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Vinyl Polymerization by Metal Complexes. XXXII.* Formation of Glycolchitosan-Copper(II) Complex and the Initiation of Vinyl Polymerization by Using the Complex

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ABSTRACT

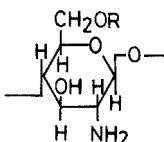
The formation of the water-soluble glycolchitosan-copper (II) complex was studied by ultraviolet and visible spectroscopy and by viscosity measurement. The structure of the polymer complex in question was found to change with pH value of the system. The glycolchitosan-copper (II) complex was active as a free-radical initiator for the polymerization of methyl methacrylate and acrylonitrile in the presence of carbon tetrachloride. The maximum conversion was observed at neutral pH, and was influenced by the presence of neutral salts. Relationship between the activity of the polymer complex for initiating the polymerization and its structure was discussed.

*For Part XXXI of this series, see Y. Inaki, M. Otsuru, and K. Takemoto, *J. Macromol. Sci.-Chem.*, A12, 953 (1978).

INTRODUCTION

In a previous paper, the polymerization of methyl methacrylate and acrylonitrile initiated by the chitosan-copper(II) complex and its monomeric form, glucosamine-copper(II) complex, in the presence of carbon tetrachloride has been reported [1]. The activity of the chitosan-copper(II) complex for initiating the polymerization was discussed in relation to its complex formation characteristics. However, as the chitosan and its copper(II) complex were insoluble in water in neutral and alkaline regions, difficulty was encountered in studying the structure of the complex in question by spectroscopic measurements.

In a subsequent investigation, a water-soluble chitosan derivative, that is, glycolchitosan was chosen to obtain more detailed information about the structure of chitosan-copper(II) complex by spectrophotometrical studies. The activity of the complex for initiating the polymerization is dealt with in detail in the present paper. Glycolchitosan is a 6-glycol derivative of chitosan which is soluble in water in neutral pH region.



EXPERIMENTAL

Commercial glycolchitosan was purified by reprecipitation from its aqueous solution into acetone. Glycolchitosan thus obtained contained still acetamide groups derived from original chitin. Free amino groups present in glycolchitosan were determined by pH titration to be 65% per unit pyranose ring.

The other reagents, including chitosan and vinyl monomers, were purified in the manner reported earlier [1].

pH titrations of glycolchitosan-copper(II) complex were made by using a Hitachi-Horiba pH meter at 25°C in a nitrogen atmosphere. The visible spectra were measured at 25°C by using a Hitachi type 124 spectrophotometer.

RESULTS AND DISCUSSION

pH Titration

At first, the glycolchitosan-copper(II) complex was studied by pH titration, UV and visible spectra, and viscosity measurements.

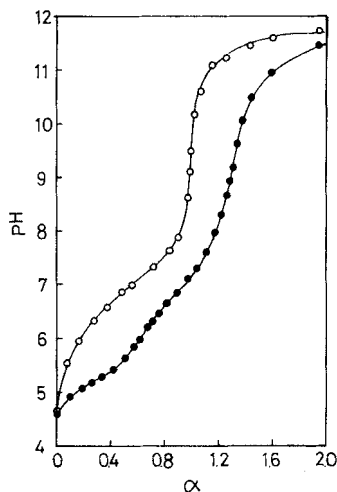


FIG. 1. pH titration curves at 25°C for the (\circ) glycolchitosan and (\bullet) glycolchitosan-Cu(II) systems. [Glycolchitosan] = 1×10^{-2} mole/liter; [Cu(II)] = 1×10^{-3} mole/liter; $\mu = 1.0$ (NaCl).

Glycolchitosan hydrochloride and its copper(II) complex were titrated with aqueous NaOH solution, which gave titration curves as shown in Fig. 1. The fact that a proton was released above $\alpha = 1$, where α denotes the degree of neutralization of amino group per glycolglucosamine unit, suggests the participation of hydroxyl groups in coordination. Below $\alpha = 1$, the modified Bjerrum plots [2] gave the average coordination number as $\bar{n} = 3$ only by coordinating to amino groups. The result was identical to that obtained in the case of chitosan-copper(II) system [1].

UV and Visible Spectra

In contrast to the chitosan-copper(II) system, the glycolchitosan-copper(II) complex was soluble in a wide pH range at low ionic concentration, which enables the spectroscopic investigation on the latter complex.

Visible spectra of the glycolchitosan-copper(II) system at different pH values are shown in Fig. 2. These spectra resemble those of the triethanolamine-copper(II) complex. The absorbance at 650 nm was

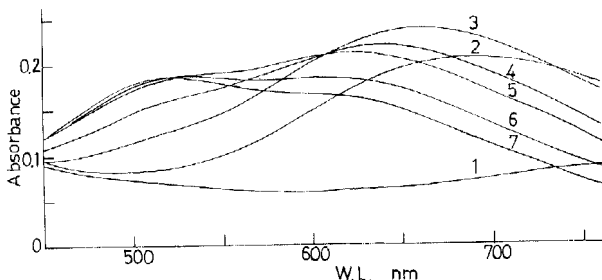


FIG. 2. Visible spectra of glycolchitosan-Cu(II) system at various pH: (1) pH 4.64; (2) pH 5.41 (3) pH 5.90; (4) pH 6.40 (5) pH 7.02; (6) pH 7.86; (7) pH 10.63-12.07.

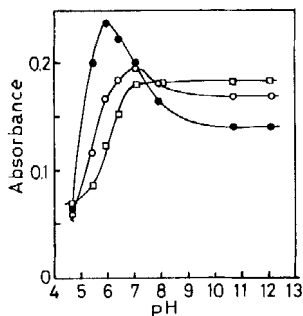


FIG. 3. Absorbance-pH relationships for the glycolchitosan-Cu(II) system: (□) 515 nm; (○) 570 nm; (●) 660 nm.

found to increase up to pH 5.9, which corresponds to the increase in the complex coordinated by amino groups of glycolchitosan. In the range between pH 6 and pH 7, this complex changed its form to that coordinated by both amino and hydroxyl groups. Above pH 7 up to pH 10, an additional hydroxyl group is considered to coordinate to copper(II) of the complex.

These changes in the structure of the glycolchitosan-copper(II) complex could also be shown clearly by plotting the absorbance against the pH, as shown in Fig. 3. The UV spectra of the copper(II) complex (Fig. 4) also suggested the presence of three kinds of copper(II) complexes. Up to pH 5.3, similar spectra were obtained. In the interval pH 5.7 to pH 7.0, the absorbances at 200 to 300 nm increased with increasing pH, and above pH 7.7, the spectra tended to have two peaks at 238 and 273 nm. Figure 5 shows that the change in the structure of the complex occurred at pH 6.

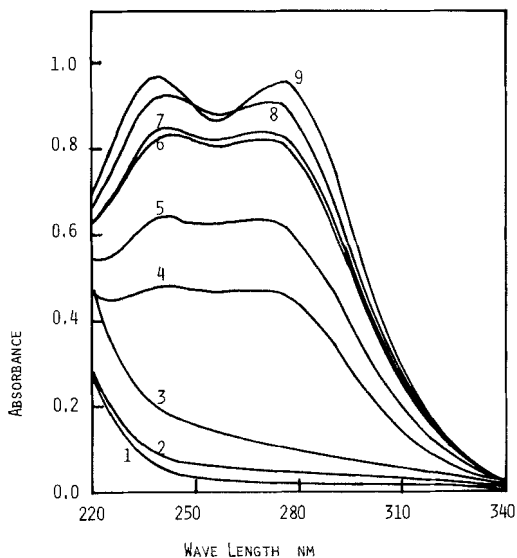


FIG. 4. Ultraviolet spectra of glycolchitosan-Cu(II) system at various pH: (1) 3.80; (2) 5.28; (3) 5.72; (4) 5.86; (5) 5.98; (6) 6.24; (7) 6.29; (8) 6.66; (9) 7.75, 10.07, 10.27, 11.26. [Glycolchitosan] = 1.6×10^{-3} mole/liter, [Cu(II)] = 2.0×10^{-4} mole/liter.

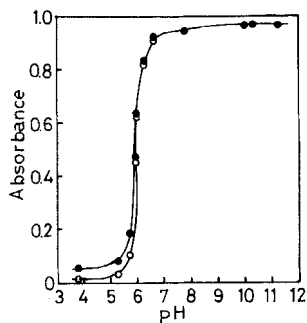


FIG. 5. Absorbance-pH relationships for the glycolchitosan-Cu(II) system: (○) 276 nm; (●) 238 nm.

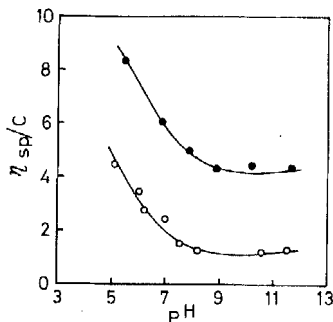


FIG. 6. Intrinsic viscosity-pH relationships for the glycolchitosan-Cu(II) system at 25°C: (●) glycolchitosan; (○) glycolchitosan-Cu(II). [Glycolchitosan] = 1.3×10^{-2} mole/liter, [Cu(II)] = 2.0×10^{-3} mole/liter.

The presence of the Cu-O band at 605 nm in the IR spectra was unfortunately not obvious because of overlapping of the absorption of glycolchitosan itself.

Viscosity of the Complex Solution

Figure 6 shows the relationship of intrinsic viscosity with pH values of the systems. At low pH, the viscosity of glycolchitosan is substantially high, suggesting its stretched conformation because the polymer consists of rigid glucosamine units in the main chain with positively charged $-\text{NH}_3^+$ units. With increasing pH values of the systems, the $-\text{NH}_3^+$ units changed to neutral $-\text{NH}_2$ units, and the viscosity tended to decrease, owing to a plausible structural change of the polymer to a more compact conformation. Addition of NaCl as a neutral salt caused lowering of the viscosity of glycolchitosan, suggesting a formation of more compact conformation, too, by repressing the electrostatic repulsion.

The character of the viscosity behavior of glycolchitosan-copper(II) complex in a wide pH region was similar to that of glycolchitosan itself, though the viscosity values were quite low. From the result, formation of intramolecular complexing of copper(II) for the case of glycolchitosan-copper(II) complex which leads to the more compact conformation as compared with the case of the polymer itself, may be considered.

In the presence of a neutral salt, the glycolchitosan-copper(II) complex precipitated in a rather neutral pH region, while the polymeric complex tended to be soluble above pH 9. The viscosity of the complex in the high pH region did not change by addition of a neutral salt, which suggests that no significant conformational change of the polymeric complex occurred.

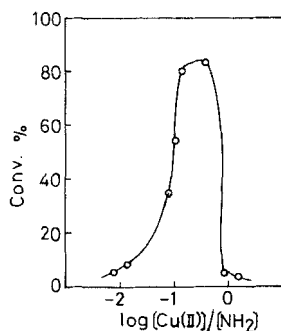


FIG. 7. Polymerization of methyl methacrylate initiated by the copper(II) complex in the presence of carbon tetrachloride at 60°C for 3 hr. [Glycolchitosan] = 3.3×10^{-2} mole/liter; [Cu(II)] = 2.5×10^{-4} to 7.5×10^{-2} mole/liter; CCl₄ = 0.2 ml; monomer = 2.0 ml; $\mu = 0$.

Vinyl Polymerization Initiated by Glycolchitosan-Copper(II) Complex

The glycolchitosan-copper(II) complex was found to initiate vinyl polymerization in aqueous solution in the presence of carbon tetrachloride. The system was active particularly for the polymerization of methyl methacrylate, acrylonitrile and styrene in that order, and in the case of the latter monomer, the polymerization was hardly initiated. Several factors affecting the initiation activity were studied.

The polymerization of methyl methacrylate was at first carried out in the presence of carbon tetrachloride, in which the concentration of glycolchitosan was kept constant and that of copper(II) was varied. Figures 7 and 8 show the relationship of the conversion at 60°C for 3 hr with the molar ratio of copper(II)/NH₂ units. Figure 7 shows the result of the polymerization in the absence of neutral salts, in which the pH values of the system have not been adjusted. The conversion showed a maximum about a molar ratio of 10^{-1} . A sharp decrease in the conversion observed at [Cu(II)]/[-NH₂] = 1 appears to be related to the decrease in pH values. Figure 8 shows the result in which the pH of the system was kept at 7 by adding a neutral salt also gave a maximum conversion about [Cu(II)]/[-NH₂] = 10^{-1} . The fact that maximum conversions of the polymerization exist suggests that the presence of sufficient amount of ligands is necessary for attaining the high activity.

The polymerization rate of methyl methacrylate was proportional to the first order of the concentration of glycolchitosan-copper(II) complex (Fig. 9). From the assumption of bimolecular termination,

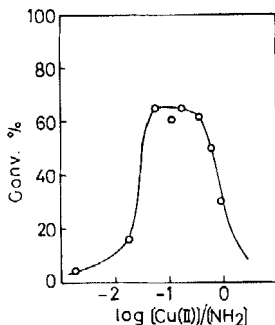


FIG. 8. Polymerization of methyl methacrylate initiated by the copper(II) complex in the presence of carbon tetrachloride at 60°C for 3 hr. [Glycolchitosan] = 2.2×10^{-2} mole/liter; [Cu(II)] = 3.8×10^{-5} to 1.9×10^{-2} mole/liter; CCl₄ = 0.2 ml; monomer = 2.0 ml; pH = 7, μ = 0.1 (NaCl).

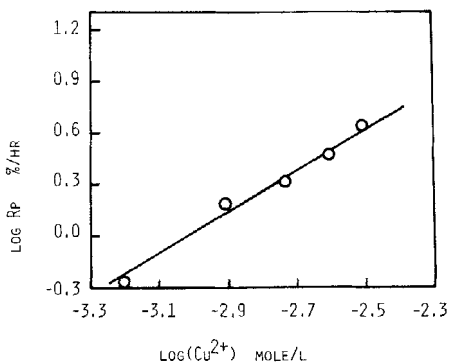


FIG. 9. Polymerization of methyl methacrylate initiated by the glycolchitosan-Cu(II) system at various Cu(II) concentrations. [Glycolchitosan]/[Cu(II)] = 5.8 molar ratio; CCl₄ = 0.2 ml; 60°C; 1.5 hr; pH = 7.3; μ = 0.1 (NaCl).

the rate of initiation should be proportional to the second order of the polymeric complex. Conversion increased with increasing amount of methyl methacrylate monomer, which reached a limiting value at about 1.5 ml of the monomer feed (Fig. 10). This feature is similar to that of the emulsion polymerization, and it appears that the maximum conversion is related to the maximum amount of free radicals formed from the initiator system.

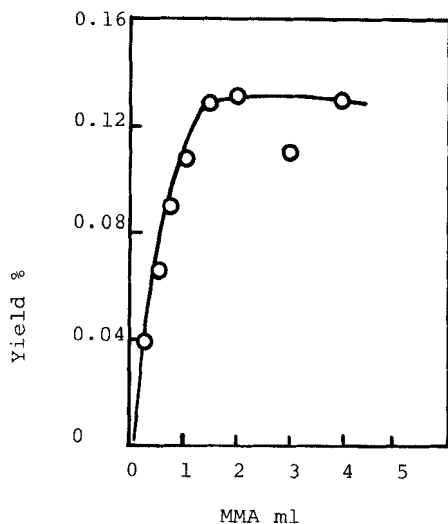


FIG. 10. Polymerization of methyl methacrylate initiated by the glycolchitosan-Cu(II) system at various monomer concentrations. $[\text{Glycolchitosan}] = 2.2 \times 10^{-2}$ mole/liter; $[\text{Cu(II)}] = 3.8 \times 10^{-3}$ mole/liter; $\text{CCl}_4 = 0.2$ ml; 60°C ; 1.5 hr; $\text{pH} = 7.3$; $\mu = 0.1$ (NaCl).

The effect of carbon tetrachloride on the polymerization behavior was studied at different pH regions, either in the presence or absence of neutral salt at 60°C (Figs. 11 and 12). While addition of a small amount of carbon tetrachloride accelerated the polymerization of methyl methacrylate, an excess of CCl_4 tended to cause the rate to decrease, which was explained as the result of decreasing the monomer concentration. Copolymerization of methyl methacrylate with styrene suggested a free-radical mechanism for the initiation by the glycolchitosan-copper(II)-carbon tetrachloride system (Fig. 13).

Finally, the polymerization of acrylonitrile and methyl methacrylate initiated by the glycolchitosan-copper(II) complex was carried out at 60°C for 3 hr at different pH values in the presence of carbon tetrachloride (Figs. 14 and 15).

In the case of acrylonitrile, the conversion was found to increase over pH 7, with increasing pH value, giving a small peak at pH 8. A small effect of the neutral salt on the conversion was observed at neutral pH.

Initiation Mechanism

From both the spectral and titrational results, it can be assumed that the glycolchitosan-copper(II) complex takes different forms at different pH regions as shown in Eq. (1).

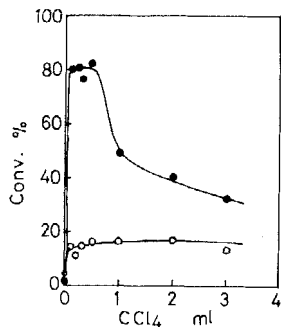


FIG. 11. Polymerization of methyl methacrylate initiated by the glycolchitosan-Cu(II) system at various CCl_4 concentrations (60°C , for 3 hr, at $\text{pH} = 6.8$): (\circ) $\mu = 0$; (\bullet) $\mu = 0.1$ (NaCl). [Glycolchitosan] = 3.3×10^{-2} mole/liter; [Cu(II)] = 5.0×10^{-3} mole/liter; monomer = 2.0 ml.

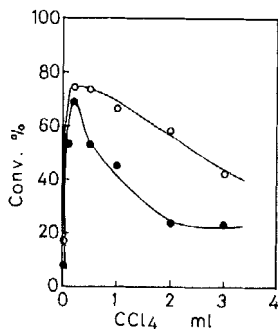


FIG. 12. Polymerization of methyl methacrylate initiated by the glycolchitosan-Cu(II) system at various CCl_4 concentrations (60°C , 3 hr, $\text{pH} = 12.3$): (\circ) $\mu = 0$, (\bullet) $\mu = 0.1$ (NaCl). [Glycolchitosan] = 3.3×10^{-2} mole/liter; [Cu(II)] = 5.0×10^{-3} mole/liter; monomer = 2.0 ml.

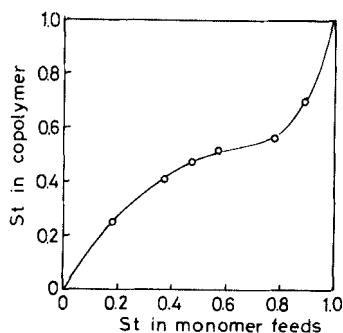


FIG. 13. Monomer-copolymer composition curve for the copolymerization of methyl methacrylate with styrene at 60°C for 1 hr. $[\text{Glycolchitosan}] = 2.2 \times 10^{-2}$ mole/liter; $[\text{Cu(II)}] = 3.8 \times 10^{-3}$ mole/liter; $\text{CCl}_4 = 0.5$ ml; total monomer = 1.5 ml, $\text{pH} = 7.3$, $\mu = 0.1$ (NaCl).

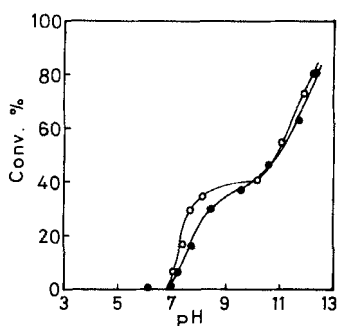


FIG. 14. Polymerization of acrylonitrile initiated by the glycolchitosan-Cu(II) system at various pH (60°C , 3 hr): (\circ) $\mu = 0$, (\bullet) $\mu = 0.1$ (NaCl). $[\text{Glycolchitosan}] = 3.3 \times 10^{-2}$ mole/liter; $[\text{Cu(II)}] = 5.0 \times 10^{-3}$ mole/liter; $\text{CCl}_4 = 0.5$ ml; monomer = 2.0 ml.

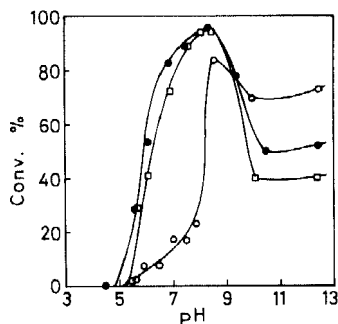
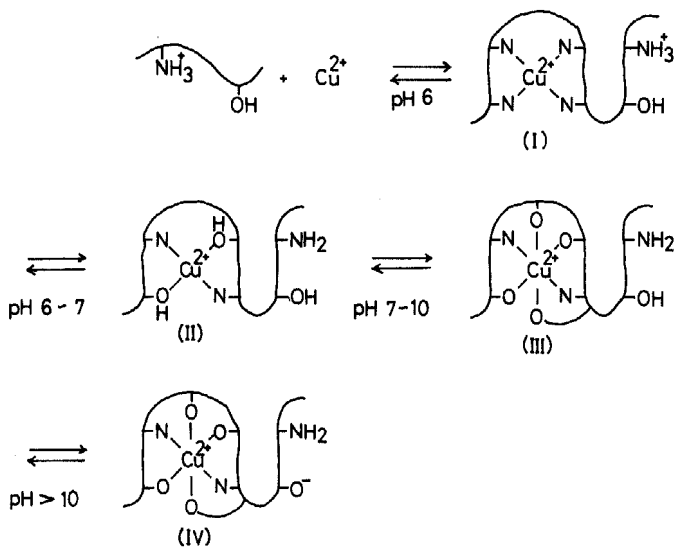
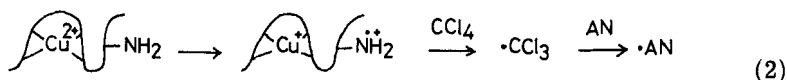


FIG. 15. Polymerization of methyl methacrylate initiated by the glycolchitosan-Cu(II) system at various pH (60°C , 3 hr): (\circ) $\mu = 0$; (\bullet) $\mu = 0.1$ (NaCl); (\square) $\mu = 0.4$ (NaCl). [Glycolchitosan] = 3.3×10^{-2} mole/liter; [Cu(II)] = 5.0×10^{-3} mole/liter; $\text{CCl}_4 = 0.5$ ml; monomer = 2.0 ml.



(1)

The initiation of acrylonitrile polymerization may be caused by interaction of the copper(II) complex with a free amino unit of glycolchitosan, followed by radical transfer to carbon tetrachloride to afford trichloromethyl radical, as shown in Eq. (2) [3].



High activity of the complex at high pH appears to be caused by a reaction of the complex with hydroxyl anion, as well as the case of the polymerization by polyvinylamine-copper(II) complex [4]. The scheme shown in Eq. (2) is supported by the results obtained in the case of polyvinylamine- and vinyl alcohol-vinylamine-copper(II) complexes [3, 4].

Conversion of the methyl methacrylate polymerization tended to increase from pH 5 and to decrease at higher pH regions after passing a maximum near pH 8. Activity of the copper(II) complex below pH 6 may be caused by the reaction of hydroxyl group and the copper(II) complex. The high activity at pH 8 may be caused in a similar way by a reaction of the hydroxyl group and the amino group with the copper(II) complex.

The difference in the conversion-pH relationship for the polymerization of methyl methacrylate (Fig. 15) from that for the polymerization of acrylonitrile (Fig. 14) seems to be caused by the difference

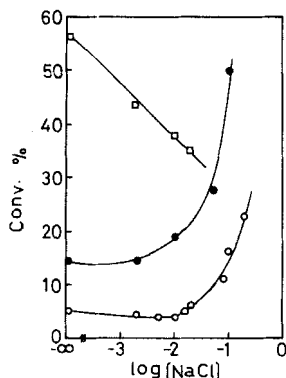


FIG. 16. Polymerization of methyl methacrylate initiated by the chitosan-Cu(II) system at various NaCl concentrations (60°C): (○) pH 6.3, 2 hr; (●) pH 6.6, 3 hr; (□) pH 11.8, 2 hr. [Glycolchitosan] = 3.3×10^{-2} mole/liter; [Cu(II)] = 5.0×10^{-3} mole/liter; CCl_4 = 0.5 ml; monomer = 2.0 ml.

TABLE 1. Polymerization of Methyl Methacrylate Initiated by Glycolchitosan-Cu(II)-CCl₄ in the Presence of Various Neutral Salts^a

Neutral salt	Conversion (%)
--	12.0
NaCl	67.0
KCl	51.2
NH ₄ Cl	55.5
NaNO ₃	60.0
NaClO ₄	51.0

^aGlycolchitosan, 1.3×10^{-4} mole; Cu(II), 2.0×10^{-5} mole; CCl₄, 0.5 ml; MMA, 2.0 ml; 60°C, for 3 hr; pH = 6.7, $\mu = 0.1$.

in the participation of the monomers in the initiation mechanism [4].

In Eq. (1) a conformational change in the polymer chain is to be noted. At acidic pH, the polymer may exist in an extended form due to electrostatic repulsion between -NH₃⁺ groups. Dissociation of the -NH₃⁺ groups to neutral -NH₂ groups with increasing the pH value changes the polymer to a coiled form which may accelerate the intra-chain reaction of the copper(II) complex with the free ligand.

By adding a neutral salt, the conversion increased markedly at neutral pH region, while the conversion decreased at high pH region (Figs. 15 and 16). At neutral pH, the neutral salt may act to depress the electrostatic repulsion between -NH₃⁺ groups and thus change the polymer chain to the coiled form. This was supported by the result of the viscosity measurement as shown in Fig. 6. At the neutral pH region, the glycolchitosan-copper(II) complex is soluble in water, but becomes insoluble in the presence of the neutral salt.

At high pH region, however, addition of the neutral salt caused a decrease in the conversion (Figs. 15 and 16). The glycolchitosan-copper(II) complex is soluble in water at high pH region regardless of the presence of the neutral salt, because of the dissociation of -OH groups to -O⁻ form. The viscosity data suggest that the conformation of the polymer complex at high pH region is similar to that at neutral pH, and that the conformational change by adding the neutral salt is small. Therefore, it should be assumed that the conformational change in the polymer chain is not responsible to the decrease in the conversion at high pH region in the presence of the neutral salt.

The spectral data of the glycolchitosan-copper(II) complex suggest the additional coordination of hydroxyl groups to copper(II) above pH 10. Above pH 10 such a rigid complex may lose the activity for the reaction with free amino or hydroxyl groups, resulting in a

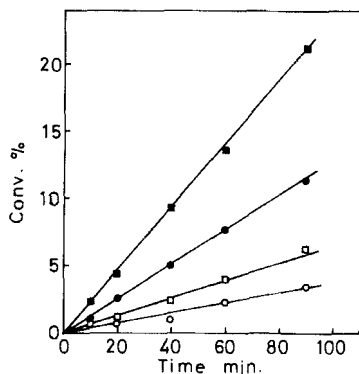


FIG. 17. Polymerization of methyl methacrylate initiated by the glycolchitosan-Cu(II) system at different temperatures: (○) 50°C; (□) 60°C; (●) 70°C; (■) 80°C. [Glycolchitosan] = 3.3×10^{-2} mole/liter; [Cu(II)] = 5.0×10^{-3} mole/liter; CCl_4 = 0.2 ml; monomer = 2.0 ml, pH = 6.9, μ = 0.

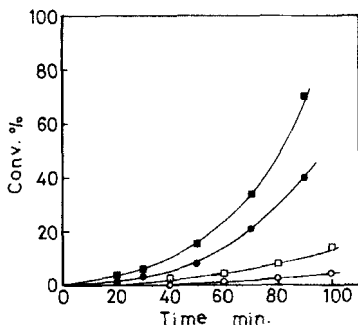


FIG. 18. Polymerization of methyl methacrylate initiated by the glycolchitosan-Cu(II) system at different temperatures: (○) 50°C; (□) 60°C; (●) 70°C; (■) 80°C. [Glycolchitosan] = 2.2×10^{-2} mole/liter; [Cu(II)] = 3.8×10^{-3} mole/liter; CCl_4 = 0.2 ml; monomer = 2.0 ml, pH = 6.9, μ = 0.1 (NaCl).

decrease in conversion at higher pH region, different at the neutral pH region. Addition of a neutral salt appears to make the complex assume a more rigid structure, thereby decreasing the activity for initiating the polymerization. Similar features were found when other types of neutral salts were added, as can be seen from Table 1.

Polymerization of methyl methacrylate was further carried out by

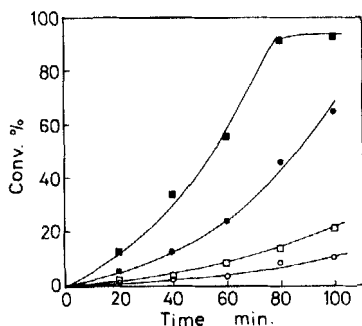


FIG. 19. Polymerization of methyl methacrylate initiated by the glycolchitosan-Cu(II) system at different temperatures: (○) 50°C; (□) 60°C; (●) 70°C; (■) 80°C. [Glycolchitosan] = 2.2×10^{-2} mole/liter; [Cu(II)] = 3.8×10^{-3} mole/liter; CCl_4 = 0.2 ml; monomer = 2.0 ml, pH = 11.5, μ = 0.

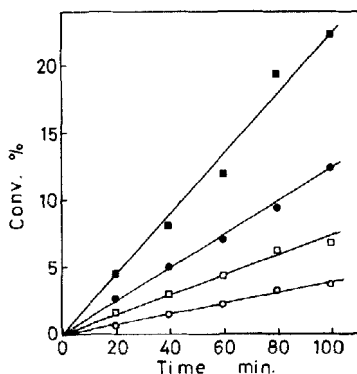


FIG. 20. Polymerization of methyl methacrylate initiated by the glycolchitosan-Cu(II) system at different temperatures: (○) 50°C; (□) 60°C; (●) 70°C; (■) 80°C. [Glycolchitosan] = 2.2×10^{-2} mole/liter; [Cu(II)] = 3.8×10^{-3} mole/liter; CCl_4 = 0.2 ml; monomer = 2.0 ml, pH = 11.5, μ = 0.1 (NaCl).

the glycolchitosan-copper(II) complex in the presence of carbon tetrachloride, at different temperatures. The relationship of the conversion with the polymerization time at pH 6.9, in the absence of the neutral salt gave straight lines (Fig. 17). In the case of addition of neutral salts, acceleration of the polymerization rate was observed with an elapse of time (Fig. 18). This fact suggests that the rate of

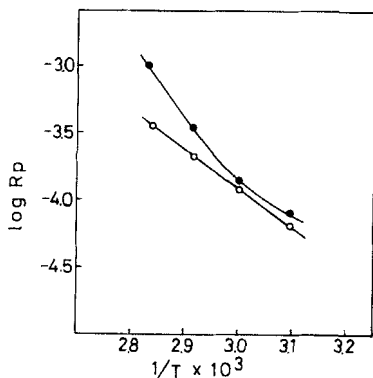


FIG. 21. Arrhenius plots for the polymerization of methyl methacrylate: (○) $\mu = 0.1$ (NaCl), (●) $\mu = 0$. [Glycolchitosan] = 2.2×10^{-2} mole/liter; [Cu(II)] = 3.8×10^{-3} mole/liter; $\text{CCl}_4 = 0.2$ ml; monomer = 2.0 ml, pH = 11.5.

initiation is faster than the rate of termination. The apparent activation energy was estimated from the results as 14.2 kcal/mole in the case of the absence of the neutral salt.

On the other hand, such an acceleration of the rate was observed at high pH region as 11.5, even in the absence of the neutral salt (Fig. 19). Arrhenius plots for the case with neutral salt, as shown in Fig. 20, gave an apparent activation energy of 12.8 kcal/mole (Fig. 21). In the case in which no neutral salt was present, deviation from the linear relationship was observed at higher temperatures, which suggests increase in the mobility of the polymer complex chain to cause an increase in the activity.

REFERENCES

- [1] Y. Inaki, M. Otsuru, and K. Takemoto, *J. Macromol. Sci.-Chem.*, **A12**, 953 (1978).
- [2] H. P. Gregor, L. B. Luttinger, and E. M. Loebel, *J. Phys. Chem.*, **59**, 34 (1955).
- [3] K. Kimura, Y. Inaki, and K. Takemoto, *Makromol. Chem.*, **176**, 2241 (1975).
- [4] K. Kimura, Y. Inaki, and K. Takemoto, *Makromol. Chem.*, **171**, 19 (1973).

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