Dynamics of photoinduced radical pairs in poly(3-dodecylthiophene)/ fullerene composite

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Abstract

Radical pair laser (660 nm) photoinduced in poly(3-dodecylthiophene)/[1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C61] (P3DDT/PCBM) composite were investigated by the X-band light-induced EPR method in a wide temperature region. Two lines with different magnetic parameters were attributed to non-interacting polaron and fullerene ion-radical. The susceptibility of these centres follow activation law and decrease drastically at $T \geq 180$ K due to their geminate recombination. The spin–lattice and spin–spin relaxation times of these paramagnetic centres were determined separately by the steady-state saturation method. It was shown that two independent spin dynamics processes are mainly realized in illuminated P3DDT/PCBM composite, namely polaron diffusion along the polymer chains with activation energy of 0.071 eV and rotation of fullerene ion-radicals with activation energy of 0.024 eV.

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1. Introduction

Electron and hole transporting materials are of growing interest and importance for photonic and electronic applications. One of the most widely studied photovoltaic devices are thin plastic solar cells [1,2]. If the composite of poly(3-alkylthiophenes) (P3AT) or other conjugated polymers with fullerene or its derivative, [1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C61] (PCBM) is irradiated by light the latter acts as strong electron acceptor attracting an electron from polymer chain. This is accompanied by the simultaneous formation of the donor–acceptor radical pairs of polarons and fullerene ion-radicals $C_6H_5^-$, both with spin $S = \frac{1}{2}$. The power conversion efficiency of solar cells should depend on dynamics properties of these pairs [3], however, spin motion in such composites has not been studied so far.

Photoinduced radical pairs are paramagnetic, therefore, the light-induced EPR (LEPR) method is widely used for investigation of such composites [4–6].

Here we report the LEPR study of magnetic, relaxation and dynamics parameters of polarons and fullerene ion radical laser photoinduced in the P3DDT/PCBM composite in a wide temperature region. We demonstrate non-interacting feature and therefore different interaction of these independent paramagnetic centres with own microenvironment. This allows to determine separately the relaxation and dynamics parameters in of these paramagnetic centres and to analyse the mechanism of spin dynamics in the P3DDT/PCBM composite. Different activation energies obtained are evidences for independence of the motion of the polaron and fullerene ion-radical charge carriers.

2. Experimental

Regioregular P3DDT (a commercial product of Aldrich®) and PCBM synthesized in the laboratory of
This spectrum was attributed to radical pair of diffusing temperatures. By the dotted line the spectrum of the composite without irradiation is shown. The dashed line shows the spectrum calculated by using the data of Table 1. Fig. 1 exhibits also LEPR spectrum calculated with the fitting magnetic parameters presented in Table 1 as well.

Fig. 3 depicts the Arrhenius dependence of spin susceptibility of both paramagnetic centres derived from their double-integrated spectra in non-saturated conditions. The photoexcitation of radical pairs normally occurs in the femtosecond time domain [11,12], therefore this parameter is mainly defined by the probability of their recombination. Assuming that polarons move by tunneling within initial site \( i \) to final site \( j \) with the energy difference \( \Delta E_{ij} \), the recombination rate is [13]

\[
v = v_0 \exp \left( -\frac{2R_c}{\alpha_0} \right) \exp \left( -\frac{\Delta E_{ij}}{k_B T} \right),
\]

where \( v_0 \) is an attempt to recombine frequency, \( R_c \) is the distance between charge carriers, \( \alpha_0 \) the Bohr radius of charge carrier and \( k_B \) the Boltzmann’s constant.

It is seen from Fig. 2 that the temperature dependence of spin susceptibility of both contributions of photoinduced radical pairs follows the Arrhenius law at \( T \leq 160 \text{K} \). The activation energies \( \Delta E_{ij} \) were determined for polaron and fullerene ion-radical diffusion from the slopes of appropriate curves to be 0.006 and 0.021 eV, respectively. If one include Coulomb interactions in this model, these would affect the activation energy for either detrapping or recombination. Assuming that polarons move by tunneling between initial site \( i \) to final site \( j \) with the energy difference \( \Delta E_{ij} \), the recombination rate is [13]

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### Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Polaron P**</th>
<th>PCBM C61*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( g_{xx} )</td>
<td>2.00320</td>
<td>2.00061</td>
</tr>
<tr>
<td>( g_{yy} )</td>
<td>2.00225</td>
<td>2.00030</td>
</tr>
<tr>
<td>( g_{zz} )</td>
<td>2.00145</td>
<td>1.99941</td>
</tr>
<tr>
<td>( g_{xx} )</td>
<td>2.00230</td>
<td>2.00011</td>
</tr>
<tr>
<td>( \Delta B_{pp}^x )</td>
<td>1.04</td>
<td>0.75</td>
</tr>
<tr>
<td>( \Delta B_{pp}^y )</td>
<td>1.04</td>
<td>0.81</td>
</tr>
<tr>
<td>( \Delta B_{pp}^z )</td>
<td>1.02</td>
<td>2.55</td>
</tr>
<tr>
<td>( \Delta B_{pp}^{iso} )</td>
<td>1.03</td>
<td>1.37</td>
</tr>
</tbody>
</table>

### 3. Magnetic resonance parameters

As the compound P3DDT/PCBM is irradiated by laser at \( T = 77–200 \text{K} \), two overlapping LEPR lines with temperature-dependent intensities are observed (Fig. 1). This spectrum was attributed to radical pair of diffusing polarons P** with effective \( g_{iso} = 2.0022 \) and rotating ion-radicals C61* with effective \( g_{iso} = 1.9996 \). Earlier it was shown [9,10], that these radicals demonstrate anisotropic magnetic parameters at 3-mm (W-band, 95 GHz) and 2-mm (D-band, 140 GHz) waveband EPR, so we have to fit both the contributions to the LEPR P3DDT/PCBM spectrum using their anisotropic \( g \)-factors and linewidths (Table 1). Fig. 1 exhibits also LEPR spectrum calculated with the fitting magnetic parameters presented in Table 1 as well.

The spectral linewidth should reflect different processes occurring in the system studied. One of them is the line broadening due to dipole–dipole interaction between mobile
and trapped polarons and rotating fullerenes by $\Delta B_{dd} = \mu_B/ R_0^3 = 4/3\pi \mu_B R_{pc}$ [14], where $\mu_B$ is the Bohr magneton and $R_0$, the distance between dipoles, is proportional to the paramagnetic centre concentration $n_{pc}$ on the polymer chain. Analysis shows that the peak-to-peak linewidth $\Delta B_{pp}$ of the $P^{**}$ and $C_{61}^{**}$ radicals changes with the temperature linearity as $\Delta B_{pp}(T) = 0.81 + 2.5 \times 10^{-3} T$ Gauss and $\Delta B_{pp}(T) = 0.64 + 2.9 \times 10^{-3} T$ Gauss, respectively. Therefore, one obtains $R_0 \approx 2.3–2.5$ nm for the dipolar distance in the P3DDT/PCBM system at the lower temperature limit, when $T \rightarrow 0$.

At the increase of magnetic term $B_1$ of the MW field in the sample the spectra of both the paramagnetic centres are broadened, whereas their linewidth first linearly increases and then starts to decrease as shown in the insert of Fig. 2. Since the signals of these paramagnetic centres were found to be independent of one another, both the spin–lattice $T_1$ and spin–spin $T_2$ relaxation times were determined separately by the steady-state saturation method [8] (insert in Fig. 3).

5. Spin dynamics

There are different dynamics of photoinduced spins in the P3DDT/PCBM system, namely the polaron diffusion along and between the polymer chains with respective diffusion coefficients $D_{1D}$ and $D_{3D}$, and the rotational diffusion of fullerene ion radical around main molecular axis with coefficient $D_c$. These processes should induce an additional magnetic field in the whereabouts of another spin, leading to the acceleration of electron relaxation of both spin ensembles. As the relaxation times of the spin reservoir is defined mainly by a dipole–dipole interaction between the spins, the following equations can be written [15]:

$$T_1^{-1}(\omega) = \langle \omega^2 \rangle [2J(\omega_e) + 8J(2\omega_e)], \quad (2a)$$

$$T_2^{-1}(\omega) = \langle \omega^2 \rangle [3J(0) + 5J(\omega_e) + 2J(2\omega_e)], \quad (2b)$$

where $\langle \omega^2 \rangle = 1/10 \pi^2 \hbar^2 (S + 1) \Sigma_{ij}$ is a constant of the dipole–dipole interaction for powder, $n$ is the number of polarons per eah monomer, $\Sigma_{ij}$ the lattice sum for powder-like sample, $J(\omega) = (2D_{1D} \omega^2)^{-1/2}$ at $D_{1D} \gg \omega_e \gg D_{3D}$ or $J(0) = (2D_{1D} D_{3D})^{-1/2}$ at $D_{3D} \gg \omega_e$ is a spectral density function for Q1D motion and $J(\omega) = \tau_\omega/(1 + \tau_\omega^2 \omega^2)$ for rotational motion with correlation time $\tau_\omega = D_{1D}/(4D_{1D}/L)^2$, $\omega_e$ is resonant angular frequency of the electron spin precession, and $L$ is a factor of spin delocalization over a polaron equal approximately to five monomer units in P3AT [16]. A similar spectral density function was earlier used in the study of spin dynamics in other conjugated polymers [17,18].

The dynamics parameters calculated from Eq. (2) for both paramagnetic centres in photoinduced radical pairs are presented in Fig. 3 as function of temperature.

To account for the LEPR mobility data obtained, the Elliot hopping model [19] has been used. The model based on a hopping of carriers over barriers $E_b$ predicts a frequency dependence of their mobility, $\nu_{1D} \propto D_{1D} \propto \omega_e^s$, where the exponent $0<s<1$ reflects the dimensionality of
the system and depends on the well depth for an isolated wall $E_b$ as $s = 1 - 2k_BT/E_b$. The value of $E_b$ was deduced for lightly doped poly(3-methylthiophene) to be 1.1 eV at $\alpha = 6$ [20]. At activation of the charge carriers through the barrier the rotational diffusion of fullerene should follow the temperature as

$$D_{1D,r}(\omega_e T) = D_{1D,r}^{0} T^{-2} \omega_e \exp\left(\frac{E_b}{k_B T}\right).$$  \hspace{1cm} (3)

The temperature dependences calculated from Eq. (3) with $E_b = 0.071$ and 0.024 eV and shown in Fig. 3 fit the experimental data obtained for radical pairs well. $E_b$ obtained for fullerene lies near that obtained for the triphenylamine/C$_{60}$ complex [21], however, is considerably lesser than that reported for a pure C$_{60}$ rotation [22]. The $E_b$ values determined are close to the energy of lattice phonons in poly(3-octylthiophene) [9] and other conjugated polymers [18].

6. Conclusion

Under excitation of the P3DDT/PCBM composite, two paramagnetic centres are formed; the positive polaron on the polymer backbone, $P^{+\ast}$ and the negatively charged fullerene ion-radical $C_{61}^{-\ast}$. Both radicals are spatially separated due to their low recombination rate, so they can be considered as non-interacting. This leads to difference in their interaction with own microenvironment and, therefore, in relaxation and dynamics parameters, which seems to be an intrinsic feature of the radicals in this composite. For the $P^{+\ast}$ this gives rise to a more noticeable saturation effect at higher microwave power. Photoinduced charge is transferred by polaron along polymer chain in frames of the activation mechanism and then hops to the fullerene molecule. The activation energy of the charge transfer by polaron differs from that determined for rotation of the fullerene molecule. This allows concluding about independence of these processes in the P3DDT/PCBM composite.

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Reference