A pyroelectric liquid crystal polymer (PLCP) for second-harmonic generation

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In order for a material to show a non-vanishing second order non-linear susceptibility, the material has to have a polar axis. This is hard to achieve in a liquid crystal system because of the strong quadrupolar order along the director. Electrostatic poling of polymers and polymer liquid crystals at high temperature and subsequent quenching to lower temperature only gives a small value of the polar order parameter and, in addition, results in materials which are not in thermodynamic equilibrium and therefore not stable over long times. Starting with a ferroelectric liquid crystal (which has polar order perpendicular to the director) we have succeeded in making a material with true polar order. It is not ferroelectric, although the ferroelectric properties of the starting and intermediate materials are basic for the procedure and for the final product which can be used for frequency doubling, of importance, for instance, in a wide area of optic communication applications.

1. Introduction

During the last decade the interest in organic materials for non-linear optics (NLO) has been constantly growing. This is due to several factors. First of all the polarization response to an externally applied field is of molecular-electronic origin and therefore practically lossless and extremely rapid. The potential of ultra-fast components for use in telecommunication technology is obvious. Furthermore, organic materials may have very high values of molecular NLO susceptibilities, but this can be used only if the material also has very high polar order. Organic single crystals offer this, but are expensive to grow. Polymer films normally have very low polar order (which may not even be stable in time), but are attractive because they are cheap, flexible and easily processable mechanically. There is thus a large interest in developing methods of increasing the polar order parameter in such polymers. As liquid crystals and liquid crystal polymers generally are characterized by intrinsic order, the recent interest has in particular been focused on these systems.

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2. The problem with liquid crystalline order

Liquid crystal molecules superficially seem to be ideal NLO materials because donor and acceptor groups may easily be attached to either end of long conjugated spacer groups (see figure 1 (a)). In the reference frame of the molecule, the induced polarization can be written

$$P_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \dots \qquad (1)$$

where α, β and γ are polarizability, hyperpolarizability and second hyperpolarizability, respectively. For a macroscopic material, we write instead, in the laboratory system (and with new meaning of ijk)

$$P_i = \chi^{(1)}_{ij}E_j + \chi^{(2)}_{ijk}E_jE_k + \chi^{(3)}_{ijkl}E_jE_kE_l + \dots \qquad (2)$$

where $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ are the first, second and third order susceptibility. Our interest is in the second order susceptibility which, in simplifying terms, can be expressed by

$$\chi^{(2)} = N\langle\beta\rangle \qquad (3)$$

where N is the number of molecules per unit volume and $\langle\beta\rangle$ is the average value of the hyperpolarizability with respect to both degree of order and local field effects. A value $\chi^{(2)} \neq 0$ is a requirement for second-harmonic generation in the material, but even if molec-

ules of the kind shown in figure 1 (*a*) have large values $\beta \neq 0$ along their axis, once they are in a nematic or smectic liquid crystal phase, $\chi^{(2)} = 0$, because β is averaged out along the director, in fact, as efficiently as if the material were completely disordered (isotropic). This is because liquid crystals are non-polar materials. They have the wrong kind of internal order, quadrupolar instead of dipolar, to be suitable as NLO materials.

In order to achieve $\langle \beta \rangle \neq 0$, the old method of producing electrets has been used, consisting in poling in an electric corona discharge at high temperature and freezing in (the very small) polar order by lowering the temperature below the glass temperature T_g in the presence of the field. Liquid crystalline polymers are, however, hardly any better than other polymers in this respect, and besides the low polar order parameter, they share the other important disadvantage of being out-of-equilibrium systems, i.e. not thermodynamically stable. Their weak NLO properties may therefore deteriorate even further with time.

3. Ferroelectric liquid crystals

Along the director, the liquid crystalline order is strictly non-polar, but there is an exception to what has been said above, in as much as polar liquid crystals do exist. These are the so-called ferroelectric and antiferroelectric liquid crystals in which an appreciable polar order can exist or be induced perpendicular to the director. In the surface-stabilized ferroelectric S_C^* state there is a macroscopic (bulk) polarization $P \perp n$. In the helicoidal S_C^* state or in the antiferroelectric state, an external field E, above a certain value, is required in order to achieve a homogenous macroscopic polarization. Along this axis $\langle \beta \rangle \neq 0$ and a light wave with a field E vibrating parallel to this direction will give rise to a wave with twice the incoming frequency. Early experiments on ferroelectric liquid crystals confirmed
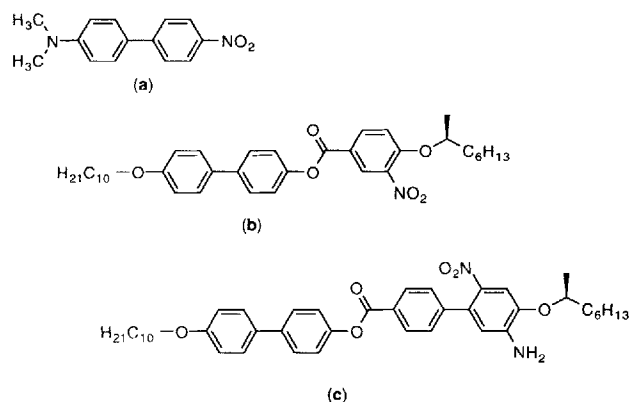
this even if the effect turned out to be extremely small [1-4]. This is not too difficult to understand: the polar order perpendicular to the director is a guarantee that $\langle \beta \rangle \neq 0$ parallel to this direction, but does not guarantee a particularly large polarizability.

Walba *et al.* [5, 6], were the first to realize this and thereby attached donor and acceptor groups across the molecule, starting with an acceptor NO_2 (a facing hydrogen will then serve as donor), cf. figure 1 (*b*). Later they included a special donor, NH_2, as well, cf. figure 1 (*c*). These were the first specially designed NLO structures with large polarizabilities in a direction which can be lined up by an external electric field. In the best case (the mixture MX 5679), the measured NLO susceptibility practically matched that of KDP. An application for such a material is in an electro-optically active waveguide, as shown in figure 2. The optic axis is homogeneously lined up by an electric field applied between the ITO-coated inner sides of the covering glass plates. The requirements for such a device would be low optical damping (freedom of absorption and scattering) and high thermal and mechanical stability, in addition to the desired high value of the polar order parameter and NLO susceptibility $\chi^{(2)}$. The high thermal and mechanical stability can hardly be achieved by using a monomeric liquid crystal. Moreover, the most attractive component would be passive, i.e. without any need of an applied electric field in order to frequency-double the incoming light. This can only be achieved by polymerizing the structure. The idea is, however, not just to make a ferroelectric liquid crystal polymer (FLCP), but to block the optic axis and its perpendicular polarization in one fixed position, which has to be done by UV polymerizing the structure in the presence of the applied electric field. It makes no difference whether the starting material is ferroelectric or antiferroelectric: the final state should be pyroelectric, i.e. with a macroscopic uniform polarization which is not switchable but fixed in space.

(a)

(b)

(c)

Figure 1.   Molecules   in   which   the   hyperpolarizability cannot (*a*) or can (*b, c*) be lined up along a polar direction in a liquid crystalline phase.
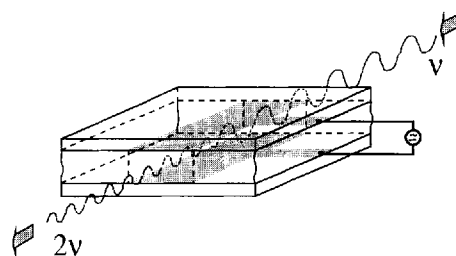

Figure 2.   Electro-optically active wave guide using a ferroelectric liquid crystal with the polar axis lined up by an electric field. The light interacts with the polarizable π-electrons.

4. The pyroelectric liquid crystal polymer (PLCP)

The advantages with the pyroelectric polymer state are obvious. The material has a uniform optic axis. It is stable thermodynamically and is not in a metastable state. The thermal (250 or 300°C is normally required in industrial applications) and mechanical stability can be assured. It can be polymerized in a sufficiently thick sample (5–100 μm) to be detached from the glass plates, as no electrodes are necessary anyway, since the polar axis has been rigidly blocked. Two non-trivial difficulties can, however, be foreseen in producing the pyroelectric polymer. One is that even if the monomer state is a tilted smectic, the phase stability will be affected by the polymerization leading to an orthogonal, and therefore non-polar polymer smectic. The second is the difficulty of performing the polymerization in such a way that the end product is a homogeneous, non-scattering material of optical quality.

Ideally, the starting material should have a wide and stable smectic C range, be provided with donor and acceptor side groups and at least one chiral end group, as well as having a reactive, polarizable end group separated from the core by a spacer. It is not easy to include all this in a single substance. Our first attempts were therefore made using one monofunctional monomer responsible for the final polar properties, mixed with a bifunctional monomer responsible for crosslinking. The effect of only partial and not complete crosslinking can be seen (exaggerated) in figure 3. Still, the crosslinking turned out to be sufficient, by excluded volume effects, to prevent motion of the optic axis even at relatively high temperature.

The starting structures **1** (chiral polar monomer) and **2** (crosslinking bifunctional monomer) shown in figure 4 were first synthesized and mixed to give a composition showing the smectic C* phase. The *in situ* UV polymerization has the advantage that it can be performed at any chosen temperature. With the chosen substances, there was a clear tendency for an orthogonal phase to be created at low temperature. At a concentration ratio of
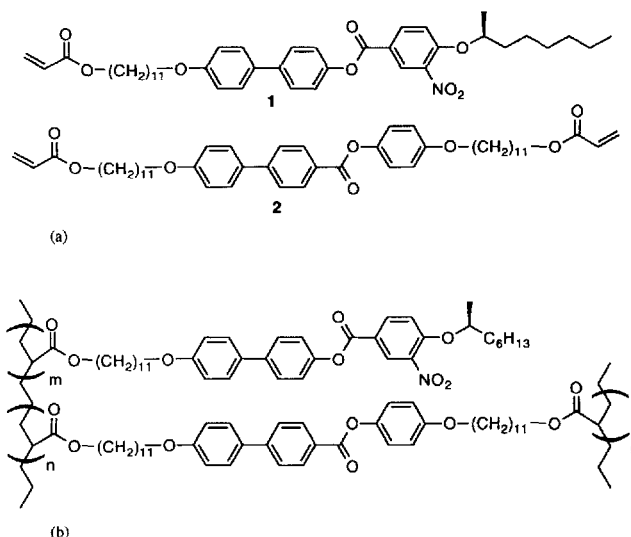
Figure 4. Structures 1 and 2 used (*a*) in the ratio 30:70 for making the PLCP (*b*).

30:70 for active (**1**) relative to crosslinking structure (**2**), the polymerization temperature had to be raised to 70°C in order for the C* phase to be preserved. This led necessarily to a very small tilt angle in the final PLCP, reducing the otherwise achievable value of $\chi^{(2)}$.

5. Experimental

Cells of conventional sandwich type, consisting of two parallel glass substrates, separated at a constant distance (2 or 4 μm) by evaporated SiO_x spacers, were used. The substrates were prepared from ITO coated glass sheets (Balzers Baltracon) on which an electrode pattern was formed. An insulating layer of SiO_x of about 1000 Å thickness was deposited onto the electrodes. The uniform book-shelf alignment of the liquid crystal material (smectic layers being essentially perpendicular to the substrates) in the cell was achieved by shearing the upper glass plate with respect to the lower, or by depositing a thin polyimide aligning layer on top of the isolating film and rubbing unidirectionally. The liquid crystal material was introduced into the cell in the smectic A* or in the isotropic phase by depositing the material on the lower glass plate near its electrode, and then placing the upper glass plate on top and assembling the cell; by capillary forces, the cell was now filled homogeneously and rapidly, sufficient in order to avoid the thermal excitation of the photoinitiator which would result in polymerization. The cell was inserted into a Mettler FP 52 hot stage controlling the temperature to within 0·1 K and investigated by polarizing microscopy. In order to avoid the undesired photopolymerization (by photoexcitation of the photoinitiator) of the liquid crystal material in the cell during the preparation procedures and investi-
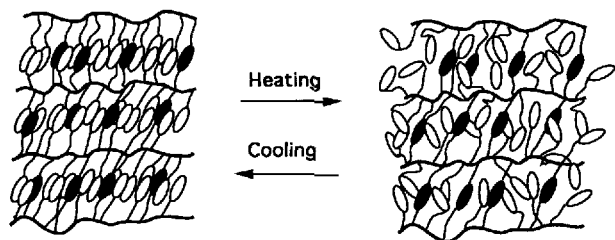
Figure 3. The effect of only partial crosslinking of a side chain polymer during heating and cooling. The mesogenic groups have a smectic C type organization. The shaded ovals represent crosslinked sites, which preserve the smectic C organization at high temperatures.

gations, yellow light was used. The cell was slowly cooled from the A* to the C* phase, thus preserving the uniform alignment achieved in the A* phase. A well-pronounced electroclinic and ferroelectric response was detected in the A* and C* phases, respectively. The electro-optic response of the cell indicated the temperature at which the ferroelectric electro-optic response in the C* phase was fully developed. At this temperature ($\approx 95°$C for the ratio 30:70 (1:2) and 92°C for 35:65 (1:2)), a d.c. electric field was applied in order to orient the spontaneous polarization in the whole cell in one direction. This gives in the bookshelf geometry a unique direction of the optic axis, tilted with respect to the layer normal, and resulting in a ferroelectric mono-domain. By rotating the turntable of the microscope, full extinction of the transmitted light could be achieved when the optic axis was either parallel or perpendicular to the transmission direction of the polarizer.

After obtaining the ferroelectric mono-domain, the cell was illuminated with UV light for about 15 min (in most cases keeping the d.c. field on) during which time the liquid crystal mixture polymerized. The texture changed slightly during the illumination. For the 4 µm cells, the birefringence colour changed from green to blue and the initial uniform bookshelf texture was disturbed by stripes oriented perpendicular to the smectic layers. The cells were studied by video camera and monitor during the UV exposure, and it seems that most of the changes in texture occurred during the first two minutes of the exposure. Rotation of the turntable after polymerization gave the lowest value of transmitted light intensity for a position corresponding to a residual tilt of the optic axis of about 15 to 20 degrees.

The polymerized material in the cells did not exhibit any ferroelectric response. Because of the absence of ferroelectric switching, we may suppose that the uniform molecular tilt in the smectic C* phase was fixed during the polymerization and thus the macroscopic polarization of the sample (in a direction perpendicular to the cell glass plates) was also fixed. The polymer network formed is temperature stable: on increasing the temperature well above the A*–isotropic phase transition pertaining to the non-polymerized liquid crystal material, the molecular tilt in the network does not change at all.

6. Measurements

Two types of experiment were performed in order to check for the presence of a second-order optical nonlinearity in the polymerized sample cells: Pockels measurement, and second-harmonic generation measurement.

The Pockels measurement was carried out in a standard set-up with a HeNe laser, polarizer, sample, Soleil–Babinet compensator, analyser and detector. The polar-

izers are crossed, and the intensity modulation δI through the set-up arising when an electric field is applied on the cell is measured as a function of the field strength. With an appropriate setting of the Soleil–Babinet compensator, δI becomes proportional to the change in phase shift, $\delta I \sim \delta\phi$, which in turn is proportional to the electric field strength. In figure 5, $\delta I/I$ is plotted as a function of electric field, and is found to be linear, as expected. I is the intensity transmitted through the set-up when $E = 0$. The linearity in figure 5 can, however, also arise from a motion of the optic axis that is linear in the electric field. This may arise if the chiral units (1) have not been frozen in completely by the polymer network. Therefore, it is necessary to check explicitly the origin of the result in figure 5.

For the second-harmonic generation measurement, the sample was mounted on a stage which could be rotated by means of a step motor so that the angle of incidence could be varied. The angle of incidence was
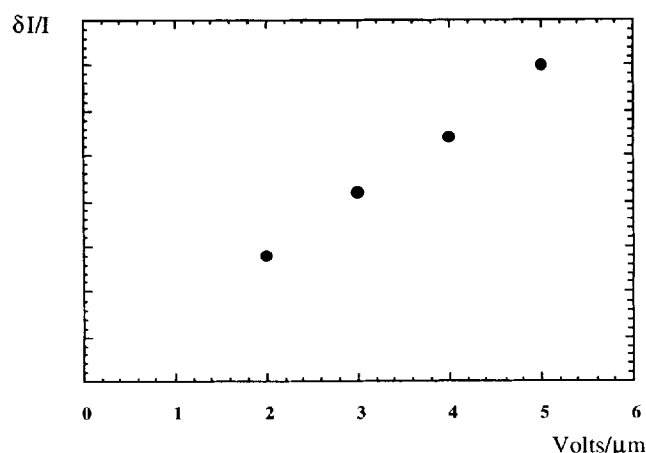

Figure 5.   Measurement of the electro-optic modulation in a set-up for Pockels measurements.
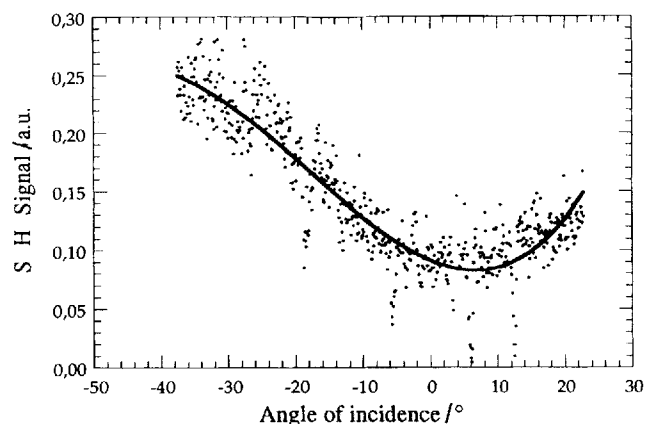

Figure 6.   Measurement of the second-harmonic signal for sample A (see text) as a function of the angle of incidence.

the angle between the beam direction and the normal to the cell glass plates; these directions define the plane of incidence. The SHG experiment was performed with a Q-switched Nd:YAG laser operating at 1064 nm wavelength, with a pulse width of about 7 ns and at a 10 Hz repetition rate. The incoming beam was linearly polarized in the plane of incidence, and was tightly focused onto the sample. The SH signal (532 nm) was separated from the fundamental beam by an edge filter placed after the sample and transmitting only wavelengths < 700 nm, and detected by a photomultiplier. It was also explicitly checked that there was no contribution to the detected signal from the fundamental beam.

Three different polymer samples were tested for SHG, and two monomeric (i.e. non-polymerized) samples were also checked for SHG for comparison. These results are presented in tables 1 and 2.

The SH signal from sample A is presented in figure 6 as a function of the angle of incidence. Due to the planar (bookshelf) geometry of the samples, the signal goes to a minimum at normal incidence. The orientation of this particular sample was achieved by shearing the monomer mixture in the S_A^* phase, and the glass plates had no rubbed polyimide layer in this case. In all other cases, the glass plates were treated with rubbed polyimide (RPI). Also in sample B an SH signal, though weaker, was detected. The fixed tilt angle remaining after the polymerization of this sample was lower than in samples A and C. Before polymerization of sample B the ferroelectric states were quite stable, so this was polymerized without the simultaneous application of a d.c. field. In sample C the SH signal was of the same magnitude as in sample A.

The monomer samples were heated to about 85°C, and a d.c. bias field was applied in order to select and hold one of the ferroelectric states. The quality of sample D was very bad, which ought to be the reason for the weak SH signal. For sample E, the concentration of the chiral end group has been increased slightly. The

SH signal was of the same magnitude as, or slightly greater than, that of samples A and C.

The SH signal was compared to that of a quartz reference at the corresponding angle of incidence, and was about 1000 times weaker. Considering the small thickness of our test cells, and the quadratic dependence of the SH signal on the cell thickness up to the coherence length of the laser beam, our material should have NLO d-coefficients (essentially $\chi^{(2)}$ values) of the same order of magnitude as those of quartz (i.e. in the range of 0.4 pm V^{-1}).

7. Work in progress

Although the results have confirmed the correctness of the ideas, much can be done to ameliorate the performance of the PLCPs. To increase the $\chi^{(2)}$ values, both or all structural ingredients should be active, double-sided, chiral and bifunctional. The starting molecules should also have longer conjugated parts with very high tilt angles in the C* phase. Antiferroelectric structures are the most promising from this point of view; this is also the case because they have very high P values and are easy to bring into a quasi-bookshelf (QBS) structure with moderate fields. A very high polar order parameter should be achievable in these materials. In the long term, an interesting possibility would be to increase $\chi^{(2)}$ by crosslinking between nearest neighbour couples in such a way that the conjugation distance across the molecules could be essentially doubled.

Table 1. Polymer samples for SHG, with the ratio 30:70 (1:2). Cell thickness: 4 μm

Sample	Orientation by	Polymerization	Fixed tilt angle	SH signal
A	Shearing	with d.c.	17–20°	+ +
B	RPI	w/o d.c.	~12°	+
C	RPI	with d.c.	19–20°	+ +

Table 2. Monomer samples for SHG, at ~85°C with a d.c. bias field of ~15 V

Sample	(1:2) ratio	Cell thickness	P_s at $T - T_C = 10$ K	SH signal
D	30:70	4 μm	20 nC cm^{-2}	+
E	35:65	2 μm	25 nC cm^{-2}	+ +

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