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Vinyl Polymerization. 405. Polymerization of Methyl Methacrylate Initiated by Poly(N-vinylimidazole) in Aqueous Solution of Copper(II) Chloride

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ABSTRACT

The polymerization of methyl methacrylate (MMA) was carried out with a system of poly(N-vinylimidazole) (PNVIm), copper(II) chloride, and water at 85°C. The effects of the amount of each component on the conversion of MMA were investigated. The initiating ability of PNVIm was much larger than that of N-ethylimidazole; the macromolecular effect of the initiator was very remarkable. The polymerization proceeded through a radical mechanism. The overall activation energy was estimated to be 24.8 kJ/mol.

INTRODUCTION

In a previous paper we reported on the radical polymerization of methyl methacrylate (MMA) initiated with imidazole (Im) [1] or substituted imidazole [2] in an aqueous solution of copper(II) chloride. We concluded that the initiating free radical was generated by the hydrogen atom transfer from water to MMA through the complex of Cu(II) ion with Im compound, water, and MMA.

Takemoto et al. [3] studied the polymerization of MMA and acrylonitrile (AN) initiated with poly-4(5)-vinylimidazole-copper(II) complex in aqueous solution. The activity of polymer chelate polyvinylimidazole was found to be higher than that of Im. However, they carried out the experiment in the presence of carbon tetrachloride, using dimethylsulfoxide as the solvent. We have studied the polymerization in a water phase and in the absence of carbon tetrachloride.

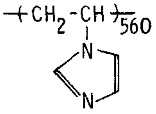
The present paper deals with the polymerization of MMA initiated with a system of PNVIm and an aqueous solution of copper(II) chloride.

EXPERIMENTAL

Materials

PNVIm was prepared by the polymerization of N-vinylimidazole at 60°C using α,α'-azobisisobutyronitrile [4]. PNVIm was purified three times by reprecipitation from ethanol and acetone. The weight-average molecular weight ($\overline{M}_w$) of PNVIm was determined to be 53,000 from measurements of its intrinsic viscosity, $[\eta]$, in 0.001 N-tetrabutylammonium bromide methanol solution at 25°C by using Tan's equation [4].

$$\log \overline{M}_w = 5.18 + 1.49 \log [\eta]$$



Poly(N-vinylimidazole) (PNVIm)

N-ethylimidazole (N-EtIm) was dried over anhydrous sodium sulfate and distilled twice under reduced pressure. Copper(II) chloride of special commercial grade was used without further purification. MMA, acrylonitrile (AN), and styrene (St) were purified by the usual methods and redistilled before use. Water was ion-exchanged and redistilled.

Procedure

The polymerization was carried out in a sealed tube with shaking in a manner similar to that reported in a previous paper. The reaction

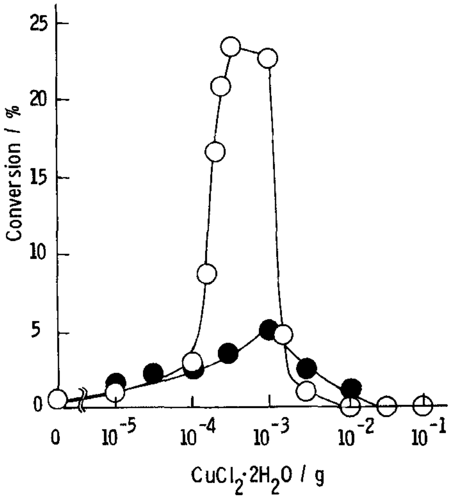


FIG. 1. Conversion of MMA vs amount of copper(II) chloride. MMA, 3 cm^3; H_2O, 10 cm^3; 85°C; with shaking. (○) PNVIm: 0.02 g (2.2×10^{-4} mol of F.U.); 2 h. (●) N-EtIm: 0.1 cm^3 (1.1×10^{-3} mol); 5 h. F.U. = functional unit.

mixture was lyophilized and then poured into a large amount of n-hexane to precipitate the polymer. The conversion of monomer was calculated by

$$\text{Conversion (\%)} = \frac{\text{weight of precipitate - weight of fed PNVIm}}{\text{weight of fed monomer}} \times 100 \qquad (1)$$

The number-average degree of polymerization ($\overline{P}_n$) of poly-MMA was measured from $[\eta]$ in benzene at 30°C by using Welch's equation [5].

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

The efficiency of grafting (E.G.) is the percentage of the grafted poly-MMA versus the polymerized MMA. The homopolymer of MMA was separated by extraction with benzene for 70 h.

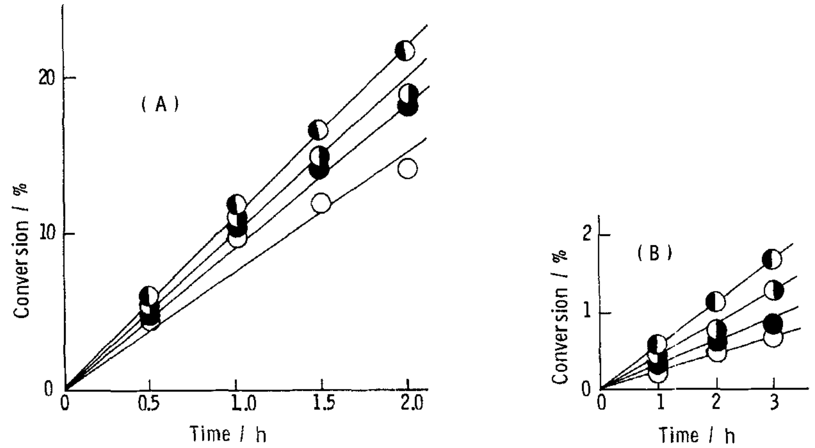


FIG. 2. Time-conversion curves for (A) polymerization in the presence of 0.02 g of PNVIm and (B) polymerization in the absence of PNVIm: MMA, 3 cm^3; $CuCl_2 \cdot 2H_2O$, 5×10^{-4} g; H_2O, 10 cm^3; with shaking. (○) 75°C; (●) 80°C; (◑) 85°C; (◐) 90°C.

RESULTS AND DISCUSSION

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

Figure 1 shows the effect of the weight of Cu(II) ion on the conversion of MMA. From this figure it is concluded that the presence of Cu(II) ion is necessary for the polymerization of MMA and that the polymerization ability of PNVIm is about 10 times as much as that of N-EtIm, which is a monomeric compound of PNVIm. This can be regarded as a remarkable macromolecular effect and may be due to a large concentration of MMA in the hydrophobic area (HA).

Estimation of Overall Activation Energy

Time-conversion curves were obtained by carrying out the polymerization at 75-90°C with a system of 3 cm^3 of MMA, 5×10^{-4} g of $CuCl_2 \cdot 2H_2O$, and 10 cm^3 of H_2O in the presence or absence of 0.02 g of PNVIm. The results obtained are shown in Fig. 2. The rate of polymerization of MMA, R_p, was calculated by

$$R_p\ (\mathrm{g/h}) = \frac{\begin{bmatrix}\text{overall poly-MMA} \\ \text{obtained in the pres-} \\ \text{ence of PNVIm (g)}\end{bmatrix} - \begin{bmatrix}\text{poly-MMA obtained} \\ \text{in the absence of} \\ \text{PNVIm (g)}\end{bmatrix}}{\text{polymerization time (h)}} \qquad (2)$$

On applying the values of R_p to the Arrhenius equation, the overall activation energy was calculated to be 24.8 kJ/mol, as shown in Fig. 3. This value was smaller than the 28.7 kJ/mol found with Im [1].

Selectivity for Vinyl Monomer

The polymerization of three kinds of vinyl monomer was carried out in the presence of PNVIm, copper(II) chloride, and water. The results are given in Table 1. The conversion of St was due to thermal polymerization. The polymerization of AN takes place easily, even in the absence of PNVIm, indicating that charge-transfer polymerization occurs only with the Cu(II) ion [6]. It is clear that only MMA can be specifically polymerized by PNVIm. The selectivity of monomer in this polymerization system is the same as that in the system of Im, copper(II) chloride, and water [1].

Proof of Radical Mechanism

In order to confirm that the polymerization proceeded through a radical mechanism, the copolymerization of MMA (M_1) with St (M_2)

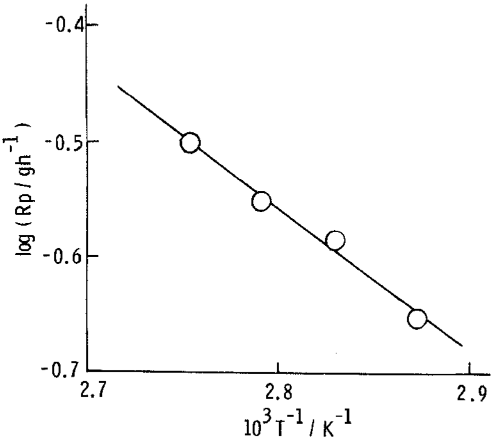


FIG. 3. Arrhenius plots.

TABLE 1. Polymerization of Vinyl Monomer[a]

PNVIm (g)	$CuCl_2 \cdot 2H_2O$ (g)	Conversion (%)		
		MMA	St	AN
0	0	0.4	1.5	0
0	5×10^{-4}	0.3	1.4	3.5
0.02	0	0.4	1.0	0
0.02	5×10^{-4}	23.3	1.8	0.4

[a] Monomer, 3 cm^3; H_2O, 10 cm^3; 85°C, 2 h, with shaking.

was carried out and the results shown in Fig. 4 were obtained. From the curve, r_1 and r_2 were calculated as 0.53 and 0.56, respectively.

Into a mixture of 3 cm^3 of MMA, 0.02 g of PNVIm, 5×10^{-3} g of $CuCl_2 \cdot 2H_2O$, and 10 cm^3 of H_2O, 0.1 g of 1,1-diphenyl-2-picrylhydrazyl(DPPH) or 1,3,5-triphenylverdazyl (TPV) was added. The polymerization was completely inhibited by DPPH or TPV. Thus the polymerization was verified to proceed through a radical mechanism.

Effect of Water on Polymerization

On keeping the amounts of MMA, PNVIm, and $CuCl_2 \cdot 2H_2O$ constant at 3 cm^3, 0.02 g, and 5×10^{-4} g, respectively, and varying the amount of water, the polymerization of MMA was carried out with shaking. The results obtained are shown in Fig. 5. It is concluded that the presence of water is necessary. MMA polymerized only thermally in the absence of water, and the initiating effect of PNVIm could not be observed.

Effect of the Amount of PNVIm on Polymerization

Keeping the fed amounts of MMA, $CuCl_2 \cdot 2H_2O$, and H_2O at 3 cm^3, 5×10^{-4} g, and 10 cm^3, respectively, and varying the amount of PNVIm, polymerization was carried out with shaking. The results obtained are shown in Fig. 6. A remarkable feature in this figure is the decrease in the conversion of MMA when the amount of dissolved PNVIm exceeds a certain limit. Such a phenomenon was also recognized in the polymerization of MMA in an aqueous starch solution [7, 8]. Such a decrease in conversion is considered to be due to the increased entanglement of PNVIm molecules, making the formation of adequate HA difficult. MMA is incorporated into HA, and polymerization commences there.

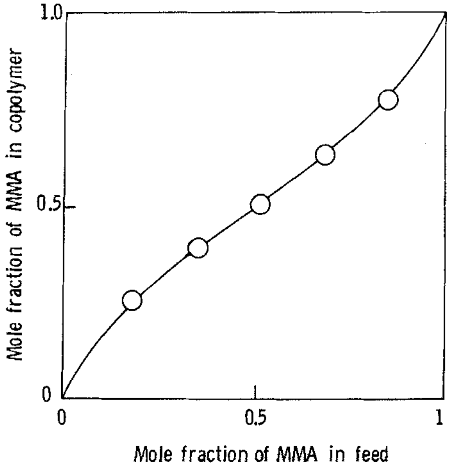


FIG. 4. Copolymerization of MMA (M_1) with St (M_2). Monomer, 3 cm^3; PNVIm, 0.02 g; $CuCl_2 \cdot 2H_2O$, 5×10^{-4} g; H_2O, 10 cm^3; 85°C; 2 h; with shaking.

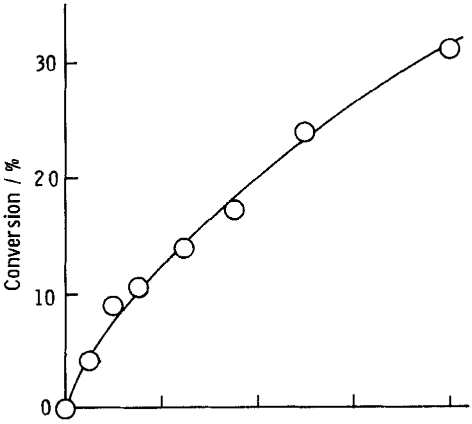


FIG. 5. Amount of water vs conversion of MMA. MMA, 3 cm^3; PNVIm, 0.02 g; $CuCl_2 \cdot 2H_2O$, 5×10^{-4} g; 85°C; 2 h; with shaking.

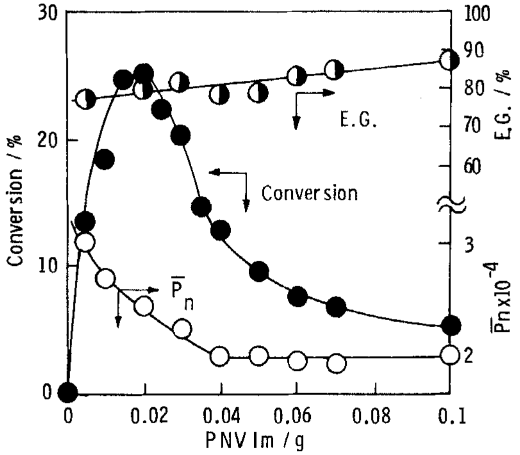


FIG. 6. Effects of amount of PNVIm on the conversion of MMA, E.G., and $\overline{P}_n$ of poly-MMA. MMA, 3 cm^3; $CuCl_2 \cdot 2H_2O$, 5×10^{-4} g; H_2O, 10 cm^3; 85°C; 2 h; with shaking.

Effect of the Amount of MMA on Polymerization

Keeping the amounts of PNVIm, $CuCl_2 \cdot 2H_2O$, and H_2O constant, and varying the amount of MMA, polymerization was carried out with shaking. The effects of the amount of MMA on the polymer yield, E.G., and $\overline{P}_n$ of poly-MMA are shown in Fig. 7. The polymer yield is independent of the amount of MMA beyond a certain period, before which the polymer yield increases with the amount of MMA. This result suggests that polymerization takes place in the water layer. In order to ascertain the phase in which polymerization took place, polymerization reactions were carried out on standing. After the polymerization, the clear layer of MMA was pipetted off and poured into methanol. The results are shown in Fig. 8. It is concluded that polymerization was initiated, propagated, and terminated in the water layer.

Observation of Hydrophobic Area

The formation of HA by PNVIm in the water layer was observed by scanning electron microscopy, using a method reported previously [9]. Figures 9(A) and 9(B) are views before and after polymerization, respectively.

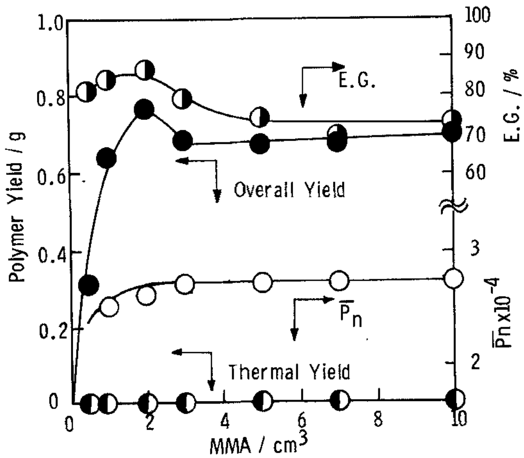


FIG. 7. Effects of amount of MMA on the polymer yield, E.G., and $\overline{P}_n$ of poly-MMA with shaking. $CuCl_2 \cdot 2H_2O$, 5×10^{-4} g; H_2O, 10 cm^3; 85°C; 2 h. (●, ◑, ○) PNVIm, 0.02 g; (◐) PNVIm, 0 g.

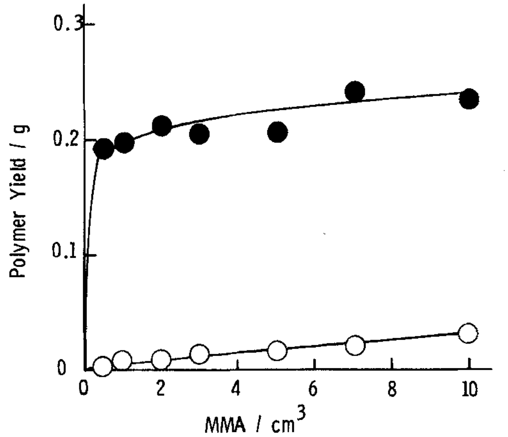
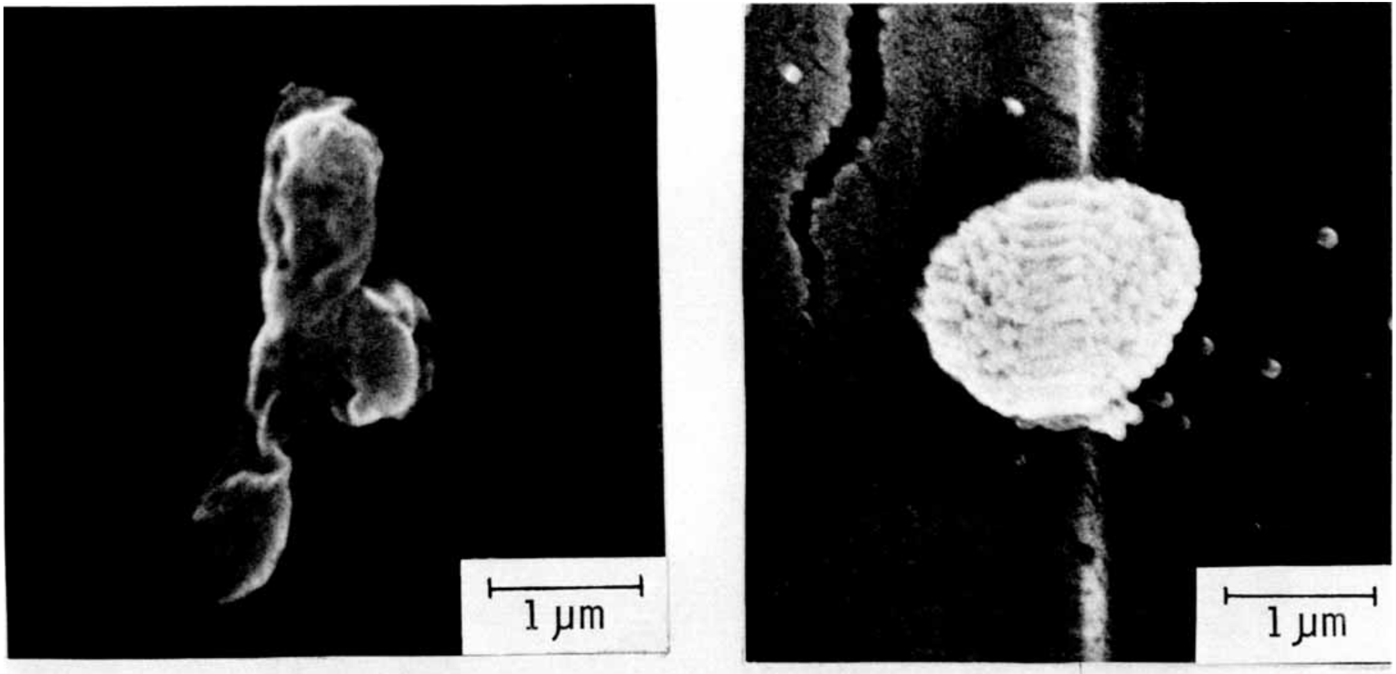


FIG. 8. Effects of the amount of MMA on the polymer yield on standing. PNVIm, 0.02 g; $CuCl_2 \cdot 2H_2O$, 5×10^{-4} g; H_2O, 10 cm^3; 85°C; 2 h. (●) Water layer; (○) monomer layer.



(A)

(B)

FIG. 9. Surface views of PNVIm. PNVIm, 0.02 g; MMA, 3 cm^3; $CuCl_2 \cdot 2H_2O$, 5×10^{-4} g; H_2O, 10 cm^3; 85°C; 1.5 h; on standing. (A) Before polymerization; (B) after polymerization.

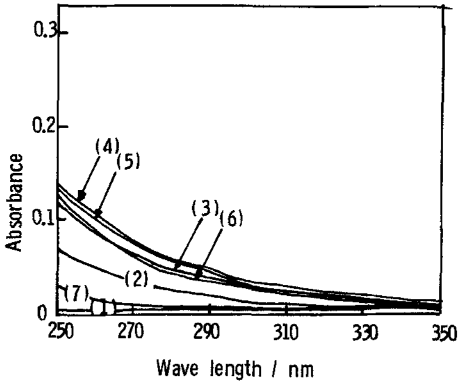


FIG. 10. Electronic spectra of system of CuCl$_2$/PNVIm in water at room temperature. [CuCl$_2$] = [PNVIm] = 1.1×10^{-2} mol/dm^3 of F.U. Mole ratios of CuCl$_2$:PNVIm = (1) 1:0, (2) 1:1, (3) 1:2, (4) 1:4, (5) 1:5, (6) 1:6.5, (7) 0:1.

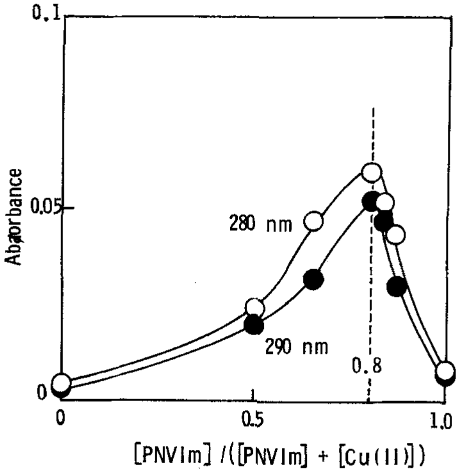


FIG. 11. Application of the results obtained in Fig. 10 to the continuous variation method.

TABLE 2. Results of Visible Spectra[a]

$CuCl_2 \times 10^3$ (mol/dm^3)	PNVIm $\times 10^3$ (mol/dm^3 of F.U.)	MMA[b]	λ_{max} (nm)
13.00	0	0	821
4.33	8.67	0	715
4.33	8.67	1 drop	705
2.60	10.40	0	645
2.60	10.40	1 drop	640

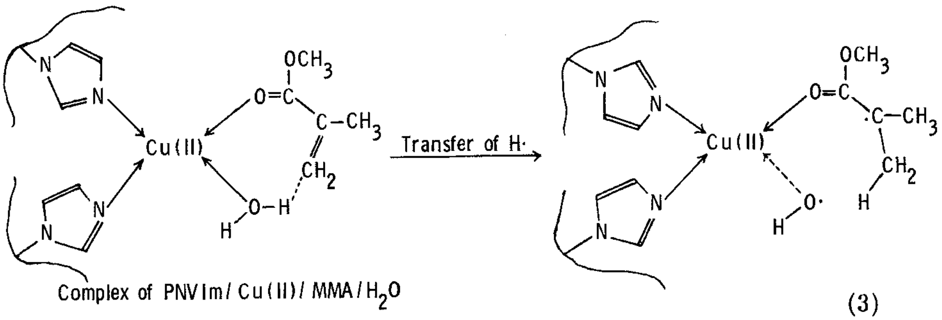
[a] Measured in water at room temperature.
[b] MMA saturated in water.

Formation of the complex of Cu(II) ion with PNVIm in water and MMA was proved by the electronic spectra. Figure 10 shows the UV spectra of the system PNVIm and $CuCl_2$ measured in aqueous solution. Solutions of PNVIm and $CuCl_2$, both at a concentration of 1.1×10^{-2} mol/dm^3 of F.U., 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 the UV region.

By using the continuous variation method, the results shown in Fig. 11 were obtained. The maximum corresponds to a mole ratio of 1:4 of Cu(II):PNVIm; it suggests that Im associated with water forms a complex with the Cu(II) ion.

On the other hand, the maximum absorption of Cu(II) ion in the visible spectra was measured (Table 2). The following conclusions can be obtained from this table. (1) The blue shift of λ_{max} from 821 nm is due to the formation of the complex of the Cu(II) ion with PNVIm and water, and (2) the blue shift observed on addition of MMA suggests that formation of a complex of Cu(II) ion, H_2O, and Im and MMA groups occurs.

Therefore, the complex can be written as in Eq. (3), as reported for the system Im, Cu(II) ion, MMA, and H_2O [1]. The initiating free radicals are assumed to be generated by hydrogen transfer from water to MMA:



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