

Vinyl Polymerization. CCCXCVII. On the Polymerization of Methyl Methacrylate Initiated with the System of Glutathione, Cu(II) Ion, Urea, and Water*

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ABSTRACT: The polymerization of methyl methacrylate (MMA) was carried out in a system of glutathione (oxidized type, GSSG), Cu(II) ion, urea, and water. GSSG having S-S bonds behaved as a lysozyme model. It was confirmed by scanning electron microscopy that GSSG formed hydrophobic areas (HA) in the water phase. The HA was not so hydrophobic and was classified as a soft HA. MMA is a monomer softer than styrene (St). Accordingly, the soft HA formed by GSSG incorporated MMA more easily than St. This was verified by copolymerization of MMA and St.

KEY WORDS Glutathione / Hydrophobic Areas / Hard and Soft Monomer /
Uncatalyzed Polymerization / Methyl Methacrylate /

Recently,¹ we reported the “uncatalyzed polymerization” of methyl methacrylate (MMA) in a system of lysozyme, Cu(II) ion, and water, and found a remarkable promotion of the polymerization by urea. Due to the four S-S bonds of the lysozyme molecule, polymerization in the presence of urea was found to involve the following four kinds of reactions.

I. The polymerization of MMA with lysozyme, Cu(II) ion, and water. This reaction belongs to the “uncatalyzed polymerization.”

II. The polymerization of MMA with urea and Cu(II) ion.

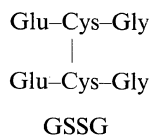
III. The polymerization of MMA initiated by the reaction of the S-S bond of lysozyme with urea.

IV. The thermal polymerization of MMA takes place in the monomer layer.

Accordingly to these manifold reaction types, a characteristic feature of the overall polymerization of MMA was found in the relationship between the conversion of MMA and the dissolved mass of Cu(II) ion, *i.e.*, the correlation curve had two peaks,

which are shown again in Figure 3 of this paper. The reasons for the appearance of the two peaks is satisfactorily explained.¹

In the present paper, glutathione (oxidized type, GSSG) having one S-S bond was used, as a simpler



polypeptide model of lysozyme. It was confirmed that GSSG gave the same curve of the conversion of MMA coordinated with the mass of Cu(II) ion, *i.e.*, the curve showed two peaks, as the curve obtained by lysozyme.

We could observe with the aid of scanning electron microscope that GSSG formed hydrophobic areas (HA) in the water phase. Considering that GSSG is not a macromolecule, the formation of HA is an interesting fact.

As has been already reported,² the uncatalyzed polymerization proceeds in three phases: (i) in the monomer phase, (ii) in HA, and (iii) in the water phase. The monomer is incorporated into the HA and there, the polymerization commences. The

* Vinyl Polymerization. CCCXCVI. T. Ouchi, M. Sakae, T. Yamazaki, H. Yamashita, and M. Imoto, *Nippon Kagaku Kaishi*, 1888 (1980).

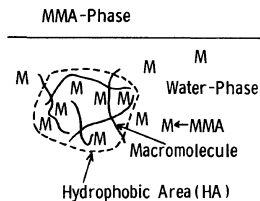


Figure 1. A schematic polymerization system.

schematic representation of the polymerizing system is shown as Figure 1.

The HA can be divided into many degrees of hardness and softness, according to hydrophobicity.³ The HA formed by *p*-dodecylbenzenesulfonate is very hard, according to its high hydrophobicity, while the HA formed by GSSG may be very soft, because the HA is formed by the loose agglomeration of the not so high molecular compound of GSSG containing many hydrophilic groups.

In regard to the incorporation of vinyl monomer in HA, the following concept is proposed³: a hard monomer, which is hydrophobic, can be easily incorporated into a hard HA and a soft monomer, which is hydrophilic, into a soft HA. Styrene (St) is a hard monomer and MMA is much softer than St. Therefore, the HA formed by GSSG incorporates MMA more easily than St. This interesting assumption was verified by the method of copolymerization, as is shown in this paper.

EXPERIMENTAL

Materials

Commercial GSSG (Sigma Chemical Company) was used without further purification. MMA and other monomers were purified by the usual methods and redistilled before use. Urea and Cu(II) chloride were of special commercial grade and used without further purification.

Procedures

MMA and other reagents were placed in a tube. The tube was sealed under vacuum after thawing with nitrogen and shaken or allowed to stand in a thermostat. After a definite time, the contents of the tube were poured into a large amount of methanol to precipitate the polymer. When the polymerization was carried out on standing, the monomer phase and the water phase were separately

pipetted out and poured into methanol. The polymer collected on the filter was thoroughly washed with methanol. After drying at 80°C under vacuum, the polymer was weighed.

The surface views of the polymerized system were observed by scanning electron microscopy (Nihon Denshi Co. JSM-35 type). One drop of the reaction system was mounted on a cylindrical brass support with nitrocellulose film, freeze-dried under vacuum, and rendered electrically conductive with a 20–30 nm coating of gold. Microscopy was performed at an accelerating voltage of 15 kV.

RESULTS AND DISCUSSION

Uncatalyzed Polymerization with GSSG and Cu(II) Ion in the Absence of Urea

GSSG could initiate the polymerization of MMA in a dilute aqueous solution of Cu(II) ion. The results obtained are shown in Figure 2. The Cu(II) ion behaved simultaneously as both an initiating reagent and a radical scavenger. Therefore, when Cu(II) ions were in excess, polymerization was inhibited.

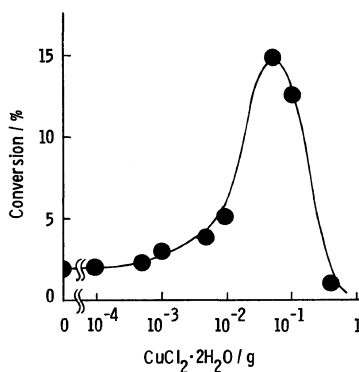


Figure 2. Conversion of MMA vs. mass of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in the absence of urea: MMA, 3 cm³; GSSG, 0.1 g; H₂O, 10 cm³; temp, 85°C; time, 6 h.

Uncatalyzed Polymerization of MMA with GSSG and Cu(II) Ion in the Presence of Urea

In the presence of urea, the effect of added Cu(II) ions on the polymerization was studied and the results are shown in Figures 3 and 4. Two peaks of conversion were clearly observed. The curve of A was obtained using lysozyme, and the curves of B and C, by GSSG. The similarity in the results by lysozyme and GSSG showed that GSSG behaves as

a model of lysozyme.

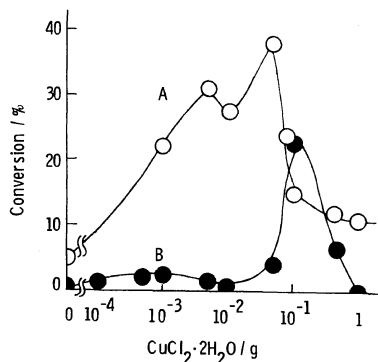


Figure 3. Conversion of MMA vs. mass of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$: MMA, 3 cm^3 ; H_2O , 10 cm^3 ; urea, 1 g; temp, 85°C ; time, 3 h; A (○), lysozyme, 0.1 g; B (●), GSSG, 0.1 g.

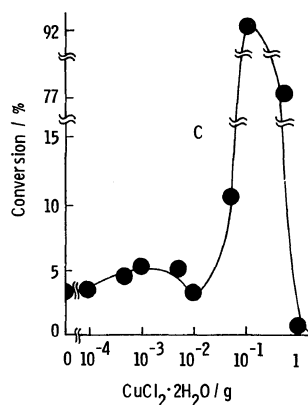


Figure 4. Conversion of MMA vs. mass of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$: MMA, 3 cm^3 ; H_2O , 10 cm^3 ; urea, 1 g; temp, 85°C ; time, 6 h; C (●), GSSG 0.1 g.

Selectivity of Vinyl Monomer

In order to observe the selectivity for vinyl monomer in polymerization by the system of GSSG, Cu(II) chloride, urea, and water, the polymerizations of three kinds of vinyl monomers were carried out.

As shown in Table I, the polymerization of MMA took place, while those of St and acrylonitrile (AN) did not, under the some conditions.

Proof of Radical Mechanism

A mixture of 3 cm^3 of MMA, 0.1 g of GSSG, 1 g of urea, and 10 cm^3 of water containing 0.1 g of Cu(II)

Table I. Polymerization with GSSG under shaking^a

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	Glutathione	Conversion/%		
		MMA	St	AN
g	g			
1×10^{-3}	0.1	5.3	4.3	0.1
1×10^{-1}	0.1	92.7	4.4	1.9
1×10^{-1}	0	4.3	4.2	—

^a Monomer, 3 cm^3 ; H_2O , 10 cm^3 ; urea, 1 g; temp, 85°C ; time, 6 h.

Table II. Effect of radical scavenger on the polymerization of MMA^a

Radical scavenger	Conversion/%	
	MMA phase	Water phase
None	1.7	16.7
DPPH	1.0	2.3
TPV	0	0

^a MMA, 3 cm^3 ; GSSG, 0.1 g; H_2O , 10 cm^3 ; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.1 g; urea, 1 g; radical scavenger, 0.1 g; temp, 85°C ; time, 3 h.

chloride was allowed to stand at 85°C for 3 h. The conversions of MMA in the water phase and monomer phase were 16.7 and 1.7%, respectively. With the addition of 0.1 g of 1,1-diphenyl-2-picrylhydrazyl (DPPH) or 1,3,5-triphenylverdazyl (TPV) as a radical scavenger, polymerizations were carried out in a similar manner. Neither in the MMA phase nor in the water phase, was there any no formation of poly(MMA) (Table II). Thus, it is concluded that the polymerization proceeded through a radical mechanism.

The Observation of Hydrophobic Areas

The formation of the HA by GSSG in the water phase could be observed with an electron microscope. Figure 5 shows the view before the polymerization and Figure 6 shows the view following the polymerization of MMA initiated with GSSG, urea, CuCl_2 , and water.

Copolymerization of MMA with St on Standing

Copolymerization of MMA(M_1) with St(M_2) was carried out. A mixture of MMA and St was placed on top of an aqueous solution of GSSG, urea, and

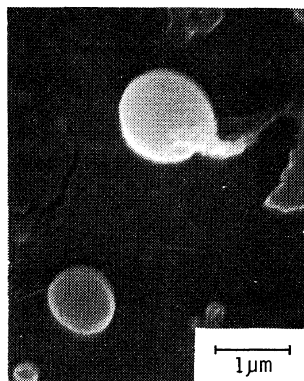


Figure 5. Surface view of GSSG: solution of 0.1 g of GSSG, 0.1 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and 1 g of urea in 10 cm^3 of H_2O , heated at 85°C for 3 h and diluted to 1000 cm^3 with H_2O .

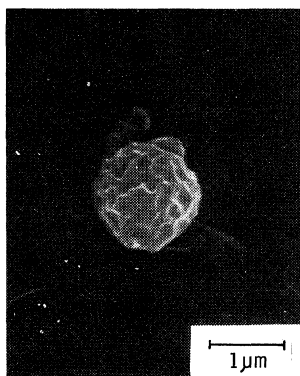


Figure 6. Surface view of the polymerized system: polymerization of 3 cm^3 of MMA in 10 cm^3 of water containing 0.1 g of GSSG, 0.1 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and 1 g of urea was carried out at 85°C for 6 h on standing. The water phase was diluted to 1000 cm^3 with water.

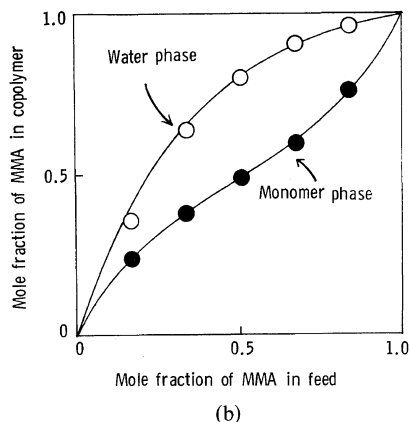
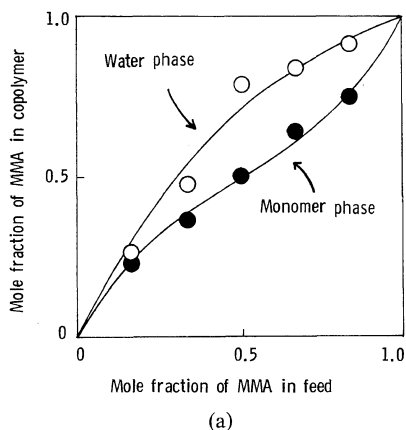


Figure 7. Composition curve of the copolymer of MMA (M_1) with St (M_2): (St + MMA), 3 cm^3 ; GSSG, 0.1 g; urea, 1 g; H_2O , 10 cm^3 ; temp, 85°C ; time, 6 h; (a), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.1 g; (b), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.001 g.

Table III. Values of r_1 and r_2 ^a

Case ^b	Copolymerization in MMA phase		Copolymerization in aqueous phase	
	r_1	r_2	r_1 ^c	r_2 ^c
(a)	0.44	0.42	1.86	0.24
(b)	0.49	0.56	5.01	0.55

^a MMA (M_1) + St (M_2), 3 cm^3 ; GSSG, 0.1 g; urea, 1 g; H_2O 10 cm^3 ; temp, 85°C ; time, 6 h.

^b (a) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.1 g; (b) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.001 g.

^c Apparent values.

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in a tube and allowed to stand at 85°C . After 6 h, the lower aqueous phase became turbid, while the upper monomer phase remained

clear. Both phases were poured separately into methanol so as to isolate the copolymer. The composition of the copolymer was determined by

elemental analysis. The results obtained are shown in Figures 7a and 7b.

According to Fineman-Ross method, the reactivity ratios, r_1 and r_2 , were calculated and are given in Table III.

As stated previously,³ the "uncatalyzed polymerization," which commences in HA, proceeds in the aqueous phase, and only the thermal polymerization takes place in the organic phase. Also in the present case, the copolymers isolated from the monomer phase gave the usual values of r_1 and r_2 , since the product was produced through radical copolymerization. On the other hand, the composition of the copolymers produced in the aqueous phase was unusual, *i.e.*, the MMA content was much larger than that determined theoretically. However, this unusual result can be satisfactorily explained by the concept of hard and soft HA and monomer. The HA formed by GSSG is soft, and

also MMA is a soft monomer. Therefore, MMA can be easier incorporated into the HA than the hard monomer of St. The concentration of MMA in the HA, which is a copolymerization site, becomes much higher than in the mixture of fed monomers. According to this, the unusual composition curve can be reasonably explained.

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