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**Vinyl Polymerization by Metal Complexes. XXXIII.*
Polymerization of Acrylonitrile Initiated
by Triazole-Copper(II) Complex
in Dimethylsulfoxide Solution**

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ABSTRACT

Polymerization of acrylonitrile initiated by triazole-copper(II) complexes was studied in dimethylsulfoxide solution. It was found that the polymerization proceeds by a free radical mechanism; however, the complexes can hardly homopolymerize methyl methacrylate and styrene. Ability of the complexes to initiate polymerization seems to depend on the substituents of triazole, the sort of solvents, and the counterions of copper(II) salts. From the data of visible spectroscopy and the spin trapping, the initiation mechanism was discussed in terms of reduction of copper(II) followed by forming active species.

*For Part XXXII of this series, see Y. Inaki, M. Otsuru, and K. Takemoto, *J. Macromol. Sci.-Chem.*, in press.

INTRODUCTION

Considerable attention seems to have been hitherto given to the chemistry of imidazole because its presence in many biological systems provides a potential binding site for metal ions, particularly for the copper(II) ion. Some authors reported previously that imidazole could initiate vinyl polymerization in the presence of carbon tetrachloride [1, 2]. It has been further reported that imidazole-copper(II) complexes could initiate the polymerization of acrylonitrile (AN) and methyl methacrylate (MMA) in dimethylsulfoxide (DMSO) solution even in the absence of carbon tetrachloride [3-5]. It was pointed out that the initiation mechanism differs significantly from that of the polymerization system containing carbon tetrachloride.

The present paper is concerned with the polymerization of AN initiated by copper(II) complexes of triazole, a related five-membered heterocycle such as imidazole, and its derivatives in DMSO solution. Effects of the substituents of triazole, the sort of solvents, and the counterions of copper(II) salts were studied and the initiation mechanism are discussed in detail.

EXPERIMENTAL

Materials

Triazole and its derivatives used here were kindly given by Sakai Chemical Industries Co. Ltd. They were purified by recrystallization from the appropriate solvents; 1,2,4-triazole (ethanol/benzene), 3,5-dimethyl-1,2,4-triazole (ethyl acetate), 3,5-diheptyl-1,2,4-triazole (acetone), 3,5-dibromo-1,2,4-triazole (ethyl acetate/benzene), 3,5-diphenyl-1,2,4-triazole (acetone), and 3-amino-1,2,4-triazole (ethanol). AN and other monomers and the solvents were distilled repeatedly under reduced pressure. The copper(II) salts and nitriles used were of analytical grade of commercial origin. A spin trapping agent, 2-methyl-2-nitrosopropane, was prepared according to the literature [6].

Polymerization

Polymerization was carried out in a sealed tube in a similar manner as described previously [7]. The monomer was charged into a glass tube containing a DMSO solution of triazole-copper(II) complexes. After sealing off the tube in vacuo, polymerization was carried out under shaking at 60°C for 3 hr. The polymer that resulted was separated by pouring the contents into a large excess of methanol, followed by filtration and drying in vacuo.

Spectral Measurements

Visible spectra were measured in a stoppered quartz cell of 10 mm optical length in the 370-850 nm absorption range at 25 or 60°C using an Hitachi 124 type UV-VS spectrophotometer with a temperature controller. ESR spectra were measured in a sealed capillary at 25 or 60°C using the X-band of the Model JES-ME-2X JEOLCO ESR instrument.

RESULTS AND DISCUSSION

Polymerization by Triazole-Copper(II) Complex

Polymerization of AN initiated by 1,2,4-triazole (Trz)-cupric nitrate complex was first carried out in DMSO solution at constant Trz concentration, varying the copper(II) concentration for optimizing concentrations of copper(II) and Trz for the polymerization (Fig. 1). With increasing copper(II) concentration, conversion increased gradually up to a concentration ratio $[Cu(II)]/[Trz]$ of 0.5 and then remained nearly constant over the concentration ratios measured. Polymerization was also carried out at constant copper(II) concentration while varying the Trz concentration (Fig. 2). Conversion was found to be nearly constant over a $[Trz]/[Cu(II)]$ of 2. These results suggest that a Trz-copper(II) complex in a 2:1 composition ratio is significant for initiating polymerization. The complex in question was also isolated in a separate experiment. An excess of copper(II) and

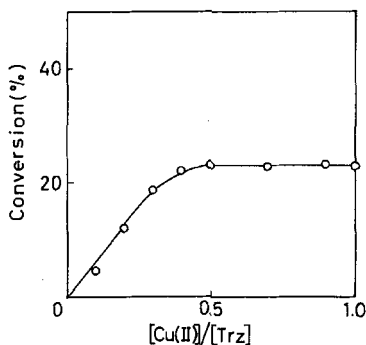


FIG. 1. Dependence of Cu(II) concentration on polymerization activity for AN. $[Cu(NO_3)_2]$, 3.4×10^{-3} to 3.4×10^{-2} mole/L; $[Trz]$, 3.4×10^{-2} mole/L; $[AN]$, 5.1 mole/L in DMSO solution at 60°C for 3 hr.

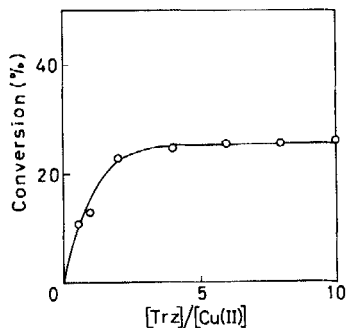


FIG. 2. Dependence of Trz concentration on polymerization activity for AN. [Trz], 4.0×10^{-3} to 1.7×10^{-1} mole/L; [Cu(NO₃)₂], 1.7×10^{-2} mole/L; [AN], 5.1 mole/L in DMSO solution at 60°C for 3 hr.

Trz appears not to take part in the initiation process, which was also understood by the fact that no polymerization was observed in the absence of copper(II) and/or Trz. Based on these findings, all of the subsequent polymerizations were performed at a [Trz]/[Cu(II)] concentration ratio of 2.

Attempts were further made to polymerize MMA and styrene by using the Trz-copper(II) complex. However, it was found unexpectedly that the complex could not initiate homopolymerization of these monomers, which implies that AN monomer itself plays an important role in the initiation step of the polymerization.

Copolymerization of AN with styrene was carried out in the presence of the Trz-Cu(II) complex in DMSO solution. Monomer-copolymer composition plots exhibited an S-shaped curve (Fig. 3), which indicates that the polymerization initiated by the Trz-Cu(II) complex proceeds by a free radical mechanism.

Polymerization of AN by Triazole Derivative-Copper(II) Complexes

Cupric nitrate complexes of 3,5-disubstituted and 3-substituted 1,2,4-triazole derivatives were next chosen for the polymerization of AN in order to study the effect of substituents of triazole on the polymerization activity. From the time-conversion plots, the rate of initial polymerization, R_p , for each polymerization system was calculated, and they are listed in Table 1 together with the λ_{\max} values of visible spectrum of each copper(II) complex in DMSO solution. The R_p value

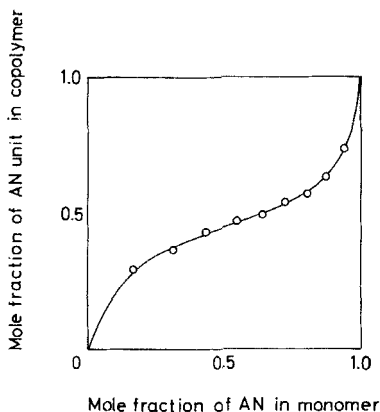


FIG. 3. Copolymerization of AN with styrene by Trz-Cu(II) complex. $[\text{Cu}(\text{NO}_3)_2]$, 1.7×10^{-2} mole/L; $[\text{Trz}]$, 3.4×10^{-2} mole/L in DMSO solution at 60°C .

for each complex decreases in the following order: 3,5-dimethyl > 3,5-diheptyl > 3-amino > (H) > 3,5-dibromo \gg 3,5-diphenyl \approx 0.

It is widely known that the more stable copper(II) complex shows a shorter λ_{max} value of visible spectrum so long as the complexes have the identical types of coordination [8-10]. In the case of 3,5-disubstituted derivatives, the stability of the copper(II) complexes is thus in the following order: (H) > 3,5-dimethyl > 3,5-diheptyl > 3,5-dibromo > 3,5-diphenyl. Since the 3-amino derivative is assumed to form a different type of coordination than 3,5-disubstituted ones because of the coordination ability of the 3-amino group to copper(II), the stability of the complex cannot be compared with those of other Trz complexes. Copper(II) complexes of 3,5-disubstituted derivatives are generally less stable than that of Trz, probably because of the bulkiness of the substituents. Electron-attracting substituents lower the basicity of nitrogen atoms of the triazole ring, which makes the copper(II) complex unstable. For example, 3,5-diphenyl derivative can hardly coordinate to copper(II).

The relation of the stability of the copper(II) complexes with R_p values allows us to note that medium stable copper(II) complexes exhibit high polymerization activity. It is thus assumed to be important for initiating polymerization that the copper(II) complexes should exist in an unstable coordination state. This was also observed for diaminoalkane-copper(II) systems [7].

TABLE 1. R_p and λ_{\max} Values of Visible Spectra for a Series of Trz-Copper(II) Systems

Substituent of Trz	R_p (%/hr) ^a	λ_{\max} (nm) ^b
(H)	6.44	795
3,5-dimethyl	16.38	815
3,5-diheptyl	10.02	825
3-amino	9.30	765
3,5-dibromo	5.94	830
3,5-diphenyl	0	835

^a[Cu(NO₃)₂]: 1.7×10^{-2} mole/L, [ligand]: 3.4×10^{-2} mole/L, [AN]: 5.1 mole/L in DMSO solution.

^b[Cu(NO₃)₂]: 1.7×10^{-2} mole/L, [ligand]: 3.4×10^{-2} mole/L in DMSO solution.

Effect of Solvents and Counterions of the Copper(II) Salts on Polymerization

Polymerization of AN initiated by the Trz-copper(II) complex was next carried out in different solvents by using various sorts of copper(II) salts. Dimethylformamide (DMF), hexamethylphosphorous triamide (HMPA), ethanol, and methanol were chosen as the solvents. For the copper(II) salts, its perchlorate, chloride, and bromide were used. The results are summarized in Table 2. With the exception of the run in DMSO solution, no polymer was obtained under the reaction conditions; the polymerization of AN by the Trz-copper(II) complex proceeds specifically only in DMSO solution. As for the effect of counterions, both cupric nitrate and cupric perchlorate complexes of Trz were found to be active for initiating polymerization, while cupric chloride and bromide complexes of Trz were inactive under similar conditions.

Table 3 shows λ_{\max} values of the visible spectra of the copper(II)-Trz complex in DMSO solution both in the absence and in the presence of AN. Addition of AN to the cupric nitrate or cupric perchlorate-Trz in DMSO solution caused a slight blue shift, suggesting the coordination to copper(II). On the other hand, no spectral change was observed on adding AN to cupric bromide and chloride-Trz systems. These results, together with polymerization data, appear to show the necessity of interaction of the AN molecule with the Trz-copper(II) complex in the initiation step.

TABLE 2. Effect of Solvents and Counterions of Copper(II) Salts on Polymerization Activity^a

Solvent ^b	Conversion (%)	Counterion ^c	Conversion (%)
DMSO	22.8	NO ₃ ⁻	22.8
DMF	Trace	ClO ₄ ⁻	13.5
HMPA	0	Cl ⁻	0
Ethanol	0	Br ⁻	0
Methanol	0		

^a[Cu(II)]: 1.7×10^{-2} mole/L, [Trz]; 3.4×10^{-2} mole/L, [AN]: 5.1 mole/L.

^bCu(NO₃)₂ was used.

^cIn DMSO solution.

TABLE 3. Visible Spectra of Trz-Copper(II) Complex in DMSO Solution

Counterion	λ_{\max} (nm)	
	In the absence of AN ^a	In the presence of AN ^b
NO ₃ ⁻	795	790
ClO ₄ ⁻	800	795
Cl ⁻	825	825
Br ⁻	825	825

^a[Cu(II)]: 1.7×10^{-2} mole/L, [Trz]: 3.4×10^{-2} mole/L in DMSO solution.

^b[Cu(II)]: 1.7×10^{-2} mole/L, [Trz]: 3.4×10^{-2} mole/L, [AN]: 5.1 mole/L in DMSO solution.

Retarding Effect of Nitriles and Polyacrylonitrile

The effect of adding various sort of nitriles on the polymerization of AN initiated by the Trz-copper(II) complex was further studied. The results are shown in Table 4. Their addition to the polymerization system apparently causes retardation of the polymerization of AN. It was found that a small quantity of poly-AN also retards the polymerization drastically (Fig. 4). It can be assumed that these nitriles compete

TABLE 4. Effect of Various Nitriles on the Polymerization of AN^a

Nitrile	Conversion (%)
Acetonitrile	16.4
n-Butyronitrile	16.5
i-Butyronitrile	20.5
n-Valeronitrile	17.1
Benzonitrile	13.9
None	22.8

^a[Cu(NO₃)₂]: 1.7×10^{-2} mole/L, [Trz]: 3.4×10^{-2} mole/L, [AN]: 5.1 mole/L, [nitrile]: 0.5 mole/L in DMSO solution at 60°C for 3 hr.

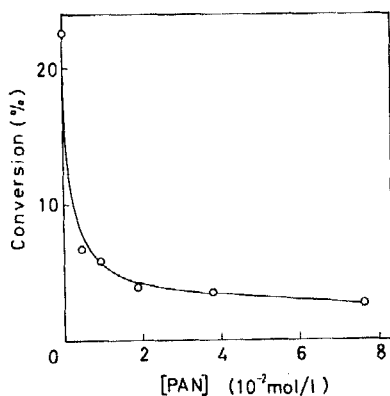


FIG. 4. Retarding effect of polyacrylonitrile on the polymerization of AN. [Cu(NO₃)₂], 1.7×10^{-2} mole/L, [Trz], 3.4×10^{-2} mole/L; [AN], 5.1 mole/L in DMSO solution at 60°C for 3 hr.

with AN in coordinating to the Trz-copper(II) complex, which prevents AN from coordinating to the copper(II) complex. These results also strongly support the concept that the coordination of the AN molecule to the Trz-copper(II) complex is substantial for initiating polymerization.

Initiation Mechanism

Parallel to the study on polymerization behavior, the change in visible spectra of the Trz-copper(II) complex during the polymerization

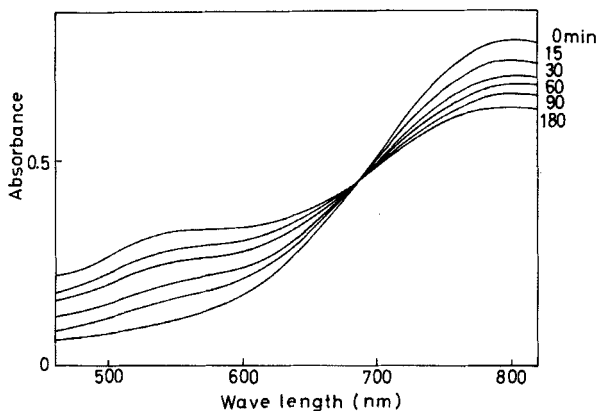


FIG. 5. Change in visible spectra of Trz-Cu(II)-AN in DMSO system. $[\text{Cu}(\text{NO}_3)_2]$, 8.5×10^{-3} mole/L; $[\text{Trz}]$, 1.7×10^{-2} mole/L; $[\text{AN}]$, 2.5 mole/L in DMSO solution at 60°C .

of AN was measured at 60°C in DMSO solution. Typical spectral changes are depicted in Fig. 5. With a lapse of polymerization, absorbance of the copper(II) complex at 795 nm tends to decrease, suggesting a decrease in the concentration of the copper(II) complex. The appearance of a new band near 560 nm was simultaneously observed with a decrease in absorbance for the copper(II) complex. The new band in question may be assigned to the copper(II) complex. The spectral change observed suggests that reduction of the Trz-copper(II) complex to the Trz-copper(I) complex occurs during polymerization. In the absence of AN, such a spectral change was not observed. The reduction of the copper(II) complex in the presence of AN was also confirmed by an ESR spectral change.

Spin trapping experiments [11] were carried out in order to get some information about the initiating free radical. 2-Methyl-2-nitrosopropane (BN) was chosen as the trapping agent. The agent was first added to the Trz-copper(II) nitrate-AN in the DMSO system, and then the mixture was heated at 60°C for 5 min in a degassed, sealed tube. After the reaction an excess of water was added to the reaction mixture and the spin adduct produced was extracted by benzene. The ESR spectrum of the spin adduct is depicted in Fig. 6. The doublet-triplet spectrum indicates a formation of a spin adduct: Since the spin trapping was made at a high concentration (0.2 mmole/L) of BN, the spin adduct obtained can possibly be assigned to (I) ($n = 1$). The result implies that (II) is the original initiating free radical.

From the polymerization activity and spectral data, the initiation

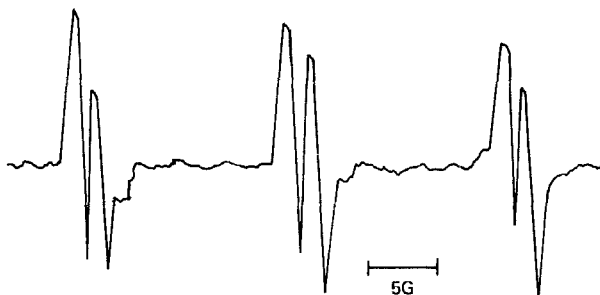
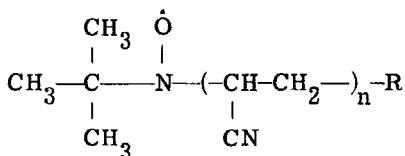
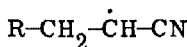


FIG. 6. ESR spectrum of the spin adduct. $[\text{Cu}(\text{NO}_3)_2]$, 1.7×10^{-2} mole/L; $[\text{Trz}]$, 3.4×10^{-2} mole/L; $[\text{AN}]$, 5.1 mole/L; $[\text{BN}]$, 2.0×10^{-1} mole/L in DMSO solution. After the reaction at 60°C for 5 min, the spin adduct was extracted by benzene.

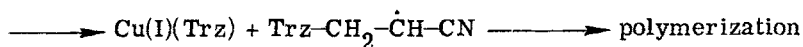
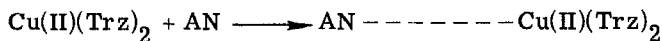


(I)



(II)

mechanism for the polymerization of AN initiated by the Trz-copper-(II) complex in DMSO solution may be assumed to be



AN molecules may first interact with the Trz-copper(II) complex, after which reduction of copper(II) to copper(I) follows. At the same time, cyanoethylation of Trz coordinated to copper(II) occurs. The initiating free radical like (II) is formed and then initiates the polymerization of AN.

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