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Nonanomalous diffusion in Vycor porous glass

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The diffusion of polystyrene in solution in the pore space of Vycor porous glass has been studied by the method of dynamic light scattering. In contrast to diffusion rates reported by others, we find results that are completely consistent with our previous measurements in other porous glass systems and that are in agreement with predictions of hydrodynamic theories and a model of chaotically connected pores. The anomalously slow diffusion of azobenzene in Vycor reported by others is possibly attributable to the residual effects of surface adsorption, which we have carefully eliminated in our experiment.

Porous glass is used in many applications, especially for adsorption and separation of compounds. It also offers a structure suitable for the study of hindered transport in restricted geometries, which is a subject of increasing theoretical and practical interest because of its relevance to many important processes such as chromatographic separation of polymers, enhanced oil recovery, membrane separation, and polymerization in the presence of heterogeneous catalysts. Porous silica glasses are highly pure, optically transparent, and mechanically stable; therefore they are ideal porous material for probe measurements using light scattering.

This laboratory has previously employed the technique of dynamic light scattering (DLS) for direct measurement of solvated polymer diffusion in porous glasses.[1-4] We have studied the dependence of polymer diffusion in pores on the molecular weight and architecture of the polymer and on solvent-polymer interaction. The ratio of polymer free-solution radius to the glass pore radius studied ranges from 0.017 to 1.4. We have also investigated the dependence of the restricted diffusion behavior on the length scale[1,2] and time scale[5] of observation.

In this work, we used DLS to study diffusion of low-molecular-weight polystyrenes in Vycor 7930, a commonly used porous glass. Diffusion of small molecules in Vycor porous glass has been studied by different techniques, such as forced Rayleigh scattering (FRS),[6-8] polarized picosecond transient grating experiments,[9] NMR,[10] the constant volume method,[11] and the tracer method.[12] Among these studies, the FRS diffusion measurement by Klafter and co-workers[6-8] is most directly comparable to our experiments, as the techniques in both studies are similar and the porous matrix used (Vycor 7930) is the same. Those authors found that the diffusion rate of an azobenzene molecule in Vycor was two orders of magnitude slower than in free unbounded solution, a result that was interpreted in terms of a parallel-pore model, or alternatively, a fractal structure model.[6] However, in later discussions some misgivings regarding these interpretations were expressed. Thus a major motivation of our study on the diffusion in Vycor porous glass was to assess other factors that could be responsible for the anomalous behavior. We suspected that some residual surface adsorption could be dominant in reducing the diffusivities. Thus in the present study the internal surfaces of the Vycor glass used were treated to minimize this possibility.

Linear polystyrenes of molecular weights $2.5\times10^3-1.3\times10^4$, each with narrow molecular weight distribution ($M_w/M_n \leq 1.1$), were used. Polystyrene was dissolved in fluorobenzene (Aldrich). The concentration of each solution was normalized to $c^*/5$, where the overlap concentration[13] c^* is estimated from $c^*=[\eta]^{-1}$, where $[\eta]$ is the intrinsic viscosity of polystyrene. The mutual diffusion coefficient D_0 in unbounded fluorobenzene solution was measured by dynamic light scattering at concentrations $c\approx c^*/5$. At $c^*/5$, D_0 is greater than at infinite dilution by about 5%. The hydrodynamic radius R_H was calculated from the Stokes equation, $R_H=k_BT/(6\pi\eta D_0)$, where η is the viscosity of the solvent. Fluorobenzene is a thermodynamically good solvent for polystyrene. It has an index of refraction closely matching that of the Vycor, thus allowing direct measurement of polymer diffusion *within* the porous fragment by dynamic light scattering.

The Vycor 7930 glass (Corning Glass Works) used in this study is made by a spinodal phase separation and leaching process[14,15] in which the sodium borosilicate glass is heat treated below the liquidus temperature to induce separation into continuous phases, and the Na_2O-B_2O_3-rich phase is then leached out with hydrochloric acid. Vycor 7930 has a narrow pore-size distribution, an average pore radius R_P of 20 Å, a porosity Φ of 0.28, and an internal surface area of 200 m^2/g (data provided by the manufacturer). Small-angle neutron-scattering and small-angle x-ray-scattering measurements[16] showed

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power-law behavior relating scattering intensity to scattering wave vector that can be interpreted in terms of a surface fractal dimension of 2.4, although this interpretation for Vycor is controversial. Levitz *et al.*[17] have provided a comprehensive analysis of the microstructure of Vycor as probed by electron microscopy, direct energy transfer, small-angle scattering, and molecular adsorption.

In this study, the internal surface of the Vycor glass was treated to minimize surface adsorption so that other potential causes for hindrance of diffusion, such as the tortuosity of the pores, could be separated. The surface treatment, the purpose of which was to replace the active hydroxyl groups with alkyl groups, consisted of the following steps. The glass was heated at 90 °C in concentrated HNO_3 to remove organic impurities and then soaked overnight in concentrated HCl to remove metal contaminants. The silica surface was activated by drying at 210 °C under vacuum for 4 h. A silanization[18] solution of 1-M hexamethyl disilazane in toluene was added to a Schlenk tube containing the glass fragments after they had been maintained under N_2 flow for 7 days at 100 °C. The reaction was terminated by the addition of dry distilled methanol. The glass was then dried and heated to 200 °C for 1 h prior to use.

Dynamic light-scattering measurements were made by using a 50-mW Spectra-Physics 125 He-Ne laser as the light source. The index matching cell holder assembly was constructed with seven windows at individual scattering angles ranging from 15° to 155°. Window axes were tilted 5° from the horizontal to reduce stray light. The photon count autocorrelation function (ACF) was measured at each of these seven angles with a Langley-Ford model 1096 digital correlator (Coulter Electronics) that had 256 contiguous channels plus 16 channels delayed by 1024 sample time intervals to measure last channel baseline.

The diffusion coefficients of the polystyrene fractions in free solution were normally obtained by using a homodyne arrangement, whereas diffusion within a porous glass bead was monitored by using heterodyne detection.[19,20] The light scattered by the solvated macromolecules was mixed with light statically scattered by the glass, which served as a strong local oscillator with an intensity ratio of about 1:50.

For the heterodyne arrangement, the measured photon-count ACF $G^{(2)}(q,t)$ is related to the normalized scattered electric-field ACF $g^{(1)}(q,t)$ by[19]

$$G^{(2)}(q,t)=B[1+f|g^{(1)}(q,t)|] \,, \tag{1}$$

where q is the scattering wave vector, t is the delay time, B is the baseline value, and f is the heterodyne coherence factor. A least-squares fit of $G^{(2)}(t)$ to a second-order cumulant expansion[21] was applied, where

$$\ln\left[\frac{G^{(2)}(j\Delta t)-B}{G^{(2)}(k\Delta t)-B}\right]=a+b(j\Delta t)+c(j\Delta t)^2 \tag{2}$$

with k the first data channel used in the fit, Δt the sample time for each channel, and j the channel number. The coherence factor f, the average ACF decay rate $\langle \Gamma \rangle$, and the variance of the decay rate distribution μ_2 were derived from the fitting parameters a, b, and c, respectively. For translational diffusion of noninteracting particles, $\langle \Gamma \rangle$ is proportional to q^2. The slope of $\langle \Gamma \rangle$ plotted as a function of q^2 defines the diffusion coefficient D of polystyrene in pores.

The translational diffusion of polystyrene molecules inside Vycor porous glass was studied by dynamic light scattering on a length scale much larger than the pore radius, i.e., $qR_P \ll 1$. The measured diffusion corresponds to a macroscopic diffusion process in which the diffusing macromolecule moves over distances that are large relative to the pore dimensions, thereby averaging over the details of the pore structure. The ACF decay rate $\langle \Gamma \rangle$ plotted as a function of the squared wave vector q^2 for a polystyrene fraction ($M_W=7000$) in Vycor glass is shown in Fig. 1. The linear relation between $\langle \Gamma \rangle$ and q^2 indicates that the macroscopic diffusion is governed by Fick's diffusion law, in which mean-squared displacement is proportional to t.

The reduction in diffusion rate inside the porous medium is characterized by the hindrance factor D/D_0, where D is the macroscopic diffusion coefficient. Figure 2 shows the hindrance factor as a function of size ratio, $\lambda_H=R_H/R_P$; as can be seen, D/D_0 decreases monotonically with λ_H, as expected. The solid line in Fig. 2 is an empirical fit of the data points.

The measured polymer diffusion rates in the pore spaces of Vycor 7930 were compared with the results of our previous studies of diffusion in a similar porous material, a controlled pore glass (CPG, Shell Development).[1,2,4] We found a general agreement between the two sets of results in terms of the magnitude of D/D_0 and its decrease with λ_H. The pore structures of CPG's and Vycor glass are fundamentally the same in that they are made by the same processes of phase separation and leaching. CPG's undergo a final controlled etching (by NaOH) to remove silica deposits from other components

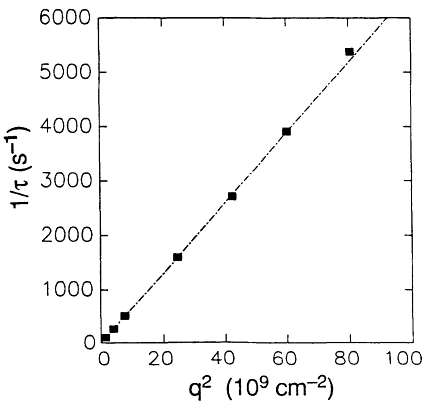

FIG. 1. Decay rate of DLS autocorrelation function $\langle \Gamma \rangle=(l/\tau)$ as a function of squared wave vector q^2, for polystyrene ($M_W=7{,}000$) in Vycor glass 7930. The straight line is a least-squares fit; the slope defines the macroscopic diffusion coefficient.

present in the Na_2O-B_2O_3-rich phase[22] and may thus have fewer surface irregularities than Vycor. Small-angle scattering measurements[16] showed that all CPG's have an apparent surface fractal dimension of 2.2, compared with the value of 2.4 for Vycor.

For polystyrenes in CPG, the hindered diffusion behavior at low λ_H was in quantitative agreement with a hydrodynamic theory for a flexible polymer chain in a cylindrical pore,[23,24] and the diffusion at high λ_H was in qualitative agreement with the prediction based on a scaling analysis of the entropy barrier effect.[25] The polymer diffusion results for Vycor reported in this study are not as extensive, being limited by the small pore size of the glass and weak scattering from low-molecular-weight polymers. Nevertheless, these results, in the range $0.64 \le \lambda_H \le 1.35$ demonstrate a trend similar to that observed for polymer diffusion in other CPG's.

A precise value of the intrinsic conductivity[26-28] X, defined as the value of D/D_0 at the limit $\lambda_H = 0$, clearly cannot be obtained from the limited number of data points. An estimate yields $X = 0.3$ to 0.7, a range that is reasonable for this kind of porous glass. Vycor glass has well-connected pores with narrow pore-size distribution. For such porous materials, the intrinsic conductivity is formally related to the tortuosity (T) of the pore structure by $X = 1/T$. It is emphasized here that for experiments such as those utilizing DLS and FRS, in which the diffusion coefficient is obtained essentially by using Fick's second law, the value of the hindrance factor D/D_0 is $1/T$ for the limiting case of point particles, rather than Φ/T, which was inappropriately used in Ref. 6 to interpret the hindered diffusion results obtained by FRS.

Pismen[28] calculated the tortuosity factor for diffusion in a porous solid, in which the model was a medium composed of random structural elements (pores) chaotically connected with one another. His expression

$$X \equiv \frac{1}{T} = 1 - \frac{2}{3}(1+\Phi)(1-\Phi)^{3/2} \tag{3}$$

yields $X = 0.48$ for Vycor 7930 ($\Phi = 0.28$), which is consistent with the data shown in Fig. 2.

Our results can be compared with the work of Klafter and co-workers.[6-8] These authors used FRS to measure the diffusion coefficient of a dye molecule (azobenzene, $R_H \approx 3$ Å) in the same Vycor glass, and they observed a "puzzlingly slow" diffusion, two orders of magnitude slower than that for free solution. The smallest polystyrene molecule used in this study ($M_W = 2500$, $R_H = 12.8 \pm 0.2$ Å) exhibits more rapid diffusion ($D/D_0 = 0.105 \pm 0.006$), even though its size is substantially greater than that of azobenzene.

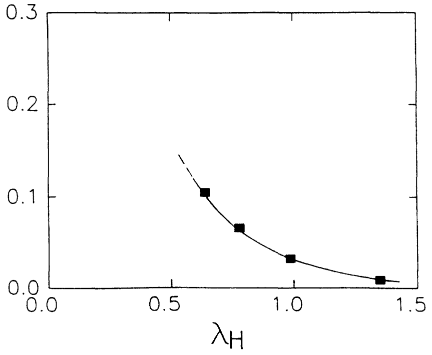

FIG. 2. Hindrance factor D/D_0 as a function of size ratio λ_H for polystyrenes ($M_W = 2500$–13 000) in Vycor. An estimate yields an intrinsic conductivity value of 0.3 and 0.7 (see text).

We suggest that the very strong hindrance to diffusion described in Refs. 6–8 can be attributed to residual surface adsorption of molecules by the glass surfaces. This "sticking" effect is not a rare phenomenon for porous materials with untreated surfaces, as we have noted in our past studies of hindered diffusion. In DLS experiments, the adsorption can be suppressed satisfactorily by silanizing the glass surface. We did briefly examine the diffusion of azobenzene in untreated Vycor, found a slow q-independent decay mode, and noted that azobenzene left a residual yellow stain that could not be washed from the sample. On the other hand, azobenzene in a silanized sample exhibited a diffusion rate too rapid to measure and left no visible stain upon rinsing. We have no explanation for the simultaneous presence of q^2 dependence and the anomalously slow diffusion of azobenzene observed in the work of Ref. 6.

In summary, the macroscopic diffusion coefficient of polystyrene molecules in a porous fragment of Vycor 7930, which had undergone thorough chemical surface treatment to minimize surface adsorption, was directly measured by dynamic light scattering. The decrease in the hindrance factor D/D_0 as a function of size ratio λ_H is in general agreement with our previous studies on controlled pore glasses. The value of D/D_0 for the smallest polystyrene ($R_H = 12.8 \pm 0.2$ Å) used in this study is approximately one order of magnitude larger than that of the diffusant azobenzene ($R_H \approx 3$ Å) in Vycor 7930 reported in Refs. 6–8. We suspect that this slower diffusion behavior reported in the previous work may be due to adsorption effects on the pore walls.

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