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Polymerization of Acrylamide in Aqueous Medium with Copper(II) Metabisulfite Redox Pair

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ABSTRACT

The kinetics of aqueous polymerization of acrylamide with the Cu^{2+} /metabisulfite redox system has been studied in an atmosphere of nitrogen at $35 \pm 0.2^\circ\text{C}$. The rate of polymerization has been found to be second power on monomer concentration, zero and 0.5 power with respect to catalyst, and 0.5 power with respect to activator concentration. The molecular weight of the polymer has been found to increase with the increase in the concentration of monomer. Catalyst has been found either to increase or decrease the molecular weight of the polymer formed, depending largely upon the fixed concentration of activator. The overall energy of activation has been calculated to be 24.95 kcal/deg.-mole between 35 and 50°C .

INTRODUCTION

The role of Cu^{2+} ion in various capacities has been studied for the polymerization of vinyl monomers [1-3]. It has mostly been used to promote the activity of the catalyst. In three-component systems,

it has been found to act as an oxidant and reductant. In the present investigation, Cu^{2+} has been used as an oxidant (I_1) with metabisulfite (I_2) reductant for aqueous polymerization of acrylamide.

EXPERIMENTAL

Preparation of Material

Acrylamide was crystallized twice from methyl alcohol and dried under vacuum over silica gel (mp 84.5°C). Copper sulfate and sodium metabisulfite were of B. D. H. grade. Solutions of metabisulfite were prepared afresh for the study of each effect.

Technique

The kinetic course of the polymerization reaction was followed iodometrically by the estimation of double bond of the monomer [4]. The apparatus and technique were similar to those used by Misra et al. in their earlier communications [5-7]. A variable induction period was found to occur in a few cases only.

Determination of Molecular Weight

Though the rate data were calculated on 15-30% conversion of monomer only, the samples for the determination of molecular weight were collected for more than 80% conversion. Samples in the study of catalyst effect in a few cases were collected within 10% conversion, i. e., until a steady state was reached. After reprecipitation from methanol, the samples were dried at 40°C . The intrinsic viscosity of dilute solutions in an aqueous medium was calculated from the Sing-Shulz relationship at 30°C . Finally the molecular weights of the polymers were determined by application of the equation of Dainton et al. [8]:

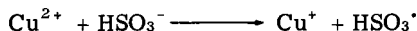
$$[\eta]_{30} = 6.8 \times 10^{-4} \bar{M}_0^{0.66}$$

where $[\eta]$ is the intrinsic viscosity of the polymer solution and \bar{M}_0 is the molecular weight.

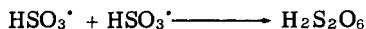
RESULTS AND DISCUSSION

Activator Dependence

The initial rate of polymerization and the limiting conversion are found to increase with the increase in the concentration of activator at a fixed concentration of acrylamide (5.0×10^{-2} mole/liter) and copper (2.0×10^{-4} mole/liter). The maximum conversion, however, decreased when the concentration of activator was raised beyond 12.0×10^{-4} mole/liter (Fig. 1). Metabisulfite alone is incapable of initiating the polymerization. Its reaction in solution is that of bisulfite ion. The polymerization of acrylamide is initiated by HSO_3^\cdot , supplied from metabisulfite by its reaction with divalent copper:



The order of the reaction calculated from the slope of the double logarithmic plot of R_p (% conversion/min.) versus the initial concentration of activator has been found to be 0.5. The decrease observed in maximum conversion after a certain concentration of activator suggests the termination of the chain by the mutual combination of active species:



Rodriguez et al. [9] also confirmed HSO_3^\cdot to be the chain initiating species for the polymerization of acrylamide with the persulfate/metabisulfite redox pair.

Catalyst Dependence

The behavior of catalyst is governed by the relative concentration of reductant. At sufficiently high concentration of activator compared to catalyst, increasing concentration of Cu^{2+} increases the initial rate of polymerization and the limiting conversion in the concentration range 2.0×10^{-4} to 8.0×10^{-4} mole/liter (Fig. 2). A further increase in the concentration of catalyst decreases both the initial rate of polymerization and the limiting conversion. The order of the reaction with respect to copper in this range is found to be 0.5. At this concentration of catalyst, HSO_3^\cdot radicals from HSO_3^- are used up in the polymerization reaction without undergoing side reactions.

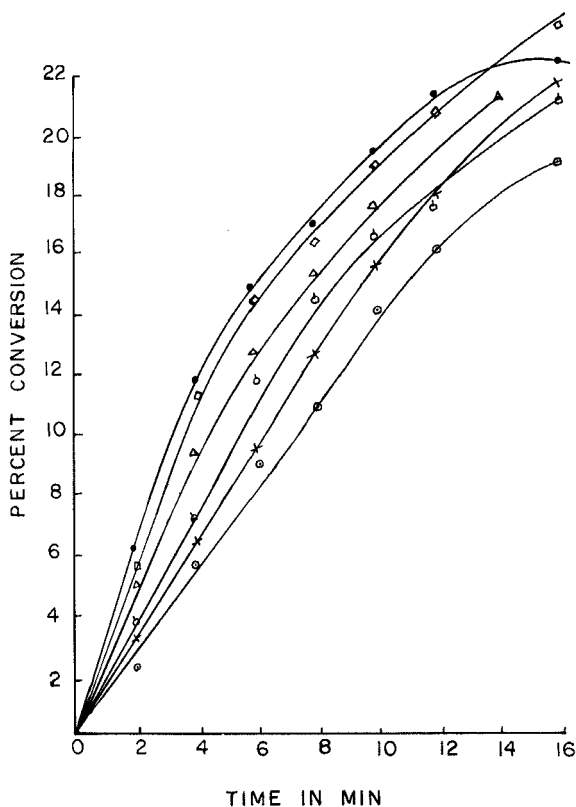


FIG. 1. Aqueous polymerization of acrylamide with $\text{Cu}^{2+}/\text{S}_2\text{O}_5^{2-}$ redox pair at fixed concentration of AAR = 5.0×10^{-2} mole/liter, and $\text{Cu}^{2+} = 2.0 \times 10^{-4}$ mole/liter with varying initial concentrations of metabisulfite (MBS): (\odot) [MBS] = 2.0×10^{-4} mole/liter; (\times) [MBS] = 4.0×10^{-4} mole/liter; (\circ) [MBS] = 6.0×10^{-4} mole/liter; (\triangle) [MBS] = 8.0×10^{-4} mole/liter; (\square) [MBS] = 12.0×10^{-4} mole/liter; (\bullet) [MBS] = 15.0×10^{-4} mole/liter.

The molecular weight of the polymer formed has also been found to increase with the increase in the concentration of Cu^{2+} in this particular range of concentration (Table 1). The plot of R_p versus $1/\bar{P}$ results in a straight line (Fig. 3).

At equivalent concentrations of activator and the catalyst, the rate of polymerization has been found to be independent of the concentration

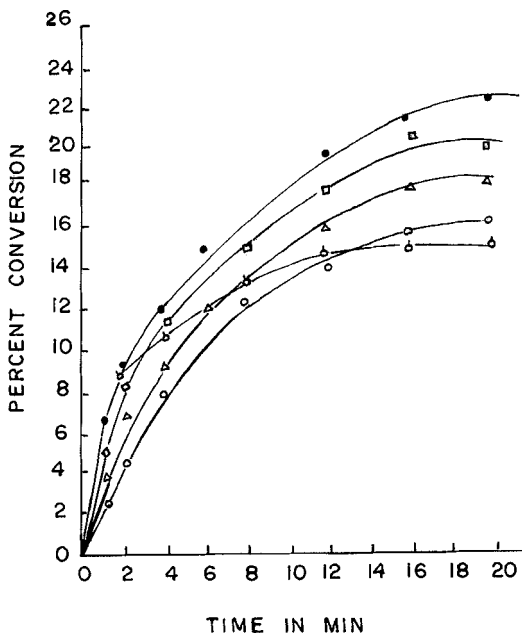
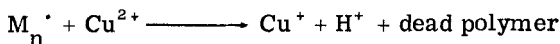


FIG. 2. Aqueous polymerization of acrylamide initiated by $\text{Cu}^{2+}/\text{S}_2\text{O}_5^{2-}$ redox pair at fixed concentrations of acrylamide = 5.0×10^{-2} mole/liter, metabisulfite = 1.0×10^{-3} mole/liter, and varying initial concentration of copper (II) at $35 \pm 0.2^\circ\text{C}$: (O) $[\text{Cu}^{2+}] = 2.0 \times 10^{-4}$ mole/liter; (Δ) $[\text{Cu}^{2+}] = 4.0 \times 10^{-4}$ mole/liter. (\square) $[\text{Cu}^{2+}] = 6.0 \times 10^{-4}$ mole/liter; (\bullet) $[\text{Cu}^{2+}] = 8.0 \times 10^{-4}$ mole/liter; (\diamond) $[\text{Cu}^{2+}] = 10.0 \times 10^{-4}$ mole/liter.

of Cu^{2+} in the concentration range 2.0×10^{-4} to 5.0×10^{-4} mole/liter. Further increase in the concentration of Cu^{2+} decreases the rate of polymerization and the limiting conversion. The molecular weight of the polymer collected after nearly the completion of polymerization reaction, decreases with the increase in the concentration of Cu^{2+} (Table 2). It appears that at higher concentrations, Cu^{2+} enters in the termination reaction by combination with polymer radical:



The propagating radical thus loses a hydrogen atom to form a dead

TABLE 1. Effect of Cu^{2+} Concentration on Viscosity-Average Molecular Weight of the Polymer at Fixed Concentrations of Acrylamide and Metabisulfite^a

Expt.	$[\text{Cu}^{2+}] \times 10^4$ (mole/liter)	R_p (%/min)	$\bar{M}_0 \times 10^{-4}$	\bar{P}	$1/\bar{P} \times 10^3$
1	2.0	7.3	2.21	311.3	3.21
2	4.0	8.35	2.42	340.8	2.93
3	6.0	8.80	2.62	369.0	2.71
4	8.0	9.52	2.84	400.0	2.50
5	10.0	8.10	1.65	232.4	4.30

^a $[\text{Acrylamide}] = 25.0 \times 10^{-2}$ mole/liter; $[\text{metabisulfite}] = 1.0 \times 10^{-3}$ mole/liter.

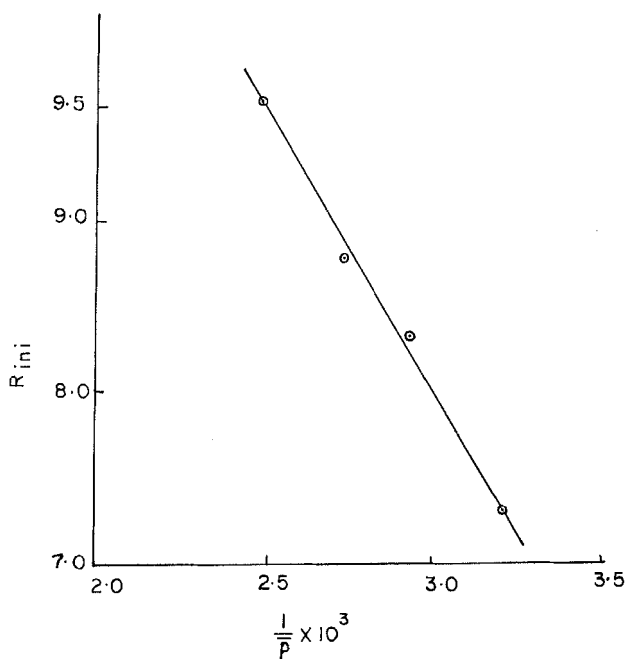


FIG. 3. Aqueous polymerization of acrylamide initiated by $\text{Cu}^{2+}/\text{S}_2\text{O}_5^{2-}$ redox system. Plot of initial rate of polymerization vs. reciprocal of degree of polymerization $1/\bar{P}$.

TABLE 2. Effect of Catalyst Concentration on Polymerization at $35 \pm 0.2^\circ\text{C}^a$

$[I_1] \times 10^4$ (mole/liter)	$\bar{M}_0 \times 10^{-4}$
2	8.77
4	8.52
6	6.28
8	6.40

^a $[M] = 0.25$ mole/liter; $[I_2] = 2.0 \times 10^{-4}$ mole/liter.

polymer with an olefinic end group. There is, however, no visual or experimental evidence of the formation of any complex with the monomer or the activator.

The high value of molecular weights observed at high conversions (Table 3) are indicative of side reactions leading to branched polymers. There is also a slight possibility of radicals being trapped due to the high viscosity of the medium. It can safely be concluded that Cu^{2+} ions act as triggers towards the production of HSO_3^\cdot initiating radicals and that Cu^{2+} is effective as an oxidant only in a very short concentration range.

Monomer Dependence

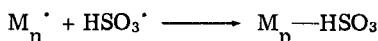
The initial rate of polymerization and the conversion are found to increase with the increase in the concentration of monomer. Monomer

TABLE 3. Effect of Monomer Concentration on Polymerization at $35 \pm 0.2^\circ\text{C}^a$

$[M]$ (mole/liter)	$\bar{M}_0 \times 10^{-4}$
0.10	4.24
0.15	4.80
0.20	6.20
0.25	8.77

^a $[I_1] = [I_2] = 2.0 \times 10^{-4}$ mole/liter.

exponent calculated from the slope of the line obtained on plotting $\log R_p$ (conversion mole/liter-min) versus $\log [M]$ has been found to be 2.01. A second-order dependence on monomer concentration $[M]^2$ is not very common in polymerization reactions. Explanation in terms of complex formation theory, cage effect or solvent transfer theory has been sought by earlier workers [10, 11]. These theories have, however, been subject to some criticism. The reason in the present case appears to be an alternative mode of termination, i. e., the termination reaction between a polymer radical and the active species,



competing [12] with the normal termination by coupling. This mode of termination, however, demands R_p to be independent of initiator concentrations [13], which has been found true in the present case. Hariharan et al. [14] and Schrijver et al. [15] have made identical observations in their study of the polymerization of acrylonitrile and styrene respectively. In both cases, however, R_p was observed to be independent of the initiator concentration.

The viscosity-average molecular weight of the polymer \bar{M}_v has been found to increase with the increase in the initial concentration of the monomer.

Rate Dependence on Temperature

The rate of polymerization was found to increase with the increase in the polymerization temperature. High temperature favors the rapid generation of primary free radicals.

The effect of temperature has been studied between 30 and 50°C. The rate was found to obey the Arrhenius equation. The energy of activation, calculated from Arrhenius plot ($\log R_p$ vs. $1/T$) was found to be 24.95 kcal/deg-mole.

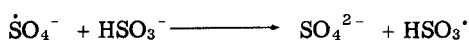
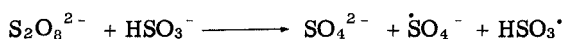
Effect of pH

The pH of the reaction medium is not altered appreciably in the course of polymerization. However, a slight decrease in pH value is observed when copper is present in higher concentrations in the reaction medium. The rate of polymerization remains unaffected in the limited pH range of 4.10 to 2.85. Further increase in the initial value of pH depresses the rate of polymerization.

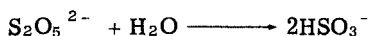
Effect of Addition of Persulfate

Metal ions greatly accelerate the rate of polymerization of vinyl monomers initiated by redox pairs. The effect of the addition of Fe^{2+} ion, in one such system consisting of $\text{S}_2\text{O}_8^{2-}/\text{S}_2\text{O}_5^{2-}$ has been studied by Rodriguez and Givey [9]. In the present system, therefore, the effect of the addition of persulfate was studied.

The initial rate of polymerization remains unaltered by the addition of a small amount of persulfate, but the steady-state period was greatly enhanced. The limiting conversion also increased to a greater extent. Further addition of either persulfate or metal ion Cu^{2+} was found to increase both the initial rate of polymerization and the limiting conversion. Cu^{2+} ions, it appears first react with metabisulfite to produce the HSO_3^\cdot chain initiating species. $\text{S}_2\text{O}_8^{2-}$ then, by its reaction with HSO_3^- , maintains the supply of active species:

Mechanism

The reaction of metabisulfite in aqueous solution is found to follow the equation:



Experimental observations clearly indicate a chain mechanism involving HSO_3^\cdot active species. Reactions (1)-(7) describe the overall mechanism.



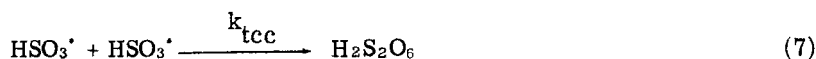
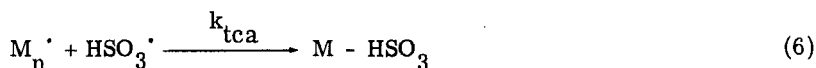
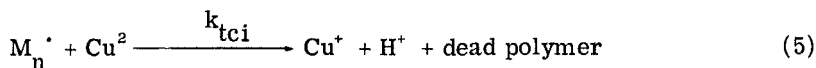
Initiation:



Propagation:



Terminations:



The polymerization reaction proceeds in the same manner as in other vinyl polymerization reactions in the initiation and propagation steps. The termination takes place by normal coupling of polymer radicals when the concentration of catalyst is sufficiently less than that of the activator. At higher concentrations of copper, step (5) competes with step (4) and possibly represents main termination step. At equal concentrations of catalyst and activator, termination takes place equally well by steps (5) and (6). At higher concentrations of activator, the possibility of chain termination by the mutual combination of active species [step (7)] cannot be ruled out.

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