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Vinyl Polymerization Initiated by the Methylated Cyclodextrin/Metal Ion System in Water

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ABSTRACT

The polymerization of the vinyl monomers methyl methacrylate (MMA), benzyl methacrylate, and styrene, has been carried out using methylated cyclodextrins, for example, heptakis(2,6,0-dimethyl)- β -cyclodextrin, and heptakis(2,3,6-O-trimethyl)- β -cyclodextrin. These methylated cyclodextrins were found to initiate polymerization of the vinyl monomers in combination with water and a small amount of Cu(II) ion, in analogy with β -cyclodextrin (β -CD). Generally, the initiating ability of the methylated cyclodextrins/Cu(II) ion system for the polymerization of MMA was larger than that of the β -CD/Cu(II) ion system. Moreover, the introduction of a phosphate group into a methylated cyclodextrin molecule was found to increase the initiating ability for the polymerization of MMA.

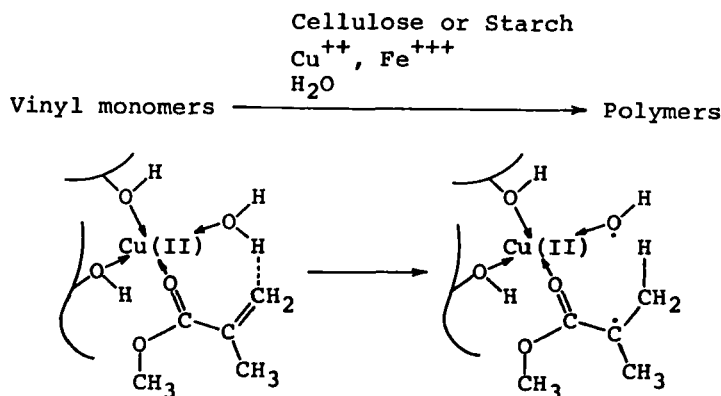
INTRODUCTION

There have been many studies on the polymerization of vinyl monomers initiated by polysaccharides/metal ion systems, so-called "uncatalyzed polymerization" [1]. A plausible initiation mechanism for the polymerization of MMA in the starch or cellulose/Cu(II) ion system, which includes complex formation among polysaccharides, Cu(II) ion, and MMA, has been proposed by Imoto and co-workers (see Scheme 1) [1f, 1g].

In a previous paper we found that α -, β -, and γ -cyclodextrins, which possess an ability to include various kinds of organic molecules in their hydrophobic cavity, can initiate the radical polymerization of such vinyl monomers as methyl methacrylate (MMA) and benzyl methacrylate (BMA) in combination with water and a small amount of Cu(II) or Fe(III) ion [2] in a similar fashion to the cases of polysaccharides such as cellulose and starch [1]. Moreover, we have also found that β -cyclodextrin (β -CD) compounds containing phosphate group, such as β -CD monophosphate ammonium salt (β -PCD) [3] and β -CD polyphosphate ammonium salt (β -PPCD) [4], possess a larger initiating ability for the polymerization of vinyl monomers than unmodified β -CD. Therefore the hydrophobic area formed by the cyclodextrins, as well as the complex formation among vinyl monomers, metal ions, and hydroxyl or phosphate group of the cyclodextrins, is considered to play an important role in these polymerizations.

Recently, Imoto et al. [5] proposed the concept of "hard" and "soft" for the hydrophobic area of polysaccharides and vinyl monomers for uncatalyzed polymerization.

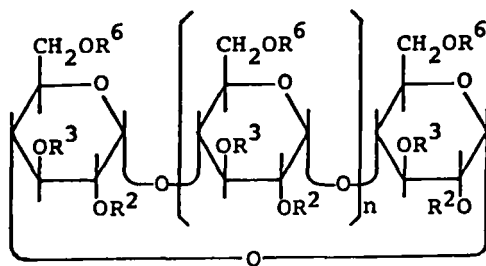
These findings prompted us to investigate the polymerization of vinyl monomers initiated by methylated β -CD compounds with various



SCHEME 1.

levels of methylation, such as heptakis(2,6-O-dimethyl)-2-cyclodextrin (DM- β -CD) and heptakis(2,3,6-O-trimethyl)- β -cyclodextrin- β -CD), and the compound (DM- β -PCD) which was prepared by the phosphorylation of DM- β -CD, in order to clarify the mechanistic feature of the polymerization of cyclodextrins/metal ion system in more detail. Actually, methylated β -CDs such as DM- β -CD have been known to form more stable inclusion complexes with organic compounds in comparison with unmodified cyclodextrins [6].

In this report we describe the results of the polymerization of MMA, BMA, and styrene initiated by methylated β -CD compounds or the DM- β -PCD/Cu(II) ion/H₂O system (Table 1).



CD compd.	n	R ²	R ³	R ⁶
β -CD	5	H	H	H
DM- β -CD	5	CH ₃	H	CH ₃
TM- β -CD	5	CH ₃	CH ₃	CH ₃

TABLE 1. Degree of Methylation of Four Kinds of Methylated β -CD Compounds

CD compound	Degree of methylation (d.m.)
M- β -CD-I	0.54
M- β -CD-II	1.28
DM- β -CD	2.0
TM- β -CD	3.0

EXPERIMENTAL

Materials

β -Cyclodextrin (β -CD): A commercial product from Tokyo Kasei Co. Ltd. was used after recrystallization from water; $[\alpha]_D^{20} +160.0^\circ$ (H_2O).

Vinyl monomers: Freshly distilled methyl methacrylate (MMA), benzyl methacrylate (BMA), and styrene (St) were used for the polymerization.

Metal salt: Cupric chloride ($CuCl_2 \cdot 2H_2O$) of commercial grade was used without further purification.

Preparation of Heptakis (2,6-O-dimethyl)- β -cyclodextrin (DM- β -CD)

This compound was prepared by methylation of β -CD with dimethyl sulfate according to the published method [7]. $[\alpha]_D^{20} +123^\circ$ ($CHCl_3$) (Ref. 7b: $[\alpha]_D^{20} +122^\circ$ ($CHCl_3$)).

Preparation of Heptakis (2,3,6-O-trimethyl)- β -cyclodextrin (TM- β -CD)

This compound was prepared using a procedure similar to that described by Boger et al. [8]. β -CD (8.9 g, 7.8 mmol) was treated with dry sodium hydride (Aldrich) (19.7 g, 0.82 mol) in 400 cm³ of dry dimethylformamide at 0°C. After being stirred for 30 min at room temperature, 104 cm³ of methyl iodide (1.67 mol) was added, and the mixture was stirred at room temperature for 5 h. The concentration of the organic layer and column chromatography on silica gel (200 mesh), using benzene/ethanol (volume ratio 4:1) as eluent, followed by recrystallization from chloroform/hexane and hot water (80°C) successively, yielded an analytically pure product. Yield 6.0 g (54%), mp 156-158°C, $[\alpha]_D^{20} +161^\circ$ (c 0.118, $CHCl_3$) (Ref. 7b: mp 156°C, $[\alpha]_D^{20} +163^\circ$ ($CHCl_3$)).

Preparation of the Partially Methylated β -Cyclodextrins, M- β -CD-I and M- β -CD-II

These compounds were prepared by the methylation of β -CD with dimethyl sulfate in the presence of BaO and $Ba(OH)_2 \cdot 8H_2O$. Elemental analyses indicated that the resulting M- β -CD-I and M- β -CD-II possessed 3.97 (the degree of methylation (d.m.): 0.57)* and 8.94 (d.m.: 1.28) methyl groups in a β -CD molecule, respectively.

*The degree of methylation (d.m.) = (total number of CH_3O groups in the methylated β -CD) \times 3/21; total number of hydroxyl groups in β -CD = 21

M- β -CD-I (C _{45.97} H _{77.94} O ₃₅)	Calcd.: C, 46.37; H, 6.60%
	Found: C, 46.37; H, 6.78%
M- β -CD-II (C _{50.94} H _{87.88} O ₃₅)	Calcd.: C, 48.54; H, 7.03%
	Found: C, 48.54; H, 7.20%

Preparation of Heptakis (2,6-O-dimethyl)- β -cyclo-dextrin Phosphate Ammonium Salt (DM- β -PCD)

This compound was prepared using a procedure similar to that described in a previous paper [4].

Polymerization Procedures

The general procedure is as follows. A mixture of methylated β -CD, a vinyl monomer, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and water was placed in a glass tube. The tube was filled with nitrogen under vacuum and sealed. Polymerization was carried out by continuous shaking in a thermostat at a preset temperature. After polymerization, the content was poured into a large amount of methanol or acetone to obtain the precipitated polymer. The resulting polymer was dried and the conversion was determined gravimetrically.

RESULTS AND DISCUSSION

Effect of the Addition of Cu(II) Ion on the Polymerization Using Four Kinds of Methylated β -Cyclodextrin

The effect of the addition of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was examined on the polymerization of MMA in the presence of M- β -CD-I (the degree of methylation (d.m.): 0.57, M- β -CD-II (d.m.: 1.28), DM- β -CD (d.m.: 2.0), and TM- β -CD (d.m.: 3.0). The polymerization of MMA was carried out in the presence of various amounts of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, keeping the amount of MMA (3 cm^3 , 2.80×10^{-2} mol), water (10 cm^3), and the methylated β -CD compounds (0.1 g , $8.81 \times 10^{-5} \sim 7.00 \times 10^{-5}$ mol) constant. The $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ content was changed from 10^{-5} to 0.1 g ($5.87 \times 10^{-8} \sim 5.87 \times 10^{-4}$ mol). The results are shown in Figs. 1 and 2 together with the result using β -CD (d.m.: 0). As shown in Figs. 1 and 2, the percent conversions of polymerization in the presence of M- β -CD-I, M- β -CD-II, and DM- β -CD increased with an increase of the amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and showed maximal values when the amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was estimated to be 0.01 g (5.87×10^{-5} mol). In polymerization in the presence of M- β -CD-I, M- β -CD-II, or DM- β -CD, a sharp conversion curve was obtained. A broad conversion curve was observed for polymerization in the presence of TM- β -CD. These results indicate that the ini-

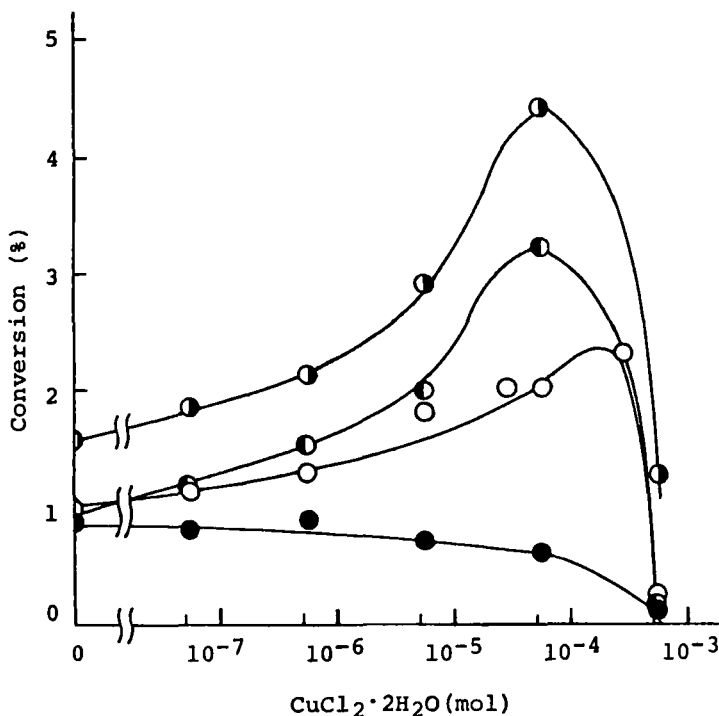


FIG. 1. Effect of the amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ on the percent conversion of the polymerization of MMA using M- β -CD-I or M- β -CD-II. MMA, 3 cm^3 (2.80×10^{-2} mol); H_2O , 10 cm^3 ; methylated β -CD, 0.1 g ($8.81 \times 10^{-5} \sim 7.93 \times 10^{-5}$ mol); 85°C ; 3 h; (●) M- β -CD-I, (○) M- β -CD-II, (○) β -CD, (●) thermal polymerization.

tiating ability of these methylated β -CD compounds for the polymerization of MMA is larger than that of unmodified β -CD.

Effect of the Degree of Methylation of β -CD on the Polymerization of MMA

Figures 1 and 2 also indicate that the percent conversion for the polymerization of MMA in the M- β -CD-I, M- β -CD-II, DM- β -CD, or TM- β -CD/Cu(II) ion system is dependent on the degree of methylation of β -CD hydroxyl groups. The initiating inability of each system increases in the order M- β -CD-II (d.m.: 1.28) > M- β -CD-I (d.m.: 0.57) > TM- β -CD (d.m.: 3.0) \approx DM- β -CD (d.m.: 2.0) > β -CD (d.m.: 0), when 0.01 g (5.87×10^{-5} mol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is used (see Fig. 3). This fact suggests that a methylated β -CD possessing a suitable sized hydrophobic

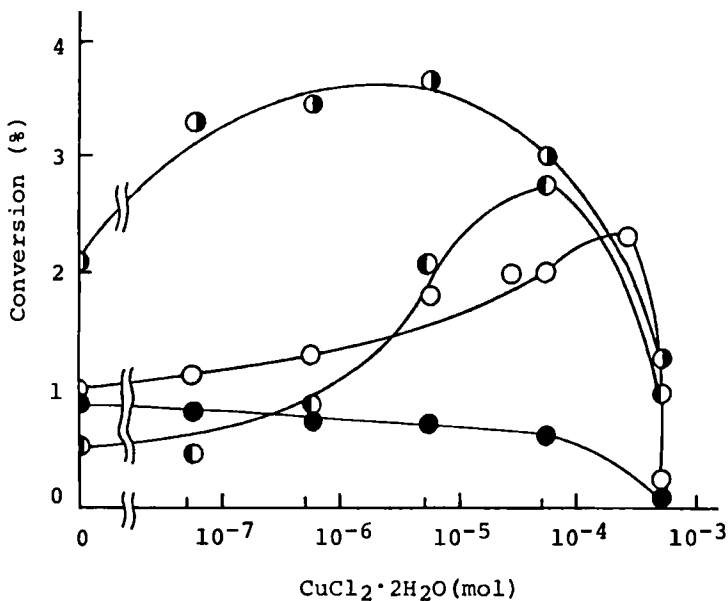


FIG. 2. Effect of the amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ on the percent conversion of the polymerization of MMA using DM- β -CD or TM- β -CD. MMA, 3 cm^3 (2.80×10^{-2} mol); H_2O , 10 cm^3 ; methylated β -CD, 0.1 g ($8.81 \times 10^{-5} \sim 7.00 \times 10^{-5}$ mol); 85°C ; 3 h; (●) DM- β -CD, (○) TM- β -CD, (○) β -CD, (●) thermal polymerization.

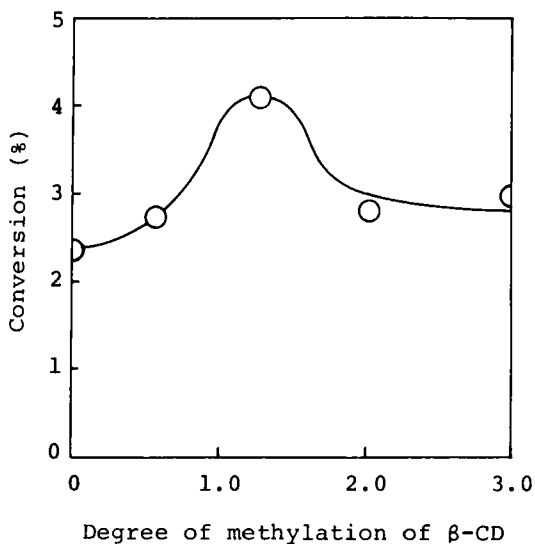


FIG. 3. Effect of the degree of methylation of β -CD for the polymerization of MMA. MMA, 3 cm^3 (2.80×10^{-2} mol); $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.01 g (5.87×10^{-5} mol); H_2O , 10 cm^3 ; methylated β -CD, 0.1 g ($8.81 \times 10^{-5} \sim 7.00 \times 10^{-5}$ mol); 85°C ; 3 h.

cavity and a certain number of hydroxyl groups is preferable to unmodified β -CD for the polymerization of MMA.

On the other hand, TM- β -CD, which does not contain a hydroxyl group in its cyclodextrin molecule, can also initiate the polymerization of MMA in analogy with the other β -CD compounds containing some hydroxyl groups. However, the conversion of the polymerization obtained is independent of the amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in the TM- β -CD/Cu(II) ion system, unlike the other systems (see Fig. 2). This finding may be attributed to the fact that the rate of thermal polymerization of MMA is accelerated by including MMA molecules within the large hydrophobic cavity of TM- β -CD.

Polymerization of Various Vinyl Monomers

The polymerization of various kinds of vinyl monomers (MMA, BMA, and St) in the DM- β -CD/Cu(II) ion or TM- β -CD/Cu(II) ion system was carried out. The results are summarized in Table 2 together with those in the β -CD/Cu(II) ion system. As shown in Table 2, the DM- β -CD/Cu(II) ion system can accelerate the polymerization of MMA, BMA, and especially St more effectively than the β -CD/Cu(II) ion system.

TABLE 2. Polymerization of Vinyl Monomers in the Presence of β -CD, DM- β -CD, and TM- β -CD^a

β -CD compound	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (10^{-5} mol)	Conversion (%)		
		MMA	BMA	St
None	0	0.88	0	2.27
	5.87	0.64	0.16	2.26
β -CD	0	0.99	0	2.37
	5.87	2.37	0.29	2.26
DM- β -CD	0	0.51	0.42	2.25
	5.87	2.70	5.53	3.14
TM- β -CD	0	2.27	0.82	2.82
	5.87	3.09	1.26	2.88

^aPolymerization condition: β -CD compound, 0.1 g ($8.81 \times 10^{-5} \sim 7.00 \times 10^{-5}$ mol); monomer, 3 cm³; H₂O, 10 cm³; 85 C; 3 h.

At a rough glance, the TM- β -CD/Cu(II) ion system seems to accelerate the polymerization of MMA and St. However, the percent conversion of thermal polymerizations for MMA and St in the presence of TM- β -CD without CuCl₂ · 2H₂O is considerably larger. Therefore, the initiating ability of the TM- β -CD/Cu(II) ion system is not as effective as that of the DM- β -CD/Cu(II) ion system. On the basis of these findings, the hydroxyl groups in the cyclodextrin compounds, which are assumed to participate in the complex formation with the Cu(II) ion, play an important role at the initiation step of polymerization.

The rate of acceleration of the polymerization in the DM- β -CD/Cu(II) ion system also indicates that the introduction of methyl groups into the β -CD molecule, which may cause expansion of the hydrophobic cavity, should be an important factor of this polymerization, since the incorporation of vinyl monomers into the hydrophobic cavity of β -CD compounds may increase with the enlargement of their hydrophobic cavity.

Next, in order to get a clue as to the dependence of the hydrophobic character of the methylated β -CD compounds and the vinyl monomers on the percent conversion of polymerization, we tried the following:

$$R = 1 - \frac{\left(\text{Conversion (\% in the } \beta\text{-CD/Cu(II) ion system} \right) - \left(\text{Conversion (\% in the Cu(II) ion system} \right)}{\left(\text{Conversion (\% in the methylated } \beta\text{-CD/Cu(II) ion system} \right) - \left(\text{Conversion (\% in the Cu(II) ion system} \right)} \quad (1)$$

This parameter, R, is associated with a characteristic mode of acceleration of polymerization in the methylated β -CD compounds/Cu(II) ion system, and it is suggested that the polymerization is efficiently accelerated as the R value approaches one. The R values obtained from the polymerizations of MMA, BMA, and St in the DM- β -CD/Cu(II) ion and the TM- β -CD/Cu(II) ion systems are compiled in Table 3. Table 3 clearly indicates that the methylated β -CD compounds, which possess a large hydrophobic character compared with β -CD, can effectively accelerate the polymerization of hydrophobic vinyl monomers containing an aryl group such as BMA and St. These results are also compatible with the concept of "hard" and "soft" in the so-called uncatalyzed polymerization proposed by Imoto et al. [5].

Effect of the Addition of Benzene on the Polymerization of MMA in the DM- β -CD/Cu(II) Ion System

In order to clarify the importance of the inclusion ability of the methylated β -CD compounds toward vinyl monomers at the initiation step of polymerization, the polymerization of MMA in the DM- β -CD/

TABLE 3. R Values Obtained from the Polymerizations of MMA, BMA, and St in the DM- β -CD/Cu(II) Ion System and the TM- β -CD/Cu(II) Ion System

Methylated β -CD compound	Monomer		
	MMA	BMA	St
DM- β -CD	0.16	0.98	1.0
TM- β -CD	0.29	0.88	1.0

Cu(II) ion system was carried out in the presence of various amounts of benzene, since benzene is known to be a good "guest" compound of DM- β -CD than is MMA. The results of the polymerization are shown in Fig. 4. The percent conversion of the polymerization in the DM- β -CD/Cu(II) ion system decreases with an increase in the amount of benzene added. That is to say, benzene seems to act as an inhibitor for this polymerization. This finding suggests that the initial incorporation of MMA into the hydrophobic cavity of DM- β -CD is essentially required for the initiation of the present polymerization. This fact is consistent with the data described above. That is, the DM- β -CD/Cu(II)

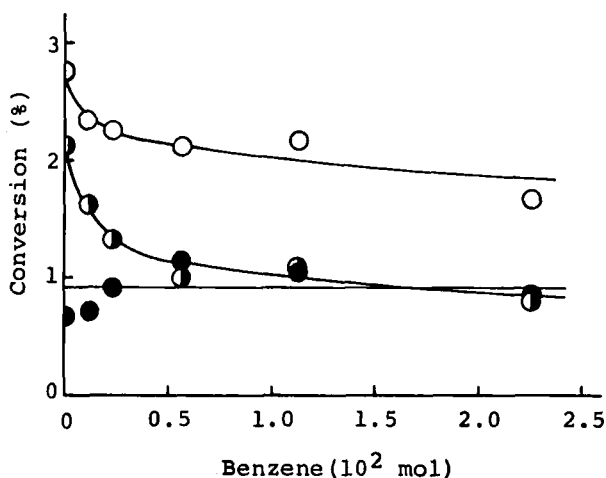


FIG. 4. Effect of the addition of benzene for the polymerization of MMA in the DM- β -CD/Cu(II) ion system. MMA, 3 cm^3 (2.80×10^{-2} mol); $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.01 g (5.87×10^{-5} mol); H_2O , 10 cm^3 ; DM- β -CD, 0.1 g (7.51×10^{-5} mol); 85°C ; 3 h; (o) DM- β -CD, (•) thermal polymerization, (◐) corrected conversion.

ion system can more effectively initiate polymerization of vinyl monomers containing an aryl group such as BMA and St in comparison with MMA.

Polymerization of MMA Initiated by the DM- β -PCD/Cu(II) Ion System

Polymerization of MMA in the DM- β -PCD/Cu(II) ion system was carried out. The result obtained is tabulated in Table 4 together with the results in the β -CD/Cu(II) ion [2], β -CD monophosphate ammonium salt (β -PCD/Cu(II) ion [3], DM- β -CD/Cu(II) ion, and TM- β -CD/Cu(II) ion systems. The initiating ability for the polymerization of MMA was found to increase in the order β -CD/Cu(II) ion system < DM- β -CD/Cu(II) ion system < TM- β -CD/Cu(II) ion system < β -PCD/Cu(II) ion system < DM- β -PCD/Cu(II) ion system. Thus the introduction of the phosphate group into the β -CD molecule seems to increase the initiating ability for the polymerization of MMA in combination with the Cu(II) ion. Rate enhancement by phosphorylated β -CD compounds is considered to be due to the high ability of complex formation of the phosphate group with the Cu(II) ion at the initiation step of the polymerization.

In summary, partially methylated β -CD compounds which possess a larger hydrophobic cavity than unmodified β -CD were found to effectively accelerate the water-insoluble vinyl monomers, such as MMA, BMA, and St, in combination with a small amount of Cu(II) ion. We previously proposed a plausible initiation mechanism for polymerization using the β -CD compound/Cu(II) ion system [3], which includes the initial incorporation of vinyl monomer, into the hydrophobic cavity of β -CD, and complex formation among β -CD, Cu(II) ion, and a vinyl

TABLE 4. Comparison of the Results for the Polymerization of MMA in the Four Kinds of β -CD Compounds/Cu(II) Ion/H₂O Systems^a

β -CD compound	Conversion (%)
β -CD	2.37
DM- β -CD	2.78
TM- β -CD	3.09
β -PCD	3.54
DM- β -PCD	4.55

^aPolymerization condition: β -CD compound, 0.1 g ($8.81 \times 10^{-5} \sim 7.00 \times 10^{-5}$ mol); MMA, 3 cm³ (2.80×10^{-2} mol); H₂O, 10 cm³; CuCl₂ · 2H₂O, 0.01 g (5.87×10^{-5} mol); 85°C; 3h.

monomer. Considering this mechanistic implication, the partial methylation of β -CD seems to increase with the initial incorporation of vinyl monomers. However, permethylated β -CD, TM- β -CD, merely accelerated the thermal polymerization even when Cu(II) ion was used.

Therefore, we propose that a certain number of hydroxyl or phosphate groups of a methylated β -CD compound, which is capable of assisting complex formation among a methylated β -CD compound, Cu(II) ion, and a vinyl monomer, is necessary for the initiation of the present polymerization.

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