Diffusion of Large Flexible Polymer Chains through Model Porous Membranes

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ABSTRACT: The diffusion of large polymer molecules through model porous membranes (pore radius \( R_p \)) has been measured as a function of both polymer concentration and molecular weight. In the limit of low concentrations, the parameter that controls the diffusion of the chains is their hydrodynamic radius \( R_H \); for \( R_H > R_p \), the diffusion is highly hindered. When the concentration is increased, our results demonstrate the existence of a new transport regime in which chains with \( R_H > R_p \) can diffuse through the membrane with an effective diffusion coefficient, \( D_{\text{eff}} \), 2 orders of magnitude larger than in the dilute concentration range. We interpret this behavior in the framework of the scaling approach to polymer solutions and show that this enhanced diffusion may be attributed to the concentration dependence of the partition coefficient between bulk solution and pores and is related to the flexibility of the chains.

Introduction

Transport of macromolecular solutes through porous media controls a wide variety of experimental situations such as gel permeation chromatography, ultrafiltration, and enhanced oil recovery.

A basic initial and intuitive idea was that solutes of size comparable to the pore radius could hardly penetrate the porous media. This simple geometrical view is well supported by a large amount of experimental data on diffusion or flow of rigid proteins and small molecular weight polymer solutions through a wide variety of porous media (compacted silica beads,\(^1\) leached vycor glass,\(^2,3\) mica or polycarbonate track-etched membranes with cylindrical pores\(^4,5\)). Large flexible macromolecules, however, seem to deviate from this straightforward hard-sphere behavior and have been shown to penetrate small pores more easily than rigid particles.\(^2,5\) Moreover, an enhancement of the permeation rate of flexible molecules has been observed in a few cases when either the flow rate or the polymer concentration are increased.\(^9,10\)

From a theoretical point of view, Casassa was the first to calculate the partition coefficient (i.e., the ratio of the solute concentration inside the pore to the solute concentration outside) for both ideal flexible chains and rigid rods at infinite dilution from a statistical analysis of the polymer conformation.\(^11\) Taking advantage of the scaling approach to polymer solutions, Daoud and de Gennes have investigated the conformations of large flexible chains in good solvent trapped into small cylindrical pores as a function of polymer concentration.\(^12\) Daoudi and Brochard have later evaluated the partition coefficient both in the very dilute regime and in the high-concentration regime where the chains become entangled inside the pore. Also, de Gennes and Brochard have calculated the diffusion coefficient of isolated chains inside a cylindrical pore\(^13\) and Daoudi and Brochard have studied the transport under flow.\(^15\)

Both approaches, static and dynamic, predict that large flexible chains penetrate small pores much more easily when the concentration is increased. Available experimental data seem in qualitative agreement with such prediction,\(^10,11,12,15\) but quantitative comparisons are difficult to handle, as they suppose both well-defined polymer chains (low polydispersity, good solvent conditions) and well-defined porous geometry (cylindrical pores of controlled radius). Nucleopore filters (track-etched membranes) provide such controlled systems, but their porosity, fixed by the manufacturer’s specifications, is generally too large for our needs.

We have thus undertaken a series of experiments using high molecular weight, low polydispersity polymers, and membranes similar to Nuclepore filters but prepared by ourselves in order to adjust their characteristics as desired, avoid pore overlap, and control the pore diameter. We have paid special attention to the case where the chain size, as defined by the hydrodynamic radius \( R_H \), is comparable to the pore size \( R_p \).

In the present paper, we examine the influence of both molecular weight and concentration of the solutions on the diffusion of the chains through the membranes in the absence of solvent flow. Our results on transport under flow will be presented in a forthcoming paper.

Experimental Procedures

1. Membranes. The detailed preparation and characterization of the membranes have been described previously,\(^18\) and we summarize here only the main features. Polycarbonate films are irradiated with heavy \( K_L^{209} \) ions, accelerated to an energy of 500 MeV or 6 MeV/N at A.L.I.C.E. synchrotron in Orsay. Under such high incident energies, latent tracks are formed in the film and later chemically etched to produce cylindrical pores spanning the membrane. The pore density is fixed by the irradiation dose, while the pore radius is governed by the duration of etching. Three techniques have been used to characterize the membranes; they are discussed below.

(a) Conductivity Measurements. The polycarbonate film has a high electrical resistivity, while the etching solution is an electrolyte (sodium hydroxide \( 2 \) N). The conductance \( \sigma \) of the membrane is related to the overall pore area and can be followed directly in the etching cell. If the pore density is known, an average value of the pore radius \( R_p \sim \sigma^{1/2} \) can be extracted. A typical evolution of \( R_p \) vs. the etching duration is shown in Figure 1. Three time domains can be distinguished: (i) for \( t < t_0 \) the conductance is that of an unirradiated film and \( R_p = 0 \); (ii) at \( t_0 \) the first pores start to be broken through and \( R_p \) increases rapidly; (iii) at longer times \( t > t_1 \) \( R_p \) increases linearly with etching time.

We can define the etching rate along the track as \( v_T = L/t_0 \), where \( L \) is the membrane thickness, and the bulk etching rate (for \( t > t_2 \)) as \( v_B = dR_p/dt \). The ratio \( v_B/v_T \) controls the final shape of the pores (cylindrical or conical) and can be made as large as \( 10^4 \) if the membranes are exposed to ultraviolet light before the etching.\(^12\) With \( v_B/v_T = 10^4 \), one obtains cylindrical pores with \( R_p = 10 \) nm and \( L = 10 \) \( \mu m \).

As discussed in ref 18, the determination of the overall pore area by conductivity has a good sensitivity for porosities smaller than 0.1% only. The calibration of the pore growth kinetics \( R_p(t) \) has thus been performed with membranes of such a low porosity and by using an independent determination of \( v_B \) by weight-loss measurements of unirradiated samples.

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