Chemistry of Materials 1990, 2, 169–172

Optical Third Harmonic Response of Amorphous Poly(3-methyl-4′-octyl-2,2′-bithiophene-5,5′-diyl) Thin Films

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Received October 5, 1989

We have measured the optical third harmonic susceptibility of thin amorphous films of poly(3-methyl-4′-octyl-2,2′-bithiophene-5,5′-diyl) (P3MOT) on fused silica substrates as a function of wavelength (1.06–2.04 μm) and film thickness. The wavelength profile of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ does not show the expected enhancement at shorter wavelengths from three-photon resonance in the visible region. For a film of 720-Å thickness, $\chi^{(3)}$ decreases monotonically from 4.4×10^{-11} esu at a wavelength of 2.4 μm to 1.8×10^{-11} esu at 1.06 μm. For film thicknesses between 400 and 3000 Å, the observed $\chi^{(3)}$ also shows an unusual dependence upon film thickness in that thinner films have increasingly higher effective values of $\chi^{(3)}$. We have observed some evidence for preferential in-plane orientation of thiophene rings in very thin films by UV–visible spectroscopy, which suggests that the enhanced response is an orientation effect.

There has been much recent interest[1] in the third-order nonlinear optical response of highly conjugated conductive polymeric materials. Because of the extensive π-electron delocalization built into the polymer chains to promote electrical conductivity, these materials may also show large optical nonlinearities. For certain compositions, convenient processability makes them attractive for optical device applications. It is this latter property that makes the 3-substituted polythiophenes[2] particularly interesting. With appropriate substituents, these polymers can be made highly soluble, and the resulting solutions can be easily cast into films by spinning or other methods. The preliminary reports of others[3] have shown that the optical nonlinear response of polythiophenes is not only large but also very fast, as expected from a nonlinearity with an electronic origin. We have made a detailed study of the third-order response of a soluble polythiophene, poly(3-methyl-4′-octyl-2,2′-bithiophene-5,5′-diyl) (P3MOT), in thin-film form by optical third harmonic generation (THG) and report here our results. The important feature of this particular polythiophene is that it is strictly amorphous in thin solid film form. Not only is the absence of crystallinity an advantage for optical device considerations, it also simplifies our attempt to understand the molecular nature of $\chi^{(3)}$ in this material.

The polymer P3MOT is made according to a method described previously[2b] by polymerizing a configurational specific dimer of 3-methylthiophene and 3-octylthiophene. Because the precursor is a dimer, the resulting copolymer has a strictly 1:1 ratio of methyl- and octylthiophene units. Further, the regiospecific placement of the methyl and octyl groups greatly reduces the probability of "head-to-head" (5′,5′) coupling so that the polymer is highly regular with a minimum of adjacent ring steric interactions. Thin films prepared by spin coating from toluene solution show no evidence of crystallinity when examined by electron diffraction, and standard X-ray diffraction of thick (≥100 μm) films cast by standing evaporation reveals minimal (<5%) crystallinity. The electronic absorption spectrum of P3MOT spun onto fused silica shown in Figure 1 is much broader than that of P3MOT in toluene solution, and the absorption maximum is red-shifted from 438 (ϵ = 4890 M cm^{-1}) to 460 nm (ϵ = 5300 M cm^{-1}). This behavior is analogous to that documented for other poly(3-alkylthiophenes)[4] and possibly indicates one or more of the following phenomena: extended coplanarity of the π system in the solid state, aggregation of chains via π interactions between thiophene rings, or inhomogeneity of the chromophoric sites in the amorphous solid. In P3MOT films, the characteristic shoulder at ~600 nm in the spectrum attributed to extended chain polymer[4a] is quite a bit less intense than is observed in other polythiophenes. A very small but noticeable absorption feature also occurs at ~600 nm in the solution spectrum; thus, this shoulder is most likely an intrinsic molecular electronic transition such as singlet–triplet ($\pi \rightarrow \pi^*$) transition. As shown in Figure 1, a very slow relaxation phenomenon takes place in spun films over a period of weeks, which is reflected in the absorption spectrum. This phenomenon can be accelerated somewhat by prolonged exposure of the films to fluorescent room light and can be entirely reversed by redissolving and recasting the film. This behavior is similar to the temperature/orientation effects seen in other polythiophenes.[5] No further evidence of degradation with time is observed in films greater than ~500 Å thick, but extremely thin films (<200 Å) tend to bleach irreversibly over a period of several weeks from orange to yellow, suggesting that the chromophore is being shortened in some way.

For THG experiments, P3MOT films 70–3000 Å thick were spun onto optically polished fused silica substrates from toluene solution and vacuum dried overnight at room temperature to remove solvent. Thickness measurements were obtained by profilometry on films >400 Å and were verified independently by ellipsometry for several samples. These measurements correlated extremely well to optical

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(1) (a) Heeger, A. J., Orenstein, J., Ulrich, D., Eds. *Nonlinear Optical Properties of Polymers*, MRS Symposium Proceedings; Materials Research Society: Pittsburgh, PA, 1988; Vol. 109, and references therein. (b) Chemla, D. S., Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987; Vol. 2. (c) Williams, D. J., Ed. *Non-linear Optical Properties of Organic and Polymeric Materials*, ACS Symposium Series; American Chemical Society: Washington, D.C., 1983; Vol. 233. (d) Kaino, K.; Kubodera, K.; Kobayashi, H.; Kurihara, T.; Saito, S.; Tsutsui, T.; Tokito, S.; Murata, H. *Appl. Phys. Lett.* **1988**, *53*, 2002.

(2) (a) Jen, K. Y.; Oboodi, R.; Elsenbaumer, R. L. *Polym. Mater. Sci. Eng.* **1985**, *53*, 79. (b) Jen, K. Y.; Oboodi, R.; Elsenbaumer, R. L. *J. Synth. Met.* **1986**, *15*, 169. (c) Sato, M.-A.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1986**, 873.

(3) Prasad, P. In ref 1a, p 271.

(4) (a) Hotta, S.; Rughoopath, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212. (b) Hotta, S.; Rughoopath, S. D. D. V.; Heeger, A. J. *J. Synth. Met.* **1987**, *22*, 79.

(5) (a) Inganäs, O.; Salanek, W. R.; Österholm, J.-E.; Laakso, J. *J. Synth. Met.* **1988**, *22*, 395. (b) Salanek, W. R.; Inganäs, O.; Themans, B.; Nilsson, J. O.; Sjögren, B.; Österholm, J.-E.; Brēdas, J.-L.; Svensson, S. *J. Chem. Phys.* **1988**, *89*, 4613.

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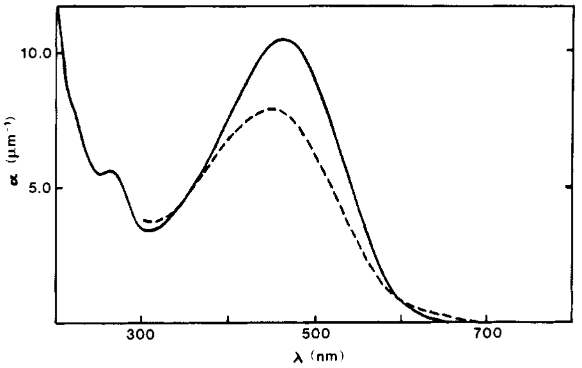

Figure 1. Absorption spectrum of a 1600-Å P3MOT film on silica immediately after drying (—) and after 30 days in the dark at room temperature (- - -).

absorption of the films so the thickness could be determined optically to ±15 Å. Film thickness could not be determined optically for films thinner than ~250 Å, as small but significant spectral changes (vide infra) indicated that the calculated absorption coefficient is no longer accurate.

The experimental apparatus and approach was similar to that used by Kajzar et al. for THG measurements on thin supported films.[6] A Spectra Physics DCR3 Nd:YAG laser operating in the "doughnut" mode pumped a PDL-2 dye laser. The 1.06-μm beam and dye laser beam were combined in a WEX wavelength extender containing an angle-tuned $LiNbO_3$ crystal to generate an infrared beam by frequency difference mixing. Spurious wavelengths were filtered out of the beam by appropriate cutoff filters. The resulting doughnut-shaped infrared beam was linearly polarized with a pulse half-width of 8 ns and an energy of 1–6 mJ/pulse and was focused to a minimum spot size on the order of 150–300 μm by a 25-cm lens. This configuration gave a depth of focus of 1.5–2 cm over the experimental range 1.06–2.4 μm. Samples were mounted vertically on a two-axis goniometer/rotation stage with the film side facing away from the incident laser beam, and the film surface was positioned at the center of tilt/rotation by means of a jig. A HeNe alignment laser was used to align the film normal to the incident laser beam. To assess the TH (third harmonic) contribution from air, the entire sample holder could be enclosed in a helium atmosphere, which has a $\chi^{(3)}$ only $^1/_{23}$ that of air.[7] After passing through the sample, the light was filtered by an appropriate combination of Schott KG and interference filters to remove the laser beam and isolate the TH wavelength. Neutral density filters were used to reduce the intensity so that it could be detected in the linear range of a nine-stage Hamamatsu photomultiplier tube operating at 1 kV. The signal was then collected and averaged over a minimum of 1000 shots by a Tektronix 2430 digitizing oscilloscope. The TH pulse had a half-width slightly narrower than that of the laser pump pulse, and the peak height was proportional to the integrated area, as expected.

Third harmonic signals for P3MOT films were large compared to a bare silica substrate, even for the thinnest films, and showed a strict cubic dependence upon incident laser intensity. No evidence of degradation of the film was observed for estimated power densities as high as 30 MW/cm². No significant change in TH intensity was noted in repeated measurements on the same film over a 4-month period, even though extensive relaxation of the film was observed spectroscopically during this time. Because the TH response of the films was so large, variation of the input beam angle did not give rise to an interference pattern from the substrate.[8] Moreover, the replacement of air by helium had a negligible effect on the magnitude of the signal. Thus, the P3MOT film could be approximated as a plane parallel slab of nonlinear material in a linear medium (see below). To determine the third-order susceptibility, TH from a P3MOT film was measured relative to a standard reference substrate of fused silica, with a known $\chi^{(3)}$.[9] In contrast to the P3MOT films, TH from the silica reference substrate showed the expected sensitivity to incident angle[6] and to the presence of air.[6b,10] To simplify the measurements, a reference substrate was used that had a thickness very close to an integral number of coherence lengths, so that the TH signal at normal incidence was a maximum (this was easily verified in any given experiment). The effect of ambient air on the reference signal was to cause a 20–30% increase in TH at normal incidence in the particular experimental geometry employed. This increase was reproducible from trial to trial and varied little with wavelength over the range studied. Therefore, the majority of measurements were made in ambient air, and a standard correction was made for the TH signal from the reference.

The nonlinear susceptibility of thin-film P3MOT was calculated by using the approximation of a plane parallel slab of nonlinear material "a" in a linear medium "b". The general solution to this problem has been previously treated by Kajzar et al.[6b,11] Because P3MOT has significant optical absorption, we have developed an expression for THG similar to that derived by Oudar[12] for SHG, which treats absorptive losses in a simple manner. We note here that for absorbing media, the complex form of the refractive index must be used. We will use the Nebraska convention in which the refractive index is written as $n = (n_r - ik)$. Dielectric constants, wave vectors, phases, and propagation angles are also complex at absorbing wavelengths ($k > 0$).

Following Kajzar et al.,[6b,11] the general expression in cgs units for THG in a plane parallel slab can be written

$$\frac{S^{3\omega}}{(S^{\omega})^3} = \frac{64\pi^4 T}{c^2}\left[\frac{\chi^{(3)}}{\Delta\epsilon}(\Delta KL)\right]^2 F_{(\Delta KL)} \tag{1}$$

S^{ω} and $S^{3\omega}$ are the magnitudes of the Poynting vectors describing, respectively, the intensity of the fundamental beam at frequency ω before entering the slab and of the third harmonic beam at frequency 3ω after leaving the slab. T is a composite transmission factor that takes into account Fresnel transmission factors and boundary conditions at the front and back faces of the slab. More specifically

$$T = \frac{n_b{}^{3\omega}}{(n_b{}^{\omega})^3}[t_{ab}{}^{\omega}]^6\left[\frac{N_a{}^{3\omega} + N_a{}^{\omega}}{N_b{}^{3\omega} + N_a{}^{3\omega}}\right]^2\left\{1 - \left[\frac{N_b{}^{3\omega} - N_a{}^{3\omega}}{N_b{}^{3\omega} + N_a{}^{3\omega}}\right]^2\right\}^{-2} \tag{2}$$

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(6) (a) Kajzar, F.; Messier, J.; Rosilio, C. *J. Appl. Phys.* **1986**, *60*, 3040. (b) Kajzar, F.; Messier, J. In ref 1b, Chapter III-2, p 51, and references therein.

(7) Ward, J. F.; New, G. H. C. *Phys. Rev.* **1969**, *185*, 57.

(8) A similar observation has been made in the case of a polydiacetylene Langmuir–Blodgett thin film.[6b]

(9) Meredith, G. R.; Buchalter, B. *Appl. Opt.* **1982**, *21*, 3221. The value of (2.79 ± 0.03) × 10^{-14} esu at 1.907 μm was corrected for wavelength by using Miller's Rule (see: Miller, R. C. *Appl. Phys. Lett.* **1964**, *5*, 17).

(10) (a) Meredith, G. R. *Phys. Rev. B* **1981**, *15*, 5522. (b) Meredith, G. R. In ref 1c, Chapter 2, p 27.

(11) Kajzar, F.; Messier, J. *Phys. Rev. A* **1985**, *32*, 2352.

(12) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446.

where t_{ab}^{ω} is the Fresnel intensity transmission factor from medium b to medium a at frequency ω. N_i^j is defined as $n_i^j \cos \phi_i^j$, where n_i^j is the index of refraction and ϕ_i^j is the propagation angle of light of frequency $j = \omega, 3\omega$ in medium i = a,b. The last term in the expression is nearly unity and may be neglected.[6b] Moreover, since the experiments were conducted at normal incidence, the expression can be simplified to

$$T \approx \frac{n_b^{3\omega}}{(n_b^{\omega})^3}\left(\frac{2n_a^{\omega}}{n_a^{\omega} + n_b^{\omega}}\right)^6\left(\frac{n_a^{3\omega} + n_a^{\omega}}{n_b^{3\omega} + n_a^{3\omega}}\right)^2 \quad (3)$$

In eq 1, $\Delta\epsilon$ is the difference in optical dielectric constant of medium a between ω and 3ω, L is the thickness of the nonlinear slab, and ΔK is the wave vector mismatch between the fundamental and TH waves, defined[11] as $(k^{3\omega} \cos \phi_a^{3\omega} - 3k^{\omega} \cos \phi_a^{\omega})$. Alternatively, $\Delta K = \pi/L_c$, where L_c is the coherence length of the material, defined as $2\pi c/6\omega(n^{3\omega} - n^{\omega})$. The function $F_{(\Delta KL)}$ describes the third harmonic intensity within the nonlinear medium,[12] including the oscillatory behavior due to wavevector mismatch and the absorptive losses at ω and 3ω. In the most general case

$$F = 2 \exp\left[-\left(\frac{\alpha_3}{2} + \frac{3\alpha_1}{2}\right)L\right] \times \left\{\cosh\left[\left(\frac{\alpha_3}{2} - \frac{3\alpha_1}{2}\right)L\right] - \cos(\Delta KL)\right\} \Big/ \left\{(\Delta KL)^2 + \left[\left(\frac{\alpha_3}{2} - \frac{3\alpha_1}{2}\right)L\right]^2\right\} \quad (4)$$

where α_1 and α_3 are standard Napieran absorption coefficients at ω and 3ω for which the optical transmittance is $\exp(-\alpha L)$. For a transparent nonlinear medium, eq 4 reduces to

$$F = \frac{2}{(\Delta KL)^2}[1 - \cos \Delta KL] \quad (5)$$

as it should. In the case of P3MOT, α_1 is negligible over the entire experimental range, but α_3 becomes significant for films thicker than 300 Å at wavelengths shorter than 620 nm.

Experimentally, the TH signal for a given P3MOT film was measured with respect to a silica reference at identical values of S^{ω}. Thus,

$$\frac{\chi_p^{(3)}}{\chi_r^{(3)}} = \left[\frac{S_p^{3\omega}}{(S_r^{3\omega})'}\,\frac{T_r}{T_p}\,\frac{F_r}{F_p}\right]^{1/2}\frac{\Delta\epsilon_p}{\Delta\epsilon_r}\,\frac{L_p}{(L_c)_p}\,\frac{(L_c)_r}{L_r} \quad (6)$$

Here, the subscripts p and r refer to polymer and reference, respectively, and $(S_r^{3\omega})'$ is the intensity of TH signal observed for the reference after correction for the effect of air as described above. In calculating T_p, we have used the index of refraction of silica instead of P3MOT for the front face boundary, as the attenuation of the incident beam is identical for both sample and reference. We also neglected transmission losses at the silica/polymer interface as well as multiple reflection within the polymer, which were judged to be incoherent as discussed in ref 11.

The sensitivity of the calculation to the values used for the indexes of refraction of both the material and the reference is clear from eq 6. A poor estimation of indexes of refraction can lead to large error in $\chi^{(3)}$ if $\Delta\epsilon$ of the film is very different from that of the reference, as is the case for P3MOT and many other highly colored materials. To avoid this source of error, we measured the complex index of refraction of P3MOT from 350 to 800 nm using a Rudolf Research S2436 scanning ellipsometer. The curves shown in Figure 2 are the result of a simultaneous fit of ellipsometric data taken at three different angles for a 1600-Å P3MOT film on silicon and analyzed according to standard theory.[13] As a cross check, k_λ was independently determined by standard UV–visible transmission spectroscopy where $T_\lambda = \exp(-4\pi k_\lambda L/\lambda)$. The ellipsometric values of k agreed with those measured by transmission to the limit of experimental accuracy (~0.002). For the fused silica reference, the indexes of refraction were calculated according to the dispersion equation developed by Malitson.[14]

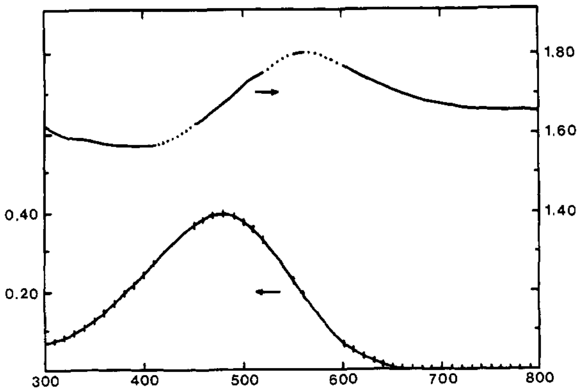

Figure 2. Variation of the optical constants n_r and k with wavelength for thin-film P3MOT. (+) Points determined by ellipsometry. Solid curve for k determined independently by optical absorption.

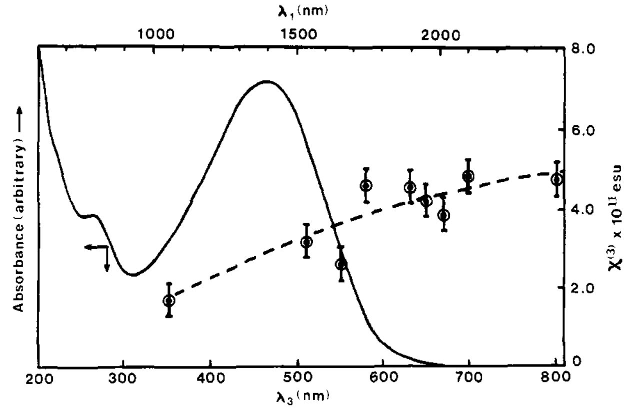

Figure 3. Variation of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ (O) with wavelength for a 720-Å film of P3MOT. Top scale, wavelength of fundamental beam; bottom scale, third harmonic wavelength.

The values obtained for $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ as a function of wavelength are shown for a 720-Å film in Figure 3. As is clear from the superimposed absorption spectrum, $\chi^{(3)}$ apparently does not show the expected three-photon resonance enhancement, nor is the increasing value of $\chi^{(3)}$ with increasing wavelength consistent with one-photon resonance; the infrared absorption spectrum of P3MOT shows no optical absorption in the range 650 nm to 50 μm. The wavelength profile does resemble the absorption spectrum of the oxidatively doped conducting polymer.[4] To test whether the apparent TH signal might in fact be coming from trace oxidized impurities in the films, we examined the third harmonic from a series of 650-Å films that were deliberately oxidized to various doping levels by dipping in acetonitrile solutions of $NOBF_4$. Partial oxi-

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(13) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North-Holland: Amsterdam, The Netherlands, 1987.

(14) Malitson, I. H. *J. Opt. Soc. Am.* **1965**, *55*, 1205.

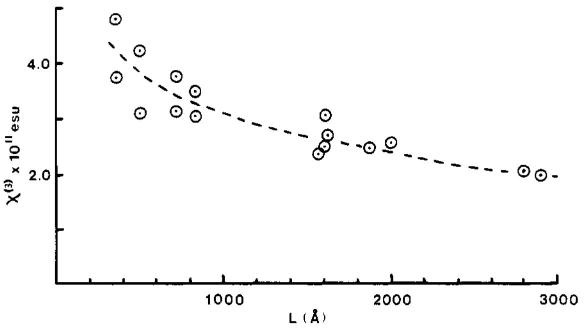

Figure 4. Variation of calculated $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ with film thickness L in P3MOT films for fundamental wavelength of 1740 nm.

dation caused the TH signal from the film to drop dramatically, and at doping levels greater than ~15%, a laser burn spot quickly developed on the sample. Extensively oxidized films were vaporized instantly by the incident laser beam, probably as a result of direct absorption of the laser beam whose wavelength fell within the envelope of the first electronic transition.[4] Thus, it appears that oxidized P3MOT is not responsible for the wavelength dependence of $\chi^{(3)}$ measured in the thin films; rather, oxidized impurities are probably quickly destroyed in the course of any given experiment.

Our observation of an amorphous wavelength profile of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ in P3MOT is consistent with those of Fichou et al.,[15] who obtained similar profiles for several thiophene oligomers. In all cases, the apparent value of $\chi^{(3)}$ in the near infrared does not follow a wavelength profile that can be explained by either one- or three-photon resonances evident from the normal one-photon absorption spectrum. There are several possibilities for this apparent anomaly. In our amorphous polymer system, we may expect a range of effective conjugation lengths. Although the one-photon absorption spectrum reflects this distribution, the weighting factors are relatively insensitive to conjugation length. The $\chi^{(3)}$, however, is dependent upon conjugation length to a high power. Thus, the observed $\chi^{(3)}$ may reflect the presence of long conjugation lengths within the polymer. Alternatively, the wavelength dependence of $\chi^{(3)}$ may result from two-photon resonance enhancement. The bandwidth of the resonant absorption is exceedingly wide, however, which suggests that more than one two-photon state may be present in the near-infrared region. A study of two-photon absorption in a representative thiophene oligomer should prove to be illuminating on this point.

The value of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ as measured in this experiment is also not constant with film thickness, a result contrary to the behavior of a bulk material. Figure 4 shows the value of $\chi^{(3)}$ calculated from data taken with 1740-nm excitation, as a function of film thickness where $L_c = 1.0$ μm and the TH wavelength falls in a slightly absorbing spectral region. We have also obtained similar results at 1064 nm where $L_c = 1.48$ μm and the TH wavelengths is in a region of anomalous dispersion as indicated in Figure 2. A similar phenomenon has been noted previously in TH measurements on polysilane thin films[16] and has been attributed to orientation anisotropy of the nonlinear chromophore at the film surfaces. As the bulk of the film becomes thinner, the TH contribution from the plane-oriented material near the surfaces becomes larger. This explanation is particularly attractive in the case of polythiophenes, since the greater π-electron conjugation obtained by increasing coplanarity of the thiophene rings in near-surface polymer will also give rise to a larger $\chi^{(3)}$,[15] which will add to the simple orientation effect. Accordingly, we searched for physical and spectroscopic evidence of orientation in thin P3MOT films. By cross-sectional transmission electron microscopy, thin films spun onto plastic substrates (for purposes of microtoming) appeared extremely smooth and homogeneous with no trace of crystallinity seen in the electron diffraction pattern. Infrared spectroscopy was likewise uninformative; spectra of very thin films taken by polarized attenuated total reflection infrared spectroscopy (in which two oriented interfaces should be important) were identical with those of thick films taken in the conventional transmission mode where surface contributions are negligible. However, the UV–visible absorption spectra of extremely thin films gave some hint of increased coplanarity of the rings. Films less than ~300 Å showed a slight red-shift of the absorption maximum from 460 to 470–480 nm. This effect was repeatable but could not be reliably quantified.

In summary, P3MOT is an example of a strictly amorphous polythiophene thin film that exhibits attractive nonlinear optical properties. The high value of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ in the preresonant wavelength region coupled with the very high damage threshold of this material in thin-film form are useful features for optical devices. The higher effective nonlinearity of very thin films may be exploitable in certain device applications. In some polymers, a thicker film may be built up by spinning several consecutive films on top of one another. It is conceivable that a polythiophene could be synthesized with the appropriate substituents at the 3-position to confer this property of spin overcoating, and that spin-oriented thin films could be easily fabricated.

Acknowledgment. We thank Dr. Jordi Marti for TEM measurements, Ken O'Brien for ATR infrared spectroscopic analysis, and Frank Chisena for technical assistance. We are very grateful to Rudolf Research (Flanders, NJ) for allowing us the use of the S2436 scaning ellipsometer and to Dr. Richard Spanier of Rudolf Research for several helpful discussions.

Registry No. P3MOT (homopolymer), 125197-71-9.

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(15) Fichou, D. L.; Garnier, F.; Charra, F.; Kajzar, F.; Messier, J. In *Proc. Intl. Conf. Org. Mat. Nonlinear Opt.* Oxford, U.K., June 29–30, 1988; Hann, R. A., Bloor, D., Eds.; The Royal Society: London, in press.

(16) Baumert, J.-C.; Bjorklund, G. C.; Jundt, D. H.; Jurich, M. C.; Looser, H.; Miller, R. D.; Sooriyakumaran, R.; Swalen, J. D.; Tweig, R. J. *Appl. Phys. Lett.* **1988**, *53*, 1147.