PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Polymeric Nonlinear Optical Materials

W. J. Feast

Phil. Trans. R. Soc. Lond. A 1990 **330**, 117-125
doi: 10.1098/rsta.1990.0006

Phil. Trans. R. Soc. Lond. A **330**, 117–125 (1990)
Printed in Great Britain

Polymeric nonlinear optical materials

By W. J. Feast
Department of Chemistry, Durham University, South Road, Durham DH1 3LE, U.K.

This paper briefly reviews the design requirements for polymeric nonlinear optical materials. Progress in synthesis that leads towards meeting some of these objectives is described with respect to the preparation, characterization and properties of conjugated hydrocarbon polymers.

INTRODUCTION

Chemists specializing in synthesis who attempt to come to terms with the theoretical physics associated with nonlinear optical behaviour of materials frequently encounter a highly repulsive intellectual energy barrier, and I am no exception to this generalization. However, as in many other fields of activity lying at the interface between solid state physics and chemistry, this field of research needs contributions from synthetic chemistry if it is to progress and, if the role of 'plumber's mate' is to be avoided, the chemist attempting to make a contribution requires a picture of what is involved in nonlinear optic phenomena. At the simplest level the questions are 'What happens?' and 'What are the structural features of the material which allow it to happen?'

The descriptive remarks presented below attempt to answer this need and to provide relevant background to the main body of the paper. Readers seeking more detailed and properly rigorous treatments of the subject are referred to more authoritative sources (Chemla 1987; Shen 1984; Williams 1984). After this brief nod in the direction of physics and technology the bulk of the paper will be concerned with the synthesis and properties of materials.

When light passes through an optically transparent material it interacts with it. The major interaction is that between the electric field of the electromagnetic radiation and the charge distribution within the material. This interaction induces a polarization $\boldsymbol{P}$ within the material that is related to the electric field $\boldsymbol{E}$ of the radiation by the expression,

$$\boldsymbol{P} = \chi^{(1)}\boldsymbol{E} + \chi^{(2)}\boldsymbol{E}^2 + \chi^{(3)}\boldsymbol{E}^3 + \dots, \tag{1}$$

where $\chi^{(1)}, \chi^{(2)}, \chi^{(3)}$ are the first-, second- and third-order optical susceptibilities of the bulk material. Theories that account for most of the familiar optical processes in, and properties of, materials only require the first term of (1); however, the existence of special effects resulting from higher-order induced polarizations have been recognized for more than a century. For example, the electro-optic Kerr effect, first detected in the observation of double refraction in transparent materials exposed to high electric fields (Kerr 1875), has a magnitude that depends on $\boldsymbol{E}^2$ and has been a subject for discussion in standard texts for many years (Partington 1953). Despite this very early observation there was, before the advent of lasers, relatively little of practical consequence stemming from the nonlinear optical behaviour of materials because the optical susceptibilities are small and consequently the effects are not big enough to be detected at the field strengths normally encountered. The advent of the laser and the very high electric fields associated with this type of radiation changed the situation dramatically. Perhaps the most obvious manifestations of nonlinear optical behaviour are second and third harmonic generation; in these processes, which depend on $\chi^{(2)}$ and $\chi^{(3)}$ respectively, part of a beam of monochromatic light passing through or being reflected from an active nonlinear material emerges as frequency-doubled or tripled radiation, a phenomenon having obvious implications for optical processing.

It was soon apparent that the availability of processable materials displaying large nonlinear coefficients offered great technological opportunities in the fields of optical information processing, telecommunications and integrated optics. The realization of the potential of this general area came first to the solid state physics community who were already familiar with inorganic systems (semiconductors, insulators, etc.) and not unnaturally the first materials investigated for their nonlinear optical behaviour were inorganic. Later it was recognized that conjugated organic systems might be particularly effective in this field, because the required nonlinear effects would, in this case, be arising from the polarization of the π-electron distribution rather than the displacement of nuclear coordinates involved when these phenomena are observed in inorganic materials. It was anticipated that the versatility of synthetic organic chemistry would be able to provide monomeric or polymeric structures with π-electron distributions matching almost any specified 'ideal design', the term 'structure' in this context referring not only to molecular structure but also to the organization of molecules or polymer chains or both in the bulk sample. It was soon established that these expectations of organic materials were justified and that extremely large nonlinear responses could be observed from appropriately organized unsaturated organic molecules (Williams 1984; Girling 1987; Neal 1986). Difficulties were anticipated, in particular the thermal, chemical and mechanical stabilities of organic materials appeared to be less attractive than those of inorganic materials.

Following this preamble, what are the necessary design criteria for nonlinear activity in organic materials? I have already introduced two factors into the discussion, namely polarizable π-electrons and the organization of the system under consideration. The detailed theoretical physics referred to above led to the conclusion that even-order effects will vanish in centrosymmetric media whereas odd-order effects do not experience this symmetry restriction. Potential practical applications of nonlinear optical materials currently focus on the utilization of phenomena that depend on the availability of materials that have large second- or third-order nonlinear susceptibilities. The practical consequence of this is that to design a material for a second-order effect, such as second harmonic generation, the detailed organization of the polarization of the π-electron cloud throughout the bulk of the sample has to be controlled. The many molecular structures that have been used to demonstrate second-order nonlinear effects have the common structural feature of a polarizable unsaturated subunit with donor and acceptor units attached at its extremities. This molecular feature must then be aligned throughout the sample by making use of the individual or combined ordering potentials of crystals, liquid crystals, Langmuir–Blodgett superlattices and oriented polymers. In the latter case the active nonlinear entities have been incorporated either as additives or as pendant groups. Such activities have been successful and are the subjects of recent conference proceedings (Prasad 1987; Heeger 1988) and several of the other contributions to this volume, I shall not consider them further. Third-order effects do not, in principle, require quite such complicated and highly organized structures; here the requirement is for the synthesis and processing of molecules or polymers containing well-defined conjugated sequences. Third-order optical nonlinearity is of interest for a number of potential applications, including fast optical switches, nonlinear memories, optical transistors and so on; already by 1983 more than 20 different processes occurring through $\chi^{(3)}$ had been observed (Williams 1984). One practical problem associated with many of the applications is the requirement for the reproducible fabrication of well-defined very thin films, which represents a severe restriction on the application of conventionally produced conjugated polymers. The remainder of this paper is concerned with progress achieved in the realization of the objective of producing well-defined processable conjugated polymers and the properties of the materials obtained so far.

Synthesis of conjugated polymers

The term conjugated polymers represents a very broad class of materials. To keep this short review within bounds I focus on the simple hydrocarbon polymers that typify the class, namely polyacetylene, polyparaphenylene, and poly(paraphenylene vinylene). I have consequently excluded all the work on polydiacetylenes, which have recently been reviewed (Schott 1987), neither do I attempt to deal with heterocyclic conjugated polymers. The review is not comprehensive, it is concerned primarily with areas of synthesis in which I have been involved and related literture reports.

Polyacetylene has been the paradigm for the field of conjugated polymers for over half a century since its appealingly simple structure first attracted theoretical speculation (Lennard-Jones 1937). In the last two decades a very large volume of theoretical and experimental studies of this material have appeared. Unfortunately, despite its simplicity it turned out to be a difficult target for synthesis and an extremely difficult material to process. The obvious route, i.e. the direct addition polymerization of acetylene, was established 30 years ago (Natta 1958). The material was obtained by solution polymerization using a typical Ziegler–Natta initiating system and was characterized as the *trans* isomer, it was found to be air sensitive, insoluble and infusible. These considerable material disadvantages discouraged much further study until several years later it was shown that free standing films of polyacetylene could be produced by polymerization of acetylene gas at the surface of a concentrated Ziegler–Natta catalyst solution (Ito 1974). Initially, these films, often referred to as Shirakawa-polyacetylene (S-PA) were rather heterogeneous in structure; usually the morphology was described as a 'fibrillar mat', but more recently quite detailed control of film density and morphology has been obtained by regulation of the reaction conditions. Much of the early work on the syntheses and properties of this material have been collected together (Skotheim 1986) and the more contemporary work has been reviewed recently (Naarman 1988).

The processing, and therefore the practical application of this type of polyacetylene still represents a considerable problem; nevertheless, values of $\chi^{(3)}$ for samples of polyacetylene produced in this way have been recorded as 1.3×10^{-9} esu at the fundamental wavelength of 1907 nm (Kajzar 1987) and 4×10^{-10} Fr† at 1064 nm (Heeger 1987), which are slightly larger than the values found for polydiacetylenes.

We introduced an alternative approach to the synthesis of polyacetylene via processable precursor polymers; some examples of the chemistry developed are shown in figure 1.

---

† 1 Fr (≡ 1 esu) ≈ 3×10^{-10} C.

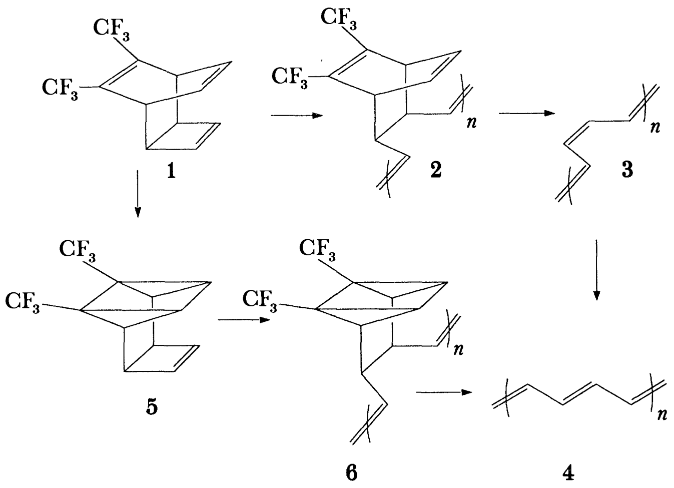


FIGURE 1. The chemistry of precursor polymers.

The first route of this kind to be established (Edwards 1984) used the readily accessible tricyclic triene **1** as the monomer in a metathesis ring-opening polymerization to give the precursor polymer **2**. Polymer **2** was produced by using a relatively ill-defined initiator derived from the reaction of WCl_6 with $(CH_3)_4Sn$, reaction occurs exclusively at the cyclobutene double bond and produces a random distribution of *cis* and *trans* double bonds in the polymer backbone. As a consequence of the method of production the polymer chain conformation is highly disordered, which is a characteristic that ensures its solubility even at high molecular mass. Solutions of this precursor can be purified by repeated reprecipitation and used to spin well-controlled thin films on a conventional resist spinner. The precursor **2** eliminates hexafluoroxylene in a process which is symmetry allowed in the ground state to give polyacetylene **3**. As a consequence of its mechanism of formation the newly formed double bond has to have *cis* stereochemistry, but the material isomerizes to give high purity, continuous uniform films of *trans*-polyacetylene **4** the thickness of which can be controlled between 10000 and 200 Å (1 Å = 10^{-10} m), this material is usually referred to as Durham-polyacetylene (D-PA). The process works well and has been fairly widely adopted. It is essential if high quality material is to be obtained to carry out *all* manipulations of both the precursor and the product in an inert atmosphere because both polymers are air sensitive. A further minor difficulty arises from the fact that the elimination reaction leading to the formation of the polyene sequences occurs slowly at room temperature, which means that it is desirable to conduct *all* the manipulations of the precursor, before the generation of polyacetylene, at ice temperature. A modification of the original route (Feast 1985) avoids this inconvenience, the monomer **1** is first photoisomerized to **5**, which can be used as a monomer for ring-opening polymerization in an analogous manner to **1** to give the precursor polymer **6**. This new precursor polymer is kinetically more stable than **2** because it has to undergo a 2+2 cycloreversion reaction, which is forbidden by symmetry in the ground state, before the elimination of hexafluoroxylene can occur. There is, of course, a large amount of strain energy stored in precursor polymer **6** and the conversion to polyacetylene is extremely exothermic. As a consequence the process is only satisfactory for thin film preparation and attempts to convert bulk material to polyacetylene result in explosions.

The picture outlined above and summarized in figure 1 is an attainable ideal; however, in practice the precursor polymers which are used have undergone a low degree of elimination of hexafluoroxylene and contain a distribution of short polyene sequences and are more accurately represented by the structures shown in figure 2.

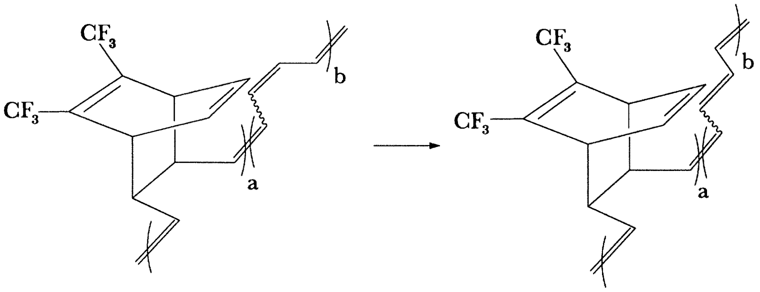


FIGURE 2. Short polyene sequences.

These polymers are, nevertheless, soluble and processable and yield high quality films of D-PA when carefully manipulated, a material that has been successfully exploited in the investigation of the novel semiconductor physics of conjugated polymers (Burroughes 1988). There are several other features of this system which merit attention. For example, the precursors shown in figure 2 undergo photo-oxidative bleaching of the polyene sequences when irradiated with ultraviolet (UV) in the presence of air, the areas of film so exposed are no longer able to be thermally converted to D-PA and become a transparent insulating film, whereas unirradiated sections of the film are thermally converted to D-PA by the usual elimination mechanism and with the usual reduction in volume. Irradiation of thin films of precursor through a mask followed by heating therefore allows the production of high-resolution (less than 1 μm) relief images which define patterns of the conjugated polymer D-PA in an insulating matrix (Allen 1990). Another consequence of this methodology for the production of D-PA is that the precursor materials can be oriented by stretching; subsequent thermal conversion gives D-PA in which the polyene chains are oriented predominantly in the direction of the stretching (Leising 1984).

Recent developments in the structural specification of the initiators used in ring-opening metathesis polymerization have allowed even greater control in the generation of polyene systems via the Durham route. By using well-defined titanium methylidene sources it has proved possible to polymerize monomer **7**, figure 3, to give precursor **8**, which yields D-PA on thermal elimination of napthalene.

The advantage of this approach is that the system shows all the hallmarks of a living polymerization and consequently narrow molecular mass distributions and well-defined block copolymers can be obtained by this methodology (Klavetter 1988). Similar advantages accrue from the use of the well-defined initiator systems $M(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ (where $M = W$ or Mo) (Knoll 1988; Krouse 1988) with the monomer **1**. Indeed in this latter work it has proved possible to establish that all the precursor backbone vinylenes are *trans* and because all the vinylenes formed in the elimination step have to be *cis* the initial polyene has alternating *cis* and *trans* double bonds. These workers have separated individual *tert*-butyl capped telomers of the precursor system by chromatography and converted them to the set of odd polymers with from seven to 19 double bonds. This provides the first synthesis of many of these compounds

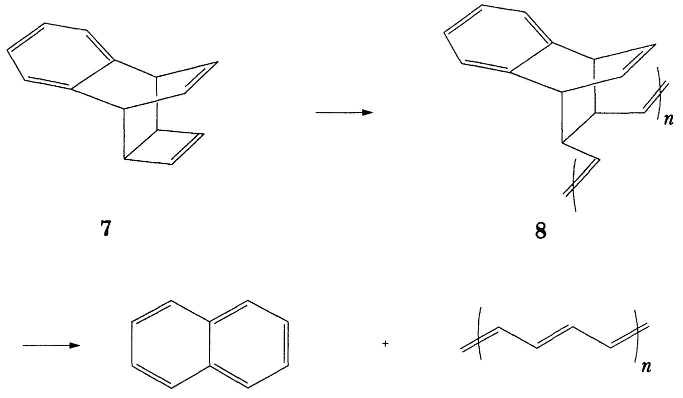


Figure 3. The polymerization of monomer **7** to give precursor **8**.

and a wealth of spectroscopic information concerning such well-defined polyenes (including nonlinear optical data) can be expected to emerge in the future.

It is clear from the foregoing discussion that the synthetic methodology now exists for the production of well-defined films of polyacetylene. Such materials are expected to have high third-order nonlinear optical susceptibilities and a recent study of third harmonic generation in oriented D-PA reports that the value of $\chi^{(3)}$ determined using a 1907 nm laser source polarized parallel to the chain direction (extension ratio 14:1) was $2.7 \pm 0.4 \times 10^{-8}$ Fr, the highest value reported for an organic polymer (Drury 1988).

Polyparaphenylene and poly(paraphenylene vinylene) are, like polyacetylene, characterized by insolubility and infusibility although in this case the materials have a much greater resistance to oxidative degradation. Precursor routes to these materials have also been established and are outlined in figures 4 and 5.

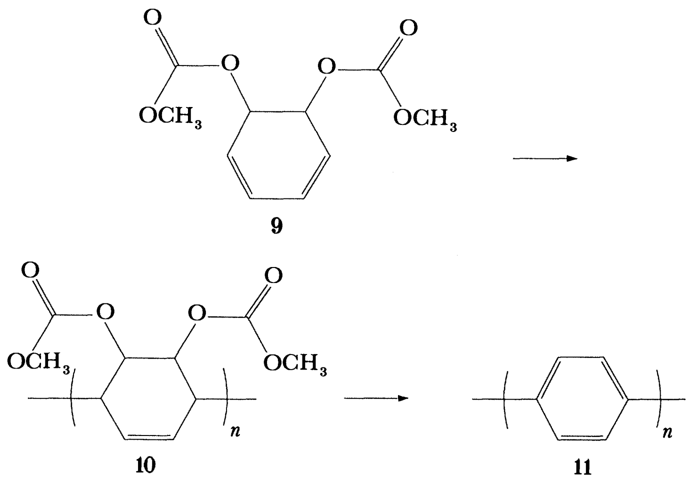
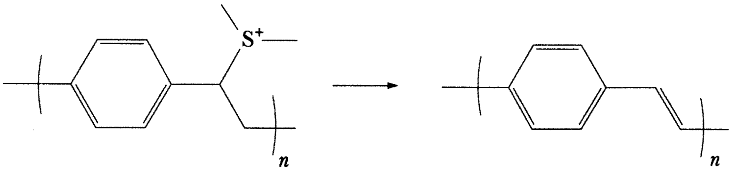


Figure 4. Precursor route.

The polymerization of the cyclic diene **9** gives a soluble precursor polymer **10**, which is somewhat more irregular in structure than figure 4 implies because of the intervention of some 1,2-addition polymerization. Thermal elimination of methanol and carbon dioxide gives a product that is substantially polyparaphenylene **11** (Ballard 1983).

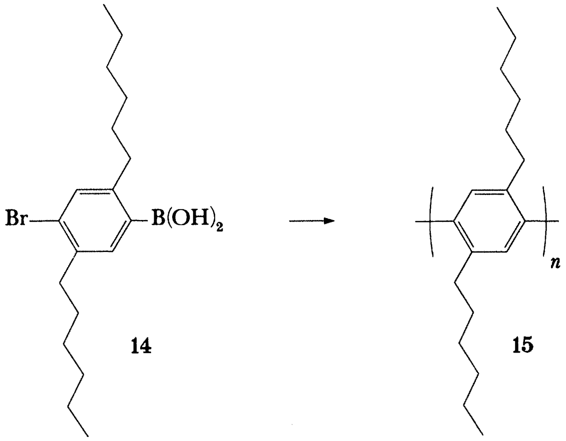


12 **13**

FIGURE 5. Precursor route.

Poly(paraphenylene vinylene) **13** is obtained as indicated in figure 5 via the methanol–water soluble polyelectrolyte precursor **12**, as with D-PA, this material can be stretched to align the molecular chains so that highly anisotropic films can be produced (Gagnon 1987).

An alternative approach to rendering intractable polymers, such as polyparaphenylene, processable is to modify the basic structure by addition of side chains that induce solubility and hence allow traditional solution phase processes to be applied. There have been many examples of this procedure reported, particularly for heterocyclic polymers, and figure 6 outlines the route which has recently been established for the synthesis of polyparaphenylenes (Rehahn 1989).



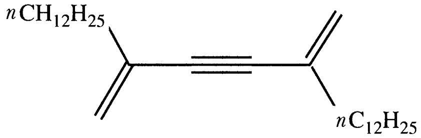
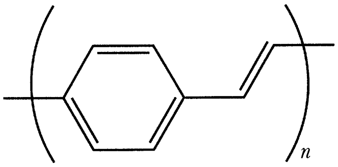
14 **15**

FIGURE 6. The synthesis of polyparaphenylenes.

In this study it was established that palladium-catalysed coupling of the bromoarylboronic acid **14** was far more efficient as a route to polyparaphenylene **15** than the nickel-catalysed coupling of bromoaryl Grignard compounds, which was limited by chain growth terminating reduction of the aryl bromide. This method provides the longest sequences of structurally regular polyparaphenylene yet reported and the material is completely soluble in toluene at DP > 30, whereas unsubstituted sexiparaphenylene has vanishingly small solubility in this solvent.

Thus it can be seen that synthetic organic chemistry provides the means to make and manipulate many kinds of structurally homogeneous and well-defined conjugated polymers. These materials can be produced in a variety of morphologies, and they conform to the design criteria set out at the beginning of this brief review. The values of third-order nonlinear optical susceptibilities so far available are collected in the table 1 and it can be seen that the expectation of large effects appears to be justified by the limited data.

Table 1. Third-order susceptibilities $\chi^{(3)}$ for hydrocarbon polymers

polymer	$\chi^{(3)}/(10^{-12}\ \mathrm{Fr})$	reference
	1.33 ± 0.68	Kajzar (1983)
trans-S-PA (isotropic)	400	Heeger (1987)
trans-S-PA (isotropic)	1300	Kajzar (1987)
trans-D-PA	27000	Drury (1988)
	7.8	Kaino (1987)

The subject is still relatively young and it seems likely that there will be considerable progress in understanding the correlation between structure and property in this general class of polymers during the next few years providing beneficial interactions between synthetic organic chemists and solid state physicists can be developed.

It is a pleasure to acknowledge the support for our work in synthesis provided by BP Research (Sunbury-on-Thames), the SERC and the BMFT. The picture of the field presented here emerged from many stimulating discussions with colleagues and students in Durham, Cambridge, Sunbury and Mainz. I am grateful for their attempts to enlighten me. They are acknowledged in the references cited, remaining errors or obscurities are my responsibility. I thank David Bloor for advice on points of detail and for pointing out two recent references. I am particularly indebted to Duncan Cadd without whose skilled assistance this manuscript would not have been completed.

References

Allen, P. C., Bott, D. C., Brown, C. S., Connors, L. M., Gray, S., Walker, N. S., Clemenson, P. I. & Feast, W. J. 1990 *Springer Series in Solid State Sciences.* (In the press.)

Ballard, D. G. H., Courtis, A., Shirley, I. M. & Taylor, S. C. 1983 *J. chem. Soc. chem. Commun.*, p. 954.

Burroughes, J. H., Jones, C. A. & Friend, R. H. 1988 *Nature, Lond.* **335**, 137.

Chemla, D. S. & Zyss, J. 1987 *Nonlinear optical properties of organic molecules and crystals.* New York: Academic Press.

Drury, M. R. 1988 *Solid St. Commun.* **68**(4), 417.

Edwards, J. H., Feast, W. J. & Bott, D. C. 1984 *Polymer* **25**, 395.

Feast, W. J. & Winter, J. N. 1985 *J. chem. Soc. chem. Commun.*, p. 202.

Gagnon, D. R., Capistran, J. D., Karasz, F. E., Lenz, R. W. & Antoun, S. 1987 *Polymer* **28**, 567.

Girling, I. R., Cade, N. A., Kolinsky, P. V., Jones, R. J., Peterson, I. R., Ahmad, M. M., Neal, D. B., Petty, M. C., Roberts, G. G. & Feast, W. J. 1987 *J. opt. Soc. Am.* B **4**, 950.

Heeger, A. J., Moses, D. & Sinclair, M. 1987 *Synthetic Metals* **17**, 343.

Heeger, A. J., Orenstein, J. & Ulrich, D. R. 1988 *Nonlinear optical properties of polymers*, *MRS Symp. Proc.*, vol. 109. Pittsburg, Pennsylvania: Materials Research Society.

Ito, T., Shirakawa, H. & Ikeda, S. 1974 *J. Polymer. Sci.* **12**(1), 11.

Kaino, T., Kubodera, K. I., Tomaru, S., Kurihara, T., Saito, S., Tsutsui, T. & Tokito, S. 1987 *Electron. Lett.* **23**, 1095.

Kajzar, F., Etemad, S., Baker, G. L. & Messier, J. 1987 *Solid St. Commun.* **63**, 1113.
Kajzar, F., Messier, J., Zyss, J. & Ledoux, I. 1983 *Optics Commun.* **45**, 133.
Kerr, J. 1875 *Phil. Mag.* **50**, 337.
Klavetter, F. L. & Grubbs, R. R. 1988 *Synthetic Metals* **26**, 311.
Knoll, K., Krouse, S. A. & Schrock, R. R. 1988 *J. Am. chem. Soc.* **110**, 4424.
Krouse, S. A. & Schrock, R. R. 1988 *Macromolecules* **21**, 1885.
Leising, G. 1984 *Polym. Bull.* **11**(5), 401.
Lennard-Jones, J. F. 1937 *Proc. R. Soc. Lond.* A **158**, 280.
Natta, G., Mazzanti, G. & Corradini, P. 1958 *Rc. Accad. naz. Lincei CI Sci. fis. mat. nat.* **25**, 3.
Naarmann, H. & Theophilou, N. 1988 *Electroresponsive molecular and polymeric systems* (ed. T. A. Skotheim), ch. 1. New York: Dekker.
Neal, D. B., Petty, M. C., Roberts, G. G., Ahmad, M. M., Girling, I. R., Cade, N. A., Kolinsky, P. V. & Peterson, I. R. 1986 *Electron. Lett.* **22**(9), 460.
Partington, J. R. 1953 *An advanced treatise on physical chemistry. IV Physico-chemical optics*, p. 278 *et seq.*
Prasad, P. N. & Ulrich, D. R. 1987 *Nonlinear optical and electroactive polymers.* New York and London: Plenum Press.
Rehahn, M., Schluter, A.-D., Wegner, G. & Feast, W. J. 1989 *Polymer* **30**, 1054; 1060.
Schott, M. & Wegner, G. 1987 *Nonlinear optical properties of organic molecules and crystals* (ed. D. S. Chemla & J. Zyss), ch. III-1.
Shen, Y. R. 1984 *The principles of nonlinear optics.* New York: Wiley.
Skotheim, T. A. 1986 *Handbook of conducting polymers.* New York: Dekker.
Williams, D. J. (ed.) 1983 *Nonlinear optical properties of organic and polymeric materials. ACS Symp. Ser.* **233**.
Williams, D. J. 1984 *Angew. Chem. int. Edn Engl.* **23**, 690.