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Synthesis of heteroatom end-functionalized polyethene with lanthanide and transition-metal catalysts

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Introduction

Incorporation of heteroatom functionalities in the catalytic formation of polyolefin materials can be accomplished either by copolymerization of the olefin with an olefinic substrate that has a heteroatom-containing substituent, or by using a heteroatom-containing chain-transfer agent. In the first case the functionalities introduced are located in side-groups on the polyolefin backbone, in the second case the functionality will cap the polymer on one end of the chain. The latter strategy has been applied recently using chain-transfer agents with reactive X-H bonds ($X = \text{Si}, \text{B}^2$) in conjunction with group 3 and group 4 metal catalysts. We have sought to apply the capacity of lanthanide metallocenes to perform ethene polymerization as well as C-H activation³ to this chemistry, using heteroatom-containing hydrocarbons with activated C-H bonds as chain-transfer agents,⁴ and to compare this with analogous cationic group 4 metallocenes.

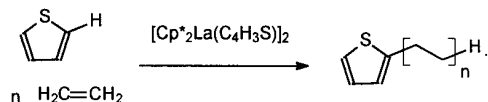
Results and Discussion

The compounds $[\text{Cp}^*_2\text{LnH}]_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{Ln} = \text{Y}$, **1a**; La , **1b**) are known to polymerize ethene readily to high molecular weight HDPE.³ These compounds also readily activate the *ortho*-CH bonds of the heteroaromatics pyridine, furan and thiophene to give $\text{Cp}^*_2\text{Ln}(2\text{-C}_5\text{H}_4\text{N})$ (**2a**,^{5b}) and $[\text{Cp}^*_2\text{Ln}(2\text{-C}_4\text{H}_3\text{X})]_n$ ($X = \text{O}$, **3a**,^{6b}; $X = \text{S}$, **4a**,^{4,6b}; $n = 2$). These systems should therefore in principle be suited to the type of polymerization/chain transfer chemistry described above.

Pyridine. Our group observed previously that the Y-pyridyl **2a** readily inserts one molecule of ethene into the Y-C bond, but that subsequent insertions are extremely slow (only a very slow formation of 2-ethylpyridine was observed with ethene and excess pyridine).⁵ The La-derivative essentially shows the same chemistry. This is due to the strong intramolecular coordination of the pyridyl nitrogen in the product of the first ethene insertion. Only in the presence of H_2 were good conversions to 2-ethyl- and 2,6-diethylpyridine observed. Thus the reactivity of these systems is similar to that of the cationic zirconocene system studied by Jordan *et al.*⁷ Dihydrogen is needed to cleave the M-C bond of the stable chelate complex that results from the first ethene insertion.

Furan. The oxygen in furan is less Lewis basic than the oxygen in THF or the nitrogen in pyridine. This is seen by the fact that coordination of furan to the Y-furyl **3a** is readily reversible. This should facilitate multiple ethene insertions into the metal carbon bond of **3**. However, the use of this substrate as chain-transfer agent is prevented by another feature of its reactivity. It turns out that the furyl C-H and C-O bonds are sufficiently reactive to let **3a** decompose in solution even at ambient temperature to give furan and a compound with the stoichiometry $[\text{Cp}^*_2\text{Y}]_2(\text{C}_4\text{H}_2\text{O})$. NMR spectroscopy suggests that cleavage of one of the furyl C-O bonds has occurred. An X-ray structure determination of the product is in progress.

Thiophene. The sulfur in thiophene is again less Lewis basic than the heteroatoms in the other substrates. This is seen by the fact that the 2-thienyl compounds **4** are dimeric, but do not give observable thiophene adducts in solution. These compounds are now stable in solution up to 100°C. The reactivity of the yttrium complex **4a** is rather sluggish, but even with a substituted olefin (1-butene) very slow catalytic formation of 2-*sec*-butylthiophene was observed. The more reactive La-derivative **4b** now readily forms low molecular weight end-functionalized polyethene $\text{H}(\text{CH}_2\text{CH}_2)_n(2\text{-C}_4\text{H}_3\text{S})$ at 80°C even in neat thiophene.



The nature of this material was evident from its NMR spectra, and the ^1H NMR spectrum in $\text{C}_2\text{D}_2\text{Cl}_4$ solvent is shown in Figure 1a. The integral ratio between the $\alpha\text{-CH}_2$ protons and the methyl end-group show that each polymer chain has one methyl and one 2-thienyl end-group. In this spectrum two small additional resonances are observed at around δ 6.6 (s) and δ 2.8 (t) ppm. These are attributed to a small amount of 2,6-di(*n*-alkyl)thiophene that can be formed by metallation and subsequent alkylation of the reactive C-H bond on the 5-position of the 2-alkylthiophene. Performing a similar reaction in neat 2-methylthiophene corroborated this. The ^1H NMR spectrum of this polymer is shown in Figure 1b. The resonances of the furyl aromatic protons and the $\alpha\text{-CH}_2$ protons in this polymer correspond well to those of the small additional resonances seen in Figure 1a.

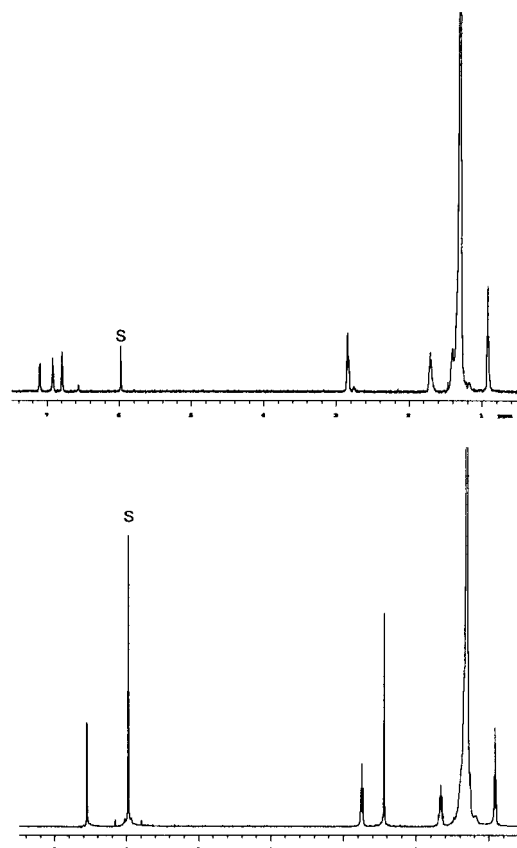


Figure 1. ^1H NMR spectra ($\text{C}_2\text{D}_2\text{Cl}_4$, 95°C) of (a, top) $\text{H}(\text{CH}_2\text{CH}_2)_n\text{-2-C}_4\text{H}_3\text{S}$ and (b, bottom) $\text{H}(\text{CH}_2\text{CH}_2)_n\text{-2-(5-Me-C}_4\text{H}_2\text{S)}$, prepared with catalyst **4b** in neat thiophene and 2-methylthiophene respectively.

The catalyst activity of **4b** is modest, but its catalyst stability is excellent. In neat thiophene at 80°C, 7.5 bar ethene pressure and a run time of 2 h the productivity is $27 \text{ kg mol}^{-1} \text{ h}^{-1}$, giving a low polymer with an M_n of 950 (by NMR). The activity and molecular weight can be increased by decreasing the concentration of thiophene. In a 10:90 volume% thiophene-toluene mixture under otherwise identical conditions the productivity of **4b** is $102 \text{ kg mol}^{-1} \text{ h}^{-1}$ of a polymer with an M_w of 3330 ($M_w/M_n = 2.0$, by GPC). This suggests there is noticeable inhibition of the reactivity by thiophene, probably by reversible coordination to the metal center. This appears to be corroborated by comparable experiments that are performed in neat thiophene and neat 2-methylthiophene. At 2.5 bar ethene pressure (80°C, 2 h run time) the productivity in thiophene ($5.0 \text{ kg mol}^{-1} \text{ h}^{-1}$) is half of that in 2-methylthiophene ($10.4 \text{ kg mol}^{-1} \text{ h}^{-1}$), but the product M_n is similar (700 vs 740). It is likely that the sterically more hindered 2-substituted thiophene is a less efficient inhibitor.

Zirconocene catalyst. In order to compare the reactivity of the neutral lanthanum catalyst with a representative of the well-known cationic group 4 metallocene olefin polymerization catalysts, we have performed some similar experiments with the $[\text{Cp}^*_2\text{ZrMe}][\text{MeB}(\text{C}_6\text{H}_5)_3]^{\delta}$ catalyst. In neat thiophene at 80°C and 2.5 bar ethene pressure (2 h run time) this system produced polyethene with an M_w of 12600 ($M_w/M_n = 2.4$ by GPC) and a productivity of 17 kg mol⁻¹ h⁻¹. ¹H NMR spectroscopy of this product showed predominantly olefinic end-groups, and only a small amount of thienyl end-capped chains. This suggests that with the zirconium catalyst used here, C-H activation cannot effectively compete with β-H transfer as chain transfer mechanism.

Conclusions

The cleavage of activated C-H bonds of thiophenes can be used as chain transfer mechanism in the catalytic polymerization of ethene by a lanthanocene catalyst. This yields polyethene (of a relatively low molecular weight) that is selectively capped on one end with a thienyl functionality. Thus far, only thiophene and substituted derivatives have been successful as chain-transfer agents, as pyridine and furan were found to be either too Lewis basic or too reactive, leading to catalyst deactivation. A first experiment using a cationic zirconocene catalyst revealed that this too can produce polyethene in neat thiophene, but in this case thiophene C-H activation cannot compete effectively with the usual route for chain transfer, β-H elimination.

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