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Vinyl Polymerization Initiated by Peroxydiphosphate. XI. Polymerization of Methyl Methacrylate Initiated by Peroxydiphosphate-Tartaric Acid Redox System

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ABSTRACT

The polymerization of methyl methacrylate was studied using the peroxydiphosphate and tartaric acid redox system as the initiator. The rate of polymerization increases with increasing peroxydiphosphate concentration and the initiator exponent was computed to be 0.5. The rate of polymerization increases with increasing monomer concentration and the monomer exponent was computed to be unity. The reaction was carried out at three different temperatures, and the overall activation energy was computed to be 3.80 kcal/mol. The effect of certain surfactants on the rate of polymerization has been investigated and a suitable kinetic scheme has been proposed.

INTRODUCTION

Among the inorganic compounds containing a peroxide bond, peroxydisulfate, $S_2O_8^{2-}$, alone or in combination with a suitable reductant, proved to be an efficient redox initiator for various vinyl polymeriza-

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tions [1, 2]. Studies involving peroxydiphosphate (PP) are very few in the literature. Edwards and co-workers [3-6] reported the photochemical oxidation of water, ethanol, propan-2-ol, and some metal complexes by peroxydiphosphate. The kinetics and mechanism of certain organic and inorganic substrates involving peroxydiphosphate have been reported by Santappa and co-workers [7-9]. Nayak et al. [10-15] have reported the aqueous polymerization of vinyl monomers using a large number of redox systems involving peroxydiphosphate ion.

This communication presents the results on the polymerization of methyl methacrylate indicated by the PP-tartaric acid (TA) redox system.

EXPERIMENTAL

Potassium peroxydiphosphate ($K_4P_2O_8$) was obtained as a gift sample from F.M.C. Corporation, U.S.A. The tartaric acid used was of analytical grade. Methyl methacrylate, acrylonitrile, and butyl acrylate were purified by standard procedures. Polymerization was carried out in the absence of air. The rate of polymerization was evaluated gravimetrically [11-16]. The molecular weights $\overline{M}_w$ of the purified polymers were determined by viscometry by use of the appropriate Mark-Houwink relationship.

RESULTS AND DISCUSSION

Methyl methacrylate, acrylonitrile, and butyl acrylate were polymerized at 50°C in the presence of the PP-TA redox system. Typical sets of time-conversion curves for the three monomers at fixed monomer, oxidant, and reductant concentrations are shown in Figs. 1, 2, and 3. The rate of polymerization increases with time in the case of all systems.

Effect of [Initiator]

The initial rate and the limiting conversion tend to increase with increasing peroxydiphosphate concentration over the range of 2.5×10^{-3} to 15.0×10^{-3} $\underline{M}$. The plots of R_p versus $[PP]^{1/2}$ (Fig. 4) and the plots of log R_p versus log [PP] (Fig. 5) with a slope of 0.5 are linear, indicating a 0.5-order with respect to peroxydiphosphate. Similar observations were made by Kamenskaya et al. [17] and Price et al. [18, 19].

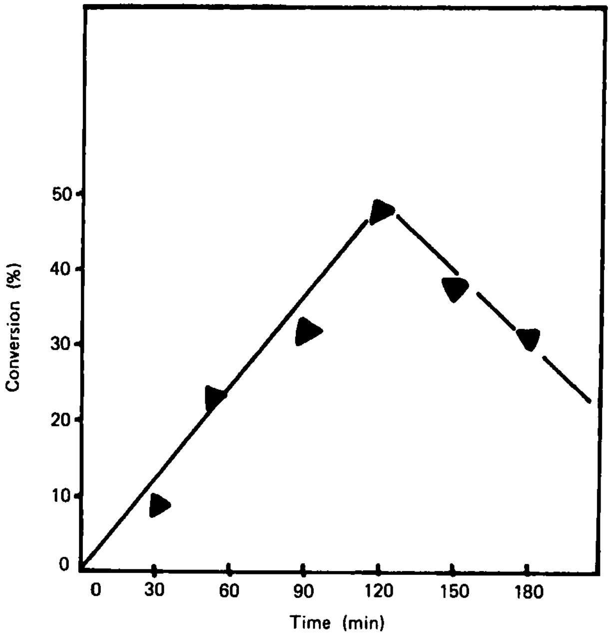


FIG. 1. Plot of % conversion of methyl methacrylate vs time in minutes: 50°C, [PP] = 5.0×10^{-3} M, [TA] = 5.0×10^{-3} M, [MMA] = 9.4×10^{-2} M.

In terms of generally accepted kinetic interpretation, this means that the termination process occurs by mutual collisions of the two active centers and the steady-state assumption is reasonably well fulfilled.

Effect of [Monomer]

The rate of polymerization, R_p, has been measured within the range of 2.35×10^{-2} to 9.4×10^{-2} M at 50°C. The plot of R_p versus [M] (Fig. 6) is linear, indicating first-order with respect to monomer. Similar results have been reported for the polymerization of methyl methacrylate initiated by the PP-sodium thiosulfate redox system [12].

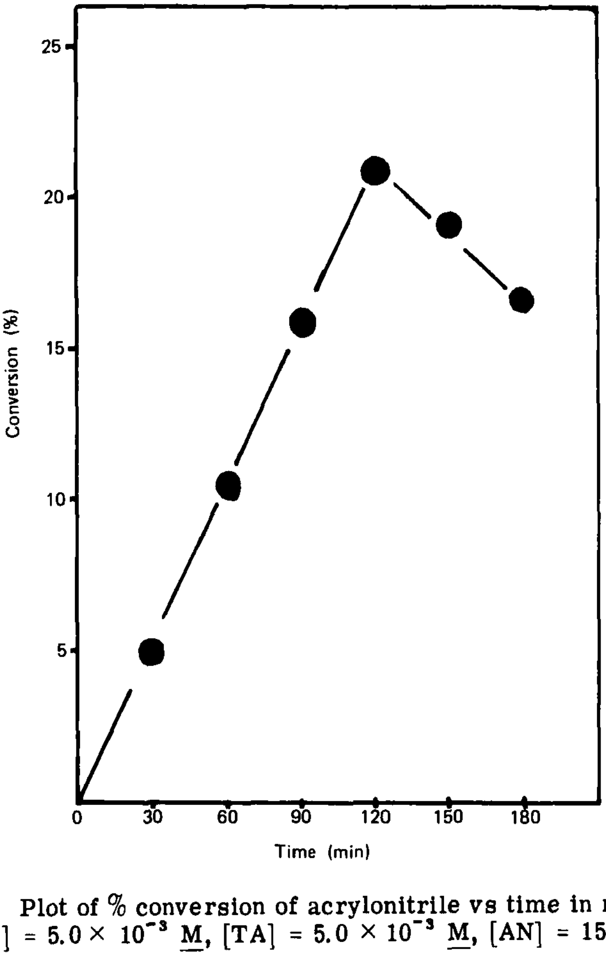


FIG. 2. Plot of % conversion of acrylonitrile vs time in minutes: 50°C, [PP] = 5.0×10^{-3} M, [TA] = 5.0×10^{-3} M, [AN] = 15.04×10^{-2} M.

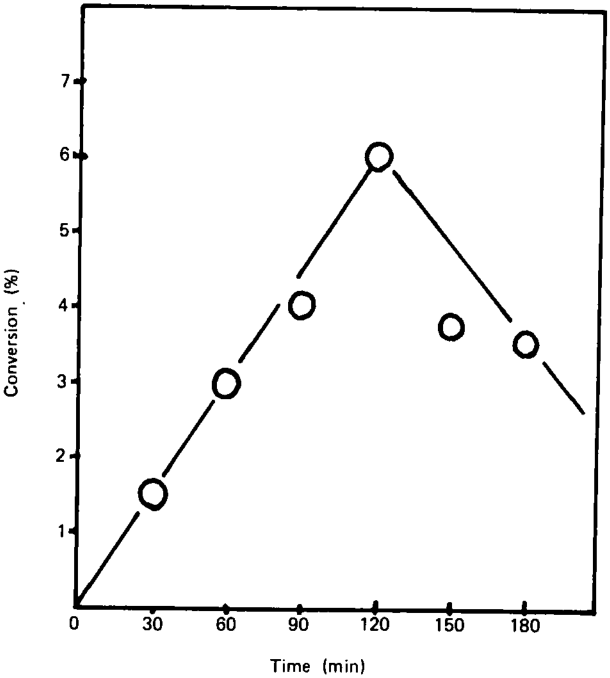


FIG. 3. Plot of % conversion of butyl acrylate vs time in minutes: 50°C, [PP] = 5.0×10^{-3} M, [TA] = 5.0×10^{-3} M, [BA] = 7.0×10^{-2} M.

Effect of [Activator]

The effect of activator concentration (tartaric acid) on the rate of polymerization has been studied by changing the activator concentration from 2.5×10^{-3} to 17.5×10^{-3} M at 50°C. The rate of polymerization was found to increase linearly with increasing tartaric acid concentration. The plot of R_p versus [tartaric acid] (Fig. 7) is linear, indicating the order of reaction with respect to tartaric acid to be unity. Further, the plot of log R_p versus log [TA] (Fig. 8) is linear with a unity slope.

Effect of Temperature

An increase in temperature causes an enhancement in the initial rate of polymerization as well as maximum conversion. The rate of

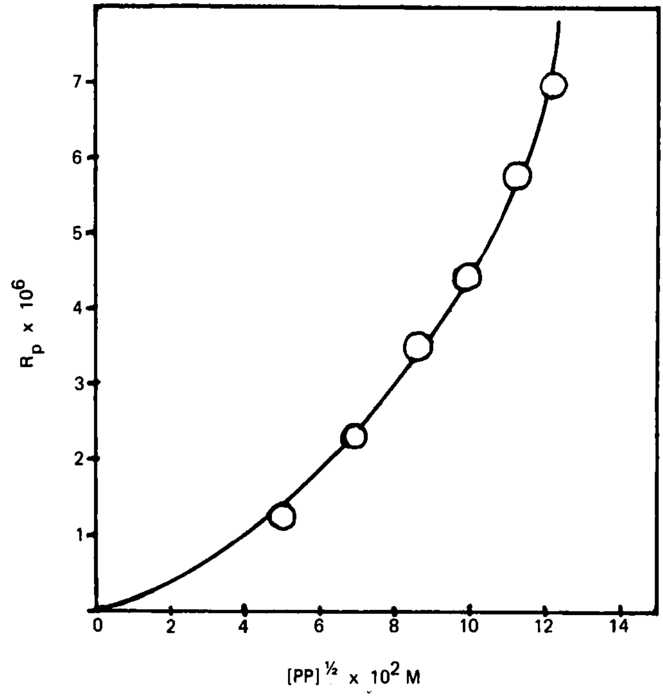


FIG. 4. Plot of R_p vs $[PP]^{1/2}$: 50°C, 2 h, [TA] = 5.0×10^{-3} M, [MMA] = 9.4×10^{-2} M.

polymerization has been studied by varying the temperature within the range of 50 to 60°C. From the slope of the Arrhenius plot of log R_p versus 1/T (Fig. 9), the value of activation energy was computed to be 3.80 kcal/mol.

Effect of Surfactant

The rate of polymerization has been investigated in the presence of certain cationic (CTABr) and anionic (NaLS) surfactants. The hydrophobic interactions and electrostatic attractions are chiefly responsible for the spectacular rate enhancements or inhibitions exhibited by micelles formed from these surfactants. Anionic micelles of sodium lauryl sulfate decrease the rate, and cationic micelles of cetyltrimethyl ammonium bromide increase the rate of polymerization.

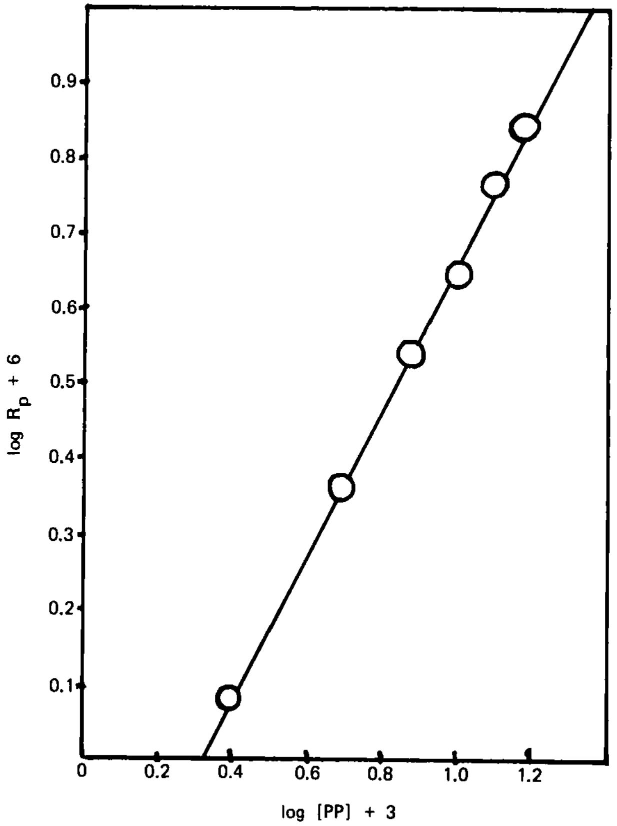


FIG. 5. Plot of log R_p vs log [PP]: 50°C, 2 h, [TA] = 5.0×10^{-3} $\underline{M}$, [MMA] = 9.4×10^{-2} $\underline{M}$.

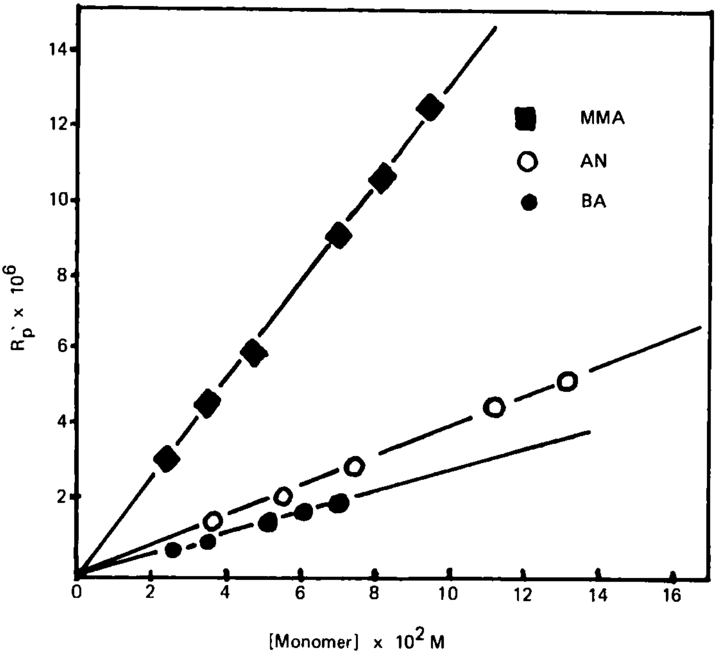
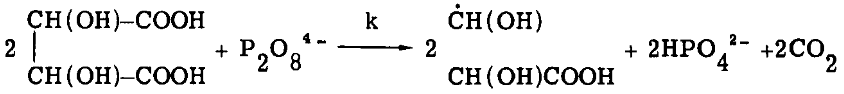


FIG. 6. Plot of R_p vs [M]: 50°C, 2 h, [PP] = 15.0×10^{-3} M, [TA] = 1.75×10^{-3} M.

Mechanism

The aqueous polymerization of methyl methacrylate initiated by the peroxydiphosphate-tartaric acid system show characteristic features of heterogeneous polymerization. The reaction system, though homogenous before the initiation of polymerization, becomes heterogeneous as soon as the polymerization starts due to the insolubility of the polymer in the aqueous phase.

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



$$2\begin{array}{l}\mathrm{CH(OH){-}COOH}\\ |\\ \mathrm{CH(OH){-}COOH}\end{array} + P_2O_8^{4-} \xrightarrow{k} 2\begin{array}{l}\dot{\mathrm{C}}\mathrm{H(OH)}\\ \\ \mathrm{CH(OH)COOH}\end{array} + 2HPO_4^{2-} + 2CO_2$$

(R•)

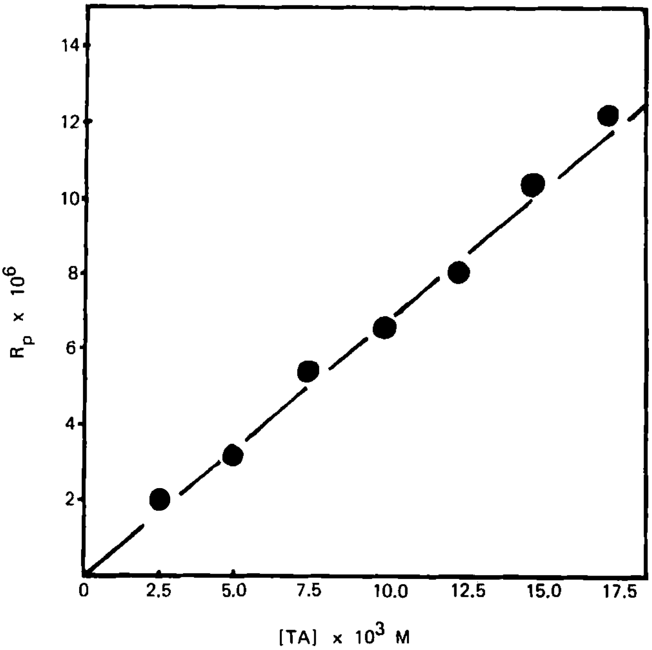


FIG. 7. Plot of R_p vs [TA]: 50°C, 2 h, [PP] = 15.0 × 10^{-3} M, [MMA] = 9.4 × 10^{-2} M.

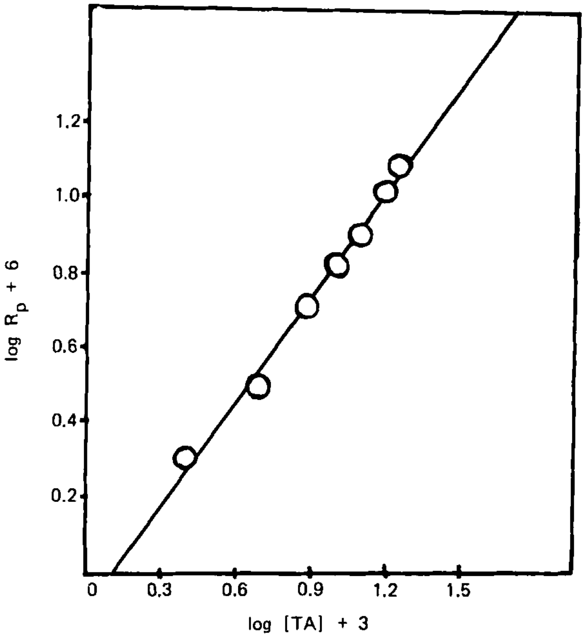


FIG. 8. Plot of log R_p vs log [TA] : 35°C, 2 h, [PP] = 15.0 × 10^{-3} M, [MMA] = 9.4 × 10^{-2} M.

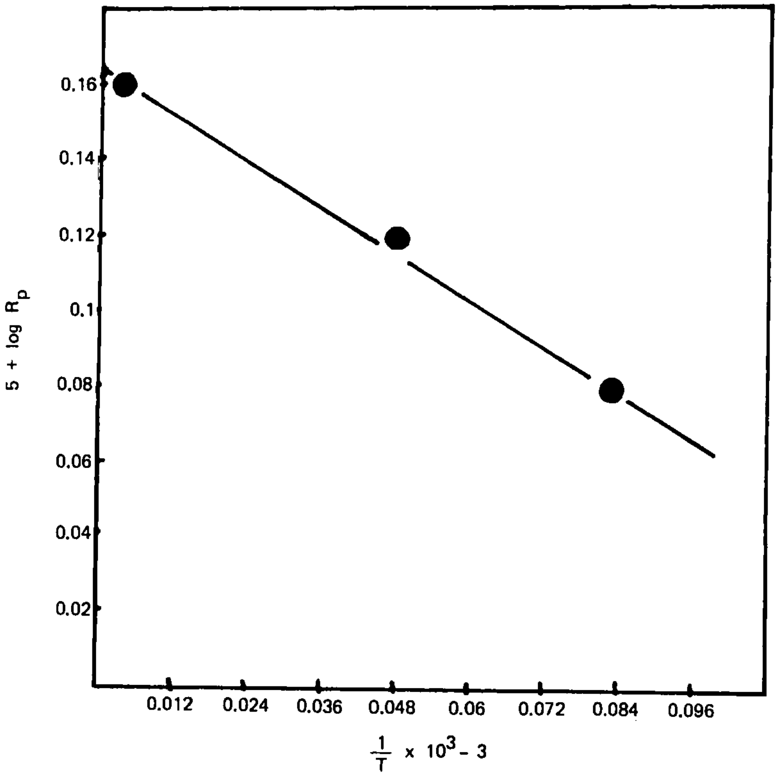


FIG. 9. Plot of log R_p vs 1/T: 2 h, [PP] = 15.0×10^{-3} M, [TA] = 17.5×10^{-3} M, [MMA] = 9.4×10^{-2} M.

Initiation:

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

Propagation:

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

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

Termination:

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

Applying the steady-state assumptions to $[R^{\bullet}]$ and $[RM_n^{\bullet}]$, the rate of polymerization R_p was derived to be

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

Thus the plots of R_p versus $[PP]^{1/2}$ (Fig. 4) and R_p versus [TA] (Fig. 7) were linear, showing the validity of the above reaction scheme.

CONCLUSION

The peroxydiphosphate-tartaric acid system is a very good initiator for the aqueous polymerization of vinyl monomers. This system could be used as a suitable initiator for grafting vinyl monomers onto a number of natural and synthetic fibers.

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