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Polymerization of Methyl Methacrylate in the Presence of Imidazole Derivatives. Additive Effect of the Initiator Adduct and Copolymerization with Acrylamide

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POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF IMIDAZOLE DERIVATIVES. ADDITIVE EFFECT OF THE INITIATOR ADDUCT AND COPOLYMERIZATION WITH ACRYLAMIDE

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ABSTRACT

In the anionic polymerization of methyl methacrylate (MMA) induced by imidazole (Im), an Im-MMA adduct forms as an initiator adduct in methanol at 30°C in an argon atmosphere by the equimolar reaction of Im with the MMA monomer. The additive effect of the adduct on the homopolymerization of MMA in tetrahydrofuran at 30°C was investigated by dilatometry. The existence of the adduct increased the duration of the propagation step without shortening the formation step of the initiator adduct. The H-D exchange reaction of the adduct was observed in D_2O by ^{1}H NMR. Proton transfer of the MMA unit in the adduct was not observable until 45 h after initiation. The copolymerizability of MMA with acrylamide (AAm) induced by the Im catalyst in THF at 30°C was also investigated. It was found that the homo- and copolymerizations proceeded at the same time. On the other hand, in the MMA homopolymerization system, the addition of AAm monomer during the initial propagation step yielded copolymer of MMA and AAm for near equimolar concentration of the charged monomers.

INTRODUCTION

In an earlier article [1] we reported on the polymerization of methyl methacrylate (MMA) induced by imidazole (Im). Our kinetic investigation [2] also revealed that polymerization could be initiated by the Im-MMA adduct (initiator adduct) anion formed in the thermodynamic equilibrium between Im and the Im-MMA adduct.

An induction period that occurs in the initial polymerization step is caused by the formation of an initiator adduct (Im-MMA). We also reported the structure and reactions of the characteristic initiator adduct obtained in the polymerization of methyl vinyl ketone (MVK) induced by Im [3]. This polymerization of MVK was investigated by use of synthesized *N*-(butyl-3-one)imidazole (as the Im-MVK adduct) as an anionic catalyst. From the measurement of the pK_a value and the ^{1}H-NMR determination of the H-D exchange reaction rate with D_2) it was found that the α-proton of the Im-MVK adduct is exchanged readily. The propagation step involves a chain reaction, as determined from gel permeation chromatography data.

The present report concerns the additive effect of the Im-MMA adduct (as the initiator adduct that was isolated from the polymerization system) on the anionic copolymerization of MMA with acrylamide induced by the Im catalyst.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) and acrylamide (AAm) were prepared as described previously [1, 2]. Imidazole (Im) was used after recrystallization from benzene [1]. Methanol, tetrahydrofuran (THF), and other solvents were purified by conventional methods [7].

Polymerization Method

The polymerization of MMA was carried out homogeneously in THF at 30°C in an argon atmosphere by use of a dilatometer, as described earlier [1]. The required amounts of Im, THF, and MMA were placed in the dilatometer which was placed in a thermostat at 30°C to start the polymerization. In the case of copolymerization of MMA with AAm, the AAm was added to the polymerization mixture during the propagation reaction step (after about 8-10 h. After the reaction, the polymerization mixture was poured into a large amount of ether containing hydrogen chloride, and the precipitate was filtered, vacuum dried, and weighed to determine the yield.

Analyses

^{1}H-NMR spectra at 90 MHz in $CDCl_3$ with tetramethylsilane as an internal standard were recorded with a Hitachi-Perkin-Elmer Model 40 cw spectrometer. Mass spectra were obtained with a JEOL Model JMS-HX100 mass spectrometer. Infrared (IR) spectra of a KBr disk or a film were recorded with a Nihon-Bunkou IRA-2 spectrophotometer. Gas-liquid chromatography (GLC) was carried out with a Yanaco Model G-1800 with helium gas as carrier. The molecular weight distributions of the polymers were estimated by gel permeation chromatography (GPC) with Gasukuro-Kogyo Model LSG-9, Toyo-Soda Model RI-8000, and Shodex GPC A-80M columns.

RESULTS AND DISCUSSION

Initiator Adduct

In our previous paper [2] a polymerization mechanism was proposed which proceeds according to

$$\mathrm{Im} + \mathrm{MMA} \xrightarrow{k_i} \mathrm{Im\text{–}MMA\ adduct} \tag{1}$$

$$\mathrm{Im\text{–}MMA\ adduct} + \mathrm{Im} \overset{K}{\rightleftharpoons} \mathrm{Im\text{–}MMA}^{\ominus} + \mathrm{Im}^{\oplus} \tag{2}$$

$$\mathrm{Im\text{–}MMA}^{\ominus} + \mathrm{MMA} \xrightarrow{k_p} \mathrm{Polymer} \tag{3}$$

The initiator adduct (Im-MMA adduct) was isolated in this study in order to elucidate the polymerization mechanism. The reaction of Im (2.0 mol/L) with the MMA monomer (2.4 mol/L) was carried out in methanol at 30°C under argon. The product, obtained as a colorless liquid which decomposes at 60°C, was soluble in acetone, THF, and water. Its IR spectrum (Fig. 1) has several absorption bands characteristic of Im (3100 cm^{-1}) and the methylene group (1720 and 1150 cm^{-1}). The ^{1}H-NMR spectrum (Fig. 1) in THF-d_8 has signals representing the β-proton (4.2 ppm), α-methine (2.8 ppm), and methoxy group (3.6 ppm). The mass spectrum (Fig. 1) has the mass numbers (m/e), 168(P), 109, 81(B), and 54.

The structural analyses confirm that the product was the Im-MMA adduct, formed in the initial polymerization step by the Michael reaction between the Im and the MMA monomer.

Polymerization of MMA in the Presence of the Im-MMA Adduct

If the polymerization of MMA is related to the existence of the Im-MMA adduct that forms in the initial polymerization step according to Eqs. (1) and (2), then the initial polymerization step can be assumed to be shortened by addition of the separately synthesized Im-MMA adduct. Hence, the polymerization of MMA induced by Im in the presence of the Im-MMA adduct in THF at 30°C was investigated by dilatometry. Typical results are shown in Fig. 2. The two distinct slopes correspond to two reaction steps, with the first step depending on the formation of an adduct and the second step depending on the polymerization (propagation) reaction. Comparison of Curve b with Curve c shows that the addition of the Im-MMA adduct to the MMA polymerization system increased the reactivity of the second propagation step without shortening the first step. However, the polymerization induced by just the Im-MMA adduct was very slow under these conditions (Fig. 2d).

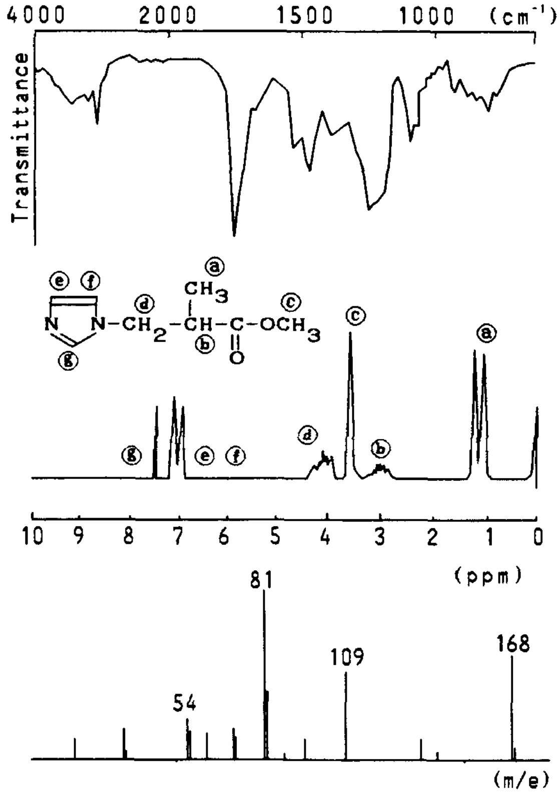

FIG. 1. IR (top) ^{1}H-NMR (center), and mass spectra (bottom) of the Im-MMA adduct.

We have previously reported that MVK monomer was readily polymerized by the Im-MVK adduct in THF at 30°C [3]. In the present study the polymerizability of MMA was also investigated in the presence of the Im-MVK adduct. Our observations clearly indicate that Im-MVK in the presence of Im shortened the first step (Fig. 2e). But again, use of just the Im-MVK adduct (Fig. 2d) led to longer reaction times (about 90 h).

From these results it is predicted that the Im-MMA adduct has a lower pK_b value than Im-MVK ($pK_b = 8.27$) and Im ($pK_b = 6.92$). In order to investigate this point, the H-D exchange reaction of the Im-MMA adduct in D_2O was observed by ^{1}H NMR in a manner similar to that described in an-

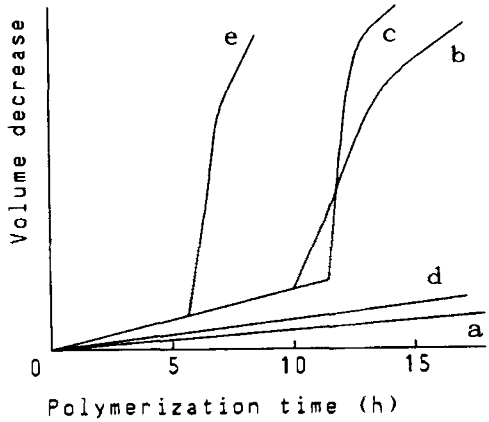

FIG. 2. Time dependence of the volume decrease in THF at 30°C. (a) Blank. (b) Im. (c) Im and Im-MMA adduct. (d) Im-MMA adduct or Im-MVK adduct. (e) Im and Im-MVK adduct.

other paper [3]. Proton transfer of the MMA unit in the adduct, however, did not occur in 45 h. It is currently considered that the Im-MMA adduct is stable in the base form. This might imply that the first step in the polymerization of the MMA monomer, which conforms to Eq. (1) or (2), requires a long reaction time. The reactivity of the initiator adducts is being investigated by use of Im derivatives containing other monomers such as methyl acrylate, acrylonitrile, acrylamide, vinyl acetate, vinyl pyrrolidone, and styrene. The details will be reported in a subsequent paper.

Gel Permeation Chromatography of Poly-MMA

In our previous work [2], $\bar{M}_v$ of poly-MMA initiated by Im was determined to be in the range 145 000 to 673 000, e.g., a poly-MMA made with a conversion of ~16.5% had mp 265-270°C and $\bar{M}_v$ 227 000. The GPC molecular weight distribution became broader with increasing polymerization time (Fig. 3). This may be explained as follows. While the monomer concentration decreases with polymerization time, the concentration of the anionic species remains unchanged (Eq. 2), and therefore, its relative concentration increases.

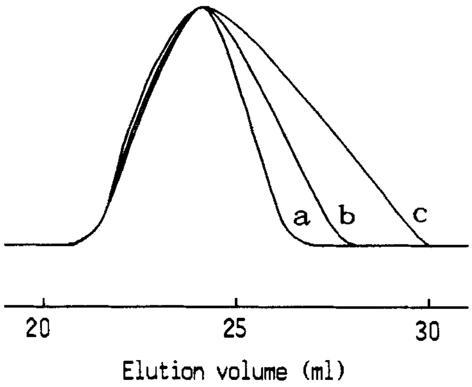

FIG. 3. Gel permeation chromatograms of the polymerization system of MMA induced by Im in THF at 30°C. Polymerization conditions: [MMA] = 2.0 mol/L, [Im] = 0.5 mol/L. (a) Time, 100 h; $\bar{M}_n$ = 276 000. (b) Time, 200 h; $\bar{M}_n$ = 244 000. (c) Time, 340 h; $\bar{M}_n$ = 128 000.

Possibility of Copolymerization of MMA with Acrylamide Induced by Im

The copolymerization of acrolein with methyl vinyl ketone and acrylamide (AAm) initiated by the Im catalyst has been reported in previous articles [4-6]. In this study the copolymerization of MMA with AAm in the presence of the Im catalyst in THF at 30°C under argon is also investigated (Table 1). The copolymerization proceeded homogeneously during the initial polymerization step and changed to a heterogeneous process for longer reaction times. This indicates the occurrence of homo- or copolymers of AAm because AAm polymer is insoluble in THF. This polymerization also required long reaction times, and mixtures of both monomers without Im catalyst did not yield polymers. Since homo- and copolymerization proceeded at the same time, the experiments are not characteristic of the typical copolymerization, and the possibility of block copolymerization is indicated.

The fractionation scheme used for these mixtures of polymers is shown in Fig. 4. However, accurate fractionation of poly-AAm and copoly(MMA-AAm) on the basis of the solubility difference is known to be difficult. Copoly(MMA-AAm) was obtained as a white powder from the fractionation described above. Interestingly, the copolymer was formed near 50-70 mol% AAm in the charged monomers. Based on our previous data [1, 2], it is concluded that the formation of the Im-MMA adduct requires a long reaction time (about 8-10 h, where-

TABLE 1. Results for the Copolymerization of MMA (M_1) with AAm. Induced by Im[a]

Monomers charged						
M_1		M_2				
mol%	mol/L	mol%	mol/L	Polymerization time, h	Total conversion,[b] %	Copolymerization conversion,[c] %
100	3.76	0	0	190	34.5	0
80	3.01	20	0.75	190	48.9	~0
70	2.63	30	1.13	190	75.1	~0
60	2.26	40	1.50	190	80.8	~0
50	1.88	50	1.88	95	74.0	13.1
40	1.50	60	2.26	95	39.7	14.0
30	1.13	70	2.63	95	59.7	19.9
20	0.75	80	3.01	95	(11.4)	(~0)
0	0	100	3.75	190	35.9	0

[a] Polymerization conditions: [Im] = 0.50 mol/L; total volume, 20 mL; solvent, THF; temperature, 30°C; atmosphere, argon.

[b] Mixture of poly-MMA, poly-AAm, and copoly(MMA-AAm).

[c] Fractionated by the method of Fig. 4.

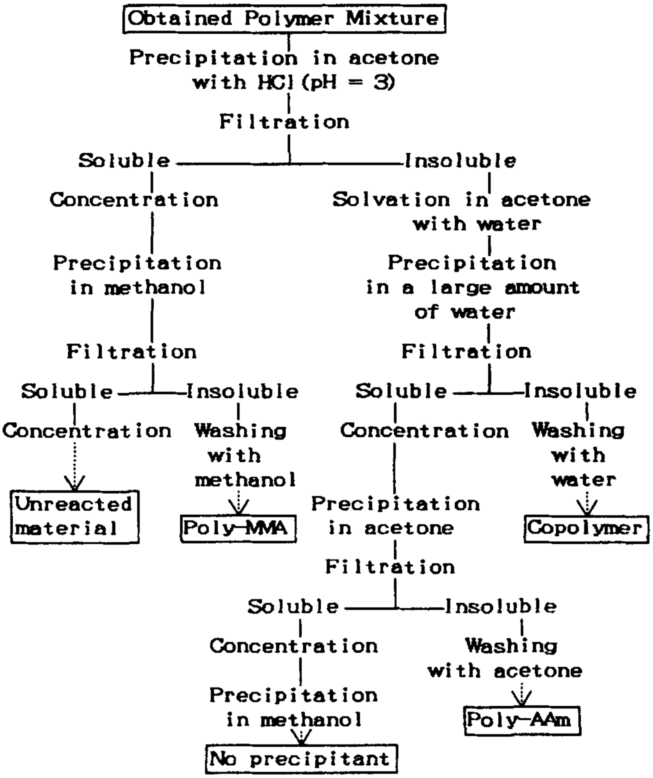

FIG. 4. Fractionation procedure.

as the polymerization of the AAm monomers occurs more rapidly. Therefore, the concentration of AAm monomer has already decreased when the initial propagation step of the MMA monomer takes place.

The IR spectra of the copoly(MMA-AAm) (Fig. 5) revealed the absorption bands characteristic of poly-AAm (3300, 1680, and 1400 cm^{-1}) and poly-MMA (2800, 1710, and 1100 cm^{-1}). The ^{1}H-NMR spectrum of the copolymer in $(CD_3)_2SO$ (Fig. 6) contains several peaks representing the amide group (near 7.0 ppm), the methoxy group (3.7 ppm), and the α-methyl group (1.0 ppm). These results support a copolymer that contains both monomer units (MMA and AAm).

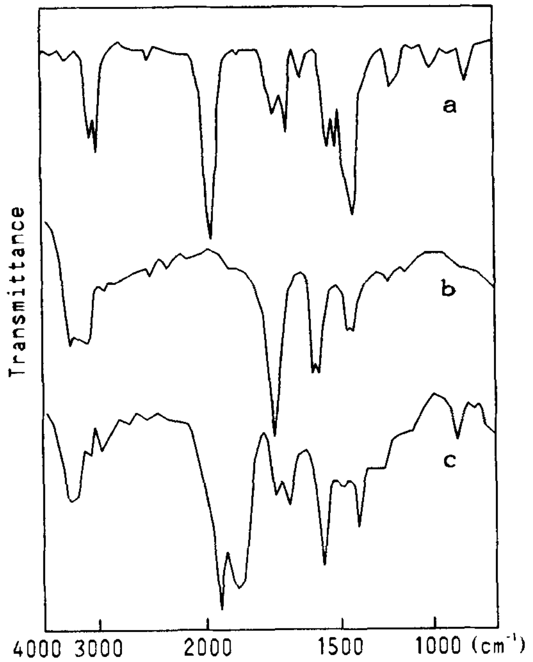

FIG. 5. IR spectra. (a) Poly-AAm. (b) Poly-MMA. (c) Copoly(MMA-AAm).

The Additive Effect of AAm to the Propagation Step of MMA

The additive effect of AAm to the homopolymerization of MMA was investigated under the same polymerization conditions as above, i.e., the homopolymerization of MMA was first induced by Im in THF at 30°C under argon. After the formation of the initiator adduct was sufficiently advanced (after 8.5 h), the AAm monomer was added during the initial propagation step.

The results in Table 2 show that copoly(MMA-AAm) is obtained by the equimolar reaction of both monomers. The poly-MMA and poly-AAm homopolymers were obtained in a highly concentrated system. This may indicate a possible chain transfer reaction.

The dependence on the MMA concentration was investigated in a similar manner, and the results are summarized in Table 3. At low concentrations

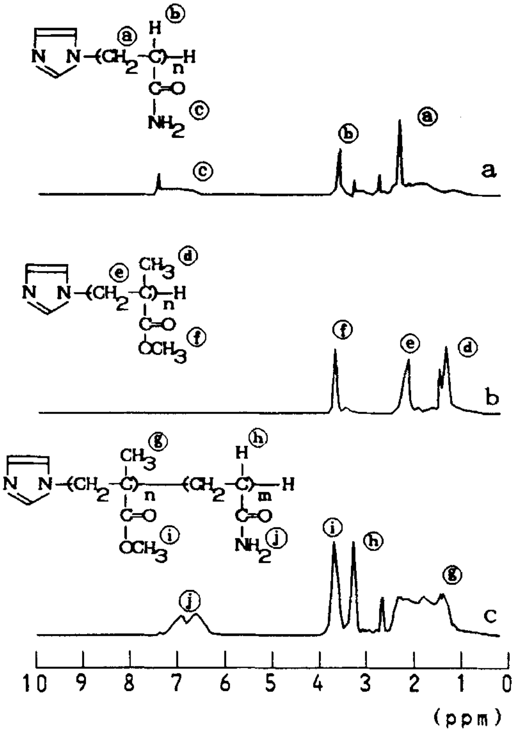

FIG. 6. ^{1}H-NMR spectra. (a) Poly-AAm. (c) Poly-MMA. (c) Copoly-(MMA-AAm).

of charged MMA, formation of the Im-MMA adduct was confirmed by thin-layer chromatography; however, some polymer was also obtained. The polymerization mixture homogeneously first became a viscous liquid and then changed gradually to a heterogeneous system. This also suggests that the MMA monomer polymerized first and that the polymerization of AAm was also initiated. These results indicate the possibility of block copolymerization, with the AAm monomer being added to the propagating poly-MMA anion in a random fashion.

TABLE 2. The Additive Effect of AAM to the Propagation Step of MMA[a]

MMA charged, mol/L	AAm added, mol/L	Conversion[b]		
		Poly-MMA, %	Poly-aam, %	Copoly(MMA-AAm), %
3.2	0.8	23.6	0	0
2.8	1.2	30.3	0	0
2.4	1.6	0.8	0	22.8
2.0	2.0	0	0	38.1
1.6	2.4	0	Trace	47.4
1.2	2.8	0	85.9	0
0.8	3.2	0	70.6	0

[a] Polymerization conditions; [Im] = 0.5 mol/L; total volume, 20 mL; solvent, THF; polymerization time, 98 h, temperature, 30°C; atmosphere, argon.

[b] Fractionated by the method of Fig. 4.

TABLE 3. Dependence on MMA Concentration of the Additive Effect of AAm to the Propagation Step of MMA[a]

MMA charged, mol/L	Im, mol/L	Polymerization time, h	Conversion[b] Poly-MMA, %	Poly-AAm, %	Copoly(MMA-AAm), %
1.0	0.25	–	0	0	0
1.5	0.25	570	Trace	0	53.1
2.0	0.25	500	Trace	65.3	67.5
3.0	0.25	500	45.0	25.5	55.2
1.0	0.50	–	0	0	0
1.5	0.50	330	3.0	27.0	69.9
2.0	0.50	260	7.6	Trace	76.3
3.0	0.50	210	Trace	4.0	91.0
1.0	0.75	500	0	14.8	40.9
1.5	0.75	330	0	24.3	56.0
2.0	0.75	260	0	52.2	58.4
3.0	0.75	210	45.7	4.8	54.3

[a] Polymerization conditions: [AAm] = 1.5 mol/L; total volume, 20 mL; solvent, THF; temperature, 30°C; atmosphere, argon.

[b] Fractionated by the method of Fig. 4.

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