(5) H. Kresse and R. V. Talrose, *Makromol. Chem., Rapid Commun.*, 2, 369 (1981).
(6) P. Törmälä, *J. Macromol. Sci., Rev. Macromol. Chem.*, C17, 298 (1979).
(7) L. Bosio, B. Fayolle, C. Friedrich, F. Lauprêtre, P. Meurisse, C. Noël, and J. Virlet, in "Liquid Crystals and Ordered Fluids", A. Griffin and J. Johnson, Eds., Plenum Press, Vol. 4 (in press).
(8) B. Fayolle, C. Noël, and J. Billard, *J. Phys. (Paris)*, **40**, C3-485 (1979).
(9) E. G. Rozantsev and V. D. Sholle, *Synthesis*, **4**, 190 (1971).
(10) R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, **11**, 3273 (1965).
(11) J. C. Williams, R. Mehlhorn, and A. D. Keith, *Chem. Phys. Lipids*, **7**, 207 (1971).
(12) H. Kelker, and R. Hatz, "Handbook of Liquid Crystals", Verlag Chemie, 1980.
(13) C. Noël, L. Monnerie, M. F. Achard, F. Hardouin, G. Sigaud, and H. Gasparoux, *Polymer*, **22**, 578 (1981).
(14) L. Liebert, L. Strzelecki, D. Van Luyen, and A. M. Levelut, *Eur. Polym. J.*, **17**, 71 (1981).
(15) F. Volino, A. F. Martins, R. B. Blumstein, and A. Blumstein, *C. R. Hebd. Seances Acad. Sci.*, **292**, 829 (1981); *J. Phys. (Paris), Lett.* **42**, L305 (1981).
(16) S. Maret, A. Blumstein, and S. Vilasagar, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **22**, 246 (1981).
(17) F. Hardouin, M. F. Achard, H. Gasparoux, L. Liebert, and L. Strzelecki, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 975 (1982).
(18) J. H. Freed, G. V. Bruno, and C. F. Polnaszek, *J. Phys. Chem.*, **75**, 3385 (1971).
(19) J. H. Freed, in "Spin Labeling: Theory and Applications", L. J. Berliner, Ed., Academic Press, New York, 1976, p 53.
(20) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).
(21) J. H. Freed, *J. Chem. Phys.*, **41**, 2077 (1964).
(22) A. Hudson and G. R. Luckhurst, *Chem. Rev.*, **69**, 191 (1969).
(23) P. L. Nordio, in "Spin Labeling: Theory and Applications", L. J. Berliner, Ed., Academic Press, New York, 1976, p 5.
(24) J. S. Hwang, R. P. Mason, L. P. Hwang, and J. H. Freed, *J. Phys. Chem.*, **79**, 489 (1975).
(25) S. Gade, A. Chow, and R. Knispel, *J. Magn. Reson.*, **40**, 273 (1980).
(26) (a) S. A. Goldman, G. V. Bruno, and J. H. Freed, *J. Phys. Chem.*, **76**, 1858 (1972); (b) R. C. McCalley, E. J. Shimshick, and H. M. McConnell, *Chem. Phys. Lett.*, **13**, 115 (1972).
(27) P. L. Nordio, *Chem. Phys. Lett.*, **6**, 250 (1970).
(28) P. M. Smith, *Eur. Polym. J.*, **15**, 147 (1979).
(29) A. L. Kovarskii, J. Plaček, and F. Szöcs, *Polymer*, **19**, 1137 (1978).
(30) A. M. Wasserman, T. A. Alexandrova, and A. L. Buchachenko, *Eur. Polym. J.*, **12**, 691 (1976).
(31) (a) P. M. Smith, R. F. Boyer, and P. L. Kumler, *Macromolecules*, **12**, 61 (1979); (b) R. F. Boyer and P. L. Kumler, *ibid.*, **10**, 461 (1977); **9**, 903 (1976).
(32) A. T. Bullock, G. G. Cameron, and P. M. Smith, (a) *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 1263 (1973); (b) *Eur. Polym. J.*, **11**, 617 (1975).
(33) M. C. Lang, C. Noël, and A. P. Legrand, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1329 (1977).
(34) A. L. Kovarskii, A. M. Vasserman, and A. L. Buchachenko, *Vysokomol. Soedin., Ser. A*, **13**, 1647 (1971).
(35) A. N. Kuznetsov and B. Ebert, *Chem. Phys. Lett.*, **25**, 342 (1974).
(36) A. S. Waggoner, O. H. Griffith, and C. R. Christensen, *Proc. Natl. Acad. Sci. U.S.A.*, **57**, 1198 (1967).
(37) S. Vivatpanachart, H. Nomura, and Y. Miyahara, *Polym. J.*, **13**, 481 (1981).
(38) S. C. Gross, *J. Polym. Sci., Part A-1*, **9**, 3327 (1971).
(39) G. P. Rabold, *J. Polym. Sci., Part A-1*, **7**, 1203 (1969).
(40) R. F. Boyer and P. L. Kumler, 10th Europhysics Conference on Macromolecular Physics: "Structure and Motion in Polymeric Glasses", Noordwijkerhout, 1980, p 190.
(41) S. Lee and I. M. Brown, *Macromolecules*, **12**, 1235 (1979). I. M. Brown, *Macromolecules*, **14**, 801 (1981).
(42) R. P. Mason, C. F. Polnaszek, and J. H. Freed, *J. Phys. Chem.*, **78**, 1324 (1974).
(43) E. L. Wee and W. Miller, *J. Phys. Chem.*, **77**, 182 (1973).
(44) P. Törmälä, *Eur. Polym. J.*, **10**, 519 (1974).
(45) Z. Veksli and W. G. Miller, *Macromolecules*, **10**, 1245 (1977).

Small-Angle Neutron Scattering and Light Spectroscopy Investigation of Polystyrene Gels under Osmotic Deswelling

Jacques Bastide,* Robert Duplessix, and Claude Picot

Centre de Recherches sur les Macromolécules, 67083 Strasbourg Cedex, France

Sauveur Candau

Laboratoire d'Acoustique Moléculaire, Université Louis Pasteur, 67070 Strasbourg Cedex, France.

Received November 29, 1982

ABSTRACT: Neutron scattering experiments on a partially labeled gel and quasi-elastic light scattering measurements are reported. The radius of gyration of the elementary mesh of the labeled network is shown to remain nearly constant when the gel is deswollen by a factor of 4 in volume. This result is in contradiction with the fundamental hypothesis of the classical theories of gel swelling; however, it can be understood by considering a rearrangement of the network at a scale larger than the mesh. The cooperative diffusion constant D_c of the osmotically deswollen gels was measured by using the quasi-elastic light scattering. The apparent scaling law of D_c vs. ϕ, the polymer volume fraction of the gel, is shown to differ significantly from that corresponding to a series of gels swollen at equilibrium in a pure solvent. This result is interpreted in the framework of a phenomenological scaling approach, consistent with the neutron scattering results. This approach allows the calculation of the variation with ϕ of K_{os} and G, the osmotic bulk modulus and the shear modulus of the gel, respectively, which appear in the expression for D_c.

Introduction

In order to understand the thermodynamic behavior of polymeric networks, a knowledge of the relation between macroscopic and microscopic properties is required. Most of the available theories of polymer networks are based on some fundamental assumptions regarding the local deformation of polymer chains as a function of the network state of strain or swelling. However, for a long time the validity of these assumptions could not be directly checked. In this regard, important progress has been achieved recently through experiments with small-angle neutron scattering (SANS). SANS associated with partial deuteration is a very efficient technique for characterizing the conformation of the elastic chains in a cross-linked polymer. The angular dependence of the neutron scattering intensity given by networks containing small amounts of

0024-9297/84/2217-0083$01.50/0

Table I

sample	nature of the synthesis	M_n of the elementary mesh	swelling degree in pure benzene	(DVB)/(LE)	C_P PS conc prior to cross-linking	fraction of mono-functional chains
A	anionic; 5% of the chains are deuterated	26 000	17.4	3	0.091	0
54	anionic	34 500	20.5	5	0.091	0
56	anionic	35 000	20.4	5	0.091	0.3
58	anionic	30 000	23.8	5	0.091	0.6
64	anionic	12 500	9.8	3	0.109	0
65	anionic	12 500	8.5	3	0.146	0
B7	radicalar		16	0.010[a]	0.3[b]	
B12	radicalar		8.5	0.013[a]	0.3[b]	
G24	radicalar		25.6			

[a] Concentration of DVB prior to cross-linking. [b] Concentration of styrene prior to cross-linking.

Table II

polymer volume fraction		swelling deg of gel
in deswelling solution	of gel phase	$Q = V/V_{\mathrm{dry}}$
o (pure benzene)	0.0575	17.4
0.0187	0.0685	14.6
0.0467	0.0909	11
0.0748	0.1149	8.7
0.1121	0.1266	7.9
0.187	0.2083	4.8

perdeuterated chains enables the determination of the mean conformation of a network chain, characterized by its radius of gyration. This can be performed in the dry state as well as in the swollen state.

The first aim of the study reported here is to investigate the variation of the radius of gyration of the elastic chains as a function of macroscopic swelling degree. For this purpose, a polystyrene network initially swollen at equilibrium in benzene is subsequently deswollen by addition of large linear polystyrene chains to the surrounding solvent. These chains do not penetrate into the gel phase[1,2] and large deswelling may be obtained (ranging from 1 to 4 in volume) without change of the local polymer–solvent interactions. The radius of gyration of the labeled network chains is measured for different concentrations of the linear polymer chains in the surrounding solution.

The second part of this paper deals with the dynamics associated with the collective fluctuations of the network. In previous papers, light spectroscopy studies performed on model polymer networks swollen at equilibrium in good solvents were reported.[3-5] The results were interpreted by using a scaling approach derived for semidilute solutions of large linear macromolecules. The cooperative diffusion constant measured for a set of networks having different cross-linking degrees was found to vary with the swelling equilibrium concentration according to the same power law as that found for semidilute solutions. In swollen networks, the restoring force for a concentration fluctuation arises from two contributions, one of purely osmotic nature and the other associated with the elasticity of the network. In the previous experiments, it was not possible to determine the relative weights of these two contributions, since both had the same scaling laws as a function of the swelling equilibrium concentration. By contrast, when a network of given cross-linking degree is progressively deswollen, the osmotic compressibility and the shear modulus exhibit different concentration dependences. In this paper, we report measurements of the cooperative diffusion constant as a function of polymer concentration for several gels prepared from different cross-linking methods under osmotic deswelling. The results suggest that some of the principal assumptions of current gel elasticity theories have to be revised.

I. Experimental Section

1. **Preparation and Characteristics. (a) Anionic Polystyrene Networks.** Such networks are obtained by anionic block copolymerization of styrene with a small amount of divinylbenzene (DVB), using a method that has been described earlier.[6,7]

First, bifunctional living polystyrene is prepared at low temperature (−70 °C) in an aprotic solvent (equivolume mixture of tetrahydrofuran and toluene) using a bifunctional initiator (α-methylstyrene tetramer). When a small amount of DVB is added to the "living" polystyrene solution, the DVB polymerization is initiated only by the living ends of the polystyrene molecules, resulting in a cross-linked network in which each linear element is connected to two different branch points consisting of poly(vinylbenzene) nodules. Prior to the reaction a small aliquot of the living precursor polystyrene was removed for characterization. The average molecular weight of the precursor polystyrene was determined by gel permeation chromatography (GPC). In Table I are listed the sample references, the molecular weight of the precursors, and the swelling degrees of the gels in benzene. Sample A was prepared from a precursor polymer containing 5% of deuterated chains for use as probes for SANS.[8-11] Samples 56 and 58 were prepared by using as a precursor a mixture of difunctional and monofunctional polystyrene chains. These last molecules react only by one end and therefore form dangling chains in the network. The characteristics and the properties of these networks were investigated in a previous study.[12] For the deswelling experiments we have used as surrounding polymer an anionically prepared polystyrene of molecular weight $M_w = 763000$ (polydispersity $M_w/M_n = 1.15$).

(b) Free Radical Networks. These networks were obtained by free radical copolymerization of mixtures of styrene and divinylbenzene, using azobisisobutyronitrile as initiator. The procedure is described in detail in ref 13 and 14. Two samples prepared from this method were investigated in this study and are listed in Table I.

2. **Deswelling Measurements.** In Table II, we have listed the equilibrium concentrations of the network A obtained for different concentrations of the swelling polymer solution in benzene. When the swelling solution is very concentrated, it is difficult to separate the gel sample from its surrounding liquid and then apply the usual weighing method. Therefore, we measured the volume swelling degree by an optical method, and the equilibrium concentration was obtained by using the following relationship:

$$\phi_e = (Q_e)^{-1}$$

Q_e is the swelling equilibrium degree.

The experimental data obtained for the internal concentration of the gel vs. the external solution concentration were studied previously and reported elsewhere.[2] Only the internal polymer volume fraction inside the gel phase, which is needed in the present work, is considered in the quasi-elastic light scattering results section.

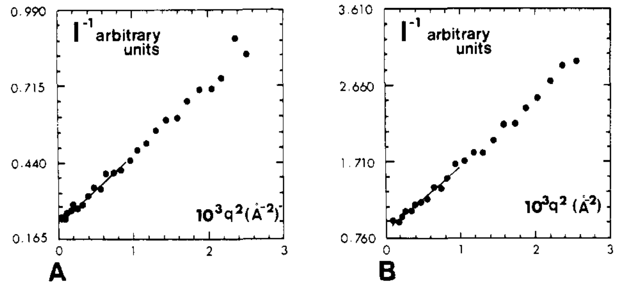

Figure 1. Inverse neutron scattering intensity vs. q^2 for a partially labeled network: (A) at the swelling equilibrium in benzene ($Q = 17.4$); (B) deswollen ($Q = 4.8$).

3. Small-Angle Neutron Scattering (SANS). SANS experiments were carried out with D11 and D17 spectrometers at the Institut Laue Langevin in Grenoble, France (neutron beam facilities at HFR available for users, ILL (Sept 1977)). The swollen polystyrene network samples were held between quartz windows, and the measurement area was defined by a 1.0-cm-front diaphragm. The coherent scattering signal of labeled chains in the swollen networks (5% of perdeuterated chains) was obtained by subtraction of appropriate incoherent scattering background. The isotopic composition of the swelling solvent (benzene H + D) was adjusted in order to match the contribution of the protonated chains. Detector normalization was performed by using the flat incoherent scattering signal given by water under identical experimental conditions. Intensities were recorded on a two-dimensional multidetector (64 × 64 cells). Two sample detector distances were used on the D11 spectrometer (10.66 and 5.66 m), and a 2.82-m distance was used on the D17. Under such conditions, scattering intensities could be measured for scattering vectors $\vec{q}$ ($|\vec{q}| = (4\pi/\lambda)\sin(\theta/2)$, where λ is wavelength and θ is scattering angle) ranging between 5×10^{-3} and 10^{-1} Å^{-1}.

The scattering intensity spectra can be used to obtain model-independent information about the conformation of deuterated chains in the network. In particular, for very small scattering vectors, q, the average radius of gyration of the labeled chains, R_g, may be obtained with the help of the Guinier approximation. Then, for $qR_g << 1$ and infinitely small concentrations of deuterated chains, the scattering intensity is[15]

$$I(q) \simeq K\phi_D N(1 - q^2R_g^2/3) \qquad (1)$$

where ϕ_D is the volume fraction of deuterated chains, N their polymerization index, and K a numerical constant (involving contrast factor and apparatus geometry). We have obtained R_g from the Zimm representation: practically, $I(q)$ vs. q^2 is well approximated by a straight line, and R_g is given by (see Figure 1)

$$R_g = \left[\frac{(I(q)^{-1} - (I(0))^{-1}}{(I(0))^{-1}}\,\frac{3}{q^2}\right]^{1/2} \qquad (2)$$

It should be stressed that such a procedure may introduce some systematic errors if the q values are of the order of $1/R_g$ and if the concentration of the deuterated chains is not small enough. However, as we estimate below, the sum of these two systematic errors is negligible as compared to the statistical error, which is about ±5% for D17 and D11 (5 m) and ±10% for D11 (10 m).

Discussion of the Systematic Errors. (i) The radii of gyration were determined from eq 2 at the limit of the Guinier range ($0.5 < qR_g < 1.7$). Therefore, in principle, the equations for the scattering intensity should be modified in order to take into account higher chain distribution moments. Such an elaborate analysis, however, is not justified by the precision of our intensity measurements. If the network chain statistics were Gaussian, the intensity would be described by the Debye scattering function. Then the apparent radius of gyration obtained from eq 12 applied to the Debye function in the sample, $0.5 < qR_g < 1.7$, would be overestimated with respect to the acutal one by about 7%. If the chain statistics are of excluded volume type rather than Gaussian, this error will be smaller (≃4%). Moreover, a slight polydispersity ($M_w/M_n \sim 1.20$) of the chain reduces further this overestimation.

(ii) The scattering intensity increases when the fraction of deuterated chains in the network is increased. However, this is a source of systematic error in the determination of the radius of gyration given by eq 2. In fact, in this equation the interchain correlation effect is neglected. If all the chains were deuterated, such correlations would be as important as the interchain correlations described by eq 1, since the overall monomer concentration in the gel corresponds to a semidilute range ($\phi \sim \phi^*$). Only a small fraction of chains is labeled in our gel; thus the contribution to the scattered intensity, due to the fluctuations of concentration of monomers belonging to different labeled chains, is small. Actually, within the mean field theory, the scattering intensity for small q vector can be expressed, for semidilute solutions as[16]

$$I(q) = K\phi_D N\left\{1 - \frac{q^2R_g^2}{3} - \frac{Nu\phi_D}{1 + Nu\phi}f(q)\right\} \qquad (3)$$

where u characterizes the effective monomer–monomer interaction and is equal to v/v_s (v is the excluded volume parameter and v_s is the molecular volume of the solvent) and $f(q)$ is an interchain correlation function normalized to unity for $q = 0$. Within the range of distances probed by the neutron scattering technique, interchain correlations should be comparable to that of a semidilute solution. At a larger scale, crosslinking inhomogeneities exist, as revealed by the quasi-elastic light scattering experiments. However, the stray scattering associated with these long-range fluctuations affects only the smallest values of the explored q range, which are not used in the determination of the radius of gyration. Therefore we estimate the error in determining R_g with eq 2 by comparison with the case of semidilute solutions (eq 3). For typical values of ϕ_D and ϕ of our gel, the error is an underestimation of about 4%. The overestimation of (i) and the underestimation of (ii) have approximately the same absolute value. Therefore, these systematic errors roughly compensate each other.

4. Correlation Time Measurements. Hydrodynamic theories of gels[17,18] predict that the time-dependent term of the autocorrelation function of light scattered from a swollen polymer network is a single exponential with a time constant τ_c given by

$$\tau_c = (2k^2D_c)^{-1} \qquad (4)$$

where D_c is the cooperative diffusion coefficient. The magnitude of the scattering vector $\vec{k}$ is given by

$$k = (4\pi n \sin(\theta/2))/\lambda \qquad (5)$$

where θ is the scattering angle, λ is the wavelength of the incident light in a vacuum, and n is the index of refraction of the scattering medium.

The optical source on the light scattering apparatus is a Spectra-Physics argon ion laser operating at 4880 Å. The scattered light is collected at a predetermined angle by a lens–aperture system and focused on a photomultiplier (ITT, FW 130) cathode. The time-dependent correlation function of the scattered intensity is derived by using a 96-channel digital correlator (Precision Devices and Systems LTD Malvern System 4300).

The cube- or cylinder-shaped samples (~1 cm^3) were put in standard glass cells containing an excess of swelling liquid. They were allowed to stand for at least 1 day to attain thermodynamica stability. All the measurements were performed at room temperature (22 °C).

In previous papers from this laboratory it was shown that the intensity scattered from longitudinal fluctuations of swollen networks is generally heterodyned to some extent by the static component due to microscopic heterogeneities. In order to check whether the scattered signal is fully heterodyned, we measured the autocorrelation function obtained by mixing the scattered signal with an external oscillator using a Michelson-type interferometer. The comparison between the results obtained with and without reference beam is discussed in the next section.

Intensity correlation data were routinely processed by using the method of cumulants[19] to provide the average decay rate $\langle\Gamma\rangle$ and the variance $\bar{v}$. The latter is a measure of the width of the distribution of the decay rates and is given by

$$\bar{v} = (\langle\Gamma^2\rangle - \langle\Gamma\rangle^2)/\langle\Gamma\rangle^2 \qquad (6)$$

$\langle\Gamma^2\rangle$ is the second moment of the distribution. The scattering from microscopic swelling inhomogeneities of the gel generally

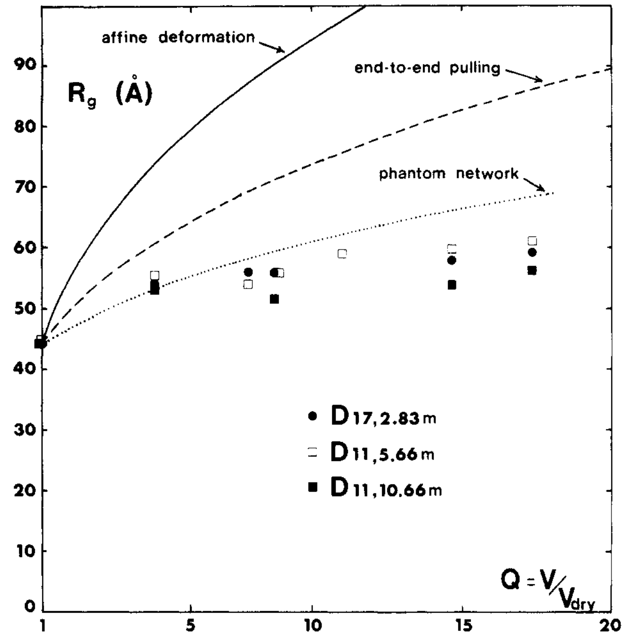

Figure 2. Radius of gyration of the labeled chains of the network as a function of the swelling degree.

exhibits long-time fluctuations, which may produce an error in the determination of the flat background B of the autocorrelation function. Therefore, instead of using the general procedure based on the mean unclipped and clipped count rates per sample time,[20] we have considered B as an adjustable parameter in the fitting procedure. For the investigated gels the ratio between the fitted and computed values of B ranges from 1.002 to 1.02.

II. Experimental Results

1. Small-Angle Neutron Scattering. SANS experimental results obtained on sample 1 are plotted in Figure 2. Dimensions of the elastic chains in this sample in the dry and the swollen (in pure benzene) states have been previously investigated.[8,10] While the values corresponding to the dry sample are in very good agreement, the repeated experiments for the sample in pure benzene lead to systematically slightly lower values. The variation of R_g resulting from the osmotic deswelling remains in the range of the experimental error. At the limit of the experimental precision of the results, only a weak variation could be invoked, in any case much smaller than the one expected from an affine deformation of the chains.

2. Intensity Correlation. The autocorrelation function of light scattered from the investigated gels contains in addition to the exponential term a quasi-static component, which has been previously attributed to the effect of microscopic swelling inhomogeneities. Experiments performed with a two-beam interferometer (cf. Experimental Section) show that the time-dependent term is fully heterodyned by the static scattering except in the case of the more dilute gels, for which a slight increase (~5%) of the decay time is observed when the reference beam is superimposed on the scattered signal. As a consequence, the average cooperative diffusion constant $\langle D_c \rangle$ is related to the time constant τ_c of the exponential term through

$$\tau_c = (k^2 \langle D_c \rangle)^{-1} \tag{7}$$

The quality of the exponential fit is very good, as can be ascertained from the very low values of the variance ($0.005 < \bar{v} < 0.05$) and of the mean square deviation per channel between the experimental curve and the exponential, which is typically of the order of 5×10^{-3}.

It must be emphasized that this behavior is very different from that of semidilute solutions, which generally exhibit nonexponential autocorrelation functions in the same range of concentrations.[21] These deviations from the exponential behavior have been attributed to the effect of concentration inhomogeneities.[22] Such fluctuations are rather similar to the microscopic swelling inhomogeneities evidenced in the gels. However, in the latter case, the inhomogeneities are more or less frozen because of the cross-links, and their motion is not coupled to the fast modes associated with network deformation. Figure 3 shows a log–log plot of $\langle D_c \rangle$ vs. the equilibrium concentration ψ of the investigated polystyrene networks swollen in pure benzene. The variation of $\langle D_c \rangle$ with ψ is similar to that observed in semidilute solutions of high molecular

Table III

A. Anionic Gels

sample	$10^2\phi_e$	$10^2\phi$	$10^7\langle D_c \rangle$, cm^2 s^{-1}
54	0	4.9	9.4
	4.7	7.3	10.6
	9.4	10.6	13.4
	14	15.4	14.5
	18.7	19.2	15.5
64	0	10.2	14.7
	4.7	13.4[a]	16.4
	9.4	16.7	
	14	20	14.8
	18.7	23.6[b]	16.2
65	0	11.8	15.8
	4.7	14.6[a]	16.8
	9.4	17.5	17.3
	14	20.4	16.9
	18.7	23.8[b]	17.1

B. Gels with Pendant Chains

sample	p[c]	$10^2\phi_e$	$10^2\phi$	$10^7\langle D_c \rangle$, cm^2 s^{-1}
56[d]	0.3	0	4.9	8.5
		4.7	7.3	9.6
		9.4	10.6	11.4
		14	15.4	12.6
		18.7	19.2	14.6
58	0.6	0	4.2	5.1
		4.7	7.7	8.4
		9.4	12.5	11.6
		14	17.8	14
		18.7	27.1	17.7

[a] Interpolated value. [b] Extrapolated value. [c] Fraction of monofunctional chains prior to cross-linking (see text). [d] For this series the deswelling degrees have not been measured and were assumed to be the same as for sample 54.

Table IV
Radical Gels

sample	$10^2\phi_e$	$10^2\phi$	$10^7\langle D_c \rangle$, cm^2 s^{-1}
B7	0	6.25	12.8
	4.7	8.8	13.7
	9.4	10.9	14.3
	14	15.6	15.8
	18.7	21.7	18.3
B12	0	11.8	16.6
	9.4	16.7[a]	16.4
	14	19.5[a]	18
	18.7	23.7[a]	18
	23.4	27.8	18.3
G24	0	3.9	8.2
	4.7	9.8	12
	9.4	11.6	12.3
	14	15.7	14.5
	18.7	20.7	17

[a] Interpolated value.

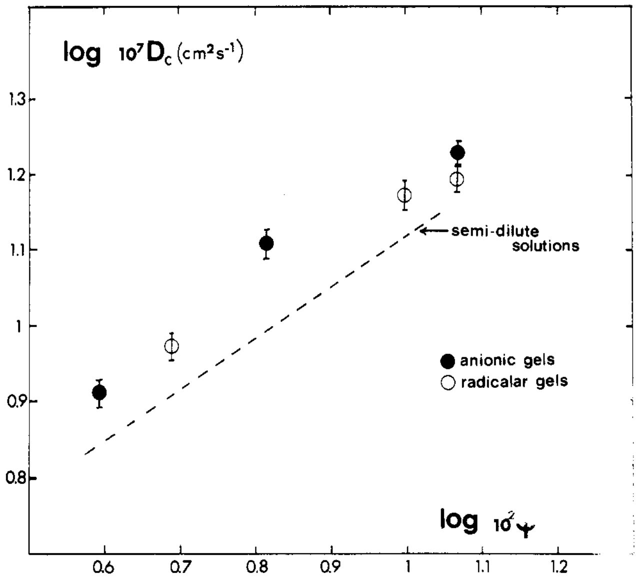

Figure 3. Variation of the cooperative diffusion constant D_c with the polymer volume fraction ψ for networks swollen at equilibrium in pure diluent.

weight polystyrene (dashed line), thus confirming our previous result on other polystyrene–benzene gels.

Figures 4 and 5 and Tables III and IV show the effect of the osmotic deswelling on the diffusion constant. For both anionic and radical gels, $\langle D_c\rangle$ is found to increase with the gel concentration. In a log–log representation, the data may be fitted approximately to a straight line. The slopes of these straight lines decrease when the equilibrium volume fractions of the networks in pure solvent increases. Furthermore, it must be noticed that the experimental values of the slopes are smaller that the value 0.67 obtained for semidilute solutions. In Figure 5 are also reported the data obtained for two gels containing pendant chains. In a previous paper,[12] it was shown that the equilibrium concentration of gels is rather insensitive to the presence of pendant chains whereas the diffusion constant decreases when the amount of such chains increases. The effect of the osmotic deswelling on the diffusion constant $\langle D_c\rangle$ depends also considerably on the amount of pendant chains. Variations of $\langle D_c\rangle$ with the polymer volume fraction ϕ_i of the gel are approximately the same for both networks 56 and 54, with 30% of monofunctional precursor polymer and with pure bifunctional precursor, respectively (curves 1 and 2 of Figure 5). On the other hand, gel 58, which contains a large amount of pendant chains, exhibits a much larger variation of $\langle D_c\rangle$ with ϕ_i than for other gels. The value of the slope of the straight line that best fits the experimental points is equal to 0.66.

III. Discussion

1. Neutron Scattering Data. (a) Classical Models. The results of Figure 2 illustrate the ability of a network to undergo large deformation without significant change of the network chain conformation. The question arises then as to whether or not this result is compatible with current theories of gel swelling. The average radius of gyration of the labeled chains, which is obtained from the neutron scattering data, can be expressed as follows:

$$\langle R_g^2\rangle = \frac{1}{2N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle r_{ij}^2\rangle \qquad (8)$$

where N is the polymerization index of the chain. The average $\langle r_{ij}^2\rangle$ can be calculated within the framework of various models. Certain rubber elasticity theories suppose an affine deformation in the macroscopic strain of the cross-link positions.[23,24] This means that a chain vector $\vec{r}_0$ in the undeformed state is transformed to $\vec{r} = \lambda\vec{r}_0$ by the strain. Within the framework of this assumption the so-called end-to-end pulling model[10,25,26] assumes that the chains are free to rearrange, provided their end-to-end vectors are affinely transformed. We recall briefly the main features of the derivation, in the more recent and elegant form given by Ullman[27]

$$\langle r_{ij}^2\rangle = \int \omega(\vec{r}_{ij}/\vec{R})\omega_\lambda(\vec{R})\,\mathrm{d}\vec{R} \qquad (9)$$

$\omega(\vec{r}_{ij}/\vec{R})$ is the conditional probability density that elements i and j of the chains are separated by $\vec{r}_{ij}$, given that the chain ends are separated by $\vec{R}$. $\omega_\lambda(\vec{R})$ is the probability density of end-to-end vectors of the network chains in the strained state. $\omega(\vec{r}_{ij}/\vec{R})$ is easily obtained from an extension to the three-dimensional case, performed by Fixman[28] of the Wang and Uhlenbeck theorem.[29] A previous work by Duplessix et al.[8,10] has shown that in the dry state the elementary chain statistics (for the same network) is Gaussian unperturbed. In the dry state the probability density of the end-to-end distances can be written

$$\omega(\vec{R}) = \left(\frac{a_N}{\pi}\right)^{3/2} e^{-a_N R^2} \qquad (10)$$

where $a_N = 3/2Nb^2$, where N is the number of statistical segments with length b.

An affine deformation of the end-to-end vectors in the strained state, characterized by the deformation tensor λ results in a modification of the distribution function:

$$\omega^\lambda(\vec{R}) = \omega(\lambda^{-1}\vec{R})/|\lambda| \qquad (11)$$

where $|\lambda|$ is the determinant of λ. In the case of isotropic swelling $|\lambda| = V/V_{\mathrm{dry}} = Q$, where V and V_{dry} are the volumes of the sample in the swollen and dry states, respectively, and $\lambda^{-1}\vec{R} = Q^{-1/3}\vec{R}$.

Under these conditions, the result is

$$\langle r_{ij}^2\rangle = |j-i|b^2 + \left(\frac{Q^{2/3}-1}{N}\right)(j-i)^2b^2 \qquad (12)$$

$$\langle R_g^2\rangle = \langle R_{g,\mathrm{dry}}^2\rangle\left(\frac{Q^{2/3}+1}{2}\right) \qquad (13)$$

This function is plotted in Figure 2. Clearly, as already noticed by Duplessix in the case of swelling by changing the diluent quality, the variation of R_g predicted from the end-to-end pulling model is much larger than the one experimentally observed. In the case of the experiments reported here, the discrepancy between the experimental behavior and the predictions of the end-to-end pulling model is even much larger, since almost no variation of the radius of gyration is observed. Therefore, in the Duplessix experiments, the variation of the radius of gyration with the swelling is more likely to be related to the change of local statistics of the chains, associated with the modification of the diluent quality rather than with a pure geometrical effect of the swelling on the chain dimensions.

Let us turn now to the comparison of the results to the predictions of the phantom network model, which is an extension of the James and Guth theory.[30-33] We adopt the approach to the problem developed by Flory[34-36] and by Deam and Edwards:[37] a phantom network is assumed to be composed of volumeless chains interacting only at the cross-links. The distribution of end-to-end vectors of the elastic chains is Gaussian in the undeformed state. The mean positions of the cross-links are supposed to be transformed affinely when the network is strained, whereas the fluctuations about their mean positions are supposed to be independent of the strain. These assumptions result in a nonaffine transformation of the instantaneous end-to-end distances and therefore of the apparent radius of gyration of the labeled elastic chains. The theoretical expression for the radius of gyration in the case of a tetrafunctional phantom network stretched uniaxially was derived first by Pearson[38] and then by Warner and Edwards.[39] It is

$$\frac{\langle R_{g}^{2}\rangle}{\langle R_{gi}^{2}\rangle} = \frac{\lambda^2 + 3}{4} \tag{14}$$

where λ and $R_{g\parallel}$ are respectively the stretch ratio of the sample and the component of the radius of gyration in the direction parallel to the stretch. R_{gi} is the radius of gyration of the chain in the undeformed network. As in the case of the end-to-end pulling model, λ can be indentified with $Q^{1/3}$ for an isotropic swelling, since the chains are undeformed in the dry state; then

$$R_g = R_{g,\mathrm{dry}}\left(\frac{Q^{2/3} + 3}{4}\right)^{1/2} \tag{15}$$

This function is also plotted in Figure 2. In the range of swelling degree $1 < Q < 5$, reasonable agreement seems to exist between the experimental results and eq 15, while in the range $5 < Q < 18$ both the absolute value of R_g and the slope of its variation with Q, calculated from (15), are larger than the experimental values. It seems then that the phantom network model overestimates, at least in the high-swelling range, the variation of the dimensions of the elementary chains, although this model is generally considered as a limiting case at small deformations. Also it must be emphasized that the swelling from the dry state to the osmotically deswollen state at $Q = 5$ is accompanied by a change of the local polymer–solvent interaction. The observed variation of the radius of gyration corresponds roughly to that of the free chain of the same length in the same environment (bulk to good solvent). Therefore, the agreement between the results and the "phantom" network predictions in this low-swelling range is presumably fortuitous. "Real" networks, which are believed by most of the authors[34-37,40] to behave in an intermediate manner between an "affine" and "phantom" network should exhibit even larger R_g variations with Q. This is not observed and it appears that new mechanisms should be put forward to explain the experimental results.

(b) Interspersion Model. Recently, it has been proposed that an important contribution to the swelling mechanism could arise from topological rearrangements.[41] A large deformation could be accounted for not only by a rearrangement of the configurations of the elementary chains but also and even mainly by a rearrangement on a larger scale than the mesh size, through an exchange of the respective positions of first-neighbor cross-links. The starting point of this line of arguments is based on a remark originally made by Flory[34] that in a dry network the chains are widely interspersed. As a consequence a given cross-link has two kinds of first neighbors:

(i) The topological first neighbors are directly connected by one elastic chain to the reference cross-link. Each junction point is surrounded by f topological first neighbors if f is the functionality of the network.

(ii) The spatial neighbors are characterized by a mutual distance shorter than or equal to the distance between topological neighbors but they are connected by a larger path through the network.

The ratio n/f of the total number of neighbors over the number of topological neighbors of a given cross-link is easily shown to be[41]

$$\frac{n}{f} \propto R_g^{\,3}N^{-1}f^{-2} \propto \frac{1.5}{f^2}N^{1/2} \tag{16}$$

n/f may be calculated by using SANS data on linear polystyrene. For tetrafunctional networks n/f ranges typically from 10 to 20. This implies that on the average the shortest path connecting two neighboring junctions is much longer than the elementary chain and is therefore embedded in the network through several cross-links. From this observation, it was conjectured that in a network subjected to macroscopic strain, topological paths constrained by a large number of cross-links are more deformed than the elementary chains.[41]. Consequently, under stretching or swelling, the distance between spatial pairs is drastically increased with respect to that of topological pairs, resulting in a rearrangement of the position of the junction pairs. The experimental results reported here are in good agreement with this description. The dimensions of the labeled chains are mainly governed by the nature of the local interaction (excluded volume in our case), and the gel can undergo large macroscopic deformations without a significant change of the molecular dimensions. Under osmotic deswelling, the gel behaves as a kind of three-dimensional accordion. It must also be remarked that the above mechanism explains previous results of SANS studies performed on polymeric networks. Measurements from Duplessix et al. on a polystyrene network swollen in cyclohexane at room temperature have shown that the radius of gyration of the elastic chains is the same as in the bulk even though the network was swollen by a factor of 3.[10] One must also mention the recent study by Beltzung et al.[42,43] of the molecular deformation induced by uniaxial extension on bulk poly(dimethylsiloxane) samples. Again, the observed deformation is lower than the predictions of the current theories and must be connected with semilocal reorganization of the network chains.

2. Quasi-Elastic Light Scattering Results. Tanaka, Hocker, and Benedek[17] presented a theory that describes the concentration fluctuations in a polymer gel and gave the following expression for the autocorrelation function of the scattered light field:

$$\langle E(\vec{k},t)E(\vec{k},0)\rangle = C\left(\phi\frac{\partial n}{\partial \phi}\right)^2 \frac{k_{\mathrm{B}}T}{K_{\mathrm{os}} + {}^4\!/_3G}\exp\left[\frac{-(K_{\mathrm{os}} + {}^4\!/_3G)k^2}{\tilde{f}}\right] \tag{17}$$

where E is the amplitude of the scattered field, $\vec{k}$ is the scattering vector, n is the refractive index, ϕ is the polymer volume fraction, k_{B} is the Boltzmann constant, T is the absolute temperature, K_{os} and G are the osmotic bulk and shear moduli of the gel, and C is a constant depending only on the optical geometry. The combination $K_{\mathrm{os}} + {}^4/_3G$ is the longitudinal elastic modulus M of the gel. The ratio $(K_{\mathrm{os}} + {}^4/_3G)/\tilde{f}$ represents the cooperative diffusion constant D_c, with $\tilde{F}$ the friction coefficient per unit volume.

(a) Expression of the Moduli (Gels Swollen by a Good Diluent). The calculation of the elastic moduli requires the knowledge of the free energy of dilution. Theoretically, this is expressed as a sum of a free energy of mixing of the polymer chains and an elastic free energy corresponding to the chain deformation associated with the swelling:[44]

$$\frac{\Delta F}{k_{\mathrm{B}}T} = \frac{\Delta F_{\mathrm{mix}}}{k_{\mathrm{B}}T} + \frac{\Delta F_{\mathrm{el}}}{k_{\mathrm{B}}T} \tag{18}$$

where ΔF_{mix} and dF_{el} are the free energy of mixing and the elastic free energy variation, respectively. ΔF_{mix} is generally identified with the free energy of mixing of uncross-linked polymer chains and then calculated in the framework of the Flory–Huggins theory. The latter is based on a lattice model, the total volume of the gel phase being divided into n_s sites of volume a^3, generally identified with v_1, the molecular volume of the solvent. In order to simplify the calculations, we deal in the following with a free energy F'' per site instead of the total free energy. des Cloizeaux[45] and de Gennes[46] have shown that the Flory–Huggins model is not well suited to the semidilute regime in good solvent since it neglects the large fluctuations of the polymer concentration. From the analogy between magnetic and polymeric systems, des Cloizeaux derived the following concentration dependence for the osmotic pressure:

$$\Pi \propto \phi^{9/4} \tag{19}$$

This law is in very good agreement with experimental data.[47]

An alternative derivation, still based on a lattice model but coupled to a renormalization procedure, has been proposed (ref 2, 46, Chapter II, and 48). An effective size ξ^3, where ξ is the screening length of the semidilute solution, is chosen for the site volume; then concentration fluctuations at a scale of distances greater than ξ can be neglected.

As a consequence, under these conditions, a mean field approach applies to the problem, and F'' can be calculated within the framework of the Flory–Huggins theory. Going back to the initial size a^3 of the site, the following expression is found:

$$\frac{F''}{k_B T} = u^*\phi^{2.25} + \frac{\phi}{N}\ln\frac{\phi}{N} \tag{20}$$

u^* is an effective polymer–solvent interaction parameter, independent of the concentration. N is the polymerization index of the polymer chains. In the case of networks, the translational term $(\phi/N)\ln(\phi/N)$ vanishes and $\Delta F''_{\text{mix}}/k_B T = u^*\phi^{2.25}$. u^* can be easily obtained from osmotic pressure data. The expression of the elastic term in eq 18 is more delicate. Since the neutron scattering experiments reported here are not compatible with any existing microscopic theory, a simple phenomenological form has been proposed for $\Delta F''_{\text{el}}/k_B T$.[2] In the case of isotropic deformation it is written as

$$\frac{\Delta F''_{\text{el}}}{k_B T} = \frac{\phi}{N}\mathcal{F}\left(\frac{\phi}{\phi^*}\right) \tag{21}$$

where N denotes the mean number of statistical units between cross-links and $\phi^* \propto N^{-4/5}$, the overlap volume fraction in pure good solvent of the elementary chains of the network.

The proposed form is proportional to the concentration of elastic chains through the term ϕ/N, and $\mathcal{F}$ is a dimensionless function of ϕ/ϕ^*. Such an expression is designed to represent the elastic free energy change associated with the deformation and the interspersion of the chains. Both of them are expected to refer to the overlap volume fraction ϕ^* of the elementary chains: if a free energy change is related to the interspersion mechanism presented above, it should be a function of ϕ/ϕ^*, the degree of interspersion of the elementary chains. On the other hand, following de Gennes,[46] the elastic free energy change corresponding to the deformation of the elementary chains is believed to depend on R/R_F (R is the average end-to-end distance of the elementary chains, and R_F is the Flory radius, the average end-to-end distance of the free chain of same length in the considered solvent). Since R/R_F must be related in a certain way to ϕ/ϕ^* ($R/R_F \sim (\phi/\phi^*)^{-1/3}$ in the case of the classical affine deformation assumption), both the deformation of the elementary chains and their interspersion (i.e., the deformation of the network at a larger scale) should depend on ϕ/ϕ^*. For the sake of simplicity, it has been proposed to take a scaled form for $F(\phi/\phi^*)$ in the considered range of concentrations.

$$\frac{\Delta F''_{\text{el}}}{k_B T} = A\frac{\phi}{N}\left(\frac{\phi}{\phi^*}\right)^{-x}, \qquad 0 < x < 1 \tag{22}$$

or

$$\frac{\Delta F''_{\text{el}}}{k_B T} = B\phi^l\phi^{*(9/4-l)}, \qquad 0 < l = 1 - x < 1 \tag{23}$$

B is a numerical constant that may depend on the functionality of the network. Therefore

$$\frac{\Delta F''}{k_B T} = u^*\phi^{9/4} + B\phi^l\phi^{*(9/4-l)} \tag{24}$$

The osmotic bulk modulus K_{os} can be derived directly from the above expression for the free energy:

$$K_{\text{os}} = \phi^2\frac{\partial^2\Delta F'}{\partial\phi^2} \tag{25}$$

where $\Delta F'$ is the free enthalpy per unit volume: $\Delta F' = \Delta F'' v_1^{-1}$.

At this point we have to make a distinction between the case of gels swollen at equilibrium in a good solvent and the case of osmotically deswollen gels. Qualitatively, we can predict that the longitudinal modulus $M_{\text{os}} = K_{\text{os}} + {}^3/_4 G$ will be smaller in the case of a deswollen gel than in the case of a gel swollen in a pure solvent at the same concentration. In the first case, the concentration of permanent cross-links and therefore the shear moduli G are smaller than in the second case, whereas the osmotic bulk moluli K_{os}, which are dominated by the dilution free energy variation, are comparable.

(i) Gels Swollen in a Pure Good Solvent. In the case of a gel swollen in a good solvent, μ_s (the chemical potential of the solvent) is easily shown to be equal to[2]

$$\mu_s = \Delta F'' - \phi\frac{\Delta F''}{\partial\phi} \tag{26}$$

The equilibrium condition in a good solvent is given by $\mu_s = 0$; this leads, by combination of (24) and (26), to

$$\psi = \left[\frac{(1-l)B}{(5/4)u^*}\right]^{1/(9/4-l)}\phi^* \tag{27}$$

where ψ is the volume fraction of the gel swollen at equilibrium in a good solvent. This constitutes another expression of the de Gennes "c^* theorem". The relevant assumption for obtaining this result is the choice of ϕ^* as a reference state. Combination of (24) and (25) yields

$$\frac{K_{\text{os}}^{\text{gel}}(\psi)}{v_1^{-1}k_B T} = (9/4)(5/4)u^*\psi^{9/4} - (1-l)lB\psi^l\phi^{*(9/4-l)} \tag{28}$$

and with the help of eq 27, we get

$$\frac{K_{\text{os}}^{\text{gel}}(\psi)}{v_1^{-1}k_B T} = (9/4 - l)(5/4)u^*\psi^{9/4} \tag{29}$$

This result may be compared to that which we would

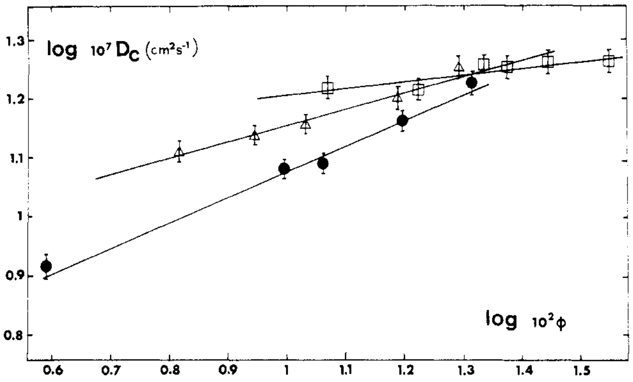

Figure 4. Variations of the cooperative diffusion constant D_c with the polymer volume fraction ϕ for deswollen radical gels (cf. Table I): (●) G24; (▲) B7; (□) B12.

obtain in the case of a semidilute solution (at zero frequency). Neglecting the translational term in the free energy of a semidilute solution (it is very weak for large N), we can write

$$\frac{\Delta F''_{\mathrm{sol}}}{k_{\mathrm{B}}T} = u^*\phi^{9/4} \tag{30}$$

and then

$$K_{\mathrm{os}}^{\mathrm{sol}}(\phi) = (9/4)(5/4)u^*\phi^{9/4}\frac{k_{\mathrm{B}}T}{v_1} \tag{31}$$

We can therefore express eq 29 as follows:

$$K_{\mathrm{os}}^{\mathrm{gel}}(\psi) = K_{\mathrm{os}}^{\mathrm{sol}}(\psi) - K_{\mathrm{os}}^{\mathrm{el}}(\psi) = (k_{\mathrm{os}} - k_{\mathrm{e}})\frac{k_{\mathrm{B}}T}{v_1}\psi^{9/4} \tag{32}$$

where $K_{\mathrm{os}}^{\mathrm{sol}}(\psi)$ is the osmotic bulk modulus at zero frequency of a semidilute solution at a polymer volume fraction $\phi = \psi$ and $K_{\mathrm{os}}^{\mathrm{el}}$ characterizes the compressibility change associated with the permanent linking of the chains:

$$\frac{K_{\mathrm{os}}^{\mathrm{el}}(\psi)}{v_1^{-1}k_{\mathrm{B}}T} = (5/4)u^*\psi^{9/4}l = k_{\mathrm{e}}\psi^{9/4} \tag{33}$$

We observe therefore that the osmotic bulk moduli of a series of gels (of the same functionality) swollen at equilibrium by a pure good diluent will scale with concentration like both the osmotic pressure and the osmotic bulk modulus of semidilute solutions. This result has been predicted by de Gennes.[46]

(ii) Gels Osmotically Deswollen by Semidilute Solutions of Polymer Molecules Much Larger Than the Mesh of the Network. In this situation, the equilibrium condition is still given by the equality of the chemical potentials of the solvent in the gel and in the surrounding solution. The detailed calculation, which has been performed elsewhere,[2] is not required here since ψ, the polymer volume fraction in the gel, can be experimentally measured. Combining (24) and (27) we get

$$\frac{\Delta F''}{k_{\mathrm{B}}T} = u^*\psi^{9/4}\left((\phi/\psi)^{9/4} + \frac{(5/4)B}{1-l}(\phi/\psi)^l\right) \tag{34a}$$

where ϕ is the polymer volume fraction of the gel at equilibrium in the considered state of osmotic deswelling and ψ is the polymer volume fraction of the same gel swollen at equilibrium in the pure good solvent. ϕ/ψ is therefore the deswelling ratio with respect to the pure good solvent.

Combination of (34a) and (25) leads to

$$\frac{K_{\mathrm{os}}^{\mathrm{gel}}}{v_1^{-1}k_{\mathrm{B}}T} = (5/4)u^*\psi^{9/4}((9/4)(\phi/\psi)^{9/4} - l(\phi/\psi)^l) \tag{34b}$$

It is immediately seen that $l(\phi/\psi)^l$ can be neglected with respect to $(9/4)(\phi/\psi)^{9/4}$ in the case of large deswelling. Futhermore, we get the following relation:

$$K_{\mathrm{os}}^{\mathrm{gel}}(\psi' = \phi) \le K_{\mathrm{os}}^{\mathrm{gel}}(\phi > \psi) \le K_{\mathrm{os}}^{\mathrm{sol}}(\phi) \tag{35}$$

where $K_{\mathrm{os}}^{\mathrm{sol}}(\phi)$ is the osmotic bulk modulus of a semidilute solution of polymer volume fraction equal to that of the considered gel. $K_{\mathrm{os}}^{\mathrm{gel}}(\psi' = \phi)$ is the osmotic bulk modulus of a gel swollen at equilibrium in the good solvent at a polymer volume fraction ψ' equal to ϕ. $K_{\mathrm{os}}^{\mathrm{gel}}(\psi' = \phi)$ and $K_{\mathrm{os}}^{\mathrm{sol}}(\phi)$ have been shown to scale with the same exponent $^9/_4$. Furthermore, since l is expected to be close to $^1/_2$,[2] the values of these moduli for a given ϕ will differ only by about 20%. Therefore, when only a first approximation is needed, we may write

$$K_{\mathrm{os}}^{\mathrm{gel}}(\phi) \propto (\phi/\psi)^{9/4} \tag{36}$$

In other words, the osmotic bulk modulus of a deswollen gel remains close to that of a gel swollen at equilibrium in a pure good solvent at the same polymer concentration. We now turn to the derivation of the shear modulus G, which is given by[49]

$$G = \frac{1}{s}\frac{\partial F'(s)}{\partial s} \tag{37}$$

where $F'(s)$ is the total free energy density (per unit volume) of a gel under a shear deformation $s = \lambda - 1/\lambda$ (λ denotes the principal stretch ratio). For a deformation performed at constant volume

$$\frac{\Delta F'(s)}{\partial s} = \frac{\Delta F'_{\mathrm{el}}(s)}{\partial s} \tag{38}$$

At this point we need an additional hypothesis concerning the dependence of $\Delta F'_{\mathrm{el}}$ on a shear strain. Similarly to the case of the affine deformation model, it was proposed to factorize $\Delta F'_{\mathrm{el}}(s)$ as follows:[2]

$$\frac{\Delta F'_{\mathrm{el}}(s)}{v_1^{-1}k_{\mathrm{B}}T} = B(s)\phi^l\phi^{*(9/4-l)} \tag{39}$$

where $B(s)$ is a function of s, with $B(0)$ taken equal to B of eq 23. Then

$$G(\phi) = \frac{1}{s}\frac{\partial B(s)}{\partial s}\left(\frac{\phi}{\psi}\right)^l\psi^l\phi^{*(9/4-l)} \tag{40}$$

The free energy is generally written as a simple linear function of the first invariant of the deformation tensor. Under this assumption and taking into account the normalization condition

$$B(s) = \frac{B(0)}{3}(s^2 + 3) \tag{41}$$

we obtain from (37), (39), and (41)

$$G(\phi) = \frac{2}{3}\frac{(5/4)u^*}{1-l}\psi^{9/4}\left(\frac{\phi}{\psi}\right)^l v_1^{-1}k_{\mathrm{B}}T = g_{\mathrm{e}}\psi^{9/4}(\phi/\psi)^l v_1^{-1}k_{\mathrm{B}}T \tag{42}$$

Again this result separates into two cases:

(i) For a series of gels swollen at equilibrium in pure good solvent, the same exponent $^9/_4$ is found again, as predicted by de Gennes.[46] This result is in good agreement with several series of experimental results.[50-54] Moreover, from

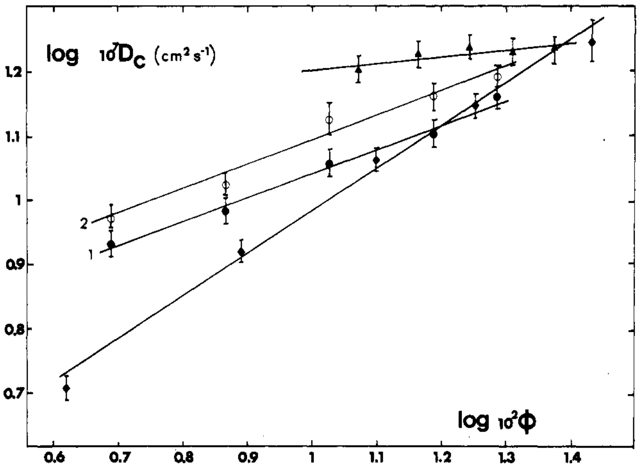

Figure 5. Variations of the cooperative diffusion constant D_c with the polymer volume fraction ϕ for deswollen anionic gels (cf. Table I): (♦) 58; (●) 56; (○) 54; (▲) 65.

eq 29 and 42, we can calculate the ratio K_{os}/G within the framework of this model (with $l = 0.5$). The result is nearly 1.3, which is in very good agreement with some experimental data by Zrinyi et al.[55]

(ii) For a given gel deswollen to different polymer volume fractions $\phi > \psi$, the scaling law $(\phi/\psi)^l$ is obtained. Summarizing, for networks swollen at equilibrium in pure good solvent, both shear and compressional modulus vary with polymer volume fraction according to the same $\psi^{9/4}$ scaling law. On the other hand, when a given gel is deswollen, K_{os} and G exhibit very different ϕ dependences, G increasing with a much lower exponent than K_{os}.

It must be noted that a classical approach based, for instance, on the affine deformation model would lead qualitatively to the same behaviors. Such an approach, which has been recently used by Horkay and Zrinyi[56] is contradicted by the elasticity measurements[2] and the neutron scattering data reported in the first part of this paper. Therefore it is necessary to consider another deformation mechanism. The expression of the elastic free energy which has been used in the above derivation is very general and does not assume any specific deformation model.

(b) Expression of the Cooperative Diffusion Constant D_c. From eq 17, 31, 34, 36, and 42, the cooperative diffusion constant can be expressed as

$$D_c = \frac{\psi^{9/4}}{\tilde{f}}\frac{k_B T}{v_1}\left[k_{os}(\phi/\psi)^{9/4} + ((4/3)g_e - k_e)\left(\frac{\phi}{\psi}\right)^l\right] \quad (43)$$

One can assume as a first approximation that the concentration dependence of the friction factor $\tilde{f}$ is the same as that of a semidilute solution. In the latter case, it was shown theoretically that in the domain of concentration of interest the asymptotic scaling behavior of $\tilde{f}$ with concentration was not reached. However, experimental studies showed that the polymer volume fraction dependence of $\tilde{f}$ was well represented by a law of the form[56,57]

$$\tilde{f} \propto \phi^\alpha \qquad \text{with } \alpha \geq 1.5 \quad (44)$$

Therefore

$$D_c \propto \frac{\psi^{9/4}}{\phi^\alpha}[k_{os}(\phi/\psi)^{9/4} + ((4/3)g_e - k_e)(\phi/\psi)^l] \quad (45)$$

For a series of networks of the same functionality but different cross-linking densities and swollen to equilibrium by a pure good solvent, $\phi/\psi = 1$; and then

$$D_c \propto \psi^{(9/4-\alpha)}[k_{os} + ((4/3)g_e - k_e)] \quad (46)$$

The exponent $^9/_4 - \alpha$ is the same as that of semidilute solutions. In this case, it has been found equal to 0.68, and this exponent has also been found in the case of a series of gels as predicted by eq 46. The only difference between the two kinds of systems arises from the different values of the prefactors g_e and k_e. The prefactor k_{os} is related to the osmotic force, which tends to equalize the concentration. Its value should be the same for both semidilute solutions and chemically cross-linked gels. On the other hand, the term $^4/_3 g_e - k_e$ depends on whether the cross-links are covalent bonds or physical entanglements. In other words, it may be reasonably conjectured that $^4/_3 g_e - k_e$ is not zero in the frequency range probed by the quasi-elastic light scattering experiments, because of the presence of entanglements at finite time scale. However, this term is expected to be smaller than its equivalent in the case of permanently cross-linked gels. This may explain the systematically higher value of the experimental diffusion constant of gels swollen to equilibrium in pure good solvents with respect to that of semidilute solutions at the same concentration.

Referring back to the osmotic deswelling experiments, the diffusion constant is given by eq 45, and its concentration dependence will depend on the value of the exponent l and on the ratio $^4/_3 g_e - k_e$. As mentioned before, previous shear modulus measurements on samples under osmotic deswelling have led to a value of l of the order of 0.5.[2] Furthermore, measurements of K_{os} and G for a poly(vinyl acetate) network swollen by toluene have shown that $^4/_3 g_e$ and $k_o - k_e$ were in the same order of magnitude as predicted by eq 31 and 42.[55] As a consequence, the cooperative diffusion constant is expected to exhibit a weaker concentration dependence in an osmotic deswelling experiment than the one obtained for a series of networks at swelling equilibrium in pure good solvent. This is in good agreement with the experimental results shown in Figures 4 and 5. It can also be observed in Figures 4 and 5 that the amplitude of the concentration dependence decreases when the cross-linking degree increases. This could be due to a relative change of the contribution of the topological rearrangements and the chain deformation to the macroscopic deformation mechanism. The latter contribution could become predominant as the network becomes tighter, with a corresponding decrease of l, in the asymptotic limit, to the value $^1/_3$ predicted by the affine deformation model. As a matter of fact, neutron scattering experiments performed on dry PDMS networks have shown that relative molecular deformation of elementary networks chains increases as the mesh size decreases. It must also be pointed out that the friction coefficient, which may reasonably be postulated to be equal to that of a semidilute solution in the case of very loose gels, can progressively differ in the case of tighter gels because of the above-mentioned change of the topology and the increase of the density of cross-linking nodules. Because of the approximation involved in this discussion, it would be hazardous to try to extract from the data quantitative information on the behavior of elastic moduli. However, the observed behavior of the cooperative diffusion constant is qualitatively well understood by the different concentration dependences of compressional osmotic bulk and shear moduli.

The phenomenological approach that has been used here for the derivation of the elastic moduli no longer applies to the case of networks containing large amounts of pendant chains. In the latter case, effective elementary chains consist of star- or comb-shaped units.[12] There is no theory that currently describes the behavior of such materials. However, the increase of the variation of D_c with ϕ could be expected for two reasons:

(i) The concentration dependence of the osmotic pressure in the semidilute regime is greater for branched polymers than for linear ones.[58] This results in a greater increase of the osmotic bulk modulus K_{os} with concentration.

(ii) When the network chains interpenetrate each other in the deswelling process, the branched units may form physical entanglements of longer lifetime, and this could result in a greater variation of G with ϕ.

Conclusion

In this paper we have reported measurements showing that the swelling degree of a network can be widely varied without a significant change of the elementary mesh dimensions. Clearly, this behavior must be related to a progressive interspersion of the chains. Such a mechanism arises as a simple consequence of the following conjectures.

1. There is a threshold distance for the affineness in the macroscopic strain: on a scale larger than the threshold the deformation is affine, whereas on a smaller scale the affineness is lost.
2. The threshold distance is not the normal spatial distance but a "topological" distance, i.e., the length of the shortest path between two points along the network. It must be emphasized that two points, separated by the same spatial distance, can be connected along the network by very different topological distances.
3. Depending on the cross-linking density, the affineness threshold may vary. Particularly in the case of loose networks, it can correspond to topological distances larger than the mesh size. In the latter case, spatial neighbors connected by a sufficiently long path will be deformed affinely whereas comparable spatial distances between two topological neighbors (small topological distances) may remain almost unchanged.

Quasi-elastic light scattering results have also been reported in this paper, and they evidence a significant difference for the variation of the cooperative diffusion constant D_c as a function of the concentration between cases of series of gels swollen at equilibrium and one that was osmotically deswollen. Although no satisfactory microscopic theory consistent with the neutron scattering data is presently available, a good semiquantitative interpretation of the results has been obtained with the phenomenological approach already used successfully in the case of the thermodynamics of deswelling.[2] Qualitatively, a gel deswollen at a given concentration will exhibit a cooperative diffusion constant D_c smaller than that of a tighter gel swollen at equilibrium in a pure solvent at the same concentration because the shear modulus, which contributes to D_c, is smaller in the first case than in the second. This kind of description could also explain the systematic shift of the law $D_c(\phi)$ in the case of gels swollen in pure good solvent in comparison with that obtained for semidilute solutions.

Acknowledgment. We are grateful to Professor H. Benoit and Dr. L. Leibler for constructive suggestions and helpful comments. We are also indebted to Dr. G. MacKenna for having carefully reviewed this paper.

Registry No. Divinylbenzene–styrene copolymer, 9003-70-7; neutron, 12586-31-1.

References and Notes

(1) Hild, G.; Froelich, D.; Rempp, P.; Benoit, H. *Makromol. Chem.* **1972**, *151*, 59.

(2) Bastide, J.; Candau, S.; Leibler, L. *Macromolecules* **1981**, *14*, 719.

(3) Munch, J. P., et al. *J. Phys. (Paris)* **1977**, *38*, 1499.

(4) Munch, J. P., et al. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1097.

(5) Munch, J. P.; Candau, S.; Hild, G. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 11.

(6) Herz, J.; Weiss, P.; Rempp, P. *C. R. Hebd. Seances Acad. Sci.* **1968**, *266*, 681.

(7) Weiss, P.; Hild, G.; Herz, J.; Rempp, P. *Makromol. Chem.* **1970**, *135*, 249.

(8) Duplessix, R. Thesis Université Louis Pasteur, Strasbourg, 1975.

(9) Farnoux, B. Thesis, Université Louis Pasteur, Strasbourg, 1976. *Ann. Phys. (Paris)* **1976**, *1*, 73.

(10) Benoit, H., et al. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 2119.

(11) Cotton, J. P., et al. *Macromolecules* **1974**, *7*, 863.

(12) Bastide, J.; Picot, C.; Candau, S. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1441.

(13) Okasha, R. Thesis, Université Louis Pasteur, Strasbourg, 1978.

(14) Okasha, R.; Hild, G.; Rempp, P. *Eur. Polym. J.* **1979**, *15*, 975.

(15) Guinier, A.; Fournet, G. "Small Angle Scattering of X-Rays"; Wiley: New York, 1955.

(16) Alexander, S.; Pincus, P. *Polymer* **1979**, *20*, 277. The equation (9) of this reference gives the following expression of the scattered intensity at $q = 0$:

$$I(0) \propto N\phi_D\left(1 - \frac{Nu\phi_D}{1 + Nu\phi}\right) \qquad \text{(a)}$$

$N\phi_D$ is simply the intrachain correlation term at $q = 0$, whereas $N^2u\phi_D{}^2/(1 + Nu\phi)$ is the interchain term. For $q \neq 0$ it can easily be shown that $I(q)$ must have the form of eq 3, which reduces to (a) for $q = 0$. The detailed calculation will soon appear in a paper by M. Benmouna and H. Benoit.

(17) Tanaka, T.; Hocker, L.; Benedek, G. B. *J. Chem. Phys.* **1973**, *59*, 5151.

(18) de Gennes, P.-G., *Macromolecules* **1976**, *9*, 587.

(19) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.

(20) See, for instance: Cummins, H. Z.; Pike, E. R., Eds. "Photon Correlation and Light Beating Spectroscopy"; Plenum, New York, 1974.

(21) Schaeffer, D. V.; Joanny, J. F.; Pincus, P. *Macromolecules* **1977**, *10*, 1229.

(22) Mathiez, P.; Mouttet, C.; Weisbuch, G. *J. Phys. (Paris)* **1980**, *41*, 519.

(23) Wall, F. T. *J. Chem. Phys.* **1943**, *11*, 527.

(24) Wall, F. T.; Flory, P. J. *J. Chem. Phys.* **1951**, *19*, 1435.

(25) Levy, S.; Benoit, H., unpublished results.

(26) Levy, S. Thesis, Université Louis Pasteur, Strasbourg, 1964.

(27) Ullman, R. *J. Chem. Phys.* **1979**, *71*, 436.

(28) Fixman, M. *J. Chem. Phys.* **1955**, *23*, 1656. See also: Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.

(29) Wang, M. C.; Uhlenbeck, G. E. *Rev. Mod. Phys.* **1945**, *17*, 323.

(30) James, H. M.; Guth, E. *J. Chem. Phys.* **1943**, *11*, 455.

(31) James, H. M. *J. Chem. Phys.* **1947**, *15*, 65.

(32) James, H. M., Guth, E. *J. Chem. Phys.* **1947**, *15*, 669; **1953**, *21*, 1039.

(33) Guth, E. *J. Polym. Sci., Part C* **1966**, *12*, 89.

(34) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1976**, *351*, 1666.

(35) Flory, P. J. *J. Chem. Phys.* **1977**, *66*, 5720.

(36) Flory, P. J. *Macromolecules* **1979**, *12*, 119.

(37) Deam, R. T., Edwards, S. F. *Philos. Trans. R. Soc., Ser. A* **1976**, *280*, 317.

(38) Pearson, D. S. *Macromolecules* **1977**, *10*, 696.

(39) Warner, M.; Edwards, S. F. *J. Phys. A* **1978**, *11*, 1649.

(40) Staverman, A. J., *Adv. Polym. Sci.* **1982**, *44*, 73.

(41) Bastide, J.; Picot, C.; Candau, S. *J. Macromol. Sci., Phys.* **1981**, *B19*, 13.

(42) Beltzung, M. Thesis, Strasbourg, 1982.

(43) Beltzung, M., et al. IUPAC 27th International Symposium on Macromolecules, Strasbourg, 1981; Reprints, p 728.

(44) See, for example, the reviews by: Dusek, K.; Prins, W. *Adv. Polym. Sci.* **1969**, *6*, 1.

(45) des Cloizeaux, J. *J. Phys. (Paris)* **1975**, *36*, 281.

(46) de Gennes, P.-G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.

(47) Cotton, J. P., Farnoux, B.; Jannink, G.; Strazielle, C. *J. Polym. Sci., Polym. Symp.* **1973**, *No. 49*, 981.

(48) Joanny, J. F. Thesis, Université Pierre et Marie Curie, Paris, 1978.

(49) Landau, L., Lifschitz, E. "Theory of Elasticity"; Pergamon Press: London, 1970.

Macromolecules **1984,** *17,* 93–100

(50) Munch, J. P., et al. *J. Phys. (Paris)* **1977,** *38,* 971.
(51) Macret, M., Thesis, Université Louis Pasteur, Strasbourg, 1980.
(52) Zrinyi, M.; Horkay, F. *Polym. Bull.* **1981,** *4,* 361.
(53) Zrinyi, M.; Horkay, F. *Polym. Bull.* **1980,** *3,* 665.
(54) Candau, S.; Peters, A.; Herz, J. *Polymer* **1981,** *22,* 1504.
(55) Zrinyi, M.; Horkay, F. *J. Polym. Sci.,* in press.
(56) Horkay, F.; Zrinyi, M. *Macromolecules* **1982,** *15,* 1306.
(57) Adam, M.; Delsanti, M. *Macromolecules* **1977,** *10,* 1229.
(58) Geissler, E.; Hecht, A. M., private communication.
(59) Candau, F.; Strazielle, C.; Benoit, H. *Eur. Polym. J.* **1976,** *12,* 95.

NMR Relaxation Study of Hydrogen Exchange in Solutions of Polyelectrolytes

Dirk Lankhorst and Jacob C. Leyte*

Gorlaeus Laboratories, Department of Physical and Macromolecular Chemistry, University of Leiden, 2300 RA Leiden, The Netherlands. *Received February 23, 1983*

ABSTRACT: Exchange rate measurements of water protons in aqueous solutions of poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMA) by NMR T_2 measurements in $H_2{}^{17}O$ are reported. The polyelectrolyte contribution to the exchange rate is found to depend linearly on the concentration. This indicates that it originates from intramolecular processes, probably proton transfer between COOH and COO^- groups via an intervening water molecule. The corresponding rate constant is an increasing function of the degree of neutralization, largely independent of molecular weight and of the concentration of added salt. The residence time of a proton in a COOH group is calculated from the obtained rate constants and is found to be longer for PMA than for PAA by a factor 5. The influence of added simple salt on the exchange rate is reported. The possibility of obtaining hydrogen ion concentrations and activity coefficients from the experimental exchange rate is demonstrated.

Introduction

An experimental investigation of water proton exchange in solutions of low molecular weight carboxylic acids was reported recently[1]. In the present paper results of ^1H exchange rate measurements using the CarrPurcell NMR method on polyelectrolyte solutions in ^{17}O-enriched water are described. The exchange rate k_{ex} is defined as the inverse mean proton residence time in a water molecule. As in the previous work[1], k_{ex} is obtained from the contribution of the exchange-modulated ^1H–^{17}O scalar coupling to the proton transverse relaxation rate $1/T_2$.

Because the water proton exchange is catalyzed by processes involving the transfer of a proton from a COOH group to a water molecule, k_{ex} may yield information on the proton residence time in a COOH group, τ_{COOH}. Knowledge of τ_{COOH} is important for the interpretation of solvent relaxation data for solutions of high molecular weight compounds.

The polyelectrolytes investigated are poly(acrylic acid) (PAA, $(CH_2(CHCO_2H))_n$) and poly(methacrylic acid) (PMA, $(CH_2(CH_3CCO_2H))_n$). The exchange rate k_{ex} was measured as a function of the polyelectrolyte concentration c_p at a number of α values (α is the degree of neutralization). For PAA, the molecular weight dependence was investigated.

Some measurements of proton exchange in PMA solutions were performed in this laboratory previously,[2] but a quantitative explanation was complicated by the fact that only ^{17}O-enriched water containing 80% deuterium was available, whereas large deuterium isotope effects on the reaction rates are expected.[1] ^{17}O line width experiments on proton exchange in PAA and PMA solutions were reported recently by Halle and Piculell.[3] However, they did not investigate the concentration dependence of the exchange rate systematically, and the method can only give reliable results over a small pH range. Experiments have been reported on proton exchange between polyelectrolytes (PAA and PMA) and indicator molecules by the temperature jump method.[4] Such experiments do not yield direct information on the residence time in COOH groups in the absence of indicator.

In order to partition the experimental k_{ex} into contributions from H_3O^+ catalysis and from polyelectrolyte catalysis, it is necessary to know the H_3O^+ concentration c_{H^+}. For the simple acid solutions studied earlier, c_{H^+} was calculated from known pK and activity corrections.[1] For polyelectrolyte solutions these quantities are not unambiguously and accurately known. To be able to separate H_3O^+- and polyelectrolyte-catalyzed contributions, two alternative approaches were taken:

(a) The exchange rate was measured as a function of c_p in the presence of excess NaCl. Then in the present α-range ($0.3 \leq \alpha \leq 0.8$), c_{H^+} is supposed to be independent of c_p.

(b) For salt-free solutions, c_{H^+} was calculated from the experimental pH and an H_3O^+ activity coefficient estimated from the single-ion activity coefficient γ_{Na^+}, which is known from the literature.

Both methods are shown to yield a polyelectrolyte-catalyzed contribution to k_{ex} (denoted k_{COOH}) that depends linearly on c_p. This indicates that intramolecular processes are responsible for k_{COOH}. The rate constant obtained for polyelectrolyte catalysis will be used to estimate the proton residence time in a COOH group.

Experiments on the influence of added simple salt on the exchange rate are reported. It is shown to be possible in some cases to determine the hydrogen ion concentration and activity coefficient from the experimental exchange rate if the relevant rate constants are known.

Experimental Section

Chemicals and Solutions. All solutions were prepared by weight. The (monomer) aquamolality, $\tilde{m}$, is used as a measure of the concentration; i.e., concentrations are given as the number of moles of monomeric units per 55.5 mol of water. Polyelectrolyte concentrations c_p are given as global concentrations, i.e., as $c_{acid} + c_{conjugated\ base}$, unless indicated otherwise. ^{17}O-enriched water was obtained from Monsanto Research Corp. in two fractions containing 43.4 and 52.4 mol % ^{17}O and 31.4 and 35.1 mol % ^{18}O, respectively. The oxygen isotopic composition of these stock solutions was checked by mass spectrometry as described in the previous paper.[1] PAA, degree of polymerization DP = 2100 and DP = 4100, and atactic PMA, DP = 2300, were synthesized and

0024-9297/84/2217-0093$01.50/0