*The Electrical Properties of the Poly(N-vinyl Carbazole)-Tetracyanoquinodimethane Charge Transfer Complex**

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(Received April 21, 1964)

Tetracyanoquinodimethane (abbreviated as TCNQ) forms a charge transfer complexes with various amines.[1] The electrical resistivity of these compounds is fairly low, and some of them show an ESR signal.[1,2]

It is to be expected that vinyl polymers with π-electron systems of aromatic amines will form charge transfer complexes with TCNQ and also that the complexes have conductive characteristics. Plasticity may also be expected to be retained in the product complex.

Charge transfer complexes derived from polyvinylanthracene,[3] polyethinylnaphthalene,[4] polyvinylpyridine,[5] polyvinylnaphthalene[6] and polyvinylmesitylene[6] have been reported.

In the present work, the electrical and optical properties of the charge transfer complex between poly(*N*-vinyl carbazole) and TCNQ have been investigated. The photoconductive properties of poly(*N*-vinyl carbazole) and its sensitization with TCNQ and other compounds acting as acceptors have already been described.[7]

Preparation. — The poly(*N*-vinyl carbazole) used is Luvican M170 (Badische Anilin u. Soda Fabrik A. G.). TCNQ was prepared by the method described in the literature.[8]

Poly(N-vinyl Carbazole)-TCNQ Charge Transfer Complexes.—These complexes were prepared easily by dissolving both components in chloroform at room temperature. The dark green material thus obtained was fairly stable thermally, with a softening point between 210 ~270°C. It was possible to make a film of the complex by evaporating the solution containing the material.

In preparing the complex, the ratio between the amounts of the two components were changed as shown in Table I. The mole ratio between the carbazole monomer unit of poly(*N*-vinyl carbazole) and TCNQ in the various complexes obtained are shown in the table. The mole ratios of the components were estimated spectroscopically from the intensities of the absorption peaks at 330 and 400 mμ.

As reference substances, an *N*-ethyl carbazole-TCNQ complex and a carbazole-TCNQ complex were also prepaped.

N-Ethyl Carbazole-TCNQ Charge Transfer Complex.—One hundred ninty-five milligrams (10^{-3} mol.) of *N*-ethyl carbazole and 204 mg. (10^{-3} mol.) of TCNQ were mixed as a chloroform solution (100 ml.). The solution immediately turned dark green, and a crystalline solid separated. The solution was evaporated to half of its volume after one hour, and the precipitated crystalline complex was filtered. Dark green needles; sublimation temperature above 160°C; yield 270 mg.

Found: C, 77.10; H, 4.59; N, 17.73. Calcd. for a one-to-one complex $C_{26}H_{17}N_5$: C, 78.19; H, 4.26; N, 17.53%.

Carbazole-TCNQ Charge Transfer Complex.—One hundred sixty-seven milligrams (10^{-3} mol.) of carbazole and 204 mg. (10^{-3} mol.) of TCNQ were mixed as in the case of ethyl carbazole. Sublimations temperature, 210~250°C; yield, 310 mg.

Found: C, 76.70; H, 4.41; N, 19.54. Calcd. for a one-to-one complex $C_{24}H_{13}N_5$: C, 78.00; H, 3.24; N, 18.55%.

Spectroscopic Properties. — The absorption spectra of the charge transfer complex between poly(*N*-vinyl carbazole) and TCNQ are shown in Fig. 1. In chloroform the main bands are at 330, 400 and 620 mμ, of these, 330 mμ is the absorption due to poly(*N*-vinyl carbazole) itself and 400 mμ, that due to TCNQ. The 620 mμ band is, consequently, the so-called charge transfer band between the two components. The absorption spectra of the glassy solid film

* Presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

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of the complex are very similar to those of the chloroform solution, having maxima at 330, 400 and 600 mμ.

As a reference, the absorption spectrum of the *N*-ethyl carbazole - TCNQ complex was also measured. In the chloroform solution, a charge transfer band was observed around 560 mμ, as is shown in Fig. 1.

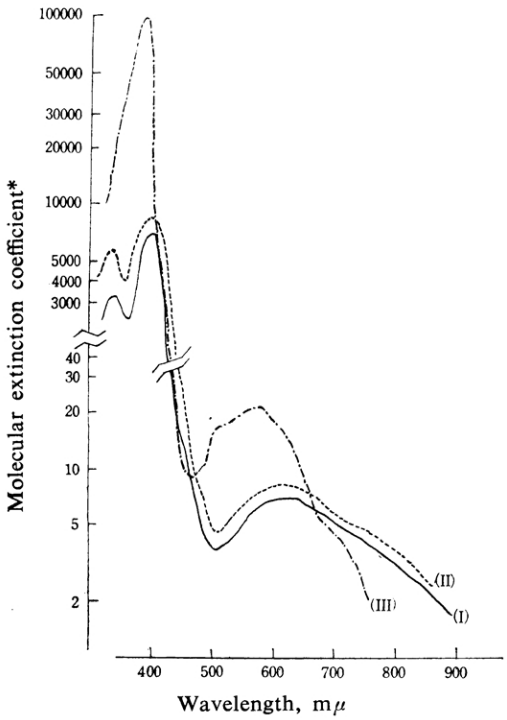

Fig. 1. Absorption spectra of some complexes.
(I) Poly(*N*-vinyl carbazole) and TCNQ were dissolved in chloroform in the ratio 10 : 1.
(II) Poly(*N*-vinyl carbazole) - TCNQ complex film (arbitrary unit).
(III) *N*-Ethyl carbazole - TCNQ complex in chloroform.
* This value is calculated by dividing the optical density of the solution as observed with the mol./l. concentration of the carbazole monomer units present in the solution.

Electrical Properties.—The electrical conductivity of the material was measured with a pellet made under 5000 kg./cm² pressure with a silver-paste electrode by the DC method, the applied voltage being 20~2000 V./cm. The relation between the current and the applied voltage obeyed Ohm's law in this range. The relationship between the logarithm of the resistivity and the reciprocal of the temperature is shown for the complexes in Fig. 2. The specific resistivity at room temperature and the band gap, ε, as calculated from the temperature dependence of the resistivity by the equation $\rho = \rho_0 \exp(\varepsilon/2kT)$ are tabulated in Table I. The specific resistivity of poly(*N*-vinyl carbazole) itself was above 10^{17} Ωcm. The conductivities of the *N*-ethyl carbazole - TCNQ complex and the carbazole-TCNQ complex are also listed in this table.

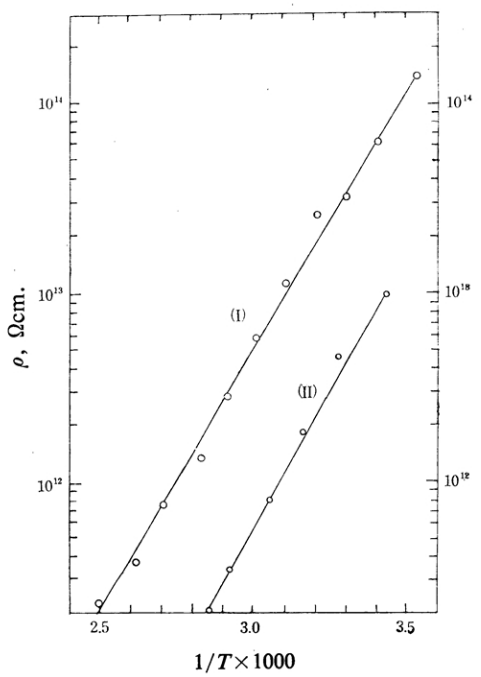

Fig. 2. Temperature dependence of the resistivity.
(I) Poly(*N*-vinyl carbazole) - TCNQ complex (sample No. 5).
(II) *N*-Ethyl carbazole - TCNQ complex

TABLE I. PROPERTIES OF VARIOUS COMPLEXES

No.	Weight ratio between both components used in preparation	Mole ratio between carbazole monomer unit and TCNQ in the complex	Specific resistivity at room temperature Ωcm.	ε eV.
Poly(*N*-vinyl carbazole) - TCNQ				
1	1 : 1	34 : 1	5.0×10^{15}	1.4
2	2 : 1	38 : 1	1.2×10^{14}	1.4
3	5 : 1	31 : 1	1.1×10^{16}	1.5
4	10 : 1	35 : 1	2.4×10^{14}	1.3
5	20 : 1	57 : 1	1.4×10^{14}	1.1
N-Ethyl carbazole - TCNQ				
6	1 : 1	1 : 1	1.8×10^{13}	1.1
Carbazole-TCNQ				
7	1 : 1	1 : 1	7.0×10^{10}	1.1

Summary

Poly(*N*-vinyl carbazole) (specific resistivity, above 10^{17} Ωcm.) gives a dark-green charge transfer complex with tetracyanoquinodimethane.

The specific resistivity of the complexes at room temperature is $10^{14}\sim10^{16}$ Ωcm. and the band-gap energy is 1.1∼1.5 eV. The film-forming property of poly(*N*-vinyl carbazole) is retained in the complex. The charge transfer band is observed at about 620 mμ.

The authors wish to thank Mr. Takuzo Fujino and Mr. Tsuneyo Shishido for their elementary analyses.

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