

## 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 photoluminescent 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

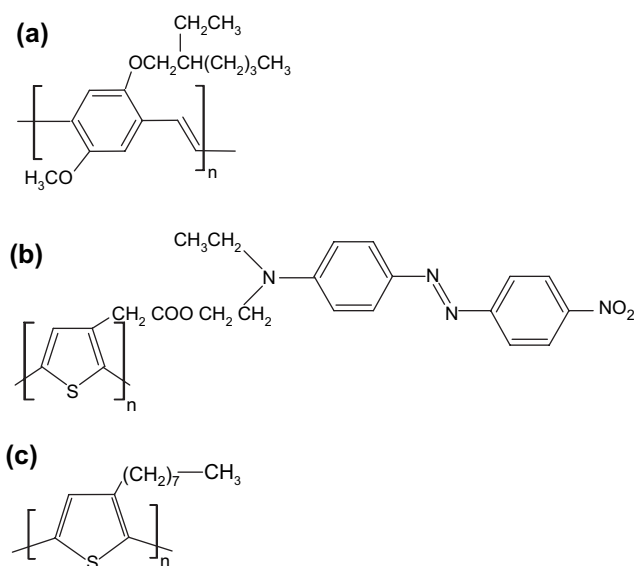


Fig. 1. Molecular structure of (a) poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV), (b) poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane-(3-thienyl)ethanoate], PAzT and (c) poly(3-octyl-thiophene), POT.

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  $\mu$ J) in the visible range was generated by employing  $\sim 0.3$  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  $\sim 2$  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)

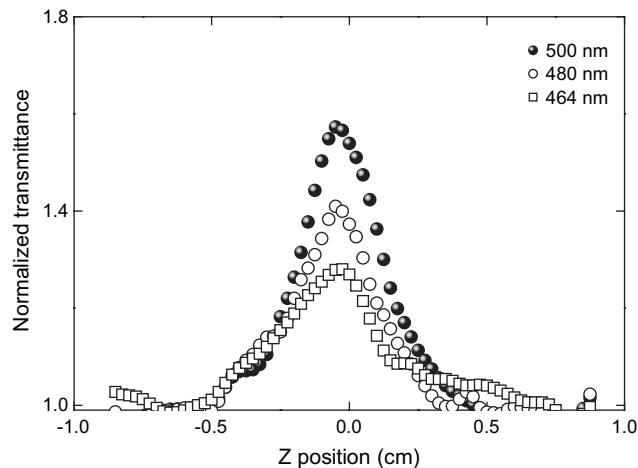


Fig. 2. Experimental Z-scan curves for PAzT obtained at 500 nm, 480 nm and 464 nm, using an input average power of 3.6 mW.

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