Rapid Communication

DIFFUSION OF LONG CHAINS THROUGH A POROUS THIN GEL NETWORK[*]

Qi-liang Song and Guang-zhao Zhang[**]
*The Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics, The University of
Science and Technology of China, Hefei 230026, China*
Chi Wu
Department of Chemistry, The Chinese University of Hong Kong, Shatin N. T., Hong Kong, China

Abstract Using a core (142 nm) made of linear polystyrene (PS) chains as a seed, we further polymerized a thin layer of cross-linked PS shell (7 nm) on it in water to form a core-shell particle. Such a particle swells in toluene, which enables 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 examined the chain diffusion process by following the change of the scattering intensity (*i.e.* the average molar mass of the particles). For the first time, we have revealed that the diffusion exhibits three stages. In the first stage, the chain diffusion through the shell is even faster than their translational diffusion in a dilute solution. The three stages respectively correspond to the change of the solution in the core from concentrated to semidilute and then from semidilute to dilute.

Keywords: Chain diffusion; Small core-shell particle; Laser lighter scattering.

INTRODUCTION

The diffusion of polymer chains through a porous membrane or a swollen gel network is important for gel permeation chromatography, controlled releasing of active chemicals and translocation of biological macromolecules[1–3]. A polymer chain confined inside a small and long pore normally diffuses much slower than a chain free in a dilute solution, which is called hindered diffusion. In theory[4], assuming no specific interaction between the pore and the chain, the diffusivity of a polymer chain inside a pore is related to the hydrodynamic viscous drag coefficient (f_h) and the partition coefficient (K) of the chain between inside and outside the pore[5]. The basic theoretical "hard sphere" model for such hindered diffusion of macromolecules is expressed by the Renkin equation $D_p/D_0 = (1 - \lambda_s)^2(1 - 2.1\ \lambda_s + 2.1\ \lambda_s^3 - 0.95\ \lambda_s^5)$, where D_p and D_0 are the diffusion coefficients of polymer chains inside the core and free in a dilute solution, respectively, and λ_s is the ratio of the Stokes-Einstein radius of the polymer chain to the pore radius (R_p)[6]. Previous experimental results agreed well with this equation in the range of $0.05 < \lambda_s < 0.4$[7–9]. Further, Davidson and Deen[10] proposed an extended theory for the diffusion of linear flexible chains inside a pore under the condition $\lambda_s < 1$. On the other hand, when $\lambda_s > 1$, the diffusion of flexible polymer chains through a small pore can be described by a scaling theory[11]. For long flexible polymer chains in an athermal solvent with $R_f \geq R_p$, we have the scaling law: $D_p/D_0 \approx a(bR_f/R_p)^{2/3}\exp(-bR_f/R_p)^{5/3}$, where R_f is the Flory radius, *i.e.*, the root mean square end-to-end distance of the chain; a and b are two constants. Therefore, D_p approaches zero when $R_f >> R_p$ without any external drive[12].

The restricted diffusion experiments were normally conducted by a diffusion cell with a track-etched separation membrane in the dilute regime[13-16]. Previous studies were concentrated on polymer chains with an average size smaller than the pore size because long chains diffusing through small pores is very difficult. In the present study, we first encapsulated linear polystyrene chains (core) inside a cross-linked polystyrene network (shell) using the seeded emulsion polymerization in water. Such core-shell particles swell in toluene so that linear PS chains inside can diffuse out through the porous shell (a swollen gel network). We used a combination of static and dynamic laser light scattering to examine such a diffusion process. Using small core-shell particles, we gain two advantages in comparison with a normal macroscopic study of diffusion of long polymer chains through small pores. Namely, 1) these small particles have a huge surface area so that the diffusion out of the chains is much fast and 2) we can use laser light scattering to *in situ* monitor the mass decrease of the particles as the chains diffuse out without any external interference.

EXPERIMENTAL

Sample Preparation

First, the seeds (core) made of uncross-linked linear PS chains were prepared by emulsion polymerization. 3.53 g of PE10500 (BASF), 0.60 g of AIBN, 39.98 g of styrene and 1000 mL deionized water were charged into a 2-liter 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. Afterward 1.18 g styrene monomers and 19 mg DVB were coated on the core (3.68 g) by the seeded emulsion polymerization under the starved condition, and small core-shell particles were obtained.

Laser-Light Scattering

A commercial LLS spectrometer (ALV/SP-125) equipped with an ALV-5000 multitau 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 can lead to the apparent weight-average molar mass (M_w) and the root-mean square z-average radius of gyration ($<R_g^2>_z^{1/2}$ or written as $<R_g>$)[17], where q is the scattering vector. In all LLS experiments, the polymer concentrations were lower than 5×10^{-6} g/mL, so that $R_{vv}(q)$ is proportional to M_w for a given concentration and a small scattering angle. In dynamic LLS, the Laplace inversion analysis of a measured intensity-intensity time correlation function $G^{(2)}(q, t)$ in the self-beating mode can lead to an average line width ($<\Gamma>$) or a line-width distribution ($G(\Gamma)$)[17, 18]. For a pure diffusive relaxation, Γ is related to the translational diffusion coefficient D by $D = (\Gamma/q^2)_{q\rightarrow 0, c\rightarrow 0}$, and further, to the hydrodynamic radius distribution $f(R_h)$ *via* the Stokes-Einstein equation, $R_h = k_B T/(6\pi\eta D)$, where T and η are the absolute temperature and the solvent viscosity, respectively[18].

Diffusion Experiments

Small core-shell particles prepared by the seeded emulsion polymerization were freeze-dried and then redispersed/swollen in toluene. The diffusion of linear polystyrene chains from the core through the swollen cross-linked porous shell into toluene was monitored in terms of the change of the apparent molecular mass of the core-shell particle. All the LLS experiments were done at 25°C. All the LLS measurements started 20 min after the particles were redispersed/swollen in toluene because the preparation of a dust-free dispersion takes a certain time. Initially, the polymer concentration inside the core should be higher than that in the shell since the shell swells before the core. For a dilute dispersion, the volume inside each core (V_{core}) is much smaller than that outside the shell, so that we have[14]

$$(c_t - c_\infty) = (c_0 - c_\infty)\exp(-\frac{D_{eff} A_{pore}}{L V_{core}} t)$$

(1)

where D_{eff}, A_{pore} and L are the effective diffusion coefficient, the total effective cross-section area of all the pores in the shell and the shell thickness, respectively. The subscripts 0, t and ∞ indicate the time at zero, t and infinite,

respectively. Therefore, c_∞ is the final equilibrium concentration after all the chains diffuse out from the core into the dispersion medium. In this study, c_0 ($\equiv m_{core}/V_{core}$) is 5.5×10^{-2} g/mL, while c_∞ is lower than 5×10^{-6} g/mL. Therefore, we can rewrite Eq. (1) as

$$\ln\frac{c_t - c_\infty}{c_0} = -\frac{D_{eff} A_{pore}}{V_{core} L} t \qquad (2)$$

RESULTS AND DISCUSSION

Figure 1 shows hydrodynamic radius distributions $f(R_h)$ of the initial cores (seed) and the finial core-shell particles in water. The relative width ($\mu_2/<\Gamma>^2$) of $f(R_h)$ is all below 0.02, indicating that they are narrowly distributed. Therefore, we do not need to worry about a possible size effect within each sample even though we simultaneously observed many particles. Assuming there was no additional nucleation in the second seeded emulsion polymerization, the theoretical radius of the core-shell particle (78 nm) can be calculated from the synthesis recipe of the second seeded emulsion polymerization and the hydrodynamic radius of the seed (71 nm), which is identical to the average hydrodynamic radius of the core-shell particle determined by dynamic LLS. Such a good agreement indicates that nearly all styrene monomers and cross-linking agents DVB added during the shell preparation were coated on the seed surface with no additional nucleation in water. The shell thickness calculated from the radius difference between the final particles and the core is 7 nm.
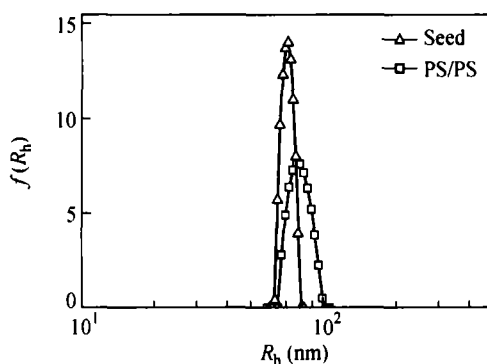

Fig. 1 Hydrodynamic radius distributions ($f(R_h)$) of seed particles (core) and core-shell particles in water
The polymer concentrations are 2.0×10^{-6} g/mL and 2.4×10^{-6} g/mL, respectively.
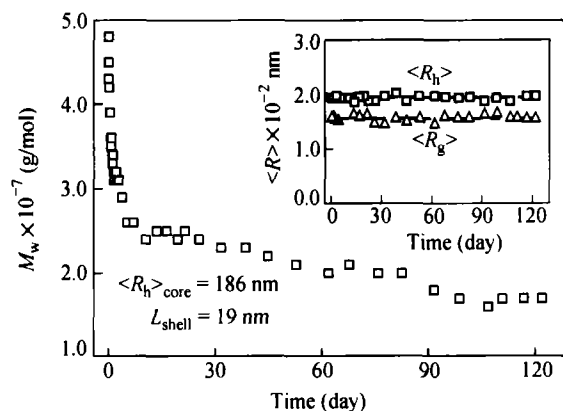

Fig. 2 Time dependence of apparent weight average molar mass of the core-shell particles swollen in toluene during an entire diffusion process
The inset shows time dependence of the average hydrodynamic radius $<R_h>$ and the average radius of gyration $<R_g>$ of the core-shell particles during the same diffusion process.

Figure 2 shows the time dependences of the weight-average molar mass (M_w), $<R_h>$ and $<R_g>$ of the core-shell particles after they were redispersed and swollen in toluene. As expected, M_w decreases as the linear PS chains inside the core diffuse out through the porous PS shell, while $<R_h>$ and $<R_g>$ remain constant during the diffusion. This is because PS chains trapped in the core are limited and the shell is thick. The diffusion out of the PS chains leads to slight changes in the $<R_g>$ and $<R_h>$. Using the size of the seed particles in water as a reference and assuming that the core and the shell swell uniformly, the average shell thickness and the average core radius of the core-shell particle after swelling are 19 nm and 186 nm, respectively. Note that the average molar mass of linear PS chains entrapped inside the core is 9.2×10^5 g/mol, much lower than that of the core-shell particles. Therefore, their contribution to the scattering intensity can be ignored after they diffuse out of the shell into toluene.

Figure 3 reveals that the diffusion process has three stages ranging in 1.0×10^{-3}–2.0×10^{-3} g/mL (the first stage), 0.7×10^{-3}–1.0×10^{-3} g/mL (the second stage), and $< 0.7 \times 10^{-3}$ g/mL (the third stage), respectively. The second stage is a transitional one between the first and third stages. The effective diffusion coefficients (D_{eff}) at first ($D_1 = 2.0 \times 10^{-7}$ cm^2/s) and third ($D_3 = 6.8 \times 10^{-9}$ cm^2/s) stages were calculated using Eq. (2), assuming that A_{pore} is the surface area of the inner shell because the cross-linked chains in the shell (a highly swollen network) occupy only a very small portion of the surface area. In the first 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^* ca. 1.37×10^{-3} g/mL. As the diffusion proceeds, the polymer concentration in the core decreases but the solution is still in semidilute regime. The diffusion enters the second transitional stage. When the polymer solution in the core becomes dilute, the diffusion enters the third stage. In the dilute regime, the average size of individual linear flexible polymer chains in the core is larger than the pore size, so that the diffusion in the third stage is extremely slow. We know that the size of the pore in the shell remain constant in the entire diffusion process, only the concentration of polymer chains in the core changes, *i.e.*, the correlation length of the polymer chains in the core increases. Therefore, we can interpret the three different diffusion stages from the change of the polymer concentration in the core or the ratio of the correlation length of the polymer chains in the core to the average size of the pore in the shell. It is interesting to note that the effective diffusion coefficient in the first stage is even faster than the same chains are free in a dilute solution (1.34×10^{-7} cm^2/s, determined by dynamic LLS of same PS seed in dilute toluene solution). The fast diffusion in the first stage can be attributed to a large difference between the correlation length in the core and the average size of the pores in the shell. The entire diffusion experiment and the different diffusion stages are schematically summarized in Fig. 4.
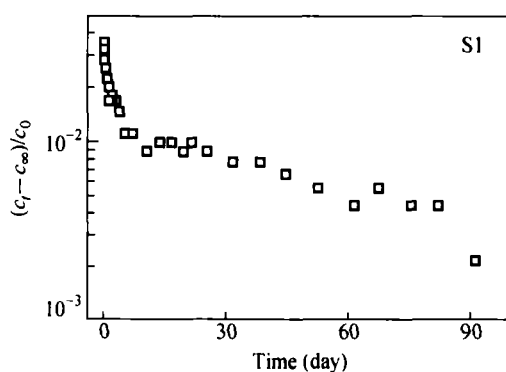

Fig. 3 Time dependence of concentration of linear polystyrene chains in the core after the core-shell particle was swollen in toluene

$c_0 = m_{core}/V_{core}$ and $c_\infty = m_{core}N_{particle}/V$ with m_{core} and $N_{particle}$ being the average mass of the core and the number of particles, respectively, and V_{core} and V being the volumes of one core and the dispersion, respectively
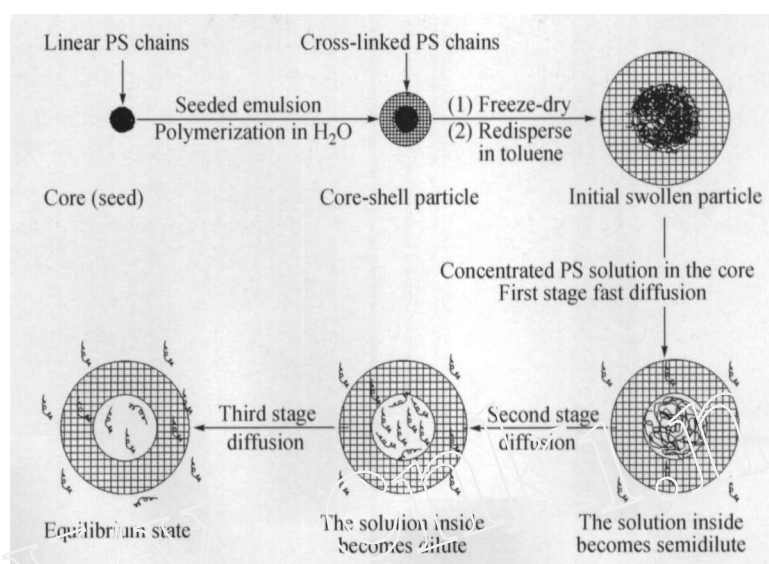
Fig. 4 Schematic of entire core-shell particle preparation and three different diffusion stages of the entire diffusion process in toluene

CONCLUSIONS

Using narrowly-dispersed core-shell particles, the diffusion out of long linear polystyrene chains in the core through the thin layer of cross-linked porous polystyrene shell has been successfully studied by using a combination of static and dynamic laser light scattering. Our results reveal that the diffusion has three different stages, which respectively correspond to the concentration change in the core. We have, for the first time, observed the diffusion through a restricted porous membrane is even faster than the translational diffusion of the same chains free in a dilute solution when the polymer concentration is much higher than the overlap concentration. Further studies of effects of the shell thickness and cross-linking density on the diffusion of polymer chains through a porous shell or a swollen gel network are ongoing.

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