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# Diffusion of Polymer Rings in Linear Polymer Matrices

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ABSTRACT: Forward recoil spectrometry has been used to determine concentration profiles and tracer diffusion coefficients $D^*$ of undeuteriated polystyrene rings of molecular weight $M$, ranging from 10 000 to 180 000, diffusing into deuteriated linear polystyrenes (PS) of molecular weight $P$, ranging from 55 000 to 915 000. Although constraint release has been proposed as the dominant diffusion mechanism for the rings, giving $D^* \sim M^{-1}P^{-3}$, this scaling is only observed at low $P$'s. For the highest $P$'s we find $D^* \sim M^{-3.2}P^{-n}$, where $n$ increases from approximately 0 at $M$ = 10 000 to 1.6 at $M$ = 180 000. In magnitude the data fall above the constraint release prediction and below the measured $D^*$'s for linear PS of the same $M$. These results indicate two additional diffusion processes for rings: (1) the restricted reptation of that fraction of rings that is unthreaded by linear $P$-chain constraints, a process recently proposed theoretically by Klein; (2) constrained ring diffusion, in which that fraction of rings threaded once by $P$-chain constraints diffuses along these linear constraints. Predictions based on these processes are in satisfactory agreement with the experimental data.

## Introduction

Studies of the diffusion of linear polymer chains of molecular weight $M$ into linear entangled polymer melts of different molecular weight $P$ have clarified the mechanisms by which such chains diffuse as well as the origin of important viscoelastic processes in the melt.[1–7] At high molecular weights of the matrix ($P > M$) the chains diffuse by reptation,[8–11] crawling along the primitive path defined by the constraints of the neighboring $P$-chains. At low enough molecular weights of the matrix the constraints are mobile on the time scale of reptation, and the $M$-chain diffuses both by reptation and the lateral diffusion of the primitive path itself due to reptation of the surrounding $P$-chains, a process called constraint release.[12–14]

The diffusion processes of nonlinear polymers are not so clear. Star polymers with entangled arms diffuse much slower than linear polymers of the same molecular weight $M$, and it is believed that constraint release processes play an important role in the diffusion of stars in linear-chain matrices even for $P > M$.[15–17] A restricted reptation process for stars, involving the drawing in of its arms to the primitive path, is postulated,[11,18–23] but not yet unambiguously observed. Ring polymers have aroused special interest since it is difficult to imagine how they can reptate. Until recently, it was thought that diffusion of rings into linear matrices must take place only by constraint release.[14]

In this paper we demonstrate that at high molecular weights of the $P$-chain matrix, processes other than constraint release are important for diffusion of ring polymers. We identify two such processes: (1) the restricted reptation of that fraction of rings that is unthreaded by linear $P$-chain constraints (this process has recently been proposed theoretically by Klein[24]); (2) a process of constrained ring diffusion, in which that fraction of rings once threaded by $P$-chain constraints diffuses along these constraints.

## Experimental Procedures

Linear deuteriated polystyrene from Polymer Laboratories Ltd. was used as the matrix for the tracer diffusion studies of the PS rings. The molecular weight ($P$) ranged from 55 000 to 915 000. The polydispersity index of the linear d-PS was never greater than 1.3.

**Table I**
**$M_w$ As Measured with Wide-Angle Light Scattering (WALS) and Small-Angle Neutron Scattering (SANS)**

| | nominal $M_w$ of rings | $M_w$ WALS | $M_w$ SANS | $M_w/M_n$ |
|---|---|---|---|---|
| PSC1 | 10 000 | 11 100 | 12 400 | 1.09 |
| PSC2 | 25 000 | 28 600 | 27 000 | 1.05 |
| PSC3 | 45 000 | 42 000 | 45 000 | 1.10 |
| PSC4 | 80 000 | 79 400 | 79 500 | 1.12 |
| PSC5 | 180 000 | 181 500 | | 1.10 |

The synthesis, fractionation, and characterization of the polystyrene ring macromolecules have been discussed in detail elsewhere.[25–28] These undeuteriated, uncatenated ring polystyrenes were synthesized by reacting bifunctional "living" polystyrene with $\alpha,\alpha'$-dibromo-$p$-xylene in dilute solution. The concentration at which the closure reaction was carried out depended on the molecular weight of the polystyrene and was less than the concentration at which the intermolecular and intramolecular reactions are equiprobable. The separation of the ring macromolecules from the polycondensate was made by fractional precipitation. The molecular weights of the polystyrene rings used in this work are shown in Table I. Studies on the molecular dimensions in the solid state as well as on the dilute solution physical chemical properties, using neutron scattering, light scattering, size exclusion chromatography, and dilute solution viscosimetric techniques, have been performed and are reported elsewhere.[28,29] Other investigators synthesize cyclic polystyrenes using similar procedures that differ somewhat from ours.[30–34] These different polymerization procedures may lead to different topological ensembles of cyclic polystyrenes as demonstrated recently by Monte Carlo simulations.[35]

Concentration profiles of the h-PS rings (molecular weight $M$) diffusing into the linear d-PS (molecular weight $P$) were measured by forward recoil spectrometry (FRES).[5,6,36] The top portion of Figure 1 shows the geometry of the FRES experiment. A $He^{2+}$ ion beam of energy $E_0$ impinges upon the polymer sample at an angle of 15°. Some of the $He^{2+}$ ions collide with $^1H$ or $^2H$ nuclei at, or beneath, the polymer surface, causing these nuclei to recoil out of the sample. The hydrogen isotopes recoiling at an angle $\theta$ are collected by an energy-sensitive detector whose output, number of ions vs. energy, is displayed on a multichannel analyzer. The forward-scattered $He^{2+}$ ions are kept from entering the detector with a 10.6-$\mu$m-thick Mylar stopper foil. The resulting forward recoil spectrum contains both nuclear composition and depth information.

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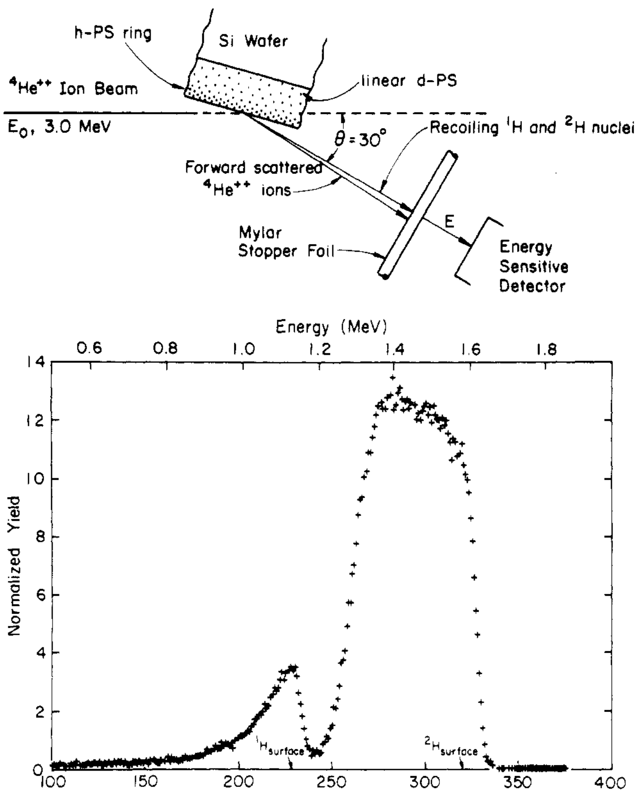

**Figure 1.** (Top) Geometry of the forward recoil spectrometry experiment. (Bottom) Forward recoil spectrum for a bilayer film sample (h-PS ring ($M$ = 45 000) on d-PS linear matrix ($P$ = 915 000) diffused for 900 s at 130 °C).

The nuclear composition information is a result of the influence of the mass of the target nucleus on its recoil energy. If a nucleus of mass $M$ is at the sample surface, that nucleus will recoil from its collision with the He$^{2+}$ of mass $m$ with an energy $E$ given by

$$E = KE_0 \tag{1}$$

From conservation of momentum and energy[37,38] it can be shown that the kinematic factor $K$ is

$$K = (4mM/(m + M)^2) \cos^2 \theta \tag{2}$$

For example at $\theta = 30°$, $^1$H has a kinematic factor of 0.48 while $^2$H has a kinematic factor of 0.67. A thin film (<50 nm) containing both $^1$H and $^2$H has a FRES spectrum consisting of two peaks at $E$'s corresponding to the $K$'s of the two H isotopes in the film. The areas under such peaks will be proportional to the differential cross section for forward scattering $\sigma$. If the cross section were Rutherford, i.e., determined solely by Coulomb repulsive forces, the cross section would be given by[39]

$$\sigma = (e^2 zZ/4E_0)^2(\sin^{-4} (\varphi/2) - 2(m/M)^2 + ...) \tag{3}$$

where $z$ and $Z$ are the atomic numbers of the He and target nucleus, respectively, and $\varphi$ is the angle between the incident and forward-scattered He$^{2+}$ ion. The increase in $\sigma$ as $\varphi$ decreases is an important advantage of FRES over Rutherford backscattering spectrometry. However, at the energies typically used for FRES (2–3 MeV) the cross section is not Rutherford because He$^{2+}$ is energetic enough to penetrate the Coulomb barrier of the H nucleus. For $^1$H, $\sigma$ is approximately independent of $E_0$ over the range 2–3 MeV and is about 3 times that given by the Rutherford formula. The same is true for $^2$H over the energy range 2.4–3 MeV, although there is a sharp peak (resonance)[40] in $\sigma$ for $^2$H at 2.14 MeV.

In a thick film the He$^{2+}$ ion loses energy to inelastic collisions with electrons as it penetrates the sample. Although these collisions do not produce significant deviations in the direction of the He$^{2+}$ ion, H isotopes recoiling from a distance $x$ below the surface will emerge with less energy than those recoiling from the surface. Since the number of recoiling H isotopes from any depth is proportional to the atom density of such isotopes at that depth, the energy spectrum of recoiling $^2$H or $^1$H nuclei, which is recorded on the multichannel analyzer, may be converted into a plot of atom fraction of $^2$H or $^1$H as a function of depth.

For the case of h-PS diffusing into d-PS the volume fraction of h-PS at any recoil energy below that of $^1$H at the surface may be found by dividing the observed spectrum by that of a thick film of the uniform $^1$H-polymer. This operation may be performed as the energy loss rates of the various nuclei are not expected to depend on whether the polymer matrix is hydrogenated or deuteriated. The energy scale is converted into a depth scale by using the stopping cross sections tabulated by Ziegler.[41] The energy loss functions of $^1$H and $^2$H in the stopper foil were found experimentally by measuring the energies of $^1$H and $^2$H recoiling from thin polymer films as a function of $E_0$.

Diffusion measurements were made on bilayer polystyrene films. A bottom layer of d-PS(linear) was spin cast from solution onto the surface of a Si wafer. A thin film of h-PS rings (10–20 nm) was produced by spin coating a glass slide with a solution of the polymer. It was removed from the glass slide by floating it onto the surface of a water bath from where it was picked up on the d-PS-coated wafer. This procedure is the direct analogue of that used for measuring the tracer diffusion of d-PS into a h-PS matrix.[5,6,36] In this case, however, one must be careful to limit the thickness of the underlying d-PS film to less than 800 nm. Deuterium nuclei originating from greater than 800 nm below the surface of the film overlap in energy with $^1$H from the surface. In this study we employed d-PS films about 600 nm thick for the bottom layer.

The bilayer films were allowed to interdiffuse at 174 °C. The diffusion times were chosen to give a diffusion distance of about 300 nm. For samples that had a tracer diffusion coefficient $D^*$ greater than $1 \times 10^{-12}$ cm$^2$/s at 174 °C the times became unrealistically short for thermal equilibrium to be obtained. For such samples the diffusion was carried out at 130 °C, and the measured $D^*$'s were scaled to 174 °C by the ratio of diffusion coefficients of selected rings measured at both 174 and 130 °C.

A fresh film was used for each measurement so that any cross-linking of the h-PS ring overlayer due to stray ions and electrons would not affect the subsequent diffusion. While there is some $^1$H and $^2$H loss due to radiation damage during analysis, it is uniform in depth and does not affect that polymer volume fraction measured.

## Results

A typical forward recoil spectrum after annealing for 900 s at 130 °C is shown in the bottom portion of Figure 1. The molecular weight of the overlying h-PS ring layer is 45 000 and that of the underlying d-PS layer is 915 000. The energies of $^2$H and $^1$H recoiling from the surface are marked. Note that after the diffusion anneal, what was a sharp peak[36] at just below 1.2 MeV due to the thin h-PS ring film on the surface of the sandwich is now spread out to lower energies due to the h-PS ring diffusion into the bottom d-PS layer. This diffusion can be followed throughout the thickness of the d-PS film, which is about 600 nm in thickness.

The h-PS ring volume fraction vs. depth profile corresponding to the spectrum of Figure 1 (bottom) is shown in Figure 2. From the integral under the profile the initial h-PS ring thickness $h$ is found to be 25 nm. At short times the solution to the Fickian diffusion equation for a thin film of thickness $h$ on the surface of a thicker film of thickness $a$ can be approximated by[42]

$$\phi(x) = 0.5(\mathrm{erf}\ [(h - x)/w] + \mathrm{erf}\ [(h + x)/w] + \mathrm{erf}\ [(h - x + 2a)/w] + \mathrm{erf}\ [(h + x - 2a)/w]) \tag{4}$$

where $\phi(x)$ is the volume fraction of h-PS rings as a function of depth $x[\phi(x) = 1$ initially for $x < h$ and $\phi(x) = 0$ for $x > h]$, and $w = (4D^*t)^{0.5}$, where $D^*$ is the infinite dilution (tracer) diffusion coefficient of the h-PS rings and $t$ is the diffusion time. The function defined by eq 4 must be convoluted with the instrumental resolution function,

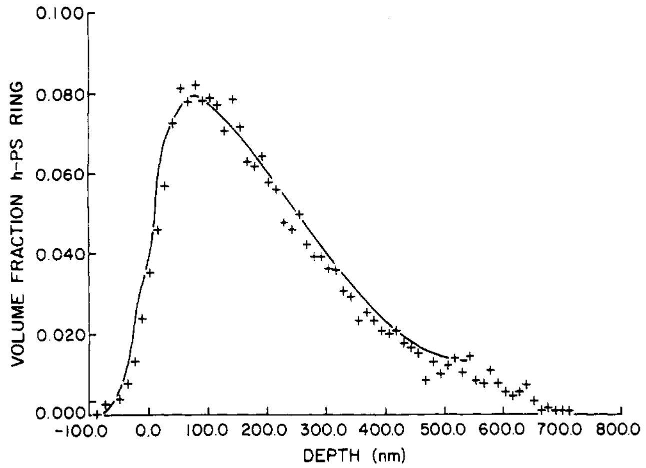

**Figure 2.** Volume fraction vs. depth profile derived from the data in Figure 1 (bottom). The solid line represents the solution to the diffusion equation (eq 4) convoluted with the Gaussian instrumental resolution function for $D^* = 4.2 \times 10^{-13}$ cm²/s.

a Gaussian with a fwhm of 80 nm, to compare it with the experimental profile. Fits to the data are obtained by adjusting $D^*$; the best fit shown as the solid curve in Figure 2 corresponds to a $D^*$ (at 130 °C) of $4.2 \times 10^{-13}$ cm²/s.

The FRES values of $D^*$ of the h-PS rings with various molecular weights $M$ are shown as a function of $P$, the molecular weight of the d-PS matrix, in Figure 3. While the $D^*$ of the high-$M$ rings depends markedly on the molecular weight $P$ of the matrix up to the highest $P$'s (915000) available, $D^*$ of the lowest $M$ rings depends little, if at all, on $P$. Figure 4 shows a cross plot of the data in Figure 3 as $D^*$ vs. $M$ at various values of $P$. Here $D^*$ is seen to decrease strongly with $M$ for the high-$P$-chain matrices but only modestly with $M$ for the shortest P-chain matrices. Even the shortest P-chains (55000) are longer than the critical molecular weight for entanglement, however. The data are in good agreement with the one previous measurement of a $D^*$ for a PS-ring ($4.3 \times 10^{-11}$ cm²/s for $M = 16000$ into a $P = 110000$ linear matrix).[3,43]

## Discussion

Linear polymer chains, and PS in particular, have been shown to diffuse by two independent mechanisms. If the molecular weight of the $P$-chain matrix is high enough, linear $M$-chains diffuse by reptation, crawling along the primitive path defined by topological constraints imposed by the $P$-chain melt.[8-10] Such a mechanism gives rise to a tracer diffusion coefficient which varies as

$$D^* = D_R = D_0 M^{-2} \quad (5)$$

where $D_0$ is given by[11]

$$D_0 = (4/15) M_0 M_e k_B T / \zeta_0 \quad (6)$$

and where $\zeta_0$ is a monomeric friction coefficient, $k_B$ is Boltzmann's constant, and $M_0$ and $M_e$ are the monomer and entanglement molecular weights, respectively. The magnitude of $D_0$ can be estimated from viscoelastic parameters of the polymer and such estimates are in good agreement with the experimental $D^*$ results, which also

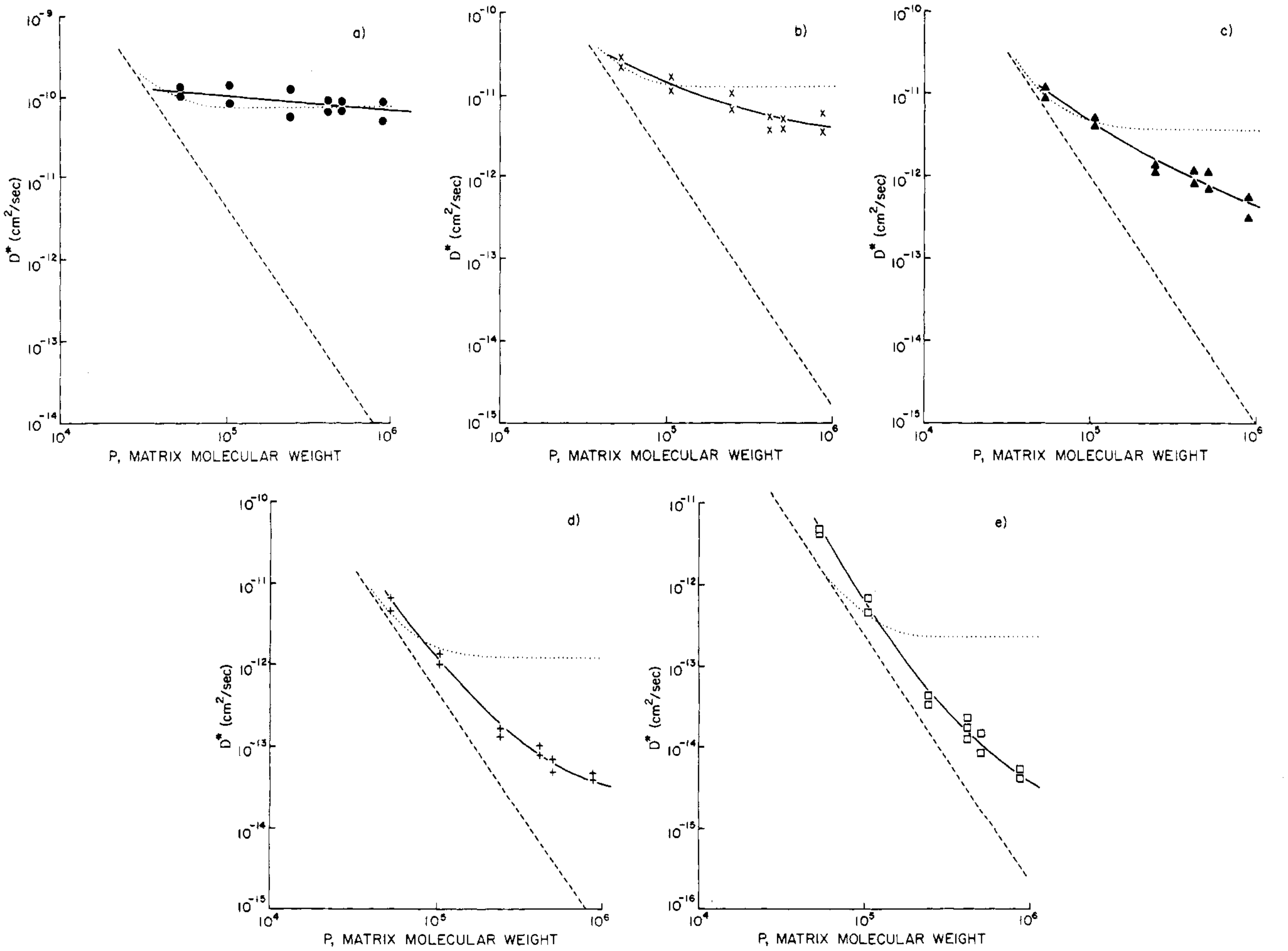

**Figure 3.** Tracer diffusion coefficient of the $M$-ring vs. $P$, the molecular weight of the linear chain matrix: (a) $M = 10000$; (b) $M = 25000$; (c) $M = 45000$; (d) $M = 80000$; (e) $M = 180000$. The dotted line represents the tracer diffusion coefficient of a linear chain of molecular weight $M$ in the $P$-chain matrix while the dashed line is the contribution expected from constraint release (eq 7).

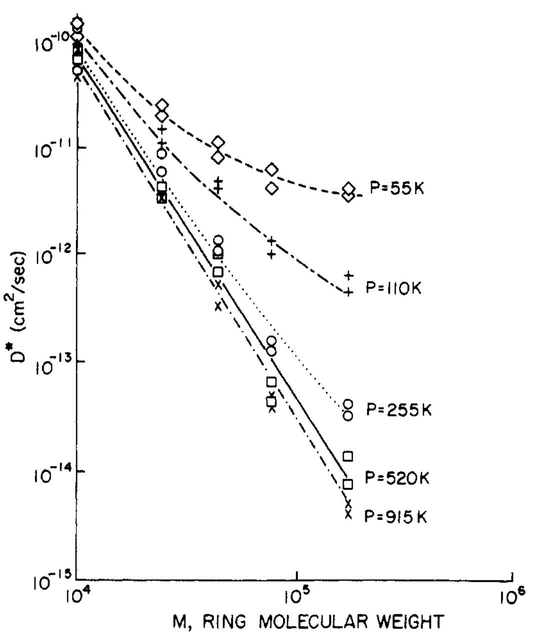

**Figure 4.** Tracer diffusion coefficient of the $M$-rings vs. $M$ at several different values of the molecular weight of the $P$-chain matrix.

confirm the $M^{-2}$ dependence of $D^*$ over a wide range of $M$'s under conditions where $P \gg M$.[6]

For long enough $M$-chains and short enough $P$-chains, other processes contribute to diffusion since the topological constraints on the $M$-chain are no longer fixed on the time scale of reptation.[12-14] One possibility is that the primitive path of the $M$-chain diffuses by reptation of the $P$-chains defining it. This motion results in a diffusion coefficient $D_{CR}$ given by[11]

$$D_{CR} = a_{CR} D_0 M_e^2 M^{-1} P^{-3} \quad (7)$$

where the constant $a_{CR} = (48/25)z(12/\pi^2)^{z-1}$, where $z$ is defined as the "number of suitably situated constraints" that define the cross section of the primitive path.[44] A more general derivation of the dependence of $D_{CR}$ on $M$ and $P$ is possible by realizing that this motion of the $M$-chain primitive path, or "tube" is formally equivalent to the diffusion of a cylinder of length $L$, the contour length of the "tube," in a medium of viscosity $\eta_0$. Since $D_{CR} \propto k_BT/L\eta_0$ and since $L \propto M$ and $\eta_0 \propto P^3$ for $P > M_c \approx 2M_e$, $D_{CR} \propto M^{-1}P^{-3}$. The effects of this constraint release mechanism have been recently observed in the diffusion of linear $M$-chains into linear $P$-chains of PS.[5,45] The $D^*$ is well described by the sum of $D_R$ and $D_{CR}$. The value of $z = 3.5$ needed to fit the data is close to that obtained from viscoelastic measurements of mixtures of polybutadienes. The $D^*$'s for linear $M$-chains of PS of the same molecular weight as the rings ($D^* = D_{CR} + D_R$) are shown as the dotted lines on Figure 3. It seems clear that the large PS rings diffuse much slower into high molecular weight linear $P$-chain matrices than do linear PS $M$-chains. This observation is especially interesting in the light of recent measurements of the $\eta_0$ of pure $M$-chain PS rings.[27,46] For these pure rings it was found that the zero-shear-rate viscosity was essentially the same as linear PS of the same molecular weight. Our diffusion measurements show large differences in the diffusion of $M$-rings and linear $M$-chains into a linear $P$-chain host.

On the other hand, recent theoretical descriptions[14] of the diffusion of high $M$-rings into linear $P$-chains assume that $D^*$ must be given by $D_{CR}$ since reptation is thought to be impossible for large rings. For comparison we have plotted $D_{CR}$ as the dashed line in Figure 3. While the $D^*$'s at relatively low $P$'s might be described approximately by $D^* = D_{CR}$, $D^*$ increasingly deviates in a positive sense, i.e., to higher $D$ values, from the $D_{CR}$ line as $P$ is increased, even for the highest $M = 180\,000$ rings. The deviation is more apparent as the $M$ of the ring is decreased, with the results at high $P$ increasing closer to the reptation prediction as $M$ is decreased. This deviation is further highlighted by the data in Figure 4. Diffusion by constraint release is predicted to vary as $D_{CR} \sim M^{-1}$ at constant $P$. The $D^*$ for the $M$-rings depends much more strongly than that on $M$, varying as $M^{-3.2}$ for our highest $P$ of 915 000. Clearly, the theoretical prediction that $D^* = D_{CR}$ does not describe well the diffusion of rings into the linear polymer.

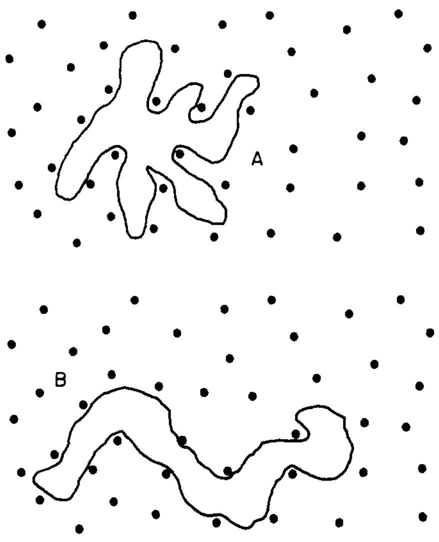

**Figure 5.** Schematic drawing of rings unthreaded by constraints: ring A, a reticulated ring; ring B, an unreticulated ring.

An alternative theoretical argument has been presented by Klein.[24] He computes the probability $P_0$ that a ring of molecular weight $M$ is not threaded by even one constraint. He finds that this probability is given by

$$P_0 = \text{const} \times (M/M_e)^{3/2} \exp(-\gamma(M/M_e)) \quad (8)$$

where $\gamma$ is a constant of order 0.6–0.7. Consider two such rings in an array of fixed constraints shown in Figure 5. Ring A has large loops that extrude between constraints. Such a ring, which Klein calls reticulated, would have to diffuse by a mechanism similar to the mechanism by which polymer stars are thought to diffuse, i.e., pulling in its loops to assume a quasi-linear conformation such as that of ring B. Quasi-linear rings, which correspond in length to a linear molecule of molecular weight $M/2$, can diffuse by reptation with diffusion coefficient given by

$$D_R = D_0(M/2)^{-2} \quad (9)$$

The tracer diffusion coefficient of the rings by this mechanism would be then $P_0$ times the probability that the ring assumes a quasi-linear conformation times $D_R$ the diffusion coefficient of such molecules. In the limit of large $M$, Klein estimates this contribution to $D^*$ to be

$$D_{RR} = \text{const} \times D_0(M/2)^{-2} \exp(-\beta(M/M_e)) \quad (10)$$

where $\beta$ is a constant approximately equal to 1.1. Since this mechanism is independent of constraint release, the total $D^*$ should be given by

$$D^* = D_{CR} + D_{RR} \quad (11)$$

The predicted $D^*$'s are plotted vs. matrix molecular weight $P$ in Figure 6 as dashed lines using $\beta = 1.1$ and const =

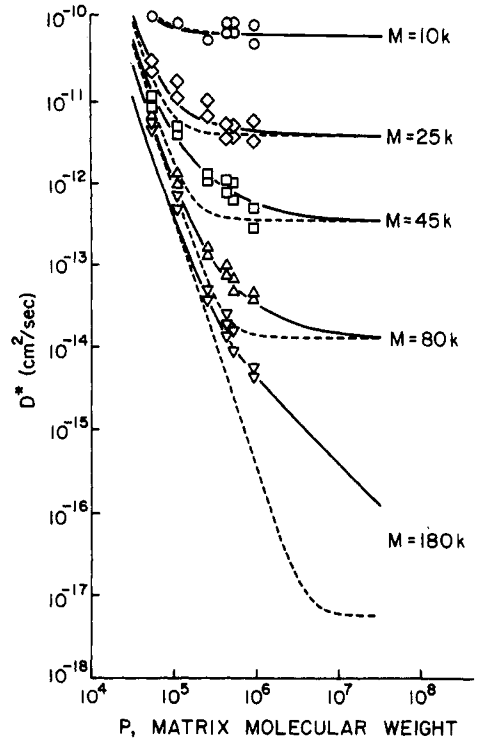

**Figure 6.** Tracer diffusion coefficient of *M*-rings vs. molecular weight of the *P*-chain matrix. Dashed lines represent the prediction based on unthreaded ring reptation and constraint release (eq 10) while the solid line represents the prediction based on the added contribution of once-threaded constrained ring reptation along linear *P*-chains (eq 13).

0.4. Because the ring reptation mechanism proposed by Klein[24] is independent of the molecular weight of the matrix, the transition from constraint release to reptation with *P* is rather abrupt, occurring over a rather small range of *P*. The experimental data, also shown in the figure, exhibit a much more gradual transition. Moreover, for the larger rings the $D^*$ prediction for ring reptation falls well below the experimental data (the probability of unthreaded rings decreases exponentially with *M*; for example, $P_0$ = 0.0009 for the 180 000 ring, which has $M/M_e = 10$). While the ring reptation mechanism may well dominate at very large *P*'s and moderate *M*'s, it clearly cannot explain most of the deviation from constraint release.

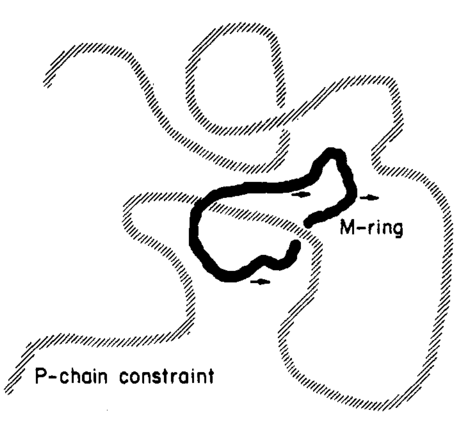

**Figure 7.** A once-threaded ring diffusing along a *P*-chain constraint.

Yet another possibility exists however. Consider a ring threaded by one constraint, represented by a single *P*-chain in Figure 7. Such a once-threaded ring can diffuse by constraint release, if the linear *P*-chain reptates so that the ring becomes unthreaded. However, if the *M*-ring is small and the *P*-chain large, another mechanism becomes more important. The *M*-chain can diffuse along, like a smoke ring, constrained to follow the contour of the *P*-chain. This mechanism can be analyzed by the same arguments used for reptation. The ring diffuses along the primitive path provided by the *P*-chain with its Rouse diffusion coefficient $D_{\mathrm{RO}} \sim M.^{-1}$ Since the contour length of the *P*-chain is proportional to *P*, the time $t_u$ required for the ring to unthread itself scales as $P^2M$. In this time the center of mass of the ring is displaced by the root mean square end-to-end distance of the *P*-chain, so the center-of-mass diffusion coefficient of the once-threaded *M*-ring should scale as $M^{-1}P^{-1}$. The diffusion coefficient should be approximately

$$D_{\mathrm{R1}} = AP_1D_0(M/2)^{-1}P^{-1} \tag{12}$$

where $P_1$ is the probability that a ring in the melt is once-threaded and unreticulated and the constant *A* takes into account any difference in the Rouse mobility of linear chains and rings. The tracer diffusion coefficient should be given by

$$D^* = D_{\mathrm{CR}} + D_{\mathrm{RR}} + D_{\mathrm{R1}} \tag{13}$$

where $D_{\mathrm{RR}}$ and $D_{\mathrm{R1}}$ represent the restricted reptation of unthreaded and once-threaded rings, respectively, and $D_{\mathrm{CR}}$ represents the diffusion of rings of all threading numbers by constraint release.

To test this hypothesis we have computed the $D^*$ from eq 13 setting $A = 1$ and adjusting $P_1$ to produce the solid lines shown in Figure 6. The previous values of $D_{\mathrm{RR}}$ computed from Klein's formula (eq 11) are retained. The values of $P_1$ used are 0.33 for $M$ = 10 000, 0.63 for $M$ = 25 000, 0.66 for $M$ = 45 000, 0.11 for $M$ = 80 000, and 0.05 for $M$ = 180 000; the corresponding values of $P_0$ are 0.67, 0.37, 0.17, 0.004, and 0.0009. The agreement with experiment is quite satisfactory, even recognizing that the adjustment of $P_1$ allows one considerable latitude to produce such agreement. $P_1$ first increases to a maximum and then decreases with increasing *M* as expected since for small enough rings $P_1$ must approach zero; at large values of *M* it is greater than $P_0$, also as expected. The gradual flattening of $D^*$ vs. *P* as *P* increases is faithfully reproduced.

These experiments suggest a number of important additional experimental checks. The diffusion coefficients of the rings into linear chain matrices with higher molecular weights will reveal important information on the asymptotic behavior, especially for the 80 000 and 180 000 rings. By diffusing the rings into cross-linked matrices, it should be possible to isolate the pure ring reptation contribution to $D^*$. Finally, the diffusion of linear chain molecules into a matrix of rings should be instructive. Will constraint release become important at molecular weights similar to those for linear chain matrices? Since the viscosity of linear and ring melts of similar molecular weights are similar,[27,46] a macroscopic view of the constraint release process suggests yes, while almost any detailed microscopic model of the process suggests no. It seems clear that further studies of diffusion of ring molecules will reveal much new information on the relationships between viscoelastic properties of polymers and their molecular topology.

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# Intrinsic Viscosity and Huggins Coefficients for Potassium Poly(styrenesulfonate) Solutions

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ABSTRACT: The intrinsic viscosities $[\eta]$ and Huggins coefficients $k_H$ measured for potassium poly(styrenesulfonate) solutions at ionic strengths of $(3 \times 10^{-5})$–3.1 M illustrate the effects of intra- and intermolecular electrostatic interactions on the viscosity of dilute solutions. With decreasing ionic strength $[\eta]$ increases monotonically as the individual chains transform from compact coils to extended rods, but $k_H$ first decreases due to coil compression before increasing substantially. Extant theories predict the variation in $[\eta]$ satisfactorily but not the behavior of $k_H$.

## Introduction

This paper is the second of two dealing with the thermodynamics and rheology of dilute polyelectrolyte solutions. The first[1] outlined an electrostatic wormlike chain theory, based on the earlier work of Odijk[2-4] and Fixman,[5-7] for thermodynamic properties such as the radius of gyration $R_g$ and the second virial coefficient $A_2$. We then combined this with the hydrodynamic wormlike chain theory of Yamakawa[8] to predict the intrinsic viscosity $[\eta]$ and the molecular friction factor $f_0$. The theory was tested with light scattering and viscometry data for potassium poly(styrenesulfonate) K-PSS).[9] Agreement was quantitative for the thermodynamic properties and semiquantitative for the hydrodynamic predictions.

To test this theory further we have conducted viscometric experiments on a series of well-characterized K-PSS samples with a narrow molecular weight distribution over a range of ionic strengths encompassing the rigid-rod and

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