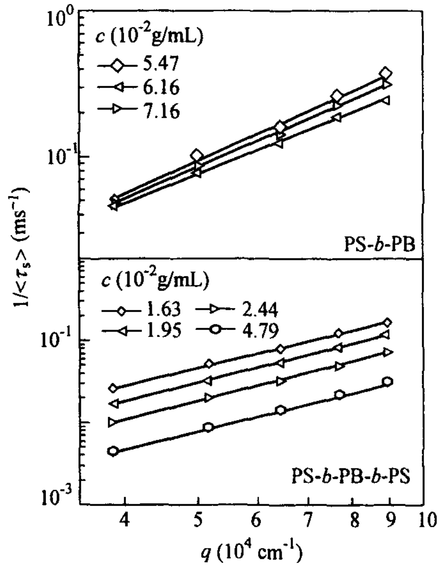

Fig. 5 Scattering vector (q) dependence of average characteristic decay time ($\langle\tau_s\rangle$) of slow relaxation for diblock and triblock chains in semidilute toluene solution

Finally, let us come back to discuss why there is a difference between the slow dynamics of PS$_{210}$-b-PB$_{960}$ and PS$_{200}$-b-PB$_{1815}$-b-PS$_{200}$ in good solvent. Our studies reveal that in the dilute regime, toluene is a relatively less good solvent for the triblock copolymer because of its smaller value of the second virial coefficient A_2, as shown in Fig. 7. This can be explained as follows. One PS$_{200}$-b-PB$_{1815}$-b-PS$_{200}$ chain can be viewed as a connection of two PS_{210}-b-PB_{960} chains. For a given good solvent, they should have a very similar change of enthalpy (ΔH), but a different change of entropy (ΔS) in the dissolution. The dissolution of the triblock chains has a smaller ΔS due to the connectivity so that the decrease of ΔG ($\equiv \Delta H - T\Delta S$) is less, resulting in a lower solubility.

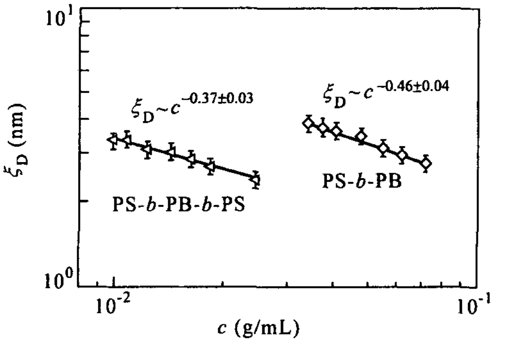

Fig. 6 Copolymer concentration dependence of dynamic correlation length (ξ_D) for diblock and triblock chains in semidilute toluene solution, where the definition of ξ_D can be found in the text

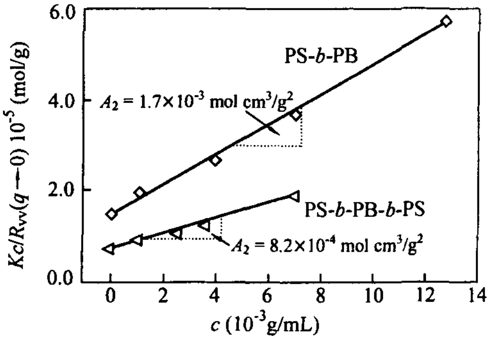

Fig. 7 Concentration dependence (c) of Rayleigh ratio ($R_{vv}(q \to 0)$) for diblock and triblock chains in dilute toluene solution, where K is a constant defined in the text

On the other hand, it is known that toluene is a better solvent for PS, even that it is also a good solvent for PB. It is reasonable for us to speculate that as the concentration increases, besides the expected overlap of the chains, the possible segregation of the PB and PS blocks could lead to transient PB or PS richer domains in semidilute solution. Based on such a speculation, we could explain why there was the middle relaxation mode for the triblock chains as well as the inverted micelle phase when toluene was quickly removed in the formation of a thin film. For the diblock chains, the transient PB richer domains are surrounded by the PS richer domains, as schematically shown in Fig. 8(a). However, we have to distinguish them from the core-shell-like micelle formed in a selective solvent because there is no strong attraction between the PB blocks and the PB blocks are still in the swollen state. The PB richer domains contain the PS blocks and the PS richer domains contain the PB blocks. The slow relaxation could be attributed to the spatial fluctuation of these transient PB and PS richer domains because each PB or PS block can move from one domain to another. It is expected that such PB and PS domains were poorly defined in space so that the slow relaxation mode was broadly distributed.

For the triblock chains, the longer PB block in the middle is even less soluble. Therefore, in the formation of transient PB and PS richer domains, some of the triblock chains are folded so that the two more soluble PS blocks would be able to stay in the PS richer domain, as schematically shown in Fig. 8(b). It is expected that such a chain folding would be enhanced with increasing copolymer concentration. It is also expected that the relaxation of the chain segments on a folded triblock chain would be slower than that on a triblock chain without the folding, but faster than that of large transient PB and PS richer domains. We intend to attribute the middle relaxation mode to the motions of the folded triblock chains. As discussed before, the Laplace inversion used to calculate $G(\tau)$ is a mathematically ill-conditioned problem. Even a small noise in the measured $G^{(2)}(\tau)$ can leads to a large uncertainty in the resultant $G(\tau)$. Therefore, we are not so confident whether the middle relaxation mode is real or is due to the splitting of a broadly distributed slow relaxation mode. However, what we do know is that the slow relaxation of the triblock chains, presumably related to the transient PB and PS richer domains, has a much broader spectrum than that of the diblock chains.

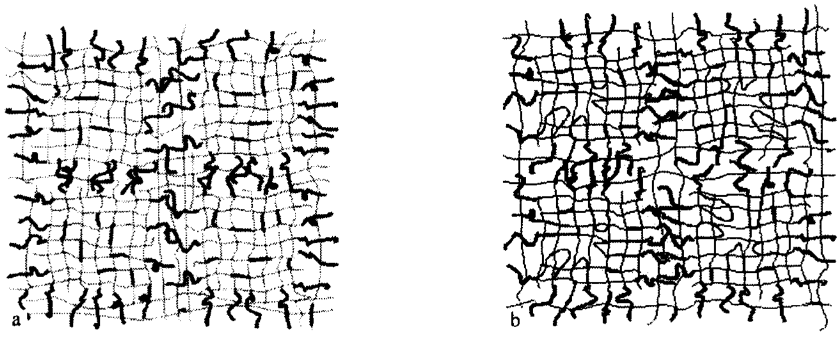

Fig. 8 Schematic of segregation of PB and PS blocks in semidilute toluene solution for (a) diblock chain (∿) and (b) triblock chain (∿), in which PB blocks (—) are relatively less soluble than PS blocks (—) even toluene is a good solvent for both PS and PB.
a) Poly(styrene-b-butadiene); b) Poly(styrene-b-butadiene-b-styrene)

To support the above speculation, we synthesized a triblock polyisoprene-b-polystyrene-b-polyisoprene (*PI-b-PS-b-PI)* copolymer and studied its chain dynamics in cyclohexane. This is because cyclohexane is a good solvent for both PS and PI at higher temperatures, but becomes a less good solvent for PS at lower temperatures. Figure 9 shows that an additional slow relaxation mode appears in the characteristic decay time distribution G(τ) at lower temperatures. It is helpful to note that for ultra-long PS chains in cyclohexane, the high critical solution temperature (HCST) is close to the θ-temperature of ~ 34.5 °C. The UCST of PS in cyclohexane sharply decreases with decreasing chain length. For example, the UCST is only ~ 28 °C for PS chains with $M_w \sim 8 \times 10^6$ g/mL[38]. For the present triblock copolymer in dilute solution (10^{-3} g/mL), the UCST of the short middle PS block is so low that no interchain aggregation was observed even at a temperature as low as 10°C, indicating that cyclohexane in the temperature range studied is not a selective solvent for the short PS block. Moreover, we found that the characteristic decay time distribution in dilute solution (10^{-3} g/mL) remains a single peak in the same temperature range. Therefore, the additional slow relaxation mode can be attributed to the transient segregation of two different polymer blocks in semidilute/concentrated solution when there is a difference in their solubility even if the solvent is not a selective solvent. More research in this direction is certainly needed.

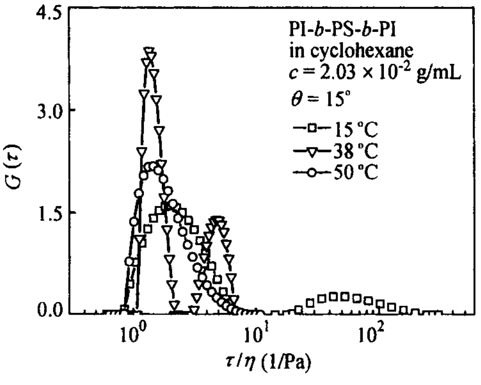

Fig. 9 Temperature dependence of characteristic decay time distribution *G(τ)* of triblock PI-b-PS-b-PI copolymers in cyclohexane
For a better comparison, the characteristic decay time (τ) in x-axis has been corrected by the solvent viscosity *(η)* at each temperature

CONCLUSION

Gradual evaporation of solvent from a diblock poly(styrene-b-butadiene) PS_{210}-b-PB_{960} or triblock copolymer poly(styrene-b-butadiene-b-styrene) PS_{200}-b-PB_{1815}-b-PS_{200} toluene solution enabled us to perform a comparative dynamic laser light scattering (LLS) study of chain dynamics during the dilute-to-semidilute transition. As expected, there is only one fast relaxation mode in dilute solution, corresponding to the mutual diffusion of individual chains. As the solution changes from dilute to semidilute, the fast relaxation remains, but becomes slightly faster. The characteristic decay time ($<\tau_f>$) of the fast relaxation is scaled to the scattering vector q as $1/\langle\tau_f\rangle - q^{2.0 \pm 0.1}$ for both the copolymers, indicating its diffusive nature. Such a fast relaxation is related to the cooperative diffusion of the chains segments (blobs) between two neighboring entanglement points. In the semidilute regime, beside the fast relaxation, the chain overlap leads to a second slow relaxation mode for both the copolymers. For the slow relaxation, the relationship of $1/<\tau_s> - q^{\alpha}$ gives an α value in the range 2.0-2.4 for PS_{210}-b-PB_{960} and in the range 2.3-2.4 for PS_{200}-b-PB_{1815}-b-PS_{200}. Considering that toluene is a better solvent for PS, we speculate that there might be a segregation to form transient PB and PS richer domains in semidilute solution. The slow mode could be attributed to the spatial fluctuation of such PB and PS richer domains. For the triblock chains, the Laplace inversion of the measured time correlation function shows an additional middle relaxation mode. This middle mode or a possible broader slow mode could be attributed to the folding of some of the triblock chains because of the segregation. The appearance of the middle mode indirectly supports the speculation of a slight segregation of the PB and PS blocks in semidilute solution. Therefore, we can attribute the previously observed inverted micelle phase to kinetically frozen morphology.

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