

# The Chemistry of Conducting Polythiophenes\*\*

By Richard D. McCullough\*

## 1. Introduction

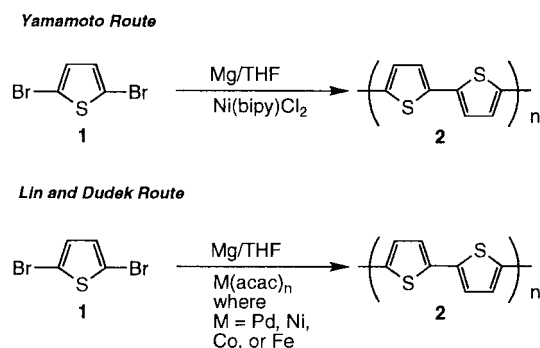
In the late 1970s, conjugated polymers were proclaimed as futuristic new materials that would lead to the next generation of electronic and optical devices. It now appears with the discoveries of, for example, polymer light-emitting diodes (LEDs)<sup>[1]</sup> and organic transistors<sup>[2]</sup> that new technologies are imminent. Polythiophenes are an important representative class of conjugated polymers that form some of the most environmentally and thermally stable materials that can be used as electrical conductors, nonlinear optical devices, polymer LEDs, electrochromic or smart windows, photoresists, antistatic coatings, sensors, batteries, electromagnetic shielding materials, artificial noses and muscles, solar cells, electrodes, microwave absorbing materials, new types of memory devices, nanoswitches, optical modulators and valves, imaging materials, polymer electronic interconnects, nanoelectronic and optical devices, and transistors.<sup>[3,4]</sup> Polythiophene and its derivatives work very well in some of the above applications and less impressively in other devices. Creative new design and development strategies of new polythiophenes has led to interesting new materials and enhanced performance in certain devices. The ability of molecular designers to begin to understand how to gain control over the structure, properties, and function in polythiophenes continues to make the synthesis of polythiophenes a critical subject in the development of new advanced materials. Here I attempt to review comprehensively the synthesis of polythiophenes. Owing to the enormous literature on this subject, some excellent work in this area will almost certainly have been inadvertently overlooked. However, I will highlight both the pioneering work and the frontiers in the synthesis of polythiophenes.

It is important to realize that, as it has become clear that structure plays a dominant role in determining the physical properties of conducting polymers, more research has focused on directing the structure and function of these materials with synthesis. Synthesis can help to determine the

magnitude of  $\pi$  overlap along the backbone and eliminate structural defects. Materials assembly (and/or processing) determines interchain overlap and dimensionality. Planarization of the backbone and assembly of the backbone in the form of  $\pi$  stacks lead to better materials and enhanced device performance in almost every category, ranging from electrical conductivity to stability. Therefore, both remarkable enhancements in the electronic and photonic properties of the resultant materials and the creation of new functions, such as new sensory materials, critically depends on the synthesis of the polythiophene. This of course leads to the exciting prospect that the properties of polythiophenes can be selectively engineered through synthesis and assembly. A large portion of both the pioneering and future work in conjugated polymers strongly depends on synthetic chemists creating new polymers that can be fabricated into new devices and whose physics and chemistry can be understood in detail.

## 2. Chemical Synthesis of Unsubstituted Polythiophene

One of the first chemical preparations of unsubstituted polythiophene (PT) was reported in 1980 by two groups.<sup>[5,6]</sup> Both synthesized polythiophene by a metal-catalyzed polycondensation polymerization of 2,5-dibromothiophene (Scheme 1). Yamamoto's synthesis treats 2,5-dibromothiophene with Mg in tetrahydrofuran (THF) in the presence of nickel(bipyridine) dichloride. The Mg reacts with either bromide to form either 2-bromo-5-magnesiobromothiophene or 2-magnesiobromo-5-bromothiophene, which is self-coupled with the Ni<sup>II</sup> catalyst to form a thiophene dimer carrying a MgBr at one end and a Br at the other. This



Scheme 1. The first chemical syntheses of polythiophene.

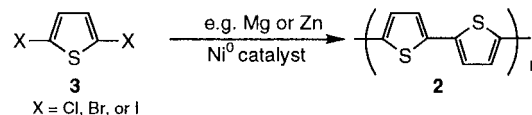
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[\*\*] This article will also appear as a chapter in the *Handbook of Oligo- and Polythiophenes*, edited by D. Fichou, to be published by WILEY-VCH, Weinheim, Germany, in 1998.

condensation reaction is propagated and eventually low molecular weight PT is formed. The polymerization is the extension of Kumada coupling of Grignard reagents to aryl halides.<sup>[7]</sup> Since PT even at low molecular weights is insoluble in THF, the precipitation of the polymer under the above reaction conditions limits the formation of higher molecular weights. The PT synthesized by this method leads to 78 % insoluble polymer that does not melt. The soluble fraction is lower molecular weight oligomers. Polythiophene polymers of molecular weight greater than 3000 are not soluble in hot chloroform.<sup>[8]</sup> The elemental analysis of this polymer indicated that 1–3 % Mg remains in the polymer sample. Similar results were found by Lin and Dudek.<sup>[6]</sup> Polymerization of 2,5-dibromothiophene in the presence of Mg in THF using palladium(acac)<sub>2</sub> (acac = acetylacetonate) or Ni(acac)<sub>2</sub> or Co(acac)<sub>2</sub> or Fe(acac)<sub>3</sub> catalyst yields low molecular weight PT containing 3 % of impurities as determined by elemental analysis.

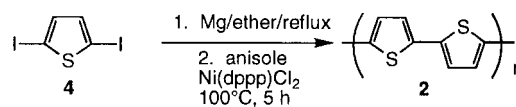
Polymerization of 2,5-dihalothiophene can be accomplished by reacting the generated bromo-Grignard reagent of thiophene with a Ni<sup>II</sup> catalyst such as Ni(dppp)Cl<sub>2</sub> (dppp = 1,3-diphenylphosphinopropane), or the 2,5-dihalothiophene can be polymerized by a polycondensation dehalogenation reaction with Ni<sup>0</sup> (Scheme 2). Systematic studies of the polymerization of 2,5-dihalothiophene have subsequently been performed primarily by Yamamoto's group<sup>[8–12]</sup> but also by others.<sup>[13–15]</sup> Varying the amounts of Mg,<sup>[13]</sup> solvent,<sup>[10,14,15]</sup> type of metal (i.e., Mg, Zn, etc.),<sup>[10]</sup> concentration of monomer,<sup>[13]</sup> type of halogen on the monomer,<sup>[8,12–15]</sup> temperature,<sup>[8,9,12]</sup> reaction time,<sup>[8]</sup> and type of catalyst used<sup>[8–13]</sup> has led to some good chemical methods for the synthesis of PT. The extension of these chemical methods to the synthesis of poly(3-alkylthiophene)s (PATs) and other polythiophenes will be noted later.

It is seen in a paper by Wudl and co-workers<sup>[14]</sup> that very good samples of PT can be prepared by the polymerization of highly purified 2,5-diiodothiophene (**4**). First 2,5-diiodothiophene is reacted with Mg in ether at reflux (Scheme 3). The formed iodomagnesiiodothiophene is isolated as a residue and redissolved in hot anisole, whereupon Ni(dppp)Cl<sub>2</sub> is added and the mixture heated at 100 °C for 5 h to induce polymerization. Extensive washing

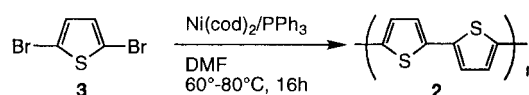


Scheme 2. Polycondensation dehalogenation route to polythiophene.

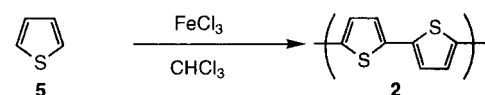
**Wudl**



**Yamamoto**



**Sugimoto and Yoshino**



Scheme 3. Specific examples of the synthesis of polythiophene.

of the isolated PT with methanol, chloroform, THF, and chlorobenzene leads to the isolation of PT with elemental analysis within 0.3 % of the calculated values for C<sub>188</sub>H<sub>97</sub>IS<sub>46</sub> (molecular weight ~4k or 46 thiophene rings and 1 butadiene unit). This high purity PT sample contains barely 50 ppm of Mg and Ni. However, it is proposed that the one butadiene unit arises from a desulfurization reaction promoted by Ni<sup>0</sup> intermediates.<sup>[7]</sup> Polymerization of the 2,5-dibromothiophene yielded PT that was analyzed as being 2–3 % low in sulfur, apparently due to this desulfurization. The Wudl sample of PT was characterized by IR, electron spin resonance (ESR), conductivity and thermopower measurements. The conductivity of the AsF<sub>5</sub>-doped material was about 10 S/cm.

Work on the polycondensation polymerization of 2,5-dihalothiophenes by Yamamoto has shown that essentially a quantitative yield of PT can be obtained from 2,5-dibromothiophene, Ni(cod)<sub>2</sub> (cod = cyclooctadiene), and triphenylphosphine (PPh<sub>3</sub>) at 60–80 °C in dimethylformamide (DMF) (Scheme 3).<sup>[8]</sup> It is also reported that the percen-



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tage of Br end groups decreases as the reaction time is increased from 8 h to 16 h, indicating that perhaps some seemingly insoluble PT continues to grow. Both less active catalysts such as  $\text{Ni}(\text{PPh}_3)_4$  and less active monomers such as 2,5-dichlorothiophene lead to lower yields of PT. The PT synthesized is exclusively coupled at the 2,5-carbons as indicated by solid-state  $^{13}\text{C}$  NMR, which exhibits peaks at 136 and 125 ppm only. Other synthetic methods can produce the conjugation-disrupting 2,4-coupled polythiophene structure. While the elemental analyses for carbon and hydrogen are within 0.3 % of the calculated values, the sulfur content of the PT is off by 3 %. Vacuum deposition of PT (estimated molecular weight of 1.5–2k) onto carbon, gold, KBr, or aluminum can be accomplished at 250–300 °C at  $10^{-4}$  Pa. Electron diffraction patterns of PT on carbon indicate the formation of crystalline PT with the PT chains arranged perpendicular to the carbon substrate—similar to oligothiophene films. Vacuum deposition of PT on rubbed polyimide films gave PT chains oriented parallel to the polyimide substrate with a dichroic ratio of 1.5. The PT films are further characterized by IR, X-ray, and conductivity measurements. Powder conductivity measurements on iodine-doped samples gave a maximum conductivity of 50 S/cm.

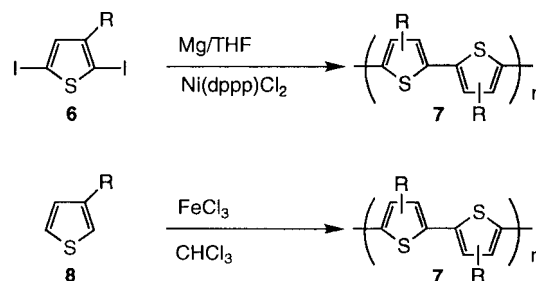
Although the above methods have been generally used to prepare high quality PT (and PATs), other methods have been reported. Early on,<sup>[16]</sup> Sugimoto described the synthesis of PT by treating thiophene with  $\text{FeCl}_3$  (Scheme 3). The treatment of thiophene with butyl lithium provides 2,5-dilithiothiophene that can be polymerized with  $\text{CuCl}_2$ .<sup>[17]</sup> The acid-induced polymerization of thiophene was reported as early as 1883, but produces tetrahydrothiophene units.<sup>[18]</sup> A novel polymerization of thiophene vapor can produce encapsulated PT in zeolites that contain transition metals.<sup>[19]</sup>

Despite the lack of processability, the expected high temperature stability<sup>[14]</sup> and potentially very high electrical conductivity of PT *films* (if made) still make it a highly desirable material. Perhaps precursor routes to PT will eventually lead to processable PT films.

### 3. Chemical Synthesis of Polyalkylthiophenes (PATs)

#### 3.1. Straight Alkyl Side Chains

In the quest for a soluble and processable conducting polythiophene, alkylthiophenes were polymerized. Poly(3-methylthiophene) (PMT) was chemically synthesized and was found to be insoluble.<sup>[9,20–22]</sup> The first chemical synthesis of environmentally stable and soluble poly(3-alkylthiophenes) (PATs)<sup>[23–25]</sup> was reported by Elsenbaumer and co-workers in 1985 (Scheme 4). Very shortly after this report, other groups<sup>[26–28]</sup> also reported both the chemical and electrochemical preparation of PATs. Poly(3-alkylthio-



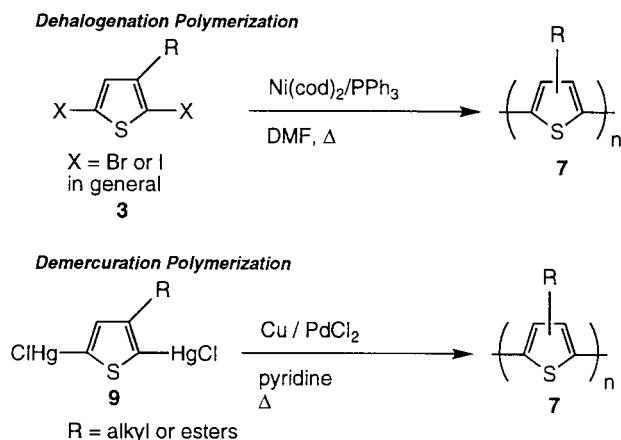
Scheme 4. The synthesis of poly(3-alkylthiophene).

phene)s with alkyl groups longer than butyl can readily be melt- or solution-processed into films, which, after oxidation, can exhibit reasonably high electrical conductivities of 1–5 S/cm.<sup>[23–28]</sup>

#### 3.1.1. Chemical Synthesis of PATs

**Metal-Catalyzed Cross-Coupling Polymerizations:** The first poly(3-alkylthiophenes) were prepared via Kumada cross-coupling,<sup>[23–25]</sup> using a method similar to that used for the chemical preparation of polythiophene.<sup>[5,14]</sup> In this synthesis a 2,5-diiodo-3-alkylthiophene (**6**) (Scheme 4) is treated with one equivalent of Mg in THF, generating a mixture of Grignard species. A catalytic amount of  $\text{Ni}(\text{dppp})\text{Cl}_2$  is then added and the polymer is generated by a halo-Grignard coupling reaction. Large quantities of PATs can be prepared by this method, and although the molecular weights were initially reported to be low (e.g.,  $M_n = 3\text{--}8\text{k}$ , polydispersity index PDI = 2), later reports show that high molecular weights are possible.<sup>[29]</sup>  $^1\text{H}$  NMR of poly(3-butylthiophene) (PBT) showed that the polymer contains only 2,5 linkages, with random regiospecificity. No 2,4 (or  $\beta$ ) couplings are observed, presumably due to steric blocking provided by the 3-alkyl group. Homopolymers of 3-alkylthiophenes with alkyl groups equal to or greater than butyl are soluble in common organic solvents such as chloroform, THF, xylene, toluene, methylene chloride, anisole, nitrobenzene, benzonitrile, and nitropropane. Casting from any of the aforementioned solvents affords thin films of PATs.

Poly(3-alkylthiophene) can also be synthesized from 2,5-diiodo-3-alkylthiophene and zero-valent nickel catalysts (Scheme 5).<sup>[8]</sup> Essentially the same conditions (monomer,  $\text{Ni}(\text{cod})_2$  and  $\text{PPh}_3$  in DMF at 60° for 16–48 h) that are used to prepare PT give yields of 60–95 % (Scheme 3). The reactions times are longer for PATs and diiodothiophenes are found to be more active monomers than dibromothiophenes. It is reported<sup>[8]</sup> that this type of organometallic coupling polymerization proceeds with predominantly 5- to 5'- (head-to-head) type of couplings. This would give a PAT with mainly head-to-head and tail-to-tail (2- to 2'-) couplings. This is interpreted as selective oxidative addition of Ni to the less sterically hindered 5-position on the alkylthiophene farthest from the bulky alkyl group. Molecu-



Scheme 5. Other chemical methods for the synthesis of PATs.

lar weights by light scattering were reported to be: number average molecular weight ( $M_n$ ) equal to 7.4k and weight average molecular weight equal to 30k (PDI = 4). The  $M_w$  measured by gel permeation chromatography (GPC) ( $\text{CHCl}_3$ ) was reported to be 52k.

**FeCl<sub>3</sub> Method for the Polymerization of PATs:** Sugimoto et al.<sup>[26]</sup> reported in 1986 a very simple method to prepare PATs (Scheme 4). The monomer, 3-alkylthiophene, is dissolved in chloroform and oxidatively polymerized with FeCl<sub>3</sub>,<sup>[26]</sup> MoCl<sub>5</sub>, or RuCl<sub>3</sub>.<sup>[30]</sup> Generally the “FeCl<sub>3</sub> method” has been used to prepare PATs.<sup>[31–36]</sup> Materials prepared by the FeCl<sub>3</sub> method produce PATs with molecular weight ranging from  $M_n = 30\text{k}$  to 300k with polydispersities ranging from 1.3 to 5.<sup>[35,36]</sup> The FeCl<sub>3</sub> method does not appear to generate 2,4-couplings in PATs.

One very good paper on the synthesis of PATs via the FeCl<sub>3</sub> method has been published by Leclerc et al.<sup>[35]</sup> This paper provides a detailed synthesis, molecular weight data, <sup>1</sup>H and <sup>13</sup>C NMR spectra, X-ray, electrochemistry, UV-vis, and electrical conductivity data on PATs synthesized chemically with FeCl<sub>3</sub> and electrochemically. In this study, alkylthiophenes in dry CHCl<sub>3</sub> (0.15 M) were treated dropwise with FeCl<sub>3</sub> in chloroform (0.4 M). The mixture was stirred for 24 h under a gentle argon stream (to help to remove generated HCl(g)). The polymer was then precipitated into methanol, filtered, redissolved in CHCl<sub>3</sub>, and the CHCl<sub>3</sub> slowly evaporated to give a free-standing film. The film was washed by Soxhlet extraction using methanol and acetone, which yields a dedoped polymer containing <0.10 % Fe. The yields ranged from 75 to 80 % with molecular weights of  $M_n = 30\text{k}–50\text{k}$  and PDIs around 5. The regioregularity, measured by the head-to-tail content (discussed in detail in Sec. 3.1.3) ranges from 70 to 80 % by this method. This paper reports that the PATs synthesized with FeCl<sub>3</sub> are more crystalline and regular than electrochemically prepared polymers.

Very high molecular weights have been reported in the synthesis of PATs using the FeCl<sub>3</sub> method by bubbling dry air through the reaction mixture during the polymerization.<sup>[36]</sup> After isolation and dedoping of the polymer with

concentrated ammonia solutions, and washing of the PATs, the molecular weights were determined by GPC using UV-vis, refractive index (RI), and light scattering detectors. All three values were compared. As an example, a single sample of poly(3-hexylthiophene) had molecular weights  $M_w$  of 175k (RI), 124k (UV-vis), and 398k (light scattering). The PATs had molecular weight ranges of 68k–175k (RI), 77k–146k (UV-vis), and 204k–398k (light scattering).

One of the major problems with the FeCl<sub>3</sub> method is that the method gives variable results. The reproducibility of the reaction has been examined, for example by Pomerantz et al.<sup>[36]</sup> The polymerization of 3-octylthiophene with FeCl<sub>3</sub> was repeated under identical reaction conditions five times. Investigations of the molecular weights of the five samples of poly(3-octylthiophene) revealed molecular weights that ranged from 54k to 122k (UV-vis) with PDIs ranging from 1.6 to 2.7. Holdcroft and co-workers<sup>[37]</sup> have reported that three identical preparations yielded three polymer samples containing three different levels of Fe impurities. The percentage of Fe impurities found in the three samples were 9.6 mol-%, 4.15 mol-%, and 0.15 mol-%. The Fe impurity level affects device performance of PT in field effect transistors<sup>[37]</sup> and in LEDs.<sup>[38]</sup>

The Finnish company Neste Oy, which has been working on cost-effective methods to synthesize PATs, has reported on the mechanism of the FeCl<sub>3</sub> synthesis of PATs.<sup>[39]</sup> The FeCl<sub>3</sub> initiates an oxidation of the alkylthiophene to produce radical centers predominantly at the 2- and 5- positions of thiophene, which propagate to form polymer (Scheme 6). Systematic studies of the optimization of the reaction conditions leading to PATs<sup>[40]</sup> and improvements in the method<sup>[41]</sup> have been reported. A new synthesis of octylthiophene, followed by FeCl<sub>3</sub> polymerization, led to a poly(3-octylthiophene) (POT) containing 84 % head-to-tail couplings in a 70 % yield. The molecular weight was reported as  $M_w = 70\text{k}$  (PDI = 2.6). The iron content was only 0.008 % and the chlorine content was 0.5 %, compared with 1 % observed in conventional POT.<sup>[42]</sup> The electrical conductivity of FeCl<sub>3</sub>-doped POT was 47 S/cm.

The FeCl<sub>3</sub> method is a well-established method to polymerize thiophenes<sup>[30–46]</sup> and even polydeuterated PATs<sup>[47]</sup> and continues to be the most widely used and straightforward method to prepare PT and its derivatives, despite the limitations and drawbacks to the method.

A related synthetic method developed by Hotta and co-workers<sup>[48]</sup> appears to provide PATs that are of high molecular weight and contain very little metal impurity. The method is the dehydrohalogenation polymerization of 2-halothiophenes with anhydrous metal halogenides (AlCl<sub>3</sub>, FeCl<sub>3</sub>, etc.).<sup>[48]</sup> Molecular weights ( $M_w$ ) of 250k were reported, along with electrical conductivities of 200 S/cm in stretch oriented (5×) samples after doping with iodine. The elemental analysis of these films shows no detectable metal or chlorine. The NMR spectrum, however, still indicates an irregular structure.

A new PAT synthesis has been recently reported by Curtis and co-workers<sup>[49]</sup> (Scheme 5). The method is reminiscent of the Yamamoto dehalogenation polycondensation polymerization of PT and PATs that was discussed above. The Curtis method polymerizes 2,5-bis(chloromercurio)-3-alkylthiophenes using Cu powder and a catalytic amount of PdCl<sub>2</sub> in pyridine. This method generates homopolymers as well as random copolymers with 3-alkyl and 3-esteric substituents. Molecular weights are reasonably high for a coupling method (for poly(3-butylthiophene),  $M_n = 26k$ , PDI = 2.5). In copolymers the proportion of the alkyl groups in the copolymers matched the ratio of their respective monomers in the reaction mixture. Furthermore, this method is tolerant to the presence of the carbonyl functionality. Most of the methods to prepare PT derivatives tolerate very few functional groups.

### 3.1.2. Comparison of the Above Methods

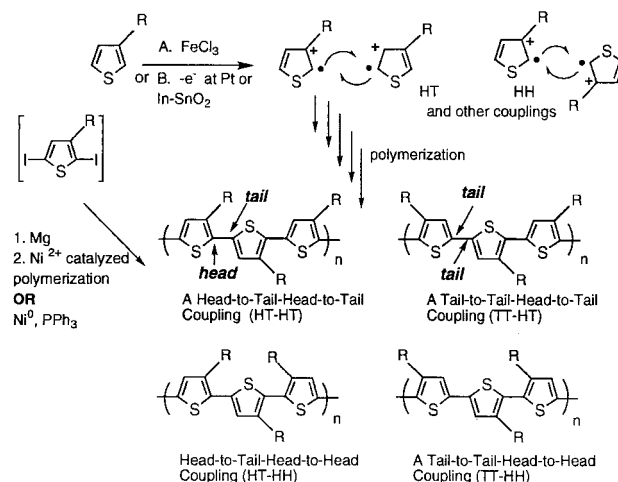
It is important to point out that the methods discussed above produce *irregular* PATs. That is to say that the self-coupling of 3-alkylthiophene occurs with *no* regiochemical control, which produces a defective PAT. This point will be discussed in detail in Secs. 3.1.3 and 3.1.4. However, three synthetic methods (FeCl<sub>3</sub> method, the Grignard coupling method using Ni(dppp)Cl<sub>2</sub>, and the electrochemical methods) have been compared by several groups. Leclerc et al.<sup>[35]</sup> who compared the electrochemical method with the FeCl<sub>3</sub> method, report that the FeCl<sub>3</sub> method produces better samples of PAT than the electrochemical method. Roncali has indirectly compared chemical methods with electrochemical methods in a review on PTs<sup>[50]</sup> and says that the electrochemical synthesis of PT leads to the most highly conjugated and most highly conductive materials as of 1992. Stein et al.<sup>[51]</sup> have recently compared the electrochemical method, the Grignard or “Ni” method, and the FeCl<sub>3</sub> method. Poly(3-dodecylthiophene) (PDDT) was prepared by all three methods and the molecular weights, NMR, UV-vis, and IR results were all compared. The regioregularity and molecular weights for the methods were as follows: the “Ni” method gave 70 % head-to-tail (HT) couplings with  $M_w = 14.5k$  (PDI = 4), the “Fe” method gave 65 % HT couplings with  $M_w = 191k$  (PDI = 9), and the electrochemical method gave 62 % HT couplings with  $M_w = 300k$  (PDI = 6). It was found that the “Ni” method gives the most conjugated PAT as judged by the sharpest UV-vis peak at 510 nm (film) and by the C=C stretch in the IR. The “Fe” method gave a film with the wavelength of the peak  $\lambda_{max} = 494$  nm. The electrochemically prepared sample gave a film  $\lambda_{max}$  of 486 nm. However, this sample had the broadest UV-vis peak, with a red-shifted tail absorbing at lower energies than the other samples. This implies that the electrochemical method gives a broad range of conjugation lengths, some of which are quite conjugated.

At this point is important to note that care must be taken

in determining the molecular weights of PATs using GPC. It has been reported by Yue et al. that extensive aggregation occurs in regioregular PATs and this can lead to errors in the GPC.<sup>[52]</sup> We have seen samples of PATs that have  $M_w$  of 130k by GPC (THF). This experiment was reproduced at least five times. However, eventually we observed (in the same sample) a  $M_w$  of 25k. Therefore, some of the reported molecular weights could be the molecular weights of aggregates.

### 3.1.3. Regioregular PATs

While all of these methods reduce or eliminate 2,4 linkages, they do not solve the lack of regiochemical control over head-to-tail couplings between adjacent thiophene rings. Since 3-alkylthiophene is not a symmetrical molecule, there are three relative orientations available when two thiophene rings are coupled between the 2- and 5-positions. The first of these is 2,5' or head-to-tail coupling (referred to hereafter as HT), the second is 2,2' or head-to-head coupling (HH), and the third is 5,5' or tail-to-tail coupling (TT). All of the above methods afford products with three possible regiochemical couplings: HH, TT, and HT (Scheme 6). This leads to a mixture of four chemically

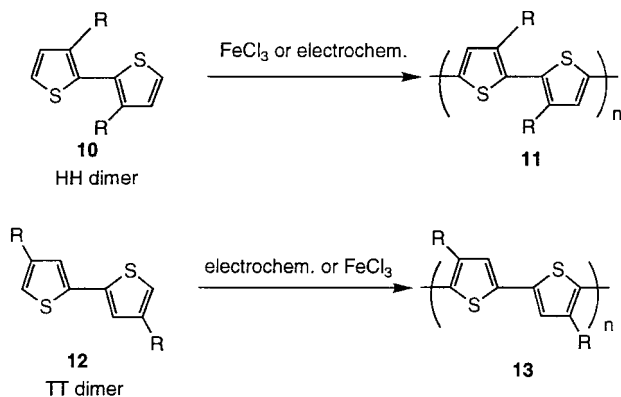


Scheme 6. Possible regiochemical couplings in PATs.

distinct triad regioisomers when 3-substituted (asymmetric) thiophene monomers are employed.<sup>[53,54]</sup> These structurally irregular polymers will be denoted as *irregular* or *non-HT*. Irregularly substituted polythiophenes have structures where unfavorable HH couplings cause a sterically driven twist of thiophene rings, resulting in a loss of conjugation. On the other hand, regioregular, head-to-tail (HT) poly(3-substituted)thiophene can easily access a low energy planar conformation, leading to highly conjugated polymers. An increase of the torsion angles between thiophene rings leads to greater bandgaps, with consequent destruction of high conductivity and other desirable properties.

The first investigation of the deleterious effects of non-HT coupling was examined by Elsenbaumer et al.<sup>[55]</sup> It was shown that the polymerization of a 3-butylthiophene-3'-methylthiophene dimer that contains a 63:37 mixture of HT:HH couplings leads to a three-fold increase in electrical conductivity over the random copolymerization of butylthiophene and methylthiophene (50:50) reaction. Therefore increases in HT coupling lead to a more highly conductive PAT.

**Regioregular HH-TT and TT-HH PATs:** Another approach to the preparation of a regiochemically defined PAT is to polymerize either the HH-dimer of alkylthiophene (3,3'-dialkyl-2,2'-bithiophene) (**10**)<sup>[56]</sup> or the TT-dimer of alkylthiophene (4,4'-dialkyl-2,2'-bithiophene) (**12**)<sup>[57-59]</sup> to yield essentially the same PAT, namely a HH-TT coupled PAT. Wudl and co-workers compared the physical properties of, for example, poly(3-hexylthiophene) (PHT) and poly(3,3'-dihexyl-2,2'-bithiophene) (PDHBT) (**11**),<sup>[56]</sup> which are synthesized by treating 3-hexylthiophene and 3,3'-dialkyl-2,2'-bithiophene with FeCl<sub>3</sub>, respectively (Scheme 7). The same polymers were also made electro-



Scheme 7. Regioregular HH-TT and TT-HH PATs.

chemically for comparison. The PHT prepared chemically had  $M_w = 140k$  (PDI = 4.4) and PDHBT had  $M_w = 120k$  (PDI = 5.3). The PHT was determined to have 80% HT couplings and the PDHBT was a regiochemically defined polymer containing alternating HH-TT couplings. Films cast from each polymer gave UV-vis  $\lambda_{max}$  of 398 nm for PDHBT and 508 nm for PHT. This very large difference in conjugation length is attributed to the intrachain sulfur-alkyl interactions. However, it was also pointed out that it is not obvious why the 3,3'-substituted polymer should be much more sterically hindered than the polymer substituted mostly in a 3,4' fashion as is found in PHT. Evidently the steric effects do not seem to affect the electrical conductivity of the HH-TT polymer, PDHBT. The conductivity of the PDHBT oxidized with NOPF<sub>6</sub> is 4 S/cm, whereas PHT's conductivity is 15 S/cm. Poly(3-methylthiophene) and poly(3,3'-dimethyl-2,2'-bithiophene) were also compared.

Krische and Hellberg<sup>[58,59]</sup> were the first to prepare regiochemically defined TT-HH PATs. The TT-dimer of al-

kythiophene (4,4'-dialkyl-2,2'-bithiophene) was first prepared electrochemically<sup>[59]</sup> and then prepared chemically by both Krische<sup>[58]</sup> and Pron and co-workers.<sup>[57]</sup> The polymers poly(4,4'-dibutyl-2,2'-bithiophene) (PDBBT) (**13**) and poly(4,4'-dioctyl-2,2'-bithiophene) (PDOBT) were prepared by polymerizing the appropriate dimer with FeCl<sub>3</sub> (Scheme 7). Again the TT-HH polymers PDBBT and PDOBT gave a solid-state UV-vis with  $\lambda_{max}$  of 392 nm and 388, respectively, with  $M_w = 15k$  for PDBBT (PDI = 1.5). The  $\lambda_{max}$  of, for example, poly(3-butylthiophene) was 494 nm ( $M_w$  of 14k, PDI = 1.4). Cyclic voltammetry shows a single oxidation for both PDBBT and PBT at 0.96 V and 0.78 V vs. Ag/AgCl (CH<sub>3</sub>CN)—another clear indication that the PBT is more conjugated in the solid state. Pron and co-workers<sup>[57]</sup> made poly(4,4'-dialkyl-2,2'-bithiophene)s with alkyl groups of octyl and decyl. The results were virtually the same as Krische. Interestingly enough, the FeCl<sub>3</sub> polymerization of 3-alkylthiophenes gave  $M_w$  of 144k (PDI = 5.5) for PHT,  $M_w$  of 142k (PDI = 3.1) for poly(3-octylthiophene), and  $M_w$  of 250k (PDI = 4.2), which is in stark contrast to Zagorska and Krische's results.<sup>[58]</sup> This again points to the variability of the FeCl<sub>3</sub> method unless specific conditions are implemented.<sup>[35,36,41]</sup>

A partial list of other recent methods that are focused on regioregular non-HT PTs include the coupling of 5,5'-dilithiobithiophenes with CuCl<sub>2</sub>,<sup>[60]</sup> a similar coupling of a 5,5'-dilithiobithiophene with Fe(acac)<sub>3</sub> in refluxing THF<sup>[61]</sup> and Stille coupling of 2,5'-dibromobithiophenes with 2,5'-bis(trimethylstannyl)bithiophenes using a catalytic amount of PdCl<sub>2</sub>(AsPh<sub>3</sub>)<sub>2</sub>.<sup>[61]</sup>

### 3.1.4. Regioregular, Head-to-Tail Coupled PATs

The conformational energetic consequences of each of the possible regioisomers that can occur in PATs (the four oligomeric triads) have been modeled in the gas phase by molecular mechanics and ab initio methods.<sup>[62,63]</sup> For the HT-HT example, both methods indicate that the thiophene rings prefer a trans coplanar orientation. Structures with the rings twisted by up to 20° (molecular mechanics) or up to 50° (ab initio-STO-3G) from coplanarity all lie within less than 1 kcal of each other on a very flat potential energy surface and accordingly are easily accessible.<sup>[57]</sup> The advantage of HT coupling is supported by crystallographic evidence from HT-HT oligomers of 3-methylthiophene.<sup>[64]</sup> HT trimers of 3-methylthiophene are calculated to have a torsional angle of 7°–8° between conjoined rings.<sup>[62]</sup> This compares favorably with the 6°–9° observed in X-ray structure of unsubstituted  $\alpha$ -terthienyl.<sup>[64]</sup>

Introduction of a head-to-head coupling, as in the HT-HH example, dramatically alters the calculated conformation at the defective HH junction. The thiophene rings maintain a trans conformation, but they are now severely twisted approximately 40° from coplanarity<sup>[62]</sup> and even a 20° twist is not favored by over 5 kcal. Planarity is impossi-

ble as indicated by gas phase calculations. The calculations indicate that head-to-head couplings destroy conjugation, inhibiting intrachain charge mobility,<sup>[65]</sup> and can result in poor electrical conduction in polythiophenes that contain non-HT connectivity. It is important to point out that Brédas has reported that the  $\pi$  orbitals must be within 30° of coplanarity in order to achieve enough overlap to generate conducting polymer band structure.<sup>[66]</sup>

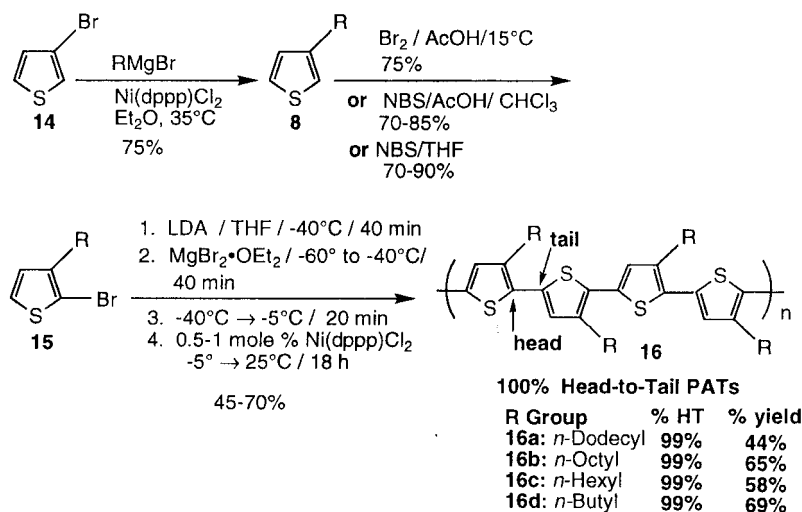
Structurally homogeneous PTs, denoted as regioregular PTs, can be obtained by one of two general strategies. The obvious, currently most common, approach is to polymerize symmetric thiophene monomers or oligomers. The number of available publications is too large to be fairly considered here and will not be addressed.<sup>[62–65]</sup> This review is directed at the alternative strategy: the utilization of asymmetric coupling of asymmetric monomers in order to achieve regioregular HT-coupled structures of polythiophene derivatives.

**The McCullough Method:** The first synthesis of regioregular head-to-tail coupled poly(3-alkylthiophenes) (PATs) was reported by McCullough and Lowe<sup>[67]</sup> early in 1992 (Scheme 8). The PATs synthesized by this method contain ~100% HT-HT couplings. This synthetic method regiospecifically generates 2-bromo-5-(bromomagnesio)-3-alkylthiophene (**17**, Scheme 9) (from monomer **15**<sup>[68–70]</sup>), which is polymerized with catalytic amounts of Ni(dppp)Cl<sub>2</sub> using Kumada<sup>[7,68–72]</sup> cross-coupling methods to give PATs with 98–100% HT-HT couplings.<sup>[62,67,73–78]</sup> In this approach, HT-PATs were prepared in yields of 44–69% (chloroform-soluble solids only) in a one-pot, multistep procedure. Molecular weights for HT-poly(3-alkylthiophenes) are typically in the range of  $M_n = 20k$  to 40k (PDI  $\approx 1.4$ ).

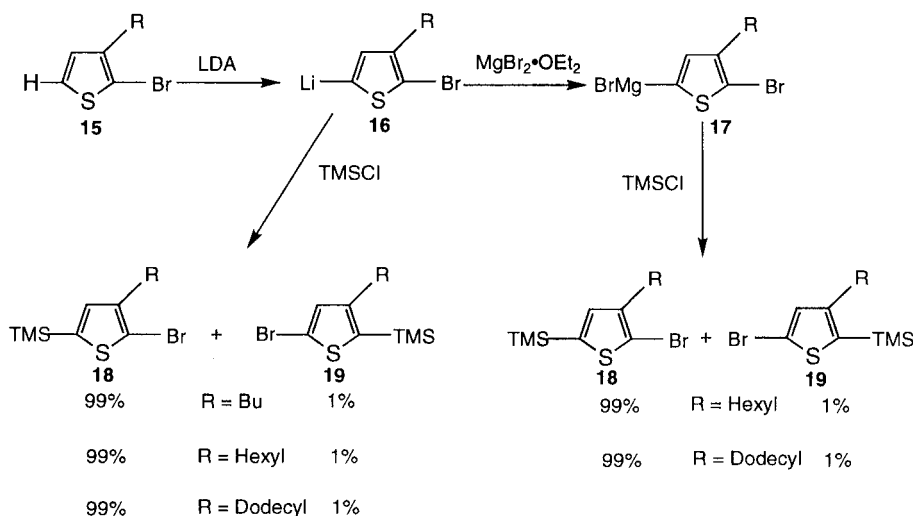
Some key features of the synthesis are the selective metallation of **15** with lithium diisopropylamide (LDA)<sup>[79,80]</sup> to generate **16**. The organolithium intermediate **16** is stable at -78 °C and does not undergo metal halogen exchange via any process, including the halogen dance mechanism.<sup>[81–85]</sup>

In addition, thienyl lithium compounds are relatively poor organolithium reagents and therefore are unlikely to undergo metal-halogen exchange reactions with 2-bromo-3-alkylthiophenes. The intermediate **16** is then reacted with recrystallized (from Et<sub>2</sub>O, in a dry box) MgBr<sub>2</sub>·Et<sub>2</sub>O which results in the formation of **17**, which does not rearrange at higher temperatures. Quenching studies performed upon the intermediates **16** and **17** indicate that 98–99% of the desired monomer and less than 1–2% of the 2,5 exchange product are produced<sup>[62]</sup> (Scheme 9). The subsequent coupling polymerization also occurs without any scrambling. The resulting HT-PAT is precipitated in MeOH, washed (fractionated) with sequential MeOH and hexane Soxhlet extractions, and then recovered by Soxhlet extraction with chloroform. The details of the synthesis have been published.<sup>[62]</sup>

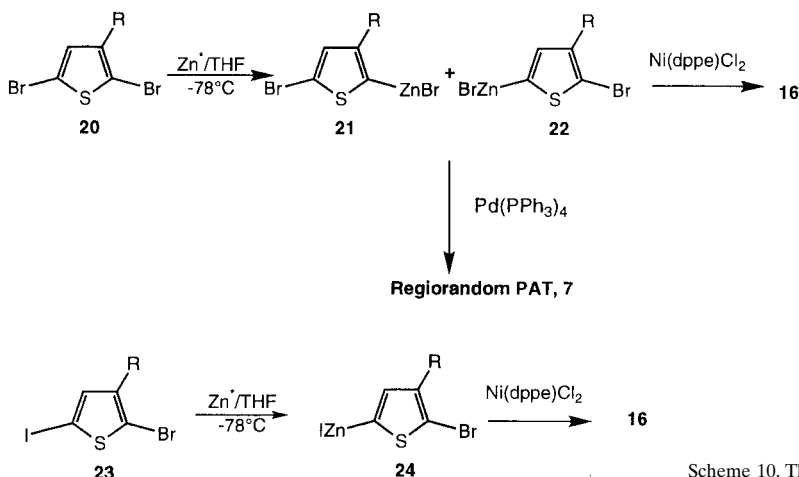
**The Rieke Method:** The second synthetic approach to HT-PAT was subsequently described by Chen and Rieke<sup>[79,80,86–88]</sup> (Scheme 10). This related coupling approach differs primarily in the synthesis of the asymmetric organometallic intermediate. In the Rieke method, a 2,5-dibromo-3-alkylthiophene (**20**) is added to a solution of highly reactive “Rieke zinc” (Zn\*). This metal reacts quantitatively to form a mixture of the isomers, 2-bromo-3-alkyl-5-(bromozincio)thiophene (**21**) and 2-(bromozincio)-3-alkyl-5-bromothiophene (**22**). The ratio between these two isomers is dependent upon the reaction temperature and, to a much lesser extent, the steric influence of the alkyl substituent. Although there is no risk of metal-halogen exchange, cryogenic conditions must still be employed because the ratio of isomers **21** and **22** produced is affected by the temperature. The addition of a Ni cross-coupling catalyst, Ni(dppe)Cl<sub>2</sub>, leads to the formation of a regioregular HT-PAT, whereas addition of a Pd cross-coupling catalyst, Pd(PPh<sub>3</sub>)<sub>4</sub>, will result in the formation of a completely regiorandom PAT. As an alternative approach, a 2-bromo-3-alkyl-5-iodothiophene (**23**) will react with Rieke



Scheme 8. The McCullough method for the regioregular synthesis of poly(3-alkylthiophenes) (PATs) with 100% head-to-tail couplings.



Scheme 9. Organometallic intermediates and quenching reactions.



Scheme 10. The Rieke method of preparing HT-PATs.

Zn to form only 2-bromo-3-alkyl-5-(iodozincio)thiophene (**24**). This species will then react in an identical fashion to form either a regioregular HT-PAT or the regiorandom equivalent, depending upon the catalyst that was used for the polymerization.<sup>[87]</sup> After precipitation and Soxhlet extraction, the yield for these reactions is reported to be ~75%. Molecular weights for polymers prepared by this method are  $M_n = 24\text{--}34\text{k}$  (with a PDI = 1.4). One advantage of the Rieke method is that highly reactive Rieke zinc affords a functional-group-tolerant synthesis. The McCullough method and Rieke method of synthesis of regioregular HT-coupled polythiophenes produce comparable materials that are not spectroscopically distinct. Both methods appear to be generally applicable to thiophenes that are tolerant to organolithium, Grignard reagents, or zinc reagents.

About the same time as regioregular, HT-PATs were prepared,<sup>[62,67]</sup> Holdcroft and co-workers<sup>[89]</sup> investigated the reaction of 2,5-diiodo-3-alkylthiophene with Mg and the subsequent polymerization of this reaction mixture. It was found that the reaction conditions and time lead to a variation in the amount of 2,5-diiodo-3-alkylthiophene, 2-iodo-5-magnesioiodo-3-alkylthiophene, and 2,5-dimagnesioiodo-

3-alkylthiophene. This, of course, greatly affects the regioregularity of the PAT synthesized. Quenching experiments on the reactive intermediates as well as the end groups were reported. Holdcroft was then able to use the above information in order to synthesize PATs containing a range of HT-HT couplings.<sup>[89]</sup> The relative configuration of the PAT can be examined from a triad (trimer repeat of alkylthiophenes) labeled as percentage of HT-HT couplings or from a dyad (dimer repeat of alkylthiophenes) labeled as percentage of HT. The two are often confused and are only important in PATs with <100% HT couplings. Holdcroft prepared PATs containing 35–58% HT-HT couplings (52–63% HT couplings, respectively). It is shown systematically how the optical and electronic properties vary with the regioregularity of the PAT, i.e., the larger the percentage of HT-HT couplings the more conjugated and more conductive the PAT will be. These results are mirrored by the physical properties of regioregular HT-PAT that have been studied by McCullough and Rieke.

*The Mechanism and Catalyst Choice:* The polymerizations described above utilize a metal-catalyzed cross-coupling technique that has been extensively investigated.<sup>[90–95]</sup> The reaction is believed to proceed by (i) oxidative addi-



tion of an organic halide with a metal-phosphine catalyst, (ii) transmetallation between the catalyst complex and a reactive organometallic reagent (or disproportionation) to generate a diorganometallic complex, and (iii) reductive elimination of the coupled product with regeneration of the metal-phosphine catalyst. Numerous organometallic species (including organomagnesium (Grignard), organozinc, organoboron, organoaluminum, and organotin) demonstrate sufficient efficiency to be utilized in cross-coupling reactions with organic halides. It should be noted that the choice of catalyst is a critical concern. It has been observed that the proportion of cross-coupling to homocoupling of the substrate, indicated by the degree of regioselectivity in the product PT, can be dependent upon both the metal and the ligands used in the catalyst.<sup>[86,87]</sup> A comparison of Ni versus Pd with monodentate (PPh<sub>3</sub>) or bidentate (Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>; dppe) ligands suggested that cross-coupling selectivity was a function of the steric environment of the catalyst. The catalyst with the greatest steric congestion, Ni(dppe)Cl<sub>2</sub>, produced almost exclusively cross-coupled product; the catalyst with the least congestion, Pd(PPh<sub>3</sub>)<sub>4</sub>, produced a random mixture of cross- and homocoupled product. However, in the Rieke case the polymerization proceeds from a mixture of regioisomers and the success of obtaining 100 % HT couplings depends on catalyst selectivity.<sup>[86,87]</sup> Where 2,5-dibromo-3-methylthiophene is reacted with Rieke Zn, the proportion of the isomers is 80:20. When 2,5-dibromo-3-cyclopentylthiophene or 2,5-dibromo-3-phenylthiophene is reacted with Rieke Zn, the proportions of isomers are 71:29 and 66:34, respectively. In contrast, in the McCullough method the polymerization proceeds from one regiospecifically generated monomer and therefore only HT couplings are found in all cases.

**NMR Characterization of HT-PAT:** Since poly(3-alkylthiophene)s and poly(3-substitutedthiophene)s are soluble in common organic solvents, <sup>1</sup>H and <sup>13</sup>C NMR can be used to determine their structure and regiochemistry.<sup>[24,35,51,53–56,62,63,67,74,86]</sup> In a regioregular, HT-PAT, for example, there is only one aromatic proton signal in the <sup>1</sup>H NMR spectrum, due to the 4-proton on the aromatic thiophene ring, at  $\delta = 6.98$ , corresponding to only the HT-HT triad sequence. Proton NMR investigations of regioirregular, electrochemically synthesized PAT reveal that four singlets exist in the aromatic region that can be clearly attributed to the protons on the 4-position of the central thiophene ring in each configurational triad: HT-HT, TT-HT, HT-HH, TT-HH. Synthesis of the four isomeric trimers by Barbarella and co-workers unambiguously assigned the relative chemical shift of each triad, with each trimer being shielded by about 0.05 ppm relative to the polymer.<sup>[63]</sup> In this analysis the HT-HT ( $\delta = 6.98$ ), TT-HT ( $\delta = 7.00$ ), HT-HH ( $\delta = 7.03$ ), TT-HH ( $\delta = 7.05$ ) couplings are readily distinguished by a 0.02–0.03 ppm shift (Table 1). These assignments are the same as the assignment by Holdcroft and co-workers<sup>[89]</sup> and different from those proposed by Sato and

Table 1. Chemical shifts corresponding to the various couplings in PT.

Configuration	Chemical shift $\delta$ [ppm]
HT-HT	6.98
TT-HT	7.00
HT-HH	7.02
TT-HH	7.05

Morii.<sup>[53,54]</sup> The relative ratio of HT-HT couplings to non-HT-HT couplings can also be determined by an analysis of the protons that are on the  $\alpha$ -carbon of the 3-substituent on thiophene.<sup>[24,55]</sup> Relative integration of the HT-HT peak relative to the other non-HT resonances can give the percentage of HT-HT couplings. From this type of NMR analysis, regioregular HT-PATs contain ~100 % HT-HT couplings.<sup>[62,67,75,86,87]</sup> Samples from the FeCl<sub>3</sub> method contain 50–70 % HT-HT couplings, in general.<sup>[62,67]</sup> End groups have also been identified in both PATs and HT-PATs<sup>[87,89]</sup> by both NMR and matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS).<sup>[96]</sup>

The degree of structural regularity is likewise apparent in the <sup>13</sup>C NMR spectrum in that only four resonances are apparent in the aromatic region, and they are attributable to the four carbons of a HT-coupled thiophene ring (e.g., PHT,  $\delta = 128.5, 130.5, 134.0, \text{ and } 140.0$  ppm). Examination of the <sup>13</sup>C NMR spectrum of regioirregular PHT shows an abundance of resonances from 125 to 144 ppm.

**IR and UV-vis:** A measure of the conjugation length can be determined by both IR and UV-vis. The intensity ratio of the symmetric IR band at ~1460 cm<sup>-1</sup> to the asymmetric band at ~1510 cm<sup>-1</sup> C=C ring stretches decreases with increasing conjugation length. For HT-PATs this ratio is 6–9, less than half of the 15–20 value measured for regiorandom samples.<sup>[87]</sup> In the UV-vis the red shift of the maximum absorption, which is the  $\pi$ - $\pi^*$  transition for the conjugated polymer backbone, is an indication of an increase in conjugation in the polymer.

If a qualitative comparison of the solution UV-vis of PATs is made, a red shift of  $\lambda_{\text{max}}$  is found in regioregular HT-PATs compared to regiorandom, regioirregular PATs.<sup>[62,67,74,75,86,87]</sup> (Table 2). As an example, the solution (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$  for HT-poly(3-dodecylthiophene) (PDDT) is about 450 nm, whereas PDDT from FeCl<sub>3</sub> has  $\lambda_{\text{max}} = 436$  nm and regiorandom PDDT has  $\lambda_{\text{max}} = 428$  nm.<sup>[62,67,74,75,87]</sup> Thus the regioregular HT-PATs have lower energy  $\pi$  to  $\pi^*$  transitions, indicating longer conjugation length.

Spectra of regioirregular PAT films contain little structure and consist of a single broad absorption for the  $\pi$  to  $\pi^*$  transition. Drop-cast films of HT-PAT, in contrast, are red-shifted and vibronic structure is apparent in the  $\pi$  to  $\pi^*$  transition.<sup>[62,67,74,75,87]</sup> It is interesting to note that this fine structure may range from shoulders to well-defined peaks with definite absorption frequencies but varying intensities, mainly varying with film thicknesses or processing conditions. Films of irregular PAT polymers prepared from the FeCl<sub>3</sub> route have  $\lambda_{\text{max}} = 480$  nm. Films of the regioregular

Table 2. Comparison of the solution UV-vis of PATs.

3-Substituent	$\lambda_{\max}$ in solution [nm]				
	Random [87] 50%HT	FeCl <sub>3</sub> [62] 70% HT	Electrochem. [126] ?% HT [a]	Rieke [87] 98–99% HT	McCullough [62] 98–99% HT
Butyl	428	436	434	449	450
Hexyl	428	436	434	456	442
Octyl	428	436	440	453	460
Dodecyl	428	436	440	453	460

[a] Holdcroft and co-workers [89] have shown that 69 % HT-HT poly<(3-hexylthiophene) has  $\lambda_{\max} = 434$  nm and 80 % HT-HT has  $\lambda_{\max} = 440$  nm.

HT-PATs have solid-state absorptions ranging from  $\lambda_{\max} = 562$  nm for “thin” films of HT-PDDT to 530 nm for “thick” films of HT-PDDT (Table 3). Analysis of thin films of HT-PATs by UV-vis spectroscopy reveal the presence of at least three distinct peaks. For example, HT-poly(3-dodecylthiophene) has  $\lambda_{\max} = 562$  nm in the solid state. The lower-intensity peaks appear at  $\lambda = 530$  and 620 nm.<sup>[57]</sup> These non- $\lambda_{\max}$  peaks are quite substantial in intensity, ranging from 60 to 100 % of the  $\lambda_{\max}$  intensity (depending on film thickness) (Table 3). The band edge for regioregular PT ranges from 1.7 to 1.8 eV,<sup>[67,75,87]</sup> a 0.3–0.4 eV improvement over the 2.1 eV reported for a regiorandom sample. Bjørn-

 Table 3. Values of  $\lambda_{\max}$  for various polymers prepared by different routes.

Polymer	$\lambda_{\max}$ in solid state [nm]			
	McCullough “thick film” >98% HT [75]	McCullough “thin film” >98% HT [78]	Rieke “thin film” >98% HT [87]	FeCl <sub>3</sub> 70% HT [75]
PBT <b>4d</b>	500*	525	522	480
	580	560*	556*	
	610	608	605	
PHT <b>4c</b>	504*	525	526	480
	550	555*	556*	
	600	610	608	
POT <b>4b</b>	520*	525	522	480
	553	559*	556*	
	603	610	608	
PDDT <b>4a</b>	526*	530	524	480
	561	562*	560	
	609	620	610	

holm and co-workers<sup>[97]</sup> have carried out nonlinear optical (NLO) studies on HT-PATs and as part of these they estimated the conjugation length from linear optical data. In irregular PDDT the conjugation length was determined to be 7 thiophene rings, while regioregular HT-PDDT has a conjugation length of 40 thiophene rings (80  $\pi$  electrons). The saturation was estimated to be roughly 100  $\pi$  electrons. Therefore, simple elimination of coupling defects, which minimizes unfavorable steric interactions of the substituents, markedly improves the solid-state order and conjugation length, resulting in a reduction in the bandgap.

The differences in the degree of conjugation and macroscopic morphological order in HT-PATs is a function of film thickness (Table 3). A similar observation was reported by Roncali, Garnier, and Yassar,<sup>[98,99]</sup> who found that regioirregular poly(3-methylthiophene) (PMT) prepared electrochemically exhibited a thickness-dependent

solid-state UV-vis spectrum, which correlated with the conjugation lengths and electrical conductivity. They found that 0.2  $\mu\text{m}$  thin films of poly(3-methylthiophene) had  $\lambda_{\max} = 510$  nm, while the thinner films 0.006  $\mu\text{m}$  thick had  $\lambda_{\max}$  values as high as 552 nm. The observation was explained by noting that, as the polymer film thickens, morphological disorder can increase, leading to a more disordered film relative to ultra-thin films. These thin films of non-HT PMT had a very high degree of structural order and extended  $\pi$  conjugation lengths with conductivities of up to 2000 S/cm. In much thicker films (1–3  $\mu\text{m}$ ) of HT-PATs, the  $\lambda_{\max}$  of POT is 559 nm and that of PDDT is 562 nm; i.e., the conjugation lengths of HT-PATs are comparable to the very highly ordered, very thin films (0.006  $\mu\text{m}$ ) of non-HT poly(3-methylthiophene). Therefore the morphological order found in the “thin film regime” has been greatly extended from 0.006  $\mu\text{m}$  to ~1–3  $\mu\text{m}$  by the regular placement of the side chains in HT-PATs.

*Self-Assembly, X-Ray, and Electrical Conductivity in HT-PATs:* One of the most fascinating physical property differences between irregular PATs and regioregular HT-PATs is that supramolecular ordering occurs in regioregular HT-PATs and not in irregular PATs. Self-assembly in regioregular HT-PATs were first discovered by McCullough.<sup>[75–78]</sup> Solution light scattering studies<sup>[100–104]</sup> by Berry and co-workers<sup>[52]</sup> coupled with X-ray studies by McCullough et al.<sup>[75]</sup> and Winokur and co-workers<sup>[105]</sup> on thin films show that macromolecular self-assembly occurs in these conducting polymers<sup>[106]</sup> (Fig. 1).

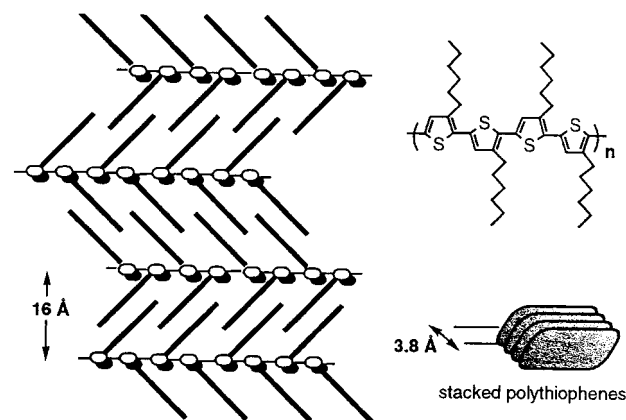
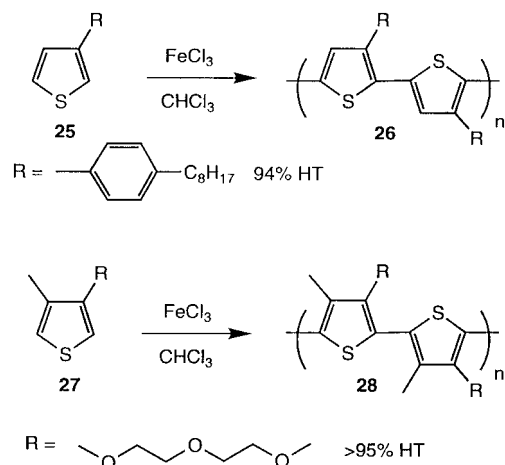


Fig. 1. Self-assembled conducting polymer superstructures form from regioregular polythiophenes as confirmed by X-ray studies and light scattering studies.

The self-assembled structure leads to a large increase in electrical conductivity in HT-PATs relative to irregular PATs. While the measured conductivity of HT-PAT films cast from the same sample can differ markedly as a result of varying morphology from film to film, for the conductivities of HT-PDDT (doped with  $I_2$ ) the maximum reported values are 1000 S/cm.<sup>[75]</sup> Values for other HT-PATs synthesized by McCullough et al.<sup>[62,67]</sup> exhibited maximum electrical conductivities of 200 S/cm (POT) and 150 S/cm (PHT).<sup>[75]</sup> McCullough et al. have routinely measured conductivities of 100–200 S/cm in these samples in HT-PDDT<sup>[77]</sup> (Fig. 2). In contrast, PDDT from  $FeCl_3$  generally gave conductivities of 0.1–1 S/cm (58–70 % HT). Rieke and co-workers have reported that their HT-PATs have conductivities of 1000 S/cm.<sup>[87]</sup> Chen and Rieke also report that the average conductivity for HT-PBT is 1350 S/cm, with a maximum conductivity of 2000 S/cm.<sup>[79]</sup>

**Other Methods:** Following the reports by McCullough and Rieke, other groups have found that specific oxidative conditions with a limited number of thiophene monomers can lead to an increase in the number of HT couplings in polythiophene derivatives. Andersson et al. report<sup>[108]</sup> that the combination of a sterically hindered, activating 3-substituent and the slow addition of  $FeCl_3$  leads to a regioselective synthesis of phenyl-substituted polythiophenes with PDIs of 2.5 (Scheme 11). It has also been shown by Levesque and Leclerc<sup>[109]</sup> that the preparation of poly(3-alkoxy-4-methylthiophenes) by  $FeCl_3$  coupling can lead to highly regioregular materials (Scheme 11). This may be due to an asymmetric reactivity of the oxidized monomers.



Scheme 11. Two monomers that give regioregular polymers by the  $FeCl_3$  method.

**Random Copolymers of Alkyl Thiophenes:** Random copolymers of 3-octylthiophene and 3-methylthiophene were prepared electrochemically and upon doping these copolymers were more thermally stable than the homopolymers.<sup>[110]</sup>

**Head-to-Tail Coupled, Random Copolymers of Alkyl Thiophenes:** Regioregular HT-random copolymers of PAT have been prepared by McCullough and Jayaraman.<sup>[111]</sup> HT-coupled PAT random copolymers were synthesized by the route shown in Scheme 12. The Grignard compounds **29** and **30** were generated using the standard procedure and polymerized to give polymers **31–35**, by simply mixing aliquots of **29** and **30** in direct proportion to the amount of

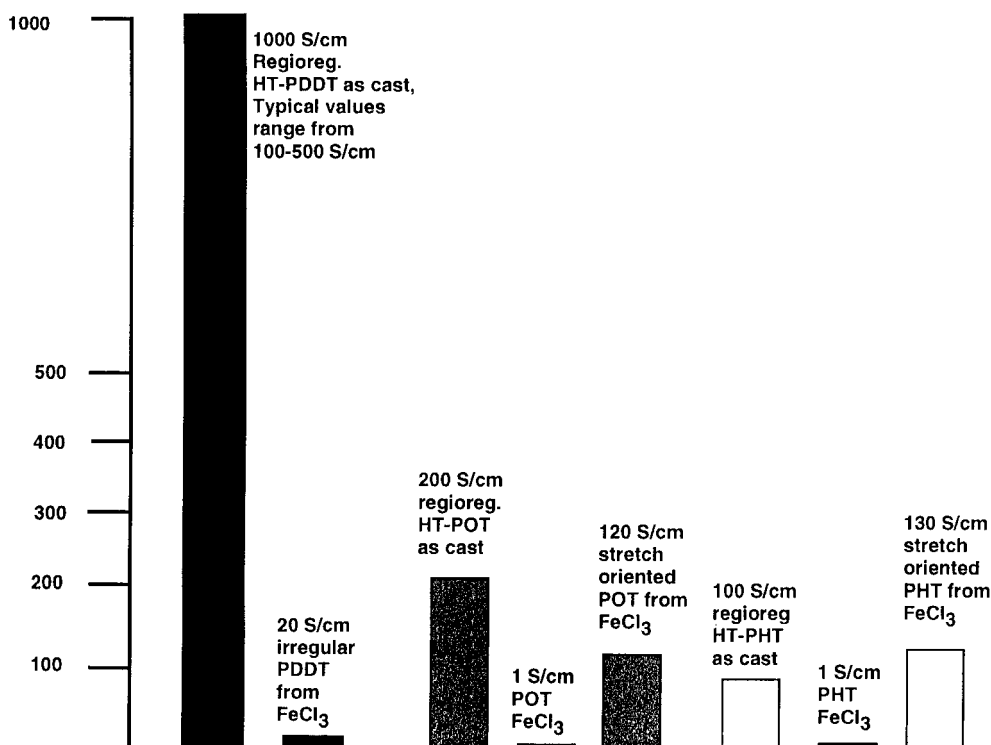
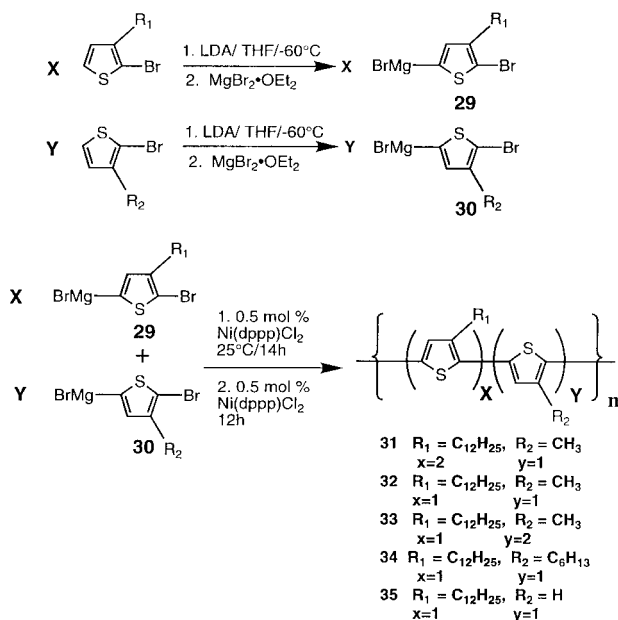


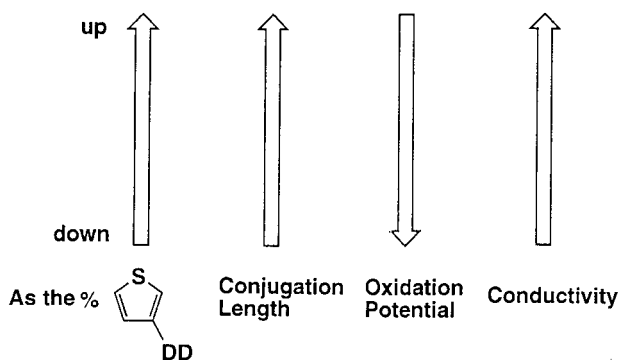
Fig. 2. Maximum electrical conductivities found in PATs. A 20- to 50-fold increase in electrical conductivity is achieved by stretch-orienting PATs. For example, the stretch-oriented PAT samples in the diagram [107] had initial conductivities of 10–20 S/cm.



Scheme 12. Synthesis of random HT-copolymers of PATs.

incorporation desired. These copolymers are very soluble in typical organic solvents and possess excellent film-forming abilities.

The solution UV-vis data for the copolymers **31–33** indicate that increasing the amount of dodecyl side chains increases the *solution* disorder, leading to a non-planar structure.<sup>[111]</sup> However, in the solid state, the polymers with a higher percentage of dodecyl side chains self-assembled, forming planar structures with long conjugation lengths. The conjugation in the solid state was greatest in polymer **31** (2:1,  $C_{12}H_{25}:CH_3$ ;  $\lambda_{max} = 565$  nm), and decreased in polymer **32** (1:1,  $C_{12}H_{25}:CH_3$ ;  $\lambda_{max} = 550$  nm), and polymer **33** (1:2,  $C_{12}H_{25}:CH_3$ ;  $\lambda_{max} = 545$  nm). In addition, cyclic voltammetry of thin films of **31–33** indicated that **31** has a longer conjugation length in the solid state and that the oxidation potential decreases as the proportion of dodecyl side chains decreases (Fig. 3).



in regioregular HT-coupled 3-dodecylthiophene/3-methylthiophene copolymers increases, the conjugation length increases, the oxidation potential decreases, and the conductivity increases

Fig. 3. Tuning the properties of electronic and photonic conjugated polymers by recipe.

Conductivity results indicate that  $I_2$ -doped thin films (0.5–4  $\mu\text{m}$ ) of polymers **31** and **33** exhibited electrical conductivities in the range of 50–200 S/cm.<sup>[75]</sup> In addition, the physical properties of these polymers were unchanged over number average molecular weights ( $M_n$ ) ranging from 9 to 28k (PDI = 1.6). Therefore, apparently the physical properties are not a function of the molecular weight.

### 3.2. Branched Alkyl PATs

Early reports indicated that 3-isopropylthiophene could not be electrochemically polymerized and therefore few branched alkyl PATs were prepared chemically. However, in 1992, Wegner and co-workers<sup>[112]</sup> prepared poly(3-cyclohexylthiophene) (PCHT) (**36**) (Fig. 4) and compared the

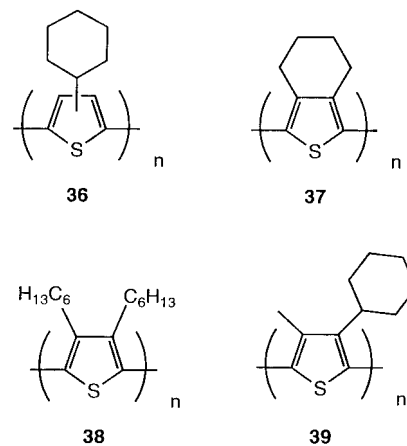


Fig. 4. Sterically encumbered PTs.

bandgap, nonlinear optical properties, and the electrical conductivity of the material with poly(3-hexylthiophene) prepared with  $FeCl_3$ . The  $M_w$  (73k) of PCHT was roughly the same as for PHT. However, PCHT was much less conjugated, by 80 nm in the solid state relative to PHT. The two polymers were electrochemically doped in the presence of  $ClO_4^-$  and the conductivities of PHT and PCHT were 0.4 S/cm and 0.0017 S/cm, respectively. These results indicated that sterically bulky side chains on PATs cause a steric twisting of the backbone and reduce the conjugation and electrical conductivity in PATs. A PT containing an annealed cyclohexyl ring, **37**, has also been prepared by Wegner and found to have a lower electroactivity, conductivity, etc. than poly(3,4-dihexylthiophene) (**38**) and PHT as prepared from  $FeCl_3$ <sup>[113]</sup> (Fig. 4).

Poly(3-cyclohexyl-4-methylthiophene) (PCHMT) (**39**) (Fig. 4) and poly(3-cyclohexylthiophene) (PCHT) (**36**) have been made by the  $FeCl_3$  method in order to test these polymers as polymers LEDs.<sup>[114]</sup> PCHMT gave  $M_w$  of 72k (PDI 2.8) and a film  $\lambda_{max}$  of 303 nm and PCHT had  $M_w$  of 56k with a very large PDI of 9 and a film  $\lambda_{max}$  of 426 nm, with 77% HT coupling. It was found that by varying the steric environment of the PT LEDs emitting from blue to near-infrared could be made.

Recently Guillerez and co-workers<sup>[115]</sup> have prepared regioregular chiral HT-PATs, namely poly(3-(*S*-3',7'-dimethyloctyl)thiophene) (**40**) (Fig. 5). They have shown that if the steric group is far enough removed from the backbone then the conjugation is relatively unaffected. Study of this PT reveals that circular dichroic spectroscopy can be used, in regioregular HT-PTs bearing a chiral group, to probe aggregation behavior, as was first pointed out by Bouman and Meijer.<sup>[116]</sup> In addition, the above polymer exhibited large conformational changes induced by minute solvent variation.

Fluorinated PTs have been prepared using the FeCl<sub>3</sub> method by Robitaille and Leclerc and the ability of these polymers to form monolayers was investigated<sup>[117]</sup> (**41,42**) (Fig. 5). In addition, the polymerization of 2-(3-thienyl)ethyl perfluoroalkanoates (**43–45**) (Fig. 5) by the FeCl<sub>3</sub> method has been accomplished by Middlecoff and Collard.<sup>[118]</sup> These polymers are being investigated for their ability to self-assemble via fluorophobic association.

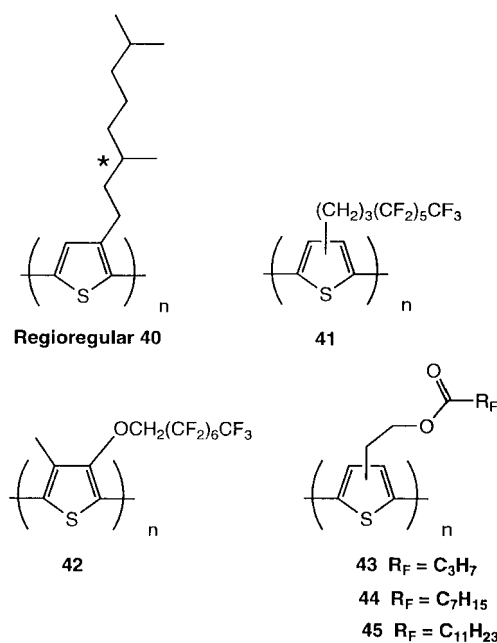


Fig. 5. Chiral alkyl- and fluoroalkyl-substituted PTs.

### 3.3. PTs with Phenyl Side Chains

Phenyl-substituted PTs were synthesized by Ueda et al.<sup>[119]</sup> using basically the polycondensation polymerization of 2,5-dihalothiophenes developed by Yamamoto<sup>[8–13]</sup> using NiCl<sub>2</sub>, PPh<sub>3</sub>, bipyridine, Zn, and *N,N*-dimethylacetamide (DMAC). The effect of solvent, amount of DMAC, NiCl<sub>2</sub>, PPh<sub>3</sub>, and bipyridine, and temperature were investigated. The solution  $\lambda_{\text{max}}$  of the poly(3-phenylthiophene) was 430 nm, which is essentially the same as sexithiophene. The polymer was soluble in typical organic solvents and films were found to be very thermally stable (10 % weight loss at 550 °C in air). Poly(3-phenylthiophene) was also prepared by the Rieke method from a mixture of regioisomers of bromo-zincbromothiophenes.<sup>[80]</sup>

Nearly regioregular (94 % HT reported) poly(3-(4-octylphenyl)thiophene) has been prepared<sup>[108]</sup> using FeCl<sub>3</sub> to oxidatively polymerize 3-(4-octylphenyl)thiophene. The film  $\lambda_{\text{max}}$  of the poly(3-phenylthiophene) was 493 nm, which increased to 602 nm upon exposure to CHCl<sub>3</sub>. Later papers reported on copolymers of thiophene and octylphenylthiophene<sup>[114]</sup> and the parent poly(3-(4-octylphenyl)thiophene).

## 4. Chemical Synthesis of Heteroatomic Functionalized Substituents on PTs: Recognition Sites for Self-Assembly and Chemical Sensing

The ability of PT to change its color and electrical conductivity in response to various analytes, solvents, and environment make the conjugated polymer an ideal candidate as an all-polymer sensor. The linear-alkyl-substituted polymers have been most widely studied because of their ease of synthesis. However, increasingly heteroatom-substituted PTs are being designed, synthesized and explored in order to engineer intelligent properties into the conducting polymer. The possibility of merging host–guest chemistry, biological macromolecular assembly, organic self-assembly, and inorganic structural chemistry to create new conjugated polymer devices and smart materials is a rapidly expanding area. In the 1980s, Wrighton, Murray, Baughman, and Garnier were among the pioneers that published general discussions of conducting polymer sensors and early demonstrations of the phenomena.<sup>[120–125]</sup> A perspectives paper by Garnier<sup>[120]</sup> specifically suggested that, due to the ease of synthesis of a large variety of PTs, functionalized polythiophenes could be used as molecular sensors. Garnier and Roncali initially demonstrated that alkoxy-substituted and chiral alkoxy-substituted PTs that were synthesized electrochemically acted as sensors for cations. The alkoxy PT **47** (Fig. 6) showed a 200 mV shift in the oxidation potential of the polymer when Bu<sub>4</sub>NClO<sub>4</sub> was used an electrolyte instead of LiClO<sub>4</sub> in solid-state cyclic voltammetry (CV). This indicates that the electrochemical response of PT can be altered by environmental effects. The chiral PT electrochemically synthesized in the study was found to recognize the complementary enantiomeric anion used as a dopant during redox cycles in the CV experiment. These results demonstrated the use of alkoxy-substituted PTs as conducting polymer sensors. The large body of work on the electrochemical synthesis of alkoxy-substituted PTs has been reviewed by Roncali<sup>[50,126]</sup> and is beyond the scope of this review.

### 4.1. Chemical Synthesis of Alkoxy Polythiophenes

Alkoxy PTs and related derivatives were the first reported to be electrochemically synthesized.<sup>[126–133]</sup> Alkoxy

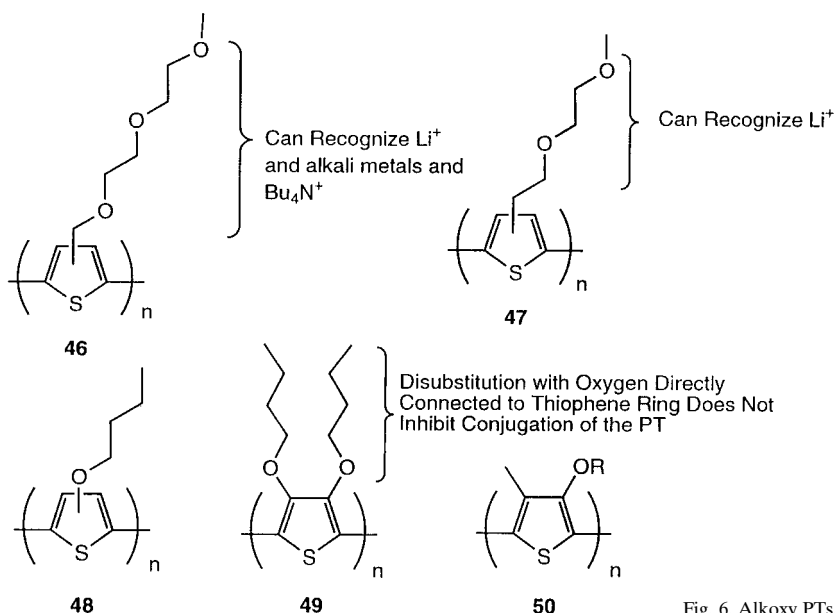


Fig. 6. Alkoxy PTs.

derivatives have several advantages over PATs. The first is that if the oxygen is directly attached to the ring, the bandgap in the conducting polymer can be reduced by a substantial amount<sup>[55]</sup> and the conducting state of the polymer is stabilized.<sup>[130,134]</sup> In addition, the side chains can act molecular recognition units for chemical sensing or as arms for directed self-assembly of the polymer. Poly(3-methoxy-2,5-thiophenediyl) was chemically synthesized using the  $\text{FeCl}_3$  method.<sup>[135]</sup> The polymer had limited solubility in dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidinone (NMP), and propylene carbonate (PC). The polymer was characterized by UV-vis-NIR, IR, CV, and electrical conductivity measurements. Short alkoxy chains on PTs that had been synthesized chemically or electrochemically generally led to low molecular weight and insoluble materials.

Two solutions to the solubility problem were provided by Bryce et al. (46),<sup>[128]</sup> Roncali et al. (47),<sup>[133]</sup> and Leclerc and Daoust<sup>[48-50]</sup> (Fig. 6). Long chain alkoxy substituents led to large increases in solubility,<sup>[128,133]</sup> while 3,4-disubstituted PTs led to the same effect.<sup>[134,136]</sup> A comparison of poly(3-butoxythiophene) (48), poly(3,4-dibutoxythiophene) (49), and poly(3-alkoxy-4-methylthiophene) (50) prepared by the  $\text{FeCl}_3$  method<sup>[134,136]</sup> shows that poly(3-butoxy-4-methylthiophene) showed the highest electrical conductivity (2 S/cm, after doping with  $\text{FeCl}_3$ ) among this group of polymers. It was found that despite 3,4-substitution on PT, poly(3-butoxy-4-methylthiophene) did not appear to exhibit a large steric twist of the PT backbone. In fact,  $\lambda_{\text{max}}$  was 420 nm ( $\text{CHCl}_3$ ) and 545 nm (film), indicating a highly conjugated PT. This is contrary to both poly(3,4-dimethylthiophene) and poly(3,4-dibutoxythiophene) polymers, where the 3,4-disubstitution causes a sterically driven twist of the conjugated backbone and leads to very low conductivity in the doped polymer. This study indicated that certain 3,4-disubstituted PTs could be highly conductive polymers. The importance of this finding led to the de-

velopment of very stable conducting polymers based on PT, namely poly(3,4-ethylenedioxythiophene) (PEDOT) (51) (Fig. 7), which will be discussed later. It is important to note that evidently oxygens directly attached to the ring not only reduce the bandgap of the polymer but also do not cause a detrimental steric twist of the polymer out of conjugation.

Cloutier and Leclerc<sup>[137]</sup> followed the above study with the chemical synthesis of poly(3,3'-dibutoxy-2,2'-bithiophene) (3,3'-PDBBT) (52) (Fig. 7) by polymerizing 3,3'-dibutoxy-2,2'-bithiophene with  $\text{FeCl}_3$  using the Sugimoto/Yoshino method. The PDBBT was a very highly conjugated

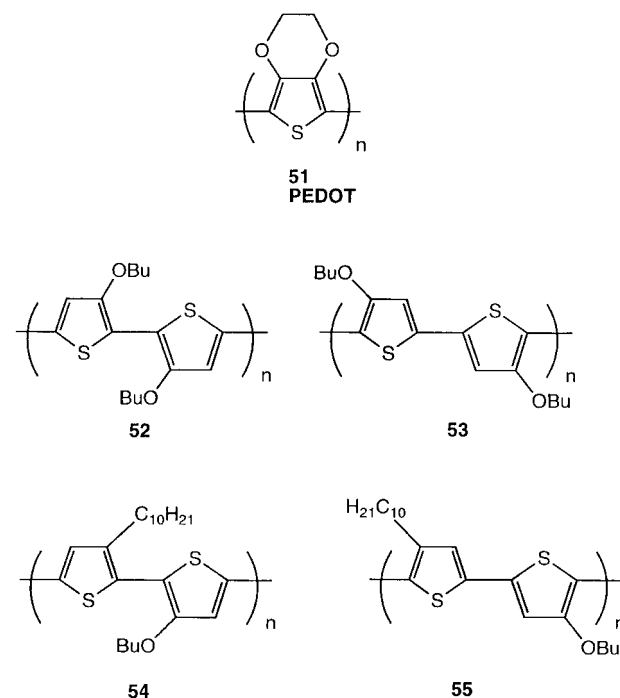


Fig. 7. More alkoxy PTs, including PEDOT.

PT, which showed a film  $\lambda_{\max}$  of about 580 nm and an electrical conductivity of 2 S/cm. One of the most interesting findings was that upon electrochemical or chemical oxidation of the polymer, the film became nearly transparent in the visible region. Further development<sup>[138]</sup> of poly(bithiophene) derivatives led to the FeCl<sub>3</sub> synthesis of poly(3-butoxy-3'-decyl-2,2'-bithiophene) (**54**), poly(4-butoxy-4'-decyl-2,2'-bithiophene) (**55**), poly(3,3'-dibutoxy-2,2'-bithiophene) (3,3'-PDBBT) (**52**), and poly(4,4'-dibutoxy-2,2'-bithiophene) (4,4'-PDBBT) (**53**). The 3,3'-PDBBT is made from the HH dimer of dibutoxybithiophene, whereas the 4,4'-PDBBT is made from the TT dimer of dibutoxybithiophene. The 4,4'-PDBBT was found to have a molecular weight three times higher than that of the 3,3'-PDBBT and the 4,4'-PDBBT was more conjugated by roughly 20 nm. However, there was very little difference in electrical conductivity or the redox behavior of the two polymers. The asymmetrically substituted polybithiophenes showed lower electrical conductivities (0.01–0.25 S/cm vs. 2–3 S/cm) than both 3,3'-PDBBT and 4,4'-PDBBT due to the presence of non-regioregular couplings. The presence of 25 % HH couplings was reported.

Other alkoxy PTs have been prepared with FeCl<sub>3</sub><sup>[139]</sup> and solubilities, molecular weights, X-ray, thermogravimetric analysis (TGA), etc. have been reported. Alkoxy PTs have also been prepared by a Cu(ClO<sub>4</sub>)<sub>2</sub> oxidation of bithiophenes.<sup>[140]</sup> Poly(3-(alkoxyphenyl)thiophene)s with *meta*- and *para*-alkoxy substituents have been prepared using the FeCl<sub>3</sub> method and the third-order nonlinear optical properties of these polymers were studied.<sup>[141]</sup> Langmuir–Blodgett films of alkoxy PTs have also been prepared and studied.<sup>[142,143]</sup> Grignard preparation via Kumada coupling has led to alkoxy PTs<sup>[144,145]</sup> that have been studied in devices such as polymer LEDs.

In 1991, poly(3,4-ethylenedioxythiophene) (PEDOT) (Fig. 7) was prepared.<sup>[146]</sup> The very stable conducting polymer was initially chemically prepared by BASF as a thin film coating for antistatic plastics. A polycarbonate film was coated with a thin layer of polyvinylacetate containing an iron(III) salt. A second coating of EDOT on top led to PEDOT in a polyvinylacetate matrix. The material showed excellent stability in the conductive state. The polymer PEDOT can also be prepared in bulk<sup>[147]</sup> by polymerizing 3,4-ethylenedioxythiophene with FeCl<sub>3</sub>. The PEDOT (doped with FeCl<sub>3</sub>) prepared in refluxing CH<sub>3</sub>CN gave a conductivity of 15 S/cm, while the polymer prepared in refluxing benzonitrile had a conductivity of 19–31 S/cm, depending on reaction time. A later paper<sup>[148]</sup> reported that chemically prepared PEDOT (using the FeCl<sub>3</sub> method) led to a polymer that was, for the most part, not soluble. On the other hand, when EDOT was electrochemically polymerized, a soluble PT resulted. Reynolds<sup>[149]</sup> found that in the synthesis of tetradecyl-substituted poly(ethylenedioxythiophene)s (PEDOT-C<sub>14</sub>H<sub>29</sub>) the solubility of the resultant polymer was very sensitive to the FeCl<sub>3</sub>/monomer ratio. When the ratio was 1, 100 %

solubility was found and the solubility decreased to 0 % solubility when the ratio was 5. The polymer PEDOT-C<sub>14</sub>H<sub>29</sub> formed deep purple films and upon electrochemical oxidation gave light green transparent films at a very low oxidation potential of 0.3 V versus Ag wire. Crown ether annelated PTs have also been polymerized using nickel catalysts.<sup>[150]</sup>

## 4.2. Chemically Prepared Alkoxy PTs as Conducting Polymer Sensors

In the preparation of conducting polymer sensors,<sup>[120–125,151–153]</sup> it is critical that the control of the structural regularity be maintained. That is to say that a PT with a regular placement of the side chains or molecular recognition units will maximize the planarity of the PT and allow for the largest response window. In addition, the chemical synthesis of PTs allows for large amounts of material to be generated. Two reports of a tunable conducting polymer and sensors that can be prepared chemically were published in 1993 by McCullough and Williams<sup>[154]</sup> and Marsella and Swager<sup>[155]</sup> (Fig. 8). McCullough reported that the conductivity and electrochemical and optical responses in regioregular alkoxy-substituted PTs (e.g., **56**) are highly sensitive to the nature and regiospecificity of the side chains.<sup>[75,154]</sup> It was found that small conformational changes due to analyte or ion detection or minute solvent polarity changes produce large effects in regioregular PTs. Swager reported on PTs where adjacent thiophene rings are linked by a crown ether-like unit (**57**). It was found that upon complexation of ions the PT conjugation is greatly reduced, thus exhibiting a sensory response.

Four related polymers **56**, **64–66** (Scheme 13) were designed and prepared in order to investigate whether the polyethylene glycol-like side-chains could help to increase electrical conductivity by increasing the ionic conductivity of the material. In addition, it was thought that, since the regioregular placement of the side chains allows for binding cavities to be created, these “sensory arms” could be used to detect various analytes. The substituent on **65** is too short to allow solubility in the growing polymer, therefore only low molecular weight materials are produced. Similarly **64** yielded only marginally better results ( $M_w = 6000$ ; PDI = 2). However, polymer **56**, determined to be >99 % HT by NMR, was markedly different. The product was regularly of high molecular weight ( $M_w = 71\,000$ ; PDI = 2; ~160 thiophene rings/chain). When doped with I<sub>2</sub> this polymer exhibited very high electrical conductivity of between 500 and 1000 S/cm on average, and a maximum conductivity of 5500 S/cm for one sample of exceptional film quality.<sup>[154]</sup> These results indicate that **HT-56** exhibits higher electrical conductivities than HT-PATs. This is in line with early reports on the high conductivity found in irregular **56**<sup>[128]</sup> and contrary to reports on other studies on irregular **56**.<sup>[126]</sup> It is possible that solid-state ion-dipole binding led to a highly ordered structure for irregular **56** polymerized in the presence

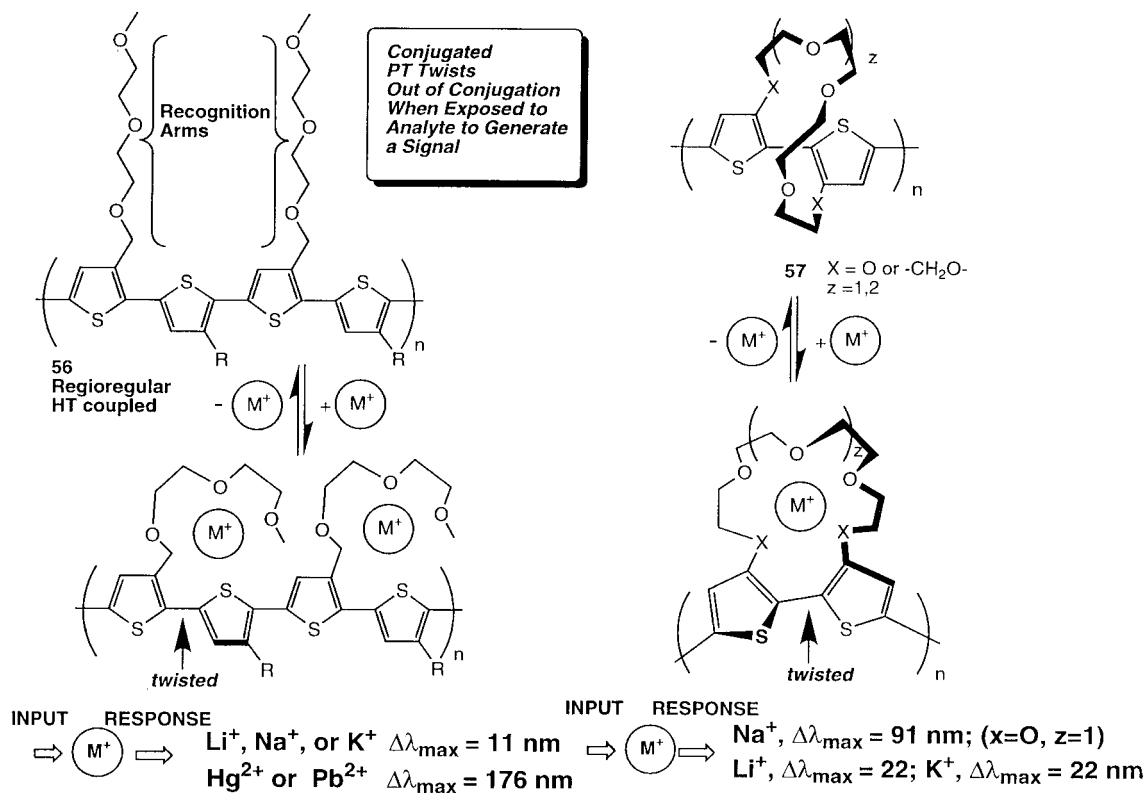
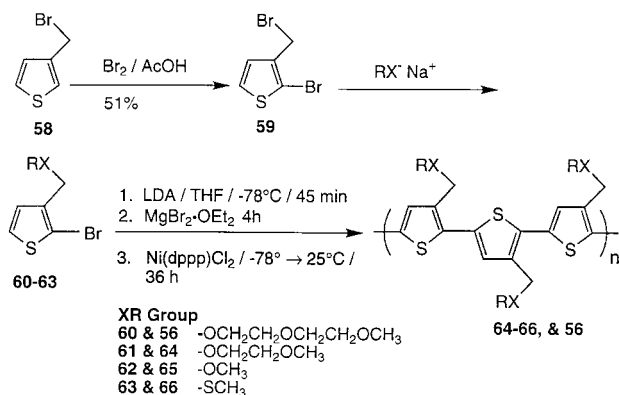


Fig. 8. PTs as chemoselective sensors.



Scheme 13. The synthesis of head-to-tail coupled, heteroatom-substituted polythiophenes.

of Bu<sub>4</sub>N<sup>+</sup> and hence led to a highly conductive sample. Molecular models show that the Bu<sub>4</sub>N<sup>+</sup> fits well in a cavity formed by polyether arms. In addition, high conductivity in **56** may also be due to a predicted increase in the ionic conductivity, facilitated by the etheric side chains, thereby increasing the charge carrier mobility. As was the case with the PATs, film morphology appears to be the limiting factor in reproducing high conductivity.

Polymer **56** does exhibit ion binding properties, and an ionochromic response occurs upon exposure to Li<sup>+</sup> in acetonitrile, leading to a blue shift of up to 11 nm.<sup>[154]</sup> A dramatic chemoselective sensory response to Pb<sup>2+</sup> and Hg<sup>2+</sup> in CHCl<sub>3</sub> was discovered for **56** as indicated by a 200 nm blue shift in

dilute solution<sup>[76,106,156]</sup> upon addition of PbCl<sub>2</sub> or HgCl<sub>2</sub>. There is no colorimetric or optical response to Li<sup>+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, and a host of other ions. In concentrated solutions the effect is different. Concentrated solutions of **HT-56** are deep magenta without added Pb salts ( $\lambda_{\text{max}} = 575\text{--}600$  nm; band edge at 700 nm). Again a striking transformation occurs upon the introduction of Pb(BPh<sub>4</sub>)<sub>2</sub> to the solution of **HT-56**. The conjugation length immediately decreases, as indicated by a blue shift of 50–100 nm upon introduction of Pb<sup>2+</sup> ion accompanied by a 50 nm blue shift in the band edge ( $\lambda_{\text{max}} = 480\text{--}550$  nm; band edge at 650 nm). A film cast from **HT-56** and Pb(BPh<sub>4</sub>)<sub>2</sub> is yellow in color ( $\lambda_{\text{max}} = 440$  nm; band edge at 550 nm). In contrast, films cast from the salt-free solution are deep crimson in color ( $\lambda_{\text{max}} = 520$  nm; band edge at 720 nm). There is a huge (170 nm) difference in the band edge between films cast in the presence and the absence of Pb<sup>2+</sup>. Since films of pure Pb(BPh<sub>4</sub>)<sub>2</sub> are colorless, the Pb<sup>2+</sup> ions induced a large disordering of the polymer. Comparison, by X-ray analysis, of a film of **HT-56** to a similar film that had been cast in the presence of Pb(OAc)<sub>2</sub> indicates that the Pb<sup>2+</sup> ions cause a significant amount of disorder in the film. X-ray diffraction shows that the very strong, wide-angle reflection, which represents interchain stacking of thiophene rings, has a half-width of 0.23 Å for a film that contains Pb<sup>2+</sup>. In contrast, the corresponding half-width for the uncontaminated film is 0.11 Å. In addition, iodine-doped films of **HT-56** that had been cast from a solution (in CHCl<sub>3</sub>) saturated with Pb(OAc)<sub>2</sub> showed a ~10 000-fold de-



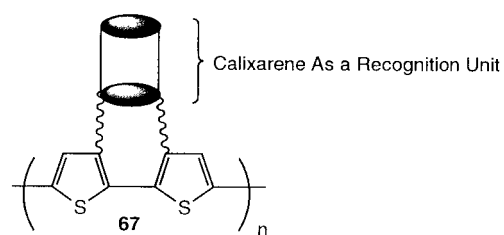
crease in electrical conductivity when compared to similar samples that contained no Pb salts ( $\sigma \approx 0.001\text{--}0.01$  versus  $\sigma \approx 100\text{--}1000$  for samples without Pb).<sup>[106,156]</sup>

Regioregular PT **56** solutions of  $10^{-6}$  M are able to colorimetrically detect Pb and Hg at minute concentrations of  $10^{-6}$  M even in the presence of multiple ions, making these PTs outstanding Pb and Hg detectors.

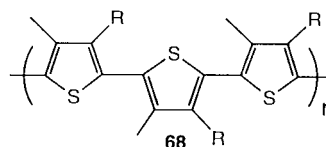
Regular polymers (e.g. **57**) (Fig. 8) were prepared and ionochromatic responses were measured in 0.1 M salt solutions in  $\text{CH}_3\text{CN}$ . Polymer **57** ( $X = \text{O}$ ,  $z = 1$ ) had  $\lambda_{\text{max}} = 497$  in solution and exhibited a chemoselective response to  $\text{Na}^+$  ( $\Delta\lambda_{\text{max}} = 91$  nm) versus  $\text{Li}^+$  ( $\Delta\lambda_{\text{max}} = 46$  nm), and  $\text{K}^+$  ( $\Delta\lambda_{\text{max}} = 22$  nm). Biothiophene copolymers containing units of **57** ( $X = \text{O}$ ,  $z = 1$ ) show selectivity for  $\text{K}^+$  ( $\Delta\lambda_{\text{max}} = 45$  nm) versus  $\text{Na}^+$  ( $\Delta\lambda_{\text{max}} = 30$  nm) and  $\text{Li}^+$  ( $\Delta\lambda_{\text{max}} = 13$  nm). Biothiophene copolymers containing units of **57** ( $X = \text{CH}_2\text{O}$ ,  $z = 1$  and  $z = 2$ ) exhibited no response, indicating that the conformational restrictions are greater when a methylene bridges the thiophene ring and the polyether chain.<sup>[155]</sup>

The design and development of conducting polymer sensory materials that are chemically prepared has led to conducting pseudopolyrotaxanes based on PT and PTs functionalized with calix[4]arene. These two copolymers of PT **67**, **69** (Fig. 9) are equipped to recognize either molecules or ions and therefore transduce molecular interactions into a measurable response ionochromatically, voltammetrically, through fluorescent responses, or through both iono- and chemoresistive responses.<sup>[157–159]</sup> The PT **69** exhibits a chemoresistive response to paraquat derivatives and forms a pseudorotaxane upon binding. A flow cell experiment indicated that the PT is “reset” after 2 min in a nonoptimized demonstration of a real-time sensory device.<sup>[158]</sup> While the calix[4]arene PTs had very large binding constants for alkali metals, they exhibited no changes in the UV-vis spectrum and only minimal changes in their voltammetric responses; however, large decreases in the polymers’ conductivities were found upon exposure to  $\text{Li}^+$  and  $\text{K}^+$ .<sup>[159]</sup> These PTs are exciting as potential new sensory materials and clearly demonstrate new creative approaches to all-plastic sensors. Although the Swager and McCullough polymers are expensive to make (from an industrial point of view), a minute amount of each polymer is needed to prepare sensory solutions or films, essentially making them cost-effective.

Regioregular, head-to-tail poly(3[ $\omega$ -(*p*-methoxyphenyl)oxy]hexyl]thiophenes)<sup>[160]</sup> have recently been prepared using the McCullough method. NMR analysis shows that the polymer is 99 % head-to-tail coupled. The regioregular polymer is much more soluble than the cross-linked irregular polymer whose preparation was also reported. The polymer is similarly thermochromic to **HT-56**. Four-probe conductivity measurements on pressed pellet samples show that the regioregular polymer shows a 1000-fold increase in the electrical conductivity compared to the irregular sample. However, no information was given about the recognition features of the polymer.

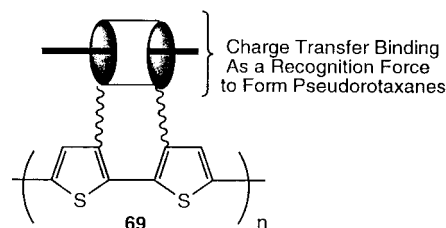


e.g. 0.5 mM  $\text{Na}^+$  response +100mV change in Oxidation Potential and 99% decrease in drain current in  $I_d\text{--}V_g$  measurements

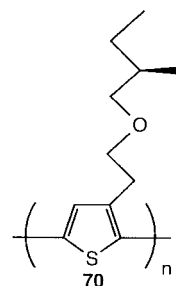


$R = \text{O}(\text{CH}_2\text{CH}_2\text{O})_m\text{CH}_3$

e.g. 10 mM  $\text{Li}^+$  response  $\Delta\lambda_{\text{max}} = 150$  nm



e.g. 50 mM Paraquat response +40mV change in Oxidation Potential and 26% decrease in drain current in  $I_d\text{--}V_g$  measurements



exposure to organic solvents and thermal response completely stereomutates polymer to give mirror image circular dichroism response

Fig. 9. Other PTs as chemoselective sensors.

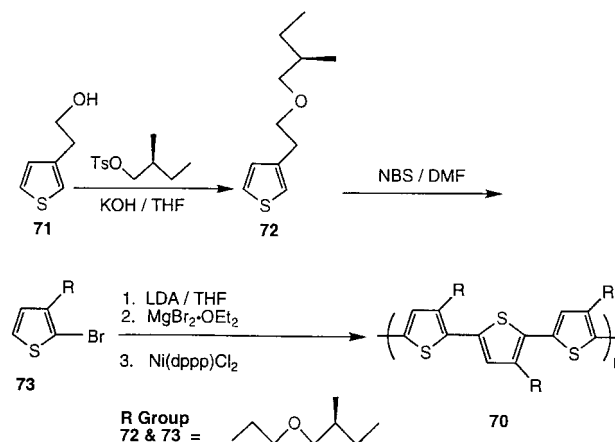
The thermochromic, solvatochromic, and piezochromic responses of polythiophenes are well-known<sup>[16,52,161–164]</sup> and are thought to be related to the reversible phase transition between a highly conjugated coplanar PT and a less conjugated, less planar conformation along the PT backbone. The chromic phenomena in both the solid state and solutions of semicrystalline regioregular and amorphous non-regioregular polythiophene derivatives has been investigated by Lecercler and co-workers.<sup>[165]</sup> A number of alkoxy PTs were tested and polymer **50** was found to sense alkali-metal ions. It turns out that  $\text{K}^+$  causes a solution self-assembly to occur and planarizes the backbone of the polymer. The response is

sensitive to  $K^+$  concentrations ranging from  $1 \times 10^{-6}$  M to  $1 \times 10^{-4}$  M. Above  $10^{-4}$  M the response is saturated. Changing the recognition unit from a (2-methoxyethoxy)ethoxy group on PT to a poly(ethyleneglycol) methyl ether (**68**) unit placed in a 95 % regioregular<sup>[62,67,75]</sup> fashion changes the response concentration window from  $1 \times 10^{-3}$  M to  $1 \times 10^{-2}$  M. The polymer exhibits an isosbestic point, indicative of biphasic conformation order/disorder and ion-induced self-assembly.<sup>[166]</sup> The regioregular PT sensor was found to chemoselective, sensitivity decreasing in the order  $K^+ > Na^+ > NH_4^+ > Li^+$ . It was found that the sensing response of PT to the ions is “molecularly amplified” by the occurrence of a “domino effect” of PT conformational twisting.<sup>[167]</sup> This type of discovery is yet another indication that regioregularity is an important factor in the development of ionoselective sensors.

The transfer of conducting polymer sensors to surfaces is a next step. Attempts to prepare Langmuir–Blodgett films of regioregular alkoxy PTs<sup>[154,156]</sup> have met with limited success<sup>[168]</sup> and variation in stability and formation of the LB films has been found. Surface-bound sensory devices for biomedical applications have recently been prepared with polydiacetylene.<sup>[169]</sup>

### 4.3. Chiral Substituents on PT

Most polymers are known to adopt helical conformations in solution, in the solid state, or in both. It is possible to induce optical activity in the main chain of such a polymer by substituting enantiomerically pure side chains. In such a system significant chirality is induced in the backbone only when the polymer forms a well-ordered aggregate, a state that is common in self-assembled, regioregular poly(3-alkylthiophene)s.<sup>[52,75]</sup> The role of chirality and optical activity as a function of regioregularity in polythiophenes can be examined by comparing the work of Roncali and co-workers<sup>[170]</sup> and Meijer and co-workers.<sup>[171]</sup> Roncali<sup>[170]</sup> has electrochemically prepared chiral polythiophenes by polymerizing (*S*)(+)- and (*R*)(-)-2-phenylbutyl ether of 3-propylthiophene to yield chiral polythiophenes with reported specific rotations of  $[\alpha]^{22} = 3000^\circ$ .<sup>[116,171]</sup> Using the McCullough method, Meijer and Bouman<sup>[116,171]</sup> synthesized an optically active regioregular polythiophene **70** (Scheme 14 and Fig. 9) that exhibits a specific rotation of  $[\alpha]^{22} = 140\,000$  for  $\lambda = 513$  nm at the sodium D line and of  $[\alpha]^{22} = -9000$  for  $\lambda = 589$  nm. This of course points to variation in the optical rotation as a function of wavelength and regioregularity and assembly. Polymer **70** also undergoes stereomutation in the solid state. Solvatochromic studies of polymer **70** ( $M_n = 16\,900$ ; PDI = 1.4) show that varying the solvent composition dramatically affects the shape and  $\lambda_{max}$  of the  $\pi$  to  $\pi^*$  transition by altering the distribution of disordered and ordered, aggregated structures. The solid-state thermochromism in **70** is typical for a polythiophene, except that at the melting point of the polymer a complete



Scheme 14. The synthesis of regioregular polythiophenes with chiral side chains.

loss of optical activity is observed. Even more interesting is the observation that when the polymer is cooled very quickly from the disordered melt (by pouring the sample into a water bath at  $0^\circ\text{C}$ ). The absorption spectra is unchanged, but a mirror image circular dichroism (CD) spectrum (relative to the original sample before melting) is found. Therefore the regioregular, chiral polythiophene **70** undergoes stereomutation. This process is thought to be driven by an aggregation effect. The effect is reversible, affording the opportunity to tune the chirality of the spectrum simply by controlling the cooling rate. Irregular chiral polythiophenes do not show this effect. The same effects are also found in poly(3,4-di[(*S*)-2-methylbutoxy]thiophene), which has been studied in some detail by both CD and circular polarized luminescence.<sup>[172,173]</sup>

Another chiral HT-PAT, namely poly(3-(*S*-3',7'-dimethyloctyl)thiophene),<sup>[115]</sup> confirms that CD spectra can be used in chiral regioregular HT-PTs to probe aggregation states.<sup>[116]</sup> This particular polymer can also act as a sensor, by exhibiting large conformational changes induced by minute solvent variation.

### 4.4. Carboxylic Acid Derivatives: Self-Assembly and Sensors

It has already been demonstrated that the torsion between thiophene rings is extraordinarily sensitive to the steric interactions of the side chains. McCullough et al. have designed regioregular carboxylic acid derivatives in order to promote self-assembly through self-molecular recognition by forming carboxylic acid dimer pairs between PT chains, “zipping up” the ordered conducting polymer structure (Fig. 10). In addition, receptor sensing could lead to a huge signal amplification due to cooperative “unzipping” and twisting of the polymer, causing both a colorimetric response and change in the electrical conduction in the molecular wire. Carboxylic acid salts were chosen as

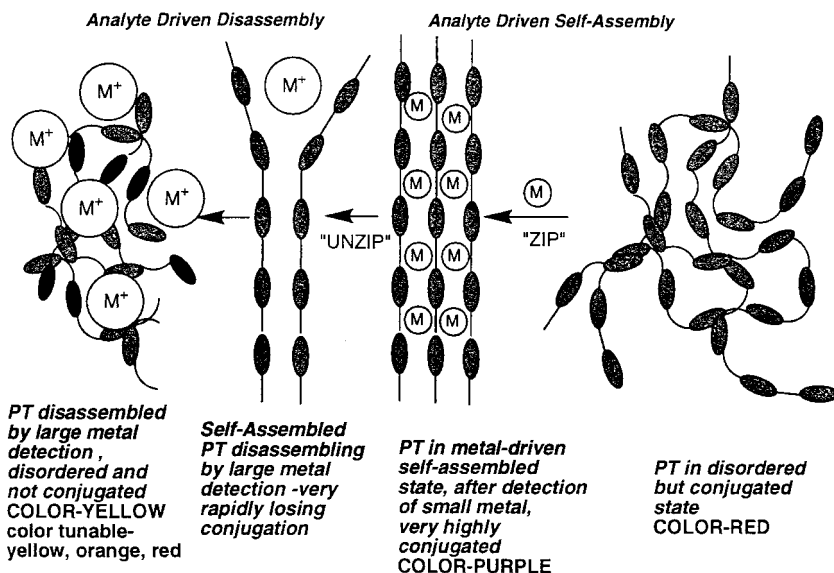


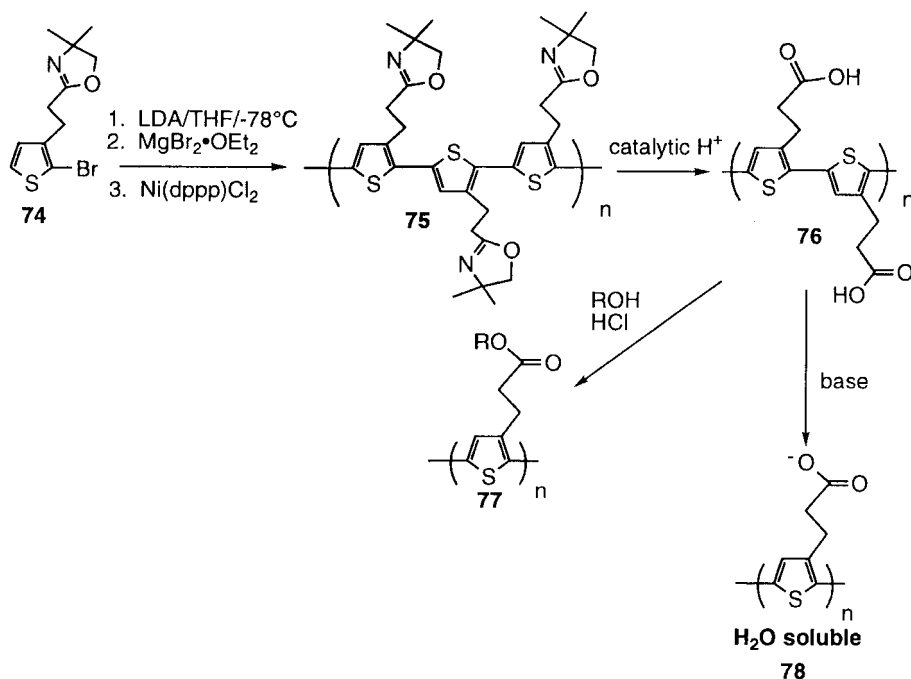
Fig. 10. PT zipper sensors.

the substituent because it is trivial to dramatically change the steric demands of the function simply by changing the size of the counter-cation. In addition, carboxylate-substituted polythiophene should be water soluble.

Regioregular carboxylic acid derivatives of PT have been prepared by employing the sturdy oxazoline protecting group. Regioregular, HT polymers **75–78** were synthesized as shown in Scheme 15.<sup>[174,175]</sup> Deprotection of **75** in aqueous HCl yields the desired product **76** as a dark purple precipitate that is completely “zipped up” into an ordered self-assembled conducting polymer. Upon deprotonation polymer **76** is converted into polymer **78**, which is completely water soluble. Most interestingly, the predicted self-assembly and ionochromic response is dramatically evident. Polymer **78** is a chemoselective ionochromic sensor in

water. The colorimetric response signal ranges from the self-assembled purple state to the disassembled, twisted yellow state and the  $\lambda_{\text{max}}$  of the polymer changes over a 130 nm range simply by varying the counterion from  $\text{NH}_4^+$  (purple), to  $\text{Me}_4\text{N}^+$  (magenta), to  $\text{Et}_4\text{N}^+$  (red), to  $\text{Pr}_4\text{N}^+$  (orange), to  $\text{Bu}_4\text{N}^+$  (yellow).<sup>[174,175]</sup> The observed chemoselective chromism is not merely counterion size dependent, but is also related to the hydrophobicity of the counterion. What happens is that a protein-like hydrophobic assembly occurs in the PT with small counterions, whereas larger counterions break up the self-assembled state, effectively disassembling the PT and amplifying the signal response.<sup>[174]</sup>

Irregular polythiophenes carrying carboxylic acids<sup>[176]</sup> have been prepared electrochemically and dramatic iono-



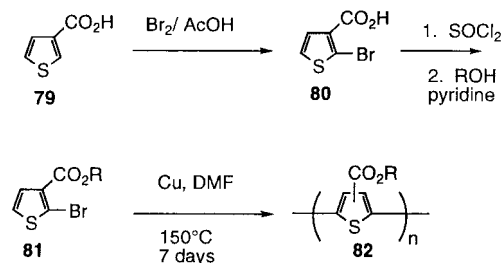
Scheme 15. Synthesis of PT zipper sensor polymers: water soluble, highly ionochromic, regioregular HT-polythiophenes.

chromism or ionic self-assembly was not reported. However, other reports have looked at irregular PT carboxylic acid derivatives in competitive immunoassays for antigens and haptens.<sup>[177]</sup> The carboxylate function attached directly to the thiophene ring has been reported to be prepared<sup>[178]</sup> from the 2,5-dichloro-3-methylthiophene carboxylate by the Yamamoto route.<sup>[8]</sup>

#### 4.5. Other Derivatives of PT

Regioregular esters of PT of any type can be prepared from the McCullough method<sup>[174,175]</sup> as shown in Scheme 15. The polymer molecular weights range from  $M_n = 12k$  to  $M_n = 5k$  with PDI = 2 with 100 % HT couplings. Irregular polythiophenes<sup>[179]</sup> containing ester side chains have been prepared with limited success. The  $FeCl_3$  method leads to partial deesterification of the isolated polymer and some ester functionalized thiophenes; it does not lead to the polymer. Modifications of the reaction media led to ester-functionalized PTs that have been well-characterized,<sup>[180]</sup> having regioregularities of around 65 %. The reported molecular weights are very large, with degrees of polymerization (DPs) of 180–1250. Aggregation was not discussed. The conductivities of  $FeCl_3$ -doped materials were in the 0.1–0.0001 S/cm range.

Ullmann coupling polymerization of 2,5-dibromo-3-alkylthiophene carboxylates as described by Pomerantz et al. is an excellent way to prepare ester derivatives of PTs<sup>[181]</sup> (Scheme 16). The molecular weight  $M_n$  of these materials



Scheme 16. Synthesis of PT esters by Ullmann coupling.

was in the 4k region with PDIs around 2. Electroluminescence and bilayer devices were subsequently studied by Pomerantz et al.<sup>[182]</sup> Efficiencies of 0.018 % were found in the ester PT polymers, which was much better than irregular poly(3-octylthiophene) ( $5 \times 10^{-5}$  %) and regioregular poly(3-hexylthiophene) ( $1 \times 10^{-4}$  %).<sup>[38]</sup>

Poly(3-(2-(methacryloyloxy)ethyl)thiophene) (**82**) has been prepared by Holdcroft by the  $FeCl_3$  method<sup>[18]</sup> (Fig. 11) and used to prepare an electronically conducting pattern by photolithography.<sup>[183]</sup> Related urethane-substituted PT has been prepared by Liu and Gregory<sup>[184]</sup> (Fig. 11) (**83**). Such a PT is thought to have very good solubility and show improved processability and may be able to be used in conducting elastomers. One example would be a blend of urethane-substituted PT and a poly-

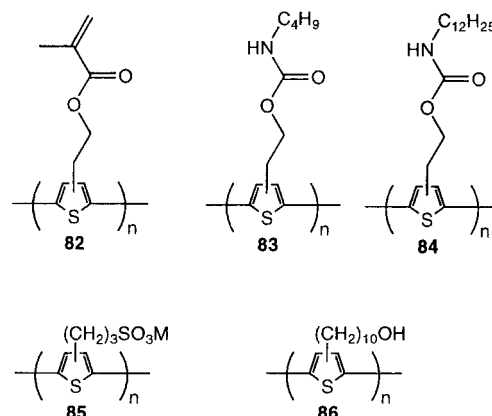


Fig. 11. Some other polar functional PTs.

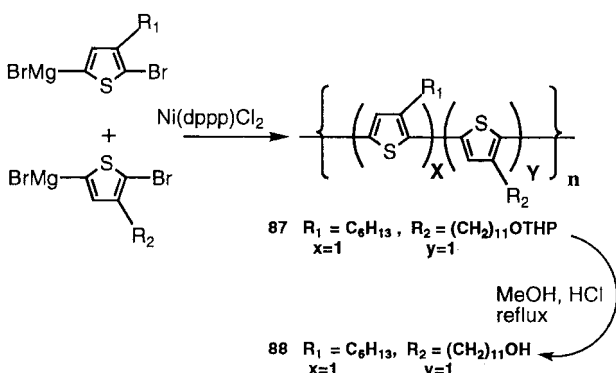
urethane elastomer that could be used for numerous applications, including electromagnetic shielding and antistatic coatings. Another application of urethane-substituted PT would be reversible thermal recording. Poly(3-(2-(*N*-dodecyl-carbamoyloxy)ethyl)thiophene) (PDDUT) (Fig. 11) (**84**) has been prepared<sup>[185]</sup> by the  $FeCl_3$  route.<sup>[26]</sup> The polymer has been characterized by NMR, IR, UV-vis, and X-ray spectroscopy. All of the data reveal 80 % HT couplings in the PDDUT. The thermochromic response of PDDUT cast onto poly(ethylene terephthalate) allows recorded letters to be imprinted using a thermal recording head.

Water-soluble, self-doped<sup>[186]</sup> PTs were first prepared electrochemically by Wudl and co-workers<sup>[187,188]</sup> in 1987. Sodium poly(3-thiophene- $\beta$ -ethanesulfonate) (P3-ETSNa) and sodium poly(3-thiophene- $\beta$ -butanesulfonate) (P3-BTSNa) are soluble in water in the doped and undoped states. The methyl esters were first polymerized and then the esters were converted to the acids with MeI. Similar sulfonate PTs have been prepared by Aldissi.<sup>[189]</sup> It was reported that long alkyl chains attached to the sulfonate group can induce lyotropic liquid crystalline behavior in the PT.<sup>[189]</sup> The ordered PTs reported in the patent possess high conductivities.

Water-soluble sulfonated PTs have also been prepared by Ikenoue et al.<sup>[190]</sup> using the  $FeCl_3$ <sup>[26]</sup> method. Later, Holdcroft and co-workers<sup>[191]</sup> chemically prepared poly(3-(3-thienyl)propanesulfonate) (P3TPSNa) also using the  $FeCl_3$  method (Fig. 11) (**85**). The aim of this study was to develop water-based photoresists that could be used in photolithography. Polythiophene films can be cast onto solid substrates and irradiated through a photomask. The non-radiated polymer is dissolved away, leaving a negative photoimage of photocrosslinked PT.<sup>[192]</sup> The HT:HH ratio was found to be 79:21. The conductivities of the  $FeCl_3$ -doped materials were about 0.001–0.0001 S/cm. Photoimaging experiments found that P3TPSNa was able to form both negative and positive images, depending on the media conditions of the irradiation and oxidation state of the polymer. One very interesting observation is that P3TPSNa films give a featureless X-ray diffraction spectra, implying a completely amorphous polymer, whereas irregular

poly(3-hexylthiophene) shows some crystallinity. Holdcroft postulates that ion-pairing promotes random disorder in the polyelectrolyte, leading to amorphous character. This is the opposite process to the self-assembly found in regioregular carboxylate PT.<sup>[174]</sup>

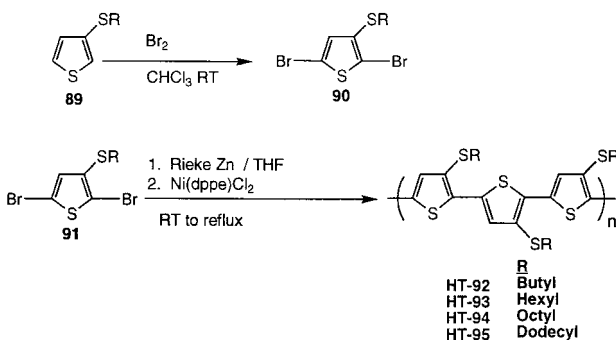
Hydroxydecyl-functionalized PT has been prepared using the FeCl<sub>3</sub> method<sup>[193]</sup> (**86**) (Fig. 11). The aim was to prepare a polymer that could self-assemble similarly to the regioregular carboxylate PT.<sup>[174]</sup> The polymer is found to be ~80% HT coupled and is quite conjugated, with a maximum absorption around 510 nm and an estimated gap of 1.8 eV, which can be compared to 2.2 eV and 1.7 eV found in regioregular and regioregular PATs, respectively. Two-probe conductivity measurement of iodine-doped samples gave values of 0.01–0.1 S/cm. Similar copolymers bearing a hydroxy functionality have been prepared in a regioregular fashion by Holmes and co-workers. A substituted HT-polythiophene copolymer containing alkyl and ω-hydroxyalkyl side chains was prepared<sup>[194]</sup> (Scheme 17). The ω-hydroxyalkyl side chain



Scheme 17. Synthesis of random HT-copolymers of polar PTs.

was first protected with a tetrahydropyranyl (THP) ether, polymerized, and deprotected to give the random copolymer **88** (Scheme 17). The copolymer **88** contains a free alcohol at the end of the side chain and can be functionalized by a number of reagents in order to tailor the properties of the conjugated polymer.

Substitution of a sulfur atom directly on the thiophene ring is expected to lower the oxidation potential of the conjugated polymer. Examples with varying alkyl chain length (Scheme 18) (polymers **HT-92**, **HT-93**, **HT-94**, and **HT-95**)



Scheme 18. The synthesis of regioregular PTs with thioether side chains.

have been synthesized with greater than 90% HT-HT linkages.<sup>[88]</sup> The solubility is notably poor though, suggesting a strong affinity between polymer chains, and the lack of solubility leads to low molecular weights ( $M_n = 4417$ ) as determined by GPC. This lack of solubility is in contrast to the regioregular polymer from 3-ethylmercaptothiophene prepared by Reynolds and co-workers.<sup>[195]</sup> This polymer is soluble in common solvents and has  $M_n = 2200$  ( $M_w = 13000$ ) and a broad polydispersity. The solution UV-vis spectrum in chloroform for **HT-93**, for example, exhibited three peaks, at 263, 324, and 513, with a shoulder at 605 nm. The destabilization of the HOMO reduces the HOMO–LUMO gap and leads to a red shift in these polymers in solution. However, the solid-state UV and conductivity do not vary markedly from those of the alkyl-substituted model.<sup>[75]</sup> The conductivity of I<sub>2</sub>-doped thin films of these polymers were reported to range from 450 to 750 S/cm. The conductivity in irregular poly(3-ethylmercaptothiophene) powder samples is about 10<sup>-3</sup> S/cm.<sup>[195]</sup> A recent study has shown that polymerization of (2,5-dibromo-3-butylthio)thiophene using Mg, followed by Ni(dppp)Cl<sub>2</sub> in refluxing anisole leads to an apparently regioregular poly[3-(butylthio)thiophene]<sup>[196]</sup> that has a molecular weight of 5k. This polymer, in contrast to the above Rieke polymer, is soluble in CHCl<sub>3</sub>, CCl<sub>4</sub>, toluene, benzene, THF, and CS<sub>2</sub>.<sup>[197]</sup>

Kanatzidis has recently prepared the thio analogue to PEDOT, namely poly(3,4-ethylenedithiathiothiophene)<sup>[198]</sup> by the FeCl<sub>3</sub> method. Unfortunately, the molecular weight of the polymer was found to be around 3–4k and the solubility was a bit low. However, this exceptionally interesting structure exhibited conductivities of around 0.4 S/cm and very interesting thermopower behavior reminiscent of a metallic state.

Other very interesting PTs have recently been prepared, including those containing liquid crystalline side chains,<sup>[199]</sup> dicyano-PTs,<sup>[200]</sup> and copolymers bearing side-chain nonlinear optical chromophores.<sup>[201]</sup>

## 5. Fused-Ring Systems

A number of fused-ring systems containing thiophene ring systems have been prepared. The pioneering design and synthesis of poly(isothianaphthene) (PITN) by Wudl et al.<sup>[202]</sup> propelled the synthesis and study of a large number of new materials. Since isothianaphthene contains essentially a four-electron cyclohexadiene system, when the benzenoid thiophene is oxidized to the conducting state and forms a quinoidal structure the cyclohexadiene will convert to a benzene structure. This means that the conducting state structure will be very stable energetically and force a large portion of quinoidal structure to be formed, leading to a highly planarized polymer with a very low bandgap of around 1 eV. Other methods for the synthesis of PITN and its derivatives have been reported, including those that are

an improvement.<sup>[203–205]</sup> Copolymers containing the isothianaphthene unit and thiophene rings have been prepared by Loray and Cava.<sup>[206]</sup>

A comprehensive presentation of PTs containing fused rings is beyond the scope of this review, however, a few examples are discussed below. Pomerantz et al. have prepared from FeCl<sub>3</sub> a dialkylated pyrazine fused PT.<sup>[207]</sup> Pomerantz and Gu have also prepared soluble fused thiophene PTs.<sup>[208]</sup> Even more elaborate fused bithiophene PTs have been reported by Inaoka and Collard.<sup>[209]</sup> Fused heterocycles on PTs and copolymers, including dithiol derivatives and others, have been prepared by many groups.<sup>[210,211]</sup>

## 6. Conclusion

Polythiophenes remain one of the most versatile conjugated polymer systems. Owing to the ease of synthesis of PT derivatives, the number that can be engineered as new materials is limited only by the imagination. Polythiophenes will continue to lead the way to new unique sensory materials, to highly stable and efficient all-polymer transistors, to very highly conductive plastics, and to new nano-electronic and nano-optical materials. New advances in the synthesis of regioregular PTs and the discovery of self-assembly in regioregular PTs provide well-defined building blocks that have increased the importance of PTs among conducting polymers. As well-defined materials become more readily available, new structure–property relationships will continue to unfold through systematic studies of structure/physical property correlations. This will allow chemists, physicists, materials scientists, and engineers to have a better grasp on the development of new technologies. The ease and low cost of processing these polymers can then be exploited for future technologies and continued commercial applications.

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