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Sudhansu Bhusan Dash[a]; Nilamber Baral[a]; Nrusingha C. Pati[a]; Padma L. Nayak[a]
[a] Laboratory of Polymers and Fibers Department of Chemistry, Ravenshaw College, Cuttack, India

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Vinyl Polymerization Initiated by Peroxydiphosphate. IV. Polymerization of Acrylonitrile Initiated by Peroxydiphosphate-Thioacetamide Redox System

SUDHANSU BHUSAN DASH, NILAMBER BARAL, NRUSINGHA C. PATI, and PADMA L. NAYAK

Laboratory of Polymers and Fibers
Department of Chemistry
Ravenshaw College
Cuttack 753003, India

ABSTRACT

The kinetics of the aqueous polymerization of acrylonitrile initiated by the peroxydiphosphate-thioacetamide redox system was investigated at 35, 40, and 50°C. The rates of polymerization were measured at different concentrations of oxidant, activator, and monomer. Peroxydiphosphate alone did not initiate polymerization under deaerated and undeaerated conditions. Addition of certain water-miscible organic solvents and neutral salts depress the rate and conversion. On the basis of experimental observations of the dependence of the rate of polymerization on various variables, a suitable kinetic scheme has been proposed.

INTRODUCTION

A literature survey reveals that the peroxydisulfate ion has been extensively used [1-3] for the polymerization of a number of vinyl monomers. But the peroxydiphosphate ion, $P_2O_8^{4-}$, which is isoelectronically and isostructurally similar, received relatively little attention till Edwards and co-workers [4-8] reported the photochemical oxidation of water, ethanol, propane-2-ol, and some metal complexes by this ion. Santappa and co-workers [9-11] have investigated the kinetics of self-decomposition of peroxydiphosphate in aqueous sulfuric acid and the oxidation of water and pinacol by peroxydiphosphate. Gupta and co-workers [12] have studied the kinetics of oxidation of a large number of inorganic substrates by this ion.

Since the oxidation potential of peroxydiphosphate ion was found to be -2.07 V which is very near to the oxidation potential of peroxydisulfate (-2.01 V), it is possible to predict that peroxydiphosphate ion might initiate vinyl polymerization like peroxydisulfate through a radical mechanism. But surprisingly, not much has been reported on using peroxydiphosphate for initiating vinyl polymerization [13].

Nayak and co-workers [14-18] have extensively studied the kinetics and mechanism of vinyl polymerization using a multitude of metal and nonmetal ions. Very recently we have reported the use of peroxydiphosphate ion as the initiator [19-23] for graft copolymerization of vinyl monomers onto wool, silk, and cellulose fibers. This communication presents the results of the aqueous polymerization of acrylonitrile initiated by the peroxydiphosphate-thioacetamide redox system.

EXPERIMENTAL

Acrylonitrile (American Cyanamid Co.) was purified following the procedure of Bamford et al. [24]. Potassium peroxydiphosphate (a gift sample from F.M.C. Corp., U.S.A.) solution (0.1 M) was prepared by dissolving it in 0.5 M sulfuric acid. The concentration of peroxydiphosphate in the experimental solution was determined by cerimetry. Other reagents such as sulfuric acid (AR, ~18 M), thioacetamide (GR, BDH), ferrous ammonium sulfate, and ceric ammonium sulfate (BDH) were used. Water distilled over alkaline permanganate and deionized by passing through a column of Biodeminolit resin (Permulit Co., U.K.) was used to prepare all solutions. Nitrogen used for deaeration of the experimental system was purified according to our previous communication [17].

The polymerization reaction was carried out according to our previous procedure [17] using peroxydiphosphate as the oxidant and thioacetamide as the reducing agent.

DISCUSSION

Effect of Peroxydiphosphate Concentration

The rate of polymerization has been investigated by changing the peroxydiphosphate concentration from 2.5×10^{-3} to 25.0×10^{-3} M. The rate of polymerization as well as the maximum conversion was

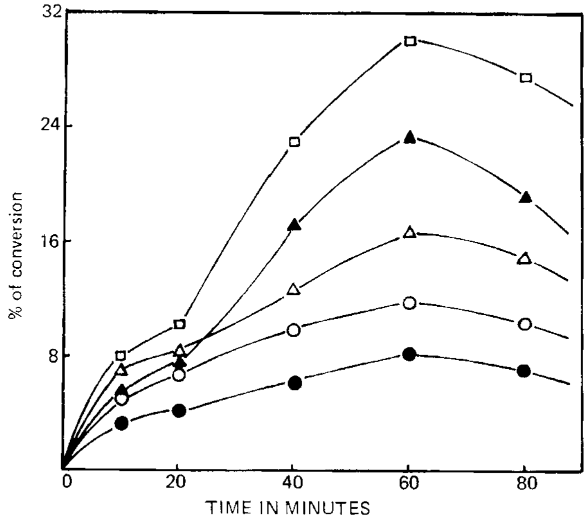


FIG. 1. Variation of rate with time at different concentrations of oxidant. [TA] = 15×10^{-3} M, [AN] = 75.39×10^{-2} M, [H^+] = 0.3 M, temperature = 35°C. [PP]: (●) 2.5×10^{-3} M, (○) 5×10^{-3} M, (△) 10×10^{-3} M, (▲) 20×10^{-3} M, (□) 25×10^{-3} M.

found to increase with increasing peroxydiphosphate concentration (Fig. 1). A probable explanation of this effect might be the production of a large number of thiol radicals ($R^{\cdot}$) produced by the interaction of peroxydiphosphate ion with isothioacetamide moiety (Eq. 1) at higher initiator concentration, which combine with the monomer to enhance the rate of polymerization.

Effect of Monomer Concentration

The rate of polymerization (R_p) was found to increase with an increase of monomer concentration over the range of 15.07×10^{-2} to 75.39×10^{-2} M, beyond which it decreased. Thus the plot of R_p versus [M] is linear up to 75.39×10^{-2} M of monomer concentration, indicating the order with respect to monomer to be unity (Fig. 2). A probable explanation for the decrease in the rate of polymerization at higher monomer concentration might be the gel effect [35], i.e., the increase in the viscosity of the medium due to the solubility of polymer in its own monomer. Similar observations have been noted by Suen et al. [25] and Nayak et al. [26, 27].

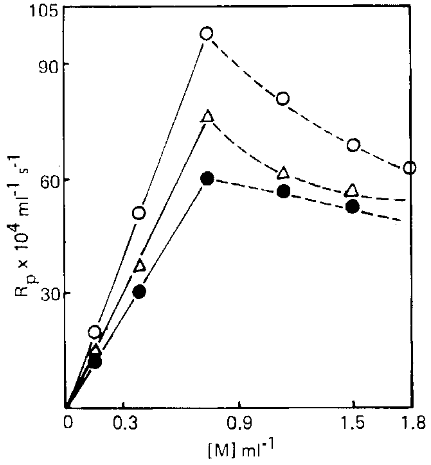


FIG. 2. Variation of rate of polymerization with monomer at different temperatures. [PP] = 20×10^{-3} M, [TA] = 15×10^{-3} M, [H^+] = 0.3 M, time = 60 min. Temperature: (●) 30°C, (○) 35°C, (△) 45°C.

Effect of Activator Concentration

The effect of activator (thioacetamide) concentration on the rate of polymerization has been studied by changing the activator concentration from 1.25 to 10.0×10^{-3} M. The rate of polymerization was found to increase linearly with increasing thioacetamide concentration up to 5.0×10^{-3} M, and at higher concentration of thioacetamide (5.0×10^{-3} M) an appreciable decrease in the rate of polymerization is observed. The plot of R_p versus [thioacetamide] is linear up to 5.0×10^{-3} M of thioacetamide, passing through the origin and indicating the order of the reaction with respect to thioacetamide concentration to be unity (Fig. 3). This agrees with observations made by Morgan [28] and Guha [29]. The decrease in the rate of polymerization at higher concentrations of thioacetamide might be due to the termination of the growing chains (1) by the primary radicals (R•), (2) by disproportionation, and (3) because some species might be forming which act as radical scavengers, thus causing a decrease in the rate of polymerization.

Effect of Acid Concentration

The rate of polymerization has been found to increase with increasing sulfuric acid concentration within the range of 15×10^{2} to 60.0×10^{-2} M (Fig. 4).

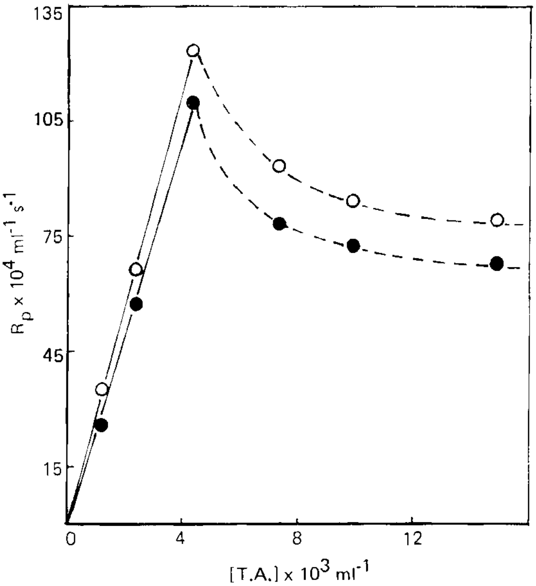


FIG. 3. Variation of rate of polymerization with activator at different temperatures. [PP] = 20 × 10^{-2} M, [AN] = 75.39 × 10^{-2} M, [H^+] = 0.3 M, time = 60 min. Temperature: (●) 35°C, (○) 50°C.

It has been known for a long time that the rate of oxyanion reactions are markedly dependent on acid concentration [30-32]. The proton will labilize oxygen by converting it from oxide ion to hydroxide ion and on to water. By the addition of protons to the oxide ion in an oxyanion, the bond is broken easily. In oxidations involving oxyanion, since covalent bonds to oxygen are generally broken simultaneously with electron transfer, they are found to be acid catalyzed. The reactions of peroxides are also subject to acid catalysis. Hence it is possible that the reactions of peroxydiphosphate, which is both a peroxide and oxyanion, i.e., oxyanion derivate of H–O–O–H, are subjected to acid catalysis strongly. Peroxydiphosphate is protonated due to its high negative charge, giving rise to various species like $HP_2O_8^{3-}$, $H_2P_2O_8^{2-}$, $H_3P_2O_8^-$, $H_4P_2O_8$, $H_5P_2O_8^+$, and $H_6P_2O_8^{2+}$. It has been stated by Santappa and co-workers [9, 11] that the reaction rate as well as the concentration of $H_3P_2O_8^-$ and $H_4P_2O_8$ increases with increasing acid concentration. In the concentration range of 15.0 × 10^{-2} to 60 × 10^{-2} M, the most active species ($H_3P_2O_8^-$) might be formed and interact with various other species, giving rise to a multitude of free radicals which enhances the rate of polymerization.

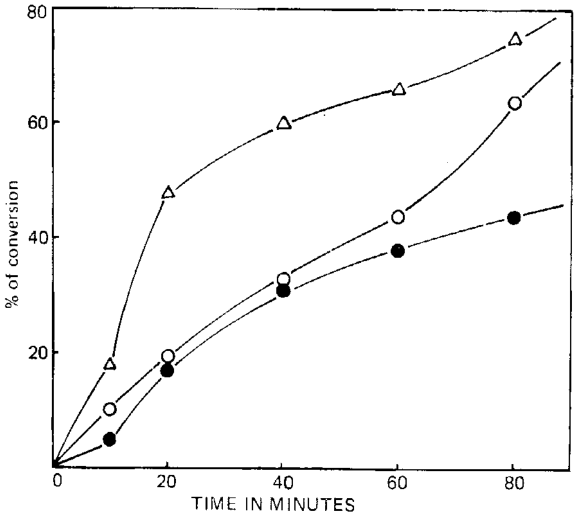


FIG. 4. Variation of rate with time at different concentrations of sulfuric acid. [PP] = 20×10^{-3} M, [AN] = 75.39×10^{-2} M, [TA] = 15×10^{-3} M, temperature = 35°C. [H^+]: (●) 15×10^{-2} M, (○) 30×10^{-2} M, (△) 45×10^{-2} M.

Effect of Temperature

The polymerization reaction has been studied at three different temperatures from 35 to 50°C. The initial rate of polymerization as well as the maximum conversion were found to increase steadily with an increase of temperature (Fig. 5). This might be due to the increase in the activation energy. The rate of diffusion of monomer and initiator into the active sites of the polymer chain also increases with an increase of temperature, thus enhancing the rate of polymerization.

Effect of Addition of Organic Solvents

The addition of 10% water-soluble organic solvents such as acetic acid, propanol, and dioxane to the reaction mixture depresses the rate as well as the maximum conversion (Fig. 6). This is probably caused by a decrease in the area of shielding of a strong hydration layer in the aqueous medium, resulting in the termination of the radical end of the growing chain, or the increase in the regulated

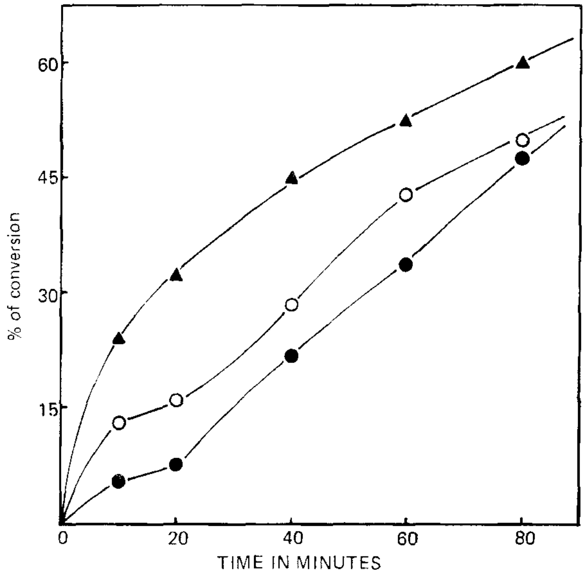


FIG. 5. Variation of rate with time at different temperatures. [PP] = 20×10^{-3} $\underline{M}$, [AN] = 75.39×10^{-2} $\underline{M}$, [TA] = 15×10^{-3} $\underline{M}$, [H^+] = 0.3 $\underline{M}$. Temperature: (●) 35°C, (○) 40°C, (▲) 50°C.

rate of production of primary radicals caused by the solvents, which under the existing experimental conditions render the termination rate relatively fast compared to the rate of growth of the polymer chains as pointed out by Kern et al. [33]. Palit et al. [34] have noticed similar observations even for the homogeneous medium in which water is the additive. The interchain hydrogen bonding interlocking the polymer chains is not rigid, which causes a premature mutual combination of the polymer chains.

Effect of Added Electrolytes

The addition of certain neutral salts such as $CuSO_4$, Na_2SO_4, and KCl to the reaction mixture reduces both the initial rate and the maximum conversion to a considerable extent (Fig. 7). This might be due to (1) the ionic dissociation of the added electrolyte which interferes with the usual polymerization reaction, resulting in the premature termination of the growing polymer chain; and (2) the reduction of the activity of the peroxydiphosphate ion due to the ion-pair coupling with the added electrolytes.

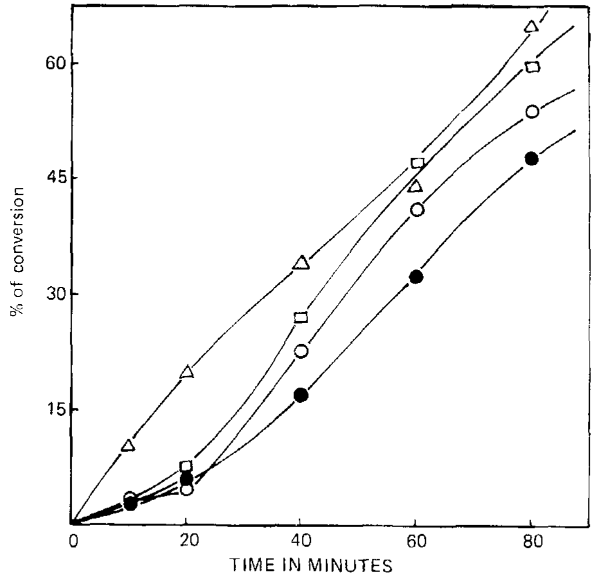


FIG. 6. Variation of rate with time in the presenee of some water-miscible organic solvents. $[PP] = 20 \times 10^{-3}$ M, $[AN] = 75.39 \times 10^{-2}$ M, $[TA] = 15 \times 10^{-3}$ M, $[H^+] = 0.3$ M, temperature = 35°C. (○) Propanol = 1% v/v. (●) Dioxane = 1% v/v. (□) Acetic acid = 1% v/v. (△) Control.

Reaction Mechanism and Rate Law

The aqueous polymerization of acrylonitrile initiated by the peroxydiphosphate-thioacetamide redox system shows characteristic features of heterogeneous polymerization. The reaction system, though homogeneous before initiation of polymerization, becomes heterogeneous as soon as the polymerization starts due to the insolubility of the polyacrylonitrile in the aqueous phase.

From the proportionalities obtained among the measurable parameters and variables, a reaction scheme, involving the initiation by organic free radicals produced by the interaction of peroxydiphosphate ion with thioacetamide and termination by mutual combination of the polymer chain, has been suggested.

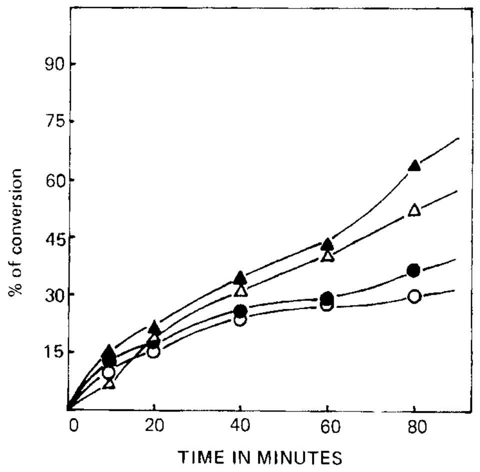


FIG. 7. Variation of rate with time in the presence of some neutral salts. [PP] = 20×10^{-3} $\underline{M}$, [AN] = 75.39×10^{-2} $\underline{M}$, [TA] = 15×10^{-3} $\underline{M}$, [H^+] = 0.3 $\underline{M}$, temperature = 35°C. (●) [KCl] = 0.02 $\underline{M}$. (○) [$MnSO_4$] = 0.02 $\underline{M}$. (△) [Na_2SO_4] = 0.02 $\underline{M}$. (▲) Control.

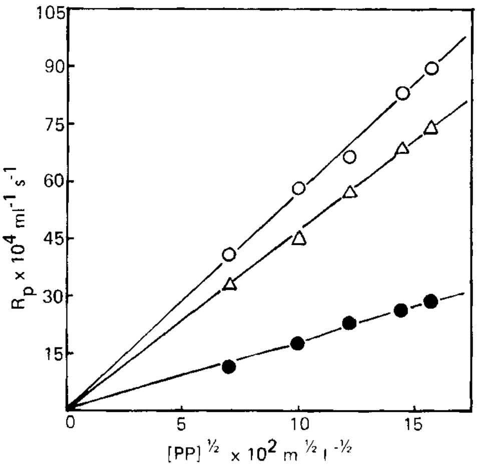
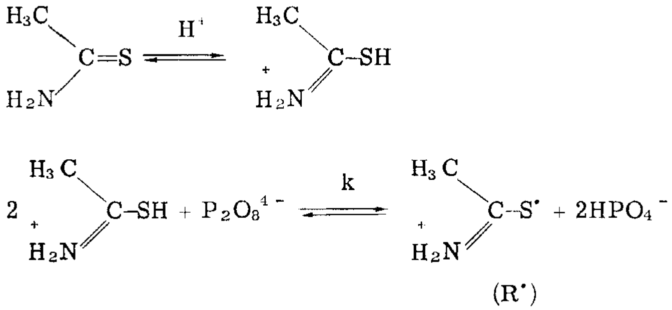


FIG. 8. Variation of rate of polymerization with oxidant at different temperatures. [AN] = 75.39×10^{-2} $\underline{M}$, [TA] = 15×10^{-3} $\underline{M}$, [H^+] = 0.3 $\underline{M}$, time = 60 min. Temperature: (●) 30°C, (△) 35°C, (○) 45°C.



(1)

Initiation:

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

Propagation:

$$RM^{\bullet} + M \xrightarrow{k_p} RM_2^{\bullet}$$

$$RM_{n-1}^{\bullet} + M \xrightarrow{k_p} RM_n^{\bullet}$$

Termination:

$$RM_n^{\bullet} + RM_m^{\bullet} \xrightarrow{k_t} \text{dead polymer}$$

Applying the steady-state assumptions to $[R^{\bullet}]$ and $[RM_n^{\bullet}]$, we get

$$\frac{d[R^{\bullet}]}{dt} = k[TA]^2[PP] - k_i[R^{\bullet}][M] = 0$$

$$[R^{\bullet}] = \frac{k[TA]^2[PP]}{k_i[M]}$$

where PP = peroxydiphosphate, TA = thioacetamide

$$\frac{d[RM_n^{\bullet}]}{dt} = k_i[R^{\bullet}][M] - k_t[RM_n^{\bullet}]^2 = 0$$

$$[RM_n^{\bullet}] = \left(\frac{k_i}{k_t}\right)^{1/2} [R^{\bullet}]^{1/2}[M]^{1/2} = \frac{k_i^{1/2}[TA][PP]^{1/2}}{k_t^{1/2}}$$

$$R_p = k_p[RM_n^{\bullet}][M] = \frac{k_p k^{1/2}[TA][M][PP]^{1/2}}{k_t^{1/2}}$$

Thus the plots of R_p vs $[PP]^{1/2}$ (Fig. 8) and R_p vs $[TA]$ (Fig. 3) are linear, passing through the origin and showing the validity of the above reaction scheme.

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