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A Modular Approach toward Block Copolymers

Mary Nell Higley, Joel M. Pollino, Eric Hollembeak, and Marcus Weck*[a]

Abstract: A novel methodology for the formation of block copolymers has been developed that combines ring-opening metathesis polymerization (ROMP) with functional chain-transfer agents (CTAs) and self-assembly. Telechelic homopolymers of cyclooctene derivatives end-functionalized with hydrogen-bonding or metal-coordination sites are formed through the combination of ROMP with a corresponding functional CTA. These telechelic homopolymers are fashioned with a high control over molecular weight and without the need for post-polymerization procedures. The homopolymers undergo fast and efficient self-assembly with their complement homopolymer or small molecule analogue to form block-copolymer architectures. The block copolymers show equivalent association constants as their small molecule analogues described in the literature, regardless of size or nature of the complementary unit or the polymer side chain.

Keywords: hydrogen bonds · polymers · supramolecular chemistry · transition metals

Introduction

The preparation of materials for electronic, optical, and biological applications becomes ever more time consuming and difficult as polymer technologies continue to evolve with increasing degrees of structural complexity. A central feature, crucial to the implementation of these materials in functional devices, is the facile preparation of complex polymers such as block or blocky copolymers that contain well-defined monomer compositions, elaborate architectures, and diverse functionalities.[1] In most cases, living polymerization techniques have been employed for the formation of block copolymers and much of today's research focused on the synthesis of block copolymers relies upon living ionic,[2] transition-metal catalyzed[3,4] and controlled free-radical[5–7] polymerization methods. Although successful, these strategies often suffer from a variety of shortcomings including functional group incompatibilities with polymerization conditions as well as low degrees of flexibility in optimizing target structures. Another method for the formation of block copolymers is the reaction of two reactive polymer chain-ends to form a covalent bond between two homopolymers.[8,9] However, quantitative yields of these post polymerization reactions are normally not obtained limiting the use of this strategy. A potential solution to overcome these difficulties is the implementation of telechelic or end-group functionalized polymers that are capable of undergoing self-assembly to form complex architectures. To that end, recent research efforts have employed metal-coordination- and hydrogen-bonding-based recognition motifs for the preparation of self-assembled block copolymers.[10–25] While these approaches use metal coordination and hydrogen bonding to prepare self-assembled polymers, in most cases the terminal recognition motifs were incorporated using a post-polymerization step,[10–14,17,20–22] often without quantitative yield, which limits the versatility and simplicity of this approach. Aside from nonquantitative yields, post-polymerization-based strategies also suffer from functional group incompatibilities during the end-group functionalization due to competitive reactions. Furthermore, ruthenium–terpyridine-based metal-coordination, one of the most used metal-coordination motifs,[12,13,17] often requires refluxing in solvents for prolonged reaction times, greatly limiting this approach to systems capable of tolerating such harsh reaction conditions. Finally, in all cases, the strategy towards the formation of the telechelic polymers is limited to one recognition motif or noncovalent interaction and no modular approach that would allow for the incorporation of a variety of recognition motifs has been reported.

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. Structures of compounds **6**–**11**, **14**, and **17**; and MALDI MS and DSC data for **20b**.

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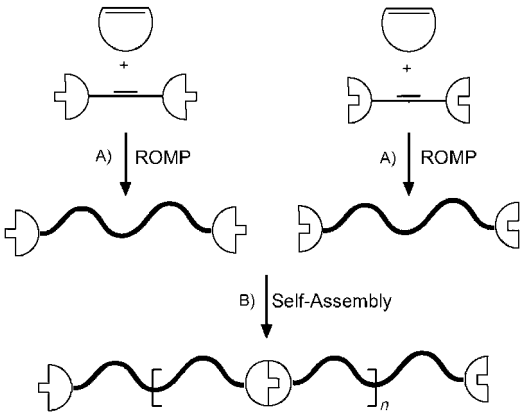
Herein, we have devised a strategy that overcomes these limitations and allows for 1) rapid and facile end-group functionalization; 2) incorporation of any functional group onto the side chain of the polymer, thereby broadening the scope for preparing complex functional polymeric materials; and 3) incorporation of any terminal recognition motif desired. Our strategy, which allows for rapid end-functionalization of homopolymers that possess recognition motifs, is based on a subsequent self-assembly step to create complex block or blocky copolymer structures quickly and efficiently in a modular fashion (Scheme 1).

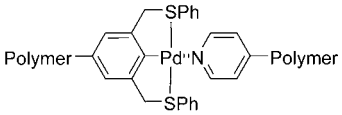


Scheme 1. Cartoon depicting A) CTA polymerization allowing for recognition motif end-functionalization and B) self-assembly of the resulting homopolymers.

Research design: Our strategy for preparing copolymers is based on the combination of chain-transfer agents (CTAs), ring-opening metathesis polymerization (ROMP), and self-assembly. Ruthenium-catalyzed ROMP is a fully functional-group-tolerant polymerization technique that allows for the facile introduction of virtually any functional group into a polymer main or side chain.[26] The inclusion of a functionalized chain-transfer agent (CTA) during the course of ROMP allows for complete polymer end-group functionalization.[26] By employing CTAs that contain different functional end-groups, such as molecular recognition units, telechelic polymers possessing any desired recognition motif can be synthesized. Additionally, this methodology allows for complete control of the molecular weight of the desired polymer through the control of the CTA to monomer ratio thereby allowing for unprecedented control over end-group functionalization, homopolymer properties, and ultimately block copolymer properties.[27–30] Following the CTA-based preparation of homopolymers possessing complementary recognition units at the chain termini, rapid self-assembly through the exploitation of noncovalent interactions allows for rapid preparation of a large variety of block copolymers.

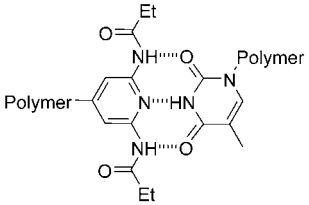
Results and Discussion

Synthesis of CTAs: The design and preparation of the functionalized CTAs must take into consideration two crucial structural components: 1) the type, strength, and behavior of the recognition motifs, and 2) the basic structural requirements of the CTA, which must allow for well-defined incorporation to the termini of the homopolymers. To demonstrate the versatility of our methodology to any noncovalent interaction, recognition units based on either hydrogen bonding or metal coordination were investigated. Specifically, palladated sulfur–carbon–sulfur (SCS) pincer ligands (**1**) were employed to explore metal coordination.[31–37] These metal complexes are known to undergo fast and quantitative self-assembly at room temperature and can accommodate a variety of ligands including functionalized pyridines, nitriles, and phosphines.[31–36] The self-assembled complex formed between a palladated-pincer complex (**1**) and a pyridine unit (**2**) is depicted here. To examine hydrogen-bonding-based



1 **2**

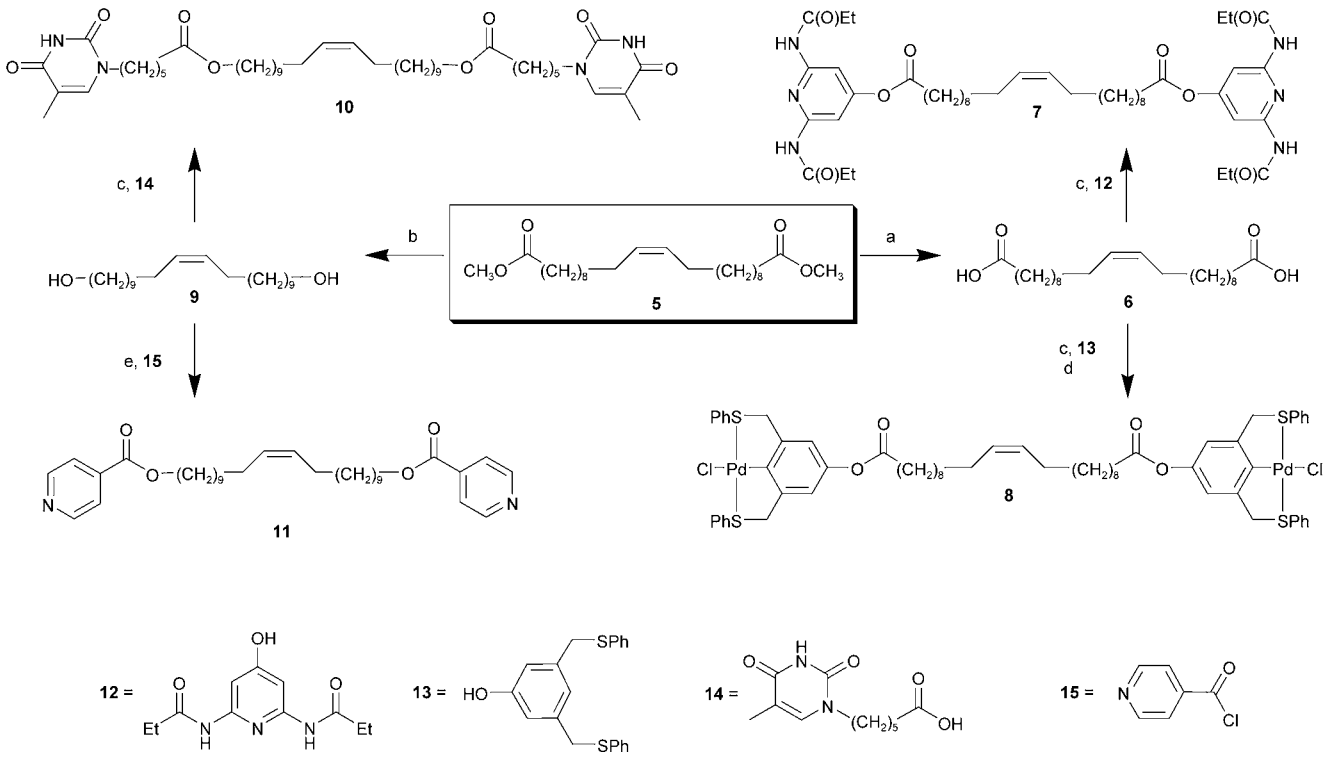
molecular recognition in our system, diaminopyridines (**3**), known to strongly bind thymine derivatives (**4**) by means of three hydrogen bonds ($K_a = \sim 10^3\ M^{-1}$), were chosen.[38–44] The basic design of CTAs employed in ROMP requires symmet-



3 **4**

ric, acyclic olefins.[26] Most CTAs reported in the literature are based on *cis*-2-butenediol derivatives.[27–30] However, we hypothesized that the large terminal recognition units employed in our investigations would be sterically demanding requiring a long alkyl spacer situated between the olefin and recognition unit. Accordingly, a series of novel CTAs (**6–11**) containing nonylalkyl spacers were chosen as synthetic targets.

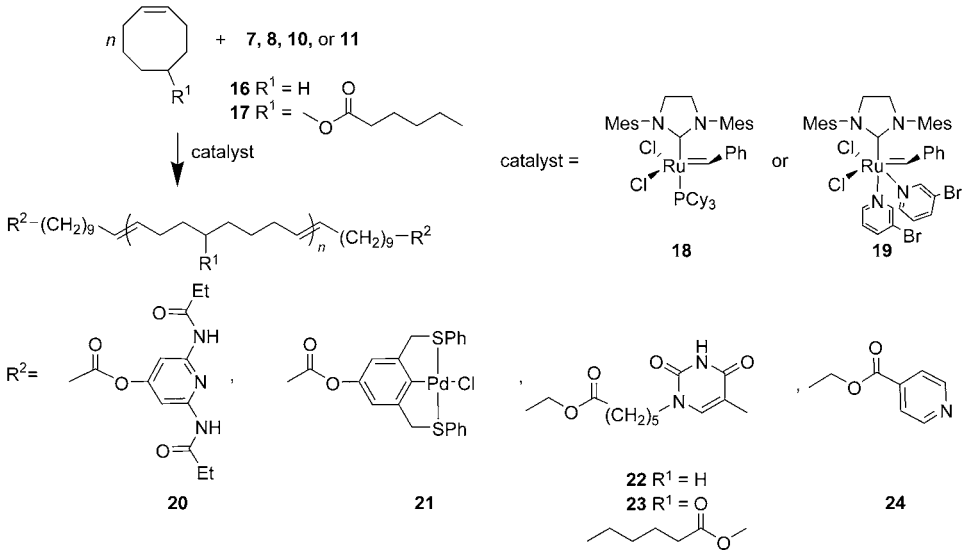
The syntheses of functionalized CTAs **6–11** commences with the preparation of methyl ester functionalized CTA (**5**) by using oxygen-assisted Wittig olefination.[45,46] Subsequent saponification of the ester groups provided diacid **6**, which could be easily functionalized with hydroxydiaminopyridine (**12**)[44] by using a DCC/DMAP esterification protocol to yield hydrogen-bonding CTA **7** (Scheme 2). Similarly,



Scheme 2. CTA syntheses. a) KOH, MeOH, H_2O, 100 °C; b) $LiAlH_4$, THF, 0 °C; c) DCC, DMAP, CH_2Cl_2, 45 °C; d) $[PdCl_2(NCPh)_2]$, $AgBF_4$, brine, CH_2Cl_2, RT; e) Et_3N, CH_2Cl_2, 0 °C.

pincer-ligand-functionalized CTA (**8**) was prepared through esterification of **6** by using the hydroxy-SCS ligand (**13**), which was subsequently palladated.[34] Reduction of **5** with lithium aluminum hydride gave access to diol **9**, which was then coupled to thymine **14** to give CTA **10**. Condensation of isonicotinoylchloride hydrochloride (**15**) with diol **9** generated pyridine-functionalized CTA **11**. The resulting CTAs contain a variety of recognition units, ranging from single hydrogen-bonding recognition units (**9** and **11**) to multiple hydrogen-bonding arrays (**7** and **10**) and metal-coordination motifs (**8** and **11**), allowing for rapid tuning of the interaction strengths. Furthermore, compound **11** can function dually as either a single hydrogen-bonding acceptor or as a ligand for metal coordination. This versatile library of CTAs allows for facile, rapid, and modular preparation of self-assembled block copolymers and offers the potential to form multiblock copolymer architectures.

Polymerization and characterization: With the desired CTAs in hand, polymerization experiments were carried out with cyclooctene (**16**) or the cyclooct-4-enyl ester of hexanoic acid (**17**) as monomers (Scheme 3). Monomer **17** was formed through the esterification of hexanoic acid with cyclooct-4-enol, which was obtained by using a literature procedure.[47] Cyclooctene derivatives were chosen for three distinct reasons: 1) their known ability to polymerize by ROMP; 2) their structural simplicity, which facilitates characterization; and 3) access to a vari-



Scheme 3. Polymerization of **16** and **17** in the presence of functionalized CTAs.

ety of highly functionalized cyclooctene-based monomers by means of asymmetric functionalization of a related compound, cyclooctadiene.[47] Polymerizations were carried out in chloroform using Grubbs' catalysts **18** or **19** in the presence of the desired CTA (**7**, **8**, **10**, or **11**) and monomer (**16** or **17**).[29] All reactions were complete within 72 h with monomer to catalyst ratios of 4000:1 for **16** and 500:1 for **17** (Scheme 3). To investigate if the ratio of monomer-to-CTA allows for control over molecular weights, a series of polymers with varying monomer-to-CTA ratios ([M]/[CTA]) were synthesized and characterized (Table 1). MALDI mass spectrometry of lower molecular-weight polymers and GPC analysis of all polymers showed no remaining monomer or CTA, demonstrating the successful and quantitative incorporation of the CTA.

Table 1. Characterization for the polymerization of **16** or **17** with CTAs **7**–**11**.

CTA	Monomer	[M]/[CTA]	Polymer	Catalyst	M_n [10^{-3}]	M_w [10^{-3}]	PDI	T_g [°C]
7	**16**	10	**20a**	**18**	5.6[a] (1.6)[b]	9.1[a]	1.6	−10
7	**16**	20	**20b**	**18**	8.7 (2.8)	14.8	1.7	−11
7	**16**	50	**20c**	**18**	17.9	32.4	1.8	−15
7	**16**	100	**20d**	**18**	26.4	49.8	1.9	−15
8	**16**	10	**21a**	**19**	6.8 (2.2)	12.8	1.9	−34
8	**16**	20	**21b**	**19**	10.3 (3.2)	15.7	1.5	−35
8	**16**	50	**21c**	**19**	14.7	36.5	2.4	−27
8	**16**	100	**21d**	**19**	49.4	69.5	1.4	−33
10	**16**	10	**22a**	**19**	6.9 (2.1)	13.5	1.9	−23
10	**16**	20	**22b**	**19**	10.8 (3.1)	25.1	2.3	−22
10	**16**	50	**22c**	**19**	15.0	30.8	2.1	−23
10	**16**	100	**22d**	**19**	29.5	48.9	1.6	−22
10	**17**	20	**23b**	**19**	7.5 (2.3)	14.8	2.0	−45
10	**17**	50	**23c**	**19**	12.0	26.5	2.2	−47
10	**17**	100	**23d**	**19**	24.3	37.6	1.6	−57
11	**16**	20	**24b**	**19**	9.0 (2.8)	16.7	1.9	−20
11	**16**	50	**24c**	**19**	36.5	72.5	1.9	−22
11	**16**	100	**24d**	**19**	54.9	90.6	1.7	−22

[a] Determined by gel-permeation chromatography in THF relative to monodispersed poly(styrene) standards. [b] Determined by matrix-assisted laser desorption/ionization.

As shown in Table 1 and Figure 1, the incorporation of CTAs **7**, **8**, **10**, and **11** allows for a high degree of control over the molecular weights of the final telechelic polymers through simple variations of the ratio [monomer]/[CTA].

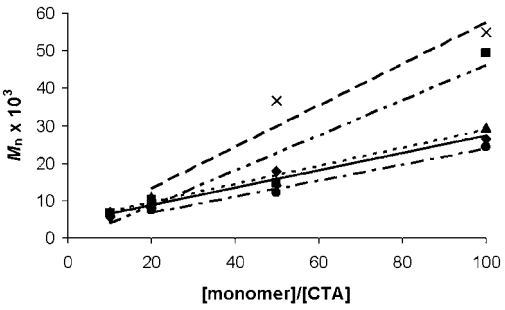
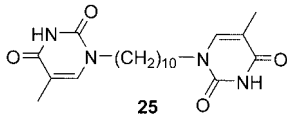


Figure 1. M_n as a function of [monomer]/[CTA] showing a linear relationship between CTA concentration and molecular weight. Key: Polymers **20** (◆) **21** (■) **22** (▲) **23** (●) **24** (×).

For example, Figure 1 shows a plot of M_n (**20**–**24**) as a function of CTA concentration. In all instances, a linear relationship was observed, which clearly demonstrates the ability to tune the molecular weight of the end-functionalized homopolymers independent of the CTA and the recognition motif used.

Copolymer formation based on 16: After establishing that cyclooctene (**16**) could be polymerized and end-functionalized with a variety of recognition motifs through a simple and controlled one-step protocol, the self-assembly of the resulting telechelic homopolymers into block copolymers was explored. To demonstrate the modular character of our strategy, two different self-assembly strategies were designed and executed. First, homoblock copolymers, that is, block copolymers based on two blocks of homopolymers of the same monomer, were directly synthesized through the self-assembly of telechelic homopolymers containing complementary terminal recognition units. Second, telechelic homopolymers were self-assembled into homoblock copolymers by employment of bisfunctionalized small molecules (**25** and **26**)[48] that possess complementary molecular recognition units. The second methodology allows for facile formation of noncovalent linkages situated between two homopolymers potentially allowing for the formation of block copolymers possessing short and long segments. The recognition units employed in both studies are identical, which facilitates direct comparison of the two self-assembly strategies. A question that could be answered by comparing these strategies is whether the self-assembly step and the strength of the noncovalent interaction are dependant on the mobility of the complimentary recognition units. If this were the case, one would expect a significantly higher bond strength of the noncovalent bond when using the small molecule self-assembly strategy, since **25** and **26** are not expected to be diffusion limited as polymer chain ends might be.



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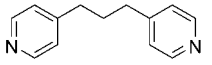

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Hydrogen-bonding-based self-assembly of **20** and **25** or **22** was carried out at room temperature in chloroform and followed in situ by means of ^{1}H NMR spectroscopy by observing characteristic shifts of the amide signals of **3** as a function of concentration.[44] In the absence of the complementary units, the proton signals of the amides of **20** were observed at 7.8 ppm for a 0.005 M solution. Upon addition of 0.4 equivalents of a 0.010 M solution of **25**, a large downfield shift to 8.4 ppm was observed. To determine the association constants of the noncovalent interaction, titration experiments were carried out by adding up to 5.2 equivalents of **25**, at 0.4 quivalents per addition, to **20**. The amide signals continued their downfield shift during the titration ending at 10.1 ppm (Figure 2), which is consistent with a K_a of $800 \pm 200\,M^{-1}$.[49] For the addition of a 0.010 M solution of **22** to a 0.005 M solution of **20**, similar shifts of the amide proton signals were observed with an association constant of $500 \pm 100\,M^{-1}$. These binding constants are identical within the error range of the titration experiments demonstrating that the hydrogen-bonding-based self-assembly is independent of the self-assembly strategy used and, for the molecular weights studied, not diffusion limited. Furthermore, these association constants are in good agreement with reported K_a values for the system diaminopyridine and thymine,[38–44] demonstrating that the formation of block copolymers through hydrogen bonding is not limited by diffusion or polymer-chain interactions (at least for the molecular weights and concentrations studied). Molecular-weight determinations by GPC could not be carried out for the hydrogen-bonded block copolymers as it has been suggested that hydrogen-bonded polymers disassociate in the GPC.[32,33,44] Therefore, to further explore the hydrogen-bonding self-assembly, flow cell IR measurements were conducted on **20**, **22**, and a 1:1 mixture of the two polymers in $CHCl_3$. The combination showed a new broad stretch at 1696 cm^{-1} after self-assembly due to the carbonyl groups of both **20** and **22** engaging in hydrogen bonding. The carbonyl group stretches for the pure polymers were found at 1766 cm^{-1} for **20** and 1684 cm^{-1} for **22**. These IR results confirmed further that self-assembly and therefore block-copolymer formation took place.

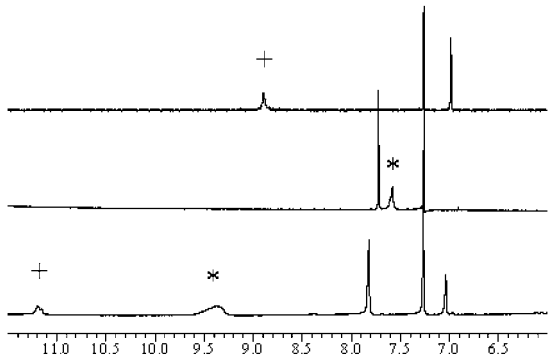

Figure 2. ^{1}H NMR spectra depicting hydrogen-bonding-based self-assembly of **20** with **25**. Top: **25** (+ = imide protons); middle: **20** (* = amide protons); bottom: addition of 1.2 equivalents of **25** to **20**.

The block copolymer formation with metal coordination of **21** was conducted with bisfunctionalized pyridine analogue **26**, or polymer **24**. The experiments were carried out at room temperature in methylene chloride and ^{1}H NMR spectroscopy was used to follow characteristic shifts that occur during the coordination step.[31–34] One equivalent of the desired pyridine system was added to **21** followed by the addition of one equivalent of $AgBF_4$, which removed the labile chlorine from **21** and allowed metal-coordination between the palladium and the pyridine to occur. Upon coordination, ^{1}H NMR measurements showed a shift of the aromatic protons of **21** upfield from 7.8 to 7.6 ppm and a characteristic broadening of the signals in the aromatic region.[32–34] Also the characteristic upfield shift of the α-pyridine signal of **26** from 8.5 to 8.0 ppm was observed.[32–34] These characteristic shifts were also observed in the self-assembly of **21** with **24** and clearly indicate that quantitative metal coordination occurred resulting in block-copolymer formation. Furthermore, a GPC experiment was conducted to compare the molecular weight of a physical mixture of the telechelic homopolymers **21** and **24** with the self-assembled block copolymer based on this mixture after metal coordination. The molecular weight increased from 9400 for the physical mixture to 17000 after metal-coordination-based self-assembly. This clearly substantiates the formation of supramolecular block-copolymers by using metal coordination.

Noncovalent assembly for polymers 20 and 23: To form true block copolymer architectures, similar self-assembly experiments were carried out with homopolymers **20** and **23**, which were formed from monomers **16** and **17**, and possess terminal complementary hydrogen-bonding recognition units. For the ^{1}H NMR spectroscopy titration experiment, the proton signals of the amides of **20** were initially observed at 7.7 ppm for a 0.006 M solution. Titration experiments were carried out by adding up to 5.6 equivalents of a 0.010 M solution of **23**, at 0.4 equivalents per addition, to **20**. The amide signals continued their downfield shift during the titration ending at 9.7 ppm, which is consistent with a K_a of $400 \pm 100\,M^{-1}$.[49] This K_a is within error of the homoblock-copolymer system, showing the side chain of **23** does not limit the block-copolymer formation. A comparable flow-cell IR spectroscopy experiment was performed with a one to one mixture of self-assembled **20** and **23** that showed the appearance of a new broad carbonyl stretch at 1709 cm^{-1}, which is similar to the carbonyl shift observed in the homoblock system and further confirmed that self-assembly took place.

Conclusion

Herein, we have demonstrated the formation of a variety of telechelic polymers containing terminal recognition motifs through the incorporation of a novel class of CTAs during

the ROMP of cyclooctene derivatives. The resulting telechelic polymers contained terminal functional groups capable of hydrogen bonding and metal coordination. The introduction of the molecular recognition units into the polymers was carried out during the polymerization without the need of post-polymerization procedures. This methodology allows for the rapid and facile end-group functionalization and incorporation of any terminal recognition motif desired in the presence of any functional group in the polymer structure or side chain. Self-assembly of the telechelic polymers into block copolymer architectures through self-assembly were fast and efficient, and were substantiated by using NMR and IR spectroscopy, MALDI mass spectrometry, and GPC. This methodology allows for the formation of block copolymers without the need of living polymerization techniques and the incorporation of any recognition unit desired. Further work includes the integration of multiple combinations of noncovalent interactions in one system to form multiblock structures using an orthogonal self-assembly approach.

Experimental Section

General methods: All reagents were purchased either from Acros Organic or Aldrich. All chemicals were reagent grade and used without further purification. Et_3N, $CHCl_3$, and cyclooctene were distilled from CaH_2. THF and CH_2Cl_2 were dried by passage through Cu_2O and alumina columns. NMR spectra were recorded on a Varian Mercury spectrometer (300 MHz). Chemical shifts are reported in parts per million (ppm), with residual solvent as an internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad), coupling constant and integration. Mass spectral analysis was provided by the Georgia Tech Mass Spectrometry Facility. Elemental analyses were conducted at Atlantic Microlab. Gel-permeation chromatography was performed on a Shimadzu 10A instrument. Differential scanning calorimetry was conducted by using a Mettler Toledo DSC 822 instrument. Infrared spectra were collected on a Shimadzu FTIR-8400s spectrometer.

***cis*-Docos-11-enedioic acid (6)**: A solution of **5** (2.46 g, 6.17 mmol) in a mixture of MeOH/H_2O (1:1, 20 mL) was stirred with KOH (0.70 g, 12.47 mmol) for six hours. The solution was poured into 1 N HCl (50 mL) and extracted with CH_2Cl_2 (2 × 50 mL). The organic layer was collected and dried ($MgSO_4$), and the solvent removed to yield **6** as a white powder (1.59 g, 70 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.27$ (br m, 24 H), 1.63 (t, $J = 7.1$ Hz, 4H), 1.99 (t, $J = 5.5$ Hz, 4H), 2.33 (t, $J = 7.7$ Hz, 4H), 5.36 (dd, $J = 4.4$, 6.7 Hz, 2H), 11.66 ppm (br s, 2H); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 25.0$, 27.5, 29.9, 30.1, 32.9, 34.5, 53.7, 128.7, 130.0, 134.0, 180.7 ppm; MS (ESI): *m*/*z* calcd $[M^+]$: 368.29; found: 368.3; elemental analysis calcd (%) for $C_{22}H_{40}O_4$: C 71.70, H 10.94; found: C, 71.95, H, 10.81.

Bis-(2,6-bis-propionylamino-pyridin-4-yl) ester of *cis*-docos-11-enedioic acid (7): Compound **6** (0.32 g, 0.84 mmol) was dissolved in CH_2Cl_2 (50 mL) and combined with dicyclohexylcarbodiimide (0.43 g, 2.10 mmol), dimethylaminopyridine (11.1 mg, 0.091 mmol), and **12** (0.52 g, 2.21 mmol). The solution was heated to reflux for 16 h and then cooled to room temperature. The solid was filtered off and the filtrate was purified by column chromatography (silica, ethylacetate/CH_2Cl_2 2:1) to yield **7** as a white solid (0.43 g, 63 %). ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 1.02$ (t, $J = 7.1$ Hz, 12H), 1.24 (br m, 24H), 1.59 (t, $J = 6.0$ Hz, 4H), 1.96 (t, $J = 5.5$ Hz, 4H), 2.39 (q, $J = 7.7$, 7.1 Hz, 8H), 2.57 (t, $J = 7.1$ Hz, 4H), 5.30 (dd, $J = 4.4$, 5.0 Hz, 2H), 7.53 (s, 4H), 10.16 ppm (s, 4H); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 9.5$, 24.9, 25.3, 25.8, 26.6, 27.5, 30.5, 31.3, 33.0, 34.4, 35.2, 56.0, 103.7, 130.0, 151.3, 161.3, 173.2 ppm; MS (ESI): *m*/*z* calcd $[M^+]$: 806.49; found: 806.6; elemental analysis calcd (%) for $C_{44}H_{66}N_6O_8$: C 65.48, H 8.24, N 10.41; found: C 65.67, H 8.17, N 10.30.

Bis-(PdCl-{3,5-bis[(phenylsulfanyl)methyl]phenoxy}) ester complex of *cis*-docos-11-enedioic acid (8): Compound **6** (0.40 g, 1.05 mmol) was dissolved in CH_2Cl_2 (50 mL) and combined with dicyclohexylcarboimide (0.54 g, 2.6 mmol), dimethylaminopyridine (32 mg, 0.26 mmol), and **13** (0.89 g, 2.63 mmol). The solution was heated to reflux for 16 h and then cooled to room temperature. The solid was filtered off and the filtrate was purified by column chromatography (CH_2Cl_2, silica) to yield the ester of *cis*-docos-11-enedioic acid (0.98 g, 0.97 mmol) as an orange solid. This ester was then combined with $[PdCl_2(NCPh)_2]$ (0.82 g, 2.13 mmol) in a 1:1 mixture of CH_2Cl_2/CH_3CN and stirred at room temperature for 45 min, then $AgBF_4$ (0.75 g, 3.87 mmol) was added and the mixture stirred for an additional 45 min. Finally, brine (180 mL) was added and stirring was continued for 18 h. The organic layer was collected and the solvent removed. The product was purified by column chromatographgy (silica, a) CH_2Cl_2; b) CH_2Cl_2/MeOH 98:2) to obtain **8** as an orange solid product (0.64 g, 47 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.26$ (br m, 24H), 1.69 (t, $J = 6.6$ Hz, 4H), 1.97 (t, $J = 6.6$ Hz, 4H), 2.47 (t, $J = 7.1$ Hz, 4H), 4.57 (s, 8H), 5.33 (dd, $J = 5.5$ Hz, 2H), 6.74 (s, 4H), 7.38 (m, 12H), 7.84 ppm (m, 8H); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 10.1$, 25.3, 27.6, 30.1, 33.3, 34.4, 34.7, 52.0, 115.8, 129.3, 129.9, 130.2, 131.7, 132.3, 135.8, 136.7, 137.6, 137.9, 139.6, 150.3 ppm; MS (ESI): *m*/*z* calcd $[M^+ - Cl]$: 1253.2; found: 1253.8; elemental analysis calcd (%) for $C_{62}H_{70}Cl_2O_4Pd_2S_4$: C 57.67, H 5.46; found: C 57.35, H 5.93.

***cis*-Docos-11-ene-1,22-diol (9)**: A solution of **5** (3.45 g, 8.65 mmol) was combined with $LiAlH_4$ (18.0 mL, 18.0 mmol) in THF (50 mL) at 0 °C and stirred for 18 h. Water (100 mL) was added to the reaction and the solid was filtered off. The solution was extracted with CH_2Cl_2 (2 × 50 mL). The organic layers were collected, dried ($MgSO_4$), and removed to yield **9** as a white powder (2.89 g, 98 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.28$ (br m, 34H), 2.00 (t, $J = 7.1$ Hz, 4H), 3.63 (t, $J = 6.6$ Hz, 4H), 5.34 ppm (dd, $J = 6.6$ Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 26.1$, 27.5, 29.5, 29.6, 29.7, 29.9, 30.1, 32.9, 33.1, 63.4, 130.1 ppm; MS (ESI): *m*/*z* calcd $[M^+]$: 340.33; found: 340.3.

Docos-11-enyl ester of *cis*-1,22-Di-6-(5-Methyl-2,4-dioxo-3,4-dihydro-2H-pyrimidin-1-yl)hexanoic acid (10): Compound **14** (1.75 g, 7.29 mmol) was combined with **9** (0.91 g, 2.91 mmol) in CH_2Cl_2 with dicyclohexylcarboimide (1.50 g, 7.29 mmol) and dimethylaminopyridine (89 mg, 0.73 mmol) and heated to 45 °C. The reaction was complete after 48 h, yielding a yellow mixture of products that were separated by column chromatography (silica, ethyl acetate) and **10** was collected as a pale yellow solid (1.645 g, 72 %). ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 1.20$ (br m, 28H), 1.52 (m, $J = 7.1$ Hz, 4H), 1.66 (br m, 4H), 1.73 (d, $J = 2.2$ Hz, 6H), 1.97 (t, $J = 3.9$ Hz, 4H), 2.26 (t, $J = 7.1$ Hz, 4H), 3.16 (t, $J = 5.0$ Hz, 4H), 3.57 (t, $J = 6.6$ Hz, 4H), 3.97 (t, $J = 6.6$ Hz, 4H), 5.38 (dd, $J = 4.9$ Hz, 2H), 7.52 (s, 2H), 11.18 ppm (s, 2H); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 12.7$, 24.7, 25.0, 25.1, 25.7, 25.8, 26.2, 26.6, 27.5, 28.9, 30.1, 31.3, 33.1, 34.3, 48.6, 64.9, 110.8, 130.0, 140.7, 150.9, 164.4, 173.6 ppm; MS (ESI): *m*/*z* calcd $[M^+]$: 784.54; found: 784.5; elemental analysis calcd (%) for $C_{44}H_{72}N_4O_8$: C 67.32, H 9.24, N 7.14; found: C 67.76, H 9.29, N 7.74.

Docos-11-enyl ester of *cis*-1,22-diisonicotinic acid (11): Compound **9** (0.40 g, 1.28 mmoles) was combined with **15** (0.68 g, 4.82 mmol) and Et_3N (0.45 mL, 3.20 mmol) in CH_2Cl_2 (50 mL) and stirred at room temperature for 18 h. The mixture was washed with 1 N HCl, 2 M NaOH, and brine, and then dried ($MgSO_4$) to yield the product as a white powder (1.19 g, 93 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.28$ (br m, 24H), 1.79 (t, $J = 7.7$ Hz, 4H), 1.99 (t, $J = 5.5$ Hz, 4H), 3.63 (t, $J = 6.6$ Hz, 4H), 4.40 (t, $J = 6.6$ Hz, 4H), 5.32 (dd, $J = 5.0$ Hz, 2H), 8.18 (d, $J = 4.9$ Hz, 4H), 8.90 ppm (s, 4H); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 26.3$, 26.6, 27.3, 27.6, 28.9, 29.5, 30.1, 33.1, 34.3, 67.3, 125.1, 130.0, 142.1, 146.2, 163.4 ppm; MS (ESI): *m*/*z* calcd $[M^+]$: 550.38; found: 550.4; elemental analysis calcd (%) for $C_{34}H_{50}N_2O_4$: C 74.14, H 9.15, N 5.09; found: C 74.28, H 9.24, N 5.00.

6-(5-Methyl-2,4-dioxo-3,4-dihydro-2H-pyrimidin-1-yl)hexanoic acid (14): 6-Bromohexanoic acid (3.95 g, 20.23 mmol) in MeOH (30 mL) was heated to 75 °C with a catalytic amount of H_2SO_4 for 16 h. The product,

the methyl ester of 6-bromo-hexanoic acid (2.70 g, 12.90 mmol, 64%), was distilled from the system and combined with thymine (4.90 g, 36.68 mmol), K_2CO_3 (1.93 g, 13.98 mmol), and NaI (1.93 g, 12.89 mmol) in dry DMSO (30 mL). The solution was heated to 90 °C for 4 h. The reaction was acidified with 1 N HCl and extracted with CH_2Cl_2 (100 mL). The organic layer was collected and removed to yield methyl ester of 6-(5-methyl-2,4-dioxo-3,4-dihydro-2H-pyrimidin-1-yl)hexanoic acid (2.53 g, 9.95 mmol, 77%). This ester was heated to 95 °C in a mixture of H_2O/MeOH (1:1, 50 mL) with KOH (1.53 g, 27.20 mmol) for 16 h. The solution was poured into 1 N HCL (100 mL) and extracted with CH_2Cl_2 (100 mL). The organic layer was collected and removed to yield **14** as a white powder (2.32 g, 97%; 48% overall yield). ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 1.22$ (m, $J = 6.6$ Hz, 2H), 1.50 (br m, $J = 7.7$ Hz, 4H), 1.72 (d, $J = 7.1$ Hz, 3H), 2.20 (t, $J = 7.1$ Hz, 2H), 3.55 (t, $J = 7.1$ Hz, 2H), 7.52 (s, 1H), 11.18 (s, 1H), 11.99 ppm (s, 1H); ^{13}C NMR (300 MHz, DMSO-d_6): $\delta = 12.7$, 24.9, 26.1, 29.0, 34.3, 47.7, 109.0, 142.1, 151.4, 164.9, 174.9 ppm; MS (ESI): m/z calcd $[M^+]$: 241.11; found: 241.1; elemental analysis calcd (%) for $C_{11}H_{16}N_2O_4$: C 54.99, H 6.71, N 11.66, O 26.64; found: C 54.75, H 6.69, N 11.43.

Cyclooct-4-enyl ester of hexanoic acid (17): Cyclooct-4-enol (2.37 g, 18.80 mmoles) was synthesized by a literature procedure[47] and combined with hexanoic acid, (3.5 mL, 27.72 mmol) dicyclohexylcarboimide (4.65 g, 22.54 mmol), and dimethylaminopyridine (0.28 g, 2.29 mmol) in CH_2Cl_2 (50 mL) at room temperature. The reaction was complete after 24 h, yielding a yellow mixture of products that were separated by column chromatography (silica, hexanes/ethyl acetate 3:1), and **17** was collected as a clear liquid (3.92 g, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.64$ (m, 2H), 4.82 (m, 1H), 2.48–2.32 (br m, 12H), 1.63 (m, 2H), 1.33 (m, 4H), 0.92 ppm (t, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 172.72$, 129.67, 129.56, 75.22, 34.71, 33.95, 33.81, 31.49, 25.01, 24.89, 22.51, 14.04 ppm; MS (ESI): m/z calcd $[M^+]$: 224.34; found: 225.2; elemental analysis calcd (%) for $C_{14}H_{24}O_2$: C 74.95, H 10.78; found: C 74.13, H 10.75.

General polymerization procedure: The desired CTA (100 mg) was placed in a dried three-necked round-bottomed flask and $CHCl_3$ (5 mL) was added. The corresponding amount of monomer ([monomer]/[CTA] = 10, 20, 50, or 100) was added, followed by the addition of **18** or **19** ([**16**]/[catalyst] = 4000, [**17**]/[catalyst] = 500) in $CHCl_3$. The solution was stirred for 72 h at room temperature, and then precipitated in cold MeOH (10 mL) to yield the desired polymer. Polymers were collected by filtration and dried.

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