The Electrical Properties of the Poly(*N*-vinyl Carbazole) - Antimony(V) Chloride (or Iodine) Charge Transfer Complexes*

By Yoshihisa Yamamoto, Seiichi Kanda, Shigekazu Kusabayashi
Takeshi Nogaito, Kazuo Ito and Hiroshi Mikawa

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Many investigations have been made of solid molecular complexes containing polycyclic aromatic hydrocarbons as donors and halogens[1,2] or antimony(V) chloride as acceptors.[3] Most of these complexes are good semiconductors and have a high conductivity, and they often show ESR absorption. Charge transfer complexes derived from polyvinylanthracene,[4] polyvinylpyridine,[5] polyvinylnaphthalene,[6] polyvinylmesitylene[6] and polyvinylcarbazole[7] have already been reported.

It may be expected that vinyl polymer with a π-electron system of aromatic amines may form a charge transfer complex with antimony(V) chloride or iodine. Although vinyl polymers are real insulating materials, some electrical conductivity may be expected in the resulting complex. It may also be hoped that plastic properties can be retained in the product complex. The present paper will deal with the electrical conductivity, ESR absorption and optical absorption of the charge transfer complexes between poly(*N*-vinyl carbazole) (abbreviated as PVCa) and antimony(V) chloride or iodine.

Preparation. — The PVCa used was Luvican M170 (Badische Anilin u. Soda Fabrik A. G.). The antimony(V) chloride was purified twice by distillation.

Poly(N-vinyl Carbazole) - Antimony(V) Chloride Complexes.—The preparation of sample No. 2 (Table I), which will serve as an example, was as follows. PVCa (0.4 g.) was dissolved in chloroform (20 cc.), and then 5 cc. of 1×10^{-3} mol./l. antimony(V) chloride solution in chloroform was stirred in at room temperature. The solution turned green, and precipitation occured. The mixture was kept overnight in a desiccator, after which precipitated complex was filtered and washed repeatedly with chloroform in order to remove the excess antimony(V) chloride. The complex thus obtained was powdered and dried under reduced pressure until a constant weight was obtained. All procedures were carefully carried out free from moisture in order to avoid the decomposition of antimony(V) chloride. In the cases of samples No. 6 and 7, precipitation did not occur, although they turned green when the two components were mixed. The solution was evaporated to dryness to give the complex as a film, which was then washed repeatedly with chloroform and petroleum ether.

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N-Ethylcarbazole - Antimony(V) Chloride and Carbazole - Antimony(V) Chloride Complexes.— The methods used were the same as those used in the case of PVCa. The complexes were soluble in chloroform.

N-Ethylcarbazole - antimony(V) chloride complexes; m. p. 129—132°C. Found: C, 29.8; H, 2.45; N, 2.40; Sb, 30.40. Calcd. for $(C_{14}H_{13}N)_2(SbCl_4)_3$: C, 28.4; H, 2.2; N, 2.37; Sb, 30.93%. Although the mole ratio of *N*-ethylcarbazole and antimony was found to be 2 : 3, Sb : Cl ratio was 1 : 4.

Carbazole - antimony(V) chloride complex; m. p. 179—183°C. Found: C, 44.38; H, 2.79; N, 4.40; Sb, 19.30. Calcd. for $(C_{12}H_9N)_2(SbCl_5)$: C, 45.54; H, 2.84; N, 4.40; Sb, 19.30%.

Poly(N-vinyl Carbazole) - Iodine Complexes.— PVCa and iodine in chloroform were mixed, the stirring was continued for two hours at room temperature, and then they were refluxed for another hour, after which the mixture was allowed to stand overnight. The green colored complex was then precipitated by petroleum ether.

Electric Properties. — Two disk electrodes, 0.2—0.3 mm. thick and 8 mm. in diameter, were prepared first by pressing graphite powder at 5×10^3 kg./cm². The powder of the material was packed between these two graphite electrodes in a mold with a diameter of 13 mm. and pressed at 6×10^3 kg./cm². The thickness of the specimen between the electrodes was about 0.7 mm. The d. c. conductivity was measured in the temperature range between 20 and 60°C.

An almost linear relationship was observed between the current and the applied voltage up to 4600—7000 V./cm. The temperature dependence of the resistivity obeyed the $\rho=\rho_0\exp(\varepsilon/2kT)$ equation (Fig. 1). The resistivity at 20°C (ρ_{20}) and the apparent energy gap (ε) as calculated from the above equation are tabulated in Table I. The ρ_{20} values of PVCa - antimony(V) chloride complexes and PVCa - iodine complexes were found to be 10^5-10^9 and $10^{11}-10^{13}$ Ωcm. The ε values were

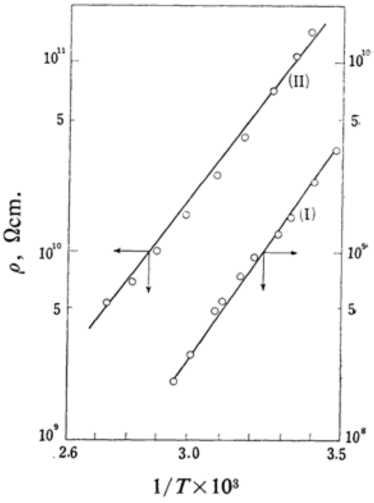

Fig. 1. Specific resistivity vs. $1/T\times10^3$.
Poly(*N*-vinyl carbazole) - $SbCl_5$ complex (I) (Sample No. 6)
Poly(*N*-vinyl carbazole) - I_2 complex (II) (Sample No. 10)

TABLE I. PROPERTIES OF VARIOUS COMPLEXES

No.	Mole ratio between both components used in preparation	Mole ratio between carbazole monomer unit and $SbCl_5$ (or I_2) in the complex	Specific resistivity at room temperature ρ_{20}, Ωcm.	ε, eV.	spin/g.
Poly(*N*-vinyl carbazole) - $SbCl_5$					
1	PVCa only		$>10^{17}$		
2	1 : 2.5	4.5 : 1	5.0×10^7	0.92	2×10^{19}
3	2 : 3		2.0×10^5	0.50	6×10^{19}
4	1 : 1	7.3 : 1	8.0×10^6	0.62	
5	2 : 1	5.3 : 1	4.0×10^5	0.47	4×10^{19}
6	5 : 1	5.6 : 1	2.5×10^9	0.80	4×10^{19}
7	10 : 1	11.3 : 1	8.0×10^7	1.0	
N-Ethylcarbazole - $SbCl_5$					
8	1 : 2.5	3.0 : 2	1.9×10^6	0.60	2×10^{19}
Carbazole-$SbCl_5$					
9	1 : 2.5	2.0 : 1	1.5×10^7	1.18	
Poly(*N*-vinyl carbazole) - I_2					
10	1 : 5	7.6 : 1	1.5×10^{11}	0.93	5×10^{17}
11	1 : 2	14 : 1	1.8×10^{13}	1.14	6×10^{16}
12	1 : 1	45 : 1	3.3×10^{12}	0.94	6×10^{16}
13	2 : 1	73 : 1	2.6×10^{13}	0.88	8×10^{16}

0.50 − 1.0 eV. for PVCa - antimony(V) chloride complexes and 0.88 − 1.22 eV. for PVCa - iodine complexes.

As a reference, the *N*-ethylcarbazole - antimony(V) chloride complex and the carbazole-antimony(V) chloride complex were also measured; there ρ_{20} values were found to be 10^6 and 10^7 Ωcm. respectively.

ESR Absorption.—The ESR absorption was examined at room temperature with a Hitachi MPS-2C spectrometer. The observed values are shown in Table I in spin/g. All the measured samples showed ESR absorption, indicating the existence of unpaired electrons. In the PVCa - antimony(V) chloride complex the number of unpaired spins is about one-tenth of the number of antimony(V) chloride present in the complex. On the other hand, in the PVCa - iodine complex the number of unpaired spins is only 10^{-3} − 10^{-4} of the number of iodine molecules in the complex.

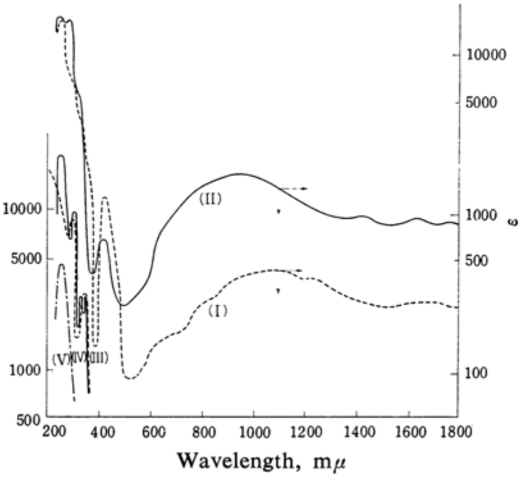

Fig. 2. Absorption spectra of some complexes.
(I) Poly(*N*-vinyl carbazole) - $SbCl_5$
(II) Ethyl carbazole - $SbCl_5$
(III) Poly(*N*-vinyl carbazole)
(V) Ethyl carbazole
(IV) $SbCl_5$

Optical Absorption.—The absorption spectra of the complexes are shown in Fig. 2. The absorption bands of the complexes in chloroform exist in four regions: <400, 420, 1000 and >1300 mμ of these, the <400 mμ bands are due to the components. The spectrum of antimony(V) chloride in chloroform did not show any absorption above 400 mμ. The 400, 1000 and >1300 mμ bands are, therefore, due to complexing between the components. The values of the energy gap as obtained from the temperature dependence of the resistivity are calculated to correspond to 1300—2500 mμ.

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The Institute of Scientific and
Industrial Reserch
Osaka University
Sakai, Osaka