Polymerization Kinetics of Acrylonitrile by Oxidation: Reduction System Using Potassium Persulfate/Ascorbic Acid in an Aqueous Medium

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ABSTRACT: The kinetics of acrylonitrile polymerization initiated by free radicals formed in situ in a potassium persulfate/ascorbic acid redox system was investigated in an aqueous sulfuric acid medium in the temperature range of 40–70°C. The rate of polymerization and the rate of the disappearance of potassium persulfate were measured. A kinetic scheme involving the production of initiating radicals from the oxidation of ascorbic acid by potassium persulfate ions and termination exclusively by the interaction of chain radicals with persulfate ions is proposed. The effects of some water-miscible organic solvents on the rate of polymerization were investigated. The temperature dependence of the rate was studied. A possible mechanism consistent with the experimental data is proposed. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1299–1303, 2011

Key words: activation energy; radical polymerization; redox polymers

INTRODUCTION

Cerium(IV) has been used as an oxidizing agent and an analytical reagent, especially in an acidic medium. Redox polymerization of vinyl monomers initiated by transition-metal ions in their higher oxidation states in an aqueous medium can provide valuable information about the mechanistic details of the elementary steps.[1–11] This article reports a kinetic study of a polymerization reaction of acrylonitrile (AN) initiated by a potassium persulfate (PPS)/ascorbic acid (AA) redox system in an aqueous sulfuric acid (H_2SO_4) medium in the temperature range of 40–55°C. Various redox systems have been used successfully for the polymerization of organic monomers in aqueous media.[12–21] Redox polymerization has the following advantages: a very short induction period, a relatively low energy of activation, the production of high-molecular-weight polymers with high yields, easy control of the polymerization reaction at low temperatures due to the reduction of side reactions, and direct experimental proof of the transient radical intermediates.[22–25] Commonly used oxidants include peroxides, persulfates, permanganates, and the salts of the transition metals. These oxidants form potential redox systems with various reducing agents such as alcohols, aldehydes, amines, amides, ketones, acids, and thiols for the aqueous polymerization of vinyl monomers.[26–31] The anomalous kinetic behavior associated with AN polymerization in aqueous solutions and the importance of polyacrylonitrile (PAN) in the fiber industry led to the choice of AN for this investigation.[32] The chemistry of AA has attracted the attention of many investigators because of its biological activity and synthetic applications. However, redox initiation in organic solvents has not been very successful. Reported peroxide/tertiary amine[33] and hydroperoxide/cobalt octate systems[34] are not applicable to all vinyl polymerizations. In fact, redox reactions are more complicated than we previously thought, and water is presumably involved in some steps of the reactions. In this investigation, the kinetics of polymerization of AN initiated by a new PPS/AA redox system in an H_2SO_4 medium was studied.

EXPERIMENTAL

Preparation of the materials

AN (S.D. Fine Chemicals, Mumbai India) was purified by the method of Bamford and Jenkins.[35] The inhibitor-free sample was washed thrice with deionized water to remove the trace of alkali water used. Solutions were prepared with triple-distilled

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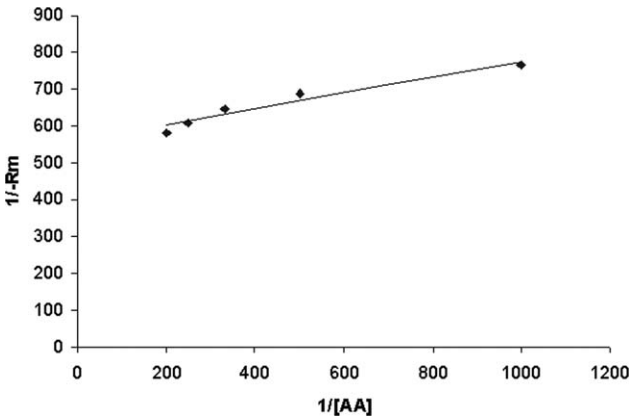


Figure 1 Inverse plot of $-R_m$ versus the AA concentration ([PPS] = 4.0×10^{-3} mol/dm^3, [AA] = 1.0×10^{-2} mol/dm^3, [M] = 0.0675×10^{-2} mol/dm^3, [H_2SO_4] = 2.0×10^{-3} mol/dm^3, temperature = 323 K).

water over alkaline permanganate and deionized by passage through Biodeminrolit resin (Permutit Co. Ltd., London, UK).[36] All other chemicals [PPS, H_2SO_4, AA, methanol, ethanol, and dimethylformamide (DMF)] were analytical-grade. A solution of PPS was prepared with triple-distilled water and standardized with a standard sodium thiosulfate solution with starch as an indicator. Triple-distilled water was used throughout the experiments, and pure nitrogen was obtained by passage through a column of Fieser's solution; distilled water was used for deaeration of all experimental systems.

Kinetic measurements

Inhibitor-free AN monomer (0.607 mol/dm^3), AA (1.0×10^{-2} mol/dm^3), and water (for a constant total volume) were placed in reaction vessels and thermostated at 40°C. The system was flushed with oxygen-free nitrogen for approximately 20–30 min to expel the dissolved oxygen. At the end of the period, a PPS solution (4.0×10^{-3} mol/dm^3) was added to the reaction vessels and shaken well. The reaction vessels were then sealed with rubber gaskets to ensure an inert atmosphere. The polymerization started without any induction period. At appropriate time intervals, the reaction was arrested by the addition of a known amount of a ferrous solution or by the cooling of the reaction mixture to 0°C. The monomer AN, converted into PAN, was filtered from the reaction mixture with funnels, was washed several times with distilled water, and was dried at 70°C to a constant weight. Finally, the rate of polymerization (R_p) and the rate of the disappearance of PPS ($-R_m$) were determined gravimetrically.[37]

Molecular weight determination

The viscosity-average molecular weight (M_v) of the purified sample of the PAN product was determined by the viscometry method. A 1% solution of the polymer in DMF was filtered through a fitted glass filter and placed in an Ubbelohde-type suspended-level dilution viscometer. The intrinsic viscosity (η) of the reaction mixture was determined, and M_v values were calculated with the Mark–Houwink equation given by Stockmayer and Cleland[38] [$|\eta| = (3.335 \times 10^{-4}) \times M_v^{0.72}$] at 30°C for PAN in DMF. The molecular weight of the polymer product under standard conditions was found to be $M_v = 6.75 \times 10^4$ g/mol. The density and refractive index were determined with a density bottle and an Abbe's refractometer (1.256 g/cm^3 and 1.353), respectively.

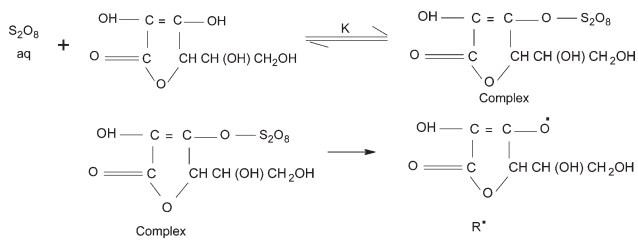
RESULTS AND DISCUSSION

At a high temperature (35°C), there was no polymerization of the monomer even after 75 min when PPS alone was used as the initiator. However, with PPS/AA as the redox initiator, the polymerization reaction proceeded without any induction period. The steady state was attained within 75 min. The polymerization of AN initiated by the PPS/AA redox system took place at a measurable rate at 40–70°C. $-R_m$ was first-order with respect to PPS and was independent of the AN concentration. It depended on the PPS and AA concentrations. A plot of $-1/R_m$ versus 1/[AA] was linear with an intercept on the rate axis indicating Lineweaver–Burk kinetics for complex formation[39] (Fig. 1).

Reaction mechanism and rate law

The polymerization of AN in an aqueous medium initiated by the PPS/AA redox system showed characteristic features of heterogeneous polymerization. The reaction mixture became heterogeneous as soon as polymerization started because of the insolubility of the polymer PAN in the aqueous medium. On the basis of the kinetic results, a reaction involving initiation by organic free radicals generated by the interaction of PPS ions with carboxyl groups is proposed (Scheme 1).

Thus, the dependences of R_p on the monomer, PPS, H^+, and AA concentrations, all of which can be observed in Scheme 1, are consistent with the experimental results. The low energy of activation is an indication of the high reactivity of the initiator and provides direct experimental evidence of the existence of transient radical intermediates generated in redox reactions. It also enables the identification of these radicals as end groups of the polymer. Further work on the kinetics of polymerization of various vinyl monomers initiated by the reaction of PPS and other transition-metal ions with suitable reductants is in progress in our laboratory.



$$AA + S_2O_8^{2-} \underset{}{\overset{k}{\rightleftharpoons}} \text{Complex}$$

$$\text{Complex} \xrightarrow{k_d} R^{\cdot} + 2H^+ + \overset{\bullet}{2}SO_4^-$$

Initiation

$$M + R^{\cdot} \xrightarrow{k_i} RM^{\cdot} \quad R^{\bullet}$$

Propagation

$$RM^{\cdot} + M \xrightarrow{k_p} RM\,M^{\cdot}$$

$$RM^{\cdot}_{x-1} + M \xrightarrow{k_p} RM\,M^{\cdot}$$

Termination

$$RM^{\cdot}_x + RM^{\cdot}_y \xrightarrow{k_t} \text{Polymer}$$

Applying steady-state approximation

$$-d[R^{\cdot}]/dt = k_d[\text{Complex}] - k_i[R^{\cdot}][R^{\cdot}] = 0$$

$$k = [\text{Complex}]/[AA][PPS]$$

$$[\text{Complex}] = k[AA][PPS]$$

$$k_d k[AA][PPS] - k_i[M][R^{\cdot}] = 0$$

$$[R^{\cdot}] = k_d k[PPS][AA]/k_i[M]$$

$$k_i[R^{\cdot}][M] = -k_t[RM^{\cdot}_n][RM^{\cdot}_n] = k_t[RM^{\cdot}_n]^2$$

$$[RM^{\cdot}_n]^2 = (k_i/k_t)[R^{\cdot}][M]$$

$$[RM^{\cdot}_n] = (k_i/k_t)^{1/2}[R^{\cdot}]^{1/2}[M]^{1/2}$$

$$R_p = k_p(k_i/k_t)^{1/2}[R^{\cdot}]^{1/2}[M]^{1/2}[M]$$

$$R_p = k_p[RM^{\cdot}_n][M]$$

$$R_p = k_p(k_i/k_t)^{1/2}\, k_p(k_d k/k_t)^{1/2}[PPS][AA]^{1/2}[M]^{3/2/}[M]^{1/2}$$

$$R_p = k_p(k_d k/k_t)^{1/2}[PPS][AA]^{1/2}[M]$$

Scheme 1 Equilibrium constant $\rightleftarrows$ K; dissociation constant = k_d; initiation constant = k_i; propagation constant = k_p; and termination constant = k_t.

Dependence of the rate on the monomer concentration

R_p increased with the monomer concentration increasing. The availability of monomer molecules in the propagation step increased, and this obviously increased R_p. The order of the reaction with respect to the monomer concentration was calculated from a plot of log R_p versus log [M] (Fig. 2). The order with respect to the AN concentration was found to be unity in the range of 0.1518–1.5188 mol/dm^3.

Dependence of the rate on the PPS concentration

R_p increased with an increase in the concentration of PPS; this was due to an increase in the concentration of active species. The order of the reaction with respect to PPS was found to be unity in the concentration range of 4.0×10^{-3}–20.0×10^{-3} mol/dm^3 (Fig. 3), and this clearly indicated that termination occurred through the unimolecular interaction of the growing polymer chain radical. M_v of PAN decreased with an increase in the PPS concentration, and this can be explained by the fact that an increase in the concentration of PPS provided more chances for premature termination of growing chain radicals, which in turn reduced the degree of polymerization.[40]

Dependence of the rate on the AA concentration

R_p increased with an increase in the AA concentration gradually. The exponent (slope) of AA was found to be a fractional order from a plot of log R_p versus log [AA] in the concentration range of 1.0×10^{-2}–5.0×10^{-2} mol/dm^3 (Fig. 4). At a higher concentration of AA, the rate became constant because of the chain transfer or mutual interaction of the growing polymer chain radicals.

Dependence of the rate on the H_2SO_4 concentration

Kinetic measurements were performed in aqueous H_2SO_4 solutions with different H^+ ion concentrations.

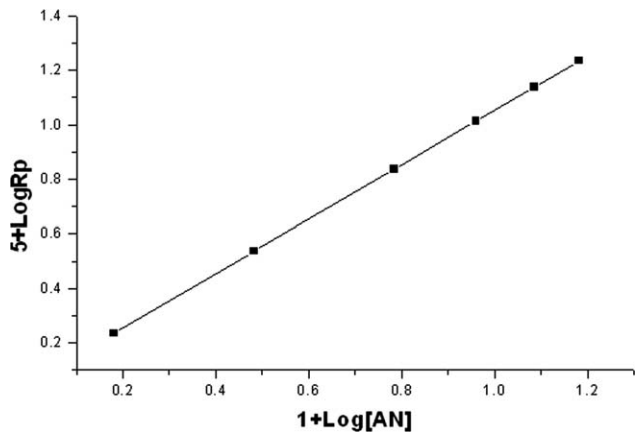


Figure 2 Effect of the monomer concentration on R_p ([PPS] = 4.0×10^{-3} mol/dm^3, [AA] = 1.0×10^{-2} mol/dm^3, [M] = 0.1518–1.5188 $\times 10^{-1}$ mol/dm^3, [H_2SO_4] = 2.0×10^{-3} mol/dm^3, temperature = 323 K).

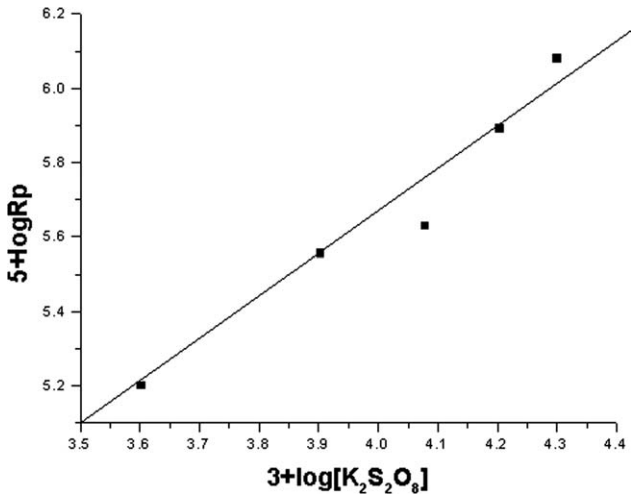


Figure 3 Effect of the PPS concentration on R_p ([PPS] = 4.0–20.0 × 10^{-3} mol/dm^3, [AA] = 1.0 × 10^{-2} mol/dm^3, [M] = 0.0675 × 10^{-2} mol/dm^3, [H_2SO_4] = 2.0 × 10^{-3} mol/dm^3, temperature = 323 K).

R_p decreased with an increase in the H^+ ion concentration, and this indicated that the hydrolyzed species of PPS was more reactive than the unhydrolyzed species and also that the unprotonated form of AA was more reactive than the protonated form. The order with respect to the H^+ ion concentration was found to be an inverse fractional order (−0.5) from a plot of log R_p versus log [H^+] (Fig. 5).

Dependence of the rate on the temperature

The polymerization reaction was studied at different temperatures ranging from 40 to 70°C. The initial value of R_p increased steadily with an increase in temperature and thereafter remained constant. This may have been due to an increase in the mobility of growing chain radicals in the system, which led to their efficient termination. The activation energy (12.10 kJ/mol) was calculated from an Arrhenius plot of log R_p versus the reciprocal of the temperature (1/T; Fig. 6) in the temperature range of 40–70°C. The other activation parameters were calculated from Eyring plots as follows: enthalpy change ($\Delta H^{\neq}$) = 49.24 kJ/mol, entropy change ($\Delta S^{\neq}$) = −158.95 J K^{-1}/mol, and Gibbs free energy change ($\Delta G^{\neq}$) = 99.30 kJ/mol. The low energy of activation was an indication of the high reactivity of the initiator and provided direct experimental evidence for the existence of transient radical intermediates generated in redox reactions.[41] It also enabled the identification of these radicals as end groups of the polymer. The existence of a rigid state

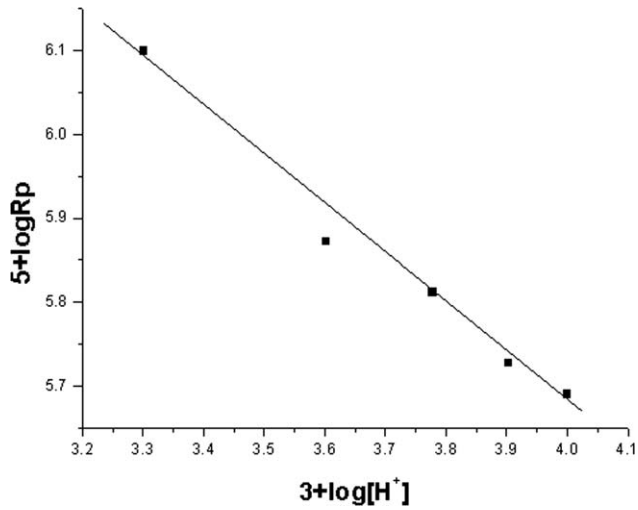


Figure 5 Effect of the H_2SO_4 concentration on R_p ([PPS] = 4.0 × 10^{-3} mol/dm^3, [AA] = 1.0 × 10^{-2} mol/dm^3, [M] = 0.0675 × 10^{-2} mol/dm^3, [H_2SO_4] = 2.0–10.0 × 10^{-3} mol/dm^3, temperature = 323 K).

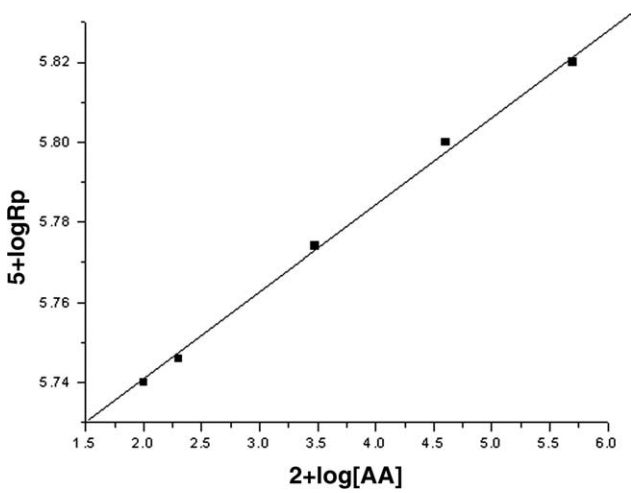


Figure 4 Effect of the AA concentration on R_p ([PPS] = 4.0 × 10^{-3} mol/dm^3, [AA] = 1.0–5.0 × 10^{-2} mol/dm^3, [M] = 0.0675 × 10^{-2} mol/dm^3, [H_2SO_4] = 2.0 × 10^{-3} mol/dm^3, temperature = 323 K).

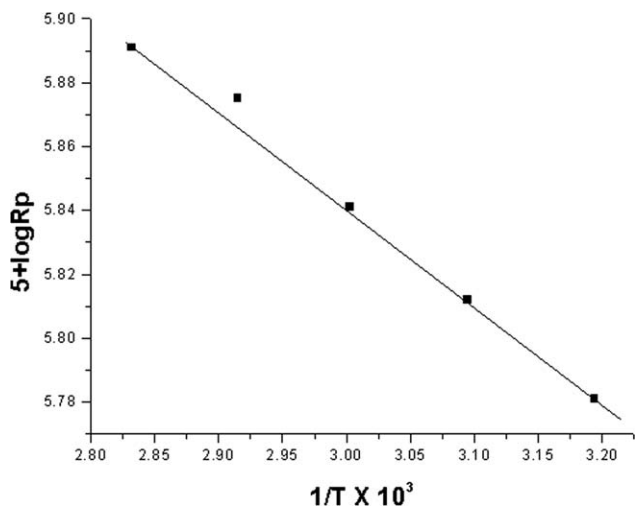


Figure 6 Effect of the temperature on R_p ([PPS] = 4.0 × 10^{-3} mol/dm^3, [AA] = 1.0 × 10^{-2} mol/dm^3, [M] = 0.0675 × 10^{-2} mol/dm^3, [H_2SO_4] = 2.0 × 10^{-3} mol/dm^3, temperature = 313–353 K).

resulting from an associative process was consistent with a negative $\Delta S^{\neq}$ value for reactions of transition-metal complexes involving an associative mechanism.[42] The highly negative $\Delta S^{\neq}$ value also suggested that the transition state involved an associated species (probably formed by salvation), which was responsible for lowering the entropy of the products and, therefore, for a highly negative value of $\Delta S^{\neq}$ and a corresponding high value of $\Delta G^{\neq}$.

Dependence of the rate on the organic solvents

Because the properties of a polymer mostly depend on the nature of the medium, various water-miscible organic solvents such as methanol, DMF, and ethanol were observed for their effect on R_p. When they were added to the reaction mixture in an equal volume (5% v/v), a depression of the initial R_p value and the limiting conversion was observed. The increasing order of depression by these solvents was methanol < ethanol < DMF.

The cause of the depression in R_p and the percentage conversion with the added organic solvents can be explained as follows:

1. When organic solvents are added to a reaction mixture, they cause a decrease in the area of shielding of a strong hydration layer in an aqueous medium, and this results in the termination of the radical end of the growing chain.
2. Some amount of the catalyst may be consumed in the oxidation of these organic solvents; as a result, the concentration of the catalyst decreases, and a depression in the rate can be observed. The sluggish radicals thus produced may not be equally capable of initiating the polymerization.

CONCLUSIONS

AN was polymerized in a nitrogen atmosphere by a PPS/AA redox system via a free-radical mechanism. The polymerization reaction with respect to the monomer concentration was 1.0, and the reaction orders related to the PPS and AA concentrations were 1.11 and 0.2, respectively. This suggested a bimolecular mechanism, and the following rate equation was derived:

$$V_p = k[\mathrm{M}]^{1.0}[\mathrm{PPS}]^{1}[\mathrm{AA}]^{0.2}$$

where k is the rate constant, V_p is the velocity of the polymerization or rate of polymerization it is also denoted as R_p.

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