

Synthesis and Properties of Chiral Donor-Embedded Polybinaphthalenes for Nonlinear Optical Applications

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The use of chirality in nonlinear optics has been theoretically studied for many years.^{1–3} Several promising phenomena (for instance, the existence of contributions inherent to chirality, which can increase the NLO response⁴) were predicted and some of them have actually been demonstrated in practice. To fully exploit the benefits of these interesting materials, there is a need for polymer materials, functionalized with chirally ordered chromophores. Unfortunately, chiral (helical) polymers for nonlinear optics were investigated only on a few occasions.^{5–9} Also, a few binaphthyl-based polymers have been studied.^{10,11} In these systems, the moieties that are responsible for the NLO response are situated in the polymer backbone and are assembled in the polymerization step. This severely restricts their possibilities for synthetical diversification. Moreover, the NLO response was quite weak since these groups show rather weak hyperpolarizabilities.

In this paper, we present preliminary results of the synthesis and properties of a new class of chiral polybinaphthalenes for nonlinear optical purposes. These materials are designed from chiral binaphthalene units, connected with rigid groups (in casu triphenylamine

derivatives). This molecular architecture gives rise to a rigid, rodlike (helical) structure.¹² Chromophores with moderate to good hyperpolarizabilities were incorporated to obtain a good NLO response. The chiral ordering of the chromophores was obtained by making the donor part of the (chiral) polymer backbone. In that way, the relation between the nonlinearity, originating from the chromophores and the chirality, situated in the polymer backbone, is as close as possible. As will be shown, this approach ensures the presence of chiral contributions to the NLO response. The polymers were obtained in a one-step reaction, by a Stille coupling of a di(trimethyltin)binaphthalene derivative and a dibromo-substituted chromophore. The advantages of our approach is (i) the fact that chromophores with large hyperpolarizabilities can be used, (ii) modifications in the molecular structure of the chromophores could easily be made so that the properties of these materials can be fine-tuned, and (iii) the polymer synthesis is convergent, which implies that many polymers, each with a different incorporated chromophore, can be prepared in a minimum of steps.

The binaphthalene monomer **3** was prepared from (S)-6,6'-dibromo-[1,1'-binaphthalene]-2,2'-diol **1**¹³ (Scheme 1). Therefore, **1** was converted into **2** by treatment with NaH, followed by hexylbromide in the presence of a catalytic amount of NaI. Finally, **3** was obtained by lithiation of **2** by *n*-BuLi at –78 °C, followed by quenching with trimethyltin chloride.

The key compound for the preparation of the chromophores is the aldehyde **5** (Scheme 2), which can readily be obtained by bromination of **4**. The chromophores **7** and **9** were prepared from the aldehyde **5** by a Knoevenagel condensation with *p*-nitrophenylacetic acid (**6**) and 2-(3,5,5)-trimethyl-2-cyclohexene-1-ylidene-propanedinitrile¹⁴ (**8**), respectively.

Finally, the polymers were prepared by a Stille coupling reaction (Scheme 3). The related Suzuki coupling (which gives rise to higher molecular weights) cannot be used since this leads to chromophore degradation. The reaction conditions were chosen^{15,16} to obtain the highest possible molecular weights.

Both polymers were soluble in common organic solvents, *s.a.* dichloromethane, chloroform, tetrahydrofuran (THF), and so forth. Their molecular structure was confirmed by ¹H NMR spectroscopy. The glass transition temperatures (*T_g*) were determined by differential scanning calorimetry (DSC) at a heating rate of 50 °C/min and were found to be 141 °C (**pol I**) and 152 °C (**pol II**). Because gel permeation chromatography (GPC) toward polystyrene standards in THF is not a suitable way to measure the molecular weights of these materials,¹⁷ we determined this parameter from end-

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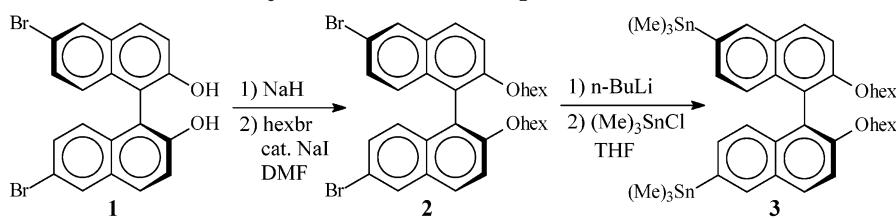
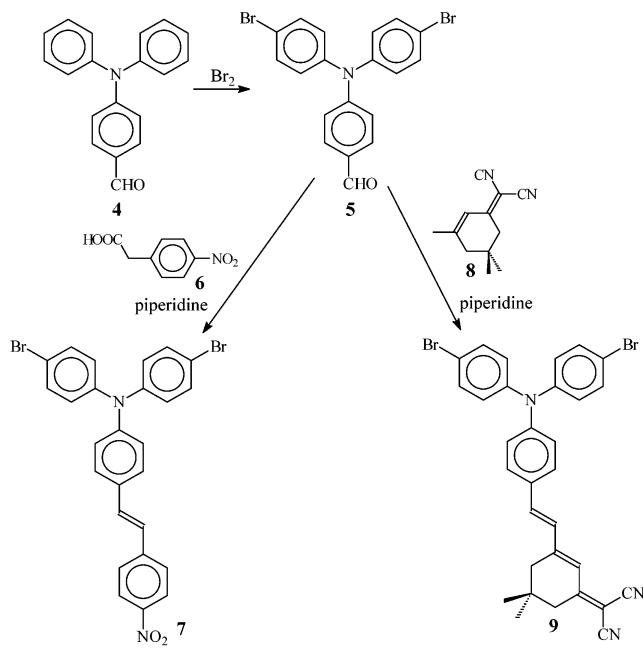
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Scheme 1. Synthesis of the Binaphthalene Monomer 4**Scheme 2. Synthesis of the Chromophores**

group analysis by ^1H NMR. ^1H NMR reveals that the polymers consist of equimolar amounts of chromophore and binaphthalene units. In that way, quantification of the trimethyltin end groups enabled us to calculate the number-average molecular weights (\bar{M}_n) on 6000 and 7000 g/mol (**pol I** and **pol II**, respectively). The molar specific rotations ($[\alpha]_D^{20}$) of the polymers are quite high, $1200^\circ \text{ dm}^{-1} \text{ g}^{-1} \text{ mL}$ (**pol I**) and $82400^\circ \text{ dm}^{-1} \text{ g}^{-1} \text{ mL}$ (**pol II**). The high optical rotations and the occurrence of a CD-band in the absorption region of the chromophore seems to suggest a chiral arrangement of the chromophores.

The polymers were spin-coated onto ITO glass slides from chloroform solution, which resulted in high-quality

Table 1. Magnitude^a of the Susceptibility Components of Poled Films of **pol I and **pol II****

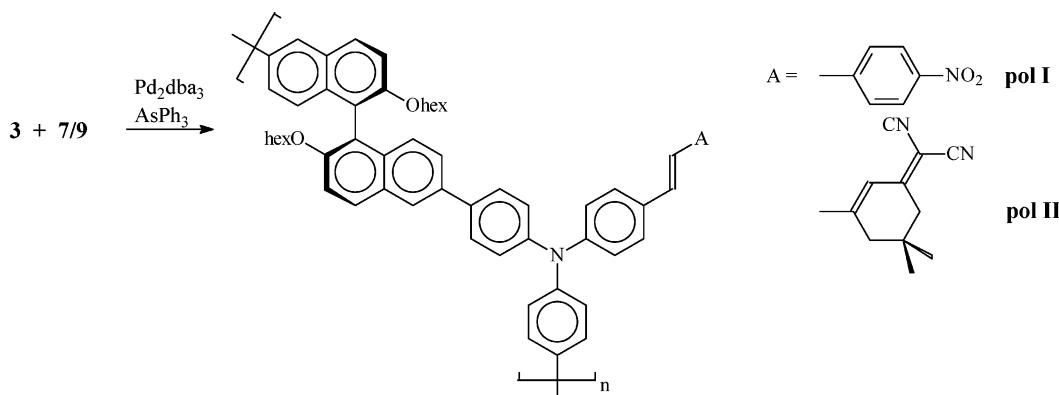
polymer	$\chi_{zzz}^{(2)}(0)$ [pm/V]	$\chi_{xxz}^{(2)}(0)$ [pm/V]	$\chi_{zxz}^{(2)}(0)$ [pm/V]	$\chi_{xyz}^{(2)}(0)$ [pm/V]
pol I	3.1	1.0	1.4	0.3
pol II	13.5	3.7	4.8	1.1

^a Experimental error is 10%.

films. Although a chiral sample is inherently non-centrosymmetric and should therefore, in principle, not be poled, the chromophores are pseudo-centrosymmetrically oriented and no NLO response was observed in the unpoled samples. Therefore, a polar ordering of the chromophores remains, in practice, necessary and was achieved by corona poling. The applied voltage was 12 kV and the samples were heated at their T_g for 15 min.

The nonlinear optical properties were analyzed using second-harmonic generation (SHG) measurements.¹⁸ Polarized UV-vis absorption and SHG showed that the poled films have a C_∞ symmetry. For such samples, there are four nonvanishing susceptibility components, that is, $\chi_{zzz}^{(2)}$, $\chi_{xxz}^{(2)}$, $\chi_{zxz}^{(2)}$, and $\chi_{xyz}^{(2)}$. The first three components originate from the polar ordering, while the latter can only be present in chiral media.

The ratio $\chi_{zzz}^{(2)}(0)/\chi_{xxz}^{(2)}(0) = 3$ confirms¹⁹ the symmetry mentioned above. The absolute values of the susceptibilities are summarized in Table 1. The magnitude of the achiral component ($\chi_{zzz}^{(2)}(0)$ for **pol II** of 13.5 pm/V) is comparable with values reported for polymers with similar chromophores.^{20–23} Considering the fact that the hyperpolarizability of the chromophores is far below the theoretical maximum limit, these polymers show great promise.^{24,25} More important, the molecular structure of these materials gives rise to chiral contributions. The chiral component $\chi_{xyz}^{(2)}$ is about 8% of the highest achiral contribution ($\chi_{zzz}^{(2)}$) and therefore significantly enhances the NLO response. Hence, we may conclude that the molecular structure of these polymers offers considerable advantages compared to their classical, achiral,

Scheme 3. Synthesis of the Polymers **pol I and **pol II****

random-coil-like analogues in which these contributions are not observed.

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Supporting Information Available: Detailed experimental procedures for the synthesis and polymerization of compounds **3**, **7**, and **9** and their 300-MHz ¹H NMR, 75-MHz ¹³C NMR, and UV-vis spectra as well as the CD spectrum of **pol II** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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