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THE EFFECT OF SUPERMOLECULAR STRUCTURE ON SOME ELECTRIC PROPERTIES OF LAYERS OF POLY(*N*-VINYLCARBAZOLE)

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Abstract—Current–voltage characteristics were measured for sandwich samples of poly(*N*-vinylcarbazole) amorphous layers and layers with pronounced supermolecular structure, similar to the fibrillar structure. Analysis of the superlinear regions of the current–voltage dependences of 3–35 μm thick samples with fibrillar structure showed that the effects of space charge are important. Results obtained for amorphous layers agree with an earlier interpretation of the current–voltage curves based on the Poole–Frenkel effect.

Of the many papers published within the last decade and dealing with poly(*N*-vinylcarbazole) (PVCA) layers, almost all concern polymer obtained by conventional polymerization. The investigations were carried out with layers prepared from solution, without characterizing their physical structure. This fact may explain the considerable scatter of experimental results. However, papers have also been published (mainly by Griffiths *et al.* [1, 2]) which are entirely devoted to the formation and investigation of the supermolecular structure of PVCA. Among papers dealing with the effect of supermolecular structure on the physical properties of layers, the fundamental one is that of David *et al.* [3], where the effect of the orientation of PVCA layers on the intensity of fluorescence is examined, and that of Turski *et al.* [4], establishing the strong influence of crosslinking on the mobility of charge carriers. Okamoto, Kusabayshi and Mikawa [5] observed the strong increase of photocurrent in crystalline heat-treated PVCA samples. Similar correlation has been reported for the γ-ray induced dark current in polyethylene films [6]. Ieda, Kosaki and Shinohara [7] found that charge carriers created in polyethylene by irradiation are captured by trapping centres in crystalline regions but not in amorphous regions. Therefore, space charge effects could be more important in crystalline samples. This problem is the object of our interest.

From analysis of the current–voltage characteristics of sandwich samples of amorphous PVCA layers, Okamoto, Kusabayshi and Mikawa [5] concluded that the non-ohmic behaviour of the dark current cannot be attributed to phenomena connected with space charge. The non-ohmic current–voltage dependences were interpreted using the Poole–Frenkel theory [5]. Recently, the Poole–Frenkel effect for amorphous PVCA layers has been proved using the shift of maxima of thermostimulated currents due to the voltage applied to the sample [8]. The current–voltage characteristics of PVCA amorphous layers and those with supermolecular structure are reported in this paper.

EXPERIMENTAL

PVCA layers with a pronounced supermolecular structure were obtained by polymerization of solid *N*-vinylcarbazole monomer on an Al support. The polymerization was initiated by radicals formed in the glow discharge. The reaction conditions have been described earlier [9]. Scanning electron micrographs of these layers are shown in Figs 1–3. Figure 1 shows formations resembling fibrils and globular formations. For electric measurements, only the layers with well developed fibrillar structure were used (see the right-hand side of Fig. 1). The results of observing the layers with a microscope with crossed nicols (Fig. 4) suggest that the structure of the fibrils is consistent with a

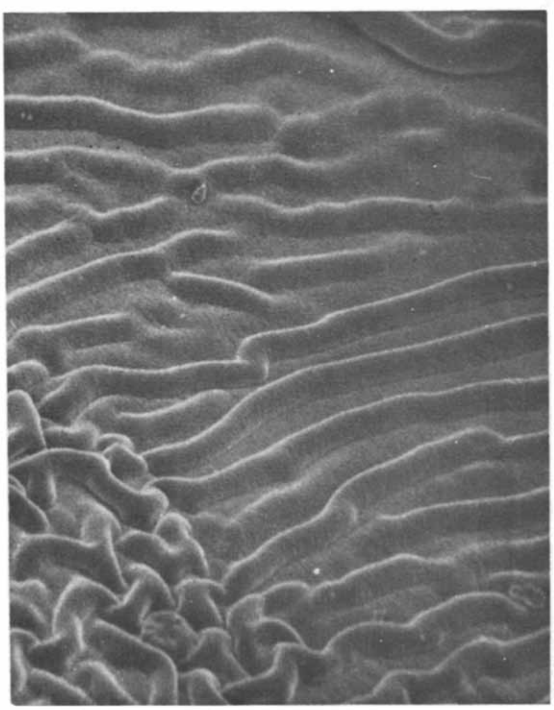

Fig. 1. Scanning electron micrograph of PVCA layer (magnified 300 ×).

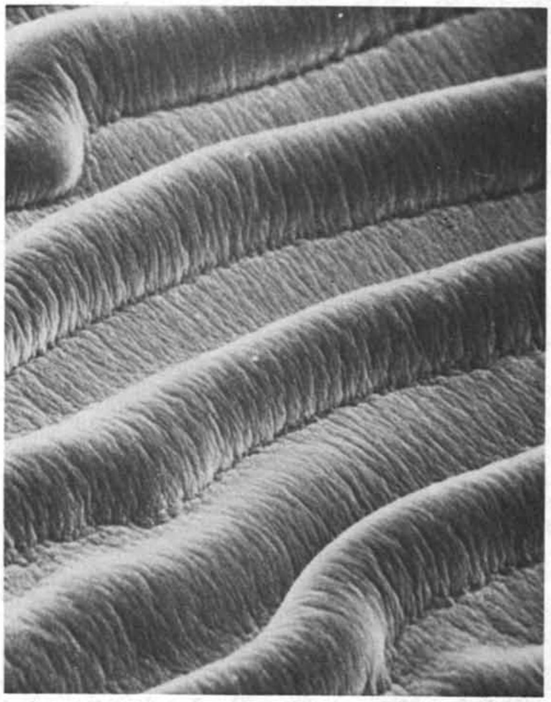

Fig. 2. Scanning electron micrograph of the PVCA layer (fragment of the surface in Fig. 1, magnified 1000 ×).

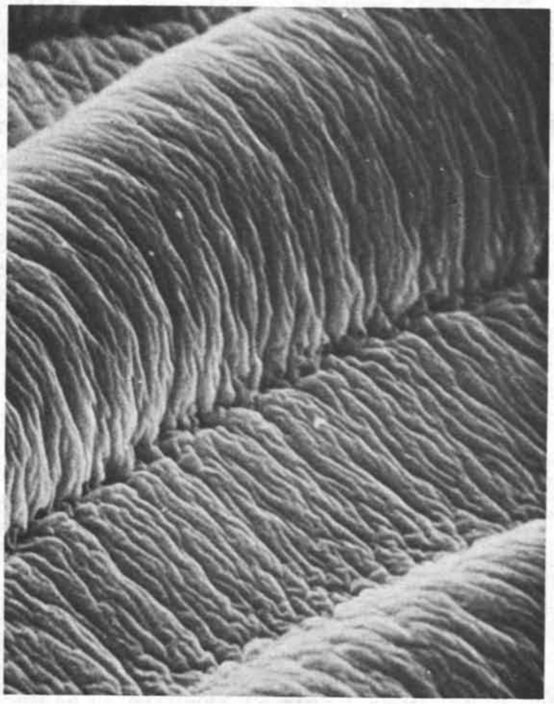

Fig. 3. Scanning electron micrograph of PVCA layer (magnified 3000 ×).

generally accepted model of on arrangement of macromolecular chains on fibrillar crystals [10] (a central fibril and a lamella growing perpendicularly to its axis).

Amorphous sandwich samples prepared by conventional radiation polymerization were obtained by coating an Al support with PVCA (mol. wt 7.4 × 10^5) in cyclohexanone–toluene solution. They were dried in vacuum at 390 K for 24 hr. The other electrode was made of Ag conducting paste.

The current was measured in a vacuum of 10^{-3} Pa by means of a Keithley 616 electrometer, with Keithley 240 A as the voltage supply.

RESULTS AND DISCUSSION

Results for amorphous PVCA samples prepared from solution agree with those reported earlier [5]. A typical current–voltage characteristic of such a sample is shown in Fig. 5. At low voltages, ohmic current is observed; for high voltages, the superlinear dependence of the type $j \sim V^n$, $n = f(V)$ is observed. Decreasing value of the coefficient n for voltages >65 V is due to limited ohmic behaviour of contact. A contact limited current is observed. The shape of the cur-

Fig. 4. Optical microphotograph of fibrillar structures observed for PVCA layers at crossed nicols (magnified 180 ×).

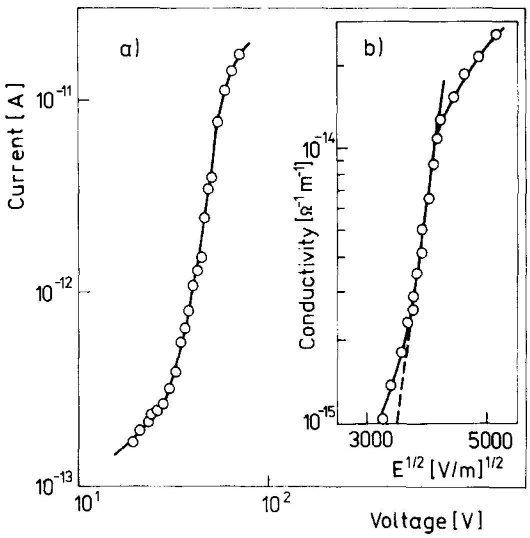

Fig. 5. Current–voltage characteristic of an amorphous PVCA layer, thickness D = 3 μm. (a) Current–voltage dependence; (b) dependence of specific conductivity σ on $E^{\frac{1}{2}}$ (in the dashed line part the ohmic conductivity component was subtracted).

rent–voltage dependence is virtually independent of change in the polarity of the electrodes; however, the absolute value of the current is lower for Al electrode substrate positivity biased. We suppose that a spatial variation of trap density across the film having higher concentration near Al electrode is responsible for this result. The course of the current–voltage dependence seems to be compatible with a model of insulator with Gaussian distribution of traps in energy [11, 12]. However, a plot of log σ vs $E^{\frac{1}{2}}$ (σ is the electric dark conductivity and E is the intensity of electric field) is sublinear for this case (seee theoretical plot Fig. 6b) while experimental results give linear dependence (see Fig. 5b). Therefore the dark conductivity of these samples at high fields may be described by the equation [5]:

$$\sigma = \sigma_0 \exp[\beta E^{\frac{1}{2}}/(kT)] \qquad (1)$$

where k is the Boltzmann constant, T is temperature of the sample. The experimentally determined value of β, 4.0×10^{-5} eV $(m/V)^{\frac{1}{2}}$, is in good agreement with the theoretical value of Poole–Frenkel coefficient $\beta = [e^3/\pi\epsilon\epsilon_0)]^{\frac{1}{2}} = 4.1 \times 10^{-5}$ eV $(m/V)^{\frac{1}{2}}$ (for $\epsilon = 3.0$ [13]) and with published experimental data [5].

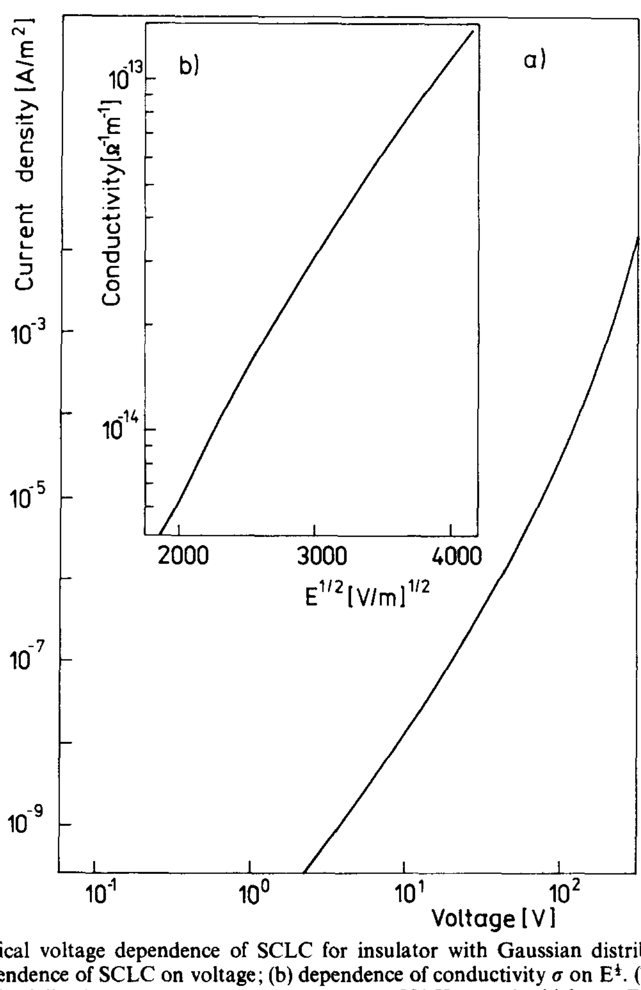

Fig. 6. Theoretical voltage dependence of SCLC for insulator with Gaussian distribution of traps in energy: (a) Dependence of SCLC on voltage; (b) dependence of conductivity σ on $E^{\frac{1}{2}}$. (Theoretical curves correspond to the following parameters: temperature T = 300 K, sample thickness D = 10^{-6} m, mobility of charge carriers $\mu = 10^{-11}$ m^2/Vsec, concentration of traps $N_t = 10^{23}$ m^{-3}, dielectric constant $\epsilon = 3.5$, effective density of states in the conduction band $N_c = 4 \times 10^{27}$ m^{-3}, trap depth (depth of distribution maxima of traps) $E_t = 0.4$ eV, half-width of the Gaussian trap distribution curve $\sigma = 0.16$ eV.)

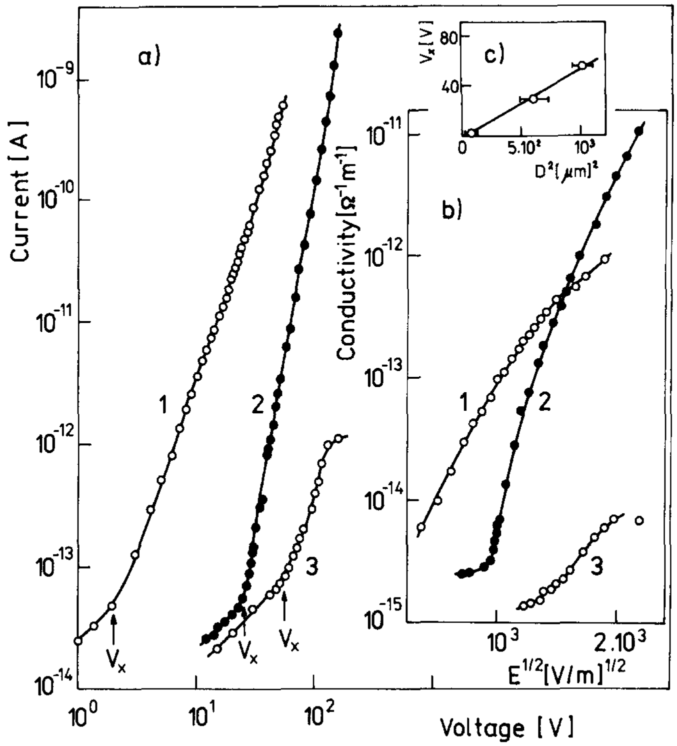

Fig. 7. Current–voltage characteristics of PVCA samples with ordered fibrillar structure, thickness (1) D = 8 μm, (2) D = 25 μm, (3) D = 33 μm. (a) Current–voltage dependence; (b) dependence of specific conductivity σ on $E^{\frac{1}{2}}$, (c) dependence of transition voltage V_x on D^2.

On the other hand, the current–voltage characteristics of samples with supermolecular structure similar to the fibrillar structure are of different character (Fig. 7). As has been shown earlier, ordered regions and their surroundings in the amorphous phase may act as charge carrier traps [14]. One may therefore expect that in layers with such a pronounced supermolecular structure (documented by Figs 1–4) effect of the space charge will be stronger. Figure 6 shows that, in samples of this type, the current–voltage slope in the superlinear part of the characteristic is steeper than in amorphous samples. Furthermore, the σ vs $E^{\frac{1}{2}}$ dependence is sublinear and the transition voltage V_x between ohmic and SCL region depends on the second power of the layer thickness (Fig. 6c). V_x/D^2 remains constant for samples of various thicknesses. This property of SCLC has been discussed by Rose [15], and Mark and Helfrich [16] and found in many materials, such as anthracene [16], *N,N′*-diphenyl-*p*-phenylenediamine [17], stilbene [18], polyethyleneterephthalate [19] etc. It has not been found in amorphous PVCA layers.

CONCLUSION

The conductivity of amorphous PVCA layers at high fields is controlled by the Poole–Frenkel effect. Effects of space charge cannot be neglected for samples with a developed supermolecular structure (of the fibrillar type in the case under investigation). Crystalline regions and their surroundings in amorphous phase act as traps and effects of charge injection become important. It is possible that both effects appear simultaneously.

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