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Excited State Absorption of Doped and Undoped Polyanyline

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Polyaniline is a conducting polymer with appealing electrical and optical properties, arising from the π-conjugation along the polymer backbone. The understanding of its excited state absorption is of prime importance for designing and fabricating optical devices. Here, we report on the study of the excited state absorption of doped and undoped PANI by using femtosecond pulses in the spectral range from 450 nm up to 850 nm. For undoped PANI, we observed saturation of absorption as well as reverse saturable absorption, depending on the excitation wavelength. For doped PANI, however, only saturable absorption was observed.

Keywords Conjugated polymer; excited state absorption; optical properties; polyaniline; Z-scan

Introduction

Conjugated polymers are materials of great technological interest due to its appealing electrical and nonlinear optical properties, owing mainly to the conjugation along the polymer backbone [1,2]. Within the class of conjugated polymers, polyaniline outstands for features such as good doping characteristics, high solubility, processability and stability [3,4]. Changes in the oxidation state of polyaniline by doping provide an increase in its conductivity [5,6], also modifying its nonlinear optical properties. Within this context, the understanding of the photoexcitation mechanism in electronic polymers is still necessary for optimizing nonlinear optical properties aiming at the fabrication of optical devices [7–10].

Several spectroscopic techniques have been used to probe the excited states of materials, including those employing white-light continuum (WLC) sources [11–14], whose outstanding characteristics include high spectral resolution and time saving. In addition, because of the WLC pulse chirp, distinct spectral components reach the sample at distinct times, enabling to monitor cumulative effects related to optical absorption in materials.

Here, we report the use of the WLC Z-scan technique [11] to study the excited state absorption spectra, from 450 nm up to 850 nm, of polyaniline (PANI) in its

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doped and undoped forms. The oxidized and reduced states of PANI, and its derivatives, are represented by the index of y, reduced unity and (1 – y), oxidized unity. The completely reduced form of PANI, the leucoemeraldine, is obtained when $(1 - y) = 0$. The oxidized form $(1 - y) = 1$ is called pernigraniline, while $(1 - y) = 0.5$ corresponds to the emeraldine form. Based on a three-level energy diagram, a set of rate equations was employed to establish the population dynamics and fit the experimental data. For doped and undoped PANI in the emeraldine form, we observed electronic transitions from the first to the second excited state. Undoped PANI presents saturation of the absorption (SA) and reverse saturable absorption (RSA) depending on the excitation wavelength, while undoped PANI presents only saturable absorption for the same spectral range.

Experimental Section

Polyaniline (PANI emeraldine) was synthesized according to reference [15], which yields a molecular weight of 40.000 g/mol and a polydispersivity of 2.5. The sample was dissolved in DMSO and placed in 2-mm thick quartz cuvette for linear and nonlinear optical measurements. Linear absorption spectrum was obtained using a Cary 17 spectrophotometer. The doping of polyaniline was carried out by adding specific volumes of a 1 M solution of hydrochloric, in order to attain the complete doping. The Mer chemical structure of PANI is displayed in Figure 1, where $y = 0.5$ (emeraldine).

We used the WLC Z-scan technique [11,12] to measure the nonlinear absorption properties of PANI. This technique consists in generating the WLC spectrum by focusing 120 fs pulses at 1100 nm in a 3 cm cell containing distilled water. The pulses at 1100 nm are generated from a optical parametric amplifier pumped by 775 nm from Ti:sapphire chirped pulse amplified system. In order to characterize the spectrum generated, from 400 to 900 nm (see inset of Fig. 2), an Ocean Optics spectrometer was employed. The positive chirp, approximately 5 ps, was measured by using Kerr Gate effect in a sample of hexane. Before reaching the sample, the WLC beam was recollimated by using a $f = 10$ cm lens and then redirected to the Z-scan setup [16]. The sample was scanned along the focused WLC beam (z-direction), and the transmitted light was measured with a spectrometer. The transmittance at distinct z-positions was normalized to the transmittance far from the focus, yielding the experimental Z-scan (normalized transmittance) curves for each wavelength.

Results and Discussion

By employing the WLC Z-scan technique, one can determine the material's nonlinear optical absorption spectrum with a single Z-scan. For instance, Figure 2 displays

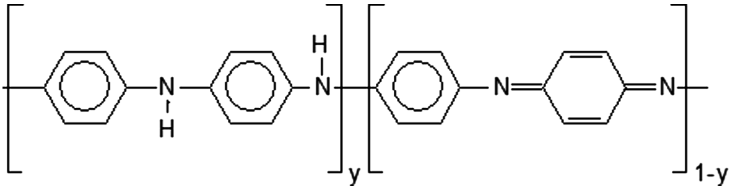

Figure 1. Mer chemical structure of PANI, in which $y = 0.5$ (emeraldine).

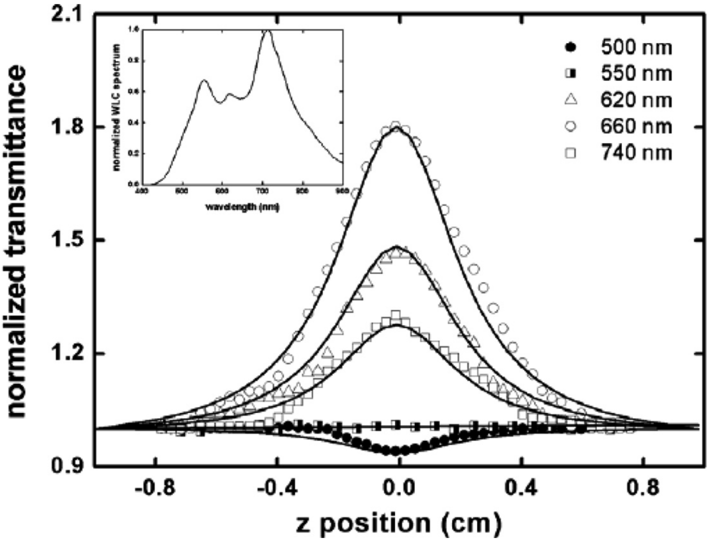

Figure 2. Experimental Z-scan curves (symbols) at distinct wavelengths for undoped PANI, obtained by using the WLC Z-scan technique. The solid lines represent the fittings by using the three-level energy model (see inset of Fig. 3). The inset portrays the normalized WLC spectrum.

Z-scan curves for distinct excitation wavelengths for undoped PANI. The increase of the normalized transmittance at positions close to the focus ($z = 0$) is a consequence of the excitation of molecules from the ground to an excited state, which has a smaller absorption cross-section. This behavior characterizes saturation of absorption (SA), providing to the material an optically induced transparency. We also observed a decrease in the normalized transmittance for wavelengths in the blue region of the WLC spectrum, which characterizes a reverse saturable absorption (RSA).

In order to explain the nonlinear optical absorption of PANI in its doped and undoped forms, we need to take into account the electronic transitions of PANI involved in the absorption. The solid lines in Figure 3(a) and (b) show the ground state absorption cross-section (σ_{01}) of undoped and doped PANI respectively. We observe that the doping causes substantial changes in the linear absorption of PANI; the σ_{01} peak for undoped PANI, around 630 nm, appears as nearly 850 nm for doped PANI [17].

Based on the three-level energy diagram displayed in the inset of Figure 3, we obtained the excited state absorption cross-sections of PANI by fitting the experimental normalized transmittance as a function of excitation wavelength. Each level in the diagram corresponds to the bottom of the respective vibronic band. Based on this diagram, molecules from the ground state, S_0, are promoted to first excited state, S_1, via one-photon absorption by the red part of the WLC spectrum. From this state, molecules can either relax to S_0 or be re-excited to a higher level S_n and then decay to S_1. According to the energy diagram, we used the following rate equations to describe the dynamic change of absorption:

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

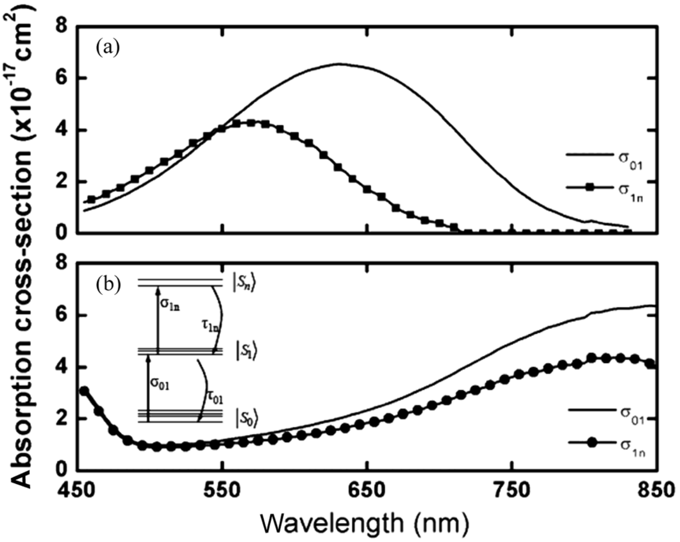

Figure 3. Ground (σ_{01}: solid line) and excited (σ_{1n}: line with symbols) states absorption cross-sections for PANI in its (a) undoped and (b) doped forms, as a function of the excitation wavelength. For both PANI, σ_{1n} was obtained by fitting the experimental data using the three-level energy diagram displayed in the inset.

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

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

where $W_{01}(\lambda) = \sigma_{01}(\lambda)I(\lambda)/h\upsilon$ is the transition rate $S_0 \rightarrow S_1$, and $W_{1n}(\lambda) = \sigma_{1n}(\lambda)I(\lambda)/h\upsilon$ is the transition rate $S_1 \rightarrow S_n$, $\sigma_{01}(\lambda)$ and $\sigma_{1n}(\lambda)$ are the ground state and excited state cross-sections respectively. $I(\lambda)$ is the excitation intensity for each wavelength. $n_1(t)$ and $n_n(t)$ are the population fraction in each state, and τ_{10} and τ_{n1} are the relaxation times of the transitions $S_1 \rightarrow S_0$ and $S_n \rightarrow S_1$ respectively. h is the Planck constant, and ν is the photon frequency.

To solve this set of equation, we consider the energy of the WLC pulse composed of a group of bandwidth limited pulses centered at the wavelengths comprising the white light spectrum. The energy of each bandwidth can be determined from the total energy and spectral distribution of the WLC. Because of the chirp of the pulse (5 ps), the red component of the WLC pulse promotes part of the population to the first excited state (S_1). Consequently, the other spectral components of the WLC pulse probe the excited state absorption of the molecules, since the first excited state presents a lifetime of nearly 100 ps [18] which is much longer than the pulse duration. During the WLC pulse width, relaxation from S_n to S_1, with a decaying time of approximately 500 fs [18], is also considered to describe the accumulation of molecules in state S_n.

The nonlinear absorption coefficient evolution can be calculated according to:

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

where N is the 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. Once the ground state absorption cross-section (solid line in Fig. 3(a) and (b)) for every spectral component is determined by the linear absorption spectrum measurements, the only adjustable parameter in our fitting procedure is the excited state cross-section $\sigma_{1n}(\lambda)$.

For undoped PANI (Fig. 3(a)), we observe that the ground state absorption cross-section (σ_{01}: solid line) remains larger than the excited state one (σ_{1n}: line with squares) from 850 nm down to 545 nm, yielding a normalized transmittance greater than one. In this spectral region, molecules are depleted from the ground to the first excited state (S_1), by the red portion of the WLC, and subsequently re-excited to S_n by the blue portion of the WLC. Because $S_1 \rightarrow S_n$ has a smaller absorption cross-section, saturation of absorption is observed. The re-excitation and accumulation of molecules in the first excited state is a consequence of the short WLC pulse chirp (~5 ps) compared to the decaying time, τ_{10}, of some picoseconds (>100 ps) [18]. However, for excitation wavelengths shorter than 540 nm, we observe in Fig. 3(a) that σ_{1n} values overpass σ_{01}, leading to a reverse saturable absorption.

For PANI in its doped form (Fig. 3(b)), we can see that the peak of excited state absorption cross-section (σ_{1n}: line with circles) accompanies the shift of the ground state cross-section (σ_{01}: solid line) towards the red region of the spectrum, when compared to undoped PANI. However, doped PANI presents excited state absorption cross-sections larger than the ground state ones along the entire spectrum studied (450–850 nm), therefore, leading only to saturation of absorption and not reverse saturable absorption.

Conclusions

We measured the excited state absorption spectrum from 450 up to 850 nm of PANI emeraldine in its doped and undoped state by using the White-Light Continuum Z-scan technique. Undoped PANI presented saturation of absorption (SA) from 850 down to 545 nm, and reverse saturable absorption (RSA) from 545 nm down to 450 nm. For doped PANI, however, we observed only SA along the spectrum region studied (850–450 nm), leading to a fast induced optical transparency. Therefore, by adjusting the doping level of PANI and choosing a proper excitation wavelength, one can select and optimize a specific nonlinear absorption process aiming at applications in optical devices.

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