

NONLINEAR ABSORPTION OF CONJUGATED POLYMERS OBTAINED BY A WHITE-LIGHT CONTINUUM SOURCE

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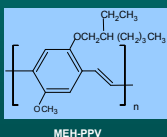
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Abstract

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: MEH-PPV, PAzT and POT. The nonlinear absorption 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. 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.

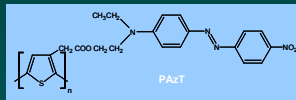
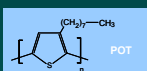
Introduction

PPV-based polymers have been studied because of its electrical and luminescent properties, which allows applications in electro- and photo-luminescent devices.



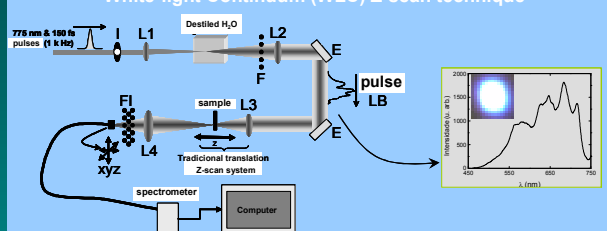
This class of material has already been proposed for photonics application, such as up-converted fluorescence devices, due to its two-photon and, more recently reported, three- and four-photon absorption properties.

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, which joint the properties of the azobenzene groups with the thiophene based polymers. Azo-polymers have been exploited for a variety of applications, such as reversible optical data storage, surface relief gratings and electro-optical devices



Experimental technique

White-light Continuum (WLC) Z-scan technique

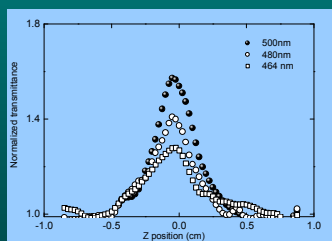


The WLC Z-scan technique was used to obtain the nonlinear absorption spectra of the polymers. The WLC was generated by focusing 150-fs pulses at 775 nm from a Ti:sapphire chirped pulse amplified system in distilled water (3 cm path length cell). 8 μ J of WLC in the visible range was generated by employing ~ 0.3 mJ at 775 nm. The WLC beam was then recollimated using a $f = 10$ cm lens. The WLC spectrum presents ~ 250 nm band in the visible region (450–700 nm), with ~ 5 ps of positive chirp. The sample was scanned along the focused WLC beam (z-direction), being the transmitted light recollimated into a spectrometer. The transmittance at distinct z-positions was normalized to the one far from the focus, yielding the normalized transmittance curves (Z-scan curves) for each wavelength.

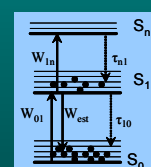
Advantages of the WLC Z-scan technique:

- The entire nonlinear spectrum measurement in a single scan!
- Less time consuming than the traditional Z-scan!

Results and discussions



Typical experimental Z-scan curves for PAzT obtained by the WLC Z-scan technique.



Two energy-level diagram used to explain the experimental results

Rate equations used to fit the experimental data

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

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

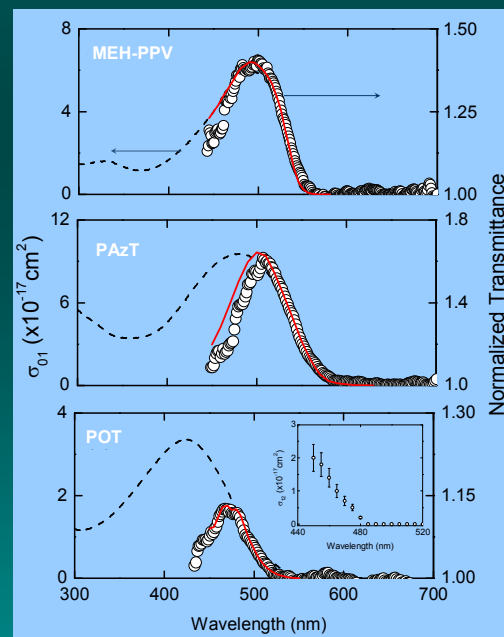
$$\frac{dn_n(t)}{dt} = n_1(t)W_{1n} - \frac{n_n(t)}{\tau_{n1}}$$

$$W_{01}(\lambda) = \sigma_{01}(\lambda)I/h\nu \quad W_{1n}(\lambda) = \sigma_{1n}(\lambda)I/h\nu \quad W_{10} = \sigma_{10}(\lambda)I/(h\nu)$$

The time evolution of the nonlinear absorption is:

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

For MEH-PPV and PAzT, we used $\sigma_{1n}(\lambda)=0$ for all excitation wavelengths, implying that there is no transition from S_1 to a higher excited state in the region between 450 and 700 nm (it becomes transparent). 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). Therefore, we have to consider the transition $S_1 \rightarrow S_n$ to occur, whose absorption cross-section values, obtained by fitting the experimental data, are displayed in the inset of figure. This assumption is in agreement with results presented in the literature reporting transitions from S_1 to higher excited states.



Conclusions

We have measured the excited state absorption cross-section spectrum between 450 and 700 nm for three important conjugated polymers: MEH-PPV, PAzT and POT. Saturable absorption is the main nonlinear mechanism for the fast optical transparency of the polymers. Higher excited absorption is negligible for MEH-PPV and PAzT. 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.

Acknowledgments

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