Diffusion of Entangled Linear Polymer Chains through a Porous Thin Gel

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ABSTRACT: Using a particle made of linear polystyrene (PS) chains as a core, we further polymerized a cross-linked PS shell on it in water to form a spherical core−shell particle (∼100 nm). Such a particle swells in toluene or tetrahydrofuran (THF). The swelling enables entangled linear PS chains inside the core to gradually diffuse out through the porous shell. Using a combination of static and dynamic laser light scattering, we have examined effects of the shell thickness and cross-linking density (pore size) on the diffusion by following the change of the scattering intensity (i.e., the average molar mass of the core−shell particles). The diffusion exhibits three stages reflecting the concentration change inside the core, or more precisely, the relative change of the correlation length (ξ_c) inside the core to the average pore size (d_{pore}) in the shell, i.e., (1) $\xi_c < d_{pore}$, (2) $R_g > \xi_c \sim d_{pore}$, and (3) $\xi_c \sim R_g \gg d_{pore}$, where R_g is the average radius of gyration of linear PS chains inside the core. It is interesting to find that in the first stage the diffusion of the chains through the porous shell is even faster than their translational diffusion in a dilute solution.

Introduction

The diffusion of polymer chains through a porous membrane or a swollen gel network is important for gel permeation (size exclusion) chromatography, ultrafiltration, controlled releasing, and translocation of biological macromolecules.[1−3] A polymer chain confined inside a small and long pore, including gels and melts, shows different diffusion behavior compared with in dilute solution and normally diffuses much slower than a chain free in a dilute solution.[4−7] In theory, the diffusivity of a polymer chain inside a pore is related to the hydrodynamic viscous drag coefficient (f_d) and the partition coefficient (K) of the chain between inside and outside the pore.[8,9] f_d can be further related to the translational diffusion coefficient (D_0) of the chain outside the pore by the Einstein equation $D_0 = k_B T/f_0$, where k_B is the Boltzmann constant, T is the solution temperature and f_0 is the molecular friction coefficient in a dilute solution. The hydrodynamic viscous drag coefficient (f_d) is normally larger than f_0 because the chains are depleted from the wall and adopt a limited number of conformations even inside a pore larger than the average radius of gyration ($\langle R_g \rangle$) of the chains. As a result, the average equilibrium polymer concentration inside the pore is normally lower than that outside, especially for pores with a size comparable to or smaller than $\langle R_g \rangle$.

Assuming no specific interaction between the pore and the chain, we have $D_p/D_0 = K(f_0/f_d)$, where D_p is the hindered diffusion coefficient inside the pore.[8] The "hard-sphere" model for such hindered diffusion is expressed by the Renkin equation,[10] $D_p/D_0 = (1 - \lambda_s)^2(1 - 2.1\lambda_s + 2.1\lambda_s^3 - 0.95\lambda_s^5)$, where λ_s is the ratio of the hydrodynamic chain radius (R_h) to the pore radius (R_p). Previous experimental results agree well with such an equation in the range of $0.05 < \lambda_s < 0.4$.[11−13] Davidson and Deen[14] extended the theory to a broader range $\lambda_s < 1$. As for $\lambda_s > 1$, the diffusion of linear flexible polymer chains through a small pore can be described by the scaling theory.[15] In

an athermal solvent with $R_f \geq R_p$, $D_p/D_0 \cong a(b\ R_f/R_p)^{2/3} \exp(-bR_f/R_p)^{5/3}$, where R_f is the root-mean-square end-to-end distance of the chain; a and b are two constants.

The partition coefficient (K) of linear flexible chains inside and outside a pore strongly depends on the polymer concentration. Namely, it remains a constant in the dilute regime but increases with the polymer concentration in the semidilute/concentrated regime. The dilute and semidilute solutions are divided by the overlap concentration (C^*) at which the chains start to touch each other. The diffusion of a long linear flexible chain in a dilute solution through a small pore without a flow field is rather difficult, if not impossible, because it is highly excluded due to a higher osmotic pressure inside the pore. In a concentrated solution, K can approach 100% even the chains are highly entangled with each other.[16]

The restricted diffusion experiments are normally conducted by using a diffusion cell with a track-etched separation membrane in the dilute regime. Previous studies were focused on polymer chains with an average size smaller than the pore because long chains cannot diffuse through a small pore.[17−20] The experimental studies of the effective diffusion coefficient of linear chains in the semidilute and concentrated regimes through a small pore have been rather limited. Note that the chain polydispersity also affects the chain diffusion. In a dilute solution, the chains with different lengths diffuse independently from each other.[21−23] It has been stated that in a semidilute or concentrated solution the diffusion of long chains through a small pore is actually accelerated by short ones.[21]

In the present study, we first encapsulated linear polystyrene chains (core) inside a cross-linked polystyrene network (shell) with different thicknesses using the seeded emulsion polymerization in water. Such core−shell particles swell in toluene or tetrahydrofuran (THF) so that linear PS chains inside the core can gradually diffuse out through the porous shell (swollen gel network). We examined effects of the shell thickness and cross-linking density on such a diffusion process. Our strategy is schematically shown in Figure 1. Using small core−shell

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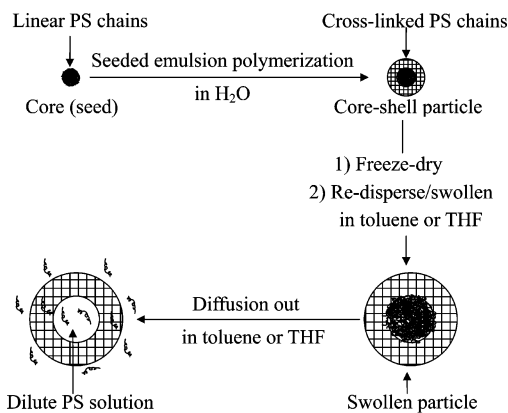‡ The Chinese University of Hong Kong.

Figure 1. Schematic of preparation of small core−shell polystyrene particles in water and their swelling in toluene or THF as well as diffusion out of linear PS chains from the core through the swollen porous shell into the dispersion medium.

particles, we gain two advantages in comparison with a normal macroscopic study of the diffusion of long linear polymer chains through a small pore. Namely, (1) these small core−shell particles have a huge surface area so that the chains from the core can diffuse out through the porous shell within a reasonable experimental time, and (2) we can use laser light scattering to in-situ monitor the diffusion out of the chains in terms of the decrease of the average mass of the core−shell particles (i.e., the scattering intensity) without any external interference or calibration.

Experimental Section

Sample Preparation. Styrene and divinylbenzene (DVB) (Shanghai Chemical Reagent Co.) were purified by reduced pressure distillation. 2,2′-Azobis(isobutyronitrile) (AIBN, Aldrich) was recrystallized from ethanol and dried in vacuum. Poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) triblock copolymer (Pluronic PE 10500, BASF) was used as received. The typical preparation of small core−shell particles is outlined as follows.

First, the seeds (core) made of linear PS chains were prepared by emulsion polymerization. 3.53 g of PE10500, 0.60 g of AIBN, 39.98 g of styrene, and 1000 mL of deionized water were charged into a 2 L three-neck flask equipped with a stirrer, a reflux condenser, and a nitrogen gas inlet. Nitrogen was bubbled for 30 min to remove oxygen. The reaction was carried out at 60 °C for 8 h. After the preparation of the seed particles, the cross-linked polystyrene shell was coated on the core by the seeded emulsion polymerization under the starved condition. The addition of different amounts of styrene monomers in the shell preparation led to small core−shell particles with the same core (71 nm) and shell cross-linking density (1.60 mol %) but three different shell thicknesses. Using the same procedure, we also prepared three different kinds of small core−shell particles with the same core (70 nm) but different shell cross-linking density (0.48, 0.64, and 0.78 mol %) by changing the monomer/cross-linking agent ratio in the seeded emulsion polymerization.

Laser Light Scattering. A commercial LLS spectrometer (ALV/SP-125) equipped with an ALV-5000 multi-tau digital time correlator and a He−Ne laser (Uniphase, 22 mW at $\lambda = 632.8$ nm) was used. In static LLS, angular dependence of the excess absolute time average scattered intensity, known as the Rayleigh ratio ($R_{vv}(q)$), of a dilute dispersion of the core−shell particles is related to the apparent weight-average molar mass (M_w), the second virial coefficient (A_2), and the root-mean-square z-average radius of gyration ($\langle R_g^2 \rangle_z^{1/2}$ or written as $\langle R_g \rangle$) as

$$\frac{KC}{R_{vv}(q)} = \frac{1}{M_w}\left(1 + \frac{1}{3}\langle R_g^2 \rangle q^2\right) + 2A_2C \tag{1}$$

where $K = 4\pi^2 n^2 (dn/dC)^2/(N_A\lambda_0^4)$ and $q = (4\pi n/\lambda_0)\sin(\theta/2)$ with n, N_A, λ_0, θ, and dn/dC being solvent refractive index, the Avogadro number, the laser wavelength in vacuum, the scattering angle, and the specific refractive index increment, respectively. In all LLS experiments, the polymer concentrations were so low (5 μg/mL) that the term $2A_2C$ in eq 1 can be ignored. Therefore, $R_{vv}(q)$ is proportional to M_w for a given concentration at a small scattering angle. Note that in the small angular range $KC/R_{vv}(q)$ is linearly proportional to q^2 for all the core−shell particles studied, well described by eq 1.

In dynamic LLS, the Laplace inversion of a measured intensity−intensity time correlation function ($G^{(2)}(q,t)$) can lead to a line-width distribution ($G(\Gamma)$).[24,25] For a pure diffusive relaxation, Γ is related to the translational diffusion coefficient (D) by $D = (\Gamma/q^2)_{q\to 0,C\to 0}$ or further to the hydrodynamic radius (R_h) via the Stokes−Einstein equation, $R_h = k_BT/(6\pi\eta D)$, where η is the solvent viscosity.[26] In the current study, the core−shell particles are so narrowly distributed that the cumulant analysis can also lead to the accurate average line width $\langle\Gamma\rangle$ and average hydrodynamic radius (R_h).

Diffusion Experiments. The core−shell particles prepared by seeded emulsion polymerization were freeze-dried and then redispersed/swollen in toluene or THF to test the solvent effect. The dispersion was immediately clarified by using a Millipore PTFE filter (1.0 μm) to remove dust particles. The diffusion out of linear PS chains from the core through the swollen porous PS shell into the dispersion medium (toluene or THF) was monitored in terms of the scattering-intensity change at 15°. All the LLS experiments were done at 25 °C. The dispersion concentration was kept at 5.0 × 10⁻⁶ g/mL. Since the preparation of a dust-free dispersion takes a certain time, all the LLS measurements started 20 min after the particles were redispersed/swollen in toluene or THF. As expected, the initial polymer content inside the core should be higher than that in the shell since the shell swells before the core. It has been known that the polymer concentration (C) inside the core follows[17]

$$C_t - C_\infty = (C_0 - C_\infty)\exp\left(-\frac{D_{eff}A_{pore}}{LV_{core}}t\right) \tag{2}$$

where D_{eff}, A_{pore}, L, and V_{core} are the effective diffusion coefficient, the total cross-section area of all the pores in the shell, the shell thickness, and the core volume, respectively. The subscripts 0, t, and ∞ indicate the time at zero, t, and infinity, respectively. As shown in Table 1, C_0, defined as M_{core}/V_{core}, is higher than 5.0 × 10⁻² g/mL. For a dilute dispersion, V_{core} is much smaller than the total dispersion volume (V). So that at $t \to \infty$, most of the chains diffuse out from the core, leading to $C_\infty \ll C_0$. Therefore, we can rewrite eq 2 as

Table 1. Characterization of Spherical Core−Shell Particles in Different Solvents at 25 °C

sample	shell cross-linking density (ρ, mol %)	no swelling in H₂O		after swelling in toluene or THF			
		L_{shell} (nm)	$\langle R_h \rangle_{core}$ (nm)	solvent	L_{shell} (nm)	$\langle R_h \rangle_{core}$ (nm)	$C_{0,core}$ (g/mL)
S1	1.60	7	71	toluene	19	186	5.5 × 10⁻²
S2	1.60	26	71	toluene	67	178	6.2 × 10⁻²
S3	1.60	32	71	toluene	74	161	8.4 × 10⁻²
P1	0.48	15	70	THF	42	197	3.1 × 10⁻²
P2	0.64	19	70	THF	46	165	5.2 × 10⁻²
P3	0.78	9	70	THF	22	168	5.0 × 10⁻²

$$\ln\left(\frac{C_t - C_\infty}{C_0}\right) = -\frac{D_{eff}A_{pore}}{V_{core}L}\,t \qquad (3)$$

where A_{pore}, V_{core}, and L are constants for a given type of swollen core−shell particles.

Results and Discussion

Figure 2 shows hydrodynamic radius distributions $f(R_h)$ of the initial seed (core) particles and three resultant core−shell samples with different shell thicknesses in water. The relative width $(\mu_2/\langle\Gamma\rangle^2)$ of $f(R_h)$ is in the range 0.01−0.02, indicating that these particles are narrowly distributed, which simplifies our study; namely, we do not need to worry about some possible size effect within each sample. The shell thickness can be calculated from the difference of the hydrodynamic radius between the resultant core−shell particle and the initial core. Note that other core−shell particles with different shell cross-linking densities are also narrowly distributed (not shown here). Table 1 summarizes shell thicknesses of six samples. Samples S1, S2, and S3 have the same shell cross-linking density, and samples P1, P2, and P3 have different shell cross-linking densities.

Figure 3 shows that the average volume per particle ($V_{particle}$ $= (4\pi/3)\langle R_h\rangle_{particle}^3$) linearly increases with the weight of additional styrene monomers (W_{shell}) added in the shell preparation for samples S1, S2, and S3. The extrapolation of W_{shell} to 0 lead to V_{core} and then $\langle R_h\rangle_0 = 72$ nm, very close to the average radius of the initial seed particles ($\langle R_h\rangle_{seed} = 71$ nm). Such a good agreement indicates that nearly all styrene monomers and cross-linking agents (DVB) added during the shell preparation (the seeded emulsion polymerization) were coated on the surface of the seed with nearly no additional nucleation in water. Otherwise, $\langle R_h\rangle_0$ would be much different from $\langle R_h\rangle_{seed}$, and the plot in Figure 3 would not be a straight line.

Figure 4 shows a typical time dependence of the weight-average molar mass (M_w) of the core−shell particles after they were redispersed and swollen in toluene. As expected, M_w decreases as linear PS chains inside the core diffuse out through the porous shell. Note that the average molar masses and polydispersity indexes of linear PS chains entrapped inside the core for two groups of samples ("S1, S2, S3" and "P1, P2, P3") are 9.2×10^5 g/mol and 2.1 and 5.5×10^5 g/mol and 2.1, respectively, much lower than that of the core−shell particles. Also note that the scattering intensity is proportional to square of the mass of a scattering object. Therefore, individual diffused-out chains in the dispersion medium scatter much less light so that their intensity contribution can be ignored in comparison with that of the core−shell particles. Initially, the polymer concentration inside the core is semidilute so that the average size of thermal blobs is independent of the chain length. Therefore, in the initial stage, the polydispersity in the chain length should have a less effect on the diffusion.

Figure 5 shows that, as expected, the average particle size remains a constant during the diffusion after the swelling reaches its equilibrium, especially $\langle R_h\rangle$. Using the size of the seed particles in water as a reference and assuming that the core and the shell swell uniformly, we can calculate the average thickness of the swollen shell and the average radius of the swollen core. The results are also summarized in Table 1. It is reasonable that for a given shell cross-linking density the core swells less when the shell is thicker because the shell swells simultaneously outward and inward. On the other hand, for a given shell thickness, both the shell and the core swell less when the shell is more cross-linked. At the swelling equilibrium, the initial
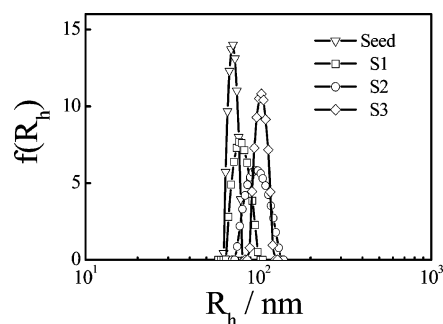

Figure 2. Hydrodynamic radius distributions ($f(R_h)$) of seed particles (core) in water before and after coated with a layer of cross-linked polystyrene shell with different thicknesses, where the particle concentration is in the range $(1-4) \times 10^{-6}$ g/mL.
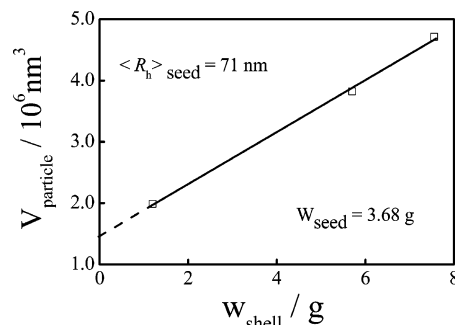

Figure 3. Shell-weight (W_{shell}) dependence of average hydrodynamic volume ($V_{particle}$) of small core−shell particles in water during seeded emulsion polymerization, where $V_{particle}$ is defined as $(4\pi/3)\langle R_h\rangle_{particle}^3$.
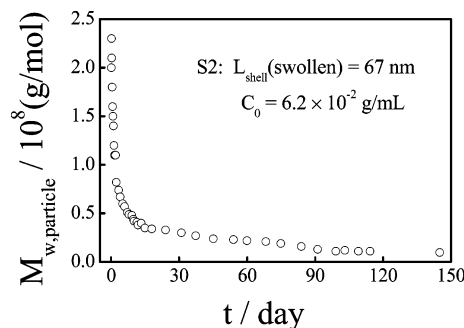

Figure 4. Time dependence of apparent weight-average molar mass of small core−shell particles ($M_{w,particle}$) after they are dispersed/swollen in toluene.
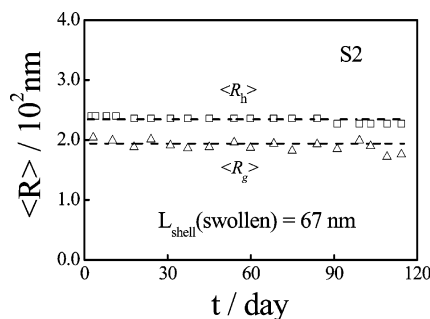

Figure 5. Time dependence of average hydrodynamic radius $\langle R_h\rangle$ and radius of gyration $\langle R_g\rangle$ of small core−shell particles after they are dispersed/swollen in toluene.

polymer concentration (C_0) inside the core can be estimated from the mass of the seed and the average radius of the swollen core $\langle R_h\rangle_{core}$ listed in Table 1. Since V_{core} is a constant during the diffusion, C_t is directly proportional to the total mass of linear PS chains inside the core and indirectly proportional to the scattering intensity.
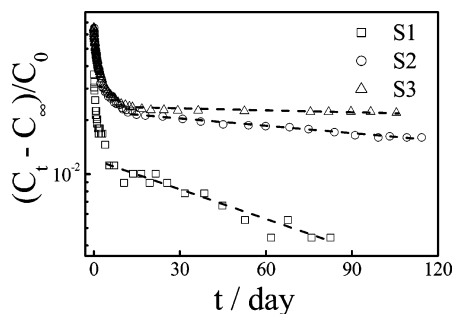
Figure 6. Time dependence of concentration of linear polystyrene chains inside the core after small core−shell particles are dispersed and swollen in toluene, where the shells have the same cross-linking density, but different thicknesses. $C_0 = M_{core}/V_{core}$ and $C_\infty = M_{core}N_{particle}/V$, where M_{core}, $N_{particle}$, V_{core}, and V are average mass of the core, average number of core−shell particles, average volumes of the core, and dispersion, respectively.
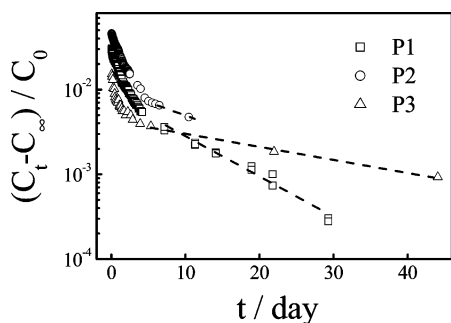

Figure 7. Time dependence of concentration of linear polystyrene chains inside the core after small core−shell particles are dispersed and swollen in THF, where the shells have different cross-linking densities. $C_0 = M_{core}/V_{core}$ and $C_\infty = M_{core}N_{particle}/V$, where M_{core}, $N_{particle}$, V_{core}, and V are average mass of the core, average number of core−shell particles, average volumes of the core, and dispersion, respectively.

Figure 6 reveals that for samples S1, S2, and S3 with the same shell cross-linking density, but different shell thickness, the diffusion process has three stages: the initial fast stage, the final slow stage, and a transitional stage between them. In the initial fast stage, the core is swollen by toluene, resulting in a concentrated PS solution. The initial polymer concentration inside the core is much higher than the overlap concentration $C^* \sim 1.37 \times 10^{-3}$ g/mL of the linear PS chains. Each linear PS chain in the core is confined inside a "tube" made of its surrounding chains. On the other hand, the average pore size in the shell (d_{pore}) can be estimated from the cross-linking density, i.e., the number of monomers (n_c) between two neighboring cross-linking points, by $d_{pore} = kn_c^\alpha$, where k and α are two scaling constants in $R_g = kN^\alpha$ for linear PS chains in toluene.[27] The three samples have the same cross-linking density (1.6 mol %) so that $d_{pore} \sim 2.6$ nm.

Note that for samples S1, S2, and S3 the initial correlation lengths (ξ_c) inside the core are 2.2, 2.0, and 1.6 nm, respectively, estimated from the initial concentrations (C_0) by using the scaling relation from dynamic laser light scattering measurements of semidilute solutions. In other words, each chain inside the core is inside a "tube" with a diameter smaller than the average size of the pores in the shell. Namely, the initial average osmotic pressure of each chain experienced inside the core (π_{core}) is larger than that inside the shell (π_{shell}) if the chain moves from the "tube" in the core into the pore in the shell. This is why the linear PS chains can diffuse into the shell with a much less resistance. On the other hand, π_{shell} is much higher than the osmotic pressure generated by a chain free in a dilute solution outside of the shell ($\pi_{outside}$). In the first initial stage,
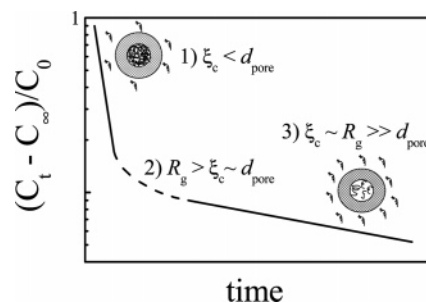

Figure 8. Schematic of three stages of diffusion out of linear polymer chains from the core through the porous shell (a swollen gel network) into the dispersion medium, where ξ_c is the correlation length of polymer solution inside the core, d_{pore} is the average size of the pores in the shell, and R_g is average radius of gyration of individual chains in a dilute solution.

Table 2. Shell Thickness and Cross-Linking Density Dependence of Effective Diffusion Coefficients of Linear Polystyrene Chains from the Core through the Porous Shell into the Dispersion Medium in the First and Third Stages (D_1 and D_3) as Well as Their Corresponding Translational Diffusion Coefficient in Dilute Solutions (D_0) at 25 °C

sample	solvent	D_0 (cm²/s)	D_1 (cm²/s)	D_3 (cm²/s)
S1	toluene	1.34×10^{-7} in dilute solution	2.0×10^{-7}	7.0×10^{-9}
S2	toluene		3.8×10^{-7}	5.0×10^{-9}
S3	toluene		3.8×10^{-7}	1.0×10^{-9}
P1	THF	2.19×10^{-7} in dilute solution	4.5×10^{-7}	1.1×10^{-7}
P2	THF		4.2×10^{-7}	7.9×10^{-8}
P3	THF		2.9×10^{-7}	1.8×10^{-8}

$\pi_{core} > \pi_{shell} \gg \pi_{outside}$. Therefore, the chains can quickly diffuse out into the dispersion medium as soon as they enter the pores of the shell.

As the diffusion proceeds, the polymer concentration inside the core decreases so that ξ_c increases even though the solution inside the core is still in the semidilute regime. When $\xi_c \sim d_{pore}$, there is no large driving force for the chains to move from the core into the shell. The diffusion is hindered and the process enters the second transitional stage. Further diffusion out of the chains finally results in a dilute polymer solution inside the core. Each chain is an independent "blob", and ξ_c becomes the size of the chain (R_g), much larger than d_{pore}. The diffusion from the core into the shell is greatly hindered and becomes extremely slow (the third stage). Note that in the above three stages the diffusion out of the chains from the shell to the dispersion medium remains the same since the polymer concentration outside the core−shell particles is so low (<5 μg/mL) that it can be considered as infinite dilution.

Figure 7 shows that for samples P1, P2, and P3 with different cross-linking densities each diffusion process also has three similar stages. The average pore sizes (d_{pore}) in the shell of samples P1, P2, and P3 are 4.7, 4.0, and 3.5 nm, respectively. In comparison, their initial correlation lengths (ξ_c) in the core are 3.3, 2.3, and 2.3 nm, respectively. In the first initial stage, $\xi_c < d_{pore}$. As shown in Table 1, six samples used have a similar seed and an initial polymer concentration inside the core. The mechanism and driving force for the diffusion out of the chains from the core are the same. Namely, $\xi_c < d_{pore}$ and the osmotic pressure inside the core is much higher than that inside the shell. On the basis of eq 3, we can calculate the effective diffusion coefficients (D_{eff}) for the first and third stages.

Table 2 summarizes the calculated values of D_{eff} for the initial fast and last slow stages, where we assumed that A_{pore} is the surface area of the inner shell because the cross-linked chains

in the shell (a highly swollen gel network) occupy only a very small portion of the surface area. As shown in Tables 1 and 2, in the first stage, in spite of different initial after-the-swelling polymer concentrations (C_0) inside the core and different thicknesses and different cross-linking densities (pore sizes) of the shell, the chains move from the core through the shell into the dispersion medium with a similar diffusion coefficient. The results show that the shell thickness and cross-linking density have nearly no effect on the diffusion out of the chains as long as $\xi_c < d_{pore}$. While in the third stage, the chains are highly excluded from the pores in the shell. For a given cross-linking density, a thicker shell means longer pores. As expected, it would take a longer time for a chain to pass a longer pore even it can enter the pore. This is why the diffusion becomes slower as the shell thickness increases.

On the other hand, for "samples P1 and P2" and "samples P3 and S1", each group has a similar shell thickness after the swelling, but different shell cross-linking densities. A comparison of Tables 1 and 2 shows that in each group the diffusion out of the chains from the core for the sample with a high shell cross-linking density is slower in the third stage. As discussed before, in the third stage, the polymer solution inside the core becomes dilute, and all the samples have a similar correlation length inside the core because the linear PS chains in the core have a similar size. A higher shell cross-linking density means smaller pores. The partition coefficient exponentially decreases with the pore size for a given chain size. This explains why the sample with a higher shell cross-linking density in each group has a smaller diffusion coefficient in the third stage.

It should be stated and interesting to note that in the first stage not only the diffusion out of the chains from the core through the porous shell has a similar diffusion coefficient but also the diffusion out of these entangled chains is even faster than the diffusion of individual chains free in a dilute solution. The diffusion coefficient (D_0) of free chains was determined by dynamic LLS in a dilute solution of the same PS chains in toluene. To our knowledge, such fast diffusion of linear chains through a porous gel network has not been reported before. Previously, Guillot et al.[28] studied the diffusion of long polymer chains ($M_w = (6.8-8.4) \times 10^6$ g/mol) from a semidilute solution through a porous membrane and found the initial diffusion coefficient through the porous gel membrane was close, but still lower than, that in a dilute solution without any membrane.

As discussed before, the fast diffusion in the first stage can be attributed to a relatively shorter correlation length inside the core, i.e., $\xi_c < d_{pore}$. In the second stage, the chains are still entangled with each other, but $\xi_c \sim d_{pore}$. There is no advantage for the chains to enter the pores of the shell. Finally, the chains inside the core completely disentangled from each other and the polymer solution inside the core becomes dilute so that $\xi_c \sim R_g \gg d_{pore}$. The partition coefficient between the shell and the core is so small in this stage that the diffusion becomes 2 orders of magnitude slower for samples S1–S3 with a highly cross-linked shell, as shown in Table 2.

Conclusion

Long linear polystyrene (PS) chains can be encapsulated inside a thin shell (7–32 nm) made of cross-linked PS chains

by seeded emulsion polymerization to form small core–shell particles (~100 nm) in water. The redispersion/swelling of these particles in an athermal solvent results in the diffusion out of linear PS un-cross-linked chains inside the core through the swollen porous shell. Such a diffusion process can be in-situ monitored by using a combination of static and dynamic laser light scattering. Our results reveal that the diffusion has three distinct stages, reflecting the change of the polymer concentration or, more precisely, the correlation length (ξ_c) of the polymer solution inside the core since the average pore size (d_{pore}) in the shell remains a constant, as schematically shown in Figure 8. The shell thickness and cross-linking density have nearly no influence on the diffusion out of the chains in the first stage but greatly affect the diffusion out of the chains in the third stage. We have, *for the first time*, observed that the diffusion of entangled chains from a semidilute/concentrated solution through a porous gel can be faster than their diffusion in a dilute solution.

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