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Supramolecular Alternating Block Copolymers via Metal Coordination

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Abstract: A bimetallic ruthenium olefin metathesis initiator was synthesized and used to polymerize functionalized norbornenes, affording polymers that are living at both polymer chain-ends. Using this bis-ruthenium initiator strategy and combining it with functional chain-terminators, highly-efficient syntheses of either SCS-Pd^{II} pincer- or pyridine-functionalized symmetrical telechelic polymers were developed. The terminal functional group incorporation was confirmed by ^{1}H NMR spectroscopy analyses. The telechelic polymers were self-assembled into block copolymers by means of metal coordination between corresponding terminal recognition units. The self-assembly process was monitored by ^{1}H NMR spectroscopy revealing nearly quantitative functionalization. The resulting supramolecular block copolymers were further characterized by viscometry and dynamic light scattering.

Keywords: block copolymers • metal coordination • polymerization • ring-opening metathesis • ruthenium • supramolecular chemistry

Introduction

The introduction of noncovalent interactions between polymeric constituents[1] allows for the modular construction of well-defined supramolecular polymeric assemblies including supramolecular block copolymers, which are of considerable interest owing to their promise for applications ranging from electronics to medicine.[2] Supramolecular block copolymers can be categorized into diblock[3] and multiblock copolymers assembled from monotelechelic and ditelechelic polymers, respectively. Multiblock copolymers are of particular interest, since unprecedented polymeric blends with tunable physical properties can be obtained easily by mixing two appropriately functionalized homopolymers.[4] A number of noncovalent interactions have been used as key interactions in multiblock copolymers including hydrogen bonding and metal coordination. For example, Sijbesma and Binder have utilized complementary hydrogen bonding to fabricate supramolecular multiblock copolymers based on telechelic poly(ester)s and poly(isobutylene)s, respectively.[5] Schubert has used terpyridine-based metal coordination to generate diblock copolymers[6] and in combination with Upy-based hydrogen bonding multiblock copolymers.[7] Meijer and Zimmerman have employed quadruple hydrogen bonds with high association constants ($K_a \approx 10^7\,\text{M}^{-1}$) between diamidonaphthyridine (DAN/Napy) and ureidopyrimidinone (Upy) or ureidoguanosine (UG), respectively, to generate supramolecular alternating block copolymers.[8]

Most synthetic strategies towards multiblock copolymers rely on post-polymerization functionalization steps to introduce the molecular recognition moiety resulting in often non-quantitative conversions and requiring reaction conditions that may be incompatible with other functionalities along the polymer. The successful synthesis of telechelic polymers with complementary binding motifs circumventing the need for post-polymerization functionalization is a desirable prerequisite for the easy and high-yielding preparation of well-defined supramolecular block copolymers. We suggest that the ring-opening metathesis polymerization (ROMP) of cyclic olefins in the presence of bifunctional chain-transfer agents (CTA) is an efficient strategy for the incorporation of supramolecular functionalities onto both chain-ends of a polymer.[9] In 2005, we employed this methodology to introduce hydrogen bonding and metal coordina-

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tion moieties at polymer chain-ends in situ and reported the self-assembly of the resulting telechelic polymers into supramolecular multiblock copolymers.[10] Although highly advantageous over traditional post-polymerization functionalization, owing to complete incorporation of almost any terminal recognition unit in situ, the ROMP-CTA strategy limits full control over the obtained telechelic polymer properties because it relies on the non-living polymerization of functionalized cyclooctenes. Herein, we report the synthesis of symmetrically end-functionalized polymers in a single step by means of ROMP using a bimetallic ruthenium initiator and functional chain-terminators (CTs). The combination of a living/controlled polymerization with metal-coordination-based self-assembly allows for the formation of well-defined supramolecular alternating block copolymers (Figure 1).

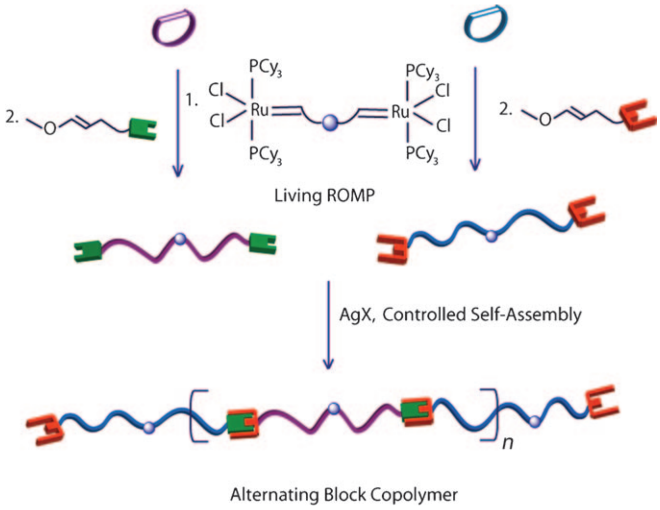
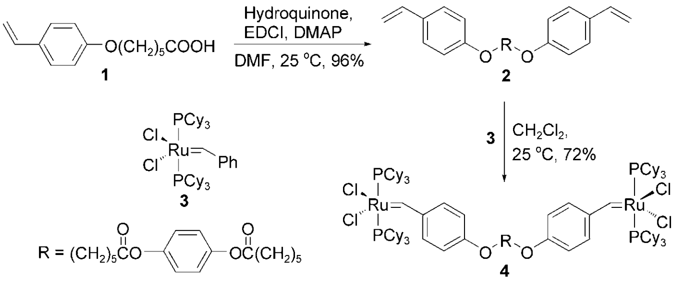


Figure 1. Schematic representation of the synthetic strategy towards supramolecular alternating block copolymers.

Research design: Our strategy is based on the self-assembly of A—A and B—B bifunctional macromonomers by means of metal coordination. The macromonomers are telechelic polymers bearing a palladated sulfur-carbon-sulfur (SCS) pincer complex or a pyridyl end group, respectively, at both chain-ends. The telechelic polymers are being synthesized by ROMP using a bis-ruthenium initiator designed to be living and tolerant to a broad range of functionalities,[11] terminated with functional CTs containing metal coordination sites resulting in the formation of perfect telechelic polymers. For our study, we employ the coordination of Pd-pincer complexes to functionalized pyridines as the noncovalent interaction. This metal coordination step is unsymmetrical, highly directional and avoids the problem of homodimerization unlike hydrogen-bonded systems.[12] Furthermore, this interaction has been used extensively in side-chain supramolecular polymers and can be tuned easily.[12] The combination of a bis-ruthenium initiator with functionalized CTs is designed to afford symmetrical telechelic polymers possessing desired recognition motifs with full control over basic polymer properties, such as molecular weight, degree of polymerization, and polydispersity. Metal coordination between SCS-Pd^{II} pincer complex-containing polymers and ones containing pyridyl end groups should lead to the self-assembly of A—A and B—B macromonomers with tunable block length by the controlled addition of the activating agent $AgBF_4$. Furthermore, use of differently substituted norbornene monomers for the A—A and B—B macromonomers allows for the preparation of supramolecular alternating block copolymers.

Results and Discussion

Synthesis of bis-ruthenium initiator 4: A bis-alkylidene ruthenium olefin metathesis initiator was used to afford poly(norbornene)s that are living at both polymer chain-ends, thereby allowing for complete incorporation of terminal recognition units. The synthesis of the bimetallic ruthenium initiator **4** is outlined in Scheme 1. 6-(4-Vinylphenoxy) hexanoic acid **1** was esterified with hydroquinone using *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride and 4-dimethylaminopyridine to afford bis-styrene **2**. Initiator **4** was synthesized by the carbene exchange of **3** with **2** in dichloromethane. ^{1}H NMR analysis indicated 95 % conversion to **4** as seen by a shift of the carbene signals to $\delta = 19.4$ ppm in CD_2Cl_2. After purification by column chromatography, **4** was isolated in 72 % yield.



Scheme 1. Synthesis of bis-ruthenium initiator **4**.

Homopolymerization using initiator 4: We investigated the polymerization behavior of norbornene octyl ester **10**. Monomer **10** was polymerized quantitatively using 2.5 mol % of **4** within 10 min at room temperature. Full initiation was observed by a complete shift of the carbene signal from $\delta = 19.4$ ppm for **4** to 18.6 ppm (for the fully initiated species) in the ^{1}H NMR spectrum. We carried out a series of homopolymerizations with monomer-to-initiator ratios ([M]/[I]) ranging from 40:1 to 200:1. A linear relationship between M_n and [M]/[I] was found for polymers **12a–e** (Figure 2) indicating the controlled nature of the polymerization of **10** using **4**. The gel-permeation chromatography (GPC) data of **12a–e** are summarized in Table 1. The living nature of the polymerization was further confirmed by the synthesis of a homoblock copolymer. First, a 40 mer was synthesized using **4**, which was then used as a macroinitiator for the polymeri-

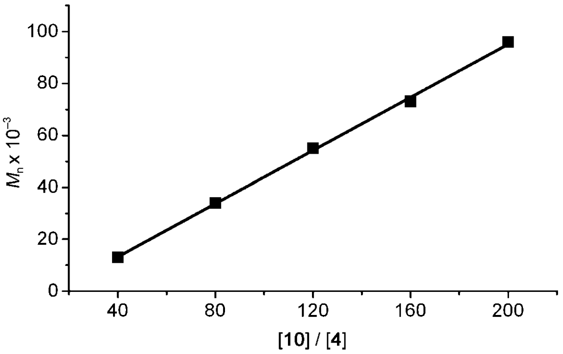


Figure 2. Plot of M_n vs. monomer **10**/initiator **4** ratios for polymer **12a–e**.

Table 1. Polymer characterization data (GPC) for **12a–e**.[a]

Polymer	[M]/[I]	M_n	M_w	PDI
12a	40	13000	20000	1.56
12b	80	34000	43000	1.27
12c	120	55000	68000	1.23
12d	160	73000	88000	1.20
12e	200	96000	114000	1.19

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

zation of a 1000 mer. The GPC traces of the homoblock copolymers were unimodal. Furthermore, we observed a complete shift to high molecular weights without traces of terminated low molecular weight polymer (Figure 3). The new bis-ruthenium initiator **4** is thus not only active toward ROMP of norbornenes, but also living at both chain-ends.

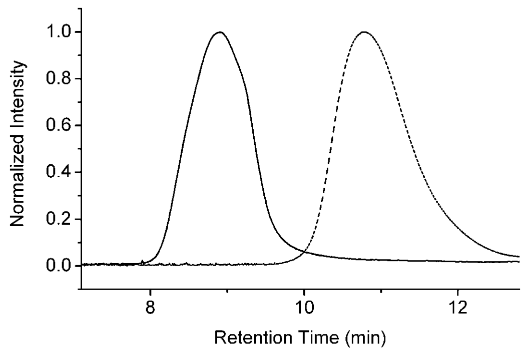
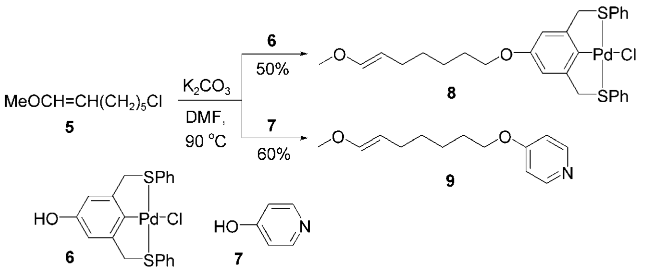


Figure 3. GPC traces of homoblock copolymers obtained from **10** by using **4**. Dashed line: polymer after complete conversion of the monomer ([M]/[I] = 40:1, M_n = 13000, PDI = 1.56). Solid line: polymer after standing for 2 h and then continued polymerization of the additional monomer ([M]/[I] = 1000:1, M_n = 258000, PDI = 1.25).

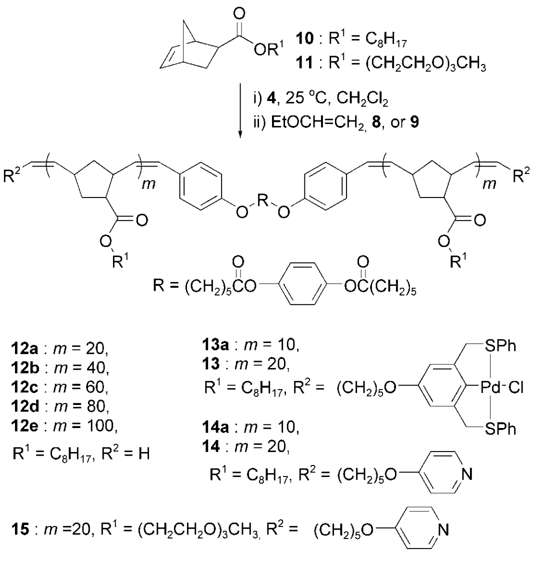
Synthesis of CTs: We can install any desired functionality in living ROMP through the use of functionalized vinyl ether derivatives that serve as chain-terminators, that is, they terminate the polymerization by incorporating the desired functionality at the polymer chain-end.[13] To install supramolecular functionalities for metal coordination at both chain-ends of the polymer, SCS-Pd^{II} pincer- and pyridine-based CTs were synthesized as outlined in Scheme 2.



Scheme 2. Synthesis of CTs **8** and **9**.

6-Chloro-1-hexenyl methyl ether **5** was reacted with SCS-Pd^{II} pincer precursor **6** or 4-hydroxypyridine **7** by using Williamson etherification to afford CTs **8** and **9**, respectively.

Preparation and characterization of telechelic polymers: ROMP of norbornene octyl ester **10** (for **13** and **14**) or norbornene methyltriglycol ester **11** (for **15**) was carried out with 2.5 mol% of **4** in CH_2Cl_2 followed by the addition of an excess of either **8** to obtain SCS-Pd^{II} pincer-functionalized telechelic polymer **13** or **9** to yield pyridine-functionalized telechelic polymers **14** and **15** (Scheme 3). Complete



Scheme 3. Synthesis of telechelic polymers **12–15**.

termination of the ROMP was observed by the disappearance of the polymeric carbene signals in the ^{1}H NMR spectra. Incorporation of each functionality at both the chain-ends of each telechelic polymer was confirmed by ^{1}H NMR analysis (Supporting Information). The molecular weights and PDIs of all the telechelic polymers were determined by GPC analyses revealing monomodal distributions (M_n = 14000, PDI = 1.62 for **13**, M_n = 13000, PDI = 1.57 for **14**, and M_n = 18000, PDI = 1.51 for **15**). Thus our methodology allows for full control over end group functionalization compared to the CTA-based ROMP in the preparation of symmetrical ditelechelic polymers.[8b,10]

Self-assembly: We also investigated the formation of supramolecular multiblock copolymers by means of metal coordination using telechelic polymers **13**–**15**. $AgBF_4$ is known to remove the Cl ligand on pincer complexes generating a cationic Pd species that can coordinate pyridyl units resulting in the formation of new pincer complexes.[12] We have previously demonstrated the functionalization of side-chain and main-chain supramolecular polymers containing Pd-pincer complexes.[10,12] We envisaged that by controlling the ratio of $AgBF_4$ in the mixture of complementary telechelic polymers to activated Pd-pincer moieties we can control the length of supramolecular block copolymers formed by metal-coordination.

The preparation of supramolecular homoblock copolymers (SHBCs) **13:14(*n*)** and supramolecular alternating block copolymers (SABCs) **13:15(*n*)** is outlined in Scheme 4. SABCs **13:15(*n*)** are based on two chemically different blocks, octyl- and methyltriglycol-substituted poly(norbornene)s, which may result in phase separation of individual blocks whereas the constituent blocks in SHBCs **13:14(*n*)** should be completely miscible. **13:14(*n*)** and **13:15(*n*)** were synthesized by the addition of ***n*** equivalents (***n***=1, 2, or 3) of $AgBF_4$ to a solution of 1 equivalent of **13** and 1 equivalent of **14** or **15**, respectively. The formation of supramolecular block copolymers was characterized by using ^1H NMR spectroscopy, Ubbelohde viscometry, and dynamic light scattering (DLS).

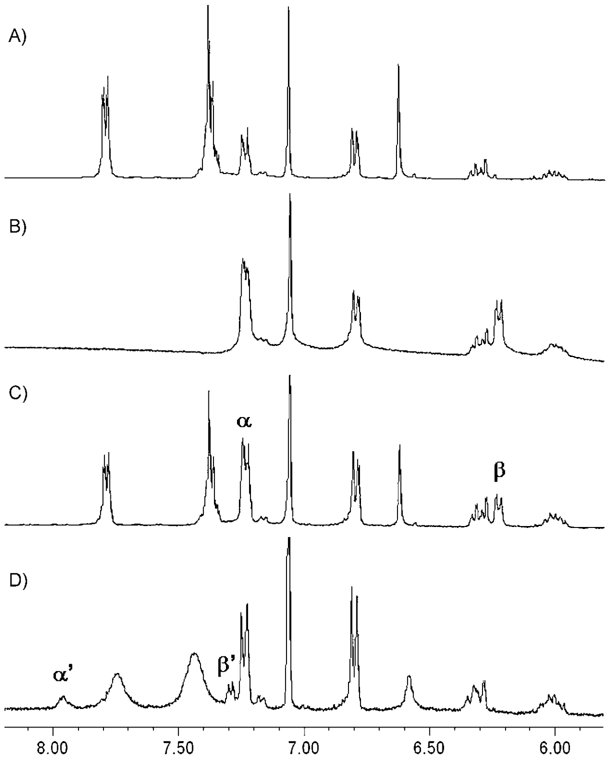
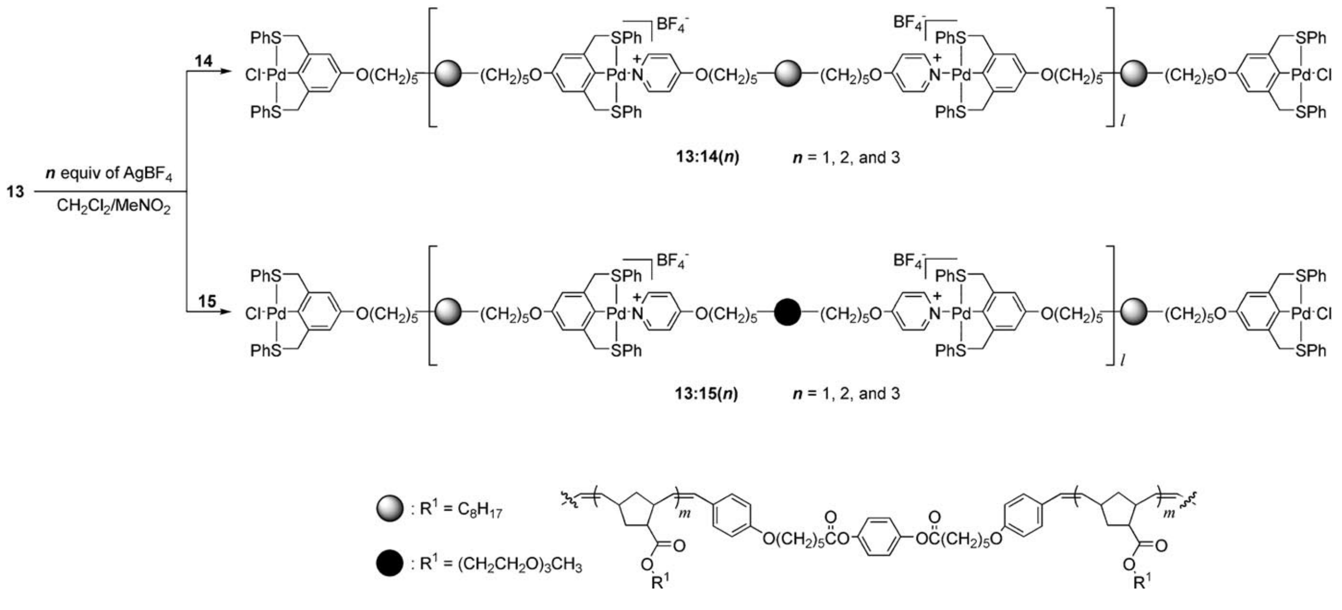


Figure 4. ^1H NMR spectra depicting metal coordination of **13a** with **14a** in CD_2Cl_2. A) Telechelic polymer **13a**; B) telechelic polymer **14a**; C) a mixture of telechelic polymers **13a** and **14a** at a 1:1 ratio: α and β = α- and β-pyridyl protons, respectively; D) self-assembled telechelic polymer **13a:14a** after addition of $AgBF_4$: α' and β' = α- and β-pyridyl protons on pyridyl pincer complex, respectively.

Telechelic polymers **13a** and **14a** were employed for the metal coordination because shorter 20 mers allow for easy ^1H NMR spectroscopy characterization. SHBC **13a:14a** was prepared by the addition of 3 equivalents of $AgBF_4$ to a solution of 1 equivalent each of **13a** and **14a** in dichloromethane. The formation of SHBC **13a:14a** was confirmed from characteristic shifts in the ^1H NMR spectrum. The ^1H NMR spectra of **13a** and **14a** is shown in Figure 4A,B, respectively. A mixture of **13a** and **14a** at a 1:1 ratio is shown in Figure 4C; no shifts in the ^1H NMR spectra are observed. Upon addition of $AgBF_4$, the resulting ^1H NMR spectrum of SHBC **13a:14a** shows the characteristic downfield shifts of



Scheme 4. Self-assembly of telechelic polymers **13**–**15**.

the α- and β-pyridyl signals from $\delta=7.23$ (α) and 6.23 ppm (β) to 7.96 (α′) and 7.29 ppm (β′), respectively. In addition to the diagnostic shifts of the pyridyl signals, the aromatic proton signals on the pincer complex broaden and shift slightly from $\delta=7.79$, 7.36, and 6.63 ppm to 7.74, 7.44, and 6.58 ppm, respectively (Figure 4D). These characteristic shifts indicate quantitative metal coordination between **13a** and **14a**, resulting in the formation of SHBC **13a:14a**.

Viscometry is a simple yet powerful technique to demonstrate the formation of supramolecular multiblock polymers.[8] The solution properties of SHBCs **13:14(*n*)** and SABCs **13:15(*n*)** in dichloromethane were examined by viscometry, and the results are shown in Figure 5. The specific viscosity (η_{sp}) of both SHBCs **13:14(*n*)** and SABCs **13:15(*n*)** increases as the equivalence of $AgBF_4$ increases from 1 to 2 to 3. Additionally, the relatively slight increases from SHBC **13:14(2)** and SABC **13:15(2)** to SHBC **13:14(3)** and SABC **13:15(3)**, respectively, represent that 2 equivalents of $AgBF_4$ are sufficient for efficient metal coordination leading to the formation of supramolecular block copolymers. Compared with SHBCs **13:14(*n*)**, SABCs **13:15(*n*)** show much larger η_{sp} values probably due to, at least partial, phase separation of the two different blocks. As a control experiment, we also carried out viscometry experiments on a 1:1 mixture of pyridine-functionalized telechelic polymer **15** and unfunctionalized polymer **12a** before and after the addition of $AgBF_4$. The η_{sp} values after addition of $AgBF_4$ were unchanged (Supporting information) supporting our hypothesis that the increase in η_{sp} values is the direct result of the formation of supramolecular alternating block copolymers.

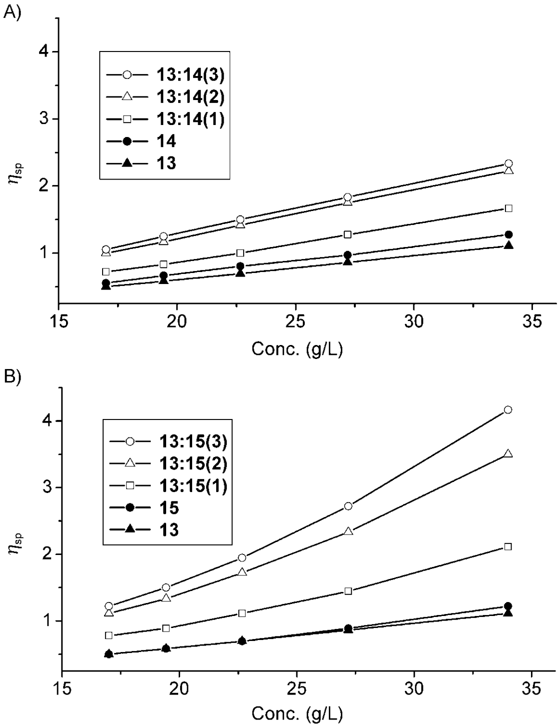


Figure 5. Specific viscosity (η_{sp}) at 25 °C in CH_2Cl_2. A) Telechelic polymers **13** and **14**, and SHBCs **13:14(*n*)** after addition of *n* equiv of $AgBF_4$; B) telechelic polymers **13** and **15**, and SABCs **13:15(*n*)** after addition of *n* equiv of $AgBF_4$.

To examine the bulk structure of SHBCs **13:14(*n*)** and SABCs **13:15(*n*)** in more detail, the hydrodynamic radii (R_h) of these materials were determined by DLS (Table 2). The particle size for both classes of materials increases with increased equivalence of $AgBF_4$ from 1 to 2 to 3, indicating that the polymeric block length can be tuned by the amount of $AgBF_4$ added. Also, a significant increase in size (almost two times) from 1 equivalent to 2 equivalents of $AgBF_4$ indicates the formation of supramolecular block copolymers. The fact that larger aggregates were observed in SABCs **13:15(*n*)** compared to SHBCs **13:14(*n*)**, suggests that the phase separation between the blocks results in increased hydrodynamic volume of SABCs with negligible effect on the metal coordination. Thus, the DLS data are consistent with the viscometry results strongly suggesting the formation of supramolecular multiblock copolymers.

Table 2. Hydrodynamic radius (R_h) of SHBCs **13:14(*n*)** and SABCs **13:15(*n*)** measured by DLS at 34 gL^{-1} (25 °C, CH_2Cl_2).

SHBC	R_h [nm]	SABC	R_h [nm]
13:14(1)	35.8	**13:15(1)**	66.8
13:14(2)	77.5	**13:15(2)**	119.3
13:14(3)	79.4	**13:15(3)**	142.0

Conclusions

We have developed a novel methodology for the synthesis of symmetrical telechelic polymers bearing terminal recognition motifs. A bimetallic ruthenium initiator was synthesized in a straight forward fashion via carbene exchange and used for the incorporation of supramolecular functionalities onto polymer chain-ends. The hydroquinone phenyl ring in the ruthenium initiator offers an opportunity to introduce stimuli-responsive functionalities in the middle of the polymeric backbone. Such functionalities could render these block copolymers pH cleavable or light responsive. Further, termination of the living ROMP with functionalized CTs afforded the symmetrical telechelic polymers in a single step. Self-assembly of the telechelic polymers to afford block copolymers was achieved by metal coordination between recognition units. The formation of supramolecular block copolymers was substantiated using ^1H NMR spectroscopy, viscometry, and DLS. We have also demonstrated that the bulk properties of the supramolecular block copolymers can be tuned by the amount of $AgBF_4$ added.

Experimental Section

General Methods. All reagents were purchased either from Acros Organics, Alfa Aesar, or Sigma–Aldrich and used without further purification unless otherwise noted. CH_2Cl_2 was dried by means of passage through copper oxide and alumina columns. NMR spectra were recorded by using a Bruker AV-400 (^1H: 400.1 MHz; ^{13}C: 100.6 MHz) spectrometer. Chemical shifts are reported in ppm and referenced to the corresponding residual nuclei in deuterated solvents. Elemental analyses were performed by using a Carlo Erba 1108 elemental analyzer. Mass spectral analyses were provided by the Georgia Tech Mass Spectrometry Facility using a VG-70 se spectrometer. Viscosity was measured in dichloromethane using a Cannon semi-micro Ubbelohde viscometer (9722-G59) at 25 °C. The hydrodynamic radius (R_h) was measured by using a Protein Solutions DLS (DynaPro) at 25 °C and analyzed with a Dynamics V6 software. Gel-permeation chromatography (GPC) analyses were carried out by using a Shimadzu pump coupled to a Shimadzu UV detector with tetrahydrofuran (THF) as the eluent and a flow rate of $1\,mL\,min^{-1}$ on an American Polymer Standards column set (100, 1000, 100 000 Å, linear mixed bed). All GPCs were calibrated using poly(styrene) standards and carried out at 25 °C. M_w, M_n, and PDI represent the weight-average molecular weight, number-average molecular weight, and polydispersity index, respectively. 6-(4-Vinylphenoxy) hexanoic acid **1**,[14] 6-chloro-1-hexenyl methyl ether **5**,[13b] SCS-Pd^{II} pincer precursor **6**,[15] and monomers **10** and **11**[16] were synthesized according to the previously published procedures.

Bis-styrene 2: To a solution of 6-(4-vinylphenoxy) hexanoic acid **1** (0.59 g, 2.5 mmol) and hydroquinone (0.13 g, 1.2 mmol) in anhydrous DMF (8 mL) were added *N*-(3-*d*imethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (0.55 g, 2.9 mmol) and 4-dimethylaminopyridine (17 mg, 0.14 mmol). After the mixture was stirred at 25 °C for 6 h, the solvent was removed under reduced pressure. Water (30 mL) was added and the mixture was extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were washed with water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a yellow oil that was further purified by column chromatography on silica gel in dichloromethane to yield 0.59 g of a white solid in 96 % yield. ^1H NMR ($CDCl_3$): $\delta = 7.34$ (d, $J = 8.8$ Hz, 4H), 7.09 (s, 4H), 6.85 (d, $J = 8.8$ Hz, 4H), 6.66 (dd, $J = 17.6$, 11.0 Hz, 2H), 5.61 (d, $J = 17.6$ Hz, 2H), 5.12 (d, $J = 11.0$ Hz, 2H), 3.99 (t, $J = 6.4$ Hz, 4H), 2.60 (t, $J = 7.6$ Hz, 4H), 1.83 (m, 8H), 1.61 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 171.9$, 158.8, 148.1, 136.3, 130.4, 127.4, 122.4, 114.5, 111.5, 67.6, 34.2, 28.9, 25.6, 24.6 ppm; elemental anal (%) calcd for $C_{34}H_{38}O_6$: C 75.25, H 7.06; found: C 74.81, H 7.03; ESI-MS: *m*/*z*: calcd for $C_{34}H_{38}O_6$, 542.2688; found, 543.2741 $[M+H]^+$.

Bis-ruthenium initiator 4: Bis-styrene **2** (0.10 g, 0.18 mmol) and Grubbs' first-generation initiator **3** (0.60 g, 0.73 mmol) were dissolved in anhydrous, degassed CH_2Cl_2 (10 mL) under an argon atmosphere and stirred at 25 °C for 1 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (hexanes/EtOAc, 4:1) to yield 0.26 g of a purple solid in 72 % yield. ^1H NMR (CD_2Cl_2): $\delta = 19.44$ (s, 2H), 8.41 (br, 4H), 7.07 (s, 4H), 6.79 (d, $J = 8.8$ Hz, 4H), 4.01 (t, $J = 6.4$ Hz, 4H), 2.58 (m, 16H), 1.94–1.12 ppm (m, 132H). ^{13}C NMR (CD_2Cl_2): $\delta = 290.6$, 172.3, 160.0, 148.6, 148.2, 134.3, 122.8, 114.4, 68.3, 34.5, 32.4, 30.0, 29.2, 28.3, 27.0, 25.9, 25.0 ppm; elemental anal (%) calcd for $C_{104}H_{166}O_6Cl_4P_4Ru_2$: C 63.08, H 8.45; found: C 62.53, H 8.42.

CT 8. To a solution of 6-chloro-1-hexenyl methyl ether **5** (0.20 g, 1.2 mmol) and SCS-Pd^{II} pincer precursor **6** (0.60 g, 1.3 mmol) in anhydrous DMF (10 mL) was added potassium carbonate (0.52 g, 3.8 mmol). After the mixture was stirred at 90 °C for 12 h, the solvent was removed under reduced pressure. Water (20 mL) was added and the mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexanes/EtOAc, 2:1) (0.38 g, 50 %). ^1H NMR ($CDCl_3$): $\delta = 7.79$ (dd, $J = 7.2$, 2.0 Hz, 4H), 7.36 (m, 6H), 6.63 (s, 2H), 6.28 (d, $J = 12.4$ Hz, 0.6H), 5.87 (d, $J = 6.4$ Hz, 0.4H), 4.70 (td, $J = 12.4$, 7.6 Hz, 0.6H), 4.64 (br, 4H), 4.33 (dd, $J = 7.2$, 6.4 Hz, 0.4H), 3.88 (t, $J = 6.4$ Hz, 2H), 3.57 (s, 1.2H), 3.50 (s, 1.8H), 2.08 (m, 0.8H), 1.94 (m, 1.2H), 1.75 (m, 2H), 1.41 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 226.8$, 157.2, 149.8, 147.2, 146.2, 132.8, 131.7, 129.8, 129.6, 108.0, 106.6, 102.8, 68.1, 59.5, 55.9, 54.5, 30.4, 29.5, 29.2, 27.6, 25.7, 25.4, 23.8 ppm; ESI-MS: *m*/*z*: calcd for $C_{28}H_{31}ClO_2PdS_2$, 604.0489; found, 569.0800 $[M-Cl]^+$.

CT 9: Potassium carbonate (1.4 g, 10 mmol) was added to a solution of 6-chloro-1-hexenyl methyl ether **5** (0.55 g, 3.4 mmol) and 4-hydroxypyridine **7** (0.35 g, 3.7 mmol) in anhydrous DMF (10 mL). After the mixture was stirred at 90 °C for 12 h, the solvent was removed under reduced pressure. Water (20 mL) was added and the mixture was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with water, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (dichloromethane/methanol, 15:1) (0.45 g, 60 %). ^1H NMR ($CDCl_3$): $\delta = 7.25$ (d, $J = 8.0$ Hz, 2H), 6.36 (d, $J = 8.0$ Hz, 2H), 6.26 (d, $J = 12.0$ Hz, 0.6H), 5.86 (d, $J = 6.4$ Hz, 0.4H), 4.65 (td, $J = 12.0$, 7.2 Hz, 0.6H), 4.33 (dd, $J = 7.0$, 6.4 Hz, 0.4H), 3.73 (t, $J = 7.2$ Hz, 2H), 3.55 (s, 1.2H), 3.48 (s, 1.8H), 2.04 (m, 0.8H), 1.91 (m, 1.2H), 1.75 (m, 2H), 1.35 ppm (m, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 147.5$, 146.6, 139.5, 139.5, 118.8, 105.8, 102.2, 59.5, 57.0, 56.9, 56.0, 30.7, 30.5, 30.1, 28.9, 27.3, 25.5, 25.4, 23.3 ppm; EIMS: *m*/*z*: calcd for $C_{13}H_{19}NO_2$, 221.1416; found, 221.1413.

General polymerization procedure: The desired amount of monomer was dissolved in anhydrous, degassed CH_2Cl_2 under an argon atmosphere. Bis-ruthenium initiator **4** was added as a solution in the corresponding solvent. Upon complete polymerization, ethyl vinyl ether (for **12**), CT **8** (for **13**), or CT **9** (for **14** and **15**) was added to quench the polymerization. The polymer was isolated and purified by repeated precipitations into MeOH (for **12**--**14**) or diethyl ether (for **15**).

Self-assembly studies: Polymer **13** was dissolved in CD_2Cl_2 and polymer **14** or **15** was added until a 1:1 equivalency was reached in relation to the Pd-pincer complexes as determined by ^1H NMR spectroscopy. The desired amount of $AgBF_4$ dissolved in $MeNO_2$ was added to the reaction mixture. After stirring at 25 °C for 4 h, the precipitated AgCl(s) was removed by centrifugation. The supernatant liquid was filtered through a plug of Celite and subsequently through a 0.2 μm syringe filter. The solvent was removed in vacuo to yield the supramolecular block copolymers.

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