Donor-embedded Polybinaphthalenes for Nonlinear Optical

Applications: Influence of the Incorporation of a Double Bond.

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Summary: In this paper two new donor-embedded polybinaphthalenes prepared by a Heck reaction, are presented. By introducing a double bond in the polymer backbone, the supramolecular structure was altered in comparison with polymers without the double bond. Comparison between the CD/UV-Vis spectra of polymers with and without the double bond (previously synthesized in our laboratory) proved this change in supramolecular structure. The double bonds also allow crosslinking upon heat treatment. NLO experiments demonstrated a more stable nonlinearity over time depending on the degree of crosslinking.

Introduction

The design and synthesis of polymeric materials for nonlinear optical (NLO) applications (such as frequency doublers, high speed modulators,...) have received considerable interest over the past years. Polybinaphthalenes show particularly interesting properties for applications in this field. Firstly, chromophore-functionalized polybinaphthalenes show a

tree-like structure: they are composed of a rigid, rod-like backbone, to which flexible chromophores are attached. This supramolecular architecture diminishes and even excludes dipolar interactions between the chromophores.^[1] Therefore, these systems allow a very high chromophore density, which cannot be obtained in random coil polymers.^[1] Secondly, chiral donor-embedded polybinaphthalenes can benefit from contributions, inherently to chirality, which can increase the nonlinear optical response.^[2] In a previous study on donor-embedded polybinaphthalenes^[1b] it was demonstrated that they are a very interesting class of polymers since (1) the dipolar interaction between the chromophores are excluded in these materials and (2) chiral contributions are present. These polymers were prepared by a Stille coupling and adopt a macromolecular helical conformation. The use of optically pure binaphthalene monomers appeared to be essential for these assets.^[1c] In this paper, the synthesis of two new donor-embedded polybinaphthalenes obtained by a Heck reaction is presented. Double bonds incorporated in the polymer backbone alter the macromolecular structure of the polymer. Moreover, the double bounds can give rise to crosslinking, which makes it possible to immobilize molecular motions and stabilizes the alignment of the chromophores and therefore the NLO response.

Experimental part

Materials

All starting materials were purchased from Acros Organics, Fluka, Merck or Aldrich and were used as received. Tetrahydrofuran (THF) was dried over a Na/K alloy and *N,N*-dimethylformamide (DMF) was distilled over CaH₂ and further dried over molecular sieve (4 Å). Acetonitrile (CH₃CN) was dried over molecular sieve (4 Å). Triethylamine was stored over NaOH pellets. Compound **1** and chromophores **a** and **b** (Scheme 1) were synthesized according to literature procedures.^[1]

Synthesis of (*R*)-(-)-2,2'-dihexyloxy-[1,1'-binaphthyl]-6,6'-dicarbaldehyde (**2**)

A solution of **1** (5.00 g, 8.00 mmol) in dry THF (80 mL) was cooled to $-78\text{ }^{\circ}\text{C}$ and purged with argon. After 15 min *n*-butyllithium (17.6 mmol, 2.5 M in hexane) was added. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 15 min. Dry DMF (2.48 mL, 32.0 mmol) was added. The reaction mixture was warmed to room temperature and stirred for 1 h. After cooling to $0\text{ }^{\circ}\text{C}$, 0.1 N HCl was added. The mixture was allowed to reach room temperature and extracted with CH_2Cl_2 . The combined organic layers were washed with a saturated NaHCO_3 solution, with brine and dried over MgSO_4 . The crude reaction product was purified by column chromatography (silicagel, hexane/dichloromethane 20/80 (v/v)) and isolated as an oil.

Yield: 2.71 g (66 %)

MS (70 eV) : m/z = 510 (M^+), 426 ($\text{M}^+ - \text{C}_6\text{H}_{13}$), 342 ($\text{M}^+ - \text{C}_{12}\text{H}_{26}$), 313 ($\text{M}^+ - \text{C}_{12}\text{H}_{26} - \text{CHO}$), 285 ($\text{M}^+ - \text{C}_{12}\text{H}_{26} - \text{CHO} - \text{CHO}$)

^1H NMR (CDCl_3): δ = 0.69 (t, 6H), 0.99 (t, 12H), 1.41 (m, 4H), 4.01 (m, 4H), 7.20 (d, 2H, J = 8.9 Hz), 7.50 (d, 2H, J = 8.9 Hz), 7.69 (dd, 2H, J = 8.9 Hz, J = 1.5 Hz), 8.12 (d, 2H, J = 8.9 Hz), 8.37 (d, 2H, J = 1.5 Hz), 10.10 (s, 2H)

^{13}C NMR (CDCl_3): δ = 14.2, 22.8, 25.5, 27.2, 31.5, 69.4, 115.8, 119.9, 123.5, 126.3, 128.2, 131.7, 132.4, 135.2, 137.6, 157.4, 192.2

$[\alpha]_D^{20}$ = $-17.8\text{ deg}\cdot\text{dm}^{-1}\cdot\text{mol}^{-1}\cdot\text{l}$ (c = 0.1 in THF)

Synthesis of (*R*)-(-)-6,6'-di(ethenyl)-2,2'-dihexyloxy-[1,1'-binaphthalene] (**3**)

A solution of **2** (2.97 g, 5.81 mmol) and methyltriphenylphosphonium bromide (8.30 g, 23.2 mmol) in dry THF (200 mL) and dry acetonitrile (100 mL) was stirred and purged with argon. After 15 min *t*-BuOK (2.6 g, 23.2 mmol) was added. The mixture was stirred overnight at room temperature under argon atmosphere. The precipitated salts were filtered off and the

solvents were evaporated in vacuo. The residue was dissolved in CH₂Cl₂, washed with water and dried over MgSO₄. The crude reaction product was purified by column chromatography (silicagel, dichloromethane) and isolated as a yellow oil, which must be kept < 5 °C.

Yield: 2.22 g (76%)

MS (70 eV) : m/z = 506 (M⁺), 421 (M⁺-C₆H₁₃), 337 (M⁺-C₁₂H₂₆), 306 (M⁺-C₁₂H₂₆-C₂H₃), 280 (M⁺-C₁₂H₂₆-C₄H₆)

¹H NMR (CDCl₃) : δ = 0.73 (t, 6H), 0.9-1.1 (m, 12H), 1.39(m, 4H), 3.94 (t, 4H), 5.23 (d, 2H, J = 11.4 Hz), 5.75 (d, 2H, J = 17.6 Hz), 6.84 (dd, 2H, J = 17.6 Hz, J = 11.4 Hz), 7.10 (d, 2H, J = 8.8 Hz), 7.34 (dd, 2H, J = 8.8 Hz, J = 2.0 Hz), 7.37 (d, J = 8.8 Hz), 7.75 (d, 2H, J = 2.0Hz), 7.88 (d, 2H, J= 8.8 Hz)

¹³C NMR (CDCl₃) : δ = 13.9, 22.4, 25.3, 29.4, 31.3, 69.7, 112.9, 116.0, 120.7, 123.4, 125.8, 126.4, 129.2, 132.7, 133.9, 137.0, 154.8

$[\alpha]_D^{20}$ = - 49.7 deg·dm⁻¹·mol⁻¹·l (c = 0.1 in THF)

Polymer Synthesis

A general procedure was as follows: a solution of **2** (112 mg, 0.22 mmol), **chr a-b** (0.22 mmol), Pd₂(dba)₃ (4.0 mg, 0.0044 mmol) and o-tolylphoshine (5.4 mg, 0.0176 mmol) dissolved in dry DMF, was purged with argon. After 30 minutes, triethylamine (0.22 ml) was added. The mixture was heated to 50 °C and stirred for 48 h under inert atmosphere. After cooling, the polymer was precipitated in methanol and filtered. For purification the polymer was redissolved in THF, precipitated in methanol and filtered. This procedure was repeated twice.

Measurements

^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) measurements were carried out on a Bruker Avance 300 MHz. The number average molecular weight $\overline{M}_n$ and polydispersity ($\overline{M}_w/\overline{M}_n$) were measured by gel permeation chromatography (GPC) with a Waters HP-GPC with tuneable absorbency detector and differential refractometer, using THF as an eluent towards polystyrene standards. UV-Vis spectra were recorded on a Varian Cary 400. Glass transition temperatures of the polymers were determined by differential scanning calorimetry (DSC) on a DSC 7 from Perkin Elmer with a heating rate of 50 °C/min. Optical rotations were measured with an Analis Optical Activity Polaar 20 Apparatus. Circular dichroism (CD) spectra were recorded on a Jasco J-810 spectropolarimeter. Spin-coated thin films from a cyclohexanone solution were coated with a thin layer of poly(acrylic acid), corona poled and measured for their second-harmonic generation coefficient at 1064 nm of induced light.

Results and discussion

The polymers **pol-A** and **pol-B** were prepared by means of a Heck reaction^[3] between a diethenylene binaphthalene compound **3** and diiodo-substituted chromophores **chr a-b**. These polymers differ from previously reported ones^[1b] in the presence of a double bond between the binaphthalene units and the chromophores in the polymer backbone. The incorporation of these double bonds influences the macromolecular (helical) structure and, consequently, their (chiral) properties.^[4] Our results show that donor-embedded polybinaphthalenes containing chromophores with distinctly different D π A-systems can be synthesized with a pure trans conformation of the substituents on the double bond as proven by ^1H NMR spectroscopy. The synthesis of the monomers and polymers is presented in *Scheme 1*. (*R*)-**2** was prepared from (*R*)-**1** by reaction of *n*-BuLi, followed by addition of DMF and subsequent hydrolysis. A Wittig reaction with methyltriphenylphosphonium bromide afforded (*R*)-**3**. Attempts were done to improve the polymerization conditions. The influence of the solvent, catalyst and the

nature and concentration of the ligand as well as the temperature were investigated. An overview of the conditions used in the test reactions is given in *Table 1*. Firstly, in several batches DMF appeared to be a better choice as solvent than THF. Secondly, the system $\text{Pd}_2(\text{dba})_3/o\text{-tolyl-phosphine (POT)}$ was the catalyst/ligand combination that resulted in the highest molecular weights as well as in the highest yields. The ratio $\text{P/Pd} = 2$ is also of high importance for the success of the polymerization. Finally, the optimal polymerization temperature was found to be 50 °C, since above this critical polymerization temperature, also cis-coupling appeared (^1H NMR spectroscopy).

The physical properties of the polymers are listed in *Table 2*. In the way described above both polymers could be prepared in reasonably high yields, without any decomposition of the chromophore as judged by ^1H NMR and UV-Vis spectroscopy. However, probably due to crosslinking, an insoluble fraction (~20 %) was obtained (vide infra). The addition of an inhibitor, 2,6-di-tert-butyl-4-methylphenol (BHT), did not change the outcome. The molecular weights, determined by gel permeation chromatography (GPC) towards polystyrene standards in THF, are satisfactory. It has been demonstrated that the molecular weights determined in this way are underestimated.^[1b, 5] In a previous publication^[1b] we have compared the molecular weight measured by GPC with the results obtained by MALDI-Tof measurements. This revealed that the real molecular weights tend to be 20% higher than the values measured by GPC.

The glass transition temperatures (T_g) of the polymers were measured by differential scanning calorimetry (DSC). It has already been shown that the observed T_g of rigid, chromophore-functionalized polybinaphthalenes is the T_g of the chromophores in the material and *not* of the whole polymer material.^[1a, 6] Therefore, the T_g of the polymer depends on the T_g of the incorporated chromophore and on the flexibility of the chromophores in the polymer

material.* The Tg of the polymer similar to **pol-A**, but without the double bond, was measured under identical conditions and found to be 186 °C.^[1] This is 18 °C lower than the Tg of the polymer synthesized by the Heck reaction. **pol-B** shows the same tendency. Hence, we must conclude that the mobility of the chromophores in this material is higher than in polybinaphthalenes without the double bonds.

The UV-Vis and CD spectra of **pol-A** and **pol-B** in THF solution are graphically presented in *Figure 1*. The absorptions < 250 and around 280 and 400 nm arise from the polymer backbone. The transition at 400 nm is due to the naphthalene group, conjugated with the double bond and the triphenylamine unit from the chromophore, while the transitions < 250 and around 280 nm is located in the naphthalene moiety only. The absorption at 500-600 nm, finally, is due to the chromophores. If these values are compared with the λ_{max} of the polymers without the double bond in their backbone^[1b], the absorption near 400 nm is significantly red-shifted[†], which can, of course, be explained by the elongation of the conjugation length. Also a slight difference in λ_{max} of the chromophores is observed (518 nm respectively 625 nm in the analogue polymer without double bonds). Since the structure of the chromophore is the same, the observed shift therefore points at a difference in the macromolecular structure: through a difference in the macromolecular structure, the lone pair on nitrogen becomes more conjugated into the chromophore, resulting in a red-shift.

All signals in the CD-spectra are localized at transitions in the polymer backbone. Since both polymers have essentially the same CD spectrum, we can conclude that the macromolecular architecture of the polymers is more or less independent of the chromophore used. The negative bisignate Cotton effect near 260 nm is due to isolated chiral binaphthalene moieties and is therefore not affected by the presence of the double bonds. The negative Cotton effect

* the Tg of **chr a** is 77 °C (DSC, 30°C/min) and **chr b** degrades before it melts and can therefore not be vitrified^[1b]

† The analogue of **pol-A** without the double bond shows a peak at 346 nm and **pol-A** itself at 392 nm. The analogue of **pol-B** without the double bond shows a peak at 344 nm and **pol-B** itself at 399 nm.

near 400 nm however, is situated in a transition in which, as mentioned before, the double bond participates. Compared with polymers, which are identical to the polymers presented here but without double bonds ^[1b], these Cotton effects are not only red-shifted, but are also significantly enhanced in intensity. These results point at a difference in macromolecular structure (altered supramolecular conformation).

As mentioned previously, we noticed the formation of insoluble material during the polymerization, which could be attributed to crosslinking. Moreover, DSC-experiments showed that degradation of the polymer started at 220 °C for **pol-A** and at 209 °C for **pol-B**, while the chromophores and polybinaphthalenes without double bonds do not degrade at a temperature < 250 °C. On the other hand, if we tried to dissolve a batch of **pol-B**, which was heated for 10 s at 250 °C, the material appeared not to be visually degraded, but it became partly insoluble. In *Figure 2*, the UV-Vis spectrum of a solution of 5 mg of **pol-B** (in THF) before and after heat treatment is shown. The two spectra show absorption maxima at the same wavelength, indicating that no chromophore degradation took place; but the incomplete dissolution of the polymer results in smaller absorption peaks. Moreover, elementary analysis of **pol-A** before and after heat treatment is, within experimental errors, the same, which again supports our hypothesis[‡]. Finally, IR spectra of a film of **pol-A** before and after heating for 15 min at 190 °C indicated the disappearance of a band at 1556 cm⁻¹, corresponding to an aromatic moiety conjugated with the double bond. All these observations must be attributed to crosslinking.

The polymers were spin-coated onto ITO glass slides from cyclohexanone solutions, which resulted in high quality films. Poly(acrylic acid) was spin-coated on top of the polymer film to prevent bleaching during the poling process. Since a chiral sample is inherently noncentrosymmetric, it should, in principle, not be poled. Nevertheless, in practice, the

[‡] Elem. Analysis (pol-A). Found; before heat treatment C 85.00, H 6.90, N 4.85; after heat treatment C 85.76, H 6.54, N 4.82. Calculated C 85.30 H 6.85 N 4.45.

chromophores are insufficiently ordered and an additional ordering of the chromophores remains, also in these polymer samples, necessary. This was accomplished by corona poling for 15 min. The applied voltage was 10 kV. Still, it remains advantageous to employ chiral samples: due to the lower symmetry of chiral samples compared to their achiral counterparts, some contributions, which must vanish in achiral samples due to symmetry reasons, can exist in chiral samples and increase the NLO properties.

The SHG results from the corona-poled films are given in *Table 2*. Although **chr a** is a weaker chromophore than **chr b**, the SHG value is remarkably higher because of higher resonant enhancement due to absorption. The chromophore alignment was reasonable for both polymers (P2 ~0.05).

The crosslinking of the polymers upon heating is also confirmed by stability measurements at elevated temperature (50 °C). **Pol-B** was poled at four different temperatures (10 °C, 6 °C and 2 °C under T_g and 2 °C above T_g). The evolution of the NLO signal in function of time (*Figure 3*) clearly demonstrates that the polymer films that were poled at a higher temperature show a more stable NLO response over time. Naturally, if the polymers are crosslinked, the (donor-embedded) chromophores are immobilized and cannot return to a random orientation. This experiment shows that the tendency to crosslink offers some considerable advantages towards applications.

The measurements of chiral contributions are still under investigation.

Conclusion

In this work, we synthesized and studied the properties of two new, chiral, chromophore-functionalized donor-embedded polybinaphthalenes. The polymers were prepared by a Heck reaction, which enabled us to introduce a double bond into the polymer backbone. The effect of the introduction of the double bond on the supramolecular (helical) structure was

demonstrated by DSC, UV-vis and CD experiments. Moreover, through the incorporation of double bonds into a polymer backbone, an interesting tool was created to introduce crosslinking upon heating. The crosslinked material resulted in a higher stability of the nonlinearity. Therefore, these materials can contribute to the design of polymeric materials with high and stable, achiral as well as chiral, NLO properties. Further investigations seem opportune to prove the importance of this synthetic way in order to obtain more stable NLO materials.

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Captions to figures/schemes

Figure 1. CD and UV-Vis spectra of the polymers

Figure 2. UV-Vis spectrum of **pol-B** before and after heat treatment

Figure 3. Stability measurements of the NLO response of **pol-B** at 50°C, poled at different temperatures.

Scheme 1. a) Synthesis of monomer **3**

b) Synthesis of the polymers: **pol-A** and **pol-B**

Table 1. Reaction conditions during the optimization of the polymerization.

Entry	Catalyst	Ligand	$\overline{M}_w /$ 10^3g.mol^{-1}	D ^{c)}	Yield / %
A-1	Pd(OAc) ₂ ^{a)}	0.08eq POT	2.1	2.3	30
A-2	Pd(OAc) ₂ ^{b)}	0.08eq PPh ₃	1.5	2.3	14
A-3	Pd ₂ (dba) ₃ ^{a)}	0.08eq POT	2.6	2.7	53
A-4	Pd ₂ (dba) ₃ ^{b)}	0.08eq POT	14	3.8	79

^{a)} 0.01 eq, 2 mol-%

^{b)} 0.02 eq, 4 mol-%

^{c)} polydispersity $\overline{M}_w / \overline{M}_n$

Table 2. Physical properties of the polymers

Polymer	Yield / %	Tg/ °C	$\overline{M}_w$ / 10^3g.mol^{-1}	D	λ_{max} / nm	$[\alpha]_D^{20}$ / $10^3 \cdot \text{deg.dm}^{-1} \cdot \text{g}^{-1} \cdot \text{ml}$	$[\chi]_{\text{xxx}}^{(2)}(\omega)$ / pm.V^{-1}
pol-A	79	204	14.2	3.8	524	6.8 ^{a)}	44.0
pol-B	62	194	6.9	2.6	663	6.3 ^{b)}	13.0

^{a)} $c = 2,2 \cdot 10^{-3}$ in THF

^{b)} $c = 1,9 \cdot 10^{-3}$ in THF

Figure 1.

Figure 2.

Figure 3.

Scheme 1.

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In this paper a new series of donor-embedded polybinaphthalenes prepared by a Heck reaction is presented. By introducing a double bond in the polymer backbone, the supramolecular helical structure was altered. This was proven with CD/UV-Vis spectroscopy. The double bond also causes crosslinking upon heat treatment. In this way a more stable NLO response in time was obtained.