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Polymerization of Acrylonitrile—Metal Halides Complexes in the Frozen State. I. Radiation-Induced Polymerization of Acrylonitrile—Zinc Chloride Complex in the Frozen State

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ABSTRACT

The radiation-induced polymerization of acrylonitrile in frozen aqueous zinc chloride solution was carried out at low temperatures. A marked enhancement both in the rate and the degree of polymerization was observed at zinc chloride/acrylonitrile molar ratios above unity, which indicated the importance of formation and stabilization of complexes in the frozen medium. The rate of polymerization R was found to follow the relation, $R \propto [M\text{-}ZnCl_2]^2 I$, where I is the dose rate and $[M\text{-}ZnCl_2]$ is the concentration of zinc chloride complexed with equimolecular monomer. It is considered that the role of zinc chloride is here dual, both as a reagent for complex formation and also as a source of initiating species on irradiation. The effect of coexisting saturated nitriles were also discussed.

INTRODUCTION

Since Bamford and his colleagues [1] first observed an accelerating effect of lithium chloride on the radical polymerization of acrylonitrile in N,N-dimethylformamide solution, a number of papers [2-8] on the polymerization of polar monomers by radical initiators in the presence of metal salts have appeared. The presence of metal salts affects the rate of polymerization and the stereospecificity as well. The enhancement in monomer reactivity was interpreted in terms of formation of complexes of monomers with metal cations [2-5, 9-12] or formation of complexes of growing radicals with monomer molecules through metal cations [13, 14].

A few studies [15-17] are also concerned with the radiation-induced polymerization in the presence of metal salts. Most of those investigations, however, are not sufficiently detailed to clarify the kinetic aspect of the polymerization.

On the other hand, we have reported the radiation-induced polymerization of acrylonitrile-urea canal complex in the frozen solvents [18], where stabilization of canal complexes was observed in frozen medium. It would therefore be of interest to examine the radiation-induced polymerization of monomers in frozen metal halide solutions from the viewpoint of the formation and stabilization of complexes in frozen media.

In the present paper the radiation-induced polymerization of acrylonitrile in frozen aqueous metal chloride solutions was studied and its kinetic features were also discussed.

EXPERIMENTAL

Materials

Acrylonitrile (AN) was purified by washing successively with 5% aqueous solutions of sodium hydroxide, phosphoric acid, and pure water, followed by drying over potassium carbonate. It was then fractionally distilled. Metal chlorides of reagent grade were not subjected to further purification.

Polymerizing Procedure

A glass ampoule containing 20 ml of an aqueous AN–metal chloride solution was sealed off under reduced pressure ($< 10^{-4}$ Torr) or in air. Generally, an AN concentration of 0.47 mole/liter and an equimolecular concentration of the metal chloride were used. The ampoule was cooled and irradiated at -78° C by using the Cobalt-60 irradiation facility of the Research Reactor Institute, Kyoto University. Polymers were washed with a methanol-water mixture containing hydrochloric acid and then with methanol. Purification was completed by repeated dissolution of polymers in N,N-dimethylformamide, followed by precipitation in methanol.

Viscosity Measurement

The determination of molecular weight was made by the viscosity measurement of polymer solutions in N,N-dimethylformamide at 25° C with an Ubbelohde dilution viscometer. The molecular weight was estimated through the equation proposed by Cleland and Stockmayer [19]:

$$[\eta] = 2.43 \times 10^{-4}\ \overline{M}_v^{\,0.75}$$

RESULTS

Type of Metal Chloride

The rates of polymerization of AN in frozen aqueous solutions containing various kinds of metal chlorides in air are summarized in Table 1. Among the chlorides examined, zinc chloride, stannic chloride, nickel (II) chloride, and stannous chloride markedly enhanced the rate of polymerization, while polymerization hardly occurred under the same conditions in the absence of metal chlorides. Cadmium chloride, magnesium chloride, manganese (II) chloride, aluminum chloride, and cobalt (II) chloride showed a moderate enhancing effect.

On the other hand no polymerization occurred in the presence of chromium (II) chloride, ferrous and ferric chlorides, and cupric chloride. These metal chlorides are known to have an inhibiting effect on radical polymerization [20-24].

Temperature

The polymerization of AN in frozen aqueous zinc chloride solution was carried out under reduced pressure. The results are shown in

TABLE 1. Effect of Metal Chlorides on the Polymerization of Acrylonitrile in the Frozen State[a]

Metal chloride	Conversion (%)	Metal chloride	Conversion (%)	Metal chloride	Conversion (%)
$ZnCl_2$	98.0	$CdCl_2$	11.5	$CrCl_2$	0
$SnCl_4$	97.6	$MgCl_2$	10.8	$FeCl_2$	0
$NiCl_2$	87.4	$MnCl_2$	10.7	$FeCl_3$	0
$SnCl_2$	60.6	$AlCl_3$	2.8	$CuCl_2$	0
		$CoCl_2$	2.4	None	0

[a] Frozen aqueous solution with a metal chloride/acrylonitrile molar ratio of unity was irradiated at -78° C in air for 10 hr at 3.44×10^4 r/hr. The monomer concentration was kept constant at 0.47 mole/liter.

Figs. 1 and 2. Figure 2 shows the dependence of the rate and the degree of polymerization on temperature. The linear decrease of the rate with decreasing temperature in the first region ends at around -30° C and is followed by an increase in the rate with further decreasing temperature to about -78° C. Below -78° C the rate again decreases. The degree of polymerization shows little change down to -63° C, having higher values below -78° C.

The fact that higher rates and the degrees of polymerization are obtained at -78° C than at -30° C suggests favored formation and stabilization of the complex of AN with zinc chloride at the lower temperature.

Zinc Chloride Concentration

AN was polymerized at a constant monomer concentration of 0.47 mole/liter in frozen aqueous solutions containing various amounts of zinc chloride at -78° C under reduced pressure. The enhancing effect on the rate of polymerization of addition of zinc chloride was obvious at molar ratios $\gamma = [ZnCl_2]/[AN]$ above unity, although the enhancement was small and complex below unity, as shown in Fig. 3. This is also clearly shown in Fig. 4; the rate of polymerization was observed to be linear with zinc chloride concentration at above 0.47 mole/liter, corresponding to $\gamma = 1$.

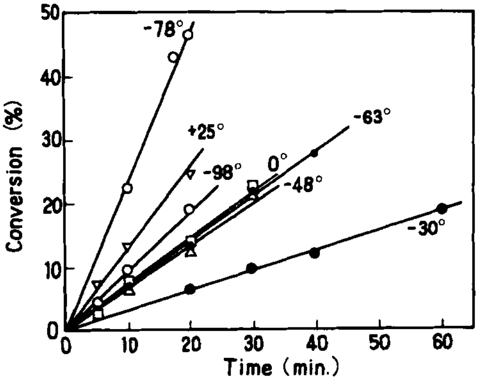

FIG. 1. Time-conversion curves at various temperatures. [AN] = [$ZnCl_2$] = 0.47 mole/liter; dose rate = 3.67×10^4 r/hr, at reduced pressure.

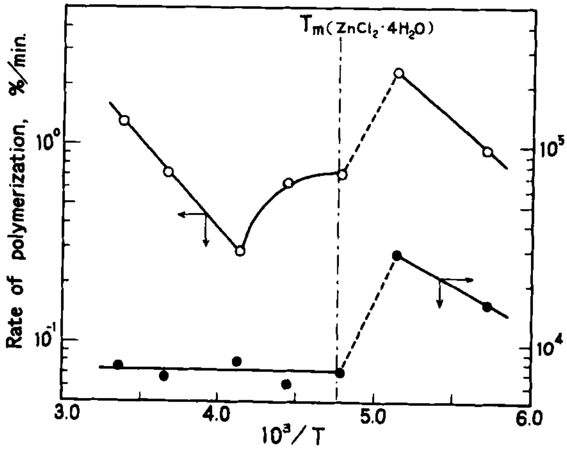

FIG. 2. Temperature dependence of (○) the rate and (●) the degree of polymerization. [AN] = [$ZnCl_2$] = 0.47 mole/liter; dose rate = 3.67×10^4 r/hr.

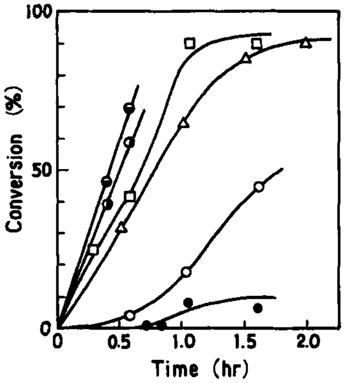

FIG. 3. Time-conversion curves for polymerization of acrylonitrile in frozen aqueous zinc chloride solution at various zinc chloride/monomer molar ratios at -78° C and 1.75×10^4 r/hr at reduced pressure: (●) γ = $[ZnCl_2]/[AN]$ = 0.3, (○) γ = 0.5; (△) γ = 1.0; (□) γ = 2.0; (◑) γ = 3.0; (⊖) γ = 4.0.

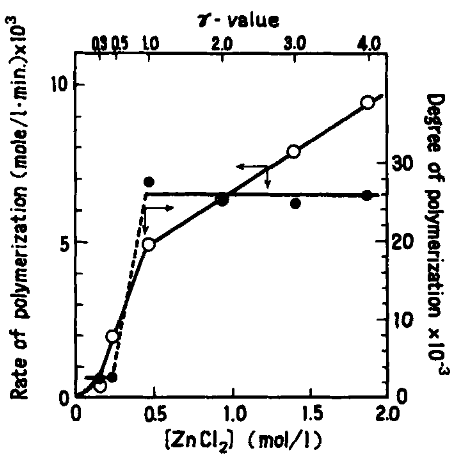

FIG. 4. Plots of (○) the rates and (●) the degrees of polymerization at a constant monomer concentration of 0.47 mole/liter as a function of the zinc chloride concentration. Irradiated at -78° C and 1.75×10^4 r/hr under reduced pressure.

TABLE 2. Effect of Zinc Chloride Concentration on Polymerization of Acrylonitrile in the Frozen State at -78° C under Reduced Pressure

$[ZnCl_2]$ (mole/liter)	$\gamma = [ZnCl_2]/[AN]$ [a]	Irradiation time (hr)[b]	Conversion (%)	Degree of polymerization	Initial rate × 10^3 (mole/liter-min.)
0.15_7	0.33	0.85	0.34	–	0.390
		1.04	8.2	–	
		1.61	6.0	2.62×10^3	
0.23_5	0.50	0.58	3.8	1.87×10^3	1.96
		1.04	18.0	2.70×10^3	
		1.61	45.5	–	
0.47	1.0	0.52	31.9	2.75×10^4	4.94
		1.00	65.1	2.66×10^4	
		1.50	86.1	2.82×10^4	
		2.01	90.4	2.74×10^4	
		4.00	96.0	2.85×10^4	
0.94	2.0	0.29	24.7	2.59×10^4	6.35
		0.58	41.3	2.50×10^4	
		1.04	90.4	–	
		1.61	89.7	–	
1.41	3.0	0.42	39.5	2.56×10^4	7.85
		0.58	58.5	2.45×10^4	
1.88	4.0	0.42	46.2	2.62×10^4	9.40
		0.58	70.0	2.60×10^4	

[a] [AN], 0.47 mole/liter.
[b] Dose rate, 1.75×10^4 r/hr.

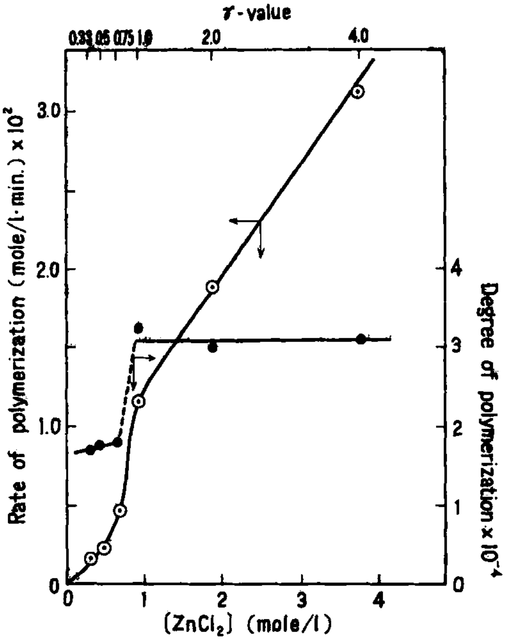

FIG. 5. Plots of (⊙) the rates and (●) the degrees of polymerization at a constant monomer concentration of 0.94 mole/liter as a function of the zinc chloride concentration. Irradiated at -78° C and 1.75 × 10^4 r/hr under reduced pressure.

The degrees of polymerization were also drastically changed above and below $\gamma = 1$, as seen in Fig. 4 and Table 2. The degrees of polymerization in the γ values above unity were quite high, around 2.5 × 10^4. Similar results were also obtained at a monomer concentration of 0.94 mole/liter, as seen in Fig. 5. These facts show that complex formation between AN and zinc chloride becomes effective for the polymerization only at γ values > 1.

A linear relation between the rate of polymerization and the zinc chloride (or monomer) concentration in logarithmic scale was obtained under the condition of a constant γ value of unity, as shown in Fig. 6. Here the exponent of the zinc chloride concentration was estimated to be 1.97. The result shows again the effect of complex formation on the polymerization.

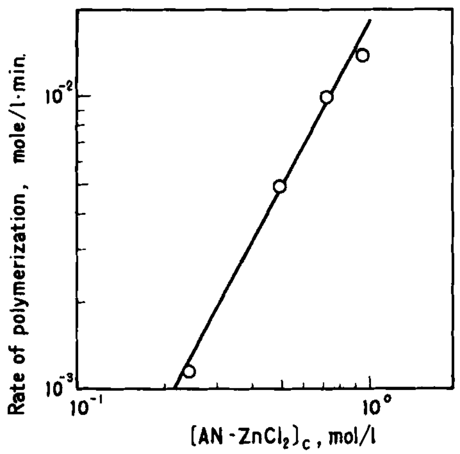

FIG. 6. Logarithmic plot of the rate of polymerization as a function of the acrylonitrile–zinc chloride (1:1) concentration. Irradiated at -78° C and 1.75 × 10^4 r/hr under reduced pressure.

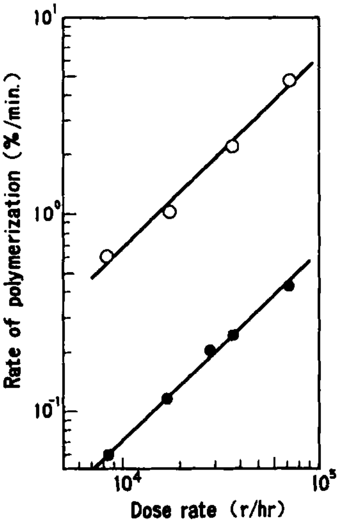

FIG. 7. Dose rate dependence of the polymerization rate of acrylonitrile in the frozen state at -78° C: (○) under reduced pressure; (●) in air. Initial rates after induction periods were adopted in air.

TABLE 3. Effect of Additives on the Polymerization of Acrylonitrile in the Frozen State at -78° C[a]

Additive	Additive concn (mole/liter)	$(R_p)_{add}/(R_p)_0$	Degree of polymerization $\times 10^{-4}$
None		1.00	2.90
Hydroquinone	2.35×10^{-2}	0.13	0.86
Benzoquinone	2.35×10^{-2}	0	–
Oxygen	Saturated	0	–

[a] [AN] = [$ZnCl_2$] = 0.47 mole/liter; dose rate = 3.67×10^4 r/hr

Dose Rate Dependence

The influence of the dose rate on the rate of polymerization was examined in the range 8.40×10^3 to 7.18×10^4 r/hr at $\gamma = 1$ and -78° C. The dose rate exponents were found to be 0.97 and 0.96 in reduced pressure and in air, respectively, as shown in Fig. 7. This suggests a unimolecular termination in these polymerizations. The degrees of polymerization were almost constant with the dose rates.

Influence of Additives

The influence of additives such as radical polymerization inhibitors were studied, and the results are summarized in Table 3. The presence of benzoquinone and saturatedly dissolved oxygen ihibited the polymerization completely. Retardation was observed in air and in the presence of hydroquinone, as seen in Fig. 8. The polymerization seems to be radical in character.

Coexisting saturated nitriles such as propionitrile (PCN, mp -91.9° C), acetonitrile (ACN, mp -45.7° C) and malononitrile (MCN, mp +31.6° C) are found to affect the rate and the degree of polymerization, as shown in Table 4. The presence of excess AN by itself (at $\gamma = 0.5$) decreases significantly both the rate and the degree of polymerization. Addition of increasing amounts of PCN at constant γ value (taken as [$ZnCl_2$]/[total nitriles]) of 0.5, decreases the rate and the degree of polymerization as well. Added PCN has more

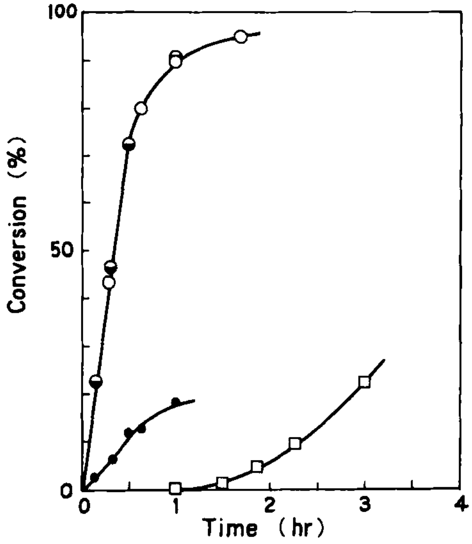

FIG. 8. Time-conversion curves for polymerization of acrylonitrile in the frozen aqueous zinc chloride solution at -78° C and at dose rate of 3.67×10^4 r/hr; (□) in air; (○) in vacuo; (◒) in N_2 ; (●) in the presence of HQ, in vacuo. [AN] = [$ZnCl_2$] = 0.47 mole/liter, [Hydroquinone] = 2.35×10^{-2} mole/liter.

effect on the degree of polymerization than on the rate. It seems that the presence of PCN and excess AN dissociates the complex to cause a decrease in the rate of polymerization. As ACN is frozen at -78° C, it is expected to have less dissociative effect. It is observed that added ACN decreases the rate and the degree of polymerization to less extent than PCN. Further, addition of MCN results in little reduction either in the rate or the degree of polymerization.

Forms of Polymers Obtained

The polymers remained after extracting the reaction mixture solution with water have a spongelike appearance with high elasticity. Observation of the polymer surface was made by scanning electron micrographs and revealed that the block of polymer has a layer structure consisting of sheets of ca. 2 μm thickness, having clearance of ca. 10 μm, as shown in Fig. 9. The layer structure changed with

TABLE 4. Effect of Coexisting Nitriles[a]

	Composition					
Nitrile	$ZnCl_2$	AN	Nitrile	$\gamma = \frac{ZnCl_2}{\text{Total nitriles}}$	$\frac{(R_p)}{(R_p)_0}$	$\overline{DP} \times 10^{-4}$
None	1.0	1.0	0	1.0	1.0	2.81
	1.0	2.0	0	0.5	0.33	1.77
PCN	1.0	1.5	0.5	0.5	0.24	1.11
	1.0	1.0	0.5	0.6_7	0.69	1.34
	1.0	1.0	1.0	0.5	0.68	1.29
	1.0	0.5	1.5	0.5	0.35	0.86
ACN	1.0	1.5	0.5	0.5	0.34	2.11
	1.0	1.0	0.5	0.6_7	0.91	2.24
	1.0	1.0	1.0	0.5	0.77	2.14
	1.0	0.5	1.5	0.5	1.06	1.70
	1.0	0	1.0	1.0	0	
MCN	1.0	1.0	0.5	0.6_7	1.02	2.69
	1.0	1.0	1.0	0.5	1.01	2.65

[a] $[ZnCl_2]$ = 0.47 mole/liter; dose rate = 1.75×10^4 r/hr; -78° C.

changing of γ values. The morphology shown here should reflect the behavior of complex formation. The complex, therefore, seems to be formed in the sheets of gaps between layers of ice.

DISCUSSION

Frozen State

Nitrile compounds are known to form σ-complexes with metal atoms in the halides. The tendency of metal chlorides to form complexes was estimated from Lewis acid strengths of metal atoms [25, 26]. No clear correlation, however, between the polymerizability and the acid strength has been reported.

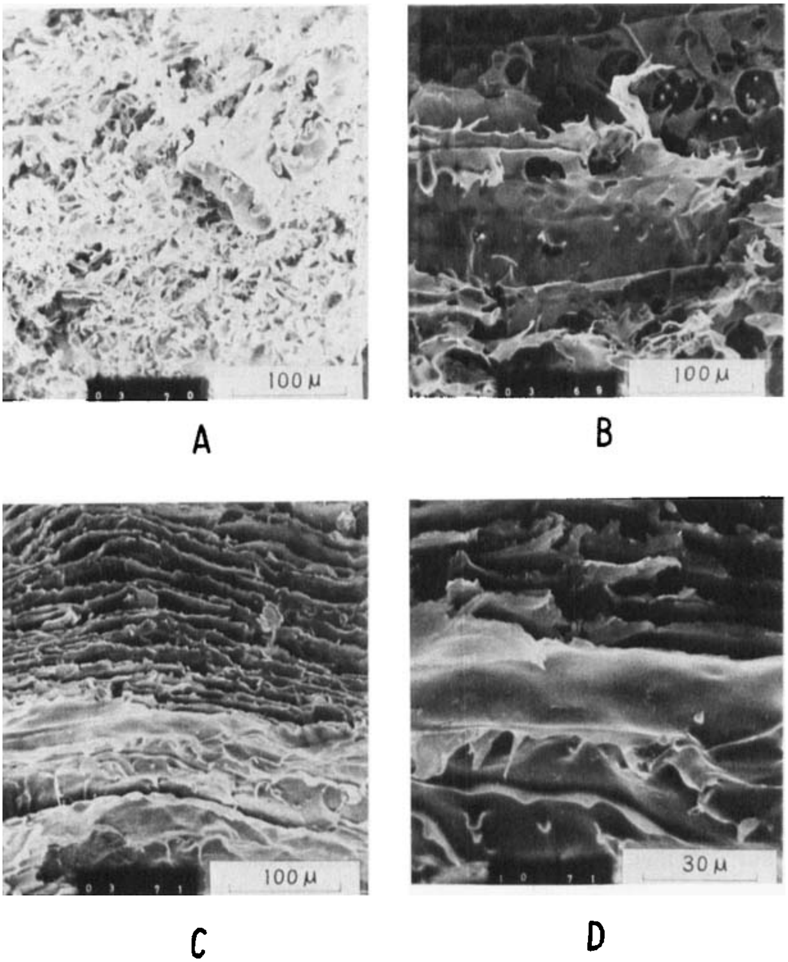

FIG. 9. Scanning electron micrographs of polymerized polyacrylonitrile prepared in frozen state at γ values of (A) 0.19; (B) 0.49; (C, D) 1.9.

The complexes seem to dissociate in polar solvents at room temperatures. In the frozen state, however, the complexes between metal chlorides and AN appear to be somehow stabilized even in an aqueous medium, since complex formation should be an exothermic reaction.

According to the phase diagram of the dilute aqueous zinc chloride solution, on cooling, ice first separates, leaving the solute concentrated.

At the zinc chloride concentration of 0.47 mole/liter, at which most polymerizations were carried out, the solution apparently freezes at about -3° C. The zinc chloride tetrahydrate, $ZnCl_2 \cdot 4H_2O$, is next frozen out in the gaps between ice at -62° C [27]. Although solution freezing temperature (-3° C) is little affected by addition of AN, the hydrated zinc chloride is believed to be modified to form hydrated zinc chloride complexes with AN, $ZnCl_2 \cdot nAN(4-n)H_2O$, the thermal behavior of which could differ from the original hydrate.

The decrease in the rate of polymerization with decreasing temperature, due to the energetic term (first region in Fig. 2), might be overcome by the enhancing effect on the rate of polymerization due to formation and stabilization of hydrated AN–$ZnCl_2$ complexes in the second region.

The marked influence of the frozen state is observed in that both the rate and the degree of polymerization are higher at -78° C than at -30° C. The degree of polymerization shows little change with conversion (Table 2).

Influence of Added Nitriles

The coexistence of PCN interferes with complex formation of AN with zinc chloride. Besides the interference with aggregation of the AN–$ZnCl_2$ complexes by the formation of a complex with PCN similar to those with AN, uncomplexed PCN might be able to dissociate the AN–$ZnCl_2$ complexes and also could act as a chain-transfer agent, which would cause a decrease in both rate and degree of polymerization.

Although a complex with ACN is also formed, from the degree of polymerization ACN has little dissociative effect because it has a higher freezing point. This is confirmed by the case of MCN with the highest freezing point among nitriles used, where no effect was observed in the polymerization.

In the frozen state, the aggregation of AN–$ZnCl_2$ complexes seems to be one of the factors in changing the rate and the degree of polymerization.

MECHANISM

Case A: $\gamma < 1$

The degree of polymerization is lower in cases of $\gamma < 1$ than in cases of $\gamma \geq 1$. It is considered that only complexed monomers could polymerize efficiently, and excess monomer seems to decrease both the rate and the degree of polymerization due to chain transfer to the excess monomers uncomplexed with zinc chloride.

Studies [28-30] on radiolysis of aqueous solutions of metal salts have offered evidence that transient Me^+ species were produced from Me^{2+} as shown in Eqs. (1) and (2).

$$H_2O \rightsquigarrow H, e^-_{aq}, OH, \text{etc.} \tag{1}$$

$$Me^{2+} + e^-_{aq} \longrightarrow Me^+ \tag{2}$$

The ESR studies revealed the formation of Zn^+ in irradiated metal complexes [31]. A possible mechanism for formation of an initiating species of radical character would be, for instance, the processes shown in Eqs. (2') and (3).

$$(AN\text{---}Zn^{2+}Cl_2) + e^-_{aq} \longrightarrow (AN\text{---}Zn^+Cl_2) \tag{2'}$$

$$(AN\text{---}Zn^+Cl_2) \longrightarrow (AN^{\overset{\cdot}{-}}\text{---}Zn^{2+}Cl_2)_= \tag{3}$$

The first-power dependence of the rate of polymerization on the dose rate, being indicative of unimolecular termination, might be attributed to the immobilization of growing polymer radicals in the rigid frozen medium containing metal halides.

The kinetic scheme for the polymerization might be as shown in Eqs. (4)-(7).

Initiation:

$$M\text{-}ZnCl_2 \rightsquigarrow R\cdot \tag{4}$$

with rate

$$R_i = f\phi[M\text{-}ZnCl_2]I$$

Propagation:

$$R\cdot + M\text{-}ZnCl_2 \longrightarrow RM\cdot \tag{5}$$

$$RM_n\cdot + M\text{-}ZnCl_2 \longrightarrow RM\cdot_{n+1} \tag{6}$$

with

$$R_p = k_p[RM_n\cdot][M\text{-}ZnCl_2]$$

Termination:

$$RM_n\cdot \longrightarrow P \qquad (7)$$

with

$$R_t = k_t[RM_n\cdot]$$

On assuming the stationary-state treatment for radicals, the overall reaction rate R is

$$R = k_p[RM_n\cdot][M\text{-}ZnCl_2]$$

$$= (k_p f\phi/k_t)[M\text{-}ZnCl_2]^2 I \qquad (8)$$

where $[M\text{-}ZnCl_2]$ is the concentration of zinc chloride complexed with AN, I is the dose rate, and f, ϕ, k_p, and k_t are the respective constants.

Case B: $\gamma \geq 1$

The degrees of polymerization are as high as 2.5×10^4, on the average. As γ increases, the concentration of the uncomplexed zinc chloride increases, and the rate of polymerization increases slowly, but the degree of polymerization remains almost constant.

In this case the initiating radicals would be additionally generated from the uncomplexed zinc chloride on irradiation, possibly by the processes shown in Eqs. (9) and (10).

$$Zn^{2+}Cl_2 + e^-_{aq} \longrightarrow Zn^+Cl_2 \qquad (9)$$

$$Zn^+Cl_2 + (AN\text{---}Zn^{2+}Cl_2) \longrightarrow Zn^{2+}Cl_2 + (AN^{\overline{\cdot}}\text{---}Zn^{2+}Cl_2) \qquad (10)$$

Then the additional initiation by the radicals derived from the uncomplexed zinc chloride, $(ZnCl_2)_u$ should be taken into account [Eq. (11)].

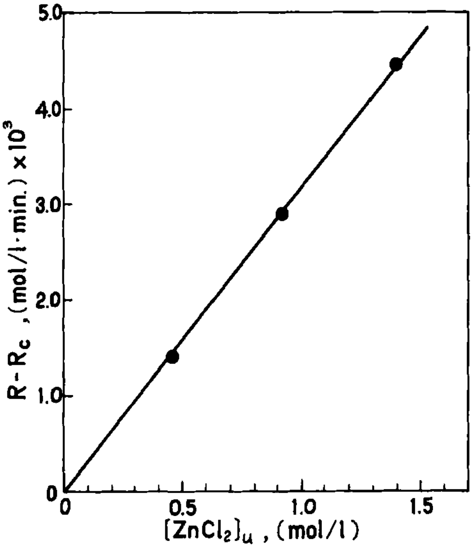

FIG. 10. Plot of the portion of the rate of polymerization attributed to initiation by uncomplexed zinc chloride against the concentration of uncomplexed zinc chloride.

$$ZnCl_2 \rightsquigarrow R\cdot \tag{11}$$

with

$$\text{Rate} = f'\phi'[ZnCl_2]_u I$$

$$R = (k_p/k_t)\{f\phi[M\text{-}ZnCl_2] + f'\phi'[ZnCl_2]_u\}[M\text{-}ZnCl_2]I \tag{12}$$

On assuming [M-ZnCl$_2$] is equal to [M] (= constant) at $\gamma \geq 1$, the first term of Eq. (12), the portion of the rate of polymerization attributable to the initiation from complexed zinc chloride R_c, is actually constant and then ($R - R_c$) becomes proportional to $[ZnCl_2]_u$:

$$R - R_c = K[ZnCl_2]_u I \tag{13}$$

where

$$[\mathrm{ZnCl_2}]_u = [\mathrm{ZnCl_2}] - [\mathrm{M}]$$

and $[\mathrm{ZnCl_2}]$ is the total concentration of zinc chloride present. This relation is found to hold in the range of $[\mathrm{ZnCl_2}]_u$ examined up to 1.4 mole/liter as shown in Fig. 10. The exponent of the concentration of uncomplexed zinc chloride is estimated experimentally to be 1.1.

Zinc chloride is here considered to play a dual role as the reagent for complex formation and the source of initiating species on irradiation.

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REFERENCES

[1] C. H. Bamford, A. D. Jenkins, and R. Johnston, Proc. Roy. Soc. (London), A241, 364 (1957).
[2] M. Imoto, T. Otsu, and S. Simizu, Makromol. Chem., 65, 174 (1963).
[3] M. Imoto, T. Otsu, and Y. Harada, Makromol. Chem., 65, 180 (1963).
[4] M. Imoto, T. Otsu, and M. Nakabayashi, Makromol. Chem., 65, 194 (1963).
[5] M. Imoto, T. Otsu, and K. Murata, Kogyo Kagaku Zasshi, 66, 1900 (1963).
[6] S. Tazuke, N. Sato, and S. Okamura, J. Polym. Sci. A-1, 4, 2461 (1966).
[7] S. Tazuke and S. Okamura, J. Polym. Sci. A-1, 5, 1083 (1967).
[8] T. Ikegami and H. Hirai, J. Polym. Sci. A-1, 8, 195 (1970).
[9] T. Otsu, B. Yamada, and M. Imoto, J. Macromol. Sci.–Chem., 1, 61 (1966).
[10] S. Tazuke and S. Okamura, J. Polym. Sci. B, 5, 95 (1967).
[11] S. Tazuke, K. Tsuji, T. Yonezawa, and S. Okamura, J. Phys. Chem., 71, 2967 (1967).
[12] S. Okuzawa, H. Hirai, and S. Makishima, J. Polym. Sci. A-1, 7, 1039 (1969).

[13] C. H. Bamford, A. D. Jenkins, and R. Johnston, J. Polym. Sci., 29, 355 (1958).
[14] V. P. Zubov, M. B. Lachinov, V. B. Golubev, V. F. Kulikova, V. A. Kabanov, L. S. Polak, and V. A. Kargin, J. Polym. Sci. C, 23, 147 (1968).
[15] H. Sumitomo, K. Kobayashi, and Y. Hachihama, Kogyo Kagaku Zasshi, 67, 1658 (1964).
[16] M. Ibonai, Kogyo Kagaku Zasshi, 70, 1267 (1967).
[17] Y. Kikuchi, Kogyo Kagaku Zasshi, 71, 296 (1968).
[18] T. Maekawa, K. Hayashi, and S. Okamura, J. Macromol. Sci.–Chem., A9, 257 (1975).
[19] R. E. Cleland and W. H. Stockmayer, J. Polym. Sci., 17, 473 (1955).
[20] M. Lee and Y. Minoura, Nippon Kagaku Kaishi, 1974, 159.
[21] E. R. Entwistle, Trans. Faraday Soc., 56, 284 (1960).
[22] N. N. Dass and M. H. George, J. Polym. Sci. A-1, 7, 269 (1969).
[23] W. I. Bengough and W. H. Fairservice, Trans. Faraday Soc., 63, 382 (1967).
[24] W. I. Bengough and T. O'Neill, Trans. Faraday Soc., 64, 1014 (1968).
[25] D. Cook, Can. J. Chem., 41, 522 (1963).
[26] A. Tomita, E. Ochiai, H. Hirai, and S. Makishima, J. Inorg. Nucl. Chem., 29, 105 (1967).
[27] F. Mylius and R. Dietz, Z. Anorg. Chem., 44, 209 (1905); Gmelins Handbuch Anorg. Chem., System-Nummer 32, 162 (1924).
[28] J. H. Baxendale, E. M. Fielden, and J. P. Keene, Proc. Roy. Soc. (London), A286, 320 (1965).
[29] M. Anbar and E. J. Hart, J. Phys. Chem., 69, 973 (1965).
[30] P. M. Moorth and J. J. Weiss, Nature, 201, 1318 (1964).
[31] J. Isoya and S. Fujiwara, Bull. Chem. Soc. Japan, 45, 2181 (1972).

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