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RADICAL POLYMERIZATION OF METHYL METHACRYLATE INITIATED WITH THE SYSTEM OF SODIUM CHONDOROITIN SULPHATE, Cu(II)-ION AND WATER*

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It was found that an aqueous solution of sodium chondroitin sulphate (ChS-Na) can initiate a radical polymerization of methyl methacrylate (MMA) in the presence of Cu(II)-ion. The kinetic behavior with respect to ChS-Na and MMA was studied. The initiation mechanism was considered to be as follow: ChS-Na forms a hydrophobic area in water. MMA is incorporated into the area, where the complex of ChS/Cu(II)-ion/MMA/H_2O generates free radicals of MMA, which initiate the polymerization.

Introduction

From the standpoint of the pollution, the effect of metallic ion on the vital issues is nowadays one of most important problems. Metallic ion is easily incorporated into the living body, particularly in peptide and not only behaves as metal containing enzyme, but also exists as free ion. Accordingly, the present authors are very much interested in the catalytic reactions with some appropriate compounds by the metal complex of the vital substance. The present paper concerns with the radical polymerization of methyl methacrylate (MMA) by the system of sodium chondroitin sulphate (ChS-Na), Cu(II)-ion and water. Chondroitin sulphate is known as a principal constituent of animal bones.

Experimental and Discussion

Reagents: ChS-Na was of commercial grade, prepared by Tokyo Kasei Kogyo Co; $[\alpha]_D^{23}$ -21.7°. MMA was purified by the usual method and distilled just before use. Water was ion-exchanged and distilled. Cupric chloride was of special grade and used without further purification.

Procedures: The reactants were placed in a tube and sealed under vacuum after thawing with nitrogen. The tube was shaken in a thermostat. After reaction, the contents were poured into methanol to precipitate the polymer. Conversion of MMA was calculated as follows:

$$\text{Conversion in \%} = \frac{\text{Polymer in g} - \text{ChS-Na in g}}{\text{Feeded MMA in g}} \times 100$$

Homopolymer was extracted with benzene from the polymer produced for 50 h, using Soxhlet extractor. Grafting efficiency of MMA onto ChS-Na was calculated by the following equation.

$$\text{Grafting Efficiency in \%} = \frac{\text{Polymer produced in g} - \text{Extracted homopoly-MMA in g}}{\text{Polymer produced in g}} \times 100$$

Effect of the Feeded Amount of $CuCl_2$ on the Conversion of MMA

As shown in Fig. 1, ChS-Na could initiate a polymerization of MMA in water solution. Cu(II)-ion is a necessary reagent for the polymerization of MMA.

Effect of the Amount of Water on the Conversion of MMA

The results obtained were shown in Fig. 2. From these results, it was clear that water was an indispensable agent.

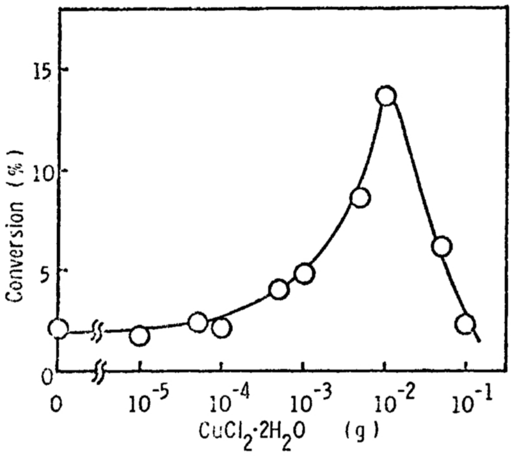


Fig. 1. Conversion of MMA vs. Amount of $CuCl_2 \cdot 2H_2O$. (MMA 3 cm^3, ChS-Na 0.1 g, H_2O 10 cm^3; 85°C, 3 h)

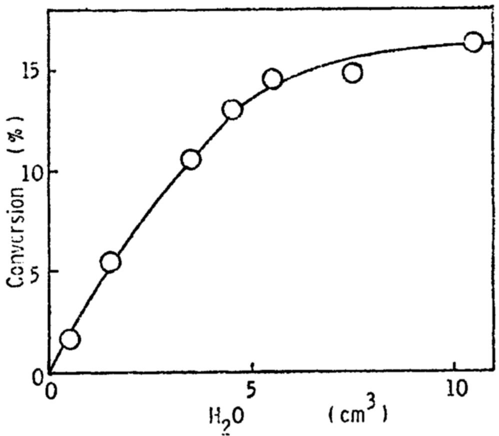


Fig. 2. Conversion of MMA vs. Amount of Water. (MMA 3 cm^3, ChS-Na 0.1 g, $CuCl_2 \cdot 2H_2O$ 10^{-2} g; 85°C, 3 h)

Proof of Free-radical Mechanism

The copolymerization of MMA with styrene (St) was carried out. The result is shown in Fig. 3. This suggests that the polymerization proceeds through a free-radical mechanism.

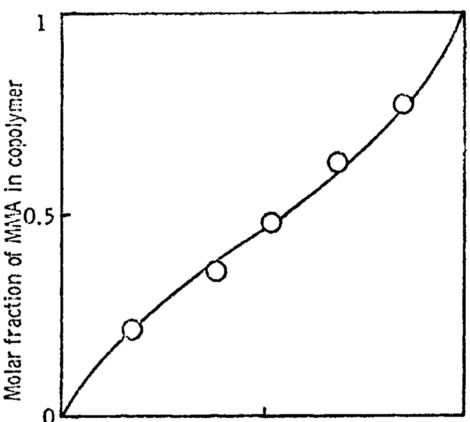


Fig. 3. Copolymerization of MMA (M_1) with St(M_2). ((MMA + St) 3 cm^3, ChS-Na 0.1 g, $CuCl_2 \cdot 2H_2O$ 10^{-2} g, H_2O 10 cm^3; 85°C, 3 h)

Estimation of Overall Activation Energy

The polymerizations were carried out at 70~90°C and the time-conversion curves shown as Fig. 4 were obtained. The rates of polymerization (R_p) calcualted from the inclinations of the lines were applied to Arrhenius equation, and Fig. 5 was obtained.

From the figure, the overall activation energy, E_a, was calculated to be 39.6 kJ mol^{-1}.

Effects of Feeded Amount of ChS-Na on the Conversion of MMA and Degree of Polymerization of Poly-MMA.

With the feeded amounts of MMA, Cu(II)-ion and water kept constant, the amount of ChS-Na was varied. The results obtained were shown in Fig. 6. As can be seen from this figure, exceeding 0.4 g of ChS-Na, the conver-

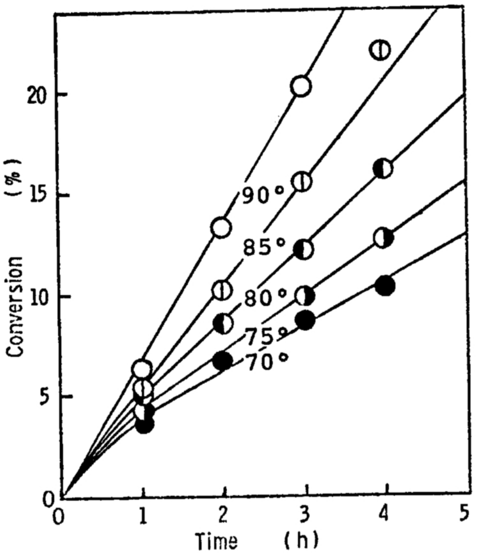


Fig. 4. Time-conversion Curves at 70-90°C. (MMA 3 cm^3, ChS-Na 0.1 g, $CuCl_2 \cdot 2H_2O$ 10^{-2}g, H_2O 10 cm^3)

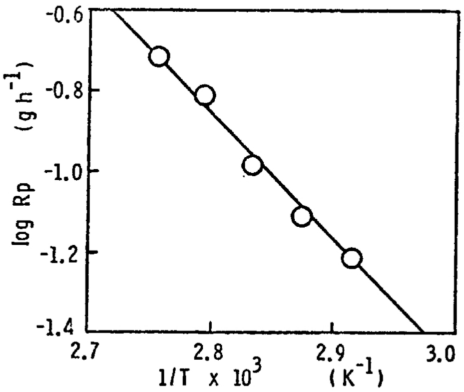


Fig. 5. Arrhenius Plots.

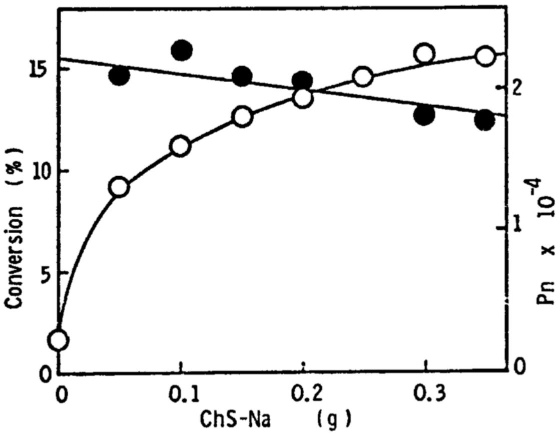


Fig. 6. Conversion of MMA or $\bar{P}_n$ of Poly-MMA vs. Amount of ChS-Na. (MMA 3 cm^3, $CuCl_2 \cdot 2H_2O$ 10^{-2}g, H_2O 10 cm^3 ; 85°C, 3 h)

sion of MMA approached gradually to the limit of 15.5%. This tendency was observed also in the polymerization of MMA when α-amylase[1)] or starch[2)] was used instead of ChS-Na. The reason was explained by the following consideration: the first step of the so-called "uncatalyzed polymerization" is the formation of hydrophobic area in the aqueous phase by the the macromolecule, i. e., ChS-Na. The second step is the incorporation of MMA into the area.[3)] Then the polymerization reaction begins. When the concentration of ChS-Na is too high, ChS-Na entangles with itself and becomes difficult to form adequate hydrophobic area. Accordingly, too large concentration of ChS-Na in water is not appropriate for the polymerization. Apparent grafting efficiency increased with the amount of ChS-Na, as shown in Fig. 7. Grafting may occur by the H· abstraction from ChS-Na with the produced free-radical.

The degrees of polymerization (P_n) of extracted homopoly-MMA has a slight tendency to decrease with the increase of ChS-Na.

Effect of Feeded Amount of MMA on the Conversion of MMA

With the feeded amount of ChS-Na, Cu(II)-ion and water kept constant, the amount of MMA was varied. The results obtained were shown in Fig. 8. The curve in this figure is very much similar to that in the enzymatic reaction. Therefore, Michaelis-Menten relationship, which was shown as Eq. (1), was applied.

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_3} E + P \qquad (1)$$

Here E,S and ES can be considered to be ChS-Na, MMA and a complex formed by E, S, Cu(II)-ion and water, respectively. From Eq. (1), Lineweaver-Burk's equation

(2) can be derived.

$$K_m = (k_2 + k_3)/k_1 \qquad \frac{1}{R_p} = \frac{K_m}{k_3[\mathrm{ChS\text{-}Na}]} \cdot \frac{1}{[\mathrm{MMA}]} + \frac{1}{k_3[\mathrm{ChS\text{-}Na}]} \qquad (2)$$

Using Eq. (2), k_3[ChS-Na] and K_m were estimated as 0.25 g h^{-1} and 1.24 g, respectively.

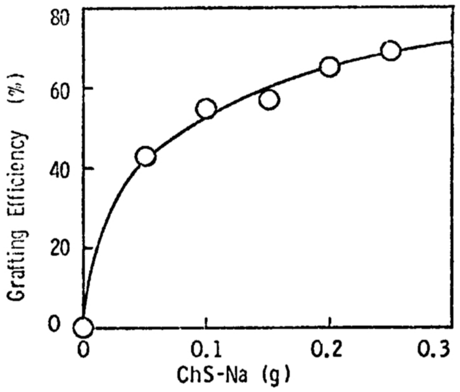


Fig. 7. Grafting Efficiency vs. Amount of ChS-Na.

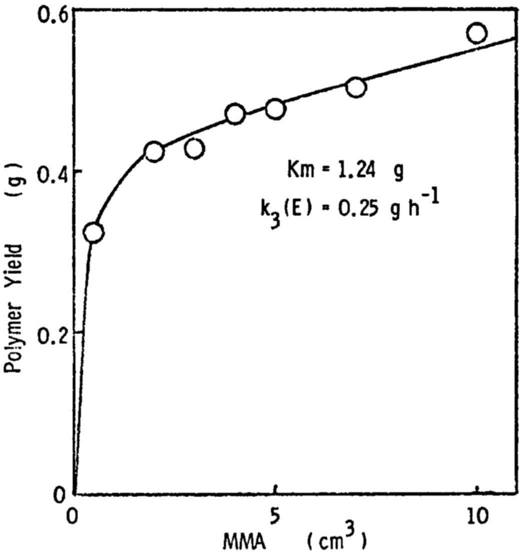
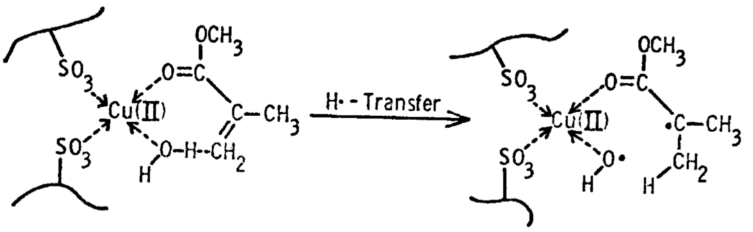


Fig. 8. Polymer yield vs. Amount of MMA. (ChS-Na 0.1 g, $CuCl_2 \cdot 2H_2O$ 10^{-2} g, H_2O 10 cm^3; 85°C, 3 h)

Furthermore, Fig. 8 suggests that the incorporation of MMA into the hydrophobic area reaches the saturation point rapidly; the space of the hydrophobic area is not so large.

Proposed Mechanism of Initiation

As shown in Scheme 1, the incorporated MMA molecule forms a complex with Cu(II)-ion, ChS-Na and water, and the radical species are generated through a hydrogen atom transfer water to monomer.



Scheme 1. Proposed Mechanism of Initiation

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* Part 370 of studies on vinyl polymerization; Part 369, see T. Ouchi, S. Kawanishi, H. Tsunoda, and M. Imoto, Tech. Rep. of Kansai Univ., in press.

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