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Effects of cyclization and pendant vinyl group reactivity on the swelling behavior of polyacrylamide gels

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Summary

A series of polyacrylamide (PAAm) gels were prepared by free-radical crosslinking copolymerization of acrylamide and N,N'-methylenebis(acrylamide) (BAAm) in water at various crosslinker (BAAm) and chain transfer agent (isopropyl alcohol, IPA) concentrations. It was shown that only 5 % of the crosslinker used in the feed forms effective crosslinks in the final hydrogels. At BAAm contents as high as 3 mole %, the equilibrium swelling ratio of the gels in water is independent of the crosslinker content in the feed. This is due to the prevailing multiple crosslinking reactions during the gel formation process. At a fixed crosslinker content, the onset of gelation is shifted towards higher conversions and reaction times as the amount of IPA increases. Addition of IPA in the monomer mixture also increases the equilibrium swelling ratio of PAAm gels. It was shown that the gel crosslinking density increases on rising IPA concentration in the feed due to the increasing rate of intermolecular crosslinking reactions.

Introduction

In recent years, hydrogels with the ability to absorb many hundred times their dry weight of water have received considerable attention. Such materials are widely used as absorbents in medical, chemical, and agricultural applications. Hydrogels are prepared mainly by free-radical crosslinking copolymerization of acrylamide (AAm) monomer in the presence of a small amount of a hydrophilic crosslinker, e.g., N,N'-methylenebis(acrylamide) (BAAm). Since the monomers are solid at the polymerization temperature, the reactions are necessarily carried out in an aqueous solution of the monomers. Previous studies have shown that the properties of hydrogels strongly depend on their synthesis conditions, i.e., on the amount of the crosslinker used in the gel synthesis as well as on the initial degree of dilution of the monomers (1-4). Although many studies have been carried out to clarify the relationship between the synthesis conditions and properties of hydrogels, the results are still inadequate to describe quantitatively the hydrogel properties from the synthesis conditions. This is mainly due to the complicated mechanism of gel formation by free-radical crosslinking copolymerization (FCC) (5-8).

It was shown that acrylamide-based hydrogels exhibit inhomogeneous crosslink distribution (9-13). It seems that the gel structure consists of more densely crosslinked domains embedded in a less densely crosslinked matrix. According to Baselga et al. (14), the difference between the reactivities of monomeric vinyls is the reason for the inhomogeneous network structure. Recent studies, however, indicate the existence of intramolecular crosslinking reactions in the form of cyclization and multiple crosslinking, which are responsible for these inhomogeneities (8,15). Moreover, a strong steric excluded-volume effect preventing the pendant vinyl groups from reacting seems to be the another reason for the inhomogeneous network structure (8). Kinetic analysis of the gel formation process indicated that the average reactivity of pendant vinyl groups decreases as polymerization proceeds, or, as the amount of the crosslinker increases (8,16).

The aim of the present study was to investigate the effects of cyclization and the pendant reactivity on the properties of the final hydrogels. Recent measurements of the pendant vinyl group conversions during FCC indicated that more than 80 % of the crosslinker BAAm are consumed for cycle formation (8,15). This would mean that more than 80 % of BAAm form "wasted" links in the final hydrogel structure. In order to test this result, a series of polyacrylamide (PAAm) gels were prepared and their equilibrium degrees of swelling in water were measured. The results of measurements were compared with the values predicted by the Flory's swelling equation, after taking into account the extent of cycle formation. To investigate the role of the excluded-volume effect in the hydrogel structure, a chain transfer agent, namely isopropyl alcohol (IPA) was included in the polymerization system. This technique controls the size of the growing macromolecules during FCC and, is known to be used to produce soluble microgels. An increase in the amount of IPA in the feed would decrease the degree of polymerization of the primary molecules, i.e., the size of the microgels. As a result, steric effects would decrease, that is, the reactivity of pendant vinyl groups would increase on rising IPA concentration, leading to the formation of more effective crosslinkages in the final network structure.

Experimental

PAAm gels

PAAm gels were prepared by free-radical crosslinking copolymerization of acrylamide (AAm) with a small amount of N,N'-methylenebis(acrylamide) (BAAm) in aqueous solution. Commercially available AAm and BAAm monomers were purified by usual methods. Ammonium persulfate (APS) and N,N,N',N'-tetramethylethylenediamine (TEMED) were respectively the initiator and the accelerator. Isopropyl alcohol (IPA, Merck) was used as the chain transfer agent. The reactions were carried out at room temperature (21±2°C). The gels were prepared according to the following scheme: 5 g AAm, 40 mg APS and varying amounts of BAAm and IPA were dissolved in double distilled water to give a total volume of 100 mL. After addition of 0.24 mL of TEMED, the solution was transferred to small tubes of 5.8 mm in diameter. After 1 day, the gels were cut into specimens of approximately 10 mm in length and immersed in a large excess of distilled water to remove the unreacted species.

The swelling experiments were carried out at 21±2°C. In order to reach the equilibrium degree of swelling, the gels were immersed in water at least for one week. The swelling ratio was determined by weighing the specimens in the swollen and dry states. In order to dry the gel samples, the swollen gels were successively washed with solutions whose composition were changed gradually from water to pure acetone. This solvent exchange process facilitates final drying of the gel samples. The collapsed samples after the treatment with acetone as a final solvent were dried in vacuum at 60°C to constant weight. The weight swelling ratio, q_w, was calculated as:

$$q_w = \frac{m_\infty}{m_o} \qquad (1)$$

where m_∞ and m_o are the masses of the gel in the swollen state and the dry state, respectively. Each swelling ratio reported in this paper is an average of at least two separate measurements; standard deviations of the measured swelling ratios were less 5% of the mean. Assuming additivity of the volumes of water and PAAm, the volume fraction of the network after preparation, ν_2^0, was calculated as:

$$\nu_2^0 = \frac{m_o / \rho}{(m_o / \rho) + (m - m_o) / d_1} \tag{2}$$

where m is the mass of the gel sample after preparation, ρ and d_1 are the densities of PAAm and water, respectively.

Kinetics of the pre-gelation period

With TEMED as an accelerator, gelation occurred in the absence of IPA within a few minutes. Therefore, in order to focus on the pre-gel period of the reactions, the redox system APS / TEMED was replaced with potassium peroxodisulfate ($K_2S_2O_8$) / sodium thiosulfate ($Na_2S_2O_3$) system. The copolymerization reactions were carried out in water at 40±0.1°C and in the presence of $NaHCO_3$ buffer. The conversion of monomers up to the onset of macrogelation and the gel points were followed by dilatometry. The polymerization technique used was described in detail elsewhere (17). Concentrations used were 0.25 M for the monomers, 1 mole % for BAAm, and 1×10^{-3} M for $K_2S_2O_8$, $Na_2S_2O_3$ and $NaHCO_3$. These concentrations were taken to be constant throughout the kinetic studies, and only the amount of IPA was varied from 0 to 1.5 mol/mol AAm. To measure the gel points, a special dilatometer containing a steel sphere of 4.8 mm diameter was used. The midpoint between the last time at which the sphere moves magnetically and that at which it stops moving is taken as the gel point.

Results and Discussion

In Figure 1, the equilibrium swelling ratios of PAAm gels in water, q_w, are plotted as a function of the crosslinker (BAAm) concentration. The gels were prepared at 5 % monomer concentration and in the absence of IPA. Experimental data points are shown as symbols. As expected, at low crosslinker contents, q_w decreases as the crosslinker content in the monomer mixture increases. However, above 3 mole % BAAm, q_w becomes independent of the crosslinker content in the initial monomer mixture. This finding is in accord with our previous observations with PAAm gels prepared at 1.8 % monomer concentration (8). According to the Flory's swelling equation, swelling ratio of a tetrafunctional affine network is related to its crosslink density through the equation (18)

$$\ln(1 - \nu_2) + \nu_2 + \chi \nu_2^2 + \bar{N}^{-1}\left(1 - 2\bar{N} / \bar{X}_n^{\bullet}\right)\left(\nu_2^{1/3} \nu_2^{0\,2/3} - \nu_2 / 2\right) = 0 \tag{3}$$

where ν_2 is the volume fraction of polymer in the equilibrium swollen gel, i.e.,

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

χ is the polymer-solvent interaction parameter, $\overline{N}$ is the average number of segments in a network chain, and $\overline{X}_n^{\bullet}$ is the number-average degree of polymerization of the primary chains. The values $\overline{N}$ of PAAm networks can be calculated from the crosslinking ratio in the feed X (mol BAAm/mol AAm) as:

$$\overline{N} = \left[2X\left(1 - k_{cyc}\right)\right]^{-1} \tag{5}$$

where k_{cyc} is the fraction of BAAm engaged in cycles. For the following calculations, the values used were ρ = 1.35 g/mL, d_1= 1.00 g/mL, and χ = 0.48 (4). Neglecting cyclization reactions, i.e., k_{cyc} = 0, and assuming $\overline{X}_n^{\bullet} >> \overline{N}$, solution of eqs (3) - (5) for q_w gives the dotted curve in Figure 1. It is seen that the gel swells much more than predicted by the theory, if cyclization is neglected. As a next step, a least square analysis of the swelling equations (3) - (5) with the experimental swelling ratio data q_w was carried out. Taking k_{cyc} as a fit parameter, the sum of the squared residuals between the calculated and experimental q_w values was minimized. The solid curve in Figure 1, which is the best - fit to the experimental data, yielded k_{cyc} = 0.95. This value of the cyclization parameter is comparable with the value 0.8 - 1 found by an analytical titration method using pre-gel polymers (8). Thus, only 5 % of BAAm used in the feed forms effective crosslinks in the final hydrogels. Another point shown in Figure 1 is that, at BAAm contents as high as 3 mole %, experimental q_w values are independent of the crosslinker content in the feed and, they are higher than the predicted values. Since this deviation is real and it is outside of estimated experimental uncertainty, the result can be explained with prevailing multiple crosslinking reactions during the gel formation process. At high BAAm contents, since the concentration of pendant vinyl groups in a molecule increases rapidly after the formation of each crosslink (Figure 2), a large number of multiple crosslink is expected to occur after each single crosslink. This leads to the formation of highly crosslinked regions in the final gel acting as single junction points. Thus, increase in the BAAm content in the feed only increases the compactness of these junctions whereas the distance $\overline{N}$ between them remains constant.

Another factor determining the hydrogel structure is the reactivity of pendant vinyl groups for intermolecular crosslinking reactions. This reactivity strongly depends on the size and compactness of the molecules, to which pendant vinyl groups belong (7). Here, we used isopropyl alcohol (IPA) as a chain transfer agent to alter the size of the primary molecules. In Figure 3A, fractional monomer conversion (x) versus time plot is given for 3.5 % initial monomer concentration and for various IPA/AAm mole ratio. The concentration of BAAm in the feed was fixed at 1 mole % BAAm. No change in the polymerization rate was observed in the presence of IPA up to 1.5 mol IPA/mol AAm, indicating that IPA does not alter the kinetics of the copolymerization. In Figure 3B, the delay in the gel point in terms of the monomer conversion Δx_c and the reaction time Δt_c, due to the addition of IPA, is shown as a function of the mole ratio of IPA to the monomers. The onset of gelation is shifted towards higher conversions and reaction times as the amount of IPA in the feed increases. This is due to the decreasing primary chain length $\overline{X}_n^{\bullet}$ on rising IPA concentration. According to the Mayo equation, the variation of $\overline{X}_n^{\bullet}$ with the IPA concentration in the feed is given as follows (19):

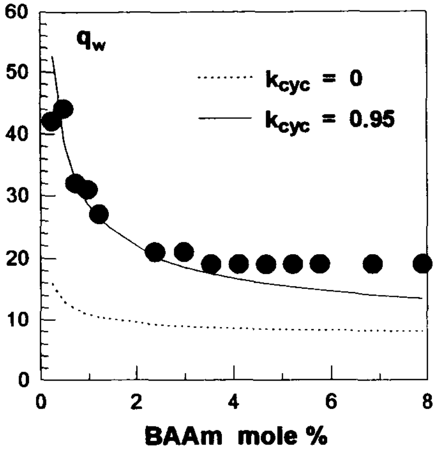

Fig. 1. Variation of q_w of PAAm gels with the BAAm concentration in the feed. Dotted and solid curves were calculated using eqs (3) - (5) for k_{cyc} = 0 and 0.95, respectively.

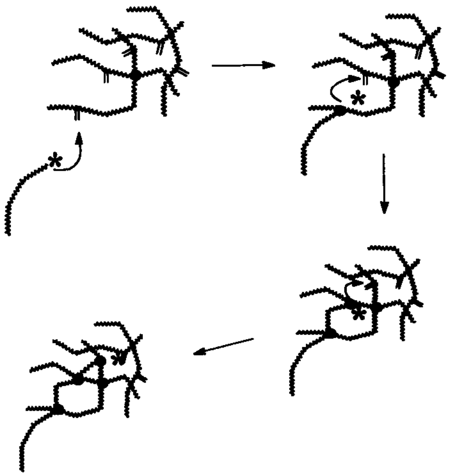

Fig. 2. Schematic representation of multiple crosslinking reactions leading to the formation of highly crosslinked regions in the final hydrogels. • = crosslink, ╨ = pendant vinyl. * = radical center.

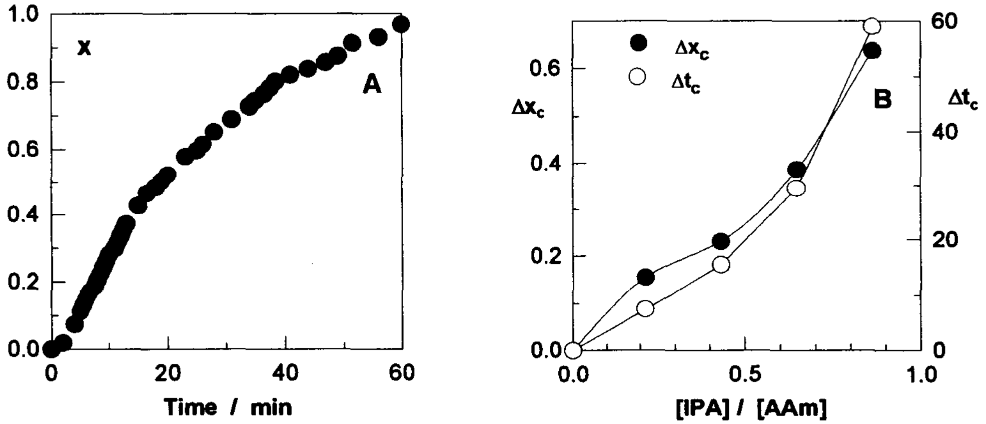

Fig. 3. (A): Monomer conversion x versus time history in AAm/BAAm copolymerization in the presence of 0, 0.25, 0.5, 0.75, 1.2, and 1.5 mol IPA / mol AAm. Standard deviation between the experimental data points obtained at different IPA concentrations was less than 0.05. (B): Delay in the gel point in terms of the monomer conversion Δx_c and the reaction time Δt_c shown as a function of the mole ratio of IPA to the monomers. Gel point conversion and the gelation time in the absence of IPA were 0.29 and 7.5 min, respectively.

$$\frac{1}{\overline{X}_n^{\bullet}} = \frac{1}{\overline{X}_{n,0}^{\bullet}} - C_s \frac{[IPA]}{[AAm]} \tag{6}$$

where $\overline{X}_{n,0}^{\bullet}$ is the number-average degree of polymerization of the primary chains in the absence of IPA, C_s is the chain transfer constant of IPA (19×10^{-4} (19)), [IPA] and [AAm] represent the molar concentrations of IPA and monomers, respectively. Increase in the IPA concentration decreases the chain length of the primary chains and therefore, more crosslinkages are needed for the onset of macrogelation.

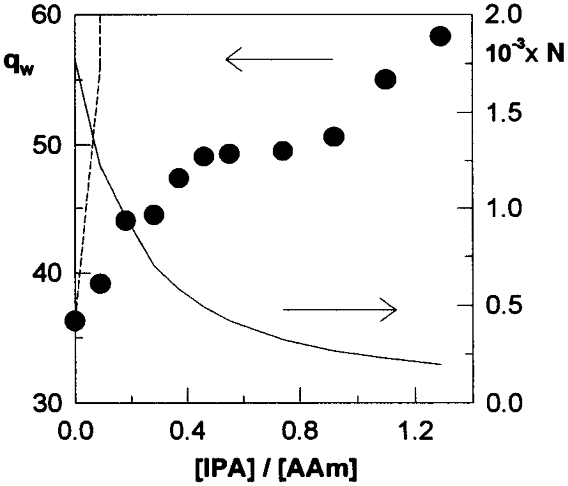

Fig. 4. Variation of the swelling ratio q_w (●) and the average number of segments in a network chain $\overline{N}$ (——) as a function of the IPA / AAm mole ratio. The dashed curve represents calculated q_w values using eqs (3) - (6) for a fixed $\overline{N}$. Synthesis conditions of the gels: Monomer concentration = 5 %, BAAm = 1 mole %.

In Figure 4, the equilibrium swelling ratios of PAAm gels in water, q_w, are shown as a function of the IPA concentration in the feed. The gels were prepared at a fixed crosslinker ratio (1 mole % BAAm) and at 5 % monomer concentration. The extent of swelling of PAAm gels increases with increasing concentration of IPA in the monomer mixture. This is due to the increasing number of chain ends in the final hydrogels on rising IPA/AAm mole ratio. However, assuming $\overline{N}$ is independent of the IPA concentration, solution of eqs (3) - (5) in combination with eq (6) for q_w gives the dashed curve in Figure 4. It can be seen that the gel actually swells in water much less than predicted for a fixed crosslinking density. Eqs (3) - (6) predict actual swelling ratios if the number of segments between successive junctions $\overline{N}$ is a function of the IPA content. The calculated $\overline{N}$ values are shown in Figure 4 as the solid curve as a function of the

IPA/AAm mole ratio. $\overline{N}$ strongly depends on the amount of IPA in the mixture and, it decreases as the IPA concentration increases. Thus, although the swelling ratio of the gels increases on rising IPA concentration, their crosslinking density also increases. This is due to a looser microgel structure with decreasing size of primary molecules, which makes the pendant vinyls more accessible for the macroradicals of other particles and facilitates the intermolecular crosslinking reactions.

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