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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Taguchi, Hiromu, Kunieda, Norio and Kinoshita, Masayoshi (1982) 'Vinyl Polymerization Initiated by Cycloheptaamylose Phosphate Ammonium Salt/Metal Ion System in Water', *Journal of Macromolecular Science, Part A*, 18: 2, 271 – 284

To link to this Article: DOI: 10.1080/00222338208074424

URL: <http://dx.doi.org/10.1080/00222338208074424>

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Vinyl Polymerization Initiated by Cycloheptaamylose Phosphate Ammonium Salt/Metal Ion System in Water

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ABSTRACT

Cycloheptaamylose phosphate ammonium salt (β -PCD) was found to initiate the radical polymerization of vinyl monomers in combination with water and a small amount of Cu(II) or Fe(III) ion, in analogy with the cycloheptaamylose (β -cyclodextrin: β -CD). The initiating ability of this system was larger than that of the β -CD/metal ion system. Detailed investigations were conducted in order to elucidate a plausible initiation mechanism of this polymerization.

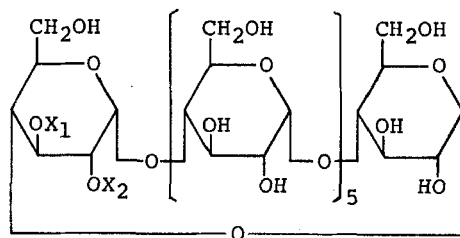
INTRODUCTION

Recently we reported that α -, β -, and γ -cyclodextrins, which possess the ability to include various sorts of organic compounds in their hydrophobic hole in water, initiated the polymerization of vinyl monomers in combination with water and a small amount of Cu(II) or Fe(III) ion [1], in a fashion similar to the cases of polysaccharides such as cellulose and starch [2].

We have now found that cycloheptaamylose phosphate ammonium salt (β -PCD), which possesses one phosphate group at the 2- or 3-position in β -cyclodextrin (β -CD) molecule, can also serve as an

initiator of radical polymerization. Meanwhile, Imoto et al. [3] recently reported that the polymerization of methyl methacrylate (MMA) was initiated with a polymer possessing a phosphate group, such as polyethylenephosphate sodium salt, in the presence of water and a small amount of Cu(II) ion.

The present paper is concerned with a study of the polymerization of several vinyl monomers initiated by the cycloheptaamylose phosphate ammonium salt (β -PCD)/metal ion/H₂O system:



CD Comps

β -CD

$X_1 = X_2 = H$

β -PCD

X_1 or $X_2 = \begin{array}{c} \text{O} \\ \parallel \\ \text{---P---O}^{\ominus}\text{---NH}_4^{\oplus} \\ | \\ \text{OH} \end{array}$

EXPERIMENTAL

Materials

β -Cyclodextrin (β -CD): A commercial product (Nippon Starch Refining Co., Osaka) was used after recrystallization from water; $[\alpha]_D^{160.0} (C 0.637, H_2O)$.

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

Metal salts: Commercial grade cupric chloride ($CuCl_2 \cdot 2H_2O$) and ferric chloride ($FeCl_3 \cdot 6H_2O$) were used without further purification.

Radical scavengers: Commercial grade of 1,1-diphenylpicrylhydrazyl (DPPH), hydroquinone (HQ), 1,3,5-triphenylverdazyl (TPV), and t-butylcatechol (t-BC) were used.

Preparation of Cycloheptaamylose Phosphate Ammonium Salt (β -PCD)

β -PCD was prepared according to the method developed by Breslow et al. [4]. The treatment of β -CD (5.45 g, 4.78 mmol) with bis-3-nitrophenyl phosphate (0.440 g, 1.30 mmol) [5] in 0.1 M sodium hydroxide solution afforded a mixture of cycloheptaamylose 2- and 3-phosphates and β -CD recovered. The resulting mixture was chromatographed using a column packed with Amberlite CG-400 Type 1 anion exchange resin using a NH_4HCO_3 buffer solution as the eluent to give a mixture of cycloheptaamylose 2- and 3-phosphate ammonium salts (1.21 g, 75% yield). The mixture was used for polymerization without separation.

Polymerization Procedures

A typical procedure is as follows. A mixture of β -PCD, a monomer, a metal salt, and water was placed in a glass tube. The air in the tube was replaced by nitrogen and sealed. Polymerization was carried out with continuous shaking in a thermostat at a preset temperature. After polymerization the content was poured into a large amount of methanol to give the polymer precipitate. The polymer was filtered and washed well with hot water to remove the residual β -PCD. The resultant polymer was dried and subjected to determination of the percent conversion by weight.

Polymerization was also carried out on standing under conditions similar to those used for polymerization with shaking as described above. After being left for an adequate time without shaking, the aqueous layer and the organic layer were separately poured into a large amount of methanol. The polymeric products were obtained in the same manner as above.

RESULTS AND DISCUSSION

Effect of the Addition of Cu(II) or Fe(III) Ion on Polymerization with β -PCD

In our previous work [1] the addition of a small amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was found to be effective for polymerization initiated by β -CD. Therefore, these metal salts were used in the present investigation. First the polymerization of MMA with β -PCD was carried out in the presence of various amount of Cu(II) ion, keeping the amount of MMA (3 cm^3), water (10 cm^3), and β -PCD (0.1 g) constant. The amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was changed from 10^{-6} to 0.1 g. The results at 85 and 50°C are illustrated graphically in Figs. 1 and 2,

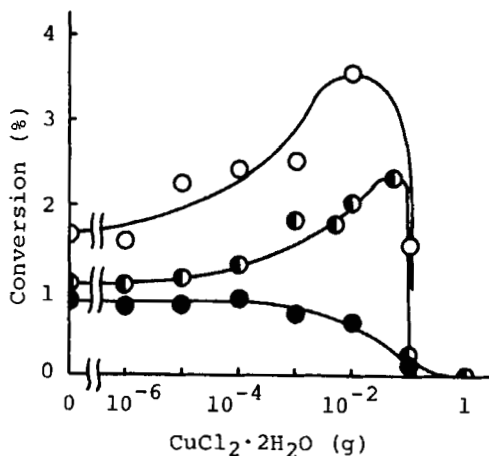


FIG. 1. Effect of the amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ on the percent conversion (at 85°C). MMA 3 cm^3 , H_2O 10 cm^3 , β -CD compounds 0.1 g , 85°C , 3 h . (\circ) β -PCD, (\bullet) β -CD, (\bullet) thermal polymerization.

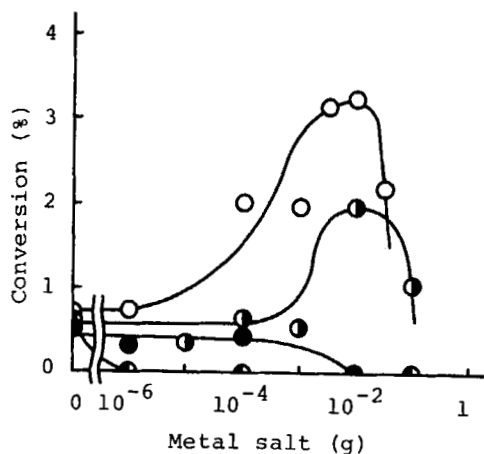


FIG. 2. Effect of the amount of metal salts on the percent conversion (at 50°C). MMA 3 cm^3 , β -CD compounds 0.1 g , H_2O 10 cm^3 , 50°C , 10 h . (\circ) β -PCD/ Cu(II) ion, (\bullet) β -CD/ Cu(II) ion, (\bullet) thermal polymerization in the presence of Cu(II) ion, (\bullet) β -PCD/ Fe(III) ion.

TABLE 1. Results of the Polymerizations of Some Vinyl Monomers in the β -PCD/Cu(II) Ion System

| Monomer | CuCl ₂ ·2H ₂ O (g) | β -PCD (g) | Conversion (%) |
|------------------|--|------------------|--------------------------|
| MMA ^a | 0 | 0 | 0.53 |
| | 0.01 | 0 | 0 |
| | 0 | 0.1 | 0.63 |
| | 0.01 | 0.1 | 2.95 |
| BMA ^a | 0 | 0 | 0.06 |
| | 0.01 | 0 | 3.30 |
| | 0 | 0.1 | 1.14 |
| | 0.01 | 0.1 | 5.53 |
| St ^a | 0 | 0 | 0.35 (0.80) ^b |
| | 0.01 | 0 | 0.61 (1.26) |
| | 0 | 0.1 | 0.63 (1.52) |
| | 0.01 | 0.1 | 0.93 (2.03) |
| AN ^a | 0 | 0 | 0 |
| | 0.01 | 0 | 2.58 |
| | 0 | 0.1 | 0 |
| | 0.01 | 0.1 | 0.19 |

^aMonomer 3 cm³, 50° C, 10 h.

^b50° C, 20 h.

respectively, together with the results of polymerization initiated by the β -CD/Cu(II) ion system. Figures 1 and 2 show that the initiating ability of the β -PCD/Cu(II) ion system is higher than that of the β -CD/Cu(II) ion system. The efficiency of the present system is especially well revealed in polymerization at 50° C (see Fig. 2).

The percent conversion of polymerization increased with an increase in the amount of Cu(II) ion, and showed the maximal value where the molar ratio of the Cu(II) ion to β -PCD to be about two. The same trend was also observed in the case of the β -PCD/Fe(III) ion system (see Fig. 2).

Polymerization of Various Vinyl Monomers

The results for the polymerizations of four kinds of vinyl monomers in the β -PCD/Cu(II) ion system are summarized in Table 1. In analogy

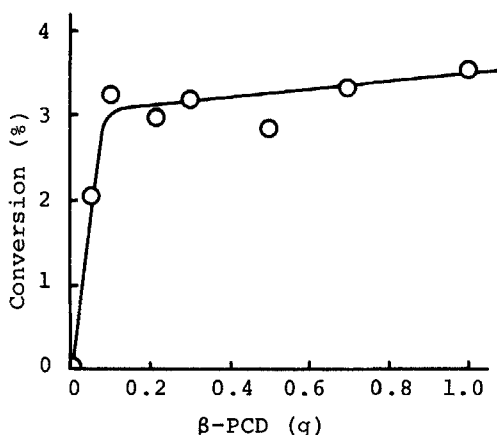


FIG. 3. Effect of the amount of β -PCD on the percent conversion. MMA 3 cm³, CuCl₂·2H₂O 0.01 g, H₂O 10 cm³, 50° C, 10 h.

with the β -CD/Cu(II) ion system, the present system was found to increase the polymerization rate of MMA and BMA. Moreover, contrary to the β -CD/Cu(II) ion system, the present system slightly accelerated the polymerization of styrene (St).

The percent conversion for the polymerizations of MMA and BMA in the present system were about sixfold (50° C, 10 h) and ninetyfold- (50° C, 20 h) larger, respectively, than for their thermal polymerizations (see Table 1).

Effect of the Amount of β -PCD

The polymerizations of MMA were carried out using varying amounts of β -PCD, keeping the amount of MMA (3 cm³), H₂O (10 cm³), and CuCl₂·2H₂O (0.1 g) constant. As shown in Fig. 3, the percent conversion increased with an increase in the amount of β -PCD, and became almost constant in the region where the molar ratio of CuCl₂·2H₂O to β -PCD was beyond ~ 2 .

Effect of the Amount of Water

As shown in Fig. 4, the polymerization of MMA using the β -PCD/Cu(II) ion system was affected by the amount of water added in a fashion similar to the cases of starch or the cellulose/Cu(II) ion system [2], the polyethylenephosphate sodium salt/Cu(II) ion system [3b], and the β -CD/Cu(II) ion system [1]. The percent conversion in

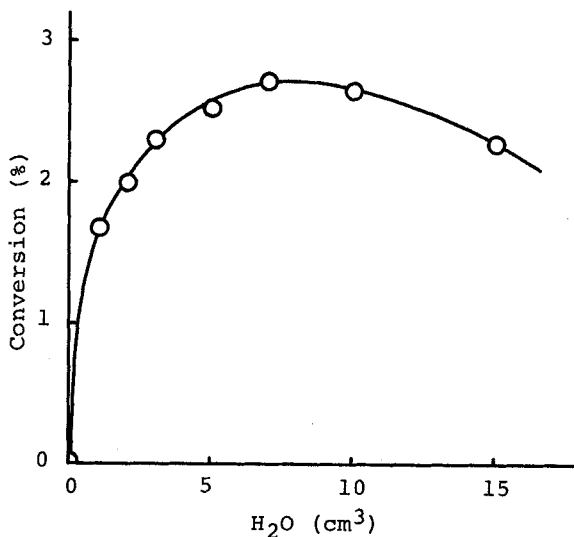


FIG. 4. Effect of the amount of water on the percent conversion. MMA 3 cm³, CuCl₂·2H₂O 0.01 g, β-PCD 0.1 g, 50°C, 10 h.

the present system increased with an increase in the amount of water; however, it decreased when more than about 7 cm³ of water was added.

Correlation of the Percent Conversion with the Polymerization Time

Time conversions for the polymerization of MMA in the systems β-PCD/Cu(II) ion/H₂O, β-CD/Cu(II) ion/H₂O, and Cu(II) ion/H₂O were determined. As shown in Fig. 5, polymerizations initiated by the β-CD/Cu(II) ion/H₂O and the Cu(II) ion/H₂O systems exhibited an induction period. However, interestingly, there is no induction period in the polymerization initiated by the β-PCD/Cu(II) ion/H₂O system. The absence of an induction period in the present system seems to indicate that β-PCD forms a tight complex with CuCl₂ in a molar ratio of 2:1 which acts as an initiator for the polymerization. No free CuCl₂ exists in the polymerization system. Actually, it has been known that a radical (R[•]) initially formed is readily captured by the metal cation [6]; R[•] + CuCl₂ → RCl + CuCl.

Effect of the Amount of MMA

The effect of the amount of MMA on polymerization in the β-PCD/Cu(II) ion system was determined. As shown in Fig. 6, polymerization

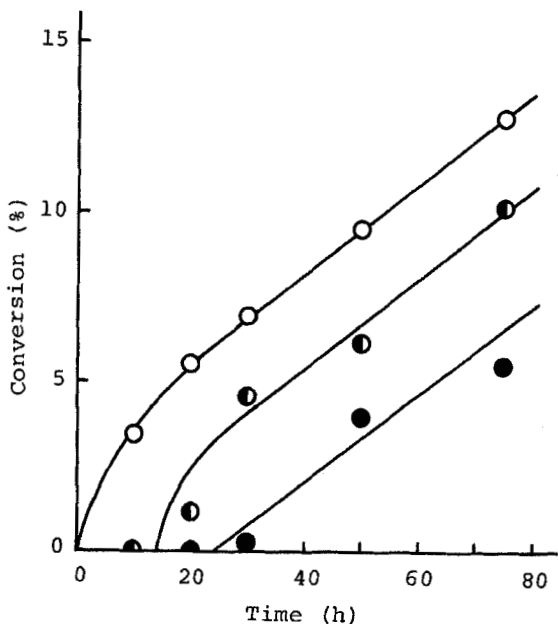


FIG. 5. Relationship between the percent conversion and the reaction time. MMA 3 cm³, β -CD compounds 0.1 g, H₂O 10 cm³, CuCl₂·2H₂O 0.01 g, 50°C. (○) β -PCD, (◐) β -CD, (●) thermal polymerization.

at 50°C for 50 h showed that the corrected polymer yield became almost constant in the region of over 7 cm³ of MMA, in a fashion similar to the case of polymerization in the β -CD/Cu(II) ion system [1]. However, an almost linear relationship was observed in polymerization at 50°C for 10 h (see Fig. 7). This fact may be understood by considering the results of the time conversion experiments described above.

Effect of Radical Scavengers

Polymerization of MMA in the β -PCD/Cu(II) ion system was carried out in the presence of several kinds of radical scavengers such as 1,1-diphenylpicrylhydrazyl (DPPH), hydroquinone (HQ), 1,3,5-triphenylverdazyl (TPV), and t-butylcatechol (t-BC). As shown in Table 2, polymerization is inhibited in the presence of radical scavengers. The results indicate that polymerization in this system should proceed through a radical mechanism.

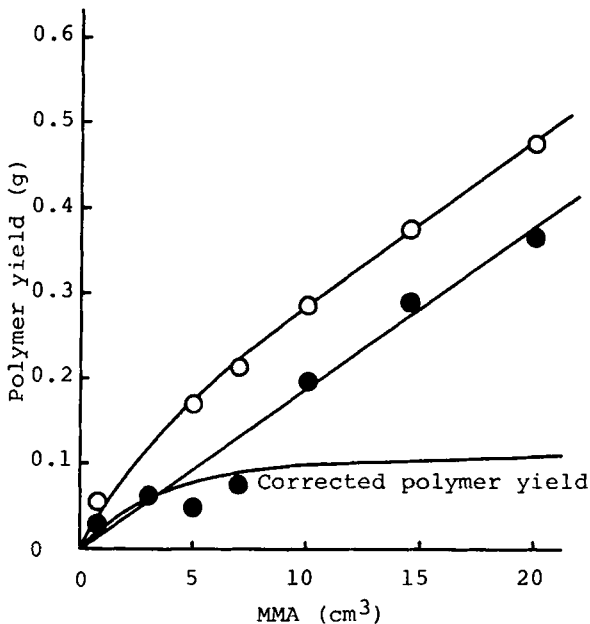


FIG. 6. Effect of the amount of MMA (50 h) on the polymer yield. H_2O 10 cm^3 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 0.01 g, β -PCD 0.1 g, 50°C , 50 h. (○) β -PCD, (●) thermal polymerization.

Results of the Polymerization without Shaking

Since the present polymerization is treated in a heterogeneous system, it is interesting to know that the polymerization proceeds in either the organic phase or the aqueous phase. Therefore, polymerization was carried out on standing without shaking. The ratio of the polymer yields obtained from the two phases are summarized in Table 3, together with data on the thermal polymerization.

Table 3 reveals that polymerization initiated by the present system proceeds in both phases to nearly the same extent. These data seem to indicate that the initiation of this polymerization takes place in the aqueous phase as in the case of polymerization initiated by the starch/metal ion system [2f].

Aspect of the Formation of β -PCD-Cu(II) Ion Complex

The UV spectrum of a mixture of β -PCD and Cu(II) ion was measured in water. As shown in Fig. 8, the UV spectrum of the mixture

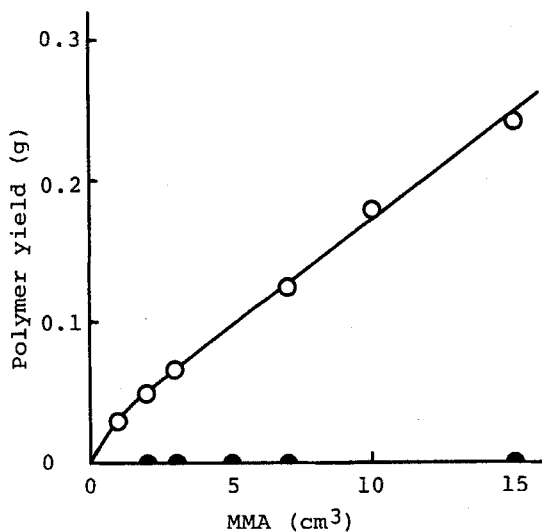


FIG. 7. Effect of the amount of MMA (10 h) on the polymer yield. H_2O 10 cm^3 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ 0.01 g, β -PCD 0.1 g, 50°C, 10 h. (○) β -PCD, (●) thermal polymerization.

TABLE 2. Effect of Radical Scavengers^a

| Inhibitor | Conversion (%) |
|-----------|----------------|
| | 2.95 |
| DPPH | 0 |
| HQ | 0 |
| TPV | 0 |
| t-BC | 0 |

^aPolymerization conditions: MMA, 3 cm^3 ; H_2O , 10 cm^3 ; β -PCD, 0.1 g; inhibitor, 0.1 g; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.01 g; 50°C; 10 h.

TABLE 3. Results of the Polymerization of MMA without Shaking in the Presence or in the Absence of β -PCD^a

| β -CD compound | Phase extracted | Conversion (%) |
|----------------------|-----------------|-------------------------|
| None | Aqueous layer | 0 (0%) |
| | Organic layer | 0.40 (100%) |
| β -PCD | Aqueous layer | 1.07 (52%) ^b |
| | Organic layer | 0.97 (48%) |

^aPolymerization conditions: MMA, 1.5 cm³; H₂O, 5 cm³; β -PCD, 0.05 g; CuCl₂·2H₂O, 0.005 g; 85°C; 3 h.

^bIn the case of the polymerization using the β -CD/Cu(II) ion system, the percent ratio was 22:78.

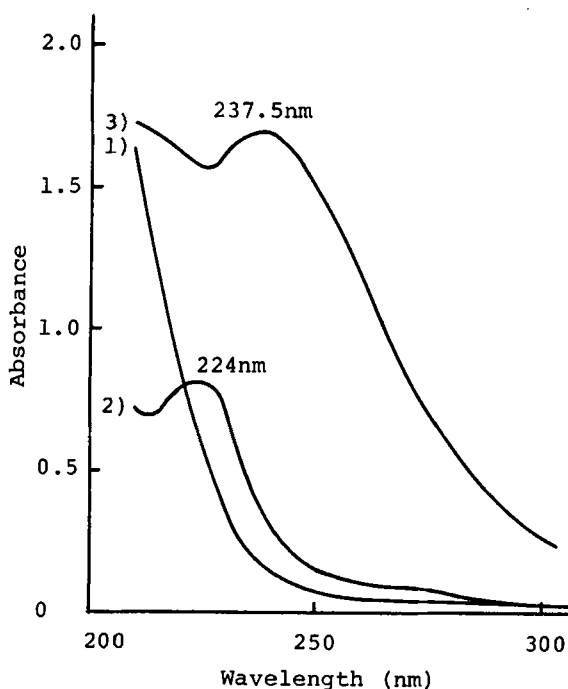


FIG. 8. UV spectra of Cu(II) ion, β -PCD, and the β -PCD/Cu(II) ion system in water (at 25°C). 1) Cu(II) ion 1.0×10^{-3} M, 2) β -PCD 1.0×10^{-3} M, 3) mixture of β -PCD (3.0×10^{-3} M) and Cu(II) ion (1.0×10^{-3} M).

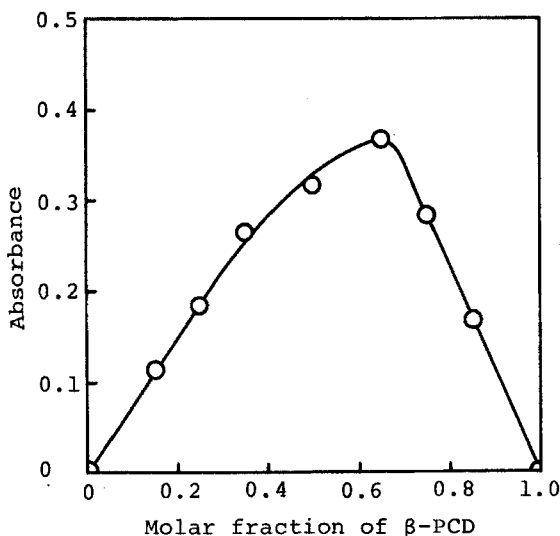


FIG. 9. The continuous variation curve for the β -PCD/Cu(II) ion system in water at 237.5 nm. $[\beta\text{-PCD}] = 0 \sim 1.0 \times 10^{-3} \text{ M}$, $[\text{Cu(II) ion}] = 1.0 \times 10^{-3} \sim 0 \text{ M}$.

has marked absorption at 237.5 nm due to the β -PCD/Cu(II) ion complex. Next, the continuous variation method [7] was carried out to determine the composition of the complex (see Fig. 9). Figure 9 indicates that the β -PCD-Cu(II) ion molar ratio is 1.80. The molar ratio method [8] also indicated that the molar ratio was about two.

Furthermore, the visible spectra of the Cu(II) ion in the presence of β -PCD and MMA were measured in water. The results are shown in Table 4. The absorption maximum shifted toward a shorter wavelength with the addition of a mixture of β -PCD and MMA, suggesting complex formation among β -PCD, Cu(II) ion, and MMA.

In summary, in analogy to the polymerizations initiated by the starch or cellulose/metal ion system [2] and the β -CD/metal ion system [1], the present polymerization using β -PCD also requires a metal ion such as Cu(II) or Fe(III) and water. The highest percent conversion has been obtained where the molar ratio of β -PCD/Cu(II) ion or β -PCD/Fe(III) ion is about two. The spectral data also indicate that β -PCD and Cu(II) ion form a complex in a molar ratio of 2:1 (see Fig. 9).

Moreover, the λ_{max} of the visible spectrum for the complex shifts toward a shorter wavelength with the addition of MMA (see Table 4), indicating that the initial formation of a β -PCD-metal ion

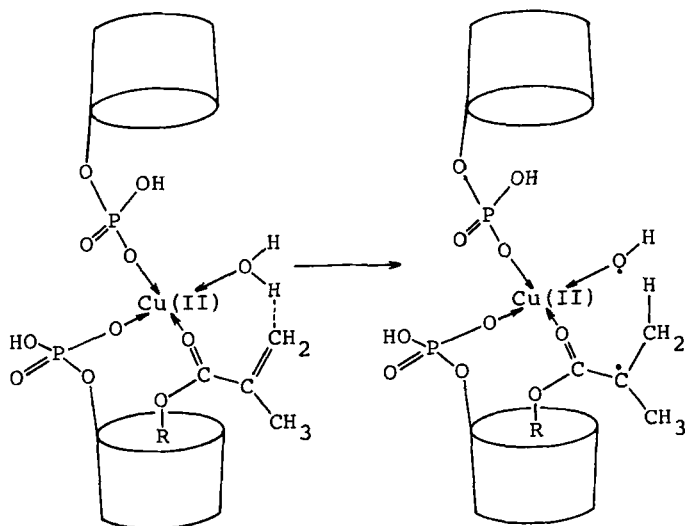
TABLE 4. λ_{\max} Values of Visible Spectra for Cu(II) Ion in the Presence of β -PCD and MMA in Water (25°C)^a

| | λ_{\max} (nm) |
|---|-----------------------|
| Cu(II) ion | 813 |
| Cu(II) ion/ β -PCD | 787 |
| Cu(II) ion/ β -PCD/MMA ^b | 748 |

^a[Cu(II) ion] = 0.02 M, [β -PCD] = 0.04 M.

^bThe mixture of Cu(II) ion (0.02 M), β -PCD (0.04 M), and MMA (0.5 cm³) was allowed to stand overnight after vigorous shaking.

complex plays an important role in the initiation step of polymerization. The experimental results using radical scavengers indicate that the polymerization proceeds through a radical mechanism. These results are similar to those for the polymerization initiated by the β -CD/metal ion system previously reported [1]. However, the present system is found to be more effective as initiator than the β -CD/metal ion system, although it is not as effective as the starch or cellulose/metal ion system [2]. Moreover, the investigation without shaking shows that polymerization in the present system takes place in the aqueous phase to a large extent, in comparison with the case of polymerization in the β -CD/metal ion system (see Table 3).



On the basis of these results and the mechanistic schemes proposed for the polymerization of MMA in the starch or cellulose/Cu(II) ion system [2] and the polyethylenephosphate sodium salt/Cu(II) ion system [3], a plausible initiation mechanism for the polymerization of MMA in the present system, which includes the complex formation among β -PCD, Cu(II) ion, and MMA, may be formulated as shown on the preceding page.

Further investigations are now under way in an effort to obtain detailed knowledge of the initiation mechanism of this polymerization.

ACKNOWLEDGMENT

We would like to express our grateful appreciation to Nippon Starch Refining Co. for supplying β -CD.

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Accepted by editor June 26, 1981

Received for publication July 7, 1981