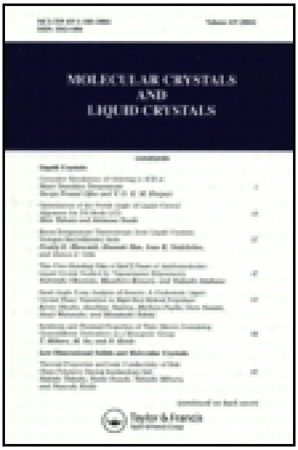

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

# Reversible Formation of Charge Carrier Traps in Poly(Phenylenevinylene) Derivative due to the Phototransformation of a Photochromic Additive

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Version of record first published: 31 Aug 2006

To cite this article: Martin Weiter, Martin Vala, Ota Salyk, Oldřich Zmeškal, Stanislav Nešpůrek & Juliusz Sworakowski (2005): Reversible Formation of Charge Carrier Traps in Poly(Phenylenevinylene) Derivative due to the Phototransformation of a Photochromic Additive, Molecular Crystals and Liquid Crystals, 430:1, 227-233

To link to this article: http://dx.doi.org/10.1080/15421400590946433

*Mol. Cryst. Liq. Cryst.*, Vol. 430, pp. 227–233, 2005
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590946433

# Reversible Formation of Charge Carrier Traps in Poly(Phenylenevinylene) Derivative due to the Phototransformation of a Photochromic Additive

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*Kinetics of photochromic reaction of spiropyran dissolved in a poly(phenylenevinylene) derivative MEH-PPV was studied by optical and impedance spectroscopy. Spiropyran forms metastable, highly polar merocyanine under illumination with light of an appropriate wavelength. Due to charge-dipole interactions, charge carrier traps are formed and affect electrical properties of the polymer matrix, namely capacitance and photoconductivity.*

**Keywords:** electrical properties; photoconductivity; photochromism; spiropyran

This work was supported by the grant 203/03/133 from the Czech Science Foundation and by the grant 4 T09A 132 22 from the Polish Committee for Scientific Research.

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## INTRODUCTION

Nowadays multistable molecular systems attract much attention because of their potential use in optical and electro-optic devices such as broadband optical modulators, holographic and image-forming media, rectifiers and switching devices [1–3]. Molecular materials offer good processibility, low cost and easy modification of mechanical, optical and electrical properties by minor modification of their chemical structure. Current research has been mainly focused on systematic synthesis of novel chromophores in order to prepare doped polymeric matrices with enhanced electro-optic coefficients. Relatively little attention has been paid to the examination of electrical properties of such systems.

Guest molecules will in general have different energy levels from the host. In particular, if ionization energies and electron affinities are suitably different, charge carrier traps can be formed. A special type of traps may occur if guest molecules possess a permanent dipole moment. The dipole moment contributes to the field acting on surrounding molecules and influences polarization energy. These dipolar traps are formed on neighboring host molecules, even though the impurity itself does not necessarily form a chemical trap. In our earlier papers [4–6] the concept of an electroactive molecular material was put forward whose electrical properties would be controlled by optical switching of photochromic species, either admixed into the polymer matrix or chemically attached to the polymer chain. The purpose of the present work is to examine the influence of charge carrier traps formed by photochromic additive on electrical properties of a $\pi$-conjugated polymer matrix.

## EXPERIMENT

The studied system consisted of $\pi$-conjugated photoconductive poly[2-methoxy, 5-(2′-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) doped with 5 wt.% of photochromic spiropyran (SP): 6-nitro-1′,3′,3′,-trimethylspiro[2H-1-benzopyran-2,2′ -indoline]. The films, typically 150 nm thick, were prepared by spin coating of chloroform solutions onto an indium tin oxide (ITO) electrode or quartz glass substrate. Vacuum evaporated 100 nm thick top Al electrodes completed the sandwich structures for electrical measurements. Dielectric properties were studied using a Hewlett Packard 4192 A impedance analyzer. The time dependences of capacitance and conductance were recorded at constant frequency (1 kHz). The reaction converting SP into its merocyanine (M) colored form was activated using a mercury discharge lamp HBO-200 with band filter (360 ± 20) nm. The measurements were performed in vacuum in the temperature range 298–350 K.

## RESULTS

The photochromic behavior of spiropyran derivatives has been investigated by many researchers [7–9]. Under irradiation spiropyran exhibits photochromism as shown in Fig. 1. The compound is stable in its colorless closed-ring isomeric form, while UV irradiation produces a metastable open-ring isomer (M) absorbing at 550–600 nm. The absorption spectra of molecules constituting the studied system are shown in Fig. 2. The maximum of absorption band of MEH-PPV is situated at 445 nm, the addition of SP increases the absorption of the sample in the UV region. After irradiation with UV light the spectra exhibit a significant absorption band at 590 nm caused by the colored merocyanine form. The photoinduced color change of SP is caused by the extension of conjugation in the M isomer [10]. Thermal fading in the dark or irradiation with a He-Ne laser gradually restores the original spectrum, the change being fully reversible. The thermal ring-closure for different temperatures is shown in Fig. 3. The changes of the reactant concentration were determined following the absorbance at $\lambda_{\mathrm{max}} = 590$ nm. The thermal reaction in solutions is a first-order process; in our experiments the decays were clearly non-exponential, being better fitted with so-called 'stretched exponential' function [11] in which the concentration of active species ($n_{\mathrm{R}}$) decays with time according to the equation

$$n_R(t) = n_R(0)\exp\left[(-t/\tau)^a\right], \tag{1}$$

where $\alpha$ is a parameter describing the deviation from a purely exponential decay ($\alpha < 1$), $n_{\mathrm{R}}(t)$ and $n_{\mathrm{R}}(0)$ is the concentration of colored species at time $t$ and $\tau$ is a time constant presumed to be described

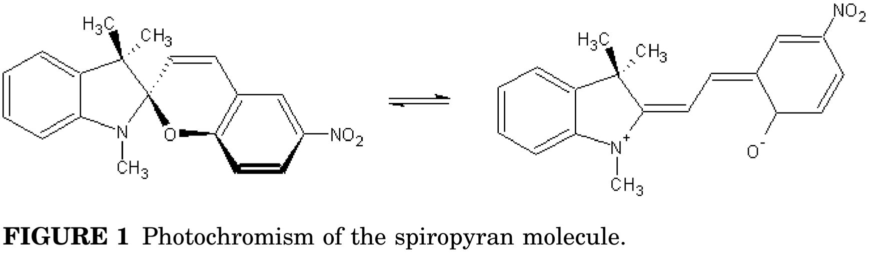

**FIGURE 1** Photochromism of the spiropyran molecule.

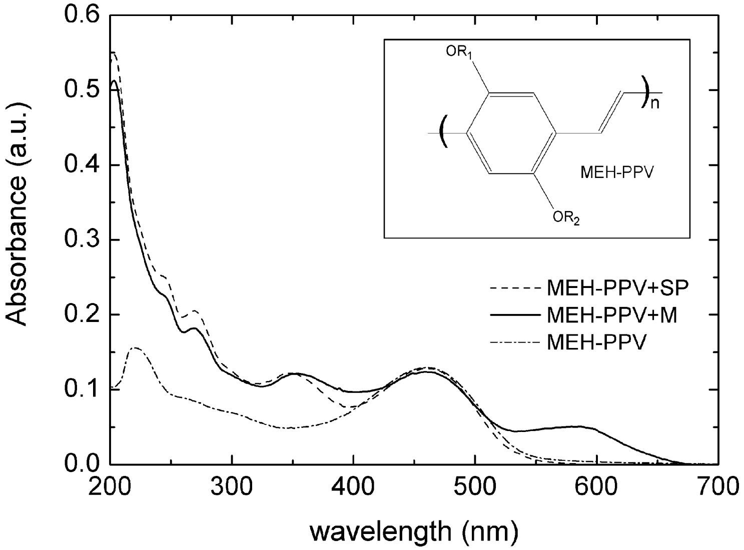

**FIGURE 2** Absorption spectra of the MEH-PPV (dash-dot line), MEH-PPV mixed with spiropyran before (dashed line) and after UV irradiation (full line). In the inset the chemical structure of MEH-PPV is depicted ($R_1$ = methyl, $R_2$ = 2-ethylhexyl).

by the Arrhenius equation

$$\tau - A^{-1}\exp(E_a/RT). \tag{2}$$

In this equation $E_a$ is the activation energy and $A$ is the pre-exponential (frequency) factor. Such a behavior can be rationalized assuming that the process is controlled by a distribution of rate constants. Using the method previously described [12], we determined the parameters of the Arrhenius equation. The analysis of the data depicted in Fig. 3 gives 107 kJ/mol for the activation energy of the dominant process and $2.9 \times 10^{13}\,\mathrm{s}^{-1}$ for the frequency factor.

Dipole moments of stable forms of spiro molecules ranges typically within (2 ~ 5) D depending on substituents attached to their backbones, whereas the moments of the merocyanine form may exceed 10 D. Thus, during the SP→M photochromic reaction dipolar species are formed. As was mentioned above, in polymer matrix they can generate dipolar traps reducing the charge carrier mobility. Consequently, a decrease of the dark current and/or photocurrent can be observed [6]. The formation of traps during the irradiation was checked by impedance measurements. The result is depicted in Fig. 4.

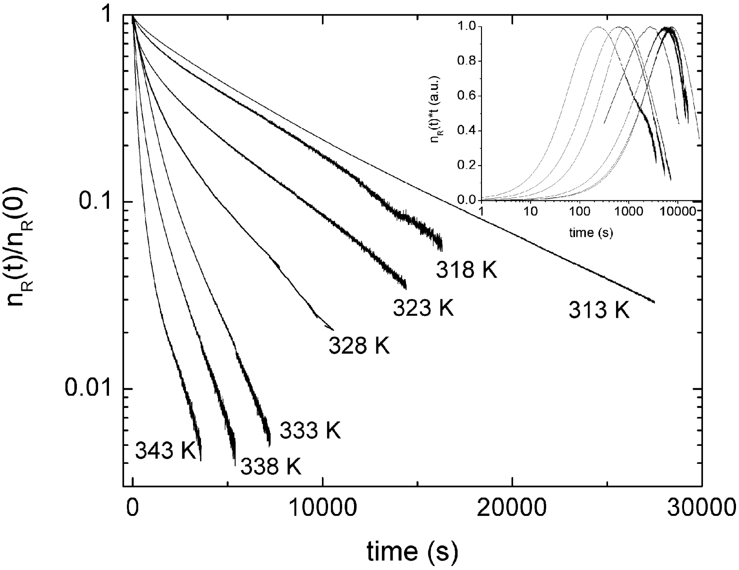

**FIGURE 3** Time evolution of normalized absorbance at 585 nm due to the dark M→SP reaction. The quotient on the vertical axis is proportional to the concentration of the reactant. Inset: (concentration × time) vs. time dependence. The position of the maxima correspond to the inverse of the dominant rate constants [12].

During the illumination of the sample a photocurrent decay was observed instead of expected current saturation; we attribute the phenomenon to the formation of the metastable species during the photochromic reaction. Simultaneously, the capacitance of the system was found to increase due to the formation of dipolar species. When the light was switched off, the rapid decrease of the photocurrent was observed, whereas the capacitance of the system was found to decrease slowly following the kinetics of the the back ring closure reaction, M → SP. The rate constant of the process follows the Arrhenius equation with $E_a = 88\,\mathrm{kJ/mol}$ and $A = 1.9 \times 10^{11}\mathrm{s}^{-1}$. The values are in a qualitatively good agreement with the results obtained from the optical measurements.

## CONCLUSIONS

The kinetics of the reversible photochromic reaction merocyanine → spiropyran, i.e. the slow disappearance of the open-form dipolar species, was studied using the optical and impedance methods. The rates

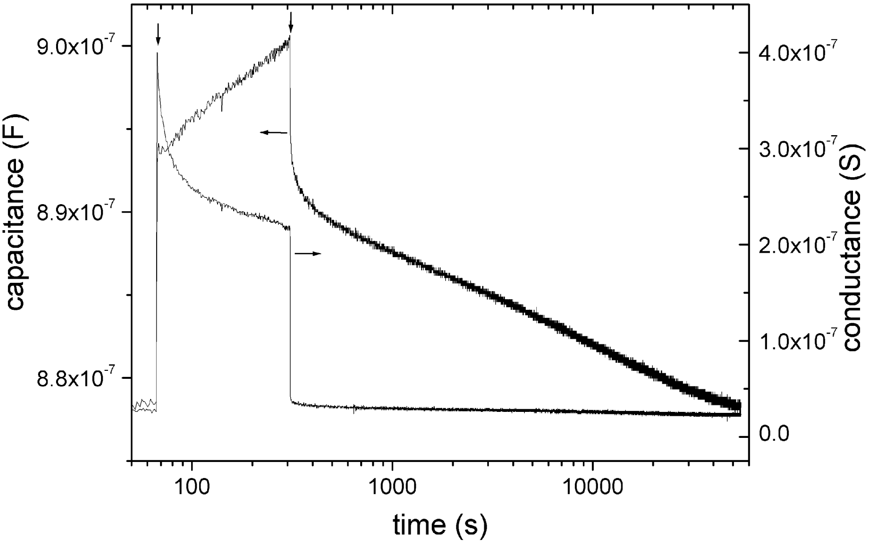

**FIGURE 4** Time evolution of the conductance and capacitance of the sample measured by impedance spectroscopy at room temperature. The vertical arrows indicate the time when the UV irradiation was switched on and off, respectively.

and characteristic parameters of the photochromic processes detected from changes in the capacitance by impedance spectroscopy qualitatively follow the parameters of photochromic changes detected optically. We can conclude that photochromic transformation of spiropyran produced charge carrier traps affecting the electrical properties of the polymer matrix, capacitance and photoconductivity in particular. Thus, an optical signal can be transformed into an electrical one and a polymeric optron can be, in principle, constructed.

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