Supporting Information

Functionalization Induced Self-Assembly of Block Copolymers for Nanoparticle Synthesis

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1. Experimental procedures

1.1 Reagents:

Dichloromethane (Chromasolv for HPLC, $\geq$ 99.9 % with 40-150 ppm amylene as stabilizer) was chemically dried with anhydrous magnesium sulfate (99.5 %, Alfa Aesar) and stored over activated molecular sieves (4 Å beads, 4-8 mesh) prior to use. Tetrahydrofuran (THF) (Chromasolv for HPLC, $\geq$ 99.9 %) was deoxygenated with nitrogen and then stored in an inert atmosphere glovebox for all cross-coupling reactions, otherwise, it was used as received. *tert*-Butyl acrylate (99 %) was filtered through an activated basic alumina (Alfa Aesar) column to remove inhibitor. Potassium fluoride (> 99.8 %), tris(dibenzylideneacetone)dipalladium (97 %), and tri-*tert*-butylphosphonium tetrafluoroborate (97 %) were stored in the glovebox before use. Ultrapure nitrogen gas (Airgas), *N,N*-dimethylacetamide (Chromasolv for HPLC, $\geq$ 99.9 %), acryloyl chloride (96 %) stabilized with phenothiazine, chloroform (Macron), methanol (99.8 %, BDH), hexanes (99.9 %, Fisher Chemical), diisopropyl ether ($\geq$ 99 %, stabilized with BHT, Macron), sodium hydroxide pellets ($\geq$ 97.0 %), aqueous hydrochloric acid (37 %), 4-bromobenzyl alcohol (99 %), *N,N*-diisopropylethylamine (99.0 %, VWR), 1-dodecanethiol, carbon disulfide, 2-bromoisobutyric acid (Alfa Aesar), potassium phosphate (anhydrous, 97 %,), ethyl acetate (ACS grade), azobisisobutyronitrile (98 %), dimethyl sulfoxide (99.9 %), phenylboronic acid (95 %,), 2-furanboronic acid (97 %, Ark Pharm), 4-hydroxybenzeneboronic acid (97 %, Alfa Aesar), trifluorobenzeneboronic acid (97%, Alfa Aesar), diphenyl-4-boronic acid (97 %, Ark Pharm), were used as received. All other reagents, unless otherwise noted, were supplied by Millipore Sigma and used as received.
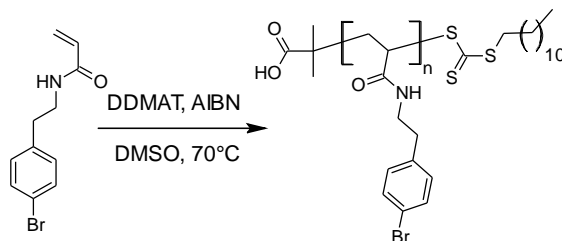
1.2 Synthesis of *N*-[2-(4-bromophenyl)ethyl]acrylamide (BPEA):

A solution of distilled acryloyl chloride (1.7 g, 19 mmol) in dry dichloromethane (10 mL) was added to a mixture of 2-(4-bromophenyl)ethylamine (3.7 g, 18 mmol), *N,N*-diisopropylethylamine (2.5 g, 19 mmol), and dry dichloromethane (20 mL). The acryloyl chloride solution was added to the amine solution in 0.5 mL increments over 45 minutes, while being stirred and submerged in a dry ice-acetone bath. Afterwards, the reaction mixture was kept in the bath overnight, and the temperature of the solution gradually rose to room temperature. The crude reaction mixture was then washed twice with 1M HCl, 1M NaOH, and deionized water, followed by filtration through three basic alumina plugs and three silica gel plugs. The solvent was removed under vacuum and the product was then recrystallized twice in a 70/30 vol. % hexanes/ethyl acetate mixture. Further details for the synthesis and characterization of BPEA are provided in our prior work.[1]

1.3 Synthesis of 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT):

DDMAT was synthesized using a modified procedure reported by Skey *et al.*[2] In a 250 ml round bottom flask, potassium phosphate (20.98 g, 98.8 mmol) and 125 ml ethyl acetate were combined under atmospheric conditions with rapid stirring at room temperature. Quickly, over the course of a couple minutes, dodecanethiol (10.0 g, 49.4 mmol) was added dropwise, followed by 10 minutes of stirring. Next, carbon disulfide (7.52 g, 98.8 mmol) was added in a similar manner, followed by 45 minutes of stirring. Finally, 2-bromoisobutyric acid was added in a similar fashion and the solution was stirred for 24 hours prior to purification. The reaction product was filtered through a coarse glass frit, aided by additions of small amounts of dichloromethane. The solvent was then evaporated under vacuum to yield a dark orange slurry. Next, the product was dissolved in dichloromethane and washed with 1M NaOH, whereupon a solid orange precipitate formed at the interface between the aqueous and organic phases. The precipitate was separated and transferred to a separate flask, and afterward dichloromethane and 1M HCl were added. Upon contact with the acid, the precipitate dissolved once again into the organic phase and the aqueous phase was discarded. The organic phase was then washed twice with deionized water. Finally, the dichloromethane was evaporated under vacuum, and the product was recrystallized twice in hexanes which was subsequently dried under vacuum to yield an orange-yellow powder

1.4 RAFT polymerization of poly(BPEA)-CTA:

N-[2-(4-bromophenyl)ethyl]acrylamide (BPEA) (1.4 g, 5.5 mmol), azobisisobutyronitrile (AIBN, 0.00045 g, 0.0027 mmol), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (0.04 g, 0.11 mmol) were dissolved in dimethyl sulfoxide (2.9 mL) within a scintillation vial. The reaction vessel was then sparged with nitrogen for one hour. The vessel was next transferred to a glove box and placed on a heating block at 70 °C. Polymerization was allowed to proceed for 4 hours. The resulting polymer solution was removed from the glovebox and exposed to air, and then the polymer was precipitated three times from tetrahydrofuran into diisopropyl ether.

1.5 Chain extension of poly(BPEA)-CTA to form poly(BPEA-*b*-tBA)-CTA:
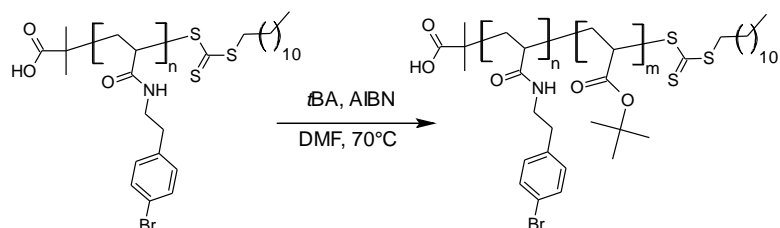
Poly(BPEA)-CTA (0.288 g, 0.040 mmol), *tert*-butyl acrylate (*t*BA, 2.047 g, 15.97 mmol), azoisobutyronitrile (AIBN, 0.000169 g, 0.00103 mmol) were dissolved in a scintillation vial with dimethyl formamide (DMF, 1.961 mL). The mixture was then vortexed to ensure dissolution and the reaction vessel was purged with nitrogen for 30 minutes. The vessel was transferred to a glove box and was placed on a heating block at 70 °C. Polymerization was allowed to proceed for 4 hours. Small aliquots were taken from this solution for SEC and NMR analysis, while the remainder of the solution was used as feedstock for the subsequent UV-initiated cleavage of trithiocarbonate end-groups, described below. Prior to NMR analysis, the NMR sample was precipitated three times in a methanol/water mixture and dried.

1.6 UV-initiated cleavage of trithiocarbonate end-groups to form poly(BPEA-*b*-tBA)-H:
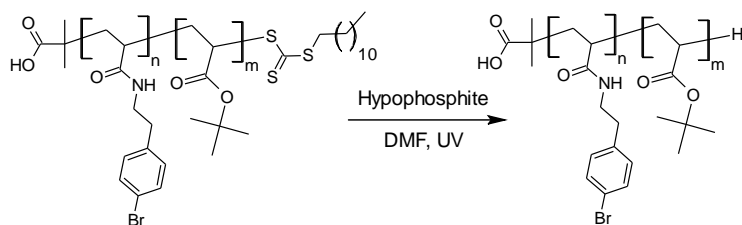
The chain-end cleavage method was based upon a procedure recently reported in the literature.[3] The crude poly(BPEA-*b*-tBA)-CTA solution (3.319 g, 0.032 mmol chain-ends) from section 1.5, 1-ethylpiperidine hypophosphite (0.012 g, 0.065 mmol), and dimethylformamide (1.6 mL) were combined in a 20 ml scintillation vial. The mixture was then vortexed to ensure dissolution of the reagents, followed by sparging with ultrapure nitrogen for ~30 minutes. The reaction vessel was then sealed and placed ~19 cm from a UV source (Spectroline Model SB-100P, 365 nm, 120 Volts) with stirring for ~24 hours. Once completed, the crude reaction mixture was exposed to air, and then the block copolymer was precipitated from a DMF/THF mixture into a 90/10 (v/v) mixture of methanol and deionized water, respectively. Afterward, the precipitated polymer was dissolved in THF and precipitated two more times into the same methanol/water mixture.

1.7 Cross-coupling of block copolymer pendant groups with functional boronic acids:

A representative cross-coupling reaction is as follows (Table S1, Entry 1): The reaction was formulated to have a ratio of $[B(OH)_2]/[Ar\text{-}Br]/[Pd]/[TTBT]/[KF] = 3.7/1/0.12/0.26/9.2$ with a polymer concentration of 100 mg/ml. To a 2 ml vial under ambient conditions were added 0.0232 g of poly(BPEA-*b*-tBA) (*i.e.* corresponding to 0.011 mmol of pendent aryl bromides (Ar-Br)), 0.0048 g of phenylboronic acid (0.039 mmol $B(OH)_2$), 0.0012 g of tris(dibenzylideneacetone)dipalladium (0.0013 mmol Pd), 0.0008 g of tri-*tert*-butylphosphonium tetrafluoroborate (0.0028 mmol TTBT), 0.0057 g of potassium fluoride (0.098 mmol KF), and a magnetic stir bar. The vial was then transferred into a nitrogen-atmosphere glovebox, initiated by addition of 0.23 ml of deoxygenated THF, and maintained at 23 °C with stirring for 5 hours. The vial was then removed from the glovebox and exposed to air. A general characterization and purification protocol for the functionalized product is provided below.

Prior to purification, a small aliquot of the cross-coupling product was set aside for DLS and SEC analysis. This aliquot, approximately 30 mg of crude solution, was diluted into 1 ml of THF and then passed through a 0.20 μm Millex-LG filter before analysis with SEC and DLS. The remainder of the solution was purified by precipitation from THF into a 10 vol % solution of deionized water in methanol. Following centrifugation at 4000 rpm, the supernatant was discarded, and the precipitate was dried overnight at 40 °C under vacuum prior to NMR analysis.

2. Analytical instruments and methods:

2.1 Size exclusion chromatography in THF (SEC-THF):

Samples for SEC-THF were typically prepared by dissolution of 2-3 drops of crude reaction solution (*i.e.*, ~2-3 mg of polymer) in approximately 1 mL of THF, vortexing for several minutes, and filtering through a 0.20 μm filter (Millex-LG). Relative number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), and dispersity ($Đ$) values were determined by analysis conducted with a Shimadzu LC-20AD HPLC pump equipped with a Shimadzu RID-20A 120V refractive index detector using HPLC grade tetrahydrofuran as the mobile phase. Polymer analytes were separated at a flow rate of 1 mL/min at 35 °C using two PLgel mixed-B Agilent columns connected in series and calibrated against 10 linear poly(methyl methacrylate) standards having M_n values ranging from 800 to 2,570,000 g/mol. SEC-THF was used exclusively for all molecular weight evaluations reported in this work except for the poly(BPEA)-CTA homopolymer which was also evaluated *via* SEC-DMAC equipped with a MALS detector.

2.2 Size exclusion chromatography in DMAC (SEC-DMAC) with MALS:

SEC in *N,N*-dimethylacetamide (SEC-DMAC): Relative number-averaged molecular weight (M_n), weight-averaged molecular weight (M_w), and dispersity ($Đ$) values were determined by size exclusion chromatography (SEC). SEC analysis was conducted with a Shimadzu LC-20AD HPLC pump equipped with a Shimadzu RID-20A 120V refractive index detector using HPLC grade *N,N*-dimethylacetamide, containing 0.03 wt. % LiCl as the mobile phase. Polymer analytes were separated at a flow rate of 1 mL/min at 55 °C using two PLgel mixed-B Agilent columns connected in series and calibrated against 10 linear poly(methyl methacrylate) standards having M_n values ranging from 800 to 2,570,000 g/mol. Size exclusion chromatography multi-angle light-scattering (SEC-MALS) in *N,N*-dimethylacetamide was carried out concomitantly on the same Shimadzu instrument for absolute molecular weight determination using a Wyatt TREOS-II MALS detector. Initial analysis was carried out to determine the *dn/dc* value of the analyte, poly(BPEA)-CTA, using the 100 % mass recovery assumption, followed by absolute molecular weight calculations. Sample preparation was similar to SEC-THF except that the sample was purified *via* multiple precipitations from THF into diisopropyl ether and dried thoroughly before analysis to ensure the correct mass was utilized for the 100 % mass recovery assumption. SEC-DMAC with MALS was only conducted on the poly(BPEA)-CTA homopolymer for absolute molecular weight determination. An absolute molecular weight value was necessary to ensure accurate formulations in subsequent post-polymerization functionalization reactions. Due to analyte solubility issues, SEC-DMAC with MALS was not pursued for the other polymers reported in this work.

2.3 Nuclear magnetic resonance (NMR):

2.3.1 ^{1}H NMR sample preparation and acquisition:

NMR samples were obtained by dissolution of purified polymer specimens in ~1 g of $CDCl_3$. Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired using a Unity Inova-500 MHz spectrometer (Varian, USA) at room temperature using 128 scans with a relaxation delay of 1 second. Chemical shifts were based on tetramethylsilane as the internal standard and were reported in ppm.

2.3.2 Percent functionalization ($f_\%$) calculations:

Each NMR spectrum was phased and baselined prior to quantitative analysis. A sample percent functionalization ($f_\%$) protocol for phenyl functionalization (FG-3) is as follows (also see Fig. S2(A)): Integral values (I) were normalized by setting the methylene peak at ~3.4 ppm equal to 2.0 (*i.e.*, $I_a = 2$), representing its two-proton equivalence (H_a). An integral value was then obtained for the aromatic region ($I_{b,c}$) at 7 ppm (+/− 1.5 ppm), designated as $I_{b,c}$. The aromatic proton equivalence from the precursor was then subtracted from the total aromatic region integral value ($I_{b,c}$) to account for the fact that the precursor compound already had 4 proton equivalents in the aromatic region ($H_b = 4$). The remaining area after subtraction represents the number of proton equivalents added to the aromatic region during functionalization, which was then divided by the number of proton equivalence of the functionality installed after cross-coupling. In the case of the phenyl functionalization (FG-3), this was equal to 5 equivalents ($H_c = 5$). For FG-3 and FG-4, spectral subtraction was used to improve accuracy for phenyl and biphenyl functionalized block polymers, by accounting for trace chloroform and residual boronic acid, respectively. For phenol functionalized block copolymers (FG-2), linear interpolation was used to compute $f_\%$ by comparing the experimentally derived ratio between the integration values of the phenol and aromatic region to the theoretical ratios expected at different $f_\%$ values (*e.g.*, a ratio of 1:8 = 100 $f_\%$, a ratio of 0.75:7 = 75 $f_\%$).

2.4 Dynamic light scattering (DLS):

2.4.1 DLS sample preparation and measurement:

Hydrodynamic diameters (D_H) and PDI values were determined at 25 °C with dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS equipped with a 632 nm wavelength, He-Ne laser with a 173° backscattering configuration allowing measurements from 0.3 nm − 10 μm. Typical measurements were reported as the average of approximately 50-300 scans using cumulant analysis. All samples were measured in THF, using a quartz cuvette, with an approximate concentration of 30 mg of crude reaction solution per mL THF (~ 3 mg/mL polymer), unless otherwise noted. DLS results were reported as number-average diameters and number distributions.

2.4.2 DLS data analysis:

Dynamic Light Scattering data analysis was primarily based upon DLS-number traces. The transformation from DLS-intensity to DLS-number is based upon the assumption of particle sphericity, which was confirmed by TEM images except for Table entry 1, which contained significant fractions of both spheres and other irregular morphologies. DLS-number peak mean and standard deviation values were obtained from the Malvern Zetasizer software. PDI for each peak was calculated according to the relationship, PDI = (standard deviation/mean)^2, as utilized in the literature.[4]

2.4.3 Serial dilutions with DLS:

Based on a procedure in the literature, DLS was used to observe an approximate critical micelle concentration of phenyl functionalized FISA micelles (Table S1 Entry 3, $f_\%$ = 100).[5] The sample was progressively diluted with 15 minutes of sonication between each dilution and DLS measurement. This procedure was repeated until the DLS number distribution generated a second population having a size consistent with poly(BPEA-*b*-tBA) precursors.

2.5 Transmission electron microscopy (TEM):

Conventional TEM imaging, scanning TEM (STEM) annular dark field (ADF) imaging, and STEM electron energy-loss spectroscopy (EELS) were performed on a JEOL 2100F microscope. The TEM was equipped with a spherical aberration coefficient, C_s, value of 1 mm and a Schottky electron emitter. The accelerating voltage was 200 kV. The conventional TEM images were acquired in bright-field mode with a defocus value of several microns. The STEM-ADF images where acquired with inner and outer collection semi-angles of 16 and 32 mrad, respectively. TEM samples were prepared by dispensing 1-3 drops of a dilute particle solution (at the same concentration as the DLS and SEC solutions described above) onto a TEM grid and allowing the THF to evaporate before placing in the TEM.

2.6 STEM electron energy-loss (STEM-EELS):

STEM-EELS was acquired with Gatan Imaging Filter Quantum and a Gatan K2 IS direct detection electron sensor operated in electron counting mode.[6] The collection semi-angle was 16 mrad. The energy dispersion was set to 0.125 eV/channel. The STEM probe was ~2 Å and the beam current was 25 pA. Spectrum-images (SIs) were acquired in multi-frame mode. The dwell time per pixel for each individual frame was 2.5 ms, and 50 frames were aligned and summed to yield to final SI. The Gatan DigitalMicrograph software package was used for SI processing. For elemental mapping, a power-law background subtraction and Slater cross-sections were used. Principal component analysis was used to improve the signal-to-noise ratio for producing the Fluorine elemental map.

2.7 LogP and molecular surface area predictions:

MarvinSketch™ software was utilized for LogP and molecular surface area predictions for quantifying polymer hydrophobicity/solvophobicity.[7,8] Each simulation was performed using twenty repeat units of the reactive portion of the diblock copolymer. Each prediction took into account the $f_\%$ determined from NMR. For LogP calculations, the Consensus method was used. For the molecular surface area simulations, the 'Solvent Accessible' mode was used, assuming a solvent radius of 1.4.
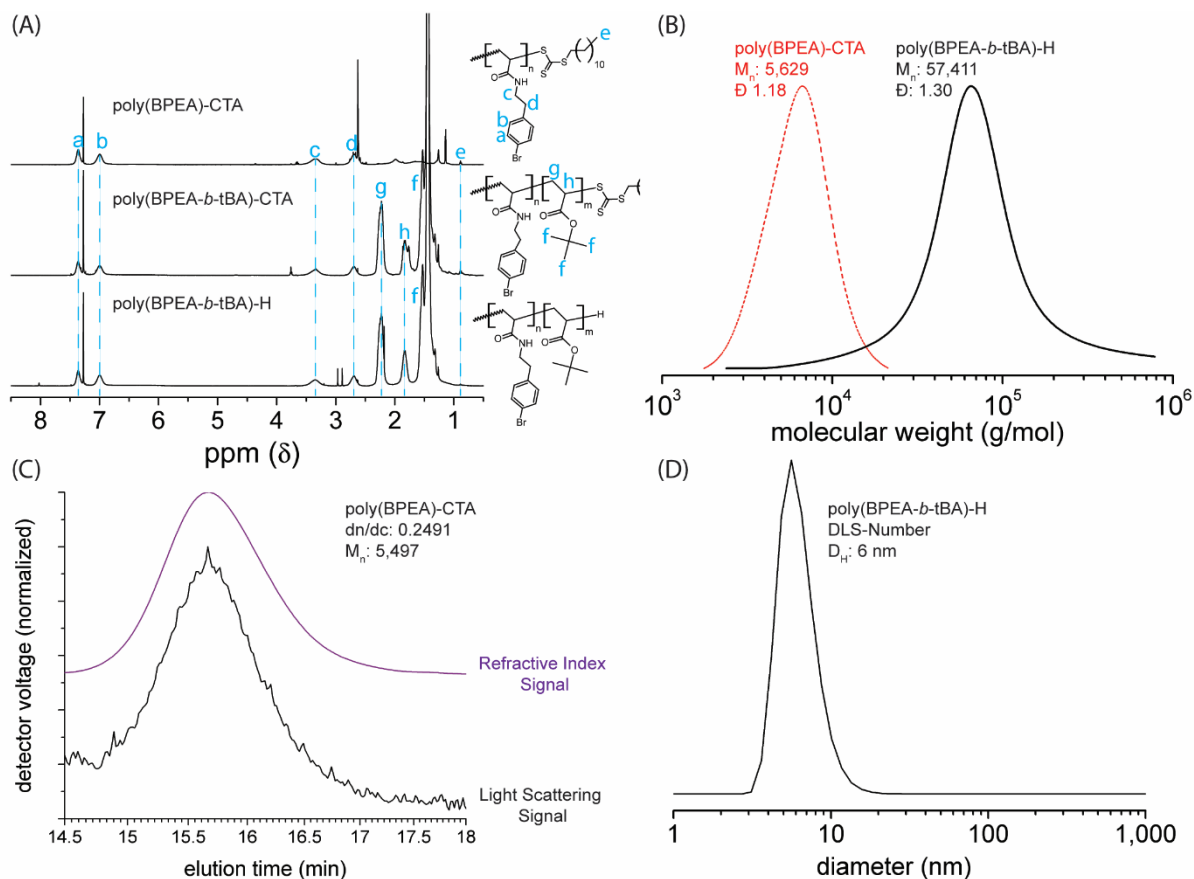
Figure S1: Supporting data for precursor synthesis including, (A) stacked NMR for poly(BPEA)-CTA, poly(BPEA-*b*-tBA)-CTA, and poly(BPEA-*b*-tBA)-H; (B) SEC-THF traces for poly(BPEA)-CTA and poly(BPEA-*b*-tBA)-H; (C) SEC-DMAC-MALS refractive index and light scattering signals for poly(BPEA)-CTA; and (D) DLS number distribution for poly(BPEA-*b*-tBA)-H.

(A) $H_a=2$, $H_b=4$, $H_c=5$ $I_a=2.00$, $I_{b,c}=7.25$

$$f_\% = \frac{(I_{b,c,7.8-6.5ppm} - H_b)/H_c}{I_a/H_a} \cdot 100$$

(B) $H_a=2$, $H_{e,f}=2$ $I_a=2.00$, $I_{e,f}=2.16$

$$f_\% = \frac{I_{e,f,6.7-6.1ppm}/H_{e,f}}{I_a/H_a} \cdot 100$$

(C) $H_a=2$, $H_d=2$ $I_a=2.00$, $I_d=0.82$

$$f_\% = \frac{I_{d,6.8-6.5ppm}/H_d}{I_a/H_a} \cdot 100$$

(D) $H_a=2$, $H_b=4$, $H_c=9$ $I_a=2.00$, $I_{b,c}=9.83$

$$f_\% = \frac{(I_{b,c,8.8-6.6ppm} - H_b)/H_c}{I_a/H_a} \cdot 100$$

(E) $H_a=1$, $H_b=4$, $H_b=4$ $I_a=1.0$, $I_{b,c}=10.77$

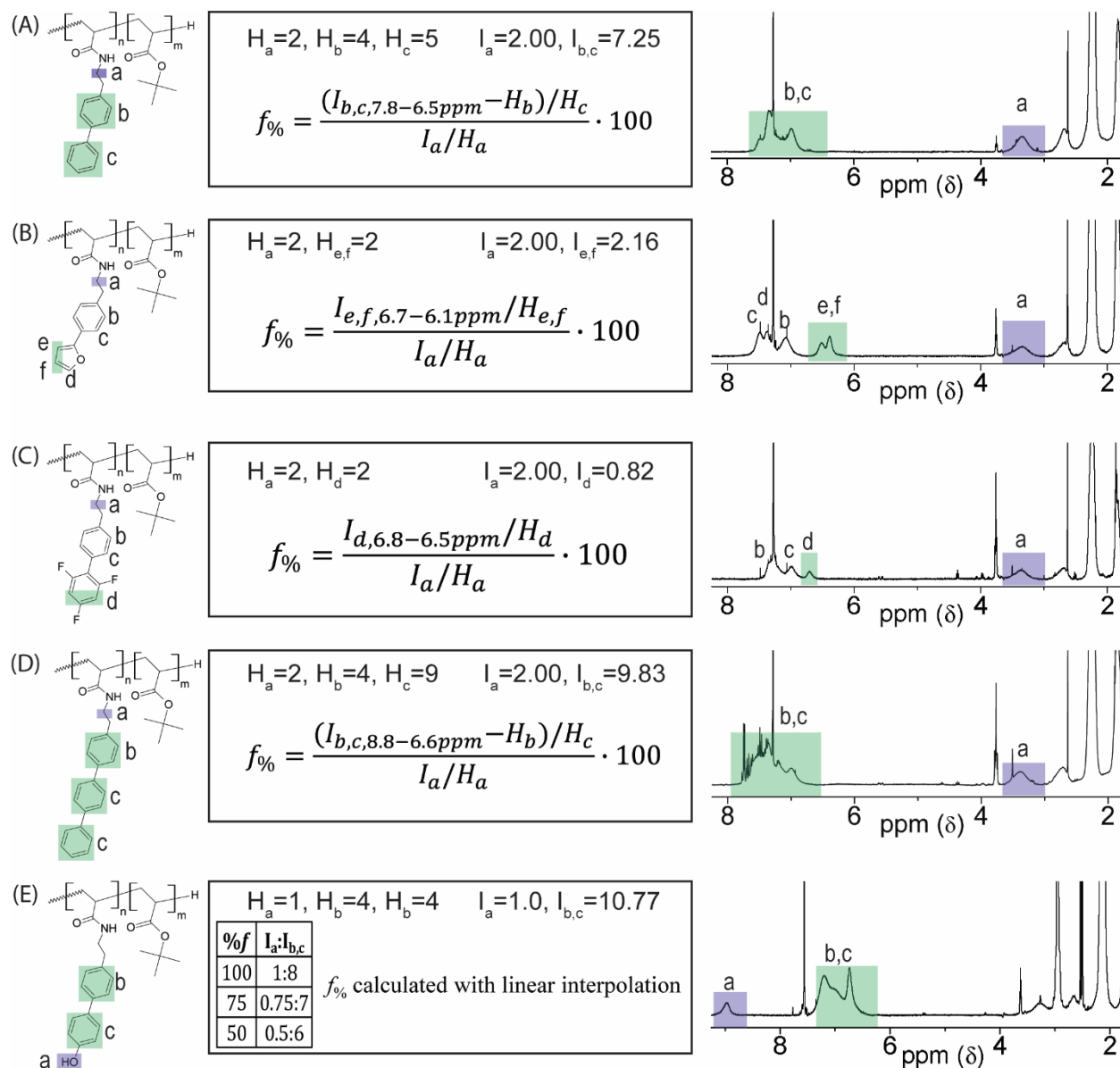| $\%f$	$I_a{:}I_{b,c}$
100	1:8
75	0.75:7
50	0.5:6

$f_\%$ calculated with linear interpolation

Figure S2: Example NMR spectra and percent functionalization calculations for each cross-coupling functional group with (A) phenyl functionality - FG-3, (B) furan functionality - FG-1, (C) trifluorophenyl - FG-5, (D) biphenyl functionality - FG-4, and (E) phenol functionality - FG-2.
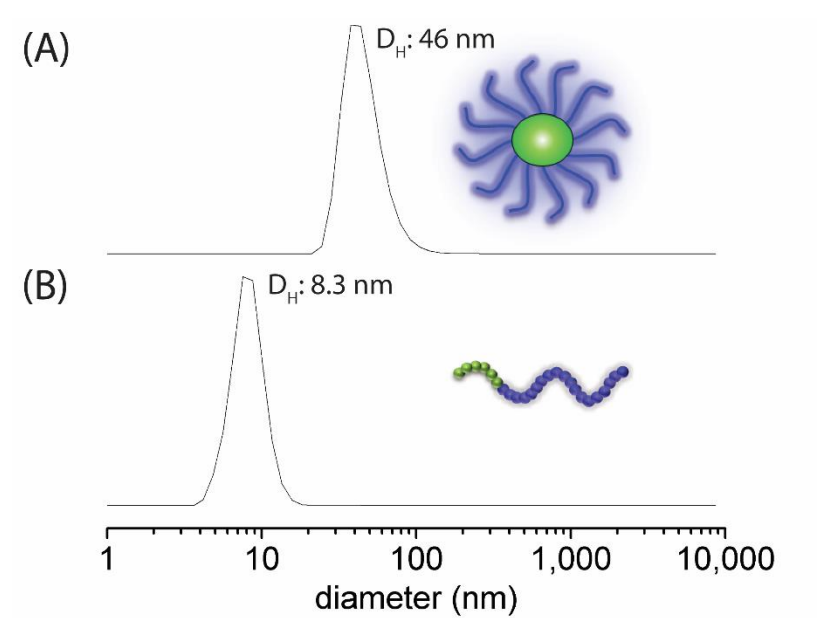
Figure S3: DLS number distributions for a phenyl-functionalized FISA sample (Table S2, Entry S3) in (A) THF and (B) chloroform at a polymer concentration of approximately 3 mg/mL.
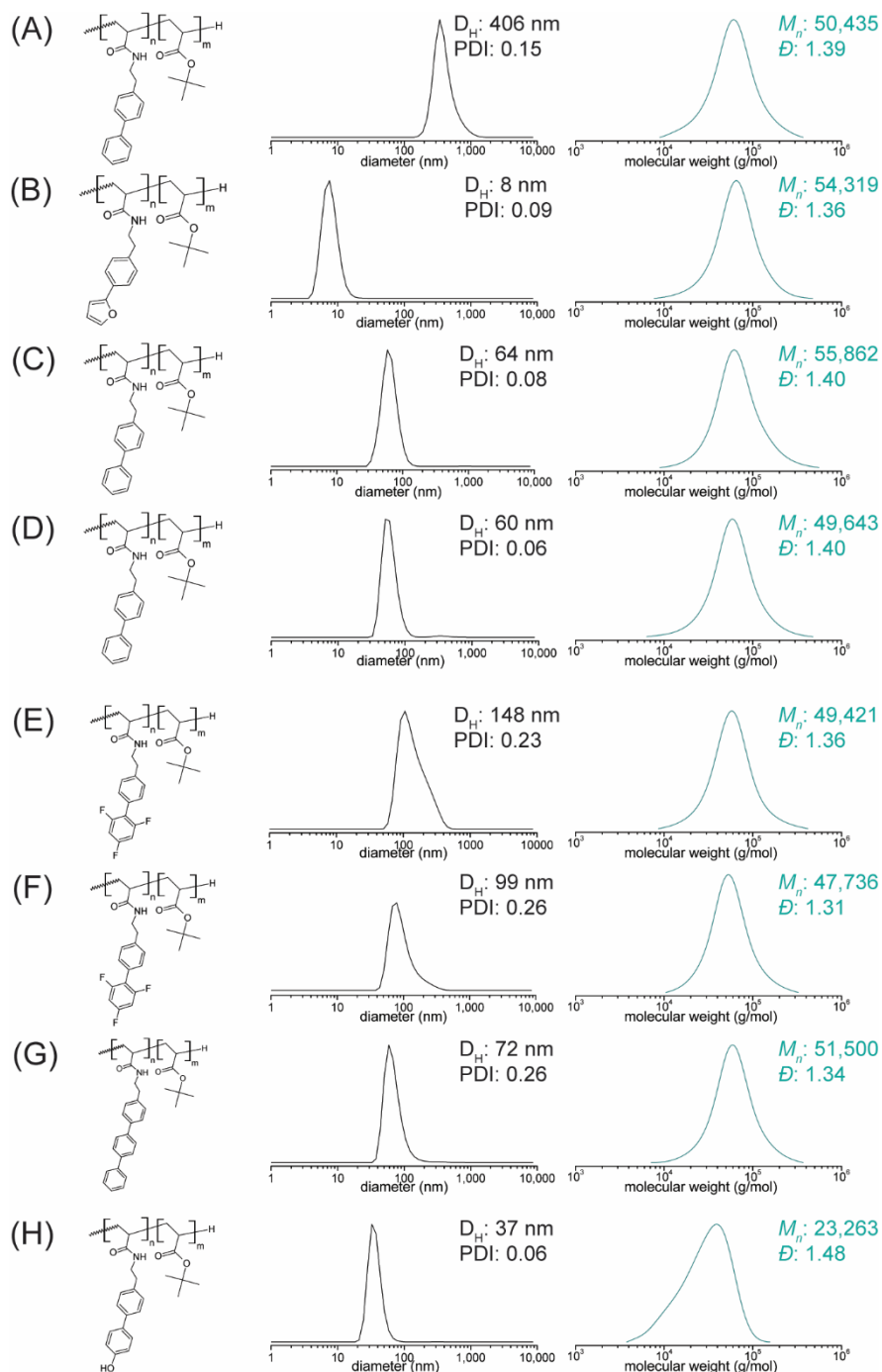
Figure S4: Chemical structures, DLS number distributions, and THF-SEC traces for Table S1. Results are provided for (A) entry 1, (B) entry 2, (C) entry 3, (D) entry 4, (E) entry 5, (F) entry 6, (G) entry 7, and (H) entry 8. All DLS measurements were carried out on approximately 30 mg/mL of crude reaction mixture diluted in 1 mL of THF, corresponding to a total polymer concentration of approximately 3 mg/mL. Reported M_n values of different block copolymer compositions are not absolute molecular weights but only relative molecular weight values from SEC-THF.

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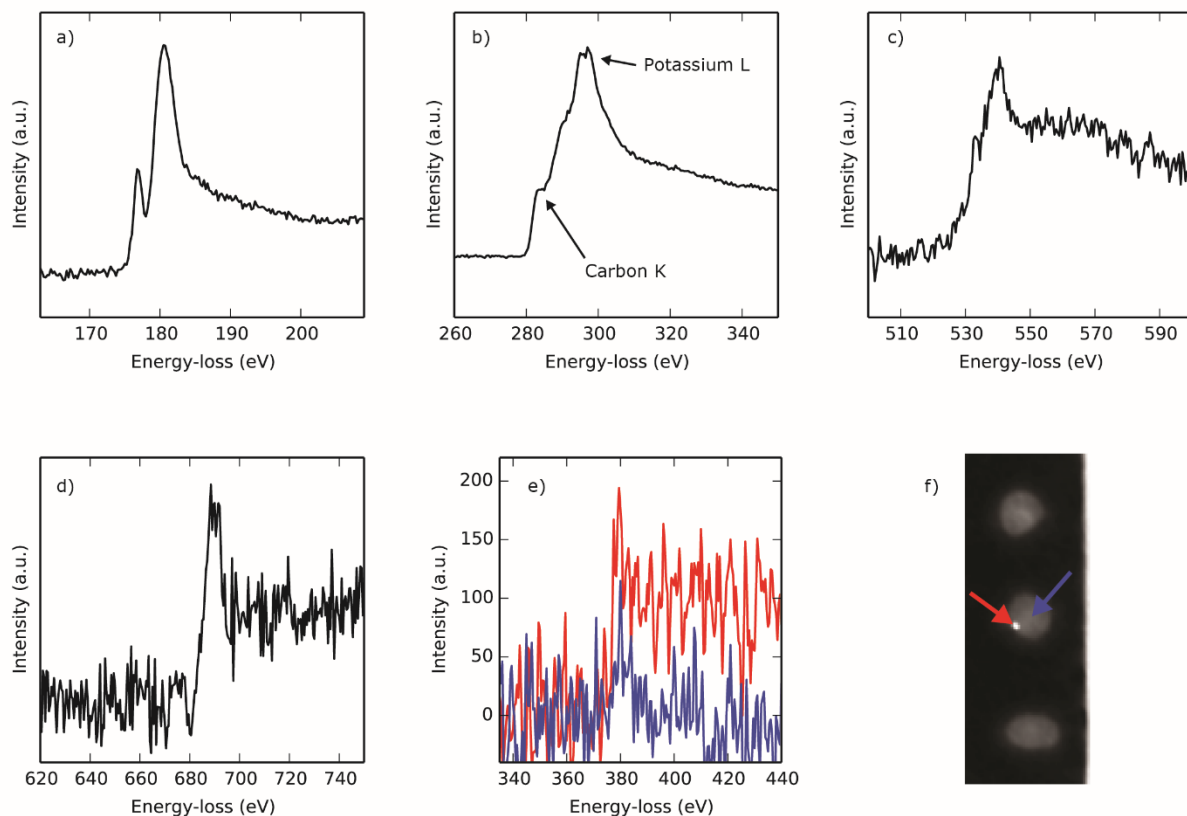
Figure S5: Various EELS spectra acquired from the core-shell polymer nanoparticles: Beryllium K edge (a), Carbon K edge and Potassium L edge (b), Oxygen K edge (c), Fluorine K edge (d). In (e), two spectra are shown, both taken from the same nanoparticle, shown in the ADF image in (d). The red and blue arrows in (f) indicate where the red and blue spectra in (e) were extracted from. There is a clear edge at 375 eV in the red spectra which corresponds to the palladium M edge, indicating that the bright spot in the ADF image is a Pd nanoparticle.

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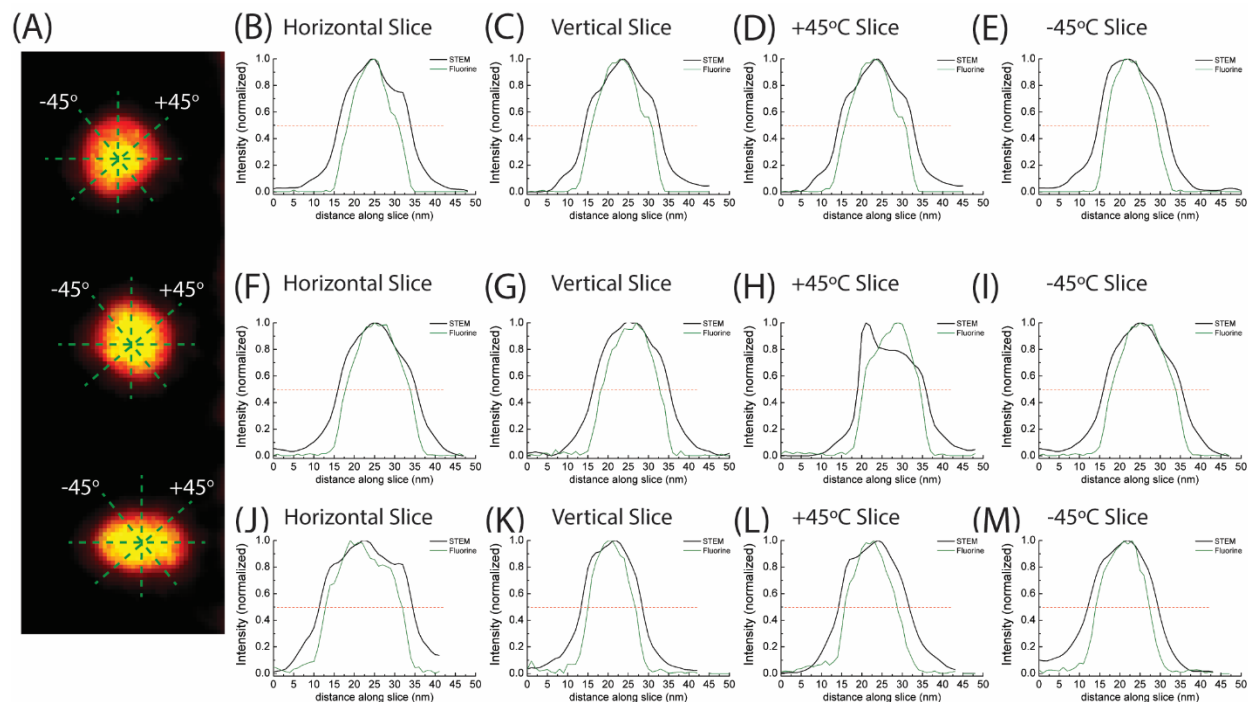
Figure S6: (A) Overlay of the ADF image and EELS fluorine concentration map, with ADF image as red and fluorine map as green (overlapping areas appear yellow) and intensity slices indicated by dashed lines on the particles, (B-E) normalized signal intensities of the ADF image and fluorine along the slices depicted on the top particle, (F-I) normalized signal intensities of the ADF image and fluorine along the slices depicted on the middle particle, and (J-M) normalized signal intensities of the ADF image and fluorine along the slices depicted on the bottom particle. The spike in the ADF signal in (H) is due to a Pd particle within the micelle.

(A) $f_\% = 100$

D_H: 64 nm

M_n: 55,862
Đ: 1.40

(B) $f_\% = 85$

D_H: 60 nm

M_n: 49,643
Đ: 1.40

(C) $f_\% = 50$

D_H: 46 nm

M_n: 48,684
Đ: 1.41

(D) $f_\% = 30$

D_H: 34 nm

M_n: 44,147
Đ: 1.43
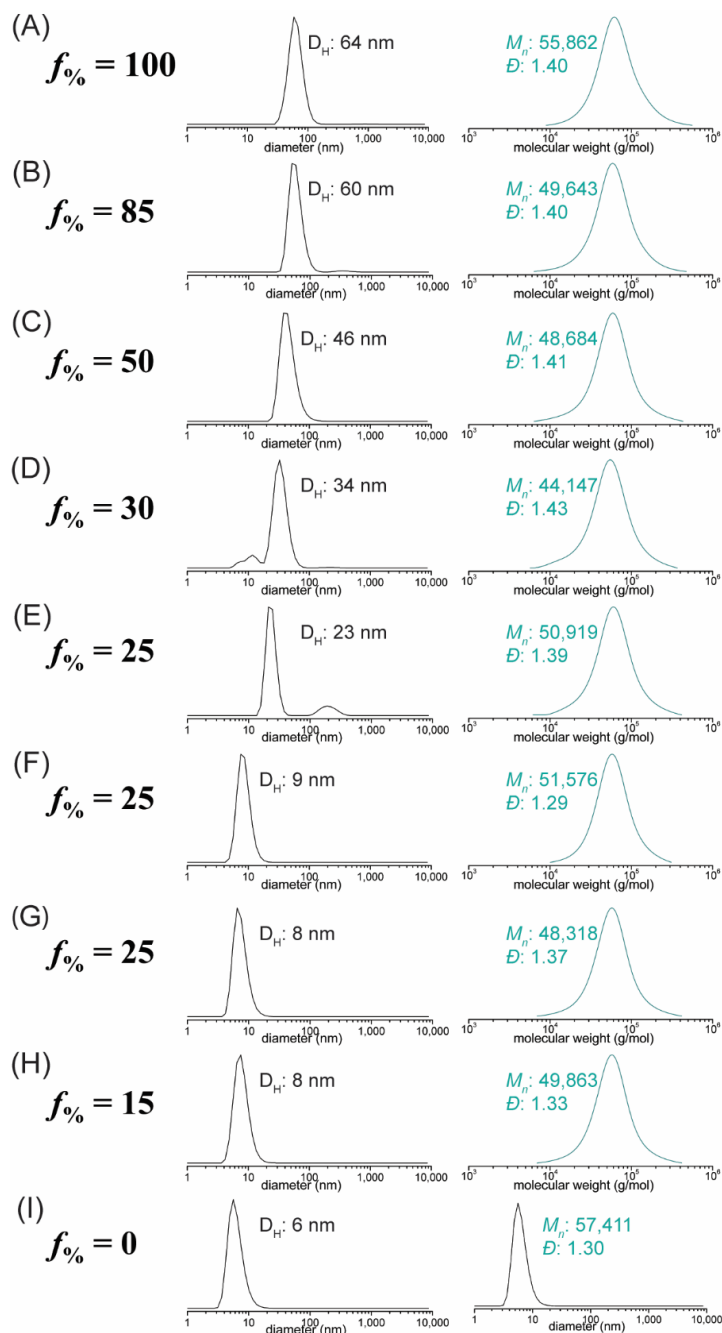
(E) $f_\% = 25$

D_H: 23 nm

M_n: 50,919
Đ: 1.39

(F) $f_\% = 25$

D_H: 9 nm

M_n: 51,576
Đ: 1.29

(G) $f_\% = 25$

D_H: 8 nm

M_n: 48,318
Đ: 1.37

(H) $f_\% = 15$

D_H: 8 nm

M_n: 49,863
Đ: 1.33

(I) $f_\% = 0$

D_H: 6 nm

M_n: 57,411
Đ: 1.30

Figure S7: DLS number distributions with mean hydrodynamic diameters reported for the primary peaks, and THF-SEC traces with M_n and dispersity values for Table S2 with (A) entry 1, (B) entry 2, (C) entry 3, (D) entry 4, (E) entry 5, (F) entry 6, (G) entry 7, (H) entry 9, and (I) entry 10. DLS was carried out on approximately 30 mg/mL of crude reaction mixture diluted in 1 mL of THF, corresponding to a total polymer concentration of approximately 3 mg/mL. Reported M_n values of different block copolymer compositions are not absolute molecular weights but only relative molecular weight values from SEC-THF.
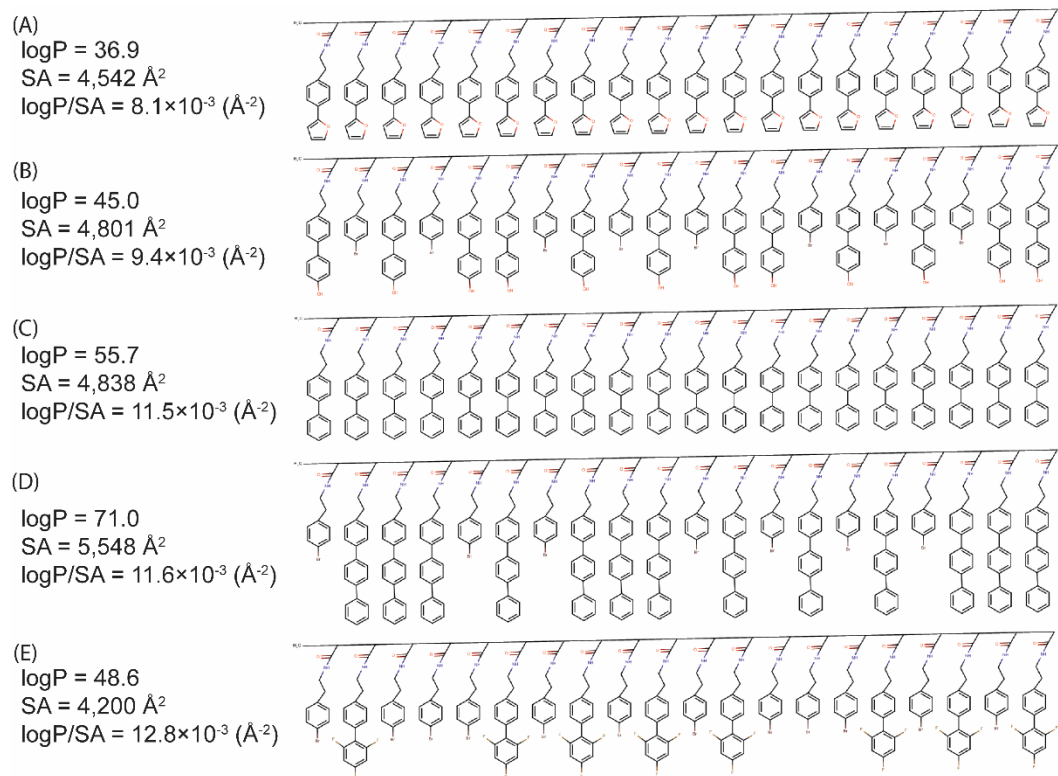
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(A)
logP = 36.9
SA = 4,542 Å^2
logP/SA = 8.1×10^{-3} (Å^{-2})

(B)
logP = 45.0
SA = 4,801 Å^2
logP/SA = 9.4×10^{-3} (Å^{-2})

(C)
logP = 55.7
SA = 4,838 Å^2
logP/SA = 11.5×10^{-3} (Å^{-2})

(D)
logP = 71.0
SA = 5,548 Å^2
logP/SA = 11.6×10^{-3} (Å^{-2})

(E)
logP = 48.6
SA = 4,200 Å^2
logP/SA = 12.8×10^{-3} (Å^{-2})

Figure S8: MarvinSketch^{TM} images of twenty repeat units of the reactive block of the block copolymer along with logP and molecular surface area (SA) predictions for the (A) furan-functionalized oligomer having a $f_\%$ = 100, (B) phenol-functionalized oligomer having a $f_\%$ = 60, (C) phenyl-functionalized oligomer having a $f_\%$ = 100, (D) biphenyl-functionalized oligomer having a $f_\%$ = 65, and (E) trifluorophenyl-functionalized oligomer having a $f_\%$ = 40.

Table S1: Reaction conditions and results for Pd-SMC and functionalization induced self-assembly. Figure 4 data points #1, #2, #3, #4, and #5 correspond to Table entries 2, 8, 3, 7, and 6, respectively.

Entry[A]	Functionality (FG-#)	Pd-SMC Molar Ratios [B(OH)$_2$]/[Ar-Br]/[Pd]	Temp. (°C)	NMR $f_\%$	DLS$_{Number}$ D$_H$ (nm)	PDI
1	3:Phenyl	3.7/1/0.12	45	65	406	0.15
2	1:Furan	3.8/1/0.15	45	100	8	0.09
3	3:Phenyl	3.7/1/0.15	23	100	64	0.08
4	3:Phenyl	3.9/1/0.02	23	85	60	0.06
5[B]	5:Trifluorophenyl	3.7/1/0.04	23	-	148	0.23
6[C]	5:Trifluorophenyl	2.9/1/0.13	23	40	99	0.26
7	4:Biphenyl	3.7/1/0.03	23	65	72	0.26
8[D]	2:hydroxy-phenyl	3.7/1/0.03	23	60	37	0.06

A - All reactions were carried out at a polymer concentration of 100mg/ml of solvent and run for 5 hours unless otherwise noted. Product characterization with SEC and DLS for each entry is provided in Fig. S4.
B – The product form entry 5 was used for EELS imaging.
C – Entry 6 employed an alternate base, Na$_2$CO$_3$ instead of KF.
D – Entry 8 was run for 24 hours instead of the standard 5 hours.

Table S2: Reaction conditions and results for $f_\%$ versus micelle size with phenyl functionalization (FG-1).

Entry[A]	Pd-SMC Molar Ratios [B(OH)$_2$]/[Ar-Br]/[Pd]	NMR $f_\%$	DLS$_{Number}$ D$_H$ (nm)	PDI
1	3.7/1/0.15	100	64	0.08
2	3.9/1/0.02	85	60	0.06
3	3.7/1/0.01	50	46	0.11
4	2.0/1/0.09	30	37	0.06
5	3.7/1/0.15	25	23	0.04
6	1.4/1/0.15	25	9	0.06
7	0.6/1/0.15	25	8	0.08
8[B]	-	-	13	0.17
9	0.6/1/0.02	15	8	0.09
10[C]	-	-	6	0.10

A - All reactions were carried out at a polymer concentration of 100mg/ml and run for 5 hours at room temperature (~23°C). Product characterization with SEC and DLS for each entry is provided in Fig. S7.
B – The mean diameter value for entries 5, 6, and 7 were averaged to create one diameter value for experiments with 25 $f_\%$.
C - DLS data for the precursor compound was used as the 0 $f_\%$ entry.

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