Novel Thermally Stable Polymer Materials for Second-Order Nonlinear Optics

Mikael Trollsås, Fredrik Sahlén, Ulf W. Gedde, and Anders Hult*

Department of Polymer Technology, Royal Institute of Technology,
S-100 44 Stockholm, Sweden

David Hermann, Per Rudquist, Lachezar Komitov,
Sven T. Lagerwall, and Bengt Stebler

Physics Department, Chalmers University of Technology, S-412 96 Göteborg, Sweden

Jan Lindström and Olof Rydlund

National Defence Research Establishment, S-172 90 Stockholm, Sweden

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ABSTRACT: A novel method of preparing thermally stable thin films with intrinsic second-order nonlinear optical activity is described. Design and synthesis yielded new ferroelectric bifunctional liquid crystalline acrylate monomer mixtures with a fast electro-optical response in the chiral smectic C (SmC*) phase. The ferroelectric liquid crystalline monomer mixtures were poled and subsequently cross-linked by in-situ photopolymerization in the surface-stabilized ferroelectric liquid crystal state. After cross-linking the polarization is no longer reversible, hence the material is pyroelectric and not ferroelectric. The cross-linked pyroelectric materials displayed a thermally stable nonlinear optical response.

Introduction

In the past decade, considerable effort has been directed toward the design, synthesis, and characterization of organic materials for second-order nonlinear optics. The advantages of using organic materials in electro-optical applications are their rapid response and their high intrinsic molecular hyperpolarizability.[1] Second-order nonlinear optical properties can only be obtained in materials with a polar order. Currently available organic nonlinear optical materials have many desired properties but normally they all suffer from a low polar order which is usually not even stable in time.

Liquid crystalline materials exhibit a high intrinsic order and have been extensively studied as materials for second-order nonlinear optics.[2] The molecular structure of many liquid crystals and liquid crystalline polymers seems at first also ideal for nonlinear optics because these materials have the required electron-donor and -acceptor groups attached to each side of the mesogen along the direction of the molecule (Figure 1).

The second-order susceptibility $\chi^{(2)}$ is given by

$$\chi^{(2)} = N\langle\beta\rangle \qquad (1)$$

where N is the number of molecules per unit volume and $\langle\beta\rangle$ is the average value of the hyperpolarizability with consideration taken to the degree of order. A requirement for second-order nonlinear optical effects is that $\chi^{(2)} \neq 0$. In nematic and smectic liquid crystalline phases, $\chi^{(2)} = 0$ because β is averaged out along the direction of the molecule. This is because liquid crystals are normally nonpolar materials and have the wrong kind of internal order, quadrupolar instead of dipolar.[3] Liquid crystalline polymers used for nonlinear optics have therefore been poled by the old corona discharge method, which has then produced materials with only limited polar order. The disadvantages of materials poled by this technique are their instability causing the nonlinear optical properties to decay with time.

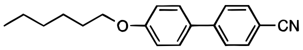

Figure 1. Structure of a strongly dipolar liquid crystal molecule which can only possess a nonpolar macroscopic order.

Along the director the liquid crystalline order is strictly nonpolar; however, perpendicular to the director, polar order can be induced.[4,5] The local polarization, $\mathbf{P} \perp n$, has the advantage of being thermodynamically stable. This can only be realized in tilted chiral smectic phases and particularly in the chiral smectic C (SmC*) state. Furthermore a macroscopic polarization can be obtained in the surface-stabilized ferroelectric state. Along the direction perpendicular to the director, $\langle\beta\rangle \neq 0$ and thus $\chi^{(2)} \neq 0$ and the materials may therefore exhibit a second-order nonlinear optical response (Figure 2). Most available ferroelectric liquid crystals have not, however, been designed to be used for nonlinear optical applications, and they therefore have a relatively small molecular hyperpolarizability, and the reported $\chi^{(2)}$ values for these materials are therefore small.[6]

Recently, several laboratories have developed ferroelectric liquid crystals and ferroelectric polymeric liquid crystals specifically devoted to second-order nonlinear optical applications (Figure 3).[6−10] Walba and coworkers showed that ferroelectric liquid crystals with non linear optical hyperpolarizability can be aligned in such a way that the resulting materials can be used for second harmonic generation.[7]

Materials for nonlinear optics must combine their unique optical properties with good mechanical and thermal properties. However, low molar mass and polymeric ferroelectric liquid crystals are ferroelectric in the SmC* phase and their polar order is limited to that state. Another drawback of low molar mass liquid crystals is their poor mechanical properties.

Stabilization of different mesophases has been accomplished by photopolymerization of bifunctional liquid crystalline monomers.[11−17] It should be possible to

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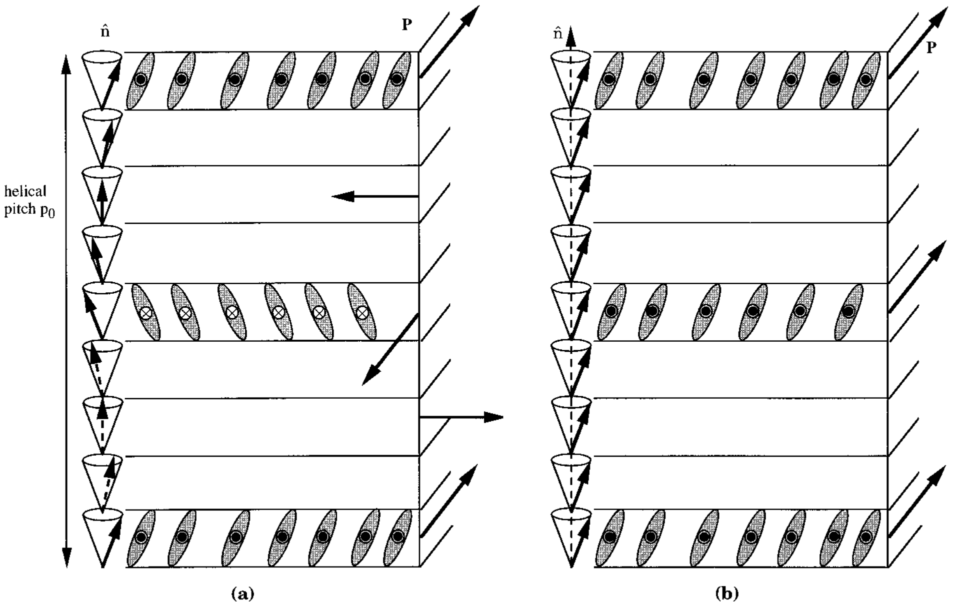


Figure 2. Illustration of a ferroelectric chiral smectic C phase (SmC*) (a) in the macroscopically nonpolar helical antiferroelectric state and (b) in the macroscopically polar ferroelectric state. **P** indicates the polarization. Each oval represents a liquid crystal molecule.

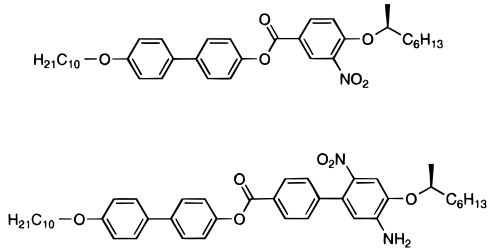


Figure 3. Structures of low molar mass liquid crystals especially devoted to nonlinear optics which can possess macroscopic polar order in the chiral smectic C (SmC*) phase.[7,9]

stabilize the polar organization of a SmC* phase thermally and mechanically using the same technique. Such stabilization would require a cross-linkable ferroelectric monomer mixture which has to fulfill at least four demands. Three of them are of a synthetic character and one is morphologically related. The synthetic demands are that the mixture has to be cross-linkable and chiral and have a nonlinear optically active chromophore oriented perpendicular to the long axis of the molecule. This chromophore will also act as the lateral dipole of the ferroelectric mixture. The fourth requirement is the demand for a SmC phase. The cross-linkable ferroelectric monomer mixture can be designed in several ways, but independent of design, it should result in a nonlinear optical material which after cross-linking is pyroelectric and not ferroelectrically switchable.

The polar order is brought to the ferroelectric system by poling in the liquid crystalline state, using dc and low-frequency ac fields, prior to the photopolymerization. When liquid crystalline vinyl ether monomers were used, the cationic polymerization using onium salts and a photosensitizer was initiated by the electric field[18] which prohibited the polar order from being formed. This problem is not present with the liquid crystalline acrylates or methacrylates used in this study which polymerize by a radical mechanism.

This paper describes the design and synthesis of novel ferroelectric monomer mixtures which were poled and in-situ photo-cross-linked by radical polymerization in the surface-stabilized ferroelectric liquid crystal state. The monomer mixtures were ferroelectric in the SmC* phase whereas after cross-linking the switchability of the polar order is lost. The result is a polar and pyroelectric polymer, and it was checked that it displayed a nonlinear optical response.

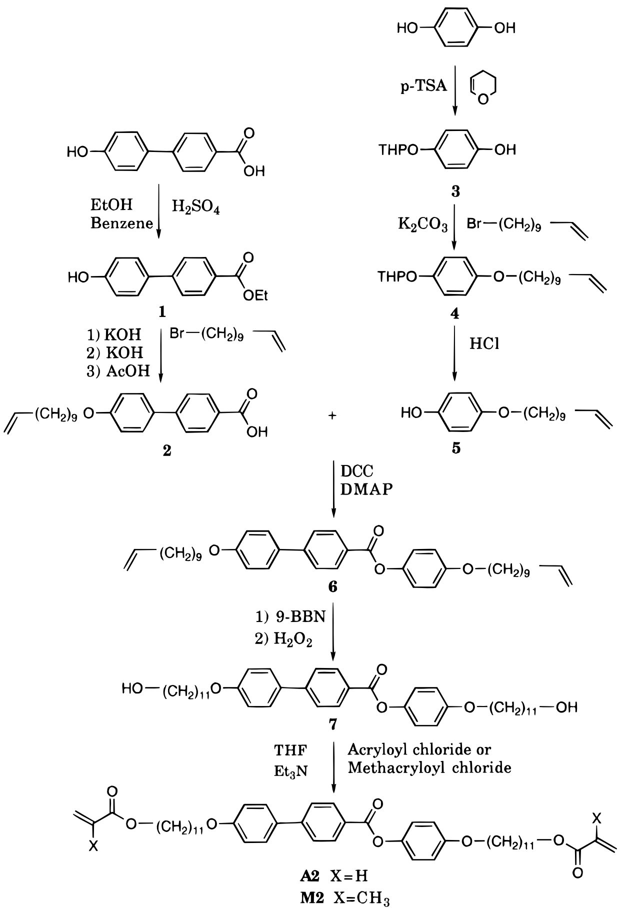
Experimental Section

Materials. 4,4′-Dihydroxybiphenyl (97%), 3,4-dihydro-2*H*-pyran, 11-bromoundecanol, *p*-TSA, triethylamine, acryloyl chloride, methacryloyl chloride, 4-hydroxy-3-nitrobenzoic acid, diethyl azodicarboxylate (DEAD), triphenylphosphine (TPP), dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine, 4′-hydroxy-4-biphenylcarboxylic acid, 8-bromo-1-octene, 11-bromo-1-undecene, 9-borabicyclo[3.3.1]nonane (9-BBN) (0.5 M in THF), hydrogen peroxide (35% in water), and triethylamine were purchased from Aldrich. Hydroquinone was purchased from BDH Chemicals Ltd. (*S*)-(+)-2-Octanol was purchased from Chomtroll Kemi HB and Aldrich and used as delivered. (2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (Lucirin), puchased from BASF, was used as photoinitiator. All substances were used without further purification.

Techniques. Chemical characterization of the synthesized substances were made by ^{1}H-NMR spectroscopy on a Bruker 250 MHz, and when necessary by FT-IR spectroscopy using a Perkin-Elmer 1760X. High-performance liquid chromatography (HPLC) experiments were performed with a Perkin-Elmer system equipped with an LC-235 diode array detector and a cartridge column (pecosphere 3 × 3CR). Acetonitrile was used as the mobile phase. 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 specified. 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 assessment of the thermal transitions of the anisotropic textures. Small-angle X-ray scattering (SAXS) patterns were recorded by a Statton camera, using Cu Kα 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). The optical activity was measured on a Perkin-Elmer 241 polarimeter.

Synthesis of Monomers. Ethyl 4-(4′-Hydroxyphenyl)-benzoate (1). 4′-Hydroxy-4-biphenylcarboxylic acid (5.27 g,

Scheme 1. Synthesis of A2 and M2



24.60 mmol) was dissolved in a solution of EtOH (17 mL, 99.5%) and benzene (10 mL). H_2SO_4 was added in a catalytic amount and the mixture was refluxed for 24 h. The reaction mixture was poured into water and extracted three times with CH_2Cl_2. The organic phase was separated and washed three times with water, dried with $MgSO_4$, and evaporated. The yellow-white powder was dissolved in $CHCl_3$, in which unreacted 4′-hydroxy-4-biphenylcarboxylic acid precipitated. The $CHCl_3$ solution was filtered and evaporated, resulting in a white crystalline powder. Yield: 4.79 g (80%). ^{1}H-NMR ($CDCl_3$): $\delta = 1.42$ (t, 3H, $-CH_2\mathit{CH_3}$), 4.40 (q, 2H, $-\mathit{CH_2}CH_3$), 6.95 (d, 2H, 3′-H and 5′-H), 7.53 (d, 2H, 2′-H and 6′-H), 7.61 (d, 2H, 2-H and 6-H), 8.10 (d, 2H, 3-H and 5-H).

4′-(11-Undecenyloxy)-4-biphenylcarboxylic Acid (2). **1** (6.0 g, 24.77 mmol) was dissolved in EtOH (30 mL). KOH (85%) (1.88 g, 28.4 mmol) dissolved in EtOH (10 mL) was then added dropwise to the solution. This turned the solution yellow. KI (1.08 g, 6.44 mmol) and 11-bromo-1-undecene (5.76 g, 24.7 mmol) were added. The solution decolored during the 24 h of refluxing. KOH (4.90 g, 74.3 mmol) was then added, and the solution was stirred for 3 h. The reaction mixture was then cooled, and the precipitate was filtered out. The product was then dissolved in a mixture of AcOH (30 mL) and EtOH (30 mL), and the solution was stirred for 1 h at 120 °C. The final product, a white crystalline powder, precipitated when the solution was cooled and was filtered out. Yield: 6.00 g (66%). ^{1}H-NMR ($CDCl_3$): $\delta = 1.34$ (m, 12H, $-OCH_2CH_2(\mathit{CH_2})_6-$), 1.80 (p, 2H, $-OCH_2\mathit{CH_2}-$), 2.05 (q, 2H, $CH_2{=}CH\mathit{CH_2}-$), 4.01 (t, 2H, $-O\mathit{CH_2}-$), 4.93 (d, 1H, $\mathit{CH_2}{=}CH-$ cis), 4.98 (d, 1H, $\mathit{CH_2}{=}CH-$ trans), 5.79 (m, 1H, $CH_2{=}\mathit{CH}-$), 6.98 (d, 2H, 3′-H and 5′-H), 7.55 (d, 2H, 2′-H and 6′-H), 7.65 (d, 2H, 2-H and 6-H), 8.11 (d, 2H, 3-H and 5-H).

4-((2-Tetrahydropyranyl)oxy)phenol (3). Hydroquinone (15.0 g, 136 mmol) was dissolved in diethyl ether with a catalytic amount of *p*-TSA at room temperature. 3,4-Dihydro-2*H*-pyran was added dropwise, and the solution was stirred for 1 h at room temperature. A mixture of $EtOH/NH_3$ (1:1) was added until the solution was basic. The reaction mixture was poured into water and extracted three times with CH_2Cl_2. The organic phase was separated and washed three times with water, dried with $MgSO_4$, and evaporated. The product was purified by column chromatography (silica gel, hexane/EtOAc as eluent) which gave a white crystalline powder. Yield: 7.40 g (56%). ^{1}H-NMR ($CDCl_3$): $\delta = 1.65$ (m, 4H, $-\mathit{CH_2CH_2}CH_2OCHO-$), 1.87 (m, 2H, $-\mathit{CH_2}CH-$), 3.62 (m, 1H, $-\mathit{CH_2}OCHO-$), 3.94 (m, 1H, $-\mathit{CH_2}OCHO-$), 4.64 (s, 1H, $\mathit{HO}Ar-$), 5.27 (t, 1H, $-\mathit{CH}-$), 6.73 (d, 2H, 2-H and 6-H), 6.95 (d, 2H, 3-H and 5-H).

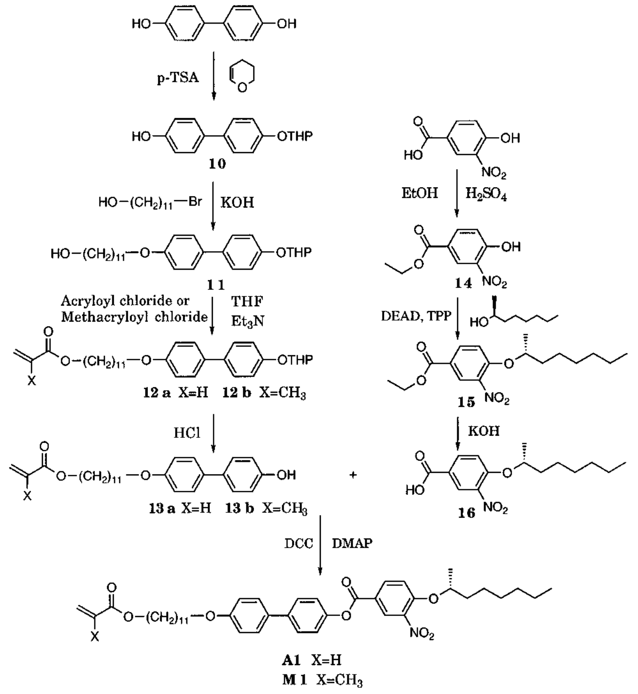
4-((2-Tetrahydropyranyl)oxy)-1-(11-undecenyloxy)benzene (4). **3** (5.00 g, 25.7 mmol) and K_2CO_3 (10.67 g, 77.22 mmol) were dissolved in DMF and stirred for 1 h at room temperature. 11-Bromo-1-undecene (6.00 g, 25.7 mmol) was added, the temperature was raised to 100 °C, and the mixture was stirred for 24 h. DMF was then removed by vacuum distillation (30 °C, 10 mmHg). The reaction mixture was poured into water and extracted three times with CH_2Cl_2. The organic phase was separated and washed three times with water, dried with $MgSO_4$, and evaporated. The product was purified by column chromatography (silica gel, hexane/EtOAc as eluent). The final product was crystalline. Yield: 5.60 g (65%). ^{1}H-NMR ($CDCl_3$): $\delta = 1.30$ (m, 16H, $-\mathit{CH_2CH_2}CH_2OCHO-$ and $CH_2{=}CHCH_2(\mathit{CH_2})_6-$), 1.66 (m, 2H, $-\mathit{CH_2}CHOO-$), 1.86 (m, 2H, $OCH_2\mathit{CH_2}-$), 2.07 (m, 2H, $CH_2{=}CH\mathit{CH_2}-$), 3.60 (m, 1H, $-\mathit{CH_2}OCHO-$), 3.91 (t, 2H, $-O\mathit{CH_2}(CH_2)_5-$), 3.94 (m, 1H, $-\mathit{CH_2}OCHO-$), 4.94 (d, 1H, $\mathit{CH_2}{=}CH-$, cis), 5.00 (d, 1H, $\mathit{CH_2}{=}CH-$, trans), 5.28 (t, 1H, $-O\mathit{CHO}-$), 5.81 (m, 1H, $CH_2{=}\mathit{CH}-$), 6.81 (d, 2H, 2-H and 6-H), 6.98 (d, 2H, 3-H and 5-H).

4-(11-Undecenyloxy)phenol (5). **4** (5.60 g, 16.7 mmol) was dissolved and well stirred in EtOH (20 mL) at room temperature. A catalytic amount of HCl was added. The solution was poured into water after 1 h and extracted three times with CH_2Cl_2. The organic phase was separated and washed three times with water and dried with $MgSO_4$, and the solvent was evaporated. The remaining product was white and crystalline. Yield: 4.23 g (90%). ^{1}H-NMR ($CDCl_3$): $\delta =$ 1.28 (m, 12H, $CH_2{=}CHCH_2(\mathit{CH_2})_6-$), 1.74 (p, 2H, $OCH_2\mathit{CH_2}-$), 2.04 (q, 2H, $CH_2{=}CH\mathit{CH_2}-$), 3.80 (t, 2H, $-O\mathit{CH_2}CH_2-$), 4.92 (d, 1H, $\mathit{CH_2}{=}CH-$, cis), 4.98 (d, 1H, $\mathit{CH_2}{=}CH-$, trans), 5.50 (m, 1H, $CH_2{=}\mathit{CH}-$), 6.76 (s, 4H, 2-H, 3-H, 5-H, and 6-H).

4″-(11-Undecenyloxy)phenyl 4-(4′-(11-Undecenyloxy)phenyl)benzoate (6). **2** (0.50 g, 1.36 mmol), **5** (0.48 g, 1.36 mmol), DCC (0.37 g, 1.77 mmol), and DMAP (0.025 g, 0.20 mmol) were dissolved in CH_2Cl_2 (15 mL) and heated under reflux for 24 h. The reaction was then cooled to −5 °C in the freezer, and the precipitate was filtered from the solution. The solvent was evaporated, and the resulting solid was recrystallized twice from EtOH to give white crystals. Yield: 0.69 g (85%). ^{1}H-NMR ($CDCl_3$): $\delta = 1.31$ (m, 24H, $CH_2{=}CHCH_2(\mathit{CH_2})_6-$), 1.79 (m, 4H, $-OCH_2\mathit{CH_2}-$), 2.05 (m, 4H, $CH_2{=}CH\mathit{CH_2}-$), 3.95 (t, 2H, $-ArArO\mathit{CH_2}CH_2-$), 4.01 (t, 2H, $-ArO\mathit{CH_2}CH_2-$), 4.93 (d, 2H, $\mathit{CH_2}{=}CH-$, cis), 5.00 (d, 2H, $\mathit{CH_2}{=}CH-$, trans), 5.82 (m, 2H, $CH_2{=}\mathit{CH}-$), 6.94 (d, 2H, 3″-H and 5″-H), 7.01 (d, 2H, 3′-H and 5′-H), 7.12 (d, 2H, 2″-H and 6″-H), 7.59 (d, 2H, 2′-H and 6′-H), 7.69 (d, 2H, 3-H and 5-H), 8.23 (d, 2H, 2-H and 6-H).

4″-((11-Hydroxyundecyl)oxy)phenyl 4-(4′-((11-Hydroxyundecyl)oxy)phenyl)benzoate (7). All glassware was dried overnight in an oven at 150 °C. **6** (1.00 g, 1.67 mmol) was added to a 100 mL flask which was flushed with argon for 30 min. Dry THF (40 mL) was added through a septum, and the solution was stirred for 30 min at room temperature under argon. 9-BBN (0.5 M in THF) (10 mL, 5 mmol) was then added through a septum and the solution was further stirred for 20 h at room temperature in an argon atmosphere. EtOH (10 mL) was added, and the oxidation was carried out by adding H_2O_2 (35%) (3 mL, 30 mmol). The oxidized solution was stirred for 1 h and then poured into water. White crystals precipitated and were filtered. Yield: 1.05 g (99%). Thermal characterization (Table 1). The product was not soluble in deuterated chloroform, acetone, or DMSO; hence no ^{1}H-NMR characterization was possible. FT-IR (KBr): 3334 cm^{-1} (O—H stretch); 2928, 2851 cm^{-1} (aliphatic C—H stretch); 1744 cm^{-1}

Scheme 2. Synthesis of A1 and M1



(C=O stretch); 1618 cm^{-1} (aromatic C=C stretch); 1517 cm^{-1} (aromatic carbon to carbonyl carbon stretch); 1299−1217 cm^{-1} (several C−O stretches).

4″-((11-(Acryloyloxy)undecyl)oxy)phenyl 4-(4′-((11-Acryloyloxy)undecyl)oxy)phenyl)benzoate (A2). **7** (0.50 g, 0.79 mmol) was dissolved in THF (40 mL) at 60 °C and stirred for 1 h. Triethylamine (0.24 g, 2.37 mmol) was then added. Acryloyl chloride (0.22 g, 2.05 mmol) dissolved in THF (10 mL) was added dropwise to the stirred solution. After 20 h, the reaction was poured into water (NH_4Cl, 10%) and extracted three times with CH_2Cl_2. The organic phase was separated and washed three times with water, dried with $MgSO_4$, and evaporated. The product was purified by column chromatography (silica gel, hexane/EtOAc as eluent). The solvent was evaporated, and the resulting solid was twice recrystallized from EtOH to give white crystals. Yield: 0.30 g (50%). HPLC: 99%. Thermal characterization (Table 1). ^{1}H-NMR ($CDCl_3$): δ = 1.32 (m, 28H, $CH_2{=}CHCH_2(CH_2)_7-$), 1.66 (m, 4H, $-COOCH_2CH_2-$), 1.80 (m, 4H, $-ArOCH_2CH_2-$), 3.95 (t, 2H, $-ArArOCH_2CH_2-$), 4.01 (t, 2H, $-ArOCH_2CH_2-$), 4.16 (t, 4H, $-COOCH_2-$), 5.82 (d, 2H, $CH_2{=}CH-$, cis), 6.11 (m, 2H, $CH_2{=}CH-$), 6.40 (d, 2H, $CH_2{=}CH-$, trans), 6.93 (d, 2H, 3″-H and 5″-H), 7.00 (d, 2H, 3′-H and 5′-H), 7.13 (d, 2H, 2″-H and 6″-H), 7.59 (d, 2H, 2′-H and 6′-H), 7.64 (d, 2H, 3-H and 5-H), 8.22 (d, 2H, 2-H and 6-H). Anal. Calcd for $C_{47}H_{62}O_8$: C, 74.77; H, 8.28. Found: C, 74.94; H, 8.17.

4″-((11-(Methacryloyloxy)undecyl)oxy)phenyl 4-(4′-((11-(Methacryloyloxy)undecyl)oxy)phenyl)benzoate (M2). **M2** was synthesized using the procedure described for **A2**. The resulting product was recrystallized from EtOH to give white crystals. Yield: 0.30 g (48%). The purity of **M2** could not be determined by HPLC because the compound was not soluble in available solvents. Thermal characterization (Table 1). ^{1}H-NMR ($CDCl_3$): δ = 1.30 (m, 28H, $CH_2{=}CHCH_2(CH_2)_7-$), 1.65 (m, 4H, $-COOCH_2CH_2-$), 1.77 (m, 4H, $-ArOCH_2CH_2-$), 1.93 (s, 6H, $(CH_2{=}CCH_3OO-)_2$), 3.95 (t, 2H, $-ArArOCH_2CH_2-$), 4.01 (t, 2H, $-ArOCH_2CH_2-$), 4.12 (t, 4H, $-COOCH_2-$), 5.51 (s, 2H, $CH_2{=}CH-$, cis), 6.08 (s, 2H, $CH_2{=}CH-$, trans), 6.93 (d, 2H, 3″-H and 5″-H), 7.00 (d, 2H, 3′-H and 5′-H), 7.13 (d, 2H, 2″-H and 6″-H), 7.59 (d, 2H, 2′-H and 6′-H), 7.64 (d, 2H, 3-H and 5-H), 8.22 (d, 2H, 2-H and 6-H). Anal. Calcd for $C_{49}H_{66}O_8$: C, 75.16; H, 8.49. Found: C, 72.94; H, 8.31.

4-Hydroxy-4′-((2-tetrahydropyranyl)oxy)biphenyl (10). 3,4-Dihydro-2*H*-pyran (1.82 g, 21.7 mmol) was added dropwise to a mixture of 4,4′-dihydroxybiphenyl (7.92 g, 43.0 mmol) and *p*-TSA (0.34 g, 1.7 mmol) in dioxane (50 mL) and THF (10 mL) at room temperature. The reaction mixture was stirred for 15 min and the reaction was then stopped by adding an EtOH/NH_3 mixture (50/50) until the solution was slightly basic. The mixture was then diluted with CH_2Cl_2 (100 mL) and mixed with an aqueous $NaHCO_3$ (15%) solution. The precipitate was filtered off and washed once with CH_2Cl_2. The eluents were collected and the organic phase was separated. The water phase was again extracted with CH_2Cl_2. All organic solvents were collected, dried with $MgSO_4$, and evaporated. The remaining solid was purified by column chromatography (silica gel, hexane/EtOAc as eluent) which gave white crystals. Yield: 2.67 g (48%). ^{1}H NMR ($CDCl_3$): δ = 1.65 (m, 4H, $-CH_2CH_2CH_2OCHO-$), 1.87 (m, 2H, $-CH_2CH-$), 3.62 (m, 1H, $-CH_2OCHO-$), 3.94 (m, 1H, $-CH_2OCHO-$), 5.21 (s, 1H, $HOAr-$), 5.47 (t, 1H, $-CH-$), 6.85 (d, 2H, 3-H and 5-H), 7.10 (d, 2H, 3′-H and 5′-H), 7.42 (m, 4H, 2-H, 6-H, 2′-H, and 6′-H).

4-((11-Hydroxyundecyl)oxy)-4′-((2-tetrahydropyranyl)oxy)biphenyl (11). **10** (2.80 g, 10.3 mmol), KOH (0.70 g, 12.4 mmol), and EtOH (40 mL) were mixed and stirred for 1 h at 60 °C before 11-bromo-1-undecanol (2.86 g, 11.4 mmol) was added. The mixture was refluxed for 16 h and then poured into water. The aqueous phase was extracted three times with CH_2Cl_2, the organic layer was then dried with $MgSO_4$, and the solvent was evaporated. The resulting solid was recrystallized from hexane/EtOAc (95/5) which gave white crystals. Yield: 3.65 g (80%). ^{1}H NMR ($CDCl_3$): δ = 1.31 (m, 14H, $-(CH_2)_7CH_2CH_2OH$), 1.54−1.68 (m, 6H, $-CH_2CH_2CH_2OCHO-$ and $-CH_2CH_2OH$), 1.80−1.90 (m, 4H, $-CH_2CH-$ and $-CH_2CH_2OAr$), 3.62 (m, 3H, $-CH_2OCHO-$ and $-CH_2CH_2OH$), 3.94 (m, 3H, $-CH_2OCHO-$ and $-CH_2CH_2OAr$), 5.47 (t, 1H, $-CH-$), 6.96 (d, 2H, 3-H and 5-H), 7.10 (d, 2H, 3′-H and 5′-H), 7.46 (m, 4H, 2-H, 6-H, 2′-H, and 6′-H).

4-[(11-(Acryloyloxy)undecyl)oxy]-4′-((2-tetrahydropyranyl)oxy)biphenyl (12a). Acryloyl chloride (1.10 g, 12.0 mmol) was dissolved in dry THF (10 mL) and added dropwise to a stirred solution of **11** (4.08 g, 9.25 mmol) and triethylamine (1.40 g, 13.88 mmol) in dry THF (25 mL) at 0 °C. After 6 h, the reaction mixture was poured into a NH_4Cl solution (15%) and was extracted three times with CH_2Cl_2. The organic phases were collected, dried with $MgSO_4$, and evaporated. The remaining solid was purified by column chromatography (silica gel, hexane/EtOAc as eluent) which gave white crystals. Yield: 2.74 g (58%). ^{1}H NMR ($CDCl_3$): δ = 1.31 (m, 14H, $-(CH_2)_7CH_2CH_2OCO-$), 1.54−1.68 (m, 6H, $-CH_2CH_2CH_2OCHO-$ and $-CH_2CH_2OCO-$), 1.80−1.90 (m, 4H, $-CH_2CH-$ and $-CH_2CH_2OAr$), 3.62 (m, 1H, $-CH_2OCHO-$), 3.94 (m, 3H, $-CH_2OCHO-$ and $-CH_2CH_2OAr$), 4.15 (t, 2H, $-CH_2CH_2OCO-$), 5.47 (t, 1H, $-CH-$), 5.84 (d, 1H, $CH_2{=}CH-$, cis), 6.14 (d, 1H, $CH_2{=}CH-$), 6.37 (d, 1H, $CH_2{=}CH-$, trans), 6.96 (d, 2H, 3-H and 5-H), 7.10 (d, 2H, 3′-H and 5′-H), 7.46 (m, 4H, 2-H, 6-H, 2′-H, and 6′-H).

4-[(11-(Methacryloyloxy)undecyl)oxy]-4′-((2-tetrahydropyranyl)oxy)biphenyl (12b). **12b** was synthesized using the procedure described for **12a**. The product was white crystals. Yield: 2.74 g (58%). ^{1}H NMR ($CDCl_3$): δ = 1.31 (m, 14H, $-(CH_2)_7CH_2CH_2OCO-$), 1.54−1.68 (m, 6H, $-CH_2CH_2CH_2OCHO-$ and $-CH_2CH_2OCO-$), 1.80−1.90 (m, 4H, $-CH_2CH-$ and $-CH_2CH_2OAr$), 1.94 (s, 3H, $CH_2{=}CCH_3COO-$), 3.62 (m, 1H, $-CH_2OCHO-$), 3.94 (m, 3H, $-CH_2OCHO-$ and $-CH_2CH_2OAr$), 4.15 (t, 2H, $-CH_2CH_2OCO-$), 5.47 (t, 1H, $-CH-$), 5.54 (s, 1H, $CH_2{=}CCH_3-$, cis), 6.09 (s, 1H, $CH_2{=}CCH_3-$, trans), 6.96 (d, 2H, 3-H and 5-H), 7.10 (d, 2H, 3′-H and 5′-H), 7.46 (m, 4H, 2-H, 6-H, 2′-H, and 6′-H).

4-Hydroxy-4′-[(11-(Acryloyloxy)undecyl)oxy]biphenyl (13a). **12a** (2.74 g, 5.37 mmol) was dissolved in a mixture of EtOH (25 mL) and THF (5 mL) at room temperature. HCl (5 mL) was added, and the solution became first milky and after a while clear. After 1 h, the reaction was stopped and poured into water. The mixture was extracted three times with CH_2Cl_2. The organic layers were then collected, dried with $MgSO_4$, and evaporated to give white crystals after recrystallization from EtOH. Yield: 1.42 g (63%). ^{1}H NMR ($CDCl_3$): δ = 1.31 (m, 14H, $-(CH_2)_7CH_2CH_2OCO-$), 1.63 (m, 2H, $-CH_2CH_2OCO-$), 1.78 (m, 2H, $-CH_2CH_2OAr$), 3.98 (m, 2H, $-CH_2CH_2OAr$), 4.15 (t, 2H, $-CH_2CH_2OCO-$), 4.78 (s, 1H, $HOAr-$), 5.84 (d, 1H, $CH_2{=}CH-$, cis), 6.14 (d, 1H, $CH_2{=}CH-$), 6.37 (d, 1H, CH_2=CH−, trans), 6.89 (d, 2H, 3-H and 5-H), 6.96 (d, 2H, 3′-H and 5′-H), 7.46 (m, 4H, 2-H, 6-H, 2′-H, and 6′-H).

4-Hydroxy-4′-[(11-(Methacryloyloxy)undecyl)oxy]biphenyl (13b). **13b** was synthesized using the procedure described for **13a**. The product was white crystals. Yield: 0.31 g (75%). ^{1}H NMR ($CDCl_3$): δ = 1.31 (m, 14H, −$(CH_2)_7CH_2$-CH_2OCO−), 1.63 (m, 2H, −CH_2CH_2OCO−), 1.78 (m, 2H, −CH_2CH_2OAr), 1.94 (s, 3H, CH_2=CCH_3COO−), 3.98 (m, 2H, −CH_2CH_2OAr), 4.15 (t, 2H, −CH_2CH_2OCO−), 4.78 (s, 1H, *H*OAr−), 5.54 (s, 1H, CH_2=CCH_3−, cis), 6.09 (s, 1H, CH_2=CCH_3−, trans), 6.89 (d, 2H, 3-H and 5-H), 6.96 (d, 2H, 3′-H and 5′-H), 7.46 (m, 4H, 2-H, 6-H, 2′-H, and 6′-H).

Ethyl 4-Hydroxy-3-nitrobenzoate (14). A single-necked 100 mL round flask equipped with a benzene-filled Dean-Stark trap and a condenser was charged with 4-hydroxy-3-nitrobenzoic acid (10.0 g, 54.6 mmol), H_2SO_4 (1 mL), EtOH (99%) (15.1 mL, 328 mmol), and benzene (10 mL). The temperature was raised to 105 °C, and the reaction mixture was stirred for 24 h. The solvents were then evaporated, and the crude product was dissolved in CH_2Cl_2 (200 mL) which was extracted twice with aqueous $NaHCO_3$ (15%) solution and twice with water. The organic phase was separated, dried with $MgSO_4$, and evaporated. Light yellow crystals were obtained. Yield: 10.6 g (92%). ^{1}H NMR ($CDCl_3$): δ = 1.40 (t, 3H, −CH_3), 4.40 (q, 2H, −CH_2CH_3), 7.21 (m, 1H, 5-H), 8.23 (d, 1H, 6-H), 8.81 (s, 1H, 2-H), 10.17 (s, 1H, −O*H*).

Ethyl 4-[(*R*)-(+)-2-Octyloxy]-3-nitrobenzoate (15). A mixture of (*S*)-(+)-2-octanol (3.00 g, 20.8 mmol) and DEAD (3.50 g, 20.8 mmol) dissolved in diethyl ether (10 mL) was dropwise added to a solution of **14** (4.40 g, 20.8 mmol) and TPP (5.40 g, 20.8 mmol) in diethyl ether, and the mixture was stirred at room temperature for 3 days. The precipitated triphenylphospine oxide was filtered off, and the solvent was evaporated. The resulting crude product was purified by column chromatography (silica gel, hexane/EtOAc as eluent) which gave a yellow oil. Yield: 5.93 g (85%). ^{1}H NMR ($CDCl_3$): δ = 0.87 (m, 3H, −$(CH_2)_5CH_3$), 1.27 (m, 8H, −$(CH_2)_4$-CH_3), 1.40 (t, 6H, −CHCH_3 and −OCH_2CH_3), 1.67 (m, 1H, −CHCH_2−), 1.81 (m, 1H, −CHCH_2−), 4.38 (q, 2H, −OCH_2-CH_3), 4.60 (m, 1H, −*CH*−), 7.09 (m, 1H, 5-H), 8.15 (d, 1H, 6-H), 8.43 (s, 1H, 2-H).

4-[(*R*)-(+)-2-Octyloxy]-3-nitrobenzoic Acid (16). **15** (1.20 g, 3.72 mmol) and KOH (0.62 g, 11.2 mmol) were mixed in ethanol (30 mL), and the mixture was stirred at 50 °C for 3 h. The reaction mixture was then acidified with HCl and poured into water and extracted three times with CH_2Cl_2. The organic phases were collected and washed twice with water, dried with $MgSO_4$, and evaporated to yield a yellow oil which solidified upon storage. Yield: 1.02 g (93%). ^{1}H NMR ($CDCl_3$): δ = 0.87 (m, 3H, −$(CH_2)_5CH_3$), 1.27 (m, 8H, −$(CH_2)_4CH_3$), 1.40 (d, 3H, −CHCH_3), 1.67 (m, 1H, −CHCH_2−), 1.81 (m, 1H, −CHCH_2−), 4.62 (m, 1H, −*CH*−), 7.11 (m, 1H, 5-H), 8.21 (d, 1H, 6-H), 8.50 (s, 1H, 2-H).

4″-[(11-(Acryloyloxy)undecyl)oxy]-4′-biphenylyl 4-[(*R*)-(+)-2-Octyloxy]-3-nitrobenzoate (A1). **13a** (1.25 g, 3.03 mmol), **16** (0.89 g, 3.03 mmol), DCC (0.81 g, 3.94 mmol), and DMAP (55 mg, 0.46 mmol) were dissolved in CH_2Cl_2 (15 mL), and the solution was stirred for 2 days at room temperature. The reaction mixture was then diluted with CH_2Cl_2 (100 mL), extracted three times with water, dried with $MgSO_4$, and evaporated. The product was purified by column chromatography (silica gel, hexane/EtOAc as eluent) which gave white crystals after recrystallization from EtOH/hexane (90/10). Yield: 1.56 g (75%). HPLC: 99.9%. Thermal characterization (Table 1). $[\alpha]_D^{20}$ = +9.7 (*c* 0.01, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 0.87 (m, 3H, −$(CH_2)_5CH_3$), 1.31 (m, 22H, −$(CH_2)_7CH_2CH_2$-OCO− and −$(CH_2)_4CH_3$), 1.40 (d, 3H, −CHCH_3), 1.63 (m, 3H, −CH_2CH_2OCO− and −CHCH_2−), 1.78 (m, 3H, −CH_2CH_2OAr and −CHCH_2−), 3.98 (m, 2H, −CH_2CH_2OAr), 4.15 (t, 2H, −CH_2CH_2OCO−), 4.62 (m, 1H, −*CH*−), 5.84 (d, 1H, CH_2=CH−, cis), 6.14 (d, 1H, CH_2=*CH*−), 6.37 (d, 1H, CH_2=CH−, trans), 6.99 (d, 2H, 3″-H and 5″-H), 7.17 (m, 1H, 5-H), 7.26 (d, 2H, 3′-H and 5′-H), 7.49 (d, 2H, 2″-H and 6″-H), 7.58 (d, 2H, 2′-H and 6′-H), 8.30 (d, 1H, 6-H), 8.50 (s, 1H, 2-H). Anal. Calcd for $C_{41}H_{53}NO_8$: C, 71.59; H, 7.77; N, 2.04. Found: C, 71.54; H, 7.76; N, 1.97.

4″-[(11-(Methacryloyloxy)undecyl)oxy]-4′-biphenylyl 4-[(*R*)-(+)-2-Octyloxy]-3-nitrobenzoate (M1). **M1** was synthesized by the procedure described for **A1**. The product was purified by column chromatography (silica gel, hexane/EtOAc as eluent) which gave white crystals after recrystallization from EtOH/hexane (90/10). Thermal characterization (Table 1). Yield: 1.78 g (75%). HPLC: 99.9%. ^{1}H NMR ($CDCl_3$): δ = 0.87 (m, 3H, −$(CH_2)_5CH_3$), 1.31 (m, 22H, −$(CH_2)_7CH_2CH_2$-OCO− and −$(CH_2)_4CH_3$), 1.40 (d, 3H, −CHCH_3), 1.63 (m, 3H, −CH_2CH_2OCO− and −CHCH_2−), 1.78 (m, 3H, −CH_2CH_2OAr and −CHCH_2−), 1.94 (s, 3H, CH_2=CCH_3COO−), 3.98 (m, 2H, −CH_2CH_2OAr), 4.15 (t, 2H, −CH_2CH_2OCO−), 4.62 (m, 1H, −*CH*−), 5.54 (s, 1H, CH_2=CCH_3−, cis), 6.09 (s, 1H, CH_2=CCH_3−, trans), 6.99 (d, 2H, 3″-H and 5″-H), 7.17 (m, 1H, 5-H), 7.26 (d, 2H, 3′-H and 5′-H), 7.49 (d, 2H, 2″-H and 6″-H), 7.58 (d, 2H, 2′-H and 6′-H), 8.30 (d, 1H, 6-H), 8.50 (s, 1H, 2-H). Anal. Calcd for $C_{42}H_{55}NO_8$: C, 71.87; H, 7.90; N, 2.00. Found: C, 71.87; H, 7.91; N, 1.92.

Polar Orientation in the Surface Stabilized Ferroelectric Liquid Crystal (SSFLC) Cell. Cells of a conventional sandwich type, consisting of two parallel glass substrates separated a distance of either 2 or 4 μm by evaporated SiO_x 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 SiO_x of about 1000 Å thickness was deposited onto the electrodes. The uniform bookshelf alignment of the liquid crystal material (smectic layers being essentially perpendicular to the plates) in the cell 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 hot stage with the temperature controlled to an accuracy of 0.1 deg, and the liquid crystalline substances were examined in a polarizing microscope (crossed polarizers).

At the temperatures (≈92 and ≈95 °C for the 70/30 and 65/35 mixtures, respectively) at which the ferroelectric electro-optic response indicated that the SmC* phase was fully developed, a dc electric field ($E \approx 30$ V/m was applied in order to orient the spontaneous polarization in the whole cell in one direction.

Thermal Stabilization by in-Situ Photopolymerization. After obtaining a ferroelectric monodomain structure for the 70/30 blend mixed with photo-initiator at the temperature (≈92 °C) at which the ferroelectric electro-optic response in the SmC* phase was fully developed, the cell was irradiated with UV light, while the dc field was kept on, for about 10 min, during which the liquid crystalline mixture polymerized. The ratio of photo-initiator to monomer was 1/250 (0.04 mol %). The low concentration of photo-initiator was sufficient to destabilize the SmC* phase, and the 65/35 mixture could not therefore be used for polymerization. In order to avoid undesired photopolymerization of the liquid crystalline material in the cell during the preparation and investigative procedures, work was performed under yellow light.

Measurement of the Pockels Effect. The Pockels effect was measured in transmission by a crossed polarizer method.[19] The electro-optic modulation of the phase difference between the incoming optical field components parallel 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 most linear detection range. The experiments were done by applying a 375 Hz sinusoidal voltage with a maximum peak-to-peak voltage of 20 V over the 2 μm electrode gap.

Results and Discussion

Design of the Cross-Linkable Ferroelectric Monomer Mixture. To incorporate the four demands described in the introduction in one monomer is possible

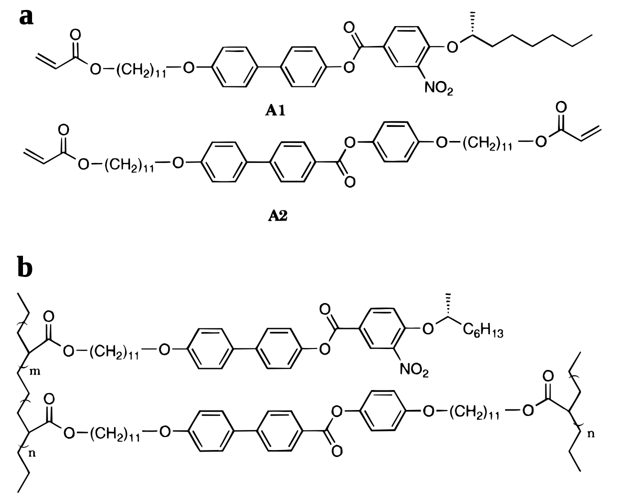


Figure 4. (a) Structures of acrylate monomers (**A1** and **A2**) in the cross-linkable ferroelectric monomer mixture and (b) structure of the cross-linked acrylate polymer.

but synthetically challenging. Therefore a two-monomer system was selected (Figure 4). Two different systems were used, an acrylate and a methacrylate system. One of the two monomers contained both a chiral part (**A1** and **M1**) and a nonlinear optical active chromophore with the dipole oriented in a direction almost perpendicular to the long axis of the molecule. This monomer had one polymerizable group attached. **A1** had an acrylic and **M1** a methacrylic polymerizable group attached. Similar structures are known to exhibit large spontaneous polarization and to display second harmonic generation.[9] The other monomers (**A2** and **M2**) were designed to generate a SmC phase, and they had two polymerizable groups attached in order to cross-link the system. Acrylates and methacrylates were selected as polymerizable groups on the basis of their inability to react due to the onset of the aligning electric field.

Synthesis of Monomers. The syntheses of the monomers and their intermediary compounds are outlined in Schemes 1 and 2.

Scheme 1, which was published in ref 17 but is for clarity reproduced here, outlines the synthesis of 4″-((11-(acryloyloxy)undecyl)oxy)phenyl 4′-(4-((11-(acryloyloxy)undecyl)oxy)phenyl)benzoate (**A2**) and 4″-((11-(methacryloyloxy)undecyl)oxy)phenyl 4′-(4-((11-(methacryloyloxy)undecyl)oxy)phenyl)benzoate (**M2**). The monomer is divided in two parts **2** and **5** which are coupled together by a low-temperature esterification using DCC and DMAP to produce **6**. **2** was synthesized by protection via esterification of 4′-hydroxy-4-biphenylcarboxylic acid with ethanol to produce **1**. **1** was further alkylated with 11-bromo-1-undecene and later deprotected by saponification with KOH to produce **2**. The other half was synthesized by monoprotection of hydroquinone with 3,4-dihydro-2*H*-pyran into **3**. **3** was then further alkylated with 11-bromo-1-undecene into **4** which was later deprotected by acidification to give **5**. The two end groups of the coupled product **6** were oxidized by using a modified version of Browns 9-BBN oxidation. The diol **7** was finally esterified using acryloyl chloride or methacryloyl chloride to produce the bifunctional monomers **A2** and **M2**.

Scheme 2 outlines the synthesis of 4″-[(11-(acryloyloxy)undecyl)oxy]-4′-biphenylyl 4-[(*R*)-(+)-2-octyloxy]-3-nitrobenzoate (**A1**) and 4″-[(11-(methacryloyloxy)undecyl)oxy]-4′-biphenylyl 4-[(*R*)-(+)-2-octyloxy]-3-nitrobenzoate (**M1**). These two monomers were also divided into two parts **13a** or **b** and **16** which were coupled by a low-temperature esterification using DCC and DMAP. **13a** and **b** were synthesized by the monoprotection of 4,4′-dihydroxybiphenyl by 3,4-dihydro-2*H*-pyran into **10**. **10** was then alkylated and further esterified using acryloyl chloride or methacryloyl chloride. HCl was produced during the esterifications, which partly deprotected the starting materials and the products into byproducts which lowered the yields, and separations on silica gel were needed. The separated products **12a** and **b** were then deprotected, in a controlled manner by HCl in ethanol, to form **13a** and **b**. **16** was synthesized by esterifying 4-hydroxy-3-nitrobenzoic acid in ethanol to give **14**. The phenol was then coupled stereospecifically to the nonracemic alcohol (*S*)-(+)-2-octanol by the Mitsunobo coupling into **15**. The Mitsunobo coupling proceeds with inversion of configuration at the stereocenter of the alcohol. Hydrolysis of the ester **15** with KOH gave the acid **16**.

Table 1. Thermal Transitions of Monomers

monomer	thermal transitions (°C) heating	cooling
A2	k 42 SmE 89 SmC 118 SmA 128 i	i 125 SmA 115 SmC 81 SmE 58 k
M2	k 84 SmE 90 SmC 123 SmA 130 i	i 127 SmA 122 SmC 74 SmE 53 k
A1	k 56 SmA* 62 i	i 61 SmA* 11 k
M1	k 43 SmA* 60 i	i 57 SmA* 17 k

Properties of the Liquid Crystalline Monomers and Their Mixtures. (a) Thermal Characterization. The mesomorphic behavior of the four monomers is summarized in Table 1. A radical inhibitor (0.1% by weight hydroquinone) was added to **A2** and **M2** in order to hinder polymerization and to permit a thermal characterization.

On cooling from the isotropic state of **A2**, a focal conic fan texture typical of SmA was formed at 128 °C. Further cooling changed this focal conic fan texture of the SmA phase into a focal conic fan texture typical of a SmC phase at 118 °C. At 89 °C, the focal conic fan texture disappeared into a texture which was identified as a SmE phase. At 42 °C, the mesophase was frozen-in and **A2** crystallized. All liquid crystalline phases of **A2** appeared on cooling and heating; i.e. they were enantiotropic. The phase behavior of **M2** was very similar to that described for **A2**. It should be noted that the phase transition temperatures may have been influenced by the admixture of inhibitor.

The nonracemic monomers **A1** and **M1** were thermally stable and did not polymerize when heated to 140 °C. The isotropic melt of **A1** was transformed into a focal conic fan texture typical of the SmA* phase at 61 °C. When **M1** was cooled, the same texture typical of SmA* phase appeared at 57 °C. The SmA* phases were enantiotropic for both **A1** and **M1**.

To obtain mixtures which had all the desired properties, one monofunctional monomer (**A1** or **M1**) and one bifunctional monomer (**A2** or **M2**) had to be mixed. Mixtures of **A1** and **A2** were thermally stable in all studied proportions. The different mixtures of the two monomers displayed enantiotropic liquid crystalline behavior. Depending on the temperature and the proportions of the two monomers, different phases were revealed, including isotropic, SmA*, SmC*, SmE*, and crystalline phases. Figure 5 shows the phase diagrams of substances **A1** and **A2**.

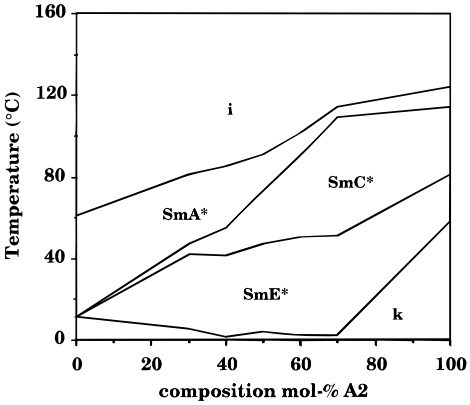


Figure 5. Phase diagram obtained on first cooling for mixtures of **A1** and **A2**.

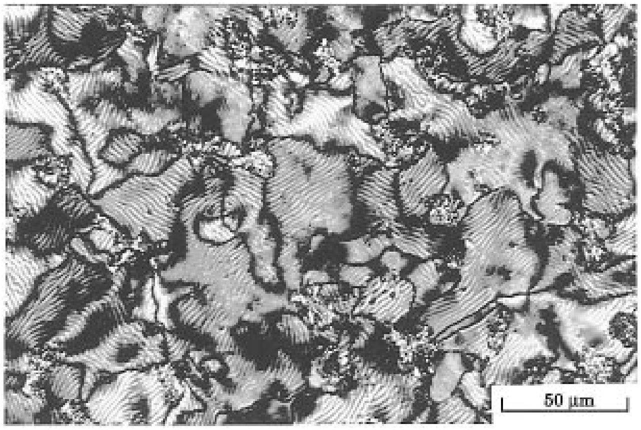


Figure 6. Polarized photomicrograph of the 50/50 blend of the **A2**/**A1** monomer mixture at 70 °C showing the liquid crystalline SmC* phase.

The desired SmC* phase, indicated by the appearance of the typical Schlieren structure texture, appeared in nearly all mixtures of the **A1** and the **A2** monomers (Figure 6).

The two methacrylate monomers **M1** and **M2** required thermal stabilization in blends with more than 70% **M1**. Mixtures of **M2** and **A1** also required thermal stabilization whereas mixtures of **M1** and **A2** were thermally stable, i.e. showed no spontaneous polymerization. Thus monomer **A2** was the more thermally stable of the two bifunctional monomers. The higher stability of **A2** is due to the higher activation energy needed to form the less stable secondary acrylic radical than the more stable and more slowly propagating tertiary methacrylic radical. This observation caused us to concentrate our further work on the acrylate system composed of **A1** and **A2**.

(b) Ferroelectric Response and Polar Orientation in the SSFLC Cell. The experiments were performed on the 70/30 **A2**/**A1** and the 65/35 **A2**/**A1** mixtures because they had the highest concentration of nonlinear optical chromophores of mixtures with stable SmC* phases (Figure 5). The 70/30 mixture consisted of 70% bifunctional monomer **A2** and 30% chiral monomer **A1** and the 65/35 mixture consisted of 65% of **A2** and 35% of **A1**.

The cell was slowly cooled from the SmA* to the SmC* phase, thus preserving the uniform alignment achieved in the SmA* phase. The two mixtures showed pronounced electroclinic and ferroelectric responses in the SmA* and SmC* phases, respectively. The behavior of the mixtures was according to expectation: where the 65/35 mixture displayed the largest spontaneous polarization and the 70/30 mixture exhibited a somewhat wider SmC* phase (Figure 7).

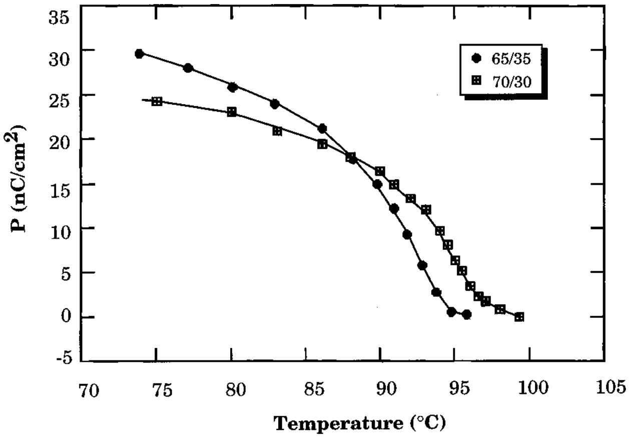


Figure 7. Polarization (**P**) obtained on first cooling as a function of temperature for the 70/30 and the 65/35 mixtures of **A2**/**A1**.

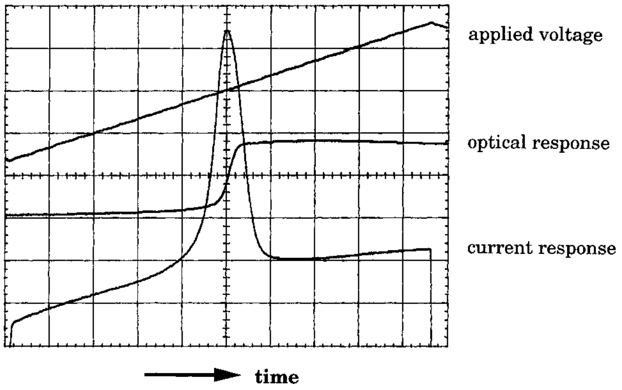


Figure 8. Ferroelectric reponse for the 70/30 blend of the **A2**/**A1** monomer mixture as observed in the oscilloscope. The upper curve shows the applied voltage, the middle curve the optical response, and the lower curve the current response.

The ferroelectric switching in the SmC* phase, here demonstrated for the 50/50 mixture, followed the applied ac field in an almost ideal way (Figure 8). Figure 8 also shows the current which flows through the cell when the applied ac field changes direction.

A homogeneous polarization direction for the whole cell was accomplished by applying a dc field. This gave a unique direction to the optic 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 or perpendicular to the transmission direction of the polarizer.

Properties of the Cross-Linked Liquid Crystals. As a consequence of the polymerization process, the texture of the sample was changed slightly after the illumination. The initially uniform bookshelf texture was disturbed by stripes oriented perpendicular to the smectic layers. Although the initial uniformity of the texture was changed after the illumination, only a small difference was found in the position of the optical axis before and after polymerization. The cross-linked polymers did not exhibit any ferroelectric response. Instead, a very weak linear electro-optical response was re-

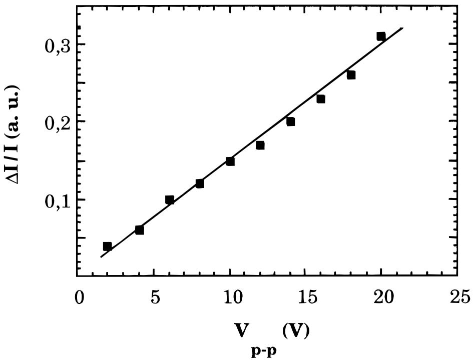


Figure 9. Modulated intensity (ac) as a function of voltage in the 70/30 mixture of A2/A1 after cross-linking at room temperature.

corded, probably corresponding to a small deviation of the molecules around their fixed position on the cone. The absence of ferroelectric switching indicates that the uniform molecular tilt in the SmC* phase was 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 the nonpolymerized liquid crystal material caused no changes in the molecular tilt of the network. DSC showed, however, a distinct endothermic peak close to 45 °C. This transition, which was observed on first and second heating and on first cooling, caused no textural changes, as revealed by polarized light microscopy. The transition has also been observed in SmA and SmB networks[13,20] but is presently not yet understood. Earlier studies have shown that the enthalpy of the transition decreases with the increasing degree of cross-linking.[13,20]

(a) Nonlinear Optical Properties. The refractive index of the isotropic material polymerized on a glass substrate was 1.556, as obtained by the *m*-line method.[21] The material is assumed to be nearly uniaxial, $n_y = n_x = n_o$ and $n_z = n_e$. If the isotropic refractive index is approximated by $n = (2n_o + n_e)/3$ and the birefringence is approximately 0.1 (visual inspection), the ordinary refractive index, $n_o = 1.52$, is obtained.

In Figure 9, $\Delta I/I$ is plotted as a function of the electric field. I is the intensity transmitted through the setup when $E = 0$.

The modulated intensity shows a linear dependence on the applied E field, as expected, for the Pockels effect (Figure 9). At an incidence angle of 26°, a value of the difference between the electro-optical coefficients ($r_{22} - r_{12}$) of 0.15 pm/V was obtained. 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 10). 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; the molecules are aligned 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 global effective 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, largest in the direction of the polar axis.

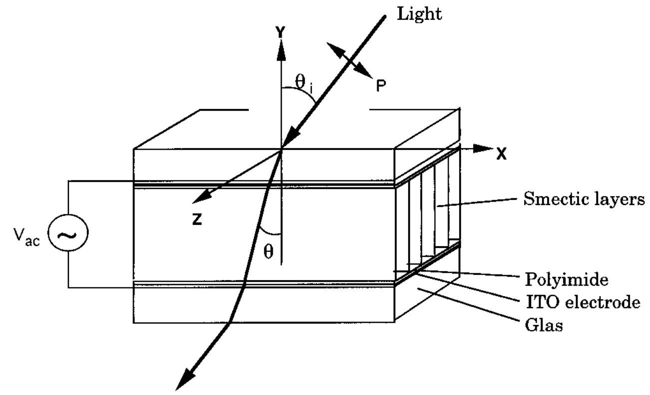


Figure 10. Configuration of the surface-stabilized ferroelectric liquid crystal (SSFLC) cell utilized in the NLO experiments.

The Pockels effect, or the linear electro-optic effect, depends on the material's macroscopic susceptibility $\chi^{(2)}$ and is observed as a modification of the material's refractive index when a low-frequency electrical field is applied.[1] The applied electric field induces a linear change in the refractive index commonly defined as

$$\Delta\left(\frac{1}{n^2}\right) = rE \tag{2}$$

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

$$\begin{pmatrix} 0 & r_{12} & 0 \\ 0 & r_{22} & 0 \\ 0 & r_{32} & 0 \\ r_{41} & 0 & r_{43} \\ 0 & r_{52} & 0 \\ r_{61} & 0 & r_{63} \end{pmatrix} \tag{3}$$

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 is related to the detected intensity variations by

$$\Delta I = \frac{1}{2} I_{\max} \Delta\Phi \tag{4}$$

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

$$\Delta\Phi = \frac{2\pi}{\lambda}\Delta n\, l \approx \frac{\pi n_0^{\,3}}{\lambda}(r_{22} - r_{12}) \sin^2 \theta \frac{l}{d} V \tag{5}$$

where λ 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} was neglected; i.e. a tilt of the refractive index ellipsoid due to the applied electric field is neglected. Measuring the second harmonic generation (SHG) in a ferroelectric liquid crystal, Schmitt and co-workers[9] found a ratio of ca. 10 to 1 between the second-order nonlinear optic coefficients d_{22} and d_{25}. If the nonlinear optic response has a purely electronic origin, the coefficients r and d

are directly inter-related. If the ratio between the electro-optic coefficients in this material is the same as that of Schmitt et al. observed between the second harmonic coefficients, the neglect of 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 9 could in principle also arise from a motion of the optic axis linear in the electric field. Therefore the nonlinear optical results were confirmed by second-harmonic generation measurements. These results will be reported in a separate paper.[22]

Conclusion

New cross-linked liquid crystalline materials with thermodynamically stable polar orders (pyroelectric) have been designed and synthesized. The starting monomer mixture in this case was ferroelectric, but could also, even to some advantage, be antiferroelectric. The Pockels effect has been observed in these pyroelectric polymer networks. The value for the difference of the electro-optic tensor $(r_{22} - r_{12})$ was determined to be 0.15 pm/V, where r_{22} is believed to give the dominant contribution. This is a very encouraging result since the cross-linked material should be more stable than the corresponding ferroelectric liquid crystal material.

The low Pockels effect observed is expected, since only 30% of the monomers had a nonlinear optical chromophore attached. A way to increase the Pockels effect, besides the use of more and stronger nonlinear optical chromophores, would be to increase the tilt angle of the optic axis prior to the polymerization. Increasing the nonlinear optical signal in the pyroelectric networks would make these substances interesting as materials for future use in electro-optic devices.

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