Structural and morphological investigations of oriented Durham polyacetylene

M. M. Sokolowski, E. A. Marseglia and R. H. Friend
Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

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Trans-polyacetylene films have been synthesized via the Durham precursor route, and have been oriented by application of stress during preparation from the precursor polymer. X-ray and electron diffraction measurements show that these Durham polyacetylene films are composed of crystallites that are highly oriented about the fibre axis. The crystallite size perpendicular to the chains and the nature of the lateral packing have been derived from a line profile analysis of *hk*0 reflections according to the paracrystalline model. The results have been verified by direct Fourier synthesis of the observed intensities of *hk*0 reflections.

(Keywords: polyacetylene; Durham route; stress alignment; orientation; crystallite size; lattice distortions; paracrystalline model)

INTRODUCTION

The polyacetylene (PA) chain is the simplest example of an extended system of conjugated carbon bonds and possesses numerous interesting optical and transport properties[1], the correlation of which to morphology and structure has been the subject of intensive research on PA over the last decade.

Morphology and structure are in turn strongly dependent on the specific conditions that have been used to prepare PA. At present there are two substantially different routes for PA synthesis. In the Shirakawa route, a net of randomly oriented fibrils (100–500 Å in diameter) is obtained by direct polymerization of acetylene gas on a Ziegler–Natta catalyst[2]. In contrast to this the Durham route utilizes a soluble precursor polymer that is cast into films and thermally transformed into PA[3]. Unoriented *trans*-PA films made by the Durham route are in a highly disordered crystalline state with short sequences of conjugation within a polymer chain of high molecular weight. Evidence for this comes from X-ray diffraction, e.s.r. and Raman spectroscopy[1,4]. Orientation of the chains along a specified direction can be brought about by stress alignment[5–7]. In Shirakawa PA the stress is applied to the crystalline material[3], but in Durham PA it is possible to apply stress during the transformation reaction from the amorphous precursor polymer, and thereby achieve more control of the orientation process. This orientation in Durham PA was first observed by electron microscopy[5], in thin films of precursor polymer cast on to electron microscope grids. The stress field was then generated by contraction of the film with weight loss during the transformation reaction. Subsequently, it was shown that free-standing precursor films could be stretch-aligned[6,7]. Under appropriate conditions these oriented films exhibit the characteristics of unstressed Shirakawa PA, i.e. longer conjugated sequences, as shown in the motionally-narrowed e.s.r. linewidth, and the resonance Raman spectrum shifted to lower frequencies[8].

In view of these two very different methods for synthesis and alignment it is important to investigate the consequent differences in structure and morphology. This paper includes results on oriented Durham PA, and it is shown that the lateral packing of PA chains can be described by a one-phase paracrystalline model. Data are also included on the degree of orientation and results are compared with those published for Shirakawa PA.

EXPERIMENTAL

Solid precursor films cast from acetone solution were clamped in a stretching apparatus and transformed under vacuum. Transformation at suitable temperatures allowed sufficient time for the films to be stretched under an appropriate stress load to final stretch ratios L/L_0 of 3–20. The films were then isomerized, still under stress, to fully *trans*-PA at 75–100°C. The resulting films are fully dense and are a few micrometres in thickness[1].

X-ray diffraction photographs were taken with Ni-filtered CuKα radiation, on a standard Weissenberg camera used as a cylindrical camera without screens. Transmission X-ray diffraction scans were performed on a Siemens single-crystal AED diffractometer. For scans along the equator (*hk*0 reflections) a sample composed of 12 aligned film layers was used. Measurements were carried out at room temperature in air. A diffuse amorphous peak at $2° < \theta < 7°$ was observed to develop owing to the presence of oxygen, but there was no observable change in the intensities of any of the peaks of interest with time, so that degradation of the sample by oxygen was assumed to be negligible for the purposes of this experiment. The instrumental broadening was estimated from Debye–Scherrer lines of Cu to be 0.4° in θ. The intensities were corrected for Lorentz and polarization factors but no corrections were made for absorption or Compton scattering.

Room temperature transmission electron microscopy was carried out with a Siemens Elmiscop 102. Only very low beam currents were used owing to the sensitivity of the sample so that exposure times of about 100 s were required.

RESULTS AND DISCUSSION

Crystal structure

The X-ray and electron diffraction diagrams of *Figure 1* and *Figure 2* show the typical fibre pattern of a material composed of uniaxially oriented crystallites. The broadening of the Bragg reflections is due to the finite size of the crystallites and disorder, and the arcing to the limited orientation of the crystallites along the orientation (fibre) axis. A diffractometer scan perpendicular to the fibre axis along the $hk0$ (equatorial) reflections is presented in *Figure 3*. Using both the films and the diffractometer scans the reflections can be indexed by an orthorhombic unit cell of parameters $a = 7.26$ Å, $b = 4.24$ Å and $c = 2.47$ Å, where the chain axis runs along the c-axis. *Table 1* compares the observed and calculated d-spacings of the equatorial reflections measured from *Figure 3*. The ratio $a^2/b^2 = 2.93$ is very close to 3, which indicates that the lateral packing of the PA chains is similar to close hexagonal packing of smooth cylinders. The exact value of a^2/b^2 is important in so far as it determines the number of next neighbour chains, $a^2/b^2 > 3$ giving two next neighbour chains and $a^2/b^2 < 3$ giving four next neighbour chains[9]. Our lattice parameters are in good agreement with published values for both Durham and Shirakawa polyacetylenes[10–15], which are listed in *Table 2*. However, the spread in these values is considerably larger than the experimental error, and values of a^2/b^2 both below and above 3 are observed. No satisfactory explanation of this fact has been provided up to now.

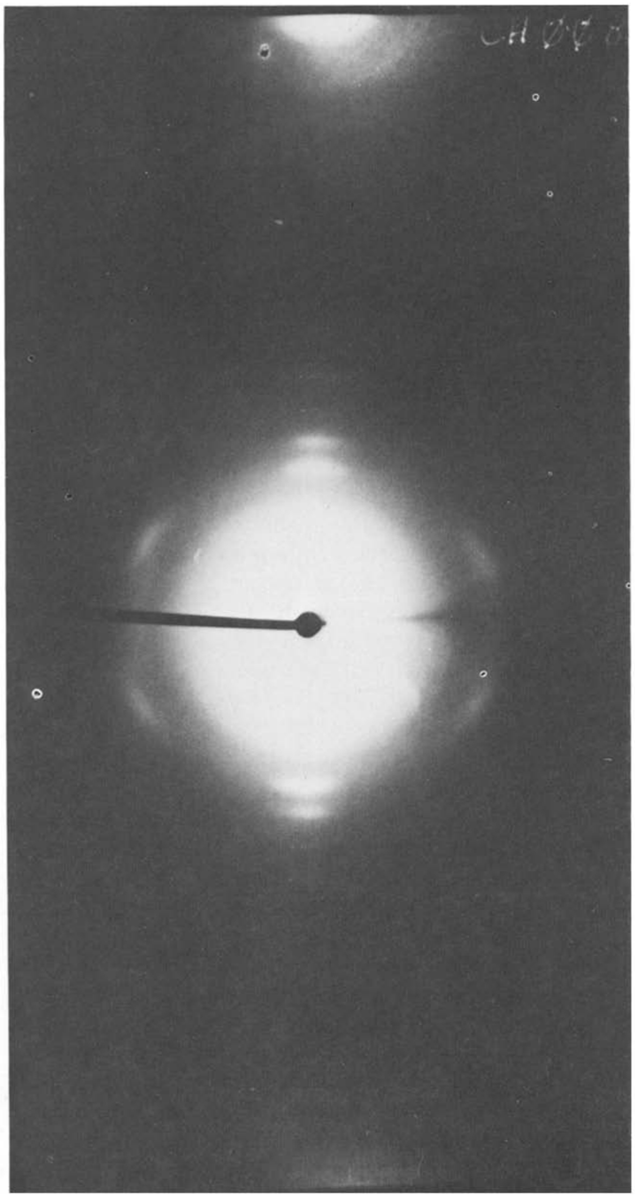

Figure 1 X-ray photograph of oriented Durham PA. The direction of applied stress is vertical, the final stretch ratio is 3

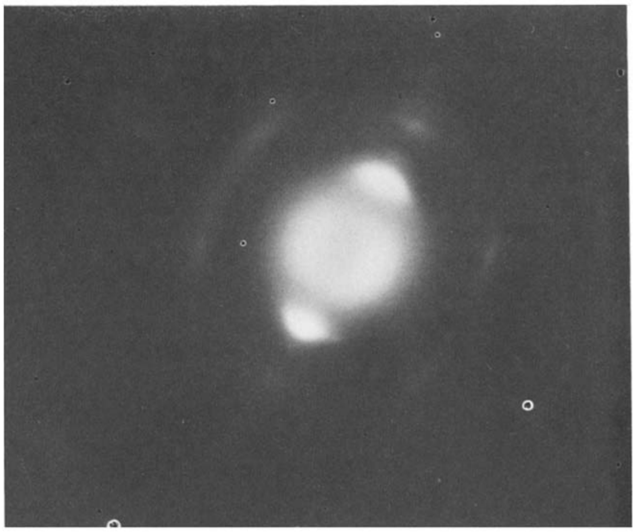

Figure 2 Electron diffraction pattern of oriented Durham PA. The apparent difference in spacings from those in *Figure 1* is due to the difference in geometries of the two cameras

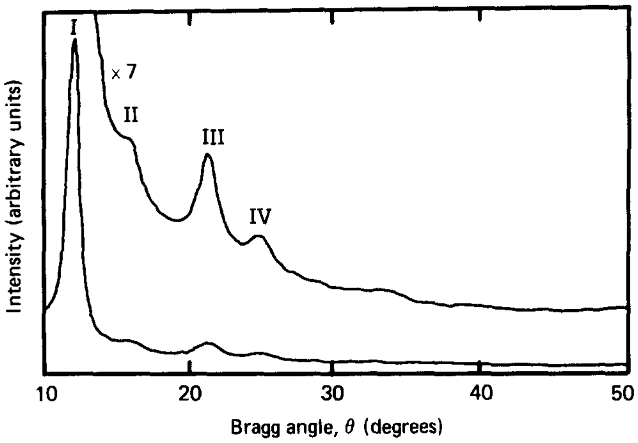

Figure 3 Diffractometer scan along the equator ($hk0$ reflections) of oriented Durham PA. $\lambda = 1.54$ Å. See *Table 1* for I–IV

The extinction rules identify a lateral packing according to the 2-D space group *pgg* (herring bone structure), see *Figure 4*. The setting angle, ϕ (the angle between the CH-backbone and the a–c plane), was estimated by the method[10] of comparing measured intensities of $hk0$ reflections with $D^2|F(\psi)|^2$, where D is the Debye–Waller factor $\exp\{-B(\sin^2\theta/\lambda^2)\}$ and F is the calculated structure factor. A reasonable match was obtained at $\theta = 55°$ and a value for $2B$ of 15 Å^2. This unusually high value for $2B$ is required to match the strong decrease of observed intensities towards higher values of θ, the origin of which will be discussed later in this paper. Considerable disagreement exists in the literature concerning the full space group of PA[10,11,16].

Table 1 Values of observed and calculated d-spacings of equatorial reflections corresponding to *Figure 3*

No. of refl.	hkl^a	d_{obsd} (Å)	d_{calc} (Å)
I	110	3.65	3.66
	200		3.63
II	210	2.80	2.76
III	020	2.11	2.12
	310		2.10
IV	220	1.82	1.83
	400		1.82
V	320	1.59	1.59
VI	130	1.40	1.39
	420		1.38
	510		1.37

[a] The reflections 210 ($d = 2.04$ Å) and 140 ($d = 1.69$ Å) are not detected as their structure factors are smaller by a factor of about 10 than those of the next neighbour reflections

Table 2 Comparison of values published for the lattice parameters a and b of *trans*-PA

Reference	PA type	a (Å)	b (Å)	ab (Å^2)	a^2/b^2
Shimamura[10]	S	7.32	4.24	31.04	2.98
Fincher[11]	S	7.32	4.24	31.04	2.98
Robin[12]	S	7.45	4.08	30.40	3.33
Perego[13]	S	7.38	4.09	30.18	3.26
Lieser[14]	D	7.20	4.20	30.24	2.94
Lieser[15]	D	7.34	4.18	30.68	3.08
Sokolowski[a]	D	7.26	4.24	30.78	2.93

[a] Data of the present work

For the dimerized chain with an alternating carbon bond length (Peierls distortion) the loss of the mirror plane perpendicular to the chain axis requires a space group of lower than orthorhombic symmetry, i.e. monoclinic. The two possibilities for the bond alternation on adjacent chains, being in or out of phase, and the possibility of exchanging the symmetries of the projections on to the a–b and a–c plane by a shift of the central chain of $c/2$ allows construction of four monoclinic space groups consistent with the 2-D space group *pgg*[17]. Perego *et al.*[16] have made the interesting suggestion that *trans*-PA is composed of regions with two different types of packing with the bond alternation being respectively in and out of phase, resulting in an overall space group *Pnam*. This would require chains to shift one against the other, which is quite possible, as the chains have a nearly uniform cross section. Nevertheless, although these shifts may be considerable they are not continuous, as the latter would smear out the *hkl* reflections into a uniform intensity along the first layer and this is *not* observed. Using formulae developed for the paracrystalline model[18] the mean square displacement of adjacent chains along the chain axis can be estimated for our materials to be about 12%, assuming, reasonably, that the layer lines are discontinuous up to the second layer (see *Figure 1*). A sufficient determination of the full space group can be obtained only from high quality X-ray diffraction data of upper layers and an analysis that makes allowances for the effects of finite crystallite size, lattice distortions and limited orientation on the intensity, shape and width of the reflections.

As mentioned above, the most significant feature of the interference maxima along the equator is their rapid decrease in intensity towards higher values of the scattering vector **s** ($s = 2\sin\theta/\lambda$). This suggests that the data should be analysed on the basis of the paracrystalline model, which was developed by Hosemann in great detail in the early 1960s[18]. This model, standing between that of an ideal crystal and an amorphous structure, describes crystal structure by correlation of nearest neighbour atoms instead of deriving it from an ideal periodic lattice. The additional type of disorder introduced is called disorder of the second kind (disorder of the first kind refers to deviations of atoms from ideal lattice points). It can be characterized by a distortion parameter, which is the mean square displacement of the distance, d, between two nearest neighbour lattice points. Disorder of the second kind shows up as a decrease in the intensities of interference maxima at higher **s** with a broadening of the line width that is additional to broadening by finite crystallite size. By assuming that the broadening by disorder of the second kind and by finite crystallite size, L, can be described by two gaussians of *FWHM* of $(\pi^2\Delta^2/d)s^2$ and $1/L$, respectively, the *FWHM* of the interference maxima is given by

$$(FWHM)^2 = 1/L^2 + (\pi^4\Delta^4/d^2)s^4 \tag{1}$$

The above formula is strictly derived for the case of a one-dimensional distorted chain but it can be extended to characterize the lateral packing of polymer chains by analysing what are in the present case the equatorial reflections. For this purpose the *FWHM*s (above the background) of the reflections I, III, and IV were measured. After subtraction of the instrumental broadening the $(FWHM)^2$ was plotted against s^4. To compare with Shirakawa PA, data published by Pouget[17] were treated in the same manner (see *Figure 5*). It should be noted that the interference maxima I and IV are composed of two reflections each and that deviations of a^2/b^2 from 3 will lead to an additional broadening. But as this deviation is very small this contribution to the *FWHM* has been neglected. The average crystallite size perpendicular to the chains was calculated from the ordinate intercept of the linear fit according to equation (1), and was found to be 50 Å for our Durham PA and 100 Å for Shirakawa PA. The choice of d is somewhat arbitrary in this analysis. For $d = a = 4.24$ Å the distortion

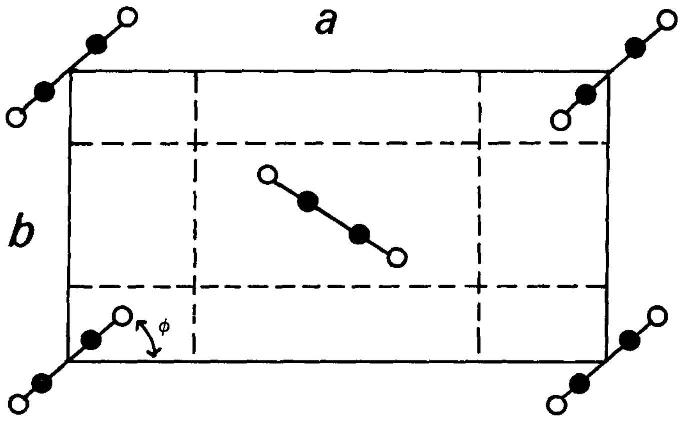

Figure 4 Lateral packing of PA chains according to the space group *pgg*. (○), hydrogen; (●), carbon atoms

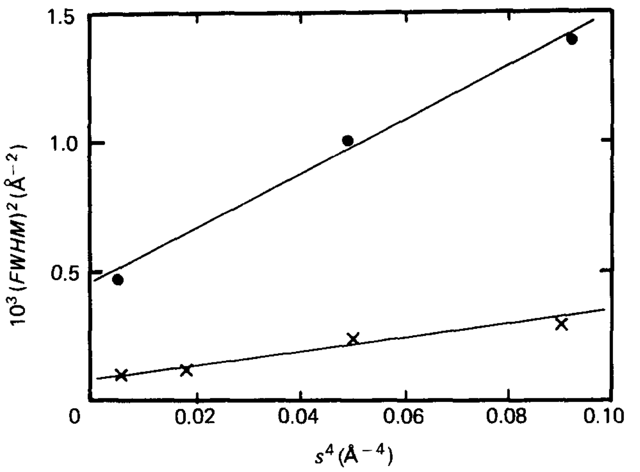

Figure 5 The $(FWHM)^2$ (corrected for instrumental broadening) of the *hk*0 reflections against s^4. (●) this work; (+) data of Pouget[14]

parameter Δ is 0.21 Å for Durham PA and 0.15 Å for Shirakawa PA. The results indicate that the lateral packing of Shirakawa PA is of higher order and possesses a longer coherence length than the packing in Durham PA. Further experiments are in progress to discover how far these differences are dependent on the preparation conditions, i.e. temperature of polymerization and isomerization, stretch ratio, etc.

To test the parameters a, b, ϕ, and the crude estimation of Δ and L found above, the equatorial intensities have been calculated by direct Fourier synthesis. For this purpose the correlation between next neighbour lattice points is described by gaussians of mean square displacement along the a and b-axes[18]. Fluctuations of the setting angle ϕ were not considered at this early stage. It is further assumed that the contribution of disorder of the first kind, which would affect the intensities in the form of a Debye–Waller factor, can be neglected. Using these assumptions the intensity can be expressed as

$$I(s)=|F(s)|^2 Z(s) * S(s) \qquad (2)$$

where $F(s)$ is the structure factor, $Z(s)$ the interference function of the second kind (in place of the Laue function for an undistorted lattice), and $S(s)$ the shape factor. $S(s)$ was chosen as a gaussian of $FWHM = 1/L$, and the convolution was performed by a Fourier transformation. *Figure 6* compares the calculated and observed intensities (a constant background was subtracted from the experimental data, and the curves were scaled to the strongest reflection, I). The two curves match reasonably well, which indicates that the main assumptions of the model are correct.

Morphology

The degree of orientation of the crystallites with respect to the fibre axis determines the amount of arcing of the reflections. To map the degree of orientation for samples of different stretch ratios L/L_0 diffractometer scans were taken along the inclination angle α (with respect to the fibre axis) through the very strong equatorial reflection 110, 200. After subtraction of an isotropic background line profiles were described by their *FWHM* and compared for different stretch ratios L/L_0 (see *Figure 7*). The width of the line profile will be given by the folding product of an intrinsic line width, due to limited coherence length along the fibre axis, and the width of the orientation distribution function that describes the probability of finding the c-axis of a crystallite at an angle α with respect to the fibre axis. The intrinsic *FWHM* of the profiles was estimated from the 002 reflection to be of the order of 1° (corresponding to an interference length of 80 Å). This is possible because the broadening due to finite crystallite size of the 002 reflections is along the fibre axis, whereas the arcing due to limited orientation is perpendicular to the fibre axis. This is considerably smaller than the observed *FWHM* of the 110, 200 reflection (6°–14°) and allows direct conclusions to be drawn about the degree of orientation from the width of the line profile. The correlation thus obtained between *FWHM* and L/L_0 indicates that the *FWHM* saturates at a value of about 6° at final stretch ratios of > 12. It should be mentioned that the increase of orientation was not

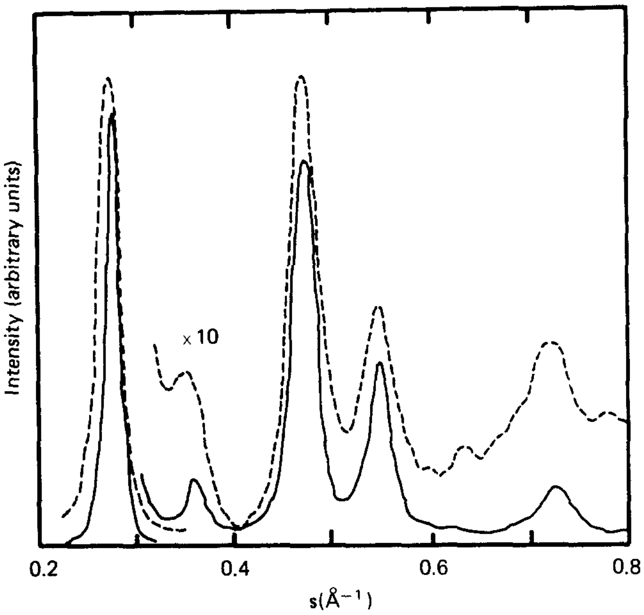

Figure 6 Comparison of observed (- - -) and calculated (———) intensity along the equator. Experimental data are not corrected for the instrumental broadening of about 0.05 $Å^{-1}$

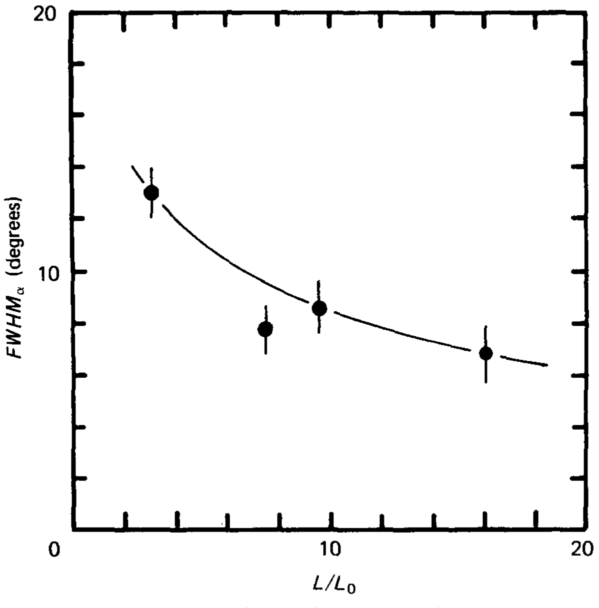

Figure 7 The *FWHM* of the reflection 110, 200 against the stretch ratio L/L_0

correlated to an increase of the crystallite size perpendicular to the chains, which would have caused a narrowing of the width of the reflections along the equator. It is interesting to compare the present results with data published by Lugli *et al.*[19] on drawn *cis*-rich Shirakawa PA. For their material the degree of orientation saturates at a stretch ratio of ~ 5. This difference arises from the method of preparation of stretched Durham PA, during which orientation and formation of the crystallites occur at the same time, which results in a higher degree of orientation and a larger range of L/L_0 over which the orientation can be increased. Further experiments should reveal how far the length of straight chain sequences along the orientation axis can be controlled by this stretching mechanism.

CONCLUSIONS

It is shown that oriented Durham PA possesses a crystal structure comparable with that of Shirakawa PA. The lateral packing of the chains is found to be of lower order than that found in Shirakawa PA, but the degree of orientation that can be gained by stress alignment during the preparation is greater than that for stress-oriented Shirakawa PA. The two last facts can be attributed to the special features of the Durham route, whereby the orientation is achieved by stretching during the transformation reaction from the precursor to polyacetylene.

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REFERENCES

1 Townsend, P. D., Bradley, D. D. C., Horton, M. E., Pereira, C. M., Friend, R. H., Billingham, N. C., Calvert, P. D., Foot, P. J. S., Bott, D. C., Chai, C. K., Walker, N. S. and Williams, K. P. J. 'Electronic Properties of Conjugated Polymers and Related Compounds', *Solid State Science* 1985, **63**, 50
2 Shirakawa, H. and Ikeda, S. *Synth. Metals* 1980, **1**, 175
3 Edwards, J. H. and Feast, W. J. *Polymer* 1982, **21**, 595
4 Calvert, P. D., Foot, P. J. S., Brown, C. S. and Vickers, M. E. to be published
5 White, D. and Bott, D. C. *Polymer* 1984, **25** (*Commun.*), 98
6 Leising, G. *Polymer Bull.* 1984, **11**, 401
7 Leising, G. *Polymer* 1984, **25** (*Commun.*), 201
8 Friend, R. H., Bradley, D. D. C., Pereira, C. M., Townsend, P. D., Bott, D. C. and Williams, K. P. J. 'Synmetals III', Los Alamos, April 1985, to be published in *Synth. Metals*
9 Lindenmeyer, P. H. and Hosemann, R. *J. Appl. Phys.* 1963, **34**, 42
10 Shimamura, K., Karasz, F. E., Hirsch, J. A. and Chien, J. C. W. *Macromol. Chem., Rapid. Commun.* 1981, **2**, 473
11 Fincher, C. R., Chen, C.-E., Heeger, A. J., MacDiarmid, A. G. and Hastings, J. B. *Phys. Rev. Lett.* 1982, **48**, 100
12 Robin, P., Pouget, J. P., Comes, R., Gibson, H. W. and Epstein, A. J. *J. Physique* 1983, **44**, 77
13 Perego, G., Lugli, G., Pedretti, U. and Cernia, E. *J. Physique* 1983, **44**, 93
14 Lieser, G., Wegner, G., Weizenhofer, R. and Bronbacher, L. *Polymer Preprints* 1984, **2**, 221
15 Leising, G., Leitner, O. and Kahlert, H. *Mol. Cryst. Liq. Cryst.* 1985, **117**, 67
16 Perego, G., Lugli, G. and Pedretti, U. *Mol. Cryst. Liq. Cryst.* 1985, **117**, 59
17 Pouget, J. P. 'Electronic Properties of Polymers and Related Compounds', Springer: Solid State Science Series, vol. 63, 1985, p. 26
18 Hosemann, R. and Baghchi, S. N. 'Direct Analysis of Diffraction by Matter', North-Holland, Amsterdam, 1962
19 Lugli, G., Pedretti, U. and Perego, G. *Mol. Cryst. Liq. Cryst.* 1985, **117**, 43