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Diffusion of Polystyrenes through Microporous Membranes

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ABSTRACT: We have measured the diffusion of monodisperse polystyrene chains through membranes containing small quasi-cylindrical pores. The effective diffusive flux decreased sharply as the polymer coil radius approached the pore diameter. This is explained equally well by the Renkin equation for solid solutes or by scaling arguments recently developed for polymer solutions. However, a drastic flux enhancement was also observed with increasing polymer concentration, a result predicted only by the scaling theory.

Partitioning and diffusion studies of flexible polymer coils in porous media have practical applications in such important fields as membranes, gel permeation chromatography, and oil recovery. They are also of fundamental interest for testing, in systems of reduced spatial dimensionality ($d < 3$), scaling arguments recently developed for polymer solutions.[1] Detailed calculations of the static[2] and dynamic[3] properties have been made for long-chain polymers trapped in small slits and cylinders, i.e., when the size of the unperturbed chains is larger than at least one dimension of the confining medium. Moreover, the scaling approach has allowed consideration of both dilute solutions, where the different chains do not overlap, and semidilute solutions, where the chains are strongly entangled. Interesting differences between the two regimes have been predicted, such as the possibility for semidilute solutions to penetrate pores much smaller than the individual coil radius of gyration.[3]

Experimental studies of the partitioning and diffusion of both rigid[4] solute molecules and polymer coils[5] in porous media immersed in solutions have been performed. Those experiments were interpreted as showing that rigid solutes reached the same concentration in the pores as in the bulk solution even when x, the ratio of the solute molecule diameter to the pore diameter, was as large as 0.5 but that their diffusion was greatly hindered. In the case of polymers, the opposite conclusions were reached, namely, completely unhindered diffusion for x as large as 1.2 but greatly reduced concentration with increasing x. Theoretically, however, one would expect not only reduced concentration due to geometric exclusion effects but also increased hydrodynamic drag,[6] and hence hindered diffusion, due to the boundary conditions on solvent flow imposed by the pore walls. Exclusion effects with polymers have also been clearly observed in a study[7] of the chromatographic behavior of dextran on porous glass, with a good correlation between the coil diameter as measured by intrinsic viscosity and the smallest pore size penetrated.

More recently, Satterfield et al.[8] have observed that the concentration of polystyrene entering porous glass cubes, relative to the concentration of the solution containing the cubes, increased sharply with concentration, which is in qualitative accord with the scaling theory predictions.

In order to provide more information in this area, and to test the scaling theory results, we have measured the net diffusive flux of various molecular weight polystyrenes through polycarbonate membranes containing small uniform pores, a measurement which is sensitive both to exclusion effects and increased hydrodynamic drag. Such membranes appear to be more easily characterized than are porous media and also provide conditions close to those treated theoretically. Since interpretation is very sensitive to pore and polymer coil radius, we measured these parameters directly, the former by flow rate and the latter by quasi-elastic light scattering.

Our results show that the diffusion of dilute polymer chains through cylindrical pores can be accurately described by a single universal function of the reduced variable r_H/r_p, where r_H and r_p are the polymer hydrodynamic radius and the pore radius, respectively, and that this universal function can be obtained from either the Renkin equation[9] or the scaling theory[2,3] results. We also find enhanced diffusion of a heavy molecular weight polymer through small pores at high concentration, a result which only the scaling theory can explain.

Experimental Section

Polystyrenes having weight-average molecular weights of 110 000, 233 000, 390 000, and 600 000 were purchased from Pressure Chemical Co. These polymers had narrow molecular weight distributions with weight-average to number-average molecular weight ratios[10] $M_w/M_n \leq 1.10$. Spectroscopic-grade ethyl acetate (Aldrich Gold Label) was chosen as the solvent because it did not attack the polycarbonate membranes. It is a fair, but not a good, solvent[11] for polystyrene. Quasi-elastic light scattering[12–15] was used to determine the translational diffusion coefficient of each of the polystyrenes in ethyl acetate in the limit of zero polymer concentration. Samples were filtered to remove dust, using membranes having 2000-Å nominal diameter pores. To within ±0.5%, results were independent of the number of times and speed with which a sample was filtered, showing that the polymer coils were not damaged by filtration. The hydrodynamic radii r_H of the various polymers were obtained from the measured diffusion coefficients, after correction to 20 °C, using the Stokes–Einstein equation, $D_0 = k_BT/6\pi\eta r_H$, where T is the absolute temperature and η the solvent viscosity. The results of these measurements are summarized in Table I. In all cases $qR_H \lesssim 0.5$, where q is the scattering wave vector, and thus the measurements should be relatively insensitive to internal motions of the polymer coils.[16]

The membranes were purchased from Nuclepore Corp. in the form of 13-mm-diameter disks ~5-μm thick. Scanning electron micrographs showed the pores to be circular, uniform in diameter, and of a density close to that specified by the manufacturer. However, a number of holes consisting of overlaps of two or more pores were observed. Use of a transmission electron microscope with a tilting stage showed the holes to be more or less uniformly distributed over angles within ±15° of normal. Thus, the probability of two holes overlapping for a distance as great as 5 μm is negligibly small.

To determine pore sizes accurately, we made flow-rate measurements by clamping the membranes between two very flat stainless steel plates containing 55 coinciding 1-mm-diameter holes through which prefiltered solvent was forced. This provided adequate support for the membrane and a well-defined area for flow. Flow rates were linear in the pressure P for all membranes, and the pore radii were determined from the flow data by using Poiseuille's equation, $Q = \pi P r_p^4/8\eta L$, where Q is the flow rate

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Table I
Hydrodynamic Properties and Relative Diffusivities D_m/D_0 for Different Molecular Weight Polystyrenes in Membranes of Various Pore Sizes r_p

					r_p, Å				
M_w	M_w/M_n	C_0, mg/cm^3	10^7D_0, cm^2/s	r_H, Å	271	396	572	928	1292
110000	≤1.06	4.0	6.17	76	0.10	0.24	0.38	0.50	0.80
233000	≤1.06	4.0	4.06	117	0.02		0.22	0.49	0.64
390000	≤1.06	4.0	3.31	145		0.04	0.16	0.37	0.60
600000	≤1.10	1.4 (47)	2.43	196	0.002 (0.016)	0.01		0.20	

per pore in cm^3/s and L is the membrane thickness. These measurements were made by using both ethyl acetate and water. The pore diameters obtained after 24-h exposure to ethyl acetate were 543, 793, 1145, 1857, and 2584 Å for membranes specified as having pore diameters of 150, 300, 500, 1000, and 2000 Å, respectively, while the diameters obtained with water were ~225 Å less than those obtained with ethyl acetate. We also observed that after a membrane was exposed to ethyl acetate the flow rate for water increased but returned to the normal value within a few hours. This effect was not caused by the membrane swelling in ethyl acetate, because even after weeks of exposure to ethyl acetate swelling was less than a few percent. We surmise instead that the pores have small lips at the membrane surface which are softened by ethyl acetate. This would explain both the observed flow behavior and the large discrepancies between the nominal values of the pore diameters quoted by the manufacturer and the values obtained by flow-rate measurements. The nominal values were obtained by scanning electron microscopy and were thus sensitive only to the pore diameter at the membrane surface.

In order to verify that polystyrene was not adsorbed to the polycarbonate membranes, we made solvent flow-rate measurements before and after 24-h exposure to polymer solutions which were forced through the pores. No changes in flow rate were observed under conditions where a 10-Å-thick layer would have resulted in an easily measurable change.

Measurements of the flux of polymer diffusing through the membranes were made by using small cells containing two chambers separated by a membrane. The membrane was tautly suspended with no supporting screen, and small Teflon-coated stirring bars were used to vigorously agitate the contents of each chamber in order to minimize any stagnant layers in the immediate vicinity of the membrane. In use, one chamber contained the polymer solution to be studied, while the other chamber initially contained pure solvent. A polymer concentration of 4 mg/cm^3 was normally used except for the largest polymer, where concentrations of 1.4 and 47 mg/cm^3 were used. The ends of the chamber initially containing solvent consisted of quartz windows, and a Cary 219 spectrophotometer was calibrated and used to measure the absorbance at 260 nm, thus providing an accurate measure of the concentration of polystyrene which had diffused across the membrane. Under these conditions one obtains the following expression for the polymer concentration in the absorbance chamber $C(t)$ as a function of time:

$$\ln\,[1 - C(t)/C(\infty)] = -(D_m n A_p/L)(1/V_1 + 1/V_2)t \qquad (1)$$

Here n is the number of pores each of cross-sectional area A_p, V_1 and V_2 are the chamber volumes, and D_m is an effective diffusion coefficient defined by

$$Q(t) = D_m A_p \Delta C(t)/L \qquad (2)$$

where Q is the polymer flux per pore in g/s, L is the membrane thickness, and $\Delta C(t)$ the difference in polymer concentration across the membrane. It should be noted that by its definition, D_m includes both the effects of restricted diffusion in the pore and any exclusion effects which tend to reduce the polymer concentration in the pore relative to the bulk concentration immediately outside the pore.

Equation 1 may be verified experimentally by plotting ln $[1 - C(t)/C(\infty)]$ vs. time to obtain a linear plot. Figure 1 shows a typical result obtained in this way. The initial curvature is almost certainly due to the rapid equilibration of low molecular weight contaminants. It was greatly reduced if the absorbance chamber was flushed with pure ethyl acetate several hours after the initial filling. The slope of the linear portion, which yields D_m, was independent of whether the absorbance chamber was flushed, and so this was not always done. Accurate values for $C(\infty)$, the equlibrium concentration, were obtained from knowledge of the chamber volumes and the total mass of polymer used to charge the cell.

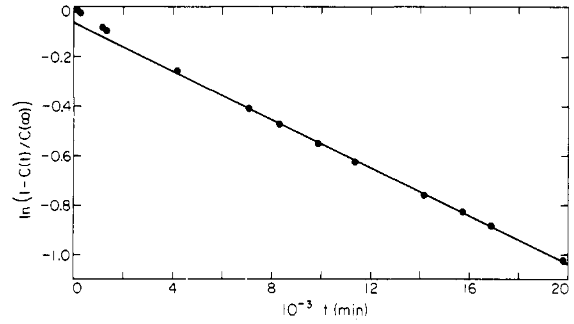

Figure 1. ln $[1 - C(t)/C(\infty)]$ vs. time, where $C(t)$ is the concentration of polystyrene which has diffused across a membrane containing cylindrical pores of radius 396 Å. The Stokes–Einstein radius of the polymer coils was 144 Å.

Since the effects of boundary-layer resistance to diffusion through the membranes can be important in studies such as the present one, some discussion of the possible magnitude of these effects is required. Such layers increase the effective resistance of the membrane to diffusion, with the effect becoming worse for small, rapidly diffusing, solutes. That the present measurements are relatively free of such artifacts is evidenced in two ways. First, the results obtained were almost completely independent of the stirring speed employed. Second, in the worst case of the smallest polymer coils diffusing through the membrane containing the largest holes, the measured diffusive flux was 80% of that which would occur for unhindered diffusion through the membrane's holes, in the absence of any stagnant-layer effects. Thus, the maximum extent to which any of the data could have been affected is 20%. One may also estimate the importance of such effects analytically. For the geometry of the cells used here, the closest approximation is provided by the solution of the problem involving diffusion from a plate immersed in a solvent flowing parallel to the plate.[17] In the worst case this solution indicates a 30% effect, which is not far from the observation that the maximum possible effect is 20%.

Results and Discussion

In several instances, quasi-elastic light scattering was used to measure the hydrodynamic radius of the polymers which had diffused through the membranes. The results showed that the polymers crossing the membranes were not simply low molecular weight contaminants. In general, the polymer passing the membrane gave a value for r_H which was ~5–10% less than that of the original sample, showing somewhat selective diffusion through the pores. As another test, in several instances an experiment was continued until a major fraction of the original polymer sample had passed the membrane.

The results of these measurements are summarized in Table I, which gives the ratio D_m/D_0 for each pore size and molecular weight combination studied. The functional dependence of these results upon the ratio of polymer coil

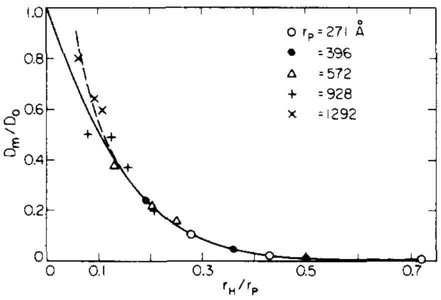

Figure 2. Ratio of membrane diffusivity to bulk solution diffusivity for various molecular weight polystyrenes dissolved in ethyl acetate as a function of the ratio of the Stokes–Einstein radius of the polymer coils to the pore radius. The solid line is the Renkin equation, using $1.45r_H/r_p$ as the variable, and the dashed line is the result obtained from scaling arguments. For $r_H/r_p > 0.3$, the dashed and solid lines are indistinguishable.

radius to pore radius is shown in Figure 2. As may be seen, the ratio D_m/D_0 is a function only of the variable r_H/r_p for the data obtained at low concentrations. On the other hand, D_m/D_0 shows a strong increase with bulk polymer concentration C_0 in the case of the 600 000 molecular weight polymer. For this polymer a factor of 8 increase in diffusion rate through 271-Å-radius pores was observed upon increasing C_0 from 1.4 to 47 mg/cm^3.

In analyzing our data, we have taken two rather different approaches. In the first, the individual polymer coils are treated as rigid spheres, while in the second, a model based on the scaling results for flexible coils is used. Both approaches give an excellent description of the low-concentration data, but only the scaling theory predicts enhanced diffusion at high concentration.

Diffusion of rigid solutes through homopore membranes has been studied experimentally,[18] and for $r_H/r_p \lesssim 0.4$ the results are fairly well described by the Renkin equation

$$D_m/D_0 = (1 - x)^2(1 - 2.1x + 2.1x^3 - 0.95x^5) \qquad (3)$$

where x is the reduced variable r_H/r_p. This equation represents a very simple model.[19] The first factor allows for the reduction of solute concentration in the pore, while the second gives the decrease in diffusion coefficient due to increased viscous drag for a sphere moving on the axis of a cylindrical pore.[6]

We find that this model is capable of an excellent description of the low-concentration data, as shown by the solid curve in Figure 2. This may not be too surprising since it is well-known that individual polymer chains in solution are generally non-free draining[20] and behave as rigid spheres hydrodynamically. This curve was obtained by using $1.45r_H/r_p$, rather than r_H/r_p, as the reduced variable in eq 3. In considering this result one should bear in mind that three different radii have been found to be useful in characterizing polymer coils in dilute solution, namely, the hydrodynamic radius r_H, the radius of gyration r_G, and the root-mean-square end-to-end distance of the chain, or Flory radius, r_F. In principle, one should probably use the ratio r_H/r_p in modeling the increased drag and r_G/r_p or r_F/r_p in considering exclusion effects; however, we do not feel that the data warrant such fine distinctions.

We shall now consider the scaling arguments of Daoud and de Gennes[2] which specifically deal with flexible long-chain polymers. Their starting point is the existence of a crossover concentration C^* in bulk solutions. C^* describes the concentration of first overlap between chains and separates the dilute regime, where one has an ideal solution of chains of "size" r_G, from the semidilute regime, where the chains overlap but can still be represented simply as ideal chains or "blobs" of size $\xi < r_G$. The correlation length ξ, which varies as $C_0^{-3/4}$, is the distance above which all excluded-volume interactions between monomers are screened out. Depending on the concentration regime, the passage of flexible chains through pores is predicted to be very different.

In the dilute regime and for $r_F \gtrsim r_p$, the concentration of chains penetrating the pore is found to decrease exponentially[2]

$$C_p = \beta C_0 e^{-(kr_F/r_p)^{5/3}} \qquad (4)$$

where β and k are proportionality constants.[21] Under the same conditions, the ratio of the coil diffusivity in the pore D_p to that in the bulk solution D_0 is given by

$$D_p/D_0 = \beta'(kr_F/r_p)^{-2/3} \qquad (5)$$

Combining eq 4 and 5, we may use these results to model the diffusivity ratio D_m/D_0 as the product of two factors

$$D_m/D_0 = (D_p/D_0)(C_p/C_0) = \alpha(kr_F/r_p)^{-2/3}e^{-(kr_F/r_p)^{5/3}} \qquad (6)$$

The dashed line in Figure 2 is eq 6 with $\alpha = 2.64^{-1}$ and the reduced variable kr_F/r_p replaced by $4r_H/r_p$. As may be seen, the fit is excellent and thus the scaling theory accounts very well for the data at low concentrations. The only serious deviation which occurs is for the point at $r_H/r_p = 0.72$, where D_m/D_0 is 0.002. In this case, the predicted value of D_m/D_0 is too small by a factor of 4. At this point, we have no explanation for this discrepancy.

In the semidilute regime the scaling theories predict that the chains are able to penetrate the pores, even when $r_F > r_p$, provided C_0 is large enough to ensure that ξ is smaller than r_p. This can be understood intuitively if one considers that, in bulk semidilute solution, each chain is already confined by the other chains over distances of the order of ξ. Therefore, it experiences large entropic repulsion only with pores smaller than ξ.

We estimate that C^* is $\sim$15 mg/cm^3 for M = 600 000 and is, of course, higher for the smaller molecular weights. Therefore, the dilute-regime behavior should be applicable for the experiments performed at C_0 = 1.4 and 4 mg/cm^3. However, for C_0 = 47 mg/cm^3 and M_w = 600 000, we expect behavior appropriate to the semidilute regime. From small-angle neutron scattering data[22] we can estimate ξ as $\sim$30 Å at 47 mg/cm^3, and thus the solution should, in theory, enter the pore freely. This may well be the basis for the factor of 8 enhancement in diffusive flux which we observe upon increasing C_0 from 1.4 to 47 mg/cm^3. However, our result pertains to the situation in which the polymer concentration is such as to be in the semidilute regime on one side of the membrane and in the dilute regime on the other. Under these conditions the polymer concentration in the pore presumably varies from semidilute to dilute in a continuous fashion, making any quantitative comparison with the theory difficult. It is also clear from Figure 2 and Table I that an increase in D_m/D_0 from 0.002 to 0.016 corresponds to only a modest decrease in r_H/r_p from $\sim$0.72 to $\sim$0.5. Thus, the relevant hydrodynamic length, if a single such length exists under our experimental conditions, has apparently decreased from r_H = 196 Å to $\sim$0.5(271 Å) or 135 Å. Obviously, this length is much greater than the actual value of ξ, but the clarification of the dependence of D_m/D_0 on ξ will require further experiments.

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References and Notes

(1) de Gennes, P. G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, N.Y., 1979.
(2) Daoud, M.; de Gennes, P. G. *J. Phys. (Paris)* **1977**, *38*, 85. Brochard, F.; de Gennes, P. G. *J. Phys. Lett.* **1979**, *40*, 399.
(3) Brochard, F.; de Gennes, P. G. *J. Chem. Phys.* **1977**, *67*, 52. Daoudi, S.; Brochard, F. *Macromolecules* **1978**, *11*, 751.
(4) Satterfield, C. N.; Colton, C. K.; Pitcher, W. H., Jr. *AIChE J.* **1973**, *18*, 628.
(5) Colton, C. K.; Satterfield, C. N.; Lai, C. J. *AIChE J.* **1975**, *21*, 289.
(6) Happel, J.; Brenner, H. "Low Reynolds Number Hydrodynamics"; Prentice-Hall: Englewood Cliffs, N.J., 1965; p 285.
(7) Haller, W. *Macromolecules* **1977**, *10*, 83.
(8) Satterfield, C. N.; Colton, C. K.; de Turckheim, B.; Copeland, T. M. *AIChE J.* **1978**, *24*, 937.
(9) Renkin, E. M. *J. Gen. Physiol.* **1954**, *38*, 225.
(10) This means that 70% of the chains are within ±30% of the number-average molecular weight. It is thus not a truly monodisperse distribution.
(11) Munch, J. P.; Candau, S.; Herz, J.; Hild, G. *J. Phys. (Paris)* **1977**, *38*, 971.
(12) Forrester, A. T.; Parkins, W. E.; Gerjuoy, E. *Phys. Rev.* **1947**, *72*, 728.
(13) Dubin, S. B.; Lunacek, J. H.; Benedek, G. B. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *57*, 1164.
(14) Cummins, H. Z.; Swinney, H. L. *Prog. Opt.* **1970**, *8*, 133.
(15) Chu, B. "Laser Light Scattering"; Academic Press: New York, 1974.
(16) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*, 1229.
(17) Levich, V. G. "Physicochemical Hydrodynamics"; Prentice-Hall: Englewood Cliffs, N.J., 1962; p 87.
(18) Beck, R. E.; Schultz, J. S. *Biochim. Biophys. Acta* **1972**, *255*, 273.
(19) For a discussion, see: Villars, F. M. H.; Benedek, G. B. "Physics with Illustrative Examples from Medicine and Biology"; Addison-Wesley: Reading, Mass., 1974; pp 2–80.
(20) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1971.
(21) Unfortunately, scaling laws are not able to predict exact numerical coefficients.
(22) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P. G. *Macromolecules* **1975**, *8*, 804.

Theory of Microphase Separation in Block Copolymers

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ABSTRACT: A microscopic statistical theory of phase equilibria in noncrystalline block copolymers of type A–B is developed. In particular, the onset of an ordered mesophase from a homogeneous melt is studied and a criterion of the microphase separation is found. The only relevant parameters of the theory turn out to be the product χN (χ is the Flory parameter characterizing A–B interactions; N is the polymerization index) and f, the fraction of monomers A in a chain. It is shown that under certain critical conditions a specific unstable mode appears in the homogeneous copolymer melt; this announces the microphase separation transition (MST). After the MST a mesophase with the periodicity equal to the wavelength of the unstable mode and with the symmetry of a body-centered-cubic (bcc) lattice should appear. For a large range of compositions a bcc mesophase is expected to be a metastable phase. Only two other ordered phases, a hexagonal mesophase and a lamellar mesophase, may be stable near the MST. The regions of stability are calculated and the phase diagram of the system is provided. First-order transitions are predicted between different ordered phases. A new method of measuring of the parameter χ, crucial for verification of the theory, is proposed.

I. Introduction

The particular chemical structure of block copolymer materials is reflected in the most fundamental and interesting way by incompatibility effects. These effects give block copolymers a number of specific, new morphologies and original physical and mechanical properties which have led to valuable technological applications (for general references see ref 1). The purpose of the present paper is to formulate a microscopic theory which, on the basis of statistical physics, would explain how and under which conditions the incompatibility of molten copolymer constituents leads to the formation of different ordered structures (mesophases). This general theory is applied to provide a phase diagram of the simplest copolymer system—molten diblock copolymer A–B. Both sequences of monomers A and B, forming a copolymer molecule, are supposed not to be able to crystallize.

The most characteristic feature of a block copolymer is the strong repulsion between unlike *sequences* even when the repulsion between unlike *monomers* is relatively weak. As a result sequences tend to segregate, but as they are chemically bonded even the complete segregation cannot lead to a macroscopic phase separation as in mixtures of two homopolymers. However, in the case of a sufficiently strong incompatibility, microphase separation occurs: microdomains rich in A (in B) are formed.

Such an effect was first observed in concentrated solutions of block copolymers and afterward in many other copolymer systems, particularly in molten block copolymers (see, e.g., review articles 3–8 and references given therein). When microphase separation occurs, the microdomains are not located at random but they may form a regular arrangement giving rise to a periodic structure (macrolattice). Several techniques (e.g., annealing, ex-

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