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J.P. Baker, H.W. Blanch, and J.M. Prausnitz

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John P. Baker, Harvey W. Blanch and John M. Prausnitz

Department of Chemical Engineering
University of California

and

Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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Popcorn-Polymer Formation During Hydrogel Synthesis

*John P. Baker, Harvey W. Blanch, and John M. Prausnitz**

Department of Chemical Engineering
University of California
Berkeley, CA 94720-9989
and
Chemical Sciences Division
Lawrence Berkeley Laboratory
Berkeley, CA 94720

*To whom correspondence should be addressed.

Abstract

Popcorn polymers were found within the matrices of two different hydrogels: (**I**) a hydrogel formed in water by copolymerizing acrylamide with the cationic monomer [(methacrylamido)propyl]trimethylammonium chloride (MAPTAC) and the divinyl monomer N,N'-methylenebisacrylamide (BIS); and (**II**) a hydrogel formed in a 60/40 (v/v) mixture of ethylene glycol/water by copolymerizing 2-hydroxyethyl methacrylate (HEMA) with the basic monomer 2-dimethylaminoethyl methacrylate (DMA) and the divinyl monomer ethylene glycol dimethacrylate (EGDMA). For **I**, popcorn-polymer formation within the gel matrix could be suppressed during synthesis by raising the initiator concentration, adding a chain-transfer agent, or by changing the mode whereby radicals are generated in the reaction mixture. For **II**, popcorn-polymer formation could be suppressed by raising the initiator concentration, or by replacing the ethylene glycol/water diluent with butanol. A proposed mechanism for popcorn-polymer formation in hydrogels is consistent with experimental observations.

Introduction

Proliferous polymerization is an abnormal reaction encountered in free-radical polymerization systems. A proliferous polymer has a popcorn- or cauliflower-like shape, and a white, opaque appearance that readily distinguishes it from the usual clear polymer obtained from normal polymerization. Proliferous polymers are hard, but flexible, and do not swell in solvent. Because of their appearance, proliferous polymers are often called "popcorn polymers." Gehrke (1986) has described popcorn polymers in hydrogels as "white clumps that look like cumulus clouds floating in a gel sky."

Yamamoto and Tatsumi (1986) present a review of proliferous polymerization. Yamamoto and Tatsumi classify popcorn polymers into three groups based on their monomers : (1) Monovinyl systems. Popcorn polymers have formed in the synthesis of poly(acrylic acid) (Breitenbach and Kauffmann, 1974). (2) Dienyl systems. Laboratory

protocols are available for making popcorn polymers from butadiene (Miller et al., 1952) and also from isoprene (Miller and Leung, 1970). (3) Monovinyl/divinyl systems. Popcorn polymers have formed in the copolymerization of styrene with divinylbenzene (Staudinger and Huseman, 1935; Seo et al., 1971). Gehrke (1986) has formed popcorn polymers in the synthesis of acrylamide-based hydrogels.

Popcorn polymers are usually not desired in swellable systems because the popcorn reduces the amount of material available for swelling per gram of monomer used in the synthesis process.

We have inadvertently formed popcorn polymers while performing free-radical crosslinking polymerizations to make hydrogels. We have produced popcorn polymers by copolymerizing acrylamide with the cationic monomer [(methacrylamido)propyl]-trimethylammonium chloride (MAPTAC) and the divinyl monomer N,N'-methylenebisacrylamide (BIS), and by copolymerizing 2-hydroxyethyl methacrylate (HEMA) with the basic monomer 2-dimethylaminoethyl methacrylate (DMA) and the divinyl monomer ethylene glycol dimethacrylate (EGDMA). In this work, we present our experience with popcorn polymers in these two hydrogel systems. We also provide a plausible mechanism for popcorn-polymer formation in network systems; that mechanism is consistent with observed experimental behavior.

Hydrogel Synthesis

We define the nominal hydrogel composition by the relative amounts of monomers and diluent (solvent) in the reaction mixture. The following three variables are convenient for defining this composition (Chrambach and Rodbard, 1971; Gehrke, 1986): $\%T$, the total mass of monomer in the reaction mixture divided by the total volume of diluent in the reaction mixture multiplied by 100; $\%C$, the mole percent monomer in the reaction mixture (diluent-free basis); and $\%CM$, the mole percent comonomer in the reaction mixture (diluent-free basis).

Synthesis of Poly(acrylamide *co*-MAPTAC) Hydrogels Containing Popcorn Polymers. We produced popcorn polymers in positively-ionized poly(acrylamide *co*-MAPTAC) hydrogels during an investigation of the swelling properties of these hydrogels (Hooper et al., 1990). We prepared a series of hydrogels with systematic variation of *%T*, *%C* and *%MAPTAC*; the hydrogel prepared with 15 *%T*, 1 *%C* and 2 *%MAPTAC* (designated A1) contained many popcorn polymers about 2 mm in diameter, as shown in Figure 1.

Materials. Acrylamide, N,N'-methylenebisacrylamide (BIS) and ammonium persulfate (APS), all electrophoresis grade, were obtained from Kodak. Dichlorodimethylsilane was also purchased from Kodak. [(Methacrylamido)propyl]trimethylammonium chloride (MAPTAC) (50% aqueous solution) was obtained from Monomer-Polymer and Dajac Laboratories. Sodium metabisulfite (SMB) was obtained from Sigma. Toluene (ACS grade) was purchased from Fisher Scientific. 3,3',3"-Nitrilotris(propionamide) (NTP) was purchased from American Tokyo Kasei. All reagents were used as received. Water was distilled, then filtered and deionized by a Barnstead Nanopure II system.

Procedure. To illustrate the procedure to prepare the poly(acrylamide *co*-MAPTAC) hydrogels, we give details for the preparation of hydrogel A1. Added to 39.6 mL water were 6.904 g of acrylamide, 0.154 g of BIS and 0.88 mL MAPTAC solution. The solution was stirred until well-mixed, then degassed under a 680-mm Hg vacuum for 90 minutes. Two initiator solutions containing, respectively, 30.0 mg of APS and 30.0 mg of SMB in 15 mL of water (for each solution) were also degassed for 90 minutes. The three solutions were transferred to a nitrogen-filled glovebox. Inside the glovebox, 0.88 mL MAPTAC solution, along with 5.0 mL of each initiator solution, was added to the monomer solution. The resulting solution was stirred until completely mixed and then poured into 10 x 75 mm silanized test tubes; silanization was accomplished by immersing the glass test tubes in a solution of dichlorodimethylsilane in toluene (3% v/v) for 1 minute. The test tubes were sealed with laboratory film; they remained in the nitrogen atmosphere at

25°C for 24 hours. The hydrogels were removed from the test tubes, sliced into disks (approximately 3 mm in width), and placed in an excess volume of water, refreshed periodically, to extract the sol fraction and initiator residues. The disks were swollen to equilibrium in water.

Synthesis of Poly(HEMA *co*-DMA) Hydrogels Containing Popcorn Polymers. Popcorn polymers in HEMA-based hydrogels were produced during attempts to prepare homogeneous, basic poly(HEMA *co*-DMA) hydrogels in the presence of widely-varying amounts of diluent. Clear, homogeneous HEMA-based hydrogels may not be prepared with the diluent concentration varying over a wide range if the diluent is water. When the water content exceeds the critical diluent concentration of approximately 0.50 volume fraction, heterogeneous, opaque HEMA-based hydrogels are formed (Peppas and Moynihan, 1987). We searched for an organic solvent or cosolvent system to use as the diluent in our syntheses, eventually selecting 100% butanol (Baker et al., 1993). We found that an 80 *%T*, 0.5 *%C*, 30 *%DMA* hydrogel (designated H1) could be produced, heavily mottled with popcorn polymers, by using a 60/40 (v/v) mixture of ethylene glycol/water as the diluent, as indicated in Figure 4.

Materials. 2-Hydroxyethyl methacrylate (HEMA) was purchased from Kodak. 2-Dimethylaminoethyl methacrylate (DMA), ethylene glycol dimethacrylate and 2,2'-azobisisobutyronitrile (AIBN) were obtained from Polysciences. Ammonium persulfate (APS), ethylene glycol (EG) and butanol, all ACS grade, were purchased from Fisher Scientific. HEMA and DMA were both vacuum-distilled using the procedure described by Chou (1991) prior to use; AIBN was recrystallized from 70/30 (v/v) water/ethanol prior to use; the other reagents were used as received. Water was distilled, then filtered and deionized by a Barnstead Nanopure II system.

Procedure. To illustrate the procedure to prepare the poly(HEMA *co*-DMA) hydrogels, we give details for the preparation of hydrogel H1. Added to a solution of 10.6 ml EG and 7.1 ml water were 9.4 mL HEMA, 4.8 mL DMA and 0.1 EGDMA. The monomer

solution was placed in an ice-water bath in order to prevent premature polymerization upon addition of the initiator, APS. While in the ice-water bath, the monomer solution was degassed by pulling a 500-mm Hg vacuum over the solution for 15 minutes. During degassing, the solution was gently stirred (no vortex formation) with a magnetic stirrer. After degassing, 10.0 mg of APS was added to the reaction mixture; the solution was gently stirred until complete dissolution of the APS. The reaction mixture was poured into silanized 3.7-mL screw-top glass vials (15 mm x 45 mm). The vials were sealed, then immersed in a water bath at 50°C. After 24 hours, the hydrogels were removed from the vials. The hydrogels were cut into disks approximately 5 mm in thickness, then immersed in a 50/50 (v/v) EG/water solution. After five days, the disks were placed in a 25/75 EG/water solution. After five more days, the disks were transferred to pure water which was refreshed periodically to extract residual diffusible species from the interior of the disks. The disks were swollen to equilibrium in water.

Results

Poly(acrylamide *co*-MAPTAC) hydrogels. A series of four 15 *%T*, 1 *%C*, 2 *%MAPTAC* poly(acrylamide *co*-MAPTAC) hydrogels (designated A1, A2, A3 and A4) was prepared; the concentrations of initiators APS and SMB (the redox couple) varied in tandem from 0.2 to 0.8 mg/mL. As shown in Figure 1, increasing the concentrations of the initiators in this manner served to eliminate the popcorn polymers from the hydrogels.

Figure 2 shows swelling equilibria in water for hydrogels A1 - A4. The swelling ratio is defined by the mass of swollen hydrogel divided by the mass of dry hydrogel. As expected, hydrogel swelling increases with removal of the unswellable popcorn polymers.

Figure 3 shows two vials containing poly(acrylamide *co*-MAPTAC) hydrogels. The left hydrogel (A1) contains many popcorn polymers, while the right hydrogel is clear. The two hydrogels were prepared identically except that the reaction mixture of the hydrogel on

the right also contained 0.2 mg/mL NTP, a chain-transfer agent for acrylamide (Sandler and Karo, 1974).

Poly(HEMA *co*-DMA) Hydrogels. A series of five 80 *%T*, 0.5 *%C*, 30 *%DMA* poly(HEMA *co*-DMA) hydrogels (designated H1, H2, H3, H4 and H5) was produced; the concentration of initiator APS varied in the reaction mixture from 0.3 to 15.6 mg/mL. Figure 4 is a photograph comparing the appearance of hydrogels H1, H3 and H5. Hydrogel H1 is heavily mottled with popcorn polymers and is completely opaque, while H5 is clear and has a much bigger diameter than either H1 or H3, indicating a higher swelling ratio.

Figure 5 shows swelling equilibria in water for hydrogels H1 - H5. As with the acrylamide-based hydrogels, increasing the initiator concentration eliminates the popcorn polymers and provides for increased swelling of the hydrogels in water.

Discussion

First, we propose a mechanism for popcorn-polymer formation in hydrogels. Then we discuss this mechanism in light of the observed results.

The heterogeneity of hydrogels synthesized via free-radical copolymerization has been confirmed by various studies (see, for example, Weiss et al., 1979; Hecht et al., 1985; Rüchel et al., 1978; Cohen et al., 1992). According to Flory (1953), gel heterogeneity is a consequence of free-radical polymerization. Each active initiator nucleates a high-density site that is initially in the sol state; polymer tends to build up around the active site. Monomers are added in shells around the site; each shell indicates that monomer is depleted as polymerization proceeds. The transfer of such sites from the sol state to the gel state occurs at the gel point. Gelation causes a rapid reduction in the concentration of available sol particles. As a result, when hydrogel polymerization occurs, the monomer is concentrated in some areas and necessarily depleted in others. Usually, the heterogeneities are smaller than the wavelength of visible light; therefore, the gels appear clear and

homogeneous to the naked eye. Under certain conditions, a high-density site may become macroscopic in scale, forming a popcorn polymer within the gel matrix.

A plausible scenario for popcorn-polymer formation during hydrogel synthesis is as follows. As the network is formed, mobility of the active initiator sites decreases as the viscosity of the solution rises. Monomer diffuses into the immobile active site. The network surrounding the active site swells to accommodate the incoming monomer. As space becomes limited for the monomer diffusing in, and for the polymer formed, the chains surrounding the active site begin to break. More radicals are formed as the result of chain breakage; these radicals are free to initiate the formation of new polymer chains. Growth of the popcorn polymer may proceed as long as unreacted monomer is available to feed the additional radicals that are formed. Formation of the additional free radicals from chain fracture has been confirmed by electron-paramagnetic-resonance spectroscopic studies on popcorn-polymer formation (Breitenbach et al., 1965).

Increasing the initiator concentration prevents polymer from building up around a relatively few active sites. We were successful in raising the initiator concentration to suppress popcorn-polymer formation in both hydrogel systems studied here. Gehrke (1986) also observed that popcorn polymers tend to form in acrylamide-based hydrogels when relatively low levels of initiator are used. In a monovinyl system, Breitenbach and Fally (1951) increased the concentration of initiator, benzoyl peroxide, 100-fold to suppress popcorn-polymer formation during the synthesis of poly(methyl acrylate).

We propose that a popcorn polymer is nucleated by an immobile radical (active site). If the mobility of radicals increases, popcorn-polymer formation could be eliminated. Chain transfer refers to the termination of a growing polymer chain and the start of a new one. In the following, $P_n\bullet$ is the growing polymer radical, XA is the chain-transfer agent, and M is the monomer:

$$\text{chain transfer} \quad P_n\bullet + XA = P_n\text{--}X + A\bullet \tag{1}$$

$$\text{reinitiation} \quad A\bullet + M = M\bullet \tag{2}$$

Through the chain-transfer reaction and subsequent reinitiation the polymer radical is exchanged for the more readily diffusible reinitiation product. A popular chain-transfer agent for acrylamide polymerization is 3,3',3"-nitrilotris(propionamide) (NTP) (Sandler and Karo, 1974) because it is similar chemically to acrylamide. We were successful in suppressing popcorn-polymer formation in an acrylamide-based hydrogel by adding a small amount of NTP to the reaction mixture as indicated in Figure 3.

We found that popcorn-polymer-free 15 *%T*, 1 *%C*, 2 *%MAPTAC* poly(acrylamide *co*-MAPTAC) hydrogels can be produced by discarding the redox couple and initiating the hydrogel synthesis using 0.2 mg/mL APS and allowing the APS to decompose thermally by heating the reaction mixture to 50°C overnight. The redox couple generates radicals relatively quickly; equilibrium for this redox reaction is reached in approximately 15 -20 minutes (Bio-Rad Laboratories, 1987). Apparently, the more uniform generation of radicals by the thermal decomposition of APS aids in avoiding the initiator-deficient condition which favors formation of popcorn polymers. Reduction or total suppression of popcorn-polymer formation by raising the reaction temperature alone has been observed by others (Yamamoto and Tatsumi, 1986).

Popcorn-polymer-free 80 *%T*, 0.5 *%C*, 30 *%DMA* poly(HEMA *co*-DMA) hydrogels may be prepared by replacing the 60/40 (v/v) EG/water diluent with butanol. APS is not soluble in butanol and may be replaced by an equal concentration of AIBN. Clear hydrogels are formed by heating the reaction mixture to 60°C overnight (Baker et al., 1993). Specific solvent effects for popcorn-polymer formation have been observed by Breitenbach and Kauffmann (1974); they propose that an optimum range of polymer-coil

dimensions exists for popcorn-polymer formation because coil dimensions are a function of solvent quality.

Conclusions

Popcorn polymers have been observed within the matrices of hydrogels. Formation of popcorn polymer was suppressed during hydrogel synthesis by raising the initiator concentration, adding a chain-transfer agent, changing the diluent, or by changing the mode whereby radicals in the reaction mixture are generated.

A proposed mechanism for popcorn-polymer formation during hydrogel synthesis is consistent with the experimental observations of this work.

Popcorn polymers do not swell in solvent; their elimination promotes swelling of the hydrogel. For the poly(acrylamide *co*-MAPTAC) hydrogel studied here, popcorn-polymer formation was completely suppressed by a four-fold increase in the initiator concentration; concomitantly, hydrogel swelling in water increased by 28% upon complete removal of the popcorn polymers. For the poly(HEMA *co*-DMA) hydrogel studied here, popcorn-polymer formation was suppressed by a fifty-fold increase in the initiator concentration; concomitantly, hydrogel swelling in water increased by 100% upon removal of the popcorn polymers. Silberberg and coworkers (Weiss and Silberberg, 1976; Weiss et al., 1979; Silberberg, 1992) have for many years argued that the initiator concentration in the pre-gel reaction mixture may have a profound effect on the ultimate properties of hydrogel networks. The findings of this work support their claim.

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Figures

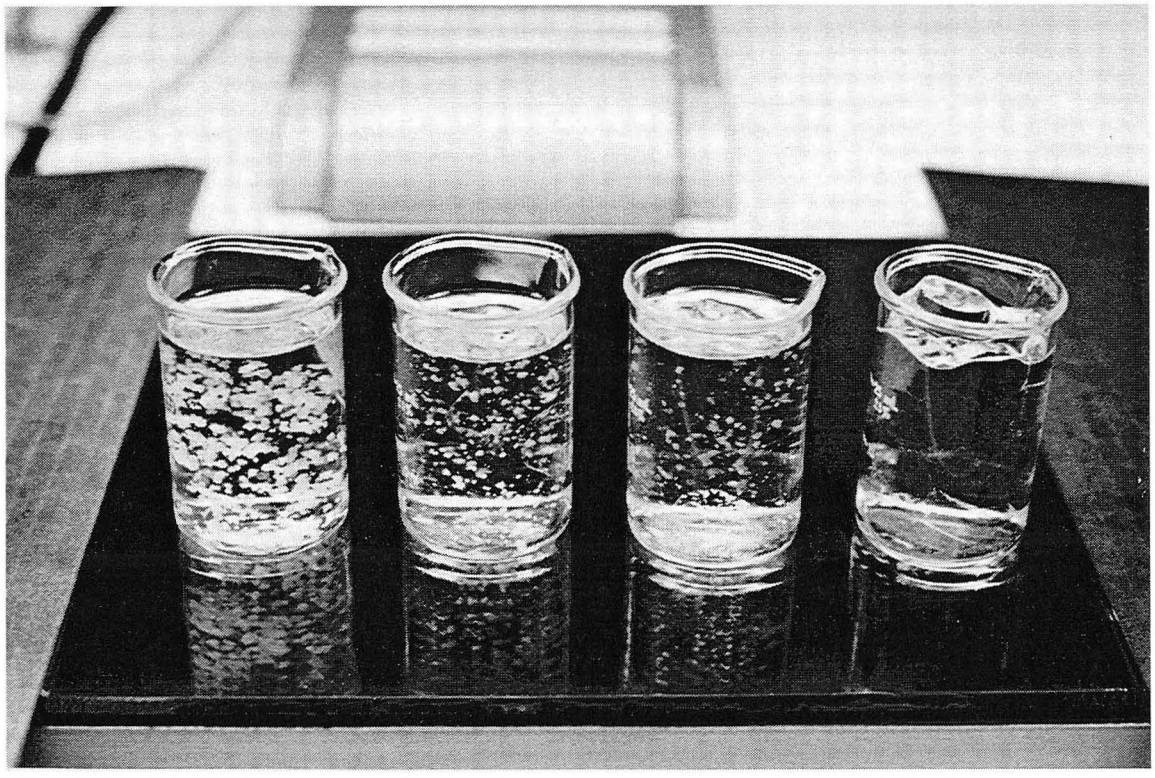

Figure 1. Photograph of 25-ml beakers containing, from left to right, poly(acrylamide *co*-MAPTAC) hydrogels A1, A2, A3 and A4. These hydrogels have reached equilibrium swelling in water.

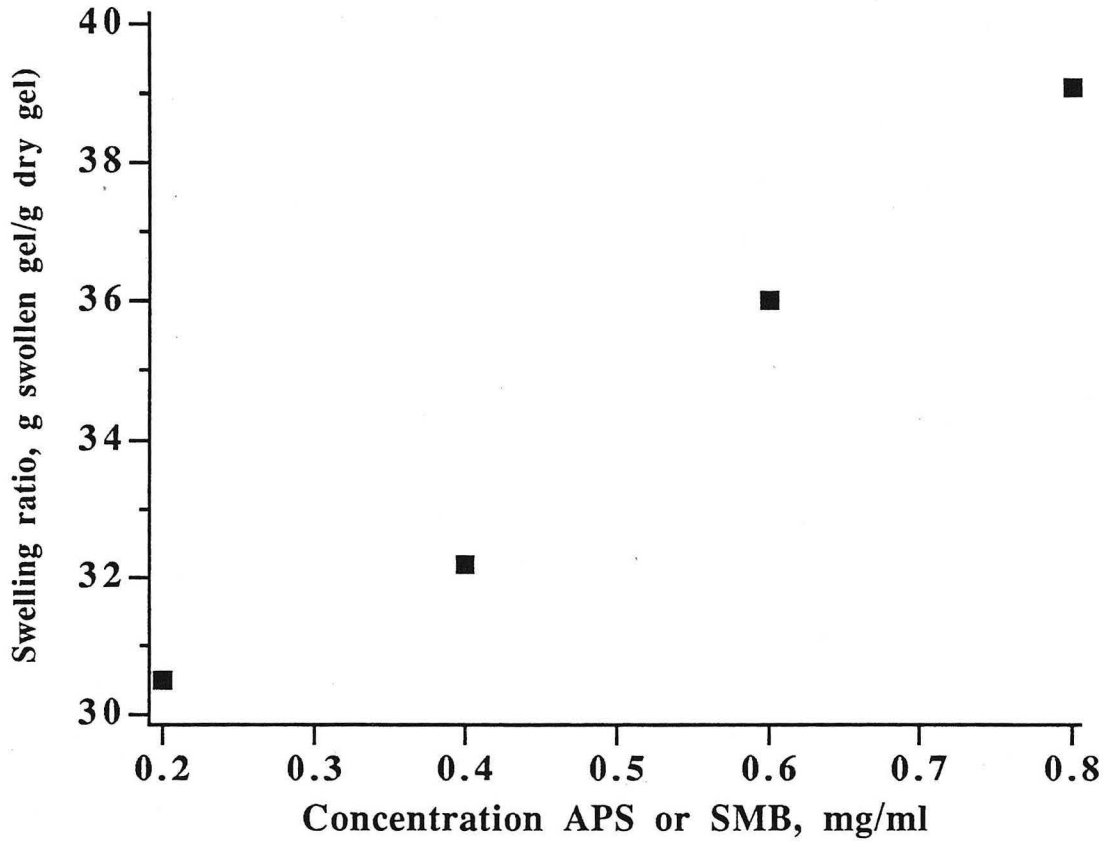

Figure 2. Swelling equilibria in water for four 15 $\%T$, 1 $\%C$, 2 $\%MAPTAC$ poly(acrylamide *co*-MAPTAC) hydrogels (A1 - A4). In the reaction mixture, the concentrations of the components in the redox couple used to initiate polymerization (APS, SMB) varied (in tandem) from 0.2 to 0.8 mg/ml.

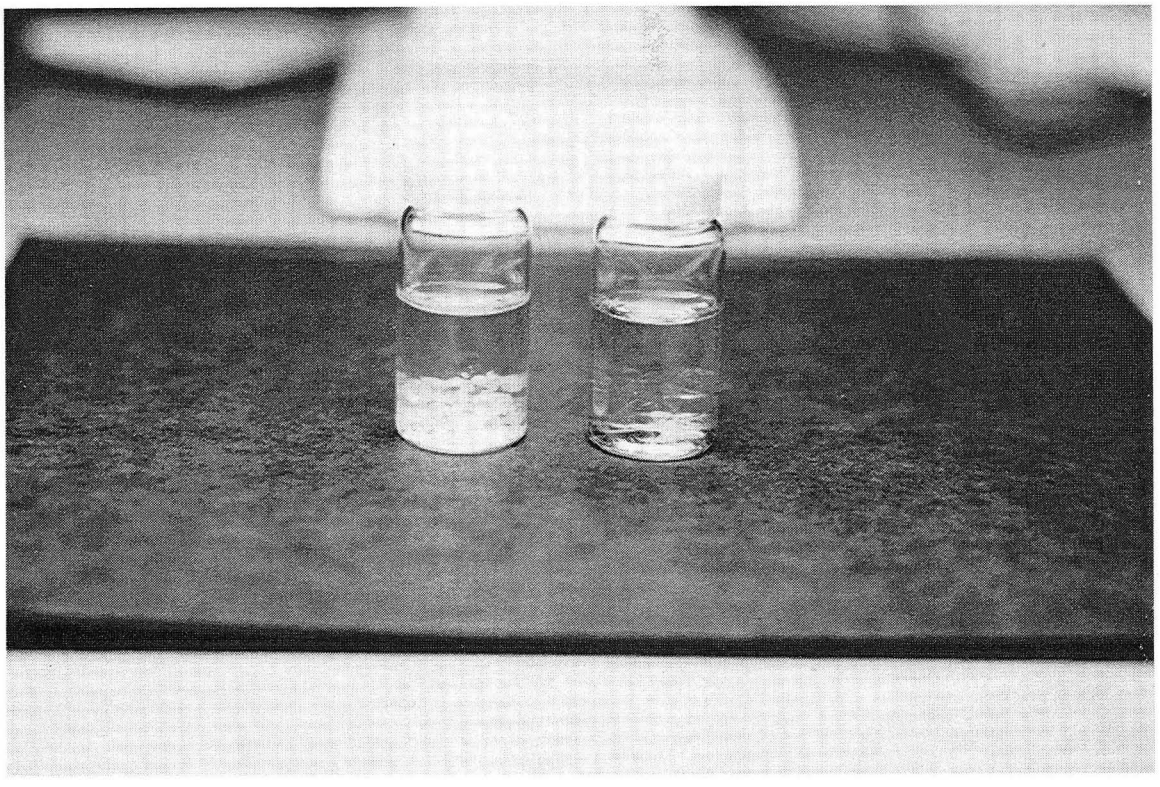

Figure 3. Photograph of two 20-ml scintillation vials containing poly(acrylamide *co*-MAPTAC) hydrogels. The left hydrogel (A1) contains much popcorn polymer while the right hydrogel is clear. The two hydrogels were identically prepared except that the reaction mixture of the hydrogel on the right contained 0.2 mg/ml of NTP.

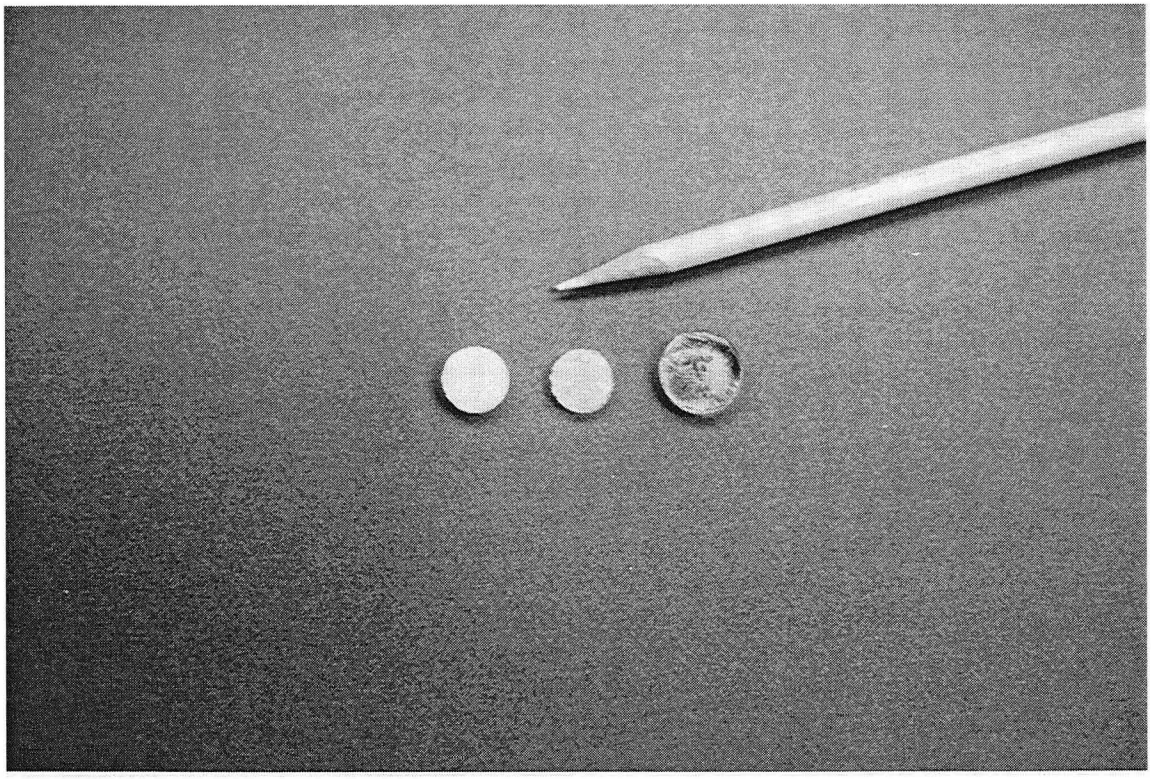

Figure 4. Photograph of three poly(HEMA *co*-DMA) hydrogels; from left to right, disks of H1, H3 and H5. H1 is mottled heavily with popcorn polymer and contains virtually no regions of clear gel; H3 is contains some regions of clear gel; H5 is clear. These hydrogels have reached equilibrium swelling in water.

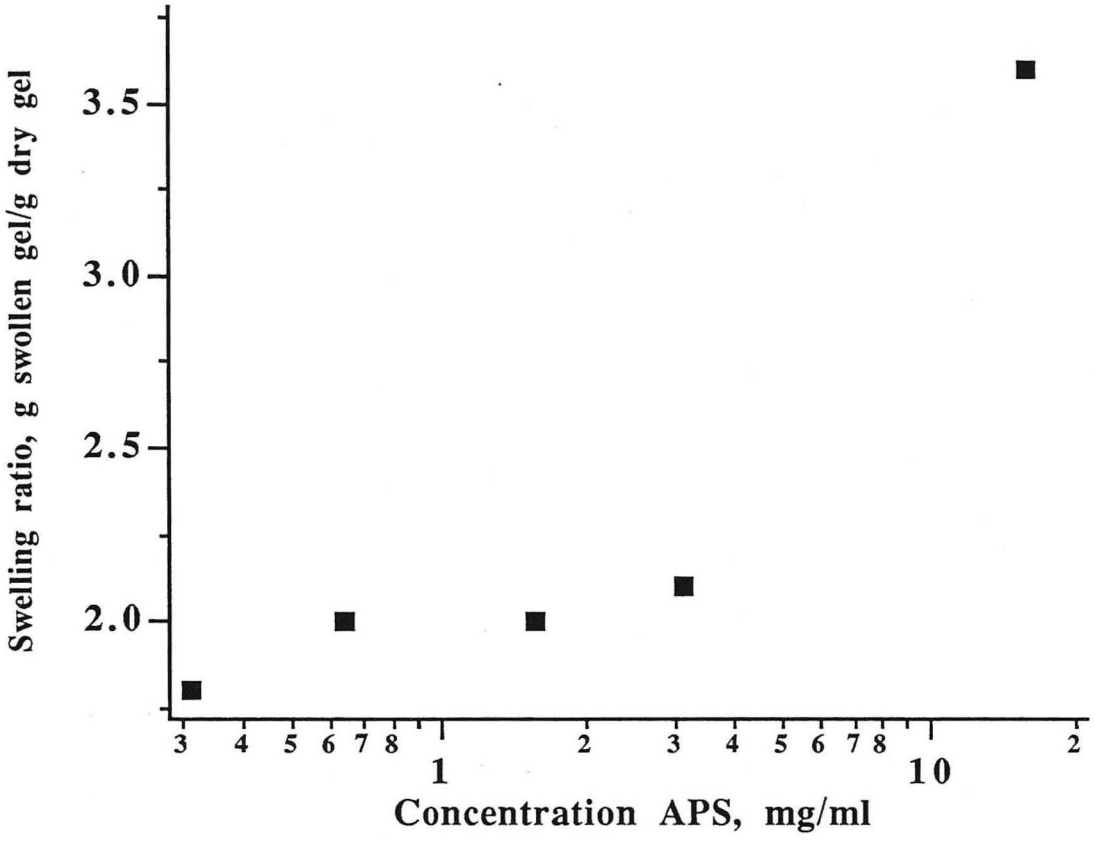

Figure 5. Swelling in water for five 80 *%T*, 0.5 *%C*, 30 *%DMA* poly(HEMA *co*-DMA) hydrogels (H1 - H5). In the reaction mixture, the concentration of APS varied from 0.3 to 15.6 mg/ml.

Tables

Table 1. Initiator concentrations and swelling ratios in water for four 15 *%T*, 1 *%C*, 2 *%MAPTAC* poly(acrylamide *co*-MAPTAC) hydrogels.

Hydrogel	Conc. each initiator in reaction mixture[a], mg/mL	Swelling ratio[b] in water
A1	0.2	30.5
A2	0.4	32.2
A3	0.6	36.0
A4	0.8	39.1

[a]Equal masses of SMB and APS were used as a "redox" initiator pair.

[b]Swelling ratio = (g swollen gel)/(g dry gel).

Table 2. Initiator concentrations and swelling ratios in water for five 80 *%T*, 0.5 *%C*, 30 *%DMA* poly(HEMA *co*-DMA) hydrogels.

Hydrogel	Initiator conc.[a] in reaction mixture, mg/mL	Swelling ratio[b] in water
H1	0.3	1.8
H2	0.6	2.0
H3	1.6	2.0
H4	3.1	2.1
H5	15.6	3.6

[a]APS was used as the initiator.

[b]Swelling ratio = (g swollen gel)/(g dry gel).

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UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720