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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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To cite this Article Sato, Tsuneyuki , Abe, Masao and Otsu, Takayuki(1981) 'Application of Spin Trapping Technique to Radical Polymerization. X [1]. Initiation Mechanism of Spontaneous Alternating Copolymerization Systems of Vinyl Sulfides with Electron-Accepting Monomers', *Journal of Macromolecular Science, Part A*, 15: 3, 367 – 379

To link to this Article: DOI: 10.1080/00222338108074377

URL: <http://dx.doi.org/10.1080/00222338108074377>

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Application of Spin Trapping Technique to Radical Polymerization. X [1]. Initiation Mechanism of Spontaneous Alternating Copolymerization Systems of Vinyl Sulfides with Electron-Accepting Monomers

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ABSTRACT

The initiation mechanism for spontaneous copolymerizations of vinyl sulfides (VS) with electron-accepting monomers such as maleic anhydride (MAn), diethyl fumarate (DEF), acrylonitrile (AN), and methyl acrylate (MA) was investigated by means of spin trapping technique using 2-methyl-2-nitrosopropane as a spin trapping agent. From the ESR spectrum observed from the system ethyl VS-DEF, two types of radicals, a vinyl radical (I; $\text{RSCH}=\dot{\text{C}}\text{H}$) and an alkyl (1,2-dicarboethoxyethyl) radical (II; $\text{C}_2\text{H}_5\text{OCOCHCH}_2\text{COOC}_2\text{H}_5$) which derived from VS and DEF, respectively, were detected as their nitroxides. Similar radicals, I and III ($\text{NCCH}_2\dot{\text{C}}\text{H}_2$), were also observed from the system VS-AN, but in the system VS-MA, three types of radicals, I, IV ($\text{CH}_3\text{OCOCH}_2\dot{\text{C}}\text{H}_2$), and V ($\text{CH}_3\text{OCO}\dot{\text{C}}\text{HCH}_3$) were trapped as their nitroxides. In the system isopropyl VS-MAn, I and a propagating radical (VI) $\sim\text{CH}_2\dot{\text{C}}\text{HSR}$, were detected. The system isobutyl vinyl ether-MAn also showed a weak ESR spectrum due to the nitroxide from Radical I. These initiating radicals were assumed to be produced from the charge transfer complex formed between

both donor and acceptor monomers. Based on these results, the cross-initiation mechanism for spontaneous alternating copolymerization is discussed.

INTRODUCTION

It has been generally accepted that electron-accepting maleic anhydride (MAN) can readily undergo alternating copolymerization with some electron-donating monomers, styrene [2], vinyl ether [3], and vinyl sulfides [4] even in the absence of radical initiators. In most of these copolymerizations it has been assumed that a charge transfer complex with a small equilibrium constant is formed between both monomers, and this plays an important role on their initiation and propagation reactions [5-11].

On the other hand, weak electron-accepting monomers such as acrylonitrile (AN) and methyl methacrylate have also been known to copolymerize thermally and alternately with styrene and butadiene in the presence of Lewis acids [12]. In these cases a ternary complex of both monomers with Lewis acid has also been considered to participate into alternating copolymerization.

In the previous results [6] on thermal copolymerization of isobutyl vinyl sulfide with various electron-accepting monomers, we have found that there is a definite correlation between the reactivities of these systems to cross-initiation and cross-propagation reactions. Therefore, it seems to be of interest to clarify the initiation and propagation mechanisms in these spontaneous copolymerizations.

The spin trapping technique has recently been recognized to be a powerful tool for analyzing the initiation mechanism of radical polymerization, and we have reported a series of the results by this technique regarding the detection and identification of primary and propagating radicals [1], and the evaluation of relative reactivities of monomers toward primary tert-butoxy radical [1h].

In a previous paper [1g] we reported the initiation mechanism of the spontaneous alternating copolymerizations of styrene with methyl methacrylate and AN in the presence of zinc chloride by means of the spin trapping technique. The present paper describes the results obtained by applying this technique to spontaneous copolymerizations of vinyl sulfides (VS) with electron-accepting monomers, MAN, diethyl fumarate (DEF), AN, and methyl acrylate (MA). For comparison, the system isobutyl vinyl ether (IBVE)-MAN is also studied. In this paper, 2-methyl-2-nitrosopropane (BNO) was used as a spin trapping agent.

EXPERIMENTAL

Materials

BNO was prepared by oxidation of tert-butylamine with *m*-chloroperbenzoic acid [13]. Di-tert-butyl peroxalate (DBPO) was synthesized

by the reaction of oxalyl dichloride with tert-butyl hydroperoxide [14]. Tri-n-butyltin hydride as a stannyl radical source was prepared by reduction of tri-n-butyltin chloride with lithium aluminum hydride [15]. Commercial triethylsilane was used as a silyl radical source after distillation. Methyl β -bromopropionate (MBP), β -bromopropionitrile (BPN), and diethyl bromosuccinate (EBS) were prepared by addition of hydrogen bromide to the corresponding unsaturated compounds [16].

Ethyl, isopropyl, and tert-butyl VS (EVS, IPVS, and t-BVS, respectively) were prepared according to the method described in a previous paper [4].

Reactions and ESR Spectrum Measurements

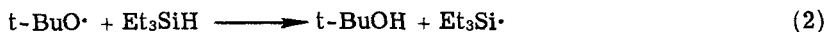
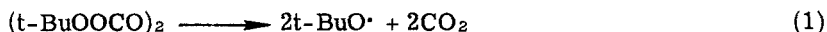
The reactions of VS with electron-accepting monomers were carried out in a degassed, sealed ESR tube in the presence of BNO as a spin trapping agent at room temperature. After the reaction had proceeded for an appropriate time, the ESR spectrum of the reaction mixture was measured by using a JES-ME-3X spectrometer with 100 kc/sec modulation.

RESULTS

IPVS-DEF, EVS-DEF, and t-BVS-DEF Systems

As reported in a previous paper [6], these systems undergo alternating copolymerization in the absence of a radical initiator. To detect the initiating radicals from this system by the spin trapping technique, the reaction of IPVS with DEF was carried out in the presence of BNO at room temperature. The ESR spectrum of the reaction mixture is shown in Fig. 1.

Figure 1 indicates that the observed spectrum consists of a mixture of two types of nitroxide, A ($A_N = 14.0$ G, $A_H^\beta = 2.5$ G) and B ($A_N = 14.5$ G, $A_H^\beta = 19.4$ G, $A_H^\gamma = 0.7$ G). Since the spectrum of the former nitroxide is quite identical with that (Fig. 2) obtained from the following reactions [Eqs. 1-4], the nitroxide A is concluded to be I-a which is formed by the reaction of intermediate radical I-b with BNO.



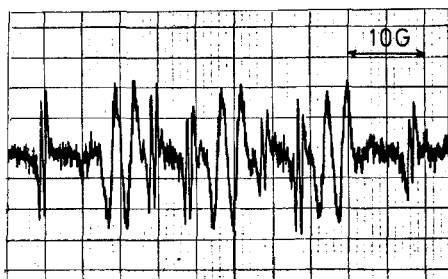


FIG. 1. ESR spectrum of the system IPVS-DEF-BNO after being reacted for 26 h at room temperature: [IPVS]/[DEF] = 50/50 in volume, [BNO] = 9.2×10^{-2} mol/L.

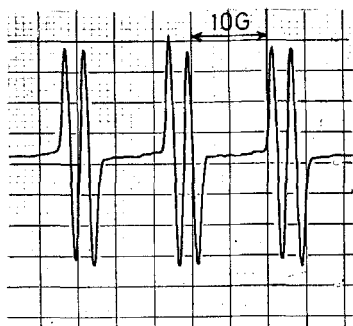
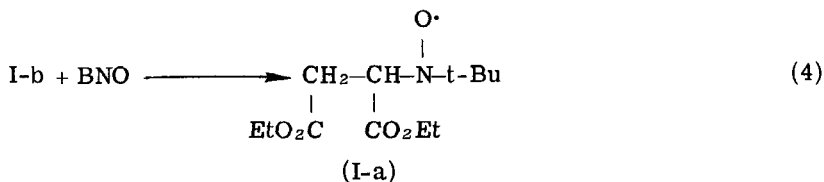
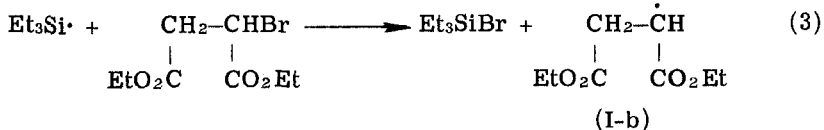
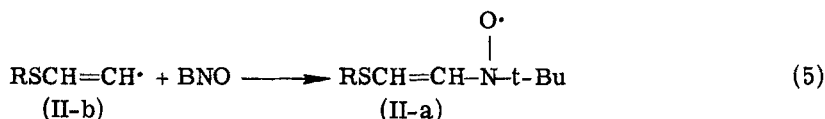


FIG. 2. ESR spectrum of the system $(t\text{-BuOOCO})_2\text{-Et}_3\text{SiH-EBS-BNO}$ after being reacted in benzene for 2 h at room temperature: [Et₃SiH]/[EBS]/[C₆H₆] = 45/9.1/45.9 in volume, [(t-BuOOCO)₂] = 6.2×10^{-2} mol/L.



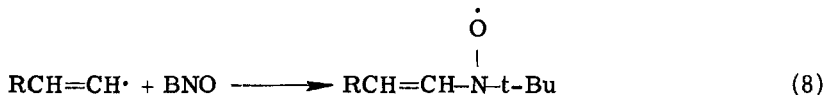
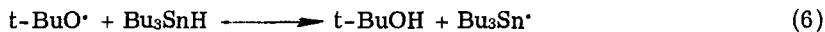
However, it may be impossible to exclude the possibility that the nitroxide A is derived from the reaction of BNO with a propagating radical which formed from the addition of a radical to DEF, because both nitroxides show spectra almost similar to Fig. 2.

The nitroxide B, in which it is noted that the coupling constant (A_H) of the β -hydrogen is very large as compared with those (1-5 G) of ordinary nitroxides carrying one hydrogen, seems to be II-a derived from the reaction of a vinyl-type radical II-b with BNO:



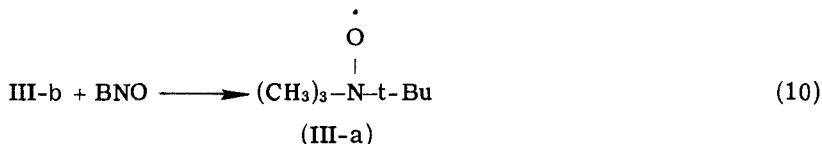
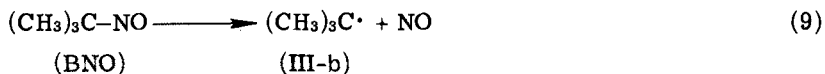
No formation of nitroxide B was found from the systems IPVS-BNO and DEF-BNO under similar conditions.

To confirm further this vinyl radical formation, we have attempted to compare it with the results obtained from well-known reactions (Eqs. 1, 6-8) for preparing vinyl radical.



where R is OC_2H_5 , C_6H_5 , and Br.

Figure 3 shows the ESR spectrum of the system $(\text{t-BuOOCO})_2 - \text{Bu}_3\text{SnH}$ -1-bromo-2-ethoxyethylene (BEE)-BNO after reacting for 1 h at room temperature. The coupling constants ($A_N = 15.1$ G, $A_H^\beta = 20.2$ G, $A_H^\gamma = 0.6$ G) of the nitroxide formed is quite similar to those of the nitroxide II-a. In this figure a spectrum due to the nitroxide III-a which is produced from the reaction of BNO with the tert-butyl radical (III-b) from the decomposition of BNO was also observed:



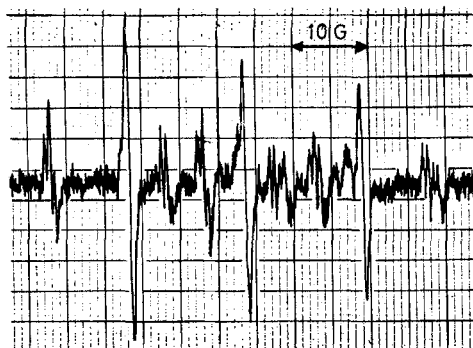


FIG. 3. ESR spectrum of the system $(t\text{-BuOOCO})_2\text{-Bu}_3\text{SnH-BEE-BNO}$ after being reacted for 1 h at room temperature: $[\text{BusSnH}]/[\text{BEE}] = 40/60$ in volume, $[(t\text{-BuOOCO})_2] = 4.3 \times 10^{-2}$ mol/L, $[\text{BNO}] = 1.9 \times 10^{-1}$ mol/L.

Similar results were also obtained in the systems which used β -bromostyrene ($A_N = 14.9$ G, $A_H^\beta = 19.6$ G, $A_H^\gamma = 0.8$ G) and 1,2-dibromoethylene ($A_N = 15.4$ G, $A_H^\beta = 20.2$ G, $A_H^\gamma = 0.7$ G) instead of BEE.

In comparing the ESR spectrum of Fig. 3 with that of Fig. 1, however, each of six lines of the nitroxide II-a shown in Fig. 1, is sharply split into two lines, while that in Fig. 3 is split into three or four lines. It seems that the nitroxide produced from BEE, which used a cis and trans mixture, probably consists of a mixture of cis and trans isomers. However, the nitroxide II-a seems to be only one isomer, strongly indicating that the formation of the vinyl radical II-b from these spontaneous copolymerizations occurs stereospecifically through a charge transfer complex formed between both donor and acceptor monomers.

When the spin trapping technique was applied to the systems EVS-DEF and t-BVS-DEF, ESR spectra similar to Fig. 1 were also observed, and they were assigned as two types of nitroxides I-a and II-a ($A_N = 14.7$ G, $A_H^\beta = 19.8$ G, $A_H^\gamma = 0.7$ G and $A_N = 14.6$ G, $A_H^\beta = 19.1$ G, $A_H^\gamma = 0.7$ G, respectively).

It is therefore concluded that both I-b and II-b radicals are produced as initiating radicals from spontaneous alternating copolymerization of DEF with VS.

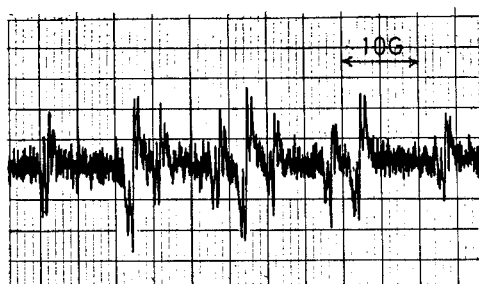
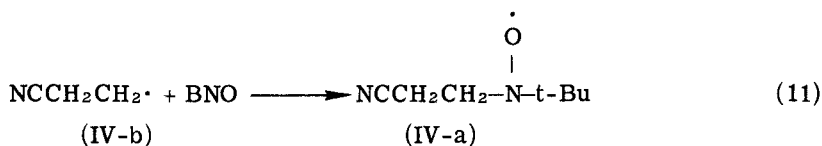


FIG. 4. ESR spectrum of the system IPVS-AN-BNO after being reacted for 76 h at room temperature: $[\text{IPVS}]/[\text{AN}] = 60/40$ in volume, $[\text{BNO}] = 9.2 \times 10^{-2}$ mol/L.

EVS-AN, IPVS-AN, and t-BVS-AN Systems

The ESR spectrum observed in the system EVS-AN-BNO, after reacting for 76 h at room temperature, also showed the formation of II-b ($A_{\text{N}} = 14.5$ G, $A_{\text{H}}^{\beta} = 19.4$ G, $A_{\text{H}}^{\gamma} = 0.7$ G) which was derived from the II-b radical. However, the spectrum (Fig. 4) observed from the system IPVS-AN-BNO indicates the formation of the new nitroxide IV-a ($A_{\text{N}} = 14.9$ G, $A_{\text{H}}^{\beta} = 11.2$ G, $A_{\text{H}}^{\gamma} = 0.7$ G), which was derived from IV-b according to



The formation of this nitroxide was also confirmed by comparing it with the spectrum (Fig. 5) of the authentic nitroxide ($A_{\text{N}} = 14.7$ G, $A_{\text{H}}^{\beta} = 11.1$ G, $A_{\text{H}}^{\gamma} = 0.6$ G) obtained from IV-b which was produced through the reaction of triethylsilyl radical (Eq. 2) with BPN.

In the system t-BVS-AN-BNO, the two initiating radicals II-b and IV-b were trapped as their nitroxides II-a and IV-a, respectively.

These results strongly indicate that the initiating radical formation from these systems occurs stereospecifically via a proton transfer as described later.

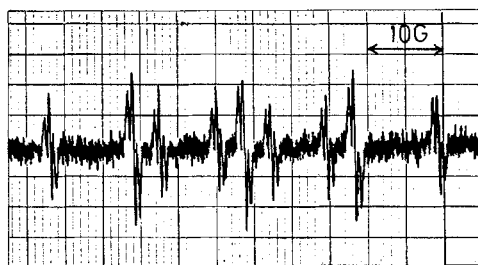


FIG. 5. ESR spectrum of the system $(t\text{-BuOOCO})_2\text{-Et}_3\text{SiH-BPN-BNO}$ after being reacted in benzene for 1.5 h at room temperature: $[\text{Et}_3\text{SiH}]/[\text{BPN}]/[\text{C}_6\text{H}_6] = 45/9.1/45.9$ in volume, $[(t\text{-BuOOCO})_2] = 5.7 \times 10^{-2}$ mol/L, $[\text{BNO}] = 9.8 \times 10^{-2}$ mol/L.

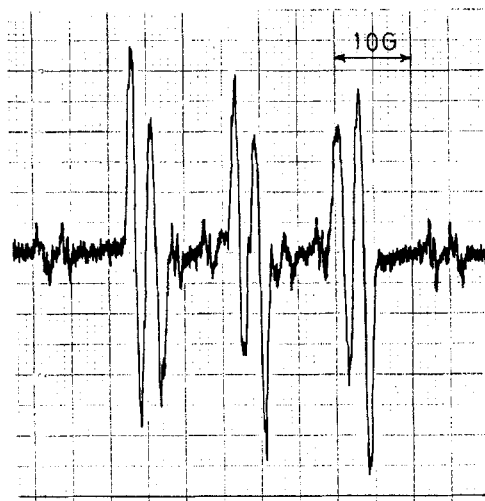
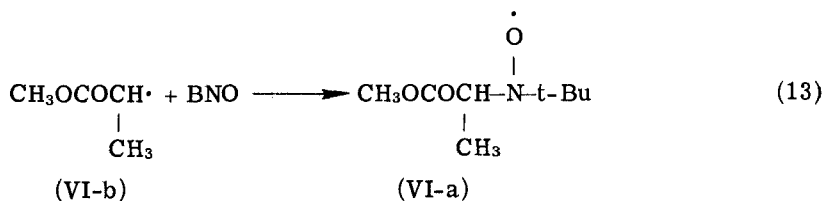
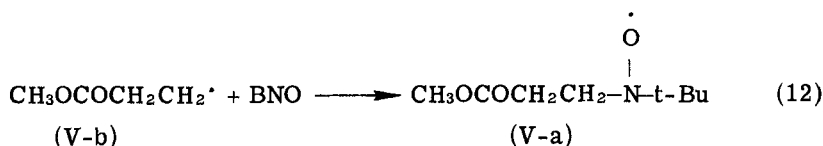


FIG. 6. ESR spectrum of the system EVS-MA-BNO after being reacted for 97 h at room temperature: $[\text{EVS}]/[\text{MA}] = 50/50$ in volume, $[\text{BNO}] = 9.5 \times 10^{-2}$ mol/L.

EVS-MA, IPVS-MA, and t-BVS-MA Systems

The ESR spectrum observed from the system EVS-MA-BNO is shown in Fig. 6, from which the three nitroxides II-a, V-a ($A_{\text{N}} = 15.3$ G, $A_{\text{H}}^{\beta} = 12.3$ G) and VI-a ($A_{\text{N}} = 14.0$ G, $A_{\text{H}}^{\beta} = 2.8$ G) were found to be formed. The last two nitroxides were probably produced by



The ESR spectra observed from the systems $(t\text{-BuOOCO})_2\text{-Et}_3\text{SiH-MBP-BNO}$ and $(t\text{-BuOOCO})_2\text{-CH}_3\text{CH}_2\text{COOCH}_3\text{-BNO}$ are shown in Figs. 7 and 8, and both spectra are found to be similar to Fig. 6. From these systems it is therefore clear that the Radicals V-b and VI-b are produced.

Similarly, three nitroxides, II-a, V-a, and VI-a, were also confirmed to be formed in the systems IPVS-MA-BNO and $t\text{-BVS-MA-BNO}$, indicating that three types of Radicals, II-b, V-b, and VI-b, are produced from the spontaneous copolymerization of VS with MA. The difference in initiating radicals between the systems of AN and MA may originate from the structures of the charge transfer complexes formed.

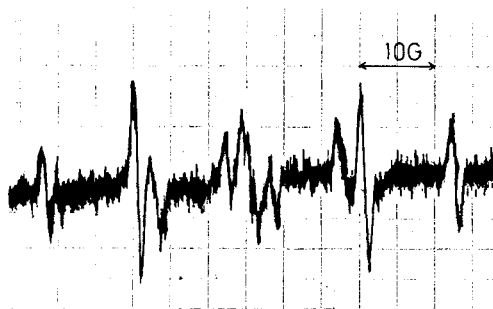


FIG. 7. ESR spectrum of the system $(t\text{-BuOOCO})_2\text{-Et}_3\text{SiH-MBP-BNO}$ after being reacted in benzene for 2 h at room temperature: $[\text{Et}_3\text{SiH}]/[\text{MBP}]/[\text{C}_6\text{H}_6] = 45/10/45$ in volume, $[(t\text{-BuOOCO})_2] = 6.0 \times 10^{-2}$ mol/L, $[\text{BNO}] = 9.8 \times 10^{-2}$ mol/L.

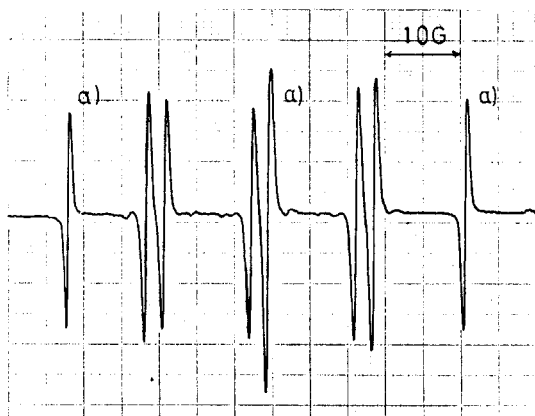


FIG. 8. ESR spectrum of the system $(t\text{-BuOOCO})_2\text{-CH}_3\text{CH}_2\text{COOCH}_3$ -BNO after being reacted in benzene for 1.5 h at room temperature: $[(t\text{-BuOOCO})_2] = 4.5 \times 10^{-2}$ mol/L, $[\text{BNO}] = 3.2 \times 10^{-2}$ mol/L. "a" indicates the spectrum due to *t*-butoxy-butyl nitroxide.

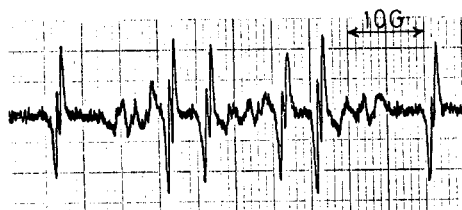
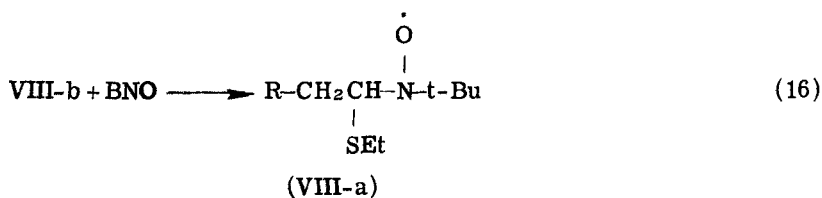
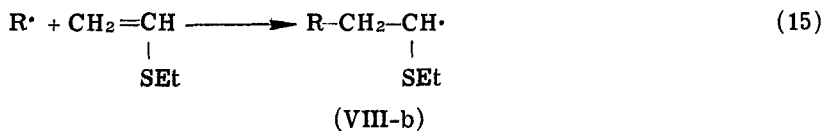
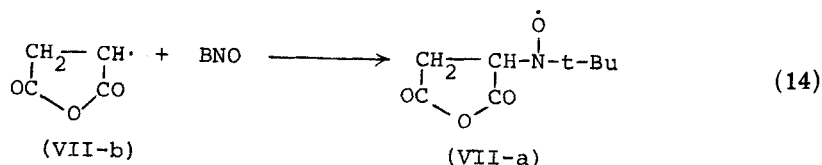


FIG. 9. ESR spectrum of the system EVS-MAN-BNO after being reacted for 1 h at room temperature: $[\text{Man}] = 4.4 \times 10^{-1}$ mol/L, $[\text{BNO}] = 7.6 \times 10^{-2}$ mol/L.

EVS-MAN, IPVS-MAN, and t-BVS-MAN Systems

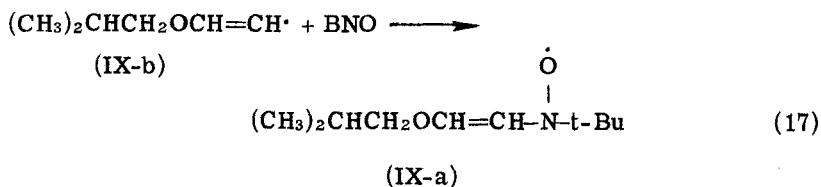
Figure 9 shows the ESR spectrum of the system EVS-MAN-BNO after reacting for 1 h at room temperature. This spectrum, assigned as a mixture of the nitroxide II-a and a new nitroxide C, is quite different from the EST spectrum due to that (VII-a) observed from the system $(t\text{-BuOOCO})_2\text{-Bu}_3\text{SnH}$ -bromosuccinic anhydride-BNO. This nitroxide C may be assigned as VIII-a which is derived from the reaction of BNO with a propagating EVS radical which was produced from the addition of a certain radical (R') formed in this system to EVS.



Similar results were also obtained in the systems IPVS-MAN and t-BVS-MAN.

IBVE-MAN System

From the ESR spectrum observed from the system IBVE-MAN-BNO, a vinyl radical IX-b was found to be trapped as its nitroxide IX-a according to



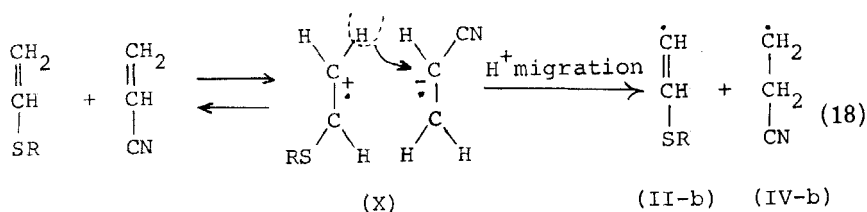
However, the rate of formation of IX-a was very low as compared with that from the systems VS-MAN.

DISCUSSION

In a previous paper [6] it was shown that EVS can form a charge transfer complex with MAN with an equilibrium constant of 0.035

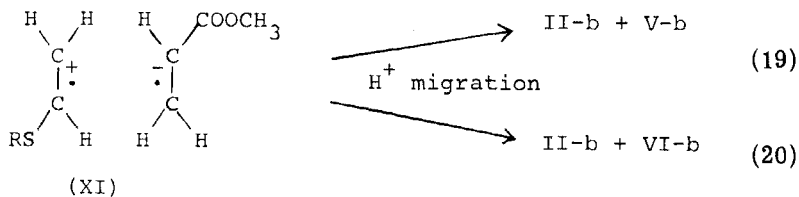
L/mol while it forms only a contact-type charge transfer complexes with weak electron-accepting monomers such as AN and MA. Since these systems readily copolymerize thermally and alternately as the result of increased reactivities in cross-initiation and cross-propagation, the initiating radical seems to be formed from the charge transfer complex.

From the results of the spin trapping technique described above, it is clear that two types of radical are produced from the donor VS and the acceptor DEF, AN, or MAn monomers. One of them is a vinyl-type radical (II-b) and the other is a substituted alkyl radical (I-b, IV-b, or VII-b). Both radicals seem to be produced via intramolecular proton migration from the cation radical of VS to the anion radical of the electron-accepting monomer in the charge transfer complex (X). For example, the initiating radical producing reaction from the system VS-AN is expressed by



The fact that only II-b and IV-b radicals are produced selectively strongly suggests that the intramolecular proton migration reaction occurs stereospecifically from a β -carbon of the VS cation radical to an α -carbon of the AN anion radical in the charge transfer complex.

In the system VS-MA, however, a vinyl-type radical (II-b) and two radicals (V-b and VI-b) are trapped as their nitroxides. The formation of the latter two radicals indicates that the two types of intramolecular proton migration reactions occur from a β -carbon of the VS cation radical to either an α - or a β -carbon of the MA anion radical:



However, since the ESR spectra due to the nitroxides of VI-b and propagating MA radicals are not so clearly distinguished, it seems

that II-b and V-b radicals are produced selectively according to Eq. (19) and then react with MA to give a propagating MA radical.

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Accepted by editor October 19, 1979

Received for publication November 13, 1979