Nonlinear absorption in azopolymer

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Abstract

The nonlinear optical properties of Poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-thienyl)ethanoate], PAzT were investigate through the open aperture Z-scan technique. This polymer bearing azobenzene moieties presents induced transparency when excited by picosecond laser pulses, which make them attractive for applications such as optical switches and storage devices. By fitting the experimental data, we obtained several parameters such as, ground and excited state cross-sections, relaxation times, etc. We also found out that the azobenzene moieties attached to the backbone are responsible for the material nonlinear response.

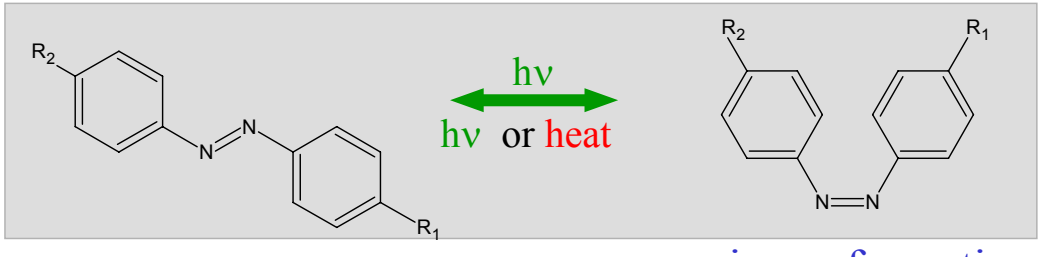
Introduction

Induced transparency – technological applications such as :

- Optical switches
- Image storage devices

Azobenzene compounds - photoisomerization

trans-conformation



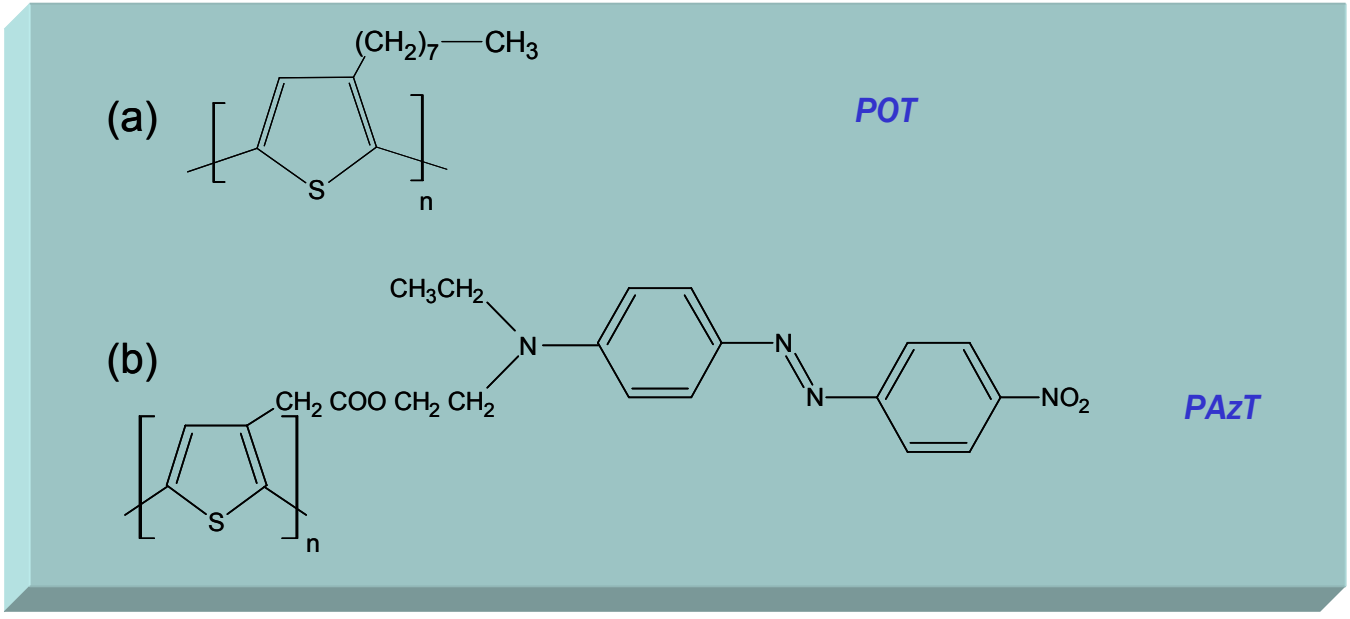
cis-conformation

✓ Increase delocalization of charges

✓π - Conjugation

PAzT

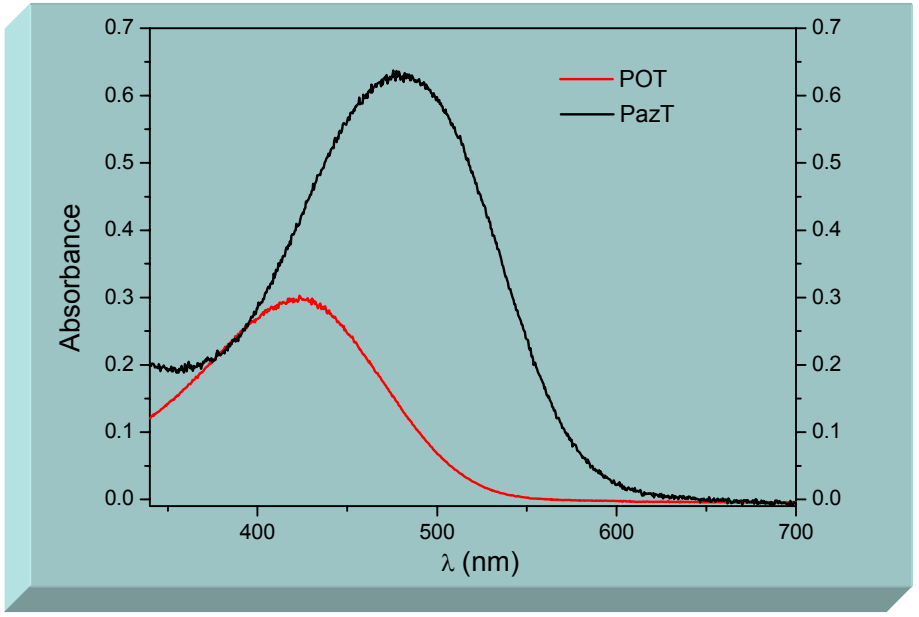
- Polythiophene derivative - synthesized by the introduction of azobenzene groups at the 3-position of the thiophene rings (polyazothiophene)
- Characteristics: polyconjugated backbone with the substituent physical properties



Absorption spectra of POT and PAzT

- Concentration of 1.25×10^{-4} mol/L

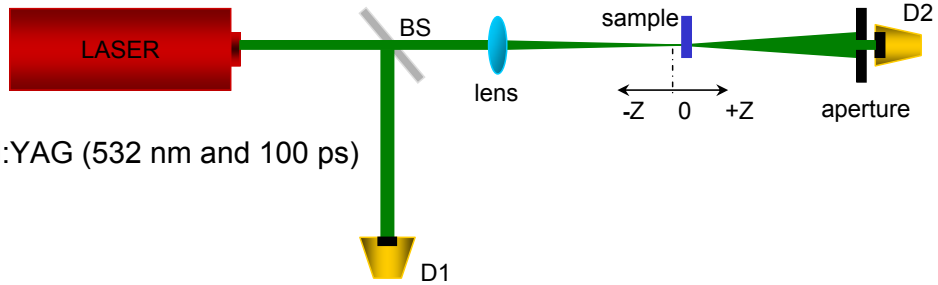
- Solvents: Toluene for POT
  N,N-dimethylformamide (DMF) for PAzT



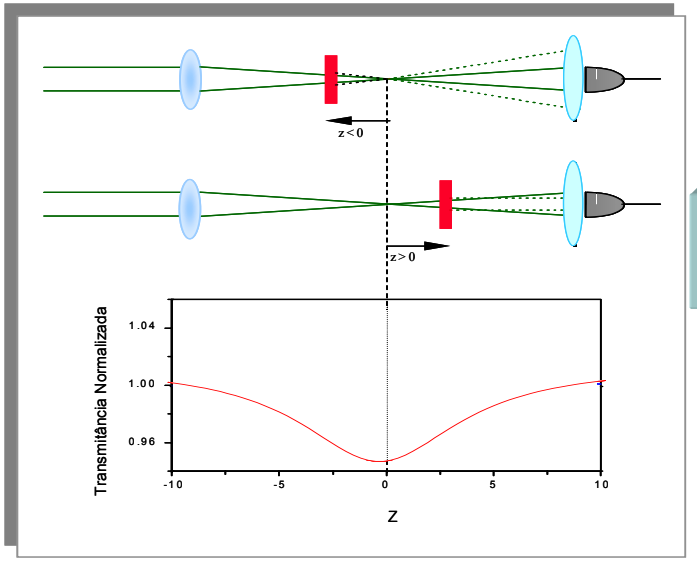
- PAzT -> λ_{peak} = 479 nm
- POT -> λ_{peak} = 425 nm

- PAzT presents red-shifted absorption – effect of the azobenzene moieties

Z-scan Technique



Nd:YAG (532 nm and 100 ps)



Z-scan signature

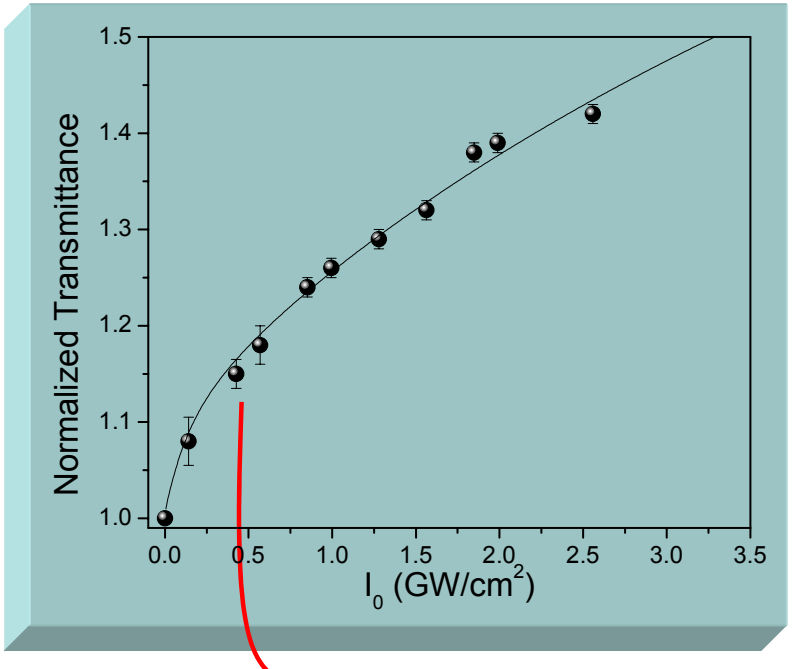
Nonlinear transmittance

$$NT_{(z)} = \exp\left\{-LN_0\left[\sigma_{01}\times n_{01(z)} + \sigma_{02}\times n_{02(z)}\right]\right\}$$

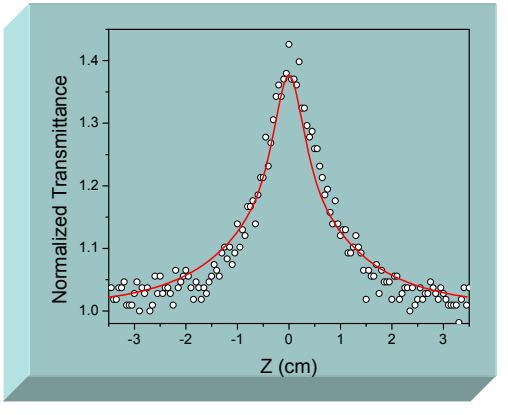
Results – Z-scan

Saturable Absorption

Single pulse



Typical signature of saturable absorption



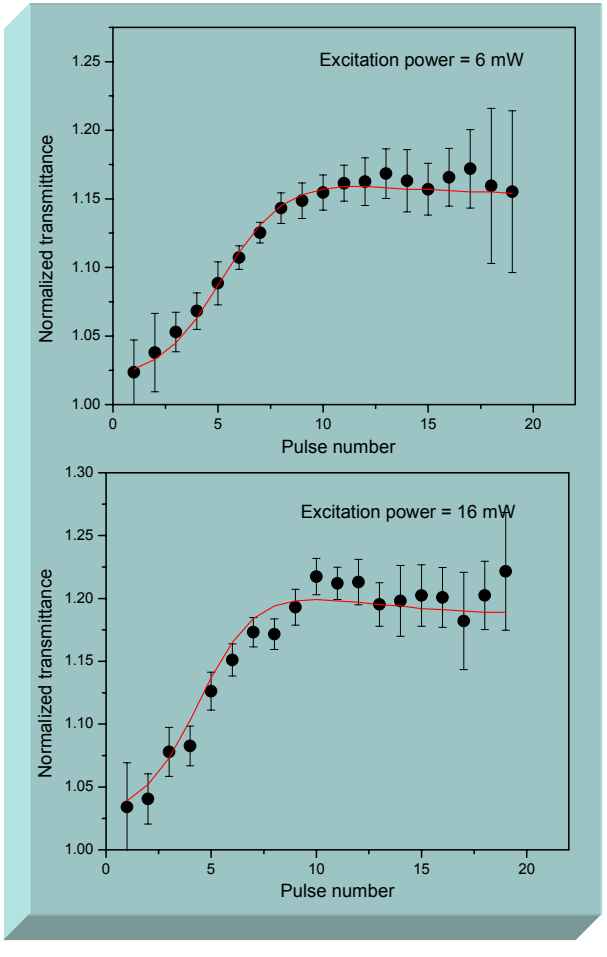
The linear transmittance increases ≈ 35 %

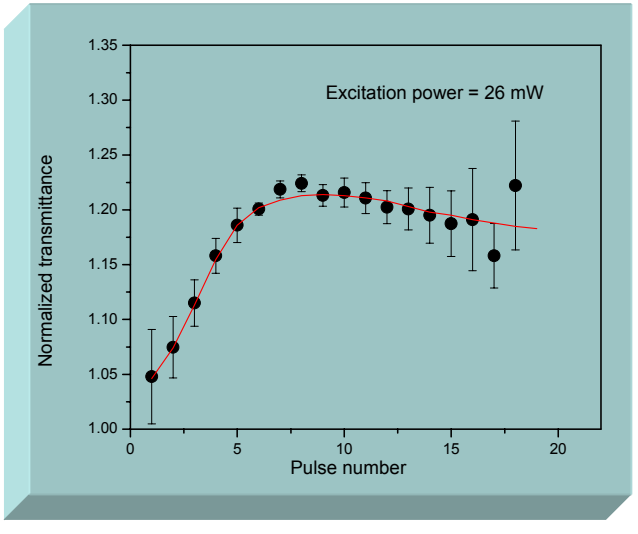
Fitting using three-level energy model

Results - Z-scan

Saturable Absorption

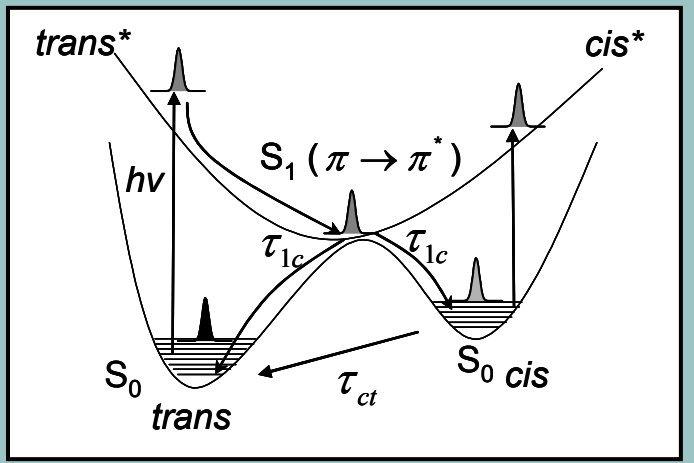
Pulse train





Results – Theoretical model

Three-level model



Constant parameters

τ_{1t} and τ_{1c} = (3,3 ± 0,3) ps

σ_t= (6,0 ± 0,1)x10^{-17} cm^2

Fitting parameters

σ_c= (4,4 ± 0,3)x10^{-17} cm^2

$\sigma_{S1} \approx 0$

τ_{ct} = 100 μs

Rate equations

$$\frac{dn_t}{dt} = -n_t W_{tS1} + \frac{n_{S1}}{\tau_{S1t}} + \frac{n_{0c}}{\tau_{ct}}$$

$$\frac{dn_c}{dt} = -n_c W_{cS1} + \frac{n_{S1}}{\tau_{S1c}} - \frac{n_{0c}}{\tau_{ct}}$$

$$\frac{dn_{S1}}{dt} = n_t W_{tS1} + n_c W_{cS1} - \frac{n_{S1}}{\tau_{S1c}} - \frac{n_{S1}}{\tau_{S1t}}$$

$$W_{tS1} = \frac{\sigma_t I}{h\nu}; \quad W_{cS1} = \frac{\sigma_c I}{h\nu}$$

$$\alpha(t) = N\left[n_t \sigma_t + n_c \sigma_c\right]$$

Conclusions

✓ The azobenzene moities attached at the polymer backbone are responsible for the nonlinear absorption

✓ This saturable absorption (SA) is a consequence of the population depletion of the ground state, causing the transparency

✓ The experimental data were well fitted by using a tree-level energy model

✓ The cis ground state cross section was found to have a value = $(4{,}4 \pm 0{,}3) \times 10^{-17}$ $cm^{2.}$

✓ The *cis-trans* relaxation time is around 100 μs.