Preface and Acknowledgements

All matter is made up of *atoms*. The term *molecule* is used to describe groups of atoms that tend to exist together in a stable form. As the term implies, *macromolecule* refers to a molecule of large size. *Intelligent macromolecules* are those large molecules, including certain polymers, dendrimers, fullerenes and carbon nanotubes, with the capability to change their conformational structures and/or properties in response to an external stimulus.

Polymers have long been used as electrically insulating materials: after all, metal cables are coated in plastic to insulate them. The visit of MacDiarmid to Shirakawa at Tokyo Institute of Technology in 1974 and, later, Shirakawa to MacDiarmid and Heeger at University of Pennsylvania, however, led to the discovery of conducting polyacetylene in 1977 - a prototype conducting polymers with the so-called *conjugated* structure of alternating single and double bonds for delocalization of ϕ-electrons. This finding opened up the important new field of polymers for electronic applications and was recognized by the 2000 Nobel Prize in Chemistry. The subsequent discovery of the electroluminescent light emission from conjugated poly(*p*-phenylene vinylene), by Friend's group at Cavendish Laboratory in 1990, revealed the significance of the use of conjugated polymers in photonic devices. Various conjugated polymers can now be synthesized to show the processing advantages of plastics and the optoelectronic properties of inorganic semiconductors or metals.

With DNA, proteins, and polysaccharides comprising the most important components of a living cell, life is polymeric in its essence. The self-assembly of lipids contributes to even larger *supramolecular* structures. Nature handles these biomacromolecular and supramolecular in a mysterious way to create various nanostructures/nanomachines that enable creatures to function. The salient feature of biomacromolecules is that they can adopt unique, well-defined conformations according to specific environmental conditions. Human beings have done

remarkable work and learned a lot from nature. Recent decades have witnessed the appearance of synthetic polymers, including dendrimers, which can respond reversibly to a change in solvent, pH, temperature, electric or optical fields, or other stimuli. These *stimuli-responsive* biomacromolecules and synthetic polymers are of significance to various potential applications, ranging from sensors/actuators to controlled release of drugs.

Sometimes history repeats itself. The visit made by Kroto in 1985 to Smalley and Curl at Rice University led also to the Noble-Prize-winning discovery of *buckminsterfullerene* C_{60} - a conjugated molecule with a soccerball-like structure consisting of 12 pentagons and 20 hexagons facing symmetrically. Just as the discovery of C_{60} has created an entirely new branch of carbon chemistry, the subsequent discovery of *carbon nanotubes* by Iijima in 1991 opened up a new era in material science and nanotechnology. These elongated nanotubes consist of carbon hexagons arranged in a concentric manner with both ends normally capped by fullerene-like structures containing pentagons. Having a conjugated all-carbon structure with unusual molecular symmetries, fullerenes and carbon nanotubes also show interesting electronic, photonic, magnetic, and mechanical properties, which make them attractive for various applications, including optical limiters, photovoltaic cells and field emitting displays.

This book deals with the synthesis, fundamentals, and device applications of a wide range of intelligent macromolecules. The diversity both in the synthesis/fabrication of intelligent macromolecules and in the development/application of various smart devices appeals to a broad group of students, teachers, scientists and engineers with backgrounds in physical, chemical, material, biological, and medical sciences and engineering. The main objective of this book is to bridge the gap between the synthesis of intelligent macromolecules and the development of smart devices through a broad treatment of the field by covering not only the materials' synthesis and structure study, but also the device construction and application. In order to cover the multidisciplinary field of such diversity, the text has been divided into three major parts after the introductory chapter. The first part from Chapter 2 to Chapter 5 deals with the basic science of various intelligent macromolecular systems. Chapters 6 and 7 follow the first part of the text to present an overview of various methodologies developed for assembling these intelligent macromolecules into multi-dimensional structures, which have been so crucial to the development of smart devices. A large variety of smart devices based on these intelligent macromolecules and functional structures are then described in the final part of the book. The above approach, I hope, will allow the reader to first review the scientific basis for intelligent macromolecules. The basic knowledge is then extended to functional devices; many of them are of practical importance. While many self-explanatory illustrations could provide an overview understanding even to those who are new to the field, the large number of updated references cited in each of the chapters should enable advanced readers to quickly review the multidisciplinary and challenging field with information on the latest developments.

At this place I wish to express my sincere thanks to Mr Oliver Jackson for his suggesting and encouraging me to write this book and also his very kind and patient

cooperation during its completion, without which this book would never have been appeared. I would also like to thank my colleagues who contributed in one way or the other to the text and authors whose work was cited, in particular: Vardhan Bajpai, Yoseph Bar-Cohen, Ray Baughman, Bruce Crissinger, Mei Gao, Zhixin, Guo, Hans Griesser, Sinan Li, Albert Mau, Darrell Reneker, Chris Strauss, Chris Toprakcioglu, Alfred Uhlherr, Gordon Wallace, Zhonglin Wang, John White, Paul White, Berthold Winkler, Junbing Yang and Zhi Yu. Last, but not the least, I thank my parents, wife Lin Zhu and two sons, Quanbin Kevin Dai, and Quanzhe Alvin Dai, for their love, unceasing patience, and continuous support. This book is dedicated to my father, who passed away from a heart attack in July, 2000.

Liming Dai
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February 2003

Chapter 2

Conducting Polymers

2.1 Introduction

Polymers have long been used as insulating materials. For example, metal cables are coated in plastic to insulate them. However, there are at least four major classes of semiconducting polymers that have been developed so far. They include conjugated conducting polymers, charge transfer polymers, ionically conducting polymers and conductively filled polymers.

The conductively filled conducting polymers were first made in 1930 for the prevention of corona discharge. The potential uses for conductively filled polymers have since been multiplied due to their ease of processing, good environmental stability and wide range of electrical properties. Being a multi-phase system in nature, however, their lack of homogeneity and reproducibility has been an inherent weakness for conductively filled polymers. Therefore, controlling the quality of dispersion to obtain homogeneous conducting polymer composites is critically important.

The report of electrical conductivity in ionic polymers in 1975 (Wright, 1975) attracted considerable interest. Since then, various ionically conducting polymers or polymer electrolytes have been prepared for a wide range of applications ranging from rechargeable batteries to smart windows. Polymer electrolytes are also highly processable. The ionic conduction mechanism requires the dissociation of opposite ionic charges and the subsequent ion migration between coordination sites, which are generated by the slow motion of polymer chain segments. Consequently, polymer electrolytes normally show a low conductivity and high sensitivity to humidity. They often become electrically non-conducting upon drying.

The discovery of electrical conductivity in molecular charge transfer (CT) complexes in the 1950s (Akamatu *et al.,* 1954) promoted the development of conducting CT polymers, and led to subsequent findings of superconductivity with molecular CT complexes in 1980 (Jerome *et al.,* 1980) and with fullerene in 1986 (Iqbal *et al.,* 1986). The conductivity in CT complexes arises from the formation of

appropriate segregated stacks of electron donor and acceptor molecules and a certain degree of charge transfer between the stacks. A desired crystal structure is, therefore, essential for good conductivity in the molecular CT complexes. However, the resultant materials are often brittle and unprocessable. To overcome this problem, attempts have been made to attach electron donor and/or acceptor moieties onto polymer backbones to produce charge transfer polymers with good processability and stacking properties.

Along with all of the activities described above, various conjugated polymers have been synthesized during the past 25 years or so which show excellent electrical properties (Skotheim *et al.,* 1986). Owing to the delocalization of electrons in a continuously overlapped ϕ-orbital along the polymer backbone, certain conjugated polymers also possess interesting optical and magnetic properties. These unusual optoelectronic properties allow conjugated polymers to be used for a large number of applications, including protecting metals from corrosion, sensing devices, artificial actuators, all-plastic transistors, non-linear optical devices and light-emitting displays. Due to the backbone rigidity intrinsically associated with the delocalized conjugated structure, however, most *unfunctionalized* conjugated polymers are intractable *(i.e.* insoluble, infusible and brittle). Some of them are even unstable in air.

The present chapter gives an overview of various methods developed for the preparation of advanced conjugated conducting polymers, charge transfer polymers, ionically conducting polymers and conductively filled polymers. The structure, conduction mechanism and electrical properties for each of these are also discussed, which underpin their applications in a wide range of smart devices as presented in later chapters.
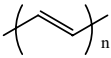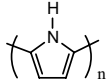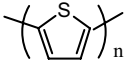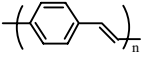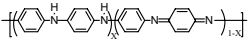
2.2 Conjugated Conducting Polymers

2.2.1 Structure and Properties

2.2.1.1 *ϕ#ϕ* Conjugation*

Table 2.1 lists the repeat units and conductivities for some common conjugated polymers (Dai, 1999). As can be seen in Table 2.1, the conjugated structure with alternating single and double bonds or conjugated segments coupled with atoms providing *p*-orbitals for a continuous orbital overlap (*e.g.* N, S) seems to be necessary for polymers to become intrinsically conducting. This is because just as metals have high conductivity due to the free movement of electrons through their structure, in order for polymers to be electronically conductive they must possess not only charge carriers but also an orbital system that allows the charge carriers to move. The conjugated structure can meet the second requirement through a continuous overlapping of ϕ-orbitals along the polymer backbone. Due to its simple conjugated molecular structure and fascinating electronic properties, polyacetylene

has been widely studied as a prototype for other electronically conducting polymers (Chien, 1984).

**Table 2.1.** Some conjugated conducting polymers

Polymer (date conductivity discovered)	Structure	$\phi\text{–}\phi^*$ gap (eV)	Conductivity[#] (S/cm)
I. Polyacetylene and analogues			
Polyacetylene (1977)		1.5	$10^3 - 1.7\times10^5$
Polypyrrole (1979)		3.1	$10^2 - 7.5\times10^3$
Polythiophene (1981)		2.0	$10 - 10^3$
II. Polyphenylene and analogues			
Poly(paraphenylene) (1979)		3.0	$10^2 - 10^3$
Poly(p-phenylene vinylene) (1979)		2.5	$3 - 5\times10^3$
Polyaniline (1980)		3.2	$30 - 200$

[#] The range of conductivities listed is from that originally found to the highest values obtained to date (after Dai, 1999, copyright 1999 Marcel Dekker, Inc.)

2.2.1.2 Doping

Since most organic polymers do not have intrinsic charge carriers, the required charge carriers may be provided by partial oxidation (*p*-doping) of the polymer chain with electron acceptors (*e.g.* I_2, AsF_5) or by partial reduction (*n*-doping) with electron donors (*e.g.* Na, K). Through such a doping process, charged defects (*e.g.* polaron, bipolaron and soliton) are introduced, which could then be available as the charge carriers. In the case of I_2-doped *trans*-polyacetylene, it was estimated that nearly 85% of the positive charge is delocalized over 15 CH units to give a positive soliton. In fact, the insulator-to-metal transition in conjugated polymers is not so simple, and the way in which charges can be stabilized on the polymer chains and the nature of the charge transport process are still a matter of debate. Nevertheless, the simple band theory can provide some useful information about the doping-induced changes in electronic structure.

According to band theory (Harrison, 1979), the electrical properties of direct gap inorganic semiconductors are determined by their electronic structures, and the electrons move within discrete energy states called *bands*. By analogy, the bonding and antibonding ϕ-orbitals of the sp^2 hybridized ϕ-electron materials (*e.g.* polyenes) generate energy bands, which are fully occupied (ϕ-band) and empty ($\phi*$-band). The highest occupied band is called the *valence band*, and the lowest unoccupied band is the *conduction band*. The energy difference between them is called the *band gap*. Electrons must have certain energy to occupy a given band and need extra energy to move from the valence band to the conduction band. Moreover, the bands should be partially filled in order to be electrically conducting, as neither empty nor full bands can carry electricity. Owing to the presence of partially filled energy bands, metals have high conductivities (Figure 2.1(a)). The energy bands of insulators and semiconductors, however, are either completely full or completely empty. For instance, most conventional polymers have full valence bands and empty conduction bands, which are separated from each other by a wide energy gap (Figure 2.1(b)). In contrast, conjugated polymers have narrower band gaps (Figure 2.1(c)) and doping can change their band structures by either taking electrons from the valence band (*p*-doping) or adding electrons to the conduction band *(n*-doping).
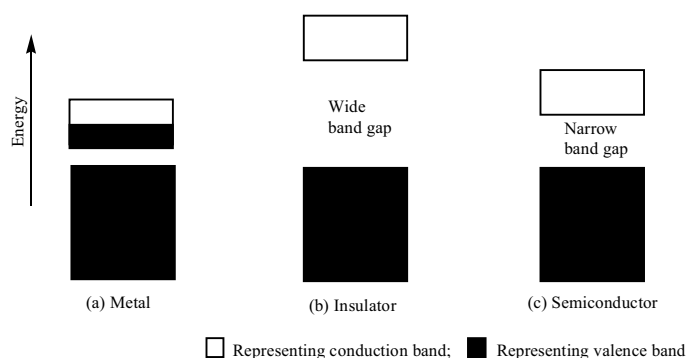
Figure 2.1. A schematic representation of energy gaps in (a) metal; (b) insulator; (c) semiconductor (After Dai, 1999, copyright 1999 Marcel Dekker, Inc.)

When an electron is added (removed) to the bottom of the conduction band (from the top of the valence band) of a conjugated polymer (Figure 2.2(a)), the conduction (valence) band ends up being partially filled and a radical anion (cation), commonly termed as a polaron (Brédas and Street, 1985), is created (Figure 2.2(b)). The formation of polarons causes the injection of states from the bottom of the conduction band and top of the valence band into the band gap. A polaron carries both spin (1/2) and charge (∂1e). Addition (removal) of a second electron on a chain already having a negative (positive) polaron results in the formation of a bipolaron (spinless) through dimerization of two polarons, which can lower the total energy (Figure 2.2(c)). In conjugated polymers with a degenerate ground state *(i.e.* two

equivalent resonance forms), like *trans*-polyacetylene, the bipolarons can further lower their energy by dissociating into two spinless solitons at one-half of the gap energy (Figure 2.2(d)). Solitons do not form in conjugated polymers with non-degenerate ground states, such as in polypyrrole, polythiophene and polyaniline (Brédas and Street, 1985). The population of polarons, bipolarons, and/or solitons increases with the doping level. At high doping levels, the localized polarons, bipolarons or solitons near to individual dopant ions could overlap, leading to new energy bands between and even overlapping the valence and conduction bands, through which electrons can flow.
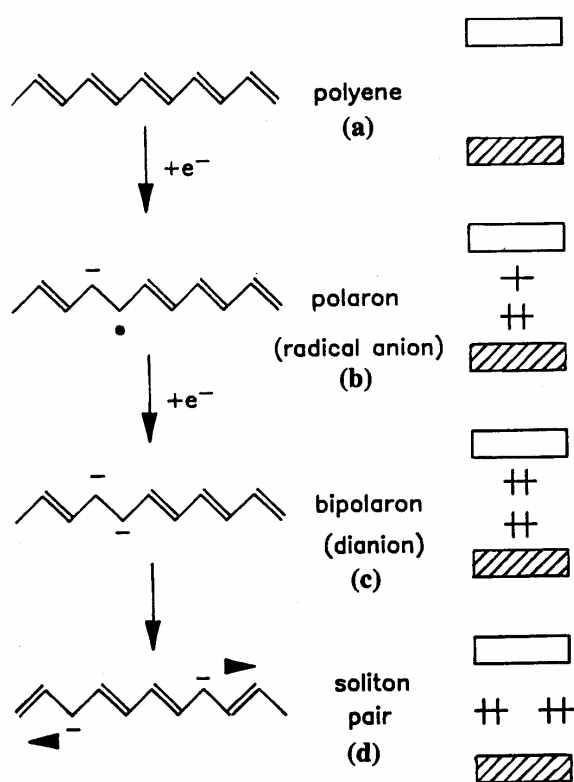
Figure 2.2. A schematic description of the formation of polaron, bipolaron, and soliton pair on a *trans*-polyacetylene chain by doping (After Dai, 1999, copyright 1999 Marcel Dekker, Inc.)

The bulk conductivity of conducting polymers should, in principle, consist of contributions from intra-chain, inter-chain and inter-domain electron transportations (Dai *et al.,* 1999). While the details for each of the transporting processes and their relative importance are still not fully understood, some of the factors that influence

conductivity have been recognized. As can be seen from the foregoing discussion, the doping process is the most obvious factor which influences conductivity of conjugated polymers. Other factors include the orientation, crystallinity and purity of the conjugated polymers. Some of the most commonly used doping methods are described below.

Chemical Doping
Almost all conjugated polymers, including those listed in Table 2.1, can be either partially oxidized (*p*-type redox doping) or partially reduced (*n*-type redox doping) by electron acceptors or electron donors. For example, the treatment of *trans*-polyacetylene with an oxidizing agent such as iodine leads to the doping reaction [Equation (2.1)] and a concomitant increase in conductivity of about 10^{-5} to 10^{2} S/cm (Figure 2.3).

$$trans\text{-}(CH)_x + 3/2xyI_2 \quad à \quad [CH^{+y}(I_3^-)_y]_x \tag{2.1}$$
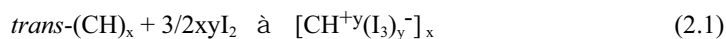
Similarly, most conjugated polymers like *trans*-polyacetylene can be doped with electron donors (*n*-doping) to gain high conductivities.

$$trans\text{-}(CH)_x + [Na^+(C_{10}H_8)^-] \quad à \quad [(Na^+)_y (CH)^{-y}]_x \quad + \quad C_{10}H_8 \tag{2.2}$$
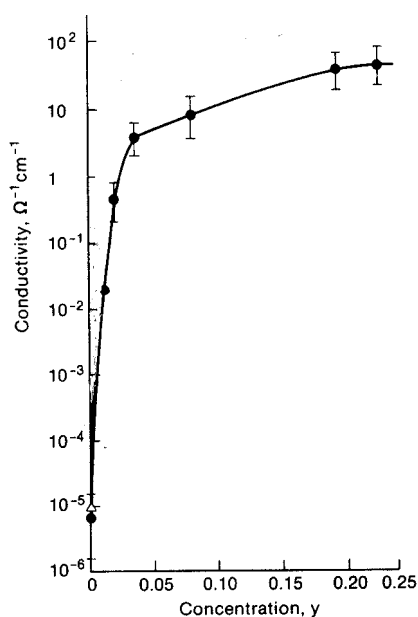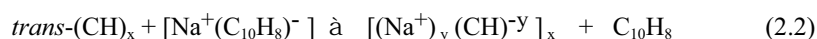
Figure 2.3. Electrical conductivity of I_2-doped *trans*-polyacetylene as a function of iodine concentration (After Chiang *et al.,* 1978, copyright 1978 American Institute of Physics)

More interestingly, it was found that the *n*- and *p*-type dopants could compensate each other. This compensation process is illustrated by the undoping of an Na-doped polyacetylene film with a composition of $(CHNa_{0.27})_x$ by I_2. As can be seen in Figure 2.4, the electrical conductivity of the Na-doped sample gradually decreases upon I_2-doping and increases, after reaching a minimum, with further *p*-doping (Chiang *et al.,* 1978).
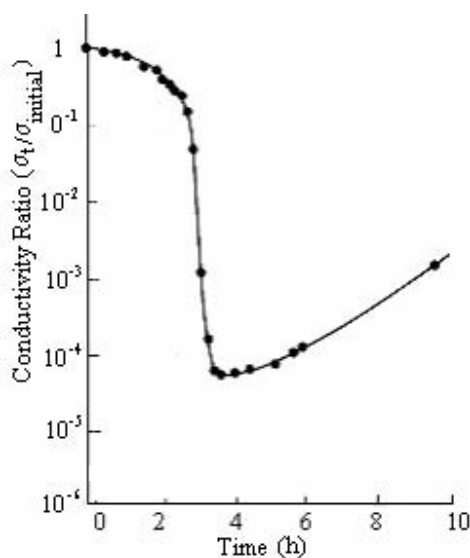
Figure 2.4. Electrical conductivity ratio of an Na-doped polyacetylene as a function of time of exposure to iodine (After Chiang *et al.,* 1978, copyright 1978 American Institute of Physics)

The relatively low conductivities attainable by the I_2-doping can be attributed to Na^+ ions remaining in the initially *n*-doped polyacetylene film in the form of NaI (0.5NaI/CH unit). Although the minimum conductivity for the fully compensated sample is still higher than that of the pristine polyacetylene film prior to Na-doping, the observed compensation process clearly demonstrates the feasibility to reversibly change the electrical properties of conjugated polymers in a controllable fashion.

Electrochemical Doping
Owing to the extensive conjugation of ϕ-electrons, conjugated polymers can also be easily oxidized (*p*-doping) or reduced (*n*-doping) electrochemically with the conjugated polymer acting as either an electron source or an electron sink. In particular, the doping reaction [Equation (2.3)] can be accomplished by applying a DC power source between a *trans*-polyacetylene-coated positive electrode and a

negative electrode. Both of them are immersed in a solution of $LiClO_4$ in propylene carbonate (Chien, 1984).

$$trans\text{-}(CH)_x + (xy)(ClO_4)^- \quad à \quad [CH^{+y}(ClO_4)_y^-]_x + (xy)e^- \quad (y \ \Omega 0.1) \qquad (2.3)$$
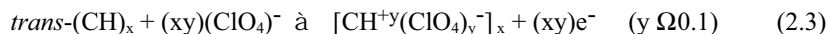
Compared with chemical doping, electrochemical doping has several distinct advantages. Firstly, a precise control of the doping level can be achieved simply by monitoring the amount of current passed. Secondly, doping-undoping is highly reversible with no chemical products requiring removal. Finally, both *p*- or *n*-type doping can be achieved even with dopant species that cannot be introduced by conventional chemical means. In both cases, however, counter "dopant" ions are introduced for stabilizing the charge along the polymer backbone. The incorporation of counter ions can be both a hindrance and an advantage. While the counter ions may cause an undesirable structural distortion and a deteriorated effect on conductivity, they facilitate conjugated conducting polymers for actuation applications (Chapter 11).

In order to eliminate the incorporation of counter ions, "photo-doping" and "charge-injection doping" methods have been exploited to achieve the redox doping effects. Besides, some conjugated polymers, such as polyaniline and poly(heteroaromatic vinylenes), can also acquire high conductivities through the protonation of imine nitrogen atoms without any electron transfer between the polymer and "dopants" occurring - *i.e.* "non-redox doping" (Epstein and MacDiarmid, 1995).

Photo-doping

The irradiation of a conjugated polymer (*e.g. trans*-polyacetylene) macromolecule with a light beam of energy greater than its band gap could promote electrons from the valence band into the conduction band, as schematically shown in Equation (2.4) (Heeger *et al.,* 1988). Although the photogenerated charge carriers may disappear once the irradiation ceases, the application of an appropriate potential during irradiation could separate electrons from holes, leading to photoconductivity.

$$trans\text{-}(CH)_x \quad \xrightarrow{h\gamma} \qquad \bigvee\!\!\bigwedge\!\!\bigvee^{+}\!\!\bigwedge\!\!\bigvee^{-}\!\!\bigvee \qquad (2.4)$$
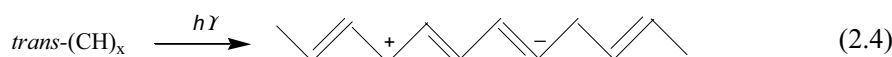
Charge-injection Doping

Using a field-effect transistor (FET) geometry (Chapter 8), charge carriers can be injected into the band gap of conjugated polymers [*e.g.* polyacetylene, poly(3-hexylthiophene), P3HT] by applying an appropriate potential on the metal/insulator/polymer multilayer structure (Garnier *et al.,* 1994). Just like photo-doping, the charge-injection doping does not generate counter ions, allowing a systematic study of the electrical properties as a function of the charge carrier density with a minimized distortion of the material structure. Using the charge-injection doping method, Schön *et al.* (2001) have recently demonstrated that a thin P3HT self-assembled film exhibits a metal-insulator transition with a metallic-like

temperature dependence. At temperatures below 2.35 K, these authors observed superconductivity when the charge density exceeds 2.5×10^{-14} cm^{-2}. This observation of superconductivity appears to be closely related to two-dimensional charge transport in the self-assembled polymer film. Although much of Schön's work is currently in question (Jacoby, 2002) and the detailed superconducting mechanism remains to be found (Tinkham, 1975), the above observation may suggest that the conductivity of conjugated polymers could be tuned over the largest possible range from insulating to superconducting.

Non-redox Doping
Unlike redox doping, the non-redox doping does not cause any change in the number of electrons associated with the polymer backbone, but merely a rearrangement of the energy levels. The most studied doping process of this type is the protonic doping of polyaniline emeraldine base (PANI-EB) with aqueous protonic acids, such as HCl, *d,l*-camphorsulfonic acid (HCSA), *p-CH$_3$*-(C$_6$H$_4$)SO$_3$H and (C$_6$H$_5$)SO$_3$H, to produce conducting polysemiquinone radical cations via the reaction shown in Equation (2.5) (Dai *et al.,* 1998a).

$$(2.5)$$
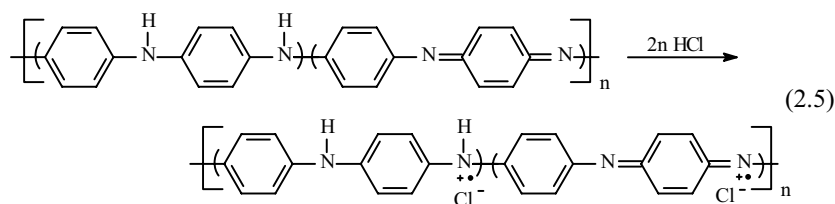
Figure 2.5 shows the evolution in time of the ultraviolet/visible/near-infrared (UV/vis/NIR) spectrum for the as-prepared PANI-EB after doping by HCSA (Dai *et al.,* 1998a).
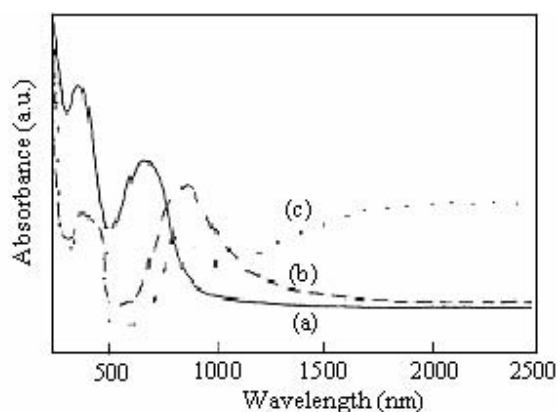

Figure 2.5. UV/vis/NIR spectra of PANI-EB: (a) pristine PANI-EB; (b) after having been doped with HCSA; (c) the HCSA-doped PANI-EB after treatment with *m*-cresol (*vide infra*) (After Dai *et al.,* 1998a, copyright 1998 The American Chemical Society. Reproduced with permission)

The absorption peaks at 322 and 625 nm for the pristine PANI-EB (curve (a)) are attributable to the ϕ-ϕ* transition of the benzenoid rings and exciton absorption of the quinoid rings, respectively (Xia *et al.,* 1995). The absorption peaks at about 420 and 800 nm seen in curve (b) appeared at the expense of the interband transitions and can be taken as evidence for the presence of localized polarons produced by the HCSA doping (Cheng and Lin, 1995).

Secondary Doping

The interaction of an HCSA-doped PANI-EB with *m*-cresol was found to cause the absorption band characteristic of the localized polarons to largely disappear at 800 nm (curve (c) in Figure 2.5), while a very intense free carrier tail commencing at *ca.*1000 nm developed (Dai *et al.,* 1998a). These spectroscopic changes have been attributed to the so-called "secondary doping" process, which causes a conformational transition of the polymer chain from a "compact coil" to an "expanded coil" due to molecular interactions between the HCSA-doped polyaniline and *m*-cresol (MacDiarmid and Epstein, 1994, 1995). The observed free carrier tail in the near-infrared region was considered to arise from delocalization of electrons in the polaron band, leading to a concomitant increase in conductivity by up to several orders of magnitude. Indeed, an increase in conductivity for a HCSA-doped polyaniline film from *ca.* 0.1 S/cm when cast from chloroform up to 400 S/cm when cast from *m*-cresol has been recorded (Cao *et al.*, 1992a, b).

The "compact coil" to "expanded coil" transition has long been ascribed to the "secondary doping" process. Some evidence from spectroscopic and viscosity measurements has been reported (MacDiarmid and Epstein, 1994, 1995). More recently, Dai *et al.* (2000, 2001) investigated the secondary doping of HCSA-doped PANI with *m*-cresol within the gallery of clay particles. They observed a significant increase in the inter-sheet distance of the polymer-intercalated clay particles (Figure 2.6), arising from the "compact coil" to "expanded coil" transition for polyaniline chains associated with the secondary doping.
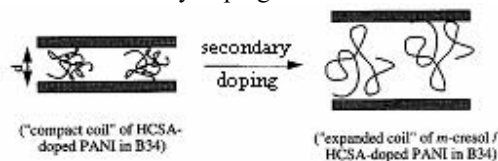
Figure 2.6. Schematic representation of the secondary doping of HCSA-doped PANI-EB with *m*-cresol within the clay gallery of Bentone 34 (B34). Note, d represents the height of the clay gallery and the diagrams are not drawn to scale (After Dai *et al.*, 2000, copyright 2000 Kluwer Academic Publishers. Reproduced with permission)

2.2.2 Syntheses

Although various catalyst systems (radiation, cationic, transition/rare-earth metal, *etc.*) can be used to initiate acetylene polymerization, the Ziegler-Natta catalyst

remains the major one for chemical polymerization of acetylene (Shirakawa, 2001). Particularly, the Ti(OBu)$_4$/AlEt$_3$ is a preferred catalyst system for producing linear polymers of high molecular weight, high crystallinity and high conductivity upon doping (Chien, 1984). In this context, Ito *et al.* (1974) have succeeded in polymerizing acetylene directly in the form of a thin film, which is often termed as *Shirakawa's polyacetylene*, on the wall of a reaction vessel by adding about 1000 times more Ti(OBu)$_4$/AlEt$_3$ catalyst than the reaction stoichiometrically required.

Meanwhile, the Luttinger catalyst (*i.e.* NaBH$_4$/Co(NO$_3$)$_2$·6H$_2$O) has also been used for acetylene polymerization (Chien, 1984; Luttinger, 1962). In both cases, acetylene is usually bubbled into a stirred catalyst solution for a homogeneous polymerization. However, the final product is often an intractable (*i.e.* insoluble and infusible) black powder (Chien, 1984). In fact, before the early 1980s no conjugated conducting polymer had been shown to be soluble in any solvent without decomposition (Dai, 1999), due to backbone rigidity associated with the delocalized conjugated structure. Furthermore, most unfunctionalized conjugated polymers were found to be unstable in air (Baker, 1988). Since then, a number of techniques have been developed to overcome these problems. Relatively stable conducting polymeric materials have been made, for example, by physically blending conjugated polymers with certain non-conjugated macromolecules (Baker, 1988) and chemically synthesizing conducting polymer colloids (Armes, 1996) or conjugated oligomers (de Meijere, 1999). On the other hand, many clever synthetic routes have now been devised for preparing processable conjugated polymers, as described below.

2.2.2.1 Syntheses of Soluble Conjugated Polymers

By Substitution
As is well known, both chemical and physical properties of a polymer material may change with substitution. Consequently, soluble forms of various conjugated polymers have been prepared by grafting suitable side groups and/or side chains along their conjugated backbones. Examples include polyacetylene, poly(*p*-phenylene vinylene) (PPV), polythiophene, polypyrrole and polyaniline grafted derivatives (Ferraro, 1987).

Polyacetylene derivatives: soluble poly(methylacetylene) and poly(phenylacetylene) have been synthesized (Yoshino, 1997). These polymers can be regarded as polyacetylene grafted with methyl or phenyl side groups. More recently, various soluble di-substituted polyacetylene derivatives, including poly(diphenylacetylene), poly(1-alkyl-2-phenylacetylene), poly(1-chloro-2-phenylacetylene) and poly[1-phenyl-2-*p*-(triphenylsilyl)phenylacetylene] have been synthesized to show electroluminescent properties (Chapter 9).

Poly(p-phenylene vinylene) derivatives: PPV is one of the most studied polymers for electroluminescent applications. The most common method to prepare PPV is the so-called Wessling route (Wessling and Zimmerman, 1968, 1972) from the sulfonium precursor polymer [Equation (2.6)].

(2.6)

Although the final product from the Wessling route is insoluble and infusible with a rigid-rod microcrystalline structure, various soluble forms of PPV have been reported. For example, the Wessling method has been extended to synthesize soluble derivatives of PPV, such as poly[2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylene vinylene] (*i.e.* MEH-PPV, Burn *et al.* 1993), poly(2-butyl-5(2'-ethylhexyl)-1,4-phenylene vinylene) (*i.e.* BuEH-PPV, Gettinger *et al.,* 1994), and poly(2,5-dimethoxy-*p*-phenylene vinylene) (*i.e.* PDMeOPV, Bradley, 1992; Brédas *et al.*, 1996), by introducing various side groups/chains onto the phenylene units. Without involving the water-soluble sulfonium salts, soluble PPVs have also been obtained from the substituted dichloro-*p*-xylene in organic solvents via the so-called Gilch route (Gilch and Wheelwright, 1966), as shown in Equation (2.7).

soluble chlorine   R = H   (DP-PPV)
precursor polymers   R = 4-biphenyl (DPbp-PPV)

(2.7)

Compared with the Wessling method, the Gilch route allows easier access to a large range of substituted PPV derivatives soluble in organic solvents (Hörhold *et al.,* 1997; Hsieh *et al.*, 1998). Using either the Wessling or Gilch route, Winkler *et al.* (1999) have recently synthesised PPV derivatives grafted with oligo(ethylene oxide) side chains of different chain lengths [Equation (2.8)].

R = (CH_2CH_2O)_mCH_3   m = 1,2,3

(2.8)

The same authors have also used the Wittig or Horner-Wadsworth-Emmons reaction to prepare phenylenevinylene oligomers/polymers substituted with crown ether rings via Equation (2.9) (Winkler et al., 2000).

	R	
1	Br	
2-1	P$^+$Ph$_3$ Br$^-$	i ⎤ ii
2-2	P(O)(OC$_2$H$_5$)$_2$	⎦

(i) Ph$_3$P, (ii) P(OEt)$_3$

(2.9)

CE-OPV
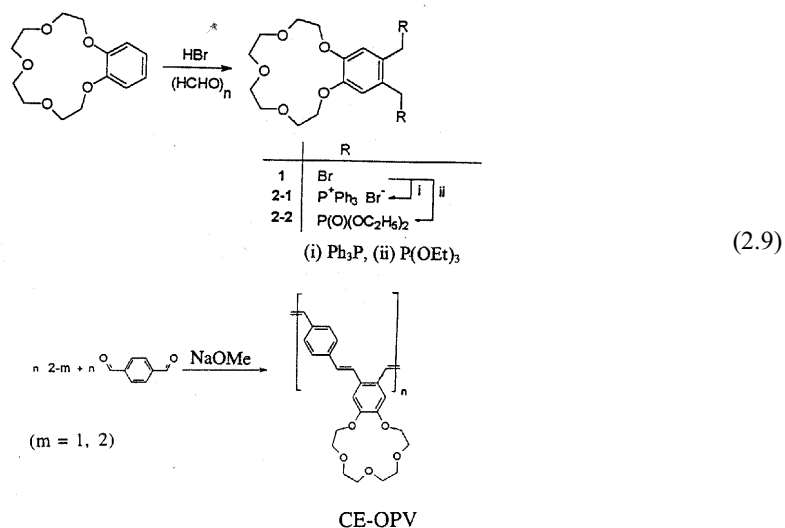
Other interesting PPV derivatives, including cyano-substituted PPVs, have been produced by a Knoevenagel condensation reaction between a diacetonitrile and a dialdehyde (Feast *et al.*, 1996), which can also be used for synthesis of hetero-aromatic cyanopolymers such as poly(thienylenephenylene vinylene) and poly(thienylene vinylene).

Polythiophenes: Equation (2.10) represents the most common route to poly(3-alkylthiophenes), P(3AT)s, in which 3-bromothiophene is used as the starting material. P(3AT)s thus prepared are meltable and soluble in most common organic solvents (Tamao *et al.*, 1982). Color tuning of photo- and electro-luminescence has been demonstrated for P(3AT)s with well-defined regioregularities (Gill *et al.*, 1994). The regioregularity also has a profound influence on crystallinity and electrical conductivity (Sentein *et al.*, 1996).

$$R\text{-}Br + Mg \xrightarrow{\text{ether}} R\text{-}Mg\text{-}Br$$

(2.10)
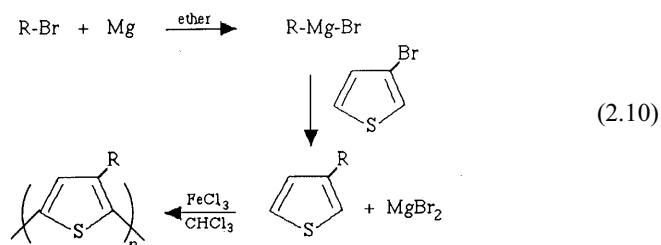
Soluble polypyrrole and polyaniline have also been synthesised by introducing alkyl side groups (Patil *et al.,* 1987; Tour, 1994). Grafting with hydrophilic side groups/chains (-SO$_3$H, -COOH, -OH, *etc.*) even allows the formation of water-soluble conducting polymers (Brédas and Silbey, 1991). Generally speaking, the high solubility of the substituted conjugated polymers is often gained at the expense of significantly reduced conductivity. For instance, the conductivities of substituted polyacetylenes*,* after doping, were shown to be lower than that of doped polyacetylene by several orders of magnitude (Chien, 1984). Polyaniline coatings with a relatively high electrical conductivity, however, have been produced from soluble polyaniline emeraldine salt generated by the protonic doping of polyaniline emeraldine-base with organic sulfonic acids containing large organic groups *(e.g.* HCSA) (Cao *et al.,* 1992a, b).
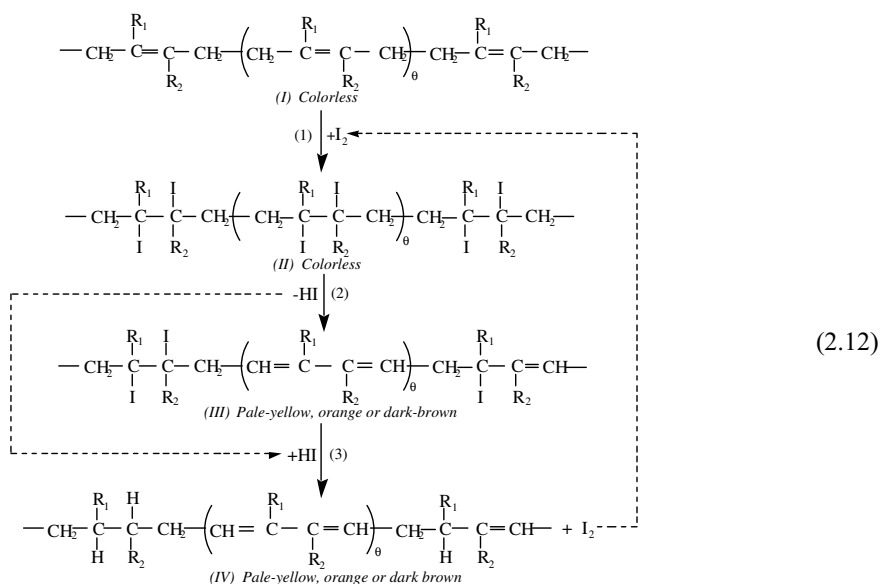
By Copolymerization
Copolymerization of conjugated polymers with various soluble segments provides an alternative way to circumvent the intractability of conjugated polymers. The combination of optoelectronic properties characteristic of conjugated structures and the solubility of the soluble polymeric segments into a single copolymer chain should, in principle, lead to a material with properties characteristic of both the constituent components.

Random and alternating copolymerization: in 1981, Chien and co-workers synthesised random copolymers of acetylene and methylacetylene (Chien *et al.,* 1981). They found that the resulting random copolymers are more tractable than polyacetylene homopolymer, being swellable in toluene and pentane when the acetylene content is less than 55%(wt). Both the intractability and conductivity, in doped form, decrease with increasing percentage content of methylacetylene, and the highest obtainable conductivity is about 45 S/cm for an AsF$_5$-doped sample. Random copolymers of acetylene and phenylacetylene have also been made (Deits *et al.*, 1982), which are soluble in methylene chloride when the acetylene content is 26%(wt). These random copolymers, after doping, also show much lower conductivities than that of the polyacetylene homopolymer. Recently, Yang *et al.* (1998) have synthesised soluble copolymers with alternating conjugated and non-conjugated segments via a Wittig-type coupling reaction between the appropriate dialdehyde and 1,4-xylylenebis(triphenylphosphonium chloride) [Eq. (2.11)].


(2.11)
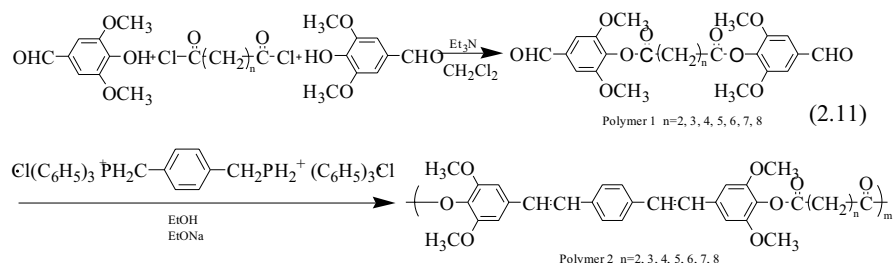
The copolymers prepared according to Equation (2.11) were found to have conductivities in the range of 10^{-3}–10^{-2} S/cm after having been cast into films from chloroform and doped with iodine (Yang *et al.,* 1994).

In 1988, Thakur (1988) claimed that a conjugated structure is not always necessary for a polymer to be electronically conducting by demonstrating high conductivities up to 10^{-1} S/cm for "I_2-doped" *cis*-1,4-polyisoprene. In view of the ease with which conducting rubber can be made and the potential challenge of Thakur's claim to modern theory of conducting polymers (Section 2.2.1.1), Thakur's work received complimentary comments from several scientific journals (Borman, 1990; Calvert, 1988; Rothman, 1988). Meanwhile, various other polymers with isolated (non-conjugated) double bonds, such as *trans*-1,4-polyisoprene, 1,4-poly-(2,3-dimethylbutadiene) and *trans*-1,4-polybutadiene, have also been found to become dark in color and conductive when "doped" with iodine in the solid state. Dai and co-workers (Dai, 1992; Dai *et al*., 1994; Dai and White, 1991) have demonstrated that the treatment of certain polydiene chains of isolated double bonds with iodine, both in solution and the solid state, produces conjugated sequences in the polydiene backbone through polar addition of I_2 into the isolated double bonds in the polymer chain, followed by HI elimination. The final products resemble random copolymers consisting of polyacetylene and polydiene segments. The reaction mechanism for the I_2-induced conjugation is shown in Equation (2.12), and the conjugated sequences thus produced have been shown to be responsible for the high conductivity of the "I_2-doped" polyisoprene.

(2.12)

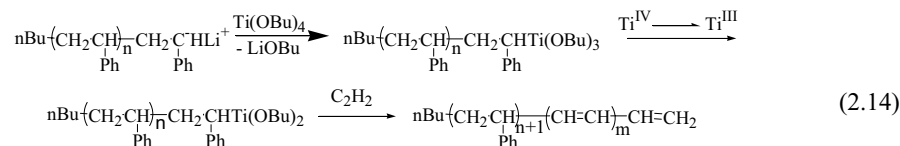R_1, R_2 refer to either H or CH_3 group.

Block and graft copolymerization: just as in the case of graft copolymers *vs*. substituted polymers, block copolymers differ from random and alternating copolymers in that relatively long conjugated polymer block(s) are attached onto a soluble polymer chain (or *vice versa*). Therefore, the integrity of conjugated structures can largely be preserved in block or graft copolymers, suggesting they possess better electrical properties than their substituted or random/alternating counterparts. In this context, Dandreaux *et al.* (1983) and Kminek and Trekoval (1984) demonstrated that ethylene oxide or methylmethacrylate (MMA) could be grafted onto a sodium-doped polyacetylene homopolymer [Equation (2.13)].
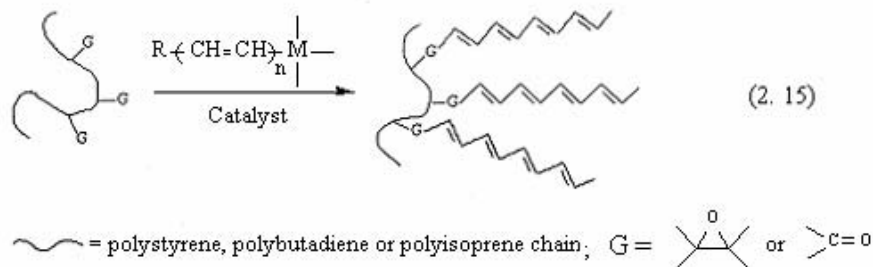

$$(2.13)$$
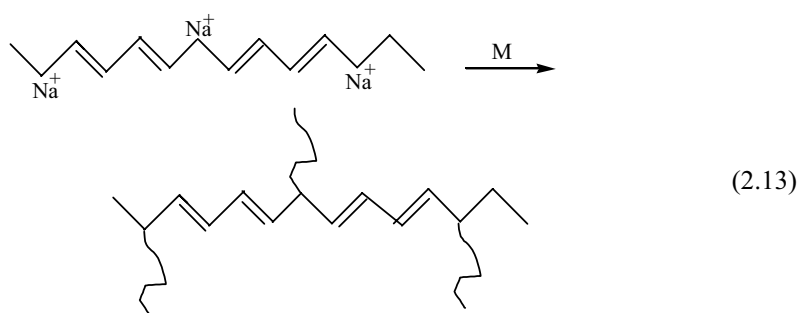
M = methyl methacrylate or ethylene oxide

The soluble graft copolymers of acetylene and ethylene oxide thus prepared were reported to have conductivities of up to 1 S/cm after I_2-doping in the solid state. This value of conductivity is still relatively low with respect to that of a polyacetylene homopolymer (Table 2.1). Possible explanations include: a) polyethylene oxide grafted chains are non-conducting; b) the grafting reaction itself introduces defects along the polyacetylene conjugated backbone.

It seems therefore more desirable to graft conjugated polymer chains onto a soluble polymer backbone. Using $Ti(OBu)_4/AlEt_3$ as a catalyst, Bates and Baker (1983), Aldissi (1986), and Galvin and Wnek (1985) have successfully copolymerized acetylene onto polystyrene, 1,4-polybutadiene, and 1,4-polyisoprene chains [Equations (2.14) & (2.15)], yielding either a block copolymer through the so-called anionic to Ziegler-Natta route [Equation (2.14)] or a graft copolymer by polymerizing acetylene in the presence of a second functionalized polymer [Equation (2.15)].

$$(2.14)$$

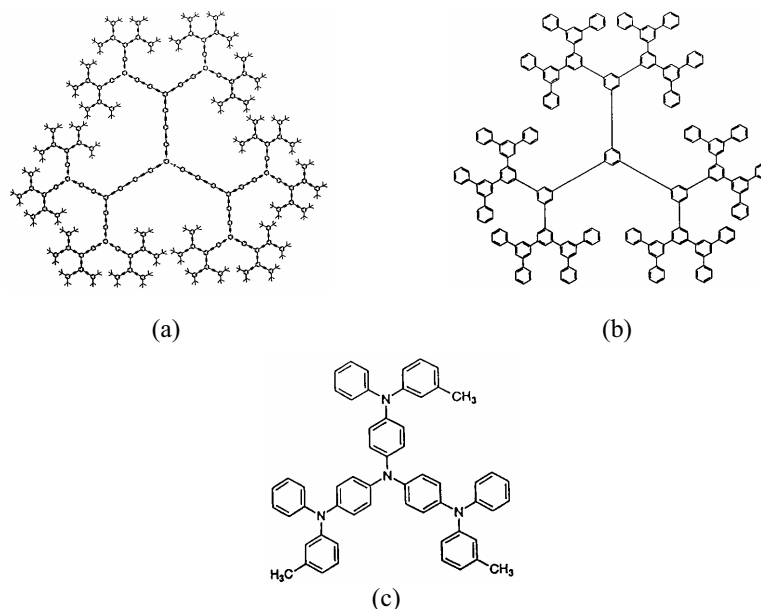$$R + CH = CH \xrightarrow[]{} M \xrightarrow[\text{Catalyst}]{} \tag{2. 15}$$

$\sim\!\!\sim$ = polystyrene, polybutadiene or polyisoprene chain ; G = (structure) or (structure)

Bolognesi *et al.* (1986) have used the same catalyst system for grafting copolymerization of acetylene onto 1,2-polybutadiene. Moreover, these authors have also grafted polyacetylene chains onto the 1,4-polydiene backbone by first lithiating polybutadiene chains with *sec*-butyllithium in the presence of tetramethylethylenediamine (TMEDA), followed by complexation with $Ti(OBu)_4$ to form a new polymeric catalyst for graft copolymerization of acetylene (Bolognesi *et al.,* 1985). It has been noted that polyacetylene chains in all of the block and graft copolymers synthesized by the Shirakawa-type titanium catalyst exist in *trans-* form. Using a novel Luttinger-type cobalt catalyst system, Armes *et al.* (1986), and Dai and White (Dai, 1997; Dai and White, 1997) have successfully synthesised both block [Equation (2.16)] and graft [Equation (2.17)] copolymers of 1,4-polydiene and polyacetylene, in which polyacetylene chains are mostly in the *cis-* form due to the low-temperature nature of the copolymerization reaction.

$H_2C=CR-CH=CH_2$

(Colourless)

n-BuLi
25 °C

$CH_2-CR=CH-CH_2$—Li

(Pale yellow)

CoCl₂
7h, -78 °C

$CH_2-CR=CH-CH_2$—Co

(dark brown)

C₂H₂
-78 °C

$CH_2-CR=CH-CH_2$

(red purple)

(R = CH₃ or H; $\sim\!\!\sim$ = PI or PB segments; $\diagup\diagdown\diagup$ = PA segments)

$$(2.16)$$

Furthermore, it was demonstrated that isomerization of the *cis*-polyacetylene blocks in a solution of the copolymers of polyisoprene and polyacetylene (PI-PA) prepared by the cobalt catalyst was retarded by some intramolecular barriers *(e.g.*

the chemically bonded polyisoprene chains), making the *cis-* isomer very stable at room temperature (Dai, 1997).

$$
\begin{array}{c}
\sim\!\!\sim\text{CH}_2\text{-CR}\!=\!\text{CH-CH}_2\!\!\sim\!\!\sim\text{CH}_2\text{-CR}\!=\!\text{CH-CH}_2\!\!\sim\!\!\sim \\[4pt]
\Big\downarrow\ \ \begin{array}{l}\textit{Sec-}\text{BuLi}\\ \text{TMEDA}\end{array} \\[6pt]
\sim\!\!\sim\underset{\overset{|}{\text{Li}}}{\text{CH}}\text{-CR}\!=\!\text{CH-CH}_2\!\!\sim\!\!\sim\text{CH}_2\text{-CR}\!=\!\text{CH-}\underset{\overset{|}{\text{Li}}}{\text{CH}}\!\!\sim\!\!\sim \\[4pt]
\Big\downarrow\ \ \begin{array}{l}\text{CoCl}_2\\ (7\text{h, }-78^{\circ}\text{C})\end{array} \\[6pt]
\sim\!\!\sim\underset{\overset{|}{\text{Co}}}{\text{CH}}\text{-CR}\!=\!\text{CH-CH}_2\!\!\sim\!\!\sim\text{CH}_2\text{-CR}\!=\!\text{CH-}\underset{\overset{|}{\text{Co}}}{\text{CH}}\!\!\sim\!\!\sim \\[4pt]
\Big\downarrow\ \ \begin{array}{l}\text{C}_2\text{H}_2\\ (-78^{\circ}\text{C})\end{array} \\[6pt]
\sim\!\!\sim\text{CH}\text{-CR}\!=\!\text{CH-CH}_2\!\!\sim\!\!\sim\text{CH}_2\text{-CR}\!=\!\text{CH-CH}\!\!\sim\!\!\sim
\end{array}
\qquad (2.17)
$$

(R = CH₃ or H; ⌣⌣ = PI or PB segments; ⌇⌇⌇ = PA segments)

The syntheses of soluble copolymers of polystyrene and polythiophene or polyparaphenylene have also been reported (Francois and Olinga, 1993; Zhong and Francois, 1991). Polystyrene-polythiophene block copolymer films were found to convert into pure polythiophene films on heating at 380°C under vacuum or argon through selective depolymerization of polystyrene sequences (Francois and Olinga, 1993). The polythiophene films thus prepared can be controlled to have a spheric or fibrillar morphology, and show conductivity of up to 60 S/cm after doping with FeCl₃.

Another interesting area closely related to the block and/or graft conjugated copolymers is the synthesis of hyperbranched/dendritic (starburst) supramolecules with conjugated moieties (Müller, 1997). Dendritic macromolecules are molecular species with a large number of hyperbranched chains of precise length and constitution surrounding a central core (Tomalia and Durst, 1993). Dendritic polymers differ from conventional linear polymers in that the former possess much more free volume and terminal end groups, and hence become more soluble than the latter (see Chapter 4 for details). Although synthesis of fully conjugated dendritic systems is difficult, Duan *et al.* (1995) have prepared electrically conducting dendrimers by modifying the periphery of a poly(amidoamine) dendrimer with naphthalene diimide anion radicals, which can aggregate into a ϕ-stacked network to provide the pathway for conductivity. Dendritic oligo(phenylene ethynylene)s up to 125 Å in diameter (Figure 2.7(a)) (Xu and Moore, 1993), along with dendritic oligophenylenes (Morgenroth *et al.*, 1997) and conjugated dendrimers of the type shown in Figure 2.7(b & c), respectively, have also been synthesized (Kuwabara *et al.,* 1994). A multilayer electroluminescence device incorporating the conjugated dendrimer shown in Figure 2.7(c) has been demonstrated to have reasonably good long-term stability.

(a)

(b)

(c)

Figure 2.7. Conjugated dendritic polymers: (a) dendritic oligo(phenylacetylene); (After Xu and Moore, 1993); (b) dendritic oligophenylene; (After Morgenroth *et al.*, 1997) (c) 4,4′,4′′-tris(3-methylphenyl-phenylamino)-triphenylamide (After Kuwabara *et al.,* 1994) (Copyrights Wiley-VCH Verlag)

Besides, Meier *et al.* (2000) have recently synthesized some highly soluble stilbenoid dendrimers with alkoxy chains substituted at the peripheral benzene rings [Equation (2.18)].

(2.18)
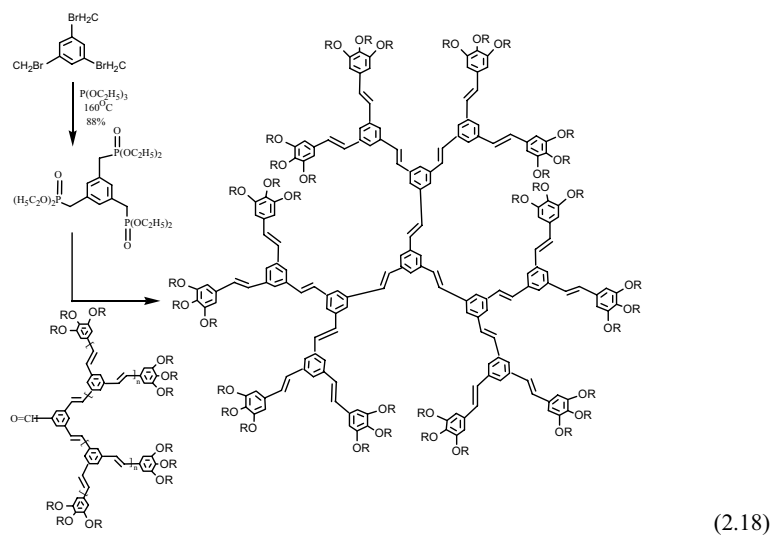
Wang *et al.* (1997) have also reported a route to conjugated star polymers with a hyperbranched 1,3,5-polyphenylene core surrounded by regioregular poly(3-hexylthiophene) arms [Equation (2.19)].

(2.19)
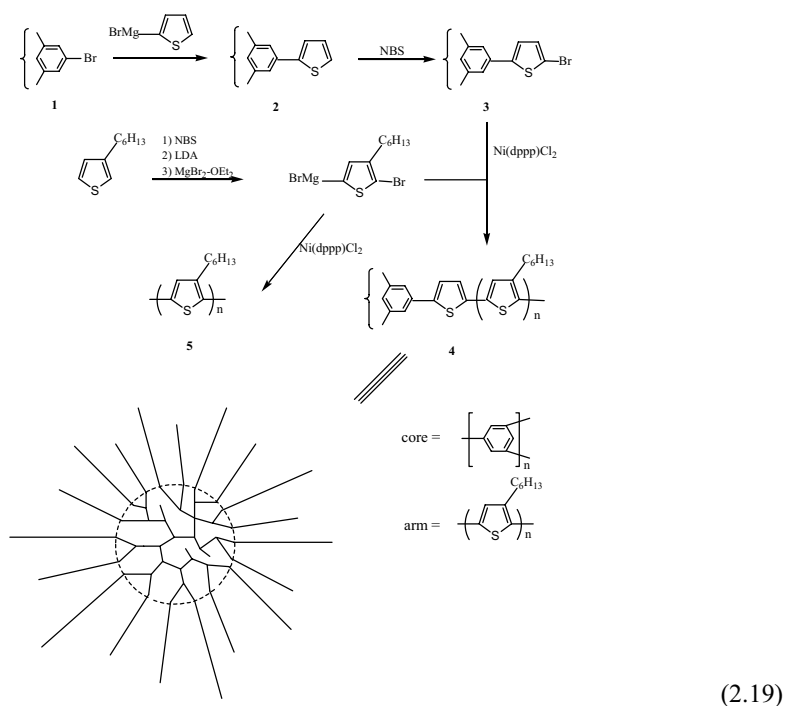
Other related examples include poly(2,5-bisphenyl-1,3,4-oxadiazole) (Herrema *et al.,* 1995), polyquinoxaline (Jandke *et al.,* 1998), hyperbranched poly-Schiff bases (Dai et al., 1998b) and hyperbranched PPV (Lin *et al.,* 2000).

2.2.2.2 Syntheses of Conjugated Polymer Films

The syntheses of soluble conjugated polymers discussed above offer excellent possibilities for advanced device fabrication using various solution-processing methods (*e.g.* spin coating). However, solution-processing techniques may cause some problems related to the quality of polymer films thus formed, including possible deterioration of the mechanical properties of conjugated polymer films by chemical modification of their structures, the reduction of device stability by trapped impurities (*e.g.* O_2, residual solvent) and difficulty in choosing suitable solvent(s) for preparing pinhole-free multilayer polymer thin films. On the other hand, some *in situ* film-forming polymerization methods, including the precursor route and electropolymerization, can be used to circumvent the above-mentioned problems associated with post-synthesis solution processing.

Precursor Route
The formation of conjugated polymers by, for example, thermal conversion of soluble non-conjugated precursor polymers has also been tried in order to circumvent the intractability of conjugated polymers. To mention but a few examples:

Durham polyacetylene: the Durham route to polyacetylene developed by Edwards and Feast has attracted a considerable amount of attention (Edwards and Feast, 1980). As seen in Equation (2.20), it involves the ring-opening metathesis polymerization (ROMP) of cyclobutene derivatives, followed by a thermal conversion into polyacetylene with the evolution of 1,2-bis(trifluoromethyl)benzene. Thermal conversion at a relatively low temperature (< 50 °C) results in the formation of a high quality polyacetylene with a low crystallinity.

(2.20)
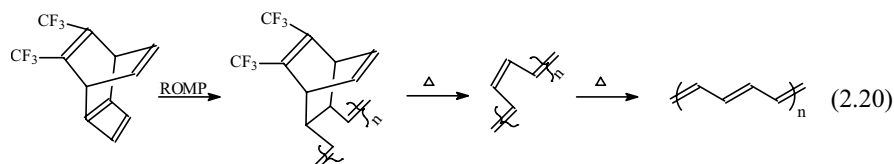
The material thus prepared could be useful for non-linear optical (NLO) applications, where the scattering of light by crystallites needs to be minimized. Changing the reaction conditions can vary the morphology of the final product.

With a refined Durham route, Knoll and Schrock (1989) were able to make polyacetylene prepolymers with a well-controlled molecular weight and its distribution close to unity. Furthermore, it is now possible to synthesize end-functionalized polyacetylene chains and to produce block copolymers with well-defined polyacetylene phase structure through the Durham route (Schrock, 1990). Based on the ROMP technique, Swager *et al.* (1988) reported an alternative precursor route to polyacetylene of low crystallinity [Equation (2.21)]. This method differs from the Durham route in that there is no mass loss upon thermal conversion. However, the resulting polyacetylene was shown to have a low conductivity after I_2-doping, and to possess a significant amount of sp^3 defects.

(2.21)
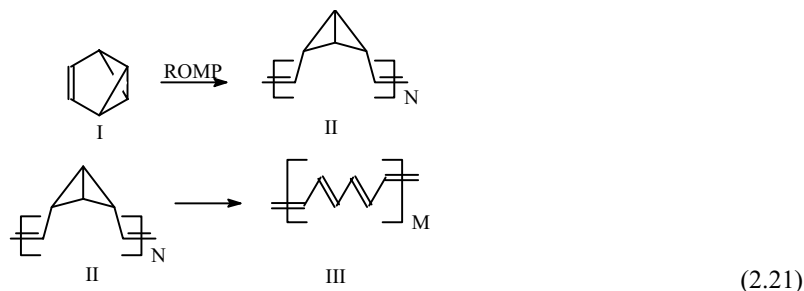
From poly(phenylvinylsulfoxide): polyacetylene-like polymers including polyacetylene-polystyrene diblock copolymers have also been made from

poly(phenylvinylsulfoxide), PPVS (Kanga, 1990) and its polystyrene copolymers (Leung and Tan, 1994) by thermal elimination of phenylsulfenic acid (Reibel, 1992), as shown in Equation (2.22).

$$(2.22)$$

Poly(phenylvinylsulfoxide)

Polyacetylene
+
Ph-S-O-H
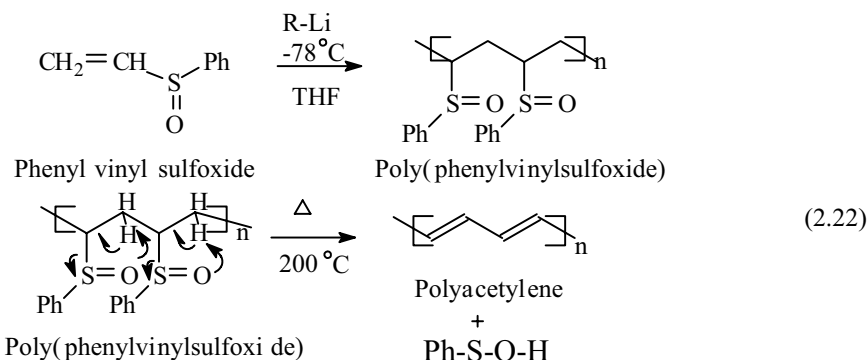
Electropolymerization

Apart from the electrochemical doping, both the potentiostatic method with a constant potential and potentiodynamic technique by scanning the potential within a certain range of voltages have been used for electrochemical polymerization of electronically conducting polymers (Chien, 1984). For instance, pyrrole can be oxidatively polymerized on a suitable anode using a simple two-electrode electrochemical cell. Equation (2.23) shows the mechanism for electropolymerization of pyrrole, which is also valid for many other conjugated conducting polymers (Skotheim *et al.,* 1986).

$$(2.23)$$
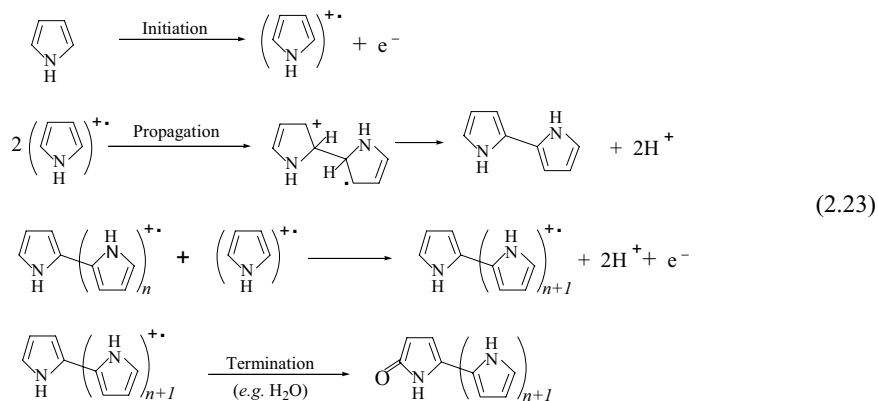
As can be seen from Equation (2.23), the electrochemical oxidation initially produces radicals. This is followed by the formation of dimers via the radical-radical recombination. Subsequent electrochemical oxidation of the dimer intermediates results in the formation of "oligomeric" radicals with a higher molecular weight, which could also combine with monomer radicals. Repeating the above steps yields

a polypyrrole film on the anode electrode. The growth of polypyrrole macromolecules is believed to be governed by the radical-radical coupling and can be terminated via the exhaustion of reactive radical species in the vicinity of the electrode or by other chain termination processes. To balance the charge on the polymer backbone, counter ions are normally incorporated into the polymer film during the chain growth process.

2.3 Charge Transfer Polymers

2.3.1 Organic Charge Transfer Complexes

In 1973, Heeger and co-workers (Coleman *et al.,* 1973; Garito and Heeger, 1974) discovered that an organic ionic salt consisting of tetrathiofulvalene (TTF – electron donor, Figure 2.8(a)) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ – electron acceptor, Figure 2.8(b)) has a low-temperature conductivity (*ca.* –220 ºC) as good as that of copper at room temperature. The observed high conductivity was attributed to a "herring bone"-type crystal structure formed by the flat TTF and TCNQ (Figure 2.8(c)), in which φ-orbitals on adjacent molecules are overlapped to form continuous one-dimensional bands. The charge carriers in this system are provided by the electron transfer between the electron donor (D) and acceptor (A) molecules.
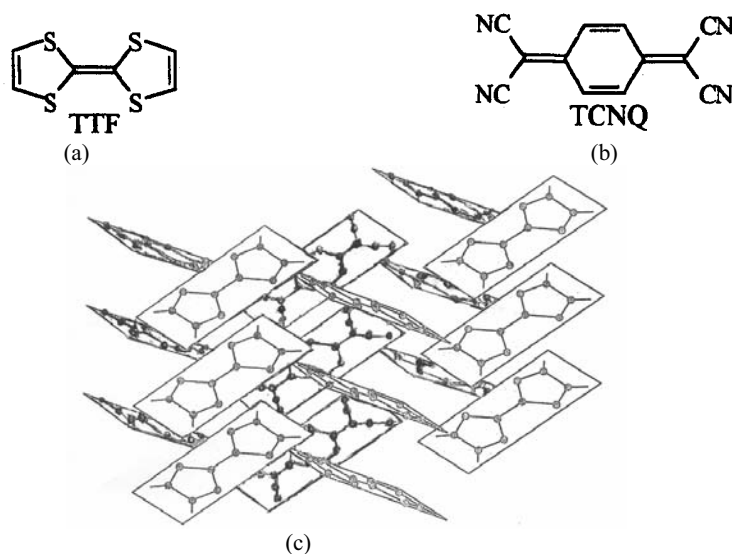
Figure 2.8. The molecular structure of (a) the electron donor TTF; (b) the electron acceptor TCNQ; (c) the crystal structure of TTF-TCNQ charge-transfer complex, in which φ-orbitals on adjacent molecules can overlap to form continuous one-dimensional bands. Transfer of electrons from TTF to TCNQ partially empties the valence band of the former and partially fills the conduction band of the latter (After Ball 1994, copyright 1994 Princeton University Press).

If there were one electron transfer from each of the TTF molecules to each TCNQ molecule, the valence band (conduction band) associated with the TTF (TCNQ) molecules would then be completely emptied (filled), forming an insulator. However, it was found that only three fifths of an electron on average is transferred per molecule in TTF-TCNQ, leading to partially filled energy bands for charge carriers to move around (Section 2.2.1.2). The TTF-TCNQ salt is a typical example of a general class of organic conductors, normally called charge transfer (CT) complexes. As these systems involve two or more different molecules, there is plenty of room for regulating the electronic properties by interchanging different donors or acceptors, or by modifying their chemical structures. Indeed, a large number of CT complexes with various TTF (TCNQ) derivatives as the electron donors (acceptors) have been reported since 1973, as have many other systems with different CT moieties. Several CT salts have been found to even have superconducting properties, as exemplified by $(BEDT\text{-}TTF)_2 \cdot X$ with BEDT being [bis(ethylenedithio)tetrathiafulvalene] and $X = ClO_4^-$, PF_6^-, AsF_6^-, I_3^-, IBr_2^-, BrI_2^-, *etc*. The major drawback for most CT complexes is that they are brittle and unprocessable.

2.3.2 Polymeric Charge Transfer Complexes

In the CT complexes discussed above, the conductivity can be attributed to two factors: the formation of appropriate segregated stacks of donors and acceptors and a certain degree of charge transfer between the stacks. Consequently, the formation of a desired crystal structure, composed of individual donor and acceptor molecules, is essential, but it is not readily susceptible to chemical control. In this regard, organic molecules or macromolecules with D and/or A moieties separated by chemically bonded spacers have been studied (Jiang *et al.,* 1998). These types of molecules possess several important advantages. Firstly, the ionization potential of D, together with the electron affinity of A, can be tuned by adjusting the nature and the mode of the chemical substitution. Hence, it is possible to prepare molecules with D and/or A in either a neutral or charged state by controlling the electron transfer from D to A. Molecules with the CT moieties in the neutral ground state should, in principle, behave like photoconductors or semiconductors, whereas their counterparts with the CT units in the charged state could be metallic conductors or superconductors. Secondly, the barrier to electron hopping along the molecules and their stacking columns may be reduced by introducing heavy atoms (*e.g.* transition metals) into the molecular spacer as certain metal atoms can overlap with the molecules through their large atomic orbitals. Finally, the incorporation of A and/or D moieties into polymer chains could increase the chances for packing segregated stacks with order (Becker *et al.,* 1989) and gain good processability and film-forming properties.

So far, various D-and/or A-containing polymers, with the CT moieties either as pendant groups or as constituent components of the polymer backbones, have been prepared. For example, Litt and Summers (1973) reported the synthesis of poly-*N*-acylethylenimines grafted with D molecules, such as 10-methylphenothiazine (MP) and 4-(methylthio)anisole (MTA) (Figure 2.9).
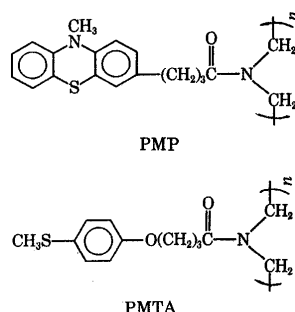
Figure 2.9. The structure of PMP and PMTA (After Litt and Summers, 1973, copyright 1973 John Wiley & Sons, Inc.)

In these polymeric electron donors, the distance between two adjacent donors along the polymer chain allows the insertion of just one electron acceptor molecule (Figure 2.10), leading to good complexing with a stack of alternating D and A.
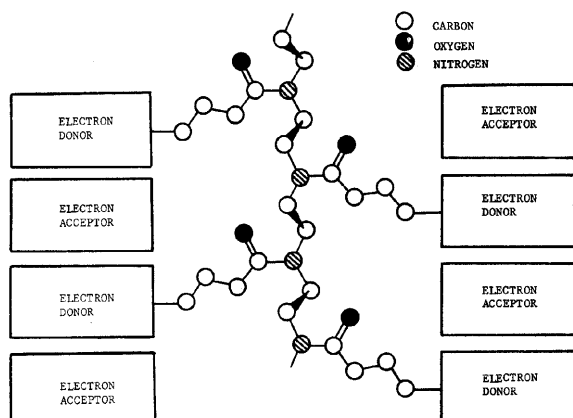

Figure 2.10. Schematic representation of the regular CT complex of polymeric electron donor with electron acceptors (After Litt and Summers, 1973, copyright 1973 John Wiley & Sons, Inc.)

Upon complexation with electron acceptors, such as dichlorodicyanoquinone (DDQ), TCNQ, tetracyanoethylene (TCNE) and tetranitrofluorenone (TNF), the aforementioned polymeric electron donors can become two hundred times as conducting as the corresponding model organic molecular complexes. The polymeric donor-TNF complex even showed photoconductivity (Summers and Litt, 1973).

More recently, Tamura *et al.* (1999) and Frenzel *et al.* (2001) have synthesized conjugated polymers containing TTF in the polymer backbone (Figure 2.11). The resulting TTF-containing polymers are soluble and have good film-forming

properties. Conductivities up to about 5.5×10^{-1} S/cm were obtained through the formation of CT complexes with iodine.
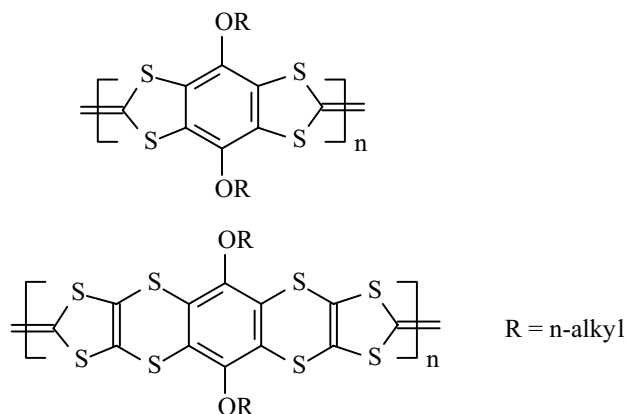
Figure 2.11. Some TTF-containing polymers with extended φ-conjugation (After Frenzel *et al.,* 2001, copyright 2001 Elsevier. Reproduced with permission)

The use of metal-containing linkage(s) to facilitate the electron transfer from a D to an A was demonstrated by the synthesis of highly conductive metal-containing polymers based on the TTF-metal bis-dithiolene type of compounds (Figure 2.12) (Rivera and Engler, 1979).
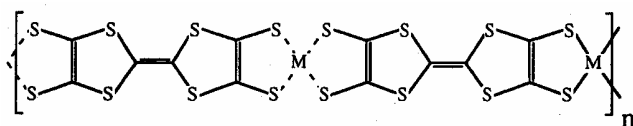
Figure 2.12. TTF-metal bis-dithiolene organometallic polymers (After Rivera and Engler, 1979, copyright 1979 The Royal Society of Chemistry. Reproduced with permission)

These compounds can show conductivities as high as 3×10^4 S/cm when the metal (M) atom is nickel. The conductivity in these metal-containing polymers arises from the charge transfer and the ability of the transition metal atom to provide the orbital overlap, implying that the conjugated structure and subsequent doping may not always be necessary for the metal-containing conducting polymers. A series of conducting polymers with porphyrin or metal-to-ligand CT porphyrin chromophores/electrophores incorporated into their backbones have been studied for potential applications ranging from artificial photosynthesis to light-emitting diodes (Jiang *et al.*, 1998).

2.3.3 Charge Transfer Between Fullerene C_{60} and Polymers

Buckminsterfullerene C_{60} has a soccerball-like structure with a diameter of 7.1 Å, consisting of 12 pentagons and 20 hexagons facing symmetrically (see Chapter 4 for details). Owing to its unusual molecular structure, fullerene C_{60} has a unique electronic structure. In contrast to benzene, double-bond resonant structures in five-membered rings of buckyballs are not favored, and the curvature of the C_{60} molecule leads to a greater intermolecular orbital overlap than graphite (Dai, 1999). As such, fullerenes have chemical characteristics different from the classical aromatic compounds and, unlike insulating diamond, they are semiconductors. The distribution in energy of the 60 ϕ-electrons in C_{60} has been determined, for example, by Hückel calculations (Haddon, 1992). The theoretically determined low-lying LUMO near to the zero of the Hückel energy axis suggests a high electron affinity for the C_{60} molecule. Therefore, C_{60} can be used as an electron acceptor in the preparation of CT compounds. Complexation of C_{60} with strong electron donors (*e.g.* cobaltocene or tetrakis(dimethylamino)ethylene, TDAE) resulted in the formation of electrically insulating CT compounds (Allemand *et al.*, 1991a), which show *ferromagnetism* below the critical temperature $T_c = 17 - 24$ K (Allemand *et al.*, 1991b). On the other hand, doping fullerene C_{60} with alkali metals (Hammond and Kuck, 1992) has led to a dramatic increase in conductivity. Surprisingly, the K_xC_{60} (typically, x = 3) combination even showed *superconductivity* (SC) below 18 K (Hebard *et al.*, 1991).

While the ability for C_{60} to provide both of the cooperative phenomena (namely, superconductivity and ferromagnetism) in its solid state CT complexes is fascinating, C_{60} has also been used as a *p*-type dopant for conjugated conducting polymers. When doping conducting polymers with C_{60}, however, the LUMO of C_{60} is located between the top of the valence band and the bottom of the conduction band (*i.e.* in the forbidden gap) of most conducting polymers (Schlebusch *et al.*, 1996), indicating that fullerenes are weak dopants (Zakhidov, 1991). Consequently, the dark conductivities of the conducting polymers could only be marginally improved by doping with fullerene C_{60} (Dai *et al.*, 1998a). Due to photo-induced CT between the fullerene molecules and conjugated conducting polymers (Figure 2.13), however, various interesting optoelectronic phenomena, including quenching of photoluminescence, photo-induced adsorption, photo-induced dichroism and enhancement of photoconductivity, have been observed (Sariciftci, 1995). For instance, C_{60}-doped photoconducting films with performances comparable to some of the best commercial photoconductors *(e.g.* thiapyryliumdye aggregates) (Yu *et al.*, 1994) have been prepared by liquid-phase mechanical mixing of PVK with fullerenes (a mixture of C_{60} and C_{70}) (Wang, 1992). The improved photoconductivity of C_{60}-doped PVK was attributed to a photo-induced charge separation of the electron transfer complex between C_{60} and PVK. Furthermore, doping a poly(3-a1kylthiophene)-C_{60}, P(3AT)-C_{60}, composite with an alkali metal, A (*e.g.* K vapor, *n*- doping), was suggested to cause extrinsic CT from A to both C_{60} and conducting polymer, leading to superconductivity for the CP-$(C_{60})_yA_x$ ternary composite ($T_c = 17$ K for 5 mol% C_{60}) (Sariciftci, 1995).
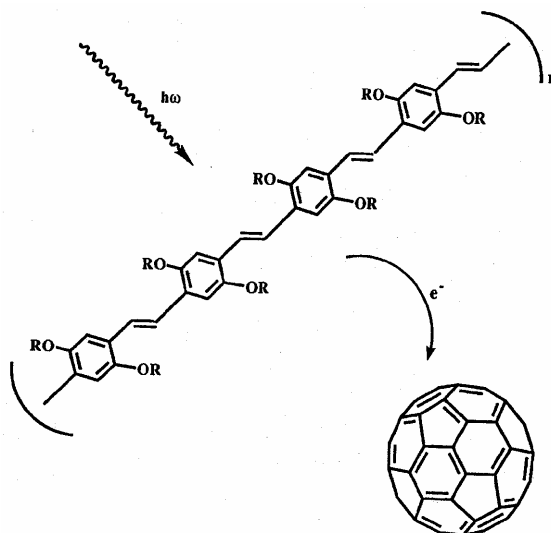
Figure 2.13. Schematic representation of the photo-induced electron transfer from conjugated polymers onto fullerene C_{60} (After Sariciftci, 1995, copyright 1995 Elsevier. Reproduced with permission)

2.4 Ionically Conducting Polymers

Just like the electronically conducting polymers (*i.e.* conjugated polymers and CT polymers) discussed above, the development of solid-state ionic conductors has been considered important because of the many uses to which they have been applied, for example, in electrochromic devices, supercapacitors, thermoelectric generators and secondary lithium batteries. The development of solid-state ionic materials based on ceramics, glasses or inorganic crystals has for decades been an active research area, while the ionically conducting polymers or polymer electrolytes represent a relatively new class of solid ionics. Since the inorganic solid-state ionics have received excellent coverage elsewhere (Vashishta *et al.,* 1979), we focus our attention here on polymer electrolytes.

2.4.1 Structural Features of Polymer Electrolytes

Polymer electrolytes are normally prepared by dissolving a salt species in a solid polymer host. Conductivity in polymer electrolytes is believed to arise from the ion migration between coordination sites repeatedly generated by the local motion of polymer chain segments. Therefore, a desirable polymer host must possess: a) electron-donating atoms or groups for the coordinate bond formation with cations, b) low bond rotation barriers for an easy segmental motion of the polymer chain, and c) an appropriate distance between coordinating centers for multiple intra-

polymer bonding with cations. Although a large number of macromolecules can meet the above requirements, poly(ethylene oxide), PEO, remains the most studied host polymer (Gray, 1991). Likewise, much attention has been focused on lithium and sodium salts, though many salts can be dissolved in PEO. Figure 2.14 schematically shows the ion transport in PEO-based polymer electrolytes.
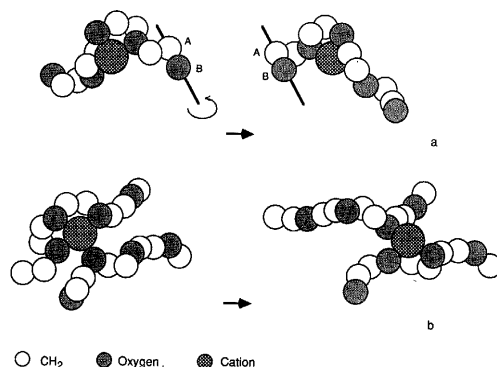
Figure 2.14. Schematic representation of the cation transport mechanism in a PEO-based polymer electrolyte. (a) Lateral displacement of the cation brought about by 180∀ bond rotation at the C‑O bond along the AB line; (b) the transfer of the cation between PEO chains, possibly along with anions as either an ion pair or an ion triplet (After Gray, 1991, copyright 1991 VCH Publishers. Reproduced with permission)

As can be seen in Figure 2.14, the ionic mobility is closely correlated to the relaxation modes of the polymer host, which become effective above the polymer glass transition temperature, T_g (*e.g.* -60∀C for PEO). Indeed, polymer electrolytes have long been considered to transport charge only above T_g, and the relatively slow segmental motion of polymer chains has limited the hopping rate of cations, and hence the conductivity. For this reason, the highest room-temperature conductivity (*ca.*10^{-4} S/cm) reported for PEO-LiX electrolytes [with X being a negative ion like Cl, ClO_4, AsF_6, CF_3SO_3 and $N(SO_2CF_3)_2$] is still several orders of magnitude less than the corresponding values of most inorganic solid-state ionics. In comparison with inorganic solid-state ionics, however, polymer electrolytes offer many advantages, including the replacement of liquid electrolytes currently used in the lithium-battery technology, the versatility for fabrication of flexible solid-state devices free from seals, and the availability in various geometries (Croce *et al.* 1998).

2.4.2 Transport Properties and Chain Dynamics

As mentioned above, the movement of ions in polymer electrolytes is mediated by the local motion of the polymer chain segments above T_g. The liquid-like motion of

polymer segments above T_g causes the local environment at any one point in the polymer sample to change with time. This has a strong influence on the charge transport in polymer electrolytes. In principle, the conductivity, $\omega(T)$, is given by:

$$\omega(T) = nq\sigma \qquad (2.24)$$

where n is the number of charge carriers, q is the charge for a single-charge carrier, and σ is its mobility. For a system with an invariant number of charge carriers and cations of a unity charge, such as PEO-LiX at a constant salt concentration, the conductivity can be related directly to the mobility of the charge species. Therefore, the ion transport in these polymer electrolyte systems can be described solely in terms of "solvent" fluidity. It is known that the temperature dependence of many relaxation and transport processes in liquid-like (amorphous) polymer systems in the vicinity of T_g can be described by the Williams-Landel-Ferry (WLF) equation (Flory, 1953):

$$log a_T = \frac{-17.4\,(T - T_g)}{51.6 + T - T_g} \qquad (2.25)$$

where a_T is a shift factor, which can be expressed in general terms as:

$$a_T = \vartheta/\vartheta_0 \qquad (2.26)$$

with ϑ and ϑ_0 being the relaxation time at temperature T and a reference temperature T_0, respectively. Now since $\sigma \propto 1/\vartheta$, the WLF equation implies that a decrease in T_g could lead to an increase in the ionic conductivity $\omega(T)$.

Indeed, it was found that the addition of various plasticizers did improve the low-temperature ionic conductivity of PEO-LiX electrolytes due to an enhanced local relaxation and segmental motion of the polymer chains. The typical plasticizers used in the PEO-LiX systems can be divided into two categories: liquid plasticizers, such as low-molecular weight polyethyleneglycols or aprotic organic solvents; and solid-state plasticizers including ceramic powders and nanoparticles (Croce *et al.,* 1998). The gain in conductivity by liquid plasticizers, however, is often accompanied by a deteriorated effect on mechanical properties and a loss of the compatibility with the lithium electrode in lithium secondary batteries. In contrast, the use of ceramic powders in the PEO-LiX electrolytes has been demonstrated to show several distinct advantages: a) increased low-temperature conductivity by promoting localized amorphous regions due to the large surface area of the particle fillers, b) enhanced mechanical stability by the network formation of the dispersed fillers, and c) improved compatibility with the lithium electrode due to the elimination of any liquids or interfacial stabilizing reagents. Figure 2.15 reproduces the temperature dependence of conductivity for nanocomposites of PEO-LiClO$_4$-10 wt% TiO$_2$ and PEO-LiClO$_4$-10 wt% Al$_2$O$_3$, along with that of a pristine PEO-LiClO$_4$ polymer electrolyte (Croce *et al.,* 1998). The enhancement of ionic conductivity for the PEO-LiClO$_4$ electrolytes by adding ceramic nanoparticles is clearly evident.
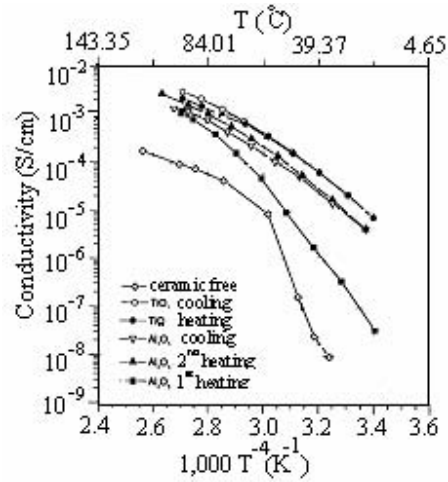
Figure 2.15. Arrhenius plots of the conductivity of ceramic‑free PEO‑LiClO$_4$, PEO‑LiClO$_4$‑10 wt% TiO$_2$ and PEO‑LiClO$_4$‑10 wt% Al$_2$O$_3$ polymer electrolytes (PEO:LiClO$_4$ = 8:1 in all cases) (After Croce *et al.,* 1998, copyright 1998 Macmillan Magazines Limited. Reproduced with permission)

Although the WLF equation does provide some useful information on the temperature dependence of the ionic conductivity in polymer electrolytes, the above transport mechanism is currently being challenged. In contrast to the general belief that ionic conductivity occurs only in *amorphous* polymers above T_g, Gadjourova *et al.* (2001) have recently shown that ionic conductivity in certain *crystalline* polymer electrolytes is even superior to that of their amorphous counterparts. In so doing, these authors prepared crystalline and amorphous PEO$_6$-LiSbF$_6$ and found that ionic conductivities of the crystalline polymer electrolytes are much higher than the corresponding amorphous materials over a range of temperatures (Figure 2.16).
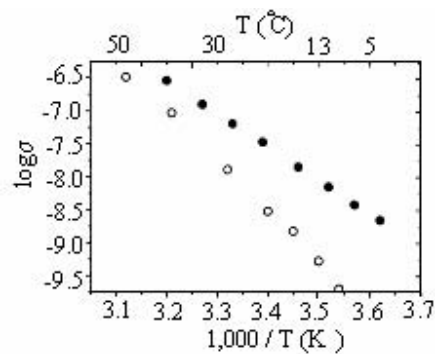
Figure 2.16. Ionic conductivity ω (S/cm) of amorphous (open circles) and crystalline (filled circles) PEO$_6$-LiSbF$_6$ as a function of temperature (After Gadjourova *et al.,* 2001, copyright 2001 Macmillan Magazines Limited. Reproduced with permission)

Detailed structural study shows that the polymer chains fold to form cylindrical tunnels inside of which the lithium ions are coordinated by the ether oxygens, whereas the anions are located outside of the tunnels with no coordinating interaction with the cations. The enhanced ionic conductivity of the crystalline materials, therefore, results from the relatively free movement of cations through the *pre-existing* tunnels.

The favored ion transport in crystalline polymer electrolytes is not inconsistent with the finding that some of the crystalline ceramics (*e.g.* $Li_{0.5}La_{0.5}TiO_3$) showed conductivities up to 1 - 3 orders of magnitude higher than the highest conductivity reported for conventional amorphous polymer electrolytes (Inaguma *et al.,* 1993). Besides, high ionic conductivity has also been recently observed in plastic crystals due to the fast lithium ion motion associated with rotational disorder and/or vacancies in the lattice (MacFarlane *et al.,* 1999). The realization that ordered structures can promote ion transport has opened up new approaches to the design of polymers with high ionic conductivity. This finding is also interesting in the context of electronically conducting conjugated and CT polymers, in which crystallinity favors electron transport.

2.5 Conductively Filled Polymers

An alternative method of inducing electrical conductivity in polymers is to make polymer composite materials with conductive additives or fillers. Typical examples of conductive components used to prepare this type of conducting polymer include conducting solids (carbon-black, carbon fibers, aluminum flake, stainless steel fibers, metal-coated fillers, metal particles, *etc.*) and conjugated conducting polymers. Because the conductivity is introduced through the addition of the conducting components, various polymer materials including both amorphous polymers (polystyrene, PVC, PMMA, polycarbonate, acrylonitrile butadiene styrene (ABS), polyethersulphone, polyetherimides, *etc.*) and crystalline polymers (polyethylene, polypropylene, polyphenylene sulphide, nylons, *etc.*) can be made electrically conducting. Various processing techniques such as hot compression, extrusion, and *in situ* polymerization have been used to prepare the conductively filled polymers for a number of applications ranging from electrostatic discharge protection to electromagnetic interference/radio-frequency interference (EMI/RFI) shielding (Olabisi, 1997).

2.5.1 Polymers Filled with Conductive Solids

As schematically shown in Figure 2.17, dispersion of conducting particles in an insulating polymer matrix can impart the conductivity when the particle volume fraction is greater than a value referred to as the percolation threshold (λ_c) (Stauffer, 1985).
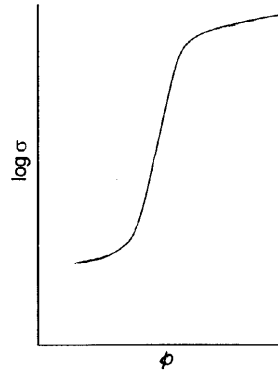
Figure 2.17. Dependence of composite conductivity, ω, on the volume fraction, λ, of conductive fillers

The conductivity of the composite is almost the same as that of the insulating polymer below λ_c. Since the number of the conductive particles is insufficient to form a continuous conducting path below λ_c (Figure 2.18(a)), the conductive domains are insulated from each other by the polymer medium and the electrical conducting behavior could not be observed. In the vicinity of λ_c, the isolated conductive particles appear to contact each other forming a continuous network for transportation of electrons (Figure 2.18(b)). Immediately after the percolation threshold (Figure 1.18(c)), a slight increase in the concentration of conductive particles may greatly increase the bridges in the conducting network. The insulating composite is thus transformed into a conducting material in a jumpwise fashion. Further increase in the concentration of the conductive particles, however, may only cause the volume of the conducting domains to increase without any significant increase in the pathways for electrons, leading to a monotonic increase in conductivity.
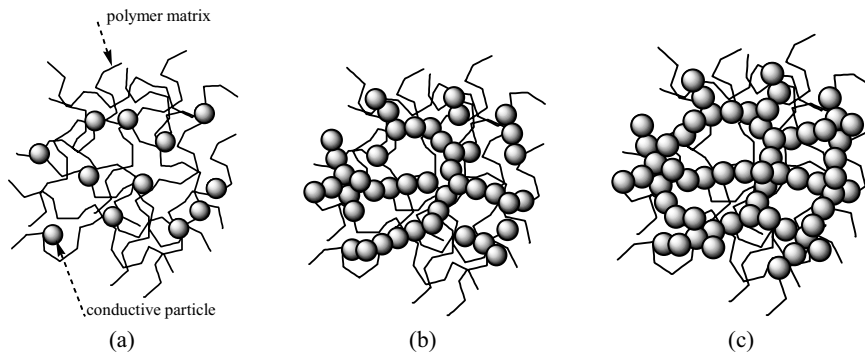
Figure 2.18. Schematic representation of conductive particles dispersed in a polymer matrix at different particle volume fractions: (a) $\lambda < \lambda_c$; (b) $\lambda - \lambda_c$; (c) $\lambda \times \lambda_c$

Obviously, the precise location of the percolation threshold is affected by many factors, including the size, aspect ratio and size/spatial distributions of the conductive particles. To a given particle volume, for example, the surface area available for conductive contact increases with a decrease in the particle size, and hence a lower λ_c. Likewise, the loading of metal particles of a high aspect ratio has been demonstrated to be more effective in enhancing conductivity than the corresponding particles of a low aspect ratio (Sichel and Rubner, 1985). For spherical conducting particles dispersed in insulating matrices, the value of λ_c was found to be *ca.* 16 vol.%.

Several theories have been developed to explain the percolation behavior observed in polymer composites filled with conducting particles (Balberg and Anderson, 1984; Mikrajuddin *et al.,* 2000; Roldughin and Vysotskii, 2000). Most of them can only predict the general feature of the conductivity change with the filler content. For example, the scaling law of percolation theory (Roldughin and Vysotskii, 2000) gives no information about possible effects of the particle size, particle size distribution and spatial distribution flocculation on the percolation threshold. Nevertheless, it can be used to predict the change in conductivity near the percolation threshold, as seen in Equation (2.27).

$$\omega - \omega_1 \vartheta^t, \quad \vartheta > 0, \qquad \omega - \omega_1 \sqrt{\vartheta}|^{-q}, \quad \vartheta < 0 \qquad (2.27)$$

where $\vartheta = (\lambda - \lambda_c)/(1 - \lambda_c)$, ω_1 and ω_2 are conductivity of the conductive particle and the polymer matrix, respectively, and t and q are scaling indexes. Numerical calculations have demonstrated that for a two-dimensional space $t = q$, while for a three-dimensional space $t > q$ (Roldughin and Vysotskii, 2000).

On the other hand, Wu (1985, 1988) deduced the correlation between the surface-to-surface interparticle distance, S (Figure 2.19), and the particle volume fraction, λ, for polymer blends with homogenously dispersed spherical particles of a diameter D as follows:

$$S = D \left[(\phi/6\lambda)^{1/3} - 1 \right] \qquad (2.28)$$
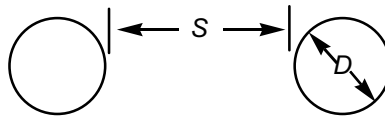
Figure 2.19. Schematic representation of conductive particles in a polymer matrix

By taking the typical electron tunneling distance of 10 nm (Doyen, 1999) as the surface-to-surface interparticle distance, the critical volume fraction (λ_c) calculated from Equation (2.28) is plotted against the particle diameter (D) in Figure 2.20 (Jing *et al.,* 2000), which clearly shows that λ_c decreases rapidly with decreasing D in the nanometer range.
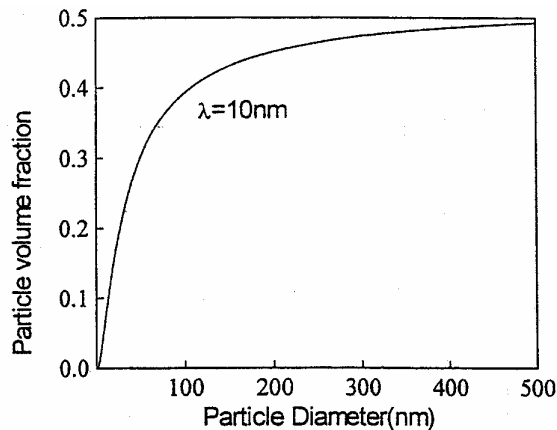
Figure 2.20. The relationship of the particle volume fraction and particle diameter for hexagonal close packed distribution at a surface-to-surface interparticle distance of 10 nm (After Jing *et al.,* 2000, copyright 2000 Kluwer Academic Publishers. Reproduced with permission)

Following the more recent formulations developed by Wu (1988), the effects of the particle size distribution and spatial distribution flocculation on the percolation threshold could also be investigated.

Consistent with Figure 2.20, a percolation threshold as low as 0.75 vol.% has recently been reported for nylon 6/graphite-conducting nanocomposites prepared by intercalation polymerization (Pan *et al.*, 2000). Furthermore, conducting polymer composites of low percolation thresholds have also been developed by using a *binary* host of *immiscible* polymer blends (Cheah *et al.,* 2000). In the binary polymer systems, the conductive particles may preferentially localize at the interface of the polymer blends or within one of the polymer phases (Gubbels *et al.,* 1998). The selective localization of the conductive particles at the interface of polymer blends is particularly interesting not only because percolation thresholds as small as 0.02 vol.% are achievable by forming a continuous conducting path at the interface region between two co-continued polymer phases but also because mechanical properties of the composites could be improved by the *in situ* interfacial modification.

In addition to the particulate conducting fillers, carbon fibers derived from polyacrylonitrile have also been used not only to generate conductivity but also to provide a degree of reinforcement of certain thermoplastic polymers for EMI/RFI shielding applications (Cogswell, 1992). Because of their high resilience, large surface area and good electrical properties, carbon nanotubes (see Chapter 5 for details) could well work better than carbon fibers for making novel conductively filled polymers with enhanced mechanical and electrical properties (Dai and Mau, 2001).

2.5.2 Polymers Filled with Conjugated Conducting Polymers

Composite materials based on conjugated conducting polymers and non-conducting polymers are another major class of conducting polymer composites that often show a low percolation threshold and improved environmental stability with respect to the conjugated polymer. To mention but a few examples, Heeger and co-workers (Reghu *et al.,* 1993; Suzuki *et al.,* 1990) have demonstrated very low percolation thresholds down to *ca.* 0.05 vol.% for spin-cast polymer composites consisting of soluble conjugated conducting polymers (*e.g.* PANI, poly(3-octylthiophene)) and certain non-conducting polymers (*e.g.* poly(methyl methacrylate), poly-(*p*-phenylene terephthalamide), polyethylene). The observed low λ_c was attributed to a multiple percolation, with which a continuous network of conducting pathways is formed on pre-existing tenuous interconnected networks of the non-conducting polymer. In addition to solution processing, compounding techniques used for processing of conventional thermoplastics have also been applied to prepare composites of polyacetylene or polypyrrole with certain thermoplastics (Wessling and Volk, 1986). On the other hand, polyacetylene lattices have been prepared by chemically polymerizing acetylene in the presence of poly[(tert-butylstyrene)-*b*-(ethylene oxide)] (Edwards *et al.,* 1983), whereas electropolymerization of pyrrole in a polymeric latex dispersion yielded conductive films after drying (Jasne *et al.,* 1986). In a separate but closely related study, polyacetylene/low-density polyethylene composites containing 1%–18% polyacetylene were prepared by exposing acetylene gas to polyethylene matrices pre-soaked with the Ziegler-Natta catalyst (Galvin and Wnek, 1982). The resultant materials showed conductivities of 5-10 S/cm, after I_2-doping, with as little as 2–4 vol.% polyacetylene. Irregular aggregates of polyacetylene were observed by transmission electron microscopy (TEM) to disperse within the insulating polyethylene matrix, which improved the environmental stability of the conducting component through physical "encapsulation". Later, this *in situ* polyacetylene polymerization method was applied to polybutadiene (Rubner *et al.,* 1983) and polystyrene-polydiene block copolymers (Lee and Jopson, 1983) to yield composite elastomers of conductivities up to *ca.* 570 S/cm. More recently, Frisch and co-workers (Frisch and De Barros, 1992; Frisch and Chen, 1994) have also prepared conducting polymer composites of conductivities up to 10^{-4} S/cm from full and psuedo-interpenetrating polymer networks of poly(carbonate-urethane) and natural rubber by I_2-induced conjugation of the polyisoprene elastomeric component (see Equation (2.12)).

2.6 References

Akamatu, H., Inokutchi, H., Matsunaga, Y. (1954) *Nature* **173**, 168.
Aldissi, M. (1986) *Synth. Met.* **13**, 87.
Allemand, P.-M., Chemani, K.C., Koch, A., Wudl, F., Holczer, K., Donovan, S., Grüner, G., Thompson, J.D. (1991a) *Science* **253**, 301.

Allemand, P.M., Khemani, K.C., Koch, A., Wudl, F., Holczer, K., Donovan, S., Gruner, G., Thompson, J.D. (1991b) *Science* **253**, 301

Armes, S.P. (1996) *Curr. Opin. Colloid Interf. Sci.* **1**, 214, and references cited therein.

Armes, S., Vincent, B., White, J.W. (1986) *J. Chem. Soc., Chem. Commun.* 1525.

Baker, G.L. (1988) In: Bowden, M.J., Turner, S.R. (eds) *Electronic and Photonic Applications of Polymers*. *Adv. Chem. Ser.* 218, ACS, Washington DC.

Ball, P. (1994) Designing *the Molecular World: Chemistry at the Frontier*, Princeton University Press, New Jersey.

Balberg, I., Anderson, C.H. (1984) *Phys. Rev. B* **30**, 3933.

Bates, F.S., Baker, G.L. (1983) *Macromolecules* **16***,* 704.

Becker, J.Y., Bernstein, J., Bittner, S., Sarma, J.A.R.P., Shaik, S.S. (1989) *Chem. Mater.* **1**, 412.

Bolognesi, A., Cattellani, M., Destri, S., Porzio, W., Meille, S., Pedemonte, E. (1986) *Makromol. Chem.* **187***,* 1287.

Bolognesi, A., Cattellani, M., Destri, S. (1985) *Mol. Cryst. Liq. Cryst.* **117***,* 29.

Borman, S. (1990) *C&E News* **May 7**, 53.

Bradley, D.D.C. (1992) *Adv. Mater.* **4**, 756.

Brédas, J.L., Cornil, J., Heeger, A.J. (1996) *Adv. Mater.* **8**, 447.

Brédas, J. L., Silbey, R. (eds) (1991) *Conjugated Polymers*, Kluwer Academic, Dordrecht.

Brédas, J.L., Street, G.B. (1985) *Acc. Chem. Res.* **18**, 309.

Burn, P.L., Kraft, A., Baigent, D.R., Bradley, D.D.C., Brown, A.R., Friend, R.H., Gymer, R.W., Holmes, A.B., Jackson, R.W. (1993) *J. Am. Chem. Soc.* **115***,* 10117.

Calvert, P. (1988) *Nature* **333**, 296.

Cao, Y., Smith, P., Heeger, A.J. (1992a) *Synth. Met.* **48**, 91.

Cao, Y., Treacy, G.M., Smith, P., Heeger, A.J. (1992b) *Appl. Phys. Lett.* **60**, 2711.

Cheah, K., Forsyth, M., Simon, G.P. (2000) *J. Polym. Sci., Polym. Phys.* **38**, 3106, and references cited therein.

Cheng, S.-A., Lin, L.C. (1995) *Macromolecules* **28**, 1239.

Chiang, C.K, Gau, S.C., Fincher, C.R., Jr., Park, Y.W., MacDiarmid, A.G., and Heeger, A.J. (1978) *Appl. Phys. Lett.* **33**, 18.

Chien, J.C.W. (1984) *Polyacetylene, Chemistry, Physics, and Material Science*, Academic Press, London.

Chien, J.C.W., Wenk, G.E., Karasz, F.E., Hirsch, J.A. (1981) *Macromolecules* **14**, 479.

Cogswell, F.N. (1992) *Thermoplastic Aromatic Polymer Composites: A Study of The Structure, Processing, and Properties of Carbon Fibre Reinforced Polyetheretherketone and Related Materials*, Butterworth-Heinemann, Boston.

Coleman, L.B., Cohen, M.J., Sadman, D.J., Yamagishi, F.G., Garito, A.F., Heeger, A.J. (1973) *Solid State Commun.* **12**, 1125.

Croce, F., Appetecchi, G.B., Persi, L., Scrosati, B. (1998) *Nature* **394**, 456.

Dai, L. (1992) *J. Phys. Chem.* **96**, 6469.

Dai, L. (1997) *Macromol. Chem. Phys.* **189***,* 1723.

Dai, L. (1999) *J. Macromol. Sci., Rev. Macromol. Chem. Phys. C* **39**, 273.

Dai, L., Huang, S., Lu, J., Mau, A.W.H., Zhang, F. (1998b) *ACS Polym. Prep.* **39***,* 171.

Dai, L., Lu, J., Matthews, B., Mau, A.W.H. (1998a) *J. Phys. Chem. B* **102**, 4049, and references cited therein.

Dai, L., Mau, A.W.H. (2001) *Adv. Mater.* **13**, 899.

Dai, L., Mau, A.W.H., Griesser, H.J., Winkler, D.A. (1994) *Macromolecules* **27**, 6728.

Dai, L., Wang, Q., Wan, M. (2000) *J. Mater. Sci. Lett.* **19**, 1645.

Dai, L., White, J.W. (1991) *Polymer* **32**, 2120.

Dai, L., White, J.W. (1997) in: Shi, L., Zhu, D. (eds) *Polymers and Organic Solids*, Science Press, Beijing.

Dai, L., Winkler, B., Dong, L., Tong, L., Mau, A.W.H. (2001) *Adv. Mater.* **13**, 915.

Dai, L., Winkler, B., Huang, S., Mau, A.W.H. (1999) In: Hsieh, B., Galvin, M., Wei, Y. (eds) *Semiconductive Polymers*, American Chemical Society, Washington DC, and references cited therein.

Dandreaux, G.F., Galvin, M.E., Wnek, G.E. (1983) *J. Physique Colloque C3* **44**, 135.

de Meijere, A. (ed.) (1999) *Carbon Rich Compounds II, Macrocyclic Oligoacetylenes and Other Linearly Conjugated Systems*, Springer-Verlag, Berlin.

Deits, W., Cukor, P., Rubner, M., Jopson, H. (1982) *Synth. Met.* **4**, 199.

Doyen, G. (1999) *The Physical Principles of STM and AFM Operation*. Wiley, New York.

Duan, R.G., Miller, L.L., Tomalia, D.A. (1995) *J. Am. Chem. Soc.* **117**, 10783.

Edwards, J.H., Feast, W. J. (1980) *Polymer* **21**, 595.

Edwards, J., Fisher, R., Vincent, B. (1983) *Makromol. Chem. Rapid. Commun.* **4**, 393.

Epstein, A.J., MacDiarmid, A.G. (1995) *Synth. Met.* **69**, 179.

Feast, W.J., Tsibouklis, J., Pouwer, K.L., Groenendaal, L., Meijer, E.W. (1996) *Polymer* **37**, 5017, and references cited therein.

Francois, B., Olinga, T. (1993) *Synth. Met.* **55–57**, 3489.

Frenzel, S., Baumgarten, M., Müllen, K. (2001) *Synth. Met.* **118**, 97.

Frisch, H.L., Chen, Z.J. (1994) *J. Polym. Sci., Polym. Chem.* **32**, 1317.

Frisch, H.L., De Barros, G.G. (1992) *J. Polym. Sci., Polym. Chem.* **30**, 937.

Ferraro, J.R., Williams, J.M. (1987) *Introduction to Synthetic Electrical Conductors*, Academic Press, San Diego.

Flory, P.J. (1953) *Principle of Polymer Chemistry*, Cornell University Press, New York.

Gadjourova, Z., Andreev, Y.G., Tunstall, D.P., and Bruce, P.G. (2001) *Nature* **412**, 520.

Galvin, M.E., Wnek, G.E. (1982) Polymer **23**, 795.

Galvin, M.E., Wnek, G.E. (1985) *Polym. Bull.* **13**, 109.

Garito, A.F., Heeger, AL. (1974) *Acc. Chem. Res.* **7**, 232.

Garnier, F., Hajlaoui, R., Yasser, A., Svrivastava, P. (1994) *Science* **265**, 1684.

Gettinger, C.L., Heeger, A.J., Drake, J.M., Pine, D.J. (1994) *J. Chem. Phys.* **101**, 1673.

Gilch, H.G., Wheelwright, W.L. (1966) *J. Poly. Sci., Polym. Chem.* **4**, 1337.

Gill, R.E., Malliaras, G.G., Wildeman, J., Hadziioannou, G. (1994) *Adv. Mater.* **6**, 132.

Gray, F.M. (1991) *Solid Polymer Electrolytes: Fundamentals and Technological Applications*, VCH Publishers, Weinheim, Germany.

Gubbels, F., Jerome, R., Vanlathem, E., Deltour, R., Blacher, S., Brouers, F. (1998) *Chem. Mater.* **10**, 1227.

Haddon, R.C. (1992) *Acc. Chem. Res.* **25**, 127.

Hammond, G.S., Kuck, V.J. (eds) (1992) *Fullerenes: Synthesis, Properties, and Chemistry of Large Carbon Clusters*, ACS Symposium Series 481, American Chemical Society, Washington DC.

Harrison, W.A. (1979) *Solid State Theory*, Dover Publications, Inc., New York.

Hebard, A.F., Rosseinsky, M.J., Haddon, R.C., Murphy, D.W., Glarum, S.H., Palstra, T.T., Ramirez, A.P., Kortan, A.R. (1991) *Nature*, **350**, 600.

Heeger, A.J., Kivelson, S., Schrieffer, J.R., Su, W.P. (1988) *Rev. Mod. Phys.* **60**, 781, and reference cited therein.

Herrema, J.K., Huten, P.F., Gill, R.E., Wilderman, J., Wieringa, R.H., Haziioannou, G. (1995) *Macromolecules* **28**, 8102.

Hörhold, H.H., Raabe, D., Opfermann, J. (1997) *J. Prakt. Chem.* **139**, 611.

Hsieh, B.R., Yu, Y., Forsythe, E.W., Schaaf, G.M., Feld, W.A. (1998) *J. Am. Chem. Soc.* **120**, 231.

Inaguma, Y., Chen, L.Q., Itoh, M., Nakamura, T., Uchida, T., Ikuta, H., Wakihara, M. (1993) *Solid State Commun.* **86**, 689.

Iqbal, Z., Baughman, R.H., Ramakrishna, B.L., Khare, S., Murthy, N.S., Bornemann, H.J., Morris, D.E. (1986) *Science* **254**, 826.

Ito, T., Shirakawa, H., Ikeda, I.J. (1974) *Polym. Sci., Polym. Chem.* **12**, 11.

Jacoby , M. (2002), *C&E News* **November 4**, 31.

Jandke, M., Strohriegl, P., Berleb, S., Werner, E., Brütting, W. (1998) *Macromolecules* **31**, 6434.

Jasne, S., Chiklis, C.K. (1986) *Synth. Met.* **15**, 175.

Jerome, D., Mazaud, M., Ribault, M., Bechgaard, K. (1980) *J. Phys. Let.* **41**, L95.

Jiang, B., Yang, S.W., Bailey, S.L., Hermans, L.G., Niver, R.A., Bolcar, M.A., Jones, Jr. W.E. (1998) *Coord. Chem. Rev.* **171**, 365.

Jing, X., Zhao, W., Lan, L. (2000) *J. Mater. Sci. Lett.* **19**, 377.

Kanga, R.S., Hogen-Esch, T.E., Randrianalimanana, E., Soum, A., Fontontanille, M. (1990) *Macromolecules* **23**, 4235 and 4241.

Kawakami, S. (1987) JP 01165603.

Kim, Y.H., Webster, O.W. (1992) *Macromolecules* **25**, 5561.

Kminek, I., Trekoval, J. (1984) *Makromol. Chem. Rapid Commun.* **5**, 53.

Knoll, K., Schrock, R.R. (1989) *J. Am. Chem. Soc.* **111**, 7989.

Kuwabara, Y., Ogawa, H., Inada, H., Noma, N., Shirota, Y. (1994) *Adv. Mater.* **6**, 677.

Lee, K.I., Jopson, H. (1983) *Polym. Bull.* **10**, 105.

Leung, L.M., Tan, K.H. (1994) *Polymer* **35**, 1556.

Lin, T., He, Q., Bai, F., Dai, L. (2000) *Thin Solid Films* **363**, 122.

Litt, M.H., Summers, J.W. (1973) *J. Polym. Sci. Polym. Chem. Ed.* **11**, 1339.

Luttinger, L.B. (1962) *J. Org. Chem.* **27**, 1591.

MacDiarmid, A.G., Epstein, A.J. (1994) *Synth. Met.* **65**, 103.

MacDiarmid, A.G., Epstein, A.J. (1995) *Synth. Met.* **69**, 85.

MacFarlane, D.R., Huang, J., Forsyth, M. (1999) *Nature* **402**, 792.

Meier, H., Lehmann, M., Kolb, U. (2000) *Chem. Eur. J.* **6**, 2462.

Mikrajuddin, A., Shi, F.G., Okuyama, K. (2000) *J. Electrochem. Soc.* **147**, 3157.

Morgenroth, F., Reuther, E., Müllen, K. (1997) *Angew. Chem., Int. Ed.* **36**, 631.

Müller, M., Morgenroth, F., Scherf, U., Soczka-Guth, T., Klärner, G., Müllen, K. (1997) *Phil. Trans. R. Soc. Lond. A* **355**, 715.

Olabisi, O. (ed.) (1977) *Handbook of Thermoplastics*. Marcel Dekker, New York.

Pan, Y.X., Yu, Z.Z., Qu, Y.C., Hu, G.H. (2000) *J. Polym. Sci., Polym. Phys.* **38**, 1626.

Patil, A.O., Ikenoue, Y., Wudl, F., Heeger, A.J. (1987) *J. Am. Chem. Soc.* **109**, 1858.

Reghu, M.; Yoon, C.O.; Yang, C.Y.; Moses, D.; Heeger, A.J.; Cao, Y. (1993) *Macromolecules* **26**, 7245, and references cited therein.

Reibel, D., Nuffer, R., Mathis, C. (1992) *Macromolecules* **25**,7090.

Rivera, N.M., Engler, E.M., Schumaker, R.R. (1979) *J. Chem. Soc., Chem. Commun.* 184.

Roldughin, V.I., Vysotskii, V.V. (2000) *Prog. Org. Coat.* **39**, 81.

Rothman, T. (1988) *Sci. Am.* **August**, 12;

Rubner, M.F., Tripathy, S.K., Georger, J., Jr., Cholewa, P. (1983) *Macromolecules* **16**, 870.

Sariciftci, N.S. (1995) *Prog. Quant. Electr,* **19**, 131, and references cited therein.

Schlebusch, C., Kessler, B., Cramm, S., Eberhardt, W. (1996) *Synth. Met.* **77**, 151.

Schön, J.H., Dodabalapur, A., Bao, Z., Kloc, Ch., Schenker, O., Batlogg, B. (2001) *Nature* **410**, 189.

Schrock, R.R. (1990) *Acc. Chem. Res.* **23**, 158.

Sentein, C., Mouanda, B., Rosi1io, A., Rosi1io, C. (1996) *Synth. Met.* **83**, 27.

Shirakawa, H. (2001) *Angew. Chem. Int. Ed.* **40**, 2574.

Sichel, E.K., Rubner, M.F. (1985) *J. Polym. Sci., Polym. Phys.* **23**, 1629.

Skotheim, T.A., Elsenbaumer, R.L., Reynolds, J.R. (eds) (1998) *Handbook of Conducting Polymers*, Marcel Dekker, New York.

Stauffer, D. (1985) *Introduction to Percolation Theory*, Taylor & Francis, Philadelphia.

Summers, J.W., Litt, M.H. (1973) *J. Polym. Sci. Polym. Chem.* **11**, 1379.

Suzuki, Y.Y., Heeger, A.J., Pincus, P. (1990) *Macromolecules* **23**, 4730.

Swager, T.M., Dougherty, D.A., Grubbs, R. H. (1988) *J. Am. Chem. Soc.* **110**, 2973.

Tamao, K., Kodama, S., Nakajima, I., Kumada, M., Minato, A., Suzuki, S. (1982) *Tetrahedron* **38**, 3347.

Tamura, H., Watanabe, T., Imanishi, K., Sawada, M. (1999) *Synth. Met.* **107**, 19.

Thakur, M. (1988) *Macromolecules* **21**,661.

Tinkham, M. (1975) *Introduction to Superconductivity*, McGraw-Hill, New York.

Tomalia, D.A., Durst, H.D. (1993) *Top. Curr. Chem.* **165***, 193.

Tour, J.M. (1994) *Adv. Mater.* **6**, 190.

Vashishta, P., Mundy, J.N., Shenoy, G.K. (eds) (1979) *Fast Ion Transport in Solids*, North-Holland, Amsterdam.

Wang, Y. (1992) *Nature* **356**, 585.

Wang, F., Rauh, R.D., Rose, T.L. (1997) *J. Am. Chem. Soc.* **119***, 11106.

Wessling, B., Volk, H. (1986) *Synth. Met.* **15**, 183.

Wessling, R.A., Zimmerman, R.G. (1968) U.S. Patent 3401152.

Wessling, R.A., Zimmerman, R.G. (1972) U.S. Patent 3406677.

Winkler, B., Dai, L., Mau, A.W.H. (1999) *Chem. Mater.* **11**, 704.

Winkler, B., Mau, A.W.H., Dai, L. (2000) *Phys. Chem. Chem. Phys.* **2**, 291.

Wright, P.V. (1975) *Br. Polym. J.* **7**, 319.

Wu, S. (1985) *Polymer* **26**, 1855.

Wu, S. (1988) *J. Appl. Polym. Sci.* **35**, 549.

Xia, Y., Wiesinger, J.M., MacDiarmid, A.G., Epstein, A.J. (1995) *Chem. Mater.* **7**, 443.

Xu, Z., Moore, J.S. (1993) *Angew. Chem., Int. Ed.* **32**, 1354.

Yang, Z., Hu, B., Karasz, F.E. (1998) *J. Macromol. Sci., Pure Appl. Chem.* **A35***, 233, and references cited therein.

Yang, Z., Karasz, F.E., Geise, H.J. (1994) *Polymer* **35**, 391.

Yoshino, K., Hirohata, M., Hidayat, R., Tada, K., Sada, T., Teraguchi, M., Masuda, Frolov, S.V., Shkunov, M., Vardeny, Z.V., Hamaguchi, M. (1997) *Synth. Met.* **91***, 283.

Yu, G., Pakbaz, K., Heeger, A.J. (1994) *Appl. Phys. Lett.* **64**, 3422.

Zakhidov, A.A. (1991) *Synth. Met.* **41**, 3393.

Zhong, X.F., Francois, B. (1991) *Makromol. Chem.* **192***, 2277.