

Supporting Information

New Method for the Synthesis of Fully Aliphatic Telechelic α,ω -Dihydroxy-Polyisobutylene

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Synthesis of Initiators

3 different initiators were employed for the synthesis of PIBs, reported in the literature: 2,4,4,6-tetramethylheptane-2,6-diol (TMHDI_{OH}), 2,6-dimethoxy-2,4,4,6-tetramethylheptane (TMHDI_{OMe}), and a new initiator: 2,6-dichloro-2,4,4,6-tetramethylheptane (TMHDI_{Cl}) in the presence of TiCl₄ coinitiator.

i. *Dimethyl 3,3-dimethylpentanedioate (DiMDiPD)*

DiMDiPD was prepared by refluxing a mixture of 3,3-dimethyl glutaric acid (100 g, 0.62 mol) with anhydrous methanol (2.5 L, 78 mol) and 125 ml concentrated sulfuric acid under reflux for 48 h. The mixture was cooled to room temperature and the methanol was removed by roto-evaporation. Re-dissolved with 500 mL of hexane and washed with NaHCO₃ solution (100 mL * 5) and then with water several times until the waste water was acid free. The solution was dried with anhydrous magnesium sulfate, filtered, and the solvent was removed. After that slightly yellow oil was recovered (yield 89 g, 76% conversion). The product was passed through an alumina column (30 g), clear oil was obtained. The ester product was dried using 3 freeze pump-thaw cycles. ¹H NMR (300 MHz, CDCl₃) δ ppm 1.07 (s, 6 H), 2.34 (s, 4 H), 3.57 (s, 6 H).

^{13}C NMR (75 MHz, CDCl_3) δ ppm 27.55 (CH_3), 32.39 (C), 44.74 (CH_2), 51.12 (OCH_3), 172.16 (C=O).

ii. *2,4,4,6-tetramethylheptane-2,6-diol (TMHDIOL)*

To a solution of *DiMDiPD* (60 g, 0.24 mol) of in 200 ml ethyl ether under a blanket of N_2 were added dropwise methylmagnesium bromide in ethyl ether (237 ml, 0.71 mol, 3.0 mol/L) and stirred for 15 h at $< 5^\circ\text{C}$. Then the charge was slowly added to a 35 g NH_4Cl -400 g ice mixture under stirring and leave to react for 5 h. The system was extracted with ethyl ether while the pH of the aqueous phase is around 7. The extract was washed with water, dried over anhydrous magnesium sulfate overnight. The product was passed through a column packed with carbon black (40 g). After that the ether is removed by roto-evaporation and crystallization with ethyl acetate help to recover the product (yield 33 g, 53% conversion). ^1H NMR (300 MHz, CDCl_3) δ ppm 1.07 (s, 6 H), 1.27 (s, 12 H), 1.73 (s, 4 H), 3.54 (s, 2 H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 33.12 (C), 33.71 (CH_3), 33.45 (CH_3), 51.46 (CH_2), 72.36 (C).

iii. *2,6-dimethoxy-2,4,4,6-tetramethylheptane (TMHDIOMe)*

Inside the dry box: TMHDIOL (16 g, 0.085 mol) was dissolved in 20 mL of freshly distilled, anhydrous THF and poured into an air-free addition funnel. NaH (8.1 g, 0.34 mol) was added in a 500 mL, 3-necked, round-bottom flask equipped with a stirrer and 80 mL of THF was added to the reaction flask rinsing the funnel used to transfer the NaH to the reactor. The reactor was sealed inside the dry box under Nitrogen atmosphere. The reactor and the air-free addition funnel that contained the alcohol intermediate were transferred to the hood. Distilled MeI (85 mL, 0.60 mmol) was transferred to an addition funnel under inert atmosphere and the walls of the funnel were rinsed with 5 mL of THF.

In the fume hood: The reactor and the air free addition funnel that contained the alcohol intermediate were connected together. The setup was flashed with vacuum and then with N₂ in order to make sure that no moisture was present. The reactor was cooled below -20 °C using hexane / dry ice bath. At - 20 °C, the dissolved alcohol intermediate was added dropwise over 30 minutes to the reactor under N₂ atmosphere. The reaction was stirred for 68 minutes. The temperature of the reaction was always maintained below -10 °C and under N₂ flow. An outlet was introduced to the reactor to prevent pressure build-up. The MeI/THF mixture was added drop-wise over 40 minutes to the reactor below -20 °C under N₂ flow. Gas evolution was monitored, by closing the N₂ gas for short periods (around 1 min). The reaction was allowed to continue for 156 minutes under N₂ flow, continuously monitoring the evolution of gas of the reaction in every 15 minutes. Then, 100 mL of heptane were added to the reactor. The reaction mixture was removed from the cold bath and allowed to come slowly to room temperature. The product was extracted with hexane, dried using MgSO₄ and the solvent was removed using roto-evaporation (T=35°C). TLC was performed over alumina plate using Hexane:ethyl acetate (5:1) eluent system which revealed one spots under UV (254 nm) lamp. The R_f value of the crude was compared with the starting alcohol. The comparison indicated that alcohol was not present in the product. Column with alumina was packed with a system of Hexane: Ethyl acetate (5:1). (yield: 14.5 g, 87% conversion).

iv. *2,6-dichloro-2,4,4,6-tetramethylheptane (TMHDiCl)*

NaCl (13 g, 0.44 mol) was placed into a 100 mL, three-necked, round-bottom flask. Concentrated sulfuric acid (12 mL, 0.44 mol) was added to the NaCl very slowly from a dropping funnel to form HCl gas. The HCl gas was bubbled into a solution of TMHDiOH (2.0 g,

0.011 mol, 0.70 mol/L) with 15 mL of CH_2Cl_2 in a 50 mL tube which was kept in an ice-water bath. The reaction flask was connected to a trap and another flask containing sodium hydroxide solution to neutralize the unreacted acid. The reaction was conducted at 0°C for 5 hours. Thin Layer chromatography was checked to follow the reaction progress, in a system of hexane: ethyl acetate (5:1 v/v). After completion of the reaction, $\text{TMHDI}(\text{Cl})$ was neutralized by the slow addition of sodium bicarbonate. The solution was filtered and the solvent was removed under vacuum (not heating). The product was purified using a column packed on alumina and a system of hexane: ethyl acetate (5:1). (yield 2.3 g, 100% conversion). ^1H NMR (300 MHz, CDCl_3) δ ppm 1.25 (s, 6 H), 1.69 (s, 12 H), 2.03 (s, 4 H). ^{13}C NMR (75 MHz, CDCl_3) δ ppm 29.64 (CH_3), 35.23 (CH_3), 37.09 (C), 57.47 (CH_2), 71.10 (C).