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Polymerization of Methyl Methacrylate by the System Ribonucleic Acid—Water in the Presence of Carbon Tetrachloride and Copper(II) Ion

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ABSTRACT

Polymerization of methyl methacrylate (MMA) was carried out in the presence of ribonucleic acid (RNA), water, carbon tetrachloride, and copper(II) ion. The overall activation energy for the polymerization is proportional to the square root of the amount of RNA. The rate increased at first with the amount of MMA, but then became independent of the amount of MMA.

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Polymerization was inhibited by the presence of air. Carbon tetrachloride and copper(II) ion are able to give RNA the ability to initiate polymerization. Conversion of MMA is accelerated by the addition of tertiary amine derivatives instead of carbon tetrachloride.

INTRODUCTION

Imoto et al. have shown that some natural and synthetic macromolecules or oligomers, such as starch, cellulose, silk, nylon 6 etc., can initiate polymerization of vinyl monomer, particularly of methyl methacrylate (MMA), in the presence of water but without so-called radical initiator through a free-radical mechanism [1]. At the same time, it has been also pointed out that the conversion of MMA increased abruptly on addition of a small quantity of carbon tetrachloride. Yamamoto et al. reported that the system of collagen fiber and water is especially effective for initiation of polymerization of MMA [2, 3]. It has been also shown that several poly(α -amino acids) initiate the polymerization of MMA in the presence of water and copper(II) ion [4, 5]. We have been particularly interested in studying such polymerization. From a brief study, we found that the polymerization of MMA was initiated by the system of ribonucleic acid (RNA) and water without any ordinary initiator [6]. The present paper is mainly concerned with a kinetic investigation of polymerization initiated by the system, RNA-water-carbon tetrachloride-copper(II) ion. In addition the contribution of a trace amount of tertiary amines and 2-tetrazenes to the polymerization was studied.

EXPERIMENTAL

Reagents

RNA was yeast nucleic acid obtained from PL biochemicals, Inc. and was used without further purification. Water was purified by the ion-exchange resin. Carbon tetrachloride was washed with 5% aqueous sodium hydroxide solution, then thoroughly with water, dried on potassium carbonate, and then distilled under nitrogen in the dark through a condenser filled with active alumina. Copper(II) chloride was a special grade reagent from Wako Pure Chemical Industries, Ltd. MMA was carefully purified by the standard method

and distilled under reduced pressure in an atmosphere of nitrogen before use. Tetramethyl-2-tetrazene (TMT), tetraethyl-2-tetrazene (TET), tetrapropyl-2-tetrazene (TPT), and tetrabutyl-2-tetrazene (TBT) were prepared by oxidation of the corresponding unsym-dialkylhydrazine with mercuric oxide, as described in a previous paper [7]. Trimethylamine (TMA), triethylamine (TEA), tripropylamine (TPA), and tributylamine (TBA) were obtained commercially and purified by standard methods.

Polymerization

The polymerization were carried out in sealed tubes. RNA, water copper(II) chloride, carbon tetrachloride, and MMA were charged in a tube in the above order, cooled in a Dry Ice-methanol bath. In all runs, the tube containing the reactants was flushed three times with oxygen-free nitrogen and sealed in vacuo. The sealed tube was shaken in the dark in a thermostat. The contents were poured into an excess of methanol to precipitate the polymer. Homopolymer of MMA was isolated by Soxhlet extraction with benzene for 30 hr. Its number-average degree of polymerization (P_n) was estimated from the intrinsic viscosity $[\eta]$ of its benzene solution determined at 30°C, by using Welch's equation:

$$\log P_n = 3.346 + 1.32 \log [\eta] \text{ (dl/g)}$$

RESULTS AND DISCUSSION

Activation Energy

In a previous communication [6], it was reported that the polymerization of MMA could be initiated in the presence of RNA, water, carbon tetrachloride, and copper(II) ion. In order to ascertain the catalytic activity of the above initiator system, heterogeneous polymerization of MMA was carried out in the absence of ordinary initiator. The polymerization was followed over the temperature range from 70 to 90°C, as shown in Fig. 1. From the slope of the lines in Fig. 1, an overall activation energy was estimated as 43.5 kJ/mole (Fig. 2). This value is close to that for the polymerization of MMA with the cupra-rayon-water-carbon tetrachloride [8] or 6-nylon-water systems [1].

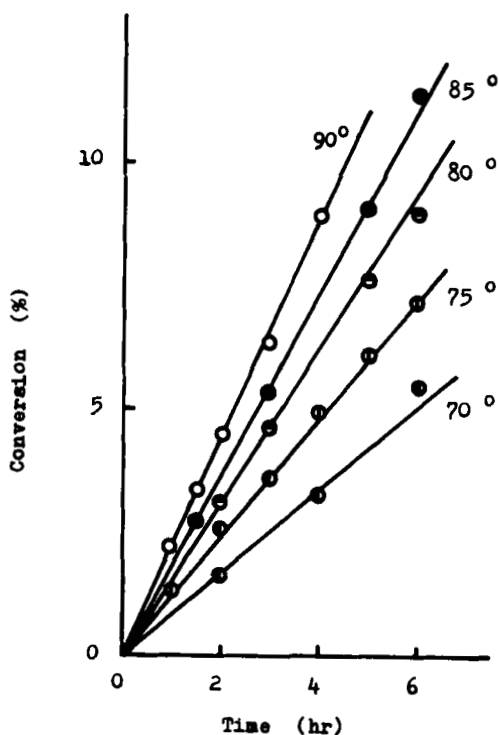


FIG. 1. Time-conversion curves for the polymerization of MMA initiated by the system RNA-H₂O-CCl₄-CuCl₂ at various temperatures. MMA, 2.82 g; RNA, 0.1 g; H₂O, 1 ml; CCl₄, 0.5 ml; CuCl₂, 5×10^{-7} g.

Effects of the Amounts of Reagents on Conversion

The dependence of the rate of polymerization R_p on the amounts of RNA and MMA was examined. The polymerization was carried out with varying amounts of MMA and at constant amounts of other components. The polymerization was also carried out with varying the amount of RNA. The rates of polymerization of MMA were calculated from the slope of the time-conversion curves, which were linear up to 5 hr. The conversions were within 15% in all experiments.

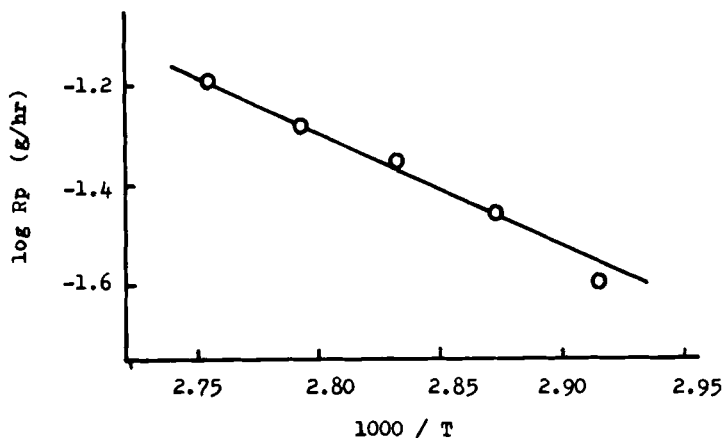


FIG. 2. Arrhenius plot for the polymerization of MMA.

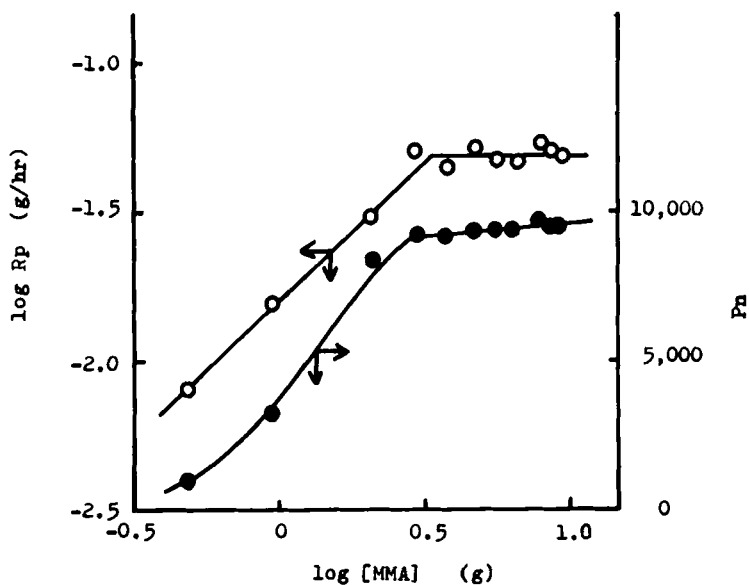


FIG. 3. Effect of the amount of MMA on the polymerization of MMA initiated by the system RNA-H₂O-CCl₄-CuCl₂ at 85°C on (○) reaction rate and (●) molecular weight of the product. RNA, 0.1 g; H₂O, 1 ml; CCl₄, 0.5 ml, CuCl₂, 5×10^{-7} g.

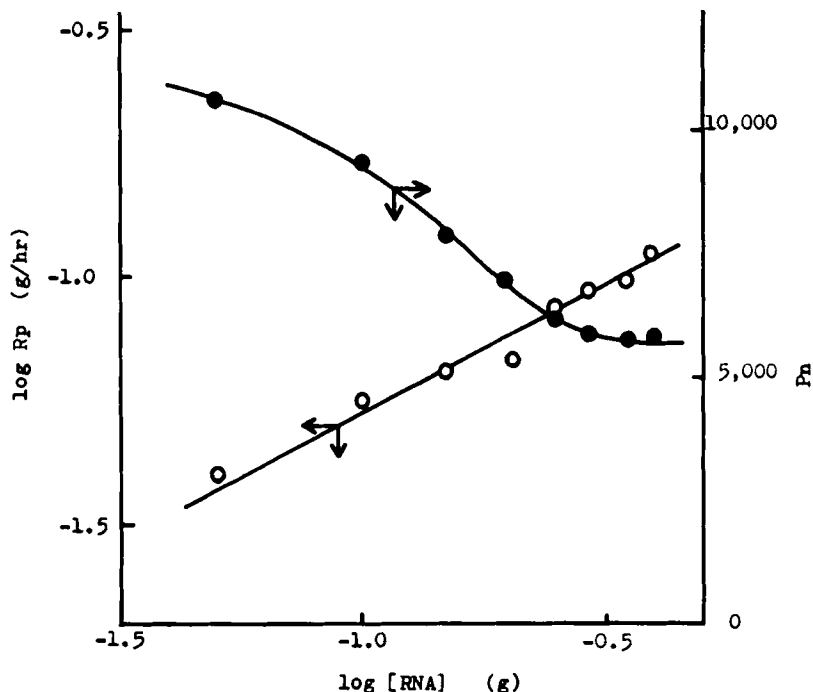


FIG. 4. Effect of the amount of RNA on the polymerization of MMA initiated by the system RNA-H₂O-CCl₄-CuCl₂ at 85°C on (○) reaction rate and (●) molecular weight of the product. MMA, 2.82 g; H₂O, 1 ml; CCl₄, 0.5 ml; CuCl₂, 5×10^{-7} g.

The results are shown in Figs. 3 and 4. Figure 3 shows that the amount of MMA is linearly proportional to R_p at the amount of MMA below about 3.76 gr, but larger amounts the rate become of zero order with respect to MMA. This phenomenon is similar to that obtained for the polymerization of MMA with macromolecule-water systems [1]. On the other hand, the rate is found, from Fig. 4, to be proportional to the square root of the amount of RNA. This fact suggests that RNA acts as radical initiator, when used in conjunction with water, carbon tetrachloride, and copper(II) ion.

From the previous experimental results [6], the amounts of water, carbon tetrachloride, and copper(II) ion are expected to affect the conversion of MMA. The effects of the amounts of additives on the conversion were then examined.

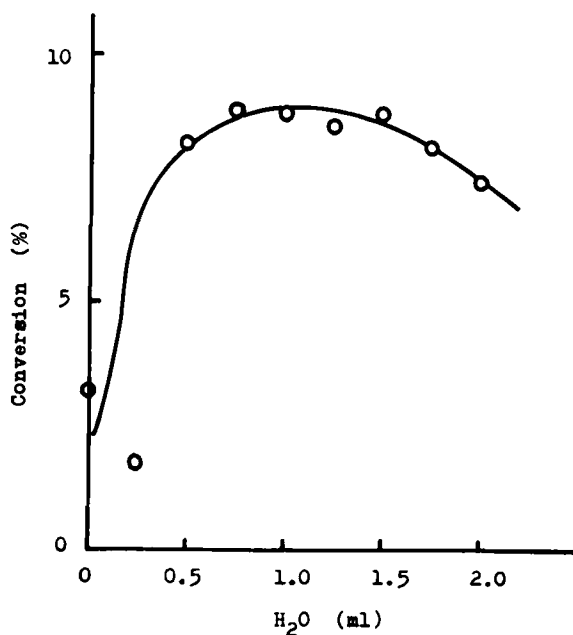


FIG. 5. Effect of the amount of water on the polymerization of MMA initiated by the system RNA-H₂O-CCl₄-CuCl₂ at 85° C for 5 hr. MMA, 2.82 g; RNA, 0.1 g; CCl₄, 0.5 ml; CuCl₂, 5×10^{-7} g.

It was found that in our system, an amount of water above 0.5 ml is necessary for the polymerization (Fig. 5). When carbon tetrachloride was absent, the conversion was near zero, while the conversion increased to 8.7%, in the presence of 0.5 ml carbon tetrachloride, (Fig. 6). Carbon tetrachloride is, thus, able to give RNA ability to initiate the system. Figure 7 shows that the polymerization of MMA initiated by the system RNA-water-carbon tetrachloride required a trace amount of copper(II) ions. This fact may be explained by the consideration that cupric ions should be absorbed onto RNA or growing polymer and to form a complex having some vacant coordination sites. The formation of a complex of poly(methyl methacrylate) with cupric ions has been described in

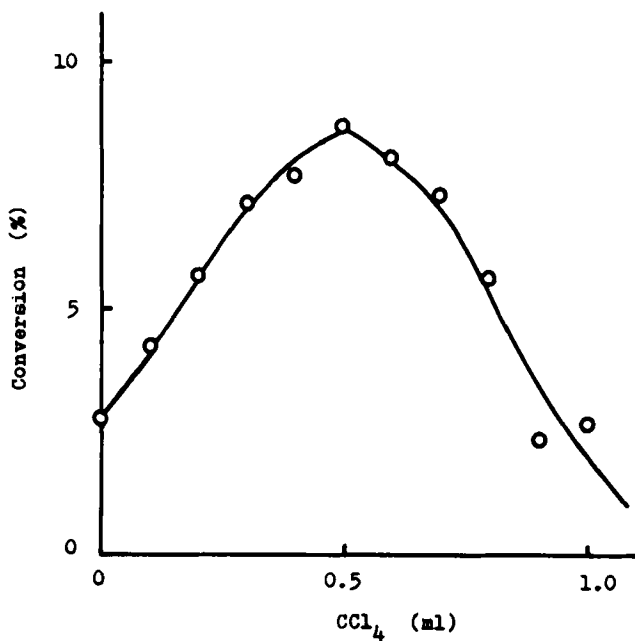
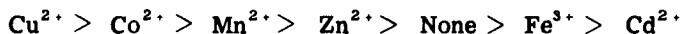


FIG. 6. Effect of the amount of carbon tetrachloride on the polymerization of MMA initiated by the system RNA-H₂O-CCl₄-CuCl₂ at 85° C for 5 hr. MMA, 2.82 g; RNA, 0.1 g; H₂O, 1 ml; CuCl₂, 5 × 10⁻⁷ g.

the literature [9]. In order to clarify this point, polymerization of MMA initiated by the RNA-water-carbon tetrachloride system was carried out in the presence of various metal cations. It is seen from Fig. 8 that the activity for the promotion of the polymerization decreases in the order:



This is roughly consistent with the order reported by Irving and Williams [10] for chelating ability.

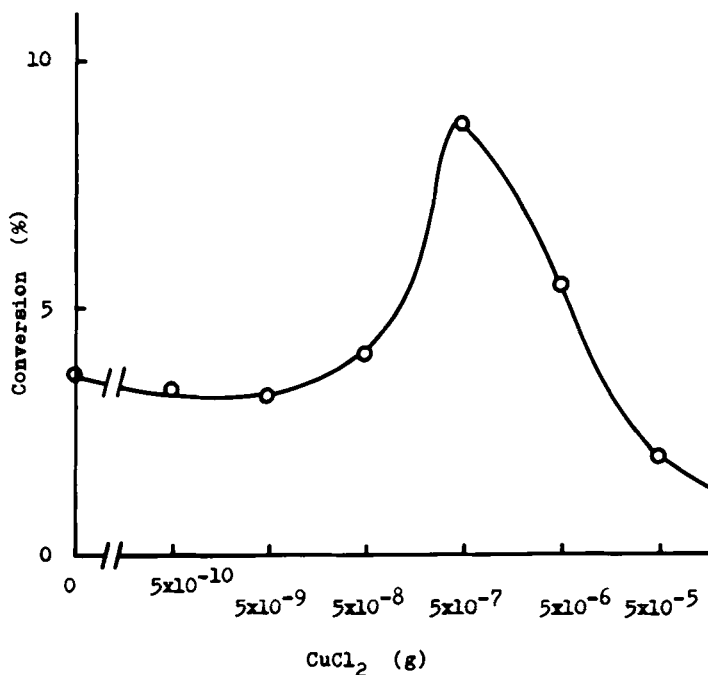


FIG. 7. Effect of the amount of copper(II) ion on the polymerization of MMA initiated by the system RNA-H₂O-CCl₄-CuCl₂ at 85 C for 5 hr. MMA, 2.82 g; RNA, 0.1 g; H₂O, 1 ml; CCl₄ 0.5 ml.

Proof of the Radical Mechanism

Polymerization in air for 5 hr gave only 0.5% conversion, because atmospheric oxygen inhibit the polymerization of MMA. Hydroquinone depressed the polymerization completely. This confirmed in two ways that the polymerization proceeds through a radical mechanism.

Effect of pH

As RNA is one component of protein, it is important to examine the effect of pH on the polymerization of MMA. The polymerization

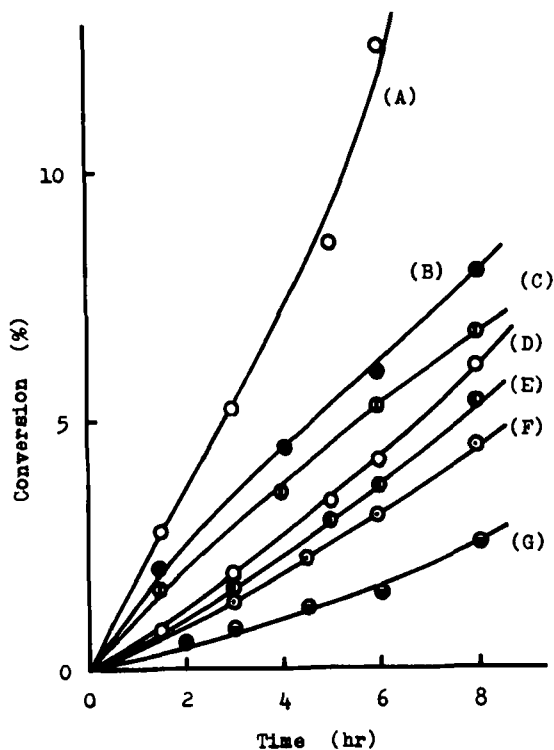


FIG. 8. Effect of metal ion on the polymerization of MMA initiated by the system RNA-H₂O-CCl₄ at 85° C: (A) Cu(II); (B) Co(II); (C) Mn(II); (D) Zn(II); (E) none, (F) Fe(III); (G) Cd(II). MMA, 2.82 g; RNA, 0.1 g; H₂O, 1 ml; CCl₄, 0.5 ml; metal chloride, 5×10^{-7} g.

was carried out in aqueous solution at varying pH at 85° C for 5 hr. Maximal conversion was obtained in the pH range of 10 to 12, as shown in Fig. 9.

Effect of Amine Derivatives

It has been described in the literature [11, 12] that the system of RNA and tertiary amines, especially TMT, could initiate the polymerization of vinyl monomers. The polymerization behavior is quite

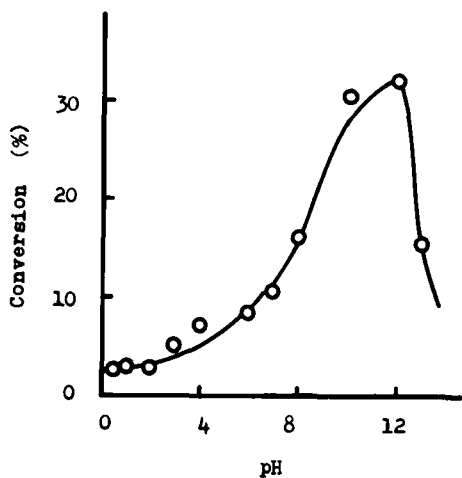


FIG. 9. Effect of pH on the polymerization of MMA initiated by the system $\text{RNA-H}_2\text{O-CCl}_4\text{-CuCl}_2$ at 85°C for 5 hr. MMA, 2.82 g; RNA, 0.1 g; H_2O , 1 ml; CCl_4 , 0.5 ml; CuCl_2 , 5×10^{-7} g.

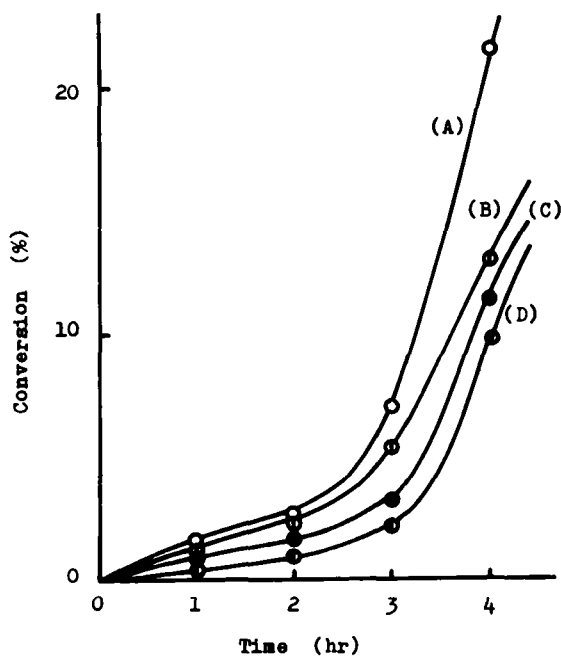


FIG. 10. Effect of tertiary amines on the polymerization of MMA initiated by the system $\text{RNA-H}_2\text{O-CuCl}_2$ at 85°C : (A) TMA; (B) TEA; (C) TPA; (D) TBA. MMA, 2.82 g; RNA, 0.1 g; H_2O , 1 ml; CuCl_2 , 5×10^{-7} g; amine, 5×10^{-5} mole.

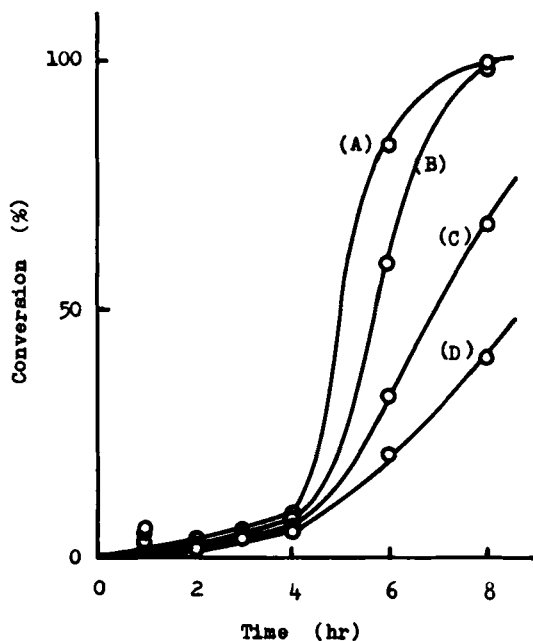


FIG. 11. Effect of 2-tetrazene on the polymerization of MMA initiated by the system RNA-H₂O-CuCl₂ at 85°C: (A) TMT; (B) TET; (C) TPT; (D) TBT. MMA, 2.82 g; RNA, 0.1 g; H₂O, 1 ml; CuCl₂, 5×10^{-7} g; 2-tetrazene, 5×10^{-5} mole.

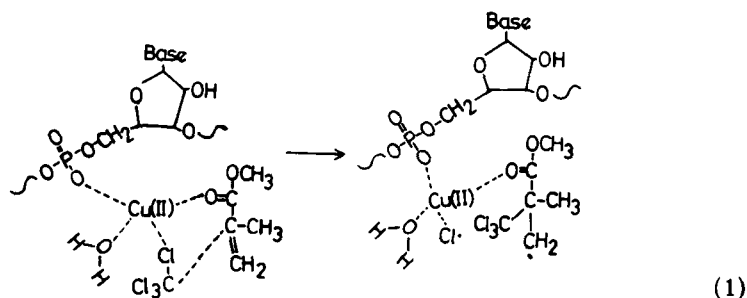
different on addition of tertiary amine derivatives instead of carbon tetrachloride for the polymerization of MMA with the system of RNA and water. Figure 10 shows that the polymerization of MMA is accelerated by the addition of a slight amount of various tertiary amines, particularly TMA. On the other hand, tetrazenes, such as TMT, TET, TPT, and TBT displayed an amazing activity for the promotion of the polymerization after an induction period (about 4 hr). The conversion increased to 100% with a very small amount of TMT and TET. The tendency for polymerization to occur decreased with the number of carbon atoms in the alkyl groups. The activity of tetrazene for the promotion of the polymerization was closely related to the effect of tetraalkyl substituents (CH₃, C₂H₅, C₃H₇, and C₄H₉) of tetrazene on its thermal decomposition [13].

The above results indicate that the presence of tertiary amine derivatives might be important for the polymerization of MMA with

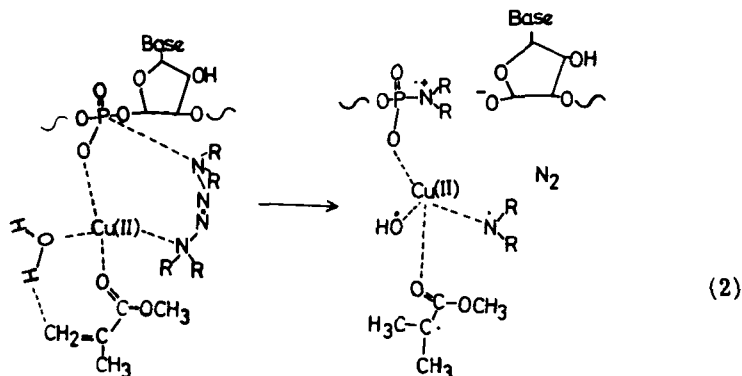
the RNA-water-copper(II) ion. It may be suggested that tertiary amines play a role in structural transformation of RNA. It has been reported [12] that the intrinsic viscosity $[\eta]$ of RNA measured in phosphate buffer solution decreased from 0.094 to 0.074 on the addition of TMT.

Mechanism of the Polymerization

As mentioned above, carbon tetrachloride and copper(II) ion were found to play an important role. A mechanism of the polymerization similar to that operating in the case of cellulose [14, 15], is proposed and is summarized in Eq. (1).



In the case of addition of 2-tetrazene instead of carbon tetrachloride, it is necessary to consider the reaction of phosphate groups of RNA with the dialkylamino nitrogen of 2-tetrazene. The reaction is believed to proceed by a nucleophilic attack of dialkylamino nitrogen on a phosphorus atom which tends to become more positive, analogous to the reaction of TMT with some electrophilic reagents, such as acetic anhydride [16], dimethyl maleate [17], and pyruvic acid [18]. The mechanism proposed is shown in Eq. (2), where R may be CH_3 ,



C_2H_5 , or C_3H_7 . In this case, $H\cdot$, $R_2N\cdot$, and $HO\cdot$ are considered initiating species.

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