Photoelectric peculiarities of electric photographic and holographic recording media with ionic dyes

N.A.Davidenko, A.A.Ishchenko*

T. Shevchenko University, 64, vul. Volodymyrska, 01033 Kyiv, Ukraine
*Institute of Organic Chemistry, NAS of Ukraine, 5, vul. Murmanska, 04094 Kyiv, Ukraine

Abstract. The features of formation and relaxation of metastable connected states of cation-radical of carbazole and negatively charged fragment of dye molecule were investigated in the films of poly-N-epoxypropilcarbazole doped with intraionic and cation dyes. In films with intraionic dye these states collapse at irradiation with light from the range of dye absorption, and in films with cation dye such states do not collapse under light action. Observed peculiarities are caused by structure features of the dyes.

**Keywords:** amorphous molecular semiconductors, electron-hole pairs, photoconductivity, ionic dyes.

Homological series of cation polymethyne dyes [1] with different anions and of organic dying cations are considered as charge photogeneration centers in amorphous molecular semiconductors (AMS) based on carbazole-containing polymers. A comparative analysis of these AMS as to efficiency of photo- and thermogeneration of charge carriers in dependency on a chemical and energetic structure of dyes was carried out. The photoconductivity of the investigated AMS within the visible and IR parts of the light spectrum was found to be proportional to a ionization potential of the dye molecule and inversely proportional to a length of polymethyne chain of chromophores conjugating. Electric conductivity of the investigated AMS in strong electric fields is a sum of three components [2]. The first component of the electric conductivity is peculiar to the PEPC films without dopants. It corresponds to holes current and is determined by thermal field generation of holes from traps occupied in the result of holes thermogeneration from uncontrolled impurity centers. The second component is also peculiar to the films without dopants and corresponds to an ionic current. The third component of the electric conductivity is determined by the thermal generation of the charge carriers from the dye molecules. For the ionic dyes an activation energy of the third component of the electric conductivity depends on the temperature. It is determined by the depth of the traps of thermogenerated holes forming in PEPC near the ionic dye molecules [3]. It was shown that the magnitude of the investigated AMS films electric conductivity upon the dye change is mainly determined by a dye and polymer capability to a formation of the traps for the holes. The last circumstance is an evidence that the electric conductivity of the AMS films with dyes within the temperature range of electric photographic and holographic

media utilization is determined by the thermofield generation of the captured holes, but not by the ionic conductivity.

The films of poly-N-epoxypropilcarbazole (PEPC) cation dyes have rather high photoconductivity [4]. It is more preferable to use intracation dyes in electrophoto-graphic and holographic media due to their photogeneration ability both as to positive charges (holes), and the negative ones (electrons). The purpose of the present work was to find out features of optical and photoelectric properties intrinsic for the PEPC films with intraionic dyes in comparison with the ionic ones.

Intraionic dye HISD
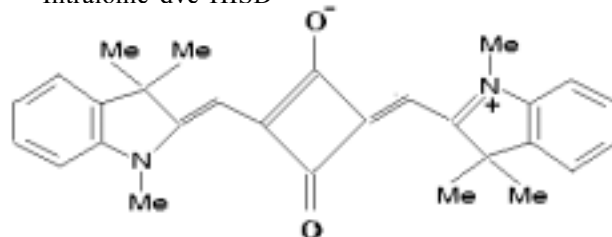
and ionic dye HIDC were used
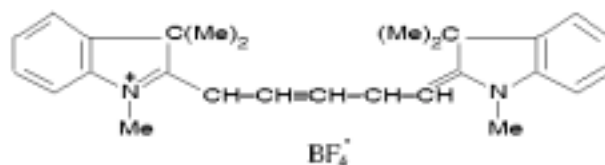
The excitation of a molecule of the first dye is accompanied by redistribution of electronic density from the negatively charged acceptor center (A^-) to the positively charged donor chromophore (D^+). The excitation of a mol-

ecule of the second dye is accompanied by redistribution of electronic density from the less charged donor chromophore (D) to positively charged donor chromophore (D$^+$), but without electronic transfer from inorganic anion (An$^-$) to cation.

The samples were prepared either as structures with a free surface: a quartz substrate-polymeric film, or as «sandwich» structures: Al-(polymeric film)-SnO$_2$. The films PEPC+Nmas.%HISD, PEPC+Nmas.%HIDC for $N = 1\cdot10^{-2}$–5 mas.% were used. The photocurrent (j_{PH}) was measured in the samples of «sandwich» structure in a mode of photoresistance during illumination of the sample from the side of SnO$_2$ electrode with wavelength $\lambda_1 = 380$ nm (intensity I_1) or $\lambda_2 = 546, 633, 680$ and 711 nm (intensity I_2). Light intensities were $I_1 = 0.1$-0.5 W/m^2 and $I_2 = 0.2$-20 W/m^2. Chosen electric filed strength was $E = 2\cdot10^7$-$3\cdot10^8$ V/m. In the samples with free surface optical spectra of absorption coefficient (k) and photoluminescence intensity (I_{PL}) were measured within the range of wavelengths $\lambda = 350$-1200 nm. An optical densities K_1 and K_2 of the films for λ_1 и λ_2, respectively, was also determined. The values ΔK_1 and ΔK_2 being deviations of the films optical density from stationary value were calculated. Changes of I_{PL}, K_1 and K_2 as a result of pulse (0.1 s) heating the polymeric films up to temperatures +(85–90) ^{o}C with the rate about 10^6 K/s were measured.

For creation of nonequilibrium concentration (n) of the seized on a trap charges the samples were irradiated with light of λ_1 wavelength during time interval t_1. Chosen light wavelength is near the edges of PEPC absorption and is not absorbed by dye. Thus, there is a photo-generation and capture of mobile holes on traps created by carbazole nuclei (Cz) PEPC. Captured hole there corresponds to a cation-radical (Cz$^-$) with optical absorption in the visible part of the spectrum. Accumulation of n was registered as reduction of K_1 and increase of K_2, and relaxation of n could be observed due to restoration of K_1 and K_2 during the time interval t_2 after the irradiation.

In the samples Al-PEPC+Nmas.%HISD-SnO$_2$, after the beginning of irradiation with light, the photocurrent at first increases up to quasi stationary value, and after switching off the light decreases down to zero. But if after the irradiation with λ_1 light in time interval t_2 the sample is subjected to irradiation with λ_2 light, then on forward front of a current pulse the maximum is observed. Then photocur-rent decreases down to the quasi stationary value as it is schematically presented by diagrams in the insert of Fig.1. Using an amplitude of this maximum it is possible to estimate concentration n of charges formed after the irradiation with λ_1 light and that taking part in photo-conductivity that is stimulated by light with wavelength λ_2. The greatest influence of a preliminary irradiation with λ_1 light is observed at $\lambda_2 = 633$ nm, and it decreases up to zero when using $\lambda_2 = 711$ nm. It could be easily seen from the diagrams of dependencies $n(t_1)$ that it is possible to approximate these dependencies by idle time exponential function with time constant 3.1±0.2 s for $I_2 = 20$ W/m^2. The value n decreases with t_2 growth, is independent on E in a time interval $t_1 + t_2$, but decreases down to zero, if during the time interval t_2 even at $E = 0$ the sample was

illuminated with wavelength λ_2. The dependencies $n(t_2)$ can not be represented by the idle exponentially falling down function, but graphics of these ones could be approximated by linear dependencies in terms $n(\ln t_2)$. Tangent of a slope angle in these plots increases with N (see Fig. 1). Dependencies of ΔK_1 and ΔK_2 on $\ln t_2$ correlate with each other as well as with dependency $n(t_2)$. The value n decreases with an activation energy 0.17 ± 0.03 eV under T growth within the temperature range of 293-370 K.

The magnitude of I_{PL} decreases during the samples illumination. But if in time or after the irradiation the polymeric film is quickly heated up, the photoluminescence intensity is restored. Simultaneously with I_{PL} restoration during the pulse heating we could observ restoration of K_1 and K_2.

In the samples Al-PEPC+Nmas.%HIDC-SnO$_2$ being previously illuminated with λ_1 light the photocurrent maximum on forward front of kinetics is not observed upon switching on the light with wavelength λ_2. The dependencies ΔK_1 and ΔK_2 on t_1 could be presented by exponential function with time constant 25±5 s, but the absolute values ΔK_1 and ΔK_2 are an order of magnitude less than that in the samples with the films PEPC+Nmas.%HISD. The plots of ΔK_1 and ΔK_2 versus t_2 could be approximated by linear dependencies in terms ΔK_1 and ΔK_2 from $\ln t_2$ (see curve 4 in Fig.1). The pulse heating of the polymeric films is accompanied by I_{PL} reduction, and the K_1 and K_2 restoration was not revealed.

The results obtained testify that during the irradiation with wavelength λ_1 accumulation of nonequilibrium particles absorbing light in visible and near IR-range occurs. In the films PEPC+Nmas.%HISD the rate of accumulation and relaxation of such particles is greater than in the films PEPC+Nmas.%HIDC. Synchronously with the change of concentration of such particles the change of photoluminescence intensity of dyes happens. The distinction of the first kind of films from the second ones shows itself in different behavior: in the first ones, after an irradiation with wavelength λ_1 and following pulse heating I_{PL} restores, and in the second ones it decreases. Besides, the excitation of HISD molecules results in acceleration of relaxation of these parti-
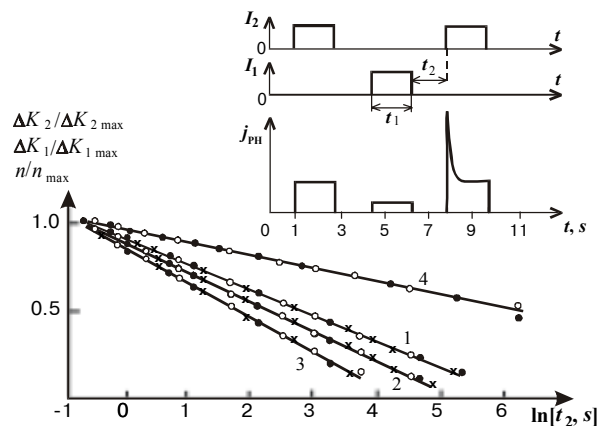

Fig.1. Dependencies of ΔK_1 (dotes), ΔK_2 (squares) and n (crosses) on $\ln t_2$ for $t_1 = 1$ c, $T = 293$ K, $\lambda_1 = 380$ nm, $\lambda_2 = 633$ nm in the samples with the films PEPC+Nmas.%HISD (1-3) and PEPC+1mas.%HIDC (4) for $N = 0.01$ (1), 0.1 (2), 5 (3).

cles concentration, and the excitation of HIDC molecules does not render such action.

The results of measurements of the dependencies $n(t_2)$ specify that after irradiation with wavelength λ_1 some connected states appear in films. These ones consisting of positive and negatively charged particles, concentration reduction of which could be considered within the framework of recombination model of charge pairs with final spatial distribution on distances between these charges [5,6]. We propose the most adequate model based on the assumption of holes capture by Cz^+ near to charged fragments of dye molecules.

For intraionic dye this model can be presented by reactions:

1. After absorption in PEPC of light quantum $h\nu_1$ and dissociation of molecular exciton, the hole capture becomes possible near the negatively charged fragment of the dye, therefore the connected state (Cz^+A^-) appears.
2. The relaxation of the state (Cz^+A^-) has an activation character and is accompanied by the recombination of Cz^+ with electron staying after exciton dissociation.
3. The increase of Cz^+ concentration causes growth of the films absorption within the range of these cation-radicals absorption and extinguishing of dye luminescence.
4. The absorption of light quantum with energy $h\nu_2$ by the dye molecule results in redistribution of electronic density in a molecule from A^- to D^+, that in turn is the reason of breaking connection between the charges in the state (Cz^+A^-).
5. After liberation of Cz^+ charge, it becomes possible either its recombination , or creation of free hole (p^+) participating in the induced photoconductivity.

For PEPC films with ionic dye HIDC the primary processes of Cz^+ creation is the same, but the connected state is formed with a dye anion An^-. At absorption of light quantum hn_2 there is a redistribution of electronic density inside dye cation of, but in such way that the connection between Cz^+ and An^- does not broken. Therefore, the excitation of dye molecules with photon energy hn_2 is not accompanied by liberation of a charge from the state (Cz^+An^-) and induced photoconductivity is absent.

The proposed model of the nonequilibrium charge carriers capture mechanism when considering PEPC films with dyes possesses also practical interest because it demonstrates opportunities of photoconductivity increase in such films for their application as recording media.

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