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Synthesis and Characterization of Repeating Sequence Copolymers of Fluorene and Methylene Monomers

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ABSTRACT: A series of well-defined multiblock (mb) copolymers consisting of alternating 9,9-dihexylfluorene and methylene segments has been prepared. Poly(9,9-dihexylfluorene-*mb*-methylene)s (PFMs) with repeat units of F_xM_y ($x = 1-4$, $y = 10$, 18 and $x = 5-8$, $y = 18$) were assembled by tandem metal-catalyzed acyclic diene metathesis (ADMET) polymerization/hydrogenation from α,ω-olefin bearing precursors. The polymers exhibited weight-average molecular weights ranging from $M_w = 10$ to 57 kDa. The PFMs exhibit photophysical properties, absorbance, and emission consistent with the length of the fluorene sequence. Glass and melting transition temperatures also increase with fluorene segment length.

Introduction

Polymers that emit light are of growing interest due to their potential applications in the field of optoelectronics.[1−5] Among this class of materials, blue-light-emitting polyfluorenes (PFs) have been the focus of much attention because of the combination of thermal stability, high quantum yields, and good charge transport properties that make them highly suitable for inclusion in organic light-emitting devices, solar cells, and thin film transistors.[6−8] As with most materials, however, there remains room for improvement and many researchers have been engaged in preparing PFs with higher stabilities, better processability, and precisely selected photophysical properties. For example, a substantial amount of research on PFs has focused on the installation of property-enhancing groups in the 9-position (Figure 1).[9−13] Although many variations have been reported, the majority of PFs feature solubilizing alkyl groups. Another general focus in creating enhanced PFs is the copolymerization of fluorene with other conjugated aryl monomers such as carbazole, naphthalene, etc.[14]

The desire to improve and understand PFs has also driven an interest in the preparation and characterization of well-defined fluorene oligomers.[17−21] This research has produced significant insight into the structure/function relationships of PFs. The optical properties, for example, were found to scale with the number of repeat units, each additional unit shifts both absorption and emission to longer wavelengths. On the basis of this correlation, the effective conjugation length in PF has been estimated at approximately 12−14 bonded fluorene units.[17,21]

In addition to providing structure/function correlations, PF oligomers have certain advantages in tunability and stability over polymeric PFs. The precise nature of the structure translates into narrow absorption and emission bands whose frequency can be selected based on the number of repeat units;[17−21] pure PF polymers cannot be as easily tuned. Another benefit of the oligomeric structure is that the materials produced can be thoroughly purified such that they contain far fewer defects than polymers produced under typical conditions. Since the presence of keto-defects has been implicated in the degradation of the characteristic blue emission to a green-yellow emission in PFs,[22−35] this property is of particular interest. Oligomeric polyfluorenes have in fact exhibited increased stability toward the production of the undesired green emission.[21,36]

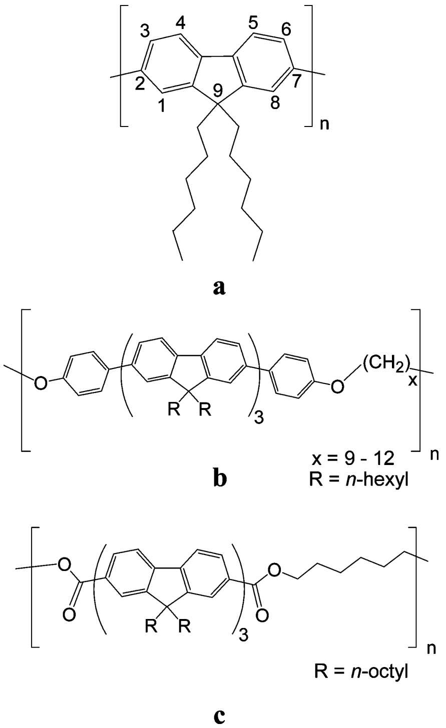

Figure 1. (a) Poly(9,9-dihexylfluorene) **PDHF**; (b) multiblock copolymers by Kallitsis and co-workers employing phenylether linkages;[15] (c) copolymer by Durocher and co-workers employing ester linkages.[16]

Despite the advantages offered by oligomers, they do not represent a universal solution to the problems inherent in making PF materials for inclusion in optoelectronic devices. Oligomeric molecules, unless they are of sufficient length to exhibit entanglement, do not typically have useful mechanical properties, and the formation of the films used in layered devices is generally achieved only by vacuum deposition.

It is our objective to combine the stability and well-defined electronic properties of oligomers with the processability and mechanical properties of polymeric materials by synthesizing macromolecules consisting of fluorene oligomers separated by alkyl spacers. Although a few multiblock copolymers in this class have been previously reported (Figure 1),[15,16] no other

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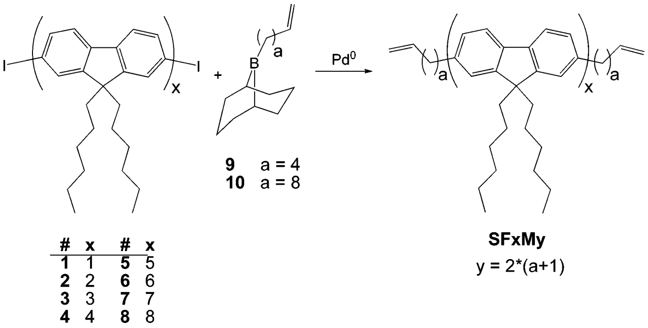
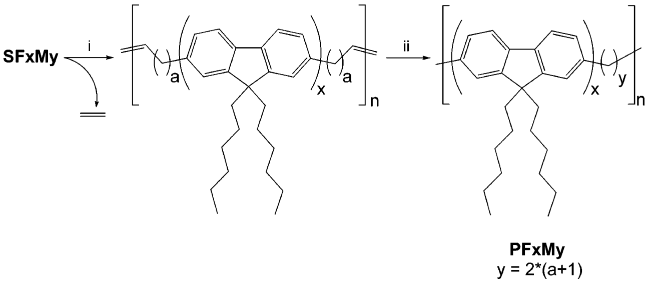
Scheme 1



Scheme 2[a]



[a] (i) 2.5 mol% Grubbs-I catalyst, Ph_2O, room temp to 45 °C. (ii) SiO_2, H_2 (180 psi), PhMe, 80 °C, 2d.

group has systematically prepared polymers with a range of fluorene segment lengths nor has anyone used the extremely advantageous acyclic diene metathesis (ADMET) process in their approach.

The ADMET reaction, which has been developed primarily by Wagener and co-workers, is particularly suitable for the preparation of multiblock copolymers.[37−39] When coupled with a postpolymerization hydrogenation step, the reaction allows the facile production of a polymer with alternating fluorene and alkyl segments. It is particularly attractive to use simple alkyl group spacers because, relative to the ester and phenylether functional groups used in previous approaches to fluorene multiblocks, they cause a smaller perturbation of the photophysical properties of the fluorene chromophore. Finally, since the only side-product of ADMET is ethylene, isolation of polymers of extremely high purity is facile.

Results and Discussion

Synthesis. Diiodo-functionalized oligomers **1**−**8**, prepared according to the procedures of Geng et al.,[20] were converted into segmers SF$_x$M$_y$ ($x = 1-4$, $y = 10$, 18 and $x = 5-8$, $y = 18$) by palladium-catalyzed Suzuki coupling with ω-alkenyl boranes **9** and **10** (as shown in Scheme 1).[40] In a typical preparation, oligomer **3** was coupled with a slight excess of ω-alkenyl borane **9** to give an 85% yield of **SF3M10** after purification by column chromatography. The segmers are colorless to pale green and are isolated as viscous oils or powders that are soluble in most organic solvents.

The segmers SF$_x$M$_y$ were then polymerized to give the polymers PF$_x$M$_y$ using the tandem ADMET polymerization/hydrogenation process reported by Wagener et al.[41] In a typical preparation, segmer **SF3M10** and Grubbs-I catalyst, Ru=CHPh)$Cl_2(PPh_3)$, in the high-boiling solvent diphenyl ether were heated under vacuum to drive the reaction by removal of the ethylene byproduct. The viscous reaction mixture was diluted with toluene, treated with silica, and without isolation, subjected to hydrogenation (as shown in Scheme 2).

Table 1. Molecular Weights of Poly(9,9-dihexylfluorene-*mb*-methylene)s and Poly(9,9-dihexylfluorene)

copolymer[a]	M_n[b] (kDa)	M_w[b] (kDa)	PDI[b]
PF1M10	14	30	2.1
PF2M10	9.2	17	1.9
PF3M10	26	44	1.7
PF4M10	7.0	9.8	1.4
PF1M18	16	33	2.1
PF2M18	13	22	1.7
PF3M18	13	20	1.5
PF4M18	13	19	1.4
PF5M18	36	57	1.6
PF6M18	24	46	1.9
PF7M18	36	57	1.6
PF8M18	14	22	1.6
PDHF	22	56	2.6

[a] PF$_x$M$_y$: polymer with alternating blocks of x fluorene units and y methylene units. PDHF: poly(9,9-dihexylfluorene). [b] Molecular weights and PDIs determined by gel permeation chromatography vs polystyrene standards.

The degree of completion of both of the reactions was monitored periodically by ^{1}H NMR spectroscopy. The polymerization was halted when the signals for the terminal olefins centered at δ 4.9 and 5.8 ppm were replaced by those of the polymer's internal olefin at δ 5.4 ppm (a mixture of cis/trans in which trans predominates). Hydrogenation was also monitored by NMR spectroscopy. The reaction was halted when the internal olefin signal at δ 5.4 ppm was no longer visible. On the basis of the sensitivity of the NMR we can set an upper limit for the number of double bonds remaining at ∼2%. As a control, the homopolymer, poly(9,9-dihexylfluorene) (**PDHF**), was prepared according to the method described by Kreyenschmidt et al.[42]

Characterization. All of the polymers exhibit high solubilities in common organic solvents such as hexanes, toluene, chloroform, tetrahydrofuran, and dichloromethane. Films are easily prepared by spin- or dropcasting from a variety of solvents.

Gel permeation chromatography (GPC) analyses in tetrahydrofuran (THF) were performed on all polymers. The results are summarized in Table 1 and are reported relative to PS standards. Most samples exhibit M_n values of 10 kDa or greater. For the polymers prepared from longer fluorene segments, the GPC distributions are not smooth. We hypothesize, given the rather large molecular weights of the individual segmers, that resolution by degree of polymerization is responsible. We were unable to calibrate these molecular weights by NMR due to the accidental overlap of key resonances.

Spectroscopy. As the PFMs prepared incorporated oligofluorenes of exact segment length, our expectation was that their solution and thin-film optical properties would track with the trends reported in the literature for the isolated oligomers.[17−21,36] As shown in Figure 2, PFMs in dilute solution ($CHCl_3$, $\sim 10^{-6}$ M based on fluorene content) give maximum light absorption and emission at progressively longer wavelengths as the number of fluorenes per sequence increases. The λ_{abs} and λ_{em} asymptotically approach those associated with the homopolymer such that polymers with seven and eight fluorene repeat units exhibit spectroscopic properties that closely mimic those of **PDHF**. The bulk-phase emission spectra show the same trend (Figure 2c). The spectroscopic data are summarized in Table 2.

Thermal Properties. The series of polymers were subjected to differential scanning calorimetry, and the results of these experiments are shown in Figure 3 and Table 3. The polymers showed weak glass transitions, some of which could not be

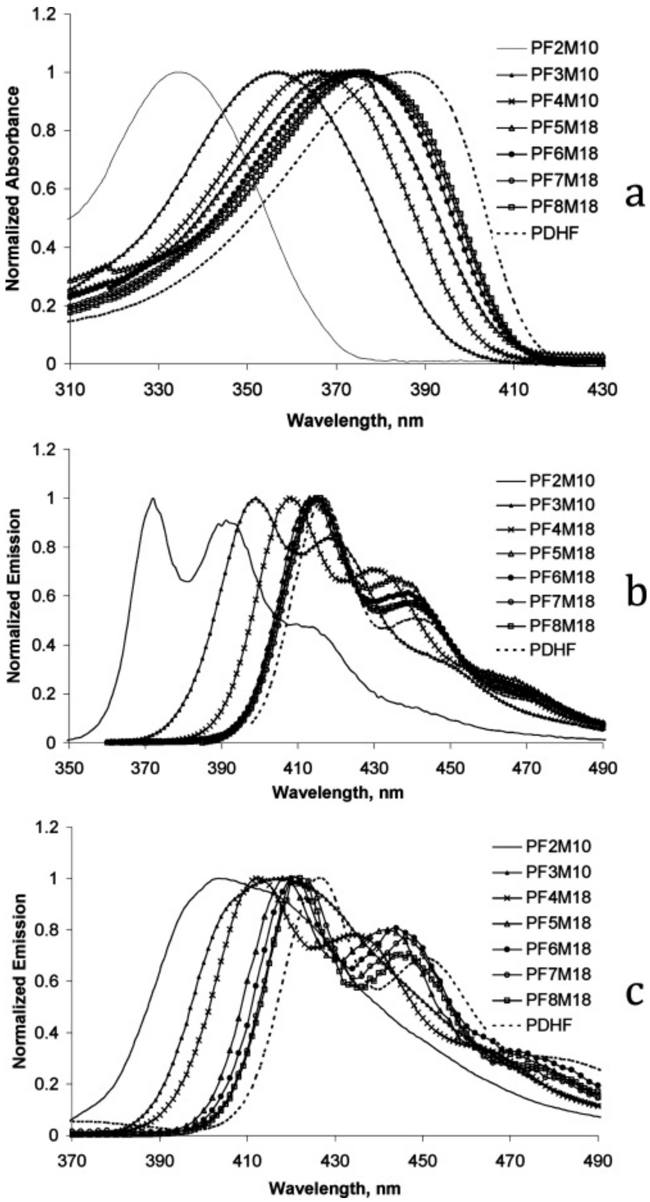


Figure 2. The absorbance (a) of poly(9,9-dihexylfluorene-*mb*-methylene)s as dilute (~10^{-6} M) solutions in $CHCl_3$. The emission spectra of indicated PFMs as dilute (~10^{-6} M) solutions in $CHCl_3$ (b) and as thin films (c). Abbreviations: **PF$_x$M$_y$**: polymer with alternating blocks of *x* fluorene units and *y* methylene units. **PDHF**: poly(9,9-dihexylfluorene).

assigned unambiguously and melting point transitions which increase with the longer fluorene segmer lengths. Cooling scans show no crystallization peaks. The DSC trace for **PF8M18** is anomalous and more difficult to interpret. We have tentatively assigned the transition at 76 °C as a glass transition. Polarized optical microscopy of the polymers did not reveal any liquid crystalline phases.

Conclusions

A series of multiblock copolymers of fluorene and methylene units were prepared and characterized. These polymers exploit exact sequence to give materials with good film-making properties and tunable emissions in the blue range. Studies are currently underway to further characterize the copolymers and to develop structure−function relationships based on fluorene and methylene segment lengths.

Table 2. Summary of Absorbance and Emission Data for Poly(9,9-dihexylfluorene-*mb*-methylene)s

copolymer[a]	λ_{abs}, $CHCl_3$ (nm)	λ_{em}, $CHCl_3$ (nm) (λ_{ex}/nm)[b]	λ_{em}, film (nm)
PF1M10	279	330 (300)	386
PF2M10	335	371 (335)	400
PF3M10	356	401 (355)	418
PF4M10	365	409 (365)	414
PF1M18	278	332 (300)	374
PF2M18	335	372 (335)	403
PF3M18	354	399 (355)	416
PF4M18	366	408 (365)	412
PF5M18	371	413 (350)	418
PF6M18	374	415 (350)	420
PF7M18	376	416 (375)	420
PF8M18	375	415 (375)	422
PDHF	385	417 (388)	427

[a] PF$_x$M$_y$: polymer with alternating blocks of *x* fluorene units and *y* methylene units. PDHF: poly(9,9-dihexylfluorene). [b] Values in parentheses are the excitation wavelengths used to collect emission spectra for both solution and film samples.

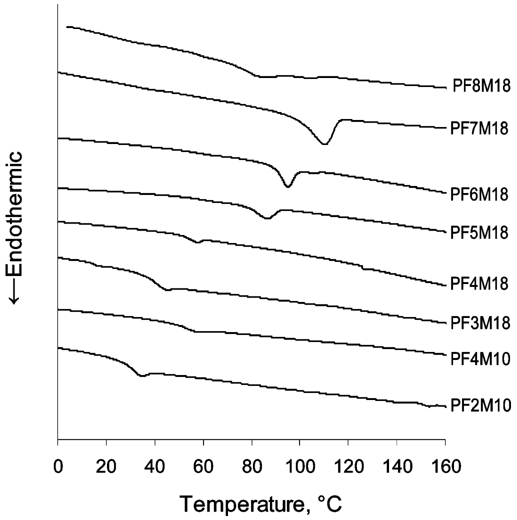


Figure 3. DSC traces for poly(9,9-dihexylfluorene-*mb*-methylene)s (first heating at 20 K/min).

Table 3. Thermal Properties[a]

copolymer	T_g (°C)	T_m (°C)
PF2M10[b]	n.d.[c]	34
PF4M10	n.d.[c]	58
PF3M18	18	46
PF4M18	n.d.[c]	57
PF5M18	59	89
PF6M18	58	95
PF7M18	61	113
PF8M18	76	

[a] Determined by DSC, first heating at 20 K/min. [b] PF$_x$M$_y$: polymer with alternating blocks of *x* fluorene units and *y* methylene units. [c] Not determined. Transition could not be unambiguously assigned.

Experimental Section

Toluene was distilled under nitrogen from sodium. 1,5-Hexadiene (98%, Acros) and 1,9-decadiene (97%, Acros and 96% Aldrich) were distilled under nitrogen from calcium hydride. $Pd(PPh_3)_4$ (Strem), $PdCl_2(PPh_3)_2$ (99.9+%, Strem), and Grubbs-I catalyst Ru-(=CHPh)$(PPh_3)Cl_2$ (Aldrich, Strem) were commercially obtained and stored in a nitrogen-filled glovebox. All other reagents were commercially obtained and used without further purification. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded with Bruker spectrometers. Chemical shifts were referenced to residual ^1H or ^{13}C signals in deuterated solvents. Column chromatography was performed using Sorbent 60 Å 40−63 μm standard grade silica. GC−MS was performed on a Hewlett-Packard Series 5980 GC/5971 A MS with a Hewlett-Packard Series 1 column. GC was performed on a Hewlett-Packard Series 6850 GC with a Hewlett-Packard Series 1 methyl siloxane column. HRMS data were obtained on a Fison VG Autospec in the Mass Spectral Facility of the University of Pittsburgh. GPC data were acquired in THF (HPLC grade, Fisher) on a Waters system equipped with a 510 pump, a U6K universal injector, and a 410 differential refractometer. GPC separations were achieved at 25 °C on Phenogel (500 and 1000 Å) or Jordi Gel DVD (500, 1000, and 10 000 Å) eluting at 0.4 mL/min. Differential scanning calorimetry was performed on a Thermal Analyst 2000 (TA instruments) DSC 2910 differential scanning calorimeter. Elemental analysis was performed independently by Atlantic Microlab, Inc., Norcross, Georgia. Diiodo(9,9-dihexylfluorene) oligomers were prepared according to the approach of Geng et al.[20] Boranes **9** and **10** were prepared according to the approach of Chung.[40]

General Procedure for the Preparation of SF$_x$M$_y$ Compounds. Method A: SF2M10. With the adaptation of the method of Peifer,[43] diiodobifluorene **2** (1.18 g, 1.29 mmol) was combined with 28 mL of dimethylformamide (DMF), 28 mL of toluene, $Pd(PPh_3)_2Cl_2$ (45 mg, 5 mol %), and K_2CO_3 (0.80 g, 5.8 mmol, 4.2 equiv) in a flame-dried Schlenk flask under nitrogen. 9-Hex-5-enyl-9-BBN **9** (0.75 mL, 3.2 mmol, 2.3 equiv) was then added under nitrogen by syringe as a solution in 5 mL of DMF. The mixture was stirred for 8 h at 45 °C, at which point the contents were poured into water for extraction with hexanes (3 × 50 mL). The organic extracts were combined, washed with brine, and dried with $MgSO_4$. After solvent removal under vacuum, column chromatography (silica, hexanes) afforded **SF2M10** as a colorless oil (0.76 g, 71%). ^1H NMR (300 MHz, $CDCl_3$) δ 0.76 (b, 20 H, $-CH_3$ and $-CH_2-$), 1.07 (b, 24 H, $-CH_2-$), 1.45 (quintet, 4 H, $-CH_2-$), 1.69 (quintet, 4 H, $-CH_2-$), 1.98−2.09 (m, 12 H, $-CH_2-CH{=}CH_2$ and $>C-(CH_2-)_2$), 2.70 (t, $J = 7.4$ Hz, 4 H, $Ph-CH_2-$), 4.95 (m, 4 H, $-CH{=}CH_2$), 5.81 (m, 2 H, $-CH{=}CH_2$), 7.13 (m, 4 H, $Ph-H$), 7.57−7.70 (m, 8 H, $Ph-H$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1 ($-CH_3$), 22.7, 23.9, 28.6, 29.8, 31.4, 31.6, 33.8, 36.2, 40.5, 55.1, 114.5, 119.6, 121.4, 123.2, 126.0, 127.2, 138.6, 139.0, 140.2, 140.5, 141.8, 151.2, 151.5. Anal. Calcd for $C_{62}H_{86}$: C, 89.57; H, 10.43. Found: C, 89.61, H, 10.51. HRMS calcd for $C_{70}H_{102}$: 830.6730. Found: 830.6846.

Method B: SF3M10. In a variation of the method of Thiem,[44] diiodoterfluorene **3** (0.63 g, 0.51 mmol) was combined with tetrabutylammonium bromide (25 mg, 0.15 mmol, 30 mol %), 17 mL of toluene, and aqueous K_2CO_3 (6.8 mL × 2.0 M, 13.6 mmol) in a Schlenk flask. The mixture was thoroughly degassed, and $Pd(PPh_3)_2Cl_2$ (17 mg, 3 mol %) and 9-hex-5-enyl-9-BBN **9** (0.43 mL, 1.8 mmol, 4 equiv) were added under nitrogen. The reaction mixture was heated at 45 °C for 8 h. Upon cooling, the organic phase was separated and the aqueous phase was extracted with hexanes (3 × 30 mL). The organic extracts were combined, washed with brine, and dried with $MgSO_4$. After solvent removal under vacuum, column chromatography (silica, hexanes, then 10% CH_2Cl_2 in hexanes) afforded **SF3M10** as a white powder (0.50 g, 84%). ^1H NMR (300 MHz, $CDCl_3$) δ 0.77 (b, 30 H, $-CH_3$ and $-CH_2-$), 1.10 (b, 36 H, $-CH_2-$), 1.42 (quintet, 4 H, $-CH_2-$), 1.67 (quintet, 4 H, $-CH_2-$) 2.02−2.11 (m, 16 H, $-CH_2-CH{=}CH_2$ and $>C-(CH_2-)_2$), 2.71 (t, $J = 7.4$ Hz, 4 H, $Ph-CH_2-$), 4.97 (m, 4 H, $-CH{=}CH_2$), 5.82 (m, 2 H, $-CH{=}CH_2$), 7.14 (m, 4 H, $Ph-H$), 7.60−7.81 (m, 14 H, $Ph-H$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.5, 23.9, 28.5, 29.7, 31.2, 31.5, 33.6, 36.2, 40.4, 55.1, 55.4, 114.3, 119.5, 119.7, 121.6, 123.1, 126.1, 126.7, 127.1, 138.7, 138.9, 140.1, 140.3, 140.6, 140.8, 141.8, 151.4, 151.6, 151.9. Anal. Calcd for $C_{87}H_{118}$: C, 89.78; H, 10.22. Found: C, 89.54, H, 10.21.

General Procedure for the Preparation of PF$_x$M$_y$ Polymers. PF3M10. With adaptation of the method of Tindall,[38] a pear-shaped flask was charged with **SF3M10** (0.99 g, 0.85 mmol). A gas adapter was fitted to the top, and the flask was evacuated thoroughly. The flask was brought into a nitrogen-filled glovebox, and Ph_2O (0.9 g) and $Ru({=}CHPh)Cl_2(PPh_3)_2$ (14 mg, 2 mol %, added as a solution in 2 mL of toluene) were added. The flask was brought out of the glovebox, and toluene was removed under high vacuum with stirring. High vacuum was then applied to the mixture until the stir bar was immobilized. Stirring was reestablished by heating the flask at 45 °C, and vacuum was applied overnight. The flask was then cooled to room temp and brought into the glove box. The reaction mixture was taken up in 11 mL of toluene and transferred to a stainless steel reaction vessel. To this vessel was added 1.5 g of silica. The vessel was brought out of the glovebox, charged with 180 psi H_2, and heated at 80 °C for 48 h. After cooling the vessel, the contents were subjected to centrifugation and the mother liquor was removed and concentrated. The polymer was isolated by precipitation into acetone with vigorous stirring to yield **PF3M10** as a white solid (0.67 g, 69%). GPC (THF, PS standards) $M_w = 44$ kDa; $M_n = 26$ kDa; PDI = 1.7. ^1H NMR (300 MHz, $CDCl_3$) δ 0.75 (b, 30 H, $-CH_3$ and $-CH_2-$), 0.95−1.45 (b, 48 H, $-CH_2-$), 1.65 (b, 4 H, $-CH_2-$) 2.01 (b, 12 H, $>C-(CH_2-)_2$), 2.68 (t, $J = 7.3$ Hz, 4 H, $Ph-CH_2-$), 7.15 (bs, 4 H, $Ph-H$), 7.59−7.80 (m, 14 H, $Ph-H$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.7, 24.1, 29.5, 29.9, 31.7, 32.0, 36.6, 40.6, 55.3, 55.6, 119.7, 119.9, 121.8, 123.3, 126.3, 126.4, 127.3, 138.8, 140.3, 140.4, 140.8, 141.0, 142.3, 151.5, 151.7, 152.1.

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Supporting Information Available: Detailed experimental procedures for all segmers and polymers and GPC data. This material is available free of charge via the Internet at http://pubs.acs.org.

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