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### Chiral effects in second-order nonlinear optics

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## Chiral effects in second-order nonlinear optics

A. PERSOONS,<sup>a</sup> M. KAURANEN,<sup>a</sup> S. VAN ELSHOCHT,<sup>a</sup> T. VERBIEST,<sup>a</sup> L. MA,<sup>b</sup> L. PU,<sup>b</sup> B.M.W. LANGEVELD-VOSS,<sup>c</sup> AND E.W. MEIJER<sup>c</sup>

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The chiral and nonlinear optical properties of polymeric Langmuir-Blodgett films are investigated

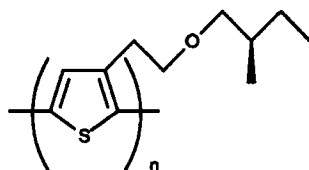
**Keywords:** nonlinear optics; chiral polymers; Langmuir-Blodgett films

## INTRODUCTION

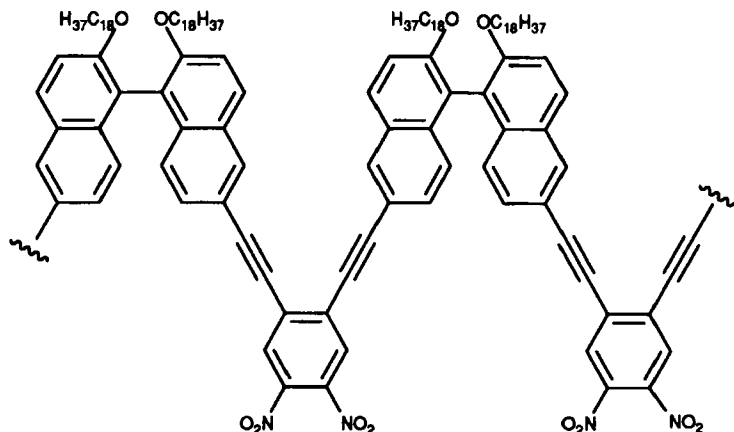
Chiral media interact differently with left- and right-hand circularly-polarized light. In linear optics this gives rise to optical activity effects like circular dichroism, optical rotation and optical rotatory dispersion.

Optical activity effects have been predicted to occur also in nonlinear optics and several examples of nonlinear optical activity have recently been observed experimentally. Nonlinear optical activity was first observed in second-harmonic generation (SHG) from chiral binaphthol molecules adsorbed at an air-water interface, and subsequently from Langmuir-Blodgett films of poly(isocyanide)s and bacteriorhodopsin.[1–3] In these experiments, the samples were illuminated with left- and right-hand circularly-polarized light and the second-harmonic efficiency was found to be different for the two circular input polarizations.

In this paper, we use second-harmonic generation as a method to study the chirality and nonlinear optical properties of Langmuir-Blodgett films of new chiral polymers.



1



2

FIGURE 1 Chemical structures of the polythiophene (polymer 1) and the propeller polymer (polymer 2).

## EXPERIMENTS AND RESULTS

The first material we investigated is a chiral polythiophene (polymer 1, Fig. 1).<sup>[4]</sup> In poor solvents or in the solid phase, this material aggregates in a stable chiral conformation and exhibits strong (linear) optical activity effects. In good solvents on the other hand, the polymer is in a random coil conformation and does not exhibit appreciable optical activity. It is very easy to distinguish the two conformations by their color. The random coil has an orange/yellow color ( $\lambda_{\text{max}} = 445 \text{ nm}$ ), while the optically active conformation has a purple/red color ( $\lambda_{\text{max}} = 512 \text{ nm}$ ).

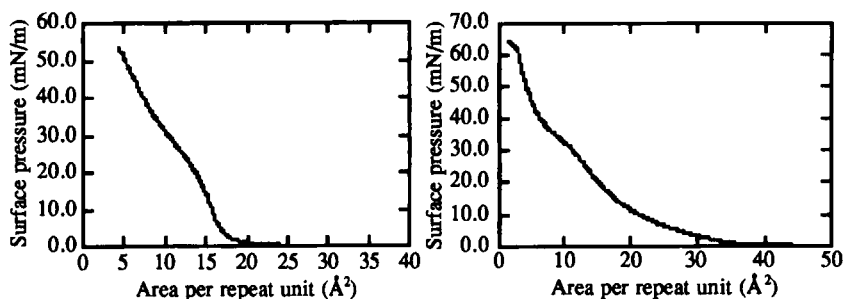


FIGURE 2 Surface pressure isotherms of polymer 1 (left) and polymer 2 (right).

The material was dissolved in chloroform ( $10^{-3}$  M of monomeric units) where it is in the random coil conformation (yellow). However, when spread on a pure water subphase the material aggregates and turns purple, indicative of the chiral conformation. Surface pressure versus surface area isotherms were taken for the floating monolayers at a constant compression rate with a Wilhelmy balance on a Langmuir trough. The monolayers were transferred to hydrophobic glass slides using the horizontal dipping technique. The dipping process was carried out at a surface pressure of 10 mN/m. 10 X-type layers were deposited. The films were of good optical quality and deep purple color, which implies that the polymer was in its optical active conformation. The absorption maximum of the films was 555 nm. Since the films of the polythiophene are sensitive to photo oxidation, measurements had to be performed in the dark and immediately after preparation of the sample.

The second material we investigated is a chiral conjugated propeller polymer (polymer 2, Fig. 1).<sup>[5]</sup> Due to the chirality of the binaphthyl units and the rigidity of the conjugated system, the dipole units in this material form a propeller-like three-dimensional configuration.

The experimental conditions for Langmuir-blodgett film formation were identical to those used for the polythiophene and a film with a thickness

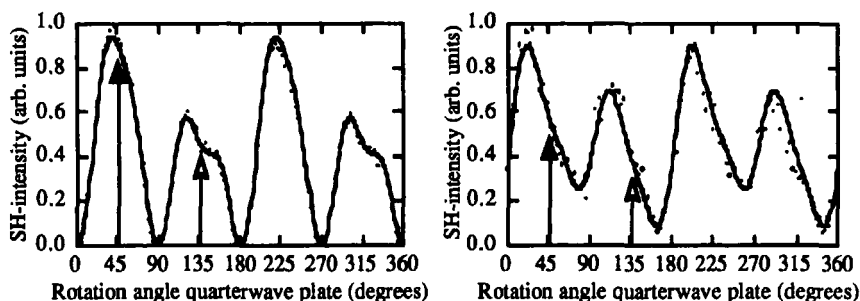


FIGURE 3 Intensity of the s-polarized transmitted second-harmonic field versus the rotation angle of the quarterwave plate for polymer 1 (left) and polymer 2 (right). The solid line is a theoretical fit to the data points. The black and white arrow indicate left- and right-hand circularly-polarized excitation, respectively.

of 10 X-type layers were obtained. The absorption maximum of the films was 430 nm.

To study the chiral and nonlinear optical properties of the Langmuir-Blodgett films, we used the fundamental beam of a Q-switched and injection-seeded Nd:YAG laser (1064 nm) to pump the chiral Langmuir-Blodgett films. The sample is oriented at a 45° angle of incidence with respect to the fundamental beam. The fundamental beam is initially p-polarized with respect to the sample and its state of polarization is varied by a quarter-wave plate. The s- and p-polarized components of the transmitted second-harmonic fields are detected. The results for the transmitted s-polarized components of the second-harmonic fields are shown in Fig. 2. A significant circular-difference response is observed in both signals. Furthermore, all signal peaks exhibit a left-right asymmetry. All these features are signatures of chirality. Analogous to linear circular dichroism, we can express the observed circular-difference effects in SHG in terms of the sum and difference of the intensities of the detected second-harmonic light for left- and right-hand circularly-polarized excitation as  $\Delta I/I = 2(I_{\text{left}} - I_{\text{right}})/(I_{\text{left}} + I_{\text{right}})$ . For polymer 2

we measured the s- and p-polarized second-harmonic signals in transmission (TS and TP) and for polymer 1 we also measured signals in reflection (RS and RP). The results are summarized in Table 1.

It is clear from Table 1 that both polymers exhibit extremely high optical activity effects. The value of the circular-difference effect  $\Delta I/I$  is orders of magnitude higher than that obtained by linear circular dichroism spectroscopy ( $\Delta\epsilon/\epsilon$ ) from solutions of the polymers.[4,5] Note also that the nonlinear technique is quite unique. Due to the inherent surface sensitivity of the SHG-process, it only probes the chirality of the surface. Therefore, SHG-CD might become a valuable and sensitive tool in fields where surface structure and chirality are important.

The polythiophene exhibits higher optical activity effects in SHG than the propeller polymer. This is in agreement with (linear circular) dichroism measurements on solution of both polymers where the polythiophene was found to have a considerably higher CD-response (at 532 nm) than the propeller derivative.

TABLE 1 circular difference response  $\Delta I/I$  for the s- and p-polarized second-harmonic signals in transmission (TS and TP) and reflection (RS and RP).

signal	$\Delta I/I$ polymer 1	$\Delta I/I$ polymer 2
TS	+39%	+65%
TP	+40%	+65%
RS	--	-4%
RP	--	+43%

## CONCLUSION

The chirality of Langmuir-Blodgett films of chiral polymeric materials was investigated using second-harmonic generation. Our results indicate that this nonlinear technique is a valuable tool in obtaining information about the chirality of surfaces and thin films.

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