Nonlinear Absorption Spectrum in MEH-PPV/Chloroform Solution: A Competition between Two-Photon and Saturated Absorption Processes

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Knowledge about the nonlinear absorption spectra of materials used in photonic devices is of paramount importance in determining their optimum operation wavelengths. It is well-know that resonances enhance the nonlinear response of a material, but in this case, slow excited states processes, propagation losses, and photodegradation can take place, which are known to be deleterious for photonic applications. With this concern, we have studied the nonlinear degenerate spectrum of poly(MEH-PPV) using femtosecond laser pulses from 460 to 1000 nm. Such a wide band spectrum has never been investigated in previous works reported in the literature. We were able to distinguish between a strong two-photon absorption (2PA) mechanism at nonresonant conditions and a saturated absorption (SA) that overcomes the 2PA process as we approach the absorptive region. The results were fitted with rate equations obtained from an energy level model.

Introduction

Among conjugated polymers, the family of poly(phenylene-vinylene) (PPV) has attracted considerable attention owing to its interesting optical and electrical properties.[1,2] PPV-based polymers are very promising for photonic applications due to the combination of their excellent film-forming properties with interesting light-emitting ability. Concerning nonlinear optics, PPV derivatives were shown to exhibit strong two-photon processes. Recent works have studied a two-photon absorption followed by emission, which opens prospects for their use for up-conversion lasing.[3,4] Even though high optical nonlinearities (absorption and refraction) have been reported for several polymers, including PPV,[5−7] most of them were measured with a single wavelength. From the application point of view, the knowledge of both linear and nonlinear absorption is important because a device must operate in a wavelength presenting high nonlinear response and low propagation losses. Besides, the optimization of nonlinear optical properties can only be done if the nonlinearity mechanism is fully understood. Again, this task can only be accomplished if a database with nonlinear optical dispersion over a wide spectral range is obtained for different materials.

In a 2PA process, which usually predominates at the nonresonant region, two photons of longer wavelength are simultaneously absorbed by a chromophore that would normally be excited by a single photon with a shorter wavelength. Besides the ability to create excited states with photons of half the required excitation energy, the I^2 dependence of 2PA allows chromophores excitation with a high degree of spatial selectivity. Therefore, the 2PA process has attracted great interest in different fields of application, such as chemistry, optical data storage,[8,9] two-photon fluorescence imaging,[10−14] and two-photon photodynamic cancer therapy.[15,16] On the other hand, at the resonant condition, nonlinear processes associated with excited state population, such as saturable absorption (SA), can

take place. The SA process has been extensively studied for use in optical switching, short pulse generation, etc., applications that require strong and fast SA processes. In this way, there is considerable interest in the design, synthesis, and characterization of new organic chromophores and polymers with potentially large absorptive nonlinear optical properties (2PA and SA). Moreover, nonlinear optical properties of organic materials may be optimized, at least in principle, by molecular engineering methods to match the application requirements. Certainly, mechanical properties and processability can be improved as well.

In this context, this work reports on the degenerate nonlinear absorption spectrum for MEH-PPV/chloroform solution, obtained through the femtosecond Z-scan technique, where a competition between two-photon and saturated absorption processes was observed. Such competition between nonlinear mechanisms is rarely explored in the literature and can lead to misinterpretation of the nonlinear effect. This kind of investigation in MEH-PPV, an important material for photonic applications, and a difference in the 2PA maximum are features never observed in previous investigations.

Experimental Section

Nonlinear optical measurements were carried out with the Z-scan technique, which is a simple and sensitive method to determine nonlinear optical properties.[17,18] Our open aperture Z-scan experiments employed laser pulses from an optical parametric amplifier (TOPAS, from Light Conversion) pumped by 150 fs pulses at 775 nm delivered by a Ti:sapphire chirped pulse amplified system (CPA-2001, from Clark-MXR Inc.) operating at a 1 kHz repetition rate. Pulse energies used here were limited to 0.01 μJ to avoid photodegradation of the polymer. Linear and nonlinear optical measurements were performed in MEH-PPV/chloroform solution (10^{-4} mol/L in repeating unit). The average number of repeating units in the polymeric macromolecule is about 200 (MW = 5.0×10^4, D = 1.6).

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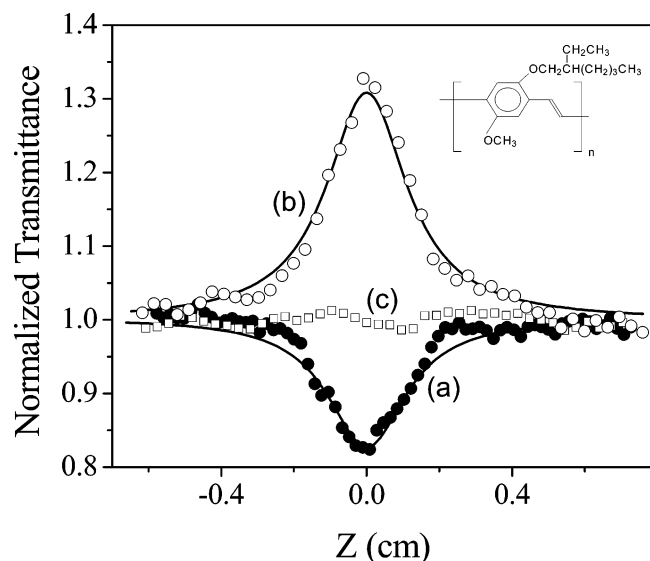
Figure 1. Open aperture Z-scan signature for MEH-PPV chloroform solution at (a) 600, (b) 555, and (c) 570 nm. The inset shows the molecular structure of MEH-PPV.
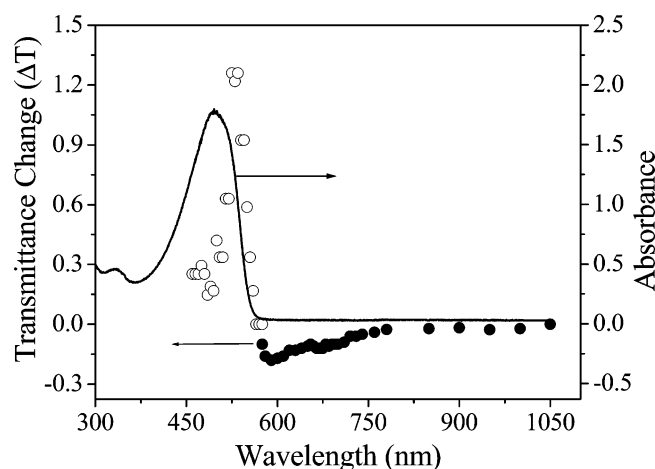

Figure 2. Linear and degenerate nonlinear absorption spectra for MEH-PPV.

Results and Discussion

Figure 1 presents open aperture Z-scan signatures for three distinct wavelengths. For nonresonant excitation ($\lambda = 600$ nm), the decrease in the normalized transmittance indicates a 2PA process, as seen in Figure 1a. When resonant excitation at 555 nm is employed (Figure 1b), an increase in the transmittance, characteristic of saturated absorption, is observed. This result indicates that excited state processes take place under resonant excitation. However, no changes in the normalized transmittance are observed at 570 nm (Figure 1c), because the 2PA and the SA effects cancel each other. The solid line in this figure represents the theoretical fitting obtained with a model including a 2PA effect[17] and a resonant process described by a three-energy-level diagram presented below. Thus, once an open aperture measurement is performed, the absorptive nonlinearity can be found unambiguously by fitting the experimental data. Similar Z-scan measurements were obtained for other wavelengths to determine the degenerated nonlinear absorption spectrum.

The transmittance change (ΔT) measured through the Z-scan experiment as a function of the wavelength (points) and the linear absorption spectrum (solid line) are plotted in Figure 2. As can be seen, the ΔT spectrum exhibits a strong SA process
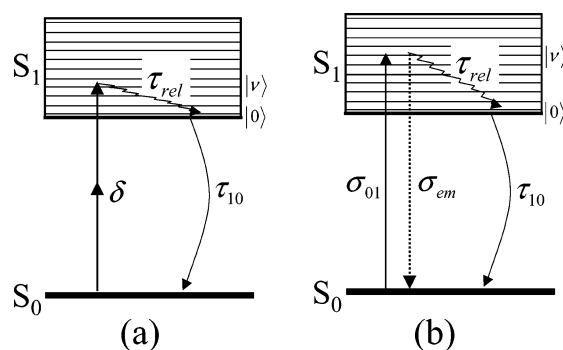
Figure 3. Three-energy-level diagram used to model the nonlinear optical processes.

in the resonant region (open circles) and a 2PA process (solid circles) away from the fundamental linear absorption band.

To understand the results of 2PA and SA presented in Figures 1 and 2, we consider the three-energy-level diagram depicted in Figure 3. According to this model, when nonresonant excitation is employed (Figure 3a) molecules at the ground state S_0 are promoted to an excited vibronic level $|v\rangle$ of S_1 by two-photon absorption. At this level molecules relax to the bottom of the vibronic band, S_1 then decaying to the level S_0 via spontaneous emission. By changing the excitation wavelength to resonant conditions, the one-photon absorption process dominates, as illustrated in Figure 3b. In this case, molecules are excited to the vibronic level $|v\rangle$ of S_1 and can either decay radiatively to the level S_0 via stimulated emission or undergo a relaxation to the bottom of the vibronic band S_1, thus radiatively decaying to level S_0 via spontaneous emission. According to this model, when the excitation wavelength is tuned from the red (nonresonant) to the blue (resonant) excitation, the nonlinear optical absorption process changes from a 2PA to a dominant SA. For wavelengths close to the bottom of the absorption band, around 570 nm, there is a competition between the two mechanisms. The rate equations used to describe the number of molecules, n_i^v, at each electronic state i and vibronic level v are

$$\frac{\mathrm{d}n_0}{\mathrm{d}t} = -W_{01}n_0 + W_{01}n_1^{\ v} + \frac{n_1^{\ 0}}{\tau_{10}} - W_{2PA}n_0 \qquad (1)$$

$$\frac{\mathrm{d}n_1^{\ v}}{\mathrm{d}t} = W_{01}n_0 - W_{01}n_1^{\ v} - \frac{n_1^{\ v}}{\tau_{rel}}W_{01} + W_{2PA}n_0 \qquad (2)$$

$$\frac{\mathrm{d}n_1^{\ 0}}{\mathrm{d}t} = \frac{n_1^{\ v}}{\tau_{rel}} - \frac{n_1^{\ 0}}{\tau_{10}} \qquad (3)$$

where $W_{01} = \sigma_{01} I(t)/(h\nu)$ and $W_{2PA} = \delta I^2(t)/(2\hbar\omega)$ are the transition rates for one- and two-photon process, respectively, with σ_{01} and δ being the ground sate and two-photon absorption cross sections. τ_{rel} and τ_{10} are respectively the intraband relaxation time and the lifetime of the first excited state. This set of equations was numerically solved, yielding the population dynamics, $n_i(t)$. The time evolution of the nonlinear absorption can be calculated according to

$$\frac{\mathrm{d}I}{\mathrm{d}z} = -[n_0(t) - n_1^{\ v}(t)]\frac{\sigma_{01}}{h\nu}I - \frac{n_0(t)\delta}{2h\nu}I^2 \qquad (4)$$

where the first term describes the SA process due to the ground state depletion, which includes stimulated emission, and the second term accounts for the 2PA process. Depending on the

Study of Nonlinear Absorption Spectra

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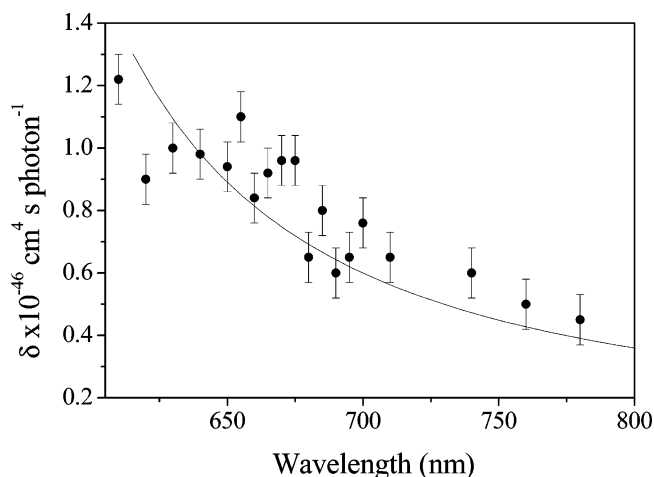
Figure 4. 2PA cross-section values experimentally determined and the SOS model.

excitation wavelength, one of these two terms will dominate. At resonant conditions the SA process overcomes the 2PA, while far from it, the 2PA process prevails. Of course in the region close to the absorption band there will be a competition between these two mechanisms. A similar description was used recently to study 2PA and saturated absorption in metalloporphyrin-doped boric acid glasses.[19]

By fitting each of the Z-scan signatures obtained at the nonresonant condition, the 2PA cross section, δ, can be determined by using the repeating unit concentration. The solid line in Figure 1a displays one such fitting. The values obtained for the 2PA cross sections range from 1.4×10^{-46} cm^4 s photon^{-1} (600 nm) to 6×10^{-47} cm^4 s photon^{-1} (740 nm). Furthermore, these values are of the same order of magnitude as those reported in the literature for femtosecond pulses.[6] To obtain the δ value using the chromophores concentration, we must use the average number of repeating units in the macromolecule given previously. Results in the spectral range from 650 to 800 nm, reported in ref 7 for a similar PPV derivative, presented a 2PA maximum around 820 nm. However, as seen in Figure 2 we covered a wider spectral range (460–1000 nm) and found a peak around 600 nm, which corresponds to the contribution of both 2PA and SA. This indicates that the pure 2PA peak should be below 600 nm. We believe that this difference is probably related to the picosecond pulse duration employed in ref 7, which allows excited-state contribution to the nonlinear absorption, once the excited-state lifetime is in the picosecond time scale. In a recent publication, Chung et al.[6] have also measured the degenerate two-photon absorption spectrum for MEH-PPV in a different spectral range (700–900 nm), using two-photon excited fluorescence measurements. They observed two peaks in the 2PA intensity around 790 and 840 nm with a decreasing trend to the blue. However, as shown in the 2PA cross-section spectrum displayed in Figure 4, a different behavior, characterized by an increase in the nonlinear absorption cross section up to about 600 nm, was observed. This behavior is in agreement with the resonant denominator in the sum-over states (SOS) model,[20–22] assuming that the $\pi \rightarrow \pi^*$ transition (corresponding to the peak of the absorption band) gives the major contribution to the virtual intermediate state, as displayed by the solid line in Figure 4. The different trend observed by Chung et al.[6] could be due to polymer photodegradation[23–25] because their experiments were performed with a high repetition rate (84 MHz) and average power (500 mW). To minimize photodegradation, our measurements were carried out with a low repetition rate (1 kHz) and low average power (<0.01 mW).

Due to the broader spectral range covered in our investigation, we were able to observe SA processes below 570 nm, at the absorptive region. The wavelength in which the SA mechanism starts to dominate is characterized by the inversion in ΔT in Figure 2. As can be seem in this figure, the SA process presents a strong band centered at around 535 nm. At 570 nm, there is a competition between the two-photon and saturable absorption processes, which cancel each other, and no changes are observed in the normalized transmittance.

To confirm this competition between two distinct nonlinear optical processes around 580 nm, we carried out excited fluorescence measurements (results not shown here), using the same laser system employed in the Z-scan experiments. The fluorescence signal as a function of the pump irradiance presents different behavior for distinct wavelengths. For wavelengths longer than about 620 nm, a quadratic dependence, characteristic of two-photon excited fluorescence, can be observed, confirming the two-photon nature of the observed process. On the other hand, at 600 nm (maximum observed in the decrease of transmittance) a dependence of 1.5 (nonquadratic) was observed, indicating clearly that a contribution from the one-photon absorption process already starts taking place.

Using the model presented previously, we were able to fit the open aperture Z-scan signatures correspondent to the SA process. The solid line in Figure 1b represents the theoretical fitting obtained with $\tau_{10} = 260$ ps and $\tau_{rel} = 1$ ps, found in the literature for MEH-PPV,[26] while $\sigma_{01}(\lambda)$ values were determined by measuring the linear absorption at each wavelength ($\alpha_0 = N\sigma_{01}$). The values found for the ground-state cross sections range from 0.5×10^{-17} cm^2 (550 nm) to 2.5×10^{-17} cm^2 (500 nm). It should be pointed out that the SA effect observed is fully described by the ground-state population depletion without any contribution from the excited-state absorption. The stimulated emission process considered in our model was found to be very important in obtaining the theoretical fitting to the experimental results.

As seen in Figure 2, the position of the SA band is red shifted in comparison to the linear absorption band. By looking carefully into the absorption spectrum of MEH-PPV, a shoulder can be seen at longer wavelengths, which is related to the absorption of polymers with long conjugation length.[27] Our results indicate that the polymer chains responsible for the SA process are, probably, those with higher conjugated structures and, consequently, a high degree of charge delocalization, once the SA band we observed seems to coincide with the exciton band.

Conclusions

In summary, the experimental degenerate nonlinear spectrum was measured in a MEH-PPV/chloroform solution by using the Z-scan technique with femtosecond laser pulses. Large 2PA cross sections were found with values comparable to those presented in the literature for this compound. It was found that the 2PA spectrum presents a strong band away from the linear absorption band, with a peak below 600 nm. A strong saturated absorption band in the resonant region was also observed, and its cross section was estimated. This competition between 2PA and SA could be understood from an energy-level diagram. The SA band peak could be attributed to polymer chains with planar high conjugated structures.

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