Electronic Supporting Information

for

Poly(propene-*co*-norbornene)s with high molar masses, tunable norbornene contents and properties, in high yield by ketimide-modified half-titanocene catalysts

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1. Experimental Section

Materials. All manipulations of air-sensitive compounds were performed under nitrogen using standard Schlenk-line and glove box techniques. Propene and nitrogen were purified by passage through BTS-catalysts and molecular sieves. Toluene was freshly distilled over Na prior to use. Norbornene (purchased from Aldrich) was distilled from Na and used as stock solution in toluene. Methylaluminoxane (MAO, 10 wt% solution in toluene, Merck Life Science Srl) was dried before use (50 °C, 3 h, 0.1 mm Hg) to remove solvent and unreacted trimethylaluminum (TMA). $CpTiCl_2(N{=}C^tBu_2)$ (**1**)[12] $Cp^*TiCl_2N{=}C^tBu_2$ (**2**) and $(Me_3SiC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**3**)[50,51] were prepared according to the reported procedure. $C_2D_2Cl_4$ was purchased from Merck KGaA and used as received.

Analytical Measurements. Microstructural analysis of the resultant polymers was conducted by NMR spectra (Bruker NMR Advance 400 instrument, 400 MHz, ^{1}H; 100.58 MHz, ^{13}C) under conditions of pulse angle = 12.50 μs, acquisition time = 0.94 s, and of delay = 16 s. Copolymer sample (ca. 100 mg) was dissolved in $C_2D_2Cl_4$ into a 10 mm NMR tube, and placed to the spectrometer (probehead preequilibrated at 103 °C). Chemical shifts were referenced to internal solvent resonance (5.86 ppm for ^1H) or hexamethyldisiloxane (HMDS, ^{13}C).

On the basis of the peak area of carbons in the ^{13}C-NMR spectra it was possible to estimate the content of norbornene and propene in the copolymers. The composition of poly(P-*co*-N) was calculated according to the following equations:[38]

$$N = \frac{I_{C_1/C_4}}{2} \quad (1)$$

Where N is the area of one norbornene carbon, I_{C_1/C_4} is the observed peak area between 37.7 and 42.8 ppm and

$$P = I_{CH_3} \quad \mathbf{(2)}$$

where P is the area of one propene carbon, I_{CH_3} is the observed peak area for propene methyl signals spanning from 12 to 20 ppm

$$\text{thus} \quad N\,(mol\,\%) = 100 * N/(N + P) \quad (3)$$

The number-average degree of polymerization, P_n, can be described as:[52]

$$P_n = \frac{M_n}{M_o}$$

in which M_0 and M_n are the molar mass of the monomer and the number-average molar mass, respectively. For a copolymer we assume that the weighted average of the monomer mass can be calculated according to the following relationship:

$$M_0 = x_P M_P + x_N M_N$$

where x_P and x_N are the molar fractions from NMR and M_P and M_N are the molar masses of propene and norbornene, respectively.

Differential scanning calorimetry (DSC) measurements of the copolymers were recorded by using a Perkin-Elmer Pyris 1 instrument in a temperature range from -50 to 250 °C using heating and cooling rates of 20 °C min^{-1}. In this heating scan, glass transition temperature (T_g) was chosen during the second scan, from the middle of the phase transition.

Molar masses (M_w) and molar mass distribution (M_w/M_n) for the prepared copolymer samples were analysed by high temperature size exclusion chromatography (SEC) (Waters, GPCV2000 high system), and the measurements were carried out in *o*-dichlorobenzene at 145 °C using a calibration curve with polystyrene standard samples.

The mechanical tensile tests were carried out by using a Zwick Roell ProLine Z010 dynamometer equipped with a XforceP (50 N) load cell at a crosshead speed of 30 $\text{mm}\cdot\text{min}^{-1}$ at room temperature. Dog-bone-shaped test specimens (thickness ca. 200 μm, length overall 75 mm, gauge length 25 mm, and width of narrow section 4 mm) were prepared by hot press as follows: i) pre-heating at 180 °C for 5 min without applying pressure; ii) moulding at 180 °C with a pressure of 50 bar for 5 min; iii) cooling by water at 20 °C min^{-1} to room temperature. The hysteresis tests (strain−stress curves, 10 cycles), elastic recovery experiments, were performed by successive stretching (loaded and unloaded) with 300% strain. The strain recovery (SR) was determined as $SR = 100(\varepsilon_a - \varepsilon_r)/\varepsilon_a$, where ε_a is the applied strain and ε_r is the strain in the cycle at zero load following the applied strain. For each material, at least five specimens were tested for tensile tests and two specimens for hysteresis experiments.

Preparation of the film sample for transparency test: the selected copolymer was fully dissolved in 1,1,2,2-tetrachloroethane at 100 °C, and the mixture was spread on a quartz glass in an oven at 100 °C for about 18 h. After the evaporation, the thickness of obtained film was measured about 20-30 μm. The transparency of the film is recorded on a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrophotometer.

Polymerization Procedure. Copolymerization reactions were carried out in a 250-mL scale Büchi stainless-steel autoclave equipped with a mechanical stirrer and with an external thermostatic bath associated to a temperature control unit for temperature regulation. Before starting the polymerization reaction, the reactor was evacuated for 120 min at 80 °C and filled with nitrogen. After cooling down to room temperature, the reactor was filled with toluene and with the solutions of norbornene and MAO in toluene, previously prepared. After thermal equilibration at 40 °C, the reactor system was saturated with propene to 4 bar. The reaction was initiated by injection of the precatalyst dissolved in toluene. The propene pressure was kept constant during the polymerization reaction. The copolymerization was quenched by addition of 2 mL of ethanol and hydrochloric acid, and precipitated in ethanol, to which a small amount of HCl had been added. The copolymer was left stirring overnight, collected by filtration and dried under vacuum at 70 °C to constant weight.

Chain End Analysis and ^{1}H NMR spectra

Poly(P-*co*-N)s synthesized by **1** and **3** based catalyst systems have higher molar masses than the corresponding poly(E-*co*-N) copolymers prepared with the same catalyst and with *ansa*-metallocenes. This is remarkable since alpha-olefins in general can give β-H elimination. Chain end analysis of copolymers could be useful to provide direct evidence for the reactions responsible for chain growth termination in a catalytic system. The amount of typical unsaturated end group signals, deriving from β-H transfer to the metal or to the monomer, indicates the possible chain transfer pathways.

Figures 1S-3S display the olefinic region of ^{1}H NMR spectra of poly(P-*co*-N), and those of poly(propene) prepared under identical polymerization conditions produced with catalysts **1**, **2** and **3**, respectively. Only the spectra of propene homopolymers show clear signals of chain end groups, despite PP homopolymers have very high molar masses. The spectra of poly(P-*co*-N)s only confirm the low tendency of the studied catalysts to give β-H eliminations.

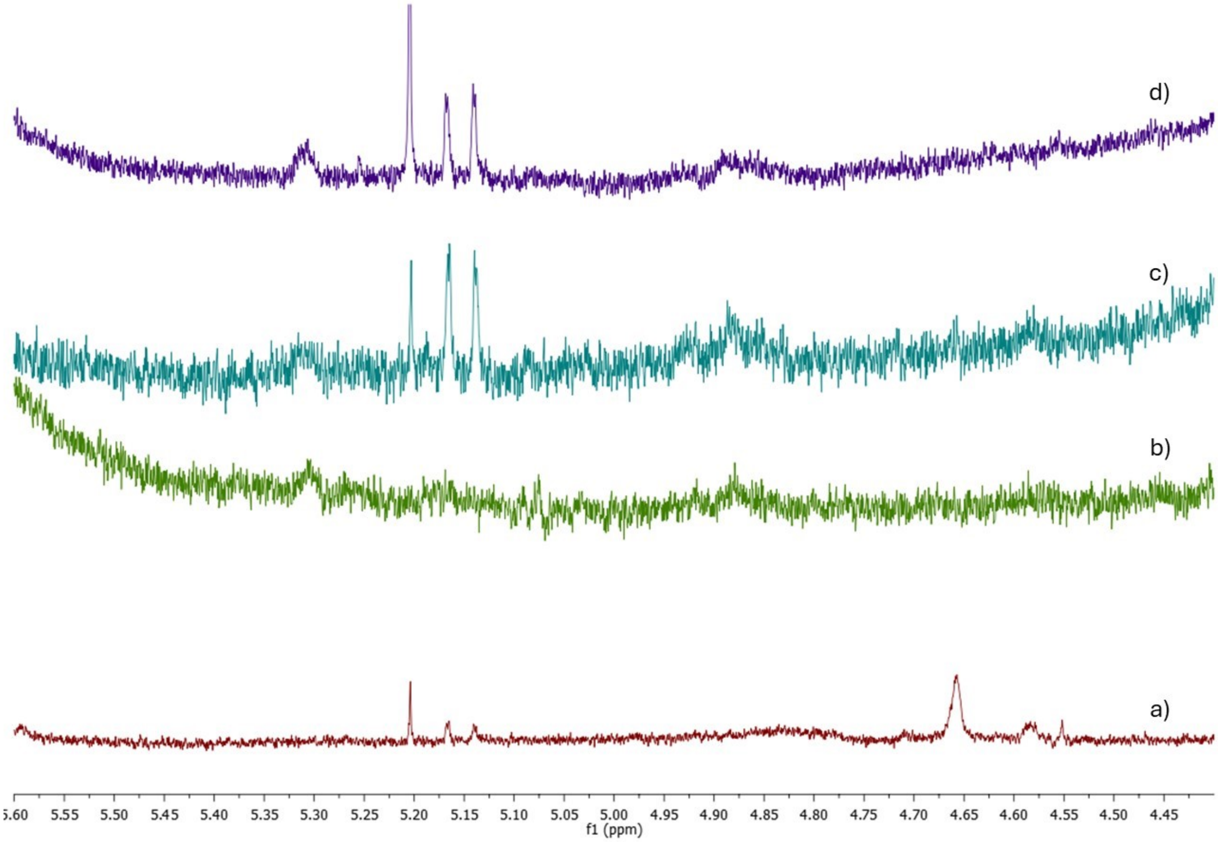

Figure 1S. Expansions of the region between 4.4 and 5.6 ppm of ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$, 103 °C) of polymers prepared by $CpTiCl_2(N{=}C^tBu_2)$ (**1**): a) polypropene (Table 1, entry 1); b) poly(P-*co*-N) (Table 1, entry 2); c) poly(P-*co*-N) (Table 1, entry 3); d) poly(P-*co*-N) (Table 1, entry 6).

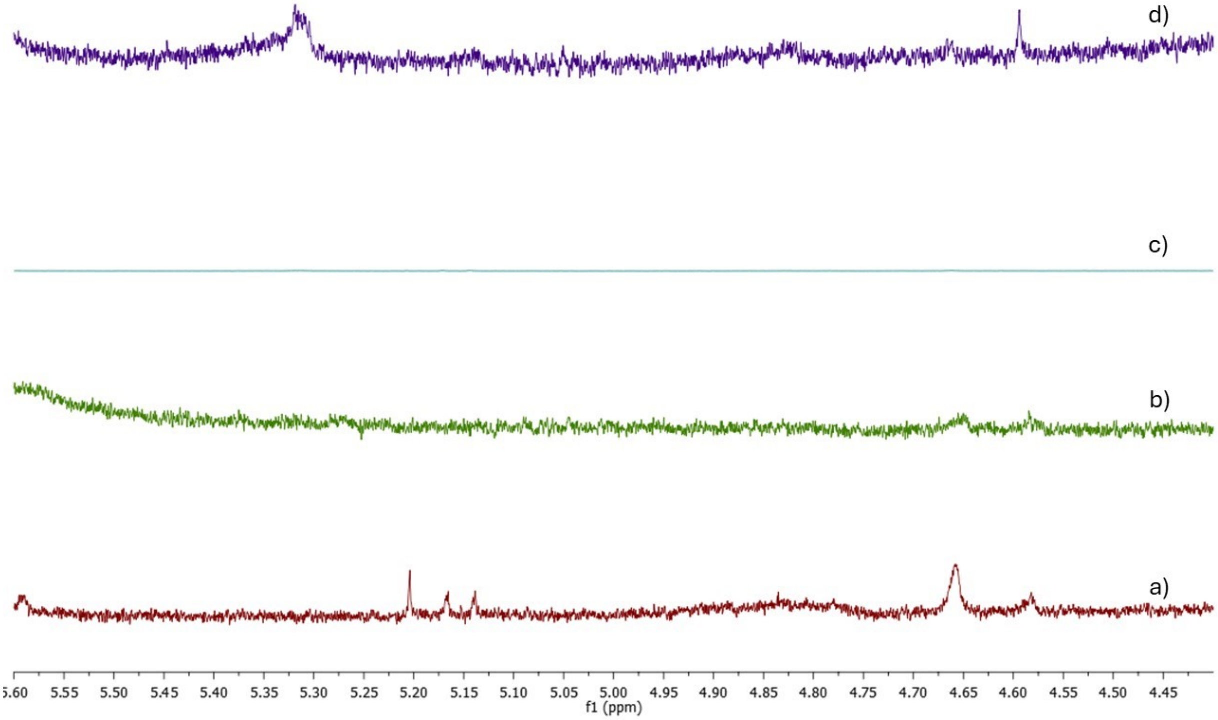

Figure 2S. Expansions of the region between 4.4 and 5.6 ppm of ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$, 103 °C) of polymers prepared by by Cp*TiCl$_2$(N=C^{t}Bu$_2$) (**2**): a) polypropene (Table 1, entry 7); b) poly(P-*co*-N) (Table 1, entry 8); c) poly(P-*co*-N) (Table 1, entry 9); d) poly(P-*co*-N) (Table 1, entry 10).

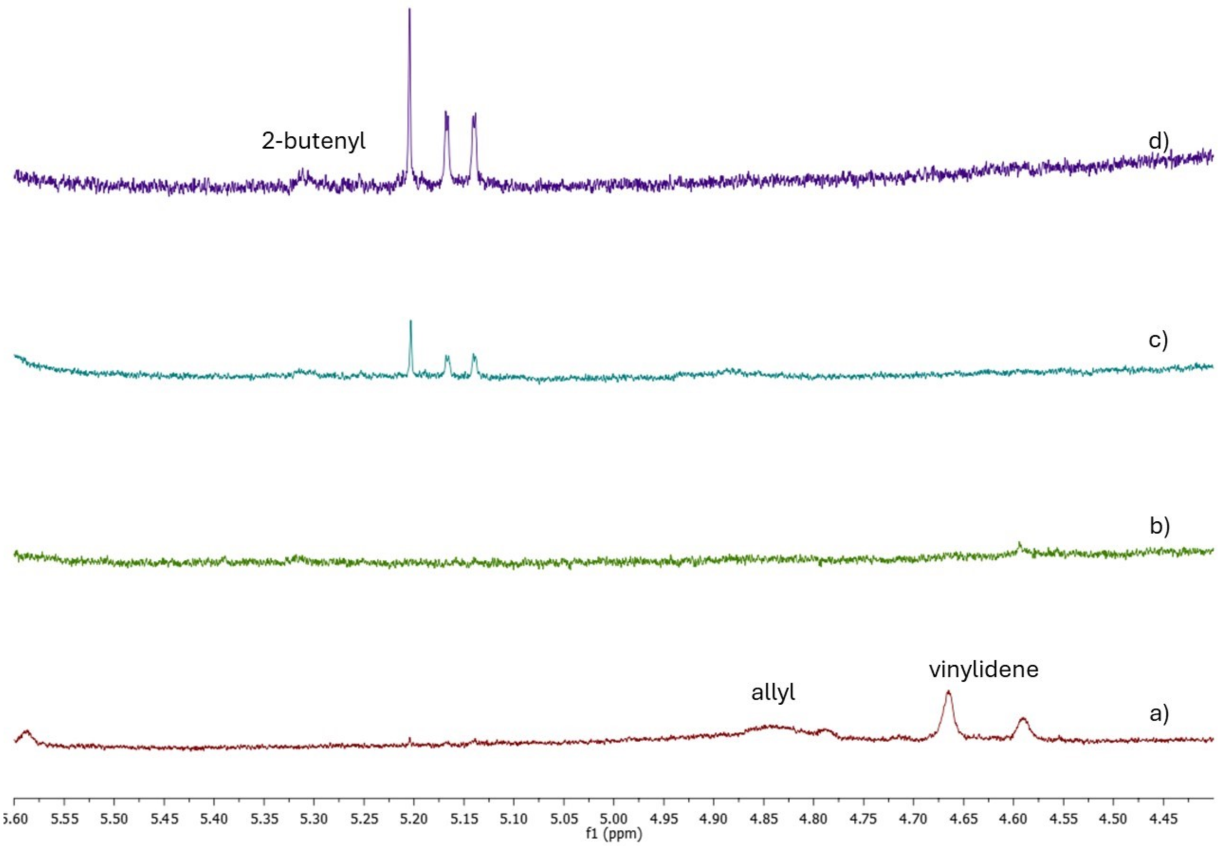

Figure 3S. Expansions of the region between 4.4 and 5.6 ppm of ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$, 103 °C) of polymers prepared by $Me_3SiCpTiCl_2(N{=}C^tBu_2)$ (**3**): a) polypropene (Table 1, entry 12); b) poly(P-*co*-N) (Table 1, entry 13); c) poly(P-*co*-N) (Table 1, entry 14); d) poly(P-*co*-N) (Table 1, entry 16).

2. DSC thermograms

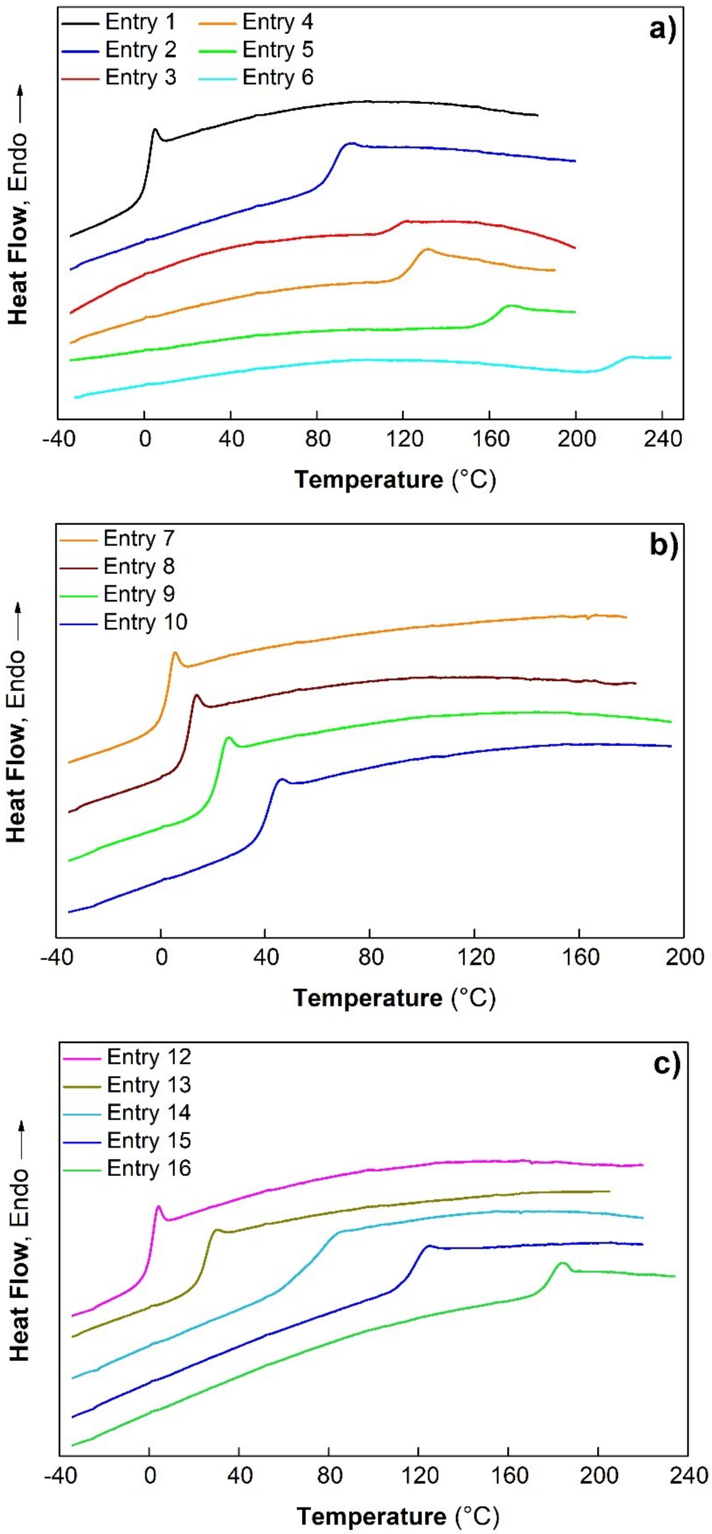

Figure 4S. DSC traces of: (a) polymers prepared by catalyst **1** (Table 1, entries 1–6), (b) polymers prepared by catalyst **2** (Table 1, entries 7–10) and (c) polymers prepared by catalyst **3** (Table 1, entries 12–16).

3. Stress-strain curves

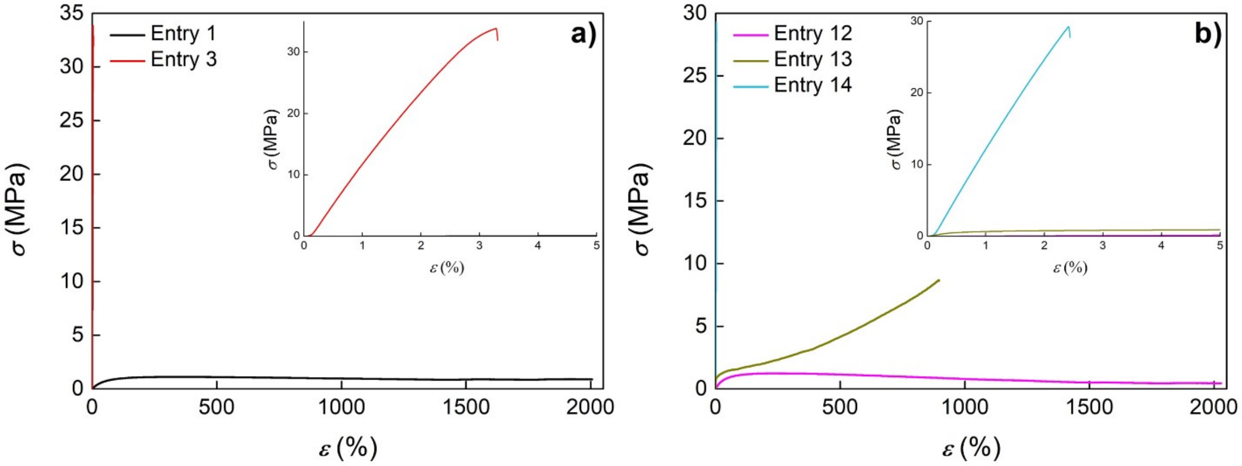

Figure 5S. Stress–strain curve in the uniaxial tensile test of polypropene and selected poly(P-*co*-N)s from catalyst **1** (a) and **3** (b).

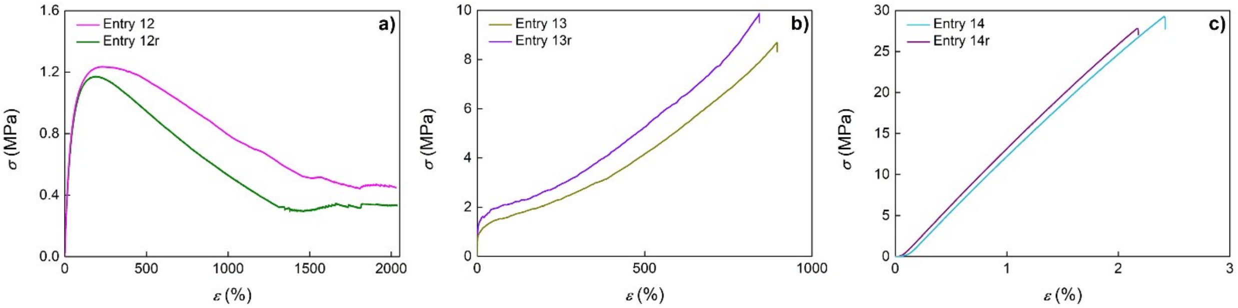

Figure 6S. Stress-strain curves of polypropene and selected poly(P-*co*-N) from catalyst **3** during monotonic tensile deformation: comparison between pristine and reprocessed samples: (a) Entry 12, (b) Entry 13 and (c) Entry 14.