Chem. Rev. **1992**, *92*, 711–738

Conjugated Poly(thiophenes): Synthesis, Functionalization, and Applications

JEAN RONCALI

Laboratoire des Matériaux Moléculaires, CNRS, ER 241, 2 rue Henry Dunant, 94320 Thiais, France

Received November 18, 1991 (Revised Manuscript Received March 10, 1992)

Contents

I. Introduction

The last few decades have been marked by the growing importance taken by two classes of materials, organic polymers and inorganic semiconductors. Thus the lightness of weight, processability, and resistance against corrosion of organic polymers have led in many applications to the replacement of metals or to the creation of original materials. On the other hand, it is almost superfluous to mention the considerable impact of inorganic semiconductors on both everyday life and on the development of many fields of modern science and technology. In such a context, it is not very surprising that materials capable of simultaneously presenting the properties of organic polymers and of semiconductors rapidly become a subject of considerable interest for both academic and industrial researchers in domains as different as chemistry, solid-state physics, and electrochemistry.

As a matter of fact and although their structure and physicochemical properties still pose a number of fundamental problems, conducting polymers (CPs) are at present intensively studied in view of their multiple potential technological applications extending from bulk utilizations such as antistatic coatings to sophisticated

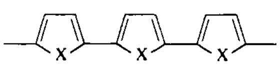
Jean Roncali was born in Paris in 1949. After technical school, he worked several years as organic chemist in industrial companies. He received his B.Sc. from Conservatoire National des Arts et Metiers and his Ph.D. degree from the University of Villetaneuse. In 1980, he joined the laboratory of Solar Photochemistry of CNRS as a research engineer and worked for 4 years on sensitization of semiconductors to solar energy by luminescence processes. In 1984, he started to work on conducting polymers in the laboratory of Molecular Materials of CNRS. His most significant results are the synthesis of highly conducting poly(thiophenes) and of hybrid conducting materials and, together with R. Garreau and M. Lemaire from the Conservatoire National des Arts et Metiers, the development of several types of functional conducting polymers. Presently Chargé de Recherche at the Laboratory of Molecular Materials of CNRS, he continues a strong interest on functional conducting polymers in view of electrochemical and electronic applications. His research interests are energy conversion, synthesis and characterization of organic conductors, modified electrodes, and molecular electronics.

molecular devices such as organic electronic components or selective modified electrodes and sensors.

The modern era of CPs began at the end of the 1970s when Heeger and MacDiarmid discovered that polyacetylene, ($(CH)_x$), synthesized by Shirakawa's method,[1] could undergo a 12 order of magnitude increase of conductivity upon charge-transfer oxidative doping.[2] The essential structural characteristic of CPs is their conjugated π system extending over a large number of recurrent monomer units. This characteristic feature results in low-dimensional materials with a high anisotropy of conductivity which is higher along the chain direction. $(CH)_x$ is the simplest model of this class of materials and despite its environmental instability which constitutes a major obstacle to practical applications, $(CH)_x$ remains the archetype of CPs and is still subject to much theoretical and experimental work.[3]

Poly(heterocycles) (2) can be viewed as an sp^2p_x carbon chain in which the structure analogous to that of cis$(CH)_x$ (1) is stabilized by the heteroatom. These CPs differ from $(CH)_x$ by (i) their nondegenerate ground state related to the nonenergetic equivalence of their two limiting mesomeric forms, aromatic and quinoid, (ii) their higher environmental stability, and (iii) their structural versatility which allows the modulation of their electronic and electrochemical properties by manipulation of the monomer structure.


(1)



(2)

An important step in the development of conjugated poly(heterocycles) occurred in 1979 when it was shown that highly conducting and homogeneous free standing films of poly(pyrrole) could be produced by oxidative electropolymerization of pyrrole.[4] The electrochemical synthesis of poly(pyrrole) from aqueous H_2SO_4 solutions had been initially reported 10 years before but the poor mechanical and electrical properties of the obtained material did not give rise to further developments.[5]

The electrochemical polymerization has been rapidly extended to other aromatic compounds such as thiophene,[6,7] furan, indole,[7] carbazole, azulene, pyrene,[8] benzene,[9] and fluorene.[10] These pioneering works have also triggered a renewal of interest for electrogenerated poly(aniline).[11-13]

Among these numerous CPs, poly(thiophene) (PT) has rapidly become the subject of considerable interest. From a theoretical viewpoint, PT has been often considered as a model for the study of charge transport in CPs with a nondegenerate ground state, while on the other hand, the high environmental stability of both its doped and undoped states together with its structural versatility have led to multiple developments aimed at applications such as conductors, electrode materials, and organic semiconductors.

PTs have been already considered in several reviews devoted to CPs in general or to some of their more specific aspects such as electropolymerization,[14-16] electrochemistry,[17,18] environmental stability,[19] or optical properties.[20] However, until now, the only review specifically focused on PTs was published in 1986 and covered the early developments of the field up to 1985.[21] However, the considerable progress accomplished in their preparation and in the characterization of their structure and electronic and electrochemical properties since this period and the fact that the essential part of the work on functional PTs has been published during the last five years outline the need for a more up to date review of this class of CPs.

II. Synthesis of Poly(thiophenes)

Although the obtention of polymeric materials from thiophene derivatives has been known for long,[22] the origin of the intensive research efforts aiming the optimization of the preparation of PTs is in keeping with the emergence of the widespread general interest for CPs in the early 1980s. PTs are essentially prepared by means of two main routes, i.e. the chemical and the electrochemical syntheses.

A. Chemical Synthesis

Thiophene oligomers have been prepared by several methods and some of them have been proposed as generalizable to the preparation of polymers. Thus, mixtures of several thiophene oligomers have been obtained by reaction of 2-iodothiophene with copper bronze.[23] Trithiophene has been prepared by cyclization of 1,4-diketones containing one or more thiophene rings.[24,25] Quater- and sexithiophene have been synthesized by coupling of α-lithiated thiophenes in presence of cupric chloride or organoboranes.[26,27] The synthesis of PT by oxidative coupling of bis-lithiated thiophene derivatives has been also reported.[28] Grignard coupling of 2,5-dihalothiophenes in presence of transition metal complexes has been extensively employed for the synthesis of PTs. Polycondensation of 2,5-dibromothiophene using respectively 2,2′-bipyridinenickel dichloride and nickel acetylacetonate as catalyst was reported almost simultaneously in 1981 by two research groups.[29,30] The polymers were obtained as powders containing 20–30% of oligomeric material soluble in chloroform. The insoluble parts yielded after doping, conductivities of 5×10^{-2} and 4×10^{-1} S cm^{-1} for PT and poly(methyl-3-thiophene) (PMeT), respectively.[31] A conductivity of 14 S cm^{-1} has been reported for PT prepared by nickel-catalyzed Grignard coupling of 2,5-diiodothiophene.[32] More recently thiophene and 3-methylthiophene oligomers have been synthesized by $NiCl_2$(dppp) (dppp = $Ph_2PCH_2CH_2CH_2PPh_2$) coupling of Grignard compounds with the appropriate bromothiophene.[33] PT has been also prepared by plasma polymerization[34] and by oxidative polymerization of thiophene and bithiophene in the gas phase using AsF_5 under pressure.[35] The highest conductivity of 2×10^{-2} S cm^{-1} was obtained using thiophene as starting material. More recently, oxidative polymerization in liquid phase, initially proposed for the preparation of poly(pyrrole),[36] has been extended to PTs.[37-39]

B. Electrochemical Synthesis

Although it is likely that chemical syntheses are the most adequate methods of preparation of oligomers of defined structure, until now, the most extensively conjugated and most conductive PTs have been prepared by electrochemical polymerization.

1. Cathodic Route

Besides the oxidative anodic electropolymerization of the monomer which is the most convenient and most widely used method, PT can be also prepared by a cathodic route involving the electroreduction of the complex (2-bromo-5-thienyl)triphenylnickel bromide in acetonitrile. This method initially proposed for the synthesis of poly(*p*-phenylene),[40] has been extended to PT.[41] The major drawback of this method is that the polymer is produced in its neutral insulating form which leads rapidly to a passivation of the electrode and limits attainable film thickness to ca. 100 nm. On the other hand, this technique presents the advantage to be applicable to electrode materials subject to anodic corrosion such as small band gap semiconductors.[42]

2. Anodic Route

Compared to other chemical and electrochemical syntheses of conducting poly(heterocycles), the anodic electropolymerization of the monomer presents several distinct advantages such as absence of catalyst, direct grafting of the doped conducting polymer onto the electrode surface (which is of particular interest for electrochemical applications), easy control of the film thickness by the deposition charge, and possibility to perform a first in situ characterization of the growing process or of the polymer by electrochemical and/or spectroscopic techniques.

The electropolymerization of bithiophene was initially mentioned in 1980,[6] whereas the first report of the electropolymerization of thiophene appeared two years latter.[7] Following these initial works, a large number of studies have been devoted to the analysis of the electropolymerization reaction and to the optimization of electrosynthesis conditions.

3. Mechanisms of Electropolymerization

The electrochemical formation of conducting polymers is an unique process. Although it presents some similarities with the electrodeposition of metals since it proceeds via a nucleation and phase-growth mechanism,[43-46] the major difference lies in the fact that the charged species precursors of the deposited material must be initially produced by oxidation of the neutral monomer at the anode surface. The consequence of this is that various electrochemical and chemical follow-up reactions are possible, making the elucidation of the electropolymerization mechanism a very complex problem.

Despite the large amount of work devoted to electrogenerated PTs, the mechanism of the electropolymerization of thiophene has been scarcely considered. This situation probably arises from the fact that it is generally admitted that the electropolymerization of aromatic compounds occurs via an unique mechanism which has been more extensively analyzed using pyrrole as a model compound.[14,44,47-50] An important aspect of the electropolymerization reaction is that it proceeds with electrochemical stoichiometry, with *n* values in the range of 2.07–2.5 Faradays/mol.[48] The oxidation of the monomer requires 2 electrons/molecule while the excess of charge corresponds to the reversible oxidation or doping of the polymer. Figure 1 represents the mechanism proposed for the electropolymerization of heterocycles,[49] by analogy to the already known coupling reactions of aromatic compounds.[51,52] The first electrochemical step (E) consists in the oxidation of the monomer to its radical cation. Since the electron-transfer reaction is much faster than the diffusion of the monomer from the bulk solution, it follows that a high concentration of radicals is continuously maintained near the electrode surface. The second step involves the coupling of two radicals to produce a dihydro dimer dication which leads to a dimer after loss of two protons and rearomatization. This rearomatization constitutes the driving force of the chemical step (C). Due to the applied potential, the dimer, which is more easily oxidized than the monomer, occurs in its radical form and undergoes a further coupling with a monomeric radical. Electropolymerization proceeds then through successive electrochemical and chemical steps according to a general E(CE)$_n$ scheme, until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the electrode surface.

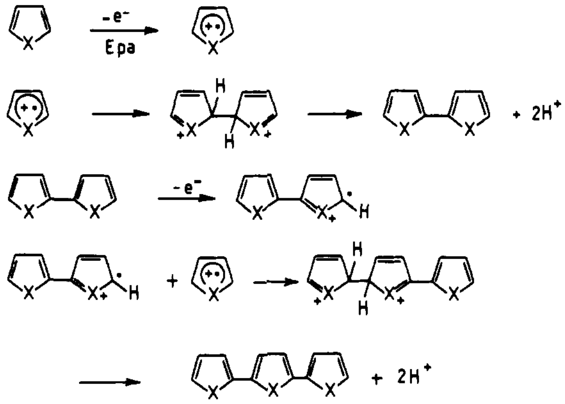


Figure 1. Mechanism of electropolymerization of five-membered heterocycles.

This mechanism leaves however several questions in abeyance concerning the nature of the rate-limiting step, the exact role of oligomers in the initial deposition step, and the subsequent growth of the polymer chains, respectively. What is firmly established is the oxidation of the monomer to its radical cation and the fact that the electropolymerization process is not diffusion-limited. Thus a first characterization of the monomeric radicals by ultrafast cyclic voltammetry has been recently reported.[53] On the other hand, chronoabsorptometric experiments have shown that during the electrodeposition of poly(pyrrole), the absorbance increases linearly with time t and not with $t^{1/2}$.[49] According to the authors, this result implies that electropolymerization is not diffusion-limited and that the rate-determining step is the radical-coupling process. A similar behavior has been observed for the electrodeposition of PMeT even in viscous electrolytic media or under high anodic potentials.[54] The initial deposition step and the process of propagation of the electropolymerization are less clearly understood and still a matter of controversy. Thus an alternative mechanism involving a radical attack on a neutral monomer has been proposed.[44,50] The radical-coupling mechanism is supported by the lack of polymerization when the applied potential is adjusted to a value sufficient to oxidize the polymer but not the monomer. However, concerning the radical–monomer mechanism, it has been stressed that the potential required by the second oxidation step might be higher than the oxidation potential of the polymer itself.[17]

In the case of the electropolymerization of pyrrole in the presence of BF_4^- it has been suggested that the polymerization process is initiated by the oxidation of the anion.[55] However, this hypothesis appears unacceptable since the oxidation of BF_4^- occurs only at a potential ca. 2 V more positive than the potential where poly(pyrrole) is formed. On the basis of theoretical calculations, the deprotonation has been proposed as the rate-limiting step in the electropolymerization of thiophenes.[56] This hypothesis is however contradicted by the absence of isotopic effect[57] on the electropolymerization rate of [2,5-$^2H_2$]thiophene and [$^2H_4$]-thiophene.[58,59]

The exact role of oligomers in both the initial steps and the propagation of the electropolymerization has been also a point of debate. On the basis of the delay observed between the rise of the current and the onset of ellipsometric signals, it has been concluded that the formation of oligomers in solution precedes the polymer deposition.[60,61] The growth of PT and poly(bithiophene) has been analyzed by time-resolved UV–vis spectroscopy. The comparison of the solution spectra with those of authentic neutral thiophene oligomers has led to the conclusion that oligomers involving ca. 7 and 12 monomer units were present in solution.[62,63] However, taking into account for the applied potential and for the high stability of oligomeric radical cations, which increases strongly with their size,[14,48] it seems likely that the observed spectra correspond to oxidized species (radical cation or dication) and hence to chain lengths considerably shorter than the assumed ones. In fact, oxidized soluble oligomers have been recently detected by rotating ring–disk experiments.[64]

The adsorption of thiophene on the electrode surface has been proposed as the first step by several groups and evidence for adsorption has been obtained by in situ IR spectroscopy.[44,65] These observations appear difficult to reconcile with the hypothesis of the formation of oligomers in solution. As a matter of fact, it is not easy to imagine why, once adsorbed, the monomer leaves the electrode surface to form oligomers in solution which reprecipitate onto the electrode. On the other hand, monomer adsorption appears consistent with NEXAFS experiments which indicate that the first polymer layer lies essentially flat on the electrode surface and that the polymeric chains are well ordered up to a thickness of 50 Å.[66] These observations are in agreement with the electronic absorption spectra recorded at various stages of the electropolymerization which reveal a steady decrease of the mean conjugation length and of the resolution of the vibronic fine structure with the progress of the electropolymerization.[67,68]

Perhaps the major argument against oligomer formation as the main reaction pathway toward the polymer is provided by the considerable deterioration of the mechanical, electrical, electrochemical, and optical properties of the polymer observed when oligomers are used as the substrate for electropolymerization instead of the monomer.[69] As discussed below, if oligomers formation was actually a necessary step between the monomer and the polymer, the same polymer should be obtained with both types of precursor. Thus, although oligomers have been detected in the synthesis medium,[61–64] or extracted from as-grown PT films,[70] these results do not constitute an unequivocal proof that the electropolymerization proceeds via oligomers formation since the observed oligomers may well result from side reactions competitive to the growth of the polymer chains.

In short, although these various investigations have contributed to elucidate some aspects of the electropolymerization mechanism, several steps of the process are not fully understood yet and are still subject to controversial interpretations.

4. Effects of Electrosynthesis Conditions

The electropolymerization of five-membered heterocycles involves many experimental variables such as the solvent, concentration of reagents, temperature, cell geometry, nature and shape of the electrodes, and applied electrical conditions. As a consequence of the diversity of these parameters and of the complexity of the electropolymerization pathways, electrosynthesis conditions determine to a large extent the structure and properties of the resulting polymer. However, due to the interdependence of many of the experimental variables, the analysis of the effects of an individual parameter and hence the optimization of electrosynthesis conditions constitute a complex problem.

The solvent of the electrolytic medium exerts a strong effect on the structure and properties of PT films. As a matter of fact, the solvent must simultaneously present a high dielectric constant to ensure the ionic conductivity of the electrolytic medium and a good electrochemical resistance against decomposition at the high potentials required to oxidize the thiophene ring ($\simeq$1.4–2.3 V/SCE depending on substitution). Although the electropolymerization of 3-methylthiophene in aqueous medium has been reported, the obtained material has not been characterized in detail.[71] In contrast, several works have shown that the presence of traces of water in the synthesis medium has deleterious consequences for the electropolymerization reaction[45,62] and for the conjugation length and conductivity of the polymer.[59] Thus it has been shown that the presence of water in the synthesis medium results in the incorporation of carbonyl groups in the polymer.[72]

The most conductive PTs obtained until now have been prepared in rigorously anhydrous aprotic solvents of high dielectric constant and low nucleophilicity such as acetonitrile,[6,7,73,74] benzonitrile,[75] nitrobenzene,[70,76–78] and propylene carbonate.[79,80] These solvents lead also to the highest current efficiency of electropolymerization.[81]

Acetonitrile leads generally to powdery deposits or to brittle films with conductivities typically comprised between 0.02 and 10 S cm^{-1} for PT and 0.1 and 50 S cm^{-1} for PMeT.[7,73,74] As shown by the main literature data on electrogenerated PT and PMeT (Table I), benzonitrile, nitrobenzene, or propylene carbonate allow the obtention of compact free-standing films with conductivities exceeding 100 S cm^{-1}.[67–70,75–80] PTs are generally electrogenerated in the presence of small anions derived from strong acids such as ClO_4^-, PF_6^-, BF_4^-, and AsF_6^-, associated with lithium or tetraalkylammonium cations.[7,67–70,73–80] HSO_4^- and SO_4^{2-} lead to poorly conducting materials.[74,76] The nature of the anion strongly affects the morphology[82,83] and electrochemical properties[84] of PTs prepared in acetonitrile. A partial crystallinity has been observed in PMeT grown in acetonitrile with $CF_3SO_3^-$.[85,86] Unlike pyrrole, the electropolymerization of thiophene in the presence

TABLE I. Electropolymerization of Thiophene (T) and 3-Methylthiophene (MeT)[a]

[monomer] (M)	solvent	electrolyte	T (°C)	electrical conditions	σ (S cm^{-1})	ref
T						
0.01	MeCN	Bu_4NClO_4	rt	1.6 V/SCE	10–100^{c}	7
0.01	MeCN	Et_4NBF_4	rt	1.9 V/SCE	0.02	74
0.4	PhCN	$LiBF_4$	rt	10 mA cm^{-2}	106	75
0.4	PhCN	$NaAsF_6$	rt	20 mA cm^{-2}	97	75
0.2	$PhNO_2$	Bu_4NClO_4	5	2 mA cm^{-2}	10	76
0.2	$PhNO_2$	Bu_4NClO_4	5	2 mA cm^{-2}	36	78
0.3	$PhNO_2$	Bu_4NClO_4	5	3 mA cm^{-2}	40	97
0.2	PC	Et_4NPF_6	5	10 mA cm^{-2}	270	79
0.1	$PhNO_2$	Bu_4NPF_6	rt	2 mA cm^{-2}	370	93
MeT						
0.01	MeCN	Et_4NPF_6	rt	1.7 V/SCE	1	74
–	MeCN	$Bu_4NSO_3CF_3$	rt	1.5 V/SCE	30–100^{c}	73
0.2	$PhNO_2$	Bu_4NClO_4	5	2 mA cm^{-2}	120	77
0.2	PC	Et_4NPF_6	5	10 mA cm^{-2}	510	79
0.1–0.4	$PhNO_2$	Bu_4NClO_4	5	2 mA cm^{-2}	750	94
0.1	$PhNO_2$	Bu_4NClO_4	5	2 mA cm^{-2}	450	70
0.2	$PhNO_2$	Bu_4NPF_6	rt	20^{p} mA cm^{-2}	740	93
0.05	$PhNO_2$	Bu_4NPF_6	rt	(3.2^{ip}), 0.25	600	92
0.05	$PhNO_2$	Bu_4NPF_6	rt	1.5 mA cm^{-2}	1975	67, 68

[a] MeCN: acetonitrile. PhCN: benzonitrile. $PhNO_2$: nitrobenzene. PC: propylene carbonate. rt: room temperature. n^{c}: compacted pellet. n^{p}: 0.5-s pulses. n^{ip}: one 0.2-s initial pulse.

of electrolytes containing aromatic anions such as halo- or alkylbenzenesulfonates or naphthalenesulfonates yields no or little polymer of low doping level and conductivity.[86,87] The temperature of electropolymerization has been reported to affect the extent of the conjugated system and hence the optical and electrical properties of the polymer, the films produced at 40 °C having a shorter mean conjugation length than those prepared at 5 °C.[70,77-80,68]

The anode material is a critical consideration since the physicochemical properties of its surface determine the nature and the strength of the bond between the polymer and the electrode, which can affect both the polymerization process and the properties of the resulting polymer. PTs are generally grown on noble metals such as platinum[7,54,60,68-70,74] and gold[46] or on optically transparent electrodes such as tin oxide or indium–tin oxide (ITO) coated glass.[54,59,69,75-80] However, PTs have been also deposited on other surfaces such as titanium[89] or iron.[90,91] Until now, the most conductive polymers have been obtained on bulk platinum, presumably because thiophene adsorbs more efficiently on platinum and also because platinum presents a larger number of potentially active sites thus leading to a high density of initial nucleation sites and to more compact materials.[67,68,92,93] The differences observed in the optical spectra of PMeT films electrodeposited in the same conditions on SnO_2 and ITO electrodes of different surface resistivities confirm the marked influence of the anode properties on the polymer structure.[68]

The applied electrical conditions exert considerable effects on the structure and properties of electrogenerated PTs. PTs have been deposited in potentiostatic[6,7,73,74] or galvanostatic[67-70,75-80,83,92-94] conditions and by recurrent potential sweeps[95,96] or current pulses.[92,93] Although, from a thermodynamical viewpoint it is likely that the applied potential is the relevant electrical parameter, the most homogeneous and conducting films are generally obtained in galvanostatic conditions,[67,68,70,79,92-94] at potentials ca. 0.5 V more positive than the oxidation potential of the monomer. The role of this overpotential is not fully elucidated; however, it has been shown that highly conducting films can be obtained at the potential corresponding to the onset of electropolymerization provided that the electropolymerization is initiated by a short pulse at high potential.[92,93] This result indicates that an initial overpotential allows the instantaneous creation of a larger number of initial nucleation sites, which contributes to improve the compactness and thus conductivity of the polymer. Besides their effects on the electrical, optical, and electrochemical properties of the films, electrical conditions have been shown to affect the orientation of the polymer chains and the mechanical properties of PTs.[97,98]

During the last few years, the optimization of the electrosynthesis of PTs has been the subject of several studies[68,70,80,94] and owing to its better stereoregularity and conductivity,[73] PMeT has been often used as model compound. Although, these works have led to significant improvements of the conductivity (Table I), this progress has been essentially accomplished by empirical approaches, and the relationships between the electrosynthesis conditions, the polymerization mechanism, and the structure and properties of the polymer have been scarcely considered. It has been shown that under constant electrical conditions (2 mA cm^{-2}), high monomer concentrations (0.5–1 M) produce loose, poorly conducting, films containing significant amounts of soluble oligomers.[70,101] The decrease of monomer concentration improves both the cohesion of the films and their conductivity which reaches values in the range of 500 S cm^{-1} for 0.1 M monomer.[70,101] Conversely, for a given monomer concentration, it is possible to define the electrical conditions leading to the polymer of optimal conjugation length and conductivity (Figure 2).[68] The decrease of conductivity observed beyond the optimal current density is probably related to the fact that PTs are unstable at the potentials required for their formation.[84] An important consequence of this so-called "polythiophene paradox"[99] is that the degradation of the polymer may compete with its electrodeposition, especially at highly anodic potentials or when the monomer concentration in the medium becomes too low to sustain the rate of polymer deposition imposed by

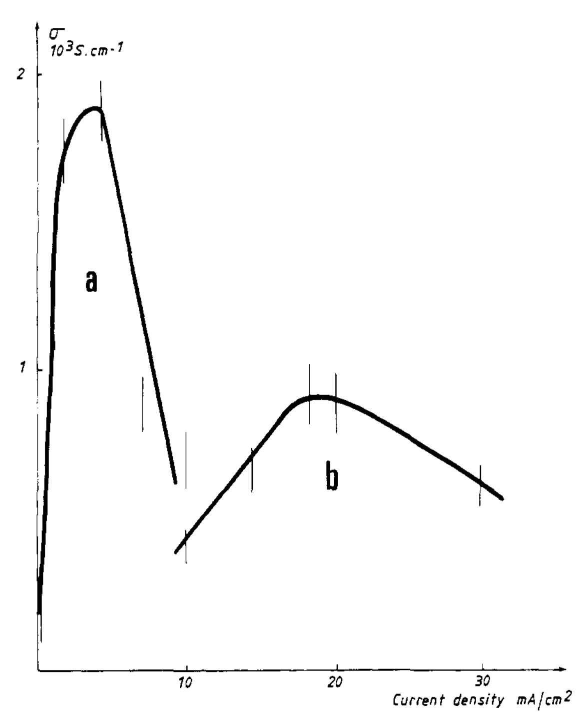


Figure 2. Effect of electrosynthesis current density on the conductivity of 200-nm-thick PMeT films prepared with (a) 0.1 M monomer on bulk Pt and (b) 0.2 M monomer on ITO.

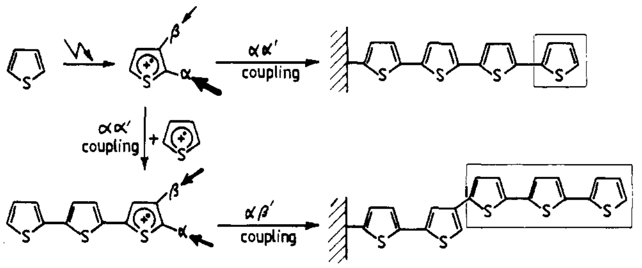


Figure 3. Competitive reactions pathways in the electropolymerization of thiophene.

the applied electrical conditions.[100]

The electrochemical and optical properties of films obtained with various monomer concentrations and electrical conditions show that the increase of the conductivity is correlated to a decrease of the oxidation potential and to a bathochromic shift of the absorption maximum, changes that are indicative of an extension of conjugation. These results have been interpreted on the basis of a reaction scheme involving two competitive pathways, the growth of polymer chains on the anode surface and the parallel formation of soluble oligomers (Figure 3), this latter process being favored when the ratio current density/monomer concentration is lower than its optimal value.[68,70,101] The occurrence of oligomers in the electrolytic medium has two main consequences. First, their limited solubility and low reactivity allow their insertion in the polymer without chemical coupling,[69,70] thus reducing the cohesion and conductivity of the material. Second, the relative reactivity of the α and β positions, which is about 95/5 in the case of the monomer,[102] decreases with the length of the oligomer,[14,48] leading thus to a statistical increase of the number of α–β' couplings and hence to a decrease of the mean conjugation length in the polymer.

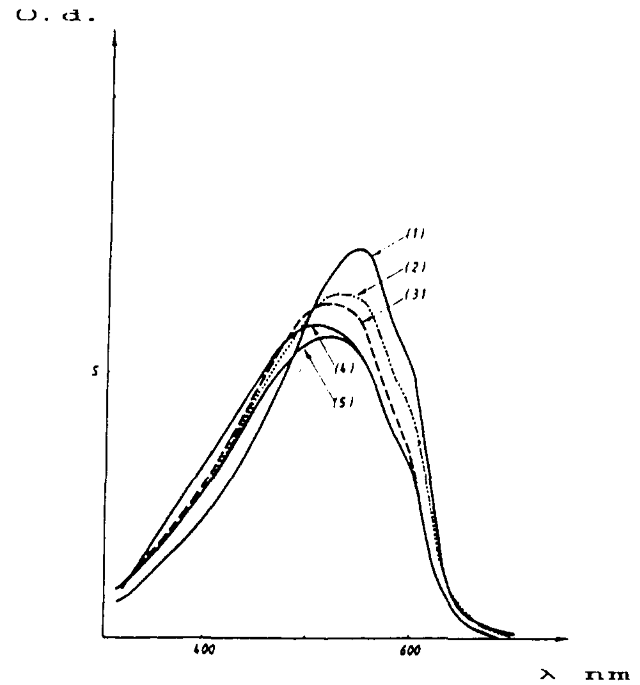


Figure 4. Effect of thickness (d) on the electronic absorption spectrum of undoped PMeT films on ITO: (1) d = 6 nm, S = 0.05; (2) d = 20 nm, S = 0.25; (3) d = 50 nm, S = 0.5; (4) d = 104 nm, S = 1; (5) d = 190 nm, S = 2.

The mean effective conjugation length along the polymer chains is determined by two parameters: the stereoregularity of the polymer, i.e. the ratio of α–β'/α–α' linkages, and the planarity of the conjugated π system. Although of different origin, these two factors are not independent. As a matter of fact, the occurrence of an α–β' linkage in a given chain modifies its electronic distribution which in turn can promote the formation of branching on sites rendered energetically more favorable than the polymer chain end. Moreover, the presence of linkage defects in a given chain can generate distortions in adjacent chains and thus modify their electronic distribution which can favor the formation of further linkage errors. It appears thus that the formation of a conjugation defect in the very early steps of electropolymerization has much more dramatic consequences for the overall stereoregularity and stacking order of the polymer chains than the occurrence of the same defect at a later stage of the process. This interpretation appears consistent with the considerable increase of morphological disorder and decrease of conductivity that accompany the progress of the electropolymerization.[88] In contrast, the limitation of the polymer growth to very thin films produces more compact material while the conductivity increases dramatically, reaching values in the range 2000 S cm^{-1} for 200-nm-thick PMeT films prepared in optimal conditions.[67,88,92,93] The analysis of the electrochemical and spectroscopic properties of the films reveals that reducing the film thickness from 200 to 5 nm produces a 100-mV decrease of the oxidation potential and a 40-nm bathochromic shift of the absorption maximum with the emergence of a fine structure in the absorption spectrum (Figure 4). These results confirm that ultrathin films are considerably more ordered and more conjugated which suggests that their conductivity should be much higher than the current experimental limits.[67,68]

TABLE II. Electropolymerization of Bithiophene (BT) and Trithiophene (TT) (NMP = *N*-methylpyrrolidinone)

[monomer] (M)	solvent	electrolyte	electrical conditions	σ (S cm^{-1})	ref
BT					
0.1	MeCN	HSO_4^-	1.17 V/SCE	0.1	74
0.01	MeCN	$LiClO_4$	0.01 mA cm^{-2}	1	109
0.1	$PhNO_2$	Bu_4NClO_4	2.00 mA cm^{-2}	2×10^{-2}	69
0.1	MeCN	Bu_4NPF_6	2.00 mA cm^{-2}	0.6	69
0.1	MeCN	$LiClO_4$	2.00 mA cm^{-2}	2.8	69
TT					
0.002	MeCN	Et_4NBF_4	1 V/SCE	10^{-2}–10^{-3}	112
0.01	MeCN	H_2SO_4	1 mA cm^{-2}	2×10^{-2}	107
0.01	MeCN	Bu_4NBF_4	1 mA cm^{-2}	1.2×10^{-2}	107
0.01	NMP	Bu_4NHSO_4	1 mA cm^{-2}	1×10^{-6}	107
0.066	$PhNO_2$	Bu_4NClO_4	2 mA cm^{-2}	5×10^{-3}	69
0.066	MeCN	$LiClO_4$	2 mA cm^{-2}	2×10^{-2}	69
–	MeCN, PC	Bu_4NBF_4	–	1×10^{-2}	114
0.1	NMP	$LiClO_4$	0.5–3 mA cm^{-2}	20	115

5. *Effects of Monomer Structure*

Besides the analysis of the electropolymerization process, the control of the structure and properties of PTs has been pursued through another strategy which involves the modification of the monomer structure. A first approach consists in the use of thiophene oligomers as substrate for the electropolymerization. Owing to their lower oxidation potential[33,103,104] electropolymerization can be performed under milder conditions,[105,106] and furthermore, since the thiophene rings are exclusively α–α' linked in the starting molecule, one could expect the resulting polymer to contain less α–β' defects than the polymer prepared from the monomer.[74,107,108]

The electropolymerization of thiophene oligomers, and in particular of bithiophene (BT) and trithiophene (TT), has been investigated by several groups.[69,99,104–118] Despite the diversity of the applied electrosynthesis conditions, consistent results have been obtained, showing that the resulting polymers differ markedly from that prepared with the monomer. As a matter of fact, these materials are generally obtained as powdery deposits with conductivities inferior by several orders of magnitude to that of PT (Table II). Thus, the conductivity of poly(bithiophene) (PBT) reaches at best a few S cm^{-1} while that of poly(terthiophene) (PTT) lies generally in the range of 10^{-2} S cm^{-1},[69,107,112,114] although a value of 20 S cm^{-1} has been recently reported for PTT prepared in 1-methyl-2-pyrrolidinone.[115] A comparative study of the electrochemical and spectroscopic properties of PT, PBT, and PTT, has shown that the increase of the length of the starting molecule leads to an increase of the oxidation potential and to a hypsochromic shift of the absorption maximum of the resulting polymer[69,101] (Figure 5). These results, and those reported more recently by others,[116,117] show that the lower conductivities of PBT and PTT are correlated to a decrease of the average length of the conjugated π system in the polymer. This limited conjugation can be explained by considering the changes in the reactivity of the substrate resulting from the delocalization of the π electrons over the entire molecule. On one hand, the overall reactivity of the substrate decreases or, in other words, the stability of the corresponding radical cation increases, which causes a decrease or even in some cases a complete loss of polymerizability. This conclusion is consistent with the limited electropolymerization of TT,[69,117,118] as shown by the fact that PTT contains large amounts of unreacted TT and of the compound resulting from an unique coupling, e.g. sexithiophene.[69,101] On the other hand and as already discussed, the conjugated structure of oligomers results in a decrease of the relative reactivity of α positions which has deleterious consequences for the stereoselectivity of the polymerization.[14,48]

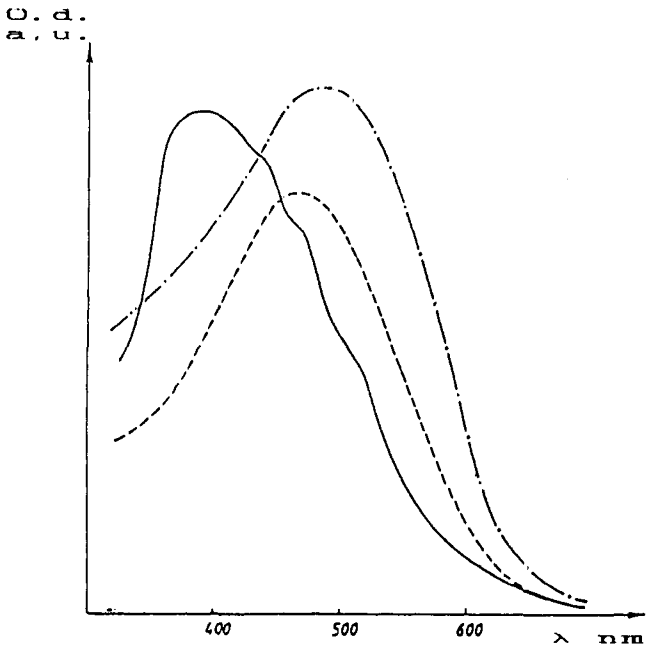
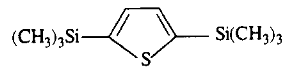


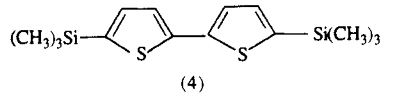
Figure 5. Electronic absorption spectra of neutral polymers on ITO electrodes: Dot-dashed line, PT; dashed line, PBT; solid line, PTT.

More generally, this behavior appears characteristic of the electropolymerization of extensively conjugated molecules. Thus the conductivity of poly(dithienothiophene),[119] poly(dithienylbenzenes),[120,121] and poly(dithienylnaphthalenes)[122] lies typically in the range of 10^{-4} to 10^{-2} S cm^{-1}, values comparable to that of PTT. Similarly, the electropolymerization of dithienylalkenes with 1–4 double bonds between the two thiophene rings[123,124] or that of heteroarylenevinylene compounds involving thiophene and *N*-methylpyrrole[125] leads in the best case to poorly conducting polymers or is even completely inhibited by the high stability of the corresponding radicals.[125,126] Although conductivities up to 15 S cm^{-1} have been obtained on poly(2,2′-bithienyl-5,5′-diylvinylene),[127] this value is still lower than that of the parent polymer poly(thienylenevinylene) prepared by chemical routes.[127,128] In summary, it is now clearly established that the electropolymerization of the monomer and oligomers does not lead to the same polymer and that, contrary to what could be expected,[107,108,112] the use of conjugated precursors for electropolymerization yields finally less conjugated and less conducting polymers. These results lead thus to the conclusion that monomeric structures remain the most appropriate for efficient electrosynthesis of extensively conjugated and highly conducting PTs. Conversely, owing to the simplicity of their structure, thiophene oligomers constitute interesting models for the study of the electronic properties of PT.[129–135] This conclusion has triggered a renewal of interest in the synthesis of these materials[33,108,113–116,136–139] that had been somewhat forsaken for more than 15 years.[140]

An alternative strategy to increase the stereoregularity of electrogenerated PTs consists in the activation of the α positions of the thiophene ring in order to increase their relative reactivity. A first attempt in this direction involved the electropolymerization of 2,5-dilithiothiophene in the presence of $CuCl_2$. The conductivity of the polymer reached 4.8 S cm^{-1} upon doping by AsF_5.[28] A more recent approach consists in the activation of the α–α' positions of the monomer by trimethylsilyl groups (TMS).[141] Although the polymer obtained from 2,5-bis(trimethylsilyl)thiophene (**3**) is rather similar to that obtained from the unactivated monomer, 2,5′-bis(trimethylsilyl)bithiophene (**4**), leads to a significant improvement of the electrochemical and electrical properties.

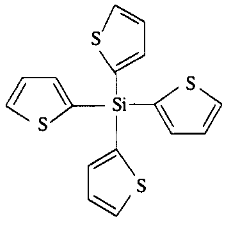


(3)



(4)

Thus, instead of the powdery deposits generally obtained with BT, the electropolymerization of **4** produces flexible, free-standing, films with a conductivity ca. 30 times larger than that of the polymer obtained from unactivated BT, a doping level 50% higher and a voltammetric response identical to that of PT.[141] These comparatively better results have been attributed to two causes: the lower α–α' selectivity of BT and the lower TMS/monomer ratio since it seems likely that the elimination of the bulky TMS group during electropolymerization can affect the morphology of the resulting polymer and hence its electrochemical and electrical properties. On the basis of these conclusions and considering that the activation of only one α position leads also to good results,[141] tetrathienylsilane (**5**), in which the ratio TMS/monomer has been reduced to its minimal value, has been synthesized and used as precursor for the electrosynthesis of PT.



(5)

Whereas it has been reported that no polymer can be formed with thiophene concentrations lower than 2 × 10^{-2} M,[99] the electropolymerization of **5** occurs at very low concentrations (2.5 × 10^{-3} M) and leads to highly conducting PT films with a highly defined electrochemical response and the lowest oxidation potential reported until now[142] (Figure 6).

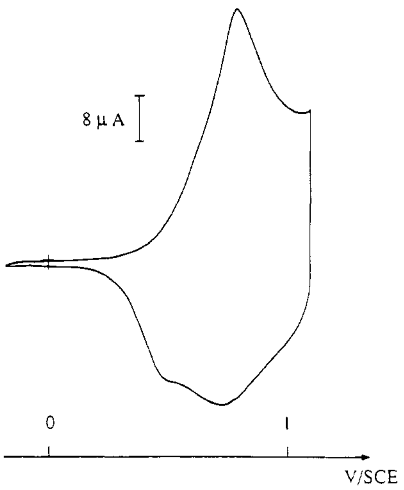


Figure 6. Cyclic voltammogram of PT synthesized from tetrathienylsilane (deposition charge 100 mC cm^{-2} on Pt; electrode area 0.07 cm^2; electrolytic medium 0.1 M $LiClO_4/CH_3CN$; scan rate 20 mV s^{-1}).

III. *Structure and Properties of Poly(thiophenes)*

A. Macromolecular Structure

The extent of the conjugated π system constitutes the essential structural parameter which controls the magnitude of the energy gap, conductivity and electroactivity of CPs.[145] In absence of distortion of the conjugated backbone, the effective mean conjugation length (MCL) of PT is determined by the stereoregularity of the α–α' linkages in the polymer.[144] Owing to the rigidity of their conjugated structure, unsubstituted CPs are generally insoluble and infusible which precludes their characterization by conventional analytical techniques. As a consequence the determination of the MCL of PT constitutes a complex problem which has been essentially approached by means of indirect methods.

IR and ^{13}C NMR spectra of neutral PTs have shown that α–α' linkages predominate in PTs.[31,145,146] Thus the IR spectrum of PT chemically synthesized from 2,5-dibromothiophene shows one sharp δ(C–H) out-of-plane vibration band at 788 cm^{-1}, characteristic of 2,5-substituted thienylene,[31,145,147] whereas the spectrum of the polymer obtained from 2,4-dibromothiophene shows two out-of-plane δ(C–H) vibration bands at 730 and 820 cm^{-1}.[31] On the other hand, XPS and IR data indicate that although PBT is considerably more ordered that poly(pyrrole),[148] electrogenerated PT has nonnegligible α–β' coupling,[73] whereas PMeT has a more regular structure.[149] The presence of a significant amount of α–β' linkages in PT has been confirmed in several works. Thus MCL values ranging from 6 to 12 α–α'-linked thiophene rings have been proposed on the basis of the conductivities of short-chain oligomers or of Raman and IR studies.[129,150,151] The IR spectra of PTs selectively labeled with deuterium at α and/or β positions led to a value of 18 for the MCL with an average degree of polymerization of 150.[59] Furthermore, these various studies have confirmed that the conductivity of PTs is essentially correlated to the MCL.

B. Conformation and Tertiary Structure

Although PTs are essentially amorphous polymers, partial crystallinity has been observed in some cases. Thus 35% crystallinity, increasing up to 56% after annealing at 380 °C has been reported for PT chemically synthesized by Grignard coupling of 2,5-diiodothiophene.[152] Two models of crystalline structure derived from that of poly(p-phenylene) have been pro-

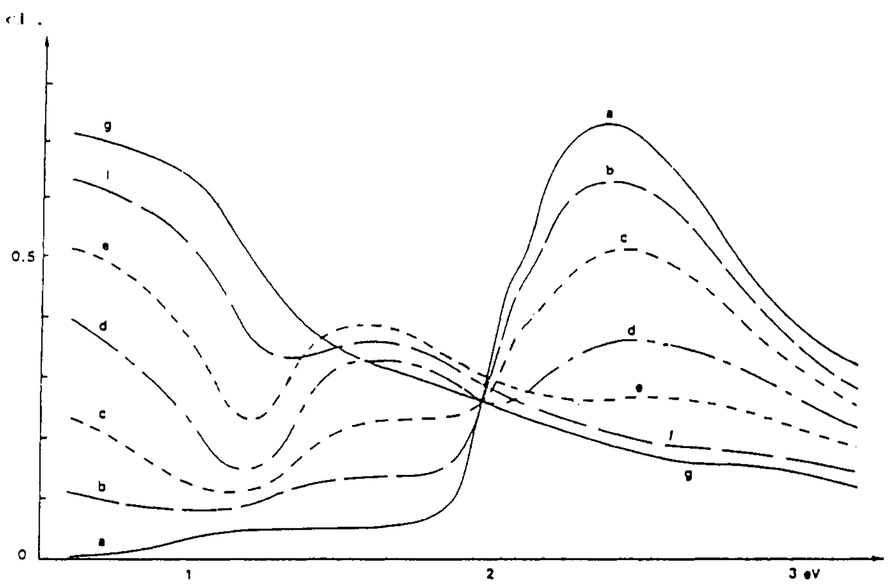


Figure 7. Evolution of the in situ electronic absorption spectrum of PMeT upon electrochemical doping: (a) −0.2 V/Ag; (b) +0.3 V; (c) +0.4 V; (d) +0.5 V; (e) +0.6 V; (f) +0.8 V; (g) +1.1 V.

posed, an orthorhombic unit cell with a = 7.80 Å, b = 5.55 Å, and c = 8.03 Å, and a monoclinic unit cell with a = 7.83 Å, b = 5.55 Å, and c = 8.20 Å and β = 96°. Similar unit cells have been proposed from theoretical studies.[153] It is worth noting that these unit cells imply planar polymer chains with a transoid conformation of the thiophene rings. TEM and X-ray studies have shown that PMeT electrogenerated in the presence of $CF_3SO_3^-$ is partially crystalline. These results have led to the proposal of a helical structure of the polymer chain, this structure implying a cisoidal conformation of the thiophene rings.[85] The existence of such a coil structure has been theoretically reexamined[154] and experimentally confirmed on electrogenerated poly(pyrrole), by scanning tunneling microscopy.[155]

C. Optical and Charge Transport Properties

The identification of the charged species responsible for the conduction mechanism in CPs has attracted much attention. In $(CH)_x$ which has a degenerate ground state, solitons have been shown to be the dominant charge storage species.[156] In contrast, polyaromatic CPs such as poly(pyrrole), poly(p-phenylene), and PT have a nondegenerate ground state and the two limiting mesomeric structures, i.e. aromatic and quinoidal are not energetically equivalent, the quinoidal form having a higher energy.[157] In these polymers, the removal of an electron from the conjugated π system provokes a local distortion of the chain and the appearance of two states in the gap corresponding to a polaron (or radical cation) with spin $^1/_2$. Theoretical calculations have shown that adjacent polarons are unstable and lead to the formation of spinless doubly charged defects e.g. bipolarons (or dications) which have been proposed as the dominant charge storage species.[157-160]

The role played by the heteroatom in the π band structure of poly(heterocycles) has been questioned in several papers. According to some authors, the influence of the heteroatom is negligible[160,161] whereas for others, the dominant effect of the heteroatom is via the direct interaction of its p-orbital lone pair with the carbon backbone π-band structure.[162]

The identification of the nature of the elementary electronic excitation has been subjected to several experimental works.[160,161,163,165-173] In situ absorption spectra of PT recorded at various doping levels show that the interband absorption around 2.5 eV decreases continuously as doping proceeds while two new absorption bands appear at ≃1.5 and 0.5 eV (Figure 7). At the highest doping level, the spectrum presents the characteristics of the free-carrier absorption of the metallic state.[80,160,163,164] On the basis of these optical features, the two subgap absorption bands have been attributed to the occurrence of bipolarons.[160,163] On the other hand, from the analysis of the evolution of the absorption spectrum of PMeT between the neutral state and the lightly doped form (1.3 mol %) it has been concluded that polarons are the primary elementary excitations in the dilute regime.[165] Evidence for transient occurrence of polarons has been also obtained by time-resolved in situ reflection spectroscopy or photoinduced absorption.[166,167]

There is much controversy about the doping level at which the polaron concentration reaches its maximum and the absolute value of spin concentration. Thus upper limit values of 1 × 10^{-3} and 3 × 10^{-3} have been proposed for the spin/charge ratios of PT and PMeT, respectively.[168,169] More recently, a spin/charge ratio close to unity has been reported for doping levels up to 10 mol % and it has been concluded that polarons are the dominant charged species in doped PMeT.[170] EXAFS experiments have revealed an absence of modification of the C–C and C–S bond lengths which should accompany the transition from the aromatic to the quinoidal structure during the formation of bipolarons.[171] This result led the authors to question the bipolaron model and they proposed that charge transport arises from the formation of a metallic state coming from the modification of the electronic structure. The oxidation proceeding through uniform extraction of electrons from the π band and continuous extension of the π and π^* bands to the Fermi level.[171,172]

In summary, although the bipolaron theory has received a large general agreement, the nature of the charged species responsible for the conduction in PTs is still a matter of debate. However, it should be emphasized that the various experimental studies devoted to this question have been carried out on polymers synthesized in very different conditions. Taking into account for the considerable effects of the synthesis conditions on the structure and properties of PTs, the existing controversies may result, for a large part, from differences in the structure of the investigated materials. Thus for instance, polarons and bipolarons differ by the minimal conjugation length required by their spatial extension.[157] Consequently, the same analysis performed on poorly or extensively conjugated polymers may lead to quite different conclusions regarding the nature of the charge storage species.

D. Electrochemical Properties

Owing to the reversibility of the transition between the neutral and the oxidized (p-doped) or reduced (n-doped) states, PTs are highly electroactive materials. However, although PTs are easily and reversibly electrooxidized, the stability of the negatively charged form is rather limited and electrochemical n doping is generally more difficult to achieve. The charging processes, which is achieved by application of an adequate potential to the polymer electrode, involves the simultaneous transport of charges and ionic species in the polymer matrix. The final doped conducting state is characterized by the presence of positive charges associated with charge-compensating anions along the polymer chains.

Since the energy of the HOMO and LUMO are closely related to the reversible half-wave oxidation and reduction potentials corrected by the solvation energies,[174,175] electrochemical techniques can provide important information regarding the magnitude of the energy gap and the extent of the conjugated π system in CPs.[176] However, this type of characterization is not straightforward since, as for others CPs, the electrochemical behavior of PTs depends on many variables such as the film thickness, the nature of the substrate electrode, and the composition of the electrolytic medium. These various parameters control to a large extent the charge propagation and mass transport in the polymer, the solvation of the ionic species and of the different polymer forms, and the Coulombic interactions between charged sites. The analysis of these variables is rendered even more complex by the fact that the number and spatial localization of charged sites, the ohmic (and probably ionic) conductivity and the capacitance vary continuously with the doping level and hence with the electrode potential. Thus whereas theoretical models have been derived to account for the electrochemical behavior of fixed-sites redox polymers,[177,178] the modelization of the electrochemical behavior of CPs remains largely, an open question.

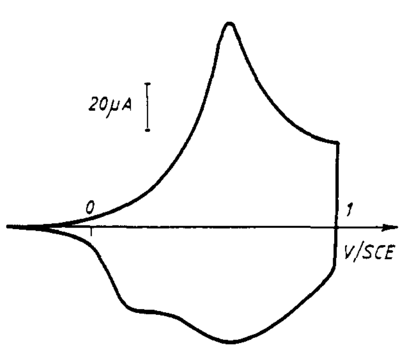


Figure 8. Cyclic voltammogram of PMeT (deposition charge 100 mC cm^{-2} on Pt; electrode area 0.07 cm^2; electrolytic medium 0.1 M $LiClO_4/CH_3CN$; scan rate 50 mV s^{-1}).

Figure 8 shows the cyclic voltammogram of a PMeT film recorded between −0.2 and +1 V/SCE in CH_3CN. Coulometric measurements have shown that the application of potential positive of ca. 1.2 V/SCE results in an irreversible loss of electroactivity while protons can be detected during the reverse scan.[84] Other experiments have shown that this degradation is accompanied by a decrease of the mean conjugation length and of the number of active sites.[179-181] The anodic branch of the CV shows a single anodic peak at 0.6 V assigned to the doping process. This peak appears rather broad with a width at half-height (PWHH) of ca. 230 mV. This value, much larger than the 90 mV expected for a surface reaction with Nernstian behavior,[182,183] has been attributed to interactions among charged sites[184] or to the distribution of the various lengths of conjugated segments in the polymer.[70] This latter interpretation could account for the much narrower PWHH observed on the polymers obtained by electropolymerization of thiophene oligomers.[69,105,117] As appears in Figure 8, the anodic peak is followed by a large residual current plateau. This residual current has been interpreted by a distribution of redox states with increasingly higher energies.[185] However this hypothesis is in contradiction with several theoretical and experimental works that have shown that the current plateau is due to capacitive charging current.[186-191] Thus, derivative cyclic voltabsorptometry experiments performed on various PT derivatives have revealed that electrochemically induced spectral changes are essentially limited to the potential region corresponding to the anodic peak.[192,193] The cathodic branch of the voltammogram, which corresponds to the undoping process, is more complex than the anodic one and exhibits two successive components. The dissymmetry between the doping and the undoping processes has been pointed out in several works and various interpretations have been proposed including: structural relaxation and conformational changes,[194,195] distinct oxidation stages with modification in the interactions among charged sites,[196,197] and differences in the properties of the oxidized and neutral polymer.[198]

The electrochemical behavior of PT derivatives depends strongly on the composition of the electrolytic medium. Although electrochemistry is generally performed in acetonitrile, other solvents have been employed. Due to their hydrophobicity, PTs present only a limited electroactivity in aqueous media.[199-202] Nitrobenzene[203] or propylene carbonate[191] lead to ill-defined voltammetric waves, probably because of their high viscosity which leads to a decrease of the heterogeneous electron-transfer rate.[204] In contrast the voltammetric response recorded in CH_2Cl_2 is very similar to that obtained in CH_3CN.[205] Liquid SO_2, which allows the polymers to be reversibly oxidized to a greater extent than conventional solvents, has been used for the study of the electrode properties of PMeT in rechargeable batteries[206] or for in situ conductivity measurements.[205] In this case, PMeT has been shown to present a finite potential window of high conductivity,[205] whereas the decrease of conductivity at high potential was not observed in other studies performed in CH_3CN.[207]

The electrochemical behavior of PTs depends significantly on the nature of the anion and cation in the electrolytic medium. Early work found significant changes in the shape and position of the voltammetric waves of poly(heterocycles) as a function of the electrolyte that was interpreted by changes in the kinetics of the redox process.[184] Recently, the aggregation of the electrolyte in the presence of crown ether has been shown to give rise to unusual transient current phenomena.[208] Systematic analyses where only the anion was replaced during cyclic voltammetry have shown that the anion affects primarily the electrodeposition process and the polymer structure and that the polymer keeps the memory of the anion used for its synthesis.[84] In contrast, the nature of the cation affects essentially the charge–discharge process.[84] These results and other studies have shown that the discharge of the polymers involves not only anion expulsion, but also the concomitant transient incorporation of cations. The relative magnitude of these two processes depends on the relative mobilities of the two species in the polymer.[209–211] With regard to the large amount of work devoted to the anion doping of PTs, the electrochemical cation doping has only been scarcely considered. This is probably due to the poor stability of reduced PTs, especially in presence of traces of water or oxygen. Electrochemical n doping of PT has been achieved in the presence of tetraalkylammonium cations and a dependence of the doping level on the size of the cation has been observed.[212,213] As discussed below, the polymer structure is a determining factor for the ability to dope n. Thus, in contrast to PT, the electrochemical n doping of PMeT has been observed only at low temperature in CH_3CN or liquid ammonia.[214]

IV. Conducting Composite Materials and Copolymers

Besides the fundamental problems related to the elucidation of their electropolymerization mechanism, structure, and properties, PTs are intensively investigated in view of their multiple potential technological uses. The wide spectrum of these applications implies profound modulations of the form, structure and properties of the polymers in order to meet the specific requirements of each type of envisioned application. The selection of the proper method of modification depends on both the desired property and the level at which the modification will occur, i.e. molecular, macromolecular, or macroscopic. Consequently, the various possible approaches for polymer modification resort to three main strategies, i.e. the derivatization of the monomer structure prior to polymerization, the synthesis of copolymers, and the association of the CP with others materials or chemical entities in order to prepare hybrid materials in which the properties of both components are associated with possible synergic effects.

A. Poly(thiophene)–Polymer Composites

Many potential applications of CPs are still hampered by their poor mechanical properties and insufficient environmental stability. A possible answer to these problems consists in the preparation of composite materials in which CPs are associated with classical insulating polymers of superior mechanical properties. Hybrid materials involving poly(pyrrole) and PVC have been initially prepared by two-step methods involving the dip coating of an electrode by a PVC film followed by the electropolymerization of pyrrole within this solid-state host matrix.[215,216] Several chemical methods involving gas- or liquid-phase polymerization of pyrrole in a host matrix loaded with an oxidant such as $FeCl_3$ have also been described.[217–219] In the case of PTs, the first examples of electrogenerated composites have been prepared by means of a one-step method which consists in the direct electropolymerization of thiophene from an electrolytic medium containing the dissolved host polymer (PMMA, PVC, poly(styrene); Figure 9).[54,200,220] This technique which leads to the simultaneous deposition of the host polymer matrix and of the conducting phase thus allows the rapid obtention of very homogeneous films whose composition, thickness, optical transmission, conductivity, and electrochemical properties can be widely tuned by means of the electrosynthesis conditions. Another advantage is that the ordered structure of the conducting polymer is retained in the composite material, thus allowing the obtention of high conductivities with small concentrations of CP. Thus transparent PVC–PMeT films showing 85% optical transmission and conductivities of 10^{-2} to 10^{-1} S cm^{-1} are obtained with less than 2% PMeT. These materials have been shown to retain the electroactivity of PT[54,200] and furthermore, the incorporation of PT in a polymeric matrix leads to a significant increase of electrochemical cyclability and long-term environmental stability of the conductivity. Other types of PT composites electrogenerated by means of multistep methods have been reported including PBT–polyTHF,[221,222] PT–PVC,[223,224] PT–poly(styrene), PT–poly(bisphenol A carbonate),[225] PT and PMeT–Nafion,[226–229] PMeT–nitrilic rubber,[230] and PBT alloyed with PVC, PVA, and polycarbonate.[231] Following the development of soluble poly(3-alkylthiophenes) (PATs) (see section V.D), conducting composite materials have been produced by the direct mixing of the PAT and the host polymer either in solution[232] or in the molten state.[233] Despite their simplicity, these methods present two main drawbacks. Since the composites are prepared in their insulating form, the obtention of a conductive material requires subsequent doping which poses the problem of the homogeneity of doping, especially with thick

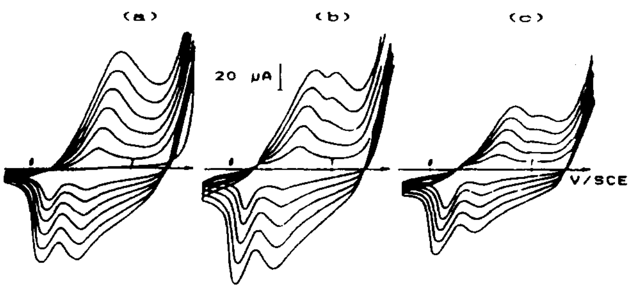


Figure 9. Electrodeposition of PMeT–PVC hybrid films by recurrent potential scans (100 mV s^{-1}): (a) 0.2 M 3-methylthiophene in 1:1 $PhNO_2/CH_2Cl_2$ + 0.1 M Bu_4NClO_4; (b) same as a plus 10 g/L PVC; (c) same as a plus 30 g/L PVC. Electrode area was 0.07 cm^2.

films. Furthermore, substantial conductivity appears only beyond the percolation threshold which lies generally in the range of 10–20%.[232,233]

B. Poly(thiophene)–Metal Composites

A quite different approach consists in using the CP not as active element but as host matrix in which metal particles are incorporated by electrodeposition. PATs electrogenerated in acetonitrile with triflate anions appear particularly interesting for this purpose owing to their fibrillar morphology and large surface-to-volume ratio.[82] Thus PMeT electrodes containing electrodeposited particles of Ag, Pt, or Cu have been reported to exhibit important electrocatalytic activity for proton reduction.[234,235] In the case of the inclusion of Cu^{2+} ions, it has been proposed that the interactions between Cu^{2+} and the sulfur atoms in PMeT chains increase the long-range order in the polymer.[236] An important problem posed by the preparation of such hybrid structures concerns the control of the concentration, size, and distribution of the metal particles in the CP matrix. As a matter of fact, the reduction of metallic salts occurs generally in the cathodic potential region where PTs are in their undoped insulating form. A detailed analysis of the PMeT–Pd system has shown that the application of cathodic potential pulses shorter than the time needed to fully undope the polymer allows the homogeneous incorporation of the Pd particles. Furthermore, their size, concentration, and 3D distribution in the PMeT matrix can be straightforwardly controlled by means of the characteristics of the potential pulses.[237] In addition, the electrocatalytic properties of PMeT–Pd-modified electrodes for O_2 reduction are tightly correlated to the characteristics of the Pd particles.[238] The inclusion of metals or metal ions in PTs has been also achieved by others methods such as, complexation of transition metal ions used for the chemical synthesis of the polymer,[239] or reduction of metal ions (Zn^{2+}) by the photoexcited PMeT.[240]

C. Other Systems

More recently, several new types of organic–inorganic conducting hybrid structures have been developed. In these systems, the in situ intercalative polymerization of a thiophene derivative in host matrixes like FeOCl, zeolites, or xerogels leads to a new class of nanoscale composite structures.[241–244]

D. Copolymers

Copolymerization is another powerful approach of modification of the structure and properties of PTs. The various possible methods of copolymerization differ by the mode of polymerization, i.e. chemical or electrochemical, by the structure of the obtained copolymers, random or block, and also by the conservation or not of a fully π conjugated system in the copolymer backbone. Random copolymers have been prepared by electropolymerization of a mixture of terthienyl and pyrrole.[112] However, this method poses the problem of the distinction of a true copolymer from a composite material involving individual poly(pyrrole) and PTT chains. A thiophene–pyrrole block copolymer showing electrical and electrochemical properties intermediate between those of PT and poly(pyrrole) has been prepared by electropolymerization of 2,2′-thienylpyrrole.[245] Various block copolymers have been prepared by electropolymerization of a basic structure involving two thiophene rings linked by a foreign moiety such as one or several double bonds,[123–126] phenyl groups,[120,121] biphenyl,[246] naphthalene,[122] pyrrole and N-substituted pyrroles,[115,125,247] furan,[104,115] and substituted thiophenes.[114] However, as discussed in section II.B, such conjugated substrates lead generally to incomplete electropolymerization and to poorly conducting materials. Because of these problems, better results are generally obtained by chemical synthesis. Thus thiophene has been copolymerized with benzene, biphenyl, or substituted phenyl groups by means of various chemical syntheses including Grignard coupling,[248] Stetter reaction followed by ring closure,[249] or oxidative dehydrogenation.[250] Poly(2,5-thienylenevinylene) can be viewed as the intermediate structure between $(CH)_x$ and PT and thus as a particular case of thiophene copolymer. This polymer, which was prepared 20 years ago by the Wittig reaction,[251] has been subject to a renewal of interest since it has been shown that highly conducting films (σ = 60 S cm^{-1}) could be obtained by means of soluble precursors.[127,128] Furthermore, the substitution of the thiophene ring by electron-donating groups allows a significant reduction of the band gap.[252] Copolymers of 3-methylthiophene and methyl methacrylate have been prepared by reaction of the Grignard 3-methylthiophene monomer and methyl methacrylate. Although the copolymers show good solution processability, the conductivity remains rather limited (0.2–6.5 S cm^{-1}) due to the interruption of conjugation caused by the methacrylate bridges.[253,254] Carbon atom bridged poly(terthiophenes) are another recent example of interrupted conjugation in the polymer backbone.[256]

V. Substituted Poly(thiophenes)

A. Structural Basis of Functionalization

Among the various possible strategies for modification of CPs, the polymerization of monomers modified by the covalent grafting of functional groups represents the most straightforward method to achieve a molecular level control of the structure and electronic and electrochemical properties of functional CPs. However, despite its elegant simplicity, this approach poses several complex problems. As a matter of fact, the synthesis of a modified CP in which a specific function will be coupled to the conjugated π system requires that the modification of the monomer structure remains compatible with both the polymerization and the conservation of an extensively conjugated system in the resulting polymer in order to preserve its relevant electronic, optical, and electrochemical properties. Consequently, the synthesis of a functional CP from a substituted monomer in respect of the above prerequisites implies a detailed comprehension of the structural effects of substitution (inductive, mesomeric and steric) at the various stages of organization of the material i.e.:

molecular	reactivity of the monomer
	propagation of the polymerization

macromolecular	planarity of the conjugated system
	mean effective conjugation length intrachain conductivity electronic and electrochemical properties
macroscopic	crystallinity, morphology, porosity
	mechanical properties macroscopic conductivity electrochemical properties

1. *Electronic Effects*

A linear correlation has been found between the oxidation potential of substituted thiophenes and the σ^{+i} Hammet substituent constant.[14,74] This result clearly shows that electronic effects drastically affect the electronic density of the thiophene ring and hence its reactivity. Thus monomers substituted by strongly electron-withdrawing groups like 3-thiophenecarboxylic acid, 3-thiophenecarboxaldehyde, 3-cyanothiophene, and 3-nitrothiophene that have oxidation potentials ca. 0.5–0.7 V higher than thiophene do not electropolymerize.[14,74] The electropolymerization of monomers with less electron-withdrawing substituents such as 3-thiopheneacetonitrile, or 3-thiopheneacetic acid, proceeds with low-current efficiency and requires highly anodic potentials.[74,256] Halogen-substituted monomers, i.e. 3-chloro-, 3-bromo-, 3,4-dibromo-, and 3-iodothiophenes, are generally difficult to electropolymerize and lead to poorly conducting polymers with high oxidation potentials.[74,141,194,257] However, in this latter case, the observed effects probably arise from a combination of electronic and steric factors.[14,257] The impossibility or difficulty to electropolymerize monomers of high oxidation potentials has been attributed to the high reactivity of the corresponding radicals which can thus undergo rapid reactions with the solvent or anions to form soluble products rather than to electropolymerize.[14]

In the other extreme case, the substitution of thiophene by electron-donating groups produces a decrease of oxidation potential and hence a stabilization of the corresponding radicals. These radicals can thus diffuse away from the electrode surface to form soluble oligomers in solution. Thus attempts to electropolymerize 3-(methylthio)-, 3-(ethylthio)-, and 3,4-bis(ethylthio)thiophenes were unsuccessful[258] or led to the formation of soluble oligomers.[259] Theoretical calculations have shown that the spin density in the corresponding radicals was maximum on the sulfide function and not on the α positions of the thiophene ring, which is a necessary condition for electropolymerization.[258] A similar explanation could account for the failure to electropolymerize tetrahydrathieno[3,4-*c*]thiophene which, in contrast, acts as a radical scavenger capable to inhibit the electropolymerization of 3-methylthiophene.[260,261] Monomers substituted by thioalkyl groups have been chemically polymerized; however, the conductivity and electrochemical stability of the obtained polymers are significantly lower than those of unsubstituted PT.[258,262] Although of lesser magnitude, similar effects result from the grafting of alkoxy groups on the thiophene ring. In this case, the electron-donating effect of the oxygen decreases the oxidation potential of the monomer[263] which stabilizes the resulting radicals and favors the formation of soluble short-chain oligomers. The electropolymerization of 3-methoxythiophene has been investigated by several groups.[263–268] There are large discrepancies concerning the degree of polymerization which ranges from 5–10[263,265] to 80[268] and the oxidation potential of the polymer for which values as different as +0.28 V[263] and –0.2 V[268] vs Ag/Ag^+ have been reported. The polymer had a conductivity of 0.3 S cm^{-1} which was reported to increase by a factor of 50 after rinsing with *n*-hexane.[266] This result appears to be consistent with the presence of large amounts of soluble short-chain oligomers in the as-grown polymer. More recently, PTs containing methoxy groups have been prepared from 3,3′-dimethoxybithiophene[269] and 4,4′-dimethoxybithiophene.[270] Although these two substrates should lead ultimately to the same polymer structure, the properties of the obtained polymers differ considerably. Poly(4,4′-dimethoxybithiophene) shows significantly lower oxidation potential and energy gap.[270] These differences probably arise from the different reactivities of the two substrates since only 4,4′-dimethoxy-2,2′-bithiophene is expected to have planar conformation. It appears thus that electronic effects play a determining role on the reactivity of substituted thiophenes and that the obtention of extensively conjugated and highly conducting substituted PTs requires that the monomer reactivity is kept within defined limits.

2. *Steric Effects*

Although steric factors do not significantly affect the oxidation potential of the monomer, they exert considerable effects on the structure and properties of the substituted polymer and, in some extreme cases, on the electropolymerization reaction. As a matter of fact, the distortion of the conjugated backbone caused by steric interactions between substituents grafted on adjacent monomers results in a decrease of the overlap between the π orbitals on consecutive rings and hence in a shortening of the effective mean conjugation length. This departure from planarity produces an increase of the ionization potential and a drop of the maximum conductivity upon doping. Theoretical calculations have shown that the electronic properties of PT evolve according to a cosine law. Consequently, substitutions leading to a torsion angle smaller than 40° between consecutive rings are acceptable.[271]

B. Poly(3,4-disubstituted thiophenes)

A first illustration of the effects of steric factors is provided by the electronic properties of PTs 3,4-disubstituted by simple alkyl groups. It has been recognized early that the introduction of a methyl group at the β-position of the thiophene ring leads to a significant increase of the conjugation and conductivity.[73,74] This effect has been attributed to the statistical decrease of the number of α–β' couplings and to the decrease of the oxidation potential (ca. 0.2 V) caused by the inductive effect of the methyl group. As a further step, disubstitution at the β,β' positions has appeared as an interesting method to synthesize perfectly stereoregular polymers by suppressing any possibility of α–β' coupling. However, this approach is severely limited by the steric interactions between substituents grafted on consecutive monomers that distort the conjugated

TABLE III. Poly(3,4-disubstituted thiophenes)

polymer R3	polymer R4	E_{pa} (V/SCE)	λ_{max} (nm)	σ (S cm^{-1})	ref
H	CH_3	0.56	520	500	260
CH_3	CH_3	1.00	350	0.5	260
cyclopenta[*c*]thiophene		0.76	510	20	260
H	C_2H_5	0.72	470	180	192
CH_3	C_2H_5	1.06	-	-	194
C_2H_5	C_2H_5	1.10	280	-	194
CH_3	OCH_3	-	530	220	267
H	OC_4H_9	0.34	520	8×10^{-4}	272
OC_4H_9	OC_4H_9	0.70	460	1×10^{-5}	272
CH_3	OC_4H_9	0.60	545	2	272
CH_3	OC_8H_{17}	0.64	545	1	272
CH_3	$OC_{12}H_{25}$	-	550	5	267
H	SC_2H_5	0.90	450	1×10^{-3}	262
SC_2H_5	SC_2H_5	1.16	390	1×10^{-7}	262

π system, producing a considerable loss of effective conjugation. As shown in Table III, poly(3,4-dialkylthiophenes) have higher oxidation potentials, optical bandgaps, and lower conductivities than monosubstituted polymers.[194] Although cyclization between the 3 and 4 positions achieved in dihydrocyclopenta[*c*]-thiophene allows a significant reduction of the steric hindrance, this monomer is more difficult to electropolymerize than 3-methylthiophene. Furthermore, the electrical and electrochemical properties of the corresponding polymer remain inferior to those of PMeT.[260] The comparison of the properties of PTs mono- and disubstituted by alkoxy[272] or thioalkyl groups[262] (Table III) reveals also significant steric hindrance in these cases. On the other hand, unsymmetrically disubstituted polymers such as poly(3-methoxy-4-methylthiophene), poly(3-butoxy-4-methylthiophene), poly-[3-(octyloxy)-4-methylthiophene], and poly[3-(dodecyloxy)-4-methylthiophene] show lower oxidation potentials and smaller bandgaps than to their monosubstituted or symmetrically disubstituted analogs (Table III).[267,272] However, due to the electronic effects of alkoxy groups, a precise evaluation of the reduction of steric hindrance is difficult. Poly[3,4-(ethylenedioxy)thiophene], which represents another interesting approach for the reduction of steric hindrance in 3,4-disubstituted PTs, has been recently mentioned in a conference paper but no characterization has been reported yet.[273]

C. Fused Rings Systems

Several types of conducting polymers have been prepared using as precursors, fused rings systems containing one or more thiophene units (Figure 10). Poly(isothianapthene) (PITN), which can be viewed also as a particular case of disubstituted PT, has been prepared by both electrochemical and chemical syntheses.[274,275] Due to the instability of the monomer, the electrochemical synthesis requires very special conditions.[274] A conductivity of 50 S cm^{-1} has been reported for the iodine-doped polymer.[276] The optical spectrum presents a maximum at 1.4 eV and an absorption onset at ≈1 eV, showing that PTIN has the smallest energy gap among CPs.[276] Poly(5,6-(dioxymethylene)isothianaphtene) has been recently described, however, contrary to what could be expected, this structural modification did not lead to significant changes in the electrochemical and optical properties of PTIN.[277] Over the past few years, CPs have been prepared by electropolymerization of several other fused rings systems such as: dithieno[3,2-*b*:2,3′-*d*]thiophene and thieno[3,2-*b*]thiophene,[278-281] thieno[3,2-*b*]-pyrrole,[282] dithieno[3,4-*b*:3′,4′-*d*]thiophene,[283] dithieno-[2,1-*b*:3,4-*b*′]benzene and dithieno[1,2-*c*:3,3-*c*′]benzene[284] and cyclopenta[2,1-*b*:3,4-*b*′]dithiophen-4-one.[285] Due to their conjugated structures, these substrates electropolymerize at lower potentials than thiophene (Table IV). However, as in the case of the electropolymerization of oligomers, the resulting materials are generally poorly conjugated and conducting except poly(dithieno[3,4-*b*:3′,4′-*d*]thiophene) and poly(cyclopenta-[2,1-*b*:3,4-*b*′]dithiophen-4-one) which have been reported to have a smaller bandgap than PT.[283,285]

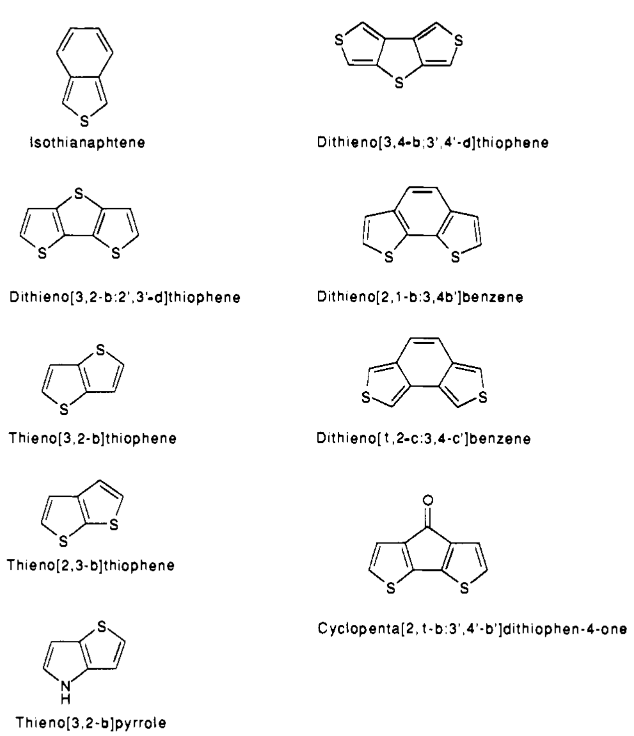


Figure 10. Fused rings system precursors of conducting polymers.

TABLE IV. Conducting Polymers Obtained by Electropolymerization of Fused Ring Systems

monomer	monomer oxidation potential (V/SCE)	λ_{max} (nm)	σ (S cm^{-1})	ref
dithieno[3,2-*b*:2,3′-*d*]thiophene	1.2	460	3×10^{-3} to 4×10^{-1}	278, 281
thieno[3,2-*b*]thiophene	1.4	435	3×10^{-6} to 8×10^{-4}	279, 281
thieno[2,3-*b*]thiophene	1.58	-	-	280
thieno[3,2-*b*]pyrrole	0.6[a]	-	5×10^{-3}	282
dithieno[3,4-*b*:3′,4′-*d*]thiophene	1.04	590	1	283
dithieno[2,1-*b*:3,4-*b*′]benzene	1.33	340	1×10^{-7}	284
dithieno[1,2-*c*:3,3-*c*′]benzene	0.92	390	1×10^{-7}	284
cyclopenta[2,1-*b*:3,4-*b*′]dithiophen-4-one	1.26	425, 740	-	285

[a] Vs Ag/AgNO$_3$.

TABLE V. Poly(3-alkylthiophenes)[a]

polymer	synthesis	σ (S cm^{-1})	solvent	% solubility	$\lambda_{\max\,\mathrm{soln}}$ (nm)	$\lambda_{\max\,\mathrm{film}}$ (nm)	N_{dp}	ref
PC2T	E, 5 mA cm^{-2}	180				470		192
PC2T	E, 5 mA cm^{-2}	270				460		80
	GC		3					288
PC3T	E, 5 mA cm^{-2}	160				472		192
PC4T	GC	4	THF, tol, Xyl			460	20–60	288
PC4T	E, 2 mA cm^{-2}	50				486		192
PC4T	E, 5 mA cm^{-2}	150				488		192
PC4T	E	0.3	Xyl	50%	455		11	114
PC4T	E, 2 mA cm^{-2}	40	Chl, Tol, THF		434	460	300	94, 289
PC5T	E, 1 mA cm^{-2}					500		192
PC5T	E, 5 mA cm^{-2}	140				512		192
PC6T	E, 2 mA cm^{-2}	95	Chl, THN				230	286
PC6T	E, 2 mA cm^{-2}	30	Chl, THF		434	488	300	94, 289
PC6T	E, 2 mA cm^{-2}	1.5	Chl			480	100	296
PC6T	OP, $FeCl_3$		MeTHF	200 g/L		505	1500	38
PC7T	E, 2 mA cm^{-2}	45				455		192
PC7T	E, 10 mA cm^{-2}	110				495		192
PC8T	E, 2 mA cm^{-2}	40	Chl, PhCl	50%	440	498		192
PC8T	E, 10 mA cm^{-2}	90		3%	440	517		192
PC8T	E, 2 mA cm^{-2}	78	Chl, THN				140	286
PC8T	E, 2 mA cm^{-2}	0.1	Chl			480	180	296
PC8T	OP, $FeCl_3$	28	Chl			505–10	195	296
PC8T	GC	30	Chl, THF		440		50	292
PC8T	OP, $FeCl_3$	30	Chl		440		150	292
PC9T	E, 2 mA cm^{-2}					518		192
PC9T	E, 5 mA cm^{-2}	85				525		192
PC9T	E, 10 mA cm^{-2}	100				542		192
PC10T	E, 2 mA cm^{-2}	40				485		192
PC10T	E, 5 mA cm^{-2}	70				498		192
PC10T	E, 2 mA cm^{-2}	0.3	Chl		440	480		296
PC10T	OP, $FeCl_3$	25	Chl		440	505–10	250	296
PC12T	E, 2 mA cm^{-2}	67	Chl, THN				90	286
PC12T	3 mA cm^{-2}	95	THF	partial			120	295
PC12T	E, 2 mA cm^{-2}	4	Chl		440	480	190	296
PC14T	E, 2 mA cm^{-2}	7				461		192
	E, 4 mA cm^{-2}	16	Chl, PhCl	10%		462		192
PC18T	E, 2 mA cm^{-2}	2				456		192
	E, 2 mA cm^{-2}	17	Chl, THN					286
PC20T	E, 2 mA cm^{-2}	11	Chl, THN					286

[a] E: electrosynthesis. GC: Grignard coupling. OP: oxidative polymerization. Chl: chloroform. Tol: toluene. Xyl: xylene. PhCl: chlorobenzene. THF: tetrahydrofuran. THN: tetrahydronaphthalene.

D. Poly(3-substituted thiophenes)

1. Linear Alkyl Chains

Since their first synthesis in 1986, poly(3-alkylthiophenes) (PATs) have attracted increasing interest, owing to the significant improvement of solubility and fusibility resulting from the grafting of flexible hydrocarbon chains on the conjugated PT backbone. The electrochemical and chemical synthesis of PATs was reported simultaneously by several groups.[286–289] Poly(3-butylthiophene) (PC4T) and random copolymers of 3-methylthiophene and 3-butyl- or 3-octylthiophene were obtained by nickel-catalyzed Grignard coupling of the 2,5-diiodothiophene monomers. The average molecular weights were in the range 3000–8000 and the doped polymers had conductivities in the range of 1–5 S cm^{-1}.[288] PATs with alkyl chains containing 1 (PMeT) to 20 (PC20T) carbons have been prepared by electrosynthesis.[192,286,287,289] The degree of polymerization (N_{dp}) ranged from 300 for PC6T[289] to 90 for PC20T.[286] The conductivity was found to decrease with the length of the alkyl chain but remained at a high level. Thus the conductivity of poly(3-decylthiophene) is still as high as 70 S cm^{-1} although the PT backbone represents only one-third of the polymer weight[192,290] (Table V). More recently, PATs have been prepared also through oxidative polymerization by $FeCl_3$.[37,38,291,292] The average molecular weights of the obtained polymers were reported to be higher than those of the polymers prepared by Grignard coupling or by electrochemical synthesis.[38,292]

Owing to the rigidity of their conjugated backbone and to strong interchain interactions, CPs are generally insoluble. Until recently, this insolubility has constituted a major obstacle to their characterization by classical analytical techniques and also to their technological applications. It had been recognized early that the preparation of PT by Grignard coupling yields ca. 20% of $CHCl_3$ soluble material.[30,31] This soluble fraction, which contains short chain oligomers, shows nevertheless rather high conductivity (up to 5 S cm^{-1}).[293] Soluble oligomers have been also detected in electrogenerated PTT or PMeT.[69,70] Besides these few examples, which are in fact the undesired consequences of incomplete polymerization, the solubilization of PTs has been achieved by polymerization with AsF_5 in AsF_3 solution.[294] However, in spite of their scientific interest, the practical applications of these results are very limited. In this context, the discovery that the grafting of long alkyl chains on PT led to polymers soluble in common organic solvents has immediately attracted much attention. Thus, PATs with alkyl groups equal

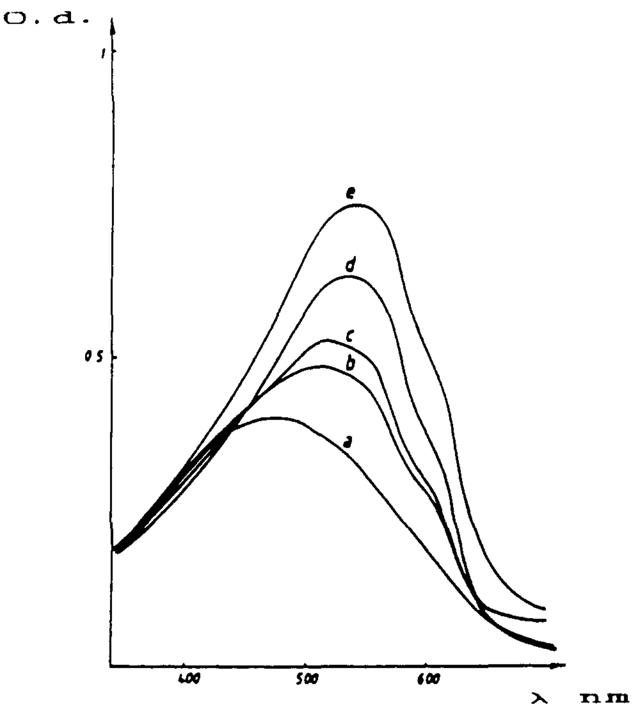


Figure 11. Effects of electrosynthesis current density (J), on the electronic absorption spectrum of undoped PC9T films deposited on ITO using 100 mC cm^{-2}: (a) J = 0.5 mA cm^{-2}; (b) J = 2; (c) J = 5; (d) J = 10.

or greater than butyl have been reported to be readily soluble at room temperature in tetrahydrofuran, dichloromethane, chloroform, benzene, toluene, xylene, nitrobenzene, benzonitrile, and tetrahydronaphthalene.[286,283,289] These soluble polymers can subsequently be processed into films from their solutions.[38,286,268,289] These solution-cast films show electrochemical and optical properties resembling those of as-grown polymer films.[38,286,289] Although the conductivity of doped solution-cast films is lower than that of as-grown electrogenerated films,[38,192,286] stretched films show considerably higher conductivities. Thus the conductivity of solution processed poly(3-hexylthiophene) films increases from 27 to ca. 200 S cm^{-1} at a stretching ratio of 5.[38]

Perhaps as a consequence of the strong immediate interest for these polymers, several questions have not been examined in detail. Thus, contradictory results have been reported concerning the effects of the alkyl chain length on the solubility. This parameter has been reported to increase[268] or decrease[268] the solubility of the polymer. Although it is perfectly clear that alkyl substituents strongly enhance the solubility of the PT backbone, clear conclusions are difficult to draw since the length of the alkyl chain affects also the N_{dp}.[286] Whereas in initial reports PATs were implicitly considered as fully soluble, further analyses on electrogenerated PATs have shown that solubility, conjugation and conductivity depend strongly on the applied electrical conditions and that this dependence increases with the length of the alkyl chain. This dependence is clearly illustrated by the considerable modifications of the optical spectrum, resulting from changes in the electrosynthesis conditions (Figure 11). The increased conjugation of polymers deposited in optimal conditions is correlated to a spectacular increase of conductivity and to a loss of solubility which decreases down to a few percents.[192] More recent works have confirmed the partial insolubility of electrogenerated PATs and its dependence on the electrosynthesis conditions.[114,295–297] These effects have been attributed to the cross-linking of the polymers.[295,297] However, this interpretation is in contradiction with the observed increase of conjugation and conductivity and it seems more probable that the differences of solubility are related to different N_{dps}. The precise determination of this parameter is not straightforward. As a matter of fact, although MW determinations using polystyrene standards generally indicate high values (up to 2.5 × 10^5),[38] a comparative analysis of the results obtained with polystyrene standards and authentic alkylthiophenes oligomers has shown that polystyrene standards lead to an overestimation of at least 1 order of magnitude of the MW of the PATs soluble fractions. Thus, in the case of electrogenerated PC4T, the soluble fraction (50% of the polymer) was shown to contain oligomers with $N_{dp} \simeq$ up to 11.[114]

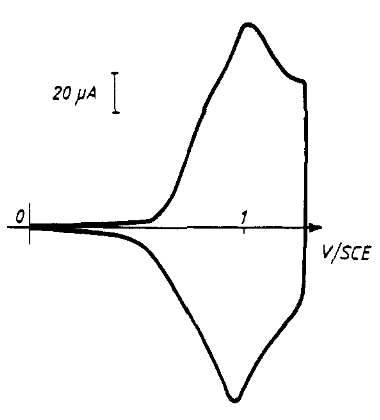


Figure 12. Cyclic voltammogram of poly(3-nonylthiophene) in 0.1 M LiClO$_4$/CH$_3$CN (deposition charge 100 mC cm^{-2} on Pt; scan rate 50 mV s^{-1}; electrode area 0.07 cm^2).

The grafting of alkyl chains on PT leads also to important modifications in the morphology of the polymers[192] and in the electrochemical and optical properties of the conjugated backbone. Thus increasing the length of the alkyl chain to 7–9 carbons produces simultaneously an extension of the mean conjugation length and an increase of the electrochemical reversibility. This reversibility is illustrated by the symmetry of the voltammogram (Figure 12) and by the disappearance of hysteresis in the Nernst plots (Figure 13).[192,197] This higher reversibility appears consistent with the faster thermal undoping observed on PATs.[298] Interestingly, this length of the alkyl chain corresponds to the optimal length of the alkyl spacers used in polymeric liquid crystals and represents a compromise between the constrained flexibility of the side chain observed with short alkyl chains ($n \simeq 3$) and the side-chain crystallization occurring with long alkyl chains ($n > 10$).[299]

The doping process of PC6T solutions has been analyzed by UV-vis and ESR spectroscopies and it has been concluded that bipolarons are the lowest charge-storage configurations in dilute solutions.[300] PATs solutions have been shown to undergo thermochromism and solvatochromism. Thus, besides the main absorption band at 430 nm, the low-temperature optical spectra of PATs solutions present a FS involving additional bands at 560 and 607 nm.[301] Thermochromism

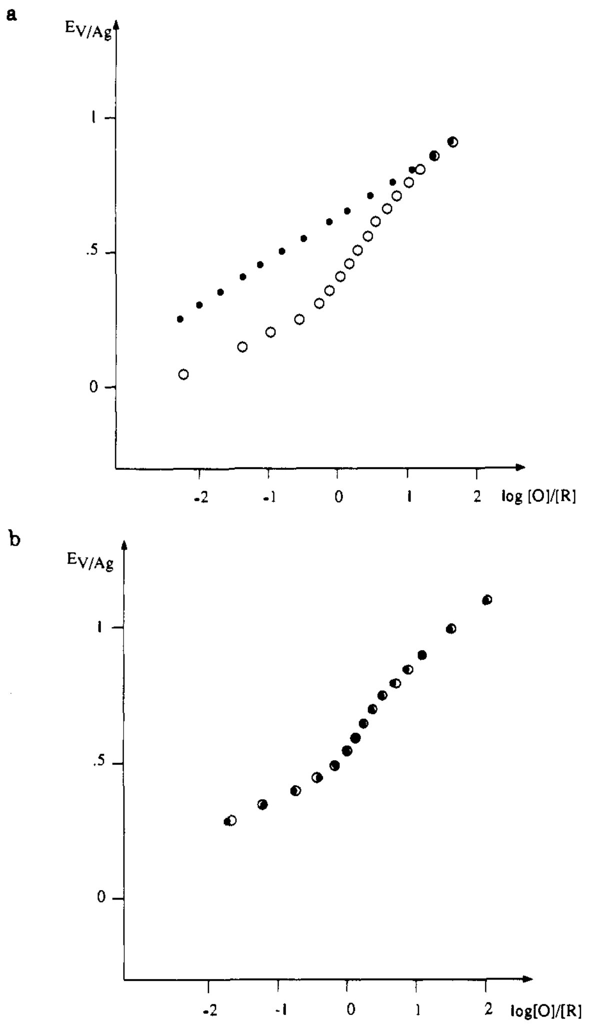


Figure 13. Nernst plots obtained in 0.1 M $LiClO_4/CH_3CN$ from in situ absorptometry at various ratios of the concentration of oxidized and reduced sites [O]/[R]: (a) PMeT; and (b) PC9T.

has been also observed on solution-cast PATs films.[302] The origin of FS in the electronic spectra of PATs has given rise to much debate and it has been attributed either to vibrational coupling involving the C=C stretching mode in the thiophene ring (1450 cm^{-1}, 0.18 eV)[301] or to rotational defects around single bonds leading to discrete lengths of conjugated segments.[303] However, the former interpretation seems now more widely accepted.[304] PATs have been reported to be fusible and to undergo piezochromism.[291,305] Photoluminescence has been found to increase with the length of the alkyl chain and with temperature with a maximum around the melting point.[306]

The structure of PATs is not fully established and different models have been proposed. Planar chains with alternating "up and down" thiophene rings,[307] or alternation occurring each two monomers, i.e. "up-up-down-down",[308] have been inferred from X-ray experiments. On the other hand, experimental and theoretical works have led to the proposal of an helical chain structure implying a syn conformation for electrogenerated PATs.[154,192,290] From this point of view, the distinction between chemically and electrochemically synthesized polymers can be of importance since until now, helical structures have been observed only on electrogenerated polymers,[65,155] and one can imagine that the highly dissymmetric electrochemical interface submitted to potentials of several thousands volts per centimeter can produce structures differing strongly from that of polymers chemically prepared in the homogeneous liquid phases.

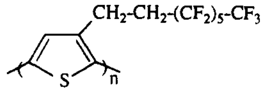
Recently, regiochemically defined PATs have been prepared using 3,3′- or 4,4′-dialkylbithiophenes as starting materials.[269,309-311] Although the obtained polymers are considerably less conjugated than PATs due to their large proportion of head-to-head linkages, this pronounced steric effect is not reflected in the conductivity. Thus poly(3-hexylthiophene) and poly(3,3′-dihexyl-2,2′-bithiophene) prepared in the same conditions have conductivities of 15 and 3.7 S cm^{-1}, respectively.[310]

2. Branched Alkyl Chains

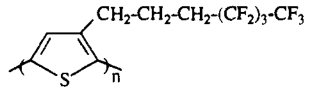
In contrast to linear chains, branched alkyl groups drastically affect the effective conjugation of the PT backbone and in some cases the polymerizability of the monomer. Thus attempts to electropolymerize 3-isopropylthiophene were unsuccessful while 3-isobutylthiophene leads to a polymer considerably less conjugated and less conductive than its linear analog.[94,192] In contrast, the oxidation potential and absorption maximum of poly(3-isoamylthiophene) are similar to those of poly(3-amylthiophene).[192,193,290] These results have been interpreted by a progressive decrease of the torsion angle between adjacent monomer units as the distance between the secondary carbon and the thiophene ring increases. Molecular models suggest that only a cisoidal conformation of adjacent thiophene rings leads to a progressive decrease of the torsion angle corresponding to the observed evolution of the polymers properties, the steric hindrance being roughly equivalent for the three polymers in the case of a transoidal conformation.[192] It is worth noting that 3-isobutylthiophene and 3-isoamylthiophene lead to films approximately twice as thick than those obtained with the same deposition charge from their linear analogs. This result shows that branched alkyl chain affect considerably the morphology and the density of the polymers.[192] Although PTs substituted by branched alkyl chains are not of specific practical interest, they provide interesting information on the effects of steric factors in PT substitution.

3. Fluoroalkyl Chains

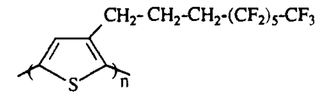
Fluoropolymers are generally known for their high thermal stability, chemical inertness, low coefficient of friction, and hydrophobicity. The association of these properties with the electronic properties of CPs could lead to new materials of interesting properties from both scientific and industrial viewpoints. Polymers **6–8** have been recently synthesized electrochemically.[312] Alkyl spacers were inserted between the thiophene ring



(6)



(7)



(8)

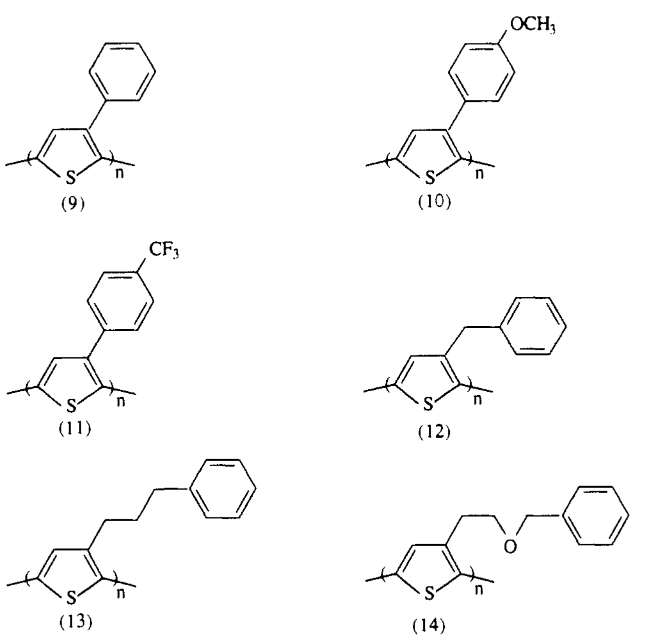


Figure 14. Poly(thiophenes) substituted by aryl groups.

and the fluoroalkyl groups in order to neutralize their electronic effects. In these conditions, the introduction of up to 50% of fluorine in the structure has been shown to lead to elastomeric materials with higher electroactivity than PATs.[312]

4. Aryl Groups

PTs derivatized by aryl groups are interesting from several viewpoints. On the one hand, the analysis of the electronic and steric effects of such substituents represents an important step in the study of structure–properties relationships in substituted PTs. On the other hand, phenyl groups constitute interesting anchoring sites for further functionalization.

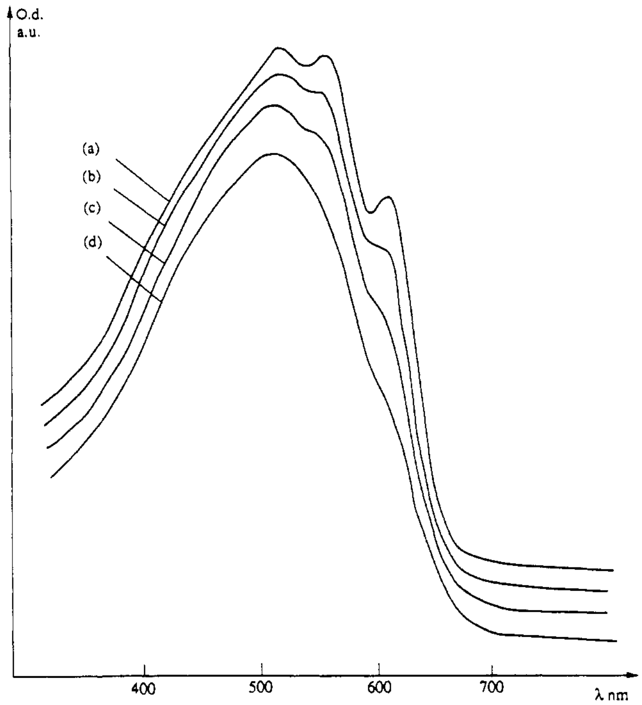


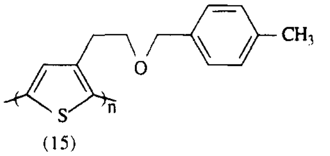
Figure 15. Effects of the substitution of the phenyl ring on the electronic absorption spectra of neutral poly[3-[2-(benzyloxy)ethyl]thiophenes]: (a) **18**; (b) **16**; (c) **19**; and (d) **20**.

TABLE VI. Poly(thiophenes) Substituted by Aryl Groups

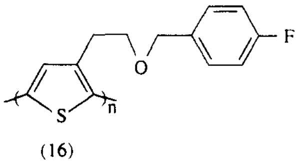
polymer	E_{pa} (V/SCE)	λ_{max} (nm)	σ (S cm^{-1})	ref
9	0.76[a]	560	140	313
9	0.96	545	5	314
9[b]		438[c]		315
10	0.65	545	40	313
11	1.00	535	1.8×10^{-3}	313
12	0.95	435	0.5	290
12	0.74[a]	440	13	316
13	0.85	485	25	317
14	0.85	510	20	317

[a] Vs Ag/Ag$^+$. [b] Chemical synthesis. [c] In CHCl$_3$.

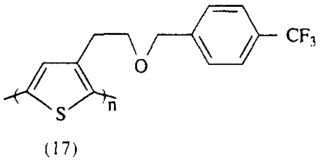
Poly(3-phenylthiophene) (**9**, Figure 14) has been prepared by both chemical and electrochemical syntheses and polymers showing quite different properties have been obtained (Table VI).[313-315] Different results have also been reported concerning the conductivity and electrochemical properties of electrogenerated **9**. Thus a conductivity of 140 S cm^{-1} and doping levels of 78 and 72% for, respectively, p and n doping, have been claimed.[313] In the same paper, a p-doping level of 69% was found for PT. Since the doping level of PT generally does not exceed 25% in the best case,[14,15,20,142] these doping levels appear clearly overestimated. Although the direct grafting of a phenyl group on the thiophene ring is expected to induce an important steric hindrance to the coplanarity of the PT backbone, the conjugation of the two cycles does not allow a clear distinction between the steric and electronic effects of the phenyl ring. The conjugation of the two cycles is supported by the large modifications of properties resulting from the para substitution of the phenyl ring by a methoxy or by a trifluoromethyl group (**10** and **11**, respectively).[316] Evidence for the steric effect of the phenyl ring has been provided by poly(3-benzylthiophene) (**12**).[290,314,315,317] The similarity of the optical electrochemical and electrical properties of this polymer with those of poly(3-isobutylthiophene) (Tables III and VI) confirms that it is less conjugated and less conductive than PT itself. On the other hand, the results obtained on polymers **12**, **13**, and **14** (Table VI) shows that increasing the length of the spacer produces an extension of conjugation and an increase of conductivity consistent with a progressive reduction of steric hindrance.[314,317] The effects of the substitution of the phenyl ring have been analyzed in polymers **14–18**. Substitution by a methyl group (**15**) inhibits the electropolymerization. This effect has been attributed to the decrease of the oxidation potential of the phenyl ring which enables parasitic side reactions.[314] The electronic and steric decoupling of the phenyl ring



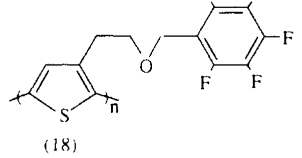
(15)



(16)



(17)



(18)

TABLE VII. Poly(thiophenes) 3-Substituted by Alkoxy Groups

polymer, R3	E_{pa} (V)	λ_{max} (nm)	σ (S cm^{-1})	N_{dp}	ref
OCH_3	0.33/SCE	480		5–10	264
	−0.20/Ag/Ag$^+$	465	0.33, 15[a]	79	266, 268
	0.28/Ag/Ag$^+$	430			263
				25–30	265
		475	1×10^{-2}		267
OCH_2CH_3		485	1×10^{-2}		267
$O(CH_2)_2CH_3$		490	6×10^{-3}		267
$O(CH_2)_9CH_3$		525	3×10^{-3}	10–40	267
$O(CH_2)_{10}CH_3$			3×10^{-3}		267
$O(CH_2)_{11}CH_3$		530	6×10^{-2}	10–50	267
$O(CH_2)_{12}CH_3$			2×10^{-3}		267
$O(CH_2)_{13}CH_3$		525	2×10^{-3}	10–40	267
$O(CH_2)_{14}CH_3$			1×10^{-3}		267
$O(CH_2)_2O(CH_2)_2OCH_3$			5×10^{-2}		320

[a] After rinsing with hexane.

in polymers 14, 16, 17, and 18 is confirmed by the invariance of the absorption maximum (520 nm) (Figure 15). However, the dependence of the resolution of the vibronic FS on the substitution of the phenyl ring shows that interactions among substituted phenyl groups indirectly affect the ordering and rigidity of the polymer framework.[318] Furthermore, the correlation of the n-doping level with the resolution of FS suggests that cation doping depends much more on these structural parameters than anion doping.

These results together with those obtained with branched alkyl chains allow a first attempt to rationalize the structural effects involved in the substitution of PT. This rationalization is illustrated by the concept of functionalization space, defined as the volume in which a given substituent must be introduced in order to preserve (i) the polymerizability of the monomer and (ii) an extended effective conjugation length in the resulting polymer (Figure 16). This volume is determined by means of three parameters, the length of the spacer needed to neutralize the electronic substituent effects and the acceptable limits of intra chain distortion and inter chain distance.[192,317]

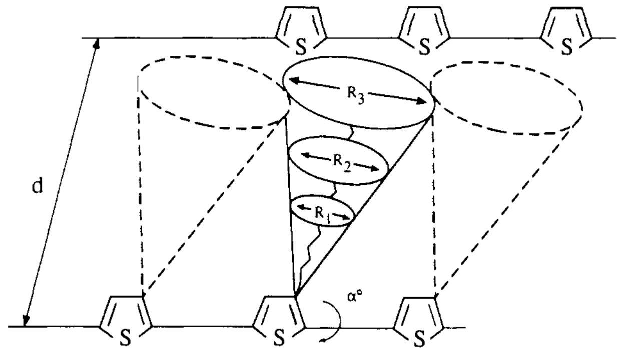


Figure 16. Functionalization space of poly(thiophene).

5. Ethers and Polyether Chains

Conjugated polymers substituted by polyether complexing groups are another class of potentially very promising electroactive materials. As a matter of fact, substitution of PT by oligo(oxyethylene) chains leads to interesting new properties such as solubility, hydrophilic character, and original electrochemical and optical behaviors. Such polymers could find interesting applications in selective electrodes and membranes and all-polymer solid-state batteries.[319] Furthermore, the formation of an ether function also constitutes an interesting method of derivatization. However, the preparation of such functional PTs requires the control of the electronic effects of the oxygen atom in order to preserve both the polymerizability of the monomer and the electronic properties of the polymer. Depending on its position in the side chain, the oxygen diversely affects the reactivity of the monomer and the properties of the resulting polymer. As already discussed (section V.A), the direct grafting of an alkoxy group at the 3-position limits the polymerization reaction to short-chain oligomers[264,267,320] (Table VII). However, this negative effect can be partly compensated by increasing the length of the alkyl residue. Thus, 3-(dodecyloxy)thiophene or 3-(octyloxy)-4-methylthiophene lead to more conjugated polymers than 3-methoxythiophene.[267,272] The conductivity of polymers with a first oxygen atom introduced after one methylene group has been reported to increase with the number of ether groups and hence with the overall size of the substituent. Values exceeding 1000 S cm^{-1} have been claimed for a polymer containing three ether groups[320] (Table VII), while other studies led to quite different conclusions.[322]

The effects of the position of the first oxygen atom in the side chain have been analyzed on two basic structures, PC4T and PC9T.[317,322] In both cases, the introduction of the oxygen after one methylene group raises the oxidation potential of the monomer and decreases the conjugation and conductivity of the corresponding polymer (Table VIII). In contrast, the insertion of a $-(CH_2-CH_2)-$ spacer brings back the oxidation potential to a value similar to that of 3-alkylthiophenes and leads to more conjugated and more conducting polymers.[317,322] A recent work has confirmed the positive effects of such a spacer.[323] The increase of the number of ether groups in the side chain leads to a progressive inhibition of the electropolymerization. Thus, attempts to electropolymerize a monomer containing seven ether groups remained unsuccessful.[322]

In the course of these studies, poly[3-(3,6-dioxaheptyl)thiophene)] (PDHT) has appeared as an interesting compromise between the conservation of an extensively conjugated structure, as confirmed by the position of its absorption maximum at 556 nm[193] and the emergence of original properties associated with the oligo(oxyethylene) side chain.

Thus, a considerable increase of hydrophilicity has been observed which allows PDHT to remain fully

TABLE VIII. **Poly(thiophenes)** 3-**Substituted by Oxyalkyl Groups**

polymer, R3	$E_{\text{pa mon}}$ (V/SCE)	$E_{\text{pa pol}}$ (V/SCE)	λ_{max} (nm)	σ (S cm^{-1})	ref
CH_2OCH_3				3.1×10^{-1}	320
$CH_2OCH_2CH_3$	1.90	1.10	435	1×10^{-2}	322
$(CH_2)_2OCH_3$	1.80	0.88	460	10	317
$CH_2O(CH_2)_6CH_3$	1.94	1.10	460	1×10^{-1}	317
$(CH_2)_2O(CH_2)_3CH_3$		0.90	498	55	323
$(CH_2)_2O(CH_2)_5CH_3$	1.80	0.88	517	50	317
$(CH_2)_3O(CH_2)_4CH_3$	1.80	0.88	500	10	322
$CH_2O(CH_2)_2OCH_3$				51	320
$CH_2O(CH_2)_2O(CH_2)_2OCH_3$				1050	320
$CH_2O(CH_2)_2O(CH_2)_2OCH_3$	1.94	1.10	420	1×10^{-3}	322
$(CH_2)_2O(CH_2)_2OCH_3$	1.80	0.80	552	250	325
$(CH_2)_2O(CH_2)_2O(CH_2)_2OCH_3$	1.80	0.80	440	10	322
$(CH_2)_2O(CH_2CH_2O)_7CH_3$	no electropolymerization				322

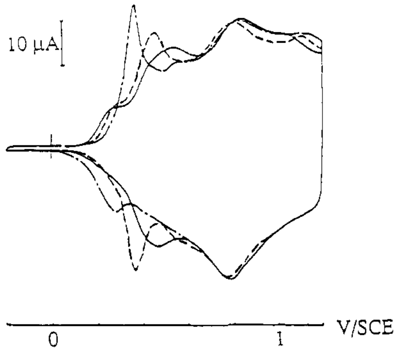


Figure 17. Effect of [Li$^+$] on the cyclic voltammetric response of PDHT (deposition charge 100 mC cm^{-2} on Pt; scan rate 30 mV s^{-1}; electrode area 0.07 cm^2; electrolytic medium $LiClO_4/CH_3CN$): [Li$^+$] = 0.1 M, (solid line), 0.5 M (dashed line), and 1 M (dot-dashed line).

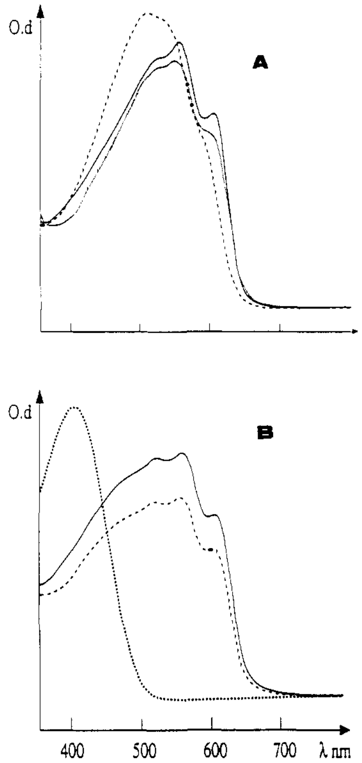


Figure 18. (A) In situ electronic absorption spectra of PDHT (60 mC cm^{-2} on ITO) recorded at 0 V/Ag after a voltammetric cycle in 1 M Bu_4NClO_4/CH_3CN (dotted line), 1 M $LiClO_4/CH_3CN$ (solid line), and 1 M $LiClO_4/H_2O$ (dashed line). (B) In situ electronic absorption spectra of PDHT (60 mC cm^{-2} on ITO) Recorded at 0 V/Ag after a voltammetric cycle in 1 M $LiClO_4/CH_3CN$ (solid line), same film immersed in hexafluoro-2-propanol (dotted line), and same film after recycling in 1 M $LiClO_4/CH_3CN$ (dashed line).

electroactive in aqueous media, contrary to PATs.[326] Furthermore, PDHT exhibits a specific electrochemical response in presence of Li$^+$ (Figure 17). These specific interactions with Li$^+$, make PDHT the first example of poly(heterocycle) capable to dope n with alkali cations.[324,325] As consequences of this high sensitivity toward environmental factors, reversible modifications of the optical spectrum can be induced by the solvent or the cation of the electrolytic medium in which the polymer has been cycled, or by immersion in strong hydrogen-bonding solvents[327] (Figure 18). These first evidences of solid-state solvatochromic and ionochromic effects have been interpreted in terms of feed-back control of the conformation and rigidity of the conjugated backbone by the interactions between the oligo(oxyethylene) side chains and the chemical environment.[327,328]

An interesting extension of this new class of functional CPs would consist in the derivatization of PT by macrocycles. However, the size of such substituents and the steric constraints imposed by the conservation of the effective conjugation will require spacer groups of considerable length. Such long spacers will drastically limit the interactions between the crown ether and the conjugated π system and hence the possibility to address the complexing properties of the macrocyclic cavity through the conjugated PT backbone. This difficulty is illustrated by the poor electrical and electrochemical properties of PT 3-substituted by nickel-cyclam through a $-(CH_2-CH_2)-$ spacer.[329] A possible answer to this problem consists in the simultaneous formation of the macrocyclic cavity and conjugated backbone by using as substrate for electropolymerization two thiophene rings linked together by an oligo(oxyethylene) chain (Figure 19). Preliminary investigations have shown that, in presence of Li$^+$, this substrate electropolymerizes at a potential 300 mV lower than PATs, indicating possible template-assisted ring closure. Furthermore, although less conjugated than some PTs substituted by linear polyether chains, the obtained polymer is highly electroactive, demonstrating thus the feasibility of this new approach.[332]

6. Redox Groups

With regard to the considerable amount of work devoted to poly(pyrrole) substituted by redox centers,[333] only a few examples of derivatization of PT by redox active groups have been described. This situation is partly due to the much higher oxidation potential of the

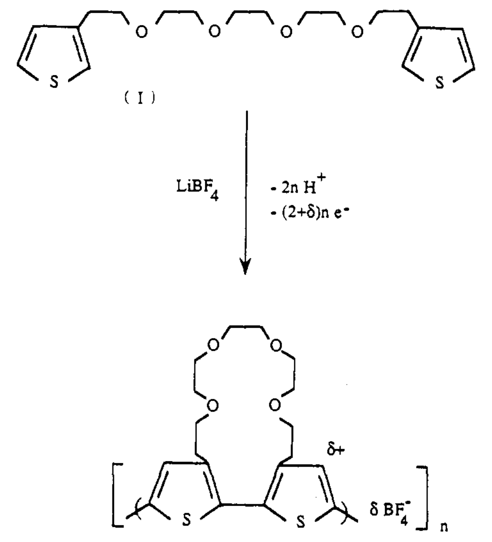


Figure 19. Electrosynthesis of poly(thiophenes) containing macrocyclic cavities.

thiophene ring which, in some cases, may lead to the degradation of the attached redox center during electropolymerization and also to the more drastic steric conditions imposed by the conservation of polymerizability in substituted PTs. Nevertheless, PTs 3-substituted by bipyridyl,[332] benzoquinone,[333] viologen,[205,334] ferrocene,[335] and tetrathiafulvalene[336] have been reported. Although not all of these materials have been characterized in detail, the electrochemical signature of the attached redox group is generally apparent in the voltammetric response of the obtained polymers.

7. Self-Doped Poly(thiophenes)

The concept of self-doped conducting polymers was introduced a few years ago with the synthesis of poly(3-thiophene-β-ethanesulfonate) and poly(3-thiophene-δ-butanesulfonate).[337] In these polymers, the charge-compensating anion is covalently bound to the polymeric backbone. Consequently, instead of anion incorporation, the charge compensation upon doping involves the expulsion of cationic species. Furthermore, the presence of the sulfonate group makes these polymers the first examples of water-soluble CPs. Due to the impossibility to polymerize the monomers in their acidic or sodium salt forms, the polymers have been prepared by electropolymerization of the corresponding methyl esters, followed by conversion to the polyelectrolytic form by methyl iodide in acetone.[337] Films cast from water solutions exhibited rather short conjugation (λ_{max} = 425 nm), and conductivities of ca. 10^{-2} S cm^{-1} increasing up to 1–10 S cm^{-1} upon exposure to bromine.[338] Higher conductivities have been reported for poly(3-thiophenepropanesulfonate) prepared by direct chemical polymerization of the monomer with FeCl$_3$.[339] A self-doped PT has been prepared from 3′-propanesulfonate trithiophene. Unlike the previous ones, this monomer electropolymerizes in acetonitrile without addition of supporting electrolyte, providing thus unambiguous evidence for self-doping.[114] This result has been attributed to the lower oxidation potential of the trimer compared to the monomer. The fact that the counteranion/monomer ratio is closer to its usual value of 25% is probably also a favorable factor. More recently, self-doped PTs with lower oxidation potentials and improved electrochemical behavior have been prepared from 3-(ω-carboxyalkyl)thiophenes with alkyl chains containing 4–14 carbons.[340]

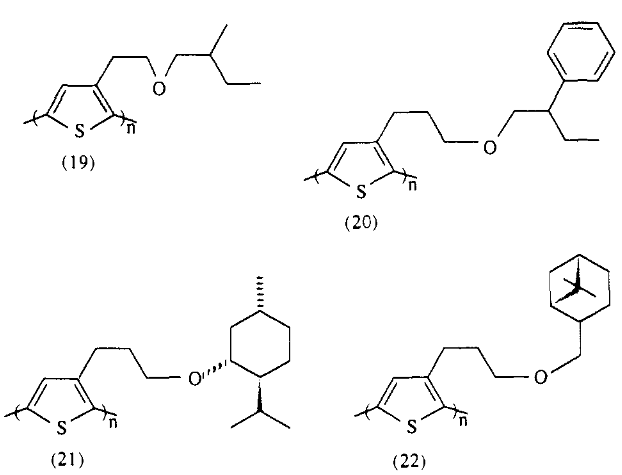


Figure 20. Chiral Poly(thiophenes).

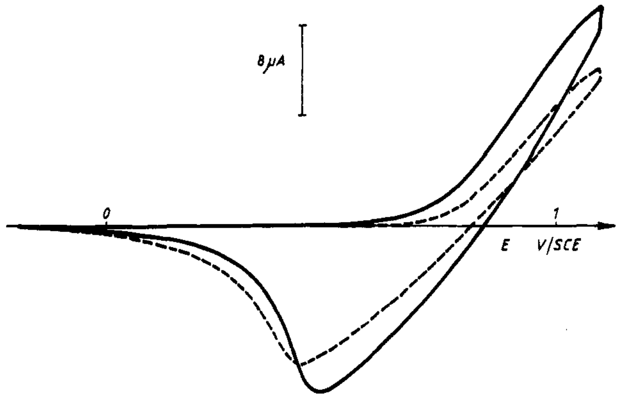


Figure 21. Cyclic voltammograms of **22** (deposition charge 400 mC cm^{-2} on Pt; electrode area 0.07 cm^2; scan rate 50 mV s^{-1}): solid line, 0.1 M (1*S*)-(+)-10-camphorsulfonic acid/CH$_3$CN; and dashed line, 0.1 M (1*R*)-(−)-10-camphorsulfonic acid/CH$_3$CN.

8. Chiral Poly(thiophenes)

Conjugated polymers substituted by optically active groups have potential technological applications as materials for enantioselective modified electrodes and membranes or for microwaves absorbers.[341] On the basis of the analyses of structural factors in PT functionalization,[192,314,317] polymers **19–22** have been synthesized by electropolymerization of enantiomeric monomers (Figure 20).[342] The polymers exhibited high stability and conductivities lying typically in the range of 1–10 S cm^{-1}. The high specific rotations measured on the two antipodes of **20** $\alpha^{22}{}_{D}$ = +3000° and −3000° have been interpreted by a macromolecular asymmetry arising from an helical polymer structure.[343] The analysis of the electrochemical behavior of the two antipodic forms of **20** using *d*- and *l*-camphorsulfonates as supporting electrolyte has shown that the amount of charge reversibly exchanged during voltammetric cycles is 50% higher in the presence of the *d*-anion for the (2*S*)-(+) polymer, whereas the reverse response is obtained with the (2*R*)-(−) polymer (Figure 21). These results constitute the first evidence of enantioselective molecular recognition on a chiral-conducting polymer (Figure 22).[344,345] More recently, the electropolymerization of (*S*)-(+)-3-(2-methylbutyl)thiophene provided another example of chiral PT.[346]

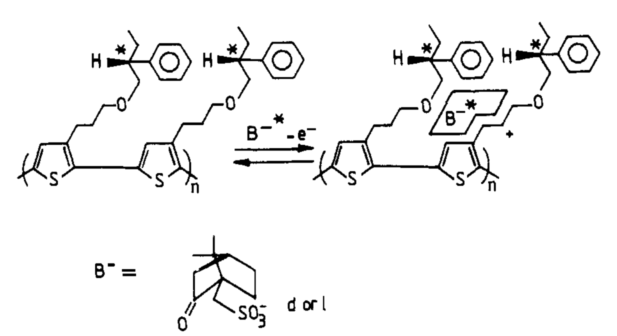


Figure 22. Enantioselective doping process of chiral poly(thiophenes).

VI. Applications of Poly(thiophenes)

Besides the fundamental problems posed by the elucidation of their structure, electronic, and electrochemical properties, the considerable research effort invested in the development of PTs is largely motivated by their multiple potential technological applications. These applications can be divided into three main groups resorting to (i) the electrical properties of the doped conducting state, (ii) the electronic properties of the neutral semiconducting state, and (iii) the electrochemical reversibility of the transition between the doped and the undoped states. A detailed survey of these various applications is beyond the scope of the present work and would deserve a specific review. Therefore, in this last section, the main fields of applications of PTs will be only briefly presented.

A. Applications of the Doped State

The development of a first domain of application, which concerns essentially antistatics and EMI shielding,[231] is conditioned by the processability of the materials and by the environmental long-term stability of the conductivity. Although these applications have not been intensively investigated yet, the recent development of conductive hybrid materials and of soluble PTs can trigger interesting new developments.

The sensitivity of the conductivity of PTs toward gases has been analyzed in several papers.[347-349] Exposure of PT films to NO and NO_2 increases their conductivity, whereas H_2S and NH_3 have opposite effect.[348,349] These results have led to the proposal of PT-based gas sensors; however, the selectivity of such devices is rather poor. A PT-based radiation detector has also been proposed on the basis of the conductivity changes observed upon irradiation with an electron beam in the presence of SF_6.[350]

Photoelectrodes used in photoelectrochemical solar cells generally involve small bandgap semiconductors such as Si, GaAs, CdS, or CdSe that are subject to rapid photocorrosion under illumination. In order to solve this problem, the use of electrodeposited thin films of poly(pyrrole) has been proposed.[351,352] These films which act as a barrier limits the photocorrosion while allowing electronic transfers between the semiconductor and the electrolytic medium. As an extension of this idea, GaAs photoanodes have been stabilized by thin films of electrogenerated PTs.[353,354] One of the main problem posed by this approach concerns the rapid undoping of the PT film which increases its resistivity and thus limits the efficiency of charge transfer between the electrode and the solution. Improved stabilizations have been achieved by means of copolymers of PBT and poly(pyrrole)[355,356] and more recently by the use of composite films of the same copolymer and PVC.[357]

B. Applications of the Undoped State

1. Electronic Devices

Various types of electronic devices involving the electronic properties of neutral PTs have been described. Photovoltaic cells based on electrogenerated PTs have been shown to present rather high quantum efficiencies under monochromatic illumination, but the overall conversion yield under polychromatic light remains low ($\simeq$0.15%).[358-360] Photoelectrochemical cells based on PTs- and CdS-PT junctions have been described[361-364] as well as a photochargeable device based on a bilayer membrane of PMeT and Prussian blue.[365] PT-GaAs and all organic PT-poly(pyrrole) p-n junctions have been also reported.[366,367] Schottky barriers and FETs involving electrogenerated PT[368-371] or solution cast PATs films[372,373] have been described by several groups. Thiophene oligomers, initially investigated as active material in photovoltaic devices in 1974,[140] have been used recently for the realization of Schottky diodes by vacuum sublimation.[374] Although these various works have demonstrated the feasibility of the use of PTs in electronic devices, the performances of these systems are still largely inferior to those of inorganic semiconductors.

The concept of molecular electronics is probably one of the most exciting in modern chemistry. Although it is sometimes abusively used to qualify almost any kind of electronic devices in which organic materials are involved, in its strict acception, molecular electronics or "chemionics"[375] refers to the possibility to achieve basic computer functions such as amplification, memory, and logical operations by means of single molecules.[376-378] This futuristic concept is expected to lead to fast switching speed and to allow the previsible limit to circuits miniaturization imposed by inorganic semiconductors to be surpassed. Although interesting experimental works have been carried out to test the feasibility of this concept,[379-381] its demonstration is still to be made. Besides enormous efforts of synthetic chemistry, the communication with and between molecular logical functions constitutes perhaps one of the most difficult problems. Recent developments in this field are oriented toward the synthesis of model molecules which could act as molecular wires,[375] or molecular rectifiers,[381] or to the preparation of LB films.[381,382] In this context, orthogonally fused thiophene oligomers have been recently synthesized,[383] whereas LB films containing thiophene oligomers[136,137] or PATs[384] have been also prepared.

2. Nonlinear Optics

The third-order nonlinear optical response of conjugated polymers has recently received much attention in general and PTs have attracted particular interest owing to their highly conjugated structure and to the recent improvements of their processability. Experiments carried out on PT and on several of its substituted derivatives have shown that PTs present a large and very fast nonlinear optical response.[385-388]

C. Electrochemical Applications

1. Energy Storage

Perhaps the most worldwide-discussed application of CPs concerns their use for electrical energy storage in rechargeable batteries. Although initial enthusiasm based on too optimistic performance evaluations has been tempered by several unresolved problems such as self-discharge and unsufficient cycle life, interest in this field of research remains high. Initial works used PT–iodine adducts in conjunction with Zn or Li electrodes. Primary and secondary cells were constructed using chemically and electrochemically prepared PTs, the latter leading to better performances.[389-391] More recent studies have confirmed the high voltage and good energy and power densities of PTs cells,[392-396] although self-discharge has been recognized as a serious problem.[395,396] Solid-state lithium cells involving poly(ethylene oxide)–$LiClO_4$ electrolytes and PT cathodes have been also assembled. However, these cells operate only beyond the phase-transition temperature of the electrolyte, i.e. 70 °C.[397] More recently, several substituted PTs have been investigated as possible electrode materials[398-400] and studies on PATs cells[398,399] have confirmed the influence of the polymer structure on the electrochemical behavior.

2. Electrochromic Devices

The considerable spectral changes in the visible region associated to the doping/undoping process of PTs have led to several proposals of electrooptical systems such as display devices or electrochromic windows. Initial characterizations revealed good optical contrast, response times ranging from 10 to 300 ms[401,402] and cycle life up to 1.2×10^5 charge–discharge cycles for PMeT films on bulk Pt electrodes.[403] Poly(isothianaphtene) films on semitransparent gold electrodes have been shown to retain ca. 75% of their initial optical density after 6×10^3 cycles.[404] More recent studies have underlined the essential role of the electrosynthesis conditions on the cycle life.[179] A comparative study of the electrooptical properties of poly(bithiophene), poly(dithieno(3,2-*b*:2′,3′-*d*)thiophene] and PMeT has shown that the latter led to the best results, confirming the influence of the polymer structure on the performance and durability of the devices.[405] Since PT derivatives are subject to overoxidation, the doping level and hence the potential at which the system is switched plays a determining role on its long-term stability. Thus cycle lives exceeding 10^7 cycles have been obtained on alkyl- and polyether-substituted PTs films operated at 10% of their maximum capacity.[192,406]

3. Electrochemical Sensors and Modified Electrodes

Selective modified electrodes and electrochemical devices appear as one of the most promising fields of application of PTs. Modified electrodes for electrocatalysis have been prepared from PMeT[407] or PT–metal hybrid materials.[234,237] On the other hand, the molecular and ionic recognitions observed with some functional PTs could find applications in selective modified electrodes for electrocatalytic or electroanalytical purposes.[325,345] The reversible electrochemical doping of a PT derivative with a neurotransmitter has been applied in a drug-release device.[408] All-organic electrochemical transistors have been realized in which the gate is constituted by a PMeT film deposited between the source and the drain, the drain current being driven by the electrochemically controlled conductivity of the PMeT film.[409] The device has been shown to be sensitive to oxidants and reductants and to amplify signals up to a kilohertz frequency.[410] More recently this concept has been extended to solid-state organic transistors using an ionic conductor solid electrolyte.[411]

VII. Conclusions and Perspectives

After 10 years of development, PTs occupy an original position in the growing class of conjugated electroactive polymers. As a matter of fact, in addition to their stability, electroactivity, and conductivity, PTs represent an almost unique class of materials in which structural versatility is associated with a moderate loss of conductivity. This particularity makes PT one of the most interesting substrates for the study of structure–properties relationships in conjugated polymers and for the design of functional conducting polymers.

Although the development of hybrid materials has significantly contributed to solving some important problems inherent to CPs such as insufficient mechanical properties and environmental stability, the most important advances have been accomplished through the manipulation of the monomer structure. Conducting polymers processable by conventional polymer techniques are now available, thus suppressing one of the main obstacles to their technological applications. On the other hand, the derivatization of the monomer has also triggered the emergence of a new generation of CPs in which the electronic and electrochemical properties of the conjugated backbone are coupled to specific functions, such as redox activity or molecular recognition, which can be addressed through the conjugated backbone. This new class of advanced molecular materials allows exciting sophisticated applications in the fields of selective sensors and molecular electronics to be envisioned.

The only important point where the manipulation of the monomer structure has not yet succeeded concerns the increase of the conductivity. Thus, until now, the most significant progress in the improvement of the molecular order and conductivity has been accomplished with the simplest thiophene derivatives, and the obtained conductivities are still far below the expected intrinsic conductivity of conjugated polymers.[412] Further progress in this area requires a better understanding of both the electropolymerization reaction and the structure–property relationships in PT substitution. As a matter of fact, although electropolymerization has been shown to lead to the most conducting PTs and to original structures such as helical poly(heterocycles), the mechanisms involved in several intermediate steps are not fully elucidated and it seems evident that a more detailed comprehension of these elementary processes can significantly contribute to the obtention of highly oriented defect-free polymers. On the other hand, the knowledge of the structure–properties relationships in PT substitution is still rather rudimentary. Progress in this direction will require enormous basic research effort since, as shown by many of the above examples, rather simple substitutions can have considerable consequences as they can affect both the formation and the various levels of organization of the material. Solutions to these fundamental problems may not be sufficient, but they are certainly necessary conditions if the idea, already envisioned 25 years ago, of synthesizing an ambient temperature superconducting polymer[413] should some day become a reality.

VIII. References

(1) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 11.
(2) Chiang, C. K.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098.
(3) Proceedings of ICSM '88, *Synth. Met.* **1989**, vol. 27–29.
(4) Diaz, A. F.; Kanazawa, K. K.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1979**, 635.
(5) Dall'Ollio, A.; Dascola, Y.; Gardini, G. P. *C.R. Acad. Sci.* **1969**, *267*, 4336.
(6) Diaz, A. F. *Chem. Scr.* **1981**, *17*, 142.
(7) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1982**, *135*, 173.
(8) Bargon, J.; Mohamand, S.; Waltman, R. J. *IBM J. Res. Develop.* **1983**, *27*, 330.
(9) Delamar, M.; Lacaze, P. C.; Dumousseau, J. Y.; Dubois, J. E. *Electrochim. Acta* **1982**, *27*, 61.
(10) Rault-Berthelot, J.; Simonet, J. *J. Electroanal. Chem.* **1985**, *182*, 187.
(11) Diaz, A. F.; Logan, J. A. *J. Electroanal. Chem.* **1980**, *111*, 111.
(12) McDiarmid, A. G.; Chiang, J. C.; Halpern, M.; Huang, H. S.; Mu, S. L.; Somasiri, N. L. D.; Wu, W.; Yaniger, S. I. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 173.
(13) Genies, E. M.; Tsintavis, C.; Syed, A. A. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 181.
(14) Waltman, R. J.; Bargon, J. *Can. J. Chem.* **1986**, *64*, 76.
(15) Diaz, A. F.; Lacroix, J. C. *New J. Chem.* **1988**, *12*, 171.
(16) Adamcova, Z.; Dempirova, L. *Prog. Org. Coat.* **1989**, *16*, 295.
(17) Chandler, G. K.; Pletcher, D. *Spec. Period. Rep. Electrochem.* **1985**, *10*, 117.
(18) Heinze, J. *Topics in Current Chemistry*; Springer-Verlag: Berlin, 1990; Vol. 152, p 1.
(19) Baker, G. L. *Electronic and Photonic Applications of Polymers*; Bowden, M. J., Turner, S. R., Eds.; ACS Advances in Chemistry Series 210; American Chemical Society: Washington, DC, 1988; p 271.
(20) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183.
(21) Tourillon, G. *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; p 294.
(22) Meisel, S. L.; Johnson, G. C.; Hartough, H. D. *J. Am. Chem. Soc.* **1950**, *72*, 1910.
(23) Steinkopft, W.; Leitsmann, R.; Hofmann, K. H. *Liebigs Ann. Chem.* **1941**, *546*, 180.
(24) Kooreman, H. J.; Wynberg, H. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 37.
(25) Wynberg, H.; Metselaar, J. *Synth. Commun.* **1984**, *14*, 1.
(26) Kagan, J.; Arora, S. K. *Heterocycles* **1983**, *20*, 1937.
(27) Kagan, J.; Arora, S. K. *Tetrahedron Lett.* **1983**, *24*, 4043.
(28) Berlin, A.; Pagani, G. A.; Sannicolo, F. *J. Chem. Soc., Chem. Commun.* **1986**, 1663.
(29) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 9.
(30) Lin, J. W. P.; Dudek, L. P. *J. Polym. Sci.* **1980**, *18*, 2869.
(31) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1503.
(32) Kobayashi, M.; Chen, J.; Moraes, T. C.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1984**, *9*, 77.
(33) Cunningham, D. D.; Laguren-Davidson, L.; Mark, H. B.; Pham, C. V.; Zimmer, H. *J. Chem. Soc., Chem. Commun.* **1987**, 1021.
(34) Hernandez, R.; Diaz, A. F.; Waltman, R. J.; Bargon, J. *J. Phys. Chem.* **1984**, *88*, 3333.
(35) Kossmehl, G.; Chatzitheodorou, G. *Makromol. Chem. Rapid Commun.* **1981**, *2*, 551.
(36) Gardini, G. P. *Adv. Heterocycl. Chem.* **1973**, *15*, 67.
(37) Sugimoto, R.; Takeda, S.; Gu, H. B.; Yoshino, K. *Chem. Express* **1986**, *1*, 635.
(38) Hotta, S.; Soga, M.; Sonoda, N. *Synth. Met.* **1988**, *26*, 267.
(39) Inoue, M. B.; Velasquez, E. F.; Inoue, M. *Synth. Met.* **1988**, *24*, 223.
(40) Fauvarque, J. F.; Petit, M. A.; Pfluger, T.; Jutand, A.; Chevrot, C. R. *Makromol. Chem. Rapid Commun.* **1983**, *4*, 455.
(41) Zotti, G.; Schiavon, G. *J. Electroanal. Chem.* **1984**, *163*, 385.
(42) Xu, Z.; Horowitz, G.; Garnier, F. *J. Electroanal. Chem.* **1988**, *246*, 467.
(43) Fleischmann, M.; Thirsk, H. R. *Advances in Electrochemistry and Electrochemical Engineering*; Delahay, P., Ed.; Wiley-Interscience: New York, 1963; Vol. 3, p 123.
(44) Asavapiriyanont, S.; Chandler, G. K.; Gunawardena, G. A.; Pletcher, D. *J. Electroanal. Chem.* **1984**, *177*, 229.
(45) Downward, A. J.; Pletcher, D. *J. Electroanal. Chem.* **1986**, *206*, 147.
(46) Hillman, A. R.; Mallen, E. *J. Electroanal. Chem.* **1987**, *220*, 351.
(47) Diaz, A. F.; Bargon, J. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; 1986; Vol. 1, p 82.
(48) Waltman, R. J.; Bargon, J. *Tetrahedron* **1984**, *40*, 3963.
(49) Genies, E.; Bidan, G.; Diaz, A. F. *J. Electroanal. Chem.* **1983**, *149*, 113.
(50) Inoue, T.; Yamase, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 985.
(51) Ambrose, J. F.; Nelson, R. F. *J. Electrochem. Soc.* **1968**, *115*, 1161.
(52) Adams, R. N. *Acc. Chem. Res.* **1969**, *2*, 175.
(53) Andrieux, C. P.; Audebert, P.; Hapiot, P.; Savéant, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2439.
(54) Roncali, J.; Garnier, F. *J. Phys. Chem.* **1988**, *92*, 833.
(55) Prezja, J.; Lundström, I.; Skotheim, T. *J. Electrochem. Soc.* **1982**, *129*, 1685.
(56) Takakubo, M. *J. Electroanal. Chem.* **1989**, *258*, 303.
(57) Melander, L.; Saunders, W. H. *Reaction rates of isotopic molecules*; Wiley: New York, 1980.
(58) Lemaire, M.; Delabouglise, D.; Garreau, R.; Roncali, J. *Recent Advances in Electro-Organic Synthesis*; Torii, S., Ed.; Elsevier Science Publishers: Amsterdam, 1987; p 341.
(59) Delabouglise, D.; Garreau, R.; Lemaire, M.; Roncali, J. *New J. Chem.* **1988**, *12*, 155.
(60) Lang, P.; Chao, F.; Costa, M.; Garnier, F. *Polymer* **1987**, *28*, 668.
(61) Hamnett, A.; Hillman, A. R. *J. Electrochem. Soc.* **1988**, *135*, 2517.
(62) Hillman, A. R.; Mallen, E. *J. Electroanal. Chem.* **1988**, *243*, 403.
(63) Hillman, A. R.; Swann, M. J. *Electrochim. Acta* **1988**, *33*, 1303.
(64) Tanaka, K.; Shichiri, T.; Wang, S.; Yamabe, T. *Synth. Met.* **1988**, *24*, 203.
(65) Christensen, P. A.; Hamnett, A.; Hillman, A. R. *J. Electroanal. Chem.* **1988**, *242*, 47.
(66) Tourillon, G.; Dartyge, E.; Fontaine, A.; Garrett, R.; Sagurton, M.; Xu, P.; Williams, G. P. *Europhys. Lett.* **1987**, *4*, 1391.
(67) Roncali, J.; Yassar, A.; Garnier, F. *J. Chem. Soc., Chem. Commun.* **1988**, 581.
(68) Yassar, A.; Roncali, J.; Garnier, F. *Macromolecules* **1989**, *22*, 804.
(69) Roncali, J.; Garnier, F.; Lemaire, M.; Garreau, R. *Synth. Met.* **1986**, *15*, 323.
(70) Roncali, J.; Garnier, F. *New J. Chem.* **1986**, *4–5*, 237.
(71) Czerwinski, A.; Zimmer, H.; Pham, C. V.; Mark, H. B., Jr. *J. Electrochem. Soc.* **1985**, *132*, 2669.
(72) Turcu, R.; Pană, O.; Bratu, I.; Bogdan, M. *J. Mol. Electron.* **1990**, *6*, 1.
(73) Tourillon, G.; Garnier, F. *J. Phys. Chem.* **1983**, *87*, 2289.
(74) Waltman, R. J.; Bargon, J.; Diaz, A. F. *J. Phys. Chem.* **1983**, *87*, 1459.
(75) Kaneto, K.; Kohno, Y.; Yoshino, K.; Inuishi, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 382.
(76) Hotta, S.; Hosaka, T.; Shimotsuma, W. *Synth. Met.* **1983**, *6*, 69.
(77) Hotta, S.; Hosaka, T.; Shimotsuma, W. *Synth. Met.* **1983**, *6*, 317.
(78) Tanaka, S.; Sato, M.; Kaeriyama, K. *Makromol. Chem.* **1984**, *185*, 1295.
(79) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1985**, 713.
(80) Sato, M.; Tanaka, S.; Kaeriyama, K. *Synth. Met.* **1986**, *14*, 279.
(81) Imanishi, K.; Satoh, M.; Yasuda, Y.; Tsushima, R.; Aoki, S. *J. Electroanal. Chem.* **1988**, *242*, 203.
(82) Tourillon, G.; Garnier, F. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, 22, 33.
(83) Reynolds, J. R.; Hsu, S.-G.; Arnott, H. J. *J. Polym. Sci., Part B. Polym. Phys.* **1989**, *27*, 2081.
(84) Marque, P.; Roncali, J.; Garnier, F. *J. Electroanal. Chem.* **1987**, *218*, 107.
(85) Garnier, F.; Tourillon, G.; Barraud, J. Y.; Dexpert, H. *J. Mater. Sci.* **1984**, *161*, 51.
(86) Warren, L. F.; Walker, J. A.; Anderson, D. P.; Rhodes, C. G. *J. Electrochem. Soc.* **1989**, *136*, 2286.
(87) Nilsson, J. D.; Inganäs, O. *Synth. Met.* **1989**, *31*, 359.
(88) Tanaka, K.; Shichiri, T.; Yamabe, T. *Synth. Met.* **1986**, *16*, 207.
(89) Deng, Z.; Smyrl, W. H.; White, H. S. *J. Electrochem. Soc.* **1989**, *136*, 2152.
(90) Yassar, A.; Roncali, J. Unpublished results.
(91) Aeiyach, S.; Kone, A.; Dieng, M.; Aaron, J. J.; Lacaze, P. C. *J. Chem. Soc., Chem. Commun.* **1991**, 822.
(92) Roncali, J.; Yassar, A.; Garnier, F. *Synth. Met.* **1989**, *28*, C275.

(93) Roncali, J.; Yassar, A.; Garnier, F. *J. Chim. Phys.* **1989**, *86*, 85.
(94) Hotta, S. *Synth. Met.* **1988**, *22*, 103.
(95) Zotti, G.; Cattarin, S.; Comisso, N. *J. Electroanal. Chem.* **1987**, *235*, 259.
(96) Otero, T. F.; de Larreta-Azelain, E. *J. Chim. Phys.* **1989**, *86*, 131.
(97) Ito, M.; Shioda, H.; Tanaka, K. *J. Polym. Sci.* **1986**, *24*, 147.
(98) Ito, M.; Tsuruno, A.; Osawa, S.; Tanaka, K. *Polymer* **1988**, *29*, 1161.
(99) Krische, B.; Zagorska, M. *Synth. Met.* **1989**, *28*, C263.
(100) Gratzl, M.; Duan-Fu Hsu; Riley, A. M.; Janata, J. *J. Phys. Chem.* **1990**, *94*, 5973.
(101) Roncali, J.; Garreau, R.; Garnier, F.; Lemaire, M. *Synth. Met.* **1987**, *18*, 139.
(102) Gamaggi, G. M.; Deluca, G.; Tundo, A. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1594.
(103) Diaz, A. F.; Crowley, J.; Bargon, J.; Gardini, G. P.; Torrance, J. B. *J. Electroanal. Chem.* **1981**, *121*, 355.
(104) Galal, A.; Lewis, E. T.; Ataman, O. Y.; Zimmer, H.; Mark, H. B., Jr. *J. Polym. Sci.* **1989**, *27*, 1891.
(105) Heinze, J.; Mortensen, J.; Hinkelmann, K. *Synth. Met.* **1987**, *21*, 209.
(106) Eales, R. M.; Hillman, A. R. *J. Electroanal. Chem.* **1988**, *250*, 219.
(107) Yumoto, Y.; Yoshimura, S. *Synth. Met.* **1985**, *13*, 185.
(108) Martinez, F.; Voelkel, R.; Naegele, D.; Naarmann, H. *Mol. Cryst. Liq. Cryst.* **1989**, *167*, 227.
(109) Druy, M. A.; Seymour, R. J. *J. Phys. (Paris) Colloq. C3* **1983**, *44*, 595.
(110) Druy, M. A.; Seymour, R. J.; Tripathy, S. K. *A.C.S. Symp. Ser., Polymers in Electronics* **1984**, *37*, 473.
(111) Funt, B. L.; Lowen, S. V. *Synth. Met.* **1985**, *11*, 129.
(112) Inganäs, O.; Liedberg, B.; Wu, C. R.; Wynberg, H. *Synth. Met.* **1985**, *11*, 239.
(113) Krische, B.; Hellberg, J.; Lilja, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1476.
(114) Havinga, E. E.; Van Horssen, L. W. *Makromol. Chem. Makromol. Symp.* **1989**, *24*, 67.
(115) Ferraris, J. P.; Hanlon, R. T. *Polymer* **1989**, *30*, 1319.
(116) Laguren-Davidson, L.; Chiem Van Pham; Zimmer, H.; Mark, H. B., Jr. *J. Electrochem. Soc.* **1988**, *135*, 1406.
(117) Zotti, G.; Schiavon, G. *Synth. Met.* **1990**, *39*, 183.
(118) Eales, R. M.; Hillman, A. R. *J. Mater. Sci.* **1990**, *25*, 3806.
(119) Di Marco, P.; Mastragostino, M.; Taliani, C. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 241.
(120) Danieli, R.; Ostoja, P.; Tiecco, M.; Zamboni, R.; Taliani, C. *J. Chem. Soc., Chem. Commun.* **1986**, 1473.
(121) Pelter, A.; Maud, J. M.; Jenkins, I.; Sadeka, C.; Coles, G. *Tetrahedron Lett.* **1989**, *30*, 3461.
(122) Tanaka, S.; Kaeriyama, K. *Polym. Commun.* **1990**, *31*, 172.
(123) Tanaka, S.; Sato, M.; Kaeriyama, K. *Makromol. Chem.* **1985**, *186*, 1685.
(124) Bäuerle, P.; Wrighton, M. S.; Chyan, O. M. R.; Spangler, C. R. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 889.
(125) Berlin, A.; Wernet, W.; Wegner, G. *Makromol. Chem.* **1987**, *188*, 2963.
(126) Martinez, M.; Reynolds, J. R.; Basak, S.; Black, D. A.; Marynyck, D. S.; Pomerantz, M. *J. Polym. Sci.* **1988**, *26*, 911.
(127) Jen, K. Y.; Maxfield, M. R.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1987**, 309.
(128) Yamada, S.; Tokito, S.; Tsutsui, T.; Saito, S. *J. Chem. Soc., Chem. Commun.* **1987**, 1448.
(129) Cao, Y.; Guo, D.; Pang, M.; Qian, R. *Synth. Met.* **1987**, *18*, 189.
(130) Alberti, A.; Favaretto, L.; Seconi, G. *J. Chem. Soc., Perkin Trans.* **1990**, 931.
(131) Fujimoto, H.; Nagashima, U.; Inokuchi, H.; Seki, K.; Cao, Y.; Nakahara, H.; Nakayama, J.; Hoshino, M.; Fukuda, K. *J. Chem. Phys.* **1990**, *92*, 4077.
(132) Jones, D.; Guerra, M.; Favaretto, L.; Modelli, A.; Fabrizio, M.; Distefano, G. *J. Phys. Chem.* **1990**, *94*, 5761.
(133) Zerbi, G.; Chierichetti, B.; Inganäs, O. *J. Chem. Phys.* **1991**, *94*, 4637.
(134) Caspar, J.; Ramamurthy, V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 600.
(135) Fichou, D.; Horowitz, G.; Garnier, F. *Synth. Met.* **1990**, *39*, 125.
(136) Tasaka, S.; Katz, H. E.; Hutton, R. S.; Orenstein, J.; Frederickson, G. G.; Wang, T. T. *Synth. Met.* **1986**, *16*, 17.
(137) Nakahara, H.; Nakayama, J.; Hoshino, M.; Fukuda, K. *Thin Solid Films* **1988**, *160*, 87.
(138) Hotta, S. *Synth. Met.* **1989**, *32*, 395.
(139) Yamamoto, T.; Kashiwazaki, A.; Kato, K. *Makromol. Chem.* **1989**, *190*, 1649.
(140) Schoeler, U.; Tews, K. H.; Khun, H. *J. Chem. Phys.* **1974**, *61*, 5009.
(141) Lemaire, M.; Büchner, W.; Garreau, R.; Huynh, A. H.; Guy, A.; Roncali, J. *J. Electroanal. Chem.* **1990**, *281*, 293.
(142) Roncali, J.; Guy, A.; Lemaire, M.; Garreau, R.; Huynh, A. H. *J. Electroanal. Chem.* **1991**, *312*, 277.
(143) Brédas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1981**, *105*, 6555.
(144) Tanaka, K.; Schichiri, T.; Yamabe, T. *Synth. Met.* **1986**, 271.
(145) Hotta, S.; Hosaka, T.; Soga, M.; Shimotsuma, W. *Synth. Met.* **1984**, *10*, 95.
(146) Hotta, S.; Hosaka, T.; Shimotsuma, W. *J. Chem. Phys.* **1984**, *80*, 954.
(147) Cao, Y.; Qian, R. *Solid State Commun.* **1985**, *54*, 211.
(148) Pfluger, P.; Street, G. B. *J. Chem. Phys.* **1984**, *80*, 544.
(149) Neugebauer, H.; Nauer, G.; Neckel, A.; Tourillon, G.; Garnier, F.; Lang, P. *J. Phys. Chem.* **1984**, *88*, 652.
(150) Furukawa, Y.; Akimito, M.; Harada, I. *Synth. Met.* **1987**, *18*, 189.
(151) Sauvajol, J. L.; Chenouni, D.; Père-Porte, J. P.; Chorro, C.; Moukala, B.; Petrissans, J. *Synth. Met.* **1990**, *38*, 1.
(152) Mo, Z.; Lee, K. B.; Moon, Y. B.; Kobayashi, M.; Heeger, A. J.; Wudl, F. *Macromolecules* **1985**, *18*, 1972.
(153) Orchard, B. J.; Freidenreich, B.; Tripathy, S. K. *Polymer* **1986**, *27*, 1533.
(154) Cui, C. X.; Kertesz, M. *Phys. Rev. B* **1989**, *40*, 9661.
(155) Yang, R.; Dalsin, K. R.; Evans, D. F.; Christensen, L.; Hendrickson, W. A. *J. Phys. Chem.* **1989**, *93*, 511.
(156) Suzuki, N.; Ozaki, M.; Etemad, S.; Heeger, A. J.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1980**, *45*, 1209.
(157) Brédas, J. L.; Thémans, B.; André, J. M.; Chance, R. R.; Silbey, R. *Synth. Met.* **1984**, *9*, 265.
(158) Brédas, J. L.; Chance, R. R.; Silbey, R. *Phys. Rev. B* **1982**, *26*, 5843.
(159) Lauchlan, L.; Etamad, S.; Chung, T. C.; Heeger, A. J.; MacDiarmid, A. G. *Phys. Rev. B* **1981**, *24*, 3701.
(160) Chung, T. C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1984**, *30*, 702.
(161) Tourillon, G.; Gourier, D.; Garnier, F.; Vivien, D. *J. Phys. Chem.* **1984**, *88*, 1049.
(162) Mintmire, J. W.; White, C. T.; Elert, M. L. *Synth. Met.* **1986**, *16*, 235.
(163) Kaneto, K.; Kohno, Y.; Yoshino, K. *Solid State Commun.* **1984**, *51*, 267.
(164) Marque, P. Ph.D. Thesis, University of Paris VI, 1988.
(165) Harbeke, G.; Meier, E.; Kobel, W.; Egli, M.; Kiess, H.; Tosatti, E. *Solid State Commun.* **1985**, *55*, 419.
(166) Murao, K.; Suzuki, K. *Solid State Commun.* **1987**, *62*, 483.
(167) Kaneto, K.; Uesugi, F.; Yoshino, K. *Solid State Commun.* **1987**, *64*, 1195.
(168) Chen, J.; Heeger, A. J.; Wudl, F. *Solid State Commun.* **1986**, *58*, 251.
(169) Colaneri, N.; Nowak, M.; Spiegel, D.; Hotta, S.; Heeger, A. J. *Phys. Rev. B* **1987**, *36*, 7964.
(170) Schärli, M.; Kiess, H.; Harbeke, G.; Berlinger, W.; Blazey, K. W.; Müller, K. A. *Synth. Met.* **1988**, *22*, 317.
(171) Tourillon, G.; Flank, A. M.; Lagarde, P. *J. Phys. Chem.* **1988**, *92*, 4397.
(172) Jugnet, Y.; Tourillon, G.; Duc, T. M. *Phys. Rev. Lett.* **1986**, *56*, 1862.
(173) Sun, Z. W.; Frank, A. J. *J. Chem. Phys.* **1991**, *94*, 4600.
(174) Loutfy, R. O. *J. Chem. Phys.* **1977**, *66*, 4781.
(175) Lyons, L. E. *Aust. J. Chem.* **1980**, *33*, 1717.
(176) Kaner, R. B.; Porter, S. J.; Nairns, D. P.; MacDiarmid, A. G. *J. Chem. Phys.* **1989**, *90*, 5102.
(177) Laviron, E. *J. Electroanal. Chem.* **1980**, *122*, 37.
(178) Andrieux, C. P.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Electroanal. Chem.* **1982**, *131*, 1.
(179) Marque, P.; Roncali, J.; Garnier, F. Extended abstracts of the 38th Meeting of the International Society for Electrochemistry, 14–18 Sept. 1987, Maastricht, Netherlands.
(180) Krische, B.; Zagorska, M. *Synth. Met.* **1989**, *28*, C257.
(181) Chao, F.; Costa, M.; Baudoin, J. L. *J. Chim. Phys.* **1990**, *87*, 1109.
(182) Hubbard, A. T.; Anson, F. C. *Anal. Chem.* **1966**, *38*, 1887.
(183) Laviron, E. *J. Electroanal. Chem.* **1972**, *39*, 1.
(184) Diaz, A. F.; Castillo, J. I.; Logan, J. A.; Lee, W. Y. *J. Electroanal. Chem.* **1981**, *129*, 115.
(185) Heinze, J.; Störzbach, M.; Mortensen, J. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 960.
(186) Feldberg, S. W. *J. Am. Chem. Soc.* **1984**, *106*, 4671.
(187) Vieil, E.; Oudard, J. F. *Ann. Phys. Colloq.* **1986**, *11*, 17.
(188) Bull, R. A.; Fan, F. R.; Bard, A. J. *J. Electrochem. Soc.* **1984**, *129*, 4671.
(189) Mermilliod, N.; Tanguy, J.; Petiot, F. *J. Electrochem. Soc.* **1986**, *133*, 1073.
(190) Tanguy, J.; Slama, M.; Hoclet, M.; Baudoin, J. L. *Synth. Met.* **1989**, *28*, C145.
(191) Servagent, S.; Vieil, E. *Synth. Met.* **1989**, *31*, 127.
(192) Roncali, J.; Garreau, R.; Yassar, A.; Marque, P.; Garnier, F.; Lemaire, M. *J. Phys. Chem.* **1987**, *91*, 6706.
(193) Roncali, J.; Marque, P.; Garreau, R.; Garnier, F.; Lemaire, M. *Macromolecules* **1990**, *23*, 1347.
(194) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1984**, *161*, 51.

(195) Heinze, J.; Bilger, R.; Meerholz, K. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 1266.
(196) Zotti, G.; Schiavon, G. *Synth. Met.* **1989**, *31*, 347.
(197) Marque, P.; Roncali, J. *J. Phys. Chem.* **1990**, *94*, 8614.
(198) Chao, F.; Costa, M. *Synth. Met.* **1990**, *39*, 97.
(199) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1984**, *161*, 407.
(200) Roncali, J.; Garnier, F. *J. Chem. Soc., Chem. Commun.* **1986**, 783.
(201) Pern, F.-J.; Frank, A. J. *J. Electrochem. Soc.* **1990**, *137*, 2769.
(202) Sunde, S.; Hagen, G.; Ödegård, R. *Synth. Met.* **1991**, *41–43*, 2983.
(203) Roncali, J. Unpublished results.
(204) Zang, X.; Leddy, J.; Bard, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 3719.
(205) Ofer, D.; Crooks, R. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7869.
(206) Mammone, R. J.; Binder, M. *J. Electrochem. Soc.* **1988**, *135*, 1057.
(207) Ochmanska, J.; Pickup, P. G. *J. Electroanal. Chem.* **1991**, *297*, 211.
(208) Lee, I. C.; Zimmer, H.; Mark, H. B., Jr. *J. Chem. Soc., Chem. Commun.* **1989**, 497.
(209) Zhou, Q.-X.; Kolaskie, C. J.; Miller, L. L. *J. Electroanal. Chem.* **1987**, *223*, 283.
(210) Baudoin, J. L.; Chao, F.; Costa, M. *J. Chim. Phys.* **1989**, *86*, 181.
(211) Servagent, S.; Vieil, E. *J. Electroanal. Chem.* **1990**, *280*, 227.
(212) Kaneto, K.; Ura, S.; Yoshino, K.; Inuishi, Y. *Jpn. J. Appl. Phys.* **1984**, *23*, L189.
(213) Aizawa, M.; Watanabe, S.; Shinohara, H.; Shirakawa, H. *J. Chem. Soc., Chem. Commun.* **1985**, 264.
(214) Crooks, R. M.; Chyan, O. M. R.; Wrighton, M. S. *Chem. Mater.* **1989**, *1*, 21.
(215) De Paoli, M. A.; Waltman, R. J.; Diaz, A. F.; Bargon, J. *J. Chem. Soc. Chem. Commun.* **1984**, 1015.
(216) Niwa, O.; Tamamura, T. *J. Chem. Soc., Chem. Commun.* **1984**, 817.
(217) Ojio, T.; Miyata, S. *Polym. J.* **1986**, *18*, 95.
(218) Bocchi, V.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1986**, 148.
(219) Yassar, A.; Roncali, J.; Garnier, F. *Polym. Commun.* **1987**, *28*, 103.
(220) Roncali, J.; Mastar, A.; Garnier, F. *Synth. Met.* **1987**, *18*, 857.
(221) Druy, M. A. *J. Electrochem. Soc.* **1986**, *133*, 353.
(222) Druy, M. A.; Rubner, M. F.; Walsh, S. P. *Synth. Met.* **1986**, *13*, 207.
(223) Niwa, O.; Tamamura, T. *Synth. Met.* **1987**, *20*, 235.
(224) Kathirgamanathan, P. *J. Electroanal. Chem.* **1988**, *247*, 351.
(225) Wang, H. L.; Toppare, L.; Fernandez, J. E. *Macromolecules* **1990**, *23*, 1053.
(226) Shigehara, K.; Hara, M.; Yamada, A. *Synth. Met.* **1987**, *18*, 721.
(227) Orata, D.; Buttry, D. *J. Electroanal. Chem.* **1988**, *257*, 71.
(228) Hirai, T.; Kuwakata, S.; Yonehama, H. *J. Electrochem. Soc.* **1988**, *135*, 1132.
(229) Bidan, G.; Ehui, B. *J. Chem. Soc., Chem. Commun.* **1989**, 1568.
(230) Zoppi, R. A.; De Paoli, M. A. *J. Electroanal. Chem.* **1990**, *290*, 275.
(231) Dubois, J. C.; Sagnes, O.; Henry, F. *Synth. Met.* **1989**, *28*, C871.
(232) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J. *Synth. Met.* **1987**, *22*, 79.
(233) Laakso, J.; Österholm, J. E.; Nyholm, P. *Synth. Met.* **1989**, *28*, C467.
(234) Tourillon, G.; Garnier, F. *J. Phys. Chem.* **1984**, *88*, 5281.
(235) Tourillon, G.; Dartyge, E.; Dexpert, H.; Fontaine, A.; Jucha, A.; Lagarde, P.; Sayers, D. E. *J. Electroanal. Chem.* **1984**, *178*, 357.
(236) Gourier, D.; Tourillon, G. *J. Phys. Chem.* **1986**, *90*, 5561.
(237) Yassar, A.; Roncali, J.; Garnier, F. *J. Electroanal. Chem.* **1988**, *255*, 53.
(238) Yassar, A.; Roncali, J.; Garnier, F. *J. Chim. Phys.* **1989**, *86*, 241.
(239) Czerwinski, A.; Zimmer, H.; Amer, A.; Chiem van Pham; Pons, S.; Mark, H. B., Jr. *J. Chem. Soc., Chem. Commun.* **1985**, 1158.
(240) Shinohara, H.; Aizawa, M.; Shirakawa, H. *J. Chem. Soc., Chem. Commun.* **1986**, 209.
(241) Kanatzidis, M. G.; Tonge, L. M.; Marks, T. J.; Marcy, H. O.; Kannewurf, C. R. *J. Am. Chem. Soc.* **1987**, *109*, 3797.
(242) Enzel, P.; Bein, T. *J. Chem. Soc., Chem. Commun.* **1989**, 1326.
(243) Kanatzidis, M. G.; Marcy, H. O.; McCarthy, W. J.; Kannewurf, C. R.; Marks, T. J. *Solid State Ionics* **1989**, *32/33*, 594.
(244) Kanatzidis, M. G.; Chun-Guey, Wu; Marcy, H. O.; DeGroot, D. C.; Kannewurf, C. R. *Chem. Mater.* **1990**, *2*, 222.
(245) Naitoh, S.; Sanui, K.; Ogata, N. *J. Chem. Soc., Chem. Commun.* **1986**, 1348.
(246) Mitsuhara, T.; Tanaka, S.; Kaeriyama, K. *Makromol. Chem.* **1988**, *189*, 1755.
(247) Ferraris, J. P.; Andrus, R. G.; Hrncir, D. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1318.
(248) Monthéard, J. P.; Pascal, T.; Seytre, G.; Boiteux, G. *Makromol. Chem. Rapid Commun.* **1985**, *6*, 679.
(249) Pouwer, K. L.; Vries, T. R.; Havinga, E. E.; Meijer, E. W.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1988**, 1432.
(250) Ruiz, J. P.; Child, A. D.; Nayak, K.; Marynick, D. S.; Reynolds, J. R. *Synth. Met.* **1991**, *41–43*, 783.
(251) Kossmehl, G.; Hartel, M.; Manecke, G. *Makromol. Chem.* **1970**, *131*, 15.
(252) Jen, K. W.; Eckhardt, H.; Jow, T. R.; Shacklette, L. W.; Elsenbaumer, R. L. *J. Chem. Soc. Chem. Commun.* **1988**, 215.
(253) Huang, W.-S.; Park, J. M. *J. Chem. Soc. Chem. Commun.* **1987**, 856.
(254) Nalwa, H. S. *Synth. Met.* **1990**, *35*, 387.
(255) Jenekhe, S. *Macromolecules* **1990**, *23*, 2848.
(256) Albery, W. J.; Fengbin, L.; Mount, A. R. *J. Electroanal. Chem.* **1991**, *310*, 239.
(257) Li, H. S.; Roncali, J.; Garnier, F. *J. Electroanal. Chem.* **1989**, *263*, 155.
(258) Ruiz, J. P.; Nayak, K.; Marynick, D. S.; Reynolds, J. R. *Macromolecules* **1989**, *22*, 1231.
(259) Tanaka, S.; Sato, M.; Kaeriyama, K. *Synth. Met.* **1988**, *25*, 277.
(260) Roncali, J.; Garnier, F.; Garreau, R.; Lemaire, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1500.
(261) Garreau, R.; Roncali, J.; Garnier, F.; Lemaire, M. *J. Chim. Phys.* **1989**, *86*, 1, 93.
(262) Tsai, E. W.; Basak, S.; Ruiz, J. P.; Reynolds, J. R.; Rajeshwar, K. *J. Electrochem. Soc.* **1989**, *136*, 3683.
(263) Dian, G.; Barbey, G.; Decroix, B. *Synth. Met.* **1986**, *13*, 281.
(264) Chang, A.-C.; Blankespoor, R. L.; Miller, L. L. *J. Electroanal. Chem.* **1987**, *236*, 239.
(265) Lowen, S. V.; MacInnes, D.; Funt, B. L. *J. Polym. Sci. A.* **1989**, *27*, 4087.
(266) Tanaka, S.; Sato, M.; Kaeriyama, K. *Polym. Commun.* **1985**, *26*, 303.
(267) Feldhues, M.; Kämpf, G.; Litterer, H.; Mecklenburg, T.; Wegener, P. *Synth. Met.* **1989**, *28*, C487.
(268) Tanaka, S.; Sato, M.; Kaeriyama, K. *Synth. Met.* **1988**, *25*, 303.
(269) Zagorska, M.; Kulszewicz-Bajer, I.; Lapkowski, M.; Laska, J.; Hasik, M.; Pron, A. *Synth. Met.* **1991**, *41–43*, 3009.
(270) Dietrich, M.; Heinze, J. *Synth. Met.* **1991**, *41–43*, 503.
(271) Brédas, J. L.; Street, G. B.; Thémans, B.; André, J. M. *J. Chem. Phys.* **1985**, *83*, 1323.
(272) Daoust, G.; Leclerc, M. *Macromolecules* **1991**, *24*, 455.
(273) Jonas, F.; Schrader, L. *Synth. Met.* **1991**, *41–43*, 831.
(274) Wudl, F.; Kobayashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, *49*, 3382.
(275) Jen, K. Y.; Elsenbaumer, R. L. *Synth. Met.* **1986**, *16*, 379.
(276) Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. *J. Chem. Phys.* **1984**, *82*, 5717.
(277) Ikenoue, Y.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1991**, *40*, 1.
(278) Di Marco, P.; Mastragostino, M.; Taliani, C. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 241.
(279) Danieli, R.; Taliani, C.; Zamboni, R.; Giro, G.; Biserni, M.; Mastragostino, M.; Testoni, A. *Synth. Met.* **1986**, *13*, 325.
(280) Jow, T. R.; Jen, K. Y.; Elsenbaumer, R. L.; Shacklette, L. W.; Angelopoulos, M.; Cava, M. P. *Synth. Met.* **1986**, *14*, 53.
(281) Taliani, C.; Zamboni, R.; Danieli, R.; Ostoja, P.; Porzio, W.; Lazzaroni, R.; Brédas, J. L. *Phys. Scr.* **1989**, *40*, 781.
(282) Lazzaroni, R.; Riga, J.; Verbist, J. J.; Christaens, L.; Renson, M. *J. Chem. Soc., Chem. Commun.* **1985**, 999.
(283) Bolognesi, A.; Catellani, M.; Destri, S.; Zamboni, R.; Taliani, C. *J. Chem. Soc., Chem. Commun.* **1988**, 246.
(284) Bolognesi, A.; Catellani, M.; Destri, S.; Porzio, W.; Danieli, R.; Rossini, S.; Taliani, C.; Zamboni, R.; Ostoja, P. *Synth. Met.* **1989**, *28*, C521.
(285) Lambert, T. L.; Ferraris, J. P. *J. Chem. Soc., Chem. Commun.* **1991**, 752.
(286) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1986**, 873.
(287) Lemaire, M.; Roncali, J.; Garnier, F.; Garreau, R.; Hannecart, E. French Pat. 86.04744, April 4, 1986.
(288) Jen, K. Y.; Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1346.
(289) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212.
(290) Lemaire, M.; Garreau, R.; Garnier, F.; Roncali, J. *New J. Chem.* **1987**, *11*, 703.
(291) Yoshino, K.; Nakajima, S.; Onoda, M.; Sugimoto, R. *Synth. Met.* **1989**, *28*, C349.
(292) Österholm, J. E.; Laakso, J.; Nyholm, P.; Isotalo, H.; Stubb, H.; Inganäs, O.; Salaneck, W. R. *Synth. Met.* **1989**, *28*, C435.
(293) Cao, Y.; Wu, Q.; Guo, K.; Qian, R. *Makromol. Chem.* **1984**, *185*, 389.
(294) Frommer, J. E. *Acc. Chem. Res.* **1986**, *19*, 2.

(295) Masuda, H.; Tanaka, S.; Kaeriyama, K. *Synth. Met.* **1989**, *31*, 29.
(296) Leclerc, M.; Martinez Diaz, F.; Wegner, G. *Makromol. Chem.* **1989**, *190*, 3105.
(297) Bobacka, J.; Ivaska, A.; Grzeszcuk, M. *Synth. Met.* **1991**, *44*, 9.
(298) Gustafsson, G.; Inganås, O.; Nilsson, J. O.; Liedberg, B. *Synth. Met.* **1988**, *26*, 297.
(299) Attard, G. S.; Williams, G. *Chem. Brit.* **1986**, Oct, 919.
(300) Nowak, M. J.; Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J. *Macromolecules* **1987**, *20*, 965.
(301) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci. B* **1987**, *25*, 1071.
(302) Inganäs, O.; Salaneck, W. R.; Österholm, J. E.; Laakso, J. *Synth. Met.* **1988**, *22*, 395.
(303) Salaneck, W. R.; Inganås, O.; Nilsson, J. O.; Thêmans, B.; Brēdas, J. L. *Synth. Met.* **1989**, *28*, C451.
(304) Sundberg, M.; Inganäs, O.; Stafström, S.; Gustafsson, G.; Sjögren, B. *Solid State Commun.* **1989**, *71*, 435.
(305) Yoshino, K.; Nakao, K.; Onada, M.; Sugimoto, R. *Solid State Commun.* **1988**, *68*, 513.
(306) Yoshino, K.; Manda, Y.; Sawada, K.; Onoda, M.; Sugimoto, R. *Solid State Commun.* **1989**, *69*, 143.
(307) Winokur, M. J.; Spiegel, D.; Kim, Y.; Hotta, S.; Heeger, A. J. *Synth. Met.* **1989**, *28*, C419.
(308) Mårdalen, J.; Samuelsen, E.; Gautun, O. R.; Carlsen, P. H. *Solid State Commun.* **1991**, *77*, 337.
(309) Zagorska, M.; Krische, B. *Polymer* **1990**, *31*, 1379.
(310) Souto Maior, R. M.; Hinkelmann, K.; Eckert, H.; Wudl, F. *Macromolecules* **1990**, *23*, 1268.
(311) Bobacka, J.; Ivaska, A. *Synth. Met.* **1991**, *41–43*, 3053.
(312) Büchner, W.; Garreau, R.; Lemaire, M.; Roncalí, J. *J. Electroanal. Chem.* **1990**, *277*, 355.
(313) Sato, M.; Tanaka, S.; Kaeriyama, K. *Makromol. Chem.* **1989**, 1233.
(314) Lemaire, M.; Garreau, R.; Delabouglise, D.; Roncali, J.; Korri Youssoufi, H.; Garnier, F. *New J. Chem.* **1990**, *14*, 359.
(315) Ueda, M.; Miyaji, Y.; Ito, T.; Oba, Y.; Sone, T. *Macromolecules* **1991**, *24*, 2694.
(316) Kaeriyama, K.; Sato, M.; Tanaka, S. *Synth. Met.* **1987**, *18*, 233.
(317) Roncali, J.; Garreau, R.; Delabouglise, D.; Garnier, F.; Lemaire, M. *Synth. Met.* **1989**, *28*, C341.
(318) Roncali, J.; Korri Youssoufi, H.; Garreau, R.; Garnier, F.; Lemaire, M. *J. Chem. Soc., Chem. Commun.* **1990**, 414.
(319) Minett, M. G.; Owens, J. R. *Synth. Met.* **1989**, *28*, 211.
(320) Bryce, M. R.; Chíssel, A.; Kathirgamanathan, P.; Parker, D.; Smith, N. M. R. *J. Chem. Soc., Chem. Commun.* **1987**, 466.
(321) Bryce, M. R.; Chissel, A. D.; Smith, N. R. M.; Parker, D.; Kathirgamanathan, P. *Synth. Met.* **1988**, *26*, 153.
(322) Lemaire, M.; Garreau, R.; Roncali, J.; Delabouglise, D.; Korri, H.; Garnier, F. *New J. Chem.* **1989**, *13*, 863.
(323) Zinger, B.; Greenwald, Y.; Rubinstein, I. *Synth. Met.* **1991**, *41–43*, 583.
(324) Li, H. S.; Garnier, F.; Roncali, J. *Synth. Met.* **1991**, *41–43*, 547.
(325) Roncali, J.; Garreau, R.; Delabouglise, D.; Garnier, F.; Lemaire, M. *J. Chem. Soc., Chem. Commun.* **1989**, 679.
(326) Roncalí, J.; Li, H. S.; Garreau, R.; Garnier, F.; Lemaire, M. *Synth. Met.* **1990**, *36*, 267.
(327) Li, H. S.; Garnier, F.; Roncali, J. *Solid State Commun.* **1991**, *77*, 811.
(328) Roncali, J.; Li, H. S.; Garnier, F. *J. Phys. Chem.* **1991**, *95*, 8983.
(329) Sable, E.; Handel, H.; L'Her, M. *Electrochimica Acta* **1991**, *36*, 15.
(330) Roncali, J.; Garreau, R.; Lemaire, M. *J. Electroanal. Chem.* **1990**, *278*, 373.
(331) Mertz, A. *Top. Curr. Chem.* **1990**, *152*, 49.
(332) Mirrazaei, R.; Parker, D.; Munro, H. S. *Synth. Met.* **1989**, *30*, 265.
(333) Grimshaw, J.; Perera, S. D. *J. Electroanal. Chem.* **1990**, *278*, 287.
(334) Baûerle, P.; Gaudl, K. U. *Adv. Mater.* **1990**, *2*, 185.
(335) Baûerle, P.; Gaudl, K. U. *Synth. Met.* **1991**, *41–43*, 3037.
(336) Bryce, M. R.; Chissel, A. D.; Gopal, J.; Kathirgamanathan, P.; Parker, D. *Synth. Met.* **1991**, *39*, 397.
(337) Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1858.
(338) Patil, A. O.; Ikenoue, Y.; Basescu, N.; Colaneri, N.; Chen, J.; Wudl, F.; Heeger, A. J. *Synth. Met.* **1987**, *20*, 151.
(339) Ikenoue, Y.; Saisa, Y.; Kira, M.; Tomozawa, H.; Yashima, H.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1694.
(340) Baûerle, P.; Gaudl, K. W.; Würthner, F.; Sarciftci, S.; Neugebauer, H.; Mehring, M.; Zhong, C.; Doblhofer, K. *Adv. Mater.* **1990**, *2*, 490.
(341) Lakhtakia, A.; Varadan, V. K.; Varadan, V. V. *Appl. Opt.* **1985**, *24*, 4146.
(342) Lemaire, M.; Delabouglise, D.; Garreau, R.; Roncali, J. *J. Chim. Phys.* **1989**, *86*, 193.
(343) Vogl, O.; Jaycox, G. D. *Chemtech* **1986**, Nov, 698.
(344) Lemaire, M.; Delabouglise, D.; Garreau, R.; Roncali, J. *Recent Advances in Electro-Organic Synthesis*; Torii, S., Ed.; Elsevier Science Publishers: Amsterdam, 1987; p 385.
(345) Lemaire, M.; Delabouglise, D.; Garreau, R.; Guy, A.; Roncalí, J. *J. Chem. Soc., Chem. Commun.* **1988**, 658.
(346) Kotkar, D.; Joshi, V.; Gosh, K. *J. Chem. Soc., Chem. Commun.* **1988**, 917.
(347) Kim, D.; Reiss, H. *J. Phys. Chem.* **1985**, *89*, 2728.
(348) Yoshino, K.; Nalwa, H. S.; Rabe, J. G.; Schmidt, W. F. *Polym. Commun.* **1985**, *26*, 103.
(349) Hanawa, T.; Kuwabata, S.; Hashimoto, H.; Yoneyama, H. *Synth. Met.* **1989**, *30*, 173.
(350) Yoshino, K.; Hayashi, S.; Kohno, Y.; Kaneto, K.; Okube, J.; Moriya, T. *Jpn. J. Appl. Phys.* **1984**, *23*, L198.
(351) Noufi, R.; Franck, A. J.; Nozik, A. J. *J. Am. Chem. Soc.* **1981**, *103*, 1849.
(352) Fan, F. R.; Wheeler, B. L.; Bard, A. J.; Noufi, R. N. *J. Electrochem. Soc.* **1981**, *128*, 2042.
(353) Horowitz, G.; Tourillon, G.; Garnier, F. *J. Electrochem. Soc.* **1984**, *131*, 152.
(354) Horowitz, G.; Garnier, F. *J. Electrochem. Soc.* **1985**, *132*, 634.
(355) Garnier, F.; Horowitz, G.; Lemaire, M.; Roncali, J. *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 1261.
(356) Gningue, D.; Horowitz, G.; Garnier, F. *J. Electrochem. Soc.* **1988**, *135*, 1695.
(357) Gningue, D.; Horowitz, G.; Roncali, J.; Garnier, F. *J. Electroanal. Chem.* **1989**, *269*, 337.
(358) Glenis, S.; Horowitz, G.; Tourillon, G.; Garnier, F. *Thin Solid Films* **1984**, *111*, 93.
(359) Glenis, S.; Tourillon, G.; Garnier, F. *Thin Solid Films* **1984**, *122*, 9.
(360) Glenis, S.; Tourillon, G.; Garnier, F. *Thin Solid Films* **1986**, *139*, 221.
(361) Kenmochi, T.; Tsuchida, E.; Kaneko, M.; Yamada, A. *Electrochim. Acta* **1985**, *30*, 1405.
(362) De Saja, J. A.; Tanaka, K. *Phys. Stat. Sol. (A)* **1988**, *108*, K109.
(363) Frank, A. J.; Glenis, S.; Nelson, A. J. *J. Phys. Chem.* **1989**, *93*, 3818.
(364) Frank, A. J.; Glenis, S. *Synth. Met.* **1989**, *28*, C681.
(365) Kaneko, M.; Takahashi, K.; Tsuchida, E. *J. Electroanal. Chem.* **1987**, *227*, 255.
(366) Horowitz, G.; Garnier, F. *Solar Energy Mat.* **1986**, *13*, 47.
(367) Aizawa, M.; Yamada, T.; Shinohara, H.; Akagi, K.; Shirakawa, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1315.
(368) Tsumura, A.; Koezuka, H.; Ando, T. *Appl. Phys. Lett.* **1986**, *49*, 1210.
(369) Tsumura, A.; Koezuka, H.; Ando, T. *Synth. Met.* **1987**, *18*, 699.
(370) Tsumura, A.; Koezuka, H.; Ando, T. *Synth. Met.* **1988**, *25*, 11.
(371) Kobel, W.; Kiess, H.; Egli, M. *Synth. Met.* **1988**, *22*, 265.
(372) Tomozawa, H.; Braun, D.; Phillips, S.; Heeger, A. J.; Kroemer, H. *Synth. Met.* **1987**, *22*, 63.
(373) Assadi, A.; Svensson, C.; Willander, M.; Inganäs, O. *Synth. Met.* **1989**, *28*, C863.
(374) Fichou, D.; Nishikitani, Y.; Horowitz, G.; Roncali, J.; Garnier, F. *Synth. Met.* **1989**, *28*, C729.
(375) Lehn, J. M. *Angew. Chem., Int. Ed. Eng.* **1988**, *27*, 90.
(376) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277.
(377) *Molecular Electronic Devices*, Carter, F. L., Ed.; Marcel Dekker: New York, 1982.
(378) Aviram, A. *J. Am. Chem. Soc.* **1988**, *110*, 5687.
(379) Metzger, R. M.; Panetta, C. A.; Miura, Y.; Torres, E. *Synth. Met.* **1987**, *18*, 797.
(380) Aviram, A.; Joachim, C.; Pomerantz, M. *Chem. Phys. Lett.* **1988**, *146*, 490.
(381) Metzger, R. M.; Panetta, C. A. *Synth. Met.* **1989**, 28, C807.
(382) Proc. of 3rd Int. Conf. on LB films, Göttingen, F.R.G 26–31 July 1987, Möbius, D. Ed.; *Thin Solid Films* **1988**, *159*, Nos. 1–2.
(383) Tour, J. M.; Wu, R.; Schumm, J. S. *J. Am. Chem. Soc.* **1990**, *112*, 5662.
(384) Watanabe, I.; Hong, K.; Rubner, M. *J. Chem. Soc., Chem. Commun.* **1989**, 123.
(385) Prasad, P. N.; Swiatkiewicz, J.; Pfleger, J. *Mol. Cryst. Liq. Cryst.* **1988**, *160*, 53.
(386) Sugiyama, T.; Wada, T.; Sasabe, H. *Synth. Met.* **1989**, *28*, C323.
(387) Singh, B. P.; Samoc, M.; Nalwa, H. S.; Prasad, P. N. *J. Chem. Phys.* **1990**, *92*, 2756.
(388) Houlding, V. H.; Hahata, A.; Yardley, J. T.; Elsenbaumer, R. L. *Chem. Mater.* **1990**, *2*, 169.
(389) Yamamoto, T. *J. Chem. Soc. Chem. Commun.* 1981, 187.
(390) Yamamoto, T.; Zama, M.; Yamamoto, A. *Chem. Lett.* **1984**, 1577.
(391) Yamamoto, T.; Zama, M.; Yamamoto, A. *Chem. Lett.* **1985**, 563.

(392) Kaneto, K.; Yoshino, K.; Inuishi, Y. *Jpn. J. Appl. Phys.* **1983**, *22*, L567.
(393) Waltman, R. J.; Diaz, A. F.; Bargon, J. *J. Electrochem. Soc.* **1984**, *131*, 1452.
(394) Kaufman, J. H.; Chung, T.-C.; Heeger, A. J.; Wudl, F. *J. Electrochem. Soc.* **1984**, *131*, 2092.
(395) Biserni, M.; Marinangeli, A.; Mastragostino, M. *J. Electrochem. Soc.* **1985**, *132*, 1597.
(396) Panero, S.; Prosperi, P.; Klaptse, B.; Scrosati, B. *Electrochim. Acta* **1986**, *31*, 1597.
(397) Arbizzani, C.; Mastragostino, M.; Panero, S.; Prosperi, P.; Scrosati, B. *Synth. Met.* **1989**, *28*, C663.
(398) Kawai, T.; Kuwabara, T.; Wang, S.; Yoshino, K. *J. Electrochem. Soc.* **1990**, *137*, 3793.
(399) Kawai, T.; Kuwabara, T.; Wang, S.; Yoshino, K. *Jpn. J. Appl. Phys.* **1990**, *29*, 602.
(400) Li, F.; Albery, W. J. *J. Electroanal. Chem.* **1991**, *302*, 279.
(401) Yoshino, K.; Kaneto, K.; Inuishi, Y. *Jpn. J. Appl. Phys.* **1983**, *22*, L157.
(402) Kaneto, K.; Yoshino, K.; Inuishi, Y. *Jpn. J. Appl. Phys.* **1983**, *22*, L412.
(403) Garnier, F.; Tourillon, G.; Gazard, M.; Dubois, J. C. *J. Electroanal. Chem.* **1983**, *148*, 299.
(404) Yashima, H.; Kobayashi, M.; Lee, K. B.; Chung, D.; Heeger, A. J.; Wudl, F. *J. Electrochem. Soc.* **1987**, *134*, 46.
(405) Mastragostino, M.; Marinangeli, A. M.; Corradini, A.; Giacobbe, S. *Synth. Met.* **1989**, *28*, C501.
(406) Roncali, J.; Lemaire, M.; Delabouglise, D.; Garreau, R.; Garnier, F.; Hannecart, E., French Pat. 87.17117, Dec. 7, 1987; Eur. Pat. 88202679.2, Dec 16, 1988.
(407) Atta, N. F.; Gala, A.; Karagözler, A. E.; Zimmer, H.; Rubinson, J. F.; Mark, H. B., Jr. *J. Chem. Soc. Chem. Commun.* **1990**, 1347.
(408) Blankespoor, R. L.; Miller, L. L. *J. Chem. Soc., Chem. Commun.* **1985**, 90.
(409) Thackeray, J. W.; White, H. S.; Wrighton, M. S. *J. Phys. Chem.* **1985**, *89*, 5133.
(410) Lofton, E. P.; Thackeray, J. W.; Wrighton, M. S. *J. Phys. Chem.* **1986**, *90*, 6080.
(411) Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 2197.
(412) Kivelson, S.; Heeger, A. J. *Synth. Met.* **1988**, *22*, 371.
(413) Little, W. A. *Phys. Rev.* **1964**, *134*, A1416.