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Anionic Copolymerizations of Acrolein with Methyl Vinyl Ketone and Acrylamide by Imidazole

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ABSTRACT

The anionic copolymerizations of acrolein (AL) with methyl vinyl ketone (MVK) and acrylamide (AAm) in the presence of imidazole (Im) as an initiator have been studied in tetrahydrofuran at 0°C. The AL-MVK copolymers were found to be composed of vinyl polymer with one Im group attached and having an aldehyde and a carbonyl side chain. The monomer reactivity ratio was determined from a Fineman-Ross plot as $r_1 = 2.02$ and $r_2 = 0.06$. On the other hand, the AL-AAm copolymer were found to be composed of polymer units of 1,2 and 1,4 addition polymerization of AAm. These observations might be explained by the intermolecular hydrogen transfer mechanism of AAm. The polymerization mechanisms were discussed on the basis of these copolymerization results.

INTRODUCTION

In earlier articles [1-3] we reported that several polar vinyl monomers such as acrolein (AL), methyl vinyl ketone (MVK), and acrylamide (AAm) could be homopolymerized readily by imidazole

(Im) below room temperature. These kinetic investigations revealed that the polymerization could be initiated by the Im-monomer adduct and Im.

This investigation was performed to reveal the anionic copolymerizabilities of AL with MVK and AAm by Im and the structure of the copolymers.

EXPERIMENTAL

Materials

AL and MVK were prepared in the manner described in previous articles [1, 2]. AAm and Im were purified by the recrystallization from benzene. Tetrahydrofuran (THF) was purified in the usual way.

Polymerization Methods

The anionic copolymerization was carried out homogeneously in THF at 0°C under a nitrogen atmosphere. The required amounts of Im and THF were placed into a tube. Then fixed amounts of monomers were added to start the copolymerization reaction. The reaction mixture was poured into a large amount of ether containing hydrochloride, and the precipitate was filtered to dry.

The copolymer composition was determined by the elementary analysis. The monomer reactivity ratio was determined by the Fineman-Ross method [4].

RESULT AND DISCUSSION

Copolymerization Results of AL (M_1) with MVK

The results of the copolymerizations of AL (M_1) with MVK are given in Table 1. The decrease of AL concentration in the monomer feed decreased the copolymerization rate. The copolymer composition was determined by the elementary analysis.

The copolymers obtained were soluble in methanol and DMF. The infrared (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}) and poly-MVK (1645 and 1380 cm^{-1}). From these observations it was revealed that the AL-MVK copolymers were found to be composed of vinyl polymer with one Im group attached and having an aldehyde and a carbonyl side chain.

The monomer reactivity ratio (r_1 = 2.02 and r_2 = 0.06) was

TABLE 1. Copolymerizations of AL (M_1) with MVK[a]

Charged composition AL (M_1) (mol%)	Polymerization time (h)	Conversion (%)	Elementary analysis C (%)	H (%)	N (%)	Incorporated ratio AL (mol%)
100	30	83.0	59.98	7.41	2.94	100
90	34	29.9	60.47	6.83	4.53	95
80	39	31.3	61.09	7.17	3.91	88
70	47	27.5	61.12	7.68	4.08	87
60	69	33.2	61.74	7.50	3.50	80
50	85	27.8	61.78	7.56	3.71	79
40	129	28.0	61.94	7.42	3.54	77
30	230	20.7	62.35	7.97	3.85	73
20	637	13.5	62.98	8.13	3.92	65
0	732	79.5	68.45	8.97	0.15	0

[a] Copolymerization conditions: Total monomers, 3.08 mol/L; concentration of Im, 0.103 mol/L; solvent, THF; polymerization temperature, 0°C; atmosphere, nitrogen gas.

determined from Fineman-Ross plots (Fig. 2). The monomer-copolymer composition curve are shown in Fig. 3. The experimental values agree well with the calculated curve.

Copolymerization Results of AL (M_1) with AAm

Copolymerizations of AL (M_1) with AAm were carried out in THF at 0°C (Table 2). Both monomers homopolymerized slowly in these polymerization conditions, while it is interesting to note that the copolymerization rate is very high. On the other hand, the monomer-copolymer composition curves are shown in Fig. 4. A difference between the experimental values (Fig. 4a) and calculated curve (Fig. 4a') is clear. Meanwhile, it was proved that there was an interesting similarity between Cuves a, b, and c in Fig. 4.

Anionic copolymerization (Fig. 4c) of AL with AAm in the presence of sodium methoxide was reported by Sumitomo et al. [8], but the polymerization mechanism is not clear. On the other hand, we have also been investigating how AL can be polymerized by a mixture of pyridine and water below room temperature [5, 6]. In these

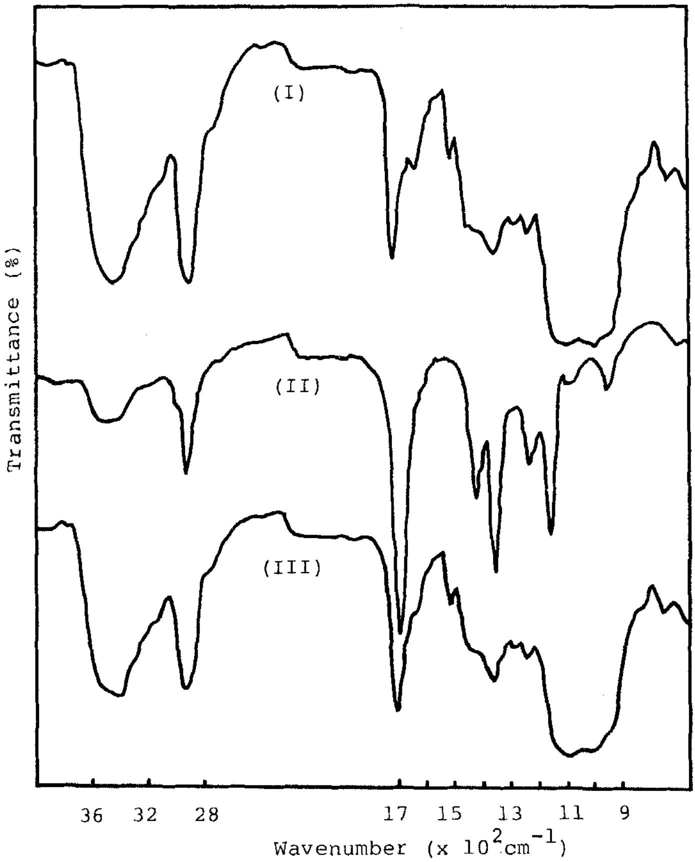


FIG. 1. IR spectra of poly-AL (I), poly-MVK (II), and AL-MVK copolymer (III).

studies the polymerization of AL in the presence of AAm by this initiation system (Fig. 6) and the results were discussed in terms of an intermolecular hydrogen transfer mechanism of AAm [7].

In order to examine the structure of AL-AAm copolymer in this study, the IR spectra were observed (Fig. 5). The IR spectrum of copolymer (Fig. 5-III) has several absorption bands depending on Im (3200, 1600-1500, and 1400-1200 cm^{-1}), and characteristic absorption bands depending on poly-AL (Fig. 5-I) and poly-AAm (Fig. 5-II). However, it is interesting that the spectrum revealed in the presence of amide I (1660 cm^{-1}) and amide II (1530 cm^{-1}) disappeared in

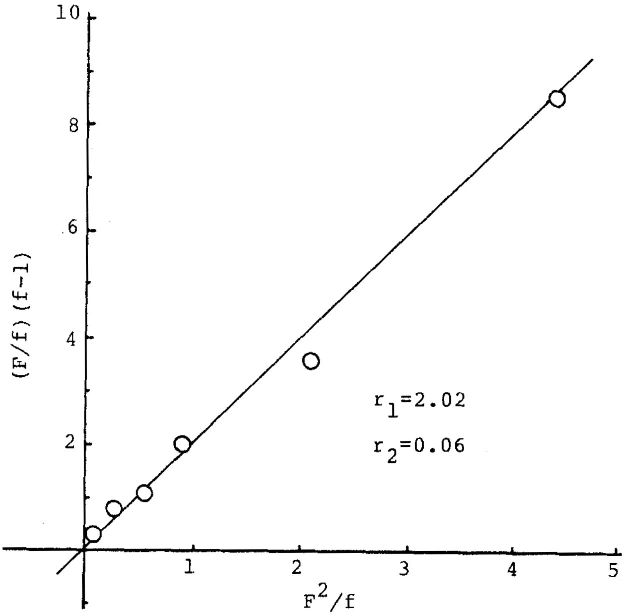


FIG. 2. Fineman-Ross plots in AL (M_1)-MVK copolymerization system.

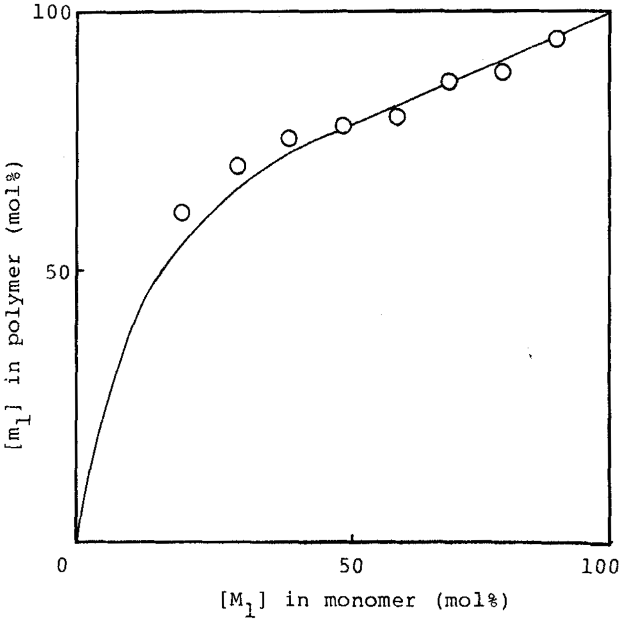


FIG. 3. Monomer-copolymer composition curve in copolymerization of AL (M_1) with MVK (M_2)

TABLE 2. Copolymerizations of AL (M_1) with AAm[a]

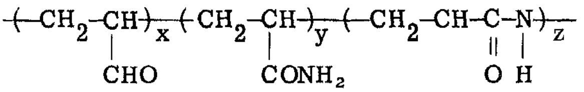
Charged composition AL (M_1) (mol%)	Polymerization time (h)	Conversion (%)	Elementary analysis			Incorporated ratio AL (mol%)
			C (%)	H (%)	N (%)	
100	568	11.2	59.98	7.41	2.94	100
90	152	28.7	59.60	6.86	4.12	92
80	52	22.0	58.82	7.00	5.08	86
70	19	23.5	58.29	6.55	5.79	81
60	19	30.1	58.94	7.18	5.94	80
50	19	23.3	56.96	6.80	6.20	78
40	19	15.5	57.14	7.09	6.99	73
30	20	11.5	56.79	6.77	8.08	66
0	865	0	-	-	-	-
0	856	47.1[b]	50.66	7.03	19.76[c]	0

[a] Copolymerization conditions: Total monomers, 1.54 mol/L; concentration of Im, 0.052 mol/L; solvent, THF; polymerization temperature, 0°C; atmosphere, nitrogen gas.

[b] Concentration of AAm, 0.20 mol/L; Im, 0.10 mol/L; polymerization temperature, 30°C.

[c] Calculated value of AAm; C, 50.69%; H, 7.09%; N, 19.71%.

the acidic hydrolysis product (Fig. 6b). From these results, the structure of the copolymer is



$$\left(CH_2-\underset{CHO}{CH}\right)_x\left(CH_2-\underset{CONH_2}{CH}\right)_y\left(CH_2-CH-\underset{O}{\underset{\|}{C}}-\underset{H}{\underset{|}{N}}\right)_z$$

(poly-AL) (poly-AAm 1,2 addition) (poly-AAm 1,4 addition)

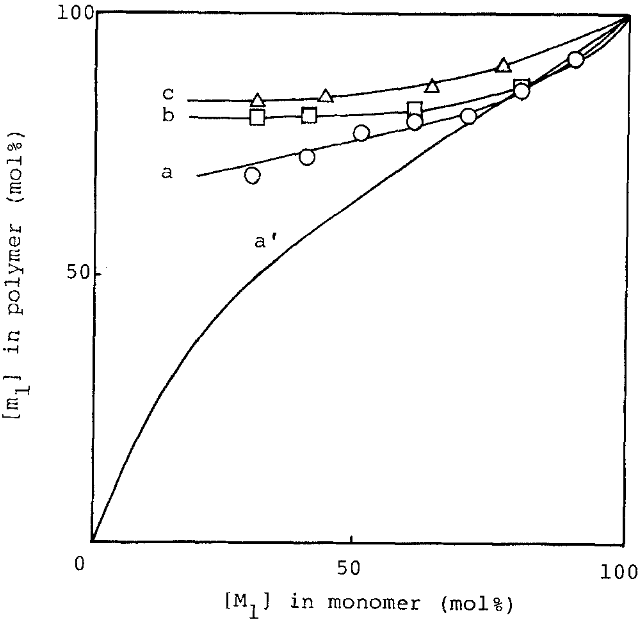


FIG. 4. Monomer-copolymer composition curves in anionic copolymerization of AL (M_1) with AAm. a: This work. a': Calculated curve by Fineman-Ross method. b: Initiated by the hydroxyanion formed in thermodynamic equilibrium between pyridine and water [5-7]. c: Initiated by sodium methoxide [8].

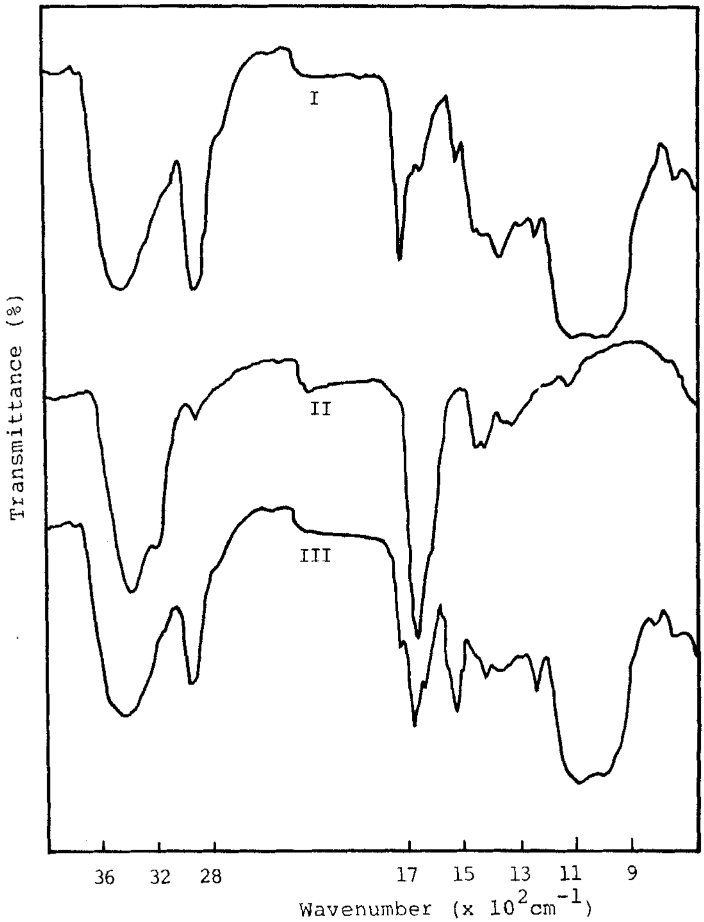


FIG. 5. IR spectra of poly-AL (I), poly-AAm (II), and AL-AAm copolymer (III).

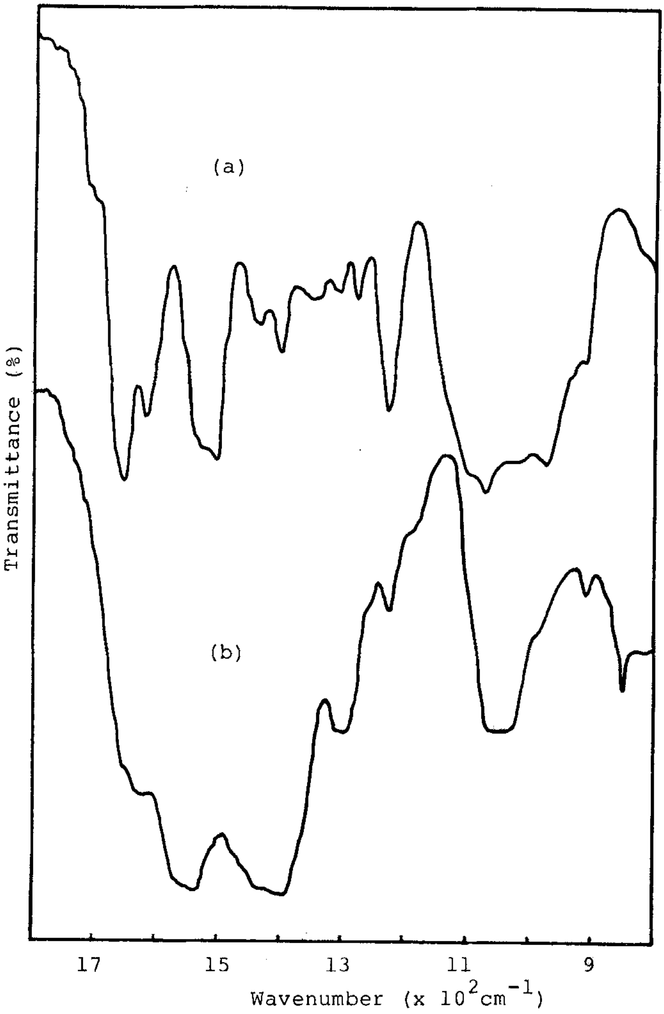
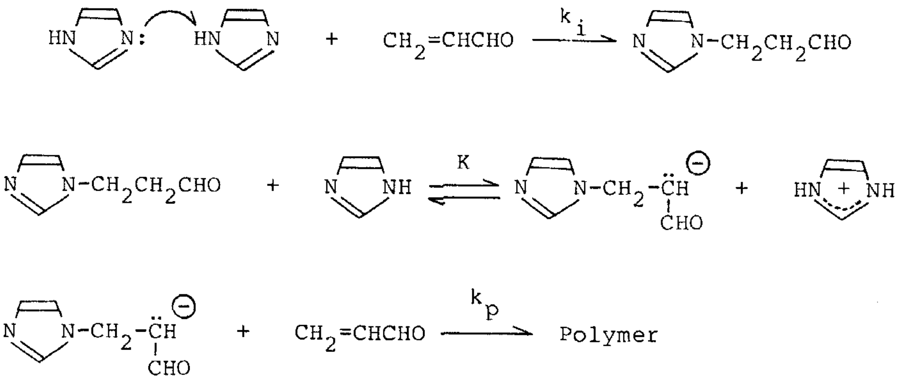


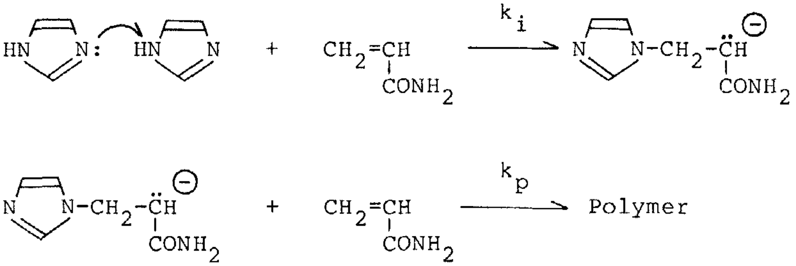
FIG. 6. IR spectra of AL-AAm copolymer (a) and hydrolysis product (b).

Polymerization Mechanism

The polymerization mechanism of AL induced by Im has been proved to be [1]:

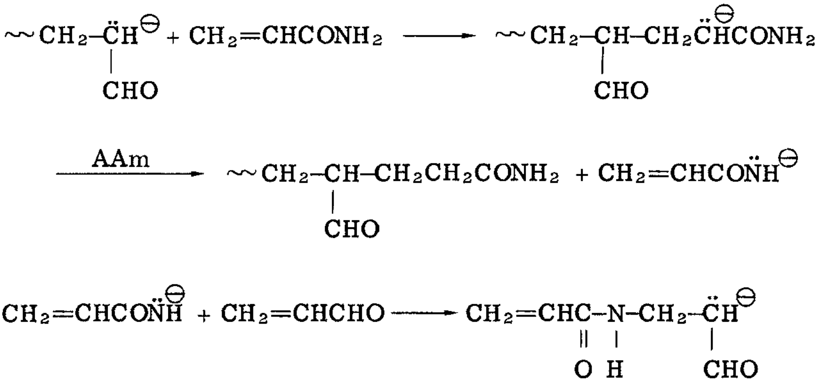


The polymerization mechanism of AAm by Im has been proved to be [3]:



On the other hand, it is well known that AAm polymerizes with intermolecular hydrogen transfer [8].

Thus, in the copolymerization of AL with AAm, the polymerization mechanism might be explained by the intermolecular hydrogen transfer mechanism of AAm. The propagating poly-AL anion was terminated by AAm to produce AAm anion, which would then reinitiate the polymerization of AL:



$$\sim\!\sim CH_2-\underset{CHO}{\underset{|}{\ddot{C}}}H^{\ominus} + CH_2=CHCONH_2 \longrightarrow \sim\!\sim CH_2-\underset{CHO}{\underset{|}{C}}H-CH_2\overset{\ominus}{\ddot{C}}HCONH_2$$

$$\xrightarrow{AAm} \sim\!\sim CH_2-\underset{CHO}{\underset{|}{C}}H-CH_2CH_2CONH_2 + CH_2=CHCO\ddot{N}H^{\ominus}$$

$$CH_2=CHCO\ddot{N}H^{\ominus} + CH_2=CHCHO \longrightarrow CH_2=CH\underset{O}{\underset{\|}{C}}-\underset{H}{\underset{|}{N}}-CH_2-\underset{CHO}{\underset{|}{\ddot{C}}}H^{\ominus}$$

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