

Strong electro-optic effect in electrically poled photoaddressable polymers

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Electrically poled photoaddressable polymers, originally designed for optical data storage, are investigated in an interferometric setup. After optimization of the corona poling conditions, we obtain Pockels coefficients r_{33} of 44 pm/V at 1555 nm. Even at nonoptimum temperatures, the material can be electrically poled quite efficiently using light to trigger *trans*-*cis* isomerization cycles. At room temperature, the degree of poling is stable over months. At elevated temperatures, after a fast initial decay, again stable or very slowly decaying electro-optic coefficients are observed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1616640]

I. INTRODUCTION

The use of suitable polymers for optical applications such as second-harmonic generation and electro-optic modulation has been studied intensely since the 1980's. Chromophores with large hyperpolarizabilities are developed, efficient poling procedures are introduced, and waveguides for polymeric integrated optics are fabricated.¹⁻³ These days, this field of research is of special importance due to fundamental bandwidth limitations of electro-optical modulators that are based on crystalline materials.⁴ Polymeric waveguides showing strong, long-term stable electro-optic effects have reached a quality that made commercial products possible.⁵ However, there is still a great demand for highly optimized materials that combine strong electro-optic effects with sufficient temporal and thermal stability. With polymers that additionally exhibit further useful properties, e.g., photorefraction, even more advanced devices could be realized.

Side-chain polymers based on azobenzene chromophores are known as photoaddressable polymers (PAPs) because they show a light-induced birefringence that is of interest for optical data storage.^{6,7} They have been optimized to give large and stable Δn values that are fully reversible, i.e., illumination with unpolarized light brings them back to an optically isotropic state.⁸ The molecular effect responsible for the large refractive-index changes is known: It is the cooperative reorientation and alignment of side chains triggered by *trans*-*cis*-*trans* transitions of azobenzene molecules after the absorption of polarized light of the appropriate wavelength. This effect, reported by Hartley in 1937,⁹ was intensely studied.¹⁰⁻¹²

Many chromophores of PAPs are highly polar, e.g., the chromophore shown in Fig. 1(a) has a large dipole moment of 7 D, evaluated by quantum chemical simulations. Furthermore, it shows a large Hyperpolarizability of $\beta_0 = 580 \times 10^{-30}$ esu, measured with the Hyper-Rayleigh scattering technique,¹³ so one can expect strong electro-optic effects.

Because the Pockels effect requires the breaking of the inversion symmetry of the material, a suitable poling process is necessary. As we have shown before,¹⁴ it is possible to electrically pole thin films of this material at temperatures near the glass transition. Due to the large molecular volume of the diazo chromophore, we expect our polymers to show excellent thermal and temporal stability,¹⁵ even without a crosslinking procedure after the poling process.

In this article, we present experiments on the magnitude of the electro-optic response of PAPs and its dependence on chromophore content. Because of the *trans*-*cis* isomerization of the chromophores under illumination we also try light-assisted electrical poling (also known as laser-induced or photoelectric poling), which has been investigated, e.g., by Sekkat *et al.*¹⁶ Finally, we show the relaxation behavior of the electro-optic coefficient during long-term storage at room temperature and at elevated temperatures since a long lifetime of the poling is one of the most important requirements for commercial electro-optic device applications.

II. EXPERIMENTS

The polymers under investigation are a homopolymer and five copolymers. The chemical structures are shown in Fig. 1. The homopolymer consists to 100% of unit (a), the copolymers are statistically built up by the two monomer units (a) and (b). Copolymers with different amounts of unit (a), that is functionalized with a side-chain chromophore, were prepared. The materials are solved in tetrahydrofuran, filtered, and spincoated onto a glass substrate that is coated with an indium-tin oxide (ITO) electrode. The resulting polymer film is dried in a vacuum oven at 80 °C for several hours. All materials are in an amorphous state and form films with excellent optical quality. Typical film thicknesses are 0.5–1 μm .

The poling procedure involves the heating of the sample above the glass temperature, waiting for approximately 30 min, and subsequent cooling to room temperature (cooling rate about 10 °C/min.). During the whole process, an external electric field is provided by applying a voltage of

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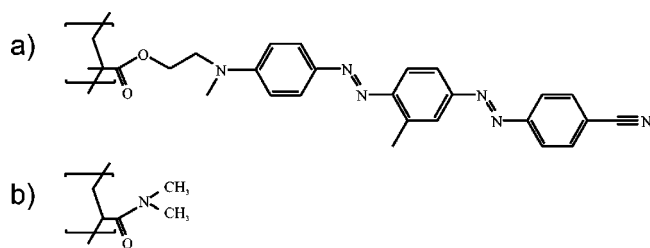


FIG. 1. Chemical structure of the investigated polymers. (a) Monomer unit functionalized with chromophore and (b) without chromophore.

+ 5 kV to a corona tip fixed 7 mm above the polymer surface, while the ITO electrode on the glass substrate is grounded.¹⁷ By this, fields can be applied that approach the breakdown threshold (in our case, about 100 V/ μm).¹⁸ Additionally, the entire sample can be illuminated during poling by light from a frequency-doubled Nd:YVO₄ laser at 532 nm. This wavelength is resonant to the *trans*–*cis* isomerization transition. After poling, a 80–100 nm gold film is sputtered on top of the polymer as the second electrode.

For measurement of the electro-optic effect, we use an interferometric setup like the one introduced by Norwood *et al.*:¹⁹ The sample is mounted at an angle of 45° as one mirror in a Mach-Zehnder interferometer. In this position, the laser beam propagates through the glass substrate, the ITO electrode, and the polymer, and is finally reflected at the gold electrode. If a voltage is applied to the sample, the electro-optic effect generates a phase retardation, which results in a small change of the interferometric signal. Even for very thin or weakly poled samples, this change can be easily detected using an ac voltage (frequency ~40 kHz) and lock-in detection. The lock-in signal varies strongly, depending on the overall phase shift between the interferometer arms. Thus, we generate an additional phase shift by piezoelectrically moving the mirror in the reference arm, yielding a slow (~1 Hz) movement of the interference fringes. At any given point in the interference pattern, we now detect sinusoidally varying signals, both for intensity and lock-in output. From the ratio of the amplitude of the lock-in signal I_{sig} to the amplitude of the moving interference pattern I_r , one can calculate the electro-optic phase shift and thus the Pockels coefficient. This method has the advantage that very thin films can be studied, even if the surface quality is not perfect. Also, different disturbances, like electrochromic effects, piezoelectricity, and even electromagnetic noise pickup, can be separated clearly.

For the interpretation of such measurements, one has to consider the phase shift $\Delta\phi$ due to a change of refractive index Δn (like shown by Norwood *et al.*),¹⁹ and also the phaseshift due to the change of the path length Δs inside the polymer, because Δn affects the propagation angle via Snell's law:

$$\Delta\phi = \frac{2\pi}{\lambda} \Delta(ns) = \frac{2\pi}{\lambda} (\Delta ns + n\Delta s). \quad (1)$$

Snell's law states that for the path length depending on the sample thickness d (with α and θ being the angle of incidence outside and inside the material, respectively):

$$s = \frac{2d}{\cos\theta} = \frac{2d}{\cos\left(\arcsin\frac{\sin\alpha}{n}\right)}. \quad (2)$$

The derivative is

$$\frac{ds}{dn} = -\frac{2d}{\cos\theta} \frac{\tan^2\theta}{n}, \quad (3)$$

and gives a phase shift

$$\Delta\phi = \frac{2\pi}{\lambda} s \Delta n (1 - \tan^2\theta). \quad (4)$$

Considering this, we get the following solution for $n^3 r$:

$$n^3 r = \frac{\lambda I_{\text{sig}}}{\pi V_{\sim} I_r} \frac{\cos\theta}{2} \frac{1}{(1 - \tan^2\theta)}, \quad (5)$$

with the amplitude V_{\sim} of the applied alternating voltage.¹⁹ Here n and r are the refractive index and Pockels coefficient for the chosen light polarization.

In principle, r_{13} and r_{33} can be determined independently in the following way. First, one measures r_{13} directly by choosing s -polarized light. Then, a superposition of r_{13} and r_{33} is obtained by using light that is p polarized with regard to the plane of incidence. With known refractive indices of both directions, one can calculate r_{33} from these measurements. However, care has to be taken because an accurate knowledge of the, sometimes poling induced, sample birefringence is necessary for this calculation, and small measurement errors have a huge impact on the resulting r_{33} .

For this reason, we concentrate on the measurement of r_{13} , keeping in mind that the tensor ratio $r_{33}:r_{13}$ is found to be 3:1 (as predicted by the oriented gas model)²⁰ or even larger in most of the literature. We also decided to make most measurements with a diode laser at a wavelength of 685 nm since this is far enough from the resonance (maximum around 490 nm) but still visible and hence convenient to handle. To measure coefficients in the technologically important wavelength region around 1550 nm, we use light from a standard telecom laser in the same setup. It has turned out that for infrared measurements, special samples on very thin ITO electrodes have to be prepared to minimize errors due to the high reflectivity of ITO in this wavelength region. For the calculation of the Pockels coefficients, we use refractive indices of 1.7 for the visible and 1.6 for the infrared measurements. These indices were determined by prism coupling measurements of poled samples.

Piezoelectric or electrostrictive contributions to the obtained coefficients, which may lead to systematic errors, can be easily measured in this setup. Turning the sample by 180° and looking at the interferometric signal for light reflected at the gold electrode directly gives the electric-field-induced expansion of the sample. However, even in well-poled samples, we find that possible systematic faults in the determination of the r values are less than 2 pm/V and hence can be neglected for the electro-optic measurements.

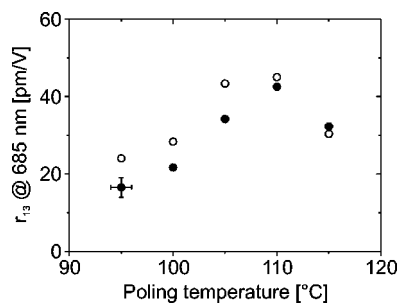


FIG. 2. Optimization of the poling temperature for the 88 wt % functionalized copolymer (glass temperature 100 °C). Data points represent Pockels coefficients r_{13} at 685 nm for samples poled in darkness (filled circles) and samples poled after green illumination with 100 mW/cm² for 5 min (open circles).

III. RESULTS

The homopolymer and copolymers with five different values of the chromophore content are synthesized and samples are prepared and poled as described above. The optimum poling temperature is determined experimentally for each material. As an example, Fig. 2 shows a typical behavior. Below a certain temperature, no efficient poling is possible. For high temperatures, the poling performance is also reduced. Here, the polymer surface becomes badly damaged by the corona discharge, even when poled in a dust-free nitrogen atmosphere. Thus, for optimum poling results, the right temperature must be picked with an accuracy of about ± 5 °C. The optimum poling temperature is 2–15 °C above the glass transition temperature T_G as it is determined by differential scanning calorimetry measurements (see Table I). However, the differences between T_G and the optimum poling temperature show no obvious systematics. Thus, it is indeed necessary to obtain the best poling temperature for each composition experimentally.

The influence of near-resonant light on the poling process is investigated as well. Below the optimum poling temperature, a 5 min exposure with 100 mW/cm² circularly polarized 532 nm light at the beginning of the poling can increase the electro-optic coefficients (“light-assisted poling”). However, longer exposures and higher light intensities lower the coefficients. The electro-optic coefficients achieved with light-assisted poling never significantly exceed those obtained by pure corona poling at optimized temperature.

TABLE I. Optimum poling temperatures for different amounts of chromophore content.

Chromophore content (wt %)	Glass temperature (°C)	Optimum poling temperature (°C)	Temperature difference (°C)
54	101	106	5
67	104	114	10
76	120	122	2
79	98	113	15
88	100	110	10
100	94	102	8

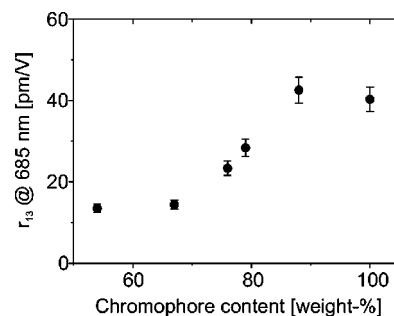


FIG. 3. Optimized Pockels coefficients r_{13} at 685 nm for different chromophore concentrations.

After tailoring the poling conditions for each material, we can plot the optimum Pockels coefficients as shown in Fig. 3. Up to 42.5 pm/V were achieved for the coefficient r_{13} at the laser wavelength 685 nm. The coefficients become larger with higher chromophore content, however, for the homopolymer (100%), a saturation is obvious.

Several samples are prepared for measurements in the infrared. Three samples that exhibit r_{13} values between 35 and 42.5 pm/V at the wavelength 685 nm are studied in the interferometric setup with infrared light at 1555 nm. We find reduction factors between 2.7 and 3.2 when moving from 685 nm to 1555 nm, with an average of 2.9. The highest r_{13} value measured at 1555 nm is 14.8 pm/V.

For the investigation of the poling stability, poled samples of the 100% functionalized homopolymer with r_{13} coefficients of about 30 pm/V at 685 nm have been stored for more than 150 days at different temperatures. The Pockels coefficients have been measured at regular intervals (Fig. 4). At 40 °C, no decay of the measured coefficients is found. At higher temperatures after a fast initial degradation, we observe a much slower relaxation or even a stabilization. About 70% of the original r_{13} value is maintained. However, heating to temperatures near the glass transition destroys the poling quite quickly.

IV. DISCUSSION AND CONCLUSIONS

The observed dependence of the electro-optic response of PAPs on poling temperature agrees well with literature data for other polymers.⁵ It is also already known that poling of azobenzene chromophores below the glass temperature is possible if the sample is illuminated.¹⁶ However, we have not

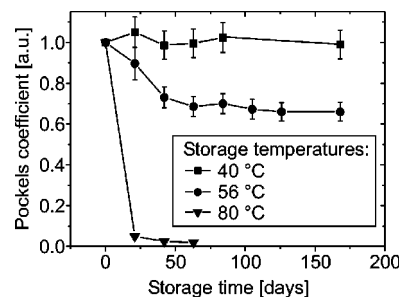


FIG. 4. Long-term stability of poled homopolymer samples at different temperatures. The glass transition temperature of this material is 94 °C.

observed a light-assisted poling that yields better r_{13} values than the optimized poling conditions without light. This indicates that the thermodynamic limit for chromophore orientation known from the oriented gas model,²⁰ is valid also for light-assisted poling. Nevertheless, with light-assisted poling, high electro-optic coefficients can be reached at lower temperatures. Also, the poling can be spatially varied quite conveniently using illumination, e.g., to create periodically poled polymers with the help of a light interference pattern.

The electro-optic coefficients increase with chromophore content up to 88 wt% (Fig. 3). For the 100% functionalized homopolymer, the coefficient is at the same level as for the 88% copolymer, presumably as a consequence of dipole–dipole interactions that hinder better unidirectional chromophore alignment.²

We find a ratio between the Pockels coefficients at 685 nm and 1555 nm of about 2.9:1, which is a realistic value considering that the Pockels effect is still very much resonance enhanced at 685 nm. Since the ratio is a property of the chromophore itself, it should be independent of the chromophore concentration. We get values of $r_{13} = 14.6$ pm/V and 13.9 pm/V for the 88% and 100% chromophores, respectively. Assuming a ratio of $r_{33}/r_{13} = 3:1$, we obtain r_{33} values of 44 pm/V and 42 pm/V at 1555 nm. To our knowledge these are the highest electro-optic coefficients for chromophores that show *trans–cis* isomerization reported so far.

The large electro-optic coefficients at 1555 nm make the material potentially interesting for integrated-optical applications, provided that the poling is stable over large time scales. As seen in Fig. 4, the poling stability at room temperature is excellent; at elevated temperatures, it is not yet sufficient. However, the samples have not been optimized for stability so far. We are confident that slower cooling rates during poling will improve stability to some degree. An increased molecular weight, or incorporation of the functional groups into different polymer hosts, will lead to higher glass temperatures and thus better stability.

An important aspect is that PAPs show other beneficial effects such as photorefraction (light-induced reorientation of chromophores leads to a change in birefringence). Thus, stripe waveguides may be written directly into planar films

by focused light beams, and waveguide electro-optic modulators can be made without much further processing. Another example is to record Bragg gratings holographically. The electro-optic effect then allows one to electrically tune the center wavelength of such a Bragg filter.

The high values of the Pockels coefficients for this material class, together with promising lifetime data and additional properties such as photorefraction, show that PAPs can be the enabling material for many advanced electro-optic devices.

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