



Aqueous Polymerization of Acrylonitrile with Cerium(IV)- *p*-Hydroxyacetophenone Redox System

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Abstract: Aqueous polymerization of acrylonitrile initiated by Ce(IV)/ *p*-hydroxy acetophenone (Ce(IV) – HAP) was studied in aqueous solution of sulfuric acid at 40 °C. The rate of polymerization was investigated at various concentrations of monomer, initiator, activator, sulfuric acid and the effect of temperature of 30-70 °C range was studied. The rate of polymerization is governed by the expression $R_p = K_p [M]^{1.44} [Ce(IV)]^{0.55} [HAP]^{0.51}$. The activation energy of polymerization was found to be 17.9 kJ/mol. A probable mechanism consistent with the observed results is proposed and discussed.

Keywords: Acrylonitrile, Ceric ion, *p*-hydroxyacetophenone, Radical polymerization.

Introduction

Ce(IV) ion either alone or in combination with various organic reducing agents such as alcohols¹, acids², amides³, aldehydes⁴ and ketones⁵ has been used to initiate vinyl polymerization. The polymerization of acrylonitrile by Ce(IV)-glucose system was studied by Padhi and Singh⁶⁻⁸. Earlier studies by different investigations indicate that the order of oxidant of ceric ion was found to be ceric perchlorate > ceric nitrate > ceric sulphate⁹⁻¹⁰. It is known that Ce(IV) is an one electron oxidant capable of oxidizing compound in sulfuric acid. Oxidation of any substrate by Ce(IV) occur through a single electron transfer from the substrate to the oxidant^{11,12}. The mechanism of oxidation of cerium in many cases is simpler than the cases with other transition metal ions such as chromate, manganite ion *etc*. This articles reports the result on the polymerization of acrylonitrile in sulfuric acid with the redox system of Ce(IV) – HAP.

Experimental

The monomer (AN) was purified by the usual procedures¹³. Sulfuric acid AR grade was used without further purification. *p*-HAP (AR) were distilled under reduced pressure. Water doubly over alkaline permanganate were employed in the preparation of the reagents and solutions. The appropriate quantities of a reaction mixture that containing ceric ammonium

sulfate, reducing agent and sulfuric acid were placed in clean conical flasks mounted in a rocking thermostat. The monomer and reducing agent were introduced under N_2 atmosphere and the reaction flasks were sealed. The polymerization was allowed to proceed at $40^\circ C$ in the dark in a thermostat. The polymerization reactions started almost instantaneously, indicated by the appearance of turbidity that increased with the progress of polymerization ultimately the polymers precipitated out. After desired intervals the polymerization were halted by adding 10 mL of 1% ferrous ammonium sulfate. The precipitated polymer were filtered off on sintered glass crucible, washed repeatedly with water and dried to constant weight at $60^\circ C$ in a vacuum oven. The polymer yield was determined gravimetrically. The rate of polymerization (R_p) was calculated from the weight of the polymer formed by using the equation:

$$R_p = 1000W/vtM$$

Where W = weight of the polymer in grams, v = volume of the reaction mixture in milliliters, t = reaction time in seconds, M = molecular weight of the monomer

Results and Discussion

The polymerization of acrylonitrile was carried out with $Ce(IV)$ in the absence of the activator, the polymerization process markedly decreased. The polymerization of acrylonitrile by $Ce(IV)$ -HAP redox system occurred at a measurable rate at $40^\circ C$.

Effect of monomer concentration on polymerization rate

The rate of polymerization was investigated by varying the concentration of monomer, acrylonitrile (AN) from 0.10 to 0.50 mol/L at $40^\circ C$, keeping the concentrations of initiator ($Ce(IV)$), ligand (*p*-hydroxyacetophenone) and sulfuric acid constant. The initial slope as well as the percentage conversion increases steadily with an increase of monomer concentration. The order dependence of the rate of polymerization on monomer concentration was determined by the double logarithmic plot of R_p versus $[AN]$, the slope of is 1.44 (Figure 1). The reaction order greater than unity with respect to monomer concentration, It may be described to a dependence of the initiation rate on monomer concentration. The order nearly 1.5 dependence of the rate of polymerization on monomer concentration as confirmed by the double logarithmic plot has widely been reported in redox initiated polymerization systems.

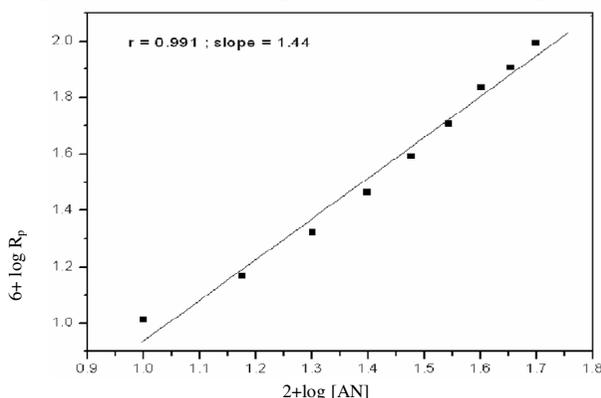


Figure 1. Effect of monomer concentration on the rate of polymerization (R_p)
 $[Ce(IV)] = 0.0025 M$; $[p\text{-HAP}] = 0.002M$; $[H^+] = 0.01M$; $Temp. = 40^\circ C$; $Time = 60 min$

Effect of initiator concentration on polymerization rate

The rate of polymerization was measured with different initiator concentrations at a fixed concentration of monomer (0.25 M), ligand (0.002 M), sulfuric acid (0.01 M) and at constant temperature 40 °C for 60 min duration. The effect of concentration of initiator (Ce(IV)) on rate of polymerization was studied by varying the [Ce(IV)] in range from 0.0025 to 0.05 M. The R_p increases with the concentration of initiator. A plot of $\log R_p$ versus $\log[\text{Ce(IV)}]$ is linear (Figure 2) with a slope of 0.55, indicating a fractional order dependence of R_p on concentration of Ce(IV) ion.

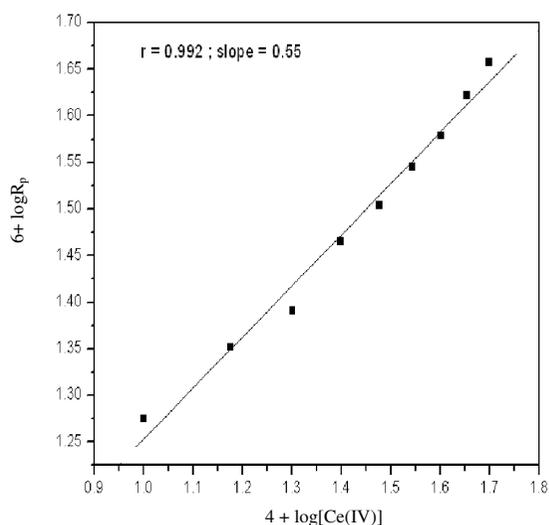


Figure 2. Effect of initiator concentration on the rate of polymerization (R_p)

$[M] = 0.25 \text{ M}$; $[2\text{-HAP}] = 0.002\text{M}$; $[H^+] = 0.01\text{M}$; $\text{Temp.} = 40 \text{ }^\circ\text{C}$; $\text{Time} = 60 \text{ min}$

Generally, the order with respect to initiator is 0.5 when termination is bimolecular in free radical polymerization processes and it drops to nearly zero when primary radical termination predominates. The initiator rate exponent of nearly 0.5 confirms bimolecular termination in the present study. The rate of polymerization rises rapidly with [Ce(IV)] until a concentration of approximately 0.05 M is reached; further increases in the concentration have a retarding effect on the rate of polymerization. The decrease of rate of polymerization at higher [Ce(IV)] can be accounted for by considering that at high concentrations, the oxidation and termination process increases.

Effect of ligand concentration on polymerization rate

The rate of polymerization was measured with different concentrations of *p*-hydroxyacetophenone at a fixed concentration of monomer (0.25 M), initiator (0.0025 M), sulfuric acid (0.01M), and at constant temperature 40 °C for 60 min duration. The rate of polymerization increases with increasing ligand concentration from 0.1 to 0.5 M. The order of reaction was found to be nearly half (0.51) from the double logarithmic plot of R_p versus [HAP] (Figure 3) and this suggests a bimolecular mechanism of growing polymer radical termination. This fractional order dependence on [HAP] indicates that the polymerization is initiated by primary radical with termination by mutual reaction of two growing polymer radicals.

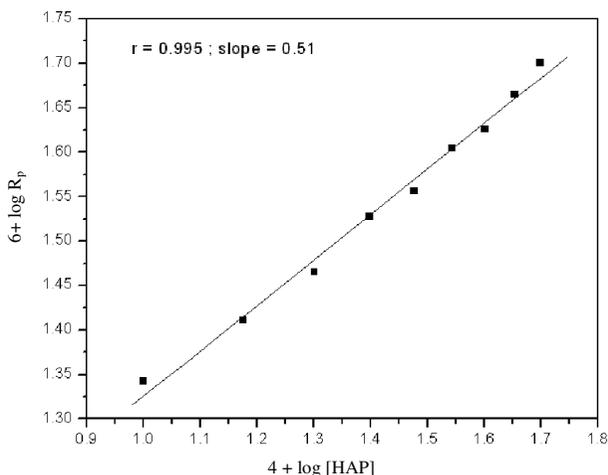


Figure 3. Effect of ligand concentration on the rate of polymerization

$[M] = 0.25 \text{ M}$; $[Ce(IV)] = 0.0025 \text{ M}$; $[H^+] = 0.01 \text{ M}$; $Temp. = 40^\circ \text{ C}$; $Time = 60 \text{ min}$

Effect of concentration of acid on rate of polymerization

The rate of polymerization was measured with different concentrations of sulfuric acid at fixed concentration of monomer (0.25 M), initiator (0.0025 M), ligand (0.002 M) and at constant temperature 40° C for 60 min duration. The effect of concentration of sulfuric acid on the conversion is shown in Figure 4. It is clear that the addition of sulfuric acid causes a substantial increase in rate of polymerization at lower concentration ranges and there after the rate of polymerization decreases. It is evident that at low acid concentrations, the reducing agent may be deprotonated so that the coordination becomes easier for the ceric salt whereas at higher acid concentrations the R_p decreases because the complexation may be high. The increase in sulfuric acid concentration causes the formation of less reactive complexes of Ce(IV) ion, which is responsible for decreasing the rate of polymerization.

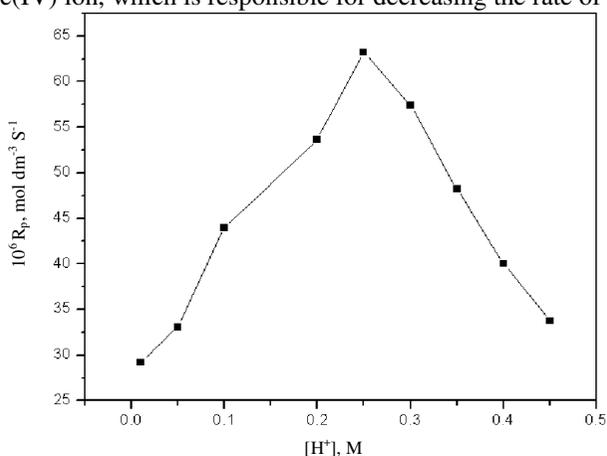


Figure 4. Effect of acid concentration on the rate of polymerization

$[M] = 0.25 \text{ M}$; $[Ce(IV)] = 0.0025 \text{ M}$; $[2\text{-HAP}] = 0.002 \text{ M}$; $Temp. = 40^\circ \text{ C}$; $Time = 60 \text{ min}$

Effect of reaction temperature on rate of polymerization

The rate of polymerization increases with an increase in temperature from 30-60 °C. This is because as the reaction rate of Ce(IV) reduction of ligand increases with temperature, there will be slow and steady generation of free radicals, and hence the polymer yield increases gradually in the temperature range 60°-80° C. At above 60 °C reduction becomes very fast, resulting in a local over concentration of free radicals. As high temperature causes an increase on the rates of chain termination reactions, a decrease was observed from 60 °C to 80 °C (Figure 5). The increase in the R_p with increasing temperature may be attributed to: increase in the mobility of monomer and initiator molecules in the polymerization medium increase in the initiation and propagation rates of polymer. The decrease in the maximum conversion as the temperature increases may be due to the side reaction.

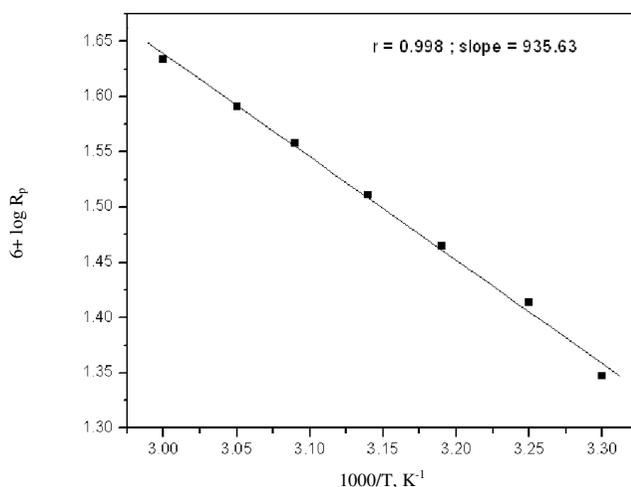
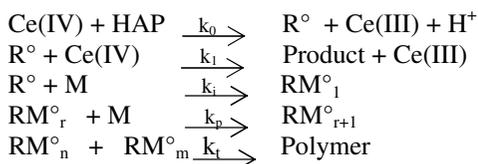


Figure 5. Arrhenius plot for the polymerization of acrylonitrile with Ce(IV)-HAP redox system
 $[M] = 0.25 M$; $[Ce(IV)] = 0.0025 M$; $[2-HAP] = 0.002 M$; $[H^+] = 0.01M$; Time: 60 min

Reaction mechanism and kinetic scheme



Applying the steady-state principle to the primary radicals R° and the growing polymeric radicals RM_n° and making the usual assumption that the radical reactivity is independent of radical size⁷, the following equation for R_p can be derived

$$d[R]/dt = k_1[Ce(IV)][HAP] - k_i[R^\circ][M], [R^\circ] = k_1[Ce(IV)][HAP]/k_i[M]$$

The rate of polymerization may given by

$$R_p = k_p[RM^\circ][M], R_p = k_p(k_0)^{1/2} (k_i/k_t)^{1/2} [Ce(IV)]^{1/2} [HAP]^{1/2} [M]^{3/2}$$

This rate expression explains clearly the dependence of R_p on HAP and monomer concentrations.

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