

## Polymerization of Acrylamide Initiated by Copper(II) Amino Acid Chelate- $\text{CCl}_4$ Systems III<sup>†</sup>

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**ABSTRACT:** It was found that copper(II) amino acid chelates initiate polymerization of acrylamide thermally, in the presence of  $\text{CCl}_4$ . Amino acids used were glutamic acid, serine and valine. Analysis of the results shows that at lower concentrations of the initiator the rate of polymerization is proportional to  $[\text{initiator}]^{1/2}$  and  $[\text{monomer}]^{3/2}$ . At higher concentrations of the initiator polymerization was found to be inhibited. Kinetics indicate a radical mechanism of polymerization. The initiating radicals seem to be  $\cdot\text{CCl}_3$  radicals, that are formed between  $\text{CCl}_4$  and "a loose adduct" resulting from the complex and the monomer. The effect of temperature was also studied. A possible reaction scheme is proposed to explain various reactions occurring in polymerization. Thermal initiation efficiencies of these chelates were found to be much greater than their photochemical counterpart in the absence of  $\text{CCl}_4$ .

**KEY WORDS** Thermal Polymerization / Acrylamide / Copper-Bis(amino acid) Chelates / Carbon Tetrachloride /

Several papers are dealing with the thermal polymerization of vinyl monomers, initiated by transition metal complexes.<sup>1-8</sup> Such initiation systems might be of interest which create free radicals by chelate interaction with another component of the initiation system. The chelate itself and the other component of the initiation system do not necessarily act as effective initiators for radical reactions when they are used independently. Bamford *et al.*<sup>6</sup> described an initiation system of copper(II) acetylacetonate with ammonium trichloroacetate. They proposed that a molecular complex is formed between the copper acetylacetonate and ammonium trichloroacetate. This molecular complex directly leads to the formation of  $\cdot\text{CCl}_3$  radicals, which are able to initiate radical reactions. Amano *et al.*<sup>9</sup> assumed the formation  $\cdot\text{CCl}_3$  radicals as intermediates in the reaction between bis(-)

ephedrine copper (II) chelate and  $\text{CCl}_4$ . Barton *et al.*<sup>7</sup> studied the kinetics of styrene polymerization initiated by the above system. Recently we<sup>10</sup> have shown photopolymerization of acrylamide initiated by copper(II)-bis(amino acid) chelates. Incidentally we found that these complexes also initiate acrylamide polymerization thermally, but in the presence of  $\text{CCl}_4$ . In the present paper we report on the kinetics of the polymerization initiated by three kinds of copper(II) amino acid chelates, namely, bisglutamato cuprate(II),  $\text{Cu}(\text{glu})_2$ , bisserinatocopper(II),  $\text{Cu}(\text{ser})_2$ , and bisvalinatocopper(II),  $\text{Cu}(\text{val})_2$ .

### EXPERIMENTAL

#### Materials

Acrylamide (BDH) was purified by recrystallizing twice from chloroform.  $\text{CCl}_4$  was of

<sup>†</sup> For Parts I and II, see ref 11 and 10, respectively.

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Analytical reagent grade (BDH). The copper amino acid complexes were available from previous studies.<sup>11</sup> The purity of the complexes was checked by measuring the absorption spectra and by carrying out elemental analysis as given in ref 10.

#### Apparatus and Procedures

Polymerizations were carried out in pyrex tubes of 60 ml capacity. The tubes were provided with an inlet and outlet for deaeration. 3 ml of  $\text{CCl}_4$  were taken in the tubes for polymerization. Solutions for polymerizations were deaerated thoroughly for 40 min using oxygen free nitrogen.<sup>14</sup> After deaeration, the tubes were sealed with gas-cuts and kept in a thermostat, kept at  $60 \pm 0.1^\circ\text{C}$ . Monomer conversion was determined gravimetrically as before.<sup>10</sup> The viscosity of the polymer solution was measured in water at  $30 \pm 0.1^\circ\text{C}$  using an Ubbelohde viscometer. The number-average molecular weight of the polymer was determined using the following relationship.<sup>15</sup>

$$\eta = 6.80 \times 10^{-4} M_n^{0.66} \quad (30^\circ\text{C}, \text{ dl g}^{-1}, \text{ water})$$

## RESULTS AND DISCUSSION

Polymerizations of acrylamide with the complex or  $\text{CCl}_4$  were carried out at  $\text{pH} = 7$  in aqueous solution at  $60^\circ\text{C}$  for 5 h. In both the cases, polymerization was not observed. Only in the presence of both, complex and  $\text{CCl}_4$ , polymerization occurred. Plots of the percent conversion of monomer and rate of polymerization,  $-d[M]/dt$  versus reaction time are shown in Figures 1—3. The steady state of polymerization was reached in 1 h as shown in Figures 1—3 for all three initiators. Polymerization of acrylamide was carried out for 1 h in the kinetic studies. The results of the studies of polymerization at various concentrations of initiator at a given concentration of monomer and particular temperature show that there is an optimal concentration of the initiator at which maximum conver-

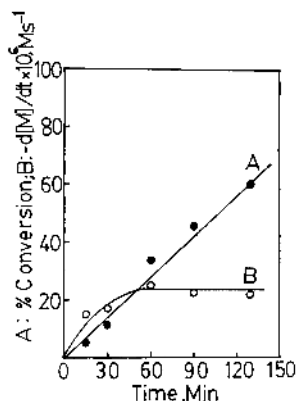


Figure 1. A) Percent monomer conversion vs. time of reaction and B) rate of monomer disappearance vs. time of reaction for  $\text{Cu}(\text{glu})_2$ .

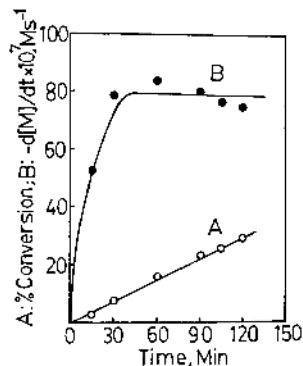


Figure 2. A) Percent monomer conversion vs. time of reaction and B) rate of monomer disappearance vs. time of reaction for  $\text{Cu}(\text{ser})_2$ .

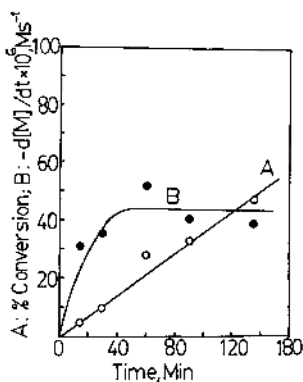
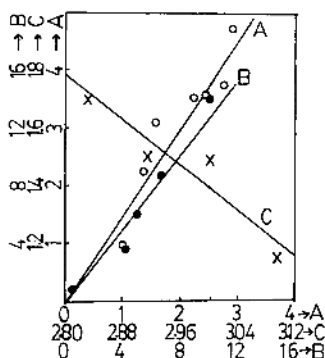
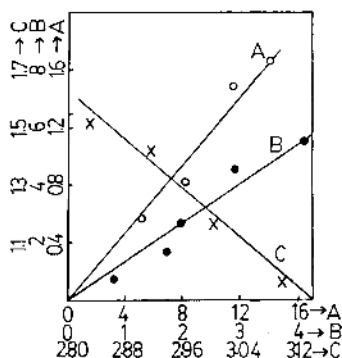


Figure 3. A) Percent monomer conversion vs. time of reaction and B) rate of monomer disappearance vs. time of reaction for  $\text{Cu}(\text{val})_2$ .

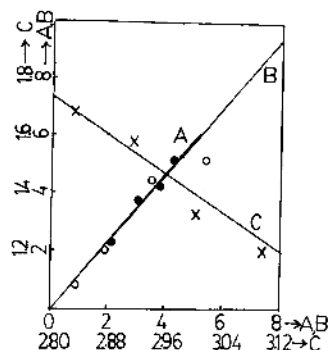


**Figure 4.** Plots of the rate of polymerization vs. the initiator concentration, the monomer exponent, and the apparent activation energy A:  $\circ$ ,  $-d[M]/dt \times 10^5/\text{Ms}^{-1}$  vs.  $[C]^{1/2} \times 10/M^{1/2}$ . B:  $\bullet$ ,  $-d[M]/dt \times 10^5/\text{Ms}^{-1}$  vs.  $[M]^{3/2} \times 10/M^{3/2}$ . C:  $\times$ ,  $\log(-d[M]/dt) + 6$  vs.  $1/T \times 10^3/\text{K}^{-1}$  for  $\text{Cu}(\text{glu})_2$ .



**Figure 5.** Plots of the rate of polymerization vs. the initiator concentration, the monomer exponent, and the apparent activation energy A:  $\circ$ ,  $-d[M]/dt \times 10^5/\text{Ms}^{-1}$  vs.  $[C]^{1/2} \times 10/M^{1/2}$ . B:  $\bullet$ ,  $-d[M]/dt \times 10^5/\text{Ms}^{-1}$  vs.  $[M]^{3/2} \times 10/M^{3/2}$ . C:  $\times$ ,  $\log(-d[M]/dt) + 6$  vs.  $1/T \times 10^3/\text{K}^{-1}$  for  $\text{Cu}(\text{ser})_2$ .

sion of monomer occurred. At lower concentrations of initiator [ $< 8.5 \times 10^{-2}$  M in the case of  $\text{Cu}(\text{glu})_2$ ,  $< 2.0 \times 10^{-2}$  M, in the case of  $\text{Cu}(\text{ser})_2$  and  $< 1.8 \times 10^{-3}$  M in the case of  $\text{Cu}(\text{val})_2$ ] the rate of polymerization was found to be proportional to the square root of the initiator concentration (Figures 4A, 5A, and 6A) and the monomer exponent was 1.5 (Figures 4B, 5B, and 6B). The rate of polymerization was found to be independent of  $[\text{CCl}_4]$ . The apparent activation energy,  $E_a$  for the polymerization was



**Figure 6.** Plots of the rate of polymerization vs. the initiator concentration, the monomer exponent, and the apparent activation energy A:  $\bullet$ ,  $-d[M]/dt \times 10^5/\text{Ms}^{-1}$  vs.  $[C]^{1/2} \times 10^2/M^{1/2}$ . B:  $\circ$ ,  $-d[M]/dt \times 10^5/\text{Ms}^{-1}$  vs.  $[M]^{3/2} \times 10/M^{3/2}$ . C:  $\times$ ,  $\log(-d[M]/dt) + 6$  vs.  $1/T \times 10^3/\text{K}^{-1}$  for  $\text{Cu}(\text{val})_2$ .

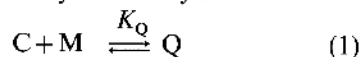
calculated from the Arrhenius plot of  $\log(-d[M]/dt)$  versus  $1/T$  (Figures 4C, 5C, and 6C). The effect of pH on monomer conversion is shown in Table I.

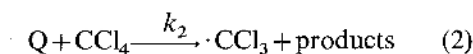
#### Reaction Mechanism

Kinetic data indicate a radical mechanism, operating in all three systems. In the light of our experimental observations the following mechanism is proposed for all three.

#### Production of Initiating Radicals

Here, a loose molecular adduct (Q) between the initiator (C) and the monomer (M) is proposed to be formed. Acrylamide is known to interact with cerium,<sup>16</sup> iron nitrate,<sup>17</sup> and  $\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})\text{Cl}_3$ <sup>18</sup> forming labile complexes which undergo subsequent decompositions leading to initiating free radicals. Formation of a loose adduct between the copper-bisamino acid complex and acrylamide is indicated by the change in the spectrum in the UV region. It is also proposed that the "loose molecular adduct" interacts with  $\text{CCl}_4$  to produce  $\cdot\text{CCl}_3$  radicals. The  $\cdot\text{CCl}_3$  radicals are known to initiate polymerization of acrylamide<sup>7,19</sup> and methyl methacrylate.<sup>24</sup>





where  $K_Q$  = equilibrium constant for the formation of Q.

It is assumed that the termination of polymerization occurs by combination or disproportionation of polymer radicals. Under steady state formation of  $\cdot\text{CCl}_3$ , the following expression for the rate of monomer disappearance,  $-d[M]/dt$ , is obtained.

$$\frac{-d[M]}{dt} = k_p[M]^{3/2}[C]^{1/2} \left[ \frac{k_2' K_Q}{k_t} \right]^{1/2} \quad (3)$$

where

$$k_2' = k_2[\text{CCl}_4],$$

$k_p$  = rate constant for propagation,

$k_t$  = rate constant for termination,

$$\frac{-d[M]}{dt} = K_h[M]^{3/2}[C]^{1/2} \quad (4)$$

where

$$K_h = \left[ k_p \frac{k_2' K_Q}{k_t} \right]^{1/2}$$

Our experimental results show that the dependence of  $-d[M]/dt$  on  $[C]$  and  $[M]$  and the independence of  $-d[M]/dt$  on  $[\text{CCl}_4]$  are consistent with the above proposed mechanism. At lower concentrations of initiator  $[[C] < 8.5 \times 10^{-2} \text{M}$  in the case of  $\text{Cu}(\text{glu})_2$ ,  $[C] < 2.0 \times 10^{-2} \text{M}$  in the case of  $\text{Cu}(\text{ser})_2$  and  $[C] < 1.8 \times 10^{-3} \text{M}$  in the case of  $\text{Cu}(\text{val})_2$ ] we observed an initiator exponent of 0.5 and monomer exponent of 1.5 in accordance with eq 4 indicating that bimolecular termination is predominant at lower concentrations of initiators. At higher concentrations of initiators, the percent monomer conversion decreased and the mechanism of termination became complicated.

#### Effect of pH on Monomer Conversion

As the pH of the solution decreased (from 7 to 5) the monomer conversion decreased with

**Table I.** Effect of pH on % conversion of acrylamide monomer by initiators  $\text{Cu}(\text{glu})_2$ ,  $\text{Cu}(\text{ser})_2$ , and  $\text{Cu}(\text{val})_2^a$

pH	% Monomer conversion		
	$\text{Cu}(\text{glu})_2$	$\text{Cu}(\text{ser})_2$	$\text{Cu}(\text{val})_2$
9.0	44.2	30.2	25.2
8.0	43.2	28.8	23.8
7.0	42.9	28.1	24.6
6.0	37.5	20.1	11.6
5.0	7.7	7.6	5.3

<sup>a</sup> [initiator],  $\text{Cu}(\text{glu})_2$   $2.5 \times 10^{-2}$ ,  $\text{Cu}(\text{ser})_2$   $1.3 \times 10^{-2}$ , and  $\text{Cu}(\text{val})_2$   $1.8 \times 10^{-3} \text{M}$ ; reaction time, 1 h; [Monomer],  $\text{Cu}(\text{glu})_2$  0.25,  $\text{Cu}(\text{ser})_2$  0.19, and  $\text{Cu}(\text{val})_2$  0.31 M; temp, 60°C.

all three initiators. On increasing the pH from 7 to 9, the monomer conversion was not found to change (Table I). In the distribution diagram<sup>10</sup> of various  $\text{Cu}(\text{II})$ -amino acid complex species at different pH, it can be seen that the concentrations of 1:1 and 1:2 complex species and free  $\text{Cu}(\text{II})$  ions remain nearly the same at  $\text{pH} \geq 7$ . The concentration of 1:2 complex species decreased from ca. 90% at  $\text{pH} = 7$  to ca. 35% at  $\text{pH} = 5$ , the concentration of 1:1 complex species increased from ca. 5% at  $\text{pH} = 7$  to ca. 60% at  $\text{pH} = 5$ , the concentration of free  $\text{Cu}^{2+}$  ions gradually increased from ca. 0% at  $\text{pH} = 7$  to ca. 3.5% at  $\text{pH} = 5$ . The decrease in the monomer conversion as the pH is lowered is attributed to the corresponding decrease in the concentration of 1:2 complex species and to the scavenging of the polymer radicals by the free  $\text{Cu}(\text{II})$  ion present in the solution.<sup>20-23</sup> Since the concentration of 1:2 complex species remained almost constant at  $\text{pH} \geq 7$  the monomer conversion did not change.

#### Effect of Temperature on the Rate of Polymerization

The activation energy  $E_a$  was calculated from the plots of  $\log(-d[M]/dt)$  vs.  $1/T$  for the three initiators.  $E_a$  of 2.0, 2.2, and 1.6 kcal  $\text{mol}^{-1}$  were obtained for the initiators  $\text{Cu}(\text{glu})_2$ ,  $\text{Cu}(\text{ser})_2$ , and  $\text{Cu}(\text{val})_2$ , respectively.

**Table II.** Values of proportionality constant,  $K_h$ 

Initiator system	Proportionality constant, $K_h$	
	From $-d[M]/dt$ vs. $[M]^{3/2}$	From $-d[M]/dt$ vs. $[C]^{1/2}$
Cu(glu) <sub>2</sub> -CCl <sub>4</sub>	$1.47 \times 10^{-3}$	$1.10 \times 10^{-3}$
Cu(ser) <sub>2</sub> -CCl <sub>4</sub>	$1.49 \times 10^{-3}$	$1.36 \times 10^{-3}$
Cu(val) <sub>2</sub> -CCl <sub>4</sub>	$2.66 \times 10^{-3}$	$2.19 \times 10^{-3}$

**Table III.** Comparison of photo- and thermal polymerizations

Initiator system	Maximum % monomer conversion obtained	
	Photochemical <sup>a</sup>	Thermal <sup>b</sup>
Cu(glu) <sub>2</sub> -CCl <sub>4</sub>	15	65
Cu(ser) <sub>2</sub> -CCl <sub>4</sub>	7	35
Cu(val) <sub>2</sub> -CCl <sub>4</sub>	12	25

<sup>a</sup> Initiator, Cu(glu)<sub>2</sub> and Cu(ser)<sub>2</sub>  $3 \times 10^{-3}$ ; Cu(val)<sub>2</sub>  $2.4 \times 10^{-3}$  M. Irradiation time, Cu(glu)<sub>2</sub> and Cu(val)<sub>2</sub> 120; Cu(ser)<sub>2</sub> 150 min. Light intensity, Cu(glu)<sub>2</sub> and Cu(ser)<sub>2</sub>  $1.3 \times 10^{-7}$  and Cu(val)<sub>2</sub>,  $1.0 \times 10^{-7}$  ein  $I^{-1} s^{-1}$ .

<sup>b</sup> [Initiator], Cu(glu)<sub>2</sub>  $8.5 \times 10^{-2}$ , Cu(ser)<sub>2</sub>  $2 \times 10^{-2}$ , and Cu(val)<sub>2</sub>  $1.8 \times 10^{-3}$  M; reaction time, 1 h; temp, 60°C.

#### Proportionality Constant, $K_h$

Proportionality constant,  $K_h$ , in eq 4 was obtained from the slopes of the plots  $-d[M]/dt$  vs.  $[M]^{3/2}$  and  $-d[M]/dt$  vs.  $[C]^{1/2}$  in the case of each initiator (see Table II). Values of  $K_h$  from the plots  $-d[M]/dt$  vs.  $[M]^{3/2}$  and  $-d[M]/dt$  vs.  $[C]^{1/2}$  were nearly the same indicating the validity of the proposed reaction mechanism.

#### Comparison of Photo- and Thermal Polymerizations

A comparison of the photochemical and thermal polymerizations indicates that the thermal polymerization gives greater monomer conversion than the photochemical counterpart (see Table III). Number-average molecular weight,  $M_n$ , of the polymers obtained in both the cases are high.  $M_n$  of the poly(acrylamide) obtained by photochemical and thermal polymerizations were found to be  $8.5 \times 10^8$  and  $1.06 \times 10^9$  respectively. Such an

extraordinary high molecular weight of the polymer may be attributed to the presence of a gel. It may be concluded that the amino acid chelates of copper(II) used in this investigation, namely Cu(glu)<sub>2</sub>, Cu(ser)<sub>2</sub>, and Cu(val)<sub>2</sub> show better initiating efficiency as thermal initiators than as photo initiators. The initiating species was a copper(I)-amino acid radical in the case of photo-polymerization<sup>11</sup> and  $\cdot CCl_3$  radical in the case of thermal polymerization reactions.

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