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Supporting Information

Polyisobutylene oligomer-bound polyoxometalates as efficient and recyclable catalysts for biphasic oxidations with hydrogen peroxide

Rana Yahya,[a] Michael Craven,[a] Elena F. Kozhevnikova,[a] Alexander Steiner,[a] Peerada Samunual,[b] Ivan V. Kozhevnikov,[a]* and David E. Bergbreiter[b]*

Chemicals

Dibenzothiophene (98%), cis-cyclooctene (95%), heptane (99%), dodecane (99%), 30% H_2O_2 and heteropoly acid hydrates $H_3PW_{12}O_{40}$ (99%), $H_3PMo_{12}O_{40}$ (99.9%) and $H_4SiW_{12}O_{40}$ (99.9%) containing approximately 20 H_2O molecules per Keggin unit were purchased from Sigma-Aldrich. The amount of crystallization water in heteropoly acids was determined by TGA. Diethylamine terminated PIB_{1000} (PIB_{1000}-$CH_2N(CH_2CH_3)_2$) and its quaternary salt (PIB_{1000}-$CH_2N(CH_2CH_3)_2CH_3^+I^-$) were synthesized from commercially available[1] PIB_{1000} by a sequence using ozonolysis, a haloform reaction, amidation, reduction, and alkylation with CH_3I (see below for experimental details). The products were in the form of viscous oils and used most conveniently as a 0.5 M solution in heptane (based on the terminal amine functionality as measured by end group analysis by ^1H NMR spectroscopy).

Two-phase oxidation reactions

Oxidation of DBT and epoxidation of cyclooctene were carried out in a two-phase system containing heptane as an organic solvent and aqueous H_2O_2 at 25-60 °C in a 50-mL glass reactor equipped with a magnetic stirrer, a reflux condenser and a heat circulator. In a typical run, heptane (10 mL), dodecane (GC internal standard), diethylamine terminated PIB, aqueous H_2O_2 and heteropoly acid in specified quantities were added into the reactor. Once the reactor was heated to the required temperature, the substrate (DBT or cyclooctene), was added to start the reaction. DBT oxidation was carried out at a DBT/H_2O_2 molar ration of 1:3, which is typical of this reaction.[1] Alkene epoxidation with H_2O_2 is usually carried out at a large excess of alkene over H_2O_2 to increase reaction selectivity and H_2O_2 efficiency.[2] For these reasons and also in order to determine accurately reaction rates, a ten-fold excess of cyclooctene over H_2O_2 was applied in the epoxidation reaction. Both reactions were carried out at a stirring speed of 1000 rpm; at stirring speeds above 500 rpm, the reaction rate did not depend on the stirring speed. Blank experiments showed that no reaction occurred in the absence of POM, and practically no reaction was observed in the presence of POM without PIB. The reactions were monitored by taking aliquots from the organic phase and submitting them to GC analysis (Varian CP-3380 gas chromatograph equipped with FID and a 25 m × 0.32 mm × 0.5 μm BP1 capillary column) to determine substrate conversion and product yield. After reaction, the amount of remaining H_2O_2 was determined by titration with $KMnO_4$ for the efficiency of hydrogen peroxide use to be estimated.

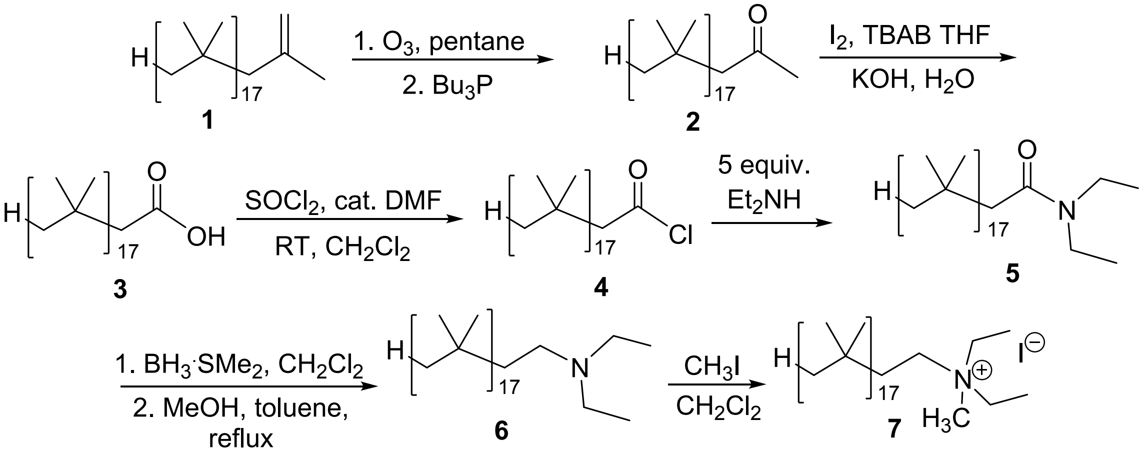
Catalyst reuse in DBT oxidation was carried out as follows. After each run, DBT sulfone was extracted by MeCN and fresh DBT and 30% H_2O_2 were added. After that the reaction was repeated as described above. In cyclooctene epoxidation the catalyst was separated by complete evaporation of the reaction mixture, washed with methanol and reused. Similar procedure for alkene epoxidation was employed by K. Kamata et al.[2]

UV-Vis study of POM phase transfer

For UV-Vis study of PW phase transfer facilitated by PIB, PW (0.648 µmol, 2 mg), H_2O (3 mL) and PIB_{1000}-$CH_2N(CH_2CH_3)_2$ in heptane (10 mL) were added to a stoppered test tube and shaken vigorously at room temperature (~20 °C). The mixture was then left to settle for 2 h at room temperature. An aliquot of the organic phase was taken, spun in a centrifuge and analysed via UV-Vis spectrophotometry (CARY 50 Probe UV-Vis spectrometer) at 275 nm.

Synthesis and characterization of amine terminated polyisobutylene oligomers

Synthetic schemes, experimental procedures, and ^1H and ^{13}C data for the synthesis of polyisobutylene (PIB) with a terminal amine group (**6**, $PIB_{1000}CH_2CH_2N(CH_2CH_3)_2$ and with a terminal trialkylammonium group (**7**, $PIB_{1000}CH_2CH_2N(CH_2CH_3)_2CH_3^+I^-$) are provided in the discussion below.



Scheme 1. Synthesis of a PIB_{1000}-amine and PIB_{1000}-quaternary ammonium salt.

General Procedures

^1H NMR spectra were obtained using Varian Inova 300, Mercury 300, AvanceIII 400, or Varian Inova 500 spectrometers at 300 MHz, 400 MHz, or 500 MHz. ^{13}C NMR spectra were obtained using Varian Inova 300, Mercury 300, AvanceIII 400, or Varian Inova 500 spectrometers at 75 MHz, 100 MHz or 125 MHz. The spectra were calibrated using residual non-deuterated solvent as an internal reference (e.g. $CDCl_3$: ^1H NMR = δ 7.27 ppm; ^{13}C NMR = δ 77.2 ppm).

Vinyl-terminated PIB_{1000} (1). Vinyl-terminated PIB_{1000} (Glissopal 1000) was obtained from BASF. This commercial sample, which contains some saturated PIB and a small amount of alkene isomer, was used without further purification.[3]

PIB_{1000}-$COCH_3$ (2). The starting vinyl-terminated PIB_{1000} (40.29 g, 40.29 mmol) Glissopal 1000)[3] was dissolved in 200 mL of pentane. The resulting solution was cooled in an acetone-dry ice bath and was purged with oxygen for 10 min. Ozone was bubbled into the reaction mixture until the solution turned blue. Then the reaction mixture was purged with oxygen again to remove excess ozone from the solution until the solution became colorless. To reduce the ozonide, tributylphosphine (20 mL, 80 mmol) was added to the reaction mixture. The reaction mixture was stirred at room temperature under nitrogen for 24 h to complete this reaction. At this point, the reaction mixture was tested for peroxides with Baker Testrips. The solution was concentrated by removing pentane under reduced pressure only after the test was negative. The resulting mixture was dissolved in 200 mL of hexane, which was washed with 90% EtOH (4 x 50 mL) and brine (1 x 50mL). The organic phase was dried over anhydrous sodium sulfate and filtered. Hexane was removed under reduced pressure, and the crude product was purified with silica gel column chromatography to obtain an isolated yield of 90% (36.40 g, 36 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.00-1.49 (m, 220 H), 2.12 (s, 3 H), 2.44 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: multiple peaks between 30.0 and 38.4, multiple peaks between 56.1-59.8, 209.0.

PIB-COOH$_{1000}$ (3). PIB$_{1000}$-$COCH_3$ (2) (19.91 g, 19.91 mmol) was dissolved in 600 mL of THF. Iodine (19.20 g, 75.65 mmol) was added into the reaction mixture, followed by a solution of KOH (70.53 g, 1.07 mol) in 600 mL of deionized water. Tetrabutylammonium bromide (TBAB) (4.56 g, 14.15 mmol) was added into the reaction mixture and the resulting biphasic mixture was stirred for 48 h under nitrogen. After the iodoform reaction was complete, the aqueous layer was removed by extraction and THF was removed under reduced pressure. The crude product was dissolved in 150 mL of hexanes and this hexane solution was washed with 6 M HCl (2 x 40 mL), 90% EtOH (4 x 40 mL), and brine (1 x 40 mL). The organic phase was dried over anhydrous sodium sulfate and filtered and the solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography to afford an isolated yield of 79% (15.66 g, 15.59 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.01-1.52 (m, 211 H), 2.35 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: multiple peaks between 28.2 and 60.0, 178.8.

PIB$_{1000}$-COCl (4). PIB$_{1000}$-COOH (4.25 g, 4.23 mmol) was dissolved in 40 mL of dichloromethane. Thionyl chloride (1 mL, 13.77 mmol) and a catalytic amount of DMF (8 drops) were added and the reaction was stirred at room temperature under nitrogen for 24 h. The solvent was then removed under reduced pressure. The crude PIB$_{1000}$-COCl was used without further purification.

PIB$_{1000}$-CON(CH_2CH_3)$_2$ (5). PIB$_{1000}$-COCl (4.25 g, 4.16 mmol) was dissolved in 40 mL of dichloromethane. Diethylamine (2.50 mL, 21.28 mmol) was added into the solution, which was stirred at room temperature for 24 h. After the reaction was complete, the solvent was removed under reduced pressure. The viscous oil residue was dissolved in 80 mL of hexanes and this hexane solution was washed first with 90% EtOH (4 x 40 mL) and then brine (1 x 40 mL). The organic phase was dried with anhydrous sodium sulfate, filtered, and the solvent was removed by reduced pressure. The isolated yield of the amide product was 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.00-1.53 (m, 200 H), 2.28 (s, 2 H), 3.33-3.38 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.4, 14.6, multiple peaks between 30.1 and 45.7, multiple peaks between 57.0-59.8, 171.3.

PIB_{1000}-$CH_2N(CH_2CH_3)_2$ (6). PIB_{1000}-$CON(CH_2CH_3)_2$ (21.46 g, 20.26 mmol) was dissolved in 200 mL of dichloromethane. The solution was placed under nitrogen for 15 min at which point 10 M $BH_3{\cdot}SMe_2$ (10.73 mL, 107.3 mmol) was added. The reaction was stirred at room temperature for 24 h. After the reaction was complete, solvent was removed under reduced pressure. The viscous residue was dissolved in 200 mL of toluene. Then 20 mL of methanol was added and the solution was stirred under reflux for 24 h to form trimethylborane. At this point, toluene was removed under reduced pressure and 150 mL of hexanes was used to dissolve the crude **6.** The hexane solution was washed with 90% EtOH (4 x 50 mL) and brine (1 x 50 mL), dried with anhydrous sodium sulfate, filtered, and the solvent was removed under reduced pressure.

Two methods were used to purify PIB_{1000}-$CH_2N(CH_2CH_3)_2$. First, the amine could be purified using column chromatography (Brockmann aluminum oxide). Alternatively, a sequestration/release method we developed earlier using Amberlyst 15 could be used.[4] In this latter method, the crude amine (17.19 g, 16.45 mmol) was dissolved in 160 mL of dichloromethane. The Amberlyst 15 (22.3 g, 0.104 mol eq.) was added. This suspension was then shaken for 24 h. At this point, the Amberlyst-bound ammonium salt formed by an acid-base reaction was isolated by filtration and washed successfully with hexane, acetonitrile, and dichloromethane. The Amberlyst species was then placed in a flask with 160 mL of dichloromethane and treated with triethylamine (40 mL, 0.28 mol). The mixture was again shaken for 24 h. The triethylammonium salt on Amberlyst 15 was then removed from the solution of **6** by filtration. Dichloromethane were removed under reduced pressure using rotary evaporator. To insure that all the triethylamine was removed, the viscous oil product was dissolved with 150 mL of hexane and washed with 90% EtOH (4 x 50 mL) and brine (1 x 50 mL). The hexane solution was then dried with anhydrous sodium sulfate, filtered, and the solvent was removed by reduced pressure to afford the amine **6**. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.00-1.50 (m, 190 H), 2.52 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 11.8, multiple peaks between 30.0 and 38.2, 46.9, 48.17, multiple peaks between 56.0-59.5.

PIB_{1000}-$CH_2N(CH_2CH_3)_2CH_3I$ (7). PIB_{1000}-$CH_2N(CH_2CH_3)_2$ (3.6 g, 3.44 mmol) was dissolved in 30 mL of dichloromethane. Iodomethane (0.325 mL, 5.27 mmol) was added and the reaction solution was stirred at room temperature overnight. Dichloromethane was removed from the product ammonium salt by reduced pressure and the crude product was purified by aluminum oxide column chromatography to afford the ammonium salt **7**. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.00-1.56 (m, 221 H), 3.30 (s, 3 H), 3.35 (m, 2 H), 3.60 (m, 2 H), 3.73 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 8.4, multiple peaks between 28.9 and 38.1, 48.3, multiple peaks between 56.6 and 59.5.

References

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3. http://www.performancechemicals.basf.com/ev/internet/polyisobutene/en/content/EV3/polyisobutene/glissopal (accessed August 26, 2014).
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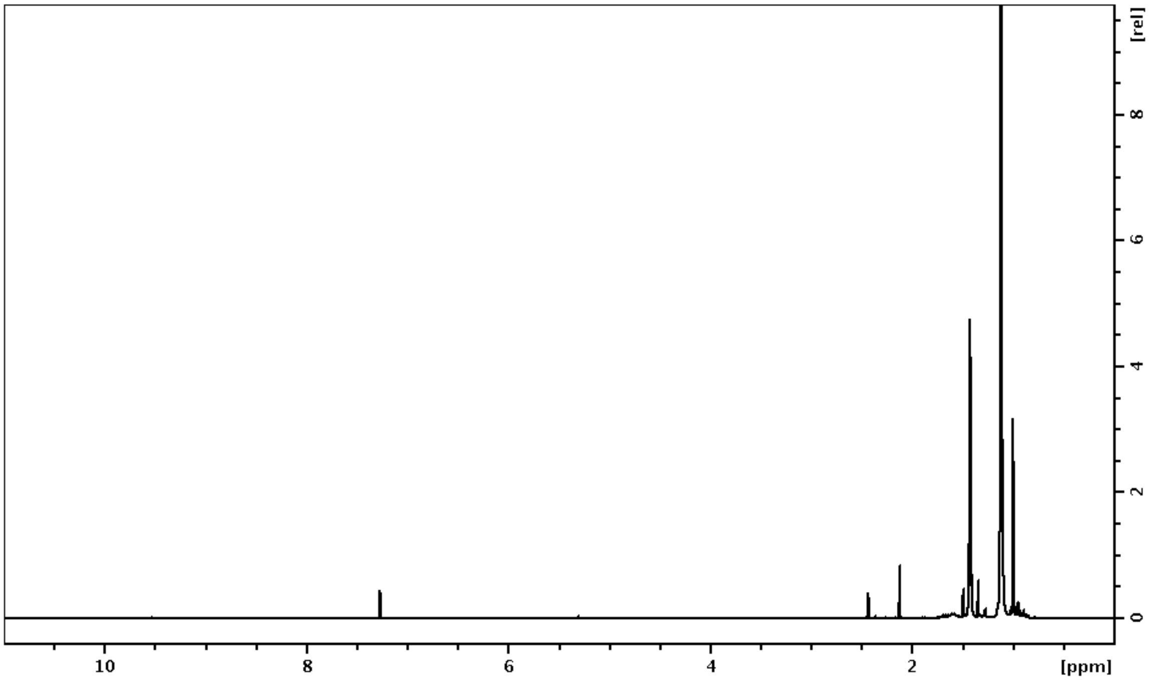
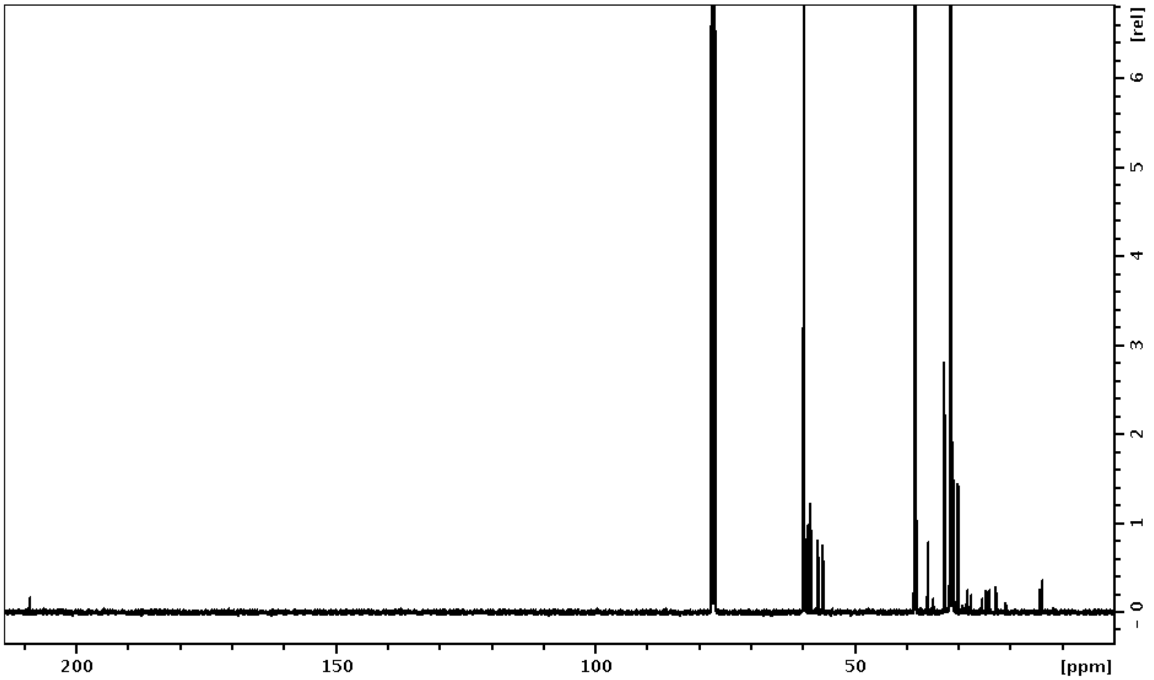
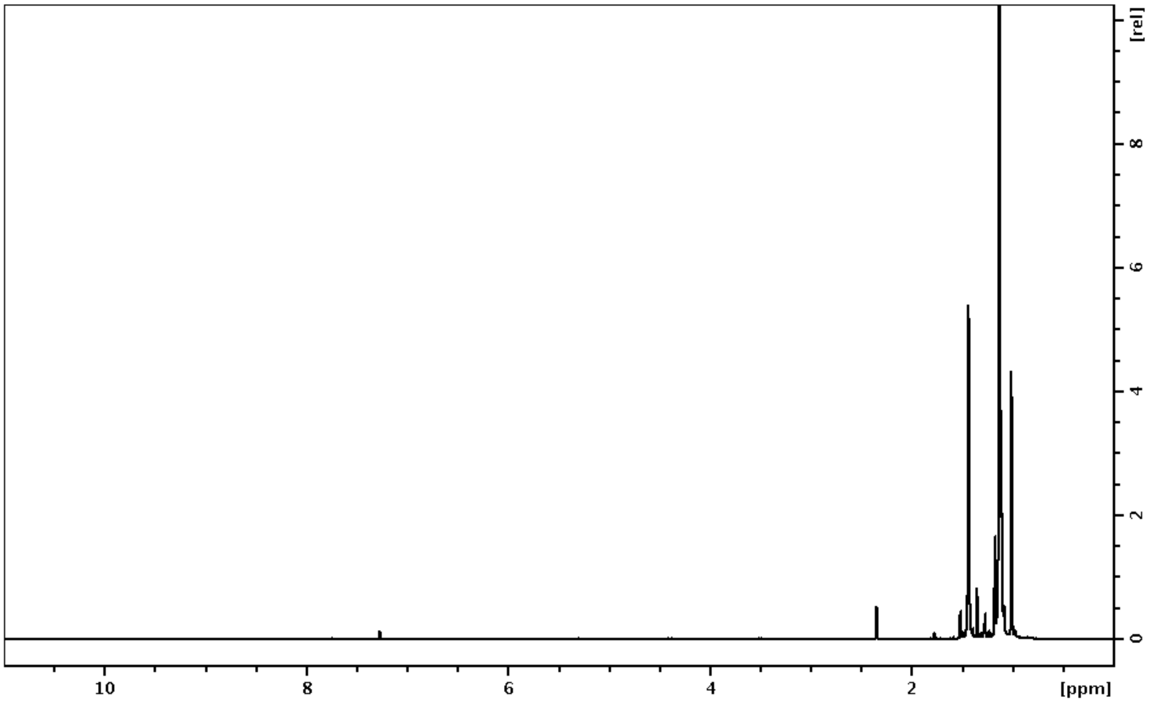
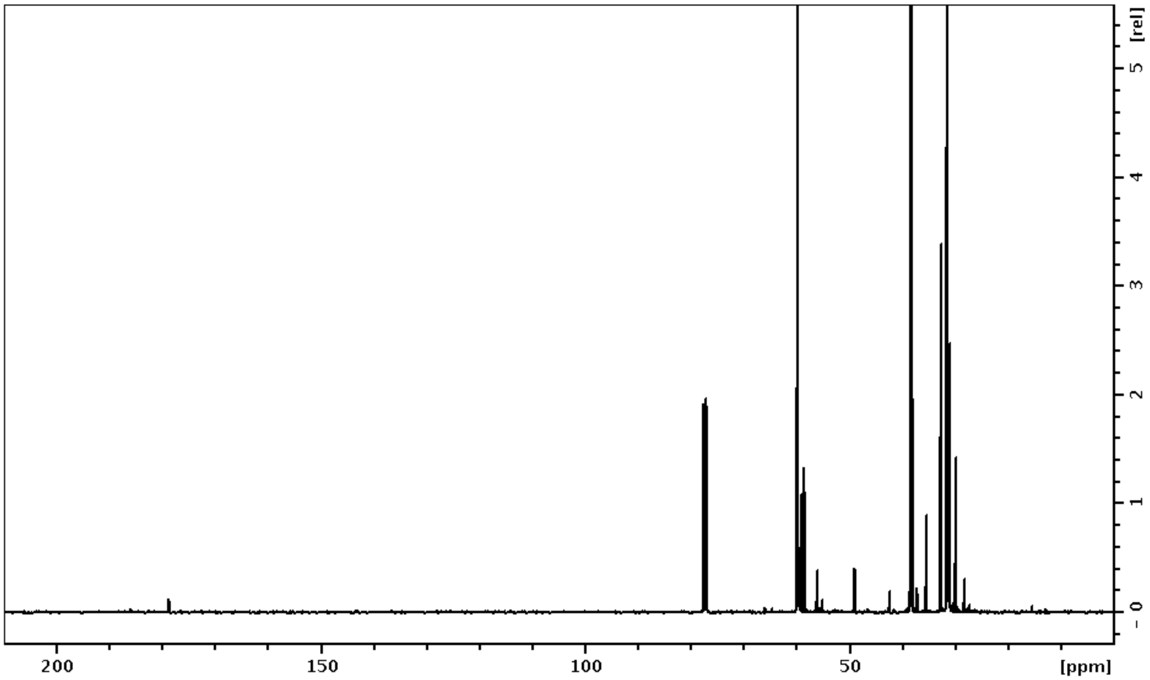
PIB$_{1000}$-COCH$_3$ (2) ^{1}H and ^{13}C NMR spectra (CDCl$_3$)



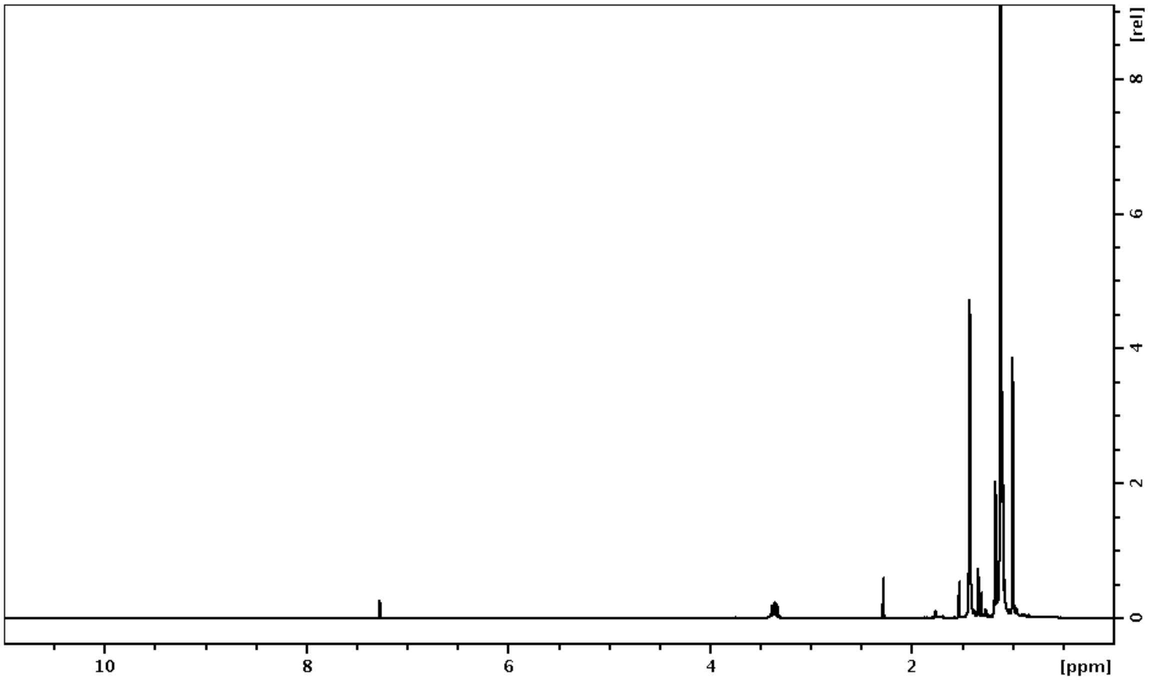


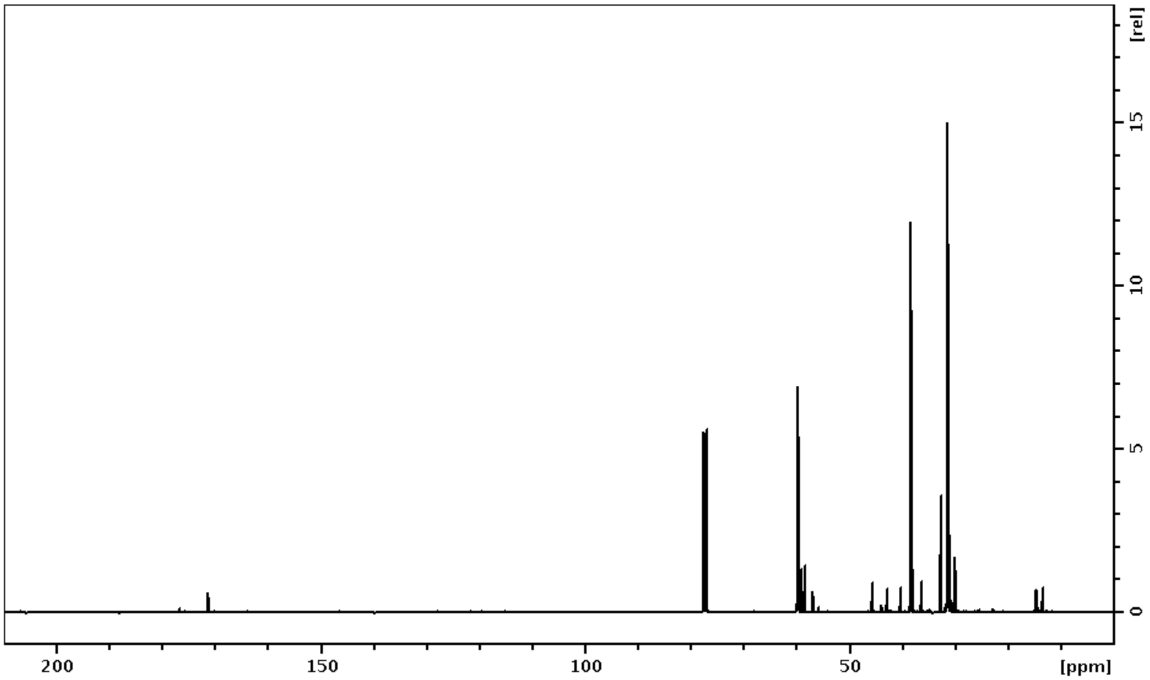
PIB$_{1000}$-COOH (3) ^{1}H and ^{13}C NMR spectra (CDCl$_3$)



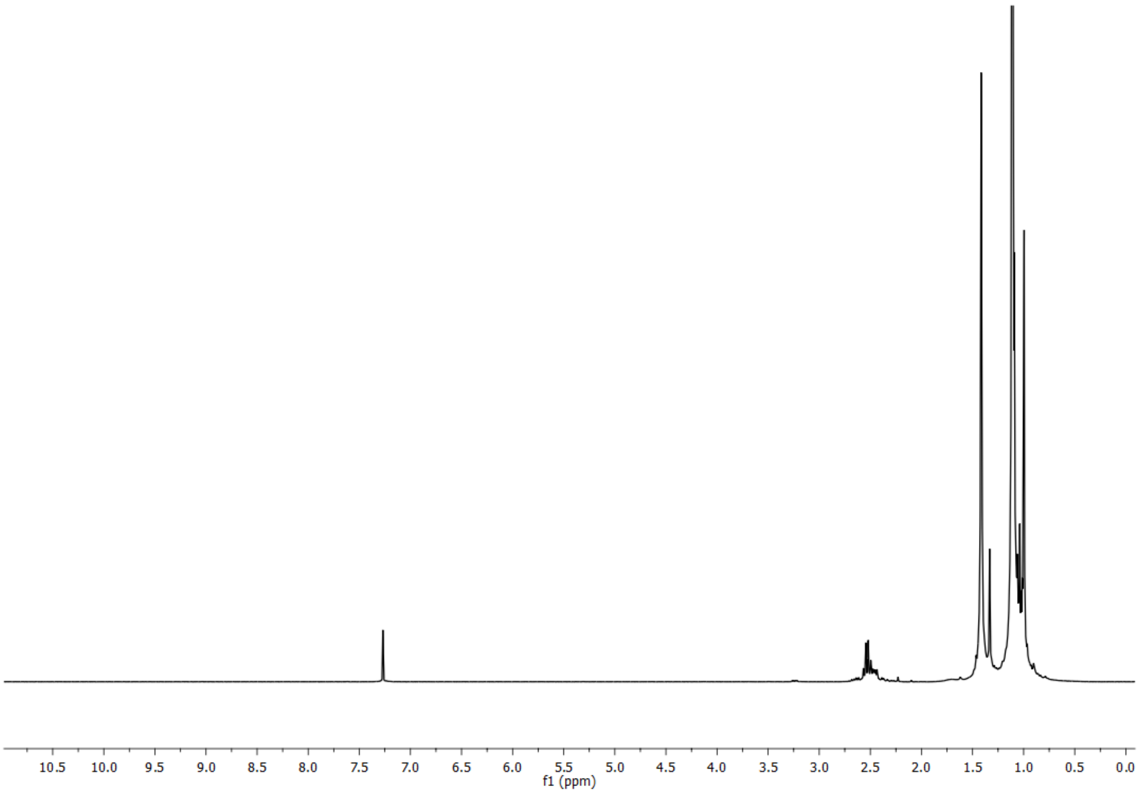


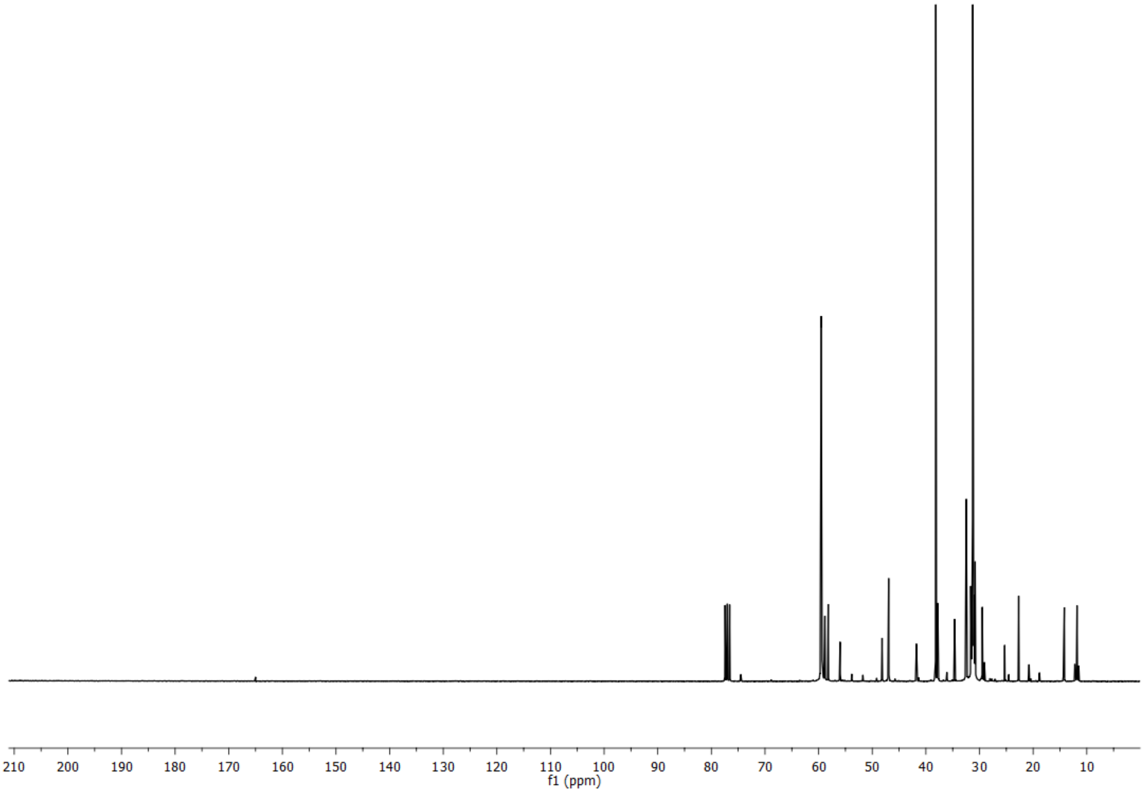
PIB$_{1000}$-CON(CH$_2$CH$_3$)$_2$ (4) ^{1}H and ^{13}C NMR spectra (CDCl$_3$)





PIB_{1000}-$CH_2N(CH_2CH_3)_2$ (6) ^1H and ^{13}C NMR spectra ($CDCl_3$)





PIB_{1000}-$CH_2N(CH_2CH_3)_2CH_3^+I^-$ (7) ^1H and ^{13}C NMR spectra ($CDCl_3$)