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# Optical spectroscopy of photoinduced and field-induced excitations in polyacetylene prepared by the Durham 'photoisomer' route

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**Abstract.** We present a study of the optical, electronic and electro-optical properties of polyacetylene prepared by the Durham 'photoisomer' route. This modification of the standard Durham precursor route gives enhanced thermal stability of the precursor, but the resultant polyacetylene is considerably more disordered than that produced from the standard precursor polymer. This is evident in the electronic properties in the increased  $\pi$  to  $\pi^*$  bandgap, with the peak in the optical absorption at 2.6 to 2.7 eV. We show here that electronic and vibrational excitations of the polymer, although affected by the disorder, are not fundamentally changed in character and that, in particular, we still find evidence for electron states associated with soliton defects on the chain, which are of non-bonding character and lie in the centre of the gap. Photoinduced absorption measurements show the 'mid-gap' band to 'soliton' transition associated with charged photoexcitations at about 0.65 eV, significantly higher than that found for better ordered polyacetylene. We observe the doping-induced IR modes at high frequencies (pinned mode above  $1000\text{ cm}^{-1}$ ). We see no evidence for the photoinduced absorption feature seen at 1.35 eV in Shirakawa polyacetylene, and at 1.5 eV in the unoriented standard Durham polyacetylene. The electronic and electro-optical properties of the field-induced charge accumulation layer formed in MIS device structures are also investigated. We calculate from these measurements charge-carrier concentrations in the range  $6 \times 10^{14}$  to  $7 \times 10^{17}\text{ cm}^{-3}$ , comparable with the standard Durham material. We have measured the 'mid-gap' optical absorption band associated with the charge present in the accumulation layer, and we find a broad absorption feature which peaks at 0.9 eV. We discuss the electronic properties of this form of polyacetylene and, in particular, the modelling of disorder on the electronic structure.

## 1. Introduction

There is continuing interest in the nature of the self-localized electronic excitations in conjugated polymers. Calculations for isolated chains show formation of soliton-like excitations for *trans*-polyacetylene, with associated non-bonding electronic states at mid-gap, upon removal or addition of charges [1, 2] (for polyacetylene) and of polarons and bipolarons for systems with non-degenerate groundstates [3, 4]. For polyacetylene, it has been shown that these states can be created through photoexcitation [5], chemical doping [6] and can also be formed via charge injection into accumulation

layers in device structures [7]. Many of the observed optical and vibrational excitations associated with these states are apparently well described by theory [8–11], despite the fact that the experiments have been performed on materials which are far from ideal. The effects of finite chain length and of the associated conformational defects on the electronic excitations remain an important issue. Experimental control of the straight chain length (which is loosely equivalent to the ‘conjugation’ length used by other authors) has not been easy to achieve or to characterize, though there has been considerable work carried out with polyacetylene prepared by the Shirakawa route [12]. We have worked with polyacetylene prepared via a solution-processible precursor polymer, the Durham route [13], and have shown that the nature of the precursor polymer can determine the electronic structure of the polyacetylene eventually obtained [14].

The advantage of using a solution-processible precursor polymer is principally that the polymer can be processed in the precursor phase and converted *in situ* to polyacetylene, which is itself intractable. The most widely used of the precursor polymers, the standard Durham route, is shown as A, B, C and D-PA in figure 1 [13]. The precursor polymer, B, is readily handled in solvents such as 2-butanone, and polyacetylene films of very high quality can be obtained. These have recently been used for the construction of semiconductor devices including MISFETs [7]. The dense Durham polyacetylene can be obtained either as disordered (solution cast or spin-coated) or highly crystalline stretch-oriented films, as was demonstrated by Leising *et al* [15–18].

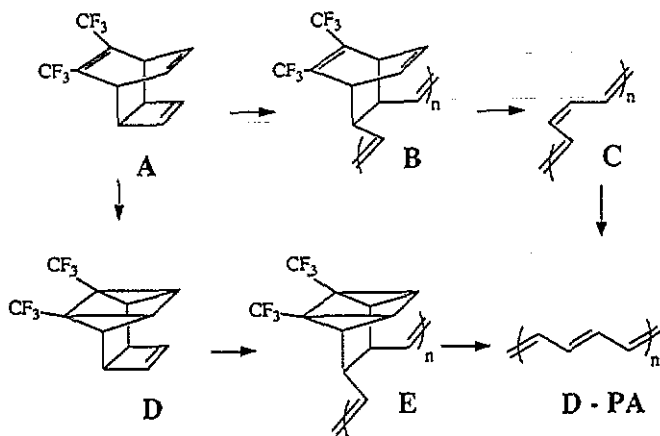


Figure 1. Synthetic routes to polyacetylene. A, B, C is the standard Durham route [13]; A, D, E is the ‘photoisomer’ route [19].

An alternative route (A, D, E, D-PA in figure 1) has been developed by Feast and Winter [19, 20]. In this approach, A is first converted to its photoisomer, D, 3,6-bis(trifluoromethyl) pentacyclo[6.2.0.0<sup>2,4</sup>.0<sup>3,6</sup>.0<sup>5,7</sup>]dec-9-ene, which gives the precursor polymer E on ring-opening metathesis polymerization. We refer to this as the ‘photoisomer’ route. The advantage here over the standard route is that the conversion of the precursor polymer to polyacetylene is no longer symmetry-allowed so that the precursor is thermally stable at room temperature, with conversion to the final polyacetylene conveniently carried out at between 100 and 120 °C [14]. There are

disadvantages with this route. First, the elimination reaction is strongly exothermic [20] and there is risk of thermal runaway (or explosion) if bulk samples or thick films are converted, though dilute solutions and thin films of the precursor can be handled safely. Second, the resultant polyacetylene shows evidence for increased disorder [14]. There is evidence from IR and XPS measurements for retention of fluorine in the thermally treated polymer, and it is considered that this is due to the opening of some of the side-groups on the precursor polymer, rather than their elimination. Polyacetylene produced, as here, in the form of thin unoriented films is highly disordered, with a coherence length for interchain order determined from x-ray scattering of only 1.8 nm. The electronic and vibrational structure of these films is much affected by the disorder, with the peak in the  $\pi$ - $\pi^*$  optical absorption band at 2.65 eV, and correspondingly high Raman-active vibrational modes [14]. We report here an investigation of the electronic and vibrational excitations achieved through chemical doping, photoexcitation of electron-hole pairs, and by charge injection to form a charge accumulation layer in MIS structures. Our interest in this is to learn how the differences in structure affect the elementary excitations of the chain, and we have used as a further experimental variable the control of the precursor polymer chain length that can be achieved with the addition of a chain transfer agent in the precursor polymer synthesis [14].

Measurements of the optical properties of polyacetylene provide important characterization of the electronic structure; we now list these.

(1) The position of the  $\pi$ - $\pi^*$  interband optical absorption is found to vary with the level of disorder, with peak absorption at just below 2 eV for oriented Durham and Shirakawa polyacetylene [21], at 2.3 to 2.4 eV for unoriented Durham polyacetylene [21], and at 2.6 to 2.7 eV for unoriented photoisomer polyacetylene [14]. The effect of disorder on the bandgap has been modelled within the framework of the Peierls electron-phonon coupling model [22] by a modified effective electron-phonon coupling constant [14].

(2) Optical transitions are observed at approximately one-half of the bandgap, attributed throughout the literature to transitions between the  $\pi$  or  $\pi^*$  band states and the non-bonding states associated with the self-localized soliton-like excitations on the polymer chain. The position of this absorption band depends critically on the order of the material and on the presence or absence of counter-ions (dopants). For photoinduced charges, it is observed at about 0.45 eV for the better ordered samples (Shirakawa and oriented Durham), at about 0.55 eV for the disordered samples (Durham) and at considerably higher energies for charges introduced through chemical doping [21]. The shift in this feature with increasing disorder can also be seen from the formation of accumulation layers in MIS (metal-insulator-semiconductor) device structures with different insulator layers [7, 23, 24].

(3) There are vibrational modes which become IR-active for charged excitations through symmetry breaking, and arise through coupling of the translational motion of the charge on the chain to those modes of the unit cell that modulate the amplitude of the bond dimerization [22]. These infrared active vibrations (IRAV) are seen with doping, photoexcitation and charge injection in MIS structures. The frequencies of these IRAVs give information about disorder such as that due to Coulomb interactions due to dopant-counter-ions [9, 25, 26].

(4) A further absorption band, in addition to the 'mid-gap' soliton to band edge feature, is seen in measurements of photoinduced absorption, at around 1.35 eV [27]. This high-energy (HE) peak has been assigned to neutral excitations on the chain, and it has been shown that its appearance upon photoexcitation depends strongly on the type

of polyacetylene used; it has thus been assigned to an extrinsic, or disorder-related, feature [28, 29]. This excitation is not described by one-electron models, and there have been proposals that this excitation is the  $A_{2g}$  excited state lowered by Coulomb interactions below the  $B_u$  state [30]. We note that the study of materials with different types of disorder can help to distinguish between extrinsic and intrinsic excitations, and our studies here on the photoisomer-route polyacetylene suggest that this excitation is indeed extrinsically stabilized.

## 2. Experimental details

The preparation of the precursor solutions of different average molecular weight and the subsequent preparation of the thin films of polyacetylene have been described [14, 20]. Conversion conditions were usually 3 to 5 h at temperatures between 100 and 120 °C. All sample-handling, storage, doping and measurements were performed in either inert Ar atmosphere or in high vacuum. We used wide-field-spectrosil (WFS) substrates for UV/visible measurements and KBr for IR measurements. MIS devices were fabricated with doped Si substrates with thermally grown oxide as the insulator layer or WFS substrates with semi-transparent metal bottom-contacts and either  $SiO_2$  (electron-beam evaporated) or  $Si_3N_4$  (CVD) as insulators on top. After spin-coating and conversion of the polymer these devices were finally covered with a semi-transparent Au top-contact. Film thicknesses were usually several 100 Å for the device structures and films of optical density at the peak of the absorption between 0.5 and 3 (typically 1) for the other samples. Most films have been prepared from the precursor with a very high average molecular weight ( $M_n = 56\,000$ ,  $M_w = 96\,000$ ,  $M_w/M_n = 1.72$  [14]) as these give films of the best quality.

Optical measurements were performed with a Perkin-Elmer  $\lambda$ -9 spectrophotometer or in the dispersive monochromator arrangement which we have also used for the temperature-dependent optical measurements and the photoinduced absorption. Different lines (mainly 457.9 nm = 2.7 eV) of a mechanically chopped CW Ar<sup>+</sup> laser served as pump source for the photoinduced absorption and the samples were mounted in an Oxford He cryostat. We have made these measurements at different temperatures, pump intensities and chop frequencies. For the IR measurements we have used a Nicolet FTIR spectrometer, and for this work the samples were vapour-phase doped with iodine. The electrical and electro-optical measurements on the MIS structures were again made in a He cryostat which was placed in a dispersive monochromator setup where we could also carry out the electrical impedance analysis (HP 4192A LF Impedance Analyser). The probe beam for the MIS electromodulation measurements and also the photoinduced absorption measurements was provided by a W lamp, dispersed with a grating monochromator and detection using standard lock-in techniques was made with a range of Si, Ge, InSb and InAs photodetectors.

## 3. Optical absorption

Figure 2 shows the optical absorption, measured as  $-\log(\text{transmission})$ , of a film of polyacetylene prepared with the high molecular weight precursor at room temperature. The peak of the interband absorption is at about 2.6 eV, in comparison to about 1.9 eV for Shirakawa and oriented Durham and about 2.4 eV for the standard Durham

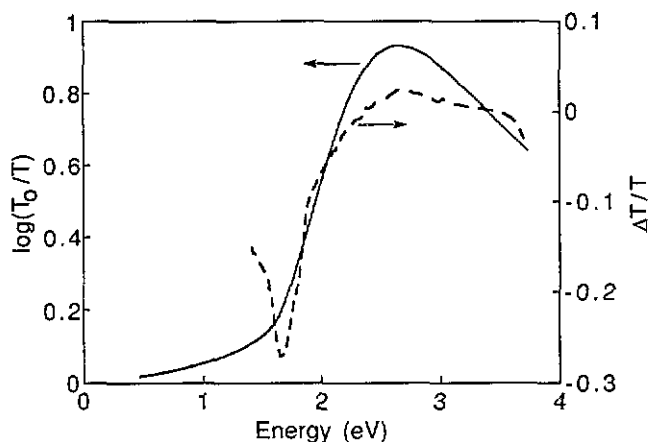


Figure 2. Optical absorption (measured as  $-\log(\text{transmission})$ ) of a spin-coated film of high molecular weight photoisomer polyacetylene. Also shown is the temperature derivative of the transmission,  $-\{T(300\text{ K}) - T(45\text{ K})\}/T(300\text{ K})$ .

polyacetylene [29, 31, 32]. The absorption band is very much broadened from that found for the better ordered forms of polyacetylene, and there is still a clear onset for strong absorption at around 1.5 eV. We consider that this broadening is due to the distribution of the local bandgap on chains with different degrees of disorder. We note that the measured transmission indicates that there is a tail into the IR extending as low as 0.5 eV. The origin of this tail is not well understood, and we stress that we have not made corrections here for reflectivity. The temperature dependence of the absorption has been measured by direct comparison of the absorption spectra at room temperature (300 K) and at low temperature (45 K), and is also shown in figure 2. The shift of the absorption edge with temperature is similar to that found for standard Durham polyacetylene [29], with increased absorption at low temperatures on the low-energy side of the absorption band and decreased absorbance at higher energies. The energy at which the thermal derivative changes sign is found here to be at 2.35 eV, although this value is not easily determined because it is hard experimentally to avoid shifts in the measured transmission on different runs, and we do not set great reliance on this figure. It is useful to measure the magnitude of the thermal modulation of the absorption in order to check whether it can contribute to the photoinduced response. We find, as reported previously for unoriented films produced from the standard Durham precursor [29], that thermal modulation has a negligible effect under the experimental conditions used here.

#### 4. IR absorption, doping

Measurements of the IR absorption have been used to control the conversion conditions from the photoisomer precursor polymer to the polyacetylene films, to characterize them, and to monitor their quality [14]. Here we have carried out iodine doping of films of two different batches of precursor polymer, one with high average molecular weight ( $M_n = 56\,000$ ,  $M_w = 96\,000$ ,  $M_w/M_n = 1.72$ ) and the other of a low to medium value ( $M_n = 23\,000$ ,  $M_w = 41\,000$ ,  $M_w/M_n = 1.78$ ), labelled respectively as H and L.

Figure 3 shows the changes in absorption due to doping with iodine at room temperature. The characteristic IRAVs of the polyacetylene chain are observed, although the frequencies of these modes are shifted to higher values than those found for more ordered polyacetylene. The peaks are at  $1030$ ,  $1289$  and  $1432$   $\text{cm}^{-1}$  for the H-polymer and at  $980$ ,  $1289$  and  $1417$   $\text{cm}^{-1}$  for the L-polymer. The lowest of the three modes is found, in principle, at zero frequency in the absence of the disorder, and is therefore found at finite frequency as a result of disorder [22]. The values of  $980$  and  $1030$   $\text{cm}^{-1}$  are considerably higher than those found elsewhere. Usually this peak is observed around  $500$   $\text{cm}^{-1}$  upon photoexcitation and around  $900$   $\text{cm}^{-1}$  upon doping [8, 9, 21, 26, 33-35]. This observation is a clear indication of the high level of disorder in the material, which is due here to the combination of the structural disorder of the chains and the Coulomb potential due to the iodide counter-ions. The shifts in position of the other two modes are less marked, as expected [22].

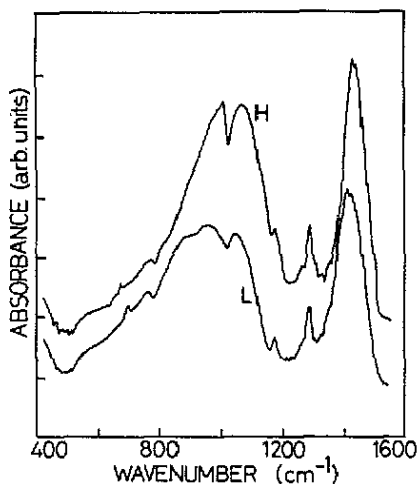


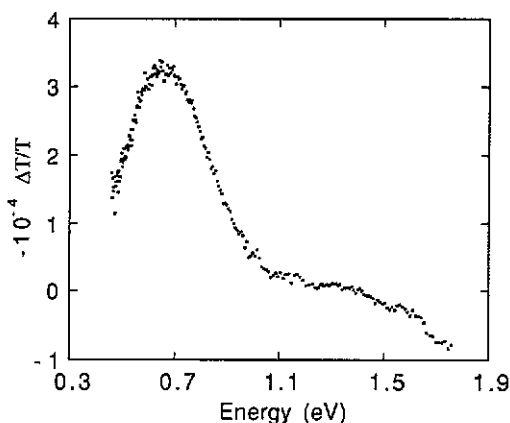
Figure 3. IR absorption spectra for two iodine-doped samples prepared from precursor polymers of high (H) and medium/low (L) molecular weights.

## 5. Photoinduced absorption

We have measured the photoinduced absorption for polyacetylene prepared from the high molecular weight precursor. Optical densities at the peak of the  $\pi$ - $\pi^*$  interband transition were chosen to be in range 0.8 to 1.5, with lower values for measurements in the region of the interband absorption, and higher values for measurements at lower energies. Measurements on different samples, at different pump intensities, chop frequencies and temperatures as well as the use of different detectors with overlapping spectral ranges allowed us to get a clear and consistent picture of the photoinduced processes in this material.

Figure 4 shows the spectral dependence of the photoinduced change in transmission of a sample with optical thickness of about 1.5 at 2 eV. The mid-gap transition is at 0.65 eV, as observed in all samples, and we note that this value is higher than

in standard unoriented Durham polyacetylene (0.55 eV) [29] and in better ordered material (around 0.45 eV) [8, 9, 25, 33]. In comparison with the standard Durham unoriented films, the mid-gap transition here is of about the same width and magnitude [29], and we also obtain very similar signal variations with temperature, chop frequency and pump intensity, as shown in figures 5 to 7. The temperature dependence in figure 5 shows an onset to a rapid decrease at about 190 K, with the signal vanishing in the noise at about 270 K. The chop frequency dependence in figure 6 shows that the charged excitations that are responsible for the mid-gap transition are very long-lived. With decreasing chop frequency we observe an increase in the signal even at frequencies below 10 Hz. We have also made preliminary measurements of the temperature, frequency and intensity variation at the energies of 1.5 and 2 eV (bleaching). The behaviour is very similar to that of the mid-gap transition, as also observed for the standard Durham material [29], with minor differences in the chop frequency dependence.



**Figure 4.** Photoinduced absorption at 50 K; pump intensity approximately  $150 \text{ mW cm}^{-2}$  at 457.9 nm (2.7 eV) and 19 Hz chop frequency.

We have checked all our measurements very carefully for any sign of major temperature effects. The data shown in figure 2, show a sharp peak of 'thermal bleaching' at about 1.65 eV and a broad 'thermal absorption' peak at the high-energy side of the former, with a crossover at 1.8–1.9 eV. This is very similar to the thermal modulation spectrum for standard Durham unoriented polyacetylene, with a blue shift of about 0.25 eV for the photoisomer. None of our measurements of the photoinduced absorption on the (rather thin) samples of the photoisomer polyacetylene shows any structure similar to that of the thermal modulation of the absorption spectrum.

Figure 4 shows, besides the mid-gap absorption, two further results of interest: there is no 'high-energy' absorption feature peak, seen at 1.35 eV in Shirakawa polyacetylene [5, 10, 33], and at 1.5 eV in unoriented standard Durham polyacetylene [29], and the onset of the bleaching is at about 1.35 eV, very much lower than that usually observed [29, 33]. The high-energy feature has been shown to be associated with a neutral excited state [5, 10], and there has been considerable discussion as to its origin [36]. Measurements on Durham polyacetylene have indicated that the excited state probed at long times is extrinsically stabilized; oriented films show no



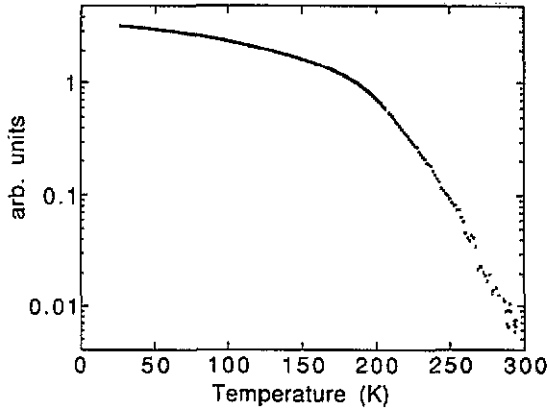


Figure 5. Temperature dependence of the photoinduced absorption at 0.6 eV; 9 Hz chop frequency, approximately  $150 \text{ mW cm}^{-2}$  pump intensity at 457.9 nm.

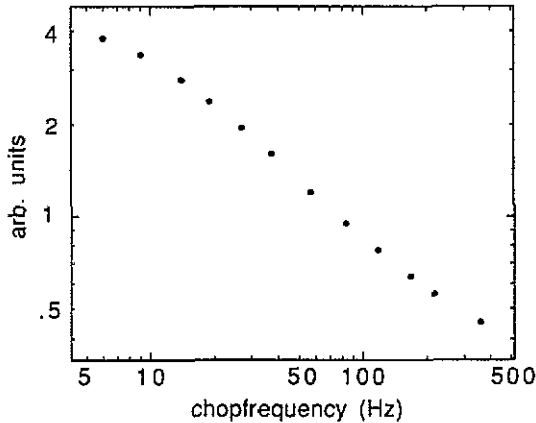


Figure 6. Chop frequency dependence of the photoinduced absorption at 0.6 eV at 45 K; approximately  $150 \text{ mW cm}^{-2}$  pump intensity at 457.9 nm.

preferred polarization of the induced absorption indicating that the excited state is present in an unoriented region of the sample [28], and the size of the response is very strongly dependent on the treatment of the polymer, with a very weak response for the better ordered stretch-oriented samples than for the unoriented films [29]. In this respect, it is perhaps surprising that we do not see the high-energy feature in the photoisomer material, as it is more disordered than the standard Durham route materials. However, it has been noticed that increased temperatures for the conversion and isomerization from the precursor polymer to polyacetylene (e.g. from 80 to  $100^\circ\text{C}$ ) result in a greater degree of local order [37] and also a decreased high-energy feature [29], whereas the optical absorption shows almost no change [38]. Because of its increased thermal stability, the photoisomer precursor requires temperatures above about  $100^\circ\text{C}$  to start conversion to polyacetylene. Furthermore, this elimination reaction itself is strongly exothermic. Therefore we have conversion temperatures well above  $100^\circ\text{C}$ , and it is possible that these temperatures are sufficient to remove the

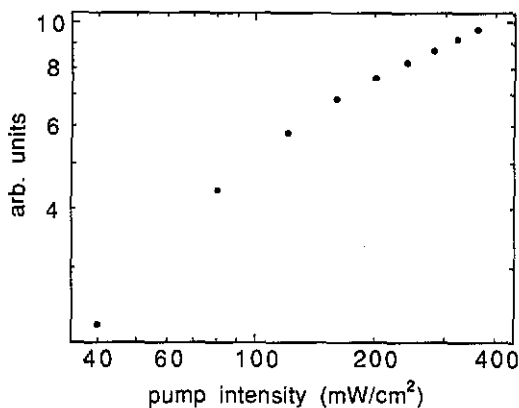


Figure 7. Intensity dependence of the photoinduced absorption at 0.65 eV, 457.9 nm pump wavelength, 50 K, 9 Hz.

extrinsic defect which stabilizes this excited state.

The onset of bleaching at about 1.35 eV, which holds for all of our samples, occurs at considerably lower energies than that found in other forms of polyacetylene (between 1.6 and 1.8 eV). We expect that the excited charges will be stored in states of lowest potential energy, and at the relatively low values of charge concentration found under these experimental conditions, these charges can migrate to the small fraction of the polymer with the lowest bandgap. If there are states associated with disorder within the gap, then it is possible that these may be involved in charge storage. This proposal has been made in relation to the spin half defects found in Shirakawa polyacetylene, for which the charge storage process is then considered as ionization of pairs of such defect states [39]. There is evidence in some samples of Shirakawa polyacetylene for photoinduced bleaching below the bandgap, at 1.35 eV, which is considered to be bleaching of the optical transitions of the uncharged spin defects [5, 39], though other samples of Shirakawa polyacetylene show only bleaching above the band edge [33], as also is the case for unoriented Durham polyacetylene [29]. The transition to bleaching observed here at such a low energy (though the peak in the bleaching response is in a broad band near 2 eV) is not readily explained.

## 6. MIS field effect devices

It has been shown that MIS devices provide a very useful tool for the investigation of polymeric semiconductors [7, 23, 24]. We have carried out capacitance against bias voltage ( $C$ - $V$ ) measurements to determine the extrinsic charge-carrier concentration ( $N_a$ ) and electro-optical measurements to investigate the behaviour of charged excitations in the polymer, formed in accumulation layers in the MIS device.

Figures 8(a) and (b) show the capacitance against bias voltage behaviour, including hysteresis effects, for MIS devices fabricated with different batches of the photoisomer polyacetylene. For the sample shown in figure 8(a) we have used a precursor polymer with a high average molecular weight (H, see above) which was prepared with a highly purified (oxygen and water-free) solvent (2-butanone). The solvent used for the sample in figure 8(b) was purified in a standard way and the precursor with the medium/low average molecular weight (L, see above) was used. Both curves show the typical

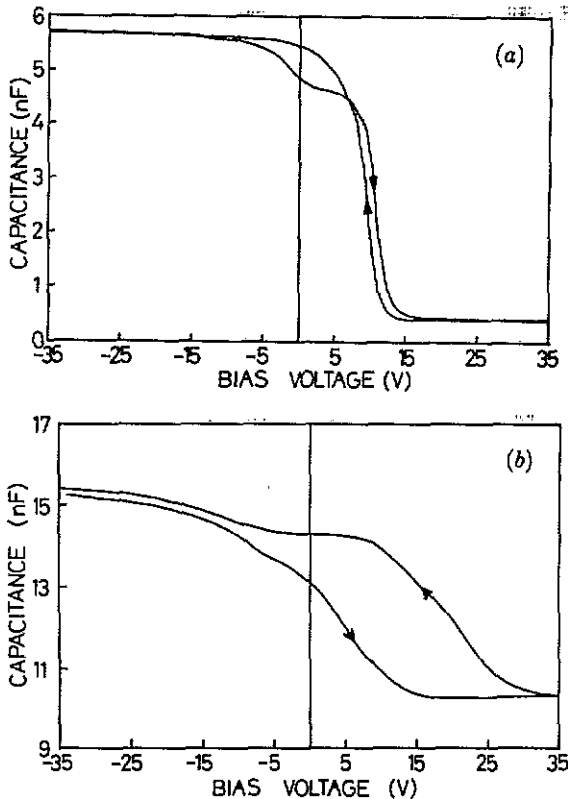


Figure 8. Differential capacitance against bias voltage for two different samples: (a) prepared with a high molecular weight precursor; and (b) with a medium/low molecular weight precursor (see text). Conditions of measurement were similar for both samples; AC modulation of 0.5 V and 50 Hz; sweep rate of 6 V min<sup>-1</sup>; direction of the sweeps see arrows in the curves; the samples were kept 5 min at either -35 V or +35 V before the start of the scan, depending on the direction (i.e. -35 V for the scans from negative to positive bias voltages). (The low value of the capacitance in depletion in (a) in comparison with (b) is due to differences in the device geometry for the two devices.)

behaviour of a p-type semiconductor with deep depletion (high positive voltages), accumulation (negative voltages) and the transition range (depletion) [40, 41]. From plots of  $1/C^2$  against the bias voltage in the depletion regime we can calculate  $N_a$ , the concentration of charged acceptor ions present in the depletion layer, through the relation [41]

$$\left(\frac{C_i}{C}\right)^2 - 1 = \left(\frac{C_i}{A}\right)^2 \frac{2(V - V_f)}{qN_a\epsilon_r\epsilon_0}$$

where  $A$  is the device area,  $\epsilon_r$  the relative dielectric constant of the semiconductor (taken here to be 2.75) and  $V_f$  the flat-band voltage. For standard Durham polyacetylene, values in the range  $10^{16}$ – $10^{17}$  cm<sup>-3</sup> are found [7, 23, 24] and  $N_a$  in the previous study on the photoisomer was found to be about the same [14]. By the use of precursor polymers of different quality in the present study we have calculated values varying from about  $6 \times 10^{14}$  cm<sup>-3</sup>, figure 8(a) to about  $7 \times 10^{17}$  cm<sup>-3</sup>, figure 8(b)

(we use the same value for the dielectric constant, 2.75, as was used for unoriented standard Durham polyacetylene). Typical values were in the range  $1-3 \times 10^{17} \text{ cm}^{-3}$ , the same as for the standard Durham polyacetylene. We have seen a clear tendency to higher values of  $N_a$  and stronger hysteresis in the  $C-V$  curves with ageing of the once-prepared precursor solutions. Hysteresis in the transition between accumulation and depletion is considered to be due to slow migration of the p-type dopant counter-ions, and is to be very much more severe in MIS devices based on poly(3-alkyl thienylenes) [42]. As can be seen in figure 8 and the calculated values for  $N_a$ , the electrical behaviour of the sample depends critically on the nature and the amount of the extrinsic impurities/dopants, although they have very little influence on the results in the electro-optical analysis (see later).

It has been argued that the unavoidable presence of impurities in this material stems from catalyst residuals from the polymerization of the monomer [14], which gives it its intrinsic doping and the behaviour of a p-type semiconductor. As mentioned, we have obtained lowest concentrations of this doping, of about  $6 \times 10^{14} \text{ cm}^{-3}$ , for the photoisomer. It can be seen from the very small hysteresis in figure 8(a) that these dopants hardly diffuse, which supports the suggestion that these catalyst groups are bound to the polymer chains. Impurities added to the precursor polymer and subsequently to the polyacetylene by solvents, possibly oxygen and/or water, may also dope the material, but are likely to be more mobile to give the strongly increased hysteresis, as in figure 7(b). We have checked the influence of the molecular weight and also the relationship between  $N_a$  and the hysteresis and we consider that the size of the hysteresis is not solely due to the concentration of dopants but depends also on the type of the impurity. We have observed in all of our samples a step in the  $C-V$  curve which is dependent on the direction of the scan, and which occurs just before full accumulation. It has been noticed for similar Shirakawa-polyacetylene MIS devices that such a behaviour is due to either interface states or a bias-dependent carrier concentration [43]. Hysteresis and this step have not been seen in standard Durham polyacetylene and interface states have been shown to be of minor importance [7, 23, 24]. However, interface states and hysteresis, as well as charge injection, are of crucial interest [44-46]. A detailed characterization of the electrical properties of these effects (interface states, hysteresis, mobile dopants, frequency and temperature effects), including the photoisomer polyacetylene, is in progress.

Figure 9 shows the 'mid-gap' soliton to band optical transition in a MIS device, measured from the change in optical transmission with gate voltage on the MIS device (i.e. with the formation of an accumulation layer at negative biases and the depletion at positive biases.) The sample was prepared on a  $\text{SiO}_2$  insulating layer and the 'mid-gap' absorption feature is broad, but peaks at about 0.9 eV. (The values which we have found for other samples on  $\text{SiO}_2$  insulator layers are between 0.9 and 0.95 eV, without a clear correlation to the precursor polymer used. This slight variation in the peak energy is presumably due to the presence of a different degree of order at the interfaces.) This value of 0.9 eV is 0.1 eV higher than that reported for standard Durham polyacetylene on the same insulators [7, 23, 24], and we consider that this corresponds to the higher degree of disorder in the material used here.

We have also observed a slight shift of the peak towards higher energies with increasing negative bias voltage. It has been suggested that this is due to a stronger confinement of the accumulation layer at the  $\text{SiO}_2$ -polymer interface at higher biases, as the disorder is very likely to increase near the interface of these two very different materials [7]. This is also consistent with the fact that the 'mid-gap' transition

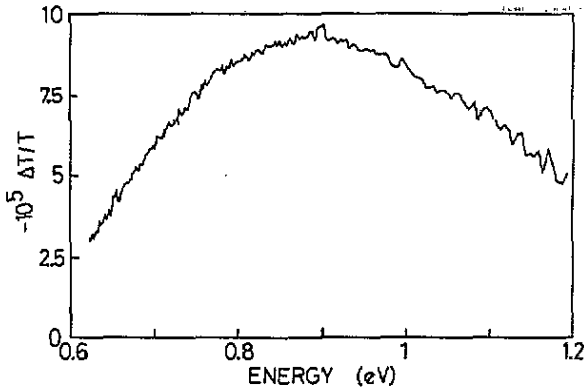


Figure 9. Change in transmission of the polymer layer in a MIS device upon applied oscillating electrical field; no bias voltage, oscillating voltage of 10 V (peak-to-peak) at 390 Hz, room temperature.

appears at lower energies when polymers (PMMA, polyamide) are used as insulating layers [23, 24].

Figure 10 shows the bias voltage dependence of the low-energy peak (at 0.9 eV) in the electro-optical experiments on the MIS devices. It has been found in standard Durham polyacetylene that this bias dependence closely matches the  $C-V$  curve from the electrical characterization of the devices [7], which indicates that charge injected into the accumulation layer is all stored in soliton-like states which cause the 'mid-gap' optical absorption. However, as mentioned, hardly any hysteresis effects have been found in the standard Durham polyacetylene. Here we observe a broad transition in the bias dependence of the electromodulation and we notice that the width and position of the transition region (from about  $-10$  V to about  $+5$  V in figure 10) matches the range where we have found hysteresis in the differential capacitance, as shown in figure 8. The width of the transition is greater in samples with larger hysteresis effects. This is very likely to be caused by a shift of the flat-band voltage [40] due to the movement of ionic charge.

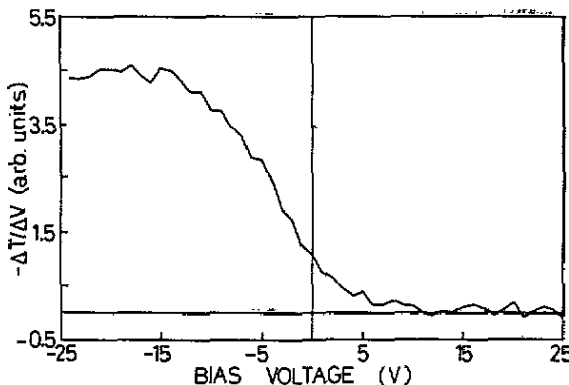


Figure 10. Bias voltage dependence of the change in transmission in a MIS device at 0.9 eV; AC voltage of approximately 4 V peak-to-peak at 270 Hz; room temperature.

## 7. Electronic structure in disordered polyacetylene

The measurements presented here demonstrate clearly that the excited states produced through chemical doping, photoexcitation or charge injection in MIS devices all show the characteristics of the 'charged solitons' that are seen in well-ordered polyacetylene. However, the polymer produced by the photoisomer precursor route is known to be very much more disordered, and the characteristic optical responses of the charged solitons found here are all shifted to higher energies in comparison with those for the well ordered materials.

**Table 1.** Comparison between energies of the optical transitions for the ground ( $\pi \rightarrow \pi^*$ ) and excited ( $\pi \rightarrow S^+$ ,  $S^- \rightarrow \pi^*$ ) states for polyacetylene produced by the various Durham precursor routes.

	Stretched Durham <sup>a</sup>	Unoriented standard Durham <sup>b</sup>	Unoriented photoisomer Durham <sup>c</sup>
$\pi \rightarrow \pi^*$ peak	1.9 eV	2.3 eV	2.65 eV
$\pi \rightarrow S^+$ , $S^- \rightarrow \pi^*$ measured in photoinduced absorption	0.45 eV	0.55 eV	0.65 eV
$\pi \rightarrow S^+$ in MIS structures formed with SiO <sub>2</sub> as insulator	—	0.8 eV	0.9 eV

<sup>a</sup> Data from [21].

<sup>b</sup> Data from [7, 23, 25].

<sup>c</sup> This work.

Disorder in the polyacetylene prepared from the photoisomer precursor is characterized by retention of fluorine after thermal conversion of the precursor, and it is postulated that the conversion reaction from the precursor may result in ring opening in such a way that the trifluoromethyl groups which remain are directly attached to the conjugated chain [14]. We would expect that such trifluoromethyl groups would have a strong electron-withdrawing interaction with the  $\pi$  electron system on the chain. However, we think that a more significant effect on the electronic structure will arise through the structural disorder that these groups introduce, and we note that x-ray measurements show directly that there is reduced crystallinity in this material [14]. In order to model the effect of disorder on the electronic structure we would need to have very detailed information about the nature of the disorder. Termination of conjugation by a  $sp^3$ -bonded carbon [12], for example, will have a much more severe effect on the electronic structure than a conformational defect of the chain (bend or twist) that weakens, but does not destroy, conjugation.

The question of basic interest is whether the 'soliton' excitation, which is calculated for the long chain, can survive in the presence of disorder, or whether the broken symmetry confines the soliton-antisolitons to polarons. In the context of the optical excitations which are measured here, the distinction between 'soliton' and 'polaron' is defined by the survival of the single 'mid-gap' state, or its splitting to form a pair of gap states. We find here that the 'mid-gap' state does survive, even though the nature of the delocalization of the  $\pi$  electrons is strongly affected by the disorder present, as

measured by the increase in the energy gap between  $\pi$  and  $\pi^*$  states, and in the energy of the 'mid-gap' to band edge transitions. We have found similar trends in the comparison between photoexcitations in stretch-oriented and unoriented standard route Durham polyacetylene [25], and also in the measurements of the accumulation layer in MIS structures, with control of disorder in the surface layer of the polyacetylene through choice of the insulator layer [23, 24].

We have previously shown that the parameterization of disorder through an effective electron-phonon coupling constant,  $\lambda$ , within a simple Peierls model for the dimerization and bandgap, first suggested by Horowitz *et al* [47], is able to model the effects of disorder over the very wide range of strength of disorder encountered in the various Durham route materials [14, 23]. The results obtained here thus provide yet further extension of the applicability of this phenomenological characterization of disorder. Thus, we find that the energy of the 'mid-gap' optical transition is increased by disorder over the value found for well ordered material by the same factor as that by which the  $\pi$ - $\pi^*$  interband transitions are raised. This is summarized in table 1. The task still remains to derive this phenomenological law from microscopic models for the disordered polymer chains.

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