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# Spin Trapping Study on Addition Reaction of Organic Radicals to Methyl Methacrylate and Methyl Tiglate

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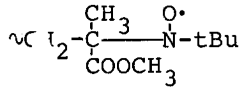
## Summary

The addition reaction of the radicals formed from 2,2'-azobisisobutyronitrile(AIBN), diisopropyloxydicarbonate(DISOP), or benzoyl peroxide(BPO) to methyl methacrylate-β-d2(MMA-β-d2) or methyl tiglate(MTA) has been investigated at 30°C by the spin trapping technique. The tail and head addition of the radicals were detected for MMA-β-d2, and only the tail addition was observed for MTA.

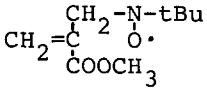
## Introduction

The spin trapping technique has been widely used for the detection of active species in radical reactions (JANZEN 1971; PERKINS et al. 1970). An application of the spin trapping technique to radical polymerization has also been developed by several groups of workers (CHALFONT et al. 1968; KUNITAKE et al. 1974), and has given some information concerning the initiation reaction in radical polymerization (SATO et al. 1973, 1975, and 1977a). In addition, the reactivities of various kinds of monomers have been estimated by this technique (SATO et al. 1977b).

It has been reported that MMA allowed to react with the radical initiator in the presence of 2-methy-2-nitrosopropane (BNO) as a spin trapping reagent gives a 9-line spectrum and that the spectrum is due to the following radicals A and B:

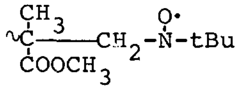


$\sim CH_2-C(CH_3)(COOCH_3)-N(O\cdot)-tBu$ (A)



$CH_2=C(COOCH_3)-CH_2-N(O\cdot)-tBu$ (B)

This implies the existence of the addition of the initiating radical to MMA and the hydrogen abstraction from the α-methyl group (KUNITAKE et al. 1974; SATO et al. 1977b). Contrarily, in the spin trapping technique for the radical reactions of MMA-β-d2 and of MTA, we found that the radicals spin-trapped are radicals A and C, which show respectively the head and tail additions of the initiating radical to MMA rather than the head addition and the hydrogen abstraction. In this paper, new information concerning the addition of an initiating radical to MMA and MTA are reported.



$\sim C(CH_3)(COOCH_3)-CH_2-N(O\cdot)-tBu$ (C)

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## Results and Discussion

Figure 1 shows ESR spectra of the polymerization system of MMA-β-$d_2$ with AIBN or with DISOP as an initiator in the presence of BNO. From the intensity distribution, the spectra are interpreted to consist of a 3-line spectrum and a 15-line spectrum. The 3-line spectrum is attributable to the adducts of scheme I and scheme II.

$$\sim CD_2-\overset{CH_3}{\underset{COOCH_3}{C}}\cdot \quad + \quad tBuNO \longrightarrow \sim CD_2-\overset{CH_3}{\underset{COOCH_3}{C}}-\overset{O\cdot}{N}-tBu$$

(I)

$$CH_3-\overset{CH_3}{\underset{CN}{C}} \quad + \quad tBuNO \longrightarrow CH_3-\overset{CH_3}{\underset{CN}{C}}-\overset{O\cdot}{N}-tBu$$

(II)

The 15-line spectrum is a triplet ($a_N$=15 Gauss) of quintets ($a_D$=1.5 Gauss), and is assigned from the intensity distribution to the radical formed by the tail addition in scheme III.

$$\sim\underset{COOCH_3}{\overset{CH_3}{C}}-CD_2\cdot \quad + \quad tBuNO \longrightarrow \sim\underset{COOCH_3}{\overset{CH_3}{C}}-CD_2-\overset{O\cdot}{N}-tBu$$

(III)

It has been described that MMA reacts with initiatin radicals in the presence of BNO to give a 9-line spectrum, which is composed of a triplet ($a_N$=15 Gauss) of triplets ($a_H$=10 Gauss) and a triplet ($a_N$=15 Gauss) (KUNITAKE et al. 1974; SATO et al. 1977b). The spectrum has been assigned to be due to two kinds of radicals. The strong 3-line spectrum was attributed to radical A formed by scheme I, and the 9-line spectrum to radical B formed by scheme IV. If this mechanism were true, a similar spectrum should be observed in the case of MMA-β-$d_2$. However, the observed spectrum is not the case. Therefore, the spectrum is not considered to be the radical formed by the hydrogen abstraction. The result of these spectra suggests that the 9-line spectrum previously observed should be assigned to radical C formed by scheme III. The proton hyperfine splitting constant is 6.6 times as large as the corresponding deuterium one (WERTZ et al. 1972). Therefore, the β-H hyperfine splitting constant in the radical formed from MMA must be about 10 Gauss because the β-D one is 1.5 Gauss. The value is in fair agreement with the experimental value ($a_H$=10 Gauss), showing that the tail addition is more likely to occur than the hydro-

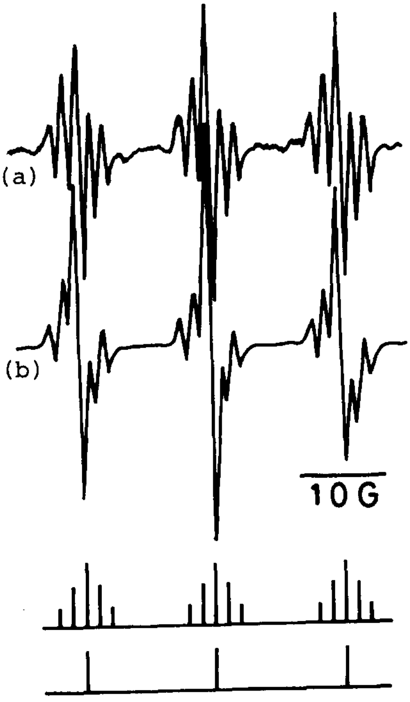
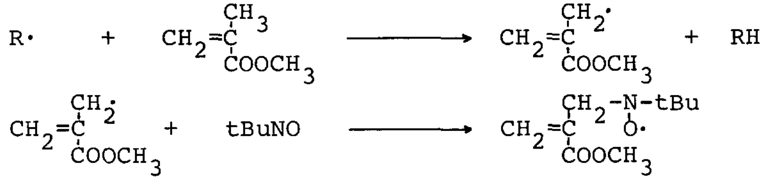


Figure 1 ESR spectra from MMA-β-$d_2$ at 30°C. (a) BNO $5\times10^{-3}$M and DISOP $4\times10^{-3}$M. (b) BNO $2\times10^{-2}$M and AIBN $4\times10^{-2}$M.

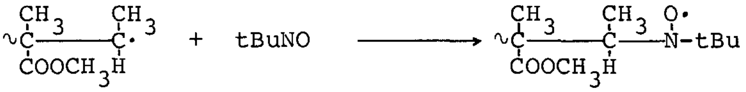
gen abstraction in the initiation process of the radical polymerization.



$$\mathrm{R\cdot} + \mathrm{CH_2{=}\overset{CH_3}{\underset{COOCH_3}{C}}} \longrightarrow \mathrm{CH_2{=}\overset{CH_2\cdot}{\underset{COOCH_3}{C}}} + \mathrm{RH}$$

$$\mathrm{CH_2{=}\overset{CH_2\cdot}{\underset{COOCH_3}{C}}} + \mathrm{tBuNO} \longrightarrow \mathrm{CH_2{=}\overset{CH_2-\underset{O\cdot}{N}-tBu}{\underset{COOCH_3}{C}}}$$

(IV)



$$\mathrm{\sim\overset{CH_3}{\underset{COOCH_3}{C}}\!-\!\!-\!\overset{CH_3}{\underset{H}{C}}\cdot} + \mathrm{tBuNO} \longrightarrow \mathrm{\sim\overset{CH_3}{\underset{COOCH_3}{C}}\!-\!\!-\!\overset{CH_3}{\underset{H}{C}}\!-\!\!-\!\overset{O\cdot}{N}-tBu}$$

(V)

$$\mathrm{\sim\overset{CH_3}{\underset{H}{C}}\!-\!\!-\!\overset{CH_3}{\underset{COOCH_3}{C}}\cdot} + \mathrm{tBuNO} \longrightarrow \mathrm{\sim\overset{CH_3}{\underset{H}{C}}\!-\!\!-\!\overset{CH_3}{\underset{COOCH_3}{C}}\!-\!\!-\!\overset{O\cdot}{N}-tBu}$$

(VI)

For further information on such an addition, the spin trapping technique was performed on MTA which was allowed to react with three kinds of initiators. As shown in Figure 2, the spectra observed are composed of a triplet ($a_N$=15 Gauss) of doublets ($a_H$=2.5 Gauss) and mainly attributable to the radical formed by scheme V. If the addition like scheme VI were predominant, the spectrum should be a triplet. This is not the case. Furthermore, if the hydrogen abstraction from the α-methyl group occured in MTA, the 9-line spectrum, a triplet of triplets, should be observed. However, the spectra from MTA show that the radical is mainly formed by scheme V. This result of MTA suggests that the 9-line spectrum from the MMA radical is atributable to radicals A and C rather than A and B.

To our knowledge, there is no report that poly(MMA) contains a detectable amount of the tail-to-tail bonding. Thus, the result obtained by the spin trapping technique does not seem to reflect quantitatively the mode of addition in the radical propagation. The existence of small amounts of radical C has been found in the reaction of methyl radical with MMA in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (SOLOMON, 1981).

In the spin trapping technique, there are two suggestive steps for the formation of trapped radicals: the first step is the formation of radicals by the reaction between the initiating radical and MMA (head and tail addi-

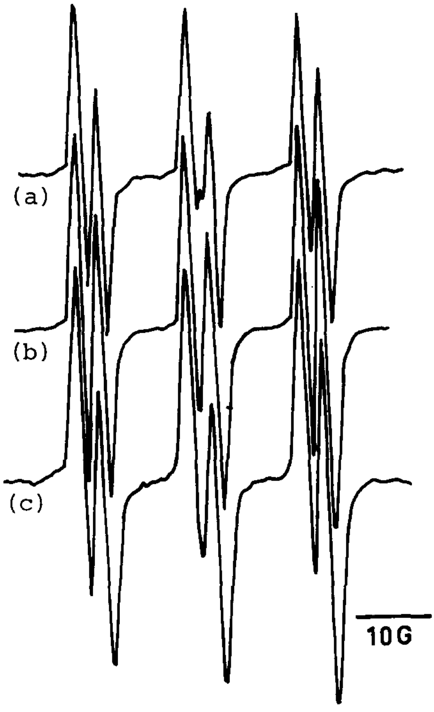


Figure 2 ESR spectra from MTA at 30°C. BNO×2 $10^{-2}$M (a) DISOP 4×$10^{-2}$M (b) AIBN 4×$10^{-2}$M and (c) BPO 4×$10^{-2}$M.

tions), and the next one is their addition to the spin trapping reagent in such schemes as I, III, and IV. Since each reaction in both steps is not diffusion-controlled but needs activation energy, the rate constants for these reactions are considered to be different, respectively. Therefore, the amount of the tail-to-tail bonding detected by the spin trapping reagent cannot be directly related to the content of the tail-to-tail bonding in the polymer. In order to correlate them the rate constants in both steps must be determined. Detailed study on this point is in progress.

## Experimental

BNO was prepared according to Holman et al. (HOLMAN et al. 1970). MMA-$\beta$-$d_2$ was prepared as described elsewhere (KAMACHI et al. 1978). MTA was commercially obtained, and distilled for purification.

DISOP, commercially available, was used as a 25% toluene solution without purification. AIBN and BNO obtained commercially were recrystallized.

ESR measurement was made using a Japan Electric Optics Model JES-FE 1X ESR with a variable temperature adaptor (ES-VT-3A). A spectrocil sample tube (2mm diameter) was degassed under vacuum and sealed.

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