# Macromonomer Approach toward Fluorene-Based Monodisperse Conjugated Polymers

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Chain length is one of the factors determining optoelectronic properties of conjugated polymers.[1–5] For examples, energy gap decreases with increasing chain length;[1] film morphology and therefore device performance are chain length dependent.[4,5a] However, direct characterizations of conjugated polymers with different molecular weight to gain sound physical data of chain length−property relationship are generally hampered by the polydisperse nature of synthetic polymers.[6] Monodisperse conjugated oligomers (MCOs) are characterized with well-defined and uniform chemical structures.[6,7] These features qualify them as finite model compounds to attain specific information on their corresponding polydisperse high molecular weight analogues by extrapolation.[1,8] However, since macromolecules differ from oligomers in chain conformation and solution and solid-state properties, it is very difficult to obtain accurate information by extrapolation.[9] This make the synthesis of monodisperse conjugated polymers (MCPs) very intriguing. However, MCOs are usually synthesized by a stepwise approach.[6] The multistep synthetic route and reduced yield with an increase in molecular weight make the synthesis of the MCOs with molecular weight close to macromolecular counterparts very difficult, and only few MCOs/MCPs with molecular weight over 5000 g/mol have been reported to date.[9,10] A previous report has shown that monodisperse conjugated oligomers with few repeating units can be obtained via separation of the polymerization mixture by means of high performance liquid chromatography (HPLC).[11] Therefore, in principle, MCPs can be prepared from separation of the macromonomer polymerization mixture. Herein, we report the successful preparation of the fluorene-based MCPs by combination of the macromonomer polymerization and the separation with recycling preparative size-exclusion chromatography (PSEC).

Scheme 1 outlines the synthesis of macromonomers **PF12-1** and **PF15-1**, which have molecular weights of 4875 and 6041 g/mol, respectively. The boronic acid **2** was synthesized in two steps from **1** in a yield of 88%. The aldehyde group has to be protected before debromination with *n*-BuLi. Suzuki coupling of **2** with 2,7-dibromo-9,9-dioctylfluorene (**3a**) and 7,7′-dibromo-2,2′-bifluorene (**3b**) afforded bifluorene **4a** and terfluorene **4b** in yields of 78 and 70%, respectively. The formyl group in **4b** was then reduced to $-CH_2OH$ with $NaBH_4$ in good yield. Transformation of $-CH_2OH$ to $-CH_2Br$ followed by refluxing with $P(OC_2H_5)_3$ afforded phosphonate ester **7** in a two-step yield of 74%. Formyl-terminated hexafluorene **9** and nonafluorene **11** were synthesized by means of Suzuki coupling in yields of 79 and 90%, respectively. Finally, the Horner−Emmons reaction of **9** and **11** with **7** yielded macromonomers **PF12-1** and **PF15-1** in yields of 66 and 77%, respectively. Since yields in all steps are reasonably high, the macromonomers can be synthesized in gram scale. The chemical structures of **PF12-1** and **PF15-1** were confirmed by means of $^1$H NMR, elemental analysis, and MALDI-TOF mass spectroscopy.

Macromonomers **PF12-1** and **PF15-1** were polymerized by means of Yamamoto coupling reactions as shown in Scheme 2. For ease of separation, the ratio of catalyst and polymerization time were optimized in order to obtain the mixture of polymers with low polymerization degree. Shown in Figure 1a is the PSEC profile of polymerization mixture of **PF15-1** with 2.0 equiv of $Ni(COD)_2$ and a polymerization time of 24 h. The peaks corresponding to MCPs with polymerization degree of 1−4 (**PF15-*n***, $n = 1-4$) became distinguishable after three cycles, and **PF15-1** and **PF15-2** can be completely separated in the first cycle and the second cycle, respectively. In real separation process, polymers with polymerization degree >4 (corresponding to the profile tail at the short retention time) were carefully disposed and separable **PF15-*n*** were collected in each cycle for simplifying the process. After three cycles, all **PF15-1** and **PF15-2** and most of **PF15-3** were successfully collected. The mixture of **PF15-3**, **PF15-4**, and higher **PF15-*n*** was collected and reinjected into PSEC for multirecycling to obtain pure **PF15-3** and **PF15-4**. Finally, **PF15-2**, **PF15-3**, and **PF15-4** were obtained in yields of 16.1, 13.0, and 7.4%, respectively. Separation of MCPs based on **PF12-1** was much easier as indicated in Figure S1 (see Supporting Information). For a polymerization mixture with 1.4 equiv of $Ni(COD)_2$ and a polymerization time of 24 h, **F12-2**, **PF12-3**, and **PF12-4** were obtained in yields of 20.6, 11.9, and 6.7%, respectively, after three cycles.

All MCPs, i.e., **PF12-*n*** and **PF15-*n***, were characterized with gel-permeation chromatography (GPC) with polystyrene (PS) and chloroform as standard and eluent, respectively. Weight-average molecular weights ($M_w$), polydispersity indices (PDIs), and calculated molecular weights ($M_{cal}$) are collected in Table 1. MCPs with $M_{cal}$ of 4875−23 685 and $M_w$ of 7800−58 300 were successfully obtained. It should be pointed out that the longest MCP, i.e., **PF15-4**, has a $M_{cal}$ of 23 685 and a $M_W$ of 58 300 and is the longest linear conjugated molecule reported to date. All MCPs exhibit a narrow GPC profile (see Figure 1b and Figure S2 in Supporting Information), and the corresponding PDIs are ≤1.08. These are consistent with their monodisperse characteristic. $M_w$ obtained from GPC measurements deviates from real molecular weights because of the different geometry of these MCPs from PS, a random-coil polymer. This inflation of molecular weights is a general phenomenon for rodlike long conjugated oligomers and polymers.[9,10,12] It should be noted that this deviation is molecular weight dependent. As molecular weight increases, the deviation increases from 1.60 for **PF12-1** to 2.46 for **PF15-4**. From the tendency, the deviation can be even larger as molecular weight further increases. From five samples with $M_{cal} > 10\,000$ in Table 1, we found that $M_{cal}$ and $M_w$ fit a formula: $M_{cal} = (M_w)^{0.917}$. This empirical formula allows one to estimate molecular weight or polymerization degree of structurally similar conjugated polymers from GPC measurements more accurately. However, it should be pointed out that this formla need further revision once MCPs with even higher molecular weight are prepared. Polarizing optical microscopic (POM) observations reveal that all **PF12-*n*** and **PF15-*n*** are

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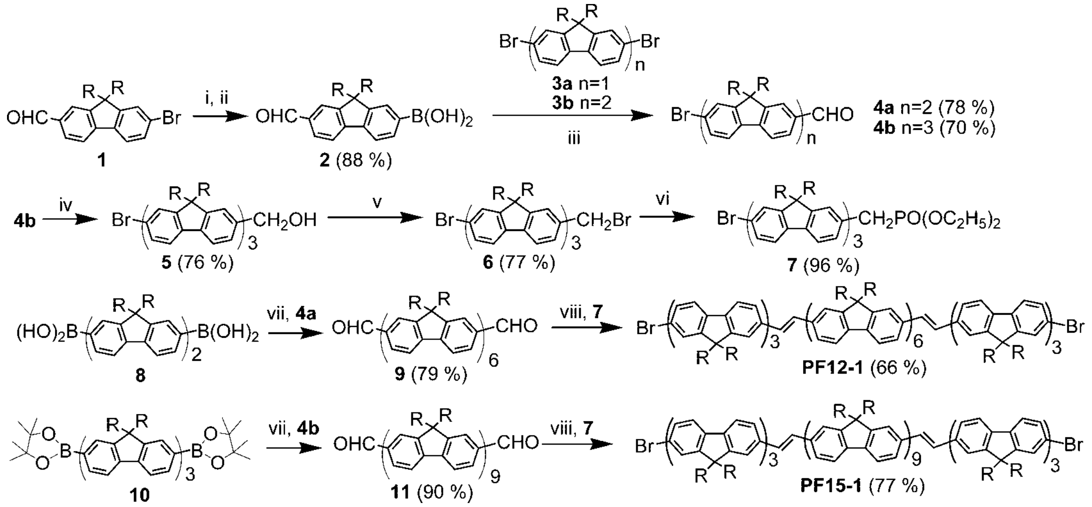
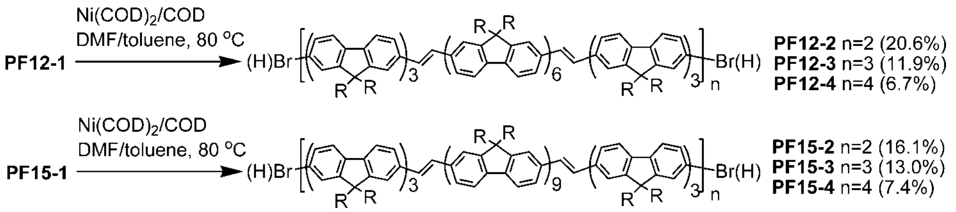
**Scheme 1. Synthesis of Macromonomers PF12-1 and PF15-1**[a]



[a] (i) $HOCH_2CH_2OH$, *p*-TsOH, toluene, reflux; (ii) (1) *n*-BuLi, THF, −78 °C, (2) $(CH_3O)_3B$, room temperature, (3) 2.0 M aqueous HCl; (iii) $Pd(PPh_3)_4$, $Na_2CO_3$, toluene/$H_2O$, 90 °C; (iv) $NaBH_4$, THF, room temperature; (v) $CBr_4/PPh_3$, THF, 0 °C to room temperature; (vi) $P(OC_2H_5)_3$, refluxing; (vii) $Pd(PPh_3)_4$, $Na_2CO_3$, THF/$H_2O$, refluxing; (viii) KO*t*Bu, THF, 0 °C to room temperature. R = *n*-octyl.

**Scheme 2. Yamamoto Polymerization of Macromonomers PF12-1 and PF15-1**



nematic mesomorphic, and the nematic-to-isotropic transition temperature ($T_c$) dramatically increases from **PF12-1** and **PF15-1** to **PF12-2** and **PF15-2** and then slowly increases with the further increase of the molecular length. This probably implies that the polymers begin to deviate from rigid-rod geometry while $n \geq 2$. Solution absorption and photoluminescence spectra (see Supporting Information) are identical with $n = 1-4$ for both **PF12-*n*** and **PF15-*n*** and are red- and blue-shifted compared to polyfluorenes[4] and poly(fluorene vinylene)s,[13,14] respectively.

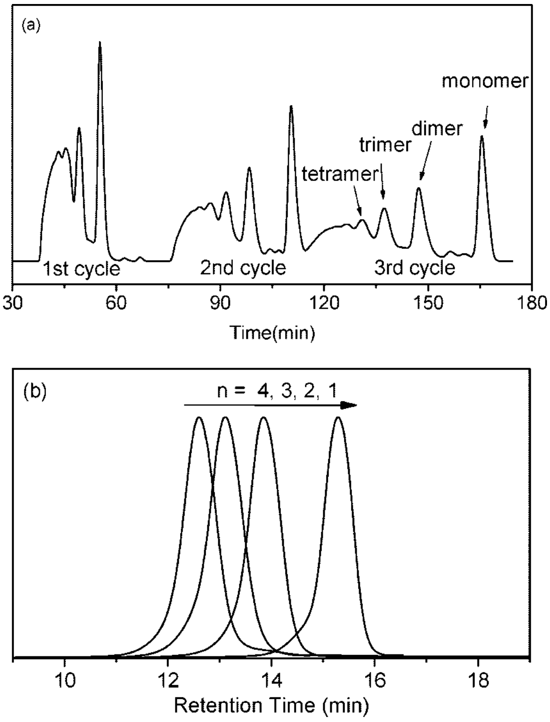


**Figure 1.** PSEC profile (a) of polymerization mixture of **PF15-1** with toluene as eluent and GPC profiles (b) of **PF15-1**, **PF15-2**, **PF15-3**, and **PF15-4** at 40 °C with chloroform as eluent.

**Table 1. Calculated Molecular Weight ($M_{cal}$), Weight-Average Molecular Weight ($M_w$), and Polydispersity Index (PDI) and Nematic-to-Isotropic Transition Temperature ($T_c$)**

| compound | $M_{cal}$ (g/mol)[a] | $M_w$ (g/mol)[b] | PDI[b] | $M_w/M_{cal}$ | $T_c$ (°C)[c] |
|---|---|---|---|---|---|
| **P12-1** | 4 875 | 7 800 | 1.04 | 1.60 | 120 |
| **P12-2** | 9 591 | 20 300 | 1.04 | 2.12 | 220 |
| **P12-3** | 14 306 | 33 900 | 1.05 | 2.37 | 240 |
| **P12-4** | 19 022 | 46 200 | 1.06 | 2.43 | 265 |
| **P15-1** | 6 041 | 10 900 | 1.05 | 1.80 | 145 |
| **P15-2** | 11 922 | 27 100 | 1.05 | 2.27 | 245 |
| **P15-3** | 17 804 | 42 900 | 1.07 | 2.41 | 250 |
| **P15-4** | 23 685 | 58 300 | 1.08 | 2.46 | 275 |

[a] Calculated based on Br-terminated structure; however, partially debromination products cannot be excluded according to $^1H$ NMR spectra. [b] Measured by GPC with PS as standard and chlororm as eluent. [c] Identified by polarizing optical microscopy.

In summary, we have demonstrated that it is possible to obtain monodisperse conjugated polymers (MCPs) from polymerization of macromonomers. We believe that this approach can be used to synthesize MCPs with different unit structures for fully establishing the molecular weight (or chain length)−property relationship.

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**Supporting Information Available:** Synthesis details of all compounds, PSEC profile of polymerization mixture of **PF12-1**, GPC profiles of **PF12-1**, **PF12-2**, **PF12-3**, and **PF12-4**, and solution absorption and photoluminescence spectra of **PF12-*n*** and **PF15-*n***. This material is available free of charge via the Internet at http://pubs.acs.org.

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