ROLE OF MOLECULAR CHAIN ORIENTATION ON CARRIER TRAPPING AND TRANSPORT EFFECTS IN POLYMER BLENDS

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We have investigated carrier trapping and transport effects influenced by molecular chain orientation in the samples of poly(9-vinylcarbazole) (PVK) doped with 30% wt 4-dibutylamino-4'-nitrostilbene (DBANS). The orientation of polar DBANS molecules was achieved by applying the electric field above the glass transition temperature; and its effect was investigated by means of Thermally Stimulated Currents (TSCs) method and current–voltage ($I$–$V$) characterization. We demonstrate that the molecular chain orientation causes significant changes both in $I$–$V$ dependences and the TSC spectra. Changes of the TSCs induced by orientation were best expressed in the temperature range of 280–290 K. They could be attributed to the thermally activated process with activation energy of about 0.38 eV.

**Keywords:** carrier transport and trapping, polymers PVK and DBANS, molecular chain orientation

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1. Introduction

Organic electronics is one of the promising and fast developing fields. Particularly, organic-based photovoltaics (PV) can give unique advantages over the traditional silicon based approach from the point of view of production simplicity and convenience. The components used for organic PV devices are potentially cheap, non-toxic, widely available and can be tailored to suit specific needs (e.g., for selective light harvesting). Manufacturing of organic PV devices is straightforward since the low temperature fabrication steps can be used, such as screen-printing, ink-jet printing, and solution spraying. As compared to present (inorganic) PV technologies, the energy and equipment requirements for producing organic PV devices are thus only minor. Furthermore, such deposition routes are compatible with non-heat resistant substrates such as plastics, allowing high throughput reel-to-reel manufacturing of flexible and lightweight PV modules by integrating well-known thermoplastic processing technologies. Organic photovoltaics could thus become a major technology for sustainable electricity generation in the long term.

Organic solar cells might promise a strong cost reduction if fast improvements of the power efficiency and the lifetime can be achieved. To build up efficient photovoltaic cells, a rectifying junction is necessary to effectively spatially separate the photogenerated carriers. One approach to realize such a junction extended over the whole device thickness may be the use of molecular rectification in an oriented amorphous polymer layer incorporating polar molecules. In such layer an internal electric field is introduced and stored and therefore the structure behaves as a distributed homojunction within a single-polymer thin film [1, 2]. This new principle enables one to avoid the necessity of the deposition of several layers, as in the cases of the Schottky or $p$–$n$ junctions. Moreover, bulk of the device could be used more effectively as charge separation occurs in the whole layer. The principle relies on the intrinsic polar nature of organic molecules, and therefore it cannot be readily applied to inorganic semiconductors which are built from spherical atoms, polarity being a crystal cell property. Oriented diode-like molecules – the so-called push–pull molecules used in second-order nonlinear optics [3] – are contained inside a polymer binder. They induce a rectifying effect behaving as a distributed homojunction within a single-polymer thin film [1]. Orientation of dopant molecules can be achieved by application of a static electric field through the polymer film, while heating near the glass transition temperature. Molec-
ular orientation is characterized by an order parameter $\langle \cos \theta \rangle$ [4]. It was demonstrated experimentally that the current–voltage characteristics of oriented Disperse Red 1 (DR1, 4-(N-(2-hydroxyethyl)-N-ethyl)-amino-4'-nitroazobenzene) films attached onto poly(methyl methacrylate) (PMMA) become strongly asymmetric [5]. Moreover, molecular order can be controlled using second harmonic generation (SHG). A new method – voltage-dependent SHG – was proposed to probe the internal field induced in the structure. It was called SEFISHG (Solid Electric Field Induced Second Harmonic Generation) [6] and was demonstrated to be related to the induced rectification behaviour [7].

On the other hand, device efficiency also depends on carrier transport properties, which are given by carrier mobility and trapping. Engineering of macroscopic devices is necessarily based not only on the technological advances and skills, but, in the same amount, on the purposeful control of carrier flows, which in their turn are given by microscopic material properties. Both carrier mobility and trapping effects can be foreknown to depend in different manner on molecular chain type and structure, and on their orientation, too. Usually in conjugated polymers the charges are severely trapped by defect states. This results in reduced electron or hole mobility and imbalance of electron and hole flows, the equality of which is of primary importance for many modern applications of polymer materials, e.g., light-emitting and harvesting devices. Increase of the carrier mobility after the orientation of diode-like molecules was evidenced by the Time of Flight (TOF) method [1]. In this paper we will analyze effect of molecular orientation on charge carrier transport and trapping in the samples of poly(9-vinylcarbazole) (PVK) doped with 30% wt 4-dibutylamino-4'-nitrostilbene (DBANS).

2. Samples and experiment

Effect of molecular chain orientation on thermally stimulated carrier transport was investigated by thermally stimulated current (TSC) and current–voltage characteristics in the samples of PVK (poly(9-vinylcarbazole)) blended with 30% wt DBANS (4-dibutylamino-4'-nitrostilbene). The choice of the DBANS molecules was motivated by the fact that they can be oriented in some polymer matrices (results from nonlinear optics). We used PVK because it is easier to perform orientation within this matrix than within poly(3-alkylthiophene)s (P3ATs) or poly(phenylene vinylen)s (PPVs) and because it is more conductive than para-methoxymethamphetamine (PMMA) (in which it is still easier to orientate). And as for PPV and P3AT, they are most used polymers in photovoltaic cells.

The polymer structures are presented in Fig. 1. Samples were prepared by the spin coating and were 1.3 $\mu$m thick. The blend was deposited on an indium tin oxide (ITO)-coated glass substrate. The samples were provided with evaporated Al contacts on the top.

The molecular chain orientation was performed at 394 K by applying 105 V voltage. The reverse bias was applied to create polarization field oriented in the forward direction and vice versa. The bias was maintained while cooling the samples down to the room temperature. The TSCs and the dark currents were measured after the white-light excitation and without excitation at liquid nitrogen temperature, respectively. During the heating a constant heating rate of 10 K/min was maintained. After each heating cycle the chain orientation procedure was repeated.

3. Methodological background

To quantitatively analyze the trap parameters by fitting the experimental curves we used a TSC model proposed in [8], as it is described in detail in [9, 10]. The kinetics of carrier density at the traps may be described as [8]

$$\frac{dn_t}{dT} = \frac{f_t n_t}{\beta} \exp\left(-\frac{E_t}{kT}\right),$$

(1)

here $n_t$ is carrier density at traps with an activation energy $E_t$, $T$ is temperature, $\beta$ is heating rate, $k$ is Boltzmann constant, $f_t$ is a carrier attempt-to-escape frequency. Assuming that $f_t$ is temperature independent and the initial condition is $n_t(T_0) = n_{t0}$, an approximate solution of Eq. (1) can be obtained that can further be used to calculate the current caused by thermally generated carriers [8]:

$$I = \frac{1}{2} e L A f_t n_{t0}$$
The mobility is given by \[ \mu = \mu_0 \exp \left( -\frac{E_0 - \alpha \sqrt{F}}{kT_{\text{eff}}} \right) \] with \[ \frac{1}{T_{\text{eff}}} = \frac{1}{T} - \frac{1}{T_R}, \] where \( F \) is an electric field strength, \( E_0 \) is an activation energy of the carrier transport at zero electric field, and \( T_R \) is the empirical reference temperature at which mobility is supposed to be known.

In the GDM model the charge transport in disordered organic conductors is supposed to proceed by hopping transport character in disordered organic solids and are based either on a modified Poole–Frenkel (PF) model [12] or a Gaussian disorder model (GDM) [17]. The latter was later extended to include correlation effects [18–20]. In the Poole–Frenkel model the mobility can be described as a field and temperature assisted detrapping process of a carrier from the Coulomb potential of a charged trap. The mobility is given by [12]

\[ \mu = \mu_0 \exp \left( -\frac{E_0 - \alpha \sqrt{F}}{kT_{\text{eff}}} \right) \] (3)

with

\[ \frac{1}{T_{\text{eff}}} = \frac{1}{T} - \frac{1}{T_R}, \] (4)

where \( F \) is an electric field strength, \( E_0 \) is an activation energy of the carrier transport at zero electric field, and \( T_R \) is the empirical reference temperature at which mobility is supposed to be known.

\[ \mu(F, T) = \mu_{\infty} \exp \left[ -\left( \frac{2\sigma}{3kT} \right)^2 \right] \times \exp \left\{ C \left[ \left( \frac{\sigma}{kT} \right)^2 - \Sigma^2 \right] \right\} \sqrt{F}. \] (5)

This equation was derived from Monte Carlo simulations of the hopping processes of charge carriers in a material with energetic \( \sigma \) and positional disorder \( \Sigma \) described by Gaussian distribution functions. \( \mu_{\infty} \) is the high temperature limit of the mobility and \( C \) is a specific parameter that is obtained from the simulations as \( C = 2.9 \times 10^{-4} \text{ (cm/V)}^{1/2}. \)

Behaviour, approximated by both these empirical equations, has been observed in many materials. Experimentally, the main difference between both models is the temperature dependence. A consequence of hopping in a Gaussian DOS is the non-Arrhenius behaviour of the mobility [17]. Nevertheless, within the limited temperature range it is practically impossible to discriminate between both dependences. Furthermore, as stated in [16], the simulations of the GDM reproduced the \( \ln \mu \sim \sqrt{F} \) dependence only in a narrow field range at high fields \((10^8 \text{ V/m})\). Apart from that, both models require many parameters that can be used to fit the experimental data, depending on the preferred model. This causes that actually both approaches can be applied to fit experimental results, basing on the chosen physical mechanism, that in many cases is not known \textit{a priori} [21]. Therefore there are rare examples where a clear distinction between the two models has been possible [22].

Moreover, in hopping systems the thermally activated mobility behaviour can cause appearance of the thermally stimulated current maxima [23]. Therefore in general it is difficult to make a final decision if the results are caused by the change of carrier concentration or their mobility. On the other hand in the latter case the TSC maxima should demonstrate an expressed dependence on the heating rate and applied electric field [23].

4. Results and discussion

First of all the possible effect of orientation was tested by investigating the current–voltage (I–V) characteristics. To avoid a clearly expressed long living sample polarization by high applied electric fields (as it was also observed in, e.g., poly[2-methoxy-5-(2’-ethyl-hexyloxy)1,4-phenylene vinylene] (MEH-PV) and reported in more detail in [10, 24]), measurements were always started from zero fields, and voltage was increased in small steps of 10 mV allowing sufficient relaxation time between the steps. Under such conditions we did not observe any influence of the molecular orientation at 300 K temperature. On the other hand at lower temperatures below about 250 K an expressed effect of the molecular orientation was identified, as it is demonstrated in Fig 2. It is clearly seen that if molecules were oriented in forward direction, i.e., their dipole field to be of the same direction as an external electrical field, creating forward current,
a built-in electric field was created in the sample. This field caused the current flow in an opposite direction at low values of applied reverse bias up to about \(-3.3\) V. Similarly, upon reverse orientation, the built-in field could be compensated by applying about 3.5 V forward bias. Characteristically the observed behaviour can be attributed primarily to the ohmic conduction of the layer volume itself. Meanwhile, e.g., contact effects make only minor influence. It is evidenced by Fig. 3, in which \(I-V\) curves are presented at 300 K in linear scaling. It can be seen that at least up to the electric field strength of \(4\times10^3\) V/cm the sample demonstrates ohmic behaviour with the sample resistance of about \((3.6-4.2)\times10^{12}\) \(\Omega\) and resistivity of about \((1.3-1.7)\times10^{16}\) \(\Omega\) cm. This does not enable evaluation nor of contact parameters, nor of carrier mobility, as it would be possible in case of other prevailing current-limiting mechanisms, e.g., thermionic emission over the contact potential barrier, Fowler–Nordheim tunnelling, or space-charge-limited currents.

Clear effect of the molecular orientation could be observed also in the thermally stimulated current spectra, as presented in Fig. 4. In all the cases marked differences are induced by the light excitation in the thermally stimulated regime, as compared to the unexcited dark currents. As far as PVK has an energy gap of about 6 eV, the observed excitation effects could be attributed to DBANS. The TSCs had the effective thermal activation energies of about 0.037 eV in the temperature region of 166–240 K. Such small values are most probably caused not by carrier generation from traps, but rather by the thermally stimulated mobility growth. This means that mobility can be varied by light excitation. Changes of the TSCs induced by orientation were expressed best in the temperature range of 260–290 K. In the unoriented and oriented in reverse direction samples a clear current dip appears in this region in contrast to the samples oriented in the forward direction.

As can be seen from Fig. 4 near the room temperature higher conductivity is assured upon excitation after the orientation in forward direction, what can offer increase of the light-harvesting device efficiency. Therefore to analyze differences between this case and unoriented sample, we modelled the experimental dependences by taking into account thermal carrier generation from the trap states as well as their mobility changes given by the Gaussian disorder (GDM) and Poole–Frenkel (PF) approximations according to Eqs. (2)–(5). Results are presented in Fig. 5. Nearby
the curves indicating carrier thermal generation, the trap parameters, i.e., their thermal activation energy and initial filling are presented. Values used for the calculation of mobility effect are as follows. Poole–Frenkel model: \( \mu_0 = 5.40 \times 10^{-11} \text{ cm}^2/(\text{V s}), E_0 = 0.152 \text{ eV}, T_R = 1000 \text{ K}, \alpha = 1.95 \times 10^{-4} \text{ eV/(cm/V)}^{1/2} \). Gaussian disorder model: \( \mu_\infty = 1.25 \times 10^{-7} \text{ cm}^2/(\text{V s}), \Sigma = 4.9, \sigma = 0.039 \text{ eV}, C = 5.00 \times 10^{-4} \text{ (cm/V)}^{1/2} \). It is necessary to note that these values used for mobility calculations are only indicative ones, because very similar trends of the curves could be obtained by different sets of parameters. As it is seen from Fig. 5, the important issue is that most fitting parameters were kept unchanged in both cases, evidencing that orientation induces definite changes in the thermally stimulated behaviour. These changes relate to the varying influence of the thermally stimulated process with effective activation energy of about 0.38 eV. This peak appears on the background of the other thermally stimulated process with even higher activation energy, therefore it could be associated not only with thermal carrier generation from the trap state, but also with mobility change.

Notably, the reversely oriented sample exhibits the TSC and the dark current both running significantly higher than in other cases. This indicates a noticeably increasing effect of the thermally stimulated mobility. Unfortunately, usually orientation in reverse direction did not give well reproducible results in contrast to other two cases, therefore additional investigations are necessary to explain its nature. One of the reasons of the steeper mobility increase with temperature could be the necessity for the carriers to overcome higher potential barriers induced by the reverse orientation of molecules.

Above about 310 K the current increase begins with the activation energy of about 0.9 eV. Probably it can be attributed to the carriers thermally excited over the potential barrier at one of the contacts.

5. Summary and conclusions

Carrier transport and trapping effects, as they are influenced by molecular chain orientation, were investigated by thermally stimulated currents and current–voltage characteristics in the samples of poly(9-vinylcarbazole) (PVK) doped with 30% wt 4-dibutylaminoo-4'–nitrostilbene (DBANS). The orientation of molecules was performed by electric field at 394 K. The reverse bias was applied to create polarization field oriented in the forward direction and vice versa. The TSCs and the dark currents were measured after the white-light excitation at liquid nitrogen temperature and without excitation, respectively. We demonstrated that the molecular chain orientation induces significant changes both in \( I–V \) dependences below about 250 K temperature and in the TSC spectra. Well expressed differences between the TSCs and dark currents were evidenced experimentally, depending on the orientation of polar DBANS molecules. The TSCs could be modelled by taking into account mobility variation according to the Gaussian disorder and Poole–Frenkel approximations as well as carrier thermal generation from traps. In the temperature region of 166–240 K the effective thermal activation energies of TSC curves were
about 0.037 eV. Such small values are most probably caused not by carrier generation from traps, but rather by the thermally stimulated mobility growth. This means that mobility can be varied by light excitation. Changes of the TSCs induced by orientation were expressed best in the temperature range of 280–290 K. The numerical fitting revealed that they could be attributed to the thermally activated process with activation energy of about 0.38 eV. Above about 310 K the current increase took place with an activation energy of 0.9 eV, that could be caused by the carriers thermally excited over the potential barrier at one of the contacts.

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References

Santrauka

Buvo tirtos polvinilkarbazolo – PVK (angl.: poly(9-vinylcarbazole)), papildyto 30% masės santykiu DBANS (4-dibutylamino-4′-nitrostilbene) polimeru krūvio pernašos ir pagavimo ypatybės, priklausomai nuo DBANS polinių molekulių grandžių erdvines orientacijos. Molekules buvo orientuojamos išoriniame elektriniame lauke 394 K temperatūroje. Prijungus įtampos laidumo kryptimi, buvo sukurtas poliarizacijos laukas užtvarine kryptimi, ir atviršciai. Taip orientavus bandinio molekules, buvo matuojamos voltamperines charakteristikos (I–V) ir šiluma skatinamųjų srovii (ŠSS) spektrai. Įrodyta, jog molekulių grandžių orientacija turi lemiamą įtaką I–V kreives formai emiu 250 K temperatūros. Taip pat gauti ryškūs ŠSS skirtumai, kuriems išanalizuoti buvo atliekamas ŠSS modeliavimas, atsižvelgiant tiek į krūvininkų šiluminę nerciją iš pagavimo lygmens, tiek į krūvininkų judrijo kitimą, nusakomą Gauso netvarkos (Gaussian disorder) bei Pulio ir Frenkelio (Poole–Frenkel) empiriniai modeliai.

Temperatūros srityje nuo 166 iki 240 K efektingai ŠSS aktyvijos energija tebuvo apie 0,037 eV. Tokios mažos vertės aiškintos ne krūvininkų tankio, bet jų judrijo kitimu. Tai įrodo, jog polimeruose krūvininkų judris priklauso nuo išankstinio suadinimo. ŠSS pokyčiai dėl DBANS molekulių orientacijos buvo ryškiausi temperatūros intervale nuo 280 iki 290 K. Skaitmeninė analizė parodė, jog šie pokyčiai susiję su vienu termiškai aktyvuotu procesu, kurio aktyvijos energija yra apie 0,38 eV. Kai temperatūra didesne nei maždaug 310 K, gautas srovės augimas, pasižymi maždaug 0,9 eV aktyvijos energija, kuris gali būti dėl krūvininkų šiluminės aktyvijos per vieno iš bandinio kontaktų potencialinių barjerų.