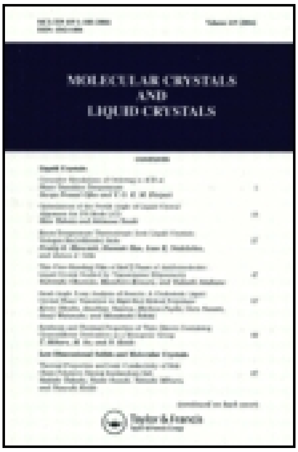

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Sensitization of Photosemiconducting Properties of Holographic Recording Media Based on Glycidylcarbazole Cooligomers by Organic Dyes

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Version of record first published: 03 Mar 2011

To cite this article: N. A. Davidenko, S. V. Dehtarenko, Yu. P. Getmanchuk, A. A. Ishchenko, A. V. Kozinetz, L. I. Kostenko, E. V. Mokrinskaya, S. L. Studzinsky, V. A. Skryshevsky, O. V. Tretyak & N. G. Chuprina (2011): Sensitization of Photosemiconducting Properties of Holographic Recording Media Based on Glycidylcarbazole Cooligomers by Organic Dyes, Molecular Crystals and Liquid Crystals, 535:1, 148-155

To link to this article: http://dx.doi.org/10.1080/15421406.2011.537969

Mol. Cryst. Liq. Cryst., Vol. 535: pp. 148–155, 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.537969

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Sensitization of Photosemiconducting Properties of Holographic Recording Media Based on Glycidylcarbazole Cooligomers by Organic Dyes

N. A. DAVIDENKO,[1] S. V. DEHTARENKO,[1] YU. P. GETMANCHUK,[1] A. A. ISHCHENKO,[2] A. V. KOZINETZ,[1] L. I. KOSTENKO,[3] E. V. MOKRINSKAYA,[1] S. L. STUDZINSKY,[1] V. A. SKRYSHEVSKY,[1] O. V. TRETYAK,[1] AND N. G. CHUPRINA[1]

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Photophysical and information properties of the holographic recording media (HRM) based on films of ferrocenyl-containing siloxane oligomer, glycidylcarbazole-butylglycidylic ether cooligomer, ferrocenemethylated oligoglycidylcarbazole, and cooligomer of o-carboxybenzoilferrocene glycidylic ether doped with squarilic dye and(or) with merocyanine dye based on ferrocene and tetranitrofluorene are investigated. It is found that the holographic sensitivity is absent for the media based on ferrocenyl-containing siloxane oligomer, and that the holographic sensitivity is present for the films based on glycidylcarbazole. It has been found that the holographic sensitivity and the photoconductivity of the media based on glycidylcarbazole cooligomers increases with the ferrocene content. This effect has been explained by the influence of iron ions on the rate of singlet–triplet conversion in photogenerated pairs of charges.

Keywords Electron-hole pair; ferrocene; holographic recording media; oligomers; photoconductivity; spin catalysis

1. Introduction

The films of polymeric composites (FPC) which contains ferrocene $Fe(C_5H_5)_2$ or its derivatives can have photosemiconductor properties [1,2]. These properties are promising for the use of ferrocene-containing FPC in the information media for optical information recording and storage. Such FPC can be used in holographic recording media (HRM) for the recording of photothermoplastic holograms [2]. The FPC photoconductivity in the visible range of the spectrum is provided by

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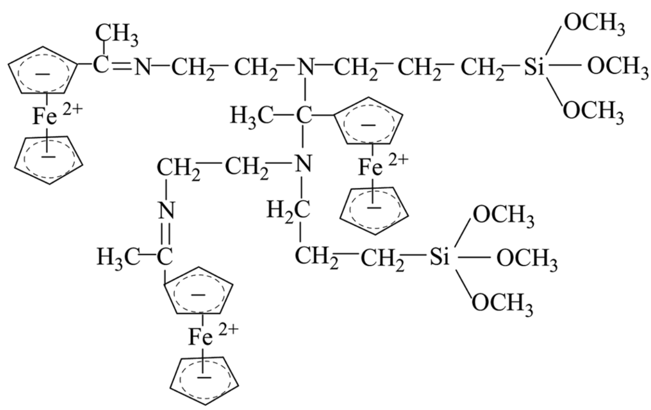
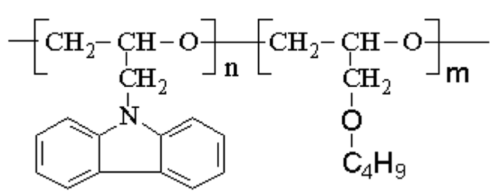
additives of organic dyes, whose molecules after the light quantum absorption are capable of nonequilibrium charge carriers photogeneration [3]. However, the possibility to use the ferrocene-containing FPC in HRM was studied insufficiently. In the present work, we report on the results of the comparative investigation of the FPC photoconductivity and information characteristics of HRM on their basis. As the light absorption centers and charge carriers photogeneration centers, we used intraionic dyes: squaraine and merocyanine dye based on ferrocene and tetranitrofluorene [4].

2. Samples and Experimental Technique

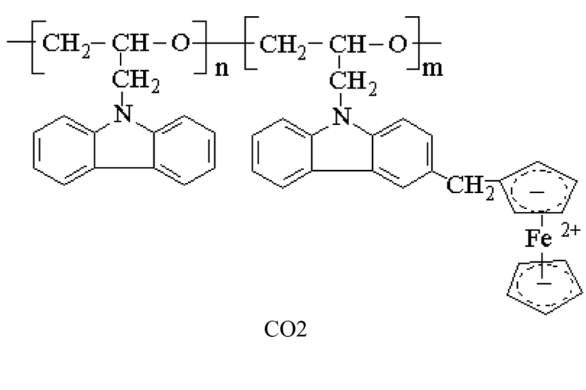
The ferrocenyl-containing siloxane oligomer (FSO), cooligomer of glycidylcarbazole with 10 mol.% butylglycidylic ether CO1, and ferrocenyl-containing cooligomers CO2 and CO3 were used for FPC prepared. In the investigated oligomeric systems, the concentration of ferrocenyl groups ($Fe(C_5H_5)(C_5H_4)$) increases in the series CO2, CO3, and FSO:



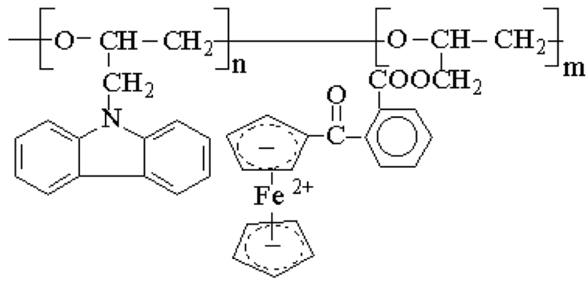
FSO



CO1

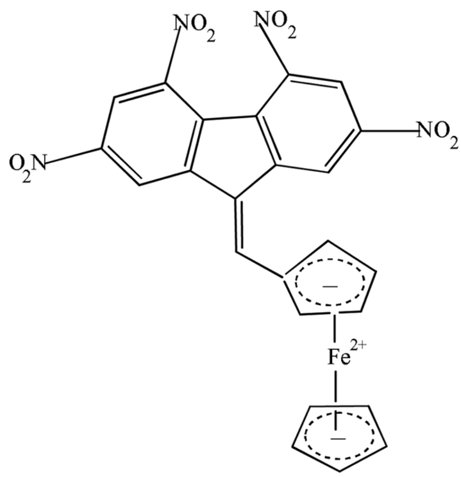


CO2

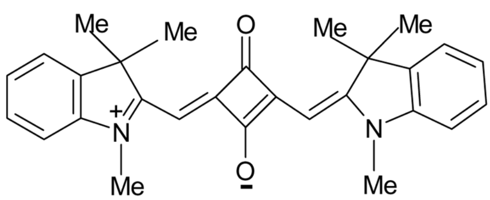


CO3

As a photoconductivity sensitizer, we used merocyanine dye (Fe-MD) for FPC based on FSO and squarilic dye (SQ) for CO1-CO3 – based FPC.



Fe-MD



SQ

The basis of the choice of such dyes is as follows: the Fe-MD molecules contain ferrocenyl ($Fe(C_5H_5)(C_5H_4)$) terminal groups; in the FSO-based FPC after their (Fe-MD molecules) excitation by light, the intermolecular electronic transitions (transfer) between Fe-MD and FSO molecules are not forbidden. The latter is caused by the approximate equality of the energies of frontier orbitals of Fe-MD and FSO molecules [3]. SQ molecules in the excited state are able to capture electrons with carbazolyl fragments in photoconducting FPC [5].

The samples were prepared both with an open surface of a polymeric film applied onto glass substrates (glass substrate – SnO_2: In_2O_3 – FPC) and as sandwiched structures of films of polymeric composites with ITO (SnO_2:In_2O_3) and Ag contacts (glass substrate – SnO_2: In_2O_3 – FPC – Ag). In these films, the concentrations of Fe-MD and (or) SQ were 1 wt.%. To determine the information characteristics of HRM in the recording mode of photothermoplastic holograms [2,6], FPC were applied onto glass substrates $50 \times 40\,mm^2$ in size coated with a transparent SnO_2: In_2O_3 conductive sublayer with a resistance of $20\,\Omega$, with two Ag-contacts on opposite sides of the substrate. The thickness of FPC films was $1.0\,\mu m$. A semiconductor laser with the light emission wavelength $\lambda = 650\,nm$ was used as a coherent light source. The controlled parameter was the maximum diffraction efficiency (ϕ) of the recording of a flat wave front hologram. The value of ϕ was determined for the -1 light diffraction order depending on the energy ($I \cdot t$) of light incident on HRM, where I is the light intensity, and t is the exposure time. To determine ϕ, the hologram was developed from the initial temperature $T = 293\,K$ to a temperature above the hologram erase temperature to the complete curing of FPC's surface relief.

The optical density (D) spectra of investigated films were measured in free surface samples in the wavelength range 400–1000 nm. Samples of the sandwich structure were used to measure the photocurrent density (j_{PH}) as functions of the external electric field strength (E) applied to electric contacts and the external magnetic field strength (H). Irradiation was performed from the conductive layer's SnO_2:In_2O_3 side. The value of E in the samples films was varied in the range of 10^4–$10^8\,V/m$. To measure changes of j_{PH} in the external magnetic field, we used an electromagnet. The value of H was varied in the range of 0–5.5 kOe. From these data, we calculated the value $\delta j_{PH} = (j_{PH}(H) - j_{PH}(0))/j_{PH}(0)$, where $j_{PH}(H)$ and $j_{PH}(0)$ – photocurrent density values with ($H > 0$) and without ($H = 0$) the magnetic field applied, respectively.

3. Results

Figure 1 shows the optical absorption spectra for investigated FPCs. Samples with CO1 films without intentionally introduced additives are transparent and have no photoconductivity in the visible region. The same ones based on FSO and CO2-CO3 without introduced dyes additives are characterized by the absorption red edge near $\lambda = 540\,nm$ and $\lambda = 400\,nm$, respectively. The short-wavelength absorption maximum of CO2- and CO3-based FPC near $\lambda = 490\,nm$ is caused by the optical transition in $Fe(C_5H_5)(C_5H_4)$-fragments of FPC.

Therefore, the absorption maximum of FPC doped with Fe-MD near $\lambda = 630\,nm$ (curves *2, 8*) is caused by the absorption of Fe-MD molecules, and the absorption maximum of FPC based on CO1-CO3 with SQ near $\lambda = 650\,nm$ (curves *5–7*) is due to the long-wavelength's optical transition in SQ molecules. We have not registered the hologram recording in HRM based on FPC with FSO. It is found that these FPC have no thermoplastic properties. The last can be supported by the absence of the so-called "frozen" deformation of the FPC surface ("frozen" noise) after the FPC charging in an electric corona discharge and the heating up to temperatures higher than the FSO softening temperature. A "frozen" deformation of the FPC surface is one of the important criteria which indicates the presence of thermoplastic properties and the FPC applicability as the HRM. In addition, we have not recorded the holograms in the HRM based on FPC with CO1 + Fe-MD. This fact can be explained by the insignificant photoconductivity of such FPC (with CO1 + Fe-MD) in the red spectral region.

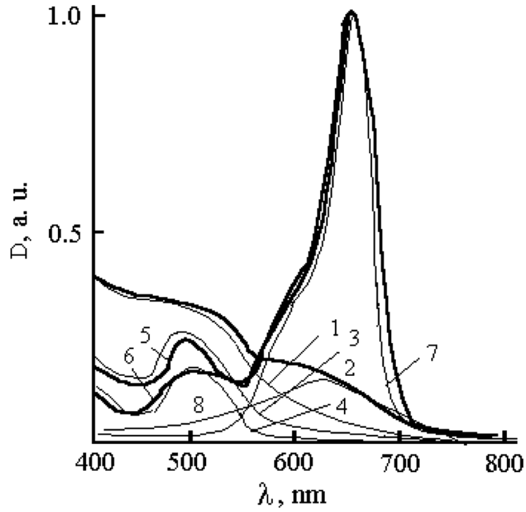


Figure 1. Absorption spectra of the investigated films based on FSO (*1*), FSO +1 wt.% Fe-MD (*2*), CO2 (*3*), CO3 (*4*), CO1 + 1 wt.% SQ (*5*), CO2 + 1 wt.% SQ (*6*), CO3 + 1 wt.% SQ (*7*), CO1 + 1 wt.% Fe-MD (*8*).

However, the photoconductivity of FPC based on FSO doped with Fe-MD is sufficiently high, and its value is comparable with that for FPC based on carbazolyl-containing cooligomers doped with SQ (Fig. 2). The $\lg j_{PH} - E^{1/2}$ dependence (Fig. 2) can be approximated by straight lines and represented by the analytical expression $j_{PHst}(E) \sim \exp[-(W_{0PH}\text{-}\beta E^{1/2})/k_B T_{eff}]$. Here, W_{0PH} is the activation energy of the photogeneration at $E = 0$, k_B is the Boltzmann constant, $T_{eff}^{-1} = T^{-1} - T_0^{-1}$, and T_0 is the characteristic temperature. The coefficient β can be calculated from the experimental results. This expression can be used to describe the photogeneration of charge carriers in the FPC which are used as HRM [2,7].

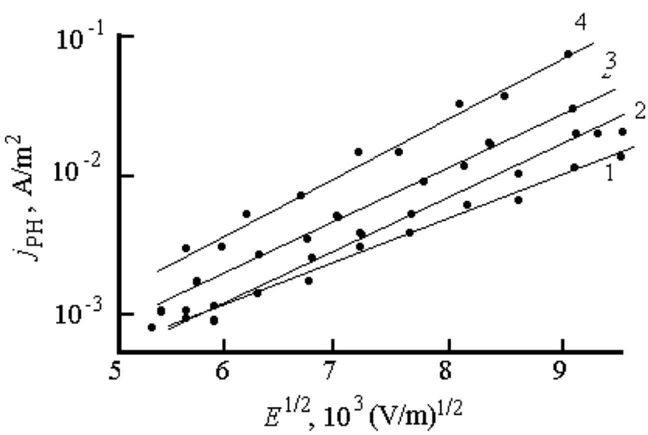


Figure 2. Dependences of $\lg j_{PH}$ on $E^{1/2}$ in the FPC samples of sandwich-structures based on FSO + 1 wt.% Fe-MD (*1*), CO1 + 1 wt.% SQ (*2*), CO2 + 1 wt.% SQ (*3*), CO3 + 1 wt.% SQ (*4*). Here, $I = 50\ \mathrm{W/m^2}$.

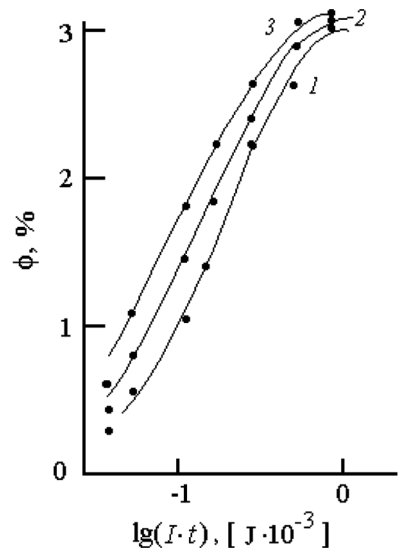


Figure 3. Dependences of the diffraction efficiency ϕ on the exposure $(I \cdot t)$ measured during the recording of the flat wave front holograms (a semiconductor laser with $\lambda = 650\,\text{nm}$) with a spatial frequency of $500\,\text{mm}^{-1}$ in HRM with films CO1 + 1 wt.% SQ (*1*), CO2 + 1 wt.% SQ (*2*), CO3 + 1 wt.% SQ (*3*).

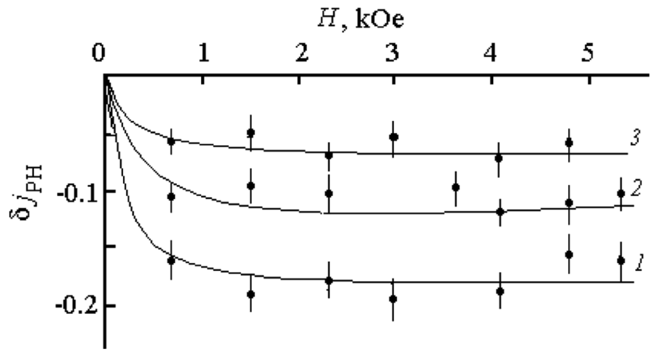


Figure 4. δj_{PHst} vs. H for the s samples of sandwich-structures based on CO1 + 1 wt.% SQ (*1*), CO2 + 1 wt.% SQ (*2*), CO3 + 1 wt.% SQ (*3*). Here, $E = 2 \cdot 10^7\,\text{V/m}$.

In Figure 3, we present the dependence of ϕ on $I \cdot t$ which indicates that the HRM photosensitivity increases in the series SQ-doped FPC CO1-CO3. The last fact correlates with the photoconductivity increase in this FPC series (Fig. 2).

It is also established that, in these FPC series, the influence of an external magnetic field (H) on j_{PH} decreases (Fig. 4).

4. Discussion of Results

It is known that FPC for HRM should have thermoplastic properties, the low dark electroconductivity, and the high photoconductivity at the used laser light emission wavelength [2]. According to the previously accepted model of photogeneration and transport of charge carriers in FPCs with organic dyes [3], the internal photoeffect in the investigated FPC is related to the generation of nonequilibrium current carriers after the light absorption by dye molecules and the transport of current carriers in the polymeric matrix. In the FPC based on FSO doped with Fe-MD, the current carriers are formed. In an external electric field, they are transferred between the ferrocene fragments of FSO. However, the absence of thermoplastic properties of FSO does not allow using these FPC in HRM. In the CO1- based FPC doped with Fe-MD, the low efficiency of the photogeneration of charge carriers is related to the fact that the ferrocenyl-group ionization potential (I_p) in a Fe-MD molecule less than the ionization potential of carbazolyl fragments in CO1 (6.72 eV and 7.46 eV, respectively). Therefore, the process of electron capture by Fe-MD molecules from carbazolyl fragments is impossible.

Among all investigated FPC, the CO1-CO3 based FPC with SQ additions is considered to be the most promising for the use in the HRM. The increase in j_{PH} in the series of FPC based on CO1-CO3 can be associated with an increase in the concentration of oxidized ferrocenyl-fragments (ferrocenium cation-radicals) playing the role of a spin catalyst of the singlet-triplet conversion in EHPs [8,9]. To clarify this assumption, let us suppose that, after the light absorption by SQ molecules, electron-hole pairs (EHP) are formed in the singlet state. The EHP dissociation probability can be increased due to an increase in the singlet-triplet conversion rate in EHP, namely, due to the presence of paramagnetic particles near EHP [8,9]. Such particles are oxidized by ferrocenyl-fragments, whose concentration increases from $2.7 \cdot 10^{26}\,\mathrm{m}^{-3}$ to $1.3 \cdot 10^{27}\,\mathrm{m}^{-3}$, when CO3 is used instead of CO2. During the EHP photogeneration, carbazolyl cation-radicals which are oxidizers of ferrocenyl groups are formed. In this case, high-spin ferrocenium cation-radicals (with a central Fe^{+3} ion) are formed as well. These high-spin paramagnetic fragments affect the singlet-triplet transition rate in EHP. The last is supported by the measurements of the dependence of δj_{PH} on H which is shown in Figure 4. The negative sign of δj_{PH} dicates the formation of EHP mainly in the singlet state [8]. Flattening the dependence δj_{PH} on H for $H \leq 1$ kOe suggests the need to consider the spin-dependent effects in the mechanism of photogeneration of charge carriers for the studied FPCs, of which the hyperfine interaction mechanism is characteristic. Since $|\delta j_{PH}|$ decreases for $H > 1$ kOe, when CO2- and CO3-based FPC are used instead of CO1-based FPC (as the ferrocenyl-groups concentration in FPC increases), we can conclude that an increase in the $Fe(C_5H_5)_2$ concentration in FPC facilitates an increase in the EHP singlet-triplet conversion rate, hence, an increase in j_{PH} and ϕ values.

The low diffraction efficiency and the low photosensitivity obtained in our experiments are explained by low squarilic dye-sensitizer SQ concentrations (1 wt.%) in the investigated systems. Such cooligomer media can be used as convenient model systems to realize the spin catalysis effect of ferrocene-fragments on the holographic recording. On the other hand, it is well known that, at the use of this squarilic dye SQ with a concentration of 3–5 wt.% for CO1 coolygomer composite films, it is possible to obtain a diffraction efficiency of 20–25% and a high photosensitivity [2,3]. But, at such concentrations, dye SQ can aggregate [2,3] (both the hole- and electron-type photoconductivities appear in the system), and the correct analysis of both the spin catalysis phenomenon and the effect of an external magnetic field on the photoprocesses in the dye nonaggregated monomer in these systems becomes very difficult.

5. Conclusions

The FPC based on FSO doped with Fe-MD have photoconducting properties in the Fe-MD light absorption range, but they cannot be used as HRM due to the absence of thermoplastic properties of FSO. However, ferrocene-containing FPC may be effective for their use in HRM. It is established that the photoconductivity and the holographic sensitivity of HRM based on carbazolyl-containing FPC doped with SQ increase, if ferrocenyl-groups is introduced into the FPC composition. This effect is caused by the influence of oxidized ferrocenyl-fragments, ferrocenium cation-radicals, on the spin conversion of photogenerated EHPs, namely with the increase in the singlet→triplet transition rate in EHP. The triplet EHPs have a longer life-times and a less EHP dissociation probability into free current carriers. The obtained results can be used to develop not only new HRM, but also media for OLEDs, photoelectric converters of solar energy, and photomagnetic and magnetooptical information media.

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