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Metal-Containing Initiator Systems. 30. Vinyl Polymerization Initiated with Bis(ethyl acetoacetato)copper(II) and Maleimide

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Metal-Containing Initiator Systems. 30.* Vinyl Polymerization Initiated with Bis(ethyl acetoacetato)copper(II) and Maleimide

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ABSTRACT

Some electron-accepting compounds such as maleimide (MIm), maleic anhydride (MAn), and tetracyanoquinodimethane were found to show pronounced accelerating effects on vinyl polymerization initiated with metal chelates. The polymerization of methyl methacrylate (MMA) initiated with bis(ethyl acetoacetato)-copper(II) (Cu(eacac)$_2$) and MIm was studied kinetically in benzene. The overall activation energy of the polymerization was calculated to be 11.5 kcal/mol. This value was much lower than that (17.6 kcal/mol) for the polymerization of MMA with Cu(eacac)$_2$ alone. The polymerization rate (R_p) was expressed as

$$R_p = k[\mathrm{MIm}]^{1/2}[\mathrm{Cu(eacac)_2}]^{1/2}[\mathrm{MMA}]$$

The first-order dependence of R_p on the monomer concentration indicated that the monomer had no participation in the initiation

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*For Part 29 of this series see T. Otsu and Y. Mun, J. Macromol. Sci.–Chem., A11(10), 1783 (1977).

step, in contrast with polymerization in the absence of MIm (where a monomer concentration dependence of 1.4th order was observed). Electronic spectroscopic study revealed that a complex between MIm and Cu(eacac)$_2$ had been formed. The ligand radical, an acetylcarboethoxymethyl radical, was trapped by 2-methyl-2-nitrosopropane in the reactions of Cu(eacac)$_2$ with MIm and with MAn in benzene. From these results the mechanism of the initiation of polymerization is discussed.

INTRODUCTION

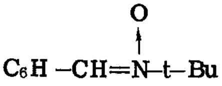
In previous papers [1-4] we studied the mechanism of vinyl polymerization initiated with metal chelates such as tris(acetylacetonato) manganese(III) (Mn(acac)$_3$) and bis(ethyl acetoacetato)-copper(II) (Cu(eacac)$_2$). From the kinetic results it has been concluded that the monomer and the metal chelate are in equilibrium with a coordination complex which produces a ligand radical to initiate polymerization.

On the basis of this conclusion some workers have investigated the effects of electron-donating compounds on polymerization with metal chelates. Pyridine [5], dimethylsulfoxide [6], and phenanthroline [7] have been reported to have high accelerating effects. Particularly, the presence of phenanthroline reduces the monomer concentration dependence of the polymerization rate from 1.9th to 1st order in the polymerization of styrene (St) with Mn(acac)$_3$.

On the other hand, Yamamoto et al. [8] have found that the stability constants of coordination complexes of vinyl monomers with dipyridylnickel and with dialkyl(dipyridyl)nickel are correlated to the e-values of the monomers, and they have concluded that back-donation of electron density from the metal atom to the monomers is an important factor governing the equilibrium constant. This might be responsible for the fact [1] that the initiating activities of metal chelates are relatively high for electron-accepting monomers such as acrylonitrile (AN) and methyl methacrylate (MMA).

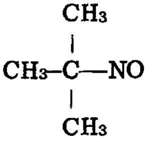
Uehara et al. [9] have found a high accelerating effect of tetracyanoethylene (TCNE) on the polymerization of MMA with bisacetylacetonatocopper(II). They have assumed that this accelerating effect originates from an interaction between TCNE and the chelate ring.

The present paper deals with the effects of some electron-accepting compounds such as maleimide (MIm) and maleic anhydride (MAn) on vinyl polymerization with metal chelates, and with the initiation mechanism investigated by means of spin trapping technique. Phenyl-tert-butylnitrone (PBN) and 2-methyl-2-nitrosopropane (BNO) were used as spin trapping reagents.



$C_6H-CH=\overset{\overset{O}{\uparrow}}{N}-t-Bu$

PBN



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-NO$

BNO

EXPERIMENTAL

$Cu(eacac)_2$ was prepared by reaction of cupric acetate with ethyl acetoacetate, and purified by recrystallization from chloroform [2]. Other metal chelates, commercially available guaranteed reagents, were used without further purification.

MIm was prepared by pyrolysis of N-carbamylmaleimide according to the method of Tawney et al. [10] and was purified by sublimation. Mp, 92°C (literature [10], 92-94°C). PBN was prepared by pyrolysis of the oxaziridine obtained by oxidation of N-tert-butylbenzaldimine with peracetic acid according to the method of Emmons [11]. BNO was prepared by oxidation of tert-butylamine with m-chloroperbenzoic acid according to the method of Perkins [12]. Monomers, solvents, and other reagents were purified by the usual methods.

The polymerizations of vinyl monomers with metal chelates and electron-accepting compounds were carried out in sealed tubes as described in a previous paper [2]. The resulting polymer was isolated by pouring the mixture into a large excess of methanol. The intrinsic viscosity ($[\eta]$) of poly(methyl methacrylate) was measured in benzene at 30°C, and the number-average degree of polymerization ($\overline{P}_n$) was calculated according to [13]

$$\log \overline{P}_n = 3.35 + 1.32 \log [\eta]$$

The reactions of $Cu(eacac)_2$ with MIm and with maleic anhydride were carried out in the presence of BNO or PBN in a degassed ESR tube, and the ESR spectra of the reaction mixtures were recorded by using a JES-ME-3X spectrometer with 100 kHz field modulation.

The visible spectrum of the $Cu(eacac)_2$/MIm system was recorded by a Hitachi ESP-2T spectrometer.

RESULTS AND DISCUSSION

Effects of Some Electron-Accepting Compounds on the Polymerization of MMA with Metal Chelates

The polymerization of MMA with metal chelates was carried out in benzene at 60°C in the presence of some electron-accepting

TABLE 1. Effect of Some Electron Acceptors on the Polymerization of MMA with Metal Chelates in Benzene at 60° C for 5 h

Metal chelate	Acceptor	mol/L	Yield (%)	$\overline{P}_n \times 10^{-2}$
$Cu(eacac)_2$	None	-	0	-
	MIm[a]	0.2	27.0	7.6
	MAn	0.2	27.2	15.6
	$AlEt_3$	0.2	4.4	2.3
	TCNQ	0.025	17.9	-
	Chloranil	0.08	0	-
	$B(OCH_3)_3$	0.4	0	-
	$SiCl_4$	0.4	0	-
	$TiCl_3$	0.05	0	-
	$SnCl_4$	0.4	0	-
	Br_2	0.9	0	-
	$Et_2O{\cdot}BF_3$	0.4	0	-
$Ni(acac)_2$	None	-	Trace	-
	MIm	0.2	Trace	-
	MAn	0.2	0.14	-
	$AlEt_3$	0.2	32.0	1.4
$Co(acac)_2$	None	-	0	-
	MIm	0.2	Trace	-
	MAn	0.2	4.9	128.0
	$AlEt_3$	0.2	37.0	1.0

[a] 1.5 h, [metal chelate] = 1.00×10^{-2}, [MMA] = 4.68 mol/L.

compounds. Bisacetylacetonatonickel(II) ($Ni(acac)_2$), $Cu(eacac)_2$, and bisacetylacetonatocobalt(II) ($Co(acac)_2$) were used as the metal chelates because these four-coordinated complexes tend to receive another ligand and because they show only slight initiating activities for MMA in the absence of the additives.

Table 1 summarizes the results obtained. Although $Cu(eacac)_2$ alone induces no polymerization under the present conditions [the bulk polymerization of MMA with $Cu(eacac)_2$ at 80° C proceeds at a moderate rate [2]], addition of MIm, MAn, or tetracyanoquinodimethane (TCNQ) to this system is found to cause considerably high polymer yields.

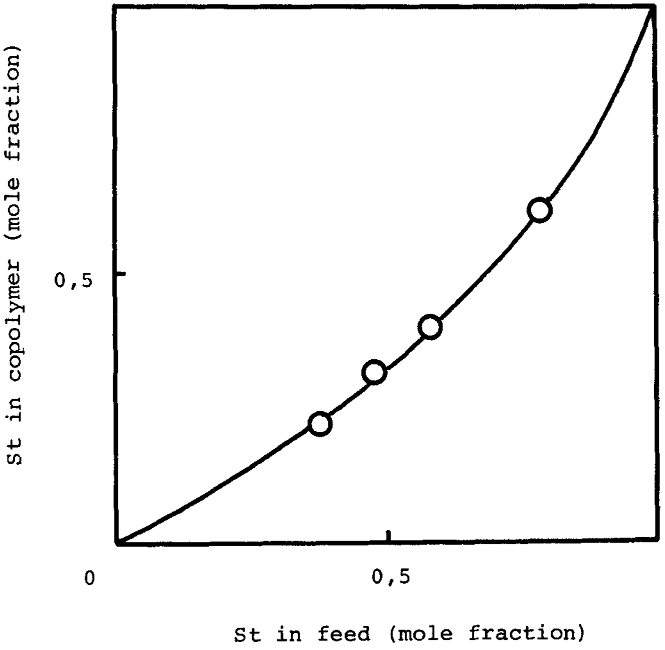


FIG. 1. Copolymerization of MMA with St initiated with the $Cu(eacac)_2/AlEt_3$ system at 60°C in benzene; $[Cu(eacac)_2] = 1.0 \times 10^{-2}$, $[AlEt_3] = 0.2$ mol/L.

The systems of metal chelates and triethylaluminum ($AlEt_3$) are also found to give good polymer yields, but the resulting poly(MMA) has very low molecular weight. Further, as shown in Fig. 1, the copolymerization of St with MMA with the $Cu(eacac)_2/AlEt_3$ system gives a monomer-copolymer composition curve indicating that the copolymer formed contains a somewhat higher MMA content than that from the usual radical polymerization. These findings suggest that the propagating species in this polymerization has some anionic character. Deshpande et al. [14] have studied the polymerization of St with the trisacetylacetonatochromium(III) ($Cr(acac)_3$)/$AlEt_3$ system, and on the basis of the kinetic results and the effect of $ZnEt_2$ as the chain transfer reagent, they have concluded that the polymerization proceeds via a coordinated anion mechanism. Simionescu et al. [15] have also reported an anionic polymerization of phenylacetylene with systems of $AlEt_3$ and metal chelates such as $Cr(acac)_3$ and trisacetylacetonatocobalt(III).

Combinations of $Cu(eacac)_2$ and halogenated compounds such as $AlCl_3$, $SiCl_4$, $SnCl_4$, $BF_3 \cdot O(C_2H_5)_2$, and bromine give no polymer. Chloranil also inhibits this polymerization. The additive effects of MIm and MAn on the polymerization with $Ni(acac)_2$ and $Co(acac)_2$

TABLE 2. Polymerization of Some Vinyl Monomers with the $Cu(eacac)_2$/MIm System at 60° C in Benzene for 5 h

Monomer	Acceptor	Yield (%)
AN	MIm	32.9
	None	13.2
MMA[a]	MIm	27.0
	None	0
St	MIm	1.1
	None	0
VAc	MIm	6.4
	None	0

[a] 1.5 h, $[Cu(eacac)_2] = 1.00 \times 10^{-2}$, $[MIm] = 0.20$ mol/L.

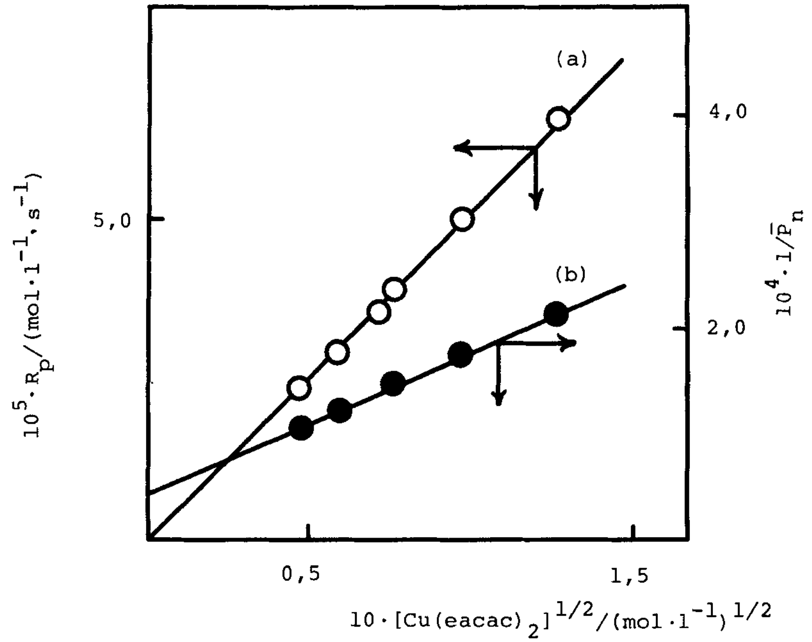


FIG. 2. Effect of the $Cu(eacac)_2$ concentration on R_p and on $1/P_n$ at 60°C in benzene; $[MIm] = 1.00 \times 10^{-2}$, $[MMA] = 4.68$ mol/L.

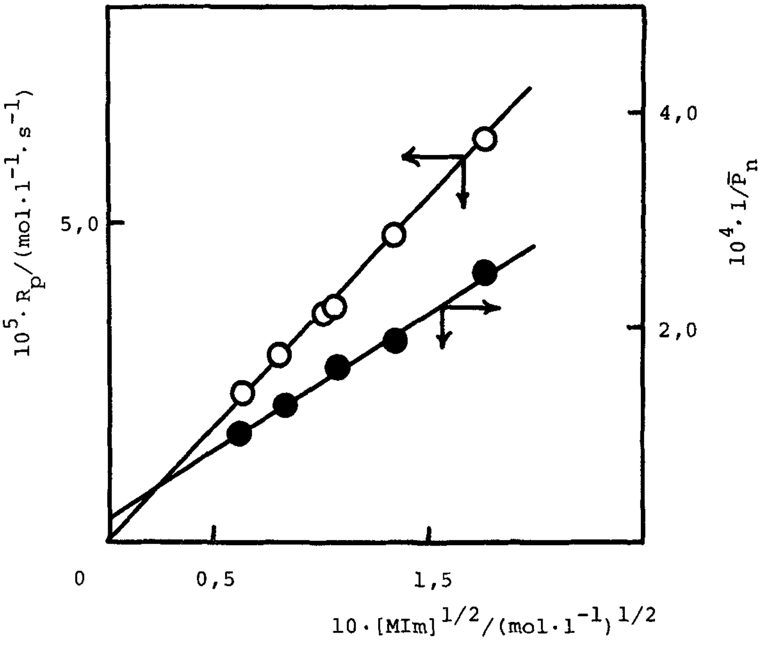


FIG. 3. Effect of the MIm concentration on R_p and on $1/\bar{P}_n$ at 60°C in benzene; [Cu(eacac)$_2$] = 5.00×10^{-3}, [MMA] = 4.68 mol/L.

are found to be much smaller compared with the polymerization with Cu(eacac)$_2$.

Polymerization of Some Vinyl Monomers with the Cu(eacac)$_2$/MIm System

As mentioned in the preceding section, the Cu(eacac)$_2$/MIm system is found to have a considerably high initiating activity for MMA. Further, some vinyl monomers were polymerized in benzene at 60°C by using this binary system as initiator. The monomers used were AN, St, and vinyl acetate (VAc). Table 2 summarizes the results obtained, together with those in the polymerizations with Cu(eacac)$_2$ alone for comparison. Some acceleration by the presence of MIm is observed for every monomer used.

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

The polymerization of MMA with the $Cu(eacac)_2$/MIm system was studied kinetically in detail in benzene. The results obtained were compared with those of the polymerization with $Cu(eacac)_2$ alone [2].

The effects of the concentrations of the initiators on the polymerization rate (R_p) were investigated at 60°C. As shown in Fig. 2 (graph a), a linear relationship is observed between R_p and the square-root of the chelate concentration when the concentrations of MMA and MIm were kept constant at 4.68 and 1.0×10^{-2} mol/L, respectively. The straight line (b) shows a relationship between the square-root of the chelate concentration 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 growing poly(MMA) radical and the chelate is negligible under the present conditions.

From Fig. 3 it is shown that both of R_p and $1/\bar{P}_n$ are also linearly dependent upon the square-root of the MIm concentration, where the

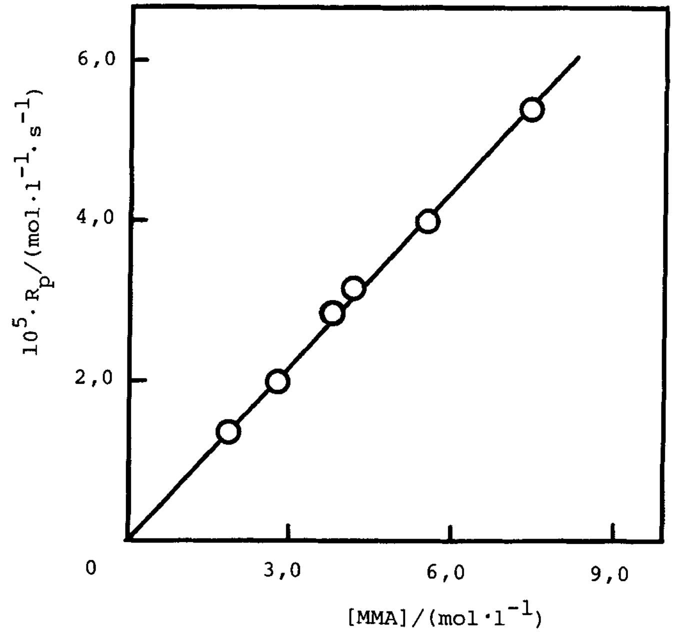


FIG. 4. Effect of the monomer concentration on R_p at 60°C in benzene; $[Cu(eacac)_2] = 5.00 \times 10^{-3}$, $[MIm] = 1.00 \times 10^{-2}$ mol/L.

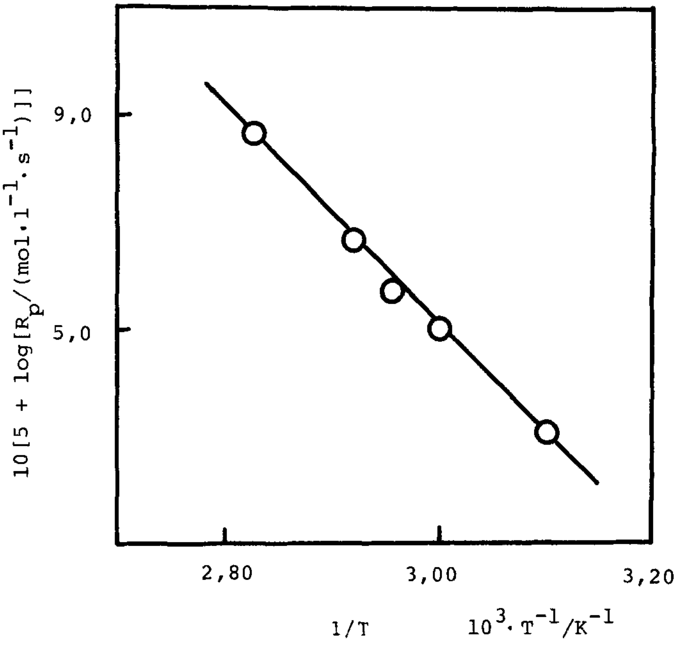


FIG. 5. Effect of temperature on R_p in benzene; [$Cu(eacac)_2$] = 5.00×10^{-3}, [MIm] = 1.00×10^{-2}, [MMA] = 4.68 mol/L.

concentrations of the chelate and MMA are kept constant at 5.0×10^{-3} and 4.68 mol/L, respectively. This finding shows that the chain transfer reaction to MIm also seems to be negligible.

Furthermore, the relationship between R_p and the monomer concentration was studied at 60°C where the concentrations of MIm and $Cu(eacac)_2$ were kept at 1.0×10^{-2} and 5.0×10^{-3} mol/L, respectively. As can be seen from Fig. 4, R_p is found to be proportional to the first-order of the monomer concentration. This fact differs from the result observed in the polymerization initiated with $Cu(eacac)_2$ alone [2], in which R_p depends on the 1.4th order of the monomer concentration.

From these kinetic results the following rate equation is derived for the polymerization of MMA with the $Cu(eacac)_2$/MIm system:

$$R_p = K[Cu(eacac)_2]^{1/2}[MIm]^{1/2}[MMA]$$

This rate equation indicates that the polymerization is induced by the

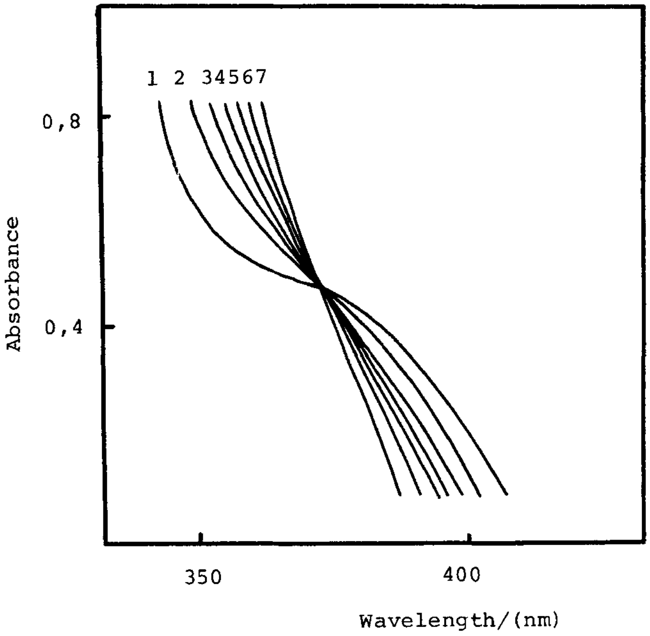


FIG. 6. Electronic spectrum of the $Cu(eacac)_2$/MIm system in benzene at room temperature; $[Cu(eacac)_2] = 2.18 \times 10^{-3}$, [MIm] = 1, 0; 2, 8.64×10^{-4}; 3, 2.59×10^{-3}; 4, 4.30×10^{-3}; 5, 7.20×10^{-3}; 6, 1.20×10^{-2}; 7, 2.00×10^{-2} mol/L.

reaction of $Cu(eacac)_2$ with MIm without any participation of the monomer in the initiation step.

Finally, the temperature effect on R_p was studied in the range from 40 to 70°C. Figure 5 shows an Arrhenius plot of the results observed. From the slope of the straight line obtained in the figure, the overall activation energy of this polymerization is calculated to be 11.5 kcal/mol. This value is much lower than 17.6 kcal/mol for the polymerization with $Cu(eacac)_2$ alone [2].

Electronic Spectrum of the $Cu(eacac)_2$/MIm System

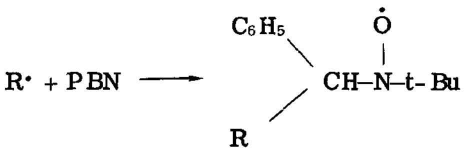
As described above, the system of MIm and $Cu(eacac)_2$ is found to induce radical polymerization without any participation of the monomer in the initiation step. In order to obtain information about the mechanism of acceleration by MIm, the effect of MIm on the electronic spectrum of $Cu(eacac)_2$ was investigated in benzene at room temperature. Figure 6 shows the results observed. In the absence of MIm, a benzene solution of Cu(eacac)$_2$ (2.18×10^{-3} mol/L) shows Spectrum 1. This spectrum is changed to Spectrum 2 by addition of MIm (8.64×10^{-4} mol/L), and then from 2 to 7 with an increase in the concentration of MIm. Thus these spectra give an equiabsorbance point around 375 nm, suggesting that an equilibrium occurs between two different copper complexes. This is considered to originate from the formation of a new coordinated complex from MIm and Cu(eacac)$_2$.

Application of Spin Trapping Technique to the Reactions of Cu(eacac)$_2$ with MIm and MAn

PBN and BNO are known to react readily with short-lived free radicals to form very stable aminyl oxide radicals [16, 17].

To detect radicals from the reaction of Cu(eacac)$_2$ with MIm, the reaction was carried out in benzene in the presence of PBN. Figure 7 shows the ESR spectrum of the reaction mixture together with that obtained in the system containing only Cu(eacac)$_2$ for comparison.

When a benzene solution containing Cu(eacac)$_2$ (2.5×10^{-3} mol/L) alone is allowed to stand for 0.5 h at room temperature, it gives only the spectrum of cupric ion ("a" in Fig. 7), while the presence of MIm (1.03×10^{-1} mol/L) is found to cause the appearance of another spectrum due to the aminyl oxide radical which is derived from the reaction of PBN with radical R$\cdot$ formed in the system (Eq. 1) (spectrum c).



(1)

I

When these reaction mixtures are further heated for 0.5 h at 60° C, spectra (b) and (d) are observed. The ESR signal of the aminyl oxide radical I in the system containing both of MIm and Cu(eacac)$_2$ becomes much stronger compared with that of the cupric ion. These observations indicate a high accelerating effect of MIm on the radical formation, and it is compatible with the kinetic and electronic spectroscopic results obtained above.

To identify the radical formed, the reaction of MIm with Cu(eacac)$_2$ was carried out in the presence of BNO at room temperature in benzene. Figure 8 shows the ESR spectrum of the reaction mixture after being reacted for 4 h. The triplet-doublet spectrum ($A_N = 14.1$ G, $A_{\beta\text{-H}} = 3.6$G) (SI-unit: $1 \text{ G} = 10^{-4} \text{ T} = 10^{-4} \text{V}\cdot\text{S}\cdot\text{M}^{-2}$) is assignable to the aminyl oxide radical III which is formed by the trapping by BNO of the ligand radical (II) from Cu(eacac)$_2$ (Eq. 2):

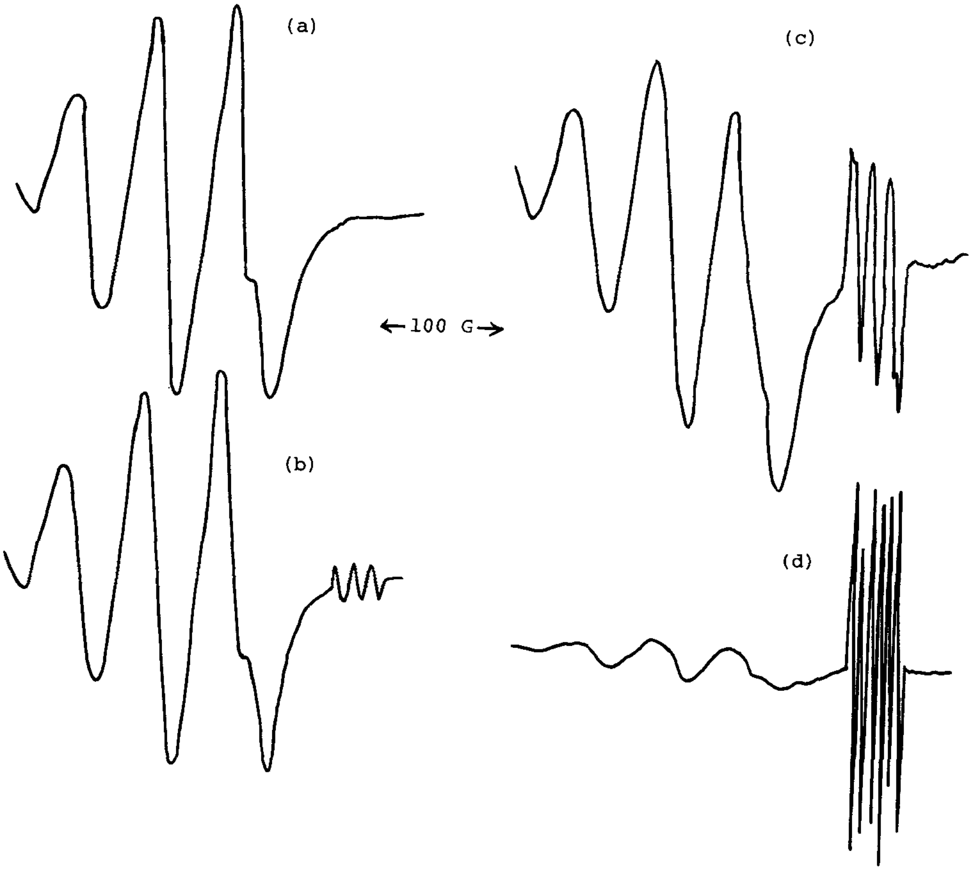


FIG. 7. ESR spectra of the reaction systems Cu(eacac)$_2$/PBN and Cu(eacac)$_2$/MIm/PBN. (a): After being reacted for 0.5 h at room temperature in benzene, [Cu(eacac)$_2$] = 2.5×10^{-3}, [PBN] = 1.1×10^{-1} mol/L. (b): After being further reacted for 0.5 h at 60°C. (c): After being reacted for 0.5 h at room temperature, [Cu(eacac)$_2$] = 2.5×10^{-3}, [MIm] = 1.03×10^{-1}, [PBN] = 1.1×10^{-1} mol/L. (d): After being further reacted for 0.5 h at 60°C.

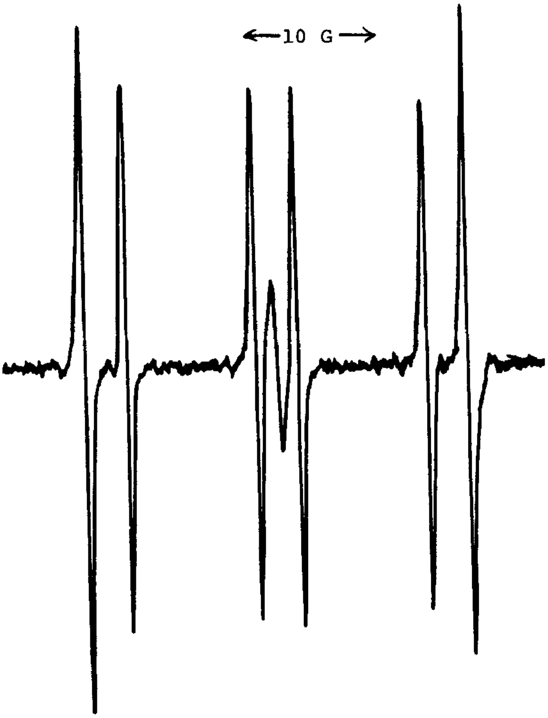
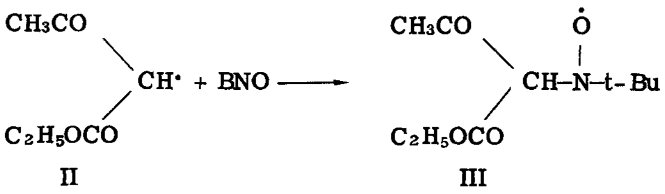


FIG. 8. ESR spectrum of the reaction system Cu(eacac)$_2$/MIm/BNO after being reacted for 4 h at room temperature in benzene; [Cu(eacac)$_2$] = 1.5 × 10^{-3}, [MIm] = 2.6 × 10^{-2}, [BNO] = 4 × 10^{-2} mol.



(2)

The authentic aminyl oxide radical (A_N = 14.2 G, $A_{\beta\text{-}H}$ = 3.8 G) of III was prepared by decomposition of di-tert-butyl peroxalate in ethyl acetoacetate in the presence of BNO (Eqs. 3-5). The ESR spectrum of the reaction mixture is shown in Fig. 9. Small differences in the coupling constants depending on the preparation methods seem to be due to the effect of the solvent used. Aminyl oxide radicals IV and V (similarly prepared) show similar spectra with narrow linewidths.

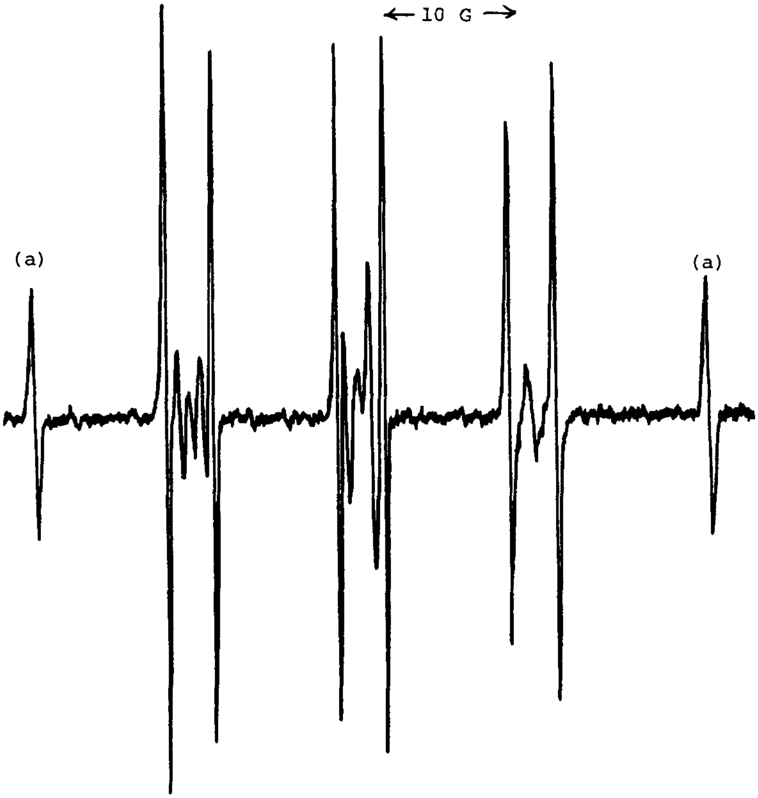


FIG. 9. ESR spectrum of the reaction system ethyl acetoacetate/di-tert-butyl peroxalate (DBPOX)/BNO after being reacted for 1 h at room temperature. (a): N-tert-Butoxy-tert-butylaminyl oxide, [DBPOX] = 4.3 × 10^{-2}, [BNO] = 2 × 10^{-2} mol/L.

$$\text{t-BuO–OCO–COO–O–t-Bu} \longrightarrow 2\text{BuO}\cdot + 2\text{CO}_2 \qquad (3)$$

$$\text{t-BuO}\cdot + \text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5 \longrightarrow \text{II} + \text{t-BuOH} \qquad (4)$$

$$\text{II} + \text{BNO} \longrightarrow \text{III} \qquad (5)$$

As shown in Fig. 10, the reaction of MAn with Cu(eacac)$_2$ in the presence of BNO is also found to give aminyl oxide III although another unassignable spectrum is also observed.

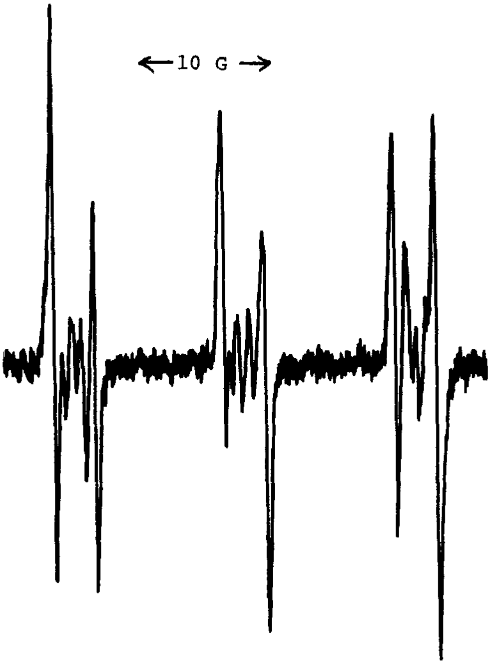
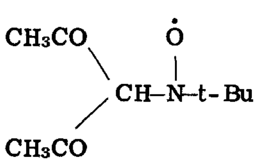
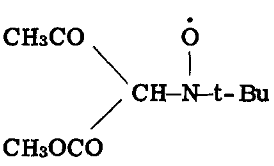


FIG. 10. ESR spectrum of the reaction system Cu(eacac)$_2$/MAn/BNO after being reacted for 45 min at room temperature in benzene; [Cu(eacac)$_2$] = 3.0 × 10^{-3}, [MAn] = 6.2 × 10^{-2}, [BNO] = 4 × 10^{-2} mol/L.



IV



V

Initiation Mechanism

As mentioned above, the polymerization of MMA is much accelerated by MIm. The presence of MIm excludes any participation of the monomer in the initiation step and hence reduces the monomer concentration dependence of R_p from 1.4th to 1st order. Further, the overall activation energy of the polymerization decreases from 17.6 to 11.4 kcal/mol. Investigation of the electronic spectrum of the MIm/Cu(eacac)$_2$ system reveals the formation of a complex between MIm and Cu(eacac)$_2$. An ESR spectroscopic study of the reaction of MIm with Cu(eacac)$_2$ in the presence of PBN showed that the MIm/Cu(eacac)$_2$ system produces the radical species much faster than Cu(eacac)$_2$ alone. A spin trapping investigation using BNO revealed that the reaction of MIm and Cu(eacac)$_2$ can readily give ligand radical II without any participation of monomer.

From these observations the initiation mechanism of the polymerization is visualized as

$$\mathrm{MIm} + \mathrm{Cu^{II}(eacac)_2} \rightleftharpoons \underset{\mathrm{VI}}{(\mathrm{MIm{\cdot}Cu^{II}(eacac)_2})} \qquad (6)$$

$$\mathrm{VI} \longrightarrow (\mathrm{MIm{\cdot}Cu^{I}(eacac)}) + \mathrm{II} \qquad (7)$$

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