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Jim Feast: a career in polymer science

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Abstract

To mark the occasion of Prof. W. J. (Jim) Feast's official retirement, an international symposium was held in Durham on July 16th and 17th 2004. This article, written by some of the participants in that symposium, highlights the contributions that Jim Feast has made in the areas of ring-opening metathesis polymerisation, electroactive polymers and dendrimers and hyperbranched polymers. In particular, the 'Durham route' polyacetylene, prepared from a precursor polymer itself prepared by ROMP, paved the way for the work in the field of conducting and semi-conducting organic polymeric materials by Richard Friend and others. In addition to the description of Jim's scientific contributions, a brief synopsis of his education and career progression is provided.

Jim Feast receiving the SCI's Baekeland medal at the end of the meeting from Professor John Ebdon (former Macro Group UK Chairman).

Keywords: Polymer chemistry; Polymer synthesis; Polymer materials

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1. Introduction

In this article, a brief description of the contributions by Jim Feast in three of areas of science in which he is highly active (ring opening metathesis polymerisation, or ROMP; electroactive polymers; dendrimers and hyperbranched polymers) is provided. Each section is written by an expert in that area who is also a close personal friend of Jim, so there are many examples of the additional benefits, other than scientific, that Jim has brought to each discipline. On reading the subsequent sections, two things stand out: (i) the wide variety of science (not just chemistry) in which Jim has been involved in his career; (ii) his inventive approach to science—doing research that leads to a step-change in the development of that field. In addition to the scientific sections, the scene is set by a synopsis of Jim's upbringing, education and scientific career development. This serves to highlight some of Jim's character traits, which enable the reader to form a picture of the man and begin to understand how his science and scientific relationships are conducted.

2. Jim Feast: an appreciation (R. W. Richards)

Jim Feast was born in 1938 in Birmingham, was a student at Sheffield University leaving with a degree in Chemistry in 1960, whereupon he returned to his roots to do research in organo-fluorine chemistry at Birmingham University gaining a PhD in 1963 and following this up with two years as a post-doctoral research fellow in the same group. He was then successful in obtaining a lectureship at Durham University in 1965 and remained there until his retirement in 2003.

These are the prosaic facts that summarise a professional life but bespeak nothing of the man, the influences that have shaped him and the influences he has had on people and the world with which he interacted, engaged and that he observed. Like Jim, I am also from the Midlands of the UK (although born some years later) and my childhood was spent in the clanging Mephistophelian atmosphere that characterises a region sometimes known as the foundry of England. Jim was more fortunate since his family moved fairly soon after he was born to the more rural and contemplative surroundings of Lichfield. Still in the Midlands to be sure but Lichfield was the city of Dr Johnson and Erasmus (grandfather of Charles) Darwin which neatly encapsulate two aspects of Jim's character as I hope to illustrate below.

According to Jim he spent most of his schooldays loafing about the fields and woods around Lichfield, not exactly 'bunking off' from school but making the most of a rural England that was about to disappear forever. I am not sure that I believe this fully, after all his father was a school teacher and a man who clearly had a significant influence on Jim, and his mother was a women of great independence of thought and spirit, both of which aspects are clearly evident in Jim when you know him well, and maybe not so well! At this time he also took up athletics, eventually becoming a sufficiently good middle distance runner to represent his club and University (I will not recite the stories of the influence of copious amounts of Guinness on running performance, except to say he won!) He must have assimilated some knowledge and displayed some ability because he was sufficiently able to apply for a place at University in an era when only circa 5% of any year group were eligible. It may be a bit of a surprise that Jim's first choice of subject was mathematics but an interview with Rudolf Peirls at Birmingham University enlightened Jim that maybe this was not a wise choice. Not that Peirls was brutal with the young Feast, just guided him to a more appropriate choice of future career.

This set Jim on the path of Chemistry and ultimately to a PhD in the growth area of the time, organo-fluorine chemistry. From some of what I heard, it is evident that Jim did all the things that chemistry students of that time did and are now unimaginable because of safety regulations and a greater awareness that many of the materials need to be treated with respect. After five years at Birmingham he arrived at Durham as a young lecturer in the third oldest University in England that had recently parted company with its 'satellite', Kings College in Newcastle which became Newcastle University. Durham was, and is still, a collegiate University, maybe not as strongly so as Cambridge and Oxford but the colleges fiercely defend their unique characters. Membership (either as student or tutor) entails a responsibility to preserve and defend the reputation of the college. Jim became a tutor at Van Mildert College, living 'over the shop' and thus constantly on hand. Whilst there he met and married Jenneke and his first daughter was born, all this whilst being tutor in residence and having to take care of some 'sticky' problems in addition to the usual 'high spirits' of undergraduates.

The Chemistry Department at Durham at that time could have been described as a rather unique Department, at least from what I gathered during my time there in later years. Some eminent people had been instrumental in reviving the Department after WWII (Paneth, Coates, Musgrave) but to have members of staff who were also part time farmers and popped out occasionally to castrate the odd pig or two seems rather strange in these Research Assessment Exercise-focussed days. Nonetheless, it was and is a happy Department where everyone knows everyone else and has a strong loyalty to the Department with a willingness to get the Chemistry done. In such an atmosphere a young chemist can thrive, seek out new challenges and when Jim arrived there was sufficient resource around to enable people to get on with it. A feature of the Department when Jim arrived in 1965 was the very strong organo-fluorine research group, but within five years Jim switched his primary research interest to polymer chemistry focussing mainly on novel polymer synthesis using innovative routes that built firmly on his knowledge and experience of small molecule organic chemistry. A significant product of this switch was the Durham route to polyacetylene, which is dealt with in a subsequent section, leading to enduring collaborations with Richard Friend and David Bott. It is instructive to note that this area of research begun some 30 years ago has lead to the current perception that carbon-based electronics now are probably at the point where silicon-based systems were in the early 1970s.

Over the 1970s and 1980s the expertise and knowledge of polymer synthesis that was being built up in Jim's group became more and more evident with various invited lectures around the world and culminating in working for two months of the year in the Max Planck Institut für Polymerforschung in Mainz with Gerhard Wegner. During this period, Jim became interested in ring opening metathesis polymerisation forming a fruitful collaboration over many years with Ken Ivin. The key to control in these polymerisations is the catalyst and to gain this knowledge and import the expertise into the Department Jim encouraged a young colleague to go to the US to learn how to make the catalysts. Subsequently, that young colleague, Vernon Gibson, became Professor of Inorganic Chemistry at Imperial College. An example of early talent spotting? A long lasting friendship with Bob Grubbs (personal and professional) also resulted from the continuing fascination with metathesis polymerisation, although Jim does say that Bob can walk his legs off when they go a-wandering up Teesdale or on the North Yorks Moors!

Like many academics, Jim progressed through the ranks at Durham, lecturer, senior lecturer, skipped Reader, Professor. Along the way there are various awards, achievements and honours (see Appendix A), perhaps the most notable of which was election to the Royal Society in 1996, where many are called but few are chosen.

I really got to know Jim in 1989 when I was recruited into the Department at Durham coincidentally with (but not connected to) the establishment of the Interdisciplinary Research Centre in Polymer Science and Technology. For me there followed a very happy and productive 14 years where Jim was both a professional colleague and a personal friend (and remains so). I learned that Jim can quote reams of poetry and has a fascination with words (despite a weakness with regard to spelling) which is only right and proper for a native of Dr Johnson's birthplace. I also learned that Jim has an insatiable fascination with science (perhaps the subliminal influence of Erasmus Darwin in his youth) and putting chemistry to work usefully, a facet newer generations would do well to emulate. Working with Jim is not a challenge as long as you appreciate what the objectives are; to get the best science done within the confines of what is available in terms of equipment, resources and people. Despite his early flirtation with mathematics, I did the figures and budgets and Jim believed me! Jim did the charm offensive and people believed him! I learned of Jim and Jenne's love of the countryside, good food, good wine and good company. He experienced dry martinis and ribald humour. Jim exhibited his generosity of spirit in encouraging and enabling younger colleagues to explore bold chemistry and have courage in their abilities, a facet that he still has.

With Jim's retirement it is all too easy to say that it is the end of an era, I do not believe that is so. The spirit lives on in all who have worked with Jim over the years and have been touched by that spirit of curiosity, enthused by the desire to find out what is happening even if it does not turn out as expected and hopefully acquired that generosity of spirit and pleasure in other people's success referred to above. Indeed, the reality lives on because, although he may have retired, it is only a partial retirement since he is overseeing some of the North East of England's activity in nanotechnology and continues as a Research Professor in the Department he first joined almost 40 years ago. It is therefore inappropriate to wish Jim a long and happy retirement but at least he is now able to do the things he wants to do rather than what he has to do—and long may that continue.

3. Ring opening metathesis polymerization (ROMP) (R. H. Grubbs)

The contributions that Jim Feast has made to olefin metathesis have been two-fold. Scientifically, he has provided outstanding examples of the applications of metathesis to the solution of important problems in polymer science. Personally, he has played a significant leadership role in the metathesis community, not only through his organization and participation in meetings but also through his example, he has kept the field friendly and cooperative. Jim's first major contribution to metathesis chemistry was the use of fluorinated monomers for the production of interesting new materials, reflecting his scientific upbringing (vide supra). Although Feast has made many contributions to metathesis and polymer science in general, only a few of the highlights will be discussed below.

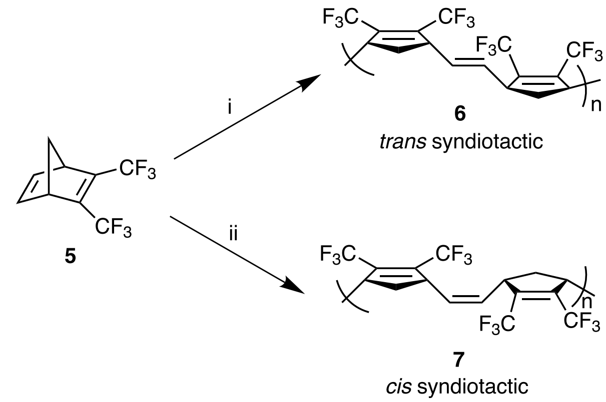
Jim Feast used olefin metathesis to overcome a long-standing problem in polyacetylene chemistry. Until Feast developed the Durham route, polyacetylene was an intractable material that could not be processed easily [1]. Combining olefin metathesis with a clever precursor route, he produced a new form of polyacetylene that could be oriented and used in the preparation of devices [2]. For Feast, these developments opened his eyes toward the application of the general area of metathesis in the production of other functional polymers and polymer types. For the remainder of the community, Feast's approach to the synthesis of new controlled structures of electro-active materials provided a guide to the creative coupling of polymer and organic chemistry. In a broader sense, the Feast approach to polymer chemistry attracted a number of organic and organometallic chemists to the field.

Conjugated polymers show a wide variety of electrical and electro-optical properties that are continually finding uses in evolving devices. For many applications, optimization of the material's properties requires alignment of the individual polymer chains. The need for close stacking and long conjugation results in intractable, insoluble materials that are difficult to process. Feast designed a monomer that (1) would polymerize to a soluble processable polymer and (2) could then be converted to polyacetylene in the solid state [1]. This precursor approach has since been used by many others to generate tractable polymers [3]. His initial approach involved the polymerization of a protected cyclobutadiene by ROMP followed by thermal deprotection (Scheme 1).

Because this synthesis allowed for the processing of polyacetylene, the Durham group helped introduce the use of conducting organic polymers for the construction of devices. Feast became an early user of well-defined, 'living' metathesis catalysts and not only applied them to the synthesis of conjugated polymers but also to the synthesis of a wide variety of polymers with precisely controlled structures [4]. In the conjugated polymer area, he used the Schrock molybdenum catalysts to prepare conjugated polymers with controlled lengths and polyacetylenes that were end-capped with mesogens that would aid in the control of the morphology of the thermally generated polyacetylene [5].

Feast has made significant contributions to the stereocontrol of metathesis and has delineated the role that stereochemistry plays on the physical properties of polymeric systems. Polymerization of 2,3-bis(trifluoromethyl)norbornene with the Schrock molybdenum catalysts resulted in high *cis* or *trans* polymers, depending on the substituent present on the catalytic metal complex (Scheme 2). The *t*-butoxy catalyst produces *trans* polymer while the hexafluoro-*t*-butoxide complex produces the *cis* isomer. The tacticity of the polymer could not be determined by NMR spectroscopy but it was elucidated in a clever way. Highly polarized polymers with the proper relative orientation show useful pyroelectric properties. The polarized susceptibility of the *trans* polymer (45.5) was an order of magnitude higher than that of the *cis* isomer. These results are consistent with both isomers being syndiotactic where the dipoles of the molecular units correlate additively in the *trans* material but are destructive in the *cis* isomer. The pyroelectric coefficient of the *trans* material is sufficiently high to have potential applications [6].

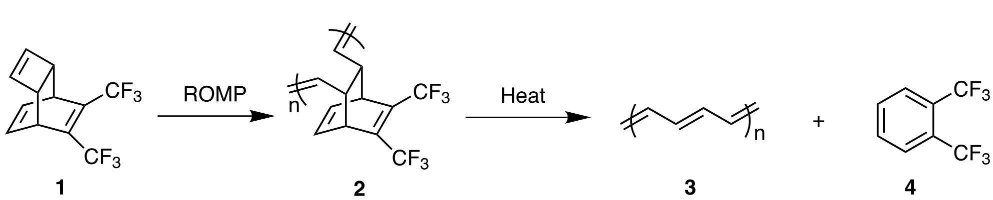
The introduction of living catalysts for metathesis opened many opportunities for controlling the architecture



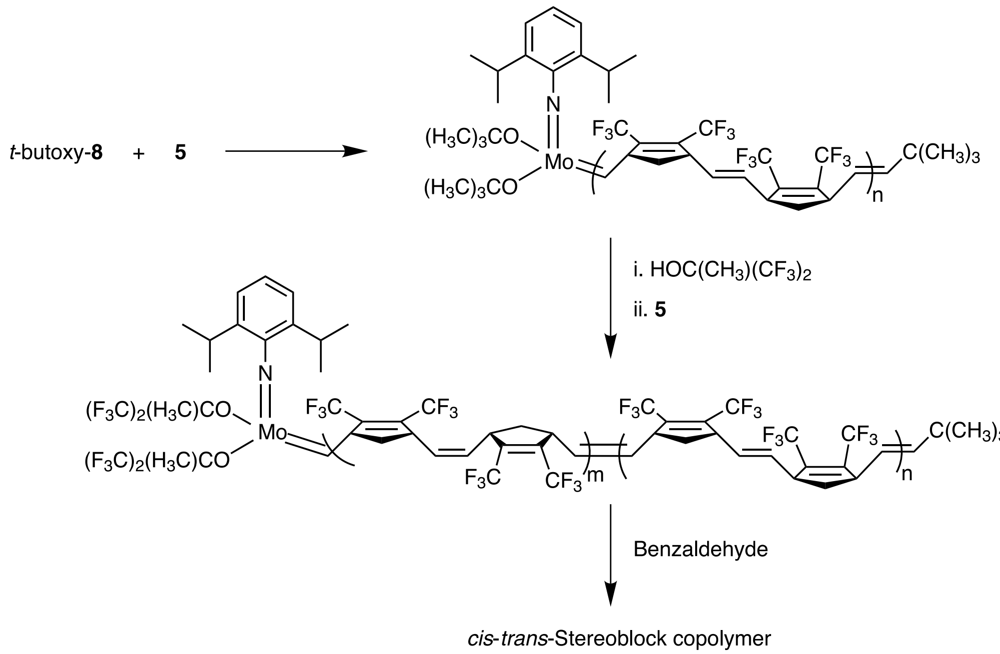
Scheme 2. Catalyst-mediated stereocontrol in ROMP. The Schrock catalyst Mo(=CH-*t*-Bu)(=N-2,6-C_6H_3-*i*-Pr_2)$(OR)_2$ (**8**) was employed, where R = –$C(CH_3)_3$ (i) or –$C(CH_3)(CF_3)_2$ (ii).

of polymers. Feast was one of the first to use the well-defined living catalysts to generate an array of important and interesting polymer structures. Each of these takes advantage of the special features of these initiators that allow for precise control of polymer stereochemistry, molecular mass, and geometry. For example, control of the stereochemistry of the polymerization of **5** by the structure of the catalyst was used to create a stereoblock polymer (Scheme 3) [7]. The polymerization of **5** using *tert*-butoxy-**8** produced a living polymer with *trans* stereochemistry. The resulting living polymer was freeze-dried and then treated with a solution of hexafluoro-*tert*-butanol, freeze-dried again and treated with a fresh solution of hexafluoro-*tert*-butanol. This procedure was repeated four times. As shown by NMR, this process converted the alkoxide ligand of the molybdenum catalyst at the end of the living polymer from a *tert*-butoxy ligand to a hexafluoro-*tert*-butoxy ligand. When the converted living polymer was treated with more **5**, the polymerization continued to produce a block of *cis* polymer. After terminating with benzaldehyde, the resulting polymer showed two thermal transitions of 95 and 145 °C which is consistent with a phase-separated stereoblock polymer.

The Feast group demonstrated the use of well-defined initiators to prepare another multiphase polymer system using macromers that had been prepared by a different polymerization mechanism [8]. In one case the macromer was prepared by the end capping of an anionically polymerized, living polystyrene with propylene oxide which was then esterified with *exo*-5-norbornene-carbonylchloride to produce a norbornene terminated



Scheme 1. The Durham route to polyacetylene.



Scheme 3. Synthesis of a stereoblock copolymer by ROMP using the Schrock catalyst by exchanging the alkoxy ligand between the synthesis of the first and second blocks.

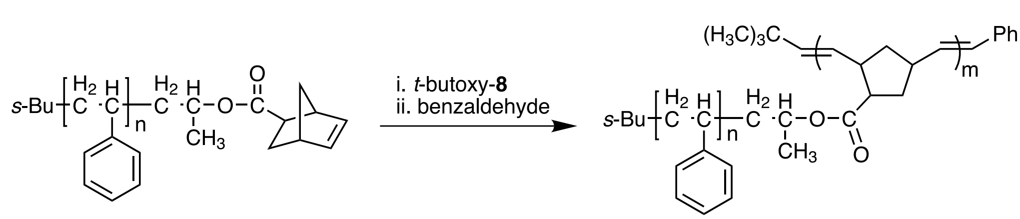
polystyrene. The resulting macromer could be polymerized using the *tert*-butoxy Schrock initiator **8** to provide narrow polydispersity graft copolymers of defined molecular mass (Scheme 4). These macromers gave more controlled polymers than other more hindered/functionalized macromers.

These graft polymers showed only one T_g suggesting that they do not give discrete phases. Other polymer structures that can be prepared by living ROMP are stars and similiar multi-arm structures (Scheme 5). A polyethylene star was produced by the living ROMP of cyclopentene using the Schrock tungsten complex W(=CH-*t*-Bu)(=N-2,6-C_6H_3-*i*-Pr_2)(O-*t*-$Bu)_2$ to produce polypentenamer **9**. Polymer **9** was allowed to react with trialdehyde **10** to produce **11** through a 'Wittig-type' reaction. Hydrogenation of the resulting polymer resulted in a star polyethylene [9].

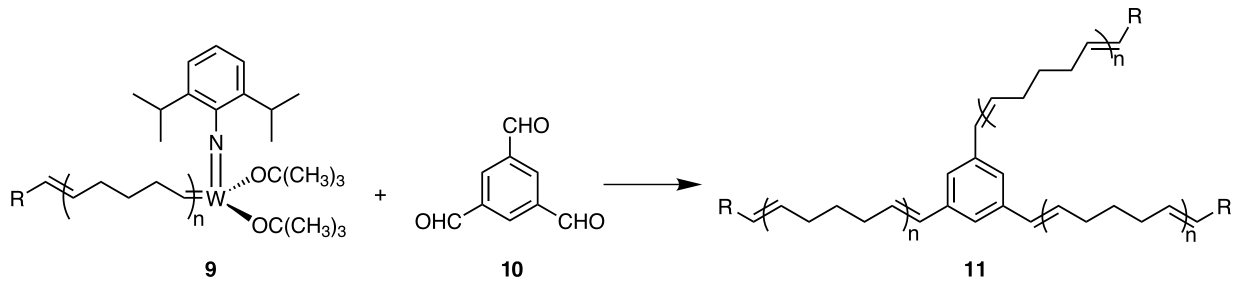
The Feast group exploited ROMP to prepare polymers with controlled functionality and functional group geometry for use in aqueous solutions to control the crystal form and crystallization rate of salts. Molybdenum and ruthenium-based living initiators were used to prepare norbornene-based polymers with controlled length and dispersity. In addition, a variety of different water-solubilizing functional groups were incorporated stereoselectively on each monomer [10]. The resulting polymers were tested for the control of the crystallization of calcium carbonate [11]. Although many of the polymers exerted a negligible control over crystal growth, the saponified and hydrogenated polymer formed from *endo*-*exo*-norbornene-5,6-dimethylcarboxylate gave good control of crystal form (calcite), shape, and face of modification. The molecular weight of the polymer also had a strong effect on crystal growth.

The above are only a few examples of the applications of ROMP from the Feast laboratory. Results continue to flow from the Durham polymer groups that use ROMP for a variety of applications from electrooptics to structural materials [12]. Papers that appear on a search of 'Feast and Metathesis' but are not referenced in this text are included in the reference list [13].

As is all of the science coming from the Feast group, the contributions to ROMP are varied and creative applications of the unique features of the chemistry. He was one of the first to exploit the newly emerging catalysts in this area to prepare polymers with precise structures. His work is a combination of the fundamental and the practical. He provides excellent examples of how the precise



Scheme 4. Comb copolymer synthesis by ROMP of polystyryl norbornene macromer.



Scheme 5. Preparation of polyethylene 3-arm star by coupling of living ROMP polymer to tri-functional core followed by hydrogenation.

stereochemical and length control of polymers translates into practical properties of the resulting materials. We look forward to the continuing work from Durham resulting from the vision and creativity of Jim Feast.

4. Polyacetylene (R. H. Friend)

Electronic conduction along a π-conjugated polymer backbone giving, when 'doped', a metallic material, was first realised with polyacetylene by the groups of Heeger, MacDiarmid and Shirakawa in 1977 [14]. This work generated a huge level of interest, both because it seemed to promise new materials with commercially-useful properties and because it demonstrated that the electronic properties of long-chain conjugated materials were considerably more interesting than previously considered possible, and was the work cited for the 2000 Nobel prize in Chemistry awarded to Heeger, MacDiarmid and Shirakawa.

Polyacetylene was not then a 'new' material, but it had not previously been available in a tractable form for measurements. The demonstration of conducting properties was made possible because polyacetylene was produced in the form of thin 'films' (in fact, low-density fibrillar mats) by Ziegler–Natta polymerisation of acetylene gas on a catalyst-containing surface. These films were made conducting by controlled oxidation (later also, reduction) by chemical or electrochemical treatment. In the early work, exposure of these 'films' to iodine vapour at room temperature produced an increase in conductivity from a low, doped-semiconductor level (typically 10^{-7} S/cm) to metallic values above 1000 S/cm. In the case of iodine, this diffuses between the polymer chains within the fibrillar structure, and abstracts electrons from the delocalised π-electron system on the polyacetylene backbone, to form a charge-transfer complex, with I_3^- anions sitting alongside positively-charged polymer chains. The non-integral oxidation state of the polyacetylene (up to typically 0.4 electrons per repeat unit can be removed) is then responsible for the metallic conduction, which can be crudely associated with conduction within a partially-filled pi valence band.

This 'Shirakawa-route' polyacetylene supported a huge research effort until the mid 1980's, because the material was relatively easily produced. However, it was not susceptible to useful post-processing because polyacetylene is a rigid-rod polymer and the extended chains are not readily soluble in tractable solvents. Thus, as a convenient material for doping post synthesis, the open, fibrillar structure was very suitable, but as a more generally useful and processible material, it was not.

The importance of a film-forming and processible conjugated polymer was well appreciated, and this became available through the elegant precursor route developed by Jim Feast and colleagues at the University of Durham (vide supra) [15]. This has come to be known as the 'Durham route' to polyacetylene, and provided exactly the processibility that was needed to incorporate polyacetylene into more practical structures. Particularly in its use as the active semiconductor in devices such as Schottky diodes and Field-Effect Transistors (FETs), it provided an excellent model material.

The 'precursor polymer' is non-conjugated, and therefore readily soluble in for example isopropanol, and can be spin-coated from solution to give thin and coherent films of polymer, that can then be readily converted to polyacetylene by heating to modest temperatures (100 °C), when the strained six-membered side ring is released (as a fluorinated xylene, volatile under these conditions), and putting a carbon–carbon double bond in its place. It is therefore very easily formed as thin films on a wide range of substrates, and can be used as a free-standing film after lifting off from a suitable substrate. The ring-opening metathesis polymerisation used to prepare the precursor polymer is discussed elsewhere in this article. As also with Shirakawa polyacetylene, the material shows substantially *cis* linkages along the chain as first prepared, but is converted during the heating process into the all *trans* isomer.

These dense-film-forming virtues of Durham polyacetylene at first caused it to be regarded as of lesser value than Shirakawa polyacetylene, because it is less easy to 'dope' to form the metallic charge-transfer complexes such as are formed with iodine. Lower conductivity values are generally reported, and this is due to the difficulty in introducing large volume fractions of intercalating 'dopant' into a dense and entangled polymer film well below its glass transition temperature. Physical characterisation of Durham-route polyacetylene was carried out very extensively [16], and reveals little crystallinity in as-prepared films, consistent with the disordered structure carried over from the precursor polymer. There are clear indications that the 'straight-chain' lengths of polyacetylene are relatively short, for example in the relatively high energy for the peak of the optical absorption across the pi–pi* energy gap (2.3 rather than 1.9 eV for Shirakawa polyacetylene), and this is in contrast with the full chain length (these are high polymers with molecular weight averages up to 10^6) which must therefore contain a large number of conformational defects (chain bends and twists) which interrupt chain conjugation.

Kahlert and Leising [17] reported that free-standing films of the Durham precursor polymer could be stretch-oriented during the thermal conversion to polyacetylene, to produce very highly-oriented films, with the polyacetylene chains oriented parallel to the stretch direction. This has been of great interest because it provided a means to measure some of the anisotropies in electronic properties (optical absorption, electrical conductivity, and charge photogeneration [18]), and the process of stretching also brought about a large increase in the intra-chain order, with resultant electronic properties more similar to those of Shirakawa polyacetylene.

The more important role of Durham polyacetylene, however, has probably been its use as a semiconductor in devices such as diodes and FETs. As prepared, both Shirakawa and Durham polyacetylene are lightly-doped p-type semiconductors, with hole concentrations dependent on preparation conditions, but typically in the range 10^{16} to $10^{18}\ \mathrm{cm}^{-3}$. This doping has never been unambiguously assigned, but is probably due both to residual catalyst and/or adsorbed oxygen. In the lower range of doping, this is a convenient level for both diode and FET operation, and the convenience of solution processing allowed the Durham route material to be used successfully [19,20]. FETs were fabricated on structures built up on silicon wafers, as illustrated in Fig. 1. In this device, a layer of thermally-grown oxide sits on a doped silicon wafer which acts as gate. Gold source and drain contacts were then processed onto the dielectric layer using standard photolithographic methods, and the final steps, of spin-coating the Durham precursor solution onto this structure and thermally converting precursor to polyacetylene then produces the complete FET. p-Type operation is produced by biasing the gate negative, thus inducing an accumulation layer of positive charges at the SiO_2/semiconductor interface, and these surface-charges then provide a conducting path between source and drain. Typical electrical characteristics for such devices are shown in Fig. 2, and it can be seen that device operation is clean, with 'textbook' characteristics. The figure of merit for such transistors is the mobility of the field-induced charges, and this is typically in the range 10^{-5} to $10^{-4}\ \mathrm{cm}^2/\mathrm{Vs}$.

Though it was very encouraging to see such clean semiconductor operation in polyacetylene, this value of mobility is low, considerably lower than values found for example in amorphous silicon (0.1–1 $\mathrm{cm}^2/\mathrm{Vs}$), and too low for practical use. These low values are in the range found in the hole transport molecular semiconductors used in electrophotography [21], where conduction is considered to be due to hopping between localised states (localised by disorder). One of the challenges therefore was to raise the degree of order in the polyacetylene film, to the point where charge carrier transport might be significantly extended along the polymer chain. One approach taken by Feast and colleagues was to engineer order into the precursor polymer by attaching mesophase-forming end-groups to the polymer chain [22]. The control of architecture through ring-opening metathesis polymerisation allows selection of the end-groups at both the start and end of the chain, and Feast and colleagues were able to attach alkyl biphenyl and alkyl triphenyl groups at the start of the chain. Both gave improved transistor performance, particularly biphenyl, which under comparable conditions (same 'dark' conductivity) showed an improvement in field-effect mobility of a factor of 100, up to $3\times10^{-3}\ \mathrm{cm}^2/\mathrm{Vs}$ [22]. This was the first evidence that improved order could be used to bring field-effect mobility into a useful range (this is at about the threshold for use in transistor arrays for active-matrix display drivers).

The description of the FET operation above has been

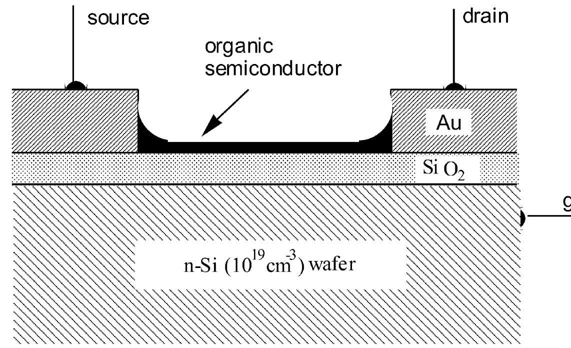


Fig. 1. Structure of a Field-Effect Transistor, fabricated using a top layer of Durham polyacetylene on a SiO_2 dielectric layer, with gold source and drain contacts. The doped Si wafer acts as substrate and gate.

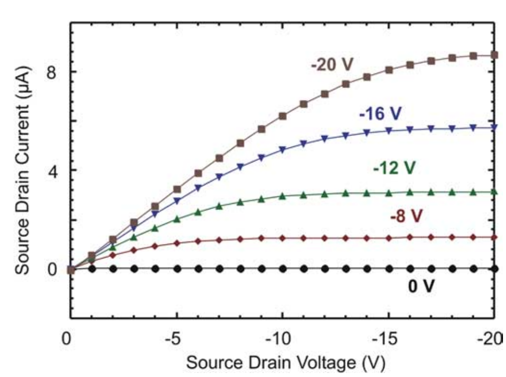


Fig. 2. Electrical transfer characteristics for polyacetylene transistors as shown in Fig. 1. The source-drain separation (channel length) is 5 μm, the channel length is 90 cm (interdigitated electrodes), and the SiO_2 thickness 200 nm.

made using wholly traditional inorganic semiconductor models, which consider holes to be carriers in valence band states, and electrons in the conduction band. Though the models are applicable, the character of the mobile charge carriers is however, very different. One of the great interests in the electronic properties of polyacetylene in its *trans* isomer is that the presence of an extra charge on the chain (such as a field-induced hole in the field-effect device) causes a region of the polymer chain to form in which the sense of bond alternation (between 'double' and 'single' bonds) is reversed. On either side of this region, there must be topological defects which separate this region from the rest of the chain, and these regions have the character of solitary waves or solitons, as is illustrated in Fig. 3 [23]. The electronic structure associated with these regions is very simple: each possesses one non-bonding π orbital, which by definition sits midway between valence and conduction band states. It is these mid-gap states onto which the extra charge is stored, so that rather than band-edge states being filled, states at mid gap are created and populated. Within this model it is then these soliton-like states which carry the current in the FET. Solitons can be considered as special examples of the more general phenomenon of 'polaron' formation, where the presence of an extra electronic charge causes a local rearrangement of chain geometry. The involvement of local structural relaxation generally increases the effective mass of the charge carrier, and for the special case of the soliton on *trans* polyacetylene, might be expected to restrict inter-chain motion.

One of the clearest pieces of evidence for the presence of these states is the optical absorption found at half the optical band gap when charges are introduced, either by chemical doping, or photoexcitation, or, as is possible here, by charge injection in the field-effect device. The schematic arrangement of the optical transitions for hole-doped polyacetylene is shown in Fig. 3, with mid-gap optical transitions between filled valence band states and empty mid-gap states. Field-induced charge injection, as used in the FET, provides a clean way of introducing charge onto the polymer chain without disorder associated with a chemical dopant, and by modulating the gate voltage on the device it is possible to detect the change in optical transmission due to the injected charge [19]. Fig. 4 shows results [24] for both the regular form of polyacetylene and also for polyacetylene with the biphenyl chain termination that provides improved field-effect mobility [22]. Broad asymmetric absorption bands are clearly seen, peaking near 0.7 eV for the regular Durham polyacetylene, but at significantly lower energies for the biphenyl-terminated material (peak at 0.6 eV, shoulder near 0.53 eV). These energies are a little lower than 50% of the ground state optical absorption; one reason for this is that charge injected onto the polymer chains will preferably be stored on the lowest energy gap material, so that more disordered parts of the sample do not contribute to the mid-gap response. We associate the higher field effect mobility in the material with the biphenyl chain termination and its lower 'mid-gap' optical absorption energy with increased order in the material—disorder both traps electronic charges and also increases the π to π^* energy gap. In addition to the electronic mid-gap optical transitions seen in Fig. 4, soliton-like charge excitations also show specific vibrational signatures, in IR (translational modes of the soliton) and in Raman (shape modes of the soliton), and both of these are also seen in field-modulated device measurements [19,20].

In summary, this section has reviewed very briefly the role that the Durham route to polyacetylene has played in the development of semiconducting polymers as processible and therefore useful electronic materials. Though polyacetylene is no longer the favoured material for applications, largely because of its extreme sensitivity to photo-oxidation, it did provide the prototypical semiconducting polymer for much of the early scientific study, and the Durham route enabled this class of materials to make the jump from 'dirty' metals to 'clean' semiconductors. The latter are now finding their way into the market in polymer light-emitting diodes, and in the near future, as arrays of FETs.

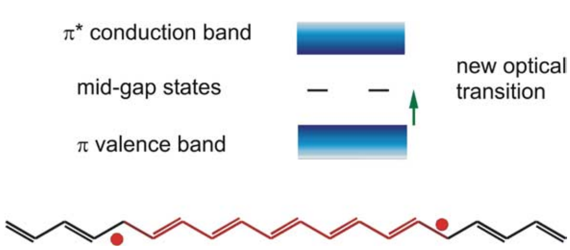


Fig. 3. Schematic illustration of a region of reversed sense of bond alternation on a *trans* polyacetylene chain, with soliton-like topological defects to either side. The associated electronic structure (for p-doped material) is shown in the band scheme.

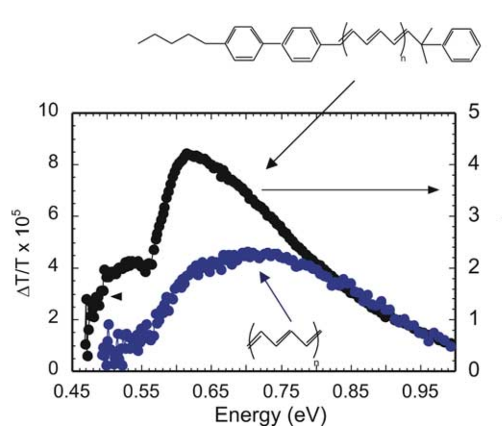


Fig. 4. Extra optical absorption due to field-induced charge in a polyacetylene field-effect structure versus photon energy. Data are shown for both the standard form of Durham polyacetylene and for polyacetylene with biphenyl chain ends.

5. Dendrimers and hyperbranched polymers (E. W. Meijer)

In his classic book on the 'Principles of Polymer Chemistry', Paul J. Flory dedicates one chapter to the molecular mass distributions in nonlinear polymers and the theory of gelation [25]. The random branching without network formation is discussed as a special case. The polymerisation of an AB_2 monomer yields a randomly branched molecule. The first synthesis of a branched polymer was probably the phenol-formaldehyde condensation polymerisation as reported by Baekeland as early as in the 19th century. Despite the elegance of these branched structures, they did not get the proper attention in academia. Industry, on the other hand, knew how to use the branching as for instance the compact disc is made out of a branched polycarbonate. The branching reduces the flow birefringence.

It was not until after the introduction of dendrimers that both organic and polymer chemists saw the many opportunities of hyperbranched polymers. As many others, Jim Feast was intrigued by the beauty of the spherical architecture of dendrimers. Probably he was also inspired by the beautiful review by Donald A. Tomalia et al. in Angewandte Chemie on dendrimers in 1990 [26]. Dendrimers are the perfect highly branched macromolecule and as an example the fifth generation of the poly(propylene imine) dendrimers is shown in Fig. 5 [27]. Jim's key knowledge in polymer and organic chemistry and his fascination for these spherical objects, made his entrance in the field of dendrimers and hyperbranched polymers possible.

Characteristic of all of Jim's scientific work, including in the area of hyperbranched polymers and dendrimers, is his search for the ultimate challenge. 'The Synthesis and Properties of Aramide Dendrimers' was the title of the first dendrimer publication from the Durham team with S. C. E. Backson as first author [28]. These aramide dendrimers combined their highly branched structure with multiple-intermolecular hydrogen bonding, leading to interesting solubility issues. This work was followed by the synthesis of aryl ester dendrimers that were used in blends, while hyperbranched polyimides were investigated in detail as well [29]. Blending dendrimers or hyperbranched polymers with linear analogues gives rise to materials with very

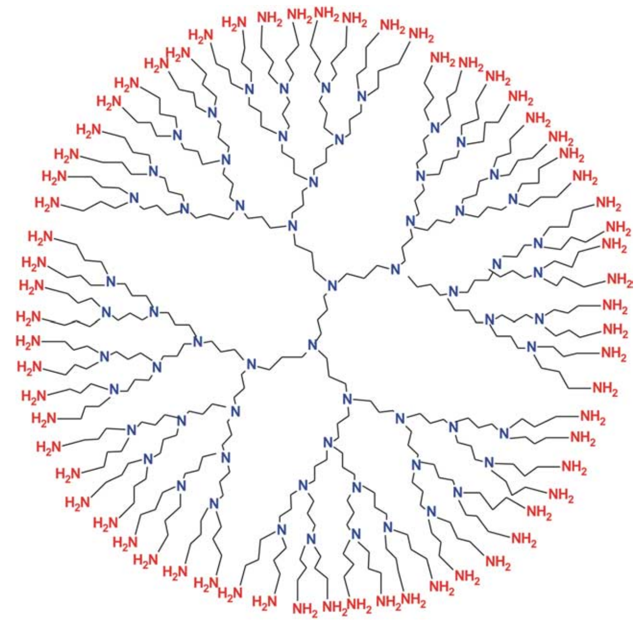


Fig. 5. The fifth generation of the poly(propylene imine) dendrimers.

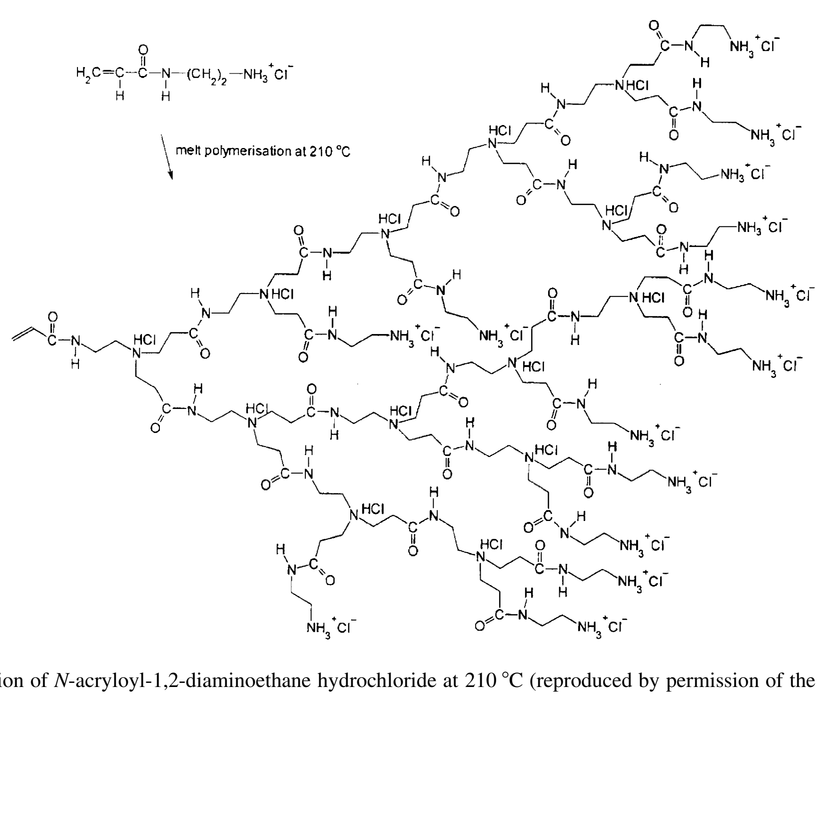


Fig. 6. The melt polymerisation of *N*-acryloyl-1,2-diaminoethane hydrochloride at 210 °C (reproduced by permission of the Royal Society of Chemistry).

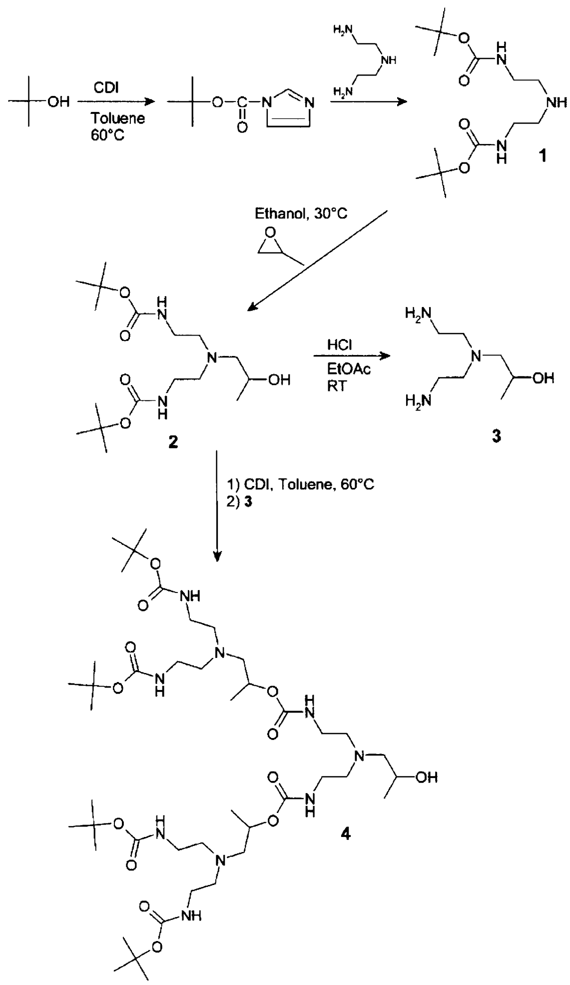


Fig. 7. The synthetic sequence to polyurethane dendrimers using CDI (reprinted with permission from [32]. Copyright (2003) American Chemical Society).

interesting melt viscosity properties. The Durham team disclosed many interesting features and the fields of both dendrimers as well as hyperbranched polymers progressed very well. However, despite the analogy in branching structure, most in the field stressed the differences between them; dendrimers are made in a very sophisticated fashion by the multiple replication of a sequence of two steps, while hyperbranched polymers are made in one pot.

Tomalia's poly(amidoamine) dendrimers, the so-called PAMAMs, were the most studied dendrimers at that time [26], and it was obvious to all of us that these structures could only be made by the repetitive sequence in the divergent approach. That is, until a paper appeared in Chemical Communications by Lois J. Hobson, Alan M. Kenwright and W. James Feast on AB_2 hyperbranched polymers [30]. The results surprised the whole dendrimer society. The authors announced a simple 'one pot' route to the hyperbranched analogues of the PAMAM dendrimers, and as a special case they reported the close-to-perfect branching in the melt polymerisation of *N*-acryloyl-1,2-diaminoethane hydrochloride (Fig. 6). A one-pot synthesis of a perfectly branched PAMAM is unique [31]. Although there remained the difference with dendrimers in that the wedges had varying sizes, these close-to-perfect hyperbranched polymers with the unique PAMAM structure were sensational. Many regard this masterpiece of chemistry as one of the most interesting syntheses of hyperbranched polymers. It is another example of the unique way Jim Feast and his group have contributed to the different fields of polymer chemistry.

In more recent years, Jim's long-lasting and exciting collaboration with Steve Rannard of Unilever Research at Port Sunlight brought a new highlight to his work on dendrimers [32]. The very creative and excellent PhD student Alison Stoddart was using 1,1-carbonyl diimidazole (CDI) to synthesize a series of aliphatic polyurethane dendrimers (Fig. 7). The selective reaction of primary amines over secondary amines of CDI is a key step to the success.

Many more insights into Jim Feast's ideas about dendrimers and hyperbranched polymers were presented during his lecture at the symposium in Durham honouring his many contributions to polymer science. As always it had a challenging title: 'Branching polymerisations and branched polymers: Baekeland's legacy and some recent developments' [33].

6. Conclusions

Jim Feast has made a highly significant contribution to polymer science and it would be a sad loss to the community if he were to retire from research. Therefore, we are extremely pleased that he will continue, for the next two years at least (and hopefully for many more to follow), and we look forward to many more exciting developments from his group. Indeed, in recent years his research has branched out from that described in this article into areas such as biomaterials [34] and self-assembling electroactive oligomers and polymers [35]. We wish him all the best for the future.

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Appendix A. William James Feast FRS Curriculum vitae

Born 25th June 1938, Birmingham, UK

PhD 1963 Birmingham University (UK)—Organic Fluorine Chemistry.

B.Sc. 1960 Sheffield University (UK).

Secondary school. King Edward VI Grammar School, Lichfield (UK).

Married Jenneke E.C. v.d. Kuijl 1967; two daughters Saskia and Marieke

Currently

Emeritus Research Professor, Department of Chemistry, University of Durham

1989–2003:

Courtaulds Professor of Polymer Chemistry, Interdisciplinary Research Centre in Polymer Science and Technology/Chemistry Department, Durham University.

1994–2002:

Director of the Interdisciplinary Research Centre in Polymer Science and Technology

1989–1994:

Associate Director of the Interdisciplinary Research Centre in Polymer Science and Technology.

1986–1989:

Professor of Chemistry, Durham University.

1975–1986:

Senior Lecturer in Chemistry, Durham. University.

1965–1975:

Lecturer in Chemistry, Durham University.

1963–1965:

Postdoctoral Research Fellow, Birmingham University.

1968–1969:

Gillette International Research Fellow in Universiteit te Leuven (Belgium).

1985–1988:

Visiting Professor and Consultant in Polymer Synthesis at the Max Planck Institut fur Polymerforschung, Mainz, FRG.

1991:

DSM Visiting Professor, International Polymer Institute, Universiteit te Leuven (Belgium).

1993:

Miles Lecturer, Cornell University, USA.

1999:

Visiting Professor, California Institute of Technology (R.H. Grubbs group).

2002:

Sabbatical visitor, Technical University of Eindhoven (E.W. Meijer group).

Chairman (1989–1992) of the Macro Group (UK) of the R.S.C. and S.C.I.

Chairman (1999–2002) of the North East Polymer Association of the Institute of Materials.

Member of the Editorial Board of the journal Polymer Photochemistry.

Sometime Editor of Polymer and remains a member of the Advisory Board.

Advisory Board member of Polymer Bulletin, Journal of Materials Chemistry, the Bulletin of the Korean Chemical Society and Polymer Journal (Japan).

Royal Society of Chemistry Medal for Macromolecules and Polymers, 1986'

Swinburn Medal of the Institute of Materials, 1994.

Miles Lectureship, Cornell University USA, 1994.

Royal Society of Chemistry's Tilden Lectureship and Medal, 1996/1997.

Royal Society of Chemistry MacroGroupUK Medal Lecture 1999

Xerox Distinguished Scientist Lectureship, Canada 1999.

Royal Society of Chemistry Interdisciplinary Award 2001.

SCI Baekeland Lectureship 2003

Election to Fellowship of the Royal Society 1996.

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