Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polymer 44 (2003) 3785–3794
polymer
www.elsevier.com/locate/polymer

Synthesis and properties of chiral helical chromophore-functionalised polybinaphthalenes for second-order nonlinear optical applications

Guy Koeckelberghs[a], Sonja Sioncke[b], Thierry Verbiest[b], André Persoons[b], Celest Samyn[a,*]

[a]*Laboratory of Macromolecular and Physical Organic Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium*
[b]*Laboratory of Chemical and Biological Dynamics, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Heverlee, Belgium*

Received 10 February 2003; received in revised form 17 April 2003; accepted 23 April 2003

Abstract

Chiral, helical, nonlinear optical polybinaphthalenes were prepared by covalent bonding of chromophores to the backbone of polybinaphthalenes via a Mitsunobu reaction. This was achieved in a two-step reaction, with the formation of a precursor polymer by a Suzuki coupling reaction, which was afterwards functionalised with chromophores. It was tried to achieve a chiral ordering of the chromophores by attaching them to a chiral, helical polymer backbone. Poled films of the polymers were measured for their second-harmonic generation effect and showed nonresonant nonlinear susceptibilities ($\chi^{(2)}_{zzz}(0)$) up to 10.6 pm/V.

Keywords: Polybinaphthalenes; Nonlinear optics; Chirality

1. Introduction

In the past decade, chromophore-functionalised polymer systems have been intensively studied for their nonlinear optical (NLO) properties [1], because of their potential applications as high speed frequency doublers and mixers, amongst others. This interest has led to the development of a large number of new chromophores with moderate to superb hyperpolarisabilities. Since polymer materials show additional advantages compared to their inorganic analogues, s.a. a good processability, a low dielectric constant, a large architectural diversification,… nearly all organic NLO materials are polymeric. Most of these polymers adapt a random coil conformation. Only a few [2] chiral, helical, rod-like polymer systems have been investigated as NLO materials. Polybinaphthalenes, with chromophores attached as side-chain, are to the best of our knowledge even novel polymer materials, although they may be interesting NLO candidates. When incorporated as side-chains, the chromophores can easily be poled (as in random coil-like systems). But, since the chromophores are attached to a rigid, nonbendable backbone, the undesired dipolar interactions between the chromophores will be largely reduced in these systems. Moreover, if chiral, helical polymers are used, these systems can benefit from the chirality of the sample. The use of chirality in second-order nonlinear optics has been theoretically thoroughly investigated [3]. These studies have demonstrated that chirality can relax the requirement for a polar ordering. Moreover, chiral contributions can increase the NLO response.

In this paper polybinaphthalenes were chosen as polymer system, since these polymers are helical (if appropriately designed) and show excellent thermal, chemical and photochemical stability. Chirality was obtained by polymerisation of chiral (*S*) dibromo-binaphthalene monomers and a bis(boronic acid) derivative. To enhance solubility, film forming properties and possibilities to synthetical diversification, the chromophores were linked as side chains. Therefore, these polymers meet with all requirements, necessary to be useful as NLO materials.

2. Experimental

2.1. Materials 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

* Corresponding author. Tel.: +32-16-327-438; fax: +32-16-327-990.
E-mail address: celest.samyn@chem.kuleuven.ac.be (C. Samyn).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00356-2

distillation. The glass transition temperatures were measured with a DSC-7 apparatus from Perkin–Elmer at a heating rate of 50 °C/min (polymers) or 30 °C/min (chromophores). Gel permeation chromatography (GPC) measurements were done with a Waters 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 spectra were recorded with a Varian Cary 400. The optical rotations were measured with an Analis Optical Activity Polaar 20.

2.2. Second-harmonic generation measurements

Thin films were obtained by spincoating a solution of the polymer in chloroform onto ITO substrates. After drying, poly(acrylic acid) was spincoated above the chromophore-functionalised polymer film to prevent bleaching during poling. The films were carefully dried. Subsequently, they were corona-poled at approximately T_g. The corona-poling set-up consisted of a thin wire, positioned 1 cm above the polymer film, that was charged to 8 kV. The NLO properties were measured by second harmonic generation (SHG). All susceptibility components were determined by analysing the polarisation of the second-harmonic signal emanating from the samples, for different input polarisations of the fundamental beam [4].

2.3. Synthesis of S-(−)-6,6′-dibromo-2-hexyloxy-2′-methoxymethoxy-[1,1′-binaphthalene] **3b**: Fig. 1

2.3.1. Synthesis of S-(+)-6,6′-dibromo-2′-hexyloxy-[1,1′-binaphthalene]-2-ol **2**

A solution of 14.4 g (32.4 mmol) of **1** [5], dissolved in 70 ml of dry *N*,*N*-dimethylformamide (DMF), was slowly added to a suspension of 0.78 g (32.4 mmol) of NaH in 30 ml of dry DMF under argon atmosphere. After 15 min, 4.6 ml (32.4 mmol) of hexylbromide and 100 mg of anhydrous NaI were added and the mixture was stirred overnight at 50 °C. After cooling, the reaction mixture was poured into 200 ml of water and extracted with dichloromethane. The organic layer was washed with a saturated $NaHCO_3$ solution and brine and dried over $MgSO_4$. After removal of the solvents, the crude compound was purified by column chromatography (silicagel; eluent: hexane/dichloromethane (60:40 v/v)) and isolated as an oil.

Yield: 8.2 g (48%). $[\alpha]_D^{25} = +32.4$ deg dm^{-1} mol^{-1} l ($c = 0.06$ in $CHCl_3$); ^{1}H NMR ($CDCl_3$, ppm): δ 8.05 (d; $J = 1.5$ Hz; 1H), 8.00 (d; $J = 1.5$ Hz; 1H), 7.93 (d; 1H), 7.80 (d; 1H), 7.46 (d; 1H), 7.34 (d; 1H), 7.34 (dd; 1H), 7.28 (dd; 1H), 7.02 (d; 1H), 6.86 (d; 1H), 4.89 (d; 1H), 3.99 (m; 2H), 1.43 (qu; 2H), 1.01 (m; 6H), 0.75 (t; 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 155.7, 151.6, 132.5, 132.2, 130.6, 130.4, 130.2, 130.1, 130.0, 129.6, 128.9, 126.6, 126.5, 118.7, 118.1, 117.0, 116.2, 115.7, 114.9, 69.6, 31.2, 29.0, 26.9, 22.4, 13.9. MS: m/z = 528 (M^+), 444 ($M^+ - C_6H_{12}$), 364 ($M^+ - C_6H_{12}$, −Br), 284 ($M^+ - C_6H_{12}$, $-Br_2$).

2.3.2. Synthesis of S-(−)-6,6′-dibromo-2-hexyloxy-2′-methoxymethoxy-[1,1′-binaphthalene] **3b**

A solution of 5.28 g (10.0 mmol) of **2**, dissolved in 30 ml of dry THF, was slowly added to a suspension of 573 mg (12.0 mmol) of NaH in 20 ml of dry THF under argon atmosphere. After 15 min, 0.90 ml (12.0 mmol) of chloromethylmethylether was added very slowly and the mixture was stirred overnight at room temperature. The reaction mixture was poured into 100 ml of water and extracted with dichloromethane. The organic layer was washed with a saturated $NaHCO_3$ solution, with brine and dried over $MgSO_4$. After removal of the solvents, the crude compound was purified by column chromatography (silicagel; eluent: hexane/dichloromethane (60:40 v/v)) and isolated as an oil.

Yield: 4.70 g (82%). $[\alpha]_D^{25} = -156$ deg dm^{-1} mol^{-1} l ($c = 3.30$ in $CHCl_3$); ^{1}H NMR ($CDCl_3$, ppm): δ = 8.01 (d (br); 2H), 7.85 (d; 1H), 7.82 (d; 1H), 7.56 (d; 1H), 7.42 (d; 1H), 7.34 (dd; 1H), 7.28 (dd; 1H), 7.00 (d; 1H), 6.94 (d; 1H), 5.30 (s; 1H), 5.07 (d; 1H), 4.96 (d; 1H), 3.95 (m; 2H), 3.17 (s; 3H), 1.37 (m; 2H), 1.0 (m; 6H), 0.73 (t; 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 154.7, 152.8, 150.5, 134.0, 133.7, 133.2, 130.6, 129.9, 129.4, 129.2, 128.4, 128.2, 121.5, 120.4, 95.4, 69.9, 55.9, 31.3, 29.3, 25.3, 22.4, 14.0. MS: m/z = 572 (M^+), 444 ($M^+ - C_6H_{12}$), 364 ($M^+ - C_6H_{12}$, −Br), 284 ($M^+ - C_6H_{12}$, $-Br_2$).

2.3.3. Synthesis of the precursor polymers: Fig. 2

ppol I was synthesized according to literature procedure [6], by reaction of **3a** [7] and **4** [6]. The synthesis of **ppol II** was as follows: 2.65 g (5.00 mmol) of **3b**, 1.82 g (5.00 mmol) of **4** and 290 mg (250 μmol) of Pd(0)$[PPh_3]_4$ were dissolved in 25 ml of THF. The solution was purged with argon and 15 ml of a K_2CO_3 solution (1 M in water) was added. The reaction mixture was refluxed for two days under argon atmosphere while vigorously stirred. After

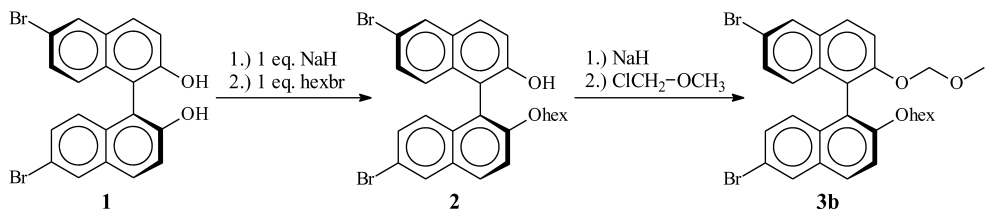

Fig. 1. Synthesis of **3b**.

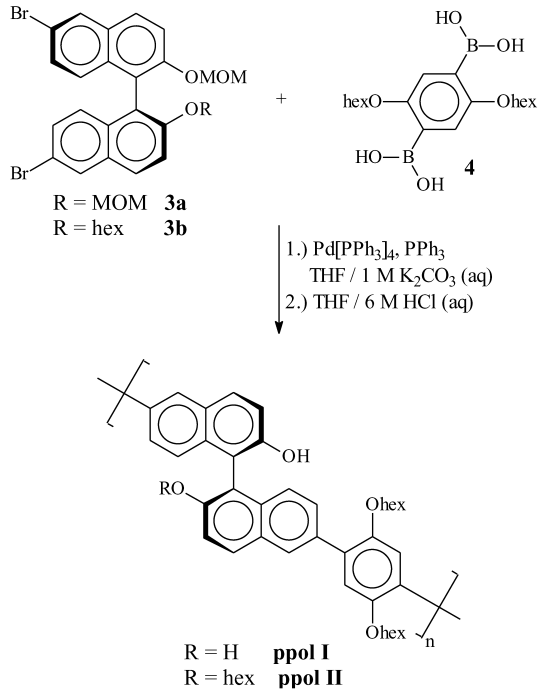

Fig. 2. Polymerisation of the binaphthalene monomers via a Suzuki reaction.

cooling, water was added and the polymer was extracted with dichloromethane. The polymer solution was washed with brine, dried over anhydrous Na_2SO_4 and concentrated. The polymer was isolated by precipitation in methanol and collected by filtration. Finally, the polymer was redissolved in THF, reprecipitated in methanol and dried under reduced pressure.

The obtained MOM-protected polymer was dissolved in 25 ml of THF. The solution was purged with argon, treated with 25 ml of HCl (6 M) and the mixture was refluxed overnight under argon atmosphere. After cooling, water was added and the polymer was extracted with dichloromethane. The organic layer was washed with a saturated $NaHCO_3$ solution, with brine and dried over anhydrous Na_2SO_4. The polymer solution was then concentrated and the polymer was precipitated in methanol. After filtration and drying, the polymer was redissolved in THF and reprecipitated in methanol. This procedure was repeated twice.

Yield: 2.8 g (86%). ^{1}H NMR ($CDCl_3$, ppm): $\delta = 8.13$ (s; 1H), 8.09 (s; 1H), 8.04 (d; 1H), 7.90 (d; 1H), 7.57 (d; 1H), 7.52 (d; 1H), 7.46 (d; 1H), 7.34 (d; 1H), 7.28 (d; 1H), 7.13 (d; 1H), 7.07 (d; 2H), 4.98 (s; 1H), 3.9 (m; 6H), 1.6 (m; 4H), 0.9–1.6 (m; 20H), 0.75 (m; 9H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 155.6$, 151.4, 150.5, 134.4, 134.3, 133.3, 133.2, 133.1, 132.9, 131.0, 130.9, 130.5, 130.4, 130.0, 129.5, 129.3, 129.1, 128.4, 127.9, 124.5, 117.5, 116.3, 115.8, 115.2, 69.8, 69.6, 31.4, 31.3, 29.3, 29.2, 25.8, 25.2, 22.5, 13.9.

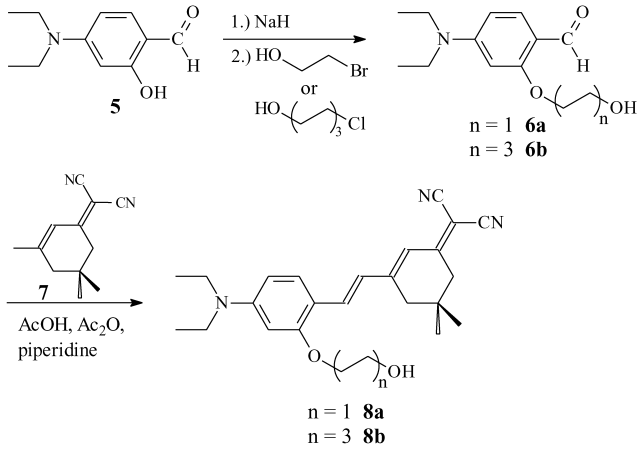

Fig. 3. Synthesis of chromophores **8a**,**b**.

2.4. Synthesis of chromophore *8a*: Fig. 3

2.4.1. Synthesis of 4-(N,N-diethylamino)-2-(2-hydroxyethoxy)benzaldehyde *6a*

Under argon atmosphere a solution of 19.3 g (100 mmol) of 4-(*N*,*N*-diethylamino)-6-hydroxybenzaldehyde **5** in 100 ml of dry DMF was added dropwise at 0 °C to a solution of 2.88 g (120 mmol) of NaH in 50 ml of dry DMF. After 15 min of stirring, 8.52 ml (120 mmol) of 2-bromoethanol and 750 mg (5.0 mmol) of anhydrous NaI were added and the reaction mixture was stirred overnight at 60 °C under argon atmosphere. The mixture was cooled and poured into 250 ml of water. The product was extracted with dichloromethane and the combined organic layers were washed with a saturated $NaHCO_3$ solution, with brine and dried over $MgSO_4$. After evaporation of the solvent, the crude compound was purified by column chromatography (silicagel; eluent: dichloromethane/ethylacetate (90:10 v/v)).

Yield: 19.5 g (82%). Mp: 80.5 °C; ^{1}H NMR ($CDCl_3$, ppm): $\delta = 10.0$ (s; 1H), 7.64 (d; $J = 9.1$ Hz; 1H), 6.31 (dd; $J = 9.1$, 2.2 Hz; 1H), 6.07 (d; $J = 2.2$ Hz; 1H), 4.18 (t; 2H), 4.00 (q; 2H), 3.42 (q; 4H), 2.83 (t; 1H), 1.22 (t; 6H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 187.6$, 163.3, 153.9, 132.2, 114.4, 104.6, 94.2, 70.2, 61.0, 44.8, 12.6. MS: $m/z = 237$ (M^+), 222 ($M^+ - CH_3O$).

2.4.2. Synthesis of chromophore *8a*

In a round-bottomed flask, equipped with a $CaCl_2$ tube, 5.93 g (25.0 mmol) of **6a** and 5.10 g (27.5 mmol) of **7** [8] were dissolved in 50 ml of dry DMF. 4.8 ml of acetic acid, 4.8 ml of acetic acid anhydride and 9.6 ml of piperidine were added and the mixture was stirred overnight at 40 °C. After cooling, 200 ml of water was added and the product was extracted with dichloromethane. The combined organic layers were washed with a saturated $NaHCO_3$ solution, with brine and dried over $MgSO_4$. After evaporation of the solvent, the compound

was purified by column chromatography (silicagel; eluent: dichloromethane/ethylacetate (90:10 v/v)).

Yield: 7.40 g (73%). Mp: 163 °C $\lambda_{max} = 526$ nm ($\varepsilon = 4.0 \times 10^4$ l mol^{-1} cm^{-1}); ^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.44$ (d; $J = 9.1$ Hz; 1H), 7.00 (d; $J = 16.1$ Hz; 1H), 6.85 (d; $J = 16.1$ Hz; 1H), 6.72 (s; 1H), 6.34 (dd; $J = 9.1$, 2.2 Hz; 1H), 6.14 (d; $J = 2.2$ Hz; 1H), 4.17 (t; 2H), 4.04 (q; 2H), 3.41 (q; 4H), 2.56 (s; 2H), 2.45 (s; 2H), 1.93 (t; 1H), 1.21 (t; 6H), 1.07 (s; 6H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 169.2$, 159.0, 156.3, 150.6, 132.9, 129.1, 124.1, 120.9, 114.6, 113.8, 112.9, 105.6, 95.4, 69.9, 61.5, 44.7, 43.1, 39.2, 32.0, 28.1, 12.7. MS: $m/z = 405$ (M^+), 390 ($M^+ - CH_3O$). IR (cm^{-1}): 3524, 2959, 2926, 2869, 2208.

2.5. Synthesis of chromophore ***8b***: Fig. 3

2.5.1. Synthesis of 4-(N,N-diethylamino)-2-(6-hydroxyhexyloxy)benzaldehyde ***6b***

The procedure, described for **6a**, was followed, starting from 9.66 g (50.0 mmol) of **5** and 7.96 ml (60.0 mmol) of 6-chlorohexanol. The compound was purified by column chromatography (silicagel; eluent: dichloromethane/ethylacetate (90:10 v/v)) and isolated as an oil.

Yield: 13.1 g (91%). ^{1}H NMR ($CDCl_3$, ppm): $\delta = 10.2$ (s; 1H), 7.70 (d; $J = 9.1$ Hz; 1H), 6.26 (dd; $J = 9.1$, 2.2 Hz; 1H), 6.01 (d; $J = 2.2$ Hz; 1H), 4.03 (t; 2H), 3.66 (t; 2H), 3.41 (q; 4H), 1.85 (qu; 2H), 1.5 (m; 6H), 1.21 (t; 6H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 187.2$, 163.9, 153.9, 130.2, 114.3, 104.3, 93.2, 67.9, 62.8, 44.9, 32.6, 29.1, 26.0, 25.4, 12.6. MS: $m/z = 293$ (M^+), 278 ($M^+ - CH_3O$).

2.5.2. Synthesis of chromophore ***8b***

The procedure, described for chromophore **8a**, was followed, starting from 7.19 g (25.0 mmol) of **6b** and 5.10 g (27.5 mmol) of **7**. The compound was purified by column chromatography (silicagel; eluent: dichloromethane/acetonitrile (90:10 v/v)).

Yield: 13.1 g (91%). Mp: 109 °C $\lambda_{max} = 530$ nm ($\varepsilon = 4.2 \times 10^4$ l mol^{-1} cm^{-1}); ^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.35$ (d; $J = 9.1$ Hz; 1H), 7.33 (d; $J = 16.1$ Hz; 1H), 6.97 (d; $J = 16.1$ Hz; 1H), 6.68 (s; 1H), 6.29 (dd; $J = 9.1$, 2.2 Hz; 1H), 6.10 (d; $J = 2.2$ Hz; 1H), 4.04 (t; 2H), 3.66 (q; 2H), 3.41 (q; 4H), 2.56 (s; 2H), 2.46 (s; 2H), 1.91 (qu; 2H), 1.55 (m; 7H), 1.21 (t; 6H), 1.06 (s; 6H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 169.2$, 159.8, 156.8, 150.7, 134.5, 130.5, 124.3, 120.5, 114.7, 113.8, 112.7, 104.8, 94.7, 68.2, 62.8, 44.7, 43.1, 39.2, 32.8, 32.0, 29.3, 28.1, 26.3, 25.7, 12.8. MS: $m/z = 461$ (M^+), 446 ($M^+ - CH_3O$). IR (cm^{-1}): 3531, 2931, 2870, 2210.

2.6. Synthesis of chromophore ***15a***: Fig. 4

2.6.1. Synthesis of 2-thienylmethylenetriphenylphosphonium bromide ***10***

68.5 ml (600 mmol) of 2-thiophenemethanol was added to a solution of 206 g (600 mmol) of triphenylphosphine hydrobromide in 600 ml of acetonitrile. The reaction mixture was refluxed for 4 h and cooled down. The precipitate was filtered off, dried and used without further purification in the next step.

Yield: 250 g (95%). Mp: 153.3 °C; ^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.92$ (t; 3H), 7.74 (m; 12H), 7.48 (m; 1H), 6.97 (dd; $J = 5.0$, 3.1 Hz; 1H), 6.78 (d; $J = 3.1$ Hz; 1H), 5.52 (d; $J = 14.6$ Hz; 2H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 135.6$ (d; $J = 2.9$ Hz), 134.3 (d; $J = 10.3$ Hz), 130.9 (d; $J = 8.0$ Hz), 130.5 (d; $J = 12.6$ Hz), 128.8 (d; $J = 9.8$ Hz), 128.3 (d, $J = 4.0$ Hz), 127.7 (d; $J = 2.9$ Hz), 118.1 (d; $J = 85.6$ Hz). MS: $m/z = 358$ ($M^+ - HBr$).

2.6.2. Synthesis of 2-[N-ethyl-N-[4-[2-(2-thien)ethenyl] phenyl]amino]ethanol ***11a***

48.3 g (250 mmol) of **9a** and 110 g (250 mmol) of **10** were dissolved in 500 ml of absolute ethanol. To this solution, 250 ml (375 mmol) of a NaOEt solution (1.5 M in ethanol) was added dropwise and the reaction mixture was refluxed for 5 h under argon atmosphere. The cooled reaction mixture was poured into 500 ml of iced water and extracted with dichloromethane. The combined organic layers were washed with a saturated $NaHCO_3$ solution, with brine and dried over $MgSO_4$. After evaporation of the solvents, the compound was purified by column chromatography (silicagel; eluent: dichloromethane/ethylacetate (90:10 v/v)). The product was isolated as a mixture of *cis* and *trans* (*cis*/*trans*: 4:6).

Yield: 51.7 g (76%). Mp: 101.2 °C; ^{1}H NMR ($CDCl_3$, ppm): *trans*: $\delta = 7.34$ (d; 2H), 7.10 (m; 1H), 7.03 (d; $J = 15.7$ Hz; 1H), 6.95 (m; 2H), 6.85 (d; $J = 15.7$ Hz; 1H), 6.74 (d; 2H), 3.81 (q; 2H), 3.45 (m; 4H), 1.64 (t; 1H), 1.17 (t; 3H).

cis: $\delta = 7.26$ (d; 2H), 7.10 (m; 1H), 6.95 (m; 2H), 6.72 (d; 2H), 6.54 (d; $J = 12.1$ Hz; 1H), 6.48 (d; $J = 12.1$ Hz; 1H), 3.81 (q; 2H), 3.45 (m; 4H), 1.64 (t; 1H), 1.17 (t; 3H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 146.4$, 146.3, 143.0, 139.7, 129.2, 128.8, 127.7, 126.6, 126.3, 126.1, 125.4, 123.5, 123.4, 123.3, 123.0, 121.8, 119.0, 116.1, 110.7, 110.1, 59.7, 51.4, 44.4, 11.2. MS: $m/z = 273$ (M^+), 242 ($M^+ - CH_3O$).

2.6.3. Synthesis of 2-[2-[4-[N-ethyl-N-[2-[(t-butyldimethyl) silyloxy]ethyl]amino]phenyl]ethenyl]thiophene ***12a***

In a 250 ml flask, equipped with a $CaCl_2$ tube, 51.7 g (189 mmol) of **11a** and 34.2 g (227 mmol) of *t*-butyldimethylsilylchloride were dissolved in 100 ml of dry DMF. The solution was cooled in an ice bath and 30.9 g (454 mmol) of imidazole was added in several portions. The reaction mixture was stirred overnight at 40 °C. After cooling, water was added and the mixture was extracted with pentane. The combined organic layers were washed with a saturated $NaHCO_3$ solution, with brine and dried over $MgSO_4$. After evaporation of the solvent, the product was isolated as an oil and used without further purification (*cis*/*trans*: 3.7:6.3).

Yield: 74.7 g (100%). ^{1}H NMR ($CDCl_3$, ppm): *trans*:

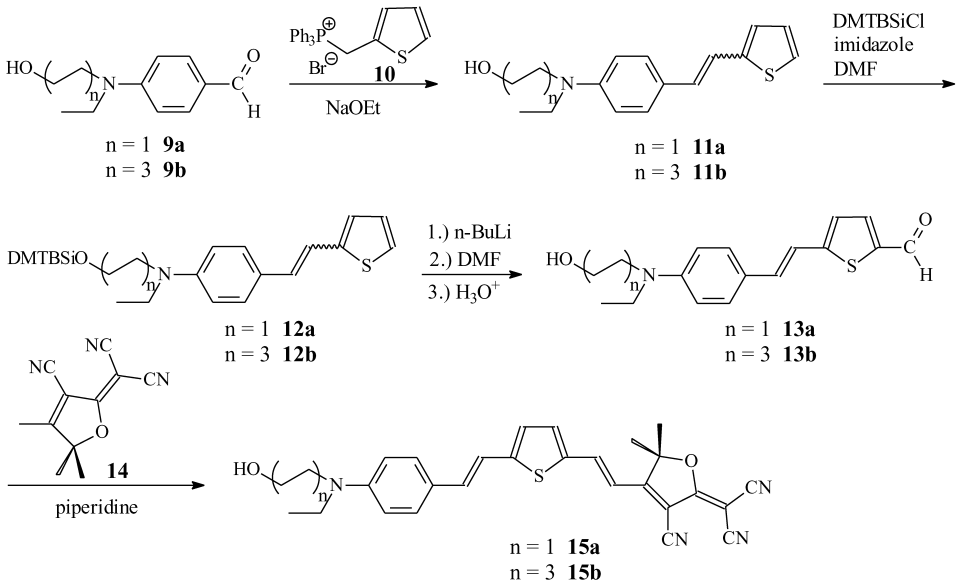

Fig. 4. Synthesis of chromophores **15a**,**b**.

$\delta = 7.29$ (d; 2H), 7.05 (m; 1H), 7.03 (d; $J = 16.4$ Hz; 1H), 6.87 (m; 2H), 6.80 (d; $J = 16.4$ Hz; 1H), 6.74 (d; 2H), 3.72 (t; 2H), 3.39 (m; 4H), 1.12 (t; 3H), 0.83 (t; 9H), 0.06 (s; 6H).

cis: $\delta = 7.26$ (d; 2H), 7.05 (m; 1H), 6.87 (m; 2H), 6.72 (d; 2H), 6.54 (d; $J = 12.1$ Hz; 1H), 6.53 (d; $J = 12.1$ Hz; 1H), 3.72 (t; 2H), 3.39 (m; 4H), 1.12 (t; 3H), 0.83 (t; 9H), 0.06 (s; 6H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 146.5$, 146.3, 143.1, 139.7, 129.0, 128.8, 127.7, 126.6, 126.4, 126.1, 125.5, 123.5, 123.4, 123.3, 123.0, 121.8, 119.1, 116.1, 110.6, 110.2, 59.6, 51.4, 44.4, 24.7, 17.2, 11.2, −6.4. MS: $m/z = 387$ (M^+), 242 ($M^+ - C_7H_{17}OSi$).

2.6.4. Synthesis of 2-[2-[4-[N-ethyl-N-(2-hydroxyethyl) amino]phenyl]ethenyl]thien-5-al *13a*

41.8 g (108 mmol) of **12a** was dissolved in 300 ml of dry THF. The solution was purged with argon, cooled to −78 °C and 94 ml (220 mmol) of *n*-butyllithium (2.34 M in hexane) was added. The solution turned dark blue. The temperature was slowly raised to −30 °C and 35 ml of dry DMF was added. Upon addition, the solution became yellow. After 2 h of stirring at −30 °C, 500 ml of HCl (2 M) was added (the solution turns deep red) and the mixture was vigorously stirred at 40 °C for 4 h. After cooling, the reaction mixture was neutralised with NH_3 solution (5 M) and extracted with dichloromethane. The combined organic layers were washed with a saturated $NaHCO_3$ solution, with brine and dried over $MgSO_4$. After evaporation of the solvents, the compound was purified by column chromatography (silicagel; eluent: dichloromethane/ethylacetate (90:10 v/v)), followed by recrystallisation from chloroform/hexane. No *cis*-isomer was detected.

Yield: 24.2 g (74%). Mp: 106.2 °C; ^{1}H NMR ($CDCl_3$, ppm): $\delta = 9.81$ (s; 1H), 7.62 (d; $J = 4.0$ Hz; 1H), 7.37 (d; 2H), 7.08 (d; $J = 16.1$ Hz; 1H), 7.05 (d; $J = 4.0$ Hz; 1H), 6.98 (d; $J = 16.1$ Hz; 1H), 6.73 (d; 2H), 3.82 (q; 2H), 3.52 (t; 2H), 3.46 (q; 2H), 1.71 (t; 1H), 1.19 (t; 3H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 182.4$, 154.3, 148.6, 140.0, 137.7, 133.4, 128.5, 125.0, 123.8, 116.1, 112.1, 60.1, 52.2, 45.5, 11.9. MS: $m/z = 301$ (M^+), 270 ($M^+ - CH_3O$), 242 ($M^+ - CH_3O$, −CO).

2.6.5. Synthesis of 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-(2H,5H)-furan *14* [9]

10.0 g (100 mmol) of 3-hydroxy-3-methyl-2-butanone and 13.2 g (200 mmol) of malononitrile were dissolved in 250 ml of absolute ethanol. The solution was purged with argon and 1.0 ml of LiOEt (1.0 M in ethanol) was added. The flask was equipped with a Soxhlet extraction apparatus, containing a thimble, filled with molecular sieve, and the mixture was refluxed for 8 h under argon atmosphere. The solution was concentrated and cooled down (−20 °C). The precipitate was filtered off, washed with cold ethanol and recrystallised from ethanol.

Yield: 16.0 g (81%). Mp: 197.5 °C; ^{1}H NMR ($CDCl_3$, ppm): $\delta = 2.36$ (s; 3H), 1.63 (s; 6H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 182.5$, 175.2, 111.0, 110.4, 109.0, 104.8, 99.8, 58.5, 24.4, 14.2. MS: $m/z = 199$ (M^+), 174 ($M^+ - CH_3$).

2.6.6. Synthesis of chromophore *15a*

2.3 g (7.50 mmol) of **13a** and 1.8 g (9.00 mmol) of **14** were dissolved in 25 ml of chloroform. The solution was purged with argon and 0.2 ml of triethylamine was added. The mixture was refluxed under argon atmosphere, until **13a** had completely disappeared (takes about 12 h). Then, the reaction mixture was cooled and 25 ml of hexane was added. The chromophore was filtered off and recrystallised twice from ethylacetate/hexane.

Yield: 1.0 g (30%). Mp: 239 °C $\lambda_{max} = 635$ nm ($\varepsilon = 4.7 \times 10^4$ l mol^{-1} cm^{-1}); ^{1}H NMR (acetone-d6, ppm): $\delta =$ 8.13 (d; $J = 15.7$ Hz; 1H), 7.75 (d; $J = 4.0$ Hz; 1H), 7.48

(d; 2H), 7.20 (s; 2H), 7.19 (d; $J = 4.0$ Hz; 1H), 6.80 (d; $J = 15.7$ Hz; 1H), 6.76 (d; 2H), 3.86 (t; 1H), 3.73 (q; 2H), 3.51 (m; 4H), 1.87 (s; 6H), 1.17 (t; 3H). ^{13}C NMR (DMSO-d6, ppm): $\delta = 177.0$, 174.6, 153.8, 148.8, 140.6, 139.2, 137.7, 134.6, 129.2, 127.7, 123.0, 115.8, 113.2, 112.5, 111.6, 111.4, 99.4, 96.4, 58.5, 52.8, 25.7, 12.2. MS: $m/z =$ 482 (M^+), 451 ($M^+ - CH_3O$), 184 ($C_{10}H_6N_3O$). IR (cm^{-1}): 3522, 2929, 2869, 2224.

2.7. Synthesis of chromophore ***15b***: Fig. 4

2.7.1. Synthesis of 6-[N-ethyl-N-[4-[2-(2-thien) ethenyl]phenyl]amino]hexanol ***11b***

The procedure, described for **11a**, was followed, starting from 57.2 g (229 mmol) of **9b**. The product was isolated as an oil (*cis/trans*: 3.5:6.5).

Yield: 65.1 g (86%). ^{1}H NMR ($CDCl_3$, ppm): *trans*: $\delta =$ 7.34 (d; 2H), 7.19 (m; 1H), 7.08 (d; $J = 16.1$ Hz; 1H), 6.97 (m; 2H), 6.86 (d; $J = 16.1$ Hz; 1H), 6.64 (d; 2H), 3.67 (t; 2H), 3.40 (q; 2H), 3.28 (t; 2H), 1.61 (m; 4H), 1.42 (m; 4H), 1.22 (t; 3H). cis: $\delta = 7.27$ (d; 2H), 7.19 (m; 1H), 6.97 (m; 2H), 6.62 (d; 2H), 6.51 (d; $J = 12.1$ Hz; 1H), 6.46 (d; $J =$ 12.1 Hz; 1H), 3.67 (t; 2H), 3.40 (q; 2H), 3.28 (t; 2H), 1.61 (m; 4H), 1.42 (m; 4H), 1.22 (t; 3H). ^{13}C NMR ($CDCl_3$, ppm): $\delta =$ 147.7, 147.4, 144.1, 140.9, 130.1, 130.1, 128.8, 127.6, 127.5, 127.0, 126.6, 124.5, 124.3, 124.1, 123.6, 122.8, 119.9, 117.0, 111.5, 111.2, 63.1, 50.4, 44.9, 32.9, 27.6, 27.0, 12.4. MS: $m/z = 329$ (M^+), 314 ($M^+ - CH_3$).

2.7.2. Synthesis of 2-[2-[4-[N-ethyl-N-[6-[(t-butyldimethyl) silyloxy]hexyl]amino]phenyl]ethenyl]thiophene ***12b***

The procedure, described for **12a**, was followed, starting from 65.1 g (198 mmol) of **11b**. The product was isolated as an oil (*cis/trans*: 3.2:6.8).

Yield: 77.9 g (89%). ^{1}H NMR ($CDCl_3$, ppm): *trans*: $\delta =$ 7.34 (d; 2H), 7.11 (m; 1H), 7.03 (d; $J = 15.7$ Hz; 1H), 6.92 (m; 2H), 6.86 (d; $J = 15.7$ Hz; 1H), 6.63 (d; 2H), 3.63 (t; 2H), 3.40 (q; 2H), 3.28 (t; 2H), 1.60 (m; 4H), 1.38 (m; 4H), 1.18 (t; 3H), 0.91 (s; 9H), 0.06 (s; 6H). *cis*: $\delta = 7.26$ (d; 2H), 7.11 (m; 1H), 6.92 (m; 2H), 6.61 (d; 2H), 6.51 (d; $J = 12.1$ Hz; 1H), 6.46 (d; $J = 12.1$ Hz; 1H), 3.63 (t; 2H), 3.40 (q; 2H), 3.28 (t; 2H), 1.6 (m; 4H), 1.38 (m; 4H), 1.18 (t; 3H), 0.91 (s; 9H), 0.06 (s; 6H). ^{13}C NMR ($CDCl_3$, ppm): $\delta =$ 147.6, 147.4, 144.1, 140.8, 130.1, 130.0, 128.8, 127.6, 127.4, 127.0, 126.5, 124.5, 124.3, 124.2, 123.6, 122.8, 119.8, 117.0, 111.6, 111.2, 63.0, 50.4, 44.9, 32.9, 27.6, 27.0, 25.8, 18.1, 12.4, −4.8. MS: $m/z = 443$ (M^+), 428 ($M^+ - CH_3$), 242 ($M^+ - C_{11}H_{25}OSi$).

2.7.3. Synthesis of 2-[2-[4-[N-ethyl-N-(6-hydroxyhexyl) amino]phenyl]ethenyl]thien-5-al ***13b***

The procedure, described for **12a**, was followed, starting from 44.4 g (100 mmol) of **12b**. The product was isolated as an oil.

Yield: 28.4 g (79%). ^{1}H NMR ($CDCl_3$, ppm): $\delta = 9.81$ (s; 1H), 7.62 (d; $J = 4.0$ Hz; 1H), 7.36 (d; 2H), 7.08 (d; $J = 16.1$ Hz; 1H), 7.04 (d; $J = 4.0$ Hz; 1H), 6.96 (d; $J =$ 16.1 Hz; 1H), 6.62 (d; 2H), 3.66 (q; 2H), 3.40 (q; 2H), 3.30 (t; 2H), 1.58 (m; 4H), 1.39 (m; 4H), 1.23 (t; 1H), 1.18 (t; 3H). ^{13}C NMR ($CDCl_3$, ppm): $\delta =$ 182.3, 154.5, 148.5, 140.0, 137.7, 133.7, 128.4, 124.8, 122.9, 115.6, 111.5, 62.8, 50.3, 45.0, 32.7, 27.6, 27.0, 25.7, 12.4. MS: $m/z = 357$ (M^+), 270 ($M^+ - C_5H_{11}O$), 242 ($M^+ - C_5H_{11}O$, −CO).

2.7.4. Synthesis of chromophore ***15b***

The procedure, described for chromophore **15a**, was followed, starting from 4.00 g (11.2 mmol) of **13b**. The product was purified by column chromatography (silicagel; eluent: dichloromethane/ethylacetate (90:10 v/v)).

Yield: 2.56 g (42%). Mp: 177 °C $\lambda_{max} = 640$ nm ($\varepsilon = 5.0 \times 10^4$ l mol^{-1} cm^{-1}); ^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.78$ (d; $J = 15.7$ Hz; 1H), 7.39 (d; 2H), 7.38 (d; $J = 3.7$ Hz; 1H), 7.03 (d; $J = 3.7$ Hz; 1H), 6.99 (d; $J = 16.1$ Hz; 1H), 6.66 (d; 2H), 6.56 (d; $J = 15.7$ Hz; 1H), 3.68 (q; 2H), 3.43 (q; 2H), 3.33 (t; 2H), 1.76 (s; 6H), 1.65 (m; 4H), 1.45 (m; 4H), 1.23 (t; 1H), 1.21 (t; 3H). ^{13}C NMR ($CDCl_3$, ppm): $\delta =$ 175.8, 172.9, 154.7, 148.9, 146.4, 137.7, 137.3, 129.1, 122.8, 112.3, 111.6, 111.5, 111.1, 96.9, 95.8, 62.9, 50.4, 45.1, 32.7, 27.6, 26.9, 26.6, 25.7, 12.4. MS: $m/z = 538$ (M^+), 523 ($M^+ - CH_3$), 184 ($C_{10}H_6N_3O$). IR (cm^{-1}): 3499, 2930, 2869, 2225.

2.8. Functionalisation of precursor polymers: Fig. 5

General procedure. Prior to reaction, the chromophores were recrystallised (**16a**,**b** and **17a**,**b** from ethanol, **8a**,**b** and **15a**,**b** from ethylacetate) and all reagents and solvents were thoroughly dried. 0.333 mmol of naphthol groups (**ppol I-II**), 0.400 mmol of chromophore and 0.666 mmol of PPh_3 were dissolved in 15 ml of dry THF. The solution was purged with argon and 0.666 mmol of diethylazodicarboxylate (DEAD) was injected. The reaction vessel was sealed and the mixture was stirred for two days at room temperature. The polymer was isolated by precipitation in methanol, collected by filtration and dried. Finally, the polymer was redissolved in THF, reprecipitated in methanol and dried. This procedure was repeated until the filtrate was only slightly coloured.

3. Results and discussion

In this paper, the synthesis and properties of chromophore-functionalised polybinaphthalenes are reported. Several parameters in the molecular structure, including the spacer length, the nature of the chromophore and the number of chromophores per binaphthalene unit, were varied, in order to investigate the influence of these parameters on the (NLO) properties of these materials.

The polymer backbone consists of chiral binaphthalene unit, connected with rigid groups, to ensure the chiral, helical conformation [6–7,10]. Hexyl groups were

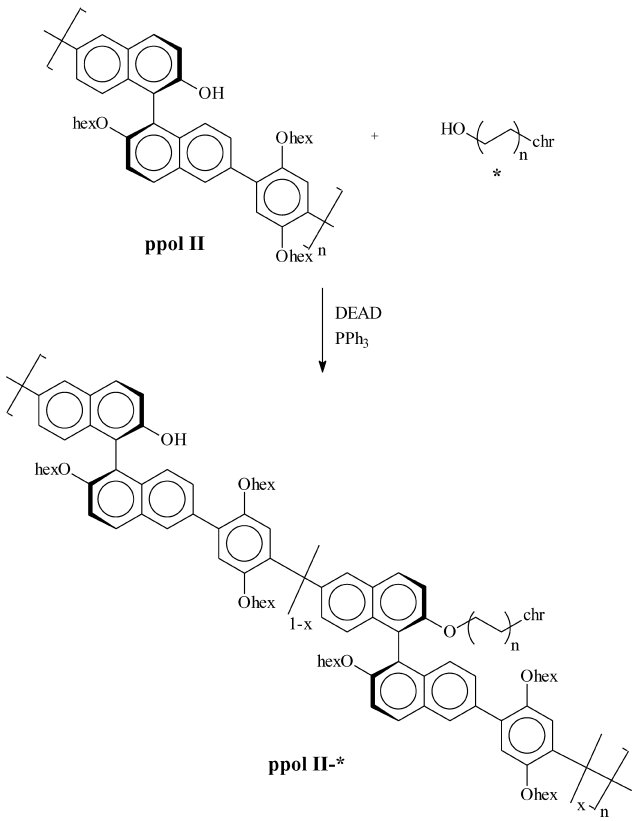

Fig. 5. Functionalisation of the precursor polymers (**ppol II**) with chromophores.

incorporated for solubility reasons and the chromophores were linked to the polymer backbone through the naphthol functions. The precursor polymers were prepared by means of a Suzuki reaction, because this pathway yields the highest molecular weights [7]. Direct polymerisation of chromophore-functionalised monomers to obtain chromophore-functionalised polymers, is not possible under this conditions, since this would lead to chromophore degradation. Therefore, the synthesis of chromophore-functionalised polybinaphthalenes was a two-step process, in which chromophores were introduced into precursor polymers in a second, separate step.

Two precursor polymers, with different number (1 or 2) of naphthol groups per binaphthalene unit, were synthesized. The number of naphthol groups per binaphthalene unit, available for functionalisation, was varied, since the two naphthol groups in a binaphthalene unit point in the opposite direction. It is therefore very likely that, when both are substituted with chromophores, the two chromophores will point in an opposite direction as well. This would result in a quasi centrosymmetrical ordering, which makes large second-order NLO responses impossible. As a consequence, systematically blocking one of the two naphthol groups with an alkyl group, can—in principal—increase the NLO response.

These precursor polymers were functionalised with eight chromophores. The molecular structure of chromophores **16a**,**b** and **17a**,**b** is presented in Fig. 6. **16a** is a commercial product (disperse red 1) and **16b**, **17a** [11] and **17b** [11] were synthesized according to literature procedures. The synthesis of chromophores **8a** and **8b** is schematically shown in Fig. 3 and corresponds to a Knoevenagel condensation between the aldehyde **6a**,**b** and **7**. For the synthesis of **15a**,**b**, the pathway, described in the literature [12] for analogous chromophores, was modified. In general, the key aldehyde **13a**,**b** is prepared from the acetyl protected derivative of **9a**,**b**, which is reacted with diethylthiophenephosphonate in a Horner reaction. Subsequently, the aldehyde functionality is introduced using a classical Vilsmeyer reaction and finally, the alcohol group is deprotected. This pathway is characterised by its low yield ($<10\%$). In our alternative procedure, **9a**,**b** was reacted with the phosphonium salt **10**, which can be readily obtained from 2-thiophenemethanol and triphenylphosphonium hydrobromide, in a classical Wittig reaction. In the next step the alcohol is converted into a silylether. The aldehyde group is then introduced by treatment with *n*-butyllithium, followed by addition of DMF and hydrolysis. Under proper reaction conditions, the conversion of the intermediary amino alcohol to the aldehydes **13a**,**b** could be performed together with the deprotection of the silyl ether to the alcohol. The overall yield in this procedure exceeds 60%, which is about eight times higher than in the classical route. Moreover, the intermediary compounds are more easily purified. The chromophores **15a**,**b** were finally obtained by a condensation of **13a**,**b** with the tricyano acceptor **14**.

With these chromophores, the influence of the chromophore on the NLO properties was investigated. The chromophores differ from each other in their spacer length and the DπA-structure. While the DπA-structure of the chromophore clearly determines the NLO properties (amongst others), one can expect that the spacer length influences the ordering of the chromophores in these systems. In case of shorter, more rigid spacers, the backbone tends to impose its chiral ordering more efficiently to the chromophores, which may benefit the NLO response. However, we must notice that if an additional ordering is performed, s.a. an electrical poling, the chiral ordering can be overruled and the advantages, proper to chirality, can in that case decrease or even disappear.

The chromophores were attached to the polymer backbone under Mitsunobu conditions. This reaction is known

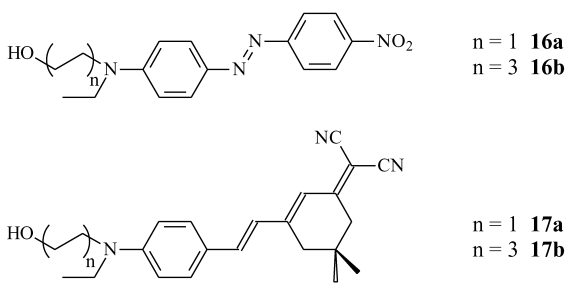

Fig. 6. Structure of chromophores **16a**,**b**, **17a**,**b**.

for its very mild reaction conditions. In this work, this is reflected in the fact that no decomposition of the chromophores, neither of the polymers, was observed during the functionalisation.

The physical properties of the polymers are listed in Table 1. The degree of functionalisation (DF) is defined as the percentage of naphthol groups that were successfully substituted by chromophores and was determined by UV–Vis and ^{1}H NMR spectroscopy. These data show that the applied method, the functionalisation of precursor polymers by means of a Mitsunobu reaction, is very suitable to prepare these molecules.

The molecular weights and polydispersities were measured with GPC towards polystyrene standards. Although they seem quite low, we may assume that they are underestimated [13] and should be estimated about two times higher. In any way, they are sufficiently high to ensure good film forming properties and chiral ordering of the chromophores—as was experimentally proven.

^{1}H NMR experiments confirm the structure of both precursor polymers and chromophore-functionalised polymers. No end groups were detected, which indicates that the materials are of (relative) high molecular weight. Finally, no evidence for structure inhomogeneity was found.

Concerning the glass transition temperatures (T_g), it is remarkable that the chromophore-functionalised polymers show a clear T_g, while no T_g could be observed from the precursor polymers (without chromophores). We assume that the observed phenomenon is the weakening of the chromophores in the polymer system and not of the whole material. It is clear that this cannot be explained by the classical model of chromophore-functionalised polymers. In this model, the two components (polymer matrix and chromophores) mix perfectly well with each other. In that case, Fox's law counts, which means that the inverse of the T_g of the mixture is a weight average of the inverses of the T_g of the components. The T_g's of the chromophores are given in Table 2. Since the T_g of the chromophores is lower then the T_g of the polymer matrix, the chromophore acts as a plasticizer. Clearly, the chromophore-functionalised polybinaphthalenes do not fit in this model. The polymer backbone is helical, which is an ordered structure and the polymers without chromophores do not show a glass transition. What is observed, is not the weakening of a mixture of polymer backbone-chromophore, but the weakening of the chromophores in the polymer system. In that case, the T_g of the system should increase when the T_g of the chromophore increases, which is experimentally confirmed. Moreover, we will show in a following paper that the T_g of the system is also increased when both, and not just one, naphthol groups per binaphthalene unit are functionalised with chromophore and when the chromophore concentration (i.e. the DF) is increased, which is in contrast with Fox's law. (Unfortunately, it is not possible to investigate the influence of these parameters with this polymer systems, because the chromophore concentration cannot be varied under controlled condition.) Indeed, attaching the chromophore to a rigid, rod-like backbone reduces the mobility of the chromophores, which increases the T_g. Therefore, the T_g of polybinaphthalenes, functionalised with chromophores with a long, flexible spacer, is lower than the T_g of analogous systems with a short, more rigid spacer.

The optical rotations are quite high. It is important to notice that they increase dramatically when chromophores,

Table 1
Physical properties of the precursor polymers and chromophore-functionalised polymers

Polymer	DF[a] (mol%)	$\bar{M}_n$ (10^3 g mol^{-1})	D[b]	T_g (°C)	$[\alpha]_D^{25}$, (10^2 deg dm^{-1} g^{-1} ml (c/10^{-2} g ml^{-1}))
ppol I	–	7.8	2.4	–[c]	3.3 (0.021)
ppol II	–	7.1	2.4	–[c]	1.5 (0.034)
pol I-16a	30	12	2.0	151	2.9 (0.010)
pol I-16b	45	10	2.0	141	3.6 (0.008)
pol I-17a	70	13	2.3	160	125 (0.009)
pol I-17b	40	15	2.0	123	145 (0.010)
pol I-8a	50	14	2.0	153	174 (0.010)
pol I-8b	50	14	2.0	126	185 (0.008)
pol I-15a	10	7.5	2.3	143	671 (0.002)
pol I-15b	10	7.7	2.0	118	681 (0.002)
pol II-16a	60	8.7	2.2	85	4.0 (0.010)
pol II-16b	45	8.5	2.1	93	1.5 (0.013)
pol II-17a	25	10	2.0	128	149 (0.010)
pol II-17b	50	7.5	2.1	100	129 (0.012)
pol II-8a	25	7.0	2.3	116	178 (0.008)
pol II-8b	15	8.5	2.1	114	148 (0.018)
pol II-15a	35	7.9	2.2	162	1.28×10^4 (0.003)
pol II-15b	35	7.6	2.1	138	1.20×10^4 (0.004)

[a] Degree of functionalisation.
[b] Polydispersity: $D = \bar{M}_w/\bar{M}_n$.
[c] Could not be detected.

Table 2
Glass transition temperatures of the chromophores

	16a	16b	17a	17b	8a	8b	15a	15b
T_g/°C	–[a]	–[a]	46	16	52	23	108	66

[a] Could not be made amorphous.

of which λ_{max} is close to the applied wavelength (589 nm), are introduced. This seems to suggest that the chiral helical polymer backbone imposes its chiral ordering to the chromophores [2d]. Analogous results are obtained from CD experiments.

Thin films were spincoated from polymers with the highest optical rotations (**pol I-8a**, **pol I-8b**, **pol I-15a**, **pol I-15b**, **pol II-15a** and **pol II-15b**). Although NLO processes can, in principal, be observed in isotropic chiral media, it remains in practice necessary to perform a polar ordering. Therefore, the chromophores were aligned by corona poling. The NLO properties were analysed by second-harmonic generation. The results are presented in Table 3. The symmetry of the poled samples was investigated by polarised UV–Vis and second-harmonic generation. These experiments showed that all samples had a C_∞-symmetry with four nonvanishing susceptibility components, i.e. $\chi^{(2)}_{zzz}$, $\chi^{(2)}_{xxz}$, $\chi^{(2)}_{zxx}$ and $\chi^{(2)}_{xyz}$. The *xyz*-type component can only be present in chiral samples, while the other components can be observed in any sample, chiral or achiral. Our experiments showed that the chiral component is very weak and in most cases even negligible. Probably, the chiral ordering of the chromophores is lost during poling, resulting in a vanishing *xyz*-component. This hypothesis was partially confirmed by CD-experiments, in which the chromophore peak largely and in most cases completely disappeared (Fig. 7). On the other hand, the magnitude of the other susceptibility components was much larger. The reason is that these components are not linked to the chirality of the system, but instead originate from the polar order, introduced by the poling procedure. Susceptibility values of over 100 pm/V were observed, which illustrates the potential of these materials for NLO applications.

Table 3
Nonlinear properties of the chromophore-functionalised polymers **pol I-8a**–**pol I-15b** and **pol II-15a**–**pol II-15b**

Polymer	$\chi^{(2)}_{zzz}$ (pm V^{-1})	$\chi^{(2)}_{zzz}(0)$ (pm V^{-1})	$\chi^{(2)}_{xxz}$ (pm V^{-1}	$\chi^{(2)}_{zxx}$ (pm V^{-1})
pol I-8a	103	6.6	36.5	46.6
pol I-8b	112	7.8	35.8	40.7
pol I-15a	32.2	10.6	9.0	14.9
pol I-15b	23.8	8.6	7.3	12.3
pol II-15a	19.9	5.8	4.8	9.0
pol II-15b	18.7	6.3	5.6	8.8

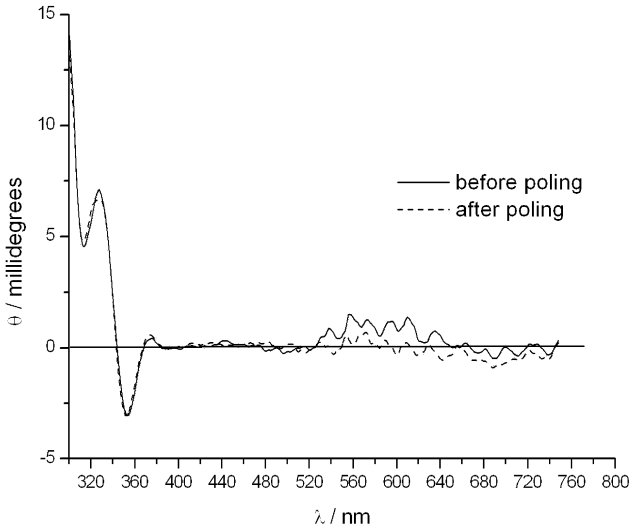

Fig. 7. CD-spectrum of **pol I-8b** before and after poling.

4. Conclusions

In this work chiral, helical chromophore-functionalised polybinaphthales were synthesized. These polymers were obtained in a two-step process. First, precursor polymers were prepared via a Suzuki-coupling. In a second step, chromophores could be incorporated under Mitsunobu conditions. With this pathway, several parameters in the molecular structure of the materials could be varied, which has made this class of polymers accessible to the field of (chiral) nonlinear optics. The NLO properties of these materials were measured and show reasonable high (achiral) responses.

Acknowledgements

We are very grateful to KVH Industries, Inc, Middletown, RI, USA for their financial support. This work was also supported by the Fund for Scientific Research-Flanders (FWO-Vlaanderen; G. 0308.96) and from the Katholieke Universiteit Leuven (GOA/2000/03). G.K. and S.S. are doctoral fellows and TV is a postdoctoral fellow of the fund for Scientific Research-Flanders. We also acknowledge S. Ermer and P. Bedworth for their synthetic advice.

References

[1] Burland DM, Miller RD, Walsh CA. Chem Rev 1994;94:31.
[2] (a) Verbiest T, Samyn C, Boutton C, Houbrechts S, Kauranen M, Persoons A. Adv Mater 1996;8:756. (b) Bouman MM, Havinga EE, Janssen RAJ, Meijer EW. Mol Cryst Liq Cryst 1994;256:439. (c) Teerenstra MN, Hagting JG, Oostergetel GT, Schouten AJ, Devillers MAC, Nolte RJM. Thin Solid Films 1994;248:110. (d) Koeckelberghs G, Van Beylen M, Samyn C. Mater Sci Engng C 2001;18:15. (e) Ma L, Hu QS, Vitharana D, Pu L. Polym Prepr 1996;37:462. (f) Ma L, Hu QS, Vitharana D, Wu C, Kwan CMS, Pu L. Macromolecules 1997;30:204.

[3] (a) Verbiest T, Kauranen M, Persoons A. J Mater Chem 1999;9:2005. (b) Kauranen M, Verbiest T, Persoons A. J Nonlinear Opt Phys 1999;8:171.
[4] Maki JJ, Kauranen M, Persoons A. Phys Rev B 1995;51:1425.
[5] Sogak GDY, Cram DJ. J Am Chem Soc 1979;101:3035.
[6] Hu QS, Huang WS, Vitharana D, Zheng XF, Pu L. J Am Chem Soc 1997;119:12454.
[7] Hu QS, Vitharana D, Zheng XF, Wu C, Kwan CMS, Pu L. J Org Chem 1996;61:8370.
[8] Van den Broeck K, Verbiest T, Van Beylen M, Persoons A, Samyn C. Macromol Chem Phys 1999;200:2629.
[9] Ermer S, Bedworth P. Lockheed Martin Space Systems-MSO, personal communication.
[10] (a) Nakano T, Okamoto Y. Chem Rev 2001;101:4013. (b) Hill DJ, Mio MJ, Prince RB, Hughes TS, Moore JS. Chem Rev 2001;101: 3893.
[11] Ermer S, Lovejoy SM, Leung DS, Warren H, Moylan CR, Twieg RJ. Chem Mater 1997;9:1437.
[12] (a) Saadeh H, Wang L, Yu L. Macromolecules 2000;33:1570. (b) Wang F. PhD Thesis, Design, synthesis and characterization of novel, organic chromophores and polymers for electro-optic applications, University of Southern California, 1998.
[13] Ma L, Hu QS, Musick KY, Vitharana D, Wu C, Kwan CMS, Pu L. Macromolecules 1996;29:5083.