

Gel Forming Waterborne Dispersion Polymerization of Sodium *p*-Styrene Sulfonate with Glycidyl Methacrylate

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Received 11 September 2017; accepted 2 December 2017; published online 00 Month 2017

DOI: 10.1002/pola.28936

ABSTRACT: Water soluble monomer like sodium *p*-styrene sulfonate (SSS) is copolymerized with hydrophobic and reactive monomer glycidyl methacrylate (GMA). The polymerization proceeds as dispersion and forms gels. The gel forming nature prevails even with other hydrophobic and hydrophilic monomers to form ternary polymeric systems. The swelling is dependent on polymer composition as well as the treatment history of polymers. SSS also induces ring opening of GMA to form 1,2-diols as confirmed independently by various model reactions. The ability of hydrogels to absorb various dyes

indicates that owing to the anionic nature, hydrogels absorb cationic dyes nearly quantitatively. Because of their strong affinity to cationic species these hydrogel forming polymers are potentially useful in water purification applications as well as purification of proteins. © 2017 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *00*, 000–000

KEYWORDS: copolymerization; crosslinking; degradation; dispersion; ring opening of epoxide

INTRODUCTION Aqueous polymerization is one of the widely practiced polymerization techniques in the modern era with millions of tons of latexes being produced annually through this process.^{1,2} Arguably, this is the earliest example of using water as a reaction medium in industrial scale processes with the exception of bioprocesses like fermentation. Solubility as well as stability of reactants and reagents in water during the reaction are some of the issues which prevent water from being used widely as a reaction medium. However, this is not of great concern for polymerization of most of the vinyl monomers in the aqueous medium. Even functional monomers like glycidyl methacrylate (GMA) have been used either on its own or as a comonomer in emulsion polymerization.^{3–6} GMA is particularly suited for post-curing purposes because of its reactivity toward nucleophiles as well as protic sources of both acidic (–COOH) and basic (–NH) origin.^{7–11} Indeed stable latexes have been formed by the aqueous emulsion polymerization of GMA.³ GMA has been copolymerized with sodium *p*-styrene sulfonate (SSS) in 5 and 15 mol% (feed ratio) using 1:1 water: *N,N*-dimethylformamide (DMF) mixtures as reaction medium.¹² The reaction reportedly proceeded normally to yield soluble copolymers.

The combination of SSS and GMA is interesting because of their contrasting interaction with water as well as the differing chemical nature like ionic and neutral, respectively. Also,

because of the attractive features such as atom economy and facile reaction with nucleophiles associated with GMA bearing copolymers we were interested to make copolymers of GMA in aqueous medium. We were interested in higher concentration of reactive comonomer so that it would enable higher loading of functional components after post polymerization modifications involving epoxy group. SSS can function as reactive surfactant in the copolymerization. SSS has been used for making surfactant free copolymers with common vinyl monomers for making high solid content polymer dispersions.^{13,14} Sulfonates are also well-known anionic surfactants. However, to our surprise, when GMA was subjected to emulsion polymerization with SSS under conventional free radical polymerization conditions in a molar ratio of approximately 2:3, the polymerization invariably yielded not only hydrogels but also accompanied with the ring opening of epoxide to yield 1,2-diols. Predominantly hydrogels are formed by using crosslinking agents such as divinyl benzene, di(meth)acrylates and di(meth)acrylamides while polymerizing water soluble monomers.^{15–17} Aqueous emulsion polymerization of GMA is well known for many decades to proceed normally without any side reactions like ring opening of epoxide during polymerization.³

Even though at the outset it might appear that the formation of hydrogel could be a result of combining water soluble

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monomer (SSS) with hydrophobic monomer (GMA)¹⁸ we preferred to probe this polymerization further. Hence model reactions were conducted to understand the formation of hydrogels. These model reactions unambiguously confirmed that ring opening of epoxide occurred during polymerization and the same was promoted by the comonomer SSS. It is useful to note here that hydrogels are very useful and industrially important materials for a variety of applications.^{19–29} Introducing other hydrophilic and hydrophobic monomers to make ternary polymeric systems did not disrupt hydrogel formation. However, the equilibrium swelling ratio was affected. Due to the ability of these polymers to swell in water and also the ability to absorb the matter dissolved in water while swelling the polymers reported here are potentially useful in water purification applications.

EXPERIMENTAL

Characterization

Nuclear magnetic resonance (NMR) measurements were recorded on Bruker UltraShield Avance 400 MHz FT-NMR instrument using deuterated dimethyl sulfoxide (DMSO-*d*₆) as the solvent. FTIR measurements were performed on Bio-Rad Excalibur Series FTS 3000 instrument using potassium bromide (KBr) pellets. GPC was conducted on a Viscotek GPCmax VE 2001 consisting of integrated solvent and sample delivery module. PLgel 5 μm Mixed-C × 2 columns were applied in sequence for separation. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1 mL/min at 30 °C and molecular weight values were determined against polystyrene standards. Thermal stabilities were determined by thermogravimetric analysis (TGA) on a TA instrument (SDT-TGA) at a heating rate of 10 °C min⁻¹ under N₂ atmosphere by heating the sample from 25 to 800 °C.

Swelling Experiments

Equilibrium swelling ratio was determined by placing known quantity of polymer either in deionized water or 0.9% NaCl solutions for 24 h at room temperature. After filtering and wiping off the excess water with the help of filter paper, the gels were weighed (*W*_s). The swollen gels were subsequently dried in a vacuum oven at 50 °C for 24 h and weighed again to note the dry weight (*W*_d). The equilibrium swelling ratio was calculated using the equation:

Swelling ratio (%) = (*W*_s - *W*_d) / *W*_d × 100. The equilibrium swelling ratio was determined by performing the experiments on three samples and therefore the values reported are the average of three experiments. Similarly the time taken to reach equilibrium swelling was determined by following water uptake by polymers at different time intervals for example, 5, 10, 15, 30, 60, 120, 180, 300, and 900 min. The results reported are the average of three measurements.

Materials

Sodium *p*-styrenesulfonate (SSS, ≥90%), methyl methacrylate (MMA, 99%), ammonium persulfate (APS, ≥98%), sodium *p*-toluenesulfonate (Na-PTSA, 95%), azoisobutyronitrile (AIBN, 98%), 1,2-epoxy-5-hexene (EH, 97%), methylene

blue (MB), and sodium acrylate (97%) were purchased from Sigma-Aldrich. Glycidyl methacrylate (GMA, 97%) was purchased from Alfa Aesar and sodium chloride (NaCl, 99%) from Merck KGaA. Acid yellow 3 (AY) and fast green FCF (FG, >85%) were purchased from TCI Chemicals. All chemicals were used as received without further purification. Deionized water was used for swelling experiments. Solvents used were obtained from Glass Contour solvents purification system.

Polymer Preparation

Preparation of P-1

Deionized water (15 mL) was purged with nitrogen for 30 min in a 2-necked RB flask fitted with a reflux condenser. SSS (2.0 g, 9.69 mmol) was added and dissolved by stirring vigorously using a hot plate magnetic stirrer. GMA (0.92 g, 6.48 mmol) and APS (60 mg) were added to the mixture under nitrogen atmosphere. The RB flask was then immersed in a preheated oil bath maintained at 75 °C. The solution turned viscous and formed a gel within an hour. The reaction was continued for further 3 h and cooled. Then the gel was washed with water, followed by acetone to remove unreacted monomers and dried in a vacuum oven at 50 °C for 24 h. Yield: 1.90 g. A portion of the gel was also dried by freeze-drying for 12 h to isolate a white powder (Yield: 0.30 g).

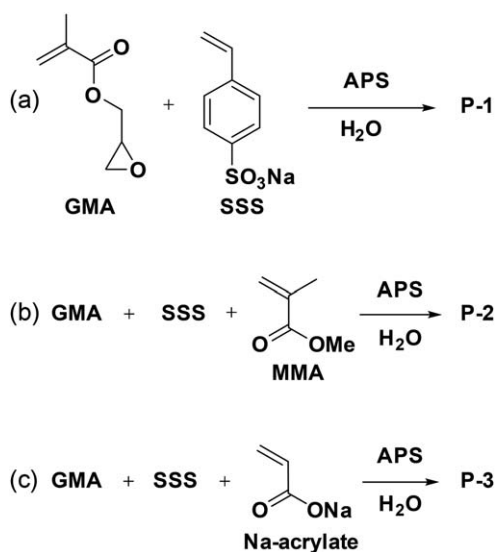
P-2 and P-3 were prepared by employing similar procedure as described above for P-1. The monomers used were SSS (2.0 g, 9.69 mmol), GMA (0.83 g, 5.84 mmol), and MMA (0.39 g, 3.89 mmol) or sodium acrylate (0.36 g, 3.83 mmol). In both polymerizations gel formation occurred within 2 h. The reaction mixture was heated for additional 3 h. Then gels were washed with water and excess acetone and dried at 50 °C in a vacuum oven for 24 h. Yield: P-2: 2.10 g; P-3: 1.75 g. From both polymerization reactions dried polymer samples were obtained by subjecting a portion of the gel to freeze-drying.

Model Reaction to Determine Ring Opening of GMA by SSS

SSS (2.0 g, 9.69 mmol) was dissolved in 15 mL of deionized water under nitrogen atmosphere. GMA (0.92 g, 6.48 mmol) and catalytic amount of hydroquinone (5 mg) were added to the aqueous solution. The mixture was heated for 6 h at 75 °C and cooled to rt. The crude reaction mixture was subsequently analyzed by ¹H NMR and FTIR spectroscopic techniques. The product, 2,3-dihydroxypropyl methacrylate (DHMP) was isolated as yellow orange liquid by extracting the freeze-dried mixture with chloroform. Yield: 0.54 g. ¹H NMR (DMSO-*d*₆, 400 MHz, δ ppm): 6.05 (s, 1H), 5.67 (s, 1H), 4.95 (d, *J* = 5.1 Hz, 1H), 4.67 (t, *J* = 5.6 Hz, 1H), 4.11 (m, 1H), 3.98 (m, 1H), 3.68 (m, 1H), 3.40 (m, 1H), and 1.88 (s, 3H). FTIR (cm⁻¹): 3400 (νOH), 1720 (νC=O str), 1122 and 1053 (νC—O—C).

Blank Reaction

GMA (1 mL) was suspended in water (10 mL) and heated at 75 °C for 6 h. The reaction mixture was analyzed after cooling to determine if the epoxy ring was affected. ¹H NMR



SCHEME 1 Preparation of polymers P-1, P-2, and P-3.

(DMSO- d_6 , 400 MHz, δ ppm): 6.06 (s, 1H), 5.72 (s, 1H), 4.46 (d, $J = 12.4$ Hz, 1H), 3.91 (dd, $J = 12.4, 6.4$ Hz, 1H), 3.24 (m, 1H), 2.79 (t, 1H), 2.65 (m, 1H), and 1.88 (s, 1H). The ^1H NMR was in agreement with that of the starting material, GMA.

Dispersion Polymerization of GMA

GMA (1.0 g, 7.03 mmol) was suspended in water (8 mL) and the suspension was purged with N_2 for an hour. After adding APS (32 mg, 0.14 mmol), the reaction mixture was stirred at 75 °C for 12 h. PGMA particles were isolated by centrifuging the reaction mixture, washing with water followed by methanol and dried in a vacuum oven (Yield: 0.95 g). FTIR (cm^{-1}): 3431, 2941, 1720, 1276, 1166, 908, and 843.

Solution Polymerization of GMA

GMA (1.0 g, 7.03 mmol) was dissolved in THF (10 mL) under N_2 atmosphere. AIBN (23 mg, 0.14 mmol) was added under nitrogen atmosphere. The polymerization was carried out at 70 °C for 15 h under N_2 atmosphere. After cooling, PGMA was precipitated as a white powder in excess of diethyl ether. Yield: 0.79 g. ^1H NMR (CDCl_3 , 400 MHz, δ ppm): 4.30 (broad, 1H), 3.80 (broad, 1H), 3.22 (s, 1H), 2.83 (s, 1H), 2.63 (s, 1H), 1.89 (broad, 2H), 1.08 (s, 1H), and 0.92 (s, 2H). $M_n = 5500$ (by GPC).

Homopolymerization of SSS

A solution of SSS (1.0 g, 4.85 mmol) in water (8 mL) was degassed by purging with N_2 . APS (22 mg, 0.09 mmol) was added and the mixture was heated to 75 °C for 15 h. The polymer thus obtained was separated by dialysis followed by freeze-drying to obtain a white solid. Yield: 0.78 g. FTIR (cm^{-1}): 3450, 2916, 1637, 1190, 1035, 1006, and 835.

Preparation of Poly(DHPM-co-SSNa)

A solution of DHPM (obtained by hydrolysis of GMA, 200 mg, 1.25 mmol) and SSS (257 mg, 1.25 mmol) in 3 mL water was degassed with N_2 for 30 min. APS (5 mg, 0.025

mmol) was added and the solution was stirred at 75 °C under N_2 atmosphere. Gel formation was observed in an hour and the reaction was continued further for 2 h. After washing with water and acetone, the gel was dried by freeze-drying to yield an off-white solid. Yield: 280 mg. FTIR (cm^{-1}): 3450, 1720, 1640, 1188, and 1124.

Preparation of Poly(DHPM)

A solution of DHPM (500 mg, 3.12 mmol) in 5 mL water was degassed with N_2 for 30 min. APS (14 mg, 0.06 mmol) was added and the solution was heated to 75 °C for 10 h. The viscous solution was freeze-dried, dissolved in MeOH and precipitated in chloroform to get a brown solid. Yield: 380 mg. ^1H NMR (MeOD, 400 MHz, δ ppm): 4.15–3.85 (broad, 2H), 3.80–3.45 (broad, 3H), 2.30–1.55 (broad, 2H), 1.30–0.70 (broad, 3H). FTIR (cm^{-1}): 3420 (broad), 1720, 1456, 1170, and 1050.

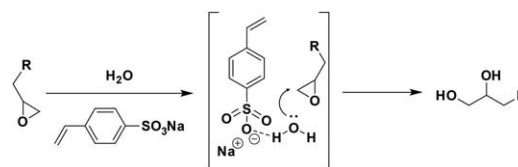
RESULTS AND DISCUSSION

Preparation of Polymers

The polymers, P-1, P-2 and P-3 were prepared by conventional free radical polymerization in a procedure typical for surfactant-free polymerization in aqueous medium as shown in Scheme 1. In all polymerizations a ratio of 2:3 was maintained between GMA and SSS respectively. The comonomer SSS is a reactive surfactant.^{13,14} Gelation of polymerization reaction mixtures occurred within an hour and the reaction was continued for additional 3 h by which time stirring of reaction mixture stopped. Formation of gels in the absence of crosslinking agent is unexpected since GMA has been reported to form soluble polymers previously.^{30,31} To understand the nature of reactions which induced gel formation, model reactions were performed as described in the succeeding sections.

Reaction of SSS with GMA

It is well known that ring opening of epoxy groups are generally initiated by hydroxyl,^{7,8} amine,^{9,10} or carboxylic acid¹¹ functionalities present in the reaction medium either as part of comonomers or as crosslinking agents. Interestingly, SSS also induced the opening of oxirane ring as confirmed by model reactions. It is worthwhile to note here that the only previously reported copolymerization of SSS with GMA in 1:1 H_2O :DMF mixture yielded soluble copolymers.¹² Thus, neither gels nor ring opening of epoxide functionality has been discussed in the published article. A possible mechanism of SSS promoted ring opening reaction is shown in Scheme 2.



SCHEME 2 Proposed mechanism for the SSS promoted ring opening of epoxide group.

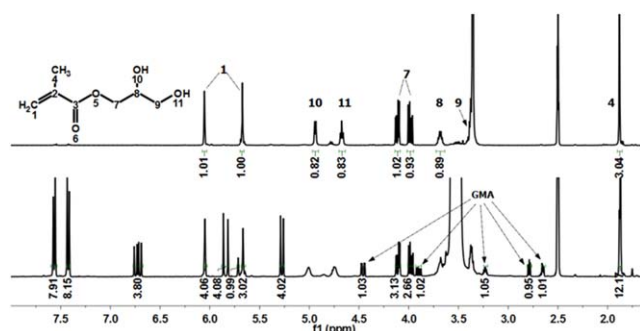


FIGURE 1 ^1H NMR spectra of crude reaction mixture containing GMA, SSS, and DHPM (bottom) and pure DHPM (top). [Color figure can be viewed at wileyonlinelibrary.com]

At first GMA was heated in water at $75\text{ }^\circ\text{C}$ with and without (blank experiment) SSS, in the absence of radical initiator (APS). Catalytic amount of hydroquinone was added as a free radical inhibitor to prevent polymerization during model reaction. After heating for 6 h, ^1H NMR was recorded by dissolving the crude reaction mixture in $\text{DMSO-}d_6$ (Fig. 1). Additional signals due to the formation of new product were observed quite apart from the signals corresponding to GMA and SSS. The product obtained by the model reaction was separated by freeze-drying the reaction mixture followed by extraction with chloroform. The product was confirmed to be 2,3-dihydroxypropyl methacrylate (DHPM) (i.e., glyceryl methacrylate) by ^1H NMR spectroscopic analysis (Fig. 1). In addition, FTIR spectroscopic analysis (Fig. 2) confirmed the presence of hydroxyl groups (broad and strong absorption centered at 3400 cm^{-1}) as well as the absence of oxirane ring in the product, DHPM, which was originally observed at 908 and 842 cm^{-1} in the FTIR spectrum of GMA. Signals corresponding to C—O—C stretching of DHPM were also observed at 1122 and 1053 cm^{-1} .³² The prevalence of strong H-bonding interaction between C=O oxygen of ester and hydroxyl groups in DHPM is obvious from the shift in carbonyl absorption frequency ($\nu\text{C=O}$) to lower values than that of GMA ($\nu\text{C=O} = 1720\text{ cm}^{-1}$) as highlighted in Figure 2. In the blank experiment, heating GMA in water did not yield

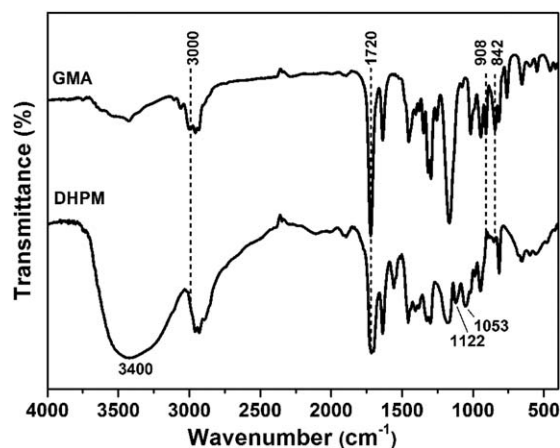
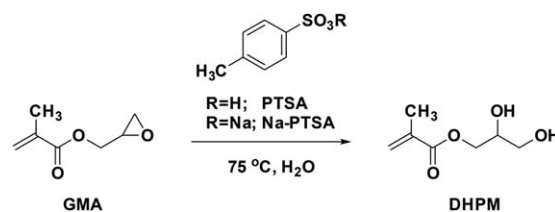


FIGURE 2 FTIR spectra of GMA and DHPM.



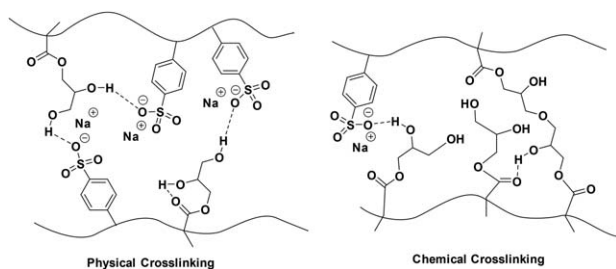
SCHEME 3 General and versatile nature of ring opening of oxiranes by aryl sulfonic acid and its salt.

DHPM as confirmed by NMR and FTIR spectroscopic analyses of the reaction mixture thereby confirming the role of SSS in the opening of oxirane ring of GMA. The findings of blank experiment are in good agreement with those reported in refs. 30 and 31. Even though it could be argued that impurities in SSS could have caused ring opening of epoxide functionality, additional experiments ruled out this proposition. To verify the role of impurities, ring opening of epoxide was studied using *p*-toluene sulfonic acid (*p*-TSA) under similar reaction conditions. As compared to SSS, *p*-TSA catalyzed ring opening reaction quantitatively at much lower concentrations. This undoubtedly highlights the reduced catalytic activity of sodium salt of sulfonic acid as compared to sulfonic acid.

General Nature of Sodium Salt of Aromatic Sulfonic Acids as Catalysts in the Ring Opening of Epoxides

To confirm the versatility of this reaction, 1,2-epoxy-5-hexene (EH) was heated in the presence of sodium *p*-toluenesulfonate (Na-PTSA) as shown in Scheme 3.

Ring opening of 1,2-epoxy-5-hexene occurred to yield hex-5-ene-1,2-diol as the major product. The yield of ring opened product increased with reaction time as indicated by the increasing ratio of hex-5-ene-1,2-diol relative to the starting material in the spectroscopic analysis (Figs. S1 and S2). This reaction confirmed that sodium salt of sulfonic acid acts as catalyst to form ring opened products of epoxy groups cleanly in the presence of conjugated as well as isolated unsaturated bonds. Previously, sulfate groups ($-\text{SO}_4^{2-}$) have been reported to be involved in crosslinking reaction with hydroxy functional groups at $75\text{ }^\circ\text{C}$ forming network structures.³³ However, sulfonate mediated ring opening of epoxy groups along with the *in situ* gel formation has not been reported to the best of our knowledge. The process reported here is useful for preparing hydrogels without additional nucleophiles or crosslinkers. There are two possible mechanisms by which hydrogel formation could take place as shown in Scheme 4. Hydrogels may be formed by physical interactions through strong intra- and interchain H-bonding interactions or through chemical crosslinking that occur when hydroxyl group of one polymer chain attack the oxirane ring of another chain. Chain transfer reactions could also be the source of chemical crosslinking. The existence of strong H-bonding interactions between C=O group of ester and hydroxyl functionality has already been highlighted as evidenced from Figure 2. In addition to the ester functionality the presence of copolymerized SSS units also offers



SCHEME 4 Possible chain interactions leading to hydrogels.

additional and even stronger H-bonding sites. Unlike chemical crosslinking, physically crosslinked gels are more prone to treatment history and thus the extent of swelling could vary to a greater degree on how the polymers were dried. Usually drying of physically crosslinked gels at high temperatures (≥ 100 °C) could substantially lower the swelling ratio as compared to those dried at 50 °C or below.

The interest in GMA is due to the presence of epoxide ring. Since GMA is one of the most preferred comonomers for applications involving curing after coating, it is important to identify the conditions under which it can undergo ring opening reaction during polymerization. This is because the extent of ring opening has serious consequences for the post-cured coated surfaces. Ring opening during polymerization to a greater extent would minimize the number of epoxy groups available for curing thereby affecting surface properties like hardness which in turn would impact durability of coated surfaces. The problem is more pronounced because of the fact that the concentration of GMA in monomer feed is already low. Therefore, it is vital to understand the mechanism of unwanted side reactions like ring opening during polymerization. To establish the crosslinking mechanism, we reacted glyceryl methacrylate (DHPM) obtained by ring opening of GMA, with SSS in a similar procedure as the preparation of gels (Scheme 5). In addition, we also polymerized DHPM in water in the absence of SSS. The FTIR spectra of these two polymers are provided in ESI (Fig. S3). Poly(DHPM) was soluble in water. Poly(DHPM) which has been previously synthesized mainly by RAFT polymerization was also water soluble.^{34–36} In contrast, polymerizing DHPM with SSS formed a gel with a swelling ratio of 5850%.

Even though this value is lower when compared with the swelling ratio of **P-1** (~7500%), the amount of water absorbed is significantly higher for a hydrogel and points to a similar network structure. It is useful to note that the mode of treatment of polymer plays an enormous role in determining the swelling of polymers where swelling is caused by physical crosslinking. But for the difference in intensity, the FTIR spectra of **P-1** and poly(DHPM-co-SSS) looked similar (Fig. S3). The difference in intensity could be due to factors such as difference in molecular weight and copolymer composition. This in turn is due to the difference in solubility of monomers in the aqueous medium. The comparative experiment convincingly confirms the physical nature of interactions. It is also useful to note that in the model reactions involving either GMA or EH,

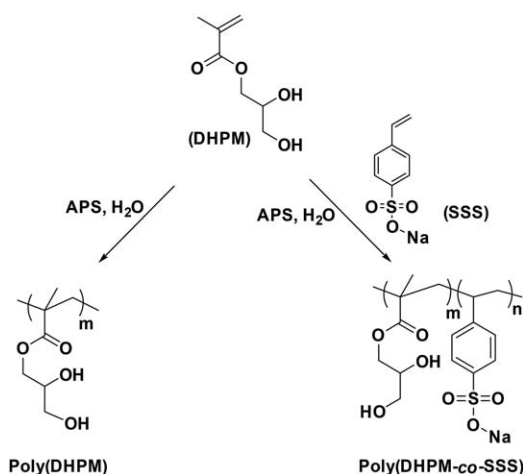
only ring opened products were obtained and no hydroxyl ether was noticed in the spectroscopic analysis which rule out chemical crosslinking mechanism. Additional evidence for the absence of chemical crosslinking arose from the observation that these polymers did not swell in common organic solvents of protic, aprotic, polar, and non-polar nature as well as in dipolar aprotic solvents like DMF and DMSO either under ambient conditions or upon heating to 60 °C. Fluoroalcohols like hexafluoroisopropanol (HFIPA) are well known to dissolve semi-crystalline and strongly hydrogen bonding polymers. However, copolymer of SSS-GMA neither dissolved nor swelled in HFIPA as well. In general, the effect of crosslinking on swelling is complex. Crosslinking at low levels induces swelling to a greater extent than higher degree of crosslinking. However, up to a point, the strength of swollen polymer is greater at higher degree of crosslinking. Crosslinked polymers show greater swelling than the corresponding linear polymers because of the prevalence of voids created by networks formed as a result of crosslinking. Solvent molecules populate these voids to form swollen polymers.

Swelling behavior of hydrogels was greatly influenced by the choice of comonomers. The effect exerted by hydrophobic and hydrophilic functionalities on the swelling properties was studied by preparing two additional derivatives of **P-1** using MMA and sodium acrylate as comonomers to make **P-2** and **P-3**, respectively. The monomers were introduced during polymerization of GMA and SSS to incorporate these as comonomers in a facile manner. The dispersion of water insoluble and hydrophobic monomers like MMA and GMA was ensured by the water soluble and surfactant nature of comonomer SSS. Crosslinked polymers of sodium acrylate are well-known super absorbents produced commercially that are largely used in diapers and sanitary napkins.^{37,38} MMA is a hydrophobic monomer and its polymers are used in various applications.³⁹

Characterization of Polymers

FTIR Analysis

Figure 3 compares the FTIR spectra of homopolymers PGMA, PSSS, and the copolymers **P-1** to **P-3**. The copolymers were



SCHEME 5 Preparation of poly (DHPM) and (DHPM-co-SSS).

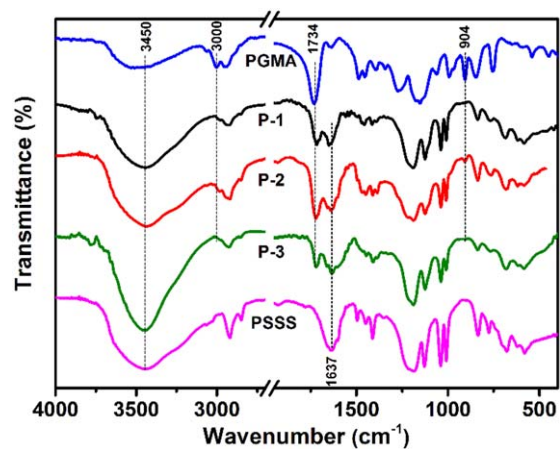


FIGURE 3 FTIR spectra homo- and copolymers. [Color figure can be viewed at wileyonlinelibrary.com]

prepared in aqueous media with APS as free radical initiator at 75 °C under conditions similar to the preparation of gels. The absorption frequency at 1734 cm^{-1} corresponding to stretching of ester $\text{C}=\text{O}$ was observed in the spectra of PGMA as well as in copolymers **P-1** to **P-3**. Similarly the frequency associated with $\text{C}=\text{C}$ stretching of aromatic unit at 1637 cm^{-1} was prevalent in all the spectra with the exception of PGMA. A stronger absorption observed in the $\text{C}=\text{O}$ region of FTIR spectra of **P-2** as compared to **P-1** and **P-3** was due to the presence of PMMA units in **P-2**. Similarly the broadening of absorption band at 1637 cm^{-1} in the case of **P-3** indicates the presence of polyacrylate (COO) groups, which typically vibrate at 1560 cm^{-1} . In the FTIR spectra of **P-1** to **P-3**, the epoxy stretching vibrations noticed at 904 cm^{-1} for PGMA completely disappeared, thus suggesting the near quantitative opening of oxirane ring in these copolymers. Two other characteristic observations that can be noticed in Figure 3 are the broad absorption bands centered around 3450 cm^{-1} due to the OH groups formed as a result of opening of oxirane ring and also the disappearance of C-H stretching of oxirane ring present around 3000 cm^{-1} in the homopolymer, PGMA. Due to the strong hygroscopic nature of homopolymer PSSS, broad absorption band centered around 3450 cm^{-1} was highly apparent.

Thermal Properties

Thermogravimetric analyses of the dried gels (**P-1**, **P-2**, and **P-3**) and homopolymers PSSS and PGMA are shown in Figure 4. With the exception of PGMA, the strong hygroscopic nature of copolymers as well as homopolymer PSSS can be noticed by loss of weight below 100 °C which is due to the loss of surface water. The weight loss noticed between 200 and 400 °C in the case of both **P-1** and **P-2** is likely due to the loss of pendant groups formed as a result of opening of oxirane ring as well as loss of pendant groups from PMMA moiety. This is not more prominent in the case of copolymer **P-3** probably due to the fact that the pendant group may have been either shielded, the interaction was stronger or its concentration was comparatively lower due to its ternary polymeric nature.

Among the polymers studied, PGMA showed the lowest thermal stability. By comparing thermograms of PGMA with that of **P-1** to **P-3**, it could be deduced that, (i) **P-1** to **P-3** are truly copolymers and (ii) as confirmed by FTIR analysis, **P-1** to **P-3** completely lack GMA units because of the ring opening reaction. As expected, PGMA degraded completely without leaving any trace because of its aliphatic nature as well as due to the absence of any inorganic moieties. All the other copolymers as well as the homopolymer PSSS yielded residue due to its ash content derived from sodium salt. The fact that copolymers have left some residue corroborates the observations made from FTIR analysis. As expected, residue varies with the nature of polymer with PSSS showing the highest ash content of 50.5%. **P-3** showed higher ash content (45.7%) than **P-1** and **P-2** due to the presence of additional ash source in the form of copoly(sodium acrylate). Between **P-2** and **P-3** the lower ash content of **P-3** (33.3% vs. 38.4%) was due to its ternary nature and thus the concomitant dilution of backbone caused by the presence of PMMA units which do not produce any ash. Thus, TGA results not only supported the FTIR analysis of polymers but also confirmed that the copolymer composition by and large matched feed ratio of monomers during polymerization.

Swelling Experiments

The results of swelling studies are summarized in Table 1. The equilibrium swelling ratios were determined by soaking dried copolymers in deionized water and 0.9% NaCl solution for 24 h at room temperature. The copolymer **P-1** showed a maximum equilibrium swelling in deionized water which was about 74 times its dry weight (swelling ratio of 7380%). The other two copolymers **P-2** and **P-3** showed swelling ratios of 1676% and 445%, respectively. Surprisingly, the swelling ratio of **P-3** which is a terpolymer with all of its constituents supposedly strongly hydrophilic was lesser than **P-2**, another ternary polymer possessing hydrophobic units. This prompted us to have a closer look to find the reason behind this unexpected observation. Therefore, the protocol employed to separate the polymers from the gels obtained after polymerization was modified. Thus

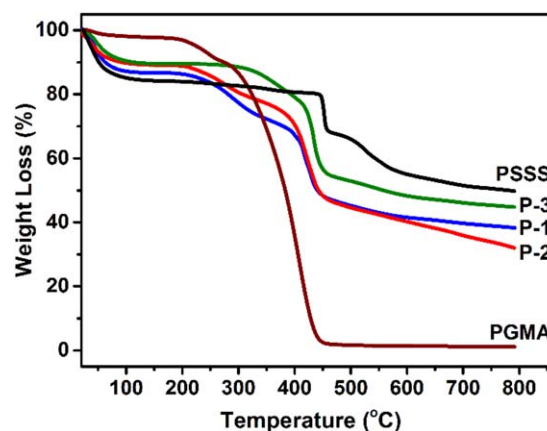


FIGURE 4 Thermogravimetric analysis of homo- and copolymers. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Equilibrium Swelling Ratio of Copolymers in Deionized Water and 0.9 wt% NaCl Solution at 25 °C

Co-Polymer	Eqbm. Swelling in DI Water		Eqbm. Swelling in 0.9% NaCl Soln	
	Dried at 50 °C	Freeze Dried	Dried at 50 °C	Freeze Dried
P-1	7380	7520	1623	810
P-2	1676	3330	970	1075
P-3	445	16120	337	864

instead of drying the polymerized gels at higher temperatures, copolymers were obtained from the gels by employing freeze drying technique. In freeze-dried samples the swelling pattern changed and followed the expected pattern based on the composition of copolymers. In freeze-dried samples, the swelling of **P-3** increased by 161 times of its dry weight and it was the highest swelling polymer followed by **P-1**. Swelling in the case of freeze-dried copolymers increased uniformly though the extent of swelling varied greatly in **P-2** and **P-3**. Such changes in swelling ratio according to sample treatment or processing method are typical of polymers crosslinked through physical interactions, in the present case through a combination of inter- and intrachain H-bonding. The physical nature of interactions was further confirmed by the loss of swelling in polymers which were subjected to heat treatment of above 90 °C. Figure 5 shows dynamic swelling behavior of **P-1**, **P-2**, and **P-3** in deionized water.

The equilibrium swelling was attained within approximately 90 min of soaking in deionized water. Swelling experiments with aqueous solution of NaCl of 0.154 mM concentration (0.9 wt%, equivalent to physiological saline) showed decrease in swelling ratio in a similar order as above: **P-1** >> **P-2** >> **P-3**. However, this order of swelling changed in the freeze-dried samples as **P-2** > **P-3** > **P-1**. Even though cross-linked sodium acrylate is the source of super absorbent

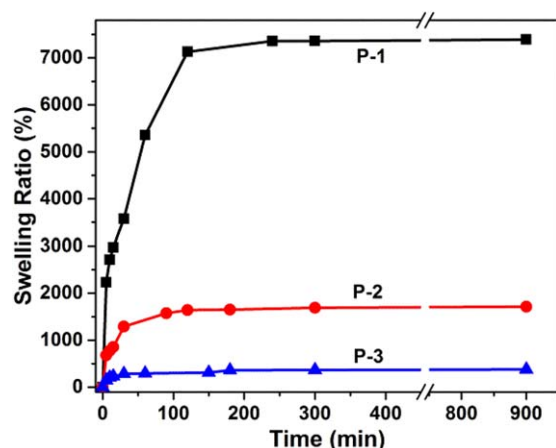


FIGURE 5 Equilibrium swelling of copolymers in deionized water. [Color figure can be viewed at wileyonlinelibrary.com]

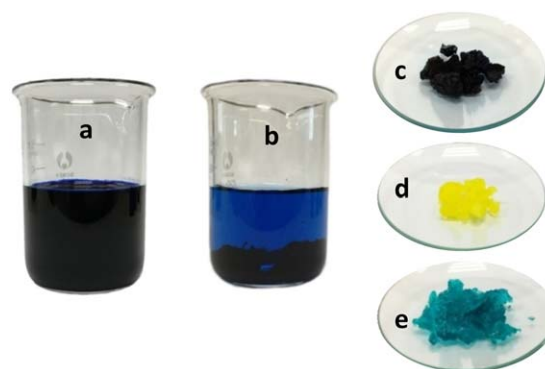


FIGURE 6 Absorption of dyes by hydrogels (a) aqueous solution of methylene blue, (b) polymer swollen with entrapped methylene blue in aqueous medium, (c) methylene blue absorbed by hydrogel separated from b, (d) acid yellow entrapped by hydrogel, and (e) polymer swollen with fast green. [Color figure can be viewed at wileyonlinelibrary.com]

polymers, the presence of acrylate unit did not change the swelling behavior in either of the samples. Apparently, NaCl solution induced disruption of network structure formed through physical interactions possibly via salt screening unlike deionized water.

The hydrogels formed in deionized water showed a tendency to absorb dyes dissolved in water. Thus, hydrogels formed *in situ* in dye solutions entrapped the dye in its network and settled down. The swollen polymer with dye can be separated from the aqueous medium conveniently by decanting off the aqueous layer. Three different dyes, namely Methylene Blue (MB), Fast Green FCF (FG), and Acid Yellow 3 (AY) were chosen to demonstrate the ability of these hydrogels to trap compounds dissolved in water.

Figure 6 shows the separation of methylene blue along with swollen polymer bearing other dyes, fast green and acid yellow. MB is a well-known cationic dye whereas both FG and AY are anionic in nature. All of these dyes absorb in the visible region with λ_{\max} 664 nm (MB), 624 nm (FG), and 413 nm (AY). Hence, using UV-vis spectroscopy, it is possible to determine the amount of dye absorbed by the hydrogels.

P-1 of known quantity (about 150 mg) was added to 20 mL of aqueous dye solutions with 200 ppm (MB and AY) and 50 ppm (FG) concentrations. The gel was allowed to equilibrate in dye solutions under ambient conditions for 6 h. Initially swollen by water, the hydrogel soon absorbed dyes. The solutions were then analyzed by UV-vis spectrophotometer to measure the drop in dye concentration. Thus by plotting a standard curve of known concentration of dye solution, the change in concentration posttreatment was determined. The UV-vis spectra of dye solutions before and after treating with **P-1** are shown in Figure 7.

The adsorption efficiency, Q_e of **P-1** was calculated by the following equation.⁹

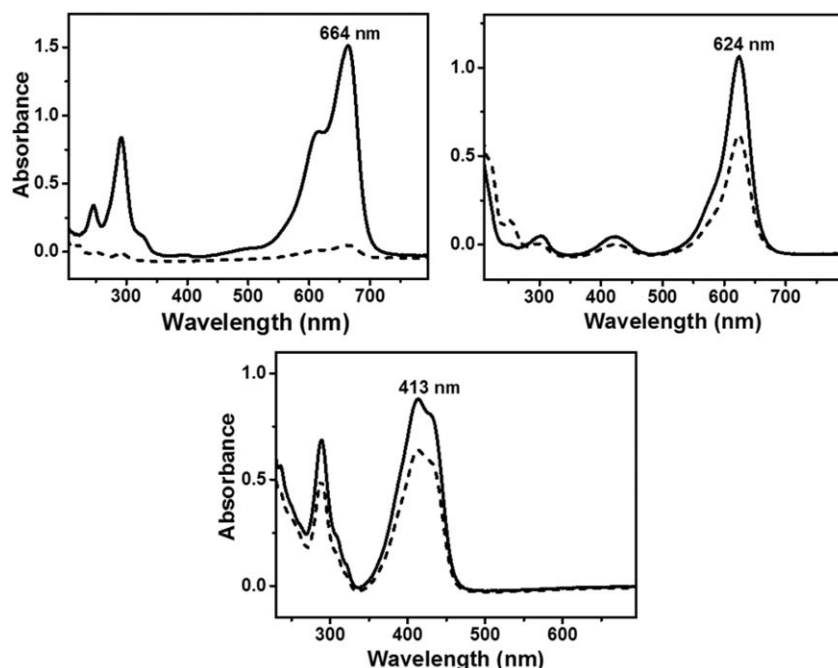


FIGURE 7 UV-vis spectra of dyes before (solid line) and after treatment (dotted line) with P-1: (a) MB, (b) FG, and (c) AY.

TABLE 2 Extraction Studies of P-1 with 3 Dyes and Their Corresponding Q_e Values

Dye	C_0 , mg/L	C_e , mg/L	V , mL	m , mg	Q_e , mg/g
MB	200	16.2	20	164	22.41
FG	50	29.6	20	143	2.85
AY	200	146.6	20	173	6.17

$$Q_e(\text{mg/g}) = (C_0 - C_e) \times V / m,$$

where C_0 and C_e (mg/L) are initial and equilibrium concentration of dye solutions, V is the volume of solutions in mL, and m is the adsorbent weight in mg. Table 2 summarizes the initial and final concentration of dye solutions and the extraction efficiency values for the adsorption of 3 dyes.

It can be noticed from the UV-vis spectra as well as from Q_e values, the extraction of the cationic dye, MB was the highest. Owing largely to the electrostatic interactions between the anionic sulfonates in gels with cationic functionality of MB, the absorption of MB was the highest. In other cases prevailing electrostatic repulsion between like charges reduced the absorption efficiency in spite of gelling behavior remaining unaffected. The gels can thus be potentially applied in selective extraction of dyes, also possibly to trap other cationic pollutants in water and thus can be explored further in the field of water purification.

CONCLUSIONS

Hydrogels were formed by the free radical polymerization of GMA with SSS in water. Model experiments confirmed that SSS catalyzed the opening of oxirane ring for the first time

in aqueous polymerization reactions involving GMA. The swelling of polymers was strongly dependent on the nature of treatment that the polymers were subjected to after polymerization. Heating the polymer samples below 50 °C as well as freeze drying the polymerized reaction mixture helped to preserve the network formed through inter- and intrachain H-bonding interactions while heating the samples above 90 °C caused the disruption of physical network thereby affecting the swelling. The swelling reduced considerably in 0.9 wt% NaCl solution as compared to that of deionized water. This lowered swelling in electrolyte solution may be caused by the screening of charges of SSS units by NaCl solution thereby disrupting the physical network formed through H-bonding interactions. It is interesting to note that homopolymer of SSS and that of 2,3-dihydroxypropyl methacrylate formed water soluble polymers whereas its copolymer formed hydrogel. Hydrogels derived from such 1,2-diols have been used in the preparation of magnetic nanoparticles⁴⁰ and also in solid phase extraction techniques.⁴¹ These hydrogels are also potentially useful in selected water purification applications as demonstrated by the absorption of dyes from aqueous solutions. Hydrogels have many applications in daily life. Polymers such as P1 because of their ability to swell in water are useful for applications in personal care and also in ion exchange membranes. The dye absorption studies demonstrate its suitability for applications like purification of industrial waste water.

ACKNOWLEDGMENTS

This work was funded by the Agency for Science, Technology and Research (A*STAR), Singapore under Environmentally

Friendly Specialty Products Programme headed by Alexander M. van Herk. The authors gratefully acknowledge the guidance provided by Tan Wui Siew of the Institute of Materials Research and Engineering, A*STAR and also thank Heng Teck Huat for assisting in TGA analysis.

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