Studies on Mechanical and Swelling Behavior of Polymer Networks on the Basis of the Scaling Concept. 7. Effect of Deformation on the Swelling Equilibrium Concentration of Gels

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ABSTRACT: Poly(vinyl acetate) networks equilibrated with a good diluent (toluene) were deswollen by two methods: (i) cylindrical form gel specimens were subjected to unidirectional compression at fixed activity of the diluent in the outer phase; (ii) the activity of the diluent around the freely swollen gel specimens was lowered by dissolving a polymer in the surrounding media. Modulus measurements (at fixed volume) were performed at each stage of dilution. The power law exponent of the concentration dependence of elastic moduli of gel homologues equilibrated with pure diluent was found to be equal to 2.33. The experimental volume fractions (ϕ) of deswollen gels were close to that calculated on the basis of the equation $\phi = \phi_e\Lambda_e^{-4/9}$, where ϕ_e is the volume fraction of the polymer in the freely swollen gel and Λ_e is the deformation ratio relative to the length of the freely swollen undeformed gel. The results of Treloar[4] on natural rubber samples equilibrated with heptane or benzene were also discussed, with particular reference to the dependence of the swelling degree on unidirectional deformation. The chemical potential of the diluent in the deswollen gel was obtained not only from the osmotic pressure of the polymer solution being in equilibrium with the gel but also from the mechanical properties of the deswollen gel. Relationships were evaluated between the swelling pressure, elastic modulus, deformation ratio, and polymer concentration.

Introduction

The dependence of the equilibrium swelling degree of a swollen network on the extent of deformation had long been recognized and discussed by Flory and Rehner.[1,2] Their theoretical treatment based on the ideal chain approximation was confirmed by elongation experiments performed on butyl rubber rings swollen by xylene. Gee[3] studied the effect of the extension on swelling of natural rubber vulcanizates both in good and poor diluents. He found that in good solvent conditions the swelling behavior of gels can satisfactorily be described by the Flory-Rehner statistical theory; however, in poor solvents the agreement was only qualitative.

The theory was further developed by Treloar,[4,5] who discussed the general case of a homogeneous strain of any type and derived equations for a number of particular types of strain, including single elongation, two-dimensional extension, and unidirectional compression. On the basis of experimental data referring to vulcanized natural rubber samples swollen by good solvents, i.e., benzene and heptane, he concluded that the effect of strain on the swelling equilibrium concentration is satisfactorily accounted for by the statistical theory under the three entirely different types of strains examined.

In order to evaluate the molecular parameters characterizing the network, Rijke and Taylor[6] studied the stress-strain behavior of a cross-linked nitrile rubber sample equilibrated with a number of diluents. They found that for networks cross-linked in solution the effect of solvent power on the relaxed degree of swelling must be taken into consideration.

If the swollen gel equilibrated with a diluent is deformed, the chemical potential of the diluent inside the gel is altered through the influence of the isotropic component of the stress arising from the deformation of the network. Thus the swelling degree of the gel changes, although the activity of the diluent in equilibrium with the gel remains the same.

Deswelling can also be induced by lowering the chemical potential of the swelling agent around the freely swollen network. This can be carried out either by dissolving a polymer in the equilibrium liquid phase or through the vapor phase by reducing the partial pressure of the diluent. According to these methods the volume change is not accompanied by distortion of the isotropic gel as in the case of deformation-induced deswelling. Due to lowering the activity of the swelling agent in the surrounding media the gel loses certain amount of diluent, but its shape remains unchanged.

Although several experimental methods are available, the dependence of the swelling degree on both the activity of the diluent and the extent of deformation at fixed diluent activity was not reported yet.

The present work is mainly intended to compare the effect of deformation and that of diluent activity on the equilibrium concentration of poly(vinyl acetate) gel homologues swollen by a good diluent. For this reason two different experimental methods were used: gels immersed in pure diluent were deswollen by unidirectional compression and deswelling of the same gels was also achieved by lowering the activity of the diluent around the freely swollen undeformed specimen.

An attempt is made to establish relationships between swelling pressure, elastic modulus, and deformation ratio. Shear moduli measurements performed at different stages of dilution as well as solvent activity measurements designed to ascertain the utility of the proposed relationships are reported.

Theory

The free energy of a gel (ΔA_{tot}) in swelling equilibrium with a diluent is considered to be the sum of the elastic free energy (ΔA_{el}) due to the network and of the free energy of mixing (ΔA_{mix}), representing the thermodynamics of the interaction of polymer and solvent:[7,8]

$$\Delta A_{\text{tot}} = \Delta A_{\text{el}} + \Delta A_{\text{mix}} \tag{1}$$

According to the theory of rubber elasticity, ΔA_{el} can be expressed as

$$\Delta A_{\text{el}} = \frac{\nu kT}{2}(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \tag{2}$$

where ν is the number of elastically active network chains, α_x, α_y, and α_z are the principal deformation ratios related to the reference state of the network, and kT has its usual meaning.

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For unidirectional deformation

$$\alpha_x = l/l_0 \qquad \alpha_y = \alpha_z \qquad \alpha_x\alpha_y\alpha_z = V/V_0$$

where l_0 is the length of the isotropic network in the reference state of volume V_0 and l is the length of the swollen distorted sample of volume V.

By identification of the reference state with the dry volume ($V_0 = V_d$) and introduction of molar quantities, the elastic contribution to the chemical potential of diluent is given by

$$\frac{(\Delta\mu_1)_{el}}{RT} = \frac{1}{RT}\left(\frac{\partial \Delta A_{el}}{\partial n_1}\right)_{T,P,\alpha_x} = \frac{\nu}{V_d}\bar{V}_1\alpha_x^{-1} \qquad (3)$$

where n_1 is the number of moles of solvent and $\bar{V}_1$ is the partial molar volume of the diluent.

α_x can be expressed either by the deformation ratio relative to the undeformed length of the freely swollen gel, Λ_e, or by the deformation ratio relative to the undeformed length of the same volume as for the deformed gel, Λ. Substitution of $\alpha_x = \Lambda_e\phi_e^{-1/3}$ or $\alpha_x = \Lambda\phi^{-1/3}$ yields the expression

$$\frac{(\Delta\mu_1)_{el}}{RT} = \frac{\nu}{V_d}\bar{V}_1\phi_e^{1/3}\Lambda_e^{-1} = \frac{\nu}{V_d}\bar{V}_1\phi^{1/3}\Lambda^{-1} \qquad (4)$$

where ϕ_e and ϕ are the volume fractions of polymer in the freely swollen network and in the distorted swollen specimen, respectively. According to eq 4 the relationship between Λ and Λ_e is given by

$$\Lambda = \Lambda_e(\phi/\phi_e)^{1/3} \qquad (5)$$

Introducing the shear modulus[7,9]

$$G(\phi) = \frac{RT\nu}{V_d}\phi^{1/3} \qquad (6)$$

yields the alternative expression for the elastic contribution to the chemical potential

$$(\Delta\mu_1)_{el} = G(\phi_e)\bar{V}_1\Lambda_e^{-1} = G(\phi)\bar{V}_1\Lambda^{-1} \qquad (7)$$

where $G(\phi_e)$ is the shear modulus of the freely swollen network. The combination of eq 5 and 7 results in

$$G(\phi) = G(\phi_e)(\phi/\phi_e)^{1/3} \qquad (8)$$

which means that the reduced modulus $G(\phi)/G(\phi_e)$ is the only function of ϕ/ϕ_e.[22,28-30]

The mixing contribution to the chemical potential of the diluent follows from the Flory–Huggins formulation of the mixing free energy as

$$\frac{(\Delta\mu_1)_{mix}}{RT} = \frac{1}{RT}\left(\frac{\partial \Delta A_{mix}}{\partial n_1}\right)_{T,P} = \ln(1-\phi) + \phi + \chi\phi^2 \quad (9)$$

where χ is the Flory–Huggins interaction parameter. The substitution of the logarithmic term of eq 9 by its second-order series expansion yields

$$\frac{(\Delta\mu_1)_{mix}}{RT} = -\left(\frac{1}{2} - \chi\right)\phi^2 \qquad (\phi \ll 1) \qquad (10)$$

As a result of recent progress in theoretical approaches, de Gennes[9,10] and des Cloiseaux[11] showed that the Flory–Huggins model was not well suited for semidilute solutions in good solvent condition, since it neglected the large fluctuations of the polymer concentration. Taking into account the effect of monomer correlations, eq 10 can be written

$$(\Delta\mu_1)_{mix}/RT = -u^*\phi^{9/4} \qquad (11)$$

where u^* is the effective (renormalized) interaction parameter, which may be determined, for instance from osmotic pressure measurements. Analysis of previous experimental results confirmed the validity of eq 11.[12,13]

By combination of eq 7, 10, and 11 the total chemical potential of the diluent is obtained

$$\Delta\mu_1 = (\Delta\mu_1)_{el} + (\Delta\mu_1)_{mix} = G(\phi)\bar{V}_1\Lambda^{-1} - K\phi^m \quad (12)$$

K is a constant and the exponent $m = 2$ or $9/4$ according to the classical or the scaling theories, respectively.

It should be mentioned that Flory's theory contains a further term, usually designated as a cross-linking term, the role of which has not been well justified yet.[7,14]

For freely swollen gels ($\phi = \phi_e$, $\Lambda = 1$, $\Delta\mu_1 = 0$) eq 12 results in

$$G(\phi_e) = \frac{K}{\bar{V}_1}\phi_e^m \qquad (13)$$

According to eq 13 the shear moduli of gel homologues equilibrated with pure diluent follow the same power law dependence as the osmotic pressure of polymer solutions in the semidilute regime predicted by de Gennes on the basis of the c^* theorem.[9] The validity of eq 13 has been strongly supported by several experimental findings.[15-22]

Introducing eq 13 into eq 12 we get

$$\Delta\mu_1 = K(\phi/\phi_e)^{1/3}\phi_e^m\Lambda^{-1} - K\phi^m \qquad (14)$$

Equation 14 predicts that at fixed chemical potential of the diluent in the outer phase, the elongation of the gel ($\Lambda > 1$) results in the decrease of ϕ, while in the case of compression ($\Lambda < 1$) ϕ increases.

If the gel is equilibrated with a pure swelling agent ($\Delta\mu_1 = 0$) the two terms of eq 14 compensate each other and the deformation ratio can be expressed as

$$\Lambda = (\phi_e/\phi)^{m-1/3} \qquad (15)$$

or using eq 8 one gets

$$\Lambda_e = (\phi_e/\phi)^m \qquad (16)$$

Comparison of eq 15 and 16 yields eq 5. Equations 15 and 16 gives the concentration of the deformed gel equilibrated with pure diluent in terms of easily accessible quantities, i.e., the equilibrium concentration of the freely swollen undeformed gel and the deformation ratios relative to either the undeformed length of the freely swollen gel or to that of the deswollen gel. It should be mentioned that eq 15 and 16 also hold for any activity of the swelling agent in the equilibrium liquid or vapor phase. If the activity of the diluent in the surrounding media differs from that of the pure swelling agent ϕ_e and Λ_e should be replaced by the actual volume fraction of the isotropic gel and the deformation ratio relative to its undeformed length, respectively.

In the foregoing section we discussed the effect of deformation on the concentration of gels equilibrated with swelling agent at fixed chemical potential. Let us focus now on the case when swelling or deswelling is induced by changing the chemical potential of the diluent in the outer phase. It follows from eq 12 that the solvent chemical potential difference required to shift the volume fraction of a freely swollen, undeformed gel from ϕ_e to ϕ can be given by

$$\Delta\mu_1 = G(\phi)[1 - \Lambda^{-1}]\bar{V}_1 \qquad (17)$$

It is convenient to introduce the swelling pressure of the gel $\omega(\phi) = -(\Delta\mu_1/\bar{V}_1)$ instead of the chemical potential of the diluent. Taking into account that $\Lambda = (\phi_e/\phi)^{m-1/3}$ we get

$$\omega(\phi) = G(\phi)[(\phi/\phi_e)^{m-1/3} - 1] \qquad (18)$$

Equation 18 predicts that the ratio of the swelling pressure to the elastic modulus is a function of ϕ/ϕ_e only.

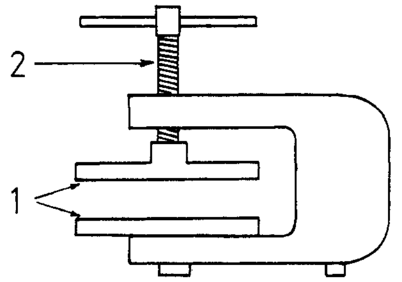

Figure 1. Schematic diagram of the apparatus for unidirectional compression experiments.

An alternative form of eq 18 can be given with eq 5, 8, and 17

$$\frac{\omega(\phi)}{G(\phi_e)} = \frac{1 - \Lambda_e^{(3m-1)/3m}}{\Lambda_e} \qquad (19)$$

According to eq 19 the swelling pressure of the gel can be obtained from data relevant to the freely swollen gel.

Experimental Section

Gel Preparation. Experiments were performed with chemically cross-linked poly(vinyl acetate) PVAc) gels swollen by toluene. The PVAc gels were prepared by a polymer analogous reaction from poly(vinyl alcohol) (PVA) networks according to a method described previously.[23,24] A hydrolyzed and fractionated Poval 420 PVA (Kuraray Co. Japan) sample was dissolved in a mixture of dimethyl sulfoxide (90 v/v %)–water (10 v/v %) and cross-linked with glutaraldehyde (Merck, GFR) in the presence of HCl (pH = 1.5) as catalyst. Cross-linking reaction took place at 25 ± 0.1 °C in solutions of polymer concentrations c° = 3.0, 6.0, 9.0, and 12.0 wt %. At concentrations 6.0, 9.0, and 12.0 wt %, four series of gels were prepared differing in degree of cross-linking (DC = 50, 100, 200, and 400). At c° = 3.0 wt % two series of gels (DC = 50 and 100) were obtained. DC is the moles of monomer units relative to the moles of cross-linking agent. Cylindrical gel specimens of equal height and diameter (approximately 1 cm) were prepared in the holes of a suitable frame. After completion of gelation the diluent was replaced with a mixture of pyridine (50 v/v %)–acetic anhydride (40 v/v %)–acetic acid (10 v/v %). Acetylation was performed at 90 °C for 8 h. A fresh mixture was provided each hour. In the last 3 h, acetic acid was omitted from the fresh mixture in order to shift the equilibrium of the acetylation reaction in the direction of acetate formation. Then the gels were immersed in large excess of acetone. The solvent exchange was continued until no foreign matter was detected in the wash even by interferometry. The washing cycle took over 6 weeks to complete, including at least 30 solvent exchanges. The gels were dried after removing traces of the acetylation mixture. Drying was completed by subjecting the gels to vacuum for 48 h at room temperature. The height, the diameter, and the mass of the dry cylindrical form network specimens were measured. The mass balance calculated on the basis of stoichiometry indicated that the extent of polymer analogous transformation was close to 100%. The dried gels were transferred to pure toluene and allowed to reach swelling equilibrium at 25 °C.

Methods

Deformation-Induced Deswelling at Fixed Activity of the Diluent. Deswelling by unidirectional compression was performed in an apparatus shown schematically in Figure 1. Gel cylinders equilibrated with pure toluene were compressed between the parallel flat plates (1), the distance of separation of which could be adjusted in order to impose the desired compression on the sample by a screw (2). During the experiments the apparatus was immersed in toluene and placed in a thermostat at 25 ± 0.1 °C. The time required to reach equilibrium was determined in subsequent experiments. Figure 2 shows the kinetics of deswelling induced by unidirectional compression for two PVAc gels differing in degree of cross-linking. It can be established that equilibrium was attained within 4–5 days. After allowing about 14 days for equilibration, the height and diameter as well as the mass of the gel cylinders were measured. In several experiments the measurements were performed at successively decreasing compression ratios following the sequences of measurements carried out with increasing compression ratios. The two sets of experimental data showed no appreciable differences. Finally the swollen samples were dried again and measured. Detectable loss of mass was not observed as a result of the swelling and drying cycle. Swelling ratios were calculated from height and diameter data of the swollen and dry cylinders as well as from the masses of the swollen and dry specimens. In the latter case density values of d_{PVAc} = 1.17 g cm^{-3} and d_{toluene} = 0.866 g cm^{-3} were used. Table I shows that the agreement between the swelling degrees calculated from independent data is within the limit of experimental uncertainty; i.e., in the studied concentration range the specific volumes of polymer and solvent can be considered additive.

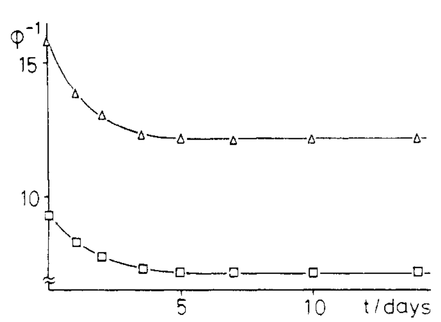

Figure 2. Kinetics of deswelling induced by unidirectional compression. PVAc/toluene: (□) 6/100; (△) 6/200.

Table I
Swelling Data of 9/400 Poly(vinyl acetate)/Toluene Gel Cylinder at Different Stages of Dilution

		vol swelling deg	
height, nm	mass, g	from mass	from dimension
5.271	0.135	1.00	1.00
12.669	1.399	13.89	13.87
12.850	1.458	14.49	14.50
13.109	1.547	15.38	15.39
13.463	1.675	16.67	16.69
13.776	1.794	17.86	17.87
14.032	1.895	18.87	18.86

Deswelling Induced by Lowering the Activity of the Diluent. Deswelling was also induced by the equilibrium deswelling method described previously.[25] This method differs from other osmotic deswelling techniques as the swollen gel is surrounded by a semipermeable membrane, which prevents the diffusion of polymer molecules used for lowering the activity of the diluent into the gel. The diluent activity in the gel can be calculated from the known osmotic pressure–concentration dependence of the dissolved polymer through the relationship

$$\ln a_1 = -\frac{\Pi \bar{V}_1}{RT} \qquad (20)$$

where Π is the osmotic pressure of the polymer solution. In order to adjust the activity of toluene, low molecular mass polystyrene (M_w = 37 000, M_m = 34 000) was used. The activity of the diluent was calculated from high-precision (±0.1%) osmotic pressure data obtained for a similar polystyrene sample dissolved in toluene.[26] Deswelling measurements were performed in the activity range 0.9950 < a_1 < 1.000. The time required to reach the equilibrium was found to be 10–12 weeks. The height, the diameter,

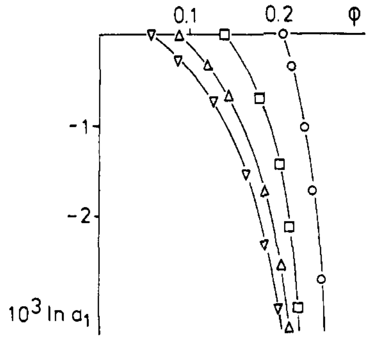

Figure 3. ln a_1 versus polymer volume fraction (ϕ) plots for PVAc/toluene gel samples. Cross-links were introduced at 9 wt % initial polymer concentration. PVAc/toluene: (○) 9/50; (□) 9/100; (△) 9/200; (▽) 9/400.

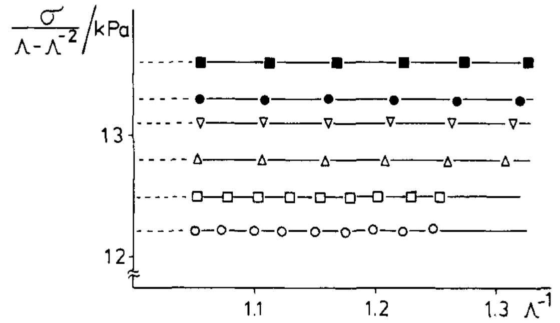

Figure 4. Mooney–Rivlin plots for 9/200 PVAc/toluene gel sample at different stages of dilution. ϕ: (■) 0.128; (●) 0.119; (▽) 0.113; (△) 0.107; (□) 0.100; (○) 0.092.

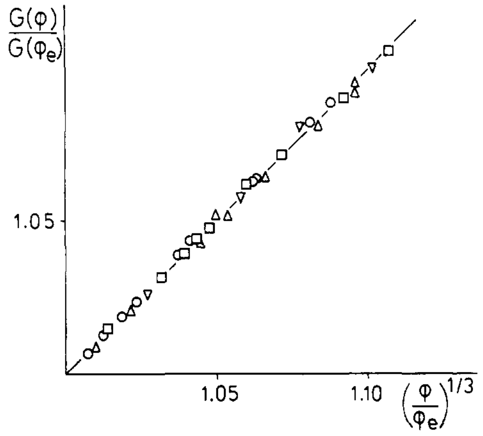

Figure 5. Variations of the reduced moduli $G(\phi)/G(\phi_e)$ as a function of $(\phi/\phi_e)^{1/3}$ for different PVAc/toluene gels. Polymer concentrations when cross-links were introduced: (○) 12; (□) 9; (△) 6; (▽) 3 wt %.

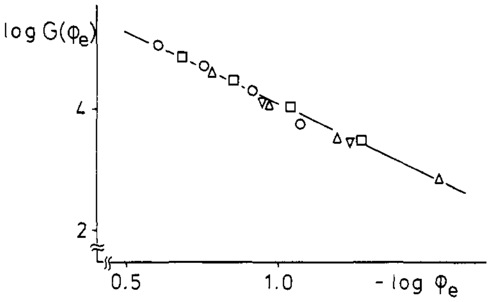

Figure 6. Double-logarithmic representation of the elastic modulus, $G(\phi_e)$, versus the polymer volume fraction of PVAc gels equilibrated with toluene ($a_1 = 1$). Symbols are the same as used in Figure 5.

and the mass of the gel samples were determined when equilibrium was attained. In several cases the reversibility of the deswelling process was also controlled by transferring the deswollen gels into polymer solutions with solvent activities increasing up to that of the pure swelling agent. No significant deviation was found between swelling ratios obtained by decreasing or increasing the activity. The height and diameter data of partially deswollen gels indicated that the deswelling process was isotropic. In Figure 3 the dependence of ln a_1 on the volume fraction of the network polymer is shown for some PVAc/toluene gels.

Modulus Measurement. The elastic moduli of the gels were evaluated from unidirectional compression measurements performed at constant volume on both freely swollen and partially deswollen gels at different stages of dilution by means of a homemade apparatus described earlier.[27] Force–deformation relations were determined over a wide range of force (from 0.0001 to 2.000 N) and deformation (from 0.006 to 3.333 mm) with an accuracy of ±0.0001 N and ±0.006 mm, respectively. Gel cylinders were deformed between two flat glass plates in the thermostable sample holder of the apparatus. The absence of barrel distortion and volume change during the measurements was checked. The experimental data were evaluated according to the Mooney–Rivlin equation:

$$\sigma = 2C_1(\Lambda - \Lambda^{-2}) + 2C_2(\Lambda - \Lambda^{-2})\Lambda^{-1} \qquad (21)$$

where σ is the nominal stress referring to the swollen undeformed cross-section of the gel, Λ is the deformation ratio, and C_1 and C_2 are constants. For all the PVAc gels, the constant C_2 was found to be equal to zero within the experimental accuracy, independent of the swelling ratio. Unidirectional compression measurements were carried out at deformation ratios $0.7 < \Lambda < 1.0$. In Figure 4 the $\sigma/(\Lambda - \Lambda^{-2})$ versus Λ^{-1} plots are shown for the 9/200 PVAc/toluene gel at six stages of dilution. One can see that experimental points scatter along straight lines parallel with the abscissa. The value of $2C_1$ can be identified with the shear modulus of the gel.[8]

All the experiments were carried out at a constant temperature of 25 ± 0.1 °C. The accuracy of the measurement of equilibrium concentration and deformation ratio was better than 0.5%. The reproducibility of activity measurements was found to be within 2–3%, while that of modulus measurements did not exceed 5%. In all cases at least three gels prepared in the same way were investigated and the arithmetic mean of the parallel measurements was used for evaluation.

Results and Discussion

Concentration Dependence of the Elastic Moduli of Gel Homologues. We start the discussion with the concentration dependence of the elastic modulus.

In Figure 5 the ratio of $G(\phi)/G(\phi_e)$ is presented as a function of $(\phi/\phi_e)^{1/3}$ for the 14 gel systems under study. The continuous line refers to the theoretical dependence given by eq 8. It can be established that the elastic modulus follows the concentration dependence $G(\phi) \propto \phi^{1/3}$, and the value of $G(\phi)$ can be expressed by the modulus of the freely swollen gel and by the ratio of the volume fraction of the network polymer to that of the freely swollen gel.

In Figure 6 experimental data referring to gel homologues equilibrated with pure swelling agent are presented. The slope of the straight line equals 2.33, which is close to the value $^9/_4$ predicted by the scaling theory and in good agreement with several previously published results.[15–23,29–32]

Effect of Unidirectional Deformation on the Equilibrium Concentration. We now turn our attention to the case when the distorted gel immersed in pure diluent

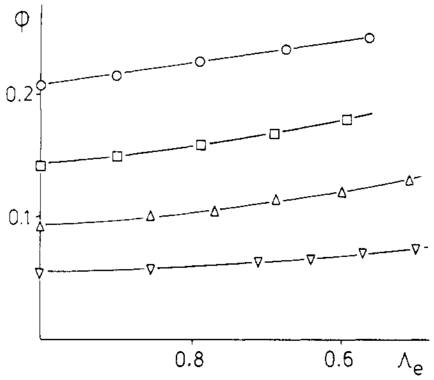

Figure 7. Variations of polymer volume fraction, ϕ, as a function of deformation ratio relative to the undeformed length of the freely swollen gel, Λ_e, for PVAc/toluene gels. Symbols are the same as used in Figure 3.

Table II
Volume Fraction Data for Natural Rubber/Benzene Systems; Comparison of Experimental Results of Treloar[4] with Calculations According to Equation 22

exptl data		calcd ϕ	
Λ_e	ϕ	$m = {}^9/_4$	$m = 2$
0.770	0.208	0.214	0.217
0.902	0.196	0.199	0.201
1.000	0.191	0.191	0.191
1.144	0.180	0.180	0.178
1.277	0.173	0.171	0.169
1.410	0.167	0.164	0.161
1.451	0.163	0.162	0.158
1.549	0.160	0.157	0.153
1.642	0.157	0.153	0.149

is allowed to attain the new equilibrium concentration due to the influence of the hydrostatic component of the applied stress. In Figure 7 the dependence of the equilibrium volume fraction of the network polymer is shown as a function of the deformation ratio. It is apparent that ϕ increases with decreasing Λ_e; i.e., the gel deswells under the applied pressure. The relative volume change depends on the cross-linking density, and it was found to be higher for slightly cross-linked networks.

In parts a and b of Figure 8 experimental data are presented according to eq 15 and 16, respectively. In Figure 8a the results of Treloar obtained for natural rubber samples swollen by benzene and heptane are also shown. The continuous lines in the figures were calculated with $m = {}^9/_4$, while the dotted lines with $m = 2$. It is apparent that experimental points scatter around the curves calculated with $m = {}^9/_4$.

In Tables II and III deformation ratios and volume fractions are given for natural rubber/benzene[4] and PVAc/toluene gels, respectively. Both elongation ($\Lambda_e > 1$) and compression ($\Lambda_e < 1$) measurements were performed on natural rubber/benzene systems. The volume fraction data given in the third column were calculated from experimentally determined ϕ_e and Λ_e values by using equation

$$\phi = \phi_e \Lambda_e^{-1/m} \tag{22}$$

with $m = {}^9/_4$ and those in the fourth column with $m = 2$. Calculations with $m = {}^9/_4$ are in better agreement with the experiments in both types of deformation.

In order to check the validity of eq 5, in Figure 9 the ratio Λ/Λ_e is plotted against $(\phi/\phi_e)^{1/3}$. The experimental points follow closely the theoretical curve, indicating the self-consistency of the experimental results.

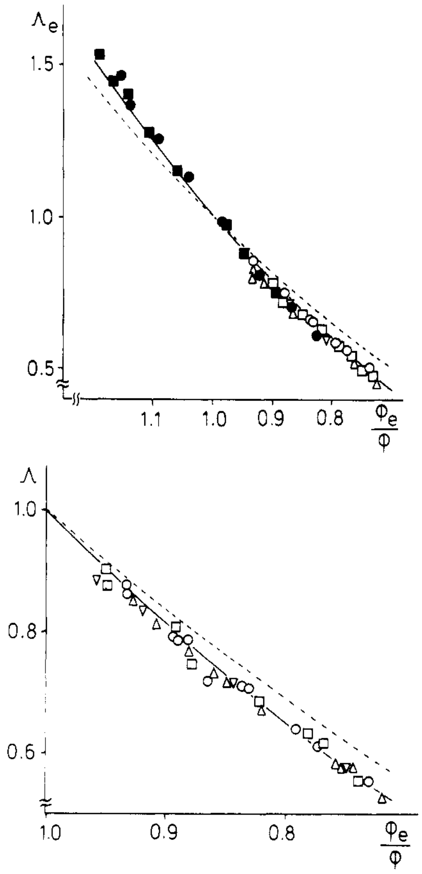

Figure 8. (a, Top) Deformation ratio relative to the undeformed length of the freely swollen gel, Λ_e, as a function of ϕ_e/ϕ for different gel systems. Curves have been calculated according to eq 16 with exponent ($m = {}^9/_4$ (solid curve) or $m = 2$ (dashed curve). The points ● and ■ represent experimental results of Treloar for natural rubber samples swollen by heptane and benzene, respectively.[4] Other symbols are the same as used in Figure 5. (b, Bottom) Deformation ratio relative to the undeformed length of the deswollen gel, Λ, as a function of ϕ_e/ϕ for PVAc/toluene gels. Curves have been calculated according to eq 15 with $m = {}^9/_4$ (solid curve) or $m = 2$ (dashed curve). Symbols are the same as used in Figure 5.

Table III
Volume Fraction Data for Poly(vinyl acetate)/Toluene Gels; Comparison of Experimental Results with Calculations According to Equation 22

	exptl data		calcd ϕ	
symbol	Λ_e	ϕ	$m = {}^9/_4$	$m = 2$
12/100	1	0.175	0.175	0.175
	0.863	0.188	0.187	0.188
	0.767	0.196	0.197	0.200
	0.671	0.210	0.209	0.214
	0.575	0.225	0.224	0.231
12/200	1	0.121	0.121	0.121
	0.849	0.130	0.130	0.131
	0.763	0.137	0.136	0.139
	0.678	0.145	0.144	0.147
	0.593	0.153	0.153	0.157
	0.509	0.165	0.164	0.170
6/100	1	0.107	0.107	0.107
	0.724	0.122	0.123	0.126
	0.620	0.130	0.132	0.136
	0.515	0.141	0.143	0.149

Comparison between Concentration Changes Induced by Unidirectional Compression of the Gel and Due to Lowering the Chemical Potential of the Diluent. Now we compare the effect of deformation (at fixed activity of the swelling agent) and that of diluent activity on the equilibrium concentration of the gel. The relationship between the elastic modulus, the deformation ratio, and the chemical potential of the swelling agent is

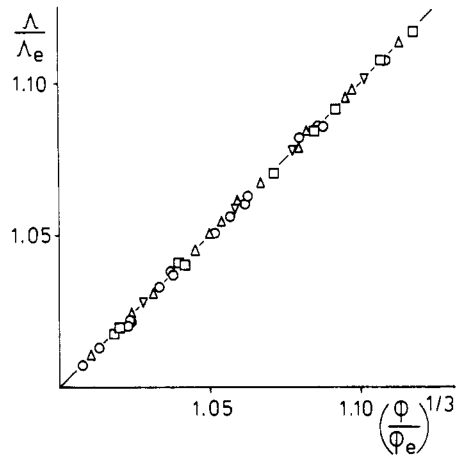

Figure 9. Ratio of deformation ratios, Λ/Λ_e, plotted against $(\phi/\phi_e)^{1/3}$ for PVAc/toluene gels. The diagonal full line has been calculated according to eq 5. Symbols are the same as used in Figure 5.

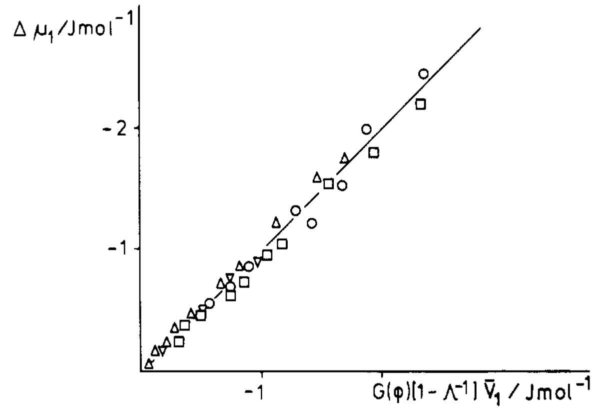

Figure 10. Chemical potential change of the swelling agent ($\Delta\mu_1$) plotted against $G(\phi)[1 - \Lambda^{-1}]\bar{V}_1$. The diagonal solid line denotes equivalence of the response of network to deswelling induced by lowering the diluent activity in the outer phase and to deswelling induced by unidirectional compression. Symbols are the same as used in Figure 5.

given by eq 17. According to that equation the chemical potential difference required to change the volume fraction of the network polymer from ϕ_e to ϕ can be obtained directly from experimental data relevant to the gel. On the other hand $\Delta\mu_1$ can also be determined from osmotic pressure measurements performed on the polymer solution equilibrated with the gel. Using eq 23 we get the chemical

$$\Delta\mu_1 = -\Pi\bar{V}_1 \qquad (23)$$

potential of the solvent in the solution phase, which should be equal to that of the swelling agent in the gel.

In Figure 10 the $\Delta\mu_1$ values calculated from osmotic pressure data are presented as a function of $G(\phi)(1 - \Lambda^{-1})\bar{V}_1$. The experimental points scatter around the theoretical straight line. This fact demonstrates the equivalence of the response of the network to isotropic shrinking and to unidirectional compression. The difference is within the limits of the experimental errors attending the separate determinations of the quantities studied.

In Figure 11 the ratio $\omega(\phi)/G(\phi)$ is plotted against ϕ/ϕ_e. The value of $\omega(\phi)$ was calculated from the osmotic pressure of the polymer solution equilibrated with the gel, while $G(\phi)$ was known from unidirectional compression measurements. It is apparent that calculations with $m = {}^9/_4$ are in quite good agreement with experimental data.

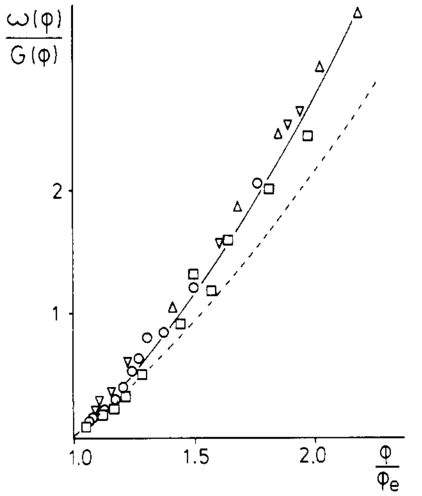

Figure 11. Ratio of $\omega(\phi)/G(\phi)$, where $\omega(\phi)$ is the swelling pressure and $G(\phi)$ is the elastic modulus, plotted against ϕ/ϕ_e. The solid curve has been calculated according to eq 18 with $m = {}^9/_4$, the dashed line with $m = 2$. Symbols are given in Figure 5.

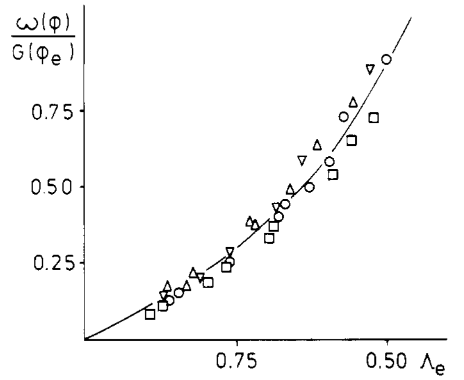

Figure 12. Values of $\omega(\phi)/G(\phi_e)$ against Λ_e for PVAc/toluene gels. The continuous curve corresponds to eq 19 with $m = {}^9/_4$. Symbols are given in Figure 5.

On the basis of eq 19 the swelling pressure of the deswollen gel can be expressed by $G(\phi_e)$ and Λ_e. In Figure 12 experimental data are presented for PVAc/toluene gels according to eq 19. The continuous curve was calculated with exponent $m = {}^9/_4$. The ratio of $\omega(\phi)/G(\phi_e)$ is a unique function of Λ_e. All the gels follow the same universal behavior, independent of the preparation conditions, i.e., the cross-linking density and the concentration of the polymer chains at the time of cross-linking.

Conclusions

In this work the effect of deformation and that of the activity of diluent on the equilibrium concentration of poly(vinyl acetate) gels swollen by toluene was demonstrated.

Elastic moduli of gel homologues equilibrated with pure swelling agent exhibited the concentration dependence predicted by the scaling theory. The elastic modulus ($G(\phi)$) of a partially deswollen gel at each dilution can be given by the modulus of the freely swollen gel ($G(\phi_e)$) and by the ratio of the actual volume fraction of the network polymer to that of the freely swollen gel.

Experimental volume fraction data referring to unidirectionally deformed gels being in equilibrium with pure diluent were compared with calculated values. The agreement between measured and calculated volume fraction data was satisfactory in cases of both natural rubber samples swollen by benzene and heptane and poly(vinyl acetate) networks swollen by toluene.

The correspondence between isotropic deswelling induced by lowering the activity of the diluent around the freely swollen gel and anisotropic deswelling due to unidirectional compression at fixed diluent activity was also studied. Experimental results proved the equivalence of the response of the network to isotropic shrinking and to unidirectional compression.

An attempt was made to evaluate the relationship between elastic modulus, swelling pressure, and equilibrium concentration of the gel. The swelling pressure was expressed in terms of the elastic modulus of the gel equilibrated with pure swelling agent and the deformation ratio relative to the undeformed length of the freely swollen gel. The validity of the proposed relationships was confirmed by experimental results.

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Registry No. Toluene, 108-88-3; benzene, 71-43-2.

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Diffusion of Homopolymers into Nonequilibrium Block Copolymer Structures. 1. Molecular Weight Dependence[†]

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ABSTRACT: The diffusion of deuteriated polystyrene (d-PS) and deuteriated poly(methyl methacrylate) (d-PMMA) into nonequilibrium symmetric diblock copolymer structures was studied by using elastic recoil detection (ERD). The diffusion coefficient, D_{HC}, of the d-PS and d-PMMA homopolymer chains of degree of polymerization N_{H} diffusing into the copolymer hosts was found to vary as N_{H}^{-2} for chains where $N_{\mathrm{H}} \lesssim N_{\mathrm{C}}/2$. N_{C} is the total number of monomer segments of the copolymer chain. In cases where N_{H} was sufficiently larger than N_{C} the dependence of D_{HC} on N_{H} was considerably greater than N_{H}^{-2}. D_{HC} was found to be an order of magnitude lower than D_{HH}, the diffusion coefficient of the homopolymer chains diffusing into their respective homopolymer hosts. It was found that varying the rate of solvent evaporation, changing the solvent used for preparing the samples, and preannealing the samples for sufficiently long periods of time before the diffusion process had a marked influence on the diffusional transport properties.

Introduction

The diffusion of homopolymer chains into phase-separated copolymer structures has received virtually no attention. Studies done thus far have primarily been concerned with the diffusion of homopolymer chains into homopolymer hosts.[1] It is clear from experiment that the tracer diffusion coefficient, D^*, of a chain of molecular weight M diffusing into a host of chains of sufficiently high molecular weight is described by $D^* = D_0M^{-2}$. This is consistent with theory.[2,3] D_0 is proportional to the molecular weight between entanglements and inversely proportional to the monomeric friction coefficient. Predictions

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