Base-Free Suzuki Polymerization for the Synthesis of Polyfluorenes Functionalized with Carboxylic Acids

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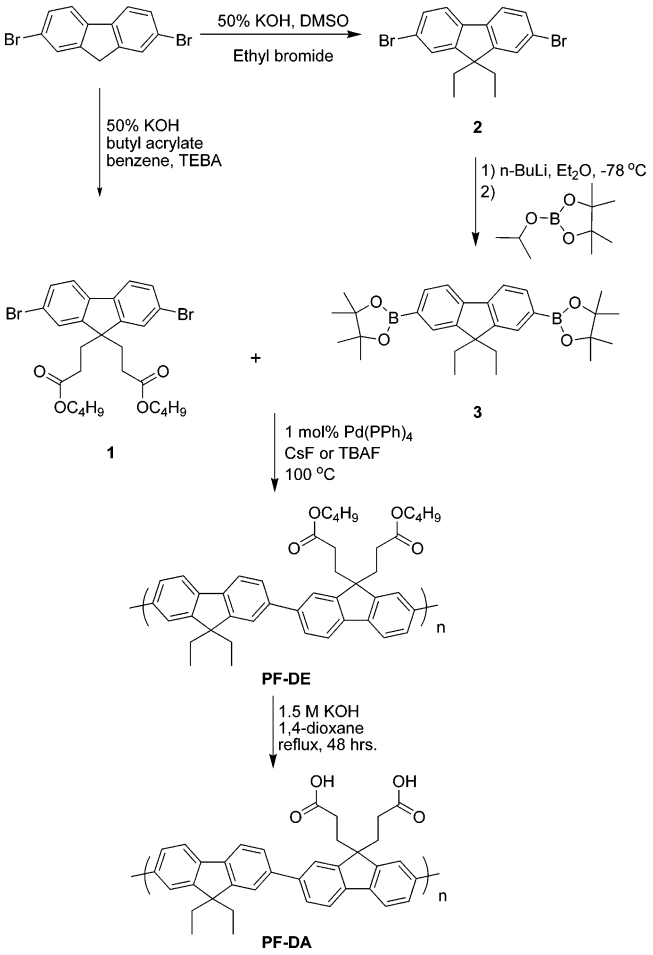
Conjugated polyelectrolytes (CPEs) are a potentially interesting class of conjugated polymers because of their solubility in polar solvents[1] and processability via various solution methods such as layer-by-layer assembly[2] and adsorption to polar substrates.[3,4] Additionally, their charged side chains give CPEs novel solution properties as rigid-rod polyelectrolytes influencing the intrachain conformational freedom and the interchain interactions.[5] These properties have made CPEs of particular interest for optoelectronic applications such as light-emitting diodes,[6,7] photovoltaics,[8−11] and sensors.[12−16]

The synthesis of conjugated polymers with ionic pendant groups follows either a direct method (where the polymerization conditions are compatible with the ionic pendant groups) or an indirect method (where the polymerization yields a precursor that can be subsequently converted to the polyelectrolyte in high yield). Direct methods have been used in the synthesis of poly(*p*-phenylenes) and poly(phenylene ethynlenes) bearing carboxylic acids[17] and sulfonates,[16,18] for example. These direct routes have been used with great success but are limited in two important ways in comparison to an indirect route. First, the indirect route allows a greater variety of pendant groups and molecular structures to be incorporated into a CPE. Additionally, the precursor polymer affords a neutral polymer that can be characterized by traditional means (e.g., GPC, NMR, elemental analysis) without the difficulties associated with polyelectrolytes (e.g., aggregation in solution, hygroscopicity, identity of counterion).

Here, we report on the first synthesis of a carboxylic acid-functionalized CPE via a base-free Suzuki polymerization. The traditional Suzuki coupling uses basic reagents to activate the boronic acid/ester to undergo the catalytic cycle and to form the new aryl−aryl bond.[19] An ester-functionalized conjugated polymer (a precursor to the carboxylic acid CPE) is subject to hydrolysis under comparable conditions. However, previous work on Suzuki coupling for small molecule synthesis illustrated how fluoride salts such as cesium fluoride and tetrabutylammonium fluoride activate boronic acids.[20] This Communication presents the optimization of the base-free Suzuki polymerization for the synthesis of the first reported polyfluorene functionalized with carboxylic acids. Characterization of this polymer's absorption and photoluminescence indicates an intrachain ordering controlled by the nature of the solvent used.

The polymerization employed the dibromide and diboronate ester of two fluorene derivatives that were subsequently polymerized, as shown in Scheme 1. The dibromide monomer was synthesized from 2,7-dibromofluorene with the 9-position functionalized via Michael addition of this bridging carbon with 2 equiv of butyl acrylate.[21] The diboronate ester was synthesized from 2,7-dibromo-9,9-diethylfluorene. The 2- and 7-positions are converted to boronate esters by lithiation at −78 °C followed by the addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to give monomer **3** in 71% yield.

Scheme 1. Synthesis and Polymerization of Fluorene Monomers



The polymerization of these monomers was tested under a variety of conditions with cesium fluoride (CsF) and tetrabutylammonium fluoride (TBAF) used as fluoride sources, as illustrated in Table 1. A comparison of entries 1 and 2 shows that excess fluoride was required to give a polymer with molecular weight $>10^3$ g mol^{-1}. With TBAF as the fluoride source, the polymerization shows no significant influence of the solvent system (entries 2 and 4) on the molecular weight, providing polymers with M_n within a range of 1500 g mol^{-1}. Cesium fluoride showed a more dramatic effect of the solvent system on the molecular weight. Biphasic systems (entries 6 and 7) which are commonly used in Suzuki polymerization[22] gave similar results to those used with TBAF. DMAC and DME (entries 5 and 8) were also used, and though neither solvent fully dissolves cesium fluoride at the applied concentrations, both gave high polymers with the latter giving a notably larger number-average molecular weight.

The diester-functionalized polyfluorene (PF-DE) was converted to its diacid form (PF-DA) by hydrolysis in refluxing dioxane/1.5 M KOH as shown in Scheme 1 and recovered by acidifying the solution and collecting the precipitate. ^{1}H NMR

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Table 1. GPC Results for Conditions Employing Base-free Suzuki Polymerization

entry	fluoride source (equiv[a])	solvent system	M_n[b] (g/mol)	PDI
1	TBAF (2)	DME	4 100	
2	TBAF (4)	DME	12 700	1.76
3	TBAF (4)	DME[c]	13 200	1.89
4	TBAF (4)	toluene	14 000	1.92
5	CsF (4)	DMAC	10 900	2.10
6	CsF (4)	toluene/water[d]	9 900	1.64
7	CsF (4)	DME/water	12 600	2.87
8	CsF (4)	DME	22 000	2.57

[a] Equivalents relative to monomer **3**. [b] Polymers were isolated by precipitation into methanol. [c] Reaction diluted over the course of the reaction, varying the monomer concentration from 0.1 to 0.03 M. [d] Reaction also includes Aliquat 336.

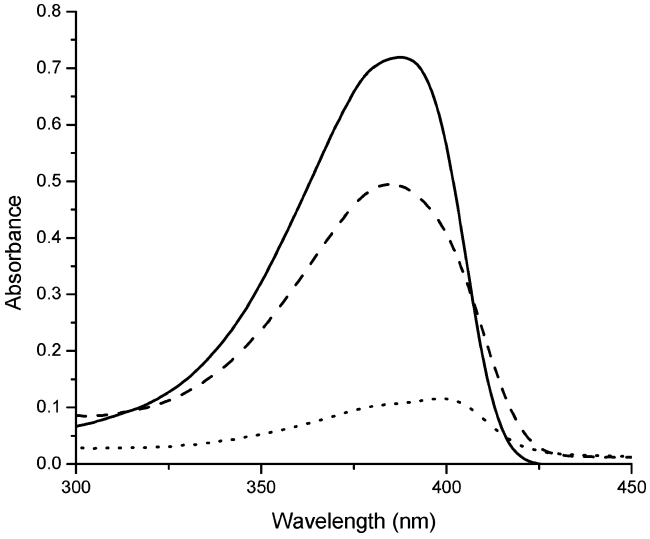

Figure 1. UV−vis absorbance of (—) PF-DE in THF, (- - -) PF-DA in methanol, and (• • •) PF-DA in basic aqueous solution (pH = 9.7). All solutions are 12 μM.

was used to characterize the PF-DA which indicated complete hydrolysis of the esters (see Supporting Information).

The spectral properties of PF-DA and PF-DE were studied as dilute solutions ($c \sim 10^{-5}$ M) to examine the effect of solvent and ionization state on the UV−vis absorbance and photoluminescence of the polyfluorene backbone chromophore(s). Figure 1 compares the absorption spectra of solutions of PF-DE in THF, PF-DA in methanol, and PF-DA in a basic aqueous solution. The spectra are all dominated by a band with λ_{max} in the near-UV region. The band shape and λ_{max} for the PF-DE/THF and PF-DA/methanol systems are very similar to those of poly(9,9-dioctylfluorene) (PFO) in a good solvent such as $CHCl_3$.[23] At room temperature in good solvents, PFO exists predominantly in the "α-phase",[24,25] in which the conformation of individual fluorene repeat units within the backbone is relatively disordered, and the π-conjugation length is low. By inference, we conclude that for the PF-DE/THF and PF-DA/methanol systems the polyfluorene backbone is in a comparatively disordered state and the conjugation length is low. A pronounced effect seen when comparing the spectra shown in Figure 1 is that the apparent oscillator strength of the near-UV absorption band decreases in the order PF-DE/THF > PF-DA/methanol > PF-DA/basic solution. In addition, the absorption band maximum of PF-DA in a basic solution is red-shifted compared to the band maxima for the other two cases. Despite the low polymer concentration, it is probable that PF-DA exists in an aggregated state to some extent in methanol and to an even greater extent in water. This interchain interaction is likely

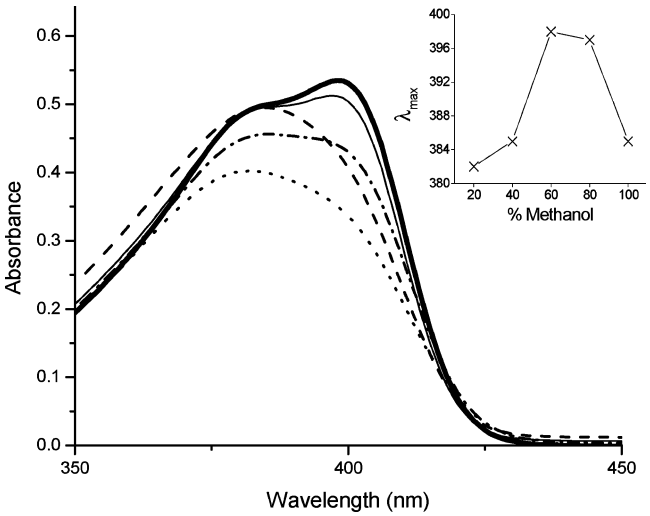

Figure 2. UV−vis absorbance of 12 μM solutions of PF-DA: (- - -) 100% methanol, (—) 80% methanol/20% water, (−) 60% methanol/40% water, (• − •) 40% methanol/60% water, and (• • •) 20% methanol/80% water. Inset: change in λ_{max} as a function of the composition of the methanol/water solution.

the origin of the reduced oscillator strength for the absorption as well as the pronounced red shift of the polymer's absorption in water.

Figure 2 compares the UV−vis absorption spectra of the acidic form of PF-DA in methanol and methanol/water solvent mixtures. This study was carried out to explore the effect of increasing water content in the solvent on the optical properties of the polymer. As noted above, in 100% methanol, PF-DA features a single absorption band with $\lambda_{max} = 385$ nm; however, for 80% methanol and 60% methanol solutions, a low-energy "shoulder" appears on the absorption band with $\lambda_{max} = 400$ nm. Concomitant with the addition of more water to the solvent (e.g., 40% methanol and 20% methanol), the absorbance band decreases in oscillator strength. These solvent-induced changes in spectral band shape and intensity are attributed to several effects that occur simultaneously. First, the red shift that is seen for the 80% and 60% methanol solutions signals that the conformation of the polyfluorene backbone is altered so as to increase the effective conjugation length.[24,25] This effect may arise solely from interaction of the solvent with the side chains which influences the backbone conformation, or it could be due to the effect of interchain aggregation on the conformation of the polymer backbone. Second, the pronounced decrease in absorption band oscillator strength that is seen for the water-rich solutions clearly arises due to interchain interactions (i.e., polymer aggregation).

Finally, in preliminary experiments we have explored the fluorescence of PF-DA in its acidic form in 100% methanol and 60% methanol. In both solvent environments, the fluorescence appears as a broad band with a distinct vibronic progression (see Supporting Information). Interestingly, the vibrational progression is the same in both solvents; however, the entire fluorescence band is red-shifted by ~10 nm in the 60% methanol solution. This red shift is consistent with the suggestion above that the conjugation length of the polymer increases with increasing water content in the solvent.[24,25]

In conclusion, a novel variation of the Suzuki polymerization is presented and optimized which operates under base-free conditions. Number-average molecular weights greater than 10 000 g mol^{-1} were achieved under a variety of conditions, with the highest molecular weight being 22 000 g mol^{-1}. This method allows for the synthesis of ester-functionalized conju-

gated polymers that can be converted to carboxylic acids postpolymerization. Carboxylic acid-functionalized polyfluorenes have been synthesized by this method with these polymers showing a significant influence of these pendant groups on the polyfluorenes' absorptive/emissive properties.

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Supporting Information Available: Experimental procedures for monomer synthesis and polymerization; fluorescence data of PF-DA and ^{1}H NMR of **1**−**3**, PF-DE, and PF-DA. This material is available free of charge on the Internet at http://pubs.acs.org.

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