Synthesis and Characterization of Polyacrylamides Containing *meso*-2,3-Dimercaptosuccinic Acid End Groups

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ABSTRACT: By using *meso*-2,3-dimercaptosuccinic acid-cerium(IV) sulfate and *meso*-2,3-dimercaptosuccinic acid-potassium permanganate redox systems, the polymerization reaction of acrylamide (AAm) monomer was examined in aqueous acidic medium at low temperatures. Water-soluble polyacrylamides bearing *meso*-2,3-dimercaptosuccinic acid end groups were synthesized using *meso*-2,3-dimercaptosuccinic acid as a reducing agent. The effects of parameters such as the molar ratio of acrylamide to initiator, temperature, polymerization time, and sulfuric acid concentration on the yields and molecular weights of polymers were investigated. The augmentation in initiator concentration resulted in a decrease in molecular weight but an increase in the yield of polymers. The increase in reaction temperature from 20 to 60°C led to a decrease in the yield from 56.80% to 20.58%. Ce(IV) and Mn(VII) ions are reduced to Ce(III) and Mn(II) ions in the polymerization reaction and the synthesized acrylamide polymers containing *meso*-2,3-dimercaptosuccinic acid end groups can absorb these ions at the end of the polymerization reaction. Ultraviolet-visible and atomic absorption measurements of polymer solutions were performed to indicate complexation between polyacrylamide and Ce(III) ions or Mn(II) ions. © 2010 Wiley Periodicals, Inc. Adv Polym Techn 29: 45–53, 2010; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/adv.20180

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Introduction

Polyacrylamides (PAAms) and their copolymers have found numerous applications as soil conditioner, in wastewater treatment, in cosmetics, paper, and textile industries, and in laboratories as a solid support for the separation of proteins by electrophoresis.[1–3] After manure application on soil surfaces, pollution of surface and groundwater from water flowing over irrigated fields is an important vector for transport of microorganisms. Polyacrylamides efficiently remove or immobilize microorganisms in flowing water, increase water infiltration, and reduce soil erosion.[4–8] The graft copolymers of acrylamide on neutral polymers such as cashew gum, carboxymethyl cellulose, guar gum, sodium alginate, and xanthan gum have potential applications to improve flocculation efficiently, decolorize textile dyes, increase solution viscosity, enhance the drag reduction effectiveness and shear stability, and prepare controlled drug delivery systems.[9–13] In addition, copolymers of acrylamide with methacrylic, maleic, acrylic, and crotonic acids, which are known super absorbent polymers for water uptake, were synthesized and used for the removal of toxic metal ions and dyes from wastes or waste solutions.[14–18] In previous studies given in literature for the polymerization and copolymerization reactions of acrylamide, the initiator systems such as Fenton reagent, persulfate, various reductants, ceric salts, or potassium permanganate-organic reducing agents containing amino, carboxyl, thiol, or hydroxyl functional groups were used.[19–32] The acrylamide polymers bearing amino, thiol, hydroxyl, and carboxylic acid end groups are potential sources for the preparation of high-molecular-weight polymers containing weakly bound structures that can be destroyed under physiological conditions and have potential to remove trace elements from waste solutions.[33–36] In addition, *meso*-2,3-dimercaptosuccinic acid as a reducing agent is an effective chelating agent and used to sequester heavy metals such as mercury for extraction. For this reason, PAAms containing *meso*-2,3-dimercaptosuccinic acid end groups may find applications to remove metal ions from wastes and find some practical applications in various industries.

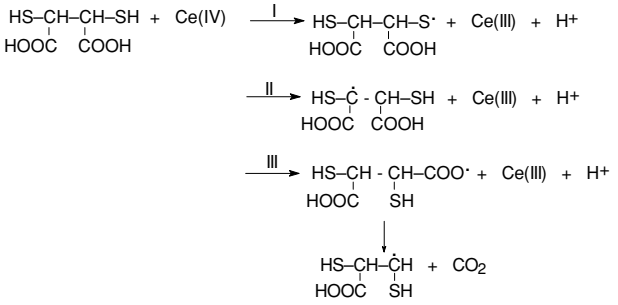
The aim of this work was to study the acrylamide polymerization in aqueous acidic medium at ambient temperatures, using *meso*-2,3-dimercaptosuccinic acid-Ce(IV) initiator system, and to synthesize water-soluble PAAms containing *meso*-2,3-dimercaptosuccinic acid end groups. In the polymerization reaction, the effects of parameters such as the molar ratio of acrylamide to cerium(IV) sulfate [$n_{Ce(IV)} = 0.5n_{DMSA}$, where cerium(IV) sulfate tetrahydrate and *meso*-2,3-dimercaptosuccinic acid are represented as Ce(IV) and DMSA, respectively], polymerization time, temperature, and the concentration of sulfuric acid on the polymerization yield and molecular weights of polymers were investigated. The obtained PAAms were characterized by viscosity, ultraviolet (UV), Fourier-transformed infrared (FT-IR), atomic absorption, and particle-size distribution measurements.

Experimental

meso-2,3-Dimercaptosuccinic acid (DMSA; Fluka), acrylamide (AAm; Merck), and cerium(IV) sulfate tetrahydrate [Ce(IV); Merck] were used without further treatment.

Polymerization reactions were carried out in a round-bottomed flask equipped with a stirrer by adding the calculated amount of ceric salt or $KMnO_4$ solution to aqueous solution of AAm and DMSA. For this purpose, the oxidant, Ce(IV) or $KMnO_4$, was dissolved in a calculated amount of sulfuric acid solution. The solution volume of oxidant was kept constant at 20 mL. The total volume of polymerization solution was 100 mL. After polymerization was completed, the solution was poured into an excess of acetone to precipitate the raw polymer. The volume ratio of acetone to polymer solution was kept constant at 7:1 for the precipitation of polymers. The weight of isolated polymer was determined by direct weighing of PAAm dried in air and the yield was calculated by using Eq. (1).

$$\text{Yield } \% = \frac{\text{Weight of isolated polymer (g)}}{\text{Weight of monomer (g)}} \times 100 \quad (1)$$



SCHEME 1. Radical formation mechanism between *meso*-2,3-dimercaptosuccinic acid and cerium(IV) sulfate tetrahydrate.

Polymerization of AAm was studied in various time-temperature conditions, using different monomer/initiator ratios [$n_{Ce(IV)} = 0.5n_{DMSA}$] in aqueous acidic medium.

In redox reaction between DMSA and Ce(IV), the radical generation is believed to occur by one-electron transfer from reducing agent to Ce(IV) according to the reaction given in Scheme 1, as reported in literature.[21,25,37,38]

Because of low S—H bonding energy, the formation of free radicals in reaction I in Scheme 1 is more likely than other reactions to initiate polymerization of AAm. It was reported that the formation of free radicals on carboxyl groups might be possible.[19–21,25,37] However, the probability of radical formation on carboxyl groups is less than other radical formation reactions given in Scheme 1 because of the influence of acid (proton). The redox reaction between Ce(IV) and reducing agents bearing S—H functional groups in acid-aqueous medium occurs at lower temperatures as described in previous studies.[21,25,37,38] This supports the idea of formation of —S• in the redox reaction in the polymerization of AAm monomer and oxidative termination of polymeric radicals is also possible by Ce(IV) ions.[21,25,37] Thus, after the polymerization reaction is completed, water-soluble PAAm having more likely structures given in Scheme 2 have been obtained.

Infrared measurements were carried out with an ATI Unicam (Mattson 1000) FT-IR spectrometer and the spectra of polymers were determined using KBr disks. For this purpose, pallets of about 300 mg of KBr containing finely grained powder of DMSA, AAm, or PAAm sample (7–8 mg) were made. The FT-IR spectra of DMSA, AAm, and PAAm synthesized using DMSA-Ce(IV) redox system were recorded on an ATI Unicam (Mattson 1000) FT-IR spectrometer.

Viscosities of polymer solutions were determined by capillary viscometer technique on a Ubbelohde viscometer at 30 ± 1°C. The intrinsic viscosities ($|\eta|$) of polymer solutions were calculated by using the following equation[19,21,25,38,39]:

$$|\eta| = \frac{\eta_{sp} + 3\ln(\eta_r)}{4C}$$

where C is the concentration of polymer solution (0.5 g/dL). The relative (η_r) and specific (η_{sp}) viscosity values were calculated using the following equations:

$$\eta_r = \frac{t}{t_0}$$

and

$$\eta_{sp} = \frac{t - t_0}{t_0} = \eta_r - 1$$

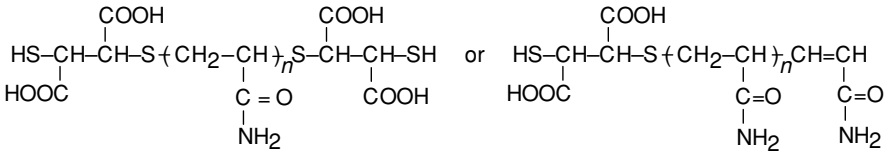
where t_0 and t are the flow times of water and polymer solution of defined volume in Ubbelohde capillary viscometer, respectively.

The molecular weights of polymers were determined by the Mark-Houwink equation given as follows:

$$|\eta| = K\ M_v^{\alpha}$$

where K and α are constants, which are dependent on the solvent, the type of polymer used, and the temperature of the system. For the aqueous solution of PAAm at 30°C, the values of K and α are 6.88×10^{-4} and 0.66, respectively.

The UV measurements (200–400 nm) were performed using a JASCO V-530 UV-visible



SCHEME 2. Chemical structure of the synthesized polyacrylamide.

spectrometer equipped with a temperature control attachment.

A Zetasizer Nano ZS light scattering system was used to measure the distribution of particle sizes in polymer solution. For this purpose, 0.25 g of polymer was dissolved in 100 mL of distilled water.

An Analytik Jena Vario 6 AAS flame atomic absorption spectrometer was used for determining Mn(II) in polymers. Manganese hallow cathode lamps were operated at a wavelength of 297.5 nm and a slit width of 0.2 nm.

Results and Discussion

The formation of —S•, in the polymerization reaction of AAm initiated by Ce(IV)-DMSA or $KMnO_4$-DMSA in aqueous acidic medium, was energetically most favorable because of low S—H bonding energy. The use of other cerium-based redox pairs such as ethylenediamine tetraacetic acid, iminodiacetic acid, amino acids, and nitrilotriacetic acid has been studied for the aqueous polymerization of AAm in different time-temperature conditions.[39–42] The initiation of AAm polymerization using organic reducing agent with thiol groups is more efficient than other organic compounds with amino or carboxylic acid groups.[27–32]

The effect of initiator concentration at constant acid and monomer concentrations ($C_{H_2SO_4}$ = 0.05 mol/L, C_{AAm} = 0.7 mol/L) on the yield and molecular weight of the polymer is shown in Fig. 1. The augmentation in the molar ratio of AAm to initiator, $n_{Ce(IV)} = 0.5n_{DMSA}$, resulted in an increase in molecular weight but a decrease in the yield of the polymer that contained DMSA end groups.

The increase in temperature in the polymerization reaction resulted in an increase in the molecular weight of the polymer and a decrease in the yield of the polymer (Fig. 2). This unexpected result must be due to the side reactions of the primary radicals generated from DMSA. These side reactions might result from a recombination of the initiating primary radicals or any other radical addition to the amide carboxyl. Similar unusual behavior has been reported by Lozinsky et al.[43] in the polymerization reaction of PAAm initiated with tertiary amine-persulfate redox couple.

The dependence of the yield and molecular weight of the polymer on the acid concentration and the polymerization time is shown in Table I. On examining the table, it is seen that an increase in acid concentration resulted in a decrease in the molecular weight of the polymer and an increase in the polymerization yield. No significant change was observed in the molecular weights by extension of the polymerization time. Polymerization

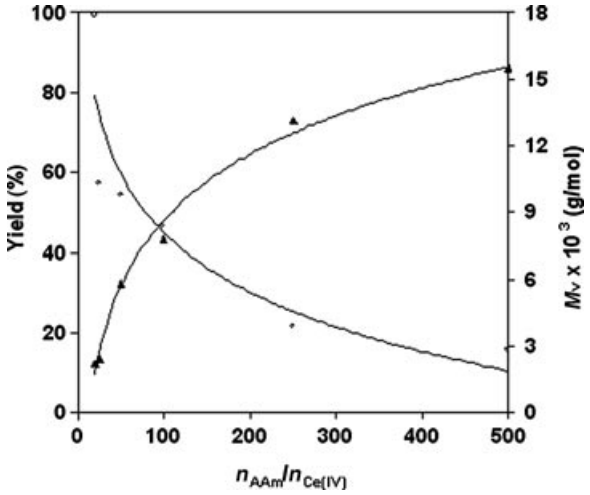


FIGURE 1. The effect of the molar ratio of acrylamide to initiator on the yield (○) and molecular weight (▲) of the polymer synthesized using *meso*-2,3-dimercaptosuccinic acid-Ce(IV) redox system. $C_{H_2SO_4}$ = 0.05 mol/L; C_{AAm} = 0.7 mol/L; $T = 30°C$; t = 1 h; $n_{Ce(IV)} = 0.5n_{DMSA}$. Abbreviations: AAm, acrylamide; Ce(IV), cerium(IV) sulfate tetrahydrate; DMSA, *meso*-2,3-dimercaptosuccinic acid.

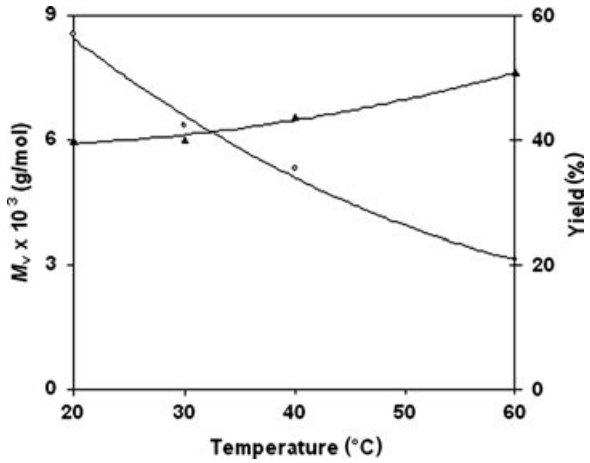


FIGURE 2. The dependence of the yield (○) and molecular weight (▲) of the polymer on the temperature. $C_{H_2SO_4}$ = 0.05 mol/L; $C_{Ce(IV)}$ = 0.007 mol/L; C_{AAm} = 0.7 mol/L; t = 1 h; $n_{Ce(IV)} = 0.5n_{DMSA}$. Abbreviations: AAm, acrylamide; Ce(IV), cerium(IV) sulfate tetrahydrate; DMSA, *meso*-2,3-dimercaptosuccinic acid.

TABLE I
The Dependence of the Yield and Molecular Weight of the Polymer on the Acid Concentration and the Polymerization Time

$C_{H_2SO_4}$ (mol/L)	Polymerization Time (min)	Yield %	M_v (g/mol)
0.025	60	31.30	11,850
0.050	60	46.60	6,700
0.100	60	45.30	6,600
0.200	60	51.70	6,000
0.400	60	58.45	5,850
0.200	5	20.60	3,900
0.200	10	42.50	7,300
0.200	20	44.70	6,750
0.200	30	44.50	6,200
0.200	40	45.00	6,450
0.200	60	51.70	6,000

C_{AAm} = 0.7 mol/L; T = 30°C; $n_{AAm}/n_{Ce(IV)}$ = 100; $n_{Ce(IV)} = 0.5n_{DMSA}$.

yield increased up to polymerization time $t = 10$ min and then remained constant at around 42.5% to 51.7% of polymerization yield for polymerization time from 10 to 70 min.

The UV spectrum of PAAm obtained using Ce(IV)-organic acid or amino acid (with or without thiol group) redox system indicates generally a peak at 254 nm because of complex formation between Ce(III) ions and polymer containing reducing agent as end groups.[21,25,30–32,37] A peak at 254 nm was observed in the UV spectrum of AAm polymer synthesized using DMSA-Ce(IV) redox system (Fig. 3). It was reported that similar peak at around 254 nm was obtained in the UV-visible spectra of PAAms synthesized using Ce(IV)-thioglycolic acid, 3-mercaptopropionic acid, or mercaptosuccinic acid redox system.[21,25,37] The obtained spectrophotometric data from peak values at 254 nm are shown in Fig. 3 and the values of molar ratios of AAm to Ce(IV) in polymerization reactions are shown in Fig. 4. As can be seen from these figure, the decrease in the initiator concentration in the polymerization reaction led to a decrease in the absorbance values of PAAm solutions (0.25 g of polymer/100 mL of solution in water) at 254 nm. Since PAAm itself does not show any absorption within this range, the observed adsorption bands indicates the presence of cerium(III) salt retention in free form or bonded to the polymer.

The FT-IR spectra of AAm, DMSA, and PAAm containing DMSA end groups are given in Fig. 5. As can be seen from the figure, the band at 3400 cm^{-1},

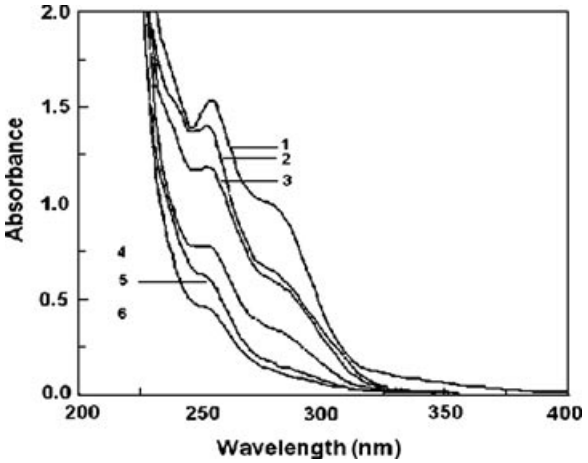


FIGURE 3. Ultraviolet-visible spectra of polymer solutions obtained using Ce/(IV)-*meso*-2,3-dimercaptosuccinic acid redox system at different initiator ratios. $n_{AAm}/n_{Ce(IV)}$ = 20 (1), 35 (2), 50 (3), 100 (4), 250 (5), and 500 (6). $C_{H_2SO_4}$ = 0.05 mol/L; C_{AAm} = 0.7 mol/L; t = 1 h; $n_{Ce(IV)} = 0.5n_{DMSA}$; $C_{polymer}$ = 0.25 g/dL. Abbreviations: AAm, acrylamide; Ce(IV), cerium(IV) sulfate tetrahydrate; DMSA, *meso*-2,3-dimercaptosuccinic acid.

which can be assigned to symmetrical and asymmetrical stretching vibrations of N—H group observed in the FT-IR spectrum of AAm monomer, has been observed to shift to a band at 3430 cm^{-1} in the spectrum of PAAm. The peak which appears at

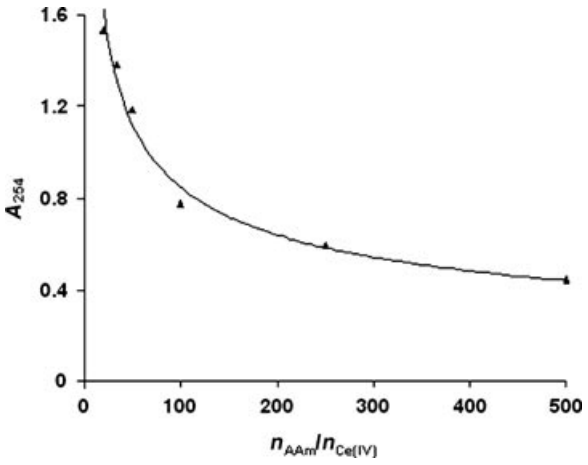


FIGURE 4. The relationship between the absorbance (A) values at 254 nm of polymer solutions (0.25 g of polymer/100 mL in distilled water) and the $n_{AAm}/n_{Ce(IV)}$ ratio in the polymerization reaction at 30°C. C_{AAm} = 0.7 mol/L; $C_{H_2SO_4}$ = 0.2 mol/L; $n_{Ce(IV)} = 0.5n_{DMSA}$. Abbreviations: AAm, acrylamide; Ce(IV), cerium(IV) sulfate tetrahydrate; DMSA, *meso*-2,3-dimercaptosuccinic acid.

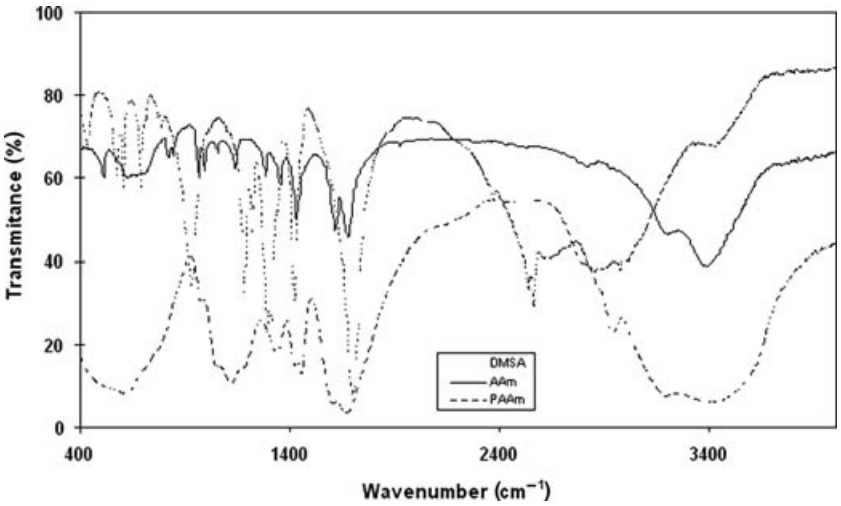


FIGURE 5. FT-IR spectra of *meso*-2,3-dimercaptosuccinic acid (DMSA), acrylamide (AAm), and polyacrylamide (PAAm) obtained using DMSA-cerium(IV) sulfate redox system.

2950 cm^{-1} in the FT-IR spectrum of PAAm has been attributed to the —CH stretching vibration band. The characteristic C=O stretching vibration bands of amide and acid groups have been observed at 1680 and 1700 cm^{-1}, respectively. The peaks observed at 900–1000 cm^{-1} and 1620 cm^{-1}, which have been attributed to the —CH=CH_2 group observed in the FT-IR spectrum of AAm monomer, disappeared in the FT-IR spectrum of PAAm. The band at 1430 cm^{-1} indicates O—H bending, the existence of C—O stretching in the plane of C—O—H bending in DMSA, and N—H stretching in AAm and PAAm. There are also peaks at 1280, 1140, and 1130 cm^{-1}, which are seen in the FT-IR spectra of AAm, PAAm, and DMSA. These peaks belong to N—H stretching of amide groups or O—H bending of DMSA and PAAm containing DMSA end groups. The peaks observed at 600–700, 935, and 2340–2600 cm^{-1} indicate the vibration band of —SH groups in the FT-IR spectra of DMSA. Moreover, the peaks in the spectrum of PAAm can arise due to metal ions absorbed in the polymer.

To measure the particle-size distribution of AAm polymers, 0.25 g of each polymer synthesized at different initiator ratios [$n_{AAm}/n_{Ce(IV)} = 20$, 100, 250, and 500; $n_{Ce(IV)} = 0.5n_{DMSA}$] was dissolved in 100 mL of distilled water and the Zetasizer Nano ZS light scattering system was used to measure the particle-size distribution of polymers in solutions. The curves of particle-size distributions determined from polymer solutions are given in Fig. 6. As can be seen from the figure, the average particle size increased with decreasing initiator concentration in polymerization reactions. This indicates that the lower initiator concentration in polymerization reaction leads to the formation of polymers having larger particle sizes. The formation of high-molecular-weight polymer might also be due to the chelating effect of Ce(III) as described previously.[30,31]

The initiation mechanism based on Ce(IV) or Mn(VII) ions is rather complicated and debatable in various aspects such as kinetics and limiting conversions because of their specific behaviors against monomers and type of reducing agents. According to the generally accepted mechanism, powerful oxidizing agent, potassium permanganate, acts on vinyl monomers to give Mn(IV) or Mn(III) ions, which are

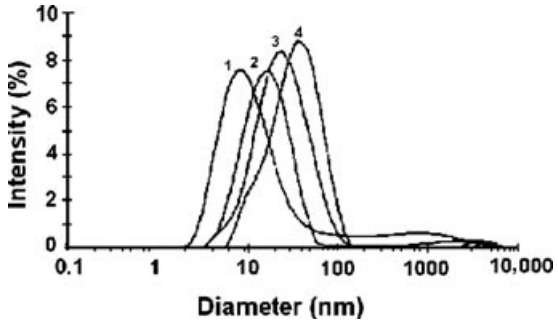
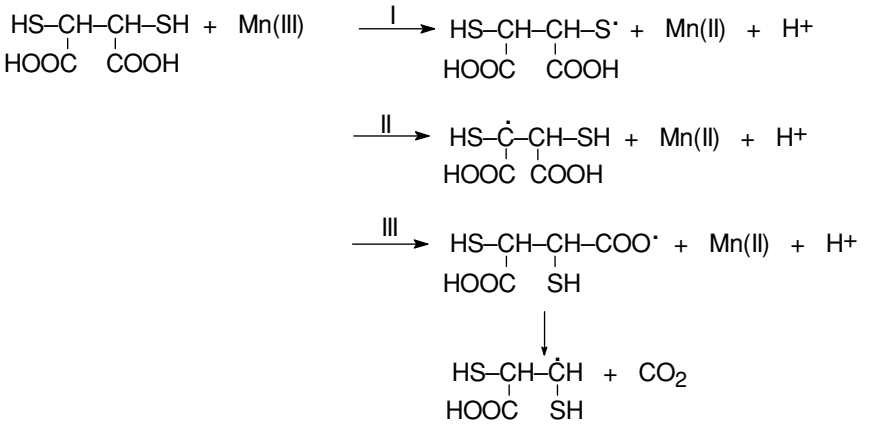


FIGURE 6. Particle-size distribution curves of aqueous solutions ($C_{polymer} = 0.25$ g of polymer/dL in distilled water) of polyacrylamides synthesized at different initiator ratios. $n_{AAm}/n_{Ce(IV)} = 20$ (1), 100 (2), 250 (3), and 500 (4). $C_{H_2SO_4} = 0.05$ mol/L; $C_{AAm} = 0.7$ mol/L; $t = 1$ h; $n_{Ce(IV)} = 0.5n_{DMSA}$. Abbreviations: AAm, acrylamide; Ce(IV), cerium(IV) sulfate tetrahydrate; DMSA, *meso*-2,3-dimercaptosuccinic acid.



SCHEME 3. Radical formation mechanism between *meso*-2,3-dimercaptosuccinic acid and Mn(III).

responsible for initiating polymerization by producing radicals from reducing agents with hydroxyl or carboxyl groups.[19–21,37] The simplified mechanism of initiation by the redox reaction between Mn(III) and DMSA is given in Scheme 3.

The formation of free radicals given in reaction I of Scheme 3 is more probable than other reactions for the initiation of AAm polymerization because of low S—H bonding energy, as explained in the redox system of DMSA-Ce(IV). As described in previous investigations, oxidative termination of polymeric radicals is also possible by Mn(III) or Mn(IV) ions[21,25,37] and PAAms having chemical structures given in Scheme 2 can be obtained in the polymerization reaction of AAm monomer initiated with $KMnO_4$-DMSA redox system in acid aqueous medium.

Using DMSA-$KMnO_4$ redox system, the polymerization reaction of AAm monomer was performed at different initiator concentrations at 30°C. It was observed that an increase in potassium permanganate concentration in the polymerization reaction resulted in an increase in the yield but a decrease in the molecular weight of the polymer (Table II). It is reported that manganese dioxide is produced by the interaction of vinyl monomer with permanganate and then manganese dioxide dissolves in acid producing highly reactive Mn(III) ions.[19,20] Both Mn(IV) or Mn(III) ions are reduced to Mn(II) ions during the polymerization reaction. The Mn(II) species that are formed at the end of the polymerization reaction are absorbed by the polymer.[21,25,30–32,37] The dependence of the concentration of Mn(II), which is incorporated into the polymer, on the initiator concentration in the polymerization reaction is given in Fig. 7. It is seen that the amount of Mn(II) bound to

TABLE II
The Effect of Initiator Concentration on the Yield and Molecular Weight of Acrylamide (AAm) Polymer

$n_{AAm}/n_{Ce(IV)}$	Yield (%)	M_v (g/mol)
35	100.00	8,050
100	52.00	12,400
250	31.20	28,600
400	22.10	29,150
500	4.65	–

$C_{H_2SO_4}$ = 0.20 mol/L; C_{AAm} = 0.7 mol/L; T = 30°C; t = 60 min.

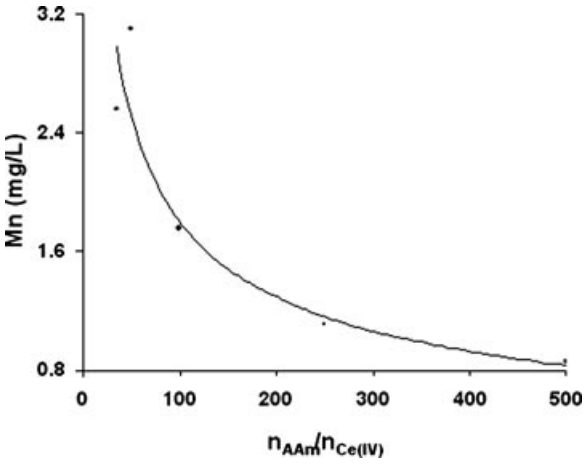


FIGURE 7. The relationship between the concentration of Mn(II) bound to the polymer and the molar ratio of acrylamide to initiator at the beginning of polymerization reaction. T = 30°C; t = 1 h; C_{AAm} = 0.7 mol/L; $C_{H_2SO_4}$ = 0.05 mol/L; $n_{Ce(IV)} = 0.5n_{DMSA}$; $C_{polymer}$ = 0.25 g/dL. Abbreviations: AAm, acrylamide; Ce(IV), cerium(IV) sulfate tetrahydrate; DMSA, *meso*-2,3-dimercaptosuccinic acid.

the polymer changes with the initial concentration of permanganate.

Conclusion

The effects of temperature, polymerization time, sulfuric acid concentration, and initiator concentration on the yield and molecular weight of the polymer were investigated in the synthesis of PAAms containing DMSA end groups. The obtained AAm polymers were characterized by spectrometric (UV and FT-IR), atomic absorption, and particle-size measurements. The results of atomic absorption measurements indicated that there is an increase in the amount of Mn(II) bound to the polymer with increasing initial concentration of permanganate in the polymerization reaction. The UV spectrum of the polymer shows a new adsorption band at 254 nm, which can be ascribed to the complexation of the polymer with Ce(III). In addition, the FT-IR spectrum of the polymer shows a reasonable chemical shift of the position of N—H stretching vibration band at 3430 cm^{-1}. This implies the complexation tendency of Ce(III) with the amido groups. The formation of high-molecular-weight polymer might also be due to the chelating effect of Ce(III) as described previously.[30,31] In the polymerization reaction of AAm initiated by Ce(IV)-DMSA or $KMnO_4$-DMSA redox systems in aqueous acidic medium, the formation of —S• is energetically most favorable because of low S—H bonding energy. As a result, DMSA is a convenient radical source for the generation of radicals to initiate AAm polymerization at room temperatures and these low-temperature polymerization methods provide advantages because it is an energy-saving process and gives polymer with low branching.

Acknowledgments

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