60 wt % P-*t*-BA is clearly a superposition of the spectra of the two pure homopolymers, thus revealing a high degree of incompatibility at the microscopic level. On the other hand, no additional MWS peak is detectable, probably because the constituent phases possess similar electrical conductivities.

Conclusions

The shape and position of the molecular relaxation peaks appearing in block copolymers and polyblends studied in this paper are generally similar to those observed in the pure constituent homopolymers while no relaxation effect ascribable to a possible diffuse interface has been detected. These results, although not disproving the existence of such a diffuse boundary, show that the amount of molecular mixing, if any, is weak and that the relaxations involving ionic charge carriers are to be attributed to interfacial polarization resulting from the existence of well-separated phases rather than to space charge polarization. The present experimental evidence thus suggests that the thermally stimulated depolarization technique is well suited to the study of the relaxational behavior of heterogeneous materials. Obviously, several problems remain to be solved for a quantitative analysis of the spectra in terms of phase volumes and microdomain morphology. This will be the subject of a further paper.

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Aging and Thermodynamics of Polyacrylamide Gels

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ABSTRACT: Arguments that the large changes observed in the swelling of polyacrylamide gels "cured" for different lengths of time are due to the formation of a heterogeneous structure rather than an increase in cross-link density as was recently suggested are presented. Torsion pendulum measurements indicate that the effective cross-link density remains practically constant over a period of 40 days. To interpret the swelling data we use a simple two-phase model which despite its simplicity reproduces reasonably well the experimental data and indicates that the aging phenomenon may be the result of the development of such a heterogeneous structure.

The thermodynamics of gels describe the swelling or collapse phenomena that are observed when a gel network is brought into contact with a solvent. The underlying idea, due to Flory,[1] is the interpretation of the swelling equilibrium as an osmotic pressure equilibrium of the solvent outside and inside the gel network. Flory's equation predicting swelling of *dry* gels in good solvents has been tested with good agreement on various systems, including natural rubber,[2] butyl rubber,[3] and polystyrene gel.[4] For gel networks which are formed in the presence of a solvent, Hermans'[5] or Dušek's[6] modifications of Flory's equation are commonly used. Recently, Tanaka[7] proposed an equation for the osmotic pressure of a gel–solvent system which was thought to have the unique feature of a sharp collapse (transition) as a function of polymer–solvent interaction (or temperature) when the gel possesses a cross-link density above a certain critical value. Such a sharp transition from swelling to collapse over a very narrow range of polymer–solvent interaction (or temperature) was observed by Tanaka for *aged* polyacrylamide gels in water–acetone mixtures as a function of acetone concentration, and more extensive results are presented below. The sharp transition exhibited by Tanaka's equation is not unique to that equation, and Hermans' (or Dušek's) equation exhibits a similar behavior,[8] although at higher values of the interaction parameter, χ, where χ is taken to be equal to $\Theta/2T$, with Θ being the Flory temperature of the polymer–solvent system. There are, how-

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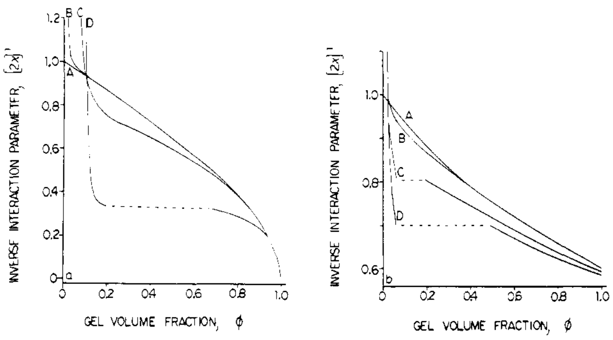

Figure 1. Volume fraction of polymer in the gel network at equilibrium for various values of cross-link density. (Left) Using Hermans' equation: (A) $\upsilon_1\nu_e/V_0 = 0$; (B) $\upsilon_1\nu_e/V_0 = 10^{-3}$; (C) $\upsilon_1\nu_e/V_0 = 10^{-1}$; (D) $\upsilon_1\nu_e/V_0 = 1$. (Right) using Tanaka's equation: (A) $\nu_0 = 0$; (B) $\nu_0 = 5.5 \times 10^{-5}$; (C) $\nu_0 = 3.0 \times 10^{-4}$; (D) $\nu_0 = 10^{-3}$.

ever, some serious difficulties with Tanaka's interpretation[7] of the swelling and collapse phenomena of polyacrylamide gels in water–acetone solutions in terms of the thermodynamic transition exhibited by the theoretical equations. These difficulties are described below and are due, we believe, to the fact that the "curing" and the collapse behavior of polyacrylamide gels are brought about by a different mechanism owing to the *heterogeneity* of these gels.

In the various thermodynamic equations for gel–solvent equilibrium mentioned above there are three contributions to the osmotic pressure which balance out to zero at equilibrium. In Flory's mean-field calculation the first two contributions are the familiar lattice entropy of mixing term and van Laar's expression for the enthalpy of mixing; the third contribution to the osmotic pressure arises from the elastic contribution of the cross-links. Recently the scaling approach developed by de Gennes[9] for semidilute solutions of entangled polymers has been applied with success to predict the dependence of the compressional modulus and the cooperative diffusion coefficient of cross-linked polystyrene gels on the swelling equilibrium concentration.[10] The dimensional analysis of the scaling approach lacks, however, the precise numerical coefficients needed for comparison with our experimental equilibrium data; we have, therefore, restricted our comparison to the mean-field approach but this should not affect the conclusions of our work. The important point is that the transition obtained from the thermodynamic equations occurs above a certain *critical* cross-linking density and represents the *coexistence* curve of *two gel phases* which should disappear and reappear by changing temperature or solvent composition.[8] These are not the phenomena observed in the swelling curves of the polyacrylamide gels.

We report here measurements of the cross-link density via the storage shear modulus G[11] as a function of aging time using torsion pendulums. We observed that curing time had little effect on the measured cross-link density. These results are in contradiction with Tanaka's proposition that the change in the behavior of the swelling curve with curing time is attributable to an order-of-magnitude change in the cross-link density with curing time. Such an assumption is necessary[7] if the polyacrylamide gel swelling behavior were to be interpreted as a thermodynamic transition of the type discussed above. There are, furthermore, several other important qualitative discrepancies between the thermodynamic transition curves (Figure 1, left) Hermans' equation, or Figure 1, right); Tanaka's equation) and the experimental swelling data (Figures 3 and 6): (a) For a good solvent, such as pure water, where $(2\chi)^{-1} > 1$, the thermodynamic equations predict *less* swelling with an increase of cross-link density (Figure 1, left) or at most no change in swelling (Figure 1, right); a large increase in swelling is, however, observed with aging. (b) As the cross-link density increases, the transition point is predicted to shift appreciably to lower values of T/Θ [$\equiv(2\chi)^{-1}$], whereas a very small shift, if any, is observed experimentally. (c) Finally, the equations predict an *increase* in swelling or a *decrease* in collapse at lower values of T/Θ (values less than unity) as a function of cross-link density, and, although an *increase* in swelling is observed as a function of curing time at the relatively high values of T/Θ, an *increase* in collapse is observed at the lower values of T/Θ.

One of the difficulties in testing a thermodynamic equation for a gel is the determination of the interaction parameter χ. This is particularly true in the case of polyacrylamide in acetone–water mixtures, where acetone is a poor solvent and the polymer precipitates (at 30 °C) in mixtures of 37% acetone. This concentration corresponds to the gel transition to the collapse state, so that the standard method of obtaining interaction parameters from solutions is not possible at the high acetone concentration where collapse occurs. Estimates of the χ parameters in the swelling region for acetone concentration lower than ~35% were obtained by applying the Flory–Fox expansion factor relation to the swelling of 6-h-old gel relative to its "prepared" size.[12] A reasonable estimate of χ for pure water, which compares well with values from other sources, is obtained and gives some confidence on the values obtained for the acetone mixtures. Although these estimates are limited to the swelling region (acetone concentration below 35% acetone), they will be used as guiding values of the interaction parameters to be used in the fitting of the theoretical predictions to the experimental data.

Attempts to fit the experimental swelling data of gels cured for various lengths of time by varying the cross-link density in Tanaka's equation were unsuccessful even in the case of pure water, where the interaction parameter is established to be around 0.48. We show, however, that Hermans' equation can be reasonably well fitted to the experimental swelling and collapse data by using a *constant* cross-link density and an *inhomogeneous* two-phase structural model proposed by Weiss and Silberberg.[13] These authors concluded from permeation studies of water through polyacrylamide gels that these gels must have an inhomogeneous structure. This conclusion is supported by our fitting of the experimental swelling data to Hermans'equation using a *constant* effective cross-link density and *apparent* interaction parameters χ_{app} (which change with curing time), obtained directly from the swelling and collapse data themselves. Since the interaction parameter for a given polymer–solvent mixture should be independent of time (under identical conditions), this fitting procedure is only meaningful insofar as it points out that the apparent change in χ may be the effect of a changing structure (entropy of mixing term) rather than a change in the cross-link density (elastic term) which could not explain the experimental data. This possibility, along with our experimental observation of a negligibly small change in the elastic term, suggests the probability of an *inhomogeneous* structure as pointed out by Silberberg and his co-workers.[13,14] Nonhomogeneous gel structures are not uncommon and have been observed via electron microscopy in both radiation cross-linked poly(ethylene oxide) gels[15] and collagen gels formed by glutaraldehyde cross-linking.[16] Furthermore, several thermodynamic arguments for phase separation that lead to inhomogeneous gel structures are reported in the review article of Dušek and

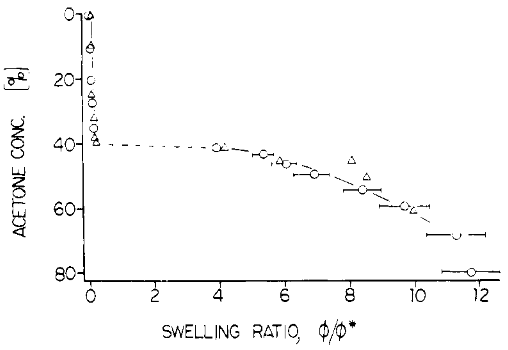

Figure 2. Comparison of the 30-day gel collapse data with Tanaka's results obtained under similar conditions: (○) present work (T = 25.0 °C); (△) Tanaka's data (T = 23 °C).[7] Error bars in the swelling region are negligible.

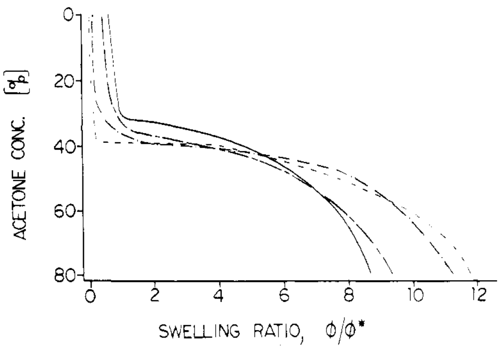

Figure 3. Acetone concentration vs. swelling ratio at 25 °C: (—) 6-h gel; (– – –) 3-day gel; (– – –) 15-day gel; (- - -) 30-day gel. The actual data points are presented in Figure 6.

Prins[8] where references to experimentally observed phase separation in gels are also quoted.

Preparation and Procedure

A standard method[7,17] was used to prepare the gels for all the experiments reported here. The ingredients consisted of 5 g of acrylamide, 0.133 g of *N,N'*-methylenebisacrylamide (BIS), 40 mg of ammonium persulfate, and 150 μL of tetramethylethylenediamine (TEMED). All ingredients except TEMED were dissolved in water, after which the TEMED was added and the solution taken to 100-mL volume. The solution was thoroughly mixed and poured into the test tubes and pendulum molds for use in the various experiments. The molds were covered with Parafilm to make an airtight seal and were left on a lab bench of a temperature-controlled room (25 ±2 °C) to allow for gelation and aging. Two types of torsion pendulums were used in measuring the storage modulus of the gels as a function of aging: a gas-bearing torsion pendulum with a Bentley-Nevada proximetor and an associated recorder described elsewhere[18] and several less sophisticated simple test tube pendulums. The simpler pendulums were used to permit the study of a large number of gels over a long period of time and permit direct observation of the gels for possible degradation. The moment arms of these pendulums were horizontal aluminum bars 22-cm long with metal washers weighing 15.26 g on each end to increase the moment of inertia of the system. The bobs were 20-cm long, and 0.5-cm-diameter glass rods were directly connected to the moment arm. The lower end of the glass rods was pointed and acted as a bearing for the system. The cups holding the gel were glass test tube molds, 12.5-cm long and 2.54 cm in diameter, giving a clearance of 1.02 cm between the cup and bob. The moment of inertia of the system was determined to be 3225 g cm^2. The frequency of oscillation in these pendulums was measured by monitoring cycle frequency with a stopwatch.

Swelling and collapse experiments were performed on 0.5-cm-thick cylindrical samples cut from the central part of gels molded in the test tubes. Gel samples were initially placed in pure water. After swelling equilibrium was reached, the samples were removed from pure water and placed in a 10% acetone in water solution. When the new swelling equilibrium was established and the measurement of the diameter made, the process was then continued on to higher acetone concentrations such that the relationship between acetone concentration and swelling was determined reversibly from one gel sample.

Experimental Results

A. Swelling and Collapse Curves. Figure 2 shows a plot of acetone concentration vs. swelling ratio for a 30-day gel sample. The swelling ratio, ϕ/ϕ^*, is defined as the ratio of the volume fraction of the polymer in the gel network after equilibration (ϕ) in an acetone–water mixture to the volume fraction of the polymer in the gel as prepared (ϕ^*). Assuming no volume change due to mixing solvents and polymer, one has[7]

$$\phi/\phi^* = V^*/V = (D^*/D)^3 \tag{1}$$

where D is the diameter of the sample and the asterisk refers to the prepared state. The last equality in eq 1 implies isotropic swelling. The "curing time" or age of the gel is measured from the time of the addition of the initiator to the beginning of the swelling experiment. From Figure 1, it is observed that swelling occurs for all acetone concentrations less than 37% acetone, where the swelling ratio is less than 1. Whenever the swelling ratio is greater than 1, the gel has shrunk and we shall say that it has collapsed from its initial state. Figure 2 also shows the data points previously obtained by Tanaka for the same gel at the same age. Agreement between the two sets of results is good and is even better for the 3-day gel (not shown). Apart from the 3- and 30-day gel swelling–collapse curves we have also obtained these curves for the 6-h, 15-day, and 45-day gels. Figure 3 shows the results for all the gels except the 45-day gel which gave results, within experimental error, identical with the results of the 30-day gel. Unlike the 6-h, 3-day, and 15-day curves which show a smooth transition from the swelling to the collapse region, the 30- and 45-day curves show a discontinuous-like behavior which occurs over a very narrow concentration range when moving from the swelling to the collapse region. Although not immediately obvious from Figure 3, variations of swelling with curing time are much more pronounced than variations of collapse in solutions of 60% acetone and higher. For example, at acetone concentrations of less than 20% the volume increase of a 3-day gel is 85% of its initial prepared volume, whereas for the 30-day gel it is 1100%; on the other hand, the collapse of a 3-day sample in 70% acetone is 88% and increases only to 92% for the 30-day gel.

B. Cross-Link Density. For free oscillatory shearing between a cup and a bob separated by a viscoelastic material, the storage modulus is given by[11]

$$G = (\omega^2 I/b)(1 + \Delta^2/4\pi^2) \tag{2}$$

where

$$b = \frac{4\pi L}{(1/R_1^2) - (1/R_2^2)} \tag{3}$$

ω is the frequency oscillation (rad/s), Δ is the logarithmic decrement, L is the length of the bob (cm), R_1 is the radius of the bob (cm), R_2 is the radius of the cup (cm), and I is the moment of inertia (g cm^2). The logarithmic decrement is defined as the natural logarithm of the ratio of the amplitudes of two successive oscillations, and for the gas-bearing pendulum it was determined by measuring the amplitude of the oscillations from the recorder. Geometry and characteristics of the gas-bearing pendulum are found in the earlier work of Hamed and Rodriguez.[18] The logarithmic decrement could not be measured in the simple

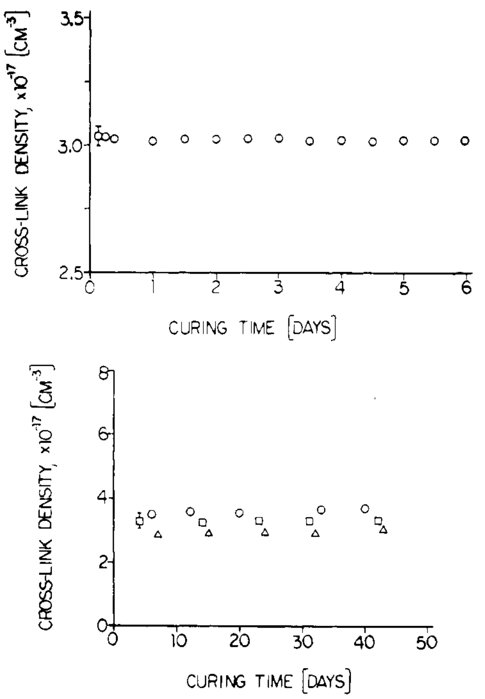

Figure 4. Cross-link density N as a function of curing time at 25 °C. (Top) Using the gas-bearing pendulum and letting a = 2 in eq 4. Error bar shown for the first point only. (Bottom) Using glass test tube pendulums for three different samples with a = 2 in eq 4. Error bar shown for the first point only.

test tube pendulums and was neglected; this resulted in a small error in the evaluation of G from these pendulums. The storage modulus is related to the cross-link number density N by the equation[11]

$$G = aNkT \qquad (4)$$

where a is a constant of order unit, k is Boltzmann's constant, and T is the temperature (K).

Figure 4, top, represents the data obtained with the gas-bearing torsion pendulum. The first measurmement of G (and of cross-link density) was 3 h after the sample was made. The figure shows that the cross-link density remains approximately constant over a 6-day period. A longer term effect of curing time on the cross-link density is shown in Figure 4, bottom, where the less accurate test tube torsion pendulum data are reported. It is obvious, nonetheless, that the increase in the number of cross-links as calculated by the above procedure is small (being at most several percent), up to 40 days of curing time.

Assuming that each molecule of *N,N'*-methylenebisacrylamide forms one cross-link, a straightforward stoichiometric calculation leads to the value of 5.2×10^{18} cross-links/cm^3. The values measured according to Figure 4 range from 2.7×10^{17} to 3.7×10^{17} cross-links/cm^3, which accounts for only 5–7% of the expected cross-links. This discrepancy may be mainly attributed to the great extent of intramolecular cross-linking (cyclization) which occurs in high dilution and which also leads to the formation of inhomogeneities.[19] Pendent chains[20] and the very close proximity of several cross-link units acting as one "effective" cross-link[13] would also contribute to this discrepancy.

C. Apparent Interaction Parameters from Swelling Data. The apparent interaction parameters calculated here from the swelling data of the 6-h, 3-day, 15-day, and 30-day gels and the relationship of Flory and Fox[21] relating the polymer expansion factor α to the interaction parameter are only meaningful in the sense that it is possible to use these values to fit the experimental data to Hermans' thermodynamic equation, provided that the cross-linking density is kept constant (Figure 5). Attempts to fit the experimental data by varying the cross-link density with curing time in Tanaka's or Hermans' equation and using reasonable estimates of the interaction parameters that are kept constant (with gel age) were tried but failed. Fairly constant χ values should be expected for this system, and the apparent curing-time-dependent values calculated here only serve to indicate that for a constant cross-link density, as is observed experimentally, the entropy of mixing term is inadequate and is compensated for by these apparent changes in χ.

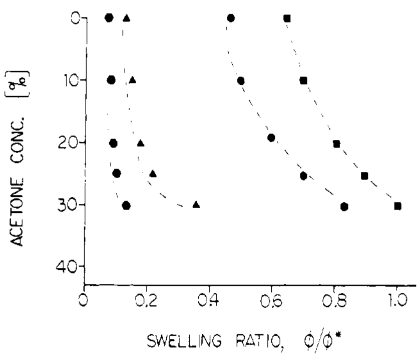

Figure 5. Experimental data points for (■) the 6-h gel, (●) the 3-day gel, (▲) the 15-day gel, and (●) the 30-day gel for several acetone concentrations compared to the predictions of Hermans' equation (dashed curves) using $\nu_e/V_0 = 2.90 \times 10^{-5}$ mol cm^{-3} and the apparent interaction parameters listed in Table II.

Table I
Values of the Molar Volume
of the Pseudo-One-Component Solvents at T = 25 °C

[acetone], vol %	v_1, cm^3/mol	[acetone], vol %	v_1, cm^3/mol
0	18.1	40	33.6
10	21.6	50	38.4
20	25.4	60	43.8
25	27.1	70	49.8
30	29.5	80	56.6
35	31.8		

The Flory–Fox relation gives

$$\alpha^5 - \alpha^3 = 2C_m(\tfrac{1}{2} - \chi)M^{1/2} \qquad (5)$$

where α, the expansion factor, will be taken here to be the expansion from the prepared gel state such that $\alpha = D/D^*$, with D^* = 1.75 cm; M is the molecular weight which we have taken to be the average molecular weight of the polymer prepared by the same procedure as the gel but with no cross-linking agent added. This was determined to be 271 000 g mol^{-1}. The constant C_m is given by the expression

$$C_m = \frac{27}{2^{5/2}\pi^{3/2}} \frac{v_{sp}^2}{N_A v_1} \left(\frac{\langle r_0^2 \rangle}{M} \right)^{-3/2} \qquad (6)$$

The value of $(\langle r_0^2\rangle/M)^{1/2}$, where $\langle r_0^2\rangle^{1/2}$ is the unperturbed dimension of the chain, is given by Immergut and Brandrup[22] to be 10^{-8} cm mol$^{1/2}$ g$^{1/2}$, and v_{sp}, the specific volume of the pure polyacrylamide, is taken to be[13] 0.7 cm^3 g^{-1}. N_A is Avogadro's number and v_1, the molar volume of the acetone–water mixture, is measured via a specific gravity densitometer (values listed in Table I). The values of χ_{app} obtained by this procedure are listed in Table II. It is interesting to note that the apparent interaction parameters for the 6-h gel are close to the values we have obtained from viscometric methods and Fixman–Stockmayer plots.[12] Other sources[22] lead to an estimate of 0.48

Table II
Values of the Apparent Interaction Parameter of the 6-h, 3-day, 15-day, and 30-day Gels

curing time	[acetone], vol %	α	χ_{app}
6 h	0	1.162	0.486
	10	1.129	0.488
	20	1.075	0.493
	25	1.042	0.496
	30	1.000	0.500
3 days	0	1.294	0.463
	10	1.263	0.464
	20	1.180	0.477
	25	1.131	0.485
	30	1.067	0.493
15 days	0	1.964	−0.039
	10	1.874	0.008
	20	1.761	0.098
	25	1.622	0.199
	30	1.433	0.374
30 days	0	2.361	−0.999
	10	2.321	−1.130
	20	2.207	−0.956
	25	2.113	−0.719
	30	1.974	−0.405

for the interaction parameter of polyacrylamide in pure water, and, since the polymer precipitates in acetone concentration of 37% or higher, the interaction parameter in these mixtures is expected to be greater than 0.5[1] as shown by the trend in χ_{app}'s of the 6-h gel.

Numerical Results and Comparison with Experiments

Using a quasi-chemical approach to cross-linked polymer networks in solution, Dušek[6] has obtained the following relation for the osmotic pressure, Π, in the network:

$$\Pi v_1 = -RT\left[\ln(1-\phi)+\phi+\chi\phi^2+\frac{v_1\nu_e}{V_0}(\phi^{1/3}\phi^{*2/3}-B\phi)\right] \tag{7}$$

R is the gas constant, ν_e/V_0 is the cross-link density in the dry network, ϕ^* is the volume fraction of the polymer in the prepared gel, and $B = 2/f$, with f being the effective functionality of the cross-linking agent. The parameters χ, T, and v_1 have been defined earlier. Equation 7 reduces to Hermans' equation[5] when $B = {}^1/_2$ and to Flory's equation for the swelling of dry networks[1] when $\phi^* = 1$ and $B = {}^1/_2$. Tanaka recently[7] modified Flory's equation and wrote

$$\Pi v_1 = RT\phi_0^3\left[\frac{1}{2\phi_0}(1-2\chi)\times\left(\frac{\phi}{\phi_0}\right)^2+\frac{1}{3}\left(\frac{\phi}{\phi_0}\right)^3+S\left(\frac{\phi}{2\phi_0}-\left(\frac{\phi}{\phi_0}\right)^{1/3}\right)\right] \tag{8}$$

where $S = \nu_0/\phi_0^3$, with ν_0 being a dimensionless cross-link number and ϕ_0 being the volume fraction of un-cross-linked polymer. Equation 8 may be obtained from Flory's analysis by interpreting the expansion factor α to be that relative to the prepared gel rather than the dry gel. The assumptions that ϕ is small and that v_1, the molar volume of the solvent, is approximately equal to the effective molar volume of the cross-link unit are also built into eq 8.

A. Hermans' Equation with Curing-Time-Dependent χ. Figure 5 shows plots of acetone concentration vs. swelling ratio for gel samples cured for 6 h, 3 days, 15 days, and 30 days. The dashed curves represent numerical solutions of ϕ from eq 7 set equal to zero. The volume fraction of polymer in the prepared gel, ϕ^*, was determined from the preparation to be 0.035 and the values of the molar volume of the solvent, v_1, are listed in Table I. The value of the interaction parameter was taken to be the appropriate value of χ_{app} listed in Table II and the fit was obtained by minimizing the mean average deviation of the experimental points, using $\nu_e/V_0 = 2.9 \times 10^{-5}$ mol/cm^3, which is in the range experimentally observed if, in eq 4, $a \simeq 1$. Despite the unsatisfactory aspect of using curing-time-dependent interaction parameters which the subsequent procedure will avoid, this procedure serves to demonstrate that the experimental swelling data could be reproduced by using Hermans' equation and keeping the number of cross-links constant. None of the attempts using eq 8 came close to fitting the set of swelling data as eq 7 was able to do. Unsuccessful attempts were made both by using the χ_{app}'s and by changing the number of cross-links with curing time.

The large variation of χ_{app}'s with curing time and the experimental near-constancy of cross-link density indicate the inadequacy of the one-phase entropy of mixing term in eq 7. To remedy this inadequacy, the simple inhomogeneous two-phase gel model[13] mentioned earlier was used.

B. Inhomogeneous Two-Phase Gel Model. To account for the permeability data of water through various preparations of polyacrylamide gels, Weiss and Silberberg have proposed a simple two-phase structure of the gel: one phase, nondraining, contains a high volume fraction of gel substance and is denoted "phase 1"; the other, free-draining and containing a low concentration of polymer and cross-links, is labeled "phase 2". By assigning different permeability and flux to each region, Weiss, Van Vliet, and Silberberg have been able to account successfully for their permeability data.[14] We apply this model here to our swelling data by assuming that the two phases are weakly bound to each other such that they swell independently. The nondraining regions are pictured as spheres of average radius a, randomly distributed in the gel media and separated by an average distance R. The volume fraction of polymer in the equilibrated gel is then written as

$$\phi = \beta\phi_1 + (1-\beta)\phi_2 \tag{9}$$

where $\beta = (a/R)^3$ is the volume fraction of phase 1. We can write a similar relation for the prepared gel such that

$$\phi^* = \beta^*\phi_1^* + (1-\beta^*)\phi_2^* \tag{10}$$

where the ϕ_i^*'s represent volume fractions in the prepared gel and β^* is the volume fraction of phase 1 in that state. The parameters β and β^* are simply related by

$$\beta = \beta^*\phi_1^*\phi_2[\beta^*\phi_1^*\phi_2 + (1-\beta^*)\phi_1\phi_2^*]^{-1} \tag{11}$$

The cross-link density may also be written as

$$S = \beta^*S_1 + (1-\beta^*)S_2 \tag{12}$$

where $S = \nu_e/V_0$. To fit the model to the experimental swelling and collapse data obtained, we apply Hermans' equation—eq 7—to each of the phases 1 and 2 separately, such that

$$0 = \ln(1-\phi_1) + \phi_1 + \chi\phi_1^2 + v_1S_1(\phi_1^{1/3}\phi_1^{*2/3} - \phi_1/2) \tag{13}$$

and

$$0 = \ln(1-\phi_2) + \phi_2 + \chi\phi_2^2 + v_1S_2(\phi_2^{1/3}\phi_2^{*2/3} - \phi_2/2) \tag{14}$$

where the interaction parameter is assumed to be concentration independent and hence identical in both phases.

Equations 9–14 form a set of six coupled equations. The polymer volume fraction in the prepared gel, ϕ^*, is ob-

Table III
Values of the Effective Interaction Parameter in Various Acetone-Water Mixtures

[acetone], vol %	χ_{eff}	[acetone], vol %	χ_{eff}
0	0.4860	40	0.5706
10	0.4863	50	0.5944
20	0.4890	60	0.6214
25	0.4912	70	0.6346
30	0.4937	80	0.6452
35	0.5387		

Table IV
Values of ϕ_1*, ϕ_2*, S_1, S_2, and β* from Fits to the 6-h and 3-, 15-, and 30-day Experimental Swelling and Collapse Data

curing time	β^*	$10\phi_1^*$	$10^2\phi_2^*$	10^3S_1	10^7S_2
6 h	0.95	0.36	1.36	0.26	1.00
3 days	0.89	0.38	0.80	0.28	0.90
15 days	0.20	1.59	0.40	1.25	0.70
30 days	0.12	2.70	0.30	2.08	0.30

tainable from the preparation recipe to be 0.035; also known are the values of the molar volume of the various solvents listed in Table I and the value of the total cross-link density $S = 2.50 \times 10^{-4}$ mol/cm^3. We would like to predict the equilibrium values of ϕ obtained experimentally. For each acetone concentration, we are left, however, with nine unknowns, ϕ_1*, ϕ_2*, ϕ_1, ϕ_2, χ, S_1, S_2, β* and β, and six equations. We have, though, two restrictions to satisfy: (a) for a given gel age, β*, ϕ_1*, and ϕ_2* are constant, and (b) for a given acetone concentration, χ is constant. We therefore fit the experimental ϕ's to the predicted ϕ's by using a three-parameter fit subject to the given restrictions. As adjustable parameters, we chose ϕ_2*, S_2, and β*. The fitting procedure is divided into two parts: first, the effective values of χ for acetone concentrations from 0 to 80% are determined with the experimental 6-h gel swelling data. These values of χ are then held constant and the values of ϕ_2*, S_2, and β* are adjusted to best fit the 3-, 15-, and 30-day data.

The values of the interaction parameters obtained from the 6-hour gel data, χ_{eff}, are shown in Table III. The values and trend of these χ_{eff}'s from 0 to 30% acetone in water correspond within a few percent to those obtained from Stockmayer–Fixman plots. The values of χ_{eff} in Table III are used to fit the 3-, 15-, and 30-day swelling–collapse data and the values of ϕ_2*, S_2, and β* obtained are shown in Table IV along with those used for the 6-h gel. The value of $S_2 = 1 \times 10^{-7}$ for the 6-h gel was taken to be of the same order of magnitude as that used by Weiss et al.[14] We also find that the equilibrium values of ϕ_1 and ϕ_2 in water that we obtain for the 6-h and 3-day gels are consistent with those reported by these authors.

Figure 6 shows the comparison between the numerically calculated curves based on the parameters in Tables III and IV and the data points experimentally measured. The 3-, 15-, and 30-day data in Figure 6 are the true test of the model since the exact fit of the 6-h gel in Figure 6 provided the values of the interaction parameters to be used in the three other curves. Very good agreement is obtained in the swelling region, and the collapse region above 60% acetone is also well predicted except for the 30-day gel. The transition region between swelling and collapse is, however, poorly predicted, particularly for the 30-day gel. The curves drawn on the basis of the numerical solutions are left discontinuous between the swelling and collapse region because of the discrete nature of the available calculated interaction parameters. The model predicts, in agreement with experimental results, a collapse at an approximately constant acetone concentration. Overall, the qualitative agreement and the reasonable quantitative results obtained (despite the numerous assumptions) indicate that the two-phase model can go much further in interpreting the swelling–collapse data from cured gel samples than can a homogeneous model. The values of β*, ϕ_i*, and S_i, obtained for the different gels and shown in Table IV, indicate that in terms of the two-phase model, aging may be interpreted as a slow phase separation where the gel domains of nondraining, denser cross-linked polymer contract and leave more volume to the draining phase of the heterogeneous gel. Such a phase separation in gels kept under nonequilibrium swelling conditions, such as those examined here, had been postulated earlier.[8]

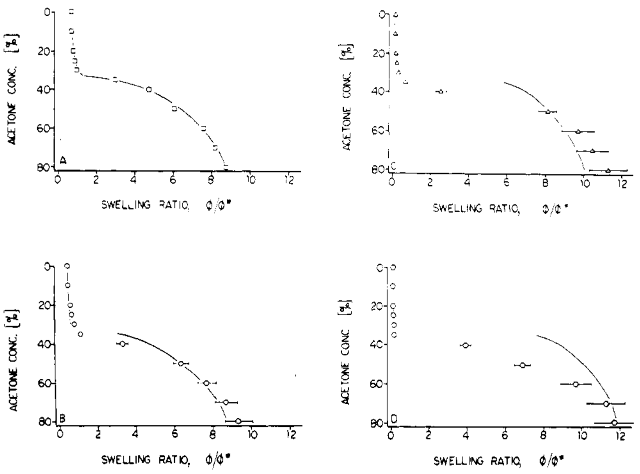

Figure 6. Fitting the experimental swelling ratios to those predicted by the two-phase gel model: (top left) the 6-h gel data specify the interaction parameters χ to be used for the older gels; (bottom left) comparison with the 3-day gel data; (top right) comparison with the 15-day gel data; (bottom right) comparison with the 30-day gel.

Conclusion

Of the thermodynamic equations for gels based on a homogeneous distribution of cross-links, the modified Flory equation due to Hermans (or Dušek) can provide a quantitative description of the swelling data of aged polyacrylamide gels only if the interaction parameter, expected to remain constant, changes drastically with curing time. We argue that these apparent large changes in the interaction parameter are due to a changing heterogeneous structure rather than an increase in cross-link density which we have measured and found to be practically constant over the curing time. To interpret our swelling data we use a simple two-phase model recently proposed.[13,14] The results we obtain on the basis of this model coupled to Hermans' equation applied to each phase separately indicate that the two-phase model represents a simplified but adequate approach to the properties of the polyacrylamide gels investigated here and that the aging phenomenon may be the result of the development of such a heterogeneous structure.

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Amphoteric Behavior of Tetrakis(methoxycarbonyl)quinodimethane in Alternating Copolymerizations with Various Comonomers

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ABSTRACT: Tetrakis(methoxycarbonyl)quinodimethane (TMCQ) was found to copolymerize alternatingly as an electron-acceptor monomer with such conventional electron-donor comonomers as styrene, isobutyl vinyl ether, *n*-butyl vinyl ether, 2-chloroethyl vinyl ether, phenyl vinyl ether, and vinyl acetate. In a study of the charge-transfer absorption band between TMCQ and conventional donor compounds, TMCQ was found to be an electron acceptor, but much weaker in electron-accepting character than tetracyanoquinodimethane (TCNQ). Moreover, TMCQ copolymerizes alternatingly and spontaneously with TCNQ, indicative of its electron-donating character toward the very strongly electron-accepting TCNQ. These results appear to be the first demonstration of amphoteric behavior in alternating radical copolymerizations.

Tetracyanoquinodimethane (TCNQ) was found previously to copolymerize with styrene (St) alternatingly and even spontaneously,[1] indicating that TCNQ can participate in radical copolymerization as an acceptor monomer. Moreover, polymerizations of TCNQ with isobutyl vinyl ether (*i*-BVE), *n*-butyl vinyl ether (*n*-BVE), 2-chloroethyl vinyl ether (CEVE), phenyl vinyl ether (PhVE), and vinyl acetate (VAc) were carried out in acetonitrile.[2] The first two vinyl ethers homopolymerize in the presence of TCNQ and the last three compounds copolymerize in an alternating fashion with TCNQ. The two polymerization modes correlate well with the electron-donating character of the monomers by Taft's substituent constants for vinyloxy compounds.

Tetrakis(methoxycarbonyl)quinodimethane (TMCQ) is a quinodimethane derivative with an electron-withdrawing functional group similar to that of TCNQ, but TMCQ is expected to be a much weaker electron acceptor than TCNQ. When TMCQ is heated above 175 °C or exposed to light, it is reported[3] to polymerize, even though the product is suggested to be a dimeric or trimeric structure, whereas TCNQ does not homopolymerize with any type of initiator. The difference in polymerizability is suggested to correspond to differences in the electron density on the exocyclic carbon atoms.[4] Therefore, the polymerization behavior of TMCQ as an acceptor monomer deserves study, especially in relation to TCNQ.

In this work, copolymerizations of TMCQ with various comonomers are described. Surprisingly, it was found that, in these copolymerizations, TMCQ copolymerizes alternatingly in an amphoteric fashion; TMCQ changes its polar character from electron-accepting to electron-donating, depending upon the nature of the comonomer.

Experimental Section

Materials. TMCQ was prepared according to the method of Acker and Hertler:[3] mp 149.5–151.0 °C (lit.[3] mp 147 °C); yield 23% (lit.[3] yield 26%); IR $\nu_{C=O}$ 1710 cm^{-1}; NMR (CDCl$_3$) δ 3.83 (12 H, s), 7.83 (4 H, s). Anal. Calcd $C_{16}H_{16}O_8$: C, 57.14; H, 4.80. Found: C, 57.36; H, 4.87. Commercial TCNQ was purified by recrystallization from acetonitrile and was sublimated (twice), mp 294.5–296.0 °C. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol and freed of solvent under reduced pressure.

N,*N*-Dimethylaniline (DMA) and hexamethylbenzene (HMB) (Nakarai Co. Guaranteed reagent grade) were used as electron donors without further purification. St [bp 58 °C (32 mmHg)], *n*-BVE (bp 94.5 °C), *i*-BVE (bp 82 °C), CEVE (bp 109 °C) and VAc (bp 72.6 °C) were purified from commercial products by conventional methods.

PhVE [bp 54 °C (17 mmHg)] was prepared from phenol and dibromoethane according to the procedure of McElvain et al.[5,6] Monomer purity was checked by gas chromatography (purity, 99.6–99.8%). Acetonitrile was refluxed with phosphorus pentoxide and then distilled at 81.7 °C. Benzene was refluxed over sodium and distilled at 80 °C. Other solvents were purified by conventional methods.

Charge-Transfer Absorption Band. An absorption spectrum of the charge-transfer transition of the TMCQ–St system was taken in benzene at room temperature. For the HMB–TCNQ,

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