Paramagnetic Resonance Absorption in Solution of the Sodium Adducts of Styrene and 1, 1-Diphenylethylene*

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As reported already¹⁾, paramagnetic resonance absorption with hyperfine structure could be observed on the red adduct of styrene with sodium in tetrahydrofuran (THF) solution. Such absorption has been observed by Weissman and his collaborators²⁾ in caces of polynuclear condensed aromatic hydrocarbons, e. g., naphthalene, anthracene, and naphthacene. Moreover, it is interesting that the adduct of styrene polymerizes easily, turning into a so-called " living polymer". The research, therefore, was continued with an apparatus of higher sensitivity, thus obtaining more interesting and confirmative results. It is the object of the present communication to report them and also a similar research on 1, 1-diphenylethylene (DPE), which also forms a living polymer³⁾.

As shown in Figs. 1a and 1b, two kinds of spectrum were observed in the adduct of styrene, and it was found that they could be observed in the solutions when the adduct of high degree of polymerization was depolymerized with metallic sodium, and after repeated experiment it

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1) K. Hirota, K. Kuwata and K. Morigaki, This Bulletin, **31**, 538 (1958).

2) D. Lipkin, D. E. Paul, J. Townsend and S. I. Weissman, *Science*, **117**, 534 (1953); T. L. Chu, G. E. Pake, D. E. Paul, J. Townsend and S. I. Weissman, *J. Phys. Chem.*, **57**, 504 (1953); S. I. Weissman, J. Townsend, D. E. Paul and G. E. Pake, *J. Chem. Phys.* **21**, 2227 (1953); T. R. Tattle, Jr. and S. I. Weissman, ibid., **25**, 189 (1956).

* Part of this communication was already spoken at the meetings of the Phys. Soc. of Japan (March 1958, Tokyo), and of the Chem. Soc. of Japan (April 1958, Tokyo).

3) K. Kuwata, S. Ishida and K. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), to be published.

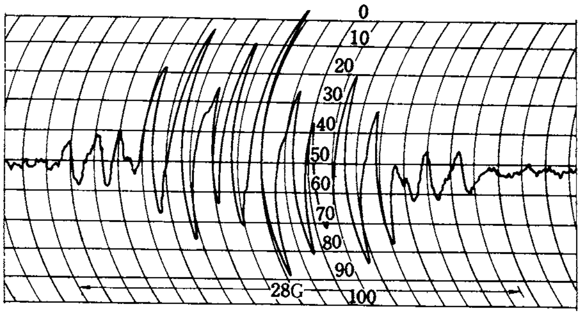


Fig. 1a. Resonance spectrum of styrene radical.

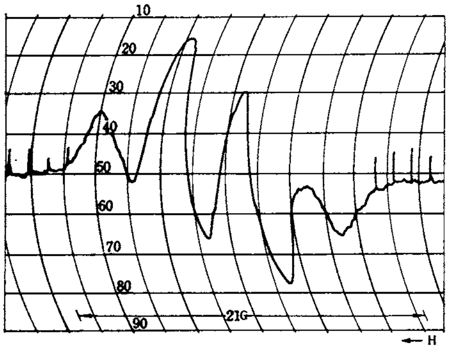


Fig. 1b. Resonance spectrum of styrene radical.

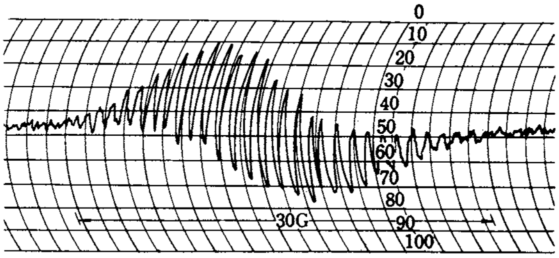


Fig. 2a. Resonance spectrum of DPE radical.

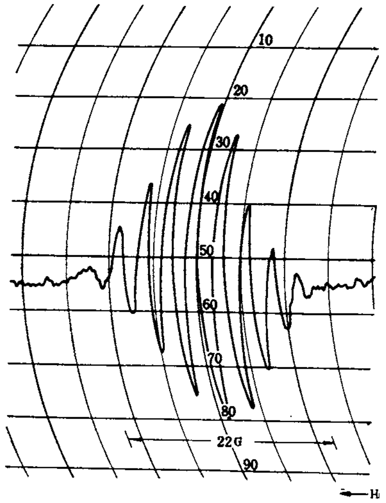
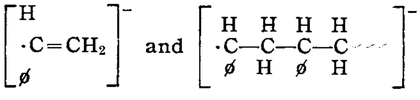


Fig. 2b. Resonance spectrum of DPE radical.

was confirmed that, according as the depolymerization is performed to much extent or not, the spectra observed were composed of about 23 lines or of four lines, as shown in Figs. 1a and 1b, but the reproducibility of the former was not confirmed. It is noteworthy that the spectrum of four lines did not separate into more lines when the measurment was done at such low temperature as about −100°C and when dioxane was used as the solvent, or potassium was substituted for sodium to prepare the adduct.

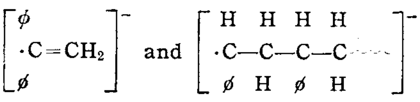
Similar situation was found on the adduct of DPE whose spectra are shown in Figs. 2a and 2b. The spectrum composed of 32~33 lines (Fig. 2a) could be obtained on the adduct freshly prepared from DPE monomer and sodium in THF. The spectrum, changed into the one composed of nine lines (Fig. 2b), when the sample was kept at 110°C for two days. Now it is clear that solutions of the sodium adducts of styrene and DPE contain some free radicals. Taking such fact into consideration, some discussions on the nature of these adducts were attempted.

These radicals in the adduct of styrene are considered to have the following structures on the view of the polymerization reaction, it is believed that these two radicals are the origin of such two resonance spectra*:



$$\left[\begin{array}{l} H \\ \cdot C{=}CH_2 \\ \phi \end{array}\right]^- \quad \text{and} \quad \left[\begin{array}{l} \;\;H \;\;\; H \;\;\; H \;\;\; H \\ \cdot C—C—C—C\cdots \\ \;\;\phi \;\;\; H \;\;\; \phi \;\;\; H \end{array}\right]^-$$

In case of DPE the situation is similar, but is more confirmative by the analysis of the spectra. The structures of the radicals corresponding to the spectra shown by Fig. 2a and Fig. 2b are as follows, respectively:



$$\left[\begin{array}{l} \phi \\ \cdot C{=}CH_2 \\ \phi \end{array}\right]^- \quad \text{and} \quad \left[\begin{array}{l} \;\;H \;\;\; H \;\;\; H \;\;\; H \\ \cdot C—C—C—C\cdots \\ \;\;\phi \;\;\; H \;\;\; \phi \;\;\; H \end{array}\right]^-$$

The detailed result and discussion will be published in near future.

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* By these formulae all resonace formulae are represented for both adducts.

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