

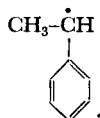
Electron Spin Resonance Study on Irradiated Styrene in Crystalline and Glassy States

By

Kozo TSUJI*, Takeo IWAMOTO*, Hiroshi YOSHIDA*,
Koichiro HAYASHI** and Seizo OKAMURA*

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Styrene was irradiated at -196°C to give a five-line spectrum with a coupling constant of about 16 gauss. This is attributed to the free radical



When a mixture of styrene and 2-methyltetrahydrofuran was irradiated, a broad singlet spectrum (total width 33 gauss) was superposed on the seven-line spectrum due to the methyltetrahydrofuran radical and no sharp singlet spectrum due to trapped electrons was observed. This broad singlet spectrum is thought to be due to styrene anion radicals. This spectrum was bleached by visible light and saturated appreciably with increasing microwave power.

Similar phenomena were observed for a styrene-3-methylpentane mixture.

Introduction

Radiation-induced polymerization of styrene in a dried system is thought to proceed from a cationic mechanism.¹

Hamill, *et al.*² observed absorption peaks at 400, 590 and 460 $m\mu$ in γ -irradiated 3-methylpentane-styrene system. They assigned the absorption bands at 400 and 590 $m\mu$ to the styrene anion radical and that at 460 $m\mu$ to the styrene cation radical. However, the yield of the latter was very small. They observed only the anion radical in the γ -irradiated 2-methyltetrahydrofuran-styrene system.³

Bagdasarian, *et al.*⁴ observed a singlet ESR spectrum after γ -irradiation of the tetrahydrofuran-styrene system. The singlet spectrum saturated with increasing microwave power and was bleachable with ultraviolet light. From these facts they attributed the singlet spectrum to the styrene anion radical.

* Department of Polymer Chemistry

** Faculty of Engineering, Hokkaido University

In this investigation we observed the ESR spectra of styrene, 3-methylpentane-styrene and 2-methyltetrahydrofuran-styrene systems irradiated at -196°C . The formation of the styrene anion radical in the glassy states has been confirmed.

Experimental

After purification of commercial styrene by the usual method, it was dried three times with barium oxide which had been heated in the vacuum. 2-methyltetrahydrofuran was distilled three times over sodium, and dried five times with Na-K alloy. 3-Methylpentane was distilled over sodium after passing through activated alumina. It was dried four times with Na-K alloy. Samples were mixed in ESR sample tubes by vacuum distillation and sealed off after evacuating to about 10^{-4} mm Hg. In the case of pure styrene, solid blocks were made at 77°K after degassing, put into ESR sample tubes, and evacuated. The samples could move in the tube in order to anneal color centers produced in the tube by irradiation.

Irradiation was made mainly by γ rays from Co^{60} (6×10^5 r/hr). Electron beams from Van de Graaff accelerator were used only for pure styrene. A conventional X-band ESR spectrometer was used with 100 Kc field modulation. Microwave power was less than 1 mw. Irradiation and ESR measurements were carried out at -196°C in the dark.

Results and Discussion

1) Pure Styrene

Styrene was frozen at -196°C to form a polycrystalline sample. It was irradiated with a dose of 2×10^7 rad and give a broad ESR spectrum as shown in Fig. 1(a). After warming up the sample to about -152°C , a five-line spectrum

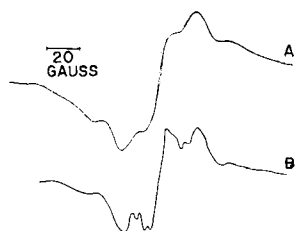
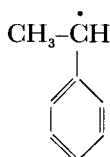


Fig. 1. ESR Spectra of Irradiated Styrene.

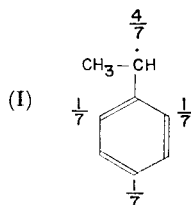
dose = 2×10^7 rad

ESR spectra were measured (a) at -196°C and (b) at -52°C .

with a coupling constant of about 16 gauss was observed clearly (Fig. 1(b)). A similar value for the coupling constant has been obtained from the spectrum of γ -irradiated styrene in ethyl alcohol glass observed at -177°C ⁵. This spectrum can be attributed to the free radical



The spin density distribution on this free radical was calculated by means of the Hückel MO method and is shown in (I). The coupling constants of the methyl protons are about $28 \times 4/7 = 16$ gauss and that of the α -proton is also about the same value. Therefore, a five-line spectrum is expected. This free radical was probably produced by hydrogen atom addition to the vinyl group. Many free radicals of this type have been observed after irradiation of vinyl compounds.



2) Styrene-2-methyltetrahydrofuran (MTHF)

When MTHF was γ -irradiated to a dose of 10^5 r at -196°C in the dark, a seven-line spectrum and a sharp singlet were observed as shown in Fig. 2(a). This

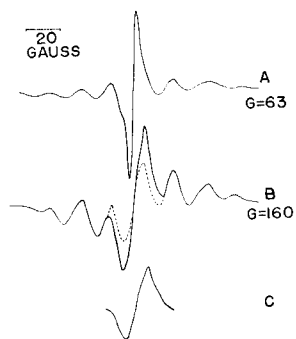


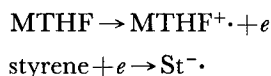
Fig. 2. ESR Spectra of Irradiated Styrene-2-methyltetrahydrofuran
dose = 10^5 r

- (a) pure 2-methyltetrahydrofuran
 (b) 2-methyltetrahydrofuran-styrene (0.5 mole %)
 solid line — before bleaching with visible light
 dotted line — after bleaching with visible light
 (c) spectrum disappeared by bleaching
 G represents an amplifier gain.

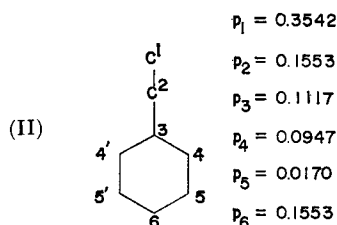
sharp singlet has been assigned to the trapped electron.⁶ This sample was blue after irradiation.

When 0.5 mole % of styrene was added to MTHF, the sharp singlet due to the trapped electron was not observed after γ -irradiation but instead a broader singlet spectrum was superposed on the seven-line spectrum of the MTHF free radical, (Fig 2(b)). This sample was blue-violet instead of blue as for pure MTHF. The

singlet spectrum observed here saturates somewhat with increasing microwave power. The singlet spectrum and the blue-violet color were bleached with visible light after 20 min irradiation for a 0.5 mole % sample, and after 2 hrs irradiation for a 2.1 mole % sample (Fig. 2 (b) dotted line). The spectrum which disappeared here was the singlet one with the total width of about 33 gauss (Fig. 2 (c)). From these facts, it appears that the broader singlet spectrum which appeared in place of the sharp singlet one due to the trapped electrons can be assigned to the styrene anion radical formed by electron capture by styrene



The same electron capture process has been observed with nitroethylene⁷. The spin density distribution was calculated by Hückel MO method and is shown in



(II). Using these values, coupling constants for each of the protons were calculated on the assumption that $Q=23$ gauss⁸ for the α proton. The results are as follows:

$$A = Q\rho (\rho = \text{spin density})$$

$$A_1 \doteq 8 \text{ gauss}$$

$$A_2 \doteq A_6 \doteq 4 \text{ gauss}$$

$$A_4 \doteq 2 \text{ gauss}$$

$$A_5 \doteq 0 \text{ gauss}$$

A total width of about 28 gauss is expected from these values. The value of 33 gauss obtained experimentally would agree with this value.

When methyl bromide was added to the styrene-MTHF system and irradiated, the ESR spectrum shown in Fig. 3 (a) was obtained. This spectrum changed at -196°C in the dark, and the spectrum of Fig. 3 (b) was obtained 1 hour after irradiation. The spectrum which had disappeared during this period consists of a quartet with a coupling constant of about 23 gauss. The intensity ratio is nearly 1:3:3:1, and this is identified as the methyl radical. The styrene anion

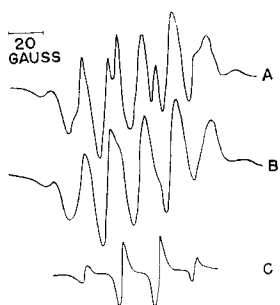
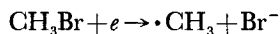


Fig. 3. ESR Spectra of Irradiated 2-methyltetrahydrofuran-styrene (0.7 mole %)- CH_3Br (3.1 mole %) dose= 10^5 r
(a) immediately after irradiation
(b) after one hour
(c) spectrum disappeared within one hour

radical did not form and the methyl radical was produced by the addition of methylbromide. This behavior is due to dissociative electron capture by methyl bromide and confirms the former identification of the styrene anion radical.



3) Styrene-3-methylpentane (3MP)

After 3-methylpentane was irradiated at -196°C , a six-line spectrum with a coupling constant of 22.3 gauss and a sharp singlet were observed. The latter is due to the trapped electrons. The sample is colorless.

When 1~10 mole % of styrene was added to 3MP, the ESR signal due to the trapped electron was no longer observed and the sample became blue-violet. With higher microwave power, the spectrum changed as shown in Fig. 4(b), where the resolution in the central part is better. It is evident that there is some signal at the center. When the sample was bleached with visible light for 18 seconds, both the signal at the center and blue-violet color disappeared

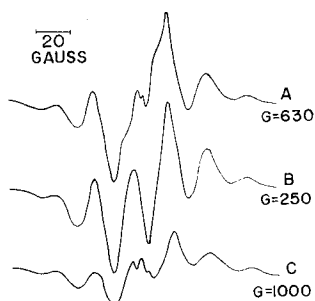


Fig. 4. ESR Spectra of Irradiated 3-methylpentane-Styrene (10 mole %) dose= 10^5 r
(a) immediately after irradiation, 20 db
(b) 10 db of microwave power attenuation
(c) after bleaching with visible light, 20 db
C represents an amplifier gain.

The six-line spectrum characteristic of 3MP radical remained. By comparison with the styrene-MTHF system; these facts indicate that the spectrum at the center is due to the styrene anion radical. Hamill, *et al.*,² observed styrene cation

radicals in addition to the styrene anion radicals in the same system. The ESR spectra of anion and cation radicals are expected to be the same, so we cannot deduce anything about the possible existence of styrene cation radicals discussion.

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