Alternating Arene−Perfluoroarene Poly(phenylene ethynylenes)

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ABSTRACT: We report the synthesis of two poly(phenylene ethynylene)s (PPEs) with alternating dialkylbenzene−perfluorobenzene repeating units. The combination of low volume fraction of solubilizing side chains and enhanced intermolecular $\pi-\pi$ stacking renders these materials insoluble. A soluble polymer analogue was realized by using a 1,2,4,5-tetralkoxy benzene in the place of dialkyl benzenes, and its properties are compared to a nonfluorinated analogue. The effects of fluorination and side-chain identity on supramolecular and thermal behavior were investigated by wide-angle X-ray diffraction, differential scanning calorimetry, and polarized optical microscopy. Single-crystal X-ray diffraction from small-molecule model compounds provided further insight, including indication that PPE's composed of alternating 1,2,4,5-tetralkoxy- and 1,2,4,5-tetrafluorobenzenes can assemble to close face-to-face π-stacks. Initial efforts to prepare these same polymers and small-molecule model compounds by alternate pathways are also described.

Introduction

Attractive interactions between fluorinated (πF) and nonfluorinated (π) π-electron units provide fairly predictable control over supramolecular behavior. This has been most clearly demonstrated with small molecules,[1] but the supramolecular consequences in polymeric materials have yet to be demonstrated. Partial or full fluorination of organic π-electron systems can also lead to *n*-type organic electronic materials.[2] Several πF-containing conjugated polymers such as oligo- and poly-(phenylene vinylene)s,[3] thiophene copolymers,[4] and poly-(phenylene ethynylene)s (PPEs)[5] have been reported. Detailed structure−property relationships are lacking, but it can be expected that fluorination should raise oxidation potential/oxidative stability,[6] and perfectly alternating structures should lead to enhanced π-stacking. Distant π-stacking or a total lack thereof[7] is desirable for sensors[8] and to increase quantum yields[9] for light emitting materials, but closer π-stacking can be advantageous for charge-carrier transport in organic semiconductors.[10] Whether PPE's in general π-stack at all has recently been questioned based on photophysical measurements.[11]

We present here our initial efforts to establish structure−property relationships for perfectly alternating $\pi-\pi$F PPEs. The primary goals here are to begin to understand the effects of side-chain identity and $\pi-\pi$F interactions on solid-state packing and to achieve solution processability. Up until now, the only published soluble $\pi-\pi$F PPEs contained very bulky iptycene[5c] or sugar-derivatized benzenes as comonomers.[5a] We report the synthesis of three new $\pi-\pi$F PPEs with differing side chains and substitution densities, as well as one nonfluorinated control, and their characterization by wide-angle X-ray diffraction (WAXD), variable-temperature polarized optical microscopy (VT−POM), and differential scanning calorimetry (DSC). Good correlation is reported between polymer packing arrangements and those displayed by newly prepared small-molecule model compounds as determined by single-crystal X-ray crystallography. We also report alternate synthetic routes to PPE oligomers and small molecules enabled by highly fluorinated aromatics, such as C−C bond formation via fluoride-substitution

reactions, and alkyne cross-metathesis (small-molecule synthesis only).
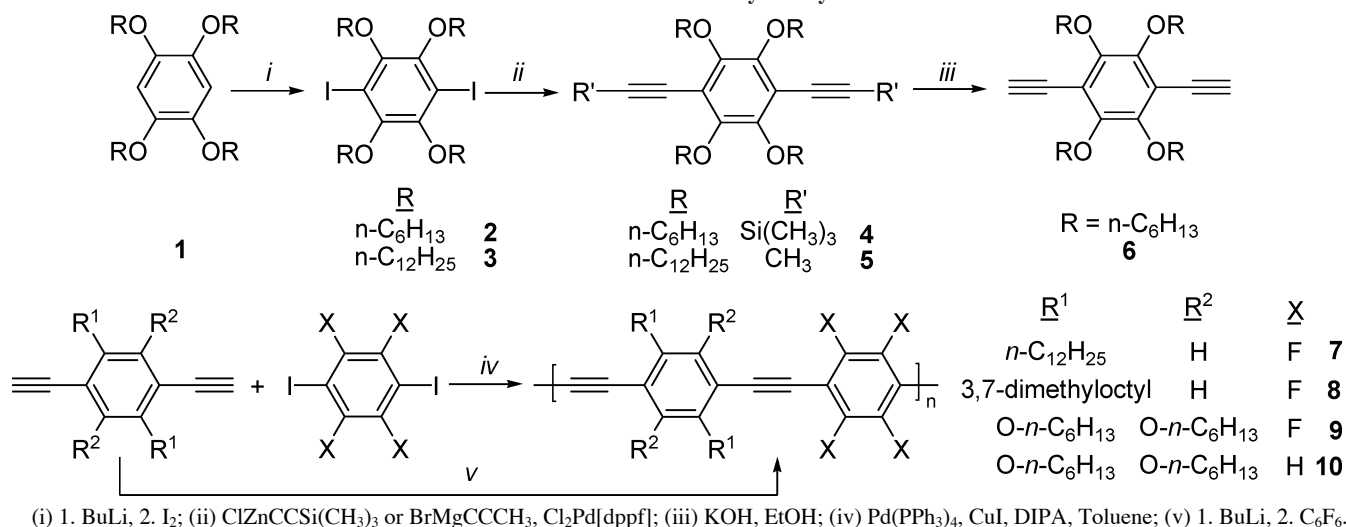
Results and Discussion

Monomer and Polymer Synthesis. 2,5-Dialkylated monomers were synthesized by published procedures.[12] All polymers (**7**−**10**) were prepared by Sonogashira coupling and isolated as yellow solids (Scheme 1. For modifications in the syntheses of **7** and **8**, see Supporting Information). Polymers **7** and **8** carrying only two alkyl chains on each repeat unit were completely insoluble. Attempts to produce soluble oligomers with number average degree of polymerization (P_n) = 10−20 via varied monomer stoichiometry and/or inclusion of monofunctional iodobenzene also led to insoluble materials.

We turned to 1,2,4,5-tetra-alkoxy benzenes as nonfluorinated comonomers to compensate for the lack of solubilizing side chains on the πF portion of the polymer repeating unit. Compounds **1** can be dilithiated with excellent conversion in hydrocarbon solvents, without the need for chelators such as TMEDA, and quenched with I_2. Negishi coupling at elevated temperatures in a sealed vessel produced **4** in good to excellent isolated yields. Sonogashira coupling of **6** with the appropriate 1,4-diiodobenzenes yielded polymers **9** and **10**.
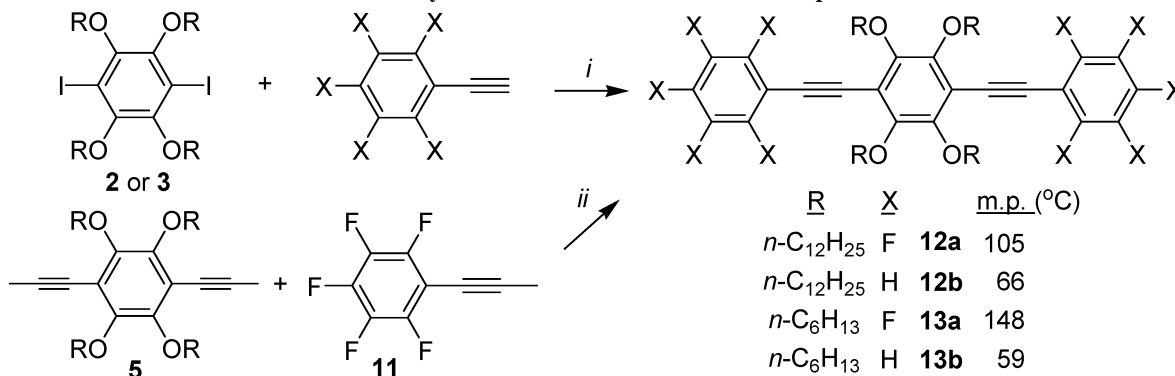
The tendency of C_6F_6 to undergo regioselective substitution reactions[13] with nucleophiles has been exploited to prepare nonconjugated high-performance polymers[14] and alternating $\pi-\pi$F oligomers and polymers.[15] We exploited the regioselective nucleophilic reaction of lithium acetylides with the 1,4-positions of C_6F_6[16] to prepare PPE **9** with well-defined end groups. Despite expected difficulties in achieving perfect stoichiometry in the lithiation step, ^{1}H, ^{13}C, and ^{19}F NMR spectra indicate high chemical purity (see Supporting Information for full spectra.). The only detectable end groups are C_6F_5, as defined by a stoichiometric imbalance during polymerization. [19]F end group analysis indicates a degree of polymerization P_n = 9−10 (18−20 benzene rings), which is greater than the published[17] effective conjugation length of PPEs. The well-defined reactive C_6F_5 end groups qualify these as macromonomers, which could later be end-functionalized with nucleophiles or copolymerized with telechelics terminated by nucleophilic sites to produce block copolymers.

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Scheme 1. Monomer and Polymer Synthesis

	R		
	n-C$_6$H$_{13}$	**2**	
	n-C$_{12}$H$_{25}$	**3**	

	R	R'	
	n-C$_6$H$_{13}$	Si(CH$_3$)$_3$	**4**
	n-C$_{12}$H$_{25}$	CH$_3$	**5**

R = n-C$_6$H$_{13}$ **6**

R^1	R^2	X	
n-C$_{12}$H$_{25}$	H	F	**7**
3,7-dimethyloctyl	H	F	**8**
O-n-C$_6$H$_{13}$	O-n-C$_6$H$_{13}$	F	**9**
O-n-C$_6$H$_{13}$	O-n-C$_6$H$_{13}$	H	**10**

(i) 1. BuLi, 2. I$_2$; (ii) ClZnCCSi(CH$_3$)$_3$ or BrMgCCCH$_3$, Cl$_2$Pd[dppf]; (iii) KOH, EtOH; (iv) Pd(PPh$_3$)$_4$, CuI, DIPA, Toluene; (v) 1. BuLi, 2. C$_6$F$_6$.

Scheme 2. Synthesis of Small-Molecule Model Compounds

R	X	m.p. (°C)	
n-C$_{12}$H$_{25}$	F	105	**12a**
n-C$_{12}$H$_{25}$	H	66	**12b**
n-C$_6$H$_{13}$	F	148	**13a**
n-C$_6$H$_{13}$	H	59	**13b**

(i) Pd(PPh$_3$)$_4$, CuI, DIPA, Toluene. (ii) Mo(CO)$_6$, 2-fluorophenol, C$_6$H$_5$Cl, reflux.

Synthesis of Small-Molecule Model Compounds. Four different model compounds (Scheme 2), with or without fluorination, and with dodecyloxy or hexyloxy chains were prepared. In addition to Sonogashira coupling, we employed acyclic diyne metathesis (ADIMET).[18] The drastically altered electron density of πFs begs their investigation as selective cross-ADIMET[19] partners. Cross metathesis of **5** with **11** produced the target "trimer" **12a** in 46% isolated yield. It is not expected that the analogous polymerization, cross-ADIMET of monomer **5** with 1,4-propynyl-tetrafluorobenzene, would lead to high-molecular-weight polymer. The high temperature required for catalyst activity and inert gas sparge necessary to drive out 2-butyne would upset stoichiometry due to evaporation of the πF monomer. Perhaps less volatile butynylated monomers or (pre)catalyst systems that operate at lower temperature would permit high molecular weight.[20]

Structure−Property Studies. The insolubility of **7** and **8** was expected as analogous *nonfluorinated* PPE's carrying alkoxy side chains on only every other backbone ring[21] show lower solubility than those carrying solubilizing chains on every benzene ring. The increased side-chain substitution density of polymers **9**, **10** substantially increases solubility. PPE **10** dissolves in many organic solvents at room temperature unlike its published[21] analogue carrying only two hexyloxy chains on every second benzene ring. Fluorinated **9** is also soluble in common organic solvents, albeit only at temperatures exceeding 100 °C. This lower solubility relative to **10** likely results from enhanced aggregation due to $\pi-\pi$F interactions. Dilute solutions of **9** and **10** yield UV−vis absorbance profiles typical of PPEs with $\lambda_{max} = 390-410$ nm, depending on solvent.

Thermal behavior was recorded using differential scanning calorimetry (DSC) and variable temperature polarized optical microscopy (VT-POM). WAXD diffractograms obtained from aligned fibers of each polymer are included in Figure 1, and the diffraction and thermal data are collected in Table 1. For each polymer except **10** (severely limited number of reflections) there is a series of equatorial intensity maxima at low to intermediate angles with relative d-spacings of L, $L/2$, $L/3$, etc., with intensities decreasing in that order. This indicates alternating, parallel zones of polymer backbones separated by alkyl side chains (lamellar packing). At wider angle, each shows intensity maxima (enclosed in dashed crescents) with d-spacing and intensity that do not fit into this series. This is assigned as the face-to-face (π-stacking) distance between the polymer backbones.

The π-stacking distance for **7** (4.1 Å) is significantly greater than for **8** (3.6 Å) as a consequence of side-chain packing. Polymer **8** shows very diffuse scattering at $d \sim 5$ Å arising from amorphous side chains, while **7** shows sharp reflections centered on the meridian at $d = 4.6$, 4.3, and 3.6 Å, indicating crystalline n-dodecyl side chains. The interlayer spacing (π-stacking) is dictated by the side chains of **7**, while the side chains of **8** are disordered, allowing packing to be dominated by backbone intermolecular interactions. *We have noted exactly analogous differences between bithiophene-based $\pi-\pi$F co-polymers carrying branched or unbranched alkyl chains, to be published elsewhere.* Distant π-stacking, dictated by side-chain packing, could explain a recent report[11] that a PPE carrying n-dodecyl side chains displays bulk photophysical behavior commensurate with noninteracting chromophores. It is important
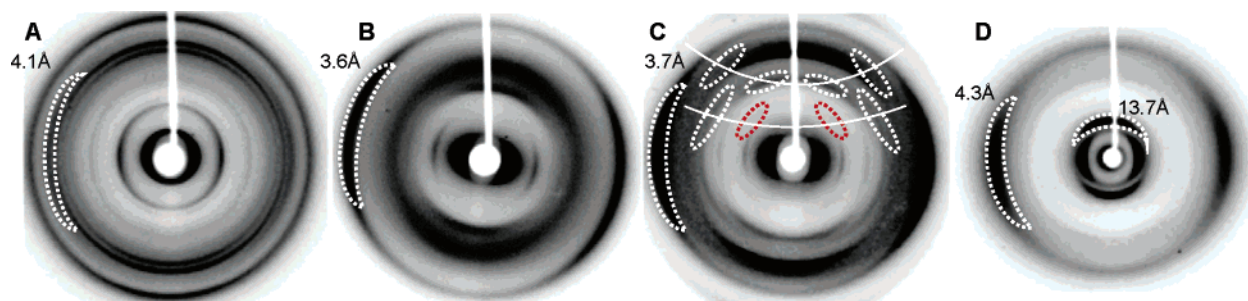
Figure 1. Fiber WAXD measurements from oriented samples of polymers: (A) **7** [extruded 165 °C], (B) **8** [extruded 100 °C], (C) **9** [annealed 240 °C], and (D) **10**. Fiber/polymer orientations are approximately vertical. Ellipses in (C) accentuate weak off-meridianal intensity maxima forming layer lines.

Table 1. WAXD and Thermal Data from Polymers 7−10

polymer	equatorial *d*-spacings (Å)[a]	meridianal *d*-spacings (Å)	thermal transitions (°C)[b]
7	18.6, 9.2, 6.1 (4.1)	4.6, 4.3, 3.6	179 {solid → lc},[c] 320−350 (dec)
8	17.9, 8.9, 5.9 (3.6)	6.7, 5.0, 3.2, 2.7	320−350 (dec)
9	19.6, 9.8, 6.5 (3.7)	4.6, 3.2, 3.0, 2.3	274 {solid → lc}, 320−350 (dec)
10	16.7 (4.3)	13.7	40 {lc → lc}, 320−350 (dec)

[a] Values in ( ) indicate π-stacking distance. Text in { } are transitions assigned from VT−POM. [b] DSC, 10 °C/min. [c] Annealed 170 °C.
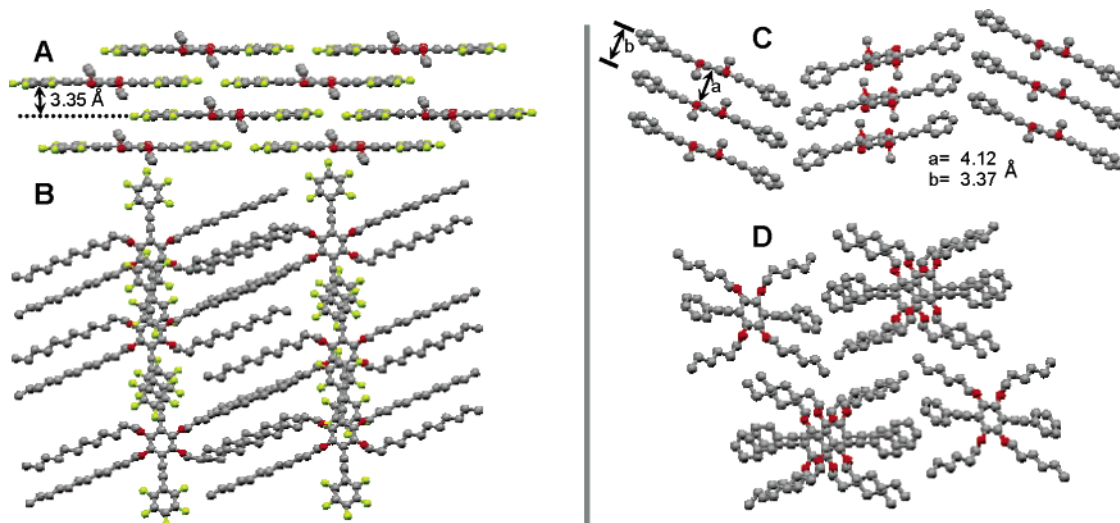

Figure 2. Crystal packing of small molecules. (A−B) Views parallel and perpendicular to the calculated best planes containing the unsaturated carbons of **12a**. (C−D) Analogous views of **13b**. Alkyl chains truncated beyond the α-CH₂ groups for clarity in (A) and (C). Double-headed arrows indicate perpendicular distances (given in Å) between the π-faces.

to note that powder diffraction measurements of unoriented samples of **7** and **8** would not have allowed clear differentiation between their packing.

These differences in packing are clearly reflected in the DSC and VT-POM experiments. On heating, **7** undergoes very broad endothermic processes with maxima at 140 and 178 °C, which do not appear in subsequent heating scans unless the sample is annealed above 100 °C. This may reflect the opposing driving forces for ordering (side-chain vs main-chain packing). Annealing at progressively higher temperature shifts the lower endothermic maximum to progressively higher values until a single, sharp transition is observed at 179 °C (Supporting Information). VT-POM shows a distinct increase in birefringence near 180 °C, suggesting a solid to liquid-crystalline transition. Polymer **8** shows no transitions until the onset of decomposition at 320 °C, which is in the same range for decomposition of all the polymers (VT-POM, DSC, TGA). Branched racemic chains might normally be expected to decrease the thermal stability of a given phase and increase the π−π stacking distance due to entropic and steric factors. In this case, it is side-chain crystallization that destabilizes π-stacking.

Before discussing the diffraction data from polymers **9** and **10**, we show by X-ray crystallography of model compounds that close π-stacking is possible with phenylene−ethynylene structures bearing such highly substituted benzene rings. Using various solvents and thermal conditions, we could only obtain very thin flexible platelets from **12b** and **13a**. Suitable crystals could be obtained from **12a** and **13b**, and their crystal packing arrangements are illustrated in Figure 2. Within single molecules, the benzene rings of **12a** are essentially coplanar. The perpendicular distance between the parallel π-faces of adjacent molecules is 3.35 Å, proving close π-stacking is possible. The "rigid" rod core of **13b** is significantly distorted from planarity (largest dihedral angle between benzene rings = 24.7°) and curved along its long axis. These features accommodate two different π−π stacking distances: a close face-to-face packing (3.37 Å) of terminal phenyl rings and a larger spacing between the central rings (4.12 Å). The melting points of the fluorinated small-molecule models are 40−90 °C greater than the nonfluorinated ones within each pair carrying identical side chains, indicating more thermally stable crystal packing.

Similar differences are reflected by the analogous polymers: the room-temperature phase of **9** is substantially more thermally

stable than that of **10**. DSC revealed a broad, reversible endothermic transition (30−40 °C wide) for **10** with onset just above room temperature. Unlike the other three polymers, as-cast thin films of **10** show strong birefringence between cross-polars with scattered maltese crosses. Polymer **10** is likely the only one that is plastic- or liquid-crystalline at room temperature. Fluorinated **9**, on the other hand, showed no thermal transitions until approximately 280 °C, followed by a substantial exotherm with onset near 320 °C (presumably decomposition). Near 280 °C, VT-POM revealed a distinct increase in birefringence, indicating a solid to liquid-crystalline transition.

Polymers **9** and **10** allow a direct comparison of the solid-state packing of fluorinated and nonfluorinated polymers. In the intermediate angle range, polymer **10** shows single pairs of intense equatorial ($d = 16.7$ Å) and meridianal ($d = 13.7$ Å) reflections, indicating short-range order at best. The strong meridianal reflection corresponds closely to the length of repeat unit, suggesting overlapping oxygenated rings similar to the small-molecule model **13b**. The fiber from **9** produces a series of equatorial intensity maxima typical of lamellar ordering. There is also some three-dimensional registry for polymer **9**, not seen for any of the other polymers, as indicated by weak off-meridianal reflections forming parabolic layer lines (accentuated by dashed ellipses and curved lines in Figure 2C). The points at which these layer lines are estimated to cross the meridian are within 2 Å, but not equal to, the length of the repeating unit and one-half of that value. Without more data, a unit cell cannot be determined with certainty. The π-stacking distance for **10** (4.3 Å) is noticeably greater than that for fluorine-containing **9** (3.7 Å), in analogy to the differences in packing for the small molecule models.

Photophysical studies will be carried out and reported later as more polymers become available. The widely variable properties of polymers **7**−**10** severely limit the number of meaningful conclusions that could be drawn in this case. There is no pair of polymers with differing substitution patterns, both of which are soluble at room temperature, or both of which that can undergo thermal relaxation in the solid state, allowing equilibration and erasure of thermal/processing history.

Concluding Remarks

π−πF PPE's may be rendered soluble with appropriate side-chain substitution. Nucleophilic attack on πFs by carbanions is a promising method to prepare such alternating copolymers. Fluorination reduces solubility, increases thermal stability of room-temperature packing arrangement, and enhances supramolecular order, all presumably due to interactions between the fluorinated and nonfluorinated units. In the case of dialkyl π−πF PPE's, crystallizable *n*-docyl side chains seem to dominate self-assembly, while amorphous branched chains are more or less space-filling spectators. Evaluation of these two polymers demonstrates the importance of utilizing oriented samples to diminish ambiguity in diffraction experiments.

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