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A Connectivity Model for Covalent Cross-linking in a Thermally Reversible Gel. Evidence for Latent Covalent Network Formation in the Formaldehyde Cross-linking of Gelatin Gel

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Abstract: A connectivity model is proposed to account for the abrupt melting point rise that occurs with covalent cross-linking in gelatin gel. The thermally reversible gel phase is treated as a lattice of elements that is spanned by a network of reversible pairwise connections. The elements are taken to be the polymeric gelatin chains and the connections are bonds. On the basis of the model a spanning network will be present when a critical fraction of the total possible pairwise connections has been exceeded. In the thermally reversible gel phase covalent bonds are assumed to be formed randomly and independently of the existing reversible bonds. By considering the criteria for gelation to be met when the sum of the nonredundant fractions of the two types of bonds exceeds the critical value a new gel melting point equation is derived, $1/T_m = (R/\Delta E) \ln (1 - C/C_*) + B$. This equation, in which the melting point of the gel is a function of the extent to which the concentration of covalent cross-links C has approached a critical value C_*, gives a good fit to the melting point data for formaldehyde cross-linked gelatin gel.

I. Introduction

In this paper a new model is presented to explain the rise in gelatin gel melting point that occurs with covalent cross-linking in the gel state. It has been previously shown[1,2] that the melting point rise cannot be simply related to Flory's equation for the melting of swollen polymers. Alternatively it was suggested that the melting point rise is related to the reduction in the entropy of melting resulting from the cross-linking of the ordered structure as proposed by Flory.[3] However, no attempt was made to directly utilize the relevant equation[4] to fit the melting point data of chemically cross-linked gelatin gels.

The central premise of this work is that gelation is a connectivity property and the melting point of a thermally reversible gel a measure of the connectivity state of the system. Hence an equation or model describing gel melting point must incorporate a method of assessing the connectivity state of the system and cannot be based on thermodynamics alone.[5] This was realized in an early attempt[6] to relate gelatin gel melting point to gelatin molecular weight and concentration via the classical Flory–Stockmayer gelation theory.[7,8] It has been subsequently shown[9] that the connectivity model of this classical gelation theory is a special case of the percolation connectivity model.[10,11] This new model is based on the fact that if a lattice of elements has adjacent elements pairwise connected in random fashion then a network spanning the lattice will exist if the fraction, p, of the total possible connections exceeds a critical value, p_*. The model is illustrated for a two-dimensional lattice (Figure 1). The connectivity model for the classical theory is the special case where only noncyclic or treelike structures are allowed. The essence of the percolation model is that there are only two possible connectivity states for a lattice of elements. Either the lattice has a spanning network or it does not. This description applies whether or not cyclic connections are present. A characteristic of the model is that for a macroscopic lattice measurable parameters of the system either diverge (become infinite) or vanish at the critical transition point between the states. While the critical point is a function of the type of lattice, it need not be a regular periodic lattice as the elements can be placed arbitrarily in space.[12] Thus the critical point is system dependent and not a universal quantity.[13]

In applying the percolation model to molecular systems the elements are taken to be monomers and the pairwise connections bonds. The gel–sol transition, which is characterized by abrupt changes in the viscoelastic properties of the medium, is attributed to network formation or dissolution[14] as in the classical theory. When the critical point is approached in the sol the viscosity diverges whereas when approached from the gel side the elasticity vanishes. An elastic gel and macroscopic network are present when $p > p_*$ and do not exist for $p < p_*$.

The approach taken here is to develop a connectivity model from which can be derived an equation relating the melting point of a thermally reversible gel to the extent of covalent cross-linking in the gel phase. The thermally reversible gel phase will itself be treated as a lattice upon which covalent cross-links can form a macroscopic covalent network. The model developed posits, cyclic linkages notwithstanding, the existence of a critical point for covalent cross-linking and the divergence of a measurable system parameter, the melting point of the gel.

II. Experimental Section

A. Gelatin. An alkaline processed bone gelatin was used having an assayed moisture of 10.9%, Bloom strength of 227, and isoelectric point of 4.8. Unless otherwise noted references to gelatin are uncorrected for moisture content. The molecular weight of the gelatin was determined[15] by size exclusion chromatography on a DuPont HPLC with a TSK G4000 SW column, $M_w = 143\,021$, $M_n = 53\,827$, and $M_w/M_n = 2.657$. Solutions were prepared by swelling 4.50 g of the gelatin in 50.0 mL of deionized water for from 1 to 4 h and then melting the gelatin at 55 °C. To these solutions, pH 5.71 (40 °C), were added 4.00 mL of 1.00 M sodium acetate raising the pH to 6.13. The solutions, in stoppered Erlenmeyer flasks, were thermally equilibrated for 1 h in a 37 °C bath.

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(15) I thank Dr. Felix Viro and the Kind and Knox Gelatine Co. for the molecular weight determinations.

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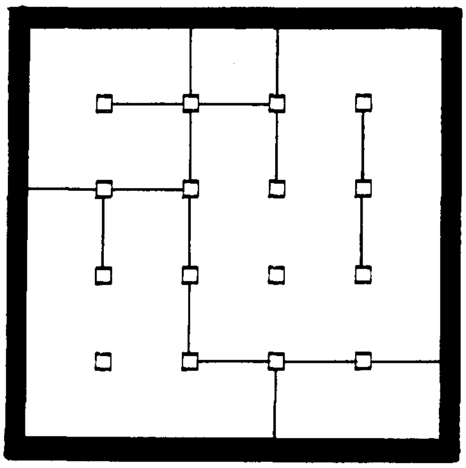

Figure 1. A square lattice with $N = 40$ and p_* assumed to be (16/40). A single network spans the lattice. If the bonds are thermally reversible then $p_r = (N_r/N) = (17/40) > p_*$. The system is just above the critical point and at a temperature just below the gel melting point.

There was then added, with stirring and at 37 °C, 3.00 mL of a formaldehyde solution ranging in concentration from 0.170 M up to 0.652 M. The time of this last addition was taken as t_0 for the kinetic runs. The pH immediately after the formaldehyde additions was 6.05 ± 0.05. The weight percent gelatin for all kinetic runs was 7.30%. The total reaction volume of the gel phase, 60.2 mL, was obtained by difference after allowing the solution to gel in a 100-mL volumetric flask. This gives a gel-phase gelatin concentration of 0.0748 g of gelatin/mL. Formaldehyde levels given in mmol/g of gelatin are thus directly convertible to formaldehyde concentrations. When the solution having the highest formaldehyde level was kept at 41 °C, for the time required for the melting point of its gel phase counterpart to rise above 90 °C, a decline of 0.25 pH units was observed.[16,17] The pH drop during the gel phase reactions is estimated to be no greater.

B. Melting Points. A simple capillary melting point technique, which has the advantage of rapid thermal equilibration, was used. Via capillary action an aliquot of the 37 °C gelatin solution was drawn 1.0 cm into one end of a both ends open 150 × 0.1 mm glass capillary tube. The tubes, one per kinetic point, were immediately sealed at both ends with plastic "microhematocrit" capillary sealing caps[18] and placed in a thermostated chamber at 25.0 ± 0.1 °C. The melting points, as a function of holding time at 25 °C, were determined with tubes which were periodically removed from the chamber. The sealing caps were removed and the tube immersed in a 400-mL beaker filled to a depth of 6.0 cm with deionized water. The temperature of the bath was raised, from approximately 10 °C below the melting point, at 5 °C per min. The melting point of the network, corresponding to a gel-to-sol transition and an abrupt drop in viscosity, was taken as the temperature at which the surface of the fluid in the capillary rose 1.0 cm under the applied hydrostatic pressure differential of 5 cm of water.[19] The requirement of a 1.0-cm rise eliminated mistaking gel swelling or deformation[20] for melting. This method gave melting points reproducible to within 0.3 °C.

C. Gelation Time. It was desirable for the time interval, between the addition of formaldehyde to the 37 °C gelatin solution and the gelation in the capillary, to be minimal.[21] The time required for the formaldehyde free gelatin solution at 37 °C to cool to a gel when drawn into the melting point capillary at ambient temperature 23.0 ± 0.1 °C was determined in a viscosity study. Lines were drawn at 6 and 10 cm from the top of the capillary. The 37 °C gelatin solution, with 3.00 mL of water added in place of formaldehyde, was drawn by suction to within 1 cm of the top of the capillary. When the solution rose above the upper mark the time, T_i, was noted. At T_f, after residence time in the capillary $T = T_f - T_i$, the time t required for the solution to drop the 4.0 cm between the marks was determined. From the data and assuming a cooling rate independent of solution height in the capillary, gelation is estimated to occur within 0.5 min. Allowing for stirring subsequent to the addition of the formaldehyde, solution-phase cross-linking accounts for less than 1 min of the total reaction time in the melting point studies.

T (s)	t (s)	T (s)	t (s)
5	3.2	17	3.6
10	3.6	19	4.7
13	3.6	21	∞

D. Gelatin Degradation. The limiting viscosity number,[22] LVN, of the formaldehyde free gelatin solution was used to check for gelatin degradation. Aliquots of the formaldehyde free gelatin solution, with 3.00 mL of water added in place of formaldehyde, were placed in capped glass vials. After storage in the thermostated chamber at 25.0 ± 0.1 °C the vials were warmed at 50 °C to melt the gel, and 3.00 mL of the resulting solution was diluted to give a 2.00×10^{-3} g of gelatin/mL solution (based on dry gelatin) which was 1.00 M in NaCl. The original saline solution contained sufficient sodium bicarbonate to give a final solution pH of 7.0. Viscosities were determined at 40.00 ± 0.01 °C with a Cannon-Ubbelohde dilution type viscometer having a constant of 0.004430 cSt/s. The initial LVN value of 41 was unchanged after 15 400 min which was the time required for the melting point of the gel containing the lowest concentration of formaldehyde, 0.113 mmol/g of gelatin, to rise to 60 °C. Since the principal conclusions of the study rest on kinetic data for melting points up to 60 °C, no significant degradation was found to have occurred.

E. Nonlinear Least-Squares Regressions. The regressions were performed with the SAS Institute NLIN regression procedure.[23]

F. Critical Point Determination. The data below (see also Table I and the Discussion section), were substituted into eq 10, and for a given value of C_* the square of the correlation coefficient, r^2, was determined. C_* was incremented by 1×10^{-4} from 0.0298 to 10 and r^2 rose monotonically to a maximum, $r^2 = 1$, for $C_* = 0.0302$ followed by a monotonic decline.

$10^3/T_m$ (K^{-1})	C (mmol of cross-links/g of gelatin)
3.1731	0.0135
3.1681	0.0208
3.1432	0.0297

III. Results

A. The Model. Consider a macroscopic three-dimensional lattice of elements. The square lattice of Figure 1 is used illustratively. Equivalent bonds form randomly pairwise between adjacent elements, and each bond is formed independently of any other. Each element here is a polymer chain, and the bonds are cross-links. Let N equal the total number of possible bonds, N_r equal the number of thermally reversible bonds, N_c the number of covalent bonds, and N_0 the number of nonbonded pairs. Let p denote the fraction of bonds formed, i.e., for reversible bonds, $p_r = N_r/N$.

B. Thermally Reversible Gelation, $p_c = 0$. Initially only thermally reversible bonds between the elements are considered to have formed. In accordance with percolation theory, when a critical fraction of bonds, p_*, is exceeded an infinite network percolates through the lattice (Figure 1). The critical condition is then simply $p_* = p_r$.

Paralleling the literature approach,[5,9] each adjacent pair of elements comprises a two-state system consisting of a nominally unbound state with statistical weight ρ and a ΔE more stable bound state with weight $(1 - \rho)$. From Boltzman statistics it follows that

$$N_0/N_r = ge^{-\Delta E/RT} \qquad (1)$$

where $g = \rho/(1 - \rho)$, the ratio of available unbound to bound states. Accordingly, each polymer chain is taken to have a number of equivalent independent branches or segments equal to the number of adjacent lattice elements. A pair of chain segments from adjacent elements may then, for example, either be loosely associated random coils or be bound in a ΔE more stable configuration where both have helical regions stabilized by a series of interchain hydrogen bonds.[24] Since this kind of bond is possible only to a very few of the possible conformations of the pair of chain

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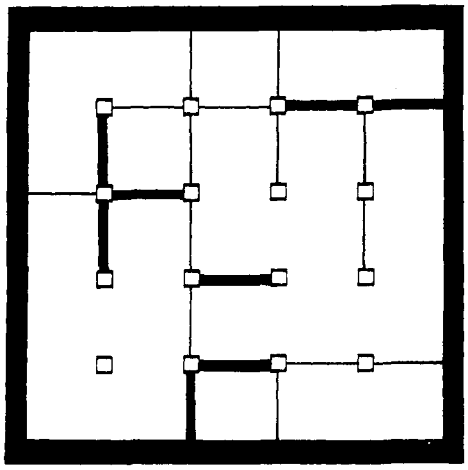

Figure 2. Superimposed on the thermally reversible network gel of Figure 1 are $p_c = (8/40) < p_*$, covalent cross-links. (For clarity the redundant reversible bonds are not shown.) The melting point of the system is now higher since a smaller value of p_r, $p_r = (N_r'/N') = (8/32)$, will now suffice at the critical point.

segments, g should be an exceedingly large number.

For this system with only thermally reversible bonds between the polymer chains, $p_r = N_r/(N_r + N_0)$, so that

$$p_r = \frac{1}{1 + g e^{-\Delta E/RT}} \tag{2}$$

where p_r is the fraction of the total possible number of reversible bonds formed or equivalently the probability that any reversible bond has formed. As $T \rightarrow \infty$, $p_r \rightarrow 1/(1 + g)$ which for g extremely large is nearly zero.[25] As $T \rightarrow 0$, $p_r \rightarrow 1$ for g extremely large but finite. At the critical point

$$p_* = \frac{1}{1 + g e^{-\Delta E/RT_m}} \tag{3}$$

where T_m is the melting point temperature of the thermally reversible gel.

C. Covalent Cross-linking in a Thermally Reversible Gel Phase. Let the lattice elements also be connectable by a covalent set of bonds. Let the two sets of bonds, reversible and covalent, be completely independent. Consider that the system is at a temperature such that $p_r > p_*$ and is therefore in the gel state. We now superimpose on the p_r linked system p_c random covalent bonds pairwise between the lattice elements (Figure 2). The covalent and reversible bonds are independent and are not mutually exclusive so the covalent bonds may form between two elements not previously bonded or between elements already connected by a reversible bond. Since the covalent bonds are distributed randomly, the residual noncovalently linked population, $N' = N - p_cN$, itself constitutes a random sample of the parent population. The expected number of reversible bonds in the residual population, N_r', is given by

$$N_r' = p_r(N - p_cN) \tag{4}$$

The existence of a gel now only requires that the sum of the fractions of nonredundant bonds exceed the critical value. Since the covalent bonds exist independent of temperature the critical point is reached if

$$p_* = p_c + p_r' \tag{5}$$

where $p_r' = N_r'/N$. It follows that $p_r' = p_r(1 - p_c)$ and at the critical point then

$$p_* = p_c + p_r(1 - p_c) \tag{6}$$

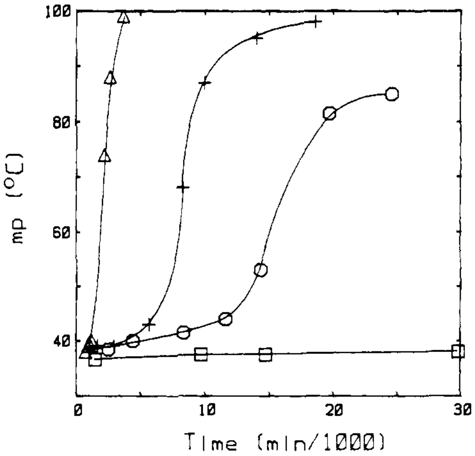

Figure 3. Gel melting point vs. time curves as a function of formaldehyde level (mmol/g of gelatin): □ = (0.000), ○ = (0.113), + = (0.139), Δ = (0.260). Not shown: (0.122), (0.156), (0.174), (0.435). Weight percent gelatin for all runs was 7.30%.

For $p_c < p_* < 1$, the fraction of thermally reversible bonds required to keep the system at the critical point, $p_r = (p_* - p_c)/(1 - p_c)$, decreases to zero as the fraction of covalent cross-links, p_c, increases toward the critical value p_*. When $p_c > p_*$ a covalent network will exist embedded in the extant reversible network. The melting point of the gel must therefore diverge as $p_c \rightarrow p_*$. Of course covalent bond breaking and decomposition of the network will preclude the unbounded increase in T_m.

Substituting for p_r gives

$$p_* = p_c + (1 - p_c)\frac{1}{1 + g e^{-\Delta E/RT_m}} \tag{7}$$

and at temperature T_m sufficient thermally reversible bonds are present so that the p_c cross-linked system is at the critical point. On rearranging eq 7 and taking logs

$$\frac{1}{T_m} = \frac{R}{\Delta E} \ln\left(1 - \frac{p_c}{p_*}\right) + B \tag{8}$$

where

$$B = \frac{R}{\Delta E} \ln \frac{g}{\left(\frac{1}{p_*} - 1\right)} \tag{9}$$

Since the lattice elements are polymer chains eq 8 relates the melting point of the thermally reversible gel to the extent to which covalent cross-linking, p_c, has approached a critical value p_*.

A test of the applicability of this model to covalent cross-linking in gelatin gel is possible via eq 8. Since p_c/p_* is given by the ratio C/C_*, where C is the level of cross-links in mmol/g of gelatin and C_* is its value at the critical point we obtain

$$\frac{1}{T_m} = \frac{R}{\Delta E} \ln\left(1 - \frac{C}{C_*}\right) + B \tag{10}$$

With a kinetic model for the cross-linking reaction the required relationship between the gel melting point, T_m, and the level of covalent cross-linking C can be obtained.

D. A Kinetic Model for the Formaldehyde Cross-linking of Gelatin Gel. A series of gel melting point vs. time curves, i.e., rate curves, were obtained, each at a different formaldehyde level and all at a fixed gelatin concentration (Figure 3). Formaldehyde cross-links in gelatin are known to undergo an increasingly rapid hydrolysis above 60 °C,[2,16] which reasonably accounts for the shape of these curves above 60 °C.[26] The kinetic analysis will therefore be restricted to melting point temperatures up to 60 °C. The time, t, required to attain a given melting point was determined for each of seven initial formaldehyde levels, A_0, from its curve. A set of

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(25) Equation 2 and all subsequent relations derived therefrom are subject to the limitations discussed in ref 9, footnote 19.

(26) For a system where the rate curves are unaffected by cross-link hydrolysis, see: Wexler, A *Image Technology 1985 SPSE's 38th Annual Conference, Advance Printing of Paper Summaries*, p 102.

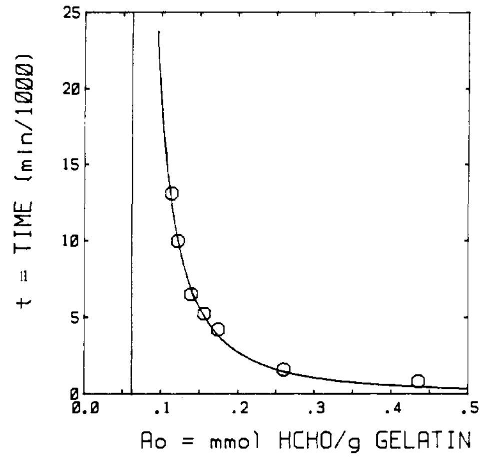

Figure 4. The time required to attain a mp of 47.5 °C as a function of initial formaldehyde level. The least-squares fit of eq 11 is plotted along with the asymptote at $A_0 = 2C$.

Table I. Cross-link Levels and Their Corresponding Melting Points[a]

T_m (°C)	$10^4 k_2$[b]	C[c]	T_m (°C)	$10^4 k_2$[b]	C[c]
41.0	-1.7	-0.019	55.0	3.7	0.031
42.0	1.6	0.014	60.0	3.5	0.031
42.5	2.7	0.021	65.0	3.5	0.031
45.0	4.1	0.030	70.0	3.6	0.032
47.5	4.1	0.031	75.0	3.8	0.034
48.0	4.1	0.031	80.0	3.9	0.035
49.0	4.1	0.031	90.0	7.2	0.047
49.5	4.0	0.031			

[a] $R > 0.99$ for all values in the table. [b] g of gelatin per mmol per min. [c] mmol of cross-links per g of gelatin.

points is obtained which approaches an asymptote as shown for $T_m = 47.5$ °C in Figure 4. A nonlinear least-squares regression on the data gives an excellent fit to eq 11, which can be derived

$$t = \frac{1}{2k_2}\left(\frac{1}{A_0 - 2C} - \frac{1}{A_0}\right) \qquad (11)$$

by assuming that cross-linking in the gel obeys the following solution phase kinetic model,[17] given in Scheme I.

Scheme I

$$\text{Gel-NH}_2 + \text{HCHO} \xrightarrow{k_1} \text{Gel-NHCH}_2\text{OH}$$

$$2\text{Gel-NHCH}_2\text{OH} \xrightarrow{k_2} \text{Gel-NHCH}_2\text{OCH}_2\text{NH-Gel} + \text{H}_2\text{O}$$

If $k_1 \gg k_2$, [Gel-NHCH$_2$OH] = A and [Gel-NHCH$_2$OCH$_2$NH-Gel] = C then

$$\mathrm{d}C/\mathrm{d}t = k_2 A^2$$

but $A = A_0 - 2C$, where $A_0 = [\text{HCHO}]_0$, so

$$\mathrm{d}C/\mathrm{d}t = k_2[A_0 - 2C]^2 \qquad (12)$$

which on integration gives eq 11.[27]

Thus the time required to attain a fixed melting point corresponds to the time required to reach a fixed level of cross-links, C, and this is a function of the initial formaldehyde level A_0. Table I presents the results of this kinetic model for a series of melting point temperatures. A simple linear extrapolation of the cross-link levels vs. melting points below 45 °C gives a melting point of the noncovalently cross-linked gel of $T_m^0 = 41.0$ °C. A plot of melting points vs. cross-link level affords a phase diagram that is characterized by an abrupt increase in the gel melting point at 0.031 mmol crosslinks/g of gelatin (Figure 5). The fit of eq 10 to these data will test how well the model accounts for the phase diagram.

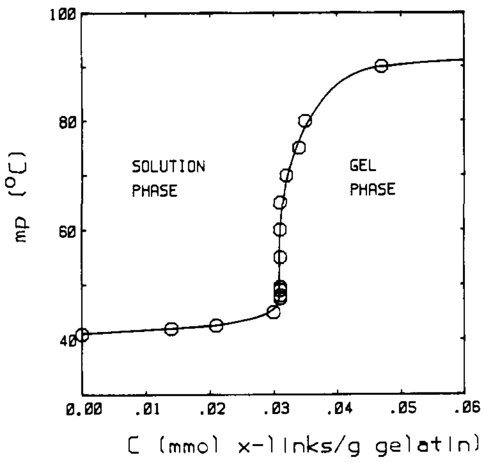

Figure 5. A critical point in the phase diagram of formaldehyde cross-linked gelatin gel.

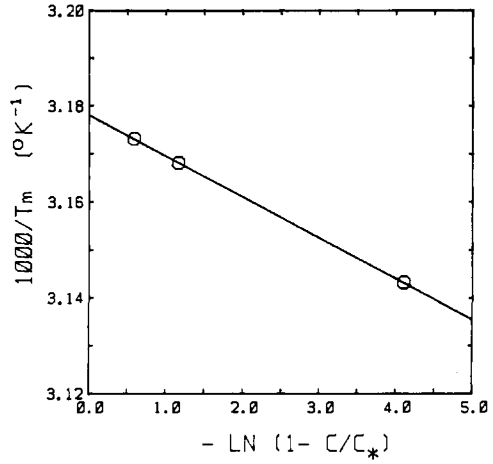

Figure 6. Optimized fit of eq 10, $C_* = 0.0302$, to the melting point $T_m < 47.5$ °C vs. cross-link level data (Table I). Found, $1/T_m = 8.511 \times 10^{-6} \ln(1 - C/0.0302) + 3.178 \times 10^{-3}$, with $r^2 = 1$.

E. Fit of the Connectivity Model to the Melting Point vs. Cross-link Level Curve. The melting point vs. cross-link level data come from Table I. The onset of the critical point is so abrupt that the same level of cross-links is found for T_m at or above 47.5 °C. C_* is determined by optimization to the best least-squares fit of eq 10 to the remaining data.[31] (The data used were rounded for significant figures only following the optimization. See the Experimental Section.) An excellent optimum fit was found for $C_* = 0.0302$ mmol of cross-links/g of gelatin (Figure 6). The stability of the reversible bond is $\Delta E = 2.3 \times 10^2$ kcal mol^{-1}, and from the intercept the melting point of the noncovalently cross-linked gel, T_m^0, is 41.5 °C. In terms of p_*, $g = [(1/p_*) - 1]e^{370}$. The stability of the reversible bond found here is similar to that previously reported for gels having the stablest possible reversible bonds.[6]

IV. Discussion

The approach taken here is that a thermally reversible gel phase can serve as a lattice for covalent cross-linking. The existence of a network furthermore is taken to depend on whether the fraction of randomly formed nonredundant linkages, irrespective of type, exceeds the critical value for the lattice. This approach provides a model for the connectivity of the system at the critical point, and hence serves as the basis for a melting point equation.

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[27] As discussed in ref 17 and elsewhere[28,29] there are conflicting reports about the formaldehyde cross-link. Accordingly, eq 12 is also obtained directly from the rate law for the cross-linking reaction[17] if methylene-ether cross-links are produced and Ostwald isolation conditions for formaldehyde prevail.[30]

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[31] Reference 10, p 109.

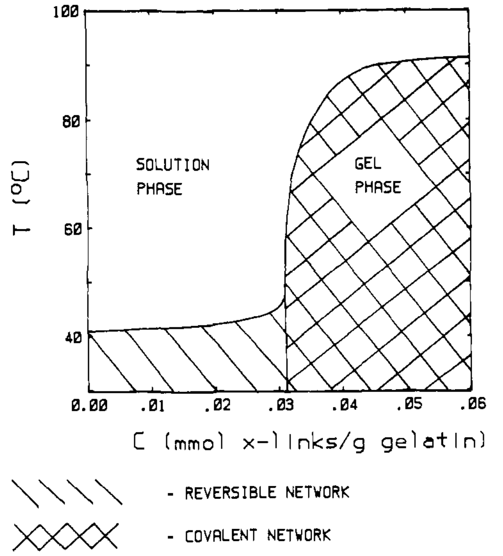

Figure 7. The phase diagram of formaldehyde cross-linked gelatin gel.

Applying this model to the gelatin system presupposes independence between the covalent and reversible cross-links. The reversible cross-links in gelatin, which result from interchain hydrogen bonds between helical regions having the nonpolar Gly-Pro-Hypro tripeptide sequence,[24] are distinct from the formaldehyde produced covalent linkages involving polar side chain lysine amino groups in the mobile amorphous regions of the polymer. That the two sets of cross-links utilize different groups on the gelatin chains suggests that a sufficient degree of independence exists to warrant application of the model. A further assumption in the approach taken here is that the increase in melting point is due solely to the covalent cross-linking. Gelatin gel does undergo an increase in melting point[32] in an annealing process.[33,34] This increase, however, is nearly completed shortly after gelation and is small relative to the very large melting point rise reported here.[35] That the T_m° obtained from extrapolation of the kinetic data is slightly higher than observed experimentally for the formaldehyde free gel may reflect some enhancement of this process in the formaldehyde-containing gels.

The close correspondence between the level of covalent cross-links resulting in the abrupt melting point rise seen in the phase diagram (Figure 7) and the critical level of covalent cross-links, C_*, determined via eq 10, supports this connectivity model. The gel region of the phase diagram, up to the critical value of 0.031 mmol of cross-links/g of gelatin, is the domain of solely the thermally reversible network. As the level of covalent cross-links increases in this domain, a decreasing fraction of the nonredundant reversible bonds is required to maintain the system as a gel and the melting point increases. The sudden increase in the thermal stability of the gel occurs with the incipient formation of the covalent network. Usually network formation is associated with a sol-to-gel transition. The formation of the covalent network here, however, takes place in the gel phase, and the network formed is in this sense a latent covalent network. The formation of this covalent network is made apparent only by the drastic change in the melting point of the system. Above the critical level of covalent cross-links the gel-to-sol transition necessarily occurs with degradation of the covalent network at what are more properly regarded as decomposition temperatures.

The melting point of a thermally reversible gel is here newly identified as a physical quantity which diverges at a critical point. Just as viscosity diverges at a critical point in solution-phase cross-linking of polymers, gel melting point diverges when the cross-linking of the polymer takes place in a thermally reversible gel phase.

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[35] The melting point of the formaldehyde free gel (Figure 3), after increasing from 33 to 36.5 °C in the interval from 30 to 450 min, increased only to 38.0 °C at 30 × 10^3 min.

Bond Paths and Bond Properties of Carbon-Lithium Bonds

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Abstract: Twenty-three organolithium compounds were analyzed by using the topological theory of molecular structure. The geometry of each compound was first optimized, making use of the 3-21G basis set. Then integrated lithium charges and quantities characterizing the carbon-lithium bond critical point, such as ρ_c(C-Li), $\nabla^2\rho_c$(C-Li), and the local energy density, were calculated. The results confirm the nature of the carbon-lithium bond to be primarily ionic. Bond path networks of these compounds were also calculated and proved surprising. Coordination numbers of lithium, as assigned by the topological theory, range from one to four. Similarly defined coordination numbers of carbon range as high as nine. Unexpectedly, some putatively bridging lithiums are not bridging in a topological sense. Additional unexpected features of the bond path networks are bond paths connecting essentially neutral carbons with lithiums and bond paths connecting highly negatively charged carbons that are widely separated. No lithium-lithium bond paths are found. Finally, unstable topological structures occur at potential energy minima. Polarization of electrons toward what are essentially lithium cations accounts for the carbon-lithium bond paths observed.

Bonds are a fundamental construct of chemistry.[1] Nevertheless, many chemists are hard pressed to define exactly what a bond is and, instead, rely upon intuition to identify bonds in unusual structures. The dotted lines that appear in representations of nonclassical cations, transition states, and "weakly" interacting systems, for example, are a sign of the uncertainty and imprecision in defining "chemical bonds".

In contrast, by a detailed examination of the behavior of the electron density distribution, the topological theory rigorously defines bonds, rings, and cages in molecules.[2] For a wide variety

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