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### **Kinetics of the Copolymerization of Methyl Vinyl Ketone and Acrylamide Initiated by the Adduct of Methyl Vinyl Ketone and Imidazole**

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## KINETICS OF THE COPOLYMERIZATION OF METHYL VINYL KETONE AND ACRYLAMIDE INITIATED BY THE ADDUCT OF METHYL VINYL KETONE AND IMIDAZOLE

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### ABSTRACT

*N*-(Butyl-3-one)imidazole acts as an initiating adduct which is formed in the anionic polymerization of methyl vinyl ketone (MVK) induced by imidazole (Im) and is directly formed from Im and the MVK monomer. The kinetics of the anionic homopolymerization of MVK and acrylamide (AAm) under argon in the presence of the adduct were investigated in tetrahydrofuran (THF). The rate of polymerization for the MVK system is expressed as  $R_p = k[\text{Adduct}][\text{MVK}]$ , where  $k = 3.1 \times 10^{-6}$  L/(mol·s) in THF at 30°C. The overall activation energy,  $E_a$ , was found to be 5.34 kcal/mol. The  $R_p$  for the AAm system is expressed as  $R_p = k[\text{Adduct}][\text{AAm}]$ , where  $k = 6.8 \times 10^{-6}$  L/(mol·s) in THF at 30°C, with  $E_a$  7.78 kcal/mol. The mechanism of the polymerization induced by the initiator adduct is discussed on the basis of these results.

## INTRODUCTION

In earlier papers [1-6] we reported data on the homo- and copolymerization of acrolein induced by imidazole (Im). The imidazole-initiated polymerization of several polar vinyl monomers, such as methyl vinyl ketone [1, 2], acrylamide [2, 6, 8], and methyl methacrylate [2, 9] were also investigated. Our investigations of the kinetics revealed that the polymerization could be initiated by the Im-monomer adduct anion that is formed in the thermodynamic equilibrium between Im and the Im-monomer adduct (initiating adduct). An interesting point of these polymerization reactions is that the observed changes in the slope of the time-conversion curves appear to be related to the polymerization mechanism.

This observation may indicate that the initiating adduct described above is formed during the initial polymerization step. The overall polymerization rate,  $R_p$ , is described by the equation  $R_p = k[\text{Im}][\text{Monomer}]^2$ , which holds in tetrahydrofuran at 0-30°C [1, 2, 6, 8, 9]. The present report aims to establish the formation of the initiating adduct with methyl vinyl ketone as a monomer. We also aim to establish the initiation capability of the adduct for methyl vinyl ketone and acrylamide monomers.

## EXPERIMENTAL

### Materials

Methyl vinyl ketone (MVK) and acrylamide (AAM) were prepared as described in previous papers [1, 7]. Imidazole (Im) was used after recrystallization from benzene [1]. Tetrahydrofuran (THF), diethyl ether, and *n*-hexane were purified by conventional methods [11].

### The Polymerization Method

The polymerization of MVK was carried out in THF at 30°C under an argon atmosphere. THF solutions containing the required amounts of Im and MVK were placed in the main and side arms of the polymerization tube, respectively. The tube was placed in a thermostat kept at 30°C, and both solutions were mixed to start the polymerization reaction. The polymerization was stopped with a large amount of diethyl ether or methanol containing hydrogen chloride, and the precipitate was filtered, vacuum dried, and weighed to determine the yield.

### Kinetics

The initial polymerization rate,  $R_p$ , was estimated from the decrease in the amount of monomer, which was determined by gas-liquid chromatography (GLC). A linear relationship between the reaction time and the consumption of monomer was observed during the initial period of reaction.

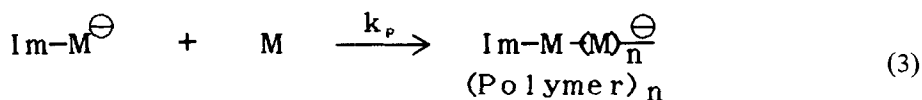
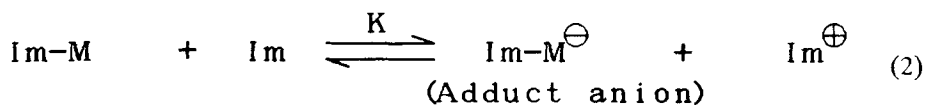
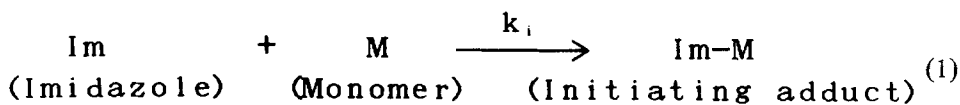
### Techniques and Analyses

Nuclear magnetic resonance ( $^1\text{H NMR}$ ) spectra in  $\text{CDCl}_3$  were recorded at 90 MHz with tetramethylsilane as an internal standard with a Hitachi-Perkin-Elmer Model 40 cw spectrometer. Mass spectra were obtained with a JEOL Model JMS-HX100 mass spectrometer. Infrared (IR) spectra were recorded with KBr disk or film samples by employing a Nihon-Bunkou IRA-2 spectrophotometer. Gas-liquid chromatography was carried out with a Yanaco Model G-1800 instrument, and helium gas was used as the carrier. The molecular weight distributions of the polymers were measured by gel-permeation chromatography (GPC) with Gasukuro-Kogyo Model LSG-9, Shodex GPC A-80M, and Toyo-Soda Model RI-8000 chromatographs.

## RESULTS AND DISCUSSION

### Synthesis of the Im-MVK Adduct and its Structure

We reported in earlier articles [1, 7] that the Im-monomer adduct may be formed as an "initiating adduct" in the initial polymerization setp. The polymerization could be initiated by the Im-monomer adduct anion formed in the thermodynamic equilibrium between Im and the Im-monomer adduct. This polymerization is assumed to proceed according to Eqs. (1)-(3):



The Im-monomer adducts formed during the initial polymerization step were confirmed by  $^1\text{H-NMR}$  spectroscopy [2]. However, the isolation of these unstable products and the structure of these products have not been previously investigated in detail.

In order to investigate these points, *N*-(butyl-3-one)-imidazole was synthesized as an initiating adduct by the equimolar reaction of Im with MVK. Crystalline Im (0.5 mol) was added directly to MVK (0.6 mol) and allowed to stand overnight at room temperature under an argon atmosphere. After the excess MVK monomer in solution was removed with diethyl, extraction with *n*-hexane gave a highly viscous oily substance which decomposed thermally at  $130^\circ\text{C}$ , as determined by GLC.

The IR spectrum of this compound (Fig. 1a) has several absorption bands characteristic of *N*-(butyl-3-one)imidazole, such as the Im group ( $3150\text{ cm}^{-1}$ ), the  $-\text{CH}_3$  group ( $2950\text{ cm}^{-1}$ ), and the  $>\text{C}=\text{O}$  group ( $1700\text{ cm}^{-1}$ ) bands. The  $^1\text{H-NMR}$  spectrum (Fig. 1b) contains several peaks from the Im group (7.4 and 6.9 ppm), the methylene chain of the added MVK monomer (4.2 ppm of  $\beta$ -proton and 2.8 ppm of  $\alpha$ -proton), and its methyl group (2.1 ppm). The mass spectrum (Fig. 1c) indicated a mass number ( $m/e = 138$ ) for the parent peak and several molecular fragments, such as  $-\text{CH}_3^+$  ( $m/e = 15$ ),  $\text{CH}_3\text{C}=\text{O}^+$  ( $m/e = 43$ ), and  $\text{Im}-\text{CH}_2^+$  ( $m/e = 68$ ). As the above experimental results show, the reaction product is *N*-(butyl-3-one)imidazole, as the Im-MVK (initiating) adduct.

#### Basicity of the Im-MVK Adduct

The  $\text{p}K_b$  value of this new Im derivative has not been previously determined. The pH of a solution of the Im-MVK adduct (0.07 mol/L) in water at  $30^\circ\text{C}$  was measured with a pH meter. The  $\text{p}K_b$  was calculated from the pH (9.0) as follows:

$$\text{p}K_b = -\log K_b = -\log \frac{[\text{Im-MVK adduct}^+][\text{OH}^-]}{[\text{Im-MVK adduct}]}$$

The  $K_b$  and  $\text{p}K_b$  thus obtained were  $3.06 \times 10^{-9}$  and 8.51, respectively. The latter is higher than that of Im ( $\text{p}K_b = 6.92$ ). The considerably higher basicity of Im compared to the Im-MVK adduct suggests a ready transfer of the  $\alpha$ -proton of the MVK unit of the adduct to Im.

The rate of the H-D exchange reaction of the Im-MVK adduct in  $\text{D}_2\text{O}$  was measured by  $^1\text{H-NMR}$  spectroscopy (Fig. 2). The proton peak of the  $\alpha$ -methylene group (at 2.7 ppm) decreased gradually with increasing reaction

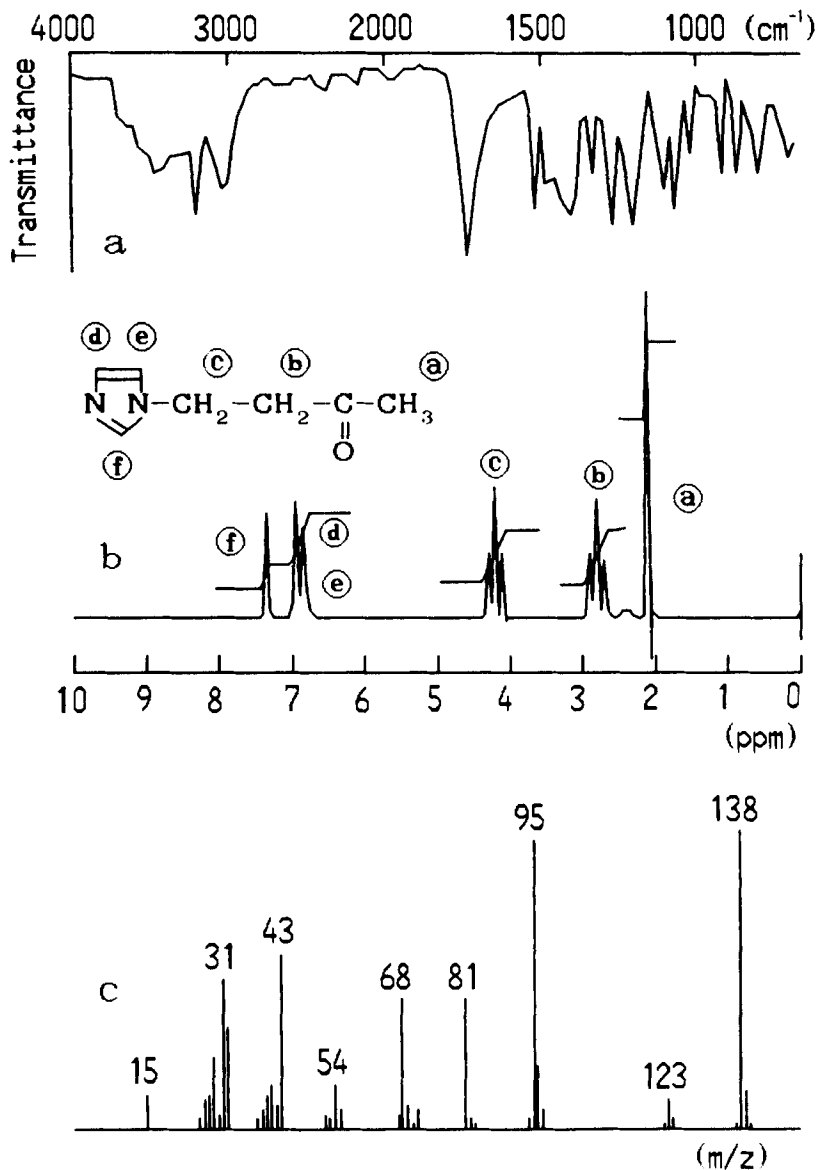


FIG. 1. IR,  $^1\text{H-NMR}$ , and mass spectra of *N*-(butyl-3-one)imidazole prepared as an Im-MVK adduct.

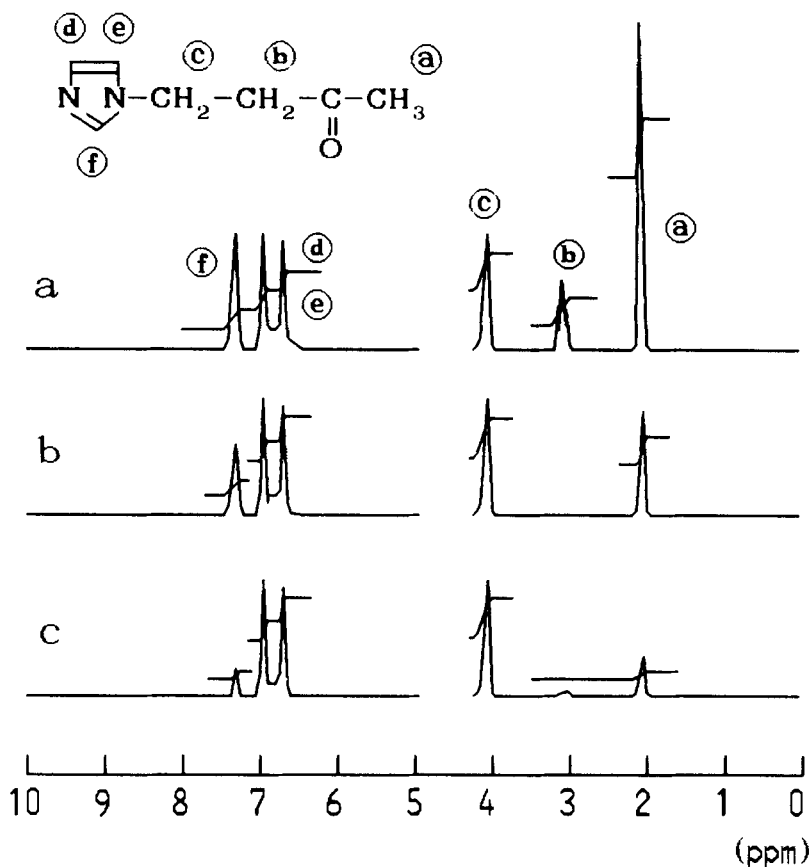



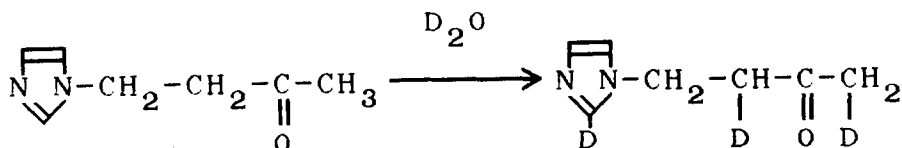
FIG. 2.  $^1\text{H-NMR}$  observations of the H-D exchange reaction of the polymer in  $\text{D}_2\text{O}$ . (a) At the start of the reaction, (b) after 18 h, (c) after 45 h.

time. The triplet peaks of the  $\beta$ -methylene group (at 4.2 ppm) changed to a singlet band without any shift of the center peak, whereas the proton signals of the Im ring (at 7.4 and 7.0 ppm) and that of the methyl group (at 1.9 ppm) did not change. The half-lives of the H-D exchange reactions are listed in Table 1. These results support our proposed polymerization mechanism.

TABLE 1. Half-Lifetime of the H-D Exchange Reaction<sup>a</sup> for *N*-(Butyl-3-one)imidazole Prepared as an Im-Adduct

Exchange position by D <sub>2</sub> O		Half-lifetime, <sup>b</sup> h
α-Position of methylene	-CHD-	9
Methyl group	-CO-CDH <sub>2</sub>	11
2-Position of imidazole	 $\text{N} \begin{array}{c} \text{N} \\ \text{Y} \\ \text{D} \end{array} \text{N}-\text{CH}_2-$	45

<sup>a</sup>Reaction conditions: [Im-MVK adduct] = 30 mg/500 μL; solvent, D<sub>2</sub>O; temperature, 25°C; atmosphere, argon gas.



<sup>b</sup>Measured by <sup>1</sup>H NMR.

### Polymerization of MVK with Im and the Im-MVK Adduct

We reported previously [1, 2, 5] the kinetics and polymerization mechanisms of acrolein, methyl methacrylate (MMA) and acrylamide (AAM) induced by Im. The rate of polymerization was determined as  $R_p = k[\text{Im}][\text{M}]^2$ , where  $k = 5.73 \times 10^{-2} \text{ L}^2/(\text{mol}^2 \cdot \text{s})$  in THF at 0°C for the acrolein system, and  $k = 3.00 \times 10^{-6} \text{ L}^2/(\text{mol}^2 \cdot \text{s})$  in THF at 30°C for the MMA system; and as  $R_p = k[\text{Im}][\text{M}]$ , where  $k = 9.33 \times 10^{-7} \text{ L}/(\text{mol} \cdot \text{s})$  in THF at room temperature (23°C) for the AAM system. The  $R_p$  value for MVK is similar to that reported earlier [1] and determined previously from unpublished data [10].

The polymerization of MVK in the presence of Im was carried out in THF at 30°C under an argon atmosphere. The resulting relationship between the conversion rate, based on monomer consumption, and the reaction time is shown in Fig. 3. This time-conversion curve (Fig. 3-I) indicates that the formation of Im-MVK adducts proceeds as a first step (from Point A to Point B). The propagation reaction begins at Point B and is induced by the initiating adduct, whereas the polymerization initiated directly by the Im-MVK



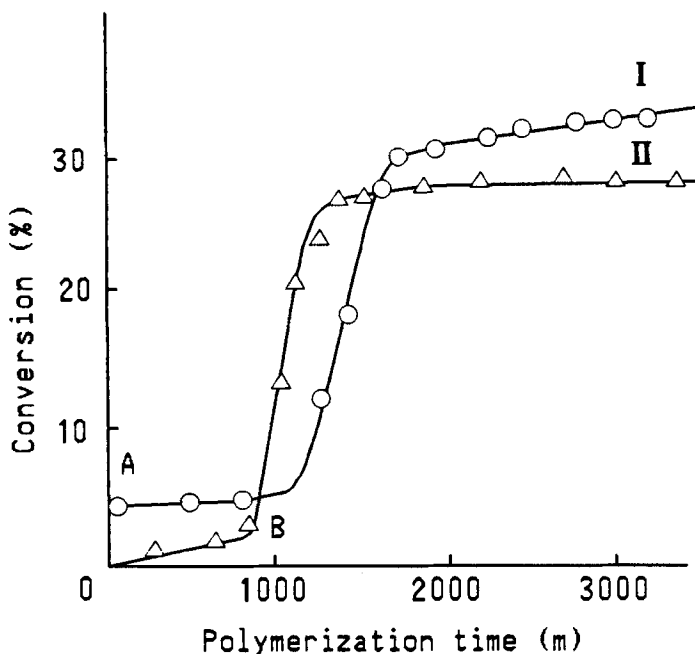


FIG. 3. The time-conversion curve of the polymerization of MVK induced by (I) Im and by (II) Im-MVK.  $[\text{Im}] = [\text{Im-MVK adduct}] = 0.13 \text{ mol/L}$ ;  $[\text{MVK}] = 3.60 \text{ mol/L}$ ; solvent, THF; temperature,  $30^\circ\text{C}$ ; atmosphere, argon gas. The conversion was calculated from the monomer consumption.

adduct (Fig. 3-II) is accompanied by a shortening of the first step. Figure 4 shows that maximum conversion is reached with an initial MVK concentration of about  $3 \text{ mol/L}$  and that the presence of a large quantity of Im impedes the polymerization reaction. This tendency may be explained by the fact that the monomer is used up for the formation of the initiating adduct during the initial polymerization step. These facts also support the polymerization mechanism described above by Eqs. (1)-(3).

On the other hand, gel-permeation chromatograms of poly-MVK were needed to investigate the mechanism of the propagation step (Fig. 5). The peak height for poly-MVK increased with increasing polymerization time, whereas its elution volume (i.e., average MW) remained unchanged. Our data thus clearly indicated that the propagation reaction is a chain reaction.

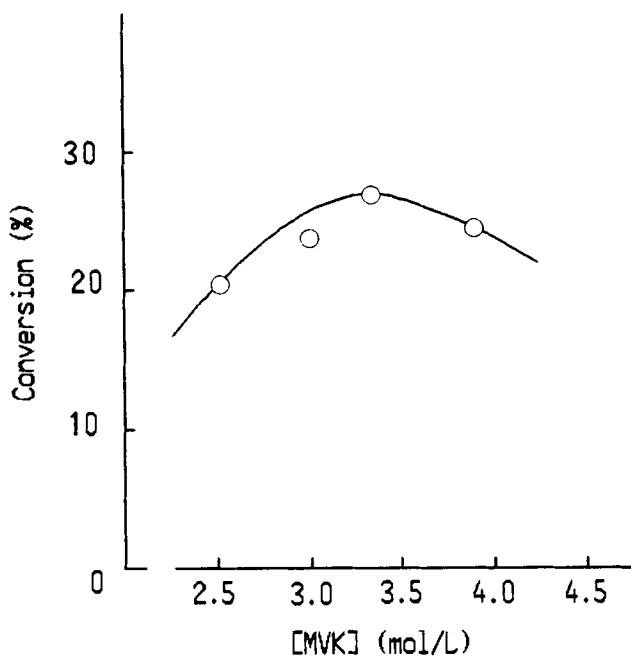


FIG. 4. The relationship between the MVK concentration and the conversion determined from the monomer consumption.  $[Im] = 0.10$  mol/L; solvent, THF; temperature,  $30^{\circ}C$ ; polymerization time, 70 h; atmosphere, argon gas.

The kinetics of polymerization of MVK initiated directly by the Im-MVK adduct (synthesized *N*-(butyl-3-one)imidazole) in THF was also carried out at  $30^{\circ}C$  under an argon atmosphere. The characteristic period for formation of the Im-MVK adduct (Point A to Point B in Fig. 3) was shortened. The  $R_p$  was estimated from the consumption rate of the monomer by means of GLC. A linear relationship was observed between  $R_p$  after Point B and the concentration of MVK or the Im-MVK adduct (Figs. 6 and 7). The rate, expressed as

$$R_p = k[Im-MVK \text{ adduct}][MVK],$$

led to  $k = 3.2 \times 10^{-6}$  L/(mol·s) in THF at  $30^{\circ}C$ . From this kinetic result and the H-D exchange data described above, the reaction mechanism is explained

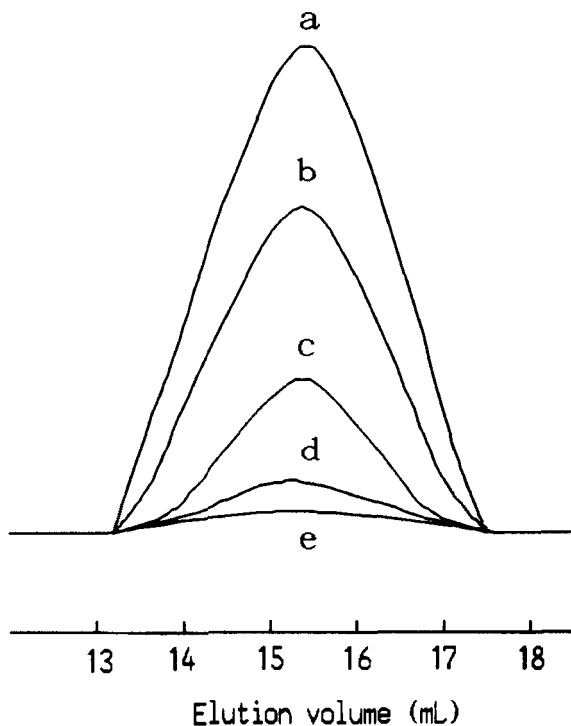
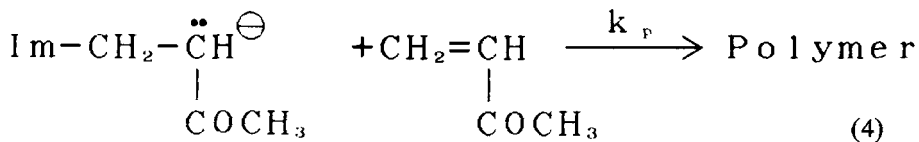


FIG. 5. Gel permeation chromatogram of poly-MVK obtained from the polymerization of MVK induced by the Im catalyst. [Im] = 0.09 mol/L; [MVK] = 3.0 mol/L; solvent, THF; temperature, 30°C; atmosphere, argon gas. Polymerization time: (a) 41 h, (b) 34 h, (c) 23 h, (d) 9.5 h, (e) 3 h.

on the basis of a general anionic propagation mechanism (Eq. 4), i.e., the initiating adduct could readily dissociate to the initiating anion.



The overall activation energy,  $E_a$ , obtained from the Arrhenius plot (Fig. 8) was 5.34 kcal/mol for this initiation reaction. That for the polymerization

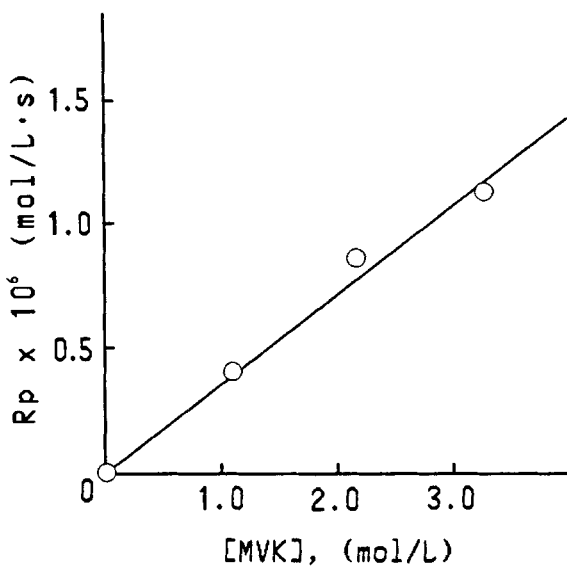


FIG. 6. Relationship between the polymerization rate,  $R_p$ , and the MVK concentration. [Im-MVK adduct] = 0.10 mol/L; solvent, THF; temperature, 30°C; atmosphere, argon gas.

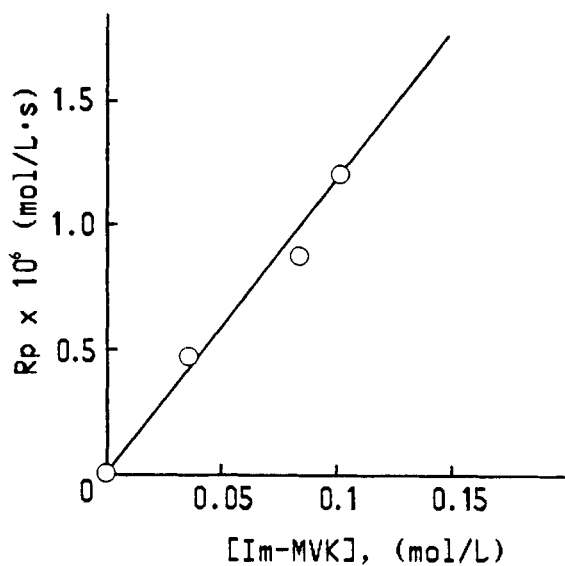


FIG. 7. Relationship between the polymerization rate,  $R_p$ , and the Im-MVK adduct concentration. [MVK] = 3.30 mol/L; solvent, THF; temperature, 30°C; atmosphere, argon gas.

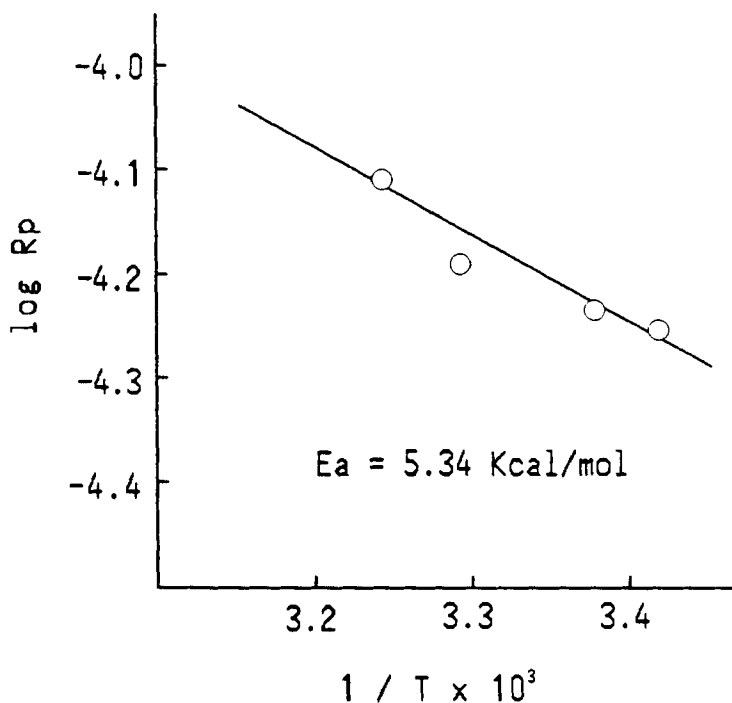


FIG. 8. Arrhenius plot for the Im-MVK adduct system.

of MVK induced by Im, obtained from the  $R_p$  dependence of the propagation step (second step of the reaction) in Fig. 3, was very similar 5.24 kcal/mol (Fig. 9). Both  $E_a$  values support the idea that the reaction proceeded by an anionic polymerization mechanism.

All polymers that we obtained were readily soluble in acetone, dioxane, and THF. The IR spectra of the polymers induced by the Im catalyst (Fig. 10a) and by the Im-MVK catalyst (Fig. 10b) revealed absorption bands characteristic for Im ( $3150 \text{ cm}^{-1}$ ) and MVK ( $3000\text{-}2900$ ,  $1720\text{-}1680 \text{ cm}^{-1}$ ), which suggests a structure similar to that of the polymers obtained by anionic polymerization, in agreement with the idea that poly-MVK contains the Im group as an end group [1].

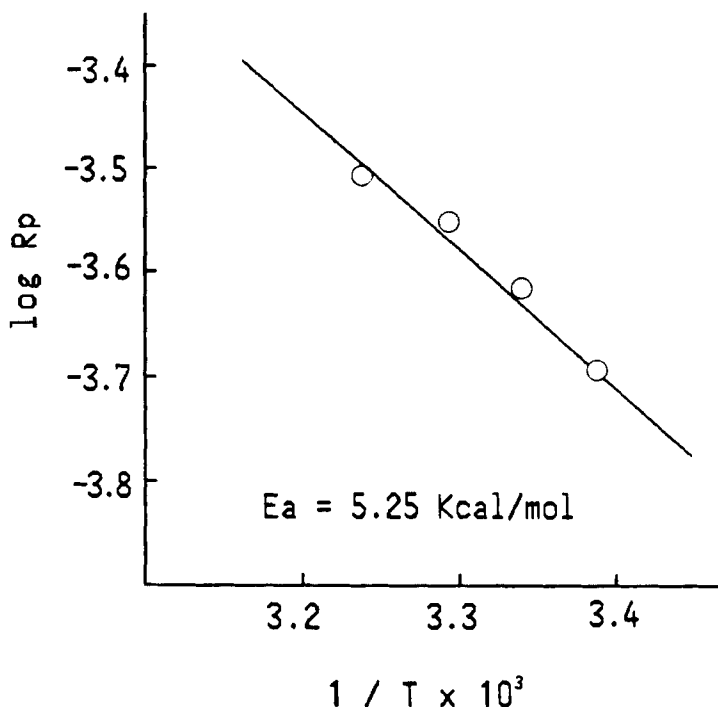


FIG. 9. Arrhenius plot for the Im system.

#### Polymerization of AAm Induced by the Im-MVK Adduct

Polymerization of AAm in the presence of Im has been described in our previous papers [2, 7]. The polymerizability of this monomer induced by the Im-MVK adduct will now be discussed. The polymerization of AAm in the presence of the Im-MVK adduct in THF was carried out at 30°C under an argon atmosphere (Figs. 11 and 12). The  $R_p$  value, determined from the equation

$$R_p = k [\text{Im-MVK adduct}] [\text{AAm}],$$

gave  $k = 6.83 \times 10^{-6}$  L/(mol·s) in THF at 30°C. The  $E_a$  was 7.78 kcal/mol, whereas  $E_a$  for the Im system has been reported as 9.6 kcal/mol [7]. The

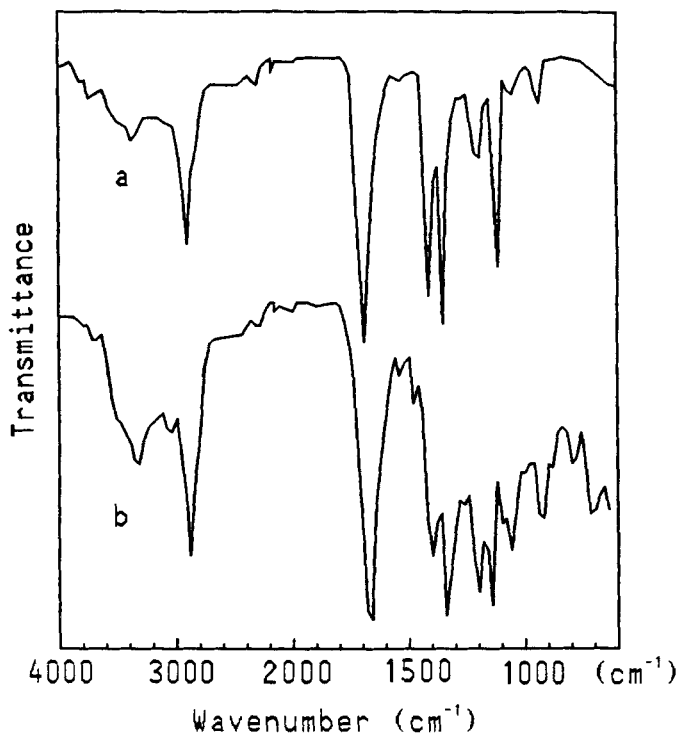


FIG. 10. IR spectra of poly-MVK. (a) Im system. (b) Im-MVK adduct system.

fact that the later value was higher than that of the Im-MVK system suggests the existence of a mechanism involving the formation of a complex during the propagation step.

The polymers obtained were in the form of white powders and were soluble in water. The IR spectrum (conversion, 38.4%;  $\bar{M}_n$ , 3907) revealed absorption bands corresponding to Im (3200, 1600-1500, and 1400-1200  $\text{cm}^{-1}$ ), and the characteristic absorption bands of poly-AAm (1700-1600  $\text{cm}^{-1}$ ), corresponding to the 1,2-addition vinyl polymer of AAam, as described previously [7, 11].

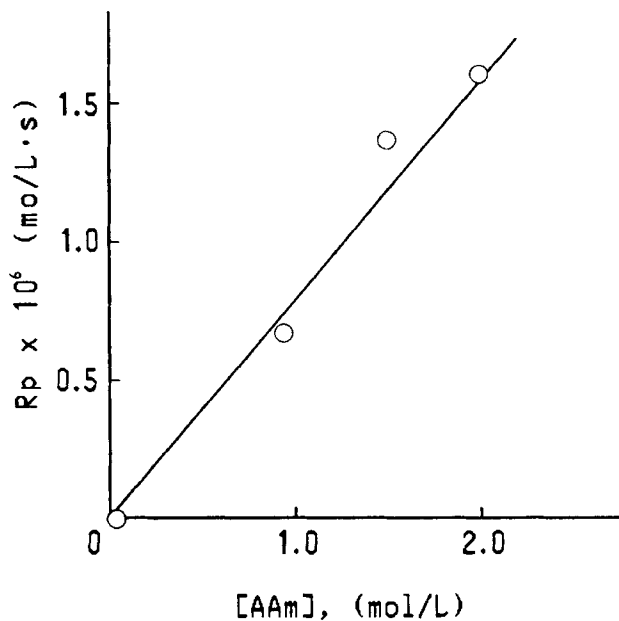


FIG. 11. Relationship between the polymerization rate,  $R_p$ , and the AAm concentration. [Im-MVK adduct] = 0.10 mol/L; solvent, THF; temperature, 30°C; atmosphere, argon gas.

### CONCLUSIONS

In the time-conversion curve of the polymerization of MVK by the Im catalyst, there are two distinct slopes. This was explained by the presence of two reaction steps, with the first step corresponding to the formation of the Im-MVK adduct (initiating adduct) and the second step representing the polymerization propagation reaction.

In the first reaction step an adduct is formed by Im and the MVK monomer. The amount of polymer obtained at this stage is very small. The  $^1\text{H-NMR}$  and mass spectrometry results for the *N*-(butyl-3-one)imidazole synthesized as an Im-MVK adduct show that the  $\alpha$ -proton in the MVK unit of the adduct is subject to proton transfer. The polymerization kinetics for MVK and AAm in-



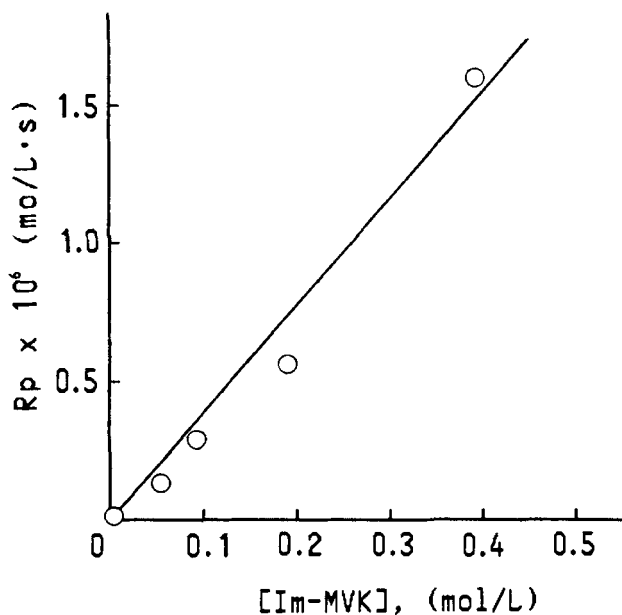


FIG. 12. Relationship between the polymerization rate,  $R_p$ , and the Im-MVK adduct concentration.  $[A_m] = 1.00$  mol/L; solvent, THF; temperature,  $30^\circ\text{C}$ ; atmosphere, argon gas.

duced by the adduct as an anionic catalyst were confirmed to be  $R_p = k[\text{Im-MVK adduct}][M]$ , where  $M$  represents MVK or AAm monomer.

From the above described facts we conclude that the formation step of the initiating adduct is part of the polymerization mechanism.

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## REFERENCES

- [1] N. Yamashita, S. Morita, and T. Maeshima, *J. Macromol. Sci.—Chem.*, **A12**(9), 1261 (1978).
- [2] S. Morita, K. Ikezawa, H. Inoue, N. Yamashita, and T. Maeshima, *Ibid.*, **A17**(9), 1945 (1982).
- [3] N. Yamashita, S. Morita, H. Yoneyama, and T. Maeshima, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 13 (1983).
- [4] N. Yamashita, S. Morita, M. Nishino, and T. Maeshima, *J. Polym. Sci., Chem. Ed.*, **21**, 239 (1983).
- [5] M. Horiba, N. Yamashita, and T. Maeshima, *J. Macromol. Sci.—Chem.*, **A23**(9), 117 (1986).
- [6] N. Yamashita, A. Tadokoro, E. Ozu, T. Maeshima, I. C. Baianu, and L. S. Wei, *Ibid.*, **A24**(10), 1223 (1987).
- [7] S. Morita, H. Inoue, N. Yamashita, and T. Maeshima, *Ibid.*, **A16**(5), 1003 (1981).
- [8] N. Yamashita, K. Ikezawa, Y. Yamamoto, H. Kinugasa, and T. Maeshima, *Ibid.*, **A21**(3), 291 (1984).
- [9] N. Yamashita, H. Tanaka, S. Deguchi, and T. Maeshima, *Ibid.*, **A24**(9), 1121 (1987).
- [10] N. Yamashita, E. Ozu, and L. S. Wei, Unpublished Data.
- [11] T. Otsu and M. Kinoshita (eds.), *Experimental Method of Polymer Syntheses*, Kagaku Doujin, Kyoto, Japan, 1975; The Society of Polymer Science Japan (ed.), *Syntheses of Monomers*, Kyouritsu Syuppan, Tokyo, Japan, 1958.

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