

DETECTION OF ACTIVE RADICALS FORMED DURING THE SONOLYSIS OF POLYMERS*

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ABSTRACT

Active radicals formed during the sonolysis of PVK (polyvinyl carbazole) and PMMA (polymethyl methacrylate) have been studied with the combination of spin trapping technique and ESR spectroscopy. The results show that:

1. For PVK, radicals $\text{CA}\cdot$ and $-\text{CH}_2-\dot{\text{C}}\text{H}-$ are produced during the ultrasonic irradiation and only the later can be trapped by MNP.

2. For PMMA, radicals $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{C}\cdot \\ | \\ \text{COOCH}_3 \end{array}$ and $-\dot{\text{C}}\text{H}_2-$ are generated by sonolysis and both can be trapped by ND.

It is well known that many chemical reactions can be initiated by ultrasonic irradiation^[1-2]. Some of them proceed by an ionic mechanism^[3-5], others involve free radical intermediates^[6-7]. Although no direct evidence has been provided, the combination of decrease in molecular weight of polymer caused by ultrasonic irradiation and theoretical analysis leads one to conclude that the main-chain scissions are mechanically induced by the action of ultrasonic waves on the polymer solutions^[8-10]. However, it is possible that the scissions are secondary effects due to chemical reaction initiated by active intermediates, such as either free radicals or ions produced by sonolysis. Recently, the method of combination of spin trapping technique with ESR offered us a useful tool for detection of active free radicals^[11-13]. In this paper, the free radicals produced during the sonolysis of polyvinyl carbazole (PVK) and polymethyl methacrylate (PMMA) have been studied with this method.

EXPERIMENTAL

Reagents

Spin trapping reagent such as nitrosodurene (ND) and 2-methyl 2-nitroso propane (MNP) were prepared according to the references [14] and [15]. The average molecular

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weight of PVK and PMMA are about 4×10^5 and 1×10^5 respectively.

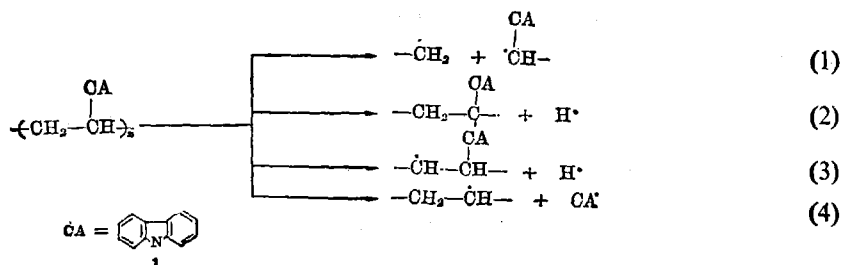
ESR spectra

The ESR spectra of samples were measured before and after ultrasonic irradiation (20W, 40KHz) at room temperature by using a Bruker ER-200D ESR spectrometer with 100KHz modulation and a X-band klystron.

RESULTS AND DISCUSSION

Sonolysis of PVK

No ESR signal was observed from PVK-benzene (100 mg/cm^3) solution or MNP-benzene ($1 \times 10^{-2} \text{ mg/cm}^3$) solution after ultrasonic irradiation for 40 min. Triple-doublet (3 (1:1:1) $\times$ 2 (1:1)) ESR signal, as shown in Fig. 1, was observed from PVK-MNP-benzene (0.9 mg MNP was added in 1 ml PVK-benzene (100 mg/cm^3) solution) system after ultrasonic irradiation for 40 min. The results indicate that not only the homolysis of PVK occurred during the ultrasonic irradiation but also the active free radical produced in the homolysis process can be trapped by MNP to form stable spin adduct. The triple doublet spectrum is attributed to the hyperfine coupling interaction of unpaired electron with a β -proton and a ^{14}N . For PVK, the following homolysis processes are possible:



From the knowledge of average bond energies, $D_{\text{C-H}} = 99 \text{ kcal mol}^{-1}$; $D_{\text{C-O}} = 83 \text{ kcal mol}^{-1}$; $D_{\text{O-N}} = 70 \text{ kcal mol}^{-1}$. The probabilities occurred of these processes are decreasing according to the following order:

$$(4) > (1) > (2) \doteq (3)$$

On the other hand, the N-centered free radical is more difficultly trapped by MNP than C-centered free radical. Therefore, we predicate that the free radical $\text{-(CH}_2\text{-}\dot{\text{C}}\text{-)}$ produced

in eq. (4) can be trapped by MNP to form spin adduct $\text{-(CH}_2\text{-}\dot{\text{C}}\text{-N(C(CH}_3\text{)}_3\text{))}$ and give a rational explanation of the ESR spectrum as shown in Fig. 1.

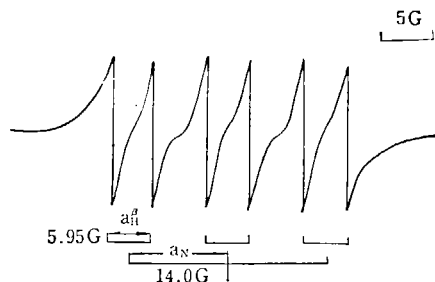
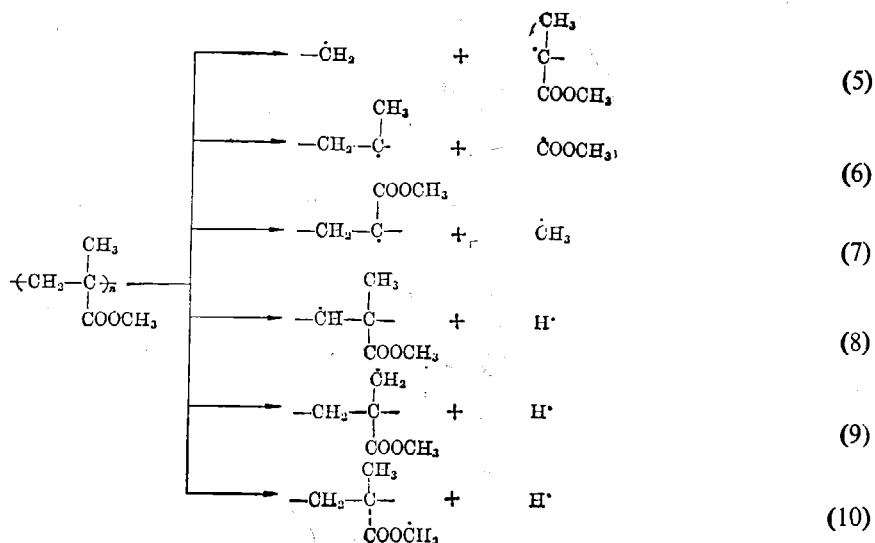


Fig. 1 ESR spectrum of PVK-MNP-benzene system (0.9 mg MNP was added in 1 ml PVK-benzene (100 mg/cm³) solution) after ultrasonic irradiation for 40 min

Sonolysis of PMMA

No ESR was observed from PMMA-benzene or ND-benzene solution after ultrasonic irradiation for 40 min, ESR spectrum as shown in Fig. 2 appeared from PMMA-ND-benzene system (1.6 mg ND was added in 1 ml PMMA-benzene (100 mg/cm³) solution) after irradiation for the same time. It is easily to find that the spectrum is superimposed of two components, one is triple-triplet (3 (1:1:1) $\times$ 3 (1:2:1)), which is due to the interaction of unpaired electron with two β -protons and a ¹⁴N, the other one is triplet (3 (1:1:1)) which is originated from the interaction of unpaired electron with a ¹⁴N alone. These reveal that two kinds of free radical formed in the sonolysis of PMMA and can be trapped by ND to form two kinds of spin adduct. One of them has two β -protons, and the other has no β -proton. For PMMA, there are six possible homolysis pathways as follows:



The experimental results only can be illustrated by spin adducts I and II formed from the free radicals produced in eq. (5) with ND.

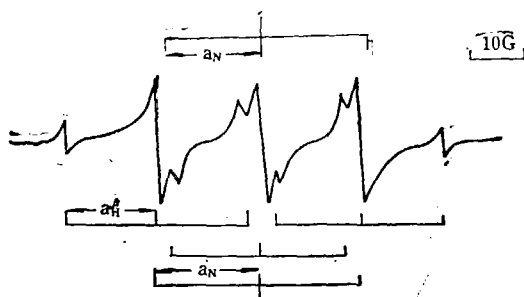
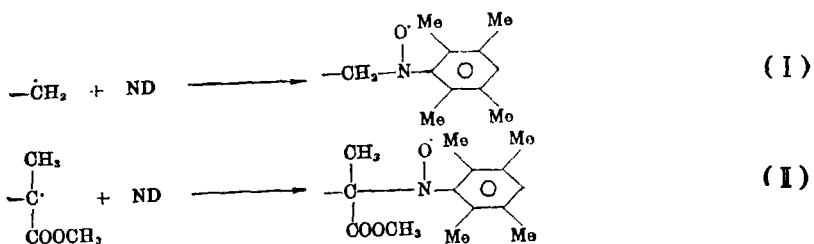


Fig. 2 ESR spectrum of PMMA-ND-benzene system (1.6 mg ND was added in 1 ml PMMA-benzene (100 mg/cm³) solution) after ultrasonic irradiation for 40 min

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