Light-Induced Change of Charge Carrier Mobility in Semiconducting Polymers

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Summary: Light-driven devices based on reversible change of carrier mobility in semiconducting polymers were investigated. The mobility was altered using a photochromic spiropyran capable of a reversible change of permanent dipole moment and ionization potential. While the latter attribute may result in formation of chemical traps and is more important for matrices with similar ionization potential such as PVK, the former phenomenon results in formation of polar traps and is more pronounced in the case of lower-band-gap materials.

Keywords: charge transport; conducting polymers; poly(phenylenevinylene); poly(vinylcarbazole); supramolecular structures

Introduction

This contribution deals with the concept of a current switch built from polymer materials doped by photochromic compounds capable of reversible switching between ON and OFF states by changing the charge carrier mobility in the semiconducting polymers.[1,2] The colour changes due to the photochromic transformations are also accompanied by changes of other chemical and physical properties, such as emission spectra, refractive index, dielectric permittivity and enthalpy. These modifications are intrinsic in photochromic phenomena and thus offer wider possibilities for practical applications of photochromic compounds. 6-nitro substituted spiropyrans, which can change their dipole moment from ca. 6 D to 12 ÷ 20 D due to a photochromic reaction,[3–5] can be mentioned as examples. The changes in physical or chemical properties transferred to the microenvironment or supramolecular structure further induce modification in the surrounding environment.

It has been shown that dopants added to a surrounding charge-transporting material can produce: (i) chemical traps based on the formation of local centres by the dopant with ionization energy lower and/or electron affinity higher than in the virgin material (for further discussion, see e.g. ref.[6] and references therein), and (ii) dipolar traps created by dopant with high dipole moments. Dipolar traps are based on modification of local values of polarization energy (leading to modification of ionisation energy and/or electron affinity) and broadening of the hopping-states distribution due to the charge-dipole interactions in the environment.[7] Other types of traps, such as traps produced by structure defects will not be discussed in this paper. Based on the calculations performed on model systems, a concept of optoelectrical switch was put forward. The proposed device consists of bistable polar species capable of switching between low-dipole and high-dipole states. In consequence, the created polar traps modify the effective mobility of charge carriers in a reversible and controlled manner.[1,2,8,9] This contribution extends the research to another semiconducting polymer poly(vinylcarbazole).

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Since the structure of the polymer differs from those previously reported, a different switching mechanism is expected.

Experimental Part

All the samples were prepared in the form of sandwich cell of the diode type. The samples were fabricated on a transparent ITO (indium tin oxide) electrode using the spin-coating technique. As a polymer matrix, poly(vinylcarbazole) (PVK) was used. As the active photochromic unit 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-[2H]-indole] (SP) was used. All the chemicals were supplied by Aldrich and were used as recieved. The preparation conditions of the active materials were optimised to obtain typically 150 nm thick layers. The structures were finished by vacuum evaporation of 100 nm thick top aluminium electrode. The average device area was 3 mm^2. The current-voltage characteristics were measured with a Keithley 6517A electrometer. All electric measurements were performed at room temperature under vacuum. Absorption and photoluminescence spectroscopies were used to monitor the photochromic reaction. For optical measurements, thin layers of the same thickness were spin-coated on quartz glass substrates. A xenon arc lamp (450 W) with selected wavelength (360 ± 20 nm) and IR filter were used to switch the photochromic moiety from the stable to metastable state.

Results and Discussion

The photochromic behaviour of spiropyrans was first reported in 1952.[10] Since that time it has been intensively studied for their use as a binary element for computer memories (for further information, see [3]). Absorption of UV light by the spiropyran results in a cleavage of the oxygen-spiro carbon bond leading to the formation of the coloured open-form ($\lambda_{max} = 600$ nm) isomer having a high dipole moment as opposed to the closed form, which is colourless and possess a lower dipole moment. The open form is often called (photo)merocyanine (MC) because it is similar to merocyanine dyes. The MC form reverts thermally to the closed form, which manifests itself as bleaching of the samples. The reverse reaction can be accelerated by absorption of visible light. The reaction scheme and the absorbance change during the reaction is depicted in Figure 1 and 2. It can be seen that, even before the photochromic conversion, some MC forms are present as the system is in its thermodynamic equilibrium (note the logarithmic scale on the y axis). The change of the absorbance is only neat. The electric properties, however, were modified dramatically.

Figure 2 shows the photoswitching of the electric current of the PVK:SP samples with various concentrations of the photochromic SP. It can be seen that addition of a higher amount of SP already led to a decrease in current before the photochromic conversion. The photochromic reaction caused a further reversible decrease in all cases. This behaviour differs from our previous observations where we investigated the influence

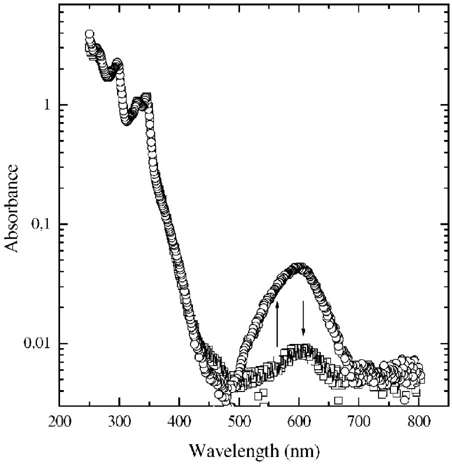

Figure 1.
The absorbance spectra of the PVK:SP 5% (by weight) before (□) and after the photochromic reaction (○). The reverse reaction can be accelerated by illumination with VIS light (longer wavelength absorption band of MC).

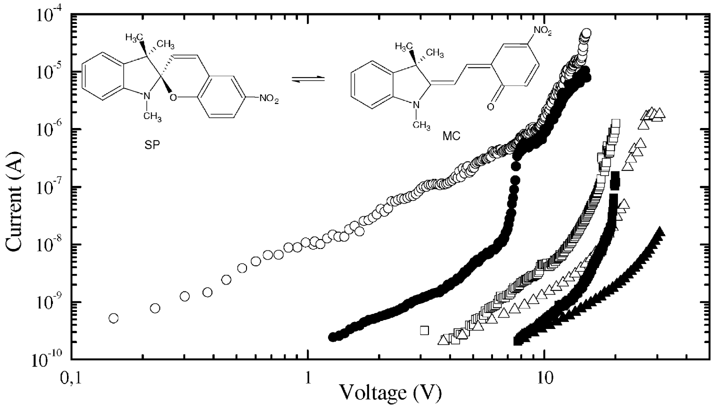

Figure 2.
Current-voltage characteristics of the PVK:SP blends measured before (open symbols) and after (full symbols) the photochromic reaction. Circles represent 2.5%, squares 5% and triangles 10% (by weight) mixtures. The inset shows the photochromic reaction: under illumination of UV light the spiropyran (SP) converts to the metastable (photo)merocyanine (MC) form.

of SP on a series of poly(phenylenevinylene) (PPV) derivatives.[4,9] The addition of SP molecules up to 30% (by wt.) into the PPV matrix does not lead to such decrease.

The carbazole units in the polymer act as individual molecules[11] and the electronic coupling is weaker compared with the PPV polymers. The addition of dopant (SP) led to a more pronounced disorder and thus lowered charge carrier mobility in comparison with the PPV-based systems where few percent of dopant hardly influenced the transport. This results in a lowering of the electric current after addition of SP.

Another remarkable difference is in the behaviour after photochromic conversion. In the case of PPV-based system, the yield of the photochromic reaction was poor[12] and also the reversibility of the current switching was unsatisfactory.[4] These drawbacks are improved in the system based on the PVK matrix.

Figure 2 shows a drop of the current and a change of the shape of the current-voltage characteristics after photochromic reaction. The shape can be interpreted in terms of the space-charge-limited current (SCLC) theory. When the applied electric field is increased, the traps are filled, which is equivalent to a shift of the quasi-Fermi level with electric field. This causes the occupancy of electronic states to change and enables the scanning of the distribution of energy from the current changes. In terms of the present work, the distribution of charge traps describes those induced by the spiropyran–merocyanine photochromic conversion. At a certain voltage the Fermi level crosses over the trap level and the current is no more influenced by this trapping level, approaching the values similar to those before the photochromic conversion (for further discussion, see [13]).

In our previous papers the current switching was explained as a reversible decrease in hole mobility due to the increased trap concentration caused by the presence of an additive with permanent dipole moment forming polar traps.[4] Using the Hoesterey-Letson formalism,[14] it has been shown that the carrier mobility with relative trap concentration c is the product of mobility of the trap-free system μ_0 and trapping factor:

$$\mu(c) = \mu_0 \left[1 + c\exp\left(\frac{E_t}{kT}\right)\right]^{-1}, \qquad (1)$$

where E_t is the energy of trapping level, k is the Boltzmann constant and T is the temperature. It follows that the current flowing through the sample is reduced when the concentration of traps is increased.

Table 1 shows calculated ionization potentials (IP) and electron affinities (EA) reported in literature for the SP and

Table 1.
Energy levels of the compounds.

	EA [eV]	IP [eV]	Ref.
SP – closed	−1.10	−8.79	[15]
SP – opened (MC)	−1.76	−7.09	[16]
PVK	−1.50	−7.60	[11]
MEH-PPV	−1.87	−4.57	[17]

polymers considered in this study. It should be noted that these IP and EA values are for isolated molecules. Therefore they differ from the IP and EA values of the corresponding solid films because of the large solid-state polarization corrections. Since there are no data on SP values of EA and IP in the solid state, we will use these gas phase values to explain the observations.

After the photochromic conversion, the SP molecules change the electronic properties and the IP gain value higher than PVK matrix. This new energetic level inside the PVK band-gap can acts as a trapping level for holes. The photoproduct (MC) also possesses a higher dipole moment and, therefore, also polar traps are produced. The concentration of SP dopant can thus drop to several percent compared with several tenths of percent for the PPV-based systems to achieve current switching withing two orders of magnitude.

The situation in PPV-based systems is different. Since the calculated IP of MEH-PPV is higher than that of the MC form, it is unlikely that the photochromic conversion produces a new trapping level in the MEH-PPV band-gap. Even for rough estimation of the gas-phase IP from the widely used solid-state value (ca. –5.35 eV [18]) considering polarization effect ca. 1.5 eV, we obtain a higher value than the IP of MC. Therefore, the formation of chemical traps is less likely to occur and only polar traps are present.

Conclusions

Charge mobility switching in semiconducting polymers using a photochromic spiropyran was demonstrated. It has been shown that the PVK:SP-based devices allow high performance with a ten-times-lower concentration of the active units compared with the PPV-based devices where the switching process is rather inefficient. However, the actual switching mechanism differs since also the formation of chemical traps is likely to occur as opposed to the PPV-based devices where the position of IP does not allow such behaviour.

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