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Polymerization of Acrolein by Imidazole

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ABSTRACT

Polymerization of acrolein(AL) in the presence of imidazole(Im) has been investigated in tetrahydrofuran or methanol below room temperature. The polymers obtained, white or pale yellow powders, were found to be composed of vinyl polymer with one Im group attached and having an aldehyde side chain, of which 70-80 mole % of the aldehyde revealed bridge structure. The number-average molecular weight ($\overline{M}_n$) of these polymers was determined to be in the range of 317 to 691. The rate of polymerization R_p was expressed by the equation, $R_p = k[Im][AL]^2$. The addition of water or dimethyl sulfoxide accelerated the polymerization reaction, while the presence of benzaldehyde or N,N'-dimethylformamide decreased R_p. The structure of addition products in the initial polymerization step was confirmed by IR and NMR spectra, and the observations of polymerization system was carried out by UV and NMR spectra. The polymerization mechanisms were discussed on the basis of these results.

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INTRODUCTION

Numerous reports have been published [1] on the polymerizability of acrolein by such polymerization methods as radical, cationic, and anionic polymerization. It is well known that the polyacrolein structure is generally composed of polymer units formed through both vinyl and aldehyde polymerization. Further, these polyacroleins are converted to the insoluble and infusible polymer by intramolecular cyclization and/or the intermolecular crosslinking of side chains.

Our previous papers [2-6] described how acrolein could be polymerized by a mixture of pyridine and water below room temperature. The kinetic investigations revealed that polymerization might be initiated by a hydroxyl anion formed through thermodynamic equilibrium between pyridine and water. However, the polymerization of acrolein in the presence of imidazole and benzimidazole gives a soluble polyacrolien containing the imidazole ring. The present investigation was performed in order to reveal the mechanism of polymerization of acrolein by imidazole and the structure of the resulting initial products and polymers.

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EXPERIMENTAL

Materials

Acrolein (AL) and methyl vinyl ketone (MVK) were prepared in the manner described in previous papers [3, 4]. Imidazole (Im) and benzimidazole (BIm) were purified by the recrystallization from benzene and water, respectively. Tetrahydrofuran (THF), methanol, N,N'-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and benzaldehyde were purified in the usual way.

Polymerization Methods

All operations were carried out in the vacuum line. The polymerization was carried out homogeneously in THF or methanol at 0°C in vacuo or under a nitrogen atmosphere. The required amounts of catalysts and solvent were placed into a tube. Then a fixed amount of monomer was added to start the polymerization reaction. The polymerization was stopped in a large amount of ether containing hydrochloride, and the precipitate was filtered to dry.

Kinetics

The initial polymerization rate R_p was estimated from the decreasing rate of monomer by means of gas chromatography (GLC). A straight-line relationship between the reaction time and the consumption of monomer was observed at the initial step of the reaction.

RESULT AND DISCUSSION

Results of Polymerization and Structure of Polymer

The results of polymerization are shown in Table 1. The atmosphere under which polymerization is carried out (vacuum or nitrogen) made no difference to the yields. The addition of water or DMSO tended to accelerate the polymerization reaction. In the initial step of polymerization, no polymer could be obtained in all systems. The number-average molecular weight $\overline{M}_n$ of polymers increased with increasing polymerization time and with the addition of water or DMSO. The polymers obtained, white or pale yellow powders, were soluble in carbon tetrachloride, chloroform, methanol, and DMF.

The IR spectra (Fig. 1) of these polymers revealed absorption bands depending on Im (3200, 1600-1500, and 1400-1200 cm^{-1}), and characteristic absorption bands depending on poly-AL (1700-1680 and 1140-900 cm^{-1}). In addition, the spectra of all polymers initiated by Im, Im-water, and Im-DMSO systems were sufficiently similar to suggest the same structure of polymer.

The results of quantitative analysis for the carbon-carbon double bond and the aldehyde group are given in Table 2. No difference in iodine number between Im and polymer suggests the absence of vinyl groups in the polymer. The contents of aldehyde groups in the polymer were found to be in the range of 20 to 30 mole %. These observations might be explained by a polymer structure composed of an Im ring, vinyl polymer of AL, and a bridge structure of aldehyde groups (about 70-80 mole %).

Polymerization Equation

The polymerization of AL has been kinetically investigated in the presence of Im in methanol at 0°C. The overall polymerization rate R_p was determined as

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TABLE 1. Results of Polymerization[a]

Run	Co-catalyst charged: Water (mole/liter)	Co-catalyst charged: DMSO (mole/liter)	Polymerization time (min)	Conversion (%)	Content of N (%)	$\overline{M}_n$
I[b]	-	-	150	37.0	7.68	345
II	-	-	150	41.1	7.83	317
III-1	-	1.41	60	0	-	-
III-2	-	1.41	120	46.6	6.56	407
III-3	-	1.41	150	79.5	4.76	-
III-4	-	1.41	160	81.8	4.68	-
III-5	-	1.41	180	90.9	4.37	-
III-6	-	1.41	240	99.2	4.09	460
IV	1.41	-	60	92.8	4.45	691

[a]Polymerization conditions: [AL] = 3.08 mole/liter, [Im] = 0.30 mole/liter in THF at 0°C under N_2.
[b]In vacuo.

$$R_p = k[Im][AL]^2$$

($k = 5.73 \times 10^{-2}$ liter/mole-sec) with varying concentrations of monomer and catalyst.

Effect of Addition of Water

We noticed, as previously described, that the addition of water tended to accelerate the polymerization reaction. This kinetic result is shown in Fig. 2. R_p increased depending upon the quantity of water added, regardless of the polymerization equation. This may be possibly explained by an equilibrium between Im or the hydrogen of AL with water [Eqs. (1) and (2)].

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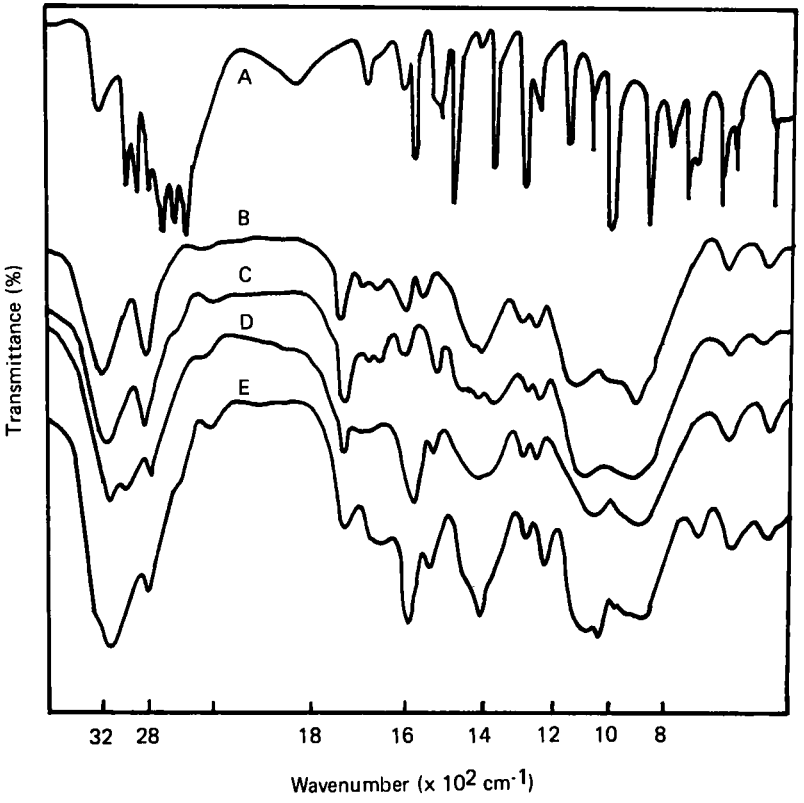
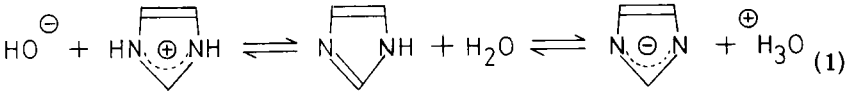


FIG. 1. IR spectra of polymer (KBr disk): (A) Im; (B) polymer IV; (C) polymer III-5; (D) polymer II; (E) polymer I.



(1)

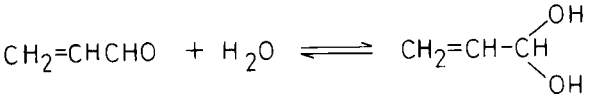


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TABLE 2. Analysis and Structure of Polymer

Sample	M_n	N (%)	Iodine number[a]	N of phenyl-hydrazone (%)	Crosslinked units (mole %)	Free aldehyde (mole %)
I	345	7.68	48.2	14.3	80	20
II	317	7.83	44.9	15.7	75	25
III-2	407	6.56	72.9	9.2	80	20
III-6	460	4.09	61.3	13.3	67	33
IV	691	4.45	66.5	10.3	73	27

[a]Iodine number of Im = 64.6.

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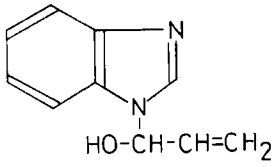
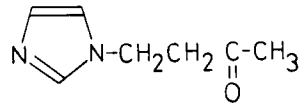
Adduct of Initiation Polymerization

In this study, polymer was not obtained in the initiation period of the polymerization. Moreover, the polymerizations seem to progress by a stepwise reaction. In order to investigate this, equimolar reactions of monomer with catalyst were carried out in THF at 0°C in case of AL and BIm, and the polymerization mixtures were examined by GLC. The structure of separated product, a white crystal line material (mp 199°C) was confirmed by IR (Fig. 3) and NMR (Fig. 4) spectra, and by the elementary analysis (contents of nitrogen, 15.10%). Its structure is shown as A. The addition product of the equimolar reaction of MVK and Im has the structure B.



(A)



(B)

Effect of Addition of Benzaldehyde and DMF

In this case, the initiation mechanism is really complicated. In order to investigate the effect of addition of benzaldehyde or DMF,

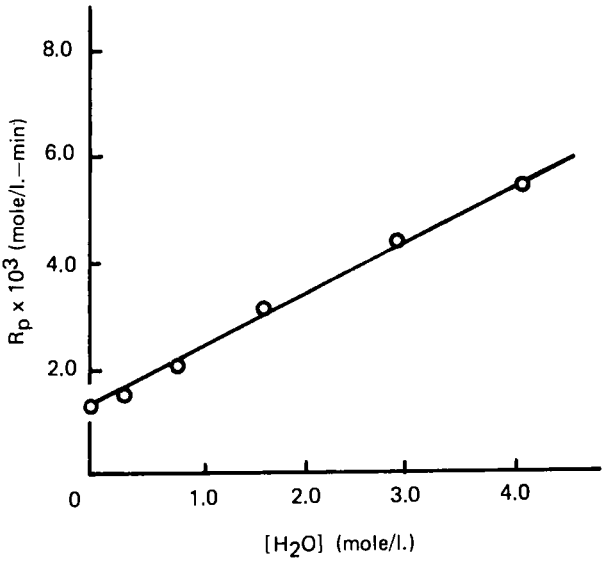
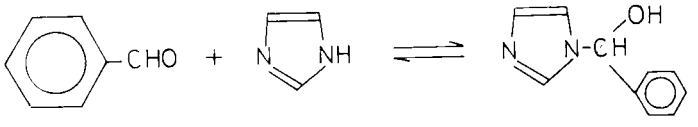


FIG. 2. Effect of addition of water on R_p; [Im] = 0.004 mole/liter; [AL] = 0.39 mole/liter; in THF at 0°C under N_2.

the polymerization of AL in the presence of Im was carried out in THF at 0°C and followed kinetically (Table 3). The increase in the amount of additive produces a decrease of R_p especially in the case of benzaldehyde. This fact suggest that there is an equilibrium between benzaldehyde and Im [Eq. (3)].



(3)

UV and NMR Spectra of the Polymerization System

In order to examine the process of formation of these adducts, the UV and NMR spectra of Im-AL and Im-MVK systems were observed under the same conditions. The UV spectra of Im-AL system are shown in Fig. 5. The absorption with λ_{max} at 328 nm depending on

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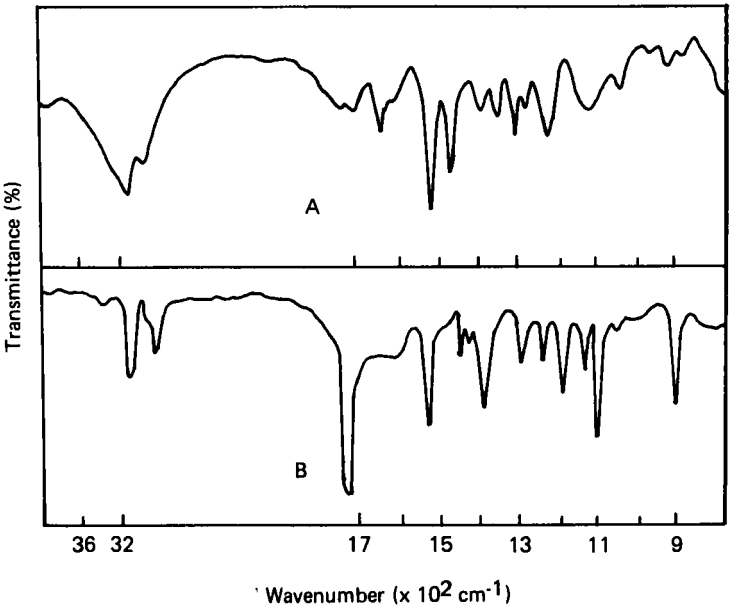

FIG. 3. IR spectra of initial products; (a) product of BIm-AL system; (B) product of IM-MVK system.

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the carbonyl group disappeared in the initiation step, while an absorption at 262 nm gradually appeared as the reaction time increased. However, in the Im-MVK system (Fig. 6), the absorption at 318 nm is shifted to 278 nm, obscuring the distinction between aldehyde and ketone. In the case of AL, it is supposed that the addition of Im occurs at the aldehyde group of AL.

Observations of the Im-AL and Im-MVK systems by NMR spectra were carried out in $CDCl_3$ (Figs. 7 and 8). The signal (13.5 ppm) of the NH proton depending on Im disappears in the initiation step of the reaction, and the signal attributed to the methylene proton depending on the vinyl polymerization readily appears. These observations support the addition of the NH proton of Im to the vinyl group of monomer.

By considering these all results, the process of polymerization may be assumed to proceed as follows.

$$\text{Monomer} + \text{Im} \longrightarrow \text{Adduct} \longrightarrow \text{Polymer}$$

or

$$\text{Monomer} + \text{Im} \longrightarrow \text{Adduct} + \text{Monomer} \longrightarrow \text{Polymer}$$

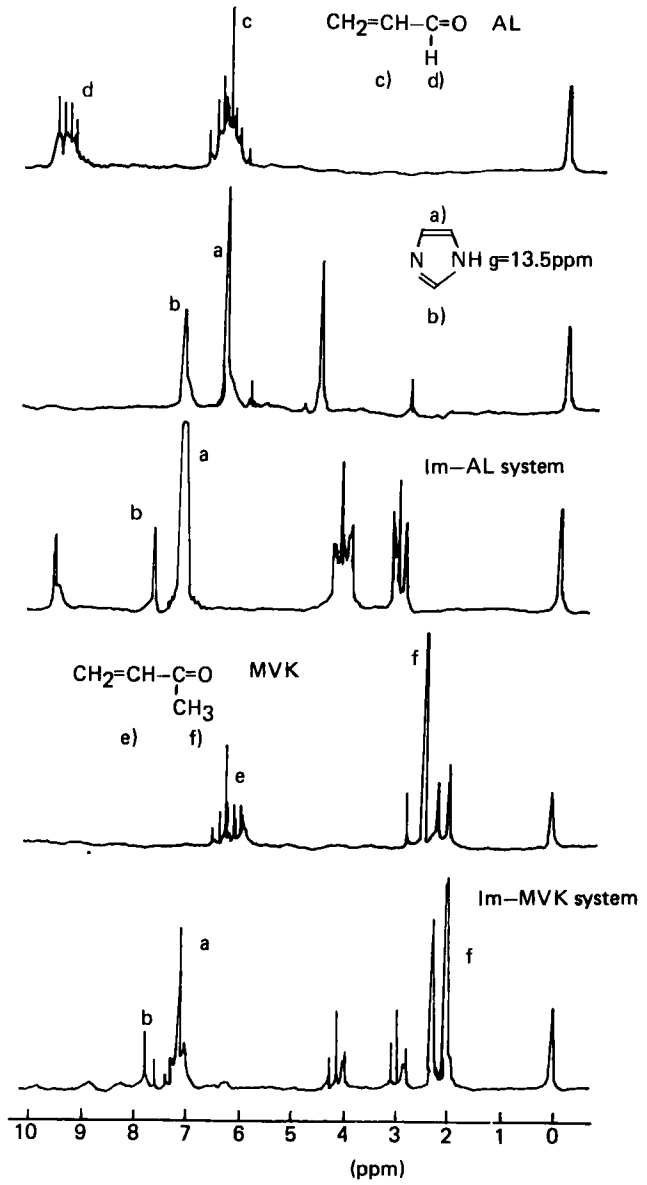

FIG. 4. NMR spectra of Im, monomers, and initial products (in $CDCl_3$).

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TABLE 3. Addition Effect of Benzaldehyde and DMF[a]

Additive (mole/liter)	DMF system		Benzaldehyde system	
	$R_p \times 10^5$ (mole/liter-sec)	R_p/R_{p_0}	$R_p \times 10^5$ (mole/liter-sec)	R_p/R_{p_0}
0	12.17	1	12.17	1
0.28	9.54	0.78	1.42	0.12
0.50	9.06	0.75	1.24	0.10

[a]Polymerization conditions: [AL] = 0.769 mole/liter, [Im] = 0.004 mole/liter, in THF at 0°C under N_2.

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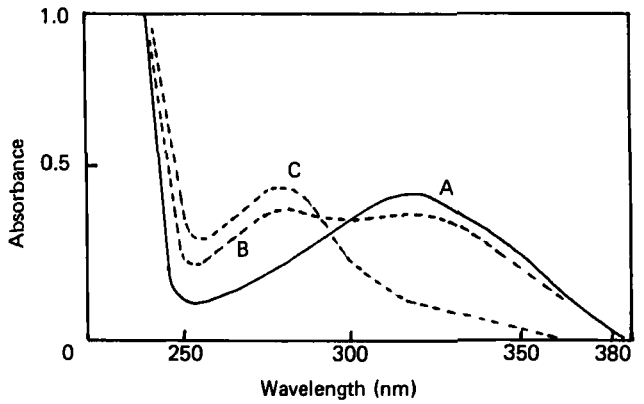

FIG. 5. UV spectra of Im-AL system at various reaction times: (A) 0 hr; (B) 12 hr; (C) 864 hr. Im/AL = 1/5 (mole ratio).

Mechanism of Polymerization

The polymerization might be initiated by the addition of Im and monomer [Eq. (4) or (5)]. The effect of addition of benzaldehyde and UV spectra support Eq. (5) while the structure of polymer, UV and NMR spectra supported Eq. (4). However, the initial adducts were the aldehyde addition product in the BIm-AL system and the vinyl

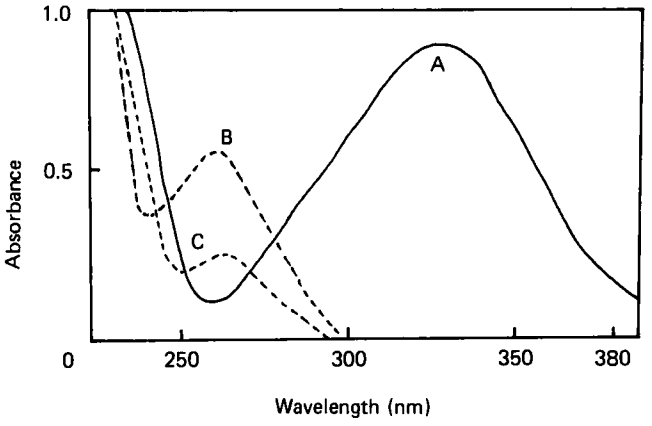

FIG. 6. UV spectra of Im-MVK system at various reaction times: (A) 0 hr; (B) 48 hr; (C) 432 hr. Im/MVK = 1/5 (mole ratio).

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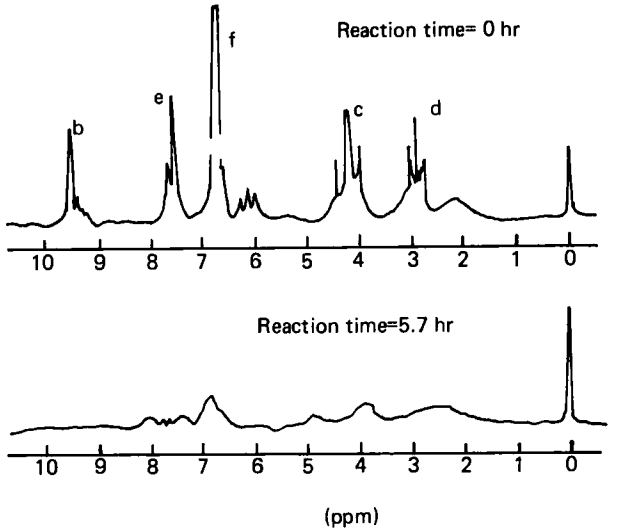


FIG. 7. NMR spectra of Im-AL system in $CDCl_3$; Im/AL = 1/1 (mole ratio); g(NH) = 13.5 ppm. $CH_2{=}CH{-}HC{=}O$; $R_2N{-}CH_2{-}CH_2{-}COR_1$; $\underset{e}{\text{CH}}{=}\underset{e}{\text{CH}}{-}\underset{f}{\text{NH}}{-}\text{CH}{=}\text{N}$.
a b c d

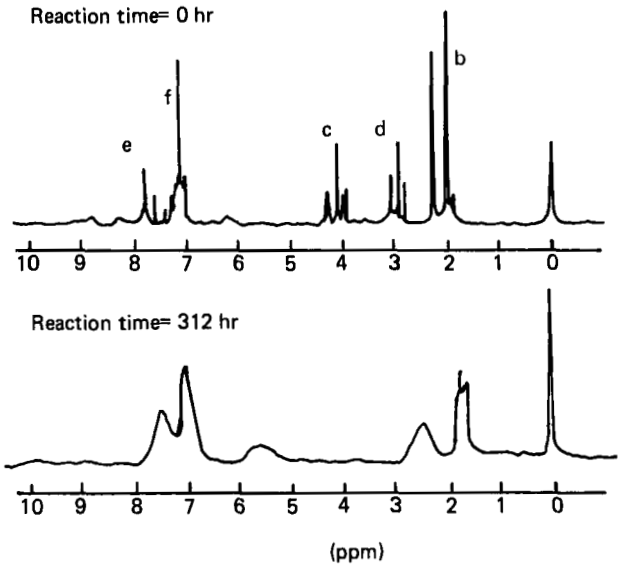
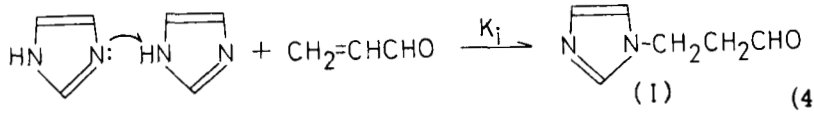


FIG. 8. NMR spectra of Im-MVK system; in $CDCl_3$; Im/MVK = 1/1 (mole ratio); g(NH) = 13.5 ppm. $CH_2{=}\underset{a}{CH}{-}\underset{b}{HC}{=}O$; $R_2N{-}\underset{c}{CH_2}{-}\underset{d}{CH_2}{-}COR_1$; $\underset{e}{CH}{=}\underset{e}{CH}{=}NH{-}\underset{f}{CH}{=}N$.



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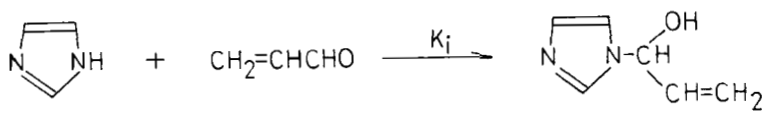

(5)

addition product in the Im-MVK system, respectively. From these observations it may be indicated that the polymerization is initiated by both schemes represented by Eqs. (4) and (5), but the adduct of Eq. (5) does not polymerize under the initiation conditions of this study.

On the other hand, the possibilities of polymerization for the adduct (I) may be considered as shown in Eqs. (6)-(9).

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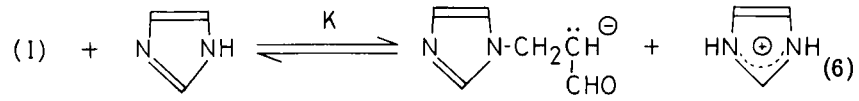

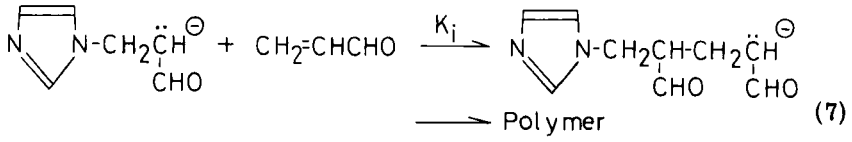

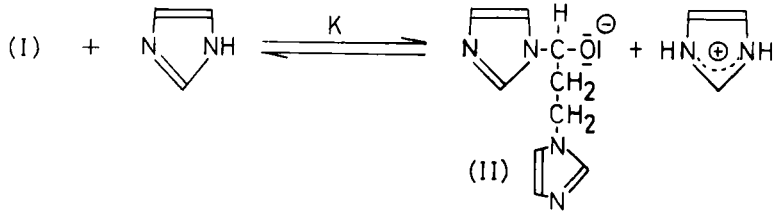

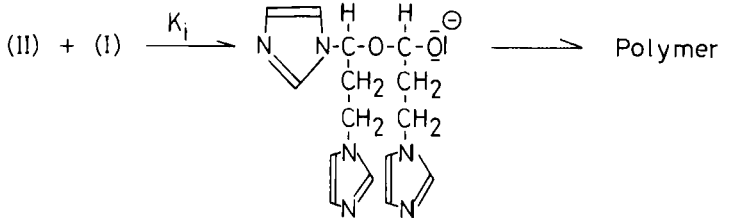

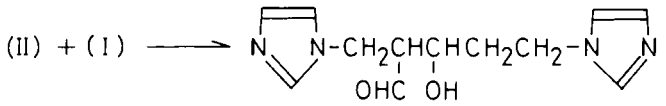

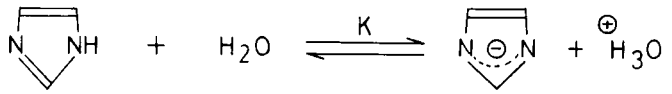

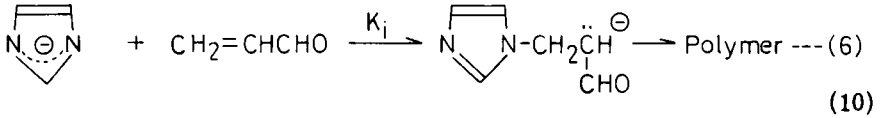

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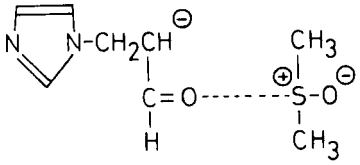
However, the structure of polymer obtained cannot support the process of Eqs. (8) and (9), but the anionic propagation as shown in Eq. (7) is strongly supported.

Meanwhile, the addition of water acted to accelerate the R_p and to increase the $\overline{M}_n$. These results are explained fairly well on the basis of the imidazole anion formed through the equilibrium between Im and water [Eqs. (10)] and by the hydration of aldehyde groups in the initiation or propagation step. In practice, the addition of DMSO also showed the same phenomenon as that for the addition of water, but the polymer obtained did not contain sulfur. The reason for this may be formation of an intermediate as in the case of AL induced by the pyridine-water system, as reported in earlier papers [3, 4].



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