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# Molecular Crystals and Liquid Crystals

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## Charge Flow Mechanism and Charge Effects in Polymer Film Structures

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The mechanisms of charge flow in organic polymer PEPC and 3,6-di-Br-PEPC films,  $V_2O_5$  xerogel and composite films of PEPC+N mas.%  $V_2O_5$  and 3,6-di-Br-PEPC+N mas.%  $V_2O_5$  are investigated. The conductivity of composite films is established to depend on the polymer nature,  $V_2O_5$  content, and presence of charge-transfer complexes between the polymers and vanadium oxides. In PEPC+N mas.%  $V_2O_5$  films the volume charge and the trap field effect play an important role as distinct from the case of bromated polymer composites.

**Keywords:** composite film; conductivity; differential slope; polymer, trap field effects; vanadium oxide (V)

#### INTRODUCTION

The investigations of polymer organic structures, especially nanocomposite polymer ones, are under a big attention of physicists and

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chemists today [1–5]. The polymers with various structures and properties can be applied in different fields of physics and technologies. So, the new organic light-emitting devices (OLEDs) of various structures on the various polymer bases with various dopants have good stability, simplicity of formation, wide possibility of color variety, etc. The new solar cells on the polymer base were designed as well. The conducting structures, various optical filters, reversible media for the optical registration of information, holograms [6], etc. have been constructed.

The purpose of this work is to investigate the electrical properties of films of polymers poly(N-epoxypropylcarbazole) (PEPC), 3,6-di-Br-poly(N-epoxypropylcarbazole) (3,6-di-Br-PEPC),  $V_2O_5$ , their composites and establish the mechanisms of charge flow in them by analyzing current-voltage characteristics (CVC) within the differential method.

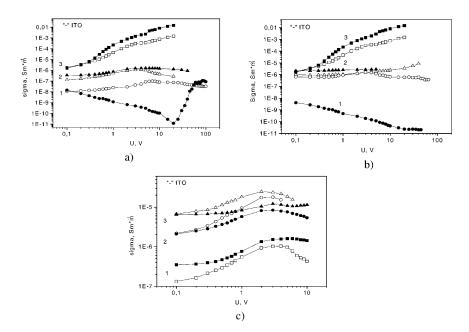
#### **EXPERIMENTAL**

The structures investigated were formed by casting from solutions on the ITO ( $In_2O_3$ : $SnO_2$ ) substrate. The sol of  $V_2O_5$  was prepared by the Bilts technique [7]. The concentration of  $V_2O_5$  in polymers was varied from 24.8 mas.% to 52.8 mas.%. An In electrode of  $2 \cdot 10^{-2} \, \mathrm{cm}^2$  in area was prepared by pressing. The CVC of the investigated structures were measured in the range  $0.1\text{--}100\,\mathrm{V}$  by an automated tester 14-TKS-100 under illumination and without illumination and processed by a PC. The CVC were treated by the differential method [8,9] as the differential slope  $\alpha = d \lg I/d \lg U$  versus applied bias. This allows determining the fine structure of CVC. The analysis of the mechanisms of charge flow sets an essential variety in the behavior of carriers and their influence on CVC.

#### **RESULTS AND DISCUSSION**

The conductivity of PEPC and 3,6-di-Br-PEPC films was very low, decreased with increase in the applied voltage without illumination, and depended on illumination strongly (Fig. 1). Under dark conditions, the carriers are captured by the traps of polymers. At a voltage of about 10 V, the traps are full and carriers are moving to the second contact. So, in the films on the PEPC base, the trap field effects are presented strongly.

The conductivity of 3,6-di-Br-PEPC films under illumination was up to 5 orders of magnitude more than that without illumination. The photosensitivity of 3,6-di-Br-PEPC was more than that of PEPC by about 2 orders of magnitude.



**FIGURE 1** The conductivity of films: a) PEPC (1),  $V_2O_5$  (3) and their composite PEPC + 33.82 mas.%  $V_2O_5$  (2); b) 3,6-di-Br-PEPC (1),  $V_2O_5$  (3) and their composite 3,6-di-Br-PEPC + 24.8 mas.%  $V_2O_5$  (2); c) composites PEPC + N mas.%  $V_2O_5$ , N=33.82 (1), 48.33 (2), 52.8 (3). \*Open symbols correspond to the film conductivity under illumination, dark ones – without illumination.

The conductivity of  $V_2O_5$  xerogel as distinct from that of the polymer was much higher, increased with the applied bias, and did not depend on illumination strongly. The ratio of the conductivity without illumination to the conductivity under illumination was up to 10.

The conductivity of  $V_2O_5$  xerogel consists of two components: conductivity inside  $V_2O_5$  fibers and conductivity between them. The first component is much higher than the second one, because the electrons can move through the crystals of  $V_2O_5$  fibers much fast than between them. This fact was confirmed by the results of the investigation of surface conductivity in various directions. The difference come to several times.

The conductivity of composite films is much more than that of polymer films by 4–5 orders of magnitude. It did not change with the applied voltage and practically did not depend on illumination. The polymers lose the high photosensitivity in composite films. Such a behaviour is caused by the compensation effect.

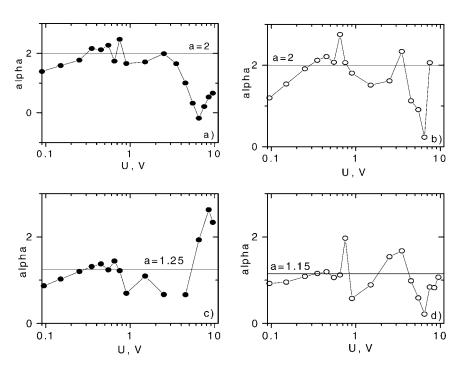
The conductivity of composite films was established to depend on the nature of polymers and the  $V_2O_5$  content in them. The presence

of charge-transfer complexes between oligomers and vanadium oxides of various levels of oxidation (III, IV, V) make easier the movement of charges in the film bulk.

The conductivity of the investigated films consists of the ionic component of a polymer or/and  $V_2O_5$ , thermogeneration of charge carriers in the film volume, and injection of carriers to the film from the contacts.

The conductivity increases up to 1 order of magnitude with increase in the  $V_2O_5$  content in composite films (Fig. 1c). The increase is caused by additional carriers from  $V_2O_5$  fibers and the significant interaction between them.

The differential treatment of CVC in the form of  $\alpha = d \lg J/d \lg U$  allowed us to discover the peculiarities of charge flow in composite films. All CVC have the regions of  $I \sim U^{\alpha}$ , where  $\alpha = (1-3)$  (Fig. 2).



**FIGURE 2** Differential slope of the curves of conductivity versus the voltage of composite films: PEPC + 33.82 mas.%  $V_2O_5$  without illumination (a); PEPC + 33.82 mas.%  $V_2O_5$  under illumination (b); 3,6-di-Br-PEPC + 24.8 mas.%  $V_2O_5$  under illumination (c).

TABLE 1 The Approximation of the Regions of CVC and Regimes of Injection and Recombination Processes in Investigated Composite structures

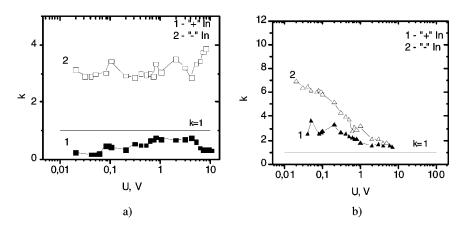
				Applied	Applied bias, V	
			Composite film of PEPC + 33.82 mas. % $V_2O_5$ , " -" In	Composite film of PEPC+33.82 as.% $V_2O_5$ , " -" In	Composite film of 3,6-di-Br-PEPC+24 mas.% V <sub>2</sub> O <sub>5</sub> , "-" In	Composite film of 3,6-di-Br-PEPC + 24.8 mas.% V <sub>2</sub> O <sub>5</sub> , " -" In
Differential slope $\alpha$	Regimes	Approximation	Without illumination	With illumination	Without illumination	With illumination
1.4 1.25			0.1	0.1		
1	contact limited current	$J(U) \sim J_0 \; U/L$			0.1	0.1
$1<\alpha<1.5,$ 1.5	low injection double injection in semiconductor, bi-molecular	$U(J) = [1-J/J_i]JL/\sigma$ $J(U) \sim J_0U^{3/2}/L^2$	$0.1-0.2 \\ 0.2$	$0.1-0.2 \\ 0.2$	$0.1-0.7 \\ 0.7$	0.1-4
63	current limited of volume charge or double injection in semiconductor, monomolecular recombination of carriers	$J(U)\sim J_0U^2$	0.35	0.3		
$\alpha > 2$ , max	traps field limited (monopolar injection) or recombination limited (daulyle injection)		0.35-1	0.3-0.8		
$0<\alpha<1$	regime of constant field		1–6		0.7–5	4–6.5
$\begin{array}{c} \alpha \\ \lambda \\ \downarrow 3 \end{array}$	contact limited current double injection in ideal dielectric, monomolecular recombination of carriers <sup>5</sup>	$J(U) \sim J_0 U/L$ $J(U) \sim J_0 U^3/L$	6–10	0.8–7	5-8	6.5-9

Usually the movement of carriers in amorphous polymers is the activation process [10]. The charge flow depends on the overlapping of wave functions of molecules, and the carriers move by hopping.

The regime of low injection was obtained in all composite films at low voltages. The differential slope  $\alpha$  of CVC was in the region  $1 < \alpha < 1.5$  (Table 1). Bromating of PEPC and illumination give no important influence on the charge flow regime.

In composite films on the PEPC base, it was possible to inject the carriers to the film bulk. The current at first was limited by the volume charge  $(\alpha=2)$ . The approximation can be described as  $J(U) \sim J_o U^2$ . Then, with increase in voltage, the current was limited by the field of traps and  $\alpha>2$  (max). At a higher voltage, the current was contact-limited and  $\alpha\to 1$ ; the approximation can be presented as  $J(U) \sim J_o U/L$ . The tendency to saturation observed at high electric fields points to the conversion from the regime of the current limited by the volume charge to the regime of the charge-limited injection from contacts [10].

We have obtained the low injection to composite films on the 3,6-di-Br-PEPC base at low voltages (1 <  $\alpha$  < 1.5). At higher voltages, the regime of the contact field between contacts ( $\alpha \rightarrow 0$ ) or contact limited current ( $\alpha \rightarrow 1$ ) was established. At a decrease in the  $V_2O_5$  content, the neutral carbazole's groups in composites don't combine to charge transfer complexes (CTC), and a fast decrease in the mobility of holes was observed. The increase of electron mobility with increase in the  $V_2O_5$  content in composites is accompanied also by an increase in



**FIGURE 3** Ratio of the current under illumination to the current without illumination k for composite films PEPC + 33.82 mas.%  $V_2O_5$  (a) and 3,6-di-Br-PEPC + 42.67 mas.%  $V_2O_5$  (b).

the concentration of  $V_2O_5$  molecules not combined to CTC [10]. So, the influence of CTC is to increase the concentration of free carriers but is not the facilitation of their movement.

The increase in the  $V_2O_5$  content in the PEPC composite decreases its photosensitivity. The higher photosensitivity was obtained on the film PEPC + 33.82 mas.%  $V_2O_5$  and the ratio of the current under illumination to the current without illumination k was up to 4 (Fig. 3a).

The increase in the  $V_2O_5$  content in the composite on the base of 3,6-di-Br-PEPC increases its photosensitivity. The ratio of the current under illumination to the current without illumination k was up to 7 at 42.67 mas.%  $V_2O_5$  (Fig. 3b).

#### **CONCLUSIONS**

Our consideration of the charge flow in the investigated polymer structures has shown the following.

The conductivity of the investigated composites is of the mixed type: electron (through  $V_2O_5$ ), hole (through polymers), and ionic (through both components) ones.

The composites of 3,6-di-Br-PEPC+N mas.%  $V_2O_5$  were much photosensitive than the composites of PEPC+N mas.%  $V_2O_5$  like 3,6-di-Br-PEPC toward PEPC. The contacts have the important role for the injection to composite films 3,6-di-Br-PEPC+24.8 mas.%  $V_2O_5$ .

The differential processing of CVC allowed us to obtain the fine structure of the current and recognize the small differences in characteristics with respect to voltage.

The injection of carriers to the composites on the PEPC base is much easy than to the composites on the base of bromated polymers. In the PEPC+N mas.%  $V_2O_5$  films, the volume charge and the trap field effects played an important role. We haven't obtained a similar situation on the bromated polymer composite because of the absence of many traps.

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