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Excited state absorption in conjugated polymers: Photoinduced transparency

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Abstract

The understanding of excited states of conjugated polymers is of great interest for photonics, especially for fabricating electroluminescent and optical devices. 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 by means of the white-light continuum Z-scan technique. Saturation of absorption was observed due to the ground state depletion for the three polymers. In addition to this effect, we also observed a small excited state absorption for POT. 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.
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1. 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 allow applications in electro- and photo-luminescent devices [1,2]. In addition, PPV derivatives have already been proposed for photonics application, such as up-converted fluorescence devices, due to its two-photon [3,4] and, more recently, three- and four-photon absorption properties [5]. Thiophene-based polymers are interesting materials given their combination of properties, such as solubility, easy processability and conductivity [6]. A novel class of thiophenic

polymers with a side-chain containing azobenzene moieties have been recently reported [7–9]. These polymers joint the properties of the azobenzene groups with the thiophene-based polymers. Azobenzene-based polymers possess interesting linear and nonlinear optical properties [10–13] given by the azoaromatic chromophores attached to the polymer backbone. Azo-polymers have been exploited for a variety of applications, such as reversible optical data storage [11,14,15], surface relief gratings [15–17] and electro-optical devices [18].

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 lasers have been used. Among these techniques, those employing white-light continuum (WLC) sources [19–22] outstand in characterizing excited states owing to its high spectral resolution and time saving. When using such techniques under resonant conditions, the WLC pulse chirp must be considered because distinct spectral components will reach the sample at distinct times, and cumulative effects such as excited state absorption might occur.

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In this work we used the WLC Z-scan technique [19] 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 nm up to 700 nm). A set of rate equations, based on the energy diagram of the polymers, were used to explain the results and fit the experimental data. We determined an electronic transition from the first excited state S_1 to a higher excited state S_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 no absorption for a higher excited state.

2. Experimental section

MEH-PPV (molecular structure in Fig. 1(a)) 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. 1(b)) was synthesized according to Ref. [7], and used in our optical experiments with a concentration of 0.037 mg/ml in *N,N*-dimethylformamide (DMF). POT (molecular structure in Fig. 1(c)) was synthesized by following a similar procedure to that describe in Ref. [23], and was used with a concentration of 0.031 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 found in Ref. [19]. The WLC was generated by focusing 150 fs pulses at 775 nm from a Ti:sapphire chirped pulse amplified system in distilled water (3 cm path length cell). WLC (8 µJ) in the visible range was generated by employing ∼0.3 mJ at 775 nm. The WLC beam was then recollimated using a $f = 10$ cm lens. The WLC spectrum used in our experiment presents a 250 nm band in the visible region (450–700 nm), with approximately 5 ps of positive chirp. The sample was scanned along the focused WLC beam (z-direction), being the transmitted light recollimated into a spectrometer, which has a resolution of ∼2 nm. The transmittance at distinct z-positions was normalized to the transmittance far from the focus, yielding the normalized transmittance curves (Z-scan signatures) for each wavelength.

3. Results and discussion

The molecular structures of MEH-PPV, PAzT and POT are shown in Fig. 1(a)–(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 [19] it is possible to determine the material nonlinear spectrum in a single scan. Fig. 2 shows experimental Z-scan curves obtained by the WLC Z-scan technique at 460 nm, 480 nm and 500 nm for PAzT. The NT increases at positions close to the focus as a consequence of molecules depletion from the ground state to an excited state, which has a smaller cross-section, causing the optically induced transparency in the sample. This behavior characterizes saturation of absorption (SA), and was also observed for MEH-PPV and POT (not shown).

The Z-scan curves for distinct wavelengths provide the NT spectra (Fig. 3 open circles) for (a) MEH-PPV, (b) PAzT and (c)
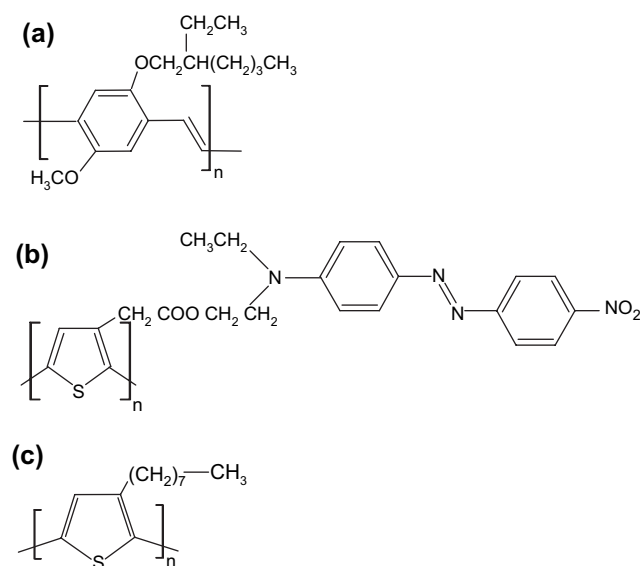

Fig. 1. Molecular structure of (a) poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV), (b) poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-thienyl)ethanoate], PAzT and (c) poly(3-octyl-thiophene), POT.
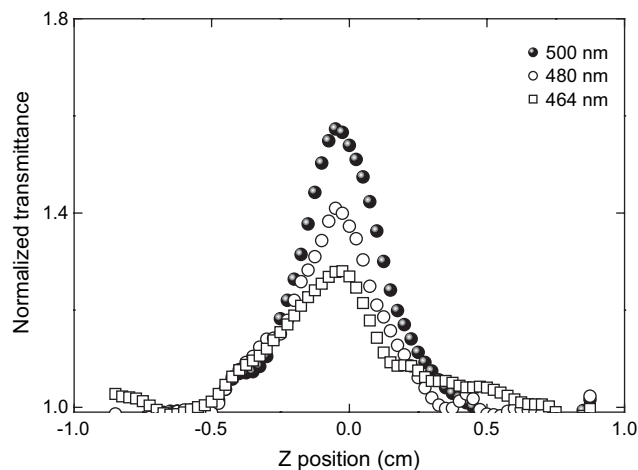

Fig. 2. Experimental Z-scan curves for PAzT obtained at 500 nm, 480 nm and 464 nm, using an input average power of 3.6 mW.
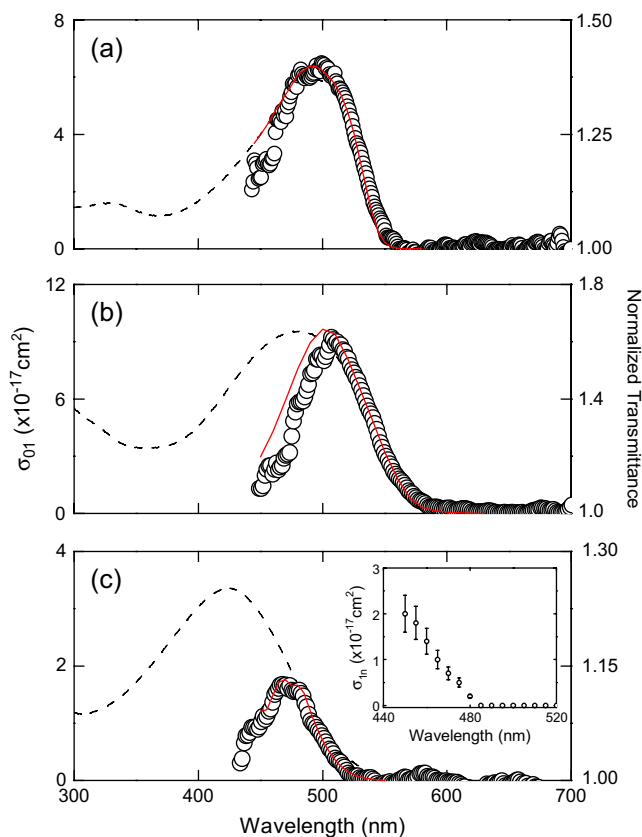
Fig. 3. Ground state cross-section (σ_{01}: dashed line), experimental Normalized Transmittance (open circles) and theoretical Normalized Transmittance (solid line) as a function of the excitation wavelength for (a) MEH-PPV, (b) PAzT and (c) POT. The theoretical Normalized Transmittance was obtained using the three-level energy diagram displayed in Fig. 4. The inset in (c) shows the values of σ_{1n} as a function of excitation wavelength for POT, obtained by fitting the experimental NT.
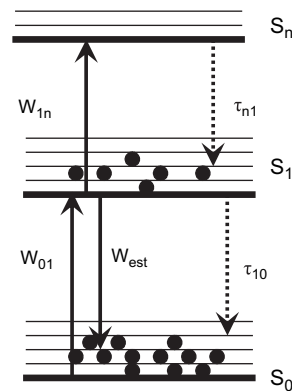

Fig. 4. Three-level energy diagram used to explain the induced transparency of the conjugated polymers and fit the experimental NT.

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—700 nm), providing the material optical transparency. However, for other spectral regions far from resonance, MEH-PPV [3,24] and PAzT [25] present NT smaller than one because of two-photon absorption processes.

In order to explain our results, we need to take into account the electronic transitions of the conjugated polymers, for which several models can be found in the literature [8,26,27]. The polymers studied here possess electronic spectra composed by an absorption peak between 400 nm and 500 nm (dashed line in Fig. 3), which characterizes their $\pi-\pi*$ transition.

Fig. 4 shows the three-level energy diagram employed to fit the experimental NT (open circles in Fig. 3), 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 τ_{n1} that is much faster than the decay time τ_{10}. Molecules at level S_1 may decay radiatively to the ground state S_0 with relaxation time τ_{10} of 260 ps for MEH-PPV [28], 3.3 ps for PAzT [10]

and longer than 500 ps for POT [29—31], as depicted in Table 1. The long τ_{10} observed for POT is caused by the high quantum efficiency of its triplet state [30], which hinders high fluorescence rates.

For MEH-PPV (Fig. 3(a)) 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 nm and 700 nm; (ii) The long lifetime τ_{10} of 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. 3(b). 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 re-absorption from the first excited state for some excitation wavelengths [10], which would contribute for PAzT to present the same behavior observed for MEH-PPV concerning NT. We believe that 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, since this time is shorter than the chirp of WLC pulse, 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 NT.

Table 1
Input parameters used in the theoretical fitting of the normalized transmittance spectra

	Power (mW)	Stimulated emission	τ_{01} (ps)
MEH-PPV	1.8	Yes	260 (Ref. [28])
PAzT	3.6	No	3.3 (Ref. [10])
POT	3.8	No	>500 (Ref. [29—31])

For POT (Fig. 3(c)) 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 480 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 480 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. As it will be presented later, attempts to describe this result with negligible excited state absorption cross-section, similarly to MEH-PPV and PAzT, were unsuccessful.

The fitting of the NT displayed in Fig. 3 (solid lines) was carried out based on the energy-level diagram displayed in Fig. 4. Each level in the diagram corresponds to the bottom of the respective vibronic band. No triplet state was considered, since the intersystem crossing time is generally much longer than the duration of the WLC pulse. The rate equations used to describe the dynamic change of absorption, according to the energy-level diagram, are as follows:

$$\frac{dn_0(t)}{dt} = -n_0(t)W_{01} + \frac{n_1(t)}{\tau_{10}} + n_1(t)W_{est} \qquad (1)$$

$$\frac{dn_1(t)}{dt} = n_0(t)W_{01} - \frac{n_1(t)}{\tau_{10}} - n_1(t)W_{est} - n_1(t)W_{1n} + \frac{n_n(t)}{\tau_{n1}} \qquad (2)$$

$$\frac{dn_n(t)}{dt} = n_1(t)W_{1n} - \frac{n_n(t)}{\tau_{n1}} \qquad (3)$$

where $W_{01}(\lambda) = \sigma_{01}(\lambda)I/h\nu$ is the transition rate for $S_0 \rightarrow S_1$, $W_{1n}(\lambda) = \sigma_{1n}(\lambda)I/h\nu$ is the transition rate for $S_1 \rightarrow S_n$, $\sigma_{01}(\lambda)$ 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's constant and ν is the photon frequency. The pump rate, $W_{est} = \sigma_{01}(\lambda)I/(h\nu)$, arises from the depopulation from S_1 to S_0 by stimulated emission, and was taken into account only for MEH-PPV (see Table 1), since this phenomenon was already observed in the literature [3,32].

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 energy of each bandwidth is determined from the total energy and spectral distribution of the WLC. 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 (5 ps).

The time evolution of the nonlinear absorption, $\alpha(\lambda, t)$, was calculated according to:

$$\alpha(\lambda, t) = N[n_0(t)\sigma_{01}(\lambda) + n_1(t)\sigma_{1n}(\lambda)] \qquad (4)$$

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. 3). 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 nm and 700 nm. As can be seen in Fig. 3(a) and (b), there is a good agreement between the experimental (open circles) and theoretical data (solid line), showing that our assumption is correct.

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 moves towards the blue region, which is not observed in the experimental NT (open circles Fig. 3). Therefore, we have to consider the transition $S_1 \rightarrow S_n$ to occur, whose absorption cross-section values obtained (σ_{1n}) by fitting the experimental data are displayed in inset of Fig. 3(c). This assumption is in agreement with results presented in the literature reporting transitions from S_1 to higher excited states [30,31]. Therefore, the induced optical transparency for this polymer is held only until 480 nm, once up to this wavelength the experimental NT starts to decrease because of light re-absorption to a higher excited state.

4. Conclusions

We have measured the excited state absorption spectrum between 450 nm 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 (the excited state absorption cross-sections are null). 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. Through this fitting we obtained the values for the excited state absorption cross-sections. 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 a desirable feature.

Acknowledgments

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