First Synthesis of Isotactic Poly(9-alkyl$_1$-9-alkyl$_2$fluorene) via Directed Aryl−Aryl Coupling of Chiral AB-Type Monomers†

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ABSTRACT: Nonsymmetrically substituted chiral 9-alkyl$_1$-9-alkyl$_2$fluorene monomers of the AB type allow for their directed, stereoregular aryl−aryl cross-coupling after Suzuki leading to isotactic poly(9-alkyl$_1$-9-alkyl$_2$fluorene). As expected, the isotactic poly(9-dodecyl-9-methylfluorene) **i-PF1-12** of this study shows an increased solid state ordering and distinctly different thermal properties when compared to its corresponding atactic, stereoirregular polyfluorene counterpart **a-PF1-12**. This and other isotactic polyfluorene derivatives will be interesting building blocks for the generation of chiral, all-conjugated block copolymers.

Introduction

Stereoregular polyolefins can be today elegantly made via stereocontrolled insertion polymerization with Ziegler/Natta- or metallocene-type catalysts. Especially iso- and syndiotactic polypropylenes are now a textbook example in the demonstration of the distinct influence of the resulting stereoregularity on the thermal, morphological, and mechanical solid state properties of synthetic polymers.[1−3] Stereoregular, π-conjugated polymers have up to now been mostly described as macromolecules with chiral side-chain substituents (e.g., chiral alkyl or alkoxy side chains)[4−13] or with (axial or planar) chiral building blocks of the main chain (e.g.. chiral binaphthyl or cyclophane units).[14−19] However, for π-conjugated polymers with nonsymmetrically arranged "out-of-plane" substituents of their planar, π-conjugated main-chain repeat units, as realized in nonsymmetrically substituted poly(9,9-dialkylfluorene)s, there also exist the corresponding iso- and syndiotactic stereoisomers. If synthetically accessible, these stereoisomers should exhibit a significantly different solid-state packing behavior when compared to their synthetically easy accessible atactic counterparts. The tactic stereo-arrangement may lead to different thermal or electronic solid state properties. The generation of such stereoregular π-conjugated polymers, however, requires up to now unknown, novel synthetic approaches. The common polycondensation schemes (transition metal catalyzed or mediated aryl−aryl couplings) generally applied for the generation of polyaromatic macromolecules do not allow for a satisfying stereocontrol toward tactic products in the coupling of suitable nonchiral or racemic monomers with the help of chiral catalysts and/or ligands via chirality transfer to the active center.

Therefore, we have studied alternate synthetic routes toward nonsymmetrically substituted, isotactic poly(9-alkyl$_1$-9-alkyl$_2$-fluorene)s. Hereby, our primary target was poly(9-dodecyl-9-methylfluorene) **PF1-12** with its two alkyl substituents of rather different alkyl length. Scheme 1 illustrates the chemical structures of atactic, isotactic, and syndiotactic poly(9-dodecyl-9-methylfluorene) **PF1-12**.

The main focus of our work was, therefore, the development of a synthetic scheme toward isotactic poly(9-dodecyl-9-methylfluorene) **i-PF1-12**. Further on, we tried to collect first structure data on the resulting solid state properties in the comparison of atactic and isotactic poly(9-dodecyl-9-methylfluorene) (**a-PF1-12** and **i-PF1-12**) with similar average molecular weights and molecular weight distributions.

Results and Discussion

The well-described and well-established standard aryl−aryl coupling schemes for polyaryls and especially polyfluorenes (Yamamoto-[20,21] or Suzuki-type couplings[22−24]) using AA- or AA/BB-type monomers/monomer couples are not applicable in the generation of isotactic poly(9-dodecyl-9-methylfluorene) (**i-PF1-12**). For the generation of our target polymers we have, therefore, switched to a directed aryl−aryl coupling of chiral, difunctional fluorene monomers of the AB type. Doing this, the step of stereocontrol is shifted to the earlier stage of monomer synthesis with a preparative enantiomeric separation of the corresponding monomer racemate. Advantageously, this novel strategy now guarantees the generation of fully (or almost fully when assuming a low amount of side reactions) isotactic poly(9-alkyl$_1$-9-alkyl$_2$fluorene)s. Using an aryl−aryl cross-coupling scheme after Suzuki, we have been, however, restricted to the use of AB-type monomers since only they will allow for a directed coupling of chiral monomers. Unfortunately, the coupling of AB-type monomers generally leads to some limitations in the molecular weight of the resulting coupling products in comparison to the coupling of the corresponding AA/BB couples.[25−28]

Our novel synthesis of isotactic poly(9-dodecyl-9-methylfluorene) **i-PF1-12** utilizes a chiral 2-bromo-9-dodecyl-9-methylfluorene-7-boronate monomer (AB type) that allows for the directed, stereoregular incorporation of the 9-dodecyl-9-methylfluorene-2,7-diyl repeat units into the growing polymer chain and is depicted in Scheme 2. The monomer synthesis starts from 2,7-dibromo-9-dodecyl-9-methylfluorene which is generated in a well-established standard procedure.[21] Next, the 2,7-dibromo-9-dodecyl-9-methylfluorene was monolithiated and subsequently converted into the corresponding racemic arylboronate (2-bromo-9-dodecyl-9-methylfluorene-7-pinakolatoboronate **F1-12**) by reaction with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Chiral, 9,9-disubstituted fluorene derivatives have been until now described for only a few examples; 9-methyl-9-alkyl-fluorene-2-carboxylic acids (alkyl: -methyl, -ethyl, -propyl, -butyl) are one of them. They have been generated via the corresponding diastereomeric chinchonidine or brucine salts.[29]

† Dedicated to Prof. Dr. Gerhard Wegner on the occasion of his retirement.

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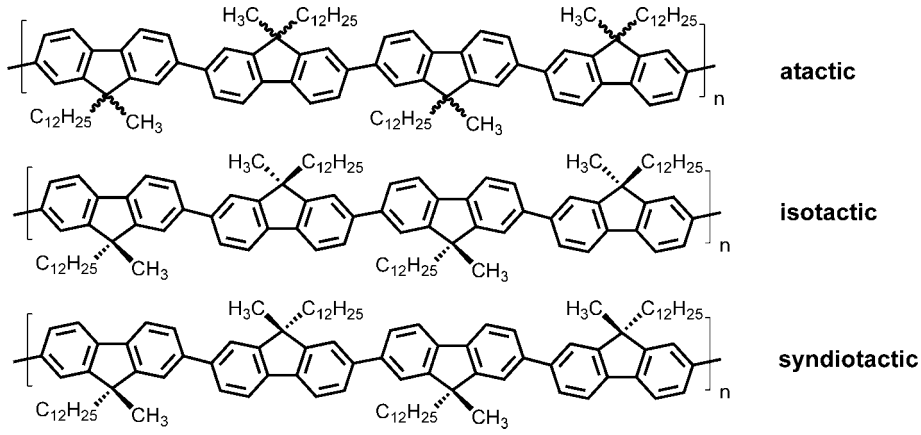
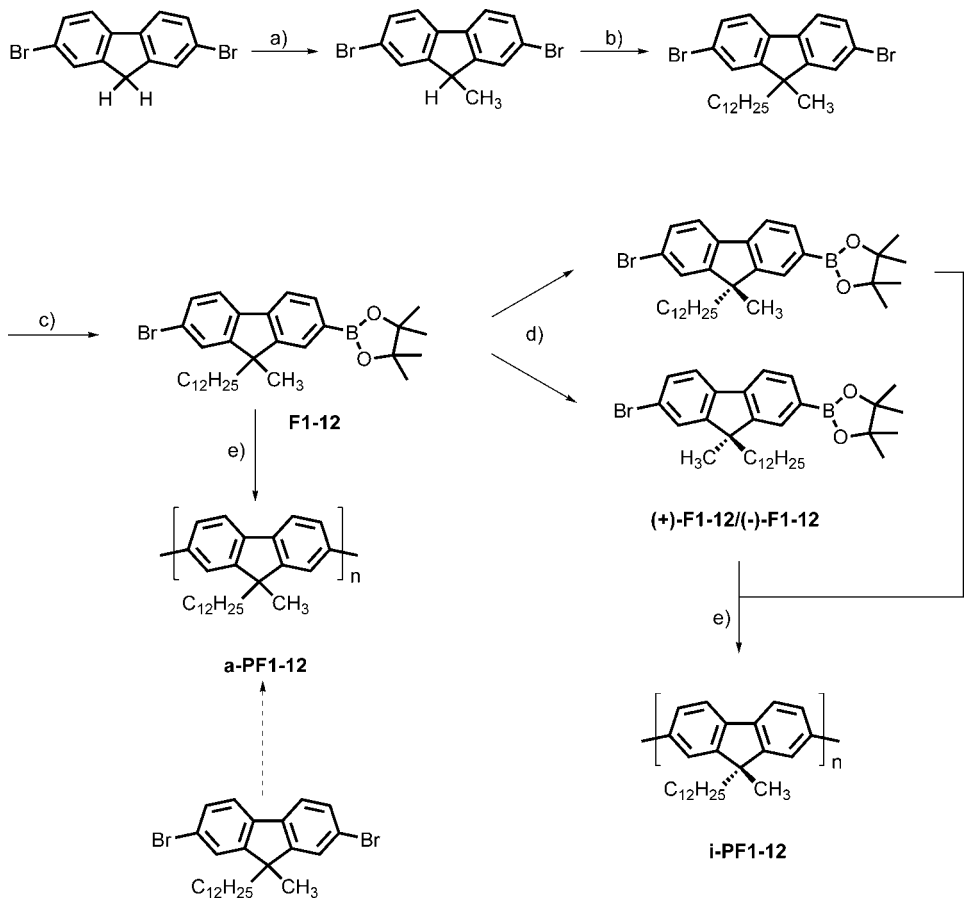
Scheme 1. Chemical Structures of Atactic (Top), Isotactic (Middle), and Syndiotactic (Bottom) Poly(9-dodecyl-9-methylfluorene) PF1-12



Scheme 2. Synthesis of Atactic (Left) and Isotactic (Right) Poly(9-dodecyl-9-methylfluorene) a-PF1-12 and i-PF1-12[a]



[a] The key step in the in synthesis of **i-PF1-12** is the column chromatographic enantiomeric separation of the racemic monomer **F1-12** (step d) and the application of enantiomerically pure AB-type monomers in the following Suzuki-type cross coupling toward **i-PF1-12** (step e). Reaction and separation conditions: (a) 1.08 equiv of *n*-butyl-Li/CH_3I in THF; (b) KOH/$C_{12}H_{25}Br$ in DMSO; (c) 1.31 equiv of *n*-butyl-Li/$[C(CH_3)_2]_2O_2)BOCH(CH_3)_2$ in THF; (d) preparative HPLC; column: Chiracel OD; eluent: 2-propanol/*n*-hexane (0.1:99.9; v/v); (e) 0.05 mol % $PdCl_2[PPh_3]_2$/KOH in THF.

The key step in our synthesis of **i-PF1-12** is a column chromatographic enantiomeric separation (HPLC on a chiral column) of monomer **F1-12** with the help of a preparative scale Chiracel OD column and 2-propanol/*n*-hexane (0.1: 99.9; v/v) as eluent.

The application of the enantiomerically pure AB-type monomers [**(+)-F1-12** and **(−)-F1-12**, with a purity of each >99% ee; see Figure 1] in the following Suzuki-type aryl−aryl cross coupling, carried out as polymer synthesis with microwave heating,[30−32] provides the expected target polymer, isotactic poly(9-dodecyl-9-methylfluorene) (**i-PF1-12**). Atactic **a-PF1-12** which is needed for comparison can be generated via a Suzuki-type aryl−aryl cross-coupling of the corresponding racemic **F1-12** monomer as well as via a Yamamoto-type homocoupling of the symmetric 2,7-dibromo-9-dodecyl-9-methylfluorene monomer (Scheme 2).

The raw polyfluorenes **i-PF1-12** and **a-PF1-12** after aryl−aryl coupling have been subsequently fractionated by preparative size exclusion chromatography (SEC) to obtain polymer fractions with similar molecular weight and molecular weight

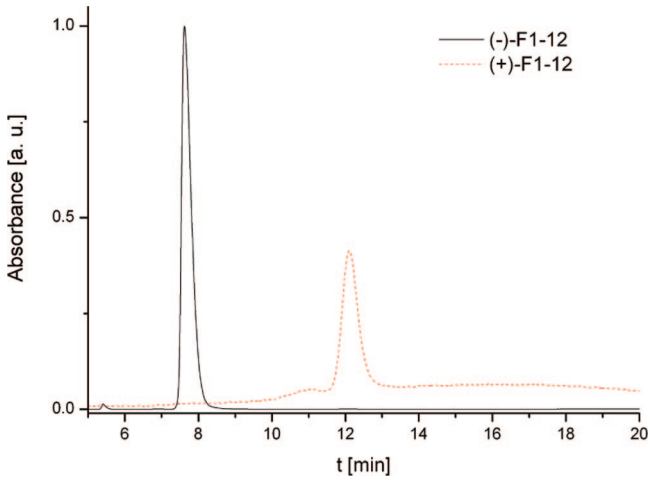


Figure 1. HPLC elugrams of the enantiomerically pure monomers (+)-**F1-12** and (−)-**F1-12** after separation step d. Column: Chiracel OD-H; eluent: 2-propanol/*n*-heptane (0.1:99.9, v/v), absorbance detected at 254 nm.

Figure 2. Aromatic carbons of the shortest connection between two stereo centers of **PF1-12** (in the ^{13}C NMR spectrum of **a-PF1-12,** the carbons C1/8 and C2/7 both form signal pairs with a $\Delta\delta$ of 0.03 and 0.04 ppm, respectively; see Figure S4).

distribution. The resulting two fractions of **i-PF1-12** and **a-PF1-12**, respectively, showed very similar average molecular weights M_n and M_w and have been used for our further characterization experiments: M_n/M_w 14 000/22 400 (PDI: 1.6) for **i-PF1-12** and M_n/M_w 15 000/25 500 (PDI: 1.7) for **a-PF1-12**, respectively (SEC, PS calibration).

The ^{1}H and ^{13}C NMR spectra of **i-PF1-12** and **a-PF1-12**, respectively, are nearly identical in a first inspection (see Supporting Information; Figures S2−S6). However, two of the six nonequivalent aromatic carbons in the ^{13}C NMR spectrum of the atactic **a-PF1-12** form signal pairs with a $\Delta\delta$ of 0.03 and 0.04 ppm, respectively, due to the presence of the two different isomeric dyads (RR/SS and RS; see Figure S4): one ternary C_{ar}−H with a chemical shift of 121.5 ppm (121.51/121.48) and one quaternary C_{ar} at 140.7 ppm (140.73/140.69). These two signal pairs have been assigned to the four central carbons of the shortest connection between two adjacent, dialkylated C9 stereo centers (C10−C1−C2−C7−C8−C13: C1/C8 as ternary, C2/C7 as quaternary carbons; see Figure 2), in full agreement with the known ^{13}C NMR data of related poly(9,9-dialkylfluorene)s.[33] Hereby, the signal splitting is somewhat more pronounced for the carbons C2/C7 of the central aryl−aryl single bond. Please note that the distance between two neighboring stereocenters of **PF1-12** approximately compares to the distance between the two outer stereocenters of stereoisomeric tetrads/pentads in polypropylenes.

The UV−vis and photoluminescence (PL) spectra of **a-PF1-12** and **i-PF1-12** in dilute solution (chloroform) are, as expected, nearly identical (Figure 3) when compared to other poly(9,9-dialkylfluorene)s from the literature with a long wavelength absorption maximum $\lambda_{max,abs}$ at ca. 387 nm and a 0−0 PL transition $\lambda_{max,em}$ at 416 nm (for comparison: poly[9,9-bis(2-ethylhexyl)fluorene] **PF2/6**: absorption: $\lambda_{max,abs}$ = 384 nm; PL: $\lambda_{max,em}$ = 415 nm[33]). When going to the solid state (Figure 4; film spectra) the long wavelength absorption edge is red-shifted by ca. 15 nm and the 0−0 PL maximum by a $\Delta\lambda$ of ca. 10 nm,

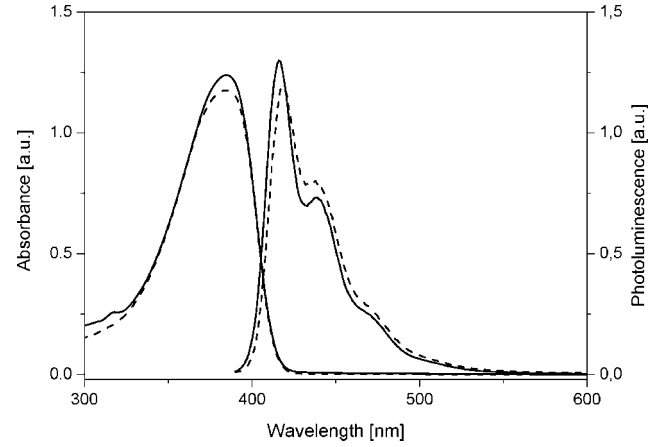


Figure 3. UV−vis absorption and photoluminescence (PL) spectra of **a-PF1-12** (solid lines) and **i-PF1-12** (dashed lines) in dilute chloroform solution (excitation wavelength: 380 nm).

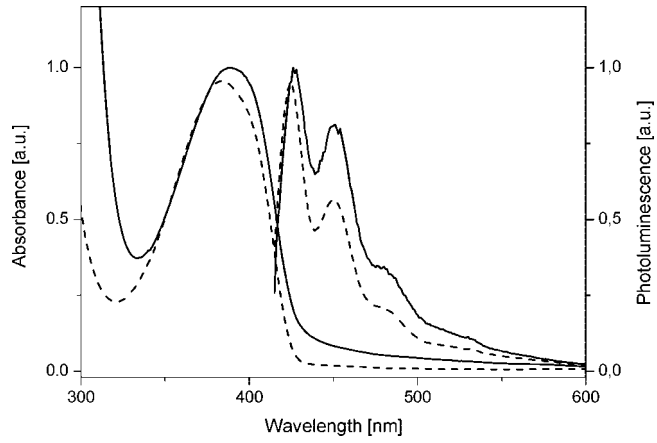


Figure 4. UV−vis absorption and photoluminescence (PL) spectra of **a-PF1-12** (solid lines) and **i-PF1-12** (dashed lines) in the solid state (film, excitation wavelength: 380 nm).

again without a significant difference between **a-PF1-12** and **i-PF1-12**. However, the more pronounced long wavelength tail for the **a-PF1-12** film (Figure 4) should result from an increased morphological inhomogenity (the formation of anisotropic, liquid crystalline (LC) mesophases in the atactic PF causes increased scattering) in comparison to the corresponding **i-PF1-12** film (please see also the next paragraph to the formation of LC mesophases). The higher intensity 0−1 PL peak and the somewhat red-shifted 0−0 PL peak in the solid state PL spectrum of **a-PF1-12** should result from reabsorption effects (due to the occurrence of the long wavelength absorption tail for this sample). The formation of a so-called β-phase with its characteristic long wavelength absorption signature (additional, sharp absorption band peaking at a $\lambda_{max,abs}$ of ca. 438 nm) as an indication of a fully planarized backbone structure and as extensively described for poly(9,9-di-*n*-octylfluorene) **PF8** (or **PFO**)[34−36] was not observed both for **a-PF1-12** and **i-PF1-12**, respectively.

An investigation of the thermal properties of **a-PF1-12** and **i-PF1-12** shows a distinctly different behavior of the two stereoisomers. The atactic **a-PF1-12** exhibits the formation of a nematic liquid crystalline mesophase (differential scanning calorimetry DSC: temperature maximum of the broad transition peak $T_{cryst} \rightarrow T_{LC}$ or $T_{LC} \rightarrow T_{cryst}$, respectively: 155−160 °C) with characteristic thread textures in polarizing microscopy images (see Figure S1, Supporting Information).[20,21,33] Such a behavior is well-known for several poly(9,9-dialkylfluorene)s with two identical alkyl substituents. In contrast, **i-PF1-12** does

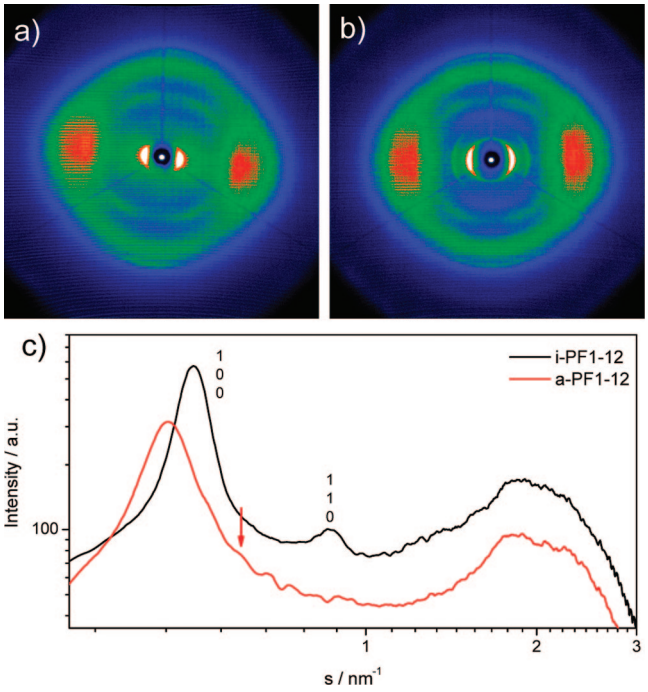


Figure 5. 2D-WAXS patterns of (a) atactic **a-PF1-12** and (b) isotactic **i-PF1-12** (recorded at 30° after annealing for 24 h to 180 °C). (c) Equatorial scattering intensities as a function of the scattering vector *s* for both compounds; the individual reflections for **i-PF1-12** are labeled with the corresponding Miller indices indicating a hexagonal lattice. The red arrow indicates the assumed [110] reflection of **a-PF1-12.**

not form any liquid crystalline mesophases up to a temperature of 300 °C. For both polymers we could not observe melting or clearing (isotropization) transitions below a temperature of ca. 350 °C, at which the thermal decomposition of the polyfluorenes starts.

The solid state organization of **a-PF1-12** and **i-PF1-12** was investigated by using two-dimensional wide-angle scattering X-ray (2D-WAXS) on annealed fiber samples made by extrusion. A detailed description of the experimental setup can be found in the Experimental Section. Figure 5 shows characteristic patterns with relatively broad reflections for both polymers, thus indicating a relatively weak overall ordering. Both patterns exhibit characteristic reflections as reported for several poly(9,9-dialkylfluorene)s: the broad equatorial wide-angle reflection corresponding to a "thickness" of 0.45 nm of the fluorene unit and a meridional scattering peak with a spacing of 0.82 nm related to the length of the planar repeat unit.[37] Reflections in the equatorial plane of the patterns are assigned to a chain-to-chain period and a macroscopic alignment of the backbones in the fiber direction. Further equatorial higher order reflections suggest a better packing for **i-PF1-12** in comparison to the atactic derivative and a hexagonal arrangement of the **i-PF1-12** chains with an interchain distance of 2.26 nm (Figure 5c). **a-PF1-12** does not exhibit this kind of distinct higher order reflections due to its lower degree of order. Only one minor reflection indicated by a red arrow in Figure 5c is detectable and was included into our further analysis. Applying a model for a ribbonlike packing of **a-PF1-12**, into which both reflections satisfyingly fit, a chain-to-chain distance of 2.34 nm is extracted, which seems quite plausible. In contrast, assuming a hexagonal lattice also for **a-PF1-12**, a unit cell parameter of 2.76 nm is derived. In comparison to **i-PF1-12** and the well-studied PF2/6 with 2-ethylhexyl side chains which shows a unit cell parameter of 1.65 nm, this value seems highly unlikely.[37] It has to be noted that both polymers **a-PF1-12** and **i-PF1-12** display an increased chain-to-chain distance in comparison to PF2/6 and poly(9,9-dioctylfluorene) **PF8**[38] although the volume fraction occupied by their alkyl chains is significantly lowered. This might be an indication for a different spatial arrangement of the methyl and dodecyl side chains of **a-PF1-12/i-PF1-12** in the solid state as compared to symmetrically substituted poly(9,9-dialkylfluorene)s.

In conclusion, these initial results with **a-PF1-12/i-PF1-12** clearly confirm the expected packing difference between atactic and isotactic **PF1-12**. Further experiments to the solid state structure of **a-PF1-12/i-PF1-12** are planned (X-ray diffraction experiments in the temperature range of 20−300 °C), also under variation of the alkyl chain length and after incorporation of substituent couples of different polarity (nonpolar/polar as −CN/−alkyl). Moreover, the synthetic availability of isotactic polyfluorenes (**i-PF**) allows now for the generation of novel chiral, all-conjugated block copolymers by using the corresponding chiral, AB-type fluorene monomers in a directed "grafting from" approach starting from suitably end-capped conjugated polymer blocks (e.g., when following the synthetic strategy described in ref 28). Such chiral, all-conjugated block copolymers are expected to exhibit unique self-assembly properties.[39]

Experimental Section

General Methods. Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification. Silica gel column chromatography was carried out with Silica Gel 60 (0.06−0.2 mm) from Carl Roth. ^{1}H and ^{13}C NMR data were obtained on a Bruker ARX 400-spectrometer. Chemical shifts are reported in parts per million (δ) using residual solvent protons as internal standards. Splitting patterns are designated as "s" (singlet), "d" (doublet), "t" (triplett), and "m" (multiplet). High-resolution mass spectrometry was accomplished on a Bruker microTOF with electrospray ionization coupled with an Agilent 1100 Series HPLC spectrometer and reported as *m*/*z* and percent relative intensity. FD masses were obtained on a ZAB 2-SE-FDP mass spectrometer. GC-MS measurements were carried out on a Shimadzu GCMS-QP5050 with an OV1 column and a quadrupole mass analyzer. Microwave-assisted synthesis was carried out using a CEM-Discovery monomode microwave apparatus utilizing an IR-temperature sensor and a magnetic stirrer. The reactions were monitored and controlled using a personal computer. Molecular weight determinations by gel permeation chromatography (GPC) were performed using a linear MZGel SD Plus GPC column set (two columns, 5 μm particles, 300 × 8 mm) with THF as eluent at room temperature with a flow rate of 1 mL/min and a concentration of the polymer of ca. 1 mg/mL. The calibration was based on polystyrene standards with narrow molecular weight distribution. A UV−vis detector at λ = 254 nm or a RI detector were used for the signal recording. The thermal properties were studied by differential scanning calorimetry (DSC) with a Mettler-Toledo DSC 1/700/356 Star System flushed with argon and a Nikon E600 polarizing microscope with a Linkam LTS350 hot stage and a Linkam TMS 94 temperature controller. The specific rotation values was determined on a Perkin-Elmer polarimeter 241 at λ = 589 nm and 20.5 °C in chloroform (aperture = 0, source/filter = Na, integration = 5 s). The UV−vis absorption spectra were recorded on a Jasco V 670 spectrophotometer (1 cm cuvettes or quartz plates). The photoluminescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrometer (1 cm cuvettes or quartz plates).

The 2D-WAXS experiments were performed with a rotating anode (Rigaku 18 kW) X-ray setup with pinhole collimation and a 2D Siemens detector. Hereby, a double graphite monochromator for the Cu Kα radiation (λ = 0.154 nm) was used. The samples were prepared by filament extrusion using a home-built mini-extruder. Therein, the materials are heated up to a temperature of 180 °C, at which they become plastically deformable and are extruded as 0.7 mm thin fiber by a constant-rate motion of the piston

along the cylinder. Before performing the measurements, the fiber samples were annealed to 180 °C for 24 h.

Monomer Synthesis. *2,7-Dibromo-9-methylfluorene.*[40] A 250 mL Schlenk flask was charged with 2,7-dibromofluorene (9.5 g, 29.7 mmol) and a magnetic stir bar. The flask was fitted with a septum and flushed with argon. 50 mL of dry THF was added via a syringe to dissolve the solid starting material. Then the mixture was cooled in a dry ice/acetone bath to −78 °C, and a 1.6 M solution of *n*-BuLi (20 mL, 32.0 mmol) in hexane was added dropwise via a syringe. The reaction mixture was stirred for 20 min, and methyl iodide (4.6 g, 32.1 mmol) was added in one portion. The reaction mixture was then stirred for an additional 2 h. The septum was removed, and 50 mL of water was carefully poured into the mixture. The mixture was transferred into a separatory funnel filled with 250 mL of chloroform. The aqueous layer was removed, and the organic layer was washed three times with water (3 × 50 mL). The organic layer was dried over magnesium sulfate and filtered. The solvent was evaporated to dryness under reduced pressure using a rotovap to yield the crude alkylation product. After recrystallization from *n*-hexane the pure product was obtained (white crystals: 5.9 g, 17.5 mmol, 59%). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ = 7.55 (bs, 2H), 7.51 (d, J = 8.14 Hz, 2H), 7.42 (dd, J = 8.14 Hz, J = 1.52 Hz, 2H), 3.84 (q, J = 7.46 Hz, 1H), 1.42 (d, J = 7.63 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.9, 138.8, 130.6, 127.8, 121.6, 121.5, 42.8, 18.2. HR-MS: m/z (%) = 334.91 (47) [M$^+$, ^{79}Br + ^{79}Br], 336.91 (100) [M$^+$, ^{79}Br + ^{81}Br], 338.91 (50) [M$^+$, ^{81}Br + ^{81}Br].

2,7-Dibromo-9-dodecyl-9-methylfluorene. In a 250 mL two-neck round-bottom flask equipped with a condenser and a stopcock 5.8 g of 2,7-dibromo-9-methylfluorene (17.2 mmol) was dissolved in 85 mL of DMSO. Then, 20 mL of a 50 wt % aqueous KOH solution was added. The mixture adopts a deep red color. 20 mg of 18-crown-6 was added. The mixture was stirred for 1 h, and 5.2 g of 1-bromododecane (21.0 mmol, 1.1 equiv) was added. The reaction mixture was warmed up to 80 °C and stirred for a further 12 h at this temperature. Then the mixture was allowed to warm up to room temperature and poured into a separatory funnel containing 100 mL of water and 100 mL of chloroform. The layers were separated and the aqueous phase three times extracted with chloroform (3 × 50 mL). The combined organic layers were washed three times with water to remove DMSO traces, dried over anhydrous sodium sulfate, and filtered. The solvent was removed by rotary evaporation, and the residual oil was purified by column chromatography over silica gel (eluent: *n*-hexane) to give 5.6 g (11.0 mmol, 64%) of 2,7-dibromo-9-dodecyl-9-methylfluorene as colorless crystals. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 32 °C): δ = 7.46 (d, J = 8.1, 2H), 7.42 (s, 2H), 7.39 (dd, J = 8.1, 1.7, 2H), 1.82 (m, 2H), 1.36 (s, 3H), 1.27 − 0.91 (m, 18H), 0.79 (t, J = 6.6, 3H), 0.66 − 0.51 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 32 °C): δ = 154.3, 138.3, 130.5, 126.5, 121.7, 121.7, 51.5, 40.6, 32.2, 30.1, 29.9, 29.8, 29.6, 29.5, 26.6, 24.5, 23.0, 14.5. FD-MS: m/z (%) = 426.5 (15), 428.5 (16), 505.7 (85) [M$^+$, ^{79}Br + ^{79}Br], 506.7 (100) [M$^+$, ^{79}Br + ^{81}Br], 507.7 (86) [M$^+$, ^{81}Br + ^{81}Br].

rac-(2-Bromo-9-dodecyl-9-methylfluorene)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **F1-12**. To a solution of 2,7-dibromo-9-dodecyl-9-methylfluorene (5.6 g, 11.0 mmol) in dry THF (40 mL) in a 250 mL Schlenk flask equipped with a septum at −78 °C a 1.6 M solution of *n*-BuLi in hexane (9.0 mL, 14.4 mmol) was added dropwise under an argon atmosphere. The mixture was stirred for 1 h at −78 °C. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.7 g, 14.3 mmol) was slowly added, and the reaction mixture was stirred for another 15 min at −78 °C. Afterward, the solution was allowed to warm up to room temperature and stirred for an additional 24 h before being poured into water. The aqueous phase was separated and then extracted with dichloromethane. The collected organic layers were dried over anhydrous sodium sulfate, and the solvent was removed by rotary evaporation. After column chromatography over silica gel (eluent: *n*-hexane) a slightly yellow oil was isolated (4.4 g, 8.0 mmol, 72%).

Preparative Enantiomeric Separation of **F1-12** *by HPLC.* Preparative HPLC was conducted using a SD1 pump system, with sample injection via an online injection pump. Preparative separations utilized a column (5 × 25 cm) packed with Chiracel OD. As mobile phase a mixture of 2-propanol/*n*-hexane (0.1:99.9) was used with a flow rate of 40 mL/min and a pressure of 4 bar. The detection was accomplished with a Prostar 320 UV−vis detector at λ = 254 nm and a Knaur RI detector. For the injection of the starting product a solution of the **F1-12** racemate with a concentration of 50 mg/mL was used.

A total of 1.0 g of the racemate as starting product yielded 320 mg (32%) of (−)-(2-bromo-9-dodecyl-9-methylfluorene)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) ($[\alpha]_D^{20.5}$ = −3.60°) in >99% ee (HPLC) and 250 mg (25%) of (+)-(2-bromo-9-dodecyl-9-methylfluorene)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) ($[\alpha]_D^{20.5}$ = +3.48°) in >99% ee (HPLC) as colorless oils of high viscosity. The absolute configuration of the two isolated enantiomers was not determined until now. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 7.6 Hz, 1H), 7.79 (s, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 1.5 Hz, 1H), 7.46 (dd, J = 8.1 Hz, J = 1.5 Hz, 1H), 1.97 (m, 2H), 1.46 (s, 3H), 1.38 (s, 20H), 1.05−1.31 (m, 12H), 0.87 (t, J = 6.9 Hz, 3H), 0.63 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.7, 155.0, 151.0, 142.0, 139.0, 134.0, 130.0, 128.9, 126.3, 121.6, 121.6, 119.2, 83.8, 51.1, 40.4, 31.9, 31.6, 29.9, 29.6, 29.5, 29.3, 29.2, 26.5, 24.9, 24.9, 24.2, 22.7, 14.1. GC-MS: m/z (%) = 383.3 (100), 385.3 (100), 473.6 (19) [M$^+$−Br], 552.4 (100) [M$^+$, ^{79}Br], 554.4 (63) [M$^+$, ^{81}Br].

Polymer Synthesis. *Atactic Poly(9-dodecyl-9-methylfluorene)* **a-PF1-12**. A 10 mL microwave tube was charged with *rac*-(2-bromo-9-dodecyl-9-methylfluorene)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **F1-12** (90 mg, 0.16 mmol), KOH (51 mg, 0.91 mmol), and $PdCl_2(PPh_3)_2$ (5 mg, 0.05 mol %) and sealed under argon. Degassed THF (4 mL) and 5 droplets of degassed water were added. Afterward, the reaction mixture was irradiated with microwaves (300 W) for 12 min at a temperature of 120 °C. The mixture was then poured into water and extracted with chloroform. The chloroform extract was subsequently washed with 2 M aqueous HCl, concentrated aqueous $NaHCO_3$ solution, concentrated aqueous titriplex solution, and brine. The solution was dried over Na_2SO_4, and the solvent was removed by rotary evaporation. The residue was redissolved in chloroform, precipitated into methanol, and Soxhlet extracted with methanol for 1 day. Reprecipitation into methanol gave a slightly yellow powder. To obtain a polymer with a narrow polydispersity and a well-defined molecular weight the **a-PF1-12** polymer was fractionated by preparative GPC utilizing a Gilson 25SC pump system with online injection. The preparative fractionation was carried out on a 2 × 25 cm column packed with MZ Gel SPlus (500 Å) with a Gilson 115 UV/vis detector at λ = 254 nm. As mobile phase THF with a flow rate of 6 mL/min was used. The polymer was injected as THF solution with the concentration of 10 mg/mL. The fractions with a retention time between 8 and 10 min were collected. Afterward, the THF was removed by rotary evaporation. The residue was dissolved in chloroform and reprecipitated into methanol to afford 25 mg (52%) of **a-PF1-12** as a slightly yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$, 32 °C): δ = 7.86 (d, J = 7.63 Hz), 7.67−7.75 (m), 2.03−2.25 (m), 1.67 (s), 1.52−1.59 (m), 1.08−1.33 (m), 0.87 (t, J = 6.9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, 32 °C): δ = 153.3 (C_{ar}), 140.69/140.74 (two signals, C_{ar}), 139.1 (C_{ar}), 126.3 ($C_{ar}H$), 121.48/121.51 (two signals, $C_{ar}H$), 120.2 ($C_{ar}H$), 51.1 (C9), 40.8 (CH_2), 31.9 (CH_2), 30.0 (CH_2), 29.6 (4 × CH_2), 29.3 (2 × CH_2), 27.0 (CH_3), 24.5 (CH_2), 22.7 (CH_2), 14.1 (CH_3).

Isotactic Poly(9-dodecyl-9-methylfluorene) **i-PF1-12**. The isotactic polymer **i-PF1-12** was prepared in the same manner as described for the atactic **a-PF1-12** utilizing (+)- or (−)-(2-bromo-9-dodecyl-9-methylfluorene)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **F1-12**. Yield: 32 mg of i-PF1-12 (67%; starting from **(+)-F1-12** and 27 mg of i-PF1-12 (56%; starting from **(−)-F1-12** as slightly yellow powders. ^{1}H NMR (400 MHz, $CDCl_3$, 32 °C): δ =

7.85 (d, $J = 7.6$ Hz), 7.66−7.76 (m), 1.66 (s), 2.06−2.20 (m), 1.51−1.58 (m), 1.09−1.36 (m), 0.86 (t, $J = 6.9$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$, 32 °C): $\delta = 153.3$ (C_{ar}), 140.7 (C_{ar}), 139.1 (C_{ar}), 126.3 ($C_{ar}H$), 121.5 ($C_{ar}H$), 120.2 ($C_{ar}H$), 51.1 (C9), 40.8 (CH_2), 31.9 (CH_2), 30.0 (CH_2), 29.6 ($4 \times CH_2$), 29.3 ($2 \times CH_2$), 26.9 (CH_3), 24.5 (CH_2), 22.7 (CH_2), 14.1 (CH_3).

Supporting Information Available: ^{1}H and ^{13}C NMR spectra and polarizing microscopy images of **a-PF1-12** and **i-PF1-12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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