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Structure and swelling of poly(acrylic acid) hydrogels: effect of pH, ionic strength, and dilution on the crosslinked polymer structure

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Abstract

The network formation of crosslinked polymer hydrogels made via a free radical polymerization mechanism is significantly influenced by the polymerization conditions. In particular, the crosslinked structure of ionic networks like poly(acrylic acid) copolymers is affected by the monomer concentration, the pH, and ionic strength during the polymerization. In this work experimental data as well as theoretical analysis are used to investigate how these factors control the degree of crosslinking and primary cyclization during the network formation of multifunctional monomers. It was found that the amount of water present during the polymerization increases primary cyclization rates, and this change affects the subsequent swelling behavior of the acrylic acid hydrogel. The effects of ionic strength and pH on the network structure are interrelated. An increase in the pH decreases the degree of primary cyclization while an increase in the ionic strength increases cyclization. To investigate further the effect of pH, a cationic polymer was formed that contained a monovinyl amine monomer and a novel diamine crosslinking agent synthesized in our laboratory. The combined effect of the ionizing backbone chain and crosslinking agent cause the degree of primary cyclization in this material to be extremely sensitive to the pH during polymerization. This result confirms the significant role of pH on the network formation in ionic materials.

Keywords: Poly(acrylic acid); Network formation; Primary cyclization

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1. Introduction

Loosely crosslinked polymeric materials that swell in the presence of water or other solvents are often used to make gel-like absorbent materials. These gels are typically made via a free radical polymerization mechanism, where monomer units are connected into long chains through their double bonds. The crosslinking agent, a monomer with two or more double bonds, provides the polymer network structure by connecting the long, linear chains in these polymerizations. Hydrogel networks formed from poly(acrylic acid) (PAA) have the ability to absorb many times their weight in water and are the basis of a class of materials called super absorbents. These polymers are used in many applications including diapers and personal hygiene products, ion exchange resins, membranes for hemodialysis and ultrafiltration and controlled release devices [1–4]. In developing super absorbent polymeric materials, it is desirable to understand how polymerization reaction conditions affect the final polymer structure and the resulting material properties. The degree of crosslinking in the polymer network structure is critical as it dictates the mechanical strength, swelling ratio, and many other properties of the polymer gel by influencing the molecular weight between crosslinks ($\bar{M}_c$).

Obviously, the degree of crosslinking of a polymer is controlled by the fraction of crosslinking agent present in the copolymerization and the double bond conversion. Smaller amounts of crosslinking agent and diminished final conversion both lead to a less densely crosslinked material. Additionally and importantly, not all of the crosslinking agent double bonds react to form crosslinks. Potential crosslinking is also lost due to intramolecular cyclization reactions, where both ends of the crosslinking agent react into the same growing polymer chain, forming a loop structure, as shown in Fig. 1. Although the equivalent amount of crosslinking agent may be present and

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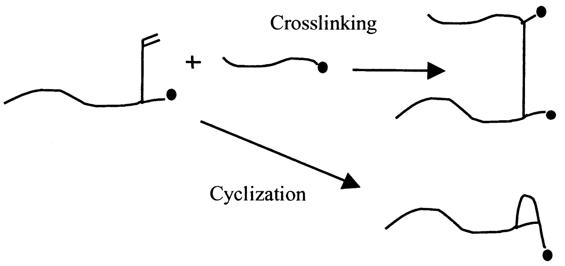

Fig. 1. Crosslinking versus cyclization reactions.

incorporated into the network, when cyclization is occurring, the polymer produced is less crosslinked and does not exhibit the expected mechanical properties, equilibrium swelling, and diffusional properties.

The ability of PAA to swell extensively is facilitated by the carboxylic acid groups on the polymer chain, which strongly associate with water molecules. These groups are readily ionizable and sensitive to the effects of pH and ionic strength. Thus, the equilibrium swelling of PAA copolymers is affected by the pH and ionic strength of the solution in which they are swelling [5–7]. Further, the pH and ionic strength are known to affect the polymerization kinetics of these systems [8–10]. How changes in pH and ionic strength during the polymerization affect the network structure, i.e. the relative cyclization and crosslinking rates, and the resulting equilibrium swelling of the resulting polymer has not been thoroughly addressed to date. It is known that the pH and ionic strength alter the chain conformation of the growing polymer chains; however, the question remains whether this change impacts the structure of the network that is created, specifically the degree of crosslinking and intramolecular cyclization.

To answer these questions and address how processing conditions influence the degree of primary cyclization in ionic networks, experimental studies have been conducted to investigate the network structure of loosely crosslinked PAA hydrogels formed by copolymerization with poly(ethyleneglycol 600) diacrylate (PEG(600)DA). PEG(600)DA was chosen as the crosslinking molecule because it was miscible with acrylic acid (AA) over a wide range of dilutions. Experiments were designed to examine the effects of monomer concentration, pH, and ionic strength during polymerization on the crosslinking density and the subsequent equilibrium swelling. Copolymers of 1 mol% PEG(600)DA and 99 mol% AA were made at various pH and ionic strengths and swollen in buffers at several pH. In conjunction with experimental data, a network formation model was utilized to analyze how dilution during polymerizations influences the structural evolution through primary cyclization. Besides the AA copolymers, an additional copolymer was designed to investigate further the effect of pH during polymerization on the crosslinked structure. To form a polymer, where both the crosslinking agent and backbone chain are ionizable, a novel ionizable crosslinking agent, *N*,*N*′-dimethyl-*N*,*N*′-diethyl methacrylate-1,6-hexanediamine (NDMH), was copolymerized with an ionizable monovinyl monomer, dimethyl aminoethyl methacrylate (DMAEMA). These experiments enabled more thorough evaluation of how changing the processing pH alters polymer structure.

2. Experimental methods

The comonomer mixture was prepared by mixing AA (Aldrich, Milwaukee, WI) and poly(ethylene glycol 600) diacrylate (PEG600DA) (Sartomer, West Chester, PA) in the mole ratio of 1% PEG600DA to 99% AA. Varying amounts of water were added (0, 25, 50, 75, and 85% by volume). Strong base (NaOH) (Fisher, Fair Lawn, NJ) and neutral salts (NaCl) (Fisher, Fair Lawn, NJ) were added to alter the pH and ionic strength of the polymerization environment. A photoinitiator, of 2,2-dimethoxy-2-phenylacetophenone (DMPA) (Ciba Geigy, Hawthorne, NY), was added at a concentration of 0.1 wt% in all experiments, based on total monomer weight.

pH measurements were taken immediately prior to polymerization using a standard pH probe (Model SA 230, Orion Research, Cambridge, MA). Thin polymer films were prepared by reacting monomer solutions between two glass plates separated by glass spacers of a thickness of approximately 1 mm (glass slide, VWR scientific). Glass interfaces were coated with Rain-X (Unelko Corp, Scottsdale, AZ) to prevent the polymer from adhering to the glass. The edges of the slides were sealed with inert silicon grease (high vacuum grease, Dow Corning) to prevent leakage and evaporation. The polymerization was initiated by $\sim 5\ \mathrm{mW/cm^2}$ of 365 UV light from a longwave UV light (Black-Ray model B, UVP), and polymerization time was 30–60 min. Complete conversion was verified using Fourier transform near infrared (near-IR) spectroscopy (Magna-IR 750, Nicolet, Madison, WI) [11].

Samples were swollen with deionized water and rinsed with deionized water to remove added NaCl or NaOH, and then dried prior to conducting the swelling experiments. The swelling behavior of the polymer films was examined by immersing sections of polymer in either water or 0.1 M buffer of pH 4 (acetic acid), 6 (phosphate), 7 (phosphate), or 9 (Tris). The water and buffers of pH 4, 6, and 9 contained additional salt, NaCl, to maintain a constant ionic strength among all of the solutions at $I = 0.225$ M. Gravimetric measurements were performed until the change in the swollen polymer weight was less then 0.001 g over a 24 h period, at which point the polymers were assumed to be at equilibrium. Two samples were swollen at each condition, and the average of the two results is presented. The two exceptions to this were swelling samples in pH 3 in Fig. 5 and samples at 0.5 M pH 7 in Fig. 8. Error bars are shown on the graphs, and in most cases the error is smaller than the size of the symbol used in the plot. Assuming ideal mixing, the swelling ratio (Q) was determined from weight measurements using Eq. (1), where w_s and w_d are the swollen and dry weights of the polymer, and ρ_p and ρ_w are the densities of the polymer and water, respectively.

$$Q = 1 + \left(\frac{w_s}{w_d} - 1\right)\frac{\rho_p}{\rho_w} \tag{1}$$

To study further the effect of ionization during polymerization on the network structure, 5 mol% ionizable crosslinking agent, NDMH, was polymerized with 95 mol% ionizable monovinyl monomer, DMAEMA. DMAEMA was purchased from Aldrich, (Milwaukee, WI) and used as received. NDMH was synthesized in our laboratory to create a crosslinking agent containing two amine groups attached to a hexanediol diacrylate-like core.

NDMH was synthesized by the following procedure. Ten grams of *N*,*N*′-dimethyl-1,6-hexanediamine (Aldrich, Milwaukee, WI) and 6 g of NaOH were dissolved in 50 ml of ethanol (Aldrich, Milwaukee, WI) and added into a three-necked flask placed in an ice-water bath. Under magnetic stirring, 10 ml of 2-bromoethanol (Aldrich, Milwaukee, WI) were added dropwise within 1 h. After all the 2-bromoethanol was added, the temperature was elevated to ambient conditions and reaction proceeded for 24 h at these conditions. Then, the reaction mixture was evaporated under vacuum to remove unreacted reactants and solvent. Thirty milliliters of water was then added to the clear liquid obtained and extracted with 20 ml chloroform (Fisher, Fair Lawn, NJ) three times. The organic phase was washed with water three times and dried with sodium sulfite overnight. After drying, it was evaporated under vacuum again to remove the solvent, and a crude product was obtained. Five grams of this product, 15 ml triethylamine (Aldrich, Milwaukee, WI), and 0.001 g hydroquinone (Aldrich, Milwaukee, WI) were dissolved in 50 ml chloroform, and added to a three-necked flask with a nitrogen purge in an ice bath. Five ml of methacryloyl chloride (Aldrich, Milwaukee, WI) were added dropwise within two hours. The reaction mixture was elevated to ambient conditions and stirred for 12 h while under a nitrogen purge. Then, 30 ml of water were added and the reaction was stirred for two more hours. Thirty milliliters of chloroform were added to the reaction mixture and the organic phase was washed three times with water and dried with sodium sulfite (Aldrich, Milwaukee, WI) overnight. After drying, it was evaporated under vacuum to remove the remaining solvent. The slightly yellow, crude product was further purified by column chromatography (silica gel (70–230 mesh) eluent: ethyl acetate/hexane, 50/50(v/v)). Fig. 2 depicts the synthesis process, and the final product was characterized with both FTIR and ^{1}H NMR.

Copolymers of 5 mol% NDMH/95 mol% DMAEMA were mixed with 50 vol% 0.1 M HCl (Aldrich, Milwaukee, WI) or NaOH (Fisher, Fair Lawn, NJ) to control the degree of ionization. Samples were photopolymerized with 0.1 wt% DMPA at 4 mW/cm^2 of 365 UV light from a longwave UV light (Black-Ray model B, UVP) between glass slides as described for the acrylic acid polymerization. The swelling behavior of the polymer films was examined by immersing sections of polymer washed with deionized water in either 0.1 or 0.5 M phosphate buffer of pH 7, or deionized water. Samples were weighed until the change in the swollen polymer weight was less than 0.001 g over a 24 h period, at which point the polymers were assumed to be at equilibrium.

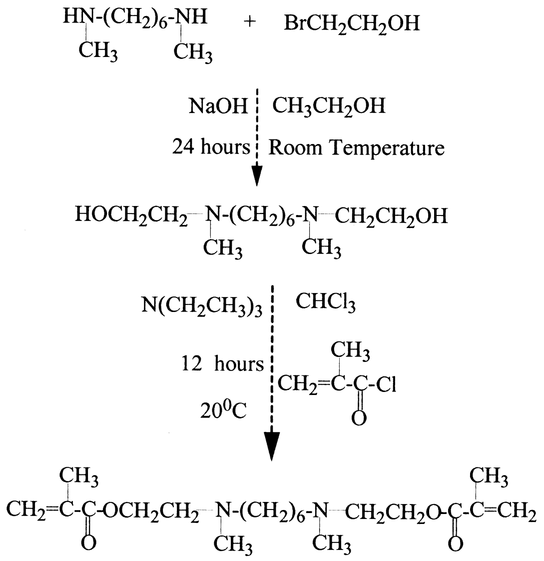

Fig. 2. Synthesis of *N*,*N*′-dimethyl-*N*,*N*′-diethyl methacrylate-1,6-hexanediamine (NDMH).

3. Computational methods

To interpret the experimental results and relate them to fundamental changes in the polymer structure, a model was developed and used that describes the network structural formation of multifunctional monomer polymerizations like the AA/PEG(600)DA copolymerization This first principle model has been described in detail in the previous work [12, 13]. The model's strength is that it does not assume that monomeric and pendant double bonds, i.e. double bonds attached to the polymer backbone, react equivalently during the propagation step like many other statistical and kinetic models. The pendant double bond is the remaining double bond when a multifunctional monomer like PEG(600)DA is added to the growing polymer chain. Because this pendant double bond is now attached to the polymer chain backbone, it will have an enhanced reactivity with the propagating radical in close proximity. Thus, the pendant double bonds are consumed by two mechanisms: the reaction with radicals in the bulk solution (bulk radicals) to form crosslinks and reaction with the radical on the same propagating chain (local radical) in cyclization reactions. The reaction of monomeric double bonds, the creation of pendant double bonds, and their subsequent reactions by either crosslinking or cyclization are each tracked over time.

The varying reactivity of pendant double bonds is incorporated by using expressions for the radical concentration that represent the apparent concentration of the bulk and local radicals seen by each pendant double bond as a function of the time since it was formed.

Several parameters are required to specify the AA/PEG600DA system in the model including the propagation kinetic parameter, k_p, termination kinetic parameter, k_t, cyclization kinetic parameter, k_{cyc}, crosslinking kinetic parameter, k_{xl}, crosslinking agent size, r_o, and characteristic ratio for calculating the end-to-end distance, C_n. All kinetic parameters are assumed to be constant throughout the reaction. The values of the kinetic parameters for propagation, k_p, and termination, k_t, were taken from experimental data for AA as 1120 and 1.4×10^{-4} l/mol s, respectively, [9]. The rate constants for cyclization, k_{cyc}, and crosslinking, k_{xl}, are assumed to be equivalent to k_p, as the varying pendant reactivity is included by accounting correctly for the different radical concentrations. As both the AA and PEG(600)DA are acrylates, their chemical reactivity was assumed to be equivalent. The length of the crosslinking agent, r_o, input as 6.4 Å for PEG(600)DA. This value is calculated from the molecular weight of the monomer, assuming a spherical molecule with the double bonds on the radius. In general, r_o depends on the size of the crosslinking agent and how relaxed or coiled it is during the polymerization. The characteristic ratio, C_n, is a measure of how extended the backbone polymer chains are in solution and varies with solvent quality and the degree of solvation of the polymer chains. Because the value of C_n is specific to the polymer composition and solvent quality, it is extremely difficult to determine experimentally in crosslinked polymers. For these reasons the value of C_n was fit to the experimental data in Fig. 3 and found to be 3.4. The parameters r_o and C_n are both size measures for different segments of the growing polymer and are affected by molecular size, stiffness, and solvent characteristics. The difference between r_o and C_n is that the former is a measurement of the distance between the pendant double bond and the polymer backbone, where it is attached. The latter is a measure of the stiffness or extension of the polymer backbone relative to that of a freely jointed chain. Because in a loosely crosslinked copolymer the polymer backbone consists mainly of the comonomer, it may have different properties than the crosslinking agent which hangs off of the backbone with a pendant double bond. The effect of r_o and C_n on primary cyclization can be calculated analytically through the modeling work. The fraction of pendants born at a particular birth time that cycle, ψ, is calculated by Eq. (2) [12,14]

$$\psi = 1 - \exp\left(\frac{-3}{8\pi N_A [\mathrm{DB}] r_o C_n l^2}\right) \tag{2}$$

Here, N_A is Avogadro's number, [DB] is the total double bond concentration, r_o is the crosslinking agent size, C_n is the characteristic ratio [15], and l is the length of a carbon–carbon bond. Clearly, r_o and C_n both have a significant impact on the amount of primary cyclization and the subsequent network structure and polymer properties.

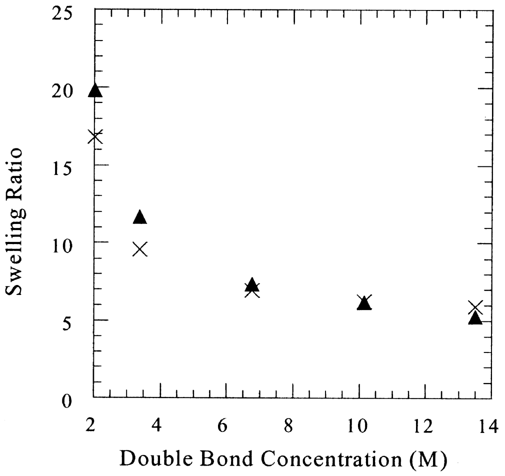

Fig. 3. Swelling ratio in pH 4 buffer of unneutralized 1/99 PEG600DA/AA copolymers made with varying concentration of deionized water; experimental, (▲), and modeling, (×).

4. Results and discussion

The results of the swelling experiments demonstrate that the monomer concentration during the polymerization significantly affects the subsequent equilibrium swelling. In Fig. 3, the equilibrium swelling ratio (swollen volume/dry volume) of 1/99 AA/PEG(600)DA copolymers swollen in pH 4 buffer is plotted versus the double bond concentration for samples with varying amounts of deionized water present during polymerization. The polymers were not neutralized during polymerization. These results show that by increasing the amount of water present during polymerization, a hydrogel with different equilibrium swelling properties is formed. A dramatic increase in the amount of swelling is observed with the increase in the amount of water present during the polymerization, though the polymers themselves all have the same chemical composition and the same relative amount of crosslinking agent. The equilibrium swelling ratio increased from 5.3 to 11.7 when the dilution was increased from 0 to 75% water. This relationship between solvent concentration and swelling behavior has been observed previously in the literature [13,16–19]. Clearly, the processing conditions leave an imprint on the polymer network. Using the kinetic model, we will show the change in swelling is a direct result of the different network structure formed because of primary cyclization.

The kinetic model was used to predict the swelling ratio as a function of the monomer concentration present during polymerization (Fig. 3). Using the model predictions of the molecular weight between crosslinks, $\bar{M}_c$, and the number average molecular weight, M_n, for the 1% PEG(600)MDA/

99% AA system, the equilibrium swelling ratio (volume swollen/volume dry) of the polymers was predicted by the Flory–Rehner equation assuming complete double bond conversion [20]. A Flory interaction parameter of 0.495 was used in all simulations [21], and the value of C_n was determined by least squares analysis and found to be 3.4. The Flory–Rehner equation neglects ionic effects on swelling, but yields a reasonably good fit of the data. Like the experiments, the model shows a large increase in swelling ratio with monomer concentration. The important contribution of the model is that it both explains and predicts this trend. It reveals that the extent of primary cyclization is increasing with the concentration of water present during polymerization. Thus, the polymer network formed at the different conditions is not the same even though it has the identical chemical composition and conversion. The network created with less water during polymerization is more crosslinked and therefore swells less. At low monomer concentration more primary cyclization occurs, and a less crosslinked network is formed. The experiments found that above 95 vol% water, gelation no longer occurred due to extensive cyclization and insufficient crosslinking.

The model provides detailed information about how much the primary cyclization increases with decreasing monomer concentration during polymerization. Fig. 4 shows the predicted integral fraction of pendants that undergo cyclization reactions that corresponds to the swelling data presented in Fig. 3. Assuming 100% conversion, which is typically obtained in these polymerizations, the differences in swelling from 0 to 85% dilution are caused by a 150% increase in cyclization. The relative increase in cyclization due to increased dilution is an important trend, and the model has been shown in previous work to be accurate at predicting the effect of solvent concentration [13]. The results indicate that by simply changing the degree of dilution during polymerization, especially beyond 50% water, the extent of cyclization and the network structure created are both radically different. Further, it can be seen in the theory behind the model, shown in Eq. (2), that decreasing the double bond concentration ([DB]) increases cyclization.

The reason behind this effect is also explained conceptually. In the high monomer concentration case, when little or no water is present during the polymerization, the propagating radical is surrounded by unreacted double bonds and reacts quickly away from the pendant double bond. There is only a limited opportunity to react in a primary cyclization reaction with a pendant double bond. Hence, less cyclization and more crosslinking will occur. When the water concentration is high during polymerization, propagating radicals are surrounded by many water molecules, the double bond concentration is lower, and the radical reacts away from the pendant double bond more slowly. Thus, the pendant double bond is still in close proximity, and there will be an increased time for the radical to react with the pendant double bond. More cyclization and less crosslinking will occur with higher concentrations of water or any other solvent present during the polymerization. The differences in swelling observed by changing the amount of water during polymerization are caused by increased primary cyclization that occurs with dilution.

It is well known that the pH of the solution in which an ionic polymer is swollen affects the extent of swelling. Polymers made with the same amount of crosslinking agent (1/99 PEG600DA/AA) and varying amounts of water (0, 25, 50, 75 or 85 vol%) were swollen in solutions at several pH (Fig. 5). The varying pH were made using buffers or salt solutions: pH 3 (water with NaCl, unbuffered), pH 4 (acetic acid buffer), pH 7 (NaOH and NaCl, unbuffered), and pH 9 (Tris buffer). All solutions had a constant ionic strength of 0.225 M maintained by adding the appropriate amount of NaCl. The ionic strength was maintained at 0.225 M

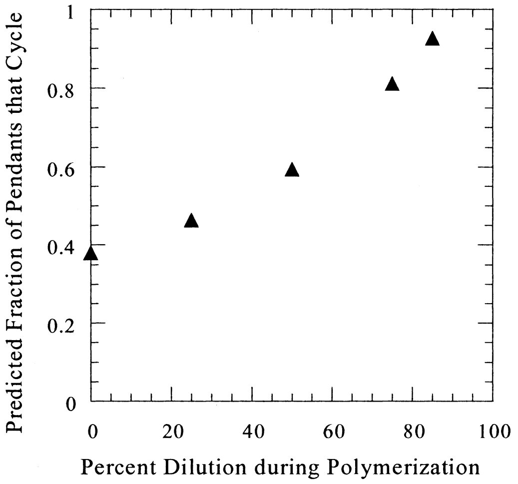

Fig. 4. Predicted fraction of pendants that cycle in unneutralized 1/99 PEG600DA/AA copolymers made with 0, 25, 50, 75 and 85% deionized water.

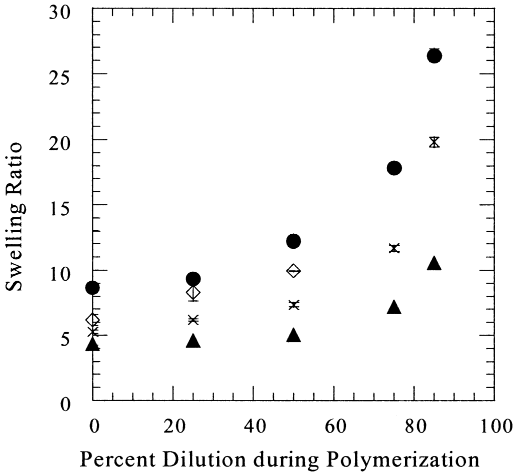

Fig. 5. Equilibrium swelling of unneutralized 1/99 PEG600DA/AA copolymers made with 0, 25, 50, 75 and 85% deionized water swollen in pH 3, (▲); pH 4, (×); pH 7, (◇) and pH 9, (●).

because it is the inherent ionic strength of 0.1 M pH 7 phosphate buffer. Because the increase in pH causes ionization of the carboxylic acid groups, the polymer chains extend more in the higher pH as the ionic groups repel each other. This result is observed in the higher swelling ratios seen as the pH increased from 3 to 9. Clearly, pH changes the polymer chain conformation.

The more interesting question is related to how the pH during polymerization affects the cyclization and subsequent equilibrium swelling behavior of poly(acrylic acid) gels. The polymer chain conformation during the formation of the network should also be altered by changes in the solution pH, and this change will in turn alter the network that is formed. Polymers were made at 85% dilution in aqueous solutions at pH 2.2, 3, 4, 5, 6, and 7. The pH of these mixtures was raised above 2.2 by adding NaOH. Equilibrium swelling after polymerization was measured in a buffer of pH 7, and these results are presented in Fig. 6. All samples have the same comonomer ratio. Although the samples have the same potential for crosslinking and near complete conversion, differences in equilibrium swelling imply that the crosslinking density is, in fact, not the same. The resulting trend is rather intriguing. The equilibrium swelling initially decreases with pH during polymerization and then increases. The trend is analogous to the manner the polymerization rate, k_p, and k_t are all affected by pH [8–10]. When the pH is increased by neutralization, OH^- ions are added which deprotonate the carboxylic acid groups on the acrylic acid. The chains then become highly ionic in nature. These charges repel each other, inhibiting chain propagation, and decreasing the polymerization rate as the pH is increased from 2 to around 4.5, as acrylic acid groups become more fully neutralized. The pK_a of acrylic acid groups in PEG copolymers is approximately 5 [7]. The repulsion force of the negative charges also causes the growing polymer chain to be more extended (increases the characteristic ratio, C_n) so the propagating radical is further away from pendant double bonds on its own chain. This effect on C_n decreases the primary cyclization rate occurring during the polymerization (see Eq. (2)). The decreased swelling ratio, observed when the pH during polymerization is changed from pH 2 to 4, is consistent with this explanation. In polymerizations, where the pH is above 5, the system is more fully neutralized and the addition of more NaOH serves only to increase the ionic strength of the solution further. The increasing concentration of ions shields the negatively charged carboxylic acid groups. An increase in the polymerization rate has been observed as the pH is further increased and propagating chains and monomers are not as strongly repelled. Similarly, it is proposed here that polymer chains collapse and coil more because of the increase in the ionic strength and ion shielding, causing the pendant double bonds to be in closer proximity to the propagating radical. The greater proximity of the pendant and the propagating radical will result in enhanced cyclization rates, reducing crosslinking, and subsequently increasing swelling as seen in Fig. 6. It is also possible at higher ionic strengths that the PEG600DA is salting out and reducing the expected crosslinking density.

The effect of ionic strength during polymerization was isolated for further study by polymerizing samples at different ionic strengths. Polymerizations were performed under the following conditions: unneutralized with no salt added, with $I = 0.5$ and 1.0 M. Results of the equilibrium swelling at pH 7 are shown in Fig. 7. There is not a significant difference between the no salt and $I = 0.5$ M samples. However, the 13% increase in swelling for the $I = 1.0$ M samples shows that increasing the ionic strength above a critical level during polymerization does reduce crosslinking in the resulting polymer network.

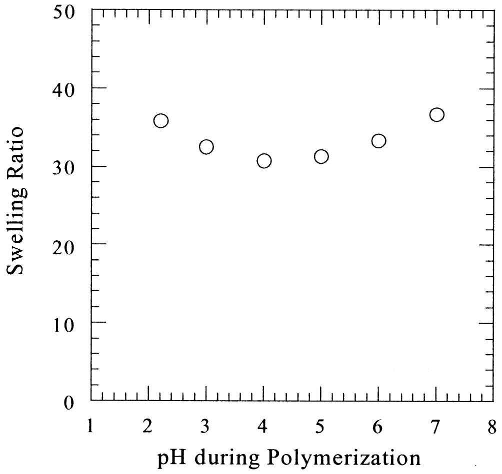

Fig. 6. Equilibrium swelling in pH 7 buffer of 1/99 PEG600DA/AA copolymers made with 85% water polymerized at pH 2.2, 3, 4, 5, 6, and 7.

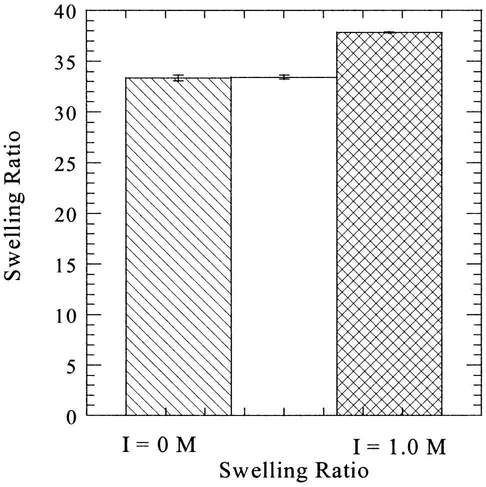

Fig. 7. Equilibrium swelling in pH 7 buffers of 1/99 PEG600DA/AA copolymer with 85% water polymerized with no additional ionic strength added, $I = 0.65$ and 2.09 M.

These results show pH during polymerization is an important influence on the polymer structure. To investigate further how ionization alters the network structure in crosslinked polymers, a novel polymer was designed using NDMH, an ionic crosslinking agent with two tertiary amine groups, which has been synthesized in our laboratories. These crosslinking molecules will alter their chain conformation with pH, allowing unique control over the network structure. When the pH is decreased, the amine groups become positively charged and repel each other, causing the crosslinking agent to be more fully extended. The polymer is expected to cycle much less as the pendant double bond is further away from the propagating radical. This novel crosslinking agent was copolymerized with 95 mol% of a monovinyl amine monomer, DMAEMA, to form a network, where both the crosslinking agent and polymer backbone are similarly ionizable. Experiments were conducted with either 50 vol% 0.1 M HCl or 0.1 M NaOH added during the polymerization to determine how the pH during polymerization affects the final equilibrium swelling ratio of the resulting polymer. The networks were washed after polymerization and swollen in pH 7 buffers and deionized water.

Here, dramatic differences in the swelling caused by changing the pH during polymerization are observed (Fig. 8). Polymers formed under acidic conditions swelled about one third less than the identical polymer made under basic conditions. The two polymer samples are made of the same chemical composition, simply polymerized at different pH. Again, the different material properties are due to changes in the amount of primary cyclization is affected by the polymer and crosslinking agent conformation during polymerization. Under acidic conditions, a more extended network forces the pendant double bond and propagating radical away from each other, causing less cyclization. The combined effect of the ionized amines on the backbone and on the crosslinking agent favors the extension of both the backbone and the crosslinking agent. In the model, this effect results from an increase in value of both r_o and C_n. This influence is much greater than when only the backbone chain conformation (C_n) was altered in the PAA/PEG600DMA system (Fig. 6). In fact, the polymer made in acidic conditions has a crosslink density 30% higher than the same polymer made in basic conditions. This calculation assumes large degrees of swelling ($Q > 10$) such that the Flory–Rehner relationship results in the swelling ratio being approximately proportional to the crosslink density to the 3/5 power [20]. Using the theoretical model, the change in the product of r_oC_n is required to alter the crosslinking density to the degree observed experimentally was calculated. For the basic conditions, r_o is estimated as 5.1 Å by assuming the crosslinking agent has a spherical shape in the collapsed neutral state. C_n is approximated as 6.9 (from methyl methacrylate [16]) for the neutral polymer backbone in the basic conditions. Thus, under the basic conditions the product r_oC_n is estimated as 35.3 Å. Using these values and the ratio of the crosslink densities, we calculated that r_oC_n is 53.6 Å under the acidic conditions, which is more than 50% greater than in the basic conditions. These results illustrate how the combined effect of changing the chain extension of both the crosslinking agent (r_o) and backbone (C_n) (causing a significant change the product r_oC_n) has a dramatic influence on the crosslinking and cyclization rate and subsequent swelling. Both the model predictions and experimental data (Fig. 8) show how in the basic conditions less crosslinking and more cyclization occur with the more coiled network. These experiments illustrate again how pH during polymerization affects the network structure created when using ionic monomers.

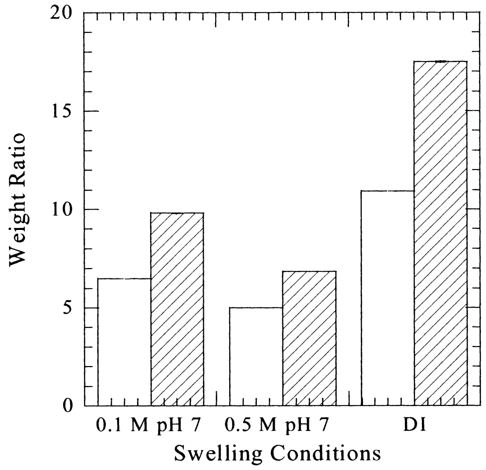

Fig. 8. Equilibrium mass swelling ratio in deionized water and pH 7 buffers of 95/5 monovinyl amine monomer/dimethyl aminoethyl methacrylate polymerized with either 50 vol% 0.1 M HCl (white bar) or 0.1 M NaOH (black bar).

5. Conclusions

In conclusion, processing conditions such as the monomer concentration during polymerization, ionic strength, and pH are important in controlling the crosslinked polymer network structure. Dilution during polymerization increases the extent of primary cyclization as seen by both experiments and modeling, and this change affects the subsequent swelling behavior. Hydrogels polymerized with more water have a higher degree of cyclization, which creates a less crosslinked mesh. Cyclization increases with dilution because the rate at which a propagating radical consumes double bonds is reduced (less monomer in solution), thus the propagating radical will spend more time in proximity of pendant double bonds attached to the polymer chain. The effects of ionic strength and pH are interrelated in ionic networks as was observed in the swelling results of PAA. The increase in pH with the addition of NaOH decreased the extent of cyclization because the negatively ionized acrylic acid chains were further extended during the polymerization, forcing the pendant double bond and propagating radical further away from each other. This effect was observed when the pH was raised from pH 2.2 to 6. Above this pH the carboxylic acid groups were fully ionized and the addition of NaOH only serves to increase the ionic strength of the solution. Increasing the ionic strength leads to ion shielding, diminishing the degree to which the negative carboxylic acid groups will repel each other. This change in conformation will bring the pendant double bond and propagating radical in closer proximity to each other and allow more primary cyclization. Finally, the cationic polymer made with the novel diamine crosslinking agent confirmed the significant role of pH on the network formation in ionic polymeric materials. With both the backbone and crosslinking agent ionizable, the swelling changed by a factor of three as the polymerization conditions were changed. This work shows how pH, ionic strength and dilution are all important conditions to consider when trying to control the network properties of ionic polymer materials.

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