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ELECTRICAL PROPERTIES OF POLYVINYLCARBAZOLE–TETRACYANOQUINODIMETHANE CHARGE TRANSFER COMPLEXES

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Abstract—Electrical properties of polyvinylcarbazole–tetracyanoquinodimethane (PVK:TCNQ) charge transfer complexes were investigated as a function of the composition of the mixture, temperature, pressure and the method of sample preparation. It was shown that the electrical conductivity of the PVK:TCNQ complex (for TCNQ content <10% by weight) increased only slowly with increasing concentration of TCNQ and was only slightly higher than the conductivity of pure PVK. At higher TCNQ concentrations however an abrupt increase of the complex conductivity was observed. This effect may be attributed to the formation of semi-conductive tracks composed of uncomplexed neutral TCNQ molecules. The electrical conductivity of PVK:TCNQ complex was lower than the conductivity of TCNQ alone. The activation energy for electrical conductivity in the complex decreased with increasing TCNQ concentration from 0.99 eV for pure PVK to 0.37 eV for PVK:TCNQ (6:1) complex. The high field conductivity of the PVK:TCNQ complex could be explained by using the Poole–Frenkel model.

INTRODUCTION

Polyvinylcarbazole (PVK) forms charge-transfer (CT) complexes with many compounds having acceptor properties. The complexes are characterized by high photo-electric sensitivity in the visible region and for this reason these materials are used in electrophotography. In PVK:TCNQ (tetracyanoquinodimethane) complexes, monomeric PVK is a donor and TCNQ an electron acceptors. The appearance of a new band, the so-called "charge-transfer band", is observed in the absorption spectrum at 600 nm [1, 2] and is the result of PVK–TCNQ complex formation. The PVK–TCNQ complex is a weak CT complex. In its absorption spectrum, the radical entities are not observed, neither is there an EPR signal for the complex. As for the frequently investigated CT complex of PVK with trinitrofluorenone (PVK:TNF), in the PVK:TCNQ complex complete complexing of PVK monomeric units with TCNQ molecules does not occur. The degree of complexing, defined as the ratio of complexed molecules of the acceptor to all the acceptor molecules, depends on the component mole ratio, and decreases with increase of acceptor concentration from 80% for PVK:TCNQ mole ratio 50:1 to 60% for 10:1 ratio [3].

PREPARATION OF SPECIMENS AND MEASUREMENTS

To prepare the PVK–TCNQ complex, PVK was obtained by thermal polymerization of *N*-vinylcarbazole* at 423 K for 30 h. After polymerization was complete, the polymer was purified by repeated reprecipitation using benzene as solvent and methanol as precipitant. TCNQ was synthesized and purified by a well known method [4]. For measurements, samples of PVK–TCNQ complex were obtained both by prolonged grinding together of the pure components in a mortar and by mixing the components in dioxane solution. The advantage of preparing the complex from pure components by grinding is the elimination of solvent occlusion as well as of possible reactions between solvent and dissolved components [5]. The degree of complexing in this method, however, depends strongly on the procedure and the grinding time.

The samples of complex obtained by this method were prepared by press moulding under a pressure of 16 kbar, to form a disc of diameter 16 nm and thickness of about 2 mm. Silver electrodes (dia. 11.6 mm) were then applied on both sides of the disc by means of vacuum deposition. Samples of the complex obtained by complexing in dioxane solution were prepared by press moulding of the substance ground in a mortar after solvent evaporation in the same way as before, as well as by pouring the dioxane solution containing complex onto a glass or PTFE substrate. By the latter method, it was possible to obtain thin layers of thickness of 100–400 μm. On the surface of layer-type samples, after heating in vacuum at 80°C for several hours (in order to remove the solvent), gold electrodes were vacuum deposited to have an area of 0.1 cm^2. Due to precipitation of TCNQ from solution, it was possible to obtain homogenous complex layers representing weight ratios not lower than 12:1. By solvent evaporation at higher temperature (70°C), the complex layers of PVK:TCNQ having weight ratio 6:1 could be obtained. On the surfaces of the specimens, Ag or Au electrodes were then deposited in vacuum (10^{-6} Tr) followed by fixing wire

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leads by means of a epoxysilver paste. Prior to investigation, the samples were conditioned by applying electric fields exceeding those used in the measurements and also by heating and then cooling the samples with the leads short circuited, down to temperatures lower than those used in the measurements. The samples thus conditioned showed good reproducibility of results. Conductivity measurements were carried out in vacuum (10^{-5} mmHg) in a darkened chamber. The voltage was fed from a supply unit with the current flow measurement performed by an electrometer. The temperature was measured by using a Constantan–Cu thermocouple situated adjacent to the sample.

Pressure effect measurements were carried out with moulded specimens of the complex using equipment described previously [6], within the pressure range 0–5.0 kbar.

RESULTS

Samples of PVK and PVK:TCNQ complex having component weight ratio >12:1 showed high electrical resistance and also exhibited strong polarization effects. After the voltage was applied, the current was observed to decrease with time. This dependence could be described by a relation $I = t^{-n}$. At higher temperatures the plots of the current–time dependences showed a bend of the curve. After initial rapid drop of the current, a slower drop was observed. Since PVK is a polar polymer (dipole moment of carbazole group is 1.5 D) and in its relaxation spectrum maxima α, β, γ appear [7], the dipole type relaxation may be responsible for the initial current drop. Further, slower drop of the current is presumably caused by charge carrier trapping. Such an effect of time dependent current decrease caused by carrier trapping is observed even in molecular crystals with ohmic electrodes [8]. For these long-lasting polarization effects, the current values given are quasi-steady values. In samples of TCNQ and in semiconducting samples of PVK:TCNQ (12:1, 8:1, 6:1), polarization effects are very small. The conductivity measurements were carried out in vacuum (10^{-5} mmHg). No effect of air on electrical conductivity of either insulating or semiconducting samples of PVK:TCNQ complex was observed (Fig. 1).

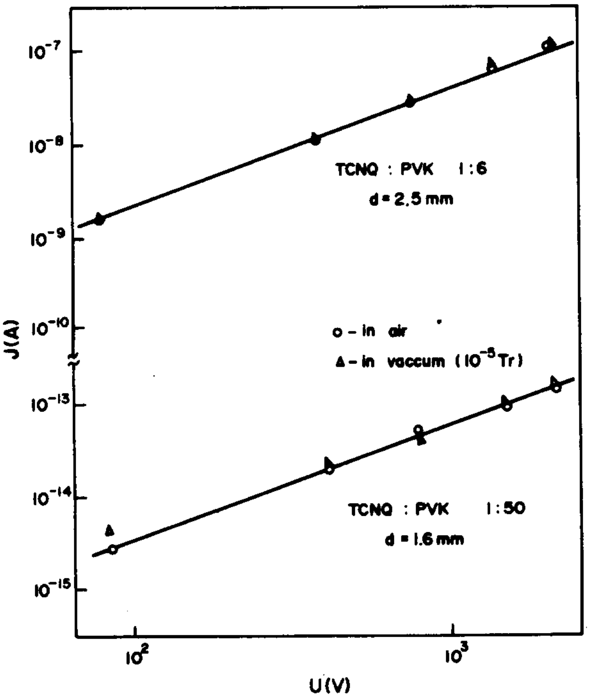

Fig. 1. Current–voltage characteristics of the two press moulded samples of PVK–TCNQ complex. The first—semi-conducting, PVK:TCNQ 6:1; the second—insulating, PVK:TCNQ 50:1. △—measurements in vacuum 10^{-5} mmHg; O—measurements in air.

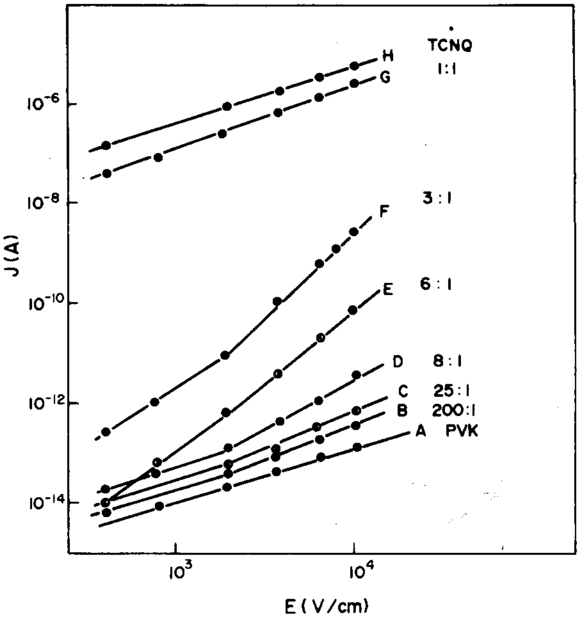

Fig. 2. Current–voltage characteristics of press moulded samples of PVK–TCNQ complex prepared by prolonged grinding of pure components in a mortar.

Current–voltage characteristics of the sample could be described by the relation $I = AE^n$, where A and n are constants. Figure 2 presents current–voltage characteristics of a PVK:TCNQ complex obtained as a result of grinding of the pure components in a mortar for 30 min. From the I–V plots, it can be seen that electrical conductivity of the PVK:TCNQ complex sample (containing <10% by weight TCNQ) is only slightly higher than the conductivity of pure PVK. Samples having PVK:TCNQ weight ratio not lower than 1:1 exhibit conductivity close to that of pure TCNQ.

Samples of the complex with intermediate TCNQ concentrations show strongly non-linear I–V dependence. The current voltage characteristics of the PVK:TCNQ complex obtained by complexing in dioxane solution and moulding are presented in Fig. 3 and for specimens in form of a thin layer, in Fig. 4. Figures 2 and 3 show for comparison the I–V characteristics for moulded samples of pure PVK and TCNQ; Fig. 4 refers to PVK layer-type sample.

I–V characteristics of PVK:TCNQ complex layers with component ratios of 1:12, 1:8 and 1:6 showed at field intensity $<10^3$ V/cm the ohmic dependence

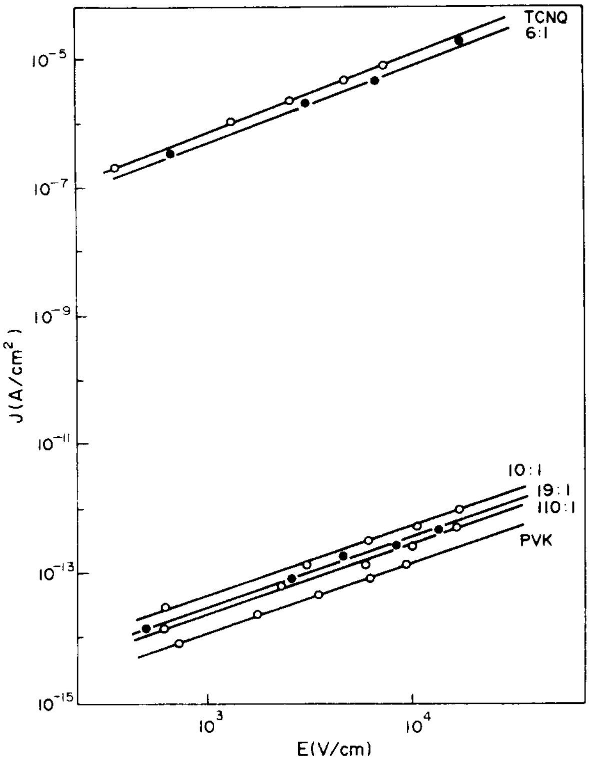

Fig. 3. Current-voltage characteristics of press moulded samples of PVK-TCNQ complex prepared by complexing in dioxane solution.

(n = 1, not shown in Fig. 4, whereas at higher field intensities n assumed values >2; Fig. 4 and Table 1).

The remaining complex samples in the form of layers or moulded discs showed deviations from the ohmic dependence not earlier than at field intensity $>5 \cdot 10^4$ V/cm. The temperature dependence of electrical conductivity of PVK:TCNQ complex exhibited thermally activated behaviour. Activation energy for conductivity of this complex decreased with increase of TCNQ concentration; at high TCNQ contents, it assumed values lower than the corresponding quantities for pure TCNQ (Table 1). Activation energies of conductivity in the complex samples did not exhibit the field type dependences for field intensities up to $5 \cdot 10^4$ V/cm. When comparing the conductivity and activation energy for moulded and layer-type specimens, it is seen that the former lead to higher values of conductivity and of activation energy. This is probably caused by barrier effects at the grain interfaces of the moulded specimens. Measurements of electrical conductivity vs pressure for the PVK:TCNQ complex were carried out with moulded specimens obtained by complexing in dioxane solution. The pressure was increased gradually by 0.1 kbar steps from 0 to 5.0 kbar. In all the investigated specimens, increase of conductivity with pressure was found (positive value of conductivity pressure coefficient). Relative changes of conductivity with increase of pressure up to 5.0 kbar were contained within one order of magnitude. The natures of relative pressure induced conductivity changes were different for PVK and for TCNQ (Fig. 5).

For PVK the conductivity increase was monotonic with pressure rise; for TCNQ, after a rapid increase, stabilization of conductivity above 3 kbar was observed. The current-voltage characteristics of PVK:TCNQ complex have an intermediate nature as discussed above. Activation energies of conductivity, determined from I–V characteristics, show a distinct drop with pressure increase (Fig. 6). Activation energy changes are proportional to (pressure)$^{1/2}$.

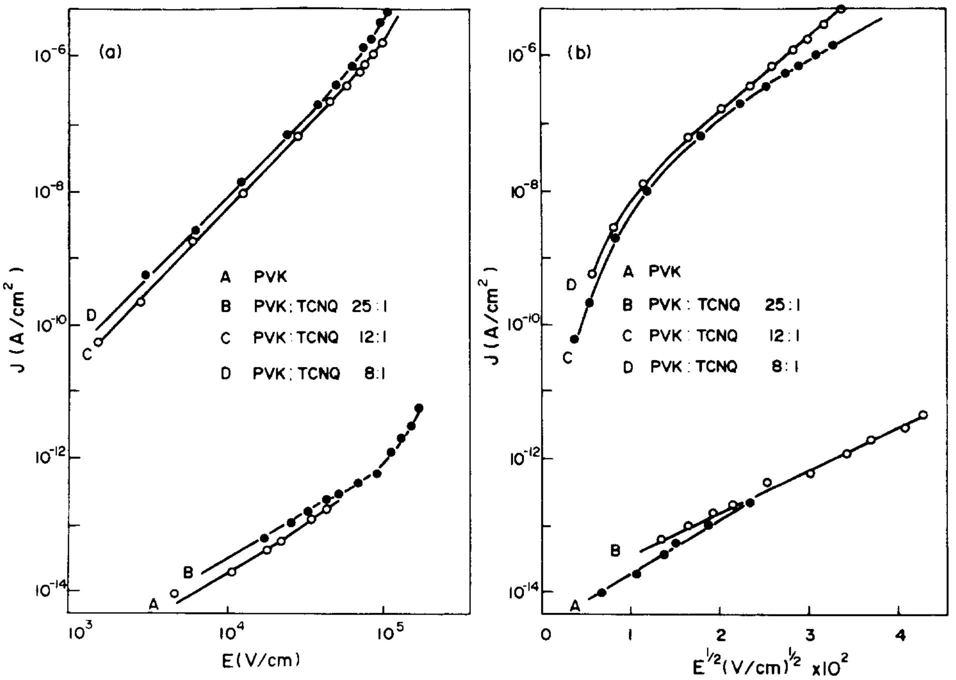

Fig. 4. Current-voltage characteristics of layer-type specimen of PVK-TCNQ complex. (a) $I = f(E)$; (b) $\log I = f(\sqrt{E})$.

Table 1. Electrical properties of PVK:TCNQ charge transfer complexes

PVK:TCNQ weight ratio	Type of sample: L—layer M—moulded	Electrical conductivity at room temp. and 10^3 V/cm $[\Omega^{-1}\,\mathrm{cm}^{-1}]$	Activation energy [eV]	Power index n from formula $J = AE^n$	Experimental values of PF coefficient
PVK	L	$2.1 \cdot 10^{-18}$	0.7	1,4	5.3
PVK	M	$1.2 \cdot 10^{-18}$	0.99	1	—
110:1	M	$1.4 \cdot 10^{-17}$	0.82	1	—
50:1	L	$2.5 \cdot 10^{-18}$	0.64	—	—
25:1	L	$3 \cdot 10^{-18}$	0.45	1.34	3.9
19:1	M	$3.1 \cdot 10^{-17}$	0.74	1	—
12:1	L	$2.88 \cdot 10^{-14}$	—	(1); 2.33	4.94
10:1	M	$4.7 \cdot 10^{-17}$	—	1	—
8:1	L	$1.7 \cdot 10^{-13}$	0.3	(1); 2.14	6.82
6:1	M	$6.8 \cdot 10^{-10}$	0.37	1.3	—
TCNQ	M	$8 \cdot 10^{10}$	0.6	1	—

$\beta_{\mathrm{PF\ theoretical}} = 4.4 \cdot 10^{-5}$ eV $(\mathrm{m/V})^{1/2}$ (for $\epsilon = 3$)

DISCUSSION

PVK–TCNQ complexes, whatever the method of preparation, showed similar relationships for electrical conductivity vs TCNQ weight content (Fig. 7). Initially the electrical conductivity increased slowly, proportional to the TCNQ content; at about 10% TCNQ, there was an abrupt change of conductivity by seven orders of magnitude. This was observed for powdered samples obtained by complexing in dioxane solution. The moulded samples, obtained by grinding of pure components, showed similar behaviour up to 10% concentration; with further increase of TCNQ content, an abrupt conductivity jump was not observed but only a gradual rise.

For layer-type specimens obtained by pouring the dioxane solution, the conductivity jump was observed at slightly lower TCNQ content. The conductivity increment after the jump amounted to over four orders of magnitude. For the range of concentrations investigated (up to 12% by weight), the conductivity of the complex was lower than that of pure TCNQ. The initial increase of conductivity σ of the PVK:TCNQ complex with TCNQ concentration is typical of polymeric CT complexes in which the acceptor concentration is increasing [9]. The relationship can be expressed thus:

$$\sigma = \alpha C^{\kappa}$$

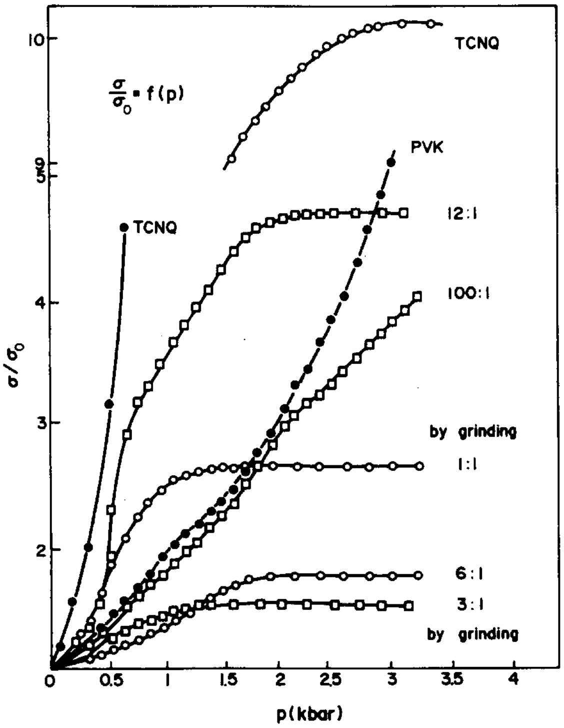

Fig. 5. Pressure dependence of relative change of electrical conductivity in press moulded samples of PVK, TCNQ and PVK–TCNQ complex prepared by grinding of pure components and by complexing in dioxane solution.

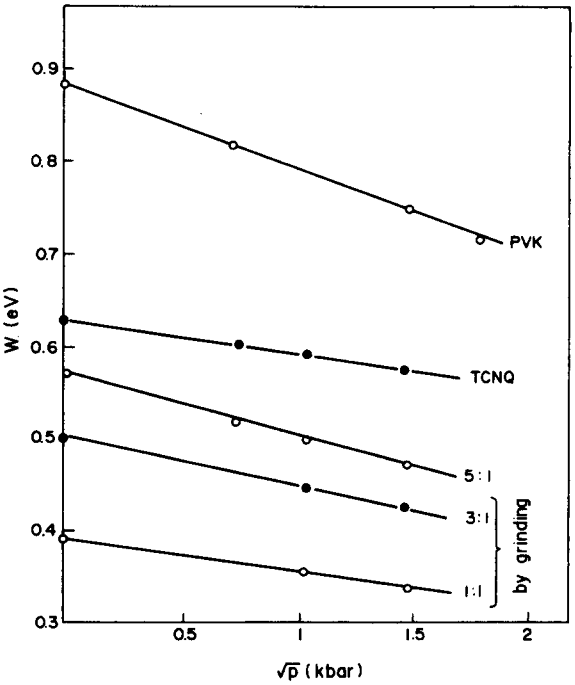

Fig. 6. Square root pressure dependence of activation energy for conductivity in press moulded samples of PVK, TCNQ and PVK:TCNQ complex.

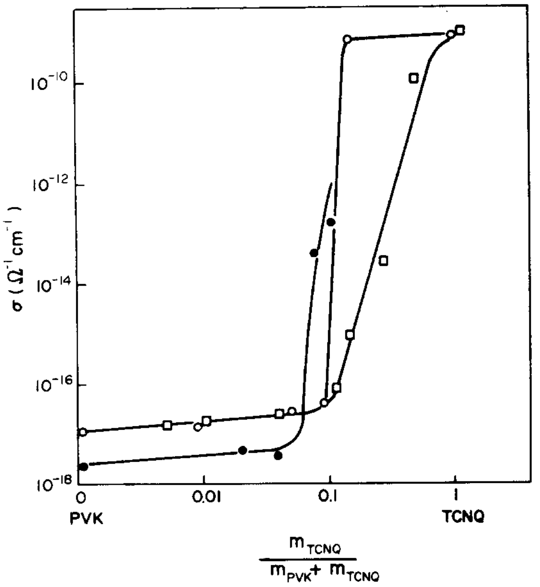

Fig. 7. Electrical conductivity of PVK:TCNQ complex vs TCNQ weight content. ○—moulded samples of complex prepared by complexing in dioxane solution; □—moulded samples of complex prepared by grinding of pure components; ●—layer of PVK–TCNQ complex obtained from dioxane solutions.

where:
α, κ are constants for a given complex
C—defines molar ratio of acceptor to donor.

Coefficient κ, characterizing concentration conductivity dependence, was identical for PVK:TCNQ complexes obtained in different ways and was 0.19. The low value of this coefficient is a characteristic feature of CT polymeric complexes typical of hole type electric conductivity [9]. In PVK, the spacings between side carbazole groups are 3.4 Å [10]; they are not large enough to distribute even flat acceptor molecules (TCNQ) between them. It may be therefore supposed that, in a PVK:TCNQ complex, a high concentration of acceptor molecules (TCNQ) occurs only in the vicinity of structural defects in the donor (PVK). Within such a TCNQ concentration range, only slow conductivity rise is observed. When, all available defects are saturated, the acceptor molecules (TCNQ) start to form semi-conductive tracks. Such a concentration corresponds to an abrupt conductivity jump. In PVK:TCNQ complex, the conductivity jump occurs at a TCNQ weight content of about 10%. Since the complexing degree at this point is about 62% (from spectroscopic measurements [3]), the concentration of free TCNQ molecules at which formation of semiconductive tracks is possible may be estimated as about 4% by weight of TCNQ. This value is close to that obtained by Lupinski *et al.* [12] for polymeric salts of TCNQ with excess of the latter. These authors found that, at 5% excess of TCNQ, a conductivity jump was observed by 5–7 orders of magnitude in polymeric salts of TCNQ. High conductivity of these compounds is a consequence of the formation during solvent evaporation of semiconductive tracks determined by the TCNQ$^-$/TCNQ systems. Maximum conductivity of such compounds was much higher than of individual components and was $10^{-3}\,\Omega^{-1}\,\text{cm}^{-1}$. It was worth noting that the radical form TCNQ$^-$ does not exist in the PVK:TCNQ complex (from spectroscopic investigations) and so the complex conductivity after the jump was not higher than the conductivity of pure TCNQ. Semiconductive tracks are formed by neutral TCNQ molecules. The results of examination of effects of pressure on conductivity of PVK:TCNQ complex confirm the assumption that acceptor molecules are initially packed in structural defects of the donor, and then take the form of semiconductive tracks. If it is assumed that the pressure induced increase of conductivity of the complex is caused by intensified overlapping of molecules orbitals, then the relationship regarding the relative change of conductivity as affected by pressure with TCNQ content, will reflect relative volume changes. Figure 8 shows that the lowest relative conductivity changes take place for the PVK:TCNQ (10:1) complex. In this complex, the lowest relative volume changes appear because all the structural defects are filled by TCNQ molecules. On further increase of TCNQ content, a separate phase is formed therefore the relative volume changes are greater. The conductivity pressure dependence can be expressed thus:

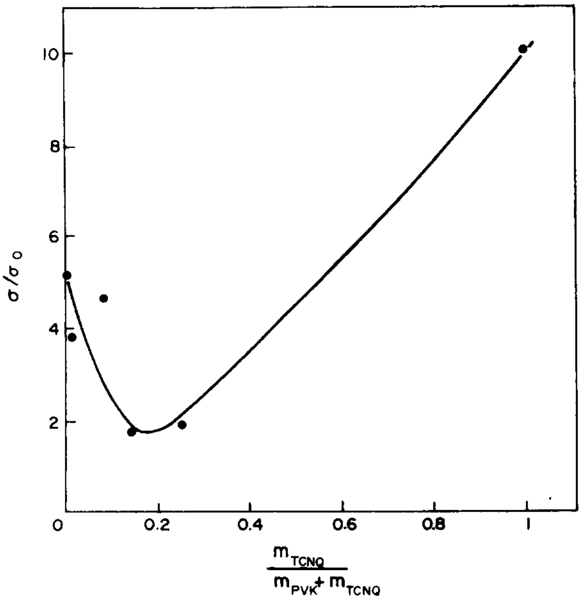

Fig. 8. Electrical conductivity relative pressure changes of PVK:TCNQ complex vs TCNQ content (pressure 3 kbar).

$$\sigma = \sigma_0 \exp - \left\{\frac{W_0 - \beta p^{1/2}}{kT}\right\}$$

where:
W_0—activation energy at p = 0
p—pressure
β—constant.

Such a pressure dependence of conductivity results both from the Pohl *et al.* [12] model of effective contacts, and from the Boon [13] model of random micro-fields.

According to Pohl *et al.* [12], change of the activation energy for conductivity with rising pressure is induced by an increase of the effective area of intermolecular contacts. Boon [13] has started from entirely different assumptions. He made use of the Down and Redfield [14] hypothesis regarding the existence of random local electrical micro-fields inside amorphous organic semi-conductors. The values of those local field intensities are proportional to the pressure. The local field causes decrease of the energy necessary to cause movement at the charge carriers by modification of coulombic interactions between the localized carrier and trapping centre. D.c. measurements seem to confirm the validity of Boon's model. At high field it is observed in PVK layers and in PVK:TCNQ complexes that the Pool–Frenkel effect occurs. Presumably both the high electric field intensity and the high pressure cause lowering of potential barriers confirming that the carriers are in localized states, which is the reason for the conductivity augmentation.

The superlinear behaviour of current–voltage characteristics, observed in PVK:TCNQ complex at high (Fig. 8) electrical field, may be explained by occurrence of the Poole–Frenkel (PF) or Richardson–Schottky (RS) effect. Both when the high intensity field induced conductivity is determined by field related decrease of the potential barriers with traps the carriers (PF volume effect) as well as when the conductivity is determined by the field related decrease of the barrier height in the contact interface (RS electrode effect), the current–voltage characteristics show similar variation described thus [15, 16];

$$J = J_0 \exp\{\beta E^{\frac{1}{2}}\}$$

where:
E—electric field intensity
β—constant.

Theoretical values of the coefficient β are given for PF model, by

$$\beta_{PF} = \left(\frac{e^3}{\pi\epsilon\epsilon_0}\right)^{1/2}$$

and for RS model by

$$\beta_{RS} = \left(\frac{e^3}{4\pi\epsilon\epsilon_0}\right)^{1/2}$$

Since the values of coefficient β differ only by a factor of 2($\beta_{PF} = 2\beta_{RS}$), it is difficult to decide on the basis of the value of the coefficient what is the actual conduction mechanism. Theoretically, the value of Pool–Frenkel's coefficient is $\beta_{PF} = 4.4 \cdot 10^{-5}$ eV $(m/V)^{1/2}$. The values of β coefficients calculated from the slope of $\log I = f(\sqrt{U})$, for PVK layers and for PVK:TCNQ complex, support the PF effect rather than the RS effect (Table 2). When considering the conduction mechanism, it should be noted that the conductivities cited are the quasi-steady values. Simmons and Taylor [17] considered that, in layers of an insulator with blocking electrodes, there are very long times of dielectric relaxation. In this connection, this process of electrical conductivity is a non-steady state process and is limited by the volume effect. Activation energy for non-steady state conductivity differs from that for steady conductivity. In the first case, it governs the value of potential energy barrier which confines the trapped carrier: in the other case, it is equal to the energy barrier height at the site of unsulator-electrode contact. In order to solve the question connected with the high field conduction mechanism, an additional experiment has been carried out based on conductivity measurements of the PVK:TCNQ (25:1) complex layers, the surfaces of which were enriched with TCNQ. These were made by vacuum sublimation of TCNQ and its deposition on complex layer surfaces or by depositing the same component in acetonitrile solution. Enrichment of the surface layer was intended to change the height of the potential barrier in the insulator-electrode contact sites. It is known [18] that one method for producing ohmic contacts is to use an excess of surface doping which causes a system of p, p^+ or n, n^+ to be formed. The author did not, however, state a distinct conductivity change nor the conductivity assymetry (rectifying effects) in the one-side enriched complex layers. This experiment seems to confirm that, in spite of potential barriers present between metallic electrodes and the complex surface, the electrical conductivity is mainly determined by the volume PF effect.

There is very little work published regarding the electrical conductivity of PVK:TCNQ complex [1, 2]. Taniguchi *et al.* [1] investigated electrical properties of moulded specimens of PVK:TCNQ complex obtained by complexing the components in chloroform. The authors measured electrical properties within the voltage range 20–2000 V, using moulded specimens having thickness of several millimeters and provided with electrodes made of silver paste. In the voltage range mentioned, the complex specimens exhibited ohmic current–voltage characteristic behaviour. PVK:TCNQ complex samples, for component molar ratios between 31:1 and 57:1, showed resistances from $1.4 \cdot 10^{14}\,\Omega \cdot$cm to $5 \cdot 10^{15}\,\Omega \cdot$cm at room temperature. These authors [1] did not find correlation between TCNQ content and sample resistance. Activation energy had values from 0.55 to 0.7 eV.

The present work involved investigation of moulded specimens of complex having the same TCNQ concentrations as those used by Taniguchi *et al.* [1] and showed almost the same activation energies, but much higher resistance ($> 10^{16}\,\Omega \cdot$cm) had been found. The resistance difference might be explained by the retention of solvent in samples obtained by Taniguchi *et al.* [1]. Okamoto *et al.* [19] found that PVK interacts easily with chloroform which exhibits weak acceptor properties. The measurements carried out by the present author [2] with samples of PVK:TCNQ complex obtained from chloroform–acetonitrile solution showed conductivity values similar to those by Taniguchi *et al.* [1].

CONCLUSIONS

The result of doping polyvinylcarbazole with tetracyanoquinodimethane is the formation of a charge transfer PVK:TCNQ complex. Electrical conductivity of the complex increases initially slowly with TCNQ content, and can be described by the relation:

$$\sigma = \alpha C^{\kappa}$$

where:
α and κ are constant; and
C is the molar ratio TCNQ:PVK.

TCNQ molecules distribute themselves mainly in structural defects of PVK. When all the available sites in the polymer matrix are occupied, the uncomplexed TCNQ molecules start to form semi-conductive tracks and this effect is associated with an abrupt conductivity rise. With increase of TCNQ concentration in the PVK:TCNQ complex, the activation energy of conductivity decreases and, when semi-conductive tracks are already formed in the polymer matrix, the activation energy assumes a value lower than that for pure TCNQ. This indicates some influence of CT interaction on the mechanism of charge carrier generation in the PVK:TCNQ complex.

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