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Satoshi Morita<sup>a</sup>; Hiroshi Inoue<sup>a</sup>; Natsuki Yamashita<sup>a</sup>; Toshihisa Maeshima<sup>a</sup>

<sup>a</sup> Department of Applied Chemistry Faculty of Science and Engineering, Kinki University Kowakae, Higashi-Osaka, Japan

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## Polymerizabilities of Several Polar Vinyl Monomers by Imidazole

SATOSHI MORITA, HIROSHI INOUE, NATSUKI YAMASHITA, and TOSHIHISA MAESHIMA

Department of Applied Chemistry  
Faculty of Science and Engineering  
Kinki University  
Kowakae, Higashi-Osaka, Japan

### ABSTRACT

Polymerizabilities of several polar vinyl monomers in the presence of imidazole (Im) have been studied in  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$  by NMR spectra. Acrylic acid formed a bimolecular adduct with Im as the initial adduct, while methacrylic acid was not obtained. On the other hand, methyl acrylate, methyl methacrylate (MMA), acrylamide (AAm), and acrylonitrile formed the initial adduct between Im and monomer, respectively. In these monomers, AAm and MMA gave each polymer in tetrahydrofuran at room temperature. The number-average molecular weight ( $\bar{M}_n$ ) of AAm polymers was determined to be in the range of 1000 to 1500, and the  $\bar{M}_n$  of MMA polymers was found to be in the range of 2500 to 4500. The rate of polymerization  $R_p$  was expressed by the equations  $R_p = k[\text{Im}][\text{AAm}]$  and  $R_p = k[\text{Im}][\text{MMA}]^2$ , respectively. The activation energy  $E_R$  was obtained by Arrhenius's plots as  $E_R(\text{AAm}) = 9.6 \text{ kcal/mol}$  and  $E_R(\text{MMA}) = 3.8 \text{ kcal/mol}$ . These polymerization mechanisms are discussed on the basis of these results.

## INTRODUCTION

In a preceding paper [1] we reported that acrolein (AL) could be polymerized readily by imidazole (Im) below room temperature. The polymers obtained were found to be composed of vinyl polymer with one Im group attached and having an aldehyde side chain, of which 70-80 mol% of the aldehyde revealed a bridge structure.

The kinetic investigations revealed that the polymerization was initiated by a thermodynamic equilibrium between the Im and an initial adduct of Im and monomer in the initial polymerization step. On the other hand, we have been investigating the graft polymerizability of AL onto Im-containing polymers such as 4(5)-vinylimidazole homopolymer and its several copolymers [2, 3]. These proved that the graft polymerization reaction also proceeds by a similar polymerization mechanism in the Im group.

This investigation was performed to reveal the polymerizabilities of several other polar vinyl monomers such as acrylic acid, methacrylic acid, methyl acrylate, methyl methacrylate, acrylamide, and acrylonitrile by Im and the structure of the initial addition products and polymers.

## EXPERIMENTAL

### Materials

Acrolein (AL) was purified in the manner described in previous papers [1, 4]. The purification of the other monomers such as acrylic acid (AA), methacrylic acid (MMA), methyl acrylate (MA), methyl methacrylate (MMA), acrylamide (AAM), and acrylonitrile (AN) was carried out in the usual way. Imidazole (Im) was purified by recrystallization from benzene.

### Polymerization Method

All operations were carried out in the manner described in a previous paper [1]. The required amounts of Im and solvent were placed into a polymerization tube. Then a mixed amount of monomer was added to start the polymerization reaction under a nitrogen atmosphere. The polymerization was stopped in a large amount of precipitating agent, and the precipitate was filtered to dry.

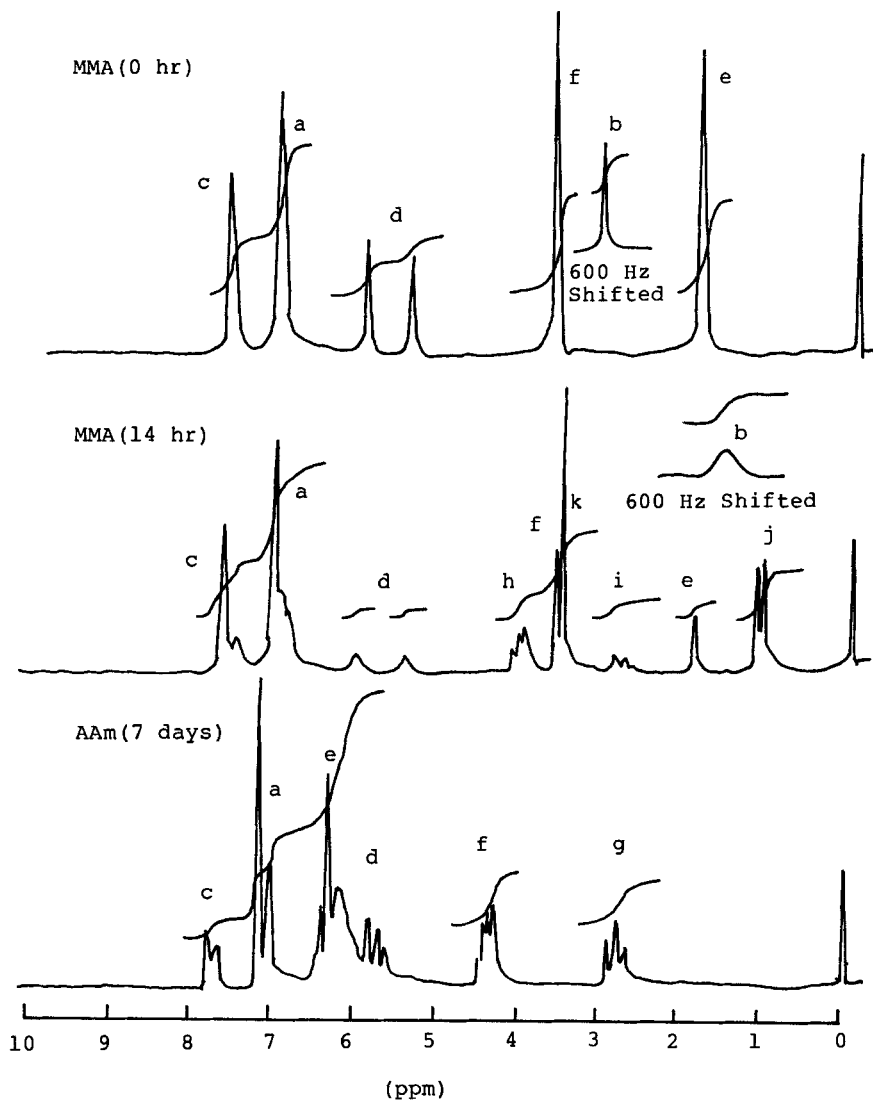


FIG. 1. NMR spectra of Im-monomer system; Im,  $\overline{\text{CH}=\text{CH}-\text{NH}-\text{CH}=\text{N}}$ ;  
MMA,  $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COOCH}_3$  and  $\text{R}_2\text{N}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{COOCH}_3$ ; AAm,  
 $\text{CH}_2=\text{CHCONH}_2$  and  $\text{R}_2\text{N}-\text{CH}_2-\text{CH}_2\text{CONH}_2$ .

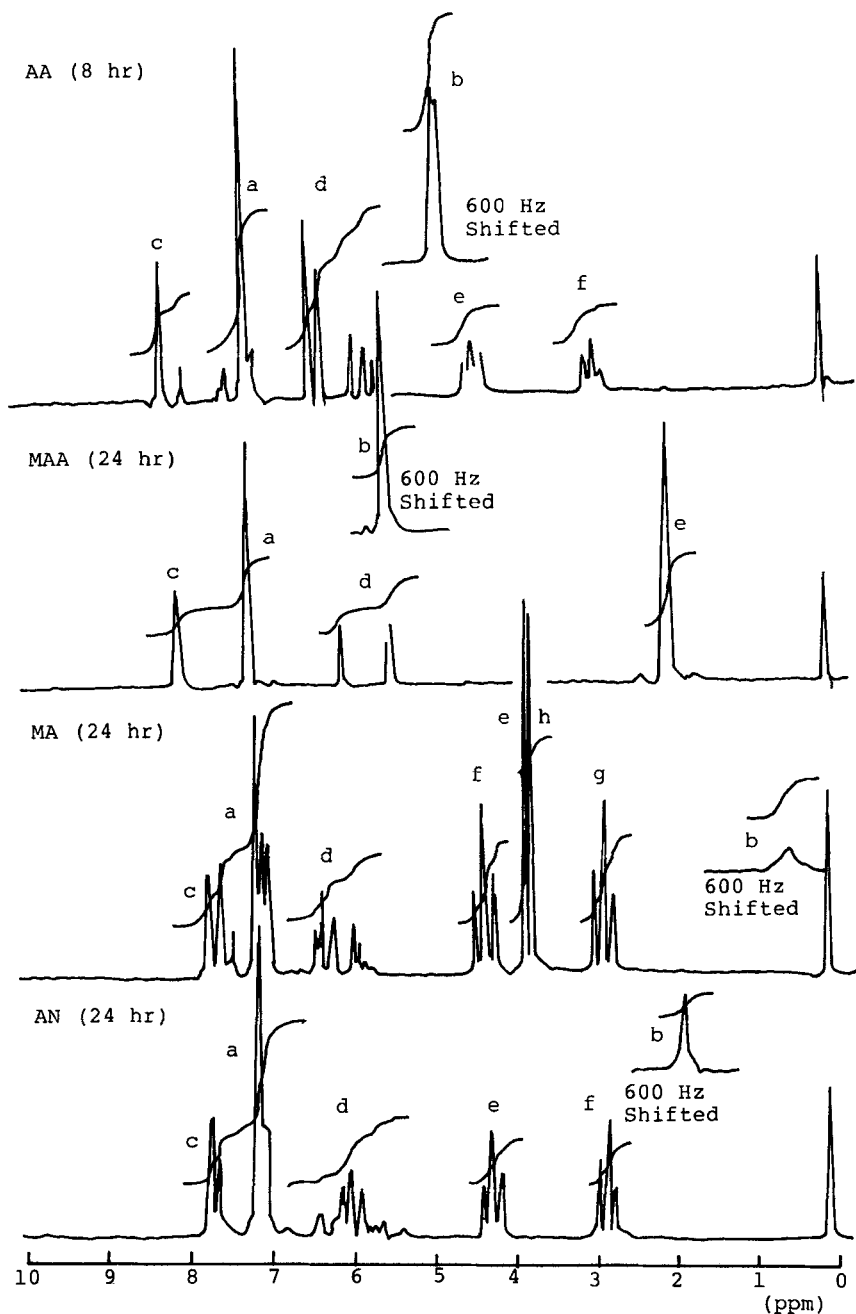


FIG. 2. NMR spectra of Im-monomer system; Im,  $\overline{\text{CH}=\text{CH}-\text{NH}-\text{CH}=\text{N}}$ ;  
AA,  $\text{CH}_2=\text{CH}-\text{COOH}$  and  $\text{R}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{COOH}$ ; MAA,  $\text{CH}_2=\text{C}(\text{CH}_3)-$   
 $\text{COOH}$ ; MA,  $\text{CH}_2=\text{CH}-\text{COOCH}_3$ , and  $\text{R}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{COOCH}_3$ ; AN,  
 $\text{CH}_2=\text{CH}-\text{CN}$  and  $\text{R}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CN}$ .  
d d d e f d e b d d e f g h

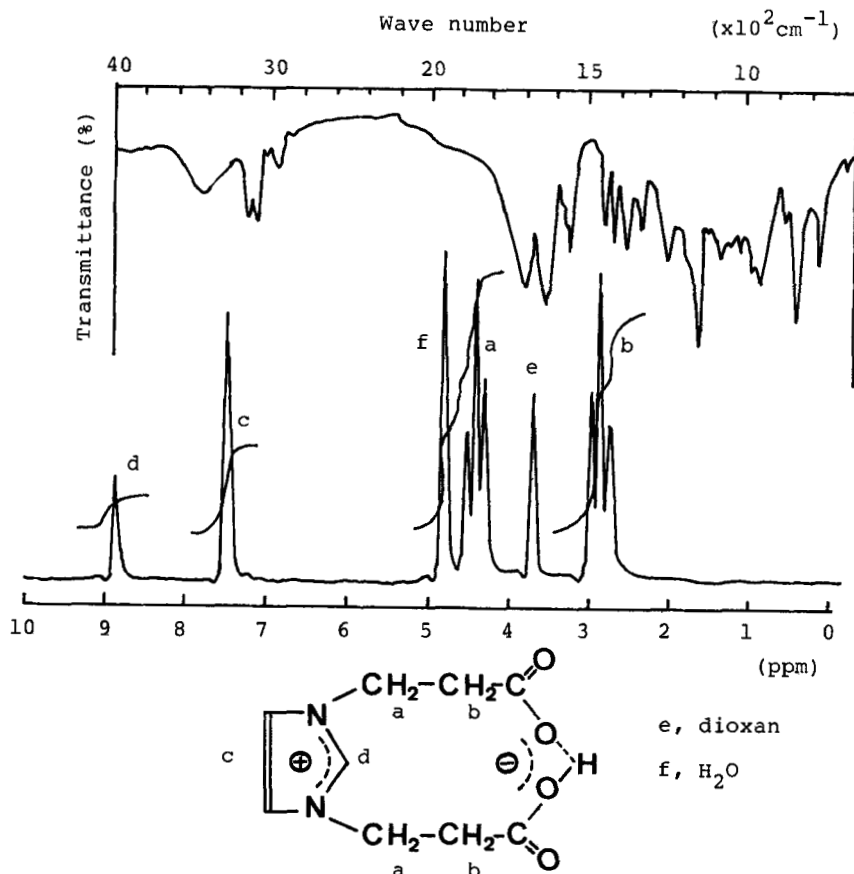


FIG. 3. IR (KBr disk) and NMR (in  $D_2O$ ) spectra of initial adduct in Im-AA system.

## RESULT AND DISCUSSION

### Observation of Initial Polymerization Step by NMR Spectra

In a previous paper [1] the reactivity of Im and monomer in the initial polymerization step was observed by NMR spectra. Similarly, in this study observations of Im and monomer mixtures by NMR spectra were carried out in  $CDCl_3$  and  $CD_3OD$  (Figs. 1 and 2). In Fig 1 the signal (13.5 ppm) of the NH proton dependent on Im disappears with a shift to high magnetic field in the initial reaction step, and the

TABLE 1. Observation of Initial Polymerization Step by NMR Spectra<sup>a</sup>

Monomers	Solvents	Initial addition product (Im:monomer)	Reaction rate, $R \times 10^4$ (mol/L·min)	Propagation to polymer
AA	CDCl <sub>3</sub>	1:2 Adduct	2.86	No
MAA	CDCl <sub>3</sub>	No	-	No
MA	CDCl <sub>3</sub>	1:1 Adduct	24.10	No
MMA	CDCl <sub>3</sub>	1:1 Adduct	0.40	Polymerize
AAM	CD <sub>3</sub> OD	1:1 Adduct	1.28	Polymerize
AN	CDCl <sub>3</sub>	1:1 Adduct	10.55	No

<sup>a</sup>[Im]/[monomer] = 1.0 mol ratio.

signal attributed to the methylene proton (2.5-4.5 ppm), which depends on vinyl addition, readily appears. These observations also support the addition of the NH proton of Im to the vinyl group of the monomer in a manner similar to the Im-AL system. The reactions of the other monomers are similarly indicated in Fig. 2. In this respect, it is interesting that AA forms a bimolecular adduct. In order to examine the process of formation of this adduct, the equimolar reaction of Im and AA was carried out in tetrahydrofuran at room temperature. The structure of the resulting product was confirmed by elementary analysis (C, 50.6%; H, 5.74%; N, 13.19%), and the measurement of the molecular weight (212-215 by the VPO method), the melting point (236°C), and the NMR and IR spectra (Fig. 3). In Fig. 2 the reason for the nonformation of the MMA adduct can be explained by the steric hindrance which depends upon the methyl group of the  $\alpha$ -carbon in the monomer.

On the other hand, all of the other monomers formed the initial adducts between Im and monomer (Table 1). The reaction rate  $R$  was calculated from the integral curves of the NMR spectra. In general, it is well known that these polar vinyl monomers polymerize by alkaline catalysts. In this study, however, the relationship between  $R$  and  $e$  values of the monomer are not perceived in Table 1. It is particularly interesting that MMA and AAM were propagated to the polymer in spite of low reactivity. This phenomenon also supports the polymerization mechanism of our previous work [1] with the equilibrium reaction between the Im and the Im-monomer adduct.

#### Polymerization of AAM by Im

Polymerization of AAM in the presence of Im was carried out in tetrahydrofuran (THF) at room temperature under a nitrogen

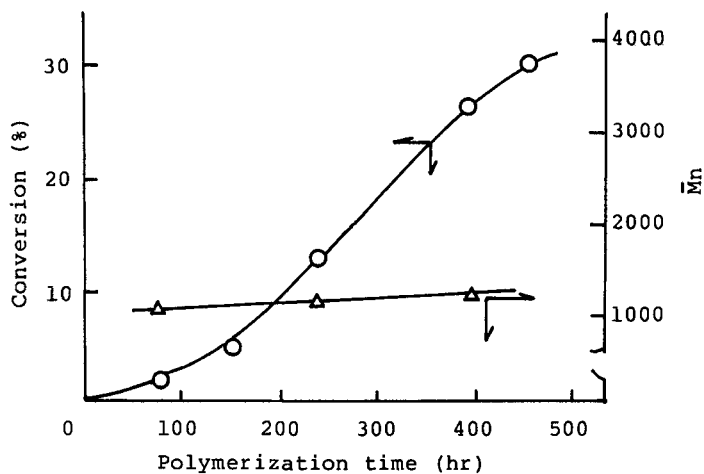


FIG. 4. Relationships between conversion,  $\bar{M}_n$ , and polymerization time in polymerization of AAm;  $[Im] = 0.1 \text{ mol/L}$ ;  $[AAm] = 0.2 \text{ mol/L}$ ; solvent, THF; room temperature.

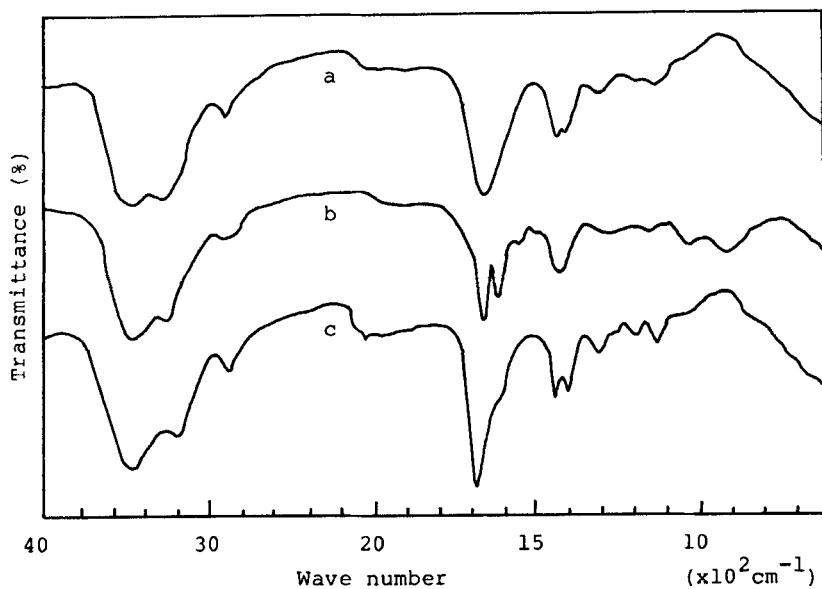


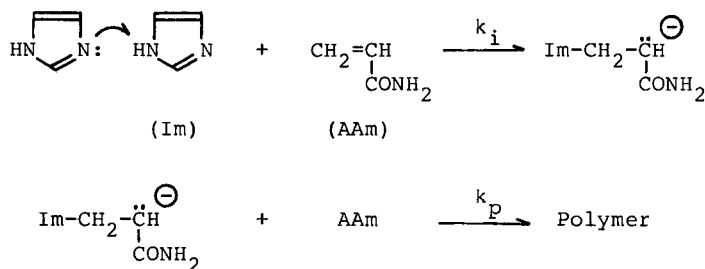
FIG. 5. IR spectra of poly-AAm; a, radical polymer; b, anionic polymer (1,4-addition) by Na; c, this study.



atmosphere (Fig. 4). The polymers obtained were in the form of a white powder and were soluble in water. The IR spectrum (Fig. 5) of a polymer (conversion, 28.5%;  $\bar{M}_n$ , 3830) revealed absorption bands depending on Im (3200, 1600-1500, and 1400-1200  $\text{cm}^{-1}$ ), and the characteristic absorption bands depended on poly-AAm (1700-1600  $\text{cm}^{-1}$ ). In addition, the spectra were sufficiently similar to suggest the same structure for the radical polymer. These results clearly support a polymer structure composed of an Im ring and the vinyl polymer of AAm.

On the other hand, the polymerization of AAm kinetically was carried out in the presence of Im in THF at 0°C. The overall polymerization rate  $R_p$  was determined as  $R_p = k[\text{Im}][\text{AAm}]$  ( $k = 5.6 \times 10^{-5}$  L/mol·min) with varying concentrations of monomer and catalyst. Overall activation energy  $E_R$  was determined as  $E_R = 9.6$  kcal/mol (in THF at 30-0°C) from Arrhenius's plots (Fig. 6).

From these kinetic results, this polymerization was explained by an anionic polymerization mechanism as follows:



In previous work [1], however, an overall polymerization equation of AL was obtained as  $R_p = k[\text{Im}][\text{AL}]^2$  ( $k = 5.73 \times 10^{-2}$  L/mol·s in THF at 0°C).

Differences are observed in these polymerization equations. This may be explained by the  $e$  value of the monomer ( $e$  value of AAm = 1.30). AN ( $e$  value = 1.20) was not polymerized (Table 1). By considering these results, it is shown that polymerization occurs only with monomers of the vinyl ketone type. In the polymerization mechanism of AAm, therefore, the participation of the carbonyl group in the monomer is needed in the initiation and propagation steps.

#### Polymerization of MMA by Im

Polymerization of MMA in the presence of Im was carried out in THF at room temperature under nitrogen (Fig. 7). The IR spectrum (Fig. 8) of the polymer (conversion, 24.5%;  $\bar{M}_n$ , 2500) revealed characteristic absorption bands which depended on Im and MMA (2950,

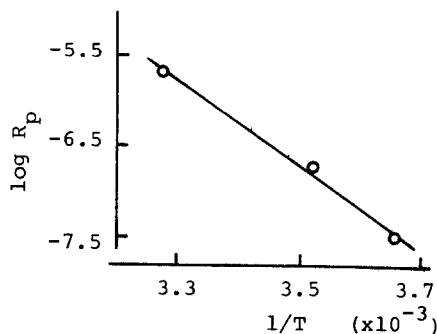


FIG. 6. Relationship between  $\log R_p$  and  $1/T$  in polymerization of AAm.

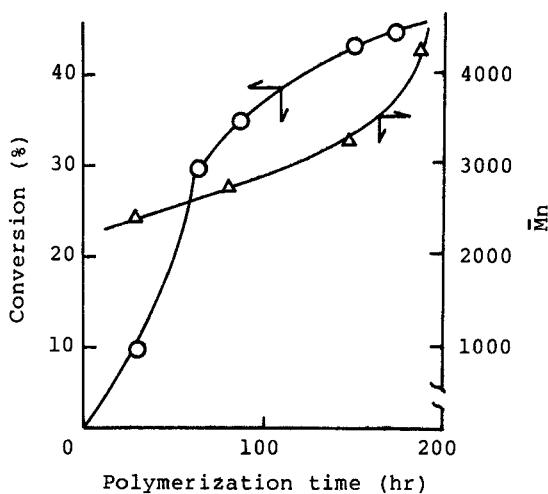


FIG. 7. Relationships between conversion,  $\bar{M}_n$  and polymerization time in polymerization of MMA;  $[I_m] = 0.5 \text{ mol/L}$ ;  $[MMA] = 1.0 \text{ mol/L}$ ; solvent, THF; room temperature.

1720, and  $1160 \text{ cm}^{-1}$ ), and similarity of the spectrum suggested the same structure as the radical poly-MMA.

The polymers obtained were very slightly soluble in acetone, chloroform, benzene, and THF. Moreover, the melting points were found to be in the range  $238\text{--}242^\circ\text{C}$ . These observations indicate that these poly-MMAs have a syndiotactic structure.

In order to examine the structure of poly-MMA, the NMR spectrum

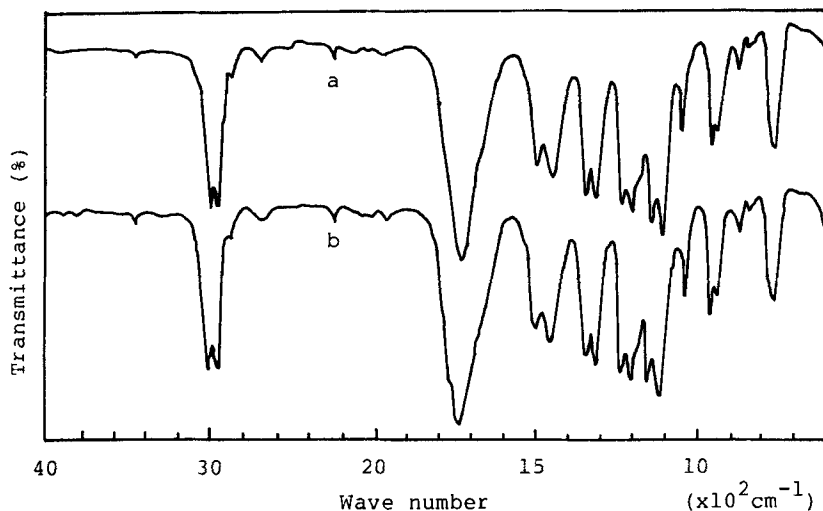


FIG. 8. IR spectra of poly-MMA; a, this study; b, radical polymer.

was observed in  $\text{CDCl}_3$  (Fig. 9D). The structure of stereospecific poly-MMA (Figs. 9A, B, and C) has been studied by NMR spectra [5]. The NMR spectrum (Fig. 9D) of poly-MMA in this study has several signals depending on the methyl group (0.5-1.5 ppm), the methylene chain (1.5-2.3 ppm), and the methyl ester group (3.7 ppm). This result clearly supports a structure composed of the vinyl polymer of MMA. Moreover, the spectra of D and C were sufficiently similar to suggest the same poly-MMA structure.

The  $R_p$  was determined as  $R_p = k[\text{Im}][\text{MMA}]^2$  ( $k = 1.6 \times 10^{-4} \text{ L/mol}\cdot\text{min}$  in THF at  $0^\circ\text{C}$ ) with varying concentrations of monomer and catalyst. The relationship (Fig. 10) between  $\log R_p$  and  $1/T$  was obtained by  $E_R = 3.8 \text{ kcal/mol}$  (in THF at  $30-0^\circ\text{C}$ ). These kinetic results also support the anionic polymerization mechanism, and it is the same as the polymerization of AL. Therefore, this polymerization mechanism may be assumed to proceed as shown in Eqs. (1)-(3). The polymerization might be initiated by the addition of Im and monomer in Eq. (1). The thermodynamic equilibrium between the initial adduct and the Im occurs with hydrogen bonding depending upon  $>\text{C}=\text{O}$  of MMA and  $\text{NH}$  of Im (Eq. 2). The reason for the formation of a stereospecific poly-MMA in this study may also be explained by the formation of an ion pair between the MMA anion and the Im cation, and by the steric hindrance of the  $\alpha$ -methyl group in the monomer.

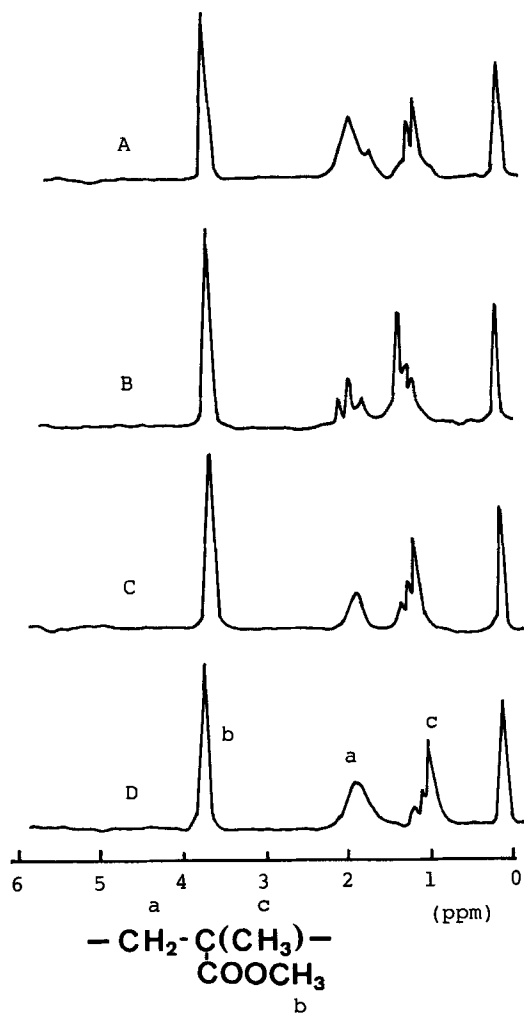


FIG. 9. NMR spectra of poly-MMA; A, atactic polymer B, isotactic polymer; C, syndiotactic polymer; D, this study.

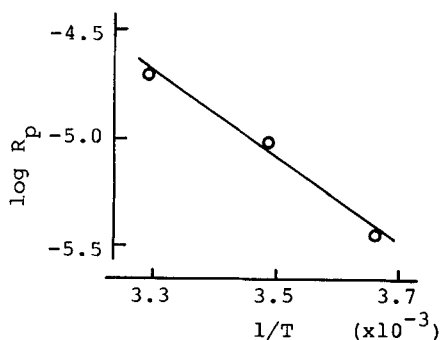
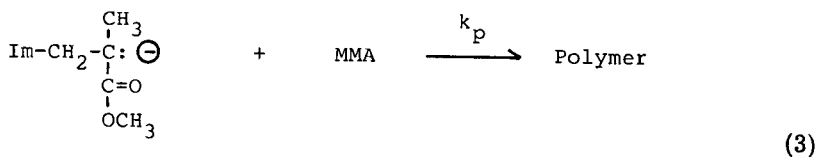
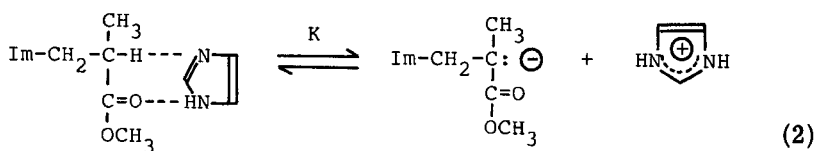
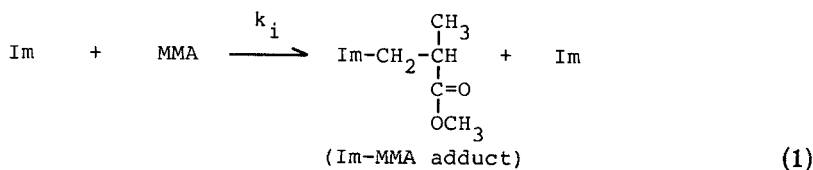


FIG. 10. Relationship between  $\log R_p$  and  $1/T$  in polymerization of MMA.



From these all results it is shown that AAm and MMA also polymerize by Im. The polymerization mechanism of MMA was explained by AL and methyl vinyl ketone as in the previous paper [1]. However, the polymerization of AAm occurred by anionic polymerization.

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