Polymerization of Racemic *β*-Butyrolactone Using Supported Catalysts: A Simple Access to Isotactic Polymers

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Supporting information

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General considerations: Manipulations were carried out under an argon atmosphere in a glove-box or by using Schlenk techniques. Solvents were dried using conventional reagents and stored in the glove-box over 3A molecular sieves. Lanthanide borohydrides were prepared by following literature procedures.[1] Aerosil 380 silica (Degussa, specific area 380 m^2 g^{-1} prior heat-treatment) was subjected to heating under secondary vacuum (10^{-6} mmHg) at 500 °C over 15 hours followed by 4 hours of heating at 700 °C, and stored in a glove-box. Grafted neodymium silylamide $[(\equiv SiO)Nd\{N(SiMe_3)_2\}_2]$ was prepared according to reported procedure.[2] Liquid-state NMR analyses were run on a on a Bruker AC-500 spectrometer. Solid-state MAS NMR spectra were recorded on a Bruker Avance 400 spectrometer (^1H: 400.1 MHz, ^{13}C: 100.6 MHz, ^{11}B: 128.4 MHz) and Bruker Avance 800 (^1H: 800.13 MHz). For ^1H experiments, the spinning frequency was 20 kHz, the recycle delay was 5 s and 64 scans were collected using a 90° pulse excitation of 3 µs. The ^{13}C CP MAS experiment was obtained at a spinning frequency of 10 kHz, with a recycle delay of 5 s and 10240 scans were collected. For the CP step, a ramped radio frequency (RF) field centered at 50 kHz was applied on protons, while the carbon RF field was matched to obtain optimal signal. The contact time was set to 1 ms. For ^{11}B MAS experiment, the pulse length was set to 0.8µsec, with a recycling delay of 1.5 s and 36864 scans. Chemical shifts were given with respect to TMS and $NaBH_4$ as external references for ^1H-^{13}C (δ=0 ppm), and ^{11}B NMR (δ= -42.06 ppm), respectively. Diffuse reflectance infrared spectra were collected using a Harrick cell on a Nicolet Avatar spectrometer fitted with a MCT detector. This setup was also used for the DRIFTS follow-up of **SiO_2-3** heat-treatment under a helium flux. Elemental analyses were carried out at the Service Central d'Analyse du CNRS (metals and boron), and in the Service d'Analyse Elémentaire, LSEO, Université de Bourgogne (C, H). Size exclusion chromatography (SEC) of PHBs was performed in THF at 20°C using a Waters SIS HPLC pump, a Waters 410 refractometer, a DAD-UV detector and Waters styragel columns (HR2, HR3, HR4, HR5E) or PL-GEL Mixte B and 100A columns. The number average molecular masses (M_n) and polydispersity index (M_w/M_n) of the resultant polymers were calculated with reference to a polystyrene calibration.

Synthesis and characterization of SiO_2-2: In the glove-box, a double-Schlenk apparatus was loaded with the molecular precursor **2** (0.220 g, 0.55 mmol) dissolved in 20 mL toluene in one compartment, and with silica dehydroxylated at 700 °C (0.820 g) suspended in 15 mL toluene in the other compartment. The complex solution was added to the -50°C cooled SiO_2-700 suspension by filtering through the sintered glass separating the two Schlenk tubes. Immediate gas evolution was observed. The reaction mixture was left to warm up to room temperature and was stirred for 15 hours. The supernatant liquid was then separated by filtration into the other compartment, from which toluene was gas-phase transferred by trap-to-trap distillation back into the compartment containing the modified support in order to wash away the residual molecular precursor. This operation was repeated twice. The resulting white powder **SiO_2-2** was then dried under secondary vacuum at room temperature for 16 hours. Elemental analysis: w%(La)= 5.10, w%(B)= 0.88, w%(C)= 3.79, w%(H)= 0.79, w%(N)= 0. ^{1}H MAS NMR (800.1 MHz): 4.0 (α-CH_2 THF), 1.8 (β-CH_2 THF), 1.0 ($LaBH_4$). ^{13}C CP MAS NMR (100.6 MHz): 70.7 (α-CH_2 THF), 24.6 (β-CH_2 THF). ^{11}B NMR: 20– -7 (8%), -23.2 (92%). DRIFTS (cm^{-1}): 2988 (m), 2967 (w, shoulder), 2940 (w), 2900 (m), 2580 (w), 2566 (w), 2453 (s), 2279 (m), 2219 (s), 2151 (s), 1462 (m, sharp).

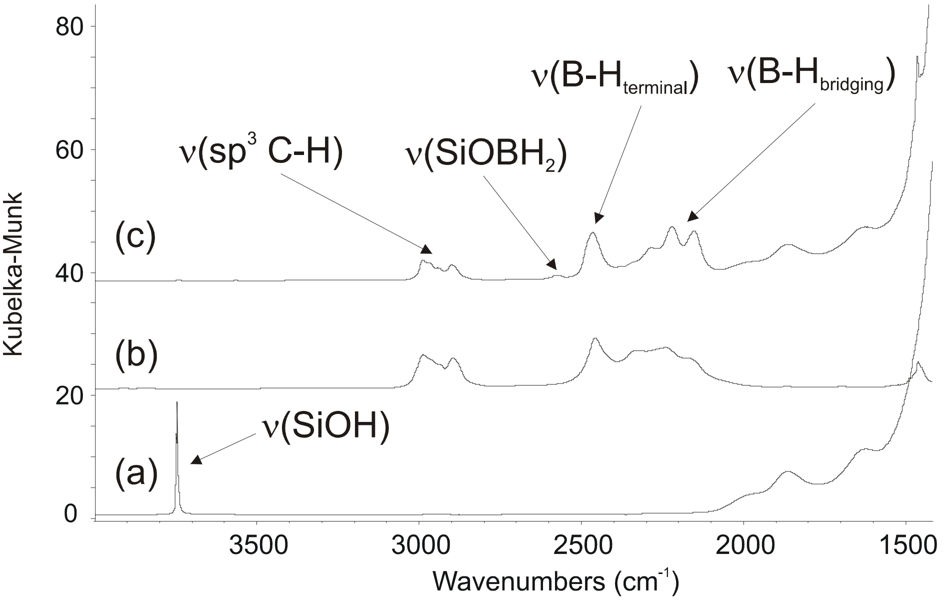

Figure S 1. Diffuse reflectance spectra of (a) SiO_2-700, (b) **2** and (c) **SiO_2-2**

^{1}H{^{11}B} MAS spectrum of SiO_2-2. It has been observed in some cases that the observed spectral linewidth could be strongly broadened by the presence of a scalar coupling with a quadrupolar nucleus. Therefore, in the present communication, we have performed a new type of decoupling sequence dedicated to quadrupolar nuclei.[3] Since ^{11}B is a quadrupolar nucleus, special care has been taken to apply the high power decoupling. In particular, the continuous wave (CW) decoupling was avoided because it tends to reintroduce some dipolar coupling, which might reduce the resolution. Figure S2. represents the ^{1}H MAS spectra without and with ^{11}B decoupling. We have used a decoupling sequence that is composed of a series of multiple pulses, slightly rotor asynchronized. The decoupling pulses are applied at a RF field strength of 80 kHz for 10 µsec, separated by a delay of 50 µsec. The MAS spinning speed was set to 20 kHz and a total of 16 transients were acquired.

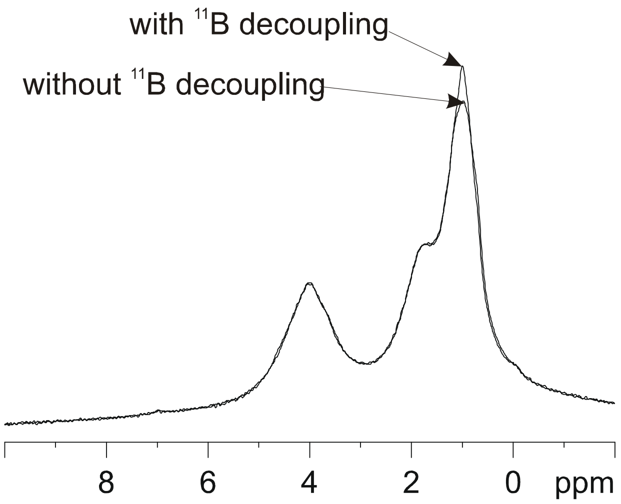

Figure S 2. ^{1}H MAS NMR spectra of **SiO$_2$-2** with and without ^{11}B decoupling.

Synthesis of SiO$_2$-3: In the glove-box, a double-Schlenk apparatus was loaded with the molecular precursor **3** (0.406 g, 1.0 mmol) dissolved in 20 mL toluene in one compartment, and with silica dehydroxylated at 700 °C (1.110 g) suspended in 20 mL toluene in the other compartment. The complex solution was added to the -50°C cooled SiO$_2$-700 suspension by filtering through the sintered glass separating the two Schlenk tubes. Immediate gas evolution was observed. The reaction mixture was left to warm up to room temperature and was stirred for 15 hours. The supernatant liquid was then separated by filtration into the other compartment, from which toluene was gas-phase transferred by trap-to-trap distillation back into the compartment containing the modified support in order to wash away the residual purple molecular precursor. This operation was repeated twice, as colorless washing fractions were obtained. The resulting white powder **SiO$_2$-3** was then dried under secondary vacuum at room temperature for 16 hours. w%(Nd)= 4.92, w%(B)= 0.81, w%(C)= 3.62, w%(N)= 0. ^{1}H MAS NMR (400.1 MHz): 0 ppm (broad). No other signal was detected in the 350 to -250 ppm range between 275 and 343 K. ^{11}B NMR (128.4 MHz): no signal detected between 400 and -350 ppm. DRIFTS (cm^{-1}): 2988 (m), 2962 (w, shoulder), 2936 (w), 2900 (m), 2580 (w), 2567 (w), 2463 (s), 2282 (m), 2218 (s), 2151 (s), 1461 (m, sharp).

Polymer Synthesis

In a typical experiment (Table 1, entry 2), in the glovebox, a silica-grafted amido complex was suspended in toluene. To this solution was added rapidly β-butyrolactone. The reaction solution was quickly removed from the glovebox and the mixture was immediately stirred at 20 °C. Conversion was monitored by comparing the relative magnitude of peaks corresponding to the methine hydrogen for BBL and PHB. After completion of the reaction, the mixture was quenched with acidic methanol (0.5

mL of a 1.2 M HCl solution in MeOH), and the polymer was precipitated with excess methanol (ca. 20 mL). The polymer was then dried under vacuum to constant weight.

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2. R.M. Gauvin, L. Delevoye, R. Ali Hassan, J. Keldenich, A. Mortreux, *Inorg. Chem.* **2007**, *46*, 1062-1070.
3. L. Delevoye, J. Trébosc, Z. Gan, L. Montagne, J.-P. Amoureux, *J. Magn. Reson.* **2007**, *186*, 94-99.