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Chiroptical Properties of Poly(*p*-phenyleneethynylene) Copolymers in Thin Films: Large *g*-Values

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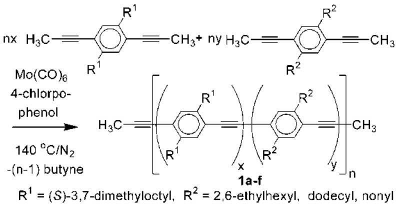
Statistical PPE copolymers **1** were obtained by co-metathesis of varying amounts of bis[(*S*)-3,7-dimethyloctyl]dipropynylbenzene with bis[2-ethylhexyl]dipropynylbenzene utilizing in situ metathesis catalysts.[1] Thin spin cast and annealed films of **1** in which 25−50 mol % of the phenyleneethynylene groups carry chiral side chains show very large *g*-values ($|g_{CD}| = 0.38$) in their circular dichroism (CD) spectra.



R^1 = (*S*)-3,7-dimethyloctyl, R^2 = 2,6-ethylhexyl, dodecyl, nonyl

Chiroptical properties of conjugated oligomers[2] and polymers[3] are of fundamental interest to understand structure, conformation, and interchain electronic interactions. They are important for the fabrication of advanced plastic semiconductor devices, which emit circularly polarized light. Most of the earlier work on the chiroptical properties of conjugated polymers has been performed on polythiophenes, but the chiroptical properties of poly(*p*-phenylene)s[2b] and of poly(*p*-phenyleneethynylene)s[1c] have likewise been reported. The measured optical dissymmetries were, however, only moderate and did not exceed values of $|g_{CD}| = 0.01$. In most cases, the chiroptical signals in absorption of conjugated polymers are bisignate and change sign where the absorption spectrum has a maximum.[2−4] According to Meijer[4] this behavior is indicative of an exciton coupling within chiral assemblies of several polymer chains (interchain effect).

This has changed recently with the closer examination of the liquid crystalline polyfluorenes, which show *g*-values in absorption and emission up to 0.25.[3c,5] The surprisingly high *g*-values in the polyfluorenes were explained by Oda et al.[3c,5] by the ability of the nonlinearly linked polyfluorenes to attain a conformation, in which the backbone assumes a steep helix, which apparently is stabilized in the solid state. We have investigated the amorphous poly[*p*-bis-(3,7-dimethyloctyl)phenyleneethynylene] (**1a**),[1c] in which all of the PE units were chirally substituted. In poor solvents and in the solid state the $|g_{CD}|$-values of **1a** were in the order of 0.006−0.008, that is, quite low even after annealing. However, when we investigated thin spin-cast and annealed films of the copolymer **1b** (5% chiral monomer) the *g*-values increased to 0.06. In statistical copolymers, where the amount of dimethyloctyl side chains is higher, the *g*-value at 432 nm increases dramatically to reach a maximum for **1d** where it exceeds $|g_{CD}| = 0.37$ (Figure 1, Table 1). The high values are observed for films, which are heated to 160 °C, just below the lc-isotropic transition for 30 s and cooled to 140 °C during 2 h, where the samples were annealed for another 16 h. Important observations are that (a) the maximum of the CD at 432 nm is at the maximum of the UV−vis spectrum (433 nm) and (b) that this prominent CD signal is fully monosignate within the range of this most prominent UV−vis peak.[6] Most important, the peak at 433 nm has previously been assigned to the absorption by a planarized polymer chain.[1b]

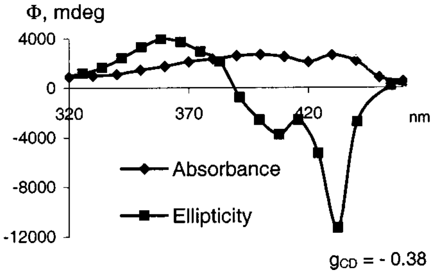


Figure 1. CD spectrum [millidegree] of a thin film of **1d** after annealing. The maximum *g*-value (−0.38) is reached at 432 nm, which corresponds to the maximum of the absorption in PPE at 433 nm.

Table 1. Substituent Key, Percentage of Chiral Monomer, and $|g_{CD}|$-Values of Thin Annealed PPE Films[a,b]

1	substituent	% chiral monomer	*g*-value annealed	*g*-value as spun
a	(*S*)-3,7-dimethyloctyl (dmo)	100	0.008	0.001
b	dmo/2-ethylhexyl	5	0.060	0.01
c	dmo/2-ethylhexyl	25	0.292	0.082
d	dmo/2-ethylhexyl	50	0.378	0.023
e	dmo/dodecyl	25	0.042	< 0.0001
f	dmo/nonyl	50	0.044	0.014

[a] If the content of dmo was higher than 50% (66%, and 75% tested) the $|g_{CD}|$ value dropped to less than 0.05. [b] All of the herein investigated films were of uniform thickness because the spatial differences in absorbance did not exceeded 8−10% in different spots of a given sample.

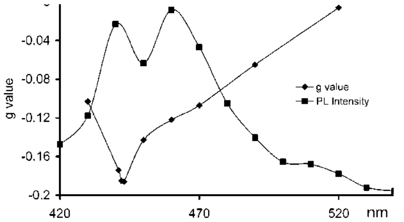


Figure 2. Solid-state emission and solid-state CPPL of **1c**. The *y*-axis depicts the *g*-value, the photoluminescence (PL) intensity is arbitrary.

Figure 2 shows the photoluminescence (PL) and circularly polarized photoluminescence (CPPL) spectra of a thin film of **1c** after annealing. As has been observed in the CD spectrum, the

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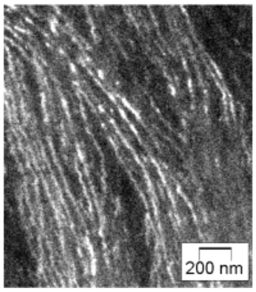

Figure 3. Transmission electron dark-field micrograph of thin polymer films of **1c** after annealing to 140 °C for 12 h.

maximum degree of CPPL at 443 nm ($g_{\mathrm{CPPL}} = -0.186$) is close to the maximum of the PL at 441 nm. The strong CPPL signal is fully monosignate within the range of its PL peak. The sign of the *g*-value is the same as for the pronounced feature in absorption at 432 nm. Therefore, we conclude that the prominent peaks in the CD and CPPL spectra have the same physical origin, which most likely is not an interchain exciton coupling. Evidence that exciton coupling is not the dominant source for the chiroptical properties stems from the rather gradual decrease in the CPPL signal within the main emission band. In particular, the absolute value of g_{CPPL} at the second emission peak (463 nm) is still more than half the value at the first emission peak (443 nm). In contrast, exciton coupling predicts a considerably smaller circular polarization for transitions to higher vibronic states in emission.[7] The shape of the CPPL spectrum shown in Figure 2 is similar to the one measured for chirally substituted polyfluorenes.[3c,5] For those polyfluorenes, a helical shape of the polymer backbone has been proposed on the basis of electron-diffraction experiments and quantum-chemical calculations.[5]

What is the structural reason for the observed high *g*-values in the annealed as compared to the pristine films of PPEs? When examined under a polarizing microscope, the “as spun” films of **1** are isotropic (black between crossed polarizers) and either show no or only a weak birefringence. Such samples of **1c,d** show a grainy, isotropic morphology without any significant ordering when viewed in transmission electron microscopy (TEM). Once the films have been annealed, the PPE molecules orient parallel, adopting a nematic texture. Between crossed polarizers a distinct Schlieren texture is observed.[1e]

For TEM and diffraction thin films were prepared from solution after drying and annealing. Electron diffraction of **1c** is similar to that of bis(ethylhexyl)PPE.[1e] However, we see additional innermost reflections corresponding to *d*-values near 15 Å. The strongest reflection is at 4.98 Å. We associate it with the lattice plane produced by a staggered array of the repeating unit of the PPEs (6.8 Å). To obtain more information a dark-field picture of a sample of **1c** was obtained in the light of the mentioned reflection. In this micrograph (Figure 3) all features originating from the 4.98 Å reflection appear bright. A stranded morphology with the strand thickness of approximately 40 nm is observed, similarly to those reported previously for PPEs.[8]

Dark-field images of nonchirally substituted PPEs display uniform brightness along the strands. Dark-field images of the stranded moieties of **1c**, however, are striated as it is visible in Figure 3. The striations are in an angle of 47° to the main axis of the strands. This angle corresponds satisfactorily with the angle under which the 4.98 Å reflection appears off the principal direction of the strand. A further interpretation is difficult due to the restricted number of diffraction peaks that could be obtained. This is particularly true when the unit cell in the crystalline state is triclinic. However, we can conclude that the crystalline strands consist of staggered PPE molecules **1c** forming a single, helically twisted, bundle. At some sites there is evidence for a helical pitch of approximately 25 nm. The screw sense of the nanoscopic twisting of multiple chains into one strand seems to be caused by the chiral substituents leading to the huge dissymmetries. The largest effect is visible for the 1:1 copolymer **1d**.

The helical twist must be induced by the subtle interplay of chiral and racemic substituents in **1c** and **1d**. The high *g*-values are therefore *not* a property of the single chain but of the strand-shaped supramolecular assemblies that form upon annealing of **1c,d**. *The nanoscopic assembly process thus seems to be critically responsible for the modulation of the chiroptical properties of **1***. It is not clear though, if this is a conformational effect of a single chain induced by chain packing, or if electronic interactions between many chains play a role.

To our knowledge, the herein reported dissymmetries are the largest that have been measured for a conjugated polymer to date. While a full understanding of the phenomenon is not possible, the observed large *g*-values are exciting and seem to be caused by the strands forming upon annealing of these materials. In the future we will explore the chiroptical behavior of other chirally substituted poly(aryleneethynylene)s.

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Supporting Information Available: Details of transmission electron microscopy/diffraction, film thickness determination, circular dichroism measurements, experimental procedures, and analytical characterization data of **1** (PDF). This material is available free of charge via the Internet at www.pubs.acs.org.

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