Polymer diffusion in porous media of fumed silica studied by forced Rayleigh scattering

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The diffusion of dye-labeled linear polystyrenes within porous media composed of fumed silica particles has been studied by using forced-Rayleigh-scattering (FRS) spectroscopy. Significant differences have been observed between results obtained by using silica R972 (made by the Degussa Corp.), which is known to adsorb labeled polystyrene chains, and silica R972-M, in which the surface hydroxyl concentration has been reduced to minimize surface adsorption. In the porous medium R972-M, the FRS signal was "normal," and the decay rate $1/\tau$ was proportional to the square of the scattering wave vector, an observation indicating diffusion by Brownian motion. In contrast, in the porous medium R972, the FRS signal was "abnormal" and there was an obvious curvature in the plot of $1/\tau$ vs q^2. We studied the effect of porosity on the hindrance to diffusion in both types of porous fumed silica; the hindrance is characterized by the ratio of the diffusion coefficient inside the pores to that in the free solution, D/D_0. For polymer diffusion inside R972-M, the hindrance can for the most part be attributed to geometric obstruction and hydrodynamic interaction with the silica surface; the experimental data are compared with predictions of the theories of Neale and Nader [Am. Inst. Chem. Eng. J. **19**, 112 (1973)] and of Prager [Physica **29**, 129 (1963)]. In the porous R972, adsorption dominated the polymer diffusion behavior, and the measured value of D/D_0, which was also a weak function of the labeling ratio, fell within the range 0.2–0.4, an observation indicating very strong hindrance. The changing diffusion rate during gelation was also monitored, and a difference in the times required for stabilization of the diffusion coefficient was found in the two silica systems. This difference is related to the mechanisms that govern diffusion behavior in each system.

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I. INTRODUCTION

The transport process in liquid-filled pores of porous materials is now a field of growing interest because of its relevance to many important processes, such as chromatography, catalysis, enhanced oil recovery, and membrane separation. A variety of porous materials, including track-etched membranes [1–6] controlled pore glasses [7–10] and sintered glasses [11], have been used as model systems for the study of hindered transport in small confining spaces. The central goal of these studies has been to relate phenomenological measurements of hindered transport to the characteristic parameters of the materials, such as pore dimension, porosity, and diffusant size. In this contribution, we describe measurements of diffusion of polystyrene molecules in porous media composed of fumed silica.

Fumed silica, also called pyrogenic silica, is produced from the hydrolysis of silicon tetrachloride in the presence of a hydrogen-oxygen flame [12]. These silica powders have extremely high surface areas and are widely used as binders, thixotropic agents, thickeners, and anticaking agents. The growth and structure of fumed silica was studied by Schaefer et al. [13], who used small-angle x-ray scattering (SAXS) and neutron-scattering (SANS) techniques. These authors found the fumed silica powders to have a fractal nature and proposed a model based on ballistic polymerization, sintering, and diffusion-limited aggregation to explain their observations.

When mixed with certain polymer solutions, the silica particles can be in either of two forms: in suspension or in a gel. In practice the transition between these forms brought about by either concentration or time is gradual. A suspension of silica greater than a certain concentration will gradually transform to gel form in a time period of several hours or several days. Although a precise definition of "gel" is historically difficult, a minimal definition characterizes a gel as a material exhibiting a three-dimensional microscopic network that exists over macroscopic distances and that holds or entraps the liquid component. Several other silica gel systems have recently been extensively used as experimental model systems for the study of the fractal nature of materials. Small-angle scattering techniques such as SAXS and SANS have been used in a number of studies concerning the fractal aspects of silica gels and their relation to gelation conditions [14–19] The silica gels that have been studied can be approximately categorized into two groups: those arising from aggregations of colloidal silica particles such as Ludox (made by DuPont) [14–17] and those originating in a sol-gel process [14,18,19].

The analytical technique employed in the present study is forced-Rayleigh-scattering (FRS) spectroscopy, which is also called holographic relaxation spectroscopy and has been widely used for the measurement of mass diffusion [20–24]. The principle of the technique is to follow the transient intensity diffracted from a sample containing

photosensitive probes that have been exposed to an optical grating created by a laser pulse. The decay of this diffracted intensity is due to the diffusive motion of the probes, which erases the refractive index gradient in the sample. Consequently, the diffusion coefficient of the polymer chains can be determined from the decay rate of the diffracted intensity. In the only application of the FRS technique used to measure diffusion inside Vycor porous glass, Dozier, Drake, and Klafter [24] measured transport of a dye molecule (azobenzene). There have been, to our knowledge, no published results concerning transport in silica gel, possibly because the abundant hydroxyl groups at the silica surfaces strongly adsorb diffusants. This problem can be addressed by chemically treating the silica surface, that is, replacing the surface hydroxyl groups by alkyl groups. Fumed silica was chosen in this study because it offers the advantage of stability in powder form, a property that facilitates the chemical treatment. The gel consisting of fumed silica can be regarded as similar to that obtained from colloidal silica aggregation. Nevertheless, there are clear differences; in fumed silica gels the basic units are ramified or fractal clusters and the gel linkage is physical and reversible, whereas in colloidal silica gels the basic units are spherical and the gel linkage is irreversible.

II. EXPERIMENTAL DETAILS

A. Sample preparation

1. Dye-labeled polystyrene

4-dimethylaminoazobenzene-4'-isothiocyanate molecules were attached to polystyrene chains to obtain photochromically active polymers. The labeling procedure involves two steps: random aminomethylation of phenyl rings in polystyrene and the subsequent reaction of aminomethyl groups with an azobenzene dye. Detailed procedures are as follows.

Selected fractions of linear polystyrene (made by Scientific Polymer Products) with narrow molecular-weight distributions were dissolved in CH_2Cl_2. Trifluoroacetic acid, used as a catalyst, was added to the polymer solution. Hydroxymethylphthalimide and trifluoromethanesulfonic acid were then added to the solution, and the solution was stirred for 8 h at room temperature. At the end of the reaction, the polymer was precipitated in methanol and washed by dissolving in tetrahydrofuran (THF) and reprecipitating in methanol. The polymer was converted to the amine form by refluxing with hydrazine in THF overnight. After reflux, the aminomethylated polystyrene was purified by again precipitating into methanol.

The aminomethylated polystyrene was dissolved in THF containing an excess of 4-dimethylaminoazobenzene-4'-isothiocyanate (DABITC made by Pierce). The solution was stirred at room temperature for 2 d. The resultant polymer was precipitated into methanol and was then extracted in a soxhlet extractor. The final DABITC-labeled polystyrene had one attached dye molecule per approximately 1000 monomer units assayed by ultraviolet-visible spectrophotometry. It was dissolved in fluorobenzene (made by Aldrich), which is a good solvent for polystyrene and has an index of refraction closely matching that of the fumed silica, a necessary requirement for the direct measurement of polymer diffusion inside the porous media by FRS.

2. Silica gel

Aerosil R972 (made by Degussa Corp.), a surface-treated fumed silica, was used in this study. The precursor silica (from hydrolysis) had basic units 10–20 nm in diameter and a surface silanol group density of 0.25–0.33 nm^2/SiOH [12]. It had been treated (by the manufacturer) with $(CH_3)_2SiCl_2$ to yield the hydrophobic product R972, which has about 20% of the initially available silanol groups. During the manufacturing process, aggregation occurred during the hydrolysis and the surface treatment, resulting in ramified (or fractal) clusters and characteristic dimensions of several hundred angstroms.

Surface silanol groups are known to adsorb many species. We examined the adsorption of labeled polystyrene on silica surface by ultraviolet-visible spectrophotometry. Silica R972 was mixed into the solution of the labeled polystyrene, and the mixture was stored at room temperature overnight. It was then washed with the solvent fluorobenzene. The washing was done by shaking the mixture, centrifuging, and removing the supernatant liquid. This process was repeated until the supernatant liquid gave no detectable absorption at a wavelength of 440 nm, where the attached azobenzene segment has an absorption maximum. A noticeable absorption peak at 440 nm was observed in the silica, a result indicating the presence of labeled polymer on the surface of R972. The amount could not be quantitatively established.

We performed additional surface treatment on the silica R972 to further remove hydroxyl groups at the surface. The silica was vacuum dried and heated to 200 °C for 4 h to activate the surface and then allowed to cool to room temperature under vacuum. Dry, distilled toluene was added, and the mixture was degassed in an ultrasonic bath. The silanizing reagent, hexamethyl disilazane, was added under flowing nitrogen to a concentration of 1 M. The reaction time was 7 d at 100 °C. After this period, the reaction was stopped by adding dry distilled methanol, and the methanol was later washed out by fluorobenzene. The washing process was the same as that described above. The silica thus treated, referred to as R972-M, was found to have negligible adsorption of labeled polystyrene, as detected by ultraviolet-visible spectroscopy.

A silica suspension was made by mixing a labeled polystyrene solution with fumed silica on a Fisher model Vortex-Genie test tube mixer. If the silica concentration used was above the critical concentration, then, in the absence of significant external perturbation, the silica suspension gradually transformed into a gel. The gelation process took several hours to several days, depending on the silica concentration. The criterion for the formation of a gel structure in this study was somewhat arbitrary. We simply tilted the sample cell containing the silica mixture to an angle of about 60°. If no appreciable flow was

observed over a time scale of several minutes, then gelation was said to have occurred. For silicas with different surface chemistries, for example, R972 with residual hydroxyl groups and R972-M without, the silica concentrations required to induce gelation were very different. The critical silica volume fraction was approximately 2.5% for R972 and 6% for R972-M, a difference implying that the surface hydroxyl groups play an important role in silica gelation. If the silica fraction was below the critical concentration, then a visually uniform suspension was formed after mixing; however, the silica particles in this type of dilute suspension precipitated and formed a distinguishable layer after several weeks. Both the silica suspensions and the silica gels are called *porous media* in this contribution.

B. FRS measurements

The experimental setup is shown in Fig. 1. The "writing beam" from a 5-W Ar^+ laser (Spectra Physics, Model 2020) was split into two beams of equal intensity, which were later converged on the sample by an off-axis parabolic mirror (focal length of 100 cm). A linear fringe pattern was created by interference of the two intersecting coherent writing beams. This optical grating induced a periodic concentration distribution of photoexcited dyes attached to the polystyrene chains. The fringe spacing d can be calculated from the expression $d = \lambda_0/2 \sin(\Theta/2)$, where the wavelength λ_0 (in air) of the writing beam was 455 nm and Θ is the angle between the two intersecting beams. The corresponding wave vector is $q = 2\pi/d$. The output power employed in the writing beam ranged from 0.003 to 0.06 W. The fringe spacing d could be varied from 3 to 30 μm by adjusting the distance between the two parallel beams impinging on the parabolic mirror. A mechanical shutter in front of the Ar^+ laser controlled the width of writing pulses, which were typically 1 ms. The reading beam was from a 1.5-mW He-Ne laser (Spectra Physics, $\lambda = 632.8$ nm), whose power was attenuated
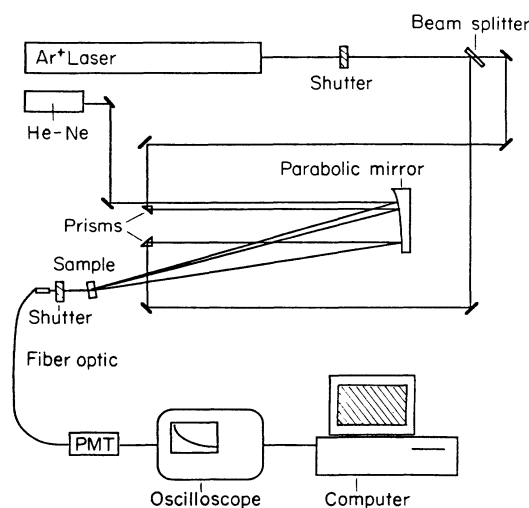
to below 0.1 mW. It was projected onto the induced fringes of the photoexcited molecules at an angle satisfying Bragg's condition. The diffracted intensity was detected with a photomultiplier tube, coupled to a digital oscilloscope (Nicolet, Model 310). The data were then transferred to and processed by a Zenith Model Z-386 Data Station Computer.

For a diffusion process, the decay profile follows an exponential function,

$$V(t) = (Ae^{-t/\tau} + B)^2 + C^2 , \tag{1}$$

where τ is the characteristic time of the decay, A is the preexponential amplitude of the diffracted optical field, B is the coherent background optical field, and C^2 is the background intensity due to incoherent scattering and stray light. The characteristic time τ can be obtained from the transient intensity measurement by a nonlinear least-squares fit of the measured intensity $V(t)$ vs t [Eq. (1)]. We used the algorithm developed by Marquardt [25], which combines the best features of gradient search and the method of linearizing the fitting function.

For single-mode diffusion processes, the characteristic decay time τ versus the squared wave vector q^2 should follow

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{life}}} + q^2 D , \tag{2}$$

where τ_{life} is the lifetime of the photochromically shifted state of the dye, and D is the diffusion coefficient. In our system τ_{life} was found to be much longer than the decay time.

III. RESULTS AND DISCUSSION

The transient diffracted optical intensity $V(t)$ from the labeled polystyrene [molecular weight (MW) of 1.13×10^6] in a silica gel consisting of R972-M (where Φ, the silica volume fraction, was 7.1%) is shown in Fig. 2(a). The FRS signal reached a maximum when the writing beams were turned off, with an immediate exponential decay. The amplitude of the initial diffraction intensity was about the same as that from the free solution under the same conditions. A nonlinear least-squares fit of $V(t)$ to Eq. (1) was reasonably satisfactory in terms of the random residuals, which are plotted in Fig. 2(b).

In contrast to the "normal" FRS signal from the R972-M gel, the FRS signal from the R972 gel usually showed a slow rise in diffraction intensity after exposure of the dye moieties to the writing beam. Figure 3(a) shows the FRS signal from the labeled polystyrene (MW of 1.13×10^6) in the R972 gel ($\Phi = 2.6\%$). The maximum diffraction intensity was 5–10 times larger than that from the free solution. We relate this abnormality to the adsorption of the polymer by the silica surface, although we do not understand the underlying mechanism at this stage of the study. The data points, excluding those at times shorter than the inflection point, were fitted to Eq. (1). Figure 3(b) plots the residuals of this fit. We note the fit is not as satisfactory as the fit for the R972-M gel because of the slow initial rise in diffraction

FIG. 1. Experimental arrangement of the forced Rayleigh scattering experiment, following the design of Eric Amis. PMT denotes photomultiplier tube.

intensity and the slow decrease in diffraction intensity at a later stage. The latter possibly accounts for the retarded movement of a small portion of the polymer molecules that were adsorbed on the surface.

The decay rates $1/\tau$ obtained at different scattering wave vectors are plotted in Fig. 4 for labeled polystyrene (MW of 1.13×10^6) in three different systems: (a) free solution, (b) R972-M silica gel, and (c) R972 silica gel. The FRS measurement in the gels were carried out several days after the gel preparation, so that the measured decay rates would be stable with time. The difference in the diffusion behavior in porous media with different surface chemistry is discussed below.

For the R972-M gel, proportionality exists between the decay rate $(1/\tau)$ and the squared wave vector (q^2). Thus, phenomenologically, standard diffusion law governs the transport process in the R972-M gel as well as in free solution. The data points for the free solution and the R972-M porous material were fitted to Eq. (2). The dashed and dotted lines in Fig. 4 represent the fitted linear functions [Eq. (2)]. The diffusion coefficients D_0 (in free solution) and D (in the R972-M gel) were obtained from the slope of $1/\tau$ vs q^2. The linear relation also indicates that the diffusion coefficient is independent of the length scale of observation, which is in the range of 3–30
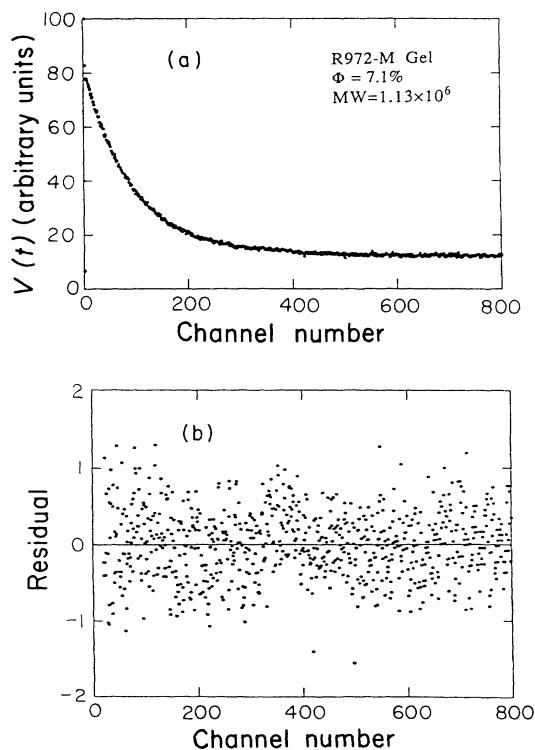
μm in our experiments. In turn, this linearity implies that the pore structure is uniform over this range of length scale being probed, as opposed to that expected for fractal pores in which the mean-square displacement of a diffusant is not proportional to time [26]. It was found that the intercept of the fitted straight line, which is equal to $1/\tau_{\text{life}}$ [from Eq. (2)] is very small. In other words, the lifetime of the excited state of the dye segments is longer than the time scale of the diffusion process being studied.

In contrast, the data for the R972 gel (Fig. 4) showed an obvious curvature. The straight lines, which are approximately tangential to the data points at the higher and lower q^2 regimes, are shown to demonstrate the trend. This curvature in $1/\tau$ vs q^2, which is not seen in the R972-M gel, is related to adsorption of the polymer chains by the silica. It may also be partly due to a larger error in the curve fitting, which can be seen in the residual plot [Fig. 3(b)]. In this study, a quantitative interpretation of the hindered diffusion largely due to adsorption in the R972 gel is not feasible. An apparent phenomenological diffusion coefficient D_a was obtained from a single-
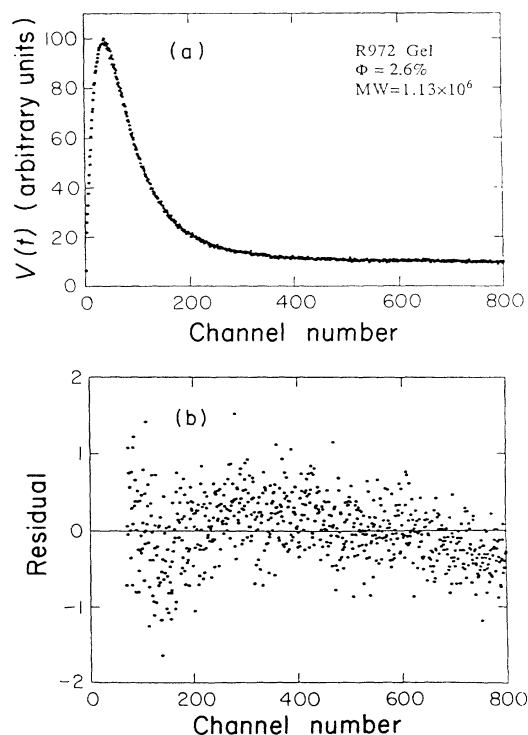

FIG. 2. (a) Typical transient diffraction intensity $V(t)$ for a dye-labeled polystyrene (MW of 1.13×10^6) in a silica gel composed of R972-M, which effectively does not adsorb the polymer. The diffracted intensity decay began immediately after the writing beam exposure of 1–2 ms. The sample time was 1 ms per channel. This FRS signal is normal. (b) A plot of the residuals [in same arbitrary units as in (a)] of a nonlinear least-squares fit of the data points in (a) to Eq. (1). These residuals are very close to a random distribution.

FIG. 3. (a) Typical transient diffraction intensity $V(t)$ for a dye-labeled polystyrene (MW of 1.13×10^6) in silica gel R972, which has a finite surface silanol density resulting in surface adsorption. The writing beam exposure time was 1–2 ms, and the sample time was typically 0.5–2 ms per channel. This FRS signal is abnormal, because there is a slow rise in the diffracted intensity after exposure of the dyes to the writing beams. Peak intensity was reached, typically, 10–20 ms after the writing pulse. (b) A plot of the residuals [in the same arbitrary units used in (a)] of a nonlinear least-squares fit of the data points in (a) to Eq. (1). The first point of fitting is approximately the inflection point. There is a systematic error in this fitting largely because of the very slow decrease in the baseline.
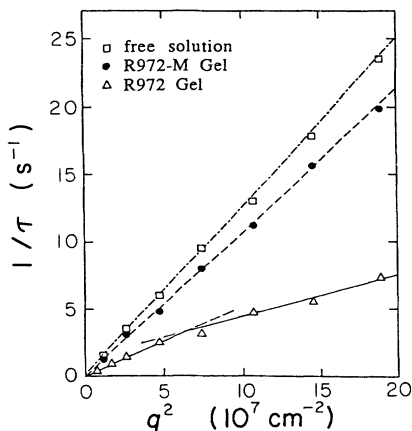
POLYMER DIFFUSION IN POROUS MEDIA OF FUMED . . .

FIG. 4. Plot of the decay rate $1/\tau$ of the transient diffraction from the grating of the excited dyes attached to a polystyrene (MW of 1.3×10^6) vs the squared wave vector q^2 in three different systems: (i) unbounded solution ($\square$), (ii) silica gel R972-M ($\bullet$), and (iii) silica gel R972 ($\triangle$). Proportionality exists in both the unbounded solution and the R972-M gel, a relation indicating Brownian motion, whereas an obvious curvature is observed in the R972 gel. The slope of $1/\tau$ vs q^2 defines the diffusion coefficient for systems (i) and (ii). The quotient $1/\tau$ divided by q^2 at $q^2 = 4.74 \times 10^7$ cm^{-2} is used as the apparent diffusion coefficient D_a to describe the porous medium R972.

angle measurement at $q^2 = 4.74 \times 10^7$ cm^{-2} (corresponding to a prism spacing of 25 cm), where $D_a = 1/(\tau q^2)$.

Polymer diffusion within a silica gel or a silica suspension is hindered relative to that in the unbounded solution. The ratio of the diffusion coefficient inside the porous medium R972-M to that in the unbounded solution D/D_0 (a ratio often referred to as the hindrance factor) is plotted in Fig. 5 as a function of silica volume fraction Φ. The general trend is that the value of D/D_0 decreases with increasing Φ, thus indicating a stronger hin-
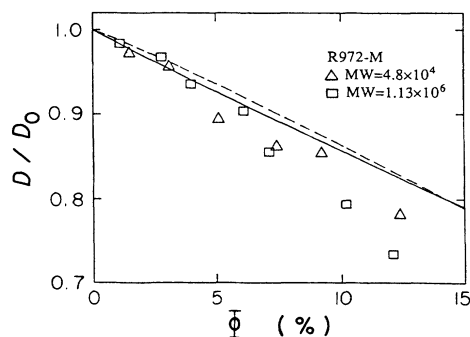
drance. In the low silica concentration ($\Phi < 6\%$) regime, the silica suspension will not gel, and the diffusion coefficient was measured before the separation of the dilute silica suspension into two layers (as a result of precipitation). In the higher silica concentration ($\Phi > 6\%$) regime, the diffusion coefficients were measured after the gels had formed.

Two labeled polystyrene samples with different molecular weights (MW of 4.8×10^4 and 1.13×10^6) were used in this study. We note that there is little difference (within experimental error) between the hindrance values for these two polymer sizes. This observation implies that the polymer molecules are still much smaller than the pore dimensions. In other words, the polystyrene molecules of both sizes can still be approximated as point particles. The use of even higher-molecular-weight polymers, although desirable, is limited by our ability to label larger molecules.

Labeled polystyrene molecules diffuse much faster in the porous medium R972-M than in the R972 porous medium (see Fig. 6), where adsorption severely reduced the freedom of the polymer. The weak hindrance in R972-M is relatively more dependent on Φ than is the diffusion behavior in R972 (see Fig. 6). These facts suggest that the effect of adsorption is negligible in R972-M, and that the hindrance can be attributed, for the most part, to geometric obstruction and hydrodynamic interaction with the silica surfaces. There exist many theories that take these two factors into account and that predict the relation between the hindrance factor D/D_0 and the porosity for different porous systems. Our experimental results are compared with the hydrodynamic theory developed by Neale and Nader [27] for a much simpler model system—that of a homogeneous swarm of spherical particles of arbitrary size distribution. Based on the nonrigorous assumption that each particle experiences the remainder as a uniform fluid, this model predicts that
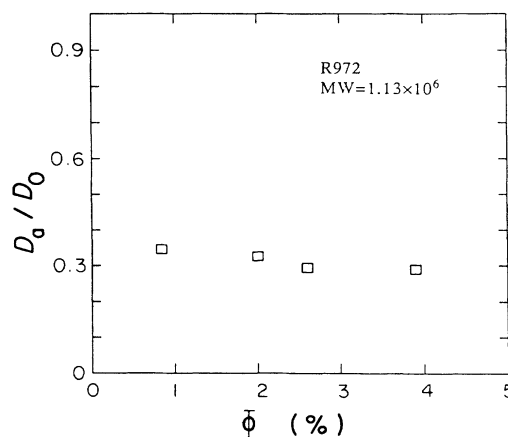

FIG. 5. Hindrance factor D/D_0 vs silica volume fraction Φ for two polystyrene samples (MW of 4.8×10^4 and 1.13×10^6) in R972-M solutions and gels. The gelation threshold is approximately $\Phi = 6\%$. The weak hindrance is attributed to geometric obstruction. The solid curve represents the theory of Neale and Nader [27] [Eq. (3)] for diffusion in a homogeneous, isotropic swarm of spheres. The dashed curve corresponds to the bound predicted by Prager [28] [Eq. (4)] for a homogeneous, isotropic suspension of solid particles of arbitrary shape.

FIG. 6. Hindrance factor D_a/D_0 vs silica volume fraction Φ for polystyrene (MW of 1.13×10^6) in R972 solutions and gels. The gelatin threshold is approximately $\Phi = 2.2\%$. The polymer diffusion is strongly hindered even at low Φ. This hindrance is only slightly dependent on Φ.

$$\frac{D}{D_0} = \frac{2(1-\Phi)}{2+\Phi} . \tag{3}$$

(Note that in Neale and Nader's original notation, Φ was used to denote porosity, which we denote as $1-\Phi$.) Equation (3), independent of the size distribution of the spheres, is in satisfactory agreement with the experimental data for diffusion in a wide range of porous media throughout the whole porosity range. The solid line in Fig. 5 represents Eq. (3). Our results in the low-Φ regime are reasonably consistent (within experimental error) with the Neale-Nader theory [Eq. (3)]. This correlation can be explained by the fact that the silica suspensions can be regarded approximately as a collection of basic spherical units, even though these units had aggregated into ramified clusters. At low solid-volume fraction Φ (or high porosity), the trend of hindered diffusion in a fumed silica gel is similar to that in an unconsolidated homogeneous swarm of spherical particles.

In the gelled systems, the formation of three-dimensional networks further deviates from the assumption of the Neale-Nader model that requires different particles in the suspension to be independent of one another in the sense that their regions of hydrodynamic influence must not overlap. This deviation is greater at higher silica concentration. We observe that at higher Φ (or lower porosity), the hindered diffusion tends to be slower than that predicted by the Neale-Nader theory. We emphasize here that the Neale-Nader model does not totally parallel our experimental system. Therefore, this comparison (as well as another comparison to follow) is thus intended only to put this work in a more general context of studies of hindered transport in random porous media.

Our results are also compared with a theory developed by Prager [28] for a homogeneous and isotropic suspension of solid particles of arbitrary shape. In this treatment, the main assumptions in the Neale-Nader model were relaxed, and the principle of minimum entropy production was applied to obtain bounds of the hindered diffusion rate:

$$\frac{D}{D_0} < (1-\Phi)\left[1-\frac{\Phi}{3}\right] . \tag{4}$$

(Again, Φ is the silica volume fraction rather than porosity, as denoted by Prager.) The dashed curve in Fig. 5 corresponds to Prager's theory [Eq. (4)]. Our experimental results obviously satisfy the inequality relation predicted by Prager.

The ratio of diffusion coefficient D_a/D_0 for labeled polystyrene (MW of 1.13×10^6) in the porous media of silica R972 is plotted against silica volume fraction Φ in Fig. 6, where D_a is as defined in Sec. II. All data in this figure were taken after the diffusion coefficient had stabilized; as will be demonstrated, the diffusion rate decreases soon after mixing the silica suspension. We found that the value of D_a/D_0 is only slightly dependent on the silica fraction Φ. This observation is explained by the fact that adsorption plays a dominant role in slowing down polymer diffusion and that even at low concentration the silica surface area is greater than that which would be

covered by the adsorbed polymer molecules. Yet the measured diffusion coefficient in the R972 gel still decreases by a small amount as Φ increases. There are three possibilities to account for this small decrease: (i) the increased ratio of surface-to-pore volume results in a higher probability of adsorption; (ii) geometric obstruction, such as tortuosity, is increased; and (iii) more silica particles cause more static scattering and stray light, which produce a poorer signal-to-noise ratio and a higher baseline value, thus introducing greater error into the data analysis. We also found that, at the two lower silica concentrations, the silica suspension will not gel and the hindrance in these two suspensions is similar to that in the gels.

Although the labeling ratio or the density of the dye segments does not affect the diffusion rate in the R972-M porous medium, it does have an effect on the diffusion coefficient for the dye-labeled polystyrene in the R972 porous medium. For polymer samples with the same molecular weight, a higher labeling ratio usually results in slower diffusion. Thus, comparison between different polymer sizes is not made, as there is no quantitative control over the labeling ratio in the labeling reactions. As an approximate generalization of this observation, for most molecular weights and labeling ratios studied, the value of D_a/D_0 is between 0.2 and 0.4 in a Φ range of about 1–5 %.

The silica gels in this work can be viewed as physical gels that are reversible in nature, because there is no chemical bonding involved in gelation. We monitored the development of hindrance during the formation of silica gels. Initially, the mixture of silica and the polymer solution was vigorously shaken on a model Vortex-Genie test tube mixer to destroy the interconnection of the silica particles. FRS measurements were then conducted to obtain the diffusion coefficient at different times during the gelation process. We observed little difference (within experimental error) between a "fresh" gel and a gel reformed from a "destroyed" one.

The diffusion coefficient for polystyrene (MW of 1.13×10^6) inside a R972-M gel ($\Phi=7.1\%$) as a function of gelation time is shown in Fig. 7. There is a slight
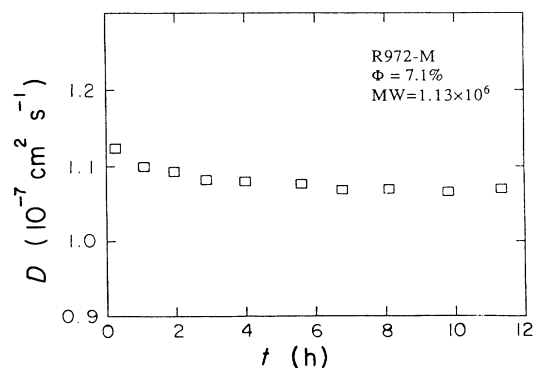

FIG. 7. Diffusion coefficient D vs time during the gelation process for an R972-M gel ($\Phi=7.1\%$). The time for stabilization of the diffusion coefficient (approximately 5 h) is comparable to that needed for the silica suspension to gel.

difference in the diffusion rate between the silica suspension immediately after mixing and that in the gel formed later. Diffusion within the gel attained a stable value in approximately 5 h. This time period is comparable to that needed for gelation. The small difference in the diffusion rate at early and late stages may be attributed to the interconnection of silica particles into networks, which were not present in the initial suspension. It is also possible that, immediately after severe mixing, turbulence and convection smear the fringe pattern of excited dyes created in the exposure to the optical grating and that the turbulence is incorrectly interpreted as faster diffusion. In the gel, however, the three-dimensional networks effectively retard such turbulence and convection.

Figure 8 shows the diffusion coefficient as a function of gelation time for a R972 gel ($\Phi=2.6\%$). The diffusion reached a stable value in a much shorter time (about 20 min) than that needed for gelation (several hours). In other words, the mixture was still visibly liquid when strong hindrance had built up. In the R972 silica gels, the hindrance is mainly due to surface adsorption of the polymer molecules. Thus, we inferred that the time needed to develop this hindrance is actually the time needed for the polymer chains to approach the solid surface and be physically adsorbed.

Dynamic light-scattering spectroscopy, a similar technique that was previously used in this laboratory for direct measurement of polymer diffusion in porous glasses [7–10] was also tested in the study of polymer diffusion in the present silica gels. It was found to be impractical to extract a diffusion coefficient from the measured autocorrelation function (ACF) [29] because of complications in the intensity fluctuation due to the oscillatory movements of the silica particles. The intensity fluctuation is mixed with that due to the polymer movement. We noted that even a pure silica gel (without polymer) gives a significant ACF, thus distinguishing itself from the situation with consolidated porous materials such as porous glasses.

IV. CONCLUSIONS

We have used the technique of FRS to study the diffusion of dye-labeled linear polystyrene inside porous
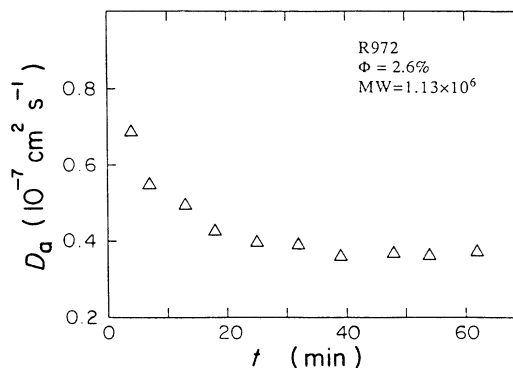

FIG. 8. Diffusion coefficient D_a vs time during the gelation process for an R972 gel ($\Phi=2.6\%$). The time for stabilization of the diffusion coefficient (approximately 10 min) is much shorter than that needed for gelation of the silica suspension.

media. For silica gel R972, which has a finite surface density of silanol, adsorption of polymer by the silica surface dominates the diffusion behavior. The diffusion in the R972 porous medium, which is not normal Brownian motion, shows a strong hindrance even at low silica concentrations. This hindrance has a slight dependence on the silica volume fraction Φ. For silica gel R972-M, adsorption is almost absent as a result of further surface treatment. In this system, diffusion is of the normal Brownian-motion type, and the weak hindrance to polymer diffusion is attributed to geometric obstruction and hydrodynamic interactions with the silica surfaces. The change in the diffusion coefficient during gelation was also monitored for both types of silica gels. The time needed for the diffusion rate to stabilize is commensurate with the mechanisms that are responsible for diffusion behavior.

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[1] M. G. Davidson and W. M. Deen, Macromolecules **21**, 3474 (1988).

[2] W. M. Deen, M. P. Bohrer, and N. B. Epstein, AIChE J. **33**, 1409 (1987).

[3] M. P. Bohrer, G. D. Patterson, and P. J. Carroll, Macromolecules **17**, 1170 (1984).

[4] M. P. Bohrer, L. J. Fetters, N. Grizzuti, D. S. Pearson, and M. V. Tirrell, Macromolecules **20**, 1827 (1987).

[5] D. S. Cannell and F. Rondelez, Macromolecules **13**, 1599 (1980).

[6] G. Guillot, Macromolecules **20**, 2600 (1987); **20**, 2606 (1987).

[7] M. T. Bishop. K. H. Langley, and F. E. Karasz, Macromolecules **22**, 1220 (1989).

[8] M. T. Bishop, K. H. Langley, and F. E. Karasz, Phys. Rev. Lett. **57**, 1741 (1986).

[9] N. Easwar, K. H. Langley, and F. E. Karasz, Macromolecules **23**, 738 (1990).

[10] Y. Guo, K. H. Langley, and F. E. Karasz, Macromolecules **23**, 2022 (1990).

[11] J. V. Brakel and P. M. Heertjes, Int. J. Heat Mass Transfer **17**, 1093 (1974), and references therein.

[12] *Hydrophobic AEROSIL: Manufacture, Properties, and Applications,* Technical Bulletin on Pigments, No. 6, Degussa Corporation (unpublished).

[13] D. W. Schaefer, A. J. Hurd, D. K. Christen, S. Spooner, and J. S. Lin, in *Better Ceramics through Chemistry III,* edited by C. J. Brinker, D. E. Clark, and D. J. Ulrich, MRS Symposia Proceedings No. 121 (Materials Research

Society, Pittsburgh, 1988), p. 305.

[14] D. W. Schaefer, Science **243**, 1023 (1989).

[15] C. Aubert and D. S. Cannell, Phys. Rev. Lett. **56**, 738 (1986).

[16] G. Dietler, C. Aubert, and D. S. Cannell, Phys. Rev. Lett. **57**, 3117 (1986).

[17] J. E. Martin, Phys. Rev. A **36**, 3415 (1987).

[18] D. W. Schaeffer and K. D. Keefer, Phys. Rev. Lett. **53**, 1383 (1984).

[19] J. E. Martin and J. P. Wilcoxon, Phys. Rev. A **39**, 252 (1989).

[20] H. Hervet, W. Urbach, and F. Rondelez, J. Chem. Phys. **68**, 2725 (1978).

[21] L. Lèger, H. Hervet, and F. Rondelez, Macromolecules **89**, 3193 (1985).

[22] J. A. Wesson, I. Noh, T. Kitano, and H. Yu, Macromolecules **17**, 782 (1984).

[23] M. Antoneitti and H. Sillescu, Macromolecules **18**, 1162 (1985).

[24] W. D. Dozier, J. M. Drake, and J. Klafter, Phys. Rev. Lett. **56**, 197 (1986).

[25] D. W. Marquardt, J. Soc. Ind. Appl. Math. **11**, 431 (1963).

[26] B. O'Shaughnessy and I. Procaccia, Phys. Rev. Lett. **54**, 455 (1985).

[27] G. H. Neale and W. K. Nader, AIChE J. **19**, 112 (1973).

[28] S. Prager, Physica (Utrecht) **29**, 129 (1963).

[29] B. J. Berne and R. Pecora, *Dynamic Light Scattering: With Applications to Biology and Physics* (Wiley, New York, 1974).