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# Vinyl Polymerization. 386. Polymerization of Methyl Methacrylate Initiated by Imidazole in Aqueous Solution of Copper(II) Chloride

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# Vinyl Polymerization. 386. Polymerization of Methyl Methacrylate Initiated by Imidazole in Aqueous Solution of Copper(II) Chloride

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## ABSTRACT

The radical polymerization of methyl methacrylate (MMA) was carried out with the system of imidazole (Im), copper(II) chloride, and water at 85°C. The effects of the amount of each component on the conversion of MMA were investigated. The polymerization proceeded through a radical mechanism. The overall activation energy was estimated to be 28.7 kJ/mole. The conversion of MMA showed a maximum at pH 8-9 of the aqueous solution. The formation of a complex of $CuCl_2$ with Im, water, and MMA was confirmed by electronic spectra. An initiation mechanism was proposed.

## INTRODUCTION

In a previous paper [1], we reported that the radical polymerization of methyl methacrylate (MMA) could be initiated with RNA in the aqueous solution of copper(II) chloride.

On the other hand, Imoto and Takemoto et al. [2] found that the polymerization of MMA was initiated by the system of imidazole (Im), water, and $CCl_4$.

Furthermore, Takemoto et al. reported that the imidazole-copper(II) complex of type $Cu(Im)_4X_2$ could initiate acrylonitrile (AN) but not MMA and styrene (St) in aprotic polar solvent such as dimethyl sulfoxide or dimethylformamide [3-6]. They found that copper(II) nitrate and perchlorate could initiate the polymerization, but copper(II) chloride and bromide did not.

By using Im as a monomeric unit of RNA, the present paper deals with the polymerization of MMA initiated with the system of Im and aqueous solution of copper(II) chloride.

## EXPERIMENTAL

### Materials

Im, which was obtained from Shikoku Kasei Ind. Co. Ltd., was recrystallized twice from acetone. Copper(II) chloride of special commercial grade was used without further purification. MMA, St, and AN were purified by the usual method and redistilled before use. Water was ion-exchanged and redistilled.

### Preparation of Buffer Solutions

These were prepared by use of following systems: pH 2-4, $\underline{M}/10$ sodium citrate-$\underline{M}/10$ HCl; pH 5-6, $\underline{M}/10$ sodium citrate-$\underline{M}/10$ NaOH; pH 7-9, $\underline{M}/20$ $Na_2B_4O_7$-$\underline{M}/5$ $H_3BO_3$ + $\underline{M}/20$ NaCl; pH 10-11, $\underline{M}/20$ $Na_2B_4O_7$-$\underline{M}/10$ NaOH.

### Procedure

Vinyl monomer, Im, $CuCl_2 \cdot 2H_2O$, and water were placed in a tube and sealed under vacuum after thawing with nitrogen. The tube was heated at 85°C with shaking or on standing. After a definite time, the contents were poured into a large amount of methanol containing a small quantity of hydrochloric acid to precipitate the polymer. The collected polymer was washed thoroughly with water and methanol and dried.

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

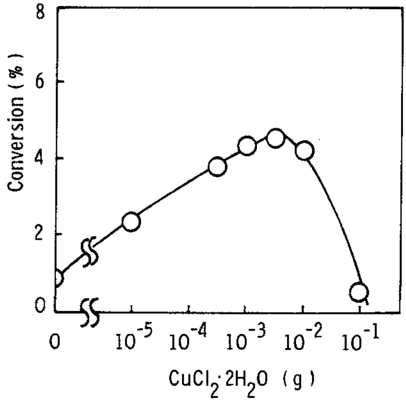


FIG. 1. Conversion of MMA vs. weight of copper(II) chloride. MMA, 3 $cm^3$; Im, 0.075 g; $H_2O$, 10 $cm^3$; 85°C; 5 hr; with shaking.

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

## RESULTS AND DISCUSSION

### Effect of the Amount of Cu(II) Ion on Polymerization

Figure 1 shows the effect of the weight of Cu(II) ion on the conversion of MMA. A maximum conversion of MMA was obtained at $5 \times 10^{-3}$ g of $CuCl_2 \cdot 2H_2O$. From this figure, it was concluded that the presence of Cu(II) ion was necessary for the polymerization of MMA.

### Selectivity for Vinyl Monomer

The polymerizations of three kinds of vinyl monomer were carried out in the presence of Im, water, and copper(II) chloride. The results are given in Table 1. The conversion of St was due to the thermal polymerization. The polymerization of AN takes place easily, even in the absence of Im, indicating the charge-transfer polymerization occurs only with Cu(II) ion [9]. It was clear that only MMA could be specifically polymerized by Im. Such selectivity of monomer in this polymerization system suggested that the monomer participated in the initiation step and then differed from that initiated with Im-copper(II) complex, reported by Takemoto et al. [5].

TABLE 1. Selectivity of Vinyl Monomer[a]

| Monomer | Im (g) | Conversion (%) |
|---|---|---|
| MMA | 0 | 0.25 |
| | 0.075 | 4.37 |
| St | 0 | 3.81 |
| | 0.075 | 3.71 |
| AN | 0 | 27.13 |
| | 0.075 | 0.82 |

[a] Monomer, 3 $cm^3$; $CuCl_2 \cdot 2H_2O$, $1 \times 10^{-3}$ g; $H_2O$, 10 $cm^3$; 85°C; 5 hr; with shaking.

## Proof of Radical Mechanism

In order to confirm that the polymerization proceeded through a radical mechanism, the copolymerizations of MMA($M_1$) with St($M_2$) were carried out, and the results shown in Fig. 2 were obtained. From the curve, $\gamma_1$ and $\gamma_2$ were calculated as 0.81 and 0.69, respectively. A radical mechanism was verified from these results.

## Estimation of Overall Activation Energy

The time-conversion curves were obtained by carrying out the polymerizations at 75-90°C, with the system of 3 $cm^3$ of MMA, $1 \times 10^{-3}$ g of $CuCl_2 \cdot 2H_2O$, and 10 $cm^3$ of $H_2O$ in the presence or absence of 0.075 g of Im. The results obtained are shown in Fig. 3. The rate of $R_p$ polymerization of MMA was calculated by Eq. (1):

$$R_p(\text{g/hr}) = \frac{\begin{array}{c}\text{Overall poly-MMA obtained}\\ \text{in the presence of Im(g)}\end{array} - \begin{array}{c}\text{Poly-MMA obtained in}\\ \text{the absence of Im(g)}\end{array}}{\text{Polymerization time (hr)}} \quad (1)$$

On applying the values of $R_p$ to the Arrhenius equation, the overall activation energy was calculated to be 28.7 kJ/mole, as shown in Fig. 4.

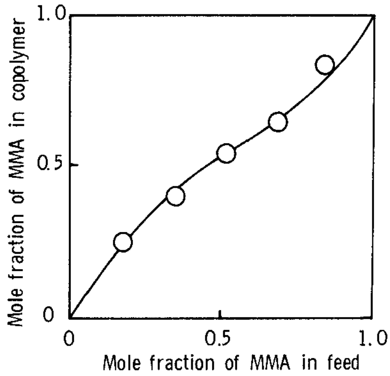


FIG. 2. Copolymerization of MMA with St. Monomer, 3 $cm^3$; Im, 0.075 g; $CuCl_2 \cdot 2H_2O$, $1 \times 10^{-3}$ g; $H_2O$, 10 $cm^3$; 85°C; 5 hr; with shaking.

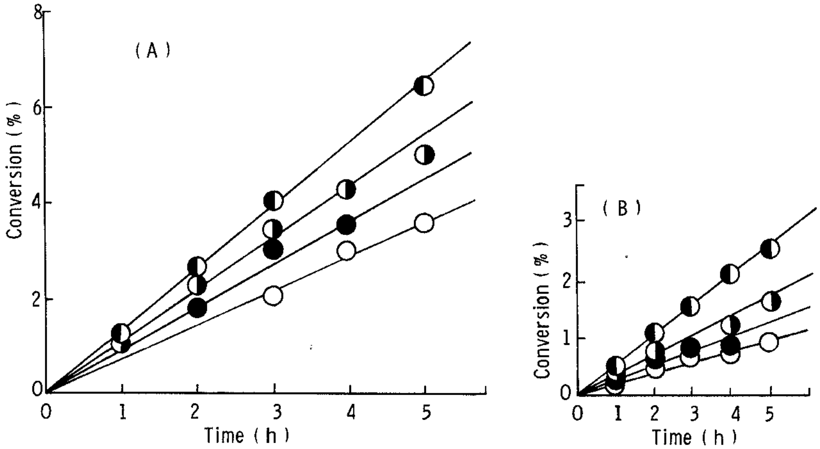


FIG. 3. Time-conversion curves for (A) polymerization in the presence of 0.075 g of Im and (B) polymerization in the absence of Im: ( ○) 75°C; ( ● ) 80°C; ( ◑) 85°C; ( ◐ ) 90°C. MMA, 3 $cm^3$; $CuCl_2 \cdot 2H_2O$, $1 \times 10^{-3}$ g; $H_2O$, 10 $cm^3$; with shaking.

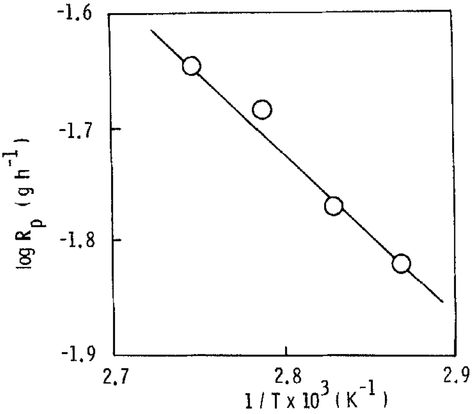


FIG. 4. Arrhenius plots.

## Necessity of Water

On keeping the amounts of MMA, Im, and $CuCl_2 \cdot 2H_2O$ constant at 3 cm$^3$, Im 0.075 g, and $1 \times 10^{-3}$ g, respectively, and varying the amount of water, the polymerizations of MMA were carried out under shaking. The results obtained are shown in Fig. 5. It was concluded that the presence of water is necessary. In the absence of water, MMA polymerized only thermally and the initiating effect of Im could not be observed.

## Phase Where the Polymerization Takes Place

In order to ascertain the phase in which the polymerization took place, the polymerization reaction was carried out on standing. The reaction tube was allowed to stand at 85°C for 5 hr. After the polymerization, the clear layer of MMA was pipetted out and poured into methanol. Also the muddy aqueous layer was poured into methanol. The results are shown in Fig. 6. It was concluded that this polymerization was initiated, propagated, and terminated in the water layer.

## Effect of Amount of Im on the Polymerization

On keeping MMA, $CuCl_2 \cdot 2H_2O$, and $H_2O$ in the feed constant at 3 cm$^3$, $1 \times 10^{-3}$ g, and 10 cm$^3$, respectively, and varying the amount of Im, the polymerizations were carried out with shaking. The results obtained are shown in Fig. 7.

Im was reported to associate in water [10]. Therefore, the strange shape of the curve for the conversion of MMA observed can be explained by the initiation mechanism which shall be later mentioned:

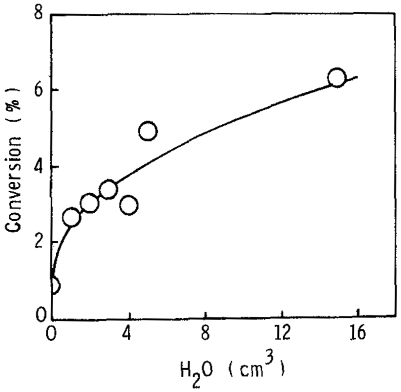


FIG. 5. Amount of water vs. conversion of MMA. MMA, 3 $cm^3$; Im, 0.075 g; $CuCl_2 \cdot 2H_2O$, $1 \times 10^{-3}$ g; 85°C; 5 hr; with shaking.

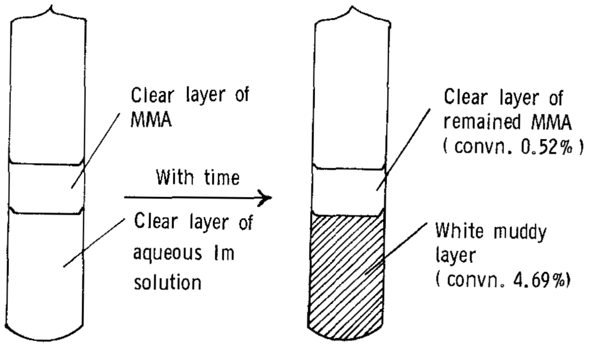
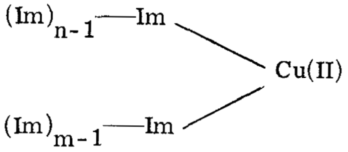


FIG. 6. Polymerization of MMA initiated with Im in aqueous solution of copper(II) chloride. MMA, 3 $cm^3$; Im, 0.075 g; $CuCl_2 \cdot 2H_2O$, $1 \times 10^{-3}$ g; $H_2O$, 10 $cm^3$; 85°C; 5 hr; on standing.



The value of (n + m) is, on the average, 6.5, as described in later section. Accordingly, the following equilibrium can be set up:

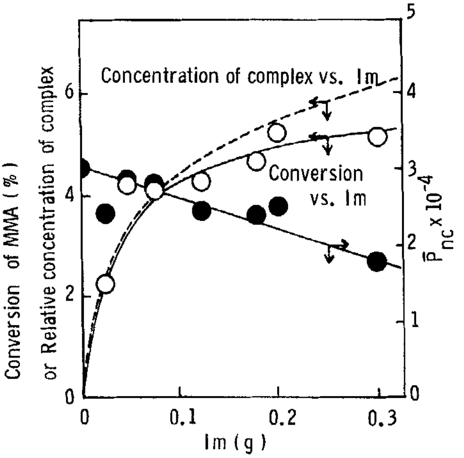


FIG. 7. Effects of amount of Im on the conversion of MMA, relative concentration of complex, and $\bar{P}_{nc}$ of poly-MMA. MMA, 3 cm$^3$; $CuCl_2 \cdot 2H_2O$, $1 \times 10^{-3}$ g; $H_2O$, 10 cm$^3$; 85°C, 5 hr; with shaking. *Corrected conversion obtained by subtracting the thermal conversion from the overall conversion.

$$\frac{2}{6.5}\ \mathrm{Im} + \mathrm{Cu(II)} \rightleftharpoons \mathrm{Complex} \tag{2}$$

Thus, the concentration of complex can be expressed by Eq. (3).

$$[\mathrm{Complex}] = K[\mathrm{Im}]^{2/6.5}[\mathrm{Cu(II)}] \tag{3}$$

where K is an equilibrium constant.

When the concentration of Cu(II) ion is constant, Eq. (3) can be rewritten as Eq. (4).

$$[\mathrm{Complex}] = \mathrm{Const.}\ [\mathrm{Im}]^{2/6.5} \tag{4}$$

The formation of this complex is the first step of the polymerization. Thus, the concentration of the complex formed in the reaction system should be proportional to the rate of initiation, and furthermore, to the rate of polymerization. Calculating the values of $[\mathrm{Im}]^{2/6.5}$, we have correlated the relative concentration of complex with [Im], as shown by a dotted line in Fig. 6. In the region of small [Im], this curve agrees with the conversion curve obtained experimentally. When [Im] becomes larger, the calculated dotted line exceeds the

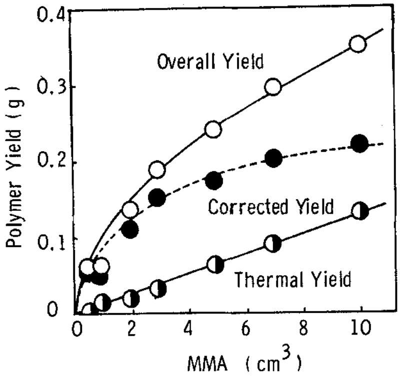


FIG. 8. Effect of the amount of MMA on the polymer yield: ( ○, ● ) 0.075 g Im; ( ◑ ) 0 g. $CuCl_2 \cdot 2H_2O$, $1 \times 10^{-3}$ g; $H_2O$, 10 cm$^3$; 85°C, 5 hr; with shaking.

conversion curve. This is due to the chain transfer reaction of the propagating chain to Im in excess.

## Effect of the Amount of MMA on the Rate of Polymerization

On keeping Im, $CuCl_2 \cdot 2H_2O$, and $H_2O$ constant and varying the amount of MMA, polymerizations were carried out with shaking. The effect of the amount of MMA on the polymer yield is shown in Fig. 8.

By subtracting the thermal yield from the overall yield, the corrected yield was calculated. Beyond a certain amount of MMA, the yield became independent of quantity of MMA. Such a relationship between the polymer yields and the MMA in the feed is similar to that in the enzymatic reaction. Therefore, application of the Michaelis-Menten equation, Eq. (5), to the present polymerization was attempted. As mentioned previously [8], the rate of reaction in the Michaelis-Menten-Lineweaver-Burk equation (7) is considered to correspond to the initiation rate of the polymerization, $R_i$.

$$\begin{array}{ccccccc} E & + & S & \underset{k_2}{\overset{k_1}{\rightleftharpoons}} & ES & \xrightarrow{k_3} & P \quad + E \qquad (5) \\ \vdots & & \vdots & & \vdots & & \vdots \\ Im/Cu(II)/H_2O & & MMA & & \text{Complex} & & MMA\cdot \\ & & & & & & \text{(Primary radical)} \end{array}$$

If we assume that the following relationship exists in the region before the saturation point of MMA:

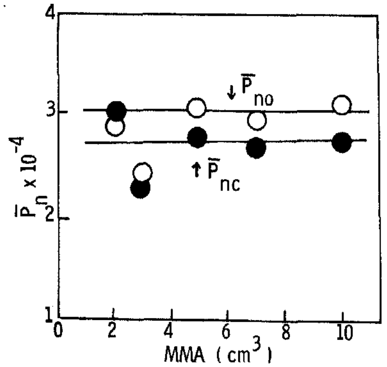


FIG. 9. Effect of the amount of MMA on $\overline{P}_n$ of poly-MMA: ( ○ ) $\overline{P}_{no}$; ( ● ) $\overline{P}_{nc}$. Im, 0.075 g; $CuCl_2 \cdot 2H_2O$, $1 \times 10^{-3}$ g; $H_2O$, 10 cm$^3$; 85°C, 5 hr; with shaking.

$$[\mathrm{MMA}]_I = \mathrm{Const.}\ (\mathrm{MMA}) \tag{6}$$

where $[\mathrm{MMA}]_I$ and (MMA) indicate the concentration of MMA formed from the complex (ES) and the MMA in the feed, respectively, then

$$\frac{1}{R_i} = \frac{K_a}{k_3[\mathrm{Im}]}\left(\frac{1}{\mathrm{Const.}\ (\mathrm{MMA})}\right) + \frac{1}{k_3[\mathrm{Im}]} \tag{7}$$

Here, $K_a$ denotes $(k_2 + k_3)/k_1$.

$R_i$ can be replaced by $(R_p/\overline{P}_{nc})\beta$ on neglecting the chain-transfer reaction, as reported in the previous paper [8]:

$$R_i = (R_p/\overline{P}_{nc})\beta \qquad \beta = 1\text{-}2 \tag{8}$$

The $\overline{P}_{no}$ and $\overline{P}_{nc}$ obtained are shown in Fig. 9. Thus, $\overline{P}_{nc}/\beta R_p$ was coordinated with 1/(MMA); and the results obtained are shown in Fig. 10. From the slope of the straight line and the intercept on the ordinate, $K_a \times \mathrm{Const.}^{-1} \times \beta$ and $k_3[\mathrm{Im}]^{-1}\beta^{-1}$ were estimated to be 3.34 g and $2.32 \times 10^{-6}$ g/hr, respectively.

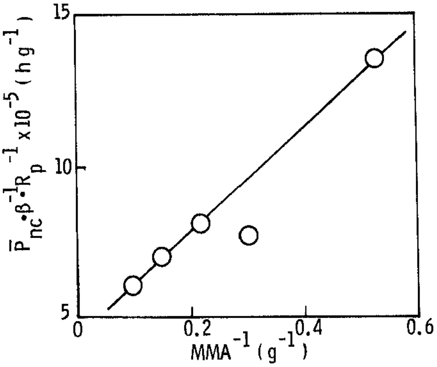


FIG. 10. Application of Eq. (7).

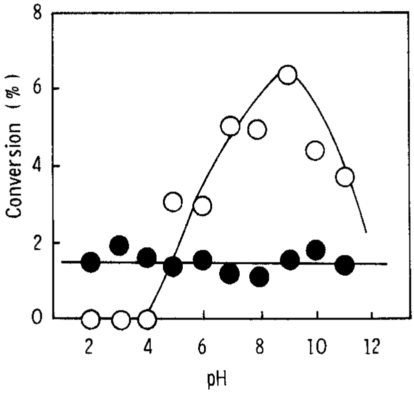


FIG. 11. Conversion of MMA vs. pH of aqueous solution ( ○ ) with and ( ● ) without Im. MMA, 3 cm$^3$, Im, 0.075 g; $CuCl_2\cdot 2H_2O$, $1 \times 10^{-3}$ g; buffer solution, 10 cm$^3$; 85°C, 5 hr; with shaking.

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

The polymerizations of MMA were carried out by varying the pH of the aqueous solution; the results shown in Fig. 11 were obtained. The conversion of MMA showed a maximum at pH 8-9. It is well known that Im dissolved into the protonated and anionic forms in acidic and basic media, respectively. Therefore, it seems that undissociated Im can easily form a complex with copper(II) ion and is effective for the polymerization.

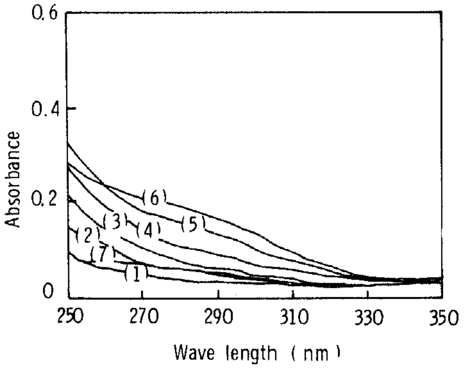


FIG. 12. UV spectra of system of $CuCl_2$/Im in water at room temperature at various $CuCl_2$: Im mole ratios: (1) 1:0; (2) 1:0.2; (3) 1:0.5; (4) 1:1; (5) 1:2; (6) 1:5; (7) 0:1.

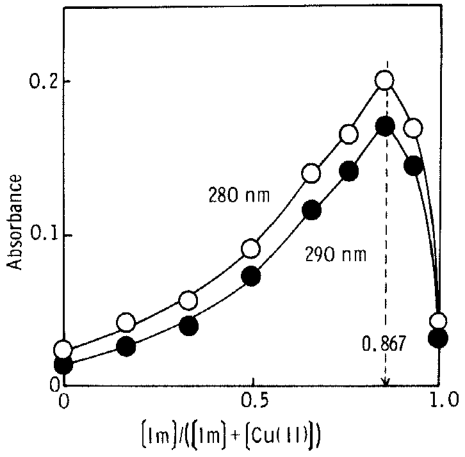


FIG. 13. Analysis by the continuous variation method. [Im] = [Cu(II)] = $1.16 \times 10^{-3}$ mole/$dm^3$, in water at room temperature.

TABLE 2. Results of Electronic Spectra[a]

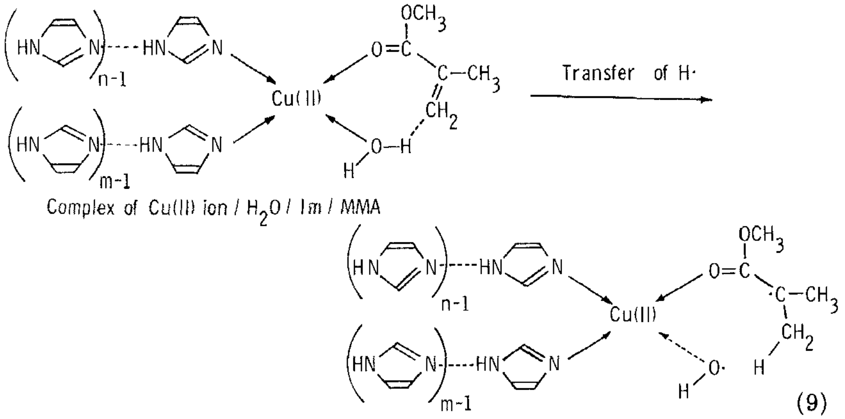
| $CuCl_2 \times 10^2$ (mole/dm$^3$) | Im $\times 10^2$ (mole/dm$^3$) | MMA[b] | $\lambda_{max}$ (nm) |
|---|---|---|---|
| 7.04 | 0 | 0 | 821 |
| 5.87 | 1.17 | 0 | 800 |
| 4.69 | 2.35 | 0 | 780 |
| 3.52 | 3.52 | 0 | 745 |
| 2.35 | 4.69 | 0 | 691 |
| 2.35 | 4.69 | 1 drop | 655 |
| 1.64 | 5.40 | 0 | 631 |
| 1.41 | 5.63 | 0 | 620 |
| 1.17 | 5.87 | 0 | 607 |
| 1.17 | 5.87 | 1 drop | 604 |
| 0.94 | 6.10 | 0 | 599 |
| 0.94 | 6.10 | 1 drop | 599 |
| 0.70 | 6.34 | 0 | 599 |
| 0.47 | 6.57 | 0 | 599 |
| 0 | 7.04 | 0 | - |

[a] Measured in water at room temperature.
[b] MMA saturated in water.

## Mechanism of Initiation

Formation of the complex of Cu(II) ion with Im water and MMA was proved by the electronic spectra. Figure 12 shows UV spectra of the system of Im and $CuCl_2$ measured in aqueous solution. The solutions of Im and $CuCl_2$ both at concentration of $1.16 \times 10^{-3}$ mole/dm$^3$, were mixed; the total volume was 3 cm$^3$. A new shoulder was observed at about 280 nm. This shoulder should be due to the complex of Cu(II) ion with Im. However, further addition of MMA to the solution of Im and $CuCl_2$ showed no peak of complexed MMA in UV region. By using the continuous variation method, the results shown in Fig. 13 were obtained. The maximum corresponds to the mole ratio of 1:6.5 of Cu(II): Im; it suggests that Im associated in water forms a complex with Cu(II) ion.

On the other hand, the maximal absorptions of Cu(II) ion in visible spectra were measured (Table 2). From this Table 2 the following conclusions can be obtained. (1) The shift of $\lambda_{max}$ from 821 to 599 nm was due to the formation of the complex of Cu(II) ion with the associated Im and water. (2) The blue shift observed on addition of MMA suggests that formation of a complex of Cu(II) ion, $H_2O$ and the associated Im and MMA occurs. Therefore, the complex can be as



(9)

shown in Eq. (9). The initiating free radicals are assumed to be generated by hydrogen transfer from water to MMA [ Eq. (9)].

## ACKNOWLEDGMENT

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