Optical waveguiding in novel phosphazene polymer films

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Summary

Planar optical waveguides of some novel phosphazene inorganic polymers with high glass transition temperatures, $T_g \geq 150°\ C$, have been prepared by spin-coating on glass and quartz substrates. Thicknesses between 0.5 and 2 μm and index steps of about $\Delta n \sim 0.2$ (for quartz) and $\Delta n \sim 0.1$ (for glass) at $\lambda = 0.633$ μm have been achieved. From one to five modes have been observed at wavelengths ranging from the green to the near infrared. Refractive indices have been well fitted to a Sellmeier dispersion equation. Waveguide losses are estimated to be around 10 dB/cm.

Introduction

Organic polymer materials are being increasingly considered for optoelectronic applications [1,2]. They have a number of potential advantages on single crystals, both organic and inorganic, due to their superior chemical flexibility, processability and low cost. Phosphazenes are inorganic-backbone polymers resulting from the repetition of the - P = N - monomer unit, and appear as an interesting alternative to organic polymers [3,4]. They present a number of useful features, for optoelectronic devices. First, controlled incorporation of covalently linked chromophores can be easily accomplished over a broad concentration range. Consequently, most physical properties (mechanical, optical,....) can be tailored by changing the side groups attached to the polymer chain by suitable molecular engineering. In particular, high refractive indexes can be achieved [5] that might allow for the fabrication of highly confining optical waveguides on a variety of substrates. Moreover, by using polar side-groups significant second-order nonlinear optical (NLO) responses have been obtained [6], suggesting a promising potential for waveguide NLO devices. For previously synthesised phosphazene polymers [4,5] the glass-transition temperature, T_g, could be modified over a large range but below an upper limit value of about 100°C [3]. Consequently, the expected performance of poled films of these polymers for electrooptic and nonlinear devices is not competitive with that achieved with a number of high T_g organic

polymers [7,8]. In fact, the low T_g of polyphosphazenes caused a relatively rapid degradation of the nonlinear response as a consequence of the relaxation of the molecular order after poling [6].

Recently, a new synthetic route has been developed [9,10] for the preparation of highly soluble and rigid novel phosphazene polymers with high glass transition temperatures ($T_g \geq$ 150° C). This should allow for highly stable molecular ordering after electric-field poling and so largely undegraded nonlinear (particularly, electrooptic) susceptibilities. Therefore, the purpose of this work has been to explore and ascertain for the first time the possibilities of these phosphazene polymers for the fabrication of optical waveguide devices. In particular, the NLO side group 4-[(4'-nitrophenyl)azo phenoxy] has been covalently attached to the polymer backbone to investigate their influence on the preparation procedures and waveguide performance. In fact, $\chi_{31}^{(2)}$ values of 2-5·10^9 esu (~ 0.6-1.7 pm/V) have been recently reported for corona-poled films of this side-chain polymer [11]. Moreover, the second-harmonic yield was stable for more than 70 days at room-temperature.

Polymer characterisation

Two poly(2,2'-dioxybiphenil) phosphazene polymers designated as **I** and **II**, illustrated in Fig. 1, were synthesised by following the procedure previously reported [3]. The dioxibiphenil group facilitates the synthesis, gives stability to the polymer chain and rises the glass-transition temperature T_g. Values measured by DSC were T_g=156°C for polymer **I** and T_g=145°C for polymer **II**. In addition, polymer **II** contained the NLO side-group 4-[(4'-nitrophenyl)azo phenoxy covalently linked to the polymer backbone. Molecular weights were 500.000 and 800.000 for polymers **I** and **II**, respectively, as determined by GPC.
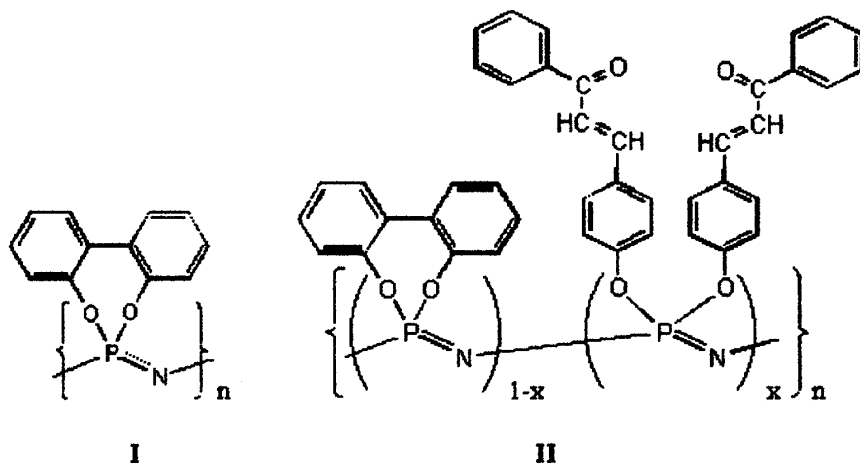
Figure 1: Chemical structure of polymers **I** and **II**.

Film preparation

Films of compounds **I** and **II** have been prepared by spin-coating a solution of the polymers in chlorobenzene at weight concentrations between 4% and 8% on clean quartz (infrasil with $n=1.457$ at $\lambda=633$ nm) and glass substrates (microscope slides with $n=1.515$ at $\lambda=633$ nm). The dispersion laws are known for both substrates. The solution was previously filtered (0.45 µm pore size) to remove impurity particles, spun at 200-500 rpm and finally baked at 90 °C during 5 h and subsequently kept at RT for 16 h. The baking and annealing processes was carried out in vacuum to remove the solvent as completely as possible. Films of good quality were obtained for the two polymers by performing the spin-coating either in air or in a class 100 clean room. The thicknesses were measured with a profilometer and with the dark m-line method [12]. They were in the range 0.5-2 µm and were critically dependent on concentration. The thickness homogeneity of the films was acceptable, since thickness variations lower than 10% were achieved over a large central area of ~5x5 mm^2 (excluding film edges). For concentrations higher than about 10% it was not possible to obtain good quality films for any of the polymers.
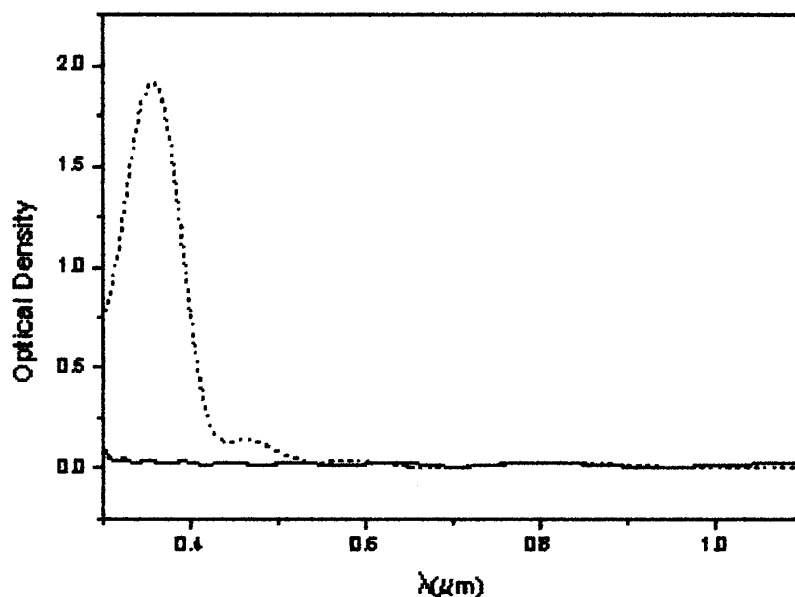
Optical and waveguide behaviour

Fig. 2.- Optical absorption spectra of polymers **I** (solid line), **II** (dashed line).

For compound **I**, the absorption spectrum of the spin-coated films on quartz substrates showed the onset of the UV-Visible at ~300 nm. A well-defined band at 375 nm, corresponding to the attached NLO chromophore is observed for polymer **II**, Fig. 2. Therefore, they offer a large one-photon transparency window for optical applications in both bulk and waveguide devices. A refractive index of n=1.62 has been, first, approximately determined at λ=633 nm from a fitting to the oscillations observed in the absorption spectra and associated to the interference fringes caused by multiple reflections in the film.

The planar waveguides have been, then, characterised in the visible and near infrared by the dark m-line method [12], using a glass prism (n = 1.8308 at λ = 633 nm) to couple the light into the waveguide. The dispersion of the prism and subtrate were taken into account for the analysis. Several wavelengths obtained from Ar (488 nm, 502 nm and 514 nm), He-Ne (633 nm), AlGaAs (810 nm), Nd:YAG (1.047 nm) and Nd:YLF (1.330 nm) lasers were used. Experiments using TE polarization geometry for films prepared with both polymers **I** and **II** show well-defined dips in the reflectivity spectra corresponding to steady propagating modes. The number of modes ranges between one and five depending on the film thickness and the index step. From the analysis of the m-line spectra and assuming a square refractive index profile, precise values for the refractive indices ($\pm$0.001) and guide thickness ($\pm$ 0.01 μm) have been obtained. The measured dependences of refractive index on wavelength are plotted in Fig. 3. The values have been satisfactorily fitted to a Sellmeier equation [13]:

$$n^2 = A + \frac{B}{(C - \lambda^{-2})} - D \cdot \lambda^2 \qquad \textbf{(1)}$$

that has a simple physical basis and is very often used for wavelength dispersion of glass and other materials. From the fitting to our data one obtains: A 2.38 $\pm$ 0.01, B = 3.0 $\pm$ 0.2, C = 11.3 $\pm$ 0.2, D = 0.028 $\pm$ 0.009 for polymer **I** and A = 2.43 $\pm$ 0.04, B = 3.2 $\pm$ 0.6, C = 10.8 $\pm$ 0.8, D = 0.034 $\pm$ 0.007 for polymer **II** and λ in microns. This equation would allow to interpolate (and extrapolate) index values for any wavelength in the visible and near infrared. The index step between the phosphazene waveguides and the substrate was $\Delta n \approx 0.1$ (for glass) and $\Delta n \approx 0.2$ (for quartz) at 633 nm. These values are much higher than those obtained in the standard waveguides prepared on some of the best inorganic electrooptic substrate as $LiNbO_3$ and $KNbO_3$. Consequently, the light intensity profiles in the propagating modes are strongly confined in the polymer region. Film thicknesses inferred from the m-line analysis were in good accordance with these measured with the profilometer.

Waveguide losses for TE modes have been determined by recording the scattered light during mode propagation with a CCD camera [14]. For the films deposited in a clean room measured losses at λ = 633 nm were ~10 dB/cm for polymer **I**. No systematic differences in the losses were found for different mode orders. The value of the losses is relatively high in comparison to those reported for the best organic waveguides [15] and cannot compete with the performance of present inorganic devices. Due to the good transparency of the films in the red (and near infrared) spectral region the losses should be associated to light scattering by film inhomogeneties and surface roughness. Therefore, one may expect a substantial improvement in waveguide transmittance through suitable optimisation of deposition

conditions and film structure. For polymer **II** losses were not measured due to residual absorption at λ=633 nm. At higher wavelengths (e. g. near infrared) they are expected to be similar to those for polymer **I**.
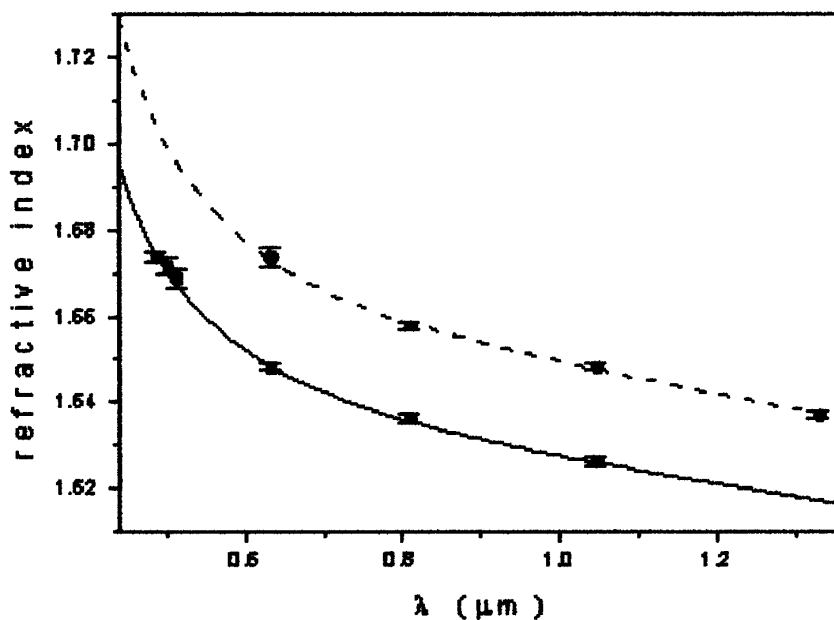
Figure 3: Fitting of the refractive indices for polymers **I** (square and solid line) and **II** (circle and dashed line) to a Sellmeier equation.

Conclusions

Highly confining optical waveguides of two soluble phosphazene (inorganic) polymers with $T_g \geq 150°\ C$ (one of them containing the 4-[(4'-nitrophenyl)azo phenoxy NLO side-group) have been prepared for the first time on glass and quartz substrates. The index step was, respectively, $\Delta n = 0.1$ and 0.2 at $\lambda = 633$ nm. From one to five well-defined modes have been observed depending on the thickness of the film and index step. The refractive index dispersion has been determined from the m-line spectra and fitted to a Sellmeier equation. Losses ~10 dB/cm have been measured at $\lambda = 0.633$ μm. Therefore, phosphazene polymers offer a potential route for optical waveguide devices (both linear and nonlinear) although additional work is still needed to reduce losses.

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