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DIFFUSION OF LINEAR POLYISOPRENE MOLECULES INTO POLYISOPRENE NETWORKS

by

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Diffusion and equilibrium absorption of polyisoprene liquids into crosslinked samples of cis-polyisoprene (natural rubber) have been studied by direct observation of volume swelling. Natural rubber was crosslinked

(Sulfur dioxide) (Hydrogen sulfide) (+ or -) (micrometers)

in the form of fine threads, about 40 ± 20 μm in diameter, using a gaseous reaction with SO_2 and H_2S (the Peachey process). An optical microscope was used to observe the relatively rapid absorption of linear high-molecular-weight polyisoprene liquids by these fine threads. From the kinetics of absorption, values of the self-diffusion coefficient D_s of polyisoprene were estimated. They ranged from 10^{-16} m^2/s to 10^{-12} m^2/s, depending upon molecular weight, and varied with molecular weight approximately as M^{-2} over the entire range employed, from 1,000 to 60,000 g/mole, i.e., both above and below the entanglement molecular weight. Amounts of polymer absorbed at equilibrium varied widely, depending upon the degree of crosslinking of the host material and the molecular weight of the absorbing liquid. They were in reasonable agreement in all cases with simple swelling theory, with the heat of mixing equated to zero. ([illegible])

Introduction.

Many physical processes depend upon the rate of diffusion of polymer molecules among themselves; for example, relaxation and flow, intermixing, self-adhesion and crystallization. And many methods have been employed to measure coefficients of self-diffusion. But, because rates of diffusion of large molecules are extremely small, rather long times are needed to observe motion, even over small distances. Indeed, it is questionable whether "fast" measurements can really study true molecular diffusion. Moreover, it is not easy to distinguish the diffusing species from its surroundings, i.e., "guest" molecules from "host" molecules, when they are identical. Thus, there are considerable difficulties in studying the self-diffusion of polymer molecules.

In an attempt to circumvent these difficulties, we have previously employed a lightly-crosslinked polymer as the host material and measured the uptake of linear molecules of the same chemical structure into it, by observing the corresponding increase in weight (1). This simple procedure was surprisingly effective. Values of diffusion coefficient $\underline{D}$ were determined readily for polydimethylsiloxane polymers having molecular weights $\underline{M}_s$ in the range 5,000 to 39,000 kg/kmol, diffusing into samples having molecular weights $\underline{M}_c$ between crosslinks covering almost the same wide range. When the two values of molecular weight were equal, the corresponding diffusion coefficient was taken as a measure of the coefficient $\underline{D}_s$ of self-diffusion for linear molecules of that size. Values obtained in this way were found to be in good agreement with other measurements, where comparison was possible. They were also found to be inversely proportional to molecular weight.

One reason for the successful outcome of those experiments was the relatively high rate of diffusion of polydimethylsiloxane at ambient temperatures, due to its low glass transition temperature. Other polymers are much more viscous and diffuse less readily. We have now adopted a slightly modified procedure, in order to be able to study more viscous polymer systems. A fine thread of polymer is prepared, and crosslinked in this form. Because the rate of swelling is strongly dependent on sample dimensions, fine threads absorb liquid polymers relatively rapidly. In this way we have been able to study the kinetics of absorption of linear polyisoprene molecules by lightly-crosslinked cis-polyisoprene, as we did before for polydimethylsiloxane materials, even though the diffusion coefficients are much smaller.

Because the rubber threads were extremely thin, with diameters ranging from 20 to 60 μm, it was not feasible to clean and weigh them to determine the mass uptake of diffusant. Instead, the thread diameter was measured at intervals of time, using an optical microscope, and the amount of diffusant taken up was calculated from the increase in thread diameter, as described later, assuming simple additivity of volumes.

The materials employed were in one way simpler than before and in one way less satisfactory. Because the polyisoprene liquids were prepared by anionic polymerization, their molecular weight distributions were fairly narrow. Typically, the ratio $\underline{M}_w/\underline{M}_n$ of weight-to-number-average molecular weight was about 1.08 ± 0.03. In contrast, the previous polydimethylsiloxane samples had broad molecular weight ranges, with a characteristic ratio $\underline{M}_w/\underline{M}_n$ of about 2.0. Thus, in the present experiments the diffusing ("guest") species had a more accurately defined molecular weight. But, because crosslinking is a random process, the molecular weight between crosslinks in the "host" natural rubber samples was still broadly distributed.

On the other hand, polyisoprene as synthesized here is not a pure *cis*-1,4 polymer; it contains about 20 percent *trans*-1,4 and 5 percent 3,4 groups. Although it appeared to be perfectly compatible with natural rubber (100% *cis*-1,4 polyisoprene), nevertheless it is structurally different and the diffusion processes studied are thus not strictly self-diffusion.

An interesting result of these and the previous measurements is the equilibrium level of absorption of linear polymer molecules by a crosslinked polymer of similar chemical structure. The thermodynamics of swelling takes a particularly simple form in this case, because we can assume with some confidence that the heat of dilution is negligibly small. Only the entropy of dilution remains as the driving force for absorption, with elastic stresses set up in the host network acting as the restraint. Measurements of this kind thus provide a powerful test of theories of swelling equilibrium of macromolecular networks.

Experimental Details

(a) Preparation of rubber threads

Fine crosslinked threads of natural rubber were prepared as follows:

Natural rubber (Standard Malaysian Rubber, SMR-L) was passed five times through the nip of a two-roll rubber mill and then dissolved in toluene, at a concentration of about 5 %. About 0.1 % of a coarse carbon black (Thermax, R.T.Vanderbilt Company) was added to the solution to make the rubber threads visible later, under the microscope, and about 0.05 % of an antioxidant (Cyanox 2246, American Cyanamid Company) was also added. The mixture was shaken for about eight hours on a mechanical shaker to induce the rubber to dissolve.

Fine threads of rubber were drawn from the solution and stretched across a narrow gap, about 1 mm wide, cut in a thin Mylar film, about 0.3 mm thick, as shown in Figure 1. After allowing them to dry for a period of about 8 h in vacuo, several threads with an average diameter of 40 μm, and a cast sheet of rubber, about 0.5 mm thick, were placed in a reaction vessel, shown schematically in Figure 2, and crosslinked simultaneously by a gaseous reaction, the Peachey process (2-4).

The Peachey process involves the joint reaction of SO_2 and H_2S within rubber, yielding sulfur that appears as polysulfide crosslinks, and water,

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O. \qquad (1)$$

Studies on model compounds indicated that the crosslinks are primarily of dialkenyl tetrasulfide type (3).

Preliminary experiments indicated that care was needed to avoid non-uniform crosslinking, especially with thicker samples. Slow diffusion and rapid reaction of these gases led to extensive crosslinking of surface regions, but much less in the interior. The diffusion coefficient of SO_2 in natural rubber is reported to be 1×10^{-10} m^2/s at 22°C (5) and that of H_2S is estimated to be about the same from a plot of gas diffusion coeficients as a function of the diameter of gas molecules (6). For sheets of 0.5 mm thickness, it is therefore inferred that a period of about 20 min is needed to reach relatively uniform concentrations. To ensure uniform absorption of the first gas, a period of 4 h exposure to a given concentration was employed with samples up to 0.5 mm thick, followed by a further 4 h exposure to the second gas. As described below, this procedure gave similar levels of crosslinking for fine threads and sheets 0.5 mm thick.

SO_2 gas was admitted to the reaction vessel, which had a volume of about 500 ml, by opening a tap from an SO_2 cylinder for a short time, between 2 and 12 sec. The gas flow rate was held at 5 ml/s and the pressure at entry was close to 1 bar, so that the corresponding gas concentration within the vessel was estimated to be from 0.8 to 4.5 mmole/l. After 4 h the vessel was swept with nitrogen for 30 s and then H_2S gas was admitted by opening a tap for twice the time allowed for SO_2, between 4 and 24 sec, at the same rate of flow. The samples were left in this atmosphere, at a concentration of H_2S estimated to be from 1.5 to 8.5 mmole/l, for a further 4 h.

Samples were prepared in this way with a wide range of crosslinking levels. Estimates of the degree of crosslinking were obtained in two ways. The equilibrium degree of swelling in decane was measured, both for thread and sheet specimens. They were found to be identical. Values of molecular weight M_c were calculated from the ratio Q of swollen to unswollen volume, using the modified Flory-Rehner relation:

$$Q^2 \ln(1 - Q^{-1}) + Q + \chi + (\rho V_1/M_c)/(Q^{5/3} - Q/2) = 0 \qquad (2)$$

where χ denotes the polymer-solvent interaction parameter, taken to be 0.44 for the natural rubber - decane system (7), ρ is the polymer density, 0.97 g/ml, and V_1 is the molar volume of the swelling liquid, 195 ml/mole in the present case. Values of M_c obtained in this way are given in Table 1.

Tensile stress-strain relations provide a second method of estimating the degree of crosslinking of rubber samples. They were measured using strips cut from the sheets crosslinked at the same time as the fine threads. Values of tensile (Young's) modulus E were obtained from the initial slopes; they are included in Table 1. Values of molecular weight M_c between crosslinks were calculated from them using the relation given by the simple kinetic theory of rubber elasticity,

$$M_c = 3\rho RT/E \qquad (3)$$

where R is the gas constant and T is the test temperature. They are given in Table 1 and are seen to be in good agreement with those deduced from swelling.

However, they correspond to surprisingly high degrees of crosslinking after exposure to high concentrations of the two gases, more than about 3 mmole/l of SO_2 and 6 mmole/l of H_2S, respectively. Even at lower gas concentrations the crosslinking reaction is remarkably effective. It should be noted that a sample of polyisoprene liquid crosslinked in the same way, included in Table 1, was much less highly crosslinked than natural rubber after equivalent exposure to SO_2 and H_2S.

(b) Preparation of polyisoprene liquids

Isoprene monomer was anionically polymerized in benzene at room temperature, using sec-butyllithium as initiator. Polymerization was terminated with anhydrous degassed methanol. One percent by weight of an antioxidant, butylated hydroxytoluene, was added to the polymer.

Molecular weights were determined by light scattering, using tetrahydrofuran as solvent, at a temperature of 30°C. Polydispersity was characterized using a Waters 150C ALC-GPC instrument, with tetrahydrofuran as the eluting solvent at a flow rate of about 1 ml/min, and at a temperature of 30°C. Calibration was carried out using standard samples of cis-polyisoprene, having narrow molecular weight distributions.

The microstructure of the polyisoprene liquids was determined using a Varian CFT-20 C^{13} NMR spectrometer. Samples were dissolved in $CDCl_3$ at a concentration of about 10 percent by weight. Tetramethylsilane was added as an internal standard.

(c) Measurements of absorption of polyisoprene liquids.

Crosslinked threads were immersed in a drop of a selected polyisoprene liquid, as shown in Figure 3. At intervals of time the cross-section of the thread was measured using an optical microscope at a magnification of about 300X. A photograph of a thread, unswollen and swollen, is shown in Figure 4. Particles of carbon black in the crosslinked thread were clearly visible throughout the absorption process. They enabled the edges of the thread to be brought into sharp focus in the microscope so that the swollen diameter could be measured accurately.

Values of the ratio d_t/d_o of the thread diameter after time t to the initial value were employed to determine the corresponding mass uptake of polymer liquid. All measurements were carried out at room temperature, about 24°C.

(d) Calculation of mass uptake

At first, cylindrical samples swell only in a radial direction because the unswollen core prevents any extension in the axial direction. The corresponding swelling ratio Q_t after a time t is then given in terms of the thread diameter d_t by the ratio $(d_t/d_o)^2$, where d_o is the original diameter of the thread. Initially, therefore, mass uptake is expected to follow the diffusion relation for one-dimensional swelling,

$$M_t/M_\infty = 8(Dt/\pi d_o^2)^{1/2} \quad (4)$$

where $M_t = M_o(Q_t - 1)$ denotes the amount taken up at time t, and $M_\infty = M_o(Q_\infty - 1)$ denotes the amount taken up at equilibrium, by a sample of initial mass M_o which is only able to expand radially outwards.

This equilibrium amount $\underline{M}_\infty$ is, of course, different from the equilibrium uptake of an unrestrained sample, denoted here $\underline{M}_\infty^*$. The relation between the two limiting values can be deduced from the thermodynamic relations for restrained and unrestrained swelling (8,9) which take the following forms when the densities of swelling liquid and host material are equal:

$$Q_\infty^2 \ln(1 - Q_\infty^{-1}) + Q_\infty + \chi + (M_s/M_c)(Q_\infty^3 - Q_\infty/2) = 0 \qquad (5)$$

and

$$Q_\infty^{*2} \ln(1 - Q_\infty^{*-1}) + Q_\infty^* + \chi + (M_s/M_c)(Q_\infty^{*5/3} - Q_\infty^*/2) = 0 \qquad (6)$$

where $\underline{Q}_\infty^*$ denotes the equilibrium volume swelling ratio in unrestrained swelling, so that $\underline{M}_\infty^* = \underline{M}_o(\underline{Q}_\infty^* - 1)$.

Predicted relations between $\underline{Q}_\infty$ and $\underline{Q}_\infty^*$ are shown in Figure 5 for various values of polymer-solvent interaction parameter $\underline{\chi}$. They allow us to take the final measured swelling of a thread, $\underline{Q}_\infty^*$, given in terms of the equilibrium swollen diameter $\underline{d}_\infty$ as $\underline{Q}_\infty^* = (\underline{d}_\infty/\underline{d}_o)^3$, and deduce from it the amount of swelling $\underline{Q}_\infty$ that would have been obtained at equilibrium if swelling had been restricted to one dimension only, throughout the experiment. Over the range of interest here, marked in Figure 5 by vertical broken lines, the two degrees of swelling differ by a factor of up to two, one-dimensional swelling being between 50 and 100 percent of the degree of swelling in the unrestricted state, depending upon the ratio $\underline{M}_s/\underline{M}_c$ of the molecular weight $\underline{M}_s$ of the diffusing species to that, $\underline{M}_c$, of network strands in the host material, and, to a lesser extent, upon the interaction parameter $\underline{\chi}$. In the present calculations, $\underline{\chi}$ has been equated to zero.

Results and discussion.

(a) Characterization of materials

Molecular weights $\underline{M}_c$ between crosslinks for the crosslinked natural rubber samples were found to range from about 1,000 to about 17,000 g/mole, Table 1. Thus, a rather wide range of crosslink densities were employed. Similarly, the molecular weights of the polyisoprene liquids varied from about 1,000 to 60,000 g/mole, a comparable range.

After crosslinking, a small amount of trans-isoprene was detected in the crosslinked natural rubber samples by solid-state MAS C^{13} NMR, but it was less than 10 percent, even for the most highly crosslinked material. This material also showed a significantly higher glass transition temperature, about 10°C above that for lightly crosslinked materials.

(b) Effect of thread diameter.

Measurements of the observed thread diameter $\underline{d}_t$ are plotted in Figure 6 against the time $\underline{t}$ of immersion in a polyisoprene liquid, for threads of two different diameters. As would be expected, the thicker thread swelled more slowly. When the results for the two threads are replotted against the ratio $\underline{t}^{1/2}/\underline{d}_o$, Figure 7, they are seen to be in good agreement. Thus, the rate of absorption appears to depend upon thread diameter in accordance with the basic diffusion relation, Equation 4.

Results for polyisoprene liquids having a wide range of molecular weights $\underline{M}_s$, diffusing into threads crosslinked to the same extent, $\underline{M}_c$ = 11,100 g/mole, are shown in Figure 8. Liquids of lower molecular weight are seen to diffuse much more rapidly, and the degree of swelling at equilibrium is much greater, than for high-molecular-weight liquids. Equilibrium absorption was attained after relatively short times, about one hour for the lowest molecular weight liquids and about three days for the highest molecular weight employed. We conclude that the present technique, using threads of 20 μm in diameter and periods of up to one month to reach equilibrium, could be utilized to measure diffusion coefficients as low as 3 x 10^{-17} m^2/s.

We now turn to the problem of calculating diffusion coefficients from measurements of this kind.

(c) Diffusion coefficients

First, from the equilibrium swelling ratio Q^*_∞, determined from the thread diameter d_∞ at long times, $Q^*_\infty=(d_\infty/d_o)^3$, we calculate the equilibrium uptake Q_∞ expected for one-dimensional swelling, using Equations 5 and 6, or Figure 5, with x assumed to be zero. Then, the mass M_t absorbed into the rubber thread after a particular time t is calculated from the observed increase in diameter, using the relation:

$$M_t/M_\infty = (Q_t - 1)/(Q_\infty - 1) \qquad (7)$$

where Q_t is given by the swelling relation valid for short times, when the thread grows only in diameter,

$$Q_t = (d_t/d_o)^2 \qquad (8)$$

The relative mass uptake determined in this way is plotted, as shown in Figure 9, against the time of exposure to the diffusing liquid. Initial slopes of these relations give the diffusion coefficient D, by means of Equation 4. Values of D determined in this way for all of the host networks and guest liquids are listed in Table 2.

As can be seen in Figure 9, the results are strongly dependent upon the molecular weight $\underline{M}_s$ of the diffusing liquid. For a natural rubber network with a molecular weight between crosslinks of 17,200 g/mole, $\underline{D}$ was found to decrease by a factor of about 1,600 as the molecular weight of the diffusing liquid increased by a factor of 70. Values obtained for $\underline{D}$ were also found to depend somewhat upon the molecular weight $\underline{M}_c$ between crosslinks of the host materials, as shown in Figures 10 and 11. Estimated diffusion coefficients were found to decrease somewhat as the molecular weight between crosslinks of the host material was increased, by a factor of about 2 as $\underline{M}_c$ was increased by a factor of 20. A similar dependence was found before in studies with polydimethylsiloxane liquids and networks (1). The effect is small but consistent for a wide range of diffusing liquids, and takes the approximate form: $D \approx M_c^{-0.2}$.

In contrast, a decrease of diffusion coefficient with increase in crosslink density was reported by Garrido et al (10), whereas Antonietti and Sillescu (11) found an initial decrease at low levels of crosslinking, a transition region where the diffusion coefficient was fairly constant or increased as the degree of crosslinking increased , and finally a decrease at high levels of crosslinking. Clearly, the effect of the degree of crosslinking of a host material upon the rate of diffusion of linear molecules within the network requires further study.

The measured kinetics of absorption usually showed good agreement with the theoretical relation for radial diffusion only, up to about 50 percent of the final (equilibrium) amount. Beyond this point, they started to diverge, absorption becoming slower than predicted for high molecular weight liquids and faster than expected for liquids of lower molecular weight. These deviations probably reflect a transition from simple radial expansion of the thread in the early stages of swelling to three-dimensional swelling in the later stages of absorption.

(d) Self-diffusion.

An estimate of self diffusion coefficients can be made from the results described above. By interpolation, as shown in Figure 12, we can infer the diffusion coefficient $\underline{D}_s$ when the molecular weight of the diffusing liquid is the same as the molecular weight between crosslinks of the host material. Values obtained in this way are listed in Table 3 and plotted in Figure 13 against molecular weight, using logarithmic scales for both axes. Within experimental error, the results can be described by a straight line in this representation, with a slope of -1.9.

(e) Comparison with other work

It is interesting to note that the observed dependence of diffusion coefficient upon molecular weight is in good agreement with that found for other polymers, by a variety of methods (12). For example, a similar dependence has been reported by Antonietti and Sillescu (11) from studies of the diffusion of polystyrene molecules in polystyrene networks, by means of a holographic grating technique. They found a slope of -2.07.

These results are in good accord with the predictions of reptation theory for diffusive motions of polymer molecules (13). It is rather surprising, however, that the dependence appears to remain largely unchanged on passing through the reported molecular weight between entanglements for polyisoprene, about 10,000 g/mole (14), although some change in slope would also be consistent with the experimental results shown in Figure 13.

Values of self diffusion coefficients $\underline{D}_s$ obtained by interpolation and extrapolation from the full line in Figure 13 are compared in Table 4 with results taken from the literature (15-17) for cis-polyisoprene. Although values of $\underline{D}_s$ for molecular weights at the extremes are not in good agreement, varying by a factor of about 7 from those obtained by others, they are in reasonable accord over the middle range of molecular weights where comparison is possible. They are about one-half as large as the values obtained by Von Meerwall for similar polymers using NMR techniques (17). It should be noted that a similar discrepancy, and in the same direction, is found with NMR results for other polymers; they tend to be generally higher than values obtained by other methods (12).

(f) Absorption of binary mixtures

Measurements were made of the kinetics of absorption of a mixture of equal amounts of two polyisoprene liquids having very different molecular weights. As shown in Figure 14, the initial uptake followed closely the relation for the low molecular weight component of the mixture, but the final level of absorption lay midway between the results for the two separate liquids. It is thus clear that molecular separation occurs in polymer diffusion, lower molecular weights diffusing much more rapidly. Estimates of diffusion coefficient using initial rates of uptake will therefore be biassed in favor of the lower molecular weight components, when liquids having a broad distribution of molecular weight are absorbed. This may be the reason for the different dependence upon molecular weight found previously for polydimethylsiloxane liquids, where an inverse proportionality was observed between diffusion coefficient and molecular weight (1). The present results are in better accord with a dependence of the form: $D \approx M^{-1.9}$, as discussed above.

(g) Equilibrium absorption

Values of equilibrium swelling ratio Q_{∞}^{*} are listed in Table 5 for all combinations of polymer swelling liquid and host network. They are plotted in Figure 15 against the ratio M_s/M_c of the molecular weight of the diffusing liquid to that of the network strands. At a ratio of 1, when the molecules of the diffusing species have the same length as the network strands, equilibrium swelling corresponds to an uptake of about 60 % of the polymeric liquid. When the ratio is much larger, so that the liquid molecules are much longer than the network strands they are diffusing into, then the final uptake is quite small, less than 10 %. (And, of course, it takes a long time to attain.) On the other hand, polymer liquids of much lower molecular weight swell the host polymer network highly, more than 200 % in the extreme cases studied here.

The curves in Figure 15 represent predictions of the Flory-Huggins theory for different values of polymer-solvent interaction parameter. Actually, the difference between them is rather small over this range of molecular weights. The experimental results lie somewhat above the highest theoretical relation, for $\underline{x}$ = 0, and thus they are in better agreement with this result than with the others. But the quantitive agreement is only fair.

It should be noted that the filled symbols in Figure 15 represent values of equilibrium absorption for networks prepared from synthetic polyisoprene, prepared in the same way as the natural rubber networks but using the polyisoprene liquids instead. The good agreement between the swelling values for the two materials suggests that they are completely compatible.

Conclusions

The following conclusions are obtained.

1. Fine threads of natural rubber, 20 to 60 μm in diameter, can be readily crosslinked to various degrees by the Peachey process.

2. They allow one to study the absorption of polyisoprene liquids having a wide range of molecular weight because equilibrium is attained within a relatively short time, 2-3 days for molecular weights as high as 60,000 kg/kmole.

3. Using narrow molecular weight fractions, measurements of diffusion coefficient were obtained in this way for molecular weights between about 1,000 and 60,000 kg/kmole. The results ranged from about 10^{-16} to about 10^{-12} m^2/s.

4. For a binary mixture of equal amounts of two quite different molecular weights, the diffusion coefficient was found to be virtually the same as that of the low molecular weight component.

5. Inferred coefficients of self-diffusion were found to be strongly dependent upon the molecular weight $\underline{M}_s$ of the diffusing liquids, varying approximately as $\underline{M}_s^{-1.9}$. This result is in good agreement with the predictions of reptation theory. It appeared to hold even for molecular weights well below the entanglement molecular weight.

6. Experimental values of equilibrium absorption of polyisoprene liquids by polyisoprene networks ranged from about 5% to over 200%, depending upon the relative molecular weights of swelling molecule and network strand.

7. Equilibrium swelling ratios were found to be in fair agreement in all cases with the Flory-Rehner theory, with the heat of mixing and

polymer-liquid interaction parameter made equal to zero, but the swelling was generally somewhat higher than expected.

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TABLE 1

Molecular Weight of Network Strands Determined from Volume Swelling and Stress-Strain Measurements

Gas Flow Time (sec.) SO_2/H_2S	Volume Swelling		Stress-Strain Measurements	
	$\underline{Q}$	$\underline{M}_c$ (g/mole x 10^{-3})	$\underline{E}$ (MPa)	$\underline{M}_c$ (g/mole x 10^{-3})
(1) 2/4	5.25	19.3	0.42 ± 0.03	17.2
3/6	4.50	13.1	0.65 ± 0.01	11.1
5/10	3.55	6.9	1.26 ± 0.08	5.7
7/14	3.14	5.0	1.83 ± 0.25	3.9
10/20	1.97	1.2	6.7 ± 0.3	1.1
12/24	1.92	1.1	7.9 ± 0.02	0.9
(2) 15/30	4.98	16.9	0.53 ± 0.02	13.6

(1) Natural rubber

(2) Synthetic cis-polyisoprene

TABLE 2

(m^2/s)

Diffusion Coefficients $\underline{D}_\wedge$ of Cis-polyisoprene Liquids Diffusing into Natural Rubber Networks

Molecular Weight of Diffusant $\underline{M}_s$ (g/mole)	Molecular Weight of Network Strands $\underline{M}_c$ (g/mole)				
	17.2 x 10^3	11.1 x 10^3	5.7 x 10^3	3.9 x 10^3	0.9 x 10^3
8.70 x 10^2	$(5.5 \pm 0.4) \times 10^{-13}$	$(6.1 \pm 0.8) \times 10^{-13}$	$(7.1 \pm 0.9) \times 10^{-13}$	$(7.3 \pm 1.2) \times 10^{-13}$	$(9.9 \pm 1.8) \times 10^{-13}$
3.10 x 10^3	$(5.8 \pm 0.5) \times 10^{-14}$	$(6.5 \pm 1.3) \times 10^{-14}$	$(1.2 \pm 0.2) \times 10^{-13}$	$(8.8 \pm 2.0) \times 10^{-14}$	$(2.0 \pm 0.8) \times 10^{-13}$
3.29 x 10^3	$(7.8 \pm 0.6) \times 10^{-14}$	$(7.7 \pm 1.5) \times 10^{-14}$	$(8.1 \pm 1.8) \times 10^{-14}$	$(6.6 \pm 1.6) \times 10^{-14}$	$(1.7 \pm 0.6) \times 10^{-13}$
7.34 x 10^3	$(1.8 \pm 0.2) \times 10^{-14}$	$(2.8 \pm 0.5) \times 10^{-14}$	$(3.3 \pm 1.0) \times 10^{-14}$	$(2.5 \pm 0.5) \times 10^{-14}$	$(6.2 \pm 2.5) \times 10^{-14}$
1.45 x 10^4	$(1.15 \pm 0.2) \times 10^{-14}$	$(1.1 \pm 0.2) \times 10^{-14}$	$(1.05 \pm 0.25) \times 10^{-14}$	$(1.4 \pm 0.4) \times 10^{-14}$	
1.71 x 10^4	$(1.1 \pm 0.2) \times 10^{-14}$	$(8.6 \pm 2.4) \times 10^{-15}$	$(1.5 \pm 0.4) \times 10^{-14}$	$(1.6 \pm 0.5) \times 10^{-14}$	
4.88 x 10^4	$(3.2 \pm 0.8) \times 10^{-16}$	$(3.6 \pm 1.1) \times 10^{-16}$	$(3.2 \pm 1.2) \times 10^{-16}$		
5.88 x 10^4	$(4.1 \pm 1.2) \times 10^{-16}$	$(5.3 \pm 1.9) \times 10^{-16}$			

TABLE 3

Inferred Self-diffusion Coefficients $\underline{D}_S$ of Cis-polyisoprene Liquids Diffusing into Natural Rubber Networks

Molecular Weight of Diffusant $\underline{M}_S$ (g/mole)	Self-Diffusion Coefficient $\underline{D}_S$ (m^2/sec)
8.70×10^{2}	1.00×10^{-12}
3.10×10^{3}	9.55×10^{-14}
3.29×10^{3}	9.12×10^{-14}
7.34×10^{3}	2.63×10^{-14}
1.45×10^{4}	1.07×10^{-14}
1.71×10^{4}	1.05×10^{-14}
4.88×10^{4}	2.57×10^{-16}
5.88×10^{4}	3.39×10^{-16}

TABLE 4

Comparison of Self-Diffusion Results with Previous Work

Previous Work	Molecular Weight of Cis-Polyisoprene (g/mole)	Self-Diffusion Coefficient $\underline{D}_s$ (m²/s)	
		Their Data	Our Data
J.D. Skewis (15) using radio-labelling	2.70×10^{5}	3.16×10^{-18}	2.22×10^{-17}*
N. Nemoto et al. (16) using forced Rayleigh scattering	3.50×10^{4}	3.06×10^{-15}	1.11×10^{-15}
E. von Meerwall et al. (17) using pulsed-gradient spin-echo NMR	2.63×10^{3}	2.95×10^{-13}	1.59×10^{-13}
	1.23×10^{3}	1.29×10^{-12}	6.81×10^{-13}
	9.10×10^{2}	2.69×10^{-12}	1.21×10^{-12}
	4.10×10^{2}	4.17×10^{-11}	5.42×10^{-12}*

*Extrapolated values

TABLE 5

Equilibrium Swelling Ratios $\underline{Q}^*_\infty$ of Natural Rubber Networks by Cis-polyisoprene Liquids

Molecular Weight of Diffusant $\underline{M}_s$ (g/mole)	Molecular Weight of Network Strands $\underline{M}_C$ (g/mole)				
	17.2 x 10^3	11.1 x 10^3	5.7 x 10^3	3.9 x 10^3	0.9 x 10^3
8.70 x 10^2	4.492	3.177	2.197	1.920	1.302
3.10 x 10^3	3.044	2.698	1.995	1.612	1.071
3.29 x 10^3	2.791	2.253	1.916	1.561	1.046
7.34 x 10^3	2.172	1.972	1.525	1.263	1.048
1.45 x 10^4	1.816	1.689	1.313	1.184	
1.71 x 10^4	1.547	1.440	1.155	1.060	
4.88 x 10^4	1.231	1.144	1.093		
5.88 x 10^4	1.232	1.074	1.030		

Figure Legends

Figure 1: Method of mounting a rubber thread.

Figure 2: Reaction vessel for crosslinking rubber threads and sheets.

Figure 3: Application of polyisoprene liquid to a crosslinked thread.

Figure 4: Photomicrograph of a rubber thread before and after absorbing a polyisoprene liquid.

Figure 5: Relations between equilibrium volume swelling ratios for unrestrained ($\underline{Q}^*_\infty$) and one-dimensional ($\underline{Q}_\infty$) swelling, calculated from Equations 5 and 6.

Figure 6: Absorption relations for threads of different initial diameter $\underline{d_o}$. $\underline{M}_s$ = 7,340 g/mole; $\underline{M}_c$ = 17,200 g/mole.

Figure 7: Results from Figure 6 replotted against a reduced time function $\underline{t^{1/2}/d_o}$.

Figure 8: Absorption relations for various polyisoprene liquids diffusing into natural rubber threads, $\underline{M}_c$ = 11,100 g/mole. $\underline{M}_s$ = 870 g/mole, ○; 3,100 g/mole, □; 7,340 g/mole, △; 17,100 g/mole, ◇; 48,800 g/mole, ▽.

Figure 9: Absorption relations for various polyisoprene liquids diffusing into natural rubber threads, $\underline{M}_c$ = 11,100 g/mole. $\underline{M}_s$ = 870 g/mole, ○; 3,100 g/mole, □; 7,340 g/mole, △; 17,100 g/mole, ◇; 48,800 g/mole, ▽.

Figure 10: Dependence of diffusion coefficient $\underline{D}$ upon molecular weight $\underline{M}_c$ of network strands, for various polyisoprene liquids diffusing into cis-polyisoprene networks.

Figure 11: Dependence of diffusion coefficient $\underline{D}$ upon molecular weight $\underline{M}_c$ of network strands, for various polyisoprene liquids diffusing into cis-polyisoprene networks.

Figure 12: Method of deducing self-diffusion coefficient $\underline{D}_s$ from diffusion coefficients for a polyisoprene liquid, molecular weight $\underline{M}_s$ = 7,340 g/mole, diffusing into cis-polyisoprene networks of various strand molecular weights $\underline{M}_c$.

Figure 13. Relation between inferred self-diffusion coefficients $\underline{D}_s$ and molecular weight $\underline{M}_s$ of polyisoprene liquids.

Figure 14. Absorption relation for a mixture (●) of equal amounts of two polyisoprene liquids, of low molecular weight ($\underline{M}_s$ = 3,100 g/mole, □) and high molecular weight ($\underline{M}_s$ = 48,800 g/mole, ▽) diffusing into a crosslinked cis-polyisoprene thread, $\underline{M}_c$ = 17,200 g/mole. The absorption relations are also shown for the two liquids separately.

Figure 15. Equilibrium volume swelling ratio $\underline{Q}^*_\infty$ of natural rubber networks (open symbols) and a synthetic polyisoprene network (filled circles) by polyisoprene liquids of various molecular weights $\underline{M}_s$, plotted against the ratio $\underline{M}_s/\underline{M}_c$ of liquid molecular weight to molecular weight $\underline{M}_c$ of network strands. The curves are calculated from Equation 6 for different values of the interaction parameter χ.

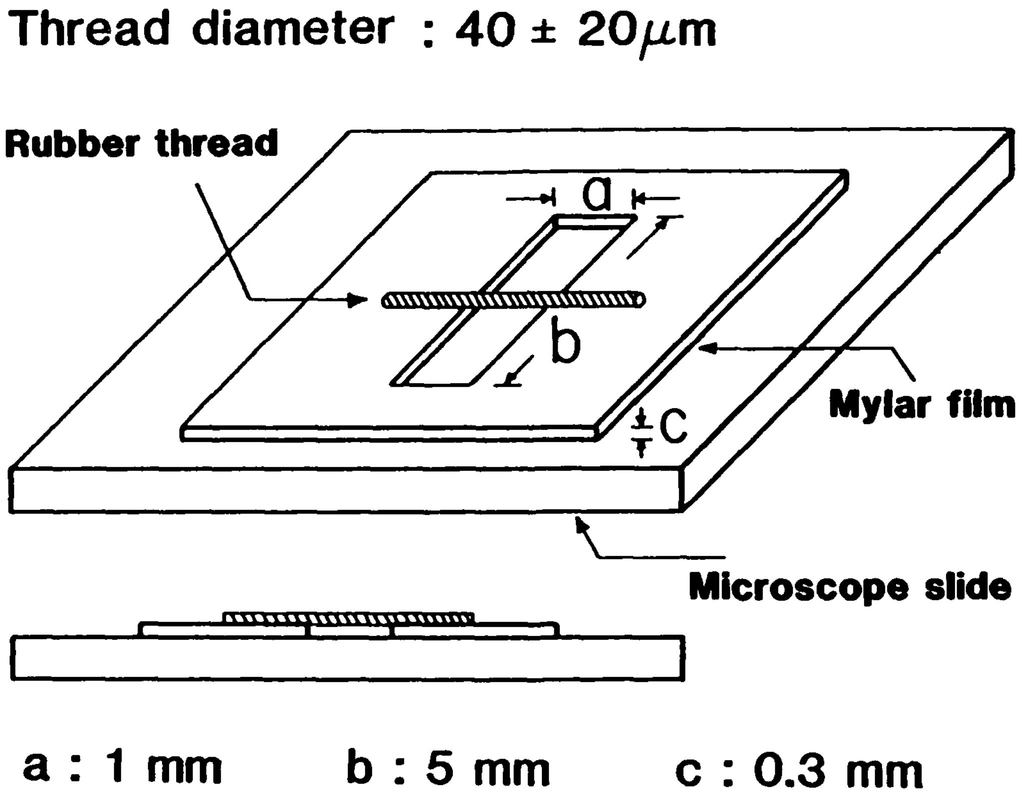
Thread diameter : 40 ± 20μm
Rubber thread
a
b
c
Mylar film
Microscope slide
a : 1 mm
b : 5 mm
c : 0.3 mm

Figure 1

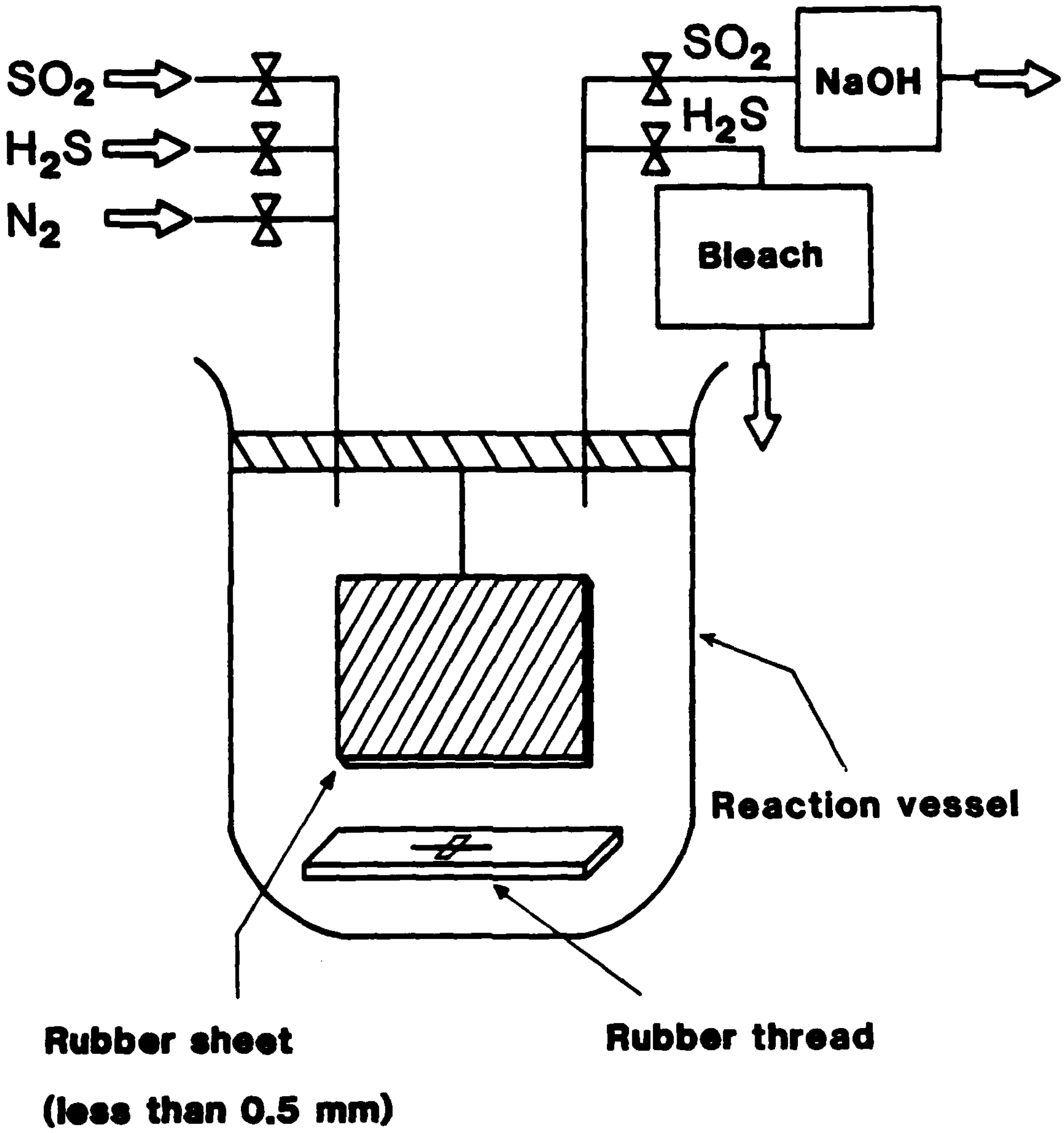
SO_2
H_2S
N_2
SO_2
H_2S
NaOH
Bleach
Reaction vessel
Rubber sheet
(less than 0.5 mm)
Rubber thread

Figure 2

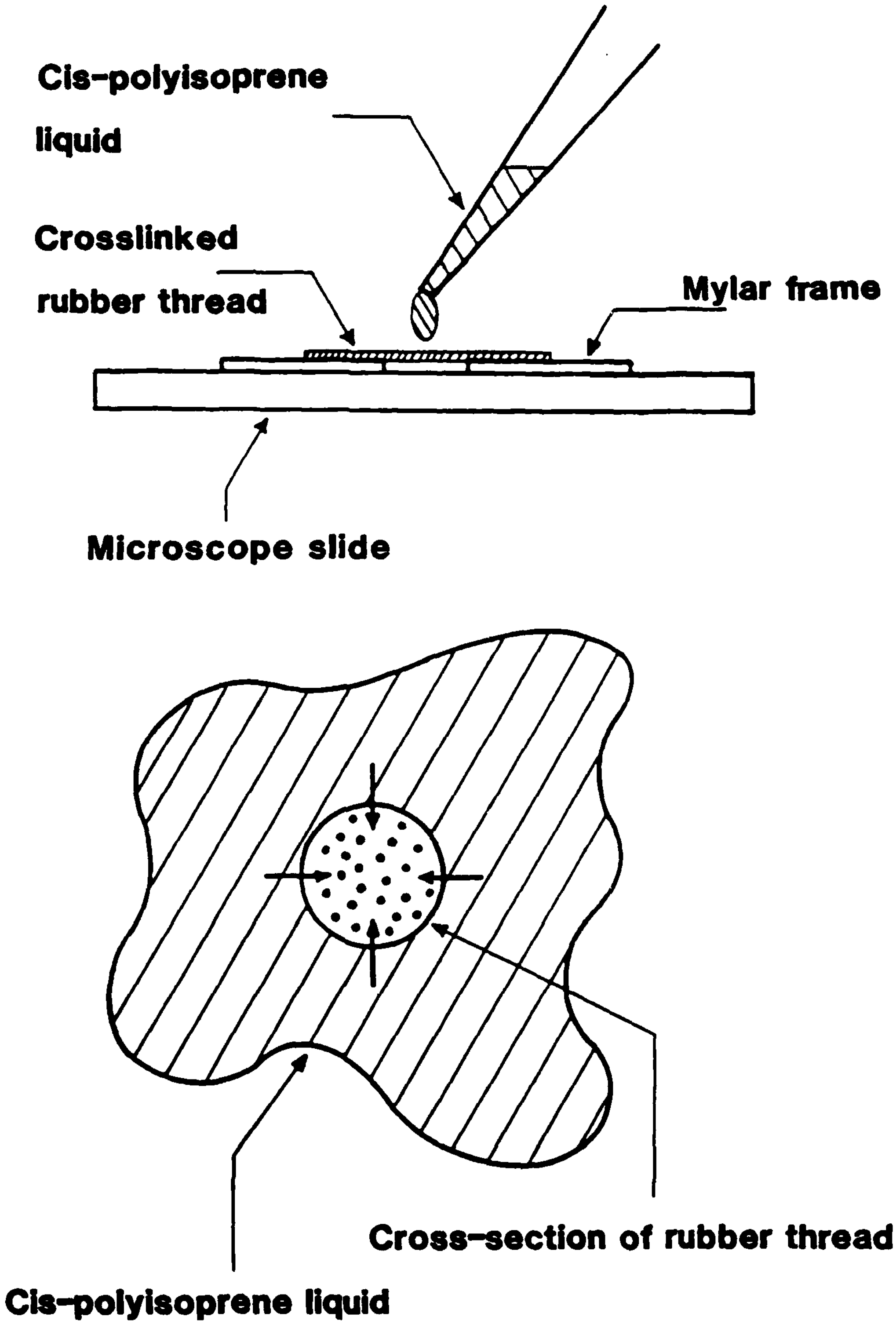
Cis-polyisoprene liquid
Crosslinked rubber thread
Mylar frame
Microscope slide
Cross-section of rubber thread
Cis-polyisoprene liquid

Figure 3

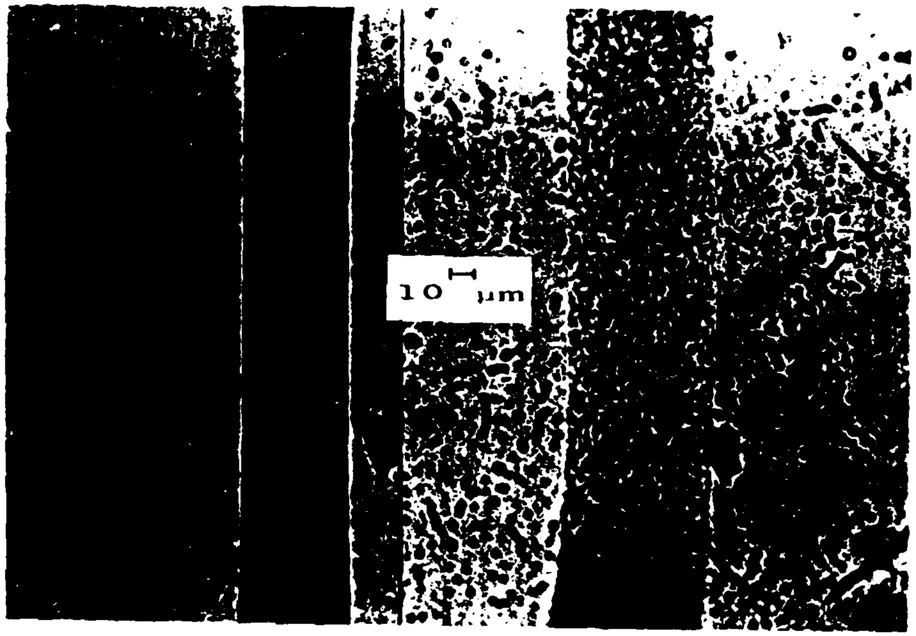

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Figure 4

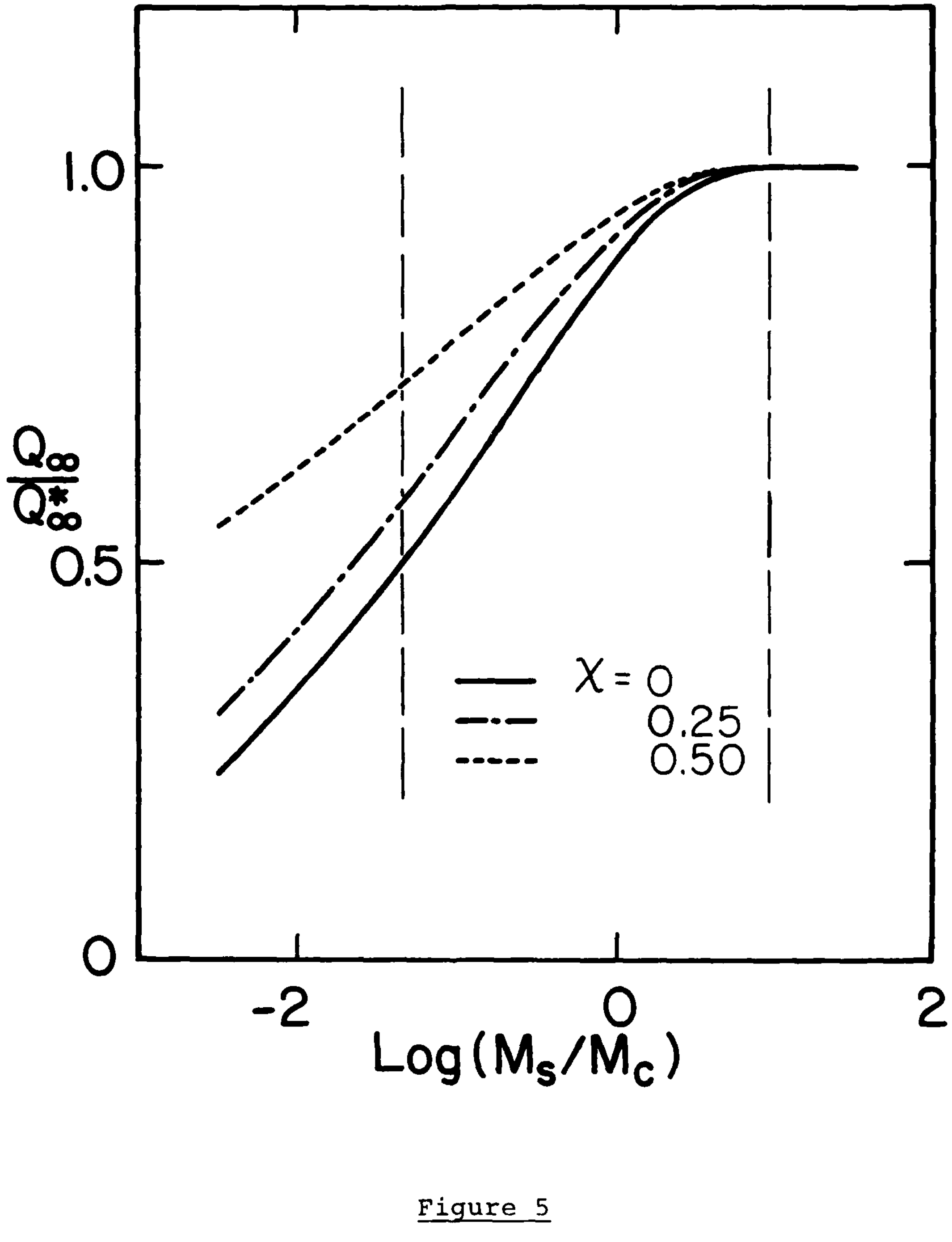


Figure 5

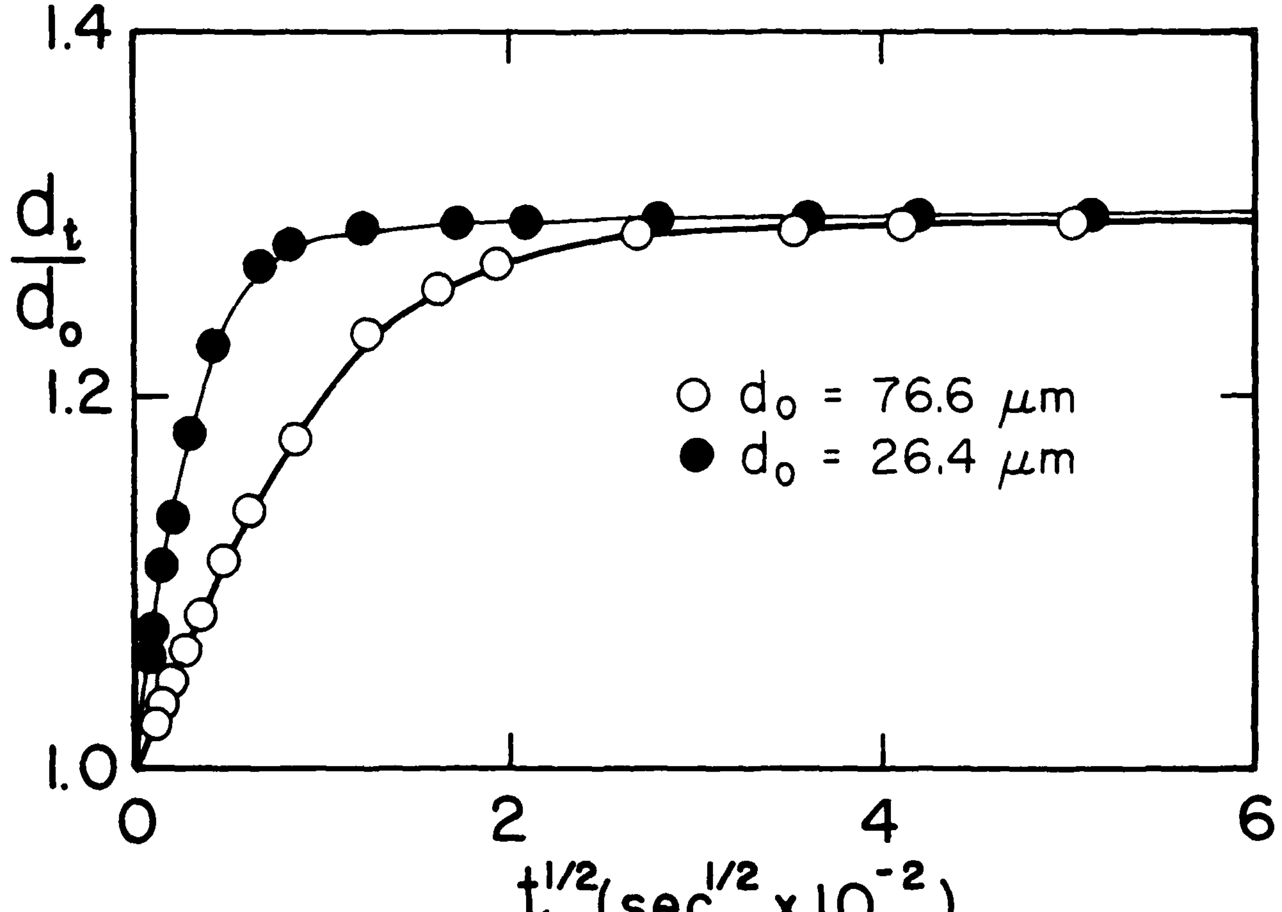


Figure 6

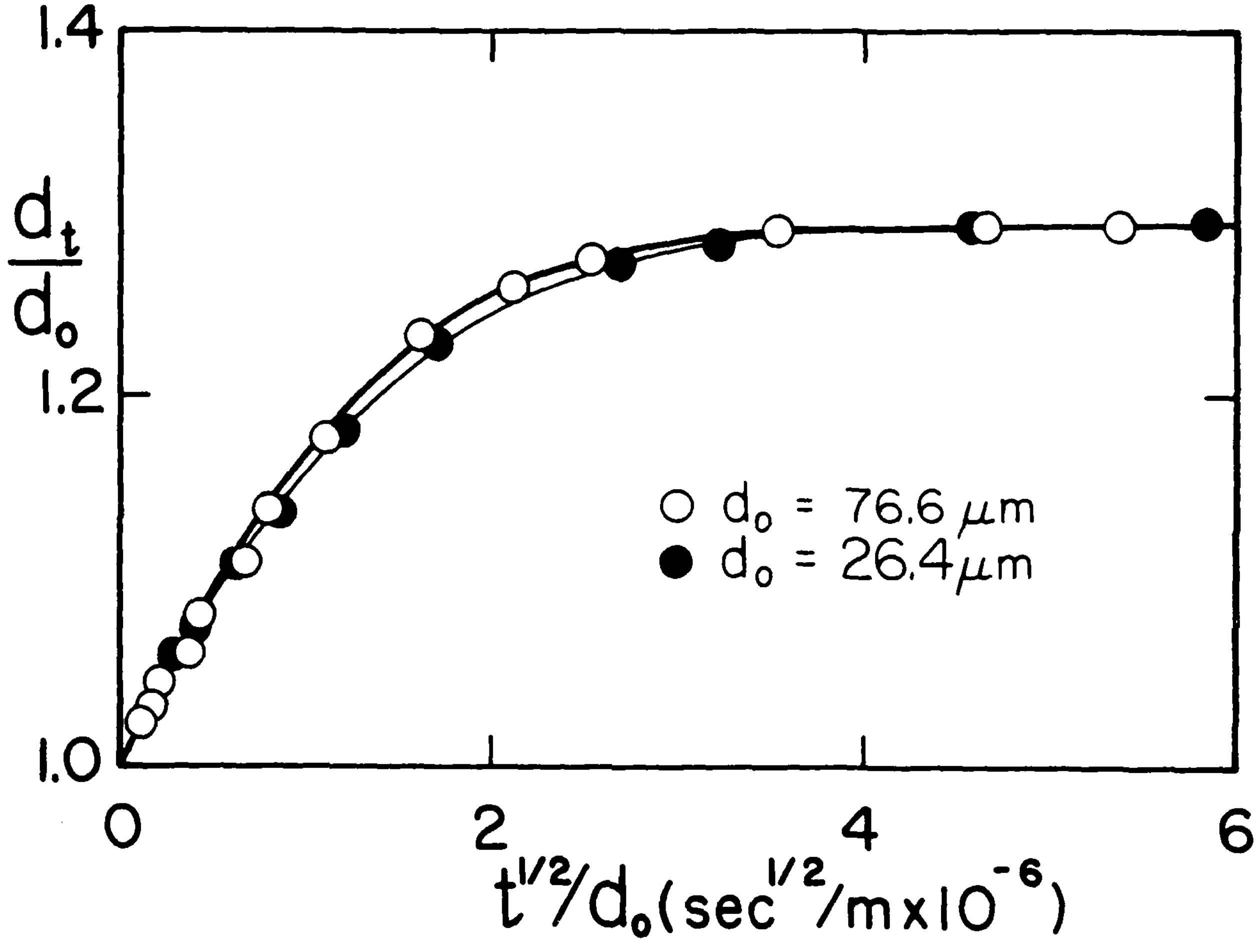
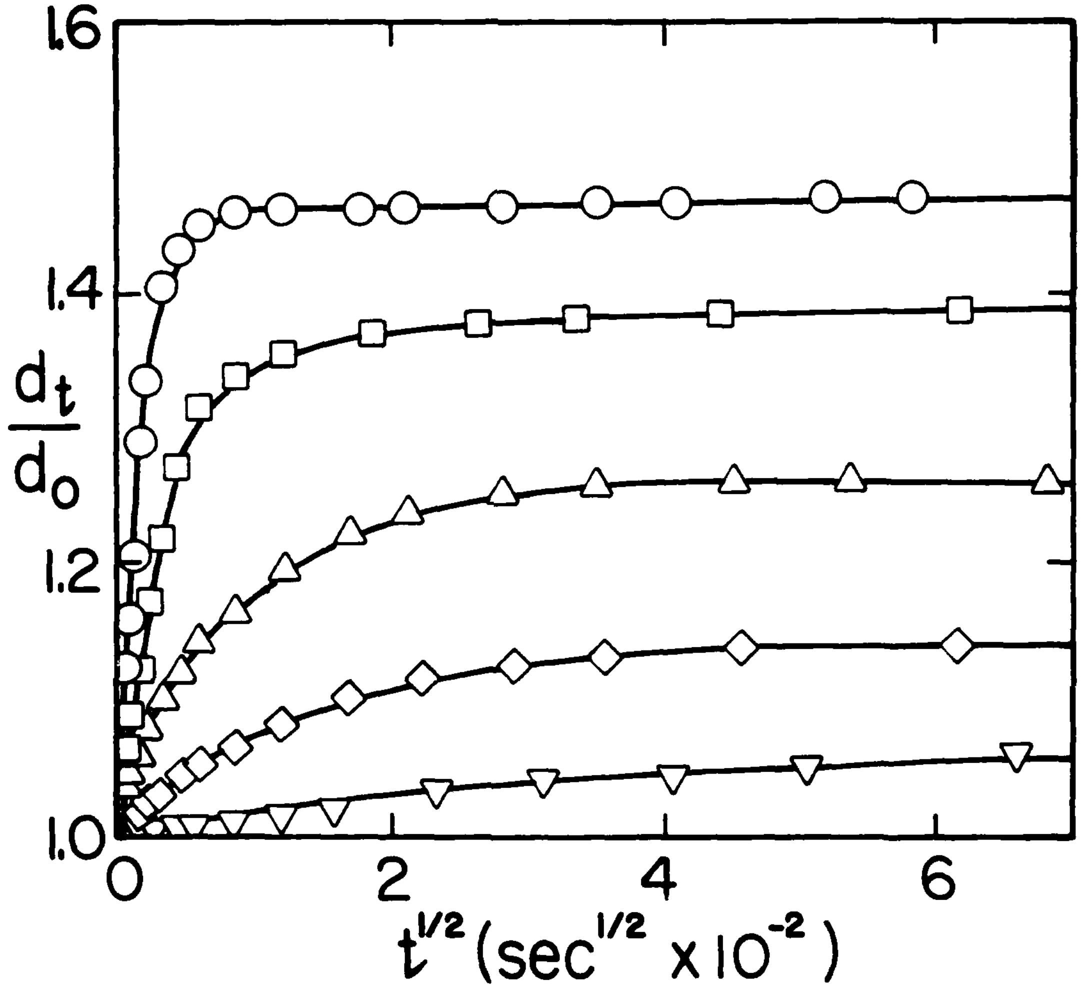
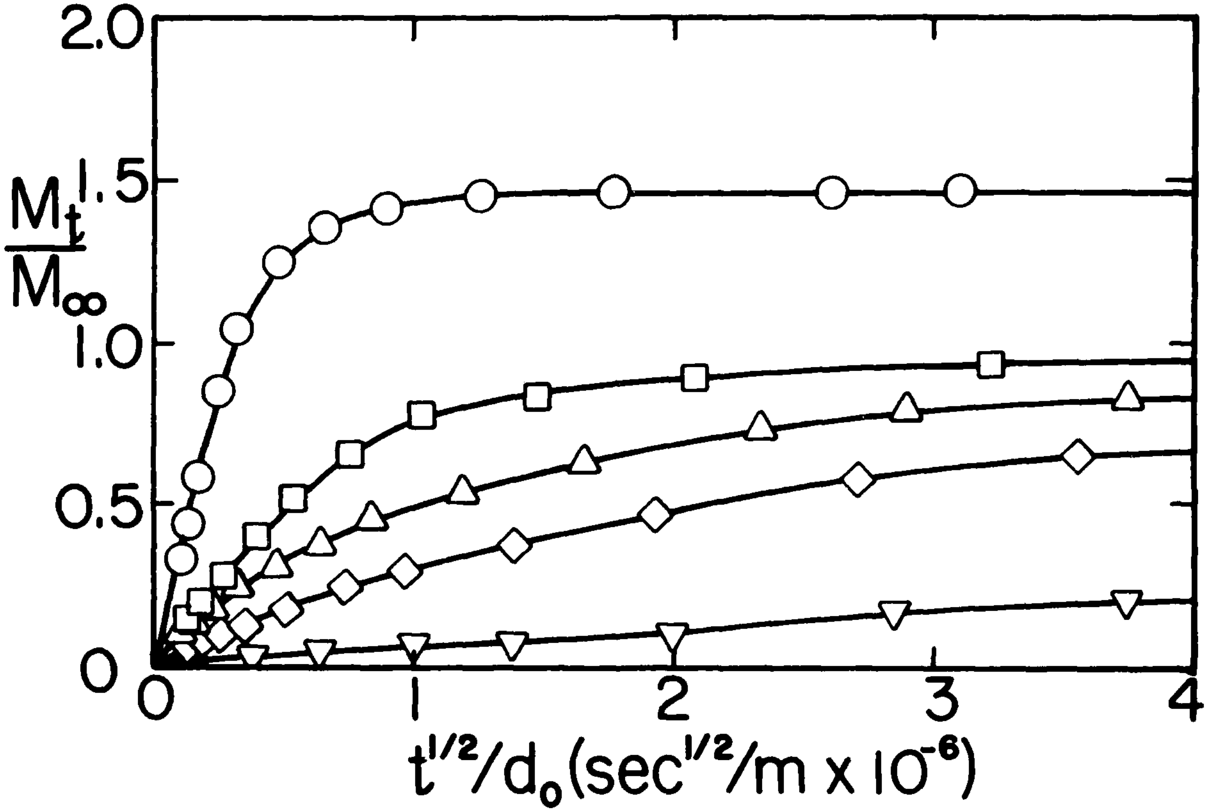

1.4
1.2
1.0
$\frac{d_t}{d_o}$
0
2
4
6
$t^{1/2}/d_o(\text{sec}^{1/2}/\text{m} \times 10^{-6})$
○ d_o = 76.6 μm
● d_o = 26.4μm

Figure 7



<u>Figure 8</u>



<u>Figure 3</u>

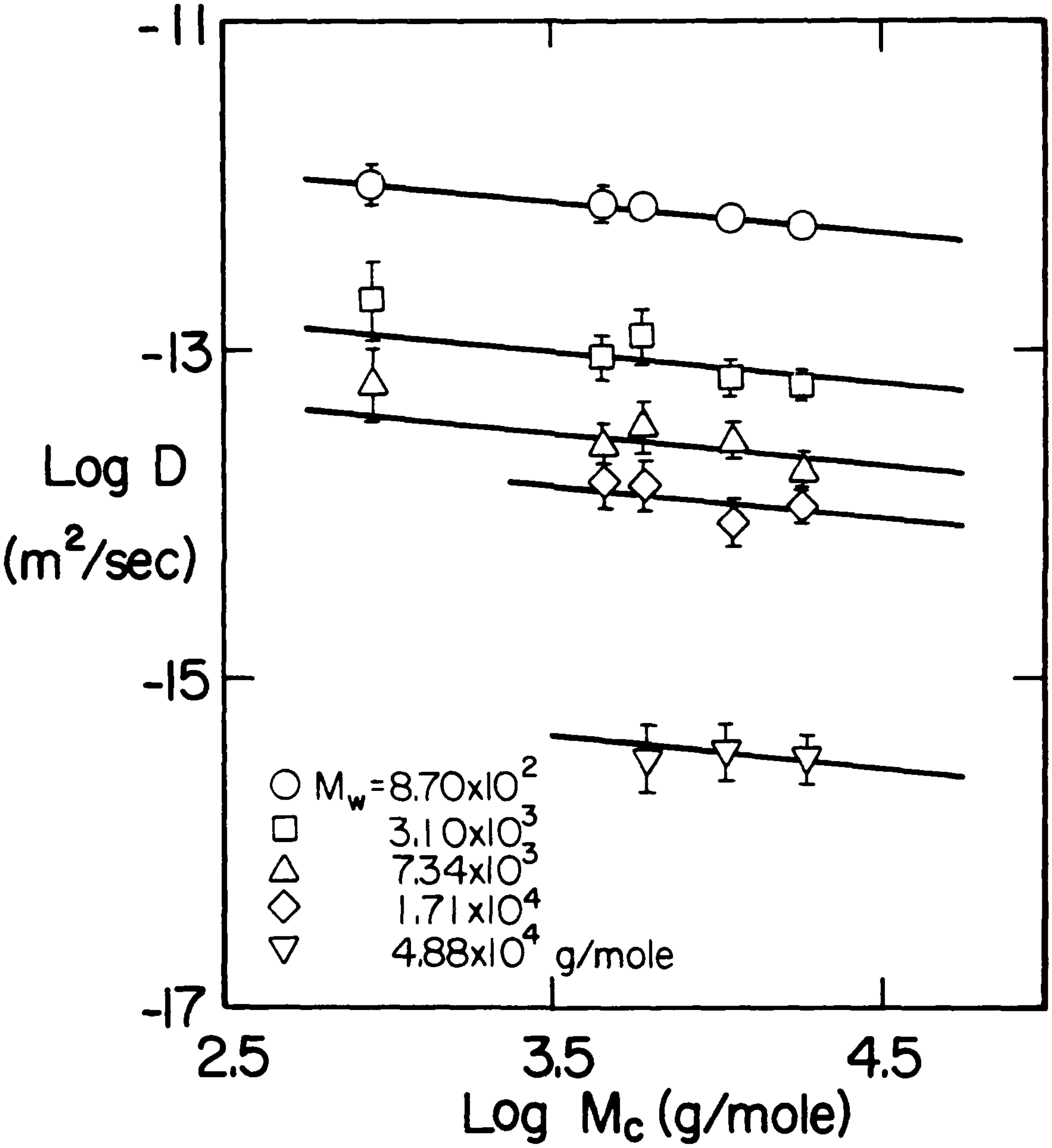

-11
-13
-15
-17
Log D
(m²/sec)
2.5
3.5
4.5
Log Mc (g/mole)
○ Mw=8.70x10²
□ 3.10x10³
△ 7.34x10³
◇ 1.71x10⁴
▽ 4.88x10⁴ g/mole

Figure 10

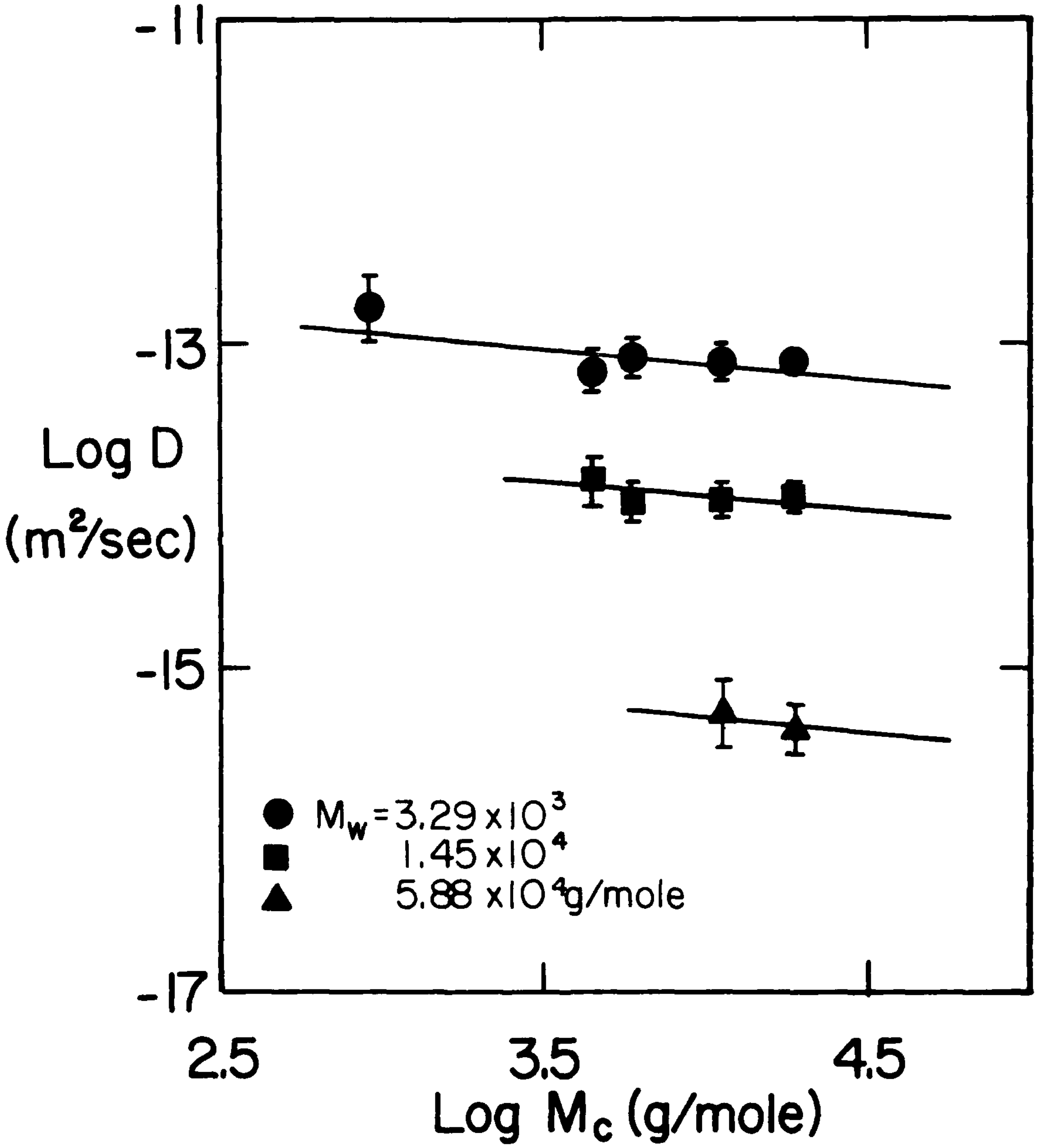

-11
-13
-15
-17
Log D
(m²/sec)
2.5
3.5
4.5
Log Mc (g/mole)
● Mw=3.29 x10³
■ 1.45 x10⁴
▲ 5.88 x10⁴ g/mole

Figure 11

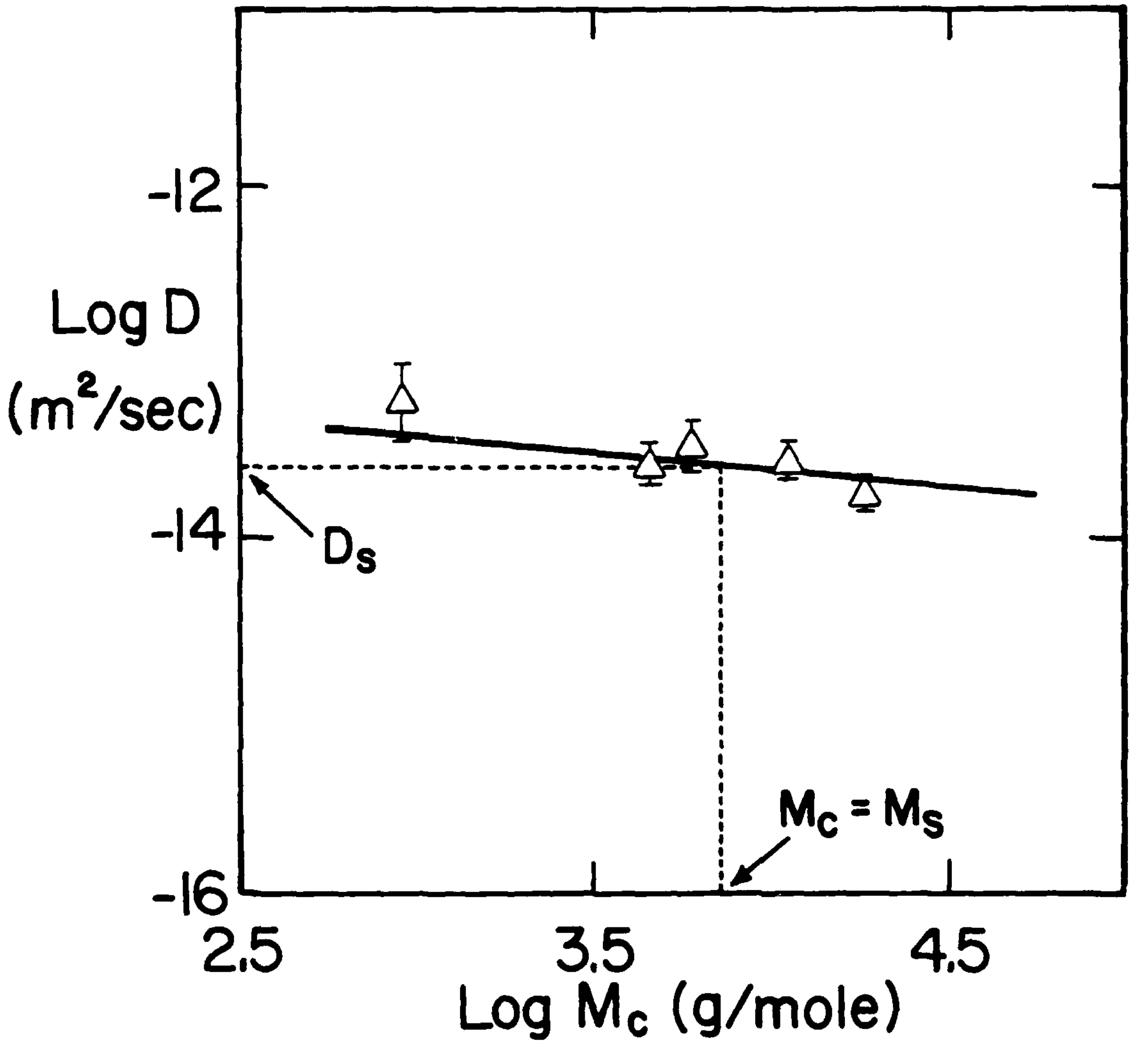


Figure 12

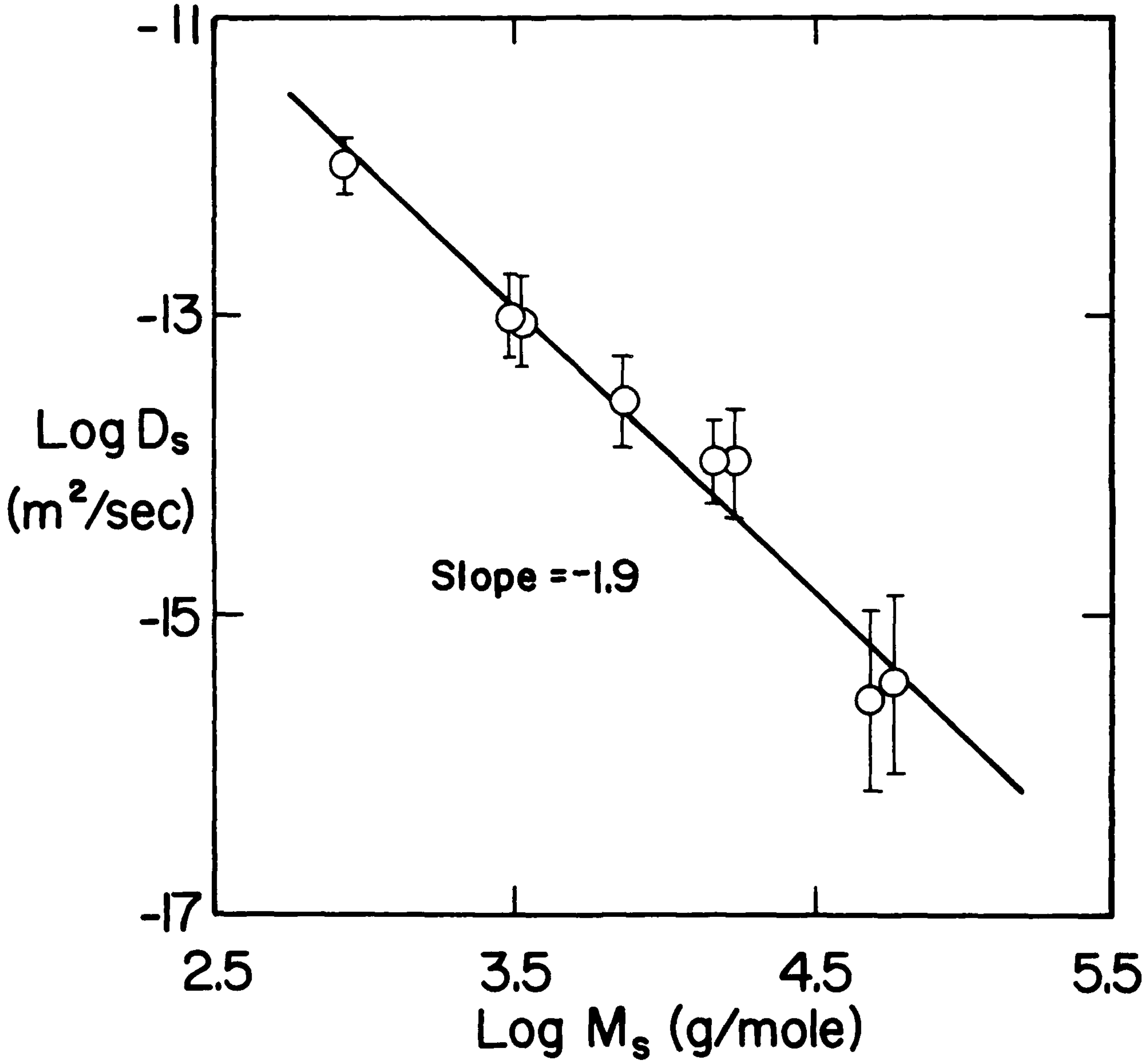


Figure 13

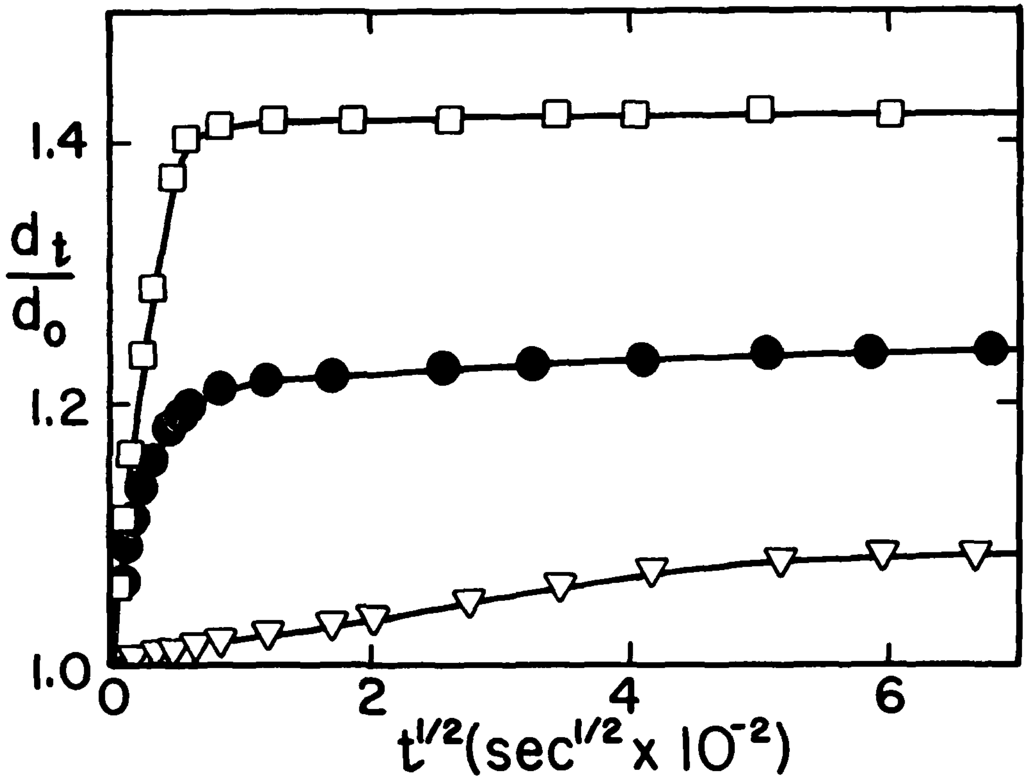
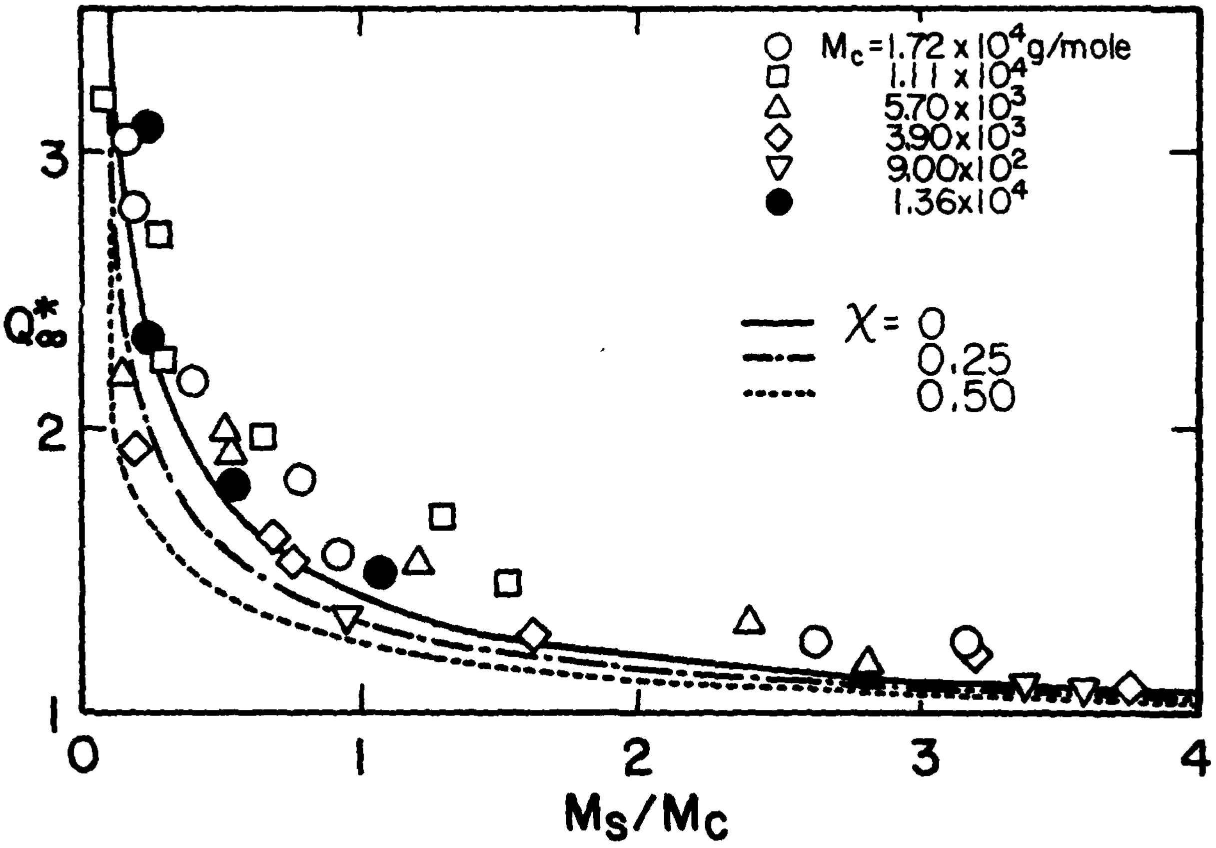


Figure 14



○ M_c=1.72 x 10^4 g/mole
□ 1.11 x 10^4
△ 5.70 x 10^3
◇ 3.90 x 10^3
▽ 9.00 x 10^2
● 1.36 x 10^4
χ = 0
0.25
0.50
Q^*_∞
M_S/M_C
0
1
2
3
4

Figure 15

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