Central European Science Journals
w w w . c e s j . c o m

Central European Journal of Chemistry
Central European Science Journals
CEJC 3(4) 2005 705–720

Oxidative polymerization of acrylamide in the presence of thioglycolic acid

Cemal Özeroğlu*, Sacide Erdoğan

Department of Chemistry, Faculty of Engineering,
Istanbul University,
34320 Avcilar, Istanbul, Turkey

Received 16 February 2005; accepted 17 June 2005

Abstract: Chemical polymerization of acrylamide at room temperature was examined by using thioglycolic acid-cerium (IV) sulfate and thioglycolic acid-$KMnO_4$ redox systems in acid aqueous medium. Water soluble polyacrylamides containing thioglycolic acid end groups were synthesized. The effects of the molar ratio of acrylamide to Ce(IV) $n_{AAm}/n_{Ce(IV)}$, the polymerization time, the temperature, the monomer concentration, the molar ratio of cerium (IV) sulfate to thioglycolic acid and the concentration of sulfuric acid on the yield and molecular weight of polymer were investigated. Lower molar ratios 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 generally resulted in a constant value for the molecular weight of polymer. With increasing polymerization time, the yield and molecular weight of polymer did not change substantially. 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 bound to polymer was investigated by UV-visible spectrophotometry and fluorescence measurements. The amount of Mn(II) incorporated into the polymer was determined using graphite furnace atomic absorption spectrometry. The mechanism of this phenomenon is discussed.
© Central European Science Journals. All rights reserved.

Keywords: *thioglycolic acid, cerium (IV) sulfate, redox polymerization, acrylamide*

1 Introduction

The use of ceric salts and $KMnO_4$-organic reducing agent redox systems in the syntheses of acrylamide, acrylonitrile, methylmethacrylate, or acrylic acid has been described in previous papers. These redox systems have been also used for the preparation of

* E-mail: ozeroglu@istanbul.edu.tr

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM

graft copolymers of vinyl monomers such as acrylonitrile, methylmethacrylate, acrylic or acrylamide [1-17]. Water-soluble polymers containing amine, hydroxyl, carboxyl or dicarboxylic end groups by using redox initiator system were synthesized [18-24]. In most previous 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 fact that it is an energy saving process and gives polymer with low branching.

In the present communication, the thioglycolic acid-cerium (IV) sulfate and the thioglycolic acid-$KMnO_4$ redox systems were used to initiate the polymerization of acrylamide in low temperature polymerization reactions. The dependence of the polymerization yield and the molecular weight of polymer on the $n_{AAm}/n_{Ce(IV)}$ ratio at constant monomer concentration, the polymerization time, the temperature, monomer concentration, the molar ratio of cerium (IV) sulfate to thioglycolic acid and the concentration of sulfuric acid was investigated. Polyacrylamides which are soluble in water and contain thioglycolic 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 synthesis of high molecular weight polymers that can be destroyed under physiological conditions due to occurring weakly bound structure in polymer and to have potential for the preconcentration and separation of some trace elements [25-29].

2 Experimental

Ceric sulfate ($CeSO_4 \cdot 2H_2O$), thioglycolic acid, acrylamide and sulfuric acid were all Merck reagent chemicals of highest purity and were used without further treatment. Ce(IV) sulfate, thioglycolic acid and acrylamide are denoted by Ce(IV), TGAc and AAm respectively.

Polymerizations were carried out in a round-bottomed flask equipped with a magnetic stirrer by adding the calculated amount of Ce(IV) salt or $KMnO_4$ solution to an aqueous solution of acrylamide monomer and thioglycolic 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 weighing the air-dried polyacrylamide and conversion % was calculated by using following equation.

$$\text{Conversion } \% = \frac{\text{polymer yield (g)}}{\text{weight of monomer (g)}} \times 100 \qquad (1)$$

In polymerization reactions, the effects of the mole ratio of acrylamide to initiator ($n_{AAm}/n_{Ce(IV)}$= 35, 50, 100, 250 and 500) at different polymerization time, the monomer concentration (C_{AAm}= 0.35, 0.525, 0.7, 1.05 and 1.4 mol/L), the temperature (T = 20, 30, 40, 60 and 70°C), the molar ratio of cerium (IV) sulfate to thioglycolic acid ($n_{Ce(IV)}/n_{TGAc}$ = 0.25, 0.5, 1 and 2) at constant monomer concentration, the polymerization time (t = 15, 30 and 60 min) and the concentration of sulfuric acid (C_{H2SO4} = 0.05, 0.1, 0.2 and 0.4

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM

mol/L) on the conversion and molecular weight were examined.

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

For determination of the average molecular weight (Mv), the flow times of dilute solutions of polyacrylamide (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) were measured by an Ubbelohde-level viscosimeter at 30 °C. The intrinsic viscosities ($|\eta|$) of polymer solutions were calculated by using single point measurements as given in the following equation [30].

$$|\eta| = \frac{\eta_{sp} + 3\ln(\eta_r)}{4C} \tag{2}$$

In standard measurements, the solution viscosity is measured in at least three different concentrations and triplicates for extrapolation of the Huggins or Kraemer plots to infinite dilution. However, this method is quite laborious and time consuming. The Mv values were calculated by using the Mark-Houwink equation [18-23].

$$|\eta| = 6.8 \times 10^4 \mathrm{M}_v^{0.66} \tag{3}$$

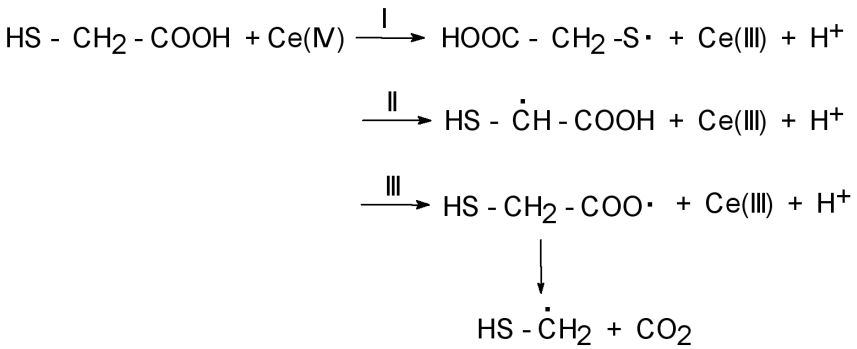
The UV-visible measurements (200-1000 nm) were made using a Shimadzu UV-160A spectrophotometer equipped with a temperature control attachment for spectrophotometric measurements.

For fluorescence measurements, 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 polymers. The Mn hollow cathode lamps were operated of a current at 30 mA, wavelength of 403.2 nm and a slit width of 0.7 nm.

3 Results and discussion

An electron transfer from thioglycolic acid to Ce(IV) leads to the formation of free radicals and the following reactions occur.

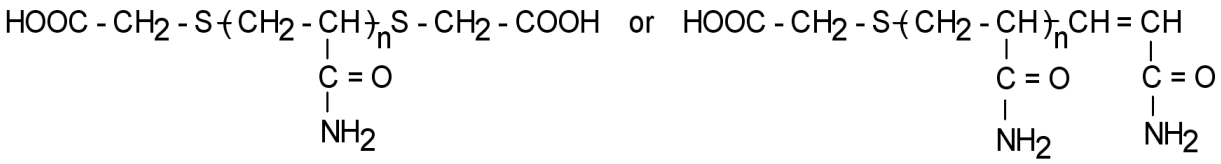


Scheme 1 Radical formation reactions.

Because of low S-H bonding energy, the formation of free radicals in reaction I in

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM

Scheme 1 is more likely than other reactions to initiate polymerization of acrylamide, and oxidative termination of polymer radicals by ceric ions is also possible. For this reason, in the polymerization reaction, water soluble polyacrylamides having probable structures given in Scheme 2 have been obtained.



Scheme 2 The probable structures of synthesized polymers.

The increase in the molar ratio of acrylamide to thioglycolic acid at different polymerization time led to an increase in the molecular weight but a decrease in the yield of polyacrylamide which contains thioglycolic acid end groups at constant monomer and acid concentrations at 30 °C (Figure 1). The molar ratio of cerium (IV) sulfate was taken as equal to the molar ratio of thioglycolic acid, i.e., $n_{TGAc} = n_{Ce(IV)}$.

The polymerization of acrylamide is also initiated by the thioglycolic acid-$KMnO_4$ redox system (Table 1). It was observed that at low initiator concentrations, the molecular weight of acrylamide polymer initiated by the thioglycolic acid-$KMnO_4$ redox system is higher than that initiated by the thioglycolic acid-cerium (IV) sulfate redox system.

n_{AAm}/n_{TGAc}	Conversion %	Mv (g/mol)
35	66.05	1000
50	53.20	2500
100	48.50	5000
250	26.15	9600
500	18.40	16800

Table 1 The effect of the permanganate concentration on the yield and molecular weight of polymer. $C_{H2SO4} = 0.1$ mol/L; $C_{AAm} = 0.7$ mol/L; T = 30 °C; t = 60 min, $n_{KMnO4} = n_{TGAc}$.

The effects of polymerization time, the temperature, the acid concentration and the mole ratio of cerium (IV) sulfate/thioglycolic acid at constant monomer concentration of 0.7 mol/L on the yield and molecular weight of polymer are given in Table 2. With increasing polymerization time, significant changes in the yield and molecular weight of polymers were not observed. This indicates that the polymerization reaction is fast and complete in a few minutes. The increase in the mole ratio of Ce(IV)/TGAc resulted in an increase in the yield. Upon increasing the concentration of sulfuric acid, the yield increased but the molecular weight of polymer decreased.

With increasing temperature, the data appeared to indicate only a small drop overall in the conversion, and there appears to be a small increase in molar mass.

The effect of monomer concentration on the yield and molecular weight of polymer is

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM

$n_{Ce(IV)}/n_{TGAc}$	C_{H2SO4} (mol/L)	Polymerization (Min.)	T (°C)	Conversion %	Mv (g/mol)
1.00	0.10	15	30	45.45	3750
1.00	0.10	30	30	55.45	3650
1.00	0.10	60	30	53.80	3100
1.00	0.05	15	30	32.65	4150
1.00	0.20	15	30	47.45	2550
1.00	0.40	15	30	51.95	2300
0.25	0.10	60	30	2.45	-
0.50	0.10	60	30	15.00	1500
2.00	0.10	60	30	50.85	3150
1.00	0.10	60	20	45.65	2900
1.00	0.10	60	40	41.00	2900
1.00	0.10	60	60	38.65	3300
1.00	0.10	60	70	29.50	3300

Table 2 The dependence of the yield and the molecular weight of polymer on the acid concentration, the temperature, the molar ratio of cerium (IV) sulfate/thioglycolic acid and the polymerization time. $C_{AAm} = 0.7$ mol/L; $n_{AAm}/n_{TGAc} = 100$.

given in Figure 2. As can be seen from Figure 2, with increasing monomer concentration, the polymerization yield increased and reached a maximum value at $C_{Aam} = 0.7$ mol/L and then showed a slight decrease; however, the molecular weight increased. The relation between conversion % and monomer concentration is unusual and unexpected and the reason is not known.

Unlike the UV-visible spectrum of homopolyacrylamide, the UV-visible spectrum of polyacrylamide obtained using 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 reducing agent end groups [21-23]. Two peaks at 238 nm and 253 nm were observed in the UV-visible spectrum of acrylamide polymer synthesized using the thioglycolic acid-Ce(IV) redox system. As can be seen from Figure 3, the increase in the molar ratio of acrylamide to initiator in the polymerization reaction led to a decrease in the absorbance values of polyacrylamide solutions (0.25 g polymer/100 mL solution in water) at 238 nm and 253 nm. This indicates that complex formation takes place between Ce(III) ions and polyacrylamide containing thioglycolic acid end groups. The relation between the absorbance values of polymer solutions (0.25 g polymer/100 mL in water) at 238 nm and 253 nm and the initiator concentration ($n_{Ce(IV)} = n_{TGAc}$) in polymerization reaction is given in Figure 4.

The FTIR spectra of polyacrylamide containing thioglycolic acid end groups are given in Figure 5. As seen from Figure 5, the peak intensities at 1050, 1130, 1190, 1355, 1460, 1680, 3220 and 3450 cm^{-1} in the polymer were determined. It has been reported that peaks representing carboxyl groups at 850-950, 1200-1300, 1350-1450, 1650-1750 and 2750-3300 cm^{-1} and amide groups at 1250-1450, 1550-1700 and 3200-3500 cm^{-1} are

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM

observed [31]. These results indicate that carboxyl and amide groups usually show peak intensities at the same wavenumbers and suggest that the observed peaks at 1000-1800, 3220 and 3450 cm^{-1} indicate the existence of carboxyl and amide groups in polymer. Moreover the spectra presented can arise from metal ions absorbed in the polymer.

Unlike the fluorescence curve of homopolyacrylamide, the fluorescence curves of polyacrylamide obtained using thioglycolic acid-Ce(IV) redox system show a peak at 356 nm (Figure 6). Ce(IV) was reduced to Ce(III) in the polymerization reaction. It was observed that with increasing Ce(IV) content in the polymerization reaction, the fluorescence intensity of polymer solution (0.25 g polymer/100 mL solution in water) at 356 nm increased. The data points of the fluorescence intensities of polymer solutions at 356 nm and $n_{AA}/n_{Ce(IV)}$ ratios in the polymerization reaction is shown in Table 3.

$n_{AAm}/n_{Ce(IV)}$	Fluorescence Intensity at 356 nm
35	6.54
50	6.12
100	5.36
250	3.02
500	2.71

Table 3 The relation between the fluorescence intensity at 356 nm of polymer solution ($C_{polymer}$ = 0.25 g polymer/dL solution in water; excitation wavelength = 260 nm) and the molar ratio of acrylamide to cerium (IV) sulfate in polymerization reaction at 30 °C. C_{AAm} = 0.7 mol/L; T = 30 °C; t = 15 min; $n_{Ce(IV)} = n_{TGAc}$.

Saraç and Misra have reported that MnO_2 is produced by the interaction of vinyl monomer with permanganate and then MnO_2 dissolves in acid, producing highly reactive Mn(III) ions [1,3]. Both Mn(IV) and Mn(III) ions reduced to Mn(II) ions in polymerization reactions. The Mn(II) species that occur at the end of the polymerization reaction are absorbed with polymer [21-23]. The effect of initiator concentration on the concentration of Mn(II) which is incorporated in the polymer is given in Figure 7. It is seen that the amount of Mn(II) bonded to polymer increases with increasing initial permanganate concentration in polymerization reactions.

In the polymerization of acrylamide initiated by Ce(IV)-thioglycolic acid in acid-aqueous medium, the formation of thiol radicals (–S·) is energetically most favorable due to low S-H bonding energy. Therefore the polymerization of acrylamide initiated with Ce(IV)-organic reducing agents such as polyamino, amino and carboxylic acids [17-22] requires higher energy, longer time and lower acid concentration than initiated with Ce(IV)-organic reducing agents containing thiol groups. In this study, the polymerization of acrylamide using thioglycolic acid-Ce(IV) or $KMnO_4$ redox system in acidic aqueous medium was examined at room temperatures. The effects of the molar ratio of acrylamide to thioglycolic acid, the temperature, the polymerization time, the monomer concentration and the concentration of sulfuric acid on the yield and molecular weight of polymer were investigated. The results indicate that this redox system is very convenient to ini-

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM

tiate acrylamide polymerization at room temperature. Low temperature polymerization is attractive both industrially and scientifically due to fact that it is an energy saving process and gives polymer with low branching.

References

[1] A.S. Saraç: "Redox polymerization", *Prog. Polym. Sci.*, Vol. 24, (1999), pp. 1149–1204.

[2] H.F. Launer and D.M. Yost: "The kinetics of the reaction between potassium permanganate and oxalic acid", *J. Am. Chem. Soc.*, Vol. 56, (1934), pp. 2571–2577.

[3] G.S. Misra and U.D.N. Bajpai: "Redox polymerization", *Prog. Polym. Sci.*, Vol. 8, (1982), pp. 61–131.

[4] J.S. Shukla and D.C. Misra: "Aqueous polymerization of acrylamide initiated by acidic potassium permanganate-ascorbic acid redox system", *J. Polym. Sci. Polym. Chem. Edit.*, Vol. 11, (1973), pp. 751–762.

[5] D. Pramanik and A.K. Chaterjee: "Mechanistic studies on ceric-thiourea-initiated polymerization in acid aqueous media from end group analysis", *J. Polym. Sci. Chem. Edit.,* Vol. 18, (1980), pp. 311–319.

[6] C. Özeroğlu and T. Yalçinyuva: "Oxidative polymerization of methyl methacrylate in acid aqueous medium", *Polym.-Plast. Technol.*, Vol. 43(3), (2004), pp. 731–743.

[7] N. Biçak and C. Özeroğlu: "Low temperature initiation by methylene bis(diethyl malonate)-Ce(IV) redox system in organic solvents", *Eur. Polym. J.*, Vol. 37, (2001), pp. 2393–2395.

[8] K.Y. Sui and L.X. Gu: "Preparation and characterization of amplihilic block copolymer of polyacrylonitrile-block-poly(ethylene oxide)", *J. Appl. Polym. Sci.*, Vol. 89(7), (2003), pp. 1753–1759.

[9] A.S. Saraç, Ş. Özkara, B. Ustamehmetoğlu and E. Sezer: "Controlled electroinduced polymerization of methyl meyhacrylate in the presence of catalytic amount of Ce(IV)", *J. Macromol. Sci. Pure A*, Vol. 40(2), (2003), pp. 193–207.

[10] V.S. Ananthanarayanan and M. Santappa: "Kinetics of vinyl polymerization initiated by ceric ion in aqueous solution", *J. Appl. Polym. Sci.*, Vol. 9, (1965), pp. 2437–2449.

[11] G. Mino, S. Kaizerman and E. Rasmussen: "The polymerization of acrylamide initiated by ceric nitrate-3-chloro-1-propanol redox system", *J. Polym. Sci.*, Vol. 38, (1959), pp. 393–401.

[12] S.V. Subramaniun and M. Santappa: "Ceric ion-reducing agent redox couple initiated vinyl polymerization", *Macromol. Chem.*, Vol. 112, (1968), pp. 1–15; "Vinyl polymerization initiated by ceric ion-reducing agent system in sulfuric acid media", *J. Polym. Sci. Part A-1*, Vol. 6(3) (1968), pp. 493–504.

[13] S.R. Palit and R.S. Konar: "Permanganate-oxalic acid as an initiator of acrylonitrile polymerization in aqueous media: (III) Kinetics and degree of polymerization", *J. Polym. Sci. Part A*, Vol. 2(4), (1964), pp. 1731–1748.

[14] S.R. Palit and R.S. Konar: "Permanganate-$H_2C_2O_4$ as an initiator in aqueous media: (I) The initiating radical and general features", *J. Polym. Sci.*, Vol. 57, (1962), pp.

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM

609–615; "(II) The kinetics and degree of polymerization", *J. Polym. Sci.*, Vol. 58, (1962), pp. 85–102.

[15] G.S. Misra and H. Narain: "Aqueous polymerization of acrylic acid initiated by potassium permanganate-oxalic acid redox system", *Makromol. Chem.*, Vol. 113, (1968), pp. 85–94.

[16] M.M. Hussain and A. Gupta: "Effect of some additions on the aqueous polymerization of acrylamide initiated by permanganate-oxalic acid redox system", *Makromol. Chem.*, Vol. 178(1), (1977), pp. 29–36.

[17] O. Galioğlu, A.B. Soydan, A. Akar and A.S. Saraç: "Block graft copolymer synthesis via ceric salt", *Angew. Makromol. Chem.*, Vol. 214, (1994), pp. 19–28.

[18] A.S. Saraç, C. Erbil and A.B. Soydan: "Polymerization of acrylamide initiated with electrogenerated cerium(IV) in the presence of EDTA", *J. Appl. Polym. Sci.*, Vol. 44, (1992), pp. 877–891.

[19] C. Erbil, C. Cin, A.B. Soydan and A.S. Saraç: "Polyaminocarboxylic acids-Ce(IV) redox systems as an initiator in acrylamide polymerization", *J. Appl. Polym. Sci.*, Vol. 47, (1993), pp. 1643–1648.

[20] A.S. Saraç, A.H. Başak, A.B. Soydan and A. Akar: "Polymerization of acrylamide by electrolytically generated Ce(IV)-organic acid redox system", *Angew. Makromol. Chem.*, Vol. 198, (1992), pp. 191–198.

[21] C. Özeroğlu, O. Güney, A.S. Saraç and M.I. Mustafaev: "Polymerization of acrylamide initiated with Ce(IV) and $KMnO_4$ redox systems in the presence of glycine", *J. Appl. Polym. Sci.*, Vol. 60, (1996), pp. 759–765.

[22] C. Özeroğlu, O. Güney and M.I. Mustafaev: "Oxidative polymerization of acrylamide in the presence of L-threonine", *Angew. Makromol. Chem.*, Vol. 249, (1997), pp. 1–9.

[23] C. Özeroğlu and A.E. Kurtoğlu: "The synthesis and characterization of acrylamide polymer containing R-(+)-cystein end groups", *Eur. Polym. J.*, Vol. 37, (2001), pp. 1053–1059.

[24] B. Ustamehmetoğlu, Z.I. Diler and A.S. Saraç: "Chemical polymerization of acrylamide initiated with Ce(IV)-dicarboxylic acid redox system: effect of chain length between the carboxyl groups", *Int. J Polym. Anal. Ch.*, Vol. 7(4), (2002), pp. 263–272.

[25] A.S. Saraç, C. Özeroğlu and M.I. Mustafaev: "Ternary complexes of bovine serum albumin and polyacrylamide derivatives in the presence of copper ions in neutral water", *J. Bioact. Compat. Polym.*, Vol. 10, (1995), pp. 121–134.

[26] C. Özeroğlu, N. Namazova, M.I. Muatafaev and A.S. Saraç: "The complex formation between polyacrylamide containing glycine end groups and bovine serum albumin in the presence of copper(II) in neutral aqueous water", *Colloid Polym. Sci.*, Vol. 274, (1996), pp. 418–427.

[27] R.V. Petrov, M.I. Mustafaev and A.Sh. Norimov: *Physicochemical Criteria for the Constraction of Artificial Immunomodulators and Immunogens on the Basis of Polyelectrolyte Complexes*, Sov. Med. Rev. D. Immunol., UK Harwood Academic Publisher GmbH, London, UK, 1992, pp, 1–113.

[28] M. Özcan, S. Akman and C. Özeroğlu: "The use of water soluble polymers for the preconcentration and separation of copper, lead and chromium prior to their

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM

determination by graphite furnace atomic absorption spectrometry", *Anal. Lett.*, Vol. 35(6), (2002), pp. 1075–1083.

[29] M. Özcan, S. Akman, C. Erbil and A.S. Sarac: "Determination of copper, chromium, manganese and zinc by graphite furnace atomic absorption spectrometry after separation on polyacrylamide modified with nitriloacetic acid", *Fresen. J. Anal. Chem.*, Vol. 355(5-6), (1996), pp. 665–666.

[30] H.H. Chuah, D. Lin-Vien and U. Soni: "Poly(trimethylene terephthalate) molecular weight and Mark-Houwink equation", *Polymer*, Vol. 42, (2001), pp. 7137–7139.

[31] J.H. Harley and S.E. Wiberley: *Instrumental Analysis*, John Wiley and Sons, Inc., New York, 1954, pp. 63–95.

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM

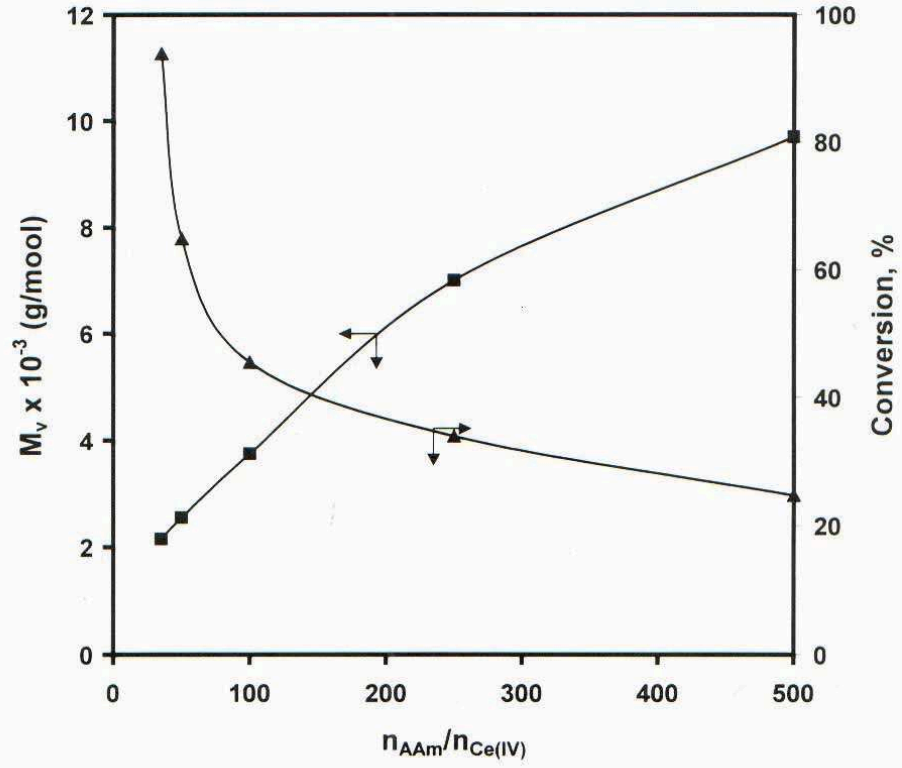


Fig. 1 The effect of the mole ratio of acrylamide to initiator on the yield and molecular weight of polymer synthesized by using thioglycolic acid-Ce(IV) redox system. C_{H2SO4} = 0.1 mol/L, C_{AAm} = 0.7 mol/L; T = 30 °C; t = 15 min; $n_{Ce(IV)} = n_{TGAc}$.

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM

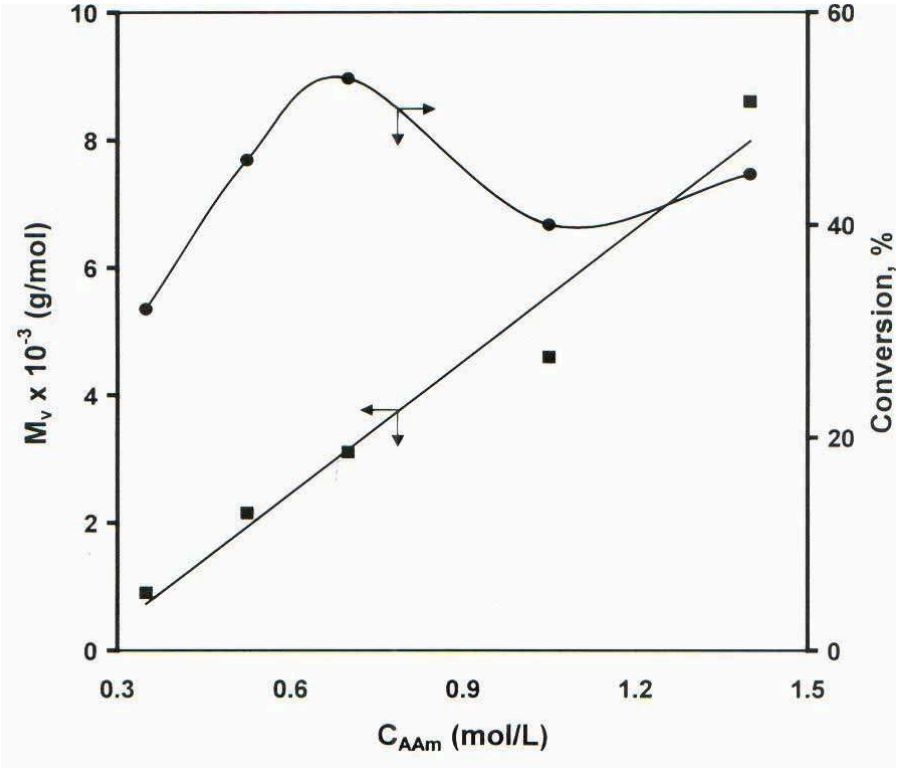


Fig. 2 The effect of monomer concentration on the yield and molecular weight of polymer. C_{H2SO4} = 0.1 mol/L; $C_{Ce(IV)}$= 0.007 mol/L; T = 30 °C; t = 1 h; $n_{Ce(IV)} = n_{TGAc}$.

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM

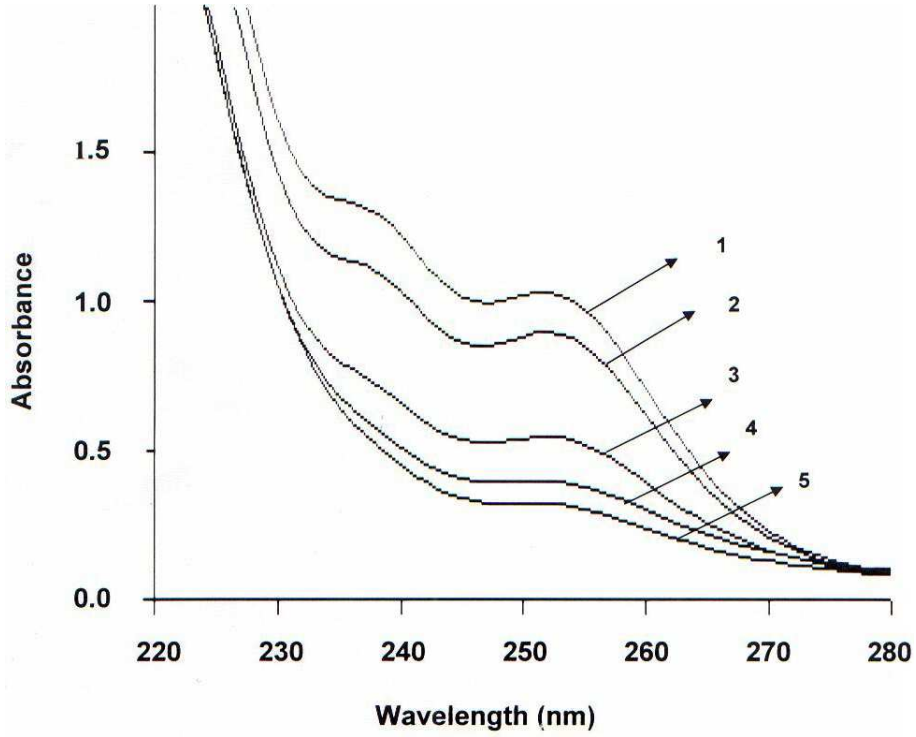


Fig. 3 UV-visible spectra of polymer solutions obtained using Ce(IV)-thioglycolic acid redox system at different initiator concentrations. $n_{AAm}/n_{Ce(IV)}$= 35(1), 50(2), 100(3), 250(4) and 500(5). C_{H2SO4}= 0.1 mol/L; C_{AAm}= 0.7 mol/L; t = 15 min; $n_{Ce(IV)} = n_{TGAc}$; $C_{polymer}$ = 0.25 g/dL.

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM

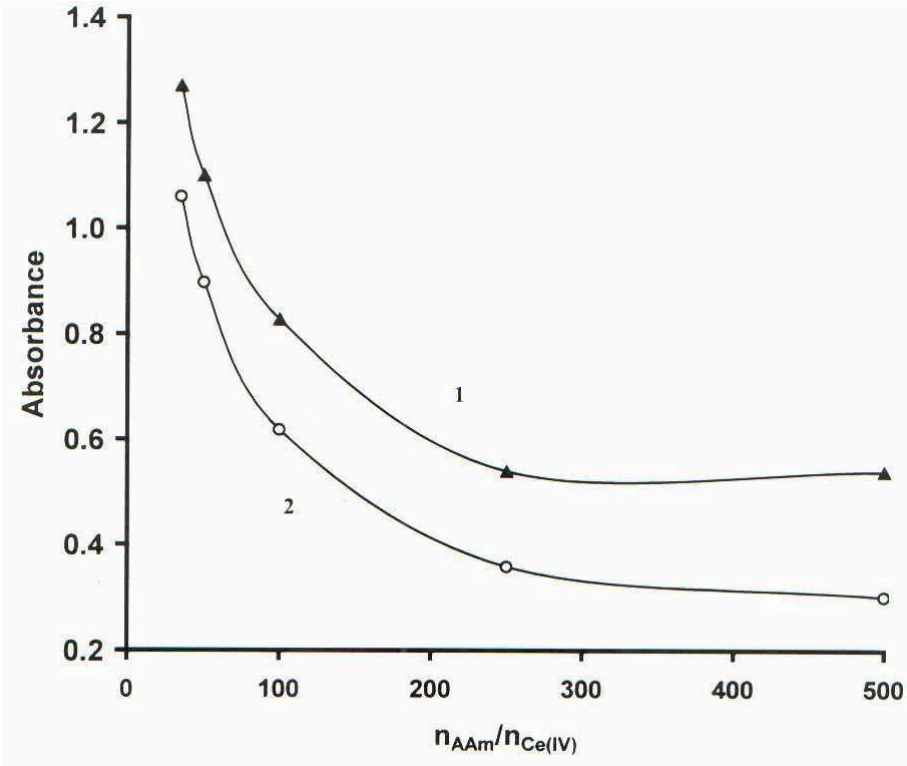


Fig. 4 The relation between the absorbance values at 238 (1) and 253 (2) nm of polymer solutions (0.25 g polymer/100 mL solution in water) and the n_{AAm}/n_{TGAc} in polymerization reaction at 30 °C. C_{AAm} = 0.7 mol/L; C_{H2SO4} = 0.1 mol/L; $n_{Ce(IV)} = n_{TGAc}$.

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM

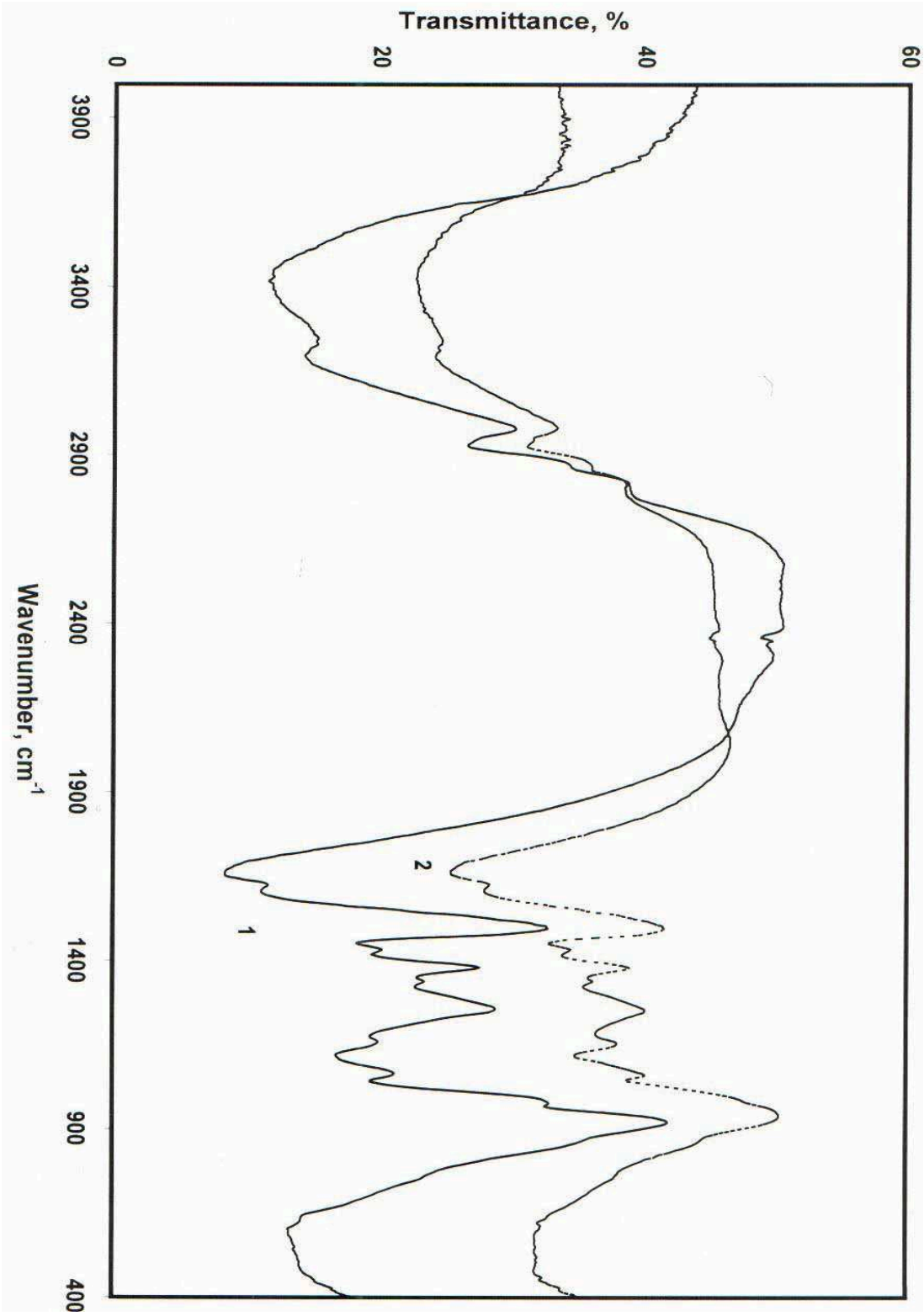


Fig. 5 FT-IR spectra of polyacrylamides obtained using thioglycolic acid-cerium(IV) sulfate(1) and thioglycolic acid-$KMnO_4$(2) redox systems.

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM

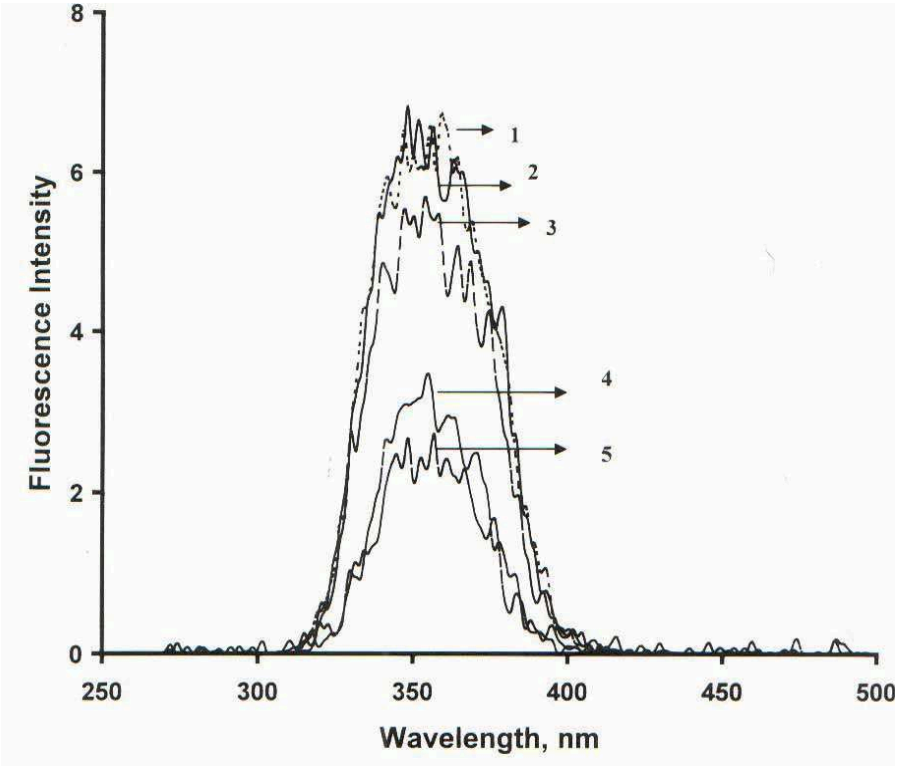


Fig. 6 The dependence of fluorescence curves of polyacrylamide solutions ($C_{polymer}$ = 0.25 g polymer/dL solution in water), obtained using thioglycolic acid-cerium (IV) sulfate redox system, on the molar ratio of monomer/initiator (excitation wavelength = 260 nm). $n_{AAm}/n_{Ce(IV)}$ = 35(1), 50(2), 100(3), 250(4) and 500(5). C_{H2SO4} = 0.1 mol/L, C_{AAm} = 0.7 mol/L; T = 30 °C; t = 15 min; $n_{Ce(IV)} = n_{TGAc}$.

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM

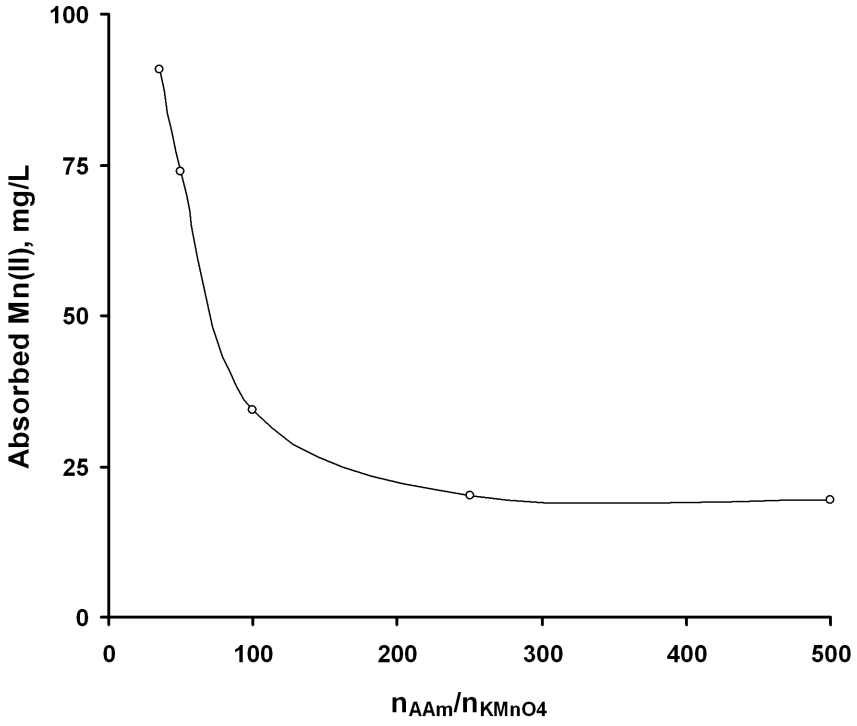


Fig. 7 The relation between the concentration of Mn(II) bonded to polymer and the permanganate concentration at the beginning of polymerization reaction. T = 30 °C; t = 1 h; C_{AAm} = 0.7 mol/L; C_{H2SO4} = 0.1 mol/L; $n_{KMnO4} = n_{TGAc}$, $C_{polymer}$ = 0.25 g/dL.

Brought to you by | Istanbul Universitesi - Istanbul University
Authenticated
Download Date | 3/5/20 5:34 PM