Restricted Diffusion of Highly Dense Starburst-Dendritic Poly(amido amine) in Porous Glasses

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ABSTRACT: The dependence of hindered diffusion on the size ratio λ_H, the ratio of the hydrodynamic radius of the macromolecule to pore radius, was studied for dendritic poly(amido amines) and linear polystyrenes in porous glasses. At low λ_H, when hydrodynamic interactions dominate the diffusion, the dendritic polymers diffuse more slowly than do the linear polymers. The diffusion results for the dendritic polymer are in quantitative agreement with a hydrodynamic theory for a hard sphere in a cylindrical pore. The diffusion results for the linear flexible polymer chains are in qualitative agreement with a hydrodynamic theory for a random coil macromolecule in a cylindrical pore.

Introduction

The diffusion of polymers or other species in restricted geometries continues to attract great interest because of its theoretical and practical importance. The central goal of the studies of hindered transport in porous materials has been to relate the results of phenomenological measurements to the microscopic parameters characterizing the polymer and the porous material. Many publications concerning restricted diffusion in pores have focused on transport across track-etched membranes,[1-8] which have pores corresponding closely to the cylindrical pore models that have been extensively used in theoretical work.[9-14] However, the various papers report different experimental results for the extent of reduced diffusion as a function of the ratio of diffusant radius to pore size, i.e., $\lambda_H \equiv R_H/R_P$, where R_H is the effective hydrodynamic radius in unbounded solution and R_P is the pore radius. These differences may be attributed to the difference in the effective hard-sphere radius of confined polymer molecules relative to that in unbounded solution. In membrane transport studies, the differences may also result from the dependence of the partition coefficient on the specific interactions between the polymer and the pore walls.

We have employed dynamic light scattering (DLS) techniques for direct measurement of polymer diffusion inside liquid-filled pores of controlled-pore glasses, without the complication of the partition effect.[15-17] Hindered diffusion of polymer molecules with different architectures, including linear flexible chains and star-branched forms, has been studied. When a polymer molecule is appreciably smaller than the pore in which it resides, its diffusion is reduced relative to that in the unbounded solution mainly because of the steric obstruction provided by the solid matrix and the hydrodynamic interactions with the pore wall. In interpreting the results, it has been assumed that the effect of the structural geometry and the effect of the hydrodynamic interaction are separable at macroscopic scales.[15] Therefore the macroscopic diffusion coefficient D, measured over a distance much larger than the pore dimension (i.e., $qR_P \ll 1$, where q is the scattering wavevector), is given by

$$D/D_0 = Xf(\lambda_H) \tag{1}$$

where D_0 is the diffusivity in unbounded solution and the ratio D/D_0 is often referred to as the hindrance factor for diffusion. The parameter X represents the intrinsic conductivity of the porous material and is inversely proportional to the tortuosity of the pore geometry, thereby accounting for the meandering paths a diffusant must take. The function $f(\lambda_H)$ is the size-dependent ratio of diffusivity within the pore space to that in the unbounded solution. The separation of structural and hydrodynamic effects in eq 1 is valid only when all the pores are well connected and when the pore size distribution is narrow. For $\lambda_H \rightarrow 0$, the function $f(\lambda_H)$ approaches 1; thus a measured value of X can be obtained by extrapolating to zero measurements of D/D_0 versus λ_H.

When the confinement is relatively weak, hydrodynamic interactions dominate the diffusion process. Brenner and Gaydos[12] developed a hydrodynamic theory for the diffusion of a hard sphere inside a cylindrical pore, which predicts that

$$f(\lambda_S) = (1 + 1.125\lambda_S \ln \lambda_S - 1.539\lambda_S)/(1 - \lambda_S)^2 \tag{2}$$

where λ_S is the ratio of the radius of an impermeable, rigid, spherical diffusant to R_P, the pore radius. Bishop et al.[15] and Easwar et al.[16] compared the measured diffusion coefficients of polymers in porous glasses to those predicted by the Brenner–Gaydos theory. Because a confined macromolecule may have an effective radius that differs from R_H, its radius in free solution, a scaling factor κ was introduced to correlate the measured hydrodynamic radius of a partial free draining polymer to the hard-sphere radius R_S in the theory:

$$R_S = \kappa R_H \tag{3}$$

Although the incorporation of κ as a fitting parameter into the Brenner–Gaydos theory may lead to a better fit of the reported experimental results, the nature of the parameter κ is not unambiguous. Bishop et al.[15] suggested several possible factors that may cause the deviation of κ from unity; of these, the most important are (1) the underestimation of the pore radius by mercury intrusion

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porosimetry and (2) the fundamental inequality of R_H and R_S for permeable polymers. Easwar et al.[16] measured the diffusion of linear, 4-arm, and 8-arm polyisoprenes in porous glasses. The fitting parameter κ was found to be 0.45, 0.80, and 0.92 for the three architecturally different polyisoprenes. These authors ascribed the increase in κ to the fact that the polymer molecule with more arms more nearly approximated a hard sphere. On the basis of the observation that the value of κ for the 8-arm polymer was close to unity, they also suggested that the underestimation of R_P is insignificant. It is logical to extend the diffusion study to even more compact, less permeable polymer molecules. The recently developed starburst-dendritic macromolecules[18] are well suited for this purpose.

The Brenner–Gaydos theory and many other hydrodynamic theories for diffusion in the restricted space of simple geometries employ a rigid, impermeable sphere as a diffusant model. Therefore, an experimental system using highly compact diffusants more closely representative of these theories is desirable to test the theories' predicting power.

Experimental Section

The dendritic poly(amido amines) were a gift from David M. Hestrand and Donald A. Tomalia at Dow Chemical Co. The fundamental building blocks for this class of polymer are referred to as dendrimers, which have extreme symmetry and highly branched and maximized (telechelic) terminal functionality density. The dendritic polymers are formed by chemically bridging the repeating units in a starburst topology with, in principle, a very high degree of uniformity.[18] Because of the high functionality of the dendrimers, the number of terminal groups increases very rapidly with generation number. Therefore, a few layers of dendrimers can result in a molecule with a compact inner body and a densely packed outer surface, giving rise to very strong resistance to solvent permeation. In the dendritic poly(amido amine) samples received from Dow, the surface amines had been modified by reaction with epoxyoctane so that they would be soluble in organic solvents. The modified, less-polar surface outside the highly polar inner body further reduces the penetration of organic solvent molecules. The molecular weights of the polymers were unknown and could not be calculated because the number of the attached epoxyoctane groups was unknown. The theoretical molecular weights for the unmodified starburst poly(amido amines) were calculated to be 10 619, 43 415, and 349 883 for the fifth, seventh, and tenth generations. Static light scattering measurements to more completely characterize the samples were unsuccessful.

The porous materials used in this study were controlled-pore silica glasses with nominal pore radii of 893 Å (denoted as R893, from Electro-Nucleonics Co.) and 275 Å (denoted as G275, from Shell Development Co.), measured by mercury intrusion (data provided by the suppliers). Detailed descriptions of these porous glass samples can be found in refs 15 and 17. The pores were approximately cylindrical in shape over small dimensions and were highly branched and highly connected.

In the experiments a porous glass fragment was immersed in a decahydronaphthalene (Aldrich) solution of end-capped poly(amido amine); the solution had an index of refraction closely matching that of the glass and thus allowed detection of light scattered from polymer molecules inside the porous fragment. The concentration of the polymer solution was scaled to be approximately 1 order of magnitude smaller than the overlap concentration of that polymer. At these levels, the polymer concentration within the pore is sufficiently low for the results to be independent of this parameter.[19] Diffusion coefficients in unbounded solution (D_0) and inside the porous glass (D) were measured by using DLS at scattering wavevectors that satisfied $qR_P \ll 1$ to ensure that D was truly a macroscopic diffusion coefficient. The effective hydrodynamic radius R_H was calculated from the measured D_0 by the Stokes–Einstein equation.

The hindered diffusion relative to unbounded solution was studied in two porous glass samples, R893 and G275, which differ in pore radius R_P as well as in intrinsic conductivity X. Because X is characteristic of the porous material and does not depend on the nature of the diffusant, it is possible to use in this work the X values measured previously, namely, X(R893) = 0.78[15] and X(G275) = 0.89.[17] These values were obtained by extrapolating to $\lambda_H = 0$ the diffusion coefficient ratio D/D_0 of linear polystyrene in 2-fluorotoluene.

Table I
Experimental Values for the Diffusion of Dendritic Poly(amido amines)

polymer[a]	D_0[b] (10^{-7} cm^2/s)	R_H[c] (Å)	D[d] (10^{-7} cm^2/s)	λ_H[e]	$D/(XD_0)$[f]
Diffusion in R893 at 35 °C					
5	4.79	29	3.30	0.032	0.883 ± 0.019
7	3.15	44	2.11	0.049	0.859 ± 0.016
10	2.02	68	1.24	0.076	0.790 ± 0.032
Diffusion in G275 at 23 °C					
5	3.76	28	2.49	0.102	0.744 ± 0.015
7	2.57	41	1.40	0.149	0.612 ± 0.013
10	1.64	64	0.66	0.233	0.451 ± 0.020

[a] Generation number. [b] Diffusion coefficient of the polymer in free solution. [c] Hydrodynamic radius in free solution. [d] Macroscopic diffusion coefficient in porous glass. [e] $\lambda_H \equiv R_H/R_P$; R_H is defined in footnote c, and R_P is the pore radius of the porous material. [f] D/D_0 is the hindrance factor for diffusion; X is the intrinsic conductivity of the porous material. $D/(XD_0)$ is termed the diffusivity ratio; see text.

Results and Discussion

Table I lists the values for the polymer diffusivity in free solution D_0, the hydrodynamic radius of the polymers R_H, the macroscopic diffusion coefficient in the pores D, the ratio of polymer to pore size λ_H, the diffusivity ratio $D/(XD_0)$, and the temperature of the DLS measurements. The experimental temperatures were selected to achieve optimal matching of the refractive indexes of the solvent solution and the glass.

It has been observed that plots of the diffusivity ratio $D/(XD_0)$ versus λ_H superimpose for polystyrenes diffusing in three controlled-pore glasses that have different pore sizes but similar pore structures.[15] It has also been observed that similar plots for polymers with different chemical or architectural structures, for example, polystyrene, linear polyisoprene, 4-arm polyisoprene, and 8-arm polyisoprene, cannot be superimposed.[16] In other words, the difference in the behavior of diffusivity ratio versus size ratio for the different conditions reflects a dependence on chemical and/or architectural structure. A plot of the diffusivity ratio $D/(XD_0)$ against λ_H for the dendritic poly(amido amines) is shown in Figure 1, together with previously published data for linear polystyrenes in the same glasses.[15,17] The diffusivity inside the pores is significantly reduced relative to the unbounded solution, a result generally consistent with most other reported observations. We note that $D/(XD_0)$ for the starburst-dendritic polymer decreases with increasing λ_H faster than does that of the linear polymer. In other words, at the same λ_H, the dendritic polymer molecule diffuses more slowly than do linear chains; and the larger the λ_H, the larger the difference in diffusion rate.

The difference in diffusion rates for the linear polystyrene and the dendritic poly(amido amine) can be conceptually understood by taking into account the compressibility of the polymer molecule as an entity. Inside the hydrodynamic volume occupied by the polymer molecule, the dendritic polymer has much less unoccupied space than the linear polymer. The conformational adjustment is more difficult for the dendritic polymer; hence, it has lower compressibility, and, once inside the

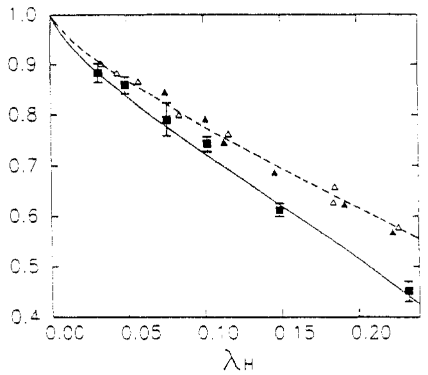

Figure 1. Diffusivity ratio $D/(XD_0)$ for dendritic poly(amido amine) in controlled-pore glasses R893 (R_P = 893 Å) and G275 (R_P = 275 Å) versus the size ratio λ_H (solid squares with error bars). The filled triangles represent data for the hindered diffusion of polystyrene in CPG R893,[16] and the open triangles represent that in CPG G275.[17] The solid curve corresponds to the hydrodynamic theory of Brenner and Gaydos (eq 2).[12] The dashed curve corresponds to the function obtained by fitting the data points for polystyrene diffusion to eqs 2 and 3; see text. The parameter κ = 0.76 was used in the calculation of the dashed curve.

confining pores, a starburst polymer has a larger effective size than a linear polymer with the same free-solution hydrodynamic radius. Consequently, the hindrance for the larger effective size diffusant macromolecule is stronger. This view is consistent with other published results.[7,16]

The diffusion results for dendritic poly(amido amines) inside pores are directly compared with those calculated with the Brenner–Gaydos theory by assuming that R_H correctly measures effective radius not only in free solution but also in confined spaces; that is, $R_H = R_S$. The curve in Figure 1 is calculated from eqs 1 and 2 (Brenner–Gaydos). We found that the function based on the Brenner–Gaydos prediction fits our results for dendritic polymer diffusion in pores reasonably well *without* any adjustable fitting parameter.

The quantitative agreement between the Brenner–Gaydos theory and the present experimental results proved the direct applicability of the theory even to nonideal pores such as those found in controlled-pore glass, if the pores are well connected and have a narrow distribution of pore radii R_P and if the spherical diffusant is appreciably smaller than R_P. This agreement also implies that the nominal pore radius R_P, measured by mercury intrusion porosimetry under the assumption of cylindrical pore geometry, is a reasonably good measure of the pore dimension that is effectively related to the transport process.

Following the approach of Bishop et al.,[15] we also incorporated the parameter κ into the Brenner–Gaydos theory by using eq 3 to fit the data for diffusion of a dendritic polymer in pores. A least-squares fit yielded $\kappa_{\text{dendritic}} = 0.98 \pm 0.06$; this fit did not include the point at $\lambda_H = 0.23$ because this λ_H value is beyond the claimed validity of the Brenner–Gaydos theory, which is stated to be $\lambda_S < 0.1$. However, inclusion of this point in the fit changed the fitted κ by only −0.01. The value of $\kappa_{\text{dendritic}}$ (0.98 ± 0.06) is compared with that for the linear polystyrene ($\kappa_{\text{linear}} = 0.76 \pm 0.02$)[15], the 4-arm star-branched polyisoprene ($\kappa_{4\text{-arm}} = 0.83 \pm 0.09$), and the 8-arm star-branched polyisoprene ($\kappa_{8\text{-arm}} = 0.94 \pm 0.09$).[16] Obviously, the parameter κ, which correlates the effective hard-sphere radius in free solution (R_H) to that in restricted spaces, increases and approaches unity with higher compactness and lower permeability of the diffusant. It is noted that $\kappa_{\text{dendritic}}$ and $\kappa_{8\text{-arm}}$ are not significantly different. This similarity is consistent with the observation of Bohrer et al.,[7] who found that the 8-, 12-, and 18-arm star polymers had almost the same reduced diffusivity in pores of track-etched membranes.

Conclusions

Diffusion of dendritic poly(amido amines) in porous glasses has been studied by using DLS. It was found that the starburst polymers diffuse more slowly than the linear polymers with the same λ_H, a behavior that is attributed to the higher structural compactness of the dendritic polymer. Quantitative agreement exists between our experimental results and the Brenner–Gaydos theory if $R_S = R_H$ is assumed. Therefore, for the highly compact dendritic polymers, the hydrodynamic radius R_H in free solution is almost the same as the effective radius R_S in constraining pores, which in reality is the overall physical size. For permeable polymers, however, there is no such equality. A least-squares fit using eqs 2 and 3 yielded $\kappa_{\text{dendritic}} = 0.98 \pm 0.06$. The comparison of this $\kappa_{\text{dendritic}}$ value with $\kappa_{4\text{-arm}}$ and $\kappa_{8\text{-arm}}$ shows that the scaling parameter κ, which correlates R_H to R_S, increases and approaches unity with higher compactness and lower permeability of the polymer.

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