for 4 h. The solvent was removed under reduced pressure, and the better isolable acetyl derivative of 1-phenylethanol was purified by thin-layer chromatography (TLC, silica gel, hexane:ethyl acetate, 20:1 for **1**, **3**, and **4** and benzene alone for **2**). The yield of the acetyl derivative in all the cases was 15% (mol/mol monomer); IR (neat) ν_{max} = 1760 cm^{-1} (O—C=OCH_3); ^1H NMR ($CDCl_3$) δ 1.5 (3 H, d, J = 8 Hz, $-CH-CH_3$), 1.9 (3 H, s, $COCH_3$), 5.8 (1 H, q, $-CH-CH_3O$), and 7.1–7.3 (5 H, m, Ar–H).

To a magnetically stirred mixture of freshly distilled styrene (0.044 mol) and cobalt complex (0.44 mmol) in THF (15 mL), a solution of $NaBH_4$ (0.44 mmol) in distilled water (5 mL) was added in one lot under an argon atmosphere. The mixture was stirred at room temperature (28 °C) for 4 h, and it was poured into methanol (150 mL) containing 10 N HCl (5 mL). Precipitated polystyrene was filtered off and was further purified by successive precipitation from benzene solution. The polystyrene was dried under vacuum at 60 °C to a constant weight (2% conversion). The molecular weight ($\bar{M}_v$) of the polymer was determined viscometrically at 30 °C in toluene,[9] by using the intrinsic viscosity [η] relation [η] = 1.1×10^{-4} $(\bar{M}_v)^{0.73}$. The values of $\bar{M}_v$ so obtained in the different cases being A ($\bar{M}_v$ = 6100), B ($\bar{M}_v$ = 4400), C ($\bar{M}_v$ = 5900), and D ($\bar{M}_v$ = 7700).

The aerial oxidation experiment proves that the radical $CH_3\dot{C}H(C_6H_5)$ is formed in the intermediate step. On the basis of this observation, the most plausible mechanism[6] of the polymerization may be given as

$$\underset{1\text{–}4}{Co^{2+}L_n} \xrightarrow{NaBH_4} \underset{Co^+ \text{ species}}{HCoL_n}$$

$$HCoL_n + C_6H_5CH{=}CH_2 \rightleftharpoons CH_3(C_6H_5)CHCo^{3+}L_n$$

$$CH_3(C_6H_5)CHCo^{3+}L_n \rightleftharpoons CH_3(C_6H_5)\dot{C}H + Co^{2+}L_n$$

$$CH_3(C_6H_5)\dot{C}H + C_6H_5CH{=}CH_2 \rightarrow \text{poly(styrene)}$$

The formation of Co^+ species ($HCoL_n$) is confirmed by quenching of polymerization reaction upon addition of methyl iodide.[6] Addition of *p-tert*-butylcatechol in the polymerization mixture significantly inhibits the polymerization, confirming the radical mechanism of the reaction. Mun et al.[10] in their ESR study of the polymerization of methyl methacrylate using ethyl acetylacetonate copper complex and sodium tetraphenyl borate binary redox system have also proved the transfer of the phenyl radical to the monomer as an intermediate step.

Thus, the above experiments demonstrate that the inhibitory role of oxygen during the radical polymerization of styrene initiated by Co^{2+}–BH_4^- redox system is due to the formation of 1-phenylethanol. And since the 1-phenylethanol formed is a stable molecule, we believe that inhibitory action of oxygen in the present case is rather permanent. Besides, this study also provides a new redox system for the room-temperature radical polymerization, though it seems to be less efficient than the known initiators[3] of this type.

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Registry No. **1**, 37981-00-3; **2**, 36423-23-1; **3**, 120173-03-7; **4**, 14566-16-6; $NaBH_4$, 16940-66-2; styrene, 100-42-5; polystyrene, 9003-53-6; oxygen, 7782-44-7; 1-phenylethanol, 98-85-1.

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Diffusion of Linear Polystyrene in Controlled Pore Glasses. Comparison of Experimental Data with a Theoretical Model of Entropic Barriers

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Diffusion of dissolved macromolecules in porous materials is central to many phenomena of scientific and technological interest. Extensive literature exists[1–4] on the experimental results on porous media, membrane separations, and polymer solutions. Recent experiments have used quasielastic light scattering as a convenient probe to measure directly the translational diffusion coefficient of polymers in porous glasses in the absence of convection, chemical reaction, and adsorption.[5–7] The measurements are made at equilibrium, without macroscopic concentration gradients, and further, since the measurements are made directly within the porous material, the equilibrium partitioning[1–3] between the unbounded solution and the pore space does not have to be known. In this note, we compare the data on the diffusion of linear polystyrene in controlled pore glasses (CPGs) reported by Bishop et al.[5,6] and Easwar et al.[7] to the predictions of the theoretical model by Muthukumar and Baumgartner.[8] This theoretical model focuses on the effects of entropic barriers on the dynamics of a polymer chain in an infinite periodic array of cavities separated by short bottlenecks. The problem has been investigated by Monte Carlo simulations and by scaling arguments, and the results demonstrate that the polymer dynamics in random media is dominantly controlled by the entropic barriers.

The CPGs used in the light-scattering measurements mentioned above are made by the phase separation upon heat treatment of sodium borosilicates followed by the selective etching of the Na_2O–B_2O_3 rich phase. The glasses were characterized by mercury intrusion porosimetry to have nominal pore sizes of 703, 893, and 1866 Å and are labeled as R703, R893, and R1866, respectively. The scanning electron micrograph shows the highly connected structure of R893.[6] Characterization by mercury intrusion porosimetry is shown in Figure 1. Although the distribution of pore sizes obtained from porosimetry appears narrow, the presence of constrictions such as bottlenecks is not inconsistent with the characterization data, as discussed by Bishop et al.[6,9] A recent analysis of the pore size

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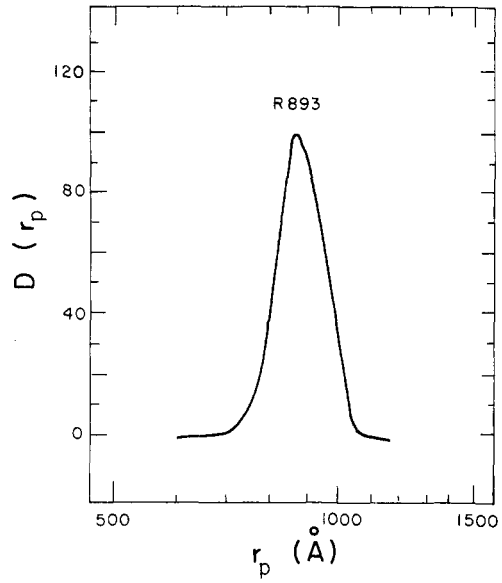

Figure 1. Pore size distribution derived from mercury intrusion porosimetry for R893. $D(r_p)$ is the relative probability that a pore has radius r_p.

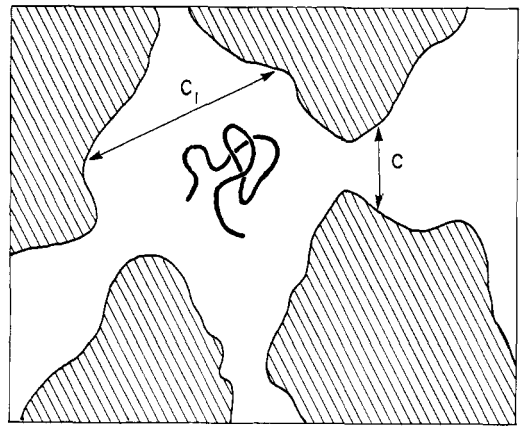

Figure 2. Schematic representation of the assumed model for the porous network.

distribution in similar porous borosilicate glasses using magnetic resonance relaxation[10] reveals the existence of two length scales while porosimetry misses this bimodal feature. The large size component from magnetic relaxation is found to agree qualitatively with the results with porosimetry and also with measurements from scanning electron microscopy.[10] This motivates the assumption that the porous media used in the light-scattering studies might consist of larger chambers or domains that are interconnected by short bottlenecks. Figure 2 schematically represents this situation. This picture makes it possible to apply the predictions of the theoretical model.

We now briefly outline the relevant details of the experiment and refer the reader to the original papers for elaborate discussions of the same. Dilute solutions of polystyrene in the thermodynamically good solvent 2-fluorotoluene filled the pore spaces of the glass. For each molecular weight (which spanned the range 17.5×10^3 to 4.4×10^6) the concentration of the solution relative to the overlap concentration c^* was held constant at approximately $c^*/8$. A single silanized porous glass fragment was mounted in the sample cell and immersed in the polymer solution. The refractive indexes of the glass and the solvent were closely matched. The local oscillator for heterodyne dynamic light-scattering measurements was provided by the scattering from the glass fragment. The

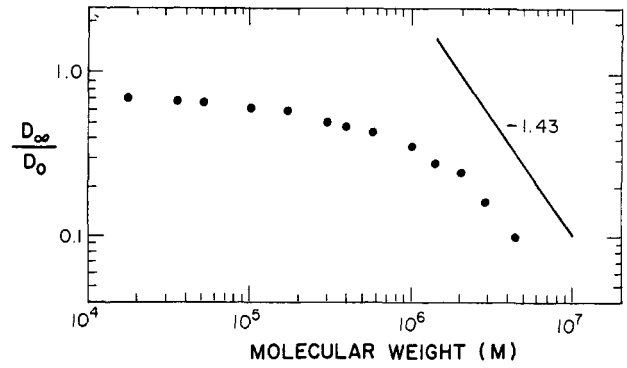

Figure 3. Macroscopic diffusion coefficient D_∞ of linear polystyrene in R893 relative to the diffusion coefficient in unbounded solution D_0 plotted as a function of molecular weight M. Since $D_0 \sim M^{-0.57}$ for polystyrene in 2-fluorotoluene, the reptation model result $D_\infty \sim M^{-2}$ predicts that the limiting variation of D_∞/D_0 with M at high molecular weight is a straight line of slope −1.43 on this plot.

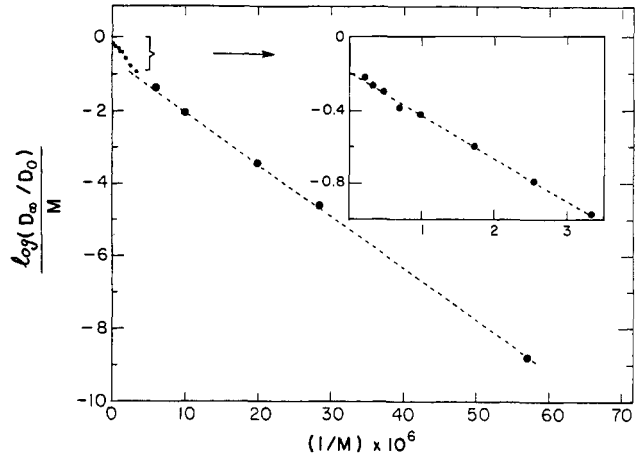

Figure 4. $(1/M) \log (D_\infty/D_0)$ plotted as a function of $1/M$. The inset is the higher molecular weight data magnified to show detail. Dashed lines have been drawn through the data for guidance.

measured intensity autocorrelation function was analyzed by the second-order cumulants method to obtain the average effective diffusion coefficient of the polymer inside the porous glass. For small values of the scattering wave vector q, satisfying $qR_p < 0.7$, where R_p is the radius of the pores, the values of the effective diffusion coefficient reach an asymptotic limit D_∞, which is the macroscopic diffusion coefficient. In each case, values of D_0, the diffusion coefficient in unbounded solution, was measured by using homodyne light scattering. Figure 3 shows the superposed data of Bishop et al. and Easwar et al. on a graph of D_∞/D_0 versus M for glass R893. We will mainly use the results for glass R893, for which extensive data exist.

The scaling prediction for the model of entropic barriers[8] corresponding to the situation of Figure 2 is

$$D_\infty/D_0 = A \exp\left\{-N\left[f\left(\frac{1}{C}\right)^{1/\nu} + \left(\frac{1-f}{Z} - 1\right)\left(\frac{1}{C_1}\right)^{1/\nu}\right]\right\} \quad (1)$$

where N is the degree of polymerization of the polymer, C_1 is the average domain size, and C is the average size of the bottleneck (as in Figure 2), Z is the average number of domains that contain the unconfined segments of the chain per bottleneck, and f is the fraction of monomers inside the bottleneck that results in the entropic barriers

for the polymer diffusion. f is actually a crossover function and depends on the degree of confinement which is related to the ratio of the polymer size to that of the bottleneck. f assumes the limits (see ref 8 for details)

$$f \rightarrow \begin{cases} 1 & \text{weak confinement} \\ N^{-1}C^{(1/\nu)-1} & \text{strong confinement} \end{cases} \quad (2)$$

The prefactor A appearing in eq 1 accounts for the modification of D_0 due to the screening of hydrodynamic interaction even in the absence of partitioning effects, as already addressed by Guillot et al.[12] A is less than 1 and is related to the ratio of the Rouse diffusion coefficient D_R to the Zimm diffusion coefficient D_0. It readily follows from eq 1 and 2 that a plot of $(1/M)$ log (D_∞/D_0) versus $1/M$ should show two linear regimes corresponding to weak and strong confinement with the slope for strong confinement greater than that for the weak confinement. Quantitative comparison with the predictions of the theoretical model requires specific knowledge of the length scales C_1 and C. Figure 4 is a plot of the data as $(1/M)$ log (D_∞/D_0) vs $1/M$. The graph clearly shows two linear regimes with a rather clear crossover between the two. The data for glasses R1866 and R703[6,7] though not as extensive as for R893, show the same qualitative features seen above. More recent data[12] in similar glasses with pore radii 275 and 75 Å, where the confinement is even stronger, also support this picture. Notice that while the crossover between the weak and the strong confinement regimes appears distinct in Figure 4, the data do not conform to any apparent power law in the double-logarithmic plot of Figure 3. Thus the data are in good agreement with the model of entropic barriers, indicating that a porous network with bottlenecks is a reasonable model for the structure of these CPGs and that the entropic barrier effects at these bottlenecks play an important role in polymer diffusion in these glasses.

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Spinodal Decomposition of an Aqueous Solution of Poly(*N*-isopropylacrylamide)

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A number of experimental studies have been performed on the spinodal decomposition of polymer mixtures. However, most of these studies were performed for organic solvent systems and very few for aqueous systems. To our knowledge, experimental studies for the latter systems have been reported only by Inoue and his co-workers,[3] for the aqueous solution of poly(vinyl alcohol). The present work has been devoted to measuring the spinodal decomposition of the aqueous solution of poly(*N*-isopropylacrylamide).

The polymer was synthesized by the radical polymerization of *N*-isopropylacrylamide in water at 0 °C with a monomer concentration 7.3 wt %, initiated with potassium persulfate (0.7 wt %) in the presence of a reaction accelerator, *N,N,N′,N′*-tetramethylethylenediamine (2 μg/L). The synthesized polymer had number- and weight-averaged molecular weights of 2.9×10^5 and 2.3×10^6, respectively. Aqueous solutions of the polymer at three different concentrations, 4.4, 5.9, and 7.3 wt %, were prepared and subjected to cloud-point and light-scattering measurements.

The cloud points were determined with thermal analysis, using a differential scanning calorimeter (Seiko I. SSC-5000) and also checked according to a common visual method. The experimental results are presented in Figure 1. Since the present system exhibits the behavior of a lower critical solution temperature,[2] phase separation occurs in a temperature region above the cloud points.

Light-scattering experiments were carried out with a light-scattering photometer (Otsuka Denshi Co., Model LS-601) equipped with a 488-nm Ar-ion laser source and a thermoregulated xylene bath. The xylene bath was maintained at a constant temperature above the cloud point. A sample cell of the polymer solution was placed in it and raised to the temperature of the bath. Then the intensities of light scattered from the sample were measured at appropriate intervals.

According to Cahn's linearized theory proposed for the initial stage of spinodal decomposition,[1] the variation of scattered light intensity with time is expressed as follows:

$$I(q,t) = I(q,0) \exp[2R(q)t] \quad (1)$$

where

$$q = (4\pi/\lambda) \sin(\theta/2) \quad (2)$$

and $I(q,t)$ is the scattered light intensity at wavenumber q and time t, $I(q,0)$ the initial value of $I(q,t)$, and $R(q)$ is the growth rate of composition fluctuation at wavenumber q, θ is the scattering angle of the light, and λ is its wavelength.

Figure 2 shows the time variations of scattered light intensity measured at various wavenumbers. The experimental temperature was 33.5 °C, and the polymer concentration of the sample used was 4.4 wt %. Figure 2 indicates that each set of data can be approximated by a linear relation until about 60 s. This linear relation is in accordance with the prediction of eq 1, and the same relation was also observed in the other experiments. Therefore the values of $R(q)$ were determined from the experimental data.

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