3-Mercaptopropionic Acid–Ce(IV) Redox Couple for Preparing Cross-Linked Gels with Moderate Swelling Ratios

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ABSTRACT: 3-Mercaptopropionic acid–Ce(IV) redox couple has been demonstrated to be useful for cross-linking polymerization of acrylamide (AAm) with *N*,*N*′-methylene bis(acrylamide) (MBAA). Effects of the cross-linker ratio, acid concentration, and Ce(IV) molar ratios on swelling behavior of the resulting hydrogels have been studied. These experiments show that increasing cross-linker content has greatly reduced the equilibrium swelling ratios as expected. Interestingly, the increase in the Ce(IV) concentration ($n_{\mathrm{Ce(IV)}} = n_{\mathrm{MPA}}$) has resulted in a decrease in the swelling ratio. Because the thiol group in 3-mercaptosuccinic acid acts as a cross-linking agent, more cross-linking occurs with an increase in the Ce(IV) concentration and Ce(III) forming in the cross-linking polymerization reaction of AAm with MBAA may provide the formation of intermolecular complexes between amide groups in polymer chains; the swelling equilibrium ratio and swelling rate decrease with an increase in their concentrations in the cross-linking polymerization reaction of AAm with MBAA. Kinetics and equilibrium swelling values have been discussed in terms of reaction parameters. © 2012 Wiley Periodicals, Inc. Adv Polym Techn 32: E241–E248, 2013; View this article online at wileyonlinelibrary.com. DOI 10.1002/adv.21270

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KEY WORDS: Acrylamide, Hydrogels, *N*,*N*′-Methylene bis(acrylamide), Redox polymers, Swelling)

Introduction

Hydrogels have recently been of increasing interest in various applications.[1,2] The gels are useful for drug delivery systems, separation operations in biotechnology, processing of agricultural products, sensors, and actuators.[3–9] The volume phase transitions of hydrogels are introduced by a continuous change in various conditions of network such as temperature, pH, electrical field, radiation of UV or visible light, solvent composition, salt concentration, and type of surfactants.[10–16]

The swelling equilibrium of gels resulted from both the free energy of elasticity and free energy of mixing. In acrylamide (AAm)–*N*,*N*′-methylene bis(acrylamide) (MBAA) hydrogel/water system, water diffuses into the network by forces determined by the difference of chemical potential of water between the network inside and outside. The swelling gel reaches the equilibrium state at a higher concentration of water in the gel phase. Contribution of elastic forces to the chemical potential of water prevents the polymer from becoming completely dissolved.[2,16–18] Numerous scientists have made great efforts to investigate the synthesis and swelling properties of gel particles. In the synthesis of gel particles, potassium persulfate or ammonium persulfate with/without *N*,*N*,*N*′,*N*′-tetramethylenediamine initiator systems have been generally used.[19–24] A ceric salt-organic reducing agent containing thiol, hydroxyl, carboxyl, and amine functional groups can be used for polymerization and copolymerization of vinyl monomers.[25–36] However, ceric salt-organic reducing agents containing the thiol functional group or groups are new sources to initiate copolymerization of vinyl monomers at low temperatures. When a reducing agent with the thiol functional group is used in a redox system of the ceric salt-organic reducing agent, the formation of the −S• radical is energetically most favorable due to low S—H bonding energy to initiate copolymerization of gel particles in acid aqueous medium at lower temperatures.[25–30,32]

In this study, the 3-mercaptopropionic acid–Ce(IV) redox system was used to synthesize the cross-linked polymer of AAm with MBAA in acid aqueous medium. The effects of parameters such as molar ratios of AAm to MBAA, AAm to cerium(IV) sulfate, and the concentration of sulfuric acid were investigated. The swelling ratios (SR) and kinetics of hydrogels synthesized at different reaction parameters such as the n_{AAm}/n_{MBAA} at a constant initiator and acid concentrations, the concentration of sulfuric acid for $n_{AAm}/n_{MBAA} = 40$ at the constant initiator concentration, and the $n_{AAm}/n_{Ce(IV)}$ at constant acid and cross-linker concentrations were also investigated.

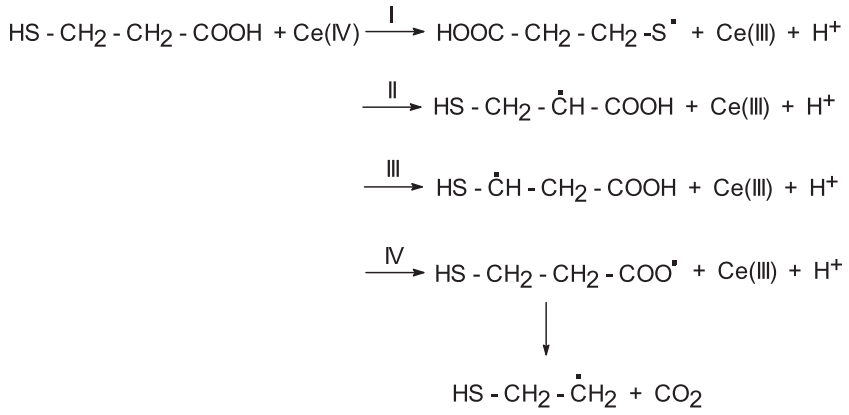
Experimental

MATERIALS

AAm (Merck, Darmstadt, Germany), MBAA (Fluka, Taufkirchan, Germany), cerium(IV) sulfate (Merck), and 3-mercaptopropionic acid (MPA) (Merck) were used as received. Sulfuric acid (Merck) with purity of 98% was used in a redox reaction of MPA and cerium(IV) sulfate.

PREPARATION OF P(AAm-MBAA) HYDROGELS

To prepare acrylamide–*N*,*N*′-methylene bis (acrylamide) (P(AAm-MBAA)) hydrogels, the solution containing the calculated amount of Ce(IV) dissolved in acidic medium was added to the aqueous solution of AAm, MBAA, and MPA in a round-bottomed flask equipped with a stirrer. For this purpose, the oxidant (cerium(IV) sulfate) was dissolved in a solution containing the calculated amount of sulfuric acid. The solution volume containing oxidant was kept constant at 20 mL. The total volume of a cross-linking polymerization solution was 100 mL. The aqueous polymerizing solutions were mixed by a magnetic stirrer for about 10 min at constant temperature ($T = 30^{\circ}C$). The formed hydrogels and each of unpolymerizing solutions filled into glass vessels (volume $\approx$ 100 mL) were stored in a water bath at 25°C for about 24 h to achieve a complete polymerization. The synthesized hydrogels were cut into pieces of 3–4 mm length, washed with water to remove unreacted compounds, and



SCHEME 1. Radical formation reactions between MPA and Ce(IV) in acid aqueous medium.

dried in a vacuum oven at 60°C. The dry hydrogels were replaced in the sintered glass funnels, which were immersed in distilled water. The swelling of the hydrogels was monitored by mass measurements depending on time. One hundred and sixty eight hours were approximately enough to reach equilibrium swelling. Once equilibrium was attained, the hydrogels were weighed, dried at 60° in vacuum for 24 h, and reweighed. The effects of parameters such as the molar ratios of AAm /cerium(IV) sulfate ($n_{AAm}/n_{Ce(IV)} = 150$, 250, and 400) at the constant cross-linker and acid concentration, the molar ratios of AAm to MBAA ($n_{AAm}/n_{MBAA} = 20$, 40, and 60) at the constant initiator concentration ($n_{AAm}/n_{Ce(IV)} = 250$; $n_{MPA} = n_{Ce(IV)}$), and the concentration of sulfuric acid ($C_{H2SO4} = 0.01$ and 0.02 mol/L) at the $n_{AAm}/n_{MBAA} = 40$ on the swelling behaviors and kinetics of synthesized hydrogels were investigated.

The radical generation in the redox reaction of MPA and cerium(IV) sulfate in acid aqueous medium is believed to occur by one-electron transfer from MPA to Ce(IV) according to the reactions given in Scheme 1 as reported in the literature.[25–30,32,37]

Because of low S—H bonding energy, the formation of free radicals in reaction (I) in the Scheme 1 is more likely than other reactions to initiate cross-linking polymerization of AAm and MBAA, and oxidative termination of polymer radicals is also possible by ceric ions.[25,27,28,30,32,37] In previous investigations, it is described that the formation of radicals on carboxyl groups may be possible.[25–33,37] However, the radical formation on carboxyl groups may appear less than that of the other radical formation reactions given in Scheme 1, due to necessity of higher energy for the formation of free radicals on carboxyl groups and formation of ionization of carboxyl groups in an aqueous medium.

After radical generation by the redox reaction of MPA–Ce(IV) in acid aqueous medium, the cross-linking polymerization of AAm with MBAA was performed and the cross-linked copolymer having a chemical formula given in Scheme 2 was synthesized.

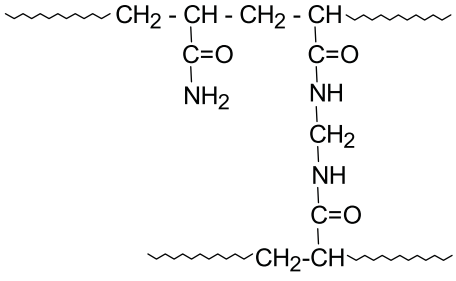
Results and Discussion

SRs and the values of equilibrium swelling ratios (ESR) of resulting hydrogels have been calculated using Eqs. (1) and (2):

$$\mathrm{SR} = \frac{m_t - m_0}{m_0} \tag{1}$$

$$\mathrm{ESR} = \frac{m_{eq} - m_0}{m_0} \tag{2}$$

where SR represents the average the swelling ratio of hydrogel in distilled water, obtained in triplicate



SCHEME 2. Chemical structure of the synthesized P(AAm-MBAA) hydrogel.

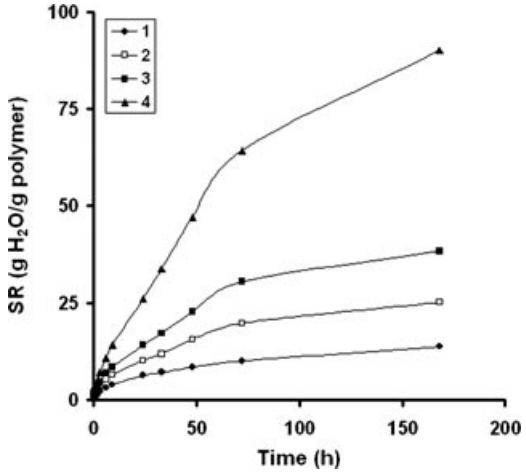


FIGURE 1. Dependence of SRs of synthesized P(AAm-MBAA) hydrogels in distilled water on a cross-linker and acid concentrations. The molar ratios of $n_{AAm}/n_{MBAA} = 20$ (curve 1), 40 (curve 3), and 60 (curve 4) for 0.01 moL/L H_2SO_4 and $n_{AAm}/n_{MBAA} = 40$ (curve 2) for 0.02 mol/L H_2SO_4 concentration. $C_{AAm} = 0.7$ mol/L, $n_{AAm}/n_{Ce(IV)} = 250$, $n_{Ce(IV)} = n_{MPA}$, and $T = 30^\circ$.

from experiments. m_t and m_0 are the weights of hydrogel at time t and dried gel at an initial time t_0, respectively. ESR denotes the equilibrium swelling ratios in terms of g H_2O/g polymer, and the m_{eq} is the weight of hydrogel at the equilibrium.

The effects of the molar ratios of (AAm/MBAA) and the acid concentration at the constant initiator ($n_{AAm}/n_{Ce(IV)} = 250$; $n_{MPA} = n_{Ce(IV)}$) concentration on SRs are shown in Fig. 1. As can be seen from Fig. 1, the increase in the molar ratio of (AAm/MBAA) at the constant acid concentration of 0.01 mol/L has increased SRs of hydrogels (Fig. 1, curves 1, 3, and 4). ESR are dependent on the n_{AAm}/n_{MBAA} in the cross-linking polymerization reaction. ESR have been determined as 13.80 g H_2O/g copolymer, 38.50 g H_2O/g copolymer, and 90.20 g H_2O/g copolymer for values of 20, 40, and 60 of the n_{AAm}/n_{MBAA}, respectively. This indicates that a hydrogel having less cross-linked bonds swells better than a hydrogel having more cross-linked bonds as expected.

It has been reported that H_2SO_4 is used to increase the solubility of oxidant (cerium(IV) sulfate) and to prevent the hydrolysis of oxidant in the redox reaction of MPA–Ce(IV).[25–29,32] For this reason, the MPA–Ce(IV) redox couple has been performed in acid aqueous medium to initiate cross-linking polymerization of AAm with MBAA. The dependence of SRs of hydrogels on the acid concentration in the cross-linking polymerization reaction at a constant cross-linker molar ratio of $n_{AAm}/n_{MBAA} = 40$ is also given in Fig. 1. The values of ESR of hydrogels synthesized at different acid concentrations of 0.02/ and 0.01 mol/L have been determined as 25.30 g H_2O/g copolymer and 38.50 g H_2O/g copolymer for $n_{AAm}/n_{MBAA} = 40$, respectively, (Fig. 1, curves 2 and 3). An increase in the acid concentration in cross-linking polymerization of AAm with MBAA has resulted in a decrease in SR and ESR of hydrogel. This phenomenon has been attributed to increasing acid concentration in the polymerization reaction. At higher acid concentration, the hydrolysis of $-CONH_2$ group in AAm has increased and some of functional groups ($-COHN_2$) in hydrogels have converted to functional groups of $-COOH$.[37,38] The functional groups $-CONH_2$ and $-COOH$ in hydrogels react with each other to form the imide functional groups ($-CONHOC-$) in P(AAm-MBAA) hydrogels. For this reason, the hydrogel synthesized at a higher acid concentration swells less than that synthesized at a lower acid concentration.

The effect of the molar ratios of AAm/Ce(IV) in the cross-linking polymerization reaction at constant acid and cross-linker concentrations on the SRs of P(AAm-MBAA) hydrogels in distilled water is illustrated in Fig. 2. The increase in the $n_{AAm}/n_{Ce(IV)}$

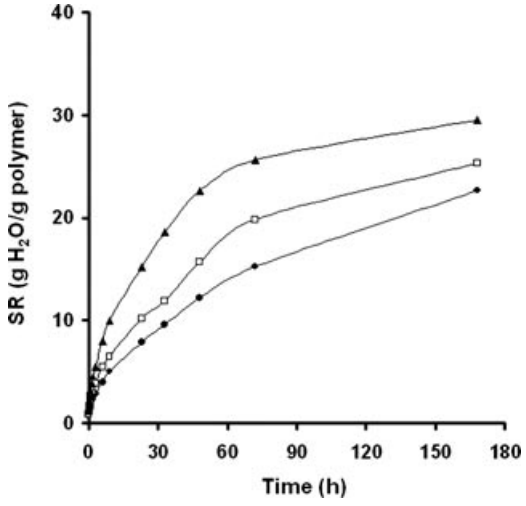


FIGURE 2. Relation between the molar ratios of AAm to the initiator in the cross-linking polymerization reaction and the SRs of P(AAm-MBAA) hydrogels in distilled water, synthesized using the MPA–Ce(IV) redox system in acid aqueous medium. $n_{AAm}/n_{Ce(IV)} = 150$ (●), 250 (□), and 400 (▲). $C_{AAm} = 0.7$ mol/L, $C_{H2SO4} = 0.02$ mol/L, $n_{AAm}/n_{MBAA} = 40$, $n_{Ce(IV)} = n_{MPA}$, and $T = 30^\circ$.

resulted in an increase in the SRs of hydrogels in distilled water. ESR of hydrogels increased from 22.65 g H_2O/g copolymer to 29.50 g H_2O/g copolymer, with increasing the molar ratios of AAm/Ce(IV) in the cross-linking polymerization reaction at the constant acid concentration (0.02 mol/L) and cross-linker ratio ($n_{AAm}/n_{MBAA} = 40$). This is evidence that the augmentation in the initiator concentration in the synthesis of P(AAm-MBAA) hydrogel using the cerium(IV)–MPA redox system has decreased SRs and ESR of synthesized AAm-MBAA hydrogels in distilled water. Ce(IV) reduced to Ce(III) in the redox reaction between cerium(IV) sulfate and MPA in acid aqueous medium. Because forming of Ce(III) in the cross-linking polymerization reaction of AAm with MBAA may lead to formation of intermolecular complexes between amide groups in polymer chains; and the increase in Ce(IV) in polymerization reaction may cause an increase in more cross-linking formation, or the thiol group in MPA may act as a cross-linking agent; the swelling equilibrium ratio and swelling rate decrease with an increase in their concentrations.

To indicate the efficiency of the redox initiation system, the yields of dried gels synthesized at different initiator concentrations ($n_{AAm}/n_{Ce(IV)} = 150$, 250, and 400; $C_{AAm} = 0.7$ mol/L; $n_{AAm} = n_{MPA}$) at the constant acid concentration (0.02 mol/L) and cross-linker ratio ($n_{AAm}/n_{MBAA} = 40$) were determined and are illustrated in Fig. 3. As can be seen from Fig. 3, the increase in the molar ratio of AAm/Ce(IV) from 150 to 400 led to a little decrease in the yield of the synthesized gel from 100% to 93.4%. This indicates that the efficiency of the redox initiation system of Ce(IV)–MPA in acid aqueous medium for the cross-linking polymerization of AAm using MBAA as a cross-linker is good enough to synthesize P(AAm-MBAA) gels, and the experimental results indicate that it may find applications in scientific and industrial areas.

The kinetic swelling results of hydrogels synthesized at various reaction parameters were examined by the Peppas kinetic formula[39–42] (Eq. (3)):

$$\frac{m_t}{m_{eq}} = kt^n \tag{3}$$

a linearized form of Eq. (3) can be written as Eq. (4)

$$\ln \frac{m_t}{m_{eq}} \ln k + n \ln t \tag{4}$$

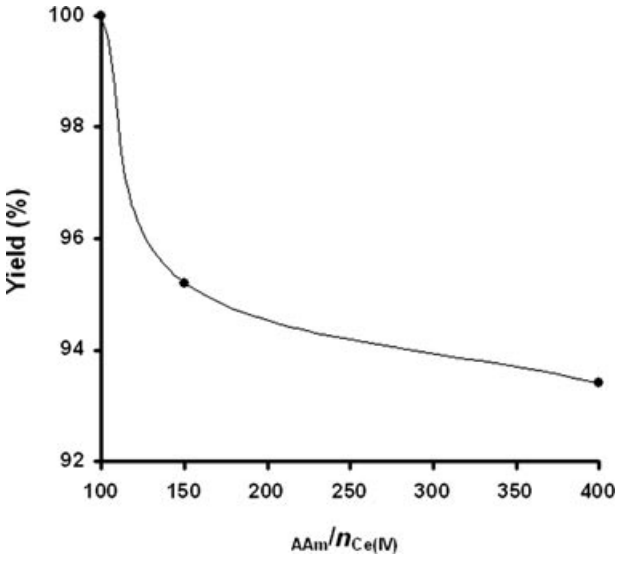


FIGURE 3. Dependence of the yield on the molar ratio of AAm/Ce(IV) for the cross-liking polymerization of AAm with MBAA as a cross-linker using the redox initiation system of Ce(IV)–MPA in acid aqueous medium. $C_{AAm} = 0.7$ mol/L, $n_{AAm} = n_{MPA}$, $C_{H2SO4} = 0.02$ mol/L, $n_{AAm}/n_{MBAA} = 40$, and $T = 30^\circ$.

where m_t and m_{eq} are the weights of hydrogels at time, t, and at equilibrium, respectively. k and n are constants. The numerical value of n provides information about a mechanism of swelling kinetics. This equation is applicable to the initial stages of swelling and yields only straight lines up to nearly 60% of the maximum amount of absorption water.[21,39,42] Using this criterion, the exponent, n, and k values are obtained from slope and intercept determined from a plot of ln (m_t/m_{eq}) versus ln t, respectively.

Figure 4 shows a logarithmic plot (ln (m/m_{eq}) versus ln t) of the swelling rate of AAm-MBAA hydrogels with various cross-linker contents. The kinetic parameters (k and n values obtained from the slop and intercept of straight lines) in the swelling kinetic equation of P(AAm-MBAA) hydrogels synthesized at different acid, initiators, and cross-linker concentrations are listed in Table 1. The results show that increasing the cross-linker ratio results in a significant rise in k whereas the n exponent slightly decreases. The effect of the acid concentration of the initiation system on the swelling behaviors has been examined (Fig. 5). As can be seen from Fig. 5 and Table 1 that at a higher acid concentration, the swelling of gels is slow, the corresponding k value increases by increasing the acid concentration, while the n value somewhat decreases.

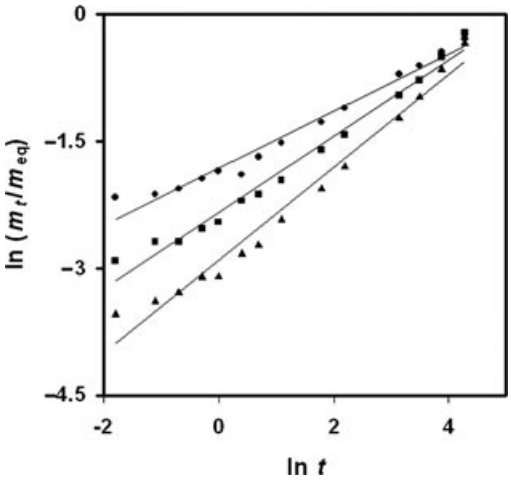


FIGURE 4. Effect of molar ratios of AAm to a cross-linker on the swelling rates of P(AAm-MBAA) hydrogels in distilled water. $n_{AAm}/n_{MBAA} = 20$ (●), 40 (■), and 60 (▲).

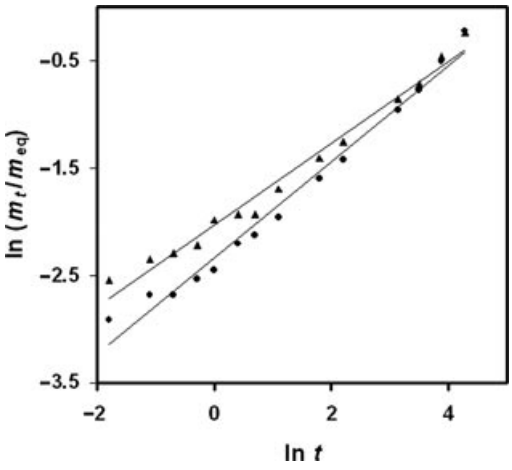


FIGURE 5. Relation between acid concentrations in cross-linking polymerization reactions at the constant cross-linker concentration ($n_{AAm}/n_{MBAA} = 40$) and the swelling rate of synthesized P(AAm-MBAA) hydrogels in distilled water. $C_{H2SO4} = 0.01$ (●) mol/L and 0.02 (▲) mol/L.

The swelling rate of P(AAm-MBAA) hydrogels synthesized at different initiator concentrations ($n_{AAm}/n_{Ce(IV)} = 150$, 250, and 400) is shown in Fig. 6. The increase in the initiator concentration in the cross-linking polymerization reaction of P(AAm-MBAA) hydrogels synthesized using the MPA–Ce(IV) redox system in acid aqueous medium has led to a decrease in the swelling rate. Moreover, it has been observed that swelling rates and equilibrium swelling values are influenced by initiator concentrations. The n values decrease with an increase in Ce(IV) and MPA concentrations (Table 1). Because the thiol group in MPA and Ce(IV) has led to more cross-linking in the synthesis of P(AAm-MBAA) hydrogel.

Conclusion

The swelling of polymeric networks is affected by the composition of polymer, that is, synthetic conditions such as the n_{AAm}/n_{MBAA} in polymeric networks and the nature of swelling media. These types of hydrogels containing functional groups have a potential to be used as colon-specific drug delivery devices and can be used for water absorption from oil–water emulsions.[43–45] The carboxylic acids that are biotechnological waste substances released in many industries can be removed by using cross-linked AAm hydrogels.[46]

TABLE I
Dependence of Kinetic Parameters in the Swelling Kinetic Equation Fitting Data Obtained from Swelling Results of P(AAm-MBAA) Hydrogels in Distilled Water on the Acid Concentration in the Cross-Linking Polymerization Reaction

C_{H2SO4} (mol/L)	$n_{AAm}/n_{Ce(IV)}$	n_{AAm}/n_{MBAA}	n	k	Correlation Coefficient, (R)
0.01	250	20	0.336	16.28×10^{-2}	0.973
0.01	250	40	0.450	9.67×10^{-2}	0.983
0.01	250	60	0.549	5.48×10^{-2}	0.978
0.02	150	40	0.370	12.08×10^{-2}	0.981
0.02	250	40	0.382	13.17×10^{-2}	0.981
0.02	400	40	0.422	14.10×10^{-2}	0.994

Each amount of dried gel was kept constant as 1 g in swelling experiments. $C_{AAm} = 0.7$ mol/L, $n_{Ce(IV)} = n_{MPA}$, and $T = 30^{\circ}$. Total volume of the solution of polymerization was 100 mL.

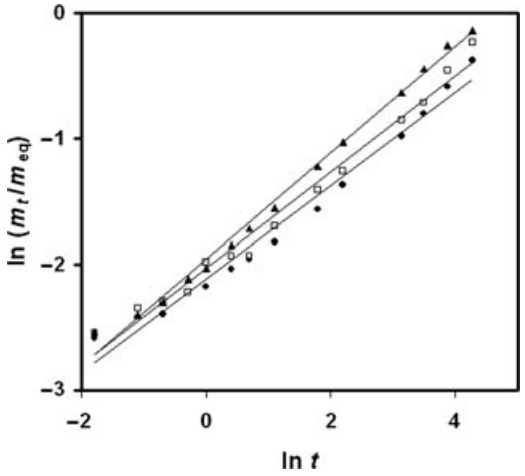


FIGURE 6. Dependence of the swelling kinetic rate of synthesized P(AAm-MBAA) hydrogels in distilled water on molar ratios of AAm/Ce(IV) in the cross-linking polymerization reaction. $n_{AAm}/n_{Ce(IV)} = 150$ (●), 250 (□), and 400 (▲).

MPA–cerium(IV) sulfate is a versatile redox initiator system for cross-linking polymerization of AAm with MBAA in acid aqueous medium at room temperatures. The dependence of SR and swelling rate of hydrogels on the parameters such as the n_{AAm}/n_{MBAA}, acid concentration, and the $n_{AAm}/n_{Ce(IV)}$ in the cross-linking polymerization reaction of AAm and MBAA initiated with the MPA–cerium(IV) sulfate redox system has been investigated. Although the n exponent of the kinetic equation remains almost constant, the ESR are greatly reduced by increasing concentration of Ce(IV). In the cross-linking polymerization reaction, the $n_{Ce(IV)}$ has been taken to be equal to the n_{MPA} and the decrease in SR with an increase in the Ce(IV) concentration might be possible due to an increase in the concentrations of MPA and Ce(IV). Because the thiol group in MPA may act as a cross-linking agent or the increase in Ce(IV) may cause an increase in more cross-linking in the polymerization reaction and Ce(III) forming in the cross-linking polymerization reaction of AAm with MBAA may provide the formation of intermolecular complexes between amide groups in polymer chains; the swelling equilibrium ratio and swelling rate decrease with an increase in their concentrations. Consequently, it seems that the redox reaction of MPA–Ce(IV) in acid aqueous medium is a promising new alternative source to initiate cross-linking polymerization of AAm with MBAA at low temperatures and the results indicate that this initiator system will find application in scientific investigations and industry.

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