Large optical birefringence in poly(p-phenylene vinylene) films measured by optical waveguide techniques

Ryszard Burzynski and Paras N. Prasad*
Photonics Research Laboratory, Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214, USA

and Frank E. Karasz
Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA

We report here the observation of a large birefringence in an as-cast unoriented film of poly(p-phenylene vinylene), a material that has a large third-order non-linear optical susceptibility. A waveguide technique in TE and TM polarization is used to obtain in-plane and out-of-plane refractive indices at several wavelengths. At 633 nm the measured refractive index values are $n_{TE} = 2.085$ and $n_{TM} = 1.612$. No dependence of the in-plane refractive index on the direction of film spreading is found, indicating an in-plane isotropic behaviour. No anomalous dispersion of refractive index is found in the wavelength range 633–1064 nm.

INTRODUCTION

Organic polymeric systems are emerging as an important class of optical materials for photonics applications[1]. Polymeric systems offer two main advantages. First, their flexibility to be fabricated in forms of films or fibres of optical quality makes them suitable for integrated-optics device structures. Secondly, conjugated polymeric structures exhibit large non-resonant (non-absorptive) third-order optical non-linearity, which leads to intensity dependence of refractive index. This intensity dependence of refractive index is what forms the basis for ultrafast all-optical switching and optical signal processing[2]. The topic of non-linear optical processes in polymers, therefore, is at the forefront of modern research because of the prospect of optical processing with speeds in the subpicosecond range[1,3].

Concentrated efforts are being placed on the measurements of non-linear optical behaviour in organic polymeric materials. However, in order fully to understand and properly to characterize the non-linear optical behaviour of these systems, one needs to have a proper understanding of their linear optical properties. The natural birefringence described by the refractive index anisotropy of polymeric materials in the form of films and fibres has to be understood. One often assumes that an amorphous polymer when cast in the form of a film is isotropic. In the case of planar optical waveguides formed by using polymeric films, this assumption is often made. There are several earlier reports that indicate that the as-spun or cast films show birefringence[4,5]. However, in these cases only small birefringence has been reported. We report here the study of refractive index anisotropy using the optical waveguide technique in a film of poly(p-phenylene vinylene) that has been processed through a water-soluble precursor route but has not been oriented by stretching. We observe what we believe is the first case of large birefringence where the in-plane and out-of-plane refractive indices are widely different. Our study is also relevant to the application of poly(p-phenylene vinylene) film as an optical waveguide for integrated-optics applications because the polymeric film is used as the waveguiding medium.

EXPERIMENTAL

Materials and sample preparation

Films investigated in our studies were made from a solution of the polymer precursor in water, supplied by Foster-Miller. Details of the polymer and polymer precursor synthesis and processing can be found elsewhere[6]. Here, we focus only on the thin-film preparation, which is essential for the light-guiding devices. Films using the polymer precursor solution containing 4% of solids were cast on two different substrates: the base of a prism of high index of refraction (heavy flint, $n_p = 1.8445$), and a fused silica slide with two ion-milled holographic gratings, with periodicity Λ of 530 nm, separated by a distance of 1 cm[7]. The doctor blading technique was used to deposit a uniform layer of the polymer precursor solution on each substrate. Thickness of the film was controlled by varying the distance between the blade edge and the substrate surface. By adjusting this distance to approximately 80 μm, we obtained resulting films of thickness ~1.5–2.8 μm depending on the dilution of the stock solution with pure methanol. Polymer precursor films were kept at room temperature for about 2–3 h to allow most of the solvent to escape. Subsequently, the dried film was placed in the

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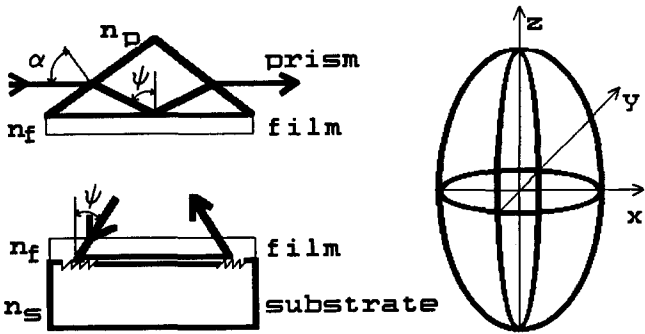* To whom correspondence should be addressed

Figure 1 Schematics of the leaky waveguide structure (top) and the grating input and output coupler waveguide structure (bottom) used in our experiment. The diagram on the right shows the refractive indices of a waveguiding film in its principal axes system

vacuum oven and slowly annealed, first at about 70°C under vacuum (50 mmHg), followed by high-temperature annealing (210°C) for 6–12 h. This high-temperature treatment is necessary to achieve a full conversion of the precursor into the poly(p-phenylene vinylene) (PPV) polymer[6]. The polymer films prepared by this procedure did not exhibit any orientation in the film plane when tested by the light scattering method. However, the films were not completely uniform in thickness, being ~15% larger at the edges than in the middle.

Integrated-optics techniques for refractive index measurements

Determination of the thin-film optical parameters was achieved by using integrated-optics techniques. Here a prism (or grating) input–output coupler was used in a leaky or true waveguide arrangement. Measurements of the coupling angles for TE and TM polarized monochromatic light to the waveguide discrete modes were made. These methods are very convenient and accurate and are very well described in the literature[8–10]. In the leaky waveguide arrangement, the guiding film is coated on the base of a prism whose refractive index is higher than that of the film. Therefore, the film–air interface at the prism base is bound (i.e. it satisfies the waveguiding condition of the film having refractive index higher than that of the cladding medium). But the prism–film interface is leaky. When a laser beam is incident at the prism–film interface at an angle larger than the critical angle, it will be internally reflected. However, the film acts as a leaky waveguide in which specific waveguide modes (see below) can still be excited at specific coupling angles. At these coupling angles, the intensity of the reflected beam would drop because the power is transferred into the guided (even though leaky) modes.

For the case where the film has a refractive index higher than the prism, it would act as a true waveguide. In such a case we have used the grating input–output coupler arrangement. One grating is used to couple light into the guided-wave form. Another grating (spatially separated from the first) can be used to decouple the light.

The film-coated prism is mounted on an optical goniometer, which has an angular accuracy better than 10^{-2} deg arc. Different laser sources were used to make measurements at many different wavelengths. The 632.8 nm line was obtained from a He–Ne laser. The 602 nm line was obtained from a dye laser pumped by a

mode-locked (82 MHz) and frequency-doubled Nd–YAG laser (Spectra Physics, model 3820). The 1064 nm wavelength was obtained from a mode-locked and Q-switched (500 Hz) Nd–YAG laser. The polarized laser beam was directed onto the prism uncoated face to enter the film (*Figure 1*). The light reflected at the prism base was monitored through the prism output face by a photodiode connected to the boxcar averager (Princeton Applied Research, model 4021). By varying the angle of incidence α on the prism base the laser light was coupled into one of the waveguide modes at the synchronous angle α_m at which the intensity of the reflected beam dropped down. Hence, by monitoring the reflected output beam as a function of angle α, one can readily detect the intensity change whenever light is coupled into a waveguide mode. This procedure is repeated for both polarizations, TE and TM, thus giving us in-plane and out-of-plane refractive indices. A similar type of study was conducted on the slide with the grating input–output coupler covered by the polymer film. This slide was placed on the goniometer. Again the angular variation of the input beam was used to determine the coupling angles for various waveguide modes.

RESULTS AND DISCUSSION

In order for the light waves confined in the film to propagate (to interfere constructively), the following waveguide mode equation has to be fulfilled[9]:

$$2kW(n_f^2 - \beta^2)^{-1/2} - 2\phi_{10} - 2\phi_{12} = 2m\pi \qquad (1)$$

where $\beta = n_f \sin\theta$ is the effective refractive index of the waveguide mode m. The angle θ is the angle of incidence measured from the waveguide normal to the wavevector k; and W and n_f are the film thickness and refractive index, respectively. The quantities ϕ_{10} and ϕ_{12} are the phaseshifts suffered by the wave upon reflections from the two interfaces: film–cladding and film–substrate. Launching a waveguide mode is accomplished with the help of an input coupler, grating or prism, which allows one to match the wavevector component of the incident radiation parallel to the film surface with the guided wavevector, $k\beta$. By adjusting the incidence angle, ψ (*Figure 1*), the phase matching conditions:

$$kn_{c,s} \sin\psi + v(2\pi/\Lambda) = k\beta \qquad \text{(grating)} \qquad (2)$$

$$kn_p \sin\psi = k\beta \qquad \text{(prism)} \qquad (3)$$

are easily achieved. In the above equations, k is the wavevector of light in the air, ψ is the incidence angle between k and the surface normal at which the light strikes the grating or the prism base, and v is the grating diffraction order. The subscripts c, s and p denote the cladding, substrate and prism media, respectively.

Figure 2 shows the observed modes for the PPV leaky waveguide film deposited on the prism base, and excited with 632.8 or 602 nm TM polarized laser radiation. It can be seen that up to four resonances could be excited, which permitted us to calculate both the refractive index and the thickness of the film. With these sets of coupling angles, the refractive index and the thickness of the film are computed using the expressions given in ref. 10. The calculated values of n_{TM} at 632.8 and 602 nm are listed in *Table 1*. This value of n_{TM} correlates very well with the previously reported values of n_{TM} from our laboratory[11]. The accuracy of the computed indices is

$\sim 1 \times 10^{-2}$, for the reason that we shall explain in the later part of this paper.

Unfortunately, the TE polarized light did not produce any appreciable change in the intensity of the reflected beam as the angle was varied. This observation indicated that for TE polarization the waves could not be coupled into the PPV film. This would suggest that the refractive index of the PPV film for TE polarization is higher than that of the prism. In such a case, the PPV film forms a regular waveguide and its mode excitation can be done by using an external input prism coupler of higher index of refraction. We selected an alternative arrangement involving grating coupling described above to determine the refractive index for TE polarization. A grating coupler is more flexible and simpler to use and it may cover a wider range of waveguide modes, depending on the grating parameters. However, for efficient coupling such couplers have to be designed for a given system (refractive indices, thickness, beam size)[7]. For our purpose, where the coupling efficiency was not of concern, we used a grating with the 530 nm spacing.

The results of our studies with the grating coupler are listed in *Table 2*. There are a few comments pertaining to the experiment that we would like to make before we proceed with the discussion.
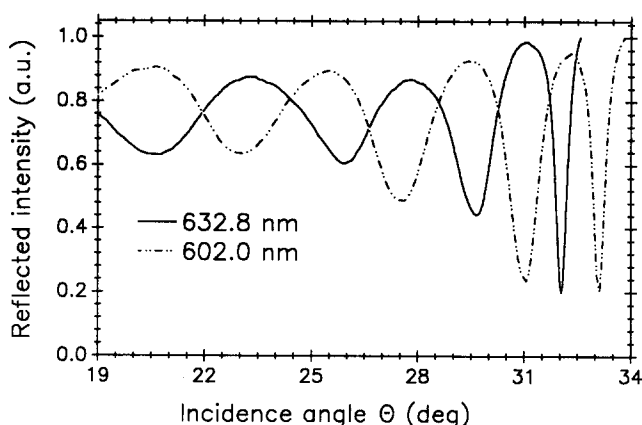

Figure 2 The observed leaky waveguide resonance curves at 602 and 632.8 nm for TM polarization. The leaky waveguide structure consisted of a high-index right-angle glass prism and a thin PPV film coated on the prism hypotenuse face (see *Figure 1*)

Table 1 Refractive index of PPV thin film obtained in leaky waveguide geometry (TM polarization)

λ (nm)	n_{TM}	$n_{\perp}^{cor\ a}$	$n_{TE}{}^{b}$
632.8	1.63	1.612	2.085
602.0	1.64	1.619	2.085

[a] Value corrected for anisotropy
[b] Index taken from *Table 2*

First, the waveguide losses at both wavelengths, 632.8 and 1064 nm, increased as the precursor film was gradually converted to PPV. For instance, for the precursor waveguide film, the TM excited modes could propagate several centimetres almost unattenuated at 1064 and 632.8 nm. In contrast, for the film fully converted in the final polymer (PPV), propagation distances were usually limited to a millimetre. This dramatic change is, in our opinion, due to strong scattering created by film inhomogeneities (different parts of the film could be converted into polymer to different extents, leading to inhomogeneity of the refractive index) as well as due to structural defects (created by the chemical elimination process) during precursor–polymer conversion. Also, at the higher laser frequency used in our experiment, the PPV polymer shows residual absorption, which caused additional attenuation of the beam coupled into the waveguide mode. Regardless of this obstacle, the coupling angles could still be determined with sufficient accuracy to compute the film parameters.

Secondly, from our observations we can conclude that the TE polarized waveguide modes were considerably more attenuated. For the fully converted PPV film, the streak of the coupled TE polarized light was less than one-tenth of that for the TM polarized mode. The strong scattering between the coupled modes, on the other hand, produced clearly visible *m*-lines on the screen placed behind the grating. It is not clear at this time why the attenuations of the TE and TM modes were dramatically different. Further investigation is needed to understand this behaviour.

The first analysis of our experimental data indicated an unusually high difference (anisotropy) between the refractive indices parallel (n_{TE}) and normal (n_{TM}) to the film plane. This anisotropy became progressively larger as the ratio PPV polymer/precursor increased. Also, the agreement between the thicknesses computed for the TE and TM polarizations was rather poor. The above observation led us to the conclusion that we cannot explain the anisotropy of the refractive indices by using a waveguide mode analysis developed for an isotropic medium. However, full analysis of an anisotropic waveguide requires detailed knowledge of the dielectric constant tensor and the orientation of its principal axes with respect to the waveguide framework. Considering the rigid highly conjugated ladder-like structure of the polymer, we can assume that the polymer chains in as-cast film lie flat, parallel to the surface, and are randomly oriented in the film plane. In such a case, the dielectric constant tensor would be of the form:

$$\varepsilon = \begin{pmatrix} \varepsilon_x & & \\ & \varepsilon_x & \\ & & \varepsilon_z \end{pmatrix} = \begin{pmatrix} \varepsilon_{\parallel} & & \\ & \varepsilon_{\parallel} & \\ & & \varepsilon_{\perp} \end{pmatrix} \quad (4)$$

Table 2 Refractive indices of the prepolymer film at different stages of conversion to the PPV polymer

	Conversion (%)							
	0		20		60		100	
λ (nm)	$n_{\perp}$	$n_{\parallel}$	$n_{\perp}$	$n_{\parallel}$	$n_{\perp}$	$n_{\parallel}$	$n_{\perp}$	$n_{\parallel}$
632.8	1.602	1.655	1.572	1.748	1.590	2.022	1.610	2.085
1064.0	1.598	1.628	1.569	1.704	1.578	1.918	1.584	1.968

Here the x, y and z directions correspond to the waveguide coordinates (see *Figure 1*). $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the dielectric constants parallel and perpendicular to the film plane respectively. Subsequently, equation (1) has to be modified to the form:

$$2kW(n_{\parallel}^2 - \beta^2)^{-1/2} - 2\phi_{10} - 2\phi_{12} = 2m\pi \quad \text{(TE modes)}$$

$$(5a)$$

$$2kW(n_{z,m}^2 - \beta^2)^{-1/2} - 2\phi'_{10} - 2\phi'_{12} = 2m\pi \quad \text{(TM modes)}$$

$$(5b)$$

where $n_{\parallel}$ denotes index of refraction in the film plane, and $n_{z,m}$ is the film index of refraction in the xz (or yz) plane along the propagation direction of the guided mode m. The expressions for the phaseshift angles ϕ_{ij} are obtained by inserting $n_{\parallel}$ or $n_{z,m}$ in place of n_f in the original equation[9]. The relation of $n_{z,m}$ to the principal indices $n_{\parallel}$ and $n_{\perp}$ of the refractive index indicatrix can then be expressed as[12]:

$$(n_{z,m}^2)^{-1} = (n_{\perp}^2)^{-1} \sin^2 \theta + (n_{\parallel}^2)^{-1} \cos^2 \theta \quad (6)$$

Here, θ is the angle between the guided wave normal and the z axis within the waveguide.

With the above assumptions, the refractive index in the film plane, $n_{\parallel}$, was determined by the analysis of the TE modes. Then with $n_{\parallel}$ known, we analysed data for the TM modes and obtained $n_{\perp}$ via equation (6). The results of this calculation are presented in *Table 2*. Using a similar procedure and with the value of $n_{\parallel}$ obtained from this calculation, we corrected $n_{\perp}$ obtained by the leaky waveguide structure. They are listed in the second column of *Table 1*.

The above computations were based on the assumption that the in-plane refractive index is isotropic. One may, however, suspect that casting the polymer film with doctor blading can induce orientation of the polymer chains in the direction of spread. Orientation of the polymer waveguide film by repetitive strokes during its casting has been reported by Schlotter *et al.*[13]. To check the validity of our assumption of in-plane isotropy, we repeated our experiments with films spread in a direction normal to the waveguiding direction. We found complete agreement between the values of refractive indices for these two sets of experiments. This result establishes that the film is isotropic in the film plane. To evaluate the effect of dispersion and examine if there is any anomalous refractive index dispersion, we have also conducted the experiments at 680 and 720 nm. The values obtained are essentially the same as those found at 632 nm.

Results obtained for the PPV polymer film show large anisotropy of refractive indices for the in-plane and out-of-plane values. For light polarized in the plane of the film (TE), the index of refraction at 632.8 nm is 2.085, much higher than the refractive index of the prism used in our leaky waveguide experiment, thus supporting our earlier presumption.

Anisotropy in the refractive indices, $\Delta n = n_{\parallel} - n_{\perp}$, in waveguides made from other conjugated polymers has been reported earlier[4,5]. Townsend *et al.*[4] observed anisotropy of the order of $\Delta n = 0.07$ for spun poly(4-BCMU) and poly(3-BCMU) films at 1064 nm. Our preliminary studies on these polymers also support the existence of a similar anisotropy, although smaller in value[14]. This anisotropy is believed to be a natural result of the spinning process. Also, evaporation of the solvent

itself can produce highly birefringent film, as was observed for the poly(4-BCMU) polymer in tetrahydrofuran (THF)[15]. However, our results give evidence of an unprecedented high anisotropy for a polymer film. The nature of this phenomenon has to be studied in more detail. We cannot give a full explanation of its existence at this time. It seems to be associated with the molecular structure of the polymer chain. The high conjugation of the polymer chain and its rigidity most probably account for the refractive index anisotropy.

The refractive index of PPV film has also been reported recently by McBranch *et al.*[16]. They used the Abeles method and found a value 2.2 ± 0.05 at 633 nm for TM polarization, which does not agree with our values reported here as well as reported earlier for the same polarization[11]. This discrepancy may be because the analysis they used for the Abeles method has an implicit assumption that the medium is isotropic. It is also possible that their method of processing produces a film of different optical property.

Finally, we would like to point out that the measured value of refractive index, $n_{\parallel}$, in the film plane relates to randomly oriented polymer chains. If any in-plane orientation is induced, for example by stretch orientation, the refractive index value along the orientation direction can be even higher than our measured $n_{\parallel}$.

ACKNOWLEDGEMENTS

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