

## Fabrication and optical testing of hybrid sio2:azo-polymer based planar waveguides for nlo/shg laser emission

V Torres-Zúñiga<sup>1</sup>, O G Morales-Saavedra<sup>2</sup>, A L Pérez-Martínez<sup>3</sup>

<sup>1</sup> Facultad de Ciencias, Universidad Nacional Autónoma de México, Circuito Interior, Ciudad Universitaria, C.P. 04360, México D.F., México.

<sup>2</sup> Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Circuito Exterior S/N, Ciudad Universitaria, A.P. 70-86, C.P. 04510, México D.F., México.

<sup>3</sup> División de Ciencias Basicas, Departamento de Química, Facultad de Ingeniería, Universidad Nacional Autónoma de México, Circuito Exterior S/N, Ciudad Universitaria, México D.F., México.

E-mail: [vicentz@gmail.com](mailto:vicentz@gmail.com)

**Abstract.** Predesigned push-pull azo-dye polymers were homogeneously dispersed within a SiO<sub>2</sub> sol-gel matrix synthesized via the sonogel (SG) route. High-quality spin-coated films were obtained with these hybrid structures in the liquid sol-phase. The spectroscopic UV-Vis analyses reveal the appropriate insertion of these organic compounds within the highly pure SG-environment whereas the thermal (DSC) analysis and photoacoustic measurements evidence the thermomechanical stability of the amorphous hybrid layers. As the optical attenuation, refractive index and film thickness values of the obtained films are adequate for opto-electronic applications; these hybrid films were implemented to fabricate optical waveguiding prototypes. In this sense, functional planar waveguides were fabricated for nonlinear optical (NLO) applications after performing a molecular ordering via a corona DC-poling procedure in order to achieve a macroscopic polar order (ferroelectric and noncentrosymmetric arrangement of the organic chromophores). The poled films were then able to exhibit stable NLO-waveguiding effects as excited with a Nd:YAG laser system in order to generate second harmonic waves travelling within the planar layer.

### 1. Introduction

Nowadays linear and NLO applications require the development of active organic compounds in order to improve the efficiency of several optical effects for practical technological applications. In this sense, the push-pull functionalized azo-benzene polymers have received increasing attention in the last decade [1]. Among their attractive features, these compounds exhibit a rod-like dipolar structure which is convenient to perform a collective molecular alignment, achievable by applying strong DC- fields on the material. This gives rise to a macroscopic ferroelectric polar order which is equivalent to a non-centrosymmetric crystalline arrangement. In this kind of polar structures quadratic  $\chi^{(2)}$ -NLO effects such as second harmonic generation (SHG) are allowable [2]. Nevertheless, poled organic compounds are susceptible to thermal relaxation which tends to annihilate the induced NLO response. Different efforts, including molecular cross-linking, preparation of Langmuir-Blodgett films and the use of high glass transition polymers have been attempted in order to produce stable NLO-polymeric materials [2]. So far, a conclusive and

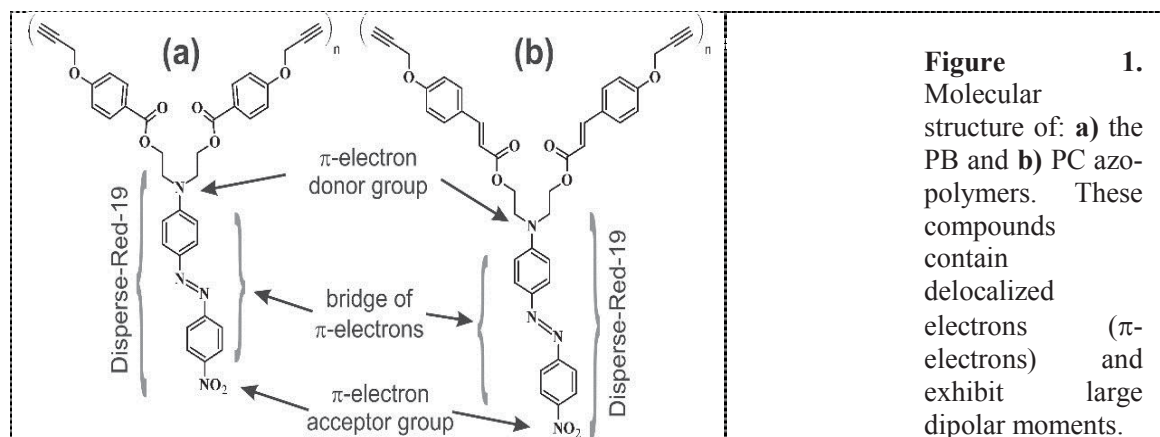


universal methodology to permanently preserve the poled phase of organic materials is still under research. Given that our research group has recently achieved some new sol–gel technology (via a physicochemical sonogel route: catalyst-free sonolysis approach) for the synthesis of high quality mesoporous  $\text{SiO}_2$  glasses, we have implemented this approach for the development of optically active organic-inorganic hybrid glasses. In the current case, we report on the fabrication of optically active sonogel hybrid films and demonstrate their plausible applicability in NLO waveguiding photonic devices implementing promising polymeric molecules with current potential applications in opto-electronic technologies. The sonogel route is a low-cost technique which has been successfully implemented to increase the thermal and mechanical stability of organic compounds embedded within a vitreous sol-gel matrix [1, 3]. The SG-glasses are optically transparent and chemically inert allowing the observation of the photophysical properties of the guest organic compounds in a quasi-pristine form. In this way, we fabricated hybrid planar waveguides implementing two predesigned azo-polymers. These organic materials were dispersed in the liquid sol-phase of the sonogel precursor and spin-coated onto ITO-glass substrates in order to obtain hybrid film layers ready for optical inspections.

## 2. Materials and experimental methods

### Chemical structure of the implemented NLO azo-benzene polymers

We implemented two photo-active push-pull polymers: Poly(hexa-2,4-diynylene-1,6-dioxydibenzoate) and Poly(hexa-2,4-diynylene-1,6-dioxydicinnamate) [4]; named here PB (para-benzoate) and PC (para-cinnamate), respectively. Both reddish polymers contain rod-like molecular units comprising electron-donor and electron-acceptor functional groups linked by an azobenzene molecule (see Fig. 1); this molecular architecture gives rise to an electronic dipolar configuration, adequate to perform electrical poling procedures for collective molecular alignment.



### 2.2 Synthesis of the highly pure $\text{SiO}_2$ -based sonogel

The sonogel synthesis is a catalyst-free sol-gel process [3]. Briefly, a stainless steel tip (Cole-Parmer- CPX) provides an ultrasonic irradiation ( $\sim 3.2 \text{ W/cm}^3$  at  $20 \text{ kHz}$ ) on the interface of the two immiscible precursors: 25 mL of tetraethyl-orthosilicate (TEOS: Fluka 99% purity) and 25 mL of tri-distilled water, stabilized at  $1^\circ\text{C}$ . After 3 h of acoustical irradiation (with 5 s on/off intermittent sequences) and 24-hrs of repose, two new immiscible phases emerge. Only the denser one is capable of producing (after drying/poly-condensation) a highly pure and transparent  $\text{SiO}_2$  amorphous network.

### 2.3 Fabrication of organic-inorganic waveguiding hybrid structures

In order to fabricate organic-inorganic sonogel hybrid films, the chromophore doping must be performed in the liquid sol-phase. Hence, highly-loaded dopant dissolutions (DD) of the PB- and PC-polymers (in Tetrahydrofuran: THF) must be prepared (at 3.0 mg/mL). These DD must be filtered through 0.22  $\mu\text{m}$  Teflon membrane, added and ultrasonically mixed to the liquid sonogel (sol-phase) in a 50-50% DD:sonogel-concentration. Undoped reference sonogel films (0.0% DD) were also prepared for reference and calibration spectroscopic purposes.

For the fabrication of planar waveguides we first deposited two thick layers of the pure sonogel (0.0% DD) onto Indium-Tin-Oxide-coated substrates (ITO: Aldrich 25  $\Omega/\text{sq}$ ) via standard spin-coating procedures (each layer deposited at 100 rpm for 6 s; drying conditions: room temperature for 48 hrs). The obtained  $\text{SiO}_2$  film showed an average thickness of  $\sim 3 \mu\text{m}$  (according to profilometry measurements), this layer plays the role of an optical buffer since its low refractive index ( $n_{\text{SG}}=1.31\pm 0.05$ , measured by the Brewster's angle methodology) is essential in the cladding of waveguide. The second film (PB or PC active hybrid layer) was deposited with a (50.0-50.0% DD:sonogel, in sol-phase. Each layer deposited at 80 rpm for 4 s). The average film thickness of the hybrid layers was  $\sim 4 \mu\text{m}$ . The refractive index values of these layers were:  $n_{\text{PB}}=(1.48\pm 0.06)$  and  $n_{\text{PC}}=(1.50\pm 0.05)$ . At this stage, the organic compounds are randomly oriented within the film geometry showing a quasi-isotropic macroscopic structure. Thus, in order to achieve a macroscopic noncentrosymmetric molecular alignment, as required for  $\chi^{(2)}$ -NLO effects, we implemented the corona-poling technique [2]. Here, the ITO-layer operates as the anode whereas a vertical non-oxidable iron needle placed above the active film layer of the sample (film-needle gap: 1 cm) works as electrode. The electrodes are then connected to a high voltage supply (at 5.2 KV) in order to apply a strong DC-electric field over the sample. During the whole electrical poling procedure the sample was mounted onto an electrical oven operated around the glass transition temperature ( $T_g$ ) of the implemented azo-polymers ( $\sim 180^\circ\text{C}$  for  $\sim 1$  hr) in order to allow highest molecular mobility for optimal collective alignment. Thereafter, the multilayered hybrid sample was cooled down to room conditions, keeping the DC-field on in order to freeze the collective molecular alignment within the sonogel network. In this way, the poled hybrid films were ready for morphological, photophysical and waveguiding characterizations.

#### 2.4. Photophysical characterization methodology

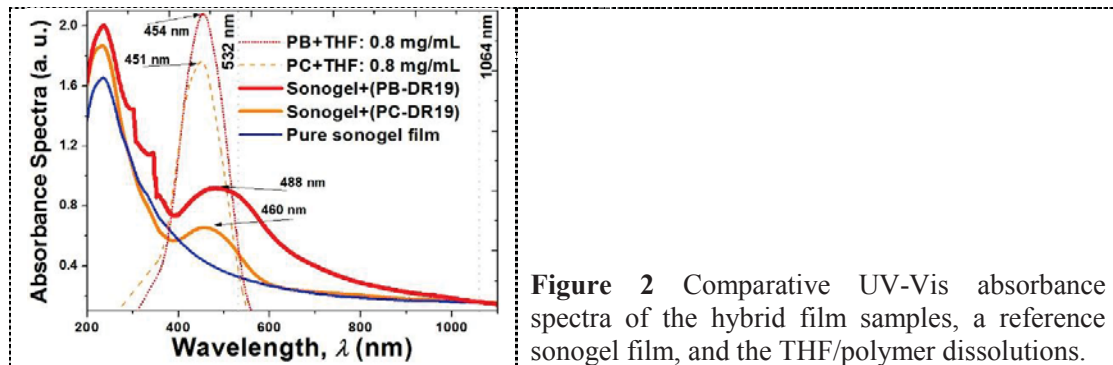
Standard characterization methodologies were applied to undoped and hybrid sonogel film samples in order to determine their thermomechanical and optical properties: **i)** The absorbance UV-Vis analysis was performed using a double beam Shimadzu UV-Vis spectrophotometer (air as reference) within the 200–1100 nm spectral range. **ii)** The thermal and structural characterization to determine the  $T_g$  parameter and the degradation temperature of the organic compounds within the SG-environment were performed via the laser photoacoustic technique (LPA) [3] and Differential Scanning Calorimetry (DSC). **iii)** The NLO/SHG characterization was performed on the hybrid waveguides mounted onto a micrometric XYZ-stage; the active layers were directly excited with a pulsed laser beam (Continuum Nd:YAG: polarization state:  $P_{\text{In}}$ , at  $\lambda=1064$  nm, pulse width: 15 ns). After overpass a linear polarizer ( $P_{\text{Out}}$ ) and an interferometric filter, the SHG-output waves (at 532 nm) were collected by a photomultiplier tube connected to a digital oscilloscope. The planar waveguides were asymmetrically cut in order to perform SHG-intensity measurements as function of the optical path.

### 3. Results and discussion

#### UV-Vis spectroscopic measurements

The UV-vis spectra of the THF/polymer-based dissolutions present sharp and intense absorbance bands (see Fig 2) distinctive of organic compounds exhibiting efficient charge transfer properties [4]. In contrast, the pure reference sonogel film exhibits low absorbance at optical wavelengths and

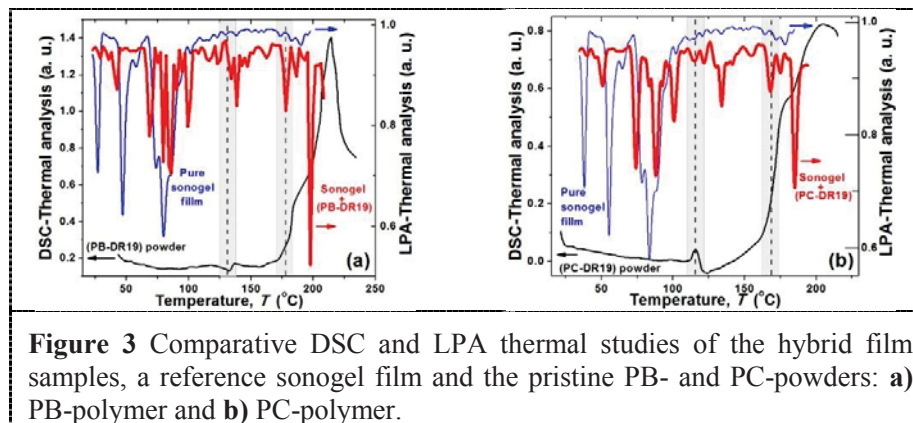
an intense UV-band which is typical of SiO<sub>2</sub> glassy materials [5]. Finally, as a result of the successful organic doping, the hybrid SG-samples exhibit the characteristic absorbance bands of their organic and inorganic constituents; with additional red-shifts of the main absorbance bands at optical wavelengths as a consequence of the extreme molecular packing (formation of head-to-tail aggregates) which is usual in the solid-state phase [3].



**Figure 2** Comparative UV-Vis absorbance spectra of the hybrid film samples, a reference sonogel film, and the THF/polymer dissolutions.

### 3.2 Thermal (DSC) and (LPA) analyses

Fig. 3 illustrates the comparative DSC and LPA thermal analyses of the hybrid films. Before 100°C, the pure sonogel displays intense LPA signal-peaks associated to the evaporation of residual water and alcohols within the glassy matrix. Thereafter, the sonogel film is thermally stable. On the contrary, the pristine PB- and PC-powders show small DSC-variations until the corresponding  $T_g$  values (at 130 and 120°C, respectively) have been reached. However, these transitions are markedly delayed in the corresponding hybrid films, namely to 140 and 135°C, respectively. Besides, the pristine PB- and PC-compounds start their degradation process around 180°C whereas in the SG-environment this phenomenon occurs until 190°C. Thus, the thermal stability of the chromophores is guaranteed and can be enhanced within the glassy sonogel environment.



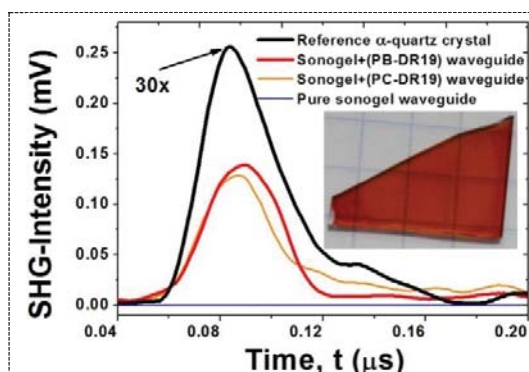
**Figure 3** Comparative DSC and LPA thermal studies of the hybrid film samples, a reference sonogel film and the pristine PB- and PC-powders: **a)** PB-polymer and **b)** PC-polymer.

### 3.3 Planar waveguiding NLO/SHG-activity of the hybrid SG-layers

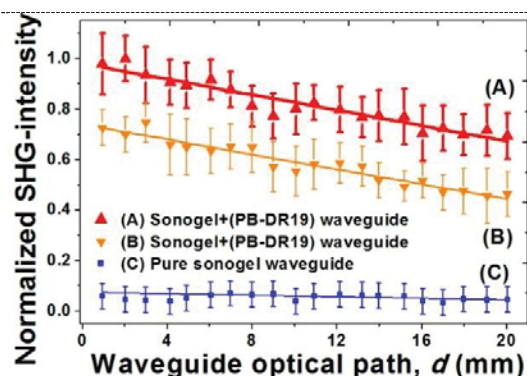
After laser excitation, both the PB- and PC-based hybrid waveguides were able to exhibit stable SHG-emission for more than 500 hrs (non-continuous working hours) at room temperature (see typical SHG-signals in Fig. 4). The SHG-conversion efficiency as function of the waveguide optical path is represented in Fig. 5 (normalized SHG-output signals). The PB-based sample show higher SHG-emissions than the PC-sample, and the optical attenuation of both PB- and PC-based hybrid waveguides is evidenced as the optical path ( $d$ ) within the planar waveguide is increased.



However, under our experimental conditions and up to the 20  $\mu\text{m}$  optical path ranges, we were not able to observe any significant oscillating behavior of the SHG-intensity signals (distinctive feature of phase-matching effects [1]). Thus, since the coherence-length cannot be measured in these samples, additional processes such as quasi-phase matching induced effects to improve the SHG-emissions were discarded for the current geometry [6]. Indeed, longer hybrid waveguides or planar samples at prepared different PB- or PC-molecular concentrations must be prepared. These experiments are currently underway in order to improve the SHG-conversion efficiency of our organic-inorganic hybrid waveguides.



**Figure 4.** Comparative SHG-signals of the hybrid waveguides, the amorphous SG-glass and the reference  $\alpha$ -quartz crystal. Inset figure: Picture of a typical hybrid waveguide with variable optical paths.



**Figure 5.** SHG-peak intensities recorded as function of the optical-path ( $d$ ): (A)- and (B)-data correspond to the PB- and PC-based hybrid waveguides, respectively. (C)-data corresponds to the reference/pure SG-waveguide.

#### 4. CONCLUSIONS

In this work, we briefly show some experimental details of the fabrication procedure and physical characteristics of planar waveguides comprising push-pull polymers embedded within a highly pure  $\text{SiO}_2$ -sonogel matrix. These low-cost hybrid materials could be important for the development of Si-based semiconductor technologies and evidenced excellent attributes such as: lower SG-refractive index (compared to the hybrid layers) or cladding effect, a stable mechanical structure (fracture-free hybrid samples), a homogeneous molecular dispersion within the host SG-network, an enhanced thermal protection of the guest organic compounds and a freezing effect in the collective molecular ordering induced by high DC/electric fields. Indeed, the corona-poling process allowed us to obtain a stable macroscopic noncentrosymmetric structuring of the hybrid SG-layers as required for quadratic SHG-effects. At this point however, it was not possible estimate the coherence-length of our samples in order to perform a periodic molecular poling along the waveguide layers, appropriate to obtain a quasi-phase-matched structure capable to enhance the SHG-activity as function of optical length of the waveguides. Future works must include several NLO-spectroscopic studies and geometry and molecular concentration variations of the samples in order to obtain the coherence-length and other optical characteristics of interest, such as the linear and nonlinear refractive index of the hybrid waveguides. Under this scope, the present work provides a starting reference in the study of the  $\chi^{(2)}$ /NLO properties of organic-inorganic SG-based photonic prototypes.

#### Acknowledgments

VTZ and OGMS acknowledge the financial support from DGAPA-UNAM (Postdoctoral Scholarship), SEP-CONACYT (Grant: 47421) and DGAPA/PAPIIT-UNAM (Grant: IG100713).

### References

- [1] Lebeau, B. and Innocenzi, P. 2011 *Chem. Soc. Rev.* **40** 886
- [2] Bosshard Ch, Hulliger J and Florsheim M 1995 *Organic Nonlinear Optical Materials* vol 1 (Switzerland: CRC Press)
- [3] Torres-Zúñiga V, Morales-Saavedra O G, Rivera E, Castañeda-Guzmán R, Bañuelos J G, and Ortega-Martínez R 2010 *J. sol-gel Sci. Techn.* **56** 7
- [4] Pérez-Martínez A L, Gómez-Sosa G and Ogawa T 2005 *J. Macromol. Sci. Pure Appl. Chem.* **42** 1561
- [5] Neuroth N 1998 *The properties of optical glass* ed. Bach H and Neuroth N (Berlin: Springer-Verlag) pp 90-93
- [6] Warren N H and L. M Hayden 1995 *J. Opt. Soc. Am. B* **12** 416