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Polymerization of Acrylonitrile-Metal Halide Complexes in the Frozen State. V. Comparison of Metal Cations and Halogen Anions in Radiation-Induced Polymerization of Acrylonitrile-Metal Halide Complexes

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ABSTRACT

The radiation-induced polymerization of acrylonitrile in the frozen aqueous solutions of various metal chlorides and zinc halides was studied to compare the accelerating effect of metal cations and halogen anions. Among metal chlorides examined, zinc, stannous, manganese, and nickel cations gave greater rates and degrees of polymerization. Of the halogen anions, the rate of polymerization decreased in the order, Br^-, Cl^-, $SCN^- \gg I^-$, $CH_3CO_2^-$, and the degree of polymerization decreased in the order, Br^-, $SCN^- > Cl^- > I^- > CH_3CO_2^-$. The increase of the rate and the degree of polymerization was confirmed below the eutectic temperatures of the hydrated metal chlorides and ice. This suggests that the increment of

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the rate and the degree of polymerization is attributed to formation of hydrated metal chloride-acrylonitrile complexes accompanied by their solidification in eutectic mixtures with ice. The radioactivation analysis of polymers obtained in frozen dilute aqueous zinc bromide solution reveals appreciable contribution of water to generation of initiating species.

INTRODUCTION

Formation of σ-type complexes with metal salts generally increases radical polymerizability of polar vinyl monomers. This increase of the reactivity could be interpreted by enhancement of conjugation of monomers on formation of the complexes [1, 2].

In the previous paper [3], kinetic features of the radiation-induced polymerization of acrylonitrile in the frozen aqueous zinc chloride solution were studied. It was shown that in this frozen medium the presence of zinc chloride is essential to the polymerization and that zinc chloride plays a dual role as the reagent for complex formation, resulting in the increase of monomer reactivity and the source of initiating species on irradiation. The rate and the degree of polymerization have maximal values a little below the eutectic temperature of ice and zinc chloride tetrahydrate.

The present paper compares metal cations and halogen anions with respect to the rate-enhancing effect in the radiation-induced polymerization of acrylonitrile in frozen aqueous solution. Further studies with some metal chlorides confirmed a parallel between the eutectic temperatures of ice and metal chloride hydrates and temperatures at which the specific rate enhancement occurs. The radioactivation analysis of polymers obtained also offered information concerning generation of initiating species.

EXPERIMENTAL

Purification of chemicals, polymerization procedure, and determination of molecular weights were described in the previous paper [3]. Radioactivation analysis of polymers was carried out as described previously [4].

RESULTS

Comparison of Metal Halides in Rate Enhancement

Comparison of Metal Cations. Polymerization of acrylonitrile (AN) was carried out in the presence of various metal chlorides in frozen aqueous solutions at -78°C under reduced pressure ($< 10^{-4}$ Torr). As shown in Table 1, the presence of Zn^{2+}, Sn^{2+}, Mn^{2+}, and Ni^{2+} cations gives large rate and degree of polymerization. These cations can form σ-type complexes with AN. No polymerization occurred with Cr^{2+}, Fe^{2+}, Fe^{3+}, and Cu^{2+}, which are known as radical polymerization inhibitors [5-9]. This tendency is almost the same as the results obtained in air [3].

Comparison of Anions. The influence of anions was examined with various zinc halides. The rate and degree of polymerization are shown in Figs. 1 and 2. Though the initial rates of polymerization with Br^-, Cl^-, and SCN^- are large and show little difference, the rates at higher conversions tend to decrease in the order: $Br^- > Cl^- > SCN^-$. The rates are lower with I^- and $CH_3CO_2^-$.

The degrees of polymerization decrease in the order: Br^-, $SCN^- > Cl^- > I^-$, but change little with conversion. The lower rate and degree of polymerization with I^- could be due to the retarding action of I^- to the radical polymerization.

Temperature Dependence of Polymerization

It was suggested [3] that the eutectic temperature T_e of ice and zinc chloride tetrahydrate correlates with the temperature at which the rate and degree of polymerization increase markedly in the frozen aqueous zinc chloride solution. The temperature dependence, therefore, of the rate and degree of polymerization was examined in aqueous solutions with $NiCl_2$, $MgCl_2$ and $AlCl_3$ which were selected because data concerning compositions and T_e values of the eutectic mixtures of their hydrates and ice are available [10-13] (see Table 2).

As seen in Fig. 3, the temperature dependence of polymerization in the case of $NiCl_2$ shows a similar trend to that in the case of $ZnCl_2$, both the rate and the degree of polymerization having maximal values somewhat below -45°C, the T_e of the eutectic mixture of $NiCl_2 \cdot 7H_2O$ and ice. In the case of $MgCl_2$ and $AlCl_3$, the specific temperatures at which the rate and the degree of polymerization increase with decreasing temperature were observed about -33 and -55°C, the T_e values of the eutectic mixtures of $MgCl_2 \cdot 12H_2O$ and

TABLE 1. Effect of Metal Chlorides on the Polymerization of Acrylonitrile in Frozen Aqueous Solution and Relevant Properties of Metal Cations[a]

Metal chloride	Conversion (%)	Degree of polymerization $\times 10^{-4}$	Formation of complex $\Delta\nu$ (C≡N) (cm^{-1})[b]	Lewis acidity $\Delta\nu$(C=O) (cm^{-1})[c]
$ZnCl_2$	96.3	2.80	34	57
$SnCl_2$	77.5	1.86	55[d]	-
$MnCl_2$	36.9	1.57	24	37[e]
$NiCl_2$	36.4	1.62	58	38[e]
$CrCl_2$	18.3	0.65	40	-
$CdCl_2$	16.5	0.90	34	34
$BaCl_2$	7.34	0.50	f	-
$TiCl_4$	6.40	0.17	45	175, 128[g]
$CaCl_2$	4.58	0.44	f	47
$MgCl_2$	3.50	0.50	f	-
$AlCl_3$	3.04	0.60	f	117[g]
$CoCl_2$	0.40	-	32	50
$CrCl_2$	0	-	-	-
$FeCl_2$	0	-	29	-
$FeCl_3$	0	-	-	141

$CuCl_2$	0	-	-	20[g]
None	0	-	-	-

[a] [AN] = [Metal chloride] = 0.47 mole/liter, 3.44 × 10^4 r/hr, 2 hr, -78°C, in vacuo.

[b] Data of Herberhold [15].

[c] Xanthone [16].

[d] Present work.

[e] Xanthone, present work.

[f] Formation of complexes was not detected by IR measurement at room temperature in the present work.

[g] Ethyl acetate, [17].

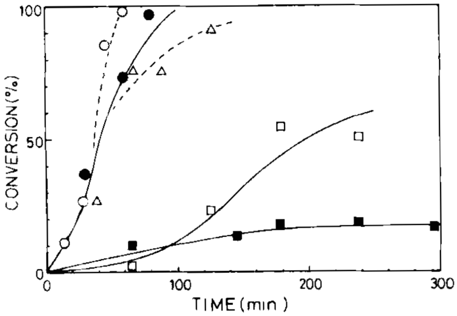

FIG. 1. Time-conversion curves in the frozen aqueous AN-ZnX_2 solutions: (○) Br^-; (●) Cl^-; (△) SCN; (□) I^-; (■) CH_3CO_2. At -78°C, dose rate 2.0×10^4 r/hr, in vacuo; [AN] and [ZnX_2] = 0.47 mole/liter.

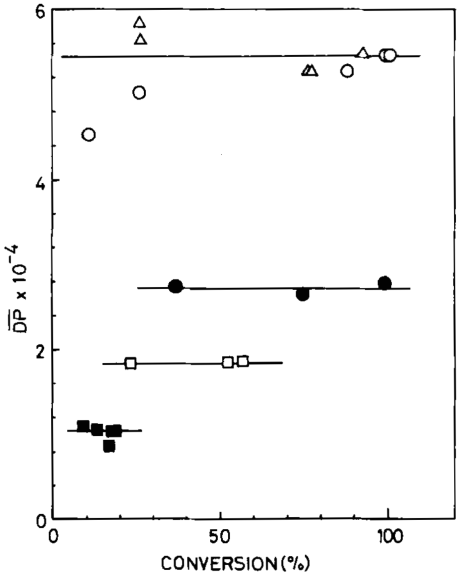

FIG. 2. Plots of degrees of polymerization as a function of conversion in the frozen aqueous AN-ZnX_2 solutions: (○) Br^-; (△) SCN^-; (●) Cl^-; (□) I^-; (■) $CH_3CO_2^-$. At -78°C, dose rate 2.0×10^4 r/hr, in vacuo.

TABLE 2. Eutectic Compositions and Temperatures of Metal Chloride Hydrates and Ice

Composition (mole ratio)	T_e (°C)	Reference
$MgCl_2 \cdot 12H_2O$ + Ice; (1: 7.46)	-33	[10]
$NiCl_2 \cdot 7H_2O$ + Ice; (1: 9.87)	-45	[11]
$AlCl_3 \cdot 6H_2O$ + Ice; (1:15.9)	-55	[12]
$ZnCl_2 \cdot 4H_2O$ + Ice; (1: 3.28)	-62	[13]

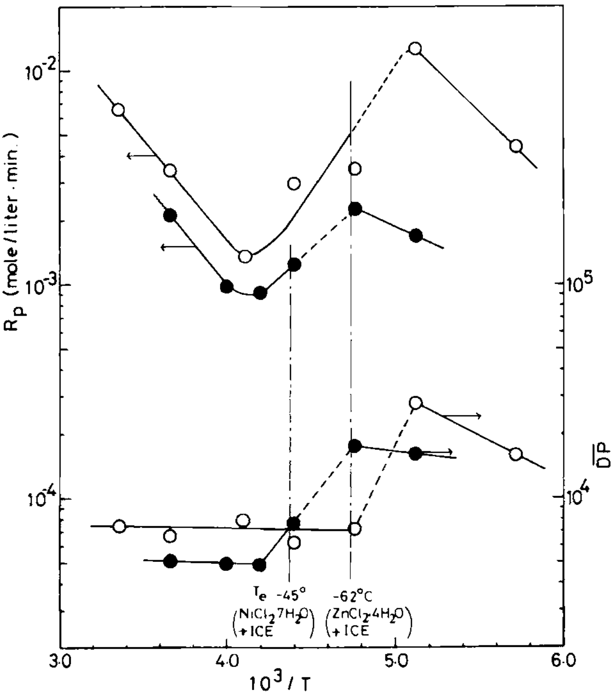

FIG. 3. Temperature dependence of the rate and degree of polymerization at dose rate 3.44×10^4 r/hr in vacuo: (○) $ZnCl_2$; (●) $NiCl_2$. [AN] and [MCl_2] = 0.47 mole/liter.

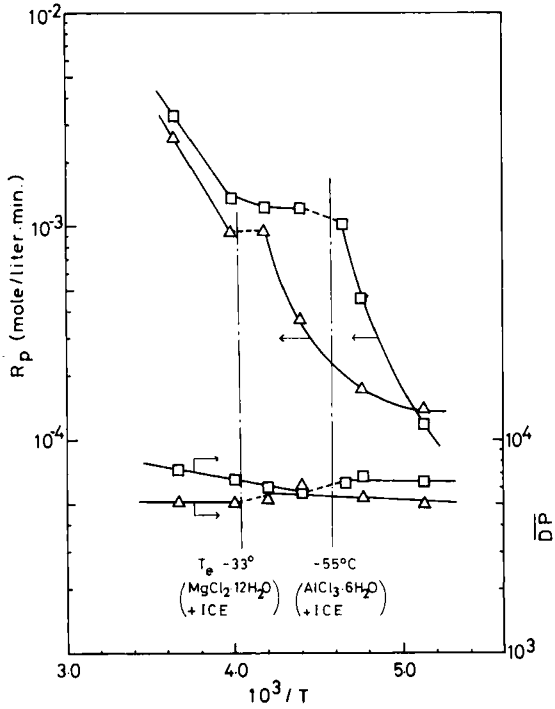

FIG. 4. Temperature dependence of the rate and degree of polymerization at dose rate 3.44 × 10^4 r/hr in vacuo: (□) $AlCl_3$; (△) $MgCl_2$. [AN], [$AlCl_3$] and [$MgCl_2$] = 0.47 mole/liter.

ice, and $AlCl_3 \cdot 6H_2O$ and ice, respectively (see Fig. 4). The increase of the rate and degree of polymerization slightly below the T_e seems due to solidification of the hydrated metal chloride-AN complex caused by its formation of the eutectic mixtures with ice.

Radioactivation Analysis of Polymers

Bromine contents in polymers prepared by polymerization of AN in frozen aqueous zinc bromide solutions were measured by radioactivation analysis in order to obtain information concerning initiating species. As shown in Table 3, the number N_{Br} of bromine atoms per polymer chain is found to be about 0.1 for polymers prepared at -78°C and is almost unchanged irrespective of conversion or mole

TABLE 3. Bromine Contents in Polymers Obtained by Polymerization in Aqueous $ZnBr_2$ Solution

Polymerization conditions[a]		Conversion (%)	$\overline{M}_n$ $\times 10^{-6}$ [b]	N_{Br} Br atoms per polymer chain
$[ZnBr_2]/[AN]$	Temp. (°C)			
1.0	-78	32.7	1.53	0.10
1.0	-78	86.5	1.54	0.11
4.0	-78	23.5	1.48	0.10
1.0	-30	19.1	0.30	0.12
1.0	+25	24.5	0.30	0.58

[a] Dose rate 3.44×10^4 r/hr.
[b] Calculated from $\overline{M}_v$ as $\overline{M}_n = \overline{M}_v/1.89$.

ratio $r = [ZnBr_2]/[AN]$. This small N_{Br} value indicates minor contribution of the bromine radical to initiation. Since the water concentration is high and the generation of initiating radical species from water is large, the water molecule seems to contribute significantly to initiation in the frozen dilute aqueous solution. Polymers prepared at 25°C have a large N_{Br} of about 0.6, which seems to indicate occurrence of chain transfer to $ZnBr_2$ because of the liquid-state reaction [14].

DISCUSSION

It was suggested [3] that for radiation-induced polymerization of AN in the frozen dilute aqueous $ZnCl_2$ solution, important factors which govern the reaction are (a) formation of the metal chloride-AN complex, (b) phase of the complex, and (c) generation of initiating species according to processes (1) and (2), where $i = 1, 2$.

$$AN_i \text{ --- } M^{2+}Cl_2 + e^-_{aq} \longrightarrow AN_i \text{ --- } M\cdot^+Cl_2 \tag{1}$$

$$AN_i \text{ --- } M\cdot^+Cl_2 \longrightarrow AN_i^{\cdot-} \text{ --- } M^{2+}Cl_2 \tag{2}$$

The factors (a) and (c) depend on properties of metal cations. AN can form the complexes with metal cations by σ-bonding through the lone pair of electrons on the nitrogen [15]. Table 1 lists increase of the $C\equiv N$ stretching frequency when AN is coordinated to various metal cations. All metal cations having a marked rate-enhancing effect are ones which form complexes with AN as judged by this increase of the $\nu(C\equiv N)$ frequency. Since an increase of monomer reactivity on formation of complexes with metal salts could be accounted for by enhancement of conjugation of monomers [1, 2], it may depend on Lewis acidity of metal salts. Lewis acidity [16] of metal chlorides, evaluated from decrease of the carbonyl stretching frequency of xanthone when it forms complexes with Lewis acids, is listed in Table 1. Distinct correlation, however, is not observed between Lewis acidity and the rate enhancement as shown in Fig. 5. This result seems to suggest that in this reaction conditions physical factors such as aggregated state of complexes function significantly as well as chemical nature of complexes. Consequently AN-zinc and -stannous chloride complexes seem to have adequate physical state and to be most suitable to propagation in the frozen aqueous solution.

Though the ionization potential IP of metal cations may function in processes (1) and (2) for generation of initiating species, there appears to be no obvious relationship between IP [18] and the polymer yields as shown in Fig. 6. This suggests that the above processes are important but are not the sole ones controlling the rate of polymerization.

According to the spectrochemical series of the ligands [19], the stability order of metal complexes is $RCO_2^- > SCN^-, Cl^- > Br^- > I^-$.

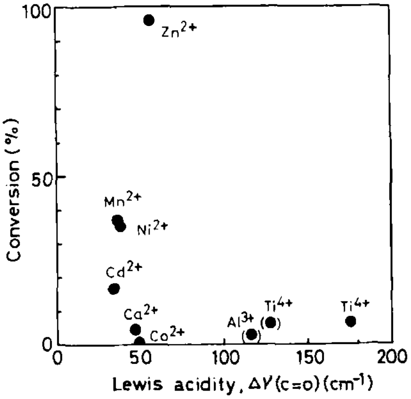

FIG. 5. Polymer yields plotted against Lewis acidity of metal cations.

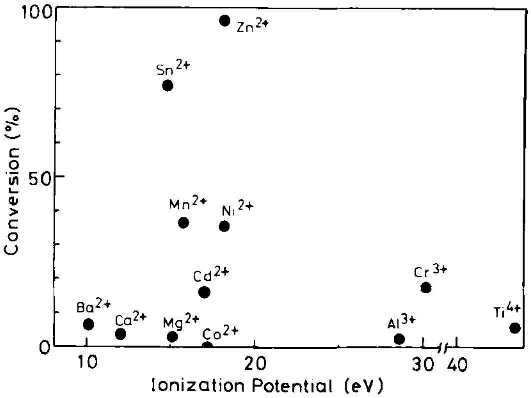

FIG. 6. Polymer yields plotted against ionization potential of metal cations.

TABLE 4. Complex Index at a Composition of ZnX_2:AN:H_2O = 1:1:3 at Various Temperatures

Zinc halide	Complex index		
	20°C	-62°C	-80°C
$ZnCl_2$	0.670	0.761	0.795
$ZnBr_2$	0.681	0.770	0.807
ZnI_2	0.685	0.773	0.811

Difficulty of formation of the Zn-AN complex is predicted to increase in the series: $Cl^- > Br^- > I^-$. The complex index J, defined in the previous paper [20] as $D_{2270}/(D_{2270} + D_{2235})$ as a measure of the concentration of AN complexed with zinc cation, and obtained by IR measurements in concentrated aqueous solutions of zinc chloride, bromide and iodide, decreases in the order: $I^- > Br^- > Cl^-$, as shown in Table 4.

The slight change of the Zn-AN complex concentration with different anions affects the degree of polymerization, but has only a slight effect on the rate of polymerization. The degree of polymerization decreases in the order Br^-, $SCN^- > Cl^- > I^- > CH_3CO_2^-$ which corresponds nearly reversely to the spectrochemical series of ligands. It seems likely that the anion which forms complexes more easily with zince cation disturbs the aggregate of the Zn-AN complex to be formed, resulting in decrease of the degree of polymerization.

Finally, the phase change of the complex is considered an important factor. When a dilute aqueous solution of a metal chloride is cooled, ice and a eutectic mixture of ice and the hydrated metal chloride freeze out successively [10-13]. By addition of AN to the solution, a eutectic mixture of ice and the hydrated metal chloride-AN complex is believed to freeze out. The appearance, therefore, of the maximal rate and degree of polymerization at the temperature somewhat below T_e in the cases of $ZnCl_2$ and $NiCl_2$ could be attributed to formation of the solid hydrated metal chloride-AN complex in the eutectic state. This hydrated $ZnCl_2$ -AN complex is solidified only in the eutectic state in the frozen dilute aqueous solution. In contrast, in the concentrated aqueous $ZnCl_2$ solution (the supercooled liquid system described previously [21]), the phase of the hydrated $ZnCl_2$-AN complex does not change above the glass transition temperature. Therefore, no specific temperature at which the rate and degree of polymerization increase is observed in the concentrated aqueous $ZnCl_2$ solution.

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