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Swelling properties of acrylamide-N,N′-methylene bis(acrylamide) hydrogels synthesized by using meso-2,3-dimercaptosuccinic acid-cerium(IV) redox couple

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Abstract. In this paper, meso-2,3-dimercaptosuccinic acid-Ce(IV) redox couple is used for crosslinking polymerization of acrylamide (AAm) with N,N′-methylene bis(acrylamide) (MBAA) in acid aqueous medium. We have investigated the effects of crosslinker ratio, acid concentration and the molar ratio of AAm/Ce(IV) on the swelling behaviors of the synthesized P(AAm-MBAA) hydrogels. The experimental results show that the increase in the n_{AAm}/n_{MBAA} and $n_{AAm}/n_{Ce(IV)}$ result in an increase in the swelling ratio and rate of resulting hydrogels. However, the swelling equilibrium ratio and rate have been decreased with increasing of acid concentration. The k and n values in the equation of swelling rate have been determined. The n exponent decreases with increasing crosslinker, initiator and acid concentrations whereas k values increase. Kinetics and equilibrium swelling values have been discussed in terms of reaction parameters.

Keywords: *polymer gels, meso-2,3-dimercaptosuccinic acid, redox initiator, acrylamide, swelling*

1. Introduction

Hydrogels that exhibit swelling changes in response to environmental changes such as temperature, pH, electrical field, radiation of UV or visible light, solvent composition, salt concentration and type of surfactants are promising as intelligent materials. As a result they attract increasing interest in various application areas such as drug delivery systems, separation operations in biotechnology, processing of agricultural products, conductive or superabsorbent composites, sensors and actuators [1–12]. The swelling equilibrium of gels is determined by both the free energy of elasticity and free energy of mixing. In acrylamide-N,N′-methylene bis(acrylamide) hydrogel/water system, water diffuses into the network by the forces determined by the difference of chemical potential of water inside and outside of the network. The swelling gel reaches the equilibrium state at higher concentration of water in gel phase. The contribution of elastic forces to the chemical potential of water prevents the polymer from becoming completely dissolved [2, 9, 13, 14]. Numerous scientists have made great effort to investigate the synthesis and swelling properties of gel particles. In the synthesis of gel particles, potassium persulfate (PPS) or ammonium persulfate (APS) with or without N,N,N′,N′-tetramethylenediamine (TEMED) initiator systems have been generally used [15–17]. Ceric salt-organic reducing agent containing thiol, hydroxyl, carboxyl and amine functional groups can be used for polymerization and copolymerization of vinyl monomers. However, ceric salt-organic reducing agent containing thiol functional group or groups are also new sources to initiate copolymerization of vinyl monomers at low tem-

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peratures. When reducing agent with thiol functional group is used in redox system of ceric salt-organic reducing agent, the formation of –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 [18–23].

The swelling of polymeric networks is influenced by the composition of the polymer i.e. by the synthetic conditions, such as the n_{AAm}/n_{MBAA} in polymeric networks and by 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 [24–26].

In this communication, meso-2,3-dimercaptosuccinic acid-Ce(IV) redox couple was used to synthesize the crosslinked copolymer of acrylamide and N,N′-methylene bis(acrylamide) in acidic aqueous medium. The effect of parameters such as molar ratios of acrylamide to N,N′-methylene bis(acrylamide), acrylamide to cerium(IV) sulfate and the concentration of sulfuric acid were investigated. The swelling ratios and kinetics of hydrogels synthesized at different reaction parameters such as the n_{AAm}/n_{MBAA} at different initiator and acid concentrations, the concentration of sulfuric acid for $n_{AAm}/n_{MBAA} = 40$ at constant initiator concentration and the $n_{AAm}/n_{Ce(IV)}$ at constant acid and crosslinker concentration were studied.

2. Experimental

2.1. Materials

Acrylamide (Merck), N,N′-methylene bis(acrylamide) (Fluka), cerium(IV) sulfate (Merck) and meso-2,3-dimercaptosuccinic acid (Merck) were used as received and represented as AAm, MBAA, Ce(IV) and DMSA respectively in the text.

Sulfuric acid (Merck) with a purity of 98% was used in the redox reaction of meso-2,3-dimercaptosuccunic acid and cerium(IV) sulfate.

2.2. Preparation of P(AAm-MBAA) hydrogels

In order to prepare P(AAm-MBAA) hydrogels, the solution containing the calculated amount of Ce(IV) dissolved in acidic medium was added to the aqueous solution of acrylamide, N,N′-methylene bis(acrylamide) and meso-2,3-dimercaptosuccinic acid 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 the oxidant was kept constant at 20 ml. The total volume of crosslinking polymerization solution was 100 ml. The synthesized P(AAm-MBAA) hydrogels were purified from contaminants by immersion and soaking for 4 hours (three times) in 300 ml of distilled water and dried at 60°C. After drying, the hydrogels were placed in the sintered glass funnels which were immersed in distilled water. The swelling of the hydrogels were monitored by mass measurements against time. In this study, swelling values at 167 hours have been taken as equilibrium swelling values of all hydrogels – although equilibrium of swelling of some hydrogels may need more time than 167 hours. Once the equilibrium was reached, the hydrogels were weighed, dried at 60°C in vacuum for 24 hours and re-weighted. The effects of physicochemical parameters on the swelling behaviors and kinetics have been investigated. These parameters are: the molar ratios of acrylamide/cerium(IV) sulfate ($n_{AAm}/n_{Ce(IV)} = 100$ and 200) at constant crosslinker and acid concentrations, the concentration of sulfuric acid ($C_{H_2SO_4} = 0.0125$ and 0.025 mol/l) at the $n_{AAm}/n_{MBAA} = 40$ and the molar ratios of acrylamide to N,N′-methylene bis(acrylamide) for different acid and initiator concentrations.

The radical generation in the redox reaction of meso-2,3-dimercaptosuccinic acid and cerium(IV) sulfate in acid-aqueous medium is supposed to occur by one electron transfer from meso-2,3-dimercaptosuccinic acid to Ce(IV) according to the reactions given in Figure 1 as reported in the literature [18–22].

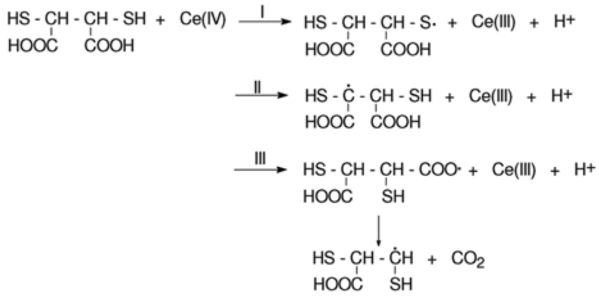

Figure 1. Radical formation reactions between meso-2,3-dimercaptosuccinic acid and Ce(IV) ions

Because of low S–H bonding energy, the formation of free radicals in reaction I in Figure 1 is more likely than other reactions to initiate crosslinking polymerization of acrylamide and N,N′methylene bis(acrylamide) and oxidative termination of polymer radicals is also possible by ceric ions [18, 20, 21]. In previous investigations, it is described that the formation of radicals on carboxyl groups may be possible [18–22]. However, the radical formation on carboxyl groups may appear less than that of the other radical formation reactions given in Figure 1, as the formation of free radicals on carcoxyl groups requires more energy.

After radical generation by redox reaction of meso-2,3-dimercaptosuccinic acid-Ce(IV) in acid-aqueous medium, the crosslinking polymerization of acrylamide-N,N′-methylene bis (acrylamide) was performed and the crosslinked copolymer having chemical formula given in Figure 2 was synthesized.

In order to characterize the crosslinking polymers, infrared measurements were carried out with ATI Unicam (Mattson 1000) FT-IR spectrometer and the spectra of crossliked polymers were determined by KBr disk method. For this purpose, pellets of about 300 mg KBr powder containing finely grained powder of crosslinked polymer sample (7–8 mg) were made. Figure 3 shows that the FT-IR spectra of crossliked polymers containing different crosslinker ratios (n_{AAm}/n_{MBAA} = 20 and 150), synthesized using DMSA-Ce(IV) redox system have been recorded by ATI Unicam (Mattson 1000) FT-IR spectrometer. As can be seen from Figure 3, the bands which can be assigned to the N–H stretching vibration in –NH-group of N,N′-methylene bis(acrylamide) or $–CONH_2$ groups of acrylamide in hydrogels appear at 3470 and 1670 cm^{-1}. The C–H stretching band is characterized by the peak at 2960 cm^{-1} due to symmetric or asymmetric stretching vibration of the CH_2 groups of acrylamide or N,N′-methylene bis(acrylamide).

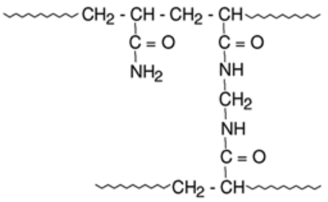

Figure 2. The chemical structure of the synthesized P(AAm-MBAA) hydrogel

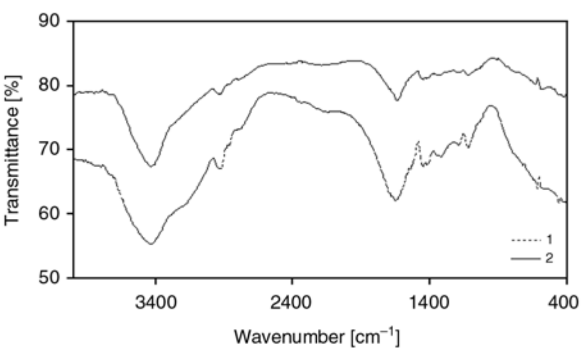

Figure 3. The FT-IR spectra of P(AAm-MBAA) hydrogels containing different n_{AAm}/n_{MBAA}, synthesized using meso-2,3-dimercaptosuccinic acid-Ce(IV) redox system. n_{AAm}/n_{MBAA} 20 (1) and 150 (2). C_{AAm} = 0.7 mol/l; $C_{H_2SO_4}$ = 0.0125 mol/l; $2n_{Ce(IV)} = n_{DMSA}$; T = 30°C.

3. Results and discussion

Swelling ratios (SR) and the values of equilibrium swelling ratios (ESR) of resulting hydrogels were calculated by using the Equations (1) and (2):

$$\mathrm{SR}=\frac{m_t-m_0}{m_0} \qquad (1)$$

$$\mathrm{ESR}=\frac{m_{eq}-m_0}{m_0} \qquad (2)$$

where SR represents the average swelling ratio of hydrogel in distilled water, obtained from triplicate experimental results. m_t and m_0 are the weights of hydrogel at time t and dried gel at initial time, 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 equilibrium.

The effects of the molar ratios of AAm/MBAA for different $n_{AAm}/n_{Ce(IV)}$ ($n_{AAm}/n_{Ce(IV)}$ = 100 and 200; $n_{DMSA} = 2n_{Ce(IV)}$) and acid concentrations ($C_{H_2SO_4}$ = 0.0125 and 0.0250 mol/l) on the swelling ratios of hydrogels in distilled water has been shown in Figures 4 and 5. The concentration of acrylamide monomer in these experiments was kept constant at 0.7 mol/l. As can be seen from Figures 4 and 5, it is observed that the increase in the molar ratio of AAm/MBAA for different acid concentrations of 0.0125 mol/l and 0.025 mol/l, and the $n_{AAm}/n_{Ce(IV)}$ values of 200 and 100 has increased the swelling ratios of hydrogels. The equilibrium swelling ratios determined from the curves of the swelling ratios of hydrogels depending on the n_{AAm}/n_{MBAA} for vari-

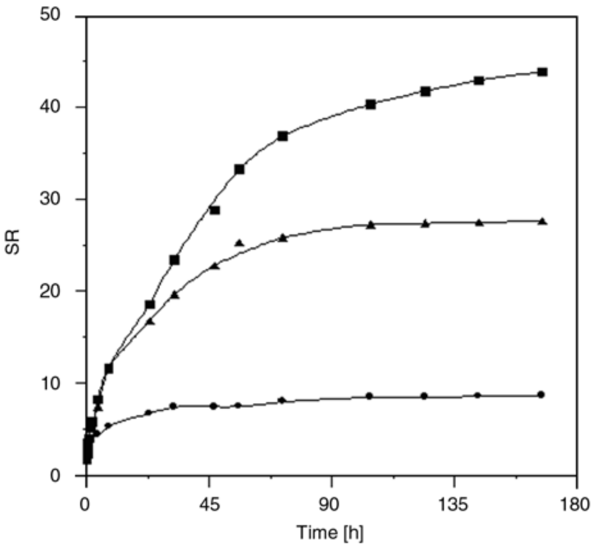

Figure 4. The dependence of swelling ratios of P(AAm-MBAA) hydrogels synthesized at the acid concentration of 0.025 mol/l and the $n_{AAm}/n_{Ce(IV)}$ of 100 on the molar ratios of AAm/MBAA. n_{AAm}/n_{MBAA} = 40 (●), 80 (▲) and 100 (■); C_{AAm} = 0.7 mol/l; $2n_{Ce(IV)} = n_{DMSA}$; T = 30°C

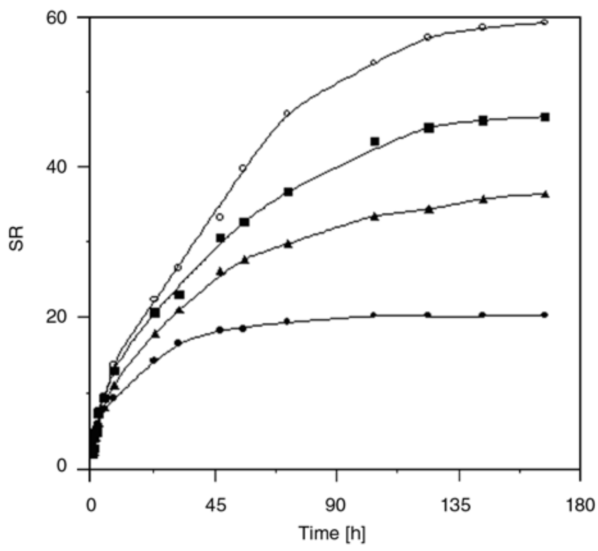

Figure 5. The effect of the molar ratios of AAm/MBAA on swelling ratios of P(AAm-MBAA) hydrogels synthesized at the acid concentration of 0.0125 mol/l and the $n_{AAm}/n_{Ce(IV)}$ of 200. n_{AAm}/n_{MBAA} = 20 (●), 60 (▲), 80 (■) and 150 (o); C_{AAm} = 0.7 mol/l; $2n_{Ce(IV)} = n_{DMSA}$; T = 30°C.

ous acid and initiator concentrations in crosslinking polymerization reaction have been listed in Table 1. As can be seen from the results given in Table 1, an increase in the n_{AAm}/n_{MBAA} values has resulted in an increase in the equilibrium swelling ratios of the synthesized hydrogels in distilled water. The photographic pictures of P(AAm-MBAA) hydrogels containing different crosslinker ratios are shown in Figure 6. The hydrogel represented with letter *A* is more opaque due to having higher crosslinker concentration (n_{AAm}/n_{MBAA} = 20), whereas, the hydrogel represented with letter *D* is more transparent due to having lower crosslinker concentration (n_{AAm}/n_{MBAA} = 150). These results show that hydrogels having less crosslink bonds swell better than hydrogels having more crosslink bonds as expected. In order to describe the phenomenon of swelling of more opaque hydrogels, phase separation is assumed in the systems and in the case of AAm-based hydrogels it is explained by entanglements between chains developing during polymerization in water medium as described in a previous study [27].

The dependence of swelling ratios of hydrogels on the acid concentration in crosslinking polymerization reaction at constant crosslinker molar ratio of n_{AAm}/n_{DMSA} = 40 is given in Figure 7. The augmentation in acid concentration has led to a decrease in the swelling ratios of hydrogels in distilled water. With increasing acid concentration in crosslinking polymerization, $–CONH_2$ groups of acrylamide may slowly undergo hydrolysis and the functional groups of –COOH may appear [28]. 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 higher acid

Table 1. The effect of the n_{AAm}/n_{MBAA} on the equilibrium swelling ratios of hydrogels synthesized at different acid and initiator concentrations. C_{AAm} = 0.7 mol/l; T = 30°C.

$n_{AAm}/n_{Ce(IV)}$	$C_{H_2SO_4}$ [mol/l]	n_{AAm}/n_{MBAA}	ESR (g H_2O/g polymer)
100	0.0250	40	8.59
100	0.0250	80	27.62
100	0.0250	100	43.91
200	0.0125	20	20.17
200	0.0125	60	36.41
200	0.0125	80	46.48
200	0.0125	150	57.18

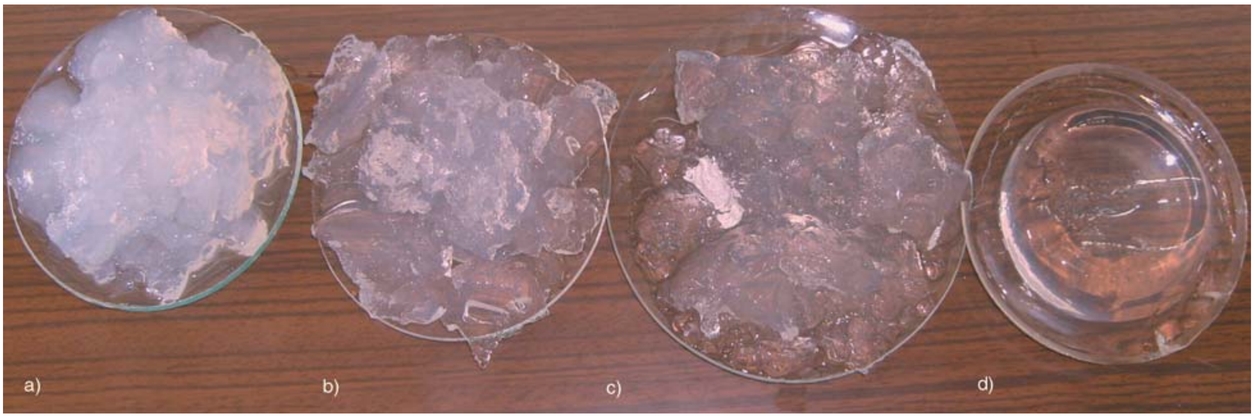

Figure 6. The photographic pictures of swelled hydrogels containing different molar ratios of AAm/MBAA. n_{AAm}/n_{MBAA} = 20 (a), 40 (b), 60 (c) and 150 (d). C_{AAm} = 0.7 mol/l; $C_{H_2SO_4}$ = 0.0125 mol/l; $n_{AAm}/n_{Ce(IV)}$ = 200; $2n_{Ce(IV)} = n_{DMSA}$; T = 30°C.

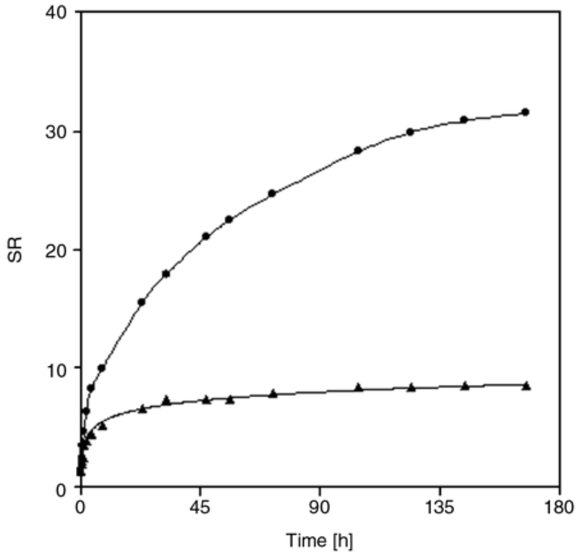

Figure 7. The swelling ratios of hydrogels synthesized at different acid concentrations. $C_{H_2SO_4}$ = 0.0125 (●) and 0.025 (▲) mol/l; C_{AAm} = 0.7 mol/l; n_{AAm}/n_{MBAA} = 40; $2n_{Ce(IV)} = n_{DMSA}$; T = 30°C.

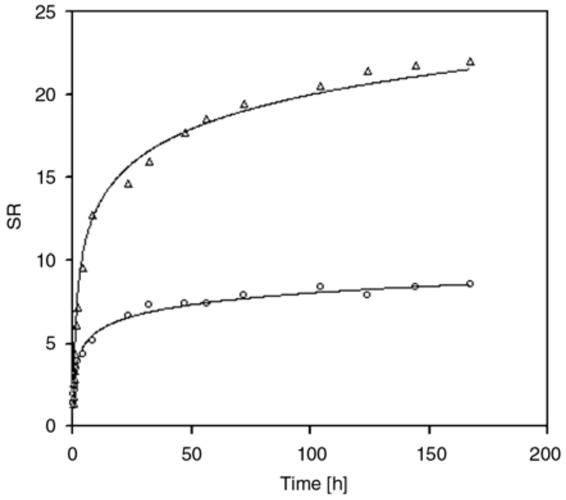

Figure 8. The relation between the molar ratios of AAm/Ce(IV) in crosslinking polymerization reaction and the swelling ratios of P(AAm-MBAA) hydrogels in distilled water, $n_{AAm}/n_{Ce(IV)}$ = 100 (o) and 200 (Δ). C_{AAm} = 0.7 mol/l; $C_{H_2SO_4}$ = 0.025 mol/l; n_{AAm}/n_{MBAA} = 40; $2n_{Ce(IV)} = n_{DMSA}$; T = 30°C.

concentration swells less than that synthesized at lower acid concentration. The values of equilibrium swelling ratios of hydrogels synthesized at different acid concentrations of 0.025 and 0.0125 mol/l have been determined as 8.59 and 31.53 g H_2O/g polymer for n_{AAm}/n_{MBA} = 40, respectively.

The effect of the molar ratios of AAm/Ce(IV) in crosslinking polymerization reaction at constant acid and crosslinker concentrations on the swelling ratios of P(AAm-MBAA) hydrogels in distilled water has been illustrated in Figure 8. The increase in the nAAm/nCe(IV) has resulted in an increase in the swelling ratios of hydrogels in distilled water. The equilibrium swelling ratios of hydrogels have been determined as 8.59 and 22.03 g H_2O/g polymer for the molar ratios of AAm/Ce(IV) of 100 and 200, respectively, in crosslinking polymerization reaction at constant acid concentration (0.025 mol/l) and crosslinker ratio (n_{AAm}/n_{MBA} = 40). It is evident that the increase in initiator concentration in synthesis of P(AAm-MBAA) hydrogel using cerium(IV) sulfate meso-2,3-dimercaptosuccinic acid redox system has decreased the swelling ratios of synthesized P(AAm-MBAA) hydrogels in distilled water.

The kinetic swelling results of hydrogels synthesized at various reaction parameters were examined by Peppas kinetic formula [29–31] (Equation (3)):

$$\frac{m_t}{m_{eq}} = kt^n \quad (3)$$

Linearized form of Equation (3) can be written as shown in Equation (4):

$$\ln\frac{m_t}{m_{eq}} = \ln k + n\ln t \quad (4)$$

where m_t and m_{eq} are the weights of hydrogels at time, t and at equilibrium respectively. k and n are constants. The values of exponent n are dependent on the amount of ionic groups in hydrogel. This equation is valid in the swelling ratio less than 60% [13, 31]. Using this criteria, the exponent, n and k values are obtained from the slope and intercept determined from a plot of $\ln(m_t/m_{eq})$ versus $\ln t$, respectively.

Figures 9 and 10 show a logarithmic plot ($\ln(m_t/m_{eq})$ versus to $\ln t$) of the swelling rate of P(AAm-MBAA) hydrogels with various crosslinker 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, initiator and crosslinker concentrations have been summarized in Table 2. The experimental results show that an increasing crosslinker ratio (n_{AAm}/n_{MBAA}) results in significant rises in the n exponent, whereas the k value decreases. The effect of acid concentration of initiation system on the swelling behaviors has been examined (Figure 11). As can be seen from Figure 11 and Table 2 that at higher acid concentrations, the swelling of gels is slow, the corresponding k values increase by increasing acid concentrations, while the n values somewhat decrease.

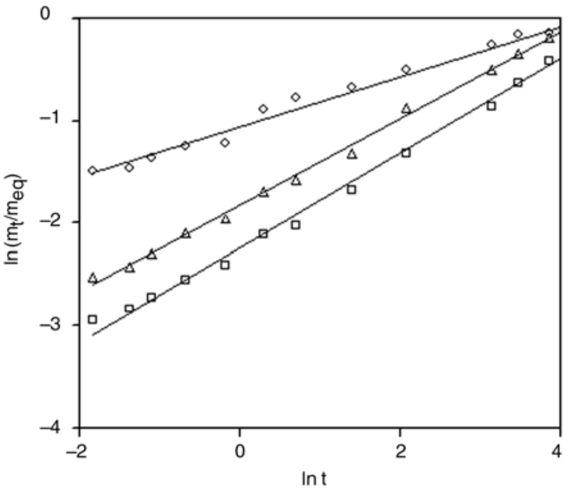

Figure 9. The effect of molar ratios of acrylamide to crosslinker on the swelling rates of P(AAm-MBAA) hydrogels in distilled water, synthesized at the acid concentration of 0.025 mol/l and the $n_{AAm}/n_{Ce(IV)}$ of 100. n_{AAm}/n_{MBAA} = 40 (o), 80 (Δ) and 100 (□).

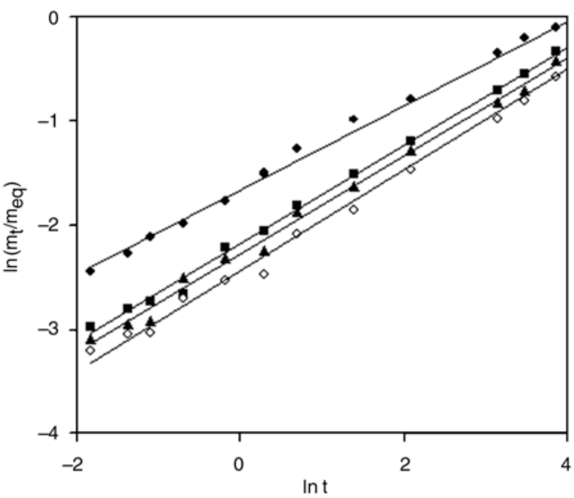

Figure 10. The dependence of the swelling rate of hydrogels synthesized at the acid concentration of 0.0125 mol/l and the $n_{AAm}/n_{Ce(IV)}$ of 200 on the n_{AAm}/n_{MBAA}. n_{AAm}/n_{MBAA} = 20 (●), 60 (■), 80 (▲) and 150 (o).

Table 2. The dependence of kinetic parameters in swelling kinetic equation fitting data obtained from swelling results of P(AAm-MBAA) hydrogels in distilled water on the acid concentration in crosslinking polymerization reaction. C_{AAm} = 0.7 mol/l; T=30°C.

$C_{H_2SO_4}$ [mol/l]	$n_{AAm}/n_{Ce(IV)}$	n_{AAm}/n_{MBAA}	n	k	Correlation coefficient, (R)
0.0125	200	20	0.405	0.191	0.995
0.0125	200	60	0.471	0.113	0.997
0.0125	200	80	0.472	0.103	0.996
0.0125	200	150	0.485	0.090	0.993
0.0125	100	40	0.457	0.119	0.990
0.0250	100	40	0.244	0.348	0.983
0.0250	100	80	0.421	0.161	0.997
0.0250	100	100	0.462	0.107	0.994
0.0250	200	40	0.371	0.210	0.967

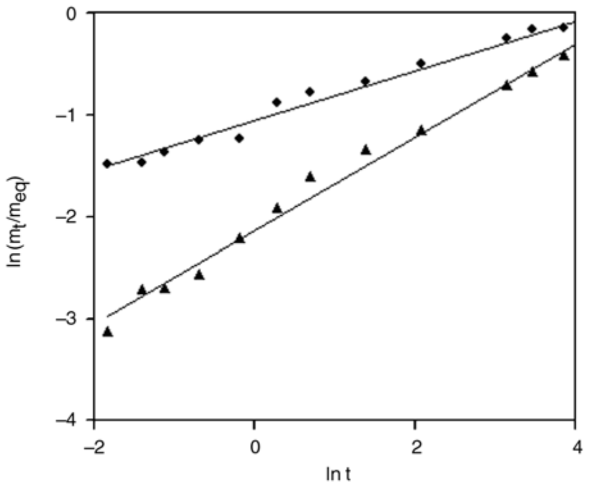

Figure 11. The relation between acid concentrations in crosslinking polymerization reactions at constant crosslinker concentration (n_{AAm}/n_{MBAA} = 40) and the swelling rate of synthesized P(AAm-MBAA) hydrogels in distilled water. $C_{H_2SO_4}$ = 0.0125 (▲) and 0.0250 (●) mol/l.

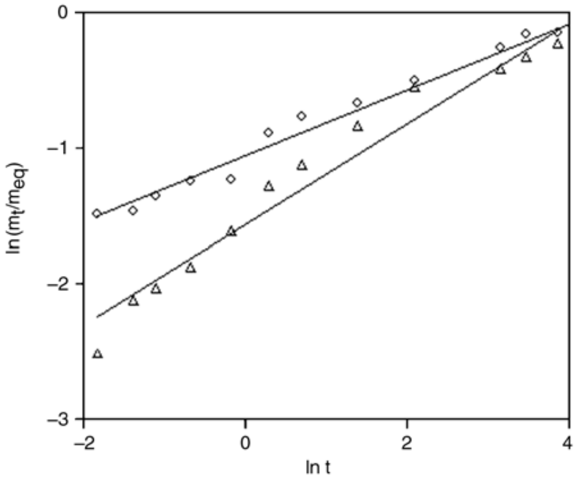

Figure 12. The dependence of swelling kinetic rate of synthesized P(AAm-MBAA) hydrogels in distilled water on molar ratios of AAm/Ce(IV) in crosslinking polymerization reaction. $n_{AAm}/n_{Ce(IV)}$ = 100 (o) and 200 (Δ).

The swelling rate of P(AAm-MBAA) hydrogels synthesized at different initiator concentrations ($n_{AAm}/n_{Ce(IV)}$ = 100 and 200) has been shown in Figure 12. The augmentation in the molar ratio of AAm/Ce(IV) in crosslinking polymerization reaction shows an increase in the *n* exponent from 0.244 to 0.371. However, the *k* value decreases from 0.348 to 0.210 (Table 2). This result indicates that the increase in initiator concentration in crosslinking polymerization reaction of P(AAm-MBAA) hydrogels synthesized using DMSA-Ce(IV) redox system in acid aqueous medium has led to a decrease in the swelling rate.

4. Conclusions

Ceric salt-organic reducing agent containing thiol functional groups are promising a new alternative initiator system for crosslinking polymerization of AAm with MBAA in acid-aqueous medium at ambient temperatures. The dependence of swelling ratio 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 crosslinking polymerization reaction of acrylamide and N,N′-methylene bis(acrylamide) initiated with meso-2,3-dimercaptosuccinic acid-cerium(IV) sulfate redox system has been investigated. It has been observed that the augmentation in the acid, initiator and crosslinker concentrations has led to a decrease in the swelling ratio and rate of P(AAm-MBAA) hydrogels in distilled water. The *k* and *n* exponent values in the kinetic equation have been calculated. The swelling ratios and *k* values decrease with increasing Ce(IV) concentration ($2n_{Ce(IV)} = n_{DMSA}$) due to increase in the concentration of meso-2,3-dimercaptosuccinic acid. This phenomenon is attributed that thiol group in meso-2,3-dimercaptosuccinic acid acts as a crosslinking agent. Therefore the swelling equilibrium ratio and swelling rate decrease with increase in its concentration.

Acknowledgements

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