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ARTICLE

Conformational Steering in Substituted Poly(3,6-phenanthrene)s: A Linear and Nonlinear Optical Study

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ABSTRACT: The synthesis of a chiral, 9,10-dialkoxy-functionalized poly(3,6-phenanthrene) and the study of its chiroptical properties in different solvents is reported. The polymer was prepared by a Suzuki cross-coupling reaction. UV−vis, circular dichroism, and fluorescence spectroscopy and hyper-Rayleigh scattering were used to demonstrate that this polymer adopts a random coil conformation in a good solvent and folds into a one-handed helical conformation in poor solvents rather than stacking in a chiral way. Hyper-Rayleigh scattering proved to be a powerful tool for the investigation of the conformation of conjugated polymers because its response strongly depends on the conformation of the polymer.

Introduction

Conjugated polymers have been extensively studied and implemented as active materials in, for instance, transistors and organic light-emitting devices.[1] Recently, poly(phenanthrene)s (PPhs) have attracted particular attention as blue emitters[2] because they show several advantages compared with conventional blue emitters,[2a] such as poly(*p*-phenylene) (PPP)[3] and poly(fluorene) (PF).[4] The main chain conjugation of PPhs is not disturbed by the introduction of solubilizing groups (in contrast with PPPs), and they potentially show a highly efficient, stable blue emission, even upon annealing (in contrast with PFs).

Although PPhs can be prepared by coupling phenanthrene moieties in either a 2,7-[2] or 3,6-fashion,[2e] mostly 2,7-PPhs were investigated. However, whereas the conformation of 2,7-PPhs is restricted to a linear consecution of repeating units, 3,6-PPhs can be expected to adopt several fundamentally different conformations, for example, a planar zigzag structure, which allows supramolecular stacking, or a helical conformation.

Although it has been suggested that alkyl-substituted 2,7- and 3,6-PPhs aggregate upon transition to film,[2e] a study of the (supra)molecular behavior in solution of these poly(3,6-phenanthrene)s still remains absent. Nevertheless, the conformation has a profound influence on the optical and electronic properties; therefore, it is of great importance for the eventual properties of the polymers.

Conjugated polymers that adopt a helical conformation can be of particular use as mimics for complex natural systems, scaffolds to align chromophores in a chiral way,[5] or for chiral sensing, in which a small amount of a chiral guest induces a large chiral effect arising from a helical, but achiral, conjugated polymer.[6] Also effects originating from the combination of chirality and conjugation, such as electrical magnetochiral anisotropy[7] and circular polarized luminescence[8] may arise. Examples of such helical conjugated polymers include cis−transoid poly(acetylene)s,[9] oligo(*m*-phenyleneethynylenes),[10] oxazoline-functionalized poly(thiophene)s,[11] and gallic-acid-functionalized poly(dithienopyrrole)s.[12]

In this article, we report the synthesis of a chiral, 9,10-dialkoxy-functionalized poly(3,6-phenanthrene) (Figure 1) and the study of its supramolecular behavior in different solvents. By a combination of CD, UV−vis, and fluorescence spectroscopy and hyper-Rayleigh scattering, it was shown that this polymer can adopt either a random coil or a helical conformation in solution, depending on the solvent used.

Experimental Section

Materials and Instrumentation. All starting materials were purchased from Acros Organics, Fluka, Merck, or Aldrich and were used as received. *N*,*N*-Dimethylformamide (DMF) and 1,4-dioxane were dried by distillation over calciumhydride. 3,6-Dibromophenanthrene-9,10-dion **1**[13] and (*S*)-3,7-dimethyloctylbromide[14] were synthesized according to literature procedures.

Gel permeation chromatography (GPC) measurements were done with a Shimadzu 10A apparatus with a tunable absorbance detector and a differential refractometer in tetrahydrofuran (THF) as eluent toward polystyrene standards. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 MHz apparatus. UV−vis and CD spectra were recorded with a Varian Cary 400 and a JASCO 62 DS apparatus, respectively. The DSC measurements were performed on a Perkin-Elmer DSC 7 apparatus. Optical rotation was done on a Polaar 20; the concentration (in grams per 100 mL) and solvent used are given in parentheses.

The hyper-Rayleigh scattering (HRS) experiments were performed at a fundamental wavelength of 800 nm. A mode-locked Ti/sapphire (Spectra-Physics, model tsunami) laser with femtosecond laser pulses was used for high-frequency demodulation technique. This technique was used to discriminate between the hyper-Rayleigh signals and the additional contributing signals from multiphoton fluorescence at the second-harmonic wavelength of 400 nm. As a reference compound, crystal violet in methanol was used (β_{xxx} = 338 × 10^{-30} esu).[15] The experimental analysis reveals that the multiphoton fluorescence is out of phase with the hyper-Rayleigh signal at a

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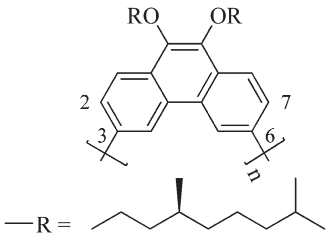


Figure 1. Structure of the polymer.

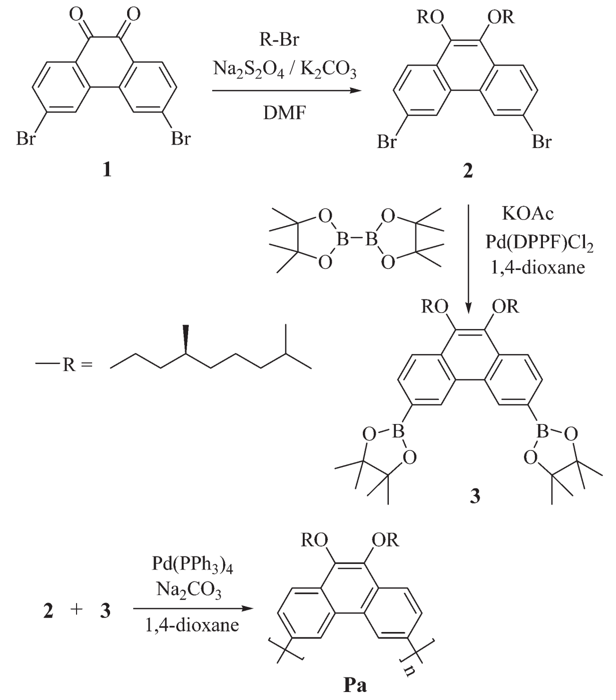
modulation frequency of 880 MHz. This means that all of the experiments are fluorescence free and that only HRS signals are detected.

Synthesis. *Synthesis of (−)-3,6-Dibromo-9,10-di((S)-3,7-dimethyloctyloxy)phenanthrene* ***2***. A solution of **1** (3.50 g, 9.56 mmol) in dry DMF (50 mL) was purged with argon, and after the addition of $Na_2S_2O_4$ (1.22 g, 7.00 mmol), the mixture was vigorously stirred at room temperature. After 10 min, K_2CO_3 (5.31 g, 38.4 mmol), tetrabutylammonium bromide (0.967 g, 3.00 mmol), NaI (0.450 g, 3.00 mmol), and (*S*)-3,7-dimethyloctylbromide (8.41 g, 38.4 mmol) were added, and the reaction mixture was stirred for an additional 16 h at 80 °C and then poured in water. The aqueous layer was extracted with dichloromethane. The combined organic layers were dried on $MgSO_4$ and concentrated in vacuo. The crude product was purified with column chromatography (dichloromethane/petroleumether 1/9), yielding a white solid. Yield: 2.30 g (37%). mp: 35.1−37.0 °C. $[\alpha]_D^{20} = -0.60$ deg·dm^{-1}·mol^{-1}·L ($c = 33$ in chloroform). ^{1}H NMR ($CDCl_3$, δ): 8.65 (s, 2H), 8.09 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 4.22 (t, 4H), 1.94 (m, 2H), 1.72 (m, 4H), 1.54 (m, 4H), 1.35 (m, 4H), 1.15 (m, 6H), 0.95 (d, 6H), 0.85 (d, 12H). ^{13}C NMR ($CDCl_3$, δ): 143.6; 130.9; 129.3; 129.1; 125.8; 124.6; 120.7; 74.4; 39.7; 37.9; 37.8; 30.3; 28.4; 25.1; 23.1; 20.2. MS *m*/*z*: 648 (M^+), 368 ($M^+ - C_{20}H_{40}$).

Synthesis of 2,2′-(9,10-Di((S)-3,7-dimethyloctyloxy)phenanthrene-3,6-diyl)-di(4,4,5,5-tetramethyl-1,2,3-dioxaborolane ***3***. A solution of **2** (500 mg, 0.770 mmol), KOAc (0.453 g, 4.62 mmol), and Pd(DPPF)Cl_2 (41.0 mg, 50.0 μmol) in dry 1,4-dioxane (2.5 mL) was purged with argon for 10 min. Then, a purged solution of bis(pinacolato)diboron (0.432 g, 1.70 mmol) in dry 1,4-dioxane (2.5 mL) was added, and the reaction mixture was heated to 80 °C. After 1 h, the solvent was removed by rotary evaporation, and the crude mixture was purified by column chromatography (SiO_2, dichloromethane/petroleumether 5/5), yielding a yellow oil. Yield: 0.281 g (49%). ^{1}H NMR ($CDCl_3$, δ): 9.21 (s, 2H), 8.22 (d, J = 6.0 Hz, 2H), 8.02 (d, J = 6.0 Hz, 2H), 4.24 (m, 4H), 1.95 (m, 2H), 1.72 (m, 4H), 1.54 (m, 4H), 1.43 (s, 24H), 1.09 (m, 10H), 0.97 (d, 6H), 0.87 (d, 12H). ^{13}C NMR ($CDCl_3$, δ): 144.6; 132.7; 132.0; 130.5; 128.7; 121.8; 84.4; 72.4; 39.7; 38.0; 37.8; 30.3; 28.4; 25.4; 25.2; 23.2; 23.0; 20.2. MS *m*/*z*: 743 (M^+), 461 ($M^+ - C_{20}H_{42}$).

Synthesis of Poly(3,6-(9,10-((S)-3,7-dimethyloctyloxy)phenanthrene) ***Pa***. A solution of **2** (0.153 g, 0.236 mmol) in 1,4-dioxane (2.0 mL) was purged with argon. Then, purged solutions of Pd(PPh_3)$_4$ (15.6 mg, 13.5 μmol) in 1,4-dioxane (1.0 mL), **3** (0.175 g, 0.236 mmol) in 1,4-dioxane (2.0 mL), and Na_2CO_3 (2.0 mL, 2.0 M in water) were added. The reaction mixture was stirred for 20 h at 100 °C, after which the resulting polymer was precipitated in methanol. The precipitate was filtered and subsequently fractionated by Soxhlet extraction with acetone and chloroform. The chloroform solution, containing the higher molar mass fraction, was concentrated in vacuo and again precipitated in methanol. Filtration yielded a gray solid. Yield: 0.160 g (69%). ^{1}H NMR ($CDCl_3$, δ): 9.10 (s, 2H), 8.41 (d, J = 8.2 Hz, 2H), 8.13 (d, J = 8.2 Hz, 2H), 4.28 (m, 4H), 1.98 (m, 2H) 1.74 (m, 4H), 1.50 (m, 2H), 1.34 (m, 4H), 1.17 (m, 8H), 0.97 (d, 6H), 0.83 (d, 12H).

Scheme 1. Synthesis of the Monomers and Polymer



Results and Discussion

Polymer Synthesis and Characterization. The synthesis of the phenanthrene-based monomers and the resulting polymer is presented in Scheme 1. Monomer **2** was obtained by radical bromination[13] of phenanthrene-9,10-dione, followed by a one-pot reduction−alkylation[2d] step with (*S*)-3,7-dimethyloctylbromide.[14]

Initials attempts to obtain compound **3** by Li−Br exchange of **2** with *n*-BuLi at −78 °C and subsequent addition of isopropoxyboronic acid pinacol ester appeared to be unsuccessful. Yet, by quenching the lithiated species at −78 °C with D_2O, ^{1}H NMR spectroscopy revealed that the three- and six-positions are indeed lithiated. However, it turned out that the lithiated species scrambles at higher temperatures, which were required for reaction with isopropoxyboronic acid pinacol ester, which explains the presence of several regio-isomers of **3**. Fortunately, compound **3** could be synthesized by a Suzuki coupling of **2** to bis(pinacolato) diboron.[2e] Finally, **2** and **3** were polymerized with a Suzuki coupling to obtain **Pa** with a number-averaged molar mass ($\overline{M}_n$) = 7.3 kg/mol (DP, degree of polymerization = 15) and polydispersity (D) = 2.5, according to GPC toward polystyrene standards.

DSC experiments revealed a glass transition at 158 °C (second heating cycle, scanning rate = 20 °C/min) for **Pa**, but no melting peak could be observed. Finally, the ^{1}H NMR spectrum of **Pa** showed no defects or end groups, which is indicative of a regular structure and a relatively high degree of polymerization.

Linear Optical Properties. The UV−vis spectrum of **Pa** in chloroform, a chloroform/methanol (3/7) mixture, and hexane is displayed in Figure 2a. The spectrum in chloroform, a good solvent, resembles the spectrum of the previously reported (achiral) dialkyl-substituted 3,6-PPhs. The band near 350 nm can be attributed to the $\pi-\pi^*$ transition of the conjugated backbone. The effect of lowering the solvent quality, either by the addition of methanol or by the use of hexane, mainly results in a decrease in the intensity of the low-energy band near 350 nm rather than a significant red shift.

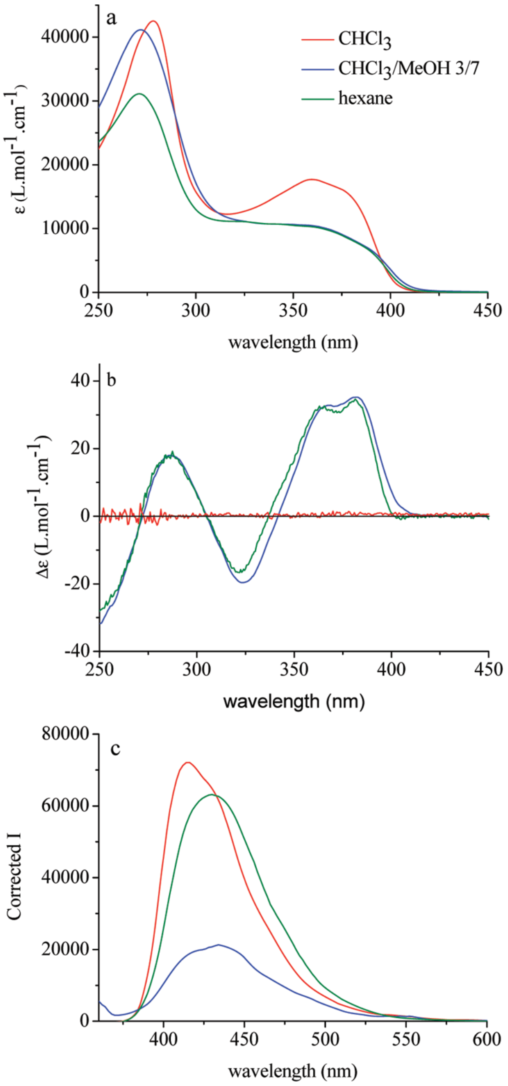


Figure 2. (a) UV−vis, (b) CD, and (c) emission spectra of **Pa** in CHCl$_3$ (c = 22 mg/L), CHCl$_3$/MeOH 3/7 (c = 22 mg/L), and hexane (c = 27 mg/L) excited at 350 nm. The fluorescence intensities are corrected for the polymer concentration and refractive index of the solvent used.

The high-energy band near 270 nm retains its intensity, but a small blue shift is observed.

The CD spectra (Figure 2b) revealed the absence of any Cotton effects in chloroform, whereas almost identical spectra were measured in the chloroform/methanol mixture and hexane. The spectra in the latter solvents seem to be a superposition of two positive bisignate Cotton effects: one corresponding to the located transition at ~270 nm (zero crossing at 271 nm) and one corresponding to the broad transition from the conjugated backbone with a zero crossing at 338 nm. The dichroic ratio, g_{abs} (= $\Delta\varepsilon/\varepsilon$), amounts to 6 × 10^{-3} (λ = ~380 nm), which is a commonly observed value for conjugated polymers in which chirality is fully expressed.

The emission spectra of **Pa** in the three solvents, excited at 350 nm, are shown in Figure 2c. The intensity of the emission is corrected for the absorption and the index of refraction of the solvent (mixture). It is worthwhile to mention that only excitation of the delocalized transition results in emission. Excitation at 270 nm only results in a very weak emission, which is indistinguishable from the emission resulting from excitation at 350 nm; that is, the high-energy excited state relaxes largely in a nonradiative way, with only a minor indication of energy transfer to the low-energy band.

The absence of any Cotton effects in chloroform is in agreement with the expected disordered (random coil) conformation of **Pa** in a good solvent. The presence of clear Cotton effects in both the chloroform/methanol mixture and hexane, in contrast, demonstrates the formation of a chiral structure. Two possibilities now arise: the chirality is either macromolecular (for instance a one-handed helical structure) or supramolecular (i.e., chirally aggregated polymer chains) in nature. To discriminate between both possibilities, the concentration dependency of the spectra was investigated: if the transition, induced by decreasing the solvent quality, corresponds to the formation of a one-handed helix, then the effects accompanying this transition are concentration-independent, whereas concentration-dependent spectra are expected for the presence of supramolecular chirality. In Figure 3, the concentration dependency of the UV−vis and CD spectra of **Pa** are displayed. For the chloroform/methanol mixture, not a (3/7) but a (7/3) mixture was used because a solvatochromism study (Figure 4) indicated that intermediate spectra are observed in this mixture. For this study, the CD spectra are particularly adequate because the transition is accompanied by only relatively small changes of the UV−vis spectra, whereas the CD spectra show a very large difference. From Figure 3, it can be concluded that within the broad concentration range studied no concentration dependence is observed for the chloroform/methanol mixture or in hexane and that, consequently, the polymer adopts a one-handed helical structure in both the chloroform/methanol mixture and hexane. It must be mentioned that the fact that the coil−helix transition does not necessarily require a dramatic change of the conjugation length brings the observed small changes of the UV−vis spectra into conformity with the proposed coil−helix transition. The same also holds for the emission spectra in chloroform and hexane. The lower intensity of the emission in the chloroform/methanol mixture might be attributed to the presence of some traps, possibly arising from polymer chains that occasionally cluster. Alternatively, it might be due to stronger π-stacking interactions between segments laying on top of each other. Both explanations might be supported by the fact that upon further increasing the methanol content, the CD as well as the emission intensity decreases.

It is intriguing that the UV−vis and CD spectra of both the chloroform/methanol mixture (very polar) and hexane (apolar) are almost identical. This suggests that the helical conformation is independent of the conditions used. However, in general, the solvent plays an important role in stabilizing a (helical) conformation; an example of this is the possibility of resolving a racemic mixture of achiral helical polymers by the addition of a chiral additive or solvent.[6,16] Similarly, it was demonstrated for the formation of a helical nucleus in the aggregation process of conjugated oligomers[17] that the solvent interacts with the helical entity. For the polymer **Pa**, the presence of the coil−helix transition demonstrates that the conformation of the polymer is not locked into a particular conformation and that multiple conformations can be adopted. To investigate the dependence of the helical conformation on the nature of the solvent further, CD spectra in other alkanes (pentane, heptane) were recorded as well, but again, no differences were observed. This suggests that although a coil−helix transition is possible in this polymer and that the helix is therefore dynamic in nature, the helical conformation seems to be insensitive to the conditions under which it is present.

It can therefore be concluded that 3,6-PPhs constitute a class of helical, conjugated polymers that remain conjugated in their helical conformation; that is, the conjugation is not

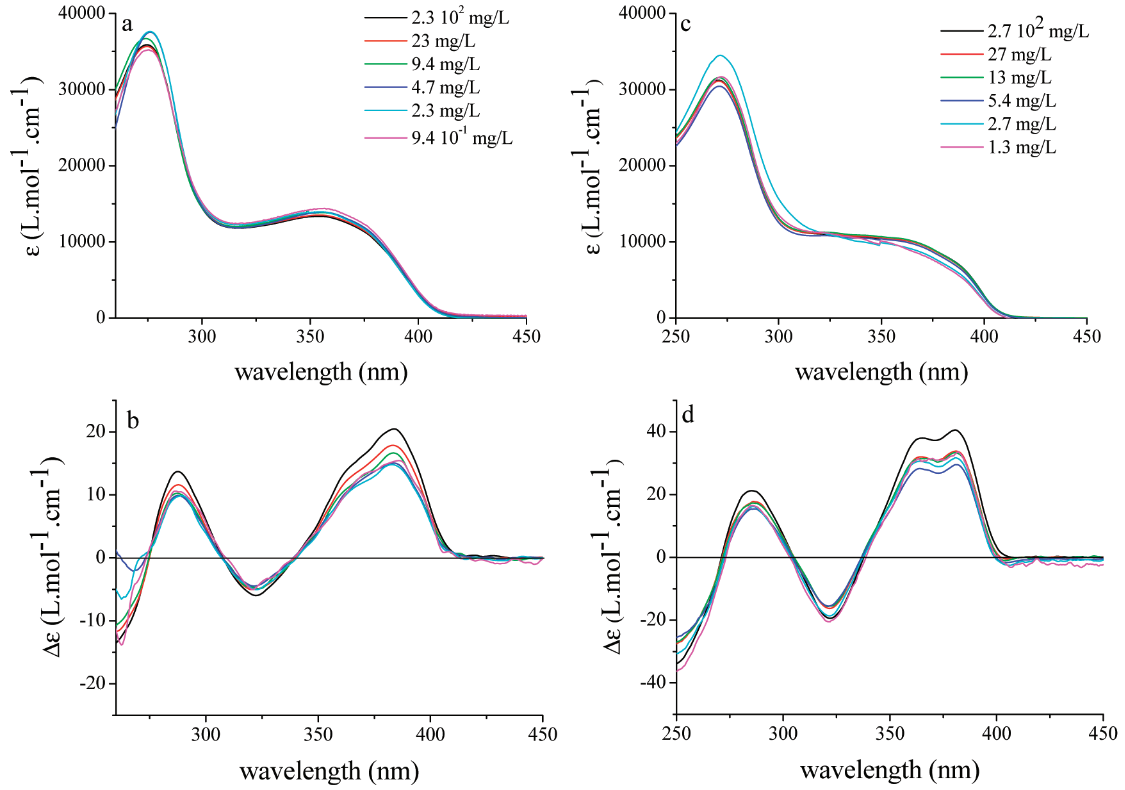


Figure 3. Dilution experiments of **Pa** in $CHCl_3$/MeOH 7/3: (a) UV−vis and (b) CD and in hexane: (c) UV−vis and (d) CD.

disrupted, as evidenced by the absence of a significant blue shift in the absorption spectra. Because the helical conformation seems to be rather insensitive toward the conditions, these polymers may be of importance in fields where a direct (and fixed) relation between chirality and conjugation is required.

Nonlinear Optical Properties. The conformation of the polymer in different $CHCl_3$/MeOH mixtures was also investigated by hyper-Rayleigh scattering (HRS). Second-order nonlinear optical properties are inherently very sensitive to symmetry and conjugation. The observation of and also the magnitude of a second-order nonlinear response can therefore reveal crucial information about the conformation of molecules, macromolecules, and polymers. In general, high conjugation combined with significant symmetry breaking should lead to a high HRS response, whereas breaking of conjugation and more centrosymmetric arrangements will decrease or even completely inhibit the HRS response.

Hyper-Rayleigh scattering[18] has been previously used for solution phase structure determination on the molecular[19e] and macromolecular scales.[19d] As a consequence, HRS is particularly interesting for probing differences in the conformation of macromolecules because a change in conformation results in a significant change in symmetry, and as a consequence, the HRS response will be drastically influenced.[19] In the case of conjugated polymers, a change in conformation can alter both the conjugation and the symmetry, rendering HRS very sensitive for their conformation.

Here we used HRS to study the conformational properties of **Pa** in several chloroform/methanol mixtures (Figure 4c). To suppress fluorescence contributions, frequency-demodulated HRS measurements were employed. The values shown are the real hyper-Rayleigh signals as measured for each solvent mixture at the same concentration. A first conclusion from this experiment is that the HRS measurements clearly point out a strong difference in the conformation state of the polymer in the different solvent (mixtures). It is therefore clear that although this experiment constitutes, to the best of our knowledge, the first example of the use of HRS to study the conformational behavior of conjugated polymers, it demonstrates that HRS is nevertheless a promising technique for this purpose.

Next, the conformational changes, induced by the decrease in solvent quality, were studied in more detail. Interestingly, because UV−vis spectroscopy, CD, and HRS are sensitive to the conformation of the macromolecule, the evolution of the absorbance, ellipticity, and hyperpolarizability as a function of solvent quality can give insight into the folding of the conjugated polymer. The results of these experiments are summarized in Figure 5. For this purpose, the following parameters were defined

$$X_{\mathrm{UV-vis}} = \frac{\varepsilon_{\mathrm{solvent,\,358nm}} - \varepsilon_{\mathrm{chloroform/methanol(3/7),\,358nm}}}{\varepsilon_{\mathrm{chloroform,\,358nm}} - \varepsilon_{\mathrm{chloroform/methanol(3/7),\,358nm}}}$$

$$X_{\mathrm{CD}} = \frac{\Delta\varepsilon_{\mathrm{solvent,\,382nm}}}{2\Delta\varepsilon_{\mathrm{chloroform/methanol(3/7),\,382nm}}} - \frac{\Delta\varepsilon_{\mathrm{solvent,\,323nm}}}{2\Delta\varepsilon_{\mathrm{chloroform/methanol(3/7),\,323nm}}}$$

$$X_{\mathrm{HRS}} = \frac{\mathrm{HRS}_{\mathrm{solvent}} - \mathrm{HRS}_{\mathrm{chloroform/methanol(3/7)}}}{\mathrm{HRS}_{\mathrm{chloroform}} - \mathrm{HRS}_{\mathrm{chloroform/methanol(3/7)}}}$$

$X_{\mathrm{UV-vis}}$, X_{CD}, and X_{HRS} measure the relative evolution (0 in chloroform, 1 in chloroform/methanol (3/7)) of the absorption, ellipticity, and hyperpolarizability, respectively, as a function of the methanol content. The absorption dependence

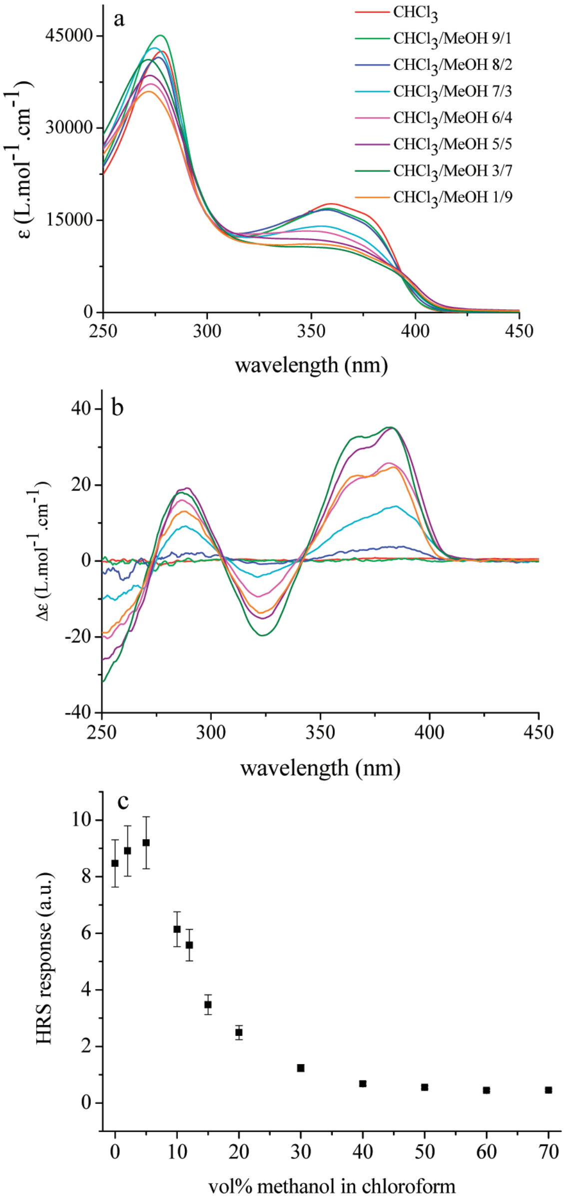


Figure 4. (a) UV−vis spectra, (b) CD spectra, and (c) HRS response of **Pa** in different $CHCl_3$/MeOH mixtures.

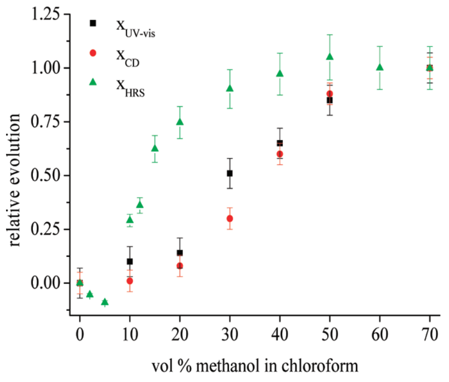


Figure 5. Dependency of the (a) UV−vis spectra, (b) CD spectra, and (c) HRS response of **Pa** in $CHCl_3$/MeOH mixtures.

was monitored at 358 nm, whereas the ellipticity was monitored at both 323 and 382 nm to increase the accuracy.

From Figure 5, it is clear that UV−vis and CD spectroscopy are both (solely) sensitive to the actual transition from (achiral) coil to the chiral helix; therefore, both trends coincide. The evolution of the HRS response, in contrast, does not coincide at all with these data. As a consequence, it can be concluded that the coil−helix transition is not a single step process but that some conformational changes occur at low methanol content in which no (one-handed) helices are formed. Because no CD response is observed under these conditions, these conformations must be achiral. The fact that the UV−vis spectra hardly change reveals, on its turn, that in the intermediate structure(s) the conjugation length, which is essentially determined by the twist angles between the monomeric units, is hardly affected.

Conclusions

It was demonstrated that 3,6-PPhs adopt a random coil in a good solvent and a helical conformation in a nonsolvent rather than stacking in a supramolecular way. Moreover, it was shown that the helical conformation is independent of the conditions used. The conformational changes were investigated by UV−vis, circular dichroism, and fluorescence spectroscopy and hyper-Rayleigh scattering. It was shown that hyper-Rayleigh scattering can be a powerful technique for probing differences in the conformation of conjugated polymers. Finally, it was demonstrated that the coil−helix transition in 3,6-PPhs is not a single step-process but that the formation of achiral structure(s) precede(s) the helix formation.

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Supporting Information Available: NMR spectra of the new compounds as well as the GPC and DSC profile of the polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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