Polymerization of Acrylonitrile-Metal Haiide Complexes in the Frozen State. III. Relationship between Rate of Radiation-Induced Polymerization and Complex Concentration

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Polymerization of Acrylonitrile-Metal Halide Complexes in the Frozen State. III. Relationship between Rate of Radiation-Induced Polymerization and Complex Concentration

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ABSTRACT

Radiation-induced polymerization of acrylonitrile (AN) in the
$ZnCl_2$-AN-H_2O ternary system was carried out at tempera-
tures ranging from 30 to -78°C, and correlation between the
polymerization rate and the concentration of complexed AN
with zinc atom was clarified. The selected systems were in
the supercooled liquid state at -78°C with the molar composi-
tion ratio of $ZnCl_2$:AN:H_2O of 1:1:3. The polymerization is
free-radical in character. The 0.5-power dependence of the
polymerization rate on the dose rate at 30°C indicates
bimolecular termination, while the 0.9-power dependence at
-78°C shows predominant unimolecular termination because
of the high viscosity of the systems at just above the glass
transition temperature. The negative temperature dependence

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of the polymerization rate is indicative of the tendency of the complex concentration to increase with lower temperatures. The polymerization rate, therefore, is proportional to the 2 and 1.5 powers of the complex concentration at -78 and 30°C, respectively. These results indicate participation of the complexed monomer both in generation of the initiating radical species on irradiation and in the propagation step. A kinetic scheme has been proposed on the basis of the results.

INTRODUCTION

Since the enhancement of polymerization of acrylonitrile (AN) in the presence of LiCl was observed by Bamford [1], numerous reports [2-9] have been published on the accelerating effect of some coordinative metal halides on the radical polymerization of certain polar vinyl monomers such as AN and methyl methacrylate.

From determination of the absolute rate constant, it was found that the rate of propagation was significantly increased in the presence of LiCl, while the termination constant remained almost constant, resulting in an enhanced rate of polymerization [6]. On the basis of these results, it was proposed that formation of a complex of the propagating radical with metal ion occurred. A similar observation and explanation were made by Kargin [9] for polymerization of AN in the presence of $ZnCl_2$.

Imoto and Otsu [3, 4] have studied the polymerization of the complex of AN with $ZnCl_2$ and have attributed the accelerating effect of $ZnCl_2$ to σ-type complex formation between AN and $ZnCl_2$ through the lone pair on the N atom of the nitrile group of the monomer.

In the previous paper [10] the radiation-induced polymerization of AN was carried out in aqueous zinc chloride solution at a mole ratio of $ZnCl_2:H_2O = 1:118$ at low temperatures; the kinetic results indicated the important roles of complex formation of AN with zinc atom.

In the present paper, in an attempt to elucidate a more direct correlation between the polymerization kinetics and complex formation in the $ZnCl_2$-AN-H_2O ternary system, the dependence of the polymerization rate on the complex concentration, determined by means of the IR technique developed in the preceding paper [11], was studied. The polymerization behavior of AN in the $ZnCl_2$-AN-H_2O ternary system of various compositions, initiated by Co-60 γ-rays at temperatures ranging from 30 to -78°C, was investigated, and the polymerization mechanism was discussed on the basis of kinetic

results. Here the composition of the ternary system was as
$ZnCl_2:H_2O$ = 1:3 or 5 in mole ratio, with $\gamma = [ZnCl_2]/[AN] \leq 1$.

EXPERIMENTAL

Materials

AN and $ZnCl_2$ were purified as previously described [11].

Polymerization Procedure

After mixing the required amount of aqueous $ZnCl_2$ solution and
AN in a glass ampoule, the solution was degassed by repeated freeze-
thaw cycles and then sealed under reduced pressure. The polymeriza-
tion was initiated by γ-rays from a Co-60 source at various tempera-
tures ranging from 30 to -78°C. The dose rate was 27.9 Kr/hr
unless otherwise noted. After certain period of irradiation, polymers
were precipitated by pouring into excess amount of a dilute aqueous
HCl solution.

Polymers were washed with a dilute HCl solution on a sintered
glass filter until $ZnCl_2$ was completely removed and dried at room
temperature under reduced pressure. The percent conversion was
determined by gravimetry.

Differential Thermal Analysis

Differential thermal analysis (DTA) was carried out on a Shimadzu
DTB-20 in accordance with the procedure described in the preceding
paper [11].

IR Spectrum

The IR spectra of $ZnCl_2$-AN-H_2O ternary system of various com-
positions were obtained by using a Shimadzu IR-27G spectrophotom-
eter, and the procedure was similar to that described in the preceding
paper [11]. The spectra of polymers were obtained by the potassium
bromide disk method.

TABLE 1. Ternary Systems under Investigation

Composition (mole ratio)			Glass transition temperature (°C)	Specific gravity (g/ml)	Monomer concentration $[A]_0$ (mole/liter)
$ZnCl_2$	AN	H_2O			
1	1	3	-82	1.5662	6.42
1	2	3	-89	1.3372	9.02
1	1	5	-96	1.4553	5.21
1	2	5	-103	1.3049	7.86

RESULTS

Systems Under Investigation

Since this investigation was designed to cover the temperature range from 30 to -78°C, the four systems selected, listed in Table 1, were ones which were in a homogeneous solution phase at 20°C and did not have any thermal discontinuity in the above experimental temperature range. The DTA curves of the systems are shown in Fig. 1.
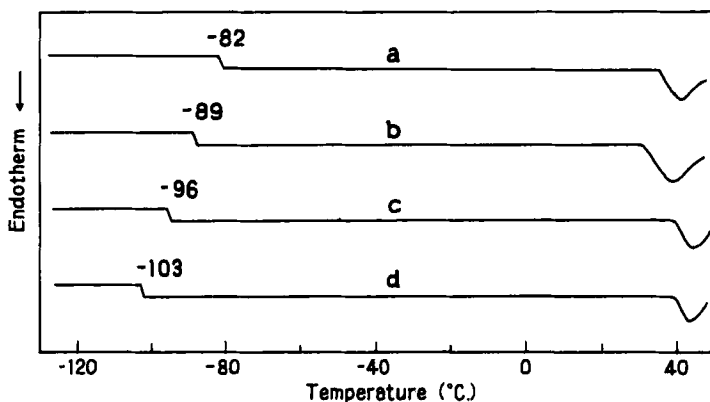

FIG. 1. Thermograms of ZnCl-AN-H_2O ternary systems of various compositions (in mole ratio of $ZnCl_2$:AN:H_2O): (a) 1:1:3; (b) 1:2:3; (c) 1:1:5; (d) 1:2:5.
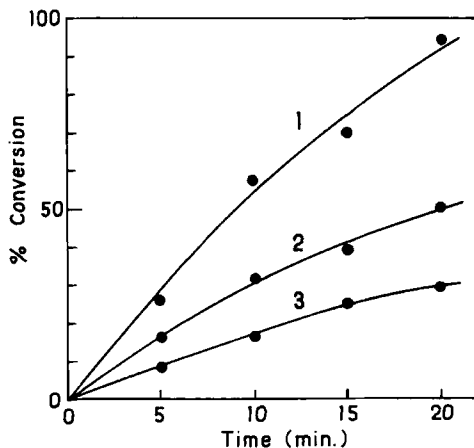
FIG. 2. Time-conversion curves for the system with composition (in mole ratio) $ZnCl_2:AN:H_2O = 1:1:3$ at (1) $-78°C$, (2) $-35°C$, and (3) $+30°C$, all at the dose rate of 27.9 Kr/hr.

Characteristics of Polymerization

A typical time-conversion curve of this polymerization system is given in Fig. 2. The acceleration effect of $ZnCl_2$ is so large that almost 90% conversion is attained within 20 min with a dose rate of 27.9 Kr/hr at $-78°C$. No polymerization takes place in the absence of $ZnCl_2$ under the same reaction condition. A higher polymerization rate results with a higher mole fraction of $ZnCl_2$ and with lower reaction temperatures, and a lower reaction rate with higher AN and/or H_2O levels. The presence of oxygen or radical scavengers such as hydroquinone inhibits the polymerization to large extent.

The resulting polymers are insoluble in such conventional solvents for poly-AN as N,N-dimethylformamide, but are only swollen, and this is considered to be due to gelation of polymers during irradiation; determination of their molecular weight was thus infeasible. The IR spectra of polymers are similar to those of the conventional poly-AN.

The rate of polymerization for kinetic study was taken from the initial slope of the time-conversion curve.

Temperature Dependence of Polymerization Rate

Figure 3 shows the dependence of the polymerization rate of temperature. As noted in the previous section, a trend of higher rate of
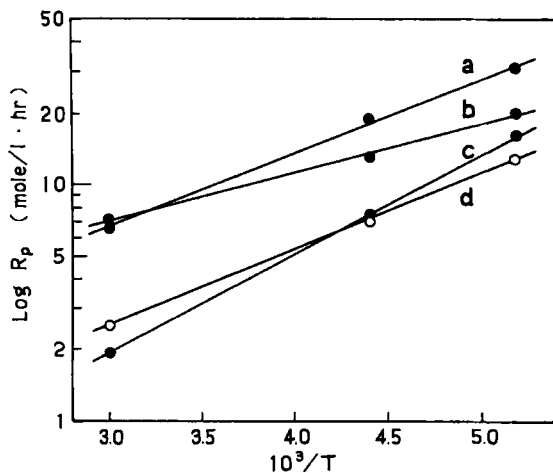
FIG. 3. Temperature dependence of polymerization rate for systems having various compositions (in mole ratio of $ZnCl_2$:AN:H_2O): (a) 1:2:3; (b) 1:1:3; (c) 1:2:5; (d) 1:1:5.

polymerization is observed with lower temperature. Plots of the rate of polymerization versus 1/T give straight lines. The apparent activation energies, calculated from the slopes of the Arrhenius plots, are -1.17, -1.63, -1.70, and -2.26 kcal/mole for the systems with compositions of $ZnCl_2$:AN:H_2O = 1:1:3, 1:2:3, 1:1:5, and 1:2:5 in mole ratio, respectively. The extent of the dependence increases with increasing mole fraction of water and of AN. A higher mole fraction of water resulted also in a lower polymerization rate.

Dependence of Polymerization Rate on Dose Rate

The dose rate dependence of polymerization rate was investigated in the range of 3.68 to 27.9 Kr/hr at -78°C and 30°C in order to obtain basic knowledge on the polymerization mechanism; results are shown in Fig. 4. Regardless of the composition of the systems, the dose rate exponents were obtained as 0.94 ± 0.02 at -78°C and 0.50 ± 0.05 at 30°C.
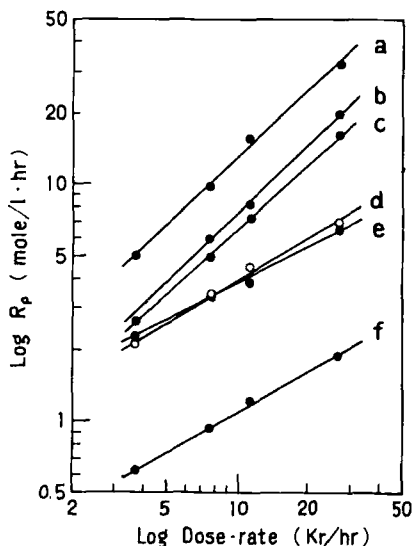
FIG. 4. Dependence of polymerization rate on dose rate at various compositions (in mole ratio of $ZnCl_2$:AN:H_2O) and temperatures: (a) 1:2:3, $-78°C$; (b) 1:1:3, $-78°C$; (c) 1:2:5, $-78°C$; (d) 1:2:3, $+30°C$; (e) 1:1:3, $+30°C$; (f) 1:2:5, $+30°C$.

Complex Index

Figure 5 shows the temperature dependence of the complex indices for various systems. The complex index J, defined as $D_{2270}/(D_{2270} + D_{2235})$, where D_{2270} and D_{2235} are absorbances at 2270 and 2235 cm^{-1}, respectively, was measured in accordance with the procedures described in the preceding paper [11].

As noted in the previous paper, the complex index has a linear relationship with $1/T$ over a wide composition range of the ternary system; that is, the complex index increases with decreasing temperature; a higher value of the complex index is obtained with a higher mole fraction of $ZnCl_2$, and a lower value of J with increasing mole fraction of AN and/or H_2O.

The concentration C of the complexed AN in the system was calculated by using the values of the complex index according to the relationship
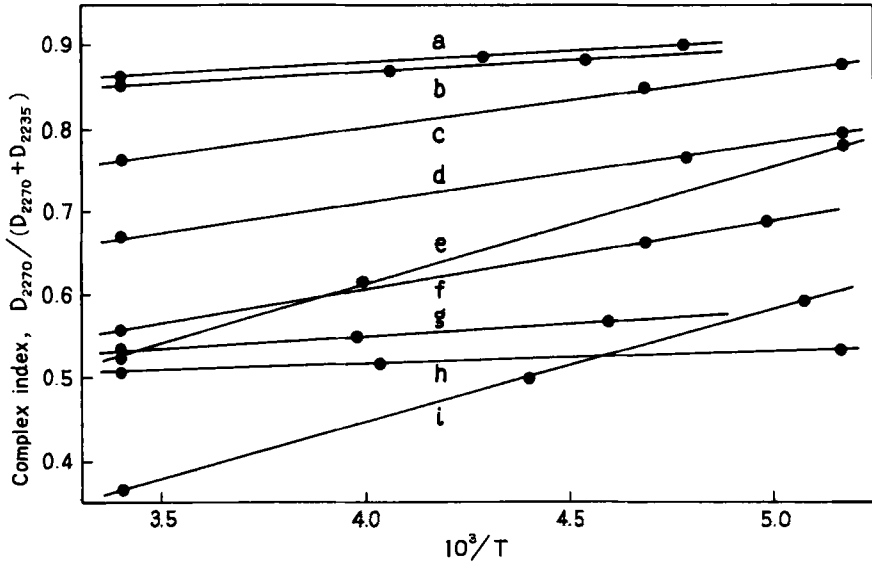
FIG. 5. Dependence on temperature of complex index J at various compositions (in mole ratio of $ZnCl_2:AN:H_2O$): (a) 1:0.1:3; (b) 1:0.2:3; (c) 1:0.5:3; (d) 1:1:3; (e) 1:2:3; (f) 1:1:5; (g) 1:2.5:3; (h) 1:3:3; (i) 1:2:5.

$$C = [A]_0 J / \{\alpha (1 - J) + J\}$$

derived in the preceding paper [11] where $[A]_0$ is the monomer concentration in the feed and α is a correcting coefficient which was provided in the preceding paper [11].

Dependence of Polymerization Rate on Complex Concentration

Figure 6 on the logarithmic scales shows the relationship between the polymerization rate and the complexed AN concentration in both 1:1 and 1:2 type $ZnCl_2$-AN complexes. The polymerization rates are found to be proportional to approximately the 2 and 1.5 powers of the complexed AN concentration at -78 and 30°C, respectively.
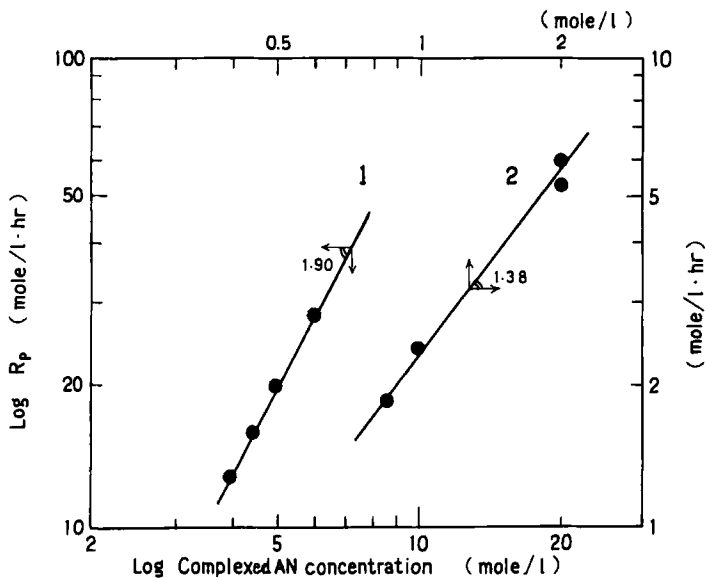
FIG. 6. Plots of the polymerization rate as a function of complexed AN concentration on irradiation (1) at -78°C and (2) at +30°C. Dose rate, 27.9 Kr/hr.

DISCUSSION

The similarity in the tendency of polymerization rate and complex index to increase with decreasing temperature suggests close correlation of the two findings. Since the complex index is an indirect measure of complex stability, the higher value of the complex index at lower temperature indicates a gradual increase in the complex concentration with decreasing temperature.

The striking feature of this polymerization system, i.e., the higher rate of polymerization at lower temperature and the negative value of the apparent activation energy shown in Figs. 3 and 5, therefore, can be explained in connection with the tendency of the complex concentration to increase with lower temperature. The increased viscosity of the system might also contribute to enhancement of the

polymerization rate at low temperature, although this aspect has not yet been treated quantitatively in this investigation.

The decreased rate of polymerization with increasing mole fraction of H_2O is further evidence of the dependence of the polymerization rate on the complex concentration. The decreased rate of polymerization is considered to be ascribed to the reduction of the complex concentration as a result of complex dissociation with increasing mole fraction of H_2O.

This can be confirmed from the results shown in Fig. 6. A close correlation between the polymerization rate and the complexed AN concentration is recognized in the polymerizations carried out at 30°C and -78°C, which reveals that the polymerization rate is dependent on the complexed AN concentration. This conclusion obtained from the kinetic study is consistent with the reported results [2, 8, 12] that the accelerated polymerization rate in the presence of metal halides is due to the enhanced monomer reactivity as a result of complex formation with metal ion.

Such facts as the inhibition effect of O_2 and hydroquinone at -78°C and the 0.5-power dependence of the polymerization rate on the dose rate at 30°C are evidence for the free-radical character of this polymerization.

The 0.9-power dependence of the polymerization rate on the dose rate in the polymerization at -78°C is considered to be a result of unimolecular termination due to the high viscosity of the polymerization systems, since the reaction temperature is very close to the second transition temperature of the systems under investigation, as noted in Table 1.

On the basis of kinetic results and other evidence mentioned above, the following scheme is considered to be applicable for the polymerization behavior of this system.

Complex Formation

ZnCl$_2$ and AN form 1:1 and 1:2 type complexes in the water medium and the complexes quickly reach equilibrium.

$$M + AN \xrightleftharpoons{k_1} M\text{-}AN \tag{1}$$

$$M\text{-}AN + AN \xrightleftharpoons{k_2} M\text{-}(AN)_2 \tag{2}$$

The concentration of 1:1 and 1:2 type complexes in the polymerization systems are as shown in Eqs. (3) and (4).

$$[M\text{-}AN] = k_1[M][AN] \tag{3}$$

$$[M\text{-}(AN)_2] = k_2[M\text{-}AN][AN] = k_1k_2[M][AN]^2 \tag{4}$$

Then, the total concentration C of the complexed AN in both 1:1 and 1:2 type complexes is

$$C = [M\text{-}AN] + 2[M\text{-}(AN)_2] \tag{5}$$

Initiation

As concluded in the previous paper [10], the complex species are considered to take part in the initiation step and to be responsible for the generation of radical species by irradiation [Eq. (6)]:

$$M\text{-}(AN)_i \rightsquigarrow R\cdot \tag{6}$$

where i = 1, 2. Then, the rate of initiation, R_i, is

$$R_i = f\phi CI \tag{7}$$

where f, ϕ and I are the initiation efficiency, the rate constant of free radical production in the complex, and the dose rate, respectively.

Propagation

Assuming the reactivity of the free monomer is negligibly small in comparison with that of the complexed monomer, as it is the case in the systems, the complexed monomer is the only species responsible for the propagation.

$$R\cdot + M\text{-}(AN)_i \longrightarrow RM_1\cdot \tag{8}$$

$$RM_n\cdot + M\text{-}(AN)_i \xrightarrow{k_p} RM_{n+1}\cdot \tag{9}$$

Then, the rate of propagation, R_p', will be

$$R_p' = k_p C[RM_n\cdot] \tag{10}$$

Termination

In the polymerization systems at 30°C with relatively low viscosity, termination occurs almost exclusively by mutual interaction of two polymer radicals,

$$2RM_n \cdot \xrightarrow{\;k_t\;} P \qquad\qquad (11)$$

and as the viscosity increases with decreasing temperature, the role of unimolecular termination becomes important. Particularly in the polymerization at -78°C, a temperature which is just above the glass transition temperature of the systems under investigation, unimolecular termination is predominant because of the high viscosity of the systems.

$$RM_n \cdot \xrightarrow{\;k_t'\;} P' \qquad\qquad (12)$$

Then, the rate of termination R_t at 30°C will be

$$R_t = k_t [RM_n \cdot]^2 \qquad\qquad (13)$$

while at -78°C it will be

$$R_t = k_t' [RM_n \cdot] \qquad\qquad (14)$$

Finally, assuming a steady state at the initial step of polymerization, the rate of polymerization R_p at 30°C and -78°C will be given by Eqs. (15) and (16), respectively,

$$R_p = \kappa k_p I^{1/2} C^{3/2} / k_t^{1/2} \qquad\qquad (15)$$

$$R_p = \kappa' k_p I C^2 / k_t' \qquad\qquad (16)$$

where κ and κ' are constant terms which stand for $(f\phi)^{1/2}$ and $(f\phi)$, respectively.

Equations (15) and (16) are consistent with the experimental results obtained. The coexistence of bimolecular termination is considered to be responsible for a slight deviation from unity in the dose rate dependence of polymerization rate at lower temperatures, since bimolecular termination is also operative to some extent even at $-78°C$, the systems being in the supercooled liquid state.

No evidence was obtained for a large difference in the reactivity of 1:1 and 1:2 type $ZnCl_2$-AN complexes as far as H_2O is involved in the systems.

ACKNOWLEDGMENT

REFERENCES

[1] C. H. Bamford, A. D. Jenkins, and R. J. Johnston, Proc. Roy. Soc. (London), A241, 364 (1957).

[2] M. Imoto, T. Otsu, and Y. Harada, Makromol. Chem., 65, 180 (1963).

[3] M. Imoto, T. Otsu, and M. Nakabayashi, Makromol. Chem., 65, 194 (1963).

[4] M. Imoto, T. Otsu, and S. Shimizu, Makromol. Chem., 65, 174 (1963).

[5] H. Sumitomo, K. Kobayashi, and Y. Hachihama, Kogyo Kagaku Zasshi, 67, 1658 (1964).

[6] C. H. Bamford, S. Brumby, and R. P. Wayne, Nature, 209, 292 (1966).

[7] S. Tazuke and S. Okamura, J. Polym. Sci., B5, 95 (1967).

[8] S. Tazuke, K. Tsuji, T. Yonezawa, and S. Okamura, J. Phys. Chem., 71, 2957 (1967).

[9] V. A. Kargin, V. A. Kabanov, and V. P. Zubov, Vysokomol. Soedin., 2, 765 (1960).

[10] T. Maekawa and S. Okamura, J. Macromol. Sci.–Chem., A10, 1565 (1976).

[11] S. Mah, T. Maekawa, and S. Okamura, J. Macromol. Sci.–Chem., A11, 687 (1977).

[12] T. Ikegami and H. Hirai, J. Polym. Sci. A-1, 8, 463 (1970).