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Metal-Containing Initiator Systems. XXXIII. Polymerization of Vinyl Monomers Initiated by Binary System of Bis(ethyl Acetoacetato)copper(II) and Sodium Tetraphenylborate

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ABSTRACT

The polymerization of vinyl monomer with the bis(ethyl acetoacetato)copper(II) ($Cu(eacac)_2$) and the sodium tetraphenylborate (TPB) system was investigated. This binary system was found to initiate effectively the radical polymerization of methyl methacrylate (MMA) and methyl acrylate (MA). The polymerization of MMA with the $Cu(eacac)_2$/TPB system was studied kinetically in acetone. The overall activation energy of the polymerization was calculated to be 15.8 kcal/mol. This value is a little lower than that (17.6 kcal/mol) for the polymerization of MMA with $Cu(eacac)_2$ alone. The polymerization rate (R_p) is represented by

$$R_p = k[Cu(eacac)_2]^{0.5}[TPB]^{0.5}[MMA]^{2.5}$$

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The high order for the monomer concentration suggests participation of the monomer in the initiation process in this polymerization. This is supported by examination of the visible and ESR spectra of the Cu(eacac)$_2$/TPB/MMA/acetone system. Reduction of Cu(II) to Cu(I) was observed from the ESR spectrum. To elucidate the initiation mechanism, the spin trapping technique was applied to the Cu(eacac)$_2$)/TPB/MMA system. Based on these results, an initiation mechanism for the binary system of Cu(eacac)$_2$ and TPB is proposed and discussed.

INTRODUCTION

In a previous paper [1] we found that the binary system of bisacetylacetonato cobalt(II) (Co(eacac)$_2$) and sodium tetraphenylborate (TPB) could effectively initiate the polymerization of methyl methacrylate (MMA) and methyl acrylate (MA). The polymerization mechanism was examined by a kinetic study and by the spin trapping technique. It was apparent that vinyl polymerization of this binary system proceeded via a radical mechanism and that the monomer participated in the initiation step. Further, the phenyl radical was trapped in this polymerization system. It was concluded that the reaction of bis(ethyl acetoacetato)copper(II) (Cu(eacac)$_2$), borate, and monomer produced phenyl radical which initiated the polymerization.

It is well known that the initiation mechanism and the initiating activity of a metal chelate in polymerization initiated with metal chelates vary with the kind of central metal atoms. We recently found that the polymerization of MMA and MA is effectively induced by the Cu(eacac)$_2$ and TPB system. Co(II) is a lower valent ion and shows a strong reducing nature, whereas Cu(II) has a high valence and a strong oxidizing nature. Therefore comparison of the initiation activities of cobalt and copper as central metals is of interest.

The present paper is concerned with the results on a kinetic study of vinyl polymerization with the Cu(eacac)$_2$/TPB system and on an ESR spectroscopic study of the initiation mechanism.

EXPERIMENTAL

Materials

Cu(eacac)$_2$ was prepared by the reaction of cupric acetate with ethyl acetoacetate, with purification by recrystallization from acetone [2]. TPB (Dotait Materials) was used without further purification.

Monomers, solvents, and additives were purified by the usual methods. 2-Methyl-2-nitrosopropane (BNO) as a spin trapping agent was prepared by oxidation of tert-butylamine with m-chlorobenzoic acid according to the method of Perkins [3].

Polymerization

The polymerizations were carried out in degassed sealed tubes without diffused light as described in a previous paper [1]. To isolate the polymer formed, the polymerization mixture was poured into a large amount of methanol containing a small amount of HCl which decomposes metal chelate. The intrinsic viscosity ($[\eta]$) of the resulting poly(MMA) was measured in benzene at 30°C, and the number-average degree of polymerization ($\bar{P}_n$) was calculated by [4]

$$\log \bar{P}_n = 3.346 + 1.32 \log [\eta] \quad (1)$$

Measurement of ESR and Visible Spectrum

The reaction of $Cu(eacac)_2$ and TPB was carried out in the presence of BNO in a monomer-acetone mixture in an ESR tube, which was degassed and sealed. After a given time the ESR spectrum of the reaction mixture was recorded by a JES-ME-3X spectrometer with 100 kc/s field modulation. The visible spectrum of the $Cu(eacac)_2$/TPB system was recorded by a Hitachi ESP-2T spectrometer.

Analysis of Products from Thermal Reaction of $Cu(eacac)_2$/TPB System by Gas Chromatography

The reaction of $Cu(eacac)_2$ with TPB was carried out in a sealed tube in acetone at 50°C for 10 h, and extracted with n-hexane. In order to analyze the reaction products, a Yanagimoto GCG-550 gas chromatograph was used with Apiezone Grease L as the column. The column was programmed for a heating rate of 4°C/min from 80 to 170°C. 4-Methylbiphenyl (MBPH) was used as an internal standard.

RESULTS AND DISCUSSION

Polymerization of Vinyl Monomers with $Cu(eacac)_2$ and Borate Ion Systems

The polymerization of some vinyl monomers with $Cu(eacac)_2$ and TPB or tetraethylborate (TEB) systems was first carried out in ace-

TABLE 1. Polymerizations of Some Vinyl Monomers with the $Cu(eacac)_2$/borate Systems in Acetone at 50°C[a]

Monomer	Borate	Time (h)	Yield (%)
MMA	TEB	3	8.3
MMA	none	3	0
MMA	TPB	3	8.5
MA	TEB	3	99.8
MA	TPB	3	39.3
St	TEB	15	4.4
St	TPB	15	3.4
AN	TEB	15	12.4
AN	TPB	15	1.0
VAc	TEB	15	2.0
VAc	TPB	15	0.3

[a] $[Cu(eacac)_2] = 8.00 \times 10^{-3}$, $[\text{borate}] = 1.00 \times 10^{-2}$ mol/L, [monomer] = [solvent] = 5 mL.

tone. The results are summarized in Table 1. The polymerization activity was found to change according to the monomer used in the following order: MA > MMA > acrylonitrile (AN) > styrene (St) > vinyl acetate (VAc). Thus, these binary systems were found to show selectivity for the monomers used. $Cu(eacac)_2$ alone or TPB alone induced no polymerization under the present conditions. The TEB system gave a somewhat higher polymer yield than the TPB system.

Effect of Solvents and Some Additives on Polymerization

Table 2 shows the effect of solvents on the polymerization of MMA with the $Cu(eacac)_2$/TPB system at 50°C. As can be seen from the table, this initiator system showed high activity in $CHCl_3$ and in CH_3CN, but more polar aprotic solvents, such as DMF and DMSO, caused a very slow polymerization rate. As described below, this result agrees well with our ESR examination. Table 3 shows the effects of some additives on the polymerization of MMA for this system. Halogen compounds such as CCl_4 and $CHCl_3$ showed a marked accelerating effect on polym-

TABLE 2. Effect of Solvent on the Polymerization of MMA with the Cu(eacac)$_2$/TPB System at 50°C for 3 h[a]

Solvent	Yield (%)	$\bar{P}_n \times 10^{-2}$
DMF	2.4	12.0
DMSO	3.5	17.0
CH_3CN	26.5	8.5
$CHCl_3$	39.0	9.7
Bz	7.8	9.7
THF	12.9	11.7
EtOH	1.3	-
Acetone	8.5	30.9

[a] [Cu(eacac)$_2$] = 8.00 × 10^{-3}, [TPB] = 1.00 × 10^{-2}, [MMA] = 4.68 mol/L.

TABLE 3. Effect of Some Additives on the Polymerization of MMA with the Cu(eacac)$_2$/TPB System in Acetone at 50°C for 3 h[a]

Additive	Yield (%)
$C_6H_5CH_2Br$	11.7
$CHCl_3$	12.8
CCl_4	46.6
Phenyl acetylene	0.4
18-Crown-6	1.7

[a] [Cu(eacac)$_2$] = 8.00 × 10^{-3}, [TPB] = 1.00 × 10^{-2} mol/L, [additive] = 0.5 mL/10 mL, [18-Crown-6] = 2.00 × 10^{-2} mol/L.

erization, but crown ether and phenyl acetylene (PA) apparently retarded polymerization. In order to clarify the mechanism of polymerization with the Cu(eacac)$_2$/TPB system, the copolymerization of MMA and St was carried out at 60°C in acetone or benzene. The composition curves obtained in both solvents were in agreement with that obtained with ordinary radical polymerization. Therefore, it is suggested that polymerization with this binary system propagates by a radical mechanism.

A Kinetic Study of the Polymerization of MMA with the Binary System of Cu(eacac)$_2$/TPB

Polymerization of MMA with the Cu(eacac)$_2$/TPB system was investigated kinetically in detail in acetone. Figure 1 shows the time-conversion curves obtained at relatively low temperatures (30-50°C). This system showed no induction period compared to that observed in

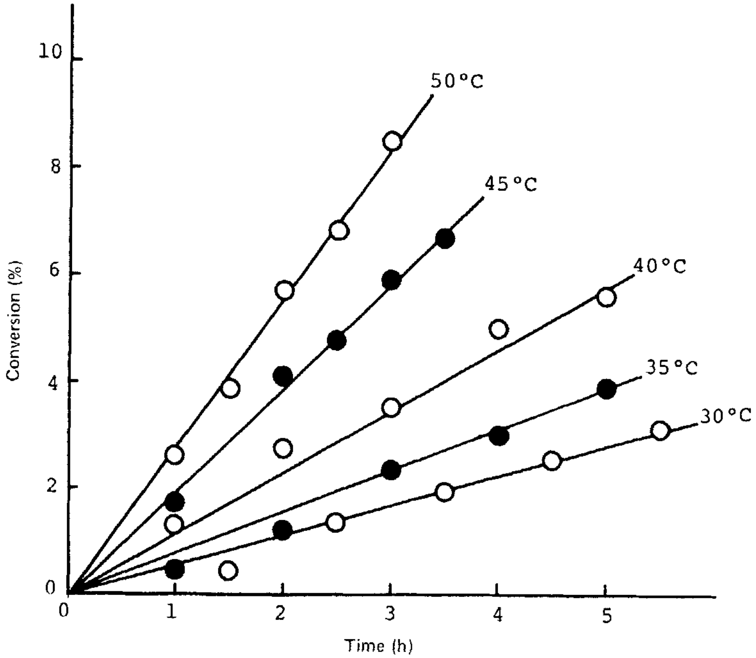


FIG. 1. Time-conversion curves in the polymerization of MMA with Cu(eacac)$_2$/TPB system in acetone: [Cu(eacac)$_2$] = 8.00 × 10^{-3}, [TPB] = 1.00 × 10^{-2}, [MMA] = 4.68 mol/L.

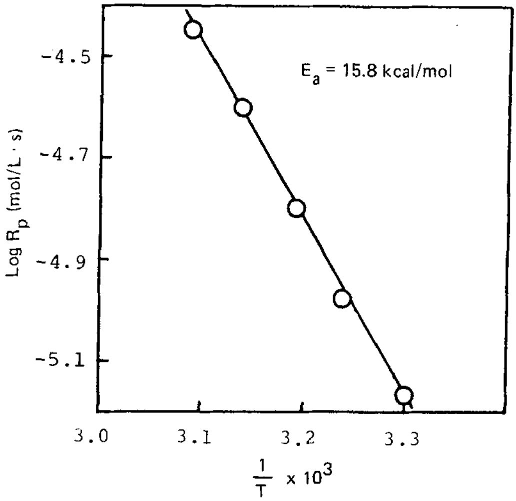


FIG. 2. Temperature effect on the polymerization rate (R_p): $[\mathrm{Cu(eacac)_2}] = 8.00 \times 10^{-3}$, $[\mathrm{TPB}] = 1.00 \times 10^{-2}$, $[\mathrm{MMA}] = 4.68$ mol/L.

polymerization with the Co(acac)$_2$/TPB system [1]. The yield of the polymer increased linearly with time at every temperature.

Figure 2 shows an Arrhenius plot of the polymerization rate (R_p) determined from these curves. From the slope of the straight line obtained in Fig. 2, the overall activation energy of this polymerization was calculated to be 15.8 kcal/mol. This value is a little lower than that (17.6 kcal/mol) of the bulk polymerization of MMA with Cu(eacac)$_2$ alone [2].

Figure 3 shows the relationship between R_p and the Cu(eacac)$_2$ concentration when the concentrations of MMA and TPB were kept constant. Similarly, Fig. 4 shows the relationship between R_p and TPB concentration. R_p was found to be proportional to the square roots of the concentrations of both initiator components. This indicates that bimolecular termination of the polymer radical occurs in this polymerization system. As shown in Figs. 3 and 4, a linear relationship is observed between R_p and the reciprocal degree of polymerization ($1/\bar{P}_n$) of the polymers obtained. This linear relationship indicates that the chain transfer reaction of the polymer radical to the initiator component is negligible under the present conditions.

Figure 5 shows the relationship between the monomer concentration and R_p. As can be seen, R_p was found to depend on the 2.5 order of the

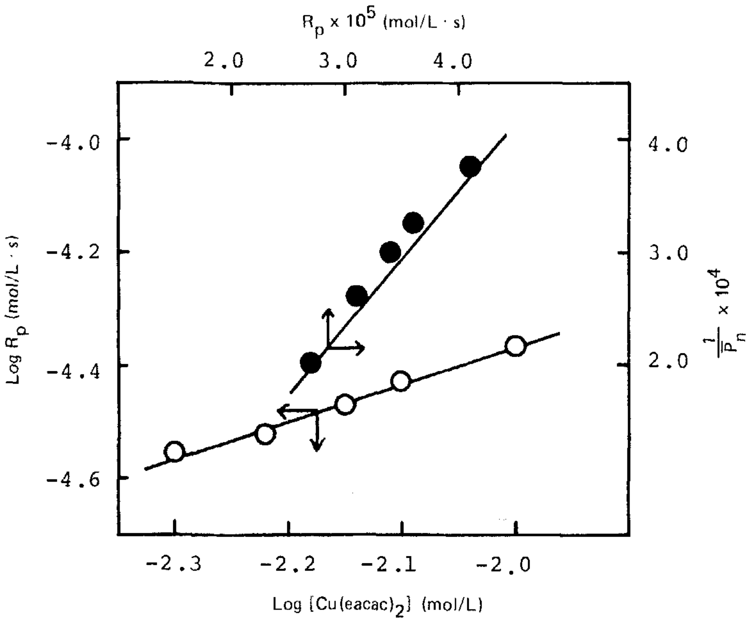


FIG. 3. Dependence of the polymerization rate (R_p) on the $Cu(eacac)_2$ concentration and on $1/\bar{P}_n$ at 50°C in acetone: [TPB] = 1.00×10^{-2}, [MMA] = 4.68 mol/L.

MMA concentration. This high-order dependence suggests a participation of the monomer in the initiation process in this polymerization. From the above results, the following rate equation was derived for the polymerization of MMA with the $Cu(eacac)_2$/TPB system:

$$R_p = K[Cu(eacac)_2]^{0.5}[TPB]^{0.5}[MMA]^{2.5} \tag{2}$$

Visible and ESR Spectra of $Cu(eacac)_2$/TPB System

Figure 6 shows the visible spectrum of the $Cu(eacac)_2$/TPB system after reaction at 50°C. The spectrum behaved differently depending upon the absence or presence of MMA. The absorption at 340-450 nm increased with time, even in the absence of monomer (A in Fig. 6), but this increase was much lower compared with that

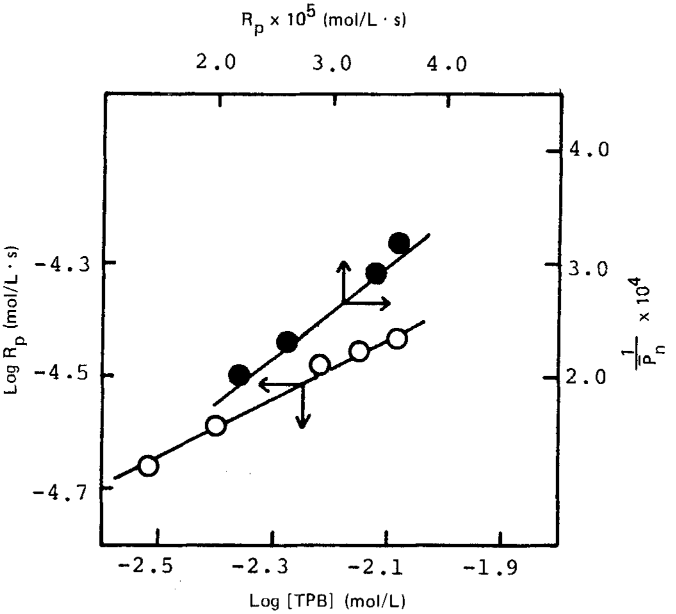


FIG. 4. Dependence of the polymerization rate (R_p) on the TPB concentration and on $1/\bar{P}_n$ at 50°C in acetone: [$Cu(eacac)_2$] = 8.00 × 10^{-3}, [MMA] = 4.68 mol/L.

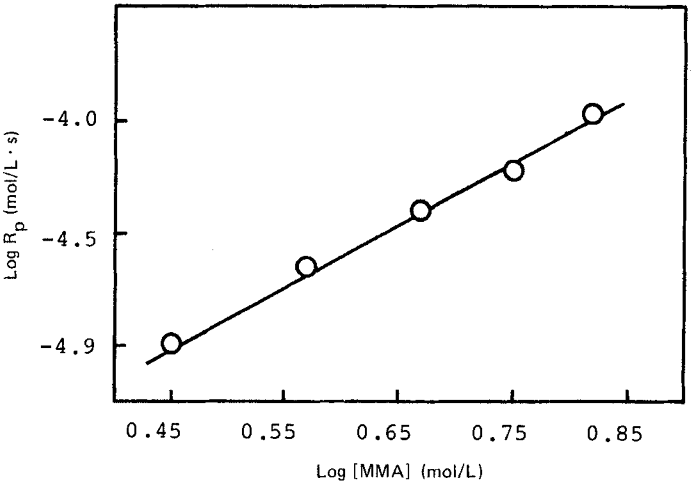


FIG. 5. Effect of the MMA concentration on R_p at 50°C in acetone: [$Cu(eacac)_2$] = 8.00 × 10^{-3}, [TPB] = 1.00 × 10^{-2} mol/L.

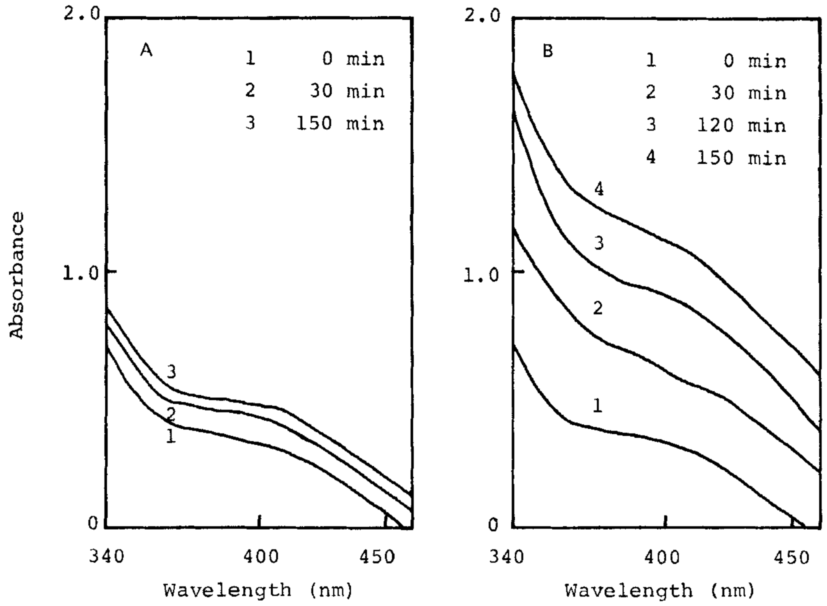


FIG. 6. Visible spectrum of the $Cu(eacac)_2$/TPB system after reaction at 50°C in acetone: $[Cu(eacac)_2] = 2.00 \times 10^{-3}$, $[TPB] = 3.00 \times 10^{-3}$, $[MMA] = 4.68$ mol/L. A: In the absence of MMA. B: In the presence of MMA.

in the presence of monomer (B in Fig. 6). In the absence of MMA, no increase of absorption was observed after about 150 min. This indicates that a complex was formed between $Cu(eacac)_2$ and TPB, but no further reaction proceeded after equilibrium was attained in a given time. However, in the presence of monomer, the reaction between the $Cu(eacac)_2$ and TPB proceeded rapidly and reduction of Cu(II) to Cu(I) occurred. The occurrence of this reduction was supported by the fact that the color of the polymerization system changed from green to green-yellow and finally to yellow.

Figure 7 shows the ESR spectrum of the $Cu(eacac)_2$/TPB system in acetone. Typical absorption of four lines of Cu(II) is observed in Fig. 7. After 2 h at 50°C, the strength of the absorption was slightly lowered. As shown in Fig. 8, however, in the presence of monomer this binary system showed only a very weak absorption after 2 h at 50°C, indicating reduction from Cu(II) to Cu(I). This result is consistent with the results from visible spectroscopic and kinetic studies, suggesting participation of the monomer in the initiation process.

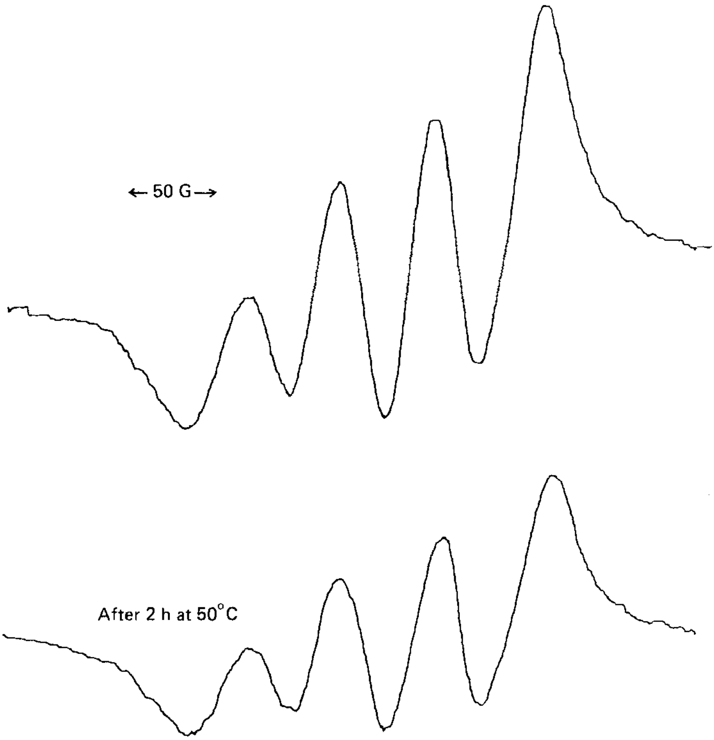


FIG. 7. ESR spectrum of the Cu(eacac)$_2$/TPB system in acetone: [Cu(eacac)$_2$] = 2.00 × 10^{-3}, [TPB] = 3.00 × 10^{-3} mol/L.

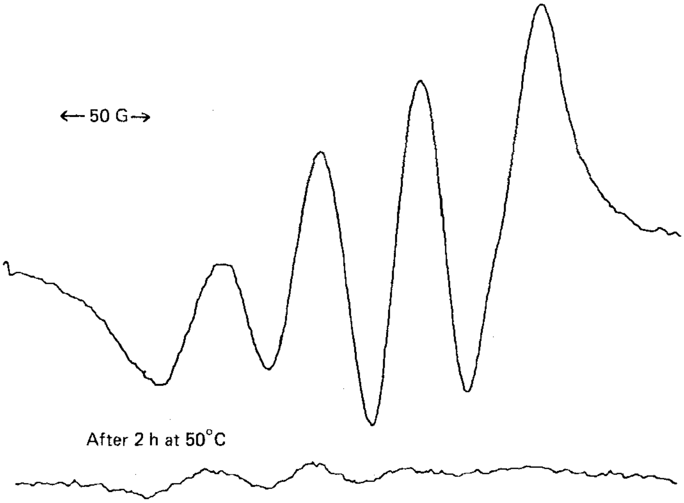


FIG. 8. ESR spectrum of the Cu(eacac)$_2$/TPB/MMA system in acetone: [Cu(eacac)$_2$] = 2.00 × 10^{-3}, [TPB] = 3.00 × 10^{-3}, [MMA] = 3.76 mol/L.

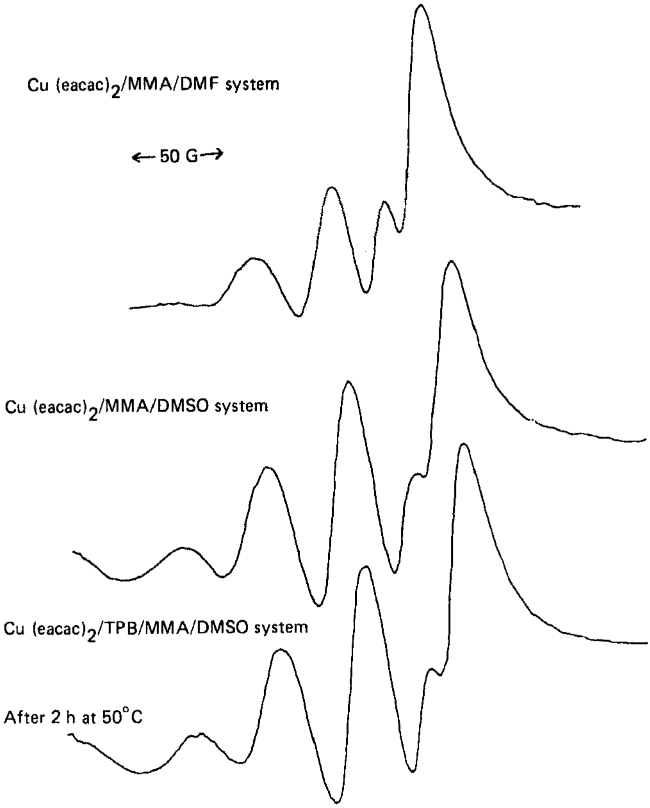


FIG. 9. ESR spectrum of the $Cu(eacac)_2$/MMA/DMF and $Cu(eacac)_2$/TPB/MMA/DMSO systems: $[Cu(eacac)_2] = 2.00 \times 10^{-3}$, $[TPB] = 3.00 \times 10^{-3}$, $[MMA] = 3.76$ mol/L.

Figure 9 shows the ESR spectra of the $Cu(eacac)_2$/MMA/DMF and the $Cu(eacac)_2$/TPB/MMA/DMSO systems. As mentioned above, polymerization by this binary system did not proceed appreciably in DMF and DMSO. As shown in Fig. 9, the ESR spectra in DMF and DMSO differed from that in acetone. It is suggested that different copper complexes are produced in those solvents. Further, the ESR spectrum in a mixture of MMA and DMSO was almost unchanged after 2 h at 50°C, indicating that reduction of Cu(II) is very difficult in DMSO. This finding is in accord with the solvent effect results on polymerization.

Reaction of $Cu(eacac)_2$ and TPB

To elucidate the initiation mechanism, the reaction between the $Cu(eacac)_2$ and TPB was carried out in acetone at 50°C for 10 h. The product analysis for the reaction was performed by gas chromatography. 4-Methylbiphenyl (MBPH) was used as an internal standard. The results are shown in Table 4. As can be seen, trace amounts of biphenyl (BPh) were produced. The production of ethyl acetoacetate (EA) was also confirmed because BPh production was accelerated by an increase in $Cu(eacac)_2$ concentration. However, it was found that the amount of BPh decreased with an increase in monomer concentration. These results suggest that BPh might be formed through a reaction other than radical formation. However, the possibility of BPh formation from the phenyl radical cannot be neglected. It has been reported that BPh is a major product of the electrooxidation of TPB [5] where the formation of phenyl radical was confirmed by the spin trapping technique [6]:

$$B(C_6H_5)_4^- \xrightarrow[\text{electrode}]{-2e} B(C_6H_5)_2^+ + (C_6H_5)_2 \qquad (3)$$

TABLE 4. Reaction of TPB with $Cu(eacac)_2$ at 50°C for 10 h in Acetone[a]

Solvents and monomer (mL)			
Acetone	$CHCl_3$	MMA	Product of biphenyl (mg)
10	-	-[b]	0.4
10	-	-	7.2
5	5	-	0.7
4	3	3	0.3
5	-	5	0.3
7	-	3	0.4
9	-	1	1.1

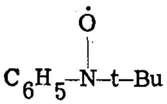
[a] Reaction condition: $[Cu(eacac)_2]$ = 16 mmol, [TPB] = 17 mmol, carrier gas, nitrogen; column temperature, 80-170°C; programmed rate, 4°C/min, injection temperature, 200°C.

[b] Reaction condition: $[Cu(eacac)_2]$ = 8 mmol, [TPB] = 17 mmol.

In the reaction of Cu(eacac)$_2$ and TPB, the formation of BPh may be suppressed by the reaction of MMA and phenyl radical.

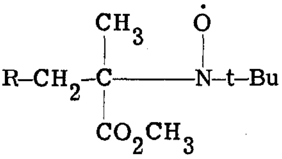
A Study of the Initiation Mechanism by Means of the Spin Trapping Technique

As described above, it is apparent that the Cu(eacac)$_2$/TPS system in acetone is a useful initiator for the radical polymerization of vinyl monomer. In order to clarify the initiation mechanism, the spin trapping technique was applied. 2-Methyl-2-nitrosopropane (BNO) was the spin trapping agent.



$C_6H_5\text{–}N(\dot{O})\text{–}t\text{-}Bu$

I



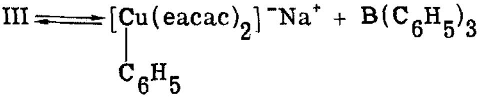
$R\text{–}CH_2\text{–}C(CH_3)(CO_2CH_3)\text{–}N(\dot{O})\text{–}t\text{-}Bu$

II

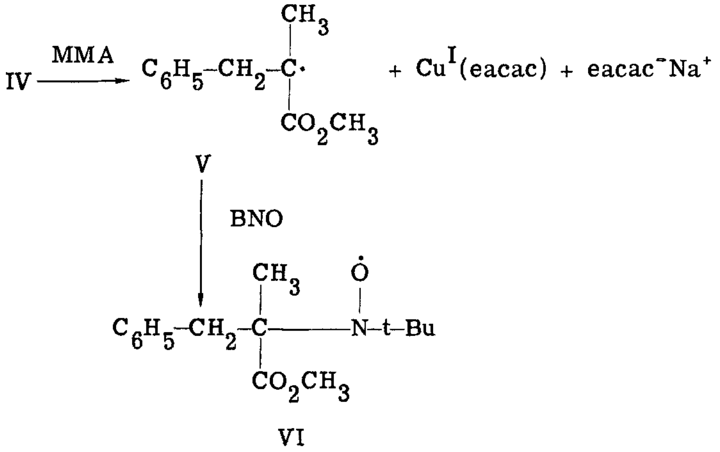
Figure 10 shows the ESR spectrum of the Cu(eacac)$_2$/TPB/BNO system in acetone. Nitroxyl Radical I produced by trapping the phenyl radical was observed, although broadening of the spectrum probably occurred by interaction of the nitroxyl radical with copper ion. In contrast to this system, nitroxyl radical I was not observed in the Co(acac)$_2$/TPB system in the absence of monomer. Figure 11 shows the ESR spectrum of the system Cu(eacac)$_2$, TPB, and BNO in the presence of monomer. Nitroxyl Radicals I and II were observed. The latter radical was produced from trapping by BNO of a radical formed by addition of some radical(R$^\bullet$) to the monomer.

From the above results, the initiation mechanism of this polymerization was considered to be as follows:

$$Na^+B(C_6H_5)_4^- + Cu^{II}(eacac)_2 \rightleftharpoons \underset{\text{III}}{[Cu(eacac)_2\cdot B(C_6H_5)_4]^-Na^+} \tag{4}$$



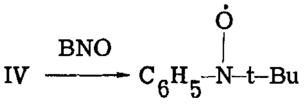
$$\text{III} \rightleftharpoons \underset{\text{IV}}{[Cu(C_6H_5)(eacac)_2]^-Na^+} + B(C_6H_5)_3 \tag{5}$$



$$\mathrm{IV} \xrightarrow{\text{MMA}} \mathrm{C_6H_5{-}CH_2{-}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CO_2CH_3}}{\mathrm{C}\cdot}} + \mathrm{Cu^{I}(eacac)} + \mathrm{eacac^{-}Na^{+}} \qquad (6)$$

$$\mathrm{V} \xrightarrow{\text{BNO}} \mathrm{C_6H_5{-}CH_2{-}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CO_2CH_3}}{\mathrm{C}}}{-}\overset{\dot{\mathrm{O}}}{\mathrm{N}}\mathrm{{-}t{-}Bu}$$

VI



$$\mathrm{IV} \xrightarrow{\text{BNO}} \mathrm{C_6H_5{-}}\overset{\dot{\mathrm{O}}}{\mathrm{N}}\mathrm{{-}t{-}Bu} \qquad (7)$$

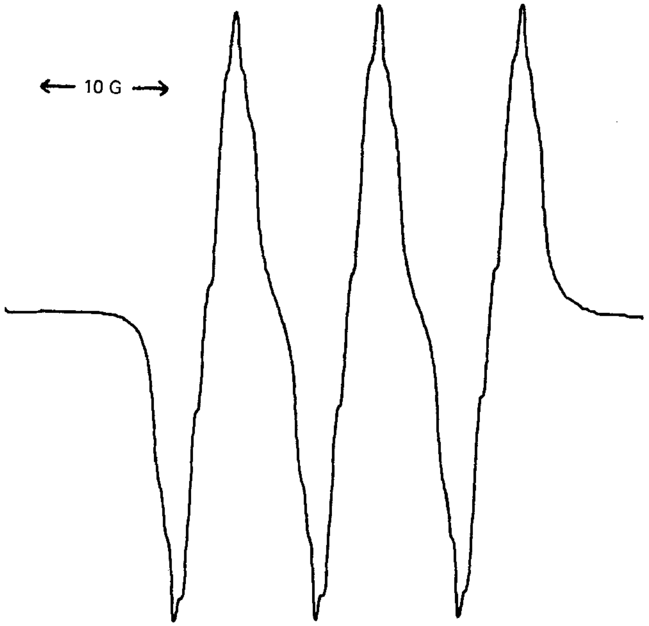


FIG. 10. ESR spectrum of the Cu(eacac)$_2$/TPB/BNO system after reaction at room temperature for 1 h in acetone: [Cu(eacac)$_2$] = 1.50 × 10^{-3}, [TPB] = 1.50 × 10^{-2}, [BNO] = 2.00 × 10^{-2} mol/L.

FIG. 11. ESR spectrum of the Cu(eacac)$_2$/TPB/MMA/BNO system after reaction at room temperature for 0.5 h in acetone: [Cu(eacac)$_2$] = 1.50 × 10^{-3}, [TPB] = 1.50 × 10^{-2}, [MMA] = 5.60, [BNO] = 2.00 × 10^{-2} mol/L.

At first, Complexes III and IV are formed by equilibrium reactions between Cu(eacac)$_2$ and TPB. Complex IV has a phenyl group coordinating to the center metal. Complex IV seems to react with MMA, and Radical V is formed and initiates polymerization. Nitroxyl radical VI is formed by trapping of this radical by BNO. As mentioned above, nitroxyl Radical I was observed in the absence of monomer, suggesting that IV reacts directly with BNO to form nitroxyl Radical I.

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