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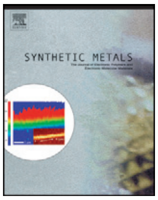

Recombination kinetics of polarons in films of alkylator-sensing co-polymers

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ABSTRACT

We report on the effect of an alkylating agent sensing of a nucleophilic unit, Pyridine-Thiophene (PyTh), on the polaron recombination in a co-polymer [Poly(3-hexylthiophene)]$_n$(PyTh)$_m$ ($m \approx 0.025n$). We show that by exposing the co-polymer to an alkylating agent, such as methyl iodide, the recombination rate increases substantially, possibly due to the introduction of additional recombination pathways created by the charge transfer between the electron deficient alkylated pyridinium sites and the electron rich thiophene polymer backbone.

We also establish the bi-molecular-dispersive nature of the polaron recombination mechanism by following the modulation frequency and excitation intensity dependencies of the polaron photoinduced absorption.

1. Introduction

Poly(3-hexylthiophene) [P3HT] is a well studied and important material for research in organic opto-electronic devices such as organic photovoltaic polymer solar cells [1–4] as well as organic light emitting diodes (OLEDs) [5] and field effect transistors (FETs) [6–8]. Being stable and relatively easy to prepare, co-polymers made of P3HT and alkylator-sensitive compounds can potentially be utilized as sensors for detecting alkylators which are highly reactive and biologically dangerous chemicals [9].

In this work we study the effect of alkylation of a nucleophilic unit, Pyridine-Thiophene (PyTh), on the polaron recombination in a co-polymer (P3HT)$_n$(PyTh)$_m$ ($m \approx 0.025n$). Polarons can readily be photogenerated in P3HT by an above band gap radiation and were thoroughly studied [10–12]. The rate by which these photoinduced polarons recombine depends not only on the polymer structure itself but also on the morphology and purity of the sample. We show that by exposing the co-polymer to an alkylator, such as methyl iodide (MeI), the recombination rate increases substantially, possibly due to additional recombination pathways that are created by the charge transfer interaction between the alkylated PyTh and the bulk polymer backbone.

2. Materials

The co-polymer (P3HT)$_n$(PyTh)$_m$ ($m \approx 0.025n$) was prepared by co-polymerization of 3-hexyl thiophene with FeCl$_3$ in chloroform by purification and de-doping with hydrazine, Fig. 1a. The resulting polymer was characterized by $M_n = 94{,}700$ and $M_w = 180{,}000$; $m \approx 0.025n$ using Gel Permeation Chromatography (GPC) and Nuclear Magnetic Resonance (NMR). More details on the synthesis and characterization will be published elsewhere [9].

All the experiments reported here were performed under reduced pressure in order to remove any volatile molecules from the film. The effect of methanol, ethanol, acetone and isopropanol vapors on the electrical and optical properties were checked and found to be very small and reversible. On the other hand, the reaction with alkylators, reported below, is not reversible and results in the formation of a new covalent bond.

3. Modulated photoinduced absorption and recombination kinetics

The photoinduced absorption (PIA) spectra were obtained by recording the negative relative differential transmission, $-\Delta T/T$, due to the application of periodically modulated (at frequency $f \equiv \omega/2\pi$) optical beam of intensity I_L [13]. The modulated PIA signal is measured using a phase sensitive lock-in technique in which both the in-phase (IP) and quadrature (Q) components are obtained. If $N(t)$ is the time dependent photoexcitation density (which is proportional to the measured $-\Delta T/T$) following the application of the modulated excitation, then the measured IP and Q components are

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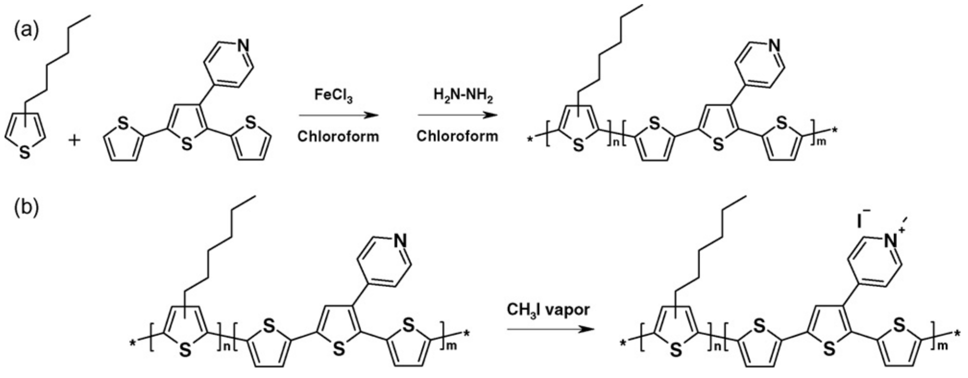

Fig. 1. (a) Preparation scheme of the $(\mathrm{P3HT})_n(\mathrm{PyTh})_m$ ($m \approx 0.025n$) co-polymer. (b) Alkylation scheme of the $(\mathrm{P3HT})_n(\mathrm{PyTh})_m$ co-polymer by methyl iodide.

proportional to

$$N_{\mathrm{IP}}(\omega) = \int_{\mathrm{period}} N(t)\cos(\omega t)\,\mathrm{d}t, \qquad N_{\mathrm{Q}}(\omega) = \int_{\mathrm{period}} N(t)\sin(\omega t)\,\mathrm{d}t. \tag{1}$$

The IP and Q components yield thus complementary information regarding the recombination mechanisms and characteristic lifetime, τ, of the photoexcitations.

The simple recombination processes can be described by the rate equation $\mathrm{d}N/\mathrm{d}t = g - U$, where $U = N/\tau$ or $U = bN^2$ for the mono- or bi-molecular mechanism, respectively. Here, $g \propto I_L$ is the photomodulated generation rate and b is the bi-molecular recombination (BMR) coefficient. The IP component is a monotonic decreasing function of the modulation frequency and it reduces to half its zero frequency value at approximately $\omega_{\max} = (\tau)^{-1}$, where for the BMR process $\tau = (bg)^{-1/2}$ and is thus becoming shorter at high excitation intensity. At this frequency the Q component, being zero at zero modulation frequency, reaches its maximum value [12]. At high frequencies, $\omega \gg (\tau)^{-1}$, for both mono- and bi-molecular processes, $N(\omega) \propto \omega^{-n}$, where $n = 1$ or 2, for the Q or IP components, respectively. Note that for these processes $N_{\mathrm{Q}} = \omega\tau N_{\mathrm{IP}}$.

When a wide recombination rate (or lifetime) distribution significantly affects the kinetics, the behavior of the photoexcitation density is drastically changed. Experimentally it was found in many cases that $-\Delta T(\omega)/T \propto \omega^{-\alpha}$, where $\alpha < 1$ [14–19]. Such a behavior may be described by a recombination process with "dispersive" kinetics, in which the photoexcitation density is expressed as,

$$N(\omega) = \frac{N_0}{1 + (i\omega\tau_0)^{\alpha}}, \tag{2}$$

where $N_0 = g\tau_0$ is the steady state photoexcitation density, g is the photoexcitation generation rate, τ_0 is a "mean" recombination time and $\alpha < 1$ is the dispersive parameter [14]. $g = \eta\Phi$ where $\Phi \propto I_L$ is the impinging photon flux and η is the efficiency of generating the measured photoexcitation. The in-phase and quadrature components are then given by: $N_{\mathrm{IP}} = Re(N)$, and $N_{\mathrm{Q}} = Im(N)$. One of the main features that distinguishes the dispersive kinetics from the "single lifetime" processes discussed above is the high frequency ($\omega \gg \tau_0^{-1}$) behavior. Unlike single lifetime processes, for the dispersive process described by Eq. (2), the high frequency dependence is sublinear: $N(\omega) \propto \omega^{-\alpha}$. For the mono-molecular process τ_0 is independent of g and $N(\omega) \propto g$ for all frequencies. For the BMR process τ_0 is excitation intensity dependent: $\tau_0 = (gb_0)^{-1/2}$, where b_0 is a "mean" BMR coefficient. In this case, it can be seen from Eq. (2) that $N(\omega, g)/\omega$ is a "universal" function of the lumped variable g/ω^2, whose shape is determined by α. Since $-\Delta T/T \propto N$ and $g \propto I_L$, it is useful to plot the experimentally measured $[-\Delta T/T/\omega]$ data as a function of the experimentally determined variable $[I_L/\omega^2]$ in order to obtain a single plot of the I_L dependence of the PIA over a wide range of frequencies [15]. The BMR dispersive kinetics is characterized by unique excitation intensity dependencies in the various modulation frequency regimes; e.g. for $\omega\tau_0 \ll 1$ $N_{\mathrm{IP}} \propto I_L^{1/2}$ (independent of α!) and $N_{\mathrm{Q}} \propto I_L^{(1-\alpha)/2}$. It is therefore important to experimentally study the recombination kinetics on a wide dynamic range, in which both I_L and ω are varied and the lumped variable I_L/ω^2 spans many orders of magnitude.

4. Experimental results and discussion

The absorption and photoluminescence (PL) spectra of films of as-made $(\mathrm{P3HT})_n(\mathrm{PyTh})_m$ ($m \approx 0.025n$) are displayed in Fig. 2 (solid lines), showing typical P3HT features with the optical gap around 2.1 eV and a Stokes shifted PL band with clear vibronic structure. Apparently, the 2.5% of PyTh do not alter significantly the spectra of the pure P3HT polymer [20]. The dotted lines in Fig. 2 represent the spectra of the same film after exposure to MeI. As seen, the main visible effect is rearrangement of the relative intensity of the vibronic side bands. This may be due to changes in morphology upon exposure to MeI that is expected because of the resulting chemical reaction and formation of a localized ion pair. The changes in morphology may also explain the extra tail absorption at around 1.5–1.8 eV.

The PIA spectrum of the as-made co-polymer film $(\mathrm{P3HT})_n(\mathrm{PyTh})_m$ ($m \approx 0.025n$) taken at 80 K and excited with the 515 nm @25 mW/cm^2 Argon ion laser is shown in Fig. 3a. The

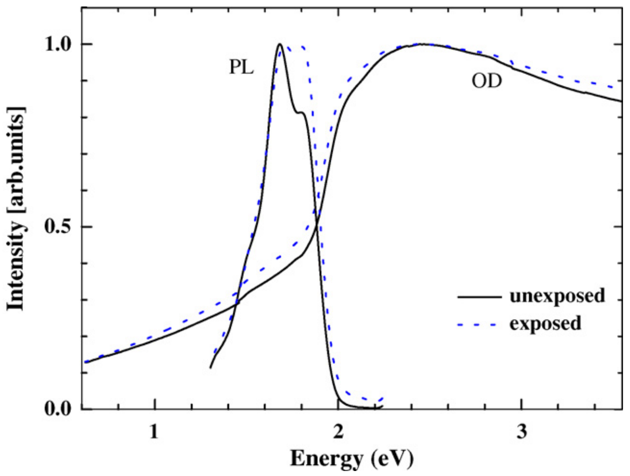

Fig. 2. Solid lines: The optical density (OD) and PL spectra at 80 K of a film of $(\mathrm{P3HT})_n(\mathrm{PyTh})_m$ ($m \approx 0.025n$). Dotted lines: The spectra of the same film after exposure to MeI.