Supporting Information

Titanium Pyridonates for the homo- and copolymerization of *rac*-Lactide and ε-Caprolactone

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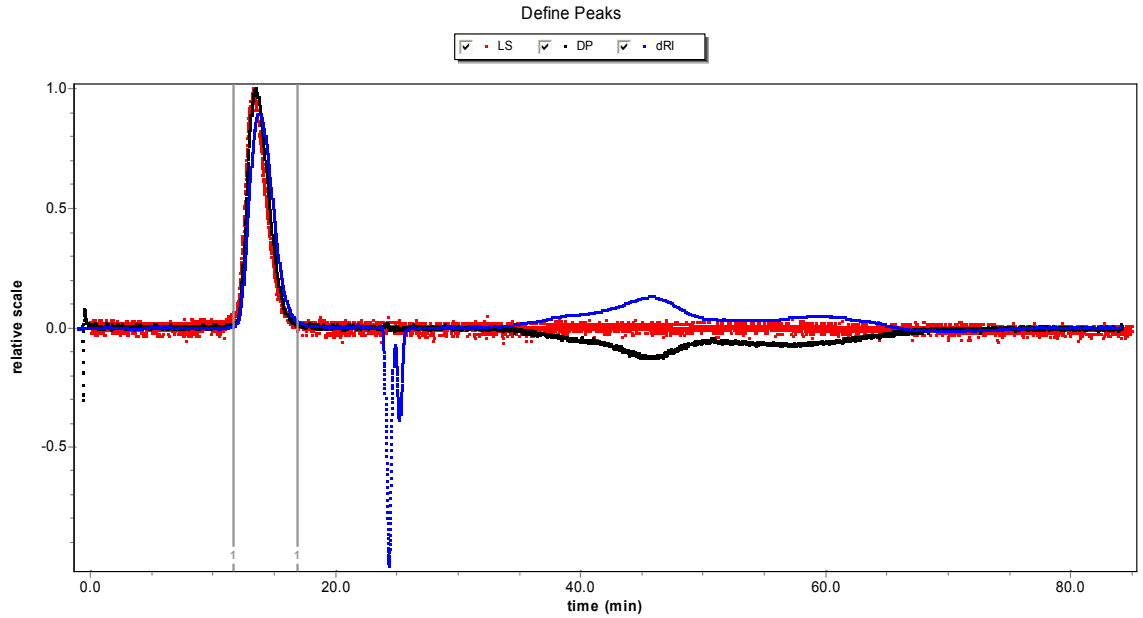
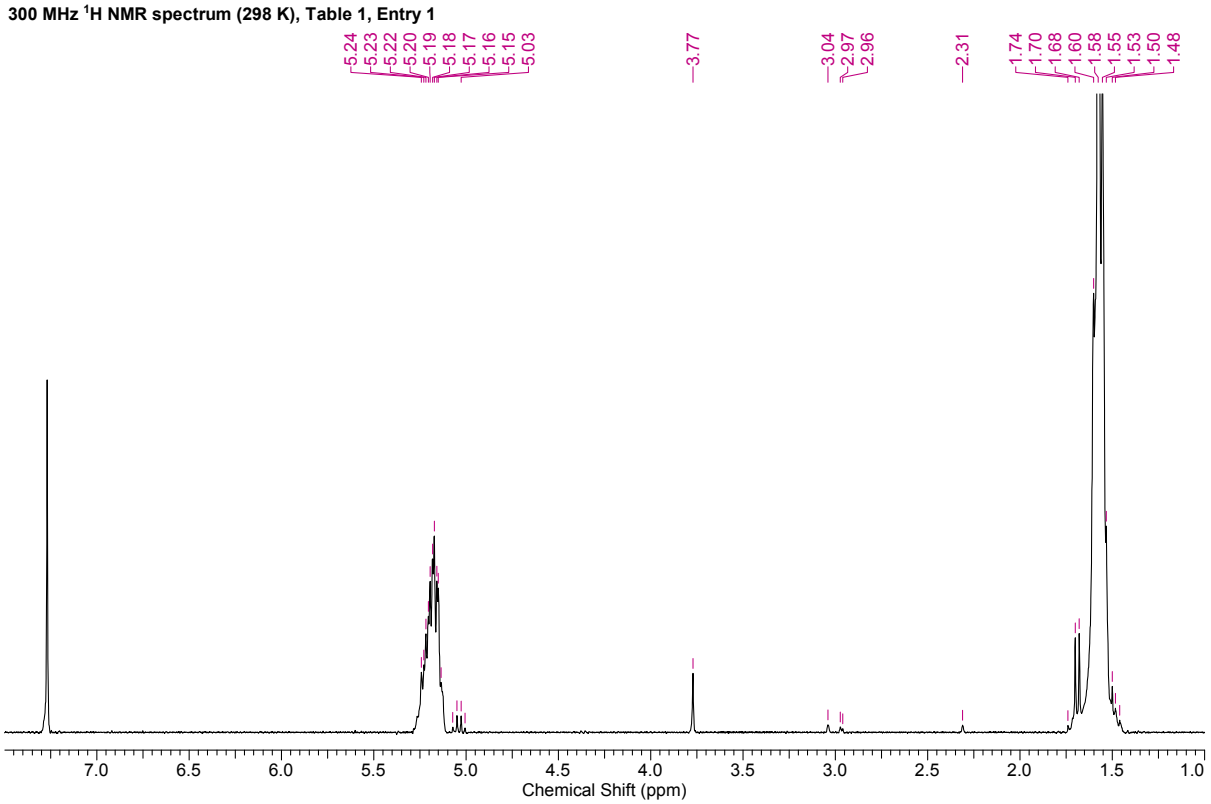
Homopolymerization of *rac*-lactide

Table 1, Entry 1

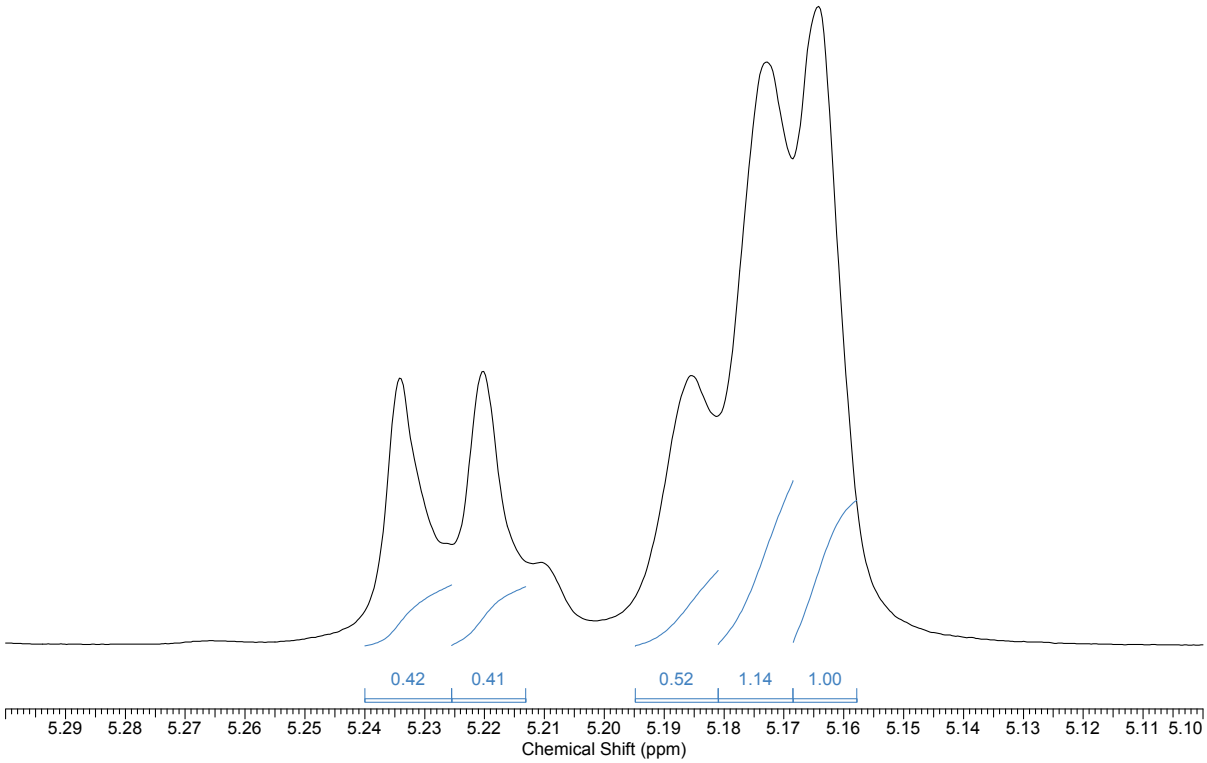
Gel-permeation chromatography trace:



Note: Detection by RI shown in blue, light-scattering in red



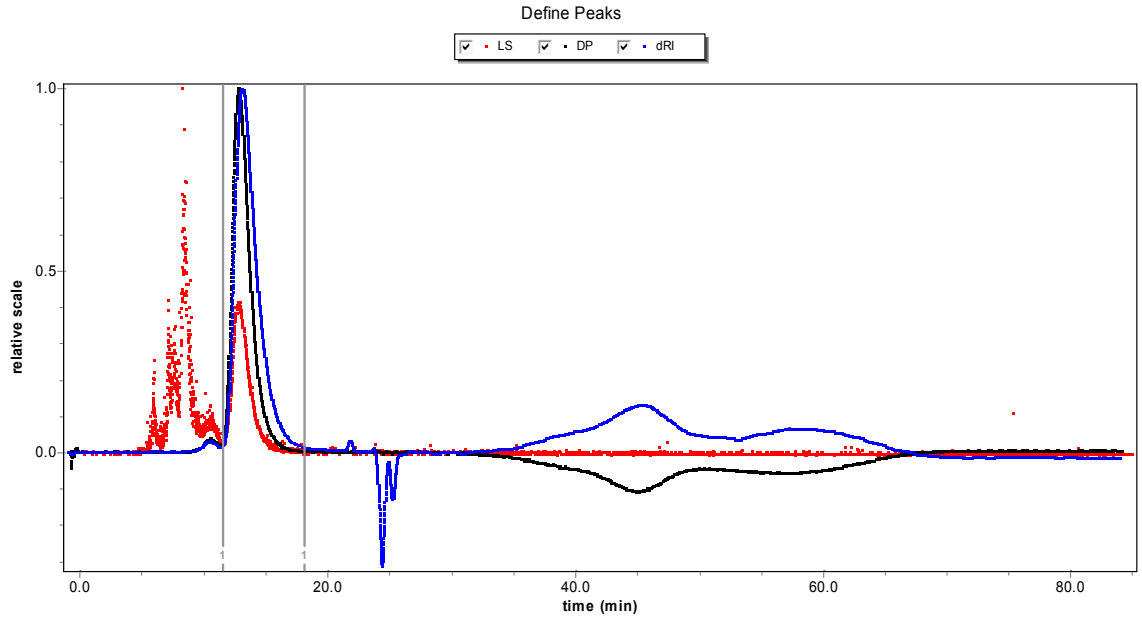
400 MHz $^{1}H\{^{1}H\}$ NMR spectrum (298 K), Table 1, Entry 1



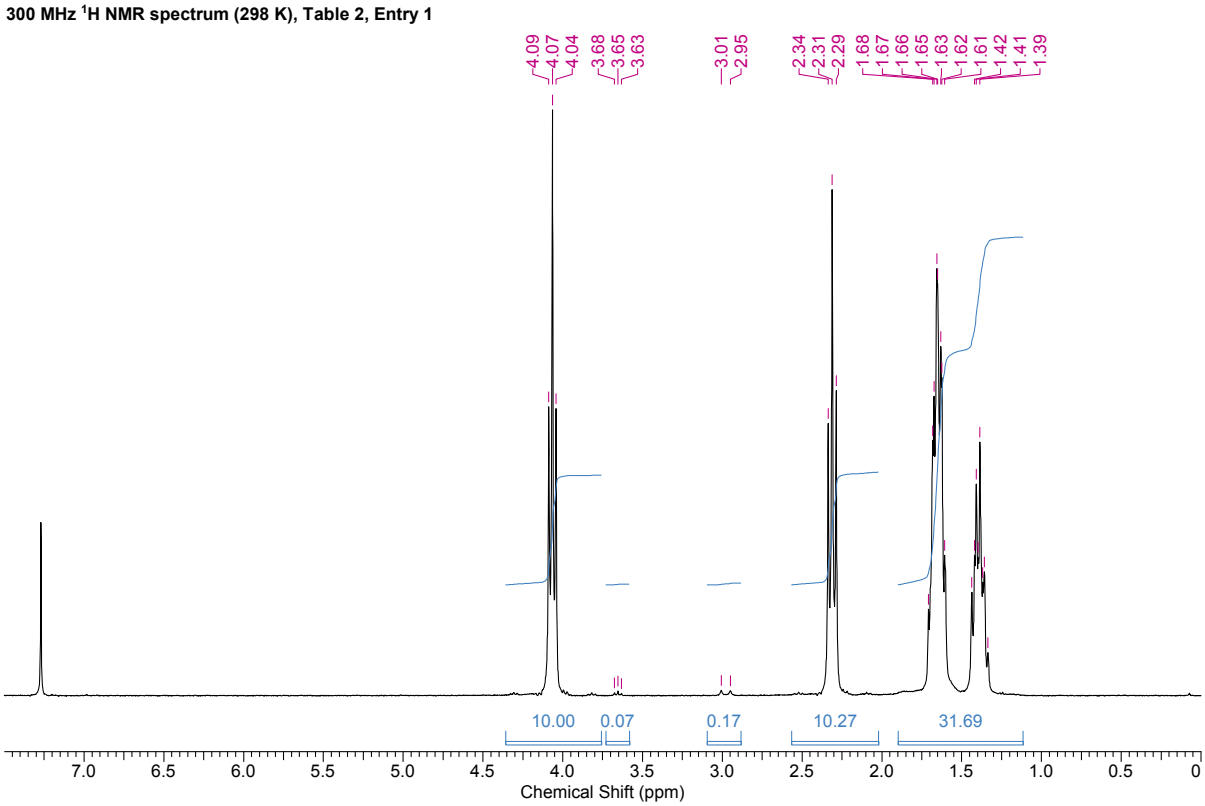
Homopolymerization of ε-caprolactone

Table 2, Entry 1

Gel-permeation chromatography trace:



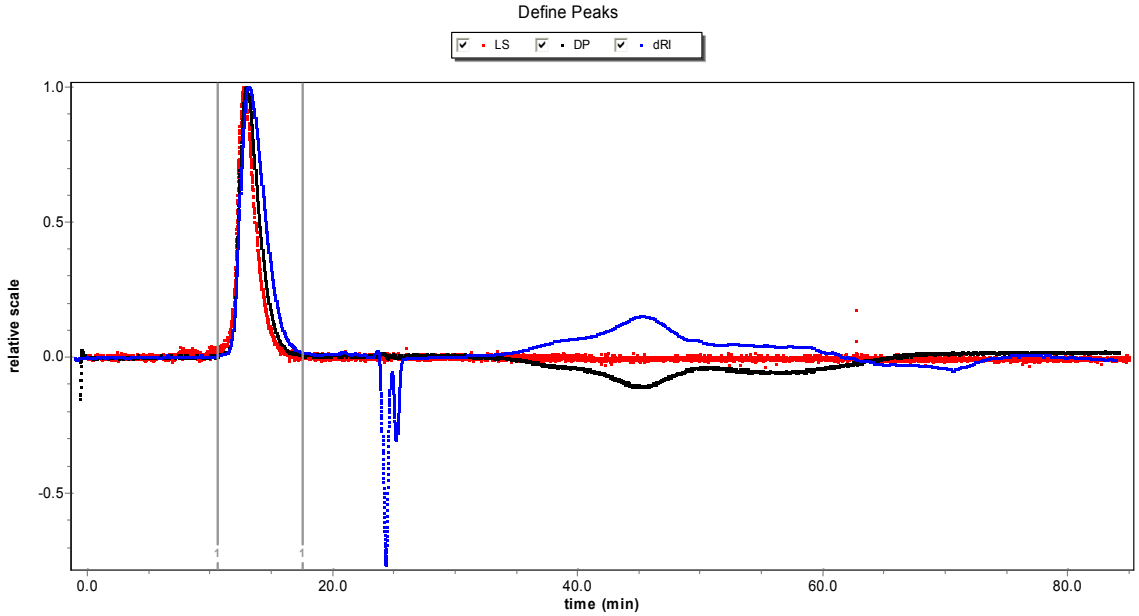
Note: Detection by RI shown in blue, light-scattering in red



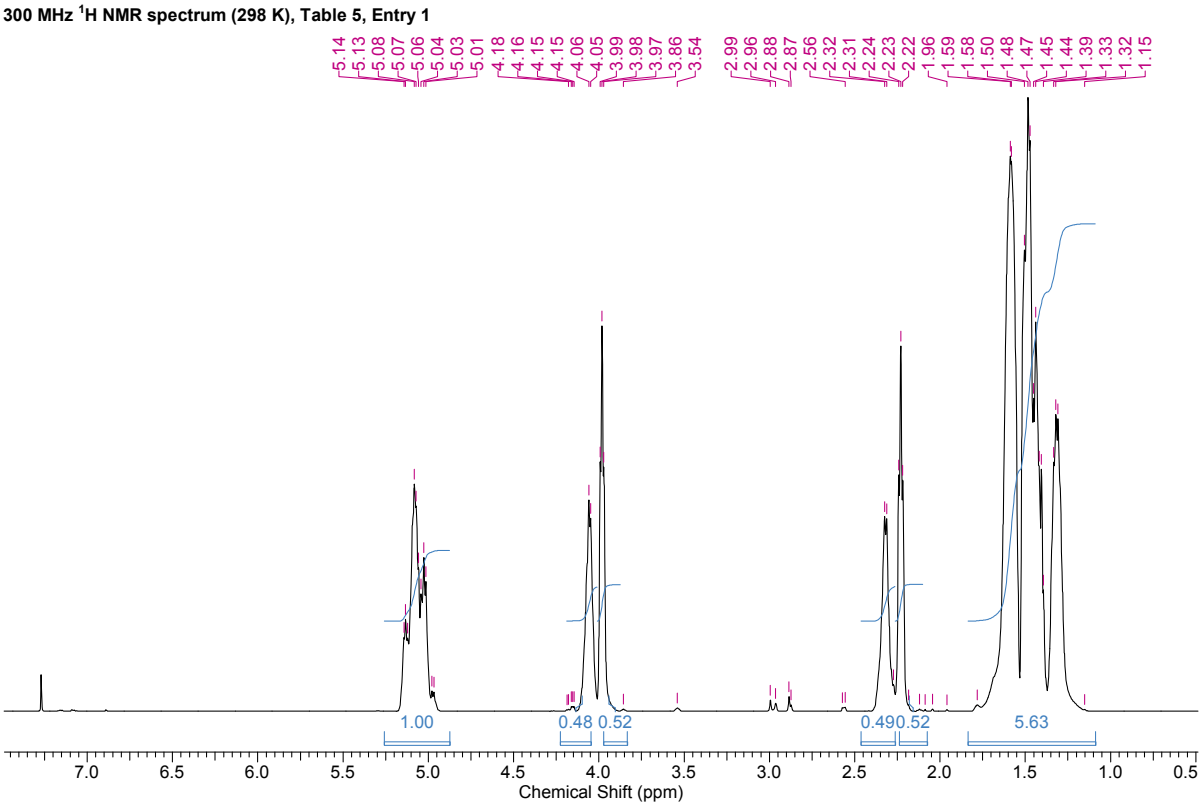
CL/LA random copolymerization

Table 3, Entry 1

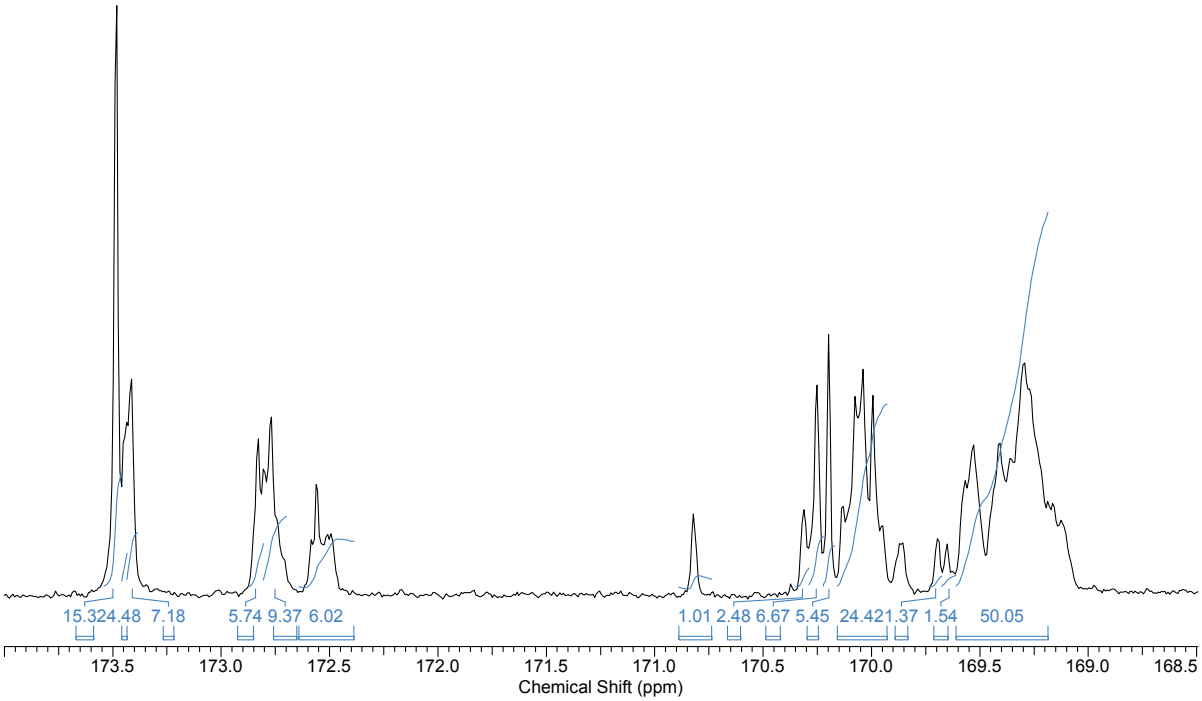
Gel-permeation chromatography trace:



Note: Detection by RI shown in blue, light-scattering in red



100 MHz $^{13}C\{^{1}H\}$ Inv. Gate. NMR spectrum (298 K), Table 5, Entry 1



Monitoring copolymerization as a function of time.

Previous work[1] has shown that Ti pyridonate complexes generate random copolymers by transesterification and not random incorporation of monomers throughout the growth of the polymer chain. Charts S1 and S2, reproduced from the supplementary data provided for our original communication, show that with initiator **2b** lactide is incorporated at a faster rate than ε-caprolactone (CL) early in the reaction and that once lactide is consumed it is not only the homodiads of CL that increase as expected, but rather heterodiad formation is observed to increase dramatically. These data can only be rationalized by extensive transesterification occuring in copolymerization where both monomers are added simultaneously. This transesterification process with pyridonate ligands results in the formation of random co-polymers with similar sequence lengths, as determined by NMR spectroscopy.[1]

Chart S1: Profile of the consumption of LA and CL during copolymerisation using **2b,** measured by integration of the unreacted LA and CL in the ^{1}H NMR spectrum ($CDCl_3$) using 1,3,5-trimethoxybenzene as a standard.

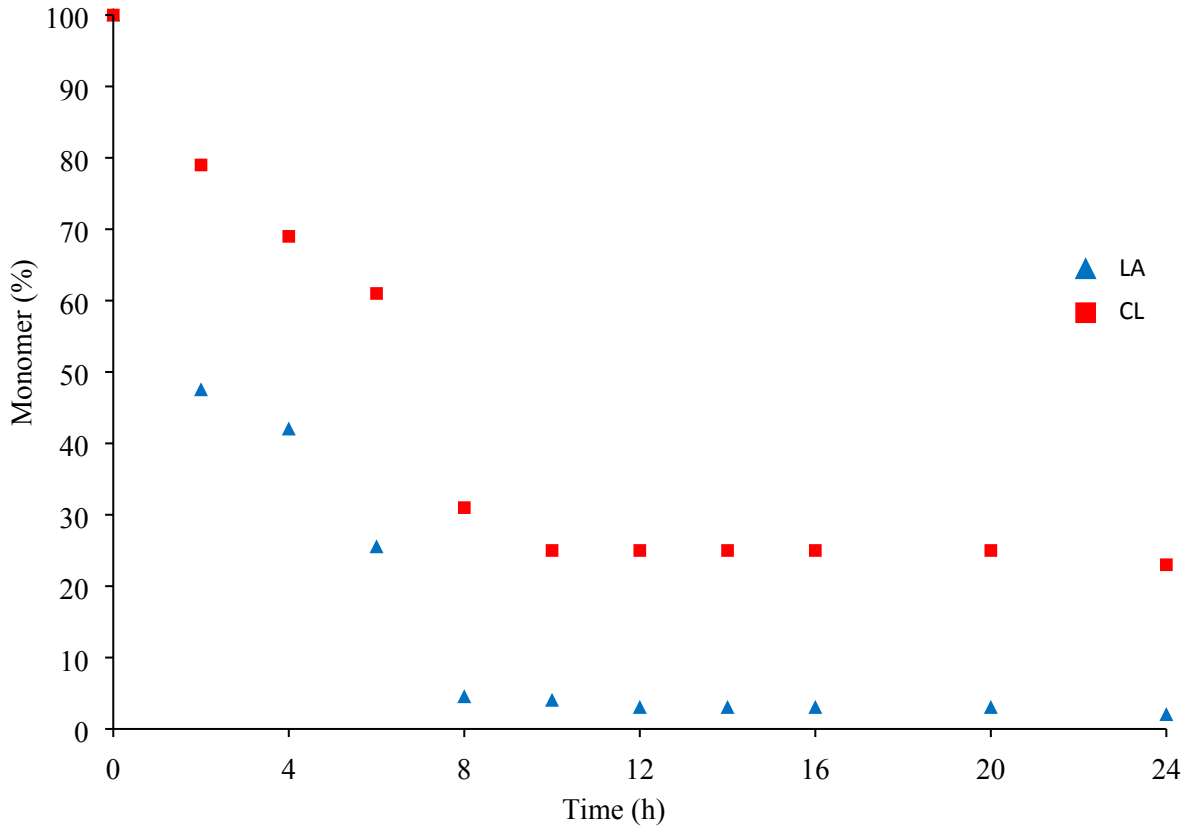
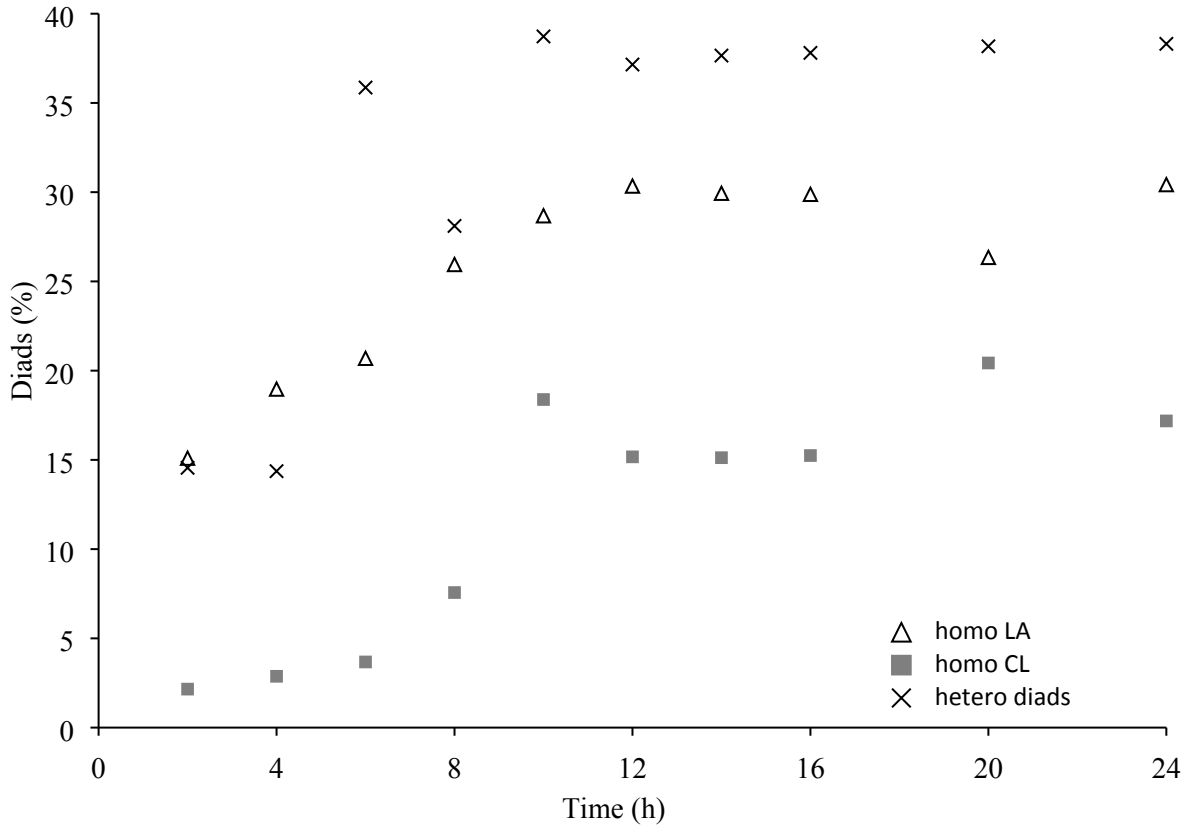


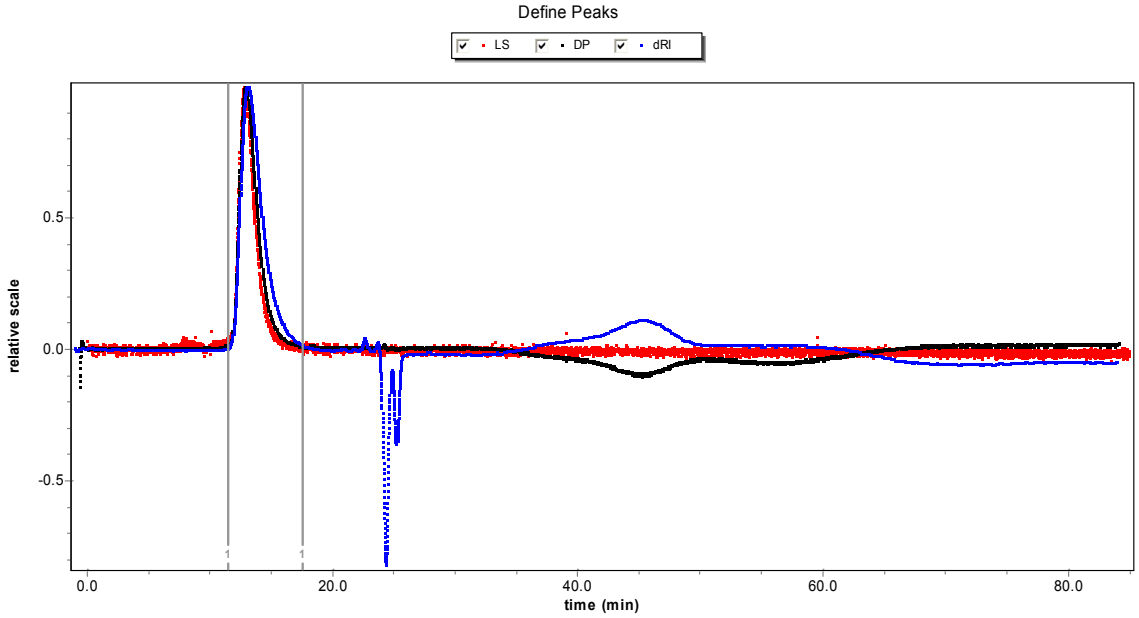
Chart S2: Monitoring the presence of homo- and hetero-diads during copolymerisation with **2b**, measured as a ratio by integration of the homo and hetero sequences in the ^{1}H NMR spectrum (d^{6}-DMSO).



CL-LA block copolymerization

Table 4, Entry 1

Gel-permeation chromatography trace:



Note: Detection by RI shown in blue, light-scattering in red

300 MHz ^{1}H NMR spectrum (298 K), Table 3, Entry 1