

The Polymerization of Acrylamide Initiated with Ce(IV) and KMnO_4 Redox Systems in the Presence of Glycine

CEMAL ÖZEROĞLU,^{1,*} ORHAN GÜNEY,¹ A. SEZAI SARAÇ,¹ and MAMED I. MUSTAFAEV^{1,2}

¹Department of Chemistry, Istanbul Technical University, 80626 Maslak, Turkey, and ²Department of Chemistry, Baku State University, Baku, Azerbaijan

SYNOPSIS

Glycine–Ce(IV) salts and KMnO_4 initiator systems were used for the polymerization of acrylamide, resulting in water-soluble polyacrylamide, which contains amino acid end groups. The dependence of polymerization yields and molecular weights of polymers on the mole ratio of acrylamide monomer to glycine, the polymerization time, the temperature, and the concentration of sulfuric acid were investigated. The decrease in the mole ratio of acrylamide to glycine resulted in a decrease in the molecular weight, and an increase in the yield of acrylamide polymer, which contains a glycine end group. With increasing acid concentration of the polymeric solution, the polymerization yield and the molecular weight of polymer decrease. Ce(IV) and Mn(IV) reduced to Ce(III) and Mn(II) in the polymerization reaction. The amounts of Ce(III) and Mn(II) bound to polymer were determined. The composition of the polymerization product was investigated and a bimodal character of the molecular weight distribution was observed. The mechanism of this phenomena is discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

KMnO_4 ¹ and ceric salts^{2–4}–organic reducing agent system in acidic solution are used as initiators for vinyl polymerization. It is well known that these salts also form very effective redox systems in the presence of organic reducing agent such as alcohols,^{5,6} aldehydes,⁷ and carboxylic acids.⁸ These methods have also been used for the preparation of graft copolymers of vinyl monomers such as acrylonitrile acrylic acid and acrylamide.^{5–12} Using a Ce(IV)–organic acid redox system, Sarac et al. recently synthesized (amino, hydroxy, carboxylic, and dicarboxylic acids) end-group-containing water-soluble polymers.^{13–17} However, in these studies, the composition (metal ions existence in the structure of the polymers) and molecular weight distribution were not investigated.

In this work, the polymerization of acrylamide monomer, initiated by cerium(IV) sulfate–glycine

and the potassium permanganate–glycine redox systems, was investigated. The dependence of polymerization yields and molecular weights of polymers on the mole ratio of acrylamide monomer to glycine, the polymerization time, the temperature, and the acid concentration were investigated. First the composition of the polymerization product was investigated and the existence of Ce(III) and Mn(II) in polymer was determined. Water-soluble polyacrylamides that contain amino acid end groups were synthesized. Such polyelectrolytes (PE) have potential for the construction of high-molecular-weight polymers containing weakly bound structure that can be destroyed under physiological conditions.^{18,19} The results of FTIR, UV-visible spectrometry, atomic absorption spectrometry, conductometric titration, viscosity, fluorescence measurement, and HPLC chromatography are given.

EXPERIMENTAL

Cerium(IV) sulfate, acrylamide, potassium permanganate, glycine, and sulfuric acid (Merck) were used without further treatment. Acrylamide, glycine

* To whom correspondence should be addressed.

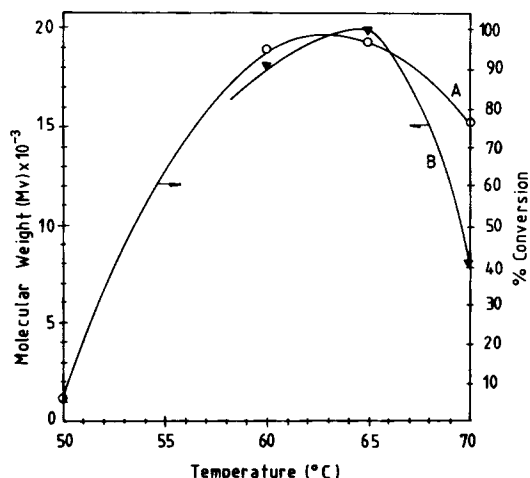


Figure 2 The dependence of yield and molecular weight of polymer on the temperature. $n_{AA}/n_{gly} = 250$; $t = 6$ h; $C_{gly} = 2.8 \times 10^{-3}$ mol/L, $C_{H_2SO_4} = 0.05$ mol/L; $C_{AA} = 0.7$ mol/L; $n_{Ce(IV)} = n_{Gly}$.

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

A Perkin-Elmer Model Zeeman-3030 atomic absorption unit equipped with an HGA-600 graphite furnace and PR-100 printer were used for determining Mn(II) in polymer. The manganese hollow cathode lamps were operated at a lamp current of 30 mA, wavelength of 403.2 nm, and a slit width of 0.7 nm.

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

Gel filtration HPLC was estimated by gel filtration chromatography using a Bio-Sil Sec. 250 column (7.8 mm \times 30 cm). The HPLC was run using a buffer containing 100 mM phosphate, pH 6.8, and 0.1M NaCl at a flow rate of 0.1 mL/min at room temperature. The eluate was monitored at 280 nm.

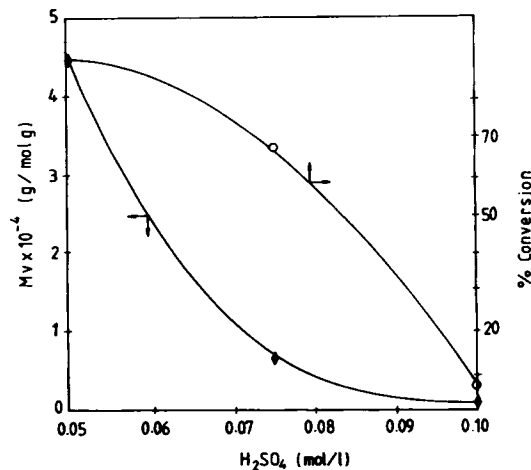


Figure 3 The effect of acid concentration on the yield and the molecular weight of polymer. $n_{AA}/n_{gly} = 250$; $t = 6$ h; $C_{gly} = 2.8 \times 10^{-3}$ mol/L; $C_{AA} = 0.7$ mol/L; $n_{Ce(IV)} = n_{Gly}$.

RESULTS AND DISCUSSION

The comparison of the effects of the temperature, the polymerization time, acid concentration and the mole ratio of monomer/initiator on the yield with other carboxylic acids¹⁵ and polyamino carboxylic acids^{14–17} shows that for the involvement of amino acid end groups to polymer, the amino acids require higher energy, longer time, and lower acid concentration for the acrylamide polymerization.

The increase in the mole ratio of acrylamide to glycine resulted in an increase in the molecular weight but a decrease in the yield of polyacrylamide, which contains glycine end groups at constant acid concentration and temperature (Fig. 1). The mole of cerium(IV) sulfate was taken as equal to the mole of glycine, i.e., $n_{Ce(IV)} = n_{glycine}$.

The polymerization of acrylamide monomer is also initiated by the potassium permanganate glycine redox system (Table I). We observed that the

Table III Molecular Weight and Conductivities of PE

PE	C_{AA}/C_{Gly}	M_v	M_n	M_v/M_n	$n = M_v/M_{AA}$	Specific Conductivity ^a ($\Omega^{-1} \text{ cm}^{-1}$) $\times 10^6$
PE1	100	20,000	19,000	1.05	280	380
PE2	250	45,000	22,200	2.02	630	296
PE3 ^b	500	230,000	—	—	3200	168

^a The specific conductance of 0.3 g polymer dissolved in 50 mL water.

^b Since polymers have high molecular weights, carboxylic end groups were difficult to determine.

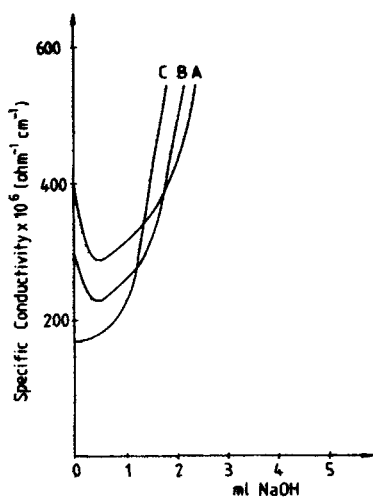


Figure 4 The conductometric titration curves of polymers at different molecular weights by using 0.09N NaOH as titrant. $M_v = 20,000$ (A); $M_v = 45,000$ (B); $M_v = 230,000$ (C).

velocity of the polymerization of acrylamide monomer initiated by the KMnO_4 -glycine redox system is faster than that initiated by the Ce(IV) sulfate-glycine redox system.

With increasing polymerization time, the yield of polymer increased, but the molecular weight of the polymer did not change. The results are shown in Table II.

The effect of temperature on the yield and molecular weight of polymer is shown in Figure 2. As

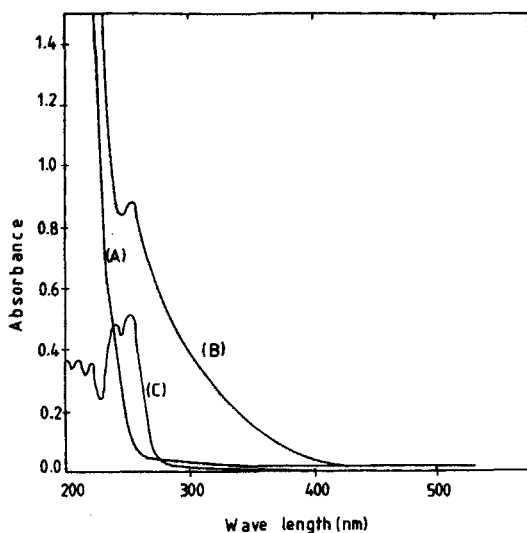


Figure 5 The UV spectra of homopolyacrylamide (A, 6×10^{-6} mol/L), polyacrylamide (B, 2.5×10^{-4} mol/L) obtained by cerium(IV) sulfate-glycine redox system and cerium(III) sulfate (C, 1.6×10^{-3} mol/L).

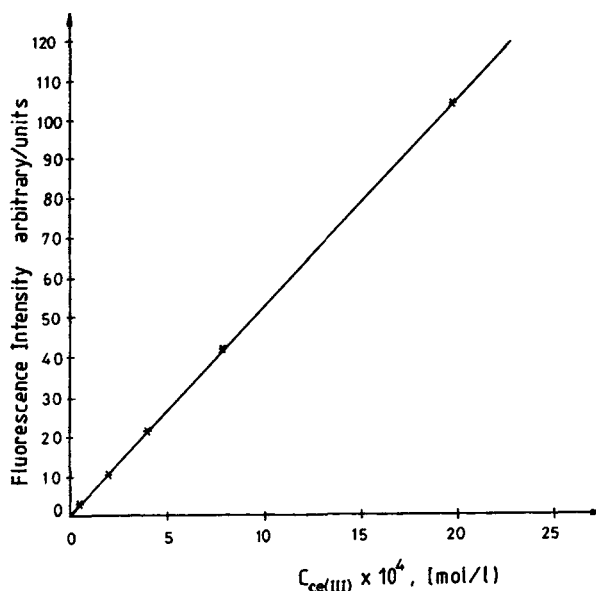


Figure 6 The dependence of intensity on cerium(III) sulfate concentration (excitation wavelength 290 nm).

can be seen from the figure, the polymerization yield and the molecular weight of polymer increase and then reach a maximum value with increasing temperature.

The effect of acid concentration on the yield and the molecular weight of acrylamide polymer is shown

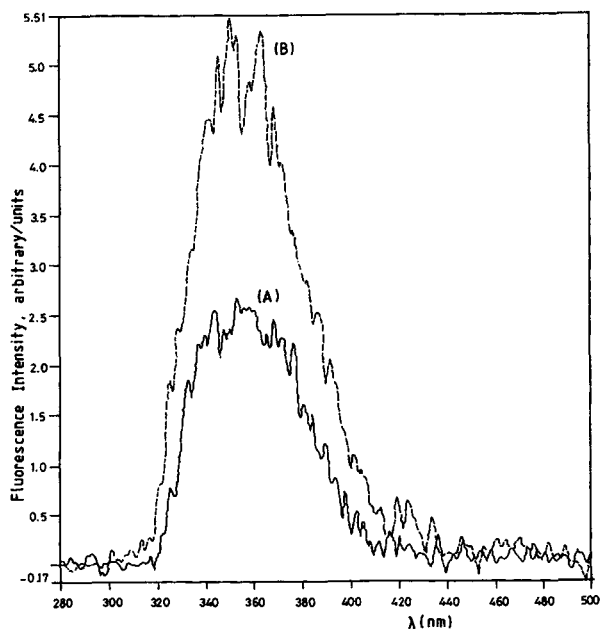


Figure 7 The fluorescence spectra of polyacrylamides initiated by cerium(IV) sulfate-glycine redox system (excitation wavelength 290 nm). $C_{\text{PE}} = 0.02$ g/dL (A), 0.04 g/dL (B).

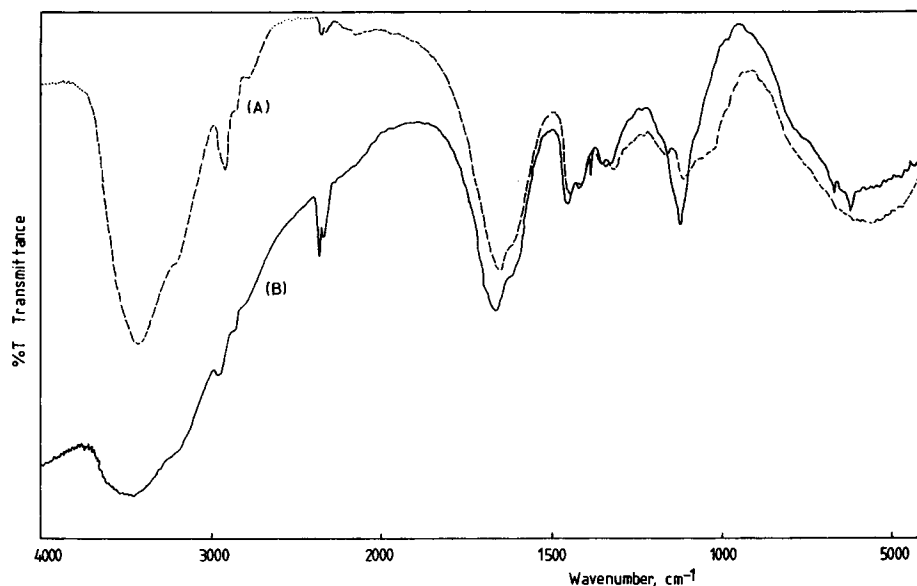


Figure 8 FT-IR spectra of polyacrylamides obtained by cerium(IV) sulfate-glycine (A) and potassium permanganate-glycine (B) redox systems.

in Figure 3. The increase of acid concentration in polymeric solution results in a decrease in the yield and the molecular weight of polymer.

The conductometric titration curves of polymers, in the case of the Ce(IV)-glycine redox system, are given in Figure 4. According to our previous results,¹⁵ the amino groups are responsible for the second peak of the titration curve. After ionization of the COOH groups is complete, by further addition of NaOH solution of known normality the number of the amino groups was determined. A comparison of molecular weight determined by conductometric titration and the viscometric method is given in Table III.

The UV-visible spectra of homopolyacrylamide, polyacrylamide obtained by cerium(IV) sulfate-glycine redox system, and cerium(III) sulfate are given in Figure 5. As can be seen from Figure 5, the UV absorbance curves of Ce(III) sulfate and polyacrylamide, obtained using the Ce(IV)-glycine redox system, contain peaks at 254 nm. The UV-visible spectrum of homopolyacrylamide does not contain any peak at 254 nm. Ce(IV) reduced to Ce(III) at the reaction of polymerization. The existence of Ce(III), which forms a complex with the polymer, was determined by the fluorescence measurements (Figs. 6 and 7). The fluorescence data show that about 75% of the initial Ce(IV) concentration forms a complex with polymer as Ce(III). The UV-visible and fluorescence measurements show that there is an interaction between polymer and Ce(III), i.e.,

complex reactions take place during the polymerization reaction.

FT-IR spectra of polymers, obtained by Ce(IV) sulfate-glycine and potassium permanganate-glycine redox systems, are shown in Figure 8. The amount of manganese in polyacrylamide obtained with the KMnO_4 -glycine redox system was determined by using the atomic absorption method (Fig. 9). As can be seen from FTIR and atomic absorption results, there is also an interaction between polyacrylamide, which contains glycine end groups, and manganese ions. The Mn(II) species that occur at the end of the reaction of polymerization form a complex with polymer. The amount of Mn(II) bounded to polymer as a complex changes with initial concentration of the permanganate. When the initial concentrations of Mn(IV) were 0.0678 and 0.0339 g/L, the concentrations of Mn(II) bound to polymer were 0.055 and 0.029 g/L, respectively.

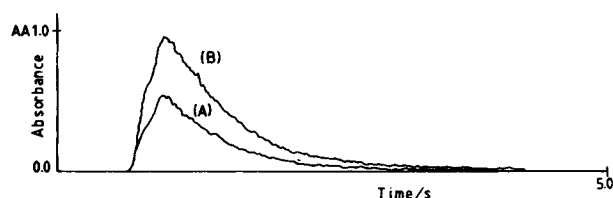


Figure 9 Atomic absorption spectra of acrylamide polymer obtained by potassium permanganate-glycine redox system. $C_{\text{Mn(II)}} = 0.029$ g/L (A), $C_{\text{Mn(II)}} = 0.055$ g/L (B).

Mainly two peaks were observed in the HPLC chromatograms of polymers (Fig. 10). As Figure 10 shows, the water solutions of PE1, PE2, and PE3 are characterized by a bimodal distribution of products. The areas of these peaks change with the concentration of initiator. The area of the peak I decreases with increasing the initiator concentration, but the area of peak II increases. Since peak I belongs to high-molecular-weight polyacrylamide, with decreasing initiator concentration, polyacrylamide having high molecular weight is obtained. The HPLC chromatograms of polyacrylamide, which has low molecular weight, are given for 254 and 280 nm in Figure 11. The peaks at 254 nm are due to low-molecular-weight polymers that contain glycine end groups. These multipeaks do not appear at 280 nm, because of complex formation; there is no absorbance at 280 nm.

The bimodal character of the polymeric product can be described as follows. Considering the reaction of Ce(IV)–Ce(III), it is considered that both cerium ions form complexes with a part of the polymer chain and the polymeric product consists of two fractions: free polymer without contained metal ions and polymer metal complexes. Complex formation between glycine end groups of PAA and cerium ions can be depicted as follows.

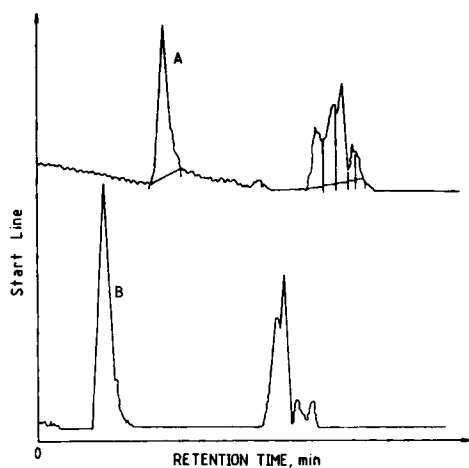
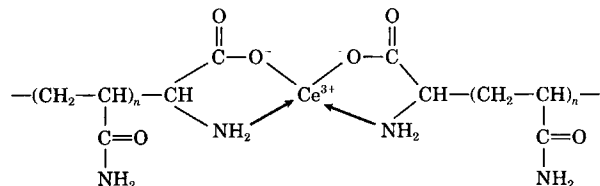


Figure 10 The HPLC chromatograms of polymers that have different molecular weight $M_v = 20,000$ (A); $M_v = 230,000$ (B); flow: 1.0 mL/min; pH 6.8.

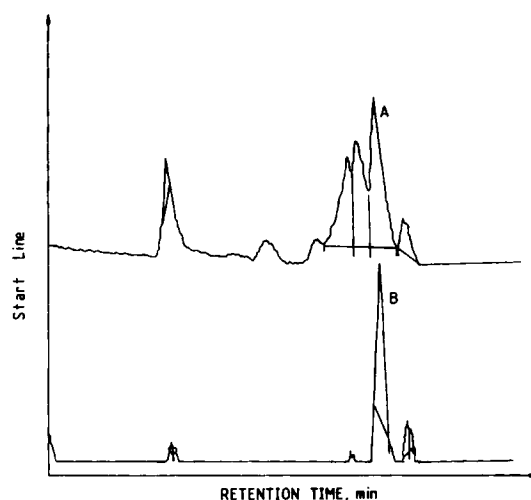


Figure 11 The HPLC chromatograms of polymer solutions at 254 nm (A) and 280 nm (B); $M_v = 45,000$; flow: 1.0 mL/min; pH 6.8; $C_{PE} = 0.1$ g/dL.

On the basis of the weak stability of PAA–metal complexes^{18,19} binding metal ions with two amino acid residues are more likely. This assumption gives two results: first, in water solution, two fractions occur at two different conformational states (coil and compact structures) that elute from HPLC chromatography with different elution volume. Second, the formation of such complexes leads to increased molecular weight of polymer and the system forms two fractions.

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