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Polymerization of Acrylonitrile-Metal Halide Complexes in the Frozen State. IV.

Radiation-Induced Polymerization of Acrylonitrile-Zinc Chloride Complexes in the Solid State and in Benzene Solution

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ABSTRACT

The radiation-induced polymerization of zinc chloride-acrylonitrile (AN) complexes, both the amorphous $ZnCl_2$ -AN (1:1) type and the crystalline (1:2) type, was carried out at 30 and $-35^\circ C$. The rate of polymerization of the 1:1 type exceeds that of the 1:2 type not only in bulk but also in their benzene (BZ) solution, which seems to be attributable to the difference in the relative concentration of $ZnCl_2$ to AN rather than to difference in their phases. The addition of a small amount of water to both type complexes results in an increase in the rate of polymerization. In the BZ solution of the 1:2 type complex ($ZnCl_2$:AN:BZ = 1:2:2), the addition of water, methanol, and acetic acid increases the rate of polymerization, and the apparent G value of initiation increases with the added amount of water. The findings indicate considerable contribution of the added ligands coordinated to

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zinc cation to formation of initiating species on irradiation. The bromine atom number N_{Br} per polymer chain was measured by means of radioactivation analysis for polymers obtained from the polymerization of $ZnBr_2$ -AN complexes. N_{Br} of 0.20 for both 1:1 and 1:2 types suggests a minor contribution of the initiation by addition of the bromine radical to monomer molecules. In the BZ solution of complexes of the 1:2 type, the N_{Br} of 0.19 was reduced to 0.13 upon addition of water (0.2 mole ratio), which indicates some contribution of water to formation of initiating species. The result is in accord with the estimation based on the rate increase.

INTRODUCTION

It is well known that presence of metal salts enhances radical-catalyzed polymerization of polar vinyl monomers. This enhancement of the rate of polymerization was accounted for in terms of formation of metal complexes with monomers. Although a few studies [1, 2] of radiation-induced polymerization of metal complexes in bulk reported rapid polymerization, mechanistic features of the polymerization still remain obscure.

The previous papers [3, 4] concerned kinetic mechanistic studies on the radiation-induced polymerizations of acrylonitrile in aqueous zinc chloride solutions, where emphasis was put on importance of formation and stabilization of zinc chloride-acrylonitrile complexes in the frozen aqueous solution and on the dual role of zinc chloride as a reagent for complex formation and also as a source of initiating species on irradiation.

Acrylonitrile (AN) can form complexes with zinc chloride to be isolated as crystalline $ZnCl_2$ -AN (1:2 in molar ratio) and amorphous (1:1) complexes [1, 2].

In the present paper, the thermal behavior of these complexes was examined by using differential thermal analysis (DTA). A comparison of polymerizabilities of the crystalline and the amorphous complexes was made in bulk and in their benzene solutions, and effect of phase difference of these complexes was discussed. Furthermore, examination of the effect on the polymerization of such additives as water and methanol coordinated to zinc cation, together with radioactivation analysis (RAA) of polymers obtained, provided information on the initiation mechanism.

EXPERIMENTAL

AN was washed with 5% NaOH, 5% H₃PO₄, and finally with water and dried over K₂CO₃, and then distilled fractionally. Zinc chloride and bromide of reagent grade were dried at about 150°C for about 7 hr under reduced pressure immediately before use. Water was distilled over acid permanganate, alkaline permanganate after refluxing overnight, and finally distilled without the salt. Methanol (MeOH), acetic acid (HAc), benzene (BZ), and N,N-dimethylformamide (DMF) were standard reagent grade chemicals.

The crystalline ZnCl₂-AN complex was prepared by dissolving zinc chloride in excess AN and cooling the solution to precipitate the crystalline product. The crystalline complex was distilled for about 15 hr under reduced pressure at room temperature to yield the amorphous complex. Benzene solutions of the complexes were prepared according to the method of Hirai [5].

A glass ampoule containing the complex was sealed off under reduced pressure ($< 10^{-4}$ Torr) and irradiated at required temperatures by using γ -rays from a Co-60 source. Polymers were washed with dilute HCl, water, and finally with methanol. To complete purification dried polymers were dissolved in DMF and precipitated in methanol repeatedly.

The molecular weights \bar{M}_v of polymers were determined by viscometry. The viscosities of polymer solutions were measured with an Ubbelohde-type dilution viscometer in DMF at 25°C. The molecular weight was estimated by using the relationship [6]:

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

DTA thermograms of the complexes and their benzene solutions were recorded on Shimadzu DT-20B instrument. Samples in the usual range of 3 to 15 mg were placed in small platinum pans and quenched in liquid nitrogen. The analyzer operated in the range -120 to 40°C. All runs were made at a scanning rate of 2°C/min under a helium gas atmosphere.

The bromine contents of polymers were quantitatively determined by the radioactivation analysis method as described in previous papers [7]. Purification of polymers for the analysis was completed by five cycles of the dissolving-precipitating procedure described above.

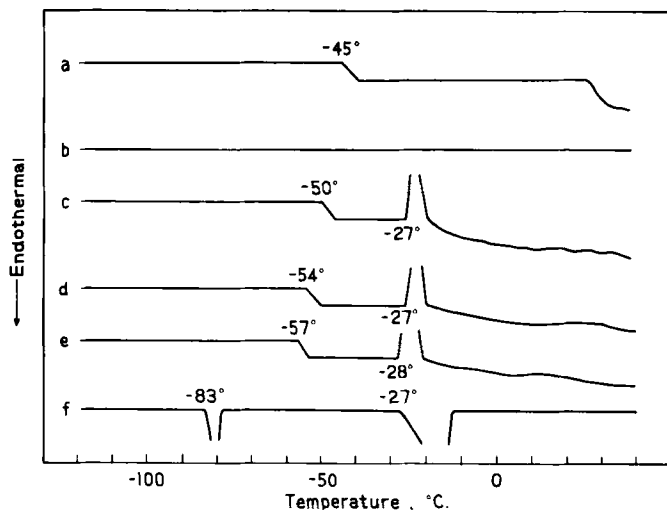


FIG. 1. DTA curves of ZnCl_2 -AN complexes and their benzene solutions: (a) ZnCl_2 :AN = 1:1; (b) ZnCl_2 :AN = 1:2; (c) ZnCl_2 :AN:BZ = 1:1:1; (d) ZnCl_2 :AN:BZ = 1:2:2; (e) ZnCl_2 :AN:BZ: H_2O = 1:2:2:0.2; (f) AN:BZ = 1:1.

RESULTS

DTA of ZnCl_2 -AN Complexes and Their Benzene Solutions

Thermal properties of two types of ZnCl_2 -AN complexes and of their benzene solutions were analyzed by DTA. Although the 1:1 complex appears to be an amorphous solid at room temperature, its DTA curve showed the presence of a glass transition temperature T_g at -45°C and a melting range at about 27°C (see Fig. 1a). The 1:2 complex is a crystalline solid with a melting point T_m at about 40°C . The benzene solutions of both type complexes, ZnCl_2 -AN-BZ (1:1:1) and (1:2:2) solutions, have T_g at -50 and -54°C , respectively, as shown in Fig. 1c and 1d. Both solutions, with crystallization temperature T_c at -27°C , melt gradually above T_c . Addition of small amount of water to the benzene solution results in slight lowering of T_g and T_c (see Fig. 1e). Consequently, the 1:1 complex is in a liquid or

supercooled liquid state in the polymerization temperature range 30 to -35°C and the 1:2 complex is in a liquid state, while the benzene solutions are viscous liquids in the polymerization range 30 to 0°C . The complexes do not dissociate in the benzene solution [4], although they do partly in the aqueous medium.

Temperature Dependence of Polymerization

Figure 2 shows time-conversion curves of the polymerization of the 1:1 and 1:2 type complexes at 30, -35 , and -78°C . The rate of polymerization is greater for the 1:1 complex than for the 1:2 type at each temperature. The temperature dependence of the rate of polymerization is shown in Fig. 3. The rates of polymerization decrease with decreasing temperature, with an apparent activation energy E of 0.26 kcal/mole for the 1:1 type in the range 30 to -35°C and 0.52 kcal/mole for the 1:2 type in the range 30 to -78°C . Besides, decreasing temperature tends to increase the degrees of polymerization slightly, as seen in Table 1.

Time-conversion curves for the benzene solutions of the complexes are shown in Fig. 4. The rate of polymerization of the 1:1 type is also found to be greater than that of the 1:2 type, even in their benzene solutions where no crystalline structural effect is expected to be operating.

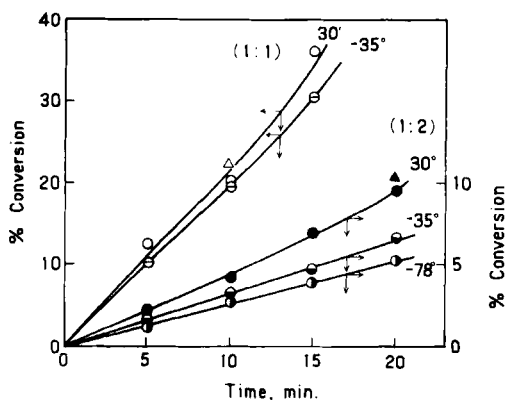


FIG. 2. Time-conversion curves of the polymerization of ZnCl_2 -AN complexes at various temperatures at a dose rate of 2.79×10^4 r/hr: (\circ , \ominus) ZnCl_2 -AN (1:1) complex; (\bullet , \ominus , \bullet) ZnCl_2 -AN (1:2) complex; (Δ) ZnBr_2 -AN (1:1) complex; (\blacktriangle) ZnBr_2 -AN (1:2) complex.

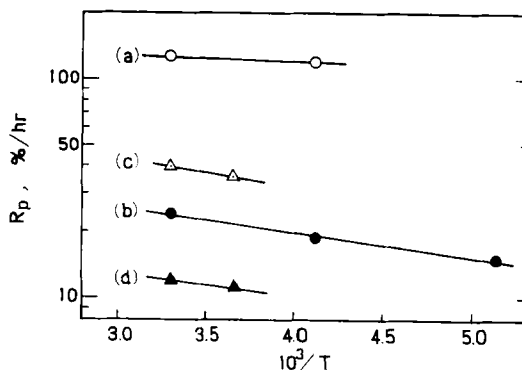


FIG. 3. Temperature dependence of the polymerization rate of $ZnCl_2$ -AN complexes at a dose rate of 2.79×10^4 r/hr: (a) $ZnCl_2$ -AN (1:1) complex; (b) $ZnCl_2$ -AN (1:2) complex; (c) $ZnCl_2$ -AN-BZ (1:1:1) complex solution; (d) $ZnCl_2$ -AN-BZ (1:2:2) complex solution.

Decreasing temperature slows the rates of polymerization but increases slightly the degrees of polymerization (see Fig. 3 and Table 1). The rates and the degrees of polymerization are greater with the complexes in bulk than with their benzene solutions.

Dose Rate Dependence of Polymerization Rate

The dose rate dependence of the rate of polymerization was examined for each complex at $30^\circ C$. The dose rate exponents were found to be 0.88 and 0.99 for the 1:1 type and 1:2 type, respectively, as shown in Fig. 5. The 0.99-power dependence in the 1:2 type complex suggests unimolecular termination common to solid-state polymerizations. The 0.88-power dependence in the 1:1 type shows coexistence of bimolecular termination beside unimolecular termination, which implies similarity of the system to a highly viscous liquid, in accordance with the DTA result mentioned above.

The rates of polymerization in the benzene solutions are proportional to the 0.84 and 0.76 power of dose rate in the 1:1:1 and 1:2:2 solutions, respectively. This suggests coexistence of unimolecular and bimolecular terminations in the systems of viscous liquids.

Effect of Additives on Polymerization

Effect of such additives as water, methanol, and acetic acid on the polymerization of the $ZnCl_2$ -AN complex was investigated at $30^\circ C$.

TABLE 1. Polymerization of $ZnCl_2$ -AN 1:1 and 1:2 Complexes and Their Benzene Solutions^a

Composi- tion of complex (mole ratio)	Tempera- ture (°C)	Time (min)	Conver- sion (%)	$\bar{M}_V \times 10^{-6}$	G_i (maxi- mum) ^b	
$ZnCl_2$ -AN (1:1)	30	5	12.4	1.10	25	
		10	20.2	1.08	21	
		15	36.0	1.12	24	
	-35	5	10.2	1.91	12	
		10	19.6	1.93	12	
		15	30.5	1.94	12	
	(1:2)	30	5	2.2	0.90	8.6
			10	4.2	0.91	8.2
			15	7.0	0.88	9.3
			20	9.4	0.91	9.1
		-35	5	1.6	0.98	5.8
			10	3.1	1.01	5.4
			15	4.7	1.03	5.4
			20	6.5	1.02	5.6
		-78	5	1.1	1.09	3.6
10			2.7	1.13	4.2	
15			3.8	1.18	3.8	
20			5.2	1.23	3.7	
$ZnCl_2$ -AN-BZ (1:1:1)	30	5	3.4	0.88	6.2	
		10	6.7	0.88	6.1	
		15	9.8	0.89	5.9	
	0	5	2.9	0.89	5.2	
		10	6.1	0.90	5.4	
		15	9.0	0.90	5.3	
	(1:2:2)	30	5	0.8	-	-
			10	2.0	0.57	3.8
			15	3.0	0.57	3.8
			20	3.9	0.58	3.6
		0	10	1.7	-	-
			15	2.8	0.60	3.3
		20	3.7	0.61	3.3	

^aDose rate 2.79×10^4 r/hr.^bBased on total energy absorbed by the complex or the solution and calculated by using $\bar{M}_n = \bar{M}_V/1.89$.

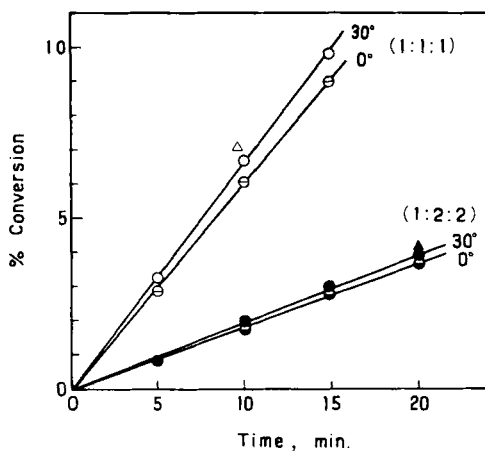


FIG. 4. Time-conversion curves of the polymerization of ZnCl_2 -AN complexes in benzene solutions at a dose rate of 2.79×10^4 r/hr: (\ominus , \circ) ZnCl_2 -AN-BZ (1:1:1); (\bullet , \bullet) ZnCl_2 -AN-BZ (1:2:2); (Δ) ZnBr_2 -AN-BZ (1:1:1); (\blacktriangle) ZnBr_2 -AN-BZ (1:2:2).

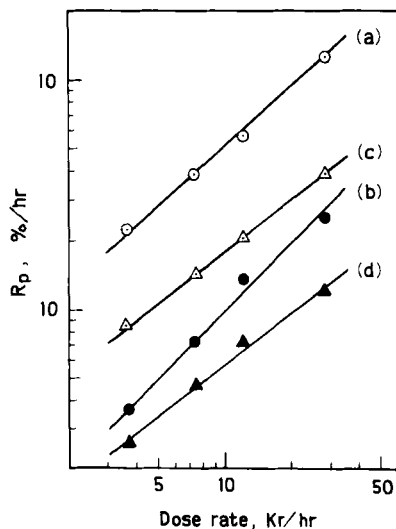


FIG. 5. Dose-rate dependence of the polymerization rate of ZnCl_2 -AN complexes at 30°C : (a) ZnCl_2 -AN (1:1) complex; (b) ZnCl_2 -AN (1:2) complex; (c) ZnCl_2 -AN-BZ (1:1:1) complex solution; (d) ZnCl_2 -AN-BZ (1:2:2) complex solution.

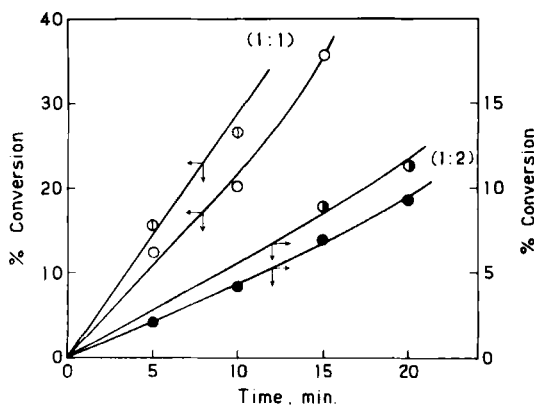


FIG. 6. Effect of water addition on the polymerization of ZnCl_2 -AN complexes at 30°C at a dose rate of 2.79×10^5 r/hr: (\circ) ZnCl_2 -AN (1:1); (\bullet) ZnCl_2 -AN (1:2); (\odot) ZnCl_2 -AN- H_2O (1:1:0.2); (\ominus) ZnCl_2 -AN- H_2O (1:2:0.2).

Addition of a small amount of water to the 1:1 and 1:2 complexes increases the rate of polymerization, although water addition causes inhomogeneity of the systems (Fig. 6).

Addition of a small amount of water, methanol, or acetic acid to the benzene solutions of the complexes does not disturb homogeneity of the solutions. Addition of these additives to the 1:2:2 solution results in an increase of the rate of polymerization, the increment decreasing in the order, $\text{H}_2\text{O} > \text{MeOH} > \text{HAc}$, as shown in Fig. 7 and Table 2.

On the other hand, as these additives partially dissociate the complexes, a complex index J , as a measure of the concentration of AN complexed with zinc cation, was obtained by IR measurements. J is defined as $D_{2270} / (D_{2270} + D_{2235})$, where D_{2235} and D_{2270} stand for infrared absorbances of the bands at 2235 and 2270 cm^{-1} of free and complexed AN, respectively. The results are listed in Table 3. Each additive decreases the J value, to show a decrease in concentration of AN complexed. Since the rate of polymerization increases with increasing concentration of AN complexed [4], the presence of the additives is expected to decrease the rate of polymerization. In spite of this expectation, the rate of polymerization increases on addition of the additives, which suggests a large contribution of additive molecules to formation of the initiating species on irradiation and consequently to an increase of the initiation rate. Table 2 shows the increase in G_1 , the G value of initiation, on addition of the additives.

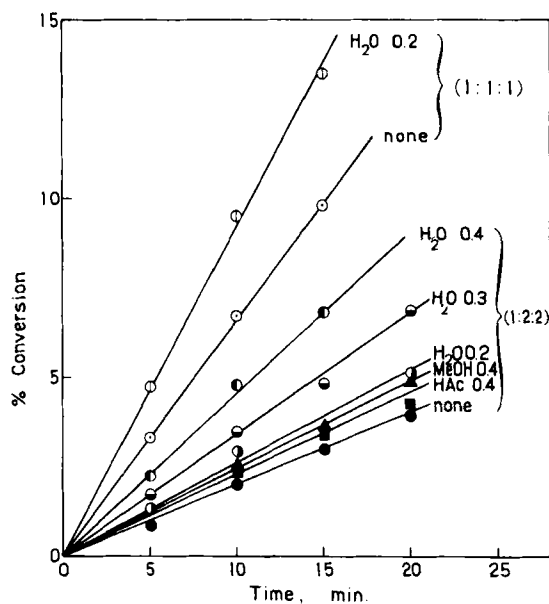


FIG. 7. Effect of additives on the polymerization of ZnCl_2 -AN complexes in benzene solutions at 30°C at a dose rate of 2.79×10^4 r/hr: ZnCl_2 -AN-BZ-additive (1:1:1:x), (\odot) none, (\oplus) H_2O , 0.2; ZnCl_2 -AN-BZ-additive (1:2:2:x), (\bullet) none, (\ominus) H_2O , 0.2, ($\omin�$) H_2O , 0.3, ($\omin�$) H_2O , 0.4, (\blacktriangle) MeOH, 0.4, (\blacksquare) HAc, 0.4.

G_1 calculated here is a maximal value, since chain transfer and polymer chain scission by irradiation are not taken into account.

Radioactivation Analysis of Polymers

Halogen contents of polymers were measured by radioactivation analysis (RAA) in order to evaluate contribution of the radical species $\text{X}\cdot$ produced from the irradiated halogen anion X^- to the initiation reaction. If it is assumed that chain transfer is negligible and that all growing chains are initiated by $\text{X}\cdot$, we expect the number N_{X} of halogen atoms per polymer chain to be maximally 1 or 2, depending on whether unimolecular or bimolecular termination is involved. Polymers for RAA were prepared from the polymerization of the ZnBr_2 -AN complexes because bromine is more advantageous in

TABLE 2. Effect of Additives on the Polymerization of $ZnCl_2$ -AN Complexes^a

Additive	Conversion (%)	$\bar{M}_n \times 10^{-5b}$	R_p (%/hr)	G(i) (maximum)
$ZnCl_2$:AN:H₂O				
1:1:none	20.2	5.7	121	21
0.2	26.8	5.6	169	29
1:2:none	4.2	4.8	25.2	8.2
0.2	8.8 ^d	4.6 ^d	31.5	12 ^d
$ZnCl_2$:AN:BZ:H₂O				
1:1:1:none	6.7	4.7	39.6	6.1
0.2	9.5	4.6	55.2	8.7
$ZnCl_2$:AN:BZ:additive				
1:2:2:none	2.0	3.0	12.0	3.8
H ₂ O 0.2	2.9	2.9	15.6	5.7
H ₂ O 0.3	3.5	2.6	20.4	7.7
H ₂ O 0.4	4.8	2.2	27.3	12
MeOH 0.4	2.5	2.9	14.7	5.0
HAc 0.4	2.4	3.0	13.7	4.6

^aPolymerization at 30°C, dose rate 2.79×10^4 r/hr, total dose 4.65×10^3 r.

^bEstimated from \bar{M}_v as $\bar{M}_n = \bar{M}_v/1.89$.

^cBased on total energy absorbed by the complex or the solution.

^dAt total dose 6.98×10^3 r.

TABLE 3. Effect of Additives on Complex Formation

Additive (mole ratio)	Complex index J^a
ZnCl ₂ :AN:BZ: Additive	
1:2:2:none	1.0
H ₂ O 0.2	0.74
H ₂ O 0.4	0.71
MeOH 0.4	0.70
HAc 0.4	0.57

^a Measured at 20°C.

analytical operations than chlorine. The ZnBr₂-AN complexes have almost same rates of polymerization as the ZnCl₂-AN complexes (see Figs. 2 and 3).

Observed N_{Br} values for polymers obtained from the ZnBr₂-AN complexes, their benzene solutions, and benzene solutions containing added water are summarized in Table 4. Polymers obtained from the 1:1 and 1:2 complexes have N_{Br} values of 0.20-0.21, and those obtained from the benzene solutions have N_{Br} in the range 0.16-0.19, which demonstrates the small contribution by addition of a bromine radical Br· to the monomer molecule to initiation. That water addition decreases N_{Br} to 0.13-0.06 implies a large contribution of water molecules to production of initiating species.

DISCUSSION

The reason why the 1:1 complex has larger rate of polymerization than the 1:2 type of complex might be either a difference in their phase or a difference in the relative concentration of ZnCl₂ to AN. The finding that the 1:1 type complex has also the larger rate in the benzene solutions in which both types show close thermal behaviors implies that the origin of the rate difference is the relative concentration of ZnCl₂ to AN.

Addition of the additives to the benzene solution of the 1:2 type complex causes partial dissociation of the complex. The J values, as a measure of dissociation, indicate that water and methanol

TABLE 4. Number of Br Atoms per Polymer Chain by Activation Analysis

Composition of complexes (mole ratio)	Polymerization temperature ($^{\circ}\text{C}$) ^a	Conversion (%)	$\bar{M}_n \times 10^{-5b}$	No. Br atoms per chain NBr
ZnBr₂:AN:H₂O				
1:1:none	30	22.9	5.9	0.20
1:2:none	30	10.1	4.9	0.21
	-78	33.6	11.3	0.24
1:1:0.2	30	27.8	5.4	0.13
1:2:0.2	30	14.2	4.6	0.12
ZnBr₂:AN:BZ:additive				
1:1:1:none	30	7.1	4.9	0.16
1:2:2:none	30	4.1	3.1	0.19
1:1:1:H ₂ O 0.2	30	9.4	4.6	0.11
1:2:2:H ₂ O 0.2	30	5.3	3.0	0.13
H ₂ O 0.4	30	6.1	2.4	0.06
MeOH 0.4	30	5.1	2.9	0.12

^aDose rate 2.79×10^4 r/hr.^bEstimated from \bar{M}_v as $\bar{M}_n = \bar{M}_v/1.89$.

TABLE 5. Donicities DN and G Values of Ligands

Ligand	DN ^a	G(R·)
BZ	0.1	0.76 ^b
H ₂ O	18.0	6.6 ^c
MeOH	19.1	6.1 ^d , 6.3 ^e
HAc	-	3.7 ^d
AN	(12-16)	0.8-1.9 ^f , 0.5 ^g

^aData of Mayer and Gutmann [8].

^bData of Swallow [9].

^cData of Ausloos [10].

^dData of Adams et al. [11].

^eData of Baxendale and Mellows [12].

^fData of Bouby [13].

^gData of Brandrup and Immergut [14].

dissociate the complex to nearly the same extent, which is in accordance with close "donicity" DN [8] values of 18.0 and 19.1 of water and methanol, respectively (see Table 5).

Table 2 shows addition effect of water, methanol, and acetic acid on G_i values. The rate enhancement by the additives is caused by an increase of initiation rather than by a decrease in termination. The order of increasing G_i values is H₂O > MeOH > HAc. This order agrees with the order of G(R·), the G value for free radical yield of the additives (see Table 5). Furthermore, the large difference in G_i as water and methanol are added might tentatively be attributed to the difference in G(e⁻) values of 3.05 and 1.9 rather than in G(R·) values of 6.6 and 6.3 for water and methanol [10, 12], respectively. This suggests a considerable contribution of electrons to generate initiating species as monomer anion radicals AN⁻. The generation of the anion radical was confirmed by ultraviolet spectra in the irradiated 2-methyltetrahydrofuran glass containing AN and ZnCl₂ [15].

An endgroup analysis of polymers by means of RAA is valid for more direct estimation of the initiating species. If the chain transfer reaction is assumed negligible, a fraction f_x of initiation by an initiating species X· generated from a halogen ion X⁻ on irradiation can be estimated from the observed N_x value. As AN polymer radicals

terminate by recombination [16-18], f_x equals $N_x/2$ or N_x , depending on whether bimolecular or unimolecular termination is involved. The observed N_{Br} is 0.19 in the 1:2:2 complex solution, where unimolecular and bimolecular termination coexist, from which f_{Br} is estimated to be between 0.095 and 0.19, probably about 0.15. This considerably small f_{Br} shows that the major initiating species are other than the bromine radical $Br\cdot$. In this case the monomer anion radical $AN\dot{-}$ formed by electron absorption by complexed AN seems to contribute considerably to initiation, since as origins of radical species other than the bromine radical AN and BZ have relatively small $G(R\cdot)$ values as seen in Table 5.

In the case of the 1:2:2 solution with added water at 0.2 mole ratio, a rate of increase of G_i , $(G - G_0)/G_0$ is equal to 0.50, where G and G_0 are G_i values with and without added water, respectively. The fractional contributions, therefore, of Cl^- and H_2O to initiation are 0.67 and 0.33, respectively. The same fractional contribution to initiation and same f_x value for both chloride and bromide are assumed; then the former of 0.67 and the latter of 0.15 give an expected N_{Br} of 0.10, which agrees considerably well with the observed N_{Br} of 0.13. Similarly, expected N_{Br} values of 0.05 and 0.11 in the cases with added water of 0.4 mole ratio and with added methanol of 0.4 mole ratio are in relatively good agreement with observed values of 0.06 and 0.12, respectively.

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