Supplementary information (ESI) for *Dalton Trans*.

Supporting Information:

Heterogeneous catalysts for the controlled ring opening polymerisation of *rac*-lactide and homogeneous silsesquioxane model complexes

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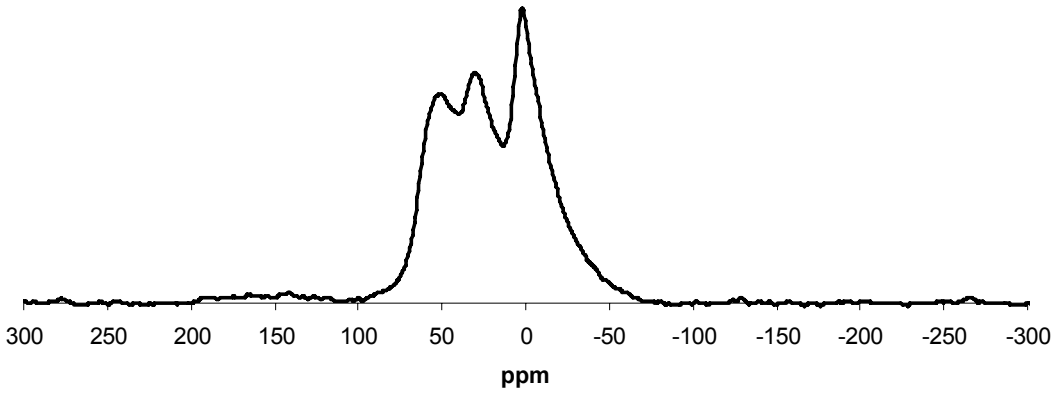
Silica

The silica materials were purchased from Aldrich, the materials have a pore diameter of 40 Å (750 m^2g^{-1}) or 60 Å (480 m^2g^{-1}), where the number in brackets represents the surface area of the material.

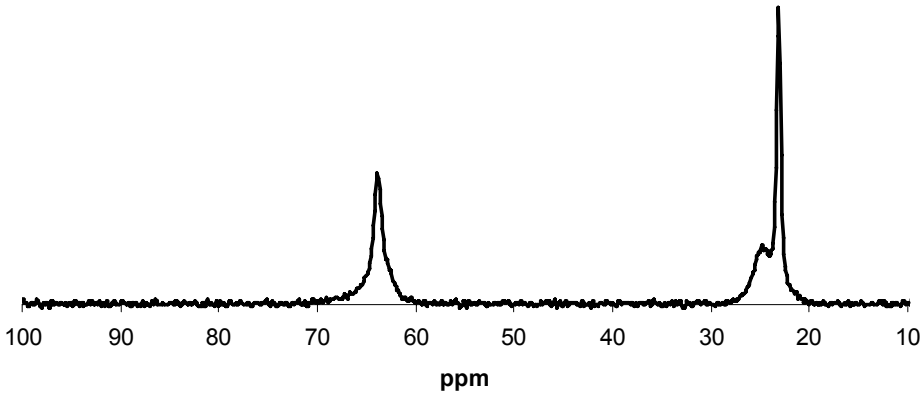
Solid-state NMR:

All spectra were recorded at the EPSRC National Solid-state NMR service centre, Durham. $^{13}C\{^1H\}$ CP/MAS were recorded on a Varian VNMRS 400 MHz spectrometer and referenced to TMS, a pulse delay of 1.0 s and contact time of 1.0 ms were employed with TPPM decoupling. ^{27}Al MAS NMR were recorded on the same spectrometer and referenced to 1M $AlCl_3$, a recycle delay of 0.2 s was used.

^{27}Al NMR for Al-SiO_2 (60 Å)



^{13}C{^{1}H} NMR for Al-SiO_2 (60 Å)



The MALDI-TOF mass spectra were recorded at the EPSRC national mass spectrometry service centre, Swansea. The polymer samples were ionised with NaOAc.

MALDI-TOF for the polymer produced with Al-SiO_2 (60 Å):