KINETIC INVESTIGATION ON AQUEOUS POLYMERIZATION OF ACRYLONITRILE: BrO_3^-/CYCLOHEXANONE REDOX SYSTEM

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: الخلاصة

يدرس البحث بلمرة الأكرايلونيترات في وسط محلول مائي باستعمال مبدء يتكون من بروميت —
سيكلوهكسانون كنظام تأكسد واختزال في محلول مخفف من حامض الكبريتيك . ثم يناقش تأثير تركيز المواد المتفاعلة
على معدل سرعة البلمرة ونسبة التحول ، وقد أدت هذه الدراسات إلى إمكانية التوصل إلى صيغة معينة تصف
معدل سرعة البلمرة بالإعتماد على تركيبة التفاعل المحتملة .
كذلك قدمت دراسة عن تأثير درجة الحرارة والمذاب والأملاح المتعادلة على معدل سرعة البلمرة .

ABSTRACT

The aqueous polymerization of acrylonitrile (AN) initiated by the bromate–cyclohexanone redox system in dilute sulfuric acid has been investigated. The effects of reactant concentrations on the rate of polymerization and percentage conversion have been studied and a rate expression based on a possible mechanism was derived. The effects of temperature, solvents and some neutral salts on the rate of polymerization have also been reported.

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INTRODUCTION

During the last few years, the use of metal ions as redox components for initiation of aqueous vinyl polymerization has been investigated [1–5]. Few studies have been reported on the initiation of vinyl polymerization by non-metal ions. Mishra and others [6] reported aqueous polymerization of methacrylamide initiated by acidifed bromate–thiourea redox system. Recently, aqueous polymerization of methyl methacrylate by the bromate–thiourea redox system has been reported [7]. In this laboratory, there is a programme to use redox systems, consisting of bromate and organic substrates, in order to induce graft copolymerization of various vinyl monomers onto modified jute fibres. As a part of the investigation, this communication presents results of studies on polymerization of acrylonitrile initiated by a redox system consisting of acidified bromate and cyclohexanone.

EXPERIMENTAL

Materials

Acrylonitrile (AN) was washed with 5% NaOH and 3% orthophosphoric acid followed by repeated washing with conductivity water, dried over calcium chloride, and finally stored in refrigerator for use. Potassium bromate (AnalaR), cyclohexanone (AnalaR), and sulfuric acid (18M, AnalaR, BDH) were used without further purification.

Polymerization

Required amounts of monomer (M), sulfuric acid and cyclohexanone were mixed in the reaction vessel (Pyrex vessel fitted with $B_{24/29}$ socket carrying a $B_{24/29}$ cone with inlet and outlet tubes) and thermostated at the desired temperature. A required amount of bromate solution was added. After a specified time, the polymerization was arrested by adding an excess of ferrous ammonium sulfate solution. The polymer formed was filtered,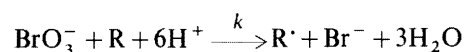 washed repeatedly with conductivity water and dried to constant weight. The percentage of conversion was calculated by using the following formula:

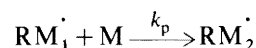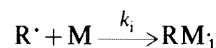$$\% \text{ conversion} = \frac{\text{Wt. of polymer}}{\text{Wt. of monomer}} \times 100$$

The rate of polymerization was calculated from the slope of the plot of yield versus time.

In the aqueous polymerization of AN by BrO_3^-/cyclohexanone initiation system, it is proposed that the acidified bromate reacts with cyclohexanone (R) to form a primary radical, which initiates the polymerization reaction of the monomer. The following mechanism may be suggested to explain our experimental findings.
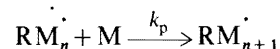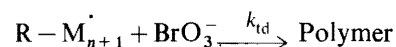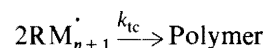
(a) *Radical Formation:*

$$BrO_3^- + R + 6H^+ \xrightarrow{\ k\ } R^{\cdot} + Br^- + 3H_2O$$

(b) *Initiation and Propagation:*

$$R^{\cdot} + M \xrightarrow{\ k_i\ } RM_1^{\cdot}$$

$$RM_1^{\cdot} + M \xrightarrow{\ k_p\ } RM_2^{\cdot}$$

$$\vdots$$

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

(c) *Termination:*

(i) By disproportionation:

$$R - M_{n+1}^{\cdot} + BrO_3^- \xrightarrow{\ k_{td}\ } \text{Polymer}$$

(ii) By combination:

$$2RM_{n+1}^{\cdot} \xrightarrow{\ k_{tc}\ } \text{Polymer}$$

(d) *Oxidation:*

$$R^{\cdot} + BrO_3^- \xrightarrow{\ k_0\ } \text{Oxidation product}$$
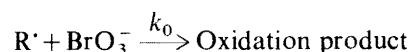
Applying the steady state principle to the primary radical $R^{\cdot}$ as well as the growing radical $RM_n^{\cdot}$ and making the usual assumption, that the radical reactivity is independent of radical size, we arrive at the following rate expressions:

(i) Termination by disproportionation:

$$R_p = \frac{k_p[M]^2}{k_{td}}\left(\frac{k[R]}{[M]+\frac{k_0}{k_i}[BrO_3^-]}\right) \quad (1)$$

(ii) Termination by combination:

$$R_p = \frac{k_p[M]^{3/2}[BrO_3^-]^{1/2}}{k_{tc}^{1/2}}\left(\frac{k[R]}{[M]+\frac{k_0}{k_i}[BrO_3^-]}\right) \quad .(2)$$

RESULTS AND DISCUSSION

Effect of Time on Percentage Conversion

Acrylonitrile was polymerized by BrO_3^- cyclohexanone initiator system both in presence and absence of nitrogen medium. A typical set of time conversion curves at 40°C has been presented in Figure 1. It was found that the percentage of polymerization in presence of nitrogen was greater than that of the atmospheric condition. It was decided, therefore, to carry out all polymerization studies in the presence of nitrogen. The limiting conversion was found to be reached in sixty minutes.

Dependence of Rate on Activator Concentration

Rate of polymerization has been investigated by varying the concentrations of cyclohexanone (activator) Figure 2. The percentage of conversion increases with increasing concentration of cyclohexanone in the range of 0.0965M (mol/liter) to 0.2892M. This may be attributed to the fact that the increasing quantity of cyclohexanone produces an increased
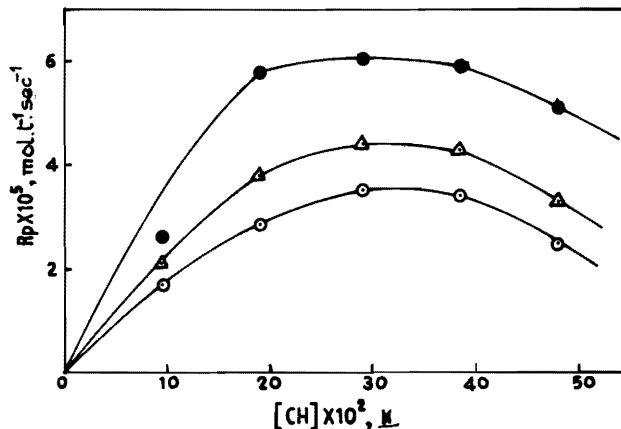

Figure 2. R_p vs[CH] Plots. $[BrO_3^-]=0.0250M$; $[M]=0.7514M$; $[H_2SO_4]=0.50M$; Time=60min, (○) Temperature=40°C; (△) Temperature=45°C, (●) Temperature=50°C

quantity of free radicals, whereby the maximum conversion is increased. As the concentration of cyclohexanone is further increased, a considerable decrease in initial rate and maximum conversion is observed. This might be due to the prevalence of primary radical termination at higher concentrations of cyclohexanone.

Dependence of Rate on Initiator Concentration

The rate of polymerization increases steadily with increasing concentration of the BrO_3^- ion (initiator) Figure 3. Beyond certain concentration of initiator $(3.25 \times 10^{-2}M)$ there is decreasing trend in the initial rate and maximum conversion of polymerization. In the increasing portion obviously it is expected that the mutual termination is more effective than the linear one. At the higher concentration of the initiator, which
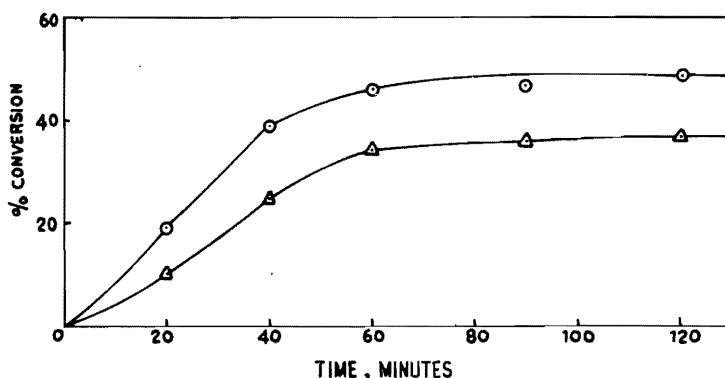

Figure 1. Time Conversion Curves. $[BrO_3^-]=0.0250M$; $[CH]=0.2414M$; $[M]=0.7514M$; $[H_2SO_4]=0.50M$; Temperature=40°C; (○) N_2 Medium; (△) Atmospheric Medium
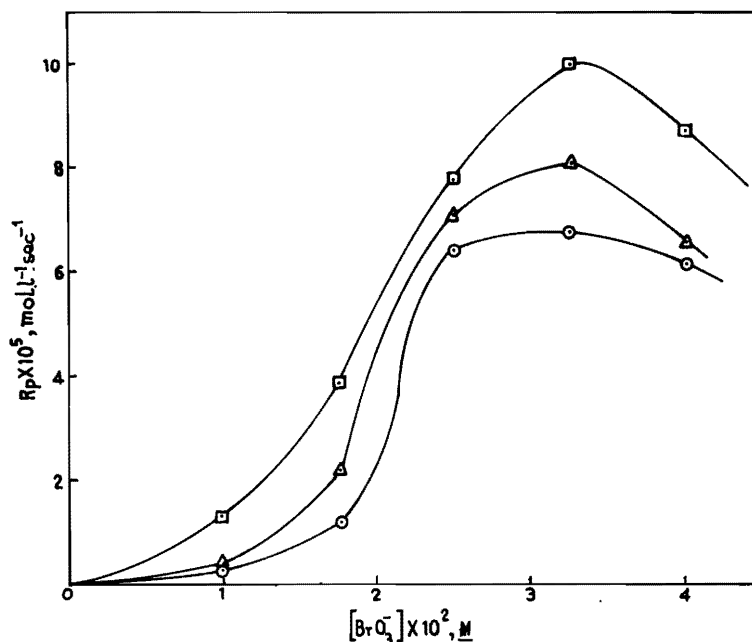
Figure 3.   Plots of R_p vs. $[BrO_3^-]$: $[CH] = 0.2414M$; $[M] = 0.7514M$; $[H_2SO_4] = 0.50M$; Time = 60 min, (○) Temperature = 40°C; (△) Temperature 45°C., (□) Temperature = 50°C

affects the colloidal stability of the system, there is a decrease in the molecular weight. Certainly, at this point BrO_3^- takes part in the linear termination. Similar observations have been reported by Evans and his coworkers [8] for the polymerization of methyl methacrylate (MMA).

Dependence of Rate on Monomer Concentration

The inital rate of polymerization as well as percentage of conversion increases with increase in monomer concentration. But the rate of increase in the value of R_p becomes less at higher concentration of

monomer (1.0519M) which may be due to the higher viscosity of the medium, thus, preventing the conversion of the monomer into the polymer. The linearity in the plots of R_p vs. $[M]^2$ for various temperatures (Figure 4) justifies the derivation of rate expression, which is based on prevalence of linear type of termination.

Effect of Temperature

The experiments were conducted at different temperatures ranging from 40°C to 50°C. An increase in temperature causes an increase in the rate of
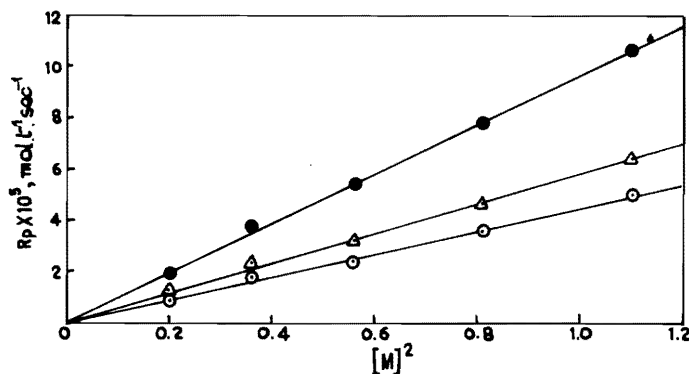

Figure 4. R_p vs. $[M]^2$ Plots. $[BrO_3^-] = 0.0250M$; $[H_2SO_4] = 0.50M$; $[CH] = 0.2414M$; Time = 60 min; (○) Temperature = 40°C; (△) Temperature 45°C; (●) Temperature 50°C

polymerization as well as maximum conversion. The effect of temperature has been demonstrated in Figures 2–4. The reaction is found to be strongly accelerated at 50°C. The overall energy of activation as calculated from the Arrhenius plot (Figure 5) is found to be 11.28 kcal mol^{-1}.
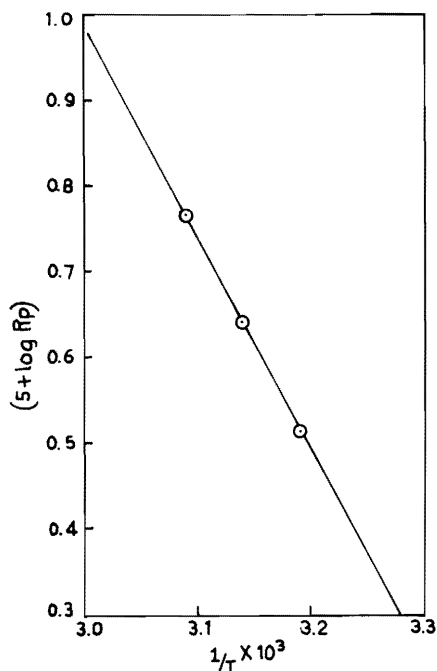
Figure 5. Arrhenius Plot of log R_p vs $1/T$ $[BrO_3^-] = 0.0250M$, $[M] = 0.7514M$, $[H_2SO_4] = 0.50M$, (○) $[CH] = 0.3863M$, Time = 60 min.

Effect of Salts and Solvents

The rate of polymerization and percentage of conversion are significantly affected by the addition of small amounts of salts (0.01M). The effect is demonstated in Table 1.

All the salts in Table 1, except sodium chloride, enhance the rate of polymerization. The decrease in the

Table 1. Effect of Salt on Percentage Conversion

Sample	Salt	% of polymer-ization	$R_p \times 10^5$ in mol $l^{-1}sec^{-1}$
1.	$CuSO_4$	30.20	6.303
2.	$MnSO_4$	25.40	5.303
3.	NaCl	9.98	2.084
4.	K_2SO_4	30.00	6.261
5.	Nil	17.55	3.663

$[BrO_3^-] = 0.0250M$; $[CH] = 0.241M$; $[AN] = 0.7514M$;
$[H_2SO_4] = 0.60M$; $[Salt] = 0.01M$ (mol/liter);   Time = 60 min;
Temperature = 40°C.

rate with sodium chloride is attributed to the ionic dissociation of the added electrolyte, which interferes with the normal polymerization process, resulting in the premature termination of the growing polymer chains. This interference is probably absent in the other salts which do not dissociate to the same extent. The effect of organic solvents when added in equal proportions (5% by volume) was investigated and found to be in the following order:

Dioxane > DMF > Control > Acetone > Methanol. The explanation of this observation is based on the polarity and dielectric properties of the different solvents.

Effect of Acid Concentration on Rate

The effect of sulfuric acid concentration on the rate of polymerization is presented in Table 2. The rates of polymerization increase with increasing acid concentration from 0.30M to 0.75M and then decrease. The increase of rate with increase in concentration of acid may be accounted for by the formation of more effective species at reasonable concentration of the acid. At higher concentration, however, a good proportion of initiating species is destroyed by side reaction.

Table 2. Effect of Acid on Percentage Conversion and Rate of Polymerization

Sample	$[H_2SO_4]$ in M	40°C		45°C		50°C	
		% Poly-meriza-tion.	$R_p \times 10^5$ in mol l^{-1} sec^{-1}	% Poly-meriza-tion.	$R_p \times 10^5$ in mol l^{-1} sec^{-1}	% Poly-meriza-tion.	$R_p \times 10^5$ in mol l^{-1} sec^{-1}
1.	0.30	9.34	1.951	10.95	2.285	15.49	3.234
2.	0.45	10.67	2.226	11.72	2.446	33.88	7.071
3.	0.60	19.07	3.980	20.36	4.249	41.29	8.617
4.	0.75	34.71	7.246	36.89	7.699	45.65	9.527
5.	0.90	31.95	6.669	33.02	6.891	38.47	8.029

$[BrO_3] = 0.0250M$; $[CH] = 0.2414M$; $[AN] = 0.7514M$; Time = 60 min.

ACKNOWLEDGMENT

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