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A Cationic Polymerization of *N*-Phenylethylenimine by Various Carboxylic Acid Catalysts

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The polymerization of *N*-phenylethylenimine was carried out using various carboxylic acid catalysts (pK_a=0.23—4.87) in acetonitrile at 0°C. The number-average molecular weight was determined by measuring the allyl-group content in the infrared spectrum of the polymer initiated with allylformate. The relationship between the number-average molecular weight and the reduced viscosity was determined. Both the conversion and the number-average molecular weight increased with the reaction time when weak acid (pK_a=2.85—4.87) was used. On the other hand, when strong acid (pK_a=0.23—2.85) was used, conversion reached a limited value which increased in proportion to the amount of the catalyst. With the strong acid, the efficiency factor of the catalyst was almost unity, and was independent of the reaction time. On the other hand, with the weak acid, it was smaller than unity and increased proportionally with the amounts of the polymer formed. The rate constants of the elementary reactions were evaluated on the basis of the kinetic study. The rates of the initiation, propagation, and termination reaction increased with a decrease in the pK_a of the acid. With a weak acid, the termination reaction is slow at a low temperature (below 50°C), and increases with the reaction temperature, whereas with a strong acid the termination reaction occurs markedly even at a low temperature (above 0°C), and increases slightly with the temperature. The mechanism of the termination reaction was discussed on the basis of a structural study of the end group of the polymer.

It has already been reported by the present authors that *N*-phenylethylenimine and β-propiolactone copolymerized with various Brönsted acid catalysts, and that the monomer reactivity ratio varies with the pK_a of the acid used as the catalyst.[1]

In order to determine the role of the catalyst in the elementary reactions in the polymerization, the polymerization of *N*-phenylethylenimine was studied with various carboxylic acids, and the rate constants of the elementary reactions were determined on the basis of the kinetics. Furthermore, the mechanism of the termination reaction was discussed on the basis of the structural study of the end group of the polymer.

Experimental

Polymerization Procedure. *N*-Phenylethylenimine was prepared according to the method described in the literature[2] from β-bromoethylaniline hydrobromide. It was dried over sodium sulfate and fractionated twice before use, bp 70—70.5°C/13 mmHg. Acetonitrile was purified by the usual method.[3] Acids of guaranteed reagents were used without further purification.

Definite amounts of a catalyst and a solvent were placed into a glass ampule under a nitrogen atmosphere, and then *N*-phenylethylenimine was added to this system at −78°C. The ampule was sealed and maintained at 0—1°C for the definite period of the reaction time. The product was then washed with diethyl ether, separated by a centrifuge, and dried *in vacuo*.

Physical Analysis of the Polymer. The melting point of the polymer was measured visually in a nitrogen atmosphere in a capillary on an electric heater. The reduced viscosity of a 0.25% solution of 99—100% formic acid was measured at 35°C with an Ostwald viscometer. The infrared spectrum was obtained with the use of the potassium bromide pellet technique on a Shimadzu infrared spectrophotometer, Model IR-27. The X-ray diffraction diagram was recorded with a powder camera on a Shimadzu X-ray diffractometer, Model GX-3B. The differential thermogram was obtained with the use of a Rigaku Denki differential thermal apparatus, Model VIP-32.

Determination of Molecular Weight. It was found that *N*-phenylethylenimine polymerized with cationic reagents, such as triphenylmethyl chloride, allyl formate or allyl acetate, as well as with Brönsted acid. The absorption peak of the infrared spectrum of the polymer initiated with allyl formate at 910 cm^{-1} assigned to the vinyl group, and that at 1600 cm^{-1} assigned to the phenyl group, were used in order to determine the number-average molecular weight of the

1) T. Kagiya, T. Tomizo, S. Narisawa and K. Fukui, This Bulletin, in press.
2) H. W. Heine, B. L. Kapur and C. S. Mitch, *J. Am. Chem. Soc.*, **76**, 1173 (1954).
3) A. Weissberger, *et al.*, "Technique of Organic Chemistry, Vol. VII, Organic Solvents," Interscience Publishers, Inc., New York (1955).

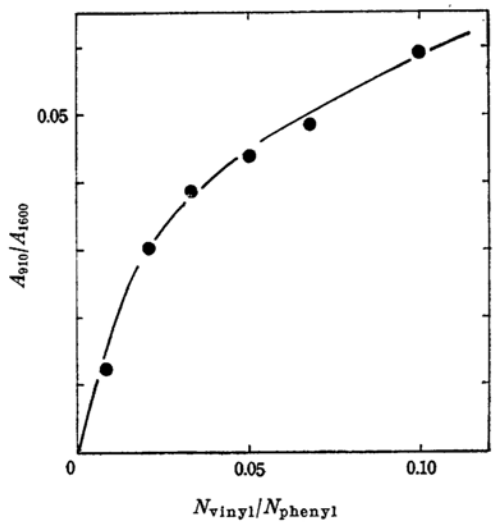


Fig. 1. Plots of A_{910}/A_{1600} *vs.* the ratio of the number of vinyl group (N_{vinyl}) in allyl urea to the number of phenyl group (N_{phenyl}) in the polymer.

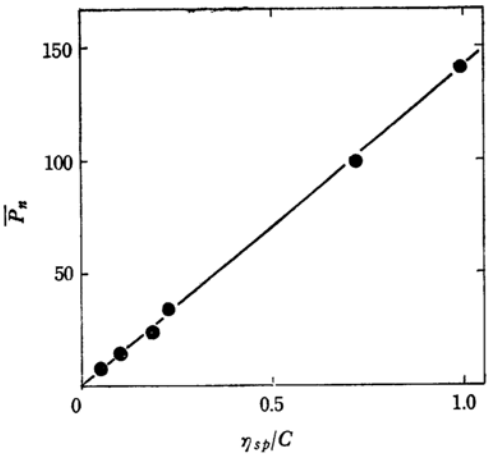


Fig. 2. The plots of the degree of the polymerization *vs.* the reduced viscosity of the polymer.

polymer. The calibration curve was obtained by plotting the optical density ratio, D_{910}/D_{1600}, in the infrared spectrum against the ratio of the number of vinyl and phenyl groups in the mixture of allyl urea and polymer obtained with formic acid (Fig. 1). The relation between the number-average molecular weight, $\overline{M}_n$, and the reduced viscosity, η_{sp}/C, is shown in Fig. 2. From Fig. 2, the following empirical equation may be obtained:

$$\eta_{sp}/C = 0.6\times10^{-4}\,\overline{M}_n$$

Results and Discussion

Physical Properties of the Polymer. The polymer is a white powdery solid soluble in formic acid, but insoluble in the other organic solvents.

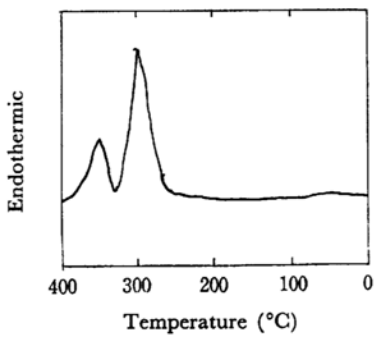


Fig. 3. Differential thermogram of the polymer.

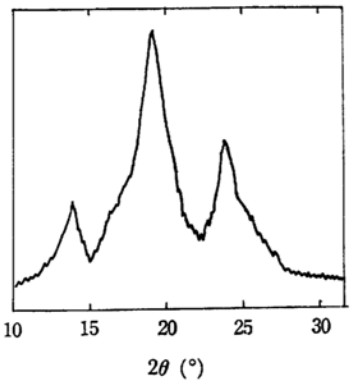


Fig. 4. X-Ray diffraction of the polymer.

The melting point of the polymer is from 287 to 292°C, and the differential thermogram of the polymer showed a sharp endothermic peak corresponding to the melting point of the polymer at 300°C (Fig. 3). In an X-ray diffraction diagram of the polymer (Fig. 4), sharp peaks were observed at 13.6, 19.4, and 23.3 θ. The figure showed that the polymer had a fairly good crystallinity.

Polymerization of *N*-Phenylethylenimine with Various Carboxylic Acids. The polymerization was carried out with various carboxylic acids (pK_a=0.23—4.87) at 0°C in acetonitrile. Figure 5 shows the variation in the polymer yield with the reaction time. With weak acid catalysts (pK_a=2.85—4.87), such as formic acid, acetic acid, and propionic acid, the polymer yield increased with the reaction time. On the other hand, with strong acids (pK_a=0.23—2.85), such as trifluoroacetic acid, dichloroacetic acid, and monochloroacetic acid, the conversion reached a saturated value ($<$ 50%) in a few minutes after the start of the polymerization. The number-average molecular weight of the polymer obtained with weak acid varied with the reaction time, whereas that obtained with strong acid remained constant (Fig. 6). With weak acid, the rate of the monomer consumption is expressed by a first-order rate equation with respect to the monomer

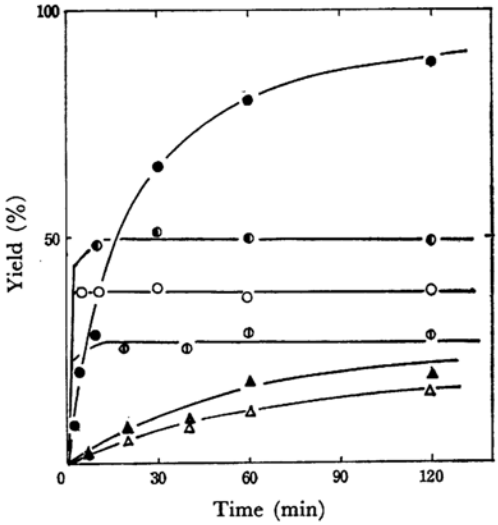


Fig. 5. Polymer yield *vs.* reaction time.
Monomer, 1 mol/*l*; Catalyst, 0.018 mol/*l*;
Solvent, Acetonitrile 5 m*l*
Reaction temperature, 0°C
○, Trifluoroacetic acid; ⓘ, Dichloroacetic acid;
◐, Monochloroacetic acid; ●, Formic acid;
▲, Acetic acid; △, Propionic acid;

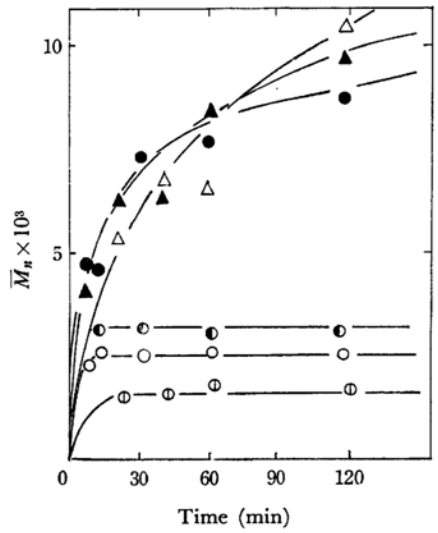


Fig. 6. The number-average molecular weight *vs.* reaction time.
(Reaction conditions and notes are the same as Fig. 5.)

concentration in the early stages of the polymerization, but not in the later stages. These facts suggest that the termination reaction occurs in this polymerization. In order to confirm that the termination reaction takes place, the following experiment was carried out. In the polymerization with monochloroacetic acid, the catalyst was added after the conversion reached the saturated value. The increase in the polymer yield in this experiment leads to the conclusion that the saturation is caused by the deactivation of the propagating species.

Kinetics of the Polymerization. The rate equations of the initiation, propagation, and transfer reactions may be assumed to be as follows:

$$R_i = k_i[\mathrm{C}][\mathrm{M}] \quad (1)$$

$$R_p = k_p[\mathrm{P}^*][\mathrm{M}] \quad (2)$$

$$R_{tr} = k_{tr}[\mathrm{P}^*][\mathrm{Y}] \quad (3)$$

where:
[C], [M], [P*], and, [Y]: the concentrations of the catalyst, monomer, the propagating species, and the substance to which the acitivity of P* is transferred.
R_i, R_p, and R_{tr}: the rates of the initiation, the propagation, and the transfer reaction.
k_i, k_p, and k_{tr}: the rate constants of the initiation, the propagation, and the transfer reaction.

The number-average degree of polymerization at a given reaction time may be written for the polymerization with no termination by recombination as follows:

$$\overline{P}_n = \int R_p dt / \left(\int R_i dt + \int R_{tr} dt \right) \quad (4)$$

By combining Eqs. (2), (3) and (4), and considering $\int R_p dt$ to be approximately equal to the polymer yield, $[\mathrm{M_p}]$, the reciprocal of the degree of polymerization may be expressed by the following equation:

$$1/\overline{P}_n = \int R_i dt / [\mathrm{M_p}] + (k_{tr}[\mathrm{Y}])/k_p \quad (5)$$

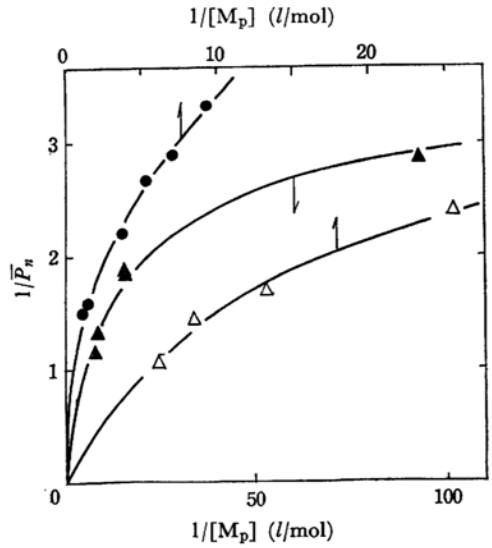


Fig. 7. Reciprocal of degree of polymerization *vs.* reciprocal of the polymer yield.
(Reaction conditions and notes are the same as Fig. 5.)

The plots of the reciprocal of $\overline{P}_n$ against the reciprocal of the polymer yield give a upward-concave curve through the point of origin, as is shown in Fig. 7. Figure 7 shows that $\int R_t dt$ increases with the reaction time. Moreover, the fact that the curve goes through the point of origin indicates that no chain transfer occurs in the polymerization with the weak acid. Equation (4) thus becomes:

$$\overline{P}_n = [M_p]/\int R_t dt \tag{6}$$

For the polymerization without chain transfer and bimolecular termination, the value of $[M_p]/([C]_0/\overline{M}_n)$ may be called the efficiency factor of the catalyst, α. The plots of α against the reaction time are shown in Fig. 8. In the polymerization with strong acid catalysts, α is independent of the reaction time and is found to be almost unity (Fig. 8). This fact indicates that this system with strong acid involves polymerization with a rapid initiation and no chain transfer reaction. On the other hand, on the basis of the findings that, with a weak acid, α is smaller than unity and increases with the reaction time, this system may be considered to involve polymerization with a slow initiation.

The relationship between α and the amount of the polymer formed, $[M_p]$, when a weak acid is used is shown in Fig. 9. Figure 9 shows that α is proportional to the amount of the polymer formed, and is independent of the pK_a of the acid. This result may be interpreted by assuming that the stationary state is applicable, and that the termination reaction occurs with the monomer

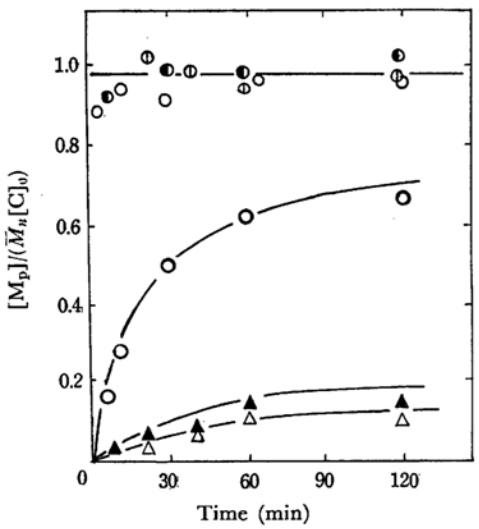


Fig. 8. The plots of efficiency factor of catalyst, *vs.* reaction time.
(Reaction condition and notes are the same as Fig. 5.)

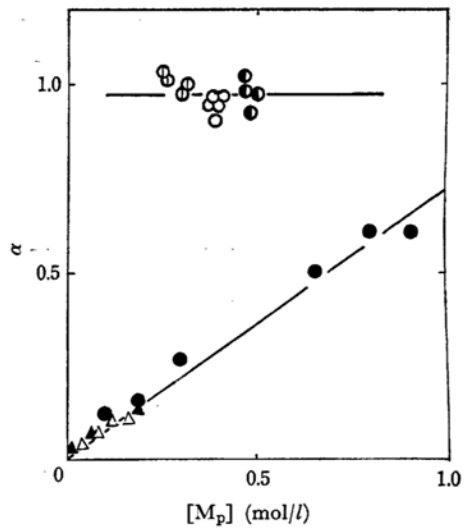


Fig. 9. The relationship between α and $[M_p]$.
(Reaction conditions and notes are the same as Fig. 5.)

as is expressed by Eqs. (7) and (9):

$$R_i = R_t \tag{7}$$

or

$$\int R_i dt = \int R_t dt = \alpha[C]_0 \tag{8}$$

$$R_t = -d[P^*]/dt = k_t[P^*][M] \tag{9}$$

where R_t and k_t are the rate and the rate constant of the termination respectively. By integrating Eqs. (2) and (9), and by then dividing the latter by the former,

$$\int R_t dt/\int R_p dt = k_t/k_p = \int R_t dt/[M_p] \tag{10}$$

From Eqs. (8) and (10), Eq. (11) is derived:

$$\alpha[C]_0 = (k_t/k_p)[M_p] \tag{11}$$

The relationship of Eq. (11) is in accord with Fig. 9; that is, α is proportional to $[M_p]$. From Eq. (11), the value of k_t/k_p was estimated to be 1.26×10^{-2}.

With a weak acid catalyst, the rate constant of the initiation reaction was obtained by using the following method. From a combination of Eqs. (1), (7), and (9), Eq. (12) is derived:

$$k_t[P^*][M] = k_i[C][M] \tag{12}$$

By substituting the $[P^*]$ from Eq. (12) into Eq. (2), the rate of the monomer consumption becomes:

$$-d[M]/dt = (k_p k_i/k_t)[C][M] \tag{13}$$

On the other hand, Eq. (11) may be expressed as Eq. (14):

$$[C]_0 - [C] = (k_t/k_p)([M]_0 - [M]) \tag{14}$$

where $[M]_0$ is the initial monomer concentration. From Eqs. (13) and (14), Eq. (15) is derived:

$$-d[M]/dt = (k_p k_i/k_t)[M]\{[C]_0 - (k_t/k_p)([M]_0 - [M])\} \quad (15)$$

or:

$$\frac{-d[M]}{(k_t/k_p)[M]^2 - \{(k_t/k_p)[M]_0 - [C]_0\}[M]} = (k_p k_i/k_t)dt \quad (16)$$

On integrating, Eq. (17) is obtained:

$$\ln\left\{\frac{k_p[C]_0}{k_t[M]_0}\,\frac{[M]}{([M]-[M]_0)+(k_p/k_t)[C]_0}\right\} = k_i\{[M]_0 - (k_p/k_t)[C]_0\}t \quad (17)$$

By substituting the value, $(k_p/k_t)[C]_0 = 1.43$ mol/l, obtained from Eq. (11), $[M]_0 = 1$ mol/l and $([M]_0-[M])/[M]_0 = x$, into Eq. (17), one obtains

$$\log\{(1-0.7x)/(1-x)\} = 0.187k_i t \quad (18)$$

A plot of the left hand of Eq. (18) against t defined a straight line through the point of origin (Fig. 10). From the slope of the line, the k_i values were evaluated. The values of k_i in the polymerization with weak acid are summarized in Table 1. The fact that k_i increases with a decrease in the pK_a of the acid may be ascribed to the larger dissociation constant of the stronger acid than that of the weaker acid.

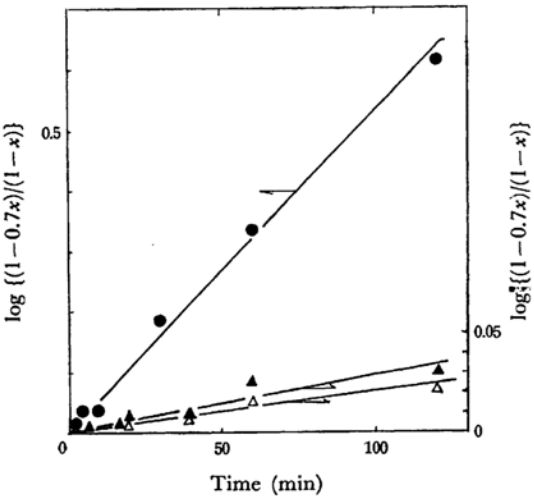


Fig. 10. The plots of $\log\{(1-0.7x)/(1-x)\}$ according to the Eq. (18).
(Reaction conditions and notes are the same as Fig. 5.)

The values of k_p and k_t with a weak acid catalyst were estimated graphically as follows. The concentrations of the propagating species are expressed by Eq. (19):

$$[P^*] = \int R_i dt - \int R_t dt \quad (19)$$

By substituting Eqs. (2), (6), and (9) into Eq. (19), Eq. (20) is derived:

$$R_p/([M][M_p]) = k_p/\overline{P}_n - k_t \quad (20)$$

As is shown in Fig. 11, the plots of $R_p/([M][M_p])$ against $1/\overline{P}_n$ gave straight lines with the weak acid catalyst. Therefore, the assumption of the rate equation is considered to be suitable.

From the slope and intercept on the ordinate axis, k_p and $-k_t$ can be obtained graphically. The rate constants obtained by this method are summarized in Table 1. It is found that, with the weak acid catalyst, the rate constant of the termination reaction is about a hundredth that of the propagation, and that both k_p and k_t increase with a decrease in the pK_a of the catalyst. In the polymerization with strong acid catalysts such as trifluoroacetic acid, the rate constants can not be evaluated by the above method because the conversion is saturated immediately after the start

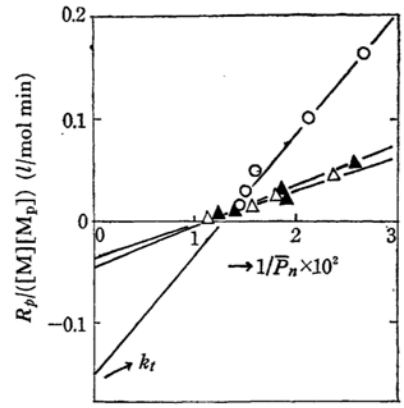


Fig. 11. The plots of $R_p/([M][M_p])$ *vs.* the reciprocal of the degree of the polymerization according to Eq. (9).
(Reaction condition and notes are the same as Fig. 5.)

Table 1. The rate constants of elementary reactions in the polymerization with weak acid catalyst

Catalyst	pK_a	$k_i \times 10^2$ l/mol min	k_p l/mol min	$k_t \times 10^2$ l/mol min	$(k_t/k_p) \times 10^2$
Formic acid	3.75	2.86	12	15	1.25
Acetic acid	4.76	0.167	3.8	4.8	1.26
Propionic acid	4.87	0.131	3.5	4.2	1.20
					mean 1.24

of the polymerization. Therefore, k_t/k_p was obtained by using the limited conversion $[M_p]_\infty$ according to the following method: From Eq. (10), Eq. (21) is derived:

$$\int R_t dt / \int R_p dt = k_t/k_p = \int R_t dt/[M_p]_\infty \quad (21)$$

On the basis of the facts that, with a strong acid catalyst, no chain-transfer reaction occurred in this polymerization, that α was almost equal to unity, and that the propagating species deactivated quantitatively, Eq. (22) can be assumed:

$$\int R_t dt = \int R_t dt = [C]_0 \quad (22)$$

By substituting Eq. (22) into Eq. (21), Eq. (23) was derived:

$$[M_p]_\infty = (k_p/k_t)[C]_0 \quad (23)$$

In the polymerization with monochloroacetic acid, the conversion reached a limited value which was dependent on the catalyst concentration. A plot of a limited conversion $[M_p]_\infty$ *versus* the initial concentration of the catalyst gave a straight line through the point of origin, as is shown in Fig. 12. This fact is in accordance with the relationship shown in Eq. (23). From the relation of $[M_p]_\infty$ and $[C]_0$ in Eq. (23), k_t/k_p can be determined.

The values of k_t/k_p are plotted against the pK_a of the catalyst in Fig. 13. This figure shows that the value of k_t/k_p decreases with an increase in the pK_a of the acid, and reaches a limited value of 1.24×10^{-2} with a weak acid. This value is almost in accord with the value, 1.26×10^{-2}, obtained from the slope of the line in Fig. 9.

Mechanism of the Termination Reaction. In order to investigate the temperature dependency of the termination reaction, the polymerization was studied with formic acid (a weak acid) or monochloroacetic acid (a strong acid) at various temperatures. A two-stage polymerization method was used. The polymerization was carried out for five minutes at a definite temperature (first stage), and then continued for 25 min at 0°C (second stage). The polymer yield obtained in the first stage, or the total of that obtained in the whole period, is plotted against the reaction temperature in Fig. 14. With the monochloroacetic

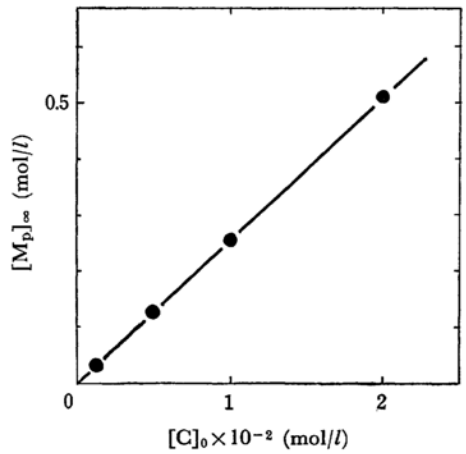


Fig. 12. Relation between the limiting conversion and initial concentration of the catalyst in the polymerization with monochloroacetic acid. (Reaction condition is the same as Fig. 5.)

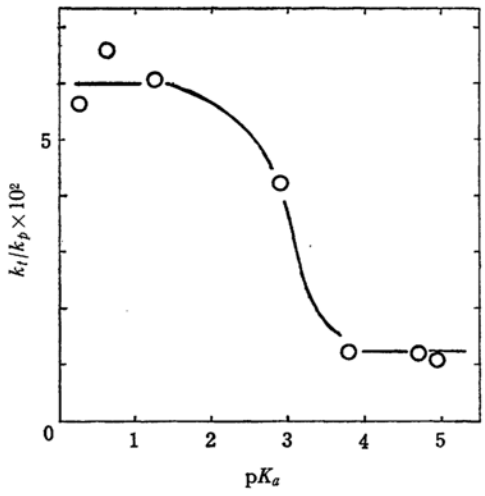


Fig. 13. The plots of k_t/k_p *vs.* pK_a of the acid catalyst.

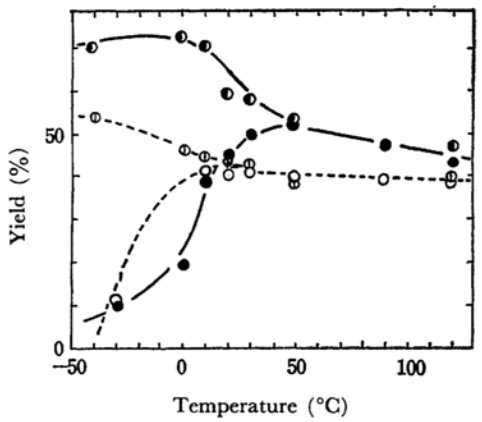


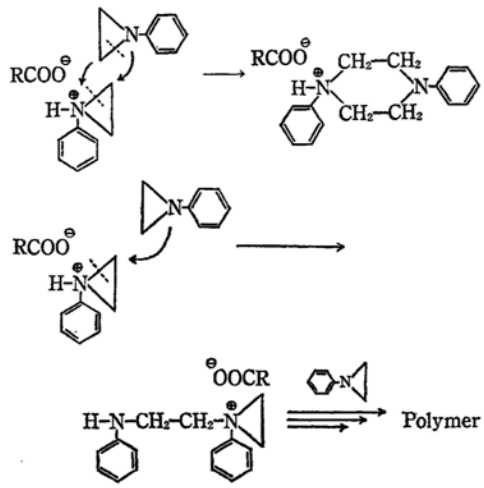
Fig. 14. The effect of temperature on the termination in the polymerization with formic acid or monochloroacetic acid.
Monomer, 1 mol/l; Catalyst, 0.018 mol/l;
Solvent, Acetonitrile 5 ml
Formic acid catalyst:
● first stage, Polymerization for 5 min at definite temperature.
◐ second stage, Continued for 25 min at 0°C.
Monochloroacetic acid catalyst:
○ first stage, Polymerization for 5 min at definite temperature.
◑ second stage, Continued for 25 min at 0°C.

acid catalyst, the conversion increased only a little in the second stage at temperatures of about 0°C. On the other hand, with formic acid the increase in conversion was observed in the second stage at temperatures below 50°C, and the termination reaction increased markedly above 50°C. This indicates that, with a weak acid, the termination reaction is slow at low temperatures and increases with the reaction temperature, while with a strong acid the termination reaction occurs remarkably at even low temperatures.

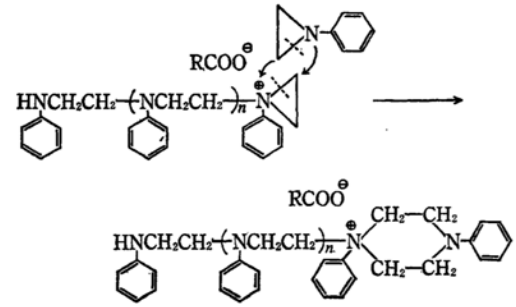
Chemical and spectral analyses of the products of the reaction of *N*-phenylethylenimine with excess amounts of monochloroacetic acid were carried out in order to elucidate the mechanism of the termination reaction. The reaction was carried out in an acetonitrile solution at room temperature for five hours. A white crystal precipitate (A) was filtered out. When this filtrate was neutralized by an 1/10 N sodium aqueous solution, a white resinous crystal (B) was precipitated. The product (A) was soluble in formic acid and insoluble in the other organic solvents. The infrared spectrum of (A) was identical to that of poly-*N*-phenylethylenimine. On the other hand, the product (B) was soluble in formic acid and ethanol, and its infrared spectrum indicated the characteristic peak at 930 cm^{-1} assigned to a piperazine ring.

It has been reported by Dick that *N*-substituted ethylenimine reacts with allyl bromide in acetone at 40°C to produce the piperazine derivatives and the polymer, and that the infrared spectrum of the polymer showed the characteristic peak of the piperazine ring at 930 cm^{-1}.[4]

In view of these facts, the *N*,*N*-diphenylpiperazine derivative and the polymer were considered to be produced in the reaction of *N*-phenylethylenimine and monochloroacetic acid by the following mechanism:



The infrared spectrum of the polymer initiated by a strong acid catalyst shows the characteristic peak of the piperazine ring at 930 cm^{-1}. Therefore, the mechanism of the termination reaction may also be considered to be piperazine ring formation at the end of the polymer.



The increase in the termination reaction with a decrease in the pK_a of the acid may be ascribed to the separation of the counter anion from the growing immonium ion.

4) C. R. Dick, *J. Org. Chem.*, **32**, 72 (1967).