Vinyl Polymerization. CCCLXXXV. Polymerization of Methyl Methacrylate Initiated with Sodium Poly(L-glutamate) in Aqueous Medium of Cu(II) Ion

Tatsuro OUCHI, Kiyotaka WATANABE, Toshiyuki YOSHIKAWA,
Eijiro MORITA, and Minoru IMOTO

*Department of Applied Chemistry, Faculty of Engineering,
Kansai University, Suita, Osaka 564, Japan.*

(Received July 19, 1979)

ABSTRACT: The polymerization of methyl methacrylate (MMA) by sodium poly(L-glutamate) (PLG-Na), copper(II) chloride and water was carried out. The effects of the pH of the aqueous solution and the mass of each component on the conversion were studied. The polymerization proceeded in an acidic medium through a radical mechanism. The initiation mechanism was discussed. The formation of the complex of Cu(II) ion with PLG-Na and water was confirmed by measurements of electric conductivity and UV spectrum of the PLG-Na aqueous solution in the presence of CuCl_2 .

KEY WORDS Sodium Poly(L-glutamate) / pH / Methyl Methacrylate / Copper(II) Chloride / Radical Polymerization / Initiation Mechanism / Electric Conductivity / UV Spectrum / Scanning Electron Microscopy /

We reported that the macromolecules having the CONH group as main chain unit, such as silk,¹ nylon 6,² nylon 3,³ α -amylase,⁴ lysozyme,⁵ and poly(α -amino acid),⁶ were able to initiate the radical polymerization of methyl methacrylate (MMA) in an aqueous solution of metal ions, particularly, Cu(II) ions. The mechanism of the polymerization is considered to be as follows.

This paper is concerned with the radical polymerization of MMA initiated with the system of sodium poly(L-glutamate) PLG-Na, Cu(II) ion and water. PLG-Na contains CONH units and pendent carboxyl groups. The carboxyl groups are also expected to be active centers for the present uncatalyzed polymerization.

EXPERIMENTAL

Materials

PLG-Na afforded by Kyowa Hakko Co. Ltd., was used without further purification (molecular weight, 40,000—50,000). MMA and other monomers were purified by the usual method and redistilled before use. Copper(II) chloride was of special commercial grade and used without further purification. Water was ion-exchanged and distilled.

Procedures

The polymerization was carried out in a sealed tube under vacuum, after thawing with nitrogen, with shaking at 85°C in the dark. After a definite time, the contents of the tube were poured into a large amount of methanol to precipitate the polymer. The collected polymer was thoroughly washed with methanol. By elemental analysis and IR, the polymer was confirmed to contain no PLG-Na and was regarded as homopoly(MMA). Thus, no grafted copolymerization of MMA onto PLG-Na was observed. The conversion was calculated by the following equation:

$$(\text{weight of polymer} / \text{weight of feeded monomer}) \times 100$$

The number-average degrees of polymerization ($\bar{P}_n$) of poly-MMA were calculated by Welch's equation,⁷ from $[\eta]$ measured at 30°C in benzene.

Preparation of Buffer Solution

Buffer solutions were prepared as follows: pH 2, (M/10) sodium citrate-(M/10) HCl; pH 3–7, (M/10) citric acid-(M/5) $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$; pH 8, (M/15) $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ -(M/15) KH_2PO_4 ; pH 9, (M/15) KH_2PO_4 -(M/20) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$; pH 10, (M/20) $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ -(M/10) NaOH; pH 11, (M/10) NaOH-(M/10) $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$.

RESULTS AND DISCUSSION

Effect of pH of the Aqueous Solution on the Conversion of MMA

The polymerizations of MMA with PLG-Na were carried out at various pH in the aqueous solution. pH adjustments were made by the buffer solutions. As can be seen in Figure 1, the polymerization took place only in an acidic medium but not in neutral or basic media.

Figure 1. Conversion of MMA vs. pH of the aqueous solution: MMA, 5 cm³; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 5×10^{-4} g; buffer solution, 10 cm³; 85°C; 5 h.

The ineffectiveness of PLG-Na in alkaline and neutral media is considered due to the following three reactions.

i) PLG-Na is known to form an α -helix conformation more easily than poly(L-glutamic acid) (PLGA).⁸

On the other hand, Fujie and Kawai⁹ studied the polymerization of MMA at 70°C in the presence of poly(α -amino acid) and copper(II) ion and found

that if poly(α -amino acid) has the α -helix conformation, the polymerization does not proceed, and in the cases of the random coil and β -conformations the polymerization occurs to a greater extent. These results are due to the ease of formation of the Cu(II) ion complex with poly(α -amino acid) having the β -conformation. Accordingly, in the present case, the formation of an adequate complex of Cu(II) ion with PLG-Na becomes more difficult than that with PLGA.

ii) As described in an earlier section, even if PLG-Na can bind with Cu(II) ion, the composition of the complex becomes that of $(\text{Glu})_3\text{Cu(II)}$, which has no capacity to initiate the polymerization.

iii) As will be shown later by scanning electron microscopy, PLG-Na cannot form any hydrophobic areas.

Hereinafter, the polymerizations were carried out in the aqueous solution buffered at pH 2.

Effect of the Mass of Cu(II) Ion on the Conversion of MMA

Figure 2 shows the effect of the mass of Cu(II) ion on the conversion of MMA. As can be seen, in the case of pH 2, a maximum conversion of MMA was obtained at 5×10^{-4} g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. From the figure, it was concluded that the Cu(II) ion could promote the polymerization of MMA.

Figure 2. Conversion of MMA vs. mass of copper(II) chloride: MMA, 5 cm³, PLG-Na 0.1 g; aqueous solution, 10 cm³; 85°C; 5 h.

Selectivity for Vinyl Monomer

In order to observe the selectivity for vinyl monomer in the polymerization, by PLG-Na, copper(II) chloride, with a pH 2 buffer solution, polymeri-

zations of three kinds of vinyl monomer were carried out.

As shown in Table I, the polymerization of MMA was accelerated by PLG-Na in the pH 2 buffer solution containing Cu(II) ion, while the polymerization of styrene (ST) and acrylonitrile (AN) were not.

Table I. Selectivity of vinyl monomer^a

PLG-Na/g	Conversion/%		
	MMA	ST	AN
0.1	6.20	4.34	0.82
0	1.49	3.77	0.68

^a Vinyl monomer, 5 cm³; CuCl₂·2H₂O, 5 × 10⁻⁴ g; pH 2 buffer solution, 10 cm³; 85°C, 5 h.

Proof of Radical Mechanism

In order to confirm that polymerization proceeded through a radical mechanism, copolymerizations of MMA(M₁) with ST(M₂) were carried out and the results are shown in Figure 3. From the curve, *r*₁ and *r*₂ were calculated to be 0.57 and 0.56, respectively. A radical mechanism was verified from these results.

Figure 3. Copolymerization of MMA with St: (MMA+ST); 3 cm³, PLG-Na 0.1 g; CuCl₂·2H₂O, 5 × 10⁻⁴ g; pH, 2 buffer solution, 10 cm³; 85°C, 5 h.

Effect of the Amount of MMA on the Polymer Yield

Keeping the concentration of PLG-Na and CuCl₂·2H₂O constant, and varying the mass of MMA, polymerizations were carried out. The effect of the mass of MMA on the polymer yield and $\bar{P}_n$ of poly(MMA) were shown in Figure 4. The corrected

Figure 4. Effect of the mass of MMA on the polymer yield: CuCl₂·2H₂O, 5 × 10⁻⁴ g; pH 2 buffer solution, 10 cm³; 85°C, 5 h; PLG-Na, 0.1 g (○, ●, ○) and 0 g (●).

yield, estimated by deducting the thermal yield from the overall yield, became independent of the mass of MMA, beyond a certain period in which the polymer yield increased with the mass of MMA. Such a figure is usually obtained in the “uncatalyzed polymerization” of MMA initiated with macromolecule. On the other hand, $\bar{P}_n$ of poly(MMA) increased up to a certain mass of MMA, and became independent beyond that mass.

Effect of the Mass of PLG-Na on the Conversion of MMA

The results obtained in the study of the effect of the mass of PLG-Na on the polymerization of MMA are shown in Figure 5. In this figure, a remarkable observation was the decrease in the conversion of

Figure 5. Conversion of MMA vs. mass of PLG-Na: MMA, 5 cm³; CuCl₂·2H₂O, 5 × 10⁻⁴ g; pH 2 buffer solution, 10 cm³; 85°C, 5 h.

MMA when the dissolved mass of PLG-Na exceeded a certain limit. Such a phenomenon was also recognized in the polymerization of MMA in the aqueous starch solution.¹⁰ Such a decrease in the

Figure 6. Conversion of MMA vs. added volume of PLG-Na solution: MMA, 5 cm³; CuCl₂ · 2H₂O, 5 × 10⁻⁴ g; 85°C; 5 h. O, the pH 2 buffer solution containing 10⁻² g dm³ of PLG-Na; ●, the pH 2 buffer solution containing no PLG-Na.

conversion is considered due to the increased entanglement of PLG-Na molecules, making formation of adequate hydrophobic areas (HA) difficult. MMA are incorporated into the HA and there the polymerization commences.

Thus by maintaining the concentration of PLG-Na solution at 10⁻² g dm³, and changing the added volume of PLG-Na solution, the polymerization of MMA was carried out. The results obtained in Figure 6 show that the conversion of MMA increased linearly with the added volume of PLG-Na solution; this figure supports the considerations mentioned above.

Surface View of Polymerization System by Electron Microscopy

Direct evidence of the formation of HA was obtained by scanning electron microscopy (SEM). The SEM procedure was the same as that reported in a previous paper.¹⁰ In Figure 7(B), the formation of HA can be observed. However, it is clear that in the case of Figure 7(A), HA is not formed.

(A) pH 8.3

(B) pH 2

Figure 7. Surface views of PLG-Na in pH 8.3 and 2.

(A) 0.1 g of PLG-Na was dissolved in 10 cm³ of water containing 5 × 10⁻⁴ g of CuCl₂ · 2H₂O, warmed at 85°C for 3 h and diluted with 1 dm³ of H₂O.

(B) 0.1 g of PLG-Na was dissolved in 10 cm³ of pH 2 buffer solution containing 5 × 10⁻⁴ g of CuCl₂ · 2H₂O, warmed at 85°C for 3 h and diluted with 1 dm³ of H₂O.

Mechanism of Initiation

In order to study the necessity of PLG-Na as a macromolecule, monomeric glutamic acid and sodium glutamate were used, instead of PLG-Na. As listed in Table II, glutamic acid and sodium glutamate could not initiate the polymerization of MMA. Thus, it was confirmed that the uncatalyzed polymerization could be initiated only by a macromolecule.

To confirm the formation of the complex of Cu(II) ion with PLG-Na, electrical conductivity and UV spectra were measured by a Yanagimoto conductometer (Type MY-8) and a Simadzu double beam spectrophotometer (Type UV-200), respectively.

Table II. Polymerization of MMA in the presence of Glu compound^a

Glu compound	Conversion/%	
	In pH 2 buffer solution	In water (pH 8.3)
PLG-Na	6.20	3.04
Glutamic acid	1.93	0.65
Sodium glutamate	1.81	1.30

^a MMA, 5 cm³; glutamic acid compound, 6.62×10^{-4} mol; CuCl₂·2H₂O 5×10^{-4} ; aqueous solution, 10 cm³; 85°C; 5 h.

Figure 8 shows the results of electrical conductivity. From this figure, it is clear that the Cu(II) ion is bonded to PLG-Na.

Figure 8. Electrical conductivity of CuCl₂ in aqueous PLG-Na solution at room temperature.

^a [CuCl₂] = 3×10^{-3} g dm⁻³.

^b 30 cm³ of PLG-Na at 1×10^{-3} g dm⁻³.

^c 30 cm³ of H₂O.

Figure 9. Analysis by the continuous variation method in water (pH 8.3); [PLG-Na] = [CuCl₂] = 1.16×10^{-3} mol cm⁻³, in H₂O at room temperature.

Moreover, the results of UV spectra obtained by continuous variation method are shown in Figure 9. As can be seen in this figure, the maximum absorbance in water (pH 8.3) appeared at the mole ratio of 1:3 of Cu(II): unit of PLG-Na; the complex of ratio of 1:3 was suggested to be formed; three coordination sites of Cu(II) ion are considered to be filled, as shown in following structure. The initiation mechanism in the present polymerization can be written as eq 1. Since, in the pH 8.3 medium, it was difficult to keep open vacant sites for MMA and water, the complex lost its catalytic activity, as was reported in the case of using nylon 3.³

Polymerization by PMAA

In order to find out directly the action of the

Figure 10. Polymerization of MMA with PMAA: MMA, 5 cm³; PMAA-Na 0.0835 g; aqueous solution, 10 cm³; 85°C; 5 h.

COONa group, the polymerization of MMA was carried out using sodium poly(methacrylic acid) (PMAA) whose main chain consists of $\text{CH}_2\text{-C}(\text{CH}_3)$ bonds. The results obtained are shown in Figure 10. from this figure, it is clear that PMAA has the ability

to initiate polymerization.

Therefore, in the case of using PLG-Na, the polymerization of MMA is also considered to be initiated by a mechanism (2) other than the mechanism (1) described above.

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