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### Application of the Spin Trapping Technique to Radical Polymerization. 21. Vinyl Polymerization with the N-Hydroxysuccinimide/Acetylacetonato Metal Chelate System

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## Application of the Spin Trapping Technique to Radical Polymerization. 21. Vinyl Polymerization with the N-Hydroxysuccinimide/Acetylacetonato Metal Chelate System

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### ABSTRACT

Some combinations of N-hydroxysuccinimide (NHS) and acetylacetonato metal chelates were found to induce radical polymerization. A kinetic study on the polymerization of methyl methacrylate (MMA) was performed by using as initiator the NHS/trisacetylacetonatomanganese(III) ( $Mn(acac)_3$ ) system, which can initiate the polymerization effectively even at room temperature. The overall activation energy of polymerization was very low (9.1 kcal/mol). The polymerization rate ( $R_p$ ) was expressed by

$$R_p = k[\text{initiator}]^{0.5}[\text{MMA}]^{1.8}$$

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\*Part 20, T. Sato, N. Fukumura, and T. Otsu, Makromol. Chem., **184**, 431 (1983).

where the initiator concentration was varied by fixing  $[\text{NHS}] / [\text{Mn}(\text{acac})_3] = 2$ .  $R_p$  showed a maximum when  $[\text{Mn}(\text{acac})_3]$  was changed while keeping  $[\text{NHS}]$  constant. Further, a spin trapping study revealed that the primary propagating radical was trapped even in the system containing only a small amount of monomer ( $1.6 \times 10^{-2}$  mol/L). These results indicate that a complex from NHS and  $\text{Mn}(\text{acac})_3$  with a very high stability constant plays an important role in the generation of initiating radicals, and that the monomer participates in the initiation process. This conclusion was also supported by electronic spectroscopic results. An initiation mechanism is proposed and discussed.

## INTRODUCTION

It is well known that hydrogen peroxide and alkyl hydroperoxides react with various metal ions to produce radicals which can initiate vinyl polymerization [1]. On the other hand, N-hydroxysuccinimide (NHS), a nitrogen analog to peracid, was found to initiate the radical polymerization of vinyl monomer [2]. This polymerization is expected to be accelerated by the presence of metal ions.

We recently found that some combinations of NHS and acetylacetonato metal chelates as metal ions effectively induce the polymerization of vinyl monomers in organic solvents. In the present paper vinyl polymerization initiated with the NHS/metal chelate system is studied kinetically, spectroscopically, and by means of the spin trapping technique. An initiation mechanism for this polymerization is proposed and discussed.

## EXPERIMENTAL

Commercial acetylacetonato complexes ( $\text{Me}(\text{acac})_n$ ) (Dotaito reagent) were used without further purification. NHS was used after recrystallization from ethyl acetate. Vinyl monomers and solvents were purified according to the usual methods. N-Methylacrylamide (NMMAm) was prepared by the reaction of acryloyl chloride with methylamine and purified by distillation. 2-Methyl-2-nitrosopropane (BNO) as the spin trapping agent was prepared according to the method of Perkins [3].

Polymerization was carried out in a degassed sealed tube for a given time with shaking. The polymerization mixture was poured into a large amount of methanol containing a small amount of hydrochloric acid which decomposes metal chelates. The polymer formed was filtrated, washed by methanol, dried in vacuum, and weighed. The intrinsic viscosity  $[\eta]$  of the resulting poly(methyl methacrylate (MMA)) was measured in benzene at  $30^\circ\text{C}$ , and the number-average molecular weight of poly(MMA) was calculated by the following equation [4]:

$$\log \bar{M}_n = 5.34 + 1.32 \log [\eta] \quad (1)$$

ESR spectra of the reaction mixtures were recorded by a JES-ME-3X spectrometer with 100 kc/s field modulation. Visible spectra were measured by using a Hitachi EPS-3T spectrophotometer.

## RESULTS AND DISCUSSION

### Polymerization of MMA with the NHS/Me(acac)<sub>n</sub> System

The effect of NHS on the polymerization of MMA initiated with some acetylacetonato metal chelates was investigated in ethyl acetate at 40°C. As shown in Table 1, Mn(acac)<sub>3</sub>, Co(acac)<sub>3</sub> and Fe(acac)<sub>3</sub> gave higher polymer yields than Mn(acac)<sub>2</sub> and Co(acac)<sub>2</sub> systems, which is in agreement with the results reported previously [5].

NHS was found to greatly accelerate the polymerization of MMA with Mn(acac)<sub>3</sub>, Co(acac)<sub>3</sub>, and Cu(acac)<sub>2</sub>. The NHS/Mn(acac)<sub>3</sub>

TABLE 1. Polymerization of MMA with the NHS/Metal Chelate (Me(acac)<sub>n</sub>) System at 40°C for 10 h in Ethyl Acetate<sup>a</sup>

Me(acac) <sub>n</sub>	Polymer yield, %	
	In the absence of NHS	In the presence of NHS <sup>b</sup>
Mn(acac) <sub>3</sub>	10.3	53.7
Co(acac) <sub>3</sub>	3.8	16.4
Cu(acac) <sub>2</sub>	0.0	10.7
Fe(acac) <sub>3</sub>	3.1	5.6
Co(acac) <sub>2</sub>	0.0	0.0
Mn(acac) <sub>2</sub>	0.0	0.0

<sup>a</sup>Me(acac)<sub>n</sub>: 50 mg, [MMA] = 4.68 mol/L.

<sup>b</sup>[NHS] = 4.3 × 10<sup>-2</sup> mol/L.

TABLE 2. Polymerization of Some Vinyl Monomers with the  $\text{Mn}(\text{acac})_3/\text{NHS}$  and the  $\text{Mn}(\text{acac})_3/\text{NHP}$  Systems at  $40^\circ\text{C}$  in Ethyl Acetate<sup>a</sup>

Monomer	Time, h	$\text{Mn}(\text{acac})_3$	Polymer yield, %	
			$\text{Mn}(\text{acac})_3$ + NHS	$\text{Mn}(\text{acac})_3$ + NHP
MA	1	0.0	41.7	2.1
MMA	4	0.0	22.2	3.9
AN	4	0.0	11.7	0.0
St	12	0.4	2.4	1.2
VAc	12	0.0	0.8	0.0

<sup>a</sup> $[\text{Mn}(\text{acac})_3] = 6.31 \times 10^{-3}$ ;  $[\text{NHS}] = [\text{NHP}] = 1.26 \times 10^{-2}$  mol/L; monomer, 5 mL; solvent, 5 mL.

system showed the highest yield. On the other hand, polymerization with  $\text{Mn}(\text{acac})_2$  or  $\text{Co}(\text{acac})_2$  did not proceed even in the presence of NHS.

#### Polymerization of Vinyl Monomers with the NHS/ $\text{Mn}(\text{acac})_3$ System

The polymerization of some vinyl monomers was carried out in ethyl acetate at  $40^\circ\text{C}$  by using the NHS/ $\text{Mn}(\text{acac})_3$  system as initiator. The combination of N-hydroxyphthalimide (NHP) and  $\text{Mn}(\text{acac})_3$  was also investigated for comparison. The results obtained are listed in Table 2. The NHS/ $\text{Mn}(\text{acac})_3$  system showed a higher initiating activity for electron-accepting monomers such as methyl acrylate (MA), MMA, and acrylonitrile (AN) than for styrene (St) and vinyl acetate (VAc). The NHP/ $\text{Mn}(\text{acac})_3$  system gave lower polymer yields compared with the NHS/ $\text{Mn}(\text{acac})_3$  system.

TABLE 3. Polymerization of MMA with the  $\text{Mn}(\text{acac})_3/\text{NHS}$  System in Various Solvents at  $40^\circ\text{C}$  for 4 h<sup>a</sup>

Solvent	Polymer yield, %			$(\bar{M}_n \times 10^{-4})$
	$\text{Mn}(\text{acac})_3$	NHS	$\text{Mn}(\text{acac})_3$ + NHS	
DMF	18.5	0.0	30.9	(12.5)
Acetonitrile	0.0	1.4	20.3	(9.7)
Acetone	0.0	0.0	20.1	(8.6)
Ethyl acetate	0.0	0.0	22.2	(7.4)
Chloroform	0.0	Trace	28.9	(8.2)
Benzene	0.0	0.0	26.5	(7.3)
Tetrahydrofuran	0.0	0.0	23.9	(6.8)
Ethanol	12.1	0.0	8.7	(12.5)
Acetylacetone	7.0	0.0	4.6	(43.5)

<sup>a</sup> $[\text{Mn}(\text{acac})_3] = 6.31 \times 10^{-3}$ ,  $[\text{NHS}] = 1.26 \times 10^{-2}$ ,  $[\text{MMA}] = 4.68$  mol/L.

#### Solvent Effect on the Polymerization of MMA with the $\text{NHS}/\text{Mn}(\text{acac})_3$ System

The polymerization of MMA with the  $\text{NHS}/\text{Mn}(\text{acac})_3$  system was carried out at  $40^\circ\text{C}$  in various solvents for 4 h. As shown in Table 3, higher polymer yields were observed in aprotic solvents such as dimethylformamide (DMF), acetone, and ethyl acetate, being almost independent of the polarity of the solvents used. On the other hand, in ethanol and acetylacetone, which are protic solvents, the polymer yield was reduced to a value similar to that for polymerization with  $\text{Mn}(\text{acac})_3$  alone. This is ascribed to repression of the reaction between NHS and  $\text{Mn}(\text{acac})_3$  by these protic solvents.

#### Polymerization of NMMAm with the $\text{NHS}/\text{Mn}(\text{acac})_3$

As reported previously [6], N-methylacrylamide and NMMAm were found to give their stable propagating polymer radicals

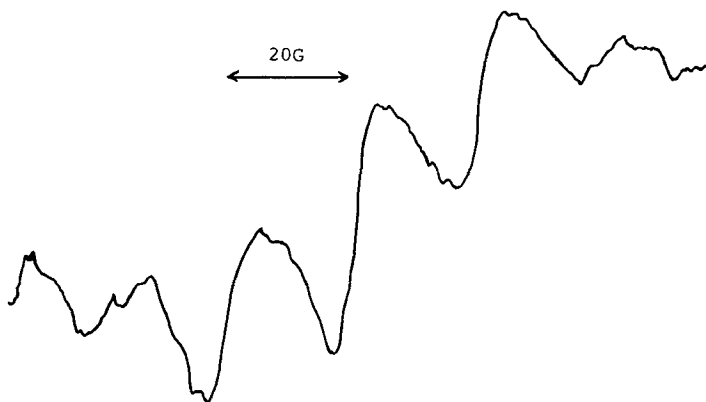
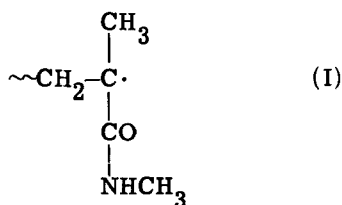


FIG. 1. ESR spectrum of the NHS/Mn(acac)<sub>3</sub>/NMMAm system after reaction at 40°C for 4 h in ethyl acetate. [Mn(acac)<sub>3</sub>] = 2.5 × 10<sup>-3</sup>, [NHS] = 2.5 × 10<sup>-2</sup>, [NMMAm] = 4.9 mol/L.

when the amide monomers were polymerized by radical initiators in adequate solvents.

To see whether the polymerization with the NHS/Mn(acac)<sub>3</sub> system proceeds via a radical mechanism, the polymerization of NMMAm was carried out at 40°C in ethyl acetate. Figure 1 shows the ESR spectrum of the polymerization mixture obtained. The spectrum is assignable to the propagating radical of NMMAm(I). Thus, NMMAm/NHS/Mn(acac)<sub>3</sub> was readily found to produce



indicating that polymerization with this binary initiator system proceeds via radical mechanism.

#### Kinetics of the Polymerization of MMA with the NHS/Mn(acac)<sub>3</sub> System

The polymerization of MMA with the NHS/Mn(acac)<sub>3</sub> system was studied kinetically in ethyl acetate. Figure 2 shows time-conversion

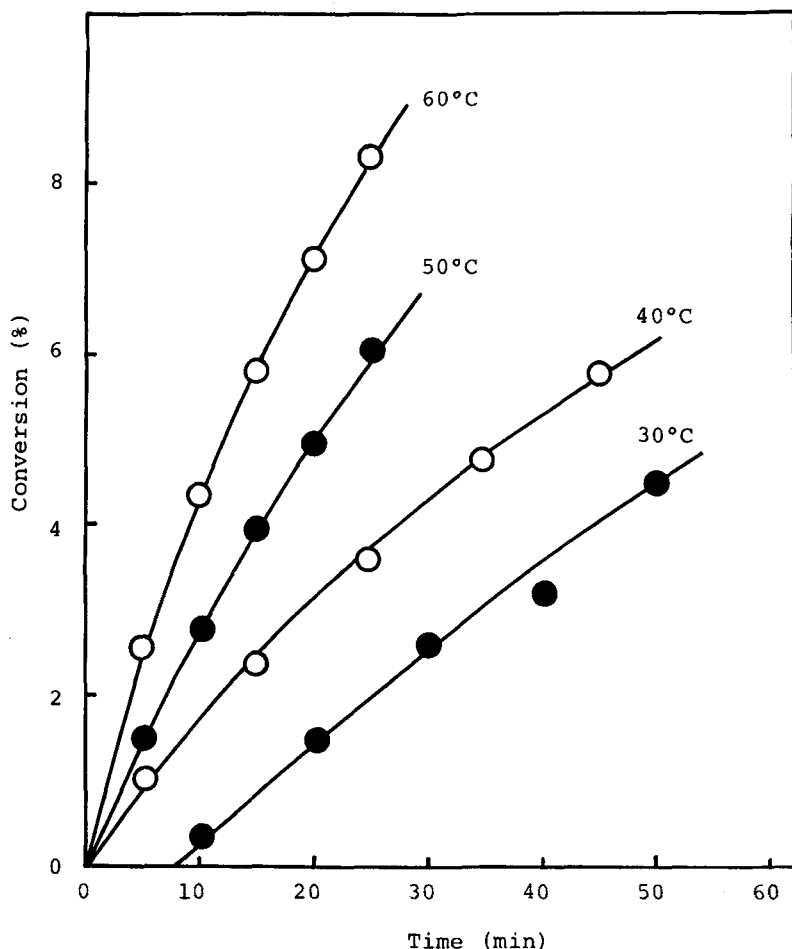


FIG. 2. Time-conversion curves in the polymerization of MMA with the NHS/Mn(acac)<sub>3</sub> system in ethyl acetate.  $[\text{Mn}(\text{acac})_3] = 1.33 \times 10^{-2}$ ,  $[\text{NHS}] = 8.62 \times 10^{-3}$ ,  $[\text{MMA}] = 4.16 \text{ mol/L}$ .

curves obtained at several temperatures. From an Arrhenius plot of the polymerization rate ( $R_p$ ) obtained from Fig. 2, the overall activation energy of this polymerization was calculated to be 9.1 kcal/mol. This low value confirms that polymerization proceeded readily even around room temperature.

Figure 3 shows the dependence of  $R_p$  on the concentrations of the initiator components. Curve (a) in Fig. 3 shows the relationship be-



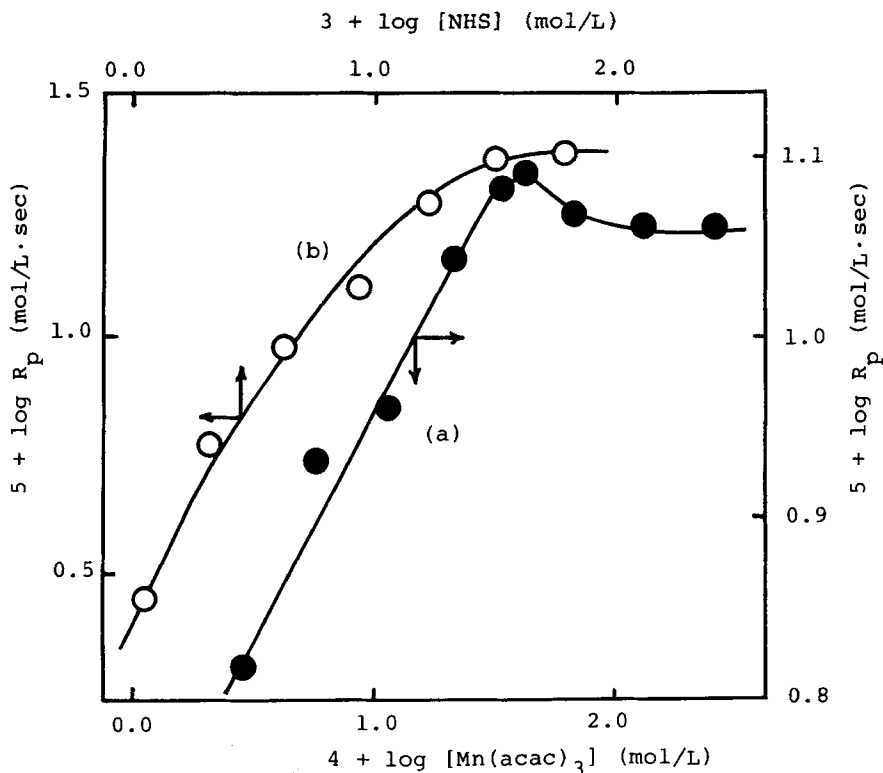


FIG. 3. Effects of the  $\text{Mn}(\text{acac})_3$  [(a)] and NHS [(b)] concentrations on  $R_p$  at  $40^\circ\text{C}$  in ethyl acetate.  $[\text{MMA}] = 4.17$ . (a)  $[\text{NHS}] = 8.64 \times 10^{-3}$ ; (b)  $[\text{Mn}(\text{acac})_3] = 4.29 \times 10^{-3}$  mol/L.

tween the  $\text{Mn}(\text{acac})_3$  concentration and  $R_p$ . The logarithmic  $R_p$  increases linearly with increasing  $\text{Mn}(\text{acac})_3$  concentration up to a certain concentration.  $R_p$ , however, becomes nearly constant above the concentration which corresponds to a molar ratio of NHS to  $\text{Mn}(\text{acac})_3$  of about 2. Curve (b) shows the relationship between  $R_p$  and the NHS concentration, which exhibits a tendency similar to that of curve (a).

Further, Fig. 4 shows a plot of  $R_p$  against NHS concentration when the concentrations of NHS and  $\text{Mn}(\text{acac})_3$  are varied simultaneously with  $[\text{NHS}]/[\text{Mn}(\text{acac})_3] = 2$ .  $R_p$  was found to be proportional to the

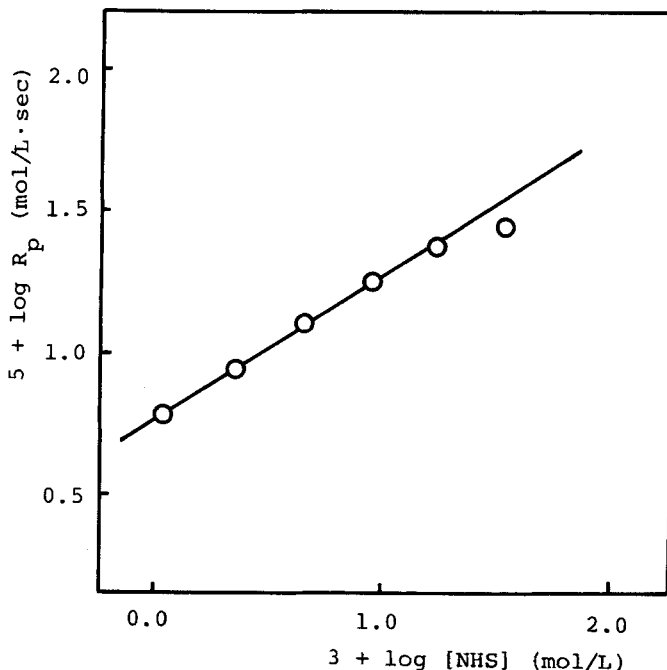


FIG. 4. Effect of the initiator concentration on  $R_p$  at  $40^\circ\text{C}$  in ethyl acetate.  $[\text{MMA}] = 4.68 \text{ mol/L}$ .  $[\text{NHS}]/[\text{Mn}(\text{acac})_3] = 2$ .

square root of the initiator concentration. These findings suggest that bimolecular termination occurs in this system and that a complex with a very high stability constant is formed between 2 mol of NHS and 1 mol of  $\text{Mn}(\text{acac})_3$ , which plays an important role in the generation of initiating radicals.

Figure 5 shows a plot of  $R_p$  vs MMA concentration when the concentrations of  $\text{Mn}(\text{acac})_3$  and NHS are kept constant.  $R_p$  depends on the 1.8th order of monomer concentration. This indicates that the monomer participates in the initiation of this polymerization.

#### Visible Spectrum of the NHS/ $\text{Mn}(\text{acac})_3$ System

An ethyl acetate solution of NHS is colorless, and one of  $\text{Mn}(\text{acac})_3$  has a brown color. On the other hand, a solution contain-

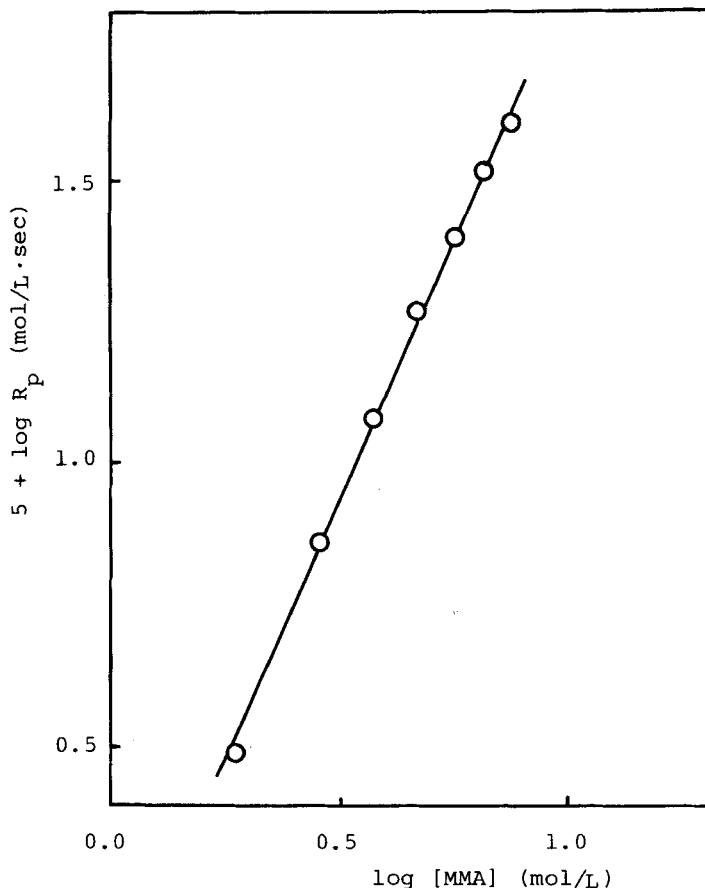


FIG. 5. Effect of the monomer concentration on  $R_p$  at  $40^\circ\text{C}$  in ethyl acetate.  $[\text{Mn}(\text{acac})_3] = 7.01 \times 10^{-3}$ ,  $[\text{NHS}] = 1.40 \times 10^{-2}$  mol/L.

ing both  $\text{Mn}(\text{acac})_3$  and NHS becomes green when the concentration of NHS is higher than twice that of  $\text{Mn}(\text{acac})_3$ . Thus, NHS is considered to interact with  $\text{Mn}(\text{acac})_3$  in ethyl acetate. The interaction of NHS with  $\text{Mn}(\text{acac})_3$  was studied in a mixture of MMA and ethyl acetate by spectroscopy. Figure 6 shows the visible spectrum of the NHS/ $\text{Mn}(\text{acac})_3$ /MMA/ethyl acetate system. As  $[\text{NHS}]$  was increased, the main absorption increased and the shoulder peak around 410 nm disappeared when  $[\text{Mn}(\text{acac})_3]$  was fixed.

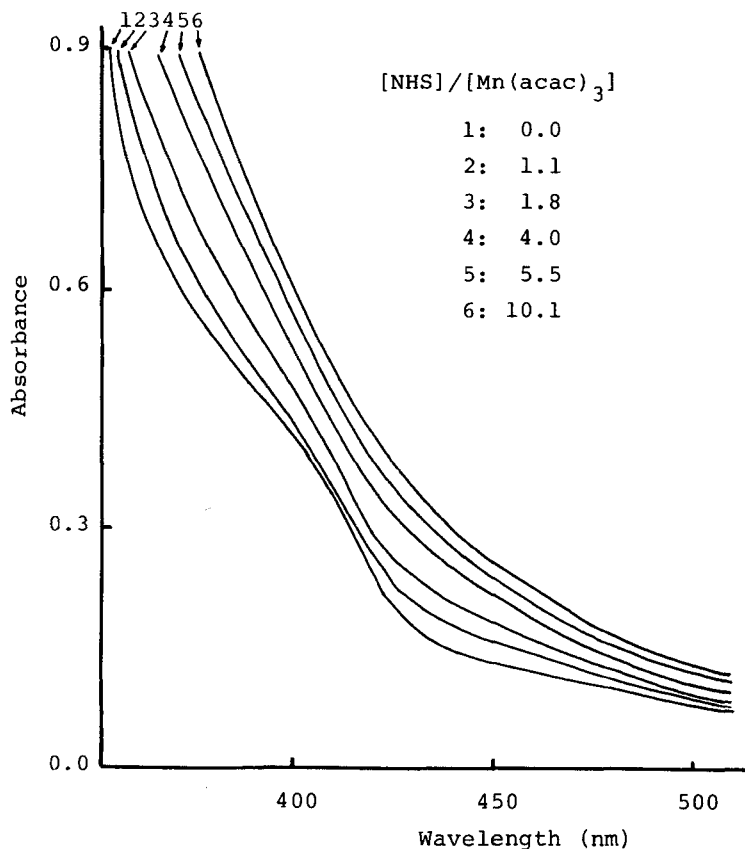


FIG. 6. Effect of NHS on the visible spectrum of  $\text{Mn}(\text{acac})_3$  at room temperature in an ethyl acetate/MMA (1:1 (v/v)) mixture.  $[\text{Mn}(\text{acac})_3] = 2.63 \times 10^{-3}$  mol/L. A 1-mm UV cell was used.

Figure 7 shows plots of  $[\text{NHS}]/[\text{Mn}(\text{acac})_3]$  against absorbance at various wavelengths obtained from Fig. 6. As can be seen, the curves vary significantly at the point where  $[\text{NHS}]/[\text{Mn}(\text{acac})_3]$  is about 2, suggesting that a 2:1 complex is formed between NHS and  $\text{Mn}(\text{acac})_3$ .

Figure 8 shows spectrum change of the reaction mixtures after the reaction of NHS and  $\text{Mn}(\text{acac})_3$  is carried out at  $50^\circ\text{C}$  in ethyl acetate in the presence of (B) and in the absence (A) of MMA in a degassed UV-cell. Absorption due to the complex in the system including MMA decreases more rapidly than in the absence of MMA. This fact sup-

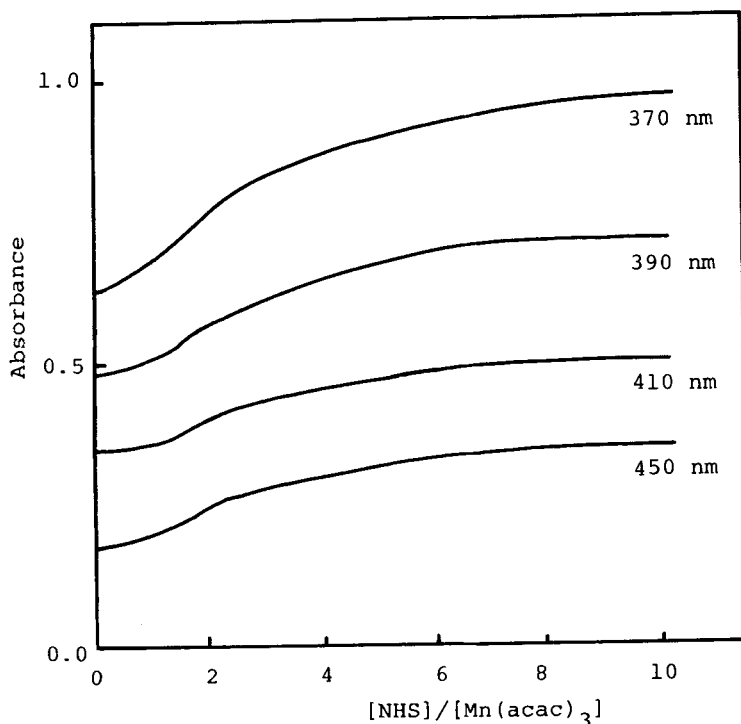


FIG. 7. Relationship between  $[NHS]/[Mn(acac)_3]$  and absorbance. Under the same conditions as shown in Fig. 6.

ports the above conclusion that MMA participates in the initiation reaction of NHS and  $Mn(acac)_3$ .

#### Application of the Spin Trapping Technique to the NHS/ $Mn(acac)_3$ System

The initiation mechanism of vinyl polymerization with the NHS/ $Mn(acac)_3$  system was investigated by means of the spin trapping technique. BNO was used as spin trapping reagent.

Figure 9 shows the ESR spectrum of the NHS/ $Mn(acac)_3$ /ethyl acetate system. This spectrum is assigned to amine N-oxyl (II) ( $A_N = 7.7$  G), which was formed by the trapping of an acyl radical ( $RCO\cdot$ ) by BNO:

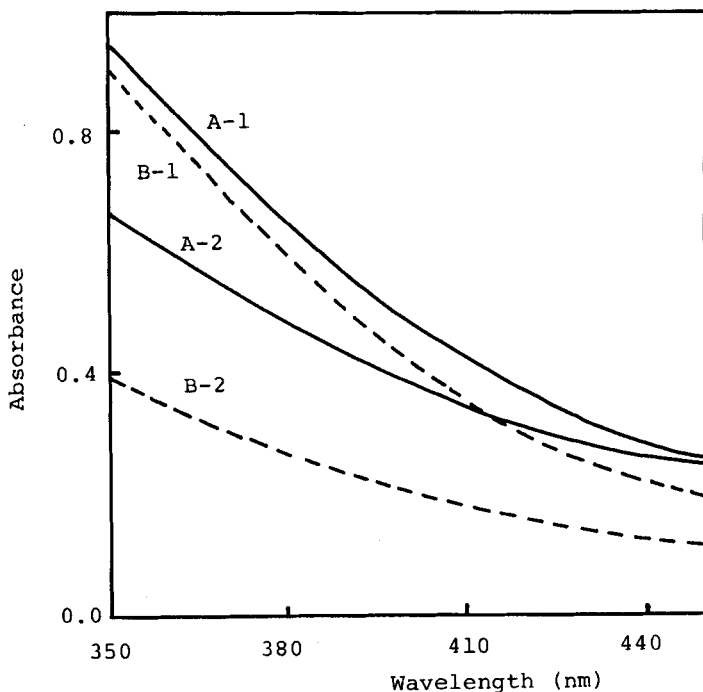
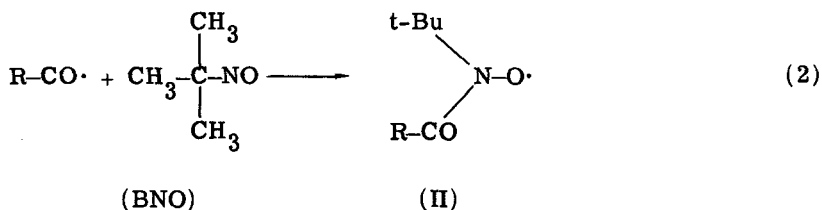


FIG. 8. Spectrum change of the  $\text{Mn}(\text{acac})_3/\text{NHS}$  system at  $50^\circ\text{C}$  in ethyl acetate (—) and in a MMA/ethyl acetate (1:3 (v/v)) mixture (---).  $[\text{Mn}(\text{acac})_3] = 2.59 \times 10^{-4}$ ,  $[\text{NHS}] = 2.70 \times 10^{-3}$  mol/L. Reaction time: 5 min (A-1, B-1), 30 min (A-2, B-2). A degassed sealed UV cell of 10 was used.



Thus, the  $\text{NHS}/\text{Mn}(\text{acac})_3$  system was found to produce an acyl radical in the absence of MMA.

As described above, kinetic and electronic spectroscopic results suggest that MMA participates in the initiation process of this polym-

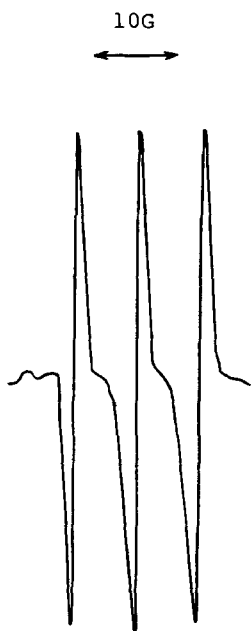
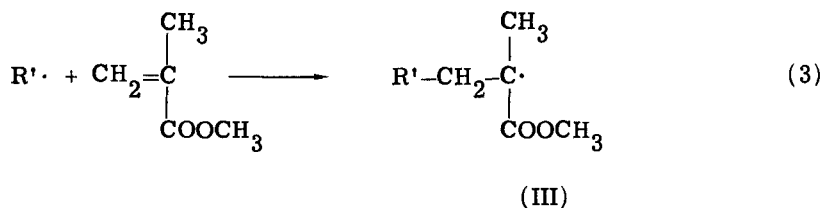


FIG. 9. ESR spectrum of the  $\text{Mn}(\text{acac})_3/\text{NHS}/\text{BNO}$  system in ethyl acetate at room temperature.  $[\text{Mn}(\text{acac})_3] = 1.9 \times 10^{-3}$ ,  $[\text{NHS}] = 1.0 \times 10^{-2}$ ,  $[\text{BNO}] = 9.2 \times 10^{-3}$  mol/L.

erization. Therefore, the reaction of NHS,  $\text{Mn}(\text{acac})_3$ , and BNO in ethyl acetate was performed in the presence of MMA. Figure 10 shows the ESR spectra of the reaction mixtures. Spectrum (a) was observed when the MMA concentration was as high (3.1 mol/L) as under polymerization conditions. Amine N-oxyl (IV) ( $A_N = 14.5$  G), observed separately, was derived from the addition of some radical ( $\text{R}'\cdot$ ) to MMA:



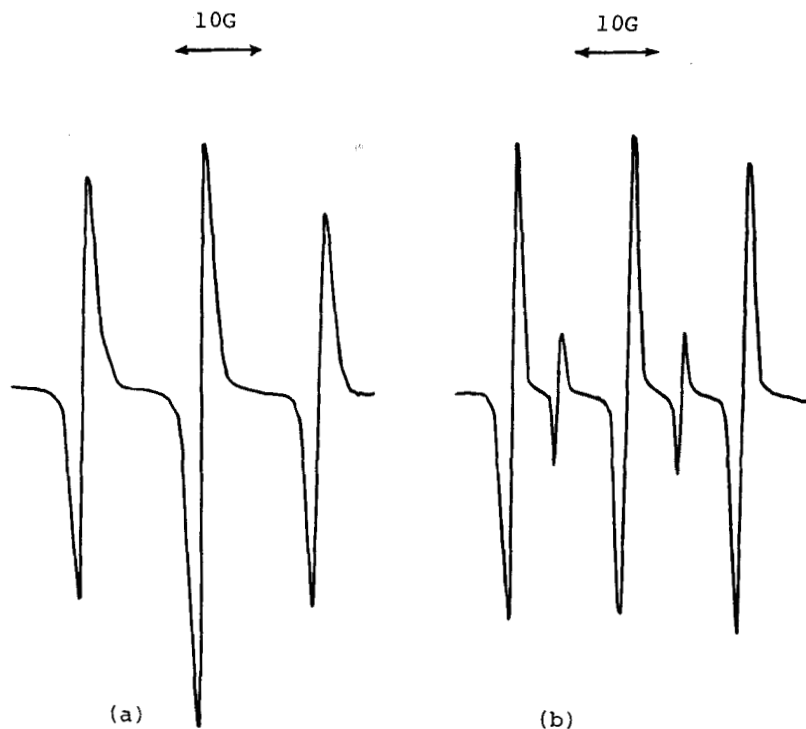
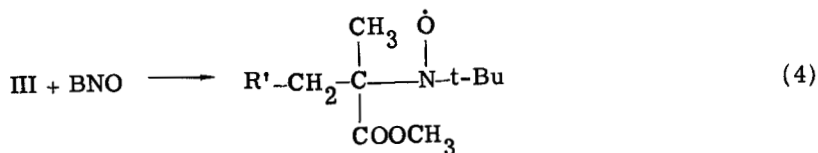


FIG. 10. ESR spectrum of the  $\text{Mn}(\text{acac})_3/\text{NHS}/\text{MMA}/\text{BNO}$  system in ethyl acetate at room temperature. (a)  $[\text{MMA}] = 3.13$ ,  $[\text{Mn}(\text{acac})_3] = 4.0 \times 10^{-3}$ ,  $[\text{MHS}] = 2.0 \times 10^{-2}$ ,  $[\text{BNO}] = 1.4 \times 10^{-2}$  mol/L. (b)  $[\text{MMA}] = 1.6 \times 10^{-2}$ ,  $[\text{Mn}(\text{acac})_3] = 1.4 \times 10^{-3}$ ,  $[\text{NHS}] = 8.6 \times 10^{-3}$ ,  $[\text{BNO}] = 8.6 \times 10^{-3}$  mol/L.



(IV)

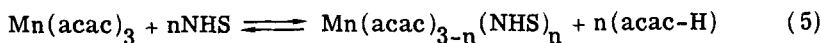
Spectrum (b) was obtained when the MMA concentration was lowered to  $1.6 \times 10^{-2}$  mol/L, which is comparable to the initiator concentration. Both amine N-oxyl (II) and (IV) were formed. Thus, the



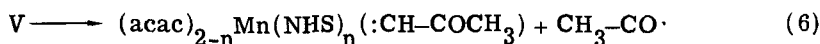
primary propagating radical (III) was found to be trapped by BNO even at the very low monomer concentrations. This indicates that the monomer-participating initiation reaction is much faster than the other reaction under these polymerization conditions. Similar results were observed when MA, AN, and St were used in place of MMA.

### Initiation Mechanism

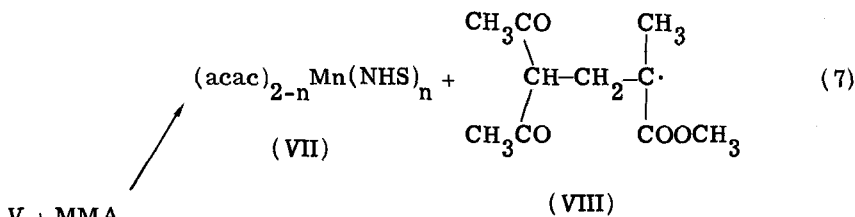
From the results mentioned above, the following initiation mechanism is proposed for vinyl polymerization with the NHS/Mn(acac)<sub>3</sub> system.



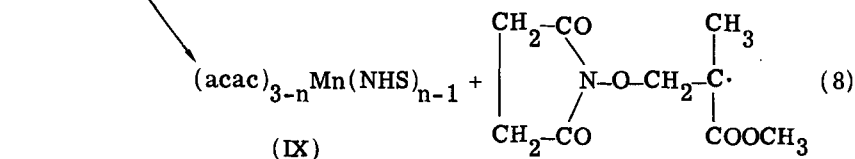
(V)



(VI)



(VIII)



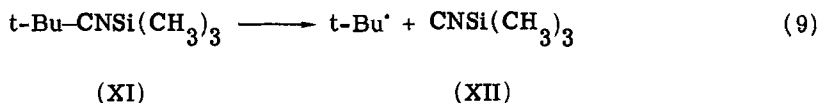
(IX)

(X)

Equilibrium (5) was derived from kinetic and visible spectroscopic results, where *n* is probably 2.

The equilibrium lies far to the right. Formation of the acetyl radical in Eq. (6) seems to be derived from alpha elimination of the ligand radical, diacetylmethyl, which might be assisted by stabiliza-

tion of the resulting carbene by the manganese ion. The following alpha elimination of an iminoyl radical (XI) has been reported to give an isonitrile (XII), being isoelectronic to carbene (Eq. 9) [7]:



Under our polymerization conditions, the direct reaction of complex (V) with MMA gives radical (VIII) or (X). The precursor radicals, diacetylmethyl and succinimidyl, are formed by oxidation of the conjugated bases of acetylacetone and NHS by the manganese ion.

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