

Thermoresponsive Super Water Absorbent Hydrogels Prepared by Frontal Polymerization

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Received 5 February 2010; accepted 10 March 2010

DOI: 10.1002/pola.24020

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Frontal polymerization was used as an alternative technique for the preparation of super water absorbent hydrogels obtained from acrylamide and 3-sulfopropyl acrylate, potassium salt (SPAK) in the presence of *N,N*-methylene-bisacrylamide as a crosslinker. All samples were synthesized in dimethyl sulfoxide, and their swelling behavior in water was investigated. It was found that their features are dependent on the monomer ratio used, which influenced the porous morphology, and consequently, the swelling capability. The swelling ratio ranges from about 1000% for the acrylamide homopolymer up to 14,000% for the sample containing

87.5 mol % of SPAK, thus indicating that this parameter can be easily tuned by using the appropriate monomer ratio. The affinity towards water was eventually confirmed by contact angle analysis. Polymer hydrogels made from at least 62.5 mol % SPAK exhibit a thermoresponsive behavior, with a lower critical solution temperature of ~ 30 °C. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 2486–2490, 2010

KEYWORDS: free radical polymerization; frontal polymerization; hydrogels; polyacrylamides; radical polymerization; stimuli-responsive polymers; stimuli-sensitive polymers; swelling

INTRODUCTION Polymer gels are three-dimensional networks belonging to the “Soft Matter” category,¹ depending on the nature of crosslinks, they can be classified as chemical or physical gels.^{2,3} These materials are able to swell in a suitable solvent without dissolving. Polymer gels exhibiting a hydrophilic behavior are called hydrogels, which are considered very interesting materials primarily because of their swelling properties.⁴ As the biologic environment is mainly composed of water, they have several applications in both pharmaceutical and biomedical fields.^{5,6} Indeed, their good biocompatibility and mechanical properties make them very useful for the preparation of a number of biomaterials in contact with biological fluids.^{7,8} In particular, they are used for soft contact lenses,⁹ drug delivery,^{10–12} artificial tendons and tissues, reconstruction of cartilage.^{13,14}

Some of these materials are stimuli-responsive in that they undergo a volume phase transition characterized by a sudden variation in the degree of swelling upon a change in environmental conditions. Namely, stimuli-responsive hydrogels exhibiting a high swelling capacity can be used in a wide number of biomedical fields¹⁵ in which a fast response rate to the external stimulus^{16,17} is needed. Examples of external stimuli are variation of pH,^{10,18,19} salt concentration,¹¹ solvent,²⁰ and temperature control,^{11,19,21,22} all of them having the effect of modifying the hydrophilic/hydrophobic balance.

Poly(*N*-isopropylacrylamide), poly(NIPAAm), is one of the most investigated thermoresponsive hydrogel polymers.²³

Although it shows a lower critical solution temperature (LCST) at around 32–33 °C, which makes it very useful in biological systems,¹⁵ this polymer is characterized by undesirable problems of biocompatibility. To overcome this problem, several copolymers were synthesized, such as those with ethylene glycol,²⁴ 2-alkyl-2-oxazoline and 2-hydroxyethyl methacrylate,²⁵ propylacrylic acid,²⁶ ethylene imine,^{27,28} lysine and glutamic acid,²⁹ and 2-carboxyisopropylacrylamide.³⁰

Another polymer with large versatility in biomedical areas is polyacrylamide, (poly(AAm)).⁶ If combined with *N,N*-methylene-bisacrylamide (BIS) as a crosslinker, it gives rise to hydrogels with large swelling capability.^{31,32} Its swelling and collapse behaviors were widely studied.^{33,34} To increase its swelling property, Okay et al.^{35,36} incorporated 2-acrylamido-2-methylpropane sulfonic acid sodium salt into the hydrogel network as a comonomer thus obtaining a stimuli-responsive copolymer.

Hydrogels with a very large swelling capability in aqueous media belong to the category called super water absorbent polymers. They are formed of highly hydrophilic crosslinked macromolecules that present high water absorption.^{37–39} This property is because of the flexibility and hydrophilicity of their polymer network, which may be high or low depending on the chemical composition of the hydrogel.^{40–42}

In 2001, Washington and Steinbock⁴³ were able to obtain poly(NIPAAm) gels by frontal polymerization (FP),⁴⁴ a technique

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 48, 2486–2490 (2010) © 2010 Wiley Periodicals, Inc.

that allows the fast conversion of a monomer into a polymer as a consequence of the heat released during the polymerization reaction itself. The result is the formation of a polymerization front able to self-sustain and propagate along the whole reactor.

FP was proposed for the first time by Chechilo and Enikolopyan.⁴⁵ Pojman and coworkers polymerized epoxy resins,^{46,47} acrylic monomers,^{48–51} ionic liquids,⁵² thermochromic composites,^{53,54} poly(dicyclopentadiene),⁵⁵ and multifunctional thiol-ene systems.⁵⁶ Crivello studied the polymerization of glycidyl ethers,^{57,58} Chen and coworkers frontally polymerized 2-hydroxyethyl acrylate⁵⁹ and *N*-methylolacrylamide systems^{60,61}; moreover, they obtained epoxy resins/polyurethane networks,⁶² polyurethane-nanosilica hybrid nanocomposites,⁶³ poly(*N*-vinylpyrrolidone)⁶⁴ and thermosensitive hydrogels.⁶⁵ Frontal radical polymerizations of vinyl monomers in nonstationary mode were investigated theoretically by Tonoyan et al.⁶⁶

Our group applied FP to get polyurethanes,^{67,68} interpenetrating polymer networks,⁶⁹ unsaturated polyester/styrene resins,⁷⁰ poly(diurethane diacrylates)⁷¹, and to the atom transfer radical polymerization of acrylic monomers.⁷² Moreover, we applied FP to the restoration area of wood⁷³ and stone⁷⁴ consolidation and to obtaining polymer nanocomposites containing polyhedral oligomeric silsesquioxanes.⁷⁵ Also, FP was exploited to obtain controlled drug release systems.⁷⁶

Recently, by FP we synthesized poly(*N,N'*-dimethylacrylamide)⁷⁷ and prepared thermoresponsive hydrogels based on NIPAAm, in some cases properly copolymerized to increase biocompatibility.⁷⁸

In this article, we report on the application of FP to the preparation of super water absorbent hydrogels⁷⁹ starting from AAm with the addition of SPAK^{38,39} as an anionic monomer and BIS as crosslinker. The swelling behavior and water contact angle (WCA) analysis were used for sample characterization.

EXPERIMENTAL

Materials

Acrylamide (AAm, 99%, FW = 71.8, mp = 84–86 °C), 3-Sulfopropyl acrylate, potassium salt (SPAK, FW = 232.3, mp = 302 °C), ammonium persulfate (AmPS, FW = 228.20), dimethyl sulfoxide (DMSO, FW = 78.13, bp = 189 °C, $d = 1.101$ g/mL), and *N,N'*-methylene-bisacrylamide (BIS, FW = 154.17, mp = 300 °C) were purchased from Sigma-Aldrich and used as received. At 25 °C, all the monomer mixtures discussed below were stable for several days, that is, without undergoing spontaneous polymerization.

Characterization

DSC thermal characterization was performed by means of a Q100 Waters TA Instruments calorimeter, with a TA Universal Analysis 2000 software. Two heating ramps, from –80 to 250 °C, with a heating rate of 10 °C/min, were carried out on dry samples: the first scan was performed to remove

TABLE 1 Composition of Samples (BIS: 2.5 mol %; AmPS: 1 mol %, DMSO)

Sample code	AAm (mol %)	SPAK (mol %)
FP1	12.5	87.5
FP2	25.0	75.0
FP3	37.5	62.5
FP4	50.0	50.0
FP5	75.0	25.0
FP6	100	0

eventual residual solvent and to establish monomer conversion; the second one was to determine the glass transition temperatures (T_g). Conversions were always quantitative and T_g were always around 190 °C.

WCAs of dried samples were determined by a Dataphysics OCA 5, 10 instrument.

To determine their swelling ratio (SR %) in water, hydrogels were heated from 10 to 50 °C in a thermostatic bath by increasing temperature at a rate of 2 °C/day, and from 50 to 80 °C by increasing temperature at a rate of 10 °C/day. SR % was calculated by applying the following equation:

$$\text{SR \%} = (M_s - M_d)/M_d \times 100 \quad (1)$$

where M_s and M_d are the hydrogel masses in the swollen and in the dry state, respectively.

Hydrogel Synthesis

A set of hydrogels was obtained by varying the molar fraction of the two monomers, from AAm homopolymer to a copolymer containing 87.5 mol % of SPAK (Table 1) keeping constant the total molar amount of the two monomers (3.2×10^{-2} mol), the amounts of crosslinker (BIS, 2.5 mol % referred to the total amount of monomers), initiator (AmPS, 1 mol % referred to the total amount of double bonds), and DMSO (2.5 mL).

A common glass test tube (i.d. = 1.5 cm, length = 16 cm) was filled with the appropriate amounts of AAm and SPAK, DMSO. The mixture was sonicated in an ultrasound bath at 30 °C for 1 min. Then, BIS and AmPS were added and the mixture was again sonicated for 1 min and shaken.

A thermocouple junction was located at about 1 cm from the bottom of the tube and connected to a digital temperature recorder. Front started by heating the external wall of the tube in correspondence of the upper surface of the monomer mixture, until the formation of the front became evident. The position of the front (easily visible through the glass wall of test tubes) against time was measured. Front temperature measurements were performed by using a K-type thermocouple connected to a digital thermometer (Delta Ohm 9416) used for temperature reading and recording (sampling rate: 1 Hz). For all samples, front temperature (T_{max} , ± 10 °C) and front velocity (V_f , ± 0.5 cm/min) were measured.

After polymerization, all samples were washed in water for several days to remove DMSO and allow them to swell.

RESULTS AND DISCUSSION

To study the effect of the relative amounts of monomers, the ratio between AAm and SPAK was allowed to vary by keeping constant all the other parameters (Table 1), including total monomer concentration, amount of initiator, crosslinker, and DMSO. This latter solvent was necessary to dissolve all the components and preparing homogeneous mixtures.

The double- Y plot (Fig. 1) shows T_{\max} and V_f values recorded during the FP experiments.

As can be seen, both parameters increase as AAm concentration is raised. It should also be highlighted that 12.5 mol % AAm is the minimum amount of this monomer that allows FP to self-sustain. T_{\max} goes from 110 °C, for the copolymer containing 12.5 mol % AAm, to 227 °C for AAm homopolymer, whereas V_f goes from 0.5 to 6.8 cm/min.

To investigate the SR % of all hydrogels, they were swollen and equilibrated in water at various temperatures from 10 to 80 °C.

As shown in Figure 2, a relationship exists between SR % and the amount of SPAK; in fact, it increases as the latter raises. Namely, the sample with the largest amount of SPAK (FP1) exhibits the highest swelling ratio, that is around 14,000% at 10 °C, whereas it is as low as ~5000% at $T = 36$ °C and about 4000% at 80 °C. Such a large SR % allows one to consider them as super water absorbent hydrogels.

It is noteworthy that SR % decrease is quite sharp and happens as the hydrogel is heated above 25 °C, thus suggesting the presence of an LCST, which can be located at ~30 °C. All samples containing up to 37.5 mol % AAm (FP1-3) exhibit a similar thermoresponsive behavior. An analogous result was also found in the NIPAAm/SPAK copolymers (Scognamillo et al., in preparation), thus suggesting that SPAK influences the possible presence of an LCST, and the amount of swelling; on the contrary, it does not seem to have large influence on the

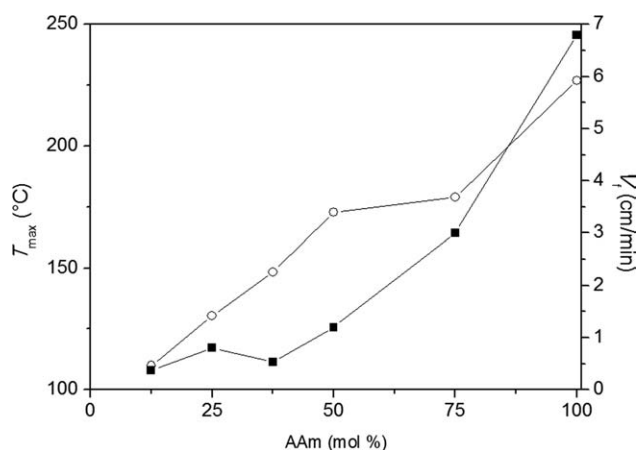


FIGURE 1 T_{\max} (○) and V_f (■) as functions of the molar amount of AAm.

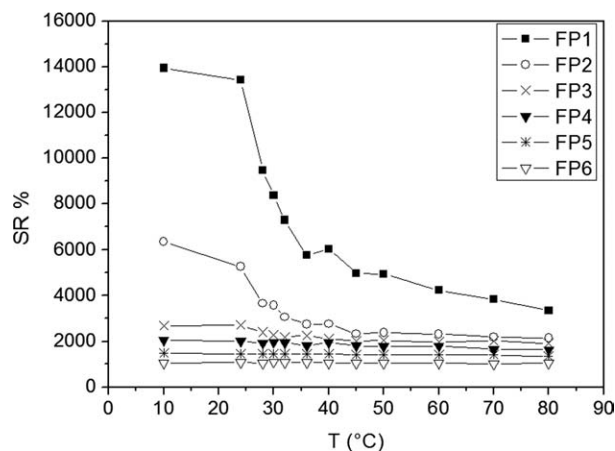


FIGURE 2 SR % as a function of temperature for samples characterized by different monomer ratio.

actual LCST value, which is always around 30–35 °C. However, it should be highlighted that the difference of SR % as temperature exceeds LCST becomes gradually smaller as the AAm content is increased in the copolymer samples. In particular, no LCST is exhibited by those samples in which the content of SPAK is not sufficiently large.

The above results suggest that the AAm/SPAK copolymer could be used as a possible alternative to poly(NIPAAm) in that it is characterized by similar LCST (i.e., around 30 °C). However, the present system has the advantage of being tunable in swelling and characterized by much lower cost.

In a recent article, Chen et al. reported on the use of contact angle analysis for the characterization of wet hydrogels.⁸¹ At variance, in this work such analysis was carried out on the dry samples.

As can be observed in Figure 3, the affinity of the polymer toward water increases as the amount of SPAK increases (decreasing angles). In detail, sample FP1, containing 12.5 mol % AAm, exhibits a WCA of 33°. This value reaches 87°

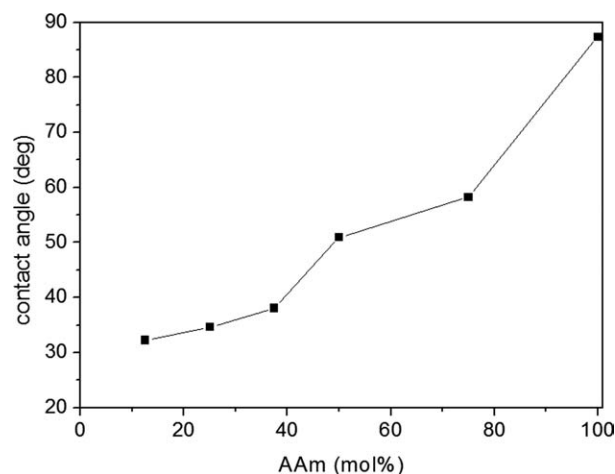


FIGURE 3 Water contact angle for hydrogels made from different AAm/SPAK ratios.

when the amount of AAm is 100 mol % (sample FP6). These data confirm the trend already discussed about SR %. In particular, the hydrophilic character of these samples is strongly dependent on the SPAK content, as one could be expected by considering its ionic nature.

CONCLUSIONS

In this work, a number of crosslinked polymer hydrogels made from AAm and SPAK were successfully prepared by FP in DMSO as a solvent, which was necessary to get a homogeneous mixture. It was found that FP can be successfully performed if the content of AAm is at least of 12.5 mol %.

The hydrogels swollen in water are characterized by SR % values that are dependent on composition and temperature. In particular, it was found that SPAK dramatically influences the degree of swelling, the SR % being larger for those copolymers prepared from large salt content. The hydrophilic character, which increases as the amount of SPAK increases, was also confirmed by contact angle analysis made on the dry samples.

However, one of the most relevant results of the present work is that, if the amount of SPAK is at least equal to 62.5 mol %, a thermoresponsive super water absorbent polymer hydrogels are obtained. Moreover, they exhibit an LCST at ~ 30 °C, which is a temperature very close to that of poly(NIPAAm), the most studied and used thermoresponsive polymer.

In particular, it can be as large as 14,000%, thus potentially allowing for a number of applications larger than that of poly(NIPAAm). Furthermore, it should be also highlighted that both SPAK and AAm are much cheaper than NIPAAm.

Finally, it should be also underlined that the super water absorbent polymer hydrogels studied in this work were prepared by using FP, which has confirmed to be a very fast and reliable technique for polymer synthesis.

The authors are in debt with Plinio Innocenzi and Cristiana Figus (University of Sassari, Italy) for the precious scientific discussions and their kind assistance in water contact angle analysis. S. Scognamillo is grateful to "Regione Autonoma della Sardegna" for the financial support ("Master and Back" program).

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