

Recent developments in the controlled synthesis and manipulation of electroactive organic polymers

F. Cacialli, R. Daik, P. Dounis, W. J. Feast, R. H. Friend, N. D. Haylett, C. P. Jarrett, C. Schoenenberger, J. A. Stephens and G. Widawski

Phil. Trans. R. Soc. Lond. A 1997 **355**, 707-714

doi: 10.1098/rsta.1997.0037

Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

To subscribe to *Phil. Trans. R. Soc. Lond. A* go to: <http://rsta.royalsocietypublishing.org/subscriptions>

Recent developments in the controlled synthesis and manipulation of electroactive organic polymers

BY F. CACIALLI¹, R. DAIK², P. DOUNIS², W. J. FEAST², R. H. FRIEND¹,
N. D. HAYLETT², C. P. JARRETT¹, C. SCHOENENBERGER²,
J. A. STEPHENS¹ AND G. WIDAWSKI²

¹*Cavendish Laboratory, Cambridge University, Cambridge CB3 0HE, UK*

²*Interdisciplinary Research Centre in Polymer Science and Technology,
Durham University, Durham DH1 3LE, UK*

This paper is concerned with making and manipulating conjugated polymers and studying their properties, particularly their behaviour when incorporated as the active components of a field effect transistor/electro-optic switch or a light emitting diode device structure. Two examples will be discussed. In the first we will show how the Durham precursor route to polyacetylene can be manipulated via the use of living polymerization techniques using well defined Schrock ROMP initiators to produce a self-ordering polyene precursor which gives significantly improved charge carrier mobilities and device performance. The second topic discussed will concern recent work on the application of McMurray coupling to the synthesis of electroluminescent poly(arylene vinylene)s.

1. Introduction

The possibility of using organic polymers as the active components of devices such as field effect transistors, electro-optic switches, light emitting diodes, pyroelectric sensors and so on has changed from speculation to practical demonstration only recently. Although the technological requirements for such materials are demanding, commercial applications are beginning to be established. This technological achievement continues to stimulate interest in basic research. In particular, the stringent materials requirements associated with the potential application of organic polymers as active components of electro-optic devices encourages the search for functional polymers with improved properties and very high levels of compositional and structural purity. Effective syntheses of well defined structures and manipulation of such materials into forms convenient for the study of their physics remain important objectives if useful structure property correlations are to be developed and new technologies established. This kind of work requires effective interdisciplinary collaborations and the realization of this has been one of the features of work in this area during the last decade. In this paper, work conducted jointly by the Cambridge physics and Durham polymer chemistry groups—which is directed to improving the performance of polyene semiconductors in FET structures by designing and making self-ordering systems—and recent progress in the application of the McMurray approach to the synthesis of electroluminescent polymers will be discussed.

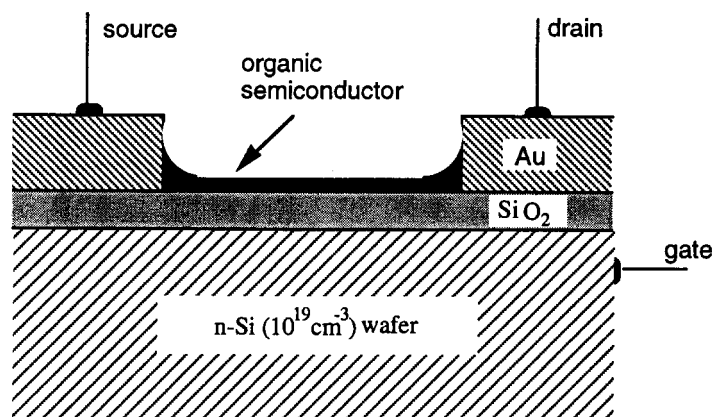


Figure 1. MISFET device structure used in studying self-ordering polyenes discussed here.

Some fifteen years ago, a precursor route to polyacetylene was established (Edwards & Feast 1980; Bott *et al.* 1983; Edwards *et al.* 1984). This route involves the ring opening metathesis polymerization of a tricyclic monomer to give a soluble precursor polymer which can be processed via conventional techniques and converted to polyacetylene when and where required. The precursor polymer is soluble in organic solvents, so the materials produced by this route may be cast as thin films by conventional techniques and produced in a wide range of morphologies and densities depending on the conversion protocol adopted (Feast *et al.* 1985; Bott *et al.* 1986; Martens *et al.* 1994). One possible application of this polymer is the convenient fabrication of hybrid polyacetylene-silicon based MISFET (metal insulator semiconductor field effect transistor) devices. The processing flexibility of the Durham route allowed the material to be incorporated into device structures of the kind shown in figure 1 which, in turn, allowed detailed study of the physics of this remarkable polymer (Burroughes *et al.* 1988).

It is established that this route allows the generation of solid, fully dense, continuous but highly disordered films of polyacetylene; thin films of such materials were used to demonstrate that polyacetylene can function as the active component in device structures. However, although the phenomenon was demonstrated, the semiconducting and optical performance of the material was not very interesting from the point of view of a real device because switching speeds and charge carrier mobilities were low. In this particular application, the mobility of the charge carriers is an important issue, and it might be optimized by improving the alignment of the polyene chains and the inherent interfacial ordering of the polymer film in the device. This view was based, in part, on the knowledge that bulk samples of the precursor polymer may be stretched before, or during, conversion to the conjugated material and that this procedure generates highly ordered films that have electrical and optical properties which are different from, and in some ways superior to, those of the disordered films (Martens *et al.* 1994). This work has been extensively documented and space limitations do not allow further review here (Edwards & Feast 1980; Bott *et al.* 1983; Edwards *et al.* 1984; Feast *et al.* 1985; Bott *et al.* 1986; Martens *et al.* 1993, 1994; Burroughes *et al.* 1988; Allen *et al.* 1989; Feast 1990; Feast & Friend 1990; Jones *et al.* 1991; Pichler *et al.* 1991, 1992*a,b*; Clemenson *et al.* 1992, 1993).

The objective of the work described here was to investigate the application of recent advances in living ring opening metathesis polymerization methodologies to

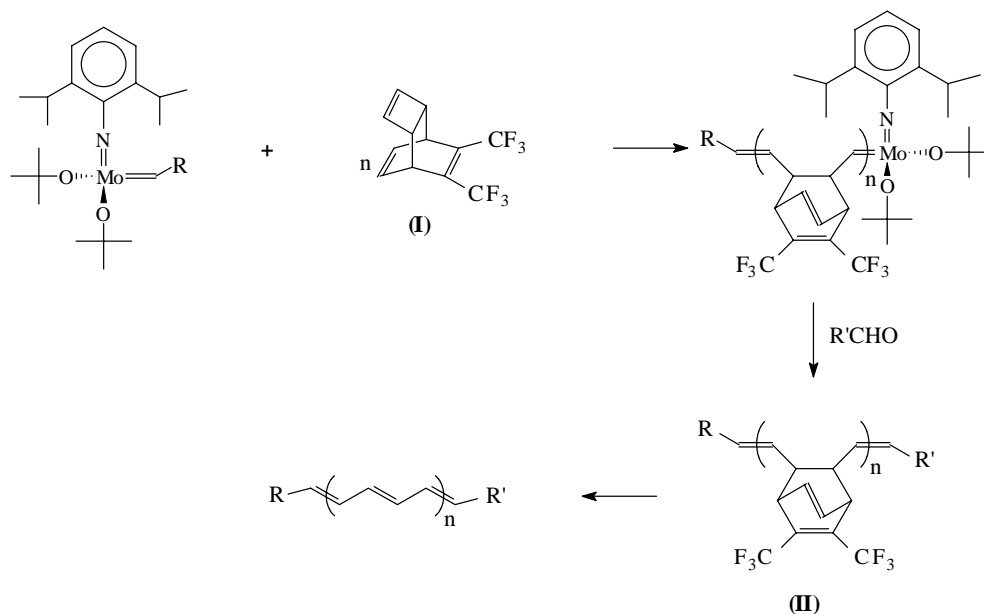


Figure 2. The 'Durham route' to polyacetylene

the synthesis of precursor polymers with an innate capability for forming ordered films of polyacetylene without the requirement for mechanical ordering by stretching; that is to say we were seeking self-ordering precursor polyene systems.

2. Synthesis of novel tailor-made polyenes functionalized via application of living ring opening metathesis polymerization (ROMP) and the Durham route

The ring opening metathesis polymerization of 7,8-bis(trifluoromethyl)-tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (I) using molybdenum alkylidene initiators of the kind developed by Schrock yields precursor polyacetylene with well defined chain-ends, molecular weights and polydispersities. The precursor polyenes (II) can be thermally converted to the equivalent polyacetylene structures by elimination of hexafluoroxylenes. The process is well established and is summarized in figure 2. In this work, the living precursor polymers were terminated by addition of an aldehyde which was also a potential phase segregating and self-ordering unit. The hope was that the polyene precursor segments and the chain end segments (R') would be incompatible and undergo phase separation. If that happened, and the chain end domains so formed were ordered, they might be expected to act as nucleating sites for the forming polyenes during the conversion stage. If all these requirements were realized, a self-ordering system would be established.

The chain end units used in this study were derived from the well known liquid crystal molecules 4-n-pentyl-4'-cyano-p-biphenyl and 4-n-pentyl-4'-cyano-p-terphenyl. The cyano group was reduced to the corresponding aldehyde using diisobutylaluminium hydride (DIBAL-H) (figure 3) and the product thus obtained used to functionalize the precursor polymer by the route outlined in figure 2.

A series of precursors were produced of controlled chain length carrying either

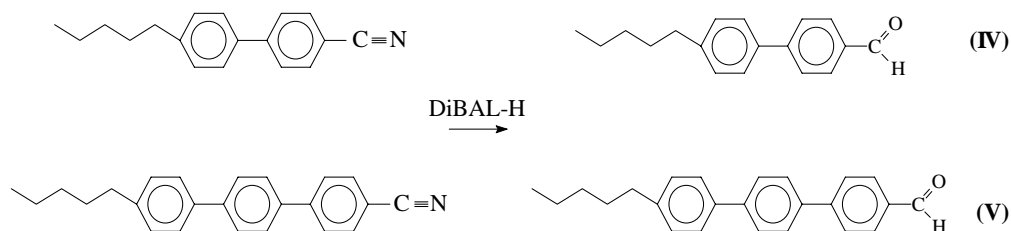


Figure 3. Synthesis of aldehydes used for termination reactions

Table 1. Structure of the different polymers studied

(The samples designated TTPA were prepared to act as references, i.e. bearing no phase segregating self-ordering end groups)

Reference	R'	R	<i>n</i>
LCBiPA			25, 50
LCterPA			7, 18, 30
TTPA			10, 20, 30

t-butyl or neophyl at one chain end and t-butyl, 4-pentylbiphenyl or 4-pentyl-paraterphenyl at the other; typical examples of materials prepared are recorded in table 1. Studies of the spectra, thermal properties and polarized microscopy of precursor films lead to the conclusion that the hoped for chain end phase segregation and self-ordering does occur (Widawski *et al.* 1995).

The important question is: can and do such well defined precursors allow improved performance in device structures? It has been suggested that low conductivity coupled with high carrier mobility, as required for efficient construction of devices of the MISFET type, cannot be simultaneously realized in an amorphous organic semiconductor, and that there may be a universal empirical relationship linking conductivity and mobility for such materials (Brown *et al.* 1994). The materials listed in table 1 have been studied as components of MISFET device structures following the procedures described previously (Burroughes *et al.* 1988). The results are summarized graphically in figure 4. It can be seen that the values of conductivity and mobility for the reference samples having well controlled chain length but no phase segregating chain ends fall on the curve for the 'universal empirical relationship for amorphous organic semiconductors' (Brown *et al.* 1994), whereas the values for the samples with the segregating chain ends depart significantly from the 'universal curve' and, for some of these samples, encouragingly high mobilities are associated with low conductivities. While these results are encouraging, the self-ordering polyene systems we have established do not have the conductivity and mobility required for application; values similar to those of amorphous silicon are required, i.e. mobilities greater than 10^{-1} . We are currently attempting to extend the concept described above via the synthesis and use of symmetrically substituted polyaldehydes derived from discotic

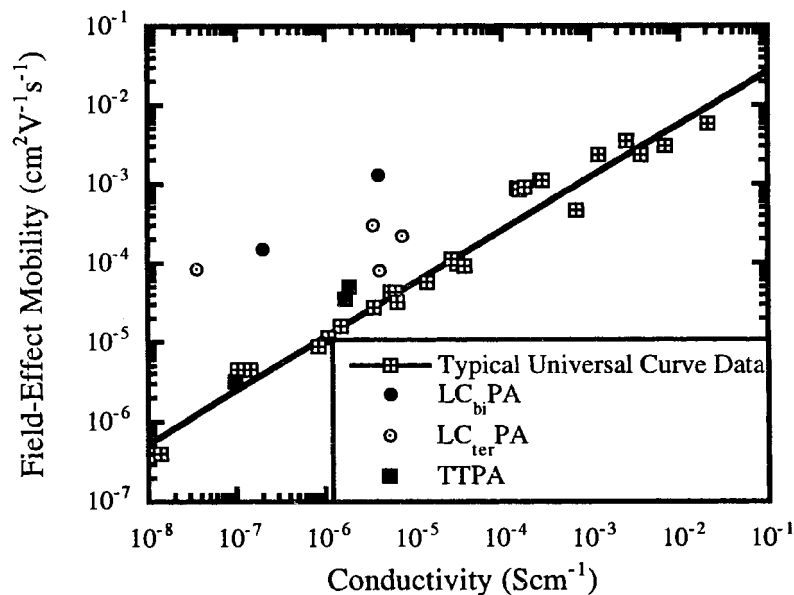


Figure 4. Conductivity versus mobility for materials described here in comparison with 'Universal curve' data (Brown *et al.* 1994).

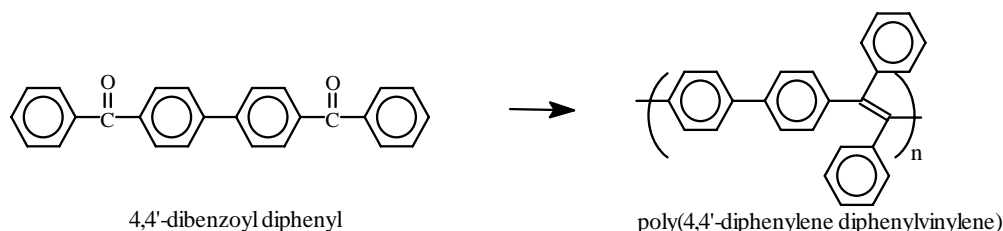


Figure 5. The McMurray route to poly(arylene vinylene)s.

liquid crystal molecules, in the hope of obtaining more highly ordered self-ordering polyene systems with further improvement of electrical properties.

3. Recent progress in the synthesis of electroluminescent materials via the McMurray approach

Some time ago, we described the synthesis of an arylene vinylene via the McMurray condensation of a diketone (Feast & Millichamp 1983). Recent interest in electroluminescence from such materials has caused us to re-examine this work with a view to producing well defined samples for study.

The polymerization of 4,4'-dibenzoyldiphenyl to poly(4,4'-diphenylene diphenylvinylene), PDPV, in tetrahydrofuran the presence of a coupling reagent formed from titanium trichloride and lithium aluminium hydride in a 1:2 molar ratio is relatively easily accomplished, since the monomer is easy to make and purify and the polymer is a soluble film forming material.

We have made fresh samples of this material and showed that the 'as made' polymer displays a solid state photoluminescence efficiency of *ca.* 50% and that thin

Phil. Trans. R. Soc. Lond. A (1997)

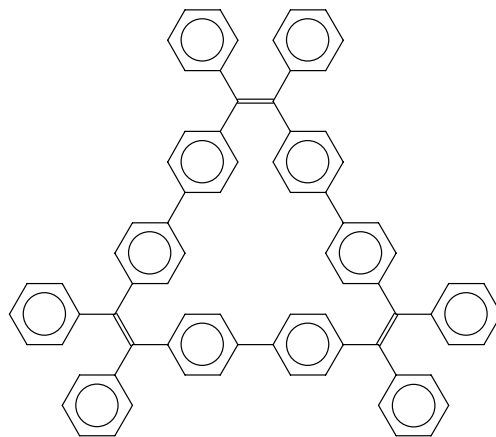


Figure 6. Cyclic trimer isolated from polymer fractionation.

films of material can be incorporated in LED device structures to give electroluminescence in the yellow–green region. The details of the device work will be reported elsewhere; here we describe briefly some recent results concerning the structure and purity of the material. The gel permeation chromatogram of the as made material shows a broad molecular weight distribution, typically $M_w/M_n \sim 6$ for a sample with $M_n \sim 5000$ Daltons, using polystyrene as calibrant. Also, there are small peaks at the low molecular weight end of the chromatogram. Materials for use in electro-optic devices should ideally be well defined structurally and of high purity. In the case of PDPV, we have a material with apparently interesting properties but we are ignorant concerning its structure and purity; thus, we do not know the frequency and distribution of cis and trans vinylenes along the polymer backbone and we do not know the nature of the low molecular weight impurities. In an attempt to rectify these deficiencies, we undertook a careful equilibrium fractionation of a sample of 15 g of the as made polymer, using chloroform as solvent and heptane as non-solvent at 20 °C. A series of 18 fractions was collected varying from $M_n \sim 88\,000$ down to ~ 1000 and from the residual solution, one of the low molecular weight impurities was obtained as a pure microcrystalline solid. The low molecular weight component isolated was shown by ^1H and ^{13}C NMR, IR and MALDI-TOF spectroscopies to be the cyclic trimer shown in figure 6.

This trimer constitutes about 2% of the as made product and this demonstrates unambiguously that the coupling process with this monomer can form cis vinylenes. The luminescence spectrum of the trimer is qualitatively blue shifted with respect to that of the polymer. The various fractions of polymer recovered have been examined for film forming characteristics and, for samples with M_w/M_n of the order of 2, polystyrene equivalent molecular weights in excess of $M_n \sim 18\,000$ Daltons are required in order to obtain good films. We have been unable to detect either a glass transition or melting point in any sample of this material below 230 °C and above this temperature it begins to decompose. This evidence encourages us in the belief that the coupling reaction is fairly indiscriminate; for this case leading to polymers that have a statistical distribution of cis and trans vinylenes and resulting in an amorphous material assembled from stiff segments. The investigation of properties, including luminescence, as a function of molecular weight and purity is in hand and will be reported elsewhere.

We acknowledge the financial support of the European Community's Human Capital and Mobility Programme, the EPSRC and the National University of Malaysia.

References

- Allen, P. C., Bott, D. C., Brown, C. S., Connors, L. M., Gray, S., Walker, N. S., Clemenson, P. I. & Feast, W. J. 1989 *Electronic properties of conjugated polymers III, Springer series in solid state sciences* (ed. H. Kuzmany, M. Mehring & S. Roth), vol. 91 pp. 456–460. Berlin: Springer.
- Bott, D. C., Chai, C. K., Edwards, J. H., Feast, W. J., Friend, R. H. & Horton, M. E. 1983 *J. Physique* **44**, 143–146.
- Bott, D. C., Brown, C. S., Chai, C. K., Walker, N. S., Feast, W. J., Foot, P. J. S., Calvert, P. D., Billingham, N. C. & Friend, R. H. 1986 *Synth. Metals* **14**, 245–269.
- Brown, A. R., de Leeuw, D. M., Havinga, E. E. & Pomp, A. 1994 *Synth. Metals* **68**, 65.
- Burroughes, J. H., Jones, C. A. & Friend, R. H. 1988 *Nature* **335**, 137.
- Clemenson, P. I., Feast, W. J., Allen, P. C., Bott, D. C., Brown, C. S., Connors, L. M., Walker, N. S. & Winter, J. N. 1992 *Polymer* **33**, 4711–4716.
- Clemenson, P. I., Cramail, H., Dyer, P. W., Feast, S., Feast, W. J., Gibson, V. C., Khosravi, E., Parker, D. & Winter, J. N. 1993 In *Conjugated polymers and related materials: the interconnection of chemical and electronic structure* (ed. W. R. Salaneck, I. Lindstrom & B. Rönby), ch. 13, pp. 171–184. Oxford University Press.
- Edwards, J. H. & Feast, W. J. 1980 *Polymer* **21**, 595–596.
- Edwards, J. H., Feast, W. J. & Bott, D. C. 1984 *Polymer* **25**, 395–398.
- Feast, W. J. 1990 *Phil. Trans. R. Soc. Lond. A* **330**, 117–125.
- Feast, W. J. & Friend, R. H. 1990 *J. Mat. Sci.* **25**, 3796–3805.
- Feast, W. J. & Millichamp, I. S. 1983 *Polymer Commun.* **24**, 102.
- Feast, W. J., Friend, R. H., Bott, D. C., Bradley, D. D. C., Chai, C. K., Foot, P. J. S., Giles, J. R. M., Horton, M. E., Pereira, C. M. & Townsend, P. D. 1985 *Phil. Trans. R. Soc. Lond. A* **314**, 37–49.
- Jones, C. A., Lawrence, R. A., Martens, J., Friend, R. H., Parker, D., Feast, W. J., Logdlung, M. & Salaneck, W. R. 1991 *Polymer* **32**, 1200–1209.
- Martens, J. H. F., Pichler, K., Marseglia, E. A., Friend, R. H., Cramail, H. & Feast, W. J. 1993 *Synth. Metals* **55–57**, 443–448.
- Martens, J. H. F., Pichler, K., Marseglia, E. A., Friend, R. H., Cramail, H., Khosravi, E., Parker, D. & Feast, W. J. 1994 *Polymer* **35**, 403.
- Pichler, K., Friend, R. H., Parker, D. & Feast, W. J. 1991 *J. Phys. Condens. Matter* **3**, 3007–3021.
- Pichler, K., Gelsen, O. M., Bradley, D. D. C., Friend, R. H., Parker, D. & Feast, W. J. 1992a *Electronic properties of polymers, Springer series in solid state Sciences* (ed. H. Kusmany, M. Mehring & S. Roth), vol. 107, pp. 238–241. Berlin: Springer.
- Pichler, K., Ziemelis, K. E. Friend, R. H., Parker, D. & Feast, W. J. 1992b *Electronic properties of polymers, Springer series in solid state sciences* (ed. H. Kusmany, M. Mehring & S. Roth), vol. 107, pp. 471–474. Berlin: Springer.
- Widawski, G., Feast, W. J. & Dounis, P. 1995 *J. Mat. Chem.* **5**, 1847–1851.

Discussion

D. VESELY (*Department of Materials Engineering, Brunel University, UK*). Could Professor Feast please explain the reason for his effort to reduce polydispersity while keeping the molecular weight high? Is this to improve the film morphology and thus the performance of the film? How is the morphology linked to the polymer properties?

Phil. Trans. R. Soc. Lond. A (1997)

W. J. FEAST. In this work, we have attempted to obtain narrow polydispersities by two methods. In the polyene work, a well defined living polymerization gave control of molecular weight, dispersity and end group structure whereas, in the arylene vinylene work, fractionation of the product gave us samples with variation of molecular weight and dispersity.

In general, both the molecular weight and polydispersity have profound effects on polymer properties, such as film formation and mechanical properties, the effect of these factors on electrooptical properties has been less well studied; we try to control these features in order to examine their importance. Although a detailed study has not been conducted, we have shown that the improved order reported for the polyenes requires a relatively low molecular weight whereas, for the arylene vinylenes, good films are only obtained above a threshold molecular weight.

In various areas of polymer technology (e.g. paints and toner resins), it is known that optimum performance is associated with complex multimodal distributions; it is clear that if you can control molecular weight, and obtain a narrow dispersity, you can formulate any desired distribution.

S. MORATTI (*Chemistry Department, University of Cambridge, UK*). Has Professor Feast tried aligning these films on rubbed surfaces?

W. J. FEAST. We have not carried out such studies in Durham, but our colleagues in Cambridge have and found that orientation of thin films is improved. Alignment on rubbed substrates is, of course, a standard technique in the liquid crystal device area.

D. D. C. BRADLEY (*Department of Physics and Centre for Molecular Materials, University of Sheffield, UK*). Professor Feast mentioned the presence of cis double bonds in some of the phenylene vinylene polymers. We have found that in a specific case, cis double bonds increase the fluorescence efficiency. Would he care to comment on the role of configuration in emissive yields?

W. J. FEAST. We know that the linear polymers have a distribution of cis and trans double bonds, but we have no method for analysis of their frequency and distribution so cannot answer the question directly. However, the cyclic trimer has only cis double bonds and has absorption and emission spectra which are quite distinct from those of the linear polymer. It seems reasonable to expect that main chain planarity will be harder to achieve in cis vinylene sequences and this is likely to influence the properties of interest. We have work in hand directed to the synthesis of materials in which the cis/trans frequency and distribution is controlled, which may allow us to examine the phenomenon to which Professor Bradley refers; it seems reasonable to assume that the details of chain microstructure will influence the spectroscopic properties of these materials.