

Radical Polymerization of Acrylamide Initiated by Ceric Ammonium Nitrate–Methionine Redox Initiator System

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ABSTRACT: The polymerization of acrylamide, initiated by a cerium (IV) [Ce(IV)] ammonium nitrate–methionine redox initiator system, was carried out in an aqueous solution at different reaction conditions. The dependence of molecular weight and polymerization yield on the concentration of Ce(IV), polymerization time, and temperature was determined. The molecular weight distributions (MWD) of the resulting polymers were examined using the HPLC method. Based on the HPLC results, optimum reaction conditions were determined that provided an opportunity to obtain a polymer that had a narrow MWD. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1643–1648, 1997

Key words: acrylamide; Ce(IV); HPLC; molecular weight distribution

INTRODUCTION

Cerium(IV) has been extensively used with various reductants in the polymerization of vinyl monomers.¹ The reducing agents used with cerium(IV) are alcohols, aldehydes, ketones, carboxylic acids, organic acids, hydroxy acids, and polyaminocarboxylic acids.^{2–8} The aim of this work was to investigate the effect of reaction conditions [the concentration of Ce(IV), polymerization time, and temperature] on molecular weight, yield, and molecular weight distribution (MWD) of the polyacrylamides using HPLC and viscosimetric methods.

EXPERIMENTAL

L-Methionine, nitric acid (65%), CuSO₄·5H₂O, acetone, and methanol were purchased from

Merck. Acrylamide (AA) was supplied from Fluka Chemical Company.

The polymerization of AA initiated with a Ce(IV)–methionine redox system was carried out at a certain temperature in a two-necked round-bottomed flask equipped with a stirrer. Methionine and monomer were dissolved in aqueous HNO₃. Then the calculated amount of Ce(IV) salt solution was added dropwise with stirring over 5 min. After a chosen polymerization time, the reaction mixture was left standing for 1 h. Polyacrylamide was isolated by pouring the reaction mixture into acetone, filtering, and drying in air.

The synthesis of homopolyacrylamide was achieved by reaction of 15 g pure AA dissolved in 150 mL of water under nitrogen for 70 min at 40 ± 1°C. Polymer was precipitated from an aqueous solution twice by methanol addition and dried in a vacuum at 35°C.

The polymer yield was determined by direct weighing of the polyacrylamide produced. The viscosity (η) of the polymer solution was measured in water at 30 ± 0.1°C using an Ubbelohde viscometer. The number-average molecular weights, \bar{M}_n ,

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of the polymers were determined using the following relationship⁹:

$$\eta = 6.80 \times 10^{-4} \bar{M}_n^{0.66}$$

In this work HPLC was performed throughout using a Waters Associates (Norwich, U.K.) model 501 pump and a model U6K universal liquid chromatograph injector, a Lamda-Max model 481 LC spectrophotometer, a Waters 746 data module integrator, and a 300×7.8 mm i.d. stainless steel column packed with a protein pak (20- μ m particle size, Waters).

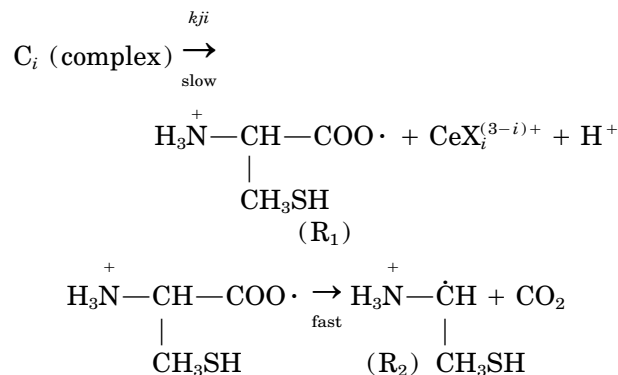
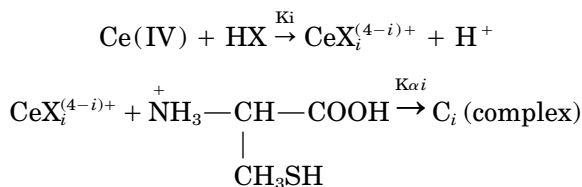
The mobile phase consisted of 1/15M KH_2PO_4 and 1/15M $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, pH 7. Elution was isocratic at a flow rate of 1 mL/min. The mobile phase and samples were filtered (0.45- μ m filter pore size, Waters). A 25- μ L volume of the samples was injected into the chromatograph. All the samples were monitored at a 254-nm wavelength where polyacrylamide has a maximum peak. The column was maintained at ambient room temperature.

RESULTS AND DISCUSSION

Polymerization of AA was undertaken to prove that Ce(IV) oxidation of the α -amino acids proceeds according to the radical mechanism. α -Amino acid or Ce(IV) alone did not initiate polymerization under experimental conditions, but the free radicals generated from an α -amino acid-Ce(IV) reaction were capable of initiating the polymerization of AA.

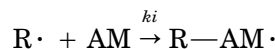
In our study, polymerization of AA was carried out with a Ce(IV)-methionine redox initiator system. The dependence of molecular weight, yield, and MWD on reaction conditions were summarized. The average molecular weights of the polymers were determined by viscosimetric measurements. The polymer yield was determined by direct weighing of the polyacrylamide produced. The MWD of the polymers were analyzed by HPLC.

The overall scheme of the reaction mechanism was postulated as follows:

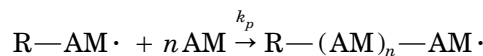


where HX indicates HNO_3 and X indicates NO_3^- . The free radicals (R_1 and R_2) may initiate the polymerization. The mechanism of polymerization of monomer (AM) may be given as follows:

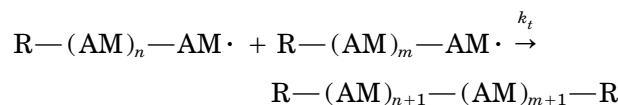
initiation:



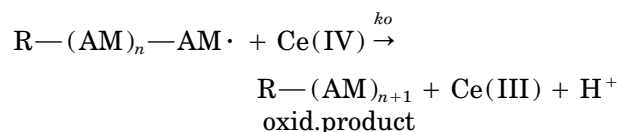
propagation:



mutual termination:



termination by Ce(IV):



Effect of Ce(IV)

Polymerization was carried out with different concentrations of Ce(IV). Figures 1 and 2 show the effect of Ce(IV) on molecular weight and polymerization yield, respectively. The results clearly show that as the concentration of Ce(IV) increases, the molecular weight decreases but the yield increases.

This probably indicates that at low catalyst [Ce(IV)] concentration, termination is due to the

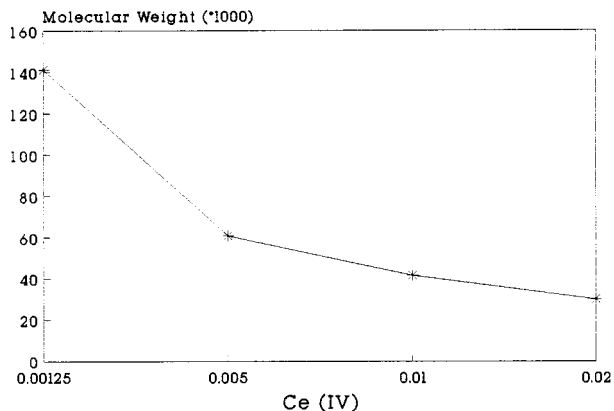


Figure 1 Effect of Ce(IV) concentration (mol/L) on molecular weight.

usual bimolecular collision between two chains. This finding eliminates the linear termination by Ce(IV) and emphasizes the mutual termination as a major process.

In fact, HPLC results support this assumption. As can be seen in Figure 3, a bimodal molecular distribution is observed at high Ce(IV) concentrations. According to size exclusion theory, the peak eluted first in the chromatogram (peak 1) corresponds to the molecules of large size and similarly, the peak eluted last corresponds to those of small size (peak 2). As the concentration of Ce(IV) decreases, the area of peak 2 diminishes and ultimately peak 2 disappears and only peak 1, corresponding to higher molecular weight, is seen in the chromatogram. Although peak 1 shows the same elution time for all the investi-

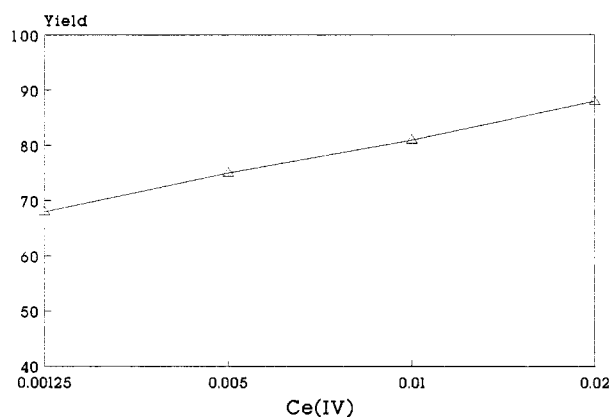


Figure 2 Effect of Ce(IV) concentration (mol/L) on yield.

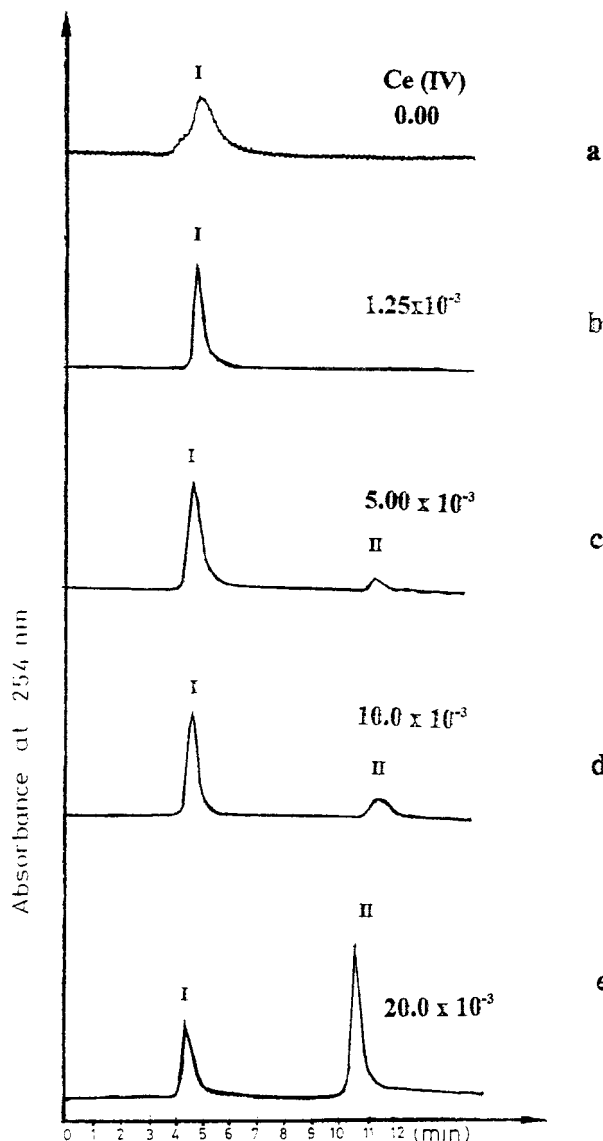


Figure 3 A series of HPLC chromatograms of polyacrylamide: (a) homopolyacrylamide and (b–e) synthesized at four different Ce(IV) concentrations (mol/L) in the presence of methionine; temperature, 55°C; reaction time, 2 h.

gated concentrations of Ce(IV), there is a significant decrease in the peak area with respect to the increasing concentration of Ce(IV).

Considering the reaction of Ce(IV)–Ce(III) and UV-visible and fluorescence measurements, it was recently suggested that the polymeric product consists of two fractions¹⁰: free polymer, which does not contain metal ions, and a polymer–metal complex.

Furthermore, the HPLC chromatograms of ho-

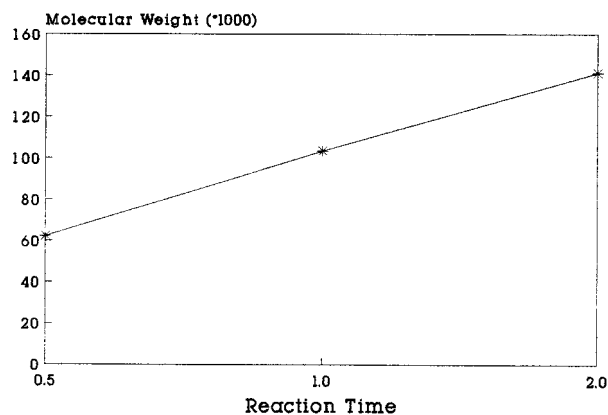


Figure 4 Effect of reaction time (hours) on molecular weight.

mopolyacrylamide and polyacrylamide obtained by the Ce(IV)–methionine redox system clearly show that the homopolyacrylamide does not contain peak 2, which corresponds to the polymer–metal complex, and only peak 1, which corresponds to free polymer, is seen in the chromatogram. Complex formation between functional groups of polyacrylamide and cerium ions can be illustrated in a method similar to that of Özeroğlu et al.¹⁰

Effect of Polymerization Time

The effect of polymerization time on molecular weight and yield was also examined at three different reaction times. The results are illustrated in Figures 4 and 5. As reaction times increase, the molecular weight and yield also increase. A series of HPLC chromatograms of the polymers obtained at different polymerization times is

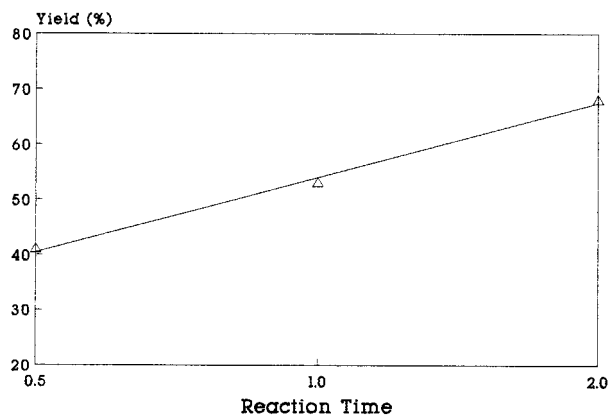


Figure 5 Effect of reaction time (hours) on yield.

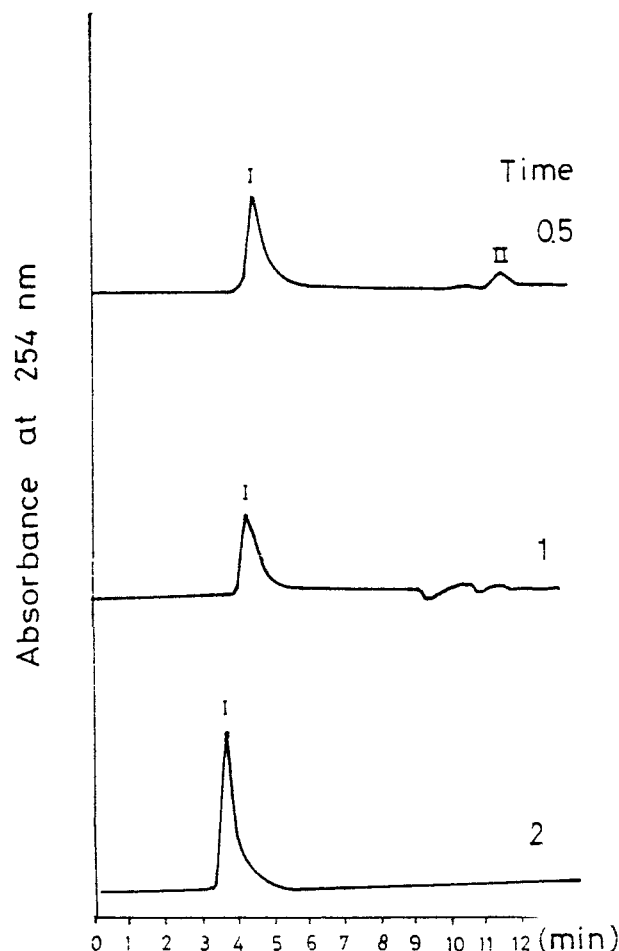


Figure 6 A series of HPLC chromatograms of polyacrylamide synthesized at three different reaction times (hours): Ce(IV) = 1.25×10^{-3} mol/L; temperature, 55°C.

shown in Figure 6. As can be seen from this figure, with an increase in polymerization time, the area of peak 1 corresponding to higher molecular weight increases whereas that of peak 2 corresponding to the molecules of smaller size decreases.

Effect of Temperature

By considering the effect of temperature on the molecular weight and yield, the polymerization was carried out at three different temperatures. The results are shown in Figures 7 and 8. The molecular weight and yield decrease as the temperature increases.

A series of HPLC chromatograms of the polymers synthesized at various temperatures is illus-

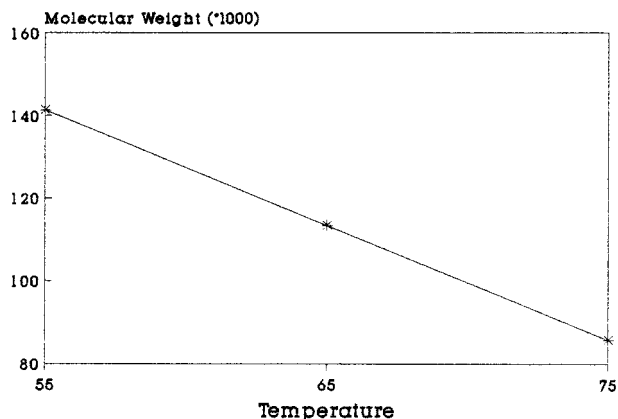


Figure 7 Effect of temperature (°C) on molecular weight.

trated in Figure 9. Following from this figure, with an increase in temperature, the area of peak 1 that corresponds to the molecules of large size decreases whereas that of peak 2 that corresponds to the molecules of small size increases. This is in conformity with kinetics of the polymerization of AA initiated by the ceric ion–methionine redox system.

Both viscosimetric and HPLC results are reflected in the fact that the initiating species is destroyed at higher temperature by side reactions.¹¹

Based on the HPLC results mentioned above, optimum reaction conditions that provide an opportunity to obtain a polymer showing only one peak in the chromatogram are as follows: $[\text{Ce(IV)}] = 1.25 \times 10^{-3}$ mol/L; reaction time, 2 h; temperature, 55°C.

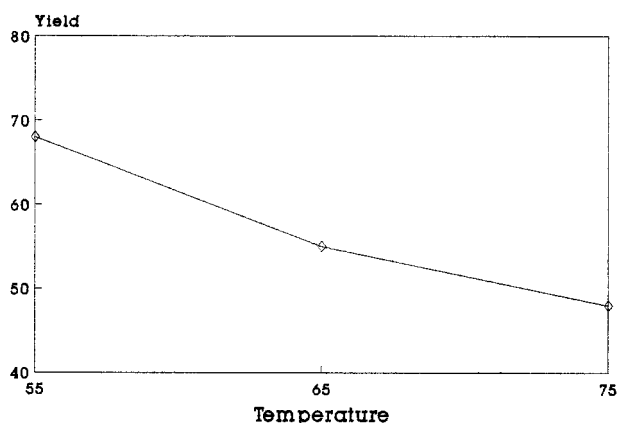


Figure 8 Effect of temperature (°C) on yield.

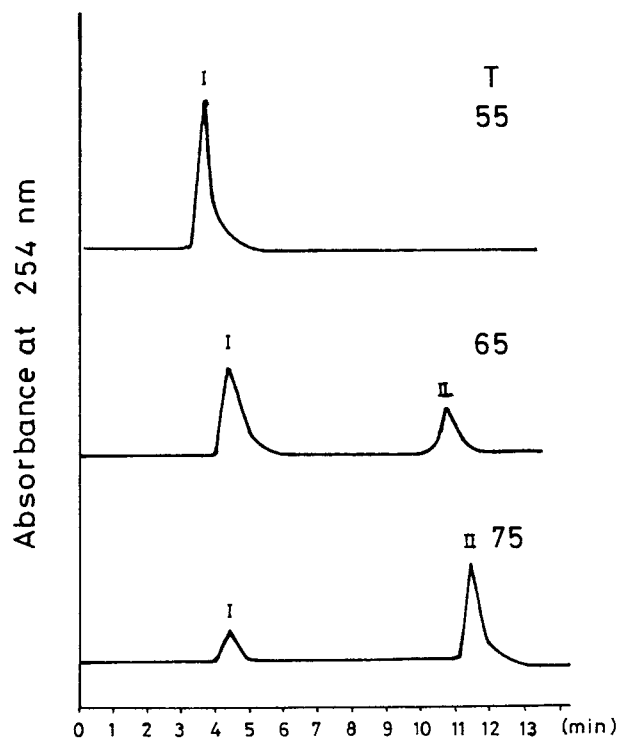


Figure 9 A series of HPLC chromatograms of polyacrylamide synthesized at three different temperatures (°C): $[\text{Ce(IV)}] = 1.25 \times 10^{-3}$ mol/L; reaction time, 2 h.

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