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Vinyl Polymerization by Metal Complexes. XXIX.* Initiation Mechanism of Vinyl Polymerization Initiated by Copper(II) Chelates of Polyvinylamine—Carbon Tetrachloride System: Spin Trapping and Gelation Studies

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ABSTRACT

The initiation mechanism of vinyl polymerization initiated by copper(II) chelates of polyvinylamine and 1,3-diaminopropane was studied both in aqueous and dimethyl sulfoxide solution, in the presence of carbon tetrachloride. The results of spin trapping and gelation experiments made clear that trichloromethyl free radical initiates the polymerization.

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*For part XXVIII of the series: K. Kumura, K. Hanabusa, Y. Inaki, and K. Takemoto, Angew. Makromol. Chem., 52, 129 (1976).

INTRODUCTION

In previous papers of this series, the polymerization of vinyl monomers by copper(II) complexes with organic amines [1], polyvinylamine (PVAm) [2, 3], poly(vinyl alcohol)(PVA) [4], and vinylamine-vinyl alcohol copolymers [5, 6] in aqueous solution in the presence of carbon tetrachloride has been reported. It has been confirmed that these systems can initiate the polymerization of acrylonitrile and methyl methacrylate effectively, and that the polymerization in question is free radical in nature. The polymerization by the PVAm-copper(II) chelate was also studied in dimethyl sulfoxide (DMSO) solution, in which all the components were kept homogeneous throughout processing of the polymerization [7, 8], in order to elucidate the initiation mechanism spectrophotometrically. Visible and ESR spectra obtained supported the reduction of copper(II) ion to copper(I) ion during the initiation step.

Recently, a spin-trapping method [9] has been developed to detect active free-radical species: that is, short-lived precursor radicals are converted to rather stable ones by the reaction with a trapping agent, and they can then be determined from the ESR spectra of the adducts [10-14].

This paper concerns the ESR study as well as gelation experiments in order to clarify the initiation mechanism for the vinyl polymerization by PVAm-copper(II) chelates both in aqueous and DMSO solution in the presence of carbon tetrachloride.

EXPERIMENTAL

Materials

Poly(vinylamine hydrochloride) was prepared from polyvinylphthalimide according to the method of Reynolds et al. [15]. Poly(vinylamine hydrochloride) was then neutralized by sodium hydroxide before use. Poly(vinyl trichloroacetate) was prepared by reacting poly(vinyl alcohol) with trichloroacetyl chloride according to the method of Bamford et al. [16]. (The chlorine content of the polymer was 50.9%, which corresponds to 69% trichloroacetylation.) 1,3-Diaminopropane (DAP) was purified by repeated distillation over potassium hydroxide. Copper(II) reagents used are of analytical grade. Other components, including monomers, solvents, and carbon tetrachloride were purified in the usual manner.

Trapping agents were all prepared according to the literature. Phenyl-N-tert-butylnitrone (PBN) was obtained by oxidizing N-benzylidene tert-butylamine with m-chloroperbenzoic acid, followed by pyrolysis of the oxaziridine to acetonitrile [17]. The N-tert-butylnitrone (BN) was prepared by the reaction of 2-methyl-2-nitrosopropane [18] with diazomethane [19]. α-(3,5-Di-tert-butyl 4-hydroxyphenyl)-N-tert-butylnitrone (BHPBN) was prepared by condensation of 3,5-di-tert-butyl-4-hydroxybenzaldehyde with N-tert-butyl hydroxylamine [17] in ethanol solution, in the presence of several drops of methanesulfonic acid [20].

Polymerization

Polymerization was carried out in sealed tubes in the same manner as reported previously. The degassed and sealed tubes were shaken in a thermostat maintained at 60 ± 0.1°C for 3 hr. The polymer was obtained as colorless precipitate by pouring the reaction mixture into a large excess of methanol and drying overnight in vacuo.

ESR Measurements

After the reaction of the initiation systems with a spin-trapping agent in benzene solution in a degassed and sealed tube at 60°C, the spin adducts produced were extracted with benzene. No monomer was added to the initiation systems, in order to reduce the complexity of the ESR spectra. The benzene solution containing the spin adducts in a degassed capillary was then subjected to ESR measurement, using the X bands of a Model JES-ME-2X JEOLCO ESR instrument at ambient temperature.

RESULTS AND DISCUSSION

Polyvinylamine-Copper(II) System in Aqueous Solution in the Presence of Carbon Tetrachloride

In the course of successive investigations [1-3] on the vinyl polymerization by copper(II) complexes with DAP and PVAm in aqueous solution in the presence of carbon tetrachloride, the initiation mechanism shown in Eqs. (1)-(3) was proposed:

$$\text{Cu(II)}-(\text{H}_2\text{N}-\text{R})_n + \text{R}-\text{NH}_2 \longrightarrow \text{Cu(I)}-(\text{H}_2\text{N}-\text{R})_n + \text{R}-\dot{\text{N}}\text{H} + \text{H}^+ \qquad (1)$$

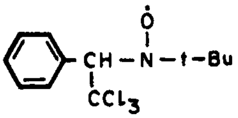
$$R\text{–}\dot{N}H + CCl_4 \longrightarrow R\text{–}NHCl + {}^{\bullet}CCl_3 \qquad (2)$$

$$R\text{–}\dot{N}H \text{ or } {}^{\bullet}CCl_3 + \text{monomer} \longrightarrow \text{monomer radical} \qquad (3)$$

Reduction of copper(II) to copper(I) may occur at first by reacting the amine-copper(II) complexes with free amines as shown in Eq. (1). Trichloromethyl radicals are then formed by radical transfer from almost all amino radicals to carbon tetrachloride [Eq. (2)]. After all, the trichloromethyl free radicals (and the amino radicals) can initiate the polymerization of vinyl monomers [Eq. (3)].

The reduction of copper(II) to copper(I) has been confirmed previously by cuproin coloration method [21]. Free amines, which do not coordinate with copper(II) ion, are indispensable to the reduction [Eq. (1)], which is supported by the fact that the polymerization could not be initiated without free amines [1, 2]. After keeping the aqueous system including PVAm, copper(II), and carbon tetrachloride at 60°C for 3 hr, the original PVAm was isolated by reprecipitation and confirmed by means of elemental analysis to contain about 10-20% chlorine. Since silver chloride was not formed by allowing the polymer to react with silver nitrate in nitric acid solution, the isolated polymer is regarded as containing no amine hydrochloride unit ($R\text{–}NH_2{\cdot}HCl$). These findings suggest that the haloamine units (R–NHCl) as shown in Eq. (2) are formed in the initiation step.

In order to determine the free-radical species, spin-trapping experiments were carried out. Trapping of the free radicals in the initiation step was performed at first by using PBN for the aqueous systems including PVAm or DAP, copper(II), and carbon tetrachloride. Figure 1 shows the spectrum. This ESR spectrum consists only of one kind of three doublets. No other signals were observed, in a wide range of PBN concentrations. The hyperfine splitting constants (hfsc) of the ESR spectrum obtained from each PBN containing system are shown in Table 1. It was also found that no such spectrum was observed in the absence of carbon tetrachloride. This fact suggests that three doublets in question can be attributed to the PBN adduct of trichloromethyl free radical, that is, α-trichloromethylbenzyl tert-butyl nitroxide (I).



I

FIG. 1. ESR spectrum obtained for PVAm–Cu(II)–H_2O–CCl_4 system containing PBN (measured for benzene extract after reaction of the system with PBN). [PVAm] = 5×10^{-2} mole/liter in H_2O; [$CuCl_2$] = 5×10^{-3} mole/liter in H_2O; [PBN] = 5×10^{-2} mole/liter in 0.5 ml benzene; CCl_4, 0.5 ml; pH 9.3 at 60°C for 10 min.

TABLE 1. Hyperfine Splitting Constants of PBN Adducts in Benzene Solution

System	a_N (G)	$a_{\beta\text{-H}}$ (G)
PVAm–$CuCl_2$–H_2O (pH 9.3)–CCl_4[a]	13.6	1.7
DAP–$CuCl_2$–H_2O (pH 12.3)–CCl_4[a]	13.6	1.7
PVAm–$Cu(NO_3)_2$–DMSO–CCl_4[a]	13.7	1.7
DAP–$Cu(NO_3)_2$–DMSO–CCl_4[a]	13.7	1.7
$BrCCl_3$–benzene[b]	13.7	1.7

[a] Hyperfine splitting constants were measured for benzene extract after allowing to react each system with PBN at 60°C for 10 min.

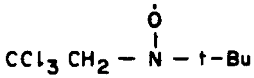
[b] UV-irradiated at room temperature.

In order to obtain an authentic spectrum of the nitroxide (I), bromotrichloromethane was photolyzed in benzene solution containing PBN.

$$\mathrm{BrCCl_3} \xrightarrow{h\nu} {}^{\cdot}\mathrm{CCl_3} \xrightarrow{\mathrm{PBN}} \underset{\mathrm{I}}{\text{nitroxide}} \qquad (4)$$

The splitting constant of the three doublets obtained by photolysis of bromotrichloromethane was consistent with that obtained from the above-mentioned initiation systems.

In order to try to catch amino free radicals [23], trapping experiments were carried out for the same systems using BN. Figure 2 shows the ESR spectrum obtained from the aqueous system containing PVAm, copper(II), carbon tetrachloride, and BN. The BN adduct of the amino free radical was not detected, however; only the BN adduct of trichloromethyl free radical, that is, 2-trichloroethyl tert-butyl nitroxide (II) (α_N = 13.1 G, $\alpha_{\beta\text{-H}}$ = 7.1 G) was confirmed. Since

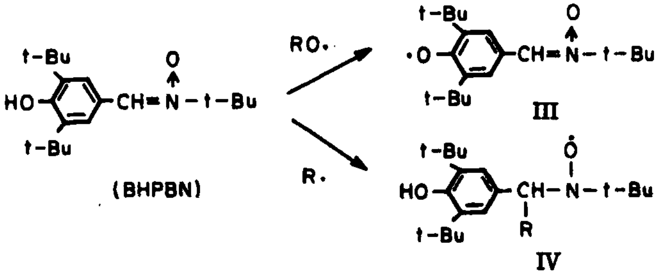


$$\mathrm{CCl_3CH_2}-\overset{\overset{\bullet}{\mathrm{O}}}{\overset{|}{\mathrm{N}}}-t\text{-Bu}$$

II

the nitroxide (II) was found to be much more stable than the nitroxide (I), BN appears to be useful as a trapping agent for trichloromethyl free radicals.

In order to determine the amino free radical ($\mathrm{R{-}\dot{N}H}$), trapping experiments were carried out next for the aqueous systems containing PVAm or DAP, copper(II), carbon tetrachloride, and BHPBN. It is known that BHPBN [20] is useful for distinguishing between the oxygen-centered radical and the carbon-centered radical (alkyl and aryl), as shown in Eqs. (5) and (6).



(5)

(6)

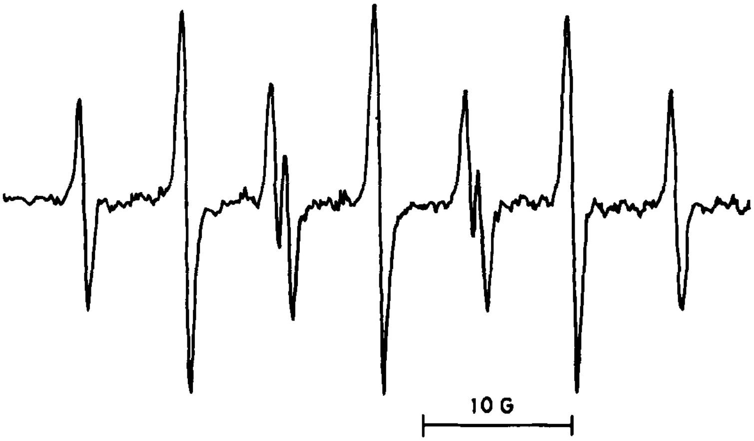


FIG. 2. ESR spectrum obtained for PVAm–Cu(II)–H_2O–CCl_4 system containing BN (measured for benzene extract after reaction of the system with BN). [PVAm] = 5×10^{-2} mole/liter in H_2O; [$CuCl_2$] = 5×10^{-3} mole/liter in H_2O; [BN] = 5×10^{-2} mole/liter in 0.5 ml benzene; CCl_4, 0.5 ml; pH 9.3 at 60° C for 10 min.

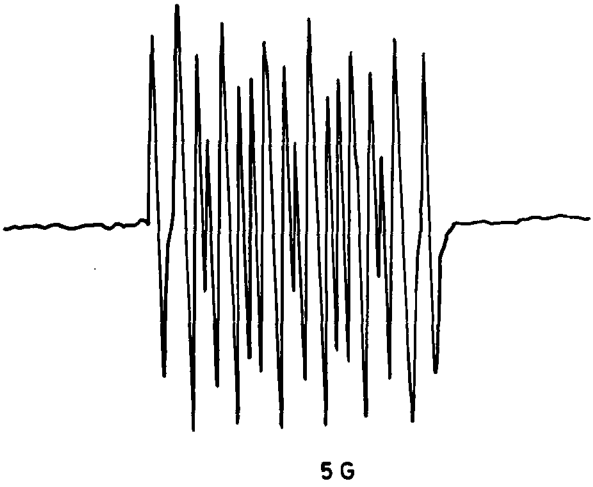


FIG. 3. ESR spectrum obtained for PVAm–Cu(II)–H_2O–CCl_4 system containing BHPBN (measured for benzene extract after reaction of the system with BHPBN). [PVAm] = 5×10^{-2} mole/liter in H_2O; [$CuCl_2$] = 5×10^{-3} mole/liter in H_2O; [BHPBN] = 1×10^{-2} mole/liter in 0.5 ml benzene; CCl_4, 0.5 ml; pH 9.3 at 60° C for 10 min.

Oxygen-centered radical abstracts the phenolic hydrogen atom of BHPBN, thereby affording phenoxyl radical (III), while carbon-centered radical adds to the α-carbon atom of BHPBN and gives nitroxide (IV). It has been shown that the phenoxyl (III) is sufficiently stable to be isolated [20].

As nitrogen-centered radicals also have some capability for hydrogen abstraction [24], formation of phenoxyl (III) by these radicals seems probable. Figure 3 shows the ESR spectrum obtained from the aqueous system containing PVAm, copper(II), and carbon tetrachloride. This spectrum contains a 18-line spectrum based on the phenoxyl (III) (α_N = 5.1 G, $\alpha_{\beta\text{-H}}$ = 2.6 G, $\alpha_{m\text{-H}}$ = 1.5 G, 1.7 G). Over a wide range of BHPBN concentrations and reaction times, only phenoxyl (III) was detected. It is also noteworthy that a similar result was obtained in the trapping experiment in the absence of carbon tetrachloride. These facts suggest that the amino free radical is formed in the initiation step of the polymerization.

For comparison, the photolysis of bromotrichloromethane was examined in benzene solution containing BHPBN, in order to establish the authentic spectrum of the nitroxide (V: IV, R = CCl_3). The change in the ESR spectra obtained with time is shown in Fig. 4. Within 10 min, both the phenoxyl (III) and nitroxide (V) ($\alpha_N \simeq 15$ G, $\alpha_{\beta\text{-H}} \simeq 2$ G) were detected. With a lapse of time the nitroxide V tended to decrease and at the same time, the phenoxyl (III) tended to increase. After 1 hr, only the spectrum of the phenoxyl was detected. It can be considered, therefore, that the trichloromethyl free radical is able to abstract hydrogen from BHPBN and also to add to BHPBN. Even if the trichloromethyl radical formed was trapped as a spin adduct (V), the latter seems to be too unstable to be immediately decomposed under the reaction conditions.

For the polymerization of acrylonitrile and methyl methacrylate initiated by the aqueous system containing PVAm, copper(II), and carbon tetrachloride, no grafting of polymer onto PVAm resulted, as reported in the previous paper [6]. It was concluded, therefore, that amino radicals generated in reaction (1) of the initiation mechanism cannot initiate the polymerization. If so, trichloromethyl radicals generated in reaction (2) should initiate the polymerization.

To determine whether trichloromethyl radical is responsible for initiating vinyl polymerization, a gelation technique was tried. For the polymerization by metal carbonyl–organic halide systems, Bamford et al. studied the initiation mechanism by using poly(vinyl trichloroacetate) (PVTCA) as halide [16, 27, 28]. We have tried to carry out gelation experiments, using PVTCA instead of carbon tetrachloride. Polymerization of acrylonitrile and methyl methacrylate

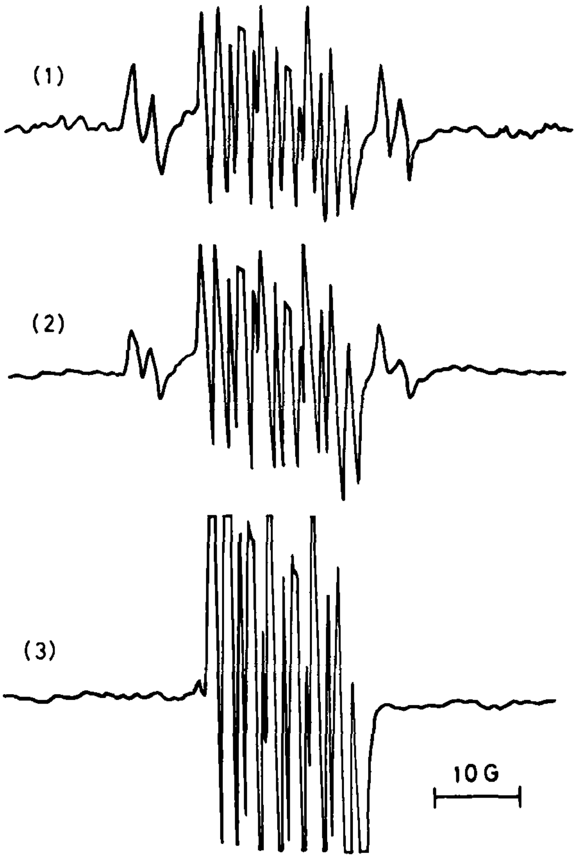
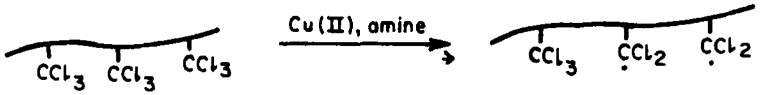
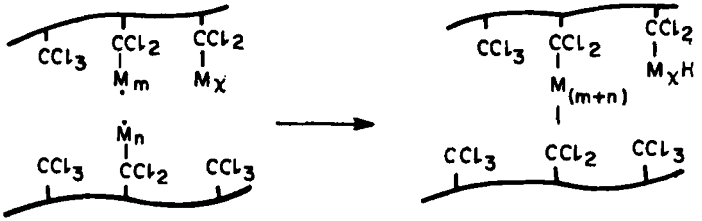


FIG. 4. Change with time in the photolysis of the system of bromotrichloromethane containing BHPBN (in benzene at room temperature): (1) 10 min; (2) 30 min; (3) 60 min. [$BrCCl_3$] = 3.44 mole/liter; [BHPBN] = 1×10^{-2} mole/liter. The "scale out" in (3) is due to ESR measurement in the same condition as in (1) and (2) (gain = 7.9 × 100, mod. width = 2 G).

was studied in aqueous systems containing PVAm or DAP, copper(II), and PVTCA at 60° C. In our case, if dichloroacetate radicals were to



(7)



(8)

form in the initiation step directly, grafted (and/or crosslinked) polymers should be formed [Eq. (7)]. Ungrafted polymers were extracted from the resulting polymer. The results, given in Table 2, indicate that considerable amounts of insoluble grafted polymers were obtained. These results confirm that dichloroacetate radicals were the main initiation species for polymerization with the initiation systems in question. The results also suggest that trichloromethyl radicals, not amino radicals, might be the main initiation species in our polymerization, and that the polymerization is initiated by either adding of halide radicals to monomer or radical transfer from the radical to monomer.

In Table 2, the apparent yield of grafted polymers for the polymerization by potassium persulfate (KPS) and AIBN in the presence of PVTCA is also tabulated; it is, however, very small. This fact seems to exclude the assumption that any initiation species other than trichloromethyl radical exist in the initiation step by the amine–copper(II)–carbon tetrachloride systems and that chain transfer from the initiation species to carbon tetrachloride occurs. Trichloromethyl radicals were thus concluded to be the sole initiating free radicals.

The composition curve for the copolymerization of acrylonitrile with styrene by the aqueous system containing PVAm, copper(II), and carbon tetrachloride is shown in Fig. 5, together with that of the case by KPS in aqueous solution. The former system shows features typical of free-radical polymerization and is almost consistent with the latter. Monomer reactivity ratios calculated by the Fineman-Ross method for the former system are: $r_1 = 0.31$ and $r_2 = 0.08$ (M_1 =

TABLE 2. Apparent Yields of Grafted Polymer in the Polymerization by Amine–Copper(II) Systems in the Presence of PVTCA

System[a]	Monomer[b]	Conversion (%)	Apparent yield of grafted polymer (%)
PVAm–$CuCl_2$–H_2O (pH 9.1)	AN	13.00	53.33
	MMA	10.04	46.33
DAP–$CuCl_2$–H_2O (pH 12.3)	AN	25.25	55.71
	MMA	12.50	48.63
PVAm–$Cu(NO_3)_2$–DMSO	AN	19.25	90.25
	MMA	16.44	60.57
DAP–$Cu(NO_3)_2$–DMSO	AN	47.52	71.00
	MMA	36.11	55.70
KPS–H_2O	AN	68.26	2.09
	MMA	15.44	1.38
AIBN–DMSO	AN	50.81	1.05
	MMA	44.02	1.73

[a] Polymerization at 60° C, for 3 hr. In cases of aqueous systems, $[-NH_2] = 5 \times 10^{-2}$ mole/liter, $[Cu(II)] = 5 \times 10^{-3}$ mole/liter, $[KPS] = 1 \times 10^{-2}$ mole/liter, $[PVTCA] = 2 \times 10^{-1}$ mole/liter in 1 ml ethyl acetate. In cases of DMSO systems, $[-NH_2] = 2.86 \times 10^{-2}$ mole/liter, $[Cu(II)] = 2.86 \times 10^{-3}$ mole/liter, $[AIBN] = 5.71 \times 10^{-3}$ mole/liter, $[PVTCA] = 5.71 \times 10^{-2}$ mole/liter in DMSO.

[b] Dimethylformamide and benzene were used for extraction of polyacrylonitrile and poly(methyl methacrylate), respectively.

acrylonitrile, M_2 = styrene); literature values are $r_1 = 0.41$ and $r_2 = 0.04$ [29].

Polyvinylamine–Copper(II) Systems in DMSO Solution in the Presence of Carbon Tetrachloride

The initiation mechanism for the polymerization by the PVAm or DAP-copper(II) chelates in DMSO solution in the presence of carbon tetrachloride has been proposed [8] as shown in Eqs. (9)-(11).

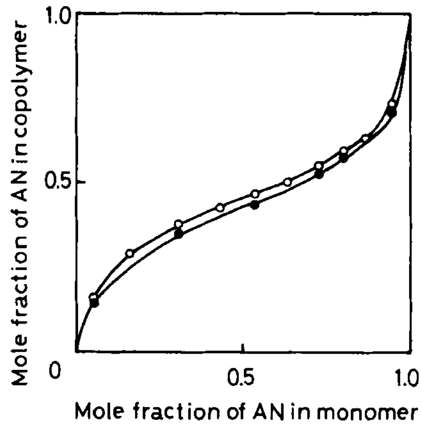


FIG. 5. Composition curve for the copolymerization of acrylonitrile with styrene by PVAm–Cu(II)–H_2O–CCl_4 system at 60° C; (○) PVAm–Cu(II)–H_2O–CCl_4 system; (●) KPS–H_2O system. [PVAm] = 5 × 10^{-2} mole/liter in H_2O; [Cu(II)] = 5 × 10^{-3} mole/liter in H_2O; CCl_4, 1.0 ml; [KPS] = 5 × 10^{-3} mole/liter in H_2O.

$$\mathrm{Cu(II)\,(R{-}NH_2)_n + CCl_4 \longrightarrow \{[Cu(II)\,(R{-}NH_2)_n] \cdots\cdots CCl_4\}} \tag{9}$$

$$\mathrm{\{[Cu(II)\,(R{-}NH_2)_n] \cdots\cdots CCl_4\} \longrightarrow}$$

$$\mathrm{\{Cu(I) + R{-}\overset{\bullet\,+}{N}H \cdots\cdots CCl_4\} \longrightarrow {}^{\bullet}CCl_3} \tag{10}$$

$$\mathrm{{}^{\bullet}CCl_3 + monomer \longrightarrow monomer\ radical} \tag{11}$$

Amine–copper(II) chelates interact at first with carbon tetrachloride, after which reduction of copper(II) to copper(I) occurs. Radical transfer reaction from the amino radical to carbon tetrachloride occurs in the "cage" immediately after the redox reaction, and thus trichloromethyl radicals are formed.

When carbon tetrachloride was added to DMSO solution containing PVAm or DAP-copper(II) systems, marked red shifts of the absorption based upon d-d transition of copper(II) were observed in the visible spectra. The red shift was referred to interaction between

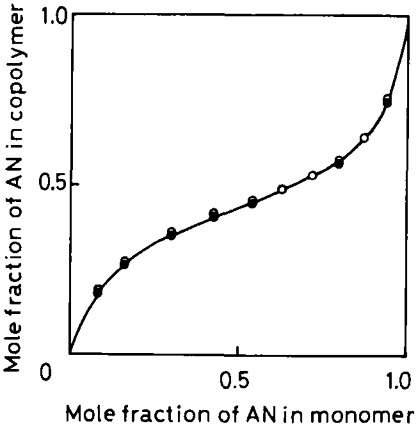


FIG. 6. Composition curve for the copolymerization of acrylonitrile with styrene by PVAm–Cu(II)–DMSO–CCl_4 system at 60° C: (○) PVAm–Cu(II)–DMSO–CCl_4 system; (●) AIBN–DMSO system. [PVAm] = 2.86×10^{-2} mole/liter; [Cu(II)] = 2.86×10^{-3} mole/liter; [AIBN] = 5.71×10^{-3} mole/liter.

the copper(II) chelates and carbon tetrachloride [8]. The reduction from copper(II) to copper(I) has been already confirmed by the decay of ESR and visible spectra during the polymerization, as well as determination of copper(I) by the cuproin method. Contrary to the case in the aqueous solution, the polymerization proceeds even in the absence of excess free amines uncoordinated with copper(II) in DMSO solution. That is, the free amines are not always necessary to initiate the polymerization, for example, in DMSO solution, though the polymerization appears to be partly initiated according to the sequence of Eqs. (1)-(3).

In order to characterize the radical species, spin-trapping experiments were carried out. In the trapping experiments of free radicals for the case of DMSO solution containing PVAm or DAP, copper(II) and carbon tetrachloride system by using PBN (Table 1) and BN, trichloromethyl radicals were trapped and confirmed to be generated during the initiation step of the polymerization.

For the polymerization with the use of PVTCA instead of carbon tetrachloride, the apparent yield of grafted polymers was found to be very high (Table 2). Table 2 shows that the apparent yield of the grafted polymers is generally higher in DMSO solution than in aqueous solution. This may be attributed to the fact that the polymerization systems are homogeneous during the polymerization and crosslinked polymer seems to be obtained rather easily, whereas in the case of aqueous system, the heterogeneous system makes the formation of crosslinked polymer more difficult, because of precipitation of the grafted polymer radicals. From the results here obtained, it is also clear that trichloromethyl radicals play an important part in initiating the polymerization in DMSO solution.

The composition curve for the copolymerization of acrylonitrile with styrene by DMSO solution containing PVAm, copper(II), and carbon tetrachloride is shown in Fig. 6. together with that of the case by AIBN in DMSO solution. The former shows a typical feature of free-radical polymerization in analogy with the latter case. Monomer reactivity ratios calculated by Fineman-Ross method for the former system are: $r_1 = 0.38$ and $r_2 = 0.08$ (M_1 = acrylonitrile and M_2 = styrene).

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