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Low Temperature Initiation by 3-Mercaptopropionic Acid-Ce(IV) or -$KMnO_4$ Redox System for Polymerization of Acrylamide Monomer

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Polymerization of acrylamide monomer was performed at low temperatures using 3-mercaptopropionic acid-cerium(IV) sulfate and 3-mercaptopropionic acid-$KMnO_4$ redox systems in acid aqueous medium. Water soluble polyacrylamides containing 3-mercaptopropionic acid end groups were synthesized. The effects of mole ratio of acrylamide to initiator($n_{MSA} = n_{Ce(IV)}$), polymerization time, temperature, and concentration of sulfuric acid on the yield and molecular weight of polymer were investigated. The decrease in the mole ratio of acrylamide/Ce(IV) at constant monomer concentration resulted in an increase in the yield but a decrease in molecular weight of polymer. The increase of reaction temperature from 20° to 70°C resulted in a decrease in the yield but indicated generally a constant value for the molecular weight of polymer. With increasing of polymerization time, the yield and molecular weight of polymer did not change mainly. Ce(IV) and Mn(VII) ions are reduced to Ce(III) and Mn(II) ions, respectively in the polymerization reaction. The existence of Ce(III) ion bonded to polymer was investigated by UV-visible spectrometry and fluorescence measurements. The amount of Mn(II) that is incorporated to the polymer was determined using graphite furnace atomic absorption spectrometry. The mechanism of this phenomenon is discussed.

Keywords 3-Mercaptopropionic acid; Cerium(IV) sulfate; Redox polymerization

INTRODUCTION

The polymerizations of vinyl monomers initiated with $KMnO_4$ and ceric salts-organic reducing agent systems in acid-aqueous medium were investigated. These methods have been also used for the preparation of graft copolymers of vinyl monomers such as acrylonitrile, methylmethacrylate, acrylic, or acrylamide[1–16]. In previous studies, water soluble polymers containing amine, hydroxyl, carboxyl, or dicarboxylic end groups were synthesized using a redox initiator system[17–24]. In most of these studies, the polymerization of vinyl monomers initiated with $KMnO_4$ or ceric salts-organic acid reducing system were performed at relatively high temperatures. However, low temperature polymerization is attractive both industrially and scientifically due to the fact that it is an energy saving process and gives polymers with low branching.

The initiator system, especially using 3-mercaptopropionic acid for the polymerization of acrylamide monomer, was used firstly in this study. Unlike other reducing agents used in most previous studies, 3-mercaptopropionic acid contains an S−H group. Due to the low bonding energy of the S−H bond, the formation of –S· is more likely at low temperatures. This gives the advantages of saving energy in the polymerization process and obtaining a polymer with low branching. Moreover, when we used 3-mecaptopropionic acid as a reducing agent, we obtained polyacrylamide containing 3-mercaptopropionic acid end groups, which may be found to have some practical applications, depending on this functional group in the polymer.

In the present communication, the polymerization of acrylamide monomer initiated by 3-mercaptopropionic acid-cerium(IV) sulfate and 3-mercaptopropionic acid-potassium permanganate redox systems was examined in low temperature polymerization reactions. The dependence of the polymerization yield and the molecular weight of polymer on the $n_{AA}/n_{Ce(IV)}$ ratio at constant monomer concentration, polymerization time, temperature, and concentration of sulfuric acid was investigated. Polyacrylamides that are soluble in water and contain 3-mercaptopropionic acid end groups were synthesized. Such polymers prepared with Ce(IV)-organic reducing agent redox system and containing amino, hydroxyl, carboxylic, and thiol functional groups or end groups seem to be potential sources for the construction of high-molecular-weight polymers containing weakly bound structure that can be destroyed under physiological conditions and to have potential for the preconcentration and separation of some trace elements[25–29].

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EXPERIMENTAL

3-mercaptopropionic acid (Merck), acrylamide (Merck), cerium(IV) sulfate (Merck), and sulfuric acid (Merck) were used without further treatment. Ce(IV) sulfate, 3-mercaptopropionic acid, and acrylamide are denoted by Ce(IV), MPA, and AA, respectively.

Polymerizations were carried out in a round-bottomed flask equipped with a stirrer by adding the calculated amount of Ce(IV) salt or $KMnO_4$ solution to aqueous solution of acrylamide monomer and 3-mercaptopropionic acid. After polymerization was completed, the solution was poured into an excess of acetone to precipitate the gross polymer. The polymer yield was determined by direct weighting of polyacrylamide dried in air and conversion % was calculated by using the following equation.

$$\text{Conversion } \% = \frac{\text{polymer yield(g)}}{\text{weight of monomer(g)}} \times 100$$

In the polymerization reaction, the effects of the mole ratio of acrylamide to initiator ($n_{AA}/n_{Ce(IV)} = 35$, 50, 100, 250, and 500), the temperature ($T = 20^\circ$, 30°, 40°, 60°, and 70°C), the polymerization time ($t = 15$, 30, 45, and 60 minutes), and the concentration of sulfuric acid ($[H_2SO_4] = 0.05$, 0.1, 0.2, 0.4, and 0.6 mol/L) on the conversion and molecular weight were examined. The $n_{Ce(IV)}/n_{MSA}$ ratio was kept constant at 1.

Infrared measurements were carried out with ATI Unicam (Mattson 1000) FTIR spectrometer and the spectra of polymers were determined by KBr disk method.

For determination of the average molecular weight (Mv), the flow time of dilute solution of polyacrylamide with 0.5 g/dL and that of water (the average value of flow times for three measurements was 163 ± 0.2 s for water at 30°C) was measured by an ubbelohde-level viscosimeter at 30°C. The intrinsic viscosity ($|\eta|$) of polymer solutions was calculated by using single point measurement as given in the following equation (30).

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

In standard measurements, the solution viscosity is measured in at least three different concentrations in triplicate for extrapolation of the Huggins or Kraemer plots to infinite dilution. However, this method is quite laborious and timeconsuming. The M_v values were calculated by using the Mark-Houwink equation[17–23].

$$|\eta| = 6.8 \times 10^4 \, M_v^{0.66}$$

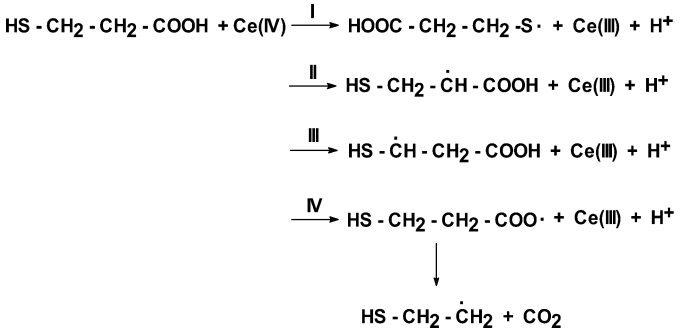
The UV-visible measurements (200–1000 nm) were done using a Shimadzu UV-160A spectrophotometer equipped with a temperature control attachment for spectrophotometric measurements.

For fluorescence measurement, a Perkin-Elmer model LS-50 fluorescence spectrometer was used to establish the existence of Ce(III) in polymer.

A Perkin–Elmer Model Zeeman-3030 atomic absorption unit with an HGA-600 graphite furnace was used for determining Mn(II) in polymer. The manganese hollow cathode lamps were operated at a current of 30 mA, wavelength of 403.2 nm, and a slit width of 0.7 nm.

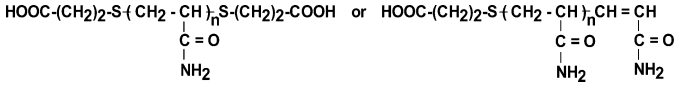
RESULTS AND DISCUSSION

An electron transfer from 3-mercaptopropionic acid to Ce(IV) leads to the formation of free radicals and the following reactions take place.



SCHEME 1.

To initiate the polymerization of acrylamide in acid aqueous medium, the formation of –S· radicals in reaction I in Scheme 1 is more probable than other reactions due to low S−H bonding energy. Termination reactions take place by combination reaction of polymer radicals and by oxidative termination of polymer radicals with Ce(IV) ions. Finally, water soluble polyacrylamides that have more likely structures given in Scheme 2 are synthesized in the polymerization reaction.



SCHEME 2.

The increase in the mole ratio of acrylamide to 3-mercaptopropionic acid resulted in an increase in the molecular weight but a decrease in the yield of polyacrylamide, which contains 3-mercaptopropionic acid end groups at constant monomer and acid concentrations at 30°C (Fig. 1). The mole ratio of cerium(IV) sulfate was taken as equal to the mole ratio of 3-mercaptopropionic acid, i.e., $n_{MPA} = n_{Ce(IV)}$.

The polymerization of acrylamide monomer is also initiated by the 3-mercaptopropionic acid-potassium permanganate redox system (Table 1). It was observed that the molecular weight of acrylamide polymer initiated by

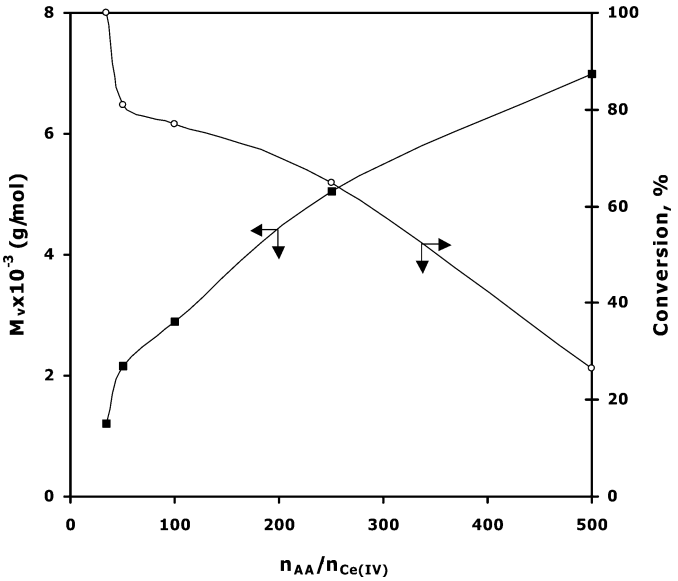


FIG. 1. The effect of the mole ratio acrylamide to initiator on the yield and molecular weight of polymer synthesized by using the 3-mercaptopropionic acid-Ce(IV) redox system. $[H_2SO_4] = 0.2\,mol/L$, $M_{AA} = 0.7\,mol/L$; $T = 30^{\circ}C$; $t = 1\,h$; $n_{Ce(IV)} = n_{MPA}$.

the 3-mercaptopropionic acid-$KMnO_4$ redox system is higher than that initiated by the 3-mercaptopropionic acid-cerium(IV) sulfate redox system.

Table 2 indicates the effects of polymerization time and acid concentration on the yield and molecular weight of polymer. With increasing of polymerization time, the yield and molecular weight of polymer did not change. This indicates that polymerization reaction is fast and completes in a few minutes.

Figure 2 shows the effect of reaction temperature on the yield and molecular weight of polymer. The increase of the temperature in polymerization reaction from 20°C to 70°C indicated a decrease in the yield of polymer due to termination of radicals at the beginning of the polymerization reaction. However, the molecular weight of polymer did not change with increasing of reaction temperature.

TABLE 1
The effect of permanganate concentration on the yield and molecular weight of polymer

n_{AA}/n_{MPA}	Conversion %	Mv (g/mol)
35	41.05	1500
50	60.55	1500
100	70.05	4550
250	89.50	9050
500	86.80	13050

$[H_2SO_4] = 0.05\,mol/L$; $[AA] = 0.7\,mol/L$; $T = 30^{\circ}C$; $t = 15$ minutes, $n_{KMnO_4} = n_{MPA}$.

TABLE 2
The dependence of yield and molecular weight of polymer on the acid concentration and polymerization time

n_{AA}/n_{MPA}	$[H_2SO_4]$ (mol/L)	Polymerization time (min)	Conversion %	Mv (g/mol)
100	0.2	15	78.40	2150
100	0.2	30	65.00	2150
100	0.2	45	72.65	2150
100	0.2	60	77.00	2900
100	0.05	60	8.30	1800
100	0.10	60	30.15	1800
100	0.40	60	68.70	2900
100	0.60	60	88.45	1850
250	0.05	60	7.90	4600
250	0.10	60	45.15	4150
250	0.20	60	64.90	5050
250	0.40	60	39.95	5050

$[AA] = 0.7\,mol/L$; $T = 30^{\circ}C$; $n_{Ce(IV)} = n_{MPA}$.

The UV-visible spectrum of polyacrylamide obtained using the Ce(IV)-organic acid or amino acid (with or without thiol group) redox system indicates a peak at 254 nm, due to the complex formation between Ce(III) ions and polymer containing functional end groups[21–23]. Such a peak was also observed at the UV-visible spectrum of acrylamide polymer synthesized by using the 3-mercaptopropionic acid-Ce(IV) redox system. Figure 3 indicates the relation between the absorbance values of polymer solutions (0.25 g polymer/100 mL in water) at 254 nm and the initiator concentration ($n_{Ce(IV)} = n_{MSA}$) in polymerization

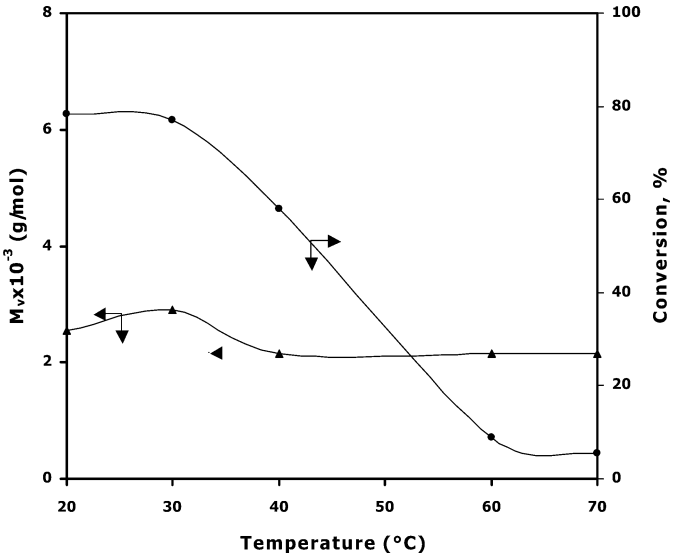


FIG. 2. The dependence of polymerization yield and molecular weight of polymer on temperature. $[H_2SO_4] = 0.2\,mol/L$; $M_{Ce(IV)} = 0.007\,mol/L$; $M_{AA} = 0.7\,mol/L$; $t = 1\,h$; $n_{Ce(IV)} = n_{MPA}$.

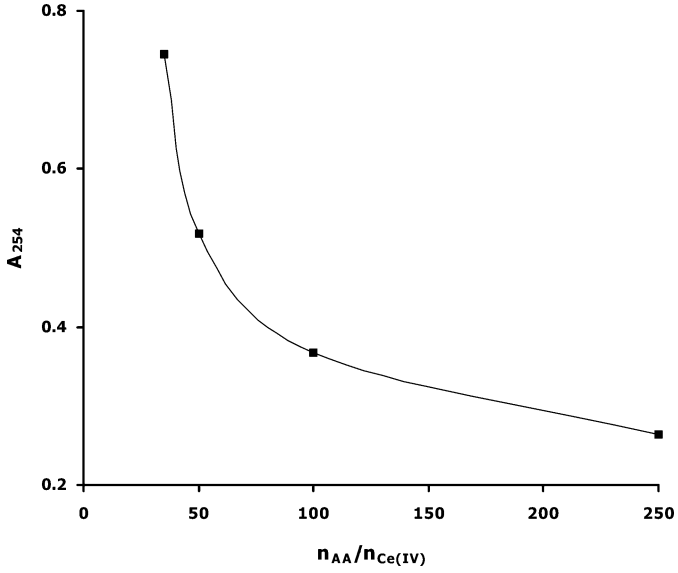


FIG. 3. The relation between the absorbance values at 254 nm of polymer solutions (0.25 g polymer/100 mL solution in distilled water) and the n_{AA}/n_{MPA} in polymerization reaction at 30°C. $M_{AA} = 0.7$ mol/L; $[H_2SO_4] = 0.2$ mol/L; $n_{Ce(IV)} = n_{MPA}$.

reaction at 30°C. As can be seen from Fig. 3, the increase of Ce(IV) concentration in polymerization reaction indicated an increase in the absorbance values at 254 nm. This indicates that complex formation takes place between Ce(III) ions and polyacrylamide containing 3-mercaptopropionic acid end groups.

In previous studies, the presence of carboxyl groups from FTIR spectra of polyacrylamide at 1390–1410 cm^{-1} was observed, unlike the FTIR spectrum of homopolyacrylamide[21–23]. Figure 4 shows the FTIR spectra of polymers as depending on the initiator concentration in the polymerization reaction. With increasing of 3-mercaptopropionic acid and Ce(IV) contents in the polymerization reaction, the intensities of the peaks at 1000–1800 cm^{-1} and 3220 cm^{-1} indicate an increase, due to carboxyl and amide groups in polymer and the complex formation between Ce(III) ions and polyacrylamide containing 3-mercaptopropionic acid end groups.

Unlike the fluorescence curve of homopolyacrylamide, the fluorescence curves of polyacrylamide obtained using the 3-mercaptopropionic acid-Ce(IV) redox system show a peak at 356 nm (Fig. 5). Ce(IV) reduced to Ce(III) in polymerization reaction. With increasing of Ce(IV) content in polymerization reaction, the fluorescence intensity of polymer solution (0.25 g polymer/100 mL solution in water) at 356 nm increases. The relationship between the values of fluorescence intensities of polymer solutions at 356 nm and the $n_{AA}/n_{Ce(IV)}$ in polymerization reaction is shown in Fig. 6.

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[1,3]. Formed Mn(IV) or Mn(III) ions reduce to Mn(II) ions in the polymerization reaction. The Mn(II) species that occur at the end of the polymerization

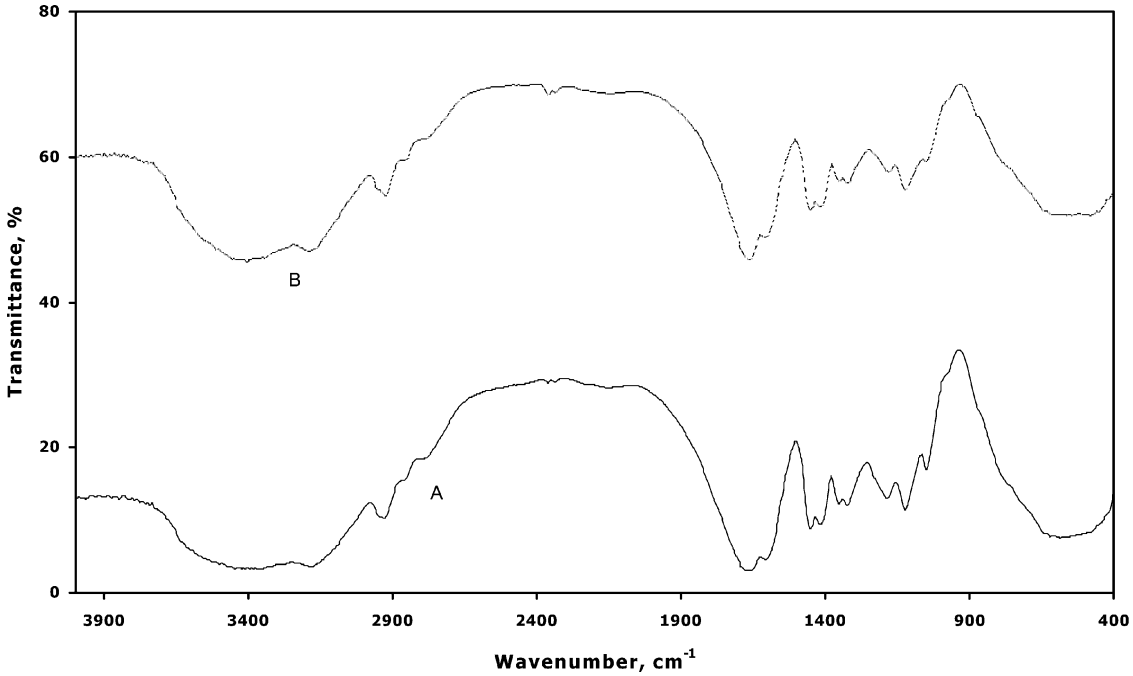


FIG. 4. FT-IR spectra of polyacrylamides containing different amounts of initiator in polymerization reaction. $n_{AA}/n_{MPA} = 100$ (A) and 500 (B); $[H_2SO_4] = 0.2$ mol/L, $M_{AA} = 0.7$ mol/L; T = 30°C; t = 1 h; $n_{Ce(IV)} = n_{MPA}$.

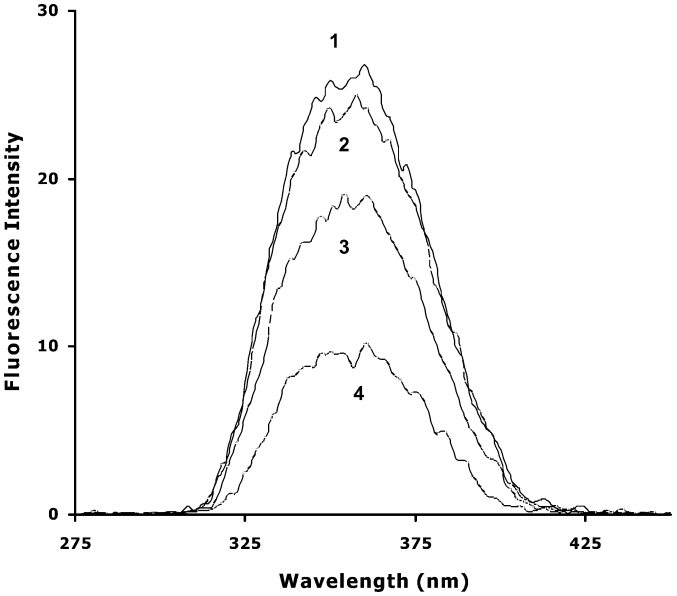


FIG. 5. The relation between fluorescence intensities of polyacrylamide solutions ($C_{polimer} = 0.25$ g polymer/dL solution in distilled water and excitation wavelength 260 nm) and the $n_{AA}/n_{Ce(IV)}$ ratios in polymerization reactions at 30°C. $n_{AA}/n_{Ce(IV)} = 35(1)$, 50 (2), 100 (3), and 250 (4). $[H_2SO_4] = 0.2$ mol/L, $M_{AA} = 0.7$ mol/L; t = 1 h; $n_{Ce(IV)} = n_{MPA}$.

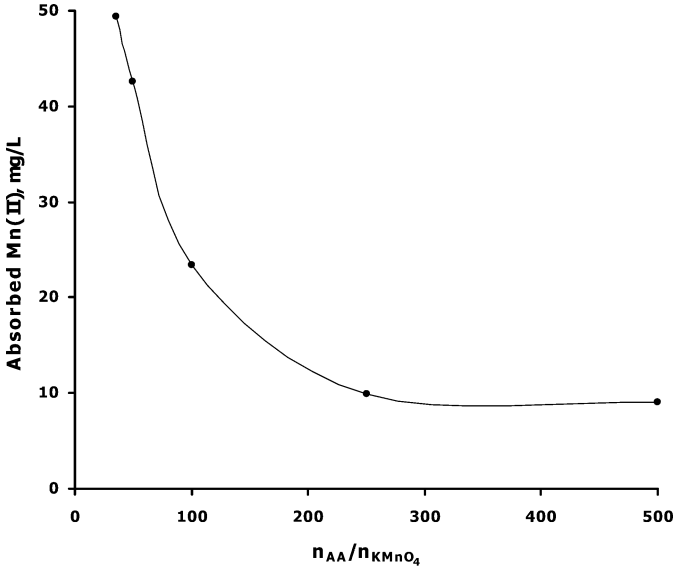


FIG. 7. The relation between the concentration of Mn(II) bonded to polymer and the permanganate concentration at the beginning of polymerization reaction. T = 30°C; t = 1 h; $M_{AA} = 0.7$ mol/L; $[H_2SO_4] = 0.2$ mol/L: $n_{KMnO_4} = n_{MPA}$, $C_{polimer} = 0.25$ g/dL.

reaction are absorbed with polymer[21–23]. The dependence of the concentration of Mn(II), which is incorporated in polymer on the initiator concentration, is given in Fig. 7. It is seen that the amount of Mn(II) bonded to polymer changes with the initial concentration of permanganate.

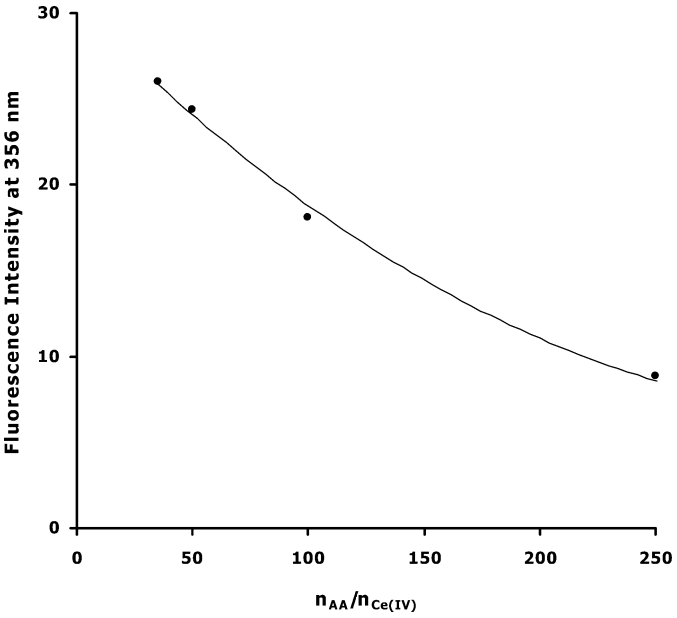


FIG. 6. The dependence of fluorescence intensities at 356 nm of polymer solution ($C_{polimer} = 0.25$ g polymer/dL solution in distilled water and excitation wavelength is 260 nm) on the mole ratio of acrylamide to cerium(IV) sulfate in polymerization reaction at 30°C. $M_{AA} = 0.7$ mol/L; $[H_2SO_4] = 0.2$ mol/L; T = 30°C; t = 1 h; $n_{Ce(IV)} = n_{MPA}$.

CONCLUSION

In this study, the polymerization of acrylamide monomer initiated by using the 3-mercaptopropionic acid-Ce(IV) or -$KMnO_4$ redox system was performed in acid-aqueous medium. The effects of the mole ratio of acrylamide to 3-mercaptopropionic acid, temperature, polymerization time, and concentration of sulfuric acid on the yield and molecular weight of polymer were investigated. The properties and compositions of obtained polymers were examined by viscosimetric and spectrometric (FT-IR, UV-visible, fluorescence, and atomic absorption) techniques. When we compared the effects of temperature, polymerization time, acid concentration, and initiator concentration on the yield of acrylamide polymer, we observed that polyamino acids, amino acids, and carboxylic acids[17–22] require higher energy, longer time, and lower acid concentration than organic acid containing thiol groups for acrylamide polymerization. Moreover, the formation of –S$^{\bullet}$ radicals is energetically most favorable due to low S–H bonding energy in the polymerization of acrylamide initiated by the $KMnO_4^-$ or Ce(IV)-3-mercaptopropionic acid redox system. This allows us to save energy in the polymerization process and to obtain a polymer with low branching.

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