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Diffusion of hairy polymeric micelles in a homopolymer solution

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ABSTRACT

Polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-PVP) forms hairy micelles with PVP and long PS block as the core and corona in toluene, respectively. Diffusion of the micelles in solution in the presence of poly(methyl methacrylate) (PMMA) or polystyrene homopolymer (h-PS), from dilute to semidilute, has been investigated by laser light scattering (LLS). Our results indicate the micelles only exhibit translational diffusion with characteristic $\Gamma = Dq^2$ in PMMA dilute and semidilute solutions, where Γ, D and q are characteristic line width, translational diffusion coefficient and scattering vector, respectively. PMMA concentration dependence of D reveals that the micelle diffusion follows a "stretched exponential" scaling law, similar to that of a hard sphere in the presence of matrix polymer. This is because the PS corona is incompatible with PMMA and no entanglement between them occurs. In contrast, in h-PS solution, due to the overlap and entanglement between the PS corona and h-PS matrix, the micelles exhibit diffusion with characteristic of $\Gamma \propto q^{\alpha}$, where $\alpha = 2$–2.6. For the same matrix polymer concentration, the micelles exhibit a faster diffusion in PMMA solution than that in h-PS solution, especially in semidilute solutions. The fact further indicates that the overlap and entanglement between the corona and h-PS matrix restrict the micelle motion.

1. Introduction

The diffusion of polymeric particles or polymer chains in another polymer solution has received considerable attention [1–14]. Such a system consists of a sphere particle or labeled polymer, a matrix polymer and a solvent. Pioneered by Mason and Weitz [15], the sphere particles have been used as probes since their Brownian fluctuation relates to the microstructure, microrheology and other behaviors of the matrix polymers [15–18]. On the other hand, proteins undergo folding and aggregation in a concentrated solution of DNA, polysaccharide and other macromolecules [19]. Study of the motion of a polymer in a solution in the presence of other polymers can help in understanding these complicated biological processes.

It is well established that the concentration has great influence on the self-diffusion of polymers. Polymer chains move nearly independently in dilute solution, where the self-diffusion coefficient is mainly determined by the polymer size. Further increasing the concentration up to the overlap concentration (C^*) leads to a crossover from dilute to semidilute regime. In semidilute and concentrated regimes, the chains are topologically constrained in a tube formed by the surrounding chains. Thus, the lateral motions of polymer chains are blocked and the chains mainly exhibit reptation motion, which can be described by the reptation model and the scaling theory [20,21]. In the case of probe diffusion in polymer solution, one of the favored models was developed by de Gennes, Langevin, and Rondelez [22,23]. However, de Gennes argued about the topological effects on probe behavior [23], because hard sphere particles without entanglements do not reptate. Considering that interchain hydrodynamic interactions dominate over the effects of topological constraints, Phillies [1] proposed an equation, that is, $D = D_0 \exp(-\kappa C^{\mu})$, to account for the concentration dependence of the self-diffusion coefficient for both spherical particles and polymer chains in dilute and semidilute solutions, where D_0 is the diffusion coefficient of the spherical particles or polymer chains in the absence of matrix polymer, C is the concentration of the matrix polymer, μ and κ are constants for a given sphere or labeled polymer chain with a certain radius and a matrix polymer with a certain molecular weight. The Phillies' equation has tested valid by some experiments, particularly those regarding flexible chain or solid sphere particle in flexible polymer solutions [24]. So far, though many theoretical models have been proposed [22,25–27], the mechanism about the translational diffusion of probes in a matrix polymer solution is still poorly understood.

In the present work, by use of laser light scattering (LLS), we have investigated the diffusion of PS-*b*-PVP micelles (probe) with long PS chains as the corona in toluene in the presence of PMMA or h-PS (matrix). Such hairy micelles are expected to have

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a combined characteristic of polymer chains and spherical particles. Moreover, the PS corona is incompatible with PMMA matrix but compatible with h-PS matrix. Namely, chain entanglement would not occur in the former case. Thus, we can examine the effects of different matrix polymers.

2. Experimental section

2.1. Materials

sec-Butyllithium in *n*-hexane/cyclohexane (1.3 M), dibutylmagnesium (1.0 M) in heptane, *n*-butyllithium in *n*-hexane (2.79 M), 1,1-diphenylethene (DPE) and 4-vinylpyridine were all purchased from Aldrich. DPE was transferred into the flask sealed with a Young® stopcock on the high-vacuum line after its reaction with dry *n*-butyllithium for 4 h. PMMA ($M_w = 3.5 \times 10^5$ g/mol, $M_w/M_n = 1.18$) was purchased from Aldrich. PS ($M_w = 3.6 \times 10^5$ g/mol, $M_w/M_n = 1.09$) was synthesized by anionic polymerization.

The overlap concentration C^* for PMMA or h-PS were estimated by $C^* = 3M_w/(4\pi N_A R_g^3)$, where M_w and R_g are the molar mass and the radius of gyration of polymer chains, respectively, N_A is the Avogadro constant [28]. Considering that toluene is a good solvent for both PMMA and h-PS [29], C^* was estimated to be ~10 mg/mL [10].

2.2. Synthesis of block copolymer

PS-*b*-PVP block copolymer was synthesized by sequential anionic polymerization following a standard procedure [30]. Styrene (St) was distilled under reduced pressure after it was washed with aqueous solution of sodium hydroxide for three times and then with water. After being stirred with CaH_2 at 60 °C for 4 h, styrene was transferred into dry dibutylmagnesium and stood on a high-vacuum line (10^{-5} Torr) until it turned slightly yellow. Anhydrous styrene was obtained by collecting the medium fraction under the high vacuum into a flask sealed with a Young® stopcock. Tetrahydrofuran (THF) was dried by sodium and further treated with PSt^-Li^+ anions which were synthesized via the reaction of *sec*-butyllithium and styrene in hexane at a molar ratio of 1/2. It was then distilled into a flask with a Young® stopcock on the high-vacuum line. Such prepared components were moved from the high-vacuum line into the dry box (MBraun Unilab®, $O_2 < 0.1$ ppm and $H_2O < 0.1$ ppm) before use.

Styrene, 4-vinylpyridine and DPE monomers were, respectively, added into a flask with Young® stopcock in dry box, which were degassed on the high-vacuum line, the flasks were connected. A certain amount of THF was transferred into a five-neck flask equipped with a magnetic stirrer in dry box so that the polymer concentration was 1 wt%. A small amount of PSt^-Li^+ solution in hexane was introduced into the THF to remove the impurity before *sec*-butyllithium was added. Then, the solution was cooled to −78 °C, and styrene was transferred to the five-neck flask. Two drops of DPE were introduced 30 min later, so the solution changed from slightly yellow to red immediately. Afterwards, 4-vinylpyridine was introduced and the solution quickly turned into green. The living polymerization was quenched with degassed methanol 2 h later. The copolymer was obtained by precipitating in methanol and dried under vacuum at 40 °C to constant weight.

PS precursor was characterized by gel permeation chromatography (GPC) with THF as the eluent and monodisperse polystyrene as the standards. The weight average molecular weight (M_w) of PS block is 145 kg/mol. The molecular weight of PVP block determined by a combination of GPC and ^{1}H NMR is $M_w = 13$ kg/mol. The polydispersity ($M_w/M_n = 1.07$) of the block copolymer was determined by GPC with $CHCl_3$ as the eluent.

2.3. Laser light scattering (LLS)

A commercial LLS spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-τ digital time correlation (ALV5000) and a cylindrical 22-mW He–Ne laser ($\lambda_0 = 632$ nm, UNIPHASE) as the light source was used. In dynamic LLS [31], the Laplace inversion of each measured intensity–intensity time correlation function $G^{(2)}(q,t)$ in the self-beating mode can lead to a line-width distribution $G(\Gamma)$. For dilute spheres in low-viscosity solvents, Γ is related to the translational diffusion coefficient D by $(\Gamma/q^2)_{C\to 0,q\to 0} \to D$, so that $G(\Gamma)$ can be converted into a transitional diffusion coefficient distribution $G(D)$ or further a hydrodynamic radius distribution $f(R_h)$ via the Stokes–Einstein equation, $R_h = (k_BT/6\pi\eta)/D$, where k_B, T and η are the Boltzmann constant, the absolute temperature and the solvent viscosity, respectively.

In the absence of matrix polymer, the micelle was prepared by directly dissolving the PS-*b*-PVP film in toluene, which was formed by evaporation of THF solution. The micelle solution in the presence of matrix polymer was prepared by dispersing micelle solution in PMMA or h-PS solutions in toluene, respectively. The final concentration of micelles was 1.0×10^{-4} g/mL. All measured solutions were clarified with a 0.45 μm Millipore Millex-LCR filter.

3. Results and discussion

The average hydrodynamic radius $\langle R_h \rangle$ and average radius of gyration $\langle R_g \rangle$ for PS-*b*-PVP micelle in pure toluene were determined to be 68 nm and 38 nm, respectively. The ratio of $\langle R_g \rangle/\langle R_h \rangle$ (~0.56) is lower than 0.774 for a uniform hard sphere, indicating the core–shell structure. Moreover, since PS block ($M_w = 145$ kg/mol) is much longer than the PVP block ($M_w = 13$ kg/mol), the block copolymers form hairy micelles.

Fig. 1 shows concentration dependence of characteristic decay time distribution $G(\tau)$ of PS-*b*-PVP micelles in PMMA solutions. Since PMMA and toluene are isorefractive, that is, PMMA has a very small refractive index increment value in toluene [32], PMMA chains cannot be detected. The micelles, however, are readily detectable. As PMMA concentration increases, the peak for the micelles shifts toward longer time, clearly indicating the matrix PMMA suppresses the micelle diffusion. By fitting the decay time (τ) at different scattering angles, we can obtain the scattering vector (q) dependence of the characteristic line width (Γ) and self-diffusion coefficient (D) of micelles (Fig. 2).

Fig. 2 shows that Γ is linearly dependent on q^2, and the extrapolation of Γ to $q \to 0$ passes the origin. The facts indicate that the micelle relaxation is related to the Brownian translational diffusion

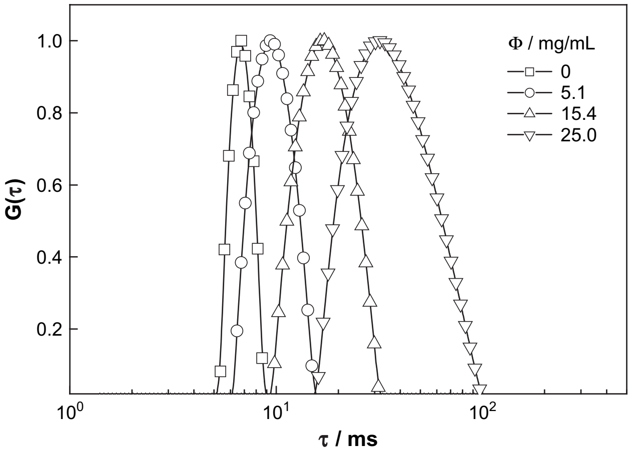

Fig. 1. Characteristic decay time distribution $G(\tau)$ for PS-*b*-PVP micelles in PMMA solution at different PMMA concentrations (Φ), where the scattering angle is 20°.

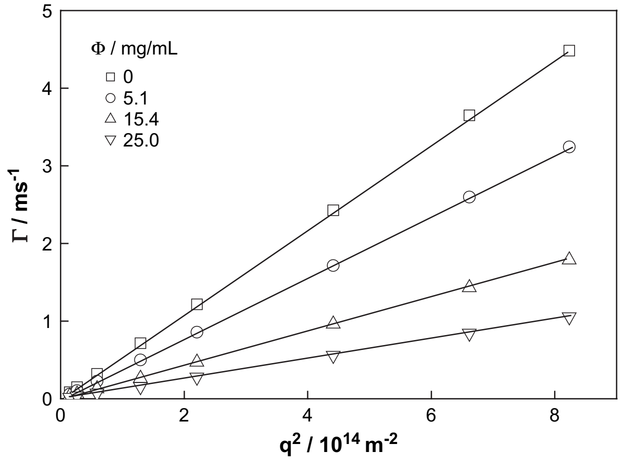

Fig. 2. Scattering vector (q) dependence of characteristic line width (Γ) of PS-*b*-PVP micelles in PMMA solutions at different PMMA concentrations (Φ).

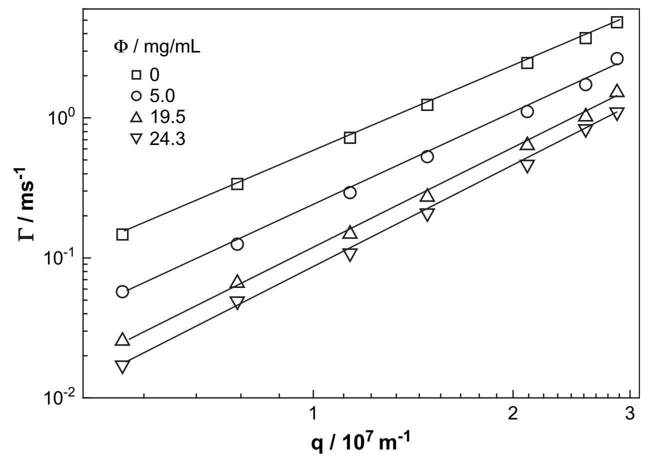

Fig. 4. Scattering vector (q) dependence of characteristic line width (Γ) of PS-*b*-PVP micelles in h-PS solutions at different h-PS concentrations (Φ).

over the whole concentration range [31]. As PMMA concentration increases to C^* ($\sim$10 mg/mL), PMMA chains begin to entangle. Since the PS corona is incompatible with PMMA matrix, no entanglement occurs in PMMA semidilute solutions. Thus, the hairy micelles are confined in the cage formed by PMMA entangled chains. The slope of $\Gamma \propto q^2$ leads to the self-diffusion coefficient (D). Obviously, as PMMA concentration increases, the self-diffusion coefficient decreases due to interchain hydrodynamic interaction. Actually, the self-diffusion coefficient of micelles in PMMA follows a “stretched exponential” hydrodynamic scaling law [1]. We will come back to this point later.

Fig. 3 shows the matrix concentration dependence of $G(\tau)$ for PS-*b*-PVP micelles in h-PS solutions. Two relaxation modes can be observed. The modes at short and longer time can be attributed to h-PS matrix chains and micelles, respectively. As h-PS concentration increases, the peak for the micelles shifts toward longer time, indicating the decay time of micelles becomes longer. This is similar to the case regarding PMMA matrix. At the same time, the decay time of h-PS chains becomes shorter. This can be attributed to the entanglement of h-PS chains. Namely, as h-PS concentration is higher than C^*, the “blobs” or subchains between two neighboring entangled points instead of the whole polymer chains are detected by LLS. Such blobs become smaller with the increasing entanglement increases, so that their diffusion becomes faster [33]. The insert shows the normalized intensity–intensity time correlation functions $G^{(2)}(q,t)$ of micelles in h-PS solutions. As h-PS concentration increases, the scattering light intensity contribution from h-PS chains increases. A fast and a slow relaxation modes corresponding to h-PS chains and micelles diffusion, respectively, can be clearly observed particularly at high h-PS concentrations.

Note that the long PS corona of micelle is incompatible with PMMA matrix but miscible with h-PS matrix. Thus, the micelle diffusion in the former is different from that in the latter. Fig. 4 shows double logarithmic plot of q dependence of Γ for micelles in h-PS solutions. For each h-PS concentration, Γ is linearly dependent on log(q). The slope leads to the exponent (α) for $\Gamma \propto q^{\alpha}$ relation. As h-PS concentration increases, α is over 2.0, implying that the relaxation of the micelles is in a non-diffusive mode. As reported before [34], the micelles act as transient physical cross-linker in a concentrated matrix polymer solution.

Fig. 5 shows the matrix concentration (Φ) dependence of α for micelles in PMMA and h-PS solutions, respectively. α holds 2 in the range $\Phi = 0$–30 mg/mL in PMMA solutions. However, α has concentration dependence in h-PS solutions. In dilute h-PS solutions, as h-PS concentration increases, α slightly increases from 2 to 2.2. This can be attributed to the dynamical entanglement between micelles and h-PS chains. When h-PS concentration is higher than C^* ($\sim$10.4 mg/mL), α gradually increases from 2.2 to 2.6. The deviation of α value from 2 clearly indicates the non-Brownian translational

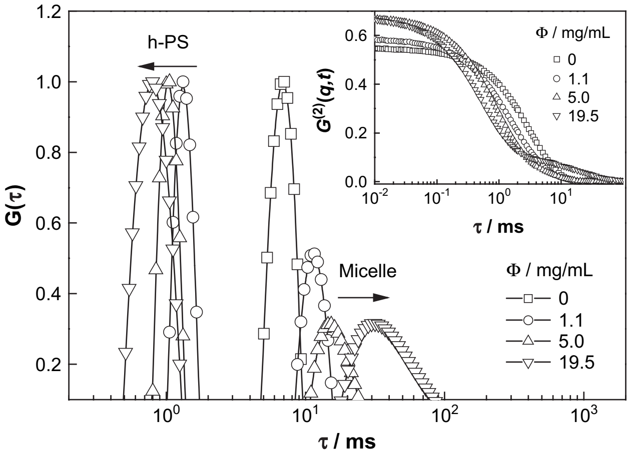

Fig. 3. Characteristic decay time distribution $G(\tau)$ for PS-*b*-PVP micelles in h-PS solution in toluene at different h-PS concentrations (Φ), where the scattering angle is 20°. The insert shows the normalized intensity–intensity time correlation functions $G^{(2)}(q,t)$ of the micelles in h-PS solutions.

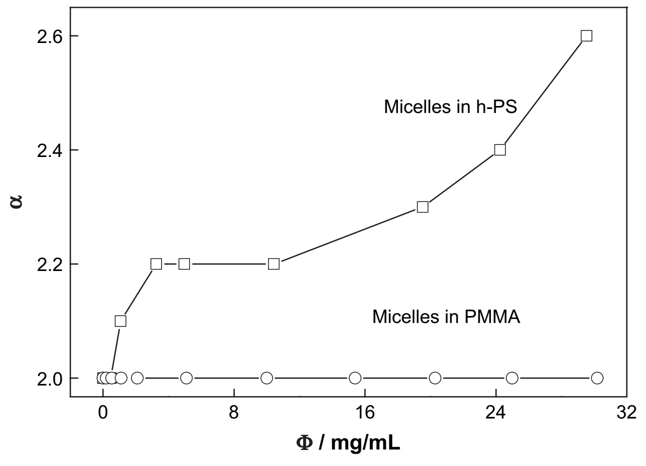

Fig. 5. Matrix concentration (Φ) dependence of α for PS-*b*-PVP micelles in PMMA and h-PS solutions in toluene, respectively, where α is the exponent for the scaling relation $\Gamma \propto q^{\alpha}$.

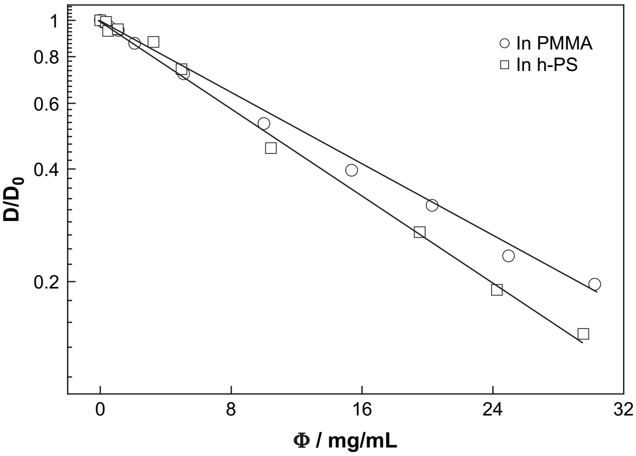

Fig. 6. Matrix concentration (Φ) dependence of diffusion coefficient (D/D_0) of PS-*b*-PVP micelles in PMMA or h-PS solutions, where D_0 is the diffusion coefficient of the micelles in the absence of the matrix polymer.

diffusion of the micelles [35,36]. This is probably because the PS chains in the micelle corona and in the matrix are compatible, and they can penetrate and overlap each other when h-PS concentration is higher than C^*. In other words, the micelle forms a complex with PS chains around in the matrix.

Fig. 6 shows matrix concentration dependence of diffusion coefficient (D/D_0) of micelles in PMMA and h-PS solutions, respectively. The self-diffusion coefficient (D) of micelles in h-PS semidilute solutions was obtained by linear fitting of plot of Γ versus q^2 at lower scattering angles. This is reasonable because the diffusion of the whole micelle can be observed at lower scattering angles with large observation scale $1/q$ [28]. Clearly, in either PMMA or h-PS solutions, $\log(D/D_0)$ has linear matrix concentration dependence. In other words, the experimental results agree well with the fitting results on the basis of the Phillies' stretched exponential equation, $D = D_0 \exp(-\kappa C^{\mu})$. Note that the diffusions of the micelles in the two matrix polymer solutions exhibit the same μ values (~ 1) but different κ values. This is probably because PS/PMMA interaction is much weaker than the PS/h-PS interaction, and the microscopic viscosities of PMMA and h-PS at the micelle surface are different, leading to the difference in κ values.

4. Conclusions

Diffusion of PS-*b*-PVP hairy micelles in toluene in the presence of PMMA or h-PS has been investigated by laser light scattering. The micelles exhibit Brownian translational diffusion over the whole concentration in PMMA solutions. In contrast, the micelles exhibit more complex diffusion in h-PS solutions, especially in semidilute solution. At the same matrix concentration, the micelles have a larger diffusion coefficient in the former than that in the latter. The facts indicate that the interactions between the micelle corona and matrix polymer have great effects on the diffusion.

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