Varying Anionic Functional Group Density in Sulfonate-Functionalized Polyfluorenes by a One-Phase Suzuki Polycondensation

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ABSTRACT: A series of anionically functionalized polyfluorenebased conjugated polyelectrolytes were synthesized by the Suzuki polycondensation of the boronic ester 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di(1-(2-(2-methoxyethoxy)ethoxy)ethyl)fluorene with the ionic and nonionic dihalides 2,7-dibromo-9,9-di(6-sodium sulfonate-hexyl)fluorene and 2,7-dibromo-9,9-di(1-(2-(2-methoxyethoxy)ethoxy)ethyl)fluorene. The latter monomer served as a diluent to control the ionic functional group density. The use of the triethylene glycol monomethyl ether derivatives made possible a one-phase polycondensation in a THF/methanol/ Na₂CO₃(aq) mixture using Pd(PPh₃)₄. The one-phase nature of



the polymerization was essential to balancing the reactivity of the dihalides so that they were both incorporated into the same polymer and so that the polymer composition became dictated by the monomer feedstock composition. In closely related twophase reactions, a mixture of polymers, one ionic and one nonionic, was isolated with no control over ionic functional group density possible. Using the one-phase approach, polyfluorene-based polyelectrolytes were synthesized with 2–20 aromatic rings per sulfonate group.

INTRODUCTION

Phenylene-based conjugated polymers, such as poly(p-phenylene) and poly(fluorene), are prototype luminescent conjugated polymers that have been widely studied for applications ranging from electroluminescence to biological sensing. In the study and application of these materials, ionic functionality has proven useful because it can strongly alter key physical and chemical properties. Ionic functional groups can impact solubility, impart ionic or mixed ionic/electronic conductivity, influence excitons dynamics, provide a mechanism for strong 1-8intermolecular interactions, and alter doping mechanics.^{1–} One of the central compositional parameters of conjugated polyelectrolytes (CPE), also known as ionomers, is the density of ionic functional groups. In reference to phenylene-based polymers, we define the parameter χ as the molar ratio of ionic functional groups to aromatic rings. Despite its importance, there have been relatively few reports on methods to control χ in phenylene-based conjugated polymers. The goal of the work in this paper is the synthesis of a family of soluble, anionically functionalized poly(fluorene)s with variable ionic density and similar backbone electronic structure. The synthesis developed to achieve this goal utilizes the direct polymerization of ionic monomers, permits for the facile control over the ionic density in the polymers, and through judicious selection of monomer and solvent pairs avoids complications introduced by the twophase nature of typical Suzuki cross-coupling reactions.⁵

Metal-catalyzed cross-coupling reactions are the most commonly employed reactions for synthesizing phenlyene-based conjugated polymers.^{2,9,10} Typically, the Suzuki coupling

of an aryl dihalide with an aryl diboronic acid or acid ester is used in the synthesis of ionically functionalized derivatives.^{2,7} Other approaches include Ni-catalyzed Colon coupling^{2,11} and Pd-catalyzed Sonagashira coupling to form poly(phenylene ethylenes).^{2,12–15} Ionic functionality is introduced either by the direct polymerization of ionic monomers or indirectly through postpolymerization conversion.

In the direct route, an ionic monomer A containing one or more ionic functional groups is coupled with a nonionic monomer B resulting in an alternating copolymer poly(AB). In the indirect route, a monomer A' containing precursors to ionic functional groups (e.g., esters or amines) is coupled to a nonionic monomer B resulting in an alternating nonionic copolymer poly(A'B) that can be converted into an ionically functionalized polymer. Within either the direct or the indirect route, χ can in principle be controlled by synthesizing analogous monomers with varying ionic functional group density or by the introduction of a third diluent monomer C to yield poly(AB-CB) or poly(A'B-CB). With the indirect route, it is also possible to control ionic functional group density by only converting a fraction of the A' moieties to ionic groups.

The most widely explored method for controlling χ has been the indirect postpolymerization route. Using this route, χ has been controlled in a single poly(A'B) polymer by the extent of conversion postpolymerization¹⁶ or through the addition of a

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diluent monomer C with the same functionality (boronic ester or arylhalide) as the monomer to be later converted to an ionic group.^{11,17,18} If complete conversion of the precursor monomer can be achieved, the ionic functional group density is controlled by the polymerization step rather than the conversion step. Complete conversion is rare postpolymerization, as conversions of 80-90% are commonly cited, and it has been reported that this approach is not necessarily reproducible.^{19*} To date, postpolymerization conversion routes to controlling ionic density have nearly all involved the quaternization of an amine to form a cationic polymer. There are far fewer examples of anionic polymer formation, with these involving the hydrolysis of an ester to form a carboxylate, phosphate, or sulfate.²⁰⁻²² It is noted that in studies reporting phenlyenebased CPEs with varying ionic functional group density such variation was not typically the primary focus. As a result, some report only two different ionic functional group densities (including the parent AB polymer) or use a third monomer not really intended to dilute ionic functionality, but to serve a different purpose such as being an electron acceptor.

Although less explored, the direct polymerization of ionic monomers is of interest because the polymer is synthesized in a single step, it eliminates possible issues with the intentional or unintentional incorporation of unconverted precursor groups, and it is potentially applicable to a wider range of ionic functional groups. While in theory both changing monomer structure and dilution using a three-monomer system can be applied in the direct route, only the former has been reported.² For instance, Kim et al. demonstrate the direct polymerization of an anionic monomer with a phenyl diboronic ester and a different reaction with biphenyl diboronic ester to give two densities of anionic monomer along the backbone of the polymer.²³ Regardless, this approach requires the synthesis of a new monomer for each desired ionic functional group density.

One possible reason that control of ionic functional group density of phenylene-based polyelectrolytes has not been reported using the direct polymerization of ionic monomers in the presence of a diluent monomer is the two-phase nature of many Suzuki cross-couplings.⁹ In the synthesis of nonionic polymers, the two monomers A and B are typically dissolved in an organic phase with the base catalyst in an aqueous layer. With ionic monomers, the situation is somewhat different because the ionic monomer, say A', will partition into the aqueous layer while the nonionic monomer B stays in the organic layer. The addition of a nonionic monomer C to compete with A' in the coupling reaction will, in many cases, partition into the nonaqueous layer. As demonstrated more fully herein, this will favor the formation of a poly(BC) because both of these monomers are in the same phase rather than the desired poly[(A'B)(CB)]. The preferential coupling of the monomers in the same phase over those in different phases is referred to as the "two-phase problem" herein.

By choosing amphiphilic monomers and carefully selecting solvent systems, we were able to overcome the two-phase problem and take advantage of the control afforded by direct polymerization in the synthesis of a family of soluble, phenylene-based, anionically functionalized, conjugated polymers with variable ionic density. Specifically, we report a series of sulfonate functionalized poly(fluorene-*co*-alt-fluorene)s (SPFs) polymers with varying χ incorporating either hexyl (to illustrate the two-phase problem) or triethylene glycol monomethyl ether (TEG) functionality. The polymers in this series are referred to as SPF_{χ}^{Hex} and SPF_{χ}^{TEG} , respectively, where the χ indicates the molar ratio of sulfonate functional groups to aromatic rings in the monomer feedstock and hence represents an idealized polymer composition. As will be shown later, the initial feedstock corresponds well to the final composition.

RESULTS AND DISCUSSION

The Suzuki polycondensation of 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (1) and sulfonated fluorene derivative, 2,7-dibromo-9,9-di(6-sodium sulfonatehexyl)fluorene (2), was initially explored in the synthesis of SPFs. The initial choice of the hexyl-substituted boronic ester monomer was motivated by previous reports on the successful polymerization of closely related monomers.² The dihexyl-fluorene monomer is commercially available and has been widely used in the synthesis of nonionic polymers because the flexible alkyl side chains promote solubility. The monomer 2 was synthesized by the sulfonation of 2,7-dibromo-9,9-di(6-bromohexyl)fluorene (3) in water using sodium sulfite with cetyltrimethylammonium bromide (CTAB) and 2 as phase transfer agents (Scheme 1). The 3 was synthesized according to a previously published procedure.¹⁸

Scheme 1. Synthesis of the Sulfonated Fluorene Monomer 2



The use of 2 as a phase transfer agent in its own synthesis of course required its initial synthesis by another means. This alternate means and the motivation for using 2 in its own synthesis developed out of a number of attempted approaches to 2 as summarized in Scheme 2. Sulfonation of the 3 alkyl halide chains using sodium sulfite and CTAB alone as a phase transfer agent was unsuccessful in water, water/methanol mixtures, and dimethyl sulfoxide/water mixtures. Sulfonation of the iodo-functionalized analogue 4 (2,7-dibromo-9,9-di(6-

Scheme 2. Reactions Explored during the Original Synthesis of the Sulfonated Fluorene Monomer 2^a



^{*a*}Key (i) Na₂SO₃, CTAB; (ii) NaI in acetone; (iii) thiourea in EtOH, reflux, 16 h; (iv) NaOH in H₂O, reflux, 3 h; (v) H₂SO₄; (vi) boiling HNO₃, (vii) 5% 6, Na₂SO₃, CTAB in water.

Scheme 3. Synthesis of SPF^{Hex}_{0.5}



iodohexyl)fluorene) synthesized by halide exchange was also not successful under similar conditions. An alternative approach to introducing the sulfonate group functionality is through the oxidation of a precursor such as thiol or dithiol. Toward this end, the thiol-functionalized 2,7-dibromo-9,9-di(6-thiolhexyl)fluorene (5) was synthesized via the diisothiuronium salt. The sulfur was introduced through nucleophilic attack by thiourea in refluxing ethanol, which was then hydrolyzed with sodium hydroxide and neutralized with sulfuric acid. The resulting thiol 5 was then oxidized using refluxing nitric acid to give the desired sulfonate functional group, but unfortunately, the fluorene monomer was also nitrated yielding monomer 6. More gentle oxidation conditions (30% hydrogen peroxide in acetic acid) only oxidized to the dithiol. Regardless, we suspected that the monomer 6 would be a good phase transfer agent, and so it was tried as such in the direct substitution of 3 with sodium sulfite. When used together with CTAB, near complete conversion was observed. Some of the newly synthesized 2 along with CTAB was then used successfully as a phase transfer reagent resulting in 2 in >80% yield. The inclusion of \sim 5% of 2 was needed, and without it, the reaction did not proceed even when refluxed for several days. All 2 used in the synthesis of SPFs was synthesized with 2 as a catalyst, not 6.

The sulfonated fluorene monomer 2 was reacted with 1 to yield $SPF_{0.5}^{Hex}$ as shown in Scheme 3. The sulfonated monomer 2 and 1 were coupled using $Pd(PPh_3)_4$ in a mixture of THF, methanol, and 2 M K₂CO₃(aq). Precipitation of a polymer from the two-phase mixture was observed after 48 h and continued over the full course of the reaction (5 days). The needed reaction times were longer than typically required for the Suzuki polycondensation of nonionic monomers, but they were consistent with other polymerizations involving ionic monomers.^{2,9} The structure of the isolated polymer SPF_{0.5}^{Hex} was confirmed by ¹H NMR, and the polymer was found to be soluble in DMSO to a level of >5 mg/mL. The apparent molecular weight of the polymer was determined to be 17 kDa by gel permeation chromatography (GPC). The GPC was carried out using a Waters Styragel HR4 column with a nominal molecular weight range of $5 \times 10^3 - 6 \times 10^5$ Da with 0.1 M LiNO₃ in H₂O/DMSO 25/75 (v/v) as an eluent. The sodium salts of polystyrenesulfonate standards were used to calibrate the column and solvent system. The 0.1 M LiNO₃ was used to screen the charge of the polymers from the charge on the column. Because of the differences in the structure of the standards and polymers, the reported molecular weights should be considered apparent (see Table 1).

In an effort to control the functional group density, the commercially available dihalide analogue of 1, 2,7-dibromo-9,9dihexylfluorene (7), was incorporated as a diluent monomer. As with $SPF_{0.5}^{Hex}$, the polymerization of 1 with 2 and 7 resulted in the precipitation of a yellow solid from the reaction mixture. This solid, however, could be separated into two polymers with differing solubilities. Analysis of the separate polymers revealed

Table 1. Molecular Weight and Photophysical Properties of Sulfonate-Functionalized Poly(fluorene-*co-alt*-fluorene)s

CPE	$\overset{a}{\chi_{ ext{monomer}}}$	$\mathcal{X}_{ ext{polymer}}$	MW ^c (kDa)	$\frac{\mathrm{ex}{\lambda_{\max}}^d}{\mathrm{(nm)}}$	$\operatorname{em}_{\operatorname{max}}^{e}$ $\binom{e}{\operatorname{nm}}^{e}$
SPF ^{Hex} _{0.50}	0.5	0.55	17	380	425
$SPF_{0.50}^{TEG}$	0.50	0.51	14	380	425
$SPF_{0.25}^{TEG}$	0.25	0.21	19	380	425
$SPF_{0.20}^{TEG}$	0.20	0.18	15	380	425
$SPF_{0.16}^{TEG}$	0.17	0.17	23	380	425
$SPF_{0.05}^{TEG}$	0.050	0.048	12	380	425

^{*a*}From initial monomer concentration. ^{*b*}From ¹H NMR of the purified polymer. ^{*c*}Apparent molecular weights as determined by GPC vs polystyrenesulfonate standards in 0.1 M LiNO₃/25% water-75% DMSO. ^{*d*} $\lambda_{\rm max}$ of the excitation spectrum. ^{*e*} $\lambda_{\rm max}$ of the emission spectrum.

them to be $SPF_{0.5}^{Hex}$ and $SPF_{0.0}^{Hex}$, which are the polymers formed by reaction of monomer 1 with 2 and 7, respectively.

It is believed that a mixture of polymers was obtained in the attempt to dilute ionic functionality because of the two-phase nature of the polymerization. Nearly all Suzuki polycondensations are two-phase systems. In the synthesis of nonionic polymers, both the aryl halide and boronic ester partition into the organic layer, thereby providing optimal contact between monomers. In the synthesis of ionic polymers, as with $SPF_{0.5}^{Hex}$, the aryl halide and boronic ester are in separate phases leading to poorer contact, which requires longer polymerization times. In the copolymerization of boronic ester 1 with ionically functionalized dibromide 2 and the nonionically functionalized dibromide 7, it is possible for polymerization to occur both within the organic layer and across the organic/aqueous interface. It is hypothesized that the 1 preferentially reacts with the 7 over the 2, which is within a separate phase, leading to the rapid formation of $SPF_{0.0}^{Hex}$, with the slower formation of $SPF_{0.5}^{Hex}$ at the organic/aqueous interface.

The two-phase problem was not unique to the copolymerization of solely fluorene-based monomers. During the course of this study, we also explored an analogous sulfonatefunctionalized poly(fluorene-co-alt-phenylene) (SPFP) system. The polymerization of 1 with 2,5-dibromobenzylsulfonate (8)to yield a SPFP was successful, but as in the SPF system, polymerization of 1 with both 8 and dibromo-p-xylene as a diluent monomer resulted in a mixture of polymers. This was particular evident when the polymerization was carried out in acetonitrile. In this solvent, the 1/dibromo-p-xylene polymer is observed to precipitate immediately upon addition of catalyst. No 1/8 polymer SPFP_{0.33}^{Hex} is observed at these early stages of the reaction, and the 8 can be nearly quantitatively recovered by simple separation of the aqueous layer. At later stages, whether or not the 1/dibromo-p-xylene was separated out, the polymer of 1 and 8 (SPFP^{Hex}_{0.33}) was observed.

Returning to the SPF system, a variety of approaches were pursued in an effort to better balance the activity of 2 and 7 in the attempted synthesis of SPF^{Hex}. Mixtures of polymers, rather



than the desired three component polymers, were obtained for polymerizations under a range of conditions: solvents were varied (CH₃CN/H₂O, MeOH/THF/H₂O); phase transfer agents, such as CTAB and tetrabutylammonium bromide, were added in an attempt to emulsify the reaction; and Pd(OAc)₂ was used as an alternate catalyst because of its greater solubility in polar solvents relative to Pd(PPh₃)₄. Ultimately, the very different solubilities of the nonionic monomers (1 and 7) and the ionic monomer (2) could not be overcome through modification of reaction conditions.

As an alternate strategy, the nonionic monomers were redesigned to include triethylene glycol monomethyl ether (TEG) functionality promoting better solubility in polar solvents. In particular, the TEG-functionalized dibromofluorene 2,7-dibromo-9,9-di(1-(2-(2-methoxyethoxy)ethoxy)ethyl)fluorene (9) and its boronic ester derivative 2,7-bis(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di(1-(2-(2methoxyethoxy)ethoxy)ethyl)fluorene (10) were synthesized (see Scheme 4). The target polymer in this case for $\chi = 0.5$ is similar to that reported by Zhu et al., but control over ionic functional group density was not reported.²⁴ The monomer 9 is an oligoether derivative of commercially available 2,7dibromofluorene. Functionalization was accomplished using LDA to deprotonate the 9-position of fluorene followed by the addition of excess Br(CH₂CH₂O)₃CH₃. The monomer 10 is the boronic acid ester of 9, functionalized by lithium halide exchange of 9 using *n*-butyllithium at -78 °C followed by quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

The polymerization of **2**, **9**, and **10** using the Suzuki polycondensation reaction was carried out with monomer compositions targeting the following polymers $SPF_{0.2}^{TEG}$, $SPF_{0.25}^{TEG}$, $SPF_{0.26}^{TEG}$, $SPF_{0.16}^{TEG}$, and $SPF_{0.05}^{TEG}$ (see Scheme 5). With the TEG-functionalized monomers, it was possible to identify conditions where the reaction did not break into two phases, which ultimately led to the successful synthesis of copolymers with varying χ . All of these polymerizations used an 8:1 organic solvent to aqueous base ratio, instead of the more common 3:2,

Scheme 5. Synthesis of Sulfonate-Functionalized Polyfluorenes (SPF $_{\chi}^{\text{TEG}}$) with Varying Ionic Density



using $Pd(PPh_3)_4$ as a catalyst. With the organic solvent being a mixture of equal volumes of THF and methanol, the reaction was single phase over the full range of monomer compositions. The reactions all proceeded with the formation of a yelloworange precipitate that began forming around 18 h. The resulting polymer was washed with CHCl₃, THF, and water. The organic washes were found to contain unreacted monomer and reaction byproducts but no polymer. It is noted that the polymer of 9 and 10 is known to be soluble in both CHCl₃ and THF.²⁵ The water wash was found to contain a small amount of unreacted ionic monomer but again no polymer. The isolated polymers were all found to be soluble in DMSO to a level of at least 5 mg/mL, and $SPF_{0.5}^{TEG}$ and $SPF_{0.25}^{TEG}$ were soluble in methanol. These solubility characteristics strongly argue against the formation of a mixture of polymers. In particular, no component of the polymers with lower ionic concentration was soluble in either methanol or THF, whereas the end point polymers from the reaction of 10 with either 2 or 9 are soluble in methanol or THF, respectively.

The ionic density in the SPF $_{\chi}^{\text{TEG}}$ series was determined by ¹H NMR of the purified polymers in DMSO- d_6 using the integral of two sets of resonances. The first set is from four equivalent methylene protons on the sulfonate side chains (the fifth carbon from the sulfonate). The second integral is the total number of aromatic protons. Table 1 and Figure 1 compare the polymer compositions from ¹H NMR to the idealized compositions based on the monomer feedstock. The polymer composition was successfully varied between $\chi = 0.05$ and $\chi = 0.5$. As can be seen, there is a good correlation between input monomer ratio and the ratio of monomers incorporated into



Figure 1. Correlation between χ_{monomer} and χ_{polymer} for SPF $_{\chi}^{\text{TEG}}$ (red squares), SPFP $_{0.33}^{\text{Hex}}$ (black circle), and SPF $_{0.50}^{\text{Hex}}$ (green triangle).

the CPEs. The percent yields for the polymerizations were between 50 and 75%. The agreement between monomer feedstock and polymer composition at less than 100% conversion is consistent with random incorporation of the monomers into the polymer.

Gel permeation chromotography on all of the polymers in a 0.1 M LiNO₃ DMSO/H₂O 75/25 (v/v) eluent revealed a single broad peak. The apparent molecular weights are reported in Table 1. There comes a point where the ionic density is so low that it is statistically improbable, or impossible, for each polymer chain to contain an ionic monomer. The solubility characteristics of the isolated polymers and the absence of any substantial quantity of the nonionically functionalized polymer 9/10 in the CHCl₃ and THF washes used during purification argue that this point was not reached in any of the polymers. A molecular weight of 9.2 kDa is needed for the lowest concentration of $SPF_{0.05}^{TEG}$ to have on average one ionic functional group. This argues that the polymer molecular weight is greater than 10 kDa, which is consistent with the apparent molecular weight of 12 kDa determined in relation to polystyrenesulfonate standards.

Excitation, emission, and/or absorption spectra were collected for the synthesized SPF_{χ}^{TEG} polymers to understand how ionic functional groups affect the optical properties and solution aggregation of these materials. Figure 2 shows a



Figure 2. Three-dimensional total luminescence plot for $SPF_{0.5}^{TEG}$.

representative total luminescence spectrum for SPF_{0.5}^{TEG}. As can be seen, the intensity of the emission changes with excitation wavelength, but the shape of the emission spectrum does not. This was also the case for the other polymers studied. More conventional excitation and emission spectra correspond to slices through the total luminescence spectrum at both a particular emission and excitation wavelength, respectively. Figure 3 show these spectra for the family of SPF^{TEG}_{χ} polymers in DMSO. Also shown are the absorption spectra of the polymers. The shapes of the absorption, excitation, and emission spectra were observed to be similar to that observed for the analogous nonionic polymers that have been reported in the literature.²⁶ Both the absorption and excitation spectra are characterized by a single broad peak with λ_{max} in the UV (350–



Figure 3. Normalized excitation (filled), emission (open), and absorbance (lines) spectra for the SPF_{0.5}^{TEG} (black squares), SPF_{0.25}^{TEG} (red circles), SPF_{0.16}^{TEG} (green triangles), SPF_{0.05}^{TEG} (blue down triangles), and SPF_{0.5}^{Hex} (orange lozenges) polymers. The SPF_ χ^{TEG} excitation spectra were collected while observing at 425 nm, and emission spectra were recorded while the polymer was excited at 380 nm.

380 nm range). The overlap of the emission and absorption spectra indicates that the species in solution doing the majority of the absorption is also doing the majority of emission. The emission spectra exhibit the vibronic structure typical of fluorene-based polymers, but there is some difference in the relative strengths of the emission peaks for the various polymers. The two polymers where the lowest energy peak of the vibronic progression is the most intense are also the two polymers with the lowest molecular weights. A similar dependence on molecular weight has been previously observed by Gao et al.²⁶

One of the goals in the work herein was to make a family of soluble luminescent CPEs with similar backbone electronic structures. This was indeed achieved with the SPF^{TEG}_{χ} series as evidenced by the very similar excitation and emission spectra across the family (see Figure 3). This is perhaps not surprising because the bridging carbon on fluorene-based polymers tends to help lock in planarity. Further, the straight-chain oligoethers used in this family of polymers also minimize steric bulk close to the backbone, relative to often used branched side chains.

The SPF^{TEG'} CPEs exhibit solvatofluorochromism as illustrated by comparing the polymers' emission in pure methanol to its binary mixtures with dichloromethane and water. A 12 nm bathochromic shift is observed for all of the polymers in going from methanol to a more polar methanol/ water mixture, so-called positive solvatofluorochromism. This bathochromic shift suggests increasing polymer aggregation as the nonsolvent water is added. Interestingly, all but $SPF_{0.5}^{TEG}$ show a bathochromic shift upon going from methanol to a less polar methanol/dichloromethane mixture, so-called negative solvatofluorochromism. This shift is smaller (~4 nm), but it is again consistent with an increase in aggregation due to the addition of a nonsolvent, in this case dichloromethane. It is somewhat puzzling that the polymer with the greatest ion content $SPF_{0.5}^{TEG}$ does not show any shift as the solvent polarity is decreased. Other than this observation, these data seem to suggest little dependence of the fluorescence and aggregation on ion density. These data, however, only reflect end points of solvent polarity.

A more comprehensive study of solvatofluorchromism was conducted for three compositions of the SPF^{TEG}_{χ} family by dissolving the polymers in methanol and then adding either water or dichloromethane in small increments. Controls were run to ensure that any change in wavelength was not due to dilution, and the spectra did not change upon filtering the solution through a 0.2 μ m filter, as evidence that gross precipitation had not occurred. The polarity of the solvent mixture was calculated using the $E_{\rm T}(30)$ scale. The $E_{\rm T}(30)$ is an an empirical polarity scale for quantifying the polarity of a binary mixture, and it is defined by the equation

$$E_{\rm T}(30) = E_D \ln \left(\frac{c_p}{c^*} + 1\right) + E_T^0(30) \tag{1}$$

where $E_{\rm T}^0(30)$ is the $E_{\rm T}(30)$ value of the pure, less polar component, c_p is the molar concentration of the more polar component, and E_D and c^* are parameters determined experimentally when the equation was developed.²⁷ E_D is a measure of the sensitivity of the $E_{\rm T}(30)$ scale to changes in c_p while c^* is used to divide the equation into a linear and logarithmic portion. The c^* term is the threshold value of c_p , at which the transition from a linear to a logarithmic relationship between the two solvents occurs.²⁷

Figure 4 shows the change in λ_{max} of emission as a function of $E_{\rm T}(30)$. The end points of each curve in Figure 4 illustrate



Figure 4. λ_{max} of the fluorescence emission spectra of SPF polymer solutions as a function of the polarity of the solvent. The value in pure methanol is indicated by the vertical red dashed line and has an $E_{\text{T}}(30)$ value of 55.4 kcal nm mol⁻¹.

the same trends in solvatofluorochromism as discussed earlier. With the exception of SPF_{0.5}^{TEG} where there is little to no shift, the λ_{max} for the remaining polymers shift similarly and continuously upon lowering $E_T(30)$ from pure methanol (left side). However, the shift in λ_{max} upon increasing $E_T(30)$ from pure methanol (right side) occurs over a somewhat more narrow region of solvent polarity. Further, the region of this transition depends on the nature of the functionality and ion concentration. As the ion content increases, so does the $E_T(30)$ at which the shift happens. SPF_{0.5}^{TEG} has its shift centering at 58.3 kcal nm mol⁻¹, SPF_{0.25}^{TEG} centers at 58.8 kcal nm mol⁻¹, while SPF_{0.5}^{TEG} does not shift until 59.1 kcal nm mol⁻¹. Given the possibility for strong interactions between water and ions, it is perhaps not surprising that increasing the ionic functional group density causes the polymer to stay unaggregated up to a

higher solvent polarity. Also significant is the nature of the nonionic functionality on the polymer. When comparing $SPF_{0.5}^{TEG}$ with $SPF_{0.5}^{Hex}$, the solvent polarity at which aggregation occurs for $SPF_{0.5}^{Hex}$ is much lower than solvent polarity at which $SPF_{0.5}^{TEG}$ aggregation occurs even though they have the same value of χ . This is consistent with the greater polarity of the TEG side chains, which help promote solubility in more polar solvents.

The solvatofluorochromism of fluorene-based polymers somewhat complicates direct comparison of the CPEs synthesized in this work with their nonionic counterparts. Nevertheless, the excitation and emission of all of the CPEs studied herein are comparable to other fluorene-based polymers. The family of SPF^{TEG}_{χ} CPEs and SPF^{Hex}_{0.5} all have very similar excitation and emission spectra, which correspond very well to the literature values for other ionically functionalized PFs.²⁸ Note that in these comparisons the data in methanol were used because of the most limited aggregation in this solvent.

The tuning of ionic functional group density over the range achieved in the SPF $_{\chi}^{\text{TEG}}$ system has not been demonstrated in other luminescent ionically functionalized conjugated polymers. Most typically, an ionic monomer (or its precursor) is coupled with either another ionic monomer or a nonionic monomer in a one-to-one ratio leading to relatively high ionic functional group densities. This is the case with anionic poly(fluorene) CPEs where carboxylate,²⁰ sulfonate,²¹ and phosphonate²² examples are known, with $\chi = 0.5$, 0.5, or 1, respectively. More broadly speaking, there are very few examples of CPEs with ionic functional group densities much lower than this or where deliberate variation has been demonstrated. The most notable examples come from the nonexhaustive quaternization of amine-derivatized conjugated polymers to yield cationic CPEs. For instance, Liu et al. have demonstrated using this approach the synthesis of polyfluorene-phenylenes with $\chi = 0.2, 0.4,$ and 0.53. In their work, the varying level of quaternization was achieved by control over reaction conditions, including solvent, temperature, and time.¹⁶ Quaternization yields in similar reactions have also been reported by Mikroyannidis et al. to be very sensitive to such conditions.

SUMMARY

The synthesis and characterization of soluble, sulfonatefunctionalized poly(fluorene)s with varying ionic density were reported. The study reveals the challenges of using traditional two-phase Suzuki polycondensations in the competitive polymerization of a nonionic boronic ester with ionic and nonionic dihalides. The partitioning of the dihalides into separate phases leads to vastly different reactivities, thereby preventing their incorporation into a single polymer. A singlephase synthesis was developed through the use of amphiphilic, oligoether-functionalized monomers and a carefully selected solvent system. The synthesis utilizes direct polymerization of ionic with nonionic monomers, allows for easy control over ionic density through monomer feedstock composition, and avoids the vastly different reactivities encountered in two-phase Suzuki polycondensations involving ionic and nonionic monomers. The synthesized SPF_{χ}^{TEG} family included CPEs with χ values varying between 0.5 and 0.05, a range not seen in other luminescent anionic CPEs. This illustrates the possibility of using direct polymerization in the presence of a diluent monomer to control ionic functional group density in phenylene-based polymers, an approach which in principle is

amenable to a wide variety of ionic functionality. This development advances the study of CPEs because χ is a central parameter in determining and understanding their properties. For instance, the aggregation state of the polymers in solution was observed to depend on the ionic functional group density and hence could be controlled through both this quantity and solvent polarity.

EXPERIMENTAL SECTION

Monomer Synthesis. Sodium 2,5-Dibromobenzylsulfonate (8). α ,2,5-Tribromotoluene (3.29 g, 10 mmol) was added to a solution of of Na₂SO₃ (1.26 g, 10 mmol) in 40 mL of H₂O. The tribromotoluene did not dissolve in the water, but as the water heated, the tribromotoluene melted and formed a puddle on the bottom of the flask. This biphasic mixture was brought to reflux and refluxed for 60 h. The starting material was not all reacted as evidenced by a small puddle of molten α ,2,5-tribromotoluene, but the reaction was removed from heat and from stirring and allowed to cool to room temperature because it did not seem to be progressing anymore. Product crystallized from the water upon cooling and was separated by filtration while washing with ice cold water and ether. The recovered crystals were the monohydrate of the desired product and dehydrated by placing them under vacuum and heating to 100 °C for 48 h. Yield = 2.376 g (67.5%). ¹H NMR (d_2 -H₂O, 300 MHz): δ (ppm) 4.24 (2H, s), 7.30 (1H, dd, ${}^{4}J_{\text{HH}} = 2.8 \text{ Hz}$, ${}^{3}J_{\text{HH}} = 9.0 \text{ Hz}$), 7.44 (1H, d, ${}^{3}J_{\text{HH}} = 9.0 \text{ Hz}$), 7.56 (1H, d, ${}^{4}J_{\text{HH}} = 2.8 \text{ Hz}$). ${}^{13}\text{C}$ NMR (d_2 -H₂O, 70 MHz): δ (ppm) 55.6, 120.6, 124.4, 131.6, 134.6, 135.1, 138.2. TOF-MS ES negative mode $C_7H_5Br_2SO_3^- = 328.82$.

α,2,5-Tribromotoluene (4). 3 (500 mg, 2.0 mmol), N-bromosuccinamide (534 mg, 3.0 mmol), benzoyl peroxide (5 mg, 0.02 mmol), and CCl₄ (10 mL) were added to a round-bottom flask and refluxed overnight. The reaction mixture was then washed with copious amounts of of H₂O, and the organic layer was removed, dried over MgSO₄, and filtered. Silica gel (30 g) was added to the organic layer, and the solvent was removed *in vacuo*. The loaded silica was placed in filter and washed with hexanes until no more material came through. Solvent was removed leaving an off-white solid. Yield = 644 mg (98%). ¹H NMR (d_1 -CHCl₃, 300 MHz): δ (ppm) 4.52 (2H, s), 7.29 (1H, dd, ⁴J_{HH} = 2.6 Hz, ³J_{HH} = 8.5 Hz), 7.43 (1H, d, ³J_{HH} = 8.5 Hz), 7.80 (1H, d, ⁴J_{HH} = 2.6 Hz).

2,7-Dibromo-9,9-di(6-sodium sulfonate-hexyl)fluorene (2). The initial synthesis of 2 was conducted using 6 as a phase-transfer agent, but subsequent syntheses used 2 as a phase transfer-agent in its own synthesis. The method in either case was the same, with the specific procedure for the latter given below. It is noted that 6 was not detected in the initially isolated 2 and that any remaining trace of this compound was further diluted with each round of synthesis. 3 (5.5 g, 8.46 mmol), Na₂SO₃ (10.6 g, 84 mmol), 2 (0.150 g, mmol), and cetyltrimethylammonium bromide (CTAB) (0.308 g, 0.84 mmol) were added to 100 mL of H₂O and refluxed for 48 h. The solvent was removed, and the solids were washed with CHCl₂ to remove leftover starting material and CTAB. The white solids were sonicated with 200 mL of methanol. The undissolved solids were filtered off and again sonicated with 200 mL of methanol, and the solids were again filtered. Methanol was removed to give a white solid. Yield: 4.97 g (84%) (d_4 -CH₂OH, 300 MHz): δ (ppm) 0.544 (4H, quint), 1.13 (8H, m), 1.59 (4H, quint), 2.03 (4H, m), 2.67 (4H, m), 7.48 (2H, dd, ${}^{3}J_{HH} = 8.0$ Hz, ${}^{4}J_{\rm HH}$ = 1.6 Hz), 7.56 (2H, d, ${}^{4}J_{\rm HH}$ = 1.6 Hz), 7.66 (2H, d, ${}^{3}J_{\rm HH}$ = 8.0 Hz). ¹³C NMR (d_2 -H₂O, 125 MHz): δ (ppm) 22.72, 24.44, 28.03, 29.15, 39.01, 51.24, 55.34, 121.12, 121.45, 126.52, 130.12, 138.67, 152.85.

2,7-Dibromo-9,9-di(6-bromohexyl)fluorene (3). 50 g of KOH in 100 mL of H_2O was heated to 75–80 °C at which point 2,7dibromofluorene (1.620 g, 5.0 mmol), dibromohexane (12.20 g, 50 mmol), and tetrabutylammonium bromide (0.161 g 0.5 mmol) were added and stirred vigorously for 45 min. The reaction was then extracted with CH₂Cl₂. The organic layer was washed with dilute HCl (100 mL), brine (100 mL), and H₂O (100 mL). The organic layer was dried over MgSO₄, and the solvent removed under vacuum, resulting in a yellow oil. Oil was distilled under vacuum to remove excess dibromohexane (about 100 °C). The remaining yellow oil was run through a column of silica using chloroform/hexane (1/9), giving a white crystalline solid. Yield: 2.93 g (90%). ¹H NMR (d_1 -CHCl₃, 300 MHz): δ (ppm) 0.578 (4H, m), 1.08 (4H, m), 1.20 (4H, m), 1.64 (4H, quin), 1.92 (4H, m), 3.29 (4H, t), 7.43 (2H, d, ⁴J_{HH} = 1.8 Hz), 7.46 (2H, dd, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 1.8 Hz), 7.53 (2H, d, ³J_{HH} = 8 Hz). ¹³C NMR (d_1 -CHCl₃, 70 MHz): δ (ppm) 23.67, 27.52, 27.99, 29.18, 32.72, 32.82, 33.92, 40.27, 55.75, 121.47, 121.80, 126.31, 130.56, 139.27, 152.39.

2,7-Dibromo-9,9-di(6-iodohexyl)fluorene (4). 3 was dissolved in acetone, and NaI (10 equiv) was added to the reaction flask. The reaction was brought to reflux and stirred for 12 h. The acetone was removed under vacuum, leaving a white solid. The solids were extracted with chloroform. The organic layer was dried with MgSO₄. The organic layer was removed, leaving an off-white solid. Yield: 1.89 g (98%). ¹H NMR (d_1 -CHCl₃, 300 MHz): δ (ppm) 0.575 (4H, quint), 1.11 (8H, m), 1.62 (4H, quint), 1.92 (4H, m), 3.06 (4H, t), 7.43 (2H, d, ⁴J_{HH} = 1.8 Hz), 7.47 (2H, dd, ³J_{HH} = 8.0 Hz, ⁴J_{HH} = 1.8 Hz), 7.52 (2H, d, ³J_{HH} = 8 Hz). ¹³C NMR (d_1 -CHCl₃, 70 MHz): δ (ppm) 7.46, 28.94, 30.20, 33.53, 40.21, 55.75, 121.51, 121.47, 121.85, 126.32, 130.54, 139.36, 152.46.

2,7-Dibromo-9,9-di(6-thiolhexyl)fluorene (5). 3 (0.650 g, 1.0 mmol) and thiourea (0.166 g, 2.2 mmol) were dissolved in 50 mL of refluxing ethanol and stirred for 16 h. NaOH (6 mL of 1.0 mL) was added to the reaction, causing it to become cloudy. The reaction mixture was refluxed for 3 h during which time the solution cleared. The total reaction volume was reduced by half, and 6 M H_2SO_4 was added dropwise until precipitation of white solid stopped. The reaction volume was reduced to 20 mL and extracted with ether (3 × 100 mL). The organic extractions were combined and dried with MgSO₄. Solvent was removed to give a sticky thick colorless oil. Yield: 0.550 g (98%).

2,7-Dibromo-9,9-di(6-sulfonic acid-hexyl)fluorene (6). Concentrated nitric acid (15 mL) was added to 5 (0.55 g, 1.0 mmol) and refluxed during which time the 5 dissolved in the nitric acid. After 12 h, water (50 mL) was added to the reaction mixture. Solvent was removed under vacuum to give a red oil, which was used without further purification.

2,7-Dibromo-9,9-di(1-(2-(2-methoxyethoxy)ethoxy)ethyl)fluorene (9). A dry three-neck round-bottom flask was charged with diisopropylamine (1.856 g, 18.35 mmol) and 15 mL of freshly distilled THF. A magnetic stir bar was added, and the solution was cooled to -78 °C. After 10 min n-butyllithium (8.08 mL, 20.19 mmol) was added and stirred for 10 min. While LDA was stirring, 2,7dibromofluorene was dissolved in 25 mL of freshly distilled THF and added dropwise to the now formed LDA solution and stirred at -78 °C for 30 min. Upon addition, a dark orange solution formed. 1-(2-(2-Methoxyethoxy)ethoxy)ethyl bromide (5.0 g, 22 mmol) was added to the orange solution. The orange color lightened, and the reaction was stirred at -78 °C for $1^{1}/_{2}$ h and allowed to come to room temperature overnight, during which time the solution turned green. Water was added to the solution and stirred for an hour. The organic layer was removed and washed with water $(3 \times 100 \text{ mL})$, and then the aqueous layer was extracted with $CHCl_3$ (2 × 50 mL). The organic layers were combined and dried over MgSO₄ and concentrated to give an orange yellow oil. The oil was purified by column chromatography on silica with hexanes until all colored bands (3) moved off the column. After hexanes, 2:5 ethyl acetate:hexanes was used to give two bands. The second band is the product. ¹H NMR (d₁-CHCl₃, 300 MHz): δ (ppm) 2.33 (4H, t), 2.76 (4H, t), 3.20 (4H, m), 3.34 (6H, s), 3.39 (4H, m), 3.29 (4H, t), 3.45–3.55 (8H, m), 7.46 (2H, dd, ${}^{3}J_{HH} =$ 8.0 Hz, ${}^{4}J_{HH}$ = 1.8 Hz), 7.50 (2H, d, ${}^{3}J_{HH}$ = 8 Hz), 7.53 (2H, d, ${}^{4}J_{HH}$ = 1.8 Hz). ¹³C NMR (d_1 -CHCl₃, 125 MHz): δ (ppm) 39.51, 51.90, 59.01, 66.78, 70.07, 70.46, 70.49, 71.00, 121.22, 121.61, 126.72, 130.65, 138.45, 150.98.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di(1-(2-(2-methoxyethoxy)ethoxy)ethyl)fluorene (10). Monomer 9 (1.5 g, 2.4 mmol) was dissolved in 30 mL of freshly distilled THF and cooled to -78 °C. n-Butyllithium (2.44 mL, 6.11 mmol) was added dropwise to the cooled reaction and stirred at -78 °C for 30 min, resulting in an orange solution. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.59 g, 8.55 mmol) was added to the solution and stirred for 1.5 h at -78 °C and then allowed to warm to room temperature overnight, resulting in an opaque colorless solution. Water was added and stirred for 30 min. The organic layer was removed and washed with water (2 \times 50 mL), and the aqueous layer was washed with ethyl acetate. The organic layers were combined, dried over MgSO4, and solvent removed under vacuum to give off-white orange solid. The solids were washed with hexanes to give pure white solid. ¹H NMR (d_1 -CHCl₃, 300 MHz): δ (ppm) 1.39 (24H, s), 2.44 (4H, t), 2.67 (4H, t), 3.18 (4H, m), 3.33 (6H, s), 3.39 (4H, m), 3.43-3.54 (8H, m), 7.70 (2H, d), 7.81 (2H, d), 7.84 (2H, d). ¹³C NMR (*d*₁-CHCl₃, 125 MHz): δ (ppm) 24.97, 39.52, 51.02, 58.98, 66.94, 69.99, 70.45, 70.49, 71.86, 83.84, 119.53, 129.25, 134.07, 143.14, 148.59.

1,2-Di-(4,4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1-ethene (13). 15 (1.00 g, 2.95 mmol) was dissolved in dry THF (30 mL) and cooled to -78 °C. *n*-BuLi (2.48 mL, 6.21 mmol) was added via syringe, and the reaction was warmed to 0 °C over 1 h, during which time the reaction turned red. The reaction was cooled back to -78 °C, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.11 g, 6.21 mmol) was added dropwise and allowed to come to room temperature overnight.

Water was added until fizzing stopped, and the layers were separated. The organic layer was washed with saturated KCl brine and twice with H₂O. The water layers were extracted with CHCl₃. The organic layers were combined, dried over MgSO₄, and evaporated *in vacuo*. Solids were recrystallized from hot hexanes to give white needles. Yield = 523 mg (41%). ¹H NMR (d_1 -CHCl₃, 300 MHz): δ (ppm) 1.35 (24H, s), 7.18 (2H, s), 7.52 (4H, d, ³J_{HH} = 8.3 Hz), 7.80 (4H, d, ³J_{HH} = 8.3 Hz). ¹³C NMR (d_1 -CHCl₃, 70 MHz): δ (ppm) 24.8, 83.8, 125.9, 129.5, 135.1, 135.2, 135.3, 139.8.

Polymer Synthesis. SPFP_{0,33}^{Hex} Monomer 8 (352 mg, 1 mmol) and K₂CO₃ (1.382 g, 10 mmol) were dissolved in 5 mL of H₂O. 9,9-Dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (502 mg, 1 mmol) was dissolved in THF (20 mL). The organic and aqueous solutions were both placed in a three-neck round-bottom flask along with a magnetic stir bar and fitted with a water cooled condenser. The mixture of solutions was deoxygenated by bubbling N₂ through the solutions and heated to 85 °C. After purging with N₂ for 10 min, the catalyst was added, and the reaction was stirred for 72 h. The reaction was poured into water, and the solids were collected via centrifugation. The solids were washed with chloroform, dissolved in methanol, and precipitated into water. This washing and precipitating process was repeated three times. ¹H NMR (d_4 -methanol, 300 MHz): δ (ppm) 0.5–1.5 (22H, m), 2.1 (4H, m), 4.25 (2H, s), 7.4–8.2 (9H, m).

SPF^{Hex}_{0.5}. Monomer 2 (524 mg, 0.5 mmol) and 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (251 mg, 0.5 mmol) were dissolved in 8 mL of THF/methanol 50/50 (v/v). 1 mL of 2 M Na₂CO₃ and the organic solution were both placed in a round-bottom flask fitted with a magnetic stir bar and condenser. The mixture of solutions was deoxygenated by bubbling N₂ through the solutions and heated to 85 °C. After purging with N₂ for 10 min, the Pd(PPh₃)₄ (0.05 equiv) catalyst was added, and the reaction was stirred for 48–72 h. The reaction proceeded with the formation of a yellow-orange precipitate that began forming around 18 h. The resulting polymer was washed with CHCl₃, THF, and water. ¹H NMR (*d*₆-DMSO, 300 MHz): δ (ppm) 0.682 (8H, m), 1.10 (22H, m), 1.33 (4H, m), 2.4 (289H, m), 7.55–8.07 (70H, m).

 SPF_{χ}^{TEG} . General polymerization procedure: *n* equiv of **2**, *m* equiv of **9**, and *n* + *m* equiv of **10** were dissolved in 8 mL of THF/methanol 50/50 (v/v). 1 mL of 2 M Na₂CO₃ and the organic solution were both placed in a round-bottom flask fitted with a magnetic stir bar and condenser. The mixture of solutions was deoxygenated by bubbling N₂ through the solutions and heated to 85 °C. After purging with N₂ for 10 min, the Pd(Ph₃)₄ (0.05 equiv) catalyst was added, and the reaction was stirred for 48–72 h. The reactions all proceeded with the formation of a yellow-orange precipitate that began forming around 18

h. The resulting polymer was washed with $CHCl_3$, THF, and water. The organic washes were found to contain both unreacted monomer and reaction byproducts but no polymer. Yields were in the 50-75% range.

 $SPF_{0.5}^{TEG}$. ¹H NMR (d_6 -DMSO, 300 MHz): δ (ppm) 0.840 (4H, m), 1.22 (12H, m), 2.4–2.9 (16H, m), 3.1 (14H, m), 3.25 (8H, m) 7.65–8.00 (12H, m).

SPF^{TEG}. ¹H NMR (d_6 -DMSO, 300 MHz): δ (ppm) 0.820 (4H, m), 1.25 (19H, m), 2.4–2.9 (88H, m), 3.1 (38H, m), 3.25 (56H, m) 7.55–8.07 (28H, m).

SPF^{TEG}_{0.20}. ¹H NMR (d_6 -DMSO, 300 MHz): δ (ppm) 0.819 (8H, m), 1.21 (64H, m), 1.49 (16H, m), 1.97 (8H, m), 2.48 (64H, s), 2.79 (48H, m), 3.12–3.54 (289H, m), 7.55–8.07 (70H, m).

 $SPF_{0.17}^{TCG^{-1}}$ H NMR (d_{6} -DMSO, 300 MHz): δ (ppm) 0.820 (4H, m), 1.25 (17H, m), 2.5 (41H, m), 2.7 (14H, m), 3.1–3.4 (104H, m) 7.55–8.07 (35H, m).

 $SPF_{0.05}^{TEG}$ ¹H NMR (d_{c} -DMSO, 300 MHz): δ (ppm) 0.819 (4H, m), 1.11–1.49 (93H, m), 2.2 (37H, m), 2.79 (53H, m), 3.12–3.54 (315H, m), 7.55–8.15 (124H, m).

Characterization. NMR spectra were recorded with a Varian INOVA 300 MHz spectrometer with CP solutions in DMSO- d_6 . Visible absorption spectroscopy was performed on either DMSO or methanol solutions using a Hewlett-Packard 8452A diode array spectrometer. Gel permeation chromatography was performed on a Waters chromatography system utilizing a Styragel HR4 size exclusion column, a 515 pump, and 2410 differential refractometer. The flow rate of the GPC was 0.1 mL/min.

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Notes

The authors declare no competing financial interest.

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