CONDUCTING POLYMERS

1. Introduction

The discovery that polyacetylene could be prepared with a high electronic conductivity initiated a major research effort on organic conducting polymers, and was recognized by the award of the Nobel Prize for Chemistry in 2000 to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa. A variety of organic conducting polymer materials has now been developed for applications ranging from electromagnetic shielding and "plastic electronics" to light-emitting devices and corrosion-inhibiting paints.

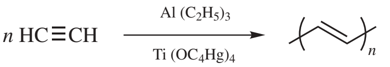
This article gives an overview of the synthesis, properties, and applications of redox dopable electronically conducting polymers, updating the previous article in the fourth edition of *ECT* by Reynolds and co-workers (1). Inorganic conducting polymers also exist, eg poly(sulfur nitride), which was discovered before the organic conducting polymers, and found to have a high conductivity (2). However, these materials will not be discussed here because of their lack of development for applications; a brief summary of their electrical conduction properties is given in an earlier review (3). Carbon nanotubes can be regarded as conducting polymers composed entirely of carbon, but are usually discussed in conjunction with fullerenes (see NANOTECHNOLOGY). We consider only intrinsically conductive polymers—excluding polymer composite materials containing metal particles or carbon black, where the electrical conductivity is the result of percolation of conducting filler particles in an insulating matrix (4) or tunneling between the particles. Ionically conducting polymers, where charge transport is the result of the motion of ions and is thus a problem of mass transport (5), are not discussed here.

The key feature of the electrically conductive organic polymers is the presence of conjugated bonds with π-electrons delocalized along the polymer chains. In the undoped form, the polymers are either insulating or semiconducting with a large band gap. The polymers are converted to the electrically conductive, or doped, forms via oxidation or reduction reactions that form delocalized charge carriers. Charge balance is accomplished by the incorporation of an oppositely charged counterion into the polymer matrix. The conductivity is electronic in nature and no concurrent ion motion occurs in the solid state. The redox doping processes are reversible and can be accomplished electrochemically. Note that during electrochemical switching, ions do move into and out of the polymers as charge-balancing species for the charge carriers on the polymer backbone. Most applications of conducting polymers utilize their electronic (electrically conducting and optical) properties, but some (eg, battery or sensor electrodes) involve their ionic properties.

2. Synthesis of Electrically Conductive Polymers

A number of synthetic routes have been developed for the preparation of conjugated polymers. The diversity has been driven by the desire to examine many different types of conjugated polymers and attempts to improve material properties. Material property enhancement has centered on the synthesis of polymers that are processible in various forms. In some cases, high molecular weight precursor polymers are prepared that can be converted into the conjugated form after processing. The conjugated polymer itself can also be soluble or fusible and is processed prior to doping. Five primary classes of conjugated polymers have been shown to exhibit high levels of electrical conductivity in the doped state. These include polyacetylenes, polyarylenes and polyheterocycles, poly(arylene vinylenes), and polyanilines. In addition, a number of multicomponent materials, usually polymer blends and composites, have been prepared in which at least one of the components is a conducting polymer.

2.1. Polyacetylenes. The first report of the synthesis of a strong, flexible, free-standing film of the simplest conjugated polymer, polyacetylene [26571-64-2], $(CH)_x$, was made in 1974 (6). The process, known as the Shirakawa technique, involves polymerization of acetylene on a thin-film coating of a heterogeneous Ziegler-Natta initiator system in a glass reactor, as shown in equation 1.

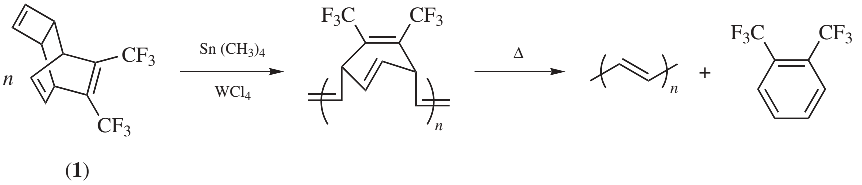


(1)

The resulting porous, fibrillar polyacetylene film is highly crystalline, so is therefore insoluble, infusible, and otherwise nonprocessible. It is also unstable in air in both the conducting and insulating forms.

Much effort has been expended toward the improvement of the properties of polyacetylenes made by the direct polymerization of acetylene (7). Variation of the type of initiator systems (8,9), annealing or aging of the catalyst (10,11), and stretch orientation of the films (12,13) has resulted in increases in conductivity and improvement in the oxidative stability of the material. The improvement in properties is due to producing a polymer with fewer defects.

Even with improvement in properties of polyacetylenes prepared from acetylene, the materials remained intractable. To avoid this problem, soluble precursor polymer methods for the production of polyacetylene have been developed. The most highly studied system utilizing this method, the Durham technique, is shown in equation 2.



(1)

(2)

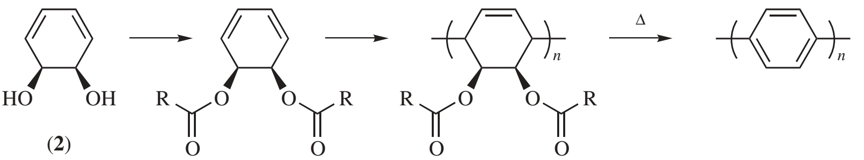
This method involves the metathesis polymerization of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.02.5]deca-3,7,9-triene (**1**), to form an acetone-soluble precursor polymer (14,15). After purification, thin films are cast from solution and the polymer is converted to polyacetylene by thermal treatment (16). This technique is useful only for the production of thin films because of the high exothermicity of the thermal conversion, which is a potential explosion hazard.

However, the films produced in this manner are much less fibrillar and of higher density than the films made by the Shirakawa technique. Variable morphologies are also available using this method; cast films have a much higher amorphous content than Shirakawa films, but stretching of the precursor polymer before or during thermal treatment yields highly oriented and crystalline materials (17–19).

A drawback to the Durham method for the synthesis of polyacetylene is the necessity of elimination of a relatively large molecule during conversion, which can be overcome by the inclusion of strained rings into the precursor polymer structure. This technique was developed in the investigation of the ring-opening metathesis polymerization (ROMP) of benzvalene (20).

Copolymerizations of benzvalene with norbornene have been used to prepare block copolymers that are more stable and more soluble than the polybenzvalene (21). Other copolymerizations of acetylene with a variety of monomers and carrier polymers have been employed in the preparation of soluble polyacetylenes (22–26). In most cases, the resulting copolymers exhibit poorer electrical properties as solubility increases.

2.2. Polyphenylenes. Poly(*p*-phenylene) [25190-62-9] (PPP), synthesized using direct polymerization methods, yields oligomers of a largely intractable material (27–30). Although it is generally difficult to use intractable polymers in practical applications, sintering techniques are available that may make this polymer technologically useful. Electrochemical polymerization affords one route to produce intractable conducting polymers as useful films (31). Soluble precursor methods have been applied to PPP syntheses to circumvent this problem. Bacterial oxidation of benzene using the microorganism pseudomonas putida to prepare 5,6-*cis*-dihydroxycyclohexa-1,3-diene (**2**), followed by esterification and free-radical polymerization, has made it possible to form a soluble PPP precursor as shown in equation 3 (32). A variety of esters (diacetate, dibenzoate, etc) have been investigated to yield high molecular weight, processible precursor polymers. Thermal conversion of thin films and fibers produce fully aromatic PPP. The cis diesters were also prepared using conventional chemical routes (33). The polymers were found to contain 10–15% 1,2 linkages rather than the desired all 1,4-linked structure.

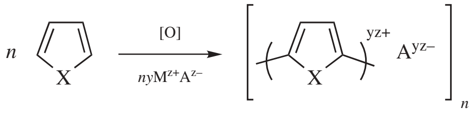


(**2**)

(3)

In both studies described, the resulting PPP was completely intractable. Preparation of a soluble and processible form of PPP has been accomplished using dialkyl-substituted benzenes in the polymerization (34,35). Originally, Grignard coupling of alkyl-substituted 1,4-dibromobenzenes was employed, but low molecular weights were obtained because of loss of chain end functionality. Subsequently, an A–B step-growth polymerization technique was developed, and the resulting PPP had a significantly higher degree of polymerization. Other organometallic routes to produce PPP and its derivatives have been investigated (36,37).

2.3. Polypyrroles. Heterocyclic monomers, such as pyrrole and thiophene, form fully conjugated polymers with the potential for doped conductivity when polymerization occurs in the 2,5 positions as shown in equation 4. The heterocycle monomers can be polymerized by an oxidative coupling mechanism, which can be initiated by either chemical or electrochemical means.



(X = NH,S,O) (**3**) (4)

The electrochemical polymerization of pyrrole is generally believed to follow a radical step-growth mechanism (38). The process is illustrated in Figure 1. The monomer is oxidized at the anode to form radical cations, which quickly couple and eliminate two protons to rearomatize. The pyrrole dimer thus formed is more easily oxidized than the pyrrole monomer, and is reoxidized to allow further coupling reactions to proceed. As the chain length of the growing oligomer increases, it becomes insoluble and deposits on the surface of the cell anode as a black film, where solid-state polymerization continues to occur. The polymer is further oxidized to a positively charged state (**3**) (redox doped) and, to compensate for this charge, negatively charged ions from the electrolyte are incorporated into the film. To avoid corrosion problems, the anode material for oxidative polymerization is normally a noble metal such as platinum, but surprisingly successful electropolymerization has also been obtained on a few commodity metals such as iron, steel, or even aluminum (39,40). Studies have indicated that coupling is primarily at the 2 and 5 positions, with small amounts at the 3 position, which leads to structural disorder in the final polymer (41–44). Pyrrole can also be polymerized using chemical oxidants such as $FeCl_3$ in the presence of an electrolyte to form the conducting polymer in the form of a powder or coating.

Significant variations in the properties of polypyrrole [30604-81-0] are controlled by the electrolyte used in the polymerization. Monoanionic, multianionic,

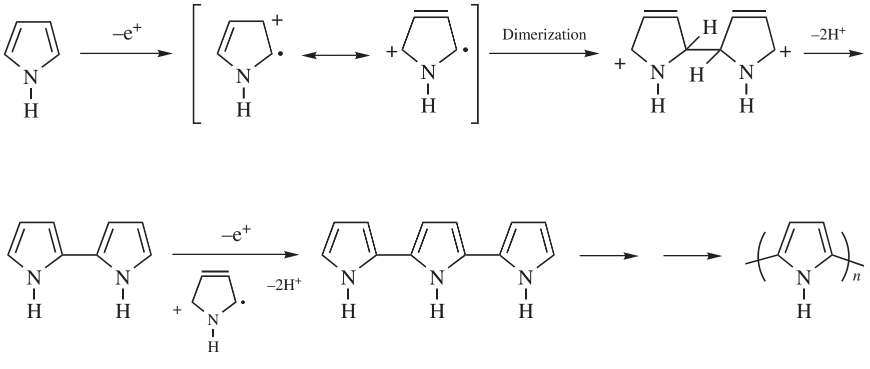
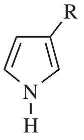
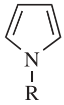


Fig. 1. Mechanism of electrochemical polymerization of pyrrole.

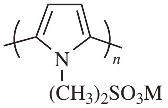
and polyelectrolyte dopants have been studied extensively (38,45–49). Properties can also be controlled by polymerization of substituted pyrrole monomers, with substitution being at either the 3 position (**4**) (50–52) or on the nitrogen (**5**) (53–55). An interesting approach has been to substitute the monomer with a group terminated by an ion, which can then act as the dopant in the oxidized form of the polymer forming a so-called self-doped system such as the one shown in (6) (56–58).



(**4**)



(**5**)

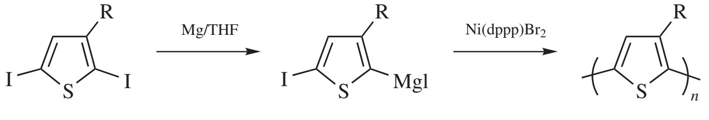


(**6**)

Both electrochemically and chemically polymerized unsubstituted polypyrroles are intractable in both the conducting and insulating forms. Some of the above substituted polypyrroles are appreciably soluble in common solvents, but generally an increase in solvent processibility is accompanied by a loss of conductivity.

2.4. Polythiophenes. In contrast to the intractability of many polypyrroles, a substantial number of substituted polythiophenes have been found to be processible both from solution and in the melt. The most studied of these systems are the poly(3-alkylthiophenes) (P3ATs).

Electrochemical synthesis of P3ATs was accomplished in 1986 (59). In the same year, a technique was reported for the chemical synthesis of P3ATs as shown in equation 5.

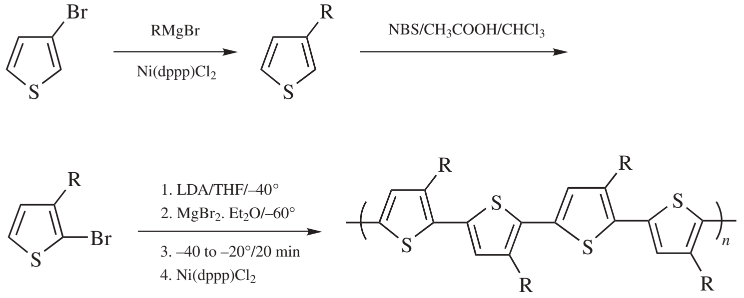
 (5)

THF = tetrahydrofuran

The synthesis involves the nickel-catalyzed coupling of the mono-Grignard reagent derived from 3-alkyl-2,5-diiodothiophene (60). Also in that year, transition-metal halides, ie, $FeCl_3$, $MoCl_5$, and $RuCl_3$, were used for the chemical oxidative polymerization of three-substituted thiophenes (61). Poly(3-hexylthiophene) prepared with an $FeCl_3$ oxidant is highly thermoplastic and soluble, with a conductivity of 40 S/cm when doped by I_2 vapor (62); however, it is difficult to remove the last trace of Fe residues from this product, and this was found to have an adverse effect on its electronic device properties (63). Much more substantial decreases in conductivity were noted when branched side chains were present in the polymer structure, due to twists in the backbone causing a substantial loss of conjugative delocalization (64).

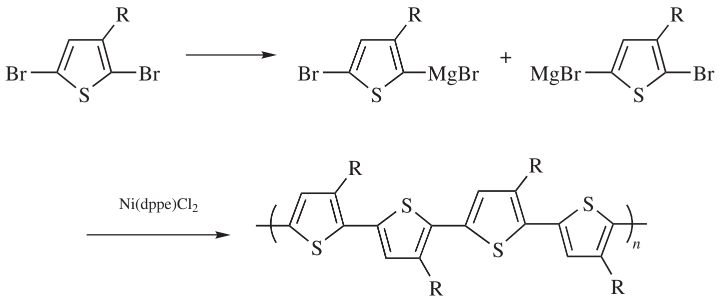
By contrast, significant increases in conductivity (>1000 S/cm) have been reported for regioselectively coupled P3ATs. McCullough and co-workers

(65,66) used an organometallic coupling route (equation 6) to produce highly regioregular polymers. In place of the traditional Grignard route, they prepared 2-bromo-3-alkylthiophene, converted it regioselectively at low temperature into 2-bromo-5-(bromomagnesio)-3-alkylthiophene and polymerized this with Ni(dppe)Cl_2 [dppe = 1,3-bis(diphenylphosphino)ethane] into 98–100% regioregular P3AT products with number-average molecular masses of $(20–40) \times 10^3$. An alternative method described by Chen and co-workers used 2,5-dibromo-3-alkylthiophene as a starting point; it was reacted with highly active "Rieke zinc" at −78°C to form 2-(bromozincio)-3-alkyl-5-bromothiophene and 2-bromo-3 alkyl-5-(bromozincio)thiophene (equation 7). This unpromising mixture of isomers was regioselectively coupled by Ni(dppp)Cl_2 [dppp = 1,3-bis(diphenylphosphino)propane] to produce near-perfect polymer chains with high molecular mass (67,68). Subsequently, Budd and co-workers (69) showed that up to 90% regioregularity could be obtained in a single step by the addition of divalent nickel or cobalt compounds to the reaction mixture for ordinary oxidative polymerisation, at ~0°C; this method has the advantage of producing P3ATs of high conductivity (up to 200 S/cm for cast, undrawn films doped with iodine), and of being readily scaled-up for commercial production.



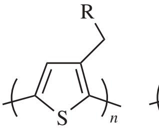
(6)

LDA = lithium diisopropylamide

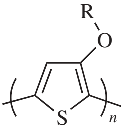


(7)

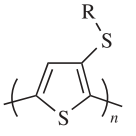
Polythiophenes with substituents other than alkyl groups at the 3 position have been prepared by the polymerization of substituted monomers. Many of these polymers have been substituted alkylthiophenes (**7**), where example side chains are (R =) $-C_6H_5$ (70–73), $-OCH_3$ (50), $-NHC(O)(CH_2)_{10}CH_3$ (50), and $-OSO_2(CH_2)_3CH_3$ (74). Poly(3-alkoxythiophenes) (**8**) (75–79) and poly(3-alkylthiothiophenes) (**9**) (80–82) have been prepared by both chemical and electrochemical methods.



(7)

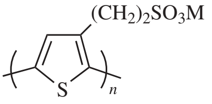


(8)

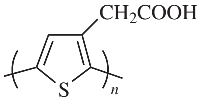


(9)

There are now many other poly(3-substituted thiophenes) and poly(3,4-disubstituted thiophenes), synthesized for a wide variety of scientific and technological purposes (83,84). Among the former group may be mentioned the poly(3-perfluoroalkylthiophenes), which are hydrophobic, "electron deficient", and hard to dope *p*-type (see the section on Doping Processes); they have doping potentials ~ 0.3–0.4 V higher than those of P3ATs. In contrast, poly(3-fluoroalkyloxythiophenes) have similar oxidation potentials to P3ATs and show fairly high conductivities (1–10 S/cm) (85,86). The "self-doped" poly(3-thiophene-β-ethanesulfonate) (**10**) (56,87), its propane analogue (88), and poly(3-thiopheneacetic acid) (**11**) (89) are hydrophilic and in some cases water soluble. They appear to exist as micellar dispersions in aqueous media, from which they can be cast as conductive thin films.

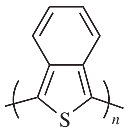


(10)

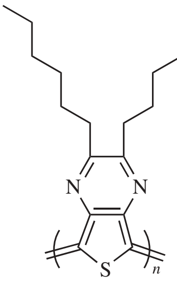


(11)

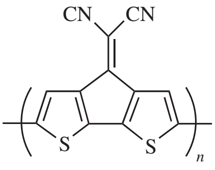
A substantial amount of research has been done on poly(3,4-disubstituted thiophenes) (84). Those having two separate substituents at the 3 and 4 positions generally suffer from steric crowding, which leads to twisting of the backbone, and hence poor π-overlap, large energy gap, and low conductivity. In contrast, those with both substituents in a single ring have high conductivities, and frequently have even smaller energy gaps than P3ATs (see the section on Optical Properties). This finding is partly due to the impeded ability of the ring atoms to cause steric hindrance between adjacent monomer units, and partly to the annelation forcing an increased double-bond character upon the links between the monomers. The principle was first demonstrated in 1984 (90) with the classic example of poly(isothianaphthene) (**12**), which has an energy gap (E_g) of ~1 eV; the polymer may be prepared in a single step by reacting phthalic anhydride with P_4S_{10} (91). Since 1984 there has been a great deal of research to produce other small-gap conducting polymers (92), including polythiophenes such as poly(2,3-dihexylthieno[3,4-*b*]pyrazine) (**13**) (93), the "tethered" polybithiophene (**14**) (94), and the alternating copolymer (**15**) (95); the last-named have E_g values of 0.9, 0.8, and 0.3 eV, respectively.



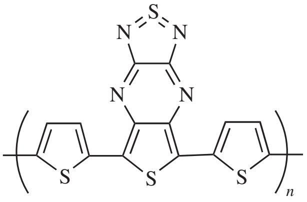
(**12**)



(**13**)

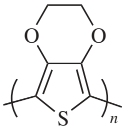


(**14**)



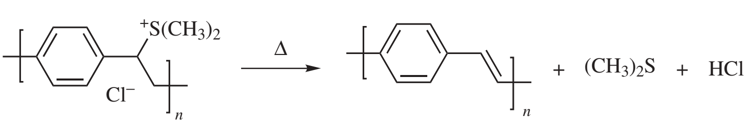
(**15**)

Poly(3,4-ethylenedioxythiophene) or PEDOT (**16**) (96) shows a similar effect of substitution on band gap (E_g ~1.5 eV), and the ether groups in the dioxin ring enable the polymer to complex with metal cations. The idea of polydentate complexation by a poly(3,4-substituted thiophene) has been extended to include polymers with crown ether moieties (97–99), which exhibit cation-selective optical properties.



(**16**)

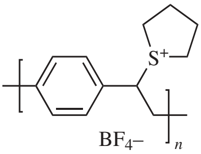
2.5. Poly(arylene vinylenes). The use of the soluble precursor route has been successful in the case of poly(arylene vinylenes), both those containing benzenoid and heteroaromatic species as the aryl groups. The simplest member of this family is poly(*p*-phenylene vinylene) [26009-24-5] (PPV). High molecular weight PPV is prepared via a soluble precursor route (100,101). The method involves the synthesis of the bis(sulfonium) salt from 1,4-bis(chloromethyl)benzene, followed by a sodium hydroxide induced elimination polymerization reaction at 0°C to produce an aqueous solution of a polyelectrolyte precursor polymer (**17**). This polyelectrolyte is then processed into films, foams, and fibers, and converted to PPV thermally (eq. 8).



(8)

(**17**)

The nature of the sulfonium structure affects the yield and quality of the resulting PPV, and it has been found that use of cyclic sulfonium structures (**18**) is preferable (102). With cyclic sulfonium polyelectrolytes, more efficient elimination of sulfur and the counterion occurs during thermal conversion, so fewer sp^3 defects are present in the final PPV.

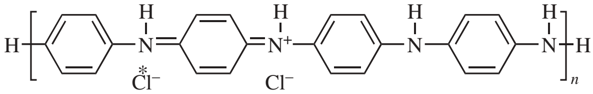


(**18**)

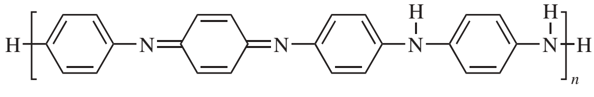
Substituted PPVs have been prepared using similar techniques, especially those with alkoxy substituents on the aromatic ring (103–106). The advantage of long-chain alkoxy (butoxy or hexyloxy) substituents is that not only is the precursor polyelectrolyte soluble, but after conversion the substituted PPV is also soluble (107,108). Heteroaromatic ring structures can also be incorporated into poly(arylene vinylene) structures using the same precursor polymer method shown for PPV. Poly(thienylene vinylene) (109–113) and poly(furylene vinylene) (114,115) have been prepared in this manner. In addition, alkoxy-substituted poly(thienylene vinylenes) (114,116) and poly(pyrrylene vinylenes) (117) have been synthesized. Various copolymers containing phenylene, thienylene, and furylene moieties have been produced (115,118,119). The benzannelated analogue of PPV, poly(1,4-naphthalenevinylene), has also been prepared by a cyclic sulfonium precursor route (120).

Alternative precursor routes to PPV and its derivatives have been investigated, eg, a bromo precursor that thermally eliminates HBr to produce trifluoromethyl-substituted PPV (121). Nonprecursor routes have also proven to be valuable, eg, ring-opening metathesis polymerization (ROMP), especially for the study of polymers with very high molecular mass (122–124).

2.6. Polyanilines. Polyaniline [25233-30-1] (PAni) is commonly prepared by polymerization of aniline using $(NH_4)_2S_2O_8$ in HCl (125,126). As prepared, it has structure (**19**) known as emeraldine hydrochloride. In this form, PAni is highly conductive but completely insoluble. When emeraldine hydrochloride is deprotonated with NH_4OH, the highly soluble emeraldine base (**20**) is produced. It is processible from organic solvents such as aqueous acetic acid (127). It must then be treated with HCl to regenerate the insoluble conducting form of the polymer.

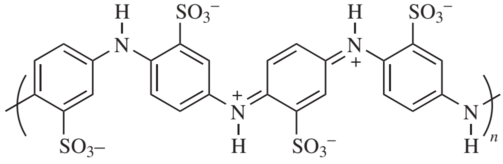


(**19**)



(**20**)

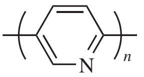
As was the case for polythiophenes, substitution along the PAni backbone has been utilized as a means of improving processibility. Many derivatives are known for PAni because of the possibility of substitution of the monomers at either the main-chain nitrogen atoms, or on the aromatic ring (128–136). Substituents studied have included alkyl, aryl, sulfonyl, and amino groups. The presence of a substituent dramatically decreases the yield of the polymerization and polymer molecular weight, the extent of the effect being proportional to substituent size. Most of the simply substituted (eg, alkyl) PAnis are insoluble as prepared, but treatment with base yields polymers that are highly soluble in common organic solvents. However, the sulfonated, self-doped PAnis have some solubility in water and polar organic solvents (eg, *N*-methylpyrrolidinone) in the conductive state (137,138). Poly(metanilic acid) (**21**) was found to be soluble in water and organic solvents, and is reportedly *n*-dopable (139).



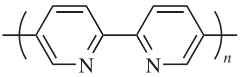
(**21**)

A much-improved combination of high conductivity and excellent processibility has come about through the use of counterion induced solubilization, especially through the use of sulfonate counterions such as 4-dodecylbenzenesulfonate (140) and camphorsulfonate (141).

2.7. Polypyridine and Ladder-Structured Polyquinoxalines. Unlike most other heterocyclic monomers for conducting polymers, pyridine cannot be polymerized directly by oxidation. However, polypyridine, poly(2,5-pyridinediyl), (**22**) can be prepared by chemical or electrochemical reductive debromination of 2,5-dibromopyridine (142). Polypyridine is somewhat soluble in polar solvents such as formic acid and it is found to be relatively electron accepting; hence it can be doped *n*-type much more easily than *p*-type, and it has been found to have a doped conductivity in the *n*-type form of ~0.1 S/cm. A 95% regioregular polymer has been synthesized (143), and it displays significantly higher conductivities. The isomer poly(2,2′-bipyridine-5,5′-diyl) (**23**) (144) has a similar conductivity to irregular polypyridine; it also complexes strongly with metal ions such as Ru(II), Os(II), and Rh(III), and the luminescent and conductive properties of these complexes have been the subject of keen interest (145).

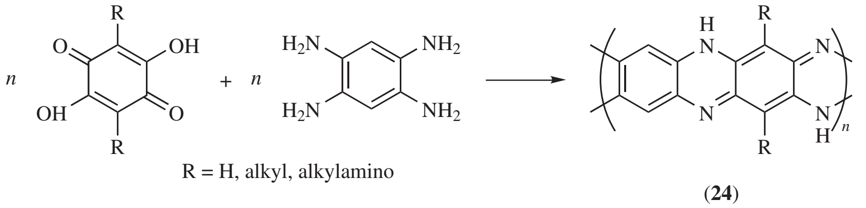


(**22**)



(**23**)

Ladder polymers are those having double strands rather than single linkages between the monomer units; conjugated ladder polymers are of considerable interest through being expected to have small energy gaps (146); some of them, like polypyridines, also have potential commercial interest as possible electron-transporting layers in light-emitting devices. The ladder polyquinoxalines (**24**) and their oligomers (147–150) can be synthesized by Stille-type condensation reactions (eq. 9) between derivatives of 1,2,4,5-benzenetetramine and 2,5-dihydroxy-1,4-benzoquinone, taking care to keep the reactants in solution. They may be regarded as ladder-structured analogues of polyanilines, in common with which they possess great chemical stability. Other conducting ladder polymers have been synthesized by a variety of methods (150).



R = H, alkyl, alkylamino

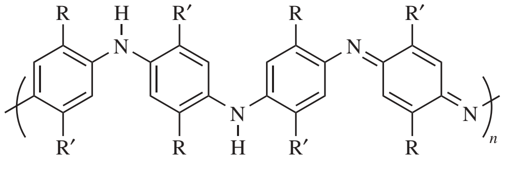
(9)

(**24**)

2.8. Liquid Crystalline Conducting Polymers (LCCPs). Since the electronic properties of conjugated polymers are sensitive to the extent of π-orbital delocalization, and hence to chain alignment and planarity, there has been considerable interest in the effects of solvation (in solution) and of drawing (in the solid state). An alternative method of modifying the backbone conformation is to use the self-organizing properties of liquid crystals (LCs) to control it, either by blending or by chemical functionalization of the conducting polymer with mesogenic groups. This offers potential benefits from switchable electronic properties or from the use of electric or magnetic fields as an aid to orienting conjugated polymers during processing.

Park and co-workers (151) used the alignment capability of LCs to produce partially aligned conducting polymers in the 1980s; they polymerized acetylene with a catalyst trapped in a magnetically aligned LC matrix. Subsequently, polythiophenes with surfactant-like substituents were shown to have lyotropic LC properties and to be magnetically alignable in the presence of solvent (152). Later, polythiophene (153,154), polypyrrole (155,156), and poly(*p*-phenylene) (157) were functionalized with LC substituents in attempts to produce thermotropic LCCPs. Most of these were β-substituted polyaromatics with side groups consisting of short alkylene or oxyalkylene spacer moieties (typically 6–8 atoms long), terminated by common mesogens such as cyanobiphenyl. Polymerization was most commonly carried out by chemical oxidation using $FeCl_3$, although reductive dehalogenation using Ni(0) as a catalyst was used for the synthesis of LC polyphenylenes.

The first processible thermotropic LC polyanilines (**25**) were produced by Gabaston (158) and N-substituted polypyrroles by Ibison (159) and Hasegawa and co-workers (160). These all show typical LC self-organization and an ability to be switched or aligned by the application of electric or magnetic fields.



R = H, allkyl

(**25**)

R′ = -O$(CH_2)_x$ O-Ph-Ph-CN,
-O$(CH_2)_x$O-Ph-Ph-CO-OAr

LCCPs based on poly(phenylene vinylenes) are now being studied as emissive materials in organic light-emitting devices (O-LEDs; see the section Polymer OLEDs and Diode Lasers) to produce polarized light emission. Apart from having useful bulk alignment properties, some LCCPs have been found to be microprocessible by scanning the surface of cast, amorphous films with a finely focused laser beam (161). In this way, local conductivity enhancements of five orders of magnitude have been obtained.

The orienting effects of LCs on conducting polymers should be even more potent for ferroelectric LCCPs, and the synthesis of such a polymer (based on polyacetylene) has been reported (162).

In the syntheses of all the LCCPs above, the mesogenic substituents sterically impede the coupling of monomers in solution and, consequently, the time scale required for polymerization is considerably longer for LCCPs than for most conducting polymers; hence it is not easy to produce high molar mass polymer by conventional step-growth reactions. Nevertheless, by optimizing the conditions and concentrations, average molar masses of $(10\text{–}20) \times 10^4$ may be obtained.

2.9. Conducting Polymer Blends, Composites, and Colloids.

Incorporation of conducting polymers into multicomponent systems allows the preparation of materials that are electroactive and also possess specific properties contributed by the other components. Dispersion of a conducting polymer into an insulating matrix can be accomplished as either a miscible or phase-separated blend, a heterogeneous composite, or a colloidally dispersed latex. When the conductor is present in sufficiently high composition, electron transport is possible.

There are several approaches to the preparation of multicomponent materials, and the method utilized depends largely on the nature of the conductor used. In the case of polyacetylene blends, *in situ* polymerization of acetylene gas into a polymeric matrix has been a successful technique. Low density polyethylene (163) and polybutadiene (164) have both been used in this manner.

Because of the aqueous solubility of polyelectrolyte precursor polymers, another method of polymer blend formation is possible. The precursor polymer is codissolved with a water-soluble matrix polymer, and films of the blend are cast. With heating, the fully conjugated conducting polymer is generated to form the composite film. This technique has been used for poly(arylene vinylenes) with a variety of water-soluble matrix polymers, including polyacrylamide, poly(ethylene oxide), polyvinylpyrrolidinone, methylcellulose, and hydroxypropylcellulose (165). These blends generally exhibit phase-separated morphologies.

The true thermoplastic nature of poly(3-alkylthiophenes) and of some polyanilines, ie, solubility and fusibility, allows the use of compounding methods commonly used in the plastics industry for the preparation of composites of these polymers. The polymers can be codissolved with a matrix polymer, then processed from organic solution. Again the resulting blends are phase separated (70,166–172), but if the composition of conducting polymer is high enough, the conducting component forms the matrix with the insulating polymer dispersed within it, and high conductivity is possible. Melt processing has also been applied to poly(3-alkylthiophenes) (173–175). Films and sheets of blends of poly(3-octylthiophene) with polystyrene, polyethylene, poly(ethylene-*co*-butyl acrylate), and poly(ethylene-*co*-vinyl acetate) have been prepared using compression molding and film-blowing extrusion techniques.

Electrochemical polymerization of heterocycles is useful in the preparation of conducting composite materials. One technique employed involves the electropolymerization of pyrrole into a swollen polymer previously deposited on the electrode surface (176–178). This method allows variation of the physical properties of the material by control of the amount of conducting polymer incorporated into the matrix film. If the matrix polymer is an ionomer such as Nafion (179–181) it contributes the dopant ion for the oxidized conducting polymer and acts as an effective medium for ion transport during electrochemical switching of the material. Other matrix polymers used for polypyrrole have included cross-linked poly(vinyl alcohol) (PVAL) (182), poly(arylether ketone) (183), polyoxyphenylene (184), polyimide (185–187), poly(vinyl chloride-*co*-vinyl acetate) (PVC–PVA) (188), and hydrogels (189). Polythiophenes have also been polymerized electrochemically in analogous fashion, the hosts including polyamide (190) and natural and synthetic rubbers (191).

A number of heterocyclic polymers have been formed chemically within host polymer matrices; the most widely used monomer was pyrrole, which has been polymerized into highly conductive composites after sorption into polyethylene (192,193), poly(methyl methacrylate) (193), polypropylene (193,194), polyurethane (195), PVC–PVA (188), polycarbonate (196), epoxy resins (193,197), and polyvinylpyrrolidinone (198).

Conducting polymer composites have also been formed by coelectrodeposition of matrix polymer during electrochemical polymerization. Because both components of the composite are deposited simultaneously, a homogeneous film is obtained. This technique has been utilized for both neutral thermoplastics such as PVC, as well as for a large variety of polyelectrolytes (46–49,199–201). When the matrix polymer is a polyelectrolyte, it serves as the dopant species for the conducting polymer, so there is an intimate mixing of the polymer chains and the system can be appropriately termed a molecular composite.

The preparation of molecular composites by electropolymerization of heterocycles in solution with polyelectrolytes is an extremely versatile technique, and many polyelectrolyte systems have been studied. The advantages of this method include the use of aqueous systems for the polymerization. Also, the physical and mechanical properties of the overall composite depend on the properties of the polyelectrolyte, so material tailorability is feasible by selection of a polyelectrolyte with desirable properties.

Polypyrrole has been used in the preparation of colloidally dispersed latexes for processing into conducting polymer blends. Electrochemical polymerization of pyrrole in the presence of latex particles having a high concentration of bound sulfonate or sulfate groups on their surface results in the formation of thick heterogeneous films. These films are then ground, solvent swollen, and sheared to yield dispersions from which conducting films can be cast or spin coated (202). Chemical polymerization of pyrrole or aniline in aqueous solutions of sterics stabilizers such as methylcellulose or PVA also results in colloidal systems suitable for the casting of films of conducting polymer blends (203–206).

By using related chemistry, conducting-polymer-coated particles of colloidal dimensions (micro- or nanometer scale) have been prepared via chemical polymerization of pyrrole or aniline adsorbed onto finely divided inorganic powders. The resulting coated particles are eminently suitable for incorporation into a wide variety of blends or composites with conventional thermoplastic polymers. Maeda and Armes (207) produced the first conductive polypyrrole-silica nanocomposites, and Perruchot and co-workers (208) improved the surface concentration of conductive component by the use of a common silane coupling agent, aminopropyltriethoxysilane (APS) prior to the introduction of monomer.

3. Doping and Optical Properties

In order to induce high electrical conductivity in organic conjugated polymers, charge carriers must be introduced. These charge carriers are created by removing electrons from, or adding electrons to, the delocalized π-electron network of the polymer, creating a conducting unit that is now a polymeric ion rather than a neutral species. The charges introduced are compensated by ions from the reaction medium. This process is called doping by analogy to the changes that occur in inorganic semiconductors upon addition of small quantities of electronic defects. However, it proceeds through a different mechanism and is more precisely termed a redox reaction (12,173). The doping level, or ratio of charge carriers per polymer repeat unit, is generally between 0.2 and 0.4 in most polyarylenes (174) and can be determined by measuring the content of charge-balancing counterions. The ability to control the electrical properties of conducting polymers over wide ranges, by adjusting the redox doping level, has created interest in these materials for a number of emerging applications (15).

3.1. Charge Carriers in Conducting Polymers.

Metals have unpaired electrons and their highest occupied electronic levels are half-occupied. Electrical conductivity results from the fact that the electrons can move readily under an electric field since there is no forbidden gap between the highest occupied and lowest unoccupied electronic levels. Conductivity is limited, therefore, by defects in the lattice and vibrational distortions (also called phonons). Since this phonon activity increases with elevated temperatures, the conductivity of metals increases as the temperature is decreased. However, the electrons in conjugated organic polymers, as in inorganic semiconductors, are paired, creating a gap between the highest occupied levels (the valence band) and the lowest unoccupied levels (the conduction band). The energy difference between these bands gives rise to the intrinsic insulating or semiconducting properties of conjugated organic polymers. The moderate conductivity of these materials is a result of thermal excitation of valence electrons into the conduction band. Therefore, the conductivity of semiconductors and conjugated organic polymers increases with increasing temperature in the neutral or undoped state.

The mechanism for the conductivity increase resulting from doping in inorganic semiconductors involves the formation of unfilled electronic bands. Electrons are removed from the top of the valence band during oxidation, called p-type doping, or added to the bottom of the conduction band during reduction, termed n-type doping. Extension of this argument to the case of conjugated organic polymers was found to be inaccurate as the conductivity in many conducting polymers was found to be associated with spinless charge carriers.

In situ electron spin (epr)/electrochemistry techniques have shown that the conducting entity in polyacetylene (175), polypyrrole (176), polythiophene (177,178), and poly(*p*-phenylene) (179) can be spinless, although evidence exists for mixed-valence charge carriers as well (180).

The conductivity increase following doping in conjugated polymers is explained in terms of local lattice distortions and localized electronic states. In this case, the valence band remains full and the conduction band remains empty so that there is no appearance of metallic character. When the polymer chain is redox doped, a lattice distortion results and the equilibrium geometry for the doped state is different than the ground-state geometry. This is evident in many small organic molecules, eg, the ground-state geometry of biphenyl is benzenoid but the geometry of its radical cation is quinoidal (181).

Many conjugated polymers have nondegenerate ground states that behave similarly upon redox doping. When one electron is removed (or added) to the polymer chain a radical cation (or anion) is formed. This results in a lattice distortion that leads to an upward shift of the highest occupied molecular orbital (HOMO) and a downward shift in the lowest unoccupied molecular orbital (LUMO). Although the radical ion is expected to be delocalized over the entire polymer chain, the species is localized, with a localized lattice distortion creating a localized electronic state. Since the geometry of the chain between the radical and the ion must be distorted, and the energy of the distorted geometry is normally higher than that of the ground state, separation, and delocalization of the radical ion results in energetically unfavorable further lattice distortions. This radical ion associated with a lattice distortion is called a polaron (182) as shown in Figure 2 for PPP. A similar argument can be used when a second electron is removed from (or added to) this site. The resulting species is a dication (or dianion), with a lattice distortion separating the two charges. This species is termed a bipolaron and is also illustrated in Figure 2.

Although this model can be applied to most conducting polymers, polyacetylene is a special case because of the degeneracy of its ground state. The energy of the distorted geometry, where the single and double bonds are simply reversed, is equivalent to the energy of the initial structure (Fig. 3). This fact allows the charges formed during the doping of polyacetylene to readily separate

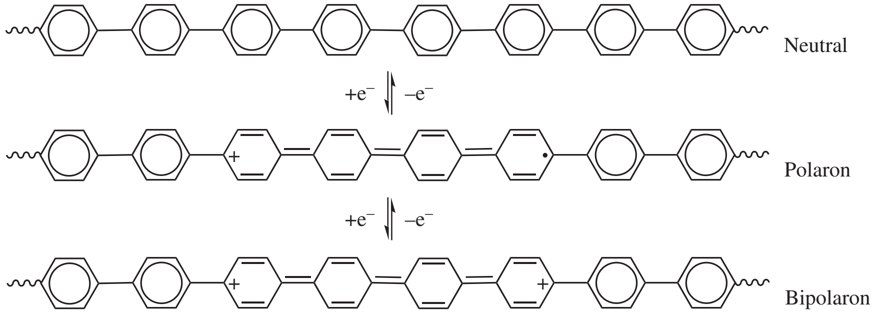


Fig. 2. Lattice distortions associated with the neutral, polaron, and bipolaron states in poly(*p*-phenylene).

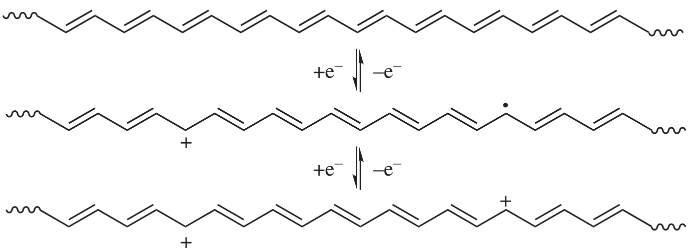


Fig. 3. Lattice distortions associated with the neutral and soliton states in polyacetylene.

because there is no increase in distortion energy. This type of charge carrier is called a soliton and is unique to conjugated polymers, that have degenerate ground states such as polyacetylene (16,183).

3.2. Doping Processes. Redox doping can be accomplished through both chemical and electrochemical means. Vapor-phase doping of neutral polyacetylene has been carried out using AsF_5 and I_2 as oxidants. During this process, the dopant is reduced to form a charge-balancing ion such as AsF_6^- and I_3^-. Polypyrrole can be doped with oxygen because of the low oxidation potential of the neutral polymer (16). Solution doping of many conjugated polymers in suspension or, in the case of processible derivatives, in solution, has been accomplished using a variety of oxidizing and reducing agents. Typical chemical dopants include $FeCl_3$, $NOPF_6$ (184), and sodium naphthalide. Conducting polymers that are synthesized using oxidative coupling techniques are obtained in the oxidized form.

These conjugated polymers can be chemically and electrochemically reduced and reoxidized in a reversible manner. In all cases, the charges on the polymer backbone must be compensated by ions from the reaction medium, which are then incorporated into the polymer lattice. The rate of the doping process is dependent on the mobility of these charge compensating ions into and out of the polymer matrix.

Electrogenerated conducting polymer films incorporate ions from the electrolyte medium for charge compensation (185). Electrochemical cycling in an electrolyte solution results in sequential doping and undoping of the polymer film. In the case of a *p*-doped polymer, oxidation of the film results in the formation of cations on the polymer backbone and the introduction of anions into the film. Since the ions that are transported into the polymer matrix generally make up 20–40% of the doped polymer, the choice of electrolyte has a marked influence on the mechanical and electrochemical properties of the film. Tetraalkylammonium salts are often utilized because of their high solubility in electrochemical solvents and their large electrochemical window. Their perchlorate, fluoroborate, and hexafluorophosphate salts are commonly used in the electrochemical doping of polythiophenes and polypyrroles. However, superior film-forming properties have been observed in the electrosynthesis and doping of polypyrrole using organic sulfonates, such as toluenesulfonate and other arylsulfonates (186).

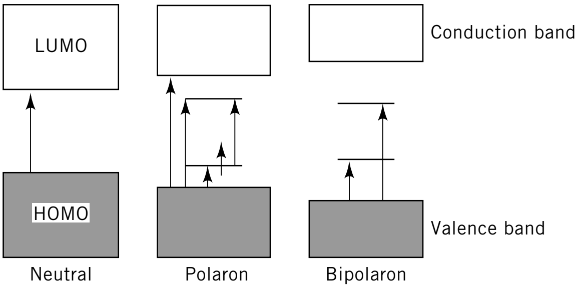


Fig. 4. Band diagram of a nondegenerate ground-state conducting polymer.

In the special case when polyelectrolytes (187) or multivalent anions (188) are used as the electrolyte during electrochemical polymerization, the dopant anion is entrapped because of its large size and multiple charges. As such, it cannot be transported into and out of the films. Cations from the electrolyte medium move into the film during electrochemical reduction to compensate the negative charges on the polyelectrolyte when the electroactive polymer is in its neutral form. Conversely, when the electroactive polymer is oxidized, the cations are expelled into the electrolyte medium and the negative charges on the polyelectrolyte are free to compensate the newly formed positive charges on the conducting polymer backbone.

3.3. Optical Properties. The energy difference between the valence band and the conduction band in conjugated polymers is referred to as the band gap and can be determined using optical spectroscopy. In the neutral (or insulating) form, conducting polymers exhibit a single electronic absorption in either the visible or ultraviolet (uv) region attributed to the electronic transition between the HOMO and LUMO levels as shown in Figure 4. The band gap is generally determined from the onset of this transition. This figure shows a band diagram of a conjugated polymer with a nondegenerate ground state, and the possible transitions in the neutral, polaron, and bipolaron states. Table 1 displays optically determined band gaps for several conducting polymers.

In the doped form, transitions between the band edges and newly formed intragap electronic states are observed in the optical spectra of conducting polymers. When polarons are present as charge carriers, an additional transition is apparent that corresponds to the electronic transitions between the two gap

Table 1. **Optical Band Gaps for Conjugated Polymers**

Polymer	Band gap, eV	Reference
polyacetylene	1.4	209
polypyrrole	2.5	210
polythiophene	2.0	211
poly(3-methylthiophene)	2.2	212
polyfuran	2.7	213
poly(3-hexylfuran)	2.5	213,214
poly(*p*-phenylene vinylene)	2.4	215
poly(*p*-phenylene)	3.0	216
polly(isothianaphene)	1.0	90

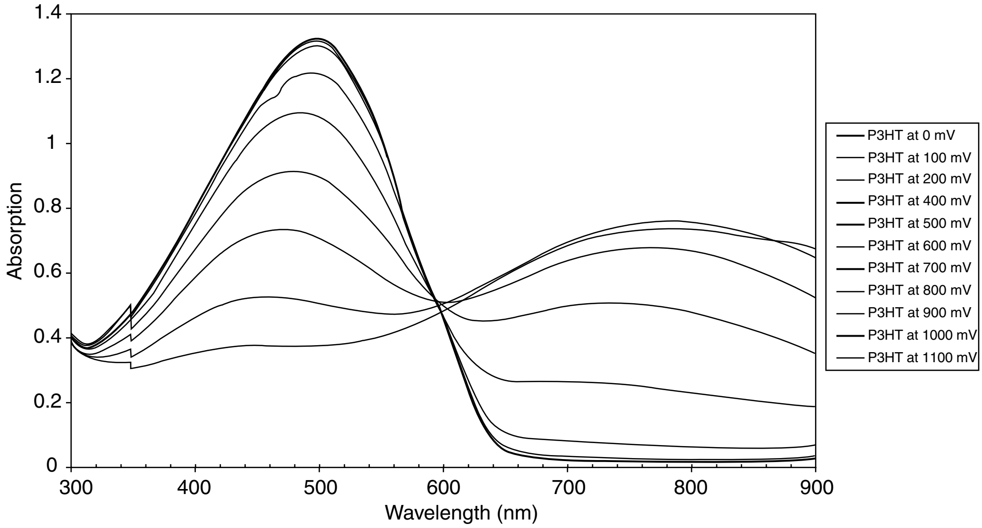


Fig. 5. Evolution of optical spectra of poly(3-hexylthiophene) during electrochemical doping.

states. Since the intragap electronic states are taken from the band edges, the band gap increases with increasing doping levels. Also, since a bipolaron creates a larger lattice distortion than a polaron, the gap states are further away from the band edges in the bipolaron model.

The changes in the optical absorption spectra of conducting polymers can be monitored using optoelectrochemical techniques. The optical spectrum of a thin-polymer film, mounted on a transparent electrode, such as indium tin oxide (ITO) coated glass, is recorded. The cell is fitted with a counter and reference electrode so that the potential at the polymer-coated electrode can be controlled electrochemically. The absorption spectrum is recorded as a function of electrode potential, and the evolution of the polymer's band structure can be observed as it changes from insulating to conducting (16).

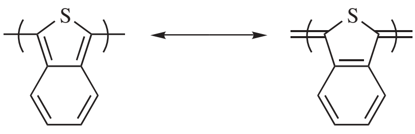
An optoelectrochemical spectrum of poly(3-hexylthiophene), showing the changes in the band structure at various applied voltages, is shown in Figure 5 (217). The spectrum at low voltages contains a single absorption at $\sim$500 nm, corresponding to a band gap transition. At higher voltages an absorption at 740–780 nm appears, which corresponds to a transition between gap states, indicating the presence of polaronic charge carriers. At higher voltages the band gap absorption diminishes significantly and decreases in wavelength.

Since the formation of these types of charge carriers is essential for electrical conductivity in conjugated organic polymers, an important factor in the structural design of conducting polymers is the ease with which they can be oxidized or reduced. The ionization potential of a class of conducting polymers can be altered by modification of the chemical structure. Substitution of the polymer with electron-donating groups has been shown to lower the ionization potential for *p*-type doping. The increased electron density along the conjugated system allows for easier removal of electrons during oxidation.

Another important factor affecting the electronic properties is the steric barrier to planarity along the polymer chain. Since polyheterocycles and polyarylenes must adopt a planar geometry in the ionized state to form quinoid-like segments, steric factors that limit the ability of the polymer to adopt geometries that are planar with respect to adjacent rings have a detrimental effect on the electronic properties (184).

In the case of polythiophenes, eg, the band gaps of alkoxy-substituted derivatives, substituted in either the 3 position (197) or both the 3 and 4 positions (198), are lower than that of the parent polymer, however the band gaps of 3-alkyl derivatives are slightly higher than polythiophene (190). The electron-donating ability of the alkoxy groups are able to outweigh the steric interactions they create. Conversely, the steric factors involved with the alkyl groups at the 3 position of the thiophene ring create geometric strains that outweigh the contribution of these substituents to the electron density of the polymer chain.

The structural effects on the band gap of conjugated organic polymers have been used to create materials with unique optical properties. Design of low band gap polymers has centered on decreasing the energy difference between the ground state and distorted geometries. One example of such a polymer is poly(isothianaphthene) (**26**) (195). The six-membered ring fused to the thiophene backbone becomes aromatic when the thiophene moiety assumes a quinoid-like geometry (**27**). This significantly reduces the energy difference between these two geometries and yields a polymer with a band gap of 1.0 eV.



(**26**) (**27**)

When doped, low band gap polymers have optical transitions in the infrared (ir) region of the spectrum, and therefore transmit more visible light in the conducting form than in the insulating form. This feature enables this class of conducting polymers to be investigated for a number of optical applications where both electrical conductivity and optical transparency are desired.

4. Electrical Conduction Properties

The electrical conductivity σ of a material, which is the inverse of its specific resistivity ρ, is a measure of a material's ability to transport electrical charge. It is determined by measuring the electrical resistance R of a sample of length L and cross-sectional area A through which the current is passing:

$$\sigma = 1/\rho = L/RA$$

The resistivity and conductivity are intrinsic properties of the material, ie, independent of the sample dimensions, unlike resistance that depends on sample size. Electrical conductivity is commonly measured in units of S/cm (ie, $\Omega^{-\varnothing}\mathrm{cm}^{-1}$). The most common method of measuring conductivity is the 4-probe method, in which the outer pair of contacts are used to feed current into the sample, while the inner pair is used to measure the voltage developed (218). The Van der Pauw method and later modifications (219–221) are also used.

Quite generally, the magnitude of the conductivity of organic conducting polymers depends not only on the doping level, but also on the degree of disorder and structural aspects of the polymer. These include main-chain structure and π-overlap, molecular weight and polydispersity, interchain interactions controlled by both main- and side-chain structures, and chain orientation that can be affected by sample processing conditions. Sample morphology plays a key role in limiting or assisting in charge transport. Important factors are the ratio of crystalline-to-amorphous material content, and whether the polymer has a bulk dense morphology or a highly open fibrillar morphology.

No reproducible observation of superconductivity has so far been made in organic polymers (an initial report of superconductivity in a polythiophene derivative is now discredited). Superconductivity does, however, occur in the inorganic polymer poly(sulfur nitride) at temperatures below about 0.3 K (222).

4.1. Metallic Polymers. A compilation of measurements of the room-temperature conductivity of several of the common organic conducting polymers (223) is shown in Figure 6.

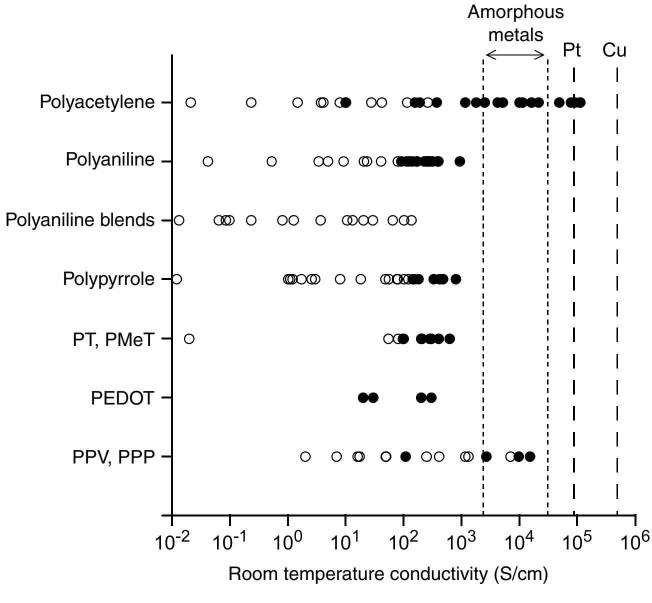


Fig. 6. Measured magnitudes of the room-temperature conductivity of different conducting polymers: polyacetylene (PA) (224–233) polyaniline (PAni) (234–239) and its blends (240–242), polypyrrole (PPy) (243–247), polythiophene (PT) (248,249) and its derivatives poly(3-methyl thiophene) (PMeT) (250,251) and poly(3,4-ethylenedioxythiophene) (PEDOT) (96), poly(*p*-phenylene) (PPP) (252) and poly(*p*-phenylene vinylene) (PPV) (253,254). The solid circles indicate metallic polymer samples and the open circles semiconducting samples. The conductivities of copper, platinum and typical conventional amorphous metals are indicated for comparison.

It is clear that the conductivity reaches remarkably high values considering that the density of carriers is much less than that in conventional metals. Conductivities of 10,000–30,000 S/cm for stretched polyacetylene are widely reproduced, while the highest reported conductivities are 80,000–150,000 S/cm (225,230,231). These conductivities exceed that of copper at room temperature on a weight basis, given that the density of copper is 8.9 gm/cm^3, while that of polyacetylene is only 1.1 gm/cm^3. The highest conductivities are for polyacetylene stretched by a factor of ~6 to improve alignment of the polymer chains—the conductivity perpendicular to the stretch direction is much lower. The doping levels of $FeCl_4^-$ or I_3^- ions for maximum conductivity are ~8% of the number of carbon atoms (225,255).

Apart from the high conductivity values, the metallic character of these highly conducting polymers is demonstrated most decisively by the observation (Fig. 7) that their conductivity remains nonzero as the temperature tends to absolute zero. In contrast, semiconductors show zero conductivity at the absolute zero of temperature owing to the gap between valence and conduction bands or localization of states. (We have used this as the criterion to separate metallic and semiconducting polymers in Fig. 6.) Further evidence is provided by the observation of a metallic Pauli susceptibility (256), a linear electronic specific heat term (257), and a linear diffusion thermoelectric power (223,258), all of which are signatures of delocalized metallic states at the Fermi level.

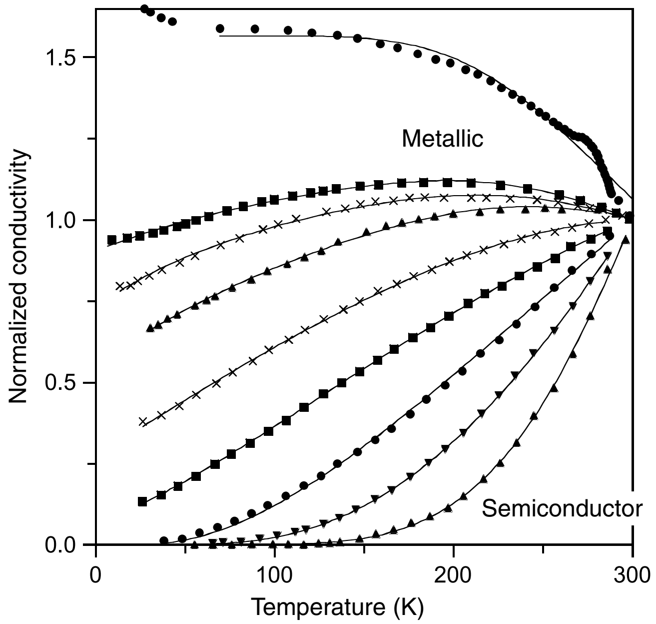


Fig. 7. Temperature dependence of the conductivity of polyacetylene (normalized to its value at room temperature), showing the transition from disordered semiconductor to metallic behavior as doping level increases. The data sets are for polyacetylene doped with ClO_4^- (224) (top two data sets [•, ■]), $FeCl_4^-$ (225) (third from top [×]) or $MoCl_6^-$ (226) (the other data sets). The lines are fits to the heterogeneous disorder model (223) as mentioned in the text.

In spite of this metallic character, the temperature dependence of the conductivity shows a predominantly nonmetallic sign, ie, the conductivity increases as temperature increases, as illustrated in Figure 7. Only near room temperature in the most highly conducting samples does the temperature dependence change to the expected metallic sign [a rare exception is a perchlorate-doped polyacetylene sample, which shows a metallic sign for the conductivity temperature dependence down to very low temperatures (224)]. A similar pattern of temperature dependence is seen for polyaniline, while for polypyrrole, polythiophene, and PPV the nonmetallic sign for temperature persists even up to room temperature (note, however, that the best of these polymers are also clearly metallic in that their conductivity is still nonzero in the zero-temperature limit).

The origin of this mixed metallic–nonmetallic behavior lies in the incomplete crystallinity of the conducting polymers, which is a feature of almost all polymers (259). Detailed studies show that highly conducting polyacetylene is $\sim$90% crystalline with crystallite size of the order of 10 nm (260). The anomalous nonmetallic temperature dependence of conductivity arises from the contribution to resistance of the disordered nonmetallic "barriers" between the metallic crystallites [as shown by the fits in Fig. 7, a heterogeneous disorder model (223) gives a good account of the experimental data for the polymers with nonzero conductivity in the zero-temperature limit]. An interesting consequence of this is that the intrinsic conductivity of the metallic polyacetylene crystallites must exceed that of copper. The remarkably large magnitude of this conductivity is ascribed to the quasi-one-dimensional character of conduction along the polymer chains, which reduces the usual scattering of the metallic charge carriers by lattice vibrations (3,261,262).

This picture of disordered regions around metallic crystalline regions appears to be a general feature of highly conducting polymers (223,232,234, 258,263), with polypyrrole showing a greater overall degree of disorder than polyaniline and polyacetylene.

4.2. Semiconducting Polymers. As the doping level of conducting polymers is reduced, the conductivity changes from mixed metallic–nonmetallic behavior to disordered semiconductor behavior, as clearly shown by the lower data sets in Figure 7 that have zero conductivity in the zero-temperature limit. For a wide variety of semiconducting polymers, the shape of the temperature dependence agrees with that for variable-range hopping conduction (ie, tunneling between localized electronic states assisted by thermally excited lattice vibrations) (223). This finding illustrated by the fits of the hopping expression (264) to the lower curves for semiconducting polymers in Figure 7. It appears that conduction is dominated by hopping between the states created in the semiconductor gap by the doping process (233).

Dispersions of metallic conducting polymer particles in an insulating polymer matrix show a similar temperature-dependent conductivity (242), which is consistent with charging-limited tunneling between mesoscopic metallic islands (265). Owing to the similarity of the predicted conductivity for this mechanism and variable-range hopping, it is difficult to identify the precise nature of the tunneling conduction mechanism in semiconducting polymers.

In high electric fields, the conductivity of conducting polymers shows significant nonohmic behavior, ie, a nonlinear current–voltage (I–V) characteristic.

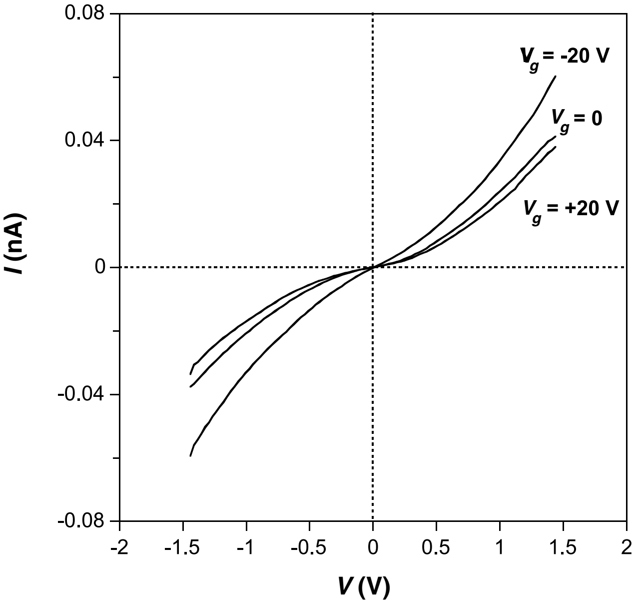


Fig. 8. The I–V characteristic of a polyacetylene nanofibre (lightly doped with iodine) of diameter 4.4 nm, with different gate voltages V_g applied to the Si back gate at a temperature of 233 K (266).

Of particular interest is the I–V characteristic of polyacetylene nanofibres (such nanofibers have potential applications in nanoscale electronics). Electric fields $>10^5$ V/cm can easily be applied to the sample when placed across electrodes only 100–200-nm apart. An example is shown in Figure 8, where the electrodes are deposited on a SiO_2 layer on a Si substrate that acts as a back gate (266). It can be seen that a negative gate voltage significantly changes the current, demonstrating operation of the polyacetylene nanofibre as a field-effect transistor (FET).

5. Stability

The rapid development of many processible conducting polymers that can now be obtained as films, fibers, and molded shapes, suggests that they will be quite useful in a number of applications. One of the concerns presently being addressed is the stability of the conductive polymers during these specific uses.

Although polyacetylene has served as an excellent prototype for understanding the chemistry and physics of electrical conductivity in organic polymers, its instability in both the neutral and doped forms precludes any useful application. In contrast to polyacetylene, both polyaniline and polypyrrole are significantly more stable as electrical conductors. When addressing polymer stability it is necessary to know the environmental conditions to which it will be exposed; these conditions can vary quite widely. For example, many of the electrode applications require long-term chemical and electrochemical stability at room temperature while the polymer is immersed in electrolyte. Aerospace applications, on the other hand, can have quite severe stability restrictions with testing carried out at elevated temperatures and humidities.

The intrinsic stability of undoped conjugated polymers (even polyacetylene) is quite high, but in most practical applications the polymers are doped and exposed to moist air. Herein lie the main stability problems, all of which can be related to the electronic properties of the polymers. Oxygen has a high electron affinity, and forms a charge-transfer complex with polymers such as polyacetylene. This “doping” process leads to the production of the superoxide ion $(O_2)^-$, which is an aggressive oxidant and rapidly leads to irreversible oxidation, chain scission, and loss of conductivity (267). Polymers with a large energy gap such as polyphenylene have high ionisation potentials and cannot be doped by oxygen; they are extremely resistant to oxidation. Polythiophenes, polyanilines, and polypyrroles have an intermediate behavior: All are somewhat susceptible to oxygen doping in their neutral states, but when doped (*p*-type) they have high ionisation potentials and are completely resistant to oxygen. However, a combination of oxygen and a nucleophilic agent, such as water or ammonia, can have a synergic effect due to the loss of dopant, low level incorporation of oxygen and then irreversible degradation and loss of conjugation; the environmental stability can then depend greatly on the ease of removal of the original dopant that is the first stage of the degradation process.

It is well known that the doped polypyrroles exhibit *some* of the best stabilities of electrical conductivity. Typically, poly(pyrrole tosylate) undergoes about a 10% conductivity decrease in a year at room temperature in air. The stability of the conductivity of polypyrrole and a series of poly(3-alkylthiophenes) has been compared in detail (201,202) under systematically controlled environmental and thermal conditions. When poly(pyrrole tosylate) is exposed to a dry N_2 atmosphere at 120°C, there is no evident conductivity change for at least 24 h. Poly(3-alkyl-thiophene tetrachloroferrates), on the other hand, show distinct conductivity decreases because of a thermal undoping process (203). The conductivity change is a function of the length of the pendent alkyl chain, with higher stability exhibited by polymers having the shortest alkyl chains. For example, poly(butylthiophene) exhibits a one-half order of magnitude drop in conductivity in the same amount of time that the conductivity of poly(3-octylthiophene) drops two orders of magnitude.

Poly(pyrrole tosylate) exhibits a slightly lower stability in air at 120°C with conductivity changes in the order of 10% in 24 h, as a result of reactions with environmental O_2 and H_2O. To circumvent this, a study of the mechanical integrity and thermal stability of polypyrroles containing a broad range of dopant ions (204) showed that encapsulation of the conducting polymer in an epoxy matrix led to a great improvement in stability. This finding is illustrated in Figure 9, where an electrochemically prepared poly(pyrrole tosylate) film and a polypyrrole-coated textile were encapsulated and their electrical resistivities monitored during exposure to 80°C and 95% relative humidity (rh) for 1 month. After an initial conductivity change, the film maintains a high conductivity throughout the entire time. The polypyrrole-coated textile, although exhibiting no change in conductivity over the entire experiment, has a higher overall resistivity than the film.

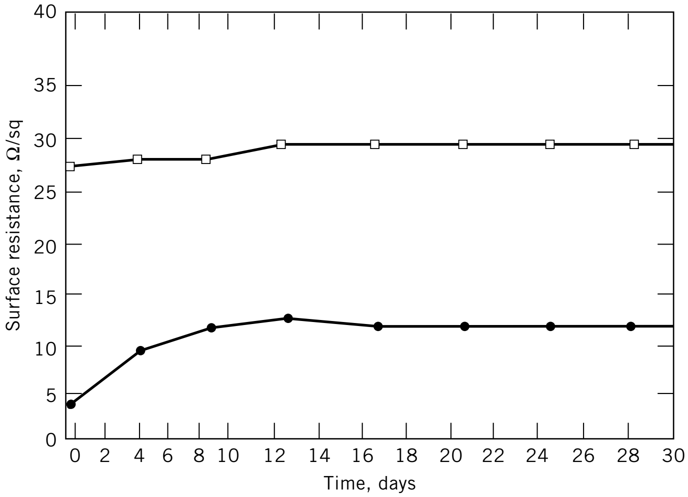


Fig. 9. Thermal stability of epoxy-encapsulated poly(pyrrole tosylate) film, dark squares, 0.5 Ω/sq, and polypyrrole-coated textiles, open squares, 20 Ω/sq, with exposure to 80°C and 95% rh.

PAni is rendered conductive by protonation rather than oxidation of a polyene; consequently its backbone has N^+ rather than C^+ sites in the doped state, and it has far more resistance to nucleophilic attack than a carbon. This confers a very high environmental stability at ambient temperatures. The thermal stability of doped PAni is high, and it is the loss of volatile dopant that leads to conductivity loss and subsequent oxidation at high temperatures (268,269). This PAni–HCl quite readily loses HCl on heating to 130°C, but the use of tosylate or dodecylbenzenesulfonate dopants confers a high thermal stability because the corresponding sulfonic acids are quite nonvolatile.

6. Applications

The novel and varied electrical, electrochemical and chemical properties of conducting polymers are leading to their development for a large variety of applications. In many cases the polymers have unique advantages over other materials, eg, low density, mechanical flexibility, tunable optical properties, and their ability to be functionalized for diferent purposes (270). There are of course disadvantages: eg, the poor stability of polyacetylene mentioned in the previous section severely limits its usefulness for applications.

The range and versatility of conducting polymers in technology is demonstrated in the following sections covering some of the main applications. Where possible, references to books or journal articles are given for each application, and relevant company websites are mentioned for detailed information on specific products and brand names.

6.1. Electromagnetic Shielding and Charge Dissipation. One of the first applications was the general area of electromagnetic shielding (271).

The surface-confined chemical oxidative polymerization of pyrrole and aniline has been used by Milliken Corp. (Spartanburg, South Carolina) to produce textile materials with electrically conductive polymer coatings (272,273). Exposure of various fabrics, including nylons, polyester, and quartz, to an appropriate oxidant leads to a preferential surface adsorption. Subsequent addition of dopant anion and monomer leads to polymerization on the fiber surfaces and formation of coherent, well adhered, conductive polymer coatings $\sim$1 μm in thickness. Polypyrrole-coated fabric can be used as radar camouflage (218,272).

Polyaniline has been used as a charge disspation layer for electron-beam lithography (274,275), as a removable SEM discharge layer (276), as a conducting electrode for electrolytic metallization of copper on through-holes in circuit boards (277), and to provide a solderable finish in printed circuit board (PCB) technology (278).

The processibility of some of the conducting polymers has enabled them to be prepared in forms applicable to typical industrial processes for applications. For example, polyaniline has been dispersed in PVC to produce a family of conducting blends (278,279) marketed by Ormecon Chemie (www.ormecon.com.de), a subsidiary of Zipperling Kessler and Co. (www.zipperling.com.de). Thin films of polyaniline form lightly colored transparent films for antistatic coatings.

6.2. Corrosion-Inhibiting Paints. An application of PAni is its use to inhibit corrosion (280). Studies have shown reduction of corrosion of steel plates exposed to brine and acid environments when coated with a thin layer of PAni (281). The mechanism of this effect could be that the PAni leads to the formation of a thin, uniform layer of unhydrated iron oxide that acts as a barrier to the rusting process (278,282). Polyaniline-based anticorrosion paints have been developed by Ormecon and are in commercial use (283).

6.3. Charge Storage Batteries. The reversible redox chemistry of conductive polymers has allowed the materials to be used as electrodes in rechargeable storage batteries (284). Initially, it was hoped that the low density of polymer electrodes would yield lightweight high-energy-density batteries. This has not been realized because the polymers have low charge densities relative to metal electrodes. The charging and discharging reactions (redox doping and undoping) create charged carriers along the conjugated backbones with concurrent insertion or emission of charge-balancing counterions from the electrolyte. As such, there is no deposition or dissolution of the electrode material and it can be dimensionally stable. This is one limitation of metal electrodes in battery cells where repeated deposition and dissolution cause morphological features at the electrode surface that can separate and break from the electrode. In some instances, high-surface-area dendrites can form on metal surfaces, ultimately leading to an electrical contact between the two electrodes.

Conductive polymer batteries were developed by VARTA/BASF who investigated a series of polypyrrole-based cells (285). Bridgestone/Sienko market a polyaniline/lithium coin-type, or button, cell (286). These cells exhibit near 100% Coulombic efficiencies up to cell voltages of 3.5 V, with recommended use voltages of 3.0 V. At this cell voltage the battery exhibits discharge characteristics of 3.0 mAh or 60 Ah/kg. These cells have cycle lives that are a function of discharge depth. At low discharge depths ($<$10%) the battery could be recharged up to 10,000 times. These cells proved to be quite stable with storage.

6.4. Actuators. Conducting polymers can be used in electromechanical applications (270), since they show a volume change of up to 10% on oxidation or reduction as ions and solvent move into the polymeric structure (286,287). Bilayer constructions can act as artificial muscles (289,290), and the compatibility of conducting polymers with the human body makes implants feasible (291). Polypyrrole–gold bilayer microactuators that bend out of the plane of the wafer can be used to position other microcomponents (292).

6.5. Chemical and Biochemical Sensors. The sensitivity of the electrical properties of conductive polymers to chemical stimuli means that they have proved useful in a number of sensing applications (293). One early program carried out at Allied Signal proposed the use of conductive polymers in remotely readable indicators (294). Conductivity changes induced in the conductive polymer could be read externally and the history of the sample known. Systems designed to detect time–temperature, temperature limit, radiation dosage, mechanical abuse, and chemical exposure were developed.

Conductive polymers can change their electrical conductivities by many orders of magnitude when exposed to specific gaseous reagents (295,296). The reactivity of polypyrrole to NH_3, NO_2, and H_2S was tested to examine this phenomena. These sensors proved to be quite sensitive with large resistance changes occurring with exposure to an atmosphere containing 0.01–0.1% of the reactive gas. In all three cases, the reactions were shown to be reversible as removal of the gas from the atmosphere led to recovery of the original conductivity. “Electronic noses” to detect odors at low concentrations have been marketed, eg, by Osmetech (www.osmetech.plc.uk).

Entrapment of biochemically reactive molecules into conductive polymer substrates can be used to develop electrochemical biosensors (297). This has proven especially useful for the incorporation of enzymes that retain their specific chemical reactivity. Electropolymerization of pyrrole in an aqueous solution containing glucose oxidase (GO) leads to a polypyrrole in which the GO enzyme is codeposited with the polymer. These polymer-entrapped GO electrodes have been used as glucose sensors. A direct relationship is seen between the electrode response and the glucose concentration in the solution that was analyzed with a typical measurement taking between 20 and 40 s.

6.6. Gas Separation Membranes. Studies suggest that, because of the fixed ionic sites along the polymer backbones, conducting polymers are useful as gas separation membranes (298–301). The ability to switch the polymers between charge states (doped and undoped) suggests that external control of gas permeability and selectivity may be possible. Studies of polyaniline (299) showed it served as an excellent membrane material for the separation of the hydrogen–nitrogen, oxygen–nitrogen, and carbon dioxide–nitrogen gas pairs with extremely high selectivities. By utilizing dopants of varied sizes the separation properties of the membranes to different gases can be controlled.

6.7. Electrochromic Applications. During electrochemical switching, distinct changes occur in the optical properties (color and extinction coefficient) of conducting polymer films. This has led many investigators to examine the feasibility for use in electrically switchable, electrochromic, or “smart windows” with polymer layers that darken on application of a voltage (302). As exemplified by polyisothianaphthene (90), thin polymer films are relatively transparent when held in the conducting state and opaque in the insulating state. By using the concepts originally put forth for polyisothianaphthene, a number of low band gap polymers have been synthesized with similar properties.

6.8. Polymer OLEDs and Diode Lasers. The application of a high electric field across a thin conjugated polymer film showed the materials to be electroluminescent (303–305). Until recently the development of electroluminescent displays has been confined to the use of inorganic semiconductors and a limited number of small molecule dyes as the emitter materials (see CHROMOGENIC MATERIALS, ELECTROCHROMIC).

One of the most exciting developments in applications of conducting polymers (306–313) is the use of their electroluminescent properties in organic light-emitting diodes (OLEDs). (Note that OLEDs also include devices based on organic molecules rather than polymers, so OLEDs based on conducting polymers are identified as "polymer OLEDs" or "PLEDs".)

In the basic construction of an OLED based on an electroluminescent polymer, electrons are injected at a cathode and holes at an anode, and their recombination in the bulk polymer leads to the emission of visible photons with an energy roughly equal to that of the polymer's energy gap. A material such as ITO glass is used as the anode, since its electron energies are comparable to those in the valence band of a luminescent polymer. It serves the dual purpose of injecting holes into the device and (being transparent) of allowing the light generated to escape and be seen. Other materials such as thin layers of silicon have been used for this purpose with greater injection efficiency but generally poorer transmission of light. The cathode material is a low work function metal, whose Fermi energy roughly matches the energy of the polymer's conduction band; this serves to inject electrons into the device. The emissive polymer is usually PPV or a soluble alkyl-substituted derivative, although regioregular poly(alkylthiophenenes) such as poly(3-hexylthiophene) have shown good electroluminescent properties for red/ir light.

The initial efficiency of polymer LEDs based on the above principle was minute (0.001%), but a level as high as 10% now seems feasible. These improvements have been brought about by ensuring the efficient and symmetrical injection and transport of carriers into the emissive region. Reactive metals such as calcium have been used as cathodes with improved electron-injection efficiency compared to aluminium, although Heeger and co-workers (314) have demonstrated high efficiency with an aluminium alloy cathode combined with a surfactant layer. A hole transporting layer such as polyaniline is normally interposed between the anode and the emissive polymer, and an efficient electron transporter based on poly(methyl methacrylate) or a polydiazole is sandwiched between the emissive layer and the cathode (315).

Polymer OLEDs have the advantage of flexibility, coverage of a wide area, low power consumption, high intensity at low voltages, fast response times, thinness, and wide viewing angles. The thin film of light-emitting polymer is typically sandwiched between a transparent electrode and a metal electrode. Companies involved in development include Cambridge Display Technologies (CDT), Uniax, Covion, Philips, Toshiba, and others.

In 2002, Philips claimed the first high volume production polymer LED product (the battery charging indicator for an electric razor), based on technology developed by CDT, and further products are planned. Toshiba has demonstrated a 17-in. diagonal full color OLED, also using CDT technology, and commercial display products from other companies are expected (316–319).

6.9. Photovoltaic Cells. The inverse effect to electroluminescence, ie, the generation of electricity from incident light (the photovoltaic effect), also operates in conducting polymers, which can therefore be used to make photovoltaic cells (320–322). Quantum efficiencies of up to 29% with overall power conversion of approximately 2% (for a simulated solar spectrum) have been obtained (320) using polythiophene as the hole acceptor and a PPV derivative as the electron acceptor. Hybrid photovoltaic cells incorporating fullerenes and conducting polymers are under development (323,324), and solar cells using inorganic CdSe nanorods in semiconducting organic polymers could make solar power more affordable (325).

6.10. Plastic Electronics. Electrolytic capacitors using polypyrrole as a solid-state electrolyte can achieve very high values of capacitance (218,326), producing a very thin dielectric layer without short circuits.

The first conducting polymer FET transistor (327) has been followed by more promising developments (328). Cheap disposable all-polymer integrated circuits (ICs) being developed by Philips (329) are likely to find application in smart labels to replace bar codes in supermarkets, eg, that allow automatic pricing without the need to unload goods from the trolley. “Line patterning” of conducting polymer circuits could lead to very inexpensive production (330–332). In this process, a circuit pattern printed on a substrate is exposed to fluid containing a conducting polymer that reacts differently with substrate and printed line. After evaporation of the solvent, the lines can be removed by sonication, leaving a conducting polymer circuit.

7. Acknowledgments

We acknowledge the authors (John R. Reynolds, Andrew D. Child, and Melinda B. Gieselman) of the previous article on this subject in ECT, from which part of the material has been retained. We thank many collaborators and colleagues for discussions, and Dr. Ben Chapman for his assistance in the final stages. ABK thanks the Marsden Fund administered by the Royal Society of New Zealand for support.

BIBLIOGRAPHY

“Polymers, Conductive” in *ECT* 3rd ed., Vol. 18, pp. 755–793, by C. B. Duke and H. W. Gibson, Xerox Corp.; “Electrically Conductive Polymers,” in *ECT* 4th ed., Vol. 9, pp. 61–88, by J. R. Reynolds and A. D. Child, University of Florida and M. B. Gieselman, 3M Specialty Adhesives and Chemicals; “Electrically Conductive Polymers” in *ECT* (online), posting date: December 4, 2000, by John R. Reynolds, Andrew D. Child, University of Florida, Melinda B. Gieselman, 3M Specialty Adhesives and Chemicals.

CITED REFERENCES

1. J. R. Reynolds, A. D. Child, and M. B. Gieselman, *Electrically Conductive Polymers, ECT* 4th ed., Vol. 10, 1994, pp. 61–85.
2. V. V. Walatka, M. M. Labes, and J. H. Perlstein, *Phys. Rev. Lett.* **31**, 1139 (1973).
3. A. B. Kaiser, *Rep. Prog. Phys.* **64**, 1 (2001).
4. W. M. Wright and G. W. Woodham, in J. M. Margolis, ed., *Conductive Polymers and Plastics*, Chapman and Hall, New York, 1989.
5. A. J. Polak, in Ref. 4.
6. T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Educ.* **12**, 11 (1974).
7. H. Shirakawa, *Handbook of Conducting Polymers*, 2nd ed., Marcel Dekker, New York, 1998, p. 197.
8. A. Munardi, R. Aznar, N. Theophilou, J. Sledz, F. Schue, and H. Naarmann, *Eur. Polym. J.* **23**, 11 (1987).
9. I. Kminek and I. Trekoval, *Makromol. Chem. Rapid Commun.* **7**, 53 (1986).
10. H. Tanaka and T. Danno, *Synth. Met.* **17**, 545 (1987).
11. K. Akagi, K. Sakamaki, H. Shirakawa, and H. Kyotani, *Synth. Met.* **69**, 29 (1995).
12. H. Naarman and N. Theophilou, *Synth. Met.* **22**, 1 (1987).
13. G. Lugli, U. Pedretti, and G. Perego, *J. Polym. Sci. Polym. Lett. Ed.* **23**, 129 (1985).
14. J. H. Edwards and W. J. Feast, *Polymer* **21**, 595 (1980).
15. J. H. Edwards, W. J. Feast, and D. C. Bott, *Polymer* **25**, 395 (1984).
16. P. J. S. Foot, P. D. Calvert, N. C. Billingham, C. S. Brown, N. S. Walker, and D. I. James, *Polymer* **27**, 448 (1986).
17. G. Lieser, G. Wegner, R. Weizenhofer, and L. Brombacher, *Polym. Prepr., Am. Chem. Soc. Div. Poly. Chem.* **25**, 221 (1984).
18. C. S. Brown, M. E. Vickers, P. J. S. Foot, N. C. Billingham, and P. D. Calvert, *Polymer* **27**, 1719 (1986).
19. D. D. C. Bradley, R. H. Friend, T. Hartmann, E. A. Marseglia, M. M. Sokolowski, and P. D. Townsend, *Synth. Met.* **17**, 473 (1987).
20. T. M. Swager, D. A. Dougherty, and R. H. Grubbs, *J. Am. Chem. Soc.* **110**, 2973 (1988).
21. T. M. Swager and R. H. Grubbs, *J. Am. Chem. Soc.* **111**, 4413 (1989).
22. J. C. W. Chien, G. E. Wnek, F. E. Karasz, and J. A. Hirsch, *Macromolecules* **14**, 479 (1981).
23. M. E. Galvin and G. E. Wnek, *Polym. Bull.* **13**, 109 (1985).
24. M. Aldissi and A. R. Bishop, *Polymer* **26**, 622 (1985).
25. J. A. Stowell, A. J. Amass, M. S. Beevers, and T. R. Farren, *Makromol. Chem.* **188**, 2535 (1987).
26. G. L. Baker and F. S. Bates, *Macromolecules* **17**, 2619 (1984).
27. P. Kovacic and M. B. Jones, *Chem. Rev.* **87**, 357 (1987); and references cited therein.
28. C. E. Brown and co-workers, *J. Polym. Sci., Polym. Chem. Educ.* **24**, 255 (1986).
29. T. Yamamoto, Y. Hayashi, and Y. Yamamoto, *Bull. Chem. Soc. Jpn.* **51**, 2091 (1978).
30. S. A. Arnautov and V. M. Kobryanskii, *Makromol. Chem. Phys.* **201**, 809 (2000).
31. V. M. Kobryanskii and S. A. Arnautov, *Synth. Met.* **55**, 1371 (1993).
32. D. G. H. Ballard, A. Curtis, I. M. Shirley, and S. C. Taylor, *Macromolecules* **21**, 294 (1988).
33. P. R. McKean and J. K. Stille, *Macromolecules* **20**, 1787 (1987).
34. M. Rehahn, A.-D. Schlüter, G. Wegner, and W. J. Feast, *Polymer* **30**, 1054 (1989).
35. Ibid., p. 1060.
36. W. Heitz, *Angew. Makromol. Chem.* **223**, 135 (1994).
37. A. D. Schluter, *Handbook of Conducting Polymers*, 2nd ed., Marcel Dekker, New York, 1998, p. 209.

38. A. F. Diaz and B. Hall, *IBM J. Res. Dev.* **27**, 342 (1983).
39. M. Schirmeisen and F. Beck, *J. Appl. Electrochem.* **19**, 401 (1989).
40. J. Rodriguez, T. F. Otero, H. Grande, J. P. Moliton, A. Moliton, and T. Trigaud, *Synth. Met.* **76**, 301 (1996).
41. A. F. Diaz, A. Martinez, K. K. Kanazawa, and M. Salmon, *J. Electroanal. Chem.* **130**, 181 (1981).
42. M. Salmon, A. F. Diaz, J. A. Logan, M. Krounbi, and J. Bargon, *Mol. Cryst. Liq. Cryst.* **83**, 265 (1982).
43. T. C. Clarke, J. C. Scott, and G. B. Street, *IBM J. Res. Dev.* **27**, 313 (1983).
44. J. C. Scott, P. Pfluger, M. T. Krounbi, and G. B. Street, *Phys. Rev. B* **28**, 2140 (1983).
45. K. J. Wynne and G. B. Street, *Macromolecules* **18**, 2361 (1985).
46. L. F. Warren and D. P. Anderson, *J. Electrochem. Soc.* **134**, 101 (1987).
47. D. T. Glatzhofer, J. Ulanski, and G. Wegner, *Polymer* **28**, 229 (1987).
48. T. Shimidzu, A. Ohtani, T. Iyoda, and K. Honda, *J. Electroanal. Chem.* **224**, 123 (1987).
49. M. B. Gieselman and J. R. Reynolds, *Macromolecules* **23**, 3118 (1990).
50. M. R. Bryce, A. Chissel, P. Kathirgamanathan, D. Parker, and N. R. M. Smith, *J. Chem. Soc., Chem. Commun.*, 466 (1987).
51. J. Ruhe, T. Ezquerra, and G. Wegner, *Makromol. Chem., Rapid Commun.* **10**, 103 (1989).
52. H. Masuda, S. Tanaka, and K. Kaeriyama, *J. Chem. Soc., Chem. Commun.*, 725 (1989).
53. A. Deronzier and J.-C. Moutet, *Acc. Chem. Res.* **22**, 249 (1989).
54. G. Bidan and M. Guglielmi, *Synth. Met.* **15**, 49 (1986).
55. J. R. Reynolds, P. A. Porapatic, and R. L. Toyooka, *Macromolecules* **20**, 958 (1987).
56. A. O. Patil, Y. Ikenoue, F. Wudl, and A. J. Heeger, *J. Am. Chem. Soc.* **109**, 1858 (1987).
57. P. G. Pickup, *J. Electroanal. Chem.* **225**, 273 (1987).
58. J. R. Reynolds, N. S. Sundaresan, M. Pomerantz, S. Basak, and C. K. Baker, *J. Electroanal. Chem.* **250**, 355 (1988).
59. M. Sato, S. Tanaka, and K. Kaeriyama, *J. Chem. Soc., Chem. Commun.*, 873 (1986).
60. R. L. Elsenbaumer, K.-Y. Jen, and R. Oboodi, *Synth. Met.* **15**, 169 (1986).
61. R. Sugimoto, S. Takeda, H. B. Gu, and K. Yoshino, *Chem. Express* **1**, 635 (1986).
62. S. Marchant and P. J. S. Foot, *Chemtronics* **5**, 131 (1991).
63. M. S. A. Abdou, X. Lu, Z. W. Xie, F. Orfino, M. J. Deen, and S. Holdcroft, *Chem. Mater.* **7**, 631 (1995).
64. M. Lemaire, R. Garreau, F. Garnier, and J. Roncali, *New J. Chem.* **11**, 703 (1987).
65. R. D. McCullough, R. D. Lowe, M. Jayaraman, and D. L. Anderson, *J. Org. Chem.* **58**, 904 (1993).
66. R. D. McCullough and co-workers, in L. R. Dalton and C. Lee, eds., *Electrical, Optical and Magnetic Properties of Organic Solid State Materials*, Vol. 328 and references therein.
67. T.-A. Chen and R. D. Riecke, *J. Am. Chem. Soc.* **114**, 10087 (1992).
68. X. Wu, T.-A. Chen, and R. D. Riecke, *Macromolecules* **28**, 2101 (1995); and references therein.
69. U.K. Pat. GB 2, 304, 346B (1998) D. Budd, R. Davis, and P. J. S. Foot, PCT/GB97/00742 (Baxenden Ltd., UK).
70. S. Hotta, S. D. Rughooputh, and A. J. Heeger, *Synth. Met.* **22**, 79 (1987).
71. K. Kaeriyama, M. Sato, and S. Tanaka, *Synth. Met.* **18**, 233 (1987).
72. M. Sato, S. Tanaka, K. Kaeriyama, and F. Tomanaga, *Polymer* **28**, 107 (1987).
73. J. Roncali, R. Garreau, D. Delabouglise, F. Garnier, and M. Lemaire, *Synth. Met.* **28**, C341 (1989).

74. A. O. Patil, *Synth. Met.* **28**, C495 (1989).
75. S. Tanaka, M. Sato, and K. Kaeriyama, *Polym. Commun.* **26**, 303 (1985).
76. K. Kaeriyama, S. Tanaka, M. Sato, and K. Hamada, *Synth. Met.* **28**, C611 (1989).
77. M. Feldhues, G. Kaempf, H. Litterer, T. Mecklenburg, and P. Wegener, *Synth. Met.* **28**, C487 (1989).
78. G. Daoust and M. Leclerc, *Macromolecules* **24**, 455 (1991).
79. S.-A. Chen and C.-C. Tsai, *Macromolecules* **26**, 2234 (1993).
80. R. L. Elsenbaumer, K.-Y. Jen, G. G. Miller, and L. W. Shacklette, *Synth. Met.* **18**, 277 (1987).
81. J. P. Ruiz, K. Nayak, D. S. Marynick, and J. R. Reynolds, *Macromolecules* **22**, 1231 (1989).
82. J. R. Reynolds, Jose P. Ruiz, Fei Wang, Cynthia A. Jolly, Kasinath Nayak, and Dennis S. Marynick, *Synth. Met.* **28**, 621 (1989).
83. J. Roncali, *Chem. Rev.* **92**, 711 (1992).
84. J. Roncali, *Handbook of Conducting Polymers*, 2nd ed., Marcel Dekker, New York, 1998, p. 311.
85. A. El Kassmi, W. Buchner, F. Fache, M. Lemaire, *J. Electroanal. Chem.* **326**, 357 (1992).
86. L. Robitaille and M. Leclerc, *Chem. Mater.* **59**, 301 (1992).
87. Y. Ikenoue, N. Outani, A. O. Patil, F. Wudl, and A. J. Heeger, *Synth. Met.* **30**, 305 (1989).
88. Y. Ikenoue, Y. Saida, M. Kira, H. Tomozawa, H. Yashima, and M. Kobayashi, *J. Chem. Soc., Chem. Commun.*, 1694 (1990).
89. P. Bauerle, *Adv. Mater.* **2**, 490 (1990).
90. F. Wudl, M. Kobayashi, and A. J. Heeger, *J. Org. Chem.* **49**, 3382 (1984).
91. D. Vanderzande, R. Van Asselt, I. Hoogmartens, J. Gelan, P. E. Froehling, M. Aussems, O. Aagaard, and R. Schellekens, *Synth. Met.* **74**, 65 (1995).
92. M. Pomerantz, *Handbook of Conducting Polymers*, 2nd ed., Marcel Dekker, New York, 1998, p. 277.
93. M. Pomerantz, B. Chaloner-Gill, L. O. Harding, J. J. Tseng, and W. J. Pomerantz, *Synth. Met.* **55**, 960 (1993).
94. J. P. Ferraris and T. L. Lambert, *J. Chem. Soc., Chem. Commun.*, 752 (1991).
95. S. Tanaka and Y. Yamashita, *Synth. Met.* **69**, 599 (1995).
96. A. N. Aleshin, R. Kiebooms, and A. J. Heeger, *Synth. Met.* **101**, 369 (1999).
97. J. Roncali, H. S. Li, and J. Roncali, *J. Electroanal. Chem.* **95**, 8983 (1990).
98. P. Bauerle and S. Scheib, *Adv. Mater.* **5**, 848 (1993).
99. M. J. Marsella and T. M. Swager, *J. Am. Chem. Soc.* **115**, 12214 (1993).
100. D. R. Gagnon, J. D. Capistran, F. E. Karasz, and R. W. Lenz, *Polym. Bull.* **12**, 293 (1984).
101. I. Murase, T. Ohnishi, T. Noguchi, M. Hirooka, and S. Murakami, *Mol. Cryst. Liq. Cryst.* **118**, 333 (1985).
102. R. W. Lenz, C.-C. Han, J. Stenger-Smith, and F. E. Karasz, *J. Polym. Sci., Polym. Chem. Ed.* **26**, 3241 (1988).
103. I. Murase, T. Ohnishi, T. Noguchi, and M. Hirooka, *Synth. Met.* **17**, 639 (1987).
104. S. Antoun, D. R. Gagnon, F. E. Karasz, and R. W. Lenz, *Polym. Bull.* **15**, 181 (1986).
105. K.-Y. Jen, L. W. Shacklette, and R. L. Elsenbaumer, *Synth. Met.* **22**, 179 (1987).
106. P. L. Burn, D. D. C. Bradley, A. R. Brown, R. H. Friend, and A. B. Holmes, *Synth. Met.* **41–43**, 261 (1991).
107. C.-C. Han and R. L. Elsenbaumer, *Synth. Met.* **30**, 123 (1989).
108. S. H. Askari, S. D. Rughooputh, and F. Wudl, *Synth. Met.* **29**, E129 (1989).
109. K.-Y. Jen, M. Maxfield, L. W. Shacklette, and R. L. Elsenbaumer, *J. Chem. Soc., Chem. Commun.*, 309 (1987).

110. PCT Int. Pat. WO 88 00,954 (1988), K.-Y. Jen, R. L. Elsenbaumer, and L. W. Shacklette.
111. I. Murase, T. Ohnishi, T. Noguchi, and M. Hirooka, *Polym. Commun.* **28**, 229 (1987).
112. Ger. Pat. DE 3,704,411 (1987), I. Murase, T. Ohnishi, and T. Noguchi.
113. S. Yamada, S. Tokito, T. Tsutsui, and S. Saito, *J. Chem. Soc., Chem. Commun.*, 1448 (1987).
114. K.-Y. Jen, T. R. Jow, and R. L. Elsenbaumer, *J. Chem. Soc., Chem. Commun.*, 1113 (1987).
115. K.-Y. Jen, R. Jow, L. W. Shacklette, M. Maxfield, H. Eckhardt, and R. L. Elsenbaumer, *Mol. Cryst. Liq. Cryst.* **160**, 69–77 (1988).
116. K.-Y. Jen, H. Eckhardt, T. R. Jow, L. W. Shacklette, and R. L. Elsenbaumer, *J. Chem. Soc., Chem. Commun.*, 215 (1988).
117. M. A. Takassi, W. Chen, R. E. Niziurski, M. P. Cava, and R. M. Metzger, *Synth. Met.* **36**, 55 (1990).
118. J.-I. Jin, H.-K. Shim, and R. W. Lenz, *Synth. Met.* **29**, E53 (1989).
119. H.-K. Shim, R. W. Lenz, and J.-I. Jin, *Makromol. Chem.* **190**, 389 (1989).
120. J. D. Stenger-Smith, T. Sauer, G. Wegner, and R. W. Lenz, *Polymer* **31**, 1632 (1990).
121. A. B. Holmes, A. C. Grimsdale, X. -C. Li, S. C. Moratti, F. Cacialli, J. Grüner, and R. H. Friend, *Synth. Met.* **76**, 165 (1996).
122. E. Thorn-Csanyi and H. D. Hohnk, *J. Mol. Catal.* **76**, 101 (1992).
123. A. Kumar and B. E. Eichinger, *Makromol. Chem., Rapid Commun.* **13**, 311 (1992).
124. A. Greiner, *Adv. Mater.* **5**, 477 (1993).
125. A. G. MacDiarmid, J.-C. Chiang, A. E. Richter, N. L. D. Somasiri, and A. J. Epstein, in L. Alcacer, ed., *Conducting Polymers*, Reidel, Dordrecht, Holland, 1987, p. 105.
126. K. L. Tan, B. T. G. Tan, S. H. Khor, K. G. Neoh, and E. T. Kang, *J. Phys. Chem. Solids* **52**, 673 (1991).
127. M. Angelopoulos, A. Ray, A. G. MacDiarmid, and A. J. Epstein, *Synth. Met.* **21**, 21 (1987).
128. E. M. Genies, M. Lapkowski, and J. F. Penneau, *J. Electroanal. Chem.* **249**, 97 (1988).
129. G. D'Aprano, M. Leclerc, and G. Zotti, *J. Electroanal. Chem.* **351**, 145 (1993).
130. G. D'Aprano, M. Leclerc, G. Zotti, and G. Schiavon, *Chem. Mater.* **7**, 33 (1995).
131. Y. Wei, W. W. Focke, G. E. Wnek, A. Ray, and A. G. MacDiarmid, *J. Phys. Chem.* **93**, 495 (1989).
132. J. Guay, M. Leclerc, and L. H. Dao, *J. Electroanal. Chem.* **251**, 31 (1988).
133. M. Leclerc, J. Guay, and L. H. Dao, *Macromolecules* **22**, 641 (1989).
134. L. H. Dao, J. Guay, M. Leclerc, and J.-W. Chevalier, *Synth. Met.* **29**, E377 (1989).
135. L. H. Dao, J. Guay, and M. Leclerc, *Synth. Met.* **29**, E383 (1989).
136. J.-W. Chevalier, J.-Y. Bergeron, and L. H. Dao, *Polym. Commun.* **30**, 308 (1989).
137. J. Yue and A. J. Epstein, *J. Am. Chem. Soc.* **112**, 2800 (1990).
138. X.-L Wei, Y. Z. Wang, S. M. Long, C. Bobeczko, and A. J. Epstein, *J. Am. Chem. Soc.* **118**, 2545 (1996).
139. K. Krishnamoorthy, A. Q. Contractor, and A. Kumar, *J. Chem. Soc., Chem. Commun.*, 240 (2002).
140. Y. Cao, P. Smith, and A. J. Heeger, *Synth. Met.* **48**, 91 (1992).
141. R. Menon, Y. Cao, D. Moses, and A. J. Heeger, *Phys. Rev. B* **47** (1993).
142. T. Yamamoto, T. Ito, and K. Kubota, *Chem. Ind.*, 337 (16 May 1988).
143. T. Yamamoto, T. Nakamura, H. Fukumoto, and K. Kubota, *Chem. Lett.*, 502 (2001).
144. T. Yamamoto and co-workers, *Chem. Lett.* 223 (1990).
145. F. Barigelletti and L. Flamigni, *Chem. Soc. Rev.* **29**, 1 (2000).
146. M. Kertesz, *Macromolecules* **28**, 1475 (1995).
147. L. R. Dalton and co-workers, *Polymer* **28**, 543 (1987).

148. L. P. Yu and L. R. Dalton, *Macromolecules* **23**, 3439 (1990).
149. P. J. S. Foot, V. Montgomery, and P. Spearman, *Mater. Sci. Forum* **191**, 251 (1995).
150. U. Scherf, *J. Mater. Chem.* **9**, 1853 (1999).
151. Y. W. Park and co-workers, *Synth. Met.* **17**, 539 (1987).
152. M. Aldissi, *Mol. Cryst. Liq. Cryst.* **160**, 121 (1988).
153. M. R. Bryce and co-workers, *Synth. Met.* **39**, 397 (1991).
154. N. Koide, *Mol. Cryst. Liq. Cryst. A* **261**, 427 (1995).
155. F. Vicentini and co-workers, *Liq. Crystals* **19**, 235 (1995).
156. P. J. Langley, F. J. Davis, and G. R. Mitchell, *J. Chem. Soc., Perkin Trans. II*, 2229 (1997).
157. V. Percec and co-workers, *Macromolecules* **32**, 2597 (1999).
158. L. I. Gabaston, P. J. S. Foot, and J. W. Brown, *J. Chem. Soc., Chem. Commun.*, 429 (1996).
159. P. Ibison, P. J. S. Foot, and J. W. Brown, *Synth. Met.* **76**, 297 (1996).
160. H. Hasegawa, M. Kijima, and H. Shirakawa, *Synth. Met.* **84**, 177 (1997).
161. U.K. Patent, GB 2 318 119B, (2000) P. Ibison and co-workers.
162. K. Akagi, H. Goto, and H. Shirakawa, *Synth. Met.*, **84**, 313 (1997).
163. M. E. Galvin and G. E. Wnek, *J. Polym. Sci., Polym. Chem. Ed.* **21**, 2727 (1983).
164. M. F. Rubner, S. K. Tripathy, J. Georger, and P. Cholewa, *Macromolecules* **16**, 870 (1983).
165. J. M. Machado, J. B. Schlenoff, and F. E. Karasz, *Macromolecules* **22**, 1964 (1989).
166. L. W. Shacklette, C. C. Han, and M. H. Luly, *Synth. Met.* **57**, 3532 (1993).
167. L. M. Gan and co-workers, *Polymer Bull.* **31**, 347 (1993).
168. T. Vikki and co-workers, *Macromolecules* **29**, 2945 (1996).
169. J. Stejskal and co-workers, *Polymer International* **44**, 283 (1997).
170. M. Zilberman, G. I. Titelman, A. Siegmann and co-workers, *J. Appl. Polymer Sci.* **23**, 243 (1997).
171. W. A. Gazotti, Jr., R. Faez, and M-A. De Paoli, *Eur. Polymer. J.* **35**, 35 (1999).
172. H. Morgan, P. J. S. Foot, and N. W. Brooks, *J. Mater. Sci.* **36**, 5369 (2001).
173. J.-E. Österholm and co-workers, *Synth. Met.* **28**, C435 (1989); ibid., C467 (1989).
174. H. Isotalo and co-workers, *Synth. Met.* **28**, C461 (1989).
175. J.-O Nilsson and co-workers, *Synth. Met.* **28**, C445 (1989).
176. S. E. Lindsey and G. B. Street, *Synth. Met.* **10**, 67 (1984).
177. M.-A. DePaoli, R. J. Waltman, A. J. Diaz, and J. Bargon, *J. Polym. Sci., Polym. Chem. Ed.* **23**, 1687 (1985).
178. O. Niwa, M. Kakuchi, and T. Tamamura, *Polym. J.* **19**, 1293 (1987).
179. F.-R. F. Fan and A. J. Bard, *J. Electrochem. Soc.* **133**, 301 (1986).
180. R. M. Penner and C. R. Martin, *J. Electrochem. Soc.* **133**, 310 (1986).
181. G. Nagasubramanian, S. Di Stefano, and J. Mascanin, *J. Phys. Chem.* **90**, 447 (1986).
182. R. Gangopadhyay and A. De, *Sensors Actuators B* **77**, 326 (2001).
183. F. Selampinar, U. Akbulut, and L. Toppare, *Polym.—Plast. Technol. Eng.* **37**, 295 (1998).
184. J. Aguilar-Hernandez, J. Skarda, and K. Potje-Kamloth, *Synth. Met.* **95**, 197 (1998).
185. F. Selampinar and co-workers, *Polym. Sci. Polym. Chem.* **35**, 3009 (1997).
186. F. Selampinar, U. Akbulut, and L. Toppare, *Synth. Met.* **84**, 185 (1997).
187. idem., *Macromol. Sci.—Pure Appl. Chem.* **A33**, 309 (1996).
188. N. Balci and co-workers, *J. Appl. Polym. Sci.* **64**, 667 (1997).
189. K. Gilmore and co-workers, *Polymer Gels Netw.* **2**, 135 (1994).
190. F. Vatansever and co-workers, *Polym. Int.* **41**, 237 (1996).
191. S. Yigit and co-workers, *Synth. Met.* **79**, 11 (1996).
192. B. Aydinli, L. Toppare, and T. Tincer, *J. Appl. Polym. Sci.* **72**, 1843 (1999).
193. M. Omastova and co-workers, *Synth. Met.* **81**, 49 (1996).

194. J. P. Yang and co-workers, *Polymer* **37**, 793 (1996).
195. Y. Lee and J. Kim, *Polym.—Korea* **22**, 953 (1998).
196. U. Gessler, M. L. Hallensleben, and L. Toppare, *Adv. Mater.* **3**, 104 (1991).
197. J. Fournier, G. Boiteux, G. Seytre, and G. Marichy, *Synth. Met.* **84**, 839 (1997).
198. A. Mohammadi and co-workers, *J. Polymer Sci. Pol. Chem.* **32**, 495 (1994).
199. R. E. Noftle and D. Pletcher, *J. Electroanal. Chem.* **227**, 229 (1987).
200. L. L. Miller and Q.-X Zhou, *Macromolecules* **20**, 1594 (1987).
201. T. Shimidzu, A. Ohtani, and K. Honda, *J. Electroanal. Chem.* **251**, 323 (1988).
202. S. J. Jasne and C. K. Chiklis, *Synth. Met.* **15**, 175 (1986).
203. S. P. Armes, J. F. Miller, and B. Vincent, *J. Colloid Interfac. Sci.* **118**, 410 (1987).
204. S. P. Armes, M. Aldissi, M. Hawley *et al.*, *Langmuir* **7**, 1447 (1992).
205. H. Nakao, T. Nagaoka, and K. Ogura, *Anal. Sci.* **13**, 327 (1997).
206. R. Gangopadhyay, A. De, and G. Ghosh, *Synth. Met.* **123**, 21 (2001).
207. S. Maeda and S. P. Armes, *J. Mater. Chem.* **4**, 935 (1994).
208. C. Perruchot and co-workers, *Synth. Met.* **113**, 53 (2000).
209. A. O. Patil, A. J. Heeger, and F. Wudl, *Chem. Rev.* **88**, 183 (1988).
210. J. R. Reynolds, *J. Molec. Elec.* **2**, 1 (1986).
211. T. C. Chung, J. H. Kaufman, A. J. Heeger, and F. Wudl, *Phys. Rev. B* **30**, 702 (1984).
212. S. N. Hoier, D. D. Ginley, and S.-M Park, *J. Electrochem. Soc.* **135**, 91 (1988).
213. S. Wang, T. Kawai, K. Yoshino, K. Tanaka, and T. Yamabe, *Jpn. J. Appl. Phys.* **29**, L2264 (1990).
214. K. Nishioka, S. Wang, and K. Yoshino, *Synth. Met.* **41–43**, 815 (1991).
215. K. F. Voss, C. M. Foster, L. Smilowitz, D. Mihailovic, S. Askari, G. Srdanov, Z. Ni, S. Shi, A. J. Heeger, and F. Wudl, *Phys. Rev. B* **43**(6), 5109 (1991).
216. H. Eckhart, L. W. Shacklette, K.-Y Jen, and R. L. Elsenbaumer, *J. Chem. Phys.* **91**, 1303 (1989).
217. C. M. Pratt, Ph.D. Thesis, Kingston University (2003).
218. S. Roth, One-Dimensional Metals, VCH, Weinheim (1995).
219. Van der Pauw, *Philips Res. Repts.* **13**, 1 (1958).
220. Van der Pauw, *Philips Res. Repts.* **16**, 187 (1961).
221. H. C. Montgomery, *J. Appl. Phys.* **42**, 2971 (1971).
222. R. L. Greene, G. B. Street, and L. J. Suter, *Phys. Rev. Lett.* **34**, 577 (1975).
223. A. B. Kaiser, *Adv. Mater.* **13**, 927 (2001).
224. Y. W. Park, E. S. Choi, and D. S. Suh, *Synth. Met.* **96**, 81 (1998).
225. J. Tsukamoto, *Adv. Phys.* **41**, 509 (1992).
226. Y. W. Park, *Synth. Met.* **45**, 173 (1991).
227. F. Körner, G. Thummes, and J. Kötzler, *Synth. Met.* **51**, 31 (1992).
228. Y. Nogami, H. Kaneko, H. Ito, T. Ishiguro, T. Sasaki, N. Toyota, A. Takahashi, and J. Tsukamoto, *Phys. Rev. B* **43**, 11829 (1991).
229. R. Zuzok, A. B. Kaiser, W. Pukacki, and S. Roth, *J. Chem. Phys.* **95**, 1270 (1991).
230. T. Schimmel, W. Riess, J. Gmeiner, G. Denninger, M. Schwoerer, H. Naarmann, and N. Theophilou, *Solid State Commun.* **65**, 1311 (1988).
231. N. Basescu, Z.-X Liu, D. Moses, A. J. Heeger, H. Naarmann, and N. Theophilou, *Nature (London)* **327**, 403 (1987).
232. K. Ehinger and S. Roth, *Philos. Mag. B* **53**, 301 (1986).
233. A. J. Epstein, H. Rommelman, R. Bigelow, H. W. Gibson, D. M. Hoffmann, and D. B. Tanner, *Phys. Rev. Lett.* **50**, 1866 (1983).
234. J. P. Travers, B. Sixou, D. Berner, A. Wolter, P. Rannou, B. Beau, B. Pépin-Donat, C. Barthet, M. Guglielmi, N. Mermilliod, B. Gilles, D. Djurado, A. J. Attias, and M. Vautrin, *Synth. Met.* **101**, 359 (1999).
235. S. J. Pomfret, P. N. Adams, N. P. Comfort, and A. P. Monkman, *Polymer* **41**, 2265 (2000).

236. E. R. Holland, S. J. Pomfret, P. N. Adams, and A. P. Monkman, *J. Phys.: Condens. Matter* **8**, 2991 (1996).
237. C. O. Yoon, J. H. Kim, H. K. Sung, J. H. Kim, K. Lee, and H. Lee, *Synth. Met.* **81**, 75 (1996).
238. A. Raghunathan, G. Rangarajan, and D. C. Trivedi, *Synth. Met.* **81**, 39 (1996).
239. Z. H. Wang, J. Joo, C.-H Hsu, and A. J. Epstein, *Synth. Met.* **68**, 207 (1995).
240. G. Du, J. Avlyanov, C. Y. Wu, K. G. Reimer, A. Benatar, A. G. MacDiarmid, and A. J. Epstein, *Synth. Met.* **85**, 1339 (1997).
241. B. Sixou, C. Barthet, M. Guglielmi, and J. P. Travers, *Phys. Rev. B* **56**, 4604 (1997).
242. C. K. Subramaniam, A. B. Kaiser, P. W. Gilberd, C.-J Liu, and B. Wessling, *Solid State Commun.* **97**, 235 (1996).
243. N. T. Kemp, A. B. Kaiser, C.-J Liu, B. Chapman, A. M. Carr, H. J. Trodahl, R. G. Buckley, A. C. Partridge, J. Y. Lee, C. Y. Kim, A. Bartl, L. Dunsch, W. T. Smith, and J. S. Shapiro, *J. Polym. Sci. B: Polym. Phys.* **37**, 953 (1999).
244. T. H. Gilani and T. Ishiguro, *J. Phys. Soc. Jpn.* **66**, 727 (1997).
245. W. P. Lee, Y. W. Park, and Y. S. Choi, *Synth. Met.* **84**, 841 (1997).
246. K. Sato, M. Yamaura, T. Hagiwara, K. Murata, and M. Tokumoto, *Synth. Met.* **40**, 35 (1991).
247. D. S. Maddison, R. B. Roberts, and J. Unsworth, *Synth. Met.* **30**, 47 (1989).
248. J. A. Reedijk, H. C. F. Martens, S. M. C. van Bohemen, O. Hilt, H. B. Brom, and M. A. J. Michels, *Synth. Met.* **101**, 475 (1999).
249. S. Masubuchi and S. Kazama, *Synth. Met.* **74**, 151 (1995).
250. D. Berner, J.-P Travers, and D. Delabouglise, *Synth. Met.* **101**, 377 (1999).
251. S. Masubuchi, T. Fukuhara, and S. Kazama, *Synth. Met.* **84**, 601 (1997).
252. L. W. Shacklette, H. Eckhardt, R. R. Chance, G. G. Miller, D. M. Ivory, and R. H. Baughman, *J. Chem. Phys.* **73**, 4098 (1980).
253. M. Ahlskog, M. Reghu, A. J. Heeger, T. Noguchi, and T. Ohnishi, *Phys. Rev. B* **53**, 15529 (1996).
254. J. M. Madsen, B. R. Johnson, X. L. Hua, R. B. Hallock, M. A. Masse, and F. E. Karasz, *Phys. Rev. B* **40**, 11751 (1989).
255. R. H. Baughman, N. S. Murthy, G. G. Miller, and L. W. Shacklette, *J. Chem. Phys.* **79**, 1065 (1983).
256. A. J. Epstein, H. Rommelman, M. A. Druy, A. J. Heeger, and A. G. MacDiarmid, *Solid State Commun.* **38**, 683 (1981).
257. D. Moses, A. Denenstein, A. Pron, A. J. Heeger, and A. G. MacDiarmid, *Solid State Commun.* **36**, 219 (1980).
258. Y. W. Park, A. J. Heeger, M. A. Druy, and A. G. MacDiarmid, *J. Chem. Phys.* **73**, 946 (1980).
259. M. P. Stevens, *Polymer Chemistry: An Introduction*, 2nd ed., Oxford University Press, Oxford, 1990, p. 91.
260. J. P. Pouget, Z. Oblakowski, Y. Nogami, P. A. Albouy, M. Laridjani, E. J. Oh, Y. Min, A. G. MacDiarmid, J. Tsukamoto, T. Ishiguro, and A. J. Epstein, *Synth. Met.* **65**, 131 (1994).
261. L. Pietronero, *Synth. Met.* **8**, 225 (1983).
262. S. Kivelson and A. J. Heeger, *Synth. Met.* **22**, 371 (1988).
263. A. J. Epstein, in P. Bernier, S. Lefrant, and G. Bidan, eds., *Advances in Synthetic Metals*, Elsevier, Amsterdam, The Netherlands, 1999, p. 349.
264. N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, 2nd ed., Clarendon Press, Oxford, 1979.
265. P. Sheng, *Philos. Mag.* **65**, 357 (1992).
266. J. G. Park, G. T. Kim, V. Krstic, S. H. Lee, B. Kim, S. Roth, M. Burghard, and Y. W. Park, *Synth. Met.* **119**, 469 (2001).

267. N. C. Billingham, P. D. Calvert, P. J. S. Foot, and F. Mohammad, *Polymer Degradation Stability* **19**, 323 (1987).
268. D. Poussin, H. Morgan, and P. J. S. Foot, *Polymer Inter.* **52**, 433 (2003).
269. A. A. Pud, *Synth. Metals* **66**, 1 (1994).
270. G. G. Wallace, G. M. Spinks, P. R. Teasdale, *Conductive Electroactive Polymers*, Technomic, Lancaster, Pa., 1997.
271. N. F. Colaneri and L. W. Shacklette, *IEEE Trans. Intr. Meas.* **41**, 291 (1992).
272. R. V. Gregory, W. C. Kimbrell, and H. H. Kuhn, *Synth. Met.* **28**, C823 (1989).
273. R. V. Gregory, W. C. Kimbell, and H. H. Kuhn, *J. Coated Fabrics* **20**, 1 (1991).
274. M. Angelopoulos, J. M. Shaw, R. D. Kaplan, and S. Perreault, *J. Vac. Sci. Tech. B* **7**, 1519 (1989).
275. M. Angelopoulos, *IBM J. Res. Develop.* **45**, 1 (2001).
276. M. Angelopoulos and J. M. Shaw, *Microelect. Eng.* **13**, 515 (1991).
277. W. S. Huang, M. Angelopoulos, J. R. White, and J. M. Park, *Mol. Cryst., Liq. Cryst.* **189**, 227 (1990).
278. B. Wessling, *Chem. Innov.* **31**, 34 (2001).
279. B. Wessling, *Synth. Met.* **85**, 1313 (1997).
280. D. W. Berry, *J. Electrochem. Soc.* **132**, 1022 (1985).
281. W.-K Lu, R. L. Elsenbaumer, and B. Wessling, *Synth. Met.* **71**, 2163 (1995).
282. B. Wessling, *Adv. Mater.* **6**, 226 (1994).
283. J. Posdorfer and B. Wessling, *Fresenius J. Anal. Chem.* **367**, 343 (2000).
284. M. D. Levi, Y. Gofer, and D. Aurbach, *Poly. Adv. Tech.*, **13**, 697 (2003).
285. D. Naegele and R. Bittihn, *Solid State Ionics* **28–30**, 983 (1988).
286. T. Matsunaga, H. Daifuku, T. Nakajima, and T. Kawagoe, *Polymers Adv. Technol.* **1**, 33 (1990).
287. L. W. Shacklette, M. Maxfield, S. Gould, J. F. Wolf, T. R. Jow, and R. H. Baughman, *Synth. Met.* **18**, 611 (1987).
288. R. H. Baughman, *Makromol. Chem. Macromol. Symp.* **51**, 193 (1991).
289. T. F. Otero, J. Rodriguez, E. Angulo, and C. Santamaria, *Synth. Met.* **55**, 3715 (1993).
290. Q. Pei and O. Inganas, *Synth. Met.* **55**, 3718 (1993).
291. E. Smela, *Adv. Mat.* **15**, 481 (2003).
292. E. W. H. Jager, E. Smela, and O. Inganas, *Science* **290**, 1540 (2000).
293. L. Dai, P. Soundarrajan, and T. Kim, *Pure Appl. Chem.* **74**, 1753 (2002).
294. R. H. Baughman, R. L. Elsenbaumer, Z. Iqbal, G. G. Miller, and H. Eckhardt, *Proceedings of the International Winter School on Conducting Polymers*, Kirchberg, Austria, March 1987.
295. G. Gustafsson and I. Lundstrom, *Proceedings of the Second International Meeting on Chemical Sensors*, Bordeaux, France, July 1986.
296. J. Janata and M. Josowicz, *Nature Mat.* **2**, 19 (2003).
297. N. C. Foulds and C. R. Lowe, *J. Cem. Soc., Faraday Trans. 1* **82**, 1259 (1986).
298. W. Liang and C. R. Martin, *Chem. Mater.* **3**, 390 (1991).
299. M. R. Anderson, B. R. Mattes, H. Reiss, and R. B. Kaner, *Science* **252**, 1412 (1991).
300. J. Sarrazin, M. Persin, and M. Cretin, *Macromol. Sym.* **188**, 1 (2002).
301. J. Pellegrino, *Adv. Memb. Tech. Ann. N. Y. Acad. Sci.* **984**, 289 (2003).
302. D. R. Rosseinsky and R. J. Mortimer, *Adv. Mat.* **13**, 783 (2001).
303. J. H. Burroughes and co-workers, *Nature (London)* **347**, 539 (1990).
304. D. Braun, A. J. Heeger, and H. Kroemer, *J. Electron. Mater.* **20**, 945 (1991).
305. Y. Ohmori, M. Uchida, K. Muro, and K. Yoshino, *Jpn. J. Appl. Phys.* **30**, L1938 (1991).
306. M. Granstrom, K. Petritsch, A. C. Arias, A. Lux, M. R. Andersson, and R. H. Friend, *Nature (London)* **395**, 257 (1998).
307. A. Kraft, A. Grimsdale, and A. B. Holmes, *Angew. Chem. Int. Ed.* **37**, 402 (1998).

308. R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, and W. R. Salaneck, *Nature (London)* **397**, 121 (1999).
309. M. T. Bernius, M. Inbasekaran, J. O'Brien, and W. Wu, *Adv. Mater.* **12**, 1737 (2000).
310. P. K. H. Ho, S. Thomas, R. H. Friend, and N. Tessler, *Science* **285**, 233 (1999).
311. I. D. Rees, K. L. Robinson, A. B. Holmes, C. R. Towns, and R. O'Dell, *MRS Bull.* **27**, 451 (2002).
312. C. D. Muller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirn, P. Rudati, H. Frohne, O. Nuyken, H. Becker, and K. Meerholz, *Nature (London)* **421**, 829 (2003).
313. A. Holmes, *Nature (London)* **421**, 800 (2003).
314. Yong Cao, Gang Yu, and Alan J. Heeger, *Synth. Met.* **102**, 881 (1999).
315. M. S. Weaver and co-workers, *Thin Solid Films* **273**, 39 (1996).
316. M. D. McGehee and A. J. Heeger, *Adv. Mater.* **12**, 1655 (2000).
317. C. Kallinger, M. Hilmer, A. Haugeneder, M. Perner, W. Spirkl, U. Lemmer, J. Feldmann, U. Scherf, K. Müllen, A. Gombert, and V. Wittwer, *Adv. Mat.* **10**, 920 (1998).
318. N. Tessler, *Adv. Mat.* **11**, 363 (1999).
319. G. Kranzelbinder and G. Leising, *Rep. Prog. Phys.* **63**, 729 (2000).
320. M. Grandstrom, K. Petritsch, A. C. Arias, A. Lux, M. R. Anderson, and R. H. Friend, *Nature (London)* **395**, 257 (1998).
321. N. S. Saraciftci, *Curr. Opin. Solid-State Mater. Sci.* **4**, 373 (1999).
322. G. G. Wallace, P. C. Dastoor, D. L. Officer, and C. O. Too, *Chem. Innov.* **30**, 14 (2001).
323. G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science* **270**, 1789 (1995).
324. C. J. Brabec, F. Padinger, J. C. Hummelen, R. A. J. Janssen, N. S. Sariciftci, *Synth. Met.* **102**, 861 (1999).
325. W. Huynh, J. J. Dittmer, and A. P. Alivisatos, *Science* **295**, 2425 (2002).
326. J. S. Miller, *Adv. Mater.* **5**, 671 (1993).
327. J. H. Burroughes, C. A. Jones, and R. H. Friend, *Nature (London)* **335**, 137 (1988).
328. H. Sirringhaus, N. Tessler, and R. H. Friend, *Science* **280**, 1741 (1998).
329. G. H. Gelinck, T. C. T. Geuns, and D. M. de Leeuw, *Appl. Phys. Lett.* **77**, 1487 (2000).
330. I. Chun, D. H. Reneker, H. Fong, X. Fang, J. Dietzel, N. B. Tan, and K. Kearns, *J. Adv. Mat.* **31**, 36 (1999).
331. A. G. MacDiarmid, *Angew. Chem. Int. Ed. Engl.* **40**, 2591 (2001).
332. D. Hohnholz and A. G. MacDiarmid, *Synth. Met.* **121**, 1327 (2001).

PETER J. S. FOOT
Materials Research Group, Kingston University

ALAN B. KAISER
MacDiarmid Institute for Advanced Materials and
Nanotechnology and Victoria University of Wellington