

Linear and nonlinear optical properties of *trans*- and *cis*-poly(1-ethynylpyrene) based sonogel hybrid materials

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Abstract

The synthesis of sol–gel materials induced by ultrasonic action (sonolysis) is implemented as an alternative method for the fabrication of highly pure organic–inorganic composites with good monolithic and optical properties. The resulting SiO₂ glass exhibits high porosity and allows the inclusion of organic compounds in the colloidal sol-state. In this work, optical properties of *trans*-poly(1-ethynylpyrene) (*trans*-PEP) and *cis*-poly(1-ethynylpyrene) (*cis*-PEP) ($M_w = 24,000$ g/mol) incorporated in this kind of gels were studied by absorption and fluorescence spectroscopies. Absorption spectra of the polymers showed that *trans*-PEP possesses a higher degree of conjugation than its homologue *cis*-PEP in sol–gel. Intramolecular interactions occur between adjacent pendant pyrene units (associated pyrenes) present in each polymer, giving rise to static excimer emissions, strongest in *cis*-PEP because of the shorter distances between aromatic rings. The results were compared to those previously reported for these polymers in solution. Besides, *trans*- and *cis*-PEP exhibited nonlinear optical properties like third harmonic generation (THG), which were measured in sol–gel phase for spin-coated film samples.

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1. Introduction

Over the last 30 years, π -conjugated polymers have been regarded as promising materials for the development of electronic and photonic devices such as light emitting diodes, photovoltaic cells and nonlinear optical systems [1–5]. The opto-electronic properties vary remarkably depending on the conjugation length between the consecutive repeat units. Polyarylacetylenes (particularly polyphenylacetylene) have been widely studied by many research groups. In general, polyarylacetylenes exhibit *trans*-*transoidal*, *cis*-*transoidal*, *trans*-*cisoidal* and *cis*-*cisoidal* geometries as shown in studies involving FTIR and ¹H NMR investigations of polyphenylacetylene [6,7].

In a previous work [8], we reported the preparation of *trans*-poly(1-ethynylpyrene) (*trans*-PEP) and *cis*-poly(1-ethynylpyrene) (*cis*-PEP) in function of the selected catalytic system. The structures of *trans*-PEP and *cis*-PEP are shown in Fig. 1.

Polymerization of 1-ethynylpyrene (EP) with WCl₆ led to the formation of *trans*-PEP with molecular weights ranging from 24,000 to 470,000 g/mol and polydispersities between 2.9 and 11 [9]. By contrast, the polymerization of EP with (1-Me-indenyl)(PPh₃)Ni–C=C–Ph and methylaluminumoxane (MAO) led to the formation of soluble *cis*-*transoidal* *cis*-PEP with molecular weights from $M_w = 2200$ –24,000 g/mol and polydispersities about $M_w/M_n \approx 2$ [8].

Since the properties of polyarylacetylenes depend on a big measure of the geometry of the polyacetylene backbone, we carried out a comparative study of thermal, optical, electrochemical properties and conductivity between two samples of *trans*-PEP and *cis*-PEP bearing the same molecular weight ($M_w = 24,000$ g/mol) [10,11]. Absorption spectra of these polymers in tetrahydrofuran (THF) solution showed that *trans*-PEP possesses a higher degree of conjugation than its homologue *cis*-PEP. Fluorescence spectroscopy revealed that intramolecular interactions occur between adjacent pendant pyrene units (associated pyrenes) present in each polymer, giving rise to static excimer emissions, strongest in *cis*-PEP because of the shorter distances between aromatic rings [10].

On the other hand, the sol–gel technique has been intensively used in the last 10 years as a standard method to confine and encapsulate different dopant species into a glassy

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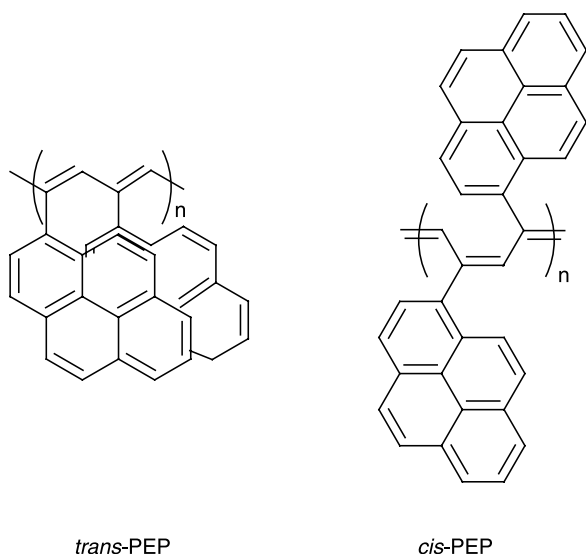


Fig. 1. Structures of *trans*- and *cis*-PEP.

SiO₂ matrix in order to obtain novel advanced materials with interesting optical and mechanical properties [12–17]. Potential applications have been proposed in recent years for organic doped SiO₂ networks in several research fields like nonlinear photonics, photocromic materials, photorefractivity, sensing devices, biomedicine, and tunable solid state dye-laser systems, among others [18–25]. The investigation of nonlinear optical (NLO)-processes are particularly interesting since they offer potential applications in photonics. Emphasis has been put on materials suitable for electro-optical systems and integrated optical circuits adopting the guided-wave format, which provide additional routes to the conception and production of photonic and telecommunication devices. Other important aspect to develop efficient devices suitable for optical sciences and photonics are the material malleability and mechanical stability required in several technological implementations, for example, in waveguiding, sensing devices and quasi-phase-matched (QPM) structures. In these cases, deposition of organic spin-coated films is required to fill up the guiding optical channels generated by standard photolithographic techniques, which have to remain stable for long periods of time. From the sol–gel sciences point of view, easy material processing offered by the colloidal state and recent developments on the deposition of doped sol–gel thin film layers, satisfy largely the requirements mentioned above [17]. Since the gelation process may take long time before the doped colloidal mixture reaches a dry and stable state, it allows an efficient deposition of doped colloidal dispersions (sols) onto the micrometric integrated structures registered in different kind of wafers and substrates. The high malleability of these materials permits them to adopt a wide variety of shapes required for photonic purposes. Once the drying process is completed, the rigidity of the hybrid sol–gel material in the desired format is achieved. The incorporated organic compounds will provide a desired physical or chemical property, whereas the inorganic part of the hybrid composite increases its mechanical and thermal strength [26,27]. These

materials can show a very stable behavior within a wide range of temperatures depending on the purity of the sol–gel precursor solvents. Thus, the different optical properties of the dopant species are preserved, without decomposition of the fragile guest molecules.

In the present work, we report the development of *trans*- and *cis*-poly(1-ethynylpyrene) based sol–gel hybrids generated by ultrasonic action (sonogel materials). The SiO₂-matrix obtained by sonolysis exhibit high porosity and purity, which provides a favorable environment for the inclusion of organic dopants. In this case, ultrasonic irradiation, instead of commonly used basic or acidic catalyst is implemented to produce acoustical cavitation within the liquid H₂O/tetraethoxysilane (TEOS) reactants. This procedure gives a hydrolyzed-TEOS colloidal dispersion (sol), which forms, after drying process, a highly pure SiO₂ network. In the colloidal state, the sol can be easily doped with *cis*-PEP and *trans*-PEP. After drying, these composites form stable and high quality hybrid optical materials suitable for several applications. The optical properties of *trans*-PEP and *cis*-PEP in bulk sol–gel samples have been studied by absorption and fluorescence spectroscopies and the results were compared to those previously obtained for these polymers in solution. Besides, we measured the cubic $\chi^{(3)}$ nonlinear optical response of *trans* and *cis*-PEP in this new environment using two samples with the same molecular weight ($M_w = 24,000$ g/mol) by means of the THG-technique. Therefore, the doped colloidal solution was spin-coated on fused silica substrates to form, after drying, hybrid film layers with a thickness of 1.2 μm .

The experiments reported in this work, have been carried out as a first attempt to the development of photonic organic–inorganic devices, implementing sonogel materials, as a practical alternative instead of expensive inorganic crystals. Here, the use of specially designed NLO-organic molecules plays an important role.

2. Experimental section

2.1. Catalyst free sonogel sample preparation

The sol–gel method has been traditionally used to synthesize amorphous SiO₂, based on the hydrolysis of different precursors such as TEOS, TMOS, etc., followed by condensation reactions of the hydrolyzed species. This method has been widely adopted as a suitable way to obtain glassy doped materials with good optical quality. Both, hydrolysis and condensation reactions normally occur in the presence of acidic or basic catalysts, where ethanol or methanol are used as standard solvents for the precursor and water reactants. Fundamental and experimental details for the sol–gel synthesis of SiO₂ can be extensively found in the literature [12]. On the other hand, several articles reporting emulsification action of the reactive mixtures induced by ultrasonic irradiation have been published in recent years, where no solvents have been used [28–31]. In such way, it is possible to obtain sonolyzed-gel materials with an elastic modulus several orders of magnitude higher than those prepared by conventional methods

[32]. In this work, a new approach for the preparation of highly pure SiO_2 sonogels is exploited (avoiding the use of both, solvents and catalysts). Here, the hydrolyzed species are substituted by molecular radicals generated by ultrasonic waves. More details about the synthesis, chemistry, and methodology to produce this new kind of materials can be found in Ref. [33], where the manufacture of free catalyst sol-gel samples implementing the sonolysis method is extensively discussed. Besides, only a brief explanation of this technique is presented and the implemented methodology to obtain organic-doped catalyst free hybrid composites with the *trans*- and *cis*-PEP polymers is presented for the first time.

Fig. 2 shows the implemented experimental device to prepare sonogel samples. A two compartments polymethacrylate cylinder was used as reaction chamber. A hole in the middle point of the chamber acts as support for a Pyrex glass vessel (100 ml), which is the reaction container. Two neoprene o-rings seal the upper from the lower part of the chamber allowing perfect isolation conditions. Several holes placed on the top and the wall of the reaction chamber allow different applications:

- (1) Hole (A) serves as an input for the ultrasonic tip; hole (B) is used to introduce electrodes in order to sense the pH-value continuously. Holes (C) and (D) are used as input and output valves in order to regulate a selected gas-flow, which rules the reaction environment of the system. Moreover, a thermocouple (type K) is also introduced through hole (C), parallel to the feed pipe of the selected gas, so that the reaction temperature can be accurately sensed. For the present application, only an oxygen-environment was used (300 ml min^{-1}), because it has been shown, that this atmosphere provides optimal conditions for the fabrication of SiO_2 networks with the current methodology [33].
- (2) Points E and F correspond to the input and output valves of a water cooling system, which control the reaction temperature. Low temperature conditions ($\sim 5^\circ\text{C}$) should be maintained in order to avoid excessive overheating of the reactant water produced by energetic ultrasonic wave irradiation.

As precursor solution, 25 ml of tetraethoxysilane (TEOS, Fluka 99%, cat. Nr. 86578) and 25 ml of three-distilled water were mixed into the glass vessel. The three-distilled water was

previously boiled in order to eliminate dissolved gases and then cooled to room temperature. The initial pH-value of water was 6.5. In order to avoid any possible over-heating of the reactants by the incidence of ultrasonic waves, the temperature was stabilized at 1°C for 1 h before irradiation. Variations on this temperature were carefully maintained below 2% in optimal experimental conditions. The tip of the ultrasonic-wave generator (Cole-Parmer-CPX) acts as an ultrasonic-homogenizer too. In order to fix the reaction atmosphere, the experimental system was sealed and isolated from room conditions, while an oxygen tube (AGA-ONU1072) was coupled to hole (C). Before the ultrasonic irradiation takes place, the selected gas was bubbled for ca. 15 min through the vessel. The metallic ultrasound tip, carefully located at the TEOS/ H_2O surface interface, is then started at 60 Hz and 180 W. Oxygen flow is maintained during the whole sonolysis process. After 3 h of programmed ultrasonic irradiation (on/off-intermittent sequences of 5 s), the chemical reaction takes place to produce the sol-gel product. A detailed study concerning to the influence of the ultrasound energy and variations of the gas-atmosphere to give good quality sol-gel samples, is discussed elsewhere [33]. An increment on the temperature of the TEOS/ H_2O reactant solution of about 5°C has been observed during ultrasonic action. Twenty four hours after irradiation, two phases appear in the reaction vessel: the upper product corresponds to unreacted TEOS, whereas the lower condensed product appears as a colloidal suspension containing the induced hydrolyzed reaction (H-TEOS). The unreacted TEOS is extracted and removed, while the remaining colloidal suspension was dropped and poured at different volumes into Teflon-containers. A solution of the dopant compounds in THF were added to the deposited colloidal suspension in order to start the gelation process and the insertion of the dopant agents within the porosity of the SiO_2 network. The resulting bulk hybrid materials possess higher purity compared to other traditional sol-gel hybrid materials, because the use of the ultrasonic waves instead of the reactive solvents and catalyst, gives samples with higher optical quality.

In order to estimate the surface area generated within the porous media of the sonolyzed SiO_2 matrix; 25 mg of the sol-gel reference sample were studied by the Brunauer–Emmett–Teller (BET)-method [34] from 25 to 1000°C (RIG-100 equipment). BET-studies showed large surface areas varying from 500 to $700 \text{ m}^2 \text{ g}^{-1}$, compared to those obtained by traditional catalyst-based sol-gel methodologies. In last case, typical surface areas in the range of 100 – $500 \text{ m}^2 \text{ g}^{-1}$ have been commonly reported [12,35]. Novel methodologies have been recently developed for the fabrication of amorphous SiO_2 with large surface areas, such as the xero-gel and aerogel-route, where surface areas up to 1000 and $2000 \text{ m}^2 \text{ g}^{-1}$ have been reported, respectively. Last kind of composites are, nevertheless, very difficult to synthesize [36,37]. Beside their adequate porosity, our samples showed high stability from 20 to 600°C . After 600°C , the sample shows a drastic structural collapse and the average surface area drops from 550 to $2 \text{ m}^2 \text{ g}^{-1}$ when the temperature reaches 1000°C [33].

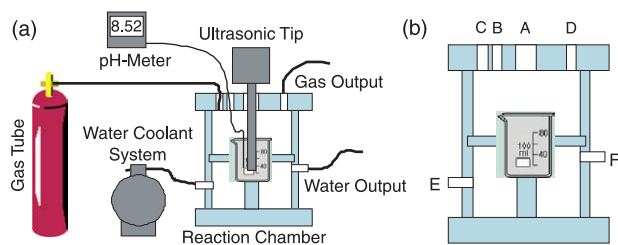


Fig. 2. (a) Experimental device for catalyst free sonogel sample preparation and (b) details of the reaction chamber: (A) ultrasonic tip, (B) pH-electrode, (C) gas input, (D) gas output, (E) cooling water input, (F) cooling water output.

2.2. Hybrid sample preparation

For the present application, a solution containing 2 mg of the dopant compounds and 8 ml of the corresponding solvent (THF) was prepared. The doses of the hydrolyzed-TEOS (H-TEOS) versus dopant-dissolution (D-D) were prepared with a precise volumetric pipe and deposited into teflon-containers in order to obtain different doped optical glasses. It has been noted that solutions of the dopants in THF are better incorporated into the SiO₂ network, since the S₄ geometry of TEOS implies a zero dipolar moment and would not accept the inclusion of highly polar THF based solutions. However, H-TEOS becomes highly polar too, and provides an optimal environment for molecules dissolved in THF (dipolar moment $\mu=1.6$ D).

The synthesis and characterization of *trans*-PEP [9] and *cis*-PEP [8] were previously reported. Two samples of these polymers bearing identical molecular weights ($M_w=24,000$ g/mol) were selected for this investigation. All *trans*-PEP and *cis*-PEP based hybrids were generated with a starting total volume of 2 ml, varying the concentrations of H-TEOS: D-D as follows: 1.0:1.0, 1.2:0.8, 1.3:0.7, 1.4:0.6, 1.5:0.5, 1.6:0.4, 1.7:0.3, and 1.8:0.2 ml. Undoped sonogel samples (2:0) were also prepared for reference and calibration purposes. The samples were isolated with a plastic cover to avoid any atmosphere and temperature variations, and conserved for 2 weeks at room conditions in a clean-dry-dark environment (closed recipients with a small hole on the cap). Afterwards, the drying process of the samples is completed and the formation of bulk samples is achieved. Monolithic cylindrical samples with diameters from 6 to 8 mm and thickness about 0.8–1.2 mm were obtained in most cases for very slowly drying speeds. For thin film sample preparation, a home-made spin-coating system was implemented; deposition conditions were varied from 1000 to 1300 rpm. The thickness of the films was measured with a profilometer system (Dektak IIA, 0.5 nm resolution) on the step formed right after drying.

2.3. Absorption and fluorescence measurements in solution and sol–gel-phase

For absorption and fluorescence spectroscopies in solution, tetrahydrofuran (THF) was purchased from Aldrich (spectrophotometric grade). Prior to use, the solvent was checked for spurious emission in the region of interest and found to be satisfactory. The absorption spectra in solution were recorded on a Varian Cary 1 Bio UV/vis spectrophotometer (model 8452A) using 1 cm quartz cells and solute concentrations of $1-3 \times 10^{-5}$ M for the polymers. It has been verified that the Beer–Lambert law applies for the concentrations used. Fluorescence spectra corrected for the emission detection were recorded on a Spex Fluorolog-2 spectrophotometer with an F2T11 special configuration. Each solution was excited near the absorption wavelength maximum using a 1 cm quartz cell. For polymers a concentration of about $1-3 \times 10^{-6}$ M was used giving absorbances of less than 0.1 in order to avoid any inner filter effect.

For sol–gel hybrids, the absorption spectra were recorded in a double beam Shimadzu UV–vis. model 260 spectrophotometer taking the air in the reference beam. Photoluminescent studies were obtained with a FluoroMax-3 Jobin-Yvon-Horiba spectrofluorometer. Each bulk sample (5.91×10^{-5} M) was excited near the maximum absorption wavelength ($\lambda_{exc}=350$ nm).

2.4. THG measurements

Prepared sol–gel hybrid spin-coated layers (1.2 μ m thickness after drying) have been studied as active media for THG. Fig. 3 depicts the THG set-up, where a commercial optical parametric oscillator (Panther-OPO Laser system from Continuum, USA) tunable in the range $\lambda_{\omega}=200-2500$ nm at 10 Hz repetition rate and $\tau=7$ ns pulse width, was implemented to provide the fundamental wave. High power focused pulses of tens of megawatt per square centimeter were used in order to irradiate the samples at $\lambda_{\omega}=1543$ nm. The focal length of the focusing lens is less than 50 mm in order to make the air contribution to the THG-signal negligible [38,39]. The fundamental wave was filtered with an IR-glass to avoid parasitic light coming from anti-Stokes radiation. The third harmonic waves ($\lambda_{3\omega}$) were detected with a sensitive photomultiplier tube (HAMAMATSU, R928) behind interference optical filters centred at the suitable wavelength. A rotation stepping motor system (OWIS, GmbH, Germany, 0.1° resolution) was implemented in order to perform angle dependent THG-measurements. The THG-device was calibrated using a fused silica plate ($\chi^{(3)}=1.47 \times 10^{-14}$ esu, at $\lambda_{\omega}=1543$ nm), which is frequently used as standard reference for cubic NLO-effects [40,41].

A simple experimental configuration for the determination of the $\chi^{(3)}$ -coefficient, in the most general case when phase-matching conditions cannot be assured, is the Maker-fringes configuration. It consists in detecting the intensity of the generated beam at third-harmonic frequency as a function of the incidence angle of the fundamental beam. In this way, as the incidence angle is varied, the effective optical path within the sample is tuned, leading alternatively to experimental conditions of phasematching and of phase-mismatch. The result is an interference pattern of the detected THG-intensity, from which the evaluation of $\chi^{(3)}$ is obtained by theoretical fitting. In the present case, the Maker-fringes technique has been applied to film samples, deposited on transparent substrates. In principle, both the film and the substrate

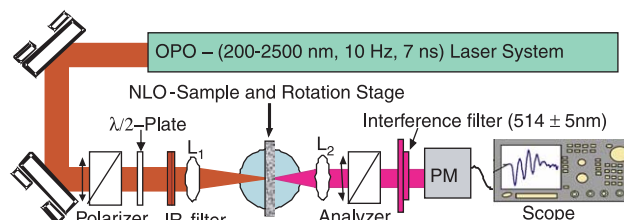


Fig. 3. Experimental device for THG measurements in *trans*- and *cis*-PEP based hybrids.

contribute to the detected THG-signal and the two contributions must be separately identified. Moreover, since the film is deposited only on one side of the substrate, the experimental configuration is asymmetric from a geometrical view point and different relations have been developed in order to fit, respectively, the ‘front’ configuration where the fundamental beam enters the film first, or the ‘back’ configuration, where the films stays behind the substrate. The equations for the interpretation of Maker-fringes experimental patterns have been derived by several authors [40,42–44].

By measuring the Maker-fringes patterns of our samples, the modulus of the nonlinear coefficient can be estimated, once the nonlinear coefficient of the substrate and the linear optical constants are known. For this reason, fused silica has been chosen as reference and substrate material, because its optical constants are well known and its nonlinear coefficient has been determined with high accuracy for the wavelength used in these experiments [38–41].

3. Results and discussion

Optical properties of *trans*- and *cis*-PEP in THF solution were previously reported by us, and both absorption and emission spectra were discussed in detail [10,11]. Fig. 4 shows the UV–vis spectra of pure sol–gel, *trans*-PEP and *cis*-PEP in sol–gel and THF solution. In sol–gel, both polymers exhibit an absorption band at 340 nm due to $S_2 \leftarrow S_0$ transition of pyrene groups (Fig. 4). This band is also observed in THF solution and appears at 350 nm. On the other hand, the absorption spectrum of *cis*-PEP in sol–gel and THF solution exhibit a second absorption band at 453 nm resulting from the formation of intramolecular pyrene–pyrene complexes in the polymer [10]. Beside the band at 340 nm, the absorption spectrum of *trans*-PEP in sol–gel exhibits a maximum absorption wavelength at $\lambda_{\max} = 591$ nm, due to the highly conjugated polyacetylene backbone. This band is also observed in THF solution at $\lambda = 580$ nm [10]. By contrast, *cis*-PEP shows only a tail in sol–gel around 570 nm, which indicates a lower conjugation degree in this polymer. A similar tail was also observed for *cis*-PEP in

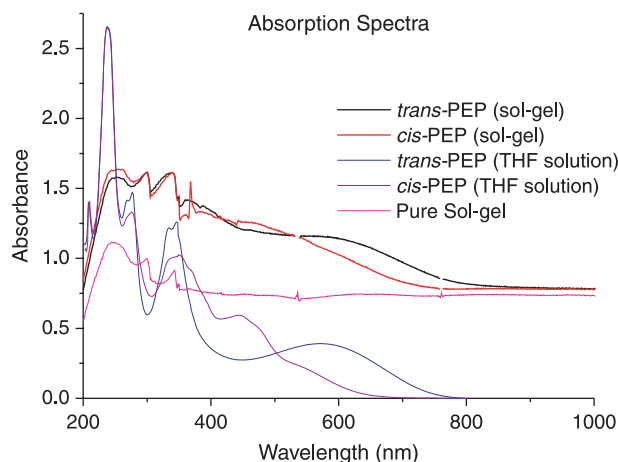


Fig. 4. Absorption spectra for pure sol–gel, *trans* and *cis*-PEP (in THF solution and sol–gel).

THF solution at $\lambda = 537$ nm. The absorption spectrum pure sol–gel (Fig. 4) only showed a band at 246–299 nm, which is less intense than those observed for the doped samples, so that we can be sure that the bands observed for the doped samples are due to the PEP polymers and the sol–gel matrix does not contribute remarkably to the absorption spectrum. On the other hand, the fact that the lowest energy band of *trans*-PEP is significantly red-shifted in sol–gel compared to that observed in THF solution, reveals that in this media the polyacetylene main chain of this polymer is better aligned to planarity. A similar behavior was observed in cast films of *trans* and *cis*-PEP [11], where the absorption bands are red-shifted compared to those observed in solution. This phenomenon can be explained in terms of the viscosity of the environment. In solution, polymer molecules can move and display rotations along the σ bonds, whereas in sol–gel they reach their optimal conformation during the drying process. Once the sol–gel is completely dry, the rigidity of the media restrains the mobility of the molecules avoiding them to adopt other conformations.

The fluorescence spectra of pure sol–gel (not normalized), *trans*-PEP and *cis*-PEP in sol–gel and THF solution ($\lambda_{\text{exc}} = 350$ nm) are shown in Fig. 5. As we can see, pure sol–gel shows a weak emission between 400–500 nm, which does not modify significantly the emission spectra of the doped samples. On the other hand, *trans*-PEP in sol–gel exhibits an emission band at 400 nm coming from the pyrene groups in the non-associated state or ‘monomer emission’. This band is better structured in the fluorescence spectrum of this polymer in THF solution and appears in the 360–465 nm region. Besides, *trans*-PEP shows also an emission tail in sol–gel from 413 nm to beyond 600 nm. Similarly, in THF solution, this polymer shows considerable emission beyond 500 nm [10,11]. It is very well known that pyrene itself does not emit at this wavelength [45] so that this emission can be only due to intramolecular interactions between pendant pyrene groups in *trans*-PEP. Indeed, part of the emission is absorbed by the highly conjugated polyacetylene backbone [11], that is why in both fluorescence spectra (in sol–gel and THF solution) no excimer emission seems to occur.

On the other hand, the fluorescence spectrum of *cis*-PEP in sol–gel (Fig. 5) exhibits a ‘monomer emission’ band at 416 nm

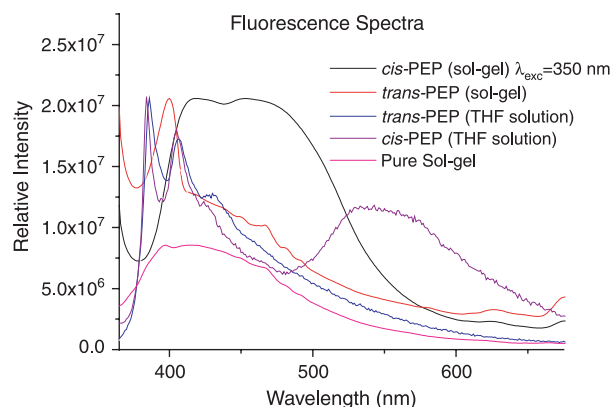


Fig. 5. Fluorescence spectra of pure sol–gel (not normalized), *trans*-PEP *cis*-PEP (in THF solution and sol–gel, $\lambda_{\text{exc}} = 350$ nm).

followed by an intense excimer emission band at 453 nm. This band results also from intramolecular interactions between adjacent pyrene units along the molecular frame in *cis*-PEP. In fact, in the fluorescence spectrum of the same polymer in THF (Fig. 5), this band has a vibronic structure and appears around 550, 50 nm red-shifted compared to that observed in sol-gel. This shift reveals that in sol-gel the *cis*-polyacetylene chain is more twisted and intramolecular interactions between adjacent pendant pyrene groups are stronger than in solution. Indeed, the rigidity of the environment confine the molecules to narrower spaces, thereby restraining their mobility and favoring interactions between pyrene groups at shorter distances. Previous molecular modeling studies performed on *trans*-PEP and *cis*-PEP segments, jointly with absorption spectra demonstrated that in *cis*-PEP the *cis*-polyacetylene main chain is twisted and pyrene groups are randomly oriented, whereas in *trans*-PEP the *trans*-polyacetylene main chain adopts a nearly planar conformation and pyrene pendant groups are placed perpendicular to it bearing a regular stacking [8]. We believe that the sol-gel environment intensify these conformational phenomena in both polymers.

Excitation spectra of *trans*-PEP and *cis*-PEP in sol-gel (Fig. 6) were carried in order to verify if only intramolecular interactions occur. For both polymers, excitation spectra were

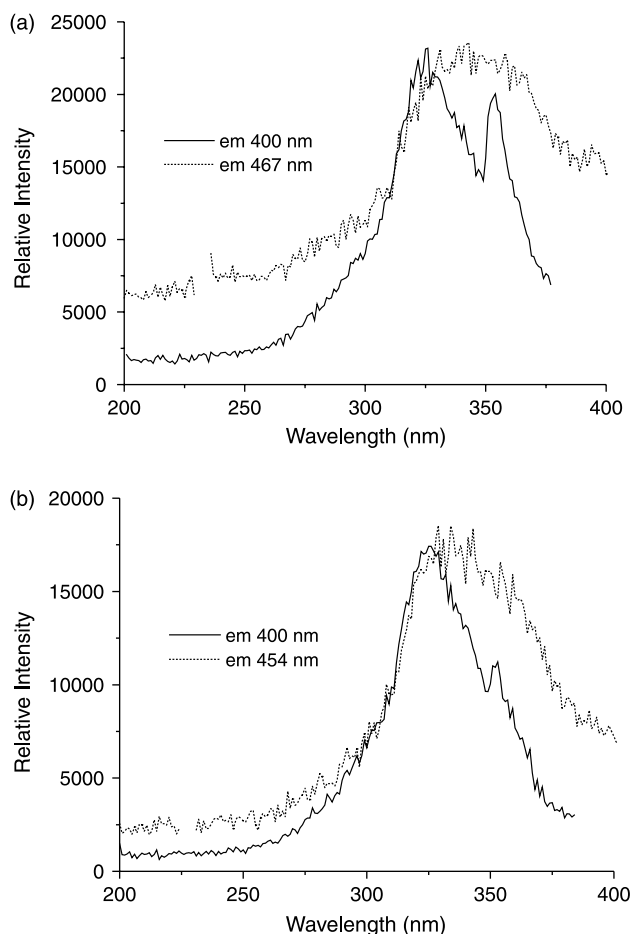


Fig. 6. Excitation spectra in sol gel of (a) *trans*-PEP at $\lambda_{FM}=400$ nm and $\lambda_{FE}=467$ nm. (b) *cis*-PEP at $\lambda_{FM}=400$ nm and $\lambda_{FE}=454$ nm.

recorded, at the fluorescence wavelength of the monomer emission (λ_{FM}) and at the wavelength of the excimer emission (λ_{FE}), and compared. Fig. 6(a) shows the excitation spectra of *trans*-PEP in sol gel at $\lambda_{FM}=400$ nm and at $\lambda_{FE}=460$ nm and they showed to be different, which is against the rule of the formation of a dynamic excimer [45], thereby proving that no intermolecular interactions take place in this system. Similarly, the excitation spectra of *cis*-PEP in sol-gel were recorded at $\lambda_{FM}=400$ nm and at $\lambda_{FE}=454$ nm and they were not identical, showing also a lack of intermolecular interactions. In order to confirm these results, the fluorescence spectrum of pyrene in sol-gel was recorded at high concentration (1.15×10^{-2} M) (not shown) and this compound exhibited a monomer emission band at $\lambda_M=396$ nm followed by a intense excimer emission band at $\lambda_E=554$ nm. Moreover, excitation spectra were recorded for this compound at λ_{FM} and λ_{EM} and showed to be identical, revealing the presence of intermolecular interactions, which was not observed in the case of the polymers. This can be explained in terms of concentration and geometry. The concentrations of our polymer doped samples were about 5.9×10^{-5} M, very diluted to give rise to intermolecular interactions. In addition, the high steric effects of *trans*-PEP and *cis*-PEP prevents aggregation.

Finally, experimental techniques based on THG give direct access to the cubic nonlinear $\chi^{(3)}$ -coefficient, which is completely originated by the ultra-fast electronic response. Thus, vibrational, orientational, and thermal effects, which may contribute to the overall nonlinear response of the material, are excluded. THG-studies were performed on spin-coated hybrid layers.

In Fig. 7, we show a typical Maker-fringes pattern (front-configuration, near-resonant configuration: $\lambda_{\omega}=1543$ nm, $\lambda_{3\omega} \sim 514$ nm) of 1.4:0.6 and 1.2 μm thick *cis*-PEP and *trans*-PEP hybrid films. These films were deposited by spin-coating onto a 1 mm thick fused silica substrate. The Maker-fringes of the hybrid samples are compared to the fringes pattern generated by the reference substrate. The Maker-fringes pattern of the film-plus-substrate system does not show any

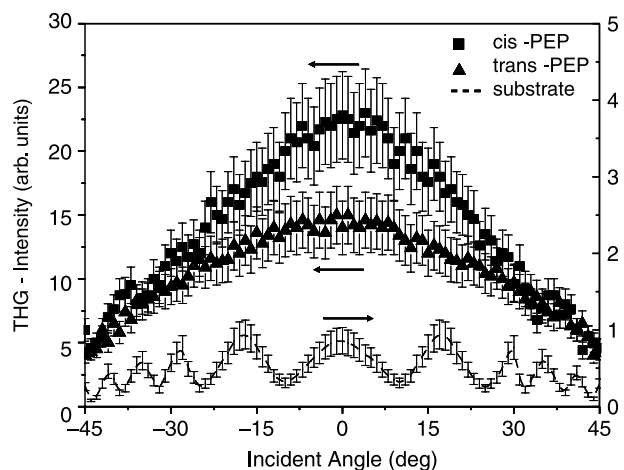


Fig. 7. Angle dependent THG-response of the reference substrate (dashed line) and the 1.4:0.6 *trans*-PEP (triangle) and *cis*-PEP (squares) hybrid films. ($\lambda_{\omega}=1543$ nm, $\lambda_{3\omega} \sim 514$ nm).

significant oscillating behavior and is approximately 30 (20) times more intense than that of the reference substrate for the *cis*-PEP (*trans*-PEP) film samples. This lack of oscillations is due to the fact that the thickness of the doped films is smaller than its characteristic coherence length (typically in the order of few microns) and the THG of the reference substrate is negligible compared to that of the hybrid films. Besides, due to the near-resonant conditions of our experiment where the free wave is highly absorbed by both, the *cis*-PEP and *trans*-PEP based hybrids (Fig. 4), the THG-intensity will not longer follows the phasematching dependent oscillations with the medium thickness [46]. However, for film samples under resonant (absorption) conditions, the determination of $\chi^{(3)}$ may be estimated by the following expression [38,47]

$$\chi^{(3)\text{-Film}} \propto \chi^{(3)\text{-Substrate}} \left(\frac{2I_c^{\text{Substrate}}}{\pi} \frac{\alpha/2}{1 - \exp(-\alpha I^{\text{Film}}/2)} \right) \left(\frac{I_{3\omega}^{\text{Film}}}{I_{3\omega}^{\text{Substrate}}} \right)^{1/2}, \quad (1)$$

where I^{Film} is the sample thickness, α is the absorption coefficient of the film sample and $I_c^{\text{Substrate}}$ represents the coherence length of the substrate ($\sim 12 \mu\text{m}$). $\chi^{(3)\text{-Film}}$ and $\chi^{(3)\text{-Substrate}}$ are, the values of the cubic nonlinear coefficients of the doped film sample and the fused silica substrate, respectively. $I_{3\omega}^{\text{Film}}$ and $I_{3\omega}^{\text{Substrate}}$ are the peak intensities of the Maker-fringes pattern of both, the film sample and the reference substrate. Estimated errors about 15 and 20% associated with the nonlinear optical measurement are indicated as error bars in Figs. 7 and 8, respectively.

By assuming that the dopant agents are homogeneously dispersed within the SiO_2 matrix, only $\chi^{(3)}$ resonant enhancements are permitted in such amorphous systems, and no SHG were measured in our samples, we believe that $\chi^{(3)}$ is dominated by a three-photon resonance $\chi^{(3)}(-3\omega, \omega, \omega, \omega)$ and no cascading effects are considered [41,48]. From the Maker-fringes experiment, the cubic NLO coefficients were evaluated according to Eq. (1) to: $\chi_{\text{cis-PEP}}^{(3)} = 0.28 \times 10^{-11}$ esu and

$$\chi_{\text{trans-PEP}}^{(3)} = 0.17 \times 10^{-11} \text{ esu} \quad (0.39 \times 10^{-19} \text{ and } 0.24 \times 10^{-19} \text{ m}^2/\text{V}^2, \text{ respectively}).$$

Fig. 8 shows the calibrated $\chi^{(3)}$ -values obtained according to the Maker-fringes experiments of different *cis*-PEP and *trans*-PEP hybrid films prepared with the selected H-TEOS:D-D (note that Fig. 7 shows the Maker-fringes pattern of our best 1.4:0.6 NLO-samples for both, *cis*-PEP and *trans*-PEP hybrid films). The $\chi^{(3)}$ -values measured at room temperature for the selected samples reveal an optimal concentration ratio between the H-TEOS and the *cis*-PEP and *trans*-PEP doped solution, in order to obtain the best possible THG signal. The moderate 1.4:0.6 doped films show highest $\chi^{(3)}$ -coefficient for *cis*-PEP and *trans*-PEP hybrid films, which is about 200 and 100% of the reference value, respectively. As expected, negligible THG-signal arises from the pure 2:0 reference sample.

Last results on the synthesis and characterization of hybrid sonolized sol-gel composites have been carried out as a first attempt for the development of photonic organic-inorganic devices like planar waveguiding structures. Current studies in order to improve the SiO_2 -gel:chromophore concentration ratio and the cubic NLO-response are at present under way. THG-investigations performed with the OPO-laser system will be also required in order to obtain the dispersion of $\chi^{(3)}$ over a wide spectral range in the IR-spectra ($\lambda_\omega \sim 1.2\text{--}2.0 \mu\text{m}$), which may be promising for optical communication devices.

4. Conclusions

The synthesis of sol-gel materials induced by ultrasonic action (sonolysis) is implemented as an alternative method for the fabrication of highly pure organic-inorganic composites with good mechanical and optical properties. Novel synthesized *cis*-PEP and *trans*-PEP were incorporated as dopant agents within the SiO_2 network in order to prepare active nonlinear optical hybrid materials at room temperature. Optimal concentrations of hydrolyzed tetraethoxysilane (H-TEOS) and the polymers in solution have been determined, in order to improve nonlinear optical properties of the selected film samples. From angle dependent THG experiments, the calibrated $\chi^{(3)}$ -values of the selected hybrid film glasses were evaluated showing $\chi^{(3)}$ -coefficients in the interesting range of 10^{-12} – 10^{-11} esu. Optical properties of *trans*-PEP and *cis*-PEP in sol-gel were determined by absorption and fluorescence spectroscopies and compared to those previously obtained in THF solution. Fluorescence spectra of both polymers in sol-gel exhibited monomer emission and static excimer bands resulting from intramolecular interactions between pyrene pendant groups. These static emission bands come from intramolecular pyrene-pyrene interactions, which was confirmed by excitation spectra. No intermolecular interactions were detected for these polymers in sol-gel.

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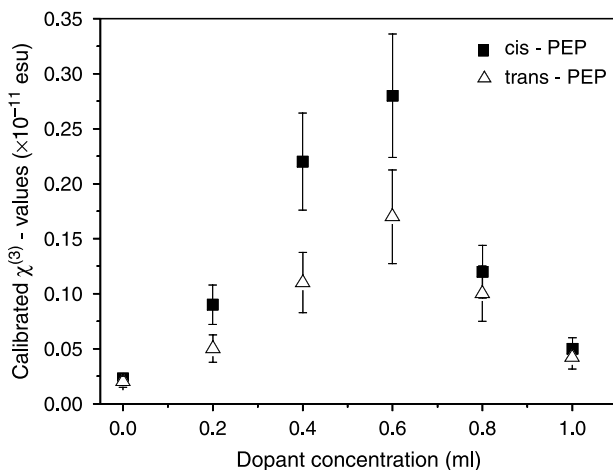


Fig. 8. Relative calibration of the nonlinear $\chi^{(3)}$ -coefficients for different *trans*- and *cis*-PEP doped hybrid films, deposited on fused silica substrates ($\lambda_\omega = 1543 \text{ nm}$, $\lambda_{3\omega} \sim 514 \text{ nm}$).

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