CHEMISTRY LETTERS, pp. 1119-1122, 1975. Published by the Chemical Society of Japan

VINYL POLYMERIZATION. 338. GENERATION OF FREE RADICAL BY THE REACTIONS OF α-AMYLASE OR SYNTHETIC POLY-α-AMINO ACID WITH COPPER(II) ION IN THE PRESENCE OF METHYL METHACRYLATE

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The polymerization of methyl methacrylate initiated with the system of α-amylase or poly-α-amino acid in the presence or absence of copper(II) ion was carried out at 85°C. It was found that the coexistence of water was indispensable. Even in the absence of copper(II) ion, the polymerization occurred to some extent. However, metallic ion was concluded to give a preferable effect.

As one of the problems of pollution, the uptake of metal in biological systems attracts much attention. Metal may react with various substances, particularly with protein, to generate some uncommon active species. Accordingly, studies on catalytic reaction of the complex of metal and protein with a third compound have an interesting meaning.

The present letter concerns with the generation of free radical by the reaction of α-amylase or synthetic poly-α-amino acid with copper(II) ion in the presence of methyl methacrylate(MMA). It was determinantly concluded that the radical polymerization of MMA took place. Recently, toxic properties of some vinyl monomers are brought up to discussion. The results obtained here may make a suggestion on this important problem.

Experimental and Discussions

Materials: α-Amylase was of commercial, prepared by Sigma Chemical Company. Its grade was "Bacterial crude type III-A" (Lot. 93C-1970) and had 67 units / mg (one unit can hydrolyze 1.0 mg of maltose from starch in 3 min. at pH 6.9 at 20°C). All poly-α-amino acids were afforded by Prof. Noguchi.

Procedures: Reagents and MMA were placed in a tube. The tube was flushed with nitrogen, frozen, evacuated at 0.1 mmHg, and sealed. Poly-α-amino acids did not dissolve both in water and in vinyl monomer. α-Amylase dissolved only in water. The tube was shaken in a thermostat. After reaction, the content of the tube was poured into a large amount of methanol to precipitate the polymer. The polymer obtained were collected on a glass filter, washed with methanol and dried. Homopolymer of MMA was isolated by extracting with benzene for 50 hr, using Soxhlet apparatus. Efficiency of grafting(E.G.) was calculated by the following eq.;

$$\text{E.G.} = \frac{\text{(Total Polymer)} - \text{(Extracted Polymer)}}{\text{(Total Polymer)}} \times 100$$

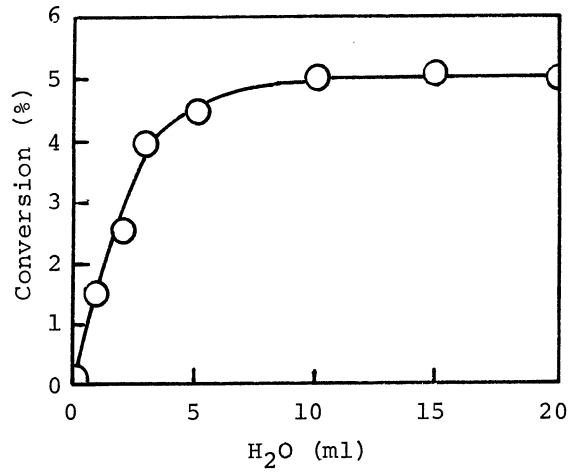


Fig.1. Conversion of MMA vs. amount of water.
MMA 3 ml, α-amylase 0.1 g, $CuCl_2 \cdot 2H_2O$ 0.01 g; 85°C, 3 hr

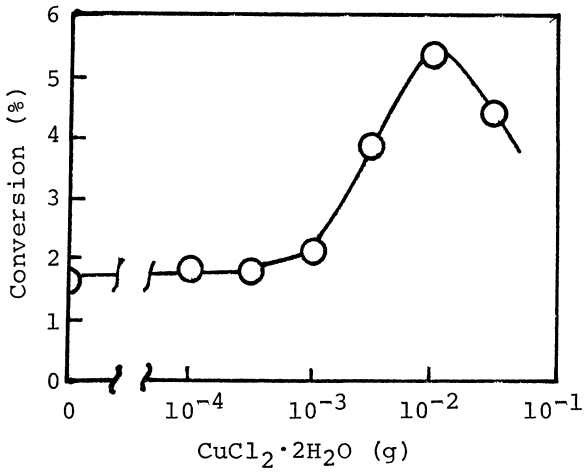


Fig.2. Conversion of MMA vs. amount of cupric ion.
MMA 3 ml, α-amylase 0.1 g, H_2O 10 ml; 85°C, 3 hr

Degree of polymerization($\bar{P}n$) of poly-MMA was estimated by Welch's eq.[1] from [η] measured at 30°C in benzene.

Polymerization of MMA with the system of α-amylase and copper(II) ion.

Fig. 1 shows the effect of water on the polymerization of MMA. As can be seen clearly, water is indispensable for the reaction.

In order to determine whether the polymerization requires coexistence of metallic ion, copper(II) ion was added to the reaction system. The result was shown in Fig. 2. Even in the absence of copper(II) ion, the polymerization of MMA took place in a small amount of 1.8 %. However, the preferable effect of metallic ion is evident.

Table 1 is a proof of radical mechanism of the polymerization.

Table 1. Effect of radical scavengers on the conversion of MMA
(MMA 3 ml, $CuCl_2 \cdot 2H_2O$ 0.01 g, H_2O 10 ml, α-amylase 0.1 g; 85°C, 3 hr)

Added scavenger		Conversion
In air		~0 %
DPPH	0.1 g	~0 %
1,3,5-Triphenyl-verdazyl	0.1 g	~0 %

Polymerization of MMA with poly-α-amino acids.

In 1965, Imoto et al.[2] found that silk fiber could polymerize MMA very effectively in the presence of water. Later, Watanabe and Yamamoto[3] carried out the polymerization of MMA initiated with collagen (cowhide powder). Very recently, Fujie and Kawai[4] studied the polymerization of MMA at 70°C in the presence of synthesized poly-α-amino acid and copper(II) ion, where poly-L-alanine, polyglycine, poly-L-valine and copolymer of glycine and L-alanine were used. They found that,

Table 2. Polymerization of MMA initiated with poly-α-amino acid in the absence or presence of copper(II) ion (MMA 3 ml, H_2O 10 ml, $CuCl_2 \cdot 2H_2O$ 10^{-3} g; 85°C, 3 hr)

NO.	$\{CO-\underset{R}{CH}-NH\}$				Cu(III) ion	Conversion (%)	Efficiency of Grafting	$\bar{P}n$ of poly-MMA
	Name ****)	R	$\bar{P}n$*)	Feed**)				
1	Poly-Gly.	H	57	0.0803 g	No	1.63	-	-†)
				0.0803	Yes	3.98	11.2	25600
2	Poly-L-Ala	CH_3	62	0.1000	No	3.25	-	-
				0.1000	Yes	2.25	47.3	12500
3	Poly-L-Val	$-CH(CH_3)_2$	25	0.1394	No	0.47	-	-
				0.1394	Yes	4.32	4.2	15300
4	Poly-L-Leu	$-CH_2-CH(CH_3)_2$	50	0.1595	No	19.48	-	-
				0.1595	Yes	15.84	45.3	13500
5	Poly-L-Phe	$-CH_2C_6H_5$	40	0.2070	No	2.61	-	-
				0.2070	Yes	10.12	30.0	13500
6	Poly-L-Glu	$-CH_2CH_2-COOH$	560	0.1817	No	12.24	-	-
				0.1817	Yes	7.71	78.2	29900
7	Poly-β-Me-L-Asp	$-\underset{CH_3}{CH}-COOH$	48	0.1817	No	2.34	-	-
				0.1817	Yes	5.07	21.5	21200
8	Poly-γ-Bz-L-Glu	$-CH_2-\underset{CH_2C_6H_5}{CH}-COOH$	136	0.2112***)	Yes	0.89	0	5100

*) $\bar{P}n$ of poly-α-amino acid were measured by Noguchi and his coworkers.

**) All the amounts of the feed correspond to 0.00142 mol by unit.

***) 0.000962 mol by unit.

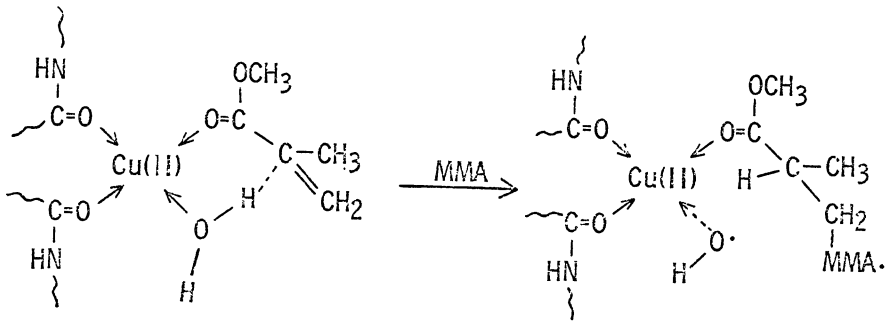
†) "-" means "not measured".

****) Gly : glycine, Ala : alanine, Val : valine, Leu : leucine, Phe : phenylalanine, Glu : glutamic acid, Asp : aspartic acid.

if the poly-α-amino acid had the α-helix conformation, the polymerization did not proceed, and in the cases of random coil and β-conformations, the polymerization occurred to a higher extent.

In the present letter, by using eight kinds of poly-α-amino acids, the polymerization of MMA was carried out in the presence and absence of copper(II) ion. The results on conversion of MMA, efficiency of grafting and degree of polymerization of extracted homopoly-MMA were shown in Table 2. The results appear to be too random and too complicated to explain systematically. However, even in the absence of copper(II) ion, the polymerization of MMA occurred to some extent; for example, in the cases of poly-L-glutamic acid and poly-L-leucine the conversions of 12.24 % and 19.48 % were recorded respectively.

According to the formerly reported mechanism, also in the present cases, the polymerization was considered to be initiated as follows:



The authors wish to express their hearty thanks to Prof. Noguchi for his affording of poly-L-amino acids.

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(Received August 1, 1975)