Preparation of a Novel Cross-Linked Polymer for Second-Order Nonlinear Optics

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Abstract: A novel cross-linked pyroelectric polymer with pronounced second-order nonlinear optical properties has been prepared. A multistep synthesis with several selective transformations including a kinetic resolution (trans-esterification) with the highly enantioselective Candida antarctica lipase B, yielded the monomer 4′-{(R)-(−)-2-[(10-acyloxyloxy)decyloxy]-3-nitrophenyl}-4-[[11-acyloxyloxy]undecyloxy]phenyl benzoate A2c which displayed a ferroelectric chiral smectic C phase with large spontaneous polarization (175 nC/cm²). The monomer was poled and subsequently cross-linked by in-situ photopolymerization in the surface-stabilized ferroelectric liquid crystalline state. The cross-linked pyroelectric polymer exhibited an electro-optical coefficient (r22 − r12) of 15−35 pm/V.

1. Introduction

Ferroelectric liquid crystals (FLC) are known to exhibit relatively low second-order nonlinear optical susceptibility (χ(2)). However, in 1990, Walba et al.2 synthesized a low molar mass compound I specially designed for second-order nonlinear optics, and this compound showed a second harmonic coefficient (d2) of 0.6 ± 0.3 pm/V in the chiral smectic C (SmC*) phase.3 The NLO chromophores aligned in the direction of the polarization, perpendicular to the long axis direction of the molecule, were later improved by Schmitt et al.4 by the addition of an electron-donating amino group in the para position to the electron-accepting nitro group (II).

The thermal and mechanical stability of these NLO materials were improved by Zentel et al.5 when they synthesized a ferroelectric liquid−crystalline side-chain polymer based on I. Recently Keller et al.6 presented a similar ferroelectric main-chain polymer designed for nonlinear optics.

The thermal and mechanical stability and the long-term properties of NLO materials are improved by cross-linking.7 We therefore developed a cross-linkable monomer exhibiting a Sm mesomorphism over a wide temperature range. A mixture based on this monomer and a chiral monomer with a NLO chromophore was ferroelectric.8 The mixture with 30% NLO active chiral monomer, aligned and photo-cross-linked into a pyroelectric polymer III, displayed a small Pockels constant (r22 − r12 = 0.15 pm/V) and a clear second harmonic signal (d-coefficient = 0.4 pm/V). The chiral monomer had one polymerizable group, and the NLO chromophore itself was therefore not cross-linked. Later this mixture was modified in attempts to increase the NLO activity.10

In this paper, we report the preparation and characterization of a new material with a higher concentration of NLO chromophores. The densely cross-linked material is based on a single monomer A2c. The new synthesis presented was possible through the use of the enantioselective biocatalyst Candida antarctica lipase B. The monomer displayed a large spontaneous polarization (175 nC/cm²) in the chiral smectic C phase at 23 °C. The in-situ photopolymerization at that temperature gave a pyroelectric polymer (poly (A2c)) with more

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than a hundred-fold higher NLO activity (Figure 3). The Pockels effect observed in A2c Structure of the new cross-linked pyroelectric polymer (poly-(A2c)) displays a Pockels effect which is 100\(^{-}\) times the second harmonic signal has not yet been measured.

Keller et al.\(^{6}\) used the stereospecific ring-opening of (5)-(−)-methylxirane by Grignard reagents catalyzed by copper (I) iodide in the synthesis of bifunctional main-chain monomers. The approach developed here, yielded similar intermediates in large enantiomeric excess (>99.5% ee).

2. Experimental Section

2.1. Materials. 2,4,6-Trimethylbenzoyldiphenyl phosphine oxide (Lucrin), purchased from BASF, was used as photoinitiator. The lipase, Candida antarctica (component B), Novozym preparation SP 435, containing 1% (w/w) protein with an activity typically of 25 000 LU/g, was kindly supplied by NOVO-Nordisk A/S, Denmark. 10-Undecen-\(^{−}\)-2-(11-undecenyloxy)-4-biphenylcarboxylic acid (A2c) was used as delivered. The syntheses of ethyl-4-(4-hydroxy)phenyl benzoate (1) and 4-((11-undecenyloxy)-4-biphenylylcarboxyl acid (2) have been described elsewhere.\(^{11}\)

2.2. Techniques. Chemical characterization of the synthesized substances was made by \(^{1}H\) NMR spectroscopy on a Bruker 400 MHz and when necessary by FT-IR spectroscopy using a Perkin-Elmer 1760X. A Perkin-Elmer DSC-7 differential scanning calorimeter was used for the assessment of thermal transitions. In all cases, heating and cooling rates were 20 °C min\(^{-}\)1 unless otherwise stated. A Leitz Ortholux POL BK II optical polarized microscope (magnification 100×) equipped with a Mettler Hot Stage FP 82 and an FP 80 central processor was used for the determination of the thermal transitions of the anisotropic textures. Small-angle X-ray scattering (SAXS) patterns were recorded by a Statton camera, using Cu Ka radiation from a Philips PW 1830 generator. Heating of the samples was controlled by a resistive oven in the Statton camera. Photopolymerization was performed by illumination with an Osram Ultra-Vitalux lamp (300 W). Gas chromatography was performed on Varian 3300 and Carlo Erba Fractovap instruments. Chrompack Cp-cyclohextrin-B-2,3,6-M-19 (25 m, 0.25 mm i.d., 0.25 μm film) and Astec Chiralalx G-TA (10 m, 0.25 mm i.d., 0.25 μm film) columns were used for enantiomeric excess determinations. Trifluoroacetate derivatives of the free alcohol were injected. Absolute configuration was assigned by optical rotation measurement (Perkin Elmer 241 polarimeter) and comparison with literature data. Spontaneous polarizations were measured by the capacitance bridge method,\(^{12}\) reading the hysteresis loop from a Tektronix 2430 oscilloscope.

2.3. Synthesis of Monomers. (4'-Benzyloxyphenyl)benzoate (3). 4-Benzylxenol (24.6 g, 124.9 mmol) was dissolved in CH\(_2\)Cl\(_2\) (500 mL) before Et\(_3\)N (37.9 g, 375 mmol) was added, and the solution was cooled to 0 °C. Benzylox chloride (22.8 g, 162 mmol) was then added dropwise while stirring vigorously. After 20 h the reaction mixture was poured into water and extracted three times with CH\(_2\)Cl\(_2\). The organic phases were separated and combined, washed three times with water (NH\(_4\)Cl, 10% (w/w)), dried with MgSO\(_4\), and filtered. The resulting solid was obtained after evaporation of the solvent. Twice repeated recrystallization from ethanol gave a white crystalline powder. Yield: 35.8 g (94%). \(^{1}H\) NMR (CDCl\(_3\)): \(d = 5.09\) (s, 2H, −OH), 7.02 (d, 2H, 2′-H and 6′-H), 7.14 (d, 2H, 3′-H and 5′-H), 7.40 (m, 5H, 2′-H, 3′-H, 4′-H, 5′-H and 6′-H), 7.53 (m, 2H, 3-H and 5-H), 7.63 (m, 1H, 4-H), 8.20 (d, 2H, 2′-H and 6-H).

(4'-Hydroxyphenyl)benzoate (4). 3 (20.0 g, 304 mmol) was dissolved in ethyl acetate (200 mL) at 70 °C. Pd/C (2.5%, 10% w/w) was added, and the system was evacuated from air and filled with H\(_2\)(g). The reaction began immediately and consumed about 1400 mL of H\(_2\) in about 1 h. The reaction was stopped, and the catalyst was then filtered. The solvent was removed by distillation which resulted in white crystals. Yield: 13.8 g (98%). \(^{1}H\) NMR (CDCl\(_3\)): \(d = 5.17\) (s, 1H, −OH), 6.83 (d, 2H, 2′-H and 5′-H), 7.05 (d, 2H, 2′-H and 6′-H), 7.51 (m, 2H, 3-H and 5-H), 7.62 (m, 1H, 4-H), 8.21 (d, 2H, 2′-H and 6-H).

(4'-Hydroxy-3-nitrophenyl)benzoate (5). 4 (7.15 g, 33.4 mmol) was dissolved in diethyl ether (180 mL) at room temperature. NaNO\(_3\) (2.84 g, 33.4 mmol) and La(NO\(_3\))\(_3\)-6H\(_2\)O (0.15 g, 0.33 mmol) in water (15 mL) were mixed with concentrated HCl (10 mL). The acidic salt solution was added to the diethyl ether solution and stirred for 3 h at room temperature. The colorless suspension turned yellow and then orange-brown. The reaction product was poured into water and extracted three times with diethyl ether. The organic phases were separated and combined, washed three times with water, dried with MgSO\(_4\), and filtered. A solid was obtained after evaporation of the solvent, which after recrystallization from ethanol gave yellow needle crystals. Yield: 6.60 g (76%). \(^{1}H\) NMR (CDCl\(_3\)): \(d = 7.73\) (d, 2H, 2′-H, 5′-H), \(J_{\text{1,2}} = 9\) Hz), 7.50 (d, 1H, 6′-H, \(J_{\text{5,6}} = 3\) Hz, \(J_{\text{5,6}} = 9\) Hz), 7.53 (m, 2H, 3-H and 5-H), 7.67 (m, 1H, 4-H), 8.03 (d, 1H, 2′-H, \(J_{\text{3,4}} = 3\) Hz, 8.18 (d, 2H, 2′-H and 6-H), 10.36 (s, 1H, −OH).

(±)-2-Hydroxy-9-decene (6). A suspension of LiH\(_2\) (2.72 g, 124 mmol) in 175 mL of anhydrous diethyl ether was vigorously stirred at room temperature under an Ar(g) atmosphere for 0.5 h. 1,2-Epoxyc-9-decene (12.8 g, 83 mmol) and anhydrous MeOH (4.0 g, 124 mmol) in diethyl ether (50 mL) were added dropwise, and the mixture was refluxed for 3 h. The reaction was subsequently quenched by the addition of a slightly acidic (HCl) aqueous solution. The solution was extracted with diethyl ether (3 × 150 mL). The organic phases were separated and combined, washed three times with water, dried (MgSO\(_4\)), and filtered. The solvent was evaporated to give an oil. Yield: 6.33 g (49%). \(^{1}H\) NMR (DMSO): \(d = 1.00\) (d, 3H, −CH\(_3\)(CH\(_2\))\(_{2}\)), 1.24−1.30 (m, 10H, \(−\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}−\) and \(−\text{CH}_2\text{CH}_2\text{CH}−\)), 1.97−2.02 (m, 2H, \(−\text{CH}_2\text{CH}_2\text{CH}−\)), 3.56 (1H, 1H, −OH), 4.27 (d, 1H, −OC\((\text{CH}_2\text{CH}−\)H\(_2\text{CH}−\)−)), 4.93 (d, 1H, \(−\text{CH}−\text{CH}_2\text{cis}\)), 5.00 (d, 1H, \(−\text{CH}−\text{CH}_2\text{trans}\)), 5.73 (m, 1H, \(−\text{CH}−\text{CH}_2\text{trans}\)).

(±)-2-Hydroxy-9-decene (7). The enzyme preparation (0.65 g) was added to a 100 mL three-necked round-flask containing

The reaction was initiated by the rapid addition of the acyl donor, S-methyl thioacetate (5.00 g, 55.5 mmol), and left overnight. The conversion was stopped after 13 h, and the reaction was quenched by filtering off the enzyme. 

\[
\text{Ee}_s \text{ and } \text{ee}_p \text{ were found to be }>99.5 \text{ and } 97.2\%, \text{ respectively (GC as described above). According to } c = \frac{\text{ee}_s}{\text{ee}_s + \text{ee}_p}, \text{ this gives a conversion of 51\% and an enantiomeric ratio } E > 400. \text{ Isolated yields were } 40\% (2.01 \text{ g}) \text{ and } 44\% (2.76 \text{ g}), \text{ and optical rotations were } [\alpha]_D^\text{+} = 8.7^\circ (c 0.1, \text{CH}_2 \text{Cl}_2) \text{ and } [\alpha]_D^\text{-} = -2.4^\circ (c 0.1, \text{CH}_2 \text{Cl}_2) \text{ for the remaining alcohol 7 and acetate, respectively. The literature provides absolute configurations for 2-octanol, and the Kazlauskas rule}^{15} \text{ allows the prediction of the absolute configuration (S)-(+)-7.}

\[4'-(\text{R})-(\text{R})-2-(9-\text{Decenyl})\text{oxy}-3'-\text{nitrophenyl} \text{benzoate (8).} \text{ 7 (1.32 g, 8.86 mmol) and diethylazodicarboxylate (DEAD) (1.54 g, 8.86 mmol) were dissolved in diethyl ether (10 mL) and added dropwise to a mixture of 5 (2.29 g, 8.86 mmol) and triphenylphosphine (TPP) (2.32 g, 8.86 mmol) in diethyl ether (10 mL). The mixture was stirred for 48 h at room temperature and then put into the freezer. Triphenylphosphine-oxide precipitated and was filtered off. The solvent was removed, and the remaining product was purified by column chromatography (silica gel, hexane/CH}_2 \text{Cl}_2 as eluent). The final product was a slightly yellow oil. Yield: 2.70 g (81%).} \]
three times with NaHCO₃ (aqueous, 10%), once with water, dried over MgSO₄, and evaporated to give a slightly yellow oil which solidified upon standing. Yield: 1.37 g (98%). ¹H NMR (CDCl₃): δ = 1.32 (m, 2H, -CH₂(OC₂H₅)-), 1.37 (d, 3H, -CH₃), 1.60 (m, 6H, -CH₂(OC₂H₅)-CH₂-), 2.03 (m, 2H, -CH₂CH₂=CH₂), 3.43 (m, 1H, -OC-(CH₂)₄H₂), 4.51 (t, 2H, ArOCH₂C=C(CH₂)₄H₂), 5.81 (m, 1H, -OHCH₂COO-, cis), 4.51 (t, 2H, ArOCH₂C=C(CH₂)₄H₂), 6.12 (d, 2H, CH₂), 4.01 (t, 2H, ArOCH₂C=C(CH₂)₄H₂), 1.77 (m, 2H, ArOCH₂C=C(CH₂)₄H₂), 6.96 (d, 2H, 2°-H), 7.28 (d, 1H, 5°-H). The aqueous phase was extracted three times with CH₂Cl₂. The final product was liquid and was purified by column chromatography (silica gel, hexane/CH₂Cl₂ as eluent). The final product was liquid and was purified by column chromatography (silica gel, hexane/CH₂Cl₂ as eluent). The final product was liquid and was purified by column chromatography (silica gel, hexane/CH₂Cl₂ as eluent). The final product was liquid and was purified by column chromatography (silica gel, hexane/CH₂Cl₂ as eluent). The final product was liquid and was purified by column chromatography (silica gel, hexane/CH₂Cl₂ as eluent). The final product was liquid and was purified by column chromatography (silica gel, hexane/CH₂Cl₂ as eluent).

<table>
<thead>
<tr>
<th>Compd</th>
<th>Heating</th>
<th>Cooling</th>
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<tbody>
<tr>
<td>A2c</td>
<td>k 29 Sc- 33 Sα- 39 i</td>
<td>1 i 34 Sα- 29 Sc- 8 k</td>
</tr>
<tr>
<td>11</td>
<td>k 28 Sc- 58 Sα- 71 i</td>
<td>1 i 63 Sα- 50 Sc- 3 k</td>
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2.4. Polar Orientation in the Surface Stabilized Ferroelectric Liquid Crystal (SSFLC) Cell. Cells of a conventional sandwich type, consisting of two parallel glass substrates kept 2 µm apart by evaporated SiO₂ spacers, were used for the ferroelectric, poling, polymerization, and nonlinear optical experiments. The substrates were prepared from ITO-coated glass sheets (Balzers Baltracon) on which an electrode pattern was formed. An insulating layer of SiO₂ about 1000 Å thick was deposited onto the electrodes. The uniform bookshelf alignment of the liquid crystal material in the cell (smectic layers being essentially perpendicular to the plates) was achieved by using a thin unidirectionally rubbed polyimide aligning layer deposited on top of the insulating layer.

The liquid–crystalline substance was introduced into the cell in the SmA* or in the isotropic phase by capillary forces. The cell was inserted into a Mettler FP 52 stage with the temperature controlled to an accuracy of ±0.1 °C, and the liquid crystalline substances were examined in a polarizing microscope (crossed polarizers).

At the temperatures (∼23 °C) at which the ferroelectric electro-optic response indicated that the SmA* phase was fully developed, a dc electric field (E ≈ 100 V/µm) was applied in order to orient the spontaneous polarization in the whole cell in one direction. This gave a unique direction to the optical axis, tilted with respect to the smectic layer normal and thus resulting in the formation of a ferroelectric monodomain between the electrodes. The uniformity of the orientation was examined in the polarizing microscope, and the applied dc field was sufficient to cause full extinction of the transmitted light when the optical axis of the cell was either parallel to or perpendicular to the transmission direction of the polarizer.

2.5. Thermal Stabilization by in-Situ Photopolymerization. After obtaining a ferroelectric monodomain structure for the monomer/photo-initiator mixture at the temperature (∼23 °C) at which the ferroelectric electro-optic response in the SmA* phase was fully developed, the cell was irradiated with UV-light, while keeping the dc-field on, for about 10 min during which the liquid–crystalline mixture polymerized. The ratio of photo-initiator to monomer was 1:200 (0.5 mol%). The low concentration of photo-initiator did not destabilize the SmA* phase. In order to avoid undesired photopolymerization of the liquid–crystalline material in the cell during the preparation and investigative procedures, the work was performed under yellow light.

2.6. Measurement of the Pockels Effect. The Pockels effect was measured in transmission by a crossed polarizer method.¹⁶ The electro-optic modulation of the phase difference between the incoming optical field components parallel to and perpendicular to the plane of incidence was converted into intensity modulation by a polarization analyzer. A Soleil-Babinet compensator placed between the crossed polarizers was adjusted so that the transmitted intensity was half the maximum intensity, in order to achieve the maximum linear detection range. The experiments were carried out by applying a 375 Hz sinusoidal voltage with a maximum peak-to-peak voltage of 20 V over the 2 µm electrode gap.

3. Results and Discussion

3.1. Design of the Monomer. The monomer (A2c) was designed to generate a cross-linkable ferroelectric liquid crystal intended for second-order nonlinear optics. Compound I which is a ferroelectric liquid crystal for second-order nonlinear optics was therefore substituted with two acrylate groups. The cross-linkable monomer A2c requires a bifunctional nonracemic chiral spacer.

3.2. Synthesis of the Monomer. The synthesis of 4'-((R)-(+)-2-[10-acryloyloxy]decyl)oxy)-3-nitrophenyl 4'-[[11-acryloyloxy]undecyloxy]phenyl]benzoate A2c is outlined in Scheme 1. In the synthesis of this compound, several selective reactions have been used. The syntheses of 1 and 2 have been reported elsewhere.¹¹ La(NO₃)₃ was used as catalyst in the aromatic ortho nitration of the phenol 4. The two-phase reaction gives almost exclu-
sively ortho nitration when para-substituted phenols are used, which was confirmed by \textsuperscript{1}H NMR.\textsuperscript{17}

The 1,2-epoxy-9-decene was reduced in an anti-Markovnikov fashion to yield the racemic secondary alcohol 5. This was done with a LiBH\textsubscript{4}−MeOH reducing system described by Soai \textit{et al.}\textsuperscript{18} The alcohol was then resolved kinetically with S-methyl thiocetate as acyl donor and the \textit{Candida antarctica} lipase B as catalyst. The remaining substrate 7 was isolated in a 40\% yield (50% theoretical maximum) with high enantioselectivity. The enantiomeric excess of the alcohol, ee, was >99.5\% (only one enantiomer detected) and that of the product, ee\textsubscript{p}, was 97.2\% as determined by chiral GC. This gave a conversion (\(c = e e / (e e + e e_p)\))\textsuperscript{15} of 51\% which is optimal for maximizing the optical purity and chemical yield of the remaining substrate. 7 showed positive optical rotation, and the absolute configuration of the alcohol was predicted to be (\(S\)) by 2-octanol analogy and the empirical rule of lipase selectivity.\textsuperscript{15}

The nitro-substituted phenol 5 was coupled to the chiral alcohol 7 in the Mitsunobu synthesis using diethylzodialcoholate (DEAD)/triphenylphosphine (TPP) which proceeds by inversion of the configuration, converting the \(S\)-alcohol to an \(R\)-ester. The chiral moiety 8 was then deprotected by KOH.

8 was subsequently coupled with 2 using dicyclohexylcarbodiimide (DCC) as dehydrating agent and dimethylaminopyridine (DMAP) as catalyst. The product 10 was hydroborated with 9-BBN and subsequently oxidized by \(\text{H}_2\text{O}_2\) using a modified procedure first reported by Sahlen \textit{et al.}\textsuperscript{11} The bifunctional monomer A2c was finally prepared by the esterification of the diol 11 using acryloyl chloride.

3.3. Liquid–Crystalline Properties of the Monomer. 3.3.1. Thermal Characterization. The thermal transitions of the monomer A2c and of the intermediate substance 11 are shown in Table 1. The DSC thermogram of monomer A2c revealed two different mesophases. On cooling A2c from the isotropic state, a focal-conic fan texture typical of “smectics”, probably SA*, was formed at 34 °C. Further cooling caused a phase transition, as observed in the DSC, which was not observed in the polarized microscope. X-ray scattering and electro-optical methods indicated that this transition involved the SA* phase. The liquid–crystalline phases of A2c appeared both on heating and cooling, i.e., they were enantiotropic. However, on heating, the liquid–crystalline phases were present in only a narrow temperature range. The monomer A2c was thermally stable and did not polymerize spontaneously on heating to 140 °C.

X-ray scattering patterns of the SA* phase of A2c consisted of diffuse wide-angle reflections and a sharp inner ring reflection, corresponding to a layer thickness of 33 Å. Simple calculations indicate that the 33 Å layer thickness is consonant with a monolayer smectic A phase. The length of the mesogenic group including the ether oxygens is 16 Å. The length of two spacer groups assuming a trans content of 70\% is 16 Å.\textsuperscript{19} The repeating distance of a perfectly smectic monolayer is the sum of the length of one mesogenic group, two spacer groups, and two acrylate groups (7 Å), i.e., 40 Å, which is only slightly more than the 38 Å obtained by X-ray diffraction.

The X-ray scattering of the low temperature phase of A2c consisted of a diffuse wide-angle reflection corresponding to an intermesogenic distance of about 4 Å, and, at small angles,
tilt in the $S_{c}^*$ phase became fixed during the polymerization and that the macroscopic polarization of the sample (in a direction perpendicular to the cell glass plates) was made permanent.

The polymer network formed showed good thermal stability. Heating above the isotropization temperature of $A_{2c}$ caused no changes in the molecular tilt of the network, nor were any textural changes revealed in the optical microscope.

3.4.1. Nonlinear Optical Properties. The refractive index of the isotropic material polymerized on a glass substrate was 1.556, according to the m-line method. The material is assumed to be almost uniaxial, $n_0 = n_e = n_o$ and $n_i = n_c$. If the isotropic refractive index is approximated by $n = (2n_o + n_i)/3$ and the birefringence is approximately 0.1 (visual inspection), the ordinary refractive index, $n_o$, is obtained.

In Figure 7, $\Delta I/I$ ($I$ is the intensity transmitted through the set-up when $E = 0$) is plotted as a function of the electric field. The modulated intensity shows a linear dependence on the applied $E$ field, as expected for the Pockels effect (Figure 7). At an incidence angle of 26°, values of the difference between the electro-optical coefficients ($r_{22} - r_{12}$) of 15–35 pm/V were obtained. This is of the same order as that of organic crystals. The dominant coefficient is expected to be $r_{22}$, since it is directed along the polar axis.

In the SSFLC-cell utilized for the experiments, the smectic layers have a bookshelf organization (Figure 8). Polyimide, rubbed in the $z$-direction, orients the smectic layers parallel to the $xy$-plane, perpendicular to the $z$-axis. This geometry makes only two orientations of the molecules possible; alignment of the molecules with their effective dipole moment in either the positive or the negative $y$-direction. The molecular dipole moments were forced to align in one of the two possible directions by the applied electric field, which after polymerization gave the polymer a $C_2$ symmetry. The effective global dipole moment of the polymer network had its orientation parallel to the $y$-axis, perpendicular to the glass/electrode plates. The magnitude of the electro-optical coefficient was, as expected, greatest in the direction of the polar axis.

The Pockels effect depends on the material’s macroscopic susceptibility $\chi^{(2)}$ and is observed as a modification of its refractive index when a low frequency electrical field is applied. The applied electric field induces a change in the
refractive index according to

\[ \Delta \left( \frac{1}{n^2} \right) = rE \]  

(1)

where \( r \) is the electro-optic tensor. For a material with \( C_2 \) symmetry, the tensor is given by

\[
\begin{pmatrix}
0 & r_{12} & 0 \\
0 & r_{22} & 0 \\
0 & r_{32} & 0 \\
r_{41} & 0 & r_{43} \\
0 & r_{52} & 0 \\
r_{61} & 0 & r_{63}
\end{pmatrix}
\]  

(2)

Assuming Kleinman degeneracy to be valid, the number of independent tensor components is reduced to four: \( r_{41} = r_{52} = r_{63}, r_{32} = r_{43}, \) and \( r_{12} = r_{61} \). Thus, the modulation of the birefringence causes a modulation of the phase retardation, \( \Delta \Phi \). If the modulated phase retardation is small, it can be related to the detected intensity variations by

\[ \Delta I = \frac{1}{2} I_{\text{max}} \Delta \Phi \]  

(3)

If the incoming polarized light propagates in the xy-plane with the electric field vector in the same plane, the phase retardation, modulated by an applied electric field parallel to the y-axis, is

\[ \Delta \Phi = \frac{2\pi}{\lambda} \Delta n l \approx \frac{\pi n^3}{\lambda} (r_{22} - r_{12}) \sin^2 \theta \frac{l}{d} V \]  

(4)

where \( \lambda \) is the wavelength, \( l \) is the length in the polymer traversed by the light, \( d \) is the distance between the electrodes, and \( V \) is the applied voltage.

In order to simplify the analysis, the term \( r_{52} \) corresponding to a tilt of the refractive index ellipsoid due to the applied electric field was neglected. Measuring the second harmonic generation (SHG) in a ferroelectric liquid crystal, Schmitt and co-workers\(^4\) found a ratio of approximately 10:1 between the second-order nonlinear optic coefficients \( d_{22} \) and \( d_{25} \). If the ratio between the electro-optic coefficients in this material is the same as that observed by Schmitt et al.\(^4\) between the second harmonic coefficients, neglecting \( r_{52} \) will not seriously affect the results. If this assumption is valid, the increase in the uncertainty in \( (r_{22} - r_{12}) \) will be less than 10%.

The linearity in Figure 7 could in principal also arise from a motion of the optical axis in the electric field. This would be the case if the monomers were free to move as in the ferroelectric state. The sample was therefore examined in other areas where the material was not made permanent in a polar organization. These areas showed no detectable modulation of the intensity. The Pockels coefficient obtained is therefore believed to be of true electronic origin, but this has to be confirmed by measurement of the second harmonic generation. If the nonlinear optic response has a purely electronic origin, the coefficients \( r \) and \( d \) are directly inter-related:\(^{21}\)

\[ r = -\frac{4\pi d}{n^4} \]  

(5)

The values of the \( d \)-coefficients, expected from SHG, should be 6.4–14.9 pm/V, calculated for a refractive index of 1.52.

Conclusions

A new pyroelectric polymer exhibiting a large Pockels effect \( (r_{22} - r_{12} = 15–35 \text{ pm/V}) \) was prepared by in-situ photo-cross-linking of a novel ferroelectric monomer. The large nonlinear optical activity, in the range of organic single crystals, is very encouraging, but it has to be confirmed by measurement of the second harmonic generation. The magnitude of the signal makes the new material interesting for use in electro-optic devices.

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