Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Spin-dependent Effects in Charge Photogeneration Mechanism in Amorphous Molecular Semiconductors

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Version of record first published: 04 Oct 2006

To cite this article: Nikolay Davidenko, Nkolay Kuvshinsky, Leonid Kostenko & Dmitriy Misik (1998): Spin-dependent Effects in Charge Photogeneration Mechanism in Amorphous Molecular Semiconductors, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 324:1, 71-76

To link to this article: http://dx.doi.org/10.1080/10587259808047136

*Mol. Cryst. Liq. Cryst.*, Vol. 324, pp. 71–76
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# Spin-dependent Effects in Charge Photogeneration Mechanism in Amorphous Molecular Semiconductors

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The paper is devoted to the investigation of multiplicity and evolution of multiplicity in the course of life of electron-hole pairs in the films of poly-N-epoxypropylcarbazole, containing the CT-complexes, the compounds with intramolecular charge transfer as the electron-hole pair photogeneration centres. The main results were obtained from the analysis of the effects of external magnetic and electric field influence on photoconductivity.

Keywords: electron-hole pairs; multiplicity; photoconductivity

The results of investigation of amorphous molecular semiconductor (AMS) films based on carbazole containing polymers (poly-N-epoxypropylcarbazole (PEPC), polystyrol with N-isopropylcarbazole) doped with organic acceptors, for example TNF, or compounds with intramolecular charge transfer (CICT) are given. In a visible part of spectrum electrons and holes in these films arise as result of photogeneration from excited states: from CT-complexes between carbazole and TNF or from CICT. The value of photoconductivity (G) is proper for these films utilization as the recording medium for holography[1]. However, limit significance G yet has not been reached at the present time, because during the first stage of photogeneration the probability of electron-hole pair

(EHP) formation is not equal to 1. Only a part of photogenerated EHP could dissociate due to small time of singlet EHP annihilation as compared with time of EHP dissociation. That is why the effects of magnetic (H) and electric (E) fields influence on G and AMS films photoluminescence were studied within the region of photoabsorbtion of photogeneration centers. The investigations were carried out in the samples of sandwich structure with blocking contacts for different temperatures, concentrations and molecule types. In AMS with CT-complexes growth of probability of EHP photogeneration under H influence was observed. The time constant of this effect is comparable with time of magnetic nucleus spin-lattice relaxation. Besides that, a multiplicity change of dissociating EHP was found under H influence. It was concluded, that multiplicity change occurs in accordance to UFI mechanism[2] for EHP with distances between charges r>13Å, as well, as for EHP with distances r<13Å. Therefore, initial EHP spin state alters with low efficiency if carrier mobilities increase. The last conclusion was confirmed by growth of quick effect of H influence on G under temperature the growth and acceptor molecules concentration increase. The correlation between the concentrations of photogenerated singlet and triplet EHP depends on light quantum energy ($h\nu$), because quick effect of H influence on G depends on $h\nu$. On $h\nu$ increase the probability of intercombination conversion in photogeneration center grows and a part of photogenerated triplet EHP increases correspondingly. Free current carriers appear, mainly, as result of triplet EHP dissociation. The highest degree of triplet EHP existence was observed in AMS with CICT employed as the photogeneration centers[3,4]. In these AMS under E=0 the probability of singlet EHP photogeneration is small and photoluminescence probability is great. For E>>0 singlet EHP photogeneration is possible, besides triplet EHP. Thus, in AMS with CICT G growth may be reached by means of amplification of a intramolecular interconversion channel.

Samples were of a sandwich-structure Al-PEPC+Nm.%TNF-$SnO_2$, where PEPC+Nm.%TNF are the PEPC films with Nm.% 2,4,7-trinitro-9-fluorenone (TNF) with thicknesses L=1-5 μm. The peculiarities of an external magnetic field influence on G were investigated in these samples. The magnitudes of G were calculated from the linear dependence of experimentally measured values of saturation photocurrent $j_f$ on L: $j_f = qGL$, where q is the electron charge.

Features of H on G were investigated using the results of the measurements of G kinetics in magnetic field. Kinetics of H on G was found from the experimentally measured $\{(j_f(H)-j_f(0)\}/j_f(0)=\delta$ on t. After magnetic field switching on $\delta(t)$ increases within the region of negative values, reaches maximum values and then changes the direction and passes to the saturation stage. Dependence $\delta(t)$ growth within the region of negative values occurs during the time $t<3\cdot10^{-2}$ s. The value $\delta$ decrease until the saturation occurs approximately during 1s. Described character of current behavior after magnetic field switching off allows to suppose, that bouth positive and negative effects of H on G are present simultaneously in $\Delta G/G(H)$. The value $\delta_-=-\Delta G/G$ in the maximum of $\Delta j_f/j_f(0)$ corresponds to the stationary value of a negative effect. The difference between $\Delta G/G$ in the maximum and in the saturation of this dependence corresponds to the stationary significance of positive effect ($\delta_+$). It should be noted that the stationary values of both positive $\delta_+$ and negative $\delta_-$ effects are independent on the sample orientation in respect to the magnetic field direction. Besides, the measurements of spin-lattice relaxation time ($T_1$) of protons in the films PEPC and PEPC+Nm.%TNF were carried out using NMR spectrometer "BRUKKER" in magnetic field H=47 kOe at T=77-350K.

Time constants of G decrease under magnetic field H is less than the time constant of magnetic induction increase. The time constant of slow $\delta_+$ is equal to $0.6 \pm 0.1$ s and is independent on E, N and λ, but it changes with T and

reaches a maximum value 0.9 $\bar{+}$0.1 s at the temperatures T=200 $\bar{+}$15 K. It should be stated, that although in magnetic field H=47 kOe the time $T_1$ of spin-lattice relaxation of protons differs by 3-4 times from the time constant of $\delta_+$ for H<6.2 kOe. However, the dependencies of the time constants on temperature are in correlation.

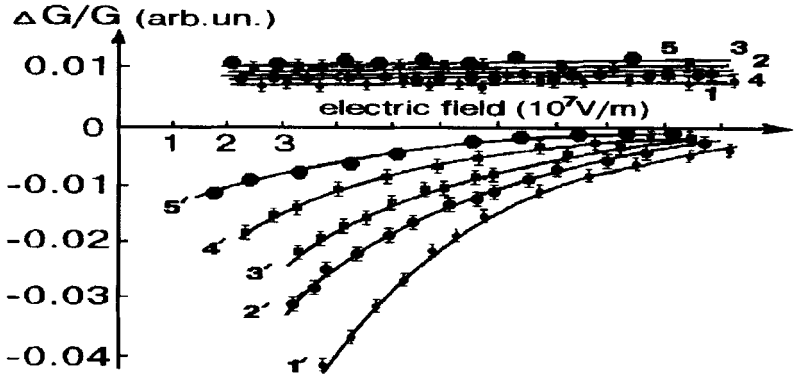


FIGURE 1. The dependencies of the respective change of current carriers photogeneration efficiency in magnetic field H=1 kOe on the electric field strength in the sample Al-PEPC+11m.%TNF-$SnO_2$ for $\lambda$=630 nm (1, 1'), 576 nm (2, 2'), 511 nm (3, 3'), and in the sample Al-PEPC+1m.%TNF-$SnO_2$ for the light wavelength $\lambda$=630 nm (4, 4'), 511 nm (5, 5'). T=293 K.

The dependencies of $\delta_+$ and $\delta_-$ on magnetic field strength are plotted in Fig.2. Temperature dependencies of $\delta_-$ and $\delta_-$ are plotted in Fig.3. The dependencies of the same effects on the number of $CH_2$ groups in the chain R of acceptor molecules, that determines the molecular weight M are shown in Fig.4. These dependencies were measured in the samples Al-PEPC+0.5m.%TNF-$SnO_2$ and Al-PEPC+3m.%R-DDFK-$SnO_2$ respectively, where R-DDFK is the 2,7-dinitro-9/dicyanmethylene/fluorene-4-oic acid.

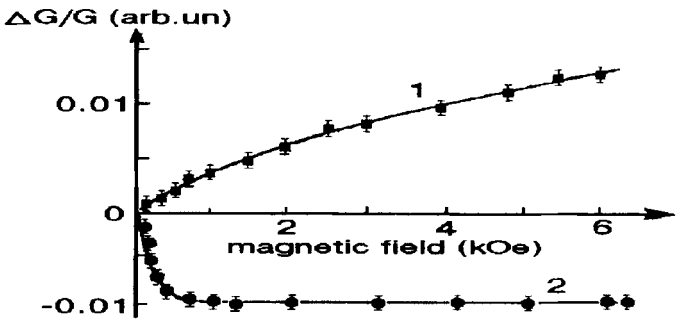


FIGURE 2. Changes of the positive (1) and negative (2) effects of magnetic field influence on the current carriers photogeneration efficiency in magnetic field in the sample Al-PEPC+5m.%TNF-$SnO_2$ for the light wavelength $\lambda$=576 nm, temperature T=293 K, electric field strength $E=5\cdot10^7$ V/m.

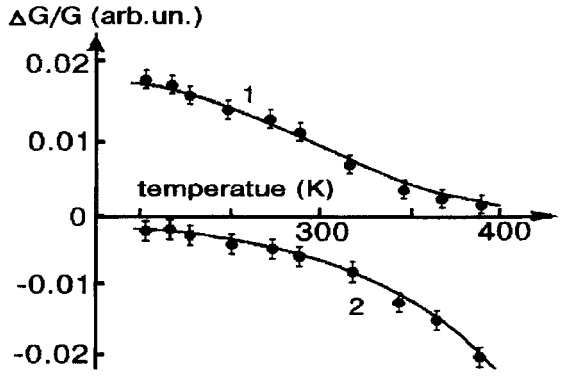


FIGURE 3. Temperature dependencies of the positive (1) and negative (2) effects of magnetic fields influence on the current carriers photogeneration efficiency in the film PEPC+5m.%TNF for H=1 kOe, $E=5\cdot10^7$ V/m, $\lambda$=511 nm.

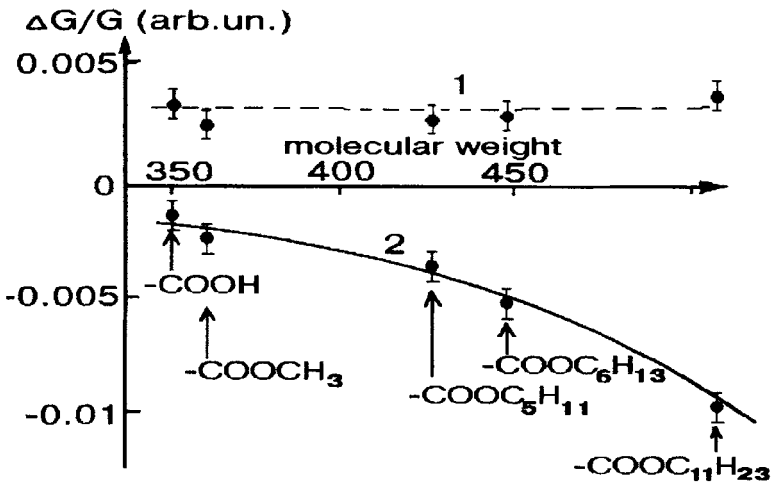


FIGURE 4. Changes of positive (1) and negative (2) effects of magnetic field influence on the current carriers photogeneration efficiency with the acceptor's molecular weight alterations in films PEPC+3m.%R-DDFK for $E=5\cdot10^7$ V/m, T=293 K, λ=630nm.

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