Isospecific Living Polymerization of 1-Hexene by a Readily Available Nonmetallocene C2-Symmetrical Zirconium Catalyst

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The search for new α-olefin polymerization catalysts based on transition metal complexes is a field of major interest involving many academic and industrial research groups. The ligands surrounding the metal play a crucial role in determining the activity as well as the stereospecificity of the catalyst, by affecting the steric and electronic properties at the metal. Over the last two decades, this field has been dominated by the metallocene complexes of group IV metals. Especially, ansa-metallocenes of C2 symmetry were found to induce isospecificity in the resulting polymers.1 Recently, there has been a growing interest in the development of non-cyclopentadienyl ligands for the polymerization of α-olefins.2 Most attention was drawn to chelating di(amido) ligands,3 some of whose group IV transition metal complexes induce polymerization in a living manner,3a whereas chelating di(alkoxy) ligands4 drew a more limited attention. The number of nonmetallocene systems, which were found to induce tacticity in the resulting polymer, is, however, quite small.5 In this communication we introduce a novel family of di(alkoxy) complexes, one member of which is the first nonmetallocene C2-symmetrical complex, which, upon activation, leads to a highly isospecific living polymerization of 1-hexene.

Recently, we introduced the amine bis(phenolate) family of ligands to group IV transition metals.6 We found that the presence of an extra donor group on a sidearm leads to octahedral LigMX6-type complexes, in which the two labile X groups are forced into a cis geometry.6a Catalysts derived from these complexes (e.g. 1a) lead to highly reactive 1-hexene polymerization catalysts.6b

The C2-symmetry of 1a allows olefin approach from the two possible directions in each active position without preference, thus the polymer obtained is atactic. Therefore, we aimed at complexes of a different symmetry which may induce tactic polymerization, that incorporate ligands having similar functional groups yet having a different connectivity. Our approach is based on replacing the “branched” mode of connectivity of donor atoms with a sequential connectivity mode, namely diamine bis(phenolate) ligands.

This new family of dianionic tetradentate chelating ligands is easily synthesized by a one-pot Mannich condensation between readily available di(secondary) amines, formaldehyde, and substituted phenols as demonstrated in eq 2, a structural isomer of 1, was synthesized by mixing $N,N'$-dimethyl-ethylenediamine, 2 equiv of formaldehyde, and 2 equiv of 2,4-di-tert-butyl-phenol in methanol, and heating to reflux for 2 h. 2 precipitated as a colorless solid and was isolated in 70% yield.

Upon reaction with tetra(benzyl) zirconium, a sequential [ONN]2−type ligand may wrap around the metal to afford several possible isomers, as shown in Figure 1.
may result in either a C1- or a C2-symmetrical complex, and the
cis(Bn,Bn)-cis(O,O) mode,6 leading to C1-symmetrical complexes
(Figure 1). The preferred C2-symmetrical complex may induce
tacticity independently of polymeric chain rearrangement rate,10a
and may therefore be considered an ansa-metallocene analogue.1

2 reacted cleanly with 1 equiv of tetra(benzyl) zirconium at
65 °C yielding a single isomer of a dibenzyl zirconium complex
[ONNO]ZrBn2, 2a, quantitatively, as a yellow crystalline solid.
The spectral data of 2a indicated the formation of a C2-
symmetrical complex, evident from the symmetry-related phen-
olate rings, the symmetry-related benzyl groups, and the three
AX spin systems which appear for three CH2 units. The
crystallographic analysis indicated that 2a adopts the desired
cis(Bn,Bn) C2-symmetrical structure (Figure 2).

The asymmetric unit contains two homochiral molecules of
the slightly distorted octahedral complex, and three molecules
of toluene. The two nitrogen donors are in a cis configuration, as
expected, and the two oxygen atoms of the phenolate rings are
in a trans configuration. The cis configuration between the two
benzyl groups is evident from the C–Zr–C angle of 110.5°.

Upon activation with tris(pentafluorophenyl)borane, 2a was
found to be an active 1-hexene polymerization catalyst. The
addition of 32 μmol of 2a and 1.1 equiv of B(C6F5)3 to neat
1-hexene at room temperature yielded 300 mg of poly(1-hexene)
after 30 min, corresponding to an activity of 18 g mmolcat
−1-hexene at room temperature yielded 300 mg of poly(1-hexene)
and a PDI of 1.15. The narrow PDI
and the linear dependence of the polymer molecular weight on
the consumption of the monomer shown in Figure 3 suggest that
the polymerization system is living. Furthermore, six narrow
singlets in the 13C NMR indicate an isotactic 1-hexene
polymerization, affording >95% isotactic poly(1-hexene).11

Figure 2. Molecular structure of 2a exhibiting the C2 symmetry and
cis(Bn,Bn) geometry (one of two molecules in the asymmetric unit shown;
H atoms and phenyl groups omitted for clarity). See Supporting
Information for complete molecular structure.

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Supporting Information Available: Synthesis and characterization of
ligand precursors 2 and 3, complexes 2a and 3a, and poly(1-hexene);
crystal data, atomic coordinates and bond lengths and angles for 2a (PDF).
This material is available free of charge via the Internet at http://pubs.acs.org.

Figure 3. Dependence of polymer weight average molecular weight (Mw)
on consumption of monomer (mg) using 32 μmol of 2a and 1.1 equiv of
B(C6F5)3 in 10 mL of neat 1-hexene at room temperature and PDI values.

A possible source of this high isotacticity is the bulk of the
t-Bu groups which direct the approaching olefin (Figure 2). To
evaluate the effect of steric bulk on the tacticity, we synthesized
the ligand precursor 3 in a similar manner (eq 1). 3
was obtained by mixing N,N’-dimethyl-ethylenediamine, 2
equiv of formaldehyde, and 2 equiv of 2,4-dimethylphenol
in methanol, and heating to reflux for 2 h. 3 precipitated as a
colorless solid and was isolated in 50% yield.

3 also reacted cleanly with 1 equiv of tetra(benzyl) zirconium
at 65 °C yielding the dibenzyl complex [ONNO]ZrBn2, 3a,
quantitatively as a yellow crystalline solid. The spectral data of
3a indicated the formation of a single isomer having analogous
symmetry to 2a.

Upon activation with tris(pentafluorophenyl)borane, 3a exhibits
a somewhat higher activity in the polymerization of 1-hexene
relative to 2a at 35 g mmolcat−1 h−1, leading to a polymer having
a molecular weight of 23 000 and a PDI of Mw/Mn = 1.57.
In contrast to the polymer obtained from 2a, the polymer obtained
from 3a was atactic according to 13C NMR.11 Thus, the size of the
substituents was shown to have a significant influence on the
tacticity of the poly(1-hexene) produced using these C2-sym-
metrical [ONNO]Zr-type catalysts.

To the best of our knowledge, this novel [ONNO] system is the
first nonmetallocene C2-symmetrical system which is active
in isospecific and living polymerization of high-olifins.9,12
Furthermore, this is a rare example of living polymerization of
high-olifins at room temperature. The extreme ease of synthesis
of a variety of ligand precursors and the resulting metal complexes
make this new family of catalysts a potential alternative to the
well-established ansa-metallocene family. We are currently
studying the parameters responsible for the catalysts polymeri-
ization activity, as well as looking for further applications of this
ligand family.

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(11) See 13C NMR spectra of isotactic poly(1-hexene) derived from 2a and
atactic poly(1-hexene) derived from 3a in Supporting Information.
(12) 1- Octene was also polymerized by 2a/B(C6F5)3, yielding a highly
isospecific poly(1-octene).