

KINETIC STUDIES ON THE POLYMERIZATION OF ACRYLONITRILE INITIATED BY METALLIC MAGNESIUM-NITRIC ACID SYSTEM

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ABSTRACT

This article reports the polymerization kinetics of acrylonitrile initiated by metallic magnesium-nitric acid system. The rate of polymerization is independent of the amount of magnesium used; when the concentration of nitric acid is higher than acrylonitrile, the equation of polymerization kinetics may be expressed as

$$R_p = 1.91 \times 10^6 e^{-15000/RT} [\text{Mg}]^0 [\text{AN}]^{2.2} [\text{HNO}_3]^{0.46}$$

The result of copolymerization of acrylonitrile and methyl acrylate supports a free-radical mechanism.

In the studies of polymerization kinetics of acrylonitrile initiated by electrolysis, it has been found that the rate of polymerization and the molecular weight of polymer not only depend upon the electric quantity in electrolysis, but also relate closely to the amount of corrosive materials from the electrode in the polymerization medium—aqueous nitric acid solution^[1]. In order to clarify the effect of the corrosive process on the polymerization reaction, the polymerization kinetics of acrylonitrile initiated by the corrosion of metallic magnesium in aqueous nitric acid solution has been investigated.

EXPERIMENTAL

Acrylonitrile (crude product) was obtained from Jilin Chemical Company, purified with Kurokawa's method^[2]. All other reagents used were of analar grade.

Monomer and the aqueous nitric acid solution were mixed in 60 ml ground-glass stoppered bottles immersed in a thermostat. After 20 minutes, the magnesium strip was added. Polymerization was carried out without shaking and after a given time stopped by an addition of ethyl alcohol. The products were filtered with sintered glass filtering crucible, washed with 2% sodium carbonate solution and then with distilled water. Dried under vacuum at 50°C until to constant weight.

The intrinsic viscosity of the polyacrylonitrile in dimethylformamide was determined at $25.0 \pm 0.1^\circ\text{C}$ and estimated by Cheng's single point method^[3].

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_r)}}{C}$$

The number average molecular weight of the polyacrylonitrile was calculated from Onyon's equation^[4].

$$[\eta] = 3.92 \times 10^{-4} \bar{M}_n^{0.75}$$

The copolymerization of acrylonitrile and methyl acrylate was carried out as described above. The nitrogen content of the copolymers was determined by Kjeldahl method and the reactivity ratios of the monomers were calculated by Fineman-Ross's method.

RESULTS AND DISCUSSION

The polymerization of vinyl monomers initiated by the reaction of metals with acids have not been reported so far. Therefore, it is necessary to determine what type of initiating centres is in order to treat correctly the polymerization kinetics and the initiation mechanism.

As a result of this work, the reactivity ratios of acrylonitrile (AN) and methyl acrylate (MA) are 0.82 and 1.20, respectively (Fig. 1). In comparison with the values quoted from the references in Table 1, the present copolymerization process belongs to free radical in nature.

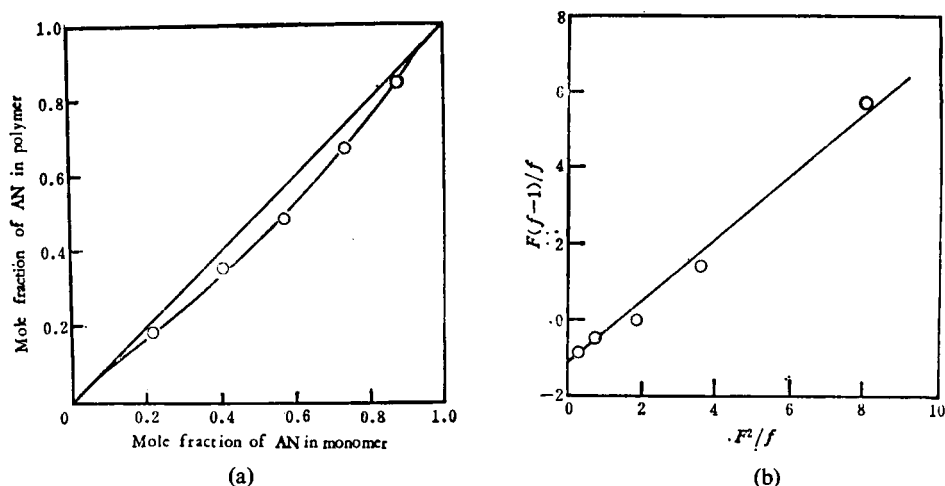


Fig. 1 Copolymerization of AN (M_1) and MA (M_2) initiated by metallic magnesium in aqueous nitric acid solution

Polymerization solution: 28.0 ml;

$[Mg] = 1.47 \times 10^{-3}$ gram-atom/l (10.0 ± 0.1 mg);

$[HNO_3] = 2.60$ mol/l; AN + MA = 3.00 ml;

Temperature: $25.0 \pm 0.5^\circ C$; time: 2hrs.

Table 1 The reactivity ratios of AN and MA in free radical copolymerization

r_{AN}	r_{MA}	References
0.84	0.83	[5]
0.70	1.07	[6]
0.67	1.26	[7]
0.86	1.25	[8]
0.82	1.20	This work

When acrylonitrile is polymerized in aqueous medium, the reaction rate depends on the concentration of initiators (Table 2).

Table 2 Free radical polymerization of acrylonitrile in aqueous solution

Equation	Temp. (°C)	E_0 (kcal / mole)	Ref.
$R = K[\text{APS}]^{1/2}[\text{AN}]^2$	45	13.3	[9]
$R = K F[\text{KPS}]^{1/2}[\text{AN}]$	60	17.5	[10]
$R = K[\text{KPS}]^{1/2}[\text{KCNS}]^{-1}[\text{AN}]^2$	45	15	[11]
$R = K \left\{ \frac{[\text{KPS}][\text{NaHSO}_3]}{k_2[\text{NaHSO}_3] + k_4[\text{KPS}]} \right\}^{1/2} [\text{AN}]^{3/2}$	30	13.0	[12]
$R = K[\text{KMnO}_4]^{0.75}[(\text{COOH})_2]^{0.5}[\text{AM}]^{1.9-2.0}$	20	9.3	[13]

On the contrary, if acrylonitrile is polymerized in aqueous nitric acid solution initiated by the reaction of nitric acid with metallic magnesium, the overall rate of polymerization does not vary essentially with the amount of magnesium used within the concentration range stated as shown in Fig. 2, whereas the number average molecular weight of polymer decreases rapidly (Fig. 3).

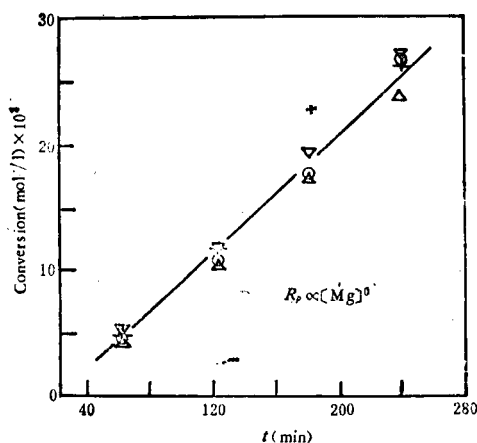


Fig. 2 Effect of amount of metallic magnesium used on the conversion of AN

Polymerization solution: 35.0 ml;

[AN] = 2.15 mol / l;

[HNO₃] = 3.43 mol / l;

[Mg]: (gram-atom / l) × 10²;

○—0.98; △—1.98; ▽—2.97; +—3.95;

Temperature: 25.0 ± 0.1°C.

It is interesting that the corrosion rate of metallic magnesium in aqueous nitric acid solution is independent of the amount, viz., the area of magnesium strip used (Table 3).

It is evident that chain radicals are formed immediately and locate in situ at the moment of magnesium reacting with nitric acid. As a result, large number of oligomers are generated

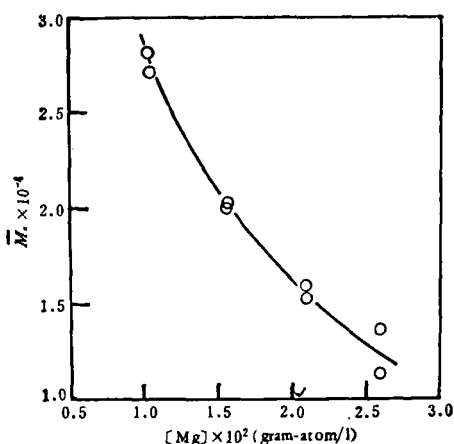


Fig. 3 Effect of amount of metallic magnesium used on the molecular weight of PAN
Conversion: $5.16 \pm 0.08\%$

Table 3 Corrosion of metallic magnesium in aqueous nitric acid solution*

Magnesium (mg)	Complete corrosion time (sec.)	H_2	
		ml in standard conditions	% (Theoretical value = 100%)
6.70	8.4	0.65	10.53
10.10	—	1.02	11.17
13.45	7.1	1.33	10.73
16.80	9.1	1.50	9.69

* $[HNO_3] = 3.43 \text{ mol/l}$; temp.: $25.0 \pm 0.1^\circ C$.

after these chain radicals have been terminated with relatively high collision frequency, and equilibrium concentration is reached within a short time. Then, the remaining radicals are added with monomers to continue the propagation by mutual diffusion.

The solubilities of acrylonitrile in aqueous nitric acid solution have been determined by the author. The results show that the increment of solubility of acrylonitrile is only affected slightly by temperature, but it changes notably with the initial concentration of nitric acid. For example, the solubility of acrylonitrile is related to the initial concentration of nitric acid at $25.0^\circ C$ as follows,

$$\log S_{AN} = 0.07624C_{[HNO_3]_0} + 1.855 \text{ (g. AN/l soln.)}$$

When the concentration of nitric acid is higher than that of acrylonitrile, the ratio of $[AN] / [NO_3^-]$ is near unity (Table 4). It is possible that the phenomenon of increase in solubility of acrylonitrile in aqueous nitric acid solution is due to the formation of the complex $AN-NO_3^-$, which has been confirmed by Cornish by means of infrared absorption spectroscopy^[14].

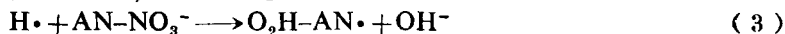
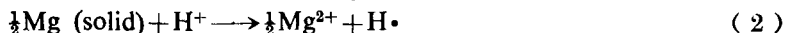
Metallic magnesium reacts with hydrogen ion to generate atomic hydrogen which reacts instantaneously with the complex $AN-NO_3^-$ to give the monomeric radical $M\cdot$, polymerization is thus initiated.

Table 4 The solubility of acrylonitrile in aqueous nitric acid solution at 25.0 ± 0.1°C

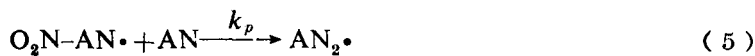
[HNO ₃] ₀ (mol / l)	Component of saturation solution			[NO ₃ ⁻]* (gram-ion / l)	[AN] / [NO ₃ ⁻] (mol / gram-ion)
	[AN]		[HNO ₃] (mol / l)		
	(g / l)	(mol / l)			
0	71.6	1.35	—	—	—
1.000	85.4	1.61	0.89	0.88	1.8
2.000	101.7	1.92	1.75	1.67	1.2
3.000	121.2	2.28	2.54	2.36	1.0
4.000	144.5	2.73	3.28	2.88	1.0
5.000	172.2	3.25	3.92	3.25	1.0
6.000	205.1	3.87	4.46	3.46	1.1

* Corrected with activity coefficient.

Chain initiation



Chain propagation



Under the study of polymerization of AN in toluene initiated by Bz₂O₂, Nakatsuka has pointed out that the chain radicals are terminated spontaneously by single-molecule process on slurry polymerization of acrylonitrile^[5]. Our experimental result shows that the dependence of molecular weight of polymer on conversion of polymerization ranging from 4 to 70 percent is a linear relation which is essentially the same as that for the process of formation of living polymers (Fig. 4).

With radical polymerization, the degree of polymerization is

$$P_n = \frac{R_p}{R_t + \sum R_{tr}} \quad (7)$$

$$\frac{1}{P_n} = \frac{k_t [\text{M}\cdot]^x + k_{trM} [\text{M}\cdot] [\text{M}] + k_{trI} [\text{M}\cdot] [\text{I}] + k_{trS} [\text{M}\cdot] [\text{S}]}{k_p [\text{M}\cdot] [\text{M}]} \quad (7a)$$

Chain radicals are terminated by combination if $x=2$



$$R_t = 2k_t [\text{M}\cdot]^2 \quad (9)$$

Eq. (7a) may be reduced as

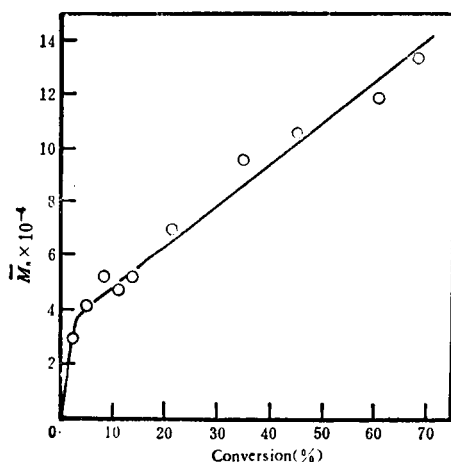


Fig. 4 Relation between conversion and molecular weight of PAN

Polymn. soln: 35.0 ml;

[AN] = 2.15 mol/l;

[HNO₃] = 3.43 mol/l;

[Mg] = 1.97×10^{-2} gram-atom/l;

Temp.: $25.0 \pm 0.1^\circ\text{C}$.

$$\frac{1}{P_n} = \frac{2k_t}{k_p^2} \frac{R_p}{[M]^2} + \frac{k_{trM}}{k_p} + \frac{k_{trI}}{k_p} \frac{[I]}{[M]} + \frac{k_{trS}}{k_p} \frac{[S]}{[M]} \quad (10)$$

In the case of $x=1$, the growth chains are terminated by single-radical process



$$R_t = k_t [M \cdot] \quad (12)$$

Substitution for Eq. (7a), thus

$$\frac{1}{P_n} = \frac{k_t}{k_p} \cdot \frac{1}{[M]} + \frac{k_{trM}}{k_p} + \frac{k_{trI}}{k_p} \cdot \frac{[I]}{[M]} + \frac{k_{trS}}{k_p} \cdot \frac{[S]}{[M]} \quad (13)$$

Let $[M] : [I] : [S] = \text{constant}$ in a series of polymerization runs, Eqs. (10) and (13) at lower conversion may be expressed as

$$\frac{1}{P_n} = \frac{2k_t}{k_p^2} \cdot \frac{R_p}{[M]^2} + K_1 \quad (14)$$

and

$$\frac{1}{P_n} = \frac{k_t}{k_p} \cdot \frac{1}{[M]} + K_2 \quad (15)$$

respectively. Plots of $\frac{1}{P_n}$ versus $\frac{R_p}{[M]^2}$ and $\frac{1}{[M]}$ are linear parallel to abscissa and coincide with each other as shown in Fig. 5.

It is clear that $\frac{1}{P_n} = K$. Substitution for Eqs. (14) and (15), we obtain

$$\frac{k_t}{k_p^2} \cdot \frac{R_p}{[M]^2} = 0; \quad \frac{k_t}{k_p} \cdot \frac{1}{[M]} = 0$$

Since polymerization is going on with normal rate, viz., $R_p > 0$, or $k_p > 0$, it can only be true that $k_t = 0$. Under steady state condition,

$$R_i = \sum R_{tr} \quad (16)$$

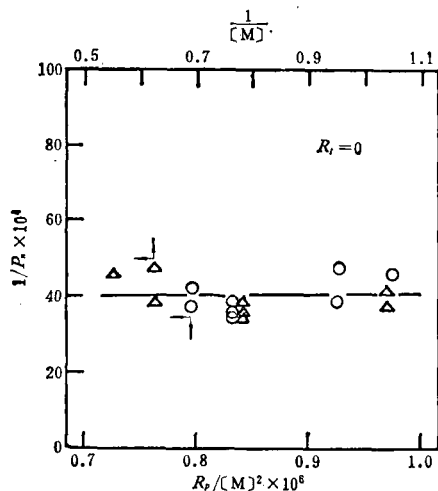


Fig. 5 Plots of $\frac{1}{P_n}$ versus $\frac{1}{[M]}$ or $\frac{R_p}{[M]^2}$

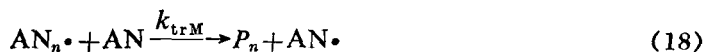
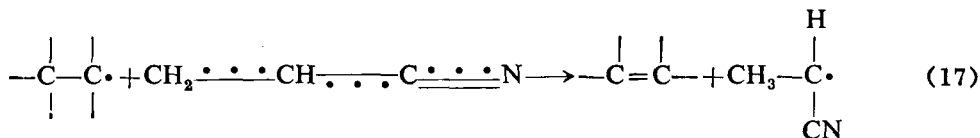
Polymer. soln.: 26.5 ml; [AN] : [HNO₃] : [Mg] = 1.0:2.24:1.63 $\times 10^{-2}$ molar ratio;
Temperature: 35.0 $\pm$ 0.1°C; conversion: 5.02 $\pm$ 0.15%;

Runs	[AN] (mole/l)	[HNO ₃] (mole/l)	[Mg] (gram-atom/l)
1	1.82	4.08	2.97×10^{-2}
2	1.60	3.58	2.61×10^{-2}
3	1.28	2.86	2.07×10^{-2}
4	0.96	2.15	1.57×10^{-2}

Because of the transfer process of chain radicals to initiator has finished before the steady-state is established, Eq. (16) may now be described as

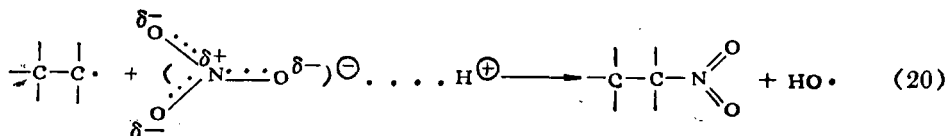
$$R_i = R_{trM} + \sum R_{trS} \quad (16a)$$

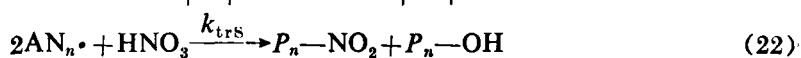
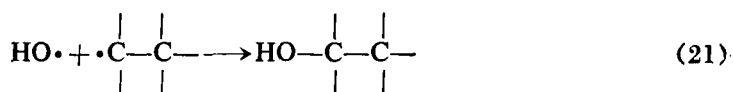
1) Chain radical transfers to monomer



$$R_{trM} = k_{trM} [AN \cdot] [AN] \quad (19)$$

2) Chain radical transfers to solvent





$$R_{\text{trs}} = \frac{1}{2} k_{\text{trs}} [\text{AN}\cdot] [\text{HNO}_3]^{\frac{1}{2}} \quad (23)$$

Substitution of Eq. (4) for Eq. (16) and then using (19) and (23), we obtain

$$[\text{AN}\cdot] = \frac{k_i [\text{Mg}]^0 [\text{AN}] [\text{HNO}_3]}{k_{\text{trM}} [\text{AN}] + \frac{1}{2} k_{\text{trs}} [\text{HNO}_3]^{1/2}} \quad (24)$$

Substitution of Eq. (24) for Eq. (6)

$$R_p = \frac{k_i k_p [\text{Mg}]^0 [\text{AN}]^2 [\text{HNO}_3]}{k_{\text{trM}} [\text{AN}] + \frac{1}{2} k_{\text{trs}} [\text{HNO}_3]^{1/2}} \quad (25)$$

The results of this work show that the reaction order of monomer is between 1.0 to 2.2 (Fig. 6) and that of nitric acid is 0.86 to 0.45 (Fig. 7). Such results are quite significant. Obviously, the reaction orders of monomer and nitric acid depend upon the transfer processes of chain radical to monomer or nitric acid under experimental conditions.

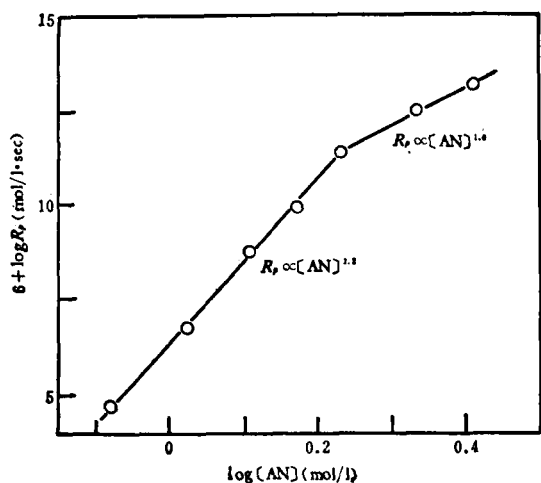
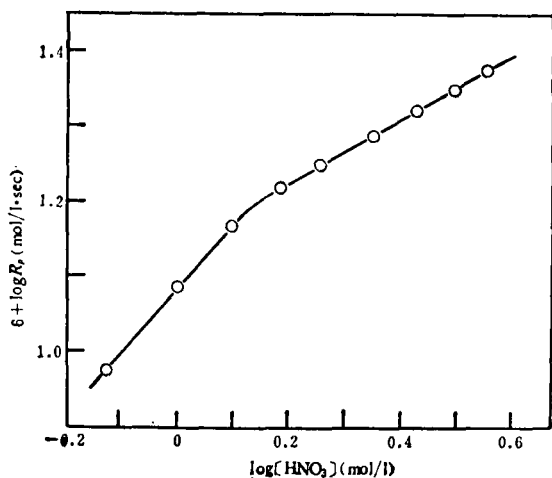


Fig. 6 Dependence of overall rate of polymerization on the concentration of monomer

Polymn. soln.: 35.0 ml;
 $[\text{HNO}_3] = 3.58 \text{ mol/l}$;
 $[\text{Mg}] = 1.97 \times 10^{-2} \text{ gram-atom/l}$;
 Temp.: $25.0 \pm 0.1^\circ\text{C}$.

Fig. 7 Dependence of overall rate of polymerization on the concentration of nitric acid

Polymn. soln.: 26.5 ml;
 $[\text{AN}] = 1.60 \text{ mol/l}$;
 $[\text{Mg}] = 2.61 \times 10^{-2} \text{ gram-atom/l}$;
 Temp.: $25.0 \pm 0.1^\circ\text{C}$.



As shown in Table 4, complexing equilibrium of 1:1 type between acrylonitrile and nitric acid exists within a finite range of concentrations. When one component is in excess, the free molecules or ions would be targets for attack by chain radicals.

1) If $[\text{HNO}_3] \leq [\text{AN}]$, then $\frac{1}{2}k_{\text{trs}}[\text{HNO}_3]^{\frac{1}{2}} \ll k_{\text{trM}}[\text{AN}]$, Eq. (25) can be written as

$$R_p = \frac{k_i \times k_p}{k_{\text{trM}}} [\text{Mg}]^0 [\text{AN}] [\text{HNO}_3] \quad (26)$$

2) When $[\text{HNO}_3] > [\text{AN}]$, the term $\frac{1}{2}k_{\text{trs}}[\text{HNO}_3]^{\frac{1}{2}} \gg k_{\text{trM}}[\text{AN}]$ may be obtained, the overall rate of polymerization is then

$$R_p = \frac{2k_i \times k_p}{k_{\text{trs}}} [\text{Mg}]^0 [\text{AN}]^2 [\text{HNO}_3]^{\frac{1}{2}} \quad (27)$$

Practically, the component ratio is so controlled such that $[\text{HNO}_3] > [\text{AN}]$ to keep the polymerization proceeds in homogeneous medium. Under this condition, the value of C_M determined is zero (Fig. 8), the overall rate of polymerization based on the experimental values above (see Figs. 6 and 7) is

$$R_p = K[\text{Mg}]^0 [\text{AN}]^{2.2} [\text{HNO}_3]^{0.45} \quad (28)$$

Eq. (27) is found to be in agreement with Eq. (28).

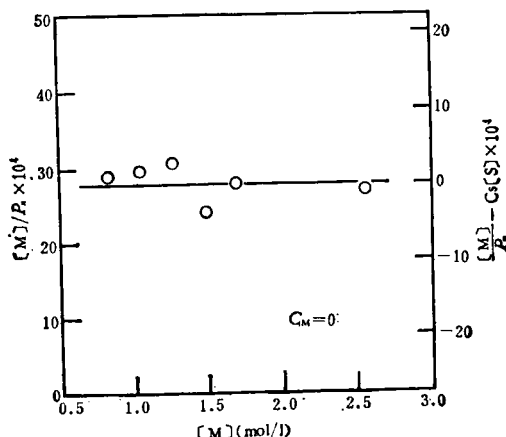


Fig. 8 Chain radicals transfer to monomer

Conversion: $8.0 \pm 0.1\%$;

$[\text{AN}] / [\text{HNO}_3] = 0.22 - 0.77$ molar ratio.

(Other conditions of this polymerization reaction are the same as in Fig. 6)

If the concentrations of monomer and nitric acid as well as the amount of metallic magnesium used are changed in such a way to keep the proportion $[\text{M}]:[\text{I}]:[\text{S}] = \text{constant}$ under the case of $[\text{HNO}_3] > [\text{AN}]$, the overall rate of polymerization R_p against $[\text{Mg}]^0 [\text{AN}]^{2.2} [\text{HNO}_3]^{0.45}$ plotted in Fig. 9 is a straight line, the slope $k = 4.4 \times 10^{-6} / \text{sec}$. Substitution for Eq. (28)

$$R_p = 4.4 \times 10^{-6} [\text{Mg}]^0 [\text{AN}]^{2.2} [\text{HNO}_3]^{0.45} \quad (29)$$

From the Arrhenius plots (Fig. 10) we obtain the apparent activation energy $E_0 = 15.0$ kcal/mol. It is quite close to the values of apparent activation energy of acrylonitrile poly-

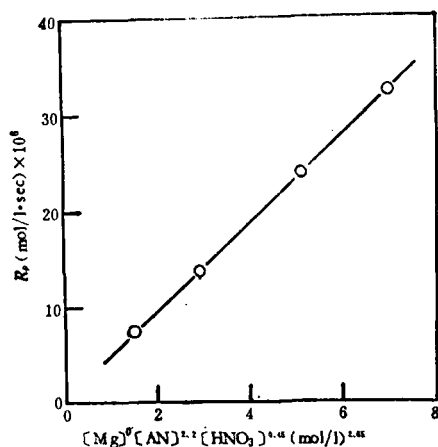


Fig. 9 Effect of polymerization conditions on the overall rate of polymerization of acrylonitrile (polymerization conditions are the same as in Fig. 5)

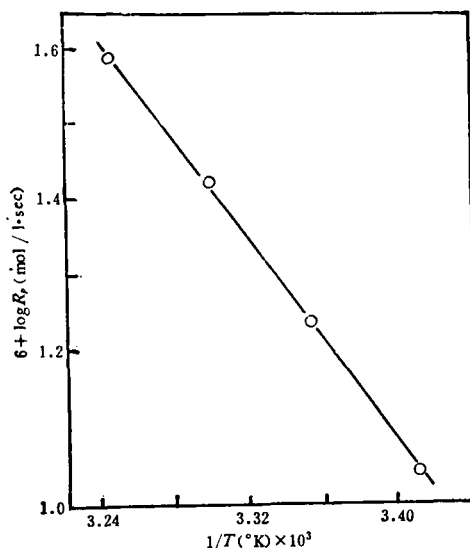


Fig. 10 Effect of temperature on the overall rate of polymerization of acrylonitrile
Polymn. soln.: 35.0 ml;
[AN] = 2.15 mol/l;
[HNO₃] = 3.43 mol/l;
[Mg] = 1.97×10^{-2} gram-atom/l.

merized by free radical mechanism in aqueous solution which are quoted in Table 2. Substitution of this value into Eq. (29), the overall rate equation of polymerization can be expressed as

$$R_p = 1.91 \times 10^5 e^{-15,000/RT} [\text{Mg}]^0 [\text{AN}]^{2.2} [\text{HNO}_3]^{0.45} \quad (30)$$

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