

Tandem Catalysis and Self-Assembly: A One-Pot Approach to Functionalized Polymers

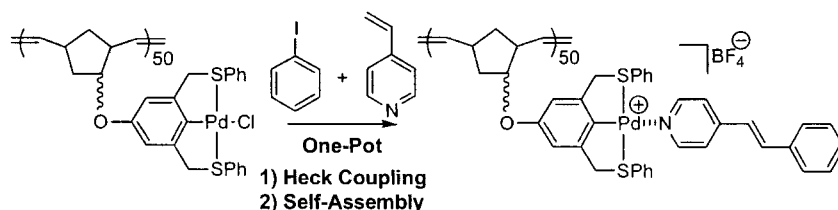
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ABSTRACT



Side-chain functionalized polymers possessing terminal palladated SCS pincer complexes at each repeat unit were synthesized via ring-opening metathesis polymerization. These palladium centers function as both well-defined Heck catalysts and recognition units capable of quantitative self-assembly of pyridine-containing molecules. Exploitation of both the catalytic and self-assembly properties has led to the development of a controlled, one-pot tandem catalysis/self-assembly sequence for the synthesis of functionalized polymers.

It is well-known that self-assembly is a prevalent force in the fabrication of complex biological entities.¹ The efficiency of natural systems can partially be attributed to Nature's ability to utilize recognition units in both catalysis and self-assembly, which often go hand in hand.¹ In this communication, we present a strategy toward the synthesis of materials that attempts to mimic this bifunctional behavior on a very basic level. In particular, we introduce a facile methodology for the synthesis of highly functionalized side-chain polymers based upon a one-pot tandem catalysis and self-assembly reaction sequence (Scheme 1).

Self-assembly of small molecules onto polymer backbones gives rise to a parallel route to materials in which a functional group or mesogen is bound to a prefabricated polymeric backbone through noncovalent interactions.² This strategy is superior to conventional synthesis because it eliminates extensive monomer synthesis and avoids problems associated with the intolerance of some polymerization techniques

toward deactivating functional groups. To this end, we envisaged a synthesis of highly functionalized materials via a route that commences with commercially available starting materials and utilizes both catalysis and self-assembly.

Pincer ligands, named for their chelating shape, are tridentate ligand systems that allow for insertion of transition metals into the aromatic C–H bond situated between donor atoms such as phosphorus, sulfur, or nitrogen.³

Such complexes have previously been described as simple, highly efficient, and robust catalysts for a variety of organic transformations.⁴ Additionally, pincer complexes have been employed as metal-coordination motifs in the synthesis of metallodendrimers and polymers.⁵

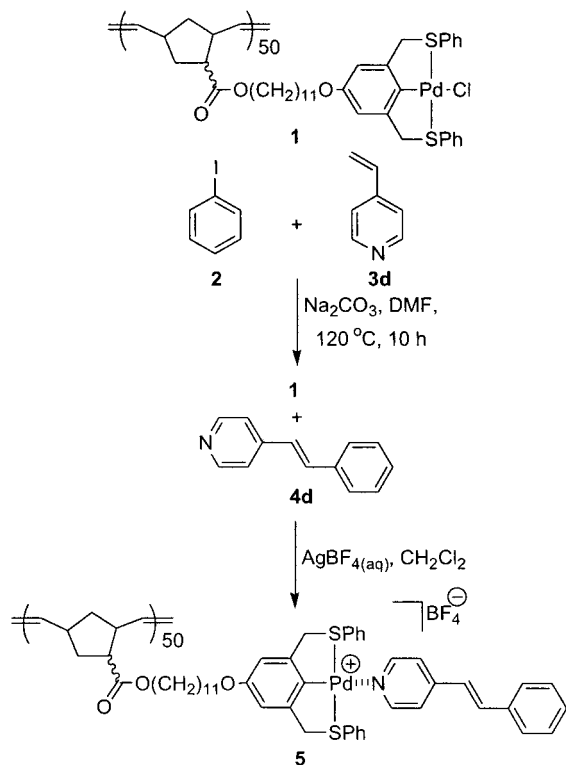
We rationalized that the bifunctional nature of pincer ligands could provide a simple and efficient route to the synthesis of highly functionalized polymers via a controlled tandem catalysis and self-assembly sequence. To this end, polymer **1** was designed possessing terminal palladated SCS

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Scheme 1. Tandem Catalysis and Self-Assembly



pincer complexes at every repeat unit, resulting in the highest catalyst loading of all pincer-ligand based polymeric Heck catalysts. Norbornene was chosen as the polymerizable unit to provide a well-controlled route to polymers via ring-opening metathesis polymerization.⁶ A flexible C₁₁ alkyl chain was introduced between the backbone and the terminal palladated SCS pincer ligand to decouple the side-chain from the polymer backbone and to increase solubility.⁷

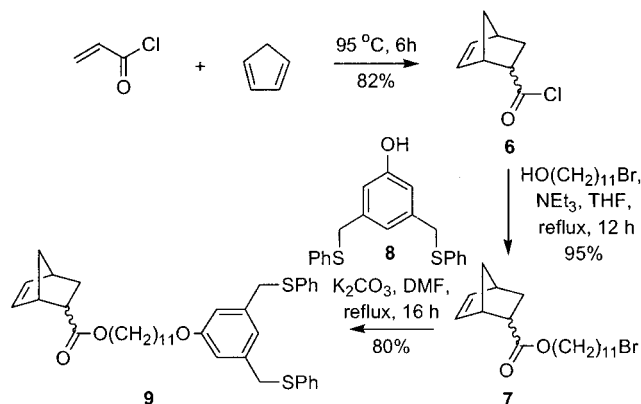
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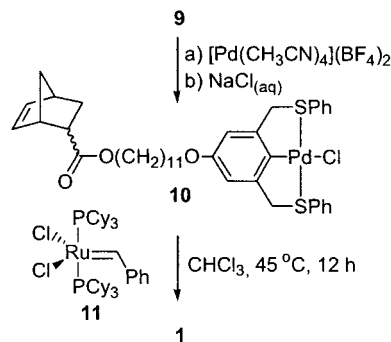
Synthesis of the desired monomer commences with formation of acid chloride **6**⁸ followed by condensation with 11-bromo-1-undecanol to provide bromoester **7** in 95% yield. Hydroxy functionalized pincer ligand **8**, synthesized as previously reported,^{5a} was coupled to the C₁₁ spacer to form the nonmetalated SCS ligand **9** in 80% yield (Scheme 2).

Scheme 2. Ligand Synthesis



Palladation of **9** was carried out by ligand exchange of [Pd(CH₃CN)₄](BF₄)₂⁹ to form the cyclopalladated monomer **10** in quantitative yield. Further ligand exchange of the resultant cationic Pd–BF₄ complex to form the neutral Pd–Cl complex required stirring with brine to provide **10** in 80% isolated yield.¹⁰ Monomer **10** was polymerized using **11** at 45 °C in chloroform to yield polymer **1** (Scheme 3).¹¹

Scheme 3. Metalation and Polymerization



To provide insights into the catalytic activity of **1**, Heck coupling experiments between **2** and various alkene acceptors

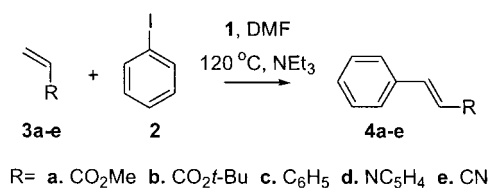
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(10) All compounds have been characterized by ¹H NMR and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis.

Scheme 4. Heck Reactions



3a–e were carried out (Scheme 4).¹² Compounds possessing electron-withdrawing substituents (**3a** and **3b**) accelerate the reaction when compared to those with electron-donating substituents (**3c** and **3d**) (Table 1). In addition to electronic

Table 1. Results for Heck Reactions

entry	product	yield ^a (%)	time (h)	TON ^b	TOF ^c
1	4a	>99	2.5	1000	400
2	4b	>99	3.5	1000	286
3	4c	97	11	1000	91
4	4d	92	16	1000	63
5	4e	95	10.5	1000	95

^a Yield of isolated product. ^b Turnover numbers are expressed as mol 4/mol **1** [Pd]. ^c Turnover frequencies are expressed as TON/h.

effects, the overall decrease in reactivity of nitrogen-containing olefins (**3d** and **3e**) can be attributed to partial deactivation of the catalyst through competitive metal coordination. These results clearly demonstrate the efficiency and versatility of **1** as a Heck catalyst.

To investigate the self-assembly of **1**, experiments leading to the coordination of **4d** to the polymer backbone were carried out and followed in situ by ¹H NMR spectroscopy (Figure 1). Stilbene **4d** was employed as a model compound for several reasons. First, stilbenes provide an efficient route to liquid crystalline materials.² Second, retrosynthetic analysis of stilbene **4d** suggests a facile synthesis by Heck reaction of vinyl pyridine and iodobenzene. Moreover, pyridyl recognition units have previously been employed as donor ligands to palladated SCS pincer complexes in supramolecular chemistry.⁵

Self-assembly experiments were carried out by adding 1 equiv of AgBF_{4(aq)} to a dichloromethane solution of a 1:1 mixture of **1** and **4d**. Instantaneously, AgCl precipitated, opening a free coordination site, which was subsequently ligated by the pyridyl moiety of the stilbene. Figure 1A and B shows the spectra of pure **4d** and **1**, respectively. Figure

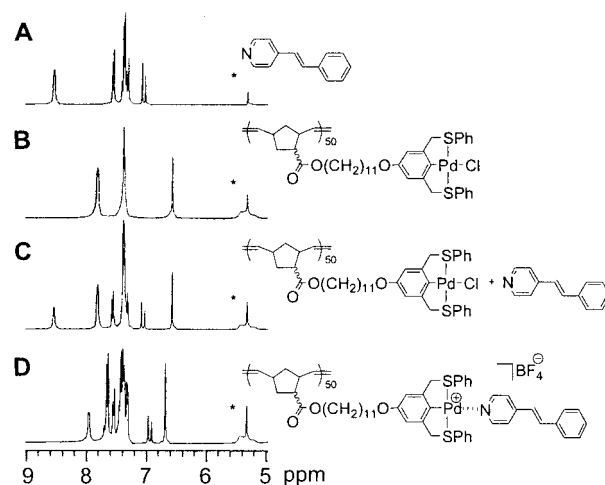


Figure 1. The aromatic and olefinic region of the ¹H NMR spectra depicting the metal coordination of stilbene **4d** onto **1** (*CD₂Cl₂). (A) Stilbene **4d**. (B) Polymer **1**. (C) A 1:1 mixture of **4d** and **1**. (D) The 1:1 mixture after addition of 1 equiv of AgBF_{4(aq)}.

1C depicts a 1:1 mixture of **4d** and **1**, which clearly shows all signals characteristic of the individual components. Figure 1D displays the 1:1 mixture after self-assembly. Of particular interest are the chemical shifts for the α-protons of the pyridyl moiety at 8.56 ppm and the singlet at 6.58 ppm assigned as the protons in the *meta* position of the palladated phenyl ring. In Figure 1D an upfield shift of the pyridyl α-protons from 8.56 to 7.97 ppm with complete disappearance of the signal at 8.56 ppm and a slight downfield shift of the *meta* pincer protons from 6.58 to 6.68 ppm were observed. This shows that the α-pyridyl groups have coordinated to the Pd center.^{5b,13} Also, shifts of the alkene protons of the stilbene from 7.09 and 7.03 ppm to 6.97 and 6.91 ppm, respectively, and other minor shifts throughout Figure 1D provide additional support for the self-assembly process. The products could be isolated by precipitation from hexanes to afford polymer **5**.

After establishing that **1** possesses both excellent catalytic activity and capability to serve as a recognition unit for self-assembly, we examined the use of both properties in a one-pot Heck coupling/self-assembly sequence. Polymer **1** was employed in tandem experiments as both catalyst for the synthesis of **4d** and recognition unit for the self-assembly of **4d**. Analogous to the method used above, the progress of the reaction was followed in situ by ¹H NMR (Figure 2).

Quantitative Heck coupling of **2** and **3d** (spectrum of a mixture of the pure compounds is shown in Figure 2A) was carried out at 120 °C for 10 h in the presence of **1** (Figure 2B) to provide exactly 1 equiv of stilbene **4d** (Figure 2D). The disappearance of the olefinic signals at 6.85–6.75, 6.20–6.14, and 5.56–5.52 ppm in Figure 2C (a 1:1:1 mixture of **1**, **2**, and **3d**) and the appearance of new signals at 7.70

(11) Polymerization reactions were carried out using a 50:1 monomer-to-catalyst ratio; 1 mL of solvent was used for every 100 mg of monomer converted. The polymerization reactions were terminated by addition of a small amount of ethyl vinyl ether, and the polymer was collected by precipitation from cold hexanes. Representative GPC data: *M*_w = 35000, *M*_n = 29000, PDI = 1.19.

(12) Heck reactions were carried out at 120 °C in DMF. To a vessel charged with 0.002 mmol of **1** were added 2 mmol of vinylpyridine, 3 mmol of olefin, and 3 mmol of NEt₃. The reaction was monitored by GC–MS. The products were isolated by precipitation in water followed by extraction with dichloromethane.

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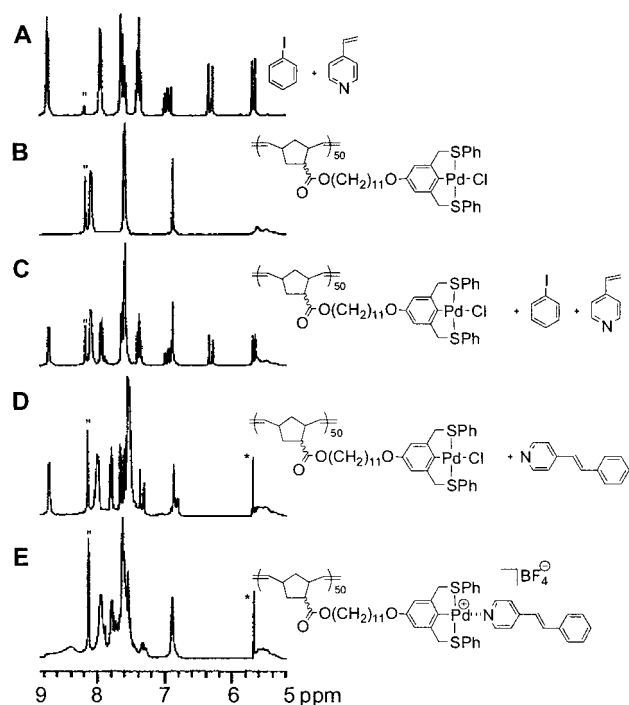


Figure 2. The aromatic and olefinic region of the ¹H NMR spectra depicting the tandem catalysis/self-assembly sequence ("DMF-*d*₇, *CD₂Cl₂). (A) A 1:1 mixture of **2** and **3**. (B) Polymer **1**. (C) A 1:1:1 mixture of **1**, **2**, and **3d**. (D) The 1:1 mixture of **4d** and **1** following catalytic Heck coupling. (E) The 1:1 mixture following the addition of 1 equiv of AgBF₄(aq).

ppm (Figure 2D) are direct evidence for this transformation. Catalyst decomposition is not evident (by NMR) throughout this conversion, revealing the robust nature of the catalyst

to the reaction conditions. Prior to self-assembly, one volumetric equivalent of CD₂Cl₂ was added to the DMF solution to solubilize the noncoordinated intermediate. Addition of AgBF₄(aq) resulted in instantaneous and quantitative self-assembly (Figure 2E). Comparison of Figure 2E and 2D provides evidence for the coordination of the in situ prepared **4d** to the Pd center with the diagnostic upfield shift and broadening of the α-pyridine protons from 8.61 to 8.28 ppm.^{5b,13} A change in chemical shifts of the signals arising from protons on the phenyl group of the thioether of the pincer ligand were also evident, with shifts from 7.88 and 7.43 ppm to 7.84 and 7.52 ppm, respectively. The final polymer could be isolated by precipitation from hexanes. The NMR spectra of isolated polymer **5** (in CD₂Cl₂) synthesized by both the tandem and stepwise routes were identical, indicating that the tandem catalysis/self-assembly route is a viable strategy toward the synthesis of functionalized polymers.

In conclusion, a bifunctional polymer system was synthesized that can be used (A) as a Heck catalyst, (B) as a recognition motif in self-assembly, or (C) in a tandem catalysis/self-assembly sequence to provide a simple and efficient route to the synthesis of self-assembled polymers. Polymer **1** possesses the highest catalyst loading of all pincer ligand-based polymeric Heck catalysts reported to date. Furthermore, our approach facilitates ease of synthesis when compared to the stepwise functionalization strategy because separation of small molecules is not required when prepared in situ.

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