Copolymer of Ketonic Resin–Polyacrylonitrile

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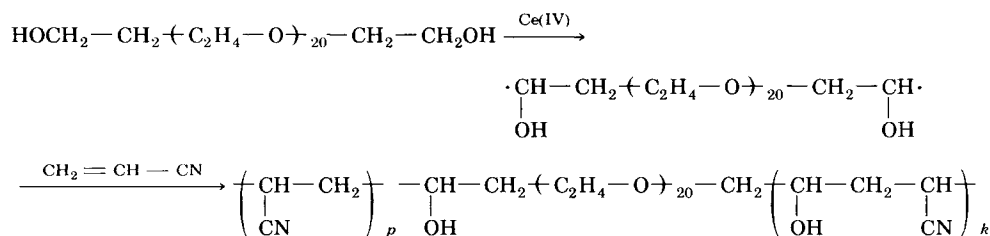Department of Chemistry, Maslak 80626, Istanbul, Turkey*

Synopsis

The polymerization of acrylonitrile in the presence of Ce(IV) salts and ketonic resin such as methyl ethyl ketone/formaldehyde and cyclohexanone/formaldehyde resin was investigated. Block copolymer of ketonic resin–polyacrylonitrile was produced. The effect of Ce(IV) concentration, temperature, time, and monomer concentration on the yield and molecular weight was studied. Maximum yield was obtained at 50°C and ceric ammonium nitrate concentration of 0.033 mol/L.
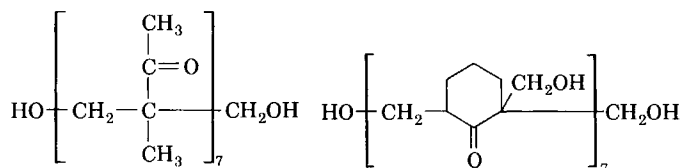
INTRODUCTION

Ce(IV) salts in aqueous acidic solution, either by themselves[1] or in combination with reducing agents,[2] are well known initiators for vinyl polymerization, especially for graft copolymerization of vinyl monomers such as acrylonitrile and acrylamide. Starch[3] and cellulose[4] were the most used polymers for grafting. The basic reaction is a redox reaction between Ce(IV) and—CH_2OH groups of cellulose or starch and free radicals are generated. These free radicals initiate polymerization of vinyl monomers.[5] Generation of free radicals, the reaction mechanisms, and initiation ability of these free radicals in Ce(IV)/reducing agent system was studied in detail before.[6,7]

The reducing agent may also be alcohol,[8] polyol,[7,9] ketone,[10] aldehyde,[11] amine,[12,13] amide,[12] and carboxylic acid.[10,14] The resulting polymer was suggested to have corresponding chain ends.[8,10] This method was also used for the preparation of block copolymer of polyacrylonitrile and polyoxyethylene (PEO) and polyoxypropylene (PPO).[14-16] PEO and PPO which contained methylol groups at both chain ends were used as the reducing agent. It was suggested that the polymerization proceeds in accordance with the following scheme:

$$HOCH_2-CH_2 \overline{(\!} C_2H_4-O\overline{)}_{20}-CH_2-CH_2OH \xrightarrow{Ce(IV)}$$

$$\cdot CH-CH_2 \overline{(\!} C_2H_4-O\overline{)}_{20}-CH_2-CH\cdot$$
$$\quad | \qquad\qquad\qquad\qquad\qquad | $$
$$\quad OH \qquad\qquad\qquad\qquad\qquad OH$$

$$\xrightarrow{CH_2=CH-CN} \left(\!\!\begin{array}{c} CH-CH_2 \\ | \\ CN \end{array}\!\!\right)_p -CH-CH_2\overline{(\!}C_2H_4-O\overline{)}_{20}-CH_2\left(\!\!\begin{array}{cc} CH-CH_2- & CH \\ | & | \\ OH & CN \end{array}\!\!\right)_k$$

The yield of block copolymer increased with increasing PEO concentration. In this case, copolymerization may proceed mainly from one chain end of PEO[17] and termination by generated free radicals may also be possible.[17]

In this work, the Ce(IV)–ketonic resin redox system was used to initiate the polymerization of acrylonitrile. The effects of temperature, time, catalyst, and monomer concentration were studied. Ketonic resins were methyl ethyl ketone/formaldehyde resin and cyclohexanone/formaldehyde resin with the following representative structures. Both ketonic resins contain free $-CH_2OH$ groups. Polymerizations of vinyl monomers such as styrene, acrylamide, and acrylic ester are under progress:

$$HO-\left[CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{|}{\underset{|}{C}}}=O}\right]_7-CH_2OH \qquad HO-\left[CH_2-\overset{CH_2OH}{\underset{O}{\bigcirc}}\right]_7-CH_2OH$$
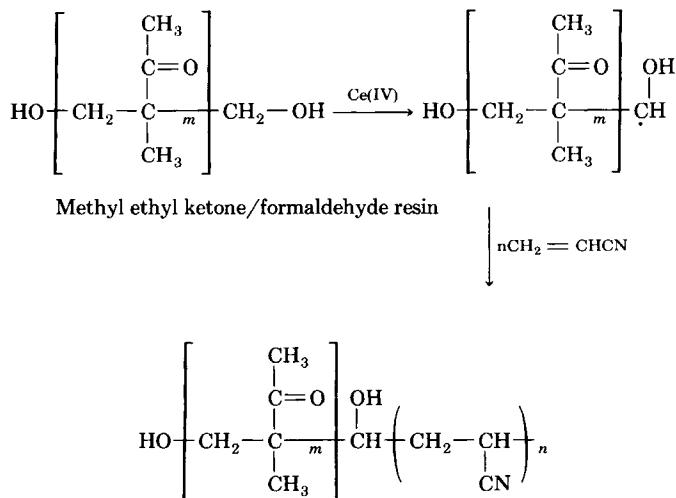
Methyl ethyl ketone/formaldehyde resin
Cyclohexanone/formaldehyde resin

RESULTS AND DISCUSSION

The product, ketonic resin–polyacrylonitrile copolymer, was purified by dissolving in dimethylformamide (DMF) and then precipitating in ethanol. This enabled us to remove any unreacted ketonic resin from the product. It was assumed that polyacrylonitrile homopolymer was not produced in this system since no polyacrylonitrile formed under a similar condition without ketonic resin (blank experiment).

The copolymer has similar solubility properties to polyacrylonitrile homopolymer. IR spectra of copolymer, ketonic resin, and polyacrylonitrile are shown in Figure 1. IR spectrum of copolymer shows peaks of both ketonic resin and polyacrylonitrile. Peaks due to $C\equiv N$, $O-H$, and $C=O$ stretchings are seen at 2250, 3400, and 1710 cm^{-1}, respectively.

Formation of copolymer of methyl ethyl ketone/formaldehyde resin–polyacrylonitrile was proposed to proceed via free radical generation followed by vinyl polymerization of acrylonitrile, as shown below.

$$HO-\left[CH_2-\underset{CH_3}{\overset{C=O}{\overset{|}{\underset{|}{C}}}}\right]_m-CH_2-OH \xrightarrow{Ce(IV)} HO-\left[CH_2-\underset{CH_3}{\overset{C=O}{\overset{|}{\underset{|}{C}}}}\right]_m-\overset{OH}{\underset{}{\overset{|}{C}H}}$$

Methyl ethyl ketone/formaldehyde resin

$$\downarrow nCH_2=CHCN$$

$$HO-\left[CH_2-\underset{CH_3}{\overset{C=O}{\overset{|}{\underset{|}{C}}}}\right]_m-\overset{OH}{\underset{}{\overset{|}{C}H}}-\left(CH_2-\underset{CN}{\overset{}{\overset{|}{C}H}}\right)_n$$
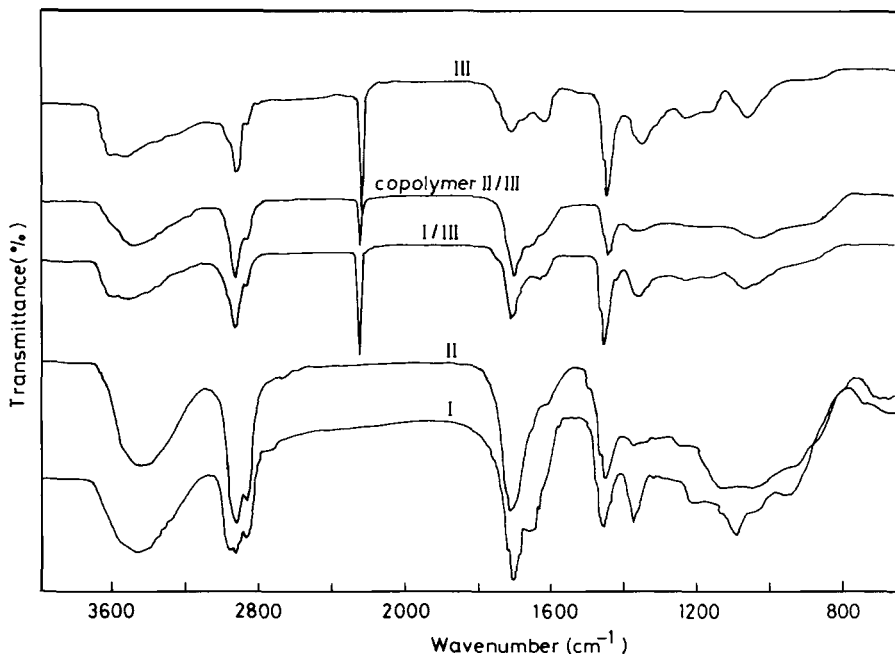
Fig. 1. IR spectra of ketonic resins and copolymers: methyl ethyl ketone/formaldehyde resin (I); cyclohexanone/formaldehyde resin (II); polyacrylonitrile (III); copolymer of methyl ethyl ketone/formaldehyde resin–polyacrylonitrile (copolymer I/III); copolymer of cyclohexanone/formaldehyde resin–polyacrylonitrile (copolymer II/III).

In the first step, Ce(IV)/methylol redox reaction occurs and free radicals are generated. These free radicals initiate polymerization of acrylonitrile. Polymerization may proceed from other —CH$_2$OH groups of ketonic resin molecule also. This occurs when Ce(IV) concentration is increased. Termination of growing chains by Ce(IV) (linear termination) or combination by themselves (mutual termination) may both be possible, by depending on the Ce(IV) concentration. Increasing Ce(IV) concentration results in a linear termination. The Ce(IV) concentration seemed to have a marked effect on the yield (Fig. 2). The yield increased linearly when Ce(IV) concentration was above 0.023 mol/L. The effect of the polymerization temperature on the yield and molecular weight showed a different pattern. The yield and the molecular weight showed a maximum at 50°C. Further increase in the temperature caused a drop in the yield and molecular weight (Fig. 3). This was probably due to solvent swelling of the copolymer precipitated during the polymerization. Diffusion and segmental diffusion of two growing polymer chain and diffusion of Ce(IV) should increase above 50°C. Thus, mutual termination of two growing chain and linear termination by Ce(IV) increased. The increase in k_t caused both R_p and molecular weight to decrease since both of them are proportional to $k_t^{-1/2}$ for mutual termination and k_t^{-1} for linear termination.[8,18] On the other hand, molecular weight of the copolymer was somehow 10–15 times higher if it was produced in DMF: water rather than in acetone : water. Much lower yield (weight increase: 0.25 g/g) was obtained when ceric ammonium sulfate was used as a reducing agent under experimen-
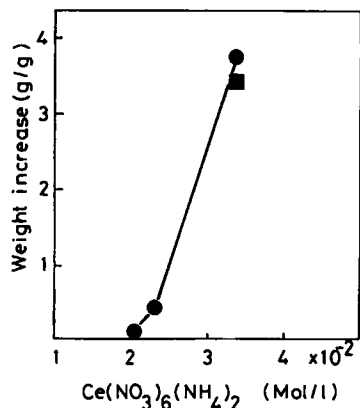
Fig. 2. The effect of $Ce(NO_3)_6(NH_4)_2$ concentration on the weight increase. Methyl ethyl ketone/formaldehyde resin, 5 g/L; [acrylonitrile] = 0.35 mol/L; Temperature, 50°C; (●) solvent: water/acetone (5:3), time, 4 h; (■) solvent: water/DMF (5:3), time, 0.5 h.

tal conditions similar to those in Figure 3 (solvent : acetone/water). In this case, the molecular weight of the copolymer was 2850.

The effect of polymerization time on the yield was examined at two different Ce(IV) concentrations (Fig. 4). When Ce(IV) concentration was 0.023 mol/L, a longer polymerization time was required to achieve good yield. However, a much higher yield was obtained in a shorter period of time if Ce(IV) concentration was 0.033 mol/L. Molecular weight of copolymer seemed to show similar pattern with the polymerization time.

Increasing monomer concentration caused the expected increase in the yield and molecular weight of copolymer (Fig. 5). However, this effect seemed to be
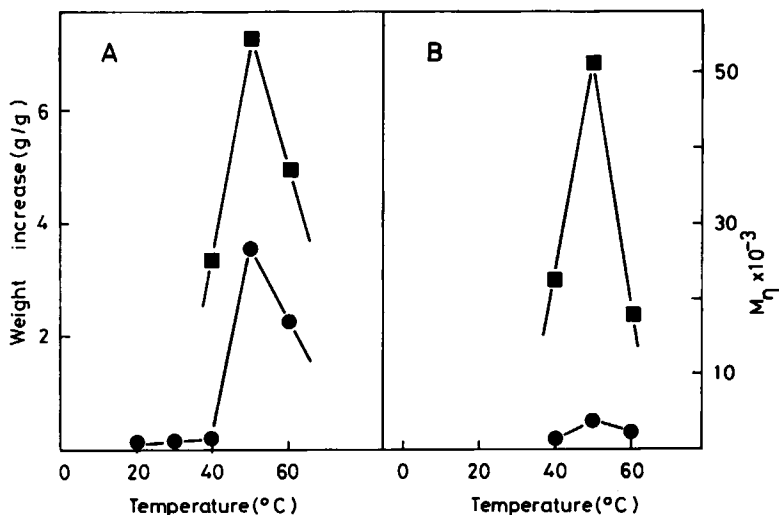

Fig. 3. The effect of temperature on the weight increase (A) and the molecular weight (B). [Acrylonitrile] = 0.35 mol/L; methyl ethyl ketone/formaldehyde resin, 5 g/L, $[Ce(NO_3)_6(NH_4)_2]$ = 0.033 mol/L; (●) solvent: water/acetone (5:3), time, 4 h; (■) solvent: water/DMF (5:3), time, 0.5 h.
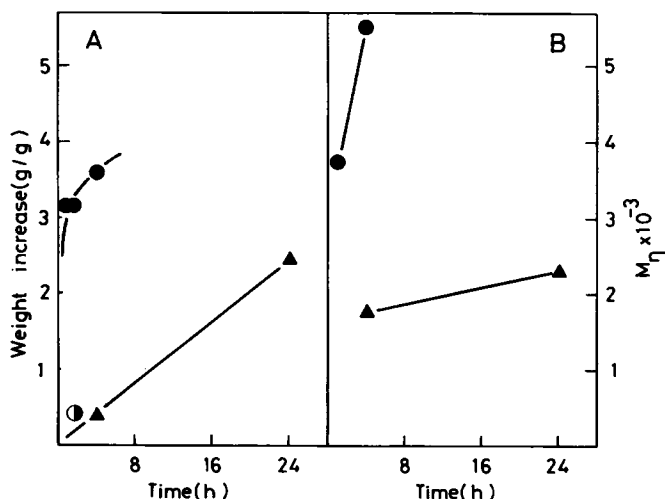
Fig. 4. The effect of time on the weight increase (A) and the molecular weight (B). [Acrylonitrile] = 0.35 mol/L; solvent, water/acetone (5:3); temperature, 50°C; methyl ethyl ketone/formaldehyde resin, 5 g/L; [Ce(NO$_3$)$_6$(NH$_4$)$_2$]: (▲) 0.023 mol/L; (●) 0.033 mol/L; (◑) cyclohexanone/formaldehyde resin.

significant if Ce(IV) concentration was 0.033 mol/L. Lowering acrylonitrile concentration resulted two different product, i.e., copolymer and water-soluble resin. If acrylonitrile was not added to the system, Ce(IV) oxidized the ketonic resin to a water-soluble resin.

Polymerization of styrene with ketonic resin/Ce(IV) system was carried out under the similar experimental conditions (50°C, 1.5 h, [Ce(IV)] = 0.033 mol/L). The yield was 4.8 g of copolymer/g ketonic resin. Both peaks due to ketonic resin and polystyrene was observed in the IR spectrum of the copolymer.
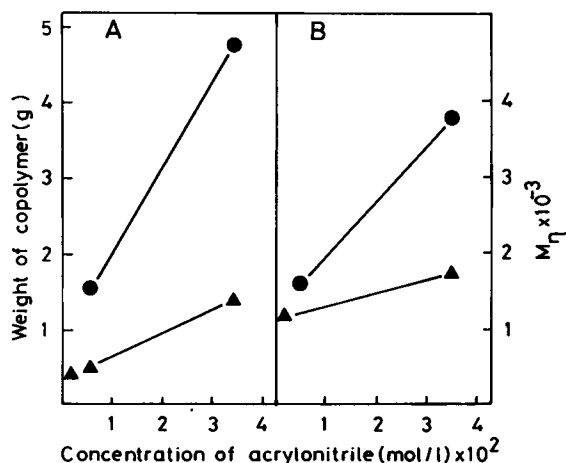

Fig. 5. The effect of monomer concentration on the weight increase (A) and the molecular weight (B). Solvent, water/acetone (5:3); methyl ethyl ketone/formaldehyde resin, 5 g/L; temperature, 50°C; [Ce(NO$_3$)$_6$(NH$_4$)$_2$]: (▲) 0.023 mol/L; (●) 0.033 mol/L.

EXPERIMENTAL

1. $Ce(NO_3)_6(NH_4)_2$ stock solution ($0.1M$) was prepared by dissolving 11.964 g of dried ceric ammonium nitrate (Fluka) in 100 mL $1M$ HNO_3 and storing in a refrigerator.

2. Preparation of ketonic resins: Methyl ethyl ketone/formaldehyde and cyclohexanone/formaldehyde resin were prepared according to Refs. 19 and 20, respectively.

3. Preparation of copolymer of ketonic resin–polyacrylonitrile: Ketonic resin was dissolved in the solvent (acetone or DMF) and water and acrylonitrile were added. Then Ce(IV) stock solution was added dropwise under stirring. After polymerization, some water was added. The recovered copolymer was then washed with water several times, dried under vacuum, and purified by dissolving in DMF and precipitating in ethanol.

4. Blank experiment: To acrylonitrile monomer, Ce(IV) stock solution was added under stirring. No polymer was recovered in about 1 h at 50°C.

5. Preparations of copolymer of ketonic resin–polystyrene: 1 g of methyl ethyl ketone/formaldehyde resin was dissolved in 140 mL acetone and 30 mL water, and 76 mL purified styrene was added, consequently. An emulsion was formed. To this emulsion, 68 mL Ce(IV) stock solution was added dropwise under stirring. Two phases occurred as the polymerization proceeded. After 1.5 h, the copolymer was recovered from the upper phase and purified. The yield was 4.8 g.

6. Molecular weight: Molecular weight of copolymer was calculated from a single point viscosity value. Viscosity of polymer solution in DMF was measured at 25°C. Following equations were used[21,22]:

$$[\eta] = \frac{\eta_{sp}/c}{1 + 0.28 \times \eta_{sp}}, \qquad [\eta] = 2.33 \times 10^{-4} \times M_w^{0.75}$$

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