via syringe. The reaction mixture was stirred overnight at room temperature and quenched and purified as described above.

Fractional Precipitation. The graft copolymer (1.0 g) was dissolved in ca. 30 mL of THF. Concentrated acetic acid was added dropwise (ca. 20 mL) until a bluish white iridescent solution persisted. Several aliquots were centrifuged, and the combined precipitates were analyzed by ^{31}P NMR spectroscopy (δ 7.9). A blend [10% poly(methylphenylphosphazene) and 90% polystyrene by weight] was treated in the same manner. Polystyrene was completely precipitated after addition of ca. 4 mL of acetic acid (no ^{31}P signal). A second blend [50% poly(methylphenylphosphazene)-*graft*-polystyrene and 50% polystyrene] was also treated in the same manner. In this case, the addition of ca. 10 mL of acetic acid gave a cloudy solution, but it was necessary to add ca. 40 mL of acetic acid to acquire sufficient precipitate for ^{31}P NMR spectroscopic analysis (no signal).

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Registry No. BuLi, 109-72-8; ($Me_3SiN{=}P(Ph)(Me)OCH_2CF_3)(PhCH{=}CH_2)$ (graft copolymer), 118336-37-1.

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Notes

Effect of Cross-Links on the Swelling Equation of State: Polyacrylamide Hydrogels

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Introduction

In the literature there exists a body of rather precise experimental observations of vapor pressure differences between swollen polymer networks and the equivalent polymer solutions.[1-3] The clearly distinguished deviations in thermodynamic activity between these two states are attributed to an anomalous elastic contribution to the total free energy of swollen gels, the mixing contributions being assumed to be the same for the two states. This anomaly has been taken as qualitative evidence in favor of the junction fluctuation model of networks,[3] but quantitative agreement with this or any other single model remains elusive,[4] and the additivity of elastic and free energy terms has been called into question.

The conclusions drawn from the investigations of ref 1–3 are founded on the Flory–Rehner theory of polymer network swelling, the only allowed adjustable parameters of which are the second-order interaction parameter χ and the volume elastic modulus G_v. In this theory, interactions of an order higher than 2 follow a fixed protocol defined by the series expansion of a mixing term log $(1 - \varphi)$, where φ is the polymer volume fraction. Difficulties arise when the additional restrictive assumption is adopted that χ is the same in the un-cross-linked solution as in the cross-linked gel.

The purpose of this note is to show that network cross-linking can severely perturb the potentials between polymer segments, not only in the second order but also in higher order interactions. Consequently, for the purpose of deducing the elastic contribution to the chemical potential of the network, the use of the un-cross-linked solution as a reference state is not necessarily valid and could be misleading.

One can write for the osmotic pressure Π_u of a neutral un-cross-linked polymer solution (indicated by the subscript u)

$$\Pi_u = RT\rho\varphi/M + A_{2u}\varphi^{9/4} + A_{3u}\varphi^3 + \sum_{n>3} A_{nu}\varphi^n \qquad (1)$$

in which R is the gas constant, T the absolute temperature, ρ the density of the pure polymer, and M the mass of the polymer chains. The 9/4 power in the second-order term is the consequence of polymer–polymer correlations in the semidilute excluded volume condition (i.e., large M, $\varphi \ll 1$, $A_{2u} \gg A_{3u}\varphi^{3/4}$) for which simple scaling theory applies.[5] This nonintegral power loses its theoretical justification close to and below the Θ temperature ($A_{2u} < 0$), since the simple scaling used to derive it does not hold in this region, but this consideration is not important for the purposes of this note. The terms in eq 1 with $n > 3$, neglected in simple scaling, must be included to describe the higher order interactions at concentrations above the semidilute range.

In the cross-linked network (designated by the subscript c), the thermodynamic activity is defined by the swelling pressure, ϖ

$$\varpi = \Pi_c - G_v = A_{2c}\varphi^{9/4} + A_{3c}\varphi^3 + \sum_{n>3} A_{nc}\varphi^n - G_{vo}\varphi^{1/3} \qquad (2)$$

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Table I
Fitting Parameters to Swelling Pressure Measurements in Polyacrylamide Gels at 25 °C

sample[a]	n[b]	m[b]	φ_e[c]	A_{2c},[d] MPa	A_{3c}, MPa	G_{vo}, kPa
8/1	2.61	0.38	0.0358	5.5	21.7	12.1
8/2	2.82	0.26	0.0475	2.8	29.6	15.9
8/3	2.96	0.33	0.0574	0.6	33.9	18.9
8/4	2.98	0.40	0.0648	−0.2	34.6	24.5
8/5	3.10	0.35	0.0662	−1.3	37.1	20.9
lightly X-linked samples[e]	2.23 ± 0.01	0.33 ± 0.01	0.007–0.062	10.5	−1.0 ± 1.0	0.75–46.5

[a] Samples copolymerized with 8% w/v acrylamide and between 0.1% and 0.5% w/v bisacrylamide. [b] Apparent power dependence obtained by fitting the data to $\varpi = A\varphi^n - B\varphi^m$ between $\varphi = \varphi_e$ and $\varphi \approx 0.20$. [c] Equilibrium volume fraction. Calculated by using density of pure polyacrylamide $d = 1.30$ g/cm^3 (ref 8). [c] Coefficients obtained from fitting data to $\varpi = A_{2c}\varphi^{2.25} + A_{3c}\varphi^3 - G_{vo}\varphi^{1/3}$. [d] Data from ref 7: set of samples prepared with initial acrylamide monomer concentration in the range 3–15% w/v.

in which $G_v = G_{vo}\varphi^{1/3}$ is the volume elastic modulus. Any anomaly in the elastic term will naturally cause G_{vo} to be concentration dependent. In most experimental observations of the difference $\Pi_u - \varpi$, the concentration φ and the mass M are such that the first term on the right-hand side of eq 1 is entirely negligible. Thus one may write

$$\Delta = \Pi_u - \varpi = \Delta_2\varphi^{9/4} + \sum_{n>2} \Delta_n\varphi^n + G_{vo}\varphi^{1/3} \qquad (3)$$

in which $\Delta_n = (A_{nu} - A_{nc})$.

The Flory–Rehner theory assumes that all $\Delta_n = 0$ for $n > 2$. If, in addition, the Flory–Huggins interaction parameter χ is assumed not to change upon cross-linking, then Δ_2 is also equal to zero. Thus any unforeseen physical reason causing a deviation from zero in any Δ_n would be detected as a discrepancy in G_{vo}.

Below, we describe results of swelling pressure measurements in a series of polyacrylamide gels, in which strong variations are observed in the coefficients A_2 and A_3 upon cross-linking.

Experimental Procedure

A set of five polyacrylamide–water gels was polymerized with a total acrylamide content of 8% w/v and a varying bisacrylamide content: 0.1%, 0.2%, 0.3%, 0.4%, and 0.5% w/v. The gels were all prepared under the same conditions: 23 °C ambient temperature in the presence of 7×10^{-4} g/cm^3 ammonium persulfate and 2.8×10^{-7} v/v tetramethylethylenediamine (TEMED). Gelation took place in 15–20 min. After being left for 24 h for the reaction to go to completion, the gels were removed from their molds and steeped in distilled water for 1 month, in order to remove any sol fraction present and to allow gels to swell to equilibrium. During this time, the water was renewed at regular intervals.

The gels were cut to size, weighed, and inserted into dialysis bags, which were in turn placed in thermostated solutions at 25 °C of poly(vinylpyrrolidone), the activity of which is known.[6] After osmotic equilibrium was reached, the gels were removed from the dialysis bags and weighed and then evaporated to dryness in a vacuum oven at 80 °C. In this way the equilibrium concentration of each gel sample was measured as a function of the osmotic activity.

Results and Discussion

Analysis of the data was performed in a first approximation by assuming that the mixing energy can be replaced by its leading term alone, i.e.

$$\varpi = A_c\varphi^n - G_{vo}\varphi^m \qquad (4)$$

with n and m being adjusted by successive steps to minimize the mean square error. Convergence is obtained rapidly, giving $m \approx {}^1/_3$ and n, for these samples, in the range 2.6–3.1. These results are shown in Table I. For comparison, earlier experiments[7] on lightly cross-linked polyacrylamide gels gave $m = 0.33 \pm 0.01$, $n = 2.23 \pm 0.01$, and $A_c = 10.5$ MPa.

A more detailed approach to the data can be achieved by retaining the first two mixing terms in eq 2, i.e.

$$\varpi = A_{2c}\varphi^{9/4} + A_{3c}\varphi^3 - G_{vo}\varphi^{1/3} \qquad (5)$$

Further terms in the series expansion of eq 2 could also be included, but this is warranted neither by the accuracy of the data nor by the extra physical insight provided. The results of this fit for A_{2c} and A_{3c} are also listed in Table I.

Inspection of the results in Table I indicate that both A_{2c} and A_{3c} vary significantly with cross-linking density. For the higher cross-linking densities, A_{2c} vanishes, as for a Θ solution. Such a result is not intrinsically surprising, since chemical cross-linking alters the electronic configuration of the constituent polymer chains, so good solvents of the un-cross-linked polymer will tend to have a more unfavorable interaction parameter in the cross-linked gel. This effect is solvent dependent. Another contribution to this effect can also arise from the fact that cross-links, in binding together two otherwise free chains, generate a permanent local increase in concentration. The result is to reduce the effective overall concentration of polymer chains participating in concentration fluctuations, even though the total polymer mass present is unchanged; i.e., the effective interaction between polymer chains is reduced.

The increase in the third-order virial coefficient A_{3c} apparent in Table I is more surprising, probably because its significance is less intuitive. The fact that A_{2c} and A_{3c} depart substantially from their values in more lightly cross-linked samples, however, underlines the need for exercising extreme caution in using the Flory–Rehner theory to deduce information about the volume elastic moduli of cross-linked gels.

Our conclusion, based on the above observations, is that the equivalence of the mixing contribution to the free energy of a swollen network with that of the corresponding un-cross-linked polymer solution cannot be taken for granted. The conclusions of investigations that assume such equivalence therefore remain in doubt, in particular concerning the elastic anomaly and the nonadditivity of the elastic and mixing contributions to the free energy.

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Note Added in Proof. The replacement of the infinite series in eq 2 by the polynomial of eq 5 may be subject to criticism. The coefficients of the terms retained and their variation are not necessarily those of the true virial coefficients. This objection can be avoided by adopting the

Flory–Rehner free energy of mixing[1] and fitting the data to a Flory–Huggins parameter $\chi = \chi_2 + \chi_3\phi$. When this is done, a difference in χ subsists between the present samples and the more homogeneous gels of ref 7, which indicates a short fall in swelling pressure (i.e., an apparent excess elastic energy) at $\phi \simeq 1$ of the same sign and order of magnitude as found for other systems in ref 2 and 3. The conclusions of this note remain unchanged in this analysis.

Registry No. (Acrylamide)(methylenebisacrylamide) (copolymer), 25034-58-6.

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Prediction of Ternary Effects in Polymer–Mixed Solvent Systems

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Polymers in mixed solvents present new interesting phenomena; among them, cosolvency and preferential adsorption are notable examples. Properties measuring coil dimensions and excluded volume, such as intrinsic viscosity, $[\eta]$, second virial coefficient, A_2, or the interaction parameter from a Stockmayer–Fixman plot, B, are solvent composition dependent in a mixed solvent. The simplest behavior to be imagined is that the value of the property in a mixed solvent be intermediate between the values in the two pure liquids. However, the behavior observed is more complex. Large deviations from the linear interpolation between the two pure liquid values are often found.[1-6] Differences between measured and interpolated $[\eta]$ as large as 200% have been reported in cosolvent systems.[6]

The preferential adsorption coefficient, λ, can also present peculiar variations with solvent composition. The simplest behavior to be imagined for λ is that the solvent preferentially adsorbed always be the better solvent of the polymer. But the real situation is also more complex. There are numerous examples in which the poor solvent is preferentially adsorbed.[7] Even strong precipitants of the polymer can adsorb preferentially to it.[4,8] Often, one of the two liquids in the mixed solvent is preferentially adsorbed in a certain range of solvent compositions, while the other liquid is preferentially adsorbed in the rest of the composition range, giving thus an inversion in λ.[1,4,6,8-10]

For the theoretical description of excluded volume properties ($[\eta]$, A_2, B) and of preferential adsorption (λ), thermodynamic theory has been applied, first, the Flory–Huggins model (FH)[11,12] and, later, equation of state theory (Flory, Prigogine, Patterson formalism, FPP).[13-15] In the FH formalism, the noncombinatorial part of ΔG_M (Gibbs mixing function) for a ternary 1,2,3 system is written as a sum of binary terms (1-2, 1-3, 2-3), each one depending on a binary interaction parameter, g_{ij}. The form of these binary terms is $n_i\phi_j g_{ij}$ (n = amount of substance; ϕ = volume fraction).

This FH formalism was found to cause difficulties in interpreting the properties of ternary systems composed of a polymer and a mixed solvent. Its applicability was then extended by introducing a ternary interaction parameter, g_T, contributing a term $n_1\phi_2\phi_3 g_T$ to ΔG_M.[16,17] This extra ternary term is a correction that destroys the additivity of binaries in ΔG_M and has been considered as taking into account "ternary effects".

The principles underlying the FPP formalism are different. In no moment is ΔG_M assumed to be a sum of binary terms. All terms depend simultaneously on the properties of the ternary system, because the variable on which ΔG_M depends is the reduced temperature of the system, $\tilde{T}$, defined as[15]

$$\tilde{T} = (n_1p_1{}^*V_1{}^*\tilde{T}_1 + n_2p_2{}^*V_2{}^*\tilde{T}_2 + n_3p_3{}^*V_3{}^*\tilde{T}_3)/(n_1p_1{}^*V_1{}^*\tilde{T}_1 + n_2p_2{}^*V_2{}^*\tilde{T}_2 + n_3p_3{}^*V_3{}^*\tilde{T}_3 - n_1\theta_2V_1{}^*X_{12} - n_1\theta_3V_1{}^*X_{13} - n_2\theta_3V_2{}^*X_2) \quad (1)$$

($p_i{}^*$, $V_i{}^*$, $T_i{}^*$ = reduction parameters for pressure, molar volume, and temperatures; $\tilde{T}_i = T/T_i{}^*$; θ_i = molecular surface fraction; X_{ij} = exchange interaction energy density). The composition and characteristic parameters of the three components, as well as the exchange interaction energy densities for all three pair interactions (X_{12}, X_{13}, X_{23}), contribute simultaneously in defining $\tilde{T}$ of the ternary system.

Thus, one of the advantages of FPP formalism over FH for ternary systems is that it obviates any assumption about the additivity of binary terms. This advantage can be of use not only for polymer–mixed solvent systems but *also for two polymers in one solvent systems.*

Since FPP results are intrinsically ternary, it is possible to obtain with them a theoretical derivation of the error, which is committed when additivity of binaries is assumed. In other words, with the FPP formalism it is possible to estimate the ternary correction (g_T) needed in the FH results. This evaluation of the ternary correction for λ and for Y has already been given in detail.[15] (Y = total sorption potential, obtained from $[\eta]$, from A_2, or from B).

The FPP theory takes into account the dissimilarity in contact surface and in free volume between polymers and liquids, which the FH theory neglects. Since these dissimilarities have an important effect on λ and Y, it is reasonable to think that the ternary correction (g_T) needed in FH is in part due to these neglected dissimilarities. This idea was developed in detail before to calculate the ternary (g_T) corrections to λ and Y, showing that in fact these dissimilarities make an important contribution.[15] For some systems, they may be the only source of g_T corrections. In other systems, the deviations from FH behavior due to specific interactions may be an additional contribution to the corrections.[8,18]

Recently, it has been shown that an empirical relationship exists between $g_T{}^\circ$, $(\partial g_T/\partial\phi_3)^\circ$, and the liquid mixture interaction parameter, g_{12}.[19,20] (1 and 2 = liquids; 3 = polymer; degree sign = dilute solution values). Six different systems of the polymers PS, PMMA, and PDMS were studied. For those systems, enough data are available to determine all three quantities involved in the correlation: g_{12} is obtained from G^E of the liquid mixture, $g_T{}^\circ$ from λ, and $(\partial g_T/\partial\phi_3)^\circ$ from A_2. Careful analysis of the experimental data showed that in each one of the systems

$$\frac{g_T{}^\circ}{g_{12} + (\partial g_T/\partial\phi_3)^\circ} = K \quad (2)$$

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