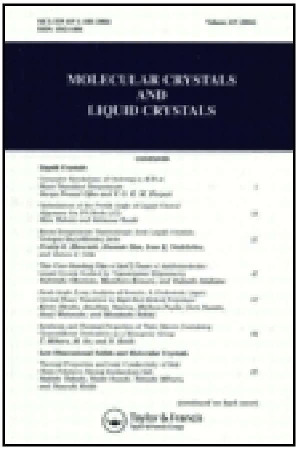

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photoconducting Polymeric Compositions Based on Acrylonitrile Copolymers Doped with Organic Dyes

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Version of record first published: 22 Sep 2010

To cite this article: S. L. Studzinsky, N. A. Davidenko, V. G. Syromyatnikov, A. N. Karapetyan & A. A. Ishchenko (2007): Photoconducting Polymeric Compositions Based on Acrylonitrile Copolymers Doped with Organic Dyes, Molecular Crystals and Liquid Crystals, 467:1, 275-283

To link to this article: http://dx.doi.org/10.1080/15421400701224348

Mol. Cryst. Liq. Cryst., Vol. 467, pp. 275–283, 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701224348

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The films of polymeric composites based on a copolymer of acrylonitrile with styrene (SAN) with the low concentration of an anionic (AD) and (or) cationic polymethine dye (CD) are obtained. The increase of the electroconductivity of SAN films, that contained dye additives, is detected by comparison with the electroconductivity of pure SAN films. The photoconductivity of SAN films with cationic dye additions wasn't found out on the irradiation in the visible region of light. On the contrary, the photoconductivity of the SAN films with AD addition was detected on the photo-excitation in the region of dye absorption. Some features of the photoconductivity and electroconductivity of such composites doped with AD are investigated.

Keywords: acrylonitrile copolymers; anionic dye; electroconductivity; photoconductivity; photogeneration

INTRODUCTION

Photoconducting polymeric composite materials doped with organic dyes are of interest as information storage media, the reversible media for optical writing of information, light emitting devices with good characteristics [1,2], and photovoltaic solar cells [3,4]. Ionic polymethine dyes are effective photoconduction sensitizers of the amorphous molecular semiconductors based on photoconducting

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polymers [5]. Therefore, such semiconductors are successfully used as recording media for electrophotography and holography [6].

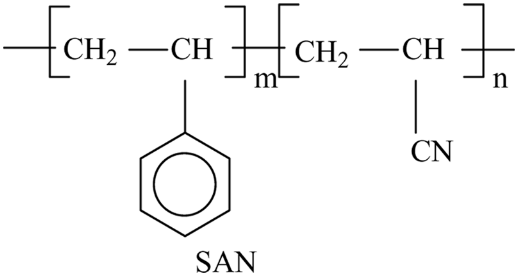
In addition, these media can be used in electroluminescent devices, since the bimolecular recombination of free charges in the molecules of dye has irradiative nature [7]. Most of the known systems of such a type are based on electron-donor polymers doped with cationic polymethine dyes and are characterized by the hole-type of conductivity [5,6]. However, anionic polymethine dyes in polymeric compositions can exhibit the properties of electron photogeneration centers [8], since they are characterized by a positive lowest unoccupied molecular orbital (LUMO) energy [5,8] and a low ionization potential I_{gc}. It was shown [9] that the photoconducting polymeric compositions based on an electron-accepted polymeric matrix sensitized by anionic polymethine dyes are characterized by the electronic type of conductivity and have some advantages (high yield of photogeneration, etc.,) in comparison with last ones.

Therefore, such polymeric systems are of interest as objects of investigations of their optical and photoelectrical properties. In order to develop new photoconducting polymeric materials with electronic conductivity, we obtained the polymeric compositions based on electron accepted copolymers of acrylonitrile (which is contained in macromolecules accepting nitrilic groups (nitrilic (CN) groups possess high electron affinity A_{ea} and are thereby capable of trapping electrons from the LUMOs of dye excited molecules)) with styrene (SAN) sensitized by ionic polymethine dyes (of anionic and cationic types) and studied their photophysical properties.

SAMPLES AND EXPERIMENTAL METHODS

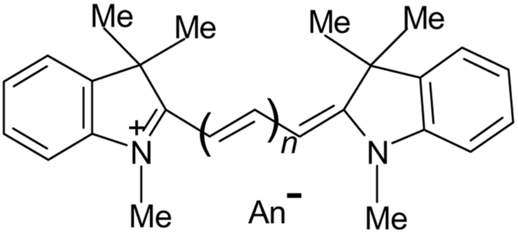
The copolymer of electron acceptor acrylonitrile with styrene (SAN) was synthesized by the free-radical copolymerization of acrylonitrile with styrene in DMF with AIBN as a free radical initiator (1.5 wt.% of monomers) according to [10].

The copolymer of acrylonitrile with styrene (SAN) was used as an electron-accepting polymeric matrix



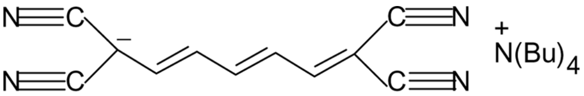
SAN

The following anionic polymethine dye (AD) and cationic polymethine dye (CD) were used as sensitizers of photoconductivity:



CD

where $n = 1$, $An^{-} = BF_4^{-}(1)$;



AD

The films of polymeric composites based on SAN with 1%wt. addition of anionic (AD) and (or) cationic polymethine dye (CD) as photoconduction sensitizers were obtained. The samples were prepared both with the open surface of a polymeric film applied onto glass substrates and as the sandwiched structures [2] of polymeric composites films with ITO (SnO_2:In_2O_3) and Ag contacts. In these films, the molar concentrations (N) of AD and (or) CD were 2.10^{-5} mol g^{-1}. Higher dye concentrations are impractical, because these molecules can form the aggregates of clusters in polymeric films, thus not allowing us to identify the films with solid solutions [11]. The thickness of the films was $1.2 \pm 0.1\,\mu m$.

The absorption coefficient and luminescence spectra of films samples were measured in the wavelength range $\lambda = 400$–1000 nm with a KSVIP-23 complex. The density and the kinetics of a dark current (j_d) and a photocurrent (j_{PH}) in the sandwiched samples were measured using a storage oscilloscope. The value of j_{PH} was determined as an increment in j_d upon the irradiation of samples with monochromatic light at $\lambda_{irr} = 630$ nm and 532 nm close to the absorption maximum of dyes. The light intensity (I) in the range of 0.2–5 W/m^2 was varied by neutral light filters. The external electric field strength (E) in the samples films was varied in the range of $(1\text{–}7)\cdot 10^7\ V\cdot m^{-1}$. All experiments were carried out at a temperature of 295 K, at which the films of photoconducting polymeric compositions generally operate in practice.

RESULTS AND DISCUSSION

The copolymer SAN was synthesized. The films of polymeric composites based on SAN with 1% (weight) addition of anionic (AD) and (or) cationic polymethine dye (CD) were obtained. The films of pure SAN are transparent in the visible and near infrared regions, and they haven't photoconductivity in this area. In SAN films which contains dye additives, the bands of absorption ($\lambda_{max} = 540–550\,nm$) and photoluminescence ($\lambda^{L}{}_{max} = 570–580\,nm$) (Fig. 1) are determined by excitation and relaxation of the excited states of dye's molecules.

The increase of the electroconductivity of SAN films that contained dye additives was detected by comparison with the electroconductivity of pure SAN films (Fig. 2).

The current density of electroconductivity was greater in the case of a negative voltage on the Ag-contact of investigated sandwich-structures (Fig. 3).

The photoconductivity of SAN films with AD addition was detected on the photoexcitation in the dye absorption region (Fig. 4).

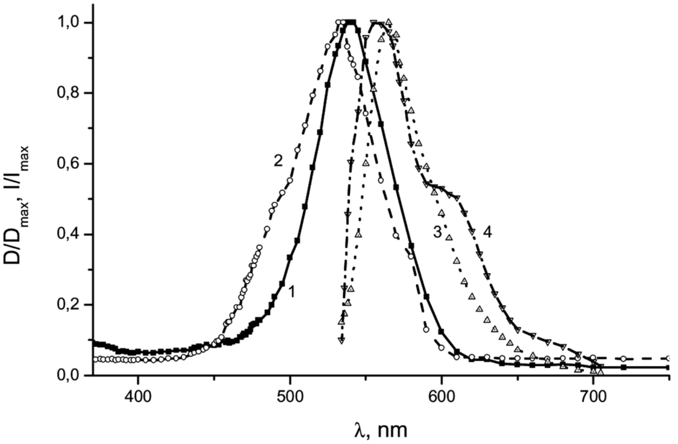


FIGURE 1 Normalized absorption (1–2) and photoluminescence (3–4) spectra of the investigated composites films based on SAN + 1%wt. AD–(1–3) and SAN + 1%wt. CD–(2–4).

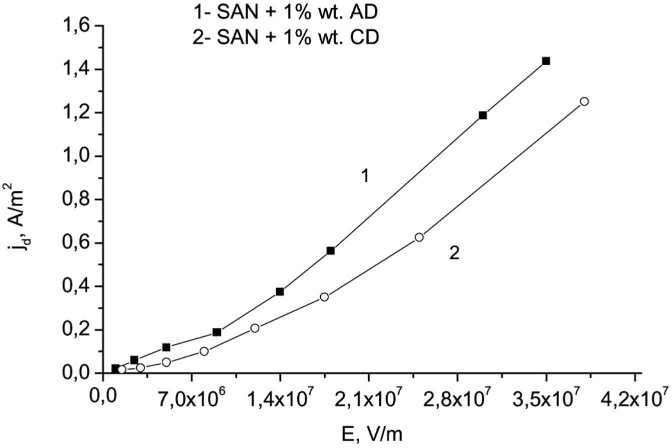


FIGURE 2 j_d vs. E dark dependences in samples of sandwich-structures (+) ITO-SAN + 1%wt. AD-Ag (–) (1) and (+) ITO-SAN + 1%wt. CD-Ag (–) (2) in the case of a negative voltage on the Ag-contact.

The photoconductivity of SAN films with CD additions wasn't found out on the irradiation in the visible region of light. The dependence of the current density of photoconductivity (j_{PH}) on the external electric field (E) can be approximated by straight lines in the coordinates

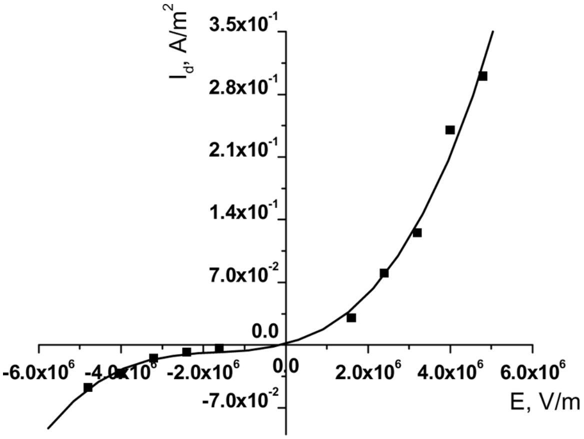


FIGURE 3 Current-Voltage (j_d–E) dark characteristics of the sandwich-structure ITO-SAN + 1%wt. AD-Ag at the different polarities of the applied voltage. The current density of electroconductivity j_d is greater in the case of a negative voltage on the Ag-contact. Here, $\lambda_{irr} = 532\,nm$ and I = 1 W/m^2.

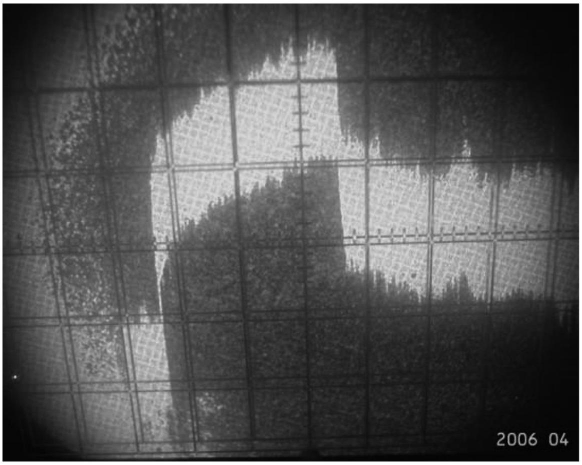


FIGURE 4 Photograph of a kinetic oscillogram of the time dependence of the photocurrent j_{PH} after the beginning of irradiation and after switching-off the light in the sandwich-structure (+) ITO-SAN + 1%wt. AD-Ag (–). Here, $\lambda_{irr} = 532\,nm$ and $E = 2{\cdot}5{\cdot}10^7\,V/m$. (1 unit of time-scale = 15 s (horizontal axis)).

$\lg j_{PH} - E^{1/2}$ (Fig. 5) (from their slopes, the Poole-Frenkel constant can be calculated), and j_{PH} depends on the intensity (I) of the light of photoexcitation as $I^{1/2}$.

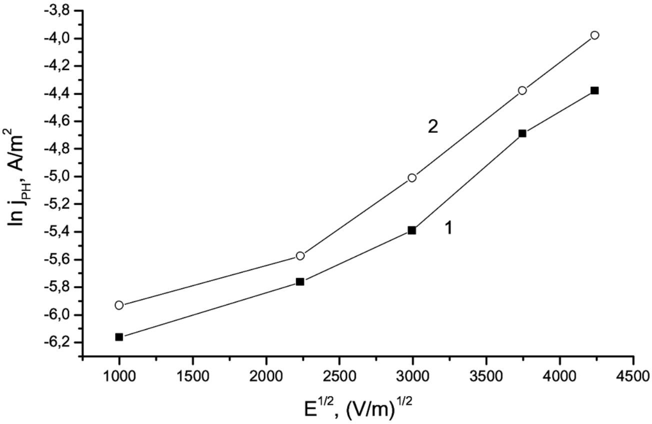


FIGURE 5 Dependence of $\ln(j_{PH})$ on $E^{1/2}$ in the samples of the sandwich-structure (+) ITO-SAN + 1%wt. AD-Ag (–) with $\lambda_{irr} = 532\,nm$, $I = 1\,W/m^2$ (1) and $\lambda_{irr} = 630\,nm$, $I = 3\,W/m^2$ (2).

The last one is an evidence for the large influence of the capture processes on deep traps and from the bimolecular recombination of charge carriers. This allows us to present the process of photogeneration in the investigated anionic dye-doped films SAN [6] by Schemes 1–3.

At the first stage of the photogeneration after the absorption by a molecule of the anionic dye(Dye^-, $N(Bu)_4{}^+$) of a light quantum with energy $h\nu$ (since the colourless counterion $N(Bu)_4{}^+$ of a dye molecule-does not absorb photons in the visible region, only a coloured anion of AD is shown below and is indicated as Dye^- in schemes 1–3), a geminal electron-hole pair (EHP) will be formed. For both researched dyes, independently of the sign of a charge of their ions, the highest occupied molecular orbital (HOMO) is occupied by two electrons. At the excitation, they separate, owing to transferring one of them on a LUMO. The presence of unpaired electrons sharply raises the reactivity of ions of a dye in the S_1 state. Therefore, the electron transfer from LUMO of the excited coloured anion $(Dye^-)^*$ of a dye molecule to the energy-lower LUMOs of adjacent acceptor nitrilic-groups CN of SAN macromolecules can occur with the formation of a geminal EHP. As a result, the neutral form of $Dye^{\bullet}$ and the negative charged form of a nitrilic group ($CN^{\bullet -}$) will be formed:

$$\mathrm{CN} + \mathrm{Dye}^- \xrightarrow{h\nu} \mathrm{CN} + (\mathrm{Dye}^-)^* \longrightarrow \mathrm{CN}^{\bullet -} + \mathrm{Dye}^{\bullet} \tag{1}$$

At the second stage of the photogeneration, the electron recombines with a hole in the dye molecule, in which it was born (geminal recombination according to scheme (2)),

$$\begin{aligned}\mathrm{CN} + \cdots + \mathrm{CN} + \mathrm{CN}^{\bullet -} + \mathrm{Dye}^{\bullet} &\longrightarrow \mathrm{CN} + \cdots + \mathrm{CN} + \mathrm{CN} + (\mathrm{Dye}^-)^* \\ &\longrightarrow CN + \cdots + \mathrm{CN} + \mathrm{CN} + \mathrm{Dye}^- + h\nu_{\mathrm{r},}\end{aligned} \tag{2}$$

or leaves a hole by transferring between adjacent CN-groups in SAN (dissociation of EHP on free charge carriers according to Scheme (3)):

$$\begin{aligned}\mathrm{CN} + \cdots + \mathrm{CN} + \mathrm{CN}^{\bullet -} + \mathrm{Dye}^{\bullet} &\longrightarrow \mathrm{CN} + \cdots + \mathrm{CN}^{\bullet -} + \mathrm{CN} + \mathrm{Dye}^{\bullet} \\ &\longrightarrow \mathrm{CN}^{\bullet -} + \cdots + \mathrm{CN} + \mathrm{CN} + \mathrm{Dye}^{\bullet}.\end{aligned} \tag{3}$$

At the recombination of charge by Scheme (2), the excessive electron can transfer from the LUMO of a negatively charged nitrilic group $CN^{\bullet -}$ on the LUMO of the neutral form $Dye^{\bullet}$ with the appearance of the excited dye-anion $(Dye^-)^*$ of an AD molecule. After the relaxation of the excited state with energy release $h\nu_r$, this molecule of an anionic dye again can absorb a light quantum and participate in the photogeneration of EHP. As a result of the dissociation of EHP by Scheme (3), the electrostatic interaction of an electron with a hole localized in Dye$^{\cdot}$(or, in detail, Dye$^{\cdot}$, N(Bu)$_4^{+}$) is weakened. With a rise of E, the probability of the dissociation of EHP and, consequently, j_{PH} are increased. On the contrary, the probability of the geminal recombination is decreased. For the cationic dye, the probability of the electron transfer from the LUMO of an excited CD-molecule to the LUMO of SAN is essentially decreased because of the strong electrostatic repulsion under the interaction between the charge of a cation of a CD-molecule and a free hole in this molecule. Therefore, CD have appeared not capable to accept a hole from SAN. For this reason, a film based on it has no photoconductivity.

A long exposure of the films to light in the anionic dye absorption region is accompanied by an increase of the electroconduction current after the blackout, when $E = 0$, and turning again on the external electric field. The recombination rate of EHP was estimated in such experiments as $k_r = 1.1{\cdot}10^{-2}\,\mathrm{s}^{-1}$ (Fig. 6) (such low value of k_r agrees with the above-mentioned conclusion).

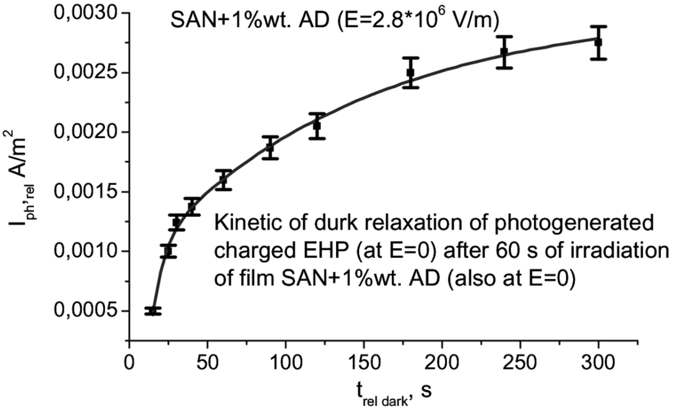


FIGURE 6 Dependence of $\Delta j_{\mathrm{PH,\ relax}} = j_{\mathrm{PH,\ relax,}\ (t\,=\,0)} - j_{\mathrm{PH,\ relax,}\ (t)}$ ($j_{\mathrm{PH,\ relax}}$ – density of the photocurrent which was registered at the turning of the external electric field $E > 0$ after irradiating the samples during 60 s (at $E = 0$) and the further dark recombinational relaxation of a photogenerated charged EHP (under conditions when $E = 0$)) on $t_{\mathrm{relax\ dark}}$ (time of dark relaxation). The recombination rate of EHP (k_r) was estimated in these experiments as $k_r = 1.1{\cdot}10^{-2}\,{\cdot}\mathrm{s}^{-1}$.

The value of the electroconduction current is repairing in the course of time after the end of irradiation.

CONCLUSIONS

Based on the above-presented facts, we conclude that the photoconductivity of composites (at the excitation by light from the dye absorption region) is caused by the electron transfer from photoexcited molecules of the anionic polymethine dye to accepting nitrilic groups of the polymer with the further transfer of electrons between nitrilic groups of SAN to SAN. The electron transfer from SAN to the light-excited dye molecule hasn't occur in the case of cationic dye (according to the scheme of the photogeneration of EHP). Therefore, we consider that the composites based on SAN with the additions of the anionic polymethine dye are characterized by the electronic type of conductivity.

Such polymeric composites could be studied for the purpose of the creation of new photoconducting materials for optoelectronic applications.

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