

neutral structure (radical) with the reduction of viologen units, and thereby the coulombic repulsion in the membrane would decrease. As shown in Table II, when the viologen content of membrane 3 with constant degree of cross-linking increased, a rate enhancement was observed. However, when the degree of cross-linking in membrane 3 with constant viologen concentration increased, the rates dropped dramatically, as indicated in Table III. This is presumably due to the decrease of mobility of the polymer chain with increasing degree of cross-linking, which interferes with access between V^{+} and Fe^{3+} .

The rate of electron transport through membrane 1a was observed to be markedly faster when the concentration of $Na_2S_2O_4$ as reducing agent was increased, as shown in Table IV.

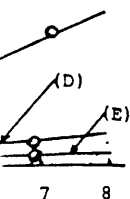
In conclusion, we have succeeded in showing that electron transport through polymeric membranes containing viologen moieties occurs. As described above, the rates of electron transport depend on the thickness, the degree of cross-linking of the membranes, the concentration of viologen units, and the location of electron carriers. These oxidation-reduction systems mediated by polymeric membrane provide a new charge separation model, and their application to the decomposition of water in photoirradiation systems can be expected.

Registry No. $Na_2S_2O_4$, 7775-14-6; $K_3Fe(CN)_6$, 13746-66-2; D, 280-57-9; [AN]:[CMS], 9080-68-6; [AN]:[CMS]:[VPy], 85613-97-4; 4,4'-bipyridyl, 553-26-4.

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Chemical Modification of Acrylamide Gels: Verification of the Role of Ionization in Phase Transitions

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ABSTRACT: We prepared "doped" acrylamide gels containing the ester *N*-acryloxysuccinimide; subsequent hydrolysis of the ester alone yielded gels of varying network ionization. After incubation in acetone-water mixtures, these gels displayed a swelling behavior qualitatively similar to that obtained from time-dependent hydrolysis of pure acrylamide gels. These results confirm that the network ionization plays a crucial role in the phase transition of these ionic gels.

Introduction

Cross-linked polymer gels of acrylamide/bis(acrylamide) that have been equilibrated in acetone-water mixtures have been observed to undergo dramatic decreases in volume with increasing acetone concentration or decreasing temperature.^{1,2} This reversible volume behavior ranges

from continuous shrinkage to a discontinuous collapse of the network, depending on the length of time (measured in days) that the gel is incubated in a basic solution (e.g., pH 12) prior to being equilibrated in the acetone-water mixture.

Tanaka et al.³ were able to explain the principal qualitative features of the unusual nonlinear dependence of the gel "swelling ratio" on solvent composition by postulating a variable degree of ionization of the polymer network due to time-dependent hydrolysis of the acrylamide groups into

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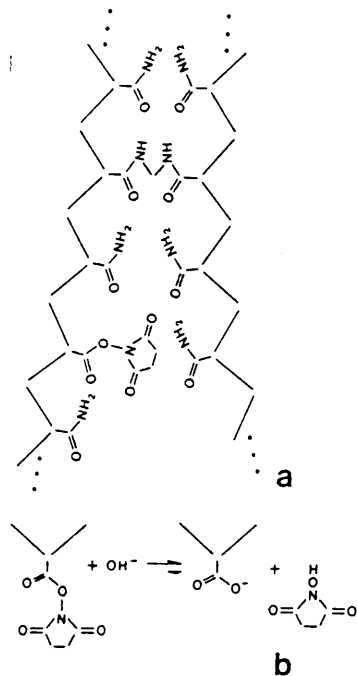


Figure 1. (a) Simplified illustration of the chemical structure of a portion of doped acrylamide gel: two cross-linked acrylamide polymer chains, with a single molecule of ester incorporated into one of the chains. (b) Hydrolysis reaction for the chain-incorporated ester *N*-acryloxysuccinimide.

ionized acrylic acid at high pH. They utilized the Flory-Huggins formula³ for the osmotic pressure of an ionic gel and included the contribution of H^+ ions dissociated from the ionizable groups. According to this theory, one of the crucial parameters that determine whether the gel exhibits continuous shrinkage or discontinuous collapse is the degree of ionization of the network² (the other being the stiffness of the constituent polymer chains). This is conveniently described by the average number of dissociated hydrogen ions per effective chain (i.e., per average length of polymer between adjacent cross-link points), denoted by f . Hence, the longer the incubation time for a gel in basic pH solution, the greater the extent of ionization of the average polymer chain⁴ and the larger the parameter f . The theory of Tanaka et al.² qualitatively confirms the existence of a critical value f_c ; when f exceeds f_c , the shrinkage in gel volume (with increasing acetone concentration) becomes discontinuous—i.e., collapse occurs. For values of f larger than f_c , the extent of volume collapse increases with increasing f , with changes as large as 350-fold observed experimentally. The crucial role of network ionization was also demonstrated recently by Ilavsky,⁵ using charged gels of polyacrylamide/sodium methacrylate.

In this article we provide direct evidence, based on chemical modification of acrylamide gels, that the ionization parameter f in the previously developed theory is, indeed, a crucial variable which determines both the nature and extent of the volume changes with solvent composition. We were able to selectively ionize the acrylamide gels by partially substituting molecules of an ester, *N*-acryloxysuccinimide,⁶ for acrylamide molecules (0–4.8%, molar basis). The ester is chemically related to acrylamide and should become randomly incorporated into the cross-linked polymer chains during gelation, as shown schematically in Figure 1a. These “doped” gels were subsequently incubated in a weakly basic solution, pH 9, for a relatively short time. Since the half-time for hydrolysis of the ester is only several minutes at this pH value,⁶ this incubation should result in virtually complete hydrolysis of the ester molecules with essentially no effect on the polymerized

acrylamide groups. The hydrolysis of the incorporated ester is illustrated in Figure 1b; the result of the hydrolysis reaction is ionized acrylic acid, incorporated into the polymer chain, plus a reaction byproduct, which is later washed away. The final gel should therefore be identical with a pure acrylamide gel that has been partially hydrolyzed, in which the ionization fraction “ x ” ideally equals the molar fraction of incorporated ester. We show that the dependence of volume swelling on acetone concentration for these doped gels strongly resembles the theoretical predictions of Tanaka et al.²

Materials and Methods

Doped acrylamide gels were prepared according to standard procedures,^{1,2,7} with the exception that a fraction “ x ” of the acrylamide monomers ($0 \leq x \leq 0.048$) was replaced by an equal number of molecules of the ester *N*-acryloxysuccinimide.⁶ Gels of approximately 5% (w/v) concentration were prepared by dissolving the following compounds at 25 °C in distilled water, brought up to a final volume of 100 mL: linear constituents, 5(1– x) g of acrylamide (Bio-Rad no. 161-0101), 5(2.38) x g of *N*-acryloxysuccinimide (prepared by A.P.); tetrafunctional cross-linking constituent, 0.133 g of *N,N',N',N'*-tetramethylethylenediamine (TEMED) (Eastman no. 8178).

The factor 2.38 in the above expression for the amount of added ester equals the ratio of the formula weight of the ester (169) to that of acrylamide (71), resulting in an ester doping fraction x that is on a molar basis. The maximum ester substitution in the gel was limited to 4.8% because of its relatively poor solubility in water.

Miniature, cylindrical-shaped gels of diameter 1.35 mm were obtained by using 100- μL micropipet tubes (Curtin-Matheson no. 5061). The gels were formed at room temperature over a period of 3 h and then extracted from the tubes by means of a water flow from a fine-gauge syringe. The gels were placed in 1-L containers of distilled water at 4 °C for 18–20 h in order to wash away residual reagents and unpolymerized components. They were then incubated for 18–20 h at 4 °C in 200-mL containers of 0.1 M $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ (+0.02% NaN_3 to retard bacterial growth) at pH ~ 9 (which should have taken the ester hydrolysis to completion with negligible hydrolysis (at pH 9) of the acrylamide). Next, the gels were removed from the basic solution and transferred to 1-L beakers of pure water at 4 °C for 8–10 h to wash away the buffer salt. Finally, the gels were removed from the water; two or three short segments were placed in individual 25-mL polyethylene bottles containing carefully measured mixtures of acetone and water (30–60% (v/v) acetone, in 1–2% increments) and incubated at approximately 25 °C for 4 days. At the end of this period the gels were removed from the acetone–water mixtures and their diameters measured with a microscope with a calibrated stage, from which the gel swelling ratios were determined.

Results and Discussion

The change in gel volume that occurs upon incubation in an acetone–water mixture at constant temperature is conveniently described by the swelling ratio ϕ/ϕ_0 , where ϕ_0 and ϕ represent, respectively, the initial and final equilibrium volume fractions of the network. This swelling ratio can be simply obtained from $(d_0/d)^3$, where d_0 (=1.35 mm) and d are, respectively, the initial and final diameter of the cylindrical gel.

Our experimental findings for ϕ/ϕ_0 vs. acetone concentration for various ester molar fractions x ($0 \leq x \leq 0.048$) are summarized in Figure 2. For ester fractions $x \leq 1.6\%$, we observe a continuous decrease in gel volume with increasing acetone concentration. For $x \geq 2\%$, the gels clearly display a discontinuous volume collapse at a critical value of acetone concentration which increases with increasing ester concentration (e.g., 46% acetone at $x = 2\%$).

These swelling curves strongly resemble those previously obtained by incubating pure acrylamide gels in a basic

Figure 2. ϕ/ϕ_0 vs. the gel swelling ratio ϕ/ϕ_0 vs. acetone concentration for gels which contain different molar fractions of ester. The dashed line represents the theoretical prediction of Tanaka et al.²

solution (4–6% acetone). In the latter case, the collapse occurs after 0–2 days of incubation, whereas in the present case, the collapse occurs after 4–6 days of incubation. The swelling ratio ϕ/ϕ_0 vs. acetone concentration for gels which contain different molar fractions of ester is shown in Figure 2. The dashed line represents the theoretical prediction of Tanaka et al.²

The swelling curves for gels which contain different molar fractions of ester are qualitatively similar to those for pure acrylamide gels, but the collapse occurs at a lower acetone concentration. The swelling ratio ϕ/ϕ_0 vs. acetone concentration for gels which contain different molar fractions of ester is shown in Figure 2. The dashed line represents the theoretical prediction of Tanaka et al.²

We next investigated the dependence of the swelling ratio ϕ/ϕ_0 on the initial diameter d_0 of the cylindrical gel. The swelling ratio ϕ/ϕ_0 vs. d_0 is shown in Figure 3. The swelling ratio ϕ/ϕ_0 vs. d_0 is shown in Figure 3. The swelling ratio ϕ/ϕ_0 vs. d_0 is shown in Figure 3.

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where $S_0 =$

$\tau = \frac{S_0 \phi_0}{r^2} \left[\left(\frac{d_0}{d} \right)^3 - 1 \right]$

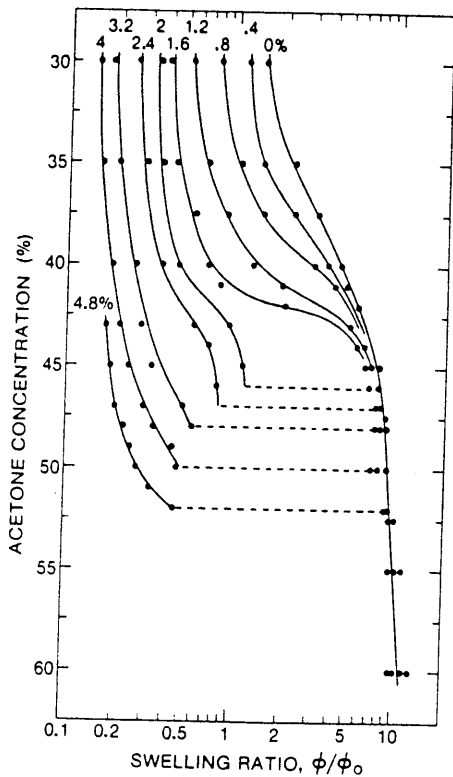


Figure 2. Experimental results of acetone concentration (vol %) vs. the gel swelling ratio ϕ/ϕ_0 for a series of ester-doped acrylamide gels which contain the ester fraction $x = 0-4.8\%$ (molar basis). The dashed lines indicate discrete collapse of the network.

solution (4% TEMED) for varying lengths of time.² In the latter study, gels immersed in this basic solution for 0-2 days showed continuous shrinkage with acetone concentration, while those incubated longer exhibited a discrete collapse. Thus, we have qualitatively confirmed the earlier hypothesis that hydrolysis of the polymerized acrylamide groups is the mechanism that is responsible for the swelling behavior observed for pure acrylamide gels.

The swelling curves for our selectively ionized gels qualitatively resemble the theoretical plots of reduced temperature τ vs. ϕ/ϕ_0 previously obtained by Tanaka et al.,² shown in Figure 3. The main difference that we observe concerns the shape of the gel swelling curves near gel collapse. Unlike the theoretical curves of Figure 3, our experimental plots exhibit substantial curvature approaching the critical acetone concentration. (For ester concentrations of 2% and 2.4% there also appears to be an inflection in the curves.) This "nonideal" behavior may be caused by incomplete incorporation of the ester into the gel network. Also, it should be kept in mind that the acetone concentration in these experiments may not be linearly related to the idealized parameter of the theory, the reduced temperature τ .

We next inquire about the quantitative agreement between the observed onset of gel collapse ($1.6\% < [\text{ester}] < 2\%$, Figure 2) and the predictions of the theory of Tanaka et al.² According to that theory, the swelling ratio ϕ/ϕ_0 ($\equiv r$) for a gel of a given composition is related to the network ionization parameter f and gel stiffness parameter S_0 through the expression for the reduced temperature τ

$$\tau = -\frac{S_0\phi_0}{r^2}[(2f+1)r - 2r^{1/3}] + 1 + \frac{2}{\phi_0} \frac{1}{r} + \frac{2 \ln(1-\phi_0 r)}{\phi_0^2 r^2} \quad (1)$$

where $S_0 \equiv \nu\nu/N\phi_0^3$.

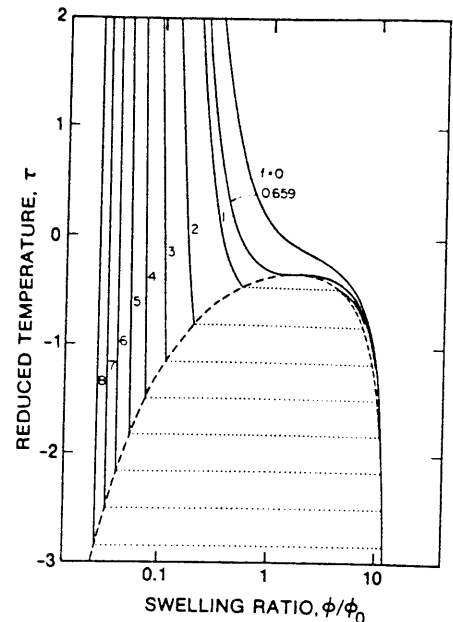


Figure 3. Theoretical plots of reduced temperature τ (eq 1) vs. swelling ratio ϕ/ϕ_0 for the network ionization parameter $f = 0-8$, with $S_0 = \nu\nu/N\phi_0^3 = 10$ (obtained from ref 2).

Here, N is Avogadro's number, ν is the solvent molar volume, and ν is the number of constituent chains per unit volume at $\phi = \phi_0$ (i.e., such that the polymer chains have random-walk configurations).

As pointed out by Tanaka et al., eq 1 predicts the possibility of gel collapse, in which the extent of the discrete volume change is approximately determined by the lumped parameter $S = S_0(1 + 2f)^4$. Hence, for a given value of S_0 (i.e., a given network stiffness), there is a "critical" value of the ionization parameter f , denoted by f_c , such that for $f \leq f_c$ the swelling curve τ vs. ϕ/ϕ_0 is continuous, while for $f > f_c$ it exhibits a discrete collapse. In Figure 3, for example, $f_c = 0.659$ for $S_0 = 10$. The value of f_c is determined by varying f until the derivative of τ with respect to ϕ/ϕ_0 ($=r$) equals zero at the point of inflection.

To obtain the theoretically predicted value for f_c , we must first establish numerical values for ϕ_0 and S_0 . The former equals the product of the specific volume of acrylamide ($\approx 0.7 \text{ cm}^3/\text{g}$) with its starting weight concentration ($0.05 \text{ g}/\text{cm}^3$), i.e., $\phi_0 = 0.035$. The gel stiffness parameter S_0 , however, is more difficult to estimate, given the ambiguity in the value of ν . The ratio of the number of acrylamide (and ester) molecules to the number of "bis" molecules before gelation equals $(5/71)/(0.133/154)$, or approximately 82. This would equal the average number, n , of monomers per chain assuming complete, ideal cross-linking, in which each molecule of "bis" forms one cross-link and there is no intramolecular cross-linking (cyclization). In this case, the ideal value for ν is $5.16 \times 10^{18} \text{ chains}/\text{cm}^3$. However, experiments of Janas et al.³ and others suggest an actual value for n that is at least a factor of 10 larger than the ideal value. For the solvent molar volume ν , we adopted the value of $36 \text{ cm}^3/\text{mol}$ (Table I, ref 7), appropriate for an acetone concentration at the onset of collapse of approximately 45% (assuming a pseudo-one-component solvent).

Consequently, we determined f_c assuming n values of 200, 500, and 1000, for which S_0 is 2.96, 1.184, and 0.592, respectively. The resulting theoretically predicted values for f_c are approximately 1.13, 1.48, and 1.80, respectively. If we assume that all of the ester is incorporated into the polymer network and, further, that it becomes 100% ion-

ized, then the predicted "critical" ester concentration (at which discrete collapse first occurs) would be given by f_c/n , or 0.57%, 0.30%, and 0.18% for $n = 200, 500,$ and $1000,$ respectively. Since the observed critical ester concentration lies between 1.6 and 2%, these predicted values are all clearly too small.

We have assumed that all of the doped ester units, after polymerization, are fully ionized. However, it is known that in a polymer solution of poly(acrylic acid), only about 20% of the ionizable units are effectively ionized. Hence, if we were to assume a similar fraction of ionization for our ester units, the effective experimental critical ester concentration would lie between 0.32 and 0.40%. In this case, the predicted range of theoretical values for f_c/n agrees with our findings. These calculations, of course, are meant only to provide qualitative verification of the experimental results. A more careful analysis would be required to obtain quantitative agreement. (For example, Ilavsky⁵ has shown that the free energy of electrostatic repulsions influences the swelling of ionic gels; this contribution should therefore be included in eq 1. Because this repulsive interaction increases the stiffness of the gel, the value of f is effectively increased.)

In conclusion, we have prepared acrylamide gels that can be ionized to differing degrees by changing the amount of an ionizable ester that is incorporated into the polyacrylamide network. In so doing, we have directly con-

firmed in a qualitative way the hypothesis that the behavior of the gel swelling ratio with respect to solvent composition depends on the degree of ionization of the gel network. Future related experiments based on chemical modifications of gels should prove useful in exploring the details of the phase transitions observed in ionic gels.

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Pressure Dependence of the Glass Transition in *cis*-Polyisoprene As Studied by Dielectric Relaxation

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ABSTRACT: Dielectric relaxation studies of the glass transition in *cis*-polyisoprene have been carried out between atmospheric pressure and 3.8 kbar. A procedure based on the Williams-Landel-Ferry (WLF) free volume formulation has been developed to analyze these data and obtain the glass transition temperature T_g and the WLF parameters $U^* = 2.3Rc_1c_2$ and $T_\infty = T_g - c_2$ as functions of pressure. The variation of T_g with pressure can be well represented by $T_g(P) = -72.0 + 17.78P - 0.673P^2$, and c_2 rises by about 8%/kbar. It is demonstrated that values of dT_g/dP obtained from data at a constant experimental frequency give rise to misleadingly high values of that coefficient. Cole-Cole analyses show that at a given pressure, the distribution of relaxation times decreases with increasing temperature. For a given relaxation time the Cole-Cole parameter, α , increases with pressure.

Introduction

cis-Polyisoprene, generally in the form of natural rubber from *hevea brasiliensis*, is a very important commercial polymer. Its elastic properties have been extensively investigated and are limited, as in all elastomers, by proximity to the glass transition temperature. Although elevated pressures are used in the processing of the polymer and often in service, studies of the effects of pressure on its properties are few. The only report in the literature of the effect of pressure on relaxation behavior is related to the dynamic compressibility of a cross-linked specimen (12% sulfur) at pressures up to 1 kbar.¹ The researchers reported a dT_g/dP coefficient of 24 °C/kbar. They also reported that the WLF equation² could be used to superpose data with invariant values of c_1 and c_2 for the frequency range studied (50-1000 Hz).

Recently, pressure-volume data have been reported over an extensive pressure range (to 8 kbar) but a narrow temperature range (15-40 °C), for which a dT_g/dP coefficient

of 13 °C/kbar was deduced from the data.³

Dielectric relaxation studies of *cis*-polyisoprene at atmospheric pressure have been reported by Norman⁴ for the frequency range 50 Hz to 1 MHz. Relaxation processes are observed in natural rubber largely because of the presence of adventitious dipoles resulting from oxidation.

The purpose of the work being reported here was to study the dielectric relaxation behavior of natural rubber at pressures up to 4 kbar, to obtain values of T_g and dT_g/dP as a function of pressure, and to investigate the applicability of the WLF equation over the pressure range studied. It is based on part of a Ph.D. Dissertation,⁵ in which the experimentation and processing of dielectric data are described in greater detail.

Experimental Section

Specimen Preparation. The natural rubber used was a grade of pale crepe supplied by the Malaysian Rubber Producers Research Association, Brickendonbury, England. It was Soxhlet extracted with benzene in order to remove the stearic acid and

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