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# Direct evidence of the failure of electric-dipole approximation in second-harmonic generation from a chiral polymer film

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Second-harmonic generation from Langmuir–Blodgett films of a polythiophene is strongly influenced by the chirality of the polymer. The polarization dependence of the process cannot be explained in the electric-dipole approximation. Evidence of contributions beyond electric dipoles is obtained directly from individual second-harmonic signals. © 1997 American Institute of Physics. [S0021-9606(97)52543-8]

Linear optical activity of chiral molecules arises from the different response of such molecules to left- and right-hand circularly polarized light.<sup>1</sup> Optical activity effects include optical rotation, circular dichroism, and optical rotatory dispersion and are usually explained by contributions of magnetic-dipole interactions to the linear optical properties of the chiral medium. Optical-activity effects can also occur in nonlinear optics.<sup>2</sup> In particular, when a chiral thin film or surface is illuminated by circularly polarized light, the intensity of the second-harmonic light generated can be different for left- and right-hand circularly polarized excitation. This and other chiral effects have been observed in second-harmonic generation from chiral monolayers adsorbed at an air/water interface or solid substrates,<sup>3–5</sup> and from Langmuir–Blodgett mono- and multilayers of chiral polymers.<sup>6–9</sup> These nonlinear optical-activity effects can occur in the electric-dipole approximation.<sup>4,10</sup> However, to properly explain the detailed experimental results for the case of Langmuir–Blodgett films of polyisocyanides, magnetic-dipole contributions to the nonlinearity must also be included.<sup>11</sup>

To date, evidence of contributions beyond electric dipoles in second-harmonic generation from chiral thin films has only been obtained by a detailed comparison of several different second-harmonic signals.<sup>7,8,11</sup> In this paper, we investigate second-harmonic generation from thin films of a chiral polymer with very strong optical activity, a polythiophene. We show that, for the case of this material, several individual second-harmonic signals contain direct evidence of significant contributions beyond electric-dipole approximation. We assume that the higher multipolar contributions have predominantly a magnetic-dipole character, because the importance of magnetic interactions in chiral media is well established. In particular, the very strong optical activity of the polythiophene indicates the presence of strong magnetic interactions in this material.

Up to first order in the magnetic-dipole interaction, the nonlinear sources at the second-harmonic frequency are<sup>12</sup>

$$P_i(2\omega) = \chi_{ijk}^{eee} E_j(\omega) E_k(\omega) + \chi_{ijk}^{em} E_j(\omega) B_k(\omega), \quad (1)$$

$$M_i(2\omega) = \chi_{ijk}^{mee} E_j(\omega) E_k(\omega), \quad (2)$$

where summation over repeated indices is implied,  $\mathbf{P}(2\omega)$  is the nonlinear polarization,  $\mathbf{M}(2\omega)$  the nonlinear magnetization, and  $\mathbf{E}(\omega)$  and  $\mathbf{B}(\omega)$  are the electric field and magnetic-induction field at the fundamental frequency, respectively.

In general, the intensity of any component of the second-harmonic field can be expressed as:<sup>12</sup>

$$I(2\omega) = |fE_p^2(\omega) + gE_s^2(\omega) + hE_p(\omega)E_s(\omega)|^2, \quad (3)$$

where  $E_p(\omega)$  and  $E_s(\omega)$  refer to the  $p$ - and  $s$ -polarized components of the (electric vector of the) fundamental field. The coefficients  $f$ ,  $g$ , and  $h$  are linear combinations of the components of the tensors  $\chi^{eee}$ ,  $\chi^{em}$ , and  $\chi^{mee}$ . For a system with  $C_\infty$  symmetry (i.e., chiral, isotropic surface symmetry) and  $s$ -polarized second-harmonic light, these coefficients are given by:<sup>8</sup>

$$f_{Ts}^{Rs} = -\sin\theta [-2\chi_{xyz}^{eee} \cos\theta - \chi_{xzx}^{em} + \chi_{zzz}^{mee} \sin^2\theta + \chi_{zxx}^{mee} \cos^2\theta \mp 2\chi_{xxz}^{mee} \cos^2\theta], \quad (4)$$

$$g_{Ts}^{Rs} = -\sin\theta [\chi_{xxz}^{em} + \chi_{zxx}^{mee}], \quad (5)$$

$$h_{Ts}^{Rs} = \sin\theta [2\chi_{xxz}^{eee} - (\chi_{xzy}^{em} + \chi_{xyz}^{em}) \cos\theta \mp 2\chi_{xyz}^{mee} \cos\theta], \quad (6)$$

where  $R$  and  $T$  refer to the second-harmonic fields generated in the reflected and transmitted directions, respectively,  $s$  refers to the polarization of the second-harmonic signal,  $\theta$  is the angle of incidence, and the surface normal is along the  $z$  direction. Note that Eqs. (4)–(6) are strictly valid in the limit where the linear indices of refraction of the thin film and the surrounding media (air and substrate) are assumed to be equal and unity. However, the inclusion of the differences in the indices of various media will only change the relative weights of the tensor components in each expansion coefficient.<sup>12</sup> Such effects are not important for the purposes of the present paper, which relies on the general properties of the coefficients. Note also that the coefficient  $h$  is nonvan-

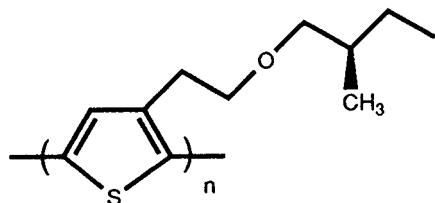


FIG. 1. Chemical structure of poly{3-[2-(2-methylbutoxy)ethyl]thiophene}. The number  $n$  of repeating units is  $\sim 50$ .

ishing for all isotropic surfaces, including achiral ( $C_{\infty v}$ ) ones, whereas the coefficients  $f$  and  $g$  are only allowed for chiral surfaces.

It is clear from Eqs. (4) to (6) that only the coefficient  $g$  depends exclusively on magnetic-dipole contributions and must vanish in the electric-dipole approximation. Therefore, a value of  $g$  different from zero provides direct evidence of the failure of the electric-dipole approximation and of the presence of magnetic-dipole contributions to the nonlinearity of the film. This argument is completely independent of the possible complex values of the various tensor components and expansion coefficients such as could be the case when the fundamental or second-harmonic light is tuned close to a material resonance. Note that in the work of Ref. 11, the coefficient  $g$  and the respective magnetic-dipole susceptibility components were too small to be observed reliably.

In our experiments, we used Langmuir–Blodgett films of a regioregular chiral polythiophene, poly{3-[2-((S)-2-methylbutoxy)ethyl]thiophene} (PT, Fig. 1). This polymer with  $M_n = 16900 \text{ g mol}^{-1}$  possesses a regioselectivity of more than 98% for the head-to-tail coupling.<sup>13,14</sup> In good solvents, like  $\text{CHCl}_3$ , the polymer is in a random coil conformation and does not exhibit optical activity in its  $\pi$ – $\pi^*$  transition. However, in the solid state, in poor solvents, or in appropriate combinations of solvents, like  $\text{CHCl}_3$ – $\text{MeOH}$ , the polymer is associated into small domains and the chiral sidegroups induce an enormous optical activity in the  $\pi$ – $\pi^*$  transition of the polythiophene. This association with a chiral conformation is accompanied by a strong solvatochromism and the films have a purple/red color ( $\lambda_{\text{max}} = 512 \text{ nm}$ ), while the random coil conformation has an orange/yellow color ( $\lambda_{\text{max}} = 445 \text{ nm}$ ). The polymer in a 40%  $\text{CHCl}_3$ –60%  $\text{MeOH}$  has an  $[\alpha]_{513}^{22} = +140.000$  and a  $g$  value  $(\Delta\epsilon/\epsilon) = 2 \times 10^{-3}$ . These values are extremely high for transitions that are predominantly electric-dipole allowed, implying that the magnetic-dipole contributions are significant in the linear optical properties. The strong magnetic effects arise from the character of the  $\pi$ – $\pi^*$  transition, which corresponds to the displacement of the electrons along the helical conjugated backbone of the polymer.

To prepare the Langmuir–Blodgett films, the polymer is dissolved in chloroform and spread on a water surface. In the solvent, PT is present in the random coil conformation. However, upon evaporation of the solvent, PT folds into the chiral conformation and changes color from yellow to purple. The surface pressure is increased to 10 mN/m and the poly-

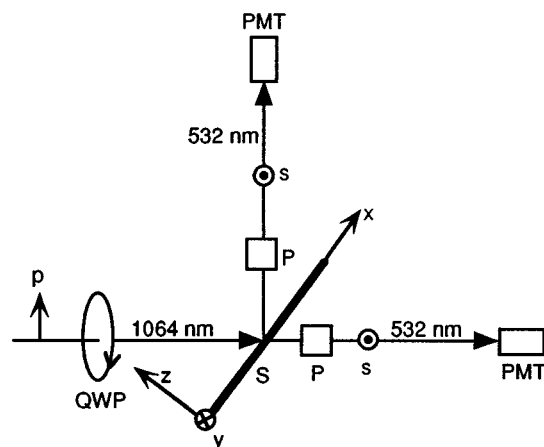


FIG. 2. A schematic representation of the experimental setup. The fundamental beam of a Nd:YAG laser (1064 nm) is  $p$  polarized with respect to the sample (S). The polarization of the beam is controlled by rotating a quarter-wave plate (QWP). The  $s$ -polarized component of the reflected and transmitted second-harmonic beams (532 nm) are detected by a photomultiplier (PMT).

mer forms a rigid layer on the water surface. The layers are transferred on hydrophobic glass substrates by horizontal dipping.<sup>15</sup> The films used in our experiments consist of ten layers of PT of good optical quality and deep purple color. The purple color, as discussed earlier, gives a clear indication of the chiral conformation of the associated polymer in the film. The films are sensitive to photo-oxidation. Therefore, the measurements were performed in the dark and immediately after fabrication of each sample.

The beam of a  $Q$ -switched and injection-seeded Nd:YAG laser (1064 nm, 10 ns pulses, 50 Hz) is weakly focused on the sample at a  $45^\circ$  angle of incidence (Fig. 2). The in-plane isotropy of the film is verified by observing no second-harmonic signal at normal incidence and by the independence of the signal on rotation about the surface normal at  $45^\circ$  angle of incidence. The polarization of the initially  $p$ -polarized fundamental beam is continuously varied by means of a quarter-wave plate and the intensity of a second-harmonic signal is measured as a function of the rotation angle of the quarter-wave plate.<sup>11</sup> This measurement technique allows a unique determination of the relative values of the expansion coefficients  $f$ ,  $g$ , and  $h$ .<sup>16</sup> The experimental results for the transmitted, glass-side-incidence,  $s$ -polarized signal are shown in Fig. 3.

The experimental results are fitted to the model of Eq. (3) with  $f$ ,  $g$ , and  $h$  as free complex parameters. Since we are only interested in the relative values of the coefficients, we finally normalize  $h = 1$ .<sup>11</sup> This fit has been shown to be unique within an overall phase factor.<sup>16</sup> The best fit is obtained for  $f = -(0.055 \pm 0.004) - (0.098 \pm 0.004)i$ ,  $g = -(0.378 \pm 0.013) - (0.300 \pm 0.008)i$ ,  $h = 1$ . Note that the coefficients  $f$  and  $g$ , which are only allowed by chirality, have significant out-of-phase parts with respect to the dominant coefficient  $h$ , which does not rely on chirality. Such phase differences between the chiral and achiral coefficients are the origin of the circular-difference response evident in Fig. 3.<sup>4,7</sup>

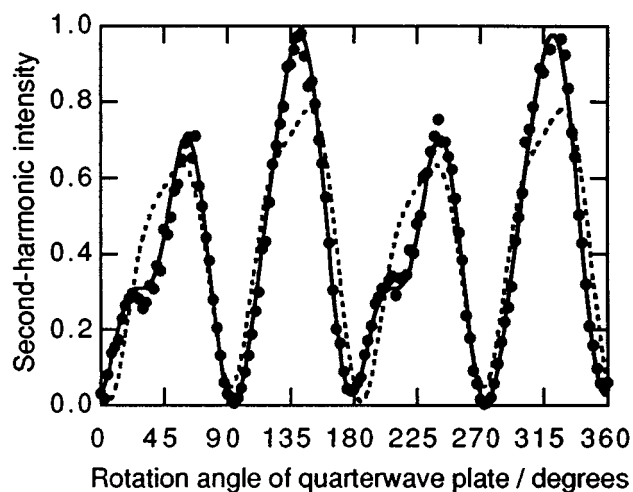


FIG. 3. Intensity of the  $s$ -polarized second-harmonic signal generated in the transmitted direction for glass-side incidence as a function of the rotation angle of the quarter-wave plate. Note the significant difference in the response for the left- ( $45^\circ$  and  $225^\circ$ ) and right-hand ( $135^\circ$  and  $315^\circ$ ) circularly polarized light. The points represent experimental data, the solid line the fit to the model of Eq. (3) with  $g$  nonvanishing, and the dashed line the fit with  $g$  vanishing.

It is noteworthy that the value of  $g$  is different from zero and relatively large. This result suggests that the electric and magnetic contributions to the nonlinearity are essentially of the same order of magnitude. This large value of magnetic contributions is probably due to the near centrosymmetric arrangement of the monomer units in the helical polymer structure, which tends to suppress the electric-dipole nonlinearity. To further illustrate the failure of the electric-dipole approximation, we have also tried to fit the results by assuming that  $g$  vanishes. This fit is also shown in Fig. 3 and clearly fails to explain the features of the experimental data. We have also verified the importance of the expansion coefficient  $g$  for the other  $s$ -polarized signals (reflected direction and both reflected and transmitted directions for film-side incidence). In all cases the fitted value of  $g$  was found to be of the same order of magnitude as for the case of Fig. 3.

In conclusion, we have shown that second-harmonic generation from Langmuir–Blodgett films of a chiral polythiophene cannot be explained in the electric-dipole approximation. Evidence of contributions beyond electric-dipole ap-

proximation was obtained directly from the dependence of the  $s$ -polarized second-harmonic signals on the state of polarization of the fundamental beam. The structure of the polymer suggests that the higher multipolar contributions are due to the effects of magnetic dipoles which were found to be comparable to the pure electric-dipole contributions. The present results also emphasize the power of polarization techniques in studying the physical origin of the second-order nonlinearity of chiral surfaces.

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- <sup>1</sup>E. Charney, *The Molecular Basis of Optical Activity* (Wiley, New York, 1979).
- <sup>2</sup>E. W. Meijer, E. E. Havinga, and G. L. J. A. Rikken, *Phys. Rev. Lett.* **65**, 37 (1990).
- <sup>3</sup>T. Petralli-Mallow, T. M. Wong, J. D. Byers, H. I. Lee, and J. M. Hicks, *J. Phys. Chem.* **97**, 1383 (1993).
- <sup>4</sup>J. D. Byers, H. I. Lee, T. Petralli-Mallow, and J. M. Hicks, *Phys. Rev. B* **49**, 14643 (1994).
- <sup>5</sup>M. J. Crawford, S. Haslam, J. M. Probert, Y. A. Grudzkov, and J. G. Frey, *Chem. Phys. Lett.* **229**, 260 (1994).
- <sup>6</sup>M. Kauranen, T. Verbiest, E. W. Meijer, E. E. Havinga, M. N. Teerenstra, A. J. Schouten, R. J. M. Nolte, and A. Persoons, *Adv. Mater.* **7**, 641 (1995).
- <sup>7</sup>M. Kauranen, T. Verbiest, J. J. Maki, and A. Persoons, *J. Chem. Phys.* **101**, 8193 (1994).
- <sup>8</sup>M. Kauranen, J. J. Maki, and A. Persoons, in *Nonlinear Optical Properties of Organic Materials VIII*, edited by G. R. Möhlmann [Proc. SPIE **2527**, 328 (1995)].
- <sup>9</sup>J. J. Maki, T. Verbiest, M. Kauranen, S. Van Elshocht, and A. Persoons, *J. Chem. Phys.* **105**, 767 (1996).
- <sup>10</sup>J. D. Byers and J. M. Hicks, *Chem. Phys. Lett.* **231**, 216 (1994).
- <sup>11</sup>M. Kauranen, J. J. Maki, T. Verbiest, S. Van Elshocht, and A. Persoons, *Phys. Rev. B* **55**, 1985 (1997).
- <sup>12</sup>J. J. Maki, M. Kauranen, and A. Persoons, *Phys. Rev. B* **51**, 1425 (1995).
- <sup>13</sup>M. M. Bouman, E. E. Havinga, R. A. J. Janssen, and E. W. Meijer, *Mol. Cryst. Liq. Cryst.* **256**, 439 (1994).
- <sup>14</sup>M. M. Bouman and E. W. Meijer, *Adv. Mater.* **7**, 385 (1995).
- <sup>15</sup>G. Roberts, *Langmuir–Blodgett Films* (Plenum, New York, 1990).
- <sup>16</sup>J. J. Maki, M. Kauranen, T. Verbiest, and A. Persoons, *Phys. Rev. B* **55**, 5021 (1997).