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Vinyl Polymerization by Metal Complexes. XXVII. Mechanistic Study on the Vinyl Polymerization Initiated by Polyvinylamine-Copper(II) Chelate in Dimethylsulfoxide Solution

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Vinyl Polymerization by Metal Complexes. XXVII.*
Mechanistic Study on the Vinyl Polymerization
Initiated by Polyvinylamine-Copper(II) Chelate
in Dimethylsulfoxide Solution

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ABSTRACT

The polymerization of acrylonitrile and methyl methacrylate
initiated by copper(II) chelates of polyvinylamine and
1,3-diaminopropane was studied kinetically in dimethyl-
sulfoxide solution in the presence and absence of carbon
tetrachloride. Time-course changes in visible as well as
ESR spectra were measured for different systems containing
the copper(II) chelates. The initiation mechanism is dis-
cussed from the spectrophotometric and kinetic data results.

INTRODUCTION

The polymerization of vinyl monomers initiated by the copper(II)
chelates of polyvinylamine (PVAm) as well as of 1,3-diaminopropane
(DAP) has been studied in the presence of carbon tetrachloride in

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*For Part XXVI of the series, see K. Kimura, Y. Inaki, and
K. Takemoto, Angew. Makromol. Chem., In Press.

dimethylsulfoxide (DMSO) solution [1] in order to compare the polymerization behavior with the study made in aqueous media [2, 3]. The activity of the DAP-copper(II) chelate for polymerization in DMSO solution was found to be higher than that of the PVAm-copper(II) chelate, contrary to the case of the polymerization of these copper(II) chelates in aqueous media. Such a difference in the activity of these copper(II) chelates for initiating the polymerization was concluded to be due to the difference in the structure of the copper(II) chelates. The DAP-copper(II) chelate can interact with monomers and carbon tetrachloride, while the PVAm-copper(II) chelate cannot interact with the monomers but only with carbon tetrachloride.

This paper reports the kinetics of the polymerization initiated by the copper(II) chelates of PVAm and DAP in DMSO solution. Both visible and ESR spectra studies were made in order to elucidate the initiation mechanism of the vinyl polymerization.

EXPERIMENTAL

Materials

PVAm hydrochloride was prepared from polyvinyl phthalimide according to the method of Reynolds and Kenyon [4]. PVAm was obtained by neutralization of PVAm hydrochloride with sodium hydroxide in water, followed by dialysis and reprecipitation. DAP of commercial origin was purified by repeated distillation. The copper(II) nitrate and cuproine (2,2'-biquinoline) used were of analytical grade. Vinyl monomers, including acrylonitrile (AN) and methyl methacrylate (MMA), DMSO, carbon tetrachloride, and trichlorobromomethane were purified in the usual manner.

Polymerization

The polymerization were carried out in sealed tubes in the absence of atmospheric oxygen. Vinyl monomer (2.0 ml) and carbon tetrachloride (1.0 ml) were added to 4.0 ml of DMSO solution of copper(II) chelate (in the case in which carbon tetrachloride was absent, an additional 1.0 ml of DMSO was added). The degassed and sealed tubes were shaken in a thermostat regulated to $60 \pm 0.1°C$ for 3 hr. The polymer was obtained as a precipitate by pouring the content into a large excess of methanol. It was dried overnight in vacuo.

Spectrophotometric Measurements

Measurements of visible spectra were made using an automatically recording Model 124 Hitachi spectrophotometer with

a degassed quartz cell of 10 mm optical length at constant tempera-
tures. ESR spectra were measured by using the X band of a Model
JES-ME-2X Jeolco ESR instrument with a degassed tube at constant
temperatures.

RESULTS AND DISCUSSION

Visible Spectra Study during the Polymerization

The time-course changes in the visible spectra of different
systems containing PVAm- and DAP-copper(II) chelate were
measured at 60°C in a degassed cell. The visible spectra of the
PVAm- and DAP-copper(II) chelates were also measured at 25°C
for chelates which had previously been kept at 80°C for 3 hr.
After heating at 80°C for 3 hr, very little change in visible
spectra were observed. The copper(II) chelates of PVAm and
DAP in DMSO solution are, therefore, assumed to be consid-
erably thermostable.

Figure 1 shows the time-course change in the visible spectra
of the DAP-copper(II) chelate in DMSO solution at 60°C in the
presence of AN. With a lapse of time the absorption at 580 nm
based on the d-d transition of copper(II) tended to decay gradually,
and the absorption based on copper(I) [4] increased, which sug-
gests the reduction of copper(II) to copper(I) by AN.

However, in the presence of MMA such a time-course change
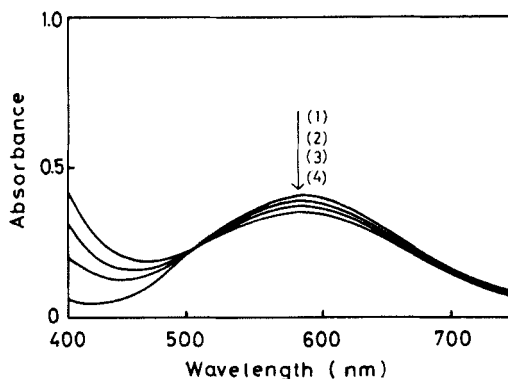was not observed in the visible spectra at 60°C. On the other

FIG. 1. Time-course change in visible spectra of DAP-
copper(II)-AN system in DMSO solution (60°C): (1) 0 min,
(2) 60 min, (3) 120 min, and (4) 180 min.

hand, the time-course changes in the visible spectra of the PVAm-copper(II) were observed neither in the presence of AN nor in the presence of MMA in DMSO solution (an example for the case of AN is shown in Fig. 2). The stability of the PVAm-copper(II) chelate appears to be reflected in the result.

Figures 3 and 4 show the time-course changes in the visible spectra for the DAP-copper(II) chelate in the presence of both
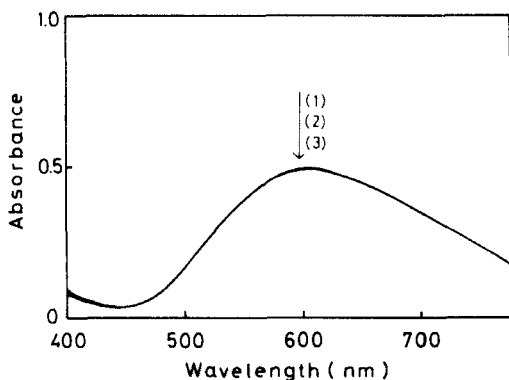

FIG. 2. Time-course change in visible spectra of PVAm-copper(II)-AN system in DMSO solution (60°C): (1) 0 min, (2) 120 min, and (3) 180 min.
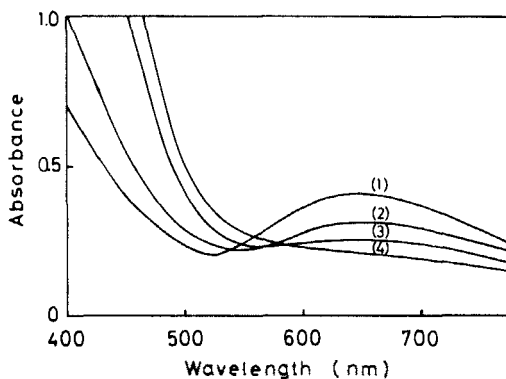

FIG. 3. Time-course change in visible spectra of DAP-copper(II)-AN-carbon tetrachloride system in DMSO solution (60°C): (1) 0 min, (2) 15 min, (3) 30 min, and (4) 60 min.
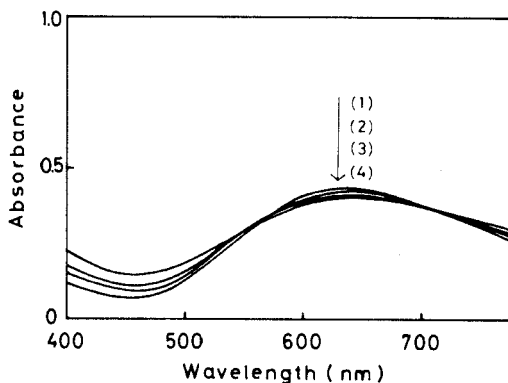
FIG. 4. Time-course change in visible spectra of DAP-copper(II)-MMA-carbon tetrachloride system in DMSO solution (60°C): (1) 0 min, (2) 60 min, (3) 120 min, and (4) 180 min.

the vinyl monomer and carbon tetrachloride at 60°C. By adding carbon tetrachloride to the DAP-AN-copper(II) system in DMSO solution, a remarkable absorption decay at 640 nm based on copper(II) was observed in the time-course changes of the visible spectra at 60°C. This fact shows that carbon tetrachloride, in cooperation with AN, had a marked acceleration effect on the reduction of copper(II). By adding carbon tetrachloride to the DAP-MMA-copper(II) system at 60°C, on the other hand, a similar absorption decay at 640 nm was readily observed, but it was not prominent as compared with the case of AN. Therefore, the reduction of copper(II) in the DAP-MMA-copper(II) system is assumed to be performed only by the action of carbon tetrachloride.

The time-course change in the visible spectra for the PVAm-AN-copper(II) system in the presence of carbon tetrachloride at 60°C is shown in Fig. 5. As shown in this figure, the reduction of copper(II) was observed only to a minor extent in this system. The time-course change in the visible spectra for the PVAm-MMA-copper(II) system was similar to that for the PVAm-AN-copper(II) system.

The rate of reduction of copper(II) to copper(I) is thus considered to be reflected in the rate of polymerization initiated by these systems, as was reported in the preceding paper [1].

ESR Study on the Chelate Systems

The reduction of copper(II) was followed by ESR measurement. Figure 6 shows the time-course changes in ESR spectra for the
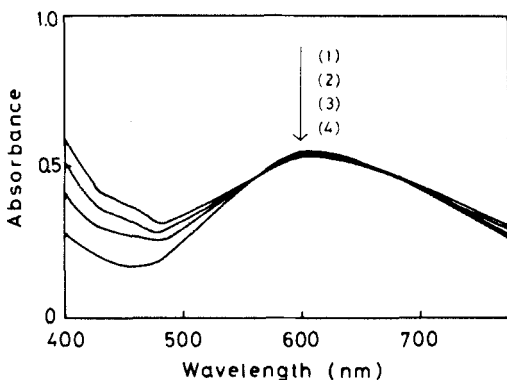
FIG. 5. Time-course change in visible spectra of PVAm-copper(II)-AN-carbon tetrachloride system in DMSO solution (60°C): (1) 0 min, (2) 60 min, (3) 120 min, and (4) 180 min.
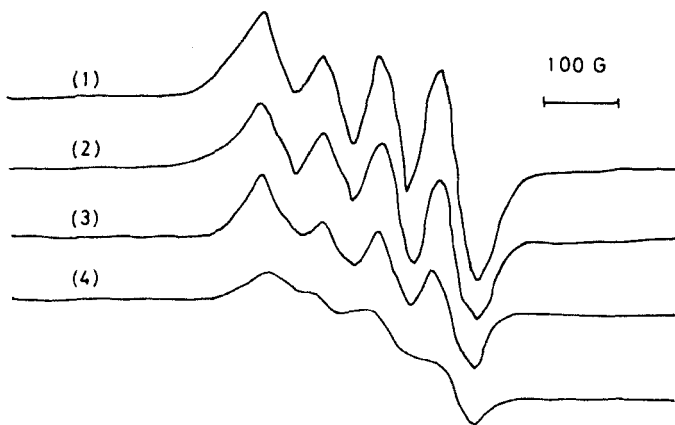
FIG. 6. Time-course change in ESR spectra of DAP-copper(II)-AN system in DMSO solution (60°C): (1) 0 min, (2) 60 min, (3) 90 min, and (4) 120 min.

DAP-copper(II) chelate in DMSO solution at 60°C in the presence of AN. The absorption band based on copper(II) tended to decay gradually with a lapse of time, and thus the copper(II) chelate was found to be reduced by AN. In the case of PVAm-copper(II) chelate in the presence of AN, even at 80°C, only a little change in the absorption was observed.

FIG. 7. Time-course change in ESR spectra of DAP-copper(II)-AN-carbon tetrachloride system in DMSO solution (60°C): (1) 0 min, (2) 30 min, (3) 60 min, and (4) 90 min.
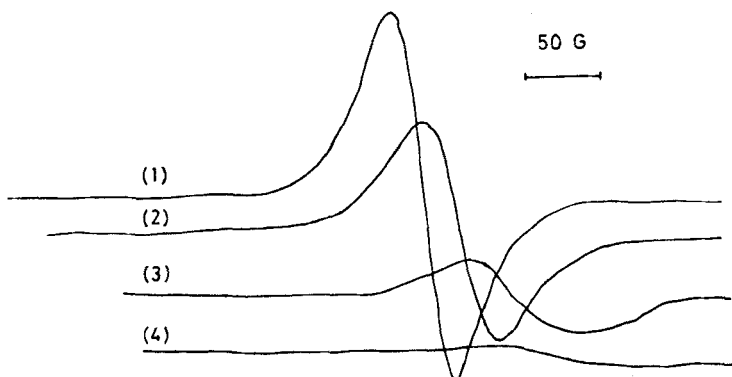
FIG. 8. Time-course change in ESR spectra of PVAm-copper(II)-AN-carbon tetrachloride system in DMSO solution (80°C): (1) 0 min, (2) 30 min, (3) 60 min, and (4) 120 min.

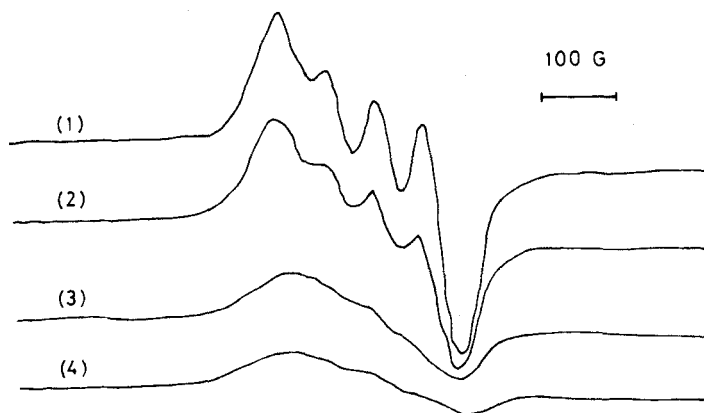Figures 7 and 8 show the time-course changes in the ESR spectra in which carbon tetrachloride was added to the above systems. For the DAP-AN-copper(II) system, the reduction of copper(II) was found to be accelerated in the presence of carbon tetrachloride. A similar change was also observed in the case of the PVAm-AN-copper(II) system.

The ESR spectra of copper(II) usually show a quartet signal centered at about 3000 G, whereas those of the PVAm-copper(II) chelate showed a singlet broad signal which is generally detected for polynuclear copper(II) chelates. The singlet broad signal of the PVAm-copper(II) chelate is interpreted in terms of the absorption which can be attributed to the dipole-dipole coupling of the copper(II) ions in the polynuclear chelate. It may be assumed that the copper(II) ions in the PVAm-copper(II) chelate are situated very close to each other.

Determination of Copper(I) Ion by Cuproine Coloration Method

The copper(I) ion concentration which was produced during the reaction was determined colorimetrically with cuproine as a reagent for the various systems containing PVAm- and DAP-copper(II) after being kept at 60°C for 3 hr [5]. The results are summarized in Table 1. They do not appear to be in agreement with the rate of

TABLE 1. Determination of Copper(I) Ion Concentration by Cuproine Coloration Method for Various Systems Containing PVAm- and DAP-Copper(II) Chelates in DMSO Solution (60°C for 3 hr)

System	Conversion of Cu(II) to Cu(I)[a]
Cu(II)	4.00
DAP-Cu(II)	4.18
PVAm-Cu(II)	3.20
DAP-Cu(II)-AN	24.60
DAP-Cu(II)-MMA	7.44
PVAm-Cu(II)-AN	5.84
PVAm-Cu(II)-MMA	4.03
DAP-Cu(II)-AN-CCl$_4$	61.27
DAP-Cu(II)-MMA-CCl$_4$	14.88
PVAm-Cu(II)-AN-CCl$_4$	12.07
PVAm-Cu(II)-MMA-CCl$_4$	10.22

[a]Determined from the absorbance for Cu(I)(cuproine)$_2$ at 550 nm ($\epsilon = 6450$).

reduction determined from both the visible and ESR spectra; however, they confirm that the absorption decay can be attributed to the forma- tion of the copper(I) ion during the reaction.

Polymerization Kinetics Initiated by PVAm- and DAP-Copper(II) Chelates in the Presence of Carbon Tetrachloride

The polymerization of AN and MMA initiated by the copper(II) chelates of PVAm and DAP was at first carried out at a constant $[Cu(II)]/[-NH_2]$ molar ratio in the presence of carbon tetrachloride, varying the monomer concentration at 60°C for 3 hr. Figures 9 and 10 show the dependence of the rate of polymerization on the monomer concentration for the polymerization of AN and MMA, respectively. The linear relationships afford the following equation for all cases:

$$R_p = k_1 [M]^{1.3 \sim 1.5}$$

The orders in this equation with respect to the monomer concen- tration are over unity for all of these systems, which means that the monomers take a part in the initiation of the polymerization,
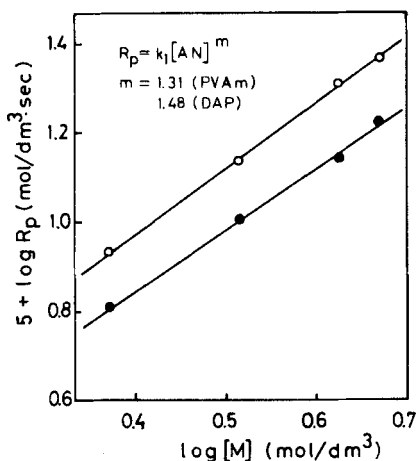

FIG. 9. Log R_p vs log[AN] (at 60°C in DMSO). $[-NH_2]$ = 2.86 × 10^{-2} mole/liter, $[Cu(NO_3)_2]$ = 2.86 × 10^{-3} mole/liter, and $[CCl_4]$ = 8.15 × 10^{-1} mole/liter. (O) DAP system. (●) PVAm system.

FIG. 10. Log R_p vs log[MMA] (at 60°C in DMSO). $[-NH_2]$ = 2.86 × 10^{-2} mole/liter, $[Cu(NO_3)_2]$ = 2.86 × 10^{-3} mole/liter, $[CCl_4]$ = 8.15 × 10^{-1} mole/liter. (O) DAP system. (●) PVAm system.
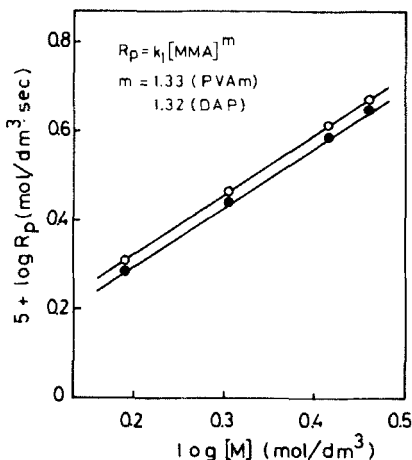
as is often observed for the redox polymerization. Since the kinetic order in question is larger for the DAP-AN-copper(II) system than that for the other systems, AN should be assumed to take an important part in the initiation of this initiation system.

The polymerization was next carried out at constant $[Cu(II)]/$ $[-NH_2]$ and monomer concentration, varying the concentration of carbon tetrachloride. Figures 11 and 12 show the dependence of the rate on the concentration of carbon tetrachloride for the polymerizations initiated by the PVAm and DAP systems,

respectively. For the relationship R_p = $k_2[CCl_4]^n$, the value of

n obtained is about 0.2 at the lower concentration of carbon tetrachloride, while it is near zero at the higher concentration.

The polymerization of AN and MMA initiated by these copper(II) chelates was then carried out at various temperatures in the presence of carbon tetrachloride, which afforded the Arrhenius plots shown in Figs. 13 and 14. From the slopes, the apparent activation energy ΔE, was obtained as 10.52 kcal/mole for the DAP-AN-copper(II) system, 11.89 kcal/mole for the DAP-MMA-copper(II) system, 10.29 kcal/mole for the PVAm-AN-copper(II) system, and 9.61 kcal/mole for the PVAm-MMA-copper(II) system. The ΔE values thus obtained are smaller than those
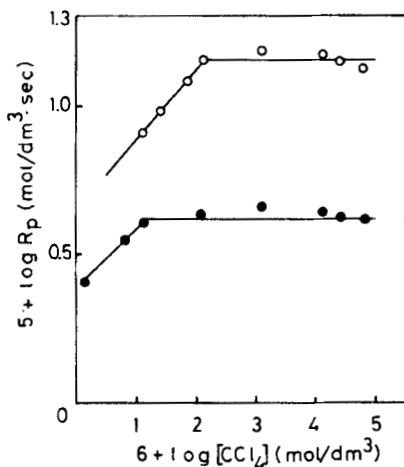
FIG. 11.   Log R_p vs log[CCl$_4$] plots for the AN and MMA polymerization initiated by PVAm-copper(II)-carbon tetrachloride system in DMSO solution (60°C).   (O) AN.   (●) MMA.

FIG. 12.   Log R_p vs log[CCl$_4$] plots for the AN and MMA polymerization initiated by DAP-copper(II)-carbon tetrachloride system in DMSO solution (60°C).   (O) AN.   (●) MMA.
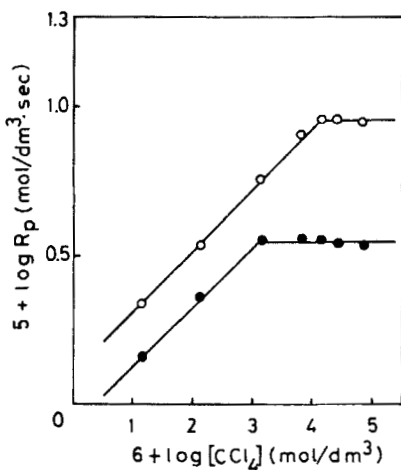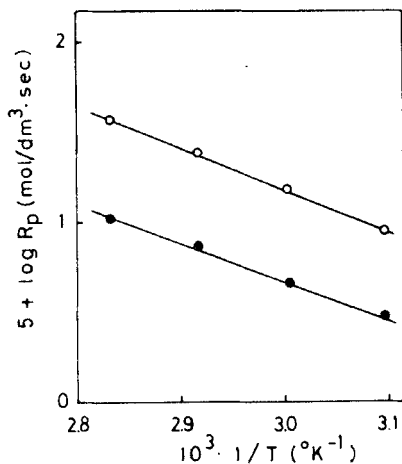
FIG. 13. Arrhenius plots for the AN and MMA polymerization initiated by PVAm-copper(II)-carbon tetrachloride system in DMSO solution. (O) AN. (●) MMA.
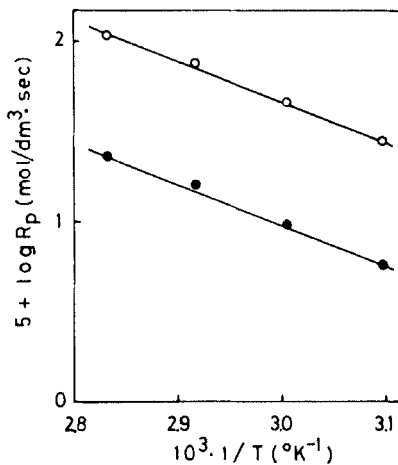

FIG. 14. Arrhenius plots for the AN and MMA polymerization initiated by DAP-copper(II)-carbon tetrachloride system in DMSO solution. (O) AN. (●) MMA.

for the usual free radical polymerization initiated by redox initiators. Since the ΔE values for all four systems are approximately a same, it should be considered that the frequency factors strongly affect the rate of polymerization.
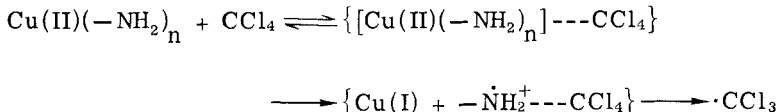
Initiation Mechanism for the Polymerizations

The initiation mechanism for the AN polymerization initiated by the DAP-copper(II) chelate in the absence of carbon tetrachloride is shown as Scheme 1. The DAP-copper(II) chelate thus interacts

$$Cu(II)(DAP)_2 + AN \rightleftharpoons \{Cu(II)(DAP)_2 \text{---} AN\} \longrightarrow Cu(I)(DAP) + R\cdot$$

SCHEME 1.
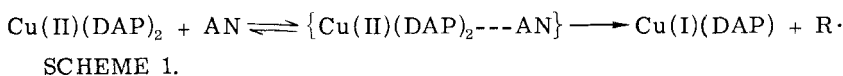
with the AN monomer [1], followed probably by cyanoethylation with the accompanying reduction of copper(II) to copper(I) to generate the initiator free radical [6].

The initiation mechanism in the presence of carbon tetrachloride is determined from the results of both visible and ESR spectra in a similar way (Scheme 2).

$$Cu(II)(-NH_2)_n + CCl_4 \rightleftharpoons \{[Cu(II)(-NH_2)_n] \text{---} CCl_4\}$$

$$\longrightarrow \{Cu(I) + -\dot{N}H_2^+ \text{---} CCl_4\} \longrightarrow \cdot CCl_3$$

SCHEME 2.

Especially for the case involving the DAP-AN-copper(II) system, polymerization is assumed to proceed cooperatively through both Schemes 1 and 2. This was supported by the fact that the kinetic order with respect to AN for this system was larger than that for all three of the other systems. Since the kinetic order with respect to the concentration of carbon tetrachloride tended to be near zero with a rise in the concentration, radical transfer from the amino free radical to carbon tetrachloride should proceed very fast as compared with the reduction of copper(II) to copper(I).

In order to examine whether any graft polymerization occurred during the polymerization, all the poly-AN and poly-MMA obtained were extracted and identified with authentic polymers by spectrophotometry. It was found that no graft polymerization proceeded in the presence of carbon tetrachloride. This fact suggests that

the amino radical cannot initiate the polymerization, and trichloro-
methyl free radical might play an important role in the initiation
by these systems.

Photopolymerization of AN and MMA was further carried out
in DMSO solution in the presence of trichlorobromomethane in
order to get some information about the monomer selectivity of
trichloromethyl free radical generated, which can be easily formed
by photoirradiation. The conversion amounted to 58.82 and 35.58%
for the polymerization of AN and MMA, respectively, in the presence
of 1.07×10^{-1} mole/liter of trichlorobromomethane at $0°C$ for 3 hr.
The conversion ratio of AN/MMA was about 1.7. All of our results
mentioned above gave the values a little below 2.0, which resembles
the result obtained here by photopolymerization. From these
findings the initiation by trichloromethyl free radicals generated
according to Scheme 2 is suggested to proceed preferably.

As has been pointed out, the activity of the DAP-copper(II)
chelate for polymerization, especially of AN, in DMSO solution
in the presence of carbon tetrachloride was higher than that of
the PVAm-copper(II) chelate, contrary to the case of polymerization
by these copper(II) chelates in aqueous media [2]. This rather
"negative polymer effect" may be explained by considering that
the interaction of AN monomer or carbon tetrachloride with the
copper(II) chelate is significant for initiation, which differs from
the case in aqueous media where the free amino units in the
polymer chain have been assumed to be necessary for initiating
polymerization [2]. To summarize, for the polymerization
initiated by the amine-copper(II) chelate in DMSO solution in the
presence of carbon tetrachloride, the difference in the interaction
of a monomer or carbon tetrachloride with copper(II) chelates,
as well as that in the stability of these copper(II) chelates, resulted
in a quite different polymerization behavior from that obtained in
aqueous media.

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