

Synthesis and Characterization of Bifunctional Liquid-Crystalline Monomers Showing Smectic C Phase. Photopolymerization and Cross-Linking

F. Sahlén, M. Trollsås, A. Hult, and U. W. Gedde*

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

Received June 22, 1995. Revised Manuscript Received November 28, 1995⁸

Novel syntheses of bifunctional liquid-crystalline acrylate and methacrylate monomers are described. Thermal and microstructural characterization of the monomers using small-angle X-ray scattering, differential scanning calorimetry, and optical microscopy revealed the presence of smectic A, smectic C, and smectic E phases. Photopolymerization of the bifunctional monomers conducted at different temperatures preserved the monomeric liquid-crystalline structure in the cross-linked polymers. The densely cross-linked polymers showed thermal reversibility. Mixtures of these monomers and chiral monofunctional liquid-crystalline monomers exhibited chiral smectic C mesomorphism that was permanentized by photopolymerization and subsequent cross-linking.

Introduction

Liquid-crystalline compounds exhibiting smectic C phase (s_c) mesomorphism in general and the chiral smectic C phase (s_c^*) in particular have received considerable attention during the past 15 years. The possibility of achieving ferroelectric properties in organic compounds is the main reason for the interest in substances exhibiting s_c^* mesomorphism.¹ Devices for fast electrooptical switching based on the surface-stabilized ferroelectric liquid-crystal (SSFLC) technique is one example of applications of these compounds.^{2,3} The s_c^* phase is present in liquid-crystalline substances containing a chiral center and with a tendency to form a s_c phase. That could be either a pure substance containing both properties or a mixture in which one compound has a chiral center and the other shows the s_c phase, resulting in a s_c^* phase for the blend. Numerous low molar mass compounds exhibiting s_c and s_c^* phases have been synthesized,^{4,5} and many mixtures thereof showing the s_c^* phase have been prepared.⁶ Side-chain liquid-crystalline polymers (SCLCP) showing s_c^* mesomorphism have also been synthesized.^{7,8} Polymers have advantages such as good processability and the possibility of freezing-in the structure below the glass transition temperature.⁹ Slight cross-linking (5–10 mol %, with reference to the mesogenes) of s_c^*

SCLCPs based on siloxane and acrylate polymer backbones has been achieved by Finkelmann et al.¹⁰ and Zentel et al.¹¹ This provides the opportunity to orient the liquid-crystalline phases mechanically in a reversible manner. In the work described in this paper, a more densely cross-linked network has been used to make the structure of the s_c phase permanent. Previous studies^{12,13} showed that densely (20–100 mol %, with reference to the mesogenes) cross-linked SCLCP structures preserved part of their orientation on heating to 200 °C. The reduction in orientation was more extensive in samples with lower cross-link density. These studies also showed that most of the heating-induced loss of orientation of these samples was recovered on the subsequent cooling to room temperature.

This paper describes a novel synthesis and characterization of bifunctional liquid crystalline monomers that exhibit s_c mesomorphism. The purpose has been to synthesize compounds suitable for making permanent, by photo-cross-linking, the s_c phase, or the s_c^* if mixed with a chiral compound. Photopolymerization from different liquid-crystalline phases were carried out. Polymerization of the bifunctional monomers led to cross-linked polymers, which were thermally stable with recoverable orientation.

Experimental Section

Materials. 4'-Hydroxy-4-biphenylcarboxylic acid (**1**, Scheme 1), 8-bromo-1-octene, 11-bromo-1-undecene, 3,4-dihydro-2H-pyran, dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)-pyridine (DMAP), 9-borabicyclo[3.3.1]nonane (9-BBN, 0.5 M in THF), hydrogen peroxide (35% in water), triethylamine, acryloyl chloride, and methacryloyl chloride were purchased from Aldrich. Hydroquinone **4** was purchased from BDH

(9) LeBarny, P.; Dubois, J. C. In McArdle, C. B., Ed. *Side Chain Liquid Crystal Polymers*; Blackie: Glasgow, 1989.

(10) Finkelmann, H.; Kock, H.-J.; Gleim, W.; Rehage, G. *Makromol. Chem. Rapid Comm.* **1984**, 5, 287.

(11) Zentel, R.; Reckert, G. *Makromol. Chem.* **1986**, 187, 1915.

(12) Sahlén, F.; Andersson, H.; Ania, F.; Hult, A.; Gedde, U. W. *Polymer*, in press.

(13) Andersson, H.; Gedde, U. W.; Hult, A. *Polymer* **1992**, 33, 4014.

* To whom correspondence should be addressed.

Abstract published in *Advance ACS Abstracts*, January 15, 1996.
(1) (a) Meyer, R. B.; Liébert, L.; Strzelecki, L.; Keller, P. *J. Phys. Lett.* **1975**, 36, 69. (b) Gray, G. W.; Goodby, J. W. *Smectic liquid crystals*; Leonard Hill: London, 1984; p 60. (c) Goodby, J. W. *J. Mater. Chem.* **1991**, 1, 307.

(2) Clark, N. A.; Lagerwall, S. T. *Appl. Phys. Lett.* **1980**, 36, 899.
(3) Lagerwall, S. T.; Dahl, I. *Mol. Cryst. Liq. Cryst.* **1984**, 114, 151.

(4) Gray, G. W.; Goodby, J. W. *Mol. Cryst. Liq. Cryst.* **1976**, 37, 157.
(5) Walba, D. M.; Slater, S. C.; Thurm, W. N.; Clark, N. A.; Handschy, M. A.; Supon, F. *J. Am. Chem. Soc.* **1986**, 108, 5210.

(6) Gray, G. W.; Hird, M.; Lacey, D.; Toyne, K. *J. Mol. Cryst. Liq. Cryst.* **1990**, 191, 1.

(7) Shibaev, V.; Kozlovsky, M.; Beresnev, L.; Blinov, L.; Platé, A. *Polym. Bull.* **1984**, 12, 299.

(8) Kapitza, H.; Zentel, R.; Tweig, R. J.; Nguyen, C.; Vallerien, S. U.; Kremer, F.; Willson, C. G. *Adv. Mater.* **1990**, 2, 539.

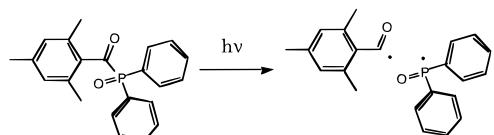
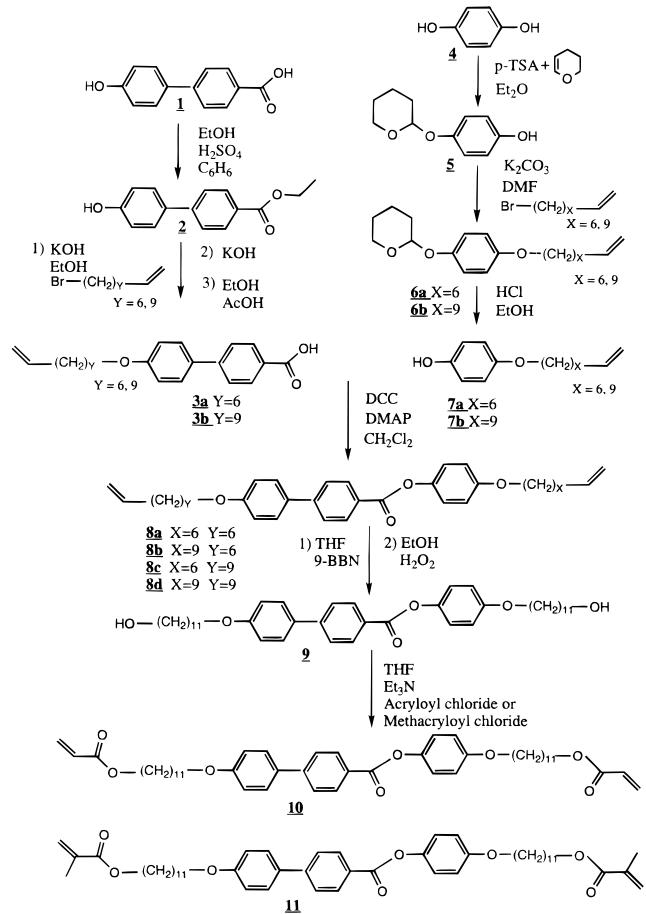


Figure 1. Photoinitiator used for radical polymerization (2,4,6-trimethylbenzoyldiphenylphosphine oxide). The substance decomposes into two active species when irradiated by ultraviolet light.

Scheme 1. Synthesis of Substances 10 and 11



Chemicals Ltd. 2,4,6-Trimethylbenzoyldiphenylphosphine oxide (Lucirin), purchased from BASF, was used as photoinitiator (Figure 1). All substances were used without further purification.

Synthesis of monomers. *Ethyl-4-(4-hydroxy)phenyl Benzoate (2).* **1** (5.27 g, 24.60 mmol) was dissolved in a solution of 50 mL of ethanol (99.5%) and 50 mL of benzene. 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 $MgSO_4$, filtered, and evaporated. The yellow-white powder was dissolved in $CHCl_3$, where unreacted **1** precipitated. The $CHCl_3$ solution was filtered and evaporated resulting in a white crystalline powder, yield 4.79 g (80%). 1H NMR ($CDCl_3$) δ 1.42 (t, 3H, $-CH_2CH_3$), 4.40 (q, 2H, $-CH_2CH_3$), 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-(8-Octenyloxy)-4-biphenylcarboxylic Acid (3a) and 4-(11-Undecenyloxy)-4-biphenylcarboxylic Acid (3b). **2** (6.0 g, 24.77 mmol), KOH (85%, 1.88 g, 28.41 mmol) and a catalytic amount of KI was dissolved in ethanol (30 mL). After 1 h 8-bromo-1-octene (4.73 g, 24.77 mmol) or 11-bromo-1-undecene (5.76 g, 24.77 mmol) was added and refluxed for 24 h. KOH (4.90 g, 74.31 mmol) was then added to hydrolyze the ester. The precipitate was filtered from the solution, washed with water,

and then dissolved in a mixture of 30 mL of acetic acid and 30 mL of ethanol and stirred for 1 h at 120 °C to prepare the carboxylic acid. The final product, a white crystalline powder, precipitated during cooling and was filtered, yield 5.20 g (60%) for **3a** and 6.00 g (66%) for **3b**. 1H NMR ($CDCl_3$) δ 1.34 (m, (6H, $-OCH_2CH_2(CH_2)_3$ for **3a**) and (12H, $-OCH_2CH_2(CH_2)_6$ for **3b**)), 1.80 (p, 2H, $-OCH_2CH_2-$), 2.05 (q, 2H, $CH_2=CHCH_2-$), 4.01 (t, 2H, $-OCH_2-$), 4.93 (d, 1H, $CH_2=CH-$ cis), 4.98 (d, 1H, $CH_2=CH-$ trans), 5.79 (m, 1H, $CH_2=CH-$), 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-Tetrahydropyranloxy)phenol (5). **4** (15.0 g, 136.23 mmol) was dissolved in diethyl ether with a catalytic amount of *p*-TSA at room temperature. 3,4-Dihydro-2*H*-pyran (5.73 g, 68.11 mmol) was added dropwise, and the solution was stirred for 1 h. A mixture of ethanol and ammonia (1:1) was added until the solution turned basic. The reaction mixture was poured into water and extracted three times with CH_2Cl_2 . The organic phase was separated and washed (3 \times H_2O), dried ($MgSO_4$), filtered, 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%). 1H NMR ($CDCl_3$) δ 1.65 (m, 4H, $-CH_2CH_2CH_2OCHO-$), 1.87 (m, 2H, $-CH_2-$), 3.62 (m, 1H, $-CH_2OCHO-$), 3.94 (m, 1H, $-CH_2OCHO-$), 4.64 (s, 1H, $HOAr-$), 5.27 (t, 1H, $-CH-$), 6.73 (d, 2H, 2-H and 6-H), 6.95 (d, 2H, 3-H and 5-H).

*4-(2-Tetrahydropyranloxy)-1-(8-octenyl)benzene (**6a**) and 4-(2-Tetrahydropyranloxy)-1-(11-undecenyl)benzene (**6b**).* **5** (5.0 g, 25.74 mmol) and K_2CO_3 (10.67 g, 77.22 mmol) were dissolved in DMF and stirred for 1 h at room temperature. 8-Bromo-1-octene (4.92 g, 25.74 mmol) or 11-bromo-1-undecene (6.00 g, 25.74 mmol) were then added. The solution was heated to 100 °C and kept at that temperature for 24 h while being stirred. DMF was then removed by vacuum distillation. The reaction product was poured into water and extracted three times with CH_2Cl_2 . The organic phase was separated, washed (3 \times H_2O), dried ($MgSO_4$), filtered, and evaporated. The product was purified by column chromatography (silica gel, hexane/EtOAc as eluent). The final product **6a** was a liquid, while **6b** was white crystals, yield 5.02 g (66%) for **6a** and 5.60 g (65%) for **6b**. 1H NMR ($CDCl_3$) δ 1.30 (m, (4H + 6H, $-CH_2CH_2CH_2OCHO-$ and $CH_2=CHCH_2(CH_2)_3-$ for **6a**) and (4H + 12H, $-CH_2CH_2CH_2OCHO-$ and $CH_2=CHCH_2(CH_2)_6-$ for **6b**)), 1.66 (m, 2H, $-CH_2CHO-$), 1.86 (m, 2H, OCH_2CH_2-), 2.07 (m, 2H, $CH_2=CHCH_2-$), 3.60 (m, 1H, $-CH_2OCHO-$), 3.91 (t, 2H, $-OCH_2(CH_2)_5-$), 3.94 (m, 1H, $-CH_2OCHO-$), 4.94 (d, 1H, $CH_2=CH-$, cis), 5.00 (d, 1H, $CH_2=CH-$, trans), 5.28 (t, 1H, $-OCHO-$), 5.81 (m, 1H, $CH_2=CH-$), 6.81 (d, 2H, 2-H and 6-H), 6.98 (d, 2H, 3-H and 5-H).

*4-(8-Octenyl)phenol (**7a**) and 4-(11-Undecenyl)phenol (**7b**).* **6a** (4.90, 16.74 mmol) or **6b** (5.60 g, 16.74 mmol) and a catalytic amount of HCl were dissolved in 20 mL of ethanol at room temperature. The solution was stirred for 1 h and then poured into water and extracted three times with CH_2Cl_2 . The organic phase was separated and washed three times with water, dried with $MgSO_4$, filtered, and evaporated. The remaining products were a liquid in the case of **7a** and white crystals for **7b**, yield 3.18 g (90%) for **7a** and 4.23 g (90%) for **7b**. 1H NMR ($CDCl_3$) δ 1.28 (m, (6H, $CH_2=CHCH_2(CH_2)_3-$, for **7a**) and (12H, $CH_2=CHCH_2(CH_2)_6-$, for **7b**)) 1.74 (p, 2H, OCH_2CH_2-), 2.04 (q, 2H, $CH_2=CHCH_2-$), 3.80 (t, 2H, $-OCH_2CH_2-$), 4.92 (d, 1H, $CH_2=CH-$, cis), 4.98 (d, 1H, $CH_2=CH-$, trans), 5.50 (m, 1H, $CH_2=CH-$), 6.76 (s, 4H, 2-H, 3-H, 5-H, and 6-H).

*4-(8-Octenyl)phenyl 4-(4-(8-Octenyl)phenyl)benzoate (**8a**).* **3a** (0.50 g, 1.54 mmol), **7a** (0.33 g, 1.54 mmol), DCC (0.41 g, 2.00 mmol), and DMAP (0.028 g, 0.23 mmol) were dissolved in 15 mL of CH_2Cl_2 and refluxed for 24 h. The solution was then cooled to -5 °C for 30 min. The precipitate was filtered from the solution before the solvent was evaporated. The resulting solid was recrystallized from ethanol twice to give white crystals, yield 0.50 g (63%). Thermal characterization is shown in Table 1. 1H NMR ($CDCl_3$) δ 1.31 (m, 12H, $CH_2=CHCH_2(CH_2)_3-$), 1.79 (m, 4H, $-OCH_2CH_2-$), 2.05 (m, 4H, $CH_2=CHCH_2-$), 3.95 (t, 2H, $-ArArOCH_2CH_2-$), 4.01 (t, 2H, $-ArOCH_2CH_2-$), 4.93 (d, 2H, $CH_2=CH-$, cis), 5.00 (d, 2H,

Table 1. Thermal Transitions and Physical Structures of Substances 8a–d and 9–11 As Obtained from Optical Microscopy, DSC,^a and SAXS

compound	thermal transitions (°C) ^b	
	heating	cooling
8a	k44s _B 117s _A 192i	i187s _A 111s _B 48
8b	k59s _B 117s _A 188i	i182s _A 112s _B 35k
8c	k61s _B 115s _C 159s _A 187i	i181s _A 153s _C 109s _B 46k
8d	k84s _B 117s _C 160s _A 181i	i176s _A 154s _C 112s _B 72k
9	k86s _E 143s _C 160s _A 170i	i165s _A 160s _C 127s _E 70k
10	k78s _E 89s _C 118s _A 128i	i125s _A 115s _C 81s _E 58k
11	k84s _E 90s _C 123s _A 130i	i127s _A 122s _C 74s _E 53k

^a Data refer to second heating and first cooling. ^b k: crystalline; s_E: smectic E; s_B: smectic B; s_C: smectic C; s_A: smectic A; i: isotropic.

*CH*₂=CH–, trans), 5.82 (m, 2H, *CH*₂=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-Undecenylloxy)phenyl 4-(4-(8-Octenylloxy)phenyl)benzoate (8b). **8b** was synthesized by the same procedure used for the synthesis of **8a**. **3a** (0.50 g, 1.54 mmol), **7b** (0.39 g, 1.54 mmol), DCC (0.41 g, 2.00 mmol), and DMAP (0.028 g, 0.23 mmol) were dissolved in 15 mL of *CH*₂Cl₂ and refluxed for 24 h. After purification the product was obtained as white crystals, yield 0.63 g (73%). Thermal characterization is shown in Table 1. ¹H NMR (CDCl₃) δ 1.31 (m, 18H, *CH*₂=CHCH₂(*CH*₂)₃– and *CH*₂=CHCH₂(*CH*₂)₆–, 1.79 (m, 4H, (OCH₂*CH*₂–), 2.05 (m, 4H, CH₂=CH*CH*₂–), 3.95 (t, 2H, –ArArOCH₂*CH*₂–), 4.01 (t, 2H, –ArOCH₂*CH*₂–), 4.93 (d, 2H, *CH*₂=CH–, cis), 5.00 (d, 2H, *CH*₂=CH–, trans), 5.82 (m, 2H, *CH*₂=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-(8-Octenylloxy)phenyl 4-(4-(11-Undecenylloxy)phenyl)benzoate (8c). **8c** was synthesized by the same procedure used for the synthesis of **8a**. **3b** (0.50 g, 1.36 mmol), **7a** (0.29 g, 1.36 mmol), DCC (0.36 g, 1.77 mmol), and DMAP (0.025 g, 0.20 mmol) were dissolved in 15 mL of *CH*₂Cl₂ and refluxed for 24 h. The product was obtained as white crystals after purification, yield 0.62 g (81%). Thermal characterization is shown in Table 1. ¹H NMR (CDCl₃) δ 1.31 (m, 18H, *CH*₂=CHCH₂(*CH*₂)₆– + *CH*₂=CHCH₂(*CH*₂)₃–, 1.79 (m, 4H, –OCH₂*CH*₂–), 2.05 (m, 4H, CH₂=CH*CH*₂–), 3.95 (t, 2H, –ArArOCH₂*CH*₂–), 4.01 (t, 2H, –ArOCH₂*CH*₂–), 4.93 (d, 2H, *CH*₂=CH–, cis), 5.00 (d, 2H, *CH*₂=CH–, trans), 5.82 (m, 2H, *CH*₂=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-Undecenylloxy)phenyl 4-(4-(11-Undecenylloxy)phenyl)benzoate (8d). **8d** was synthesized by the same procedure used for the synthesis of **8a**. **3b** (0.50 g, 1.36 mmol), **7b** (0.48 g, 1.36 mmol), DCC (0.37 g, 1.77 mmol), and DMAP (0.025 g, 0.20 mmol) were dissolved in 15 mL of *CH*₂Cl₂ and refluxed for 24 h. The product was obtained as white crystals after purification, yield 0.69 g (85%). Thermal characterization is shown in Table 1. ¹H NMR (CDCl₃) δ 1.31 (m, 24H, *CH*₂=CHCH₂(*CH*₂)₆–, 1.79 (m, 4H, –OCH₂*CH*₂–), 2.05 (m, 4H, *CH*₂=CH*CH*₂–), 3.95 (t, 2H, –ArArOCH₂*CH*₂–), 4.01 (t, 2H, –ArOCH₂*CH*₂–), 4.93 (d, 2H, *CH*₂=CH–, cis), 5.00 (d, 2H, *CH*₂=CH–, trans), 5.82 (m, 2H, *CH*₂=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-Hydroxyundecenylloxy)phenyl 4-(4-(11-Hydroxyundecenylloxy)phenyl)benzoate (9). All glassware was dried overnight in an oven at 150 °C. **8d** (1.00 g, 1.67 mmol) was added to a 100 mL flask and 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 atmosphere. 9-BBN (0.5 M in THF, 10 mL, 5 mmol) was then added through a septum, and the solution was further stirred for 3 h at room temperature under argon atmosphere. Then 10 mL of ethanol was added, and the oxidation was carried

out by adding H₂O₂ (35%, 3 mL, 30 mmol). The solution was stirred for 1 h and then poured into water. White crystals precipitated and were filtered from the solution, yield 1.05 g (99%). Thermal characterization is shown in Table 1. The product was insoluble in deuterated chloroform, acetone, or DMSO; hence no ¹H NMR characterization was possible. FT IR (KBr) 3334 (O–H stretch); 2928, 2851 (aliphatic C–H stretch); 1744 (C=O stretch); 1618 (aromatic C=C stretch); 1517 (aromatic carbon to carbonyl carbon stretch); 1299–1217 cm⁻¹ (several C–O stretches).

4-(11-Acryloyloxyundecyloxy)phenyl 4-(4-(11-Acryloyloxyundecyloxy)phenyl)benzoate (10). **9** (0.50 g, 0.79 mmol) and triethylamine (0.24 g, 2.37 mmol) was dissolved in THF (40 mL) at 60 °C and stirred for 1 h. Acryloyl chloride (0.22 g, 2.05 mmol) dissolved in 10 mL of THF was then added dropwise while the solution was well stirred. The reaction mixture was then stirred for 20 h. The reaction product was poured into water (NH₄Cl 10%) and extracted three times with *CH*₂Cl₂. The organic phase was separated and washed three times with water, dried with MgSO₄, filtered and evaporated. The product was purified by column chromatography (silica gel, hexane/EtOAc as eluent) and the resulting solid was recrystallized from ethanol twice to give white crystals, yield 0.30 g (50%), purity (HPLC) 99%. Thermal characterization is shown in Table 1. ¹H NMR (CDCl₃) δ 1.32 (m, 28H, *CH*₂=CHCH₂(*CH*₂)₇–), 1.66 (m, 4H, –COOCH₂*CH*₂–), 1.80 (m, 4H, –ArOCH₂*CH*₂–), 3.95 (t, 2H, –ArArOCH₂*CH*₂–), 4.01 (t, 2H, –ArOCH₂*CH*₂–), 4.16 (t, 4H, –COOCH₂–), 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. Found for: C₄₇H₆₂O₈; C, 74.94; H, 8.17. Calcd: C, 74.77; H, 8.28.

4-(11-Methacryloyloxyundecyloxy)phenyl 4-(4-(11-Methacryloyloxyundecyloxy)phenyl)benzoate (11). **11** was synthesized by the same procedure used for the synthesis of **10**. **9** (0.54 g, 0.85 mmol) and triethylamine (0.34 g, 3.40 mmol) was dissolved in THF at 60 °C and stirred for 1 h. Then methacryloyl chloride (0.23 g, 2.55 mmol) dissolved in 10 mL of THF was added slowly. After purification, the product was obtained as a white crystalline powder, yield 0.30 g (48%). Purity could not be measured by HPLC since the compound was insoluble in acetonitrile. Thermal characterization is shown in Table 1. ¹H NMR (CDCl₃) δ 1.30 (m, 28H, *CH*₂=CHCH₂(*CH*₂)₇–), 1.65 (m, 4H, –COOCH₂*CH*₂–), 1.77 (m, 4H, –ArOCH₂*CH*₂–), 1.93 (s, 6H, (CH₂=CCH₃OO–)₂), 3.95 (t, 2H, –ArArOCH₂*CH*₂–), 4.01 (t, 2H, –ArOCH₂*CH*₂–), 4.12 (t, 4H, –COOCH₂–), 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. Found for: C₄₉H₆₆O₈; C, 72.94; H, 8.31. Calcd: C, 75.16; H, 8.49.

Methods and Characterizations. Monomers **10** and **11** polymerized upon heating above 93 and 90 °C, respectively (Figure 2). To hinder unwanted thermal polymerization an inhibitor (hydroquinone) was mixed with the monomers, at an inhibitor concentration of 0.1 wt %. To photopolymerize the monomers in a controlled way at different temperatures, the monomer-inhibitor blend was mixed with a photoinitiator at a photoinitiator-to-monomer ratio of 1:250. The inhibitor and initiator were added to the monomer as a dilute solution in *CH*₂Cl₂. Isothermal photopolymerization was carried out between glass slides on a microscope hot stage.

Chemical characterizations of the substances shown in Scheme 1 were carried out by ¹H NMR on a Bruker 250 MHz and where necessary by IR spectroscopy (Perkin-Elmer 1760X). Purity was measured by HPLC (Vaiian 500). Thermal characterization was carried out on a Perkin-Elmer DSC-7, using a heating-cooling rate of 10 °C min⁻¹. Thermal degradation studies were carried out on a Perkin-Elmer TGA-7, using a heating rate of 10 °C min⁻¹. Polarized light microscopy (Leitz Ortholux POL BKII equipped with an FP 82 Mettler hot stage and an FP 80 central processor) was used for thermal and morphological characterization. Small-angle X-ray scattering (SAXS) patterns of the liquid-crystalline phases were recorded

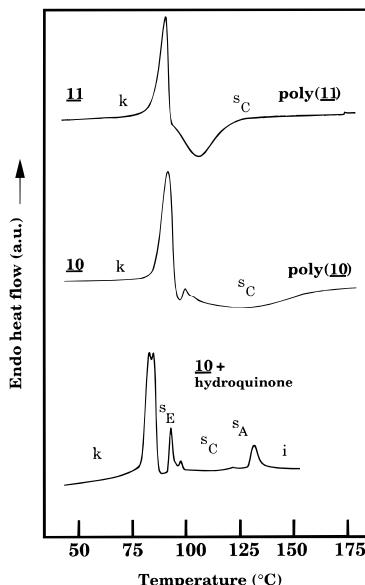


Figure 2. DSC thermograms of monomers **10** and **11** on heating. The endotherm represents a k - s_C transition via a s_E phase. The exotherm indicates thermally induced polymerization. The thermogram at the bottom shows the phase transitions of **10** mixed with an inhibitor.

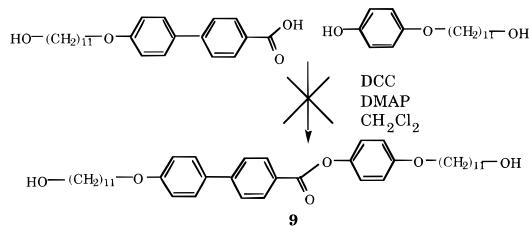


Figure 3. The reaction between 4'-(11-undecanoloxy)-4-biphenylcarboxylic acid and 4-(11-undecanoloxy)phenol intended to synthesize compound **9** did not succeed. The reason for the failure was probably that 4'-(11-undecanoloxy)-4-biphenylcarboxylic acid reacted with itself.

on a Statton camera, equipped with a resistive oven, using $\text{Cu K}\alpha$ radiation from a Philips PW 1830 generator. Infrared dichroic measurements were carried out on a Perkin-Elmer 1760X FT IR. An OSRAM Ultra-Vitalux lamp (300 W) served as ultraviolet source for photopolymerization.

Results and Discussion

Synthesis of Monomers. According to ref 4, compounds with the chemical formula $\text{C}_n\text{H}_{n+1}-\text{OArArCOOArO}-\text{C}_m\text{C}_{m+1}$ exhibit s_C mesomorphism. Reference 5 provides information about the occurrence of the s_C phase in substances of the general chemical formula: $\text{C}_n\text{H}_{n+1}-\text{CORE}-\text{C}_m\text{C}_{m+1}$, and it was suggested that the greatest possibility of obtaining the s_C phase occurred in a compound with $n = 9$ and $m = 9$. This information led to the synthesis in Scheme 1. In the first attempt to prepare **9**, the compounds 4'-(11-hydroxyundecyloxy)-4-biphenylcarboxylic acid (cf. compound **3b** with a terminal hydroxyl group instead of a vinyl group) and 4-(11-hydroxyundecyloxy) phenol (cf. compound **7b** with a terminal hydroxyl group instead of a vinyl group) were synthesized. The subsequent esterification reaction using the same conditions as in the synthesis of compounds **8a-d** did not yield **9** (Figure 3). It is proposed that 4'-(11-hydroxyundecyloxy)-4-biphenylcarboxylic acid reacted with itself or more probably reacted with DCC forming a stable amide

compound.¹⁴ This suggestion is based on the ^1H NMR spectrum of the product from the reaction between 4'-(11-hydroxyundecyloxy)-4-biphenylcarboxylic acid and 4-(11-hydroxyundecyloxy) phenol which appeared to be identical to the ^1H NMR spectrum of the product formed with 4'-(11-hydroxyundecyloxy)-4-biphenylcarboxylic acid reacted only with DCC and DMAP.

Substances **8a-d** were synthesized in order to establish which spacer lengths were needed to obtain the s_C phase. Table 1 shows that **8a** and **8b** exhibited enantiotropic s_A and s_B phases, whereas **8c** and **8d** showed enantiotropic s_A , s_C , and s_B phases. In the synthetic route, **8d** was chosen to be used as a frame for the further synthesis.

The unsaturated terminal groups of the spacers can be transformed into hydroxyl groups. Brown's hydration of an alkene via hydroboration–oxidation^{15,16} gives primary alcohols to an extent of 99%. The reaction proceeds in two steps, where the first step includes a hydroboration of the unsaturation, using 9-BBN as reagent and the second step is, according to Brown,^{15,16} initiated by adding absolute ethanol, continued by adding NaOH solution, and completed by adding hydrogen peroxide. Following this scheme, the phenyl benzoate in compound **8d** hydrolyzed in the basic environment. To avoid the hydrolyzation of the phenyl benzoate, we tried a scheme without the NaOH solution, which gave good results and resulted in a 99% yield. To our knowledge, this is a new way of transforming an unsaturation to an alcohol, on compounds sensitive to basic conditions, using Brown's hydration of alkenes via hydroboration–oxidation.

9 is a versatile substance containing two terminal hydroxyl groups, which provide the possibility of attaching various functional groups. Acrylic and methacrylic groups were selected for the photoinitiated radical polymerization. Other polymerizable groups, for example, vinyl ethers and epoxides, can also be used as end groups. Substance **9** showed enantiotropic s_A , s_C , and s_E phases (Table 1).

The final products, substances **10** and **11**, polymerized without initiators present when heated above 93 and 90 °C, respectively. Both compounds entered the s_C phase as monomers before polymerization. Figure 2 shows the heating thermograms of monomers **10** and **11**. First an endotherm appears going from the crystalline state to the s_C phase via the s_E phase. This phase sequence was clearly seen in the optical microscope but the two phase transitions are covered under the same peak in the thermogram. An exotherm is then seen when the monomer polymerizes. The polymerization was also visible in the microscope. The cross-linked polymer formed, retained the s_C phase structure. Since monomers **10** and **11** polymerized upon heating, the liquid-crystalline phases of **10** and **11** were revealed by admixing a radical inhibitor (hydroquinone) in a concentration of 0.1 wt %. The inhibitor completely hindered polymerization and allowed the phase structures to be determined. **10** and **11** showed enantiotropic s_A , s_C , and s_E phases (Table 1). In Figure 2 the thermogram

(14) Moore, J. S.; Stupp, S. I. *Macromolecules* **1990**, *23*, 65.

(15) Brown, H. C.; Knights, E. F.; Scouten, C. G. *J. Am. Chem. Soc.* **1974**, *96*, 7765.

(16) Brown, H. C.; Liotta, R.; Scouten, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 5297.

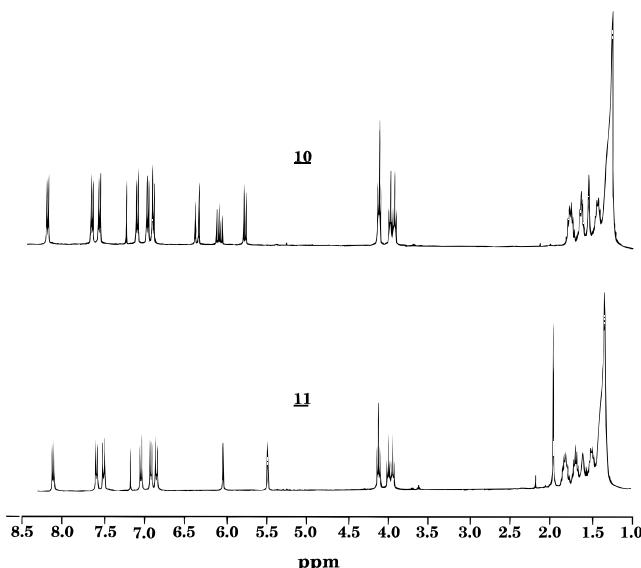


Figure 4. ^1H NMR spectra of monomers **10** and **11**.

of **10** mixed with hydroquinone is seen. The phase transition temperatures may have been influenced somewhat by the admixture of inhibitor. ^1H NMR of **10** and **11** is shown in Figure 4, where the typical acrylate peaks of **10** and methacrylate peaks of **11** are seen between 5.5 and 6.5 ppm.

Phase Characterization and Polymerization. Substances **8a–d**, **9**, **10**, **11**, poly(**10**), and poly(**11**) have been characterized according to their liquid-crystalline phases. s_A , s_B , s_C , and s_E phases were found (Table 1). In the optical microscope the s_A and the s_B phases appeared with focal conic texture as well as homeotropic texture, where the cones of the s_B phase were smoother than in the s_A phase. The s_C phase appeared with its characteristic Schlieren texture, emerging from homeotropic s_A texture, as well as blurry paramorphotic focal conic texture. The paramorphotic s_E phase appeared with sandy focal conic texture as well as homeotropic texture. Poly(**10**) and poly(**11**) made permanent the liquid-crystalline phase of the monomer by the cross-linking reaction. Unambiguous phase characterization was carried out with X-ray diffraction on aligned samples. Monomers were aligned in a magnetic field and oriented polymers were achieved by photopolymerization of surface aligned monomers. The s_A , s_B , and s_E phases, which are orthogonal phases, showed arc-shaped equatorial outer reflections perpendicular to the spotlike inner reflections on the meridian. The outer reflection recorded in the s_A phase was broad, whereas those recorded in the s_B and s_E phases were considerably sharper. In the s_E phase at least two different outer reflections appeared, originating from two different intermesogenic distances. The broad outer reflection recorded in the s_C phase was not located perpendicular to the inner spotlike reflection, revealing a tilted phase.

Photopolymerization of the bifunctional monomers was carried out to make the liquid crystalline phase of the mesogenic groups permanent. The advantage of photopolymerization over thermal polymerization is that the temperature at which the polymerization proceeds can be chosen freely. This allows a proper selection of a suitable mesophase of the monomer prior to polymerization. In situ photopolymerization of liquid-crystalline acrylates and diacrylates has been thoroughly described by Broer et al.^{17–19}.

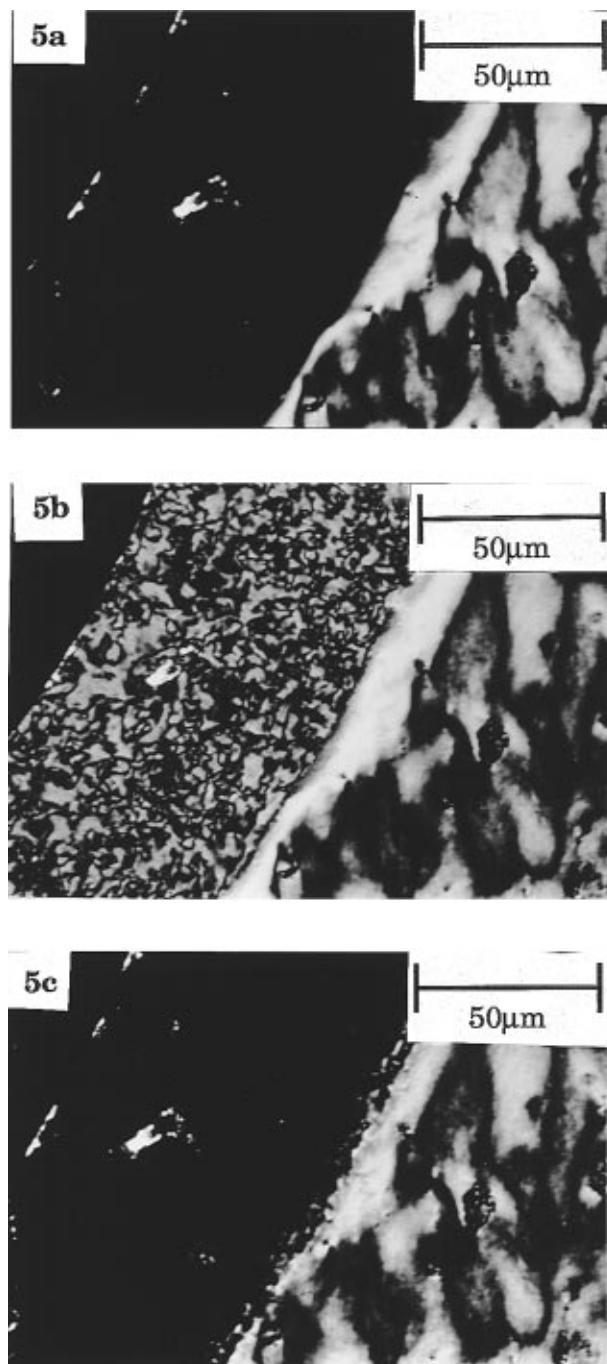


Figure 5. Polarized photomicrographs of poly(**10**) polymerized at 110 °C. Monomer residue is seen with the polymer network at (a) 125, (b) 110, and (c) 95 °C.

Photomicrographs of poly(**10**), polymerized at 110 °C (monomer in s_C state), are presented in Figure 5. Due to oxygen inhibition of the radical polymerization, there are monomer residues at the edges of the polymer samples. Figure 5a shows the texture at 125 °C with monomer residues in a homeotropically aligned s_A phase and the polymer exhibiting the typical Schlieren texture of the s_C phase. Figure 5b shows the structure at 110 °C where the monomer residues exhibited a nonorthogonal s_C phase. At 95 °C, the monomer residues

(17) Broer, D. J.; Mol, G. N.; Challa, G. *Makromol. Chem.* **1989**, *190*, 19.

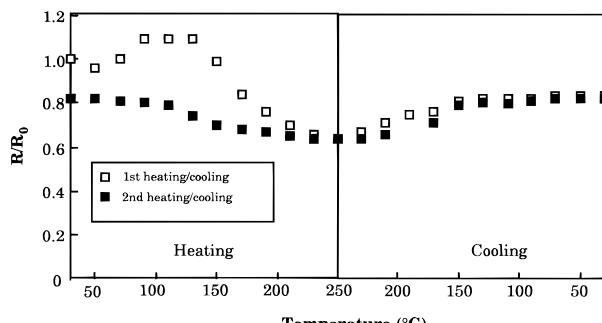
(18) Broer, D. J.; Boven, J.; Mol, G. N.; Challa, G. *Makromol. Chem.* **1989**, *190*, 2255.

(19) Broer, D. J.; Finkelmann, H.; Kondo, K. *Makromol. Chem.* **1988**, *189*, 185.

Table 2. X-ray Data of Poly(10) Polymerized at Different Temperatures (T_p)

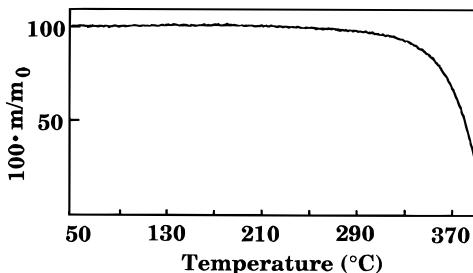
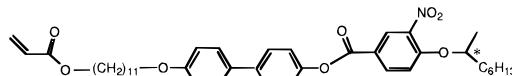
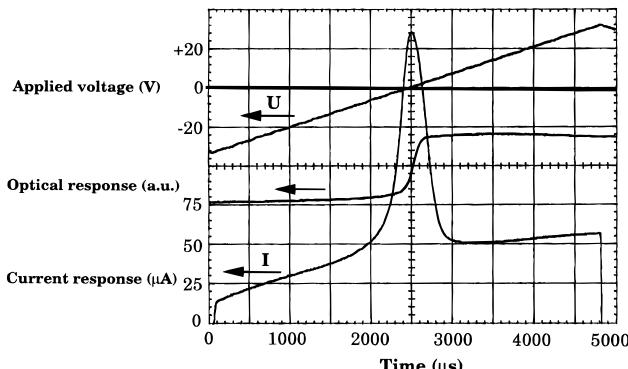
T_p (°C)	monomer phase ^a	polymer structure	spacings ^b (nm)		
			d_1	d_2	d_3
125	SA	SA	0.45	diffuse	4.6 sharp
110	SC	SC	0.45	diffuse	4.0 sharp
80	SE	SE	0.45	sharp	0.39 sharp
					4.6 sharp

^a SE: smectic E; SC: smectic C; SA: smectic A. ^b d_1 : intermesogenic distance; d_2 : intermesogenic distance; d_3 : smectic layer distance; diffuse: average distance; sharp: distinct distance.

**Figure 6.** Normalized dichroic ratio, R/R_0 , plotted versus the temperature of uniaxially aligned poly(10).

showed a homeotropically aligned s_E phase (Figure 5c). Depending on the polymerization temperature, s_A , s_C , and s_E type polymer networks were made of poly(10). The structures of the liquid-crystalline-like polymer networks of poly(10) were confirmed by X-ray diffraction. The characteristic dimensions of the mesophases were obtained from the reflection patterns (Table 2).

Thermal Stability. Aligned cross-linked polymer samples were made by *in situ* photopolymerization of monomers in contact with a uniaxially rubbed polyimide surface. The thermal stability of the alignment was investigated by infrared dichroism according to the procedure described in ref 12. A sample of uniaxially aligned **10** was polymerized in the smectic C phase at 100 °C between two potassium bromide pellets. The dichroic ratio ($R = A_{||}/A_{\perp}$) was calculated based on the absorptions parallel and perpendicular to the sample alignment and the normalized dichroic ratio (R/R_0 , where R_0 represents the dichroic ratio at the starting temperature) was plotted versus the temperature. Figure 6 shows that the alignment increased on the first heating of the sample and then decreased gradually to 65% of its starting value at 250 °C. The alignment was regained to about 80% of its original value after cooling to room temperature. Further temperature cycling led to no change in the dichroic ratio–temperature curve, and the low-temperature alignment was always regained. The increase in the alignment during the first heating was probably due to monomer residue leaving the crystal-like smectic E phase and entering the smectic C phase, thus being able to align along the director of the network. The irreversible decrease in orientation occurring during the first heating–cooling cycle was caused by the reaction of isotropic monomer residue. The permanent loss of order, of about 20%, after the first heating–cooling cycle was caused by continued thermal polymerization of the monomer residue in its isotropic phase, thus making permanent a non-ordered state. There was no sign of degradation of the polymer inside the potassium bromide cell, concluded from that the infrared spectra before and after heating to 250 °C looked identical. However, at

**Figure 7.** Thermogravimetric analysis of poly(**10**) showing thermal degradation starting at 280 °C (heating rate 10 °C min⁻¹). m represents the sample mass at a given temperature and m_0 represents the sample mass at the starting temperature.**Figure 8.** Chiral liquid-crystalline monomer **12**.**Figure 9.** Optical and current response of the monomer mixture **10** and **12** (1:1 molar ratio) at 65 °C in the ferroelectric state (s_C^*).²⁰ Data plotted from an oscilloscope.

the edges of the sample, where oxygen was present, it somewhat turned yellow-brown. Figure 7 shows a thermal gravimetric analysis of a 20 μ m thin film of poly(**10**) where the weight loss and degradation is seen to start at about 280 °C. The polymer network may contain about 10% unreacted monomer, based on the infrared dichroic measurements.

Ferroelectric Mixture. By mixing **10** with a chiral liquid-crystalline monofunctional monomer, **12** (Figure 8), a s_C^* phase was obtained. **12** exhibits an enantiotropic chiral smectic A phase, but when the two compounds were mixed in a 1:1 molar ratio the blend showed a s_C^* phase between 82 and 87 °C on heating and 85 and 57 °C on cooling. The linear electrooptical response of the monomer mixture was measured in a SSFLC cell.² In the s_C^* phase, a ferroelectric behavior was seen, where the optical response time at the fastest was of the order of 15 μ s. A triangular-wave-shaped ac voltage across the cell resulted in a square-wave-shaped optical response, while a peak occurred on the current response at the time when the molecules switched directions (Figure 9). Synthesis and characterization of **12** and electrooptical properties of different mixtures of **12** and **10** are further described in ref 20. It was possible to copolymerize and cross-link the monomer blend by radical photopolymerization in the ferroelectric state in order to make permanent the structure.

Conclusions

New bifunctional liquid-crystalline monomers that exhibit s_c mesomorphism have been synthesized. Mixtures containing these compounds show ferroelectric properties in the s_c^* phase, and after polymerization, a permanent and thermally stable structure is achieved. If the compounds contain electron donor–acceptor groups the polar order accomplished in the ferroelectric state makes these monomers and polymer networks interesting for nonlinear optical purposes.

Acknowledgment. Financial support from the National Swedish Board for Technical and Industrial Development (NUTEK) Grant 86-03476P and the Swedish Natural Science Research Council (NFR, Grant K-KU 1910-305) is gratefully acknowledged. Mr. P. Rudkvist, Dr. L. Komitov, and Dr. S. T. Lagerwall, Department of Physics, Chalmers University of Technology, Sweden, are thanked for the determination of the ferroelectric properties.

CM950282F