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Optical birefringence induced by two-photon absorption in polythiophene bearing an azochromophore

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Abstract

We carried out experiments of induced birefringence via two-photon absorption in spin-coated films of the conjugated polymer poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-thienyl)ethanoate], PAzT, at 680 and 775 nm. This process allows recording in the bulk because of the spatial confinement of the birefringence provided by the two-photon absorption. The induced birefringence is associated with molecular reorientation caused by the two-photon induced isomerization of the azochromophores attached to the polymer backbone. In addition, the two-photon absorption spectrum of PAzT was measured to help selecting the excitation wavelength for two-photon absorption induced birefringence.

Keywords: Birefringence; *Trans*–*cis* isomerization; Two-photon absorption

1. Introduction

Two-photon absorption takes place when the material absorbs two photons in a single event. Such process provides high spatial resolution, thanks to its quadratically dependence on the light intensity. Moreover, as less energetic photons can be used in two-photon absorption, improved light penetration and lower scattering are generally achieved. Two-photon absorption process has been studied by several research groups interested in the areas of photonics, medicine and physical-chemistry. The reason for this lies in the versatility of such nonlinear optical process, which has been used to manufacture photonic crystals [1–3], structures of micro and sub-micro dimensions [4,5], three-dimensional optical data storage [6], optical limiting [7], photodynamic therapy [8] and fluorescence imaging [9,10]. Three-dimensional optical storage achieved by two-photon absorption has been investigated because this process can increase the storage capability by several orders of magnitude. Two-photon induced anisotropy [11–15] and two-photon induced isomerization [16,17] have been recently reported for azoaromatic chromophores. In particular, we demonstrated two-photon induced birefringence achieved by photoisomerization and subsequent molecular orientation in guest–host films containing azoaromatic chromophores [11,12]. Such process, when induced by one-photon excitation, has already been deeply investigated for applications in surface-relief gratings and optical storage [18,19].

In this paper, we study the two-photon induced birefringence caused by the photoisomerization of the azomoieties in spin-coated films of poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-thienyl)ethanoate], PAzT. Recently, we have reported resonant nonlinear optical properties of PAzT induced by picosecond [20] and femtosecond laser pulses [21]. This polymer is a derivative of a polythiophene, synthesized by the introduction of azoaromatic groups at the 3-position of the thiophene rings (polyazothiophene), comprising the properties from the polyconjugated backbone and azoaromatic substituent. The *trans*–*cis* photoisomerization of the chromophores present in the PAzT allows its application in reversible optical data storage [18,22,23], surface-relief gratings [23–25] and electro-optical devices [26]. To select

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the proper excitation wavelengths for the two-photon induced birefringence experiments, we measured the two-photon absorption spectrum of PAzT using the *Z*-scan technique. Optical birefringence was induced in PAzT via two-photon absorption by employing femtosecond pulses at 680 and 775 nm, opening new opportunities for optical storage devices. As the azochromophores in PAzT are attached to the polymer backbone as side chain units, improved two-photon induced birefringence features were expected, in comparison to the guest–host systems previously studied [11,12].

2. Experimental

The synthesis of PAzT (poly[2-[ethyl-[4-(4-nitro-phenylazo)-phenyl]-amino]-ethane (3-thienyl)ethanoate]) used in this study was carried out according to Ref. [27], and its molecular structure is displayed in the inset of Fig. 1. The linear absorption spectrum of PAzT dissolved in *N*,*N*-dimethylformamide (DMF) was obtained in a Cary 17 spectrophotometer.

The two-photon absorption spectrum of PAzT in DMF ($N_0 = 2.2 \times 10^{18}$ molecules/cm^3 in repeating units) was obtained using the *Z*-scan technique [28], which allows the determination of the two-photon absorption coefficient β. This technique consists in moving the sample through the focal plane of a focused Gaussian beam, and monitoring the corresponding changes in the far field intensity. In the case of nonlinear absorption, the light field creates an intensity dependent absorption coefficient given by $\alpha = \alpha_0 + \beta I$, where I is the laser irradiance, and α_0 is the linear absorption coefficient. In off-resonant conditions, such as in two-photon absorption, the change in the transmitted power is integrated over time to give the normalized energy transmittance [28],

$$T = \frac{1}{\sqrt{\pi} q_0(z,0)} \int_{-\infty}^{\infty} \ln\left[1 + q_0(z,0)\, \mathrm{e}^{-\tau^2}\right] \mathrm{d}\tau, \tag{1}$$

being $q_0(z,t) = \beta I_0(t) L (1 + z^2/z_0^2)$. In Eq. (1) L is the sample thickness, z_0 is the Rayleigh length, z is the sample position, and I_0 is the pulse irradiance. The nonlinear coefficient, β, is obtained by fitting the *Z*-scan signatures using Eq. (1) [28]. The two-photon absorption cross-section, δ, is determined through the expression $\delta = h\nu\beta/N$, $h\nu$ being the excitation photon energy, and N is the number of molecules per cm^3. The unit used to express δ is the Göppert Mayer (GM), in which $1\ \mathrm{GM} = 1 \times 10^{-50}\ \mathrm{cm^4\ s\ molecules^{-1}\ photon^{-1}}$. The *Z*-scan experiment was performed using 120-fs pulses (from 620 nm to 1020 nm) from an optical parametric amplifier pumped by 150-fs pulses at 775 nm, delivered by a Ti/sapphire chirped pulse amplifier operating at 1 kHz.

To study the optically induced birefringence, we prepared films of PAzT by the spin coating method, which provides homogeneous films of regular thickness. The films were prepared from a solution of PAzT in chloroform using a concentration of 15 mg/ml, which was filtrated to separate the soluble from the insoluble fraction. The evaluation of the final concentration was performed by gravimetric methods. We submitted the samples to a thermal treatment for 16 h at 100 °C in order to eliminate residual stress arisen during the film preparation, which could produce an initial birefringence in the films. The average thickness of the films used in the birefringence measurement is 120 nm.

The two-photon induced birefringence was brought about by exposing the sample to linearly polarized 120-fs pulses from the optical parametric amplifier (writing beam). To monitor the birefringence during the fs-laser exposure, we measured the transmission of a low-power, linearly polarized 632.8 nm He–Ne laser beam (reading beam) through the sample and a set of crossed polarizers, as illustrated in Fig. 2. The polarization angle of the writing beam was set at 45° with respect to the polarization of the reading beam. The optically induced birefringence, Δn, can be determined from the reading beam transmission, T, using

$$\Delta n = (\lambda/\pi d) \sin^{-1} \sqrt{T}, \tag{2}$$

λ being the wavelength of the incident beam, and d the film thickness.

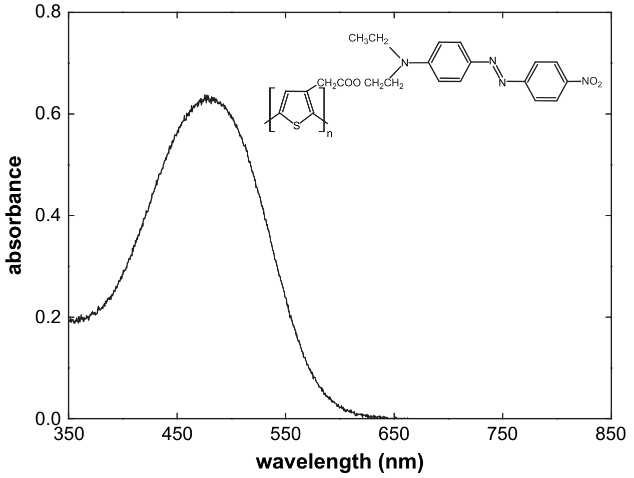

Fig. 1. UV–vis spectrum of PAzT/DMF solution. The inset shows the molecular structure of the PAzT repeating unit.

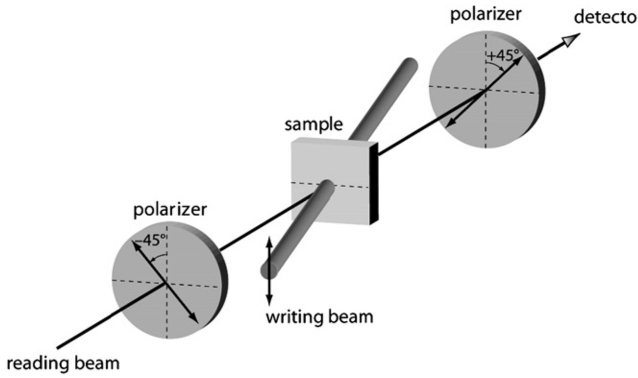

Fig. 2. Experimental setup for optical storage measurements. We used a He–Ne laser at 632.8 nm as the reading beam. The writing beams at 680 and 775 nm are produced by an optical parametric amplifier. Two crossed polarizers are used to determine the birefringence induced by the writing beam. The polarization of recording beam is set 45° off to the reading beam.

3. Results and discussion

The two-photon absorption properties presented by PAzT are not only given by the azochromophores attached to the polymer backbone, but also due to the conjugation of the polythiophene backbone, as reported in the literature [29,30]. In this study, however, we are only interested in the two-photon absorption of the azochromophores, because they are the ones responsible for the optically induced birefringence related to the *trans–cis* photoisomerization.

The linear absorption spectrum of PAzT dissolved in DMF is displayed in Fig. 1, along with the molecular structure of its repeating unit (inset). The peak at 480 nm corresponds to the $\pi \rightarrow \pi^*$ transition of the azoaromatic group, which is responsible for the *trans–cis* photoisomerization. This absorption peak has also a contribution of the thiophene backbone, but with intensity lower than that of the azoaromatic group. The sample is completely transparent for wavelengths longer than 650 nm, the spectral region where the nonlinear absorption will be excited.

The two-photon absorption cross-section spectrum of PAzT in DMF was measured through the open aperture *Z*-scan technique, and is displayed in Fig. 3. PAzT presents two-photon absorption in a large range of the NIR–vis spectrum, starting from 620 nm until 1020 nm. Higher values of δ are obtained when the excitation wavelength approaches the linear absorption band of PAzT. This behavior occurs as a consequence of the resonance enhancement of the nonlinearity, described by the Sum-Over-States (SOS) model, as reported in the literature [31–34]. In the near IR region ($\lambda > 900$ nm), we carried out *Z*-scan measurements with wavelength steps of nearly 30 nm, since this spectral region is far from the resonance enhancement, and therefore, is not very interesting for 2PA birefringence experiments. Despite the low accuracy, the two-photon absorption spectrum displayed in Fig. 3 seems to show a peak around 940 nm, which corresponds to approximately twice the wavelength of the one-photon absorption band at 480 nm (Fig. 1). Such feature was already reported for other organic molecules [32,35], and its explanation lies in the fact that the azochromophore in PAzT, responsible for the two-photon absorption, is asymmetric. In such case, transitions allowed via one-photon absorption can also be accessed via two-photon absorption, because the selection rules are relaxed. It is worth mentioning that two-photon absorption was not observed for PAzT in Ref. [21], where a white light continuum (WLC) source was used as excitation, because of the lower pulse intensity and sample concentration employed, in comparison to the ones used here. Considering the information obtained from the two-photon absorption spectrum of PAzT, we initiate the study on the two-photon absorption induced birefringence with the 120 nm thick spin-coated films. We chose two distinct excitation wavelengths for the writing beam: 680 and 775 nm. Excitation at 680 nm was chosen because at this wavelength PAzT presents a high two-photon absorption cross-section (370 GM) and, therefore, the induced birefringence should be optimized. In addition, this wavelength is far enough from the bottom of the absorption band, preventing any undesired linear absorption. Since commercially available fs-lasers operate around 800 nm, we also selected 775 nm ($\delta = 90$ GM) as a writing beam wavelength, aiming for future applications of the two-photon induced birefringence process.

Fig. 4 shows the time evolution of the reading beam transmission for both excitation wavelengths. We used excitation intensities of 1.53 GW/cm^2 and 15.3 GW/cm^2 for 680 and 775 nm, respectively. The higher excitation intensity was used to compensate the lower two-photon absorption cross-section at 775 nm. As seen in Fig. 4, before exposure ($t < A$), the probe beam transmission is zero, indicating that the chromophores are isotropically distributed. When the writing laser is switched on at $t = A$, the transmission increases as a result of the optically induced birefringence. At $t = B$ the fs-laser is switched off and the transmission decreases to a nearly constant value (see Fig. 4), remaining stable for several weeks.

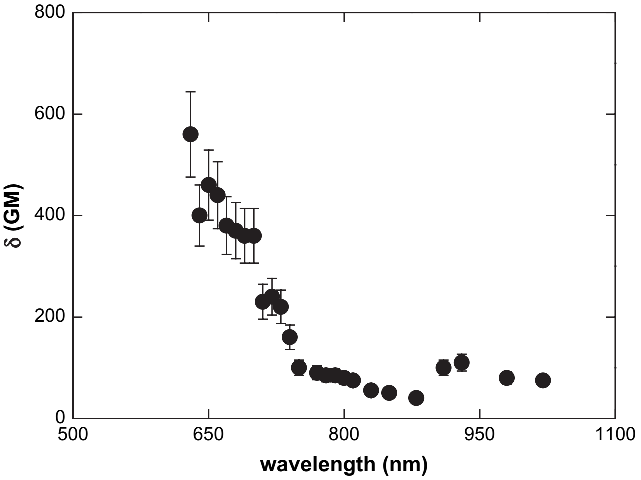

Fig. 3. Two-photon absorption cross-section spectrum of PAzT in DMF. The increase of two-photon absorption cross-section for excitations towards the beginning of linear absorbance is due to the resonance enhancement of the nonlinearity.

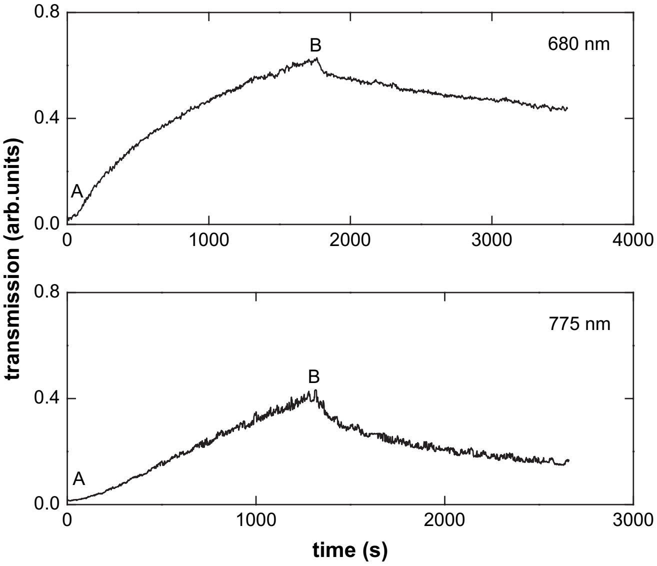

Fig. 4. Time evolution of the reading beam transmission obtained in spin-coated PAzT films via two-photon absorption at 680 and 775 nm.

The optically induced birefringence is a consequence of a change in the molecular orientation brought about by the absorption of the writing beam. Upon absorption of linearly polarized light from the writing beam, the azochromophores undergo a *trans–cis* isomerization. Subsequently, the *cis* isomer relaxes back to the more stable *trans* isomer, a process accompanied by a change in the chromophore orientation. After this isomerization–orientation cycle, the molecules with their dipole moments aligned perpendicular to the electric field no longer absorb light and, consequently, no further conversions will occur. At the end of several molecular isomerization–orientation cycles, the net result is a large number of molecules oriented perpendicularly to the laser polarization direction, creating a macroscopic birefringence [36–38]. When the writing beam is switched off, although some molecular relaxation comes about, a considerable number of molecules keep their orientation, yielding stable birefringence.

The maximum optically induced birefringence, Δn, obtained using Eq. (2), is about 1×10^{-2} for both excitation wavelengths. Fig. 4 clearly reveals that the optically induced birefringence presents two well distinct dynamics when excitations at 680 and 775 nm are employed. The slower process observed with 775 nm is due to the smaller two-photon absorption cross-section at this wavelength, which causes a smaller isomerization rate and, consequently, a slower birefringence dynamics. It is also interesting to note that an excitation intensity 10 times higher was used at 775 nm in order to obtain a Δn value comparable to the one measured at 680 nm. Again, this result is related to the lower two-photon absorption cross-section of PAzT at 775 nm. This result also indicates that the process is about twice more efficient at 680 nm, once an intensity 10 times higher have to be used at 775 nm to induce the same level of birefringence, whereas the two-photon absorption cross-section is four times smaller at 775 nm.

As mentioned before, the two-photon induced birefringence obtained for PAzT is approximately 10^{-2}. This value is about two orders of magnitude higher than the ones reported for guest–host films under two-photon excitation [11,12]. We believe that such distinct values are related to the smaller mobility of the azochromophores in PAzT after the orientation, in contrast to the higher molecular mobility expected in guest–host systems, where the azochromophores are not attached to the polymer backbone. An optically induced birefringence value of 10^{-1} was obtained for PAzT films when one-photon excitation at 514 nm was used (result not shown). This value is one order of magnitude higher than the one presented here for two-photon excitation, in agreement with Refs. [11,12], where the same difference is observed for one- and two-photon induced processes. This result also points out that the structure of PAzT favors the orientation of the azochromophores.

To confirm the two-photon nature of the observed birefringence, we measured the optically induced birefringence as a function of the writing beam irradiance at 775 nm, as shown in Fig. 5. The nearly quadratic dependence observed (slope = 1.93 and $R^2 = 0.98$) corroborates the two-photon origin of the observed process.

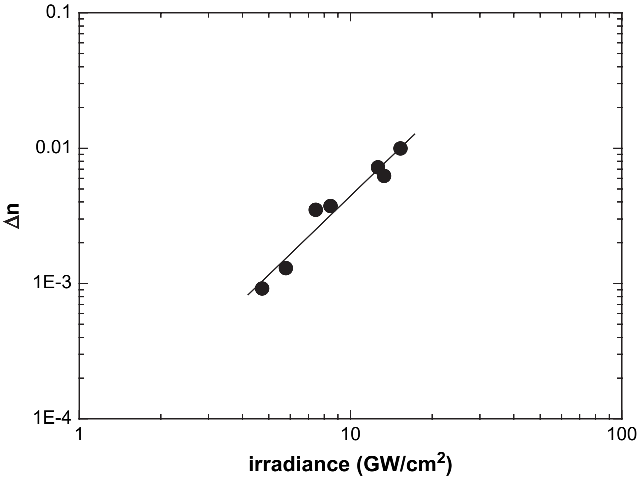

Fig. 5. Induced birefringence versus irradiance at 775 nm for the PAzT spin-coated film, showing the quadratic dependence typical for two-photon absorption processes.

Although the two-photon absorption cross-section values for PAzT are not as high as the ones reported in the literature for other molecules [39–41], they are enough to allow excitation of the azochromophores and induce the *trans–cis* isomerization. Due to the cumulative nature of the orientational process, after several cycles of isomerization–orientation, measurable birefringence is induced into the sample via two-photon absorption, which yields the optical storage. The advantage of using two-photon absorption instead of one-photon absorption to achieve birefringence into the material lies in the possibility of data recording in the bulk [11], and not only at the surface, due to the spatial localization provided by the two-photon absorption. Therefore, recording within the volume [6,42] becomes feasible, without erasing or overwriting the data previously stored on neighboring positions. As a consequence, the data density achievable by optical memory devices can be extremely increased.

4. Conclusion

The two-photon absorption cross-section spectrum of PAzT, determined through the open aperture *Z*-scan technique, increases near the edge of the linear absorption due to resonance enhancement of the nonlinearity. According to the two-photon absorption spectrum, we selected 680 and 775 nm as the wavelengths to be used in the birefringence experiments. The two-photon absorption induced birefringence arises from the molecular reorientation after several cycles of light isomerization–orientation of the azochromophore attached to the polymer backbone. This feature combined to the polymer backbone intrinsic conductivity makes this material a promising candidate to be used in photonics applications.

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References

[1] Nguyen LH, Straub M, Gu M. Advanced Functional Materials 2005; 15:209.

[2] Serbin J, Gu M. Optics Express 2006;14:3563.

[3] Scrimgeour J, Sharp DN, Blanford CF, Roche OM, Denning RG, Turberfield AJ. Advanced Materials 2006;18:1557.

[4] Maruo S, Nakamura O, Kawata S. Optics Letters 1997;22:132.

[5] Kawata S, Sun HB, Tanaka T, Takada K. Nature 2001;412:697.

[6] Parthenopoulos DA, Rentzepis PM. Science 1989;245:843.

[7] He GS, Bhawalkar JD, Zhao CF, Prasad PN. Applied Physics Letters 1995;67:2433.

[8] Dougherty TJ, Henderson BW, Schwartz S, Winkelman JW, Lipson RL. In: Henderson BW, Dougherty TJ, editors. Photodynamic therapy: basic principles and clinical applications. New York: Marcel Dekker; 1992. p. 1.

[9] Denk W, Strickler JH, Webb WW. Science 1990;248:73.

[10] Kohler RH, Cao J, Zipfel WR, Webb WW, Hansen MR. Science 1997;276:2039.

[11] Mendonca CR, Neves UM, De Boni L, Andrade AA, dos Santos DS, Pavinatto FJ, et al. Optics Communications 2007;273:435.

[12] Cardoso MR, Neves UM, Misoguti L, Ye ZH, Bu XR, Mendonca CR. Optical Materials 2006;28:1118.

[13] Si JH, Qiu JR, Guo JY, Qian GD, Wang MQ, Hirao K. Applied Optics 2003;42:7170.

[14] Maeda M, Ishitobi H, Sekkat Z, Kawata S. Applied Physics Letters 2004;85:351.

[15] Ishitobi H, Sekkat Z, Kawata S. Journal of the Optical Society of America B − Optical Physics 2006;23:868.

[16] Ishitobi H, Sekkat Z, Kawata S. Journal of Chemical Physics 2006:125.

[17] Magennis SW, Mackay FS, Jones AC, Tait KM, Sadler PJ. Chemistry of Materials 2005;17:2059.

[18] Natansohn A, Rochon P, Gosselin J, Xie S. Macromolecules 1992; 25:2268.

[19] Mendonça CR, dos Santos DS, Balogh DT, Dhanabalan A, Giacometti JA, Zilio SC, et al. Polymer 2001;42:6539.

[20] Correa DS, Goncalves VC, Balogh DT, Mendonca CR, De Boni L. Polymer 2006;47:7436.

[21] Correa DS, De Boni L, Goncalves VC, Balogh DT, Mendonça CR. Polymer 2007;48:5303.

[22] Rochon P, Gosselin J, Natansohn A, Xie S. Applied Physics Letters 1992; 60:4.

[23] Oliveira ON, dos Santos DS, Balogh DT, Zucolotto V, Mendonca CR. Advances in Colloid and Interface Science 2005;116:179.

[24] Kim DY, Tripathy SK, Li L, Kumar J. Applied Physics Letters 1995; 66:1166.

[25] Mendonça CR, Dhanabalan A, Balogh DT, Misoguti L, dos Santos DS, Pereira-da-Silva MA, et al. Macromolecules 1999;32:1493.

[26] Lanzi M, Paganin L, Costa-Bizzarri P. European Polymer Journal 2004; 40:2117.

[27] Gonçalves VC, Balogh DT. European Polymer Journal 2006;42:3303.

[28] Sheik-Bahae M, Said AA, Wei TH, Hagan DJ, Van Stryland EW. IEEE Journal of Quantum Electronics 1990;26:760.

[29] Van Keuren E, Wakebe T, Andreaus R, Mohwald H, Schrof W, Belov V, et al. Applied Physics Letters 1999;75:3312.

[30] Van Keuren E, Mohwald H, Rozouvan S, Schrof W, Belov V, Matsuda H, et al. Journal of Chemical Physics 1999;110:3584.

[31] Correa DS, Oliveira SL, Misoguti L, Zilio SC, Aroca RF, Constantino CJL, et al. Journal of Physical Chemistry A 2006; 110:6433.

[32] De Boni L, Misoguti L, Zilio SC, Mendonca CR. ChemPhysChem 2005; 6:1121.

[33] Franken PA, Ward JF. Reviews of Modern Physics 1963;35:23.

[34] Kamada K, Ohta K, Yoichiro I, Kondo K. Chemical Physics Letters 2003;372:386.

[35] Antonov L, Kamada K, Ohta K, Kamounah FS. Physical Chemistry Chemical Physics 2003;5:1193.

[36] Xie S, Natansohn A, Rochon P. Chemistry of Materials 1993;5:403.

[37] Natansohn A, Rochon P, Barrett C, Hay A. Chemistry of Materials 1995; 7:1612.

[38] Ho MS, Barrett C, Paterson J, Esteghamatian M, Natansohn A, Rochon P. Macromolecules 1996;29:4613.

[39] Oliveira SL, Correa DS, Misoguti L, Constantino CJL, Aroca RF, Zilio SC, et al. Advanced Materials 2005;17:1890.

[40] Zheng SJ, Leclercq A, Fu J, Beverina L, Padilha LA, Zojer E, et al. Chemistry of Materials 2007;19:432.

[41] Gao B, Lu CG, Xu J, Meng F, Cui YP, Tian H. Chemistry Letters 2006; 35:1416.

[42] Kawata S, Kawata Y. Chemical Reviews 2000;100:1777.