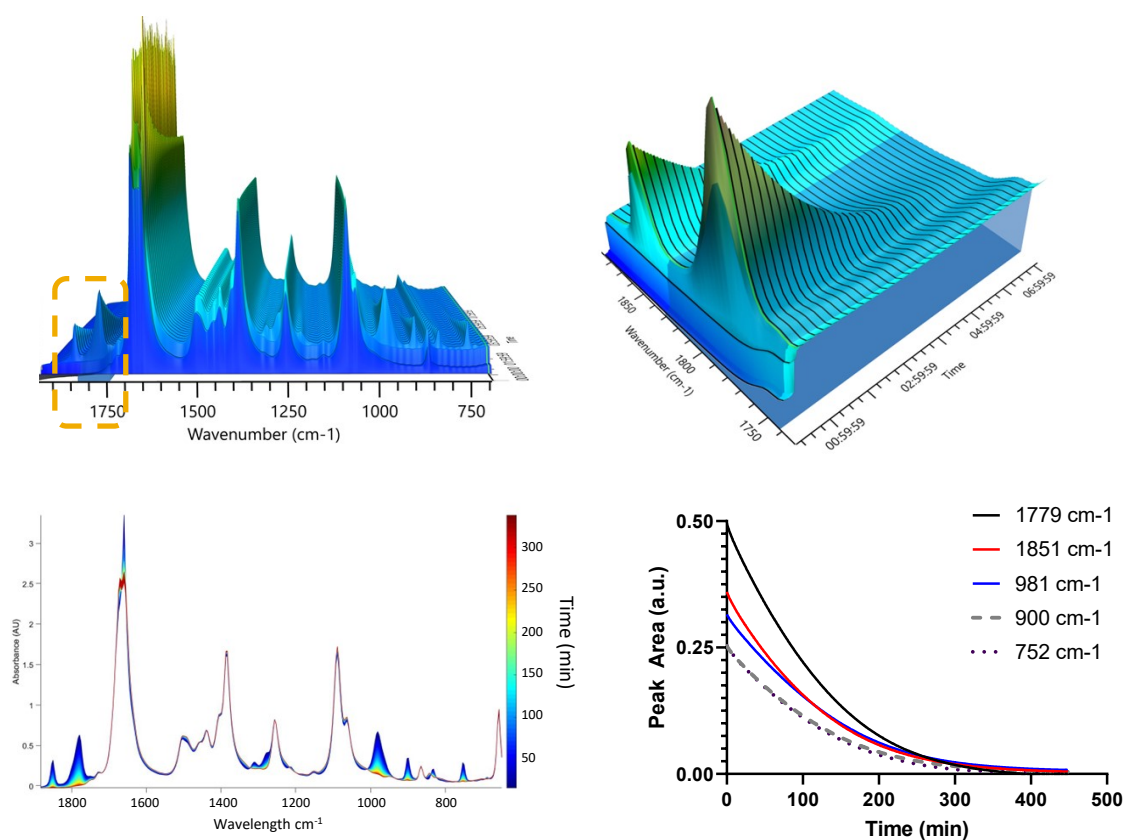


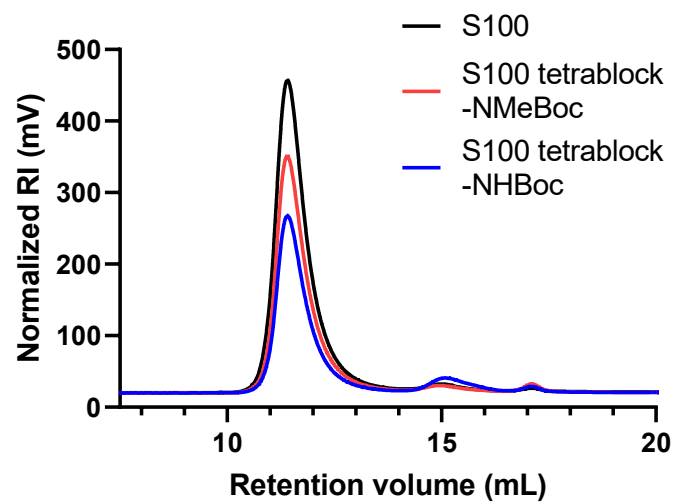
## Supporting Information

### Enhanced rate of sarcosine *N*-carboxyanhydride polymerisation from a lysine dendrimer macroinitiator driven by neighboring H-bonding effects

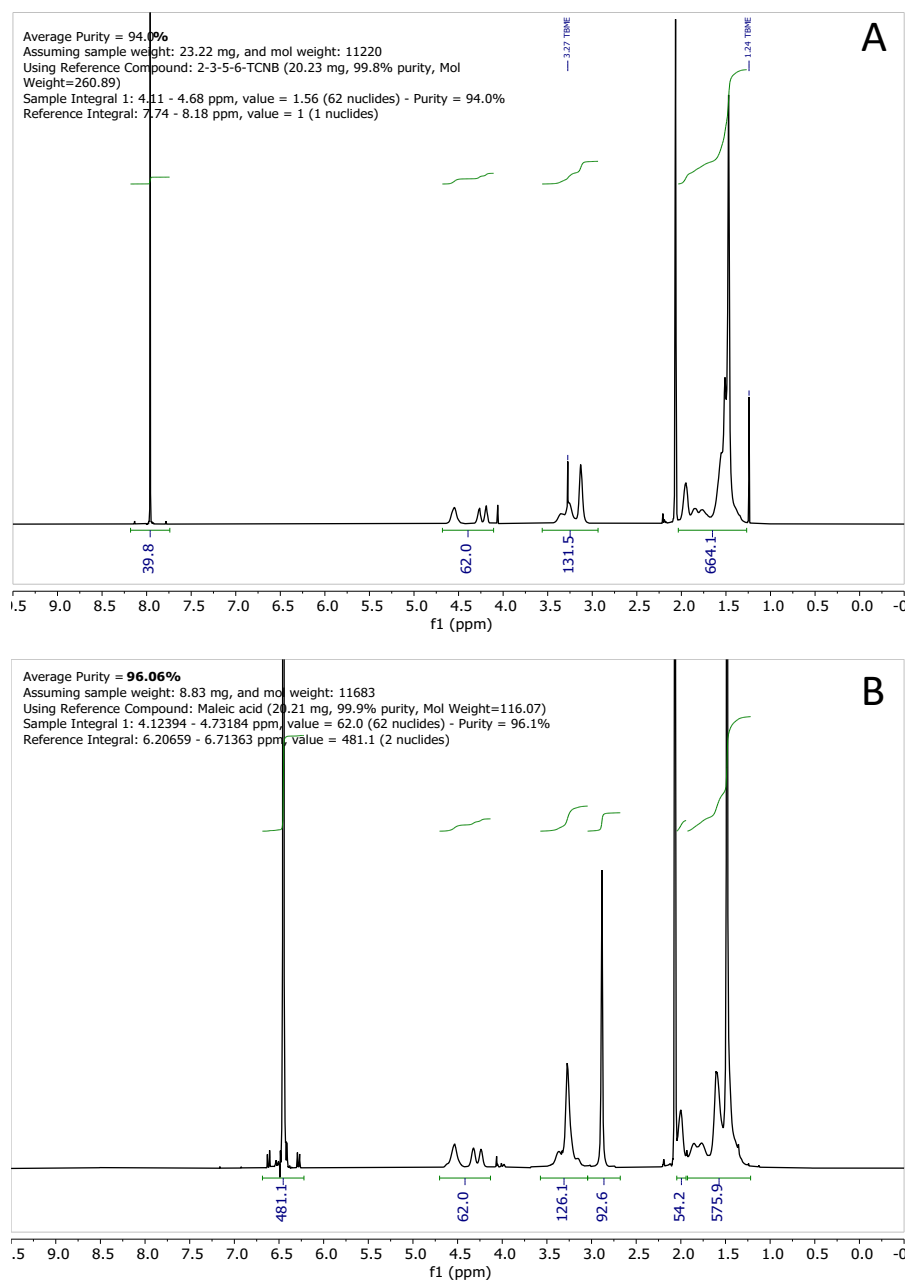
Richard M. England,<sup>\*,‡</sup> Qing Yu,<sup>‡</sup> Chloe Westley,<sup>†</sup> Carl J. Mallia,<sup>†</sup> Kevin Treacher,<sup>§</sup> Per-Ola Norrby,<sup>□</sup> Marianne Ashford.<sup>‡</sup>



**Figure S1.** Images related to the FTIR reaction monitoring of linear PSar100 (boc-N-ethylenediamine initiated). Showing the relevant wavenumber range (top left) and zoomed temporal disappearance of bands for 1779cm<sup>-1</sup> and 1851cm<sup>-1</sup> (top right). Bottom left shows the net change over the course of the experiment and bottom right shows the trends for the main absorbance bands that changed during the experiment, highlighting 1779 cm<sup>-1</sup> with the largest change in peak area over the course of the reaction.



**Figure S2.** SEC-RI chromatogram overlay of PSar stars ( $n=100$ ) synthesized from G5 lysine dendrimer either as one block of  $n = 100$  or as tetrahomoblocks with either  $\epsilon$ -NHBoc or  $\epsilon$ -NMeBoc dendrimer initiators.



**Figure S3.** Quantitative  $^1\text{H}$ -NMR of dendrimer macroinitiators showing relative purities. A) G5-PLL[NH<sub>2</sub>]<sub>32</sub>[Boc]<sub>32</sub> (500 MHz, d<sub>4</sub>-AcOD) against 1,2,4,5-Tetrachloro-3-nitrobenzene standard. B) G5-PLL[NH<sub>2</sub>]<sub>32</sub>[ $\epsilon$ -NMe,Boc]<sub>32</sub> (500 MHz, d<sub>4</sub>-AcOD) against Maleic acid standard.

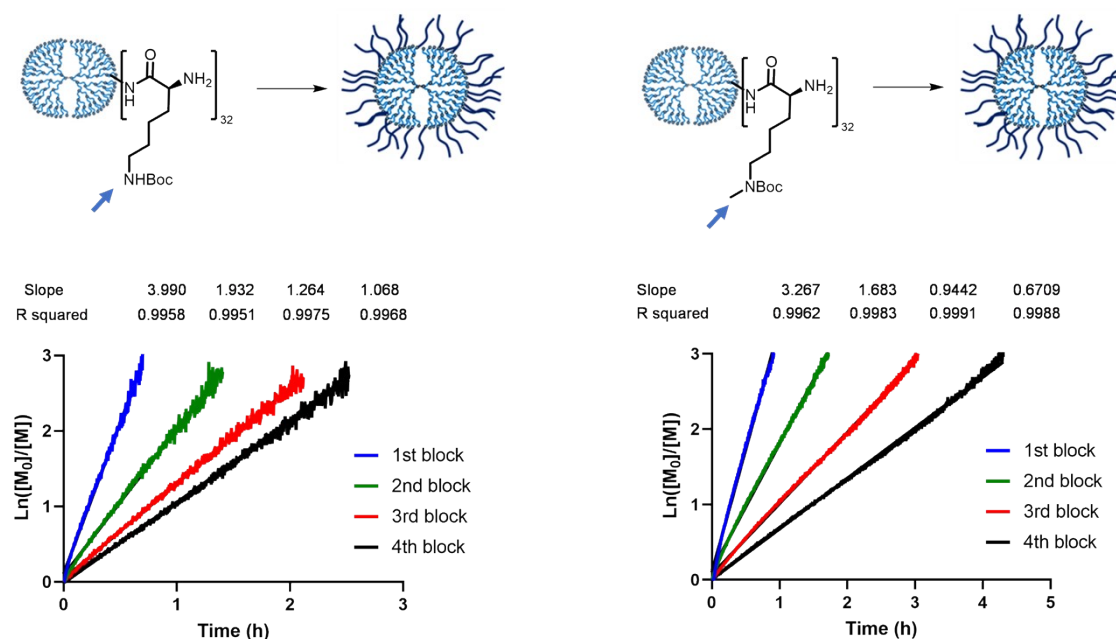
**Table S1.** Polymerization of Sar NCA initiated by star and linear initiators under various conditions

| Polymer description             | Initiator                                              | Solvent | DP (NMR)         | Mn (g/mol) (SEC-TDA) | $\bar{D}$ (SEC-TDA) | Peak <sub>max</sub> (MALDI-TOF-MS) (m/z) |
|---------------------------------|--------------------------------------------------------|---------|------------------|----------------------|---------------------|------------------------------------------|
| Linear PSar100                  | 2-methoxyethylamine*                                   | DMF     | 95               | 6200                 | 1.05                | 6100                                     |
| Linear PSar100                  | 2-methoxyethylamine                                    | DCM     | 96               | 7000                 | 1.02                | 7200                                     |
| Linear PSar100                  | n-butylamine                                           | DMF     | 99               | 6400                 | 1.04                | 6200                                     |
| Star PSar100 DCM                | G5-Lys[ $\epsilon$ -boc amine] <sub>32</sub>           | DCM     | -                | 256000               | 1.04                | 246900                                   |
| Star (PSar25) <sub>4</sub>      | G5-Lys[ $\epsilon$ -boc amine] <sub>32</sub>           | DMF     | 95               | 238700               | 1.04                | 214197                                   |
| Star (PSar25) <sub>4</sub>      | G5-Lys[Methylated $\epsilon$ -boc amine] <sub>32</sub> | DMF     | 96               | 250160               | 1.04                | 228580                                   |
| P(lys) <sub>5</sub> -b-PSar100  | MeO-poly(L-lysine) <sub>5</sub> -NH <sub>2</sub>       | DMF     | 105 <sup>‡</sup> | 7990 <sup>‡</sup>    | 1.10 <sup>‡</sup>   | ND                                       |
| P(lys) <sub>20</sub> -b-PSar100 | MeO-poly(L-lysine) <sub>20</sub> -NH <sub>2</sub>      | DMF     | 105 <sup>‡</sup> | 9540 <sup>‡</sup>    | 1.19 <sup>‡</sup>   | ND                                       |

\*With spiked boc-L-Lysine generation 5 dendrimer same molar concentration as the initiator.

<sup>‡</sup> Measured after deprotection of boc groups as ammonium trifluoroacetate form.

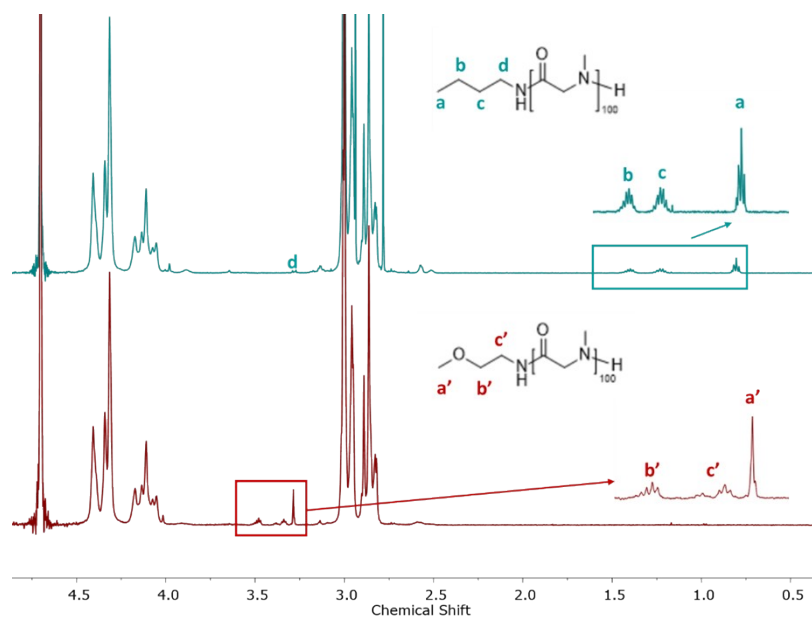
ND – Not determined.



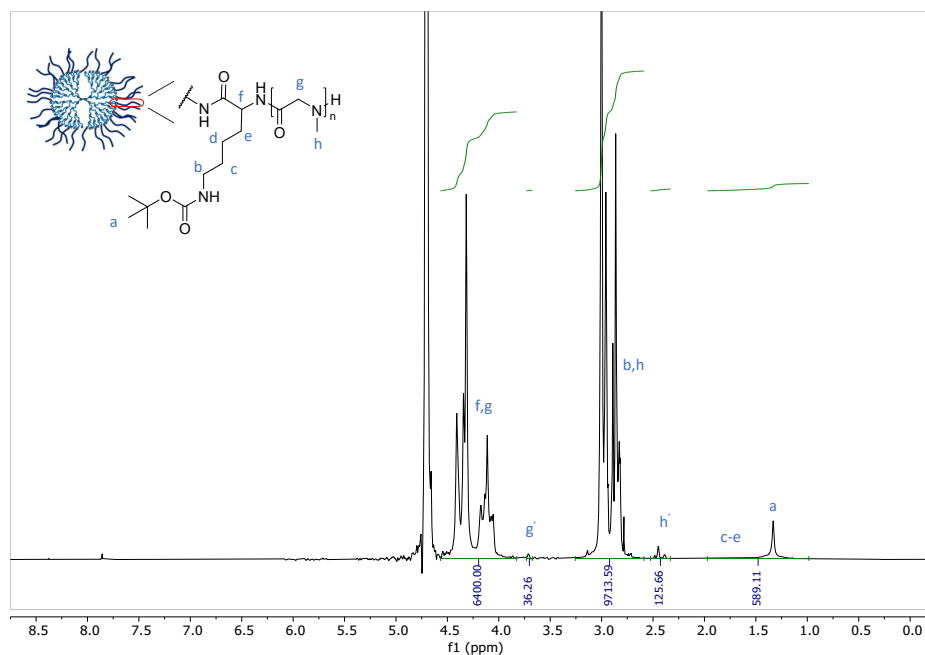
**Figure S4.** First order plots for the homo-block polymerizations with different dendrimer initiators (total n = 100 from 4 blocks of n=25). Left shows the star homoblock polymer synthesised from the G5-PLL[NH<sub>2</sub>]<sub>32</sub>[ $\epsilon$ -NHBoc]<sub>32</sub> initiator and right shows the result of using the methylated version G5-PLL[NH<sub>2</sub>]<sub>32</sub>[ $\epsilon$ -NMeBoc]<sub>32</sub>. Slope is equal to the apparent propagation rate constants  $k_p^{app}$ .

**Table S2.** Propagation rate constants calculated for the homo-block star polymers.

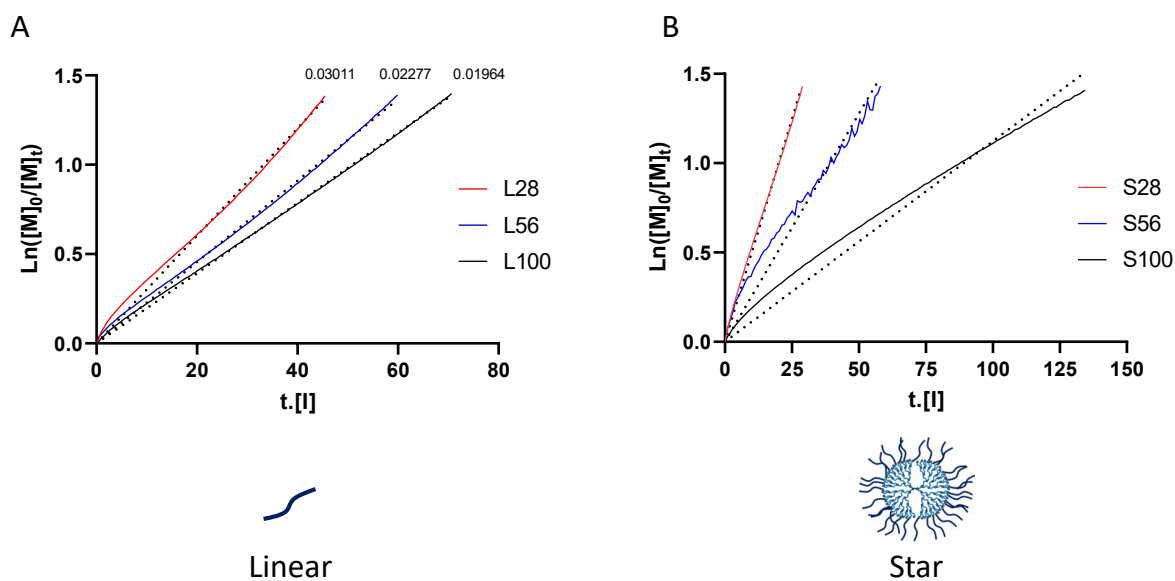
| Block number | Propagation rate constant $k_p$ (L Mol <sup>-1</sup> s <sup>-1</sup> )     |                                                                            |
|--------------|----------------------------------------------------------------------------|----------------------------------------------------------------------------|
|              | G5- PLL[NH <sub>2</sub> ] <sub>32</sub> [ $\epsilon$ -NHBoc] <sub>32</sub> | G5-PLL[NH <sub>2</sub> ] <sub>32</sub> [ $\epsilon$ -NMeBoc] <sub>32</sub> |
| 1            | 0.1228                                                                     | 0.1026                                                                     |
| 2            | 0.0595                                                                     | 0.0528                                                                     |
| 3            | 0.0389                                                                     | 0.0296                                                                     |
| 4            | 0.0329                                                                     | 0.0211                                                                     |



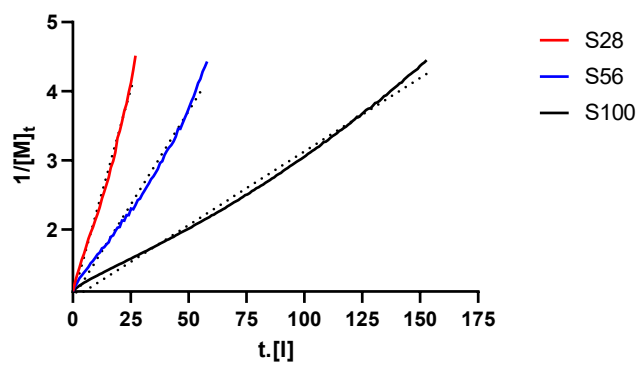
**Figure S5.** <sup>1</sup>H NMR spectra of linear PSar100 polymers initiated by *n*-butylamine (top) and 2-methoxyethylamine (bottom) (D<sub>2</sub>O, 298 K),



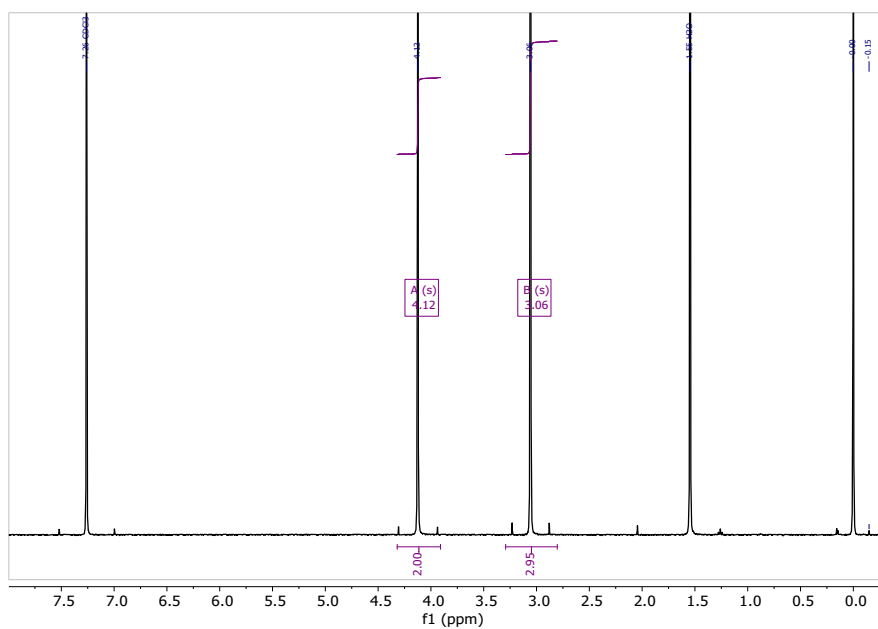
**Figure S6.**  $^1\text{H}$  NMR ( $d_2\text{O}$ , 298 K) spectrum of the 32-arm star PSar polymer ( $n=100$ ) initiated from the generation 5 L-lysine dendrimer ( $\epsilon$ -NH(Boc) macroinitiator).



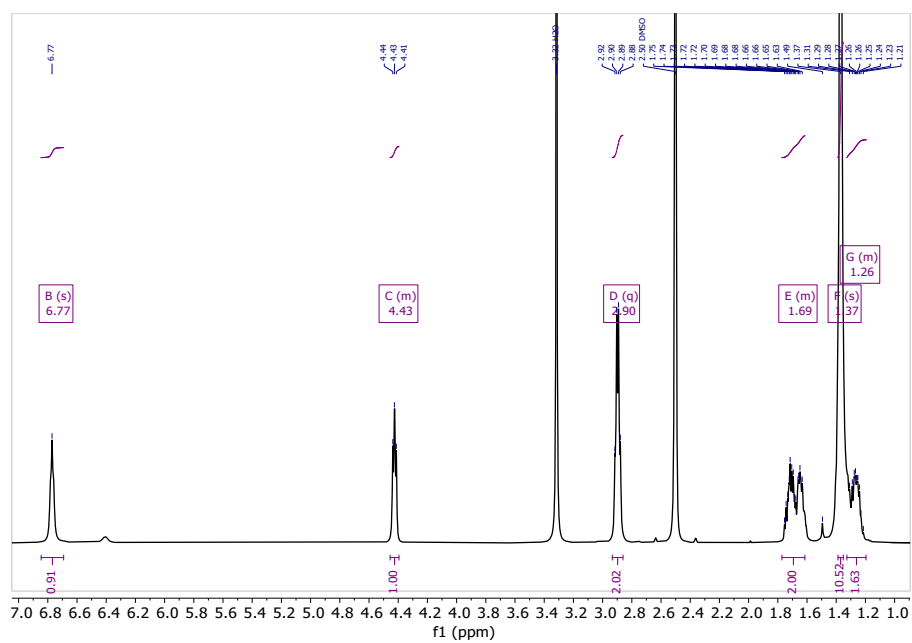
**Figure S7.** First order rate plots for linear and star polymers  $n = 28, 56$  and  $100$  at 75% monomer conversion with linear regressions plotted through the origin, showing the calculated propagation rate constant  $k_p$  derived for linear polymers.



**Figure S8.** Second order rate plots for linear and star polymers  $n = 28, 56$  and  $100$  at  $75\%$  monomer conversion with plotted linear regressions.



**Figure S9.**  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ,  $500\text{ MHz}$ ) for the sarcosine N-carboxyanhydride.



**Figure S10.**  $^1\text{H}$ -NMR ( $\text{d}_6$ -DMSO, 500 MHz) for the Boc-L-Lysine N-carboxyanhydride.