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Iterative Binomial Synthesis of Monodisperse Polyfluorenes up to 64-mers and Their Chain-Length-Dependent Properties

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S Supporting Information

Conjugated polymers have emerged as one class of advanced materials due to their applications in optoelectronic devices and sensors.[1−4] However, various fundamental issues, such as crystalline structures and chain-length-related properties, still need further study for understanding insight from the polymer viewpoint.[5−10] In principle, polymer samples with well-defined chain length and chemical structures and narrow molecular weight distribution are preferable in studying these fundamental issues. However, synthesis of well-defined conjugated polymers by polymerizations has been only realized for limited conjugated systems to date.[11,12] As one class of the most important conjugated polymers, polyfluorenes with defined molecular weights and narrow molecular weight distributions are still difficult to be prepared.

Monodisperse conjugated oligomers (MCOs) are characterized with well-defined and uniform chemical structures.[13,14] These characteristics enable them as the ideal model compounds to attain specific information, such as effective conjugation length (ECL), of their corresponding polydisperse high molecular weight analogues by extrapolation.[15,16] However, the molecular weights of the most of MCOs reported today locate in the oligomeric region since the synthesis of MCOs is a multistep process and requires carefully optimizing the reaction condition and synthetic strategy.[17−23] Their molecular weights are not high enough to serve as models of the corresponding conjugated polymers in all cases. In this regard, synthesis of monodisperse conjugated polymers (MCPs) with molecular weights beyond 10 000 g/mol is very important. Two series of MCPs based on thiophene and fluorene units with the molecular weights beyond 20 000 g/mol have been reported.[24,25] However, these MCPs were separated from the polymerization mixtures of macromonomers by preparative gel permeation chromatography (PGPC), and the methods do not allow preparing MCPs in a relatively large quantity.

The iterative binomial approach is most efficient in the synthesis of MCOs.[13,17,18] However, it has not been used in the preparation of MCPs yet. After carefully optimizing the reaction conditions, in the current paper, we first successfully synthesized monodisperse poly(9,9-dioctylfluorene)s (POFs) with molecular weights up to 25 018 g/mol in half-gram scale via iterative binomial approach. In THF, the α value of POFs in the Mark−Houwink equation was measured to be 1.15. Absorption spectroscopic measurements indicate that absorption maxima of POFs do not reach the convergent limit yet up to 64-mer, indicating that POFs are highly conjugated.

The structures of the monodisperse POFs, i.e. SiF*n*Si and F*n*, are depicted in Chart 1, where *n* and Si represent the number of fluorene units and the terminal $SiMe_3$ group, respectively. Synthesis of SiF*n*Si and F*n* is outlined in Scheme 1. In general, two orthogonal protecting groups are required in iterative binomial synthesis of MCOs, as exemplified by the synthesis of oligo(*p*-phenyleneethynylene)s.[17,18] Here, only one protecting group ($SiMe_3$) was used. Therefore, the selectivity of C−I over C−Br in the Suzuki coupling is crucial. Taking the advantage of the selectivity between C−I and C−Br, Schlüter et al. synthesized monodisperse oligophenylenes with the number of repeating units up to 16 at the refluxing temperature of toluene.[19] However, in the current conjugated system, it was found that the lower reaction temperature was necessary for achieving the satisfied selectivity. For example, at 70 °C and 16 h, BrF2Si was synthesized in a yield of 78% with 1 equiv of **1** along with a small amount of terfluorene SiF3Si (7.8%). This allowed the easy purification of the product. In contrast, the yield of SiF3Si was as high as 24% at 90 °C, resulting in difficult separation of the product. At lower temperature, the reaction time was longer than 24 h without significant enhancement of yield. In the course of the exponential growth, two groups, i.e., $SiMe_3$ and Br, could be selectively transferred to I and boronic ester groups, respectively. Treatment of BrFnSi with ICl in CCl_4 gave iodo-substituted BrF*n*I in high yields (92−97%). Organoboronic reagents BF*n*Si were prepared in modest to high yields (76−90%). BF2Si and BF4Si were prepared by debromonation of BrF2Si and BrF4Si with *n*-BuLi followed by quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Pd-catalyzed coupling reaction was used in the synthesis of BF8Si and BF16Si. As shown in Scheme 1b, Suzuki coupling of BrF*n*I and BF*n*Si at 70 °C afforded BrF*n*Si (*n* = 4, 8, 16, 32) in yields of 66−82% along with the small amount of SiF*n*Si (*n* = 6, 12, 24, 48). Even for BrF32Si, the yield was as high as 71.6% after purification. For ensuring the purity, all products with *n* > 8 were further purified by preparative GPC after the purification by the common column chromatography on silica gel.

As shown in Scheme 1c, SiF*n*Si (*n* = 8, 16, 32, 64) were synthesized by Yamamoto coupling reaction from BrF*n*Si in

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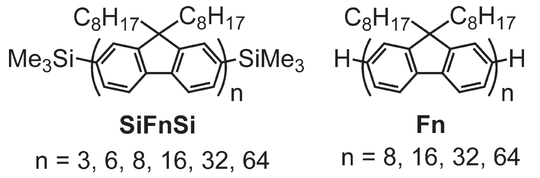
modest yields (64−81%). The protecting group $SiMe_3$ can be removed by treatment with acid.[26] We found that trifluoroacetic acid was most appropriate for the current system, and $SiMe_3$ can be eliminated quantitatively to afford F*n* in high yields of 88−93% after purification.

The molecular structures of SiF*n*Si and F*n* were validated by ^{1}H NMR, gel-permeation chromatography (GPC), matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF), mass spectrometry (MS), and elemental analysis (EA). Mass spectra of SiF*n*Si and F*n* (*n* = 8, 16, 32, 64) are displayed in Figure 1a,c. In each MS spectrum, only one peak corresponding to the molecular mass was observed. The number of the repeating units can also be validated by end-group analysis with ^{1}H NMR, as shown in Supporting Information (Figures S1 and S2). The monodisperse nature of SiF*n*Si and F*n* was confirmed by GPC measurements (Table 1 and Figure 1b,d), as evidenced by their low polydispersity indices (PDI = 1.06−1.09). However, GPC measurements overestimated the molecular weights of SiF*n*Si and F*n* because of their more rigid chain structures compared to the polystyrene (PS) standard, a random-coil polymer. The difference between number-average molecular weights ($M_{n,GPC}$) measured by GPC and calculated molecular weights (M_{calcd}) increases with an increase of molecular weight. For example, M_{calcd} and $M_{n,GPC}$ of SiF8Si are 3255.4 and 5100 g/mol (5100/3255.4 ≈ 1.57), while those for SiF64Si are 25018.6 and 59 500 g/mol (59500/25018.6 ≈ 2.38), respectively. This phenomenon was also observed for other conjugated oligomers and polymers.[22,24,25,27]

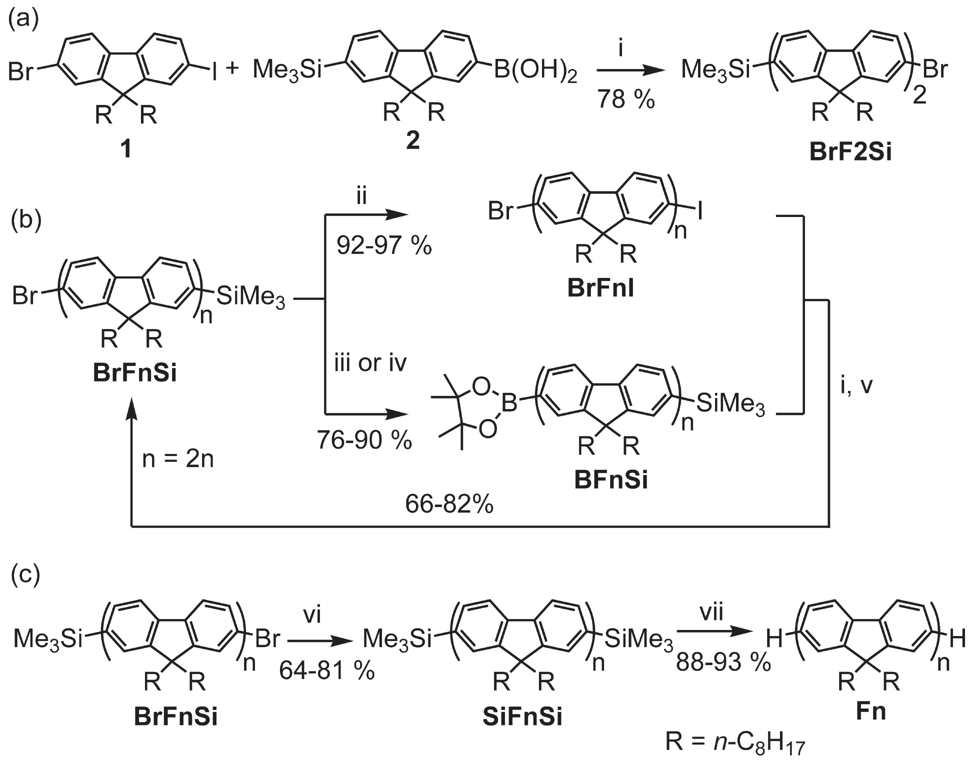
Chart 1. Structure of Monodisperse Polyfluorenes SiF*n*Si and F*n*



The α value in the Mark−Houwink equation is a parameter correlated with the rigidity of the polymer chain. The intrinsic viscosities of SiF*n*Si with *n* = 16, 32, 48, and 64 were measured with the GPC equipped with a Viscotek TDA302 triple detector. Along with the molecular weights measured by MALDI-TOF MS (M_{MS}), α value in Mark−Houwink equation was calculated to be 1.15. It is well-known that α is not constant in the entire molecular weight range[28] and is relatively lower in the low molecular weight region. For example, α of poly(methyl methacrylate) (PMMA) with molecular weight <44 000 and >44 000 g/mol in benzene are 0.5 and 0.76, respectively. The molecular weights of SiF*n*Si are in the range 6400−26 000 g/mol. Therefore, the α value of POF with significantly high molecular weight should be higher. Nevertheless, this α value implies a semirigid nature of POF backbone.

Chain-length-dependent thermotropic properties were characterized by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). Transition temperatures are reported

Scheme 1. Synthetic Route of Monodisperse Polyfluorenes SiF*n*Si and F*n*[a]



[a] Reagents and conditions: (i) $Pd(PPh_3)_4$, Na_2CO_3 (2.0 M aqueous), toluene, 70 °C; (ii) ICl, 0 °C; (iii) (1) *n*-BuLi, THF, −78 °C; (2) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, −78 °C to room temperature; (iv) 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bi-1,3,2-dioxaborolane, $Pd(dppf)Cl_2$, KOAc, DMF/toluene, 80 °C; (v) $Pd(PPh_3)_4$, Na_2CO_3 (2.0 M aqueous), THF, 70 °C; (vi) Ni(COD)/2,2′-bipyridine/COD, DMF/toluene, 80 °C; (vii) CF_3COOH, benzene, room temperature.

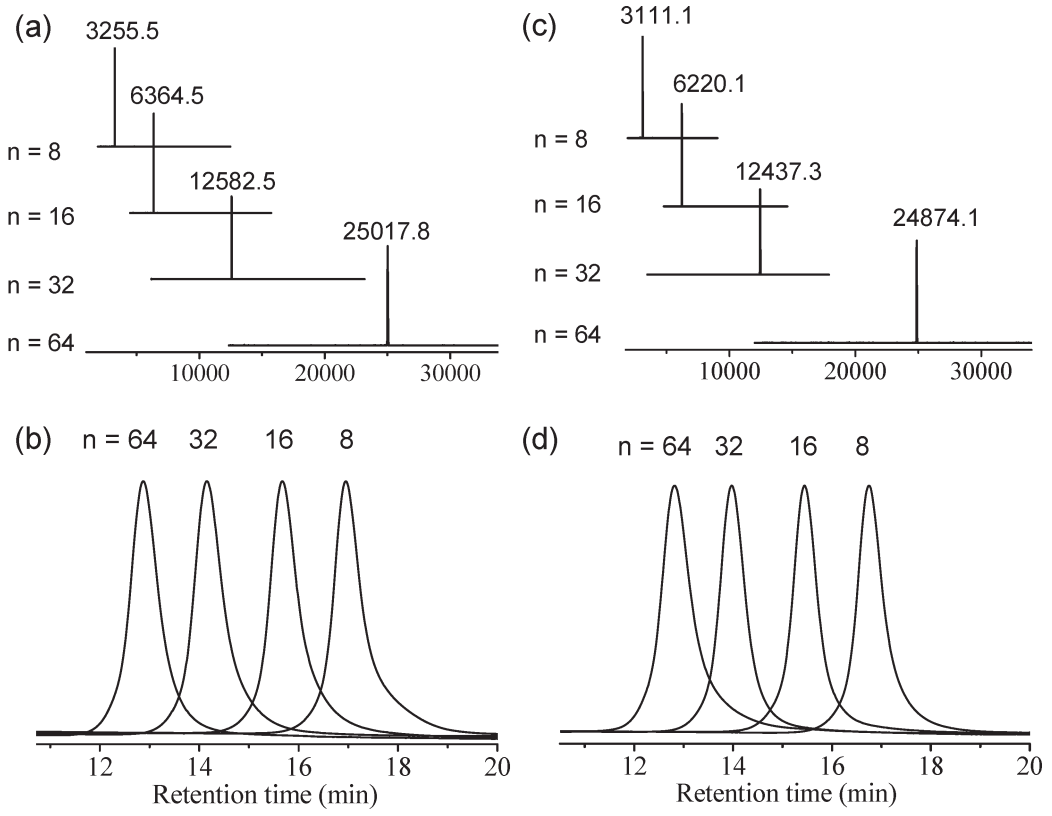


Figure 1. MALDI-TOF mass spectra (a, c) and GPC profiles (b, d) of SiF*n*Si (a, b) and F*n* (c, d). MALDI-TOF mass spectra were measured with terthiophene as the matrix in a linear mode.

Table 1. Molecular Weights and Transition Temperatures of SiF*n*Si and F*n*

sample	M_{calcd} (g/mol)	$M_{MS}{}^{a}$ (g/mol)	$M_{n,GPC}{}^{b}$ (g/mol)	PDI^{b}	$\lambda_{max,abs}{}^{c}$ (nm)	$T_m{}^{d}$ (°C)	$T_{N-I}{}^{d}$ (°C)
SiF8Si	3255.4	3255.5	5100	1.08	377.3	NA	NA
SiF16Si	6364.4	6364.5	10800	1.09	382.5	126	166
SiF32Si	12582.5	12582.5	28100	1.07	385.0	155	261
SiF64Si	25018.6	25017.8	59500	1.06	385.8	163	308
F8	3111.0	3111.1	4100	1.09	377.3	NA	NA
F16	6220.1	6220.1	9500	1.09	382.9	135	152
F32	12438.1	12437.3	23900	1.09	384.9	156	249
F64	24874.2	24874.1	56900	1.09	386.9	167	301

[a] Measured by MALDI-TOF mass spectrometry. [b] Measured by GPC equipped with refractive index detector and with polystyrene as standard. [c] Absorption spectra were measured in toluene with a concentration of 10^{-5} mol/L and an interval of 0.1 nm. [d] Melting point (T_m) and nematic–isotropic transition temperature (T_{N-I}) measured by DSC in N_2 with a heating rate of 10 °C/min. The data are reported from the second heating scans.

from the second DSC heating scans. All monodisperse POFs with $n > 8$ exhibited a melting (T_m) and a nematic–isotropic (T_{N-I}) transition. No glass transition was observed for both SiF*n*Si and F*n* with $n > 8$, indicating a highly crystalline nature. SiF8Si and F8 only showed glass transitions in the second heating, which are 22 and 18 °C, respectively. As shown in Table 1, both T_m and T_{N-I} increase with the increase of the number of fluorene units. It was found that the presence of $SiMe_3$ terminal group caused an enhancement of T_{N-I}, but a reduction of T_m. It should be noted that both two transition temperatures do not reach saturation yet with *n* up to 64.

Effective conjugation length (ECL) is one of the central concepts in the understanding of chain-length-dependent properties of conjugated polymers. Normalized solution absorption spectra of F*n* in toluene are shown in Figure 2a. The absorption maximum of F*n* continuously red-shifts with increasing *n*. F64 still exhibits a 2 nm red shift compared to F32. To find out whether the absorption maximum of F64 reaches the convergent limit, the absorption spectrum of POF with $M_{n,GPC}$ and PDI of 208 000 g/mol and 3.78, respectively, was also measured. An absorption maximum of 387.6 nm was observed. Meier et al. defined the ECL as the conjugation length at which the wavelength of the absorption maximum in the series of oligomers was not more than 1 nm above the lower limit, which is given by the infinitely long polymer chain.[15] According to this definition, the ECL of POF should be as long as 64 repeating units. However, the way often used in the literature for determining ECL is to extrapolate the linear region of the plot of absorption energies vs inverse ring number to the value of the polymer with the infinite

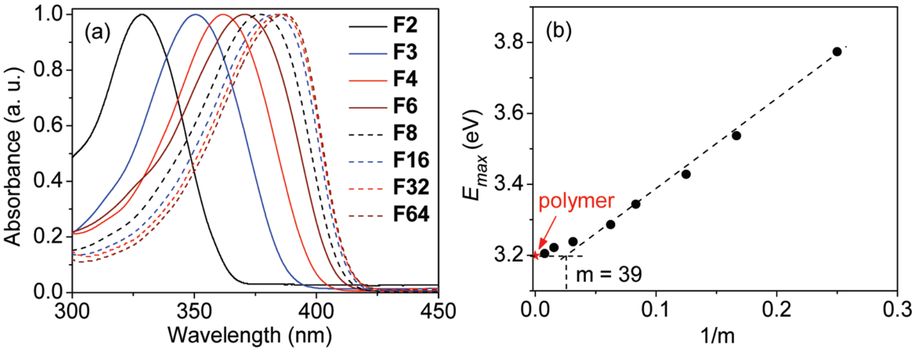


Figure 2. Solution absorption spectra in toluene (a) and correlation between absorption energies ($E_{\max}$) and inverse phenyl numbers ($1/m$) of Fn. $E_{\max}$ of polymer (red star) was calculated from the absorption maximum of POF ($\lambda_{\max,\text{abs}}$ = 387.6 nm) with $M_{n,\text{GPC}}$ and PDI of 208 000 g/mol and 3.78, respectively.

length.[22,23,29−31] For fair comparison, we also estimated the ECL with this method. Figure 2b shows the correlation between absorption energy ($E_{\max}$) and inverse phenyl ring numbers (m). For Fn with $m \leq 32$ ($n \leq 16$), the plot shows a linear correlation of $E_{\max}$ with m^{-1} following $E_{\max}$ (eV) = 3.17 + 1.17/m, but for the longer ones deviation from linearity occurs due to saturation. Assuming the absorption maximum of above POF as the convergent limit, the ECL of this conjugated system was estimated to be 39 phenyl rings, corresponding to 19.5 fluorene units. In the previous report, Miller et al. proposed that the ECL of poly(9,9-dihexylfluorene) (PHF) is about 12 fluorene units by extrapolation method, corresponding to 24 phenyl rings.[31] However, they used the absorption maximum of PHF with a number of repeating units of ~54 (measured by GPC) as the limiting value. From above discussion, it is clear that the absorption maximum does not reach the limit yet at this chain length. Meanwhile, polymers usually have broad molecular weight distribution. This means there are significant amount of short chains in above PHF, especially while considering that GPC measurements often overestimate the molecular weight.

In summary, monodisperse POFs with H and $SiMe_3$ terminal groups have been successfully synthesized in half-gram scale via iterative binomial approach. It was found that the photophysical and thermal properties are chain-length-dependent up to 64-mer. These monodisperse polyfluorenes should be ideal model compounds in the study of the various properties of polyfluorenes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Synthesis details of all compounds, ^{1}H NMR spectra of SiFnSi and Fn, logarithm of intrinsic viscosity as the function of logarithm of molecular weight. This material is available free of charge via the Internet at http://pubs.acs.org.

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