Supporting Information

for

ω- dimethyl ammonium tetrakis-pentafluorophenyl borate polyisoprene as organic template for alkylated metallocenes toward the synthesis of polyethylene beads

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Materials and General Procedures. Isoprene, *sec*-butyllithium, diphenyl ethylene (DPE), dimethylaminopropyl chloride (DMAPC) and tri-isobutylaluminium (TIBA – 1M in hexane) were purchased from Aldrich. Heptane was dried over sodium/potassium and distilled under vacuum. Dichloromethane, DPE, DMAPC were dried over calcium hydride and distilled under vacuum. Isoprene was dried over di-*n*-butylmagnesium and distilled under vacuum and kept at 5°C. *Sec*-butyllithium was filtered prior to use. Ind_2ZrMe_2 and N,N-Dimethylanilinium tetra(pentafluorophenyl)borate were purchased from Strem and kept in a glovebox under argon atmosphere.

Instrumentation. Size exclusion chromatography (SEC) was performed in THF at 40 °C at a flow rate of 1 mL/min using a differential refractometer (Varian) and a UV-visible spectrophotometer (Varian) operating at 254 nm and 4 TSK columns (G5000HXL (9 μm), G4000HXL (6 μm), G3000HXL (6 μm), and G2000HXL (5 μm)). Calibration was performed using linear (1,4)-polyisoprene standards.

The PE average molecular weight (M_w) and dispersity (D) were determined using a Waters GPCV2000 SEC instrument, equipped with three columns PLgel Olexis Guard (300 × 7.5 mm), and an online viscometer and refractive index detector, at 150 °C in 1,2,4-trichlorobenzene as a solvent at a flow rate of 1 mL/min.

Dynamic light scattering (DLS) measurements were performed using an ALV Laser goniometer, which consists of a 22 mW HeNe linear polarized laser with 632.8 nm wavelength and an ALV-5000/ EPP multiple tau digital correlator with 125 ns initial sampling time. The samples were kept at constant temperature (30 °C) during all the experiments. The dispersions were introduced into 10 mm diameter glass cells. Dynamic light scattering measurements were evaluated by fitting the measured normalized time autocorrelation function of the scattered light intensity with the help of the constrained regularization algorithm (CONTIN). Dispersions used for light scattering were prepared as follow: the desired quantity of $[PI\text{-}NMe_2H]^+[B(C_6F_5)_4]^-$ was introduced in a schlenk with 0.5mL of dichloromethane. After 1/2h under stirring, heptane is quickly added. Data were collected over different concentration from 0.07 mg/mL to 0.15 mg/mL at 30°C.

MALDI-TOF analysis were performed on a Voyager (Applied Biosystems) equipped with a N_2 pulsed laser (337 nm). Matrix was 2-[(2*E*)-3-(4-*tert*-Butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB).

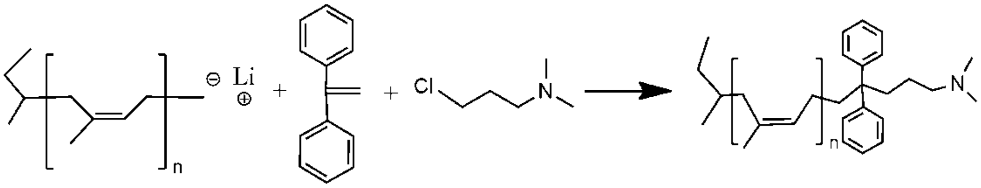
IR-TF spectra were collected thanks to a Brüker Tensor 27 device in attenuated total reflection mode (ATR) on a ZnSe crystal. The sample is dissolved in dichloromethane which was removed by flushing with azote.

Polymerization of ethylene. The desired quantity of $[PI\text{-}NMe_2H]^+[B(C_6F_5)_4]^-$ was introduced in a Schlenk tube with 1 mL of dry dichloromethane and 0.1 mL of TIBA as scavenger. The reactor mixture was stirred 1/2h at room temperature. The heptane was added and the solution was stirred 1/2h. The reaction mixture was then connected to a 1 bar ethylene gas outlet using a rubber tube. Schlenk tube was purged by ethylene for 20 minutes to remove argon. Polymerization was initiated by injection of the required amount of catalyst in toluene via a syringe. After 35 min of polymerization, the vessel was disconnected from the ethylene outlet, and the polymer was precipitated by addition of ethanol containing 10% HCl. The precipitated polymer was filtered, washed, and dried under vacuum to constant weight.

Synthesis of $[PI\text{-}NMe_2H]^+[B(C_6F_5)_4]^-$

Polyisoprene was chosen for its solubility in heptane and its synthesis achievable at room temperature in aliphatic solvent. A dry round bottom flask equipped with a magnetic stirrer was charged with 40 mL of cyclohexane, *sec*-butyllithium (1.67 mL; 0.002 mol) and isoprene (5.88 mL). After 2h of reaction, DPE (1.4 mL, 0.008 mol) was added to increase the polarity of the chain end in order to promote the self-assembly in heptane, to obtain a red coloration and to increase the functionalization yield.[1] After one night, DMAPC was added (0.8 mL, 0.006 mol) and let to react till the disappearance of the red color, to obtain a polyisoprene ω-dimethyl ammonium (PI-NMe_2) (Figure 1). The polymer was precipitated into an excess of methanol and finally dried under vacuum at room temperature. This PI-NMe_2 was then used to fix the borate activator by a quaternisation of the amine and ion exchange in a second step.[2]

Figure 1. Synthesis of PI-NMe_2 by anionic polymerization



Two PI-NMe_2 with different molecular weight, data are collected in Table 1.

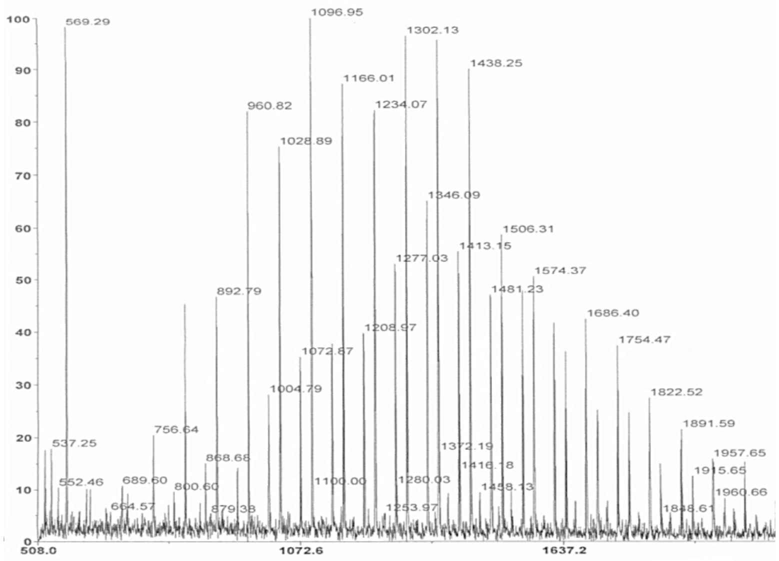
Table 1. Characteristics of PI-NMe_2 synthesized by anionic polymerization

Run	Name	M_n[a] (g/mol)	$Đ$[a]
1	PI_{15}-NMe_2	700	1.40
2	PI_{29}-NMe_2	1900	1.12

[a] Determined by SEC (THF, 1mL/min, detector Refractometer, calibration polyisoprene).

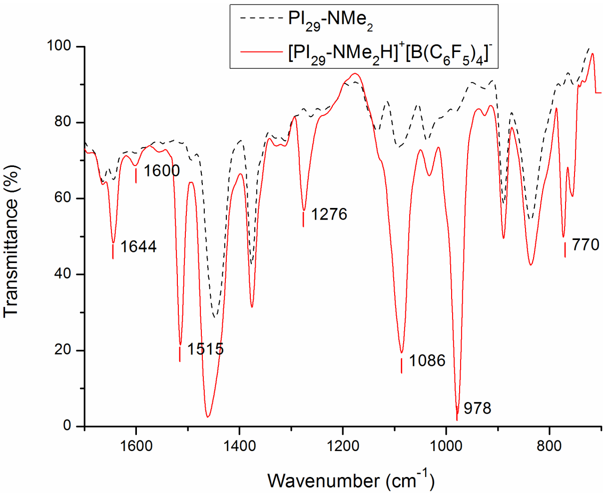
The functionalization with amine function was checked by MALDI-TOF analysis (Figure 2). Two populations are detected, the low molecular weight population corresponds to polyisoprene ω-dimethyl ammonium without DPE incorporated (Butyl (57 g/mol) + 15 isoprene units (15 x 68.11 g/mol) + DMAPC (86 g/mol) = 1164 g/mol) and a second with DPE incorporated. This incomplete incorporation of DPE comes from the slow kinetic of addition of DPE in aliphatic solvent. In all the runs, the polyisoprene was nearly 100% amine functionalized.

Figure 2. MALDI-TOF spectrum of PI_{15}-NMe_2 *(Matrix : DCTB)*



The second step was the anchorage of the borate activator through the amine PI chain-end. A dry round bottom flask equipped with a magnetic stirrer was charged with lyophilized PI-NMe_2 (0.8g, $6.15x10^{-4}$ mol) and N,N-dimethylanilinium tetra(pentafluorophenyl)borate (0.7395g, $9.23x10^{-4}$ mol) in glovebox. Dry dichloromethane was then introduced and the mixture was let under stirring for 2h. The dichloromethane was removed under vacuum and dry heptane was added to precipitate the unreacted salt. The solution was filtered under vacuum and the heptane removed under vacuum for 48h at room temperature. The functionalized PI was recovered and kept in glovebox. An analysis by FTIR allows to check the presence of the borate functions (Figure 3).

Figure 3. *IR spectra of* $[PI_{29}\text{-}NMe_2H]^+[B(C_6F_5)_4]^-$ *and* PI_{29}-NMe_2.



A comparison of the FTIR spectra, before and after functionalization, shows the presence of new bands attributed to –C=C- aryl bond (1644 cm^{-1}), N-H (1600 cm^{-1}, 1515 cm^{-1}, 772 cm^{-1}), C-N(1276 cm^{-1}, 978 cm^{-1}), C-F (1276 cm^{-1}, 1087 cm^{-1}). All these new bands agree with the presence of $B(C_6F_5)_4$ moiety. As extra quantity of the borate salt is removed by precipitation in heptane and filtration, the visible $B(C_6F_5)_4$ is then linked to the PI.

Figure 4. Photography of PE aggregates prepared with Ind_2ZrMe_2 without support (blank 1)

(1) Quirk, R. P.; Han, K.; Lee, Y. *Polymer International* **1999**, *48*, 99.
(2) Roscoe, S. B.; Gong, C.; Fréchet, J. M. J.; Walzer, J. F. *Journal of Polymer Science, Part A: Polymer Chemistry* **2000**, *38*, 2979.