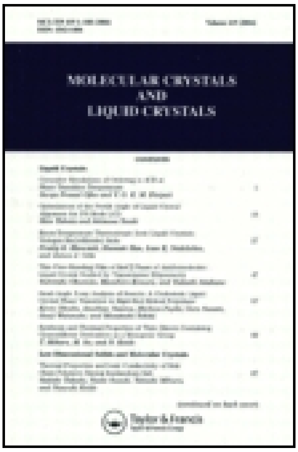

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Quadratic Electro-Optic Response of a Conjugated Porphyrin Polymer

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QUADRATIC ELECTRO-OPTIC RESPONSE OF A CONJUGATED PORPHYRIN POLYMER

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Abstract We report electroabsorption measurements of $\chi^{(3)}(-\omega; 0, 0, \omega)$ for a new conjugated porphyrin polymer formed by the edge-linking of zinc porphyrin macrocyles through conjugated acetylenic bridges. The polymer is solution processed into thin film form and experiments performed on the films indicate a very large nonlinearity, an order of magnitude larger than we have previously measured in conjugated polymers such as poly(p-phenylene vinylene) and poly(2,5-thienylene vinylene). There is clear evidence of the extension of conjugation through the acetylenic bridges. Comparison is made between results obtained for the polymer, and its monomer and dimer analogues dispersed in an inert polymer matrix.

INTRODUCTION

Macrocyclic porphyrins and phthalocyanines, have previously been studied as potentially interesting nonlinear optical materials:[1,2] They possess large 2-D delocalised π-electron systems which give rise to relatively large $\chi^{(3)}$ values and have the sharp optical transitions that are desired to allow the use of resonance enhancements. Derivatisation and central metal substitution are readily achieved and provide some tunability of the optical transition energies. In addition, excellent chemical and thermal stability are general properties of such materials. An approach to tuning transition energies further into the infrared to enhamce nonlinearity at optical communications wavelengths is to link the macrocyles together so as to provide inter-macrocyle interactions. Coordination-linked polymers have been reported in which the metalloporphyrins are held face-to-face but the inter-macrocycle coupling in these materials is found not to be strong [1].

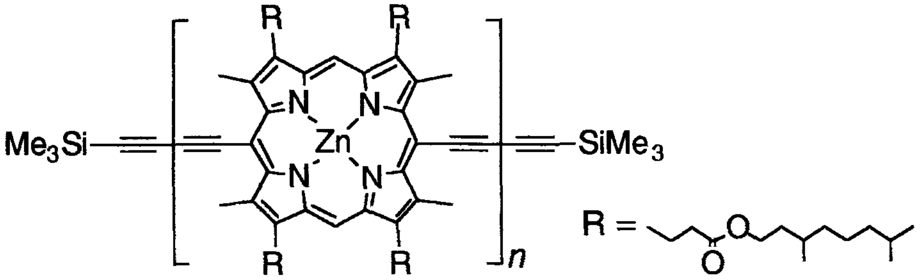

FIGURE 1 Molecular structure of the conjugated porphyrin polymer.

We report here on linear and non-linear optical studies of a new edge-linked conjugated metalloporphyrin polymer (see Figure 1) possessing butadiyne bridges between the macrocyles. These offer the possibility of inter-macrocycle π-electron interactions leading to an extension of π-conjugation. In addition to studying the polymer we have made comparative measurements on dimer and monomer analogues; solution linear optical spectra are reported here. An iterative Kramers-Kronig analysis has been carried out on the film data to determine the linear optical constants of the polymer. Electroabsorption spectra have also been measured and we have calculated both the real and imaginary parts of the corresponding DC Kerr susceptibility $\chi^{(3)}(-\omega; 0, 0, \omega)$ for the polymer. We find a large nonlinearity that peaks at a value of Re $\chi^{(3)} = -7.2 \times 10^{-8}$ esu at a wavelength of 850nm.

SAMPLE PREPARATION AND EXPERIMENTAL METHODS

The synthesis of the monomer, dimer and polymer are described elsewhere[3]. In this paper we report studies of both solution and thin film samples. The polymer is insoluble in most solvents despite possessing large sidegroups but it becomes readily soluble in chloroform or dichloromethane if pyridine is added. The pyridine is believed to coordinate to the zinc atoms and prevent aggregation of the polymer chains, allowing greater solubility. Addition of pyridine to solutions of the monomer and dimer helps to prevent aggregation and thus allows comparison of absorption spectra for un-aggregated material in each case. Films of the polymer were prepared by spin coating from chloroform solutions (containing 10% pyridine). IR absorption and NMR studies of the polymer do not detect acetylene end groups indicating a significant degree of polymerisation, that we estimate to be greater than ten. This estimate is consistent with preliminary neutron scattering studies and with the high viscosity of the polymer.

The electroabsorption measurement involves the application of a modulated electric field (typically 10-100kV/cm at 5kHz) to a thin film (300-1000Å) and the synchronous monitoring of the changes in its optical absorption. A lock-in amplifier locked to the second harmonic frequency (quadratic electro-optic response) is used to achieve the latter. The details of the spectrometer we have used have been published elsewhere.[4] Samples for electroabsorption measurements were fabricated by spin coating a thin film of the polymer onto a spectrosil disk on the top surface of which an interdigitated electrode array (finger spacing 200 μm) had been previously evaporated. The samples were held in a liquid nitrogen cold finger cryostat under dynamic vacuum ($<10^{-4}$ mbar) for the duration of the measurements. The room temperature linear absorption spectra for solutions and low temperature spectra for films were recorded using a Perkin Elmer Lambda 9 spectrophotometer equipped respectively with a quartz cuvette and a liquid nitrogen cryostat. The thicknesses of films were determined, after all other measurements had been completed, using a Dektak IIA surface profiler. In order to enumerate $\chi^{(3)}$, the real and imaginary parts of the linear refractive index, n and k, were calculated from the low temperature transmission spectrum of the polymer film using an iterative technique based on the method reported by Nilsson.[5]

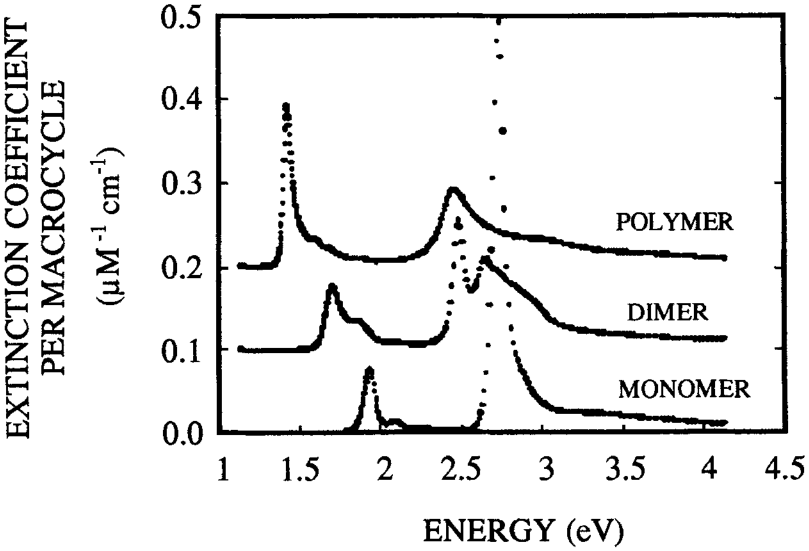

FIGURE 2 UV-VIS absorption spectra of monomer, dimer, and polymer in pyridine /chloroform solution. The dimer and polymer spectra have been offset by 0.1 and 0.2 (μM^{-1} cm^{-1}) absorbance units respectively. N.B. The absorbance is normalised as the strength per porphyrin ring.

RESULTS AND DISCUSSION

Linear Optical Response

The solution absorption spectra of the polymer and its dimer and monomer analogues are shown in Figure 2. These were recorded for each material dissolved in 1% pyridine/dichloromethane solutions which as discussed above yields spectra for the non-aggregated form. Each spectrum shows the expected pair of strong macrocycle-derived π-π^* absorption bands: A low energy or Q-band and a high energy or Soret band. The Soret band dipole strengths $\mu_B{}^2$ per macrocyle are fairly constant for monomer, dimer, polymer and a conventional zinc octaethylporphyrin[3] and the changes in spectra for this band in Figure 2 are largely associated with a splitting of the Soret band into two components (of which the lower energy one is more clearly defined) and an overall broadening of the lineshape. These changes can be understood in terms of the Kasha model for exciton coupling.[6,7,8] The Q-band however, undergoes much stronger changes with a large red shift and increase in dipole strength on going from the monomer to the dimer and on to the polymer.[3] The Q-band peaks at 642 nm (1.93 eV) for the monomer with single terminal acetylene end groups, 728 nm (1.70 eV) for the dimer and 874 nm (1.42 eV) for the polymer. We estimate a three fold increase in Q-band dipole strength, $\mu_Q{}^2$, for this series and a ten fold increase for the polymer in comparison to a conventional zinc octaethylporphyrin. In addition we note that the lineshape of the Q-band does not drastically change: It shifts, strengthens and sharpens somewhat but shows little other modification. We conclude from these observations that the changes in the Q-band spectra are not well described by the Kasha model. Indeed, the expected energy shift within this model is $\Delta E = \mu_Q{}^2/2\pi\varepsilon_0 R^3$ which for an inter-macrocylcle distance of 13.6Å (derived from molecular mechanics calculations) and an experimental $\mu_Q{}^2$ value of 100 D^2 gives a predicted red shift of some 560 cm^{-1}: The experimental shift is found however to be much greater, namely 4134 cm^{-1} (0.51 eV). These changes can be understood if, as discussed above, the bridging groups lead to an extension of π-conjugation between the macrocycles and this is our interpretation of the observed behaviour.

In Figure 3 we report the linear optical constants of an 800Å thickness spin coated film of the polymer for the spectral range overlapping the Q-band resonance region within which electroabsorption spectra were measured. These data were used to analyse the electroabsorption data reported below and thus to determine the DC Kerr electro-optic susceptibility in the Q-band one-photon resonance region.

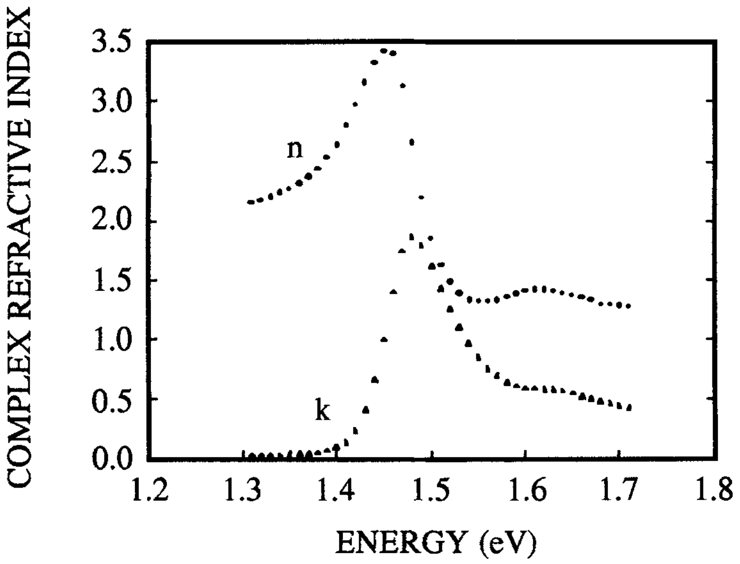

FIGURE 3 Optical constants of a spin coated porphyrin polymer film (800 Å thickness) at 77K. The real part, n, (upper curve) and imaginary part, k, (lower curve) of the refractive index were determined by Kramers-Kronig analysis of transmission data.

Nonlinear Optical Response

A typical electroabsorption spectrum (35kV/cm) at 77K for a spin coated polymer film is shown in Figure 4. We note that the lineshape of the electroabsorption signal was field invariant and its magnitude scaled quadratically with the applied field. Both were only very weakly temperature dependent, consistent with a high degree of rigidity for the polymer. The first derivative with respect to energy of the linear absorption spectrum is also shown in Figure 4 for comparison. The two sets of data have very similar lineshapes indicating that the electro-optic effect in this material can be assigned predominantly to a Stark shift for a transition in which the change in polarizability dominates.[9] A more detailed comparison of the two lineshapes reveals several differences. First the onset of the electroabsorption signal is very much sharper than that of the derivative and is at a slightly higher energy. Second the electroabsorption signal shows only very weak structure above 1.55 eV whilst the derivative spectrum shows more clearly resolved features associated with the vibronic progression of the Q-band. The apparent suppression of vibronic peaks in the electroabsorption spectrum is difficult to explain and suggests that treating the electro-optic response as a simple shift of the absorption spectrum is a rather inadequate description in this case.

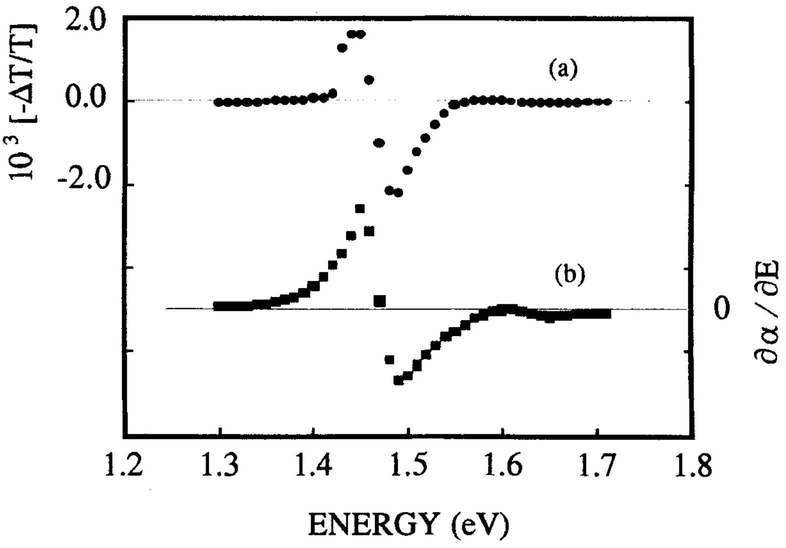

FIGURE 4 (a) Electroabsorption spectrum of a porphyrin polymer film at 77K with 35kV/cm applied field (upper curve, left scale) and (b) First derivative, ∂α/∂E, of linear absorption spectrum at 77K (lower curve, right scale arbitrary units).

Figure 5 shows the $\chi^{(3)}(\omega; 0, 0, \omega)$ spectrum calculated using the linear optical constants from Figure 3. The peak value for Re $\chi^{(3)}(\omega; 0, 0, \omega)$ of -7.24×10^{-8} esu compares very favourably with those measured for *trans*-polyacetylene (-2.5×10^{-8} esu)[10], polydiacetylene (-2×10^{-8} esu)[11] and poly(2,5-thienylene vinylene) (-7.5×10^{-9} esu)[4].

CONCLUSION

The porphyrin polymer has an enhanced nonlinearity that we assign to extended conjugation between the porphyrin macrocycles. Methods exist that may allow further enhancement e.g use of different metals and/or attachment of ligands to them. Preliminary measurements with pyridine show an enhancement by more than a factor of four.

ACKNOWLEDGEMENTS

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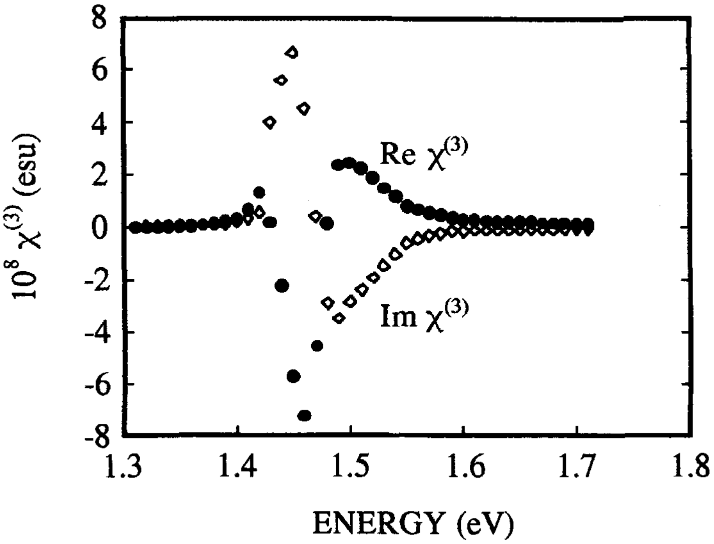

FIGURE 5 Spectral dispersion of the real (closed circle data points) and imaginary (open diamond data points) parts of the quadratic electro-optic susceptibility $\chi^{(3)}(-\omega; 0, 0, \omega)$.

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