Diffusion of Solvated Polystyrene Confined in a Porous Medium at Near-Θ Conditions

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ABSTRACT: The dynamic light scattering (DLS) technique was applied to polystyrene fractions of different molecular weights dissolved in the near-Θ solvent *trans*-decahydronaphthalene and confined in a porous glass bead. Diffusion coefficients were measured for the polymer in the interior of the porous medium and in the surrounding free solution. Diffusion, when normalized to take into account solvent viscosity and temperature, was slower in the Θ solvent than in the good solvent 2-fluorotoluene, a result being ascribed to a stronger hydrodynamic interaction for a compact Gaussian chain in the pore channels than for a chain with excluded volume. At higher temperatures, the decrease in the reduced diffusivity was larger than expected for the increased radius of gyration of the polystyrene chain in the better solvent. At the same time, the DLS autocorrelation function exhibited a pronounced deviation from a single-exponential decay. Enhanced interaction between swelling polymer chains in the narrow pore channels is considered to have increased the concentration coefficient of the friction coefficient for translational motion and thus to have resulted in the decrease of the diffusion coefficient at a low, but nonzero, polymer concentration.

Introduction

Geometrically confined solvated polymer molecules, as for example in a porous medium, exhibit static and dynamic properties distinctly different from those in unrestricted geometries. The effect of confinement is prominent when the porous materials have a pore size comparable to the dimension of the polymer molecules.

In recent years, the dynamics of polystyrene in a controlled pore glass has been intensively studied.[1−4] Dynamic light scattering (DLS) experiments have been performed with a porous glass bead immersed in a solution containing polymer molecules.[2] Index-matching of the solvent with silica, the solid phase of the porous medium, produced a situation in which the dissolved polymer was the only "observable" species in the porous medium as well as in the exterior solution. By these means, Bishop et al.[2] and Guo et al.[4] studied the dependence of the diffusion coefficient of polymer chains in the porous medium on the chain dimension. The dependence on chain architecture was also studied using star-shaped polymers with different numbers of branches.[3] It was found that, compared at the same hydrodynamic radius in free solutions, a star-shaped polymer with more branches undergoes a greater hindrance effect from the pore walls.

Application of DLS to the studies of dynamics of polymer chains confined in such porous media has been extended in the past few years to nondilute systems. The developments include (1) the measurement of mutual and cooperative diffusion coefficients of solvated polymer chains in a porous medium over a wider range of polymer concentrations[5] and (2) the measurement of the tracer diffusion coefficient of probe polymer chains in a ternary solution confined in a porous medium as a function of the matrix polymer concentration c_m.[6] In the latter measurement, the matrix polymer was selected to be isorefractive with the solvent and silica. It was found[6] that the concentration coefficient k_{Dt} in the expression for the tracer diffusion coefficient $D_t \cong D_0(1 + k_{Dt}c_m)$, where D_0 is the diffusion coefficient in the dilute solution limit, is much larger in the porous medium than in the external solution. The difference was ascribed to a stronger interaction between polymer chains in the narrow, quasi-one-dimensional pore channels.

All the studies described above were carried out using a good solvent in which there is a net repulsion between chains. A positive second virial coefficient, A_2, is associated with the chain expansion in solution. The repulsion also contributes to an increase in the mutual diffusion coefficient and a decrease in the self-diffusion coefficient as the polymer concentration increases. It is of interest to study the diffusion of solvated polymer molecules in porous media when A_2 is at or near zero.

In this contribution, we therefore report on the dynamics of solvated polymer chains within the porous medium in a Θ solvent using DLS. We take advantage of the fact that *trans*-decahydronaphthalene is nearly isorefractive with silica and is also a Θ solvent for polystyrene at around 20 °C.[7] Comparison of the measured diffusion coefficient in the Θ solvent with that in a good solvent in the porous medium will reveal the effect of the chain compactness on mobility in the pore channels. We are also interested in how changes in the chain statistics as the temperature is raised and the solvent becomes better for polystyrene are manifested in the dynamics in the pore channels.

Experimental Section

Measurement System. The dynamic light scattering measurement system has been described elsewhere.[5] The light source was a 5 mW He−Ne laser (λ = 632.8 nm). Diffusion coefficients in the external solution were measured using a Model 1096 digital autocorrelator (Langley Ford Instruments, Coulter Electronics) that has 256 linearly spaced delay channels. Diffusion coefficients in the porous glass bead were measured using a Model N4SD correlator (Coulter Electronics) with 80 quasi-logarithmically spaced delay channels. The

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absolute value of the normalized, baseline-subtracted electric field autocorrelation function $g_1(t)$ for a delay time t was analyzed in a second-order cumulant expansion: $\ln g_1(t) = -\Gamma t + (\mu/2)t^2$, where Γ is the average decay rate and μ is the variance. In the measurement of the light scattered from a porous glass bead that contains the polymer solution at various temperatures, the solvent could not always be completely index-matched to silica. We note that, in the expression of the diffusion coefficientt Γ/k^2 for the interior of the porous glass, the magnitude k of the scattering vector is still given by $k = (4\pi n/\lambda)\sin(\theta/2)$, where θ is the scattering angle and n is the refractive index of the solvent at the wavelength λ at a given temperature.

Samples. Four different molecular weight polystyrene standards (Pressure Chemical Co.) were used. The peak molecular weights M measured by size exclusion chromatography are 4.89×10^4, 9.82×10^4, 1.69×10^5, and 4.02×10^5, and the polydispersity of the molecular weights is less than 1.06 (manufacturer-supplied data). As a solvent that provides polystyrene with Θ conditions in an accessible temperature range and, at the same time, is nearly isorefractive with silica, we chose *trans*-decahydronaphthalene (TD). The refractive index n at 632.8 nm changes as a function of the absolute temperature T:[7]

$$n = 1.4662 - 4.3 \times 10^{-4}(T - 293.15)$$

The index-matching of TD with silica is optimized at temperatures around 40 °C. The viscosity η_S (cP) of TD changes as[8]

$$\log \eta_S = -1.5844 + 443.20/(T - 61.638)$$

The porous glass beads were supplied by Shell Development Co. and are coded as S980G1.5. The solid phase is silica. The nominal pore radius is 250 Å, and the pore volume is 1.0 cm^3/g. Adsorption of polystyrene onto the pore walls was avoided by careful silanization of the glass that replaces surface hydroxyl groups by trimethylsilanyl groups.

Concentrations c of polystyrene in TD were 0.43, 0.28, 0.20, and 0.14 wt % for the four samples in increasing order of the molecular weight. The respective reduced concentrations c/c^* are 0.047, 0.043, 0.041, and 0.044, at 20 °C. Here the overlap concentration c^* is defined by $c^*(2^{1/2}R_g)^3 = M/N_A$, where N_A is Avogadro's number and R_g is the radius of gyration of the polymer. We estimated R_g from the reported value[7] of 128 Å for polystyrene of molecular weight 1.79×10^5 in TD at 20 °C and the relation $R_g \propto M^{1/2}$.

After complete dissolution, the polymer solution was filtered through a 0.2 μm Millipore Teflon filter at least three times and then poured into a Pyrex test tube that held a porous glass bead at its center. At least a week was allowed to equilibrate the solvated polymer between the interior of the porous glass and the exterior. The test tube was held in a vat filled with temperature-controlled decahydronaphthalene for at least 24 h before the DLS measurements were conducted at different scattering angles (15.8, 25.5, and 35.3°). When the temperature of the vat was changed, a further 24 h of re-equilibration was used before measurements.

Results and Discussion

Molecular Weight Dependence. The Θ temperature of polystyrene in TD is about 20.5 °C.[7] In the present measurements, the diffusion coefficients D_f and D_p of polystyrene in the external free solution and in the interior of a porous glass bead for different molecular weights at 23.8 °C were obtained. The DLS autocorrelation functions observed were close to a single-exponential decay for the external solution data. In the curve-fitting by a cumulant expansion for the data points in the range $\ln g_1(t) \gtrsim -3$, μ/Γ^2 was typically less than 0.025 at the three scattering angles. The autocorrelation functions for data obtained for the interior of the glass beads showed a deviation from a single-exponential decay. In the curve-fitting for the data in the range $\ln g_1(t) \gtrsim -3$, μ/Γ^2 reached a value as large as 0.07, but the fitting was reasonably good in the range. The diffusion coefficients D_f and D_p were calculated from the relationship between Γ and k^2 (see Figure 1). It was found that the exterior diffusion coefficients D_f depended on M as $D_f \propto M^{-0.49}$. The exponent is close to -0.5, a result indicating that the system is in a near-Θ condition. We also note that the diffusion coefficient D_p for the polystyrene in the porous medium decreases much more rapidly than D_f does as the length of the chain increases.

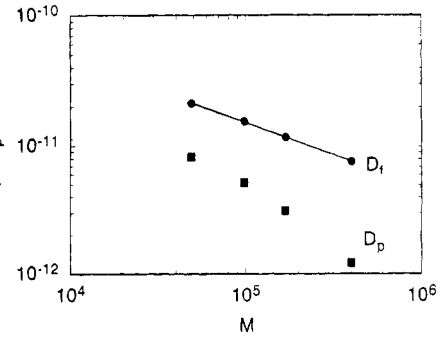

Figure 1. Diffusion coefficients of polystyrene D_f and D_p in *trans*-decahydronaphthalene at 23.8 °C in the external free solution and in the porous glass bead, respectively, plotted as a function of the molecular weight M. The straight line shows the best fit of D_f by the power law $D_f \propto M^{-0.49}$.

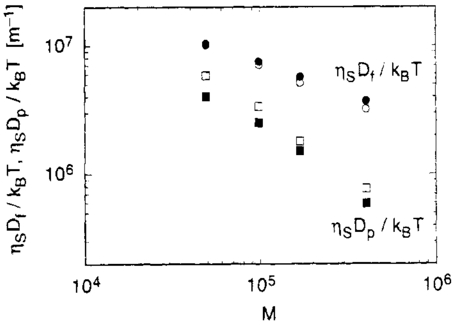

Figure 2. Reduced diffusion coefficients $\eta_S D_f/k_BT$ and $\eta_S D_p/k_BT$ in the exterior solution and in the interior of a porous glass bead, respectively. Closed symbols were obtained from the measurements for polystyrene in *trans*-decahydronaphthalene at 23.8 °C (a near-Θ condition). Open symbols are for polystyrene in 2-fluorotoluene at 34.8 °C (a good solvent).

We may compare the diffusion coefficients of polystyrene in a near-Θ condition (at 23.8 °C in TD) with those for the same polymer in a good solvent (i.e., at 34.8 °C in 2-fluorotoluene, 2FT;[6] $\eta_S = 0.569$ cP; measured at $c/c^* \cong 0.2$[9]). Reduced diffusion coefficients $\eta_S D_f/k_BT$ and $\eta_S D_p/k_BT$, where k_B is the Boltzmann constant, in the free solution and in the interior of a porous glass bead are plotted as a function of M in Figure 2. A diffusant of hydrodynamic radius R_H should obey the relation $\eta_S D_f/k_BT = 1/6\pi R_H$ in the dilute solution limit. Closed and open symbols in the figure represent the reduced diffusion coefficients in the Θ and in the good solvent, respectively. The hydrodynamic radius R_H in the Θ solvent is approximately given by $0.0254M^{0.490}$ [nm], which is favorably compared with the reported formula[10] in cyclohexane at 34.5 °C, $0.0200M^{0.508}$ [nm].

Compared at the same molecular weight, $\eta_S D_f/k_BT$ is larger in the Θ solvent than in the good solvent; the hydrodynamic radius is of course smaller in the former. As M increases, $\eta_S D_f/k_BT$ decreases both in the Θ and in the good solvent, but the relative difference increases. The decrease in $\eta_S D_f/k_BT$ for polystyrene in the Θ solvent is slower because of the difference in chain statistics. We note that the reduced diffusion coefficients plotted here have not been extrapolated to zero concentration. In the dilute solution range, D_f is expressed as $D_f = D_{f0}(1 + k_{Df}c)$, where D_{f0} is the zero-concentration asymptote and $k_{Df} = 2A_2M - k_F - \bar{v}$. Here k_F is the first-order concentration coefficient of the friction coefficient of the diffusant $f = f_0(1 + k_Fc)$, with f_0 being its asymptote, and $\bar{v}$ is the specific volume of the polymer. When extrapolated, η_SD_f/k_BT in the good solvent will be only slightly smaller. The extrapolation for the Θ solvent measurements will not make an appreciable difference, because A_2 disappears and the contribution of the hydrodynamic volume alone to k_F is not large.[11-13] Thus the difference in η_SD_{f0}/k_BT between good and Θ solvents will be larger than in η_SD_f/k_BT. The molecular weight dependence of η_SD_f/k_BT measured at a constant reduced concentration c/c^* is expected to be only weakly affected by nonzero concentration. Using the results by Huber et al.,[10] $A_2Mc^* \sim M^{0.012}$ in a good solvent (toluene, 20 °C) and $k_fc^* \sim M^{0.024}$ in a Θ solvent (cyclohexane, 34.5 °C). Thus the above discussion concerning measurements of η_SD_f/k_BT at finite concentrations will apply to the zero-concentration asymptotes essentially unchanged.

The reduced diffusion coefficient η_SD_p/k_BT for polystyrene in the porous medium shows a different tendency; η_SD_p/k_BT is smaller in the Θ solvent for the four molecular weights. Again, we examine the effect of measurements at nonzero concentrations. Our previous studies[5] on the concentration dependence of η_SD_p/k_BT in a good solvent show that D_p at $c/c^* \cong 0.2$ is nearly equal to its zero-concentration asymptote. The dependence of η_SD_p/k_BT on concentration is expected to be weak also in the Θ solvent because $A_2 \cong 0$, rendering the concentration coefficient of D_p small for diffusion in the pore channels. As we discuss below, a relatively small μ/Γ^2 for the Θ solvent measurements (compared with that for higher temperatures) also supports a small effect of finite concentrations.

We find that a Gaussian unperturbed chain that is more compact than an expanded chain in free solution experiences a larger frictional retardation in the pore channels. This result is in agreement with the report[3] that the hindrance effect of the pore channels on a diffusion is larger for a star-shaped polyisoprene that has more branches and hence is more compact. In addition to its inherent compactness, a Gaussian chain gains in monomer density when it is placed in a cylindrical pore channel. A high density of monomer units transverse to the pore diameter will help to increase the hydrodynamic interaction among such monomers as well as with the solid pore walls. The high density is explained as follows. A Gaussian chain will be represented by a trajectory of a random walk. Upon impinging on the pore wall, the random walk is simply reflected back.[14,15] The change in the coordinate of the walker appears in the radial component only. The component parallel to the pore experiences no change. This is why the dimension of a Gaussian chain along the pore does not change with confinement[14,15] whereas the monomer density across the cross section of the pore increases. In contrast, an excluded volume chain readily adopts a conformation extending along the channel.

Temperature Dependence. As the temperature increases, TD changes from a Θ to a relatively good solvent. Autocorrelation functions for the polystyrene fraction of molecular weight $M = 4.89 \times 10^4$ were measured in the exterior free solution and in the interior of the porous glass bead in the temperature range 16.2–60.0 °C. We note that the autocorrelation functions for the solution in the interior of the glass bead showed a greater deviation from a single-exponential decay at higher temperatures. The deviation was larger at a higher scattering angle. We limited the range of the data points for the second-cumulant fitting to $\ln g_1(t) \gtrsim -1.5$ to obtain a reasonable fit in the range. It is not certain whether $g_1(t)$ approaches a single-exponential decay pattern at long times; a greater mismatch in the refractive indices between TD and silica at higher temperatures hampered accurate measurements, in particular, those of baseline levels at long delay times.

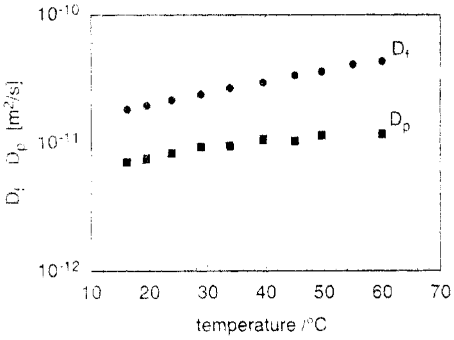

Figure 3. Diffusion coefficients D_f and D_p of polystyrene of molecular weight 4.89×10^4 in *trans*-decahydronaphthalene in the external free solution and in the porous glass bead, respectively, measured as a function of temperature. The Θ temperature of the solvent is near 20.5 °C.

Diffusion coefficients D_f and D_p in the free solution and in the porous glass bead are plotted against temperature in Figure 3. The hydrodynamic radius R_H of the polymer calculated assuming D_f at 0.43 wt % polymer concentration to be equal to that in the dilute solution limit does not exhibit a temperature dependence. This result is expected[16] when we consider the small magnitude of the parameter[17,18] $N/N_\tau = (M/416) \times [(T - T_\Theta)/T]^2 = 1.65$ at 60 °C (T_Θ is the Θ temperature). This parameter expresses the chain length N relative to a cutoff N_τ that separates Gaussian and excluded volume chains. As N/N_τ exceeds ca. 10, the solvent can be qualified as a good solvent for the polymer, and chain swelling occurs.[17,18] Furthermore, the temperature-induced increase in R_H is slower than that in R_g.[16,17] Because of the low molecular weight of polystyrene fraction used here, even at the highest temperature studied a solvent condition is not sufficiently good to expand R_H.

The increase in D_p is slower than D_f, especially at high temperatures. This may appear natural because we expect an increase in chain size R_g to some degree as TD becomes a better solvent for polystyrene. In the following, we examine whether the slower increase in D_p is due to the increase in R_g and hence to a more pronounced confinement effect. It is known[17,18] that the chain expansion factor, defined as a ratio of R_g to its value at the Θ temperature, lies on a master curve, given as a function of N/N_τ, for polystyrenes of different molecular weights at various temperatures above T_Θ. The master curve[19] enables us to estimate the expansion factor for polystyrene of different molecular weights at temperatures above 20.5 °C. The values of R_g for different molecular weights at 20.5 °C were estimated using the relationship $R_g \propto M^{1/2}$ and $R_g = 128$ Å for $M = 1.79 \times 10^5$ reported in the literature.[7] Combining the expansion factor and the estimated R_g at 20.5 °C, we evaluated R_g at higher temperatures.

To compare diffusivity in the pore channels between polystyrene of $M = 4.89 \times 10^4$ at various temperatures above T_Θ and polystyrene of the four different molecular weights at 23.8 °C, we have plotted in Figure 4 (open triangles and closed squares) η_SD_p/k_BT as a function of

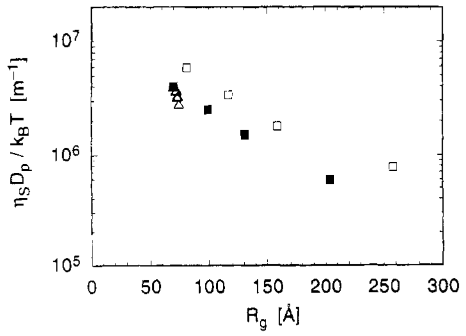

Figure 4. Reduced diffusion coefficient $\eta_S D_p/k_B T$ in the pore plotted against radius of gyration R_g of polystyrene in free solution. Closed and open squares represent the data obtained for the four different molecular weights of polystyrene in *trans*-decahydronaphthalene (TD) at 23.8 °C and in the good solvent 2-fluorotoluene at 34.8 °C. Open triangles represent the data measured for polystyrene of molecular weight 4.89 × 10^4 in TD at various temperatures.

the R_g in free solution. As the temperature increases, data points indicated by triangles deviate downward from a line drawn for the molecular weight dependence. Compared at the same R_g in free solution, the diffusivity in the pore channels is smaller at higher temperatures, although the solvent TD becomes a better solvent for polystyrene. For reference, we included in the figure $\eta_S D_p/k_B T$ for polystyrene in 2FT plotted against R_g calculated using $R_g \cong 1.562(k_B T/6\pi\eta_S D_f)$,[20] where D_f was measured at $c/c^* \cong 0.2$. Note that the data points for $\eta_S D_p/k_B T$ measured in the good solvent 2FT (open squares) lie above the straight line in Figure 4 (see also Figure 2). We therefore conclude that the slower decrease in D_p at higher temperatures is not due to simple expansion of the polystyrene chain.

Nose and Chu[7] reported that in free solution, the concentration coefficient k_F in the friction coefficient of polystyrene molecules in TD is positive and increases as the temperature increases between 20 and 40 °C. The magnitude of k_F is large enough to offset a slightly positive $2A_2M$ in $k_{Df} = 2A_2M - k_F - \bar{v}$. Thus k_{Df} is negative even at temperatures higher than the Θ temperature.

We have shown in our recent contribution[6] that k_F is increased in the narrow, quasi-one-dimensional pore channels. This was manifested as a sharp decrease in the tracer diffusion coefficient and as a deviation of the autocorrelation function from a single-exponential decay when the concentration of the matrix polymer was increased in the exterior of a porous medium, leading to a small increase in the internal concentration. When we combine the increase in k_F for polystyrene in free solution at higher temperatures and the enhancement of k_F in the pore channels, we find that k_F becomes larger in the porous medium at higher temperatures. The osmotic pressure contribution A_2M in the corresponding expression of k_{Dp} for D_p is expected to be minimized in the pore channels, especially for a larger chain dimension. Therefore, k_{Dp} should be negative, and its absolute value should be larger in the pore than in the free solution and should increase as the temperature rises. Furthermore, the increase in the osmotic pressure in the external free solution as the temperature rises will have resulted in an increased polymer concentration in the porous medium.[5] Then, the decrease in the diffusion coefficient D_p measured at a finite exterior concentration from that in the dilute solution limit should be larger in the pore, especially at elevated temperatures. We may conclude that the enhanced interaction between chains in the pores in TD at higher temperatures has caused the downward deviation in the reduced diffusion coefficient $\eta_S D_p/k_B T$ as well as the deviation in the autocorrelation function from a single-exponential decay. A further study on the concentration dependence at different temperatures will elucidate detailed characteristics of chain interaction in the pore channels.

Autocorrelation functions for polystyrenes of higher molecular weights ($M = 9.82 \times 10^4$, 1.69×10^5, and 4.02×10^5) in the porous medium at temperatures higher than 25 °C also showed a substantial deviation from a single-exponential decay. The deviations were larger than those for polystyrene of $M = 4.89 \times 10^4$. We could not obtain reasonable decay rates in the autocorrelation functions before the latter decayed to a level indistinguishable from the background, which is relatively high for the index-mismatched system. This observation is in agreement with the strong chain–chain interaction in the pore channels described earlier. As M increases and the chain dimension becomes larger, the interaction further increases to make k_F even larger.

Conclusion

The measurement of the diffusion coefficient for polystyrene in Θ solvent in a porous medium has shown that the hindrance effect due to the pore walls is larger for a Gaussian chain than for an excluded volume chain. Further, enhanced interactions between polymer chains in the narrow pore channels appear to have reduced the diffusion coefficient at finite concentrations, especially at higher temperatures. The second effect is in agreement with our previous findings[6] for the tracer diffusion of polystyrene in a good solvent.

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