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Controlling the Macromolecular Architecture of Poly(3-alkylthiophene)s by Alternating Alkyl and Fluoroalkyl Substituents

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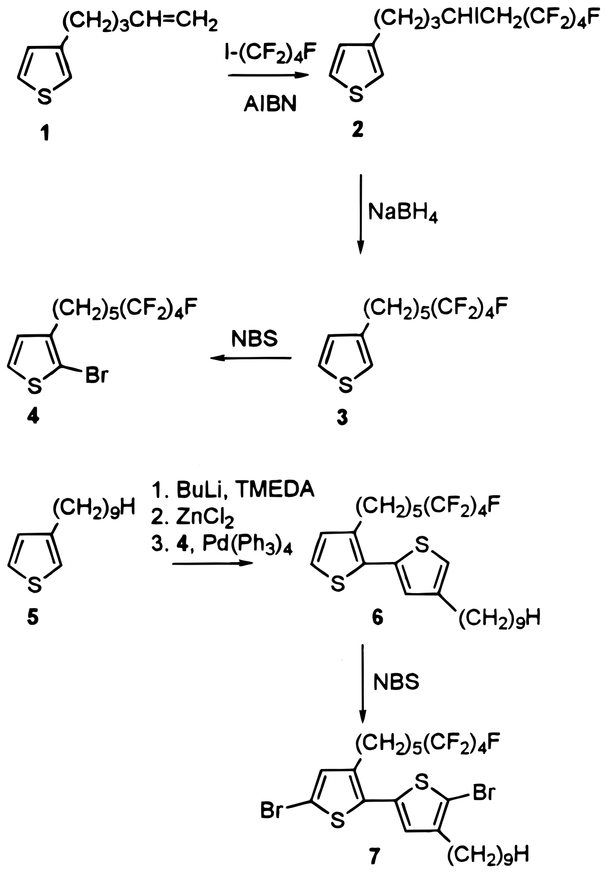
The use of semiconducting conjugated oligomers and polymers in electronic and electrooptical devices[1] relies on control of molecular order and orientation. For example, the plane of the conjugated backbones of oligothiophenes[2] and substituted polythiophenes[3] must be oriented perpendicular to the gate−insulator−semiconductor interface of a field effect transistor (FET) for maximum efficiency (i.e., high field effect mobility and on/off current ratio). The orientation of conjugated chains also gives rise to the possibility of polarized electroluminescent devices.[4]

The substitution and microstructure of oligothiophenes and polythiophenes have a dramatic effect on the assembly of the conjugated chains. While monolayers of β-substituted oligothiophenes on graphite assemble with the plane of the conjugated backbone parallel to the surface,[5] vapor phase deposition of unsubstituted oligothiophenes and α,α′-dialkyloligothiophenes results in films with the long axis of the molecules tilted only slightly from the normal to the substrate. Regioregular poly(3-alkylthiophene)s (PATs) form ordered lamellar phases[6] through interdigitation and crystallization of the side chains. The polymer chains orient along silica surfaces, with the plane of the conjugated chains oriented perpendicular to the surface. In contrast, the regiorandom analogues form more disordered phases and lay flat on silica.[3,7] The solvent from which these films are cast also effects the morphology and device performance.[8]

Besides the use of alkyl side chains to induce solid phase self-assembly and liquid crystallinity,[9] other approaches to ordered conjugated polymers include substitution of the backbones with mesogens,[10] preparation of amphiphilic monomers,[11] and polymerization in organized media.[12] To prepare ordered assemblies with control over orientation relative to a substrate surface, without introduction of ionic or hydrophilic units, we chose to develop amphiphilic polymers consisting of semifluorinated alkyl-substituted thiophenes. A previous study established routes to semifluorinated alkyl-substituted polythiophenes and compared the thermal properties of these polymers to the hydrocarbon analogues.[13] However, to make use of the amphiphilicity of a rigid polymer bearing both alkyl and fluoroalkyl substituents, it is necessary to prepare polymers with a strictly alternating sequence of 3-alkylthiophene and 3-(semifluoroalkyl)thiophene structural units. Regular placement of the substituents along the polymer (i.e., regioregular head-to-tail linkage of 3-substituted thiophene units) should further enhance the assembly of the conjugated chains into bilayer structures (as opposed to the single layer assembly of regioregular PATs).

Scheme 1. Synthesis of Monomer 7



The segregation of hydrocarbon and fluorocarbon chains, which possess different surface activity, should promote assembly of the polymer along the substrate with the plane of the conjugated backbone perpendicular to the surface to avoid interactions with both types of side chains.

Our approach to regioregular polythiophenes bearing alternating alkyl and fluoroalkyl side chains made use of the regioregular polymerization of the suitably substituted bithiophene. The fluorinated chain is separated from the thiophene ring by a hydrocarbon spacer to insulate the electronic effects of the fluorine units from the polymer backbone and for ease of synthesis.[13] The preparation of 5,5′-dibromo-3-(semifluoroalkyl)-4′-alkyl-2,2′-bithiophenes is illustrated by the synthesis of 5,5′-dibromo-3-(6,6,7,7,8,8,9,9,9-nonafluorononyl)-4′-nonyl-2,2′-bithiophene in Scheme 1. 2-Bromo-3-(6,6,7,7,8,8,9,9,9-nonafluorononyl)thiophene, **4**, was prepared by addition of perfluorobutyl iodide to 3-(4-pentenyl)thiophene followed by reduction[13] and bromination with *N*-bromosuccinimide (NBS).[14] Treatment of **4** with 2-(4-nonylthienyl)zinc chloride in the presence of catalytic Pd(PPh_3)$_4$[15] gave 3-(6,6,7,7,8,8,9,9,9-nonafluorononyl)-4′-nonyl-2,2′-bithiophene, **6**.[16] Bromination of **6** with 2 equiv of NBS was performed at 0 °C to give 5,5′-dibromo-3-(6,6,7,7,8,8,9,9,9-nonafluorononyl)-4′-nonyl-2,2′-bithiophene, **7**.[16] Attempts to brominate at higher temperatures resulted in the 4,5,5′-tribromide. The dibromide was converted to 5-bromomagnesio-5′-bromo-3-(6,6,7,7,8,8,9,9,9-nonafluorononyl)-4′-nonyl-2,2′-bithiophene by treatment with CH_3MgCl in THF at

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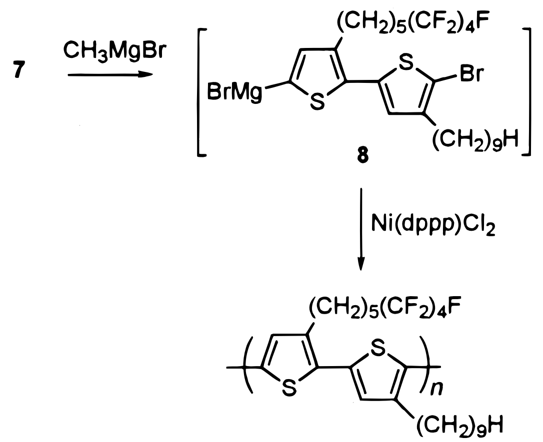
Scheme 2. Regioregular Polymerization of 7



reflux. The regiochemistry of this halogen–metal exchange was established by quenching an aliquot of the reaction mixture with methanol. This provided 5′-bromo-3-(6,6,7,7,8,8,9,9,9-nonafluoro-nonyl)-4-nonyl-2,2′-bithiophene (^{1}H NMR: 2,3-disubstituted thiophene, δ 7.16 (d, 5.4 Hz, 1H), 6.88 (d, 5.4 Hz, 1H); 2′,4′,5′-trisubstituted thiophene, δ 6.96 (s, 1H))[17] with no evidence for the formation of the 5-bromo-3-(semifluoroalkyl)-4′-alkyl analogue (shown by the absence of a pair of doublets, $J = 1.0$ Hz, in the ^{1}H NMR arising from 2,4-disubstitued thiophene). This is in contrast to the treatment of 2,5-dibromo-3-alkylthiophenes with alkylmagnesium halides which results in a mixture of metalated products (ca. 4:1 mixture of 5- and 2-magnesio derivatives which undergoes polymerization to afford the regioregular polymer[18]). Addition of a catalytic amount of $Ni(dppp)Cl_2$ to the substituted dithienomagnesium bromide **8** gave the corresponding polymer, which was precipitated with a large volume of methanol. The polymer was fractionated by extraction with methanol, acetone, hexane, and chloroform in a Soxhlet extractor. The chloroform soluble fraction (24% yield) was isolated and subjected to further study.

The deep red polymer obtained by coupling of **8** is readily soluble in common organic solvents such as chloroform, THF, methylene chloride, toluene, and xylene (unlike the poly(3-(semifluorinated alkyl)thiophene)s). The number-average molecular weight measured by GPC (in THF, polystyrene standards) is 12 700 g/mol with a polydispersity of 1.29, corresponding to a number-average degree of polymerization of 22 (i.e., the polymer chain consists of an average of 44 thiophene units).

Analysis of the ^{1}H NMR spectrum of the polymer indicates a high degree of head-to-tail coupling. Two sharp singlets with equal intensity were observed in the aromatic region (δ 6.96 and 6.94), which are assigned to protons on the two substituted thiophene structural units. The signals corresponding to the protons of the α-methylene unit of the side chains (head-to-tail, δ 2.78; head-to-head, δ 2.54) indicate that the polymers consist of 90–94% head-to-tail linkages. Since the side chain sequence is also set by the regioselectivity of the coupling reaction, the polymer consists primarily of an alternating sequence of alkyl and semifluoroalkyl substituted thiophene structural units.

The UV–vis spectrum of a solution of regioregular semifluorinated polymer derived from **8** in $CHCl_3$ has an absorption maximum, λ_{max}, at 445 nm. This is similar to that of regioregular homopolymers derived from either of the individual structural units: 3-nonylthiophene ($\lambda_{max} = 448$ nm) or 3-(6,6,7,7,8,8,9,9,9-nonafluorononyl)thiophene ($\lambda_{max} = 436$ nm), which are both red-shifted relative to the corresponding regiorandom polymers (regiorandom semifluorinated polymer prepared by $FeCl_3$-promoted polymerization of **6**: $\lambda_{max} = 428$ nm). A similar trend is observed for absorption maxima of films of these polymers (regioregular polymer derived from **8**: λ_{max} at 512 nm).

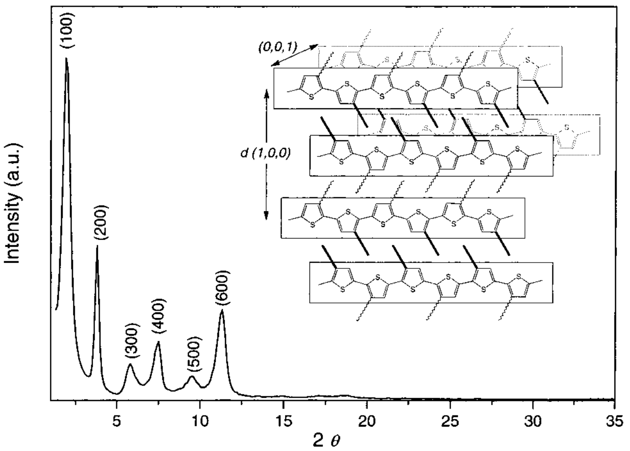


Figure 1. X-ray diffractogram (Cu Kα) of a ca. 100 μm film of alternating regioregular alkyl/fluoroalkyl substituted polythiophene. The films were cast from xylene and annealed at 150 °C for 3 h. Inset: phase structure and orientation.

Differential scanning calorimetry indicates a melting transition at 193 °C ($\Delta H_m = 12$ kJ/mol repeat unit) for the regioregular alternating alkyl–fluoroalkyl polymer and a crystallization exotherm on cooling at 173 °C. These transitions occur at higher temperatures than either of the regioregular homopolymers: poly(3-nonylthiophene), $T_m = 187$ °C ($\Delta H_m = 7.8$ kJ/mol bithiophene); poly(3-(6,6,7,7,8,8,9,9,9-nonafluorononyl)thiophene), $T_m = 170$ °C.

Films (ca. 100 μm) of regioregular alternating polymer were prepared for preliminary X-ray analysis by casting a solution (chloroform or xylene) of the polymer onto an aluminum block. The X-ray diffractogram, Figure 1, shows six strong small-angle reflections which correspond to a well-ordered lamellar structure with an interlayer spacing of 44.8 Å. This pattern is quite distinct from the case for the regioregular homopolymers which form lamellar structures with 22.4 Å interlayer spacings. On the basis of this analysis, we propose that the alternating copolymer adopts a highly ordered bilayer lamellar structure shown schematically in Figure 1 (inset). In this bilayer structure, hydrocarbon side chains pack with other hydrocarbon side chains, while fluorocarbon side chains are segregated and pack with other fluorocarbon side chains. Thus, this order is due to the immiscibility of hydrocarbons and fluorocarbons as well as the assembly of each type of chain. This structure is enhanced by high regioregularity in this copolymer; regiorandom $FeCl_3$-polymerized poly**6** is less ordered. The diffraction lines of the regioregular polymer are sharpened upon annealing the film at temperatures as high as 150 °C.

The lack of a diffraction peak corresponding to π–π stacking interactions (i.e., 001 at ca. 3.8 Å) indicates that the polymer chains are oriented such that the plane of the conjugated backbone is perpendicular to the substrate surface. This is in accord with the amphiphilic nature of the polymer in which the two side chains possess different surface activity. The interchain stacking diffraction peak is observed in unoriented (powdered) samples and also in less ordered, less oriented regiorandom poly**6**.

Thus, substituting alternating thiophene units of polythiophene with hydrocarbon and fluorocarbon side chains affords a hydrophobic amphiphilic polymer which assembles into a lamellar structure. Simply evaporating a solution of this polymer provides a highly oriented sample with the polymer chains oriented along the film and the plane of the conjugated backbone perpendicular to the interface. The films display a high degree of order relative to the all-hydrocarbon analogue (i.e., regioregular poly(3-nonylthiophene)), with strong (h,0,0) diffractions for $h = 1-6$ and a very weak broad diffraction peak for $\pi-\pi$ stacking. In addition, the amphiphilic nature of the repeat units affords a bilayer-type packing, as opposed to a monolayer motif adopted by the hydrocarbon analogue. The effect of the structure, interface, and processing conditions on the assembly and orientation alkyl−fluoroalkyl substituted polythiophenes are currently under investigation, along with their use in electronic devices.

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(16) **6**: ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 7 Hz, 3H, CH_3), 1.2−1.5 (m, 14H, 7CH_2), 1.65 (m, 6H, 3CH_2), 2.04 (m, 2H, CH_2CF_2), 2.61 (t, 2H, Ar−CH_2), 2.79 (t, 7 Hz, 2H, Ar−CH_2), 6.89 (d, 1 Hz, 1H, Ar−H5′), 6.91 (d, 5 Hz, 1H, Ar−H4), 6.94 (d, 1 Hz, 1H, Ar−H3′), 7.15 (d, 5 Hz, 1H, Ar−H5). ^{13}C NMR ($CDCl_3$, 75 MHz, ^{1}H decoupled) δ 143.6, 138.5, 135.6, 131.3, 129.7, 127.5, 123.6, 120.0, 31.93, 30.46 (t, $J_{C-C-F} = 22$ Hz), 30.41, 30.24, 29.71, 29.67, 29.57, 29.47, 29.33, 28.80, 28.73, 22.67, 19.90, 14.04 (a series of small peaks appear at δ 100−130 ppm for the CF_2 and CF_3 carbons, the signals are split into complex patterns by 1-, 2-, and 3-bond coupling between carbon and fluorine, $s = {}^1/_2$). IR (neat) 3098, 3065, 2927, 2857, 1462, 1231, 1133, 879, 725 cm^{-1}. **7**: ^{1}H NMR ($CDCl_3$) δ 0.85 (t, $J = 7$ Hz, 3H, CH_3), 1.2−1.5 (m, 14H, 7CH_2), 1.61 (m, 6H, 3CH_2), 2.02 (m, 2H, CH_2CF_2), 2.52 (t, $J = 7$ Hz, 2H, Ar−CH_2), 2.65 (t, $J = 7$ Hz, 2H, Ar−CH_2), 6.71 (s, 1H, Ar−H4), 6.84 (s, 1H, Ar−H3′). ^{13}C NMR ($CDCl_3$, 100 MHz, ^{1}H decoupled) δ 143.0, 140.2, 134.4, 132.7, 132.2, 127.9, 111.4 (C−Br), 109.7 (C−Br), 32.29, 30.85 (t, $J_{C-C-F} = 22$ Hz), 30.05, 29.94, 29.89, 29.80, 29.72, 29.63, 29.12, 29.10, 23.08, 20.35, 14.49 (two aliphatic carbon resonances are coincident; a series of small peaks appear at δ 100−130 ppm for the CF_2 and CF_3 carbons, the signals are split into complex patterns by 1-, 2-, and 3-bond coupling between carbon and fluorine, $s = {}^1/_2$). IR (neat) 2926, 2856, 1461, 1233, 1133, 879, 718 cm^{-1}. Regioregular alternating polymer: ^{1}H NMR ($CDCl_3$) δ 0.83 (m, 3H), 1.1−1.8 (m, 20H), 2.06 (m, 2H), 2.78 (m, 4H), 6.94 (s, 1H), 6.96 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz, ^{1}H decoupled) δ 140.1, 139.2, 133.9, 133.5, 130.8, 130.5, 128.8, 128.4, 31.9, 30.75 (t, $J_{C-C-F} = 22$ Hz), 30.55, 28−30 (8 carbons), 22.66, 20.00, 14.05 (a series of small peaks appear at δ 100−130 ppm for the CF_2 and CF_3 carbons, the signals are split into complex patterns by 1-, 2-, and 3-bond coupling between carbon and fluorine, $s = {}^1/_2$). IR (film) 3050, 2924, 2854, 1466, 1222, 1132, 879, 718 cm^{-1}.

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