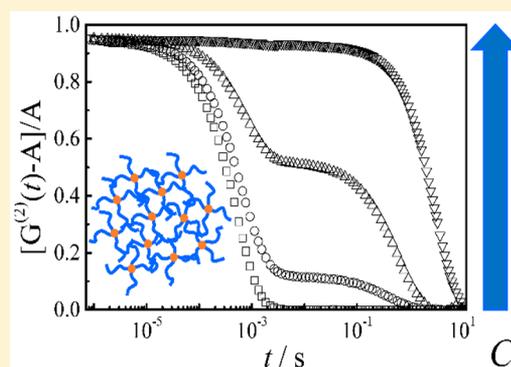


Reexamination of the Origin of Slow Relaxation in Semidilute Polymer Solutions—Reptation Related or Not?

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ABSTRACT: The origin of the slow relaxation observed in dynamic laser light scattering (LLS) measurements of semidilute polymer solutions remains controversial. Even though the chain reptation is invisible in dynamic LLS, the slow relaxation was still attributed to the reptation induced density fluctuation by those who believe that there is no other slow relaxation except the reptation. To clarify such a point, we purposely studied dynamics of semidilute solutions of narrowly distributed 4-arm star polystyrene ($M_w = 1.1 \times 10^5$ g/mol and $M_w/M_n = 1.02$) chains in cyclohexane, wherein the chains are not entangled but topologically constrained. Our results reveal that there still exists a slow relaxation mode besides a fast one that is related to the diffusion of short chain segments (“blobs”) in the semidilute regime, clearly excluding its possible reptation origin. The average diffusion coefficient ($\langle D_f \rangle$) and scattering intensity ($\langle I_f \rangle$) related to the fast mode are scaled to the polymer concentration (C) as $\langle D_f \rangle \sim C^{0.5}$ and $\langle I_f \rangle \sim C^{-0.77}$, different from those for linear chains. For the slow mode, our results show that as C increases, the relaxation slows down but the correlation length becomes shorter, apparently contradicting each other, presumably because individual “blobs” become smaller but more correlated with a correlation length of $\sim 10^2$ nm, reflected in an increase of its related scattering intensity. Since the correlation length of the scattering objects related to the slow mode is comparable to the observation length used in LLS, the average line width of the slow relaxation measured in dynamic LLS contains a mixture of internal motions and diffusion before the blobs become strongly correlated at higher concentrations.



INTRODUCTION

Dynamics of neutral flexible polymers in semidilute/concentrated solutions is an old issue in polymer science. Various theoretical and experimental studies have been designed/executed to address this problem with many fruitful outcomes in the past decades. The solution behavior of polymer chains in dilute solutions wherein polymer chains are isolated from each other has been well understood. As the concentration increases, the polymer chains start to overlap (penetrate) each other at the overlap concentration (C^*), defined as $3M_w/(4\pi N_A R_g^3)$ or $M_w/(2^{3/2}\pi N_A R_g^3)$ or $[\eta]^{-1}$ or $(A_2 M_w)^{-1}$, where M_w , R_g , N_A , $[\eta]$, and A_2 are the molar mass, the radius of gyration, the Avogadro constant, the intrinsic viscosity, and the second virial coefficient, respectively.^{1–4} Note that these definitions are not identical, and the difference between them can be as large as 5 times.⁵ Therefore, how to precisely determine C^* for a given polymer solution remains an experimental challenge. After passing C^* , the solution enters the semidilute regime, in which a fast relaxation related to the cooperative diffusion of the center of mass of short chain segment between two neighboring entanglement points is expected in dynamic laser light scattering (LLS) measurements.^{6–9} However, an additional slow relaxation mode unexpectedly/persistently appears in many polymer solutions.^{2,7,10–19} Since day one, a school of

people have attributed such a slow mode to some experimental defects, including large dust particles or possible concentration gradient introduced during the solution preparation, because there is no such a slow relaxation mode predicted in theory except the chain reptation, which should be invisible in dynamic LLS. It is true that some of earlier experimental results might be contaminated due to some imperfect solution preparation methods used at that time, especially when the solvent used is athermal.

To completely rule out possible defects introduced during the solution preparation, we previously used the high vacuum anionic polymerization to make semidilute and concentrated polystyrene solutions directly in sealed dust-free LLS cells.⁵ We found that de Gennes was correct; namely, in an athermal solvent (polystyrene in toluene), there is no slow relaxation mode even in a solution as concentrated as 50 times C^* . However, in parallel experiments wherein cyclohexane was used as a marginally good solvent, the slow relaxation mode appears and becomes irrefutable and more visible as the solution temperature decreases toward 34.5 °C at which the solvent

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quality becomes less good or the interchain interaction becomes stronger. In the past, various origins of such a slow mode were proposed by those who believe it or cannot deny it, including the reptation related slow density fluctuation,^{6,8,20} the relaxation of a transient network,^{11,21,22} the translational diffusion of large temporal chain aggregates,^{2,14,18,23–26} and internal motions of large transient chain clusters.^{27,28}

In addition to neutral polymers in solutions, we have also revisited the slow relaxation mode appearing in salt-free polyelectrolyte solutions, concentrated polymer dispersions, and polymer gels by designing and synthesizing novel polymers or developing new preparation methods as well as using a combination of static and dynamic LLS.^{29–40} On one hand, a polymer solution or dispersion has to be statically homogeneous; on the other hand, the irrefutable slow mode reveals that polymer solutions in the semidilute regime or concentrated dispersions are dynamically inhomogeneous. Namely, each chain or colloidal particle is inside a “cage” made of its surrounding chains or particles, but at the same time, it is also a part of “cages” for other chains or particles. Qualitatively, the slow mode is related to the relaxation of such “cages”. A quantitative description of the slow mode remains a challenge.

Previously, Li et al.⁵ studied the slow relaxation of linear polystyrene in cyclohexane in the semidilute regime by using two polymer solutions with a similar concentration but 10 times difference in the chain length. On the basis of the reptation theory, the relaxation time of the chain reptation (τ_r) for a linear chain and the number of Kuhn segments (N) follow the scaling of $\tau_r \sim N^3$; namely, 10 times longer chains should lead to a 10^3 -fold increase in the relaxation time.⁸ However, the observed relaxation time of the slow mode is nearly independent of the chain length, indicating that the slow mode is not related to the reptation.

The current study was designed to rule out any possibility of relating the slow relaxation to the reptation related slow density fluctuation in semidilute polymer solutions by examining dynamics of 4-arm star polystyrene chains in cyclohexane in the unentangled semidilute regime. For the star polymers, the chain reptation of f -arm star chains should be practically suppressed within our measurement time (<1 s) due to the topological constrain.⁴¹ Therefore, the center of mass of each star chain is practically localized within a small region in the semidilute regime.^{42,43} If the slow relaxation mode in semidilute polymer solutions was related to the reptation related density fluctuation, we would not be able to observe it in a star polymer solution in dynamic LLS measurements.

EXPERIMENTAL SECTION

Synthesis of 4-Arm Star Polystyrene. The 4-arm star polystyrene was synthesized by high vacuum anionic polymerization technique via the arm-first approach using SiCl_4 as the coupling agent. The crude star polystyrene product was further fractionated using a mixture of toluene (good solvent) and methanol (poor solvent). The fractionation resulted in a 4-arm star polystyrene with an average arm number $f \sim 4$, a weight-average molar mass of $M_w = 1.1 \times 10^5$ g/mol, and a polydispersity index of $M_w/M_n = 1.02$ as determined from a combination of static laser light scattering and gel permeation chromatography.

Solution Preparation. A dilute solution of 4-arm star polystyrene in cyclohexane (RCI Labscan, freshly distilled from CaH_2) was first prepared at 50 °C. The solution was clarified by a hydrophobic PTFE 0.45 μm filter (Millipore, USA) into a specially designed dust-free LLS cell to remove dust. The solvent was slowly evaporated through a 0.22 μm filter in a thermoset 50 °C air bath until a desired concentration

was reached. The solution was sealed and further placed in a thermoset 50 °C air bath for at least 1 week before LLS measurements to avoid any possible concentration gradient. The final concentration used was determined by the gravimetric method. Cyclohexane is a slightly good solvent for polystyrene at higher temperatures, and its solvent quality can be adjusted in the range of 34–50 °C.

Laser Light Scattering (LLS). The commercial LLS spectrometer (ALV/DLS/SLS-5022F) equipped with a multi- τ digital time correlator (ALV5000) and a vertically polarized 22 mW He–Ne cylindrical laser ($\lambda_0 = 632.8$ nm, Uniphase) was used. The details of LLS theory and instrumentation can be found elsewhere.^{3,44,45} In static LLS, the excess absolute time-averaged scattered light intensity at a given scattering vector q , known as the excess Rayleigh ratio $R_v(q)$, of a dilute polymer solution at a concentration C (g/mL) is related to the weight-average molar mass (M_w), the root-mean-square z -average radius of gyration ($\langle R_g^2 \rangle_z^{1/2}$) (or written as $\langle R_g \rangle$), and the second virial coefficient (A_2) as

$$\frac{KC}{R_v(q)} \approx \frac{1}{M_w} \left(1 + \frac{1}{3} \langle R_g^2 \rangle_z q^2 \right) + 2A_2 C \quad (1)$$

where $K = 4\pi^2 n^2 (dn/dC)^2 / (N_A \lambda_0^4)$ and $q = 4\pi n \sin(\theta/2) / \lambda_0$ with N_A , dn/dC , n , θ , and λ_0 being the Avogadro constant, the specific refractive index increment, the solvent refractive index, the scattering angle, and the wavelength of the incident light in a vacuum, respectively.

In dynamic LLS, the measured intensity–intensity time correlation function $G^{(2)}(q,t) \equiv \langle I(q,0)I(q,t) \rangle$, where $I(q,t)$ is the scattering intensity at a given scattering vector (q) and a given delay time (t), is related to the normalized electric field–field time correlation function $g^{(1)}(q,t)$ by the Siegert relation as

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

where $A = (\langle I(q,0) \rangle)^2$ is the measured baseline and β is the coherent factor, depending on the detection optics. For a system with different relaxation modes, $|g^{(1)}(q,t)|$ is generally related to a characteristic line-width distribution $G(\Gamma,q)$ as

$$|g^{(1)}(q,t)| = \int G(\Gamma,q) e^{-\Gamma(q)t} d\Gamma \quad (3)$$

$G(\Gamma,q)$ can be calculated from the Laplace inversion of each measured $G^{(2)}(q,t)$ using the CONTIN program provided by ALV. For a purely diffusive relaxation, the plot of Γ vs q^2 is a straight line passing through the origin, and the slope is the average translational diffusion coefficient constant ($\langle D \rangle$) of the scattering objects. The hydrodynamic radius (R_h) or the dynamic correlation length ξ_D can be calculated by using the Stokes–Einstein equation.

In the current study for two relaxation modes, a combination of the static and dynamic LLS can lead to the excess scattering intensity from each mode (a fast and a slow mode). Namely, $\langle I_f \rangle = A_f \langle I_{\text{total}} \rangle$ and $\langle I_s \rangle = A_s \langle I_{\text{total}} \rangle$, where A_f and A_s are the respective intensity contributions of the fast mode and slow mode resolved from the two peaks in $G(\Gamma,q)$ by using the CONTIN method and $\langle I_{\text{total}} \rangle$ is the time-averaged total excess scattering intensity. Note that $G^{(2)}(q,t)$ is also often analyzed by two stretching exponential decays when there are two physically meaningful relaxation modes.^{19,46,47} In the current study, we tried to avoid it because the two stretching exponential terms with five adjustable parameters are so powerful that can fit any continuous decay curves with less-defined parameters. Since two modes are well separated in this study, the CONTIN analysis provides consistent results without adjustable parameters. All the data presented were collected at 49.3 °C unless stated otherwise.

RESULTS AND DISCUSSION

Figure 1a shows that the time correlation function changes from a single exponential decay (only one fast mode at 78 mg/mL) to a two-step fully relaxed process as the concentration increases, clearly indicating the appearance of an additional slow mode in the semidilute regime of 4-arm star polystyrene in cyclohexane. Further, both the relative contribution and the

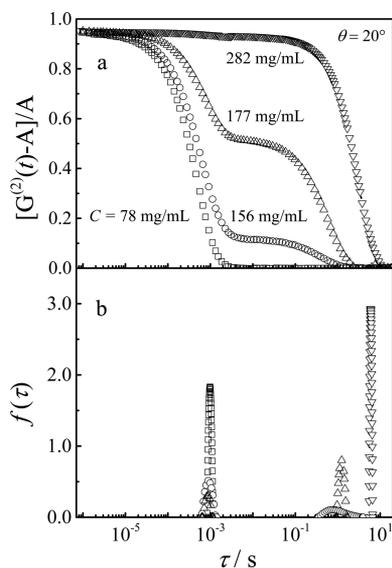


Figure 1. Concentration dependence of (a) normalized intensity–intensity time correlation function and (b) corresponding normalized characteristic decay time distribution of 4-arm star polystyrene in cyclohexane.

average characteristic relaxation time (τ_s) of the slow mode increase significantly with the concentration as indicated by peak area and position in Figure 1b, which clearly reveals that the slow relaxation should not be related to the reptation induced slow density fluctuation because there is no reptation in the unentangled semidilute regime and the reptation of star chains is expected to be extremely slow and invisible within the experimental time window used in dynamic LLS even there was chain reptation. We will address the fast and slow relaxation modes separately to make discussion more clear and avoid possible confusion.

Figure 2 shows that $\langle \Gamma_f \rangle$ is linearly dependent on q^2 , and the extrapolation to $q = 0$ passes through the origin for all the

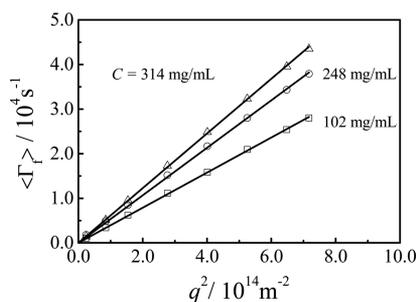


Figure 2. q^2 dependence of average characteristic line width of fast relaxation mode ($\langle \Gamma_f \rangle$) of 4-arm star polystyrene in cyclohexane.

concentrations studied, clearly indicating that the fast mode is a purely diffusive relaxation in the concentration range studied. There is no surprise here because Figure 2 just confirms previous studies on the semidilute polymer solutions in which the fast mode was attributed to the cooperative translational diffusion of the blobs.^{6–9} Each slope in Figure 2 corresponds to an average diffusion coefficient ($\langle D_f \rangle$) that can further lead to the dynamic correlation length of the fast mode ($\xi_{D,\text{fast}}$) in the range of 6–10 nm.

On the other hand, we know that each q^2 dependence of the excess scattering intensity of the fast mode ($\langle I_f \rangle = A_f \langle I_{\text{total}} \rangle$)

leads to the static correlation length ($\xi_{S,\text{fast}}$) on the basis of the Ornstein–Zernike equation, $I(q) = I(q \rightarrow 0)/(1 + q^2 \xi_{S,\text{fast}}^2)$, where A_f is the area of the peak related to the fast mode in Figure 1b and $\langle I_{\text{total}} \rangle$ is the time-averaged scattering intensity measured from static LLS.^{3,33} However, Figure 3 shows that $\langle I_f \rangle$ is nearly independent of q , indicating that $\xi_{S,\text{fast}}$ is much shorter than $1/q$, presumably due to small 4-arm star chains used here.

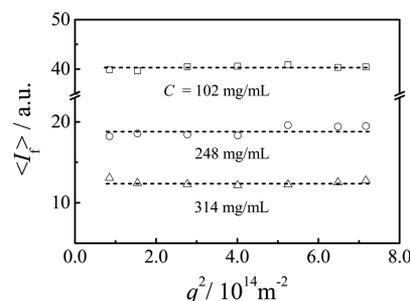


Figure 3. q^2 dependence of average excess scattering intensity ($\langle I_f \rangle$) related to fast mode of 4-arm star polystyrene in cyclohexane at different concentrations. The horizontal dashed lines are guides for the eye.

Figure 4 summarizes the strong concentration dependence of $\langle D_f \rangle$ and $\langle I_f \rangle$ of the fast mode at $q \rightarrow 0$. It is interesting to see

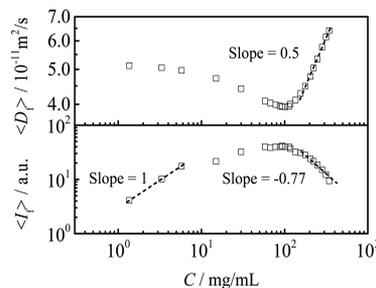


Figure 4. Concentration dependence of average diffusion coefficient ($\langle D_f \rangle$) and excess scattering intensity ($\langle I_f \rangle$) related to fast mode of 4-arm star polystyrene in cyclohexane.

that both of them turn at $C \sim 113$ mg/mL, marking the boundary between the dilute and semidilute regimes. Note that this value is reasonably close to 107 mg/mL calculated from $3M_w/(4\pi N_A \langle R_h \rangle^3)$, where $\langle R_h \rangle$ instead of $\langle R_g \rangle$ is used. When $C < 113$ mg/mL, both of them behave like those characteristically in dilute solutions, and the gradual decrease of $\langle D_f \rangle$ shows a negative dynamic second virial coefficient, presumably due to the hydrodynamic interaction in the marginally good solvent. As expected, $\langle I_f \rangle$ initially increases linearly with the concentration in the dilute regime, i.e., $\langle I_f \rangle \sim C$, then levels off in the crossover region, and finally decreases in the semidilute regime, indicating that the scattering objects change from individual polymer chains to a part comprising short chain segments (“blobs”).³ In the semidilute regime, both of them show a rough power-law dependence on C as $\langle D_f \rangle \sim C^{0.5}$ and $\langle I_f \rangle \sim C^{-0.77}$.

Note that those scalings are much more different from those predicted and measured for linear chains in an athermal solvent, $\langle D_f \rangle_{\text{linear}} \sim C^{0.75}$ and $\langle I_f \rangle_{\text{linear}} \sim C^{-0.25}$,^{8,9,48–50} presumably because 4-arm star chains are less compressible than their linear counterparts with a similar overall molar mass, and cyclohexane

at ~ 50 °C is a marginally good solvent for polystyrene. Previously, Schaefer et al.⁵¹ predicated $\langle D_i \rangle \sim C^{0.5}$ for semiflexible chains in semidilute solutions by the mean-field theory. The less good solvent quality contributes to the deviations. Such deviations were also previously reported for other polymer solutions.^{4,10,13,14,52–54} It is worth noting that this turning point experimentally marks the overlap concentration (C^*), which is more precise than those defined before. Hereafter, we will use it as the overlap concentration for the current study of 4-arm star polystyrene in cyclohexane.

Figure 5 clearly shows the time correlation function begins to show a two-step relaxation behavior at $C = 117$ mg/mL, slightly

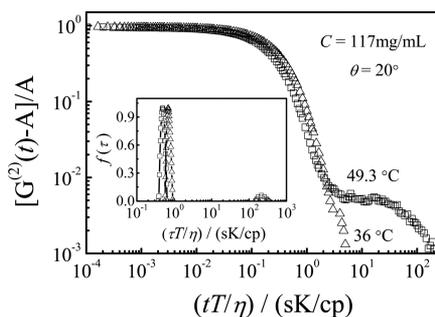


Figure 5. Temperature dependence of normalized intensity–intensity time correlation functions of 4-arm polystyrene in cyclohexane, where delay time (t) and characteristic relaxation time (τ) are scaled to remove effects of solvent viscosity (η) and temperature (T).

higher than the turning point concentration in Figure 4 at 49.3 °C. On the other hand, decreasing the solution temperature changes the relaxation from two modes to a single one, namely, from the semidilute regime to the dilute regime. Note that the concentration ($C = 117$ mg/mL) used is slightly higher than the overlap concentration ($C = 113$ mg/mL) at 49.3 °C. The shrinking of each polystyrene arm as the temperature decreases detaches star chains from each other so that the solution changes from semidilute to dilute.^{55–60} The additional relaxation at 49.3 °C is 10^2 – 10^3 times slower than the single one at 36.0 °C. A similar change was also observed for linear polystyrene chains in cyclohexane.⁵

Previously, Chu et al.^{61,62} also pointed out that the bimodal relaxation behavior could be observed in dynamic LLS during the crossover from the dilute regime to the semidilute regime. The appearance of the slow mode is a better experimental mark for the overlap concentration, which is reasonably close to the value determined from the concentration dependence of the fast mode behavior. Note that such an overlap concentration was also previously suggested.⁵²

Figure 6 shows that after the delay time (t) is normalized by q^2 , the fast relaxation appears at a similar delay time and nearly independent of the scattering angle, which is expected for a purely diffusive relaxation. Also note that the dynamic correlation length ($\xi_{D,fast}$) of the fast mode is only ~ 7.5 nm and $q\xi_{D,fast} \ll 1$. On the other hand, both the amplitude (the intensity contribution) and the characteristic decay time of the slow mode decrease with the scattering angle. The shifting of the slow mode toward a longer normalized delay time even after the q^2 scaling reveals that the slow relaxation is not purely diffusive. Note that $1/q$ is the observation length in LLS. At $\theta = 20^\circ$ and 142° , $1/q \sim 200$ and 35 nm, respectively. The diminishing of the slow mode at $\theta = 142^\circ$ indicates that the slow relaxation involves a dimension length much longer than

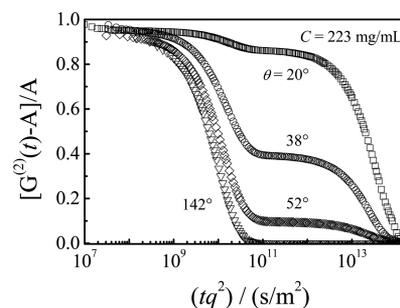


Figure 6. Angular dependence of normalized time correlation function of 4-arm star polystyrene in cyclohexane, where the delay time is scaled with q^2 .

$1/q$. The dominance of the slow mode at $\theta = 20^\circ$ further indicates that the slow relaxation occurs over a length scale of $\sim 10^2$ nm.

Figure 7a shows that the average characteristic relaxation time ($\langle \tau_s \rangle$) becomes longer and longer, following a scaling of

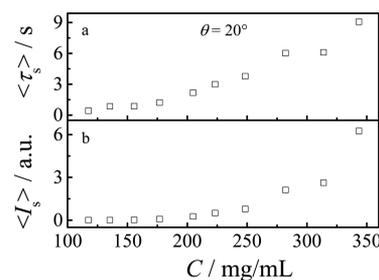


Figure 7. Concentration dependence of (a) average characteristic relaxation time ($\langle \tau_s \rangle$) and (b) excess scattering intensity ($\langle I_s \rangle$) of slow relaxation of 4-arm star polystyrene in cyclohexane in semidilute regime.

$\langle \tau_s \rangle \sim C^{2.8}$ as the concentration increases. The results in Figure 7 reveal that the slow relaxation involves a density fluctuation over a scale much longer than the blob size associated with the fast mode; namely, the movements of a number of the “blobs” become correlated, as indicated by the increase of the excess scattering intensity of the slow mode with C in Figure 7b. Qualitatively, we can define those correlated “blobs” as a “cage” in which they are affected by each other and its correlation length as the cage dimension. Note that the relaxation of the “cages” should not be linked to the diffusion away of one star chain from its surrounding ones. Instead, the “cage” means a number of correlated blobs that are agitated by the thermal energy.

Figure 8 shows that for a given scattering angle the average excess scattering intensity ($\langle I_s \rangle = A_s I_{total}$) related to the slow relaxation mode significantly increases with the concentration, reflecting that more chain segments (“blobs”) are correlated with each other. Figure 8 also shows that $\langle I_s \rangle$ scales exponentially to the scattering vector (q) as predicted by Porod’s law,⁶³ i.e., $\langle I_s \rangle \sim q^{-n}$, where n is the Porod number of a scattering object. In the LLS theory, $n = 6 - D$, where D is the mass fractal dimension of the scattering objects.⁶⁴ Figure 9 shows that n initially increases with the concentration and reaches a plateau value when $C > \sim 250$ mg/mL. The increase of n from ~ 2.8 to ~ 4.3 indicates that the density of the scattering objects changes from uniform ($D \sim 3$) to fractal ($D \sim 2$).⁶⁵

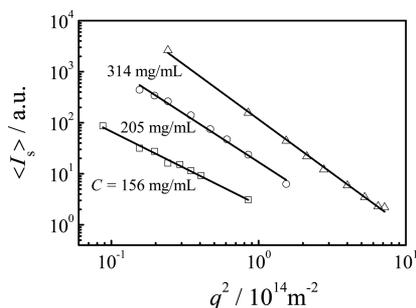


Figure 8. q^2 dependence of average excess scattering intensity ($\langle I_s \rangle$) related to slow relaxation of 4-arm star polystyrene in cyclohexane at different polymer concentrations, where solid lines are results of Porod's fitting.

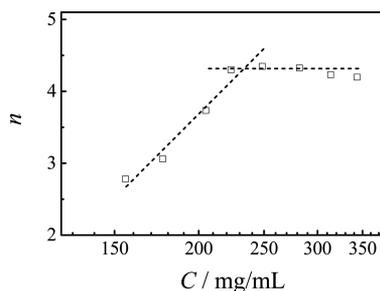


Figure 9. Concentration dependence of Porod's number (n) related to slow relaxation in semidilute regime. The dashed lines are guides for the eye.

The concentration and angular dependence of the slow mode clearly reveals that the origin of the slow mode is not the chain reptation related density fluctuation because the chains are not entangled so that there is no chain reptation here and the center of each chain should not relax a longer distance in the time window used in dynamic LLS due to the topological constrain. The origin of the slow relaxation in the semidilute solutions remains a challenging question. It should be noted that the slow relaxation mode has also been repeatedly observed in other crowded systems, including supercooled liquids, concentrated colloidal dispersions, and glassy systems.^{66–74} Theoretically, star chains could be viewed as a bridge between linear chains and microgels (soft colloidal particles).^{72,75}

Recent simulation showed a crossover from the polymer-like to particle-like behavior for star polymer chains with ~ 5 arms.⁷⁶ After considering the equivalence between the effects of decreasing the solution temperature and increasing the polymer concentration, Phillips⁷⁷ linked the slow mode observed in the glass transition to that in a neutral polymer solution. Similarly, the mode coupling theory (MCT) developed for the glassy dynamics was also adopted to analyze our current results, i.e., viewing a star chain as a soft particle.

In a glassing system, a two-step decay of the correlation function becomes a general feature as the system approaches the glass transition temperature (T_g). The MCT describes this two-step relaxation as the cage effect.^{78–80} The thermal energy ($k_B T$) agitates each particle to diffuse randomly within the “cage” made of its surrounding particles on a short time scale or over a short distance, which is the fast relaxation. On a longer time scale or over a longer distance, the dynamics is related to the cage relaxation, named as the α relaxation, phenomenologically resembling the slow mode observed in the semidilute

regime. The cage size can be calculated from the Debye–Waller relation, $A_s(q, C) \sim \exp[-q^2 \langle l \rangle^2 / 6]$,^{81–83} where $\langle l \rangle$ is the average concentration-dependent static correlation length of the “cages”. Figure 10 shows that $A_s(q, C)$ vs q^2 indeed reasonably follows the Debye–Waller relation and the slope leads to $\langle l \rangle$.

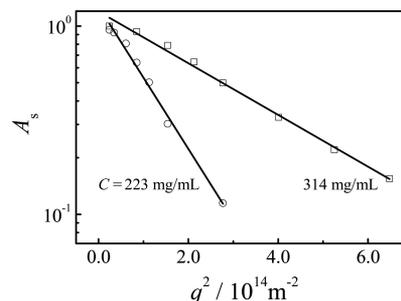


Figure 10. q^2 dependence of normalized intensity contribution of slow relaxation mode of 4-arm star polystyrene in cyclohexane, where solid lines are fittings of the Debye–Waller factor expression.

Figure 11 reveals that the average correlation length of the “cages” quickly shortens as the polymer concentration

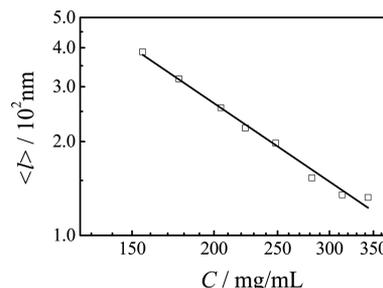


Figure 11. Concentration dependence of average static correlation length of “cages” of 4-arm star polystyrene in cyclohexane.

increases, following a scaling of $\langle l \rangle \sim C^{-1.4}$, similar to that reported for the dynamics of fractal colloidal gels.⁸⁴ Normally, for a purely diffusive process, a smaller object relaxes faster. However, a combination of Figures 7 and 11 shows that as the concentration increases, the relaxation becomes slower but the cage correlation length also shortens, and at the same time, the scattering intensity related to the slow mode increases, suggesting that the slow relaxation is not purely diffusive. Physically, as the concentration increases, the blobs become smaller but more correlated. In other words, the cage becomes smaller but also relaxes slower.

Figure 12 shows that unlike the fast mode, the average line width of the slow mode is not linearly dependent on q^2 , especially at higher concentrations, indicating that the slow relaxation is not purely diffusive. The double-logarithmic plot of $\langle \Gamma_s \rangle$ versus q leads to a scaling between them. Figure 13 summarizes the scaling exponent (α) between $\langle \Gamma \rangle$ and q for both the fast and the slow modes. Clearly, the fast relaxation is purely diffusive with $\alpha_{\text{fast}} = 2$, independent of the polymer concentration, further confirming that it is related to the diffusive relaxation of individual short chain segments (blobs) around their centers of mass. The slow relaxation behaves much more complicated, similar to what we previously found for linear polystyrene in cyclohexane in the semidilute regime at ~ 50 °C.⁵

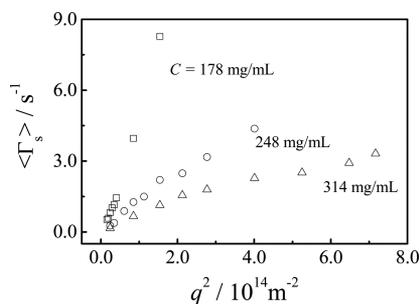


Figure 12. q^2 dependence of average characteristic line width of slow relaxation ($\langle \Gamma_s \rangle$) of 4-arm star polystyrene in cyclohexane at different concentrations.

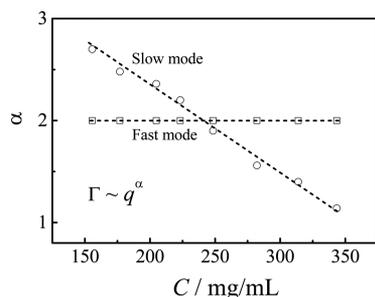


Figure 13. Concentration dependence of scaling exponent (α) on $\Gamma \sim q^\alpha$ of fast and slow relaxation of 4-arm star polystyrene in cyclohexane, where dashed lines are guides for the eye.

When $C < \sim 250$ mg/mL, $\alpha_{\text{slow}} > 2$, indicating that the slow relaxation is subdiffusive, as described by the MCT.⁸⁰ At higher concentrations $\alpha_{\text{slow}} < 2$, suggesting a hyperdiffusive behavior. The slow relaxation tends to behave like a ballistic motion ($\Gamma \sim q$) of an elastic body at much higher concentrations. The crossover point ($\alpha_{\text{slow}} = 2$ in Figure 13) is ~ 250 mg/mL, close to that shown in Figure 9, the concentration dependence of n , indicating where the MCT starts to break down, presumably because the concentrated solution made of densely packed star chains might start to behave more like an elastic body. Note that such a hyperdiffusive or ballistic behavior is also observed in fractal colloidal gels, concentrated dispersions, dense ferrofluids, and concentrated surfactant phases.^{80,85,86} Cipelletti et al.^{85,87,88} suggested that there were some random microcollapses between densely packed particles caused by the interparticle interaction, which might induce a strain field, leading to the movement of surrounding chains and resulting in the ballistic motion detected by dynamic LLS. However, we are not convinced by such a microcollapse assumption because there is no convincing evidence for such a static inhomogeneity in polymer solutions. Instead, we only know the existence of an additional slow nonpurely diffusive density fluctuation in the semidilute regime of polymer solutions when the solvent is not athermal.

Quantitatively, it indicates that as the polymer concentration increases, more and more chain segments (“blobs”) are correlated because the related scattering intensity ($\langle I_s \rangle$) increases with the concentration, but at the same time, the average correlation length of these interacted “blobs” decreases, reflected in the decrease of $\langle l \rangle$, and the relaxation significantly slows down since $\langle \tau_s \rangle$ becomes longer and longer. It should be noted that the observation length ($1/q$) in our study is only in the range of 35–200 nm. The apparent contradiction of more interacted “blobs” with a short correlation length should be

attributed to the decrease of the average size of the “blobs” as the concentration increases. If a scattering object is much larger than $1/q$, dynamic LLS probes its internal motions, i.e., $\alpha \sim 3$, even if it is diffusive; and if its size is slightly larger than $1/q$, dynamic LLS measures a combination of internal motions and diffusion so that $3 > \alpha > 2$. A combination of Figures 11 and 13 reveals that in the concentration range of 150–250 mg/mL ~ 390 nm $> \langle l \rangle > \sim 200$ nm and $2.8 > \alpha_{\text{slow}} > 2$, which is what we have expected for a mixture of internal motions and diffusion. In other words, the results in Figures 11 and 13 are consistent and agree with each other.

CONCLUSION

Using the topological constrain of star polystyrene chains in a marginally good solvent (cyclohexane at ~ 50 °C) in the unentangled semidilute regime, we have excluded the possible origin of the additional slow relaxation mode observed in dynamic LLS from the reptation-related density fluctuation. Our results demonstrate that the turning points in the concentration-dependent relaxation time and the scattered light intensity related to the fast mode mark a much better defined overlap concentration (C^*). The disappearance of the slow relaxation mode as individual star polystyrene chains shrink in cyclohexane (i.e., as the temperature decreases from 50 to 36 °C) with a concentration slightly higher than C^* reveals that the slow relaxation is indeed related to the interchain interaction. Our results further confirm that the fast mode is related to the pure diffusion of short chain segments (“blobs”) and the slow mode reflects the relaxation of the “cage” made of a number of correlated “blobs”. As the polymer concentration increases in the unentangled semidilute regime, more “blobs” are correlated, but the average correlation length decreases and the relaxation becomes slower.

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Notes

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REFERENCES

- (1) Ying, Q.; Chu, B. Overlap concentration of macromolecules in solution. *Macromolecules* **1987**, *20*, 362.
- (2) Brown, W.; Nicolai, T. Static and dynamic behavior of semidilute polymer solutions. *Colloid Polym. Sci.* **1990**, *268*, 977.
- (3) Iwao, T. *Polymer Solutions: An Introduction to Physical Properties*; Wiley: New York, 2002.
- (4) Roovers, J.; Toporowski, P. M.; Douglas, J. Thermodynamic Properties of Dilute and Semidilute Solutions of Regular Star Polymers. *Macromolecules* **1995**, *28*, 7064.
- (5) Li, J. F.; Li, W.; Huo, H.; Luo, S. Z.; Wu, C. Reexamination of the slow mode in semidilute polymer solutions: The effect of solvent quality. *Macromolecules* **2008**, *41*, 901.
- (6) De Gennes, P. G. Dynamics of Entangled Polymer Solutions. II. Inclusion of Hydrodynamic Interactions. *Macromolecules* **1976**, *9*, 594.

- (7) Adam, M.; Delsanti, M. Dynamical Properties of Polymer Solutions in Good Solvent by Rayleigh Scattering Experiments. *Macromolecules* **1977**, *10*, 1229.
- (8) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: 1979.
- (9) Wiltzius, P.; Haller, H. R.; Cannell, D. S.; Schaefer, D. W. Dynamics of Long-Wavelength Concentration Fluctuations in Solutions of Linear-Polymers. *Phys. Rev. Lett.* **1984**, *53*, 834.
- (10) Brown, W. Slow-mode diffusion in semidilute solutions examined by dynamic light scattering. *Macromolecules* **1984**, *17*, 66.
- (11) Adam, M.; Delsanti, M. Dynamical behavior of semidilute polymer solutions in a THETA solvent: quasi-elastic light scattering experiments. *Macromolecules* **1985**, *18*, 1760.
- (12) Brown, W. Diffusion of poly(ethylene oxide) in semidilute aqueous solution: Dynamic light scattering and gradient diffusion. *Polymer* **1985**, *26*, 1647.
- (13) Brown, W. Dynamic Light-Scattering on Semidilute Solutions of High-Molecular-Weight Polystyrene in Ethyl-Acetate. *Macromolecules* **1986**, *19*, 1083.
- (14) Brown, W.; Stepanek, P. Distribution of relaxation times from dynamic light scattering on semidilute solutions: polystyrene in ethyl acetate as a function of temperature from good to THETA conditions. *Macromolecules* **1988**, *21*, 1791.
- (15) Brown, W.; Mortensen, K. Comparison of Correlation Lengths in Semidilute Polystyrene Solutions in Good Solvents by Quasi-Elastic Light-Scattering and Small-Angle Neutron-Scattering. *Macromolecules* **1988**, *21*, 420.
- (16) Nicolai, T.; Brown, W.; Johnsen, R. M.; Stepanek, P. Dynamic Behavior of Theta Solutions of Polystyrene Investigated by Dynamic Light-Scattering. *Macromolecules* **1990**, *23*, 1165.
- (17) Brown, W.; Fang, L.; Stepanek, P. Dynamic behavior in poly(vinyl acetate) gels and solutions. *Macromolecules* **1991**, *24*, 3201.
- (18) Brown, W.; Stepanek, P. Dynamic behavior in concentrated polystyrene/cyclohexane solutions close to the Θ -point. Relaxation time distributions as a function of concentration and temperature. *Macromolecules* **1992**, *25*, 4359.
- (19) Stepanek, P.; Brown, W. Multiple relaxations of concentration fluctuations in entangled polymer solutions. *Macromolecules* **1998**, *31*, 1889.
- (20) De Gennes, P. G. Dynamics of Entangled Polymer Solutions. I. The Rouse Model. *Macromolecules* **1976**, *9*, 587.
- (21) Ewen, B.; Richter, D.; Farago, B.; Stuhn, B. Neutron Spin-Echo Investigations on the Segmental Dynamics in Semidilute Polymer-Solutions under Theta-Solvent and Good Solvent Conditions. *J. Non-Cryst. Solids* **1994**, *172*, 1023.
- (22) Adam, M.; Delsanti, M. Dynamical Properties of Polymer-Solutions in Good Solvent by Rayleigh-Scattering Experiments. *Macromolecules* **1977**, *10*, 1229.
- (23) Amis, E. J.; Han, C. C. Cooperative and Self-Diffusion of Polymers in Semi-Dilute Solutions by Dynamic Light-Scattering. *Polymer* **1982**, *23*, 1403.
- (24) Melnichenko, Y.; Brown, W.; Rangelov, S.; Wignall, G.; Stamm, M. Dynamic and static correlations in solutions of polymers in liquid and supercritical solvents: dynamic light scattering and small angle neutron scattering. *Phys. Lett. A* **2000**, *268*, 186.
- (25) Brown, W.; Stepanek, P. Viscoelastic relaxation in semidilute and concentrated polymer solutions. *Macromolecules* **1993**, *26*, 6884.
- (26) Konák, C.; Helmstedt, M.; Bansil, R. Dynamics in solutions of associating statistical copolymers. *Macromolecules* **1997**, *30*, 4342.
- (27) Peitzsch, R. M.; Burt, M. J.; Reed, W. F. Evidence of Partial Draining for Linear Polyelectrolytes - Heparin, Chondroitin 6-Sulfate, and Poly(Styrenesulfonate). *Macromolecules* **1992**, *25*, 806.
- (28) Chu, B.; Nose, T. Static and Dynamical Properties of Polystyrene in trans-Decalin. 4. Osmotic Compressibility, Characteristic Lengths, and Internal and Pseudogel Motions in the Semidilute Regime. *Macromolecules* **1980**, *13*, 122.
- (29) Wang, C.; Jiang, S.; Wu, C. Application of the temperature-ramped holographic relaxation spectroscopy in the investigation of physically cross-linked gels. *Macromolecules* **2001**, *34*, 6737.
- (30) Zhao, Y.; Zhang, G.; Wu, C. Nonergodic dynamics of a novel thermally sensitive hybrid gel. *Macromolecules* **2001**, *34*, 7804.
- (31) Ngai, T.; Wu, C. Effect of Cross-Linking on Dynamics of Semidilute Copolymer Solutions: Poly(methyl methacrylate-co-7-acryloyloxy-4-methylcoumarin) in Chloroform. *Macromolecules* **2003**, *36*, 848.
- (32) Ngai, T.; Wu, C.; Chen, Y. Effects of temperature and swelling on chain dynamics during the sol-gel transition. *Macromolecules* **2004**, *37*, 987.
- (33) Ngai, T.; Wu, C.; Chen, Y. Origins of the Speckles and Slow Dynamics of Polymer Gels. *J. Phys. Chem. B* **2004**, *108*, 5532.
- (34) Wu, C.; Ngai, T. Reexamination of slow relaxation of polymer chains in sol-gel transition. *Polymer* **2004**, *45*, 1739.
- (35) Li, W.; Hong, L. Z.; Ngai, T.; Huang, H. Y.; He, T. B.; Wu, C. A comparative study of chain dynamics of di- and tri-block copolymers in semidilute solution in a non-selective solvent. *Chin. J. Polym. Sci.* **2004**, *22*, 589.
- (36) Yuan, G.; Wang, X.; Han, C. C.; Wu, C. Reexamination of Slow Dynamics in Semidilute Solutions: From Correlated Concentration Fluctuation to Collective Diffusion. *Macromolecules* **2006**, *39*, 3642.
- (37) Yuan, G. C.; Wang, X. H.; Han, C. C.; Wu, C. Reexamination of slow dynamics in semidilute solutions: Temperature and salt effects on semidilute poly(N-isopropylacrylamide) aqueous solutions. *Macromolecules* **2006**, *39*, 6207.
- (38) Li, J. F.; Lu, Y. J.; Zhang, G. Z.; Li, W.; Wu, C. A slow relaxation mode of polymer chains in a semidilute solution. *Chin. J. Polym. Sci.* **2008**, *26*, 465.
- (39) Zhou, K.; Li, J.; Lu, Y.; Zhang, G.; Xie, Z.; Wu, C. Re-examination of Dynamics of Polyelectrolytes in Salt-Free Dilute Solutions by Designing and Using a Novel Neutral-Charged-Neutral Reversible Polymer. *Macromolecules* **2009**, *42*, 7146.
- (40) Li, J.; Ngai, T.; Wu, C. The slow relaxation mode: from solutions to gel networks. *Polym. J.* **2010**, *42*, 609.
- (41) Rubinstein, M.; Colby, R. H. *Polymer Physics*; OUP: Oxford, 2003.
- (42) McLeish, T. C. B.; Milner, S. T. Entangled dynamics and melt flow of branched polymers. In *Branched Polymers II*; Roovers, J., Ed.; Springer: 1999; Vol. 143, p 195.
- (43) Zamponi, M.; Pyckhout-Hintzen, W.; Wischniewski, A.; Monkenbusch, M.; Willner, L.; Kali, G.; Richter, D. Molecular Observation of Branch Point Motion in Star Polymer Melts. *Macromolecules* **2010**, *43*, 518.
- (44) Chu, B. *Laser Light Scattering: Basic Principles and Practice*; Academic Press: 1991.
- (45) Berne, B. J.; Pecora, R. *Dynamic Light Scattering: With Applications to Chemistry, Biology, and Physics*; Courier Dover Publications: 2000.
- (46) de Gennes, P. G. Relaxation anomalies in linear polymer melts. *Macromolecules* **2002**, *35*, 3785.
- (47) Raspaud, E.; Lairez, D.; Adam, M.; Carton, J. P. Triblock Copolymers in a Selective Solvent. I. Aggregation Process in Dilute Solution. *Macromolecules* **1994**, *27*, 2956.
- (48) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P. G. Solutions of Flexible Polymers - Neutron Experiments and Interpretation. *Macromolecules* **1975**, *8*, 804.
- (49) Amirzadeh, J.; McDonnell, M. E. Scaling analysis of static properties for semidilute solutions. *Macromolecules* **1982**, *15*, 927.
- (50) Wiltzius, P.; Haller, H. R.; Cannell, D. S.; Schaefer, D. W. Universality for Static Properties of Polystyrenes in Good and Marginal Solvents. *Phys. Rev. Lett.* **1983**, *51*, 1183.
- (51) Schaefer, D. W.; Joanny, J. F.; Pincus, P. Dynamics of Semiflexible Polymers in Solution. *Macromolecules* **1980**, *13*, 1280.
- (52) Huber, K.; Bantle, S.; Burchard, W.; Fetters, L. J. Semidilute solutions of star branched polystyrene: a light and neutron scattering study. *Macromolecules* **1986**, *19*, 1404.
- (53) Takahashi, M.; Nose, T. Bimodal behaviour observed by quasi-elastic light scattering in the cross-over region from Θ to critical temperature. *Polymer* **1986**, *27*, 1071.

- (54) Amis, E. J.; Han, C. C.; Matsushita, Y. Dynamic light scattering measurements of polystyrene in semidilute theta solutions. *Polymer* **1984**, *25*, 650.
- (55) Nishio, I.; Sun, S.-T.; Swislow, G.; Tanaka, T. First observation of the coil-globule transition in a single polymer chain. *Nature* **1979**, *281*, 208.
- (56) Sun, S. T.; Nishio, I.; Swislow, G.; Tanaka, T. The coil-globule transition: Radius of gyration of polystyrene in cyclohexane. *J. Chem. Phys.* **1980**, *73*, 5971.
- (57) Swislow, G.; Sun, S.-T.; Nishio, I.; Tanaka, T. Coil-Globule Phase Transition in a Single Polystyrene Chain in Cyclohexane. *Phys. Rev. Lett.* **1980**, *44*, 796.
- (58) Park, I. H.; Wang, Q. W.; Chu, B. Transition of linear polymer dimensions from THETA. to collapsed regime. 1. Polystyrene/cyclohexane system. *Macromolecules* **1987**, *20*, 1965.
- (59) Yu, J.; Wang, Z.; Chu, B. Kinetic study of coil-to-globule transition. *Macromolecules* **1992**, *25*, 1618.
- (60) Picarra, S.; Duhamel, J.; Fedorov, A.; Martinho, J. Coil-globule transition of pyrene-labeled polystyrene in cyclohexane: Determination of polymer chain radii by fluorescence. *J. Phys. Chem. B* **2004**, *108*, 12009.
- (61) Chu, B. Static and Dynamic Properties of Polymer Solutions. In *Scattering Techniques Applied to Supramolecular and Nonequilibrium Systems*; Chen, S.-H., Chu, B., Nossal, R., Eds.; Springer: 1981; Vol. 73, p 231.
- (62) Wang, Z.; Chu, B.; Wang, Q.; Fetters, L. Diffusion of Polymer in Binary and Ternary Semidilute Solutions. In *New Trends in Physics and Physical Chemistry of Polymers*, Lee, L.-H., Ed.; Springer: 1989; p 207.
- (63) Porod, G. General theory. In *Small angle X-ray scattering*; Academic Press: 1982.
- (64) Bale, H. D.; Schmidt, P. W. Small-Angle X-Ray-Scattering Investigation of Submicroscopic Porosity with Fractal Properties. *Phys. Rev. Lett.* **1984**, *53*, 596.
- (65) Schmidt, P. W.; Avnir, D.; Levy, D.; Höhr, A.; Steiner, M.; Röhl, A. Small-angle x-ray scattering from the surfaces of reversed-phase silicas: Power-law scattering exponents of magnitudes greater than four. *J. Chem. Phys.* **1991**, *94*, 1474.
- (66) Bartsch, E.; Antonietti, M.; Schupp, W.; Sillescu, H. Dynamic light scattering study of concentrated microgel solutions as mesoscopic model of the glass transition in quasiautomatic fluids. *J. Chem. Phys.* **1992**, *97*, 3950.
- (67) Van Megen, W.; Underwood, S. Glass transition in colloidal hard spheres: Mode-coupling theory analysis. *Phys. Rev. Lett.* **1993**, *70*, 2766.
- (68) Colmenero, J.; Arbe, A.; Alegria, A. Crossover from Debye to non-Debye dynamical behavior of the α relaxation observed by quasielastic neutron scattering in a glass-forming polymer. *Phys. Rev. Lett.* **1993**, *71*, 2603.
- (69) Van Megen, W.; Underwood, S. Glass transition in colloidal hard spheres: Measurement and mode-coupling-theory analysis of the coherent intermediate scattering function. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1994**, *49*, 4206.
- (70) Sciortino, F.; Gallo, P.; Tartaglia, P.; Chen, S. H. Supercooled water and the kinetic glass transition. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1996**, *54*, 6331.
- (71) Van Megen, W.; Mortensen, T.; Williams, S.; Müller, J. Measurement of the self-intermediate scattering function of suspensions of hard spherical particles near the glass transition. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1998**, *58*, 6073.
- (72) Bartsch, E. Diffusion in concentrated colloidal suspensions and glasses. *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 577.
- (73) Debenedetti, P. G.; Stillinger, F. H. Supercooled liquids and the glass transition. *Nature* **2001**, *410*, 259.
- (74) Chen, S. H.; Chen, W. R.; Mallamace, F. The glass-to-glass transition and its end point in a copolymer micellar system. *Science* **2003**, *300*, 619.
- (75) Likos, C.; Löwen, H.; Watzlawek, M.; Abbas, B.; Jucknischke, O.; Allgaier, J.; Richter, D. Star polymers viewed as ultrasoft colloidal particles. *Phys. Rev. Lett.* **1998**, *80*, 4450.
- (76) Chremos, A.; Douglas, J. F. Communication: When does a branched polymer become a particle? *J. Chem. Phys.* **2015**, *143*, 111104.
- (77) Phillies, G. D. J. Neutral polymer slow mode may signify an incipient growth-frustrated domain-forming glass. *Phys. Rev. E* **2004**, *69*, 69.
- (78) Götze, W. *Complex Dynamics of Glass-Forming Liquids: A Mode-Coupling Theory*; OUP: Oxford, 2008.
- (79) Wolfgang, G. Recent tests of the mode-coupling theory for glassy dynamics. *J. Phys.: Condens. Matter* **1999**, *11*, A1.
- (80) Cipelletti, L.; Ramos, L.; Manley, S.; Pitard, E.; Weitz, D. A.; Pashkovski, E. E.; Johansson, M. Universal non-diffusive slow dynamics in aging soft matter. *Faraday Discuss.* **2003**, *123*, 237.
- (81) Chen, S. H.; Gallo, P.; Sciortino, F.; Tartaglia, P. Molecular-dynamics study of incoherent quasielastic neutron-scattering spectra of supercooled water. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **1997**, *56*, 4231.
- (82) De Gennes, P. Incoherent scattering near a sol gel transition. *J. Phys., Lett.* **1979**, *40*, 197.
- (83) Bandyopadhyay, R.; Liang, D.; Yardimci, H.; Sessoms, D. A.; Borthwick, M. A.; Mochrie, S. G. J.; Harden, J. L.; Leheny, R. L. Evolution of Particle-Scale Dynamics in an Aging Clay Suspension. *Phys. Rev. Lett.* **2004**, *93*, 228302.
- (84) Krall, A. H.; Weitz, D. A. Internal dynamics and elasticity of fractal colloidal gels. *Phys. Rev. Lett.* **1998**, *80*, 778.
- (85) Cipelletti, L.; Manley, S.; Ball, R.; Weitz, D. Universal aging features in the restructuring of fractal colloidal gels. *Phys. Rev. Lett.* **2000**, *84*, 2275.
- (86) Robert, A.; Wandersman, E.; Dubois, E.; Dupuis, V.; Perzynski, R. Glassy dynamics and aging in a dense ferrofluid. *EPL (Europhysics Letters)* **2006**, *75*, 764.
- (87) Bouchaud, J. P.; Pitard, E. Anomalous dynamical light scattering in soft glassy gels. *Eur. Phys. J. E: Soft Matter Biol. Phys.* **2001**, *6*, 231.
- (88) Duri, A.; Cipelletti, L. Length scale dependence of dynamical heterogeneity in a colloidal fractal gel. *EPL (Europhysics Letters)* **2006**, *76*, 972.