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 Inaki, Yoshiaki , Otsuru, Masaaki and Takemoto, Kiichi(1978) 'Vinyl Polymerization by Metal Complexes. XXXI. Initiation by Chitosan-Copper(II) Complex', Journal of Macromolecular Science, Part A, 12: 7, 953 — 970

To link to this Article: DOI: 10.1080/00222337808069397

URL: http://dx.doi.org/10.1080/00222337808069397

J. MACROMOL. SCI.–CHEM., A12(7), pp. 953-970 (1978)

Vinyl Polymerization by Metal Complexes. XXXI.* Initiation by Chitosan-Copper(II) Complex

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ABSTRACT

The polymerization of methyl methacrylate and acrylonitrile can be initiated by the chitosan-copper(II) complex and its monomeric form, glucosamine-copper(II) complex, in the presence of carbon tetrachloride. The chitosan complex system was found to be more active for initiating the polymerization of methyl methacrylate than acrylonitrile at neutral pH. On the other hand, the glucosamine complex system showed no activity at neutral pH region, but had high activity at higher pH, because of the reducing endgroup of the glucosamine. Formation of the copper(II) complexes was studied by pH titration and visible spectroscopy. The relationship between complex formation and the activity for initiating the polymerization is discussed.

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*For Part XXX of this series, see K. Kimura, Y. Inaki, and K. Takemoto, Makromol. Chem., 178, 317 (1977).

INTRODUCTION

Chitosan is a polysaccharide consisting predominantly of unbranched chains of β-(1,4)-2-amino-2-deoxy-D-glucose residues. It can be readily obtained by hydrolysis from chitin, which exists naturally in fungi and arthropods, where it is a principal component in the exoskeletons [1]. Chitosan is regarded, therefore, as a cellulosic derivative and resembles cellulose in many of its properties. It is characterized by a rather nonflexible, pyranose ring structure of the main chain.

It has been reported earlier that copper(II) complexes of flexible, synthetic vinyl polymers such as polyvinylamine act as effective initiators for the free-radical polymerization of methyl methacrylate (MMA) and acrylonitrile (AN) in the presence of carbon tetrachloride, and the properties of such polymeric copper(II) complexes as well as their activities as polymerization initiators have been thoroughly studied [2].

This paper concerns a polymerization study of vinyl monomers initiated by chitosan-copper(II) complex in aqueous system in the presence of carbon tetrachloride, in order to see how the structure of the polymeric ligands reflects on their polymerization feature as compared with the cases in which flexible polymeric copper(II) complexes were used as the initiators.

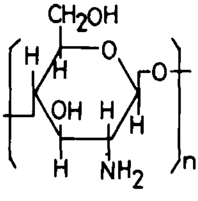
As chitosan contains both hydroxyl and amino groups, it can well be compared chemically with vinyl alcohol-vinylamine copolymer [3, 4] previously studied.

EXPERIMENTAL

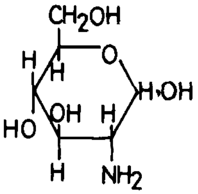
Materials

Chitosan was obtained from chitin of commercial origin by hydrolyzing with sodium hydroxide solution: Crude chitin was purified by Horowitz's method [5]. Impurities in the commercial chitin, that is, calcium carbonate, proteins, and colored matter were removed by treating it sequentially with 2 N hydrochloric acid, 10% sodium hydroxide, and 90% formic acid solution. The purified chitin thus obtained was washed thoroughly with water and dried in vacuo.

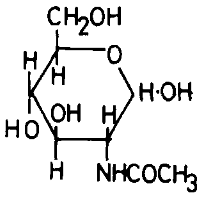
Chitin was hydrolyzed to chitosan by treating with aqueous sodium hydroxide solution at 150°C for 1 hr. Acidification by hydrochloric acid afforded colorless chitosan hydrochloride precipitation. The polymer was further reprecipitated with the water-acetone system. The degree of deacetylation of the polymer was determined to be about 90% from its NMR spectrum in D_2O solution.



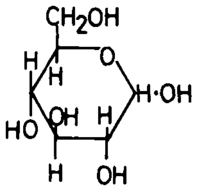
Chitosan



D-Glucosamine



N-Acetyl-D-Glucosamine



α-D-Glucose

Glucosamine, glucose, N-acetyl glucosamine, and inorganic reagents were of commercial origin and were used without further purification. Monomers as well as organic reagents were purified in the usual manner.

Polymerization

To 4 ml aqueous solution of chitosan hydrochloride and copper (II) chloride in each glass ampoule were added various concentrations of aqueous sodium hydroxide solution to form the chitosan-copper(II) complexes at different pH values. After standing overnight, 2 ml of vinyl monomer and 1 ml of carbon tetrachloride were added to the copper(II) complex system and the ampoule degassed and sealed off.

Polymerization was carried out at 60°C for 3 hr in a constant temperature bath with shaking and was stopped by cooling. Conversion was determined gravimetrically.

Titration and UV Measurement

pH titrations of the chitosan- and glucosamine-copper(II) complex systems were performed by using a Hitachi-Horiba pH meter at 25°C

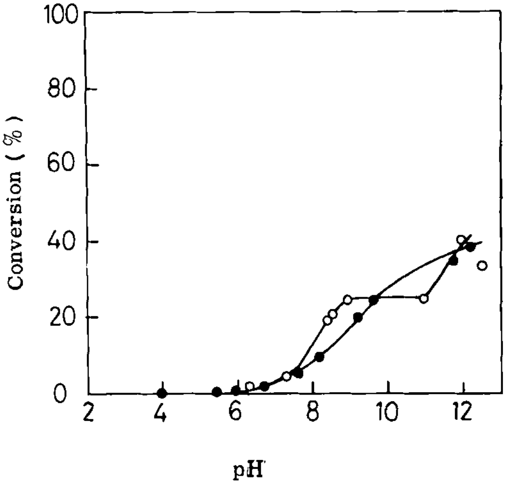


FIG. 1. Polymerization of acrylonitrile initiated by copper(II) complexes in the presence of carbon tetrachloride at 60°C for 3 hr: (○) chitosan-Cu(II)-CCl_4; (●) glucosamine-Cu(II)-CCl_4. [Amine] = 2×10^{-4} mole/liter; CCl_4 = 1.0 ml; monomer = 2.0 ml; [amine]/[Cu(II)] = 10.

in a nitrogen atmosphere [6]. The visible spectra were measured at 25°C by using a Hitachi type 124 spectrophotometer.

RESULTS AND DISCUSSION

pH Dependence

The polymerization of AN and MMA with the copper(II) complex systems at 60°C for 3 hr at different pH values in the aqueous layer was studied. Results of the polymerization are shown in Fig. 1, where the conversions after 3 hr are plotted against pH values of the aqueous layer. The chitosan-copper (II) complex was shown to be active at alkaline pH regions in the presence of carbon tetrachloride, and a characteristic activity was seen at pH 9.

The monomeric type complex, that is D-glucosamine-copper(II) also showed a similar activity for initiating the polymerization at alkaline pH regions in the presence of carbon tetrachloride. In this case, the conversion increased gradually with increasing in pH values.

The relationship between conversion and pH for the polymerization

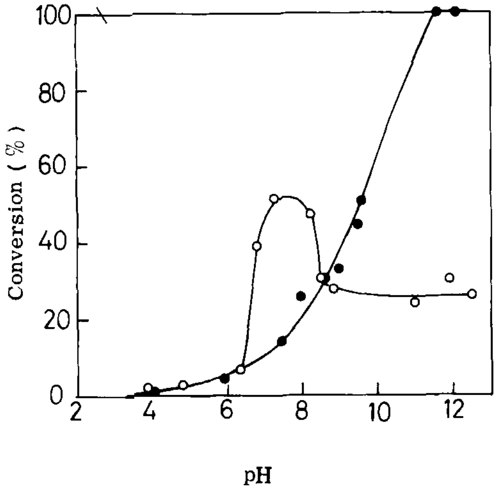


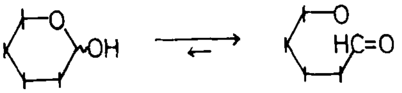
FIG. 2. Polymerization of methyl methacrylate initiated by copper (II) complexes in the presence of carbon tetrachloride at 60°C for 3 hr: (○) chitosan-Cu(II)-CCl_4; (●) glucosamine-Cu(II)-CCl_4. [Amine] = 2×10^{-4} mole/liter; CCl_4 = 1.0 ml; monomer = 2.0 ml; [amine]/[Cu(II)] = 10; μ = 1.0 (NaCl).

of MMA is shown in Fig. 2. In the case of the polymerization by the chitosan complex system, the conversion was found to increase steeply at pH 7 and decrease again at pH 9, above which the conversion seems to remain constant up to pH 13. On the other hand, conversion increased up to 100% with increasing pH values in the case of the glucosamine complex system. Such a high activity in the latter case is ascribed to the existence of the reducing endgroup of glucosamine structure which will be discussed later. The glucosamine complex system was more active for MMA than for AN polymerization. At the higher pH regions, this system was more active than the chitosan complex system, which has a much smaller amount of reducing endgroup than the glucosamine.

Effect of Reducing Endgroups on the Polymerization

Glucosamine is known to be present in the two forms in equilibrium [Eq. (1)], like those in the aldose-aldehyde sugars.

It was found that the rate of the equilibrium becomes larger at higher pH values of the system. Existence of only a trace amount of



(1)

aldehyde form would be active enough to serve as the reducing agent. It can well be assumed that a redox system consisting of such an equilibrium system containing aldehyde with copper(II) ion acts as an initiator system for vinyl polymerization.

In order to ascertain the effect of the reducing endgroups, α-methyl-D-glucose and N-acetylglucosamine were chosen besides glucose itself as a component of the initiator systems for the polymerization of MMA.

Figure 3 shows results of the MMA polymerization initiated by the N-acetylglucosamine-, glucose-, and glucosamine-copper(II) systems in the presence of carbon tetrachloride. The glucosamine-copper(II) system was found to have an extremely high activity for polymerization as compared with the glucose and N-acetylglucosamine systems, and the latter two systems showed about the same order of activity. This fact suggests that another factor is responsible for the activity for polymerization besides the presence of the reducing

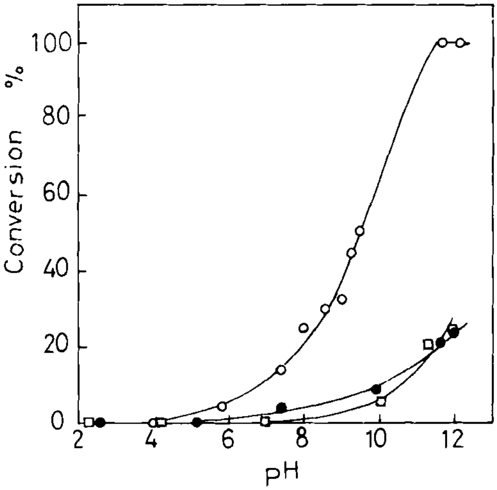


FIG. 3. Polymerization of methyl methacrylate initiated by sugar-copper (II) complexes in the presence of carbon tetrachloride at 60°C for 3 hr: (○) glucosamine-Cu(II)-CCl_4; (□) N-acetylglucosamine-Cu(II)-CCl_4; (●) glucose-Cu(II)-CCl_4. [Sugar] = 2×10^{-4} mole/liter; CCl_4 = 1.0 ml; monomer = 2.0 ml; [sugar]/[Cu(II)] = 10.

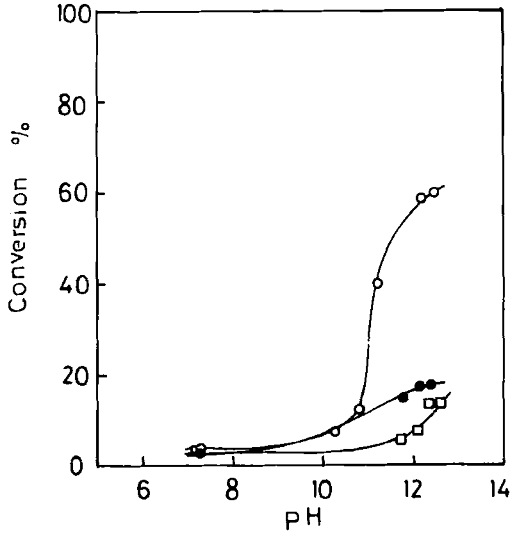


FIG. 4. Polymerization of methyl methacrylate initiated by copper (II)-trien complex in the presence of carbon tetrachloride at 60°C for 3 hr: (□) Cu(II)-trien-CCl_4; (○) α-glucose-Cu(II)-trien-CCl_4; (●) α-methylglucose-Cu(II)-trien-CCl_4. [Glucose] = 2×10^{-4} mole/liter; [Cu(II)] = 2×10^{-5} mole/liter; CCl_4 = 1.0 ml; monomer = 2.0 ml.

endgroup. The high activity of glucosamine observed may be attributed to the presence of both the ligand group, that is, amino group, coordinating to copper(II) and the reactive reducing group.

This assumption was also supported by the result shown in Fig. 4. The stable tetradentate triethylenetetramine (trien)-copper(II) complex is really inactive for the polymerization of MMA in the presence of carbon tetrachloride [7, 8]. However, if α-D-glucose was added to this trien-copper(II) complex system, the polymerization was much accelerated above pH 11, while no remarkable acceleration was observed in the case of adding α-methyl-D-glucose, which had no reducing endgroup. Thus the glucosamine system shown in Fig. 3 was found to be more active than the α-D-glucose-trien-copper(II) system, probably because glucosamine had both ligand and reacting group in the molecular structure.

Effect of Copper(II) Concentration on the Polymerization

The polymerization of MMA was then carried out at varying copper(II) concentrations and constant chitosan or glucosamine

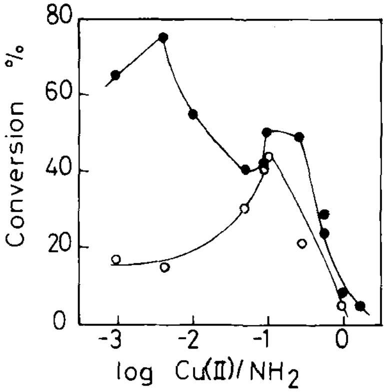


FIG. 5. Polymerization of methyl methacrylate initiated by copper (II) complexes in the presence of carbon tetrachloride at 60°C for 3 hr: (o) chitosan-Cu(II)-CCl_4; (●) glucosamine-Cu(II)-CCl_4. [Amine] = 2×10^{-4} mole/liter; CCl_4 = 1.0 ml; monomer = 2.0 ml.

concentration (Fig. 5). In these cases, equimolar sodium hydroxide was added both to the chitosan or glucosamine hydrochloride-copper(II) solutions to neutralize the systems, because of difficulty of keeping pH values constant at various copper(II) concentrations.

The chitosan-copper(II) system was found to show a maximal conversion at [Cu(II)]/[$-NH_2$ unit] = 10^{-1}, as seen in the case of the polyvinylamine-copper(II) system reported earlier [2]. The behavior observed here may suggest that the presence of an uncoordinated glucosamine unit in the chitosan molecule is necessary for generating active species for the polymerization. The glucosamine-copper(II) system showed also a peak of the conversion curve at [Cu(II)]/[$-NH_2$ unit] = 10^{-1}, and showed higher conversion at lower copper(II) concentration. This may be caused by higher pH value of the system under such reaction conditions.

Effect of Carbon Tetrachloride on the Polymerization

As can be seen from Fig. 6, carbon tetrachloride seems to play an important role in initiating the polymerization. Only a trace amount of carbon tetrachloride is enough for the initiation. Its role in the polymerization will be discussed later [9]. It should be noted here only that the initiating free radical is assumed to be trichloromethyl radical and not a free radical formed eventually in chitosan

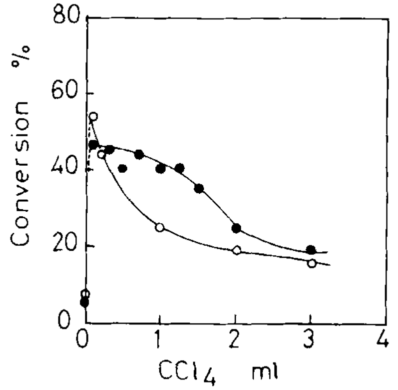


FIG. 6. Polymerization of methyl methacrylate initiated by copper (II) complexes in the presence of carbon tetrachloride at 60°C for 3 hr: (○) chitosan-Cu(II)-CCl_4; (●) glucosamine-Cu(II)-CCl_4. [Amine] = 2×10^{-4} mole/liter; monomer = 2.0 ml; [amine]/[Cu(II)] = 10.

structure; this is also supported by the following result. Poly-MMA obtained here was separated by extraction with benzene for 30 hr and further with toluene for 30 hr. The homopolymer constituted 98.65% of the product, and only 1.35% of the poly-MMA was obtained as a grafted form onto chitosan.

Effect of Neutral Salt on the Polymerization

It is generally known that polymeric electrolytes change their conformation on addition of some neutral salts in solution. A conformational change in the polymer chain could influence the activity of the polymeric copper(II) complex used for initiating the polymerization.

Figure 7 shows the results of the MMA polymerization initiated by the chitosan-copper(II)-carbon tetrachloride system with and without a neutral salt, that is, sodium chloride. The conversion was found to increase on adding NaCl at neutral pH values. This fact suggests the importance of the conformation of the polymeric copper(II) complex concerning its activity for polymerization.

Formation of the Copper(II) Complex

From the polymerization results mentioned above, it can be assumed that the formation of copper(II) complex is an important factor in initiation activity. The formation of the copper(II)

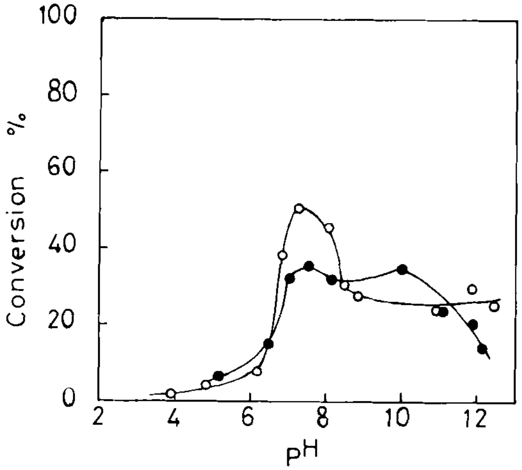


FIG. 7. Effect of neutral salt on the polymerization of methyl methacrylate initiated by chitosan-copper(II) complex in the presence of carbon tetrachloride at 60°C for 3 hr: (○) with NaCl; (●) without NaCl. [Chitosan] = 2×10^{-4} mole/liter; CCl_4 = 1.0 ml; monomer = 2.0 ml; [chitosan]/[Cu(II)] = 10.

complexes with glucosamine and chitosan was then studied by pH titrations and visible spectroscopy.

Glucosamine. pH Titration curves for the glucosamine-copper(II) system are given in Fig. 8. From the Henderson-Hasselbalch plots, the pK_a value of glucosamine was obtained as 7.73. In the case of the vinylamine-vinyl alcohol copolymer reported earlier [3], hydroxyl groups did not participate in coordination to copper(II). In the present case of glucosamine, however, treatment by considering this result afforded a divergent coordination number of amino units in the Bjerrum plots. Dissociation of protons was observed above α equal to unity, where α is the degree of neutralization based upon $-NH_2$ units. These facts indicate the participation of hydroxy units in coordinating to copper(II).

Visible spectra of the glucosamine-copper(II) system at various pH values are shown in Fig. 9. The maximum of the peak tended to shift to blue gradually with increasing pH of the system. The absorbances at 700, 615, and 550 nm in Fig. 9 were plotted against pH values to give Fig. 10. This figure suggests the formation of two kinds of copper(II) complexes.

From the results of the study on the 2-aminoethanol-copper(II) complex [10], one complex at lower pH region was estimated to be

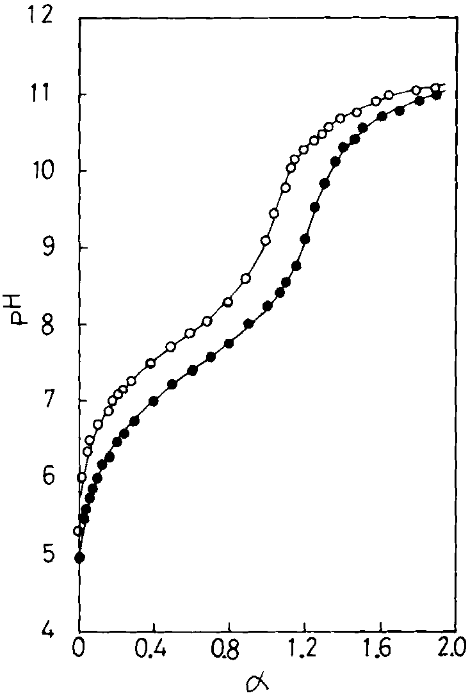


FIG. 8. pH titration curves at 25°C for the (○) glucosamine and (●) glucosamine-Cu(II) systems. [Glucosamine] = 2×10^{-3} mole/liter; [Cu(II)] = 2×10^{-4} mole/liter; $\mu = 1.0$ (NaCl).

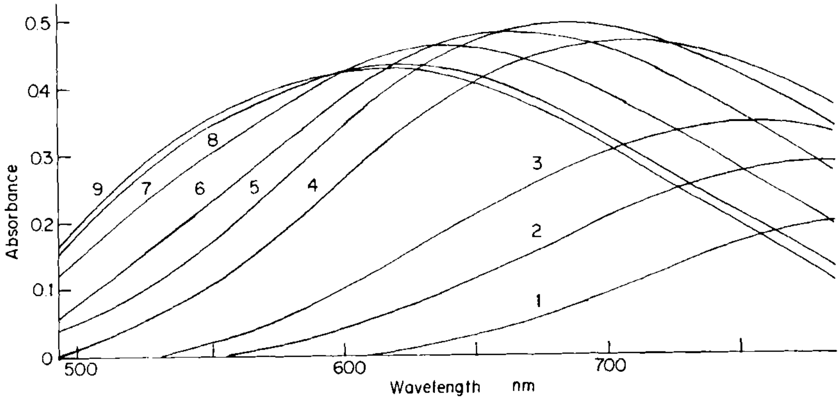


FIG. 9. Visible spectra of glucosamine-Cu(II) system at various pH: (1) pH 4.43; (2) pH 5.61; (3) pH 5.90; (4) pH 6.43; (5) pH 6.69; (6) pH 7.02; (7) pH 7.47; (8) pH 8.12; (9) pH 8.62-11.71.

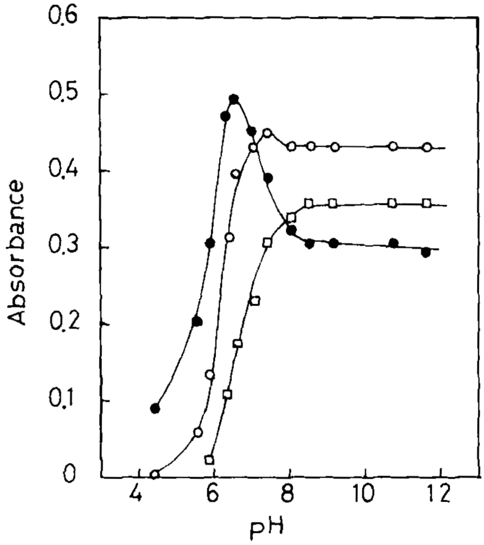
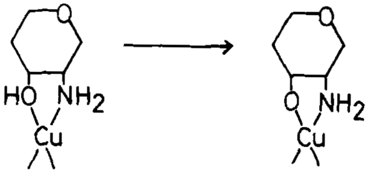


FIG. 10. Absorbance-pH relationships for the glucosamine-copper(II) system: (●) 700 nm; (○) 615 nm; (□) 550 nm.

coordinated by amino groups, and the other complexes at higher pH regions to be coordinated by both amino and hydroxy groups. The titration curve and the visible spectra show that the former complex coordinated by two amino groups is formed up to pH 6.5, and this complex changes its coordination by an amino and a hydroxy groups during pH 6.5 to pH 8.0 [Eq. (2)].



(2)

Chitosan. The titration curve of chitosan-copper(II) system was somewhat unique, as shown in Fig. 11. With increasing the degree of neutralization of amino groups, α, formation of the copper(II) complex was observed up to pH 5.0. The modified Bjerrum plots [11], as shown in Fig. 12 gave the average coordination number as $\bar{n} = 3$. After the copper(II) complex was formed by coordination with

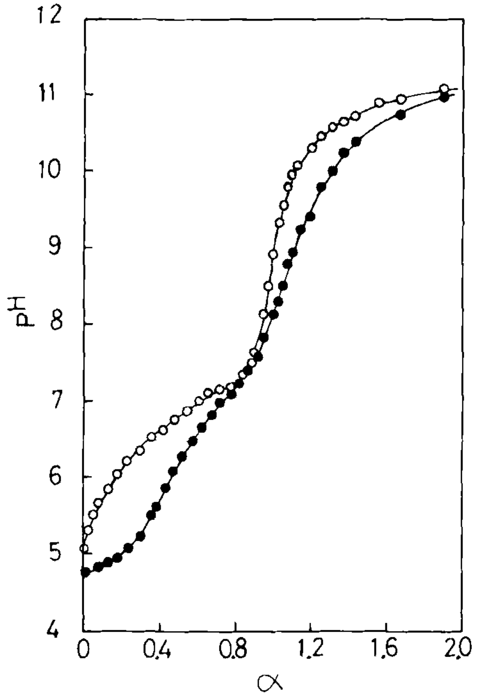


FIG. 11. pH titration curves at 25°C for the (○) chitosan and (●) chitosan-Cu(II) systems. [Chitosan] = 2 × 10^{-3} mole/liter; [Cu(II)] = 2 × 10^{-4} mole/liter; μ = 1.0 (NaCl).

three amine groups at pH = 5, free ammonium units uncoordinated to copper(II) began to dissociate to amine units with pK_a = 6.9, as shown by the Henderson-Hasselbalch plots (Fig. 13). With the increase of the degree of dissociation of $-NH_3^+$, the chitosan-copper(II) complex began to precipitate from pH = 5.5, probably because the polymer takes a compact conformation. At α = 1 about pH = 7.5, the titration curve of the chitosan-copper(II) system overlapped the curve of chitosan itself, which indicates apparently no complex formation. A probable reason for this anomalous fact is that undissociated ammonium units could be occluded in the polymeric copper(II) complex. Though the visible spectra of the chitosan-copper(II) complex could not be measured above pH = 5.5 because of precipitation, this can be reasonably estimated from the results on ethanolamine [10], glucosamine, and glycolchitosan [12]-copper(II) complex.

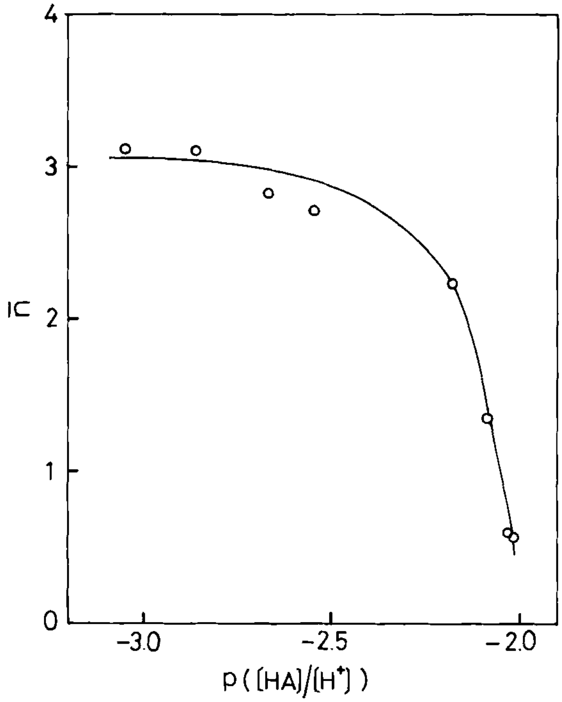


FIG. 12. Modified Bjerrum plots for chitosan-copper(II) system.

The complex coordinated by three amino groups changes its form to that coordinated by amino and hydroxy groups at neutral pH region. It is noteworthy that the pH value at $\alpha = 1$, where the titration curve of the chitosan-copper(II) complex overlapped that of chitosan itself, corresponds to high activity for initiating the MMA polymerization.

Initiation Mechanism

The initiation mechanism of the polymerization by the chitosan-copper(II) complex in the presence of carbon tetrachloride seems to be similar to that of the vinylamine-vinyl alcohol copolymer system [4] as shown in Fig. 14. Free amino units react with the copper(II) complex to afford amino free radicals, accompanied by the reduction of copper(II) to copper(I). The free radical generated then undergoes a transfer reaction to carbon tetrachloride to form trichloromethyl radical, which may initiate the polymerization of AN and MMA [9].

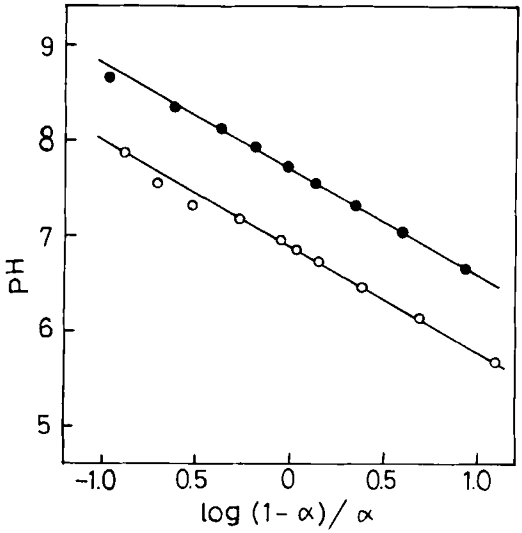


FIG. 13. Henderson-Hasselbalch plots for chitosan and glucosamine-copper(II) systems: (○) chitosan; (●) glucosamine. [Amine] = 2 × 10^{-3} mole/liter; μ = 1.0 (NaCl); 25°C.

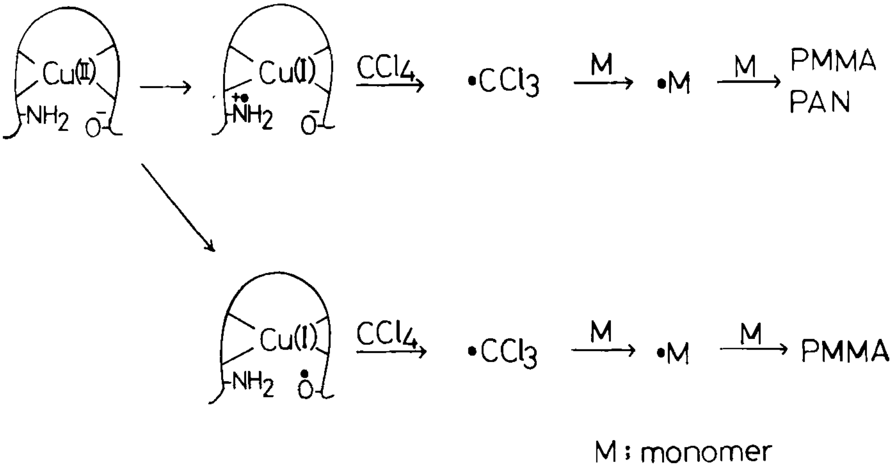
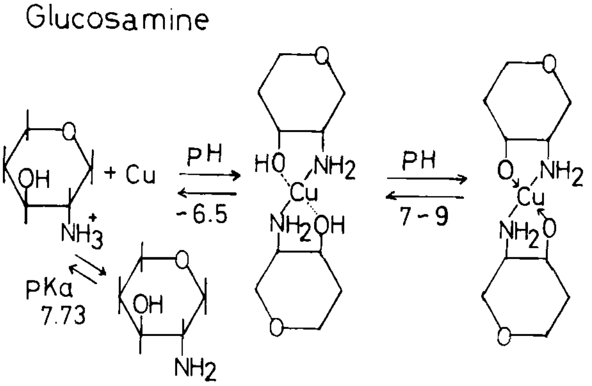


FIG. 14. Polymerization mechanism initiated by vinylamine-vinyl alcohol copolymer-copper(II)-carbon tetrachloride system.

The activity of these initiating systems should depend on the formation of the copper(II) complex as well as its structure and stability. The pH dependence of its initiation activity is also assumed to be related to these factors.

Based on the results of the titration and visible spectra, formation of the copper(II) complexes in relation to the pH value is illustrated in Eqs. (3) and (4) for the case of glucosamine and chitosan, respectively.



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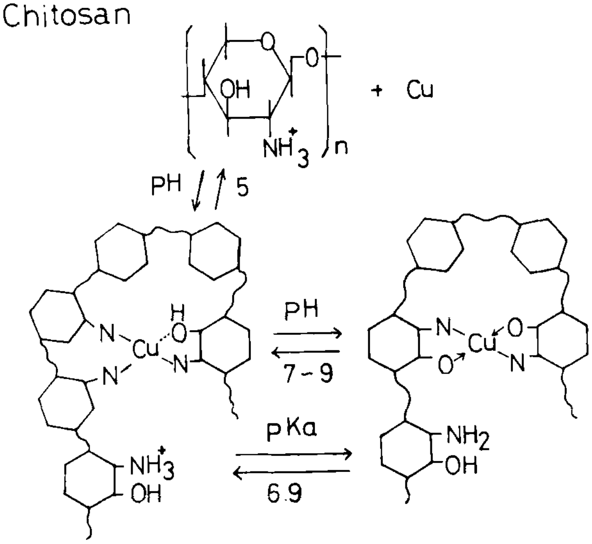

(4)

The glucosamine-copper(II) complex coordinated by two amino groups was formed from pH 4.0 to 6.5; however, the initiation of the polymerization could not be observed in this pH region. This complex was found to change its coordination to that by amino and hydroxy groups, and at the same time, free $-NH_3^+$ unit dissociated to $-NH_2$ unit with $pK_a = 7.73$, where increase of the conversion was observed. From these considerations, the primary free radical was assumed to be formed by a reaction of the copper(II) complex with free amino unit or by a redox reaction accompanying ligand substitution to give an amino free radical.

At higher pH, the predominant reaction would be a redox reaction of the reducing endgroup of glucosamine with the copper(II) complex. Such an intermolecular reaction occurs above pH = 11, as can be seen from Fig. 4. The high activity of the glucosamine-copper(II) system below pH 11 might be caused by an intramolecular reaction of the copper(II) complex with a reducing endgroup of the same molecule.

The chitosan-copper(II) complex coordinated by three amino units could be formed at pH = 5.0, though an initiating activity was not observed at this pH region. The complex in question changes its structure into a chelate type complex coordinated by both amino and hydroxy groups from pH range 7 to 9, while free $-NH_3^+$ unit dissociates to $-NH_2$ with $pK_a = 6.9$, accompanied by a conformational change of the polymer. Around this pH region, maximum conversion was attained. At neutral pH, chitosan exists as a neutral polymer which forms the most compact conformation causing the closest proximity between the units. Such a compact conformation would promote the reaction of the copper(II) complex with the free amino units. The effect of neutral salt (Fig. 7) also supports this consideration.

In the case of the vinylamine-vinyl alcohol copolymer system, an unusual increase in the conversion at neutral pH region was not observed [4]. The difference in the polymerization activity between chitosan and the vinylamine-vinyl alcohol copolymer may be explained by the fact that the former has amino and hydroxy groups at the 1 and 2 positions, while the latter has them at 1 and 3 positions, and that the structure of the former is hard and nonflexible as compared with the latter. The difference in the pK_a value of the $-NH_3$ unit may also be important.

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Accepted by editor December 22, 1977
Received for publication April 14, 1978