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End-Functionalized Polymerization of 2-Vinylpyridine through Initial C−H Bond Activation of *N*-Heteroaromatics and Internal Alkynes by Yttrium Ene−Diamido Complexes

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Supporting Information

ABSTRACT: We successfully introduced end-capping functional groups to poly(2-vinylpyridine)s by initial introduction of the functional groups on yttrium catalysts through C−H bond activation of heteroaromatics and internal alkynes to the Y center via alkylyttrium-mediated σ-bond metathesis.

Well-defined polymers with end-capping groups having a different polarity and reactivity from the backbone are attracting scientific and industrial interest for their application as building blocks and additives in the construction of new functional materials.[1] To introduce the appropriate functional groups at the chain end, two synthetic routes have been developed: living polymerization by an initiator with a desired functional group[2−4] and controlled-termination functionalization of a living polymer chain end.[5,6] Depending on the required polymerization conditions, only a limited number of functional groups can be introduced at the initiation of the polymerization. For the latter protocol, chain-transfer agents such as organoboranes and organosilanes are indispensable for selectively incorporating a functional group into the polymer chain end in coordination polymerization. To overcome these concerns, our studies are aimed at determining the most desirable and straightforward synthetic approach using a unique combination of living coordination polymerization of vinyl monomers and the C−H bond activation reaction, the latter of which directly produces catalysts bearing various kinds of terminal functional groups from the same precursor, to provide end-functionalized polymers without any sequential reactions such as termination reactions (Figure 1). In pioneering work reported by Marks and co-workers,[7] amine and phosphine end-capped polymers were prepared by initiators derived in situ from an alkane elimination reaction of alkyllanthanide complexes with N−H and P−H bonds; to extend the variability and changeability of the end-capping groups, however, a synthetic methodology for introducing organic functional groups into the polymer chain end by direct C−H bond functionalization is most desirable, even though reports of such an approach are rare.[8] We have continuously studied the reactivity and catalytic application of early-transition-metal cyclometalated complexes[9] and recently reported the multiple insertion of internal alkynes into a Hf−C bond of four-membered metallacyclic species.[9b] Here we demonstrate the end-functionalized polymerization of 2-vinylpyridine (2-VP) by yttrium catalysts. The key step is in situ generation of cyclometalated- and propargylyttrium initiators

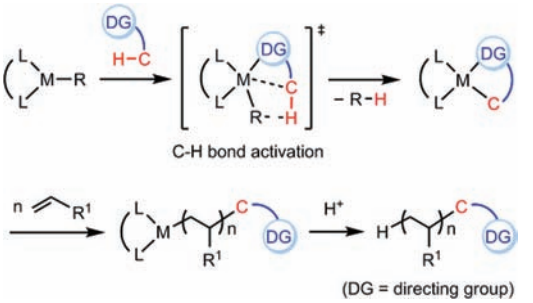
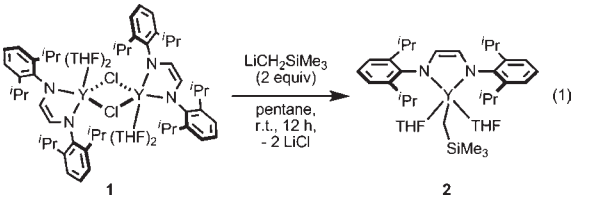


Figure 1. Direct synthesis of end-functionalized polymers via successive C−H bond activation/living polymerization.

derived from C(sp^2)−H bond activation of N-heteroaromatic compounds and C(sp^3)−H bond activation of trimethylpyridine and internal alkynes by an alkylyttrium complex.

Our catalyst precursor, alkylyttrium complex **2** bearing an ene−diamido ligand, was prepared in 63% yield by treating the chloride-bridged dinuclear yttrium complex [(2,6-^{i}Pr$_2$C$_6$H$_3$-DAD)-Y(THF)$_2$]$_2$(μ-Cl)$_2$ (**1**)[10] with 2 equiv of LiCH$_2$SiMe$_3$ (eq 1). The ^{1}H NMR spectrum of **2** at 35 °C displayed one doublet resonance at δ −0.65 ($^2J_{YH}$ = 3.0 Hz) due to the YC*H*$_2$SiMe$_3$ moiety, and the olefinic protons of the ligand backbone were observed as a singlet signal at δ 5.80, indicating a symmetric structure in solution. The doublet signal of the methylene carbon bound to the Y atom appeared at δ 25.1 ($^1J_{YC}$ = 44.8 Hz) in the ^{13}C NMR spectrum.



Complex **2** served as a catalyst for the polymerization of 2-VP in toluene at room temperature to give poly(2-VP) with a narrow molecular weight distribution (M_w/M_n = 1.2) and moderately high isotacticity ([*mmmm*] = 95%) (eq 2).[11] A trimethylsilyl group was observed at δ −0.16 in the ^{1}H NMR spectrum of the poly-(2-VP), confirming that the polymerization was initiated via insertion of the monomer into the Y−CH$_2$SiMe$_3$ bond of **2**,[12] and 2,1-insertion of 2-VP was observed, similar to the styrene

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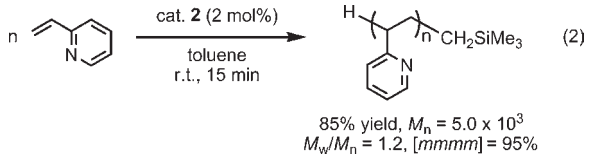
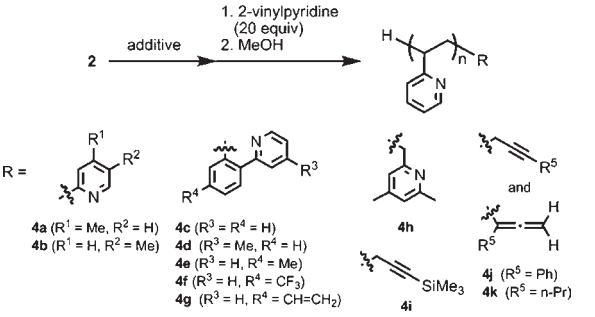
polymerization reaction[13] and 2-VP insertion into a Zr−C bond.[14] To check the living polymerization behavior, 2-VP (20 equiv) was sequentially added in each period of 15 min to the reaction mixture, and the progress of the polymerization was followed by taking the aliquots at same interval of time. A linear correlation between the reaction time and molecular weight was observed, indicating the living polymerization behavior in this system.[12] The controlled coordination polymerization of VP has rarely been explored, except in the case of the $AlEt_3$−VCl_3 catalyst.[15]



Notably, when pyridine was added to the reaction mixture (100 equiv relative to **2**), a pyridine moiety was selectively incorporated as the end group of poly(2-VP).[16] The formation of pyridyl-terminated poly(2-VP) was chracterized by electrospray ionization mass spectrometry (ESI-MS): ESI-MS measurements on the isolated low-MW polymer sample resulted in linear plots of m/z values of the peaks versus the number of 2-VP repeat units, corresponding to the molar mass of the 2-VP (Figure 2). The intercept was the sum of the masses of Na^+ and the pyridyl end group. These results clearly revealed that the polymer had a structural formula of $[H-(2\text{-VP})_n-C_6H_4N]$ (Figure 2c). To the best of our knowledge, this is the first example of the direct incorporation of a pyridyl group at the polymer chain end without preactivation of the pyridine ring. For the complete formation of pyridine-terminated polymer, addition of a mixture of excess pyridine (100 equiv) and 2-VP to the toluene solution of complex **2** was necessary; otherwise, trimethylsilyl-terminated or non-end-functionalized poly(2-VP)s were observed as contaminants.[12]

Direct functionalization of the polymer chain end was further applied to substituted pyridines and internal alkylacetylenes (Table 1). In the case of runs 1 and 2, a mixture of 4- or 3-methylpyridine (100 equiv) and 2-VP was added to a toluene solution of **2**; in runs 3−8, the toluene solution of 2-arylpyridine derivative or 2,4,6-trimethylpyridine and **2** was stirred for 15 min at room temperature before the injection of 2-VP. For internal alkylacetylenes, heating the reaction mixture to 50 °C for 3 h was necessary to achieve quantitative incorporation of the acetylenes at the terminal group of the polymers (runs 9−11). The results are summarized in Table 1. On the basis of the ESI-MS measurements, all of the poly(2-VP)s contained a terminal group corresponding to the additive molecule.[12] The poly(2-VP)s obtained in runs 1 and 2 showed low isotacticity, whereas the rest of the polymers were highly isotactic, probably because of interactions of the excess pyridine derivative (100 equiv relative to complex **2**) with the metal center during the polymerization reaction (see below). Not only the methyl-substituted pyridines but also 2-arylpyridines were introduced as the end-capping groups (runs 3−7). In the ^1H NMR spectrum of the poly(2-VP) obtained in run 7, resonances for vinylic protons assignable to the 4-vinylphenyl moiety were observed, indicating that the vinyl moiety remained intact during the polymerization reaction. The selectivity of an insertion reaction of an olefinic moiety into a metal−carbon

Table 1. End-Functionalized Polymerization of 2-VP[a]



run	additive	yield (%)	$10^3 \cdot M_n$[b]	M_w/M_n[b]	[*mmmm*] (%)[c]
1[d]	4-methylpyridine	92 (**4a**)	2.9	1.2	15
2[d]	3-methylpyridine	82 (**4b**)	3.0	1.2	20
3	2-phenylpyridine	90 (**4c**)	2.3	1.1	95
4	2-phenyl-4-methylpyridine	90 (**4d**)	2.3	1.1	95
5	2-(4-methylphenyl)pyridine	95 (**4e**)	2.1	1.2	95
6	2-(4-trifluoromethylphenyl)-pyridine	99 (**4f**)	2.0	1.1	95
7	2-(4-vinylphenyl)pyridine	91 (**4g**)	2.5	1.1	95
8	2,4,6-trimethylpyridine	99 (**4h**)	2.3	1.1	95
9[e]	1-trimethylsilyl-1-propyne	84 (**4i**)	2.0	1.2	95
10[e]	1-phenyl-1-propyne	83 (**4j**)	3.1	1.2	95
11[e]	2-hexyne	75 (**4k**)	2.5	1.1	95

[a] Reaction conditions: catalyst:additive:monomer = 0.01:0.01:0.20 (all in mmol) in toluene. The total volume was 3 mL. [b] Determined by gel-permeation chromatography. [c] Determined by ^{13}C NMR spectroscopy. [d] Excess methylpyridine (100 equiv relative to complex **2**) was added. [e] After addition of the internal acetylene, the reaction mixture was heated to 50 °C for 3 h, after which 2-VP was added.

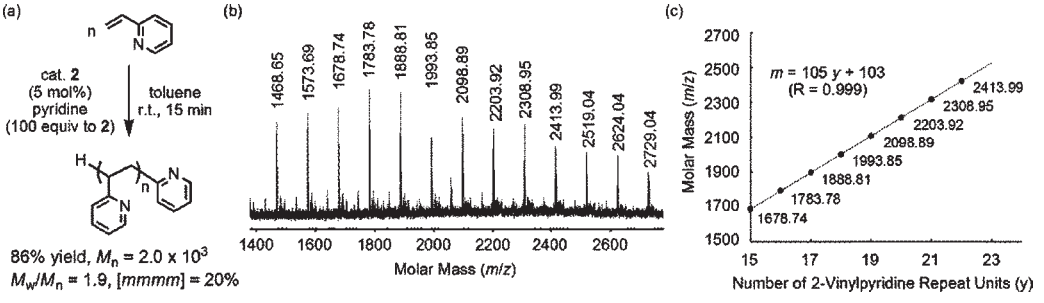


Figure 2. (a) Polymerization of 2-VP catalyzed by **2** in the presence of pyridine. (b) ESI-MS spectrum of the poly(2-VP) produced by catalyst **2** in toluene in the presence of pyridine. (c) Plot of m/z values vs the number of 2-VP repeat units.

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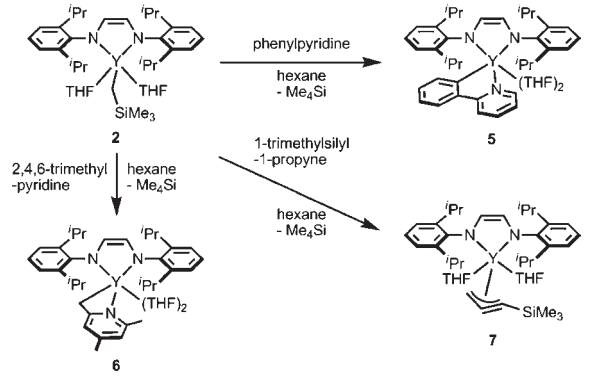
Scheme 1. C−H Activation of Heteroaromatic Compounds and Internal Alkynes by Alkylyttrium Complex 2



bond (i.e., chelation-assisted insertion of olefins into the metal−carbon bond) enabled us to prepare 2-VP-based macromonomers. When 2,4,6-trimethylpyridine was used as the additive, the C(sp^3)−H bond of the methyl group was activated, forming poly(2-VP) with a (4,6-dimethylpyridin-2-yl)methyl group at the chain end (run 8). In the case of internal alkylacetylenes, such as 1-trimethylsilyl-1-propyne, 1-phenyl-1-propyne, and 2-hexyne, a C(sp^3)−H bond at the propargylic position was activated (runs 9−11). The longer reaction time before addition of 2-VP was necessary because of the difficulty of activation of the propargylic C(sp^3)−H bond. The ^{1}H NMR spectra of the poly(2-VP)s in runs 10 and 11 displayed broad doublet resonances corresponding to the terminal allenyl groups, indicating that 2-VP inserted into the η^1-propargyl and η^1-allenyl forms of the YCH_2CCR moiety to form alkynyl- and allenyl-terminated polymers.

Alkylyttrium complexes have been reported to undergo C−H bond activation of heteroaromatic compounds and internal alkynes via σ-bond metathesis reactions.[17] Thus, we were interested in the reactions of **2** with 2-phenylpyridine, 2,4,6-trimethylpyridine, and 1-trimethylsilyl-1-propyne as model reactions for the initial step of the end-functionalized polymerization shown in Table 1. As shown in Scheme 1, treatment of **2** with 2-phenylpyridine resulted in the formation of five-membered metallacyclic compound **5** through C−H activation at the 2′-position of the phenyl ring.[17l] When 2,4,6-trimethylpyridine was used as the substrate, C(sp^3)−H bond activation afforded pyridylmethylyttrium complex **6**.[17e,f,k] 1-Trimethylsilyl-1-propyne reacted with **2** slowly at 50 °C, forming **7** via C(sp^3)−H bond activation at the propargylic position.[17b,g,h] In the ^{13}C NMR spectrum of **7**, coupling interactions with the α- and γ-carbon atoms of the YCH_2CCR moiety were observed, whereas J_{YC} for the β-carbon was not observed and the J_{CH} value for the α-carbon (155 Hz) was significantly larger, suggesting the η^3-allenyl/propargyl structure in solution.[17g,h,18] Such an η^3-coordination mode was clearly confirmed by the X-ray diffraction study of complex **7** (Figure 3). The C27−C28 and C28−C29 bonds, with lengths of 1.343(6) and 1.256(6) Å, are intermediate between C−C single and double bonds and double and triple bonds, respectively. The C27−C28−C29 angle of 164.4(5)° indicates a deviation from linearity at the central carbon, as is typical for η^3-allenyl/propargyl complexes.[17h]

Isolated yttrium complexes **5**−**7** served as catalysts for the polymerization of 2-VP, giving poly(2-VP)s with the corresponding 2-pyridylphenyl, (4,6-dimethylpyridin-2-yl)methyl, and 3-(trimethylsilyl)prop-2-ynyl groups at the terminal position (Scheme 2).[12] On the basis of the reactions in Schemes 1 and 2

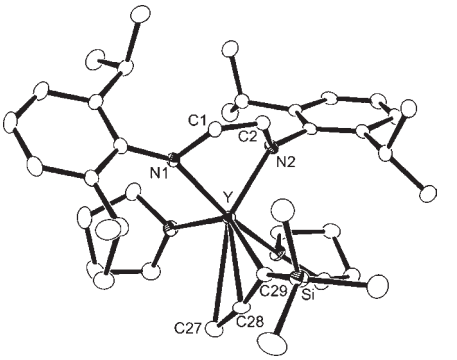
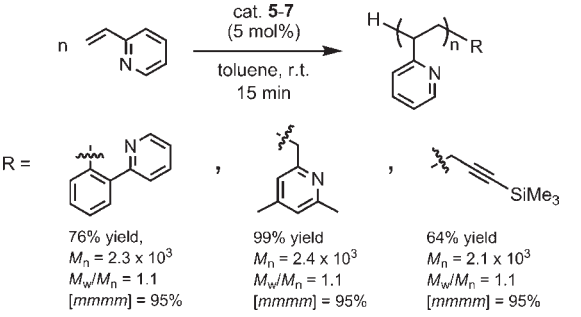


Figure 3. Molecular structure of **7** with 30% thermal ellipsoids. All H atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Y−N1, 2.229(3); Y−N2, 2.206(3); Y−C27, 2.916(5); Y−C28, 2.564(4); Y−C29, 2.513(4); N1−C1, 1.405(5); C1−C2, 1.364(6); N2−C2, 1.413(5); C27−C28, 1.343(6); C28−C29, 1.256(6); C27−C28−C29, 164.4(5). The dihedral angle between the N1−Y−N2 and N1−C1−C2−N2 planes is 128.7°.

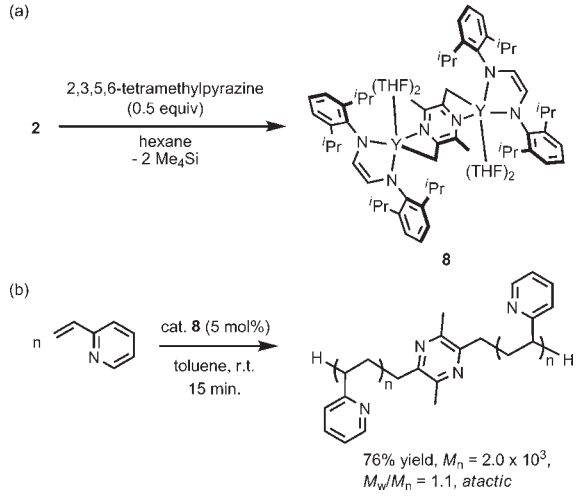
Scheme 2. Polymerization of 2-VP Catalyzed by 5−7



show that the additive molecules listed in Table 1 reacted with **2** in the first step to afford the corresponding new metallacyclic or propargylyttrium complexes. Thus, the polymerization of 2-VP proceeded via insertion of the monomer into a Y−C bond in these complexes **5**−**7**, resulting in the formation of end-functionalized poly(2-VP)s. The effect of pyridine on the tacticity of the end-functionalized polymerization was checked by the addition of excess pyridine and 2-phenylpyridine to the polymerization reaction catalyzed by complex **5**. When 100 equiv of pyridine was added to the polymerization reaction, the resulting polymer showed low isotacticity ([*mmmm*] = 60%). However, addition of excess 2-phenylpyridine (100 equiv) to the polymerization reaction did not affect the polymer microstructure, and the highly isotactic poly(2-VP) was obtained ([*mmmm*] = 95%). These results suggest that less-hindered pyridine derivatives such as pyridine, 3-methylpyridine, and 4-methylpyridine easily interact with the metal center in comparison with 2-substituted pyridine derivatives during the chain-propagation reaction.[12]

On the basis of the reactivity for chelation-assisted C−H bond activation by **2**, bimetallic initiator **8** was prepared by the reaction of **2** with 2,3,5,6-tetramethylpyrazine (Scheme 3a). The ^{1}H NMR spectrum of **8** displayed one singlet resonance assignable to the olefinic protons of the ene−diamido ligand, one broad signal for the methylene protons bound to Y, and one singlet signal due to the methyl group attached to the pyrazine ring in a 4:4:6 integral ratio, indicating a symmetric structure in solution. Complex **8** acted as a catalyst for the polymerization of 2-VP, and

Scheme 3. (a) Synthesis of Bimetallic Initiator 8 via Double C−H Bond Activation; (b) 2-VP Polymerization Catalyzed by 8



poly(2-VP) having a pyrazine unit in the main chain was isolated in 76% yield (Scheme 3b).[12] Although **6** and **8** both possess a heteroarylmethylyttrium moiety, the polymer catalyzed by **8** was atactic. We presume that the loss of stereocontrol might be due to the intramolecular interaction between two active sites.

In summary, we have demonstrated the direct synthesis of poly(2-vinylpyridine)s with various heteroaromatic and propargyl groups at the chain end of the polymers catalyzed by the single alkylyttrium complex **2**. The key to end-functionalized polymerization is activation of the C−H bond of heteroaromatics and internal alkynes to form metallacyclic and propargylic yttrium species that act as catalysts for living polymerization of 2-VP. Further development of this successive C−H bond activation−polymerization protocol using rare-earth metal complexes is ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details, NMR and ESI-MS spectra, living polymerization behavior, and a CIF file for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) 4-Vinylpyridine (**3b**) and styrene (**3c**) were not polymerized at all because of the absence of the N atom at the position ortho to the vinyl group of the monomer (see Table S1 in the Supporting Information).

(12) See the Supporting Information.

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