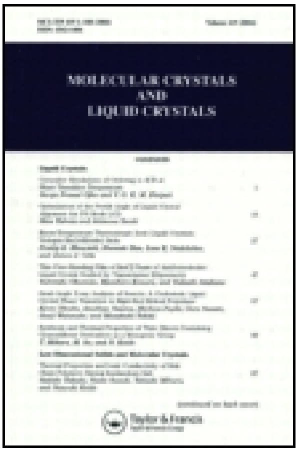

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Effect of Polymer Molecular Structure on Photosensitivity of Composites Films Based on Infra-Red Polymethine Dye

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The main results of studies of the effect of a polymer molecular structure on the photosensitivity of composites films based on infra-red polymethine dye photosensitive in a wide spectral range including the near IR region are presented.

The highest photosensitivity is observed among the studied composites in that with a polyphenylenevinylene polymer matrix. The basic reason for high integral photosensitivity of these composites is the formation of aggregates, for which the energy and efficiency of the photogeneration of charge carriers are comparable or higher than those for quasiisolated molecules of polymethine dyes.

The studied polymer composites of polymethine dyes can be used as near IR radiation sensors (800–1400 nm) and IR photoconverters including solar cells.

Keywords Photoconverters; photovoltage; polymer composites; polymethine dyes

Introduction

Polymer composites based on polymethine dyes and carbazole polymers developed by us earlier [1,2] are photosensitive in the region 400–850 nm similarly to solar cells based on CdTe, but these composites still have a more narrow region of photosensitivity comparing to Si-based solar cells. The analysis of the obtained data on the polymeric composites of polymethine dyes indicates that, for the expansion of the spectral region of absorption of these composites to the long-wave side up to 1.25 eV, it is necessary to utilize the polymethine dyes with a maximum of absorption in a solution, E_m, to be about 1.2 eV and with a considerable probability of the formation of dimer-like aggregates. For this purpose, it is necessary that their molecular structure have no bulky substituents in the mesoposition of molecules and the luminescence efficiency be small. In our recent study, it is experimentally confirmed

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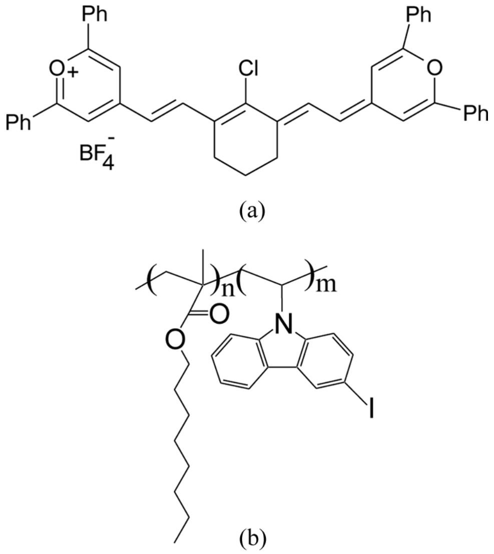

(a)

(b)

Scheme 1. Molecular structure of 4819 polymethine dye (a), MDMO-PPV (b), and I-VC-OMA (c) polymers.

that the photosensitivity is observed in the region 600–1200 nm in the composites of 4819 dye (Scheme 1a) in a polyvinylethylal (PVE) polymer matrix [3].

In order to expand more the region of photosensitivity, we proposed the technology of a deposition of more polar polymers films: soluble derivative of polyphenylenevinylene (Poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] – MDMO-PPV) and copolymer of 3-iodovinylcarbazole with octyl methacrylate(I-VK-OMA) (Scheme 1b). The first of these was shown to be photosensitive in the region 400–600 nm [4], and the total photosensitivity of the composites of the second polymer with other polymethine dyes significantly rises due to an increase of the efficiency of charge transfer between dye aggregates [1,2].

The molecular structure of 4819 polymethine dye and I-VK-OMA polymers, is shown in Scheme 1.

Experimental

The films were deposited by the spin-casting technique from the solution of both polymer and dye in methylene chloride. The concentration of dye was 30 weight %. Before the deposition, the solution was homogenized in an ultra-sound sonicator at 60°C during 1 hour. The thickness of studied films was 0.5–1 μm. For their deposition, two types of substrates were used: glass substrates for the deposition of samples to measure the absorbance and substrates with a conductive ITO layer which was deposited by magnetron sputtering and used as the electrode under measuring the photovoltaic properties of composites. The absorption spectra were measured with the help of spectrophotometers "Perkin-Elmer Lambda 8" and "Shimadzu-UV2450".

Photovoltaic properties of composites were measured by the Bergman method improved by Akimov [5]. As an advantage of this method, we indicate that there is no necessity to deposit a top ohmic electrode, for which the preparation technology is not yet designed. During measurements, a sample was illuminated by modulated monochromatic light (80 Hz) created with the help of an MDR-4 monochromator. Photovoltage (V) was measured by a Unipan 232B nanovoltmeter supplied by a preamplifier with high input impedance. The spectral dependences of V were normalized on the equal number of incident photons with the help of a calibrated pyroelement. In more details, the procedure of measurements of V is described, e.g., in [6,7].

The absorption spectra of the studied films of the composites in MDMO-PPV and I-VC-OMA are shown in Figure 1: curve 2 for PPV and curve 3 for I-VC-OMA. For the comparison, this figure also shows the absorption spectra of solutions of this dye in ethylene dichloride, curve 1.

The comparison of the spectra of these films and solutions indicates the following:

i) A relatively small (~100 meV) shift of the lowest electronic transition of a molecule ($E_m = 1.2$ eV) to the side of smaller energies is observed at the transition from a solution to a film of the composite. This is characteristic of the films of organic semiconductors and testifies to the presence of a weak (3–5% E_m) intermolecular interaction of molecules of the dye and the polymer.
ii) In the region of 1.5–2.0 eV in the absorption spectra of composite films of 4819 dye, there is the absorption band with maximum near 1.58 and 1.64 eV in

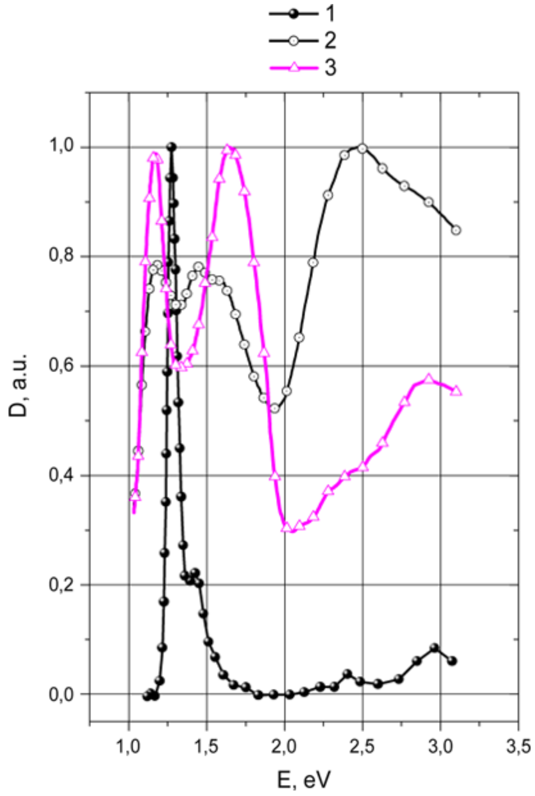

Figure 1. Absorption spectra of 4819 dye in a solution and films of this dye composites in MDMO-PPV and I-VC-OMA polymers.

different polymer matrices which have no analogs in the absorption spectra of these dyes in solutions and can be caused by the formation of two types of aggregates which are probably H-aggregates of the dimer-like type [8,9]. The absorption intensity of these bands is higher than that of the absorption of quasiisolated molecules at 1.2 eV. This testifies that the probability of the formation of dimer-like aggregates is great enough and more than that for aggregates on the basis of hexaindoletricarbocyanine tetrafluoroborate (HITC) and meso-Cl polymethine dyes [8,9]. The presence of weakly expressed shoulders in the absorption spectrum of composites in the region 2–2.5 eV can be explained by the formation of an aggregate with low efficiency and other aggregates with low absorption.

To check the efficiency of photogeneration of charge carriers under the excitation of the above-mentioned aggregates and complexes, the measurements of *V* analogous to those previously described were carried out for films of these composites. The spectral dependences of *V* are shown in Figures 2 and 3. From the comparison of the curves in Figures 2 and 3, it is seen that all aggregates and complexes, which were exhibited in the spectra of the films of 4819 dye-based

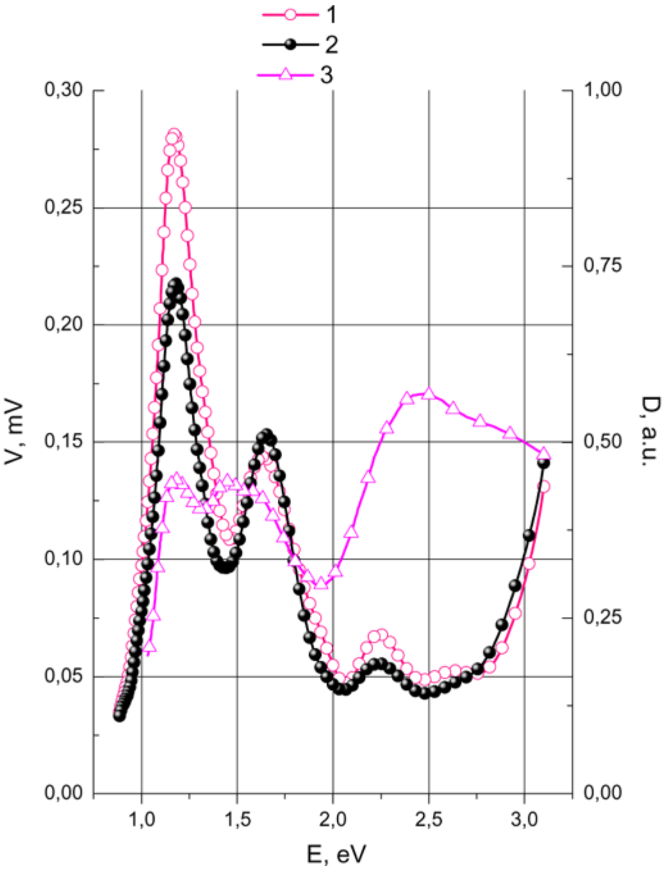

Figure 2. Spectra of photovoltage *V* of 4819 dye composites in MDMO-PPV polymer under the illumination from the side of the free surface (1) and the ITO electrode (2), as well as the absorption (D) spectrum of MDMO-PPV composite.

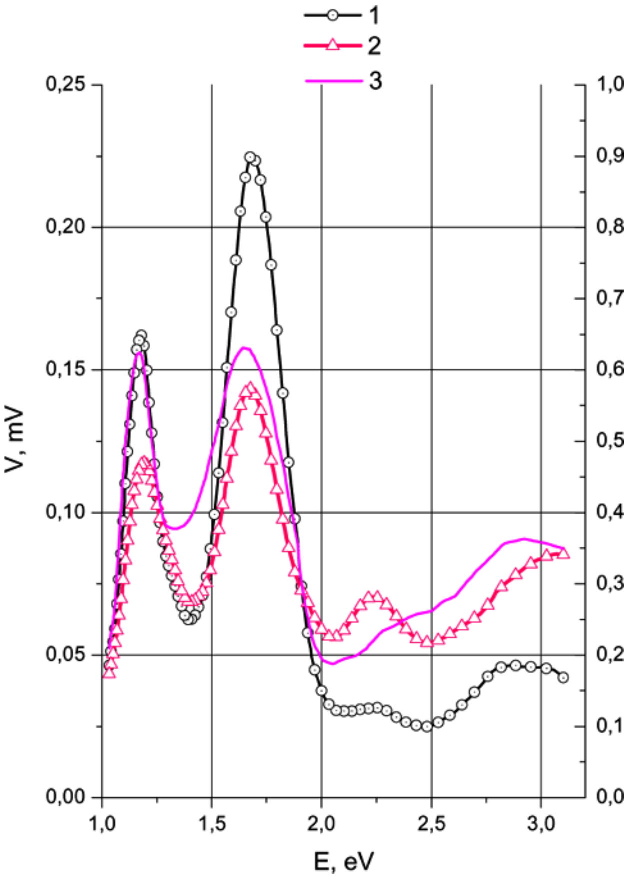

Figure 3. Spectra of photovoltage *V* of 4819 dye composites in I-VC-OMA polymer under the illumination from the side of the free surface (1) and the ITO electrode (2), as well as the absorption (D) spectrum of I-VC-OMA composite.

composites, are photosensitive and generate charge carriers under illumination. The greatest efficiency of photogeneration of charge carriers is observed for the (1.61 ± 0.03)-eV aggregate. For I-VC-OMA composite, the efficiency is greater than that under the excitation of quasiisolated molecules of 4819 dye. This peak is caused by the formation of the H-type aggregate of dye molecules, and its intensity is comparable or greater than that in the region of E_m.

Thus, the efficiency of photogeneration of charge carriers by this complex is comparable or even greater than that of a quasiisolated molecule.

The efficiency of photogeneration of charge carriers depends on the polymeric matrix. The comparison of photovoltaic parameters of different composite films is summarized in Table 1, where V_{int} is the integral arbitrary intensity of the films in the equal spectral range 1.033–3.1 eV (calculated as the area under an appropriate curve V(E) in Figures 2 and 3, the procedure was described in [10]); V_{max} is the maximal value of photovoltage; V_H is the value of photovoltage in the region of the H-aggregate band (1.61 ± 0.03 eV).

From the values in Table 1, it can be seen that the maximal photovoltage (both by absolute values V_{max} and by integral values V_{int} for both cases of the illumination)

Table 1. Photovoltaic sensitivity of 4819 based composites in different polymer matrices

Polymer matrix	Illumination from	V_{int}, a.u.	V_{max}, mV	V_H, mV
MDMO- PPV	Free surface	0.219	0.281	0.144
	ITO	0.195	0.218	0.153
I-VC-OMA	Free surface	0.154	0.225	0.225
	ITO	0.165	0.143	0.143
PVE [3]	Free surface	0.081	0.103	0.103
	ITO	0.077	0.099	0.099

is observed for MDMO-PPV based composites, and both these parameters decrease for I-VC-OMA (the average difference is ~30%) and significantly decrease for the PVE polymer matrix (more than 2 times).

It should be noted that V_{max} is observed for MDMO-PPV based composites at the energy E_m, while, for I-VC-OMA and PVE composites, V_{max} is observed in the

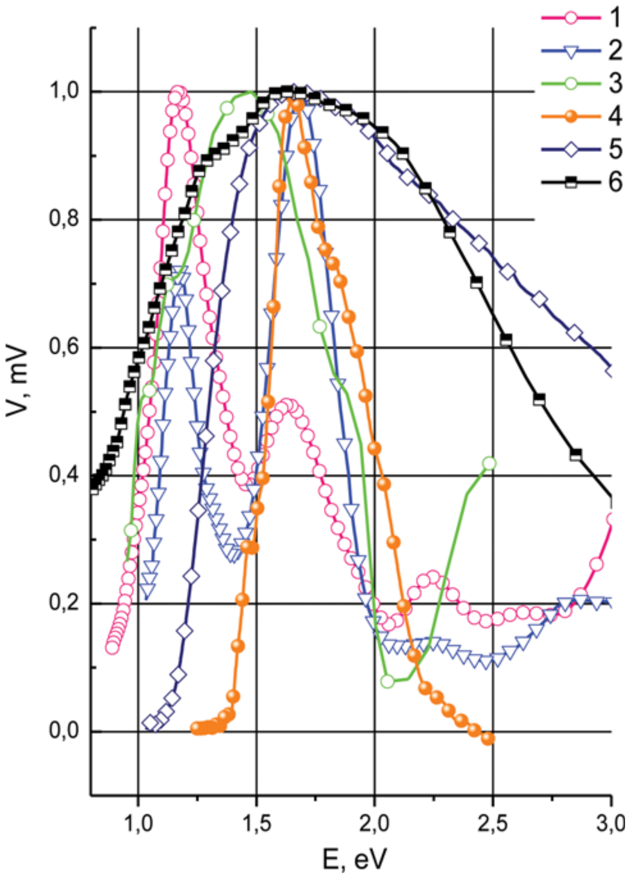

Figure 4. The spectra of photovoltage of 4819 polymethine dye in the MDMO-PPV (1), I-VC-OMA (2), and PVE (3) together with the spectra of lead phthalocyanine (4), Si photovoltaic element (5), and the absolutely black body (6).

region of H-aggregate manifestation. Thus, the process of aggregation is probably more efficient for last two polymers.

That is, the previous search for new polymethine dyes with a maximum near 1.2 eV has confirmed that they form the photosensitive composites in the region of 0.8–2.4 eV. Thus, the opportunity of the preparation of cheap photosensitive materials for the development of plastic phototransformers is experimentally confirmed.

These composites are photosensitive in the range wider than that of the composites on the basis of lead phthalocyanine [11] and Si (Fig. 4). Figure 4 shows the spectra of photovoltage of 4819 polymethine dye in different polymer matrices [MDMO-PPV (curve 1), I-VC-OMA (curve 2), and PVE (curve 3)] [3] together with the spectra of lead phthalocyanine (curve 4) [11], Si photovoltaic element (curve 5), and the absolutely black body (curve 6).

It can be seen that the studied polymethine dye composites have a wide range of photosensitivity, which is higher than that of lead phthalocyanine and is comparable to that of Si, and also demonstrate a good correspondence to the spectrum of the absolutely black body especially in the near IR region, where the maximal flux of solar photons is observed [12].

Conclusions

The high photosensitivity in a wide spectral range including the near IR region was observed in the composites with high concentration of polymethine dyes. The basic reason for widening the spectral region of photosensitivity for these composites is the formation of aggregates in them, for which the energy and efficiency of the photogeneration of charge carriers are comparable or even higher than those for quasiisolated molecules of polymethine dyes. This leads to the widening of the region of photosensitivity up to a wavelength of 1.4 μm ($E = 0.886$ eV). The maximal photovoltage (both by absolute values V_{max} and by integral values V_{int}) is observed for MDMO-PPV based composites, and both these parameters decrease for I-VC-OMA and for the PVE polymer matrix.

The studied polymethine dye composites have the maximum of photosensitivity in thenear IR region, where the maximal flux of solar photons is observed [12]. Thus, the opportunity of the preparation of cheap photosensitive composites for the development of plastic photoconverters photosensitive in a wide spectral range, such as Si-elements, has been confirmed.

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