Chirality in poly(phenylene-*alt*-bithiophene)s: a comprehensive study of their behavior in film and nonsolvents

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Abstract: New chiral, alternating copolymers of 2,5-dialkoxybenzenes and 3,3'-dialkoxy-2,2'-bithiophenes were prepared and their (chir)optical properties were studied. The polymers were prepared by a Stille-coupling reaction and show high conjugation lengths in both solution and films. Fluorescence and UV-vis spectroscopy indicate that the polymers are present as rigid, highly conjugated polymer strands in solution. In a nonsolvent mixture the polymers aggregate and, if chiral substituents are employed, supramolecular chirality is observed. In annealed films, very large Cotton effects are observed.

Keywords: Conjugated polymers, polythiophenes, alternating copolymers, chirality.

Introduction

Conjugated polymers have been attracting a lot of attention from academia as well as industry in the past decades, which has led to a thorough understanding of their physical and chemical properties.[1] Also chirality has been implemented in these materials: The chiral properties of, for instance, alkyl-[2], alkoxy-[3], aryl-substituted[4] polythiophenes, poly(phenylenevinylene)s[5] (PPVs), poly(phenylene ethynylene)s[6] (PPEs), poly(fluorene)s (PFs)[7], poly(carbazole)s[8], … have been intensively studied. Interestingly, if the polymers can be easily doped (oxidized in case of p-doping), it should be possible to construct chiral polymer conductors. In that view, we previously synthesized (chiral) regioregular poly(3-alkoxythiophene)s.[3] Since 3-substituted thiophenes are asymmetric molecules, regioregularity becomes a major issue in the polymerization of these compounds. Two possibilities for the construction of regular polymers then arise: either a regiospecific methodology is employed, rendering head-to-tail coupled poly(3-substituted polythiophene)s. This strategy has, for instance, successfully been employed in the development of head-to-tail coupled poly(3-alkylthiophene)s (HT-P3ATs).[9] On the other hand, the monomeric unit can be condensed in a HH or TT fashion to form a symmetric dimer, which can then be polymerized. In this approach, successive HH-TT couplings are present in the resulting polymer. Both strategies have been employed for the construction of rr P3AOTs.[3, 10-12]

A promising advantage of the last approach is that it enables one to copolymerize the (symmetric) bithiophene dimer with other (symmetric) conjugated moieties, such as a phenyl ring. In this way, two different conjugated moieties, with possibly different substituents, can be incorporated. Moreover, if the two different units are alternatingly connected to each other, regular alternating (co)polymers are obtained.

In this manuscript, we report the synthesis and properties of alternating copolymers of 3,3'-dialkoxy-[2,2'-bithiophene]s with 2,5-dialkoxybenzene derivatives, in which the substituents on the two different moieties can be either chiral or achiral. The symmetric benzene moiety was chosen for its synthetic versatility. The effects of the substituents on the chiral properties of the polymers will be discussed into detail.

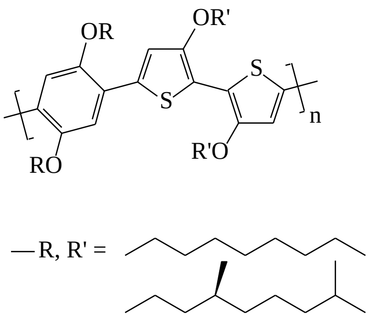


Figure 1. General structure of the alternating copolymers.

Experimental Section

Reagents and instrumentation

All reagents were purchased from Aldrich Chemical Co., Acros Organics, Merck, Fluka and Avocado. Reagent grade solvents were dried when necessary and purified by distillation.

Gel permeation chromatography (GPC) measurements were done with a Shimadzu 10A apparatus with a tuneable absorbance detector and a differential refractometer in tetrahydrofuran (THF) as eluent towards polystyrene standards. ^{1}H nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 MHz. UV-Vis and CD spectra were recorded with a Varian Cary 400 and a JASCO 810 apparatus respectively. For the CD measurements, the films were also 90 ° rotated, to ensure that no artifacts were measured. Cyclic voltammetry was performed on a Princeton Applied Research PARSTAT 2273, equipped with a standard three-electrode configuration. A Ag/AgCl (3 M NaCl) electrode served as a reference electrode and a Pt wire and disk as counter- and working electrode. The measurements were done in acetonitrile with Bu_4NBF_4 (0.1 M) as the supporting electrolyte under argon atmosphere. Ferrocene was added before each run as an internal standard. The Fe(II/III) couple of ferrocene was observed at 0.460 V (scan rate = 50 mV/s). For the measurements, a polymer film was dropcasted from chloroform solution on the Pt disk working electrode. The DSC measurements were performed on a Perkin-Elmer DSC 7 apparatus. The fluorescence measurements were done on a pTi photon Technology International apparatus. The samples were excited near the absorption wavelength and the quantum yields were determined using secondary methods.[13] The optical rotations were measured with a polAAr 20 apparatus; the solvent used and concentration (in g/100 mL) are given in parenthesis. Films for UV-vis and CD experiments were prepared by spincoating from chloroform-solution (2000 rpm, 10 s). **1a**[14], **1b**[15]were synthesized according to literature procedures.

Synthesis of the benzene monomers

Synthesis of 1,4-dibromo-2,5-dioctyloxybenzene (2a)

A solution of **1a** (5.01 g, 15.0 mmol) in dichloromethane (50 mL) was cooled to -78 °C and the flask was equipped with a $CaCl_2$-tube. A solution of Br_2 (6.71 g, 42.0 mmol) in dichloromethane (15 mL) was added drop wise. The mixture was warmed to room temperature and poured into a $NaHSO_3$-solution (60 mL). The organic layer was washed successively with a $NaHCO_3$-solution and brine. After drying over $MgSO_4$, the solvents were removed *in vacuo*. Finally, the crude product was purified by recrystallization from ethanol.

Yield: 6.58 g (89 %).

m.p.: 69.8 °C.

^{1}H NMR ($CDCl_3$): δ = 7.08 (s, 2H), 3.95 (t, 4H), 1.79 (qu, 4H), 1.47-1.28 (m, 20 H), 0.88 (t, 6H).

^{13}C NMR ($CDCl_3$): δ = 150.2, 118.6, 111.2, 70.4, 31.9, 29.4, 29.3, 26.1, 22.8, 14.3.

MS: m/z = 492.0 (M^+) (calc.: 491.8).

Synthesis of (*S*)-(-)1,4-dibromo-2,5-di(3,7-dimethyloctyloxy)benzene (2b)

The same procedure as described for **2a** is followed, starting form **1b** (5.85 g, 15.0 mmol). The crude product was purified by column chromatography (silicagel; eluent: hexane:ethylacetate (95:5 v/v)) to afford a yellow oil.

Yield: 3.76 g (46 %).

$[\alpha]_D^{20}$ = -1.55 deg.dm^{-1}.mol^{-1}.L (c = 19 in dichloromethane).

^{1}H NMR ($CDCl_3$): δ = 7.09 (s, 2H), 3.97 (m, 4H), 1.82 (m, 2H), 1.60 (m, 6H), 1.33 (m, 6H), 1.17 (m, 6H), 0.94 (d, 6H), 0.86 (d, 12H).

^{13}C NMR ($CDCl_3$): δ = 150.2, 118.5, 111.2, 68.6, 39.3, 37.6, 36.2, 29.9, 28.1, 24.8, 22.9, 19.8.

MS: m/z = 548.1 (M^+) (calc.: 548.0).

Synthesis of 1,4-diiodo-2,5-dioctyloxybenzene (3a)

1a (6.68 g, 20.0 mmol), KIO_3 (2.57 g, 12.0 mmol) and iodine (4.57 g, 18.0 mmol) were dissolved in a mixture of sulphuric acid (30%) (6.0 mL), acetic acid (36 mL) and carbontetrachloride (8.0 mL). The mixture was stirred for 3 h at 75 °C. After reaction, the precipitate was filtered off and washed with cold methanol. Finally, the crude product was recrystallized twice from ethanol.

Yield: 3.78 g (33 %).

m.p.: 56.1 °C.

^{1}H NMR ($CDCl_3$): δ = 7.17 (s, 2H), 3.92 (t, 4H), 1.80 (qu, 4H), 1.50-1.29 (m, 20H), 0.88 (t, 6H).

^{13}C NMR ($CDCl_3$): δ =152.9, 122.9, 86.4, 70.5, 31.9, 29.4, 29.2, 26.2, 22.8, 14.3.

MS: m/z = 586.0 (M^+) (calc.: 586.0).

Synthesis of 1,4-di(trimethyltin)-2,5-dioctyloxybenzene (4a)

2a (3.93 g, 8.00 mmol) was dissolved in dry THF (30.0 mL) and purged with argon. At -78°C and under argon atmosphere, *n*-BuLi (7.04 mL, 17.6 mmol, 2.5 M in hexane) was added via a syringe. After stirring for 30 minutes, a solution of Me_3SnCl (3.98 g, 20.0 mmol) in dry THF (15 mL) was added drop wise. The reaction mixture was warmed to room temperature and stirred for another 15 minutes. Then, the solvents were removed *in vacuo*. The crude product was redissolved in hexane and the precipitate was filtered off. Finally, the product was recrystallized twice from ethanol.

Yield: 3.23 g (61 %).

m.p.: 85.2-87.3 °C

^{1}H NMR ($CDCl_3$): δ = 6.84 (s, 2H), 3.89 (t, 4H), 1.74 (m, 4H), 1.29 (m, 20H), 0.88 (t, 6H), 0.25 (s, 18H).

^{13}C NMR ($CDCl_3$): δ = 157.7, 131.9, 117.3, 68.4, 32.0, 29.9, 29.5, 29.4, 26.3, 22.8, 14.3, -8.80.

MS: m/z = 660.0 (M^+) (calc.: 659.7).

Synthesis of the bithiophene monomers

Synthesis of 2-bromo-3-octyloxythiophene (6a)[10]

3-octyloxythiophene (**5a)** (6.72 g, 31.7 mmol) was dissolved in dry chloroform (40 mL), shielded from light and brought under argon atmosphere. The solution was cooled to -30°C and *N*-bromosuccinimide (5.64 g, 31.7 mmol) was added in small portions. The reaction was followed by TLC (petroleum ether). The mixture was warmed to room temperature and a $NaHSO_3$-solution (50 mL) was added. The product was extracted twice with diethyl ether (60 mL) and the combined organic layers were washed with a $NaHCO_3$-solution and brine. After drying over $MgSO_4$, the solvents were removed *in vacuo*. Finally, the crude product was purified by column chromatography (silicagel; eluent: petroleum ether).

Yield: 8.14 g (88 %).

^{1}H NMR ($CDCl_3$): δ = 7.13 (d, J = 5.5 Hz, 1H), 6.69 (d, J = 5.5 Hz, 1H), 3.99 (t, 2H), 1.73 (qu, 2H), 1.43 (m, 2H), 1.29 (m, 8H), 0.88 (t, 3H).

^{13}C NMR ($CDCl_3$): δ = 155.0, 124.6, 117.9, 91.9, 72.6, 32.3, 30.0, 29.8, 29.7, 26.3, 23.2, 14.6.

MS: m/z = 290.0 (M^+) (calc.: 291.1), 180.0 (M^+ -C_8H_{16})

Synthesis of (*S*)-(-)-2-bromo-3-(3,7-dimethyloctyloxy)thiophene (6b)

The same procedure as described for **6a**, is followed, starting form **5b** (12.0 g, 50.0 mmol).

Yield: 11.8 g (74 %).

$[\alpha]_D^{20}$ = -0.63 deg.dm^{-1}.mol^{-1}.L (c = 25 in dichloromethane).

^{1}H NMR ($CDCl_3$): δ = 7.18 (d, J = 5.5 Hz, 1H, 6.74 (d, J = 5.5 Hz, 1H), 4.06 (t, 2H), 1.77 (m, 1H), 1.66 (m, 1H), 1.52 (m, 2H), 1.31-1.16 (m, 6H), 0.93 (d, 3H), 0.86 (d, 6H).

^{13}C NMR ($CDCl_3$): δ = 154.6, 124.2, 117.5, 91.5, 70.7, 39.3, 37.3, 36.5, 29.7, 28.1, 24.7, 22.8, 19.8.

MS: m/z = 320.0 (M^+) (calc.: 319.3).

Synthesis of 3,3’-dioctyloxy-[2,2’-bithiophene] (7a)

A solution of **6a** (3.78 g, 13.0 mmol) was dissolved in dry THF (15 mL) and purged with argon. At room temperature, MeMgBr (4.33 mL, 13.0 mmol, 3.0 M in diethyl ether) was added drop wise. Then, the reaction mixture was gently refluxed for 1 h before being transferred *via cannula* to a cooled solution (0 °C) of **6a** (3.78 g, 13.0 mmol) and Ni(dppp)Cl_2 (700 mg, 0.130 mmol) in dry THF (15 mL). After refluxing for one night, the reaction mixture was allowed to cool to room temperature and poured into a 0.5 M HCl-solution. The green precipitate was filtered off, which was a first fraction of the pure product. Then, the aqueous layer was extracted twice with diethyl ether, and the organic extracts were washed with a $NaHCO_3$-solution and brine. After drying over $MgSO_4$, the solvent was removed by rotary evaporation. The residue was finally purified by recrystallization from hexane.

Yield: 2.44 g (44 %).

m.p.: 74.6–75.0 °C.

^1H NMR ($CDCl_3$): δ = 7.06 (d, J = 5.5 Hz, 2H), 6.83 (d, J = 5.5 Hz, 2H), 4.09 (t, 4H), 1.84 (qu, 4H), 1.52 (m, 4H), 1.28 (m, 16H), 0.88 (t, 6H).

^{13}C NMR ($CDCl_3$): δ = 152.3, 122.0, 116.4, 114.5, 72.4, 32.2, 30.1, 29.7, 29.6, 26.5, 23.0, 14.5.

MS: m/z = 422.0 (M^+) (calc.: 422.4), 309 (M^+ -C_8H_{17}), 197 (M^+ -$C_{16}H_{34}$).

Synthesis of (*S*)-(+)-3,3’-di(3,7-dimethyloctyloxy)-[2,2’-bithiophene] (7b)

The same procedure as described for **7a**, is followed, starting form **6b** (5.42 g, 17.0 mmol). The crude product was purified by column chromatography (silicagel; eluent: petroleum ether) and collected as an oil.

Yield: 3.67 g (45 %).

$[\alpha]_D^{20}$ = +9.29 deg.dm^{-1}.mol^{-1}.L (c = 5 in dichloromethane).

^1H NMR ($CDCl_3$): δ = 7.07 (d, J = 5.5 Hz, 2H), 6.84 (d, J = 5.5 Hz, 2H), 4.13 (t, 4H), 1.91 (m, 2H), 1.77 (m, 2H), 1.60-1.48 (m, 4H), 1.33-1.16 (m, 12H), 0.93 (d, 6H), 0.86 (d, 12H).

^{13}C NMR ($CDCl_3$): δ = 152.0, 121.7, 116.2, 114.3, 70.4, 39.3, 37.4, 36.8, 29.7, 28.1, 24.8, 22.9, 19.8.

MS: m/z = 478.0 (M^+) (calc.: 478.4).

Synthesis of 5,5'-dibromo-3,3'-dioctyloxy-[2,2'-bithiophene] (8a)

7a (1.27 g, 3.00 mmol) was dissolved in dry chloroform (20 mL). The solution was shielded from light, brought under argon atmosphere and cooled to -30 °C. Then, *N*-bromosuccinimide (1.07 g, 6.00 mmol) was added in small portions. After reaction (as monitored by TLC), a $Na_2S_2O_3$-solution (30 mL) was added. The crude product was extracted with dichloromethane, washed with a $NaHCO_3$-solution and brine. After drying over $MgSO_4$, the solvents were removed *in vacuo* and the product was purified by column chromatography (silicagel; eluent: petroleum ether:dichloromethane (90:10 v/v)) and isolated as a green solid.

Yield: 1.46 g (84 %).

m.p.: 70.1-70.4 °C

^{1}H NMR ($CDCl_3$): δ = 6.81 (s, 2H), 4.03 (t, 4H), 1.82 (qu, 4H), 1.48 (m, 4H), 1.30 (m, 16 H), 0.89 (t, 6H).

^{13}C NMR ($CDCl_3$): δ = 150.7, 119.4, 115.5, 110.2, 72.8, 32.2, 29.9, 29.6, 26.3, 23.1, 14.5.

MS: m/z = 580 (M^+) (calc.: 580.2), 467 (M^+-C_8H_{17}), 355 (M^+-2 C_8H_{17}), 275 (M^+ -2 C_8H_{17} - Br).

Synthesis of (*S*)-(-)-5,5'-dibromo-3,3'-di(3,7-dimethyloctyloxy)-[2,2'-bithiophene] (8b)

The same procedure as described for **8a** is followed, starting form **7b** (862 mg, 1.80 mmol). The crude product was purified by column chromatography (silicagel; eluent: petroleum ether) and isolated as a yellow oil.

Yield: 0.790 g (69 %).

$[\alpha]_D^{20}$ = -0.56 deg.dm^{-1}.mol^{-1}.L (c = 5 in dichloromethane).

^{1}H NMR (acetone-*d6*): δ = 7.14 (s, 2H), 4.22 (t, 4H), 1.88 (m, 2H), 1.80 (m, 2H), 1.66-1.48 (m, 4H), 1.39-1.20 (m, 12H), 0.97 (d, J = 6.4 Hz, 6H), 0.88 (d, J = 7.3 Hz, 12H).

^{13}C NMR (acetone-d6): δ = 150.5, 119.4, 114.6, 109.4, 70.5, 39.2, 37.2, 36.5, 29.4, 28.8, 28.3, 27.9, 24.7.

MS: m/z = 336.0 (M^+) (calc.: 636.6).

Synthesis of 5,5’-di(trimethyltin)-3,3’-dioctyloxy-[2,2’-bithiophene] (9a)

A solution of **7a** (6.34 g, 15.0 mmol) in dry diethyl ether (250 mL) was purged with argon. At 0 °C , *t*-BuLi (21.0 mL, 31.5 mmol, 1.5 M in pentane) was added *via cannula* and the reaction mixture was warmed to room temperature and stirred vigorously for another 15 minutes. Then, trimethyltin chloride (6.42 g, 32.2 mmol), dissolved in diethyl ether (50 mL), was added via a syringe at room temperature. After stirring for 1 h, the solvents were removed by rotary evaporation. The residue was redissolved in hexane and the precipitate was filtered off. Finally, the crude product was purified by recrystallization from acetonitrile.

Yield: 7.05 g (63 %).

m.p.: 76.3-76.7 °C

^{1}H NMR ($CDCl_3$): δ = 6.89 (s, 2H), 4.13 (t, 4H), 1.85 (qu, 4H), 1.55 (m, 4H), 1.40-1.28 (m, 16H), 0.89 (t, 6H), 0.37 (s, 18H).

^{13}C NMR ($CDCl_3$): δ = 153.9, 133.5, 123.7, 120.2, 72.1, 32.0, 29.9, 29.6, 29.5, 26.4, 22.8, 14.3, -8.19.

MS: m/z = 749.4 (M^+) (calc.: 748.3).

Synthesis of (*S*)-(+)-5,5’-di(trimethyltin)-3,3’-di(3,7-dimethyloctyloxy)-[2,2’-bithiophene] (9b)

The same procedure as described for **9a**, is followed, starting form **7b** (3.34g, 7.00 mmol). The product was collected as a dark oil and used without further purification.

Yield: 5.45 g (97 %).

$[\alpha]_D^{20}$ = +2.80 deg.dm^{-1}.mol^{-1}.L (c = 10 in dichloromethane).

^{1}H NMR ($CDCl_3$): δ = 6.87 (s, 2H), 4.14 (t, 4H), 1.90-1.75 (m, 4H), 1.63 (m, 2H), 1.53 (m, 2H), 1.38-1.10 (m, 6H), 1.16 (m, 6H), 0.95 (d, 6H), 0.86 (d, 12H), 0.35 (s, 18H).

^{13}C NMR ($CDCl_3$): δ = 153.9, 133.4, 123.7, 120.3, 70.3, 39.5, 37.5, 37.1, 29.8, 28.1, 24.9, 22.9, 19.7, -8.19.

MS: m/z = 803.2 (M^+) (calc.: 803.8)

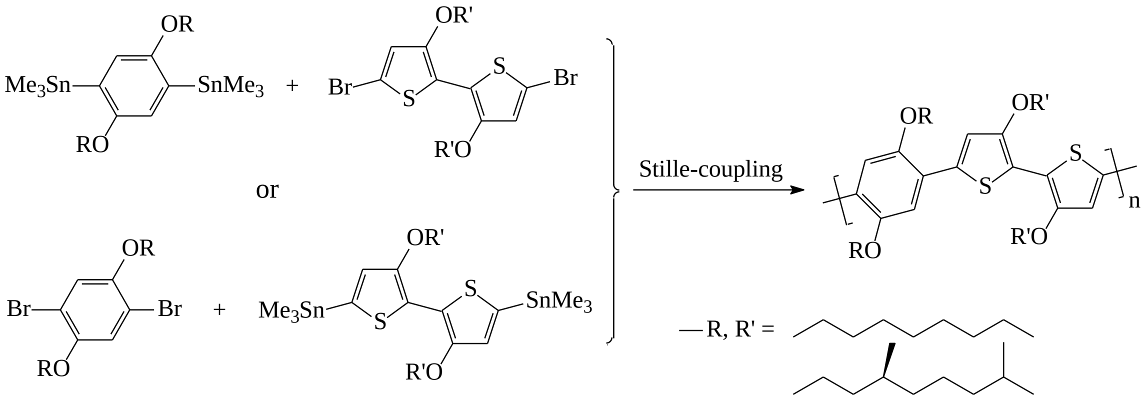
Synthesis of the polymers

A general procedure is as follows: a solution of distannylated monomer (0.500 mmol), dibrominated monomer (0.500 mmol), Pd_2dba_3 (11.4 mg, 125 μmol) and $AsPh_3$ (30.6 mg, 0.100 mmol) in dry THF (15 mL) was purged with argon for 0.5 h and then gently refluxed for 48 h. After cooling down, the polymer was concentrated and poured into methanol. The precipitate was filtered off and the polymer was further purified by Soxhlet extractions using successively acetone, hexane and chloroform. The chloroform-soluble fraction was concentrated and precipitated into methanol. Finally, the polymer was filtered off and dried.

Results and discussion

Monomer synthesis

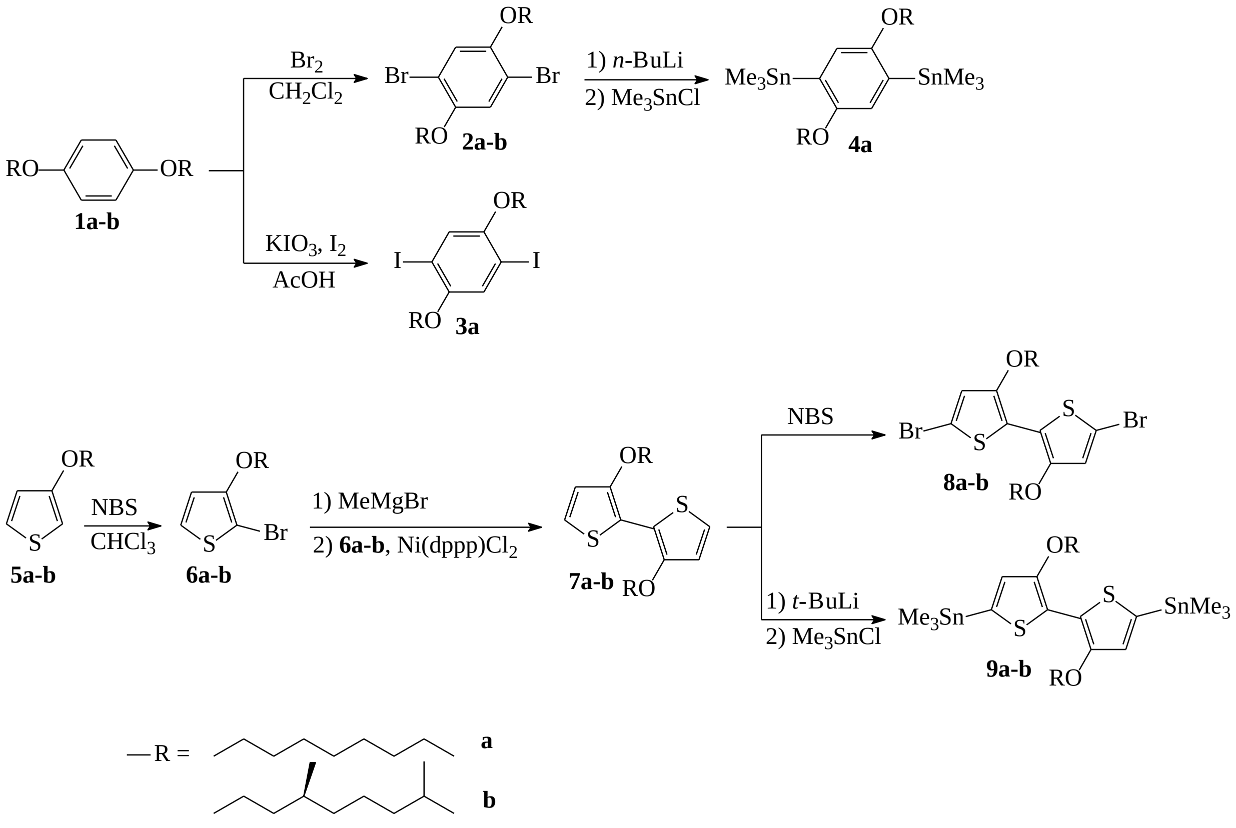
The polymers were synthesized by a polycondensation of distannylated and dihalogenated monomers using a Stille-coupling (scheme 1). Therefore, both distannylated and dihalogenated monomers were prepared. The benzene as well as bithiophene monomers were both distannylated and dihalogenated. In order to be able to investigate the chiroptical properties of the polymers as well, also achiral and chiral substituents were employed.



Scheme 1. General pathway for the preparation of the alternating copolymers.

The synthesis of the monomers is depicted in scheme 2. The benzene monomers were prepared starting from the dialkylated hydroquinone derivatives **1a-b**.[14, 15] Bromination was accomplished using bromine, while iodination was performed using KIO_3 and I_2. The distannylated monomer **4a**, finally, was conveniently prepared by bromine-lithium exchange starting from **2a** using *n*-BuLi, followed by quenching of the dilithium derivative with Me_3SnCl.

The key step for the synthesis of **8a-b** and **9a-b** was the coupling of **6a-b**, prepared by bromination of **5a-b** with NBS, to afford the bithiophene derivative **7a-b**. Therefore, **6a-b** was converted into its Grignard reagent by a Grignard metathesis reaction with methyl magnesium bromide, which was subsequently coupled to another equivalent of **6a-b** in the presence of $Ni(dppp)Cl_2$. In this way, the bithiophene derivatives could easily be prepared in good yields. **7a-b** was then brominated to yield **8a-b**. The distannylated monomers, finally, were prepared by dilithiation of **7a-b** using *t*-BuLi and quenching with Me_3SnCl. The achiral **9a** was collected as a solid and could be efficiently purified by recrystallization; the chiral **9b** is an oil, which could not be purified by column chromatography (since destannylation occurs). Fortunately, **9b** was sufficiently pure after reaction to be used without purification.



Scheme 2. Synthesis of the monomers.

Polymer synthesis

As depicted in scheme 1, alternating copolymers were prepared by a Stille-coupling between dihalogenated and distannylated monomers. Consequently, two different approaches are possible: either distannylated benzene monomers are coupled with dihalogenated bithiophene monomers or, vice versa, dihalogenated benzene monomers are coupled with distannylated bithiophene monomers. As can be concluded from Table 1, entry 1-2, the best results are obtained when dihalogenated benzene monomers are reacted with distannylated bithiophene monomers. Concerning the halogen used (entry 2-3), diiodinated compounds resulted in much larger polydispersities and, therefore, although larger yields were obtained, dibromo-substituted compounds were employed. Finally, in order to optimize the polymerization conditions, also different catalysts and solvents mixtures were tried. This reveals that in terms molecular weight, yield and especially polydispersity, the system Pd_2dba_3+$AsPh_3$[16] was the system of choice. Therefore, this protocol was used in all other polymerizations.

Table 1. Yields, molecular weights and polydispersities of the test polymerizations.

entry	benzene monomer	bithiophene monomer	Catalyst + ligand, solvent	Yield / %	$\overline{M}_n$ [a]/ kg/mol	D [a]
1	**4a**	**8a**	Pd_2dba_3 + $AsPh_3$, THF	[b]	[b]	[b]
2	**2a**	**9a**	Pd_2dba_3 + $AsPh_3$, THF	16	15.9	2.0
3	**3a**	**9a**	Pd_2dba_3 + $AsPh_3$, THF	56	15.8	11
4	**2a**	**9a**	$Pd[PPh_3]_2Cl_2$, THF/DMF	[b]	[b]	[b]
5	**2a**	**9a**	$Pd[PPh_3]_4$+ CuO, THF/DMF	54	96	4.4[c]
6	**2a**	**9a**	$Pd[PPh_3]_4$ + CuO, THF	3	54	11

[a] determined by GPC in THF towards polystyrene standards

[b] no polymer was recovered

[c] a bimodal weight distribution was obtained

All polymers were washed with acetone and hexane using a Soxhlet apparatus to remove byproducts and oligomers. Finally, the polymers were extracted with chloroform, precipitated into methanol and dried.

Apart from the four polymers prepared from the combinations between **2a-b** and **9a-b**, also a series of polymers were synthesized from the achiral benzene monomers and mixture of achiral and chiral bithiophene monomers. The code of all polymers is constituted as follows:

$$\mathbf{P(ben_x bith_y)}$$

in which x demotes the fraction of chiral benzene monomer and y the fraction of chiral bithiophene monomer in the feed. Since equal reactivity between the achiral and chiral bithiophene monomers (**9a-b**) can be expected, the ratio of chiral monomer in the feed should also be reflected in the ratio of chiral monomer built in.

Yields, GPC and DSC analysis

The yields, molecular weights, glass transition and melting temperatures of the polymers are listed in Table 2. The yields were usually quite moderate. The molecular weights were determined by GPC toward polystyrene standards. As will be shown, the polymers adopt a planar, rigid conformation even in good solvents. Therefore, the hydrodynamic volumes of the polymers and the standards can be expected to be drastically different and, consequently, the experimental error will be quite high. The real molecular weights of these polymers are probably larger. It has, for instance, been shown that GPC underestimates the molecular weight of HT-P3ATs.[17]

Most polymers showed a glass transition and melting peak, although in some cases, these transitions were rather difficult to observe. Nevertheless, it can be concluded that the polymers are semi-crystalline. Degradation always started > 260 °C. The structure of the polymers was confirmed by ^{1}H NMR spectroscopy.

Table 2. Yields, molecular weights, polydispersity and DSC data of the polymers.

polymer	Yield [a] / %	$\overline{M}_w$ [b] / kg·mol^{-1}	D [b]	T_g [c]/ °C	T_m [c]/ °C	T_d [c]/ °C
P(ben$_0$bith$_0$)	16	30	2.0	118	184	265
P(ben$_0$bith$_{0.1}$)	42	30	3.5	[d]	[d]	282
P(ben$_0$bith$_{0.2}$)	43	92	7.5	135	202	283
P(ben$_0$bith$_{0.4}$)	18	126	6.3	117	198	264
P(ben$_0$bith$_{0.7}$)	26	73	6.4	119	194	284
P(ben$_0$bith$_1$)	17	32	2.3	[d]	210	292
P(ben$_1$bith$_0$)	12	31	1.9	123	205	>300
P(ben$_1$bith$_1$)	14	37	2.3	[d]	[d]	[d]

[a] of the chloroform-soluble fraction

[b] determined by GPC in THF towards polystyrene standards

[c] determined by DSC at a heating rate of 50 °C/min

[d] not detected

Chiroptical properties in solution

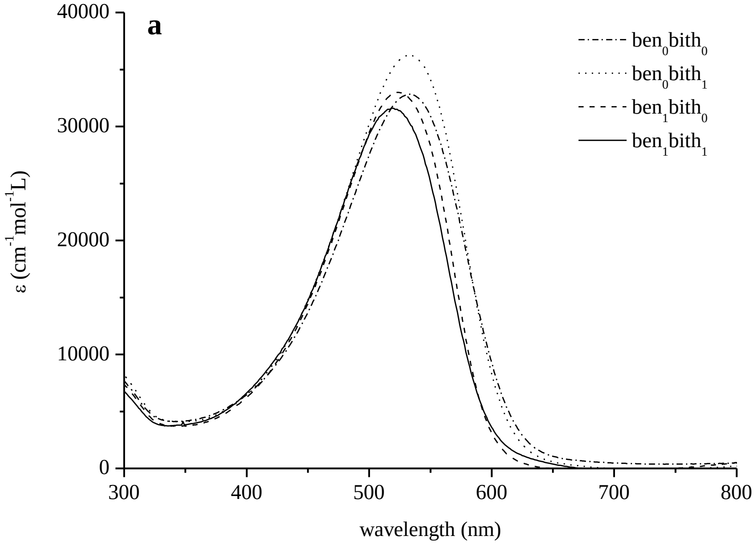
λ_{max} and the optical bandgaps are displayed in Table 3. λ_{max} in a solution of a good solvent (chloroform, THF, …) is quite high compared to HT-P3ATs (~ 445 nm), which means that much higher conjugation lengths are present, despite the presence of the benzene units. The lower λ_{max} of these copolymers compared to λ_{max} of HT-P3AOTs (~ 600 nm) and (oxidatively prepared) HH-TT-P3AOTs (~ 545 nm) can be explained by the presence of the more aromatic benzene units.

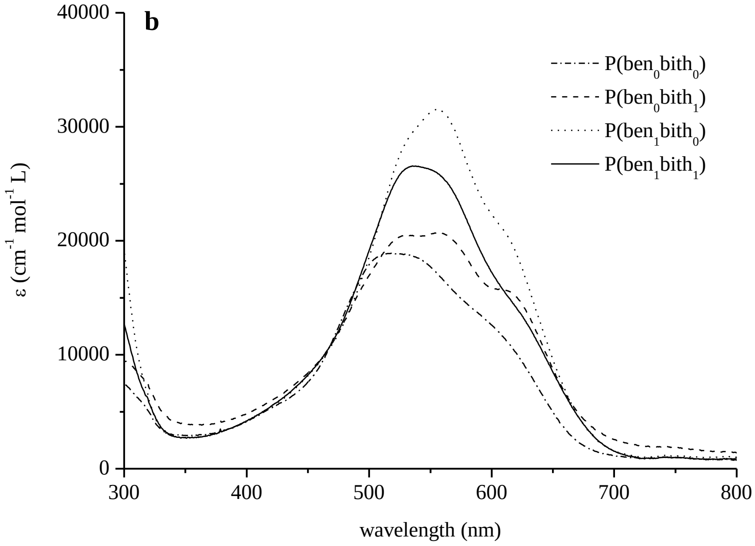
Table 3. Optical data of the polymers in film and solution.

polymer	λ_{max} in $CHCl_3$ /	λ_{max} in $CHCl_3/CH_3OH$ (4/6) /	λ_{max} in film /	bandgap /

	nm	nm	nm	eV
P(ben$_0$bith$_0$)	519	514	548	1.86
P(ben$_0$bith$_{0.1}$)	520	538	554	1.83
P(ben$_0$bith$_{0.2}$)	518	543	556	1.82
P(ben$_0$bith$_{0.4}$)	522	549	563	1.75
P(ben$_0$bith$_{0.7}$)	520	546	555	1.83
P(ben$_0$bith$_1$)	524	556	560	1.85
P(ben$_1$bith$_0$)	532	550	569	1.77
P(ben$_1$bith$_1$)	532	535	547	1.78

Upon addition of a nonsolvent (methanol), no significant red-shift is observed, but a clear vibronic fine-structure becomes present (Figure 2a-b). This points to the fact that the polymers are already present as rigid rods in chloroform and only slightly further planarize, but stack upon addition of nonsolvent. This is in contrast to more flexible conjugated polymers, such as regioregular poly(3-alkylthiophene)s, which are present as random coils in solution (low conjugation lengths), but planarize and stack upon aggregation, resulting in a significant red-shift (HT-P3ATs: ~ 65 nm).





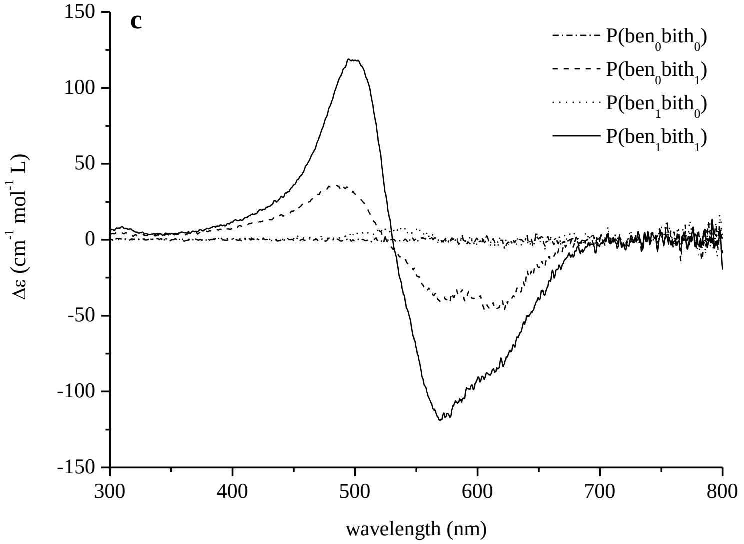
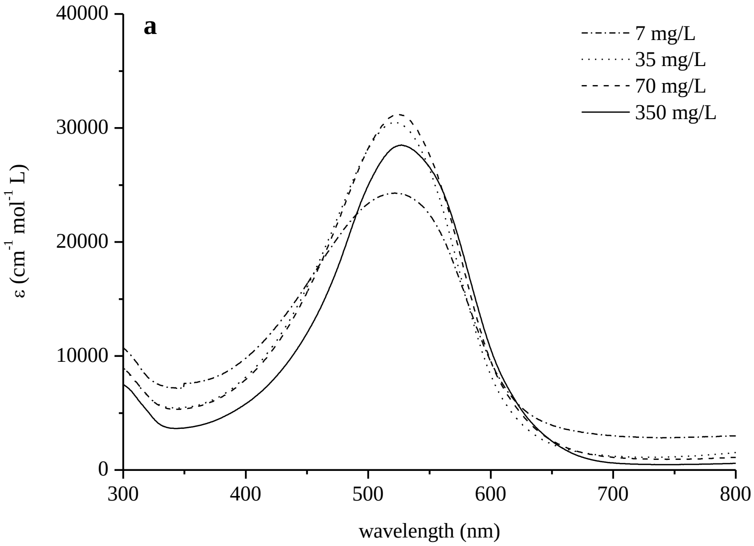


Figure 2. UV-vis spectra of **P(ben$_0$bith$_0$)**, **P(ben$_0$bith$_1$)**, **P(ben$_1$bith$_0$)** and **P(ben$_1$bith$_1$)** in a) chloroform and b) a chloroform/methanol mixture (4/6) and c) CD spectra in a chloroform/methanol mixture (4/6) (c ~ 35 mg/L).

The circular dichroism spectra reveal the occurrence of bisignate Cotton effects in a poor solvent mixture, but, interestingly, the Cotton effects of the chiral polymers **P(ben$_0$bith$_1$)**, **P(ben$_1$bith$_0$)** and **P(ben$_1$bith$_1$)** are by far not equal in intensity. Concerning the shape of the Cotton effects, Langeveld-

Voss *et al.* have indicated that the presence of bisignate Cotton effects is due to chiral exciton coupling of chirally stacked rigid, coplanar polymer strands.[18] This supramolecular behavior has, for instance, been demonstrated in chirally substituted regioregular poly(3-alkylthiophene)s[2] and PPV's[5], in which the chiral side-chains discriminate between the two possible enantiomeric supramolecular structures. This is an *inter*molecular effect and must therefore be concentration dependent.

To verify whether this explanation also holds for these polymers, we have gradually varied the content of methanol in the chloroform/methanol solvent mixture for **P(ben$_1$bith$_1$)** (Figure 1, supporting information). This indicates that starting from 20 % methanol (c = 35 mg/L), the polymers start to aggregate. Next, the concentration dependence of the chiroptical properties of **P(ben$_1$bith$_1$)** in a 20 % methanol mixture (intermediate Cotton effects) was investigated (Figure 3). A clear concentration dependence in the CD spectra is observed, which proves that the observed Cotton effects are indeed due to an intermolecular effect. Moreover, the magnitude of g_{abs} ($=\Delta\varepsilon/\varepsilon$) in the order of $7\cdot10^{-3}$ is a typical value for chiral exciton coupling of conjugated polymers[18].



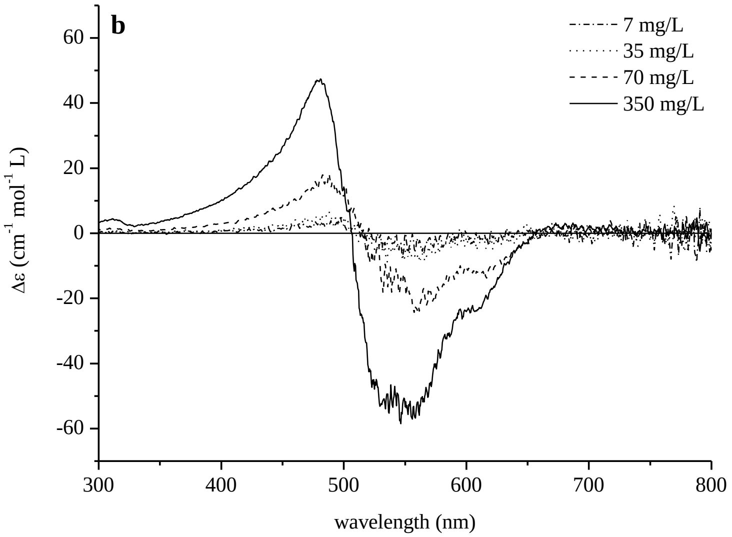
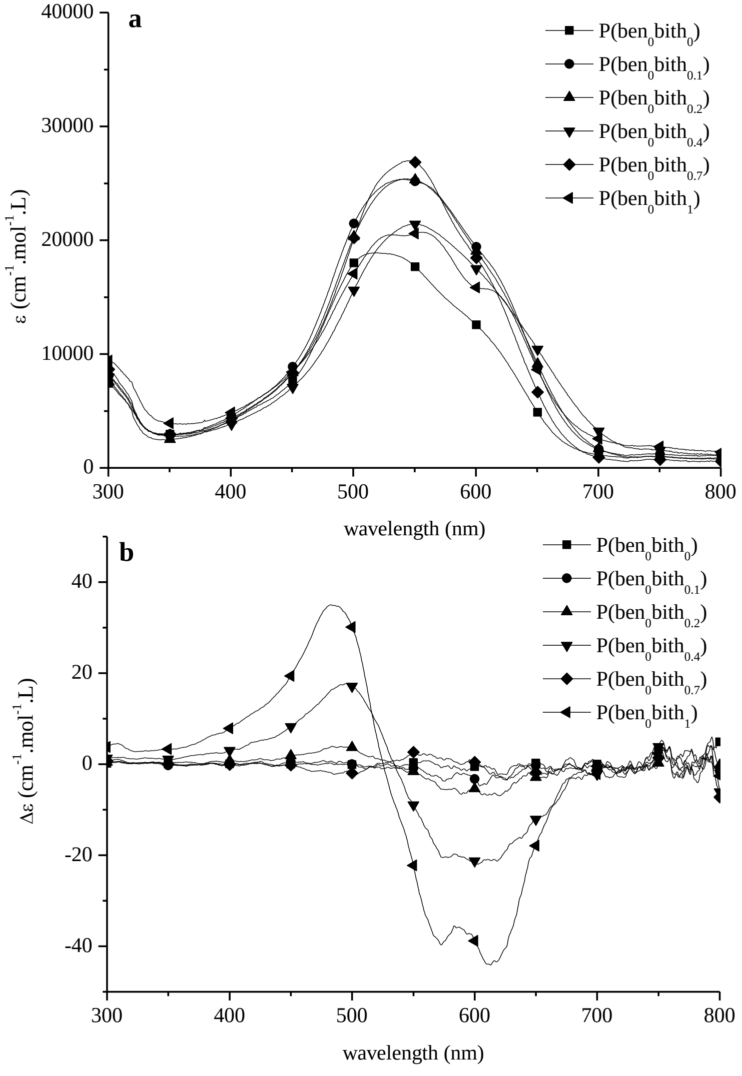


Figure 3. Concentration dependence of a) the UV-vis spectra and b) CD spectra of **P(ben$_1$bith$_1$)** in a chloroform/methanol (8/2) mixture.

Concerning the significant difference in intensity of the Cotton effects of the three chiral polymers **P(ben$_0$bith$_1$)**, **P(ben$_1$bith$_0$)** and **P(ben$_1$bith$_1$)**, we could advance three possible explanations. First, the chiral discrimination of the side-chain could be stronger if positioned on one monomer (for instance on the bithiophene) than on the other (the benzene). Second, a sergeant-and-soldiers effect could be present.[19] In that case, Δε varies (nonlinearly) with the amount of chiral substituents built in. Third, the difference in CD intensity could be explained by the fact that all four polymers are different, each with its own (chiral) supramolecular organization and corresponding CD spectrum.

The first possibility can be ruled out: if the difference between **P(ben$_1$bith$_0$)** and **P(ben$_0$bith$_1$)** were due to a stronger chiral discrimination of the chiral substituent if positioned on the bithiophene moiety, this would mean that chiral side-chain present on the benzene monomer would hardly affect the chirality of the supramolecular stacking. Therefore, the fully chiral polymer **P(ben$_1$bith$_1$)** should have approximately the same CD spectrum as **P(ben$_0$bith$_1$)**, which is not the case (Figure 2c).

To investigate whether a sergeants-and-soldiers effect is present, the chiroptical properties of the polymers **P(ben$_0$bith$_x$)**, x = 0, 0.1, 0.2, 0.4, 0.7 and 1, in which the content of chiral bithiophene moiety was thus gradually increased, were investigated as well. Sergeant-and-soldier behavior would then be observed as a nonlinear increase of the g-value in function of the amount of chiral side-chains present in the polymer. From Figure 4 it is clear that no sergeant-and-soldiers effect is present - even a reversal of the sign of the Cotton effect is observed (**P(ben$_0$bith$_{0,7}$)**). Moreover, since the chirality present in these systems is clearly supramolecular and not molecular in origin (vide supra), true sergeant-and-soldier behavior would imply stacking of some chiral and achiral polymer strands in one aggregate – in which the few chiral strands discriminate between the two enantiomeric (supramolecular) structures - rather then the aggregation of several polymer strands, each containing some chiral substituents, which stack in a way similar to polymer strands which only contain chiral side-chains. This behavior has been observed in chiral P3ATs.[20]



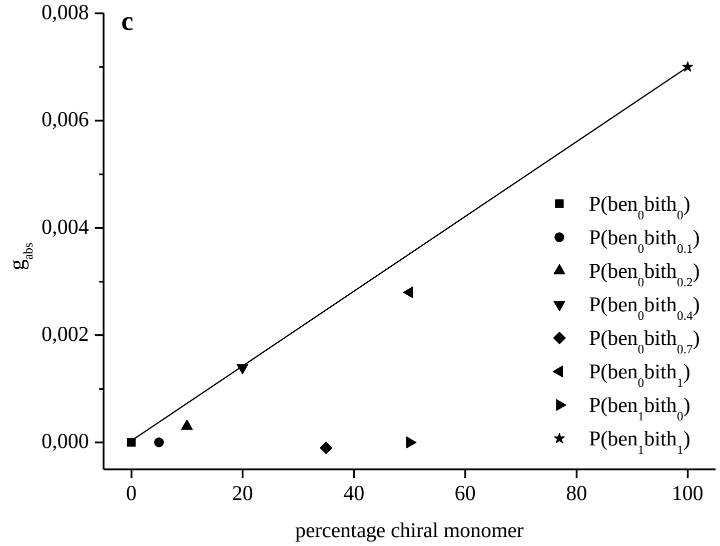


Figure 4. Influence of the ratio chiral side-chains on the chiroptical properties: a) UV-vis and b) CD spectra of **P(ben$_0$bith$_x$)**, x = 0, 0.1, 0.2, 0.4, 0.7 and 1. c) evolution of the g_{abs}-value in function of the amount of chiral substituents.

The two other possibilities being ruled out, the only explanation for the difference in CD spectra of all the polymers is the fact that they are all different, each with its own (chiral) supramolecular organization and corresponding CD spectrum.

Fluorescence

The emission data of **P(ben$_0$bith$_0$)**, **P(ben$_0$bith$_1$)**, **P(ben$_1$bith$_0$)** and **P(ben$_1$bith$_1$)** are summarized in Table 4. All spectra were recorded in chloroform. Cresyl violet perchlorate (λ_{em} = 621 nm, Φ_f = 0.54 in methanol) was used as a reference, since its λ_{em} matches closely with those of the polymers. Fluorescence is an interesting tool to probe the rigidity of the backbone: rigidification decreases the broadness of the fluorescence peak and the Stokes shift. The Stokes shifts of all polymers are quite low - much lower than the Stokes shifts of HT-P3ATs (~ 5000 cm^{-1}), which are known to adopt a rather flexible, random-coil structure in good solvent, but instead resemble those of other rigid conjugated polymers, such as poly(dithienopyrrole)s (~ 2000 cm^{-1})[21] and ladder-type polymers (~ 2000 cm^{-1})[22]. The same trend is present for fwhm_{em}. Therefore, the emission data support our hypothesis that the polymers are present in solution as (highly conjugated) rigid rods. The quantum yields amount 15-33 %.

Upon addition of nonsolvent, the polymers aggregate – as was already indicated by UV-vis and CD experiments – resulting in a complete quenching of the fluorescence (see Supporting Information).

Table 4. Emission data of the polymers in THF-solution.

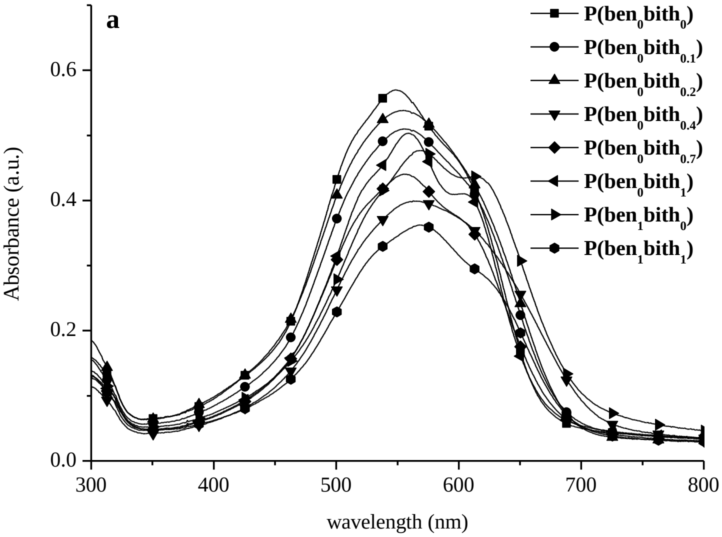
polymer	λ_{ex} / nm	λ_{em} / nm	fwhm_{em} / cm^{-1}	Stokes shift / cm^{-1}	Φ_f[a]
P(ben$_0$bith$_0$)	525	580	2040	2026	0.33
P(ben$_0$bith$_1$)	525	585	2173	1990	0.15
P(ben$_1$bith$_0$)	534	594	1886	1962	0.27
P(ben$_1$bith$_1$)	532	596	1851	2018	0.15

[a] measured towards cresyl violet perchlorate (λ_{em} = 621 nm, Φ_f = 0.54 in methanol)

Chiroptical properties in film

The UV-vis and CD spectra of films, spincoated from chloroform-solution, of **P(ben$_0$bith$_0$)**, **P(ben$_0$bith$_1$)**, **P(ben$_1$bith$_0$)** and **P(ben$_1$bith$_1$)** are shown in Figure 5. The UV-vis spectra resembles those of the polymers in poor solvents, indicating that the films also consists of (aggregates of) planar, highly conjugated polymers. The bandgaps were calculated from the onset of the absorption band and are ~ 1.8 eV. These are slightly higher than those of HT-P3AOTs (1.4-1.6 eV)[3,10-11] and HH-TT-P3AOTs (1.7 eV)[12], which can be explained by the presence of the more aromatic benzene moiety, but comparable with those of HT-P3ATs.

The shape of the CD spectra of some of the polymers, for instance of **P(ben$_0$bith$_1$)**, **P(ben$_1$bith$_0$)** and **P(ben$_1$bith$_1$)**, however, differs dramatically from the bisignate Cotton effects of the aggregates present in poor solvents. Moreover, very large g_{abs}-values ($>2\cdot10^{-2}$, after annealing, *vide infra*) are observed. It is clear that these observations cannot solely be explained by chiral exciton coupling, since in that case, bisignate Cotton effects and g_{abs}-values in the order of $10^{-3} – 10^{-2}$ would be expected[18].



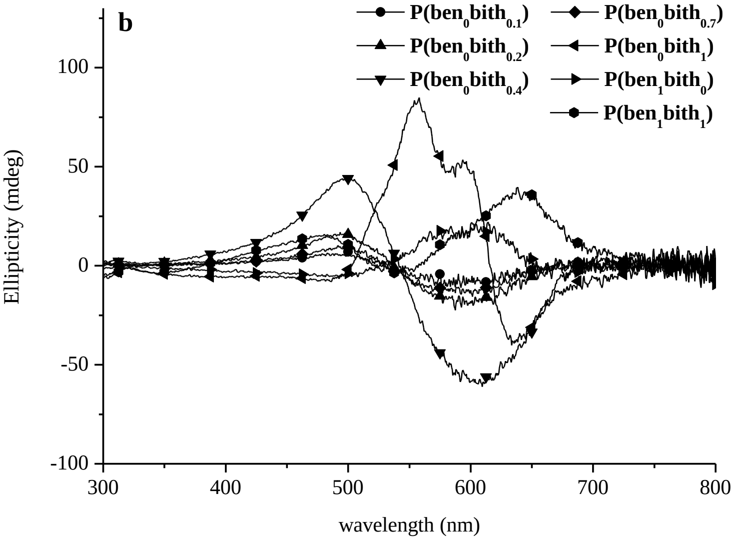


Figure 5. a) UV-vis and b) CD spectra of films, spincoated from chloroform, before annealing.

Very high g_{abs}-values in combination with CD spectra which are clearly not bisignate, have already been observed in *annealed* films of chirally substituted PPE and PF, which show liquid crystalline behavior. Several, different explanations have been given for the exceptional CD spectra of those chiral polymers. At first, the Cotton effects in PF films have been explained by a helical shape of the polymer backbone, being composed of nonlinear building blocks.[7c] The Cotton effects of PPE films, in which the monomers are attached to each other in a more linear way, are due to helically twisted bundles of planar chains. In these polymers, the highest g-values are obtained in copolymers of chiral and achiral monomers.[6] On the other hand, Geng *et al.* have shown that cholesteric stacking is the main contribution to the circular dichroism of chiral, liquid crystalline oligofluorenes.[23] This suggests that this might also be the dominant factor in the CD of liquid crystalline polyfluorenes, and even more general, of liquid crystalline conjugated polymers. Finally, the exceptional high g_{abs}-values of (annealed) PF film are explained by Craig *et al.* to be due to contributions, other than 'real' circular dichroism.[24] They indicated that, apart from 'real' circular dichroism – the statistical difference in absorption of left and right circular light -, pseudo circular dichroism increases the overall difference in absorption. For pseudo circular dichroism to be present, only ordering on mesoscale is necessary, not on macroscopic scale, so liquid crystallinity is not strictly required. In the case of pure CD, as for instance in HT-P3ATs[25], the g_{abs}-values are independent of the film thickness, while in case of pseudo circular dichroism, a clear thickness-dependence is expected.

The thickness dependence of **P(ben$_0$bith$_{0.4}$)** was investigated by evaluating the chiroptical properties of films of different thickness, which were prepared by varying the concentration of the spincoat solution (Figure 6). The films were prepared from chloroform-solutions and the spectra were recorded before annealing. By increasing the thickness by a factor ~ 6 - the thickness of the films scales with their absorbance- , the g_{abs}-value changes one order of magnitude. This clearly demonstrates that also in these polymers, apart from 'real' circular dichroism, pseudo circular dichroism plays an important role.

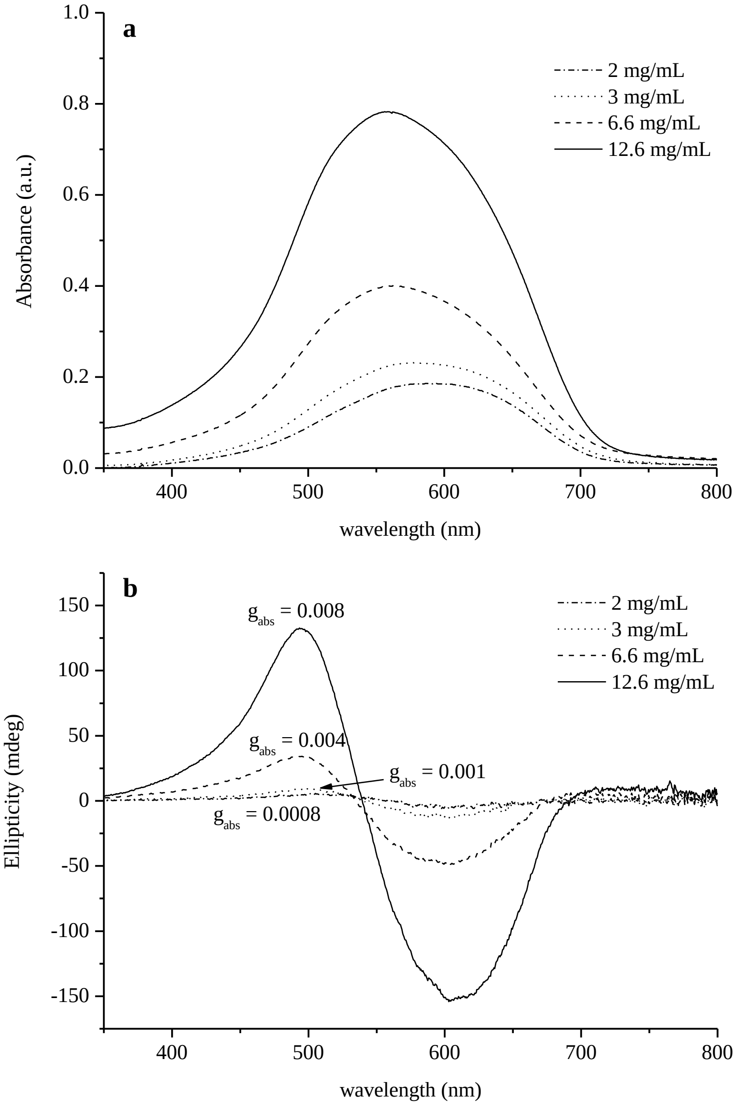


Figure 6. Thickness dependence of **P(ben$_0$bith$_{0.4}$)**: a) UV-vis and b) CD spectra.

Next, the samples were annealed for 1 min at 150 °C and , after cooling down to room temperature, immediately measured. The g_{abs}-values of the polymers before and after annealing were compared and are summarized in Table 5. In most cases, a large increase in g_{abs}-value is observed, yielding values which are several times higher than those observed in the aggregates in nonsolvent mixtures. For instance, a g_{abs}-value up to 0.023 for **P(ben$_1$bith$_1$)** was obtained by annealing. It is worthwhile to note that this was accomplished with a rather thin film. Given the fact that increasing the film thickness increases the g_{abs}-value, even higher values can be expected for thicker films.

Table 5. g_{abs}-values of the polymers before and after annealing. The films were spun from chloroform solution (c ~ 10 mg/mL).

polymer	$\lvert g_{abs} \rvert$ before annealing / 10^{-3}	$\lvert g_{abs} \rvert$ after annealing[a]/ 10^{-3}
P(ben$_0$bith$_{0.1}$)	0.6	4.5
P(ben$_0$bith$_{0.2}$)	2.5	15
P(ben$_0$bith$_{0.4}$)	5.1	15
P(ben$_0$bith$_{0.7}$)	1.1	8.8
P(ben$_0$bith$_1$)	5.5	9.1
P(ben$_1$bith$_0$)	1.2	0.7
P(ben$_1$bith$_1$)	7.5	23

[a] 1 min @ 150 °C

As mentioned earlier, extremely large g_{abs}-values have already been observed in films of PF and PPE, which show liquid crystalline behavior and the liquid crystallinity might explain the exceptional Cotton effects. Therefore, it was investigated whether our polymers show liquid crystalline behavior. Extensive polarized UV-vis spectroscopy experiments indicated that our polymers are *not* liquid crystalline. Therefore, the chirality observed in the polymers presented here, must be due to pseudo circular dichroism. Moreover, this is a good example that liquid crystallinity is not a requisite for pseudo circular dichroism.

Oxidation behavior of polymer films

Due to the use of electron-rich moieties (thiophenes) and the presence of electron-donating substituents (alkoxy groups), the polymers can readily be oxidized, especially in film. The ease of oxidation can be correlated with the electrochemical behavior of the polymer. The potential of the peak anodic current (E_{pa}) and peak cathodic current (E_{pc}) of films, deposited from chloroform solution, were measured using cyclic voltammetry. E_{pa}, E_{pc} and, consequently, $E_{1/2}$ are independent of the scanning rate. The oxidation of these polymers is pseudo-reversible.

The polymers show a $E_{1/2} \sim 0{,}55$ V. This rather low value is consistent with the ease with which the polymers can be oxidized (by I_2, $NOBF_4$, …) in both solution and thin films and the extended periods of time (in the order of days) they remain oxidized. The samples can be back reduced without any degradation. Upon oxidation, the absorption near 520 nm disappears and two new absorption peaks arize: one around 820 nm (Table 6) and one > 2000 nm.

Table 6. Electrochemical data of the polymer films.

polymer	E_{pa}[a] / V	E_{pc}[a] / V	$E_{1/2}$[a] / V	λ_{max} / nm
P(ben$_0$bith$_0$)	0.59	0.49	0.54	810
P(ben$_0$bith$_1$)	0.65	0.51	0.58	815
P(ben$_1$bith$_0$)	0.53	0.45	0.49	835
P(ben$_1$bith$_1$)	0.64	0.50	0.57	807

[a] measured at a scan rate of 50 mV/s in acetonitrile in the presence of Bu_4NBF_4 (0.1 M).

Conclusion

In conclusion, we have prepared alternating copolymers of 3,3'-dialkoxy-[2,2'-bithiophene]s with 2,5-dialkoxybenzene derivatives, in which the substituents on the two moieties were either chiral or achiral. In a solution of a good solvent, the polymers adopt a highly conjugated rigid conformation, as was indicated by UV-vis and fluorescence spectroscopy. Upon transition to a nonsolvent mixture, the polymers aggregate, given rise to rather large Cotton effects. It was shown that the difference in Cotton effects cannot be explained by a Sergeants-and-soldiers behavior, but that it is due to a different chiral supramolecular stacking of the polymers. In films, apart from 'real' circular dichroism, also pseudo circular dichroism is present, which is consistent with the thickness dependence of g_{abs}-values. Since the polymers are also easily be oxidized and show high g_{abs}-values, they can be promising candidates as chiral polymer conductors. Further research will also focus on the substitution of one or both monomers with one or two (different) functional groups.

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Supporting Information Available: UV-vis and CD spectra demonstrating the influence of the methanol/chloroform ratio of **P(ben$_1$bith$_1$)**, the quenching of the fluorescence of **P(ben$_1$bith$_1$)** upon addition of nonsolvent, the reversibility of the oxidation and back reduction of **P(ben$_0$bith$_{0.2}$)** in $CHCl_3$ as well as a representative UV-vis spectrum of an oxidized film and ^1H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References:

(1) *Handbook of Conducting Polymers*, Ed. 2 (Eds: Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R.), Marcel Dekker, Inc., New York **1998**

(2) a) Bouman, M. M.; Meijer, E. W. *Polym. Prepr.* **1994**, *35*, 309. b) Bouman, M. M.; Havinga, E. E.; Janssen, R. A. J.; Meijer, E. W. *Mol. Cryst. Liq. Cryst.* **1994**, *256*, 439. c) Langeveld-Voss, B .M. W.; Bouman, M. M.; Christiaans, M .P. T.; Janssen, R. A. J.; Meijer, E. W. *Polym. Prepr.* **1996**, *37*, 499. d) Bidan, G.; Guillerez, S.; Sorokin, V. *Adv. Mater.* **1996**, *8*, 157.

(3) Koeckelberghs, G.; Vangheluwe, M.; Samyn, C. Persoons, A.; Verbiest, T. *Macromolecules*, **2005**, *38*, 5554.

(4) Koeckelberghs, G.; Cornelis, D.; Persoons, A.; Verbiest, T. *Macromol. Rapid Commun.* **2006**, *27*, 1132.

(5) Meskers, S. C. J.; Peeters, E.; Langeveld-Voss, B. M. W.; Janssen, R. A. J. *Adv. Mater.* **2000**, 12, 589.

(6) a) Fiesel, R.; Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Scherf, U.; Bunz, U. H. F. *Macromol. Rapid Commun.* **1999**, *20*, 107. b) Wilson, J. N.; Steffen, W.; McKenzie, T. G.; Lieser, G.; Oda, M.; Neher, D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2002**, *124*, 6830. c) Babudri, F.; Colangiuli, D.; Di Bari, L.; Farinola, G. M.; Omar, O. H.; Naso, F.; Pescitelli, G. *Macromolecules* **2006**, *39*, 5206.

(7) a) Oda, M.; Meskers, S. C. J.; Nothofer, H.-G.; Scherf, U.; Neher, D. *Synth. Met.* **2000**, 111, 575. b) Oda, M.; Nothofer, H.-G.; Lieser, G.; Sherf, U.; Meskers, S. C. J.; Neher, D. *Adv. Mater.* **2000**, 12, 362. c) Oda, M.; Nothofer, H.-G.; Sherf, U.; Sunjic, V.; Richter, D.; Regenstein, W.; Neher, D. *Macromolecules* **2002**, 35, 6792.

(8) Zhang, Z.-B.; Motonaga, M.; Fujiki, M.; McKenna, C. E. *Macromolecules* **2003**, *36*, 6956.

(9) McCullough, R. D.; Lowe, R. L.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904.

(10) Sheina, E. E.; Khersonsky, S. M.; Jones, E. G.; McCullough, R. D. *Chem. Mater.* **2005**, *17*, 3317.

(11) Koeckelberghs, G.; Vangheluwe, M.; Van Doorsselaere, K.; Robijns, E.; Persoons, A.; Verbiest, T. *Macromol. Rapid Commun.* **2006**, *27*, 1920.

(12) a) Cloutier, R.; Leclerc, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1194. b) Faïd, K.; Cloutier, R.; Leclerc, M. *Macromolecules* **1993**, *26*, 2501.

(13) a) Standards in Fluorescence Spectrometry; Miller, J. N., Ed.; Chapman and Hall: New york, 1981, pp. 68 – 78. b) Handbook of Organic Photochemistry; Scaiano, J.C., Ed.; CRC Press: Boca Raton, FL, pp. 233 -236 and references therein.

(14) Nierengarten, J.-F.; Gu, T.; Hadziioannou, G.; Tsamouras, D.; Krasnikov, V. *Helv. Chim. Acta* **2004**, *87*, 2948.

(15) Ajayaghosh, A.; Varghese, R.; Malesh, S.; Praveen, V. K. *Angew. Chem. Int. Ed.* **2006**, *45*, 7729.

(16) (a) Farina, V.; Krihnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585. (b) Bao, Z.; Chan, K.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426.

(17) Liu, J.; Loewe, R. S.; McCullough, R. D. *Macromolecules,* **1999,** *32*, 5785

(18) Langeveld-Voss, B. M. W.; Beljonne, D.; Shuai, Z.; Janssen, R. A. J.; Meskers, S. C. J.; Meijer, E. W.; Brédas, J.-L. *Adv. Mater.* **1998**, *10*, 1343.

(19) Green, M. M.; Reidy, M. P. *J. Am. Chem. Soc.* **1989**, *111*, 6452.

(20) Langeveld-Voss, B. M. W.; Waterval, R. J. M.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules*, **1999**, *32*, 227.

(21) a) Ogawa, K.; Rasmussen, S. C. *Macromolecules* **2006**, *39*, 1771. b) Koeckelberghs, G.; De Cremer, L.; Persoons, A.; Verbiest, T. *Macromolecules* **2007**, *40*, 4173.

(22) Nehls, B. S.; Galbrecht, F.; Brauer, D. J.; Lehmann, C. W.; Scherf, U.; Farrell, T. *J. Pol. Sci., Part A: Pol. Chem.* **2006**, *44*, 5533.

(23) Geng, Y.; Trajkovska, A.; Culligan, S. W.; Ou, J. J.; Chen, H. M. P.; Katsis, D.; Chen, S. H. *J. Am. Chem. Soc.* **2003**, *125*, 14032.

(24) Craig, M. R.; Jonkheim, P.; Meskers, S. C. J.; Schenning, A. P. H. J.; Meijer, E. W. *Adv. Mater.* **2003**, *15*, 1435.

(25) Lakhwani, G.; Koeckelberghs, G.; Meskers, S. C. J.; Janssen, R. A. J. *Chem. Phys. Lett.* **2007**, *437*, 193.

Captions to figures

Figure 1. General structure of the alternating copolymers.

Figure 2. UV-vis spectra of **P(ben$_0$bith$_0$)**, **P(ben$_0$bith$_1$)**, **P(ben$_1$bith$_0$)** and **P(ben$_1$bith$_1$)** in a) chloroform and b) a chloroform/methanol mixture (4/6) and c) CD spectra in a chloroform/methanol mixture (4/6) (c ~ 35 mg/L).

Figure 3. Concentration dependence of a) the UV-vis spectra and b) CD spectra of **P(ben$_1$bith$_1$)** in a chloroform/methanol (8/2) mixture.

Figure 4. Influence of the ratio chiral side-chains on the chiroptical properties: a) UV-vis and b) CD spectra of **P(ben$_0$bith$_x$)**, x = 0, 0.1, 0.2, 0.4, 0.7 and 1. c) evolution of the g_{abs}-value in function of the amount of chiral substituents.

Figure 5. a) UV-vis and b) CD spectra of films, spincoated from chloroform, before annealing.

Figure 6. Thickness dependence of **P(ben$_0$bith$_{0.4}$)**: a) UV-vis and b) CD spectra.

Scheme 1. General pathway for the preparation of the alternating copolymers.

Scheme 2. Synthesis of the monomers.

Graphic for Table of Contents