

Photoelectric and Spectral Properties of Composite Films Based on GCBE-Oligomer with Different Concentrations of Polymethine Dyes

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Thin film of composites based on N-epoxypropylcarbazole and n-butylglycidyl ether co-oligomer (GCBE) sensitized by various concentrations of cationic polymethine dyes with different polymethine chain length have been prepared. Their photophysical, electrical, and spectral properties have been investigated. All studied composite films have been shown to exhibited photoconductivity effect. In film composites with high concentration of the dye photovoltaic effect have been detected. The diffusion nature of this effect and its features correlation with electronic properties of PCFs components has been established.

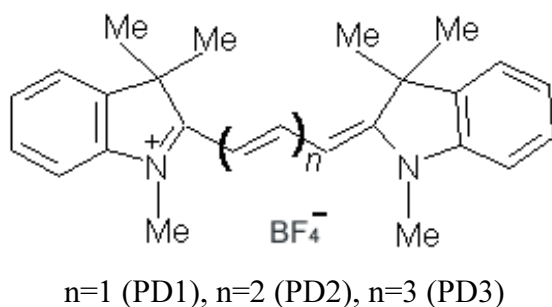
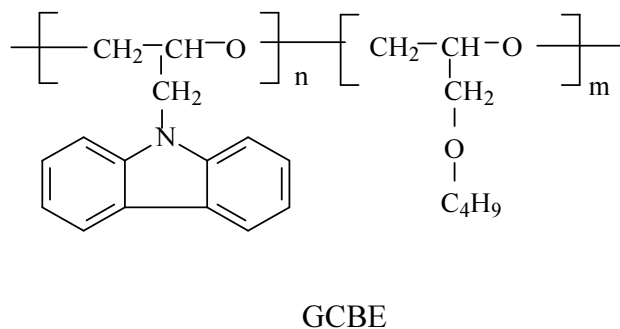
Introduction

Dye-doped polymer composite films (PCFs) are widely used in information recording, electroluminescent media, and photovoltaic solar energy converters [1-3]. Dye molecules in the composite act as the centers of light absorption and photogeneration of nonequilibrium charge carriers. To date, the significant progress has been achieved in the control of photophysical and electrical properties of the PCFs via chemical modification of dyes and polymers used [1,2,4]. It was found recently that these properties may also depend on the geometric size of the PCF components [5]. Such dependences are often associated with the changing of dopant energy structure in a polymeric binder. Therefore, it is of scientific and practical interest to develop

new photoactive PCFs, the internal photoelectric effect in which is realized due to the size/nanosize effects of dopant molecules. Among the organic dyes, the polymethine dyes (PDs) are of the greatest interest as light energy converters, since they have record values of extinction coefficient and absorb light in a very broad spectral range [1,2]. The aim of the present work was to study the spectral and photoelectric properties features of the PCFs based on the GCBE-oligomer with p-type conductivity doped with high concentration of cationic polymethine dyes with different polymethine chain length.

Results and discussion

Thin film of oligomeric composites based on GCBE-oligomer sensitized by various concentration of cationic polymethine dyes with different polymethine chain length (PD1 - PD3) have been prepared.



The films of pure GCBE are transparent in the visible and near infrared ranges, and they have no photoconductivity and photovoltaic properties in this area. In GCBE films which contains dye additives, the bands of absorption (Figure 1) are determined by excitation and relaxation of the excited states of dye molecules [2,4]. In the visible spectral range, PCFs with low concentration (1 wt%) of PD1-PD3 exhibit one absorption band. This band is attributed to the long-wavelength $\pi-\pi^*$ transition polarized along the long axis of the dye chromophore. The bathochromic shift of the $\pi-\pi^*$ absorption band in a number of PCFs with the dyes PD1-PD2-PD3 is caused by the fact that with a lengthening of

polymethine chain in this sequence of dyes energies frontier orbitals HOMO and LUMO approach [1-2].

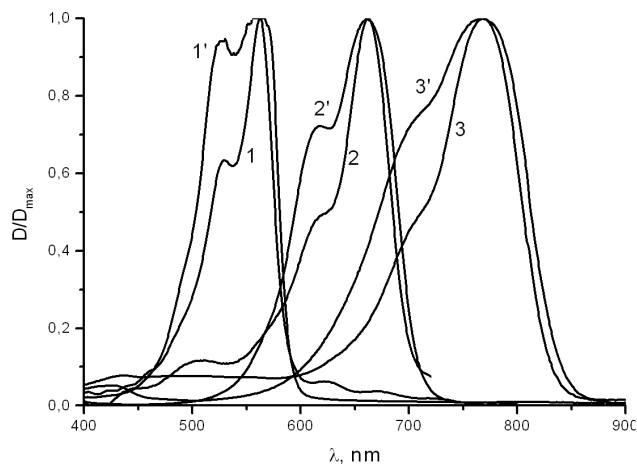


Figure 1. Normalized absorption spectra of the investigated PCFs based on GCBE doped with 1 wt% of PD1 (1), 10 wt% of PD1 (1'), 1 wt% of PD2 (2), 10 wt% of PD2 (2'), 1 wt% of PD3 (3), and 10 wt% of PD3 (3') respectively.

In the PCFs with high concentration of dyes (10 wt%) band of dye absorption showed the significant widening and band shape deviation from universal for organic dyes contour. Such changes of the absorption band width and shape are caused by the appearance of the strong intermolecular interaction between dye molecules due to the dye-dye distance decrease with the dye concentration in PCF increasing.

All studied composite films have been shown to exhibited photoconductivity effect under the photoexcitation in the dye absorption range. Character of the photoconductivity of investigated PCFs [1,4] allows us to present the process of charge carriers photogeneration in

these systems according to [1] (with mechanism which involves the stages of the dye photoexcitation, electron transfer from carbazolyl fragment to the excited dye molecule with geminal electron-hole pair (EHP) formation, and its dissociation (charges separation) with free nonequilibrium charge carriers formation).

In PCFs with high concentration of the dyes photovoltaic effect (at the excitation with light from the dye absorption range) has been detected. This effect is not observed in polymeric films with low concentration (1 %wt) of investigated cationic dyes PD1-3. The maximal absolute value of photovoltage and characteristic times of photovoltaic effect growth and dark relaxation decrease in a series of PCF-samples doped with dyes PD1, PD2, and PD3 respectively (Figure 2).

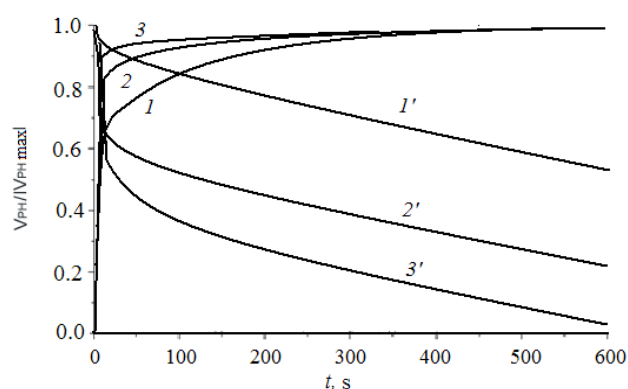


Figure 2. Normalized kinetic dependencies of the surface photovoltage growth (1-3) and relaxation (1'-3') in the samples with a free surface PCFs based on GCBE doped with 10 wt% of PD1 (1,1'), 10 wt% of PD2 (2,2'), 10 wt% of PD3 (3,3') – respectively. $I = 50 \text{ W/m}^2$.

It is suggested that this phenomenon is caused by the Dember effect, i.e. discovered effect has diffusion nature. This assumption was based on fact that observed effect appears in the range of strong light-absorption of high concentration dye-doped PCFs.

It is well known that the Dember (or photodiffusion) effect can be observed in semiconductors when the electrons and holes have different mobilities and the light-illumination of the sample leads to a non-uniform distribution of charge carriers [6]. To check the above-proposed assumption, the additional photovoltage measurements have been carried out for symmetrical sandwich structure samples of investigated PCFs. Figure 3 illustrates the scheme and results of these experiments.

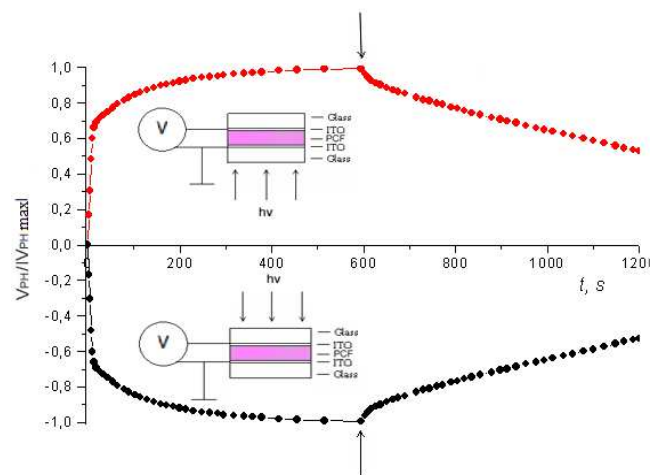


Figure 3. Normalized kinetic dependencies of the surface photovoltage growth and relaxation in the ITO-PCF-ITO sandwiched sample based on GCBE doped with 10 wt% of PD1 under illumination of the different sides of sample with white light-emitting diode irradiation, ($I = 50 \text{ W/m}^2$) and the scheme of respective photovoltage

measurements. The time moments of switching off the light illumination are shown by vertical arrows.

The Figure 3 (and the same photovoltage measurement results obtained for all other analogous sandwiched samples) shows that the sign of the photovoltage becomes inverse under exciting light illumination of the different sides of sandwiched samples. This fact confirms the correctness of our assumption about diffusion nature of the observed photovoltaic effect. In our systems case the potential of the non-illuminated (dark surface) becomes positive with respect to illuminated surface, because holes have the larger mobility. This confirms the p-type photoconductivity (hole conductivity) character of investigated PCFs [1,4,6].

It is known [1,2] that the ability of dyes to photogeneration of EHP in carbazole containing polymers is defined by a ratio between energies of frontier valence orbitals of a dye and carbazolyl-fragment. This regularity is tracked and on an example of researched number of dyes. So, with a lengthening of polymethine chain in a number of cationic dyes PD1-3 energies HOMO and LUMO approach [1], and the odds of energies HOMO of a dye and carbazole decreases. The same tendency can also occur in the dyes association case at high concentrations of dyes in the PCFs. Decrease in the energy of the HOMO in the series of dyes PD1-3 leads to a decrease in the difference in the ionization potentials of the dye molecule and

the carbazole fragment of the GCBE. This is the reason for the fact that during the photogeneration of the hole from the excited molecule onto the carbazole fragment of GCBE, contained in the hole transport band [4], the probability of formation of the electron-hole pair and its lifetime value according to [1,4] decreases. Therefore at replacement of PD1 on PD2 and PD3 lifetimes of EHP, photovoltaic effect value, and photoconductivity of GCBE-based PCFs respectively decrease. This explains the kinetics of the surface photovoltage growth and relaxation peculiarities in the samples with a free surface because long-living EHP (charge pairs) are characterized by relatively high dissociation, diffusion and charge separation ability.

Conclusions

The films of photoconductive composites based on GCBE-oligomer sensitized with various concentration of cationic polymethine dyes with different polymethine chain length have been prepared. Their spectral and photoelectrical properties have been investigated. In PCFs with high concentration of the dye photovoltaic effect have been observed. The discovered effect has been shown to have diffusion nature. The correlation of photovoltaic effect and photoconductivity features with polymethine dye and oligomer-matrix structure and electronic properties has been established. The obtained results can be used for the development of new photovoltaic media based

on photoconducting polymeric materials with organic dyes.

Experimental part

We used two types of samples:

(1) Structures with a free surface: glass substrate with or without a transparent ITO ($\text{SnO}_2:\text{In}_2\text{O}_3$) electroconducting sublayer-PCF doped with dye; and (2) closed sandwich structures: glass substrate-ITO-PCF doped with dye-ITO-glass substrate. Concentrations of dyes in all films have been 1 or 10 wt%. The thickness of the films was 1-1,5 μm . All samples have been prepared and all experiments (spectral and photoconductivity measurements) have been carried out according to [4]. Photovoltage has been measured by both the contacting method (in the sandwich structure samples) and the modified Kelvin method (under illumination of the transparent ITO-electrode side) [7]. The kinetics of photovoltage (V_{PH}) in the sandwiched samples and structures with a free surface have been measured using a memory oscilloscope Tektronix TDS1001B. The PCFs samples with a free surface have been used for spectral and photovoltage (by the Kelvin method) measurements. The sandwiched samples of PCFs were used for photoconductivity and photovoltage (by contacting method) measurements. As excitation light sources for the photogeneration

of charge carriers, we used a white semiconductor light-emitting diode and semiconductor laser emitting at $\lambda_{\text{irr}} = 780 \text{ nm}$. The light intensity has been changed by neutral light-filters within the range $I = 1\text{-}50 \text{ W/m}^2$. All experiments have been carried out at a room temperature.

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