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Self-Assembly with Block Copolymers through Metal Coordination of SCS–Pd^{II} Pincer Complexes and Pseudorotaxane Formation

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Abstract: Poly(norbornene)-based block copolymers containing side chains of palladated pincer complexes/dibenzo[24]crown-8 or palladated pincer complexes/dibenzylammonium salts were synthesized. Noncovalent functionalization was accomplished with their corresponding recognition units through simple 1:1 addition with association constants (K_a) greater than $10^5\,M^{-1}$. The self-assembly processes were monitored by using both ^1H NMR spectroscopy and isothermal titration calorimetry. In all cases, we found that the self-assembly of the recognition units along each polymer block does not preclude the self-assembly processes along the other block.

Keywords: copolymerization · crown compounds · palladium · pincer complexes · supramolecular chemistry

Introduction

As the field of materials science advances, the demand for highly functional and versatile materials will soar. Materials for applications such as organic light-emitting diodes (OLEDs), photorefractives, solar cells, drug delivery vehicles, sensors, and molecular machines will require fast and cost effective synthesis and optimization.[1–5] To meet these demands, future synthetic strategies to produce polymeric materials should be generic, such that similar functionalization techniques can be applied to a variety of applications. Nevertheless, these functionalization strategies should be tailored to a specific application. For example, a drug delivery application may require functionalities with weak noncovalent attachments to facilitate effective drug release in response to a stimulus at a target site.[6] In contrast, materials for use in electro-optics require strong and dense functionalization capable of withstanding thousands of working hours.[7]

Along the evolutionary pathway, nature has created a system with incredible fidelity in which a myriad of biomaterials can be produced from noncovalent-mediated synthesis.[8] Borrowing from this approach, our system uses similar noncovalent forces to create functionalized copolymers. Noncovalent functionalities, such as hydrogen bonding and metal coordination, have several advantages over traditional covalent functionalities; such interactions are spontaneous, allowing for fast functionalization steps. Furthermore, they are reversible, allowing for "on–off" functionalization. We have previously reported a polymeric system in which a weak interaction (hydrogen bonding) and a strong interaction (metal coordination) could be used to functionalize copolymers in an orthogonal manner, developing the first generation of so-called "universal polymer backbones" (UPBs), that is, polymer backbones that can be functionalized with multiple small molecules by using noncovalent chemistry thereby creating libraries of materials.[3,8–10] Herein, we report the next generation of UPBs by functionalizing an architecturally controlled block copolymer with two strong

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noncovalent functionalities based on 1) pseudorotaxane hydrogen bonding and 2) metal coordination between palladated sulfur–carbon–sulfur (SCS) pincer complexes and pyridines. This next generation of UPBs possesses unique advantages. First, the copolymer architecture is defined prior to functionalization, allowing for the introduction of a variety of functional groups that might otherwise hinder architectural control if introduced prior to polymerization. Second, this generation of UPBs rivals covalently functionalized copolymers by utilizing two recognition units with high binding affinities for their corresponding complementary recognition units (small molecules); this fact ensures the production of a densely functionalized and monodisperse material. Finally, our new system retains all the benefits of noncovalent modification, including reversibility, self-healing, and ease of functionalization.

In our search for the next generation of UPBs, depicted in Figure 1, we sought two important design requirements:

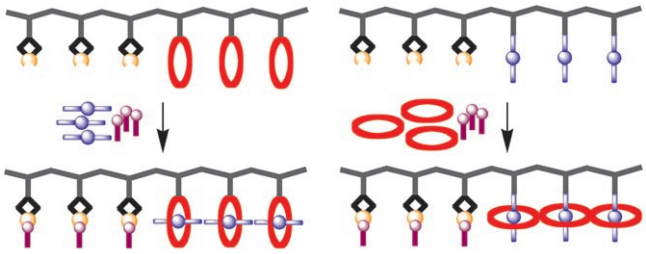
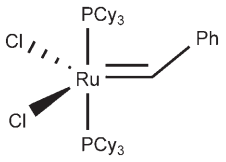


Figure 1. Schematic representation of the next generation of universal polymer backbones.

1) architectural control of the polymer scaffold, and 2) distinct recognition partners with sufficiently high noncovalent binding strengths.

Block copolymers, which have been used widely in applications ranging from drug delivery to electro-optics, form our basis for the architectural control.[11] We achieve such architectural control by the use of ring-opening metathesis polymerization (ROMP)[10,12–19] to produce block copolymers. ROMP with the ruthenium–alkylidene initiator **1** not only provides the basis of our architectural control, but **1** is also highly functional group tolerant.[20–23]



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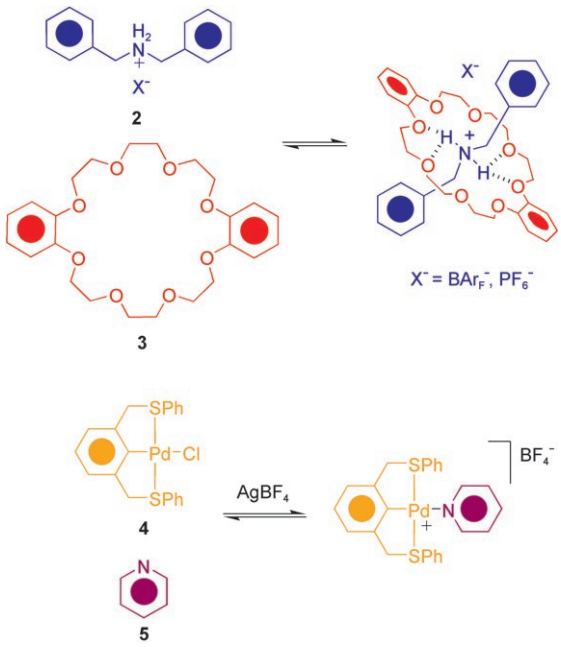
The second requirement is met with the use of two strong noncovalent interactions involving both metal coordination and hydrogen bonding as shown in Scheme 1. The hydrogen-bonding system is based on the threading of a dialkylammonium cation **2** into a dibenzo[24]crown-8 (DB24C8) macrocycle **3** to form a pseudorotaxane.[24–42] Since the discovery of rotaxane formation resulting from the threading of an ammonium cation into a crown ether macrocycle in 1995,[43] a number of interactions between ammonium cations and crown ether macrocycles have been studied, resulting in a myriad of supramolecular structures[44–50] and the evolution[51] of a "molecular meccano kit". The driving force for the formation of threadlike structures from dialkylammonium cations and crown ether macrocyles is the formation of strong hydrogen bonds between the acidic NH_2^+ protons and the oxygen atoms in the ring of the crown ether macrocyle. In addition to strong N–H···O and C–H···O hydrogen bonding, π–π stacking interactions and electrostatic forces also contribute to the strong affinity between dialkylammonium cations and DB24C8 macrocycles. Such interactions are highly solvent dependent. In apolar solvents, high association constants (K_a) are attainable for the dialkylammonium and DB24C8 system (vide supra).



Scheme 1. The two types of molecular recognition pairs employed in this study.

The metal coordination system we employ is based on a SCS–Pd^{II} pincer complex **4** which binds pyridines, nitriles, and phosphines with high efficiencies.[10,52,53] The palladium pincer complex was chosen because of its high stability and the ability of the palladium species to undergo substitution with a variety of ligands.[52] Pyridine **5** was chosen as the ligand for the pincer complex, because it can be easily displaced by a stronger coordinating phosphorous ligand.[53] Moreover, a pincer-pyridine self-assembly process can be characterized easily by using standard methods such as ^{1}H NMR spectroscopy.[9]

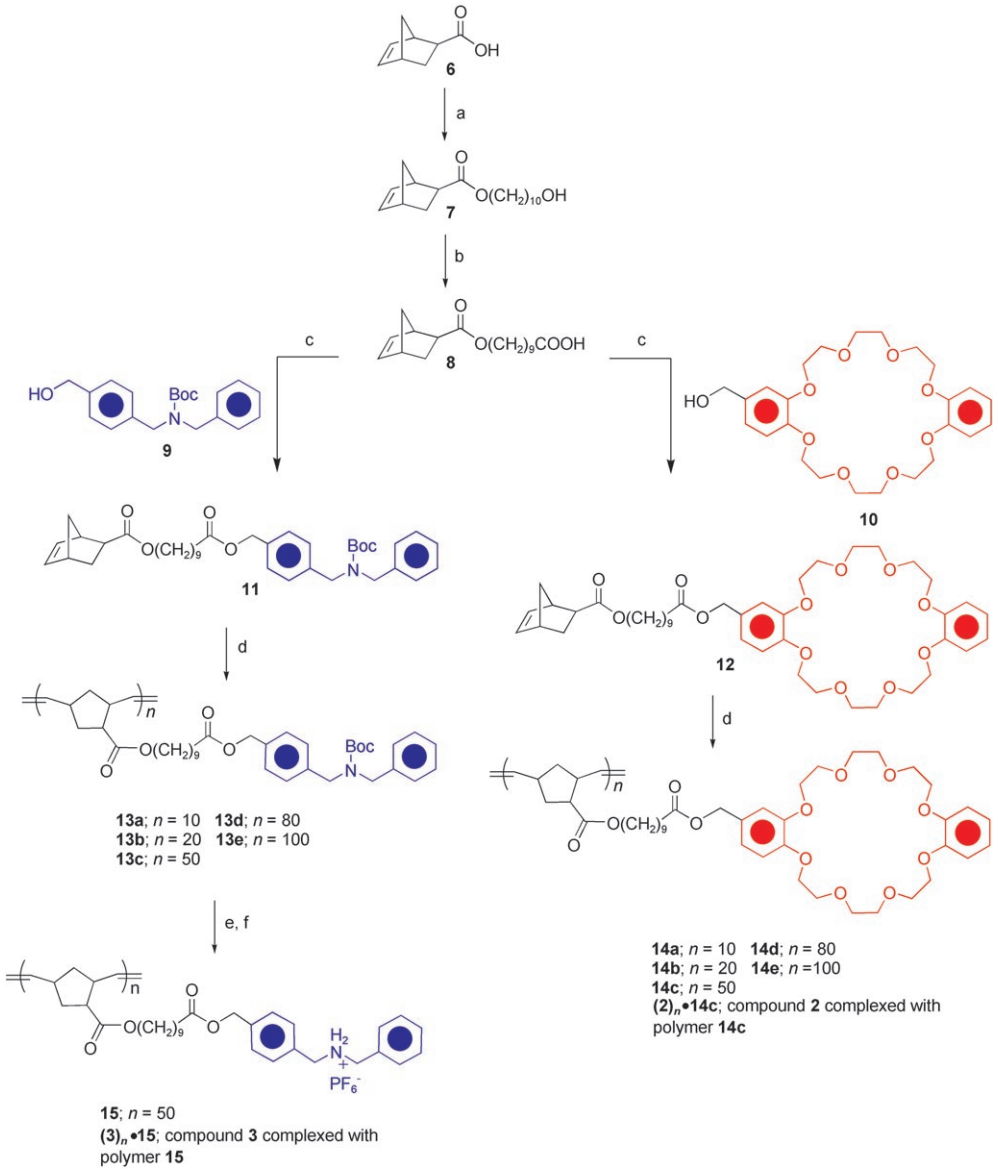
Results and Discussion

Monomer synthesis and homopolymerization reactions: Isomerically pure *exo*-norbornene esters often result in short polymerization times as well as living polymer growth.[10] Thus, *exo*-norbornene acid **6**[54–56] was chosen as the starting

point in our synthetic pathway. The addition of an alkyl spacer onto **6** was accomplished by the dicyclohexyl carbodiimide/4-dimethylaminopyridine (DCC/DMAP) esterification with 1,10-decanediol to yield **7**. The *exo*-decanol **7** was then oxidized to the corresponding carboxylic acid **8** using pyridinium dichromate (PDC) in dimethylformamide (DMF). Compound **8** was functionalized with the Boc-protected dialkyl amine **9** (Boc = *tert*-butyloxycarbonyl)[57] or the DB24C8 derivative **10**[49] by using DCC/DMAP esterification to afford **11** and **12**, respectively. Monomer **12** was polymerized by using initiator **1** to yield the resulting polymeric DB24C8 crown ethers **14a–e**. Likewise, monomer **11** was polymerized to give the polymeric Boc protected amines **13a–e**. The synthetic pathway is outlined in Scheme 2.

Monomers **11** and **12** were found to polymerize in a living fashion. The absence of chain-transfer and chain-termination in addition to controlled molecular weights are criteria for living polymerizations.[58,59] A linear relationship between M_n and [M]:[I] (M = monomer, I = initiator) was established for **11** and **12** (Figure 2). Such a linear relationship indicates the living nature of the polymerization for monomers **11** and **12**. The corresponding gel-permeation chromatography (GPC) data are summarized in Table 1.

We also investigated whether the unprotected amine **11** (**11a**), could be polymerized in a living fashion. For these experiments, **11** was deprotected by using trifluoroacetic acid (TFA), and the resulting **11a** was polymerized with **1**. Unfortunately, the polymerization behavior of **11a** was uncontrolled, and the formation of high molecular weight poly-



Scheme 2. Synthesis of molecular recognition monomers and subsequent ROMP. Reagents and conditions: a) decane-1,10-diol, DCC/DMAP, CH_2Cl_2, reflux, 12 h, 60%; b) PDC, DMF, 48 h, 80%; c) DCC/DMAP, CH_2Cl_2, reflux, 12 h, 90%; d) **1**, CH_2Cl_2, 8 h, 100%; e) TFA, CH_2Cl_2, 3 h; f) NH_4PF_6, CH_2Cl_2, 3 h, 92% from **11**.

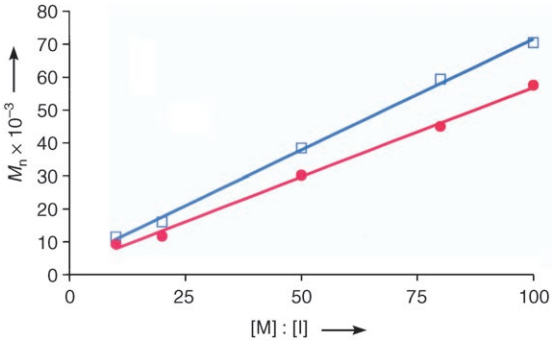


Figure 2. Plot of M_n versus monomer/initiator ratios for polymers **13** (□) and **14** (●).

Table 1. Polymer characterization data (GPC) for **13, 14, 18**, and **19**.[a]

Polymer	[M]:[I]	M_n [10^{-3}]	M_w [10^{-3}]	PDI
13a	10	11.5	14.1	1.23
13b	20	16.0	18.6	1.16
13c	50	38.2	41.4	1.08
13d	80	59.2	68.6	1.16
13e	100	70.3	93.3	1.33
14a	10	9.3	13.1	1.41
14b	20	11.6	17.4	1.49
14c	50	30.0	61.7	2.05
14d	80	44.8	83.7	1.87
14e	100	57.4	138.0	2.41
18	50	29.5	35.6	1.21
19	50	66.0	75.1	1.14

[a] M_n = number-average molecular weight; M_w = weight-average molecular weight; PDI = polydispersity index.

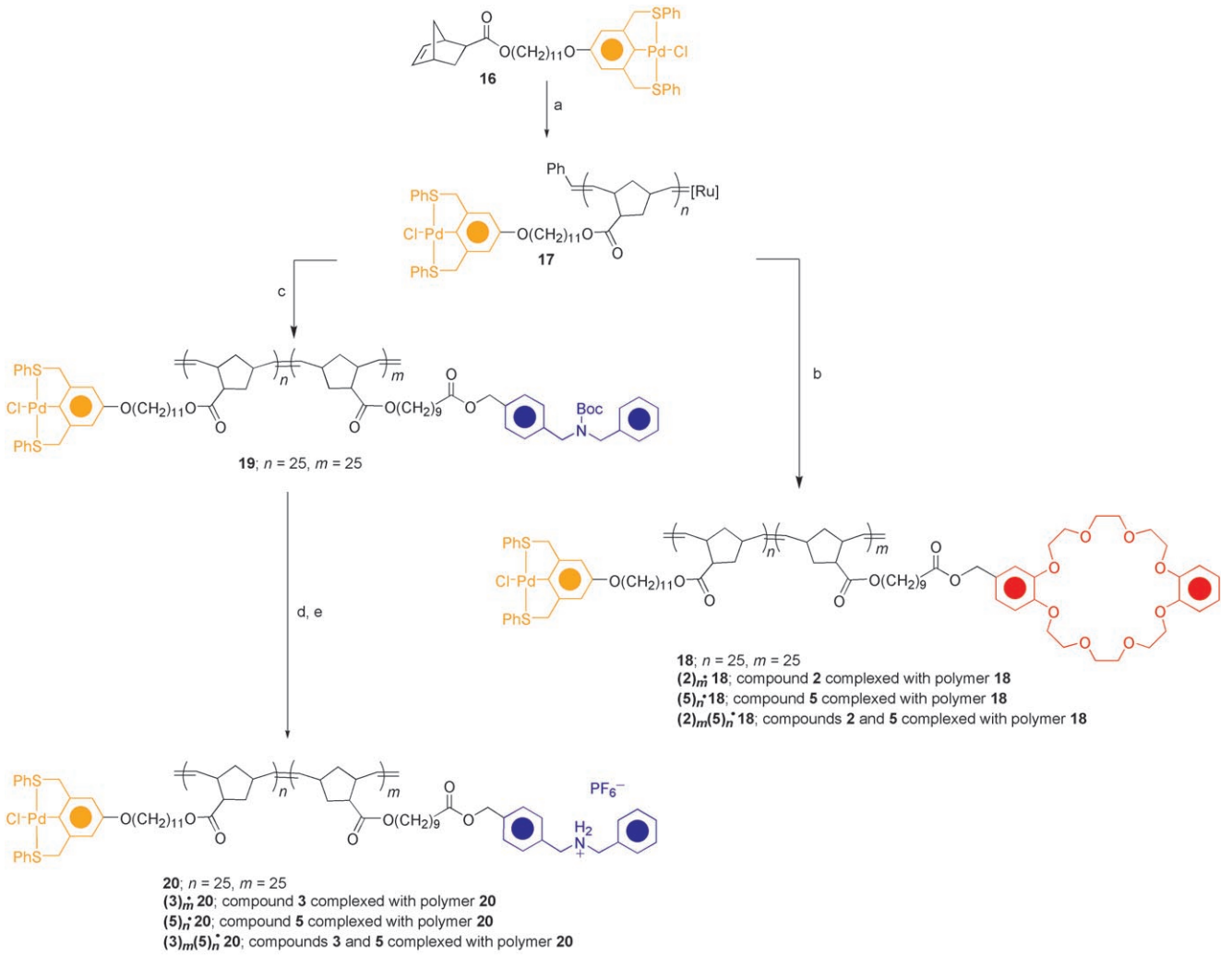
mers was observed regardless of the [M]:[I] feed ratios. Additionally, salt exchange was achieved with **11a** by using ammonium hexafluorophosphate, but the monomeric PF_6^- salt would not polymerize with initiator **1**. Thus, monomer **11** was chosen for all polymerization experiments. The conversion of polymer **13c** to the dialkylammonium PF_6^- salt **15** was accomplished by deprotection with TFA followed by salt exchange by using a 100-fold excess of ammonium hexafluorophosphate. Unfortunately, the resulting polyelectrolyte **15** could not be characterized by GPC; the charges either interacted with the column packing material or the polymer formed aggregates in an ionomeric fashion and did not elute.

Copolymerizations: After establishing that **11** and **12** could be polymerized in a controlled manner, AB block copolymerizations were carried out with the SCS–Pd pincer monomer **16** (Scheme 3). The synthesis, polymerization, and living characterization of **16** have been reported previously.[3,9,10,60] Following the polymerization of **16** by using **1**, monomers **11** and **12** were added to **17** to form the bi-functional AB block copolymers **18** and **19**. Following the deprotection of **19** with TFA and subsequent salt exchange with ammonium hexafluorophosphate, copolymer **20** was obtained. GPC analysis of copolymers **18** and **19** were carried out. Both copolymers have low polydispersities demonstrating the living character of the polymerization. Table 1 summarizes the GPC results.

Self-assembly: The aim of this study is to establish the complementarities of polymeric systems bearing the strong noncovalent recognition motifs **2, 3**, and **4**. We initially established that a polyvalent scaffold does not interfere with the self-assembly of homopolymers **14c** and **15** with their corresponding small molecule receptors. Using ^{1}H NMR spectroscopic studies, we were able to prove that both polymers **14c** and **15** can be quantitatively functionalized. Figure 3 shows the ^{1}H NMR spectra for the self-assembly of polymer **14c** with the small molecule **2**. Upon the addition of the dibenzylammonium cation **2** (in the form of **2**$[BAr_F]^-$) to homopolymer **14c**, the fully complexed polymer $(\mathbf{2})_n$·**14c** forms. The ammonium benzylic signal moves to $\delta = 4.5$ ppm from its original position at $\delta = 4.2$ ppm (spectra A and C). In addition, upon the threading of **2** into polymer **14c**, the crown ether signals move from $\delta = 4.1$, 3.9, and 3.8 ppm to $\delta = 4.0$, 3.6, and 3.2 ppm, respectively, indicating the quantitative complexation of the homopolymer (spectrum C). After the addition of excess **2**$[BAr_F]^-$ to polymer $(\mathbf{2})_n$·**14c**, a new signal at 4.2 ppm is observed that corresponds to the "free" dibenzylammonium salt. Moreover, after the deprotonation of the dialkylammonium cation **2** with triethylamine to form dibenzylamine, the benzylic ammonium signals disappear along with the complexed crown ether signals, and the original signals are evident (spectrum D). These results clearly demonstrate that self-assembly occurred and that the self-assembly step is reversible. Similar results were found for the self-assembly of **3** with polymer **15** (see Supporting Information).

Once the self-assembly of homopolymers **14c** and **15** with their small molecule receptors was found to be independent of the polymer backbone, the self-assembly behavior of block copolymers **18** and **20** was examined. Two distinct routes for the functionalization of copolymers **18** and **20** were investigated, one in which the hydrogen-bonding step precedes the metal coordination and vice versa. In the case of both copolymers **18** and **20**, the self-assembly was independent of the order of functionalization.

The DB24C8 recognition moiety **4** assembles spontaneously with the dibenzylammonium cation **2** in aprotic solvents. The palladated pincer, however, requires activation through the addition of silver tetrafluoroborate. Upon activation, the Pd^{II} pincer immediately assembles with pyridines such as **5**. The same behavior was observed for both copolymers. Figure 4 shows the ^{1}H NMR spectra of the stepwise self-assembly of copolymer **18** with **5** and **2**$[BAr_F]^-$ and the subsequent stepwise de-functionalization of copolymer $(\mathbf{2})_m(\mathbf{5})_n$·**18**. Spectrum B shows the copolymer **18** (shown by itself in spectrum A) with pyridine **5** added. Upon the addition of silver tetrafluoroborate, the pincer is activated with removal of the chloride ligand and pyridine **5** rapidly coordinates to the pincer receptor to form copolymer $(\mathbf{5})_n$·**18** (spectrum C). The diagnostic α-pyridyl proton moves upfield to $\delta = 8.1$ ppm, while the pincer methylene arms



Scheme 3. Synthesis of AB block copolymers bearing DB24C8, $DBA^+PF_6^-$, and SCS–Pd pincer recognition units. Reagents and conditions: a) initiator **1**, CH_2Cl_2, 120 min; b) 12, 8 h, 100%; c) **11**, CH_2Cl_2, 8 h, 100%; d) TFA, CH_2Cl_2, 3 h; e) NH_4PF_6, CH_2Cl_2, 3 h, 90% from **19**.

become sharper and move slightly downfield from about $\delta =$ 4.6 to 4.8 ppm. The dibenzylammonium cation **2** is subsequently added, and the crown ether complexation occurs, resulting in the fully functionalized copolymer $(\mathbf{2})_m(\mathbf{5})_n$•**18** (spectrum D). The same characteristic shifts for the complexations of $\mathbf{2}[BAr_F]^-$ with the crown ether moiety of **18** as detailed above for the complexation of $\mathbf{2}[BAr_F]^-$ with **14** are observed. The noncovalent assembly can then be reversed in a one-step or step-wise manner with the addition of triethylamine and triphenylphosphine. Triethylamine deprotonates the dibenzylammonium cation **2**, resulting in the formation of dibenzylamine, effectively de-threading the crown complexation but leaving the pyridine fully assembled to the pincer recognition unit (spectrum E). Finally, upon the addition of triphenylphospine, the pyridine ligand **5** is quantitatively displaced from the pincer complex (spectrum F). The decomplexation of **5** and $\mathbf{2}[BAr_F]^-$ from the copolymers is evident by the shifting of all signals of **18** in the ^1H NMR spectrum back to their original position that are detailed in spectrum A. It is important to note that spectrum F contains a variety of signals corresponding to non-coordinated pyridine, coordinated triphenylphosphine, dibenzylamine, and triethylamine that are all absent in spectrum A. However, all signals characteristic of the uncomplexed **18** are evident in spectrum F. These results clearly demonstrate that the functionalization of the recognition units are independent of each other and can be addressed in an orthogonal fashion.

To measure if the bond strengths of the recognition units are independent of each other, association constants for all polymers and hydrogen-bonding molecular receptors in $CHCl_3$ were obtained using isothermal titration calorimetry (ITC). The results of these experiments are summarized in Table 2. The measured K_a values were determined by using a single-site binding model; thus, the association constants are representative of the average binding strength of a single side-chain on the polymer, that is, the binding of each receptor unit is treated as an independent recognition event. In general, our ITC results show that our polymeric hydrogen-bonding system results in very high association strengths. The highest association constant ($K_a = 2\times10^6\,M^{-1}$)

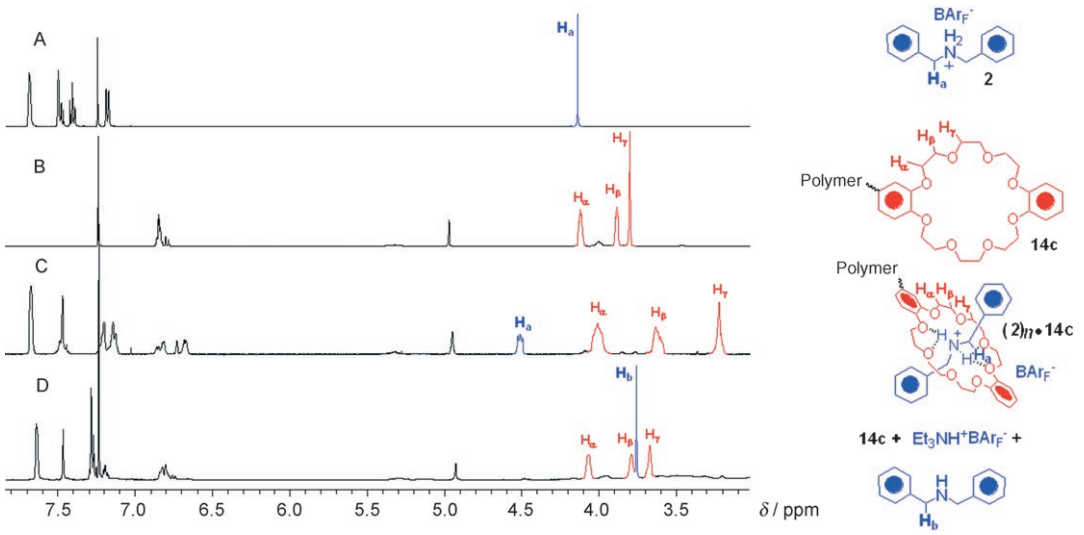


Figure 3. ^{1}H NMR spectra (500 MHz) representing the self-assembly of polymer **14c** with **2**$[BAr_F]^-$ in $CDCl_3$. A) **2**$[BAr_F]^-$: H_α = benzylic protons; B) **14c**: H_α, H_β, H_γ = nonequivalent sets of crown ether protons; C) formation of $(\mathbf{2})_n$•**14c** upon the addition of one equivalent of **2** to polymer **14c** (based on the integration of crown ether/dibenzylammonium signals): H_α = complexed benzylic proton; H_α, H_β, H_γ = nonequivalent sets of complexed crown ether protons; D) regeneration of **14c** after the addition of excess Et_3N to polymer $(\mathbf{2})_n$•**14c**: H_β = benzylic protons on dibenzylamine; H_α, H_β, H_γ = nonequivalent sets of uncomplexed crown ether protons.

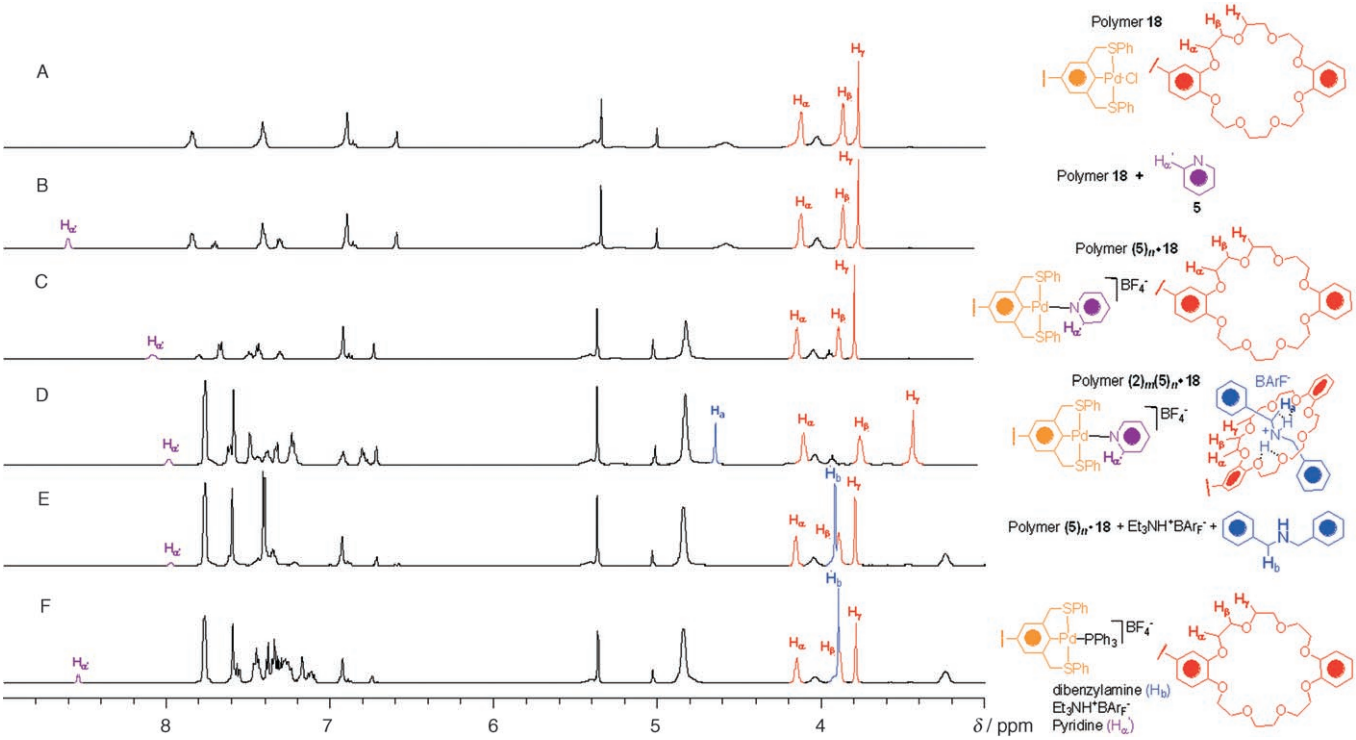


Figure 4. ^{1}H NMR spectra (500 MHz, 298 K) in CD_2Cl_2[61] showing the stepwise functionalization of copolymer **18** with **2** and **5** and the subsequent receptor removal. A) Copolymer **18**: H_α, H_β, H_γ = nonequivalent sets of crown ether protons; B) copolymer **18** and receptor **5**: H_α = α-pyridyl protons; C) activation of copolymer **18** with $AgBF_4$ to form copolymer $(\mathbf{5})_n$•**18**: H_α = α-pyridyl protons on pyridine pincer complex; D) fully functionalized copolymer $(\mathbf{2})_m(\mathbf{5})_n$•**18** after addition of **2**$[BAr_F]^-$ to $(\mathbf{5})_n$•**18**: H_α = α-pyridyl protons on pyridine pincer complex; H_α, H_β, H_γ = nonequivalent sets of complexed crown ether protons; H_α = complexed benzylic protons on **2**$[BAr_F]^-$; E) copolymer $(\mathbf{2})_m(\mathbf{5})_n$•**18** after addition of Et_3N: H_α, H_β, H_γ = inequivalent sets of uncomplexed crown ether protons; H_α = α-pyridyl protons complexed pyridine; H_β = benzylic protons on dibenzylamine. F) copolymer $(\mathbf{5})_n$•**18** after addition of PPh_3: H_α, H_β, H_γ = nonequivalent sets of uncomplexed crown ether protons; H_α = α-pyridyl protons uncomplexed pyridine.

was measured for homopolymer **14c** upon binding with the dialkylammonium cation **2**. Binding of the complementary homopolymer **15** with the small molecule **3** resulted in a slightly lower association constant ($K_a = 1 \times 10^5\,M^{-1}$). Potential reasons for the lowered association strength are steric hinderence created by the bound DB24C8 **3** along the sites

Table 2. Association constants for the hydrogen-bonding interactions in all polymers.

Polymer	Ligand	K_a [10^4 M^{-1}]	Error [10^4 M^{-1}]
14c	**2**[BAr_F]$^-$	286	±54
15	**3**	10	±4
18	**2**[BAr_F]$^-$	43	±15
(**5**)$_n$·**18**	**2**[BAr_F]$^-$	54	±17
20	**3**	9	±4
(**5**)$_n$·**20**	**3**	5	±2

of the polymer backbone, as well as different solubility behavior of the two homopolymers. In general, hydrogen-bonding association constants for all copolymers were less than the association constants of their homopolymer analogues, in part due to differences in solubility of the individual blocks of the copolymers in comparison to their homopolymer analogues. However, the hydrogen-bonding binding strengths of both copolymers **18** and **20** were independent of the metal coordination step. The association constants measured before and after metal coordination for both polymers were identical within experimental error. These results clearly demonstrate that the two employed recognition units do not interfere with each other and that the self-assembly of our copolymers can be executed orthogonally.

Conclusion

In this article, we have reported the next generation of UPBs that possess recognition moieties which self-assemble with their complementary receptor molecules with very high association strengths. We have established that through the employment of living polymerization techniques, we can control the architecture of such polymeric systems. In this contribution, we have demonstrated this control by synthesizing block copolymers. Using ^{1}H NMR spectroscopic and ITC studies, we have proven that the self-assembly of our polymers is quantitative, reversible, and can be achieved in an orthogonal fashion. Our study demonstrates the potential for the employment of such a functionalization strategy in polymeric materials. Universal polymer backbones based on such high-association-constant-based recognition units are a prerequisite for the employment of the UPB in materials science and experiments towards this goal are currently being carried out in our laboratories.

Experimental Section

General methods: Reagents were purchased either from Acros Organics, Aldrich Company, or Strem Chemicals and used without further purification unless otherwise noted. CH_2Cl_2 was dried by passage through copper oxide and alumina columns. Routine NMR spectra were recorded on a 300 MHz (^{1}H, 300 MHz; ^{13}C, 75 MHz) or 500 MHz (^{1}H, 500 MHz; ^{13}C, 125 MHz) Varian Mercury spectrometer; spectra were referenced to residual proton solvent. The Georgia Tech Mass Spectrometry Facility provided mass spectral analysis with a VG-70 se spectrometer. Atlanta Microlabs, Norcross, GA, performed all elemental analysis. Gel-permeation chromatography (GPC) analyses for all polymers were carried out by using a Waters 1525 binary pump linked to a Waters 2414 refractive index detector with HPLC grade CH_2Cl_2 as the eluting solvent on an American Polymer Standards 10 μm particle size, linear mixed bed packing columns (2×). Poly(styrene) standards were used to calibrate all GPCs. Isothermal titration calorimetry (ITC) was performed on a Microcal VP-ITC Isothermal Calorimeter. Degassed, HPLC grade solvents were used for all ITC experiments.

Dibenzylammonium BAr_F (2[BAr_F]$^-$): In a degassed flask, $NaBAr_F$[62] (380 mg, 0.43 mmol) was added to a solution of dibenzylammonium chloride (100 mg, 0.43 mmol) in anhydrous Et_2O (10 mL). The mixture was stirred vigorously for four hours and then filtered. Subsequently, the filtrate was evaporated to dryness under reduced pressure to afford the product (450 mg, 99%) as a white solid. ^{1}H NMR (CD_2Cl_2): δ=4.29 (br s, 4H), 7.18 (d, J=8.7 Hz, 4H), 7.45 (t, J=8.7 Hz, 4H), 7.50 (t, J=8.7 Hz, 2H), 7.52 (br s, 4H), 7.68 ppm (br s, 8H); ^{13}C NMR (CD_2Cl_2): δ=51.4, 117.3, 123.4, 125.5, 128.1, 129.1, 130.2, 131.0, 131.5, 134.6 ppm; MS (ESI): m/z calcd for $C_{14}H_{16}N$: 198.1277; found: 198.1386 (100) [$M-BAr_F$]$^+$; elemental analysis calcd (%) for $C_{48}H_{28}BF_{24}N$: C 52.05, H 2.66, N 1.32; found: C 52.16, H 2.69, N 1.44.

***exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 10-hydroxydecyl ester (7)**: *exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (2.6 g, 19 mmol) and decane-1,10 diol (9.9 g, 57 mmol) were dissolved in anhydrous CH_2Cl_2 (25 mL) under an argon atmosphere. DCC (3.92 g, 19 mmol) in CH_2Cl_2 (5 mL) and DMAP (catalytic amount) were added to the stirred solution at 25°C. Following stirring at reflux for twelve hours, the mixture was cooled to room temperature, and the precipitate was filtered off. The filtrate was dried ($MgSO_4$) and the solvent removed under reduced pressure to give a yellow oil that was further purified by column chromatography (SiO_2, eluant: 3:1 hexanes/EtOAc) to yield a clear oil (3.35 g, 60%). ^{1}H NMR ($CDCl_3$): δ=6.12 (m, 2H), 4.07 (t, J=6.6 Hz, 2H), 3.63 (t, J=6.6 Hz, 2H), 3.03 (m, 1H), 2.92 (m, 1H), 2.21 (m, 1H), 1.91 (m, 1H) 1.67–1.50 (m, 5H) 1.43–1.24 ppm (m, 15H); ^{13}C NMR ($CDCl_3$): δ= 176.6, 138.3, 136.0, 64.8, 63.2, 46.8, 46.6, 43.4, 41.9, 33.0, 30.5, 29.7, 29.7, 29.6, 29.4, 28.9, 26.1, 25.9 ppm; MS (ESI+): m/z: 295.2 [M+1]$^+$; elemental analysis calcd (%) for $C_{18}H_{30}O_3$: C 73.43, H 10.27; found: C 72.99, H 10.29.

***exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 9-carboxynonyl ester (8)**: Compound **7** (2.27 g, 7.77 mmol) and PDC (17.13 g, 46.64 mmol) were dissolved in DMF (50 mL) and stirred at room temperature for 48 h. Water (20 mL) was added and the mixture was extracted with Et_2O (3× 15 mL). The combined organic layers were washed with H_2O (2×20 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure to give a brown oil that was further purified by column chromatography (SiO_2, eluant: 2:1 hexanes/EtOAc) to yield a clear oil (1.89 g, 80%). ^{1}H NMR ($CDCl_3$): δ=6.12 (m, 2H), 4.07 (t, J=6.6 Hz, 2H), 3.03 (m, 1H), 2.92 (m, 1H), 2.35 (t, J=7.7 Hz, 2H), 2.20 (m, 1H), 1.90 (m, 1H), 1.63 (m, 4H), 1.53 (d, 1H, J=8.3 Hz), 1.39–1.26 ppm (m, 13H); ^{13}C NMR ($CDCl_3$): δ=180.3, 176.7, 138.3, 136.0, 64.8, 46.8, 46.6, 43.4, 41.9, 34.3, 30.5, 29.5, 29.4, 29.2. 28.9, 26.1, 24.9 ppm; MS (ESI+): m/z (%): 309.2 (100), 617.5 (25, dimer); elemental analysis calcd (%) for $C_{18}H_{28}O_4$: C 70.10, H 9.15; found: C 69.87, H 9.06.

***exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 9-{2,5,8,11,18,21,24,27-octaoxatricyclo[26.4.0.0^{12,17}]dotriaconta-1(32),12(17),13,15,28,30-hexaen-14-yl-methoxycarbonyl}nonyl ester (12)**: Compounds **8** (0.38 g, 1.23 mmol) and **10** (0.59 g, 1.23 mmol) were dissolved in anhydrous CH_2Cl_2 (25 mL) under an argon atmosphere. DCC (0.3 g, 1.45 mmol) in CH_2Cl_2 (5 mL) and DMAP (catalytic amount) were added to the stirred solution at 25°C. Following stirring at reflux for twelve hours, the mixture was cooled to room temperature and the precipitate was filtered off. The filtrate was dried ($MgSO_4$) and the solvent removed under reduced pressure to give a yellow oil that was further purified by column chromatography (SiO_2, eluant: EtOAc) to yield a white solid (0.86 g, 90%). ^{1}H NMR ($CDCl_3$): δ=6.90–6.81 (m, 7H), 6.12 (m, 2H), 5.00 (s, 2H), 4.15 (t, J=4.4 Hz, 7H), 4.07 (t, J=7.2 Hz, 2H), 3.92 (t, J=4.4 Hz, 7H), 3.83 (m, 7H), 3.03 (m, 1H), 2.92 (m, 1H), 2.32 (t, J=7.2 Hz, 2H), 2.20 (m, 1H), 1.91 (m, 1H), 1.71–1.51 (m, 8H), 1.40–1.25 ppm (m, 12H); ^{13}C NMR ($CDCl_3$): δ=176.0, 174.0, 149.1, 149.0, 138.3, 136.0, 129.3,

121.9, 121.6, 114.5, 114.2, 113.8, 71.6, 71.5, 70.2, 70.1, 69.7, 69.6, 66.3, 64.8, 46.8, 46.6, 43.4, 41.9, 34.6, 34.2, 30.5, 29.5, 29.4, 29.3, 28.9, 26.1, 25.9, 25.2, 25.1 ppm; MS (FAB+): *m/z* (%): 768.5 (30), 154.2 (100); elemental analysis calcd (%) for $C_{43}H_{60}O_{12}$: C 67.17, H 7.87; found: C 66.93, H 7.90.

***exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 9-{3-[(benzyl-*tert*-butoxycarbonylamino)methyl]benzyloxycarbonyl}nonyl ester (11)**: Compounds **8** (0.76 g, 2.5 mmol) and **9** (0.95 g, 2.90 mmol) were dissolved in anhydrous CH_2Cl_2 (25 mL) under an argon atmosphere. DCC (0.60 g, 2.75 mmol) and DMAP (catalytic amount) were added to the stirred solution at 25 °C. Following stirring at reflux for twelve hours, the mixture was cooled to room temperature and the precipitate was filtered off. The filtrate was dried ($MgSO_4$) and the solvent removed under reduced pressure to give a yellow oil that was further purified by column chromatography (SiO_2, eluant: 3:1 Hexanes: EtOAc) to yield a clear oil (1.38 g, 90%). ^{1}H NMR ($CDCl_3$): δ = 7.33–7.21 (m, 9H), 6.12 (m, 2H), 5.1 (s, 2H), 4.41 (s, 2H), 4.33 (s, 2H), 4.07 (t, J = 6.6 Hz, 2H), 3.03 (m, 1H), 2.91 (m, 1H), 2.35 (t, J = 7.15 Hz, 2H), 2.20 (m, 1H), 1.91 (m, 1H), 1.71–1.58 (m, 4H), 1.49 (s, 9H), 1.40–1.23 ppm (m, 13H); ^{13}C NMR ($CDCl_3$): δ = 176.7, 174.0, 156.4, 138.4, 136.2, 135.6, 128.9, 128.8, 128.4, 128.0, 127.7, 80.54, 66.21, 64.9, 49.2, 47.0, 46.8, 43.6, 42.0, 34.7, 30.7, 29.7, 29.56, 29.55, 29.5, 29.4, 29.1, 28.9, 26.3, 25.3 ppm; MS (ESI+): *m/z* (%): 618.5 (50); elemental analysis calcd (%) for $C_{38}H_{51}NO_6$: C 73.87, H 8.32, N 2.27; found: C 73.87, H 8.34, N 2.36.

General polymerization procedure: An amount of monomer was weighed into a glass vial with a rubber septum cap, placed under an argon atmosphere and dissolved in anhydrous, degassed CD_2Cl_2 or $CDCl_3$ (1 mL per 100 mg of monomer). A stock solution of the catalyst (in the corresponding solvent) was prepared, and the desired volume of solution was added to the polymerization vessel. Upon complete polymerization, ethyl vinyl ether was added to quench the polymerization. The polymer was isolated and purified by repeated precipitation into cold hexanes or MeOH.

Polymer 14: ^{1}H NMR ($CDCl_3$): δ = 6.90–6.78 (m, 7H), 5.42–5.10 (br m, 2H), 5.00 (s, 2H), 4.17 (m, 7H), 4.05 (br m, 2H), 3.90 (m, 7H), 3.80 (m, 7H), 2.8–2.4 (br m, 4H), 2.25 (br t, J = 7.4 Hz, 2H), 2.2–1.45 (m, 8H), 1.40–1.00 ppm (m, 12H); ^{13}C NMR ($CDCl_3$): δ = 176.2, 173.9, 149.1, 149.0, 129.4, 121.9, 121.7, 115–113, 72.9, 71.5, 71.4, 70.2, 70.1, 69.7, 69.6, 66.3, 64.7, 49.4, 34.5, 34.2, 29.6, 29–28, 26.1, 25.8, 25.1 ppm; elemental analysis calcd (%) for **14c**: C 76.17, H 7.87; found: C 66.45, H 8.14.

Polymer 13: ^{1}H NMR ($CDCl_3$): δ = 7.41–7.03 (m, 9H), 5.36–5.25 (m, 2H), 5.12 (s, 2H), 4.43 (s, 2H), 4.33 (s, 2H), 4.00 (br t, J = 6.5 Hz, 2H), 2.72–2.51 (m, 2H), 2.35 (t, J = 7.5 Hz, 2H), 2.10–1.86 (br m, 2H) 1.60 (m, 4H), 1.50 (s, 9H), 1.47–1.27 ppm (m, 13); ^{13}C NMR ($CDCl_3$): δ = 173.9, 168.1, 156.3, 152.2, 138.5, 135–127, 99.8, 86.8, 80.5, 68.6, 66.2, 64.8, 64.0, 61.0, 39.2, 34.7, 31.31, 31.26, 30.8, 29.7, 29.6, 29.3, 29.11, 28.8, 26.3, 25.3, 24.2, 23.4, 20.4 ppm; elemental analysis calcd (%) for **13c**: C 73.87, H 8.40, N 2.27; found: C 73.79, H 8.40, N 2.31.

Polymer 15: Polymer **13** (0.53 g, 0.85 mmol) was dissolved in anhydrous CH_2Cl_2 (4 mL) under an Argon atmosphere and TFA (1.0 mL, 13.51 mmol) was added. The mixture was stirred for three hours at room temperature. The solvent was removed under reduced pressure to yield the poly(DBA-TFA salt) (0.52 g, 96% yield). The resulting TFA salt (88 mg, 0.14 mmol) was dissolved in CH_2Cl_2 (10 mL) and NH_4PF_6 (2.3 g, 14 mmol) was added. The solution was stirred for three hours at room temperature to complete the ion exchange. An excess of CH_2Cl_2 was added and the mixture was washed with H_2O (2×20 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure to yield **15** as a brown oil (85 mg, 93%). ^{1}H NMR ($CDCl_3$): δ = 9.10 (br s, 2H), 7.43–6.85 (m, 9H), 5.45–5.10 (m, 2H), 5.00 (s, 2H), 4.15–3.80 (m, 6H), 3.20–2.20 (m, 5H), 2.19–1.40 (4H), 1.40–1.10 ppm (m, 14H); ^{13}C NMR ($CDCl_3$): δ = 174.0, 168.2, 156.4, 152.0, 138.5, 134–131, 99.8, 87.0, 80.6, 68.6, 66.2, 64.8, 64.0, 65.0, 61.1, 39.1, 34.7, 31.31, 31.25, 30.8, 29.6, 29.3, 28.8, 26.2, 25.3, 24.2, 23.4, 20.4 ppm.

Copolymer 18. ^{1}H NMR ($CDCl_3$): δ = 7.80 (m, 4H, SPh), 7.38 (m, 6H, SPh), 6.85 (m, 7H), 6.49 (s, 2H), 5.50–5.18 (m, 4H), 5.00, (s, 2H), 4.50 (br s, 4H), 4.17 (m, 7H), 4.05 (br m, 4H), 3.90 (m, 7H), 3.80 (m, 9H), 2.80–2.40 (br m, 4H), 2.25 (t, J = 7.0 Hz, 2H), 2.15–1.90 (br m, 4H), 1.80–1.40 (br m, 7H), 1.40–1.00 ppm (br m, 34H); ^{13}C NMR ($CDCl_3$): δ = 176.2, 176.1, 173.9, 157.2, 151.7, 150.3, 149.1, 149.0, 140.0, 134–131, 130.0, 129.4, 121.9, 121.6, 114.5, 114.3, 113.8, 110.4, 109.0, 90.5, 86.6, 71.5, 70.2, 70.1, 69.7, 69.6, 68.3, 66.3, 64.7, 57.8, 51.9, 49.8, 49.4, 47.9, 42.2, 36.6, 34.5, 34.2, 29.8, 29.5, 28.9, 26.3, 26.1, 25.9, 25.2, 24.9 ppm; elemental analysis calcd (%) for **18**: C 63.81, H 6.94; found: C 64.19, H 7.27.

Copolymer 19: ^{1}H NMR ($CDCl_3$): δ = 7.85 (m, 4H), 7.40–7.10 (m, 13H), 6.55 (s, 2H), 5.45–5.13 (m, 4H), 5.10 (s, 2H), 4.53 (br s, 4H), 4.40 (m, 4H), 4.05 (m, 4H), 3.85 (br t, J = 6.6 Hz, 2H), 2.80–2.45 (m, 6H), 2.35 (t, J = 7.6 Hz, 2H), 2.10–1.85 (m, 6H), 1.80–1.55 (m, 18H), 1.50 (s, 9H), 1.49–1.10 ppm (m, 22H); ^{13}C NMR ($CDCl_3$): δ = 173.9, 168.1, 157.4, 156.4, 152.2, 151.9, 150.5, 135–127, 109.2, 99.8, 86.8, 80.5, 68.6, 66.2, 64.9, 64.0, 61.0, 58.8, 52.1, 39.2, 34.7, 31.3, 31.2, 30.8, 29.9, 29.7, 29.6, 29.3, 29.1, 28.8, 26.5, 26.3, 25.3, 24.2, 23.4, 20.4 ppm; elemental analysis calcd (%) for **19**: C 66.65, H 7.12, N 1.01; found: C 64.96, H 7.12, N 0.83.

Copolymer 20: The block copolymer **20** was prepared analogously to polymer **15**. ^{1}H NMR ($CDCl_3$): δ = 9.00 (s, 2H), 7.85 (m, 4H), 7.40 (m, 13H), 6.60 (s, 2H), 5.40–5.10 (m, 4H), 5.00 (s, 2H), 4.60 (m, 4H), 4.30 (m, 4H), 4.10 (m, 4H), 3.90 (br t, J = 6.6 Hz, 2H), 2.80–2.40 (m, 6H), 2.30 (t, J = 7.5 Hz, 2H), 2.10–1.80 (m, 6H), 1.75–1.51 (m, 18H), 1.40–1.10 ppm (m, 22H); ^{13}C NMR ($CDCl_3$): δ = 174.5, 173.8, 168.2, 156.8, 156.2, 152.2, 151.3, 150.0, 138.4, 134–127, 108.7, 99.8, 86.8, 80.5, 68.7, 67.9 66.2, 65.0, 64.2, 64.0, 61.0, 68.6, 51.3, 47.5, 45.3, 40.0, 39.1, 37.3, 36.0, 30.8, 30.1, 29.3, 24.2, 23.4 ppm.

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