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Induced transparency in polythiophene bearing azobenzene moieties

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Abstract

The nonlinear absorption of poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane(3-thienyl)ethanoate], PAzT, was investigated using single pulse and pulse train open aperture *Z*-scan techniques to discriminate between fast and accumulative nonlinearities. We observed an induced transparency for excitation with picosecond laser pulses at resonant conditions, which was attributed to the azobenzene moieties attached to the polymer backbone. The fast transparency is caused mainly by the build up of molecules in the first excited state that have a negligible absorption cross-section compared to the ground state. When using pulse trains, the nonlinear response is mainly due to the accumulation of molecules in the *cis* configuration, which presents a ground state cross-section slightly smaller than that of *trans*. The cumulative effect arises from a combination of the less intense excitation and longer lifetime of the *cis* population. We believe that the process observed here makes PAzT an attractive polymer for photonics applications, such as optical switches and storage devices.

Keywords: trans–cis Isomerization; Azopolymer; Induced transparency

1. Introduction

The phenomenon of induced transparency in materials can be used in several technological applications, including light triggered switches and image storage devices [1,2]. Induced transparency is observed in nonlinear materials presenting smaller absorption cross-section in the excited state than that presented in the ground state. Consequently, when the material is subjected to high excitation intensity, it will exhibit higher transparency. Among organic materials for nonlinear applications, conjugated polymers have emerged as an excellent option, especially for fabricating photonic devices [3,4]. The desired optical properties arise from the electron delocalization along the polymer backbone, which is easily disturbed by the presence of electromagnetic field, generating second- and third-order nonlinear effects [5]. Another attractive class of polymers with interesting optical properties is that resulting from the incorporation of azobenzene moieties into the polymer, often called azopolymer. Azopolymers have been widely investigated owing to their potential use in a variety of optical devices employing nonlinear optics, surface relief gratings and optically induced birefringence [6–11]. These features motivated us to study the nonlinear optical properties of a new polymer that presents azoaromatic groups attached as a side chain to a conjugated backbone.

This work reports the induced transparency of a polythiophene derivative synthesized by the introduction of azobenzene groups at the 3-position of the thiophene rings (polyazothiophene). The homopolymer polythiophene is a material extensively reported in the literature owing its electrical properties [4,12] combined with good thermal and environmental stability and easier functionalization [13]. In addition, nonlinear optical properties have already been reported for some polythiophene derivatives [14]. Azobenzene moieties display the *trans–cis* photoisomerization process [15], which has been used for several applications, such as reversible optical data storage [6–8], surface relief gratings [8–10] and electro-optical devices [11]. More recently, studies have

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investigated two-photon absorption of azobenzene moieties [16,17], which makes them candidates for photonics applications. Therefore, the material investigated here should combine the properties from the polyconjugated backbone and azoaromatic substituent.

The nonlinear absorption of the polyazothiophene was characterized by the *Z*-scan technique at 532 nm, employing single pulses [18] and pulse trains [19], in order to discriminate fast and cumulative effects. Such procedure allowed one to accurately determine the *cis*-ground state cross-section of PAzT, in which the value obtained is close to that of the *trans*-ground state. This result points out that the strong induced transparency presented by this polymer is not only produced by the difference of *cis* and *trans* cross-section values, but also for accumulation of molecules in their respective excited states, which have negligible cross-sections. Our results reveal that the nonlinear absorption presented by the polymer has its origin exclusively related to the azobenzene moieties attached to the backbone. This work shows the unique nonlinear optical properties of this polythiophene derivative, which gives rise to a large number of potential applications for this class of material.

2. Experimental section

PAzT polymer was synthesized according to Ref. [20]. The solution used in our optical experiments had a concentration of approximately 0.054 mg/ml in *N*,*N*-dimethylformamide (DMF), and was characterized in a Cary 17 spectrophotometer.

The nonlinear absorption was investigated with the traditional open aperture *Z*-scan technique described in detail elsewhere [18]. Basically, this technique monitors the change in the nonlinear transmittance as the sample is scanned through the *Z*-axis, which contains a focused Gaussian laser beam. Besides single pulse *Z*-scan, in this work we also employed the *Z*-scan technique with pulse train [19,21]. This technique, which is an extension of the standard *Z*-scan method, allows investigating the time evolution of nonlinear processes, and was first proposed for close aperture *Z*-scan [19]. Subsequently, the same method was employed for open aperture experiments, in order to study the dynamics of nonlinear processes [21]. A complete description of the *Z*-scan technique with pulse train can be found in Refs. [19,21], however, a few details will be given here. The excitation source is a frequency-doubled, Q-switched and mode-locked Nd:YAG laser, delivering pulses at 532 nm and 100 ps. Each pulse train contains about 20 pulses separated by 13 ns at a 10 Hz repetition rate. This low repetition rate was used to avoid cumulative thermal nonlinearities. The beam was focused with a lens of focal length $f = 12$ cm onto a quartz cell, yielding a diameter of 50 μm at the focal plane. A detector (rise time ∼1 ns) placed in the far field coupled to a digital oscilloscope and a computer were used to acquire the pulse train signal. Each peak height is proportional to the corresponding pulse fluence, once the detection system has a rise time slower than the 100 ps pulse duration. By measuring the beam waist and the pulse train average power, we can find out the pulse fluence. The intensity can be determined by carrying out *Z*-scan measurements with CS_2. When the sample is located at the focus, the pulse train signal is acquired. Then, this signal is normalized to the one obtained when the sample is far from the focus, yielding the normalized transmittance as a function of pulse number curve. All optical measurements were carried out with the sample placed in a quartz cuvette with an optical path of 2 mm.

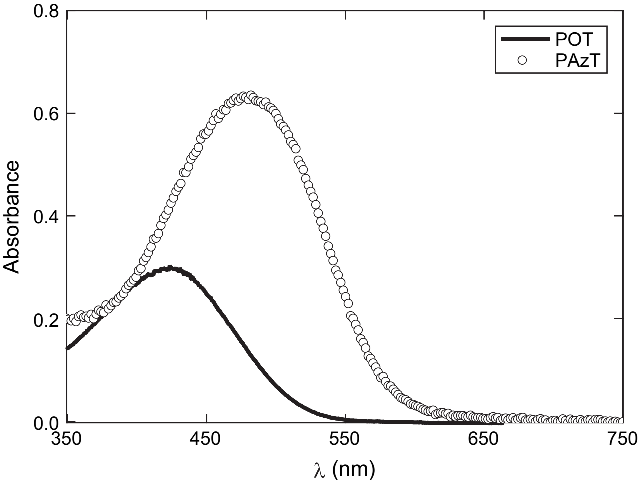

Fig. 1. Linear absorption spectrum of POT and PAzT in toluene and DMF, respectively.

3. Results

The absorption spectra of poly(3-octyl-thiophene), POT (dissolved in toluene) and poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane(3-thienyl)ethanoate], PAzT (dissolved in DMF) are displayed in Fig. 1. The use of different solvents was necessary since POT is insoluble in DMF and PAzT is poorly soluble in toluene. PAzT presents the peak of the absorption band at 485 nm, close to the $\pi-\pi^*$ of the azobenzene groups, while POT has its absorption peak at 423 nm. As both polymers are solvatochromic, the solvent has a considerable influence on the linear absorption band (e.g. PAzT solution exhibit a λ_{max} at 460 nm in toluene), affecting the excitation wavelength in which the material will present larger nonlinear effects. The molecular structures of POT and PAzT are displayed in Fig. 2(a) and (b), respectively.

A typical *Z*-scan curve for PAzT using single 100 ps pulses as excitation at 532 nm, with an intensity of approximately 2 GW/cm^2 is shown in the inset of Fig. 3. The maximum of the normalized transmittance is observed at $z = 0$ position. Fig. 3 displays the normalized transmittance (NT) as a function of the excitation intensity (dark circles) for PAzT, taken from the *Z*-scan experiments. It can be seen that the NT increases as the excitation intensity is increased, with a trend to reach a plateau.

We also carried out measurements employing the *Z*-scan technique with pulse trains, using the same laser apparatus. With this technique, processes with response times in the order of 10 ns (or longer) can be detected due to the build up of the nonlinear effect, since the separation between each pulse in the

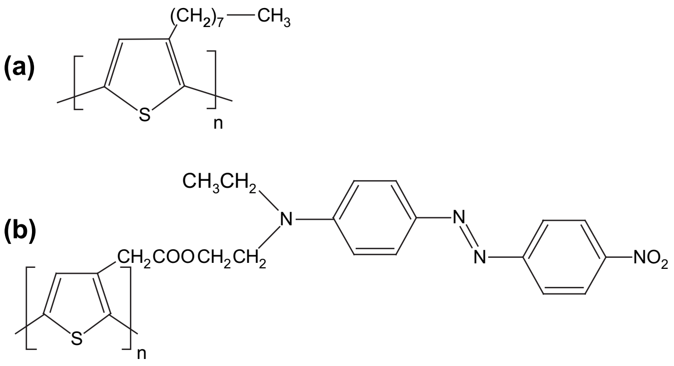

Fig. 2. Molecular structure of (a) poly(3-octyl-thiophene), POT and (b) poly-[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane(3-thienyl)ethanoate], PAzT, displaying the azo moieties attached to the backbone.

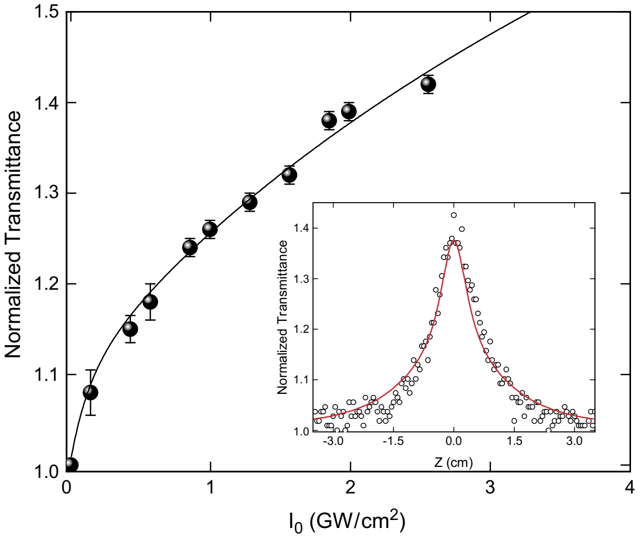

Fig. 3. Evolution of the normalized transmittance as a function of the excitation intensity for PAzT, using single pulses at 532 nm and 100 ps (dark circles). The solid line represents the fitting of the NT using the three-level energy diagram shown in Fig. 5. In the inset is shown the experimental data (open circles) and the theoretical fitting (solid line) of a typical *Z*-scan curve of PAzT.

pulse train is around 13 ns. In this way, the pulse of number *n* of the envelope (where *n* is an integer from 1 to 20) feels the effect caused by the previous pulses. However, owing to the low intensity of each individual pulse of the envelope ($\sim$0.1 GW/cm^2 for the most intense one), only a small amount of molecules can be excited to the first excited state. This implies that the excited state absorption cannot be probed inside the same pulse, as observed when single pulses of much higher intensities are employed. In Fig. 4 the normalized transmittance is displayed (taken from the *Z*-scan curves) as a function of the pulse number (closed circles). We observe that the normalized transmittance saturates before the pulse number 10. However, the normalized transmittance in Fig. 4(a) presents a higher slope than the others owing to the higher excitation power. The error bars are bigger for pulses lying among the first and last ones in the envelope because of their very low intensity, which decreases the signal/noise ratio.

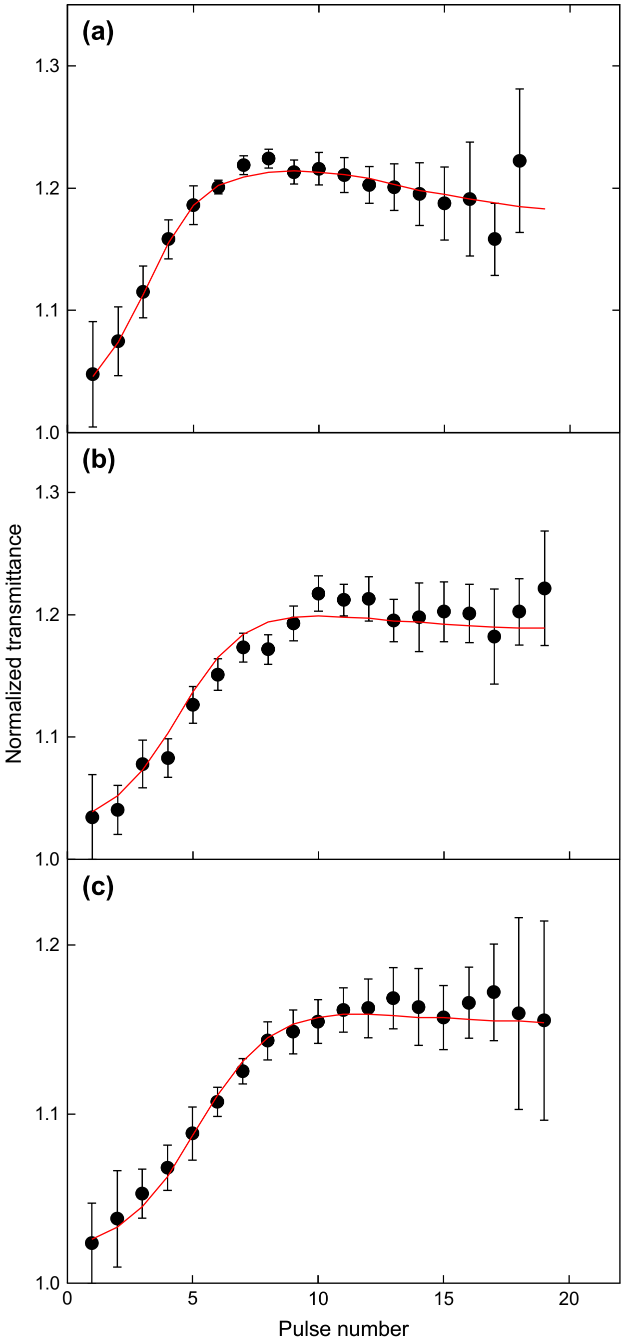

Fig. 4. Evolution of the normalized transmittance of PAzT as a function of the pulse number using an average power of the entire envelope of (a) 26 mW, (b) 16 mW and (c) 6 mW. Each envelope of pulses contains 20 pulses at 532 nm and 100 ps, which are separated by 13 ns. The solid line represents the fitting of the NT using the three-level energy diagram shown in Fig. 5.

4. Discussion

Z-scan measurements in the solution of PAzT were carried out to determine nonlinear parameters such as excited state cross-sections, *cis*-ground state cross-section and relaxation time. In the inset of Fig. 3, we observe that the normalized transmittance maximum takes place at the focus ($z = 0$), indicating an induced transparency in the material (lowering in the absorption). The induced transparency process for PAzT can be observed in Fig. 3, which shows the normalized transmittance (NT) as a function of the excitation intensity (dark circles). The increase of the NT for higher excitation intensities arises from the larger number of molecules promoted to the first excited state. It is expected that for very high excitation intensities, the NT reaches a plateau as a consequence of the saturation of the population. However, in order to avoid material degradation such intensity regime was not attained in our experiment.

The results obtained from the *Z*-scan technique with pulse trains are shown in Fig. 4. The 13 ns separation between each pulse in the pulse train makes possible the monitoring of cumulative effects. This pulse separation, however, does not allow fast induced transparencies (∼ps or faster) to be probed by this method. Only slower processes, in the order of at least a few ns, which are within the time scale for *cis*–*trans* thermal relaxation, can be monitored. Besides, each individual pulse of the envelope does not excite a very large fraction of molecules to the first excited state, due to its low intensity, assuring that the observed effect is due to cumulative processes. In Fig. 4 it can be seen that the NT is increased as the material is pumped with more pulses. In this case, in contrast to what happened with single pulses, the NT increases due to the accumulation of molecules in the *cis* state, which have a lower absorption cross-section than the *trans*-ground state. The NT reaches a plateau before the sample is irradiated by the entire envelope because a steady state is achieved.

The three-level energy diagram shown in Fig. 5 was employed to understand our results. Assuming that initially all the population is in the state S_0 (*trans*) [2,22], part of it is excited to S_1 (*trans**) by light, relaxing nonradiatively to the bottom of this band. From this configuration, two possible relaxation paths can take place: to the S_0 (*trans*) or to the S_0 (*cis*) states, both with similar relaxation lifetimes ($\tau_{1\mathrm{t}}$ and $\tau_{1\mathrm{c}}$) according to Wachtveitl et al. [23,24]. This process transfers part of the population from S_0 (*trans*) to S_0 (*cis*). A similar mechanism occurs for molecules in S_0 (*cis*). After several photoisomerization cycles, a population of molecules in the S_0 (*cis*) state is created, generating a different absorption coefficient for the sample. This population can decay to S_0 (*trans*) after a relatively long time τ_{ct} (thermal isomerization time). The rate equations describing the three-level energy diagram of Fig. 5, employed to fit the experimental data (Figs. 3 and 4), are:

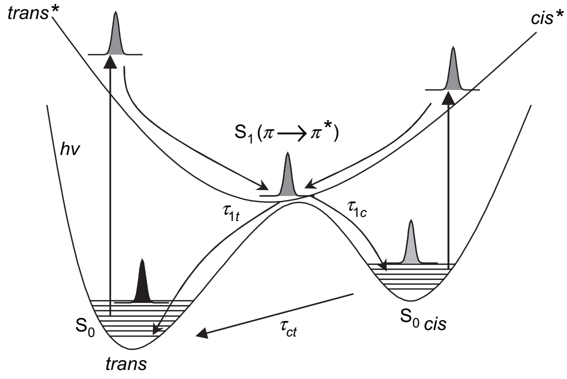

Fig. 5. Three-level energy diagram used to aid in the interpretation of the nonlinear absorption of PAzT, which is based on the change of population of the molecules from *trans* to *cis* configuration of both ground and excited states.

$$\frac{\mathrm{d}n_{\mathrm{t}S_0}}{\mathrm{d}t} = -n_{\mathrm{t}S_0}W_{\mathrm{t}S_1} + \frac{n_{S_1}}{\tau_{1\mathrm{t}}} + \frac{n_{\mathrm{c}S_0}}{\tau_{\mathrm{ct}}} \tag{1}$$

$$\frac{\mathrm{d}n_{\mathrm{c}S_0}}{\mathrm{d}t} = -n_{\mathrm{c}S_0}W_{\mathrm{c}S_1} + \frac{n_{S_1}}{\tau_{1\mathrm{c}}} - \frac{n_{\mathrm{c}S_0}}{\tau_{\mathrm{ct}}} \tag{2}$$

$$\frac{\mathrm{d}n_{S_1}}{\mathrm{d}t} = n_{\mathrm{t}S_0}W_{\mathrm{t}S_1} + n_{\mathrm{c}S_0}W_{\mathrm{c}S_1} - \frac{n_{S_1}}{\tau_{1\mathrm{c}}} - \frac{n_{S_1}}{\tau_{1\mathrm{t}}} \tag{3}$$

where $n_{\mathrm{t}S_0}$, $n_{\mathrm{c}S_0}$ and n_{S_1} are the population fractions in the states S_0 (*trans*), S_0 (*cis*) and S_1, respectively. $\tau_{1\mathrm{t}}$ and $\tau_{1\mathrm{c}}$ are the relaxation times from the excited state S_1 to S_0 (*trans*) and S_0 (*cis*) states, respectively. $W_{\mathrm{t}S_1} = \sigma_{\mathrm{t}}I/\mathrm{h}\nu$ and $W_{\mathrm{c}S_1} = \sigma_{\mathrm{c}}I/\mathrm{h}\nu$ are the transition rates from the ground states to S_1 (*trans**) and S_1 (*cis**) excited states, with σ_{t} and σ_{c} being the *trans*- and *cis*-ground state absorption cross-sections of the azobenzene moieties (in repeating units), respectively, and I the excitation irradiance. Solving numerically this equation yields to the temporal evolution of the absorption

$$\alpha(t) = N\{n_{\mathrm{t}S_0}\sigma_{\mathrm{t}} + n_{\mathrm{c}S_0}\sigma_{\mathrm{t}}\}, \tag{4}$$

where N is number of molecules/cm^3.

By measuring the linear absorption at 532 nm from Fig. 1 ($\alpha = N\sigma_{\mathrm{t}}$) and considering that azobenzene moieties are in the *trans* conformation (less energetic) at room temperature [2,22], we determined the ground state cross-section as $(6.0 \pm 0.1) \times 10^{-17}$ cm^2. The numerical calculation was carried out with $\tau_{1\mathrm{t}} = \tau_{1\mathrm{c}} = (3.3 \pm 0.3)$ ps, which is the same order of the ones presented in the literature for another family of azobenzene compounds [23,24]. Using these input parameters to solve the set of rate equations, we obtained the best fitting of the experimental data (solid lines of Figs. 3 and 4a–c) by using $\sigma_{\mathrm{c}} = (4.5 \pm 0.2) \times 10^{-17}$ cm^2. The *cis* lifetime (τ_{ct}) could not be accurately determined due to the limited sensibility of the pulse train *Z*-scan technique for response times slower than μs. As a consequence, the data of Fig. 4 could be fitted fairly well using τ_{ct} ranging from 1 μs up to 100 μs. Fig. 4 shows the fitting obtained with $\tau_{\mathrm{ct}} = 100$ μs.

Although the *cis*- and *trans*-ground state cross-sections present distinct values, they cannot hold the high nonlinear absorption presented by the polymer when single pulses are used as excitation (Fig. 3). According to our simulations, in a hypothetical situation where all molecules were in the *cis* configuration (which, actually never takes place), the NT would reach a maximum value around 1.26. Nevertheless, the experimental results obtained with the single pulse *Z*-scan technique (Fig. 3) exhibit a NT of 1.42 for an excitation irradiance of approximately 2.6 GW/cm^2, which is not the maximum value according to the curve trend. Therefore, the cumulative population in the excited S_1 band (for both *cis* and *trans*) is the major responsible for the strong transparency of this material, as depicted in Fig. 3, due to their extremely low excited state cross-sections ($\sigma_{S_{1c}} = \sigma_{S_{1t}} \approx 0\ \mathrm{cm}^2$). It is also worth mentioning that POT presented no nonlinear signal for excitation at 532 nm, showing that the azobenzene moieties attached to the polythiophene backbone are responsible for the nonlinear absorption.

In summary, our results show that the nonlinear absorption of PAzT, responsible for its transparency, arises from two phenomena: (i) accumulation of molecules in the *cis*- and *trans*-excited states (major contribution) and (ii) change of the ground state population from *trans* to *cis* (minor contribution). The first one (i) can be probed only if the material is excited by high intensity single pulses with duration smaller than the *trans*–*cis* relaxation time (result presented in Fig. 3). This process causes a large population transfer from the ground to the excited state, which has a negligible cross-section. The second phenomenon (ii) becomes measurable when the material is pumped by a pulse train, whose time scale allows the observation of cumulative effect (results presented in Fig. 4). In our case, the cumulative effect arises from *trans* to *cis* (ground state) configuration change. The low intensity of each individual pulse in the envelope excites only a negligible amount of molecules to the first excited state, keeping the NT practically unchanged for that pulse. However, in such temporal regime the excited state population can relax to the *cis* state, which has a lower cross-section compared to the *trans* state. This situation allowed us to obtain the *cis*-ground state cross-section with more accuracy.

5. Conclusion

We investigated the nonlinear absorption of a polyazothiophene derivative using single pulses and pulse train at 532 nm and 100 ps as excitation source. A three-level-diagram was employed to explain the saturation of absorption of this material. The change of population from the ground state S_0 to the excited state S_1 was found to be the main contribution for the fast transparency presented by this polymer. The ground state population change from *trans* to *cis* plays only a minor contribution to the nonlinear absorption, since both states present similar cross-section values. The induced transparency presented by this material suggests novel applications for this polythiophene derivative, such as optical switches and image storage devices.

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References

[1] Liu ZF, Hashimoto K, Fujishima A. Nature 1990;347:658.
[2] Sekkat Z, Dumont M. Applied Physics B – Photophysics and Laser Chemistry 1992;54:486.
[3] Prasad PN. Polymer 1991;32:1746.
[4] Roncali J. Chemical Reviews 1992;92:711.
[5] Spangler CW, Liu PK, Hall TJ, Polis DW, Sapochak LS, Dalton LR. Polymer 1992;33:3937.
[6] Natansohn A, Rochon P, Gosselin J, Xie S. Macromolecules 1992;25:2268.
[7] Rochon P, Gosselin J, Natansohn A, Xie S. Applied Physics Letters 1992;60:4.
[8] Oliveira ON, dos Santos DS, Balogh DT, Zucolotto V, Mendonca CR. Advances in Colloid and Interface Science 2005;116:179.
[9] Kim DY, Tripathy SK, Li L, Kumar J. Applied Physics Letters 1995;66:1166.
[10] Mendonça CR, Dhanabalan A, Balogh DT, Misoguti L, dos Santos DS, Pereira-da-Silva MA, et al. Macromolecules 1999;32:1493.
[11] Lanzi M, Paganin L, Costa-Bizzarri P. European Polymer Journal 2004;40:2117.
[12] Sirringhaus H, Brown PJ, Friend RH, Nielsen MM, Bechgaard K, Langeveld-Voss BMW, et al. Nature 1999;401:685.
[13] Zagorska M, Kulszewicz-Bajer I, Pron A, Raimond P, Kajzar F, Attias AJ. Synthetic Metals 1999;102:1141.
[14] Van Keuren E, Wakebe T, Andreaus R, Mohwald H, Schrof W, Belov V, et al. Applied Physics Letters 1999;75:3312.
[15] Zhao XY, Hu X, Yue CY, Xia XL, Gan LH. Thin Solid Films 2002;417:95.
[16] De Boni L, Misoguti L, Zilio SC, Mendonca CR. Chemical Physics Letters 2005;6:1121.
[17] De Boni L, Rodrigues JJ, dos Santos DS, Silva C, Balogh DT, Oliveira ON, et al. Chemical Physics Letters 2003;374:684.
[18] Sheik-Bahae M, Said AA, Wei TH, Hagan DJ, Van Stryland EW. IEEE Journal of Quantum Electronics 1990;26:760.
[19] Misoguti L, Mendonca CR, Zilio SC. Applied Physics Letters 1999;74:1531.
[20] Gonçalves VC, Balogh DT. European Polymer Journal, in press.
[21] Mendonça CR, Gaffo L, Misoguti L, Moreira WC, Oliveira ON, Zilio SC. Chemical Physics Letters 2000;323:300.
[22] Sekkat Z, Wood J, Knoll W. Journal of Physical Chemistry 1995;99:17226.
[23] Nagele T, Hoche R, Zinth W, Wachtveitl J. Chemical Physics Letters 1997;272:489.
[24] Satzger H, Sporlein S, Root C, Wachtveitl J, Zinth W, Gilch P. Chemical Physics Letters 2003;372:216.