# Supporting Information:

# Ethylene–*co*–norbornene Copolymerization Using a Dual Catalyst System in the Presence of a Chain Transfer Agent

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PREPARATION OF COMPRESSION MOLDED FILMS

Compression molded films were prepared by heating the as polymerized samples at temperatures 20-30 °C higher than the melting temperatures under a press. They were successively cooled to room temperature at average rate of ≈10°C/min. The applied pressure was kept low, in order to avoid preferred orientations in the samples.

X-RAY ANALYSIS

Wide angle X-ray scattering (WAXS) data were collected on compression-molded films using the multipurpose diffractometer Empyrean (PANalytical) in the θ-θ reflection geometry, with CuK$\alpha$⊚incident ⊚radiation (wavelength $\lambda$ =0.15418 nm).

THERMAL ANALYSIS

DSC thermograms were obtained with a differential scanning calorimeter Mettler Toledo DSC-1 performing scans in a flowing N2 atmosphere and heating or cooling at a rate of 10°C/min.

MECHANICAL TESTS

The mechanical tests were performed at room temperature on unoriented compression molded films using universal mechanical tester Instron, following the standard test method for tensile properties of thin plastic sheeting ASTM D882-83. Rectangular specimens 10 mm long, 5 mm wide and 0.3 mm thick were cut from compression molded films and stretched up to the break. Two benchmarks were placed on the test specimens and used to measure elongation. In the mechanical tests the ratio between the drawing rate and the initial length was fixed equal to 0.1 mm/(mm×min) for the measurement of Young's modulus, and 10 or 0.5 mm/(mm×min), depending on the rigidity, of the sample, for the measure of the stress-strain curves up to break. The reported curves and values of Young modulus were averaged over at least five independent experiments.

Values of tension set were measured on unoriented compression molded films after breaking. Two benchmarks were drawn on the specimens at distance $L_0$. Then the samples were stretched up to the break, i.e. up to achieve elongation $\varepsilon_b = [(L_f - L_0)/ L_0]100$, where Lf is the distance between the benchmarks at breaking. Ten minutes after breaking the two pieces of the sample were fit carefully together so that they are in contact over the full area of the break and the final total length $L$r of the specimen was obtained by measuring the distance between two benchmarks. The tension set $t_b$ after breaking was calculated as: $t_b = [(Lr - L_0)/ L_0]\times100$.

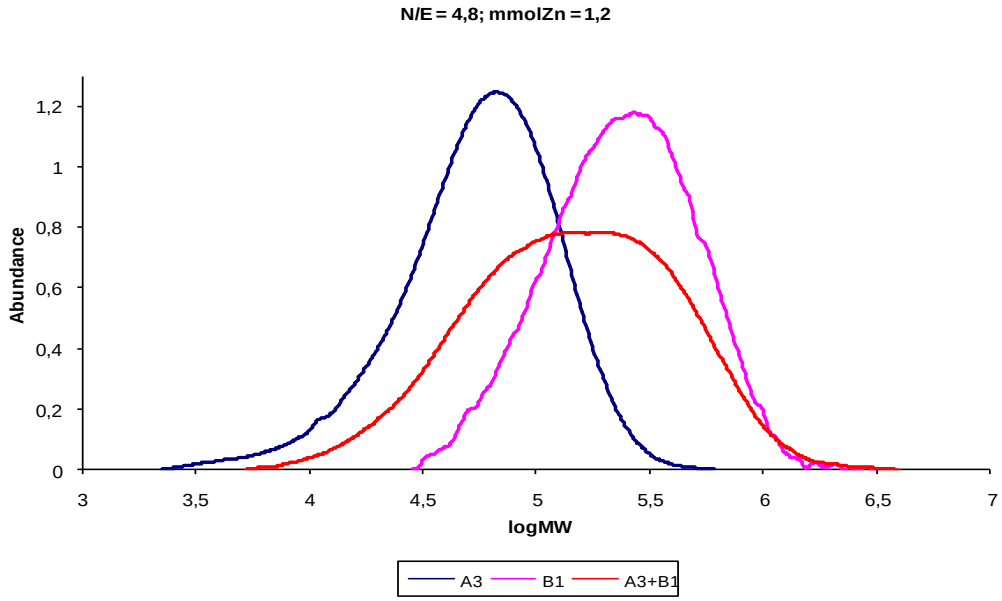


**Figure S1.** Molecular weight profiles for [N]/[E] = 4.8 and Zn = 1,2 mmol (A3 = 1; B1= 2)

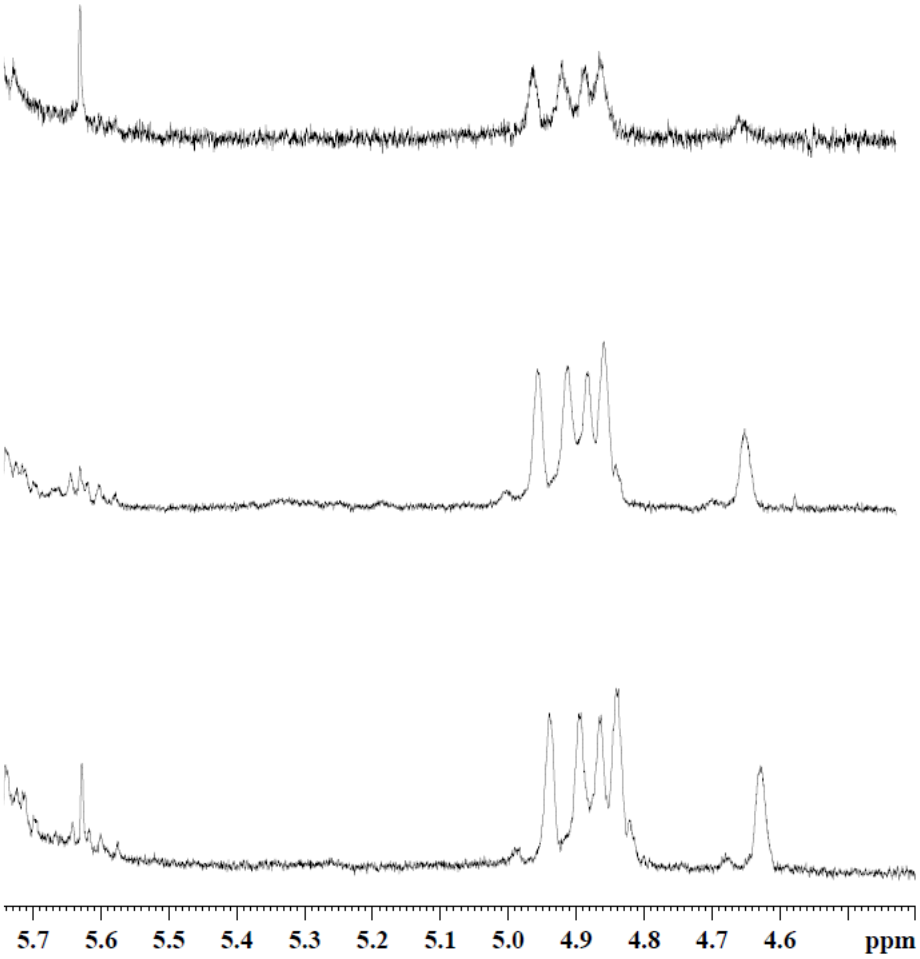


**Figure S2.** Expansions of the region between 4.4 and 5.75 ppm of $^{1}H$ NMR spectra (400 MHz, $C_2D_2Cl_4$, 103 °C) of polymers prepared by **1**:
a) (top): poly(E-co-N) without $ZnEt_2$ at [N]/[E] feed ratio of 4.8 (Table 3, entry 3 in ref. [33];
b) (middle): poly(E-*co*-N) without $ZnEt_2$ at [N]/[E] feed ratio of 1.3 (Table 1, entry 1 in ref. [33];
c) (bottom): poly(E-*co*-N) with $ZnEt_2$ at [N]/[E] feed ratio of 1.3 (Table 1, entry 8).

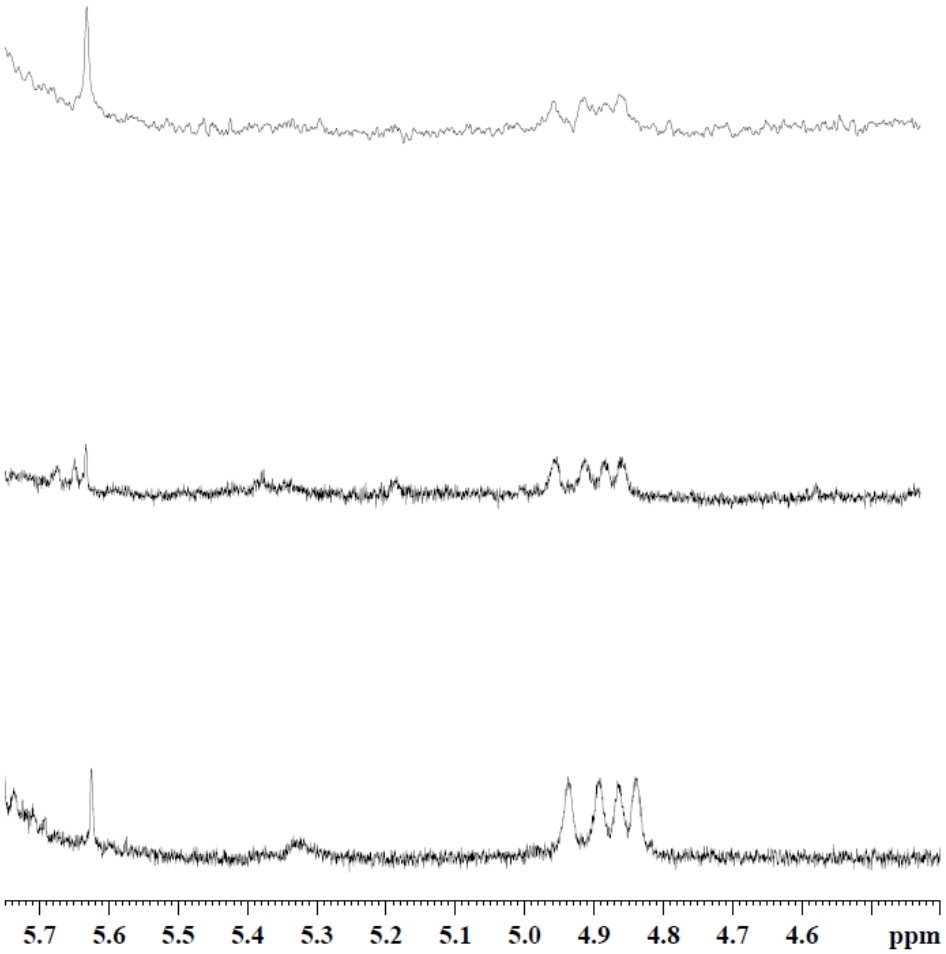


**Figure S3**. Expansions of the region between 4.4 and 5.75 ppm of $^{1}$H NMR spectra (400 MHz, C2D2Cl4, 103 °C) of polymers prepared by **2:**
a) (top): poly(E-*co*-N) without $ZnEt_2$ at [N]/[E] feed ratio of 4.8 (Table 3, entry 4 in ref. [33]);
b) (middle): poly(E-*co*-N) without $ZnEt_2$ at [N]/[E] feed ratio of 1.3 (Table 1 entry 2 in ref [33]);
c) (bottom): poly(E-*co*-N) with $ZnEt_2$ at [N]/[E] feed ratio of 1.3 (Table 1, entry 9)

$^{1}$H NMR spectra of copolymers obtained show the signals of end groups, essentially terminal vinyl groups bonded to inserted ethylene or norbornene units, depending on the N content in the copolymer.

As reported in ref. [33] by adding diethyl zinc to both systems there is no change in the terminal groups visible.

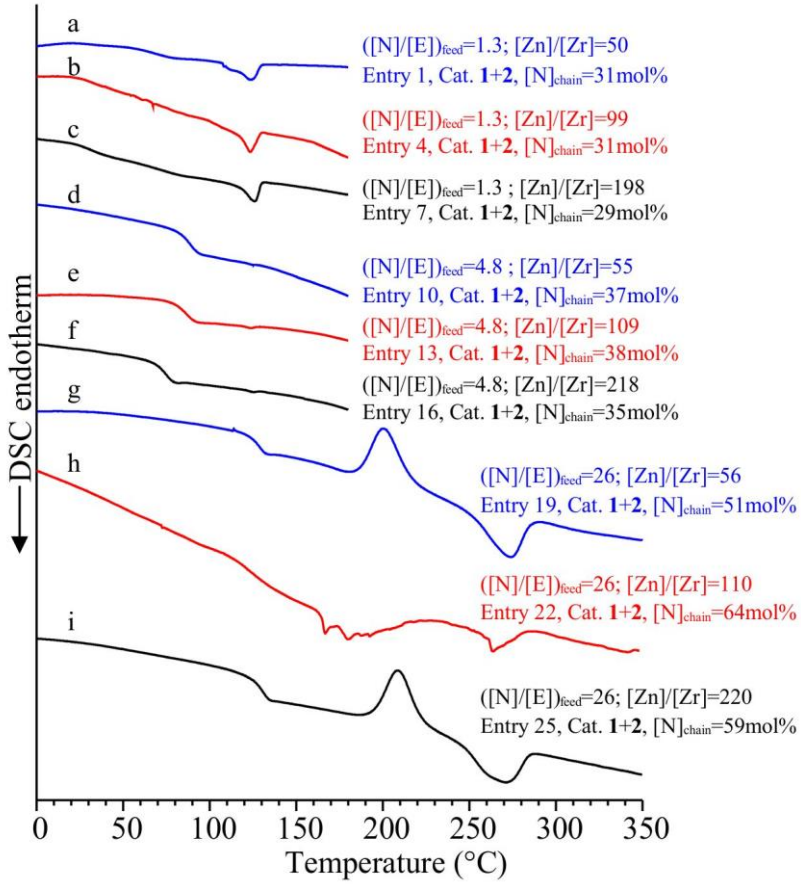


**Figure S4.** DSC thermograms recorded during the II heating scan of melt crystallized poly(ethylene-co-norbornene) samples obtained with catalysts **1**+ **2** at [N]/[E] feed ratio of 1.3, 4.8 and 26.0, using the indicated values of the [Zn]/[Zr] ratio during polymerization.

**Table S1** Reactivity Ratios of E-*co*-N Copolymerization Reactions with Catalyst **1**, **2** and **1+2** Calculated using First and Second Order Markovian Models from Tetrad Distribution

| cat | [N]/[E] | [Zn]/[Zr] | N mol %[a] | $r_1$ | $r_2$ | $r_{11}$ | $r_{12}$ | $r_{21}$ | $r_{22}$ |
|---|---|---|---|---|---|---|---|---|---|
| **1** | 1.3 | 0 | 35 | 1.65 | 0.03 | 2.21 | 0.01 | 1.35 | 0.00 |
| **1** | 1.3 | 100 | 35 | 1.34 | 0.01 | 1.45 | 0.01 | 1.29 | 0.00 |
| **1** | 1.3 | 200 | 35 | 1.40 | 0.02 | 1.63 | 0.02 | 1.30 | 0.07 |
| **1** | 1.3 | 400 | 31 | 1.57 | 0.03 | 1.62 | 0.03 | 1.54 | 0.13 |
| **2** | 1.3 | 0 | 20 | 3.76 | 0.00 | 4.27 | 0.00 | 2.21 | 0.00 |
| **2** | 1.3 | 100 | 22 | 3.26 | 0.00 | 3.81 | 0.00 | 1.98 | 0.00 |
| **2** | 1.3 | 200 | 21 | 3.48 | 0.00 | 4.08 | 0.00 | 1.98 | 0.00 |
| **2** | 1.3 | 400 | 22 | 1.57 | 0.03 | 1.62 | 0.03 | 1.54 | 0.00 |
| **1+2** | 1.3 | 50 | 31 | 1.69 | 0.03 | 2.65 | 0.01 | 1.21 | 0.30 |
| **1+2** | 1.3 | 99 | 31 | 2.06 | 0.03 | 2.89 | 0.02 | 1.40 | 0.00 |
| **1+2** | 1.3 | 198 | 29 | 1.88 | 0.04 | 2.52 | 0.02 | 1.42 | 0.00 |
| **1** | 4.8 | 0 | 45 | 2.23 | 0.05 | 3.21 | 0.05 | 2.11 | 0.00 |
| **1** | 4.8 | 100 | 46 | 2.60 | 0.05 | 3.04 | 0.06 | 2.52 | 0.00 |
| **1** | 4.8 | 200 | 45 | 2.63 | 0.05 | 2.99 | 0.06 | 2.58 | 0.00 |
| **1** | 4.8 | 400 | 46 | 2.42 | 0.05 | 1.61 | 0.06 | 2.58 | 0.00 |
| **2** | 4.8 | 0 | 33 | 5.49 | 0.00 | 6.75 | 0.00 | 4.92 | 0.02 |
| **2** | 4.8 | 100 | 34 | 3.27 | 0.00 | 4.62 | 0.00 | 3.04 | 0.00 |
| **2** | 4.8 | 200 | 34 | 4.70 | 0.01 | 5.10 | 0.01 | 4.56 | 0.00 |
| **2** | 4.8 | 400 | 34 | - | - | 5.15 | 0.02 | 3.46 | 0.00 |
| **1+2** | 4.8 | 55 | 37 | 2.89 | 0.02 | 3.53 | 0.02 | 2.78 | 0.00 |
| **1+2** | 4.8 | 100 | 38 | 3.34 | 0.03 | 4.69 | 0.03 | 3.08 | 0.00 |
| **1+2** | 4.8 | 200 | 35 | 3.46 | 0.02 | 5.74 | 0.02 | 3.02 | 0.00 |

[a] Determined from tetrads

**Table S2** Values of the Young modulus (E), stress and strain at yield ($\varepsilon_y$, $\sigma_y$) and at break ($\varepsilon_b$, $\sigma_b$), and tension set at break ($t_b$) extracted from the stress strain curves of Figure 7 for the poly(ethylene-*co*-norbornene) copolymers, obtained by catalyst **1** and/or **2**, at different concentrations of $ZnEt_2$ as CTA.[a]

| Entry | E | N | Catalyst | [Zn]/[Zr] | Zn mmol | $M_w$ ($10^{-3}$) | $v/L_0$ ($min^{-}$ | $E$ (MPa) | $\sigma_b$(MPa) | $\varepsilon_b$(%) | $\sigma_y$ (MPa) | $\varepsilon_y$(%) | $t_b$(%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$([N]/[E])_{feed}$ =1.3** | | | | | | | | | | | | | |
| 1 | 69 | 31 | **1+2** | 50 | 0.8 | 27 | 0.5 | 370±40 | 11±1 | 60±10 | 15.7±0.5 | 4.8±0.6 | - |
| 3 | 78 | 22 | **2** | 99 | 0.8 | - | 10 | 300±20 | 37±3 | 740±70 | 15.1±0.7 | 9±2 | - |
| 4 | 69 | 31 | **1+2** | 99 | 1.6 | 25 | 0.5 | 300±100 | 17±2 | 135±20 | 20±3 | 6±1 | - |
| 5 | 65 | 35 | **1** | 198 | 1.6 | 29 | 0.5/10 | 310±50 | 13±1/14±2 | 70±20/40±20 | 20±2/24±4 | 12±2/13±1 | - |
| 6 | 79 | 21 | **2** | 198 | 1.6 | - | 10 | 240±80 | 36±3 | 900±100 | 20±2 | 10.7±0.8 | 490±70 |
| 7 | 71 | 29 | **1+2** | 198 | 3.2 | 23 | 10 | 170±50 | 20±1 | 320±90 | 26±2 | 13±1 | 300±100 |
| 8 | 69 | 31 | **1** | 396 | 3.2 | 29 | 0.5/10 | 280±20 | 19±1/17±4 | 110±20/41±9 | 26±2/32±7 | 12.5±0.5/12.0±0.3 | - |
| 9 | 78 | 22 | **2** | 396 | 3.2 | - | 10 | 53±6 | 18±3 | 700±100 | 10±1 | 11.0±0.5 | 300±30 |
| **$([N]/[E])_{feed}$ =4.8** | | | | | | | | | | | | | |
| 10 | 63 | 37 | **1+2** | 55 | 1.2 | 239 | 0.5 | 650±50 | 51±6 | 8±1 | - | - | - |
| 13 | 62 | 38 | **1+2** | 109 | 2.4 | 155 | 0.5 | 600±90 | 39±6 | 8.3±1.3 | - | - | - |
| 16 | 65 | 35 | **1+2** | 198 | 4.8 | 113 | 0.5 | 470±80 | 14±2 | 24±9 | 27±4 | 7.5±0.7 | - |
| **$([N]/[E])_{feed}$ =26** | | | | | | | | | | | | | |
| 19 | 49 | 51 | **1+2** | 56 | 2.8 | 99 | 0.5 | 900±100 | 25±4 | 2.3±0.5 | - | - | - |
| 20 | 36 | 64 | **1** | 140 | 2.8 | 146 | 0.1 | 600±100 | 20±4 | 4±1 | - | - | - |
| 23 | 40 | 60 | **1** | 275 | 5.5 | 54 | 0.5 | 500±100 | 13±3 | 5±2 | - | - | - |

a) The samples have been stretched at indicated values of deformation rate v/L

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