

Table 2 Properties of polyetherurethanes

	PTHF	Atactic PPG	Optically active PPG
Appearance	Transparent	Turbid	Turbid
Optical activity [α] _D ²⁰ (degrees)	—	-0.002 ^a	-0.451 ^a
T _g (°C)	-78	-53	-50
Main endotherm (°C)	193	198	196
Hardness (° Shore A)	94	94	94
Stress at rupture (MN.m ⁻²)	38.7	26.5	34.2
Stress at 100% strain (MN.m ⁻²)	13.8	13.8	16.0
Stress at 300% strain (MN.m ⁻²)	23.2	20.4	23.9
Strain at rupture (%)	484	428	418
Tear strength (KN.m ⁻¹)	54	46	52
Infra-red analysis ^b			
Absorption at 3500 cm ⁻¹	Absent	Absent	Absent
Absorption at 3320 cm ⁻¹	Present	Present	Present
Ratio of peak heights at 1705 cm ⁻¹ and 1730 cm ⁻¹	2.0	1.78	1.76

^a 10% Solutions in dimethylformamide

^b Absorptions at 3500, 3320, 1705 and 1730 cm⁻¹ are attributed to free NH, bonded NH, bonded carbonyl and free carbonyl, respectively

pected to be virtually 100% atactic and head-to-tail whereas in the optically active PPG of the present study some head-to-head linkages would be expected to be present⁷.

The T_g processes noted in all three elastomers at temperatures somewhat higher than the T_g processes in the corresponding polyethers together with the high-temperature endothermic processes is strong evidence for the typical two-phase structure of block copolyurethanes. Whilst there is no evidence from thermal analysis of crystallinity attributable to the polyether block in any of the polyurethanes the optical activity and therefore the ability to crystallise is shown to be retained in the polyurethane derived from the optically active PPG.

There is no clue from infra-red analysis as to why the optically active PPG should provide polyetherurethanes of improved mechanical properties over those derived from atactic PPG. However, the higher proportion of hydrogen-

bonded carbonyl in the PTHF-derived analogue may be indicative of a more perfect structure in this elastomer and hence provide at least part of the explanation of its improved mechanical properties. The likelihood of a more perfect structure in this elastomer is supported by the smaller change in T_g which occurs on conversion of the polyether to a polyurethane (16°C vs. about 25°C for both PPG types).

No direct evidence is available that strain-induced crystallization is the reason for the improved mechanical properties of the optically active PPG-derived elastomer. However, this seems a likely explanation and is in accord with the conclusions of Shibutani *et al.* from a study of comparable polyetherurethaneureas⁶.

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Electrical conductivity of polyvinylcarbazole—tetracyanoquinodimethane complexes

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INTRODUCTION

Poly(vinyl carbazole) (PVK) and its charge transfer complexes have recently been investigated owing to possibilities of application of those materials in electrophotography. In comparison with other poly(vinyl carbazole) complexes, the complex with tetracyanoquinodimethane (TCNQ) has been described in only a few studies relating mainly to its spectral properties¹⁻³. The electrical properties of the complex were described only by Taniguchi and coworkers¹. By sedimen-

tation in chloroform, they obtained a series of complexes with the TCNQ:PVK molar ratio in the range 1:51 to 1:37, with a corresponding conductivity range 10⁻¹⁶ to 10⁻¹⁴ Ω⁻¹ cm⁻¹.

In this paper, results of investigations on electrical conductivity are presented for poly(vinyl carbazole) — tetracyanoquinodimethane (PVK-TCNQ) complexes of TCNQ:PVK molar ratio* from 1:111 to 1:2.2.

* The term 'molar ratio' represents here the ratio of a number of TCNQ molecules to a number of monomer units

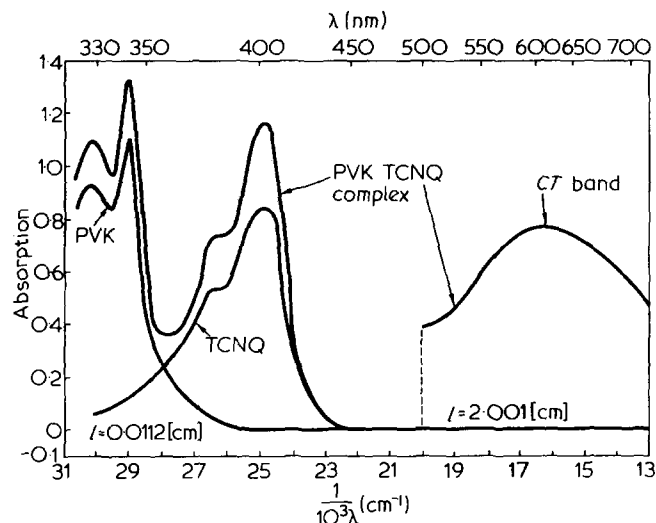


Figure 1 Absorption spectra of TCNQ, PVK and PVK-TCNQ complex dissolved in a chloroform-acetonitrile mixture. The measuring layer thicknesses were for $\lambda < 500$ nm; $l = 0.0112$ cm and for $\lambda > 500$ nm, $l = 2.001$ cm

EXPERIMENTAL

Sample preparation

The poly(vinyl carbazole) was obtained by thermal polymerization of *N*-vinyl carbazole (ICN Pharmaceuticals) at 423K. The tetracyanoquinodimethane was synthesized and purified by a well-known method⁴.

The electrical properties of two sets of samples are presented; these were prepared in various ways by the use of dioxane and a mixture of chloroform with acetonitrile in the volume ratio 4:1 as solvents. Solutions of PVK with TCNQ had a dark-green colour. In the spectrum of one of the CTs the absorption band could be observed with a maximum at a wavelength of 600 nm of the corresponding transition energy $h\nu_{CT} = 2.05$ eV (Figure 1).

The first set of samples was made (method A) by dissolution of PVK and TCNQ in dioxane, and evaporation of the solvent. The method gave homogeneous complexes of the maximum TCNQ:PVK molar ratio equal to 1:6. The solutions of complexes of molar ratio 1:25 and less were not stable and green in colour due to a decomposition process of the complex. The velocity of this process increased with the temperature rise. A similar dependence was observed by other authors⁵.

Taking the above into consideration the solvent was evaporated quickly at room temperature, immediately after the solution had been prepared. In this way stable green-coloured complexes were obtained in a vitreous form. Their colour intensity depended on the TCNQ:PVK ratio.

The samples used for the investigation of electrical properties were discs of diameter 16 mm and thickness 0.5-3 mm. They were made by powdering the complex in a mortar and by moulding under a pressure of 16 kbar. Silver electrodes each of area 1.16 cm² were shadowed onto both sides of the sample by evaporation; the conductivity of the samples was found to be stable (no change of electrical conductivity over 20 days was observed).

The second set of samples was made (method B) by dissolution of PVK and TCNQ in a mixture of chloroform and

acetonitrile and by partial evaporation of the solvent. During evaporation a sticky precipitate of the complex was separated which was then moulded to obtain samples in the form of pellets of diameter 10 mm and thickness 0.7 mm. The samples were dried for several hours at room temperature and then heated in vacuum at a temperature of 373K. Electrodes of diameter 4 mm made of silver paste were placed on both sides of each sample. The TCNQ:PVK molar ratio of the complexes was determined by spectroscopic investigation of solutions in chloroform-acetonitrile mixture, and by measuring the absorption intensities at 330 and 400 nm⁶. The accuracy of the method has been estimated to be about 8%.

RESULTS AND DISCUSSION

The investigations of electrical conductivity-temperature dependence and current-voltage characteristics for PVK, TCNQ and PVK-TCNQ complexes obtained using the two methods were then carried out.

Figure 2 shows the current-voltage characteristics of complexes obtained by solvent evaporation (method A) and also of separately moulded samples of TCNQ and PVK. The data presented show that non-ohmic characteristics were exhibited only by samples of TCNQ:PVK at a molar ratio of 1:6. The current-voltage characteristics of complexes obtained by method B are also similar (Figure 3). Samples of greater TCNQ:PVK ratio exhibited the non-ohmic characteristics.

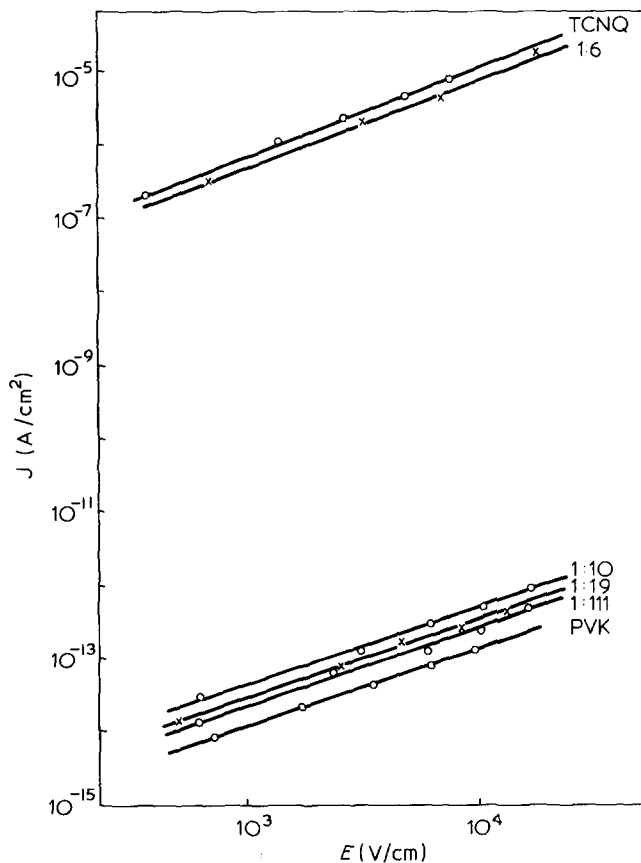


Figure 2 Current-voltage characteristics of PVK-TCNQ complexes prepared by method A

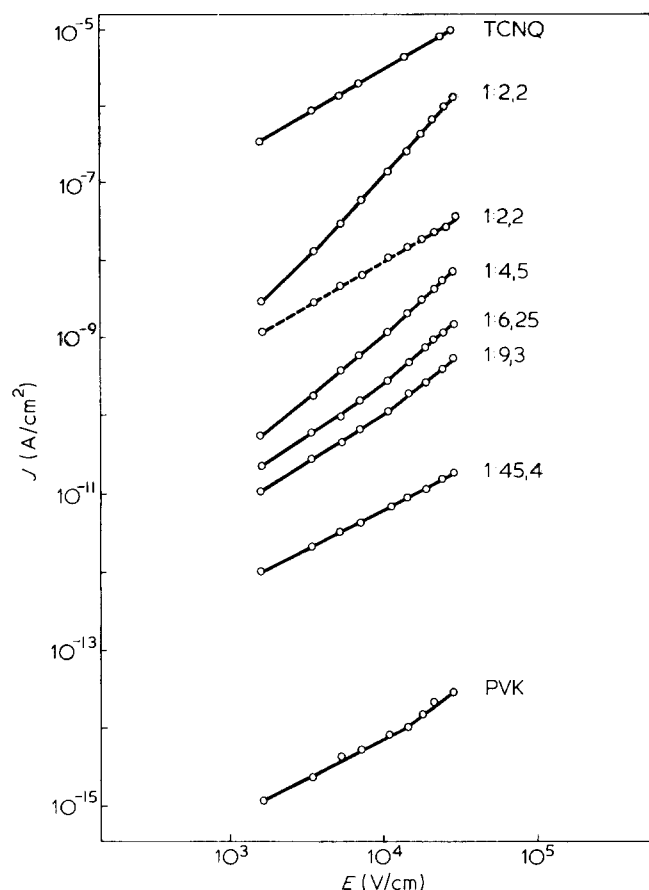


Figure 3 Current-voltage characteristics of PVK-TCNQ complexes prepared by method B

These dependences can be expressed by the equation $J = AE^n$, where A and n are constants (Table 1).

The measurements showed that index n was increasing with the rise of TCNQ:PVK ratio in the complex. Figure 3 also shows for comparison, a current-voltage characteristic for a sample made by moulding the powdered mixture of both complex components, i.e. TCNQ and PVK, at a molar ratio of 1:2.2. This relationship had been found to be ohmic.

The conductivity vs. temperature dependences for the complexes obtained are typically Arrhenius-type relations. The activation energy for conductivity of the complexes decreases with the rise in TCNQ:PVK ratio, and takes smaller values than for TCNQ alone.

The results obtained indicate a substantial influence of the preparation method on the electrical properties of PVK-TCNQ complexes. The samples which were prepared by solvent evaporation (method A) and thus exhibiting a smaller TCNQ:PVK ratio, showed slightly higher conductivity than PVK alone. Analogous samples prepared by method B showed conductivities about 2-3 ranges higher than PVK, as Taniguchi and coworkers¹ had observed earlier. The

Table 1

TCNQ:PVK molar ratio	Method of sample preparation	Electrical conductivity at room temp. and at 10^3 V/cm ($\Omega^{-1}\text{cm}^{-1}$)	Activation energy (eV)	Index n from $J = AE^n$
PVK	—	1.2×10^{-17}	0.99	1
1: 111	A	1.4×10^{-17}	0.82	1
1: 45.4	B	2.0×10^{-15}	0.68	1
1: 19	A	3.1×10^{-17}	0.74	1
1: 10	A	4.7×10^{-17}	—	1
1: 9.3	B	4.5×10^{-14}	0.63	1.3
1: 6.25	B	1.6×10^{-13}	—	1.3
1: 6	A	6.8×10^{-10}	0.37	1.3
1: 4.5	B	6.3×10^{-12}	0.59	1.5
1: 2.2	B	1.2×10^{-11}	0.49	1.9
TCNQ	—	8.0×10^{-10}	0.60	1

current-voltage characteristics of these samples were also ohmic.

The electrical conductivity of systems with higher TCNQ:PVK ratios seems not to be caused by percolation through TCNQ aggregates only. It is determined rather by the conductivity of the CT complex. The observed non-ohmic conductivity and the values of activation energy, smaller than for TCNQ alone, seem to confirm this suggestion. The relatively high conductivity of samples of TCNQ:PVK complex with molar ratio 1:6, prepared by method A is probably caused by the presence of neutral TCNQ molecules in the sample material. Associations of neutral molecules with the existing CT complex can contribute to an increase of the system conductivity. Similar explanations of electrical conductivity in high molecular complexes have been proposed by other authors^{7,8}.

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