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Vinyl Polymerization. 368.[1] Polymerization of Methyl Methacrylate with the System of RNA, Water and Cu(II) Ion

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The radical polymerization of methyl methacrylate (MMA) was carried out with the system of ribonucleic acid (RNA), Cu(II) ion and water. The generation of free radical was found to take place in the water layer where RNA and Cu(II) ion exist. Urea shows a promoting activity. The effects of pH of water medium and temperature on the conversion of MMA were investigated. A reaction mechanism was proposed.

The so-called uncatalyzed polymerization is a novel reaction, in which macromolecule (or oligomer) in water phase incorporates vinyl monomer from monomer phase, forms a complex with water, monomer and Cu(II) ion, and generates free radicals. The radical polymerization proceeds in the water phase, *i.e.*, predominantly in the hydrophobic area formed by macromolecules. The present paper deals with radical polymerization of methyl methacrylate (MMA) initiated with a system of aqueous copper(II) chloride solution and RNA which was used as macromolecule. Sugiyama and Lee independently reported the polymerization of MMA with the system of RNA, water and Cu(II) ion in the presence or absence of carbon tetrachloride.[2] They investigated in detail only the case in which carbon tetrachloride is present. The present paper is concerned with the case in which it is absent and might be of value for reference.

Experimental

Materials. Commercial RNA from yeast (Sigma Chemical Co. 6750, Lot. 124C-8150) was used. Water was ion-exchanged and redistilled. Copper(II) chloride of special commercial grade was used without further purification. MMA, styrene, and acrylonitrile were purified by the usual method and redistilled before use.

Preparation of Buffer Solutions. These were prepared by use of following systems: pH 3.0—6.0: M/10 citric acid-M/5 Na_2HPO_4; pH 7: M/15 Na_2HPO_4-M/15 KH_2PO_4; pH 8—9: M/10 HCl-M/20 $Na_2B_4O_7$; pH 10: M/20 $Na_2B_4O_7$-M/10 NaOH; pH 11—12 M/10 NaOH-M/10 Na_2HPO_4.

Procedure. Monomer, the aqueous solution of RNA and $CuCl_2 \cdot 2H_2O$ were placed in an ampoule. The ampoule was flushed with nitrogen, frozen, evacuated at 0.1 mmHg, and sealed. The ampoule was shaken in a thermostat. After the reaction, the contents of the ampoule were poured into a large amount of methanol in order to precipitate the polymer. The polymer was collected on a glass filter, thoroughly washed with methanol and water and dried. The number-average degree of polymerization (P_n) of poly-MMA was estimated by gel permeation chromagraphy, using tetrahydrofuran as an eluent.

Results and Discussion

Selectivity of Vinyl Monomer. Polymerization of vinyl monomers was carried out in the presence of RNA, water and Cu(II) ion. The results are given in Table 1. The polymerization of acrylonitrile took place easily in the absence of RNA, by the charge transfer polymerization with Cu(II) ion.[3] The conversion of styrene was due to thermal polymerization. It is evident that only MMA was polymerized by RNA.

Table 1. Selectivity of vinyl monomer
(Monomer 3 cm³, H_2O 10 cm³, $CuCl_2 \cdot 2H_2O$ 5×10^{-4} g; 85 °C, 5 h)

RNA/g	Conversion/%		
	MMA	AN	St
0	1.2	8.7	4.2
0.02	6.2	1.3	3.8

Table 2. Activity of metallic salts
(Metallic salts 2.9×10^{-6} mol. MMA 3 cm³, H_2O 10 cm³; 85 °C, 5 h)

RNA/g	Conversion/%				
	$MgCl_2 \cdot 6H_2O$	$FeCl_3 \cdot 6H_2O$	$FeCl_2 \cdot (4H_2O)$	$MnCl_2 \cdot 4H_2O$	$CuCl_2 \cdot 2H_2O$
0.02	1.7	2.6	2.5	2.6	6.2
0	1.2	1.7	1.8	1.8	1.2

Effect of Metallic Ion on Polymerization. In order to investigate the effect of metallic ion on polymerization, five kinds of metallic chlorides were added to the reaction system. The results are given in Table 2. Copper(II) chloride was the most active promotor for polymerization, and was thus used in subsequent polymerizations.

Figure 1 shows the effect of the amount of Cu(II) ion on the conversion of MMA. A maximum conver-

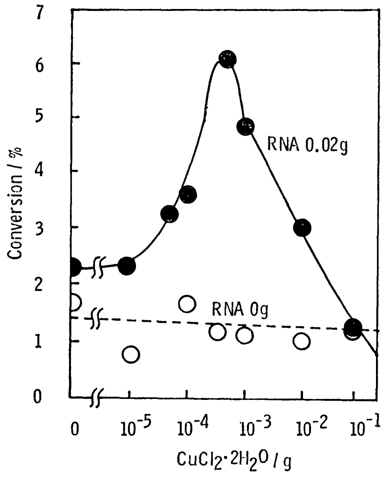


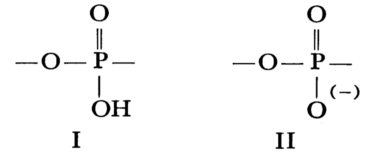
Fig. 1. Conversion of MMA *vs.* amount of Cu(II) ion. MMA 3 cm³, H_2O 10 cm³; 85 °C, 5 h.

sion of MMA was obtained at 5×10^{-4} g of copper(II) chloride. On the other hand, in the absence of Cu(II) ion, the polymerizations was hardly accelerated at all. The open circles indicate the conversion of MMA by thermal polymerization (1.2% in average). Cu(II) ion was found to be very effective.

Proof of Radical Mechanism. In order to confirm the view that polymerization proceeds through a radical mechanism, the copolymerization of MMA with styrene was carried out. The results are shown in Fig. 2. A radical mechanism was verified from the curve.

Locale of the Reaction. In order to find the locale of the generation of the initiating radical, polymerization of MMA was carried out without shaking. The ampoule containing 3 cm^3 of MMA, 0.02 g of RNA, 5×10^{-4} g of $CuCl_2\cdot2H_2O$ and 10 cm^3 of water was allowed to stand at 85 °C. The contents consist of two layers (Fig. 3(a)). As the polymerization proceeded, the water layer became turbid by the polymerized MMA (Fig. 3(b)). After 7 h, the MMA-layer was pipetted out and poured into methanol (conversion: 1.4%, $\overline{P}_n$ of poly-MMA: 1.3×10^4). The water layer was also poured into methanol (conversion: 9.8%, $\overline{P}_n$ of poly-MMA: 1.4×10^{-4}). From the results, it was concluded that the polymerization initiated with RNA takes place in the water layer. The conversion of 1.4% in MMA phase was the result of thermal polymerization.

Effects of the pH of Water Layer on the Conversion of MMA. The results obtained are shown in Fig. 4. The conversion of MMA shows a maximum at pH 8, it being assumed that in the acidic medium, the phosphonate group has the undissociated form I. The decrease in the conversion in acidic medium can be explained by the loss of ionized form II. In the basic medium, the conversion decreased. It seems that NH_2 or NH group of nucleic acid bases becomes free from protonated structure and can easily form a complex with copper(II) ion. Thus when too much NH_2 or NH group exists, the effective activity of Cu(II) ion is lost and the conversion decreases. Such a retarding effect of free NH_2 group was discussed in the polymerization of MMA initiated with Nylon-3[4].



$$\underset{\text{I}}{-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-} \qquad \underset{\text{II}}{-O-\overset{\overset{O}{\|}}{\underset{\underset{O^{(-)}}{|}}{P}}-}$$

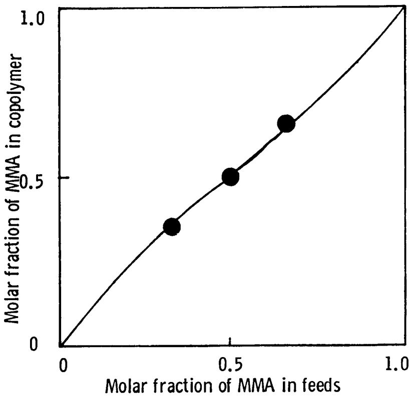


Fig. 2. Copolymerization of MMA and styrene. RNA 0.02 g, $CuCl_2\cdot2H_2O$ 5×10^{-4} g, H_2O 10 cm^3; 85 °C, 5 h.

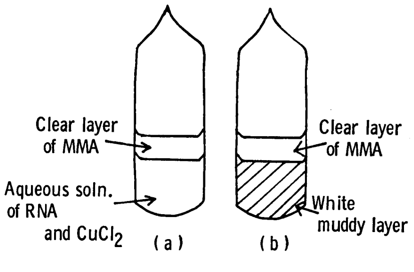


Fig. 3. Appearance of the ampoule on standing polymerization.

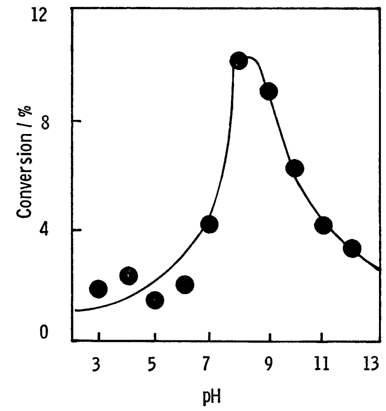


Fig. 4. Conversion of MMA *vs.* pH of aqueous phase. RNA 0.02 g, MMA 3 cm^3, $CuCl_2\cdot2H_2O$ 5×10^{-4} g, H_2O 10 cm^3; 85 °C, 5 h.

Effect of Urea on Conversion of MMA. Recently, it was found by Imoto *et al.* that urea can promote the conversion of MMA remarkably in radical polymerization initiated by the system of Cu(II) ion, water and Nylon-3[5] or α-amylase.[6] Urea is known as a denaturing agent of proteins. The tertiary structure of a protein molecule can be unfolded to form new hydrogen bonds between urea and peptide chain. Urea reveals its activity as shown in Table 3, even though the promoting effect is not so large.

TABLE 3. EFFECT OF UREA ON THE POLYMERIZATION (RNA 0.02 g, MMA 3 cm^3, $CuCl_2\cdot2H_2O$ 5×10^{-4} g, H_2O 10 cm^3; 85 °C, 5 h)

Urea/g	Conversion/g	$\overline{P}_n$ of Poly-MMA
0	6.2	—
0.05	10.5	3.5×10^4
0.10	11.2	3.4×10^4

Effect of Temperature on the Conversion of MMA. The results are shown in Fig. 5.

Mechanism of Initiation. Polymerization is considered to start by the incorporation of MMA into a

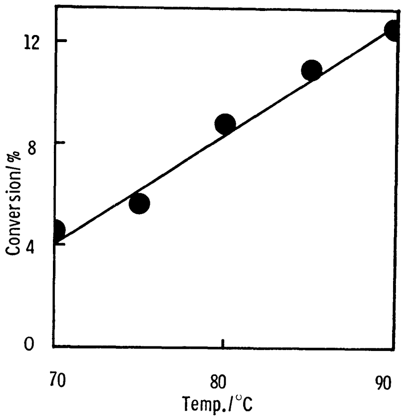


Fig. 5. Conversion of MMA *vs.* polymerization temperature. RNA 0.02 g, MMA 3 cm^3, $CuCl_2 \cdot 2H_2O$ 5×10^{-4} g, pH 8, Buffer solution 10 cm^3; 85 °C, 5 h.

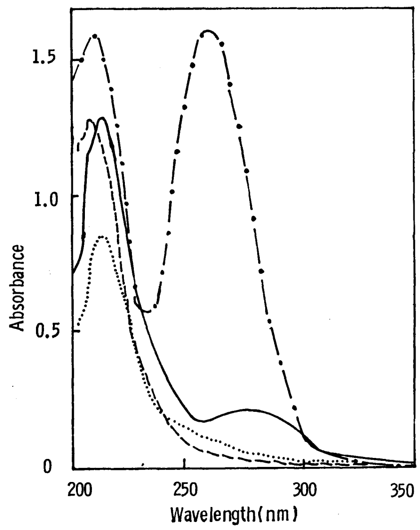


Fig. 6. UV-spectra measured in aqueous solution at 4.7—5.7 of pH.

	Reference	Sample
----	——	$CuCl_2 \cdot 2H_2O$
–·–·	——	RNA
——	RNA	$CuCl_2 \cdot 2H_2O$+RNA
······	RNA+$CuCl_2 \cdot 2H_2O$	RNA+$CuCl_2 \cdot 2H_2O$ +MMA

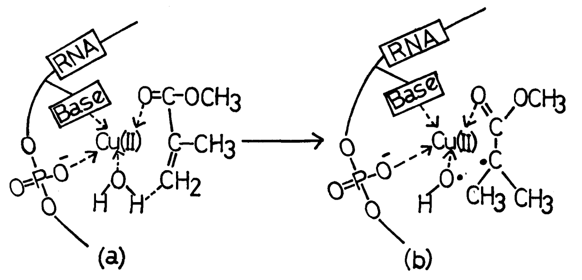


Fig. 7. Assumed initiation mechanism.

hydrophobic area formed by RNA molecules. RNA then forms a complex with Cu(II) ion, MMA and water. This is verified partially by the spectral study (Fig. 6). $CuCl_2$ solution in water showed a peak at 208 nm which corresponds to the complex $[Cu(II)(OH^-)_x(H_2O)_{4-x}]$. The λ_{max} of water (vapor) is 167 nm$^{7)}$. By complexing with Cu(II) ion, this absorption maximum is consisdered to shift to 208 nm, *i.e.*, the λ_{max} of 208 nm corresponds to $Cu(II)(OH^-)_x(H_2O)_{4-x}$. The value of x may be small in the present measurement. RNA solution in water showed a peak at 260 nm which is due to RNA. The peak shifted to 275 nm in the RNA–$CuCl_2$–H_2O solution. This is considered to be an evidence of complex formation of Cu(II) ion with RNA. However, further addition of MMA to the solution of RNA and $CuCl_2$ showed no peak of complexed MMA in this region of wavelength. The ionized phosphonate group was assumed to be necessary, too much free NH_2 or NH group retarding the polymerization. The complex is indicated in Fig. 7(a). As regards the generation of the free radical, we have repeatedly proposed the hydrogen atom transfer from water molecule to MMA as shown in Fig. 7(b).

References

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