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# Copolymerization of ethylene with α-olefins and cyclic olefins catalyzed by a Ti(IV) diisopropoxy complex bearing a tridentate [O⁻,S,O⁻]-type bis(phenolato) ligand†

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Ethylene (E) was copolymerized with some α-olefins [1-pentene (PEN), 1-hexene (HEX), and 4-methyl-1-pentene (4M1P)] and cyclic olefins [cyclopentene (CPE), norbornene (NB), and dicyclopentadiene (DCPD)] using the Ti(IV) thiobis(phenolate) complex $[2,2'\text{-}S(4\text{-Me},6\text{-}t\text{BuC}_6\text{H}_2\text{O})_2]\text{Ti(OiPr)}_2$ in combination with methylaluminoxane (MAO). The catalyst exhibited excellent activities (up to $10^6$ g $\text{mol}_{\text{Ti}}^{-1}$ $\text{h}^{-1}$). Crystalline E/α-olefin copolymers with a strong tendency for comonomer alternation were obtained with good comonomer incorporation (about 15 mol% for [Y]/[E] = 8; Y = comonomer) decreasing in the order HEX > PEN > 4M1P. Random copolymers with NB and DCPD were obtained with efficient comonomer incorporation (from 10 to 40 mol%) even for the Y/E molar ratio = 1 to 2, while the catalyst gave poor CPE incorporation. In order to collect information on the comonomer distribution in the copolymers, boiling solvent extraction was carried out and all the fractions were characterized by DSC, XRD, SEC, and NMR.

## Introduction

Ethylene copolymers with α-olefins and cyclic olefins are commercial synthetic plastics whose properties make them part of our everyday life.[1–3] The key to the successful manufacturing of such polymers has been the development of transition metal catalytic systems.[4] A major breakthrough in homogeneous olefin polymerization catalysis was the discovery of Group 4 metallocenes.[5] Successively systematic work has conceived post-metallocene complexes, including bridged- and half-metallocenes, half-titanocenes containing amide ligands such as $[\text{Me}_2\text{Si(C}_5\text{Me}_4)(\text{N}t\text{Bu})]\text{TiCl}_2$ (Constrained Geometry Catalysts),[6] anionic donor ligands of the type (Cp)MX$_2$(Y) (ref. 7) (Cp = cyclopentadienyl; M = Ti, Zr, Hf; X= halogen, alkyl; Y = anionic donor ligands such as aryloxo,[8] ketimide,[9] phosphinimide,[10] iminoimidazolidide[11]) and Cp-free multidentate ligands bearing coordinating heteroatoms,[12] *i.e.*, [O⁻SO⁻]–,[13] [O⁻SSO⁻]–,[14] [O⁻OO⁻]–,[15] [N⁻NN⁻]–,[16] [O⁻NXR]–,[17] (X = O, S, Se, P; R = alkyl or cycloalkyl). Such complexes are emerging as a new class of catalysts for the polymerization of olefins to achieve high performance in terms of activity and control of microstructure (stereoregularity, regioregularity and comonomer distribution), resulting in a new type of polymers and block copolymers for functional applications.

In particular, Group 4 complexes of chelating bis(phenolate) ligands in which the two phenolates are bridged by a sulfur donor atom,[13] or in which the two phenoxides are linked to two sulfur donors in the *ortho*- or benzyl-positions,[14] are receiving considerable attention. Such ligands are versatile in view of a large variety of possible substituents for the two phenolates, from which the electronic and steric properties of the resultant copolymers may be finely tuned. In addition, the bridging sulfur, if coordinated, provides a stereochemically rigid framework fundamental for the synthesis of stereoregular polymers. If aryloxides do not contribute sufficient electron density to be isolobal with Cp-ligands, thiobis(phenolate), in which the two phenol rings are joined in the *ortho* position by sulfur, provides an increased stabilisation of the electron-deficient metal. Indeed, although sulfur is a soft-donor atom that weakly binds to the metal {structural data for $[\text{Ti}_2(\mu\text{-X})_2\text{X}_2(\text{tbmp-}\kappa^3\text{O,S,O})_2]$ complexes showed long Ti–S distances [2.664 Å, X= Cl; 2.724 Å, X = OiPr; tbmp = $2,2'\text{-}S(4\text{-Me},6\text{-}t\text{BuC}_6\text{H}_2\text{O})_2$]},[18] it is likely to be of importance in stabilizing the active cationic species [Ti(tbmp-

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† Electronic supplementary information (ESI) available: Details of the E/4M1P copolymerizations by $C_s$-Me$_2$C(Cp)(9-Fluo)ZrCl$_2$–MAO (Table S1†), and of the boiling solvent fractionation of the E/PEN and E/CPE copolymers (Table S2†). DSC of the E/NB copolymers and boiling solvent extraction fractions (Fig. S1 and S5) and E/HEX copolymer and boiling solvent extraction fractions (Fig. S3). XRD of the ether-, THF-soluble, and residue fraction of the E/HEX copolymer (Fig. S2). $^{13}$C NMR spectra of the E/NB copolymers and boiling solvent extraction fractions (Fig. S4). See DOI: 10.1039/c3py01674a

$\kappa^3$O,S,O)Me]$^+$, and making the coordination of the counterion less tight.[19] When activated with MAO, (tbmp)Ti$X_2$ (X = Cl, OiPr) complexes were found to be (i) highly active for the polymerization of ethylene, propylene and copolymerization with styrene, much more than the 8-electron methyl-bridged (mbmp) Ti$X_2$ [mbmp = 2,2′-$CH_2$(4-Me,6-*t*Bu$C_6H_2O$)$_2$] and 2,2′-diphenolate analogues,[20] and (ii) syndiospecific catalysts for the polymerization of styrene to give syndiotactic poly(styrene)s, exhibiting melting temperatures mostly above 270 °C.[21]

Nonetheless, the full potential of titanium thiobis(phenolate) complexes for the copolymerization of various olefins is not explored yet. In this work, we report for the first time on ethylene copolymerization with some α-olefins and cyclic olefins by a (tbmp)Ti(OiPr)$_2$ (**1**)–MAO catalyst. Moreover, copolymerizations of ethylene with 4M1P by $C_s$-$Me_2C$(Cp)(9-Fluo)$ZrCl_2$–MAO are also included and the results are discussed on the basis of microstructural analysis and reactivity ratios by examining similarities and differences with respect to **1**–MAO and data reported with other efficient Group 4 complexes such as $C_2$-[*rac*-$H_2C$-(3-*t*BuInd)$_2ZrCl_2$],[22a] CGC,[22b] and Cp*$TiCl_2$(*O*-2,6-iPr$_2C_6H_3$).[23]

## Experimental section

### Materials

All manipulations of air- and/or moisture-sensitive materials were carried out under an inert atmosphere using a dual vacuum/nitrogen line and the standard Schlenk-line techniques. Toluene (Fluka, >99.5% pure) was refluxed over Na for *ca.* 8 h and then distilled and stored over molecular sieves under nitrogen. MAO (Aldrich, 10 wt% solution in toluene), Ti(OiPr)$_4$ (Aldrich, 97%) and 2-*t*-butyl-6-(3-*t*-butyl-2-hydroxy-5-methylphenyl)sulfanyl-4-methylphenol (Irganox 1081, Ciba-Geigy) were used as received. Solid MAO (d-MAO) was prepared by removing toluene and unreacted free-trimethylaluminum ($Al(CH_3)_3$) under vacuum from the commercially available MAO solution. The resulting white powder was heated further to 60 °C under vacuum to a constant weight. A stock solution was then prepared by dissolving 500 mg of d-MAO in 5.4 mL of toluene (92 mg mL$^{-1}$). PEN, HEX, 4M1P and CPE (Aldrich, ≥99% pure) were refluxed over $CaH_2$ for about 2 hours, then distilled trap-to trap. NB (Aldrich, 99% pure) was stirred over molten potassium at 80 °C under nitrogen for 4 h and then distilled. A stock solution was prepared by dissolving 50 g of freshly distilled NB in 86.21 mL of toluene (0.58 mg mL$^{-1}$). Cyclopentadiene dimer (Fluka, ~90% pure) was heated at 150 °C, and the fraction boiling at 40 °C was collected and kept at −78 °C. Ethylene was purified by flowing through BTS catalysts, molecular sieves, and $CaCl_2$. The deuterated solvent for NMR measurements ($C_2D_2Cl_4$) (Cambridge Isotope Laboratories, Inc.) was used as received. Complex **1** was synthesized according to the procedure reported by one of the authors.[18a]

### Polymerization procedure

The experiments were carried out in a 50 mL round-bottomed Schlenk flask containing a stirring bar. The polymerization reactor was first dried by heating at 110 °C and then vacuum was applied for 1 h at 40 °C. The reactor vessel was charged with toluene and the comonomer and brought to the desired polymerization temperature. MAO was added, and the solution was degassed and saturated with ethylene under vigorous stirring for 10 min. The polymerization was started by adding a solution of the titanium compound under a continuous flow of ethylene. Polymerizations were stopped with methanol containing a small amount of hydrochloric acid; the precipitated polymers were collected by filtration, repeatedly washed with fresh methanol and finally dried in vacuum at room temperature to a constant weight.

### E/4M1P copolymerization by $Me_2C$(Cp)(9-Fluo)$ZrCl_2$

The copolymerizations were performed at 45 °C, in a 300 mL glass reactor equipped with a magnetic stirrer and an inlet tube for the bubbling of the gaseous comonomer. The reactor was filled with toluene, 4M1P, and MAO. After the thermal equilibration of the reactor system, ethylene was continuously added until saturation. The polymerization was started by adding a solution of the zirconium compound under a continuous flow of ethylene.

### Polymer characterization

For $^{13}$C NMR, about 100 mg of the copolymer was dissolved in $C_2D_2Cl_4$ in a 10 mm tube. HDMS (hexamethyldisiloxane) was used as the internal chemical shift reference. The spectra were recorded on a Bruker NMR AVANCE 400 Spectrometer equipped with a SEX 10 mm probe with automatic matching and tuning, operating at 100.58 MHz ($^{13}$C) in the PFT mode working at 103 °C. The applied conditions were the following: 10 mm probe, 14.30 μs as 90° pulse angle; 64 K data points; acquisition time 5.56 s; relaxation delay 20 s; 3–4 K transient. Proton broadband decoupling was achieved with a 1D sequence using bi_waltz_16_32 power-gated decoupling. Differential scanning calorimetry (DSC) scans were carried out on a Perkin-Elmer Pyris 1 instrument equipped with a liquid subambient device under a helium atmosphere. The sample, typically 5 mg, was placed in a sealed aluminum pan, and the measurement was carried out from −80 to 150 °C using a heating and cooling rate of 20 °C min$^{-1}$. $M_w$s and $M_w/M_n$s were obtained by a high temperature Waters GPCV2000 size exclusion chromatography (SEC) system using two online detectors: a differential viscometer and a refractometer. The experimental conditions consisted of three PL Gel Olexis columns, *o*-dichlorobenzene as the mobile phase, 0.8 mL min$^{-1}$ flow rate, and 145 °C temperature. Calibration of the SEC system was carried out using eighteen narrow $M_w/M_n$ poly(styrene) standards with molar weights ranging from 162 to 5.6 × $10^6$ g mol$^{-1}$. For SEC analysis, about 12 mg of polymer was dissolved in 5 mL of *o*-DCB with 0.05% of BHT as an antioxidant. Wide-angle X-ray diffraction data (XRD) were obtained at 25 °C using a Siemens D-500 diffractometer (Cu Kα radiation, $\lambda$ = 0.154 nm). The operating voltage and current were 40 kV and 40 mA, respectively. Data were collected from 1 to 30° 2$\theta$ at 0.02° 2$\theta$ intervals.

The α-olefin content in the copolymer was determined through $^{13}$C NMR.[24] The CPE and NB content in the copolymers was calculated according to Müiller[25a] and Tritto,[25b] respectively. The composition of the copolymers E/DCPD was determined through $^1H$ NMR.[26]

## Results and discussion

Catalyst **1**/MAO displayed good activity toward the polymerization of ethylene at 50 °C (Table 1, run 1, 1900 kg $mol_{Ti}^{-1}$ $h^{-1}$), producing low molecular weight PE ($M_w$ = 13 000 g $mol^{-1}$, $M_w/M_n = 2.6$) with a $T_m$ of 127 °C. The productivity of **1**/MAO is comparable to that reported by Schaverien *et al.* for the catalyst (tbmp)$TiCl_2$/MAO (4740 kg $mol_{Ti}^{-1}$ $h^{-1}$ at 3 bar of ethylene pressure).[27] When activated with $AlMe_3$-free MAO, complex **1** yields 0.6 g of PE in 5 minutes, which corresponds to a productivity of 600 kg $mol_{Ti}^{-1}$ $h^{-1}$. The activity of **1**/MAO in the polymerization of PEN, HEX and 4M1P was very low and an oil, hardly precipitated by addition of methanol, was obtained. In contrast, **1** was not active toward the polymerization of CPE and DCPD, while the polymerization of NB gave solid powder oligomers with an activity of 20 kg $mol_{Ti}^{-1}$ $h^{-1}$.

### Copolymerization of ethylene with PEN, HEX, and 4M1P

Copolymerizations were carried out at 50 °C in toluene at the atmospheric pressure of ethylene. Different comonomer composition feedings were investigated [Y/E molar ratio from 2 to 8 (Y = comonomer)]. The results are summarized in Table 1.

The catalyst exhibited remarkable activity toward the E/α-olefin copolymerizations, producing copolymers with $M_w$s ranging from 15 000 to 33 000 g $mol^{-1}$, and $M_w/M_n$s in the range of 2.5–3.1. The activities were not strongly affected by the Y/E molar ratio but the $M_w$ values were somewhat sensitive to the comonomer content in the copolymers. Comonomer incorporation in the copolymers increased upon increasing the comonomer feed concentration and, under the same conditions at a Y/E molar ratio of 8.1, it decreased in the order HEX (run 7, 13.1 mol%) > PEN (run 4, 11.5 mol%) > 4M1P (run 10, 6.7 mol%). Incorporation of 4M1P as high as 20.3 mol% was achieved by using a large excess of 4M1P (run 11, 4M1P = 1.56 mol $L^{-1}$, 4M1P/E = 16). Compared to some Cp-free Ti(IV) complexes bearing multi-dentate ligands, the pre-catalyst **1** exhibited less efficient HEX incorporation than the β-carbonylenamine $[O^-NS]TiCl_3$ complex,[28] probably due to the much less open space around the Ti atom and also than to the phenoxyimine $[O^-NX]TiCl_3$ bearing S- or Se-donors as X sidearms, while it showed roughly the same HEX incorporation as the same complex with the O-donor.[29]

Fig. 1a shows the spectrum of a selected E/PEN copolymer (run 4, PEN = 11.5 mol%).[30] The copolymer resonances were assigned through comparison with those of the spectra reported by Galland for such a copolymer obtained with *rac*-Et(Ind)$_2$ZrCl$_2$ (PEN = 6.5 mol%).[32] In addition to resonances ascribed to the isolated PEN unit at 18.07 and 12.51 ppm, we detected a ββ methylene resonance at 22.22 ppm due to the alternating EYEYE pentad, and signals at 17.91 and 12.55 ppm assigned to the YYE triad centred on the $2B_3$ and $1B_3$ carbon atoms of the PEN side chain,[31] respectively. Fig. 1b shows the spectrum of a selected E/HEX copolymer (run 7, HEX = 13.1 mol%). The copolymer resonances were assigned according to Randall.[33] Fig. 2a shows the spectrum of a selected E/4M1P copolymer (run 11, 4M1P = 20.3 mol%). Methyl, methylene and methine carbons in the side chains were designated by the symbols $CH_3$(sc), $CH_2$(sc) and CH(sc) (C, B, and A in Fig. 2, respectively).[34] Copolymer resonances were assigned according to those reported by one of the authors.[35] Besides the characteristic signal at 42.50 ppm, corresponding to the EYE triad (centred on the $CH_2$ of the side chain), two diagnostic resonances at 21.80 and 24.54 ppm were detected and assigned to the ββ methylene carbons belonging to the completely alternating EYEYE and YYEYZ (Z means Y or E) pentads, respectively.

Table 2 reports monomer sequence (diad and triad) distributions calculated from the $^{13}C$ NMR analysis. All the copolymers had a relatively high percentage of EYE and YEY triads,

Table 1 Copolymerization of ethylene with α-olefins by 1/MAO[a]

| Run | Y (Conc./M) | [Y]/[E][b] | Time (min) | Yield (mg) | Activity[c] | $Y^d$ (%mol) | $M_w^e \times 10^{-4}$ | $M_w/M_n^e$ | $T_m/(T_g)^f$ (°C) | $\Delta H_m^f$ (J $g^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | | 5 | 475 | 1900 | | 1.3 | 2.6 | 127 | 245 |
| 2 | PEN (0.20) | 2.1 | 5 | 615 | 2460 | 4.0 | 2.3 | 2.9 | 116/113/102 | 134 |
| 3 | PEN (0.56) | 5.8 | 5 | 655 | 2620 | 8.0 | 2.6 | 2.6 | 104/100/77 | 62 |
| 4 | PEN (0.78) | 8.1 | 5 | 440 | 1760 | 11.5 | 2.0 | 2.9 | 101/97/68 | 41 |
| 5 | HEX (0.20) | 2.1 | 5 | 580 | 2320 | 3.7 | 2.2 | 2.6 | 115/112/105 | 154 |
| 6 | HEX (0.56) | 5.8 | 5 | 548 | 2192 | 8.1 | 2.3 | 2.5 | 104/100/80 | 69 |
| 7 | HEX (0.78) | 8.1 | 5 | 710 | 2840 | 13.1 | 1.5 | 2.6 | 97/92/57 | 21 |
| 8 | 4M1P (0.20) | 2.1 | 5 | 559 | 2236 | 2.5 | 2.3 | 2.9 | 121/119/111 | 163 |
| 9 | 4M1P (0.56) | 5.8 | 5 | 650 | 2600 | 5.9 | 3.1 | 2.7 | 109/105/93 | 101 |
| 10 | 4M1P (0.78) | 8.1 | 5 | 545 | 2180 | 6.7 | 2.4 | 2.8 | 104/99/84 | 92 |
| 11 | 4M1P (1.56) | 16.0 | 5 | 787 | 3120 | 20.3 | 1.0 | 2.6 | 83/57 (−54) | 6 |
| 12 | 4M1P (0.56) | 5.8 | 16 | 1070 | 1338 | 5.9 | 3.3 | 3.1 | 111/108/95 | 86 |

[a] Polymerization conditions: **1**, 3 μmol; Al/Ti, 1000; toluene, total volume 25 mL; temperature, 50 °C; ethylene pressure, 1.01 bar. [b] [Y]/[E] feed ratio (mol $mol^{-1}$) in the liquid phase. [c] Activity in $kg_{polymer}$ $mol_{Ti}^{-1}$ $h^{-1}$. [d] Comonomer content in the copolymer. [e] Molecular weight ($M_w$ in g $mol^{-1}$) and molecular weight distribution ($M_w/M_n$) by SEC in *ortho*-dichlorobenzene *vs.* poly(styrene) standard. [f] Melting temperature ($T_m$), glass transition temperature ($T_g$), and melting enthalpy ($\Delta H_m$) by a DSC second heating scan.

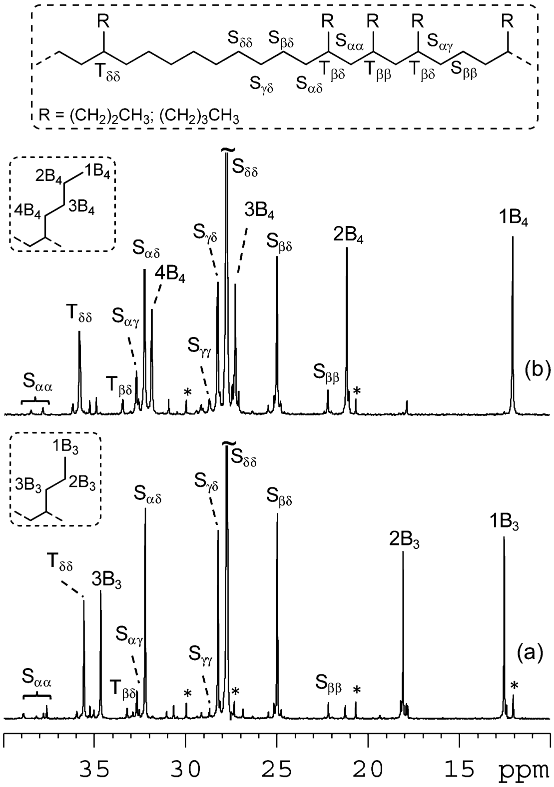

Fig. 1 $^{13}$C NMR spectra (in $C_2D_2Cl_4$ at 103 °C) of (a) E/PEN copolymer (run 4, PEN = 11.5 mol%) and (b) E/HEX copolymer (run 7, HEX = 13.1 mol%).

and the reactivity ratio product ($r_Er_Y$) values calculated from diads[36] were lower than 1, which is indicative of a rather alternating distribution of the comonomers. This result for the pre-catalyst **1** is reminiscent of that observed for $C_s$-symmetric metallocenes[5] and amine bis(phenolate) zirconium dibenzyl complexes[2g] in the E/HEX copolymerization. In contrast, ethylene copolymerization with branched 4M1P catalyzed by $C_s$-symmetric metallocenes has not been reported so far and highly alternating E/4M1P copolymers were only obtained with Cp*TiCl$_2$(*O*-2,6-iPr$_2$C$_6$H$_3$).[23] In view of this point, we copolymerized ethylene with 4M1P with the $C_s$-Me$_2$C(Cp)(9-Fluo)ZrCl$_2$ complex to examine similarities and differences with respect to pre-catalyst **1** and Cp*TiCl$_2$(*O*-2,6-iPr$_2$C$_6$H$_3$). Two copolymers produced with $C_s$-Me$_2$C(Cp)(9-Fluo)ZrCl$_2$ were selected. The samples contained 17.0 and 30.9 mol% of 4M1P, respectively (Table 3 and S1†). Fig. 2b shows the $^{13}$C NMR spectra of the E/4M1P copolymer given by Me$_2$C(Cp)(9-Fluo)ZrCl$_2$ and, for comparison, the spectra of the copolymers obtained with $C_2$-[*rac*-H$_2$C-(3-*t*BuInd)$_2$ZrCl$_2$] (ref. 22a) (Fig. 2c) and CGC (ref. 22b) (Fig. 2d) are included. In addition, Table 3 summarizes monomer sequence (diad and triad) distributions, and the $r_Er_Y$ values for the E/4M1P copolymers obtained with all catalysts that we are comparing. The product of the reactivity ratio for $C_s$-metallocene was lower than 1 ($0.32 < r_Er_Y < 0.91$, $17.0 <$ 4M1P %mol $< 30.9$) indicative of a slightly alternating comonomer distribution and closely analogous to the pre-catalyst **1**. This result is consistent with the general trend observed for ethylene copolymerization with higher linear α-olefins by $C_s$-Me$_2$C(Cp)(9-Fluo)ZrCl$_2$ (ref. 37) compared to the $C_2$-[*rac*-H$_2$C-(3-*t*BuInd)$_2$ZrCl$_2$] ($r_Er_Y \approx 17.2$ blocky distribution of comonomers)[22a] and CGC ($r_Er_Y \approx 1$ random distribution of comonomers).[22b] However, note that the Cp*TiCl$_2$(*O*-2,6-iPr$_2$C$_6$H$_3$)–MAO catalyst remains the best choice for the highly alternating E/4M1P copolymerization ($r_Er_Y = 0.27$), exhibiting both remarkable activity and 4M1P incorporation.[23]

To find a relationship between the [O$^-$SO$^-$] ligand geometry and the copolymerization results further studies are needed.

Nonetheless, the result obtained here shows unique features of complex **1** among the Cp-free multidentate ligands,[12–17] for ethylene copolymerization with linear and branched α-olefins in an efficient manner, and may be promising for designing post-metallocene catalysts for precise olefin copolymerization.

The analysis of thermal properties revealed that all the E/α-olefin copolymers were semicrystalline, in agreement with the XRD investigation. DSC thermograms of crude polymers showed a very broad endothermic transition that spans the temperature range from 10 to 125 °C. The thermograms of E/PEN copolymers are shown in Fig. 3. The overall melting event of the copolymer occurred at a lower temperature range than that of PE and it decreased with the increase of the comonomer content. Melting enthalpy decreased from 245 J g$^{-1}$ for PE to 41 J g$^{-1}$ for E/PEN copolymer (run 4, PEN = 11.5 mol%), reflecting the reduced crystallinity likely due to the comonomer incorporation. This general behaviour was observed for all the copolymers investigated. The presence of multiple endothermic peaks may be a proof of a non-homogeneous comonomer distribution. At least in principle, the peak at low temperature should be ascribed to macromolecular chain segments with high side-group content, whereas the peak at a higher temperature to segments with a lower amount of that.

### Copolymerization of ethylene with CPE, NB and DCPD

The main data for ethylene copolymerization with cyclic olefins are summarized in Table 4. Catalyst **1**/MAO exhibited moderate to high activity in the ethylene copolymerization with CPE, although the CPE incorporation never exceeded 1 mol%.[38] The $^{13}$C NMR spectrum for a selected E/CPE copolymer (run 15, CPE = 0.7 mol%) is shown in Fig. 4. Besides the resonances at 27.73 ppm due to main ethylene chain units, small signals at 40.91 (C2), 28.78 (C3), 26.77 (C1) and 20.86 (C4) ppm were detected and assigned to *cis*-1,2-enchained CPE isolated units.[39]

A remarkable improvement in the catalytic activity and comonomer incorporation was observed for the copolymerization of ethylene with NB. This may be likely due to the distortion of the NB cyclic structure with respect to CPE.[40] Excellent yields were obtained for all the comonomer composition feedings investigated (NB/E molar ratio from 1 to 5.8). More specifically, the activity increased as the NB feed concentration increased in the range of 0.096–0.20 M, but rapidly decreased for a NB concentration of 0.56 M, meaning that the copolymerization is preferred to the homopolymerization of either ethylene or the comonomer. The molecular weights of the E/NB copolymers synthesized at different NB/E molar ratios showed the same trend. Similar copolymerization behavior was observed with

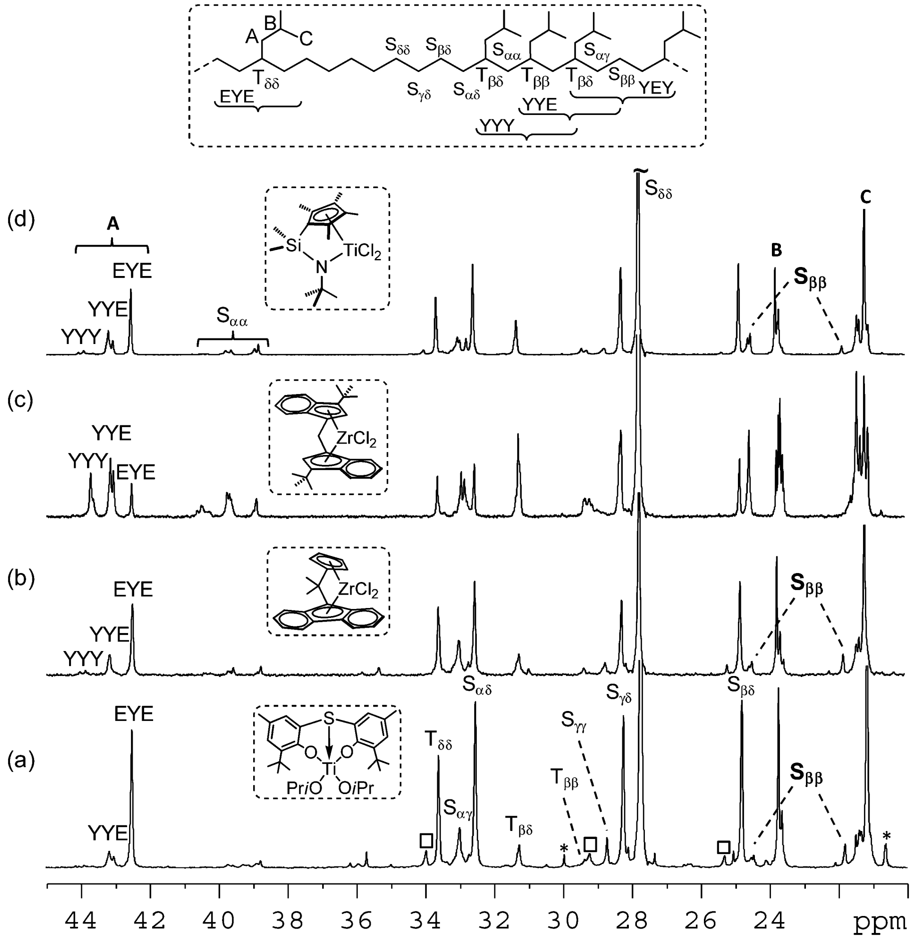

Fig. 2 $^{13}$C NMR spectra (in $C_2D_2Cl_4$ at 103 °C) of the E/4M1P copolymers prepared with (a) complex **1** (Table 2, run 11, 4M1P = 20.3 mol%), (b) $C_s$-$Me_2C(Cp)(9\text{-}Fluo)ZrCl_2$ (Table 3 and S1,† 4M1P = 30.9 mol%), (c) $C_2$-[*rac*-$H_2C$-(3-*t*BuInd)$_2ZrCl_2$] (Table 3 and S1,† 4M1P = 27.6 mol%), and (d) [$Me_2Si(C_5Me_4)(NtBu)]TiCl_2$ (Table 3, 4M1P = 20.6 mol%). Methyl [$CH_3$(sc)], methylene [$CH_2$(sc)] and methine [CH(sc)] carbons in the side chains are designated by the letters C, B, and A, respectively. 2,1 4M1P inserted units are marked with a square.[36] Chain-end groups are marked with a star.

Table 2 Monomer sequence distribution by $^{13}$C NMR of ethylene/α-olefin copolymers

| Y (type) | Run | Y$^a$ (%mol) | YY | YE | EE | YYY | YYE | EYE | YEY | YEE | EEE | $r_Er_Y{}^b$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PEN | 2 | 4.0 | 0.0 | 8.0 | 92.0 | 0.0 | 0.1 | 3.9 | 0.2 | 7.3 | 88.5 | nd |
| | 3 | 8.0 | 0.2 | 15.6 | 84.2 | 0.0 | 0.6 | 7.3 | 0.7 | 13.4 | 78.0 | 0.20 |
| | 4 | 11.5 | 0.7 | 21.6 | 77.7 | 0.8 | 1.1 | 9.6 | 1.3 | 18.0 | 69.2 | 0.44 |
| HEX | 5 | 3.7 | 0.0 | 7.4 | 92.6 | 0.0 | 0.0 | 3.3 | 0.2 | 6.0 | 90.5 | nd |
| | 6 | 8.1 | 0.2 | 15.8 | 84.0 | 0.0 | 0.6 | 7.4 | 0.6 | 14.4 | 77.0 | 0.26 |
| | 7 | 13.1 | 0.4 | 25.4 | 74.2 | 0.0 | 1.3 | 11.9 | 2.2 | 21.5 | 63.1 | 0.17 |
| 4M1P | 8 | 2.5 | 0.0 | 5.0 | 95.0 | 0.0 | 0.0 | 2.3 | 0.2 | 5.3 | 92.2 | nd |
| | 9 | 5.9 | 0.0 | 11.8 | 88.2 | 0.0 | 0.3 | 5.5 | 0.6 | 9.8 | 83.8 | nd |
| | 10 | 6.7 | 0.0 | 13.5 | 86.5 | 0.0 | 0.5 | 6.4 | 1.4 | 10.9 | 80.8 | nd |
| | 11 | 20.3 | 2.8 | 34.8 | 62.4 | 1.6 | 5.2 | 16.5 | 7.1 | 19.8 | 49.8 | 0.58 |

[a] Comonomer content in the copolymer from diad distribution as Y = (YY + 1/2YE). [b] From diad distribution as 4[YY][EE]/[EY]$^2$. nd = not determinable.

some half-titanocenes.[41] In contrast, the incorporation of NB in the copolymers increased linearly with increase in the comonomer feed concentration, reaching 40.6 mol% at NB/E = 5.8 (Table 4, run 18). The E/NB copolymers showed different thermal behaviors as a function of the NB content (Fig. S1†). The sample with 10.8 mol% of NB (run 16) was semicrystalline with a melting event at 120 °C, and an enthalpy of fusion of 60 J g$^{-1}$. As the NB content increased the melting temperature decreased (run 17, $\Delta H_m$ = 6 J g$^{-1}$) and shifted to a lower temperature range. Moreover, the glass transition event

Table 3 Monomer sequence distribution by $^{13}$C NMR and summary of the $r_E r_Y$ of E/4M1P copolymers by (tbmp)Ti(OiPr)$_2$, Me$_2$C(Cp)(9-Fluo)ZrCl$_2$, *rac*-H$_2$C-(3-*t*BuInd)$_2$ZrCl$_2$, [Me$_2$Si(C$_5$Me$_4$)(N*t*Bu)]TiCl$_2$ and Cp*TiCl$_2$(*O*-2,6-iPr$_2$C$_6$H$_3$)

| Pre-catalyst | Y[a] (%mol) | YY | YE | EE | YYY | YYE | EYE | YEY | YEE | EEE | $r_E r_Y$[b] | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (tbmp)Ti(OiPr)$_2$ (**1**) | 20.3 | 2.8 | 34.8 | 62.4 | 1.6 | 5.2 | 16.5 | 7.1 | 19.8 | 49.8 | 0.58 | This work |
| Me$_2$C(Cp)(9-Fluo)ZrCl$_2$[c] | 17.0 | 1.2 | 31.6 | 67.2 | 0.0 | 3.9 | 13.0 | 5.9 | 20.5 | 56.7 | 0.32 | This work |
| Me$_2$C(Cp)(9-Fluo)ZrCl$_2$[d] | 30.9 | 8.5 | 44.8 | 46.7 | 3.3 | 8.4 | 17.7 | 11.2 | 22.2 | 37.2 | 0.79 | This work |
| *rac*-H$_2$C-(3-*t*BuInd)$_2$ZrCl$_2$ | 27.6 | 13.9 | 27.5 | 58.6 | 7.9 | 12.4 | 3.4 | 10.5 | 5.7 | 60.1 | 17.2 | 22a |
| [Me$_2$Si(C$_5$Me$_4$)(N*t*Bu)]TiCl$_2$ | 20.6 | 4.0 | 33.2 | 62.8 | 0.6 | 7.0 | 12.7 | 7.9 | 19.9 | 51.9 | 0.9 | 22a |
| Cp*TiCl$_2$(*O*-2,6-iPr$_2$C$_6$H$_3$) | 31.4[e] | 4.9 | 54.1 | 41.0 | 1.0 | 7.7 | 22.7 | 23.2 | 8.7 | 36.7 | 0.27 | 23 |

[a] Comonomer content in the copolymer from diad distribution as Y= (YY + 1/2YE). [b] From diad as 4[YY][EE]/[EY]$^2$. [c] Polymerization conditions: total volume, 100 mL; pre-catalyst, 2 μmol; cocatalyst, d-MAO; Al/Zr, 3000 (mol mol$^{-1}$), temperature, 45 °C; time, 30 min; ethylene pressure, 1.01 bar; 4M1P feed, 1.87 mL (see also Table S1†). [d] 4M1P feed, 3.75 mL (see also Table S1†). [e] Determined from triad distribution.

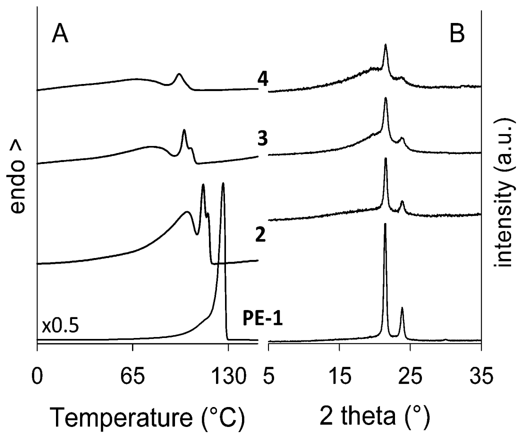

Fig. 3 DSC thermogram (A) and XRD pattern (B) of PE (Table 1, run 1) and E/PEN copolymers (Table 1, runs 2, 3 and 4).

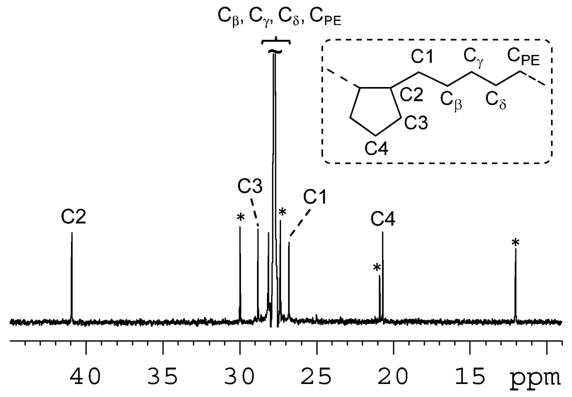

Fig. 4 $^{13}$C NMR spectra (in C$_2$D$_2$Cl$_4$ at 103 °C) of the E/CPE copolymer (Table 4, run 15, CPE = 0.7 mol%). Chain-end groups are marked with a star.

appeared at *ca.* 19 °C. At a higher NB content (40.6 mol%) sample 18 only showed $T_g$ at 85 °C, consistent with the highly amorphous character of the copolymer.

Fig. 5 shows the $^{13}$C NMR spectra of poly(E-*co*-NB)s. Peak assignments were performed based on a comparison of the observed chemical shifts with previous data by other authors[42,43,25b] and by us.[44] The signals of each chemical shift region were assigned as follows: 42.5–54.0 ppm, C2/C3; 34.5–42 ppm, C1/C4; 34.5–31.0 ppm, C7; 31–26 ppm, C5/C6, ethylene CH$_2$. The $^{13}$C NMR spectrum of sample 16 (Fig. 5c, NB = 10.8 mol%) gave eight major resonances: 27.73, 27.93, 28.05, 28.12 ppm assigned to the ethylene CH$_2$ ($S_{\delta\delta}$, $S_{\beta\delta}$, $S_{\gamma\delta}$, $S_{\alpha\delta}$,

Table 4 Copolymerization of ethylene with cyclic olefins by **1**/MAO[a]

| Run | Y (Conc./M) | [Y]/[E][b] | Time (min) | Yield (mg) | Activity[c] | Y[d] (%mol) | $M_w$[e] × 10$^{-4}$ | $M_w/M_n$[e] | $T_m$ ($T_g$)[f] (°C) | $\Delta H_m$[f] (J g$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 13 | CPE (0.56) | 5.8 | 5 | 196 | 784 | 0.6 | 5.2 | 2.8 | 128 | 202 |
| 14 | CPE (0.78) | 8.1 | 5 | 378 | 1512 | 0.9 | 3.4 | 3.7 | 127 | 216 |
| 15 | CPE (0.78) | 8.1 | 16 | 948 | 1185 | 0.7 | 2.4 | 2.8 | 125 | 211 |
| 16 | NB (0.096) | 1.0 | 5 | 760 | 3040 | 10.8 | 1.8 | 2.6 | 120[g] | 60 |
| 17 | NB (0.20) | 2.1 | 5 | 870 | 3480 | 21.1 | 3.4 | 1.4 | 80, (19) | 6 |
| 18 | NB (0.56) | 5.8 | 5 | 545 | 2180 | 40.6 | 1.7 | 1.8 | (85) | |
| 19 | DCPD (0.20) | 2.1 | 16 | 1630 | 2038 | 10.2 | 1.2 | 2.2 | [h] | 25 |
| 20 | DCPD (0.56) | 5.8 | 16 | 381 | 476 | 23.0 | 0.5 | 1.8 | nd | |

[a] Polymerization conditions: **1**, 3 μmol; Al/Ti, 1000; toluene, total volume 25 mL; temperature, 50 °C; ethylene pressure, 1.01 bar. [b] [Y]/[E] feed ratio (mol mol$^{-1}$) in the liquid phase. [c] Activity in kg$_{\text{polymer}}$ mol$_{\text{Ti}}$$^{-1}$ h$^{-1}$. [d] Comonomer content in the copolymer. [e] Molecular weight ($M_w$ in g mol$^{-1}$) and molecular weight distribution ($M_w/M_n$) by SEC in *ortho*-dichlorobenzene *vs.* poly(styrene) standard. [f] Melting temperature ($T_m$), glass transition temperature ($T_g$), and melting enthalpy ($\Delta H_m$) by a DSC second heating scan. [g] Broad endothermic transition in the temperature range 0–125 °C with a peak at 120 °C and shoulders at lower temperatures. [h] Broad endothermic transition in the temperature range 20–110 °C. nd, not determined.

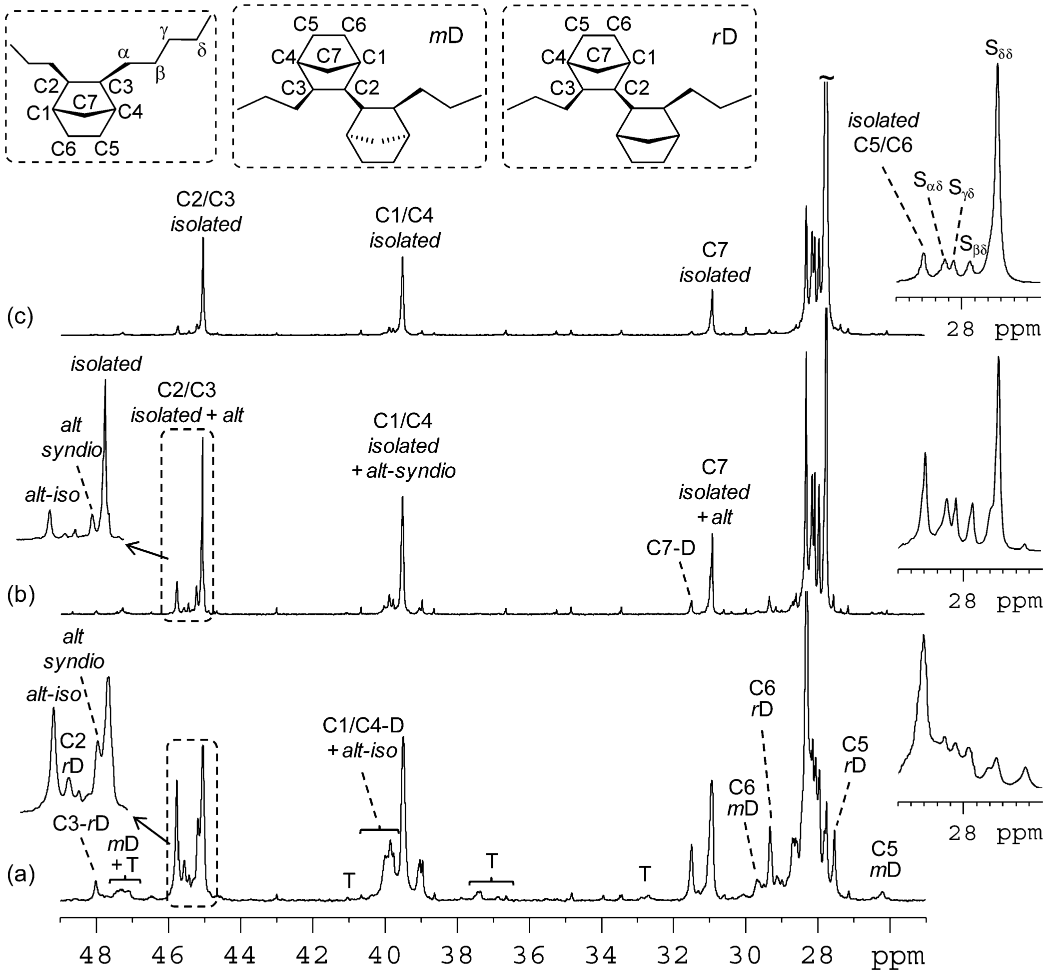

Fig. 5 $^{13}C$ NMR spectra (in $C_2D_2Cl_4$ at 103 °C) of the E/NB copolymers with NB mole percent: (a) 40.6% (Table 4, run 18), (b) 21.1% (Table 4, run 17), and (c) 10.8% (Table 4, run 16). In the inset at the top, from left to right: a segment of the E/NB copolymer chain with the isolated NB unit, showing the numbering of carbon atoms, and *meso*- and *racemic*-NB diads characteristic of E-NB-NB-E sequences (*m*D and *r*D, respectively). In the inset to the right the expanded $^{13}C$ NMR chart from 27 to 28.5 ppm is shown.

respectively), and 28.28, 30.89, 39.49, 45.04 ppm assigned to C5/C6, C7, C1/C4, C2/C3 of isolated NB units, respectively. In the methylene region (see the inset of Fig. 5) of the $^{13}C$ NMR spectrum of sample 17 (Fig. 5b, NB = 21.1 mol%) and 18 (Fig. 5a, NB = 40.6 mol%) we can track the gradual reduction of the ethylene $S_{\delta\delta}$ resonance (27.73 ppm) and the simultaneous growth of the C5/C6, $C_\alpha$, and $C_\beta$ resonances with increasing NB content. In addition to isolated NB units, the $^{13}C$ NMR spectrum of the latter copolymers also exhibited a peak at 45.75 and 45.21 ppm assigned to C2/C3 of NB in the alternating isotactic and syndiotactic YEYEY sequences, respectively. The relative peak intensities also revealed that the copolymers had a random tacticity, the ratio of syndiotactic and isotactic units being in the range from 56:44 (run 16, NB = 10.8 mol%) to 43:57 (run 18, NB = 40.6 mol%). Moreover, the $^{13}C$ NMR spectrum exhibited signals at 26.20 and 29.67 ppm, and at 27.53 and 29.32 ppm, assigned to C5/C6 of *meso*- and *racemic*-NB diads characteristic of EYYE sequences (*m*D and *r*D, respectively) which became more intense as the NB content increased. The content of *racemic*-EYYE sequences was calculated from the relative peak intensities and it was about 5 times higher than that of *meso* sequences. The higher percentage of *racemic*-[E-NB-NB-E] sequences had been observed with $C_s$-symmetric complexes such as ($t$-BuNSiMe$_2$Flu)TiMe$_2$[43] and Me$_2$C(Flu)CpZrCl$_2$.[3i]

Intrigued by the high NB incorporation capability of the precatalyst **1**, we copolymerized ethylene with DCPD. Moderate to high productivities were obtained, strongly influenced by the comonomer feed concentration. The use of more comonomer (run 20, DCPD = 14 mmol) led to a significant decrease in activity. This trend was comparable with the case of NB, although much more evident in the presence of the bulky hindered DPCD. At the same Y/E molar ratio, the catalyst showed a 2–5-fold decreased activity for Y = DCPD rather than Y = NB. This result for the ethylene copolymerization with DCPD may be likely due to the sluggish ethylene insertion into the severely encumbered bond between the Ti atom and the norbornyl bearing the cyclopentene ring. Under the conditions employed, the DCPD incorporation increased with the DCPD concentration in the feed, and easily reached 23.0 mol% at Y/E = 5.8, whilst the molecular weight dropped rapidly.

The microstructure of poly(E-*co*-DCPD)s was established through $^{13}$C and $^{1}$H NMR spectra (not shown). The peaks at 130.54 and 128.71 ppm in $^{13}$C NMR spectra (Fig. 6) as well as those at 5.56 and 5.44 ppm in the $^{1}$H NMR spectrum revealed that the copolymers contained unreacted CPE units. This suggests that the copolymerization proceeded through enchainment of the NB ring, which is consistent with the fact that the catalyst **1**/MAO was active for the E/NB copolymerization but almost inert toward the E/CPE copolymerization. The $^{13}$C NMR spectra of the aliphatic region for the E/DCPD copolymers with different amounts of comonomer are shown in Fig. 6. Sample 19 (Fig. 6b, DPCD = 10.2 mol%) consisted mainly of isolated DCPD units. The peaks observed at 51.70 (C9), 44.43 (C6), 42.87 (C7), 40.87 (C4), 38.98 (C8), 36.0 (C5), 34.28 (C10), 30.54 (C3), and 27.3–28.2 (C11, C12, $CH_2$) ppm were assigned to isolated DCPD units and PE sequences, respectively. With increasing DCPD incorporation we can track the peaks at 45.03, 43.36, 39.63 and 36.61 ppm (marked as *alt*-C*n* in Fig. 6a) characteristic of the alternating E-DCPD sequences.[45] Note that on increasing the NB and DCPD content in the copolymers, a number of small signals (marked with a cross) appeared in all the $^{13}$C NMR spectral regions, likely due to diads and cyclic olefin blocks longer than the diads. Their large number may be also due to the different comonomer stereosequences, varying lengths of the NB blocks and *meso* or *racemic* connection of the NB units.

## Boiling solvent extraction

In order to obtain information on the copolymer composition, a boiling solvent fractionation with diethyl ether and THF was carried out and all fractions were characterized by NMR, SEC, DSC, and XRD (see Table 5 and S2†). The E/α-olefin copolymers with the higher comonomer content and low molecular weight were much more soluble in boiling diethyl ether. More specifically, for the E/HEX and E/4M1P copolymers with a comonomer content of 13.1 and 20.3 mol%, respectively (Table 1, runs 7 and 11) the ether-soluble fraction accounted for over 90% of the whole copolymer, and it was indistinguishable by $^{13}$C NMR from the unfractionated copolymer. On decreasing the comonomer content in the copolymers, the fractionation yielded THF-soluble and THF-insoluble fractions whose compositions and sequence distributions matched close enough with those of the unfractionated polymer, and a small ether-soluble fraction (less than 13%) containing mainly isolated comonomer units, lower in molecular weight and crystallinity and with a lower melting point. Collectively, DSC, XRD, $^{13}$C NMR and fractionation results gave evidence that all fractions of the copolymers contained long enough crystallizable ethylene sequences (Fig. S2 and S3†).

In the fractionation of E/CPE copolymers, more than 94% of the product was THF-insoluble and the thermal behaviour of the residue fraction looked like that of neat PE (Table S2†). The results of fractionation for the ethylene copolymers with NB and DCPD are given in Table 5. For the ethylene copolymers with the higher NB and DCPD content, the THF-soluble fraction accounted for over 90% of the whole copolymer, and it was indistinguishable by DSC (Fig. S5†) and $^{13}$C NMR from the unfractionated copolymer.

Otherwise, the copolymers with the lower cyclic olefin content had a small THF-insoluble fraction (4–13%) with a low amount of comonomer (2.3–2.9 mol%), and an increased ether-soluble fraction whose $^{13}$C NMR exhibited the same features of the whole copolymer (Fig. S4†). The E/NB copolymer with 10 % mol of NB and a $M_w/M_n$ > 2.5 (Table 4, run 16) was separated

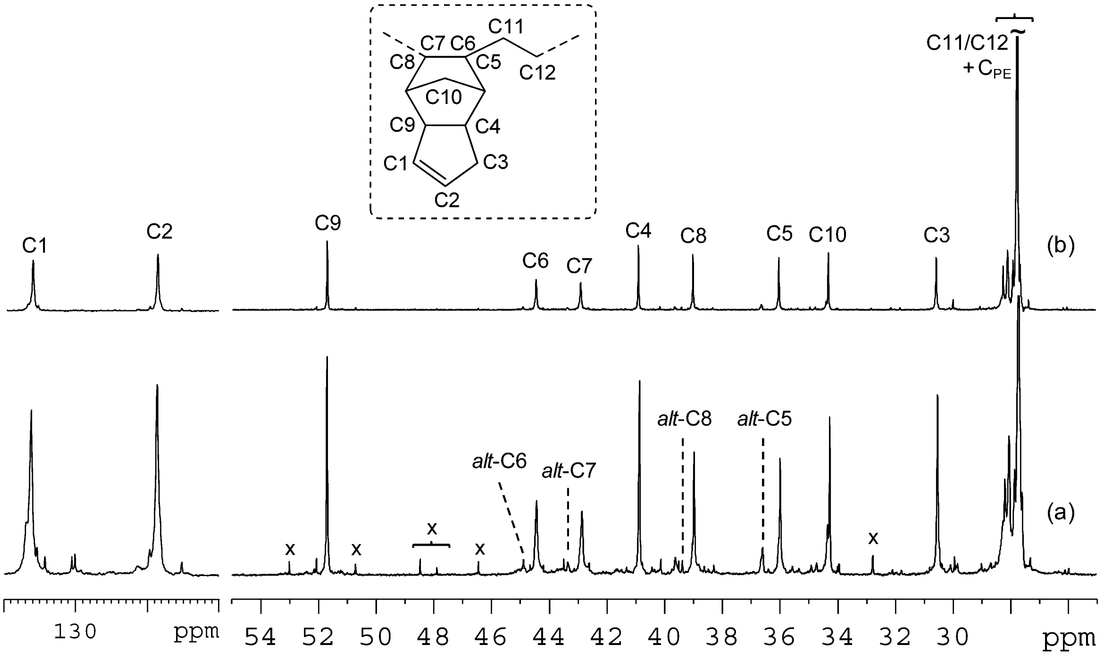

Fig. 6 $^{13}$C NMR spectra (in $C_2D_2Cl_4$ at 103 °C) of the E/DCPD copolymers with DCPD mole percent: (a) 23% (Table 4, run 20), and (b) 10.2% (Table 4, run 19). The DCPD diad and blocks longer than the diads are marked with a cross.

Table 5 Boiling solvent fractionation of the copolymers using **1**/MAO

| | | Ether-soluble fraction | | | | THF-soluble fraction | | | | Residue fraction | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Y | | | $Y^a$ | | $T_m(T_g)^c$ | | $Y^a$ | | $T_m(T_g)^c$ | | $Y^a$ | | $T_m{}^c$ |
| (Type) | Run | (%) | (%mol) | $M_w{}^b \times 10^{-4}$ | (°C) | (%) | (%mol) | $M_w{}^b \times 10^{-4}$ | (°C) | (%) | (%mol) | $M_w{}^b \times 10^{-4}$ | (°C) |
| HEX | 5 | 6 | nd | nd | 70 | 35 | 4.3 | 1.1 | 105/102 | 59 | 2.7 | 2.9 | 118/116/110 |
| | 6 | 26 | 10.4 | 1.1 | 65 | 74 | 7.5 | 2.8 | 103/98/83 | — | | | |
| | 7 | 93 | 15.5 | 1.3 | 55 | 7 | nd | 1.5 | 103/83 | — | | | |
| 4M1P | 8 | Traces | | | | 63 | 4.0 | 1.1 | 107/104 | 37 | 2.3 | 3.2 | 119/112 |
| | 9 | 13 | 9.3 | 1.1 | 83/65 | 70 | 6.4 | 2.2 | 102/98/86 | 17 | 4.0 | 6.3 | 113/102 |
| | 10 | 21 | 11.7 | 1.4 | 71 | 79 | 6.4 | 2.5 | 101/96/82 | — | | | |
| | 11 | 91 | 20.8 | 0.8 | 45 | 9 | nd | 3.5 | 93/77 | — | | | |
| | 12 | — | | | | 66 | 6.3 | 2.1 | 100/96/82 | 34 | 3.5 | 5.7 | 113 |
| NB | 16 | 52 | 17.0 | 0.8 | 52 (−10) | 35 | 14.4 | 1.1 | 93 (−11) | 13 | 3.0 | 2.5 | 124 |
| | 17 | 42 | 26.5 | 2.5 | (9) | 58 | 17.8 | 3.8 | 79 (17) | — | | | |
| | 18 | 3 | nd | nd | (60) | 97 | 41.2 | 1.7 | (81) | — | | | |
| DCPD | 19 | 48 | 14.4 | 0.5 | 46 (−7) | 48 | 9.4 | 1.2 | 85 (−1) | 4 | 2.3 | 5.7 | 117 |
| | 20 | 7 | nd | nd | nd | 93 | 23.5 | 0.5 | nd | — | | | |

[a] Comonomer content in the copolymer from diad distribution as Y = (YY + 1/2YE). [b] Molecular weight ($M_w$, in g mol$^{-1}$) by SEC in *ortho*-dichlorobenzene *vs.* poly(styrene) standard. For all fractions the $M_w/M_n$s ranged from 1.8 to 2.5. [c] Melting temperature ($T_m$) and glass transition temperature ($T_g$) by a DSC second heating scan. nd, not determined.

into three fractions (Table 5), *i.e.*, the ether-soluble (52%), the THF-soluble (35%), and the residue fraction (13%), which differed in the molecular weight, and showed a broad inhomogeneity with respect to the comonomer incorporation with an average NB content of 17.0, 14.4 and 2.9 %mol, respectively. In the same manner, the E/DCPD copolymer with 10.2 %mol of DCPD and $M_w/M_n > 2$ (Table 4, run 19) was separated into three fractions, *i.e.*, the ether-soluble (48%), the THF soluble (48%), and the residue fraction (4%), which differed with respect to the comonomer incorporation with an average DCPD content of 14.4, 9.4 and 2.3 %mol, respectively, molecular weights and thermal properties.

In agreement with the fractionation results and the fairly narrow $M_w/M_n$ of the copolymers, no PE or a comonomer homopolymer by-product was recovered even when, for example, a prolonged polymerization time or a high comonomer concentration was employed, meaning that the copolymerization is always preferred to the homopolymerization of either ethylene or the comonomer.

## Conclusions

The copolymerization of ethylene with some α-olefins and cyclic olefins catalyzed by the Ti(IV) diisopropoxy complex bearing a dianionic [O$^-$,S,O$^-$] bis(phenolato) ligand, in combination with MAO, is reported. High activity, a good comonomer incorporation (about 15 mol% for Y/E = 8; Y = comonomer), decreasing in the order HEX > PEN > 4M1P, is demonstrated for the copolymerization with α-olefins. The copolymers have a relatively high percentage of alternate EYE and YEY triads, and the reactivity ratio product values are lower than 1, confirming the tendency to fabricate copolymers with a prevalent alternation of the comonomers. The copolymerization of ethylene with cyclic olefins gives copolymers with excellent yield and, except for CPE, efficient NB and DCPD incorporation (from 10 to 40 mol%) is already achieved at Y/E = 1. The copolymers are random with isolated comonomer units together with diad, triad and longer comonomer blocks. More specifically, *racemic*-connected EYYE sequences are detected in the $^{13}$C NMR spectra, 5-times higher than the *meso* ones.

The tendency for the E/α-olefin monomer alternation, and the higher percentage of *racemic*-[E-NB-NB-E] sequences for the complex **1** are similar to those observed for some $C_s$-metallocenes.[3i,43] In consideration of this, and given that alternating copolymers with linear α-olefins were obtained with $C_s$-Me$_2$C(Flu)-CpZrCl$_2$, while no data for the ethylene copolymerization with 4M1P were reported, preliminary results for the ethylene copolymerization with 4M1P catalyzed by $C_s$-Me$_2$C(Cp)(9-Fluo)ZrCl$_2$ are reported. Similarities and differences with respect to **1**, and other efficient Group 4 complexes such as $C_2$-[*rac*-H$_2$C-(3-*t*BuInd)$_2$Zr-Cl$_2$],[22a] CGC,[22b] and Cp*-aryloxo half-metallocenes,[23] are discussed on the basis of microstructural analysis and reactivity ratios. The results illustrate the potential of the complex **1** to fabricate copolymers with a range of sequence distributions in view of a large variety of ligand substitutents. However, further studies are warranted to evaluate the role of the bis(phenolate) complex structure on the copolymerization behavior.

In conclusion, the ability to perform effectively in a variety of copolymerizations along with the ease and low-cost of preparation makes complex **1** a potential alternative to Cp-type Group 4 catalysts for the synthesis of ethylene copolymers with α-olefins and cyclic olefins.

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