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Novel Sol-Gel Systems for Application in Optical Signal Processing

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Novel Sol–Gel Systems for Application in Optical Signal Processing

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A competitive approach to obtain functionalized polymers is described in this presentation. It consists on the use functionalized sol–gel systems, known to form excellent optical quality thin films. Usually these systems suffer of the low density of active chromophores. In this approach the chromophore concentration is significantly higher. The active NLO chromophores are oriented by corona poling technique. The kinetics of poling was studied by the spectrophotometric method.

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INTRODUCTION

In recent time there one observes a lot of research activity in fabrication and characterization of efficient second order NLO materials for optical signal processing, and particularly for electro-optic modulation applications for broad band transmission. Organic molecules, and particularly quasi 1D charge transfer (CT) molecules appeared to be highly interesting materials for these applications. As they require excellent optical quality, noncentrosymmetric NLO active thin films, several more or less successful routes of material preparation are explored, such as:

- Langmuir-Blodgett X, Z or alternate layers build-up technique [1,2]
- Isotropic polymers [3–5]
- Polymer liquid crystals [6]
- Monocrystalline (epitaxy or molecular epitaxy) (or oriented thin film growth heteroepitaxy) [7]
- Self assembly [8]
- Sol–gels [9]
- Intermolecular charge transfer complexes [10]

Isotropic polymers emerged here as very interesting and promising materials, with large second order NLO susceptibilities and good optical propagation properties [3–5]. They are made from an inert, amorphous polymer matrix, functionalized with active quasi 1D charge transfer (CT) molecules, with enhanced β tensor component in the CT direction. The noncentrosymmetry is created by orienting the dipole moment by applying a high electric DC or optical fields. Broad band (>100 GHz), very efficient ($V_\pi < 1$ V) electro-optic modulators, based on these polymers were demonstrated [4].

Sol–gels, which are hybrid organic/inorganic materials represent an interesting alternative to isotropic polymers. They exhibit excellent propagation properties as the matrix is made from the presently best and very stable optical material which is silica, largely used in optics. Therefore they attracted a lot of interest (see e.g., Refs. [9,11–13]). But generally they suffer of usually small content of active molecules, introduced simply in the matrix as guest molecules. The used active species are usually quasi 1D charge transfer (CT) molecules with enhanced first hyperpolarizabilty β_{xxx} tensor component in the CT direction x.

In this paper we describe the synthesis of a functionalized sol–gel with active chromophores. The chromophores are chemically bond to the silica matrix, offering the possibility to increase their concentration. Also the stability of induced polar ordered, necessary for the targetted applications is expected to be enhanced. Preliminary results on thin film processing, characterization of linear optical properties and on polar orientation of chromophores are reported.

MATERIAL PREPARATION AND THIN FILM PROCESSING

Sol–Gel Preparation

The sol–gel was prepared in the following way:

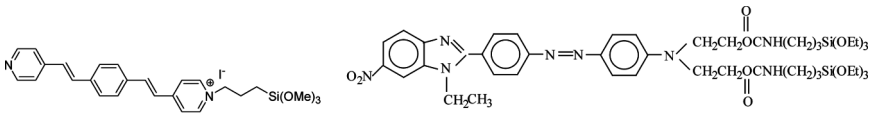
3-glycidoxypropylmethyldiimethoxysilane (GPDDMS) and N-[(3-trimethoxysilyl)propyl]-ethylenediamine) (TMESPE) were purchased by Aldrich and employed without further purification. Methoxyethanol (MeEtOH) (Prolabo) was used as the solvent as well as bidistilled water for hydrolysis.

GPDDMS and TMESPE was stirred 5 min at room temperature. The precursors were hydrolyzed in MeEtOH in basic conditions by addition of NaOH 1 N. The molar ratios H_2O:GPDDMS:NaOH = 1:1:0.002 and H_2O:TMESPE = 1.5 were employed. The final sol concentration was 150 g/L and the molar ratio TMESPE: GPDDMS was 0.4.

The chromophores BZI1-E-SGM and BPEB (cf. Fig. 1) dissolved in MeEtOH, were added to the sol. The molar ratios chromophores: Si = 0.20 were used.

Thin Film Processing

The sol–gel films, after deposition by the spin coating technique on carefully cleaned silica or glass substrates were dried in an oven at 70°C for 30 min. The film thickness was measured with a DEKTAK profilometer. Absorption spectra of so obtained films are shown in Figure 2.



BPEB BZI 1 – E – SGM

FIGURE 1 Chemical structures of the chromophores.

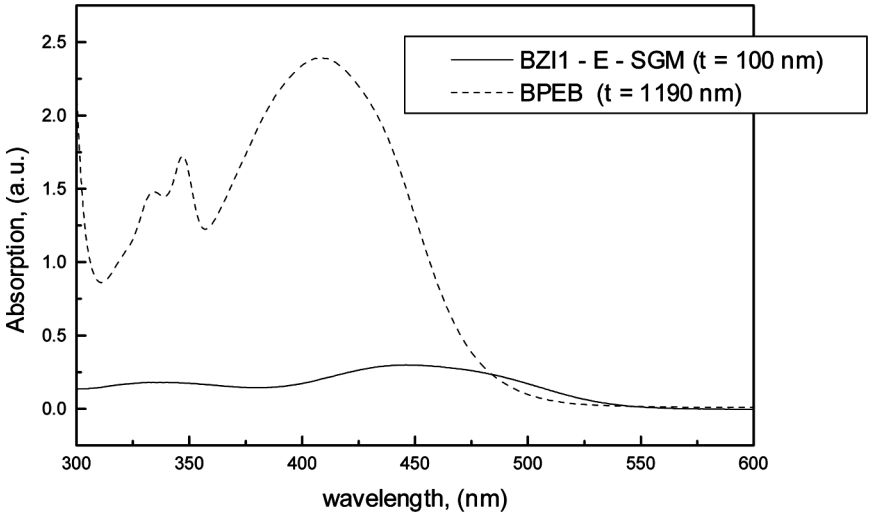


FIGURE 2 Absorption spectra of spun films.

In order to obtain thicker films, needed for refractive indices measurements, the film deposition was made simply by a deposition of a droplet on substrate followed by its curing.

OPTICAL MEASUREMENTS

Refractive Index

The ordinary and extraordinary refractive indices for all chromophores were determined by m-lines technique. The measurements were made with a MATRICON PC 2000 Prism coupler equipment and the results obtained for BZI 1-E-SGM are presented in Figure 3. The absence of optical birefringence show that the films made of this sol-gel are practically isotropic. The refractive indices are close to those of silica and show very little dispersion, in contrast to polymeric thin films. No wave coupling was obtained in the case of thin film containing BPEB chromophore, most likely to a small refractive index difference between the substrate and thin film.

POLING AND NONLINEAR OPTICAL PROPERTIES

Corona Poling

The corona poling technique was used in order to orient the active chromophores in thin film. The methodology was as follows: Firstly

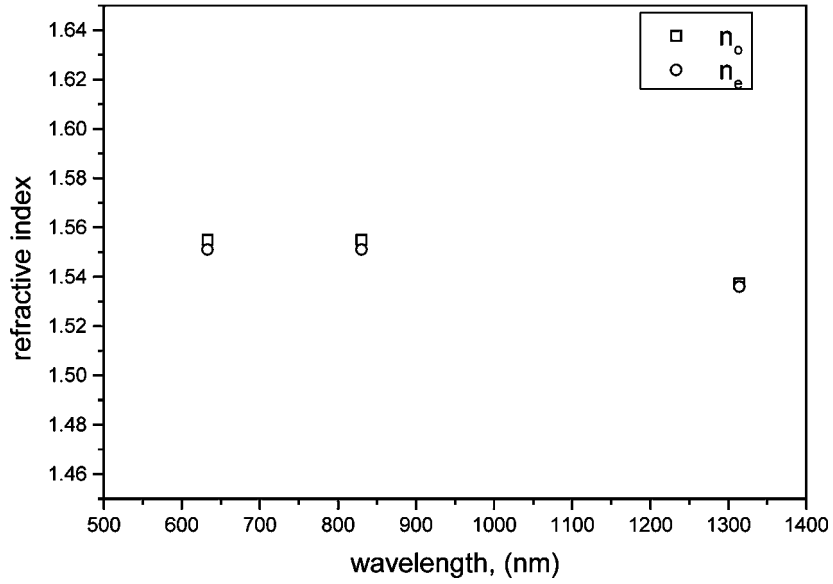


FIGURE 3 Refractive indices for the film of BZI 1-E-SGM, thin film thickness t = 10 000 nm.

the films were heated to 100°C and then the voltage of 6.0 kV was applied to the needle electrode with different periods of time. After that the sample was cooled down to room temperature under the applied the electric field.

In order to find the optimal time for the most efficient chromophore orientation the variation of optical absorption spectrum was monitored in time. Figure 4 shows the absorption spectrum recorded for a sol-gel film, functionalized with BZI 1-E-SGM chromophore, before and after applying the corona voltage, respectively. It can be seen that after 20 min of poling the absorption is increasing, and then a random behaviour is observed. This behaviour probably is due to the conductivity of sol–gels and the transformations which take place in thin film. Similar behaviour was also observed by Kim *et al.* [9] for another sol–gel system.

Figures 5 and 6 show the thin film absorption spectra recorded before and after poling for both chromophores. The poling process took place at 100°C for 60 min. One observes in the case of BZI 1-E-SGM a small shift of the maximum absorption while in the other case its increase (cf. Fig. 6). These behaviours prove that the poling process for sol-gel materials is quite complicated.

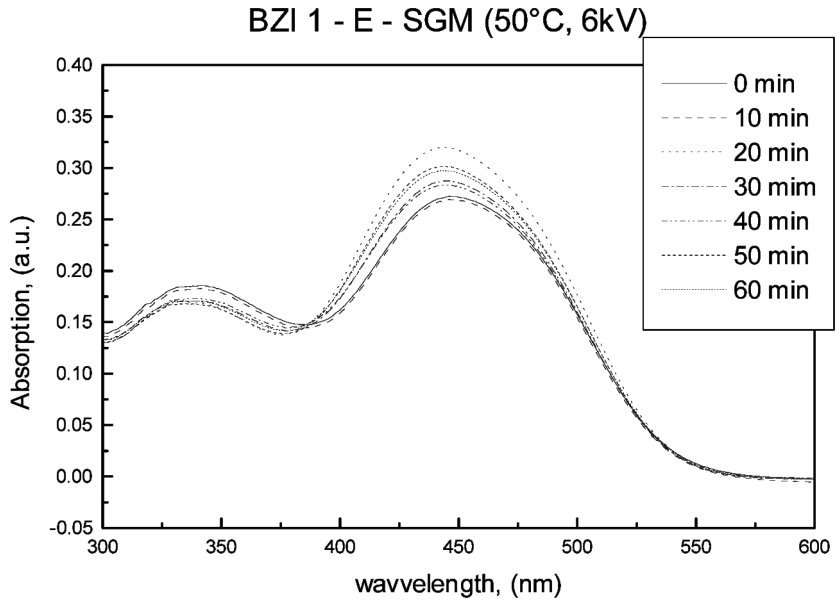


FIGURE 4 Kinetic of corona poling for a film containing the BZI 1-E-SGM chromophore (thickness t = 100 nm).

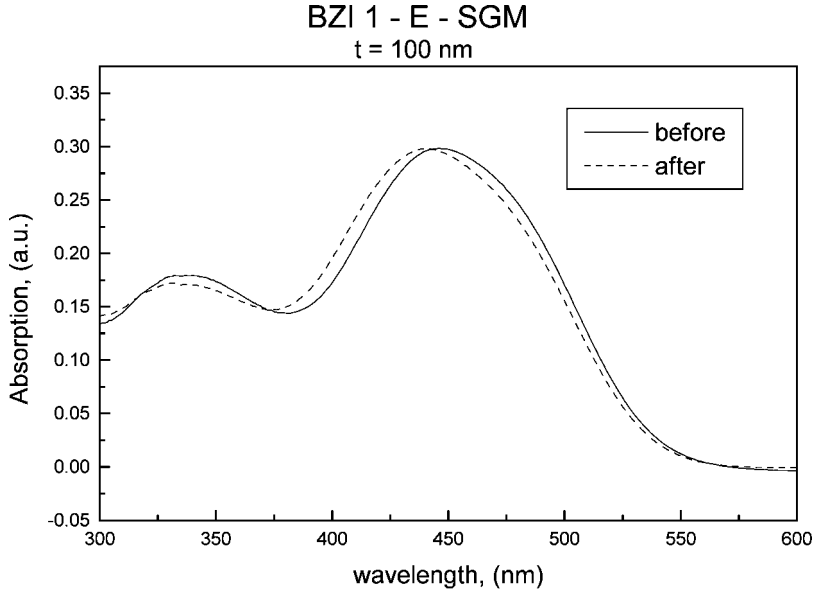


FIGURE 5 Absorption spectra of a film containing BZI 1-E-SGM chromophore, before and after corona poling for 60 mins at 100°C.

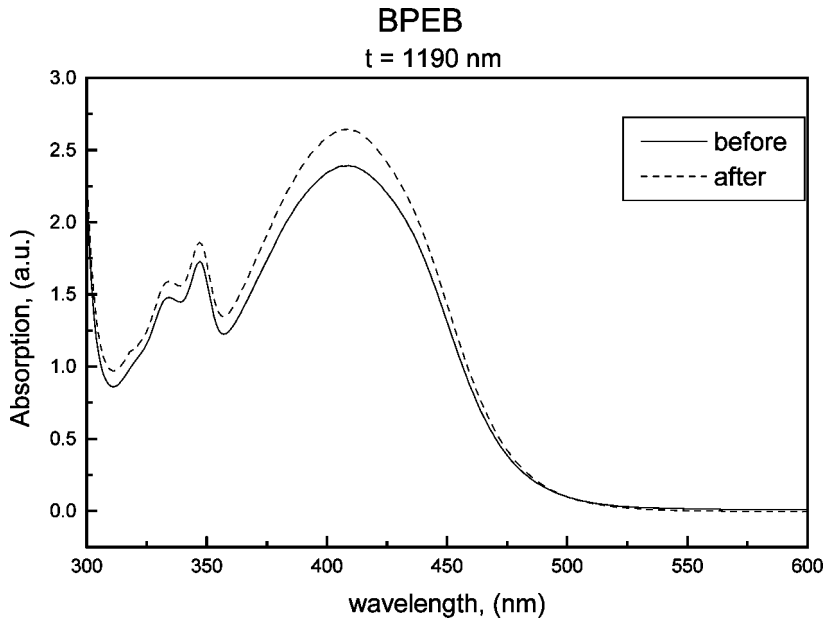


FIGURE 6 Absorption spectra of a film containing BPEB chromophore, before and after poling for 60 mins at 100°C.

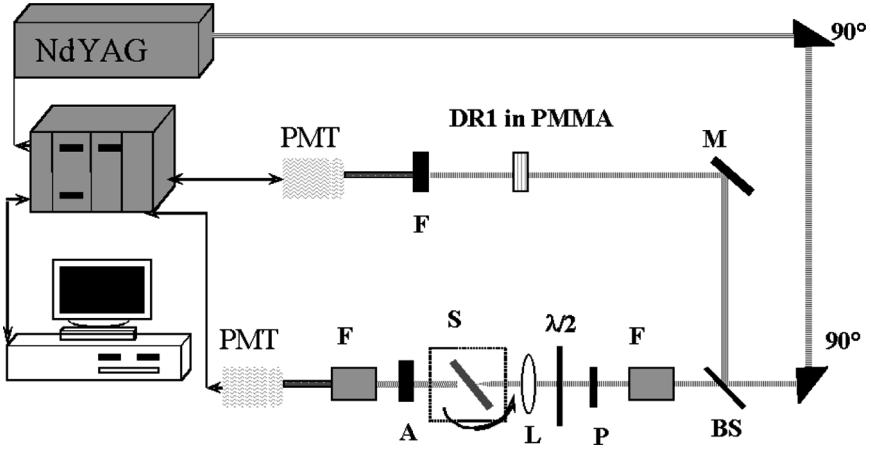


FIGURE 7 Experimental set-up for second harmonic generation. PMT-photomultiplier tube, F-filters, BS-beam splitter, L-lens, $\lambda/2$-half wave plate, A-analyzer, P-polarizer.

Second Harmonic Generation Measurements

The nonlinear optical properties of poled films were studied by optical second harmonic generation measurements. The measurements were done at 1064 nm fundamental wavelength using a Q switched ns Nd:YAG laser, delivering pulses with 13 ns duration at the rate of 10 pps. The used experimental set-up is shown in Figure 7. A part of the beam, after beam splitting, is used to correct the fundamental beam fluctuation by simultaneous SHG measurements on a standard (poled film of DR1 in PMMA matrix). In order to determine different $\chi^{(2)}$ tensor components the direction of the polarization of fundamental wave was varied by rotating the half wave plate. The SHG intensity was measured as function of incidence angle, rotating the sample around an axis perpendicular to the beam propagation direction and having with an intersection point. They were fitted using the formulas given in Ref. [15]. The two nonzero $\chi^{(2)}$ susceptibility tensor components were determined by comparison with SHG measurements on a single crystal plate of a-quartz ($\chi^{(2)}_{XXX}(-2\omega;\omega,\omega) = 1\,\mathrm{pm/V}$ [16]) done at the same conditions. The values obtained for the sol–gel film containing the BZI 1-E-SGM chromophore are as follows:

$$d_{sp} = 0.797\,\mathrm{pm/V}$$

$$d_{pp} = 1.392\,\mathrm{pm/V}\,(d_{sp}/d_{pp} = 0.542)$$

$$d_{pp} = 2.175\,\mathrm{pm/V}\,(d_{sp}/d_{pp} = 0.3)$$

In the screening of the data two approaches were used: one in which the ratio d_{sp}/d_{pp} was used as fit of experimental data and the second one in which this ratio was fixed to 0.3 as it follows from the free gas model. The fit procedure very much depends on the thin film quality. Therefore using a fixed value for d_{sp}/d_{pp} ratio allows to compare with other materials. We note that the values obtained for the studied sol–gel are significantly smaller. Particularly as they are resonantly enhanced, the static values, which are important for applications will be still smaller. Almost no SHG signal was observed from thin films made of second sol–gel.

CONCLUSIONS

The present study show that the obtained sol–gels can be easily processed into thin films by spinning technique. The refractive index measurements show that the film of BZI 1-E-SGM is isotropic. The films can be poled, but the poling is very difficult because of, most likely two factors:

(i) *Competition between hardening and orientation*. The kinetic of poling depends on temperature. Is faster at elevated temperatures but during the poling systems hardens and the rotational mobility of chromophores decreases.

(ii) *Thin film conductivity*. It is well known that sol–gel solutions contain a lot of ions. Before hardening the conductivity of films is important, thus the effective poling field is smaller. When hardening the system the conductivity is decreasing, so the electric field is increasing but the rotational mobility of chromophores is decreasing. Thus in order to increase the poling efficiency it is important to follow both the hardening and the conductivity of sol–gel films.

Presently the research work is concentrated on the understanding of these difficulties with thin film poling and on the optimisation of poling conditions.

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