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Aqueous Polymerization of Methyl Methacrylate Initiated by the Bromate-Thiourea Redox System

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ABSTRACT

The aqueous polymerization of methyl methacrylate initiated by the bromate-thiourea redox system in dilute HCl has been investigated under nitrogen atmosphere. The rate of polymerization increases with increasing concentration of thiourea in the range 5×10^{-3} - 10×10^{-3} M. The percentage of conversion increases with increasing concentration of the catalyst, but beyond 1.5×10^{-2} M, there is a decreasing trend in the rate of polymerization. The rate of polymerization increases with increasing monomer concentration, but beyond 0.184 M the polymerization rate decreases due to gel effect. The rate of polymerization increases with temperature up to 35°C and beyond 40°C a decreasing trend is noticed. The effect of water miscible organic solvents, certain neutral salts on the rate of polymerization has also been investigated.

During the last few years, the use of thiourea and N-substituted thioureas as redox components for initiation of aqueous vinyl polymerization has been investigated. Bonvicini and Caldo [1] and Sugimura et al. [2] have used these reducing agents with hydrogen peroxide for

initiation of aqueous polymerization of acrylonitrile. Mukherjee et al. [3] have used thiourea as reductant with a number of oxidants such as ferric chloride (Fe^{3+}), ethylene dibiguanide complex salt of tri-positive silver (Ag^{3+}), hydrogen peroxide and persulfate initiation for aqueous polymerization of methyl methacrylate. Palit et al. [4] have reported the general features and kinetics of vinyl polymerization with Fe(III)-thiourea as initiator system. Mishra et al. [5] have reported aqueous polymerization of methacrylamide initiated by acidified bromate-thiourea redox system. Hebeish and Bendak [6] have used hydrogen peroxide-thiourea and Fe^{3+} -thiourea redox systems for grafting vinyl monomers onto wool fibers. We have reported the aqueous polymerization of acrylonitrile, methyl acrylate, and methyl methacrylate using V^{5+} , Cr^{6+} , Mn^{3+} , and a multitude of organic substrates [7-10]. Recently, we have also reported the aqueous polymerization of acrylonitrile and methyl methacrylate using V^{5+} -thiourea [11], Cr^{6+} -thiourea [12], and Mn^{3+} -thiourea [13] redox system. In this laboratory, there is an ambitious research program to use a redox system of nonmetal ions and thiourea to induce graft copolymerization of various vinyl monomers onto wool fibers. As a part of the preliminary investigation, this communication presents results of the studies of vinyl polymerization of methyl methacrylate initiated by the redox system acidified bromate-thiourea.

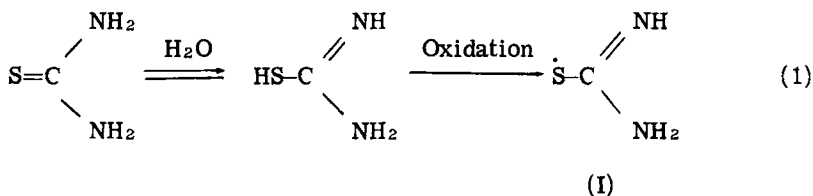
EXPERIMENTAL

Methyl methacrylate (G.R) was purified by repeated washing with 5% sodium hydroxide followed by washing with calcium chloride. Potassium bromate and thiourea were used without further purification. All reagents used were of AnalaR grade. Water distilled over alkaline permanganate and deionized by passing through a column of Biodeminrolit resin (Permutit Co., U. K.) was used to prepare all solutions. Nitrogen used for deaeration of the experimental system was purified by passing through several columns of saturated lead acetate solution and finally a wash bottle containing distilled water.

The method of polymerization study is according to our previous communications [7-10]. The polymerization was initiated with a definite amount of standard solution of bromate. Several samples were withdrawn at desired intervals and the polymerization was stopped by adding 10 ml of 1% hydroquinone solution in 2N H_2SO_4 . The precipitated polymer was filtered, washed repeatedly with water, and dried to constant weight at 60°C in a vacuum oven.

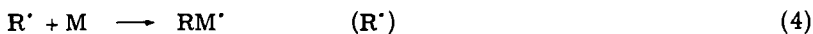
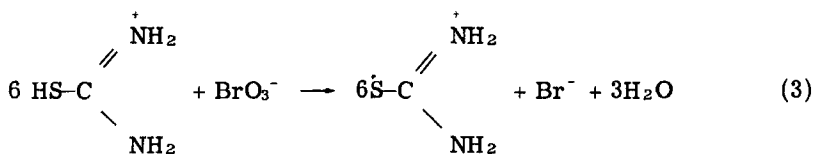
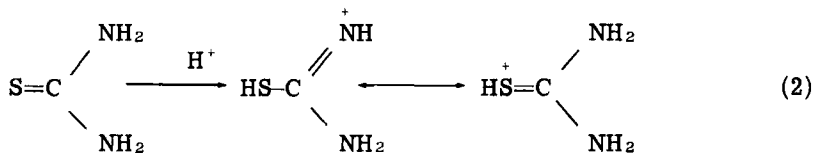
RESULTS AND DISCUSSION

Thioureas and N-substituted thioureas, although effective redox components for initiation of aqueous vinyl polymerization, do not initiate polymerization alone. In all the initiating systems containing thiourea, the redox component is isothiurea (existing in a tautomeric equilibrium with thiourea in an aqueous solution). The primary radical is formed by the abstraction of the reactive hydrogen atom attached to the sulfur atom in isothiurea, generating the amidinosulfenyl radical (I):



Various workers [14] have reported that among all the redox systems containing thiourea, the acidified bromate has the advantages over others that most of the water soluble monomers can be polymerized by it and the induction period is low. The initiation of polymerization takes place by the interaction of amidinosulfenyl radical (I) with the monomer. The initiation, polymerization, and termination reactions are shown in Eqs. (2)-(7).

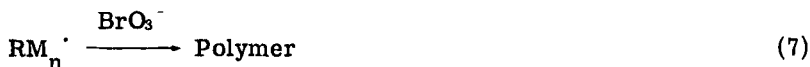
Initiation:



Propagation:



Termination:



Dependence of Rate on the Activator Concentration

The rate of polymerization has been investigated by varying the concentration of thiourea (activator) and a fixed concentration of bromate (catalyst), HCl, and monomer (Fig. 1). The percentage of conversion increases with increasing concentration of thiourea in the range 5×10^{-3} - 10^{-2} M. This may be attributed to the fact that the increasing quantity of thiourea produces an increased quantity of free radicals, whereby the maximum conversion is increased. As the concentration of thiourea increases beyond 10^{-2} M, a considerable decrease in the initial rate and the maximum conversion is observed, which might be due to several reasons: (a) the presence of free radical inhibitor in thiourea which might increase with increase of thiourea content; (b) conversion of a fixed amount of thiourea to isothiurea, which actually participates in producing initiating species; (c) an increase in amount of thiourea, possibly facilitating the formation of disulfide and thus decreasing the concentration of isothiurea radical.

Dependence of Rate upon Catalyst Concentration

The percentage of conversion increases with increasing concentration of the catalyst ($KBrO_3$) (Fig. 2) at fixed concentration of thiourea, HCl, and monomer. Beyond a certain concentration of the catalyst (1.5×10^{-2} M), there is a decreasing trend in the initial rate and the maximum conversion of polymerization. This may be due to the fact that the addition of a large quantity of initiator (which affects the colloidal stability of the system) may bring about a decrease in molecular weight. Similar observations have been reported

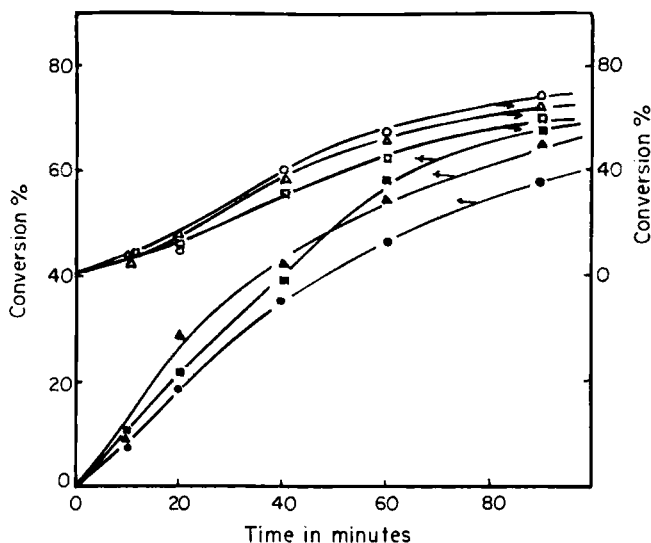


FIG. 1. Plots of percentage of conversion vs. time for aqueous polymerization of MMA-KBrO₃-TU system with various activators: (●) [TU] = 5×10^{-3} M; (▲) [TU] = 7.5×10^{-3} M; (■) [TU] = 1.0×10^{-2} M; (○) [TU] = 1.5×10^{-2} M; (□) [TU] = 2.0×10^{-2} M. [KBrO₃] = 1.5×10^{-2} M; [H⁺] = 4×10^{-2} M; [MMA] = 0.092 M; 35°C.

by Evans and co-workers [15] for the polymerization of methyl methacrylate. The plot of the logarithm of the initial rate R_i (taken from the slope of the conversion curves at zero time and expressed in % conversion per minute) against the logarithm of catalyst concentration is linear, indicating a first-order reaction with respect to the catalyst and unimolecular termination of the growing chain.

Dependence of Rate on Monomer Concentration

Figure 3 shows the dependence of the rate of polymerization on the concentration of monomer. The initial rate as well as the percentage of conversion increases with increase of monomer concentration. As the concentration of monomer increases beyond 0.184 M, the percentage of conversion decreases. A similar trend has also been noted by Mark et al. [16], Chapiro [17], and by Palit and co-workers [18] for the polymerization of vinyl acetate and methyl

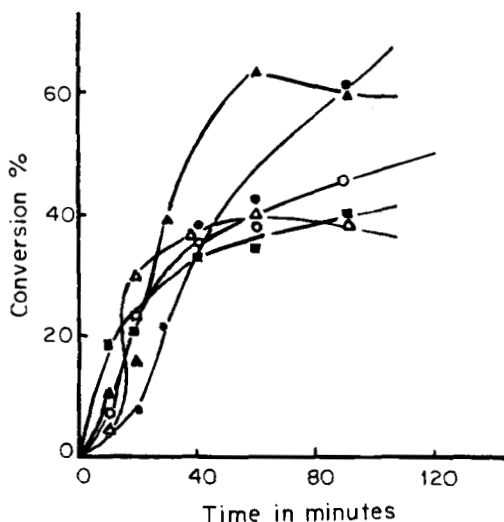


FIG. 2. Plots of percentage of conversion vs. time for aqueous polymerization of MMA-KBrO₃-TU system in the presence of different oxidants: (○) [KBrO₃] = 1 × 10⁻² M; (▲) [KBrO₃] = 1.5 × 10⁻² M; (■) [KBrO₃] = 1.8 × 10⁻² M; (◻) [KBrO₃] = 2.1 × 10⁻² M; (△) [KBrO₃] = 2.4 × 10⁻² M. [TU] = 1.0 × 10⁻¹ M; [H⁺] = 4 × 10⁻² M; [MMA] = 0.092 M; 35°C.

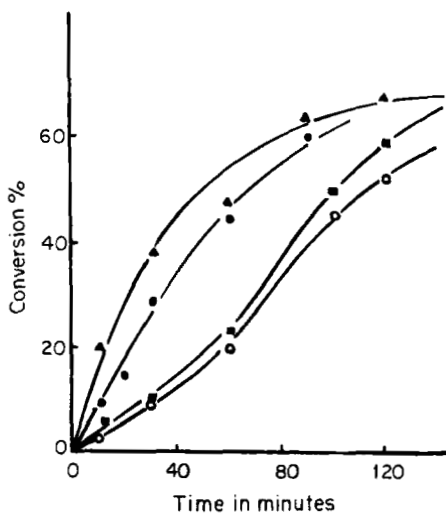


FIG. 3. Plots of percentage of conversion vs. time for aqueous polymerization of MMA-KBrO₃-TU system at various [monomer]: (●) [MMA] = 0.092 M; (▲) [MMA] = 0.138 M; (■) [MMA] = 0.184 M; (○) [MMA] = 0.276 M. [KBrO₃] = 1.5 × 10⁻² M; [H⁺] = 4 × 10⁻² M; [TU] = 1.0 × 10⁻¹ M; 35°C.

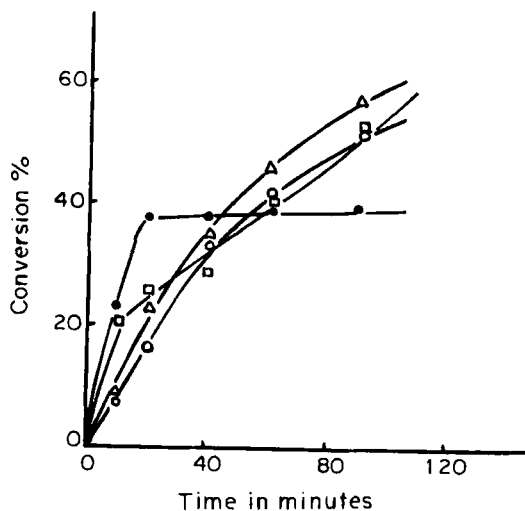


FIG. 4. Plots of percentage of conversion vs. time for aqueous polymerization of MMA-KBrO₃-TU system showing effect of temperature on rate: (○) 30°C; (△) 35°C; (□) 40°C; (●) 45°C. [KBrO₃] = 1.5×10^{-2} M; [H⁺] = 4×10^{-2} M; [MMA] = 0.092 M; [TU] = 5×10^{-3} M.

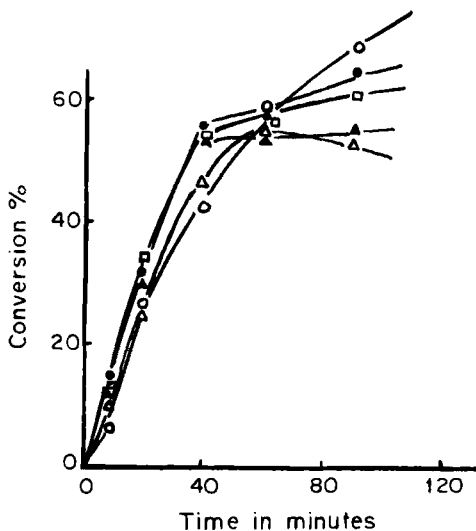


FIG. 5. Plots of percentage of conversion vs. time for aqueous polymerization of MMA-KBrO₃-TU system showing effect of water-soluble solvents on rate: (○) 5% acetone; (●) 5% methanol; (△) 5% acetic acid; (▲) 5% DMF; (■) 5% ethanol. [KBrO₃] = 1.5×10^{-2} M; [H⁺] = 4×10^{-2} M; [TU] = 10×10^{-3} M; [MMA] = 0.092 M; 35°C.

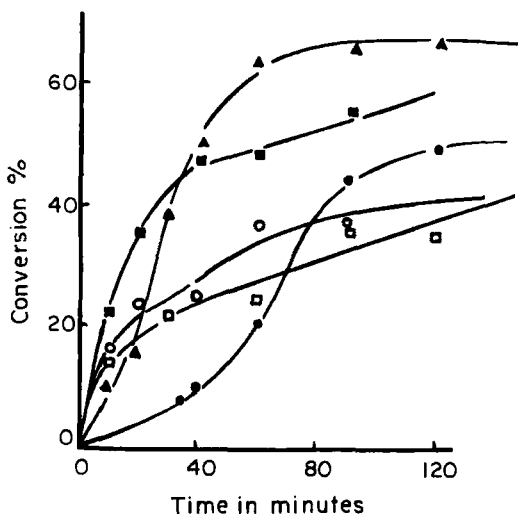


FIG. 6. Plots of percentage of conversion vs. time for aqueous polymerization of MMA-KBrO₃-TU system in the presence of acid: (•) $[H^+] = 2.5 \times 10^{-2} M$; (▲) $[H^+] = 4 \times 10^{-2} M$; (■) $[H^+] = 6.25 \times 10^{-2} M$; (○) $[H^+] = 8.75 \times 10^{-2} M$; (□) $[H^+] = 11.25 \times 10^{-2} M$. $[KBrO_3] = 1.5 \times 10^{-2} M$, $[TU] = 10^{-2} M$, $[MMA] = 0.092 M$, $35^\circ C$.

acrylate. The fall in the rate with increase in monomer concentration might be due to the gel effect, i.e., the solubility of poly(methyl methacrylate) in its own monomer, and this could be more pronounced at higher monomer concentrations. This causes hindrance in termination, particularly by coupling of the growing polymer chains.

Effect of Temperature

The effect of temperature on this system is very interesting. An increase in temperature (Fig. 4) causes an increase in initial rate of polymerization as well as maximum conversion to $35^\circ C$. However, a marked decrease in the maximum conversion is noticed beyond $40^\circ C$. This is probably due to a good portion of the initiating species being destroyed at higher temperatures by side reaction. A marked decrease in limiting conversion with increasing temperature has also been noted by Palit et al. for other redox systems [17].

Effect of Organic Solvents

The presence of small amounts (5% v/v) of water-miscible organic solvents, like methanol, ethanol, acetone, and dimethylformamide tends

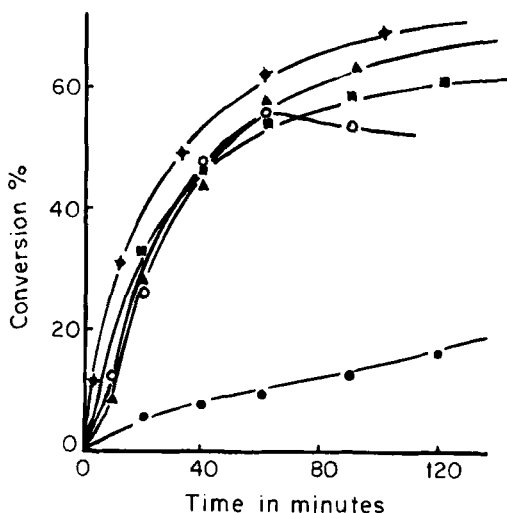


FIG. 7. Plots of percentage of conversion vs. time for aqueous polymerization of MMA-KBrO₃-TU system showing effect of different inorganic salts and complexing agents: (●) [CuSO₄] = 0.01 M; (▲) [KCl] = 0.02 M; (■) [Na₂SO₄] = 0.02 M; (○) [MnSO₄] = 0.01 M. [KBrO₃] = 1.5×10^{-2} M; [H⁺] = 4×10^{-2} M; [TU] = 1.0×10^{-2} M; [MMA] = 0.092 M; 35°C.

to depress the initial rate as well as the limiting conversion (Fig. 5). Most probably, these solvents decrease the area of shielding of a strong hydration layer in aqueous media, resulting in termination of the radical end of the growing chain. These solvents increase the regulated production of primary radicals which under the existing experimental conditions, renders the termination rate relatively fast as compared to the rate of growth of the polymer chains, as pointed out by Kern et al. [18].

Effect of Acid Concentration on Rate

The effect of HCl concentration on the rate of polymerization is represented in Fig. 6. The rate of polymerization increases with increase of HCl from 2.5×10^{-2} to 6.25×10^{-2} M and then decreases. This is because, with increase in concentration of acid, a larger amount of isothiourrea might be forming which actually participates in the initiation reaction. At higher concentration of HCl ($> 6.25 \times 10^{-2}$ M), a considerable decrease in the rate is, however, observed

due to excess of protons which might suppress the generation of the primary radical formation.

Effect of Inorganic Salts and Complexing Agents

The addition of salts such as KCl, Na₂SO₄ and Co(NO₃)₂·6H₂O brings about a decrease in the rate of polymerization (Fig. 7). This is due to the dissociation of the electrolyte with the consequent increase in the ionic strength of the medium and the premature termination of the growing polymer chains. Similar observations have been noted by Mishra et al. [19] in the case of the aqueous polymerization of acrylamide. Cobalt nitrate diminishes the rate of polymerization and the limiting conversion, because it acts as an effective chain terminator in the aqueous phase. NaF and EDTA both depress the rate of polymerization as well as the limiting conversion.

Effect of Various Monomers

Polymerization was investigated with different acrylate monomers (methyl acrylate, ethyl acrylate, and methyl methacrylate), the concentration of other reagents being kept constant. The order of reactivity, so far as percentage of conversion, is concerned is: methyl acrylate > ethyl acrylate > methyl methacrylate.

Thus as the size of the monomer is increased, the diffusion of monomer to all available sites is not possible as a result of which the percentage of conversion decreased in the case of bulkier monomers.

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