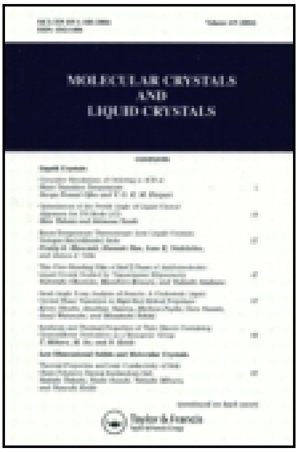

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photoconductivity of Polymeric Composites Doped with Porous Silicon Nanoparticles and Additions of Ionic Polymethine Dyes of Different Types

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Version of record first published: 03 Mar 2011

To cite this article: N. A. Davidenko, A. A. Ishchenko, V. A. Skryshevsky, S. L. Studzinsky & E. V. Mokrinskaya (2011): Photoconductivity of Polymeric Composites Doped with Porous Silicon Nanoparticles and Additions of Ionic Polymethine Dyes of Different Types, Molecular Crystals and Liquid Crystals, 536:1, 93/[325]-98/[330]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.538309

Mol. Cryst. Liq. Cryst., Vol. 536: pp. 93/[325]–98/[330], 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.538309

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Photoconductivity of Polymeric Composites Doped with Porous Silicon Nanoparticles and Additions of Ionic Polymethine Dyes of Different Types

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Features of the electrical conductivity and the photoconductivity of polyvinylbutyral films containing silicon nanoparticles and similar films doped with cationic and anionic polymethine dyes are studied. Sensitization of the photoelectric effect by dyes with various ionicities in films is explained by the possible photogeneration of holes and electrons from dye molecules and the intrinsic bipolar conductivity of silicon nanoparticles. It is assumed that the electronic conductivity in silicon nanoparticles is higher as compared with that in nanoparticles with p-*type conductivity.*

Keywords Photoconductivity; polymeric composites; polymethine dyes; silicon nanoparticles

1. Introduction

Photosemiconductor films of polymeric composites (FPC) based on organic polymers with additions of silicon-containing particles are perspective media for the development of photoelectric converters of solar energy and electroluminescent devices [1]. If silicon is included in FPC in the form of nanoparticles, the photosemiconductor band gap and the mobilities of electrons and holes can be controlled by changing the sizes of nanoparticles. As the photogeneration centers of electrons and holes in FPC, polymethine dyes can be used [2]. In this connection, the investigation of the photoconductivity sensitization of silicon nanoparticles containing polymeric composites by polymethine dyes in several spectral regions aimed at their application in photoelectric solar energy converters and other optoelectronic devices turns out very urgent.

The aim of the present work is the investigation of the electro- and photoconductive properties of FPC based on an electroneutral polymer doped with silicon nanoparticles (Si-nps) and with addition of an anionic or cationic polymethine dye.

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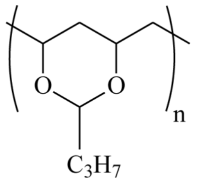
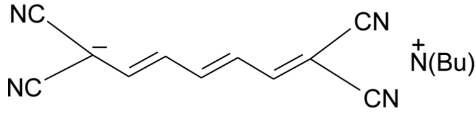
2. Samples and Experimental Methods

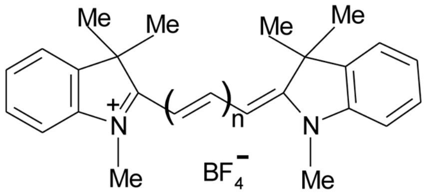
The samples for investigations were prepared with free-surface structures (glass substrate-FPC) and as sandwich structures (glass substrate – SnO_2:In_2O_3 electroconducting layer – FPC – Ag). The Ag-contacts were prepared using a silver paste. The investigated FPC were fabricated using the polyvinylbutyral (PVB) films doped with 20-wt.% silicon nanoparticles (Si-nps) or with 1-wt.% additions of anionic (Dye 1) or cationic (Dye 2) polymethine dye. Dye 1 and Dye 2 are able, respectively, to the photogeneration of electrons and holes [3–5]:



PVB



Dye 1



Dye 2, *n*=1

Silicon nanoparticles were fabricated with the use of porous silicon layers in accordance with the procedure which was described previously in [6]. A porous silicon layer was formed by the electrochemical etching of 2-in *p*-type (1–10 Ω cm) Si wafers in the 1:1 mixture (by volume) of concentrated aqueous hydrofluoric acid (48%) and pure ethanol. The obtained high-porosity (>90%) 300-μm thick porous silicon layer was washed several times in absolute ethanol. The porous silicon layer was transformed into a micropowder after the final evaporation of ethanol from its nanopores. The formed porous silicon micropowder was mechanically grinded until it became a homogeneous nanopowder, and then it was suspended in absolute ethanol. In order to perform the size selection of Si-nps, the centrifugation technique was used [6]. A saturated absolute ethanol solution with a nanopowder concentration up to 5 mg/ml was used as an initial sample for the FPC preparing. Nanoparticles were 3–5 nm in size.

FPC samples were prepared by the casting of absolute ethanol Si-nps solutions both without the addition of dyes and with dyes onto the corresponding substrates. Samples were dried at ambient temperature after the casting for 2 h at room temperature and at 75°C for 8 h in a vacuum drying chamber. The FPC thickness was

2.0–3.0 μm. The optical density (D) spectra of the investigated films were measured in free surface samples without an electroconducting SnO_2:In_2O_3 layer in the wavelength range $\lambda = 400$–1000 nm. Samples with the sandwich structure were used to measure the densities of the dark electroconductivity current (j_d) and the photocurrent (j_{PH}) as functions of the external electric field strength (E) applied to electric contacts. The density and the kinetics of a dark current and a photocurrent in the sandwiched samples were measured using a storage oscilloscope. In the measurements of photoconductivity currents, the samples were irradiated by light of a filament lamp with the use of optical filters with the light transmission band at wavelengths $\lambda > 530$ nm. The irradiating light intensity was 30 W/m^2. The irradiation was performed from the side of the conductive SnO_2:In_2O_3 layer. In the measurements of temperature dependences, we used a thermostat with an optical window. The temperature (T) and the external electric field strength (E) in the investigated samples varied in the ranges of 290–360 K and $2 \cdot 10^5$–$1 \cdot 10^8$ V/m, respectively.

3. Results and Discussion

In the visible range of the spectrum, PVB films doped with Si-nps additives and without them are characterized by a low absorption at $\lambda > 400$ nm. In the absorption spectra of FPC doped with 1-wt.% Dye 1 or Dye 2, a narrow intense band with a maximum related to the long-wavelength absorption maximum of dye molecules is observed (Fig. 1) [3].

The sandwich samples containing PVB films without additions manifest $j_d < 10^{-6}$ A/m^2, and no photocurrent in the investigated spectral region is observed. Samples based on PVB doped with 1-wt.% Dye 1 or Dye 2 and without Si-nps additives have also no photoconductivity in the visible region. In the FPC with Si-nps based additives, j_d in the samples is increased by several orders of magnitude as compared with that of PVB films without additives, and it does not depend on the applied electric voltage polarity. The dependences of j_d on E are linear in the double-logarithmic coordinates (Fig. 2) with the inclination angle tangent m_d. Therefore, they can be presented in the form $j_d \sim E^{m_d}$ used to analyze space-charge-limited currents in semiconductors [7].

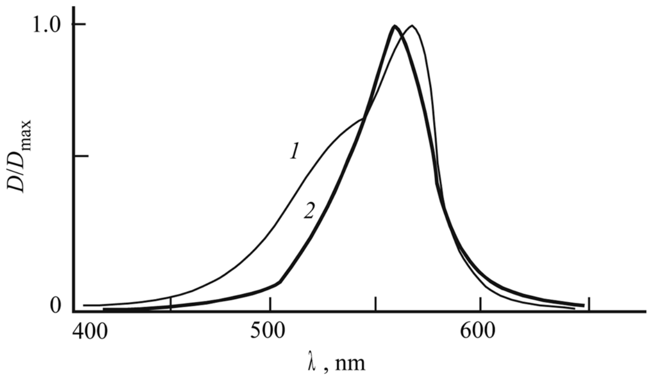


Figure 1. Normalized absorption spectra of the investigated FPC based on PVB + 20 wt.% Si-nps + 1 wt.% Dye 1 (*1*), PVB + 20 wt.% Si-nps + 1 wt.% Dye 2 (*2*).

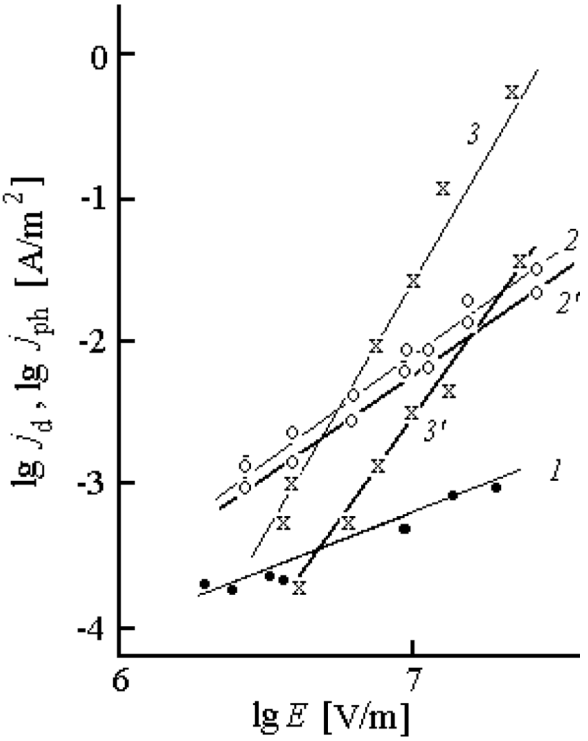


Figure 2. Double-logarithmic dependences $\lg j_d \sim \lg E$ (*1, 2, 3*) and $\lg j_{ph} \sim \lg E$ (*2', 3'*) in the FPC samples with PVB + 20 wt.% Si-nps (*1*), PVB + 20 wt.% Si-nps + 1 wt.% Dye 1 (*2, 2'*), PVB + 20 wt.% Si-nps + 1 wt.% Dye 2 (*3, 3'*). $T = 293$ K.

In Table 1, the m_d values for the FPC samples with Si-nps doped by the corresponding dyes and without such additions are presented. The value of m_d is changed insignificantly with increase in T.

The graphs of j_d vs. T in the Arrhenius coordinates can be approximated by straight lines (Fig. 3). The introduction of Dye 1 or Dye 2 into FPC increases j_d and the calculated activation energy of dark electroconductivity currents (W_d). The W_d value depends weakly on E.

The current in the FPC samples doped with Dye 1 or Dye 2 increases under light irradiation, and the current decreases to its initial value after switching-off the light radiation. The photocurrent kinetics and the stationary value of j_{ph} are independent of the applied voltage polarity, and the $j_{ph} \sim E$ dependence can be represented by the

Table 1. Electro- and photophysical characteristics of PVB + 20-wt.% Si-nps films and the same ones with the additions of 1-wt.% of Dye 1 and Dye 2

FPC	m_d	m_{ph}	W_d, eV	W_{ph}, eV
PVB + 20-wt.% Si-nps	0.8 ± 0.1	–	0.24 ± 0.03	–
PVB + 20-wt.% Si-nps + Dye 1	1.4 ± 0.1	1.3 ± 0.1	0.61 ± 0.05	0.60 ± 0.05
PVB + 20-wt.% Si-nps + Dye 2	3.8 ± 0.1	3.1 ± 0.1	1.22 ± 0.05	1.07 ± 0.05

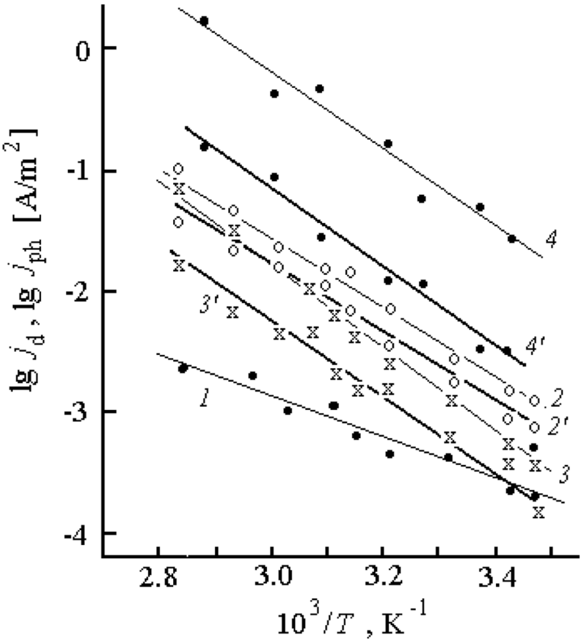


Figure 3. Temperature dependences lg$j_d \sim T^{-1}$ (*1, 2, 3*) and lg$j_{ph} \sim T^{-1}$ (*2′, 3′, 4′*) in FPC samples with PVB + 20 wt.% Si-nps (*1*), PVB + 20 wt.% Si-nps + 1 wt.% Dye 1 (*2, 2′*), PVB +20 wt.% Si-nps + 1 wt.% Dye 2 (*3, 3′, 4, 4′*). $E = 3\cdot10^6$ V/m (*1, 2, 2′, 3, 3′*), $1.1\cdot10^7$ V/m (*4, 4′*).

analytic expression $j_{ph} \sim E^{m_{ph}}$ (Fig. 2, Table 1). The dependences of j_{ph} on T in the Arrhenius coordinates can be fitted by straight lines, and the activation energy (W_{ph}) of the photocurrent can be determined (Fig. 3, Table 1).

According to the previously accepted model of photogeneration and transport of charge carriers in FPC [3,8–9], we can conclude that the photoconductivity current is caused by mobile electrons in the PVB + 20 wt.% Si-nps + 1-wt.% Dye 1-based FPC and by mobile holes in the PVB + 20 wt.% Si-nps + 1 wt.% Dye 2-based FPC. This means that the Si-nps are able to the transport of non-equilibrium electrons and holes. Sufficiently low W_d values in the PVB + 20-wt. % Si-nps-based FPC are caused by the presence of energy barriers at inorganic semiconductor particles-organic polymer interfaces. The growth of W_d and W_{ph} as a result of the introduction of ionic dyes into FPC can be related to additional Coulombic centers formed in the polymeric matrix (PVB), namely, colorless counterions. Such centers should lead, on the one hand, to an increase of the activation energy of conductivity currents and its decrease at growing E (the Pool–Frenkel or Onsager effect). But, in our experiments, the decrease of W_d and W_{ph} was not observed with increase in E. On the other hand, the addition of dyes to FPC facilitates increasing the efficiency of the formation of charge carriers. In this case, the influence of the space charge on the transport processes can increase. The last conclusion can be supported by an increase in m_d and m_{ph}. Therefore, we may assume that polymethine dyes including FPC doped with Si-nps not only increase the efficiency of the thermo- and photogeneration of charge carriers but also create conditions for the formation of a significant space charge.

4. Conclusions

It is experimentally shown that Si-nps in PVB films are characterized by both the electron- and hole-types of conductivity. The electro- and photoconductivity of films is increased in the presence of additions of Dye 1 and Dye 2. The highest photoconductivity was registered in anionic dye-based films. The obtained results can be used for the development of new photosensitive polymeric materials for photoelectric converters of solar energy and electroluminescent devices.

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