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The Kinetic Study of Copolymerization of Acrylonitrile with Allyl Alcohol in Concentrated Zinc Chloride Aqueous Solution with the Aid of a Computer

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SUMMARY

This paper presents a kinetic study of the copolymerization of acrylonitrile (AN, M_1) with allyl alcohol (AOH, M_2) in zinc chloride aqueous solution. The monomer reactivity ratios, r_1 and r_2, determined by application of the Lewis-Mayo equation to the system, are 1.60 and 0.01, respectively. The observed value of copolymer composition agrees well with one calculated by use of computer up to higher conversion. This means that the Lewis-Mayo equation may be applicable to the present system. The possibility of homopolymerization of AOH, confirmed empirically, is also sustained by numerical calculation.

INTRODUCTION

Acrylonitrile (AN) is easily changed into a high molecular weight polymer in concentrated zinc chloride aqueous solution even at low temperature

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under atmospheric pressure with radical initiator [1-4]. Various kinds of quinones which act as typical inhibitors in other solvents behave like accelerators in this system. Cupric ion, which is known to have a large effect in the system of chlorate–sulfite redox initiator in water on the rate of polymerization and the molecular weight of polymer [5], shows no remarkable effect when used in the system with the initiator in the present solvent [6].

The unusually large tendency of AN to polymerize in this solvent will be reduced to a complex formation of the monomer with the solvent, which has been demonstrated by various means, i.e., infrared (IR) [4, 7] and ultraviolet (UV) spectra, the viscosity behavior of monomer–solvent solution [1], and the dependence of solubility of monomer on the concentration of zinc chloride [8]. It is therefore reasonable to think that AN monomer exists in the solvent in at least two forms of free and complex states.

While some authors [1-3] have reported that the rate of AN polymerization in the solvent depends anomalously on the concentration of the reactant, others [4] have thought the dependence is a normal one generally found in radical polymerization. In the copolymerization of AN and ethylene sulfonic acid in the solvent, each of the monomers is linearly consumed with time [9]. This fact shows that it is possible to analyze the system by the usual kinetic treatment, but it has not been confirmed that the Lewis-Mayo equation can be applied to the system. In addition to the two forms of AN theoretically possible in the solvent, the comonomer may also exist in two forms of acid and anion.

It is one purpose of this study to determine if the Lewis-Mayo equation is valid in the copolymerization system of AN (M_1) with allyl alcohol (AOH, M_2) in zinc chloride aqueous solution. The other purpose is to find if the homopolymerization of AOH may occur in the solvent giving a small finite value of r_2, which will be derived based on empirical data of solution viscosity and calculated sequence length of AOH units.

EXPERIMENT AND COMPUTATION

Materials

AN monomer (bp 77.5°C) and AOH monomer (bp 96.3°C) were dried and distilled over CaH_2 and anhydrous Na_2SO_4, respectively.

Zinc chloride aqueous solution to be employed for the solvent was prepared by reacting zinc oxide with azeotropically distilled HCl aqueous solution, followed by evaporating excess water by heating until the concentration of zinc chloride became 60 wt%. Except for special case, the concentrations of zinc oxide, Fe^{2+}, and Cu^{2+} were brought to 0.02, 1.5×10^{-4} and 0.45×10^{-5} wt%, respectively.

Ammonium persulfate (APS) and sodium sulfite (SS) of Purissium grade were used without further purification.

Copolymerization

The total concentration of feed comonomers of AN and AOH kept constant at 10 vol% throughout the experiment. It is necessary to carry out the experiment of copolymerization at low temperature because AOH is easily hydrogen-extracted by chain radicals. APS-SS was selected as initiator for the redox system, whose temperature was set at 20°C.

SS- and APS-zinc chloride aqueous solutions were added 10 min after the monomer mixture was added to the solvent kept at 20°C. The molar ratio of $[SS]_0/[APS]_0$ was always 1.81. The experiment was carried out in batch under atmospheric pressure. In every designated time after the addition of initiator, the whole or one portion of the system was placed into excess water made weakly acidic with acetic acid. The precipitated polymer was washed by weakly acidic water repeatedly, and further by pure water until the filtrate did not show acidic, and then dried in vacuo.

The conversion was determined gravimetrically. As shown in the following section, the loss of copolymer due to washing was negligible.

Determination of Copolymer Composition

The copolymer composition determination for calculating the apparent monomer reactivity ratio was based on the results of elemental analysis of the copolymer. Typical IR spectra of copolymer and polyacrylonitrile between 1000 and 1600 cm^{-1} are shown in Fig. 1. The IR spectra were taken with KBr-disk. The plot of the ratio $D_{1040}cm^{-1}/D_{1460}cm^{-1}$ against the composition shows good linearity, at least above 80 mole-% AN content, as shown in Fig. 2. The absorption bands at 1040 and 1460 cm^{-1} corresponds to $-OH$ and $-CH_2-$ groups, respectively. The value of the ratio extrapolated to AN 100% did not fall to 0, while the one observed for the homopolymer showed good agreement with the extrapolated one. The copolymer composition in the other cases was determined by the calibration curve in Fig. 2.

Table 1. Result of Copolymerization of AN with AOH in 60 wt.% Zinc Chloride Aqueous Solution at 20°C with APS-SS[a]

No.	$[AOH]_0$ (mole-%)	Time (min.)	Conv. (%)	[η] in DMF at 30°C	[AOH] in copolymer mole %
1[b]	0	2.0	5.7	7.89	0
2[b]	4.85	2.6	5.4	3.99	1.3
3[b]	9.70	2.5	4.1	–	4.9
4[b]	14.59	6.5	5.2	–	8.7
5[b]	19.49	6.5	2.9	–	12.0
6[c]	29.32	15.0	8.5	0.90	17.4
7[c]	36.24	17.5	5.7	–	20.9
8[c]	49.20	23.0	5.7	–	26.7

[a] Solvent contains ZnO, Fe^{2+}, and Cu^{2+} in the concentrations 0.03, 1.6×10^{-5}, and 0.15×10^{-5} wt.%, respectively.

[b] $[APS]_0 = 5 \times 10^{-3}$ mole/l, $[SS]_0/[APS]_0 = 1.81$.

[c] $[APS]_0 = 10 \times 10^{-3}$ mole/l, $[SS]_0/[APS]_0 = 1.81$.

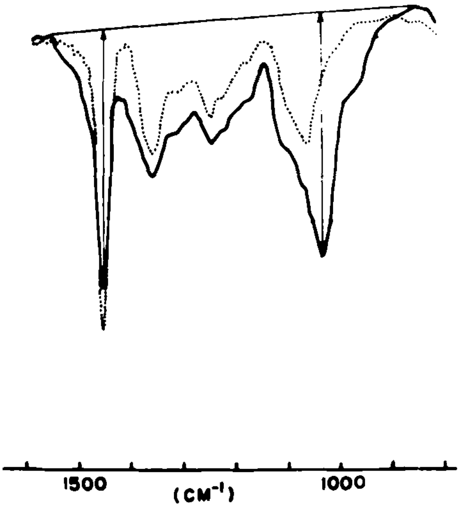

Fig. 1. Typical infrared spectra of copolymer containing 17.4 mole % AOH (solid line) and homopolymer of AN (dotted line).

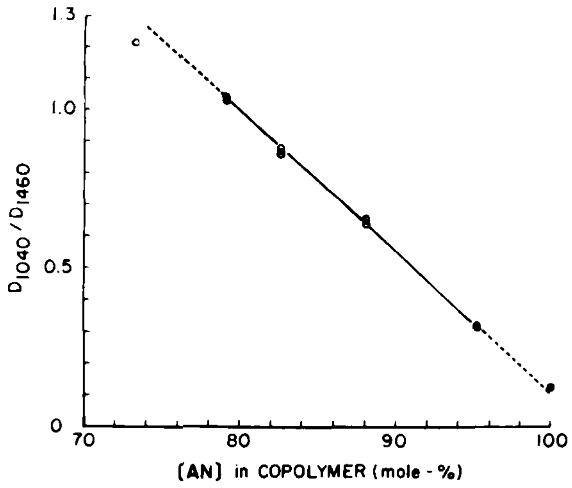

Fig. 2. The relationship of D-ratios and copolymer compositions.

Molecular Weight

The intrinsic viscosity, $[\eta]$, of the solution of polymer in N, N-dimethylformamide was determined with a Ubbelohode dilute viscometer.

The molecular weight of polyacrylonitrile, if necessary, was determined by Onion's equation [10] with $[\eta]$ measured at 25°C:

$$[\eta] = 3.93 \times 10^{-4} \bar{M}_n^{0.75} \tag{1}$$

In the other cases, $[\eta]$ at 30°C was used as a measure for the molecular weight of copolymer.

Solution Viscosity

The solution viscosity of the system in zinc chloride aqueous solution was measured with an Ostwald viscometer at 20°C.

Calculation by Computer

The calculation was made with an IBM 360 system (capacity, 64 kbytes). The calculation program was by FORTRAN IV. The calculation was carried out to obtain the instantaneous and average value of both the composition and the sequence length of monomer units of copolymer obtained at every designated conversion. The calculation was made by iterative use of the Lewis-Mayo equation in differential form with a small fixed conversion increment of 0.005 and 0.05 wt.%. The calculated results with the different conversion increments were in good agreement with each other within the computer's output (Table 3). The discussion is based on the result obtained with 0.005 wt.% increments. The calculated result was determined at every 5 wt.% of feed and at each point where 95, 99.0, and 99.9 mole-% of AN monomer was consumed. If necessary, the values at other conversions could be determined by interpolation or by extrapolation.

RESULTS

Solution Viscosity of Monomer–Zinc Chloride Aqueous Solution

The change in solution viscosity with the addition of monomer to solvent was measured at 20°C, which is shown as a relative value in Fig. 3. In the case of AN, as already reported [1], the viscosity increases with monomer concentration to a maximum point, after which it decreases. When AOH is added to solvent, the viscosity increases monotonically at a higher rate than in the case of AN, within the range of experimental conditions, suggesting the monomer might also be present in a different state in the solution, about which nothing can be mentioned here.

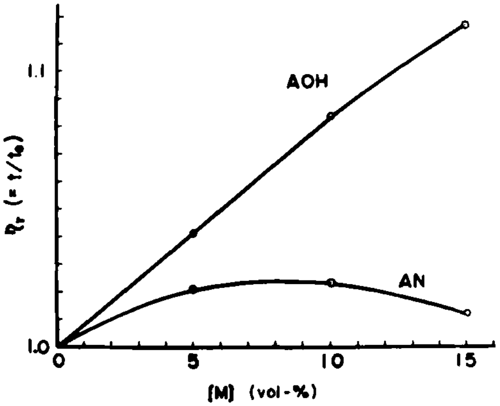

Fig. 3. Viscosity of 60 wt% zinc chloride aqueous solutions with AN and AOH, respectively.

Determination of Monomer Reactivity Ratio, r_1 and r_2

Under the assumption that the Lewis-Mayo equation may be applied to the system, r_1 and r_2 were determined based on the measured composition of copolymer obtained at low conversion. A Fineman-Ross plot is shown in Fig. 4. The values of the ratios r_1 and r_2 are 1.60 and 0.01, respectively, and were obtained by applying the least square method to the lower five points given in Fig. 4.

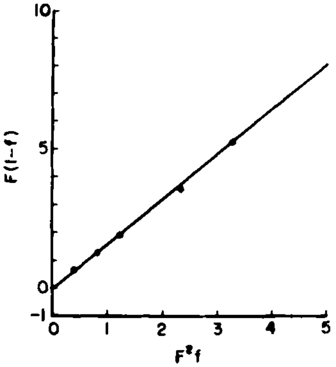

Fig. 4. Fineman-Ross' plots, where F and f are $[M_1]_0/[M_2]_0$ and $d[M_2]/d[M_1]$, respectively.

Solution Viscosity of AOH–Zinc Chloride Aqueous Solution with Initiator

The viscosity of the solution in which AOH was initially present increased with time and became finite value with addition of the initiator to the system, as shown in Fig. 5, where the viscosity is represented by the ratio of dropping time of solution in the viscometer to that of the system without initiator. This increase in viscosity may surely be ascribed to homopolymerization of AOH.

Degree of Polymerization of Initial Polymer Produced When $[M_1]_0 \gg [M_2]_0$

In order to investigate the mode of introduction of AOH into the copolymer, the degree of polymerization of copolymer produced when $[M_1]_0 \gg [M_2]_0$ was measured. The polymer obtained at low conversion can be regarded in this case as a homopolymer of AN (M_1). The result is listed in Table 2.

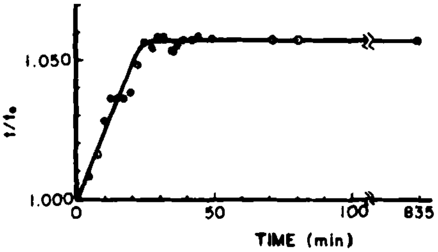

Fig. 5. Change of viscosity with time of AOH-zinc chloride aqueous solution after initiator is added at 20°C. $[AOH]_0 = 9.9$ vol.%, $[APS]_0 = 6 \times 10^{-3}$ mole/l, $[SS]_0/[APS]_0 = 1.81$.

Table 2. Copolymerization under the Condition of $[AN]_0 \gg [AOH]_0$ at 20°C[a]

$[AOH]_0/[AN]_0$ × 10^3	Time (sec.)	Conv. (%)	Conv./time (%/sec.)	$\overline{DP} \times 10^{-3}$	$1/\overline{DP} \times 10^4$
0	60	6.1	0.101	7.19	1.39
3.45	120	10.2	0.085	5.84	1.71
6.67	120	8.0	0.067	5.37	1.86
10.23	120	7.2	0.060	4.22	2.37
13.56	135	8.9	0.066	3.98	2.51
20.31	170	9.5	0.056	3.02	3.31

[a] $[APS]_0 = 5 \times 10^{-3}$ mole/l, $[SS]_0/[APS]_0 = 1.81$.

Copolymerization

Time-conversion curves at $[M_2]_0 = 20$ and 30 mole-% are shown in Fig. 6, where no induction period is found. Notwithstanding that AOH is generally known to promote degradative chain transfer reaction, it has been remarked that the final conversion obtained is relatively high. The presence of AOH in the system has lowered the copolymerization rate (%/sec) as well as the molecular weight (Table 2).

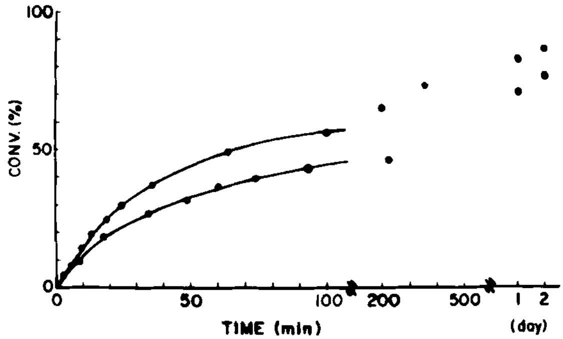

Fig. 6. Time-conversion curves at 20°C where total monomer concentration is 10 vol.%. $[AOH]_0$; 19.7 (○) and 29.7 (●) mole % in monomer mixture. $[APS]_0 = 5 \times 10^{-3}$ mole/l. $[SS]_0/[APS]_0 = 1.81$.

The conversion is given by the ratio (%) of the weight of polymer insoluble to water to that of the feed monomer mixture. In order to check that no soluble polymer could have escaped into water to give an apparent lower value of conversion than the true one, the final conversion of the system was investigated with various concentrations of initiator, especially at $[M_2]_0 = 20$ mole-% (Tables 4 and 5). It was demonstrated that the higher was initiator concentration, the lower was the molecular weight of the polymer produced. At the same time, the higher the conversion, the richer in AOH units was the copolymer. If any soluble polymer was produced, therefore, it would have been produced at higher conversion and/or with the higher concentration of initiator. An increase in the concentration of initiator would have resulted in a decrease of the final conversion. But this was not the case, as shown by Tables 4 and 5. Therefore, it can be concluded that the conversion values given in Tables 1 and 2 and in Fig. 6 are substantially the true ones.

Calculation by Computer

There are two methods by which a computer can be applied to the elucidation of the process of copolymerization at high conversion. One is by employing the Lewis-Mayo equation in integral form, which has been developed by several authors [11-15]. The other is known as iterative use of differential form, as proposed by Harwood [16]. Since the latter includes a simpler equation than the former, being appropriate to obtain continuously an output of the calculated data at any designated conversion, we have applied the latter to this study.

As indicated in the Experiment and Computation Section, we first selected 0.005 and 0.05 wt% as conversion increments in the calculations to confirm agreement between the results given by two different increment values. As shown in Table 3, good agreement has been demonstrated in the values corresponding to the range of experimental error.

Table 3. Calculated Composition with Two Different Increments for the System where $[M_1]_0$ = 70.3 mole % in Monomer Mixture

Increment	AN (mole-%) in copolymer at wt-conv.		
(wt.%)	85%	90%	A%[a]
0.005	76.94	75.99	75.18
0.05	76.93	75.98	75.18

[a] The conversion at which 99.9 mole % of $[M_1]_0$ has just been consumed. The value A lies in the range 92.68 to 93.00 wt%.

Figure 7 and Tables 4 and 5 show the comparison of observed values of composition with the calculated ones. The calculated conversion at which AN monomer feed in various amount was consumed up to 99.9 mole-% is also indicated in Fig. 7. The other calculated results are shown in Figs. 8 and 9.

DISCUSSION

By various means, such as IR and UV spectra and solution viscosity, it has been shown that AN monomer may be present, at least partly, in the

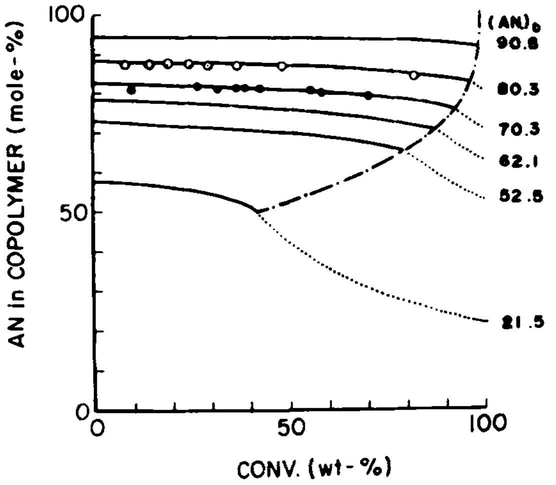

Fig. 7. Relationship between copolymer composition and conversion (experimental points are the same as in Fig. 6, and calculated lines are solid and dotted), and calculated conversion where fed AN has been consumed up to 99.9 mole %, (broken line).

form of a complex in zinc chloride aqueous solution. It is, therefore, of interest to determine if a general kinetic treatment in radical polymerization can be applied to the homo- and copolymerization of AN in the solvent, at least in the propagation step.

Alfrey and Pfeifer [9] have found that both monomers were consumed in agreement with first-order kinetics in the copolymerization of AN with ethylene sulfonic acid in 60 wt% zinc chloride aqueous solution, but they have not confirmed the application of the Lewis-Mayo equation to the system. If the comonomer may also be present in the two forms of acid and anion, sixteen types of propagation reaction should be, in principle, considered in their system.

In order to simplify this point, AOH, which is a nonconjugated monomer, has been selected in this work as comonomer. AOH itself may also be present in a complex state in the solvent, as shown in Fig. 3. The complex formation of allyl acetate with zinc chloride has been investigated by IR spectra [17] in which it has been found that a shift occurs only in the absorption bands assigned to the ester group. Consequently, it is reasonable to consider that complex formation may occur in the present case only with the –OH group of AOH with a

Table 4. Maximum Conversion and AN Content in Copolymer

$[AOH]_0$ (mole %)	$[APS]_0 \times 10^3$ (mole/l)	Conv. (wt%) at			AN (mole %)[b]		$[AN]_0$/conv.[b,c] × 100 (mole %)
		3 days	5 days	9 days	Obs.	Calc.	
0	2.5	–	100.0	–	–	100.0	–
”	7.5	–	100.0	–	–	100.0	–
”	12.6	–	100.0	–	–	100.0	–
19.7	2.5	73.5	75.6	74.2	85.1	85.4	–
”	5.0	86.8	88.0	88.1	84.6	84.1	–
”	7.5	91.2	93.8	92.5	83.9	83.4	–
”	10.1	91.1	94.5	93.4	84.2	83.2	–
”	12.6	93.4	94.5	95.1	83.7	82.9	84.1
”	”	–	94.6	–	82.8	83.0	84.5
”	15.1	–	94.7	–	83.1	83.0	84.4
”	17.6	–	95.8	–	82.6	82.8	83.5

[a] Copolymerized at 20°C under the condition $[SS]_0/[APS]_0 = 1.81$.

[b] Observed and calculated for polymers at underlined conversions.

[c] The conversion is a calculated molar value corresponding to the underlined weight conversion under the assumption that AN monomer has been consumed at the point.

Table 5. Maximum Conversion and AN Content in Copolymer[a]

$[AOH]_0$	$[APS]_0 \times 10^3$	Conv. (wt%) at			AN (mole %)[b]		$[AN]_0$/conv.[b, c]	$[\eta]$ in DMF[b]
(mole %)	(mole/l)	5 days	7 days	9 days	Obs.	Calc.	(mole %)	at 30°C
9.2	12.0	–	98.1	–	91.1	91.3	92.4	1.045
14.9	17.1	95.5	95.9	96.0	86.2	86.7	88.3	0.688
23.9	20.5	87.0	86.3	–	80.6	81.1	87.3	0.487
”	23.9	91.0	91.9	–	80.1	80.1	82.3	0.475
”	27.4	90.3	90.5	89.5	80.8	80.6	84.3	0.463
28.1	23.9	86.8	87.4	–	79.4	77.7	81.5	0.422
”	27.4	88.2	89.9	–	78.2	77.2	79.4	0.417
”	30.8	88.0	88.5	87.7	81.2	77.6	81.4	0.412
33.7	27.4	83.4	85.6	–	–	–	–	0.409
”	30.8	84.1	85.5	84.2	–	–	–	0.379
”	34.2	83.0	83.6	84.5	–	–	–	0.375
37.9	32.2	–	80.4	–	–	–	–	0.363
”	40.2	–	81.1	–	–	–	–	0.360
47.8	36.2	–	70.8	–	–	–	–	–
”	40.2	–	72.2	–	–	–	–	–
”	44.3	–	71.4	–	–	–	–	0.247

[a] Copolymerized at 20°C under the condition $[SS]_0/[APS]_0 = 1.81$.

[b] Observed and calculated for polymers at underlined conversions.

[c] The conversion is a calculated molar value corresponding to the underlined weight conversion under the assumption that AN monomer has been consumed at the point.

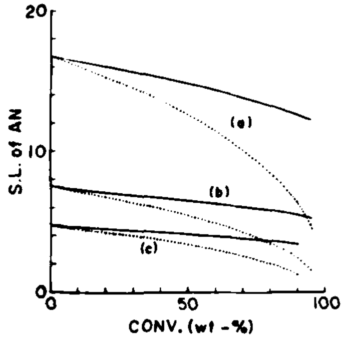

Fig. 8. Calculated relationship between average and instantaneous sequence length (solid and dotted lines, respectively) and conversion. $[AOH]_0$: (a) = 9.2; (b) = 19.7; (c) = 37.9 mole % in monomer mixture.

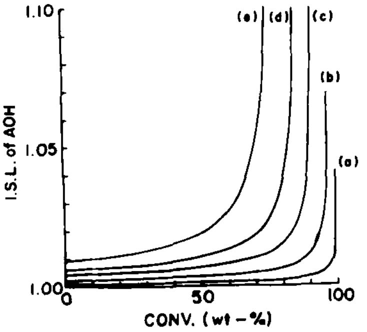

Fig. 9. Calculated relationship between instantaneous sequence length of AOH and conversion. $[AOH]_0$: (a) = 9.2; (b) = 19.7; (c) = 29.7; (d) = 37.9; (e) = 47.8 mole % in monomer mixture.

negligible effect on the chemical character of the double bond which is separated from the −OH group by the methylene group.

The apparent monomer reactivity ratios obtained in this paper (r_1 = 1.60, r_2 = 0.01) are both smaller than those in water (r_1 = 3.96 ± 0.13, r_2 = 0.11 ± 0.10 [18]. A similar effect of zinc chloride has been found in the copolymerization systems of AN-allyl compounds in ethyl acetate solvent [19]. Apparent Q and e values of AN in a so-called Q-e scheme are 9.35 and 2.34 in the present system, respectively, derived from the values of AOH given in the literature [20]. Both the values of Q and e are larger than those of free AN in the literature (Q = 0.60, e = 1.20). Even if these are apparent values, they suggest semiquantitatively that the complex formation may have been accompanied by a decrease in electron density at the double bond of AN and enlargement of the conjugation system, leading to a remarkable change in the nature of double bond.

Since allyl compounds easily suffer the chain transfer reactions which accompany degradation, AOH monomer will be introduced into the copolymer through the following reaction schemes:

$$\text{chain transfer: } \sim M_1\cdot + M_2 \xrightarrow{k_{tr_{12}}} \sim M_1 + M_2\cdot \qquad \text{(i)}$$

$$\text{recombination: } \sim M_1\cdot + M_2\cdot \longrightarrow \sim M_1 - M_2 \qquad \text{(ii)}$$

The upper value of $k_{tr_{12}}/k_{11}$ determined from the slope of the line in Fig. 10 is 8.5×10^{-3}, where k_{11} is the rate constant of propagation reaction of AN (see Appendix).

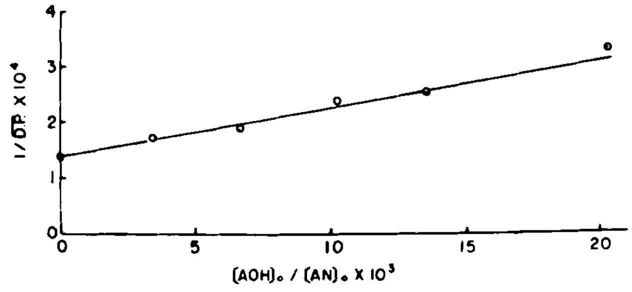

Fig. 10. $1/\overline{DP}$ vs $[AOH]_0/[AN]_0$

Since $1/r_1 = k_{12}/k_{11} = 0.625$, we have $k_{12}/k_{tr_{12}} = 73.2$. This means that AOH is introduced to the copolymer through propagation at least 73 times faster than through transfer (i) accompanying recombination (ii).

Figure 7 and Tables 4 and 5 show the comparison between the calculated and observed values of copolymer composition at high conversion. They are in good agreement with each other within experimental error.

As described under Results, any possible loss of soluble polymer is negligible. By comparing the final conversion with the calculated value at which M_1 has been consumed up to 99.9 mole % (Fig. 11), it was found that the latter was always larger than the former, with greater $[M_2]_0$. If the final conversion shows the value at which AN monomer has been consumed, the observed value of composition would be given by $[AN]_0$/final mole-conversion. Furthermore, if any soluble polymer did escape during the washing process, the observed value might be increased. The empirical data listed in Tables 4 and 5, however, show good agreement with the ones calculated by computer at any conversion.

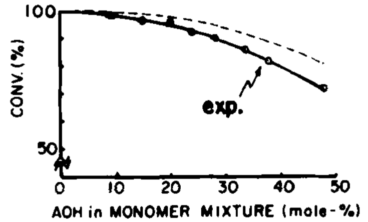

Fig. 11. Relationship between observed final conversion (solid line) and calculated conversion where fed AN has been consumed up to 99.9 mole %, (dotted line) at various monomer composition.

As mentioned above, it has been confirmed that the observed value of copolymer composition agrees well with the calculated one based on the Lewis-Mayo equation in differential form. This means that the general kinetic treatment of radical polymerization of vinyl monomer can be applied, at least in propagation reaction, not only to the homopolymerization of AN, but also to copolymerization with AOH in the present solvent, within the experimental condition. The differences between calculated and empirical final conversions suggest that any water soluble polymer could substantially be produced only beyond the observed final conversion.

If the monomer exists in the two forms described before, the assumed equation would not be accepted except in the case where the equilibrium between the free and the complexed entities in

$$\mathrm{AN} + \mathrm{ZnCl_2 \cdot X\,H_2O} \rightleftharpoons \text{complexed monomer}$$

shifted anormously to the right side, so that all the monomer molecules could exist in a complex state.

The monomer reactivity ratio of AOH, r_2, is 0.01, which could be assumed to be 0 within experimental error. The problem, if r_2 is really 0 or not, is difficult to discuss based on the copolymer composition or final conversion. For example, in the case of the system of $[M_1]_0 = 52.3$ mole % (50 wt%), the calculated copolymer composition at 70 wt% conversion at $r_2 = 0.01$ and $r_2 = 0$, are 66.9 and 67.3 mole %, respectively (given by M_1 content). The calculated final conversion, when M_1

has been consumed up to 99.9 mole %, is 79.68 and 78.43 mole %, respectively. Both the data lie within experimental error.

It is well-known that in homopolymerization AOH cannot easily be polymerized, only giving low molecular weight polymer. There are few reports of its homopolymerization being carried out at such low temperatures as 20°C. The polymer may be soluble in water, so that it would be difficult to separate the polymer from the system. Nevertheless, it will be meaningful to determine if AOH can be polymerized by itself, thus giving a nonzero value of r_2.

The calculated values of the instantaneous sequence length (ISL) of AOH at final conversion are listed in Table 6. These values have a tendency to become larger with increasing value of AOH concentration except for the case where $[\mathrm{AOH}]_0$ = 20 mole %. This means that the value of r_2 is possibly not 0 beyond the experimental error. For, if r_2 were 0 and ISL 1, the conversion at which ISL is 1.009 calculated for the system where $[\mathrm{AOH}]_0$ = 9.1 mole % could have lain within the error of the value given by (I) in Table 6. The calculated values for ISL = 1.009 are shown by (II). The difference between (I) and (II) undoubtedly increases with $[\mathrm{AOH}]_0$. The extreme case is the system where $[\mathrm{AOH}]_0$ = 47.8 mole %, where the final value becomes the difference value itself. The similar discussion can be made based on ISL at the final conversion of the system where $[\mathrm{AOH}]_0$ = 23.9 mole %.

Experimental proof for this discussion is given by the observed increase in solution viscosity of the homopolymerization system of AOH, as shown in Fig. 5.

The ratio r_2, estimated as 0.01 in this paper, cannot, therefore, be assumed to be 0, but a truly finite value.

APPENDIX

The degree of polymerization of copolymer is given by

$$\overline{DP} = R_p/(R_t + R_{tr})$$

$$= \frac{\sum_{i,j=1,2} k_{ij}\,[P_i\cdot]\,[M_j]}{\sum_{i,j=1,2} k_{t_{ij}}\,[P_i\cdot]\,[P_j\cdot] + \sum_{i,j=1,2} k_{tr_{ij}}\,[P_i\cdot\,]\,[M_j] + \sum_{i=1,2} k_{tr_i}[P_i\cdot]\,[X]} \qquad (I)$$

Table 6. Instantaneous Sequence Length (ISL) of AOH at Maximum Conversion

$[AOH]_0$ (mole %)	Max.[a] conv. (I) (wt %)	ISL[b] of AOH at max. conv.	Conv.[b] at ISL = 1.009 (II)	Conv.[b] at ISL = 1.030 (III)	(I)-(II)	(I)-(III)
0	100.0	–	–	–	–	–
9.1	98.1	1.009	98.1	–	0	–
14.9	96.0	1.013	92.5	–	3.5	–
19.7	95.8	1.037	88.0	95.3	7.8	(0.5)
23.9	91.9	1.030	80.4	91.9	11.5	0
28.1	89.9	1.036	70.5	88.6	19.4	1.3
33.7	85.6	–	–	–	–	–
37.9	81.1	1.045	40.5	77.4	40.6	3.7
47.8	72.2	1.066	0.0	62.0	72.2	10.2

[a] Maximum values are listed in Tables 4 and 5.

[b] Values calculated by computer.

where R_p, R_t, and R_{tr} are rates of propagation, termination, and chain transfer reaction, respectively, and K_{ij}, $k_{t_{ij}}$, and $k_{tr_{ij}}$ are the rate constants of the above three reactions between i- and j-reactant, respectively. k_{t_i} is the rate constant with which chain $P_i\cdot$ radical transfers to the substance X (solvent or impurities). $[P_i\cdot]$ is a concentration of polymer radical ending with i-monomer unit, and $[M_j]$ is that of j-monomer.

If copolymerization is carried out under conditions where the concentration of the more reactive monomer M_1 is much larger than that of M_2, the degree of polymerization will be approximately given as follows. $[P_1\cdot]$ is much larger than $[P_2\cdot]$ under the condition, for r_1 is larger than unity, and $k_{11}[P_1\cdot][M_1] \gg k_{12}[P_1\cdot][M_2]$. Thus, the numerator of Eq. (I) can be expressed as $k_{11}[P_1\cdot][M_1] + k_{21}[P_2\cdot][M_1]$. Under the plausible assumption of $k_{11}[P_1\cdot][M_1] \gg k_{21}[P_2\cdot][M_1]$, this is further simplified to $k_{11}[P_1\cdot][M_1]$. This assumption is reasonable, because $[P_1\cdot] \gg [P_2\cdot]$ and the polymer obtained in this paper can be regarded as a homopolymer of M_1 (AN), based on its IR spectra.

Then, Eq. (I) can be simplified with sufficient accuracy to

$$1/\overline{DP} = (R_t + R_{tr})/R_p = 1/\overline{DP_0} + (k_{tr_{12}}/k_{11})([M_2]/[M_1]) + \text{+ other positive terms} \qquad \text{(II)}$$

where $\overline{DP_0}$ is the degree of polymerization of polymer obtained with no M_2. Equation (II) is similar to the equation given by Mayo [21] for a chain transfer reaction in homopolymerization. If the plot of $\overline{DP}$ against $[M_2]/[M_1]$ shows a linear relationship, the slope will give an upper limit for $k_{tr_{12}}/k_{11}$.

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REFERENCES

[1] K. Miyamichi, T. Senoh, and M. Katayama, *Kogyo Kagaku Zasshi*, **66**, 95 (1963).

[2] K. Miyamichi, R. Suzuki, and M. Katayama, *Ibid.*, **66**, 100 (1963).
[3] H. Kiuchi and H. Uchiyama, *Ibid.*, **21**, 114 (1964).
[4] M. Yoshida and K. Tauchi, *Kobunshi Kagaku,* **20**, 545 (1963).
[5] W. M. Thomas, E. H. Gleason, and G. Mino, *J. Polym. Sci.*, **24**, 43 (1957).
[6] I. Ueda, *Kogyo Kagaku Zasshi,* **66**, 252 (1963).
[7] M. Nakajima and M. Amiya, *Ibid.*, **67**, 349 (1964).
[8] M. Nakajima and M. Amiya, *Ibid.*, **67**, 353 (1964).
[9] T. Alfrey, Jr., and C. R. Pfeifer, *J. Polym. Sci., Part A-1,* **4**, 2447 (1966).
[10] R. F. Onyon, *J. Polym. Sci.*, **22**, 13 (1956).
[11] G. E. Molau, *J. Polym. Sci., Part A-1,* **5**, 401 (1967).
[12] R. K. S. Chan and V. Meyer, *J. Polym. Sci., Part C,* **25**, 11 (1968).
[13] K. F. O'Driscoll, *Ibid., Part C,* **25**, 47 (1968).
[14] D. R. Montogomery and C. E. Fry, *Ibid., Part C,* **25**, 59 (1968).
[15] K. F. O'Driscoll and R. Knorr, *Macromolecules,* **1**, 367 (1968).
[16] H. J. Harwood, *J. Polym. Sci., Part C,* **25**, 37 (1968).
[17] V. F. Kulikova, I. V. Savinova, V. P. Zubov, V. A. Kavanov, L. S. Polak, and V. A. Kargin, Preprints of *"Proceedings of the Second Tihany Simposium on Radiation Chemistry,"* Budapest, 1967, p. 493.
[18] G. Oster and Y. Mizutani, *J. Polym. Sci.*, **22**, 173 (1956).
[19] M. Imoto, T. Otsu, and B. Yamada, *Kogyo Kagaku Zasshi,* **68**, 1132 (1965).
[20] G. E. Ham, *Copolymerization,* Wiley (Interscience), New York, 1964, p. 855.
[21] F. R. Mayo, *J. Amer. Chem. Soc.*, **65**, 2324 (1943).

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