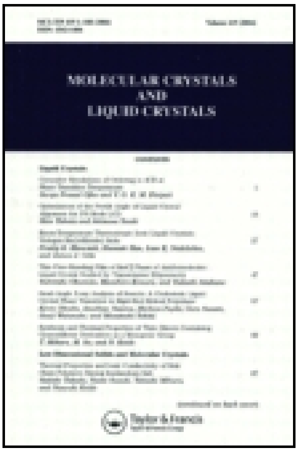

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Electroabsorption Spectroscopy of Rigid Rod Polymers PBZT and PBTPV

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ELECTROABSORPTION SPECTROSCOPY OF RIGID ROD POLYMERS PBZT AND PBTPV

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Abstract The rigid rod polymers poly(*p*-phenylenebenzobisthiazole) and poly(benzobisthiazole-*p*-phenylenebisvinylene) have been prepared as thin film samples by spin coating Lewis acid complexes from solution and regenerating the uncomplexed polymer by washing with water and drying in vacuo. This approach allows fabrication of films that show well resolved vibronic structure in their linear absorption spectra. In this paper we present results of linear- and electro-absorption spectra. From the latter we are able to deduce the average exciton radius which we find to be 13Å in PBZT and 15Å in PBTPV. The average change in polarisability accompanying the lowest energy π-π^* optical transition is also determined. Comparison of our results is made with previous studies.

INTRODUCTION

Rigid rod polymers as exemplified by poly(*p*-phenylenebenzobisthiazole) [PBZT] have been of interest over a number of years as structural materials with high mechanical strength and thermal stability. In more recent years they have attracted increasing attention as materials for nonlinear optics[1,2,3] and also luminescence emission.[4] Several studies have been undertaken to probe nonlinear optical responses including third harmonic generation [THG][1] and degenerate four wave mixing [DWFM][2], and grating coupled waveguide structures have also been tested[3]. In this paper we investigate the quadratic electro-optic response of thin film samples of both PBZT and poly(benzobisthiazole-*p*-phenylenebisvinylene) [PBTPV] by measuring their electroabsorption [EA] spectra. The results are analysed within the model proposed by Weiser[5] and we extract numerical values for the exciton radius and average change in polarisability accompanying the lowest energy π-π^* optical transition.

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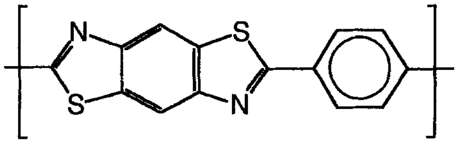
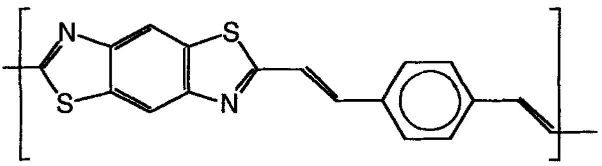
SAMPLE FABRICATION AND EXPERIMENTAL TECHNIQUES

The PBZT and PBTPV polymers (see Figure 1) were synthesised as reported elsewhere[6] and were fabricated as thin films on top of pre-prepared interdigitated gold electrode arrays by spin-coating from solutions of their metal halide ($GaCl_3$ or $AlCl_3$) Lewis acid complexes in nitromethane. The samples were washed with distilled water to remove the Lewis acid and dried in a vacuum chamber. Elemental analysis of the regenerated polymers showed only trace residues of the Lewis acid. The 20 μm spacing electrode arrays were defined by photolithographic patterning. EA measurements were undertaken in a home built apparatus in which a sinusoidal modulated electric field was applied across the electrode array and changes in sample transmission were monitored using a lock-in amplifier referenced to the second harmonic of the modulation frequency (quadratic response). Simultaneous measurement of the transmission was effected by modulation of the transmitted probe light by a mechanical chopper and detection of the resulting signal with a second lock-in amplifier. The EA signal $-\Delta T/T$ can then be determined point by point and free from fluctuations in the light source output. All EA experiments were performed in an evacuated liquid nitrogen cold finger cryostat at 80K. Linear absorption spectra were measured in a separate liquid nitrogen cold finger cryostat using a Perkin Elmer Lambda 9 spectrophotometer.



Poly(*p*-phenylenebenzobisthiazole) [PBZT]



Poly(benzobisthiazole *p*-phenylenebisvinylene) [PBTPV]

FIGURE 1 Chemical Structures of PBZT and PBTPV

RESULTS AND DISCUSSION

Linear absorption spectra

The linear absorption spectra at 80 K for both PBZT and PBTPV are shown in Figure 2 . The PBTPV absorption band is red shifted from that of PBZT by ≈ 0.25 eV consistent with an increase in π-delocalisation between the benzobisthiazole moieties through an increase in planarity associated with the hinderance of ring torsion by the vinylene groups placed either side of the phenylene ring. Well resolved vibronic peaks are observed for both materials indicating a high degree of order in these samples. Peaks appear at 2.65 and 2.84 eV, and there is a shoulder at 2.99 eV for PBZT. In PBTPV the peaks are at 2.4 and 2.59 eV and the shoulder is at 2.75 eV. We assign the absorption in both cases as a transition to the lowest lying ^1B_u exciton with a superposed vibronic progression. The observed spacings of the vibronic features are consistent with totally symmetric vibrations of the polymer backbone. There are long tails in the absorption spectra that extend to lower energies. This is believed to be due principally to scattering, a conclusion that is consistent with reports of waveguide loss measurements on both spin-coated and extruded PBZT films on fused silica substrates[3]. The losses of the spin-coated film were so high that no guided mode streak could be seen. In the extruded film, however, streaks were seen with losses measured at 15-60 dBcm^{-1} depending on wavelength and for a free standing film losses as low as 12.8 dBcm^{-1} have been measured.[3] These results suggest that with optimisation of processing procedures it should prove possible to remove or at least substantially reduce the long tail in the spectrum.

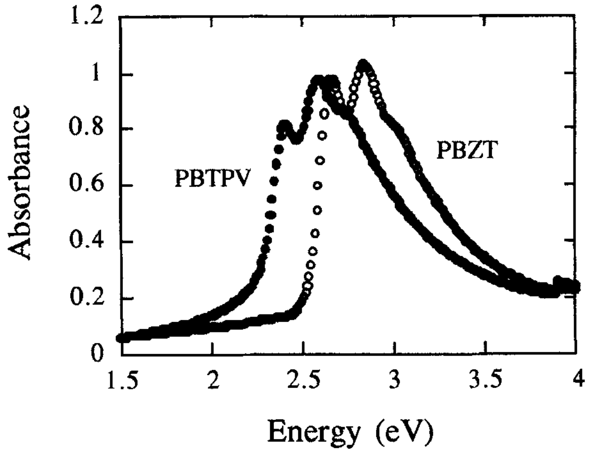


FIGURE 2 Linear absorption spectra for PBZT (open circles) and PBTPV (filled circles) measured in a liquid nitrogen cold finger cryostat at 80 K.

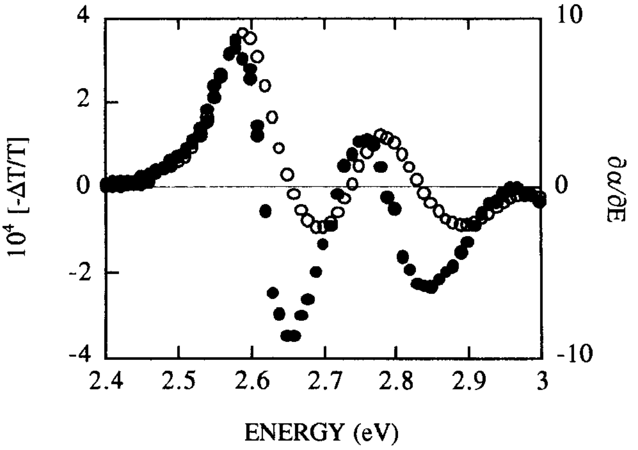
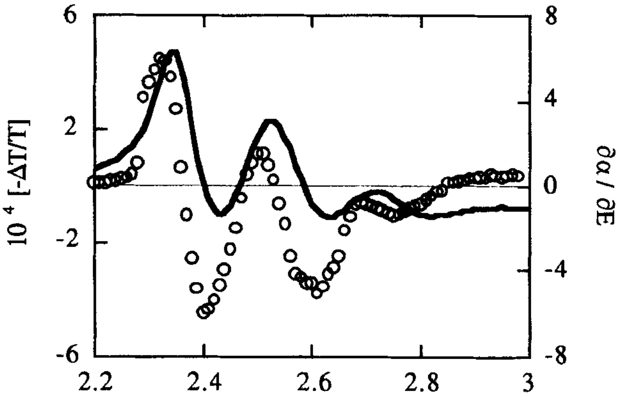


FIGURE 3 Electroabsorption spectrum (filled data points) and first energy derivative of the linear absorption (open data points) of a PBZT film.

Electroabsorption spectra

The EA spectrum for a PBZT film of thickness 550 Å is shown in Figure 3 together with the first energy derivative of its linear absorption. The corresponding spectrum for a PBTPV film of thickness 500 Å is shown in Figure 4. The applied field strength was 35 kV/cm and each spectrum was measured at 80K. The electro-optic signal in both cases was quadratic in the applied field and had a field invariant lineshape indicative of the expected Stark shift mediated DC Kerr response. The red shift of the exciton deduced from the sign of the lowest energy EA peak implies that at least three important states are involved in the field induced eigenstate mixing process. This is contrary to the earlier description for PBZT of the experimental dispersion of $\chi^{(3)}(-3\omega; \omega,\omega,\omega)$ (associated with third harmonic generation) within a two level model.[7] Vanherzeele et al.[7] discussed the problem of extending their model for $\chi^{(3)}(-3\omega; \omega,\omega,\omega)$ to predict $\chi^{(3)}(-\omega; \omega,-\omega,\omega)$ (associated with degenerate four wave mixing) and commented that difficulties could arise close to one-photon resonance excitation wavelengths where the inclusion of higher lying ^1A_g states might become important. Our results provide a contribution to this discussion in that they show for the fully single-photon resonant $\chi^{(3)}(-\omega; 0,0,\omega)$ response it is essential to include such higher lying ^1A_g states to obtain the correct sign for the imaginary part below the one-photon optical resonance. The imaginary part of $\chi^{(3)}(-\omega; 0,0,\omega)$ is directly related to the measured EA through an expression of the form Im $\chi^{(3)} = (k\ \Delta n + n\ \Delta k) / (2\pi F^2)$ where $N = n + ik$ is the complex refractive index, and Δn and Δk are the changes induced by the electric field F. The Stark red shift thus corresponds to a positive Im $\chi^{(3)}$ below the resonance whilst a two level model would predict a Stark blue shift and a negative Im $\chi^{(3)}$ below the resonance.



ENERGY (eV)

FIGURE 4 Electroabsorption spectrum (open data points) for a PBTPV thin film and the first energy derivative (solid line) of its linear absorption spectrum.

The vibronic progression seen in the linear absorption spectrum is mirrored in the EA spectrum by the oscillations in the signal. For PBZT the maxima in EA appear at 2.59, 2.76 and 2.96 eV with minima at 2.65 and 2.84 eV; the spacing between successive maxima and minima is thus in good agreement with the vibronic spacings in the linear absorption. The correspondence between the peak energies in the first energy derivative of the linear absorption and the EA is not especially good in this case, in contrast to other examples of conjugated polymer EA.[8] There is a significant red shift (0.02-0.05 eV) of the peaks in the EA response compared with the first energy derivative. This may well be due to the effect of the scattering contribution to the absorption which will influence the derivative spectrum but which will not contribute to the EA. The observation that the shift in peak energies increases with increasing energy is consistent with a Rayleigh scattering dependence on energy. Further work is however needed to clarify this point. A second deviation is that the ratio of the magnitudes of negative to positive going peaks is enhanced in EA relative to the derivative spectrum. A similar effect has been seen in poly(3-octylthiophene) and is assigned there to the effect of a transfer of oscillator strength to a transition involving a higher lying ^1A_g state.[8] In the case of PBZT we have not yet measured beyond 3 eV to see where the corresponding additional transition that should then be expected occurs.

For PBTPV the maxima in EA are found at 2.34, 2.52, and 2.7 eV and minima at 2.42, 2.6 and 2.78 eV (see Figure 4). As for PBZT, there is an offset in the peaks between EA and first derivative spectra, in this case by an amount, 0.02 eV, that is constant across the spectral range studied. Also as for PBZT the ratio of the magnitudes of negative to positive going peaks is enhanced in EA relative to the derivative spectrum. Here, however, the spectral range of the measurement allows investigation to a higher energy relative to the ^1B_u excitation energy. What we find is that the EA goes positive above 2.85 eV in a region where the derivative spectrum is still negative, indicating the onset of a new transition that is not detected in the linear absorption. We assign this to the ^1A_g state that is predominantly responsible for the red shift of the ^1B_u exciton. Again, more extended studies are required to fully characterise this state.

Analysis[9] of the EA data for both PBZT and PBTPV within the model of Weiser[5] allows extraction of the change in polarisability accompanying the ground state to ^1B_u exciton transition and also allows an estimate of the exciton radius. For PBZT we find a Stark shift of 39 μeV at 35 kV/cm applied field, which corresponds to an average change in polarisability of 6.4×10^{-18} eVm^2/V^2 and an effective exciton radius of 13 Å. For PBTPV the Stark shift is 57 μeV at 35 kV/cm applied field, which corresponds to an average change in polarisability of 9.4×10^{-18} eVm^2/V^2 and an effective exciton radius of 15 Å. The differences in Stark shift, change in polarisability and exciton radius are all consistent with a more extended π-electron system in PBTPV than PBZT.

We have not been able to compute the Re and Im $\chi^{(3)}(-\omega; 0,0,\omega)$ spectra from the measured EA data because of difficulties in obtaining reliable linear optical constants for these samples. The problem lies in the significant scattering that is present which leads to a poor convergence in our iterative Kramers Kronig analysis routine. We are working on this problem and expect to be able to obtain the $\chi^{(3)}$ data soon.

CONCLUSIONS

In this paper we have reported results for the linear absorption and electroabsorption spectra of the rigid rod polymers poly(*p*-phenylenebenzobisthiazole) and poly(benzobisthiazole-*p*-phenylenebisvinylene). We find a Stark red shift of the lowest ^1B_u exciton for both materials indicating that at least a three level model must be used to describe their electro-optic response. The vibronic structure evident in linear absorption spectra is also evident in the electroabsorption response, again indicating the importance of vibronic contributions in modelling the nonlinearity of conjugated polymers. Analysis of the Stark shift allows an estimate of the change in polarisability accompanying the excitation of the ^1B_u exciton and also of the exciton radius. Further work is necessary to more fully characterise the higher lying ^1A_g state that dominates the Stark red shift.

ACKNOWLEDGEMENTS

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