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Transition-Metal-Free Synthesis of Poly(phenylene Ethynylene)s with Alternating Aryl-Perfluoroaryl Units

Tanmoy Dutta, Kathy B. Woody, and Mark D. Watson*

University of Kentucky, Department of Chemistry, Lexington, Kentucky, 40506-0055

Received November 23, 2007; E-mail: mdwatson@uky.edu

Poly(arylene ethynylene)s (PAE) may be prepared with a broad range of (opto)electronic properties to serve as active components in solar cells,[1a] sensors,[1b] and field effect transistors (oligomers).[1c] The main routes for their syntheses are Hagihara−Sonogashira and related palladium-catalyzed couplings,[2] or acyclic diyne metathesis (ADIMET).[3] We report here a simple alternative, transition-metal-free synthesis which delivers PAEs in high molecular weight, structural fidelity, purity, and yield with minimal required purification.

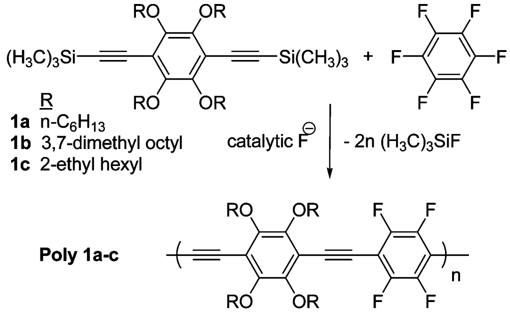
Many nucleophiles react regioselectively with perfluorobenzene (PFB), replacing two fluorides at its 1,4-positions.[4] A number of polymers have been produced this way,[5] but very few were built from carbon-centered nucleophiles.[6] Carbon-centered nucleophiles can be conveniently generated in situ from easily handled organosilanes.[7] Specifically, activated silyl acetylenes react with a number of electrophiles,[8] and we report here their reaction with PFB to prepare high molecular weight poly(phenylene ethynylene)s (PPE). The repeating structures composed of perfectly alternating fluorinated and non-fluorinated π-electron units can be expected to provide fine control over self-assembly[9] and bulk optoelectronic properties.[10]

Polymerization requires only a catalytic amount of fluoride ion to generate nucleophilic pentacoordinate silicate ions from **1**, which form new bonds with PFB (Scheme 1). The fluoride lost as volatile fluorotrimethylsilane (TMSF) with each new C−C bond is regenerated by substitution. Reactions of silyl acetylenes with perfluoropyridine are also catalytic in fluoride (not shown), unlike published reports[8b] using molar excesses of fluoride.

To minimize competing protiodesilyation, we began the synthetic study using freshly calcined CsF with 18-crown-6, which proved most effective for preparing copolymers from silylthiophenes.[11] Above 60 °C, this catalyst system is effective with monomers **1b**,**c** but with **1a** the surface of the CsF particles simply darkened. Tetramethyl- and tetrabutyl ammonium fluoride (TMAF, TBAF) are effective for all three monomers at room temperature. The differing reactivity of monomer **1a** from **1b**,**c** could be due to solubility of reactive intermediates or to subtle differences in electron donating/withdrawing ability of the alkoxy substituents dictated by rotational freedom/steric demand of the alkyl chains. The dark color fouling the CsF surface in reactions with monomer **1a** may arise from trapped reactive intermediates. Homogeneous polymerizations with **1b**,**c** catalyzed by TBAF also initially become very dark, but the solutions assume the yellow color of the polymers at high conversion when the concentration of reactive intermediates becomes low (e.g., pentacoordinate silicates or Meisenheimer complexes).

Number-average molecular weights (M_n, GPC) of a few kDa are obtained with $TBAF{\cdot}3H_2O$ and off-the-shelf solvents. M_n is increased when using a commercial “anhydrous” TBAF solution (1 M THF, 5% H_2O v/v), and further still with anhydrous TMAF in anhydrous solvents (M_n > 100 kDa). This trend is consistent with step-growth termination by unreactive C≡CH end-groups, formed via protiodesilylation by water and protic impurities resulting from Hofmann elimination of TBAF. The ratio of C_6F_5 to C≡CH end-groups can be controlled by using a molar excess of PFB under anhydrous conditions (^1H and ^{19}F NMR, Supporting Information).

Scheme 1 Synthesis of Alternating Poly(phenylene ethynylene)s



	Fluoride source	M_n (kDa) [PDI][a]	Yield (%)	λ_{max}[b] Abs[PL](nm)	T_{iso}[c] (°C)
1b	TBAF[d]	83.0 [3.76]	88	419 [441]	195
1c	TBAF[d]	34.7 [2.3]	75.1		
1c	TBAF[e]	8.91 [2.09]	83.3		
1c	CsF[f]	36.3 [2.62]	98		
1c	TMAF[d]	153 [1.54]	70	390 [495]	155

[a] GPC vs polystyrene. [b] abs:10^{-6} M THF; PL: 10^{-8} M THF. [c] Differential scanning calorimetry. [d] anhydrous, room temp. [e] $TBAF{\cdot}3H_2O$, benchtop, room temp. [f] anhydrous, 60 °C. All in toluene, except reactions using TMAF (THF).

The maximum attainable number-average degree of polymerization (P_n) for step polymerizations falls precipitously with comonomer stoichiometric imbalance as described by the Carothers equation (Figure 1). In cases where bifunctional monomer produces a more reactive intermediate, i.e., the first bond-formation is the rate-limiting step, P_n can be enhanced over practical reaction periods by using an excess of that monomer.[12] Three pieces of evidence indicate that this polymerization proceeds through a more reactive intermediate, that is, the second fluoride displacement from PFB is faster than the first:

(I) The relationship between P_n and C_6F_6:**1c** stoichiometry is plotted in Figure 1. The distinct deviation from Carothers equation allows for relatively high molecular weight despite a high molar excess of PFB, which in turn leads to well-defined C_6F_5 end-groups. Descriptions of P_n estimations by NMR and GPC are provided in the Supporting Information.

(II) During polymerization, ^{19}F NMR shows growing signals from TMSF and 1,2,4,5-tetrafluorophenyl repeating units, but the steady-state concentration of C_6F_5 end-groups remains low owing to their much higher reactivity compared to PFB.

(III) Model study (Scheme 2): Although the initial molar ratio of **2**:PFB is 1:1, ∼ 80% of **2** is converted to **5**, similar to reactions of PFB with lithium acetylides.[13] The phenyl-acetylene group of **4** activates the para-position toward further substitution, perhaps via

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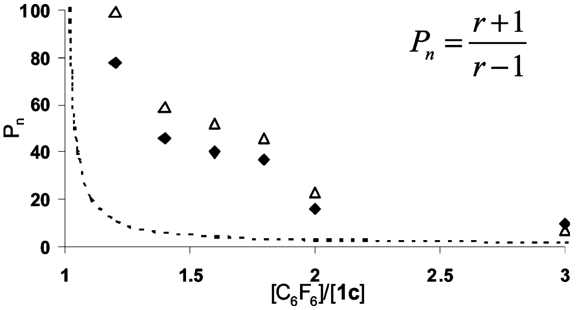
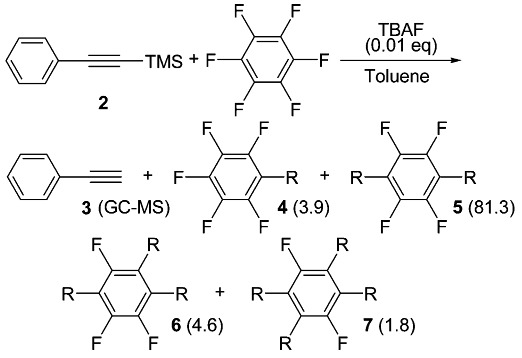


Figure 1. P_n vs C_6F_6:**1c** molar ratio (TMAF catalyst), estimated by NMR end-group analysis (◆) and GPC (△), compared to Carothers equation (dashed line). See Supporting Information for treatment of GPC data. The inset shows the Carothers equation with r = molar ratio of excess monomer to limiting monomer.

Scheme 2. Model Reaction[a]



[a] Isolated yields; R = CCPh.

additional cumulene-like resonance forms of the resulting intermediate Meisenheimer complex.

The model reaction is violently exothermic when conducted at high concentration, producing substantial amounts of **6** and **7**. At dilutions approaching those of the polymerizations, combined conversions to **6** and **7** are lowered to ~6%. These side-products correspond to branching points or cross-links in the analogous polymerizations, which could also cause deviation from Carothers equation. However, the actual percentage of such defects in the polymers is less than 1/150 repeat units based on integration of diminutive ^{19}F NMR signals. For comparison, model "defect" **6** (1 mol %) is readily detected in a solution of model polymer repeat unit **5** by ^{19}F NMR after relatively few transients. The low percentage of defects in the polymers might be attributed to steric bulk of monomers **1**. From other bis-silyl-acetylene monomers, we have prepared hyperbranched or cross-linked PAE gels, which may have their own merits[14] and will be described in a future communication.

Unlike **poly1a**,[6a] **poly1b**,**1c** are highly soluble in common organic solvents at room temperature. The solution absorbance/photoluminescence spectra of **poly1b**,**1c** differ significantly (Supporting Information). The 2-ethyl-hexyl chains of **poly1c** present greater steric bulk in the vicinity of the polymer backbone, altering rotational freedom around backbone bonds and/or the benzene−oxygen bonds. The former may affect backbone conjugation, while the latter can affect the mesomeric/inductive influence of the side chains on the chromophoric backbone. The result is a larger apparent Stokes shift and nearly featureless absorbance and PL profiles. A future communication will link solid-state optical and thermal properties to packing arrangements determined by wide-angle X-ray scattering studies.

In summary, we have shown that high molecular weight PPEs can be obtained by nucleophilic aromatic substitution. The polymers are easily purified as the only side product is a gas (TMSF), and the catalyst can be removed with a simple aqueous treatment. Their well-defined C_6F_5 endgroups might be selectively functionalized with other nucleophiles, or the polymers can be used as macromonomers. This synthetic route may enjoy broad applicability in synthesis of acetylenic scaffolds of varying geometries.[15] It may show particular importance for incorporating alkynyl monomers that are unstable[16] if desilylated prior to Hagihara−Sonogashira coupling. For example we have coupled 9,10-trialkylsilylacetylene-functionalized anthracene and the analogous 6,13-functionalized pentacene with perfluoro-pyridine and -toluene in 60−80% isolated yields (unoptimized).

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Supporting Information Available: Experimental procedures, spectroscopic and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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