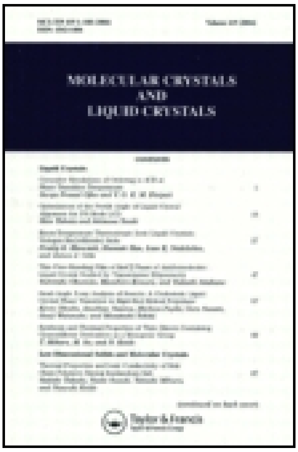

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Electro-Optic Spectroscopy of Poly(3-Octylthiophene)

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ELECTRO-OPTIC SPECTROSCOPY OF POLY(3-OCTYLTHIOPHENE)

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Abstract
Electric field induced changes in the optical properties of poly(3-octylthiophene) in the spectral region of the lowest π-π^* electronic transition are reported. The electroabsorption [EA] resembles the first energy derivative of the unperturbed spectrum, scales quadratically with the applied electric field, and its lineshape is field invariant, all consistent with a DC Kerr effect whose origin is the Stark shift of a singlet exciton. In addition, a transition that does not appear in the unperturbed absorption spectrum is detected and we assign this to the normally dipole forbidden one-photon excitation of a ^1A_g even parity exciton that becomes allowed by the symmetry breaking effect of the applied field. The optical constants of P3OT have also been determined and these are used to calculate the real and imaginary parts of the DC Kerr susceptibility, $\chi^{(3)}$ (-ω; 0,0,ω) from the EA spectrum.

INTRODUCTION

Electromodulation techniques have been widely used in the study of the electronic structure of organic molecular semiconductors. Both first and second derivative lineshapes have been reported and these are analysed in terms of the quadratic Stark effect for optical transitions dominated, respectively, by a change in polarisability or a change in dipole moment.[1] In conjugated polymers, electromodulation has been used to study the nature of the fundamental π-π^* absorption (exciton vs band description)[2,3,4], to determine the energies of excited states with the same (A_g) symmetry as the ground state[4,5,6] and to assess the size of the electro-optic nonlinear coefficients for these materials[7,8]. Here we report a study of the polymer poly(3-octylthiophene) [P3OT] which shows a response that follows the first derivative of the linear absorption. Additional features are seen and these are ascribed to the transfer of oscillator strength from the dipole allowed ^1B_u exciton to a ^1A_g state that lies at higher energy. The location of this ^1A_g state provides important information on electronic structure that is directly relevant to understanding photoluminescence and nonlinear optical properties.

SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

P3OT was synthesised following the method of Kobayashi et al.[9] The molecular weight (as determined by gpc against polystyrene standards) was M_w=13000. Samples were prepared by spin coating chloroform solutions of the polymer onto spectrosil substrates. This procedure allowed preparation of uniform films of a few hundred nanometers thickness. Interdigitated Cr/Au arrays with a 20 μm gap were pre-evaporated on the substrates and the polymer was coated on top of these. The samples were mounted in a cold finger cryostat and held at liquid nitrogen temperature. The ac modulation field was produced by amplifying the sinusoidal voltage output from a lock-in amplifier. The probe beam was obtained by pre-monochromating the mechanically chopped light from a tungsten lamp. The light was chopped at 20 Hz and polarized with a sheet of polaroid film whose transmission axis could be rotated by a known angle. The transmitted light was detected by a silicon photodiode and both the transmission, T, and change in transmission, ΔT, were simultaneously recorded using two lock-in amplifiers whose reference frequencies were, respectively, the chop frequency and twice the frequency of the applied electric field (quadratic electromodulation response). Optical constants were obtained via an iterative Kramers-Kronig analysis using transmission data recorded at liquid nitrogen temperature in a Perkin Elmer Lambda 9 spectrophotometer.

RESULTS AND DISCUSSION

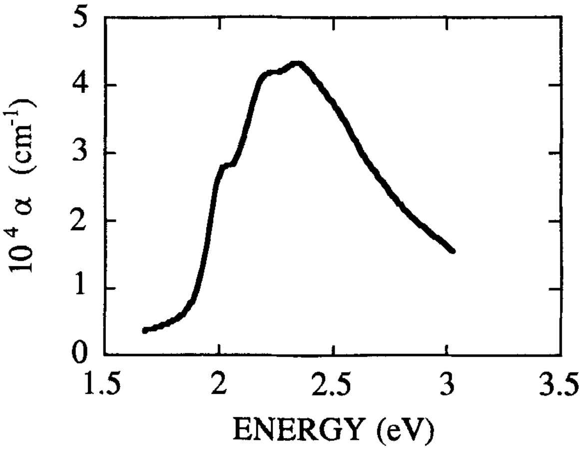

FIGURE 1 Optical absorption coefficient, α, of P3OT thin film at 77K.

Figure 1 displays the absorption coefficient, α, of the P3OT thin film sample used for electroabsorption measurements. The vibronic structure seen in the absorption indicates a relatively high degree of order in this sample. The peak value of circa 4.4 x 10^{-4} cm^{-1} is ≈ 5 times less than that seen for the precursor route polymers such as poly(*p*-phenylene vinylene), consistent with the differences in volume fraction of conjugated material.

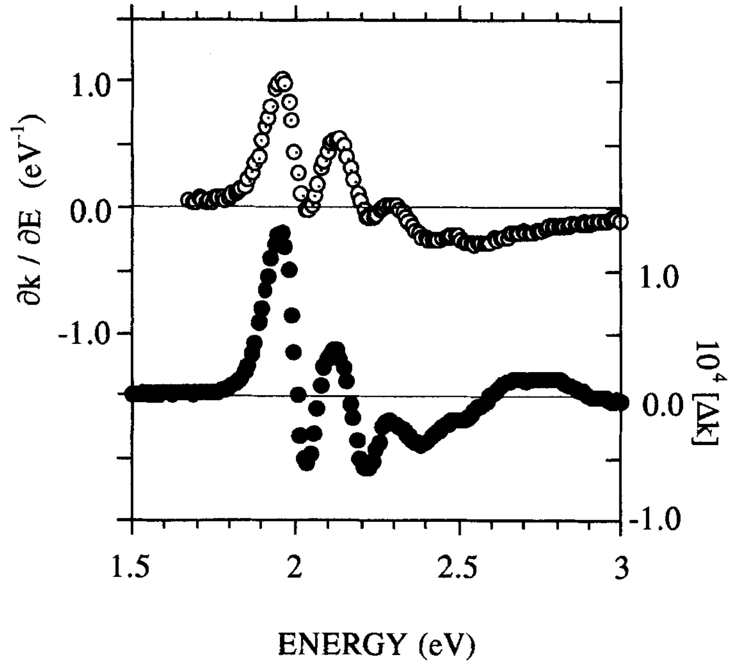

FIGURE 2 Δk spectrum (lower curve, solid circles) compared to the first derivative of the imaginary part, k, of the linear susceptibility (upper curve, open circles). N.B. both k and Δk spectra were measured at 77K.

Figure 2 shows the 77 K Δk spectrum of P3OT. The signal follows the square of the electric field and the lineshape is field independent. The Δk peaks closely match those of the first energy derivative of the k spectrum as expected for the Stark effect mediated red shift of an exciton transition for which the change in polarisability dominates over the change in dipole moment.[1] The shift of the ^1B_u exciton to lower energy requires that there be at least three important states involved in the field induced eigenstate mixing process. This is contrary to the two-level model used by Meth et al. to describe the dispersion of third harmonic generation in poly(3-hexylthiophene).[10] The appearance of the oscillatory structure demonstrates very clearly the importance for conjugated polymers of including the vibronic contributions within any physical model of their electro-optic response (and in general all of their nonlinearities). The comparison of the Δk spectrum and the first derivative of the unperturbed k spectrum indicates the presence of an additional broad bleaching between circa 2 and 2.6 eV and a positive induced absorption at around 2.7 eV. These features are unrelated to derivatives (first or second) of the unmodulated absorption and they point to the presence of an extra contribution in the Kerr response. We assign this to the electric field activation of ^1A_g exciton absorption. The broad bleaching then arises from transfer of oscillator strength from the dipole allowed excitation of the ^1B_u exciton to the dipole forbidden ground state to ^1A_g exciton transition. Supporting evidence for this assignment comes from measurements on P3OT by Pfeffer et al. using ps Kerr ellipsometry.[11] They find in tetrahydofuran solutions at room temperature a two photon absorption peak at 3.5 eV that is ≈ 0.6 eV higher than the peak in the one photon absorption. The corresponding feature in our data is at ≈ 2.7 eV which is ≈ 0.4 eV above the one photon absorption peak that we measure for film samples at 77K (see Figure 1). The differences in energy for these experiments are most likely due simply to the differences in conformation of the polymer chain in the two different environments.

The maximum Δk value obtained for P3OT is somewhat less than that found in PTV[8] and polyacetylene[7] but similar values have been reported for other poly(3-alkylthiophene)s.[12] A contributory factor in this is the volume dilution of the nonlinear active conjugated polymer main chain by the addition of alkyl side chains an effect that is also apparent in the linear absorption spectrum as discussed above.

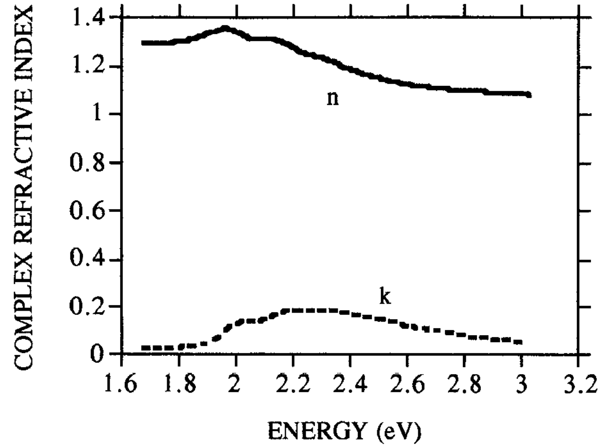

FIGURE 3 Re and Im components of the complex refractive index N = n + ik for P3OT thin film at 77K.

Figure 3 shows the linear optical constants derived from transmission data using an iterative Kramers-Kronig analysis. We find values for n and k that are very slightly lower than those reported by Jansson et al.[13] for poly(3-hexylthiophene), but are lower than those of Callendar et al.[14] for poly(3,4-dibutoxythiophene) by some 20%. The former difference can be attributed to volume fraction effects (going from octyl to hexyl side chains) and the latter to both an increase in electron density due to electron donating alkoxy groups and volume fraction effects (going from octyl to butoxy side chains).

We have used these optical constants to calculate both the real and imaginary parts of the DC Kerr susceptibility, $\chi^{(3)}$ (-ω; 0,0,ω), from the EA data as described elsewhere.[15] The data are displayed in Figure 4. The contribution from electric field activated transitions to the ^1A_g exciton can be clearly seen at the upper end of the measurement range.

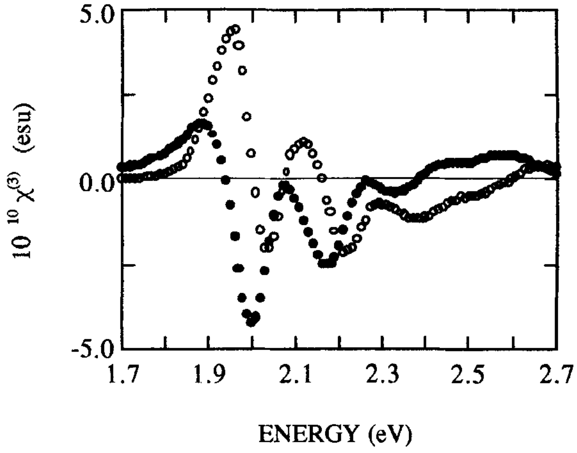

FIGURE 4 Calculated $\chi^{(3)}$ (-ω; 0,0,ω) spectrum for P3OT. Re and Im $\chi^{(3)}$ are shown by closed data points and open data points respectively.

CONCLUSIONS

In this paper we have reported measurements for poly(3-octylthiophene) that demonstrate the utility of electroabsorption measurements both in probing the electronic structure of conjugated polymers and in providing information on their nonlinear optical response. It is our intention to pursue further studies of this nature in order to more fully elucidate the fundamental nature of the excitations in this class of material and to obtain a more detailed understanding of mechanisms involved in their $\chi^{(3)}$ response.

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