Synthesis of a New Class of Low-Band-Gap Polymers with Liquid Crystalline Substituents

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ABSTRACT: New derivatives of poly(isothianaphthene methine) have been synthesized by a polycondensation reaction of 1,3-bis(*tert*-butyldimethylsilyl)isothianaphthene with benzaldehydes in the presence of $POCl_3$. In the para position the benzaldehydes possesses a liquid crystalline group, which contains a phenylcyclohexyl, phenylpyrimidine, or biphenyl moiety. The polymers are characterized by IR, UV−vis−NIR, ^1H NMR, and ^{13}C NMR spectroscopy. All polymers are soluble in common organic solvents and display band gaps between 1.2 and 1.3 eV and electrical conductivities in the range of 10^{-4}−10^{-5} S/cm upon iodine vapor doping.

1. Introduction

Low-Band-Gap Poly(arylene methine)s. At the present moment the development of stable, processable polymeric materials with a low band gap is an important issue for further advancements in the field of plastic electronics. These materials are important for application in LEDs, photovoltaic cells, transistors, and all polymer integrated circuits. The reduction of the band gap (E_g) will enhance the thermal population of the conducting band and thus increase the number of intrinsic charge carriers. This would allow to avoid oxidative or reductive doping in order to obtain intrinsic electrical conductivity. The lower oxidation potential associated with the narrow gap will also result in a stabilization of the corresponding doped state. Furthermore, the red shift of absorption and emission spectra resulting from a decrease of E_g leads to materials becoming transparent in the doped state.[1] Conjugated polymers are considered as low-band-gap materials if the value of the band gap is below the rather arbitrarily defined cutoff value of 1.5 eV.[2]

Poly(isothianaphthene) (PITN)[3,4] is one of the first polymers exhibiting a band gap below 1.5 eV (Figure 1). Important progress has been made in the synthesis of PITN,[5] but this polymer has until now remained more the subject of academic research[6,7] rather than progressing into the phase of technological application. Backed up by quantum-chemical and quantum-mechanical calculations, several other systems have been prepared that presumably had low band gaps. But none of the materials with band-gap values <1.5 eV have yet found use in long-term applications.[2] At this moment poly(3,4-ethylenedioxythiophene) (PEDOT)[8−10] is widely used (Figure 1). PEDOT has a band gap that is considered borderline by the above-defined cutoff value of 1.5 eV. As a result, the transparency of doped PEDOT is less pronounced as compared to the case of PITN.

Following the synthesis of PITN,[3] a theoretical investigation[11] of the lowering of E_g as a function of increasing quinonoid character of polyaromatics gave rise to several approaches to the design of low-band-gap materials.[12] One of these approaches suggested combining well-defined amounts of aromatic and quinonoid units to obtain poly(arylene methine).[13,14] In the case of thiophene this would allow control of the value of the band gap between the theoretically calculated value of 0.26 eV for quinonoid polythiophene and the value of 2 eV for aromatic polythiophene.[15] To control solubility, stability, and physical properties of the polyaromatics, alkyl chains have been introduced at the 3-position of five-membered heteroaromatic ring systems such as thiophene and pyrrole. Special synthetic procedures have been developed in order to control regioregularity (head-to-tail, head-to-head) in asymmetrically 3-substituted polythiophenes.[12] Lack of structural control and problems associated with irregular linked aromatic units are avoided in poly(arylene methine)s by introducing the substituents at the methine position.

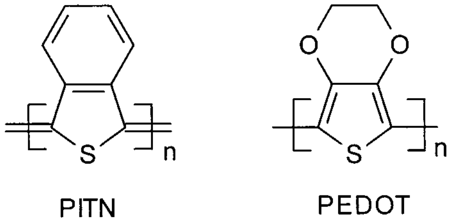

Figure 1. Poly(isothianaphthene) (PITN) and poly(3,4-ethylenedioxythiophene) (PEDOT).

Poly(arylene methine)s are synthesized through a polycondensation reaction between the appropriate aromatic compound and an aldehyde. Chen et al.[13,14] synthesized poly(thiophene methine) by heating a mixture of thiophene and an aldehyde in the presence of H_2SO_4. Goto et al.[16] used $POCl_3$ to obtain poly(thiophene methine)s containing liquid crystal side chains. The latter method, which has also been used to prepare an isothianaphthene derivative, has the advantage of higher yield and of providing a fully conjugated material.[17] As both methods finally yield a conjugated polymer, side chains have to be chosen carefully in order to obtain a soluble material. Results from the synthesis of poly(thiophene methine)s[13,14] indicate that polycondensations using benzaldehyde derivatives give the highest yields and highest molecular weights. The use of para-substituted benzaldehydes allows ample space for a wide choice of side chains which will improve the solubility of the resulting polymer. The synthesis of poly(isothianaphthene methine) has previously been demonstrated (Scheme 1).[17] The polymer bearing an hexyloxy side chain is soluble in 1,1,2,2-tetrachloroethane.

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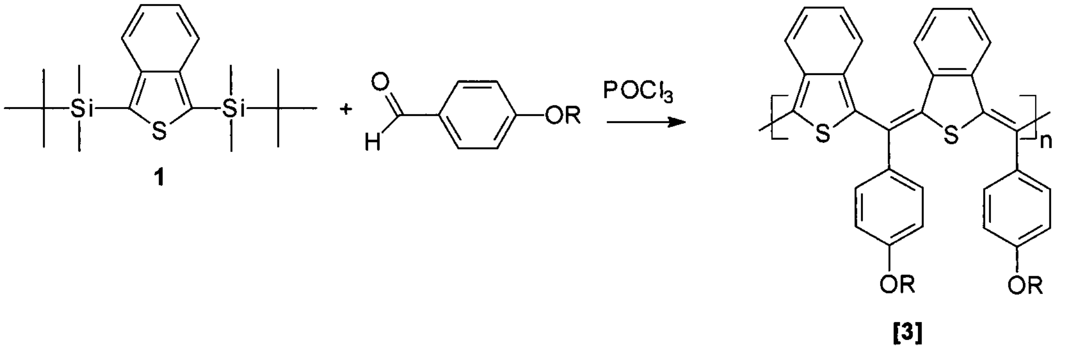
Scheme 1



It is characterized by a low band gap, which shows the possibility for switching between the dark blue non-doped state and the almost transparent doped state.

Liquid Crystalline Function and Conjugated Polymer. Among all of the conjugated organic polymers, the structure of polyacetylene is the simplest, and it shows as high an electrical conductivity as metal if doped with iodine or AsF_5.[51−53] However, its features are difficult to be characterized with standard experimental techniques due to its insolubility and infusibility. To improve the properties of polyacetylene, a variety of substituents were introduced as side chains, resulting in soluble and fusible acetylene derivatives. It is expected that the orientation of liquid crystalline side chains may enhance the main chain conjugation in conducting polymers due to the spontaneous orientation of the liquid crystalline group. As a result, the main chain orientation can be further improved and therefore result in improved electrical or optical properties. In our previous work, we successfully synthesized several side chain liquid crystalline conjugated polymers in which both liquid crystallinity and an increase in electrical conductivity were observed.[16,18−20,29−31] There are two methods to synthesize liquid crystalline conjugated polymers. One is the introduction of a liquid crystalline group such as a mesogenic group containing biphenyl or phenylcyclohexyl moieties into the polymer main chain. The other method is the introduction of long alkyl chains into the conjugated polymer (e.g., polythiophene). In the latter case, the conjugated polymer main chain plays the role of mesogenic group; this is the so-called main chain type liquid crystalline polymer. Hong et al.[49,50] recently synthesized regioregular liquid crystalline polythiophene with alkyl substituents in which the terminal carbon atoms are fluorinated. The regioregularity is an important factor in the thermal stability of liquid the crystalline phase.

Liquid Crystallinity and Low Band Gap. An approach to gain the emission of polarized light from aligned electroluminescent polymers is to use an aligned transparent cathode layer based on a low-band-gap polymer. Such a low-band-gap polymer should not only be transparent in the conducting state but also soluble and exhibit LC behavior. In principle, this can be achieved by introducing appropriate LC side chains into the backbone of a low-band-gap conducting polymer. Additionally, the higher degree of supramolecular order may even further decrease the value of the band gap of these materials.

The synthesis of poly(arylene methine)s with liquid crystalline side chains has been carried out in the framework of the applications of low-band-gap polymers in electronic devices and the aim of achieving higher structural order through liquid crystallinity. Here, we report on the synthesis of poly(isothianaphthene methine)s **3a**−**e** with of LC side chains. These LC side chains are expected to give improved solubility.

2. Experimental Section

Characterization. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM-500. The NMR spectra were measured in $CDCl_3$. The NMR data are listed in parts per million downfield (ppm) from tetramethylsilane as the internal standard. Gel permeation chromatographic (GPC) analysis was carried out at room temperature. The GPC column (Shodex KF806M column and JASCO HPLC870-UV detector) was calibrated with polystyrene standard. Tetrahydrofuran (THF) was used as eluent. ESR spectra were taken on a JEOL JES-TE ESR spectrometer. The spin concentration of each sample was determined by integration of ESR signal using those of $CuSO_4$ as standard. Optical absorption spectra were obtained at room temperature on a Hitachi U-3500 spectrometer using 1 cm quartz cell. Infrared spectra were obtained using a JASCO FT-IR 550 spectrometer. The DSC measurements were carried out with a Perkin-Elmer DSC 7 at a rate of 10 °C/min under an argon gas flow. Optical observations were made on Olympus SZH-PT polarizing optical microscope equipped with a Linkam TM-600PM hot and cooling stage.

Synthetic Procedures. All compounds were distilled or recrystallized prior to use. All experiments were performed under an argon atmosphere using Schlenk/vacuum line techniques. The synthesis of 1,3-bis(*tert*-butyldimethylsilyl)isothianaphthene (**1**) was carried out according to literature procedures.[6,21] The syntheses of the different para-substituted benzaldehydes were carried out on the basis of classical reactions to produce LC substituents: Williamson etherification, Fisher and Fisher reaction,[22] and the Mitsunobu reaction.[23] The mesogenic compound of 4-(*trans*-4-pentylcyclohexyl)phenol was purchased from Kanto Chemical Ltd. Compounds **4** and **14** were prepared by literature methods.[47,48] (*R*)-1-Chloro-3,7-dimethyloctane was a generous gift to Rafaël Kiebooms from Heinrich Becker (Hoechst).

(*R*)-(−)-4-(3,7-Dimethyl)octyloxybenzaldehyde (2a). 4-Hydroxybenzaldehyde (2.5 g, 20.5 mmol), (*R*)-1-chloro-3,7-dimethyloctane (7.2 g, 41.0 mmol), K_2CO_3 (5.7 g, 41.0 mmol), a catalytic amount of KI, and 80 mL of dry DMF were refluxed at 75 °C for 70 h. The excess K_2CO_3 was filtered off. Then DMF was removed in vacuo. The residue was taken up in $CHCl_3$ and washed with water to remove all DMF. The crude product was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate). Final purification by vacuum distillation yields 3.5 g (66%) of white liquid. $T_k = 127$ °C at 0.3 Torr. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.97; H, 10.21. FT-IR (KBr, cm^{-1}): 2955, 2928, 2870, 2731, 1697, 1602, 1577, 1509, 1470, 1312, 1260, 1160, 831. ^1H NMR ($CDCl_3$, δ from TMS, ppm): 0.77 (d, $J = 6.6$ Hz, H, CH_3), 0.85 (d, $J = 6.3$ Hz, 3H, CH_3), 1.01−1.24 (m, 6H, CH_2), 1.38−1.62 (m, 2H, CH), 1.66−1.82 (m, 2H, CH_2), 3.97 (t, $J = 7.2$ Hz, 2H, CH_2), 6.9 (d, $J = 8.6$ Hz, 2H, CH), 7.7 (d, $J = 7.9$ Hz, 2H, CH), 9.8 (s, 1H, CHO). ^{13}C NMR (CDCl$_3$, δ from TMS, ppm): 19.9, 22.8, 24.8, 28.1, 30.2, 36.7, 37.9, 39.6, 66.8, 115.9, 130.1, 132.0, 164.3, 190.7.

4-[10-[4-(Decyl-pyrimidin-2-yl)phenoxy]decyloxy]-benzaldehyde (2b). A mixture of 4-(5-decyl-pyrimidin-2-yl)-phenol (**5**) (0.82 g, 2.7 mmol), K$_2$CO$_3$ (0.46 g, 3.35 mmol), KI (0.56 g, 3.35 mmol), and 4-(10-bromodecyloxy)benzaldehyde (**4**) (1.14 g, 3.35 mmol) in 50 mL of acetone was refluxed for 24 h. After evaporation of the acetone the crude product was recrystallized from acetone/ethanol solution to yield 0.83 g (53.7%) of white solid. Mp = 79 °C. Anal. Calcd for C$_{37}$H$_{52}$NO$_3$: C, 77.58; H, 9.15; N, 4.89. Found: C, 77.42; H, 9.18; N, 4.93. IR (KBr, cm^{-1}): 2920, 2858, 1685, 1606, 1585, 1432, 1250, 1169, 978, 840, 750. ^{1}H NMR (CDCl$_3$, δ from TMS, ppm): 0.85 (t, J = 7.0 Hz, 3H, CH$_3$), 1.27−1.44 (m, br, 26H, CH$_2$), 1.58 (t, J = 7.5 Hz, 2H, CH$_2$), 1.64 (t, J = 6.5 Hz, 4H, OCH$_2$*CH*$_2$ × 2), 2.57 (t, J = 7.7 Hz, 2H, CH$_2$), 4.00 (t, J = 4.9 Hz, 4H, OCH$_2$ × 2), 6.89 (d, J = 4.9 Hz, 2H, ph), 6.95 (d, J = 4.9 Hz, 2H, ph), 7.79 (d, J = 7.1 Hz, 2H, ph). 8.31 (d, J = 7.1 Hz, 2H, ph), 8.59 (s, 2H, pyrimidine), 9.85 (s, 1H, CHO). ^{13}C NMR (CDCl$_3$, δ from TMS, ppm): 14.0, 22.6, 25.5, 25.6, 26.0, 29.1, 29.2, 30.1, 30.7, 30.8, 31.8, 66.0, 66.4, 114.4, 114.7, 129.3, 129.6, 129.7, 131.9, 132.0, 156.9, 161.1, 162.4, 164.2, 190.7.

1-[4-(*trans*-4-*n*-Pentylcyclohexyl)phenoxy]-10-bromodecane (7). A mixture of potassium hydroxide (2.4 g, 0.042 mol) and 4-(*trans*-4-pentylcyclohexyl)phenol (**6**) (10.3 g, 0.042 mol) in 100 mL of ethanol was stirred for 4 h at room temperature. Subsequently, the solution was added dropwise to a solution of 1,10-dibromodecane (50.4 g, 0.168 mol) in 200 mL of ethanol at 60 °C. The addition was completed after 4 h, and the reaction mixture was stirred for another 8 h. After evaporation of the solvent and the excess dibromodecane under reduced pressure, the solution was thoroughly washed with 1 N HCl and water and then extracted with ether. The ether layer was dried over CaCl$_2$, and the organic solvents were removed under reduced pressure. The crude product was purified by column chromatography (silica gel, ethyl acetate/hexane = 3/1) and recrystallized from ethanol to give 12.3 g of a white powder (yield 62%). Mp = 39 °C. Anal. Calcd for C$_{27}$H$_{45}$BrO: C, 69.66; H, 9.74; Br, 17.16. Found: C, 69.70; H, 9.78; Br, 17.21. IR (KBr, cm^{-1}): 2924, 2913, 2847, 1610, 1580, 1512, 1466, 1445, 1394, 1279, 1244, 1178, 1114, 1040, 1018, 970, 894, 836, 809, 765, 723. ^{1}H NMR (CDCl$_3$, δ from TMS, ppm): 0.88 (t, J = 7.2 Hz, 3H, CH$_3$), 1.01 (q, J = 7.4 Hz, 2H, CH$_2$), 1.19−1.43 (m, 23H, CH$_2$ and CH), 1.76 (m, 4H, CH$_2$),1.84 (m, 4H, CH$_2$), 2.38 (m, 1H, CH), 3.46 (t, J = 6.9 Hz, 2H, BrCH$_2$), 3.90 (t, J = 6.5 Hz, 2H, *CH*$_2$OPh, 6.70 (d, J = 8.6 Hz, 2H, Ph), 7.09 (d, J = 8.1 Hz, 2H, Ph). ^{13}C NMR (CDCl$_3$, δ from TMS, ppm): 14.1, 22.7, 25.6, 26.0, 26.6, 28.1, 28.7, 29.3, 29.4, 32.2, 32.8, 33.5, 33.7, 33.9, 34.6, 37.3, 37.4, 43.7, 67.9, 114.2, 127.5, 139.9, 157.2.

4-[10-[4-(*trans*-4-*n*-Pentylcyclohexyl)phenoxy]decyloxy]-benzalehyde (2c). A mixture of 1-[4-(*trans*-4-*n*-pentylcyclohexyl)phenoxy]-10-bromodecane (**7**) (10.0 g, 21.4 mmol), 4-hydroxybenzaldehyde (2.6 g, 21.4 mmol), and K$_2$CO$_3$ (2.9 g, 21.4 mmol) in 40 mL of acetone was refluxed for 24 h. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel, ethyl acetate/hexane = 3/1) to give 8.2 g (Y = 76%) of the desired compound of white solid. Anal. Calcd for C$_{34}$H$_{50}$O$_3$: C, 80.58; H, 9.94. Found: C, 80.55; H, 9.96. IR (KBr, cm^{-1}): 2920, 2851, 1673, 1599, 1428, 1329, 1246, 1157, 1035, 835. ^{1}H NMR (CDCl$_3$, δ from TMS, ppm): 0.87 (t, J = 7.3 Hz, 3H, CH$_3$), 1.05 (q, J = 7.1 Hz, 2H, CH$_2$), 1.21−1.46 (m, 23H, CH$_2$ and CH), 1.75−2.37 (m, 8H, CH$_2$), 2.39 (m, 1H, CH), 3.95 (t, J = 7.0 Hz, 2H, *CH*$_2$Oph), 4.03 (t, J = 6.6 Hz, 2H, phO*CH*$_2$), 6.62 (d, J = 6.8 Hz, 2H, ph) 6.99 (d, J = 7.9 Hz, 2H, ph), 7.11 (d, J = 8.6 Hz, 2H, ph), 7.61 (d, J = 8.2 Hz, 2H, ph) 9.67 (s, 1H, CHO). ^{13}C NMR (CDCl$_3$, δ from TMS, ppm): 14.1, 22.7, 25.9, 26.0, 26.6, 27.9, 29.0, 29.2, 29.3, 29.4, 29.5, 32.2, 33.6, 34.5, 37.3, 37.4, 43.7, 67.9, 68.4, 114.2, 127.5, 140.0, 157.1.

1-[4-(*trans*-4-*n*-Pentylcyclohexyl)phenoxy]-6-bromohexane (8). Sodium (4.6 g, 0.2 mol) was added to 150 mL of ethanol at room temperature. After the sodium was completely dissolved, 4-(*trans*-4-pentylcyclohexyl)phenol (**6**) (49.3 g, 0.2 mol) was added, and the mixture was stirred at room temperature for 12 h. Subsequently, this mixture was added dropwise to a stirred solution of 1,6-dibromohexane (195.2 g, 0.8 mol) in 100 mL of ethanol at 60 °C. The addition was completed after 4 h, and the reaction mixture was stirred for another 8 h. After evaporation of the solvent and the excess dibromohexane under reduced pressure, the solution was thoroughly washed with 1 N HCl and water and then extracted with ether. The ether layer was dried over CaCl$_2$, and the organic solvents were removed by reduced pressure. The crude product was recrystallized from ethanol to give 47.5 g of white crystal (yield 58%). Anal. Calcd for C$_{23}$H$_{37}$OBr: C, 67.47; H, 9.11; Br, 19.51. Found: C, 67.94; H, 9.42; Br, 19.82. IR (KBr, cm^{-1}): 3039, 2955, 2919, 2847, 1613, 1581, 1515, 1469, 1447, 1390, 1304, 1282, 1246, 1180, 1111, 1075, 966, 836, 812, 722. ^{1}H NMR (CDCl$_3$, δ from TMS, ppm): 0.89 (t, J = 7.2 Hz,3H, CH$_3$), 1.03 (q, J = 7.0 Hz, 2H, CH$_2$), 1.19−1.43 (m, 14H, CH$_2$), 1.76 (q, J = 8.5 Hz, 1H, CH), 1.86 (m, 4H, CH$_2$), 2.39 (m, 1H, CH), 3.42 (t, J = 6.7 Hz, 2H, BrCH$_2$), 3.91 (t, J = 6.4 Hz, 2H, CH$_2$-OPh), 6.80 (d, J = 6.9 Hz, 2H, Ph) 7.10 (d, J = 8.5 Hz, 2H, Ph). ^{13}C NMR (CDCl$_3$, δ from TMS, ppm): 14.0, 22.6, 25.3, 26.6, 27.9, 29.1, 32.2, 32.6, 33.6, 33.7, 34.5, 37.3, 37.3, 43.7, 67.6, 114.2, 127.5, 140.0, 157.1.

4-[6-[4-(*trans*-4-*n*-Pentylcyclohexyl)phenoxy]hexyloxy]-benzalehyde (2d). A mixture of 1-[4-(*trans*-4-*n*-pentylcyclohexyl)phenoxy]-6-bromohexane (**8**) (13.5 g, 33.0 mmol), 4-hydroxybenzaldehyde (5 g, 41.0 mmol), and K$_2$CO$_3$ (5.7 g, 41.0 mmol) in 40 mL of acetone was refluxed for 24 h. After evaporating the solvent, the crude product was purified by column chromatography (silica gel, ethyl acetate/hexane = 3/1) to give 13.1 g (yield 71%) of white solid. Anal. Calcd for C$_{30}$H$_{42}$O$_3$: C, 79.96; H, 9.39. Found: C, 79.88; H, 9. 41. IR (KBr, cm^{-1}): 2918, 2851, 1690, 1605, 1510, 1249, 821. ^{1}H NMR (CDCl$_3$, δ from TMS, ppm): 0.89 (t, J = 7.2 Hz, 3H, CH$_3$), 1.08 (q, J = 7.1 Hz, 2H, CH$_2$), 1.20−1.29 (m, 14H, CH$_2$), 1.41(q, J = 3.2 Hz, 1H, CH), 1.54 (m, 4H, CH$_2$), 1.85 (m, 4H, CH$_2$), 2.39 (m, 1H, CH), 3.95 (t, J = 6.5 Hz, 2H, *CH*$_2$Oph), 4.03 (t, J = 6.5 Hz, 2H, phO*CH*$_2$), 6.62 (d, J = 5.1 Hz, 2H, ph) 6.99 (d, J = 7.0 Hz, 2H, ph), 7.11 (d, J = 8.6 Hz, 2H, ph), 7.81 (d, J = 5 Hz, 2H, ph) 9.67 (s, 1H, CHO). ^{13}C NMR (CDCl$_3$, δ from TMS, ppm): 14.0, 22.6, 25.5, 25.7, 25.8, 28.9, 29.2, 32.1, 33.6, 34.5, 37.3, 37.4, 43.7, 67.6, 67.9, 114.2, 127.5, 140.0, 157.1.

4-Methoxycarboxycarbonyloxybenzoic Acid (9).[40] To a solution of NaOH (27 g, 0.67 mol) in water (400 mL) at −7 °C was added 4-hydroxybenzoic acid (22.3 g, 0.16 mol) while stirring. Then methyl chloroformate (22.9 g, 0.24 mol) was added slowly to the resulting suspension at −5 °C. The slurry was stirred for another 4 h and brought to pH 5 by the addition of HCl. The precipitate was filtered off and recrystallized from ethanol to give 23.8 g of a white solid (yield 76%). Mp = 85 °C. Anal. Calcd for C$_9$H$_8$O$_5$: C, 55.11; H, 4.11. Found: C, 55.15; H, 4.16. IR (KBr, cm^{-1}): 2933, 2859, 2675, 2543, 1740, 1670, 1400, 820. ^{1}H NMR (CDCl$_3$, δ from TMS, ppm): 3.91 (s, 3H, CH$_3$), 7.28 (d, J = 8.72, 2H, ph), 8.14 (d, J = 8.7 Hz, 2H, ph). ^{13}C NMR (CDCl$_3$, δ from TMS, ppm): 55.5, 121.0, 127.5, 131.9, 153.6, 155.1, 170.0.

(*S*)-1-Methylheptyl-4′-hydroxybiphenyl-4-carboxylate (11).[39] A solution of (R)-2-octanol (19.2 g, 0.14 mol) and triphenylphosphine (TPP) (30.19 g, 0.11 mol) in 200 mL of THF was added dropwise to a solution of 4-hydroxybiphenyl-4′-carboxylic acid (**10**) (25.0 g, 0.11 mol) and diethylazodicarboxylate (DEAD) (19.1 g, 0.11 mol) in 100 mL of THF at room temperature. After the solution had been refluxed for 24 h, the reaction mixture was filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate) to give 30.8 g (yield 86%) of white solid. Mp = 105 °C. Anal. Calcd for C$_{21}$H$_{26}$O$_3$: C, 77.27; H, 8.03. Found: C, 77.35; H, 8.10. IR (KBr, cm^{-1}): 3355, 2920, 2850, 1700, 1600, 1530, 1490, 1350, 1270, 1195, 1110, 1060, 830, 770. ^{1}H NMR (CDCl$_3$, δ from TMS, ppm): 0.85 (t, J = 6.9 Hz, 3H, CH3), 1.34 (d, J = 7.1 Hz, 3H, OCH*CH*$_3$−), 1.24−2.17 (m, 10H, CH$_2$), 5.20 (sextet, J = 6.7 Hz, 1H, O*CH*CH$_3$−), 6.96 (d, J = 5.9 Hz, 2H, ph), 7.33 (s, 1H, OH), 7.49 (d, J = 8.5 Hz, 2H, ph), 7.61 (d, J = 7.5 Hz, 2H, ph), 8.08 (d, J = 8.8 Hz, 2H, ph). ^{13}C NMR (CDCl$_3$, δ from

TMS, ppm): 14.0, 20.0, 22.6, 25.5, 29.2, 31.6, 36.1, 66.0, 72.2, 116.0, 126.4, 128.4, 130.8, 132.1, 145. 5, 156.6, 168.9.

(*S*)-1-Methylheptyl-4′-(4-methoxycarbonyloxybenzoyloxy)biphenyl-4-carboxylate (12). A solution of 4-methoxycarboxycarbonyloxybenzoic acid (**9**) (7.3 g, 37.0 mmol), dicyclohexylcarbodiimide (DCC) (7.5 g, 37.0 mmol), (dimethylamino)pyridine (DMAP) (4.5 g, 37 mmol), and (*S*)-1-methylheptyl 4′-hydroxybiphenyl-4-carboxylate (**11**) (12.0 g, 37.0 mmol) in 200 mL of THF was stirred for 24 h at room temperature. The reaction mixture was then filtered. The filtrate was added to a saturated $NaHCO_3$ solution and neutralized with HCl, followed by extraction with $CHCl_3$ and dried over $CaCl_2$. The solvent was evaporated, and the crude product was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate) to give 12.6 g of white solid (yield 33.6%). Anal. Calcd for $C_{30}H_{32}O_7$: C, 71.41; H, 6.39. Found: C, 71.32; H, 6.43. IR (KBr, cm^{-1}): 2933, 2856, 1740, 1705, 1594, 1277, 840, 764. ^{1}H NMR ($CDCl_3$, δ from TMS, ppm): 0.86 (t, $J = 6.9$ Hz, 3H, CH_3), 1.35 (d, $J = 7.3$ Hz, 3H, $OCHCH_3$), 1.29–2.14 (m, 10H, CH_2), 3.91 (s, 3H, CH_3), 5.18 (sextet, $J = 6.5$ Hz, 1H, O*CH*CH_3), 6.48 (d, $J = 8.6$ Hz, 4H, ph), 7.26 (d, $J = 8.6$ Hz, 2H, ph), 7.58 (d, $J = 8.6$ Hz, 2H, ph), 7.63 (d, $J = 8.4$ Hz, 4H, ph), 8.00 (d, $J = 8.5$ Hz, 2H, ph), 8.10 (d, $J = 8.7$ Hz, 2H, ph). ^{13}C NMR ($CDCl_3$, δ from TMS, ppm): 14.0, 20.0, 22.6, 25.7, 29.2, 34.1, 36.2, 55.3, 71.8, 117.6, 121.2, 121.6, 127.0, 128.4, 128.4, 130.1, 131.6, 144.7, 154.2, 155.3, 156.0, 166.0, 166.7.

(*S*)-1-Methylheptyl-4′-(4-hydroxybenzoyloxy)biphenyl-4-carboxylate (13). A mixture of (*S*)-1-methylheptyl 4′-(4-methoxycarbonyloxybenzoyloxy)biphenyl-4-carboxylate (**12**) (5 g, 9.9 mmol), ethanol (200 mL), THF (300 mL), and ammonia (30%, 200 mL) was stirred at room temperature for 1 h. The solution was then poured into a large amount of ice water. The precipitate was filtered and then purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 1/2) to give 4.0 g of white solid (yield 90%). Mp = 125 °C. Anal. Calcd for $C_{28}H_{30}O_5$: C, 75.31; H, 6.77. Found: C, 74.91; H, 7.09. IR (KBr, cm^{-1}): 3407, 2926, 2856, 1705, 1594, 1277, 840, 764. ^{1}H NMR ($CDCl_3$, δ from TMS, ppm): 0.87 (t, $J = 5.3$ Hz, 3H, CH_3), 1.29 (d, $J = 6.22$ Hz, 3H, $OCHCH_3$), 1.21–2.10 (m, 10H, CH_2), 5.19 (sextet, $J = 6.4$ Hz, 1H, O*CH*CH_3), 6.91 (d, $J = 6.3$ Hz, 4H, ph), 7.29 (d, $J = 8.6$ Hz, 2H, ph), 7.48 (d, $J = 8.6$ Hz, 2H, ph), 7.63 (d, $J = 8.4$ Hz, 4H, ph), 8.03 (d, $J = 8.4$ Hz, 2H, ph), 8.10 (d, $J = 8.7$ Hz, 2H, ph). ^{13}C NMR ($CDCl_3$, δ from TMS, ppm): 14.0, 20.1, 22.6, 25.5, 29.2, 31.3, 36.2, 72.0, 115.5, 116.0, 122.2, 126.4, 127.0, 128.5, 128.9, 130.2, 132.7, 137.8, 144.8, 151.2, 165.2, 166.4.

(*S*)-1-Methylheptyl-4′-[4-[8-(4-formylphenoxy)octyloxy]benzoyloxy]biphenyl-4-carboxylate (2e). A solution of (*S*)-1-methylheptyl-4′-(4-methoxycarbonyloxybenzoyloxy)biphenyl-4-carboxylate (**13**) (2.26 g, 5.0 mmol), 4-(8-bromooctyloxy)benzaldehyde (**14**) (1.57 g, 5.0 mmol), K_2CO_3 (0.7 g, 5.0 mmol), and KI (0.83 g, 5.0 mmol) in 20 mL of acetone was refluxed for 24 h. The reaction mixture was extracted with $CHCl_3$ and thoroughly washed with water and dried over $CaCl_3$. The organic solvents were removed under reduced pressure, and the crude product was recrystallized from acetone/ethanol solution to give 2.8 g as a white powder (yield 82%). Anal. Calcd for $C_{43}H_{50}O_7$: C, 76.08; H, 7.42; O, 16.50. Found: C, 76.15; H, 7.53. IR (KBr, cm^{-1}): 2938, 2856, 1726, 1603, 1395, 1169, 1111, 850, 768. ^{1}H NMR ($CDCl_3$, δ from TMS, ppm): 0.88 (t, $J = 7.0$ Hz, 3H, CH_3), 1.29 (d, $J = 6.2$ Hz, 3H, O*CH*CH_3), 1.21–2.15 (m, 26H, CH_2), 3.73 (t, $J = 6.9$ Hz, 2H, CH_2), 4.03 (t, $J = 6.4$ Hz, 2H, CH_2), 5.18 (sextet, $J = 6.1$ Hz, 1H, O*CH*CH_3), 6.97 (d, $J = 6.4$ Hz, 2H, ph), 7.29 (d, $J = 8.6$ Hz, 2H, ph), 7.65 (d, $J = 6.5$ Hz, 4H, ph), 7.81 (d, $J = 8.7$ Hz, 2H, ph), 8.11 (d, $J = 8.3$ Hz, 2H, ph), 8.15 (d, $J = 8.8$ Hz, 2H, ph), 9.87 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, δ from TMS, ppm): 14.0, 18.8, 20.1, 22.6, 25.5, 26.0, 26.0, 29.1, 29.1, 29.4, 29.5, 31.8, 36.2, 68.3, 68.4, 71.6, 114.1, 114.4, 121.5, 122.3, 127.0, 128.3, 129.9, 128.9, 130.1, 132.0, 132.4, 137.8, 144.7, 151.2, 163.7, 164.3, 164.9, 166.0, 190.6.

Poly[(benzo[*c*]thiophene-1,3-diyl)(*p*-(alkyloxy)benzylidene) (Benzo[*c*]thiophenequinodimethane-1,3-diyl)] (3). To a solution of 1,3-bis(*tert*-butyldimethylsilyl)isothianaphthene (**1**) (1.0 mmol) and 4-alkyloxybenzaldehyde (**2a–e**) (1.0 mmol) in 8 mL of 1,4-dioxane was added 2 mL of $POCl_3$. The reaction mixture was heated at 85 °C for 24 h. After precipitation in 150 mL of MeOH, the solid was collected and subjected to a Soxhlet extraction with MeOH. The residue was subsequently recovered by dissolving in $CHCl_3$. The pristine product was washed with dilute ammonia to yield dedoped polymer.

3a. Anal. Calcd for $C_{50}H_{58}O_2S_2$: C, 79.53; H, 7.74; S, 8.49. Found: C, 78.34; H, 7.50; S, 8.10. FT-IR (KBr, cm^{-1}): 2929, 2857, 1603, 1588, 1507, 1452, 1241, 1171, 977, 842, 737. ^{1}H NMR ($CDCl_3$, δ from TMS, ppm): 0.9 (d, 6H, CH_3), 1.3 (bm, 6H, CH_2), 1.5 (bm, 2H, CH), 1.8 (bm, 2H, CH_2), 2.4 (t, 2H, CH_2), 4.0 (t, 2H, OCH_2), 6.8 (bm, 2H, ph), 7.1 (bm, 2H, CH × 2). ^{13}C NMR ($CDCl_3$, δ from TMS, ppm): 22.8, 26.0, 26.8, 29.4, 32.3, 33.7, 34.4, 37.4, 43.8, 67.8, 114.6, 127.3, 130.1, 140.0, 157.3.

3b. Anal. Calcd for $C_{90}H_{110}N_4O_4S_2$: C, 78.56; H, 8.06; N, 4.07; S, 4.66. Found: C, 77.18; H, 8.45; N, 4.41; S, 4.93. IR (KBr, cm^{-1}): 2910, 2851, 1606, 1583, 1508, 1430, 1250, 1168, 977, 844, 797, 744. ^{1}H NMR ($CDCl_3$, δ from TMS, ppm): 0.8 (t, 3H, CH_3), 1.0–2.0 (bm, 26 H, CH_2), 2.5 (bs, 2H, CH_2), 3.9 (bs, 4H, OCH_2 × 2), 6.9–8.0 (br, ITN, arylene proton signals in LC substituents overlapped in this broad peak), 6.9 (bs, 2H, ph), 8.3 (bs, 2H, ph) 8.5 (s, 2H, pyrimidine). ^{13}C NMR ($CDCl_3$, δ from TMS, ppm): 14.0, 22.6, 25.5, 25.9, 26.9, 28.9, 29.6, 30.1, 30.7, 30.8, 31.8, 67.9, 114.1, 114.3, 122.4, 129.3, 130.0, 132.0, 137.0, 156.6, 161.1, 162.4, 165.2.

3c. Anal. Calcd for $C_{84}H_{106}O_4S_2$: C, 81.11; H, 8.59; S, 5.15. Found: C, 83.13; H, 8.21; S, 5.14. IR (KBr, cm^{-1}): 2921, 2847, 1611, 1511, 1457, 1432, 1254, 1175, 1051, 982, 849, 805, 754. ^{1}H NMR ($CDCl_3$, δ from TMS, ppm): 0.8 (t, 3H, CH_3), 1.0–2.0 (m, 33H, CH and CH_2), 2.5 (s, 1H, CH), 3.9 (bs, 4H, OCH_2 × 2), 5.7–8.0 (br, ITN, arylene proton signals in LC substituents overlapped in this broad peak), 7.9 (bs, 2H, ph), 8.3 (bs, 2H, ph), 8.5 (bs, 2H, ph). ^{13}C NMR ($CDCl_3$, δ from TMS, ppm): 14.0, 22.6, 25.6, 25.9, 28.9, 29.2, 29.3, 29.4, 29.7, 30.1, 30.8, 31.9, 68.0, 88.9, 114.3, 122.4, 129.3, 130.1, 132.0, 144.5, 161.7, 162.4.

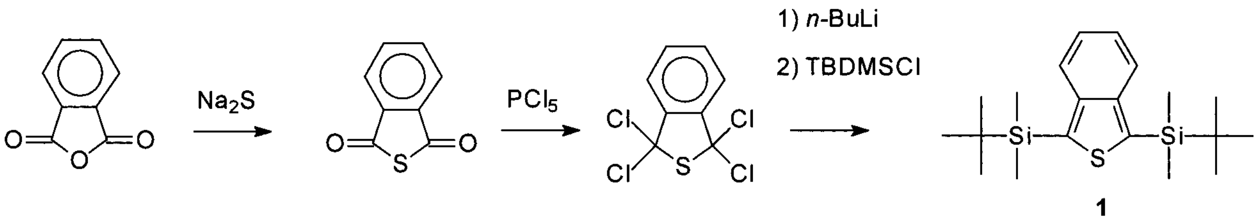
3d. Anal. Calcd for $C_{76}H_{90}O_4S_2$: C, 80.66; H, 8.02; S, 5.67. Found: C, 81.35; H, 8.29; S, 5.47. IR (KBr, cm^{-1}): 2918, 2850, 1605, 1511, 1465, 1243, 1175, 1028, 825, 747. ^{1}H NMR ($CDCl_3$, δ from TMS, ppm): 0.8 (t, 3H, CH_3), 0.9–2.0 (m, 18H, CH and CH_2), 3.9 (bs, 4H, OCH_2 × 2), 6.2–8.3 (br, ITN, arylene proton signals in LC substituents overlapped in this broad peak), 7.8 (bs, 2H, ph), 7.1 (bs, 2H, ph). ^{13}C NMR ($CDCl_3$, δ from TMS, ppm): 13.1, 21.7, 24.6, 25.1, 25.6, 26.5, 31.2, 32.7, 36.4, 42.7, 113.3, 126.5, 139.9, 143.5, 156.2, 170.5.

3e. Anal. Calcd for $C_{102}H_{106}O_{12}S_2$: C, 77.15; H, 6.73; S, 4.04. Found: C, 76.74; H, 6.86; S, 3.48. IR (KBr, cm^{-1}): 2926, 2856, 1734, 1710, 1604, 1508, 1465, 1397, 1260, 1167, 1065, 799. ^{1}H NMR ($CDCl_3$, δ from TMS, ppm): 0.8 (t, 3H, CH_3), 1.2–2.0 (m, 26H, CH, CH_2), 3.9 (bs, 4H, OCH_2 × 2), 5.1 (sextet, 2H, ph), 6.2–8.3 (br, ITN, arylene proton signals in LC substituents overlapped in this broad peak), 6.9 (bs, 4H, ph), 7.3 (bs, 2H, ph), 7.6 (bs, 6H, ph), 8.1 (d, 2H, ph), 8.2 (bs, 2H, ph). ^{13}C NMR ($CDCl_3$, δ from TMS, ppm): 13.0, 19.0, 21.6, 24.6, 26.2, 30.7, 35.1, 70.8, 113.3, 120.3, 121.3, 126.0, 127.3, 128.7, 129.1, 131.3, 136.7, 143.6, 150.1, 162.6, 163.7, 165.0, 176.0.

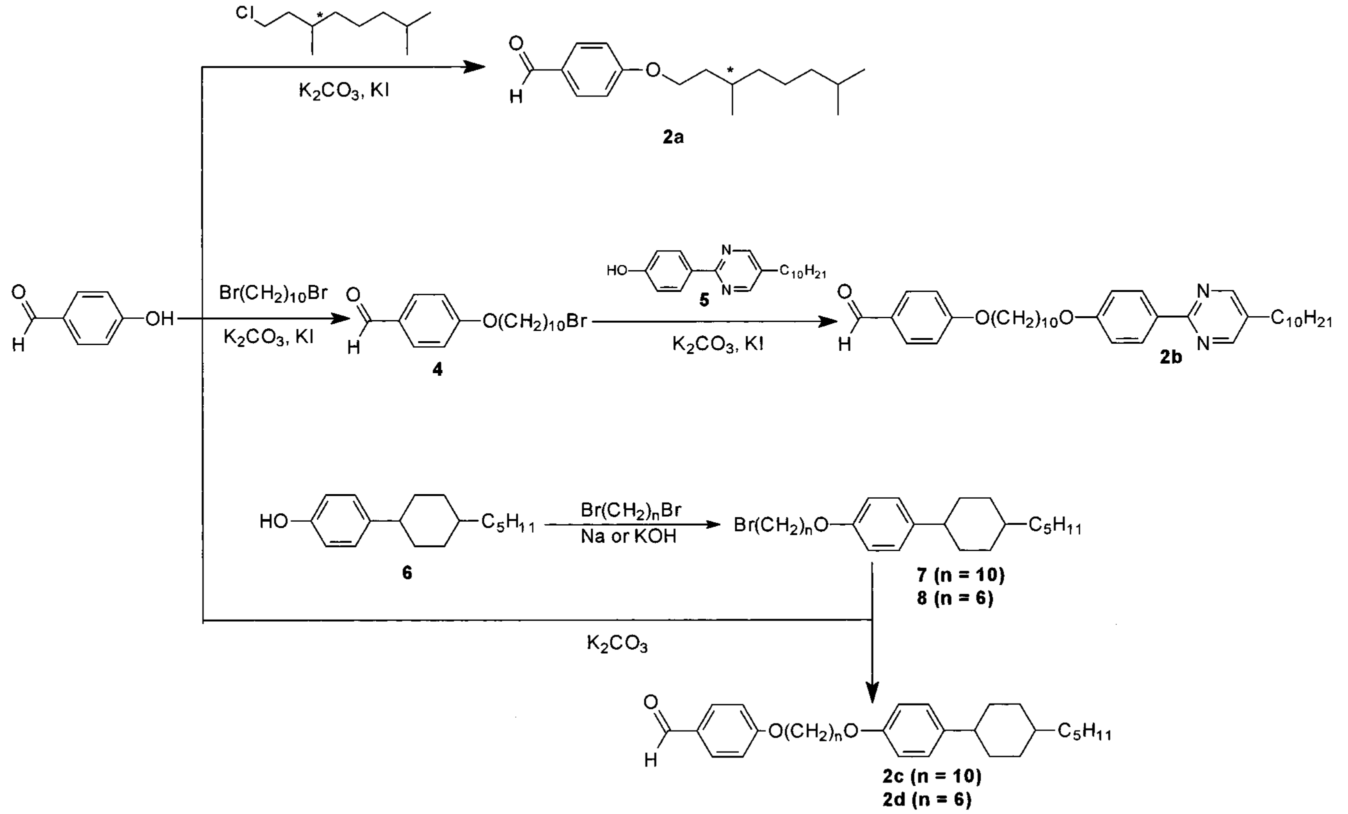
3. Results and Discussion

Synthesis of Isothianaphthene. The synthesis of isothianaphthene[24–26] is well established. The final reaction to obtain isothianaphthene consists of the pyrolysis of 1,3-dihydrobenzo[*c*]thiophene-2-oxide. Together with its well-known sensitivity toward oxidation, this renders the synthesis of larger amounts of isothianaphthene more difficult. Since we shall use the $POCl_3$ as an oxidation reagent in the present polymerization, 1,3-bis(*tert*-butyldimethylsilyl)isothianaphthene (**1**)[21] might be suitable for these types of polycondensation reactions. The above compound is very stable in air due to the steric protection by the substituents, and it can be prepared in large quantities. Another advantage is that the silicon groups activate the 1- and 3-positions

Scheme 2



Scheme 3



for electrophilic reactions. The presence of chlorine, as a consequence of the use of POCl$_3$, should facilitate the removal of the silicon leaving group during the addition reaction. The synthetic route of 1,3-bis(*tert*-butyldimethylsilyl)isothianaphthene (**1**) is shown in Scheme 2.

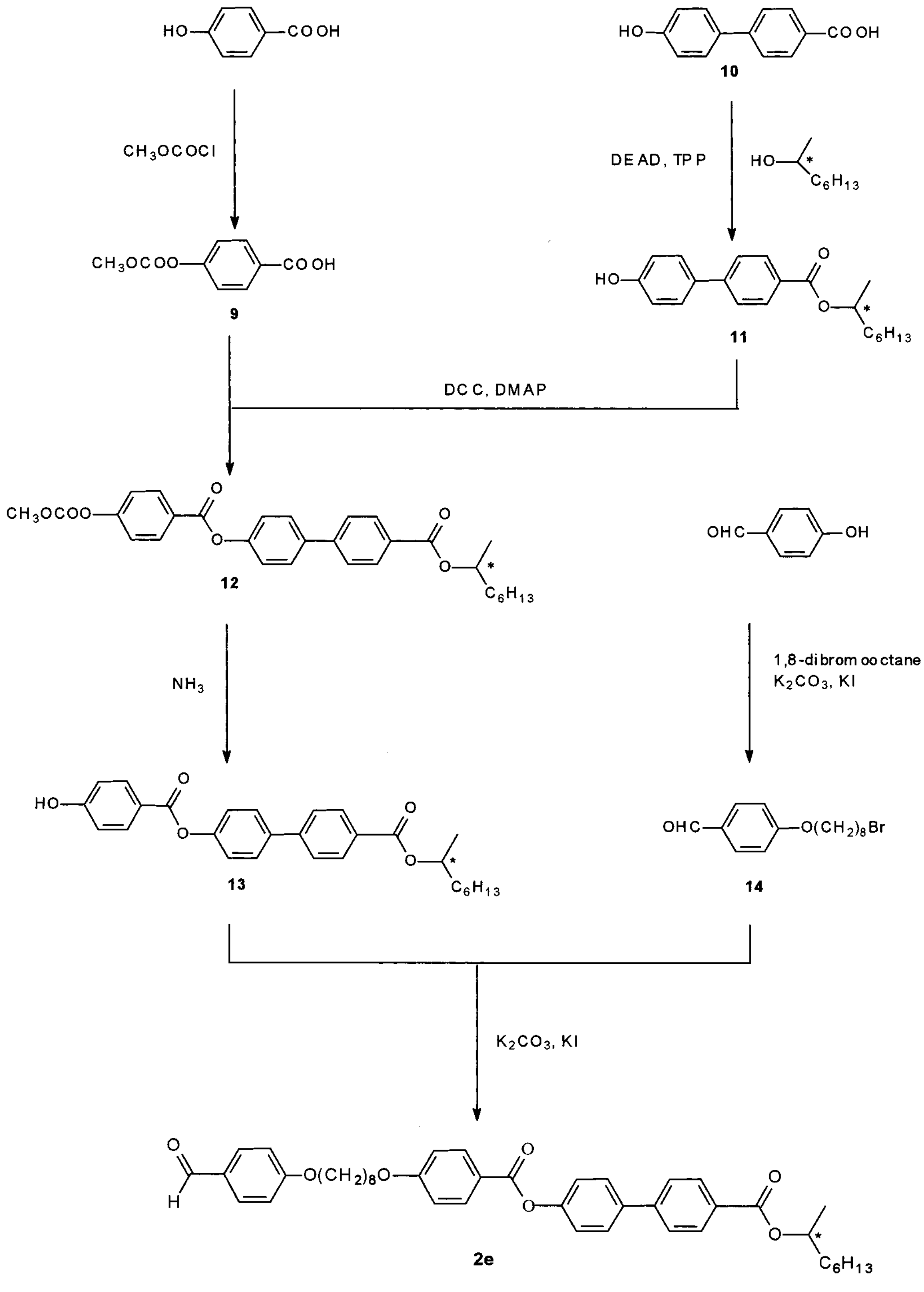
Synthesis of Para-Substituted Benzaldehydes. In order for poly(isothianaphthene methine)s to be of practical use, solubility in common organic solvents needs to be achieved. Since a hexyloxy side chain seems not to provide ideal solubility,[17] one solution is to use a longer alkyl chain. The (3,7-dimethyl)octyloxy side chain is not only a longer side chain but also contains an asymmetrically substituted carbon atom. It is known from poly(*p*-phenylenevinylene) derivatives that such side chains not only improve solubility but also enhance film-forming properties.[27] The synthesis of 4-(3,7-dimethyl)octyloxybenzaldehyde (**2a**) (Scheme 3) was carried out on the basis of a classical Williamson ether synthesis. Yield was 66% after vacuum distillation.

Para-substituted benzaldehydes also allow the introduction of liquid crystalline (LC) groups, resulting in increased solubility and a higher degree of alignment by spontaneous orientation of the LC groups. Furthermore, the presence of LC groups provides the possibility for external control of the molecular orientation and hence physical properties such as electrical conductivity. Four different benzaldehydes **2b**–**e** with LC groups in the para position were prepared. Phenylcyclohexyl, biphenyl, and phenylpyrimidine were used as mesogenic groups for the LC substituents. Besides stability and solubility, these LC groups provide the poly(isothianaphthene methine) backbone with specific LC properties associated with the corresponding mesogenic core. In the case of **2e** ferroelectricity might be one of the promising properties.

The phenylcyclohexyl group[28] has been used as a substituent for LC conjugated polymers such as LC polyacetylene,[29] LC polythiophene,[30] and LC polyphenylenevinylene[31] derivatives. These polymers show stable thermotropic LC phase. The biphenyl group with a chiral ester moiety shows the Sc* phase of ferroelectric liquid crystallinity.[19,32–35] Phenylpyrimidine derivatives show the Sc phase with tilted layer structure without having an ester group in the mesogenic core due to their relatively large dielectric anisotropy, $\Delta\epsilon$ ($\Delta\epsilon = \epsilon_{\|} - \epsilon_{\perp}$, where $\epsilon_{\|}$ and $\epsilon_{\perp}$ are dielectric constants in the parallel and perpendicular directions to the LC director, respectively).[36,37]

Phenylpyrimidine-Based LC Substituents. The pyrimidine derivative **2b** is prepared by the etherification of 4-(5-*n*-decylpyrimidine-2-yl)phenol (**5**) with 4-(10-bromodecyloxy)benzaldehyde (**4**).

Scheme 4



Phenylcyclohexyl-Based LC Substituents. The synthesis of the phenylcyclohexyl-based LC substituents containing an aldehyde moiety is also outlined in Scheme 3. The first step of this synthesis consists of a coupling reaction between 4-(*trans*-4′-pentylcyclohexyl)phenol (**6**) and an excess of a dibromoalkane in the presence of K_2CO_3 and KI to yield **7** ($n = 10$) and **8** ($n = 6$). Compounds **7** and **8** are then coupled with 4-hydroxybenzaldehyde to yield the corresponding para LC-substituted benzaldehydes **2c** and **2d**, respectively.

Ferroelectric LC Substituent. The para-substituted benzaldehyde with the ferroelectric LC side chain was synthesized as shown in Scheme 4. 4-Hydroxybenzoic acid was protected with methyl chloroformate in aqueous sodium hydroxide at 0 °C according to the Fischer and Fischer reaction to give 4-methoxycarbonyloxybenzoic acid (**9**).[22] 4′-Hydroxy-4-biphenylcarboxylic acid (**10**) was esterified according to the Mitsunobu reaction[23] using (*R*)-octanol, diethyl azodicarboxylate (DEAD), and triphenylphosphine (TPP) to give ester **11** as white solid. This reaction is characterized by a S_N2-type Walden inversion at the chiral center, but with no racemization resulting in the formation of ester **11** with (*S*) configuration.[23,38–40] The optically active compound **11** was then esterified with **9** using the combination of dicyclohexylcarbodiimide (DCC) and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) at room temperature to give **12**. Compound **12** was then deprotected using an ethanol—

Table 1. Molecular Weights of Polymer 3a–e[a]

polymer	yield	M_n	M_w	MWD
3a	78	5400	6700	1.2
3b	75	7900	11000	1.4
3c	67	8100	10100	1.2
3d	73	6000	8600	1.4
3e	61	7100	9200	1.3

[a] Polystyrene standard.

Table 2. ESR Results for Polymer 3a–c

polymer	spin/gram	spin/mru[a]	polymer	spin/gram	spin/mru[a]
3a	3.7×10^{18}	4.7×10^{-4}	**3d**	2.6×10^{18}	4.9×10^{-4}
3b	2.1×10^{18}	4.8×10^{-4}	**3e**	1.7×10^{18}	5.3×10^{-4}
3c	1.8×10^{18}	3.9×10^{-4}			

[a] Monomer repeat units.

ammonia solution at room temperature to give **13**.[23] Compound **2e** was prepared by etherification of **13** with 4-(8-bromooctyloxy)benzaldehyde (**14**) using K_2CO_3 and KI in acetone to give the desired material.

Synthesis of LC Poly(isothianaphthene methine)s (3a–e). At first a 1 M solution of the reagents was used to carry out the polymerization. But it appeared that to obtain the poly(isothianaphthene methine)s, a better procedure was to heat a 0.1 M 1,4-dioxane solution of **1** and **2** containing 20 vol % of $POCl_3$. This polymerization proceeds probably according to a side reaction of Rothemund reaction[41–43] employed for the condensation of pyrrole and aldehydes to form porphyrin ring systems. Lower molecular weight fractions were removed by Soxhlet extraction with methanol. Then the polymers were washed in dilute ammonia solution to remove residual doping that may find its origin in the use of $POCl_3$. After removal of the lower molecular weight fraction by methanol, the remaining dark lustrous solids appeared to be soluble in $CHCl_3$ and THF.

The number-average molecular weights of the different polymers vary between 5400 and 8100. The molecular weight distribution is rather narrow (1.2–1.4) and seems to be independent of the nature of the side chain (Table 1).

In the ^1H NMR spectra, the absence of the signals at 0.54 and 0.94 ppm originating from the *tert*-butyldimethylsilyl substituents of the isothianaphthene monomer unit as well as the absence of the signal corresponding to the aldehyde proton at 9.8 ppm and the aldehyde carbon at 150 ppm indicate the completion of the polycondensation reaction. Also, the broadened signals in the ^1H NMR spectrum are indicative for the polymeric nature of the material. This may be due to the paramagnetic nature of the polymer. Electron spin resonance spectroscopy (ESR) was used to probe the possible intermediates of the polymer. Table 2 shows the results of the ESR study of the polymers at 20 °C. The spin concentration of the polymer is in the range 1.7×10^{18}–3.7×10^{18}. The Dysonian line shape of the resonance was observed for these conjugated polymers such as polyacetylene.[55] The low-band-gap polymer is easily oxidized in air due to its small ionization potential. This may be the origin of the oxidation of the polymer in ambient atmosphere, the presence of conducting electrons in the polymer main chain and the oxidation of the proton attached to the methine group during the polymerization reaction. The dehydrogenation also yields radical intermediates in the polymer main chain. The spin concentration was not changed for 1 month in the air.

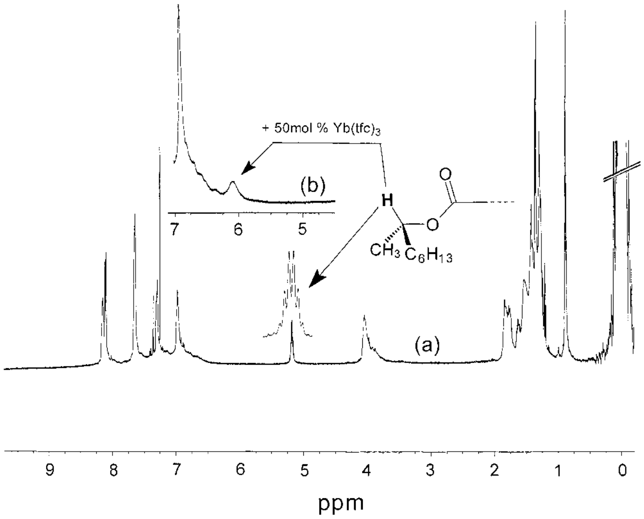


Figure 2. ^1H NMR of **3e** in $CDCl_3$ with (a) no shift reagent and (b) + 50 mol % Yb(tfc)$_3$.

In the ^1H NMR, the absence of a signal between 5 and 6 ppm indicates the formation of a fully conjugated system.[13,14,17] The ^{13}C NMR spectra of the polymers are well in agreement with those of the corresponding LC substituent, except for the absence of the aldehyde carbon signal. The presence of a signal at about 130 ppm corresponding to the methine carbon is again an indication of the presence of a fully conjugated system. The shifts corresponding with the isothianaphthene ring systems were difficult to be distinguished clearly. This may be due to the fact that the benzenoid and quinonoid structure of isothianaphthene ring give resembled but not completely the same chemical environment, resulting in indistinguishable numerous chemical shift signals.

Addition of a lanthanide shift reagent to an optical active compound can result in shift of the resonance signal. Here we used ytterbium D-3-trifluoroacetylcamphorate, Yb(tfc)$_3$, for resolving peaks from enantiomers to check the degree of chirality of the compounds **11–13, 2e**, and **3e**.[46] The induced shifts are caused by a large difference in the magnetic susceptibility tensors for the coordinated complex, and the McConnell equation, $\Delta\delta = k(1 - 3\cos^2\theta)/r^3$, qualitatively defines the relationship between the induced shift $\Delta\delta$, r is the distance from the metal center, and θ is the number of degrees that the nucleus lies away from the axial axis of symmetry.

^1H NMR spectra before and after the addition of 50 mol % Yb(tfc)$_3$ vs **3e** are shown in Figure 2. The δ value of the proton attached to the chiral center of **3e** is clearly shifted ~1 ppm to the lower magnetic field by the addition of Yb(tfc)$_3$; furthermore, no other peak was observed due to the racemization. The results of addition of Yb(tfc)$_3$ as a chiral shift reagent for the chiral compounds are summarized in Table 3. The sextet signals of protons attached to the chiral center became broad singlet after addition of Yb(tfc)$_3$. These results indicate that asymmetry in the chiral center of the compounds is maintained from the first step to the polymerization.

The FT-IR spectra of the polymers all look very similar. Figure 3 shows the FT-IR spectra of **1**, **2c**, and **3c**. The FT-IR spectrum of polymer **3c** shows no absorptions characteristic of the C=O stretching at 1700 cm^{-1} of **2c** and the *tert*-butyldimethylsilyl moiety of **1**

Table 3. NMR Chemical Shifts of Chiral Compounds

compd	$\delta_{(C^*-H)}{}^a$	$\delta_{(C^*-H)}{}^a$ (+ 50 mol % of Yb(tfc)$_3$ vs compd)	confign
11	5.20	6.21	(*S*)
12	5.18	6.16	(*S*)
13	5.19	6.17	(*S*)
2e	5.18	6.38	(*S*)
3e	5.10	6.11	(*S*)

[a] δ from TMS.

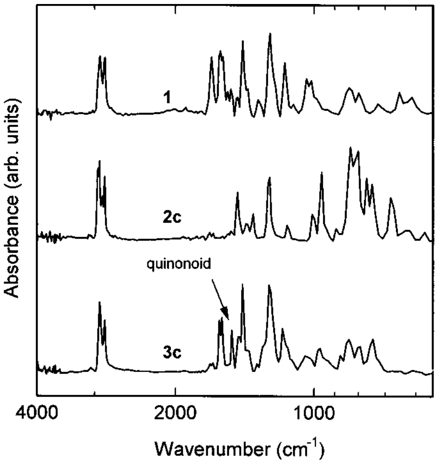


Figure 3. FT-IR spectra of **1**, **2c**, and **3c**.

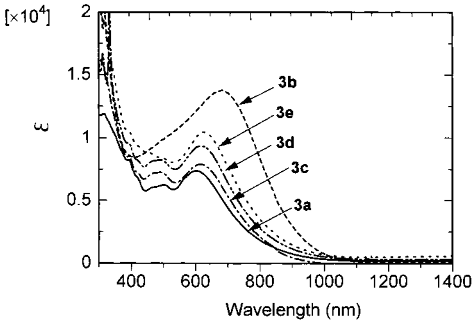


Figure 4. UV–vis–NIR spectra of the polymers in $CHCl_3$ solution (3.0 × 10^{-5} M).

at 965, 832, 802, 770, 750, and 684 cm^{-1}. According to Chen et al.,[13,14] the C=C stretching vibration of quinonoid thiophene systems is found between 1665 and 1645 cm^{-1}. In the case of poly(isothianaphthene methine), it has been reported that the bands associated with C=C vibrations are situated between 1600 and 1500 cm^{-1}.[44] All FT-IR spectra are in accordance with the spectra measured by Neugebauer et al.[44]

UV–vis–NIR spectra of the polymers in $CHCl_3$ (3.0 × 10^{-5} M) were recorded (Figure 4). All the polymers show a λ_{max} at around 600 nm, except for polymer **3b** which is characterized by a λ_{max} at 684 nm. Figure 5 shows absorption spectra of pristine and dedoped **3b**. The broad absorption of pristine **3b** at 1550 nm in the spectrum is due to doping of the polymer. These data indicate that the compound obtained after Soxhlet is still slightly doped. This residual doping probably originates from the use of $POCl_3$ in the polymerization reaction. After dedoping with dilute ammonia the broad absorption band in the near-infrared disappears. Similar results have been observed for other poly(arylene methine)s such as poly(thiophene methine),[13,14] poly(isothianaphthene methine),[17] and LC-substituted poly(pyrrylene methine).[45] All the pristine polymers are dark blue. The apparent color of the polymers was not changed after dedoping.

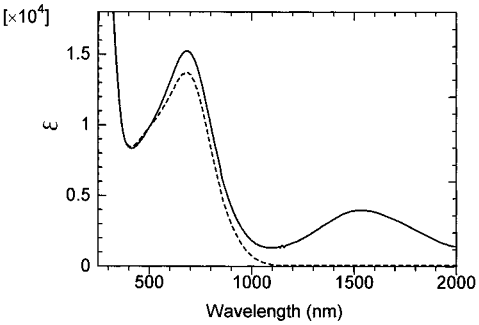


Figure 5. UV–vis–NIR spectra of **3b** in $CHCl_3$ solution (3.0 × 10^{-5} M): solid line, pristine; broken line, dedoped by ammonia.

Table 4. Band Gap of the Polymers

polymer	$E_g{}^a$ (eV)	polymer	$E_g{}^a$ (eV)
3a	1.3	**3d**	1.2
3b	1.2	**3e**	1.2
3c	1.3		

[a] Band edge band gap.

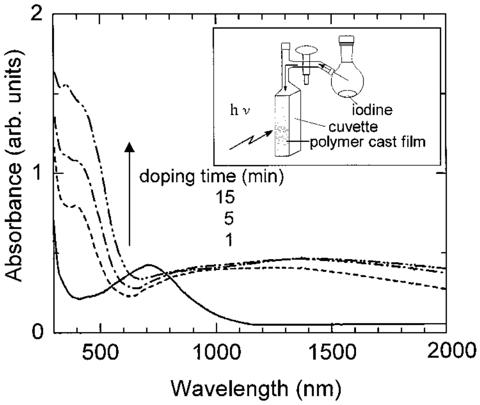


Figure 6. UV–vis–NIR spectra of in-situ iodine vapor doping for **3b**.

From the band edge in the spectra of the dedoped material, a value can be obtained that is often used as an estimation for the band gap (E_g). The values for the band gap determined from the band edge of the UV–vis–NIR spectra are summarized in Table 4. The band gaps are all in the range 1.2–1.3 eV. This is well below the cutoff value of 1.5 eV. All of the obtained polymers can therefore be considered as low-band-gap polymers.

Absorption spectra were measured in-situ vapor doping of iodine for **3b**, for which the polymer had been cast on an inner wall of a quartz cuvette, as shown in Figure 6. The absorption band of the conjugated main chain of **3b** observed at 705 nm in THF is assignable to $\pi-\pi^*$ transition of the conjugated polymer main chain. This peak was 21 nm red-shifted in the case of the cast film. This may be due to the in-plane alignment which occurred in the cast film. The ionization potential of the polymer is relatively small; hence, it should take a short time to complete iodine doping of the presented polymer. After 1 min, the absorption band at 705 nm decreased in intensity. At the same time, new broad absorption bands appeared at 1370 nm. This band could be related to the absorption band at 1550 nm in pristine polymer which is doped with $POCl_3$ during polymerization, although this broad absorption was 180 nm blue-shifted

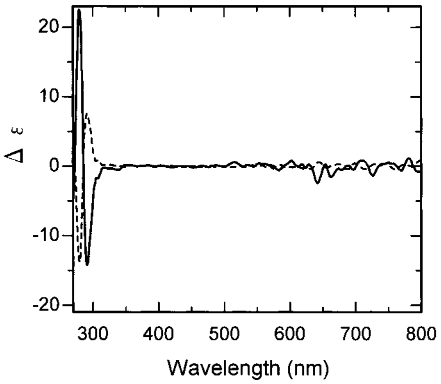


Figure 7. CD spectra of **3a** (solid line) and **3e** (broken line) in $CHCl_3$ solution (6.0×10^{-5} M).

Table 5. Electrical Conductivity of Polymer 3a−e

polymer	intact (S/cm)	iodine doped (S/cm)
3a	3.6×10^{-8}	3.2×10^{-4}
3b	6.3×10^{-8}	1.5×10^{-4}
3c	1.3×10^{-8}	1.3×10^{-4}
3d	2.8×10^{-8}	9.1×10^{-5}
3e	4.0×10^{-8}	5.2×10^{-5}

in the case of iodine doping. Figure 7 shows that there is a Cotton effect in the region between 300 and 400 nm for polymers **3a** and **3e**. This can be attributed to the presence of the optical active moiety in the LC substituents. On the other hand, there is no Cotton effect in the visible region around 600 nm. The band in this region of the spectrum originates from the $\pi-\pi^*$ transition of the conjugated polymer main chain. The polymer backbone therefore seems not to form specific second-order configurations such as a helical structure.

Electrical conductivity of the polymers was determined by the four-probe method. Upon gas vapor doping by iodine, the conductivity increased from 10^{-8} to 10^{-4} S/cm (Table 5). For low-band-gap polymers, however, one would expect the conductivity to be much higher. However, these results are in accordance with conclusions of Neugebauer et al.[44] Their infrared spectroelectrochemical investigations of poly(isothianaphthene methine) indicate that strong charge carrier localization occurs due to a decrease of the effective conjugation as a consequence of strong noncoplanarity induced by steric repulsion of consecutive units and relatively large side chains. ESR measurements elucidate that the spin concentration of the polymers was ca. 1 spin per ca. 2000 units before doping. The spin concentration of the polymers was increased 6−9 times after vapor doping of iodine for 90 min.

Liquid crystallinity (LC) of the precursor compounds was examined by polarizing optical microscopy observation and DSC measurements. The low molar mass compounds with mesogenic moieties show nematic LC, except for **7** and the compounds containing hydroxy groups. **2e** showed chiral nematic (N*) LC with helical structure. Thermal characterization by DSC indicates that these conjugated polymers show phase transitions. The DSC results are summarized in Table 6. As an example, Figure 8 shows both the cooling and the heating processes for **3c**. Three peaks corresponding to two mesophases can be observed. The phase transition temperatures of the polymer are summarized in Table 7. In general, the polymers have polymorphic texture. However, the texture was not satisfactory for typical LC phase, which may be due to randomly oriented domains as a consequence of little growth. Additionally, the extremely dark color (bluish-black) of the nondoped polymers makes it very difficult to observe apparently clear optical texture. Detailed liquid crystallinity of the polymers including XRD analysis is currently under study.

Table 6. Phase Transition Temperature of LC Compounds[a]

compd	heating	cooling
8	C 29 N 37 I	C 8 N 37 I
12	C 43 N 72 I	C 38 N 55 I
2b	C 62 N 79 I	C 38 N 74 I
2c	C 78 I	C 41 N 72 I
2d	C 57 N 85 I	C 41 N 83 I
2e	C 60 N* 102 I	C 45 N* 84 I

[a] C = crystal, N = nematic, N* = chiral nematic, I = isotropic.

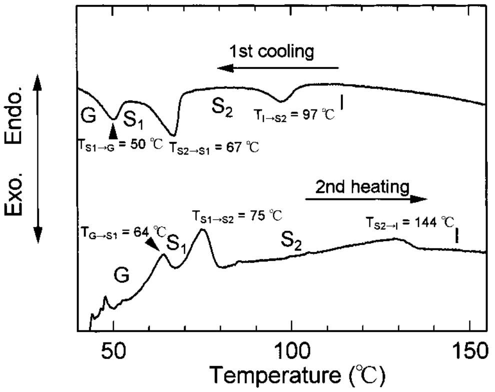


Figure 8. DSC curves of **3c**. Scanning rate: 10 °C/min.

Table 7. Phase Transition Behaviors of the Polymers

polymer	phase transition temp[a] (°C)
3a	G 44 I
3b	G 61 S 165 I
3c	G 50 S_1 67 S_2 97 I
3d	G 80 S 110 I
3e	G 48 S_1 96 S_2 118 I

[a] Determined by DSC on the first cooling scan: G = glassy, S_1 and S_2 = ordered smectic, I = isotropic.

4. Conclusion

We synthesized a series of low-band-gap polymers containing liquid crystalline side chains which exhibit enhanced solubility. These polymers are easy to be manipulated in ambient conditions. The enhanced solubility in organic solvents such as $CHCl_3$ and THF allows easier processing, which is important if these polymers are to be applied in electronic devices. The band gap of the obtained materials is well below the low-band-gap cutoff value of 1.5 eV. As such, the class of poly(isothianaphthene methine)s is one of the few polymeric materials that effectively combines a low band gap and a high solubility in different organic solvents. Conductivities are lower than would be expected from a low-band-gap polymer. However, this result is in accordance with the conclusions of Neugebauer et al.[44] and is a characteristic that should be taken into account when developing new applications. On the other hand, the chemical reaction conditions allow ample space for the introduction of a wide variety of side chains. Additionally, introducing electron-donating or electron-withdrawing substituents onto the isothianaphthene ring should allow fine-tuning of the value of the band gap depending on the specific application oriented requirements. Because of the straightforward chemical accessibility for preparing other derivatives and the possibility for fine-tuning the physical properties, poly(isothianaphthene methine)s are candidate materials for combining important electrooptical properties of synthetic metals with the exciting field of supramolecular technology.

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