Gels of Increasing Chain Rigidity: Diffusion and Deswelling by Semirigid Polymers of Varying Molecular Weight

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ABSTRACT: Linear semirigid aromatic polyamides of five different molecular lengths L were synthesized. Five cross-linked gels having rigid, semirigid, and flexible chains were prepared. The diffusion of the linear polyamides through semirigid and flexible gels was studied. It was found that the diffusion coefficient D of the semirigid macromolecules above a low molecular weight threshold scales as $D \propto 1/L$. It was also found that upon coming in contact with the polymer solutions, the gels deswell according to their chain flexibility: the flexible gels deswell very much, the semirigid gels deswell only a little, and the rigid gels do not change at all. The deswelling of the flexible gel affects the diffusion through it. The partition coefficient K of the diffusant between the gel and surrounding solution tends to decrease with increased molecular weight. The K values for rigid and semirigid gels appear to approach constant $K > 0$ values for unavailable high molecular weights. In the case of flexible gels K tends toward zero at high molecular weights, in agreement with theory and literature results. Results obtained from deswelled flexible gels in mixed solvents further substantiate the observations above.

Introduction

In recent years there has arisen a strong theoretical interest in the behavior of rodlike macromolecules under various conditions. Of prime interest have been the dynamic properties of such molecules in solutions of increasing concentration[1-4] and in entangled polymer melt or gel.[5] One of the more interesting among these properties is the translational diffusion of rodlike macromolecules. From the vast recent literature on rigid-backbone polymers, it is obvious that theoretical rodlike molecules are very often experimentally approximated by macromolecules not perfectly rodlike, which might be termed semirigid. Examples for these are the lyotropic liquid crystalline cellulose derivatives and poly(*p*-phenyleneterephthalamide), macromolecules whose persistence length is between one-half and one-quarter that of the lyotropic mesomorphic more extended poly(*p*-benzamide) and certain poly(*n*-alkyl isocyanates).[6]

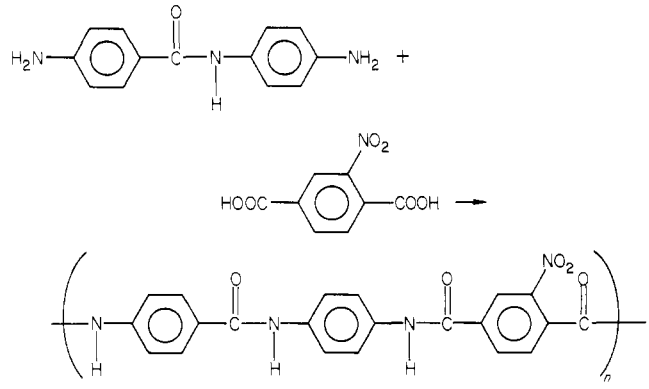
At present we are aware of only one paper describing the translational diffusion of semirigid macromolecules through a gel. In it, preliminary experimental results are presented[7] on the diffusion of semirigid aromatic polyamides through a gel of the same polymer conposition. That preliminary work constitutes a small part of the present report.

Cross-linked networks of flexible macromolecules swell and form gels when equilibrated in good solvent. The fact that they deswell (shrink) upon transfer from the good solvent to solutions of high polymers in the same solvent has been known for a long time.[8-10] Interest in this behavior of flexible gels was recently rekindled by Bastide, Candau, and co-workers[11,12] and Brochard.[13] Strictly speaking, both these treatments do not apply to the present systems. This is because the theories deal with flexible gels that do not undergo microsyneresis upon immersion in solutions of the same polymer. Our systems are semirigid or rigid gels immersed in similar polymer solutions or flexible gels in contact with semirigid polymer solutions. Furthermore, upon large deswelling in mixed solvents the gels show a tendency toward microsyneresis.[14]

In the present work we are interested in studying the swelling–deswelling behavior of polymeric gels in solutions of linear semirigid macromolecules as a function of the rigidity of the polymeric network chains in the gel and the length of the polymeric solute chains. We are also interested in the diffusion of such linear chains through gels of varied rigidity. Despite the strict inapplicability of the above theories to our systems, it was felt that at least a qualitative comparison of experiment with theory is warranted.

Experimental Section

All solvents, reagents, and monomers were of reagent grade or better and were used as received. The monomers 4,4′-diaminobenzanilide (DABA) and trimethylene glycol bis(*p*-aminobenzoate) (Polacure 740M) were obtained from Sandoz Corp. and Polaroid Corp., respectively. All other materials were obtained from chemical supply houses. The polycondensation of the linear diffusant polyamides and the cross-linked networks was by means of the Yamazaki et al.[15] procedure. Linear polyamides of five different molecular weights were prepared from DABA and nitroterephthalic acid (NTPA):



For the three low molecular weight linear polymers, amounts of monofunctional *m*-nitrobenzoic acid (NBA) were added, calculated to limit the molecular weight, M, of the products to certain desired averages. The degree of polymerization of the higher molecular weight linear polyamides was controlled by the length of time the polymerization was allowed to proceed. In all cases, the low molecular weight tail of the polymerization product was removed by precipitation of the bulk of the product in a solvent–nonsolvent mixture containing about 30:70 dimethylacetamide (DMAc) solvent and methanol nonsolvent.

In a typical polycondensation procedure, there were placed in a 500-mL round-bottom flask 100 mL of DMAc, 5 g of LiCl, and 50 mL of pyridine. The mixture was stirred by means of a magnetic stirrer and heated to about 100 °C in an oil bath. At this point the desired monomer combination was introduced. The amount of monomers was calculated to produce a 10% polymer concentration in the reaction vessel. The hot mixture was stirred until a slightly turbid solution was obtained and then 30 mL of triphenyl phosphite was added. Within a few minutes the turbid solution became transparent and after about 20 min its viscosity

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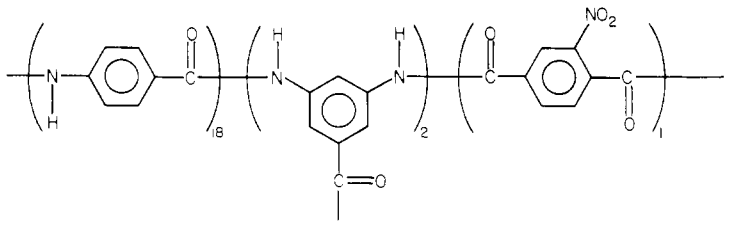
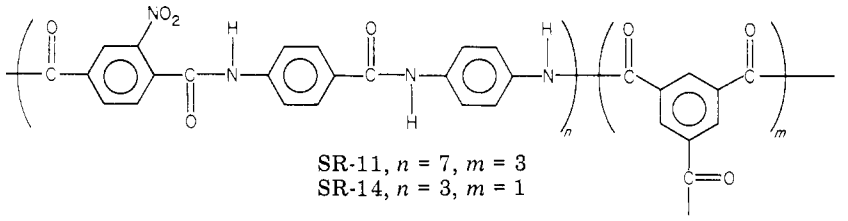
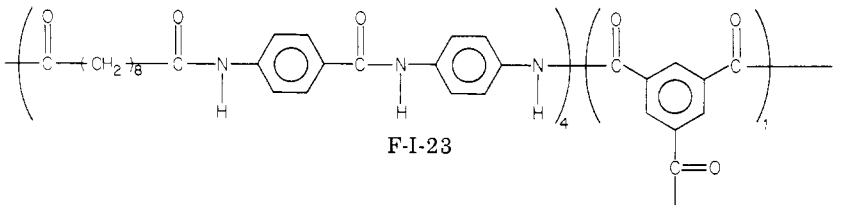
Chart I



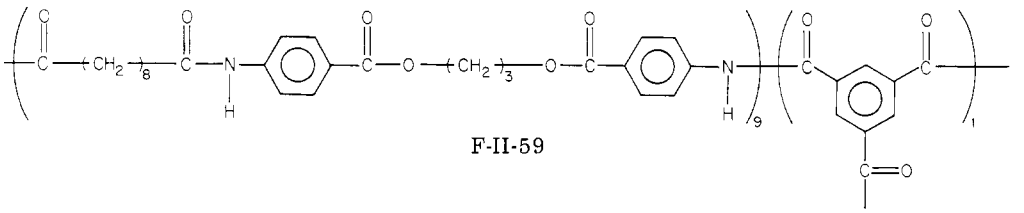
R-13



SR-11, n = 7, m = 3
SR-14, n = 3, m = 1



F-I-23



F-II-59

noticeably increased. With increased viscosity the reaction mixture became first transluscent and then opaque. From this point, the reaction was allowed to proceed for 2 h before termination. The reaction mixture was poured into a volume of methanol resulting in a 30:70 DMAc/methanol mixture. The precipitate was filtered off and then repeatedly washed with large amounts of methanol until no pyridine odor was noticed. Tests of the initial and subsequent wash solvent indicated that all reaction products shorter than a tetramer were washed away, along with spent reagents, LiCl, and trace amounts of monomers. The linear polymeric products were dried under vacuum at 130 °C for 16 h. Mass balance indicated the yield of the linear polyamides after losing their low molecular weight tail was of the order of 80% of theory.

There were five different cross-linked samples prepared for the deswelling experiments. Based on their chain rigidity and the average distance in nanometers between branch points,[16] they were encoded as follows: (a) R-13, a rigid network with 13 nm between branch points; (b) SR-11 and SR-14, two semirigid networks with 11 and 14 nm between branch points; (c) F-I-23 and F-II-59, two flexible networks of differing chemical composition and different distances between the branch points. The chemical composition of R-13 and the composition of the semirigid networks SR-11 and SR-14 are shown in Chart I. Chemically, SR-11 and SR-14 are similar to the linear semirigid polyamides described above.

The F-I-23 network (Chart I) contained the DABA monomer used for the linear polyamides and rendered flexible by the use of decanedioic acid. The F-II-59 network (Chart I) was more flexible in nature, replacing DABA by the diamine Polacure. In all systems above, the branching was effected by the use of a rigid aromatic trifunctional unit, 3,5-diaminobenzoic acid for R-13 and 1,3,5-benzenetricarboxylic acid for the others.

As was the case with the linear polyamides, the polymerization of the cross-linked networks was conducted at 10% polymer concentration. In the case of the cross-linked systems, when the reaction progressed sufficiently to turn opaque, the magnetic stirring bar became immobilized by the high viscosity of the system. From this point the reaction was allowed to continue for 2–3 h before termination. The reaction vessel was sacrificed and the solid product cut into slabs that were immersed in a large excess of methanol. The slabs usually exhibited some shrinkage and enhanced opacity. The methanol was replaced several times at intervals of 24 h each, until no pyridine was detected. Analysis of the wash indicated that at this point all the LiCl, pyridine, spent reagent, DMAc, and trace residual monomers were removed. Samples were dried in a vacuum oven at 130 °C and mass balance indicated that the polymerization yield was very close to 100% of theory. The methanol-soaked slabs were then transferred to pure DMAc, in which they swelled, and when present, the soluble polymer fraction dissolved away. No significant amount of sol fraction was detected in the cases of R-13, F-I-23, and F-II-59, and at room temperature less than 5% was leached out of the SR-11 and SR-14 networks. In all cases, the DMAc was replaced daily not less than six times before the samples reached constant weight and equilibrium. From this point the DMAc-equilibrated gels were allowed not less than 1 additional week in DMAc at room temperature before testing. With the specimen's size at hand, it was found that the first week of DMAc immersion was sufficient to reach equilibrium. Independently of the degree of network flexibility, it was found that upon equilibration in DMAc gels turned transparent.

Three sets of gel cups were prepared for the purpose of diffusion studies. Two consisted of DMAc-equilibrated SR-11 and SR-14 gels and the third was a DMAc-swollen F-II-59 gel. The initial part of the polymerization was carried out as described above. Once the reaction mixture began to increase in viscosity, it was poured into a concentric mold built from two glass vessels. Special care was taken to ensure that the distance between the inner and outer glass walls was the same all around, producing a cup-shaped mold cavity with uniform wall thickness. The mold was kept at 110 ± 5 °C throughout. The reaction mixture was stirred as before until immobilized by the increasing viscosity of the mixture. The reaction was continued for 2–3 h before termination. The assembly was carefully dismantled, often sacrificing the external glass vessel. It was found that a 24-h immersion in DMAc was sufficient to remove the gel cup from the inner glass vessel. The

Table I
Composition and Characteristics of Linear Polyamides

polymer code	DABA, g	NTPA, g	NBA, g	chain length L, nm	axial ratio L/d	M_n	$[\eta]$, dL/g
I	11.35	7.04	5.57	5.0	10	1340	0.20
II	11.35	8.79	2.78	9.5	19	2550	0.40
III	11.35	9.50	1.67	15.5	31	4150	0.67
IV	11.35	10.50	0	49.0	98	13200	2.30
V	11.35	10.55	0	68.5	137	18300	3.28

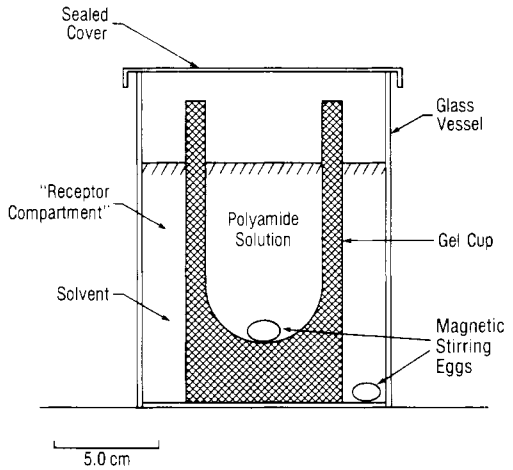


Figure 1. Experimental setup for diffusion experiments.

gel cups were then immersed in large volumes of DMAc, which were repeatedly replaced until no pyridine, LiCl, spent reagents, monomers, or soluble polymers were detected in the wash. During the solvent exchange the section of the gel cups containing the magnetic stirring bars was trimmed away. The process of solvent exchange and subsequent DMAc equilibration took over a month to complete, including not less than six solvent exchanges during the first 2 weeks of the procedure. It should be noted that during the solvent exchange, internal stresses develop in the gel cups, especially at the base of their walls where the material thickness changes, resulting in crack development and gel cup failure. Thus, a sufficiently large number of gel cups were prepared and only the blemishless ones used for the diffusion studies.

The diffusion of the linear polyamides across the gel cup walls was effected in a setup described in Figure 1, placed on a twin-head magnetic stirrer, and measured colorimetrically. The dimensions of the gel cup in Figure 1 are as prepared. They hardly changed after equilibration of SR-11 and SR-14 in DMAc but increased substantially in the case F-II-59. In all cases the starting concentration of the linear polyamides in DMAc in the gel cup was 2.0%. The receiving solvent was DMAc. The solutions in the gel cup and receptor compartment were stirred by means of magnetic stirring eggs immersed in each, keeping the concentrations constantly uniform in the compartments on both sides of the gel cup walls. Quantities of 10 mL each of the fluid in the receptor compartment in Figure 1 were siphoned (and returned after measurement) at intervals, and the percent transmittance of light through these samples was measured in a Bausch & Lomb Spectronic 20 spectrophotometer set at 450-nm wavelength. For each linear polymer sample there was prepared a light transmittance calibration curve covering the concentration interval of 0–2% in DMAc. From the measured percent transmittance, the calibration curve, and the known ratio of solution volume to the solvent volume in the receptor compartment and gel cup itself, the amount of polymer actually diffused across the gel cup walls at each time increment was determined. At the end of each run the solution in the gel cup was siphoned out and the linear polymer was precipitated in methanol, retrieved, and dried. Then the intrinsic viscosities of the initial linear and retrieved polymers were measured in concentrated sulfuric acid in Cannon-Ubbelohde viscometers and compared. The results of each pair were within experimental error of one another.

Deswelling and linear polymer pickup were measured with the solvent-equilibrated gel specimens immersed in not less than 15-fold their volume of linear polymer solution. For studies in DMAc the linear polymer concentration was 2.00%. For studies in 30:70 DMAc/acetone mixture, the linear polymer concentration was 0.60%. Volume changes were determined by allowing the specimens to reach equilibrium with the particular solvent system or solution studied, removing the specimen from it, sparingly rinsing its surface in the appropriate solvent, carefully drying with tissue paper, and weighing. When changed from one solvent to another, the measured changes in weight were corrected for the densities to yield the changes in volume. Once the gel specimens reached equilibrium in the polymer solution, they were retrieved, sparingly rinsed, dried, and weighed, and each was placed in a volume of the appropriate solvent up to 15 times larger than the volume of the specimen. The amount of linear polymer that diffused into the solvent was determined by the same colorimetric procedure used for the diffusion measurements. From it the amount of polymer that penetrated the gel specimen during the deswelling experiment and the ratio K of linear polymer in the gel to that in the surrounding solution were calculated.

Equilibration of the deswelled gels in the appropriate solvent (DMAc or 30:70 DMAc/acetone) followed by weighing showed that the deswelling process was reversible. In studies of gels in the solvent mixture, an additional transfer of the gels to pure DMAc indicated the swelling–deswelling process to be reversible over the range of pure DMAc to 0.60% polymeric diffusant in 30:70 DMAc/acetone. However, because of the large volume changes involved in the study of F-I-23 gel, this reswelled gel was more fragile than it was initially.

Results and Discussion

The monomer compositions of the five linear polyamides used in the diffusion and deswelling studies, together with the calculated number-average molecular weight M_n and chain length L of the resulting polymers and their intrinsic viscosity as determined in concentrated H_2SO_4 at 25 °C, are given in Table I. The molecular weight M_n and the chain length L of the first three linear polyamides were calculated from the monomer composition in Table I. A double-logarithmic plot of the intrinsic viscosity $[\eta]$ in dL/g against M_n of these polyamides yielded data points that fell on a straight line

$$[\eta] = 9.0 \times 10^{-5} M_n^{1.07} \quad (1)$$

with no scatter. This enabled us to estimate the M_n of the other two polyamides, IV and V, from their $[\eta]$ values. The values of L and L/d were calculated from M_n using the literature[16] value of about 0.5 nm for the length and diameter of an aromatic p-amide repeat unit. It should be noted that the $a = 1.07$ exponent in the Mark–Houwink eq 1 is large, which is usually associated with substantial chain rigidity. Studies with models indicate that the nitro group in a position ortho to an amide residue imposes a degree of nonlinearity upon the latter.[14] This renders the whole chain semirigid instead of highly rigid. Cross-polarized light microscopy studies of solutions of all linear polyamides in Table I in concentrated H_2SO_4 and in DMAc/5% LiCl revealed them to be lyotropic liquid crystals at concentrations of about 20% and higher, inversely dependent on their molecular weight. The mesomorphicity of the linear aromatic polyamides indicates them to possess a substantial backbone rigidity, placing

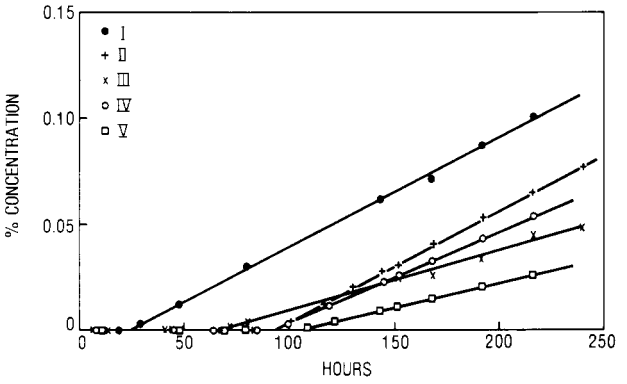


Figure 2. Diffusion of linear semirigid polyamides through SR-11 gel cups.

them in a semirigid category, definitely out of the range of common flexible polymers.

Diffusion was measured across the walls of SR-14, SR-11, and F-II-59 sets of gel cups. At the end of the diffusion studies the gel cups were thoroughly washed in DMAc and equilibrated in it for up to 3 months. The cups were then broken and parts were carefully weighed. After thorough drying to constant weight, mass balance indicated the weight percent polymers in the DMAc-equilibrated gel cups to be 9.7 ± 1.0 for SR-14, 9.6 ± 1.0 for SR-11, and 3.8 ± 0.3 for F-II-59. From this it is obvious that the SR-14 and SR-11 gels swelled in DMAc very little from the calculated 10% while the F-II-59 gel swelled substantially when transferred from the polymerization mixture to pure DMAc. Measurements of inner and outer diameters of the gel cups during the diffusion studies indicated that the SR-14 and SR-11 gels did not change their dimensions measurably, while the F-II-59 gel shrank by 25–30% of its volume in pure DMAc. The scatter of data of the SR-14 and SR-11 gel cups was not accompanied by a significant scatter in diffusion measurements.

Results of the diffusion measurements through SR-11 gel cups are plotted against time in Figure 2. The time until the point where the diffusant concentration deviates from zero is usually called the time lag, t. Knowledge of the time lag and the thickness d of the gel cup walls allows one to calculate the overall diffusion constant D. At times longer than recorded in Figure 2 some reductions in the rate of increased concentration were noticed. The constant concentration on both sides of the gel cup walls (obtained by constant stirring), the essentially linear increase in concentration with the time (in Figure 2), and obtaining the same value of D from runs repeated with different gel cup wall thicknesses (SR-14 cup no. 3 and 6 with diffusant III in Table II) indicate that the observed overall diffusion is Fickian or very close to it.

Following Edwards and Evans[17] a relationship between the free translation diffusion constant D_0 and t' for rodlike-shaped diffusants is defined as

$$D_0 = d^2/2t' \tag{2}$$

where t' is the time it would take for the particle to diffuse a distance d if no barriers were present. If barriers to free mobility are present, as in the case of the gels in the present work, the rodlike particles will take a longer time $t \gg t'$ to traverse the distance d, with the translational diffusion coefficient D being

$$D = d^2/2t \tag{3}$$

where the prolongation of t relative to t' is dependent on the ratio of L to the average distance, a, between barriers,[17]

Table II
Diffusion of Linear Aromatic Polyamides through Gel Cup Walls

gel cup	diffusant polyamide	d, cm	t', t, s	D_0, D, cm²/s
SR-14 no. 1	I	0.65	14 400	14.67×10^{-6}
SR-14 no. 2	II	0.52	24 300	5.55×10^{-6}
SR-14 no. 3	III	0.35	14 400	4.26×10^{-6}
SR-14 no. 4	IV	0.70	58 800	4.17×10^{-6}
SR-14 no. 5	V	0.70	63 700	3.84×10^{-6}
SR-14 no. 6	III	0.75	66 200	4.25×10^{-6}
SR-11 no. 1	I	0.65	86 400	24.45×10^{-7}
SR-11 no. 2	II	0.62	334 800	5.73×10^{-7}
SR-11 no. 3	III	0.48	244 800	4.68×10^{-7}
SR-11 no. 4	IV	0.55	334 800	4.53×10^{-7}
SR-11 no. 5	V	0.45	378 000	2.67×10^{-7}
F-II-59 no. 1	I	0.80	100 800	3.18×10^{-6}
F-II-59 no. 2	II	0.70	90 000	2.70×10^{-6}
F-II-59 no. 3	III	0.80	133 200	2.40×10^{-6}
F-II-59 no. 4	IV	0.70	104 400	2.34×10^{-6}
F-II-59 no. 5	V	0.80	140 400	2.28×10^{-6}

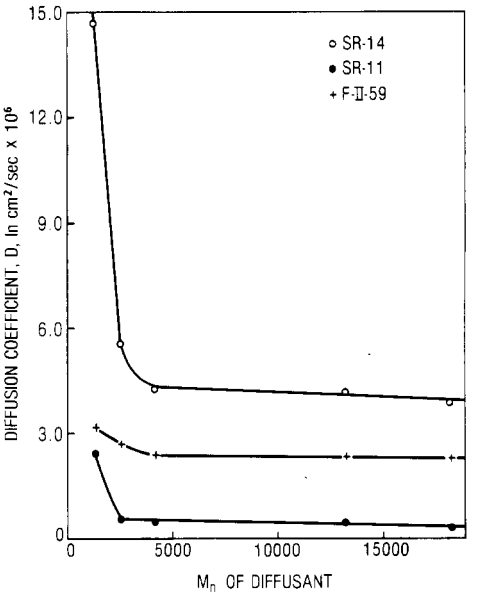


Figure 3. Diffusion coefficient D against M_n of five semirigid diffusants through (○) SR-14 gel cups, (●) SR-11 gel cups, and (+) F-II-59 gel cups.

on the time the diffusant molecule spends near each barrier,[17] and, of course, on d, the overall thickness of the gel wall to be traversed. It is clear that the higher the cross-link density in the gel, the smaller are the pores and the larger is the number of barriers in it. Hence, the higher the cross-link density, the larger is t. The linearity of the diffusion curves in Figure 2 indicates that the diffusion is independent of the concentration C of the diffusant in the receptor compartment, permitting the use of eq 2 and 3. The results in Figure 2 are typical of all the diffusion results obtained by us. The data for SR-14 were reported previously.[7]

In Table II are tabulated the overall diffusion constants D of the five linear diffusants in Table I through DMAc-equilibrated SR-14, SR-11, and F-II-59 gel cups. Also are listed the wall thickness of all gel cups and the time lag t in seconds. The diffusion coefficients are plotted in Figure 3 as a function of the molecular weight of the five diffusant polyamides.

The results in Figure 3 are very instructive. For all curves the very gentle slope of the branch associated with

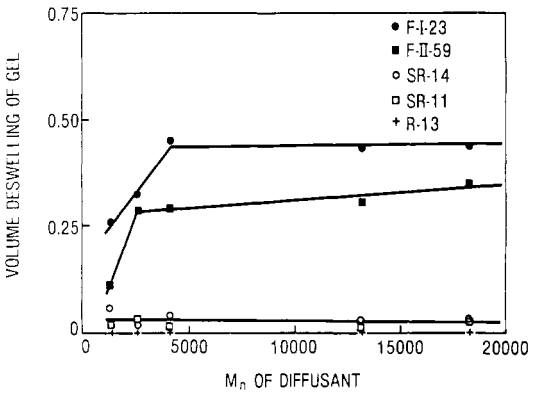


Figure 4. Volume deswelling of five gels vs. M_n of diffusant, all in DMAc.

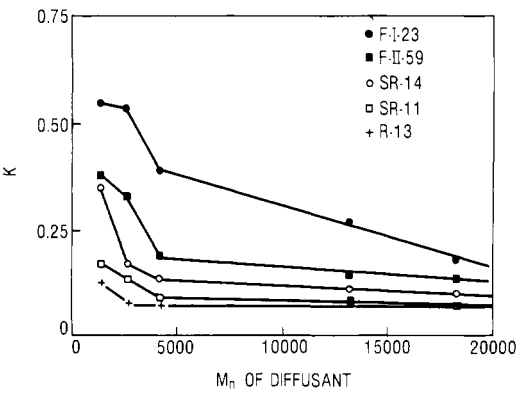


Figure 5. Diffusant partition coefficient K as a function of its M_n in five gel–solution systems. All in DMAc.

the three higher molecular weight diffusants is in reasonable agreement with a

$$D \propto 1/M_n \tag{4}$$

relationship, which can be recast as a

$$D \propto 1/L \tag{5}$$

proportionality. Attempts to fit the diffusion coefficients to a

$$D \propto 1/L^2 \tag{6}$$

relationship have failed. Thus, one concludes that the diffusion of the high molecular weight linear semirigid polyamides follows the proportionality (5) in accordance with the prediction of de Gennes[5] concerning the translational diffusion constant of stiff molecules in entangled polymer melts or gels. Because the average distance between barriers in the SR-11 gel is substantially smaller than in the SR-14 gel, the diffusion through the former is expected to be slower than through the latter.[17] The decrease in size of D values of the SR-11 gel by an order of magnitude from those of the SR-14 gel is, hence, according to expectation.

The very high values of the diffusion coefficients (in Table II and Figure 3) for the low molecular weight diffusants probably indicate that the linear polyamide I and maybe polyamide II are too short to be significantly hindered by the barriers in the gels, and the measured parameters for these two diffusants are most likely t' and D_0 and not t and D.

As can be clearly seen from Table II and Figure 3, the diffusion coefficients of all linear semirigid diffusants through F-II-59 gel were in between those obtained for SR-14 and those of SR-11. Since the average pore size of F-II-59 (59 nm between branch points) is far larger than in either semirigid gel, the diffusion results were surprising at first. Furthermore, during the diffusion studies the F-II-59 gel cups substantially shrank in size, forcing the polymer solutions inside to rise, often by several centimeters, above their initial level. The volume of liquid in the cups did not change, however. These results led us to closely examine the behavior of flexible gels and compare them with semirigid and fully rigid gels. To ensure that the observations on the F-II-59 gel cups were typical of flexible gels in general, samples of the flexible gel F-I-23 were prepared and their deswelling behavior was studied with the other gels.

Deswelling experiments were conducted as described in the Experimental Section. For specimens equilibrated in DMAc, the amount of deswelling in the presence of 2% linear polyamide is plotted in Figure 4. From it, two conclusions are obvious. First, the deswelling is very large for the two flexible gels while being of the order of 3% for the semirigid gels and 0% for the rigid gel. Second, molecular weight changes of the diffusant have no significant effect on the (negligible) deswelling of R-13, SR-11, and SR-14 gels but show strong influence on the deswelling of the F-II-59 and F-I-23 gels. Two deswelling tests with an SR-18 gel (otherwise not reported in this work) showed the same deswelling level as observed for the SR-11 and SR-14 gels.

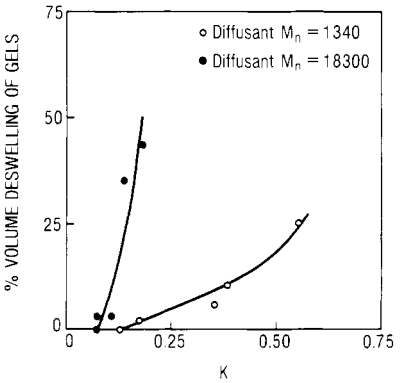


Figure 6. Volume deswelling of gels vs. partition coefficient K for two diffusants in five gels: (○) diffusant M_n = 1340; (●) diffusant M_n = 18300. All in DMAc.

The partition coefficient, K, of a diffusant is defined as

$$K = C_g/C \tag{7}$$

where C_g is the diffusant concentration in the gel and C its concentration in the surrounding solution. In Figure 5 the values of K for the five different gels are plotted as a function of the molecular weight of the linear diffusants. As expected, K decreases with increased gel rigidity. Furthermore, for each gel K increases with decreased M of the diffusant, with especially large increases for the two lowest homologues. The relationship between the volume deswelling of the five gels and the magnitude of the partition coefficient K is demonstrated in Figure 6 for the two extreme cases of linear diffusants, the one with M_n = 1340 and the one with M_n = 18300. The results of the other three diffusants fall in the interval between the two curves, in agreement with expectation. Figure 6 clearly shows that the higher molecular weight diffusant penetrates the gel less and is associated with larger deswelling than the low molecular weight diffusant. This is especially noticeable in the case of the flexible gels and is similar to the observations of Hild et al.[10] and Bastide et al.[12] concerning flexible diffusants in flexible gels.

From Figures 4 and 5 it appears that there exists a threshold where a small yet easily measurable amount of the diffusants penetrates into the R-13 gel while causing no measurable deswelling. From the base line at the R-13 gel, the volume deswelling and K values increase with increasing gel flexibility, but the increase in K for the low molecular weight diffusants is much larger than their volume deswelling while the opposite is true for the high molecular weight diffusants. This is clearly seen in Figure 6. It is interesting to note that the magnitude of K for the semirigid diffusants in the flexible gels is of the same order of magnitude as was theoretically calculated by Bastide et al.[12] and experimentally determined by Hild et al.[10] for flexible diffusants of comparable molecular weight. The situation for semirigid and, especially, rigid gels differs from that for flexible gels in that the former cannot collapse and deswell in the presence of linear polymeric diffusants as well as the latter, allowing the polymeric diffusants to penetrate the gels in significant amounts without deswelling. This behavior of the more rigid gels is different from the theoretical[12] expectations and experimental observations[8-10] for flexible gels. It may, however, approach the latter at higher diffusant concentration or molecular weight.

In a recent paper the swelling and penetration of flexible gels by homopolymer solutions were analyzed by Brochard.[13] Accordingly, there are three regimes for the penetration of linear free chains into the swollen gel. These regimes of behavior depend on the ratio L/N of the linear chain length L to the distance N between cross-links in the network and on the concentration of the linear polymer in solution. From the length and axial ratio (L/d) data in Table I and from the definition[13] of the crossover from dilute to semidilute regions, at $(DP)^{-4/5}$ (DP is the degree of polymerization) one calculates that in all diffusion and deswelling experiments for all five linear semirigid diffusants we operated in the dilute regime. Thus we must address ourselves only to the two dilute solution regimes in the Brochard paper. For flexible-chain diffusant and gel, the regimes are swollen unmixed (SUM) at $L/N > 1$, where the diffusant chains do not penetrate the gel, and swollen mixed (SM) at $L/N < 1$, where the diffusant chains penetrate the gel.

Comparison of the diffusant polymers in Table I with the characteristics of the cross-linked networks indicates that for R-13, SR-11, and SR-14 gels, the linear polymers I and II can be classified in the SM regime and polymers III, IV, and V in the SUM regime. For the flexible gels F-I-23 both linear IV and V and for F-II-59, V alone belong in the SUM regime. Based on Figures 5 and 8, it is tempting to categorize the behavior of the higher molecular weight diffusants in the various gels as SUM in the Brochard classification.[13] However, the diffusion of all diffusants through SR-11, SR-14, and F-II-59 gel cups (Figure 3) indicates that the linear polymers penetrate the gels and cannot be classified into the SUM regime. This tentative conclusion is further supported by the fact that no fractionation according to molecular weight was observed in the diffusion experiments. It is, thus, most likely that our semirigid penetrants do not conform to the Brochard model.[13]

It is important to note that the partition coefficient K and the volume deswelling appear to be qualitatively more sensitive to the rigidity of the gels than to the structural similarity between the repeat units of the linear diffusant and the gel. Within each category of gels, structural similarity between diffusant and gel may possibly cause some quantitative differences. Thus, for example, the gel F-II-59

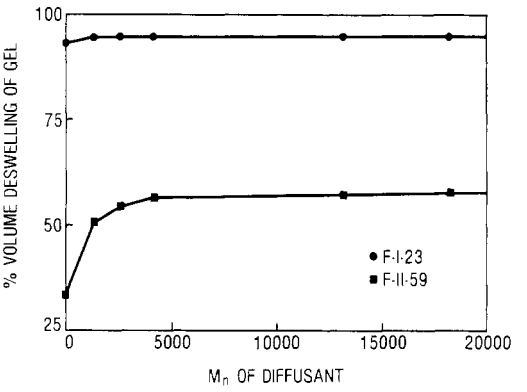


Figure 7. Volume deswelling of two flexible gels vs. M_n of diffusant. All in 30:70 DMAc/acetone.

deswells less and has a smaller K value than F-I-23, the latter being structurally closer to the linear diffusants than the former. The quantitative differences among the flexible gels are reminiscent of similar observations by Sakurada et al.[9]

It should be emphasized that in all the diffusion and deswelling studies above, when DMAc was used as a solvent, no opacity or transluscence was observed in the gels, even when deswelled in the presence of the semirigid linear polymeric diffusants. This indicates that no microsyneresis took place during the diffusion experiments and the deswelling in polymer solutions in DMAc alone.

In their work on gels of differing backbone rigidity and cross-link density, Aharoni and Wertz[14] found that semirigid and flexible polyamide gels equilibrated in the good solvent DMAc dramatically deswell and exhibit apparent microsyneresis in the form of increasing haze and turbidity only when large amounts of a nonsolvent such as acetone or methanol are introduced into the system. (Microsyneresis is a microscopic segregation of the gel into domains alternately concentrated and dilute in polymer.) Then, the deswelling and increasing turbidity occur over a relatively narrow range of solvent–nonsolvent composition. In light of the diffusion results above, it was of interest to observe the behavior of a gel that previously underwent partial or complete deswelling upon the addition of semirigid linear diffusants to the system. The solvent mixture 30:70 DMAc/acetone was chosen because all five diffusant polymers I–V in Table I were soluble in it and because one of the gels (F-II-59) was substantially deswelled and the other (F-I-23) was fully deswelled in this mixture. In this solvent mixture F-II-59 was transluscent and F-I-23 completely opaque.

The volume deswelling results are graphically shown in Figure 7. The initial points at $M_n = 0$ represent the percent volume deswelling of the gels after transfer from pure DMAc to the 30:70 DMAc/acetone mixture. The figure establishes the fact that the more deswelled the gel, the less additional deswelling it can support. The substantial deswelling of F-II-59 upon the addition of the semirigid linear diffusants is not surprising in light of the fact that the transluscent F-II-59 in the 30:70 DMAc/acetone mixture is in the middle of the steepest part of the deswelling vs. solvent compositon curve.[14] On the other hand, the small deswelling of the opaque F-I-23 is of interest. This is because once fully opaque, the deswelling of F-I-23 was not increased[14] by changes in solvent composition up to pure acetone.

Partition coefficients K of the five semirigid diffusants in two flexible gel–30:70 DMAc/acetone systems are plotted in Figure 8. Except for being about an order of magnitude smaller, they behave essentially the same as the

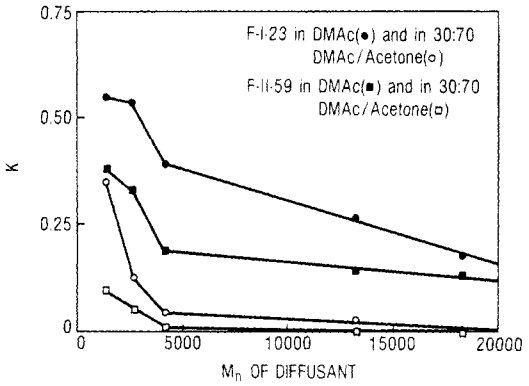


Figure 8. Diffusant partition coefficient K as function of its M_n in two flexible gels. Open symbols for 30:70 DMAc/acetone and full symbols for DMAc. Circles for F-I-23 and squares for F-II-59.

corresponding coefficients in DMAc (plotted in the same figure for comparison). As was the case in DMAc, the partition coefficients for the F-I-23 gel are consistently larger than those for F-II-59. It is of interest to note that a general similarity exists between K vs. M_n curves of the flexible gels and those calculated by Bastide et al.,[12] except that in our case the curves are displaced to much lower molecular weights. The similarity does not hold for the R-13 gel and probably the two semirigid gels that appear not to reach $K = 0$ with increased M_n of the semirigid diffusants.

The polymer network concentration in all the DMAc-equilibrated gels was higher than the solution concentration during the diffusion runs and the surrounding solution during deswelling experiments. When equilibrated in 30:70 DMAc/acetone, the flexible polymer network concentration in the deswelled gel was larger than in pure DMAc. The transluscence of F-II-59 and opacity of F-I-23 in this solvent mixture indicate an increasing amount of microsyneresis.[14,18] During the equilibration in the mixed solvent, F-II-59 shrank by 33% from 3.8% to 5.1% concentration while F-I-23 shrank by 93% from 2.22% to 31.7% concentration. It is most unlikely that the network concentration in the dilute microdomains during microsyneresis is less than it was in the DMAc-equilibrated gel, especially in the case of F-I-23. The fact that the value of K for the less concentrated F-II-59 gel in mixed solvent is significantly smaller than the value for the more concentrated F-I-23 gel may indicate that gel–diffusant compatibility effects are not negligible even though K does decrease with increased network concentration in the gel, as can be seen from Figure 8.

In the case of the deswelled flexible gels, especially F-I-23 in Figure 7, all linear diffusants may be classified in the SUM regime of the Brochard model.[13] The K values for F-I-23 in Figure 8 indicate, however, that linear diffusants do penetrate the gel even when very deswelled. Furthermore, the measured deswelling of the flexible gels in both SUM and SM regimes is in disagreement with the theoretical expectations,[13] especially for the SUM case. These observations go, we believe, against the use of the Brochard model to describe inflexible diffusants.

There are two explanations to the deviation of our observations on flexible gels from the Brochard treatment. According to one, the behavior of the semirigid diffusants with $D \propto 1/L$ is fundamentally different from that of flexible diffusants obeying[19,20] $D \propto 1/L^2$, rendering models valid for flexible penetrants invalid for semirigid or rigid diffusants. The other explanation is that models valid for flexible gels are invalid for gels of higher rigidity. At present we do not know whether either or both explanations are valid. It should be noted that the low entropy of mixing of semirigid macromolecules,[21] as compared with flexible-chain solutions,[22] may indirectly contribute to both explanations above. We tentatively conclude that the reasonable agreement between the values of K and the deswelling observed in our experiments with flexible gels and expected from the model of Bastide et al.[12] indicates that in the case of flexible gels and relatively low molecular weight diffusants this model approximates reality.

In Figure 3, the diffusion coefficient D of the F-II-59 gel falls in between the values of the SR-14 and SR-11 gels. In Figure 5 the partition coefficient K of F-II-59 is larger than K of both SR-14 and SR-11. We are not sure where the difference in behavior arises from. One possibility, which we cannot assess, is that during the deswelling experiments, measurements were always taken well after equilibrium was reached. In the case of diffusion, however, the time lag from which D is calculated is the moment when the diffusant front crossed the whole width of the gel cup wall. Until that very moment no equilibrium existed in the F-II-59 gel: it was swollen in the DMAc and undergoing deswelling in the polymer solution. It may be that this lack of equilibrium and deswelling along with the progress of the diffusant front across the gel cup wall of F-II-59 causes the time lag to increase and D to decrease for diffusion through F-II-59 gel cups. Furthermore, it is possible that the diffusion of rodlike particles through flexible gels is described by a proportionality constant different from that associated with more rigid gels, even though proportionality 5 holds true as indicated by de Gennes[5] and observed in our measurements for the diffusion of semirigid molecules in both flexible and semirigid gels. Additional, possibly interrupted, diffusion studies through thick flexible gels must be performed in order to clarify this point.

Conclusions

Above a low threshold length, linear semirigid aromatic polyamides diffuse through swollen gels, exhibiting a diffusion constant inversely proportional to their length. This is in agreement with theoretical expectations for rodlike molecules and in disagreement with flexible diffusant macromolecules, whose diffusion coefficient is inversely proportional to the square of their length.

Gels equilibrated in a good solvent deswell when brought in contact with polymer solutions in the same solvent. Qualitatively, the more flexible the chains in the cross-linked network, the larger is the deswelling. Semirigid gels deswell very little and rigid gels not at all. The degree of cross-linking appears to be far less important than the chain flexibility. The large deswelling of flexible gels appears to decrease the diffusion of semirigid macromolecules through them.

The distribution of semirigid macromolecules in a gel and the surrounding solution depends on the chain flexibility of the gel and the molecular weight (length) of the penetrant molecules. In the case of the more rigid gels a small, constant amount of linear semirigid macromolecules penetrate the gel even in the absence of meaningful deswelling. From the slopes of curves, it appears that pentration into the flexible gels will become negligible at penetrant molecular weights about tenfold higher than available in the present study. At this point the volume shrinkage of the gel will asymptotically reach its maximum. The behavior of the flexible gels in the presence of semirigid penetrants is in qualitative agreement with expectations according to the Bastide et al.[12] model. Deswelling the flexible gels in poor solvent mixture and then repeating the penetration experiments with semirigid macromole-

cules strengthened the above conclusions. In addition, it indicated that upon large deswelling, macrosyneresis appears in the flexible gels.

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Generalized Reptation Model

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ABSTRACT: The reptation model is generalized on the basis of a theory that accounts for hindered defect diffusion along the chain. A basic ingredient of the theory is a waiting time distribution for the hops of elementary defects that store length. Important rheological quantities are found to generally depend on fractional powers of the molecular mass rather than on integer powers as in the conventional reptation picture.

Recently, de Gennes proposed a theory[1] that attempts to explain the long-time dynamics of entangled polymer systems on a molecular basis. According to his reptation hypothesis, a linear polymer is restricted to a snake-like motion within a virtual tube that simulates the topological restrictions due to entanglements with other polymers. The theory was augmented by Doi and Edwards.[2] Still it exhibits some major difficulties. For example, the terminal relaxation time τ_t and the static shear viscosity $\mu(0)$ are found to depend on the third power of the molecular weight M while experiment yields $\tau_t \sim \mu(0) \sim M^\alpha$, with α in the range 3.3–3.4.[3] This discrepancy may not be explained by polydispersity effects, as is widely believed, or by fluctuations, which lead to a fractional *molecular weight* dependent exponent.[3]

From a theoretical point of view the discrepancy is very fundamental. At worst it implies a different model, i.e., a molecular mechanism different from the reptation concept since "there is no obvious correction which might increase the exponent from 3 to the experimental value of 3.3.[4] Recently, the situation has become even more confusing due to the measurements of the polymer diffusion coefficient D_3,[5] which was found to obey the law $D_3 \sim M^{-2}$ as predicted by the conventional reptation model.

Here we propose an extension of the reptation model that, depending on the time scale of interest, yields the fractional power dependences required by some experiments as well as the integer dependence required by others.

The essence of the reptation hypothesis[1] lies in the confinement of a polymer to one-dimensional diffusion. Diffusion is effected by density fluctuations of a dilute defect gas, i.e., by defects migrating freely along the chain. Each defect stores length b. The corresponding diffusion coefficient D_1 is a microscopic constant characteristic of local jump processes and is independent of the molecular mass M. The equilibration time τ_d of the defect gas is the time for a single defect to perform a mean-square displacement equal to the square of the contour length of the polymer; i.e., $\tau_d \sim (Na)^2/D_1$. Here a is the separation of two adjacent "monomers", of which there are N. Because of its M^2 dependence, τ_d cannot be identified with the terminal relaxation time τ_t. Thus de Gennes introduced the time τ_r a polymer needs to disengage completely from its initial tube. For ρb defects per length b (ρ is the defect density per unit length) it takes a time $\tau_r = \tau_d(Na/\rho b^2) \sim (Na)^3/D_1\rho b^2$ for the chain to renew its surroundings. Thus τ_r depends on the third power of M and is identified with τ_t, which is found to be proportional to $M^{3.4}$.[3]

The nature and spatial extension of a reptation defect have not been discussed. Yet, larger scale fluctuation processes can be excluded because of the large energies involved. As an example, we restrict ourselves to discussing elementary defects, gt$\bar{g}$ defects or kinks, respectively. The typical kink defect energy for polyethylene is $\Delta E \sim 1.2$ kcal/mol[6] and a conservative estimate yields a defect density of 14% at room temperature[7] compared to a saturation concentration of 25%. Thus, except for experiments on the scale of time $t \to \infty$, the assumption of a dilute freely moving defect gas is not entirely justified. This combined with the fact that the tube topology imposes strong temporary restrictions on the defect distribution, especially around points of entanglement, casts

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