Temperature Dependency of the ESR Absorption of the Diphenylamine Polymer with Reference to Its Electric Conductivity*

By Keiji KUWATA, Yoichi KAGEYAMA and Kozo HIROTA

(Received January 5, 1965)

As has been reported, a deep-brownish polymeric product can be obtained by oxidizing diphenylamine with vanadium pentoxide. This polymer is semiconductive and shows a sharp ESR absorption line.[1] Its specific conductivity, λ, and the number of unpaired electrons increases by several orders of magnitude if its complexes are formed with several electron acceptors.[2] In the present note, the temperature dependence of the number of unpaired electrons in the polymer will be reported on, as well as that of its conductivity.

Since the polymer is powdery, samples for conductivity measurement were pressed at more than 80 kg./cm^2. The apparatus used in the measurement was kindly provided by Dr. Seiichi Kanda of our University. The molecular weight of sample A (softening pt.=ca. 150°C) was ca. 3000, while that of sample B (softening pt.=ca. 200°C) was estimated to be higher than 3000 on the basis of its low solubility in ordinary solvents. The data obtained were very reproducible, irrespective of the order of measurement. In Fig. 1, the $\log \lambda$ of both samples is plotted against the reciprocal of the measuring temperature, T. Since a linear relation is given over the range between 32—120°C, we can determine the constants λ_0 and ε_0 in Eq. 1, where k is the Boltzmann constant:

$$\lambda = \lambda_0 \exp(-\varepsilon_0/2kt) \qquad (1)$$

For samples A and B, ε_0 is given as 1.1 and 0.7$_9$ eV. respectively. These numerals show the magnitude of λ, which corresponds to the semiconductive nature of the samples.

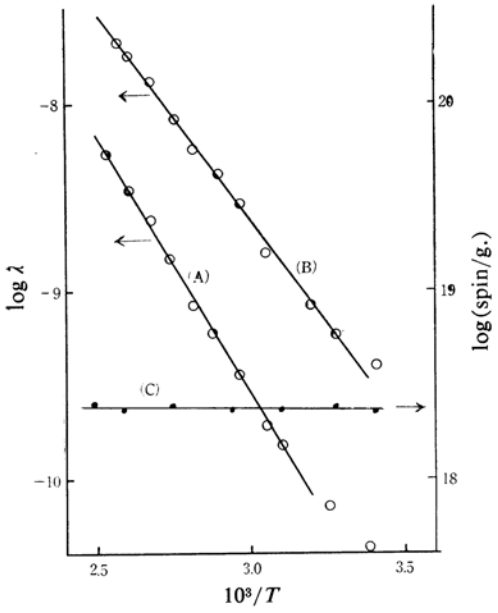

Fig. 1. Temperature variation of specific conductivity and spin concentration.
Softening pt.
(A) 150°C
(B) 200°C
(C) 220°C

The ESR measurement was the same as was hitherto adopted,[1,2] except that the rectangular cavity of the multiple mode, H_{014}, was used so as to determine the spin concentration with a greater reliability. The standard substance containing the free-radical, DPPH, was always inserted in the part of the cavity kept at room temperature, while the sample was placed in the part where the temperature could be varied independently of the standard. By the repeated determination of the spin concentration on sample C (sintering temp. 220°C and $\lambda = 1.83 \times 10^{-10}$ ohm^{-1}·cm^{-1} at 24°C; $\varepsilon_0 = 1.07_6$ (24—80°C)), it was found to be constant, 2.4×10^{18} spin/g., over the temperature range investigated (20—130°C), as Fig. 1 shows.

The results obtained above may be important, because they give us information which clarifies the conduction mechanism of organic semiconductors.

Department of Chemistry
Faculty of Science
Osaka University
Nakanoshima, Osaka

* This investigation was mostly done before Ref. 2 was published.

1) K. Hirota and Y. Kageyama, This Bulletin, 37, 793 (1964).
2) K. Kuwata, Y. Sato and K. Hirota, ibid., 37, 1391 (1964).