

# Formation and Structure of Polyacrylamide Gels

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## SYNOPSIS

Acrylamide and *N,N'*-methylenebis(acrylamide) (AAm–Bis) copolymerization has been investigated in water at a monomer concentration of 1.8 w/v %. Conversion of monomer and pendant vinyl groups was measured as a function of the reaction time up to the onset of macrogelation. Experimental results indicate that 80% of pendant vinyl groups are consumed by cyclization reactions. When the monomer concentration was kept constant at 1.8%, the critical conversion at the gel point shows a minimum at 7.5 mol % Bis. The equilibrium degree of swelling of the polyacrylamide (PAAm) gels is independent of their crosslinker content. Calculation results show that the average reactivity of pendant vinyl groups for intermolecular links decreases as the Bis concentration increases. All these results suggest formation of PAAm microgels prior to the onset of macrogelation. As the reaction proceeds, microgels are connected to a macrogel through their peripheral pendant vinyls and radical ends, whereas those in their interior remain intact. The microgels seem to act as the junction points of the final inhomogeneous networks. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Polymer gels are important materials of both fundamental and technological interest. In recent years, hydrophilic gels called “hydrogels” have received considerable attention for use as specific sorbents and as support carriers in biomedical engineering. Investigations of the swelling behavior of acrylamide-based hydrogels have been reported repeatedly in the last four decades. It is well known that the swelling behavior of polymer gels depends on their network structure whereas the latter is closely related to the conditions under which the polymer gels are formed.<sup>1</sup> Thus the understanding of the formation mechanism of polymer gels is of great interest in predicting their physical properties.

Polyacrylamide (PAAm) gels are obtained by free-radical crosslinking copolymerization of acrylamide (AAm) and *N,N'*-methylenebis(acrylamide) (Bis) monomers. Since the monomers are solid at the usual polymerization temperature, it is necessary to carry out the polymerization reactions in an aqueous

solution of the monomers. Several studies showed that the hydrogel structure, and thus the hydrogel properties, strongly depend on the initial degree of dilution of the monomers.<sup>2–6</sup> As the amount of solvent (water) present at polymerization increases, the network structure becomes increasingly loose. No continuous network is formed above a critical amount of solvent.<sup>7</sup> It was also shown experimentally<sup>8–12</sup> and theoretically<sup>13,14</sup> that acrylamide-based hydrogels exhibit inhomogeneous crosslink distribution.

Although extensive work has been reported in the literature for the physical properties of PAAm gels, the formation mechanism of only a few was concerned with free-radical crosslinking copolymerization. Baselga and colleagues studied the copolymerization of AAm and Bis monomers in an aqueous solution and found the reactivity ratio of vinyls on AAm to Bis monomers,  $r_{12} = 1.14$ .<sup>15–17</sup> They attributed the inhomogeneous crosslinking in PAAm gels to this difference in the vinyl group reactivity. However, Baselga and coworkers' explanation was contradicted by Tobita and Hamielec,<sup>14</sup> who showed theoretically that the value  $r_{12} = 1.14$  cannot produce inhomogeneities in the structure. Their experimental results indicate that a significant fraction of the

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pendant vinyl groups is consumed by cyclization and multiple crosslinking reactions, which must be responsible for the inhomogeneous crosslink distribution in PAAm gels.<sup>14</sup>

Here we present new measurements which will enable us to estimate the magnitude of cyclization and reduction in the pendant vinyl group reactivity in AAm-Bis copolymerization in highly dilute aqueous solutions. For this purpose, a series of experiments with varying amounts of the crosslinker Bis were performed at a total monomer concentration of 1.8 w/v % (0.25M). Conversion of the monomers and the gel points were determined experimentally by means of gravimetric and dilatometric techniques. The pendant vinyl group conversion was determined by an analytical titration method. The kinetic model developed recently<sup>18-21</sup> was used to study the experimental data and to evaluate the average reactivity of pendant vinyl groups as a function of the crosslinker concentration.

## EXPERIMENTAL

### Materials

Commercial available AAm and Bis monomers and the initiator potassium peroxydisulfate ( $K_2S_2O_8$ ) were purified by the usual methods. The polymerization solvent water was distilled twice before use. Sodium hydrogen carbonate ( $NaHCO_3$ ) and sodium thiosulfate ( $Na_2S_2O_3$ ) (both analytical grades) were used without further purification.

### Polymerization Procedure

AAm-Bis copolymerizations were carried out in water at  $40 \pm 0.1^\circ C$  with  $K_2S_2O_8/Na_2S_2O_3$  redox initiator system in the presence of  $NaHCO_3$  buffer. The conversion of monomers up to the onset of macrogelation was followed by dilatometry. The polymerization technique used is described in detail elsewhere.<sup>22,23</sup> The reproducibility of the kinetic data was checked by repeating the experiments and also by comparing the results with those obtained by the gravimetric technique. The deviation in the initial slopes of time versus conversion data between two runs was always less than 3%. Concentrations used were 0.25M for the monomers,  $1 \times 10^{-3}M$  for  $K_2S_2O_8$ ,  $Na_2S_2O_3$ , and  $NaHCO_3$ . These concentrations were taken to be constant throughout the study, and only the crosslinker Bis concentration was varied from 0 to 12 mol %. The polymer samples for pendant vinyl group measurements were obtained by a gravimetric technique described previously.<sup>24</sup>

### Gel Point Measurements

Two different methods were used to measure the gel points in AAm-Bis copolymerization. First, the gravimetric technique was used to follow the polymerization reactions; the gel point was determined as the midpoint between the last time at which a soluble polymer was obtained and that at which the polymer was not soluble in water. For ascertaining the insoluble gel component of samples, the latter were treated with an approximately 50-fold excess of water at room temperature. The formation of insoluble polymer was detected visually from the appearance of gel particles in water. Second, a special dilatometer containing a steel sphere of 4.8-mm diameter was used for the gel point measurements. The midpoint between the last time at which the sphere moved magnetically and that at which it stopped moving was taken as the gel point. We found remarkable consistency in the gel points determined using both methods. Each gel point reported in this paper is an average of at least four measurements. The standard deviations are shown in Figure 7 as error bars.

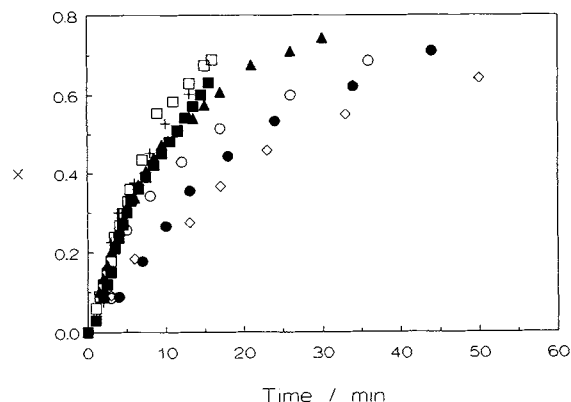
### Pendant Vinyl Groups

Measurement of the number of pendant vinyls on AAm-Bis copolymers was carried out by bromometry using the bromate/bromide titration method.<sup>25</sup> This method is based on the reaction of pendant vinyl groups with bromine produced *in situ* from the bromate/bromide reagent and back titration of the excess bromine. The method proved satisfactory with soluble polymer samples. A standard deviation of  $\pm 0.1$  mmol pendant vinyl group/g of soluble PAAm was found for this method of measurement.

## RESULTS AND DISCUSSION

### Enhancement in Polymerization Rate

It is known that in free-radical polymerization, crosslinking enhances the gel effect significantly and the autoacceleration in polymerization rate starts right at zero conversion.<sup>26-32</sup> In Figure 1, fractional monomer conversion  $x$  versus reaction time  $t$  plots are shown up to the onset of macrogelation for AAm-Bis copolymerization with different crosslinker contents. The concentrations of the monomers and the initiator were, respectively, 0.25M (i.e., 1.8 w/v %) and  $1 \times 10^{-3}M$ . The content of the crosslinker Bis in the initial monomer mixture was varied between 0 and 12 mol %. Acceleration of the rate of



**Figure 1** Variation of the conversion  $x$  versus time  $t$  histories in free-radical crosslinking copolymerization of AAm and Bis comonomers with the crosslinker concentration. Temperature = 40°C. Initial monomer concentration = 0.25M. Concentrations of  $K_2S_2O_8$ ,  $NaHCO_3$ , and  $Na_2S_2O_3$  are  $1 \times 10^{-3}M$ . Bis = 0 ( $\diamond$ ); 2.6 ( $\bullet$ ); 3.85 ( $\circ$ ); 5.06 ( $\blacktriangle$ ); 9.64 ( $+$ ); 10.71 ( $\blacksquare$ ); and 11.76 mol % ( $\square$ ).

polymerization with increasing Bis content can be seen in Figure 1. Similar time-conversion curves were also obtained at 0.5M total monomer concentration. Using a polynomial fit to the experimental data, the initial reaction rates,  $(dx/dt)_0$ , were calculated; they are shown in Figure 2 as a function of the Bis content. A significant rate enhancement can be seen even at zero monomer conversion.

Invoking steady-state approximation for the radicals in the pregel period, the initial rate of polymerization can be written as<sup>23</sup>

$$\left(\frac{dx}{dt}\right)_0 = [1 + (2r_{21} - 1)f_{20}]k_{p1}[R^*]_0 \quad (1)$$

where  $r_{21}$  is the reactivity ratio of vinyls on Bis to AAm monomer,  $f_{20}$  is the initial mole fraction of Bis in the monomer mixture,  $k_{p1}$  is the propagation rate constant for AAm homopolymerization, and  $[R^*]_0$  is the radical concentration at zero monomer conversion, which is given by

$$[R^*]_0 = (2fk_d[I]_0/k_{t0})^{1/2} \quad (1a)$$

where  $f$  is the initiator efficiency,  $k_d$  is the decomposition rate constant of the initiator,  $[I]_0$  is the initial concentration of the initiator, and  $k_{t0}$  is the termination rate constant of zero conversion radicals.

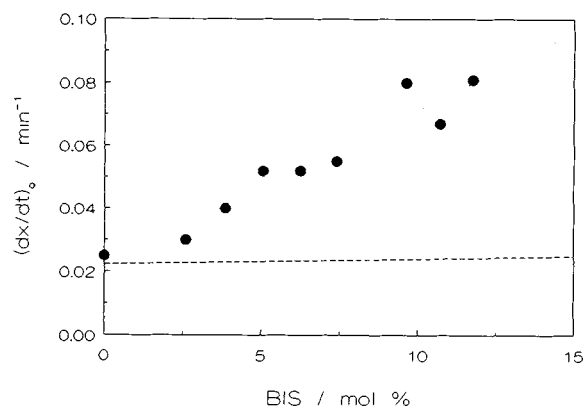
Assuming that the radical concentration at zero monomer conversion,  $[R^*]_0$ , remains constant, the increase in the initial rates shown in Figure 2 requires, according to eq. (1), a much higher reactivity

of the vinyl groups on Bis with respect to the vinyl on AAm monomer. For example, the dotted line in Figure 2, which is a best linear fit to the experimental data, assumes  $[R^*]_0 = \text{constant}$  and  $r_{21} = 11.5$ . However, the results of Baselga and colleagues indicate that the monomeric vinyl group reactivities are almost equal. The dashed line was calculated for  $r_{21} = 1.14^{-1}$ , the value reported by Baselga and co-workers.<sup>16</sup> The great discrepancy between the theoretical line and the experimental data indicates that  $[R^*]_0$  should depend on the Bis content of the initial monomer mixture. Since the concentrations of the monomers and the initiator are fixed in all experiments, this dependence must, according to eq. (1a), be due to the decrease of the termination rate constant of the radicals  $k_{t0}$ . Since we are dealing here with zero conversion radicals, i.e., polymer radicals in the absence of preformed polymers, the variation of  $k_{t0}$  with Bis content can be possible only by a change of the macroradical coil dimensions, which may result from a first-order intramolecular reaction, such as the cyclization reaction shown schematically in Figure 3.

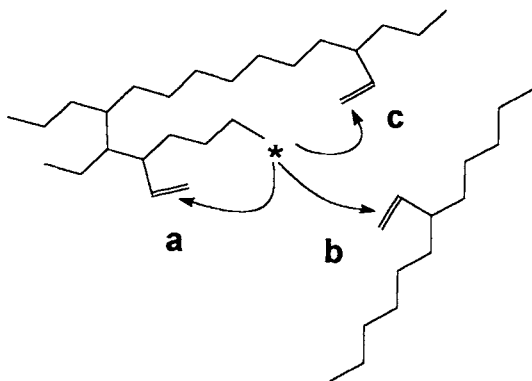
The time-conversion curves shown in Figure 1 also allow us to calculate the drift in the primary chain length during AAm-Bis copolymerization, using the following equation<sup>21</sup>:

$$\frac{\bar{M}_w^*}{\bar{M}_{w,0}^*} = \frac{(dx/dt)}{(dx/dt)_0} \exp(k_d t) \quad (2)$$

where  $\bar{M}_w^*$  is the weight average molecular weight of the primary molecules at time  $t$  and the subscript 0



**Figure 2** Variation of the initial rate of polymerization  $(dx/dt)_0$  with the crosslinker concentration. The dashed line was calculated using eq. (1) for a constant radical concentration and for  $r_{12} = 1.14$ , the value reported by Baselga and colleagues.<sup>16</sup> The dotted line is a best fit to the experimental data.

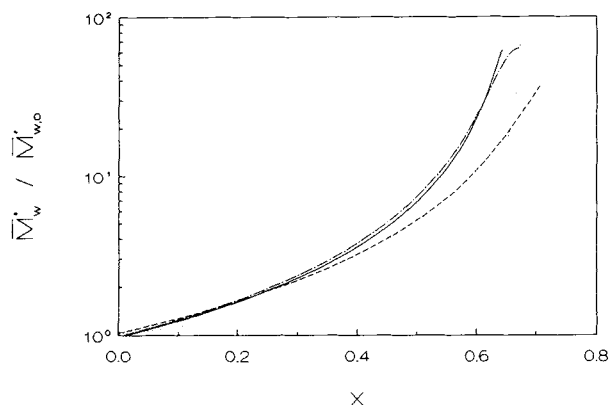


**Figure 3** Schematic drawing of the processes of cyclization (a), crosslinking (b), and multiple crosslinking (c) in free-radical crosslinking copolymerization.

denotes the initial values at the start of the reaction. Using a polynomial fit of the experimental time-conversion data shown in Figure 1, the variation of  $(dx/dt)$  with conversion  $x$  was evaluated, from which the ratio of the molecular weight of the primary chains at conversion  $x$  to that at  $x = 0$ ,  $\bar{M}_w^*/\bar{M}_{w,0}^*$ , was calculated by using eq. (2). The calculation results are shown in Figure 4 as a function of the monomer conversion. Here, we have assumed  $k_d = 0$  (constant initiator concentration). The results indicate a 10- to 100-fold increase in the primary chain length during the course of the pregelation period due to the decrease in termination rate constant (gel effect). The primary chain length first increases slightly with increasing conversion up to  $x \approx 0.5$ . The steeper increase of the primary chain length at  $x > 0.5$  can be interpreted as the result of a change from segmental diffusion to translational diffusion, being the rate controlling the termination process.

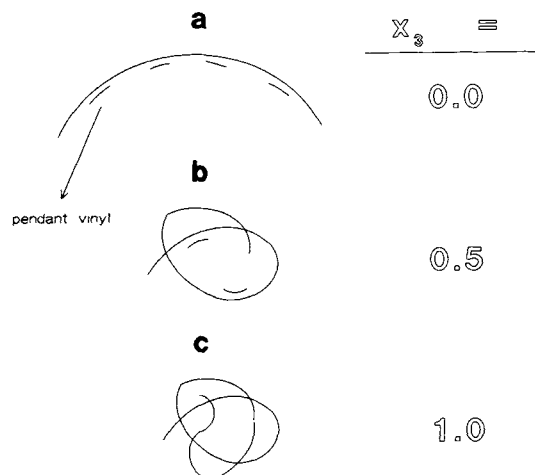
### Cyclization

In vinyl/divinyl monomer copolymerization, a pendant vinyl group is created during the course of the reaction when one of the vinyls on the divinyl monomer reacts. The pendant vinyl group thus formed can then react by cyclization, crosslinking, or multiple crosslinking reactions, or can remain pendant. With cyclization, the cycle is formed when the macroradical attacks the pendant vinyl groups in the same kinetic chain; while with multiple crosslinking, it is formed if the radical attacks double bonds pendant on other chains already chemically connected with the growing radical.<sup>1,33-35</sup> A schematic representation of cyclization, crosslinking, and multiple crosslinking reactions is shown in Figure

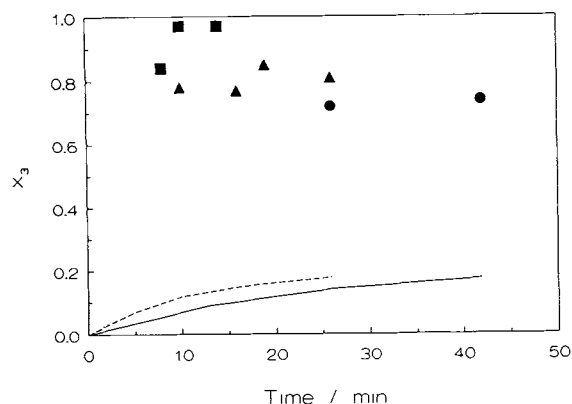


**Figure 4** Drift in the primary chain length,  $\bar{M}_w^*/\bar{M}_{w,0}^*$ , shown as a function of the monomer conversion  $x$ . See Figure 1 caption for the reaction conditions. Bis mol % = 0 (—); 2.6 (---); 5.1 (- · - ·); and 11.76 (· · · · ·).

3. Since according to the classical theory of gelation<sup>36</sup> only one crosslink per weight-average primary molecule is necessary for the onset of macrogelation, the content of pendant vinyls is a highly sensitive indicator for the formation of cycles and multiple crosslinks in finite species.<sup>14,21,23,33-35</sup> Here we define the pendant conversion,  $x_3$ , as the fraction of Bis units with both vinyl groups reacted, i.e., the fraction of fully reacted Bis units in the polymer. Thus  $x_3$  is equal to zero for linear chains bearing pendant vinyl groups, whereas it is equal to unity for chains carrying only double-reacted Bis units (Fig. 5). Theories neglecting cyclization predict that every divinyl



**Figure 5** Schematic representation of a primary chain forming cycle. Initial number of divinyl monomer units on this primary chain is equal to 4; thus there are initially four pendant vinyl groups (a). The number of pendant vinyls becomes 2 (b) and 0 (c) due to cyclization reactions.



**Figure 6** Variation of the pendant vinyl conversion  $x_3$  with the reaction time  $t$  in AAm/Bis copolymerization. Bis content = 2.6 (●), 6.25 (▲), and 11.76 (■). The curves were calculated for random polymerization with 3 (—), 6 (---), and 12 (····) mol % crosslinker.

monomer unit in the polymer should initially bear a pendant vinyl group,<sup>36</sup> i.e.,  $\lim_{t \rightarrow 0} x_3 = 0$ . Since cross-

linking is a second order reaction, deviation from zero indicates the existence of cyclization. Thus the occurrence of cyclization reactions can be reflected by extrapolating experimental  $x_3$  versus  $x$  or  $t$  plots to zero conversion or reaction time. On the other hand, the rate of change of pendant conversion  $x_3$  with the monomer conversion  $x$  or with the reaction time  $t$  is a measure of the extent of multiple crosslinkages.<sup>33,34</sup> The greater the slope of  $x_3$  versus  $x$  or  $t$  curve, the higher the number of multiple crosslinks formed per crosslink.

In Figure 6, pendant vinyl group conversion  $x_3$  versus reaction time  $t$  data are shown for AAm-Bis copolymerization at 1.8 w/v % monomer concentration. Some scatter of the data points originates from the uncertainty of the method of measurements, which is estimated to be  $\pm 0.1$ . The curves were calculated for random polymerization, that is, for equal vinyl group reactivity and absence of cyclization and multiple crosslinking reactions.<sup>21</sup> Figure 6 indicates a high extent of cyclization in AAm-Bis copolymerization at 1.8% monomer concentration. By extrapolating to  $t = 0$ , we can estimate  $\lim_{t \rightarrow 0} x_3 \cong 0.8$ ,

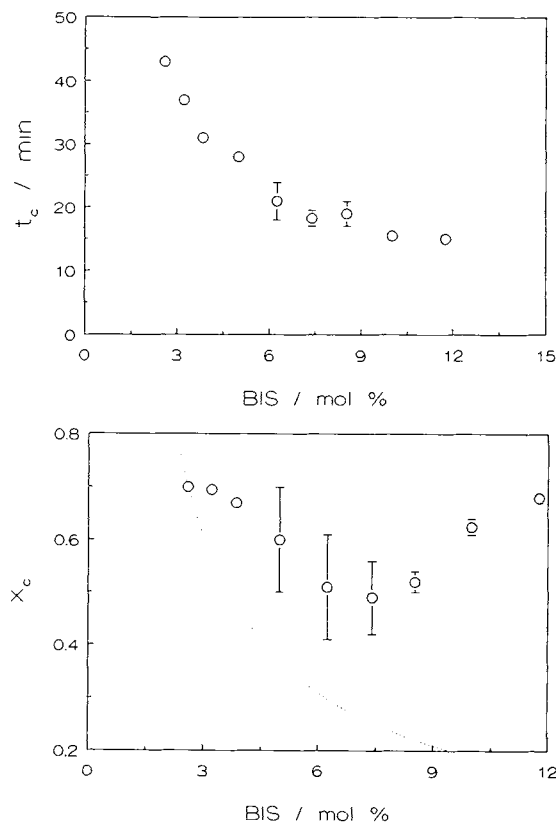
indicating that about 80% of the Bis units are consumed in intramolecular reactions. This value is close to the value found by Tobita and Hamielec<sup>14</sup> for a monomer concentration of 5.66%. The fraction of "wasted pendant vinyls" seems to be a slightly increasing function of the Bis content. Furthermore, it is difficult to derive the extent of multiple cross-

linkages from the experimental data due to the large experimental error involved in the data points.

The results on cyclization are in agreement with the reaction rate data of the previous section. The first macroradicals formed are, according to Figure 6, highly crosslinked intramolecularly; thus they should exhibit compact structures. The increase of Bis content increases the compactness of the structures formed; this will result in a decrease in the mobility of chain segments and therefore suppress the diffusion-controlled termination of radicals due to steric reasons. These phenomena are reflected in the enhancement of the rate of polymerization shown in Figure 1.

### Gel Points

Figures 7(a) and (b) show the macrogelation points in terms of the reaction time and the monomer con-



**Figure 7** Gelation points in terms of the reaction time  $t_c$  (a) and monomer conversion  $x_c$  (b) shown as a function of the crosslinker concentration. The error bars indicate standard deviations of the results of at least four measurements. The standard deviations are smaller than the symbols themselves for those without an error bar. The dotted curve in (b) was calculated using eq. (3) and assuming  $\bar{r}_{32}$  is constant.

version, respectively plotted as functions of the Bis content. The error bars indicate standard deviations of the results of at least four experiments. In terms of the reaction time, gelation occurs earlier with increasing Bis content. This is expected and also predicted by the gelation theories.<sup>36</sup> However, the critical monomer conversion at the gel point  $x_c$  shows a minimum at 7.5 mol % Bis. A similar gelation curve was also reported by Baselga and coworkers at 7% monomer concentration<sup>17</sup> (present concentration is 1.8%). They explained this unusual feature with the low probability for cyclization below 7% Bis; in this region, as predicted by the theories, gelation occurs earlier with increasing Bis concentration. Above 7% Bis, they assumed that the cyclization probability becomes significant, resulting in the delay in the gel point toward higher conversions.<sup>17</sup> However, experimental results of the previous section do not support this explanation and do require comment.

If we assume that the radical concentration and the reaction volume remain constant in the pregel regime, the critical conversion at the gel point  $x_c$  can be given as follows<sup>19</sup>:

$$x_c = \frac{1}{(1 - k_{cyc})r\rho_0\bar{X}_2^*} \quad (3)$$

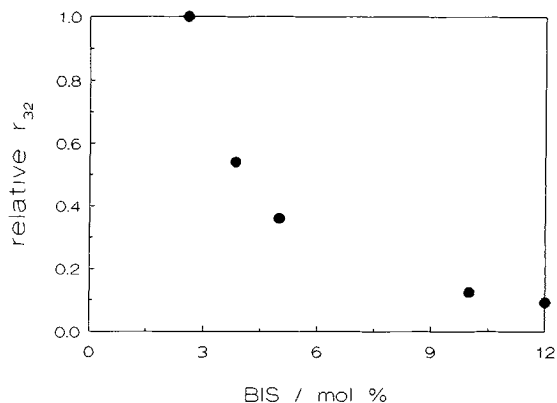
where  $k_{cyc}$  is the fraction of pendant vinyls used by cyclization reactions;  $r$  is a factor representing the unequal reactivity of the vinyl groups and is given by the equation

$$r = \frac{\bar{r}_{32}}{[r_{12} + \rho_0(1 - r_{12})]^2} \quad (3a)$$

$\bar{r}_{32}$  is the reactivity ratio of pendant to monomeric vinyls;  $\rho_0$  is the mole fraction of vinyl groups belonging to the divinyl monomer; and  $\bar{X}_2^*$  is the weight-average degree of polymerization of the primary chains, i.e.,  $\bar{X}_2^* = \bar{M}_w/\bar{M}_u$ .  $\bar{M}_u$  is the average molecular weight of a repeat unit. Note that if the variations in the radical concentration and the reaction volume are taken into account, one obtains a series of differential equations instead of eq. (3), which can also be solved numerically.<sup>18</sup> The following results, however, are not affected by these approximations.

To explain the shape of the gelation curve, we first assumed that the product  $(1 - k_{cyc})\bar{r}_{32}\bar{X}_2^*$  in eq. (3) is constant. Experimental data indicate a critical conversion of 0.7 for 2.6% Bis concentration. Thus, for  $x_c = 0.7$  at  $\rho_0 = 0.05$  and  $r_{12} = 1.14$ , eq. (3) predicts  $(1 - k_{cyc})\bar{r}_{32}\bar{X}_2^* = 36$ . This value was used for further

calculations. The results are shown in Figure 7(b) as a dotted curve. Large deviation from the experimental data indicates that the product  $(1 - k_{cyc})\bar{r}_{32}\bar{X}_2^*$ , which includes separate terms for cyclization, pendant reactivity, and primary chain length, is a function of the crosslinker concentration. The deviation becomes even larger if we include the drift in the primary chain length using eq. (2). Since the extent of cyclization (i.e.,  $k_{cyc}$ ) changes only slightly with the Bis content (Fig. 6), the variation of the pendant reactivity represented by  $\bar{r}_{32}$  with  $\rho_0$  must be the reason for the deviation. The values of relative  $\bar{r}_{32}$ —that is, the ratio of the pendant reactivity with respect to that at 2.6% Bis concentration—providing the correct gel points were calculated and are shown in Figure 8 as functions of the Bis concentration. The pendant reactivity decreases abruptly with increasing Bis content. A similar behavior was also observed recently in methyl methacrylate–ethylene glycol dimethacrylate copolymerization in toluene.<sup>32</sup> The experimental gelation curve can now be explained as follows: increasing crosslinker concentration  $\rho_0$  increases the overall concentration of pendant vinyl groups in the reaction system but decreases their average reactivity for intermolecular links. Thus the position of the gel point depends on the combination of these two opposite effects, namely the effects of the concentration and the reactivity of pendant vinyl groups. At low crosslinker contents, the increase in the overall pendant vinyl group concentration due to the increase in  $\rho_0$  dominates compared to the decrease in the pendant reactivity, resulting in earlier gelation. However, at Bis contents higher than 7% the decrease in the pendant reactivity dominates the gelation process, leading to the delay of the gel point.



**Figure 8** Variation in the relative reactivity of pendant vinyls for intermolecular reactions  $\bar{r}_{32}$  with the crosslinker concentration in AAm/Bis copolymerization. See Figure 1 caption for reaction conditions.

## Swelling Degrees

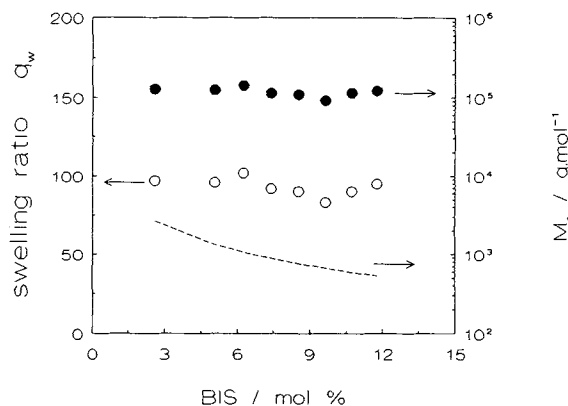
It is interesting to compare the elastically effective crosslink densities of the present PAAm gels. For this purpose, the reactions were continued for 1 week after the onset of macrogelation and the final networks were swollen in distilled water until equilibrium was reached. Then the swelling measurements were carried out as described previously.<sup>24</sup> From the equilibrium degrees of swelling of the networks, the crosslink densities were evaluated using Flory's swelling equation for tetrafunctional networks<sup>36</sup>:

$$\ln(1 - \nu_2) + \nu_2 + \chi \nu_2^2 + \frac{\rho}{M_c} V_1 (\nu_2^{1/3} \nu_2^0{}^{2/3} - \nu_2/2) = 0 \quad (4)$$

where  $\nu_2$  is the volume fraction of polymer in the equilibrium swollen gel, i.e.,

$$\nu_2 = \left( 1 + \frac{(q_w - 1)\rho}{d_1} \right)^{-1} \quad (4a)$$

$q_w$  is the weight swelling ratio of the gels, i.e., the ratio of the weights of the network in the swollen state and the dry state;  $\rho$  and  $d_1$  are the densities of the polymer and solvent (water),  $\chi$  is the polymer-solvent interaction parameter;  $V_1$  is the molar volume of solvent;  $\nu_2^0$  is the volume fraction of polymer at preparation; and  $M_c$  is the molecular weight of network chains. Using the experimental  $q_w$  data together with the values  $\rho = 1.35$  g/mL,<sup>37</sup>  $d_1 = 1$  g/mL,  $V_1 = 18$  mL/mol,  $\chi = 0.48$ ,<sup>6</sup> and  $\nu_2^0 = 0.013$ , we estimated the molecular weights of the network chains  $M_c$  using eq. (4). The results are collected in Figure 9. Here, the equilibrium swelling ratio  $q_w$  and the molecular weight of the network chains  $M_c$  are shown as symbols. The dashed curve represents the stoichiometric molecular weight of the network chains calculated from the Bis content in the reaction mixtures. The equilibrium swelling ratio and thus the molecular weight of the network chains  $M_c$  are independent of the crosslinker content in the initial monomer mixture. The results show  $M_c = 120,000 \pm 20,000$  g/mol over the entire range of the crosslinker Bis. Furthermore,  $M_c$  values are two to three orders of magnitude greater than those expected from the stoichiometry, indicating inefficient crosslinking due to cyclization and multiple crosslinking reactions. Thus we may conclude that due to the high extent of cyclization reactions, the highly intramolecularly crosslinked microgel particles formed in the pre-gel period act as junction points.



**Figure 9** Weight swelling ratio  $q_w$  (○) and the molecular weight of the network chains  $M_c$  (●) shown as functions of the crosslinker content of PAAm gels. The dashed curve represents the stoichiometric molecular weight of the network chains calculated from the Bis content of the reaction mixtures.

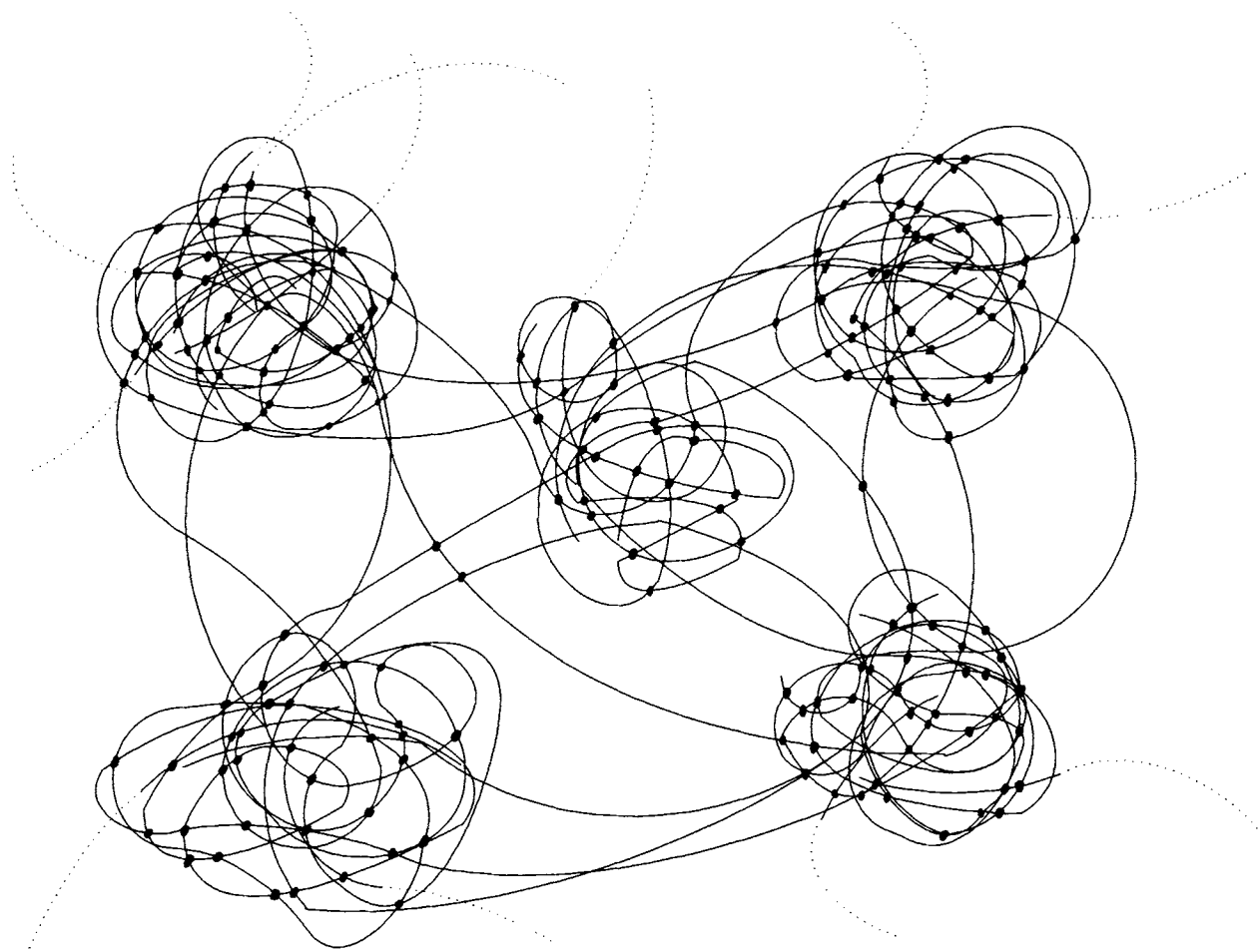
Increasing crosslinker content only increases the compactness of these junctions without changing the distance between the microgels, as shown schematically in Figure 10.

## CONCLUSIONS

The following nonidealities were observed in free-radical crosslinking copolymerization of AAm and Bis monomers in aqueous solution:

1. Bis concentration enhances the rate of polymerization;
2. 80% of the pendant vinyl groups are consumed by cyclization reactions;
3. Critical conversion at the gel point shows a minimum at 7.5% Bis concentration;
4. Average reactivity of pendant vinyls decreases abruptly with increasing Bis content; and
5. Equilibrium degree of swelling of PAAm gels is independent of their crosslinker content.

All these phenomena suggest formation of microgels prior to the onset of macrogelation. As the reaction proceeds, microgels are connected to a macrogel through their peripheral pendant vinyls and radical ends, whereas those in their interior remain intact. It seems that the scheme shown in Figure 10 best describes the structure of PAAm gels formed in dilute solutions.



**Figure 10** Schematic representation of the structure of PAAm gels prepared in dilute aqueous solutions.

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