

Internal Photoeffect in Films of Poly-N-Epoxypropylcarbazole with High Concentration of Anion Polymethine Dye

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Growth of concentration of the anion polymethine dye in the films of poly-N-epoxypropylcarbazole involves increase of quenching of photoluminescence in external electric field as well as appearance of long-wave band of the photoluminescence and photoconductivity within visible spectral range. It was ascertained that associates of ionic pairs of the dye arise when the concentration increases. Anomalous for semiconductor materials kinetics of the photocurrent growth and relaxation was observed in the films of these composites: time of the photocurrent growth is much less than the time of its relaxation after the light is switched off. Effect of memory of preliminary illumination with light was observed in the films.

Keywords: Photoconducting Polymers, Dyes, Spectra of Adsorption and Fluorescence, Associates, Kinetics of Photoconductivity, Recombination Centers.

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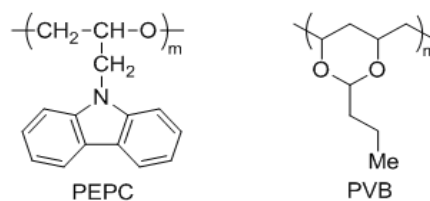
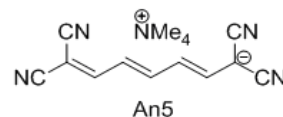
1. INTRODUCTION

The films of polymeric composites (FPC) doped with organic dyes are commonly used in informatic recording and electroluminescent media as well as in photoelectric converters of solar energy [1 – 5]. In FPC monomeric dye molecules play role of centers of light absorption and photogeneration of non-equilibrium charge carriers. Considerable progress is reached in control of photophysical and electrophysical properties of FPC by adjustment of chemical structure of the dye and polymer. But these properties also depend on geometric size of FPC components [6-10]. Such dependency is caused by transformation of energetic structure of dopants which are in polymeric matrix. Thus, there is scientific and practical interest on development of new photoactive media based on FPC where inner photoeffect is realized due to size effects in dopants. The polymethine dyes [11] are the most interesting amongst organic dyes for application for light energy conversion. The work is aimed in investigation of photoelectric and spectral-luminescent properties of the films of polymeric composites with high concentration of organic dye.

2. THE SAMPLES AND EXPERIMENTAL TECHNIQUE

Poly-N-epoxypropylcarbazole (PEPC) and anionic dye An5 were used as FPC components. For comparison the same dye was used in FPC based on non-photoconducting polyvinylbutyrate (PVB).

The samples were prepared as the structures with free surface [glass substrate – electroconducting layer SnO₂:In₂O₃ – FPC] and sandwich-structures [glass substrate – electroconducting layer SnO₂:In₂O₃ – FPC – Ag]. Concentration (N) of An5 was 0.5 – 10 mas. %, FPC thickness was 1 – 1.5 μm.



The technique of measurement of optical density (D), photoluminescence intensity (I_L) within the range λ = 400 – 900 nm, density (j_{PH}) of photocurrent is described in [2, 12]. Green laser with maximum of irradiation at λ₁ = 532 nm and He-Ne laser with λ₂ = 633 nm were used for excitation of photoluminescence and for investigation of photoconducting properties of FPC. The values D and I_L were measured before and after application of external electric field with strength E = 108 V/m. Parameters δD_E = (D_E – D₀)/D₀ and δI_{LE} = (I_{LE} – I_{L0})/I_{L0}, where D₀ and I_{L0} are the values D and I_L before application of the field (E), D_E and I_{LE} are the values D and I_L after application of the field, were calculated using experimental results. Light intensity (I) at λ₁ and λ₂ was changed by neutral light filters within the range 1 – 50 W/m². The value of electric voltage (U) which was applied to electric contacts in the samples of sandwich-structure was changed within the range 1 – 200 V. For measurements of fluorescence spectra and for excitation of fluorescence in FPC spectral fluorometer Solar CM2203 was used. All measurements were done at room temperature which corresponds to conditions of FPC practical applications.

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Quantum-chemical calculations of molecules N-methylcarbazole (as a model monomer of PEPC) and anion An5 were done by non-empirical method DFT/B3LYP in 6-31G(d,p) basis using program package PC Gamess/Firefly [13].

3. EXPERIMENTAL RESULTS AND DISCUSSION

In the samples of sandwich-structure based on PEPC with $N < 5$ mas. % An5 photocurrent was not observed. In the samples with $N > 5$ mas. % An5 photocurrent was observed both for λ_1 and for λ_2 . In the samples with $N = 10$ mas. % An5 for $U = 100$ V, $I = 50$ W/m² the value j_{PH} is 10^{-3} A/m² under illumination with light with λ_1 and $2 \cdot 10^{-4}$ A/m² under illumination with light with λ_2 . In the similar structures with PVB photocurrent was not observed. Dependencies j_{PH} on U can be described by analytical function $j_{PH} \sim U^{m_{PH}}$, which is usually used for analysis of currents in semiconductor materials. Power exponent $m_{PH} \approx 2.1$ for λ_1 and 1.4 for λ_2 . The value j_{PH} does not depend on polarity U . The dependencies of j_{PH} on I with λ_1 and λ_2 are close to linear. The last fact means that effect of photoconductivity which is not caused by two-quantum processes was discovered.

Discovered in the work photoeffect is unusual. It can not be explained by formation of electron-hole pairs (EHP) caused by electron transfer from carbazole fragment PEPC to excited molecule An5 due to difference HOMO energy (HOMO energy of the polymer which was calculated for N-methylcarbazole is -5.3280 eV and it is -2.2205 eV for An5 anion).

Additional investigations were carried out for determination of reasons of appearance of inner photoeffect upon growth of An5 concentration. Influence of external electric field on spectra of absorption and photoluminescence was observed in all investigated samples based on PEPC (Fig. 1).

When electric field is switched on the values D_0 and I_{LO} reach the values D_E and I_{LE} during time interval ~ 1 s, which is close to time of electric charge of geometric capacity of the sample. After electric field switching off all changes of spectra stop. Peculiarities of spectra changes depend on dye concentration. In FPC with $N < 5$ mas. % when electric field is switched off within short wavelength range absorption intensity increases ($\delta D_E > 0$), intensity of photoluminescence decreases ($\delta I_{LE} < 0$). Within the long wavelength range the effects are opposite ($\delta D_E < 0$, $\delta I_{LE} > 0$) (Fig. 1, c). Earlier [2, 14] the similar changes were observed in photoconducting and non-photoconducting FPC with low concentration of symmetric polymethine dyes. These changes were explained by intramolecular redistribution of electronic density under influence of external electric field. But we have ascertained that upon N growth the dependency $\delta D_E(\lambda)$ does not change whereas the dependency $\delta I_{LE}(\lambda)$ essentially transforms. The last fact reveals itself in quenching of luminescence upon application of electric field ($\delta I_{LE} < 0$) in FPC with $N > 5$ mas. %. This quenching increases upon N growth (Fig. 1, d). That corresponds to the model considerations described in [1, 2]. Luminescence quenching of organic dyes in photoconducting FPC under electric field influence is ex-

plained by formation and dissociation of EHP, namely by decrease of probability of radiative recombination of EHP.

One can suppose, that increase of An5 concentration in PEPC involves appearance of aggregates of dye molecules. But attributes of aggregation of An5 anion in FPC absorption spectra are absent. N growth involves appearance of new bands in absorption spectrum but shape of the curve changes weakly. Universal for organic dye outline of long wavelength absorption band preserves its original appearance [11]. Characteristic attributes of association are absent in photoluminescence spectrum for $N = 0.5$ mas. % as well. Photoluminescence band does not depend on light wavelength of excitation and it is inversely similar to absorption band (Fig. 1, a). More sensitive to dye concentration are spectra of excitation of fluorescence. It easily can be seen from Fig.1,a that even for $N = 0.5$ mas. % strong widening of the band is observed in the spectrum of excitation as compare to the same one in absorption spectrum. Moreover, in the first case the band possesses two maximums.

Growth of An5 concentration effects in appearance of new long wavelength band in the fluorescence spectrum (Fig. 1, b). The fluorescence spectrum of FPC becomes dependent on light wavelength of excitation. The maximal respective intensity of the long wavelength band of fluorescence was observed upon excitation in short wavelength edge of absorption band (400 – 440 nm). Increase of light wavelength of excitation results in growth of intensity of short wavelength band of fluorescence. The similar tendencies upon growth of An5 concentration were observed in FPC based on PVB.

Described effects in the spectra of excitation and fluorescence of FPC are evidence of inhomogeneous widening of absorption band due to superposition of the bands from different dye forms. In concentrated polymeric solutions those forms are dye monomers and their associates. The polymethine dyes are able to create associates of “sandwich” structure [11]. In low polar media “sandwiches” appear due to fixation of chromophores from both ends by electrostatic forces of attraction of contact ionic pairs. Upon formation of associates of “sandwich” structure the maximal splitting of the level of the first excited state (S_1) of the monomers with higher (S_1^h) and lower (S_1^l) energy is reached [11]. Bathochrome shift of An5 luminescence band is evidence of energy reduction. This reduction involves convergence of HOMO energies of dye and PEPC. That can effect in possibility of electron transfer from PEPC to dye aggregate. Conditions for appearance of non-equilibrium charge carriers arise.

Appearance of non-equilibrium charge carriers can happen due to photostimulated electron transfer from anion (An^-) to cation (Ct^+) in contact ionic pairs. Upon dye excitation anion turn into S_1 state of $(An^-)^1$. Presence of non-paired electrons creates conditions for higher reaction ability as compare to the state S_0 . Possibility of such mechanism is confirmed by quantum-chemical calculations. Upon formation of neutral radical ($An5\cdot$) HOMO energy decreases until -6.0138 eV. This value is lower than HOMO of N-methylcarbazole

(-5.3280 eV). Thus, the radical $An5^{\bullet}$ can play role of effective acceptor of electron from carbazole fragment of PEPC. It can create positive charge carrier – hole.

Effect of FPC photoconductivity on the light wavelength λ_2 also is unusual. The matter is, that λ_2 is outside the absorption band of An5 monomer. Therefore, irradiation of He-Ne laser can not involve inner photoeffect in FPC. Unusual is also kinetics of the photocur-

rent $j_{PH}(t)$ (Fig. 2, c and Fig. 2, d) with slow growth of photocurrent and quite quick its relaxation when illumination is ceased. The kinetics of photocurrent is the same for different values U and I .

Addition of conductivity current j_{PH1} and j_{PH2} for stationary dark conductivity current is similar to kinetics of j_{PH} change.

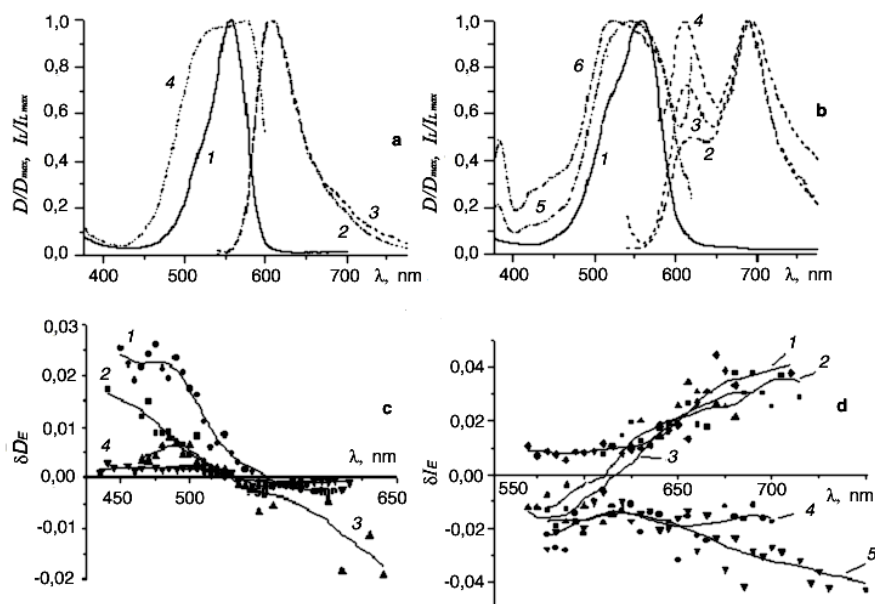


Fig. 1 – Normalized absorption spectrum (1), fluorescence spectra (2, 3) and fluorescence excitation (4) in FPC with 0.5 mas. % An5 for $\lambda_{irr} = 400$ nm (2), 520 nm (3), 640 nm (4) (a); normalized spectrum of absorption (1), spectra of fluorescence (2, 3, 4) and excitation of fluorescence (5, 6) in FPC with 10 mas. % An5 for $\lambda_{irr} = 440$ nm (2), 520 nm (3), 560 nm (4) and light wavelength of fluorescence registration 650 nm (5), 750 nm (6) (b); ΔD_E dependencies on λ in FPC based on PEPC with $N = 1.0$ (1), 2 (2), 5 (3), 10 (4) mas. % An5 (c) and dependencies of ΔD_E on λ in FPC based on PEPC with $N = 0.5$ (1), 1 (2), 2 (3), 5 (4), 10 (5) mas. % An5 (d)

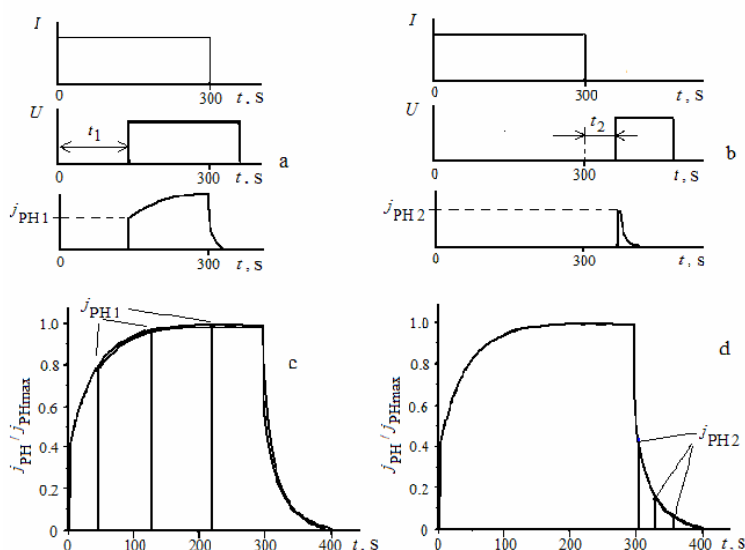


Fig. 2 – Diagrams explaining the technique of measurements of j_{PH1} depending on time of delay t_1 of electric field application after start of illumination of the samples with light (a), Diagrams explaining method of change of j_{PH2} depending on time interval t_2 of delay of application of electric field after illumination is ceased (b), kinetics of photocurrents j_{PH} and j_{PH1} for $t_1 = 45, 120, 215$ s (c) and kinetics of photocurrents j_{PH} and j_{PH2} for $t_2 = 5, 45, 60$ s (d)

4. CONCLUSIONS

Investigations of spectral-luminescent, electroconducting and photoconducting properties of the films of polymeric composites with different concentrations of anion polymethine dye are carried out. Influence of external electric field on spectra of absorption and photoluminescence, electric and photoconductivity of PEPC films doped with anion dye is studied. Widening of absorption and photoluminescence bands, quenching of

photoluminescence intensity, arising of photoconductivity effect within visible range of spectrum were observed upon growth of dye concentration. These effects can be explained by formation of associates of dye molecules. The reason of photoconductivity can be attributed to photogeneration and transport of charge carriers in the associates.

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