# Alternating stereospecific copolymerization of cyclopentene and ethylene with constrained geometry catalysts†

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**The stereoselective copolymerization of cyclopentene (cP) and ethylene (E) to generate highly alternating polymers with isotactic *cis* 1,2-cyclopentene enchainment is reported.**

Single-component olefin polymerization catalysts have provided new opportunities for the synthesis of novel polymer structures from common olefin feedstocks;[1] for these opportunities to be fully realized, control of composition, sequence distribution and stereochemistry is required. Cyclo-olefin copolymers (COCs) have been recently targeted as a new class of engineering resins.[2–7] The properties of these copolymers depend not only on the type of cycloolefin, but the composition and sequence distribution of comonomers in the chain. Random ethylene–cyclo-olefin copolymers are amorphous glasses with a range of glass-transition temperatures, good thermal stability and chemical resistance. Highly alternating isotactic ethylene–norbornene copolymers exhibit melting points up to 295 °C![2,8,9] Natta was the first to report the alternating copolymerization of ethylene and cyclopentene with vanadium catalysts.[10,11] Natta recognized that alternating copolymers were accessible due to the inability of most coordination catalysts to homopolymerize cyclopentene. Fractionation of the ethylene–cyclopentene copolymers with boiling solvents yielded a highly crystalline fraction with a melting point of 185 °C, implicating a stereoregular microstructure for these copolymers.[10] Coates and coworkers recently prepared and assigned the isotactic alternating ethylene–cyclopentene copolymer by an indirect route involving stereoselective ring-opening metathesis followed by hydrogenation;[12] the observation of a melting point of 185 °C corroborates Natta's assignment of this copolymer as the erythro-diisotactic alternating E–cP copolymer. In this communication we report the direct synthesis of the alternating isotactic ethylene–cyclopentene copolymer with a chiral constrained geometry catalyst.

Our initial attempts to prepare isotactic alternating ethylene–cyclopentene copolymers with chiral zirconocenes were unsuccessful due to competitive 1,2-[13] and 1,3-enchainment[14,15] of cyclopentene at high cyclopentene incorporations.[16,17] The lower tendency of constrained geometry catalysts (CGC) toward β-H elimination prompted us to investigate these precursors for ethylene–cyclopentene copolymerization.

The copolymerization of ethylene and cyclopentene was carried out in liquid cyclopentene at 25 and 60 °C with the complexes [Me$_2$Si(4-MeCp)(N$^t$Bu)]TiCl$_2$ and [Me$_2$Si(Ind)(N$^t$Bu)]TiCl$_2$ (Fig. 1) with MMAO; results are summarized in Table 1. In the absence of ethylene, we observed no cyclopentene homopolymerization under these conditions. Low overpressures of ethylene were introduced either by pressurizing with argon–ethylene mixtures or pure ethylene (Table 1); these conditions were necessary in order to access cyclopentene (cP) mole fractions close to 0.5 compositions.

The productivities of these copolymerizations are modest, but are several orders of magnitude higher than that reported for the bis(phenoxyimine)titanium precursors.[12] The productivities increase markedly with increasing amounts of ethylene in the feed (entries 1 *vs.* 5, Table 1), with a corresponding decrease in the incorporation of cyclopentene. Molecular weights ranged from $M_n$ = 4 600 to 72 000 with molecular weight distributions close to $M_w/M_n$ = 2.0.

Shown in Fig. 2 is the $^{13}$C NMR spectrum of the bulk copolymer (Table 1 entry 2) that was prepared with [Me$_2$Si-(Me$_4$Cp)(N$^t$Bu)]TiCl$_2$. Integration of resonances corresponding to C$_2$ between 42.0 and 44.0 ppm with those of between 28.0 and 30.0 ppm (corresponding to C$_1$, C$_\alpha$, and C$_\beta$, etc.) indicated that this polymer contains 40 mol % cyclopentene.[12,16] The presence of multiple resonances for the C$_2$ and C$_3$ carbons is indicative of an atactic but highly regioregular microstructure comprised of only 1,2-enchained cyclopentene units.[12,16] Thus, the constrained geometry catalysts are much more highly regioselective than the zirconocenes and allow for the synthesis
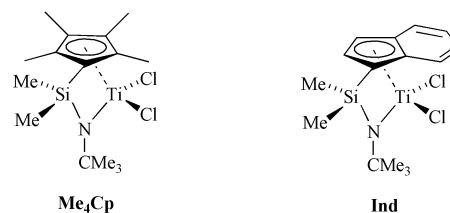


**Fig. 1** Constrained geometry pre-catalysts which were applied to the copolymerization of cyclopentene and ethylene.

**Table 1** Ethylene–cyclopentene copolymerization with [Me$_2$Si(Me$_4$Cp)(N$^t$Bu)]TiCl$_2$ (Me$_4$Cp) and [Me$_2$Si(Ind)(N$^t$Bu)]TiCl$_2$ (Ind) with MMAO

| Entry | Precat. | [Ti] (M × 10⁻⁴) | Rxn time/h | P/psi | $T_p$/°C | E:Ar ratio[a] | Yield/g | Prod[b] [kg/ (mol Ti · h)] | % cP[c] | $T_g$/°C | $T_m$/°C | $M_w/M_n$ | $M_n$[d] (g mol⁻¹ × 10⁻³) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Ind | 4.2 | 1.5 | 20 | 25 | 1:6 | 0.49 | 39 | 50 | 16.3 | 182.5 | 1.9 | 33.9 |
| 2 | Me$_4$Cp | 5.2 | 4.0 | 20 | 25 | 1:6 | 0.43 | 10 | 40 | −21.8 | 127.2 | 2.2 | 8.3 |
| 3 | Ind | 4.1 | 1.5 | 20 | 60 | 1:6 | 0.31 | 25 | 49 | 23.5 | 174.8 | 2.7 | 4.6 |
| 4 | Me$_4$Cp | 5.2 | 4.0 | 20 | 60 | 1:6 | 0.72 | 17 | 34 | −18.4 | 100.0 | 2.2 | 7.5 |
| 5 | Ind | 4.1 | 1.5 | 20 | 25 | 1:0 | 2.91 | 234 | 41 | 5.5 | 122.7 | 1.7 | 71.7 |
| 6 | Me$_4$Cp | 5.2 | 1.0 | 20 | 25 | 1:0 | 2.32 | 225 | 15 | −27.0 | 72.3 | 2.7 | 5.6 |

[a] E = ethylene; Cp = cyclopentene; Ar = argon. [b] Precat. **IND** = IndSi(Me$_2$)(tBuN)TiCl$_2$. Precat. **Me$_4$Cp** = Me$_4$CpSi(Me2)(tBuN)TiCl$_2$. [c] Determined by integration of the respective $^{13}$C NMR resonances. For all experiments the ratio of Ti:MMAO was 1:400–500 molar equivalents. [d] GPC molecular weights and polydispersities *vs.* polystyrene standards.
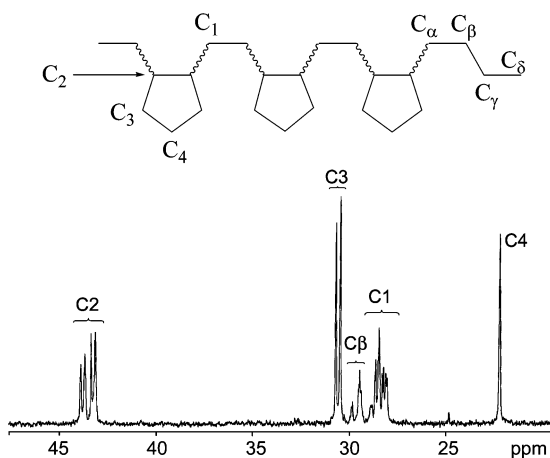
**Fig. 2** ^{13}C NMR spectrum of the atactic poly(*cis*-cP-*alt*-E) prepared with [Me$_2$Si(Me$_4$Cp)(N$^t$Bu)]TiCl$_2$.

of regioregular alternating ethylene–cyclopentene copolymers. The 1,3-enchainment of cyclopentene is known to occur with both zirconocenes[14,16,17] as well as late-metal catalysts[18] and has been attributed to the isomerization of the last-inserted cyclopentene unit by a β-H elimination–reinsertion process (Scheme 1). We attribute the high regioselectivity to the lower tendency of the titanium CGC's to undergo β-H elimination; this is consistent with the observation by Coates and coworkers that the bis(phenoxyimine)titanium complexes also exhibit high regioselectivities for 1,2-enchainment of cyclopentene.
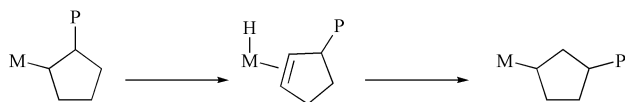


**Scheme 1** Isomerization mechanism for the generation of 1,3-enchained cP units.

Remarkably, the chiral indenyl CGC complex [Me$_2$-Si(Ind)(N$^t$Bu)]TiCl$_2$ was able to induce the stereospecific alternating copolymerization of ethylene and cyclopentene. The remarkably simple ^{13}C NMR spectrum in Fig. 3 (Table 1, entry 1) can be assigned as the alternating isotactic ethylene–cyclopentene copolymer on the basis of the model polymers reported by Coates.[12] The small resonance at ~30.0 ppm is assigned to residual E–E sequences; we found no evidence for cP–cP diads.[18] This material is crystalline (ΔH$_f$ = 36 J g$^{-1}$) and exhibits multiple melting points at 176 and 183 °C and a T$_g$ of 16 °C, consistent with data reported by Natta and Coates.[10,12]
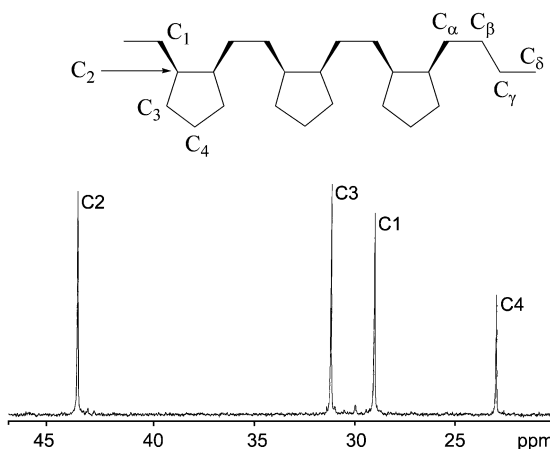


**Fig. 3** ^{13}C NMR spectrum of alternating isotactic poly(*cis*-cP-*alt*-E) prepared with [Me$_2$Si(Ind)(N$^t$Bu)]TiCl$_2$.

These high stereospecificities are preserved even at elevated temperatures; the 49% copolymer obtained at 60 °C with the indenyl catalyst was highly stereoregular, melting at 175 °C.

The stereospecific copolymerization of cyclopentene and ethylene is noteworthy in light of our previous observations that the chiral complex [Me$_2$Si(Ind)(N$^t$Bu)]TiCl$_2$ is both poorly regioselective and stereoselective for propylene polymerization.[19] While the origin of the stereoselectivity is not clear at present, we believe a chain-end control mechanism is unlikely given that the last inserted monomer unit is an ethylene. This indenyl metallocene possesses two heterotopic coordination sites; it is possible that the alternating stereospecific copolymerization of ethylene and cyclopentene occurs by a dual-site mechanism where ethylene inserts at one of the two heterotopic coordination sites and cyclopentene inserts at the other. Similar mechanisms have been proposed for ethylene–α-olefin[20–22] and ethylene–norbornene copolymerizations with C$_1$-symmetric metallocenes.[2,5] A dual-site mechanism is unnecessary to explain the tendency of the two monomers to alternate (a first order Markov single-site mechanism is sufficient with $r_2$ ~ 0);[23] nevertheless the fact that cyclopentene inserts stereospecifically suggests that cyclopentene insertion occurs at only one of the two coordination sites. Further studies are underway to illuminate the origin of these highly regio-, stereo- and sequence-selective copolymerization reactions.

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