NONLINEAR ABSORPTION IN CONJUGATED POLYMERS: INDUCED TRANSPARENCY

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Abstract - This work concerns the excited state absorption of three conjugated polymers: Poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) MEH-PPV, Poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane-(3-thienyl)-ethanoate] PAzT, and Poly(3-octyl-thiophene) POT. The nonlinear spectra from 450 nm up to 700 nm for the three polymers were obtained, revealing that saturation of absorption occurs due to the ground state depletion for the three polymers. The absorption from the first to a higher excited state is negligible for MEH-PPV and PAzT. In contrast, POT presented absorption for a higher excited state, which allowed the determination of its excited state absorption cross-section.

Introduction

Extensive research on conjugated polymers has been carried out due to its interesting technological features, such as electrical conductivity and large optical nonlinearities, properties related to the conjugation along the polymer backbone. Among the large variety of conjugated polymers, some of them deserve special attention for their unique features: i) PPV-based polymers, and ii) thiophene-based polymers. PPV-based polymers have been studied because of its electrical and luminescent properties, which allows applications in electro- and photo-luminescent devices [1,2]. Thiophene-based polymers are interesting materials given their combination of properties, such as solubility, easy processability and conductivity. A novel class of thiophenic polymers with a side-chain containing azobenzene moieties has been recently reported [3,4]. Azobenzene-based polymers possess interesting linear and nonlinear optical properties given by the azoaromatic chromophores attached to the polymer backbone, and have been exploited for a variety of applications, such as reversible optical data storage [5] and surface relief gratings [6].

Despite of intense theoretical and experimental spectroscopic studies on conjugated polymers, the deep understanding of the photoexcitation mechanism in polymers still requires some effort. In order to probe excited states of materials, spectroscopic techniques employing white-light continuum (WLC) sources [7] are useful owing to its high spectral resolution and time saving. When using such techniques under resonant conditions, the WLC pulse chirp must be considered because of distinct spectral components will reach the sample at distinct times, and cumulative effects such as excited state absorption might occur.

Here we used the WLC Z-scan technique [7] to measure the excited state absorption spectra from 450 nm up to 700 nm of three distinct conjugated polymers: (I) Poly(2-methoxy-5-(2'-


ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV), (ii) Poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane-(3-thienyl)ethanoate], PAzT, and (iii) Poly(3-octyl-thiophene), POT. The resonant nonlinear absorption spectra of the three polymers present saturation of the absorption (SA) in the spectral range studied (from 450 up to 700 nm). A set of rate equations, based on the energy diagram of the polymers, was used to explain the results and fit the experimental data. We determined an electronic transition from the first excited state S\textsubscript{1} to a higher excited state S\textsubscript{n} for POT for wavelengths smaller than 475 nm. The excited state absorption cross-sections have nearly the same magnitude as that of the ground state. In contrast, for MEH-PPV and PAzT the excited state cross-sections are negligible, which indicate none absorption for a higher excited state.

Experimental

MEH-PPV (molecular structure in Fig. 1a) was purchased from Aldrich and dissolved in chloroform solution using a concentration of 0.024 mg/ml for linear and nonlinear optical measurements. PAzT (molecular structure in Fig. 1b) was synthesized according to ref.\textsuperscript{[3]}, and used in our optical experiments with a concentration of 0.037 mg/ml in N,N-dimethylformamide (DMF). POT (molecular structure in Fig. 1c) was synthesized following the procedure similar to that describe in ref \textsuperscript{[8]}, and used with a concentration of 0.065 mg/ml in toluene. All samples were placed in 2-mm thick quartz cuvettes for spectroscopic measurements. The linear absorption spectrum was recorded using a Cary 17 spectrophotometer. The nonlinear absorption measurement was carried out using the WLC Z-scan technique, whose experimental details can be elsewhere \textsuperscript{[7]}.

Results and Discussion

The molecular structures of MEH-PPV, PAzT and POT are shown in Fig. 1a, b and c respectively. By measuring the linear absorption spectrum of these materials and knowing the concentration for each solution, we determined the ground state cross-section (GSCS) spectra for each polymer, which are displayed in Fig. 3 (dashed line).

Through the WLC Z-scan technique \textsuperscript{[7]} is possible to determine the material nonlinear spectrum in a single scan. The Z-scan curves for distinct wavelengths provide the NT spectra (Fig. 2 open circles) for (a) MEH-PPV, (b) PAzT and (c) POT, where only values bigger than one were
found. This implies that in the spectral region studied only saturation of the absorption is observed (450 nm to 700 nm), providing the material optical transparency.

Figure 2 - Ground state cross-section ($\sigma_{01}$; dashed line), experimental Normalized Transmittance (open circles) and theoretical Normalized Transmittance (solid line) as a function of the excitation wavelength for (a) MEH-PPV, (b) PAzT and (c) POT. The inset in (a) shows the three-level energy diagram used to explain the induced transparency of the three conjugated polymers and fit the experimental NT. The inset in (c) shows the values of $\sigma_{n1}$ as a function of excitation wavelength for POT, obtained by fitting the experimental NT.

In order to explain our results, we need to take into account the electronic transitions of the conjugated polymers, which possess electronic spectra composed by an absorption peak between 400 nm and 500 nm (dashed line in Fig. 2), which characterizes their $\pi-\pi^*$ transition.

The inset of Fig. 2 (a) shows the three-level energy diagram employed to fit the experimental NT (open circles in Fig. 2), where $S_0 \rightarrow S_1$ represents the $\pi-\pi^*$ transition. Using this diagram, we established the population dynamics of MEH-PPV, PAzT and POT, in which molecules from the ground state $S_0$ can be promoted to first excite state $S_1$ by one-photon absorption. From this state, molecules can be excited to a higher level $S_n$ and then decay to the first excited state $S_1$ with a relaxation time $\tau_{n1}$ that is much faster than the decay time $\tau_{10}$. Molecules at level $S_1$ may decay radiatively to the ground state $S_0$ with relaxation time $\tau_{10}$ of 260 ps for MEH-PPV [9], 3.3 ps for PAzT [10] and longer than 500 ps for POT [11,12], as depicted in Table 1.
For MEH-PPV (Fig. 3a) we see that the NT (open circles) has approximately the same profile of the GSCS spectrum (dashed line). Such behavior arises from the combination of two effects: i) excitation of molecules from $S_0$ to $S_1$ ($\pi - \pi^*$) by the WLC pulse. In $S_1$ state, MEH-PPV does not present any absorption to a higher excited state for excitation wavelengths between 450 and 700 nm. ii) the long time of $\tau_{10}$ for MEH-PPV, which causes the molecules in the excited state $S_1$ to remain in this state during the WLC pulse, which has 5 ps of positive chirp.

The perfect overlap between the NT (open circles) and the GSCS (dashed line) spectrum is not held for PAzT, as can be seen by the dissimilar profile of curves in Fig. 2b. The NT data follows the GSCS until 500 nm, but as the excitation wavelength moves towards the blue region, the NT decays more rapidly than the GSCS. It is known that this polymer does not present reabsorption from the first excited state for some excitation wavelengths $^{[10]}$. The distinct decrease in the NT for PAzT for wavelengths below 500 nm is owing to two combined effects: i) its fast decay time ($\tau_{10} = 3.3$ ps), avoiding large accumulation of molecules in the first excite state, and ii) the low intensity of the WLC pulse in the blue region (approximately zero below 450 nm), which can not promote a significant population from $S_0$ to the first excited state $S_1$, contributing to decrease in NT.

For POT (Fig. 3c) we observe an even more pronounced difference between the GSCS spectrum (dashed line) and the experimental NT (open circles) compared to PAzT. The NT follows the profile of the GSCS spectrum only until 470 nm and starts to decrease. However, POT decay time ($\tau_{10} > 500$ ps) is much longer than PazT decay time (see Table 1). Such long time contributes for the build up of molecules in the second excited state and consequently, helps to increase NT. However, we clearly see from the experimental data a pronounced decrease of NT for excitation wavelengths shorter than 470 nm. The reason for that lies in the transition of molecules from $S_1$ to a higher excited state $S_n$, which has a non-negligible absorption cross-section, in contrast to MEH-PPV and PAzT. As molecules are pumped by the WLC pulse, they accumulate in the first excited state, and because of the chirp of the pulse, the delayed spectral components excite the molecules from $S_1$ to a higher excited state $S_n$. The fitting of the NT displayed in Fig. 2 (solid lines) were carried out based on the energy level diagram displayed in inset of Fig. 2 (a). The rate equations used to describe the dynamic change of absorption, accordingly to the energy-level diagram, are:
\[
\frac{dn_0(t)}{dt} = -n_0(t)W_{01} + \frac{n_1(t)}{\tau_{10}} + n_1(t)W_{01}
\]

(1)

\[
\frac{dn_1(t)}{dt} = n_0(t)W_{01} - \frac{n_1(t)}{\tau_{10}} - n_1(t)W_{1n} - n_1(t)W_{1n} + \frac{n_2(t)}{\tau_{1n}}
\]

(2)

\[
\frac{dn_{1n}(t)}{dt} = n_1(t)W_{1n} - \frac{n_{1n}(t)}{\tau_{1n}}
\]

(3)

where \( W_{01}(\lambda) = \sigma_{01}(\lambda)I / h\nu \) is the transition rate \( S_0 \rightarrow S_1 \), \( W_{1n}(\lambda) = \sigma_{1n}(\lambda)I / h\nu \) is the transition rate \( S_1 \rightarrow S_{1n} \), \( \sigma_{01}(\lambda) \) and \( \sigma_{1n}(\lambda) \) are the ground state and excited state cross-sections respectively. \( I \) is the excitation intensity, \( n_i(t) \) is the population fraction in each state, \( \tau_{(i+1)i} \) is the relaxation time from state \((i+1)\) to \(i\), \( h \) is the Planck constant and \( \nu \) is the photon frequency. The pump rate, \( W_{ext} = \sigma_{01}(\lambda)I / (h\nu) \), arises from the depopulation from \( S_1 \) to \( S_0 \) by stimulated emission, and was taken into account only for MEH-PPV [13].

We solved this set of equation considering the energy of the WLC pulse composed of a group of bandwidth limited pulses centered at the wavelengths comprising the white light. The red portion of the WLC pulse promotes part of the population to the first excited state \( S_1 \) due to the chirp of the pulse. Consequently, the other spectral components of the WLC pulse probe the excited state absorption (ESA), since the first excite state of all polymers studied here present a lifetime longer (MEH-PPV and POT) or of the same order of magnitude (PAzT) than the pulse duration. The time evolution of the nonlinear absorption, \( \alpha(\lambda,t) \), was calculated according to:

\[
\alpha(\lambda,t) = N[n_0(t)\sigma_{01}(\lambda) + n_1(t)\sigma_{1n}(\lambda)]
\]

(4)

, where \( N \) is number of molecules/cm\(^3\). The first and the second terms in Eq. (4) provide the absorption coefficient of the ground and excited states respectively. The ground state absorption cross-section for every spectral component was determined through the linear absorption spectrum (dashed line in Fig. 2). In this way, the only adjustable parameter in our fitting procedure is the excited state cross-section \( \sigma_{1n}(\lambda) \).

For MEH-PPV and PAzT, we used \( \sigma_{1n}(\lambda)=0 \) for all excitation wavelengths, implying that the material becomes transparent when excited, that is, for both polymers there is no transition from \( S_1 \) to a higher excited state in the region between 450 and 700 nm. In contrast, using \( \sigma_{1n}(\lambda)=0 \) in the spectral region considered for POT we were not able to fit the experimental NT (open circles). If we considered the material to be transparent in the entire spectral region, the theoretical NT would increase as the excitation wavelength moved towards the blue region, which is not observed in the experimental NT (open circles Fig. 3). Therefore, we have to consider the transition \( S_1 \rightarrow S_{1n} \) to occur, whose absorption cross-section values obtained \( (\sigma_{1n}) \) by fitting the experimental data are
displayed in the inset of Fig. 3c. This assumption is in agreement with results presented in the literature reporting transitions from $S_1$ to higher excited states$^{[12,14]}$. Therefore, the induced optical transparency for this polymer is held only until 470 nm, once up to this wavelength the experimental NT starts to decrease because of light re-absorption to a higher excited state.

**Conclusion**

We have measured the excited state absorption spectrum between 450 and 700 nm for three important conjugated polymers: MEH-PPV, PAzT and POT. Saturable absorption was found to be the main nonlinear mechanism for the fast optical transparency of the polymers. In addition, we also determined that higher excited absorption is negligible for MEH-PPV and PAzT. On the other hand, for POT we had to consider the transition $S_1 \rightarrow S_n$ to occur in order to fit the experimental data. The results presented here point out these conjugated polymers, already known for their electronic and luminescent properties, as interesting materials for photonics applications, where fast optical transparency is desirable feature.

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**References**