Electric Conductivity and Electron Spin Resonance of Semiconductive Complexes of Polymer Species of Diphenylamine

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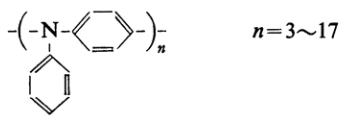
In a previous communication,[1] the formation of a stable polymer species from diphenylamine under an oxidative atmosphere with a vanadium pentoxide catalyst was reported, and the polymer structure composed of a structural unit was proposed as follows:



$n=3\sim17$

TABLE I. SPECIFIC RESISTANCE AND CONCENTRATION OF THE UNPAIRED ELECTRON FOR THE COMPLEXES AT ROOM TEMPERATURE (30°C)

Acceptor for one structural unit* mol.	Specific resistance Ω cm.	Concn. of unpaired electron spin/g.	Line width** ΔH_{msl} gauss
Complexes of iodine			
None	1.9×10^{11}	1.6×10^{18}	8
0.05	4.5×10^{8}	3.9×10^{19}	10
0.12	2.6×10^{6}	4.9×10^{19}	10
0.15	5.3×10^{5}	5.1×10^{19}	12
0.25	4.1×10^{5}	5.2×10^{19}	13
0.33	2.1×10^{5}	6.9×10^{19}	12
1.00	3.4×10^{4}	5.3×10^{19}	12
1.50	3.0×10^{4}	1.7×10^{19}	12
Complexes of chloranil			
0.25	2.4×10^{8}	2.4×10^{19}	13
0.33	2.5×10^{8}	5.5×10^{19}	13
Complexes of TCNE			
0.25	1.7×10^{6}	5.0×10^{19}	11
0.33	8.1×10^{5}	2.1×10^{20}	12
1.00	1.7×10^{6}	4.8×10^{19}	12

* Mol. wt. (Rast) of the polymer, 1.3×10^{3}.
** Broad singlets for solids, but hf structures of five lines were observed for the benzene solutions of the complexes.

Molecular complexes of the polymer species of DPA, a good electron donor because of the structure shown above, with some electron acceptors were prepared, and their semiconductive properties and concentrations of the unpaired electron were measured.

For both measurements, a benzene solution of iodine, chloranil or tetracyanoethylene (TCNE) was mixed with a benzene solution of the polymer, because of its low solubility with other solvents, and the solvent was removed, finally under a vacuum.

A sample with a high specific resistance was measured by the use of a vibrating-reed-type millivoltmeter.*

The specific resistance and concentration of each complex are shown in Table I.

The relative amount of iodine strongly bound to the polymer was determined to be about one-fifth mole to a structural unit of the polymer by the elementary analysis of a complex, which was washed repeatedly with an aqueous potassium iodide solution until no more iodine was liberated into the solution.

This relative amount of iodine is somewhat lower than that obtained for the most conductive complex, i. e., one-and-a-half mole to a structural unit, and the excess amount of iodine, more than one-fifth, obviously increases the conductivity.

The highest concentration of the unpaired electron, however, is obtained for a complex with the different composition of one mole of iodine to three structural units (cf. Table I).

This complicated phenomenon seems to be caused by the excess amount of iodine bound weakly to the complex.

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1) H. Hirota and Y. Kageyama, This Bulletin, 37, 593 (1964).

* Measurement was made at the Institute for Industry and Science of Osaka University.