BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2912—2917 (1969)

A Structural Study of the Catalytic Activity in Formaldehyde Polymerization in Liquid Carbon Dioxide

Tsutomu KAGIYA and Kōzō NARITA
Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

(Received February 17, 1969)

The catalytic activities of various acids, bases, and salts in formaldehyde polymerization in a liquid carbon dioxide solution were studied in connection with the structures of the catalysts. The activity of the catalysts increased with decreases in the pK_a of Brönsted acids and in the ion-dissociation energy of alkyl acetates, and with increases in the pK_a' of organic compounds containing a nitrogen or oxygen atom, such as triethylamine or diethyl ether, and in the pK_a of the conjugated acids of sodium salts. The activity of the salts obtained from a strong acid with various bases increased with a decrease in the pK_a' of the bases, while that of the salts from weak acids with weak bases decreased with an increase in the summation of the pK_a values of acids and the pK_a' values of bases, reaching a minimum point and then increasing. The activity of various salts decreased with an increase in the pH in an aqueous solution, reached a minimum point at pH 6, then increased.

It has been established that formaldehyde easily forms polymers with various catalysts.[1] Yokota *et al.* reported[2] that a high polymer of formaldehyde was obtained in liquid carbon dioxide. The present authors reported[3] previously that the formaldehyde polymerization in liquid carbon dioxide was initiated by the formic acid produced by the pyrolysis of α-polyoxymethylene or paraformaldehyde, and no polymer was obtained with the monomer removed from the formic acid.

The purpose of this paper is to determine quantitatively the relationship between the catalytic activity and the structure and thermodynamic nature of the catalyst, and to discuss the mechanism of polymerization on the basis of an energetic study of the catalytic activity in ionic polymerization.[4]

Experimental

Materials. Formaldehyde in liquid carbon dioxide was prepared by means of a two-step method reported previously.[3] Eighteen hundred grams (paraform), 1000 g of polyethylene glycol (degree of polymerization of about 10) (PEG), and 1.8 mol of calcium carbonate were put into a 3000 m*l* decomposer and heated at 110 to 160°C under a carbon dioxide stream (flow rate: 160 m*l*/min). The polyethylene glycol hemiformal (PEGH) was prepared by bubbling the mixed gas thus obtained into a 3000 m*l* absorber (95—110°C) containing 2000 g of PEG. Eight hundred grams of PEGH were placed in a 1000 m*l* decomposer and pyrolyzed at 130 to 180°C under a carbon dioxide stream (flow rate: 160 m*l*/min). The mixture of formaldehyde and carbon dioxide was passed through a tube cooled at −20°C and then liquefied in the monomer reservoir at −78°C. The alkyl acetates (commercial) were dried over calcium chloride and distilled before use. The Brönsted acids and bases (commercial) were purified in the usual ways. The sodium borate was dehydrated by heating before use. The other sodium compounds were used without further purification. *N*-Phenylethylenimine was prepared according to the method of the literature[5] from *β*-bromoethylaniline hydrobromide, it was dried over sodium sulfate and fractionated twice before use (bp 70—70.5°C/13 mmHg). The salts (commercial) were recrystallized from ethanol, methanol, or ethyl acetate. Triethanolamine nitrate was prepared by the reaction[6] of potassium nitrate with triethanolammonium borofluoride, and was recrystallized from ethanol (mp 99°C). Aniline trichloroacetate was prepared by the neutralization of aniline with trichloroacetic acid in ethanol, and was recrystallized from ethanol (mp 147°C). The other solid salts, which were not obtained commercially, were prepared by the same method as was triethanolamine nitrate. The aniline salt of methanol, nitroethane, or nitromethane (liquid) was used as an equimolar mixture of aniline and methanol (nitromethane or nitroethane). The dimethyl ether acetate was prepared by

---

[1] J. C. Bevington and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **A205**, 516 (1951); R. N. MacDonald, U. S. Pat. 2768994 (1956), 2828286 (1958).

[2] H. Yokota, M. Kondo, T. Kagiya and K. Fukui, *J. Polymer Sci.*, **A-1**, **6**, 425 (1968).

[3] T. Kagiya, M. Kondo, K. Narita and K. Fukui, This Bulletin, **42**, 1688 (1969).

[4] T. Kagiya, Y. Sumida and T. Nakata, *ibid.*, **41**, 2239 (1968); *ibid.*, **41**, 2247 (1968).

[5] H. W. Heine, B. L. Kapur and C. S. Milch, *J. Am. Chem. Soc.*, **76**, 1173 (1954).

[6] H. J. Emeleus and H. G. Heal, *J. Chem. Soc.*, **1946**, 1126.

the reaction⁷⁾ of monochloromethyl ether with potassium acetate, and was purified by distillation (bp 117—118°C).

Polymerization Procedure. A stainless-steel autoclave with a capacity of 30 m*l* (16 mm × 150 mm) was used as the reaction vessel. Into the vessel, which had been degassed *in vacuo* and cooled with liquid nitrogen, 0.22 mmol of the catalyst and 10 m*l* of a carbon dioxide solution of formaldehyde were introduced, after which the mixture was maintained at 20±1°C for one hour. After the polymerization, the unreacted monomer and carbon dioxide gas were purged out. The white powdery polymer thus obtained was sufficiently washed with cooled diethyl ether, dried *in vacuo* at room temperature, and then weighed. The catalytic activity of the catalyst is defined as the value of the ratio of conversion (%) to the reaction time (hr) under definite conditions.

Analysis. The number-average degree of polymerization of the polymer was measured in a manner which has been described previously.³⁾ The melting point of the polymer was visually determined under a nitrogen atmosphere in an electric heater. The infrared spectrum was obtained by using the potassium bromide pellet technique on a Japan Spectroscopic infrared spectrophotometer, Model DS-402G. The pH of the salt in an aqueous or ethanol solution with a 0.1 g equivalent/*l* was determined on a Hitachi Horiba pH meter, type M-4.

Results and Discussion

The Catalytic Activity of Brönsted Acids. The catalytic activities of various Brönsted acids in the polymerization in a liquid carbon dioxide solution were determined under definite conditions. As is shown in Fig. 1, the acids whose pK_a values are over 15 show little catalytic activity, while the activities of the acids with less than that value increased with a decreased with a decrease in pK_a.*¹ It has previously been reported⁸⁾ that this polymerization system belongs to a group of no-termination polymerizations with rapid initiations.

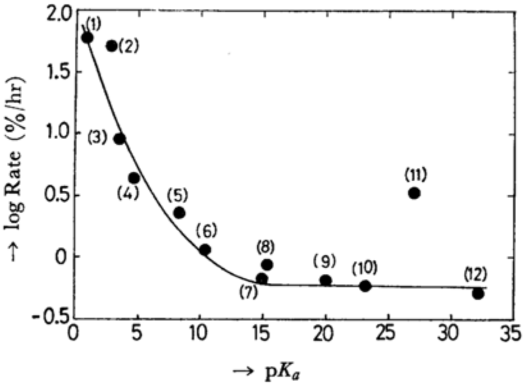

Fig. 1. Catalytic activity and pK_a of Brönsted acids: temp., 20°C; time, 60 min; monomer, 6 g; carbon dioxide, 4 g; additive/monomer (mole ratio), 1/1000; reaction vessel, 30 m*l*-autoclave.
(1) trichloroacetic acid (2) chloroacetic acid (3) formic acid (4) acetic acid (5) nitroethane (6) nitromethane (7) acetamide (8) methanol (9) acetone (10) diphenylamine (11) aniline (12) benzene

It is observed that the catalytic activity of the Brönsted acid (HB) is proportional to the rate of the propagation of the initiating species ($HOCH_2B$) produced by the reaction of formaldehyde with the acid. The propagation rate increased with a decrease in the ion-dissociation energy of the initiating species, which may be proportional to the pK_a value of the Brönsted acid. The results shown in Fig. 1 are in accordance with this theory.

The Catalytic Activity of Alkyl Acetates. Methyl acetate has little catalytic activity, while the dimethyl ether acetate produced by the reaction of methyl acetate with formaldehyde has a high catalytic activity,⁹⁾ one 20 times that of methyl acetate (Table 1). Moreover, the infrared spectrum of the polymer produced with a large quantity of benzyl acetate as a catalyst indicated the characteristic peaks of both the phenyl group (1500 (shoulder), 755, 703 cm^{-1}) and the carbonyl group (1740 cm^{-1}) (Fig. 2). These results indicate that, in this polymerization, the initiating species is

TABLE 1. THE CATALYTIC ACTIVITY OF DIMETHYLETHER ACETATE

Additive	Polymer yield (g)	Yield percent (wt%)	Degree of polymerization	Mp (°C)
Dimethyl ether acetate	3.42	57.0	1900	174—175
t-Butyl acetate	1.40	21.6	270	174
Methyl acetate	0.17	2.8	200	168—172
No additive	0.16	2.6	230	171—172

polymerization temperature: 20°C, time: 60 min, monomer: 6 g, carbon dioxide: 4 g, additive/monomer (mol ratio): 1/1000

---

7) Deutschen Chemischen Gesellschaft, "*Beilsteins Handbuch der Organischen Chemie,*" Band III, J. Springer, Berlin, (1921), p. 236.

*¹ The values of pK_a (25°C) are taken from "Ionization Constants of Acids and Bases, A Laboratory Manual," ed. by A. Albert and E. P. Serjeant, Methuen & Co., Great Britain (1962), p. 115.

8) H. Yokota, K. Kondo, T. Kagiya and K. Fukui, *J. Polymer Sci., A-1,* **6**, 435 (1968).

9) H. Yokota, M. Kondo and T. Kagiya, *ibid.*, **A-1**, **6**, 425 (1968).

methyl alkyl ether acetate ($ROCH_2OOCCH_3$), and that the reaction of alkyl acetate ($ROOCCH_3$) with the monomer to produce the initiating species is the rate-determining step.

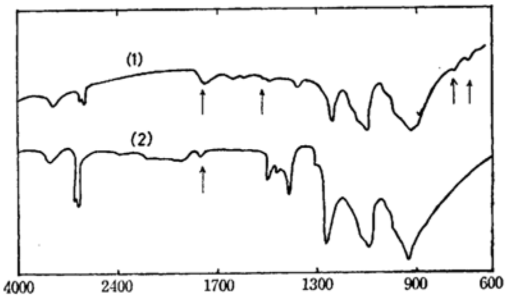

Fig. 2. The infrared spectrum of the polyoxymethylene obtained by the catalysts of both benzyl acetate and acetic acid.
(1) the polymer obtained by benzyl acetate catalyst: temp., 50°C; time, 30 min; additive/monomer (mole ratio), 1/6; (2) the polymer obtained by acetic acid catalyst: temp., 20°C; time, 60 min; additive/monomer (mole ratio), 1/1000

The catalytic activities of various alkyl acetates increased with a decrease in the ion-dissociation energy of alkyl chloride ($D(R^+,Cl^-)$) (Fig. 3). In view of the fact that the ion-dissociation energy of alkyl acetate is proportional to that of alkyl chloride,*2 it may be concluded that the rate of initiation reaction increases with a decrease in the ion-dissociation energy of alkyl acetate.

The Catalytic Activity of Organic Compounds Containing a Nitrogen or Oxygen Atom. As has been described previously (Fig. 1), aniline has a strong catalytic activity, though its pK_a value is large (27). In order to clarify the role of aniline, the catalytic activities of various organic compounds containing a nitrogen or oxygen atom, such as amines, ethers, ketones, or amides were studied. As is shown in Fig. 4, those substances with values less than the zero of pK_a',*3 such as diethyl ether, have little catalytic activity, while the activities of those with values more than 0 increased with an increase in pK_a'.

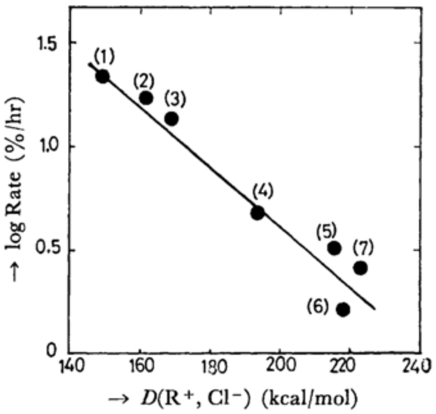

Fig. 3. Catalytic activity of alkyl acetates and ion-dissociation energy of alkyl chlorides: the condition is the same as described in Fig. 1.
(1) *t*-butyl acetate (2) alkyl acetate
(3) isopropyl acetate (4) ethyl acetate
(5) phenyl acetate (6) vinyl acetate
(7) methyl acetate

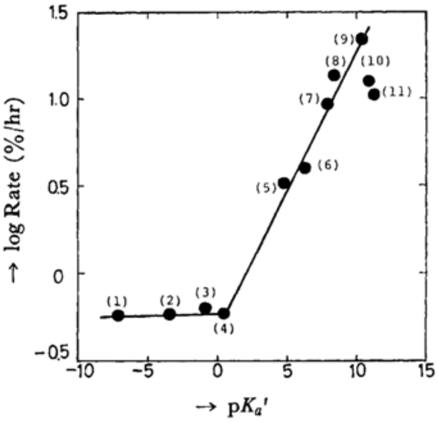

Fig. 4. Catalytic activity and pK_a' of organic compounds containing a nitrogen or oxygen atom: the condition is the same as described in Fig. 1.
(1) acetone (2) diethyl ether (3) acetamide
(4) diphenylamine (5) aniline (6) pyridine
(7) *N*-phenyl ethylenimine (8) ethylenimine
(9) *n*-butyl amine (10) triethylamine
(11) diethylamine

On the other hand, it is known that the shift of the O–D vibrational band of methanol-D in liquid organic compounds increases with an increase in the pK_a values of the compounds.10) In view of the facts presented above, it can be suggested that, in the polymerization by a basic substance (B) such as amine or ether, the initiating species

---

*2 The ion dissociation energy of organic compound (RX) is expressed as $D(R^+, X^-)=D(R\cdot, X\cdot)+I_p(R\cdot)-E_a(X\cdot)$, where $D(R\cdot, X\cdot)$ is the dissociation energy of RX; $I_p(R\cdot)$, the ionization potential of the alkyl radical, and $E_a(X\cdot)$, the electron affinity of the X radical. Therefore, the ion-dissociation energy of alkyl acetate ($D(R^+, {}^-OOCH_2)$) is expressed as $D(R^+, {}^-OOCH_3)= D(R^+, Cl^-) + \{D(R\cdot, CH_3COO\cdot) - D(R\cdot, Cl\cdot)\} - \{E_a(CH_3COO\cdot)-E_a(Cl\cdot)\}$, The difference between $D(R\cdot, CH_3COO\cdot)$ and $D(R\cdot, Cl\cdot)$ is about 7—9 kcal/mol, while the value of $D(R^+, Cl^-)$ is 150—225 kcal/mol.

10) T. Kagiya, Y. Sumida and T. Inoue, This Bulletin, **41**, 773 (1968).

*3 The pK_a' is the negative logarithm of the ion-dissociation constant of the reaction: $BH^+ \overset{K_a'}{\rightleftharpoons} H^+ + B$. Moreover, the pK_a' values of bases plotted in the figure were obtained as the values in water (25°C) according to the following equation: $pK_a'=14.17-pK_b$.

($HOCH_2OHB$) is produced by the reaction of the water in the system, the monomer, and the basic substance:

$$H_2O + CH_2O + B \rightleftarrows HOCH_2OB$$

As is suggested by the mechanism of the polymerization by Brönsted acids, the rate of the initiation reaction by amine or ether may be much larger than that of the propagation. Since the structure of the propagating species depends on the kind of basic substance, the catalytic activities of amines or ethers are proportional to the propagation rate, and increase with a decrease in the ion-dissociation energy of the initiating species, which itself may increase proportionally with a decrease in the pK_a' of amines or ethers.

The Catalytic Activity of Salts. The catalytic activity of sodium salts obtained from a strong base (sodium hydroxide) with various acids, hydrochloride salts from a strong acid (hydrochloric acid) with various bases (amines), acetate or nitrate from weak acids (acetic acid or nitric acid) with various bases (amines), and aniline salts with various acids were observed under definite condition.

a) *The Activity of Sodium Salts.* As is shown in Fig. 5, the activity of sodium salts increased with an increase in pK_a the in an aqueous solution of the conjugated acids of sodium salts. In the polymerization by sodium salt (NaB), two mechanisms of the initiation reaction may be proposed. One of them involves the polymerization by the initiating species (BCH_2ONa) produced by the reaction of sodium salt with monomer. The other involves that by the initiating species ($HOCH_2ONa$) formed by the reaction of the monomer with the sodium hydroxide produced by the hydrolysis of sodium salt with water in the system.

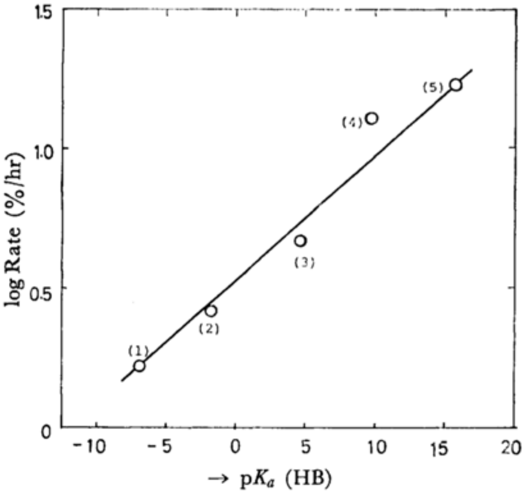

Fig. 5. Catalytic activity and pK_a of the conjugated acids of sodium salts: the condition is the same as in Fig. 1.
(1) sodium chloride (2) sodium nitrate
(3) sodium acetate (4) sodium borate
(5) sodium methoxide

The infrared spectrum of the polymer obtained with a large amount of the sodium acetate catalyst did not show the characteristic peak at 1750 cm^{-1} of the carbonyl group, but that at 3640 cm^{-1} of the hydroxy group. Therefore, it may be concluded that this polymerization proceeds by means of the initiating species of $HOCH_2ONa$. If this polymerization proceeds by the initiating species ($HOCH_2ONa$), the structure of the end group of the propagation species is the same in the polymerization with sodium salt. Furthermore, the catalytic activity of sodium hydroxide was 1.6 times that of sodium methoxide. On the basis of these facts, the formation of the initiating species may be considered to be the rate-determining step.

The rate of the formation of the initiating species may be proportional to the concentration of the hydroxy anion. On the other hand, in the hydrolysis of sodium salt, the logarithm of the concentration of the hydroxy anion is proportional to the pK_a (in an aqueous solution) of the conjugated acid of the salt.*4 These considerations lead to the conclusion that the catalytic activity of sodium salts increases with an increase in the pK_a of the conjugated acid of the sodium salt.

b) *The Catalytic Activity of the Hydrochloride Salts.* The activities of the salts obtained from hydrochloric acid with various amines increased with a decrease in the pK_a' values of the amines

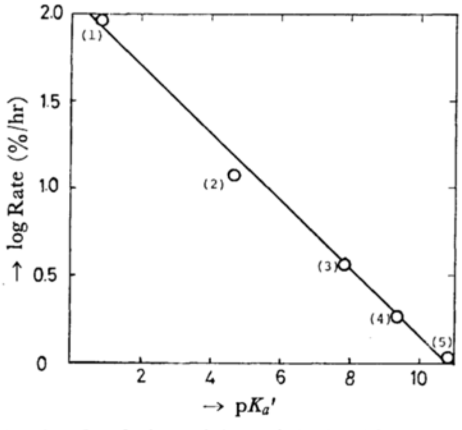

Fig. 6. Catalytic activity of hydrochloride salts and pK_a' of amines: the condition is the same as described in Fig. 1.
(1) diphenylamine hydrochloride
(2) aniline hydrochloride
(3) triethanolamine hydrochloride
(4) ammonium hydrochloride
(5) triethylamine hydrochloride

---

*4 In the reaction of $NaB + H_2O \rightleftharpoons Na^+ + OH^- + HB$, the concentration of the hydroxy anion (OH^-) is expressed as: $\sqrt{K_w(H_2O)(B^-)/K_{HB}}$, where K_w is the ionic product of water.

(Fig. 6). The salt obtained from hydrochloric acid with an amine such as R_3NHB may produce a proton and a counter anion (B^-) by hydrolysis.*5 Moreover, the initiating species ($HOCH_2B$) is considered to be produced by the reaction of a proton with a monomer in this polymerization. Just as in the polymerization by sodium salt, the formation reaction of the initiating species may be also the rate-determining step. Moreover, the rate of initiation is proportional to the concentration of the proton which increases proportionally with a decrease in the pK_a' values of the amines. This consideration is in accordance with the results shown in Fig. 6.

c) The Catalytic Activity of the Salts Obtained from Weak Acids with Various Amines. As is shown in Fig. 7, the activity of the acetate or nitrate salts decreased with an increase in the summation of the pK_a values of the acids and the pK_a' of the amines (pK_a+pK_a'), reached a minimum at *ca.* 7, and then increased with an increase to values larger than 7. Further, as is shown in Fig. 8, the activity of aniline salts also showed the same tendency as that of the acetate or nitrate salts, that is, a folded line with a minimum point.

Just as in polymerization by the sodium salts or hydrochloride salts, the formation of the initiating species may be also the rate-determining step in this polymerization.

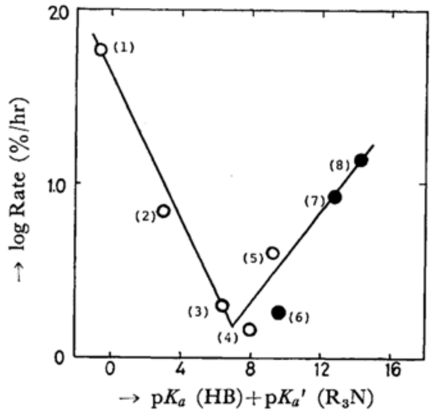

Fig. 7. Catalytic activity of acetate or nitrate salts and the summation of pK_a of acid and pK_a' of base: the condition is the same as described in Fig. 1.
(1) diphenylamine nitrate (2) aniline nitrate (3) triethanolamine nitrate (4) ammonium nitrate (5) triethylamine nitrate (6) aniline acetate (7) triethanolamine acetate (8) ammonium acetate

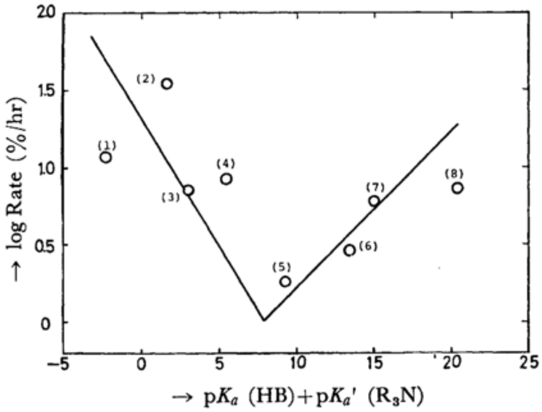

Fig. 8. Catalytic activity of aniline salts and the summation of pK_a of acid and pK_a' of base: the condition is the same as described in Fig. 1.
(1) aniline hydrochloride (2) aniline sulfate (3) aniline nitrate (4) aniline trichloroacetate (5) aniline acetate (6) aniline-nitroethane (7) anilinenitromethane (8) aniline-methanol

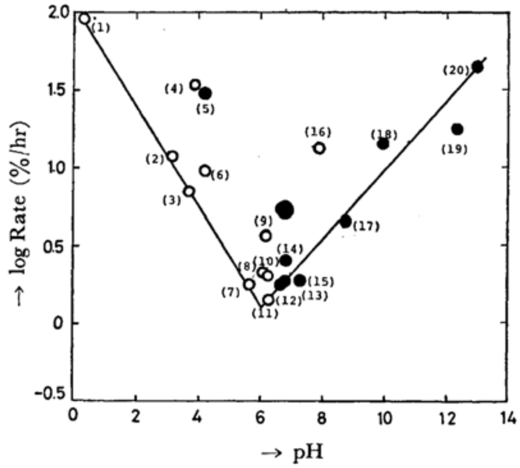

Fig. 9. Catalytic activity and pH of various salts: the condition of polymerization is the same as described in Fig. 1 the measurement of pH is carried out at 20°C with 0.1 mol/*l* aqueous (ethanol) solution.
(1) diphenylamine hydrochloride (2) aniline hydrochloride (3) aniline trichloroacetate (4) aniline sulfate (5) sodium dichloroacetate (6) triethylamine hydrochloride (7) aniline acetate (8) ammonium hydrochloride (9) triethanolamine hydrochloride (10) triethanolamine nitrate (11) ammonium nitrate (12) sodium chloride (13) tetraethylammonium iodide (14) sodium nitrate (15) tetraethylammonium bromide (16) ammonium acetate (17) sodium acetate (18) sodium borate (19) sodium ethylate (20) tetraethylammonium hydroxide

On the other hand, it is known that the hydrolysis of the salt obtained from the weak acid (HB) with a weak base (NR_3) is in equilibrium:

$$R_3NHB + H_2O \rightleftharpoons R_3NHOH + HB$$

Therefore, it may be considered that this poly-

---

*5 The hydrolysis reaction of the salt obtained from a strong acid with various amines is:

$$R_3NHB + H_2O \rightleftharpoons H^+ + B^- + R_3NHOH$$

The concentration of the proton is expressed as $\sqrt{K_a'/C}$, where C is the concentration of the salt.

merization proceeds by means of the initiating species ($HOCH_2B$ or $HOCH_2OHNR_3$) produced by the reaction of the monomer with the proton or the hydroxy anion, and that the activities of the salts depend upon the quantity of protons or hydroxy anions produced by the reaction of the salt with the water present in the system.

The proton concentration is considered to be equal to the $K_{a(\mathrm{HX})}^{1/2}\cdot K_a'^{1/2}_{(\mathrm{NR_3})}$ value, and that of the hydroxy anion, to $K_w\cdot K_{a(\mathrm{HX})}^{-1/2}\cdot K_a'^{-1/2}_{(\mathrm{NR_3})}$. The reactions shown in Figs. 7 and 8 are in good accordance with these considerations.

The relationship between the activity and the pH[*6] in aqueous solutions of various salts are shown in Fig. 9. From this finding, it may be concluded that, in the range of pH values lower than 6, the polymerization proceeds by means of the initiating species ($HOCH_2B$) produced by the reaction of proton with the monomer, while in the range of pH values higher than 6, it proceeds by means the initiating species ($HOCH_2OHNR_3$) from the hydroxy anion and the monomer.

The authors are grateful to Professor Kenichi Fukui for his valuable suggestions and to Mr. Masatsune Kondō for his helpful discussions. They also wish to express their gratitude to Mr. Hiroshi Hatta for his technical assistance in carrying out the experiments.

[*6] The pH values were determined at 20°C by using 0.1 mol/*l* of an aqueous or ethanol solution of salts.