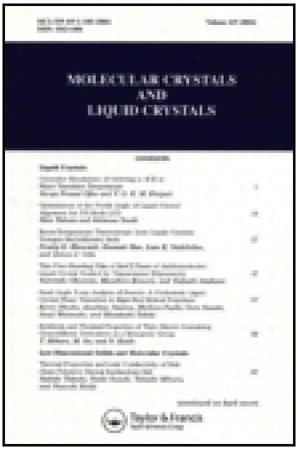

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Charge Carrier Photogeneration and Transport in Organic Photoconducting Polymer Nanocomposites Based on Polyimides

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Charge Carrier Photogeneration and Transport in Organic Photoconducting Polymer Nanocomposites Based on Polyimides

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On the base of photo- and thermostable polyimides (PI) and carbazolyl-containing polymers (CzCP) possessing predominantly p-photoconductivity and doped with perylenediimide derivative (PDID) as an acceptor with n-conductivity, the efficient bipolar polymer nanocomposites are developed. The efficient bipolar transport is obtained for microsegregated triple composites (PI-CzCP-PDID and others) in which there are p- and n-microregions with efficient charge photogeneration (quantum yield up to 0.6) at the extended microphase interface and high photoelectrical sensitivity (up to 400 m^2/J*) in the UV and visible ranges. The photovoltaic effect is investigated for sandwich cells with (Al, ITO) electrodes. The best parameters are found for triple composite films (0.7–1* μm *thickness).*

Keywords: bipolar transport; charge photogeneration; nanocomposites; perylenediimide; photoconduction; photoelectric sensitivity; photovoltaics; polyimides

High sensitive photoconducting polymer composites are of great interest for various applications: reprography, photovoltaics, and some optoelectronic devices and materials [1,2]. The efficient charge carrier photogeneration, bipolar transport, and light absorption in the UV and visible spectral ranges are the desirable features of these composites. Organic polymer composites developed as of the present moment and

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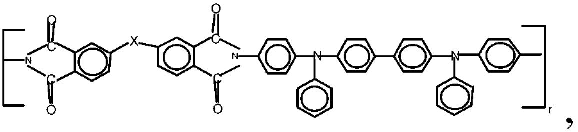
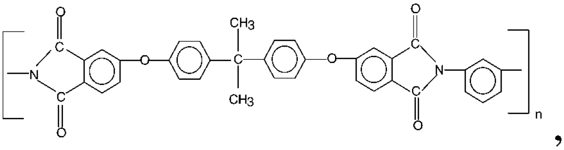
based on conjugated polymer MEH-PPV with nanoparticles of soluble fullerene derivative (PCBM) possess the high charge carrier photogeneration yield and collection efficiency in the visible range (almost 100%, AM1.5) [3]. But they have insufficient temporal and photochemical stability and need protection from O_2 and moisture. So, the more photo- and thermostable components are chosen for the development of photoconducting composites in the present work: polyimides [4] and carbazolyl-containing polymers as matrices, perylenediimide derivative (PDID) as a low molecular mass acceptor additive with *n*-conductivity and intense absorption at 430, 460, 490, and 530 nm. As was shown in [5], the high sensitivity for composite films based on *p*-photoconducting polyimides (PI) and PDID is caused by the formation of PDID molecular aggregates of a definite size (~3–4 nm).

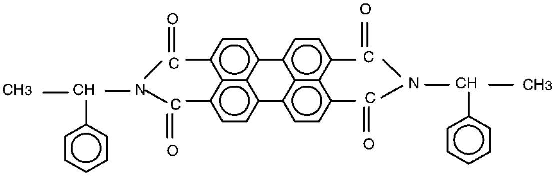
The following substances were used: *p*-photoconducting polyimides (PI) containing an active donor (double triphenylamine, $I_D = 6.8\,eV$) and an acceptor (diimide, $E_A = 1.12\,eV$ (PI-1) and 1.46 eV (PI-2, PI-3)) fragments [4], MM = 30000–60000,



where X = O (1), – (2), CO (3), nonphotoconducting polyetherimide (PEI) having no active donor fragments, MM = 20000,



poly-N-vinylcarbozole, MM = 30000 (PVCz-O) and MM = 170000 (HPVCz), poly-N-epoxy-propylcarbazole (PEPCz), MM = 740–1200, and soluble perylenediimide derivative (PDID)



Composite films were prepared by casting the combined tetrachlorethane solution onto preheated (100°C) conducting (ITO) glass substrates $2 \times 2\,cm^2$ with the next drying. It was found that the high solvent evaporation rate results in the formation of deep coloured homogeneous films containing PDID aggregates. Their size didn't exceed 100–300 nm. Aggregate formation was monitored by spectral and luminescent methods.

The photoelectrical sensitivity (PES) S_λ and charge carrier photogeneration quantum yield were measured by the convenient electrophotographic method. For the identification of carrier sign, the PES values corresponding to opposite-sign corona charges of the illuminated film surface (S_λ^+ and S_λ^-) were measured and compared with each other under inhomogeneous excitation by strongly absorbed light.

The relative composite film luminescence efficiency *f* was measured by means of a photomultiplier with glass filters, and luminescence spectra were recorded by a spectrofluorometer "Panorama".

Photovoltaic (PV) characteristics were measured in a sandwich cell with a transparent (ITO) or vacuum evaporated Al electrode.

It is found that the high PES value at a high PDID concentration C_a for PI-PDID composite films is due to the increase of the photogeneration quantum yield and efficient transport of holes exclusively: $S_\lambda^+ \gg S_\lambda^-$ (Fig. 1).

The partial electron transfer with weak charge-transfer complex (CTC) absorption in the ground state is observed for PI-PDID composite films in the 570–700 nm spectral region situated on the long-wave edge of the PDID absorption band. An electron transport network is formed in PEI-PDID composite films ($S_\lambda^- > S_\lambda^+$) in which there is no charge–transfer interaction in the ground state due to the high enough ionization potential of donor fragments ($I_D > 8.2\,\text{eV}$). These facts allow us to make conclusion that the electron mobility inside the conducting cluster of contacting acceptor particles (aggregates and molecules) is controlled by potential barriers (or trapping sites of dipole nature) between them which originate from the weak charge-transfer interaction in the ground state of acceptor particles with PI donor fragments of low ionization potential ($I_D = 6.8\,\text{eV}$).

The photoinduced electron transfer from PI donor fragments to excited PDID aggregates occurs in the PI-PDID composite films, which results in the observed strong PDID aggregate luminescence quenching in accordance with the Stern-Folmer's law. The evaluated quenching rate constant is close to the diffusion-controlled meaning, which indicates the availability of mobile excitations inside the PDID cluster. The photoinduced electron transfer leads to the photogeneration of free holes transporting through PI donor fragments and localized electrons.

More efficient electron transport is found for CzCP-PDID composite films: for $C_a > 20$–30% wt, the strong increase of S_λ^- is observed so

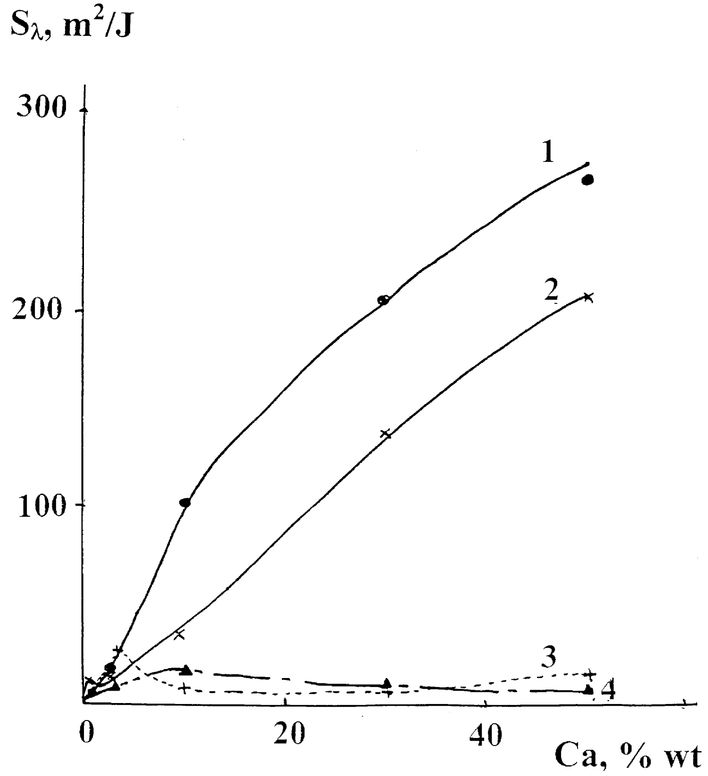


FIGURE 1 Photoelectrical sensitivity S_λ^+ (1, 2) and S_λ^- (3, 4) vs PDID concentration C_a for PI-PDID composite films: 1,3 – PI-1; 2,4 – PI-3.

that $S_\lambda^- \gg S_\lambda^+$ (Fig. 2). The S_λ^- (C_a) dependence has the threshold at $C_0 = 10$–20% wt and, for $C_a > C_0$, $S_\lambda^-(C_a)$ increases following the power law: $S_\lambda^- \sim (C_a - C_0)^p$ ($p = 1.8$–2.0). Within the frames of 3D percolation theory, this proves the electron conducting cluster formation consisting of PDID bounding particles, its conductivity being determined by the cluster correlation length.

The interaction of excited isolated (nonaggregated) PDID molecules with carbazolyl CzCP fragments and the luminescent exciplex formation are found. The long-wave shifted structureless exciplex luminescence band with a broad peak at 660–680 nm and the relative efficiency $f_{ex} = 0.02$–0.2 (as compared with the luminescence of PEI-rhodamine 6 G films) is observed. The luminescent exciplex formation indicates the absence of charge-transfer interaction in the ground state for CzCP-PDID composite films due to the higher ionization

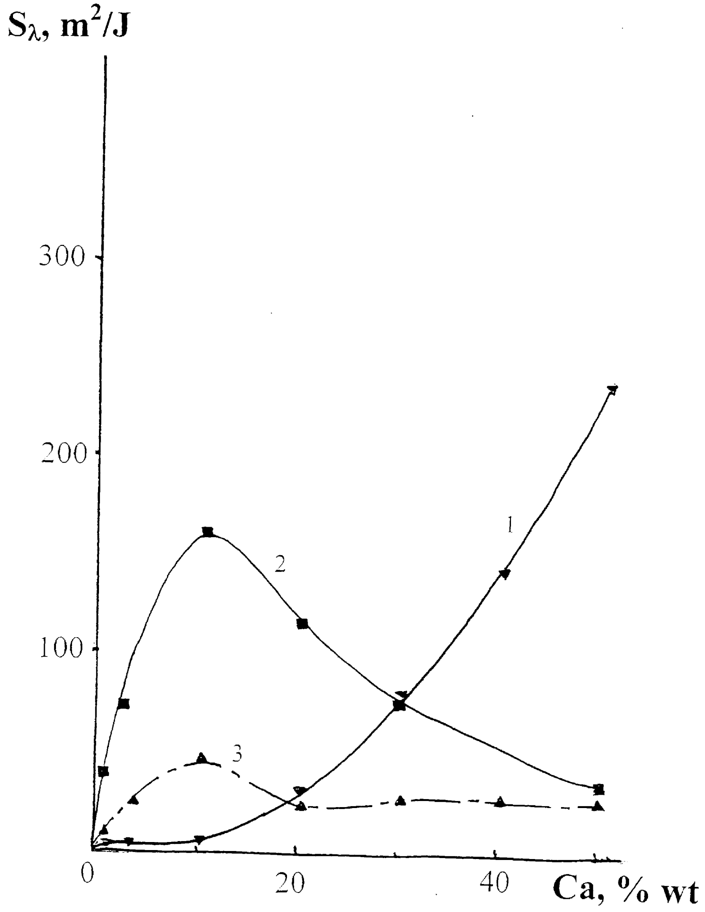


FIGURE 2 Photoelectrical sensitivity S_λ^- (1) and S_λ^+(2, 3) vs PDID concentration C_a for CzCP-PDID composite films: 1, 3 – PVCz-0 – PDID; 2 – HPVCz –PDID.

potential of carbazolyl fragments ($I_D = 7.4\,eV$) as compared with PI donor fragments. Therefore, just in contrast to PI-PDID composite, there are no potential barriers (trapping sites) between cluster particles in CzCP-PDID films, which results in a high electron mobility along the cluster and high S_λ^- (up to 300 m²/J in the PDID absorption band for $C_a = 50\%$ wt, Fig. 2) and the photogeneration quantum yield β^- (up to 0.6 for $E = 6 \times 10^5$ V/cm, Fig. 3). The latter is found to be field-dependent: $\beta^-(E) \sim E^n$ ($n = 1.5 \pm 0.1$), which evidences for the Coulomb bonded electron-hole pair (EHP) formation and its field-assisted thermal dissociation (Fig. 3). The observed difference in S_λ^- and S_λ^+ dependences on C_a (Fig. 2) indicates the difference in photogeneration and transport centers for holes and electrons. For holes transporting by hoppings between carbazolyl polymer fragments, the exciplex photogeneration mechanism takes place [6]. According to this mechanism, an EHP is formed as a result of the

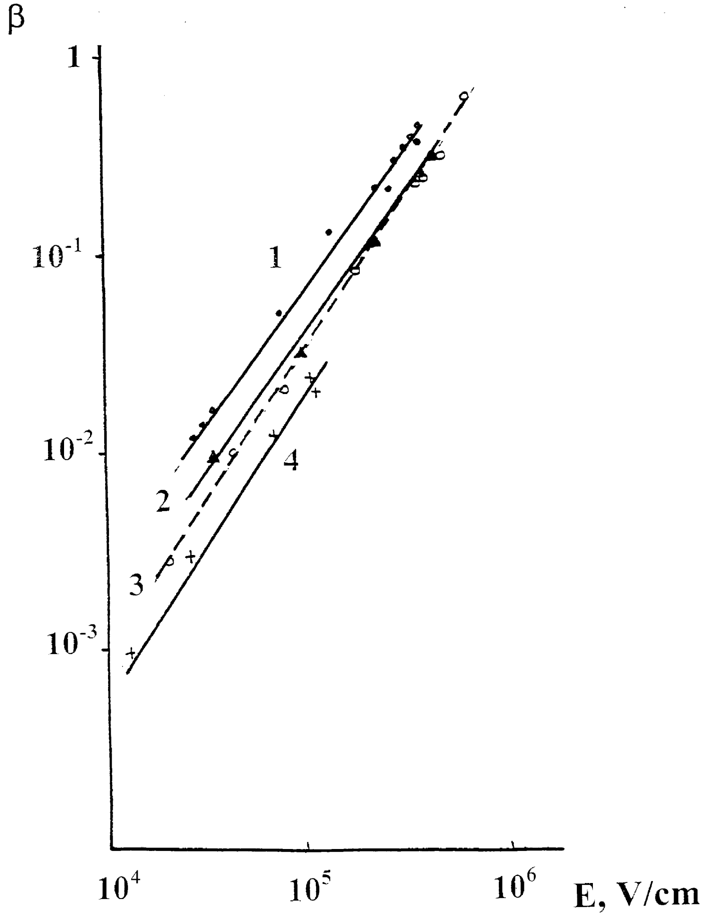


FIGURE 3 Charge carrier photogeneration quantum yield β vs electric field E for positive (1, 4) and negative (2, 3) corona charges of the illuminated surface for composite films: 1 – PVCz-0 – (PI-2)-PDID (polymer component ratio $Y = C_{PVCz}/C_{PVCz} + C_{PI\text{-}2} = 20\%$ wt); 2 – PVCz – 0 – (PI-2) – PDID ($Y = 90\%$ wt); 3 – PVCz – 0 – PDID; 4 – PI-2 – PDID; $C_a = 50\%$ wt; excitation: $\lambda = 547$ nm.

exciplex $(AD)^*$ interaction with some impurity Z characterized by enhanced electron affinity E_a (oxygen or an oxygen-containing acceptor moiety [6]):

$$\begin{array}{rll} A + h\nu \rightarrow & A^* + D \rightarrow & (AD)^* + Z \rightarrow EHP \rightarrow Z^- + h^+ \\ & \downarrow & \downarrow \\ & h\nu_{f1} & h\nu_{f2}\text{-exciplex luminescence} \end{array} \tag{1}$$

Scheme (1) results in the photogeneration of a mobile hole and a localized electron. Mobile electron photogeneration occurs also by scheme (1), but if Z is one of the PDID cluster aggregates. The higher E_a value for an aggregate as compared to an isolated molecule can be due to the enhanced electron polarization energy in PDID microcrystals as compared to polymer macromolecules. The number of these centers increases with C_a, while the number of hole generation centers involving an exciplex site surrounded by polymer donor transport fragments decreases, which explains qualitatively the data in Figure 2. It should be noted that the exciplex photogeneration mechanism is the indirect photoinduced electron transfer in polymer films when the free energy of the process, ΔG_e, is slightly positive: $0.1–0.2\,\text{eV} > \Delta G_e > 0$. Therefore, the formation of a PDID cluster of percolating particles at high C_a results in not only the appearance of an electron transport network, but of photogeneration centers as well.

The sandwich cells with (Al, ITO) electrodes based on PEPCz-PDID composite films of thickness $d = 0.7–1.0\,\mu m$ exhibit the photovoltaic effect owing to the metal-polymer interface.

On the base of *p*-(PI-PDID) and *n*-(PEI-PDID or CzCP-PDID) conducting composites, the microsegregated triple PI- PEI-PDID and PI-CzCP-PDID composites with balanced bipolar transport and enhanced charge carrier photogeneration are developed in which the PI-PDID microphase displays the hole conductivity and the CzCP-PDID (PEI-PDID) microphase does the electron one. The investigation of PES for triple composite films with varying polymer component weight ratio Y (Fig. 4) allows us to find out that there is a positive microphase interaction: $S_\lambda{}^+$ and $S_\lambda{}^-$ for triple composite films are higher than those for corresponding double PI-PDID and CzCP-PDID (or PEI-PDID) composite films (see Fig. 4 for $Y = 0$ and $Y = 100\%$, respectively). This fact evidences for the additional charge carrier photogeneration on the microphase interface. (PVCz-0)-(PI-3)-PDID triple composite films demonstrate the highest PES ($S_\lambda^+ = 350–400\,m^2/J$, $Y = 10–20\%$, $\lambda = 540\,nm$) and photogeneration quantum yield ($\beta = 0.4$ for $E = 3.5 \times 10^5\,V/cm$, Fig. 3) as well as balanced bipolar transport for $Y_m = 80\%$ (Fig. 4).

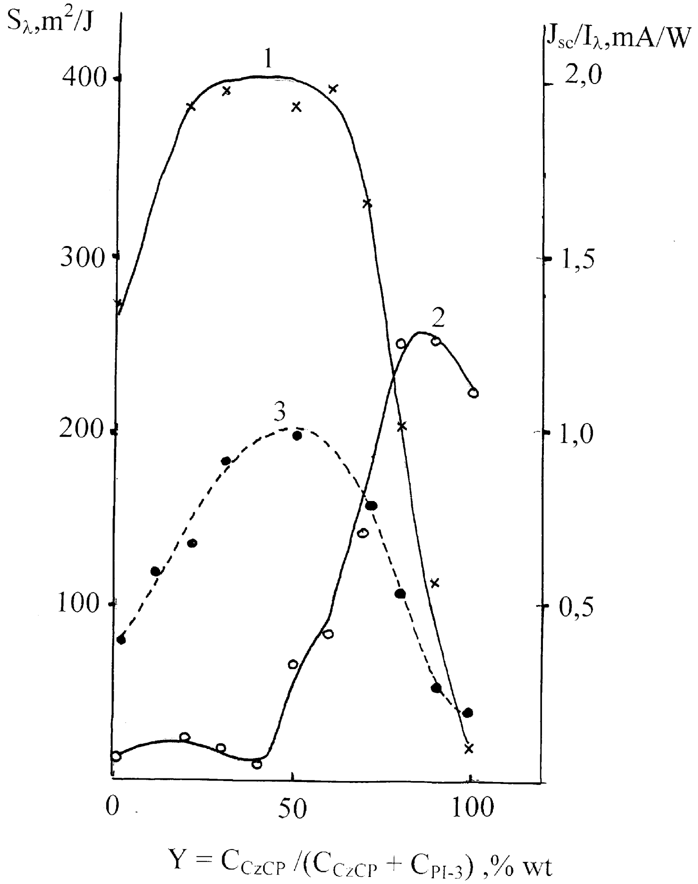


FIGURE 4 Photoelectric sensitivity S_λ^+(1), S_λ^- (2) and short circuit photocurrent density per incident light intensity J_{sc}/I_λ for PV cells (Al, ITO electrodes) (3) vs polymer component weight ratio $Y = C_{CzCP}/ C_{CzCP} + C_{PI}$ for triple composite films: 1, 2 – PVCz-0 -(PI-3) – PDID ; 3 – PEPCz-(PI-2) – PDID; $C_a = 50\%$ wt; excitation: $\lambda = 547$ nm.

The improvement of a film quality and enhancement of both the photogeneration quantum yield and carrier bipolar transport result in the improvement of PV characteristics of sandwich cells based on triple composite films of thickness $d = 0.7$–$1.0\,\mu$m: open circuit voltage $U_{oc} = 1.55$ V (higher than the electrode work function difference), short-circuit photocurrent density related to the incident light intensity $J_{sc}/I_\lambda = 2.4$ mA/W ($I_\lambda = 100\,\mu$W/cm^2), and filling factor FF = 0.31. It is found that, for these PV cells, the approximately equal

J_{sc} values are observed under excitation both through transparent ITO and semitransparent Al (of course, taking into account its transparency) electrodes, which proves the essential contribution of bulk photogeneration on the *p-n* microphase interface in addition to that on the metal-polymer interface.

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