# Elastooptic investigations in functional allyl polymer lightguides

**M. Biebricher[1], K. Pfeiffer[2], P. Schulz[1], H. Franke[1], H. J. Lorkowski[2]**

[1] Angewandte Physik, Gerhard Mercator Univ.-GH Duisburg, 47048 Duisburg, Germany
(Fax: + 49-203/379-3163, E-Mail: Biebricher@uni-duisburg.de)
[2] Angewandte Chemie Adlershof, Rudower Chaussee 5, 12489 Berlin, Germany
(Fax: + 49-30/6392-4205, E-mail: Kpeiff@aca.fta-berlin.de)

**Abstract.** Planar waveguides of the allyl polymer poly-(terephthal acid diallyl ester) (PDATP) exhibiting a particular high stress optical coefficient are investigated. Internal mechanical stress may be introduced in the waveguides by the in-diffusion of small vapour molecules or by the activation of a piezoelectric transducer in the substrate. Based on the induced stress the feasibility of gas sensors or electro acousto optic phase shifters ($V_\pi = 180$ V) with these waveguides is discussed.

**PACS:** 42.79.h; 42.79.P,Q; 42.82; 71.29.Hk

Polymers are widely used for the investigation of mechanical stress with miniaturized models in construction business. The usual material is poly-(methyl-methacrylate)(PMMA). Besides this bulk stress optics, especially in the optical disc technology the stress optical behavior of thin polymer films is important. In case of thin films there are different sources for birefringence, e.g. orientational and stress birefringence. In general the thermal expansion coefficients are higher than those of inorganic substrates like glass, $SiO_2$ or metal. Any drift of temperature causes a mechanical stress in a clamped polymer film. With a resonable stress optical coefficient this leads to a birefringence. The in-diffusion of vapor molecules may also cause a reasonable birefringence. Much work has been done to minimize the birefringence due to thermal expansion or orientation, especially in case of optical disc coatings [1].

In this paper we look into the opposite direction. A particular polymer with an extremely high stress optical coefficient is used, the functional allyl polymers [2]. Different sources for mechanical stress on a polymer film are investigated. As a method of characterization of the polymer films sensitive waveguide techniques have been used. The different light guide techniques are applicable with a high accuracy to measure the optical film parameters like refractive index in the film plane ($n_{TE}$), perpendicular to the film plane ($n_{TM}$), the birefringence $\Delta n = (n_{TE} - n_{TM})$, the film thickness and the optical losses.

With the knowledge of the influence of the different sources of mechanical stress the question of the feasibility of elasto optic polymer waveguide devices can be answered. As examples we will introduce an optical waveguide phase shifter and a monitor for vapors of the R-OH type with R=H, $CH_3$, $C_2H_5$.

## 1 Experimental

### 1.1 Material

The repeat unit of a typical polymer of the functional allyl polymer, Poly-Terephtal acid diallyl ester (PDATP) is shown in Fig. 1. This material is a crosslinkable polymer with good mechanical properties. In opposite to most other polymeric materials it is nearly mar proof when crosslinked. It is a useful material for waveguiding purposes, because of it's low losses in the visible part of the spectrum. The refractive index is $n = 1.5667$ (632.8 nm) and the birefringence is smaller than $10^{-3}$ when not processed under mechanical stress. The property which makes it really interesting for application in integrated optics as well as for basic research of stress optical behavior of polymers, is its huge stress optical coefficient of nearly +169 Brewsters [3].

### 1.2 Optical gas sensors

The measurement of change of birefringence due to in-diffusing gas molecules in thin polymer layers by waveguiding techniques has been used for a long time. Especially with polyimide films a lot of measurements were performed [4, 5]. In this paper the same principle of measurement will be presented for films of diallylic esters, but the evolution of birefringence upon in-diffusing of vapors is of a completely different origin.

A basic experimental setup is sketched in Fig. 2. In addition to the well known optical part of the equipment
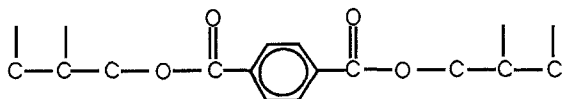
Fig. 1. Repeat unit of Poly-Terephtal acid diallyl ester

[6], there is a flow through cell clamped to the waveguide, which admits the exposure of the flow of a certain atmosphere to the polymeric material. A system of valves, tubes and sources of 'dry air', as well as vapors of water and other chemical compounds allows to adjust any concentration in the gas flow. This mixture can be controlled by a reference device, in this case a psychrometer [5]. The temperature for all measurements was room temperature ($\approx 20°C$), thus taken 2°C of deviation into account there might be a deviation of the absolute concentration of less than 3%.

Waveguiding films are produced by the method of spincoating. The performance of the experiments yields three consecutive steps: first, a certain atmosphere is adjusted by using the psychrometer. During this step, the valves are switched in a way, that the flow of gas is just in the reference channel. That means, the waveguide is not affected by it. Next the waveguide is dried, i.e. dry air is allowed to flow through the cell. During this procedure the mixture of compounds is not affected. In the third step, the previously adjusted concentration of vapors is led to the waveguide. The in-diffusing gas causes some change in the optical properties (birefringence) of the waveguide which are measured by the optical part of the setup.

A typical output upon in-diffusing of gas is shown in Fig. 3a. A change in birefringence causes a square sinus signal behind the analyzer. Since the periodicity of the square sinus function is known, it is possible to evaluate the change of birefringence $\Delta N$ from the extreme points of this measured signal. The result is shown in Fig. 3b.

$$\frac{\Delta N(t)}{\Delta N_\infty} = \exp\left(\frac{t}{\tau}\right)^\beta \qquad (1)$$

For further characterization a function of the Kohlrausch-type (1) is fitted to the curve by the method of least
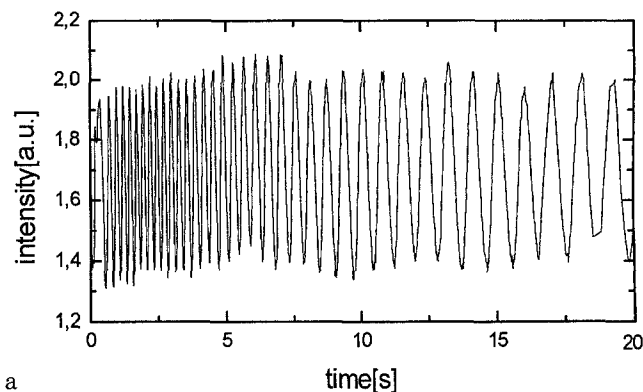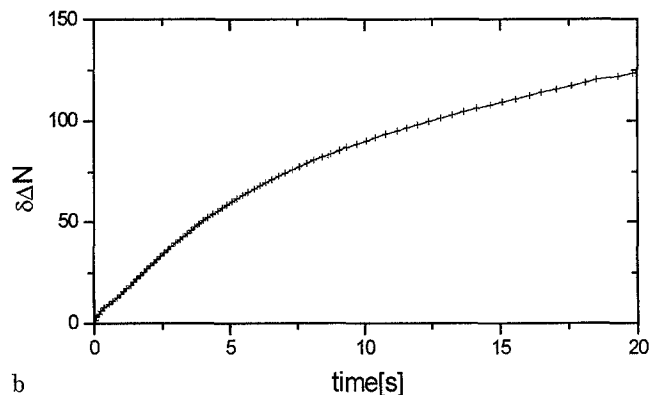


Fig. 3a, b. Principle of measurement. (a) Typical intensity signal upon in-diffusing of vapour into a PDATP film; (b) Evaluated intensity signal: course of effective birefringence upon in -diffusing (Please note, that every cross in figure b. corresponds to an extreme value of figure a.)

square error. There are three characteristic parameters: the maximal achievable birefringence $\Delta N_\infty$, the characteristic diffusion time $\tau$ and the stretching factor $\beta$.

### 1.3 Phase shifting

For phase shifting a quite similar setup is used. A sketch is given in Fig. 4. The most important part of this setup is
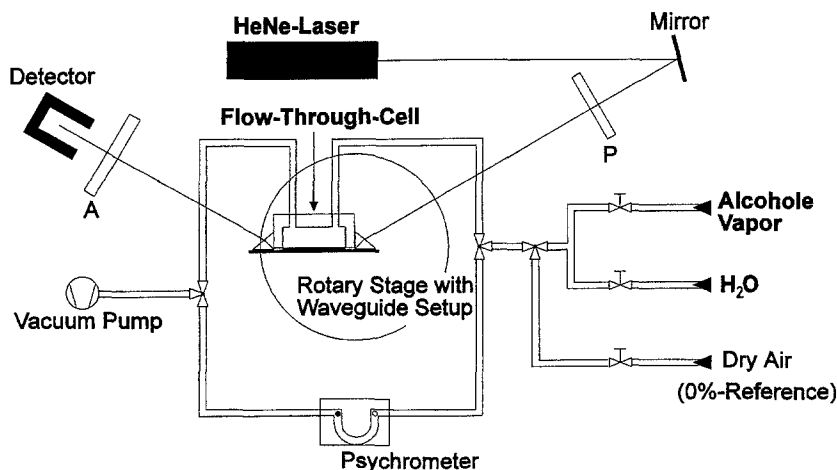


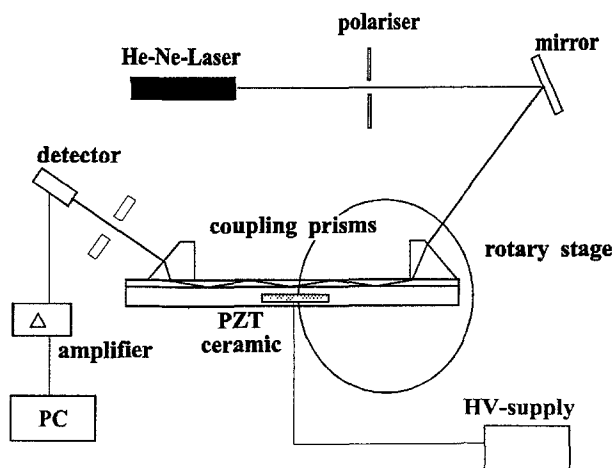Fig. 2. Experimental setup for dynamical birefringence change measurements

Fig. 4. Sketch of setup for phase shifting



Fig. 5. Maximum birefringence for various concentrations and vapors

a special waveguide. Its substrate -made of PMMA- contains a piezo (PZT, [7]) element. This piezo is connected to a voltage source, which gives the possibility to cause some mechanical stress in the substrate. The waveguide itself is made of PDATP by spincoating.

The optical part of this setup is just the same as of that for sensor purposes. It is measuring changes in effective birefringence , i.e. changes in the difference of phase velocities of TE and TM polarization; in other words phase changes.

Two types of experiments were performed, one for static phase shifting, the other one was used to modulate the phase of the optical signal. For the former, the voltage at the piezo was increased in steps between 0 and 1000 V. Some seconds after this increase, when the signal was stable again, the intensity was measured. The evaluation of the effective birefringence was achieved in the same way as for sensor experiments. The same procedure was applied to the samples while decreasing the voltage.

For the modulator experiments, the HV-supply was replaced by an amplifier giving the possibility to have AC-voltage of about 300Vpp. A silicon photo detector connected to an amplifier and an oscilloscope was used for detection. With a function generator various frequencies were applied to the piezo and checked in the optical signal. In a second step a smaller frequency (signal) was modulated on a high (carrier-) frequency.

## 2 Results and discussion

### 2.1 Allyl Polymer Light guides as Optical Gas Sensors

In Fig. 5 the maximum birefringence $\Delta N_\infty$ is plotted for several chemical compounds and concentration. For these measurements the 0th mode of a PDATP film of 3.56 μm thickness was used. The effect of in-diffusing alcohols is about one order of magnitude higher $(2.5 \cdot 10^{-3})$ than that of water, which is about $5 \cdot 10^{-4}$. The sensitivity for water was $7.06 \cdot 10^{-6}/\%$ of relative humidity, for methanol $1.58 \cdot 10^{-5}/\%$ and for ethanol $2.98 \cdot 10^{-5}/\%$, at least in the region of 40–80% of relative concentration.
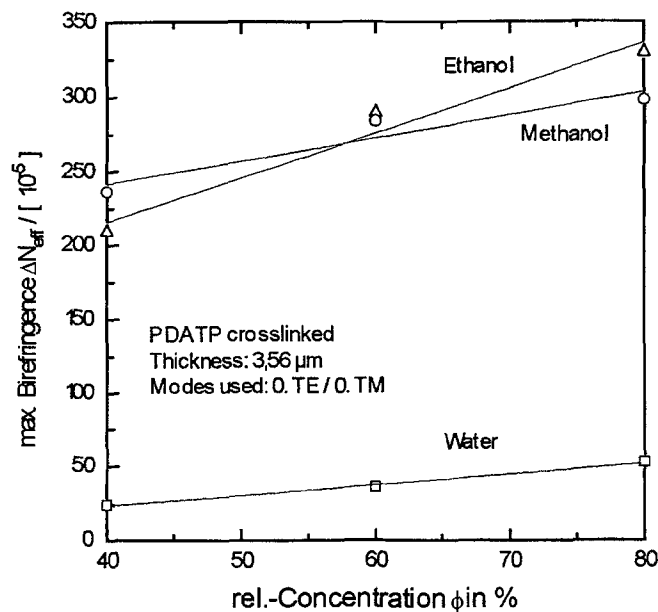
It is remarkable, that different results for different modes are obtained. In Fig. 6 this is shown for the same PDATP-waveguide of 3.56 μm thickness and a relative methanol concentration of 60%. For this reason every value given refers to the 0th mode, if nothing else is indicated. The physical background of this effect will be discussed later.

The characteristic time constant $\tau$ of the diffusion is related to the film thickness by a square function, which is shown in Fig. 7. This can be explained by a standard diffusion theory and it is in accordance with Fick's second law [8]. Furthermore, for simple, linear alcohols it is obvious, that the bigger the molecule the slower is the diffusion. The time constant for in-diffusion and out-diffusion is the same, at least for small molecules like water and methanol.

The time constant also depends on the relative concentration of the compound – in the case of large concentrations, i.e. < ca.65% – and also (weakly) on the mode used. For the stretching factor $\beta$, the values show a wide range of scattering. The fit, however is not very sensitive on this value, for all cases it is between 0.7 and 1.1.

The relation between the time constant $\tau$ and the film thickness $d$ together with the fact that there is no need for a phasematch (compare [4]) allows to adjust the film thickness to special applications. In order to get fast response, it is better to use thin films, to maximize the 'chemical resolution' thicker films will be preferred. For example, when sensing a mixture of water and ethanol with a film of 6 μm, the in-diffusion of water will be completed after some seconds. The ethanol signal on the other hand, will still rise for some minutes, and the change in birefringence is one order of magnitude higher. Thus it is possible to distinguish between the two parts of the mixture.

Waveguides of this material show real birefringence which of course also affects the effective indices of the
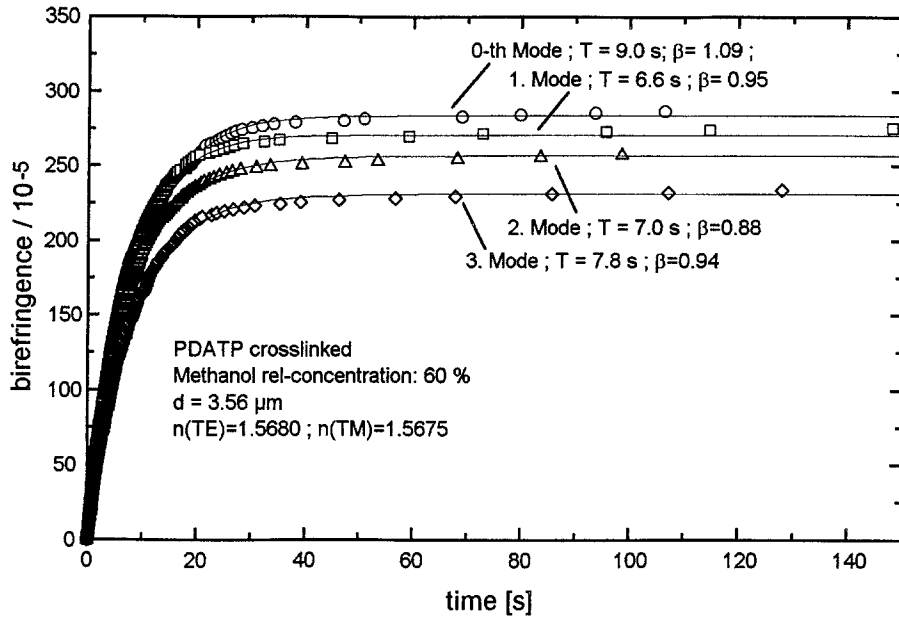
**Fig. 6.** Birefringence caused by a methanol-atmosphere in a PDATP waveguide for various modes

waveguide modes. This would not explain different results for different modes of the same waveguide (see Fig. 6). As a first approach of interpretation, we tried to consider the different amounts of the electric field, which are transported in the -isotropic-substrate and cover for higher modes. But this was not sufficient, the fraction of electric field travelling in cover an substrate is too small – in the case of the waveguide which was used – to explain such big variations of the maximum birefringence, for example.

To give some explanation for this problem, a simple model was developed, introducing a diffusion profile. Its first derivative is a measure for the mechanical stress- and therefore for the birefringence profile. To have a feeling of how much of the birefringence is 'seen' by the electric field, the overlap integral of the electric field and the birefrin-

gence profile in the wave-guiding layer was calculated. Varying the characteristics of the diffusion profile, the values of the overlap integrals would fit the values of the maximum birefringence.

The birefringence profile has to have a maximum value in the vicinity of the middle of the waveguide, because of the symmetry of the electric field distribution of the modes. For approximation a Fermi type profile was chosen. In Fig. 8 the corresponding result is shown. In the upper left picture, the electric field distribution of the TE-modes ($E_y$ component) is plotted, in the upper right the diffusion profile an the derivation of it, the birefringence profile. The product of these two graphs is demonstrated in the lower left picture of figure 8. The overlap integral of electric field and birefringence profile is shown in the lower left picture, here the values are normalized, i.e.
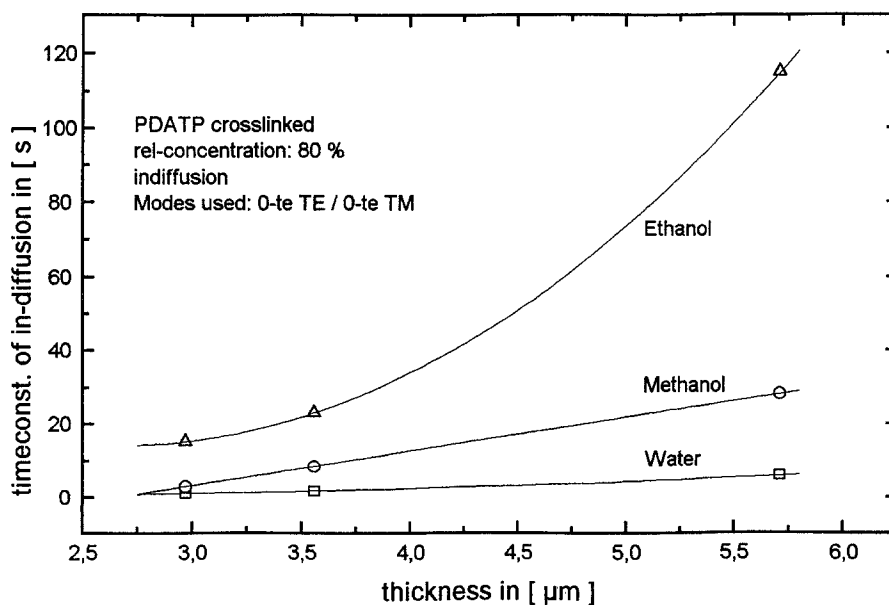


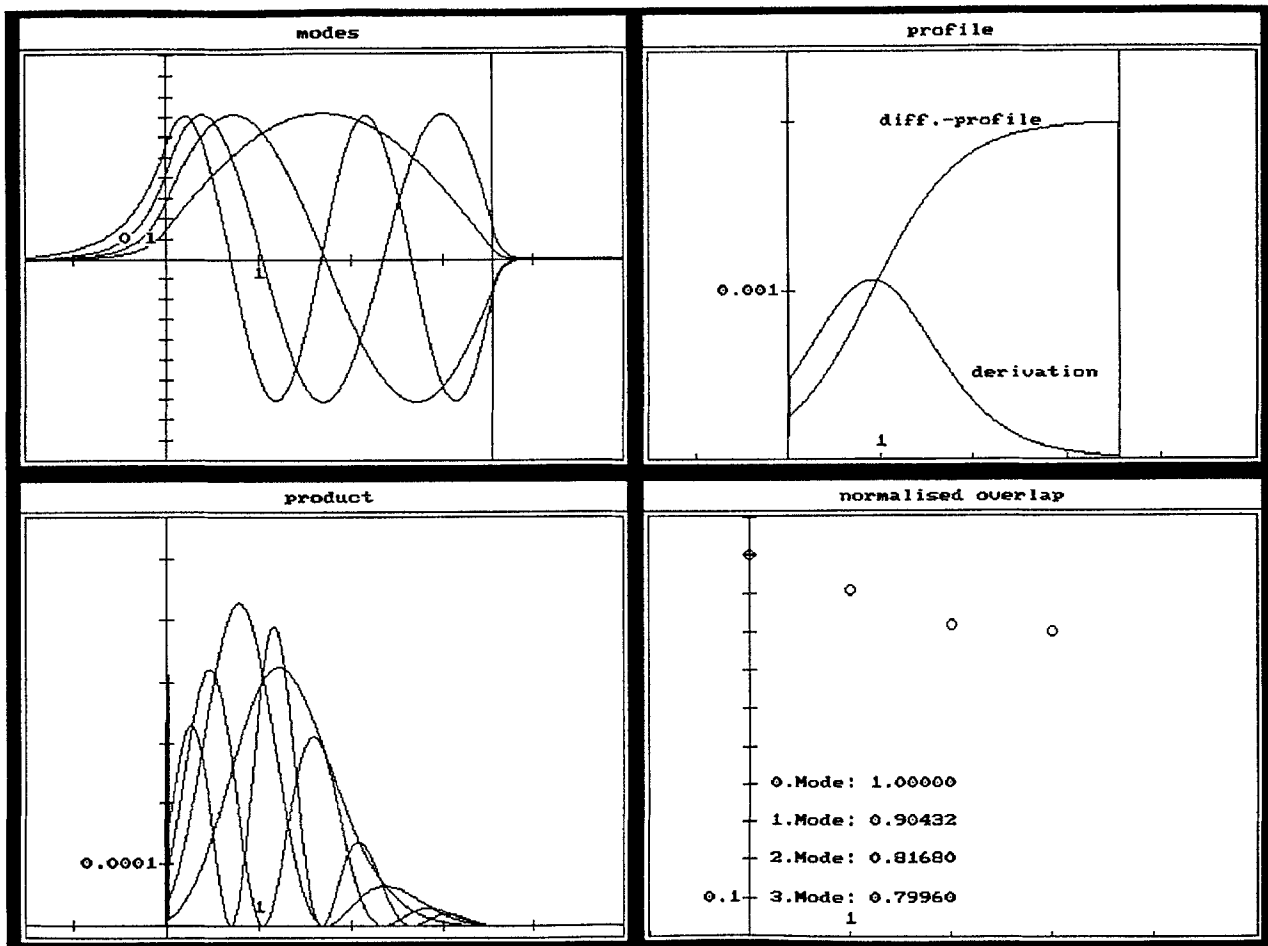**Fig. 7.** Dependence of the characteristic time constant $\tau$ on the film thickness

**Fig. 8.** Influence of the diffusion profile on the maximum birefringence of different modes

the values are divided by that for the first mode. Experimental numbers, taken from figure 6, are 1, 0.9, 0.82, 0.79 for the first, second third and fourth mode, respectively. This fits very good to the values obtained by the model. Thus it is possible to explain the different results for different modes by this model.

### 2.2 Allyl Polymer Light guides as Optical Phase Shifters

In Fig. 9 the oscillation of the intensity behind the analyzer is plotted against the applied voltage. This fluctuation is due to the change of the (effective) birefringence in the waveguide. The square sinus function is reproduced with stable frequency. Thus there is a linear relationship between effective birefringence and applied voltage. This is shown in Fig. 10; it is the evaluation of Fig. 9. In contrast to the sensor experiments, here not only the extreme values of the intensity plot were taken into account. A square sinus function was fitted to the data. Thus, the linear dependence of figure 10 is just the visualization of the argument of the square sinus function.

It is remarkable however, that the slopes of the graphs are not the same for increase and decrease of the voltage. This hysteresis may be due to relaxing stress. Anyway,

a whole period of $2\pi$ can be shifted in this configuration by about 360 Volts, in other words $V_\pi = 180$ V.

The dynamic experiments, that is the modulator experiments, resulted in a very high sensitivity for the frequency. For more than 10 kHz, an interaction with the light only was obtained for special resonance frequencies. These frequencies were multiples of 90 kHz.

There are quite simple reasons for this behaviour. The thickness of the samples – including the substrate – were about 5 mm. Provided a velocity of sound of about 2700 m/s [9], this is about the length of a quarter wave ($\lambda/4 = 7.5$ mm). Provided a ninety degree phase shift at one surface, this is a resonance frequency of the whole system. Of course there is a big deviation from the theoretical value, but it can be explained by taking the piezo in the middle into account. Thus, by optimizing the intensity of the optical signal it is also possible to measure the resonance frequencies of the whole system.

Another remarkable result of this investigation was the fact, that the reference frequency was reproduced without doubling. A double frequency was expected, because the birefringence can not distinguish between maximum and minimum of the acoustic wave. They both would produce a maximum elongation of the waveguiding film and a minimum of the birefringence signal will correspond to a crossing zero of the acoustic signal.
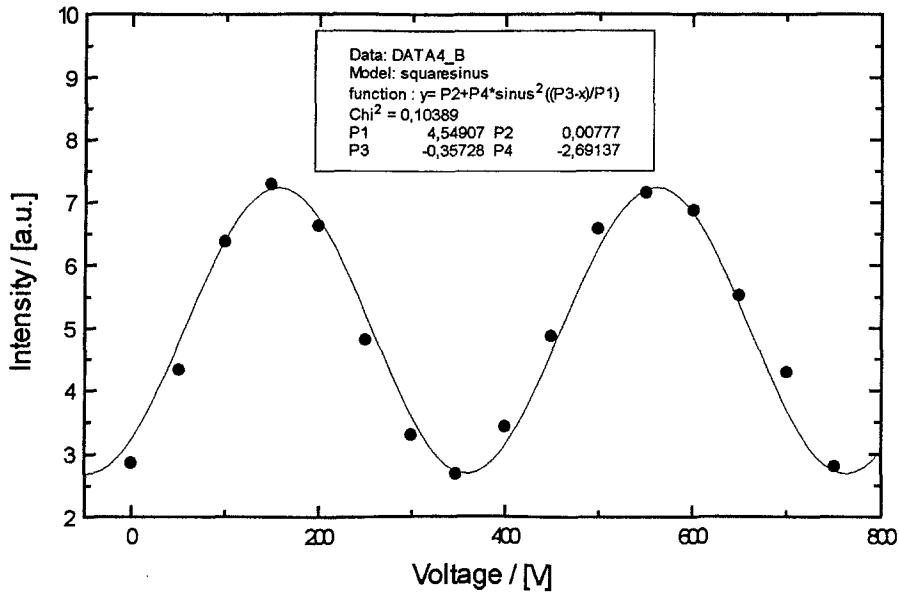
Fig. 9. Typical result of a static experiment: change of intensity due to a phase shift of a PDATP waveguide in dependence of applied voltage
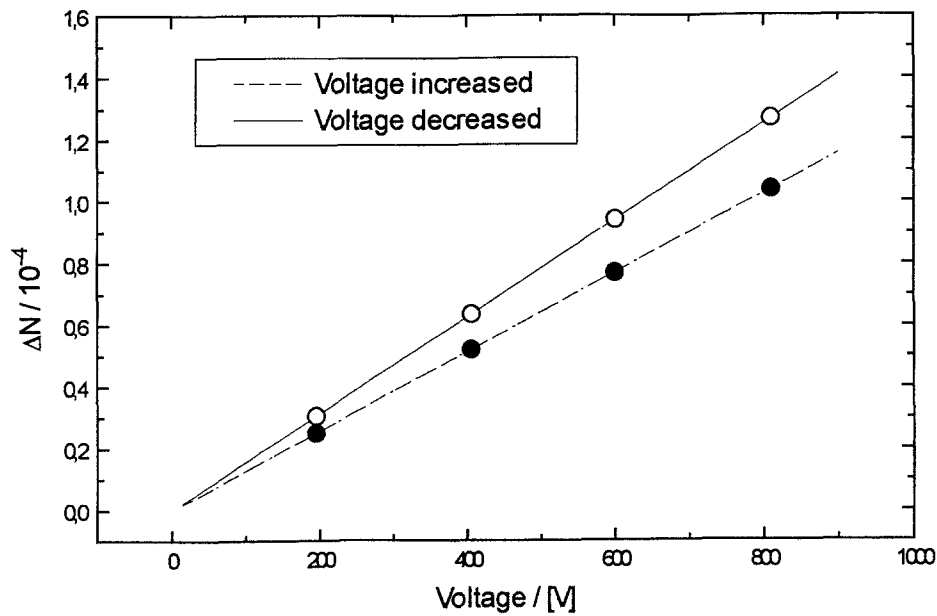


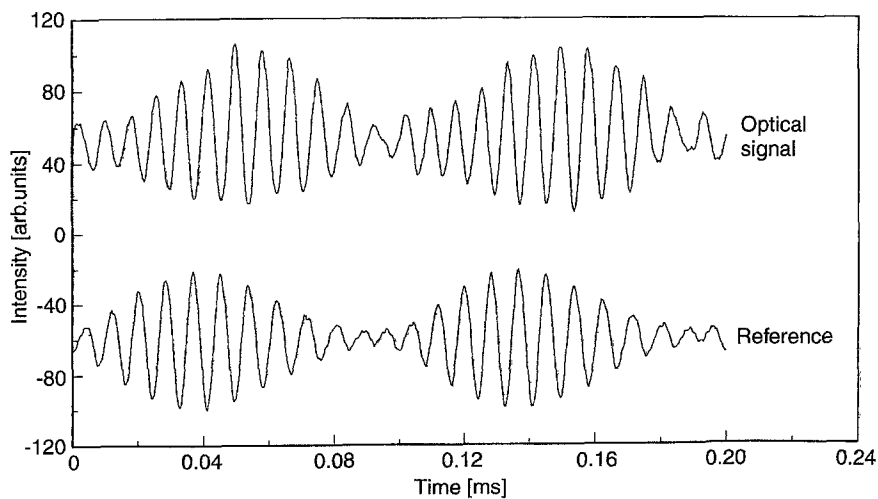Fig. 10. Result of static experiments: phase shift vs applied voltage



Fig. 11. Optical signal compared to stimulating signal ('reference'), 10 kHz am frequency, 120 kHz carrier frequency
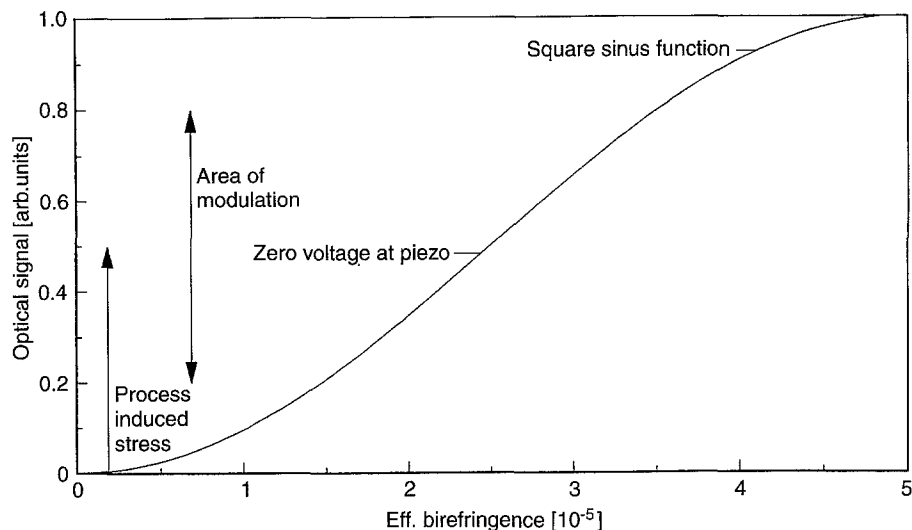
Fig. 12. Sketch of the modulator principle

On the other hand, if there is a stress offset introduced, the situation is as sketched in Fig. 12. The birefringence offset induced by this stress is of the order of $10^{-5}$. Thus it is not possible to be detected by the index and thickness measurements of $m$-line spectroscopy. Such small stresses hardly can be avoided when polymer materials are processed by spincoating to thin films [10].

In this case, and provided the stress (birefringence) induced by the piezo is not larger than the offset, there will be only a single frequency. This happens because the elongation of the film never produces enough birefringence to reach the isotropic state.

## 3. Conclusions

In this paper we have demonstrated two different applications in integrated optics for highly stress sensible polymeric films.

The mechanical stress due to in-diffusing molecules was used to develop an optical sensor for chemical compounds in the gaseous phase. The sensoring was demonstrated with water and simple alcohols in air. The possibility of varying the thickness of the films allows to design sensors for various applications and to optimize them for certain properties, e.g. for selectivity or high resolution.

The influence of diffusion profiles was demonstrated and a simple model was developed to explain different results for different modes of the waveguide.

The second possible application we realized, was phase shifting in the waveguide. Using a piezo crystal, a special setup of the waveguide gave the capability to

shift the phase of the guided light to any desired value by applying voltages of about 350 volts, the voltage needed to shift the phase by $\pi$ is $V_\pi = 180$ V.

At last, we demonstrated dynamical phase shifting, that is modulation. We observed a strong dependence on resonance frequencies of the system. Using these resonance frequencies it was possible to modulate the light up to frequencies of 180 kHz.

## References

1. M.J. Breckner in K.L. Mittal (ed.): *Polymers in Information Storage Technology* (Plenum Press, New York 1989), p. 199
2. H.J. Lorkowski, K. Pfeiffer: Plaste und Kautschuk: **22**, 945 (1975)
3. M. Biebricher, P. Schulz, H. Franke: Proc. SPIE **2349**, 211 (1994)
4. H. Franke, D. Wagner, T. Kleckers, R. Reuter, H.V. Rohitkumar, B.A. Blech: Appl. Opt. **32**, 2927 (1993)
5. R.P. Podgorsek, H. Franke: Sensors & Actuators B: Chemical **30**, 201 (1996)
6. M. Biebricher, M. Osterfeld, H. Franke, W. Lins, P. Bajons, K. Pfeiffer, H.J. Lorkowski: Proc. SPIE **2042**, 499 (1993)
7. Ferroperm Inc., DK, Product information
8. W. Jost, K. Hauffe: *Diffusion, Methoden zur Messung und Auswertung*, 2.ed., (Dr. Dietrich Steinkopf-Verlag, Darmstadt, Germany 1979) pp. 27–31
9. W. Wunderlich in: J Brandrup, E. Immergut (ed.): *Polymer Handbook*, 3.ed, (J. Wiley & Sons, New York, Chichester, Brisbane, Toronto, Singapore 1989) p. V/79
10. W.M. Prest Jr., D.J. Luca: J. Appl. Phys. **50**, 6067 (1979)