Notes

Diffusion through Coarse Meshes

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This is to examine the retardation effect of semidilute polymer solutions toward the translational diffusion of like polymer chains. The objective is simple. It is to gain insight into restricted diffusions such as organelle and macromolecular diffusion in cytosols and in the molecular sieving process, e.g., gel filtration and gel electrophoresis. Transport phenomena of this sort have been studied extensively in recent years, and some significant advances have been made. In particular, the recent development of the scaling theory of polymer physics[1] provides a new perspective in terms of hydrodynamic screening.

There is a consensus in the literature that the transport coefficients such as sedimentation coefficient, S, electrophoretic mobility, μ, and translational diffusion coefficient, D, do not scale with the macroscopic viscosity of the matrices (suspending media); they should so scale if the matrices were to act like simple homogeneous solvents (hydrodynamic continua), as would be predicted by the Stokes–Einstein equation. It is generally accepted, on empirical grounds, that these coefficients follow a stretched exponential relation,

$$Q/Q_0 = \exp(-\alpha C^{\nu}) \tag{1}$$

where Q can be S, μ, or D, C is the matrix concentration, α and ν are the empirical constants, and the subscript 0 stands for the reference state of free solution without matrix. In all cases, the diffusant concentration is assumed to be so small that it does not affect the transport coefficient, Q or Q_0. Beyond the general form of eq 1, the consensus vanishes. For instance, the value of ν varies between $^1/_2$ and 1 according to various measurements.[2-13] While it is accepted that the constant α is related to a linear dimension of the diffusant, any specific relationship is yet to be fully established.[3-7, 9, 12-18] Theoretically, there are also conflicts. The pore size distribution model of Ogston[19] has been frequently employed to explain unity for the ν value[15] such as one encounters in diffusion through gels. On the other hand, "the stochastic model" of Ogston et al.[20] is sometimes invoked to justify $^1/_2$ for the ν value.

Upon application of the scaling theory to the friction coefficient of a spherical particle with a radius, R, sedimenting through a semidilute polymer solution, Langevin and Rondelez[9] have proposed that

$$Q/Q_0 = A \exp(-R/\xi) \tag{2}$$

where Q and Q_0 are the sedimentation coefficients, A is a proportionality constant, and ξ is the hydrodynamic screening length of the semidilute solution which is the matrix. Since ξ scales with the solution concentration as $\xi \propto C^{-x}$, eq 2 is equivalent to eq 1 if α is proportional to R, which is a measure of diffusant size, be it radius or otherwise. Furthermore, Cukier[21] has recently provided a theoretical justification of eq 2 and proposed the matrix concentration exponent, ν, of eq 1 to range between $^1/_2$ and 1 depending on solvent quality. Our purpose is to test eq 2 with semidilute solutions of polystyrene in toluene as the matrices and shorter chain length polystyrenes as the diffusants.

Ideal experimental conditions require that the transport behavior of the diffusant be isolated from the rest of the system. The technique of forced Rayleigh scattering[22-25] (FRS) with photolabels only on the smaller chain diffusants should meet this requirement. Also, since eq 2 assumes a semidilute solution and stationary matrix, one must use a much higher molecular weight polymer as the matrix compared to the diffusant. We have earlier reported such a set of FRS results,[26] which span across $R < \xi$ and $R > \xi$. Our focus in that paper was in the region of $R > \xi$. Here, we report the analysis of $R < \xi$ in the context of eq 2. Hence, we deal with the translational diffusion of linear polymer through coarse meshes. Putting it differently, we pick a subset of the restricted diffusion problem by studying small linear chain diffusion through loose matrices in a good solvent such that the diffusant is well represented by a nondraining random coil configuration with fully developed hydrodynamic interactions. This should result in the diffusants behaving like hydrodynamic spheres.[1,27]

In order to test with the data set listed in Table II of ref 26, eq 2 is rewritten as

$$\begin{aligned}\log [\log (D_0/D) + \log A] &= \log R - \log \xi \\ &= \text{constant} + \log R + x \log C\end{aligned} \tag{3}$$

where $\xi \propto C^{-x}$ is used in the last line. Figure 1 shows a plot of the data points below C^* using eq 3. Note that C^* means the overlap concentration of the polystyrene diffusant. Hence, it is the concentration of the matrix where ξ is the same as R, the root-mean-square radius of gyration of the diffusant; C^* for a given diffusant is calculated with the empirical formula of Adam and Delsanti[28] for polystyrene in benzene, $C^*(\text{wt }\%) = 620M^{-0.785}$ where M stands for the molecular weight of the diffusant. The plus signs in the figure represent C^* for different diffusants. At C^*, values of D_0/D are more or less the same for all molecular weights examined, as indicated by the dashed horizontal line. This is the first prediction of eq 2 since the left-hand side is equal to a constant when $R = \xi$ *regardless of the size of diffusants*. We emphasize here that neither R nor ξ is calculated or estimated explicitly to equate the two although that can be done. Instead, only C^* is calculated for each M and indicated by + in the figure. All we have used is the condition that $R = \xi$ at $C = C^*$.

Next, we see in the plot that there exists a unique slope which is near 0.75 for different molecular weights of the diffusant. Recalling that the exponent x in eq 3 for a good solvent is 0.75, we can say that this observation confirms the second prediction of eq 3, namely, $\xi \propto C^{-0.75}$. For two samples, methyl red and polystyrene of 10K molecular weight, the data show some deviation above the concentration of 20 wt % (K stands for kilodalton in molecular weight units). This behavior was interpreted earlier as due to the changes in local friction;[26] the matrix concentration is so large that it is no longer a semidilute solution even though its calculated ξ is larger than R of the diffusants.

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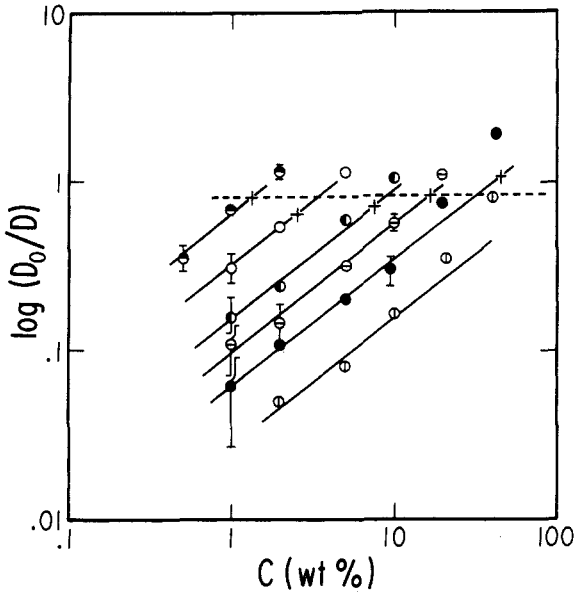

Figure 1. Log (D_0/D) plotted against matrix concentration, C, in a double logarithmic scale. The data are from ref 26. Error bars are shown for a selected few points. The plus signs stand for C^* of each diffusant, which is calculated from an empirical relation, C^*(wt %) = 620 $M^{-0.785}$ (ref 28). At C^*, R of the diffusant is equal to ξ of the matrix; hence, $D_0/D = A/e$ according to eq 2. We do not calculate ξ explicitly and equate it to the experimental R; instead we just use $R = \xi$ at $C = C^*$. The dashed horizontal line is drawn to show the constancy of D_0/D at such a state. The solid lines have the slope of 0.75. In each case, one data point above C^* is also plotted to display persistence of the same concentration dependence beyond C^*. One data point of the 390k sample at 0.5% is not shown because of its anomalous departure from the entire data set. For the 1800k sample, no data are shown in the plot since none were available for $C < C^*$. The diffusants are distinguished by 900K (⊜), 390K (○), 100K (◐), 35K ⊖, 10K (●), and methyl red (⊙).

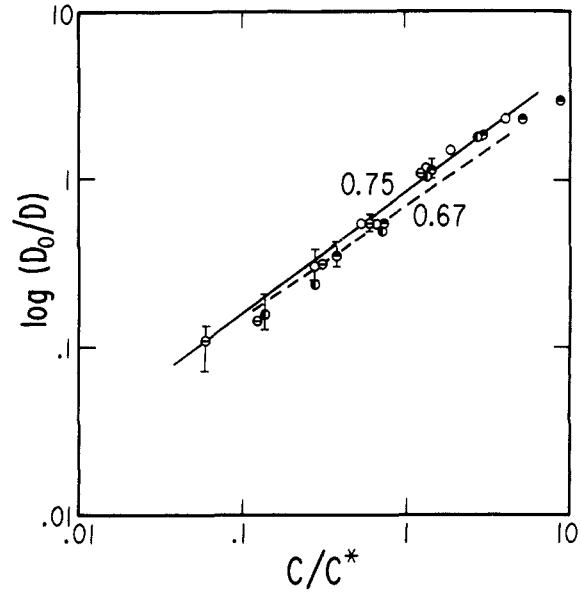

Figure 2. Double logarithmic plot of log (D_0/D) versus C/C^* where the symbols for different diffusants are the same as in Figure 1. Universal behavior for all diffusants and concentration scaling with 0.75 slope for $C/C^* < 1$ are both well represented. A dashed line with a slope of 0.67 is shown for comparison. Here, we have deleted the data for the 10k sample and methyl red (see text). More data points beyond C^* than those shown in Figure 1 are plotted here. It should be noted that the observed concentration for $C/C^* < 1$ persists for some range of C/C^* above unity before a departure from such emerges. Note also that numerical values of C^* are subject to inherent ambiguity even though we have maintained self-consistency in their evalutions.

We pursue the case when $R = \xi$. If ξ of the matrix in the semidilute solution is indeed given by

$$\xi \propto (C^*/C)^x \tag{4}$$

then a universality should be obtained:

$$\log [\log (D_0/D) + \log A] = \text{constant} + x \log (C/C^*) \tag{5}$$

for all diffusants. Such a plot is shown in Figure 2. All of the data points merge into a single line with a slope of 0.75 which is drawn over the data point. Also drawn is a dashed line with a slope of 0.67 for comparison (see below). We do not use the data for 10K sample (●) and methyl red (⊙) here because of the complications referred to above. The deviation with the 10k sample would be due to its low molecular weight so that C^* may not be calculated by using the same formula as in high molecular weights; in fact, one should define C^* with care at such a low molecular weight even with the inherent ambiguity of numerical values of C^*.

Combining both observations, we conclude that eq 2 well represents the restricted diffusion process in a polymer matrix. Further, the hydrodynamic screening concept seems to be well borne out in the mixed system consisting of high molecular weight matrix with ξ and low molecular weight diffusant with R where $R \leq \xi$. In other words, polymer coils exhibit nondraining behavior when their size is smaller than the correlation length of the matrix so that we can treat them as hydrodynamic spheres. The concentration scaling of 0.75 is the first instance of such an experimental demonstration, whereas the same for the mutual diffusion coefficient is universally observed[27] to be 0.67.

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References and Notes

(1) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1979.
(2) Ferguson, K. A. *Matab. Clin. Exp.* **1964**, *13*, 985.
(3) Hedrick, J. L.; Smith, A. J. *Arch. Biochem. Biophys.* **1968**, *126*, 155.
(4) Stellwagen, N. C. *Biochemistry* **1983**, *22*, 6180.
(5) Weber, K.; Osborn, M. In *The Proteins*, 3rd ed.; Neurath, H., Hill, R. L. Eds.; Academic: New York, 1975; Vol. 1, Chapter 3.
(6) Laurent, T. C.; Pietruszkiewicz, A. *Biochim. Biophys. Acta* **1961**, *49*, 258.
(7) Laurent, T. C.; Björk, I.; Pietruszkiewicz, A.; Persson, H. *Biochim. Biophys. Acta* **1963**, *78*, 351.
(8) Donners, W. A. B. *Colloid Polym. Sci.* **1977**, *255*, 27.
(9) Langevin, D.; Rondelez, F. *Polymer* **1978**, *19*, 875.
(10) Jamieson, A. M.; Southwick, J. G.; Blackwell, J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1513.
(11) Ullman, G.; Phillies, G. D. J. *Macromolecules* **1983**, *16*, 1947. Phillies, G. D. J. *Macromolecules* **1986**, *19*, 2637; **1987**, *20*, 559.
(12) Brown, W.; Stilbs, P. *Polymer* **1983**, *24*, 188.
(13) Brown, W.; Rymden, R. *Macromolecules* **1986**, *19*, 2942.
(14) Chen, J.-L.; Morawetz, H. *Macromolecules* **1982**, *15*, 1185.
(15) Rodbard, D. In *Methods of Protein Separation*; Catsimpoolas, N., Ed; Plenum: New York, 1976; Vol. 2, Chapter 3.
(16) Southern, E. M. *Anal. Biochem.* **1979**, *100*, 319.
(17) Lerman, L. S.; Frisch, H. L. *Biopolymers* **1982**, *21*, 995.
(18) Lumpkin, O. J.; Zimm, B. M. *Biopolymers* **1982**, *21*, 2315.
(19) Ogston, A. G. *Trans. Faraday Soc.* **1958**, *54*, 1754.
(20) Ogston, A. G.; Preston, B. N.; Wells, J. D. *Proc. R. Soc. London, Ser. A.* **1973**, *333*, 297.

(21) Cukier, R. I. *Macromolecules* **1984**, *17*, 252.
(22) Hervet, H.; Urbach, W.; Rondelez, F. *J. Chem. Phys.* **1978**, *68*, 2725.
(23) Leger, L.; Hervet, H.; Rondelez, F. *Macromolecules* **1981**, *14*, 1732.
(24) Wesson, J. A.; Noh, I.; Kitano, T.; Yu, H. *Macromolecules* **1984**, *17*, 282.
(25) Antonietti, M.; Coutandin, J.; Grütter, R.; Sillescu, H. *Macromolecules* **1984**, *7*, 798.
(26) Kim, H.; Chang, T.; Yohanan, J. M.; Wang, L.; Yu, H. *Macromolecules* **1986**, *19*, 2737.
(27) Schaefer, D. W.; Han, C. C. In *Dynamic Light Scattering: Applications to Photon Correlation Spectroscopy*; Pecora, R., Ed; Plenum: New York, 1985; Chapter 5.
(28) Adam, M.; Delsanti, M *J. Phys. (Paris)* **1983**, *44*, 1185.

Non-Gaussian Optical Properties of Bimodal Elastomeric Networks

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Introduction

Most molecular theories of rubberlike elasticity are based on a Gaussian function for the required distribution of end-to-end distances r of the network chains.[1,2] In the case of very large deformations, however, the Gaussian distribution becomes seriously inadequate. Specifically, stretching the chains close to the limits of their extensibility results in probabilities significantly lower than those given by the usual Gaussian exponential in $-r^2$.[3] As a result, there are upturns in the elastic stress,[3-10] and this "non-Gaussian behavior" is of interest both for the evaluation of non-Gaussian theories[2,3,11] and for the reinforcement effect it provides.

Very little has been done to characterize the corresponding non-Gaussian effects on the optical properties of networks.[2,12] The present investigation therefore addresses this issue, using elastomeric networks of poly(dimethylsiloxane) (PDMS). The focus is on PDMS networks having a bimodal distribution of network chain lengths since such elastomers have very high extensibilities (relative to their moduli), and the non-Gaussian characteristics of their stress–strain isotherms in elongation have been well documented.[3-10]

Experimental Details

The two PDMS samples employed were hydroxyl terminated, with the short chains having a number-average molecular weight of 880 and the long ones 21.3×10^3 g mol^{-1}. Their polydispersity indices would be expected to be in the vicinity of 2. The three compositions investigated corresponded to 60.0, 70.0, and 93.4 mol % short chains and 5.84, 8,79, and 36.9 wt %. The synthesis of the networks was carried out in the usual manner.[13,14] The required amounts of long and short chains were first thoroughly mixed with the stoichiometric amount of cross-linking agent (tetraethyl orthosilicate) and with the catalyst (stannous 2-ethylhexanoate, 0.1 wt%) and then cured for 2 days at room temperature. The resulting elastomers were extracted to remove the soluble material (~3 wt %) which they contained. They were then dried in vacuo to constant weight.

A strip of the appropriate dimensions was cut from each (unswollen) network and placed in the sample cell of the strain–birefringence apparatus, which was of conventional design.[2] The light source was a He–Ne laser (632.8 nm), the optics included Glan-Thompson prisms (polarizer and analyzer), and the detector was a photometer/radiometer using a silicon light probe. The glass sample cell had a double-walled jacket, thus permitting temperature control (at 25 °C) by means of water circulation through the parts of the cell not in the path of the laser beam. The elastic force was measured by using a Statham "strain" gauge, the signal of which was monitored by a Hewlett-Packard chart recorder.

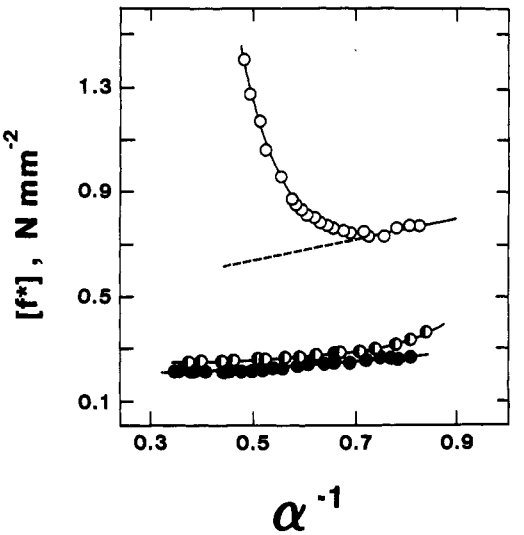

Figure 1. Stress–strain isotherms at 25 °C for the bimodal poly(dimethylsiloxane) networks[10] in the Mooney–Rivlin representation.[2,19] The elastomers consisted of network chains having number-average molecular weights of 880 and 21.3×10^3 g mol^{-1}, and the short-chain concentrations were 60.0 (●), 70.0 (◐), and 93.4 mol % (○). In this and the following figures, the linear portions of some of the curves are extended by dashed lines to facilitate characterization of the departures from linearity.

The quantities of interest were (i) the reduced stress or modulus defined by[15,16]

$$[f^*] \equiv f/A^*(\alpha - \alpha^{-2}) \tag{1}$$

where f is the equilibrium elastic force, A^* is the cross-sectional area of the unstretched sample, and $\alpha = L/L_i$ is the elongation (where L and L_i are the stretched and unstretched lengths, respectively) and (ii) the birefringence $\Delta n = R/t$, where t is the sample thickness and R is the measured relative retardation. The relationship[13]

$$C = \Delta n/\tau \tag{2}$$

defines the stress–optical coefficient C, where τ is the true stress (relative to the existing cross-sectional area). It is thus simply the slope of the line in a plot of Δn against τ. Finally, the optical-configuration parameter is defined by[17]

$$\Delta a = (45kT/2\pi)[n/(n^2 + 2)^2](\Delta n/\tau) \tag{3}$$

where k is the Boltzmann constant, T is the absolute temperature, and n is the index of refraction of the (unstretched) network. This parameter is particularly important with regard to the rotational isomeric state analysis[18] of the optical properties of a polymer.

Results and Discussion

The representation of the stress–strain data was based on the Mooney–Rivlin equation[2,19]

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \tag{4}$$

where $2C_1$ and $2C_2$ are constants. These plots, of the reduced stress against reciprocal elongation, are shown in Figure 1. They also appear in an earlier publication,[10] where they are analyzed in detail. In brief, the values of $[f^*]$ increase with increase in short-chain concentration, since this corresponds to an increase in cross-link density. Only the network containing the largest concentration of short chains (93.4 mol %) shows the upturn in modulus, at an elongation of approximately 1.4. This is consistent with earlier results[6] which show that a minimum concentration of short chains is required to observe this non-Gaussian effect. It also confirms that the deformation is

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