Living ROMP of *exo*-Norbornene Esters Possessing Pd^{II} SCS Pincer Complexes or Diaminopyridines

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ABSTRACT: Isomerically pure *exo*-norbornene esters containing either a Pd^{II} SCS pincer complex or a diaminopyridine unit were synthesized, polymerized, and copolymerized by ring-opening metathesis polymerization using a ruthenium initiator. All polymerizations are living under mild reaction conditions. A comparison between the pure *exo* monomers and the commonly employed 80:20 *endo*/*exo* mixtures was carried out. The *exo*-norbornene isomers exhibit significantly higher rates of propagation under milder conditions when compared to the *endo*/*exo* mixtures. Kinetic studies have shown that the k_p values are highly dependent upon the isomeric purity but completely independent of the terminal diaminopyridine or Pd^{II} SCS Pincer functional groups. The living character of the polymerization has allowed for the first block copolymerization of norbornene metal-containing pincer complexes and diaminopyridine-based hydrogen-bonding receptors.

Introduction

Ring-opening metathesis polymerization (ROMP) has become an increasingly popular route to side-chain-functionalized polymers and copolymers.[1,2] The high tolerance of ruthenium-based initiators to a variety of functional groups[3] coupled with high control over polymer architectures[1−6] has moved ROMP into the forefront of polymer synthesis. In particular, polymerizations of norbornenes have yielded functionalized AB and ABC block copolymers.[7−9]

Current norbornene functionalization strategies are based primarily upon elaboration of esters (**2**) synthesized as an 80:20 *endo*/*exo* isomeric mixture via the Diels−Alder reaction of cyclopentadiene and asymmetric dienophiles.[7,10−18] Our research, directed toward the synthesis of a "universal" polymer backbone through the use of functionalized norbornenes possessing metal-coordination or hydrogen-bonding recognition motifs, has revealed limitations to this methodology.[19−21] Polymerization of some elaborately functionalized derivatives of monomer **2** where R = a tethered pincer complex or a diaminopyridine recognition unit with catalyst **4** requires elevated temperatures and prolonged reaction times at low monomer-to-initiator stoichiometries ([M]:[I]). Although the polymerizations are carried out in a controlled manner, harsh reaction conditions limit molecular weights as well as block copolymerizations due to partial catalyst decomposition after several hours.

Three possible solutions to these problems can be envisaged. First, a common method used to polymerize functional group intolerant monomers has been the employment of the more active initiator **5**.[2] Although **5** is an effective polymerization catalyst,[2] the rate of propagation is much higher than the rate of initiation leaving a high concentration of uninitiated carbene available upon complete monomer consumption, resulting in nonliving behavior. A second approach is the replacement of the carbonyl ester with a pure alkyl spacer (monomer **3**),[21] which dramatically increases the rates of propagation when compared to **2**. However, the rate of initiation for these monomers (**3**) does not increase, resulting in poorly controlled polymerizations for identical reasons as those described for initiator **5**. Therefore, it can be concluded that the carbonyl group plays a critical role in retarding the rate of propagation. It is well-known for the ROMP of *endo*/*exo*-norbornene esters that the *exo* isomer reacts significantly faster than the *endo* isomer.[22] Recently, a detailed mechanistic investigation for the ROMP of *endo*- and *exo*-dicyclopentadiene has shown that the rate difference between the two isomers is primarily due to steric interactions between the growing polymer chains and the incoming monomer.[23] Furthermore, a similar preference for the *exo* isomer has been observed in the palladium-catalyzed addition polymerization of norbornene esters.[24−26] Previously, Kiessling et al. have developed a methodology that allows for the functionalization of isomerically pure *exo*-norbornene esters that has been employed extensively for the synthesis of glycopolymers.[27−31] Therefore, the utilization of isomerically pure *exo* monomers could be a potential solution to obtain controllable and efficient polymerizations by providing control over the relative rates of initiation and propagation via the carbonyl ester while simultaneously enhancing the rates of propagation by removal of any steric and/or electronic inhibition caused by the *endo* isomer. This should allow for living behavior under mild reaction conditions.

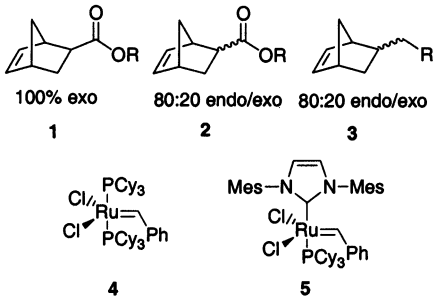

Figure 1. Monomers used in ROMP to introduce functionality at the side chain (**1**−**3**) and commercially available ruthenium olefin metathesis initiators (**4** and **5**).

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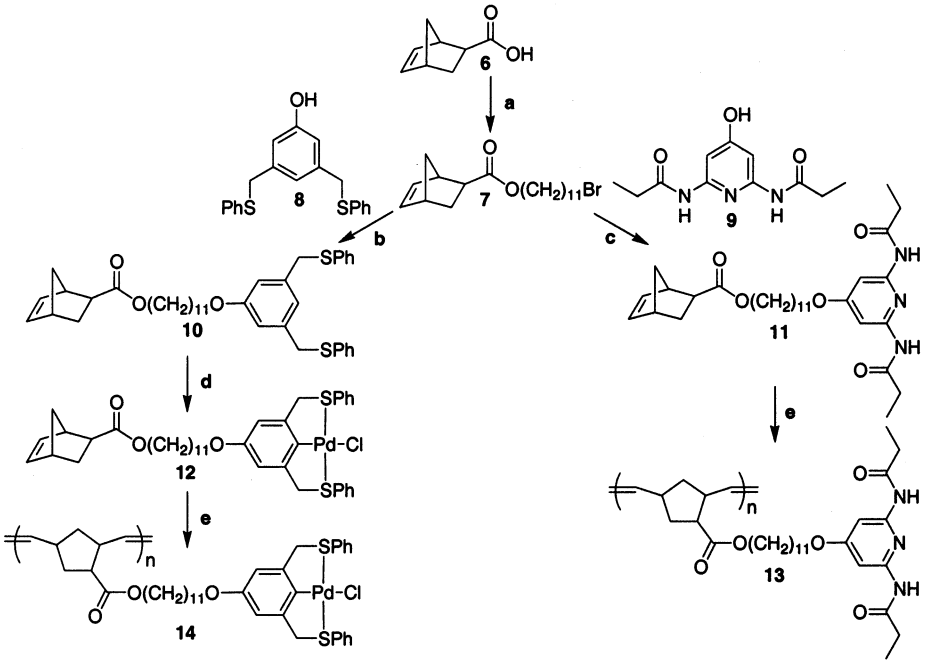
Scheme 1. Synthesis and ROMP of Isomerically Pure *exo*-Norbornene Monomers 11 and 12



a) 11-Bromo-undecan-1-ol, DCC/DMAP, CH_2Cl_2, reflux, 16 h, 87%; b) **8**, K_2CO_3, DMF, 40°C, 70 h, 96%; c) **9**, Cs_2CO_3, acetone, 70 °C, 8h, 100%; d) i. Pd $(PhCN)_2Cl_2$, CH_3CN, r.t., 30 min; ii. $AgBF_4$, 30 min; iii. $NaCl_{(aq)}$, 5 h, 87%; e) **4**, $CDCl_3$, 20-120 min, 100%.

Herein, we report (a) the use of *exo*-norbornene esters as highly efficient monomers for living ROMP of densely functionalized norbornenes containing metals and/or aromatic nitrogen containing moieties, (b) the block copolymerization of these monomers, and (c) present a detailed comparison between the isomerically pure *exo* monomers and their 80:20 *endo/exo* analogues.

Results and Discussion

Monomer Synthesis. Isomerically pure *exo*-norbornene acid **6** was synthesized via isomerization of the corresponding norbornene methyl ester from an 80:20 to a 45:55 *endo/exo* mixture followed by hydrolysis to the norbornene acid and removal of excess *endo* isomer by selective iodolactonization.[27,32,33] Functionalization of **6** was carried out via DCC/DMAP-assisted esterfication with 11-bromoundecan-1-ol to give the corresponding *exo*-undecyl bromide **7**. From **7**, monomer **11** was accessible in one step via a Williamson ether synthesis using compound **9**. Similarly, **10** was synthesized by the coupling of **8** to **7**. To avoid possible palladium-catalyzed polyadditions that are known to proceed rapidly for *exo*-norbornenes in the presence of $[Pd(CH_3CN)_4](BF_4)_2$,[24−26] we modified our previously reported metalation procedure.[19,20] Quantitative bis-palladation using 1 equiv of $Pd(PhCN)_2Cl_2$ followed by in-situ cyclopalladation using 2 equiv of $AgBF_4$ provided the tridentate Pd−BF_4 intermediate. Subsequent ligand exchange to the Pd−Cl via prolonged stirring in brine afforded monomer **12** in 87% yield.

Polymerization Studies. As described above, our previous work involving the polymerizations of 80:20 *endo/exo* mixtures of **11** and **12** was hampered by long reaction times and elevated temperatures.[19,20] For example, the 80:20 *endo/exo*-**12** required 12 h at 45 °C for the polymerization of a 50:1 [M]:[I], whereas the 80:20 *endo/exo*-**11** necessitated 24 h for polymerization under identical conditions. To investigate the behavior of isomerically pure *exo* monomers, **11** and **12** were polymerized using **4**. At 25 °C in $CDCl_3$ (20:1 [M]:[I] ratio), *exo*-**11** and *exo*-**12** were completely polymerized in less than 30 min. In sharp contrast, under identical conditions the analogous 80:20 *endo/exo*-**11** and -**12** monomers required in excess of 300 min to go to completion (Table 1).

Table 1. Representative Data for Polymers Initiated by 4

monomer	isomeric purity	time[a] (min)	[M]:[I]	M_n (10^{-3})	M_w (10^{-3})	PDI
11	80:20 *endo/exo*	300	20	13.1	19.8	1.51
12	80:20 *endo/exo*	300	20	16.0	22.8	1.42
11	100% *exo*	25	20	6.9	7.5	1.08
11	100% *exo*	65	60	23.1	24.4	1.05
11	100% *exo*	120	115	37.6	39.7	1.06
12	100% *exo*	25	20	49.9	62.6	1.25
12	100% *exo*	50	44	78.6	98.7	1.26
12	100% *exo*	120	110	186.3	222.6	1.19

[a] Time at 100% conversion.

To gain better control of the ROMP, the kinetics of the polymerization were studied. The rate of initiation was examined in situ via ^{1}H NMR spectroscopy by monitoring the carbene signal for the propagating species (δ = 18.81 ppm, solvent = $CDCl_3$) and the noninitiated species **4** (δ = 19.95 ppm, solvent = $CDCl_3$). For both **11** and **12**, complete disappearance of the noninitiated species for a 20:1 [M]:[I] ratio was evident within 5 min at ca. 30% conversion (Figure 2, Table 2). Since polydispersity is affected by the relative rates of initiation (k_i) and propagation (k_p), PDI's are broader at low [M]:[I] ratios due to higher consumption of monomer prior to complete initiation. The k_i and k_p values for monomers **11** and **12** are similar for each respective isomer, indicating that the polymerization behavior is independent of the terminal diaminopyridine or Pd^{II} SCS pincer functional groups. Comparison of the

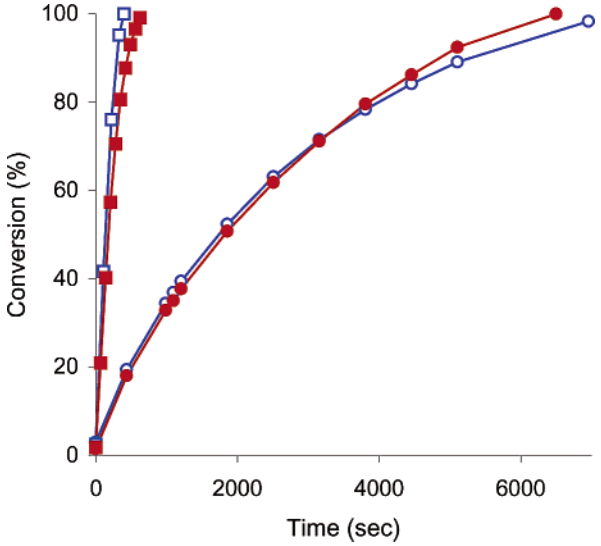


Figure 2. Plot of conversion (%) as a function of time (seconds) for the polymerization of 80:20 *endo*/*exo*-**11** (●), 80:20 *endo*/*exo*-**12** (○), *exo*-**11** (■), and *exo*-**12** (□).

Table 2. First Order Rate Constants Determined for *exo*- and 80:20 *endo/exo*-11 and -12

monomer	isomeric purity	k_i[a] (10^3 s^{-1})	k_p[a] (10^3 s^{-1})	k_i/k_p
11	80:20 *endo/exo*	7.18	0.43	16.8
12	80:20 *endo/exo*	6.91	0.41	16.7
11	100% *exo*	10.73	6.27	1.7
12	100% *exo*	9.47	6.51	1.5

[a] All values were measured using ^{1}H NMR spectroscopy with [M] = 0.222 M and [I] = 0.0111 M.

k_i values for *endo*/*exo* mixtures and the pure *exo* monomers shows that k_i is only slightly affected by the isomeric purity. In sharp contrast, the k_p values are greatly dependent upon the isomeric purity, with the *exo* isomer propagating 15 times faster than the *endo*/*exo* mixture.

Controlled molecular weights, high initiator efficiency, and absence of chain transfer and chain termination are characteristics of living polymerizations.[5,6] In accordance with these criteria, we examined whether the molecular weights are controlled by the stoichiometry of the reaction. For both monomers (**11** and **12**) a linear relationship between M_n and the corresponding [M]:[I] feed ratios (Figure 3) was observed, suggesting the living character and high control of the polymerization.

Another decisive factor in characterizing living polymerizations is the synthesis of block copolymers.[5,6] To show that the polymerizations of *exo*-**11** and *exo*-**12** fulfill this criterion, a two-step polymerization sequence was carried out for both monomers. A 20:1 [M]:[I] ratio of monomer **12** was polymerized to completion and allowed to stir for 30 min, at which time 200 equiv of additional monomer was added. As shown in Figure 4, a dramatic increase in molecular weight was observed for the original polymer (**14**) (I−A) after sequential addition of fresh monomer (**14**) (I−B). Complete absence of chain termination and chain transfer is evident by the disappearance of peak A with no residual signal in the baseline. Both chain termination and chain transfer would produce nonliving polymer chains that would not increase in molecular weight upon further addition of fresh monomer. Identical results were observed for polymer **13** (Figure 4-II). These findings, in conjunction with the linear plot of M_n as a function of [M]:[I], clearly prove the living character of these systems.

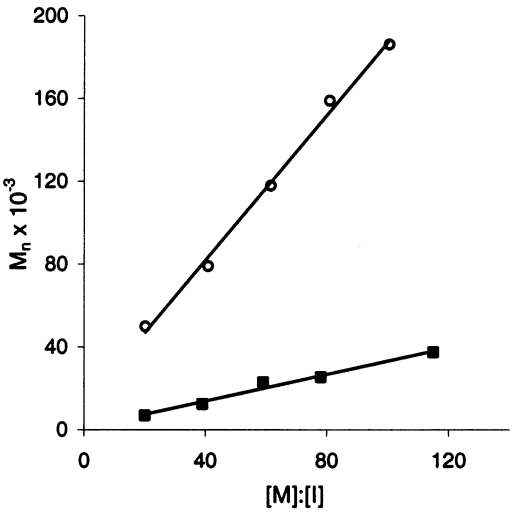


Figure 3. Plot of M_n vs monomer-to-catalyst ratios for polymers **13** (■, eluant = THF) and **14** (○, eluant = CH_2Cl_2).

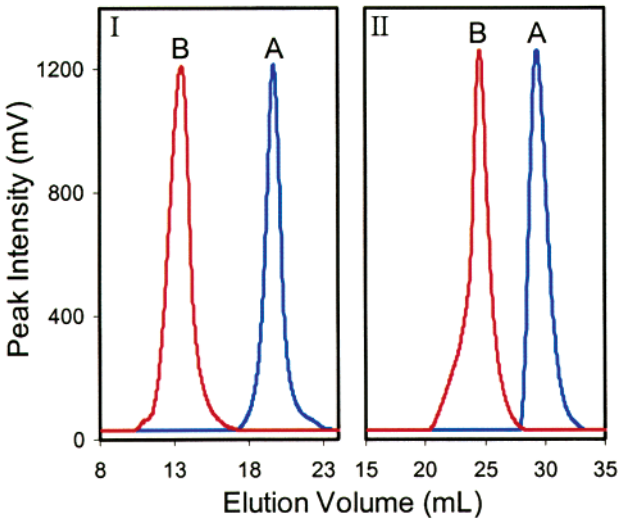
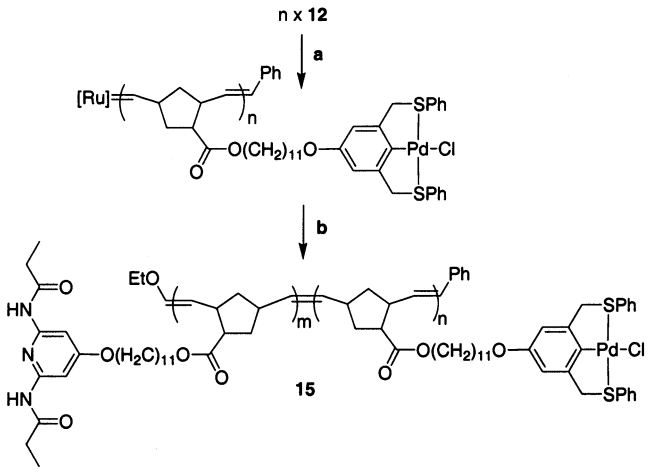


Figure 4. (I) GPC traces of polymers prepared using monomer **12.** (II) GPC traces of polymers prepared using monomer **11**. (blue —) Polymer after complete conversion ([M]:[I] = 20:1, M_w(**11**) = 8.1 × 10^3, M_n(**11**) = 7.2 × 10^3, PDI(**11**) = 1.13; M_w(**12**) = 6.3 × 10^4, M_n(**12**) = 4.9 × 10^4, PDI(**12**) = 1.29). (red —) Same polymer after standing for 0.5 h followed by polymerization of 200 equiv ([M_2]:[M_1] = 200:1, [M]:[I] = 20:1, M_w(**11**) = 1.0 × 10^5, M_n(**11**) = 7.1 × 10^4, PDI(**11**) = 1.41; M_w(**12**) = 4.5 × 10^5, M_n(**12**) = 3.4 × 10^5, PDI(**12**) = 1.32) of additional monomer.

Copolymerization Studies. Once the living nature of these monomers was established, AB block copolymerization using both monomers **11** and **12** was possible and carried out (Scheme 2). A 75:1 [M]:[I] ratio of monomer **12** was polymerized to completion, at which time 25 equiv of monomer **11** was added and allowed to stir until all monomer was consumed. The resultant AB block copolymer was isolated by precipitation from hexanes. Identical experiments were carried out for 50:50 and 25:75 compositions of **12** and **11**, respectively. GPC analyses of polymers possessing hydrogen-bonding recognition units were hampered by interactions with the columns in nonpolar eluants. Similar problems were observed for copolymers **15** when subjected to GPC analysis using CH_2Cl_2 as an eluant. These difficulties were circumvented by using DMF as an eluant. For the

Scheme 2. Synthesis of AB Block Copolymers Containing Both Diaminopyridine and Pd^{II} Pincer Receptor Units



a) **4**, $CDCl_3$, 20-120 min, 100%. b) m x **11**, 20-120 min, 100%.

25:75 composition of **11** to **12**, molecular weights of $M_w = 1.36 \times 10^5$ and $M_n = 7.82 \times 10^4$ were observed with polydispersities of 1.74, and no signs of chain transfer or chain termination were evident. However, similar analyses of 75:25 and 50:50 mixtures of **11**:**12** were unsuccessful due to poor solubility in polar media such as DMF or THF.

Conclusion

In conclusion, we have synthesized and polymerized via ROMP isomerically pure *exo*-norbornene esters containing Pd^{II} SCS pincer complexes or diaminopyridine moieties. Using standard characterization techniques, the living character of the polymerizations was proven which allowed for the synthesis of block copolymers. A comparison between 100% *exo* monomers **11** and **12** and those prepared using the more conventional route as a 80:20 *endo*/*exo* mixture clearly showed advantageous polymerization behavior for the former with faster reaction times, higher conversions, and more control. Specifically, we have shown that (i) the carbonyl ester group is central to maintaining k_i/k_p values adequate for living polymerization, (ii) the rate of propagation is dependent upon the isomeric purity of the norbornene ester moiety, and (iii) the polymerization kinetics are independent of the terminal diaminopyridine or Pd^{II} SCS Pincer functional groups. On the basis of these results, the formation of block copolymers that incorporate both metal-coordinating units and hydrogen-bonding motifs have been realized. Noncovalent functionalization of these block copolymers using hydrogen-bonding and metal coordination is currently under investigation.

Experimental Section

General Methods. All reagents were purchased either from Acros Organics, Aldrich, or Strem and used without further purification. DMF and $CDCl_3$ were distilled from calcium hydride and degassed prior to use. THF and CH_2Cl_2 were dried via passage through copper oxide and alumina columns.[34] NMR spectra were taken using a 300 MHz Varian Mercury spectrometer. All spectra are referenced to residual proton solvent. Mass spectral analysis was kindly provided by the Georgia Tech Mass Spectrometry Facility using a VG-70se spectrometer. Gel permeation chromatography (GPC) analyses for **14** were carried out using a Waters 1525 binary pump coupled to a Waters 2414 refractive index detector with methylene chloride as an eluant on American Polymer Standards 10 μm particle size, linear mixed bed packing columns (2×). GPC analysis for **13** were carried out using a Waters 510 binary pump coupled to a Waters 410 differential refractometer with THF as an eluant on an American Polymer Standards column set (100, 1000, 100 000 Å, linear mixed bed). All GPCs were calibrated using polystyrene standards. Atlantic Microlabs, Norcross, GA, performed all elemental analyses.

exo-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (**6**) was prepared according to a literature protocol.[27,32,33] 2,6-Bis(propionylamino)-4-hydroxypyridine (**9**) was prepared by acylation of 4-benzyloxy-2,6-diaminopyridine[21,35] with propionyl chloride and subsequent deprotection with H_2/Pd in 88% yield. SCS pincer ligand **8** was prepared according to literature procedure.[20,36]

***exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 11-Bromoundecyl Ester (7).** *exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid **6** (6.1 g, 0.044 mol) and 11-bromo-undecan-1-ol (11.2 g, 0.044 mol) were combined, dissolved in anhydrous CH_2Cl_2 (40 mL), and placed under an atmosphere of argon. To the stirred solution, DCC (9.1 g, 0.044 mol) in CH_2Cl_2 (40 mL) and DMAP (catalytic amount) were added at 25 °C. Immediately, the solution became turbid with formation of a white precipitate. Following stirring at reflux for 16 h, the mixture was cooled and diluted with CH_2Cl_2 (200 mL), and the precipitate was filtered off. The filtrate was dried ($MgSO_4$) and the solvent removed to give a solid residue that was further purified by column chromatography (SiO_2, eluant: 1:1 CH_2Cl_2/hexanes). Drying on high vacuum provided pure **7** as a colorless oil (14.25 g, 87%). ^{1}H NMR ($CDCl_3$): δ = 6.09 (m, 2H, CH=CH), 4.04 (t, 2H, J = 6.9 Hz, CH_2O), 3.37 (t, 2H, J = 6.9 Hz, CH_2Br), 2.99 (m, 1H), 2.88 (m, 1H), 2.18 (m, 1H), 1.92−1.76 (m, 3H), 1.65−1.55 (m, 3H), 1.55 (m, 1H), 1.53 (m, 1H), 1.41−1.19 (m, 14H). ^{13}C NMR ($CDCl_3$): δ = 176.1, 137.9, 135.6, 64.4, 46.5, 46.2, 43.0, 41.5, 33.8, 32.7, 30.2, 29.3, 29.1, 28.6. HRMS (EI): m/z = 370.15432 (M^+, calcd 370.1074) Anal. Calcd for $C_{19}H_{31}BrO_2$: C, 61.45; H, 8.41. Found: C, 61.64; H, 8.51.

***exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 11-(3,5-Bis(phenylsulfanylmethyl)phenoxy)undecyl Ester (10).** Compound **7** (2.40 g, 0.0065 mol) was slowly added to a stirred suspension of **8** (2.30 g, 0.0068 mol) with K_2CO_3 (2.40 g, 0.017 mol) in dry DMF (20 mL) at 25 °C. Once heated to 60 °C, the reaction was stirred for 60 h at which point the DMF was removed under reduced pressure. The crude product was then redissolved in CH_2Cl_2 (150 mL) and washed with H_2O (100 mL). The organic layer was dried ($MgSO_4$), the solvent evaporated, and the crude product purified by column chromatography (SiO_2, eluant: 3:2 hexanes/DCM) to afford pure **10** (3.92 g, 96%) as a viscous, colorless oil. ^{1}H NMR ($CDCl_3$): δ = 7.28−7.12 (m, 10 H, SPh), 6.80 (s, 1H, ArH), 6.69 (s, 2H, ArH), 6.11 (m, 2H, CH=CH), 4.07 (t, J = 6.6 Hz, 2H, CH_2O), 4.00 (s, 4H, CH_2S), 3.82 (t, J = 6.6 Hz, 2H, CH_2O), 3.03 (m, 1 H), 2.90 (m, 1H), 2.21 (m, 1H), 1.91 (m, 1H), 1.75−1.58 (m, 5H), 1.54 (m, 1H), 1.51 (m, 1H), 1.46−1.19 (m, 14H). ^{13}C NMR ($CDCl_3$): δ = 176.1, 159.1, 138.8, 137.9, 136.2, 135.6, 129.6, 128.7, 126.2, 121.4, 113.6, 67.8, 64.4, 46.5, 46.2, 43.1, 41.5, 38.8, 30.2, 29.4, 29.3, 29.1, 28.6, 25.9, 25.8. HRMS (EI): m/z = 628.30578 (M^+, calcd 628.304 49) Anal. Calcd for $C_{39}H_{48}O_3S_2$: C, 74.48; H, 7.69. Found: C, 74.41; H, 7.79.

***exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 11-(2,6-Bis(propionylamino)pyridin-4-yloxy)undecyl Ester (11).** 11-Bromoundecyl ester **7** (1.6 g, 0.004 36 mol), hydroxypyridine **9** (1.057 g, 0.004 24 mol), and Cs_2CO_3 (1.6 g, 0.0049 mol) were stirred in 80 mL of acetone at reflux for 12 h. The suspension was filtered, the solvent evaporated, and the residue purified by column chromatography (SiO_2, eluant: 1:1 hexanes/ethyl acetate) to afford pure **11** (2.24 g, 100%) as a colorless, viscous oil that crystallized as fine needles after several days. ^{1}H NMR ($CDCl_3$): δ = 7.94 (br s, 2 H, *NH*), 7.50 (s, 2 H, pyr), 6.08 (m, 2 H, C*H*=C*H*), 4.04 (t, J = 6.6 Hz, 2 H, CO_2CH_2), 3.97 (t, J = 6.6 Hz, 2 H, CH_2O), 3.00 (m, 1 H), 2.87 (m, 1 H), 2.34 (q, J = 7.7 Hz, 4 H, CH_2CH_3), 2.18 (m, 2 H), 1.88 (d/tr, J_1 = 12.1 Hz, J_2 = 3.8 Hz, 1 H), 1.71 (m, 2 H), 1.59 (m, 2 H), 1.48 (m, 1H),

1.40−1.20 (m, 15 H), 1.17 (t, J = 7.7 Hz, 6 H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ = 176.2, 172.3, 168.8, 150.5, 137.9, 135.6, 96.0, 68.3, 64.5, 46.5, 46.2, 43.1, 41.5, 30.6, 30.1, 29.3, 29.2, 29.1, 28.7, 28.6, 25.8, 25.7, 9.2. HRMS (EI): m/z = 527.3367 (M^+, calcd 527.3359). Anal. Calcd for $C_{30}H_{45}N_3O_5$: C, 68.28; H, 8.60; N, 7.96. Found: C, 67.76; H, 8.70; N, 7.68.

Pd−Cl *exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 11-(3,5-Bis(phenylsulfanylmethyl)phenoxy)undecyl Ester (12). Compound **10** (542 mg, 0.862 mmol) was dissolved in a 1:2 mixture of CH_2Cl_2 (5 mL)/CH_3CN (10 mL). $Pd(Ph_3CN)_2Cl_2$ (329 mg, 0.862 mmol) was then added in one portion. The dark orange solution was stirred for 30 min under an atmosphere of argon, at which point $AgBF_4$ (419 mg, 2.15 mmol) was added, and the solution was stirred for an additional 30 min. Immediately after addition of the silver salt, the solution became pale yellow in color with formation of a white precipitate. The reaction mixture was then diluted with CH_2Cl_2 (250 mL) and poured into a brine solution (250 mL). Following vigorous stirring for 5 h, the organic layer was separated and dried ($MgSO_4$), and the solvent was removed under reduced pressure. Purification by column chromatography (SiO_2, eluant: CH_2Cl_2/MeOH 99:1) yielded Pd−Cl complex **12** (570 mg, 86%) as an amorphous yellow solid. ^1H NMR ($CDCl_3$): δ = 7.82−7.79 (m, 4H, SPh), 7.36−7.32 (m, 6H, SPh), 6.56 (s, 2H, ArH), 6.10 (m, 2H, CH=CH), 4.53 (br s, 4H, CH_2S), 4.06 (t, J = 6.6 Hz, CH_2O), 3.85 (t, J = 6.6 Hz, CH_2O), 3.02 (m, 1H), 2.90 (m, 1H), 2.20 (m, 1H), 1.91 (m, 1H), 1.76−1.55 (m, 5H), 1.52 (m, 1H), 1.49 (m, 1H), 1.42−1.23 (m, 14H). ^{13}C NMR ($CDCl_3$): δ = 176.2, 156.9, 151.3, 150.0, 137.9, 135.7, 132.3, 131.3, 129.6, 129.5, 108.7, 68.0, 64.4, 51.6, 46.5, 46.2, 43.1, 41.5, 30.2, 29.4, 29.3, 29.1, 28.6, 25.9, 25.8. HRMS (FAB): m/z = 733.201 42 ($(M - Cl)^+$, calcd 733.200 14). Anal. Calcd for $C_{39}H_{47}ClO_3PdS_2$: C, 60.85; H, 6.15. Found: C, 60.40; H, 6.15.

General Polymerization Procedure. A definitive amount of monomer was weighed into a vial, placed under an atmosphere of argon, and dissolved in anhydrous, degassed $CDCl_3$ (1 mL per 100 mg of monomer). A stock solution of catalyst (in $CDCl_3$) was prepared, and the desired amount was added in one portion to the vigorously stirred monomer solution. Upon complete polymerization, a drop of ethyl vinyl ether was added to terminate the polymerization. The final polymer was obtained by precipitation from cold hexanes or by evaporation of volatiles followed by prolonged drying on high vacuum. Polymers **13** and **14** were obtained as gray and pale-yellow solids, respectively.

Polymer 13. ^1H NMR ($CDCl_3$): δ = 8.14 (br s, 2 H, NH), 7.47 (s, 2 H), 5.4−5.1 (br m, 2 H), 3.96 (br m, 4H), 3.2−2.4 (br m, 2 H), 2.33 (br m, J = 7.1 Hz, 4 H), 2.2−1.4 (br m, 23 H), 1.15 (br t, J = 7.1 Hz, 6 H).

^{13}C NMR ($CDCl_3$): δ = 176.1, 172.8, 169.1, 150.8, 134−131, 96.3, 68.6, 64.7, 49.7, 47.8, 42.1, 41.2, 37.1, 36.4, 30.8, 29.7−28.9, 26.0, 9.5.

Polymer 14. ^1H NMR ($CDCl_3$): δ = 7.78 (m, 4H, SPh), 7.32 (m, 6H, SPh), 6.55 (s, 2H, ArH), 5.50−5.17 (br m, 2H, CH=C), 4.58 (br s, 4H, CH_2S), 4.00−3.85 (m, 2H, OCH_2), 3.84−3.80 (m, 2H, OCH_2), 3.24−2.30 (br m, 3H), 2.03−1.50 (br m, 8H), 1.98−1.07 (m, 14H).

^{13}C NMR ($CDCl_3$): δ = 174.4, 156.8, 151.3, 149.9, 132.3, 131.2, 129.6, 129.5, 108.7, 108.6, 67.9, 64.2, 51.5, 48.0, 45.4, 40.4, 37.3, 36.0, 29.3, 29.2, 28.9, 28.6, 26.0, 25.8.

General Copolymerization Procedure (15). A definitive amount of monomer **12** was weighed into a vial, placed under an atmosphere of argon, and dissolved in anhydrous, degassed $CDCl_3$ (1 mL per 100 mg of monomer). A stock solution of catalyst (in $CDCl_3$) was prepared, and the desired amount was added in one portion to the vigorously stirred monomer solution. Upon complete monomer consumption, a charge of monomer **11** dissolved in anhydrous, degassed $CDCl_3$ (1 mL per 100 mg of monomer) was added to the vial and allowed to stir until all monomer was completely consumed. Upon complete polymerization, a drop of ethyl vinyl ether was added to terminate the polymerization. The copolymers were obtained by precipitation from cold hexanes. Polymers **15** were obtained as light green solids. ^1H NMR ($CDCl_3$): δ = 8.04 (br s, 2H, NH), 7.79−7.75 (m, 4H, SPh), 7.50 (s, 2H, pyr), 7.34−7.30 (m, 6H, SPh), 6.54 (s, 2H, ArH), 5.42−5.10 (m, 4H, CH=CH), 4.50 (br s, 4H, CH_2S), 4.11−3.92 (br m, 6H, CH_2O), 3.82 (t, J = 6.6 Hz, CH_2O), 3.2−1.0 (m, 60H).

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