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Living polymerization and block copolymerization of α-olefins by an amine bis(phenolate) titanium catalyst†

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An amine bis(phenolate) dibenzyl titanium complex having a methoxy donor on a side arm leads, upon activation with tris(pentafluorophenyl)borane, to unique living properties in α-olefin polymerization: exceptionally high molecular weight poly(1-hexene) is obtained in a living fashion at room temperature, living polymerization of 1-hexene is obtained above room temperature, and block copolymerization of 1-hexene and 1-octene at room temperature is described as well.

The quest for new α-olefin polymerization catalysts has involved many research groups for half a century. A recent addition to the arsenal of polymerization possibilities is the ability to produce polymers having narrow molecular weight distributions, and living polymerization processes. The vast majority of living processes are possible only below room temperature,[1] and the molecular weights of the polymers obtained in living processes are usually not very high. These systems are rarely utilized for block copolymerization of different monomers,[1c–e] since complete consumption of the monomer in a living fashion, followed by resumption of the polymerization process upon addition of the second monomer is difficult to achieve. Thus, all block copolymerization processes of α-olefins known to date are conducted below room temperature.

Recently, various Cp-free group IV metal complexes have been introduced as polymerization catalysts.[2] The most widely studied ligands are of the diamido type,[3] and one such system was the first to lead to living polymerization of α-olefins at room temperature.[1a] On the other hand, living polymerization involving alkoxo-type ligands[4] is quite rare.[1b,c] In this communication we introduce an amine bis(phenolate) titanium complex which, upon activation with tris(pentafluorophenyl)borane, leads to a polymerization process having unique living manifestations.

We recently introduced the amine bis(phenolate) group IV metal complexes and their application in α-olefin polymerization.[5–9] We revealed a unique effect of an extra donor arm in a titanium based catalyst on the complex reactivity and the termination/propagation rate ratio:[6] an [ONNO]-type complex was found to lead to living polymerization of 1-hexene, whereas an [ONO]-type complex led only to oligomerization of that monomer.

In our search for modified living catalysts of this family, we turned to a ligand having a side oxygen donor (Scheme 1).[9] We were interested in evaluating the effect of such a side donor, expected to bind strongly to the metal, on the living nature of a potential polymerization process. Furthermore, we wanted to explore the limits of the living process, in terms of polymerization time, molecular weight obtained, percentage of conversion and reaction temperature.

1 reacted cleanly with 1 mol equiv. of titanium tetra(isopropoxide) yielding the bis(isopropoxide) complex quantitatively. This complex was further reacted with 2 mol equiv. of chlorotrimethylsilane followed by reaction of the product with 2 mol equiv. of benzyl magnesium chloride, yielding the dibenzyl titanium complex **1a** in an overall yield of 95% (Scheme 1).

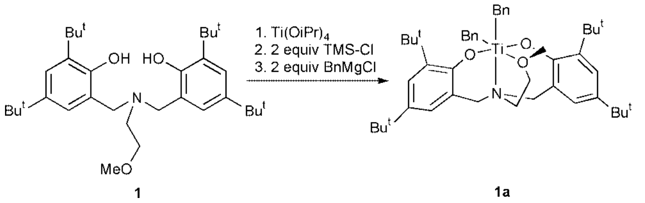
The ^{1}H NMR data are consistent with the formation of a C_s-symmetrical complex having two equivalent phenolate rings bound to the metal in a *trans* configuration, and two different benzyl groups bound in a *cis* configuration. The X-ray structure of **1a** (Fig. S1, ESI†) supported this notion, and indicated binding of the methoxy group to the titanium atom.‡

Upon activation with $B(C_6F_5)_3$, **1a** was found to be reactive in the polymerization of neat 1-hexene, exhibiting a reactivity of 20-35 g $mmol_{cat}^{-1}$ h^{-1}.§ The polymerization process induced by **1a** was found to be living for an exceptionally long time: as long as 31 hours, as expressed in the linearity of the molecular weight dependence on time (Fig. 1).[1a,e]

This system represents a rare example of living polymerization of α-olefins at room temperature.[1] Moreover, the long period at which the system remains living gives rise to a polymer having an exceptionally high molecular weight of M_w = 445 000 with a PDI of 1.12.

As this catalyst led to such a well-behaved polymerization at room temperature, it was interesting to find the temperature at which it lost its living nature. Increasing the reaction temperature to 40 °C in chlorobenzene resulted in a living process. The polymer obtained after 1 hour had a molecular weight of M_w = 16 000 with a PDI value of 1.14. Thus, this system gives rise to a rare living polymerization of α-olefins above room temperature. At 55 °C the PDI obtained was found to be 1.25 (M_w = 18 000 after one hour), and further broadening of the PDI to 1.30 (M_w = 22 000 after one hour) was obtained upon a temperature increase to 65 °C.

The most important application of living polymerization is in block copolymerization.[10] 16 μmol of **1a** were dissolved in 2.50 g of chlorobenzene, and 110 mol equiv. of 1-hexene were added. Activation with approximately 1 mol equiv. of $B(C_6F_5)_3$ dissolved in 2.50 g of chlorobenzene resulted in a living process characterized by a narrow PDI of 1.2. After 3.5 hours, complete consumption of the monomer was observed, and a polymer having a molecular weight of M_n = 9000 was obtained, supporting the polymerization of the 1-hexene employed in a living fashion (expected M_w = 9400). To further ascertain the complete consumption of the first monomer, the second monomer (1-octene) was added only after a 1.5 hours delay period (Fig. 2), resulting in resumption of the polymerization process. Stopping the polymerization after an additional 3 hours



Scheme 1

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† Electronic supplementary information (ESI) available: Fig. S1: molecular structure of **1a**. Preparation and characterization data for **1a**. Crystallographic data for **1a**. See http://www.rsc.org/suppdata/cc/b1/b105492a/

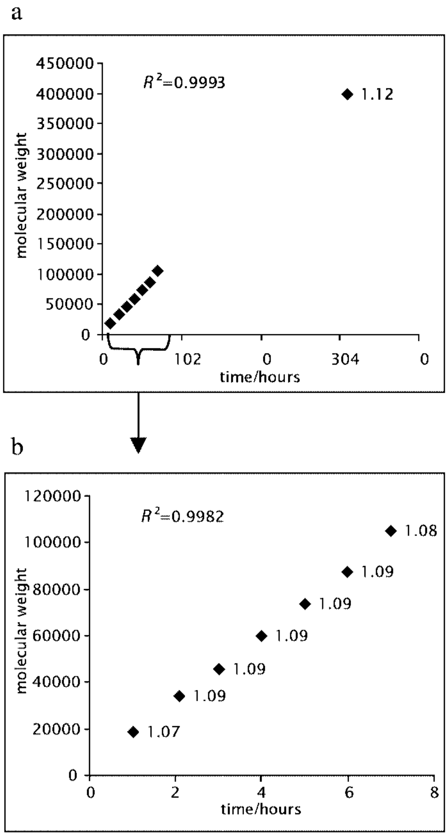

Fig. 1 Dependence of the number average molecular weight (M_n) on time (hours) using 20 mg of **1a** and 1.1 mol equiv. of $B(C_6F_5)_3$ in 30 mL of neat 1-hexene at RT and PDI values. (a) 31 hours of reaction, (b) first 7 hours of reaction.

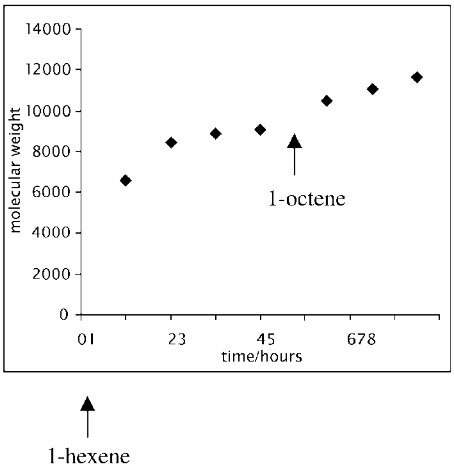

Fig. 2 Dependence of the number average molecular weight (M_n) on time (hours) in the block copolymerization of 1-hexene and 1-octene using **1a**.

yielded poly(1-hexene-block-1-octene) having M_n = 11 600 and PDI of 1.2. A ^{13}C NMR spectrum of the resulting polymer supported its assignment as an atactic copolymer of 1-hexene and 1-octene. This is a rare example of block copolymerization of α-olefins conducted at room temperature.

In summary, we present a catalytic system for polymerization of α-olefins that exhibits several unique living properties. When conducted at room temperature, the polymerization of neat 1-hexene is practically ‘immortal’. Even when the reaction is allowed to stand for days, the only cause of loss of ‘life’ is the increased viscosity of the polymerization mixture. Thus, very high molecular weights may be obtained with extremely narrow PDI values. A solution of the monomer in chlorobenzene (diluted to enable its complete consumption) was employed for block copolymerization of α-olefins to give a di-block of homopolymers, at room temperature. We are currently studying related systems and the polymerization mechanism by which they operate.

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Notes and references

‡ CCDC reference number 166843. See http://www.rsc.org/suppdata/cc/b1/b105492a/ for crystallographic data in CIF or other electronic format.

§ In a typical polymerization of neat 1-hexene, 14 mg of **1a** (19 μmol) were added to 10.0 mL of neat 1-hexene and activated with 1 equiv. of $B(C_6F_5)_3$ at room temperature. The reaction was followed by taking 0.50 mL aliquots, weighing out the non-volatile residue, and analyzing it by GPC relative to polystyrene standards. This analysis indicated a linear consumption of the monomer and linear rise in molecular weight. A sample taken after 150 min showed a reactivity of 23.5 g $mmol_{cat}^{-1}$ h^{-1}, consistent with a TOF of 280 h^{-1}, giving an expected molecular weight of 58 800. The GPC analysis gave M_w = 55 600, M_n = 50 200, and PDI = 1.11. In a typical polymerization of dilute 1-hexene, 31 mg of **1a** (42 μmol) and 27 mg of $B(C_6F_5)_3$ were added to 502 mg of 1-hexene in 5.00 g of chlorobenzene at room temperature. A sample taken after 160 min indicated that all the monomer had been consumed. The expected molecular weight is 12 000. The GPC analysis gave M_w = 11700, M_n= 10 200 and PDI = 1.15. Occasionally, the weight of the obtained polymer was found to be lower than expected, probably due to incomplete catalyst activation, however, the TOFs were consistent with the values specified above.

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