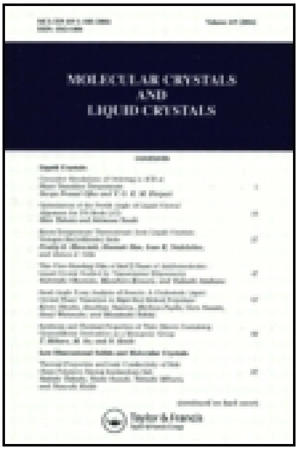

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Influence of Ionic Forms of Polymethine Dyes on the Photoconductivity of Doped Films of Poly-N-Epoxypropylcarbazole

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The features of photoconductivity of the films of poly-N-epoxypropylcarbazole doped with cationic, squarylium and merocyanine dyes are investigated. Under temperature growth starting from room the photoconductivity of the films with cationic and squarylium dyes increases more strongly as compared to the similar films with merocyanine. It was explained by a destruction of structural traps close to electrically charged fragments of dyes. In contrast to the films of the first two types, the photoconductivity of the films with merocyanine dye depends sublinearly on incident light intensity due to an effective bimolecular charges recombination.

Keywords: photoconductivity; photogeneration; recombination

INTRODUCTION

Polymethine dyes (PD) are used as sensitizers of photoconductivity and electroluminescence in photoconductive polymers due to the capacity of effective transformation of light energy. Besides, these ones have intensive bands of absorption and luminescence within the wide spectral range [1,2]. This class of dyes also can be used for photothermoplastic holograms recording [3] because the large values of photoconductivity were obtained for widely applicable recording mediums based on poly-N-epoxypropylcarbazole (PEPC). However, considerable increase of a photosensitivity of such recording mediums by means of increase of concentration of ionic or intraionic PD in PEPC has appeared inconvenient due to growth of the films electroconductivity. The comparative study of the photoconductivity of PEPC films doped with ionic, intraionic PD based on indoline is carried out in the present work aimed at clarification of a role of traps appearing in PEPC doped with the different ionic forms of dyes.

SAMPLES AND EXPERIMENTAL METHODS

Cationic (HIDC), squarylium (HISD) and merocyanine (HIM) dyes (Fig. 1) are derived from the same heterocycle 1,3,3-trimethine-3H-indoline, through which one there is an electron exchange between carbazole fragment of PEPC and PD during the elementary acts of a hole photogeneration and recombination in the films PEPC+Nmas.%PD. The compounds HIDC and HISD are characterized by charged boundary structures both in ground and in exited states, namely the HIDC exists in the monocationic form and HISD - in the form of a bipolar ion.

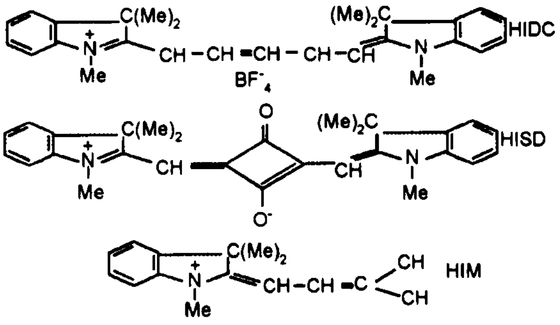

FIGURE 1 Structural formulas of the dye molecules.

The samples of «sandwich» structure (Al-polymer film-SnO$_2$) with polymer film PEPC+Nmas.% PD were used.The dye concentration N was changed from 1 10^{-1} until 5 mas.%. The thickness of the dried films was L=0,5-5 μm. The photocurrent density (j_{PH}) in a photoresistor mode was measured in the samples of sandwich-structure during their irradiation from the side of SnO$_2$ electrode with light with intensity I and wavelength λ=410-700 nm from the range of PD absorption.

RESULTS OF EXPERIMENTS

The photocurrent increases in the samples Al-PEPC+Nmas.%PD-SnO$_2$

upon E and N growth. Graphics of the dependencies $j_{PH}(E)$ are linear in terms lgj_{PH} from $E^{1/2}$. Tangents of incline angle of these graphics are the same for all investigated samples. It allows to suppose a possibility of the following analytic presentation of the dependency $j_{PH}(E)$ in the investigated films: $j_{PH}(E) \sim \exp(-(W_{0ph} - \beta E^{1/2}))(T^{-1} - T_0^{-1})/k$. Such kind of expression usually is used for the description of charge carriers photogeneration in PEPC from the photogeneration centers [3]. Here W_{0ph} is the activation energy of photogeneration, which is equal to the energy of Coulomb attraction between a hole and electron in the photogenerated electron-hole pair (EHP), k is the Boltzmann constant, T_0 is the characteristic temperature making up 490±20 K for PEPC based films. The values of β coefficient were calculated from the graphics of the dependencies $j_{PH}(E)$ in terms lgj_{PH} from $E^{1/2}$. Obtained results $(4.3\pm0.3)\,10^{-5}$ eV $(V/m)^{-1/2}$ are close to the theoretical value of Pool-Frenkel constant [3,4].

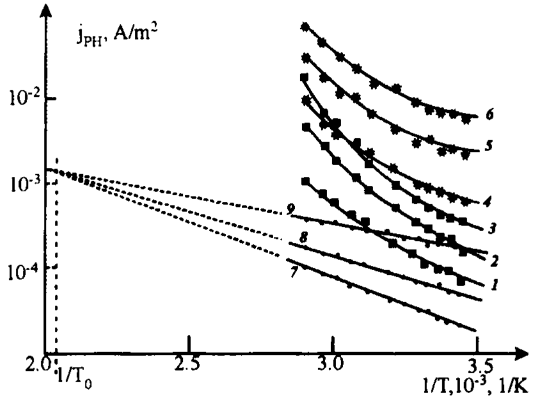

FIGURE 2 The dependencies of lgj_{PH} on 1/T for the samples Al-PEPC+1mas.%HIDC-SnO_2 (1-3), Al-PEPC+1mas.%HISD-SnO_2 (4-6) and Al-PEPC+1mas.%HIM-SnO_2 (7-9) for для E=3 10^7 V/m (1,4,7), 5 10^7 V/m (2, 5, 8), 8 10^7 V/m (3, 6, 9) measured during the samples illumination with light with wavelengths 690 nm, 650 nm and 446 nm respectively.

The temperature dependencies of j_{PH} for different E are plotted in Fig.2. These graphics are non-linear in the Arenius terms for the samples HIDC and HISD. Their non-linearity rises upon E growth. The dependencies of lgj_{PH} on 1/T are linear, tangents of their incline angles decrease with E growth. These linear graphics being extrapolated until the region of high temperatures intersect near T_0=490±20 K. The values of activation energy (W_a) of photocurrent were calculated using the tangents of incline angles of the graphics of dependencies $\lg j_{PH}$ on 1/T. Growth of external electric field strength E involves a decrease of these ones. The dependencies $W_a(E)$ are linear in terms W_a from $E^{1/2}$. A part of this graphic extrapolated until E=0 intersects the ordinate axis at the point W_{0ph}=0.49±0.3 eV.

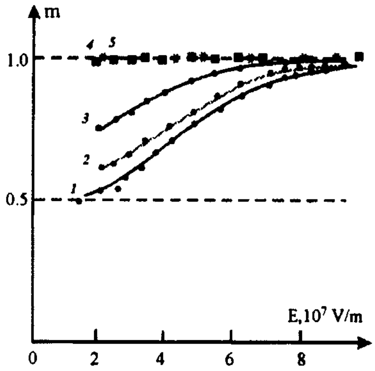

FIGURE 3 The dependencies of exponent m of lux-ampere characteristics on the external electric field strength in the samples Al-PEPC+1mas.%HIM-SnO_2 (1), Al-PEPC+0.5mas.%HIM-SnO_2 (2), Al-PEPC+0.1mas.%HIM-SnO_2 (3) Al-PEPC+1mas.%HIDC-SnO_2 (4), and Al-PEPC+1mas.%HISD-SnO_2 (5) measured during the samples illumination with light with wavelengths 446 nm, 690 nm and 650 nm respectively.

For the samples HIDC, HISD and HIM not only the temperature dependencies of photocurrent are different, but also the dependencies of temperatures intersect near T_0=490±20 K. The values of activation energy (W_a) of photocurrent were calculated using the tangents of incline angles of the graphics of dependencies $\lg j_{PH}$ on 1/T. Growth of external electric field strength E involves a decrease of these ones. The dependencies $W_a(E)$ are linear in terms W_a from $E^{1/2}$. Tangents of their incline angles make up (4.3±0.3) 10^{-5} eV $(V/m)^{-1/2}$. This value is close to the Pool-Frenkel constant. A part of this graphic extrapolated until E=0 intersects the ordinate axis at the point W_{0ph}=0.49±0.3 eV.

Connected EHP appears during the first stage of photogeneration after a light quantum absorption by the dye molecule. EHP consists of a hole, to which one there corresponds cation-radical (Cz^+) of the carbazole fragment (Cz) of PEPC, and residual electron appearing in the dye molecule after the hole going off. Non-excited molecules of the investigated PD can be presented by following simplified forms: $(D\text{-}D^{+}...An^{-})$ – for HIDC, $(D\text{-}A\text{-}A^{-}\text{-}D^{+})$ – for HISD and (D-A) – for HIM. Such presentation allows to describe the process of EHP formation in the PEPC films with HICD, HIDS and HIM by the reactions with electron transition:

$$Cz + (D\text{-}D^{+}...An^{-}) \xrightarrow{h\nu} Cz + (D^{+}\text{-}D...An^{-}) - Cz^{+} + (D\text{-}D...An^{-}) \quad (1)$$

$$Cz + (D\text{-}A\text{-}A^{-}\text{-}D^{+}) \xrightarrow{h\nu} Cz + (D^{+}\text{-}A^{-}\text{-}A\text{-}D) - Cz^{+} + (D\text{-}A^{\cdot}\text{-}A\text{-}D) \quad (2)$$

$$Cz + (D\text{-}A) \xrightarrow{h\nu} Cz + (D^{\cdot}\text{-}A^{\cdot}) - Cz^{+} + (D\text{-}A^{\cdot}) \quad (3)$$

It should be pointed out that the hole Cz^{+} photogeneration happens as a result of valence electron transition from the carbazole fragment of PEPC into the fragment D^{+} with its radical formation denoted as $PD^{\cdot}$ for the schemes (1-3).

During the second stage of the photogeneration the hole either recombines with the electron within the dye molecule, where it appeared (geminal recombination), or moves away from the electron through transitions between neighbor Cz (EHP dissociation). A relaxation of the electrostatic coupling between the hole and localized in $PD^{\cdot}$ electron is a result of EHP dissociation. During the charges recombination valence electron passes from a negatively charged form of the dye $PD^{\cdot}$ into Cz^{+} and excited form of dye PD arises. After a relaxation of the excited state with energy $h\nu_r$ emission this molecule can absorb a light quantum again and participate in EHP photogeneration.

A probability of the EHP dissociation rises under E and T. However, as it was shown earlier [4], traps for holes appear in PEPC films with ionic dyes near electrically charged PD centers due to conformational changes in polymer chains connected with electrostatic coupling between Cz and PD fragments. As result, photogenerated holes can be captured by these traps. The holes liberation and a destruction of the traps become stronger under temperature growth. This phenomenon shows itself in a non-exponential character of the dependencies $j_{PH}(T)$ (Fig.2) as well as in "splash" of thermogeneration and electric conductivity in the PEPC films with HIDC and HISD during their pulse heating.

Now, let us analyze the Fig.3. A non-linearity of the lux-ampere characteristics of the samples with HIM is an evidence of essential difference of the photoconductivity process in the PEPC films with this PD as compared to the films with HIDC and HISD. It would be natural to expect that a volume recombination of non-equilibrium charge carriers has considerable influence on the photoconductivity. It follows from the fact that the exponent m is less than unity and the dependency of j_{PH} on L is inversely proportional. It could be pointed out additionally that this conclusion agrees with observed m increase under E growth or under decrease of PD molecules concentration when velocity of free charges drift increases or concentration of the recombination centers decreases.

It was supposed, that in contrast to the PEPC films with HIDC and HISD there is no traps near the charged fragments of dye molecules in the PEPC films with HIM. However, the traps in the PEPC films with HIM are formed by its dipoles similarly to PEPC with compounds with intramolecular charge transfer (CICT)[5]. Features of these traps and their influence on the photoconductivity of the doped PEPC films were investigated earlier [5] for various CICT based on fluorene. It was ascertained, that free holes could be detained and captured within the film volume due to electrodipole coupling between CICT molecules. A depth of the traps depends on a value of the dipole momentum and CICT concentration. Therefore, it could be supposed, that (D-A) molecules can interact with the free holes as well for the HIM case. If during drift the hole appears within the active region of this coupling and there is the recombination center solid by electron in the same region, then the hole could recombine and stop a participation in the photoconductivity. An efficiency of the bimolecular recombination of charge carriers is higher in the PEPC films with HIM as compared to the PEPC films with HIDC. This fact is caused by a necessity of the hole Cz^{+} recombination with anion-radical $(D^{\cdot}\text{-}A^{\cdot})$ in the first case and electron transition from an electrically neutral radical $D^{\cdot}\text{-}D$ into cation-radical Cz^{+} is additionally required for the recombination in the second case. Therefore the Coulomb attraction between the hole and recombination center additionally contributes to the recombination of merocyanine HIM, whereas in a case HIDC such attrac-tion of the hole is directed to An-.

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