

Advances in Molecular Design and Synthesis of Regioregular Polythiophenes

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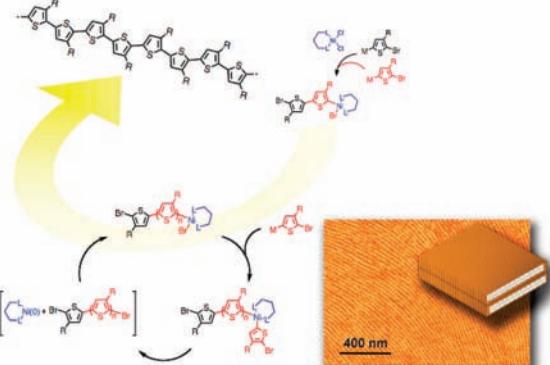
Regioregular poly(3-alkylthiophene)s (rrP3ATs) are an important class of π -conjugated polymers that can be used in plastic electronic devices such as solar cells and field-effect transistors. rrP3ATs can be ordered in three dimensions: conformational ordering along the backbone, π -stacking of flat polymer chains, and lamellar stacking between chains. All of these features lead to the excellent electrical properties of these materials. Creative molecular design and advanced synthesis are critical in controlling the properties of the materials as well as their device performance. This Account reports the advances in molecular design of new functional polythiophenes as well as the associated polymerization methods.

Many functionalized regioregular polythiophenes have been designed and synthesized and show fascinating properties such as high conductivity, mobility, chemosensitivity, liquid crystallinity, or chirality. The methods for the synthesis of rrP3ATs are also applicable to other functional side chains. Di- and triblock copolymers consisting of rrP3AT and polyacrylate or polystyrene have also been successfully synthesized, which can facilitate the assembly of the polythiophene segments. The synthesis of rrP3ATs has evolved into a simple and economical system in which the synthesis can be carried out quickly at room temperature and is thus suitable for large-scale manufacturing. Intensive study has revealed that the regioregular polymerization of 3-alkylthiophenes proceeds by a chain-growth mechanism and can be made into a living system. This feature enables precise control of the molecular weight and facile end-group functionalization of the polymer chains, leading to tailor-made regioregular polythiophenes for specific applications.

In addition, researchers have recently designed and synthesized regiosymmetric polythiophenes—these are regioregular but not coupled in a head-to-tail fashion—by various methods. These reports indicate that these regiosymmetric polymers show very high mobilities when used in field-effect transistors due to their highly ordered structure. The remarkable performance of regioregular polythiophenes in recent years has allowed for the rapid development in printable electronics and seems destined to lead to further advances in this field.

Introduction

The discovery of highly conductive polyacetylene by Shirakawa, MacDiarmid, and Heeger,¹ over 30 years ago, drew interest to π -conjugated polymers as futuristic conducting or semiconducting materials for the next generation of electronic and optical devices. One of the most interesting properties of π -conjugated polymers is that they possess excellent processability; the polymers can be



deposited by simple printing techniques. Over the past 3 decades, the field of this new class of plastic materials has developed widely and rapidly, and the initial curiosity about this field has been elevated from academic research to industrial use. Among the number of π -conjugated polymers, polythiophenes (PTs) are one of the most important and widely studied materials.² PTs, recently, have been used in a variety of applications such

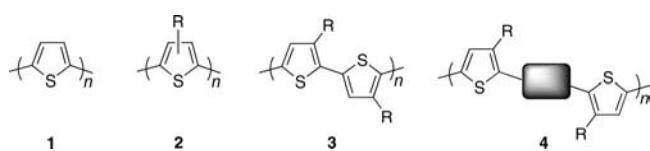


FIGURE 1. Chemical structures of unsubstituted 2,5-coupled PT (**1**), regioirregular P3AT (**2**), regioregular HT P3AT (**3**), and regiosymmetric PT (**4**).

as field-effect transistors (FETs),³ polymer light-emitting diodes (PLEDs),⁴ solar cells,⁵ and chemical sensors.⁶

At the initial stage in the history of PTs, unsubstituted polythiophene (**1**, Figure 1) was prepared through chemical polymerizations.^{7,8} This 2,5-coupled polythiophene was found to be highly conductive and environmentally and thermally stable but was insoluble. Soluble PTs with flexible side chains, poly(3-alkylthiophene)s (P3ATs, **2**), as shown in Figure 1, were then synthesized by a similar method used for 2,5-coupled polythiophene in the late 1980s.^{9,10} However, chemical and electrochemical methods create random couplings in P3ATs, leading to only 50–80% head-to-tail (HT) couplings. The loss of regioregularity is due to multiple head-to-head (HH) and tail-to-tail (TT) couplings, which causes a sterically twisted structure in the polymer backbone, giving rise to a loss of π -conjugation (Figure 2). Steric twisting of backbones leads to destruction of high conductivity and other desirable properties for PTs. In 1992, HT regioregular P3ATs (rrP3ATs, **3**), as shown in Figure 1, were synthesized first using the McCullough method,¹¹ with a similar method developed shortly thereafter by Rieke.¹² The McCullough method provided rrP3ATs with a HT regioregularity of 98–100% and later was modified as the GRIM method.¹³ The discovery of the synthesis of rrP3ATs brought about not only the development of a wide variety of new functional polythiophenes but also a dramatic enhancement in the electrical properties of rrP3ATs, due to planarization of the backbone and solid-state self-assembly to form well-defined, organized three-dimensional polycrystalline structures.^{14,15} These structures provide efficient interchain and intrachain charge carrier pathways, leading to high mobility (conductivity). For example, mobilities of regioregular poly(3-hexylthiophene) (rrP3HT) are as high as $0.2\text{ cm}^2/(\text{V s})$, while those of regioirregular P3HT are $\sim 10^{-5}\text{ cm}^2/(\text{V s})$. Additionally, regiosymmetric polythiophenes (rsPTs, **4**), another variety of regioregular polythiophenes, have recently been reported to show even more highly ordered structures and hence higher mobility, up to $0.6\text{ cm}^2/(\text{V s})$, relative to HT rrP3ATs.^{16,17}

As we have realized from the study of rrP3ATs, polymer structures are crucial for determining the electrical properties of π -conjugated polymers. It is therefore important that design,

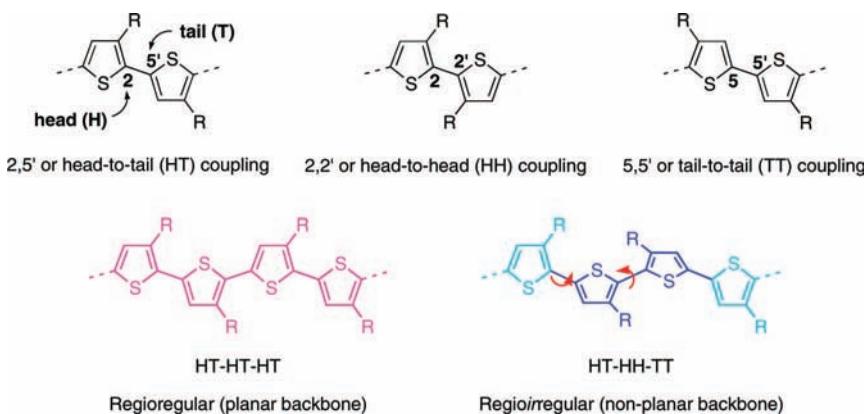
synthesis, and assembly be taken into account in the optimization of organic electronic devices. In this Account, we therefore focus on the recent progress in regioregular polythiophenes from the viewpoint of synthesis and molecular design along with their properties.

HT coupled regioregular polythiophenes

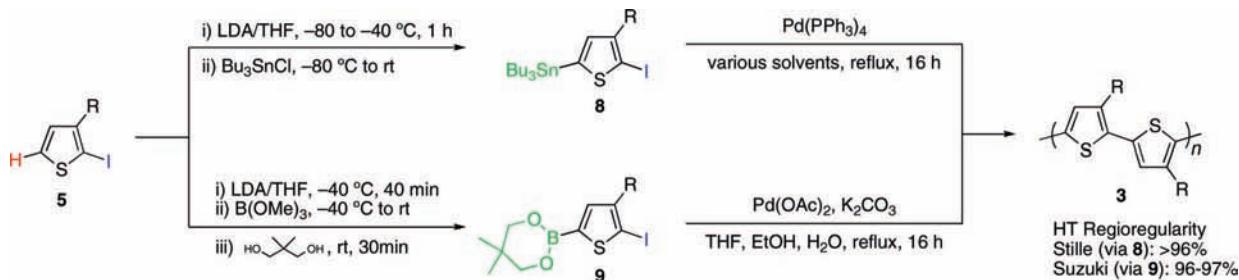
McCullough Method. The first synthesis of HT rrP3ATs is known as the McCullough method (Scheme 1).^{11,18} The key to this method is the regiospecific generation of 2-bromo-5-bromomagnesio-3-alkylthiophene (**6**, M = MgBr), which is achieved by treating 2-bromo-3-alkylthiophene (**5**, X = H, Y = Br) with LDA (lithium diisopropylamide) at -78°C followed by an addition of $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$. Quenching studies performed on intermediate **6** indicate that 98–99% of the desired monomer and less than 1–2% of 2,5-exchanged intermediate **7** are produced. The polymerization is then employed *in situ* by a cross-coupling reaction using a catalytic amount of $\text{Ni}(\text{dppp})\text{Cl}_2$, affording rrP3AT **3** (44–66% yield). The resulting rrP3ATs afford HT–HT regioregularity of 98–100% as seen by NMR study, and the number-averaged molecular weights (M_n) are typically 20000–40000 with polydispersities (PDI) of around 1.4. This procedure was later modified by replacing $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$ with ZnCl_2 , thus allowing for greater solubility of the reactive intermediate at -78°C . The resulting rrP3ATs were found to self-assemble into highly ordered crystalline arrays by X-ray diffraction (XRD) studies¹⁴ and gave electrical conductivities of 100–1000 S/cm, with an average of 600 S/cm, whereas regioirregular P3ATs give conductivities of 0.1–20 S/cm, with an average of 1 S/cm, when doped with iodine.

Rieke Method. Soon after the report of the McCullough method, the Rieke method (Scheme 1) was reported.¹³ In this method, treating 2,5-dibromo-3-alkylthiophenes (**5**, X = Y = Br) with highly reactive “Rieke zinc” (Zn^*) yields a mixture of two isomeric intermediates **6** and **7** (M = ZnBr) in a ratio of 90:10, which gives regioregular P3ATs by *in situ* addition of $\text{Ni}(\text{dppe})\text{Cl}_2$ (yield $\sim 75\%$). Molecular weights for rrP3ATs prepared by this method are $M_n = 24000–34000$ (PDI = 1.4).

GRIM Method. In 1999, an economical new synthesis for rrP3ATs, known as the Grignard metathesis (GRIM) method (Scheme 1), was reported.¹² One strong advantage of this method is that the use of both cryogenic temperatures and highly reactive metals is unnecessary; consequently it offers quick and easy preparation of rrP3ATs and enables the production of kilogram scale high molecular weight rrP3ATs. In this method, 2,5-dibromo-3-alkylthiophene (**5**, X = Y = Br) is

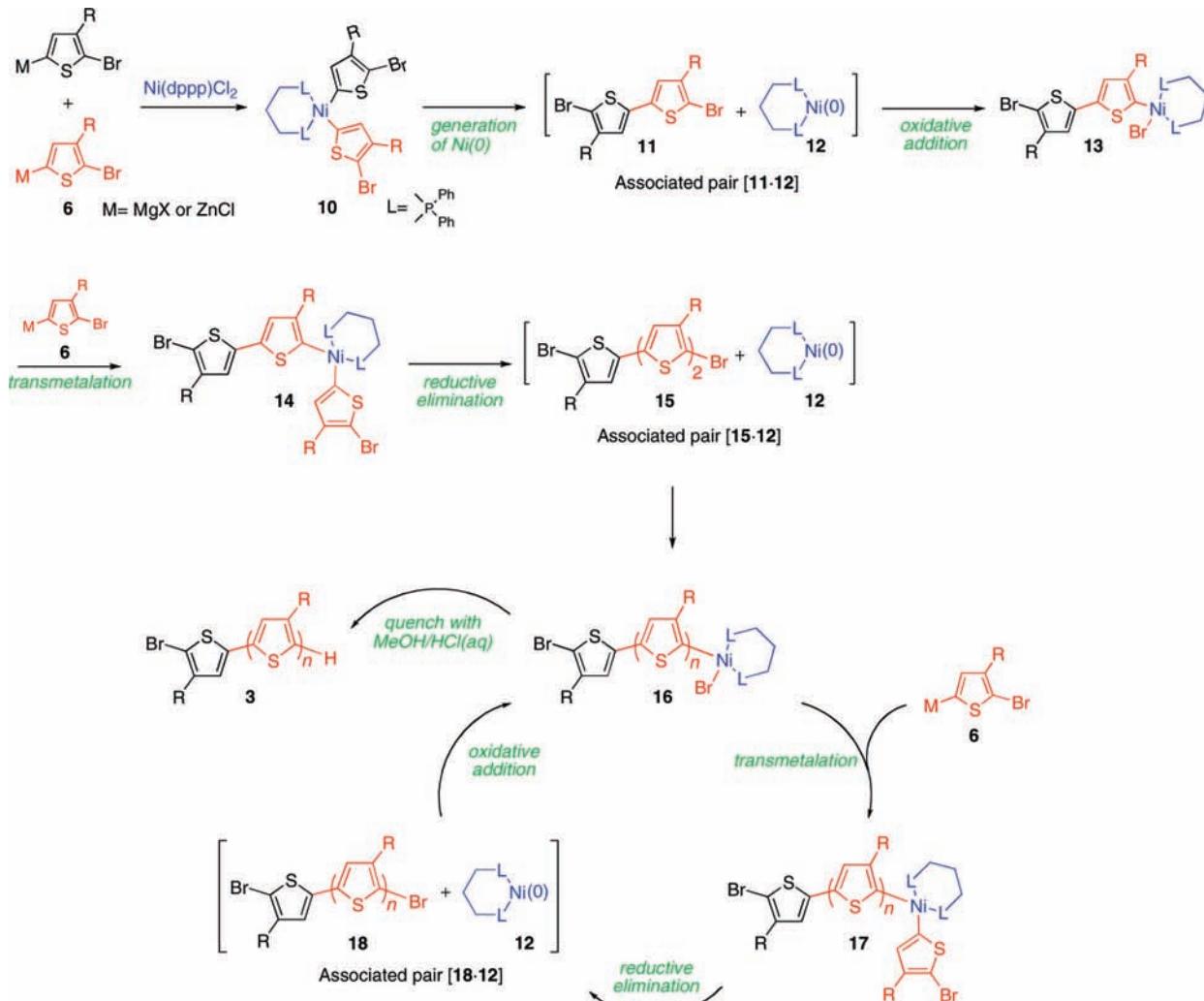
**FIGURE 2.** Regioisomeric couplings of 3-alkylthiophenes (top) and regioregular and regiorandom P3AT (bottom).**SCHEME 1.** Typical Methods for the Synthesis of Regioregular Poly(3-alkylthiophene)s

Method	X, Y	Step 1	M (ratio / 6:7)	Step 2	HT
					Regioregularity
McCullough	H, Br	i) LDA/THF, -40 °C, 40 min ii) MgBr ₂ -OEt ₂ (ZnCl ₂), -60 to -40 °C, 40 min	MgBr (ZnCl) (~98:~2) ^a	Ni(dppp)Cl ₂ , -5 to 25 °C, 18 h	98–100 %
Rieke	Br, Br	Zn ⁺ /THF, -78 °C to rt, 4 h	ZnBr (90:10)	Ni(dppe)Cl ₂ , 0 °C to rt, 24 h	97–100 %
GRIM	Br, Br	R'MgX ^b /THF, rt or reflux, 1 h	MgX' (~85:~15)	Ni(dppp)Cl ₂ , rt or reflux, < 1 h	>99 %

^a X for intermediate **7** is Br (not H) in this case. ^b R' = Alkyl, X' = Cl, Br**SCHEME 2.** Synthesis of HT rrP3ATs by Stille (Upper) and Suzuki (Lower) Coupling Reactions

treated with 1 equiv of any Grignard reagent ($R'MgX'$) to form a mixture of intermediates **6** and **7** in a ratio of 85:15 to 75:25.¹⁹ This ratio appears to be independent of the reaction time, temperature, and Grignard reagent used. Although the ratio of the desirable to undesirable isomers is higher in the GRIM method, compared with the McCullough and Rieke methods, this method still affords HT rrP3ATs with high regioregularity of >99% HT couplings. The typical M_n of rrP3ATs synthesized through this method is 20000–35000 with very low PDI of 1.2–1.4.

Other Methods. Other methods that have been applied to the synthesis of rrP3ATs include Stille²⁰ and Suzuki²¹ palladium-catalyzed cross-coupling reactions (Scheme 2). Iraqi et al. have investigated the synthesis of rrP3ATs through the Stille reaction, using 3-hexyl-2-iodo-5-(tri-*n*-butylstannyl)thiophene (**8**, $R' = n\text{-Bu}$, $X = \text{I}$) with a variety of solvents.²² In all cases rrP3ATs with greater than 96% HT couplings were obtained. Molecular weights of rrP3ATs prepared by this method are $M_n = 10000\text{--}16000$ with PDI of 1.2–1.4 after purification. The Suzuki reaction using 3-octyl-2-iodo-5-boronothiophene (**9**)

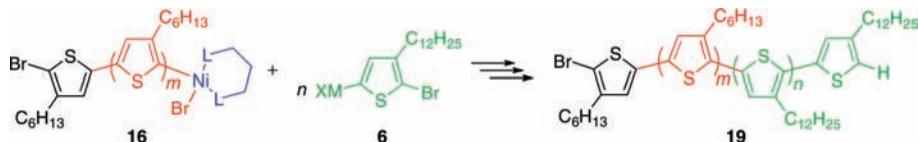
SCHEME 3. Proposed Mechanism for the Nickel-Initiated Cross-Coupling Polymerization

has been employed by Guillerez to give rrP3AT with 96–97% HT couplings and weight-averaged molecular weight (M_w) of 27000 in 51% yield.²³ However, these methods require cryogenic conditions for preparing the corresponding organometallic monomers **8** or **9**, which then must be isolated and purified.

Mechanism of the Nickel-Catalyzed Polymerization.

The synthesis of rrP3ATs is based on transition-metal-catalyzed cross-coupling reactions, of which the mechanism involves a catalytic cycle of three consecutive steps: oxidative addition, transmetalation, and reductive elimination. Since the nickel-catalyzed polymerization is formally a polycondensation reaction, it is generally accepted to proceed via a step-growth mechanism. However, it has recently been proposed by Yokozawa that the nickel-catalyzed cross-coupling polymerization (McCullough and GRIM method) proceeds via a chain-growth mechanism.²⁴ At the same time, we have proposed that this polymerization system is not only a chain-

growth system but also a living system.^{25,26} This system allows for the control of the molecular weight of the polymer as a function of reaction time and the amount of Ni catalyst. The proposed mechanism for the regioregular polymerization of 3-alkylthiophene is outlined in Scheme 3. The first step is the reaction of 2 equiv of intermediate **6** with Ni(dppp)Cl₂ affording the organonickel compound **10**, and reductive elimination immediately occurs to form an associated pair of the 2,2'-dibromo-3,3'-dialkyl-5,5'-bithiophene (tail-to-tail coupling) and Ni(0) [**11** · **12**]. Dimer **11** undergoes fast oxidative addition to the nickel center generating new organonickel compound **13**. Transmetalation with another **6**, which forms **14**, and the reductive elimination gives an associated pair of the terthiophene and Ni(0) [**15** · **12**]. Growth of the polymer chain occurs by an insertion of one monomer at a time as shown in the reaction cycle (**16** → **17** → [**18** · **12**] → **16**), where the Ni(dppp) moiety is always incorporated into the polymer chain as an end group via the formation of a π-complex. In this fash-

SCHEME 4. Synthesis of Poly(3-hexylthiophene)-*b*-poly(3-dodecylthiophene) by Chain Extension through Sequential Monomer Addition

ion, Ni(dppp)Cl₂ is believed to act as an initiator rather than a catalyst, and therefore this limits polymerization to one end of the polymer chain. The prediction of the mechanism as living is supported by two experimental results: first, the degree of polymerization of rrP3ATs has been found to increase with monomer conversion and can be predicted by the molar ratio of the monomer to the nickel initiator; second, addition of various Grignard reagents (R'MgX) at the end of polymerization results in end-capping of rrP3AT with an R' end group as described below.^{27,28} Furthermore, we have successfully achieved a chain extension of rrP3ATs. Sequential addition of monomer **6** with R = dodecyl following the polymerization of **6** with R = hexyl gave poly(3-hexylthiophene)-*b*-poly(3-dodecylthiophene) (**15**) as shown in Scheme 4.²⁶ This result strongly indicates the living nature of the polymerization system.

Supramolecular Structure in rrP3ATs. A fascinating structural feature of HT rrP3ATs that differs completely from regioregular P3ATs is the supramolecular ordering driven by the self-assembly of planar polymer backbones. X-ray study has revealed a well-ordered lamellar structure with an interlayer spacing of ~16.0 Å for rrP3HT and very close π–π stacking of facing polymer backbones with a distance of ~3.8 Å.¹⁴ Atomic-force microscopy (AFM) study on thin films of rrP3ATs show well-organized nanofibril morphologies of differing dimensions (Figure 3).

Recently, several groups (including ours) have demonstrated that rrP3HTs form various morphologies depending on molecular weight.^{29,30} AFM studies have shown that low molecular weight rrP3HTs are likely to form isolated

nanofibrils, while high molecular weight rrP3HTs are likely to form more closely packed nanofibrils indicating better inter-domain connectivity. Further investigation by our group has demonstrated that the width of the nanofibrils as well as the charge carrier mobility in FETs increase as the molecular weight increases; this correlates with the average contour length of polymer chains. However, it is interesting to note that both the nanofibril width and the mobility saturate at higher molecular weight, which is believed to be due to the “chain folding” of the rrP3HT backbones. These structural studies, accomplished through careful control of molecular weight of the polymers, have allowed better understanding the correlation of the polymer structure with physical properties and device performance.

HT Regioregular Polythiophenes with Functionalized Side Chains

The initial purpose of introducing side chains on the PT backbones was to improve solubility and hence processability. However, it has been established that the introduction of various kinds of functionalized side chains can also change the materials’ electrical and optical properties. A large number of side chain functionalized HT regioregular poly(3-substituted thiophene)s (rrPTs) have been synthesized (Table 1).

Heteroatom-Containing Groups. Introducing electron-donating groups, such as alkoxy or alkylthio groups, with the heteroatom directly connected to the ring in the 3-position of thiophene is expected to decrease the band gap by raising their HOMO level, which leads to low oxidation potentials and a highly stable conducting state. rrPTs with alkoxy substitu-

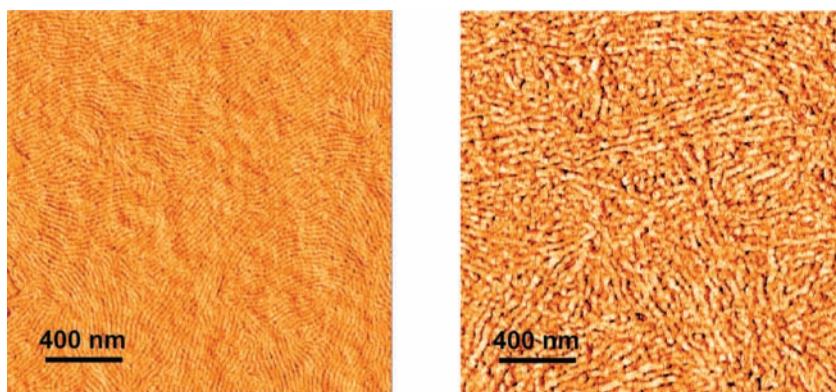
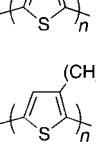
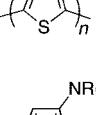
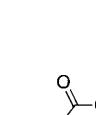
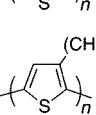
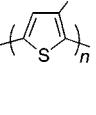
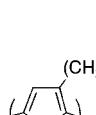


FIGURE 3. AFM phase images of rrP3HT thin films on FET devices: $M_n = 12000$ (left); 21000 (right).

TABLE 1. Summary of Side Chain Functionalized HT Regioregular Polythiophenes

Entry	Polymer structure	Side chain	Polymerization method
1		$R = \begin{array}{c} \text{---O---} \\ \\ \text{---O---C---O---} \\ \\ \text{---O---C---O---C---O---} \\ \\ \text{---O---C---O---C---O---C---O---} \end{array}$	GRIM
2		$R = \begin{array}{c} \text{---O---} \\ \\ \text{---O---C---O---} \\ \\ \text{---O---C---O---C---O---} \\ \\ \text{---S---} \end{array}$	McCullough
3		$m = 5, 6, 10$	GRIM
4		$R = \begin{array}{c} \text{---S---} \\ \\ \text{---C---} \end{array}$	Rieke
5		$R = -H \quad R' = \begin{array}{c} \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \end{array}$ $R = -CH_3 \quad R' = \begin{array}{c} \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \end{array}$	FeCl_3 NOBF_4
6		$R = \begin{array}{c} \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \end{array}$	GRIM
7		a) $l = 11, m = 3$ b) $l = 0, m = 7$	GRIM McCullough
8		a) $R^* = \begin{array}{c} \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \end{array}$ $\begin{array}{c} \text{---O---} \\ \\ \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \end{array}$ b) $R^* = \begin{array}{c} \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \\ \\ \text{---C---} \end{array}$	McCullough McCullough
9		a) $R = \begin{array}{c} \text{---O---} \\ \\ \text{---C---} \\ \\ \text{---C---} \end{array} \quad m = 2, 6$ b) $R = \begin{array}{c} \text{---Si---} \\ \\ \text{---C---} \end{array} \quad m = 10$ c) $R = \begin{array}{c} \text{---O---} \\ \\ \text{---N---} \\ \\ \text{---C---} \end{array} \quad m = 2$ d) $R = \begin{array}{c} \text{---P---O---} \\ \\ \text{---C---} \end{array} \quad m = 6$ e) $R = -Br \quad m = 6$	McCullough GRIM Stille Stille McCullough, GRIM

ents have been synthesized by the GRIM or McCullough method (entries 1–3). UV-vis absorption spectra of poly(3-(2'-(2"-methoxyethoxy)ethoxy)thiophene) (PMEET) showed that the λ_{max} was more than 100 nm red-shifted from rrP3ATs, indicating that the introduction of the electron-donating group in the side chain lowers the band gap of PTs (entry 1).³¹ PMEET showed a high conductivity of 650 S/cm upon iodine doping, and the conductivity remained high, 150 S/cm, after 2 months. A series of rrPTs with ether groups, where the oxygen is not directly connected to the ring, was synthesized by the McCullough method (entry 2).³² While the shorter side chain polymer only gave low molecular weight due to low solubility, the longer side chain polymer gave high molecular weight. These polymers, after iodine doping, exhibited very high conductivity, with averages of 500–1000 S/cm. The polymer also exhibited ion-binding properties to Li⁺, Pb²⁺, and Hg²⁺. rrPTs with a methoxy group on the end of the alkyl chains were also synthesized by the GRIM method (entry 3).³³

rrPTs with alkylthio groups were synthesized by the Rieke method (entry 4).³⁴ They showed good solubility in carbon disulfide, whereas the solubility in common organic solvents such as chloroform, THF, and xylene was fairly low. The iodine-doped polymer films showed high conductivity of 100 S/cm. UV-vis absorption spectroscopy revealed that the band gap decreased compared with that of rrP3ATs.

Alkylamino- and dialkylamino-substituted rrPTs were reported by Rasmussen et al. (entry 5).³⁵ Corresponding alkylamino and dialkylamino thiophenes were polymerized by the FeCl₃ and NOBF₄ methods, to give ~88% and ~90% HT couplings, respectively. These regioregularities show higher HT preference in these systems compared with most polyalkylthiophenes prepared by oxidative polymerization (FeCl₃ method, ~70–80% HT couplings).

The ester group, which is an electron-withdrawing functional group, was also introduced into the rrPT (entry 6).³⁶ The polymers synthesized by the GRIM method showed a slightly blue-shifted λ_{max} from that of rrP3ATs, which may be due to the electron-withdrawing nature of the carbonyl group, giving rise to a wider band gap.

Fluoroalkyl Groups. PTs bearing partially fluorinated alkyl side chains are unique materials that provide unusual properties including hydrophobicity, chemical and oxidative resistance, and self-organization of fluoroalkyl chains. Collard et al. has reported the synthesis of rrPTs with partially fluorinated alkyl side chains using the GRIM method (entry 7a).³⁷ This polymer shows liquid crystalline behavior and forms a highly ordered solid-state structure. Synthesis using the McCullough

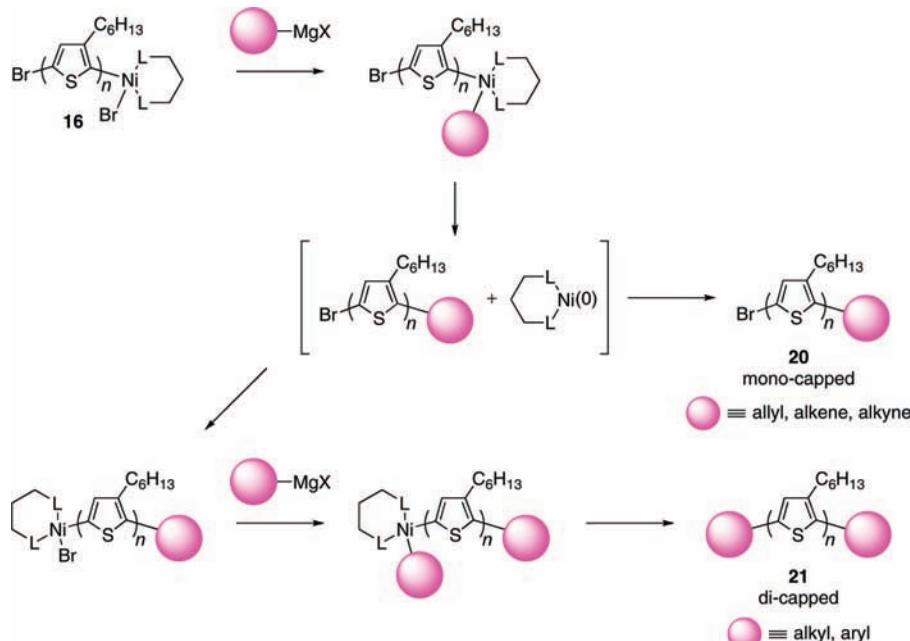
method of rrPTs with perfluoroalkyl side chains has also been reported (entry 7b), giving polymers with ~86% HT couplings.³⁸

Chiral Groups. rrPTs with chiral side chains are fascinating materials that induce a helical packing of the polymer backbone into a chiral superstructure in the aggregate, leading to optical activity (entry 8).^{39–41} The first synthesis for chiral rrPTs was reported by Meijer, in which the McCullough method was used (entry 8a).³⁹ The polymer solution showed strong CD (circular dichroism) signal at its $\pi-\pi^*$ transition at low temperature or upon addition of poor solvents, indicating the formation of a helical backbone in the aggregate, whereas the regioregular polymer showed only a weak CD signal.

Postpolymerization Functionalization at the γ Position. Functionalization at the end of the side chains on rrPTs is desirable in terms of tuning the polymer properties. The primary strategy involves using protective groups at the γ end of the side chains, which allows for the incorporation of functional groups that are usually reactive to the polymerization conditions. The tetrahydropyranyl (entry 9a)⁴² and the trimethylsilyl (entry 9b)⁴³ γ -functionalized rrPTs were synthesized through the McCullough and GRIM methods, respectively. The oxazolinyl γ -functionalized rrPT (entry 9c) was synthesized by a CuO-modified Stille coupling reaction, after which the polymer was modified by a postpolymerization hydrolysis reaction to give a carboxylic acid group on the side chain, which proved suitable for chromatic chemosensing.⁴⁴ The rrPT bearing a phosphonic ester group (entry 9d) was synthesized by the Stille method.⁴⁵ Subsequent deprotection of the ester led to the phosphonic acid functionalized rrPT, which forms a supramolecular assembly when a tetraalkylammonium hydroxide salt is added to the polymer solution. Another approach to functionalizing the side chain of rrPTs has been reported that involves incorporating reactive groups at the γ end of the side chains that are stable to polymerization conditions. rrPT with a bromohexyl side chain (entry 9e) was synthesized by Iraqi using the McCullough method and then reacted with 2-carboxyanthraquinone to give a highly redox active rrPT.⁴⁶ The bromohexyl-substituted rrPT was also synthesized by the GRIM method, and the γ end of the side chain was subsequently functionalized to various groups, such as carboxylic acid, amine, or thiols.⁴⁷

End Group Functionalization and Block Copolymers

End group functionalization of rrP3ATs is expected to lead to a number of new uses for these polymers including end group

SCHEME 5. Proposed Mechanism of End-Capping of rrP3HT by *in Situ* Functionalization

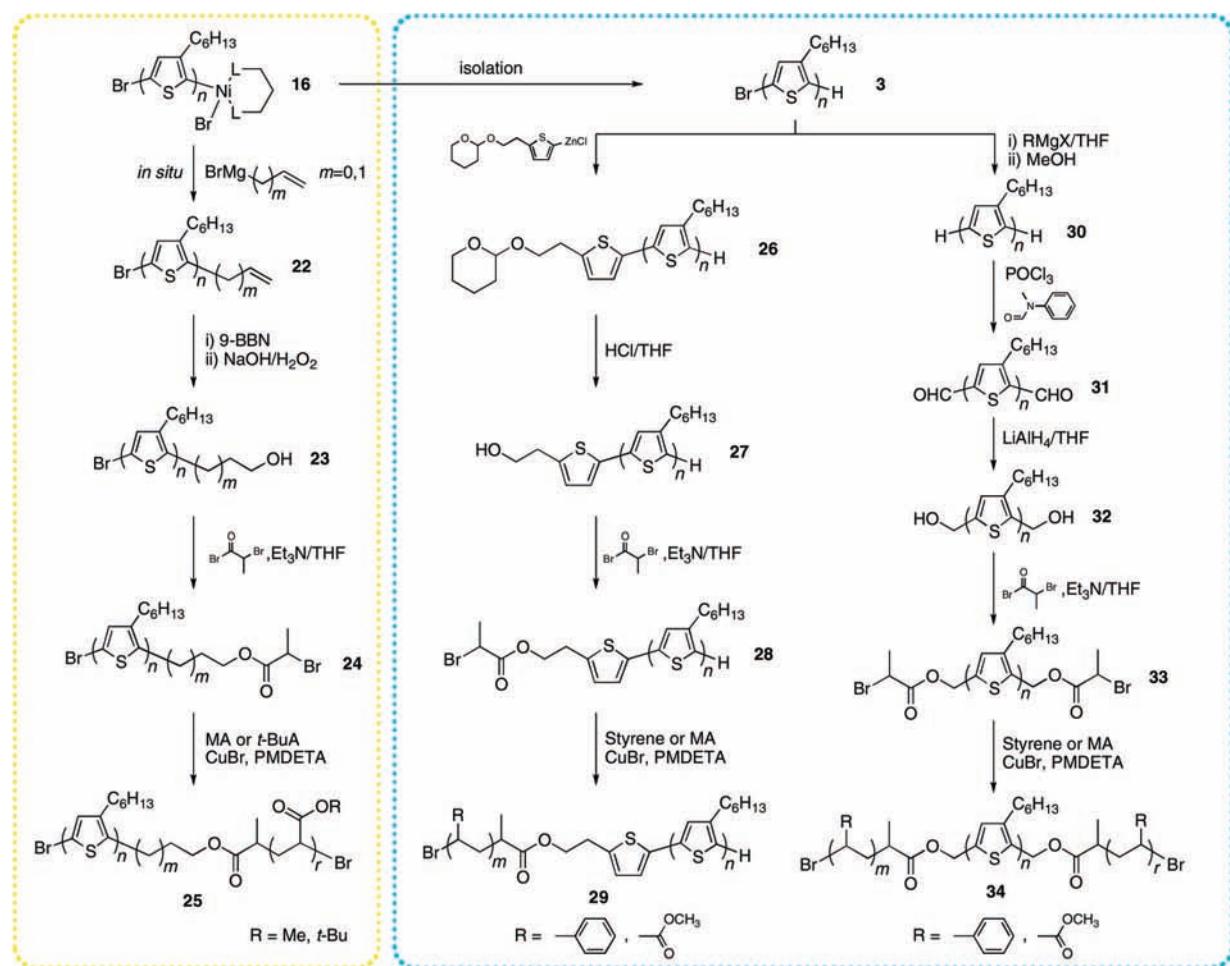
driven self-assembly onto surfaces and into conducting polymer assembled networks and the synthesis of reactive end groups that can be used as building blocks for the synthesis of block copolymers. Block copolymers comprised of conjugated and nonconjugated segments are fascinating materials that are expected to phase segregate. This phase segregation may lead to the formation of nanoscale morphologies, owing to the immiscibility of the covalently connected segments. This may in turn lead to advanced new materials for use as components in nanoelectronic devices. Moreover, incorporation with flexible segments may improve the mechanical properties and processability of conjugated polymers such as rrP3ATs. Two approaches have been investigated to alter end group composition and to create rrP3AT-based block copolymers: *in situ* and postpolymerization methods.

In Situ Method. The first attempt toward *in situ* end group functionalization was reported by Janssen using the McCullough method, in which 2-thienylmagnesium bromide or 5-trimethylsilyl-2-thienylmagnesium bromide was added to the reaction mixture with additional Ni catalyst, to give a mixture of HH and mono- and dicapped polymer chains.⁴⁸ We have reported a simple and very versatile method to achieve *in situ* functionalization of rrP3HT using the GRIM method.^{49,50} Since the GRIM method follows a living mechanism, rrP3AT is still bound to the nickel catalyst at the end of the reaction. Therefore, a simple addition of another Grignard reagent effectively terminates the reaction and “end caps” the poly-

mer chains (Scheme 5). In this system, a variety of different types of Grignard reagents (alkyl, allyl, vinyl, aryl, etc.) successfully achieved end-capping, giving both monocapped (**20**) and dicapped (**21**) rrP3AT. When the end group is allyl, ethynyl, or vinyl group, the nickel catalyst is postulated to be bound to the end group through a nickel- π complex to yield monocapped polymers, eliminating the possibility of dicapping. But when the end group is alkyl or aryl, the polymers further reacted to yield dicapped polymers. Hydroxyl, formyl, or amino groups were also successfully used to end-cap the polymer chains when properly protected.

The synthetic route for block copolymers using *in situ* end group functionalization is shown in Scheme 6. Vinyl- or allyl-terminated rrP3HT (**22**) was used as a precursor. These end groups were easily converted to the hydroxyl group (**23**) by a hydroboration using 9-borabicyclo[3.3.1]nonane (9-BBN), followed by an oxidation using H_2O_2 . The reaction of **23** with 2-bromopropionyl bromide gave rrP3HT macroinitiator **24**, and then atom transfer radical polymerization (ATRP)⁵¹ was employed to give rrP3HT containing diblock copolymers (**25**).⁵²

Postpolymerization Method. rrP3HT bearing a terminal hydroxyl group (**27**) was prepared by coupling a thiophene with tetrahydropyran-protected hydroxyl group onto the bromine end of H/Br polymer **26**.⁵³ On the other hand, the end groups of rrP3HT were converted to HH type polymer **30** by treatment of H/Br polymer **3** with excess *t*-BuMgCl and subsequent aqueous workup. Subsequently,

SCHEME 6. Synthesis of rrP3AT Containing Block Copolymers via *in Situ* (Left) and Postpolymerization (Middle, Right) End Group Functionalization

MA = methyl acrylate, *t*-BuA = *t*-butyl acrylate, PMDETA = *N,N,N,N,N'*-pentamethyldiethylenetriamine.

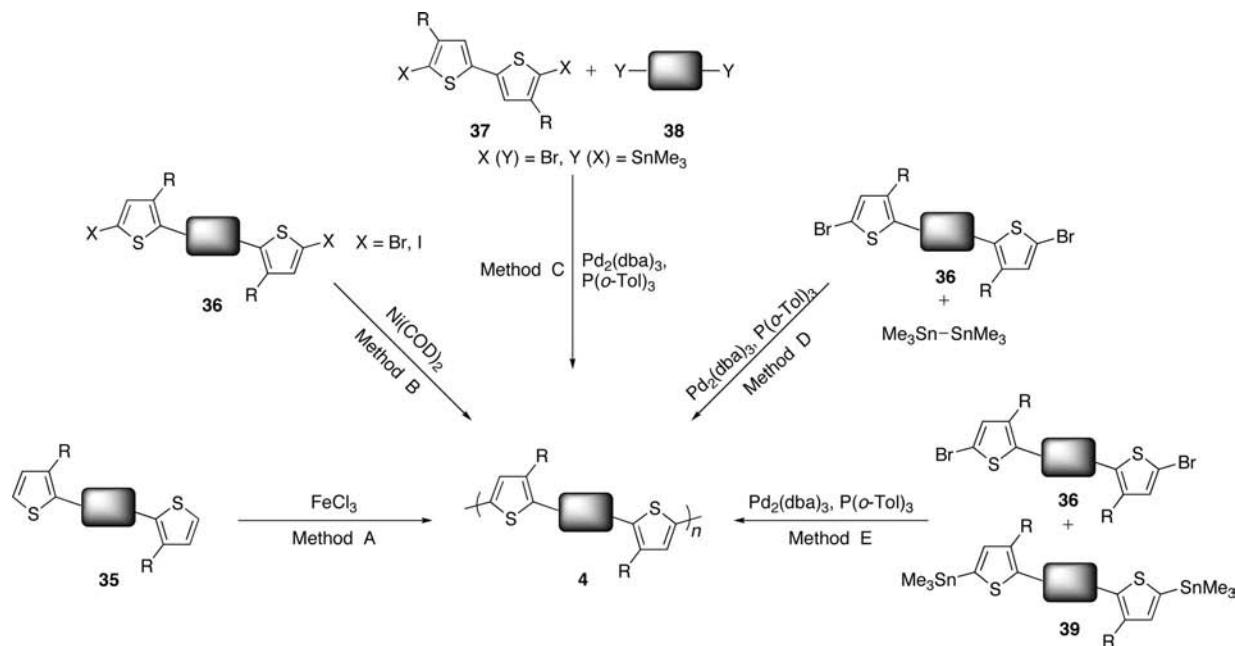
a Vilsmeier reaction was employed to install aldehyde groups onto both ends of the polymer chain (**31**). The aldehyde groups were then reduced to hydroxymethyl groups on both ends (**32**). Hydroxyl-functionalized polymers **27** and **32** were converted to macroinitiators **28** and **33** and further lead to di- and triblock copolymers **29** and **34**, respectively,⁵⁴ using ATRP.

Electrical Properties of Diblock Copolymers. The electrical conductivities of iodine-doped block copolymer films were relatively high despite the presence of the insulating block.^{52,54} Furthermore, diblock copolymer **25** ($m = 1$, R = Me) also showed high mobilities when used in FET devices.⁵⁵ These results were explained in terms of the tendency of these block copolymers to self-assemble into conducting nanofibrils of rrP3HT that are surrounded by an insulating polymer segment.

Regiosymmetric Polythiophenes

The dominant structural feature of HT rrP3ATs in determining their excellent physical and electrical properties is the almost complete absence of the HH arrangements. In another approach, regiosymmetric PT (rsPT) can be prepared where a spacer ring between HH coupled 3-substituted thiophenes is inserted, which lowers the impact of HH couplings. The reported synthesis of rsPTs are shown in Scheme 7 where one of these following methods are used: FeCl_3 -mediated chemical polymerization (method A), Yamamoto polymerization using $\text{Ni}(\text{COD})_2$ (method B), and Stille coupling reaction (methods C–E). Table 2 summarizes the representative polymers synthesized by the above methods.

Gallazzi et al. has reported the synthesis of this type of PTs for the first time by polymerizing 3,3''-dihexyl- α -terthiophene (**35**) with FeCl_3 (entry 1a).⁵⁶ Electrical conductivity of an

SCHEME 7. Synthetic Routes for Regiosymmetric Polythiophenes

iodine-doped pressed pellet was 100 S/cm, which is comparable to that of rrP3ATs. XRD study of the polymer thin film revealed a highly ordered lamellar structure as can be seen in rrP3ATs; moreover, the interlayer spacing was evaluated to be 13.0 Å, which is approximately 3 Å shorter than that of rrP3HT (16.0 Å). This indicates a closer packing of adjacent polymer backbones, which may be due to well-spaced distribution of side chains. The same polymer was also synthesized by Yamamoto polymerization.⁵⁷ Ong et al. have synthesized this type of rsPT with octyl side chain (entry 1b)⁵⁸ and rsPTs with bithiophene (entry 2)¹⁶ and benzodithiophene (entry 3)⁵⁹ as the spacer using this method. Three different routes based on the Stille reaction have been developed for the synthesis of this type of polythiophenes. McCulloch et al. have reported the synthesis of rsPTs using method C, where dibrominated dialkylbithiophene (**37**) and distannylated thienothiophene (**38**) were used as the symmetric monomers, assisted by microwave reactor (entries 4 and 5).^{17,60} Jenekhe et al. has polymerized a symmetric monomer bearing thienopyrazine (**36**) using hexamethylditin to allow corresponding rsPT (method D; entry 8).⁶¹ We have also reported on the synthesis of rsPT bearing thiazolothiazole using method E, where dibromo (**36**) and ditin (**39**) symmetric monomers consisting of the same building unit are used (entry 7).⁶² Recently, in addition, those rsPTs having bithiophene,¹⁶ benzodithiophene,⁵⁹ and thienothiophene^{17,60} were reported to exhibit higher mobility relative to rrP3HTs, due to their highly stacked crystalline structures. We have also shown that thiazolothiaz-

ole copolymer exhibited comparable mobility to rrP3HT despite having low molecular weight (entry 6).^{62,63}

Conclusions

Much of the recent research and commercial products in polymer organic electronics and/or optoelectronics has been based on regioregular polythiophenes. Solar cells and field-effect transistors are common applications of regioregular polythiophenes. This is apparently because the planar polythiophene backbones lead to the formation of self-assembled supramolecular structures and hence a dramatic increase in conductivity/mobility. Certainly, a number of remarkable contributions in this field originated with the discovery of the polymerization of 3-alkylthiophenes in a regioregular fashion. Subsequent work has given rise to large-scale manufacturing and world class devices. Intensive studies on polythiophene synthesis have led to a greater understanding of the mechanism and subsequently a living polymerization system, which is unusual in metal-catalyzed cross-coupling polymerizations. This advanced synthesis of regioregular polythiophenes has also been successful in producing a wide variety of functionalized polythiophenes, functionalized not only at the 3-position of thiophene rings but also at the end position of polymer chains. In addition, the universal use of the GRIM method has recently been reported, in which poly(*p*-phenylene) was synthesized.⁶⁴ We have also developed the universal use of the GRIM method, where polyfluorene, polycarbazole, and

TABLE 2. Summary of Regiosymmetric Polythiophenes

Entry	Polymer structure	R	Method	μ (cm^2/Vs)
1		a) $-\text{C}_6\text{H}_{13}$	A, B	—
		b) $-\text{C}_8\text{H}_{17}$	A	0.015–0.022
2		$-\text{C}_{12}\text{H}_{25}$	A	~0.2
3		$-\text{C}_6\text{H}_{13}$	A	0.15–0.25
4		$-\text{C}_8\text{H}_{17}, \text{C}_{10}\text{H}_{21}, \text{C}_{12}\text{H}_{25}$	C	~0.15
5		$-\text{C}_{10}\text{H}_{21}, \text{C}_{12}\text{H}_{25}, \text{C}_{14}\text{H}_{29}$	C	0.2–0.6
6		$-\text{C}_6\text{H}_{13}, \text{C}_{12}\text{H}_{25}, \text{C}_{14}\text{H}_{29}$	C	~0.3
7		$-\text{C}_{12}\text{H}_{25}$	D	7.1×10^{-4}
8		$-\text{C}_6\text{H}_{13}, \text{C}_{12}\text{H}_{25}, \text{C}_{14}\text{H}_{29}$	E	—

polypyrrole were successfully synthesized.⁶⁵ In addition, regiosymmetric polythiophenes incorporating various thiophene-based rings have been reported to show higher mobilities compared with head-to-tail regioregular polythiophenes. Though it has been more than 15 years since the first synthesis of the regioregular polythiophenes, this field is still growing, and we believe that there is a bright future for this class of polymers, particularly in the area of printable electronics.

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BIOGRAPHICAL INFORMATION

Itaru Osaka received his doctoral degree at University of Tsukuba (Japan) in 2002, where he worked with Professor Kazuo Akagi and Professor Hideki Shirakawa on the synthesis and characterization of liquid crystalline polythiophenes. After 4 years of

research at Fujifilm, Co. Ltd. on organic semiconductors, he joined the group of Professor Richard D. McCullough at Carnegie Mellon University as a postdoctoral fellow. His current research interest includes molecular design and synthesis of functional conjugated materials, self-assembly, and printable organic thin-film devices.

Richard D. McCullough worked with Professor Dwaine Cowan on organic metals at the Johns Hopkins University, being awarded his Ph.D. in 1988. After postdoctoral research with Professor Ronald Breslow at Columbia University, he joined the faculty of Carnegie Mellon University in 1990 and was promoted to Full Professor and Department Head in 1998. After serving as Dean for 7 years, he was appointed as Carnegie Mellon's first Vice President of Research in 2007. In 2002, he cofounded a Carnegie Mellon spin-off company based on regioregular poly(3-alkylthiophene), called Plextronics Inc. His current research interests range from synthesis and self-assembly of highly conductive organic polymers and oligomers to conjugated polymer-based transistors and solar cells and molecular electronics.

FOOTNOTES

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