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Vinyl Polymerization. 404. Polymerization of Methyl Methacrylate Initiated with Substituted Imidazoles in an Aqueous Solution of Copper(II) Chloride

TATSURO OUCHI, AKINOBU KOBAYASHI, and MINORU IMOTO

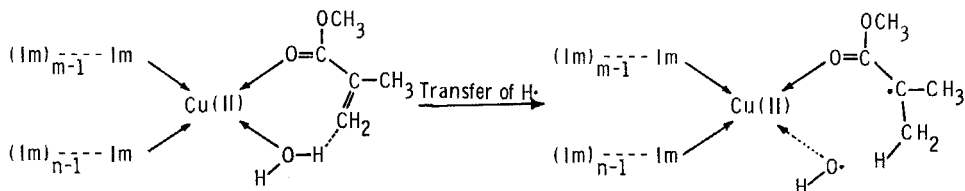
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ABSTRACT

In order to study the effect of substituent groups of imidazole (Im) on the polymerization of methyl methacrylate (MMA) initiated with the system of Im compounds, copper(II) chloride, and water, polymerizations using N-ethylimidazole (N-EtIm) and 2-methylimidazole (2-MeIm) were carried out. The initiation ability for polymerization increased in the order 2-MeIm > N-EtIm > Im. The overall activation energies of polymerization initiated with N-EtIm and 2-MeIm were estimated to be 94.3 and 61.1 kJ/mol, respectively. The formation of complexes of the Cu(II) ion with substituted Im in water was confirmed by electronic spectra. Isolated complexes of $[\text{Cu}(\text{Im})_4]\text{Cl}_2$, $[\text{Cu}(2\text{-MeIm})_2]\text{Cl}_2$, $[\text{Cu}(\text{N-EtIm})_2]\text{Cl}_2$, and $[\text{Cu}(\text{N-EtIm})_4]\text{Cl}_2$, instead of free imidazoles, were used for the polymerization of MMA. These complexes, except $[\text{Cu}(2\text{-MeIm})_2]\text{Cl}_2$, behaved as inhibitors of polymerization. This was due to the impossibility of formation of an adequate complex of MMA to initiate polymerization.

INTRODUCTION

In a previous paper [1] we reported on the radical polymerization of methyl methacrylate (MMA) initiated with imidazole (Im) in an aqueous solution of copper(II) chloride. We concluded that the initiating free radical was generated by hydrogen atom transfer from water to MMA through the complex of Cu(II) ion with Im, water, and MMA (Scheme 1).



SCHEME 1.

Takemoto et al. [3] prepared complexes of the Cu(II) ion with various kinds of 2-substituted and 2,4-disubstituted Im compounds and studied the polymerization of acrylonitrile (AN) initiated by them in aprotic solvents such as dimethylsulfoxide. However, they did not use water as the solvent.

We have studied polymerization in the water phase. In our case, AN could not be polymerized. The mechanism of polymerization in water may differ from that in aprotic solvents.

The present paper deals with the polymerization of MMA initiated with the system Im derivatives-Cu(II)-water. The Im derivatives used were N-ethylimidazole (N-EtIm), 2-methylimidazole (2-MeIm), 2-undecylimidazole (2-UnIm), and 2-phenylimidazole (2-PhIm). Isolated crystalline complexes of Im, N-EtIm, and 2-MeIm with CuCl_2 were also used for the polymerization of MMA.

EXPERIMENTAL

Materials

Im, 2-MeIm, 2-UnIm, and 2-PhIm supplied by Shikoku Kasei Ind. Co. were recrystallized three times from acetone. N-EtIm was dried over anhydrous sodium sulfate and was distilled twice under reduced pressure. Copper(II) chloride of special commercial grade was used without further purification. MMA, AN, styrene (St), and monomers

were purified by the usual methods and redistilled before use. Water was ion-exchanged and redistilled.

Preparation of Buffer Solution

Buffer solutions were prepared by use of the following systems: pH 2-4, M/10 sodium citrate-M/10 HCl; pH 5-6, M/10 sodium citrate-M/10 NaOH; pH 7-9, M/20 Na₂B₄O₇-M/5 H₃BO₃ + M/20 NaCl; pH 10-11, M/20 Na₂B₄O₇-M/10 NaOH.

Preparation of Crystalline Complexes of Imidazoles with Copper(II) Chloride

[Cu(2-MeIm)₂]Cl₂ [4], [Cu(Im)₄]Cl₂ [5], [Cu(N-EtIm)₂]Cl₂ [6], and [Cu(N-EtIm)₄]Cl₂ [6] were prepared as pure crystals according to the literature. The results of their elemental analyses are shown in Table 1.

Procedures

Polymerization was carried out in a sealed tube under shaking in a manner similar to that reported in a previous paper [1]. The polymer produced was precipitated by pouring into methanol containing a small quantity of hydrochloric acid.

The number-average degree of polymerization (\bar{P}_n) of poly-MMA was measured by its intrinsic viscosity in benzene at 30°C, using Welch's equation [7]. The \bar{P}_{no} , which is the overall \bar{P}_n , and the \bar{P}_{nt} , which is the thermal \bar{P}_n , were measured. From them and the polymer yields, \bar{P}_{nc} , which was the corrected \bar{P}_n , were calculated by using the equation derived in a previous paper [8].

Electronic absorption spectra were measured with a Simadzu double beam spectrophotometer UV-200 type.

The ESR spectra were measured at -60°C by using a JES-FE 1X spectrometer with 100 kHz field modulation.

RESULTS AND DISCUSSION

Effect of Water on the Polymerization of MMA

The polymerization of MMA was carried out by keeping the masses of MMA, Im compounds, and CuCl₂·2H₂O constant at 3 cm³, 1.1 × 10⁻³ mol, and 1 × 10⁻³ g, respectively, and varying the mass of water. The results

TABLE 1. The Results of Elemental Analyses of the Complexes of Imidazoles with Cu(II) Ion

Complex	Found (calc)			
	C (%)	H (%)	N (%)	Cu (%) ^a
[Cu(Im) ₄]Cl ₂	35.62 (35.43)	3.98 (3.96)	27.54 (27.55)	15.8 (15.62)
[Cu(2-MeIm) ₂]Cl ₂	31.39 (32.17)	4.07 (4.05)	18.13 (18.76)	21.29 (21.27)
[Cu(N-EtIm) ₂]Cl ₂	36.70 (36.76)	5.02 (4.94)	17.40 (17.15)	20.68 (19.45)
[Cu(N-EtIm) ₄]Cl ₂	45.98 (46.29)	6.20 (6.21)	21.71 (21.59)	13.28 (12.24)

^aCu(II) determination of the complexes was carried out by standard complexometric titrations.

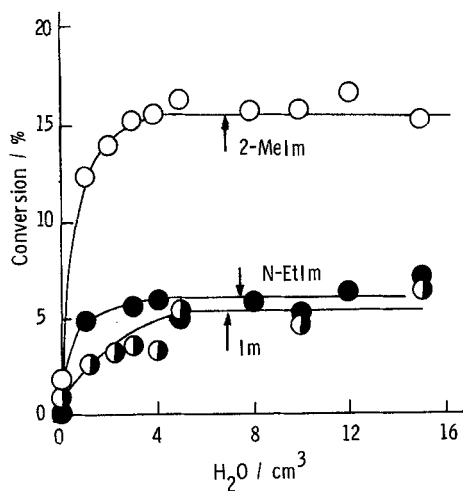


FIG. 1. Mass of water vs conversion of MMA. MMA, 3 cm³; Im compounds, 1.1×10^{-3} mol; CuCl₂·2H₂O, 1×10^{-3} g; 85°C; 5 h; with shaking.

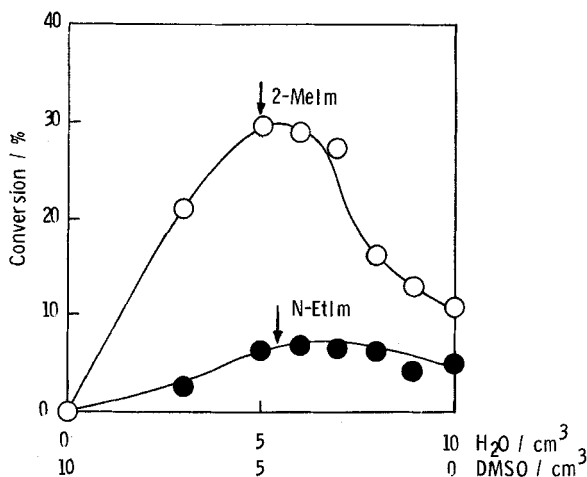


FIG. 2. Polymerization of MMA in mixed solvent of DMSO and water. MMA, 3 cm³; Im compounds, 1.1×10^{-3} mol, CuCl₂·2H₂O, 1×10^{-3} g; (DMSO + H₂O) = 10 cm³; 85°C; 5 h; with shaking.

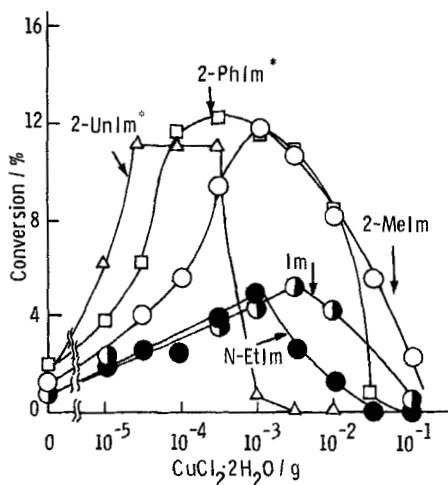


FIG. 3. Conversion of MMA vs mass of copper(II) chloride. MMA, 3 cm³; Im compounds, 1.1 × 10⁻³ mol; H₂O, 10 cm³; 85°C; 5 h; with shaking. *Partially soluble.

obtained are shown in Fig. 1. From the results, it was concluded that the presence of water is necessary.

The necessity of water was further confirmed by polymerization in the mixed solvent of water and dimethylsulfoxide (DMSO) as shown in Fig. 2. Polymerization did not take place in DMSO. A mixed solvent composed of equal volumes of DMSO and H₂O was the best.

Effect of the Mass of Cu(II) Ion on the Polymerization of MMA

In an earlier paper [1] it was concluded that the presence of Cu(II) ion was necessary to polymerize MMA by the Im and water system. In the present paper, the effects of the mass of Cu(II) ion on the conversion of MMA were studied by using five kinds of Im compounds. The results obtained are shown in Fig. 3. From this figure it is seen that the presence of Cu(II) ion is necessary for the polymerization of MMA. A maximum conversion of MMA is found in each case because excess Cu(II) ion can inhibit the propagating chain radicals.

From Fig. 3 it was clear that 2-substituted Im compounds are more effective for polymerization than N-EtIm and Im. 2-PhIm and 2-UnIm are only partly soluble in water. Therefore, soluble 2-MeIm was used in further experiments as a representative of 2-substituted Im.

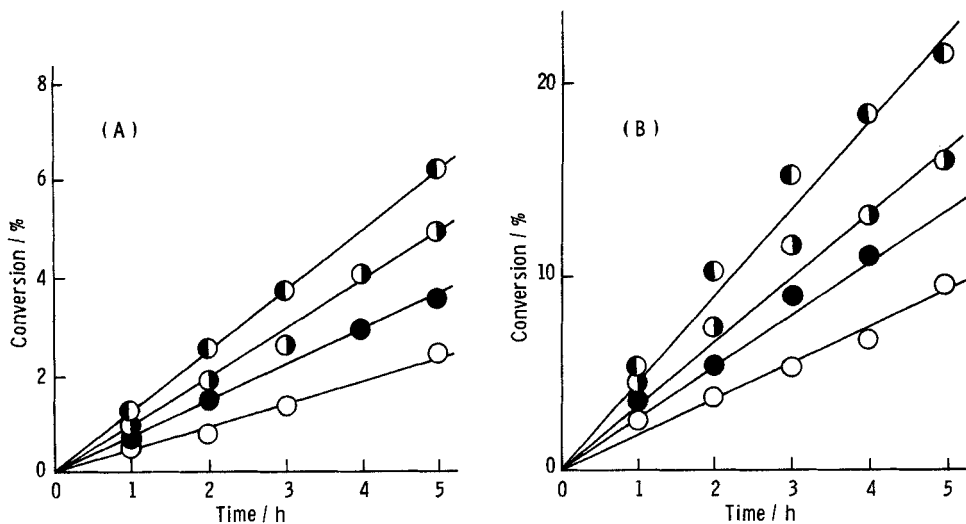


FIG. 4. Time-conversion curves in the presence of Im compounds. MMA, 3 cm³; CuCl₂·2H₂O, 1 × 10⁻³ g; H₂O, 10 cm³; (○) 75°C; (●) 80°C; (◐) 85°C; (◑) 90°C; with shaking. (A) N-EtIm, 0.10 cm³ (1.1 × 10⁻³ mol); (B) 2-MeIm, 0.090 g (1.1 × 10⁻³ mol).

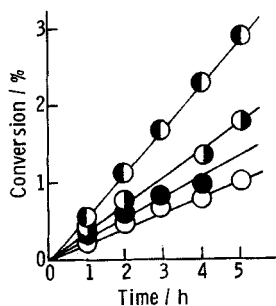


FIG. 5. Time-conversion curves in the absence of Im compounds. MMA, 3 cm³; CuCl₂·2H₂O, 1 × 10⁻³ g; H₂O, 10 cm³; (○) 75°C; (●) 80°C; (◐) 85°C; (◑) 90°C; with shaking.

Estimation of Overall Activation Energy

Polymerizations with the system 3 cm³ MMA, 1 × 10⁻³ g CuCl₂ · 2H₂O, and 10 cm³ H₂O in the presence or absence of 1.1 × 10⁻³ mol Im compounds were carried out at 70–90°C. The time-conversion curves obtained are shown in Figs. 4 and 5. Straight lines were obtained without induction periods. Accordingly, the rate of polymerization of MMA, R_p, could be calculated by

$$R_p \text{ (g/h)} = \frac{\left[\begin{array}{l} \text{overall poly-MMA obtained} \\ \text{in the presence of Im} \\ \text{compounds (g)} \end{array} \right] - \left[\begin{array}{l} \text{poly-MMA obtained} \\ \text{in the absence of} \\ \text{compounds (g)} \end{array} \right]}{\text{polymerization time (h)}} \quad (1)$$

The R_p values were applied to the Arrhenius equation as shown in Fig. 6. From the slopes of these straight lines, the overall activation energies for polymerization with N-EtIm and 2-MeIm were estimated to be 94.3 and 61.1 kJ/mol, respectively. These values were larger than the 28.7 kJ/mol found with Im [1].

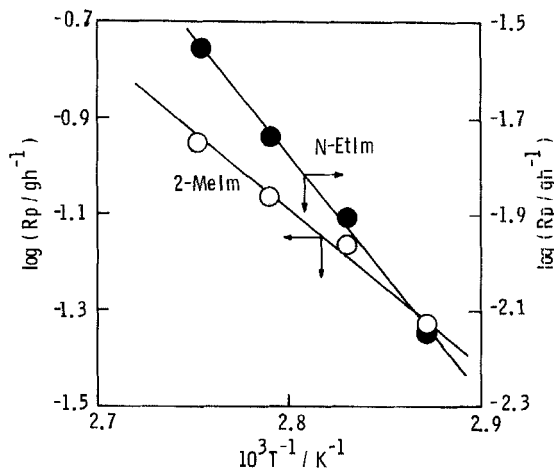


FIG. 6. Arrhenius plots.

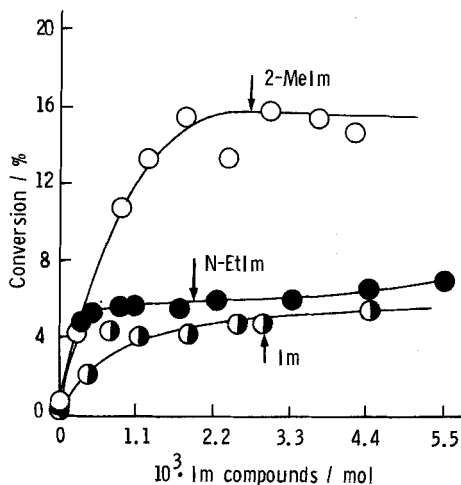


FIG. 7. Effects of masses of Im compounds on the conversion of MMA. MMA, 3 cm^3 ; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $1 \times 10^{-3} \text{ g}$; H_2O 10 cm^3 ; 85°C ; 5 h; with shaking.

Effect of the Masses of Im Compounds on the Polymerization

Keeping the feed masses of MMA, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and H_2O constant at 3 cm^3 , $1 \times 10^{-3} \text{ g}$, and 10 cm^3 , respectively, and varying the masses of Im compounds, polymerization was carried out with shaking. The results for the conversion of MMA are shown in Fig. 7.

When the Im used exceeded the defined mass, the conversion of MMA became constant. Clearly, this is due to the presence of Im in an overwhelmingly large mass compared to the $\text{Cu}(\text{II})$ ion; that is, $\text{Cu}(\text{II})$ ion was present as $5.8 \times 10^{-6} \text{ mol}$. Therefore, the results shown in Fig. 7 are considered to be reasonable.

The number-average degrees of polymerization, \bar{P}_{n0} , of the poly-MMA produced are shown in Fig. 8.

Effects of the Mass of MMA on the Polymer Yield and \bar{P}_n of Poly-MMA

Polymerization was carried out while keeping the mass of Im compounds, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and H_2O constant, and varying the mass of MMA. The effects of the mass on the polymer yield and \bar{P}_{nc} of poly-MMA are shown in Figs. 9(A) and (B), respectively.

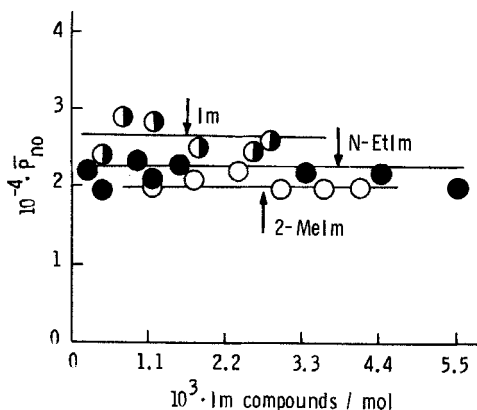


FIG. 8. \bar{P}_{no} of the poly-MMA produced in the cases in Fig. 7.

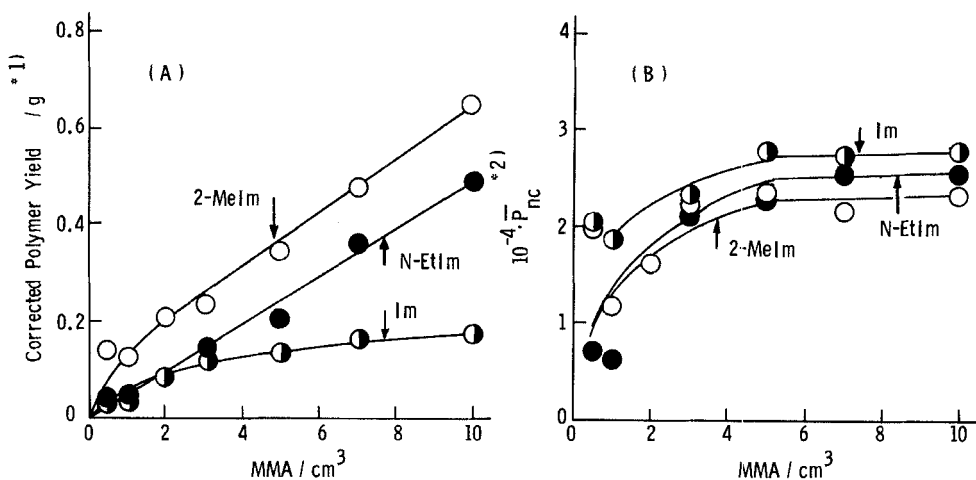


FIG. 9. Effects of the mass of MMA on the corrected polymer yield and \bar{P}_{nc} of poly-MMA. Im compounds, 1.1×10^{-3} mol; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 1×10^{-3} g; H_2O , 10 cm^3 ; 85°C ; 5 h; with shaking. *1) Corrected yield/g = (overall yield(x)/g) - (Thermal yield(y)/g). *2) $\bar{P}_{nc} = \frac{(x - y)\bar{P}_{no}\bar{P}_{nt}}{x\bar{P}_{nt} - y\bar{P}_{no}}$.

\bar{P}_{nc} = corrected \bar{P}_n . $\bar{P}_{no} = \bar{P}_n$ in the presence of Im compounds.

$\bar{P}_{nt} = \bar{P}_n$ in the absence of Im compounds.

TABLE 2. Selectivity of Vinyl Monomer^a

Im compounds	Conversion (%)		
	MMA	St	AN
None	0.3	3.8	27.1
Im, 0.075 g	4.4	3.7	0.3
N-EtIm, 0.10 cm ³	5.0	4.1	0
2-MeIm, 0.090 g	11.8	3.6	0

^a Monomer, 3 cm³; CuCl₂·2H₂O, 1 × 10⁻³ g; H₂O, 10 cm³; Im compounds, 1.1 × 10⁻³ mol; 85°C, 5 h, with shaking.

Selectivity for Vinyl Monomer

The polymerization of three kinds of vinyl monomer was carried out in the presence of Im compounds, water, and copper(II) chloride. The results are given in Tables 2 and 3. The conversion of St was considered to be by thermal polymerization. The result that polymerization of AN took place easily in the absence of Im means that redox polymerization with Cu(II) ion occurred [9]. Thus it is clear that methacrylates and acrylates can be polymerized by a system of Im compounds, Cu(II), and water.

Proof of Radical Mechanism

In order to confirm that the polymerization proceeded through a radical mechanism, the copolymerization of MMA(M₁) with St(M₂) was carried out and the results shown in Fig. 10 were obtained. From these results and the data with 2-UnIm and 2-PhIm, the values of r₁ and r₂ for the copolymerization of MMA(M₁) and St(M₂) initiated with systems of Im compounds, Cu(II) ion, and water were calculated and are listed in Table 4. This table shows that these polymerizations proceeded through a free-radical mechanism.

Effect of the pH of Water Layer on the Conversion of MMA

The polymerization of MMA was carried out by changing the pH of the aqueous solution. The results are shown in Fig. 11. A maximum conversion of MMA was obtained at pH 8-9 in each system. It is known that Im compounds change into protonated and anionic forms in

TABLE 3. Selectivity for Vinyl Monomer^a

Monomer ^b	Conversion (%)			
	None	Cu(II) ^c	N-EtIm ^d	Cu(II) ^c / N-EtIm ^d
MMA	1.2	0.3	1.3	5.0
EMA	0.9	-	0.9	10.2
iso-PMA	1.5	0.3	1.6	5.1
n-BMA	0.9	0	1.0	4.8
iso-BMA	1.6	0	1.5	4.4
iso-BA	7.0	29.7	13.5	63.6
St	3.9	3.8	3.9	4.1
AN	0	27.1	0	0.6

^a Monomer, 3 cm³; H₂O, 10 cm³; 85°C, 5 h, with shaking.

^b EMA: ethyl methacrylate, PMA: propyl methacrylate, BMA: butyl methacrylate, BA: butyl acrylate.

^c CuCl₂·2H₂O, 1 × 10⁻³ g.

^d N-EtIm, 0.1 cm³.

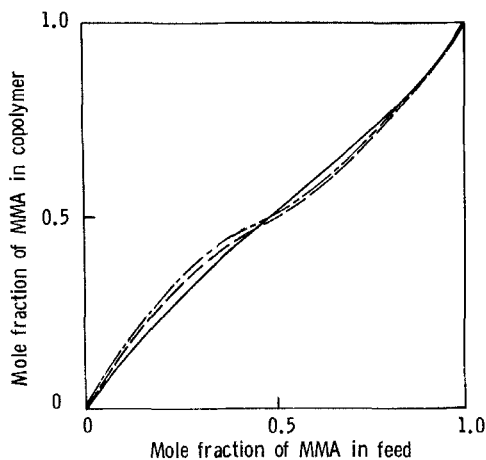


FIG. 10. Copolymerization of MMA (M_1) with St (M_2). Monomer, 3 cm³; Im compounds, 1.1 × 10⁻³ mol; CuCl₂·2H₂O, 1 × 10⁻³ g; H₂O, 10 cm³; 85°C; 5 h; with shaking. (—) Im[1], (---) N-EtIm, (- · -) 2-MeIm.

TABLE 4. The Values of r_1 and r_2^a

Im compounds	r_1	r_2
Im[1]	0.81	0.69
N-EtIm	0.50	0.58
2-MeIm	0.50	0.46
2-UnIm	0.46	0.43
2-PhIm	0.49	0.48

^a $M_1 = \text{MMA}, M_2 = \text{St.}$

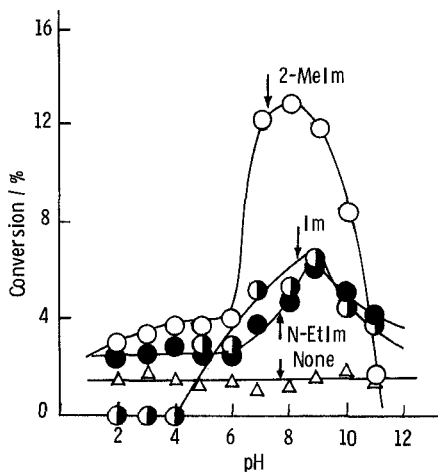


FIG. 11. Conversion of MMA vs pH of aqueous solution. MMA, 3 cm^3 ; Im compounds, $1.1 \times 10^{-3} \text{ mol}$; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $1 \times 10^{-3} \text{ g}$; buffer solution, 10 cm^3 ; 85°C ; 5 h; with shaking.

acidic and basic media, respectively. Therefore, it was concluded that undissociated Im can easily form a complex with Cu(II) ion that is effective for polymerization.

Mechanism of Initiation

The Complexes of Cu(II) Ion with Im-compounds

The formation of a complex of Cu(II) ion with Im in a mole ratio of 6.5:1 was reported in an earlier paper. In the present paper the

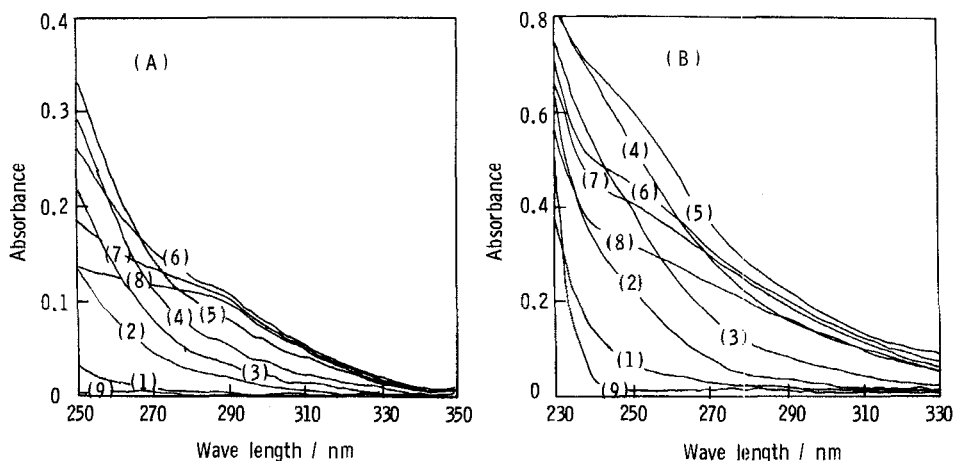


FIG. 12. Electronic spectra of system of CuCl_2/Im compounds in water at room temperature. (A) $\text{CuCl}_2/\text{N-EtIm}$ system; $[\text{CuCl}_2] = [\text{N-EtIm}] = 1.04 \times 10^{-3} \text{ mol/dm}^3$. Mole ratio of $\text{CuCl}_2:\text{N-EtIm} = (1) 1:0, (2) 1:0.2, (3) 1:0.5, (4) 1:1, (5) 1:2, (6) 1:5, (7) 1:9, (8) 1:18, (9) 0:1$. (B) $\text{CuCl}_2/2\text{-MeIm}$ system: $[\text{CuCl}_2] = [2\text{-MeIm}] = 1.10 \times 10^{-3} \text{ mol/dm}^3$. Mole ratio of $\text{CuCl}_2:2\text{-MeIm} = (1) 1:0, (2) 1:0.2, (3) 1:0.5, (4) 1:1, (5) 1:2, (6) 1:4, (7) 1:5, (8) 1:6.5, (9) 0:1$.

complex formation of N-EtIm and 2-MeIm with Cu(II) ion was studied. Figure 12 shows the results by electronic spectra.

The new shoulders recognized at about 280 nm were assigned to the complexes of Cu(II) ion with Im compounds. By using the continuous variation method, the results shown in Fig. 13 were obtained. The maximum points occurred when the mole ratios of N-EtIm and 2-MeIm to the Cu(II) ion corresponded to 5:1 and 2:1, respectively.

We have assumed that molecules of Im were associated by H bonds. However, N-EtIm has no active hydrogen atoms. It may form a Cu(II) complex with four or six ligands of N-EtIm. However, as shall be discussed in the next section, the complexes having four or six ligands are considered to have no initiating ability.

Conservation of the Valency of Cu(II) Ion

In a former paper we assumed the initiation mechanism by Im as shown in Scheme 1. However, the conservation of the valency of Cu(II) was not verified. In the present paper, 0.3 cm^3 of MMA, $1 \times 10^{-4} \text{ g}$ of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and 1.0 cm^3 of aqueous solution containing 0.0075 g ($1.1 \times 10^{-4} \text{ mol}$) of Im were allowed to stand at 85°C after thawing with nitrogen and sealing under vacuum. After definite times, the ESR spectra of the reaction system were observed. The results are

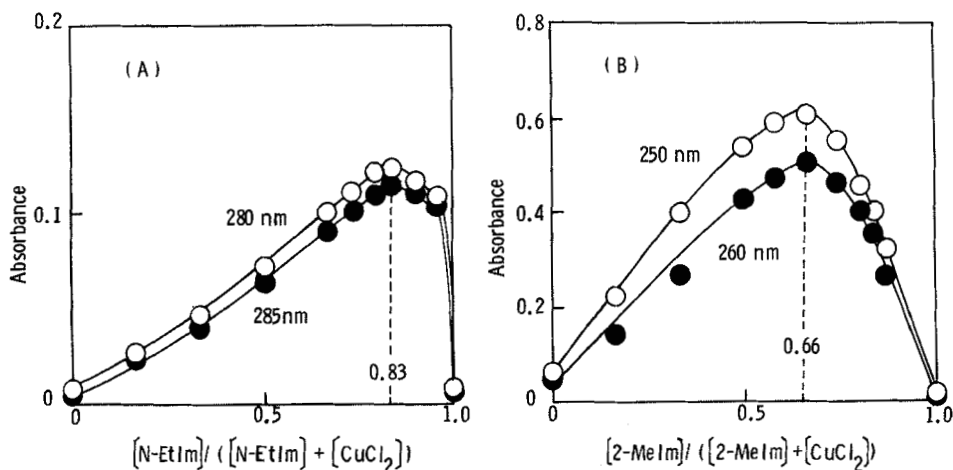


FIG. 13. Application of the results obtained in Fig. 12 to the continuous variation method.

shown in Fig. 14(A). From these, it could be considered that the valency of the Cu(II) ion did not vary. Also, in the case of 2-MeIm and N-EtIm, conservation of the valency of Cu(II) ion was verified as shown in Figs. 14(B) and (C).

The Polymerization of MMA Initiated by the Isolated Complex of Cu(II) with Im Compounds

As mentioned above, the polymerization of MMA initiated by $CuCl_2$ and an aqueous solution of Im compounds takes place through the formation of a complex of Cu(II) ion with Im compound. Therefore, we examined whether an isolated crystalline Im complex of Cu(II) and polymerize MMA in a water phase.

Polymerization of MMA Initiated with the Isolated Complexes of Cu(II) Ion Having Two or Four Ligands of Imidazoles

Figure 15 shows that only $[Cu(2-MeIm)_2]Cl_2$ can initiate the polymerization of MMA. The conversion appears to be very small. However, considering the mass of the complex, the conversion agrees with that shown in Fig. 13.

The other three complexes of $[Cu(Im)_4]Cl_2$, $[Cu(N-EtIm)_2]Cl_2$, and $[Cu(N-EtIm)_4]Cl_2$ acted as inhibitors of polymerization, while

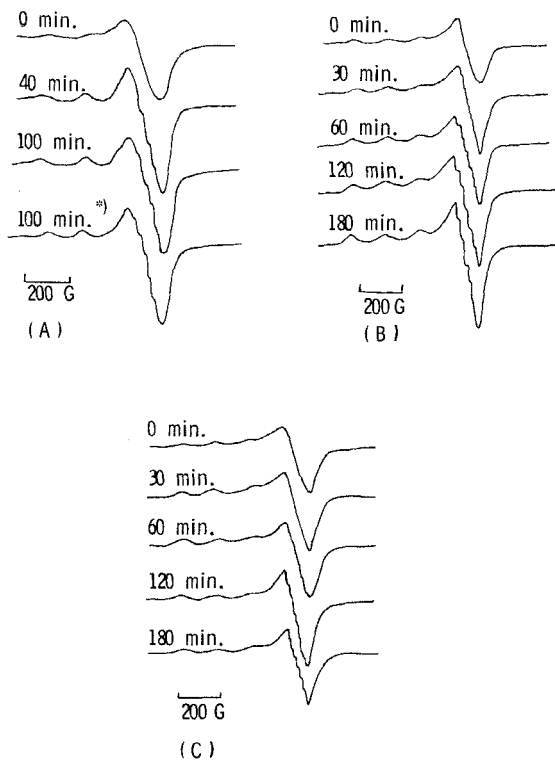


FIG. 14. Changes of ESR spectra of the polymerizing system at 85°C. (A) ESR spectra of the system of Im-Cu(II)-MMA-H₂O. Im, 0.0075 g; CuCl₂·2H₂O, 1 × 10⁻⁴ g; H₂O, 1.0 cm³; MMA, 0.3 cm³. *) Allowed to stand for 50 h at room temperature. (B) ESR spectra of the system of 2-MeIm-Cu(II)-MMA-H₂O. 2-MeIm, 0.009 g; CuCl₂·2H₂O, 1 × 10⁻⁴ g; H₂O, 1.0 cm³; MMA, 0.3 cm³. (C) ESR spectra of the system of N-EtIm-Cu(II)-MMA-H₂O. N-EtIm, 0.01 cm³; CuCl₂·2H₂O, 1 × 10⁻⁴ g; H₂O, 1.0 cm³; MMA, 0.3 cm³.

the system of Im or N-EtIm, CuCl₂, and water could polymerize MMA. Therefore, it appears that the polymerization mechanism involving the isolated complex of Im compound differs from that involving the free Im compound.

In order to confirm the difference between the two initiation systems, the visible spectra of the aqueous solutions of the isolated complexes were measured.

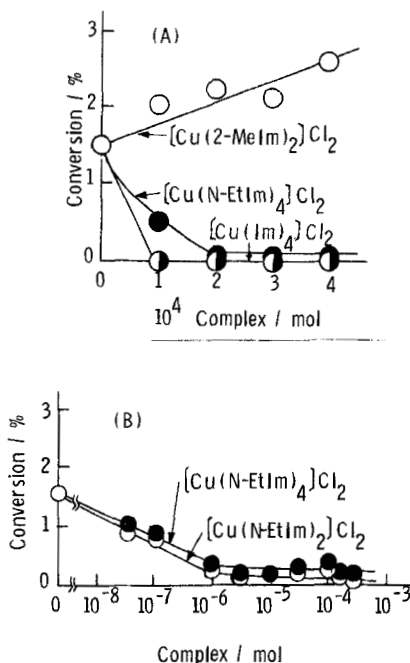


FIG. 15. The polymerization of MMA in the presence of complexes. MMA, 3 cm^3 ; H_2O , 10 cm^3 ; 85°C ; 5 h; with shaking.

Comparisons of Visible Spectra of the Complexes of Imidazoles with $\text{Cu}(\text{II})$ Ion in the Presence and Absence of MMA

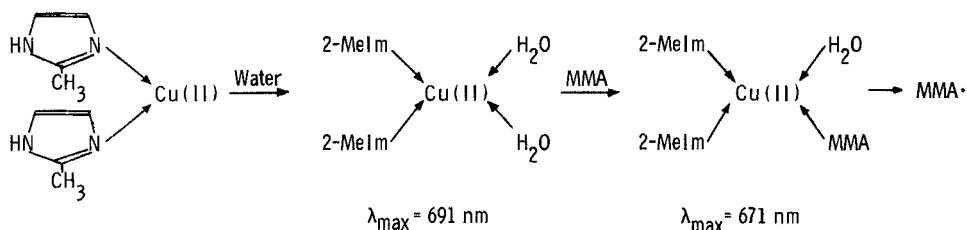
$[Cu(2-MeIm)_2]Cl_2$ is colored pale yellow. However, when it is dissolved in water, the color changes instantly to blue. On the other hand, $[Cu(Im)_4]Cl_2$, $[Cu(N-EtIm)_2]Cl_2$, and $[Cu(N-EtIm)_4]Cl_2$ do not change color in water. Furthermore, when a drop of MMA is added to the water solution of the complexes, $[Cu(2-MeIm)_2]Cl_2$ shifts its absorption maximum to a shorter range, but the λ_{max} of other three complexes remain unchanged. The results can be seen in Table 5.

From these results it is assumed that the change of the structure of the complex of $[Cu(2-MeIm)_2]Cl_2$ is explained as shown in Scheme 2.

On the other hand, the λ_{max} of the other complexes of $[Cu^{\text{II}}(Im)_4]Cl_2$, $[Cu^{\text{II}}(N-EtIm)_2]Cl_2$, and $[Cu^{\text{II}}(N-EtIm)_4]Cl_2$ do not change by the addition of MMA, as can be seen in Table 5. From these results it is concluded that these three complexes are very stable and cannot take

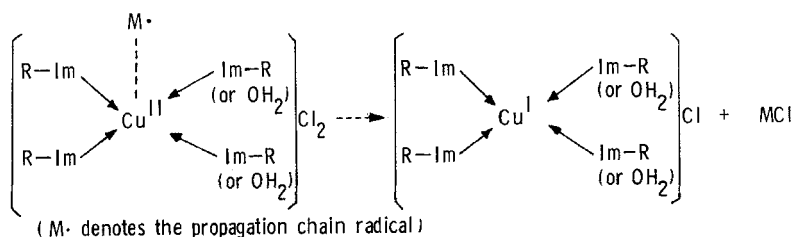
TABLE 5. λ_{\max} of the Complexes in Water in the Presence and Absence of MMA at 50°C

Solvent	λ_{\max}/nm			
	$[\text{Cu}(\text{Im})_4]\text{Cl}_2$	$[\text{Cu}(2\text{-MeIm})_2]\text{Cl}_2$	$[\text{Cu}(\text{N-EtIm})_2]\text{Cl}_2$	$[\text{Cu}(\text{N-EtIm})_4]\text{Cl}_2$
Water	620	691	674.5	609
Water + MMA	620	671	674.5	609



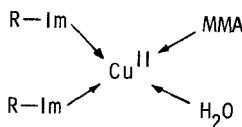
SCHEME 2.

up MMA as a ligand. As mentioned above, these complexes behave as inhibitors for thermally initiated chain radicals. The mechanism may be expressed by Scheme 3.



SCHEME 3.

Thus, excluding the case of $[\text{Cu}^{\text{II}}(2\text{-MeIm})_2]\text{Cl}_2$, the results obtained for the isolated complexes of $[\text{Cu}^{\text{II}}(\text{Im})_4]\text{Cl}_2$ or $[\text{Cu}^{\text{II}}(\text{N-EtIm})_2 \text{ or } 4]\text{Cl}_2$ differ completely from the results obtained by the system of free Im or N-EtIm and CuCl_2 in water solution. However, the mechanisms of the initiation should be identical. We have proposed Scheme 1 as an initiating mechanism. Accordingly, the formation of an adequate complex, that is, the formation of a complex having the following structure, was concluded to be a key to the initiation of polymerization:



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