Macromolecules **1990,** *23,* 3445–3450

Thermodynamic Predictions of Volume Changes in Temperature-Sensitive Gels. 2. Experiments

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Received July 19, 1989; Revised Manuscript Received January 16, 1990

ABSTRACT: This paper reports the experimental confirmation for poly(isopropylacrylamide) and poly(diethylacrylamide) gels of the molecular theory of swollen gels described in the companion paper. The predicted values of the parameters used in the theory agree closely with those measured experimentally. The theory is also qualitatively successful in accounting for the increase of the swollen gel volume with pressure.

Introduction

In the preceding paper, we presented a theory for the solution behavior of nonionic temperature-sensitive gels.[1] The theory, based on a lattice fluid model, is qualitatively capable of predicting a variety of phase behaviors in cross-linked polymer networks.

The theory is formally similar to the classical Flory–Rehner model representing the swelling of network structures.[2] However, the present theory makes allowance for empty lattice sites, thus relaxing the incompressible nature of the older model. As such, it is related to the theories developed for polymer solutions by Sanchez and Lacombe[3] and by Koningsveld and Kleintjens.[4] An equation of state for the mixture can be derived from this theory in which the pressure is just the chemical potential of the vacant sites

$$P = -\frac{\mu_o}{\upsilon_o^*} = -kT\left\{\frac{1}{\upsilon_o^*}\left[\ln\phi_o + \left(1 - \frac{\upsilon_o^*}{\upsilon_s^*}\right)\phi_s + \phi_g\right] + \nu\frac{\phi_g^\circ}{V_g^*}\left(\frac{\phi_g}{\phi_g^\circ}\right)^{1/3} + [\chi_{so}'\phi_s + \chi_{go}\phi\phi_g](\phi_o + \phi_g) - \chi_{sg}'\phi_s\phi_g\right\} \quad (1)$$

where υ_o^* and υ_s^* are the volumes of the lattice site and the solvent molecule; ϕ_o, ϕ_s, and ϕ_g are the lattice site fractions of vacancies, solvent, and gel; and $\nu\phi_g^\circ/V_g^*$ is the density of tetrafunctional cross-links per unit volume of gel at synthesis. The interaction parameters per lattice site χ_{so}', χ_{go}', and χ_{sg}', which are purely energetic in origin, are given by

$$\chi_{so}' = P_s^*/kT \quad (2)$$

$$\chi_{go}' = P_g^*/kT \quad (3)$$

$$\chi_{sg}' = (1/kT)[((P_s^*)^{1/2} - (P_g^*)^{1/2})^2 + 2Z_{sg}(P_s^*P_g^*)^{1/2}] \quad (4)$$

where P_s^* and P_g^* are the cohesive energy densities of the solvent and gel, respectively, and Z_{sg} is a correction parameter characterizing the mixture. The chemical potential for the solvent is

$$\frac{\mu_s}{\upsilon_s^*kT} = \frac{1}{\upsilon_s^*}\left[\ln\phi_s + \left(1 - \frac{\upsilon_s^*}{\upsilon_o^*}\right)\phi_o + \phi_g\right] + \frac{\nu\phi_g^\circ}{V_g^*}\left[\frac{\phi_g}{\phi_g^\circ}\right]^{1/3} + (\chi_{sg}'\phi_g + \chi_{so}'\phi_o)(\phi_g + \phi_o) - \chi_{go}'\phi_g\phi_o \quad (5)$$

The forms of eqs 1 and 5 reveal the nature of the theory employed. The first term on the right-hand side of eq 1 or eq 5, which is entropic in origin, arises from mixing three kinds of species (holes, solvent, and gel) and from the fact that both solvent and gel occupy more than one lattice site. The second term, which is also entropic in origin, is due to the extension of the network chains with an increased degree of swelling. This second term assumes that the network chains behave as Hookean springs. The remaining purely energetic terms represent the interaction of the species with each other and with the vacancies. In this paper we apply this theory to the phase diagrams of poly(isopropylacrylamide) and poly(diethylacrylamide) gels.[5,6] The predicted values for the gels' cohesive energy densities are compared with experiment by differential scanning calorimetry. The fitted cross-link densities are also compared to experimental results.

Fitted Phase Diagrams

The phase diagram fitted for a poly(isopropylacrylamide) gel is presented with the experimental data in Figure 1. These data are for the cross-linked gel shown in Figure 2 of the companion paper.[1] The values of the parameters used for this gel are presented in Table I. The phase diagram is presented as temperature vs swelling ratio instead of vs volume fraction of gel. This choice of variables is that most commonly used in experiments with these systems. The fitted and experimental phase diagrams agree closely around the critical region. The theory does predict a first-order transition at 306.1 K; the experimental transition temperature occurs at 306.5 K.

The choice of parameter values was made as follows:

a. The cohesive energy density of water, the close-packed volume of the water, and the volume of an empty lattice site are chosen to describe the pure water vapor–liquid equilibrium data.[7]

b. The gel's cohesive energy density (P_g^*), its cross-link density at synthesis conditions ($\nu(\phi_g^\circ)^{2/3}/V_g^*$), and the correction parameter Z_{sg} are chosen so the theoretical phase diagram best fits the experimental one. The values of the cohesive energy and cross-link densities of the gel are accessible by calorimetric experiments, as discussed later in this paper. The third parameter Z_{sg} indicates the extent to which the polymer–solvent interaction deviates from the geometric-mean rule. It should be noted that χ_{sg}', the parameter which actually enters into the calculation of thermodynamic properties, is sensitive to small fractional changes in the cohesive energy densities.

The fit between theory and experiment shown in Fig-

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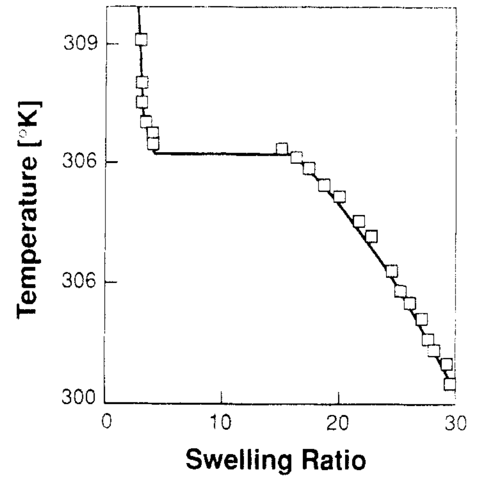

Figure 1. Phase behavior for a poly(isopropylacrylamide) gel, experiment vs theory (P = 1 atm).

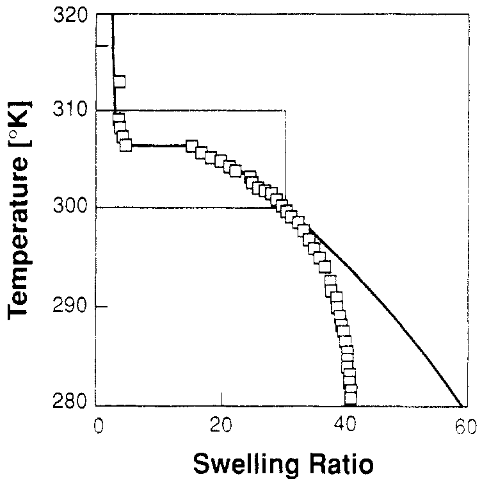

Figure 2. Phase behavior for a poly(isopropylacrylamide) gel, experiment vs theory (P = 1 atm). The rectangle corresponds to the region detailed in Figure 1.

Table I
Parameter Values for Two Gel-Water Systems

	poly(isopropyl-acrylamide)	poly(diethyl-acrylamide)
cohesive energy densities, cal/cm^3		
solvent	642.2	642.2
gel	308.8	313.9
interaction energy correction, Z_{sg}	-0.0633	-0.0595
interaction parameter, $kT\chi_{sg}'$, cal/cm^3	4.03	4.72
close-pack volume of solvent,[7,9] cm^3/mol	16.33	16.33
lattice site volume, cm^3/mol	1.93	1.93
cross-link density at synthesis, mol/cm^3	1.80 × 10^{-6}	2.00 × 10^{-6}

ure 1 is impressive evidence that the lattice theory with holes is an appropriate description of this gel. However, the theory is less accurate for highly swollen gels, as shown in Figure 2. In this figure, the area surrounded by the rectangle corresponds to that detailed in Figure 1. The poorer description of highly swollen gels reflects the failure of the elastic term in eqs 1 and 5. This elastic term assumes the phantom network formulated by James and Guth,[8] i.e., that crosslinked chains are infinitely extensible and that the only constraints on their conformations are those imposed by the cross-links. While this last assumption is a good approximation at small deformations, it is compromised by the finite extensibility of the physical chains at large swelling. The actual free energy increase is higher than that predicted by the model, and the experimental swelling ratio is lower.

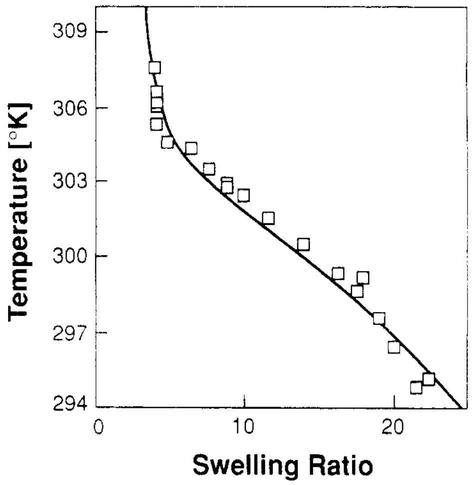

Figure 3. Phase behavior for a poly(diethylacrylamide) gel, experiment vs theory (P = 1 atm).

Theories of chains with finite extensibilities fit the data at larger deformations better. However, if we drop the assumptions of the Gaussian network model, at least one new parameter must be introduced to characterize the lengths of the chains, and the model also becomes numerically more intractable.

The theory also fits the system poly(diethylacrylamide) gel–water, as shown in Figure 3. The parameters used for this system are also presented in Table I. Poly(diethylacrylamide) does not show a first-order transition in volume with temperature.[5] Like poly(isopropylacrylamide), the fit of poly(diethylacrylamide) is more successful around the transition region. Again, the theory predicts larger swelling ratios than those encountered experimentally at high swelling.

How realistic are the adjusted values for the cohesive energy and cross-link densities in Table I? To answer this question, we must measure these values through independent experiments. Such experiments and their results will be discussed in the following two sections of this paper. Unfortunately, the interaction energy correction Z_{sg} cannot be independently tested experimentally. To do this, we could fit the low-temperature upper consolute boundary (indicated as A in Figure 1 of the companion paper) for each solvent–gel pair. Unfortunately, the mixture freezes before the appropriate temperature can be reached.

Determination of Cohesive Energy Densities

The cohesive energy densities for each gel can be determined experimentally by differential scanning microcalorimetry. Using these results with the corresponding phase diagrams and the theoretical expression for the heat of phase transition, we can calculate the values for the cohesive energy densities of the polymers.

The microcalorimeter that we used did not allow us to determine the heats of transition of the cross-linked networks because the calorimetric chamber must be filled with a syringe. Therefore, the un-cross-linked polymers were used. We are forced to assume that the presence of cross-links (bis(acrylamide) in both cases) would not dramatically alter the averaged cohesive energy densities for these systems. Thus, we construct the phase diagrams for the corresponding un-cross-linked polymers, and we use an expression for the heats of transition that does not include the elastic contribution.

The enthalpy per unit volume relative to the pure components for a mixture of polymer with an infinite molecular weight and a solvent according to our treatment is given by

$$H/V = kT[\phi_s\phi_g\chi_{sg}' = \phi_o\phi_s\chi_{so}' + \phi_o\phi_g\chi_{go}'] + P[\phi_o - (V_s\phi_s + V_g\phi_g)/V] \quad (6)$$

in which H is the enthalpy, P is the pressure of the system, V is its volume, and V_g and V_s are the volumes of the pure gel and solvent, respectively. The heat of phase separation for the system is

$$\Delta H/V = k\{T_f[\psi\phi_s^{\alpha}\phi_g^{\alpha} + (1-\psi)\phi_s^{\beta}\phi_g^{\beta}][\chi_{sg}']_{T_f} - T_i\phi_s\phi_g[\chi_{sg}']_{T_i}\} + k\{T_f[\psi\phi_s^{\alpha}\phi_o^{\alpha} + (1-\psi)\phi_s^{\beta}\phi_o^{\beta}][\chi_{so}']_{T_f} - T_i\phi_s\phi_o[\chi_{so}']_{T_i}\} + k\{T_f[\psi\phi_g^{\alpha}\phi_o^{\alpha} + (1-\psi)\phi_g^{\beta}\phi_o^{\beta}][\chi_{go}']_{T_f} - T_i\phi_g\phi_o[\chi_{go}']_{T_i}\} + kP\{[\psi\phi_o^{\alpha} + (1-\psi)\phi_o^{\beta}] - \phi_o\} \quad (7)$$

where T_f is the final temperature of the system, T_i is the initial one, ψ is the volumetric fraction of phase α (the polymer-rich phase), and $1 - \psi$ is the corresponding fraction of solvent-rich phase β. The first term accounts for the changes in solvent–polymer interactions, the second and third terms for the changes in hole–solvent and hole–polymer interactions, and the last term for the volume change on mixing. We do not expect the enthalpic contributions due to the rearrangement of holes to dominate the change of heat upon phase separation; this quantity is dominated by the solvent–polymer interactions. However, small changes in the free energy of the system can drive large ones in compositional equilibrium. Therefore, we simplify our expression for the heat of phase separations by assuming that the incompressible limit is valid, so

$$\Delta H/V = k\{T_f[\psi\upsilon_s^{\alpha}\upsilon_g^{\alpha} + (1-\psi)\upsilon_s^{\beta}\upsilon_g^{\beta}][\chi_{sg}']_{T_f} - T_i\upsilon_s\upsilon_g[\chi_{sg}']_{T_i}\} \quad (8)$$

where υ_s and υ_g are the volumetric fractions of solvent and polymer at the incompressible limit. Substituting the definition for the interaction energy parameter χ_{sg}' given by eq 4, we find that:

$$P_g^* = \frac{1}{4}\left\{2(1 - Z_{sg})(P_s^*)^{1/2} \pm \left[4P_s^*Z_{sg}(Z_{sg} - 2) + \frac{4(\Delta H/V)}{\psi(1 - \upsilon_g^{\alpha})\upsilon_g^{\alpha} + (1-\psi)(1 - \upsilon_g^{\beta})\upsilon_g^{\beta} - (1 - \upsilon_g)\upsilon_g}\right]^{1/2}\right\}^2 \quad (9)$$

This expression gives us the value of the cohesive energy density from the experimental determination of the heat of the phase transition and the value Z_{sg}.

Methodology

The polymerization reactions for both isopropylacrylamide and diethylacrylamide were carried out in an oxygen-free aqueous solution by a method similar to the one employed to synthesize the corresponding gels.[6] The redox catalyst consisted of ammonium persulfate and sodium bisulfite. No cross-linking agent such as bis(acrylamide) was added in these reactions.

The location of the phase boundary was measured both visually and with a differential scanning calorimeter. The visual observation of the temperature at which the first turbidity appeared in a solution immersed in a silicone bath as its temperature was raised provided us with the phase-transition temperature of the polymer. The experiments were carried out using a Thomas melting point apparatus at a scanning temperature rate of 5 °C/h. This transition temperature is difficult to see in dilute solutions.

The location of the phase boundary in dilute solutions and the heat of phase separation in all solutions was measured with a Microcal MC-2 differential scanning microcalorimeter. The samples were scanned at either 30 or 10 °C/h over a temperature range from 20 to 50 °C against a reference cell containing distilled and deionized water. The calorimeter response time was about 7 s. The operation of the calorimeter was digitalized using an AT&T microcomputer with the DA-2 software provided by Microcal. A typical trace after normalization is shown in Figure 4. The area under the peak between the start of the peak and 45 °C is a measure of the heat absorbed on phase separation. The responses were calibrated with the heats of fusion of indium.

Traces like that in Figure 4 are used to calculate the cohesive energy density P_g^* by use of eq 9. In this calculation, we used the cohesive energy density of the solvent estimated from vapor-liquid equilibria and the values of Z_{sg} in Table I. When two values of P_g^* were obtained, we chose the one close to the expected value of 2.

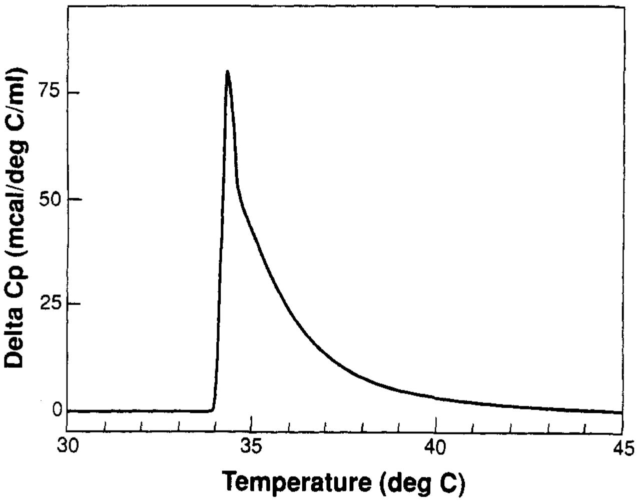

Figure 4. Change of specific heat [mcal/mL·K] with temperature for a 5% w/w solution of linear poly(isopropylacrylamide).

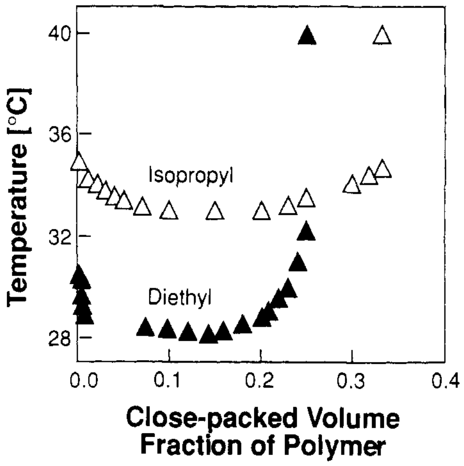

Figure 5. Phase diagrams for linear polymer chains poly(isopropylacrylamide) and poly(diethylacrylamide).

Experimental Results

The phase diagrams found for the un-cross-linked polymers are shown in Figure 5, and the transition temperatures and heats of transition are given in Table II.

The cohesive energy densities in each system calculated from these data agree with the theoretically fitted values, as shown in Table III. The difference between the fitted and experimental cohesive energy densities is less than 3%. However, these small differences may still produce large changes in the phase envelope, which is balanced delicately near the critical point. In fact, the agreement between the experimental and theoretical values of χ_{sg}' is poorer.

Table II
Heats of Phase Separation for Two Water-Gel Systems

overall volume fraction of polymer	$\Delta H_3/V$, mcal/cm^3 solution	T, °C
	Poly(isopropylacrylamide)	
0.0135	239	34.0
0.0067	125	34.3
0.0033	68	34.5
0.0007	12	34.6
	Poly(diethylacrylamide)	
0.0221	180	29.6
0.0110	36	30.3
0.0055	9	31.8
0.0011	5	31.2

Table III
Comparison of Theoretically Derived Cohesive Energy Densities and Their Ratios with the Experimentally Obtained Ones

	theory	expt
Poly(isopropylacrylamide		
cohesive energy density, P_g^*, cal/cm^3	308.8	315.4
cohesive energy density ratio, P_s^*/P_g^*	2.08	2.04
interaction parameter, $kT\chi_{sg}'$	4.03	0.55
Poly(diethylacrylamide)		
cohesive energy density, P_g^*, cal/cm^3	313.9	322.6
cohesive energy density ratio, P_s^*/P_g^*	2.05	1.99
interaction parameter, $kT\chi_{sg}'$	4.72	0.31

[a] The difference between the fitted and experimental cohesive energy densities is less than 37.

Determination of the Cross-Link Density

The stress–strain relationship for a gel composed of noninteracting ideal polymer chains is a purely configurational effect given by[2]

$$\sigma = -T\left[\frac{\partial S}{\partial L}\right]_{T,V} \qquad (10)$$

where L is the linear deformation. The phantom model of James and Guth[8] suggests that the stress–strain relationship for a tetrafunctional network is given by

$$\sigma/A_0 = RT(\nu\phi_g^{\circ}/V_g^*)[\alpha - \alpha^{-2}] \qquad (11)$$

where A_0 is the initial cross-sectional area of the sample and α is the uniaxial deformation ratio L/L_0. The unstrained dimension of the sample L_0 is in the direction of the applied stress. Therefore, a plot of σ/A_0 vs $\alpha - \alpha^{-2}$ should be linear with slope $\nu\phi_g^{\circ}/V_g^*$.

This type of plot was used to determine the cross-linking density of both gels. A disk of gel of an average diameter of 2.85 cm and height of 0.75 cm was placed between two glass slides of 13 × 10 × 0.15 cm^3. Because the gel must be in its unstrained state, freshly synthesized samples were used without washing or drying. Weights ranging from 10 to 500 g were placed on top of the upper glass slide. The resulting decrease in height was measured using a cathetometer. The stress calculated by dividing the applied weight by the cross-sectional area of the sample is plotted against $\alpha^{-2} - \alpha$, and the cross-link density in the unstrained state is found from the slope, which is accurate to ±10%.

The experimental and fitted values for the cross-link density of each gel are compared in Table IV. The fitted value is within 8% of the experimental results in the case of poly(isopropylacrylamide). The poly(diethylacrylamide) case is less successful: the fitted value is some 5 times larger than the experimental one. A possible cause of this discrepancy is the variability introduced by the need to synthesize fresh gel for every determination.[2]

Table IV
Comparison of Theoretically Derived Cross-Link Densities with the Experimentally Obtained Ones

	theory	expt[6]
Poly(isopropylacrylamide)		
cross-link density, mol/cm^3	1.8 × 10^{-6}	1.7 × 10^{-6}
Poly(diethylacrylamide)		
cross-link density, mol/cm^3	2.0 × 10^{-6}	3.9 × 10^{-7}

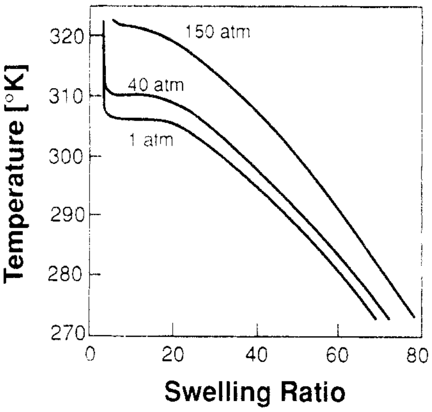

Figure 6. Predicted phase behavior of a poly(isopropylacrylamide) gel in water at 1, 40, and 150 atm. (Parameter values used are given in Table I.)

Pressure Effects on Phase Behavior of Gels

We now turn to predictions of gel behavior under conditions not yet completely studied experimentally. The gel swelling is predicted to be a strong function of pressure, particularly near the low-temperature upper consolute boundary. In these regions, the swelling increases with the pressure as shown in Figure 6 for a poly(isopropylacrylamide) gel using the fitted parameters of Table I. The transition temperature is raised by an increase in the pressure of the system.

This pressure effect, which has been experimentally observed,[10] is a direct result of the presence of holes. The increase in the pressure causes an enlargement of the swollen gel region where the phase behavior is dominated by the elastic contribution of the chains. Thus, a collapsed network initially at low pressures can see its swelling augmented by an increase in pressure. Higher pressures reduce the overall free volume of the system, thus reducing the free volume difference between the solvent and the gel. This reduction in the total entropy of the system is compensated by increasing the mixing of the solvent and polymer, which allows an expanded gel phase to exist at the higher pressures.

Discussion

The theory presented in the companion paper successfully explains the solution behavior of hydrogels at low pressures. The model correctly predicts a first-order volume transition for the poly(isopropylacrylamide) gel–water system and a second-order transition for the poly(diethylacrylamide) gel–water pair. The fitted cohesive energy densities for both pure gels are consistent with experiments, suggesting that the treatment is a realistic predictive tool. The predicted binodals are extremely sensitive to the choice of parameters. Small variations of the cohesive energy density and the correction parameter of the binary can cause large changes in the predictions.

These predictions also uncovered other characteristics of these systems. One of the more interesting is the pressure dependence of the phase diagram. The swelling is predicted to increase sharply at modest pressures, a completely unexpected effect, which is found experimentally. However, while the theory shows the correct qualitative behavior, the predicted dependence for poly(isopropylacrylamide) gels is larger than that experimentally observed.[10] This may imply that the interpretation of the observed behavior exclusively in terms of free volume is incomplete. Hydrogen bonds play a role in these systems, a role that becomes more important at high pressure. More seriously, this pressure variation may suggest that the agreement between the experimental and theoretical values shown in Tables III and IV is misleading. After all, small changes in the parameters shown in Table I do produce large changes in the phase diagrams in Figures 1 and 2. Similarly small changes in parameters might give more accurate predictions of pressure variations. Resolving this question will require more experiments on different chemical systems.

Our results form an interesting contrast with other theories of the phase transitions in gels. There are two such theories. The first, by Hirotsu et al.,[11] attempts to explain the phase behavior of poly(isopropylacrylamide) without reference to vacant lattice sites or "holes". The second, due to Prausnitz and co-workers,[12-14] explicitly includes hydrogen bonds between water and cross-linked polymer. Each theory merits comparison with the results in this paper.

With Hirotsu et al.'s hole-free theory,[11] there are also three parameters. However, the theory does not predict a discontinuous phase transition in an uncharged gel. This is inconsistent with Hirotsu et al.'s experiments and with those reported in this paper. Hirotsu et al.'s theory does not predict the pressure dependence of swelling, which is experimentally observed. Moreover, the parameters found from curve fitting the phase envelope differ from experimentally based estimates by factors of 100-1000. The theory developed here shows comparable agreements within a factor of 2.

The second, hydrogen-bonding theory, by Prausnitz and co-workers,[12-14] is more sophisticated and more successful. It basically uses three parameters, just like the Hirotsu et al. theory and like that presented here. (It can use two more parameters close to the critical point, but these are less important away from this point.) The theory, based on an incompressible lattice, does predict both continuous and discontinuous phase transitions, including those in charged gels. It sometimes predicts discontinuous transitions where continuous ones are observed, and it cannot predict pressure effects. Still, it has a major advantage in that the parameters invoke specific chemical interactions that might be detected spectrophotometrically.

Conclusions

The compressible lattice theory presented earlier[1] successfully explains the observed solution behavior of poly(isopropylacrylamide) and poly(diethylacrylamide). This generalization of the lattice model for rubbers incorporating free volume effects yields a theory richer in predictive power than might be thought possible for polar systems.

The model's success is achieved by an economy of means. While the model uses six parameters, only one is adjustable (Z_{sg}). All the remaining parameters are pure-component quantities, and they are all experimentally accessible. The fitted values obtained for the cohesive energy density and cross-linking degree are experimentally confirmed. These encouraging results confirm the validity of the theoretical treatment employed.

Acknowledgment. The authors have benefited from discussions with J. M. Prausnitz and H. H. Hooper. The work was partially supported by the National Science Foundation (Grant 89-12634) and by the Hoechst-Celanese Corp.

Nomenclature

A_o	cross-sectional area of the sample in the unstrained state
H	total enthalpy of the system
L	linear dimension of the system in the strained state
L_o	linear dimension of the system in the unstrained state
k	Boltzmann constant
P	total pressure of the system
P_s^*	cohesive energy density of the solvent
P_g^*	cohesive energy density of the gel-polymer
R	universal gas constant
S	entropy
T	absolute temperature
T_f	final temperature of system
T_i	initial temperature of system
V	total volume of the swollen gel
V_g	volume of the pure polymer (gel) phase
V_g^*	volume of the dry gel
v_g	close-packed (incompressible) lattice fraction of gel
v_o^*	empty lattice site volume fraction of component i
V_s	volume of the pure solvent phase
v_s	close-packed (incompressible) lattice fraction of solvent
v_s^*	close-packed (incompressible) molecular volume of the solvent
Z_{sg}	correction parameter for the Hildebrand rule of mixing for the solvent polymer (gel) pair
α	deformation ratio (strained to unstrained states)
$\Delta H/V$	heat of phase separation per unit volume of system
μ_o	chemical potential of empty sites or holes
μ_s	chemical potential of solvent
ν	number of inter-cross-link chains present in the gel
ν/V_g^*	number of cross-links per unit volume of dry gel
$\nu\phi_g^o/V_g^*$	number of cross-links per unit volume of gel at synthesis conditions
ϕ_g	lattice fraction occupied by gel-polymer subunits
ϕ_g^o	lattice fraction occupied by gel-polymer at synthesis conditions
ϕ_o	lattice fraction of holes
ϕ_s	lattice fraction occupied by solvent
χ_{go}'	interaction energy per lattice site of gel-polymer and holes
χ_{sg}'	interaction energy per lattice site of solvent and gel-polymer
χ_{so}'	interaction energy per lattice site of solvent and holes
σ	elastic retractive force of the network
ψ	volumetric fraction of phase α

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Steric Effect of Acyl Substituent on Homopolymerization of 7,8-Diacyl-7,8-dicyanoquinodimethanes

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Received September 13, 1989; Revised Manuscript Received January 30, 1990

ABSTRACT: Quinodimethane compounds with different substituents such as cyano and acyl groups at the 7 and 8 positions are obtainable as stable crystals and are homopolymerizable with anionic and radical initiators. Their homopolymerizations were found to exhibit a typical equilibrium polymerization behavior, the kinetics analysis of which allowed determination of their thermodynamic parameters of polymerization. Their values were compared with the substituent parameters of the acyl groups by means of linear free energy relationships, which showed that their enthalpy of polymerization is predominantly related with the Taft E_s values of the acyl groups and independent of σ^* values ($\rho = 0$), indicating that their homopolymerizability is determined exclusively by a steric effect of the acyl groups.

Introduction

Unsubstituted 1,4-benzoquinodimethane is so reactive that, when it is prepared, it polymerizes spontaneously to give the polymer and the dimers.[1] When electron-accepting substituents are fully introduced at the 7 and 8 positions, compounds such as 7,7,8,8-tetracyanoquinodimethane(TCNQ)[2]and 7,7,8,8-tetrakis(ethoxycarbonyl)quinodimethane[3] form stable crystals at room temperature that do not homopolymerize. On the other hand, it was found that quinodimethanes with two different substituents at the 7 and 8 positions, for instance, 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethane,[4-6] 7,8-diacyl-7,8-dicyanoquinodimethane,[7] and 7,8-bis(ethylthio)-7,8-dicyanoquinodimethane,[8] not only are obtainable as stable crystalline compounds but also are homopolymerizable with various types of initiators. Moreover, their polymerization kinetics interestingly revealed that their homopolymerization with radical initiators was a typical equilibrium polymerization involving considerable depolymerization.[9] The entropy change during their polymerization was in the range 35–40 J/(K·mol), which was about one-third as large as that of the corresponding conventional vinyl compounds. The enthalpy change of polymerization was also small and varied with the substituents. Thus, combination of the two values results in a negative free energy value of polymerization for these compounds, which is small near room temperature. If we prepare several equilibrium-polymerizable 7,8-diacyl-7,8-dicyanoquinodimethanes with different acyl groups, kinetics studies of their polymerizations will permit us to obtain precise values for their thermodynamic parameters of polymerization without great difficulty. We can then correlate these values with the acyl substituents by means of a linear free energy relationship to look into the nature of the polymerizability of the compounds. To date, such a relationship has not been extensively investigated, because only a limited number of equilibrium-polymerizable monomers are currently available.

In this work, some new derivatives of 7,8-diacyl-7,8-dicyanoquinodimethane (3), namely, 7,8-bis(phenylacetyl)- (**3a**), 7,8-dipropionyl- (**3b**), and 7,8-diisobutyryl-7,8-dicyanoquinodimethane (**3c**), were prepared, and the kinetics of their radical polymerization was studied to obtain their thermodynamic parameters of polymerization. These were analyzed together with the corresponding data[9] for 7,8-dibenzoyl- (BzCQ) and 7,8-diacetyl-7,8-dicyanoquinodimethane (AcCQ), which have been reported previously, by means of a linear free energy relationship (Taft's equation).

Experimental Section

Preparation of 7,8-Diacyl-7,8-dicyano-*p*-xylene (2). Sodium ethoxide (3.26 g, 48 mmol) was dissolved in 80 mL of dry *p*-dioxane, and 3.0 g (19.2 mmol) of 7,8-dicyano-*p*-xylene (1) and the appropriate ethyl ester (44 mmol), i.e., 7.22 g of ethyl phenylacetate for 7,8-bis(phenylacetyl)-7,8-dicyano-*p*-xylene (**2a**), 4.50 g of ethyl propionate for 7,8-dipropionyl-7,8-dicyano-*p*-xylene

0024-9297/90/2223-3450$02.50/0 © 1990 American Chemical Society