Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Polymer Materials with Organic Dyes of Various Ionic Ability for Photosensitive and Light Emitting Structures

Larysa Fenenko [a], Petro Smertenko [a], Sergy Svechnikov [a], Oksana Lytvyn [a], Alexander Ishchenko [b], Nikolay Davidenko [c], Micheal Hietschold [d] & Falk Mueller [d]

[a] V. E. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine

[b] Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine

[c] Kyiv Taras Shevchenko University, Kyiv, Ukraine

[d] Chemnitz University of Technology, Institute of Physics, Chemnitz, Germany

Version of record first published: 31 Aug 2006

Mol. Cryst. Liq. Cryst., Vol. 427, pp. 49/[361]–56/[368], 2005

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590891902

Taylor & Francis
Taylor & Francis Group

Polymer Materials with Organic Dyes of Various Ionic Ability for Photosensitive and Light Emitting Structures

Larysa Fenenko
Petro Smertenko
Sergy Svechnikov
Oksana Lytvyn
V. E. Lashkaryov Institute of Semiconductor Physics,
National Academy of Sciences of Ukraine,
Kyiv, Ukraine

Alexander Ishchenko
Institute of Organic Chemistry, National Academy of Sciences
of Ukraine, Kyiv, Ukraine

Nikolay Davidenko
Kyiv Taras Shevchenko University, Kyiv, Ukraine

Micheal Hietschold
Falk Mueller
Chemnitz University of Technology, Institute of Physics,
Chemnitz, Germany

The peculiarities of charge flow mechanism in polymer films on the PEPC base with organic dyes of various ionic ability were investigated. The electroconductivity was established to depend on dye nature, their ionic ability and content in polymer media. The approximation of the current-voltage characteristics as exponential function was presented and the activation mechanism of charge flow in investigated structures was established. The activation energy of various system was estimated end established to depend on the dye concentration in PEPC. The self-organization as penta- and hexagons and aggregation in investigated structures obtained.

Keywords: electroconductivity, ionic dyes, polymer, self-organization

Address correspondence to Larysa Fenenko, V. E. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, 45 Prospekt Nauki, Kyiv 03028, Ukraine. Tel.: 380-44-265-64-77, Fax: 380-44-265-83-42, E-mail: fenenko@isp.kiev.ua

INTRODUCTION

The polymer nanoscale structures are under wide investigations of chemists and physicists now [1]. The photosensitive materials for optical filters and solar cells, the reversible media for optical writing of information and for holograms, the light emitting devices with good characteristics and others have the promising perspectives in the feature.

The structure formation in such case is simple and cheap, the properties can be changed easy, the efficiency of such structures is high, the good film forming and mechanical properties are peculiar to organic polymer structure both the doped polymers and composite materials.

Poly(N-epoxypropylcarbazole) (PEPC) was used as the hole transport layer what was caused by its capability to effective transport of holes through carbazole nucleuses [2]. With addition of electron acceptors the PEPC as film forming media does both the function of hole transport and formation of photogeneration centers [3].

The organic dyes (OD) are used as sensibilizators of photoconductivity and electroluminescence of polymers because of their effective transforming of the light energy and their intensive bonds of absorption and luminescence in wide spectral range [4]. Besides, the energy of their valence orbital and carbazole are close and the holes can move from carbazole nucleases to valence orbital of OD and on the contrary [5].

The main purpose of this work is to investigate the peculiarities of charge flow in organic polymer films both doped by organic dyes of various ionic ability and their composites.

EXPERIMENTAL

The series of cationic OD 1, anionic OD 2, neutral OD 3 and intraionic OD 4 were investigated.

Casting from solutions to ITO on glass substrate formed the films investigated. The concentration of OD in polymers was in range 0–50 mas.%. The second electrode in sandwich structures was prepared by press of In or by vacuum evaporation of In with contact area of $1 \cdot 10^{-2}$ cm^2.

The current-voltage characteristics of investigated structures were measured in range 0.01–400 V by automated tester 14-TKS-100 and processed by PC. The surface morphology of investigated films was measured by Atom Force Microscopy (AFM) and by electronic microscopy.

RESULTS AND DISCUSSION

The organic dyes of various structure and various ionic ability were used [5,6] (Fig. 1). Such method let us to investigate the dependencies

TABLE 1 The Characteristics of Investigated Dyes (Table 1, Figure 1)

N	The dye classification	Ionic ability	Peak of absorption	Peak of luminescence
1	indopolycarbocianine	cationic	667	678
2	polymetine	anionic	560	602
3	merocianine	neutral	550	598
4	ionic dye with B atom coordinated	intraionic	530	612

of optical, electrical and others characteristics on the PEPC base both on the structure of dyes and their ionic ability.

The name of cationic dye OD 1 is indopolycarbocianine and it is included to polymetines. It likes salt Na^+Cl^- and falls to ions in solution. Its molecules are symmetric. The charge of such dye is positive "+1" and presence both in ground and excited states [7]. In comparison to cationic OD 1 we have investigated the anionic OD 2 like salt too. The summary charge of such dyes is "–1". OD 2 has charging structure both in ground and excited state. The neutral OD 3 was syntesied by unification of cation OD 1 and anion OD 2. The summary charge of such dyes is 0. The OD 4 is intraionic dye and has the charges "–1" and "+1" in both ground and excited states.

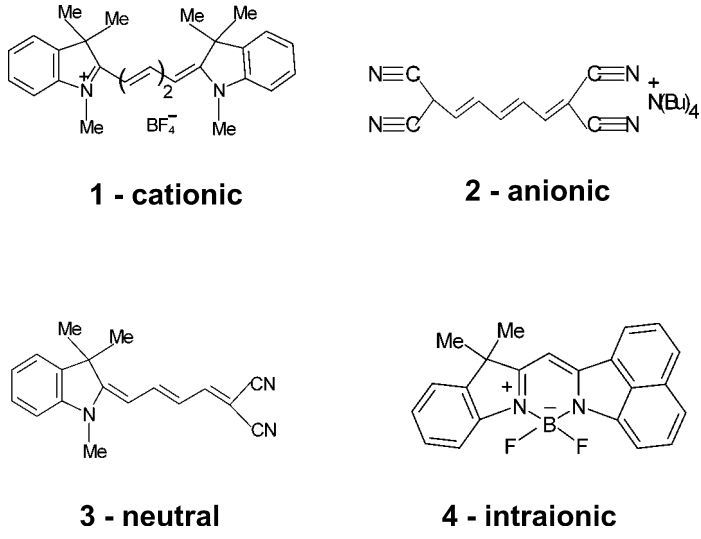


FIGURE 1 The structure of dye molecules.

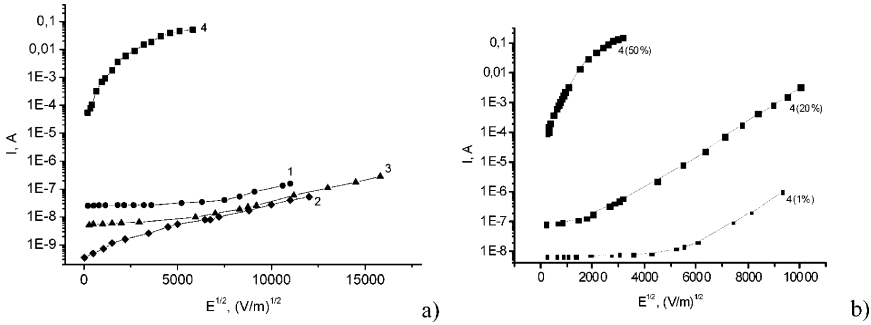


FIGURE 2 I vs E dependence: a) in the polymer structures with polymetine dyes: cationic (1), anionic (2), neutral (3) and intraionic (4). The dyes concentration was 50% mas.; b) in samples of: In–(PEPC + N% mass. dye 5)-ITO; N = 1%, 20% and 50% mas. L ≤ 1 mkm, forward applied bias.

The sandwich structures on the PEPC base with various concentration of OD were investigated. It was established that the electroconductivity of such structures increases in series (Fig. 2a):

$$\text{anionic} \rightarrow \text{neutral} \rightarrow \text{cationic} \rightarrow \text{intraionic dye}.$$

Besides, it was obtained that the structures with intraionic dyes were different from others. The conductivity of films PEPC + 50 mas. % OD 4 was more up to 6–8 orders of magnitude in comparison to structures with other dyes such consideration. So, they are more perspectives.

Dye doping of polymer films leads to increase of their EC because of contribution of thermo-field injection of carriers from dye molecules.

The dependence of electroconductivity on dye concentration in polymer media was obtained. The big difference was established at 50 mas.% for intraionic dyes. The electroconductivity of films PEPC + 50 mas. % OD 4 is more than of PEPC + 1 mas. % OD 4 one up to 6 orders of magnitude in comparison to 1 order of magnitude for other dyes (Fig. 2 b). The cause of such effect can be the presence of both positive and negative charges in intraionic dyes. Besides, in such structures was established the aggregates formation (Fig. 3a).

The CVC curves (Fig. 2b) can be approximated both exponential function:

$$J \sim \exp(-(W_t - \beta E^{1/2})/kT) \text{ and degree function } J = J_0 E^{\alpha},$$

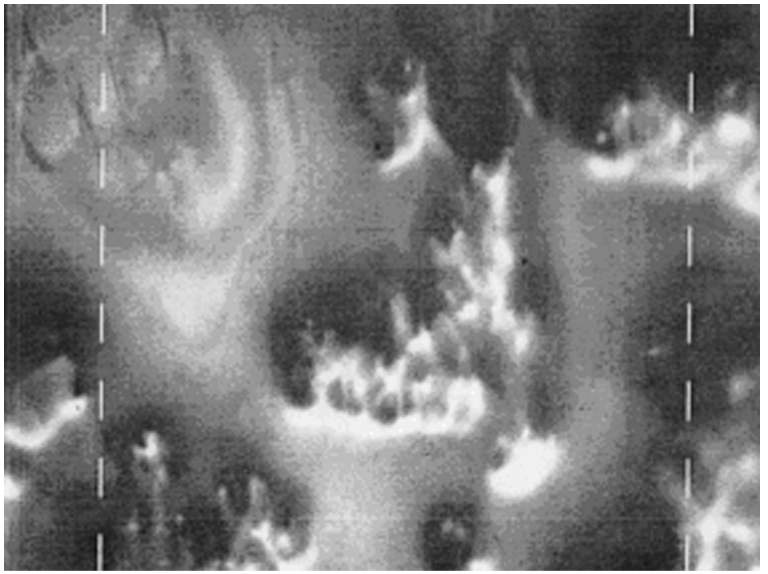
where α increases from 0.1 to 5 for PEPC + 1% mas. OD 4; from 0.2 to 5.5 for PEPC + 20% mas. OD 4; decreases from 2 to 1.5 for PEPC + 50% mas. OD 4.

The mechanism of charge flow in investigated films is presented by activation process. We have estimated the activation energy W_t for films PEPC + N mas. % OD 4:

$W_t \sim 0.45$–0.59 eV for PEPC + 1% mas. OD 4;
$W_t \sim 0.45$ eV for PEPC + 20% mas. OD 4;
$W_t \sim 0.16$ eV for PEPC + 50% mas. OD 4.

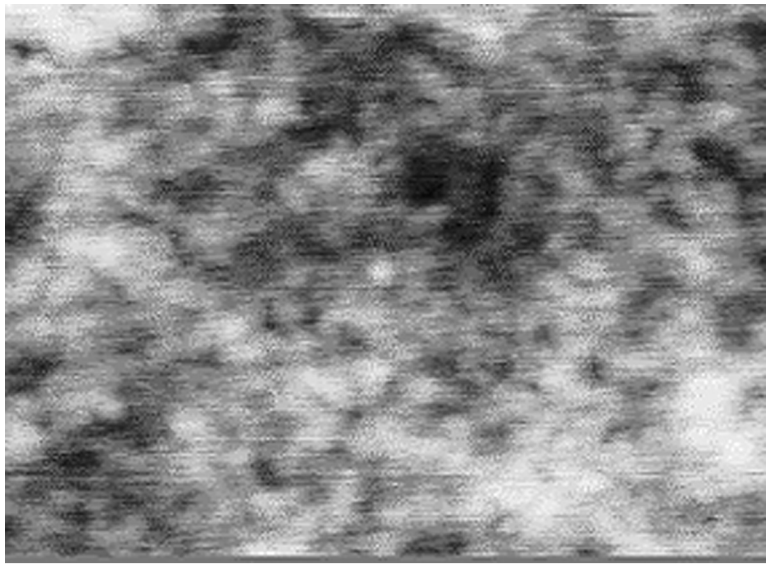
In the case of thin films we have the opportunity for EC increase because of contribution of thermo-field injection of carriers from contacts and of increase conductivity (Fig. 4).

It was obtained the aggregate formation at 50 mas.% intraionic OD in polymer media (Fig. 3a). Generally the conductivity of the films with aggregates consists of the conductivity inside aggregates and conductivity between them. In the case of aggregate size was compared to film thickness the conductivity generally take place through aggregates (Fig. 4).



(a)

FIGURE 3 The surface morphology of the polymer films: a) PEPC + 50 mas.% OD 4; the photo obtained by electronic microscope; scan rate $6 \times 8\,\mu m^2$; b) PEPC + 1 mas. % OD 1 with self-organization as penta- and hexagons.



(b)

FIGURE 3 (Continued).

Besides, the self-organization in the form of penta- and hexagons on the structures PEPC + N% mas. dyes was observed (Fig. 3b).

The electroluminescence (EL) on the samples with N% mass. OD 4 was observed (~20 V):

at N = 1% it was weak visible EL so red threads;
at N = 50% the such films give off red visible light. The effect of EL was reproduced.

The electroconductivity of investigated structures can be described as

$$\sigma = \sigma_{\text{pol}} + \sigma_{\text{i}} + \sigma_{\text{e}} + \sigma_{\text{h}} + \sigma_{\text{dye}},$$

where σ_{pol} is the thermo-field generation of carriers from polymer molecules; σ_{i} is the ion conductivity; σ_{dye} is the thermo-field generation of carriers from dye molecules; σ_{e} and σ_{h} are the thermo-field injection of carriers from contacts.

The conductivity component σ_{dye} has the biggest contribution in conductivity in the films of PEPC + 50% OD 4. The other components σ_{e} and σ_{h} carry the considerable contribution in the conductivity in thin films.

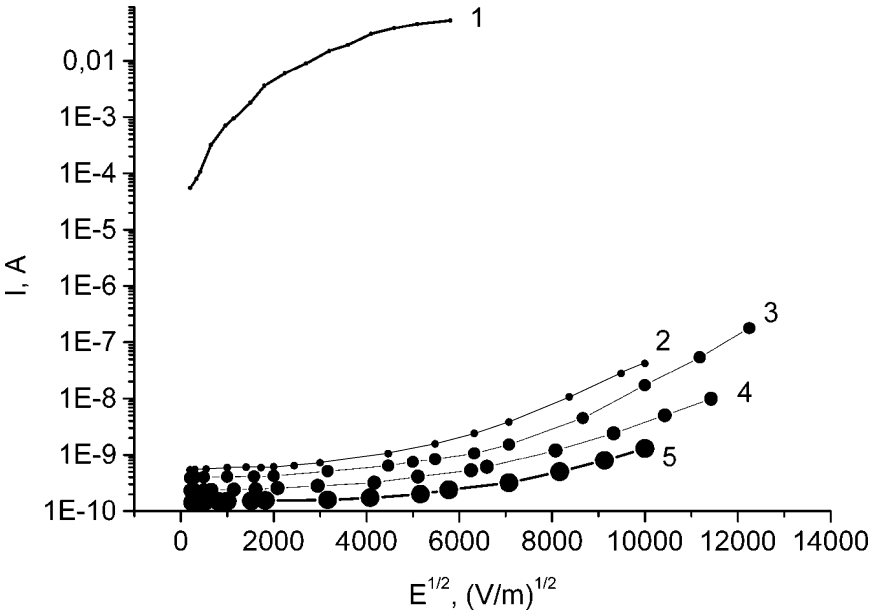


FIGURE 4 Typical I vs E dependences in samples of In–(PEPC + 50% mass. dye 5)-ITO for L = 0.55 mkm (1) 1mkm (2) 2 mkm (3) 2.3 mkm (4) 3 mkm (5) forward applied bias.

CONCLUSIONS

For increasing electroconductivity of the structures PEPC + N mas.% OD is needed to application:

- thin films with $L \leq 1$ mkm,
- dye concentrations $N > 20\%$,
- intraionic dyes.

The CVC curves can be approximated in the form of exponential function for thermofield generation of carriers $J \sim \exp(-(W_t - \beta E^{1/2})/kT)$ or degree function $J = J_0 E^{\alpha}$.

The self-organization in the films of PEPC + N mas.% OD was conditioned by interaction polymer-dye and dye-dye molecules.

In the polymer films with 50% mas. OD the aggregation take place.

Generally the film conductivity can be approximated as conductivity inside aggregates and between them $\sigma = \sigma_{\text{int } raaggr} + \sigma_{\text{int } eraggr}$.

The structures on the base of PEPC + N mass.% OD 4 with thickness less than 1 mkm are promising for OLEDs.

REFERENCES

[1] Davidenko, N. A. & Ishchenko, A. A. (2002). *Theoretical and Experimental Chemistry, 38* (2).
[2] Pope M. & Swenberg, Ch. E. (1999). *Electronic processes in organic crystals and polymers*. Oxford University Press: New York, Oxford.
[3] Kuvshinskyi, N. G. & Davidenko, N. A. (1994). *The physics of amorphous molecular semiconductors*. Lybyd': Kyiv.
[4] Kiprianov A. I. (1965). *The introduction in electronic theory of organic compounds*. Naukova Dumka: Kyiv.
[5] Davidenko, N. A. & Ishchenko, A. A. (1998). *Phys. St. Sol., 40*(4).
[6] Ishchenko A. A. (1994). *The structure and spectral-luminescent properties of polymetine dyes*. Naukova Dumka: Kyiv.
[7] Davidenko, N. A., Derevyanko, N. A., Ishchenko, A. A., & Pavlov, V. A. (2001). *Phys. St. Sol., 43*(8).