Studies on Aqueous Polymerization of Acryionitriie Initiated by Ce(IV)-Amino Acid Redox Pair

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ABSTRACT

Aqueous polymerization of acrylonitrile initiated by the Ce(IV)-glycine redox pair was studied at 35°C under nitrogen. The rate of polymerization, R_p, was found to be approximately proportional to the square of the monomer concentration within the range of 0.140-1.268 $\underline{M}$. R_p was also found to increase with glycine concentration in the interval 0.1 to 0.4 $\underline{M}$ and decrease with ceric ion concentration. The activation energy was estimated to be 25.8 kcal/mol. A suitable kinetic scheme was proposed and explained in the light of these experimental findings. The end-group in the polymer was characterized by IR spectra, and the average molecular weight of the polymer was found to be 84,100.

INTRODUCTION

Ceric salts in aqueous acidic solutions either by themselves [1] or in combination with reducing agents [2-4] are well-known initiators of vinyl polymerization. A number of studies have been conducted in the past to deal with the mechanism and kinetics of polymerization of different monomers. The reducing agents have been alcohols [4-7], aldehydes [8], secondary and tertiary amines [9], and carboxylic acids [10]. However, no attempt has been made thus far to use amino acids as reducing agents.

Recently, kinetics of glycine oxidation by Ce(IV) in sulfuric acid medium has been reported in detail [17]. The presence of free radicals during the course of the reaction has been tested by the induced polymerization of acrylamide. This observation prompted us to undertake polymerization of acrylonitrile initiated by ceric ammonium sulfate and the glycine redox pair. In view of the biological importance of amino acids, we have decided to use this system for the grafting of natural bio-fibers, like wool and silk, which will enable us to improve their useful properties. The presence of amino acids in the initiation system is expected to play the following roles:

(a) Production of reduced fibers with higher susceptibility toward grafting
(b) Decomposition of the oxidant to an appreciable extent
(c) Creation of radicals which may participate in the formation of macroradicals
(d) Lowering the extent of oxidant attack on the fibers, thereby reducing the extent of its damage

In the present communication we report a detailed study on the aqueous polymerization of acrylonitrile initiated by Ce(IV)-glycine in sulfuric acid medium at temperatures from 30 to 40°C.

EXPERIMENTAL

Chemicals

Ceric ammonium sulfate and sulfuric acid were commercial products (AnalaR, BDH). A stock solution of 0.1 M ceric ammonium sulfate was prepared by dissolving the appropriate amount in 2 M sulfuric acid.

Acrylonitrile as monomer (American Cyanamide Co., New York) was freed from inhibitors by washing with a 5% sodium hydroxide solution and then with a 3% phosphoric acid solution to remove any basic impurity. Finally, it was washed with doubled distilled water, dried over anhydrous calcium chloride, and kept in a refrigerator.

All other reagents employed in this investigation were of BDH (AnalaR) grade. Nitrogen for deaeration of the experimental system was purified by passing it through a column of Fieser's solution and a column of saturated lead acetate solution, and finally a wash bottle containing distilled water.

Polymerization Procedure

The reaction vessel was a 100-ml Pyrex tube sealed at the bottom and fitted at the top with standard joints carrying inlet and outlet tubes for nitrogen. Appropriate quantities of water, acid, monomer, and substrate (except the ceric salt solution) were placed in the reaction tube and deaerated; the ceric salt solution was then separately deaerated. Both solutions were placed inside a thermostat maintained at the desired temperature. The required amount of ceric ion was quickly added to the vessel and the components were mixed thoroughly. After a definite time, the vessels were removed from the bath and a known excess of $Fe(II)$ (0.1 $\underline{M}$) was introduced to quench the reaction mixture. The polymer was filtered off, washed, dried, and weighed. The rate of polymerization (R_p) was calculated from the initial slope of the time-conversion curve. The slope was used to deduce R_p in moles per liter per second.

Molecular Weight of Polyacrylonitrile from Viscosity Measurements

Under controlled conditions of the monomer and redox couple, the polymer was isolated after 1 h. Solutions of suitable concentrations of purified polyacrylonitrile sample in dimethylformamide were subjected to viscosity measurements from which the viscosity-average molecular weight was obtained by utilizing the Mark-Houwink equation:

$$[\eta] = 3.335 \times 10^{-4} \overline{M}_W^{0.72}$$

The molecular weight of polyacrylonitrile was thus determined to be 84,100.

RESULTS AND DISCUSSION

Relation between Conversion and Reaction Time

The relation between the conversion and reaction time for the polymerization of acrylonitrile initiated by the cerium(IV)-glycine redox pair is shown in Fig. 1. The limiting conversion is attained
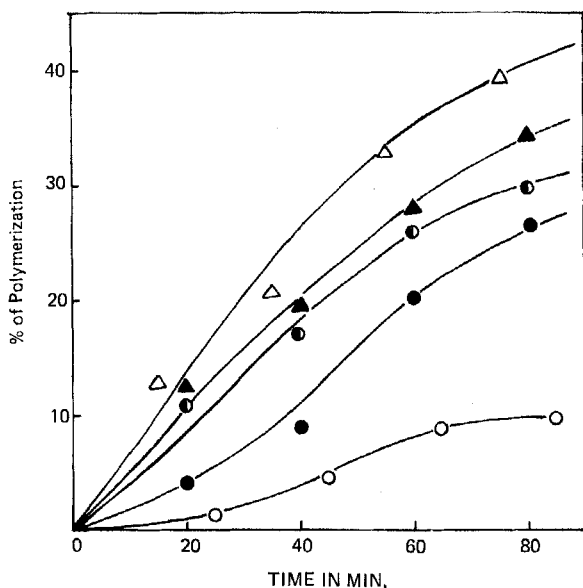
FIG. 1. Time-conversion curves: $[Ce(IV)] = 0.01$ M, $[AN] = 0.751$ M, $[H_2SO_4] = 0.2$ M. Temperature = 35°C. (○)[GLY] = nil, (●) [$\overline{GLY}$] = 0.1 M, (◐)[GLY] = 0.2 M, (▲) [GLY] = 0.4 M, (△) [GLY] = 0.6 M.

after about 1 h. The percentage of conversion has been studied at different concentrations of the substrate (glycine). It increases with an increase of glycine concentration.

Dependence of Rate on the Reductant Concentration

Figure 1 shows the course of acrylonitrile polymerization at different concentrations of the reductant (glycine). It is clearly revealed that the polymerization rate is enhanced as the concentration of glycine increases. It has been frequently reported in the literature [11, 12] that as the concentration of reductant is increased beyond a certain value, the rate and conversion decreases considerably, possibly because of the transfer of premature radicals with the reductant. In the present investigation, however, there was no evidence of a decrease within the range of glycine concentration studied. This may be attributed to the fact that the increasing quantity of glycine produces an increased quantity of free radicals whereby the maximum conversion is increased. Linear plots of log R_p vs log [glycine] with unit slopes indicate that the order with respect to [glycine] is unity.
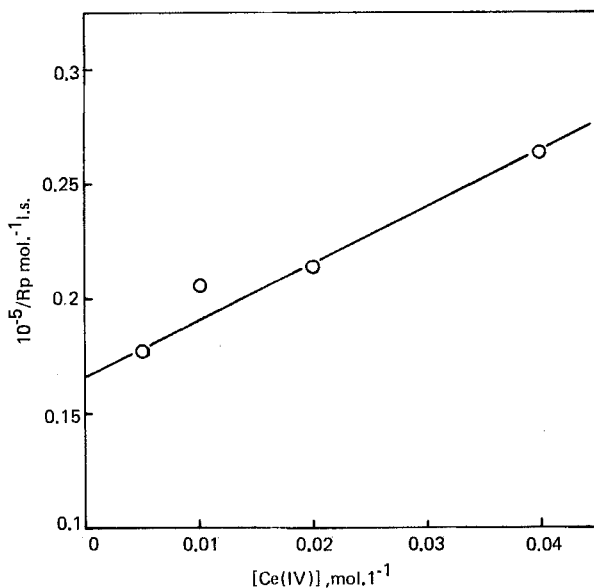
FIG. 2. Effect of metal ion on R_p: $[AN]$ = 0.751 $\underline{M}$, $[GLY]$ = 0.4 $\underline{M}$, $[H_2SO_4]$ = 0.8 $\underline{M}$, temperature = 35°C.

Dependence of Rate on the Metal Ion Concentration

The percentage of conversion as well as the rate of polymerization consistently decrease with increasing concentrations of Ce(IV). This clearly invokes the prevalence of the linear mode of termination [3] over the mutual one. The plot of $1/R_p$ vs $[Ce(IV)]$ is linear with an intercept (Fig. 2).

Dependence of Rate on Monomer Concentration

A regular increase in rate (R_p) was noticed with an increase in monomer concentration (0.375-1.126 $\underline{M}$). The plots of R_p vs $[M]^2$ were linear with zero intercepts (Fig. 3), and therefore the order with respect to $[M]$ was two. A very peculiar observation was noticed with a further increase in monomer concentration. At all the temperatures studied, there was a regular fall in the rate of polymerization beyond certain concentrations. In order to explain this behavior, Norrish and Smith [13] suggested that the excess monomer probably acts as a good solvent for its own polymer.
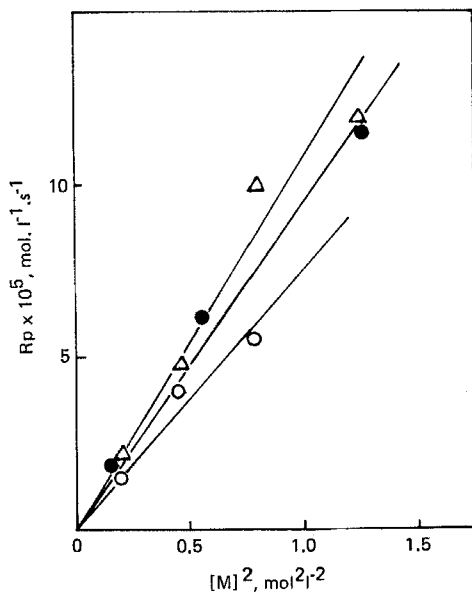
FIG. 3. Effect of monomer on R_p: $[Ce(IV)] = 0.01 \underline{M}$, $[H_2SO_4] =$ 0.6 $\underline{M}$, $[GLY] = 0.4 \underline{M}$. Temperature: ($\circ$) 30°C, ($\bullet$) 35°C, ($\triangle$) 40°C.

This increases the mobility of the growing chain, thus increasing the probability that binary collisions are necessary for premature termination and hence the rate decreases. Similar observations have been reported by Mark et al. [14], and Palit and co-workers [15] in the polymerization of vinyl acetate and methyl methacrylate.

Effect of Temperature

R_p increased with an increase of temperature from 30 to 40°C. Similar effects have been noted by many workers [2] although Thomas et al. [16] have reported that acrylonitrile polymerization is not appreciably dependent upon temperature. The overall energy of activation as calculated from the Arrhenius plot (Fig. 4) is found to be 25.8 kcal/mol.

Infrared Spectra

The infrared spectrum of the polymer shows characteristics of amino and carboxylate anion groups along with those of homopolymer. This shows that the polymer contains the substrate (glycine) as an
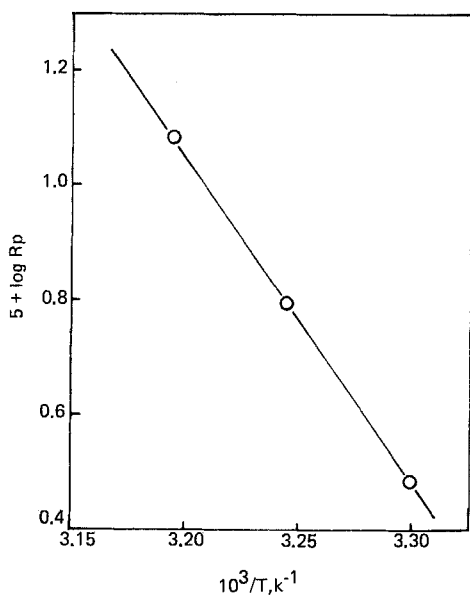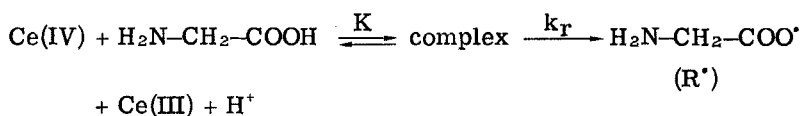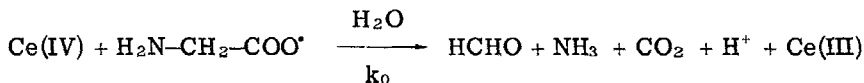
FIG. 4. Arrhenius plot of log R_p vs $1/T$.

endgroup. Formation of $H_2N-CH_2-COO^{\bullet}$ was also postulated in the oxidation of glycine [17] with Ce(IV) in sulfuric acid.
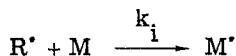
Reaction Mechanism and Rate Laws

On the basis of the above results, an attempt has been made to propose the following reaction scheme for the polymerization of acrylonitrile initiated by the acidified Ce(IV)-glycine redox system in aqueous medium. Initiation of polymerization by Ce(IV) alone was too insignificant to be considered under the experimental condition.
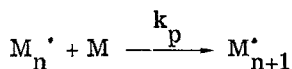
Primary Radical Production

$$Ce(IV) + H_2N-CH_2-COOH \underset{\longleftarrow}{\overset{K}{\longrightarrow}} complex \xrightarrow{k_r} H_2N-CH_2-COO^{\bullet}$$
$$(R^{\bullet})$$
$$+ Ce(III) + H^+$$

Reaction of Primary Radical with Ce(IV)

$$Ce(IV) + H_2N-CH_2-COO^{\bullet} \xrightarrow[k_0]{H_2O} HCHO + NH_3 + CO_2 + H^+ + Ce(III)$$

Initiation:

$$R^{\bullet} + M \xrightarrow{k_i} M^{\bullet}$$

Propagation:

$$M_n^{\bullet} + M \xrightarrow{k_p} M_{n+1}^{\bullet}$$

Termination:

$$M_{n+1}^{\bullet} + Ce(IV) \xrightarrow{k_t} polymer$$
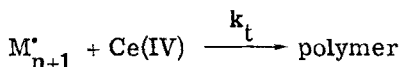
With the usual steady-state assumption, the following expression for the rate of polymerization, which is compatible with the actual experimental findings, may be deduced:

$$R_p = \frac{(k_p/k_t)k_r K[R][M]^2}{[M] + (k_0/k_i)[Ce(IV)]}$$

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