

Optical absorption and SHG in PMMA:DR1 thin films as function of poling time.

Jorge A. García-Macedo*^a, Alfredo Franco^a, Guadalupe Valverde-Aguilar^a, Carlos Aguilar-Gutiérrez^a.

^aDepartamento de Estado Sólido, Instituto de Física, Universidad Nacional Autónoma de México, Circuito Exterior s/n 04510, Ciudad Universitaria, Coyoacán, México, D.F.

ABSTRACT

Amorphous, PMMA: DR1: surfactant and PMMA:DR1:TEOS thin films were prepared by dip-coating. All films were calcined at 70 °C for 3 hours. For nanostructured thin films two ionic surfactants were used, Sodium Dodecyl Sulfate (SDS) and Cetyltrimethyl ammonium bromide (CTAB) to obtain two different nanostructures of the PMMA matrix: lamellar, and hexagonal, respectively. X-ray diffraction studies were performed to determine the long-order structure tailored in the films. The measurements of the optical absorption and the second harmonic generation (SHG) intensity were carried out at different orientation arrangements of the chromophores embedded in the films. The chromophore orientation distributions were obtained by means of the corona technique. These distributions depend on the corona poling time. We physically modeled the optical absorption and the second harmonic generation experimental results as function of the corona poling time, employing only one fitting parameter related to the matrix-chromophore interactions. The physical model and the experimental results were in an excellent agreement. The experimental results fitted by the model are shown in plots of order parameter against corona poling time and SHG intensity against corona poling time. The amorphous films provide a larger SHG intensity values than those obtained from the nanostructured films. Thin films with lamellar structure have a SHG intensity bigger than those from hexagonal and PMMA:TEOS thin films.

Keywords: Films, chromophores, second harmonic generation, optical absorption, poling.

1. INTRODUCTION

It can be induced non-centrosymmetric order in some materials by means of the application of a strong electric field under appropriate conditions of temperature, this process can be carried out for example with the procedure known as Corona poling^{1,2}. In a chromophores-containing polymeric film, the non-centrosymmetric order implies a nanoscale order of the chromophores permanent dipolar moment along a preferential direction. This phenomenon is attractive for second order nonlinear optical applications^{3,4,5}; in fact, by means of one second order nonlinear process, the SHG, it is possible to follow in situ the orientation of the chromophores embedded in the polymer^{6,7}. As the orientation of the chromophores is highly dependent of their surrounding medium it is useful to know how the local environment is around the chromophores. A good way to know the local environment effect over the chromophores is by means of studying their orientational kinetics^{8,9}. We expect that different nanostructures in the polymeric host give place to different local chromophores environments, a fact which should be reflected in SHG signal measurements as function of poling time. In fact there is a recent interest in studying the optical properties of orientable chromophores immersed in self-assembled nanostructured media¹⁰.

In this paper we present SHG dynamics results for nanostructured PMMA films containing DR1 chromophores. Two different long-range orders were detected on these films, by means of XRD measurements. Those long-range orders were: (1) a lamellar phase and (2) a mixture of lamellar and hexagonal phases.

The chromophores orientation dynamics has also been theoretically studied by J. W. Wu¹¹ and D. J. Binks et al.¹² who have proposed models for the description of this phenomenon based on a rotational diffusion equation. But to analyse the experimental results we preferred to use a model developed by us^{13,14}, which is a phenomenological one based on the harmonic movement of the chromophores embedded inside the films.

* gamaj@fisica.unam.mx; phone (55) 56 22 51 03; fax (55) 56 22 51 11.

The knowledge of the temporal behavior of the SHG signal in these kinds of materials can give information about the local interactions between the chromophores and their surrounding medium, which is very important for the optimal development of nanophotonic devices. All of these features becomes to the sol-gel films into a very interesting materials for diverse optical research and applications.

2. MATERIALS SYNTHESIS

The studied matrix was PMMA. All the films were deposited onto glass slides substrates by dip-coating. Three different kinds of the matrix organization were identified by XRD: amorphous, lamellar and mixed nanostructures. The mixed phase was obtained by adding 1.5 wt % of the cationic surfactant CTAB during the liquid phase of the PMMA matrix formation process. The long-range order lamellar nanostructure was obtained by the incorporation of 1.5 wt % of the anionic surfactant SDS during the liquid phase of the PMMA matrix formation process.

DR1 was the photoactive chromophore in all the samples. All the samples were guest-host, and the DR1 concentration was the same for all the samples.

The PMMA amorphous samples preparation was as follows: PMMA (F.W. = 120,000 g·mol⁻¹) and THF were stirred for 15 minutes at room temperature, then DR1 was added and all was stirred together for 15 minutes. This final solution was filtered with a 0.45 μm pore size syringe filter. 80% of the total weight was liquid (THF), 20% was solid (PMMA+DR1). 95% of the solid weight was PMMA and 5% was DR1. The films were deposited onto microscope glass slides by dip-coating at a constant withdrawal speed equal to 20 cm/min, and annealed at 80°C during 4 hours without controlled atmosphere.

The PMMA nanostructured samples followed a similar procedure but with as an extra step, just prior to filter, it was added the ionic surfactant in a ratio of 1.5% in weight and it was stirred for 5 minutes. The structure of the films was characterized with XRD patterns. These patterns were recorded on a Bruker AXS D8 Advance diffractometer using Ni-filtered CuKα radiation. A step-scanning mode with a step of 0.02° in the range from 1.5° to 10° in 2θ and an integration time of 2 s was used.

The SHG measurements were carried out in situ by using the experimental set-up shown in Figure 1. This set-up consists of a pulsed YAG:Nd (Nanolase NP-10620-100, wavelength: 1064 nm, frequency: 5 kHz, energy: 5μJ/pulse) as a fundamental beam of light source, two lenses, one of them focus the fundamental laser beam on the sample, the second one, which is back of the sample at a distance to the sample equal to its focal length, collect the light generated by the sample and send it to a photomultiplier (Hamamatsu H5784) through a color filter which blocks the fundamental beam of light but allows to the second harmonic to pass through it. The photomultiplier was connected to an oscilloscope (Tektronix TDS 3052B) and the data were stored by a computer each 0.5 seconds. For the measurements the films were supported just on a hole of one of the electrodes, this electrode is a copper plate which has a controlled temperature.

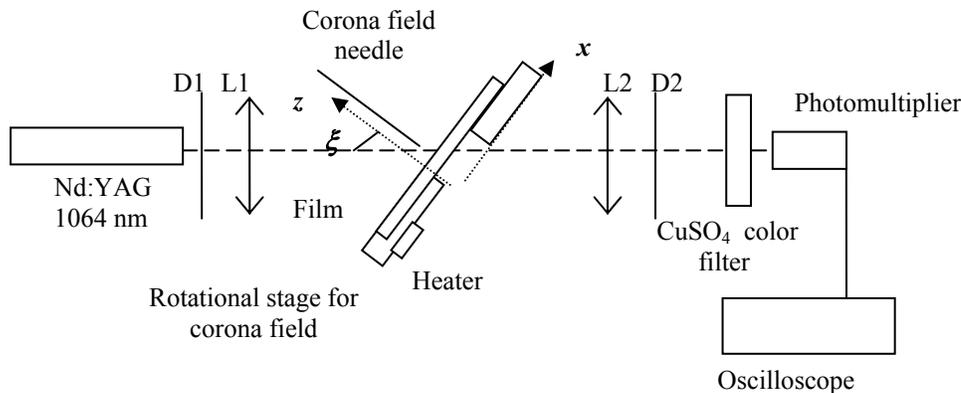


Fig 1. Schematic diagram of the SHG experimental setup.

3. RESULTS AND DISCUSSION

3.1. XRD patterns. The XRD patterns obtained for the samples with SDS and for the samples with CTAB appears in the Figure 2. Figure 2 (left) shows the XRD pattern of all the samples with SDS corresponds to a lamellar nanostructure (the peaks follow the $1q^*$, $2q^*$, $3q^*$,... sequence^{15,16}) with a d -spacing (d) equal to 3.8 nm and $q^*=2\pi/d$. Figure 2 (right) exhibits the corresponding XRD pattern for all the samples with CTAB showing a coexistence of two phases, a lamellar and a hexagonal nanostructure (the hexagonal nanostructure with a $1q_h^*$, $(3)^{1/2} q_h^*$,... sequence^{15,16}, where $q_h^*=4\pi/d(3)^{1/2}$). The lamellar phase had a d -spacing equal to 3.8 nm and the hexagonal phase had a d -spacing equal to 5.2 nm.

The studied nanostructured samples exhibit one of the X-ray spectra shown in Figure 2.

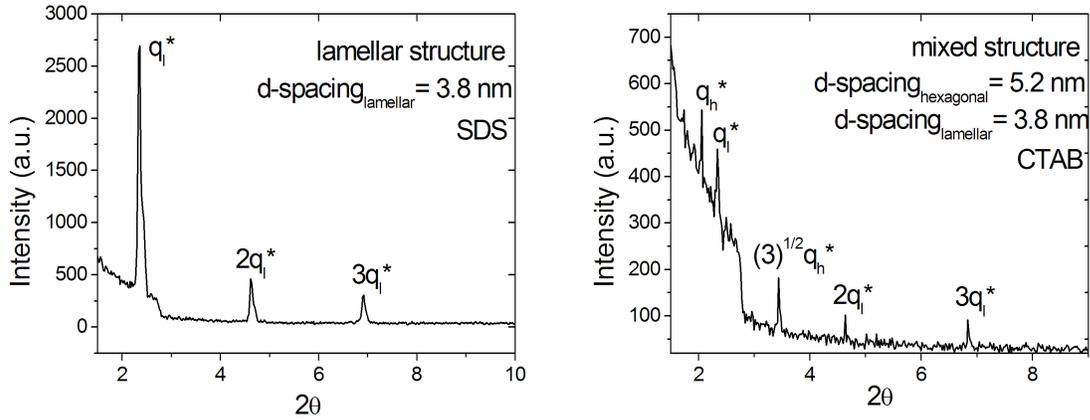


Fig. 2. XRD patterns at low angle of the samples templated with (left) SDS showing a lamellar nanostructure, and (right) CTAB showing a mixed nanostructure.

3.2. Order parameter. The experimental orientation dynamics for the PMMA:DR1 amorphous sol-gel film annealed at 80°C is shown in Figure 3. Experimental data (black squares) was fitted by using a theoretical model developed by Franco et al¹⁴. The order parameter was calculated according to:

$$\rho = 1 - \frac{A_{\perp}}{A_0} \quad (1)$$

where A_{\perp} (A_0) is normal absorption after (before) poling. Data satisfactorily fit the model, as Fig. 3 shows (blackline). The molecular orientation is corroborated by the increment in the order parameter as a function of poling time, as it is shown in Fig. 3. The figure shows saturation after 10 minutes of poling, indicating there is an asymptotical polarization from the molecules. Similar results were obtained in the other samples.

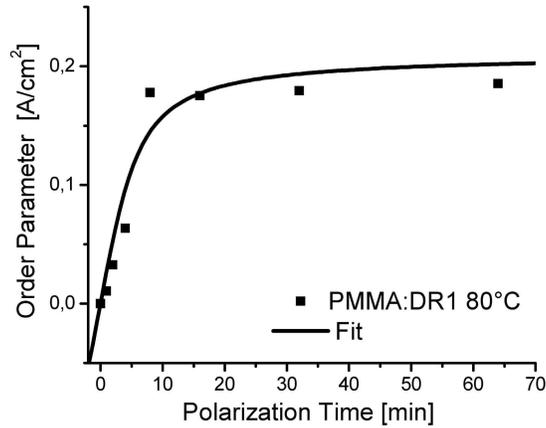


Figure 3. Order parameter as function of the poling time. Experimental order parameter data (black squares) showing the field-induced orientation as function of the poling time for amorphous PMMA:DR1 thin film. The fitting curve is represented by a continuous black line.

3.3 SHG studies. Figure 4 shows the plots of the SHG signal as function of the poling time for amorphous and nanostructured PMMA:DR1 thin films at 60, 80 and 100°C. For the amorphous samples, the SHG intensity increases when the temperature increases, too. For lamellar and mixed nanostructures, the SHG intensity for 80 and 100°C are very similar. In all the cases, the signal saturation at 60°C was observed at longer times than that at the other temperatures, and at 100°C the saturation was the fastest.

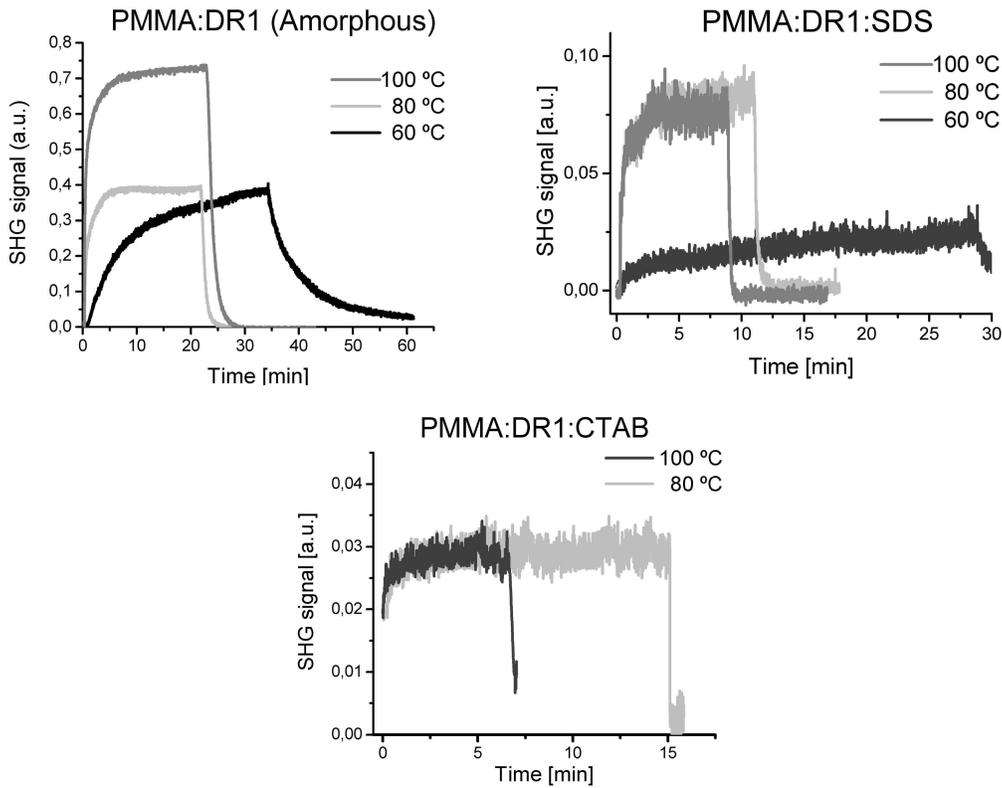


Fig. 4. SHG signal as function the poling time for amorphous, lamellar and mixed nanostructure at different temperatures.

The experimental data were fitted using a chromophores orientation model previously reported by us¹³, which requires two fitting parameters: (1) a damping constant of the material (γ), directly related to the chromophore-matrix interactions, and (2) a SHG intensity signal constant (C), proportional to $(N\beta_{333}I^\omega)^2$, where N is the number of non-linear optical active chromophores (DR1 in our case), β_{333} the second order hyperpolarizability of the chromophores and I^ω the intensity of the fundamental beam of light. Thus, larger γ values imply lower chromophores mobility, and larger C values imply larger number of molecules contributing to the non-centrosymmetry of the material. Figure 5 shows, for example, the fitting with our model to the SHG for the amorphous sample. In order to do this fitting the order parameter at long times $\rho(t = \infty)$ called A_2 and calculated from Figure 3 were used. The behavior of the A_2 parameter as a function of the temperature is observed in Figure 6.

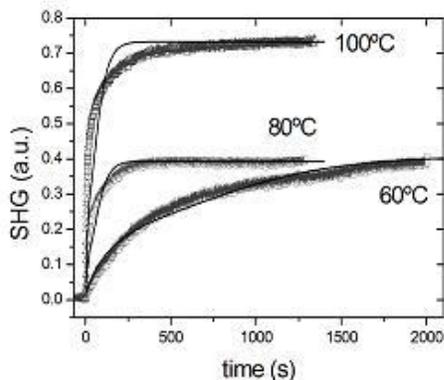


Figure 5. SHG signal as function the poling time for amorphous PMMA:DR1 thin film.

The A_2 order parameter values reflect the anomalous behaviour of the amorphous PMMA films at 80°C. While these parameter values increase as the temperature increases for the nanostructured films, the A_2 values decrease as the temperature increases for the amorphous PMMA films, furthermore there is a minimum value at 80°C. The A_2 parameter is a measurement of the orientable chromophores in the films and is directly related to the electric field inside the film (E)¹³, under the presence of the poling field, thus larger A_2 values imply larger a number of orientable molecules or a larger magnitude of the electric field (E). If we consider a set of films with the same kind of matrix and the same chromophores concentration, and the unique variable is the poling temperature, and if we assume there are not changes in the matrix of the films under the Corona procedure, then the changes in A_2 should be due to changes in the number of orientable chromophores in the material. Thus, as the temperature increases there are more orientable chromophores in the nanostructured films, but as the temperature increases there should be some matrix changes in the amorphous films because there was not detected an increase of the orientable chromophores. Figure 7 shows the electrical field E as function of temperature.

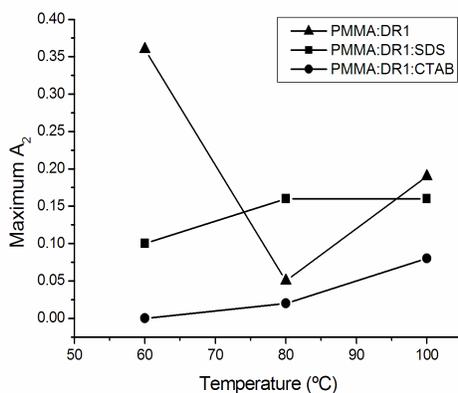


Figure 6. Optical absorption experimental results expressed in terms of the second order parameter A_2 , as a function of the temperature.

At 80°C and at 100°C the lowest value of the A_2 parameter was shown by the PMMA:CTAB films. The largest A_2 value was shown by the PMMA:SDS films at 80°C and by the amorphous PMMA films at 100°C. And at both temperatures: 80°C and 100°C, the largest value of the C parameter was shown by the amorphous PMMA films, and the lowest value was shown by the PMMA:CTAB films. It means that the amorphous PMMA films experience some structural change at 80°C, but in general, the amorphous PMMA films have the largest number of non-centrosymmetrically orientable molecules and the PMMA:CTAB films have the lowest number, even lower than the SiO₂ films, which were prepared with a considerable lower amount of DR1.

Thus, the surfactants increase the chromophores mobility but decrease the number of orientable chromophores, and how evident these features are depends on the kind of surfactant used for the films synthesis.

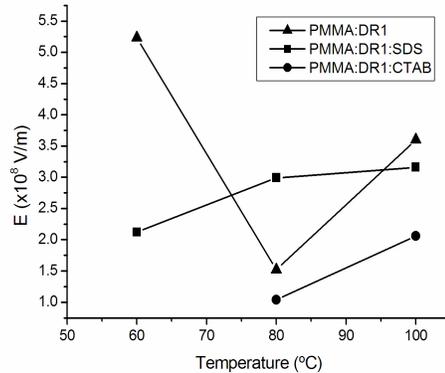


Figure 7. Theoretical local field for each film as a function of the temperature. The field was calculated as the rigid oriented gas model states^{11, 14, 17}.

The γ parameter is related with the inverse of the mobility of the molecules. Figure 8 shows the dependence of γ with temperature. Generally, the chromophores mobility increases when the temperature increases too, but the amorphous films exhibited a maximum mobility at 80°C. On these sense, the surfactants give more stability to the films, furthermore in the films with CTAB (those with mixed nanostructure) we were not able to detect an enough large chromophores mobility at 60°C, only after increasing the temperature there were chromophores orientation under the application of the corona field, obtaining practically the same mobility values at 80°C and at 100°C.

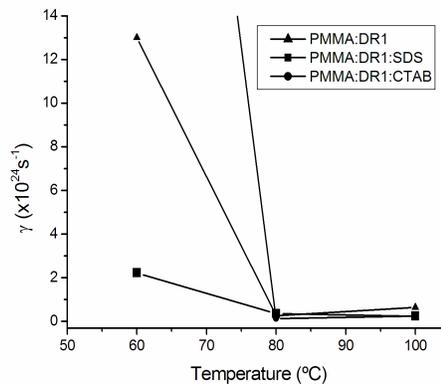


Figure 8. Damping constant (γ) for each kind of film as a function of the temperature.

By other part, as a reference, a similar kind of study was carried out on amorphous SiO₂ films, Figure 9 shows the experimental data of these samples, with their corresponding fits.

At 60°C we were not able to detect any SHG signal, just as occurred with the films with a mixed nanostructure. At higher temperatures was detected SHG signal, which showed a consistent behaviour for the chromophores mobility between the SHG signal growth and the SHG signal decay: in both cases the mobility increases as the temperature does, too.

Finally, comparing the PMMA films behaviour with the SiO₂ films one we observed that at 60°C the SiO₂ films and the PMMA:CTAB films did not show SHG signal and the chromophores mobility was larger in the PMMA:SDS films than in the amorphous PMMA films, besides the A_2 order parameter was less for the nanostructured films. At 80°C and at 100°C the largest chromophores mobility was exhibited by the SiO₂ films, and the lowest mobility was exhibited by the amorphous PMMA films. Apparently the mobility depends on how much reticulated is the matrix of the films even when the matrix has a large rigidity.

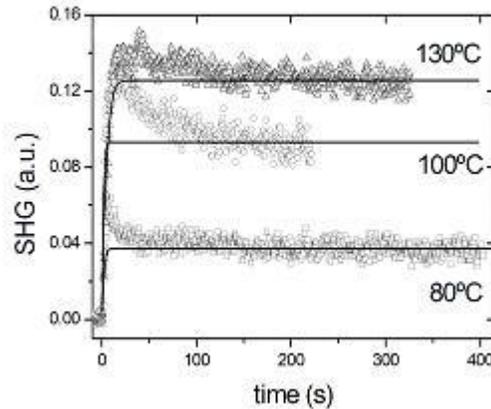


Figure 9. SHG signal as function of the poling time for SiO₂ guest-host amorphous films at 80°C, 100°C and 130°C with their respective theoretical fits (black continuous line).

5. CONCLUSIONS

High optical quality amorphous and nanostructured films doped with the chromophore DR1 were synthesized using PMMA matrixes. A long-range order nanostructure was detected in the PMMA films.

Second harmonic generation experimental results fitted as a function of the poling time in PMMA:DR1 and SiO₂:DR1 guest-host films were fitted with a physical model¹³. This macroscopic response depends on the orientation and interaction among these molecules.

The largest maximum SHG signal was detected for the amorphous PMMA films, and the lowest for PMMA films with mixed nanostructures. The SHG signal intensity varied as the next sequence indicates: Amorphous PMMA>SDS PMMA>Amorphous SiO₂>CTAB PMMA. Besides, the shortest rise time for the SHG signal was observed in the PMMA films with mixed nanostructures, the largest for amorphous PMMA films. The shortest decay time for the SHG signal was observed in the PMMA films with mixed nanostructures, the longest for amorphous PMMA films. The SHG signals grew with temperature and reached a saturation level faster at high temperature than at low one.

ACKNOWLEDGMENTS

CONACYT 43226-F, NSF-CONACYT, PUNTA, PAPIIT 116506-3 supported this work.

REFERENCES

1. M. A. Mortazavi, A. Knoesen, and S. T. Kowel, B. G. Higgings, A. Dienes. “Second-harmonic generation and absorption studies of polymer-dye films oriented by corona-onset poling at elevated temperatures”, J. Opt. Soc. Am. B **6**, 733-741 , 1989.

2. J. A. Giacometti, S. Fedosov and M. M. Costa. "Corona charging of polymers: recent advances on constant current charging", *Braz. J. Phys.* **29**, 269-279, 1999.
3. G. Della Giustina, G. Brusatin, M. Guglielmi, M. Dispenza, A. M. Fiorello, M. Varasi, M. Casalboni, A. Quatela, F. De Matteis, E. Giorgetti, G. Margheri, P. Innocenzi, A. Abbotto, L. Beverina, G. A. Pagani. "Electro-optics poled sol-gel materials doped with heterocycle push-pull chromophores", *Mat. Sci. & Eng. C* **26**, 979-982, 2006.
4. W. Shi, C. S. Fang, Q. W. Pan, Z. H. Qin, Q. T. Gu, D. Xu, J. Z. Yu. "Optimization and characterization of the guest-host polyetherketone polymer films for application in integrated optical devices", *J. Phys. D App. Phys.* **35**, 1404-1407, 2002.
5. F. Chaput, D. Riehl, J. P. Boilot, K. Cargnelli, M. Canva, Y. Lévy, and A. Brun. "New nonlinear sol-gel films exhibiting photorefractivity", *Chem. Mater.* **8**, 312-314, 1996.
6. A. W. Harper, S. Sun, and L. R. Dalton, S. M. Garner, A. Chen, S. Kalluri, and W. H. Steier, B. H. Robinson. "Translating microscopic optical nonlinearity into macroscopic optical nonlinearity: the role of chromophore chromophore electrostatic interactions", *J. Opt. Soc. Am. B* **15**, 329-337, 1998.
7. M. Eich, A. Sen, H. Looser, G. C. Bjorklund, J. D. Swalen, R. Twieg, and D. Y. Yoon. "Corona poling and real-time second-harmonic generation study of a novel covalently functionalized amorphous nonlinear optical polymer", *J. Appl. Phys.* **66**, 2559-2567, 1989.
8. T. Goodson III and C. H. Wang. "Electrochromic relaxation studies of a second-order nonlinear optical chromophore in different polymer hosts", *J. Phys. Chem.* **1996** 13920-13926, 1996.
9. I. G. Marino, D. Bersani, P. P. Lottici. "Photo-induced birefringence in DR1-doped sol-gel silica and ORMOSILs thin films", *Opt. Mat.* **15**, 175-180, 2000.
10. Yanqing Tian, Ching-Yi Chen, Marnie A. Haller, Neil M. Tucker, Jae-Won Ka, Jingdong Luo, Su Huang, and Alex K.-Y. Jen. "Nanostructured functional block copolymers for electrooptic devices", *Macromolecules* **40**, 97-104, 2007.
11. J. W. Wu. "Birefringent and electro-optic effects in poled polymer films: steady-state and transient properties", *J. Opt. Soc. Am. B* **8**, 142-152, 1991.
12. D. J. Binks, K. Khand and D. P. West. "Poling and relaxation of dipoles in dispersive media", *J. Appl. Phys.* **89**, 231-236, 2001.
13. Alfredo Franco, Guadalupe Valverde-Aguilar, Jorge García-Macedo, Michael Canva, Frederic Chaput, Yves Levy. "Modeling of the second harmonic generation in SiO₂ sol-gel films doped with nanoscopic DR1 molecules as function of the poling time", *Optical Materials* **29** (1), 6-11, 2006.
14. Alfredo Franco, Guadalupe Valverde-Aguilar, Jorge García-Macedo. "Orientational dynamics of DR1 molecules in sol-gel films", *Optical Materials* **29** (7), 814-820, 2007.
15. Juha Merta, Mika Torkkeli, Teemu Ikonen, Ritva Serimaa, and Per Stenius, "Structure of cationic starch (CS)/anionic surfactant complexes studied by small-angle x-ray scattering (SAXS)", *Macromolecules* **34**, 2937-2946 (2001).
16. Paschalis Alexandridis, Ulf Olsson, and Björn Lindman, "A record nine different phases (four cubic, two hexagonal, and one lamellar lyotropic liquid crystalline and two micellar solutions) in a ternary isothermal system of an amphiphilic block copolymer and selective solvents (water and oil)", *Langmuir*, **14**, 2627-2638, 1998.
17. M. G. Kuzyk, R. C. Moore, and L. A. King, "Second-harmonic-generation measurements of the elastic constant of a molecule in a polymer matrix" *J. Opt. Soc. Am. B* **7**, 64-72, 1990.
18. G. Valverde, J. Garcia-Macedo, Daniel Cruz, J. I. Zink, R. Hernandez, "Photoconductivity in Mesostructured Thin Films", *J. of Sol-Gel Science and Technology*, **26**, 605-608, 2003.