

## Electronic Supplementary Information

### **Synthesis and self-assembly of biobased poly(limonene carbonate)-*block*-poly(cyclohexene carbonate) diblock copolymers prepared by sequential ring-opening copolymerization**

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#### **Materials**

2,4-Pentanedione (Acros Organics, >99%), 2,6-diethylanilin (Acros Organics, 98%), hydrochloric acid (VWR Chemicals, 37%), diethylzinc solution (Sigma-Aldrich, 1.0 M in hexane), acetic acid glacial (>95%, Fisher Chemicals), (+)-limonene unstabilised (Acros Organics, 96%), cyclohexene oxide (Acros Organics, 98%), N-bromosuccinimide (Sigma-Aldrich, 99%), iodomethane (Sigma-Aldrich,  $\geq 99.0\%$ ), sodium hydride (60% dispersion in mineral oil, Sigma-Aldrich), *sec*-BuLi (Acros Organics, 1.3 M in cyclohexane/hexane (92/8)) and 1,1-diphenylethylene (Acros Organics, 98%) were used as received.

The catalyst  $[(bdi)Zn(\mu-OAc)]^1$  and *trans*-limonene oxide (LO)<sup>2</sup> were synthesized according to literature. LO and cyclohexene oxide were dried over NaH, distilled and stored under nitrogen. The monomers were freshly distilled for each polymerisation. Solid reagents were dried overnight under vacuum. The solvents hexane and toluene were purified over 1,1-diphenyl-3-methylpentyllithium, prepared *in situ* by the reaction of *sec*-BuLi with 1,1-diphenylethylene, condensed on a high vacuum line and stored under nitrogen. Carbon dioxide (4.5, Riessner Gase) was dried by passing through a column packed with 3 Å molecular sieves.

#### **Methods**

Differential scanning calorimetry (DSC) was conducted on a Mettler Toledo DSC 821c at a scanning rate of 10 K min<sup>-1</sup> under N<sub>2</sub> atmosphere.

Dynamic mechanical analysis (DMA) was conducted on a Mettler Toledo DMA 1 STAR<sup>e</sup> System at a heating rate of 2 K min<sup>-1</sup> and a frequency of 2 Hz. The sample was prepared as film and mounted in a metal strap for the measurement.

Thermogravimetric analysis (TGA) was performed on a Netzsch TG 209F1 Libra under nitrogen. The samples were heated from 25-600 °C at a heating rate of 10 K min<sup>-1</sup>.

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy was conducted on a Bruker Ultra-shield 300 using deuterated chloroform as solvent at 300 and 75 MHz, respectively.

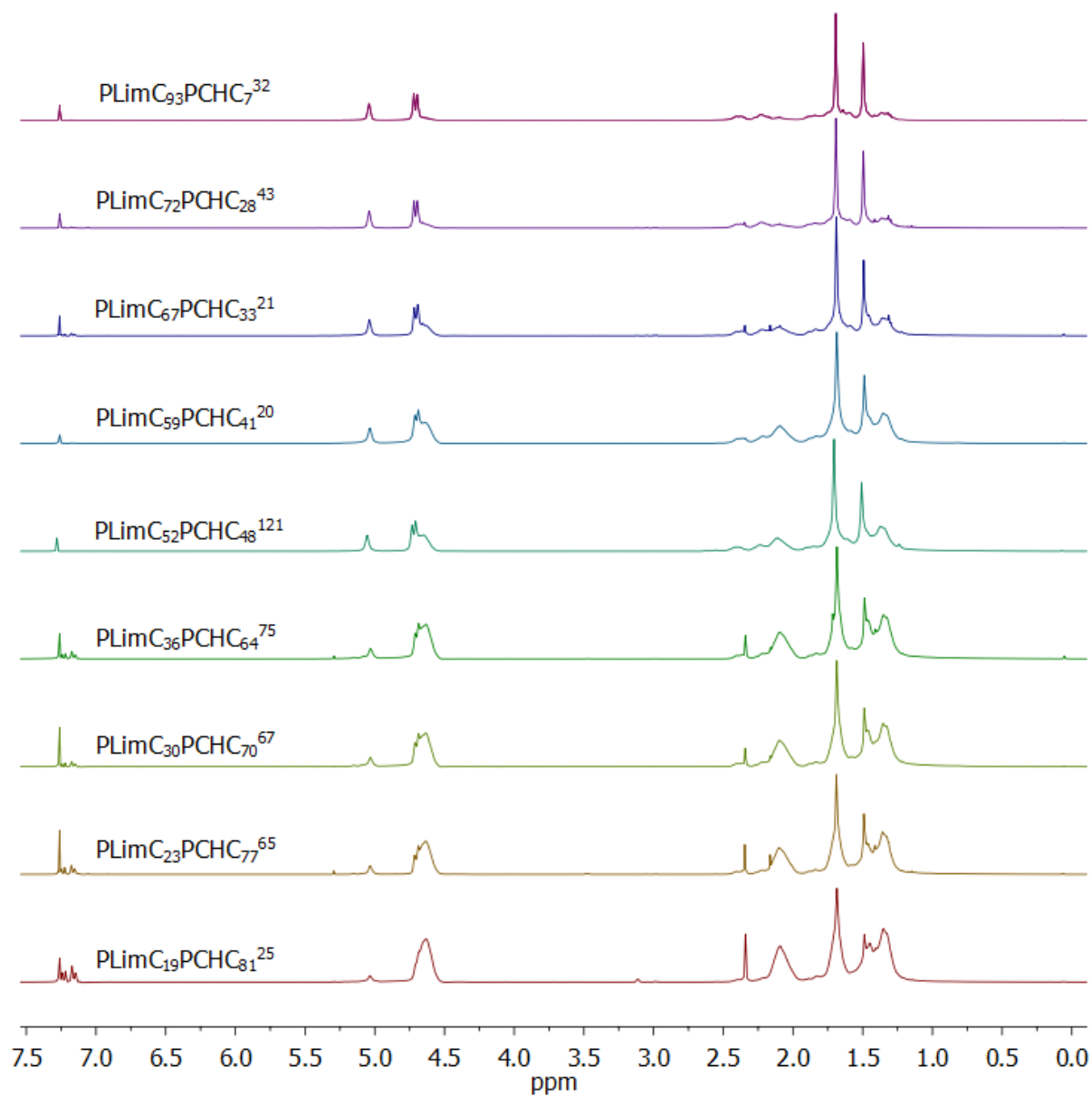
For GPC in CHCl<sub>3</sub> an Agilent 1200 system equipped with a SDV precolumn (particle size 5 µm; PSS Mainz) and a SDV linear XL column (particle size 5 µm, PSS Mainz) was used, together with a refractive index detector (G1362A, Agilent Technologies). CHCl<sub>3</sub> (HPLC grade) was used as solvent at a flow rate of 0.5 mL min<sup>-1</sup> at room temperature. The calibration was done with narrowly distributed polystyrene standards (PSS calibration kit) and toluene (HPLC grade) was used as internal standard.

MALDI-ToF MS (matrix-assisted laser desorption/ionization time-of-flight mass spectrometry) measurements were performed on a Reflex III (Bruker) equipped with a N<sub>2</sub> Laser (λ = 337 nm). An acceleration voltage of 20 kV was used in linear mode and the samples were prepared according to the dried droplet method. Therefore, matrix (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), 10 g L<sup>-1</sup> in THF), analyte (10 g L<sup>-1</sup> in CHCl<sub>3</sub>) and salt (potassium trifluoroacetate, 10 g L<sup>-1</sup>) were dissolved and mixed in the ratio of 20 : 5 : 1 and 0.5 µL of the mixture was placed and dried on the target plate.

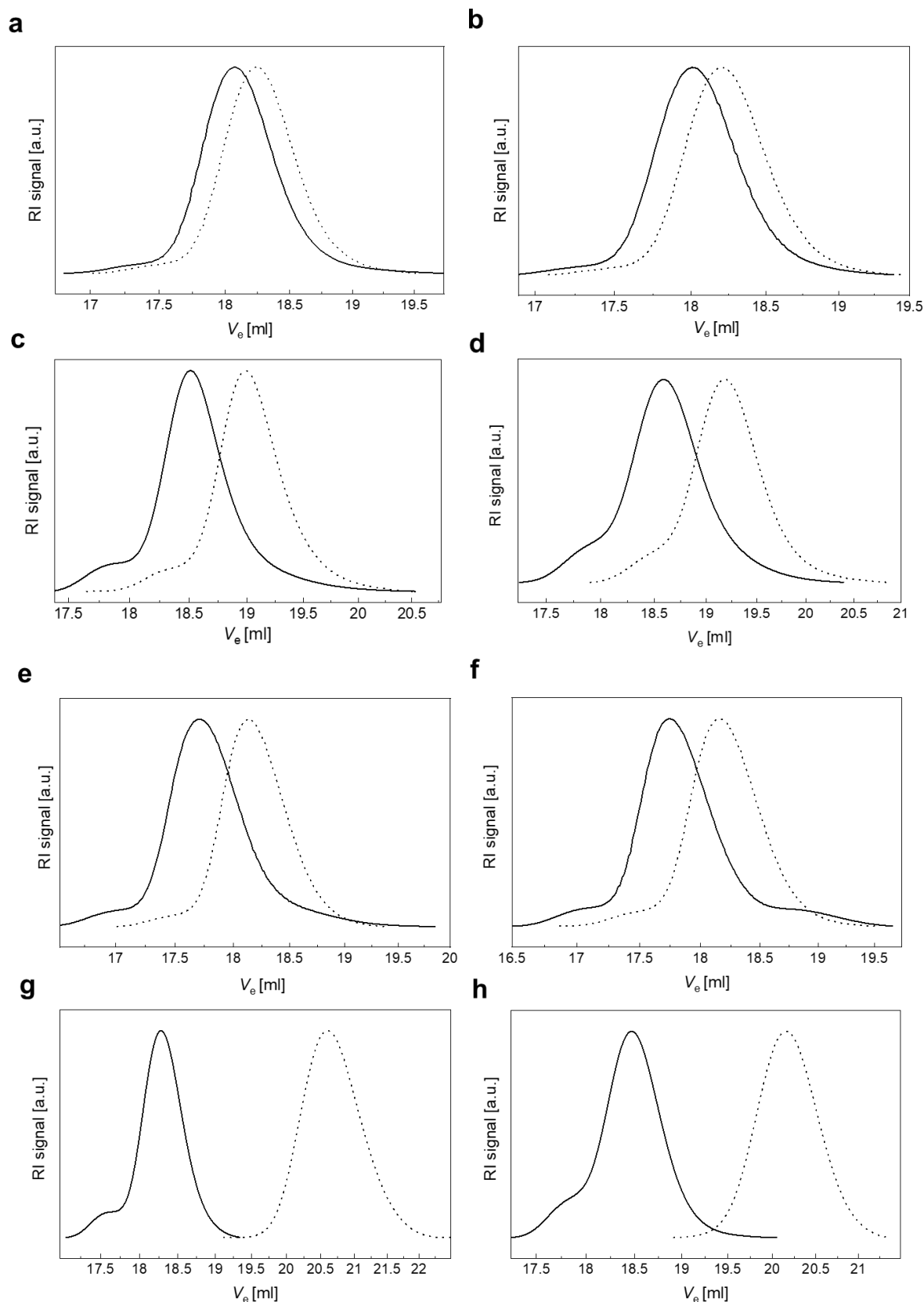
TEM measurements were performed with a Zeiss CEM902 (Zeiss Microscopy, Jena/Oberkochen, Germany) energy filtering transmission electron microscope (EFTEM) operated at an acceleration voltage of 80 kV. Zero-loss filtered micrographs (ΔE ~ 0 eV) were recorded with a side mounted CCD camera system (Orius, Gatan) and processed with DM 2.31 image processing software (Gatan). Samples for TEM were prepared by casting thin films (thickness ca. 0.5 mm) of the diblock copolymers from chloroform over 7 days, followed by vacuum drying at room temperature for 3 days. Then, ultrathin sections (< 100 nm) of the diblock copolymer films were cut at room temperature by an ultramicrotome (Leica UC7), laid on carbon coated copper grids and stained with OsO<sub>4</sub> vapour overnight to selectively stain the PLimC block. In some micrographs a background subtraction was applied for a better visibility of the microstructure. Size measurements were performed with “ImageJ” image processing software by Wayne Rasband (National Institutes of Health, USA).

All SAXS data were measured using the small-angle X-ray system “Double Ganesha AIR” (SAXSLAB, Denmark). The films were measured as received in air environment. The X-ray source of this laboratory-based system is a rotating anode (copper, MicroMax 007HF, Rigaku Corporation, Japan). The data were recorded by a position sensitive detector (PILATUS 300K, Dectris). The circularly averaged data were normalized to incident beam, an assumed sample

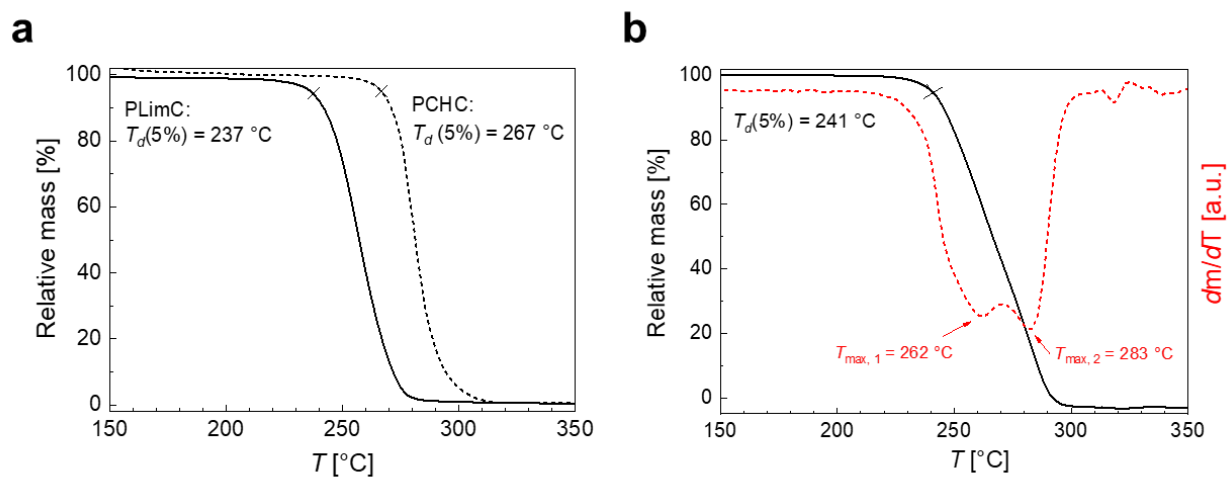
thickness of 1 mm and measurement time. In addition, the scattering contribution of the air background was subtracted.



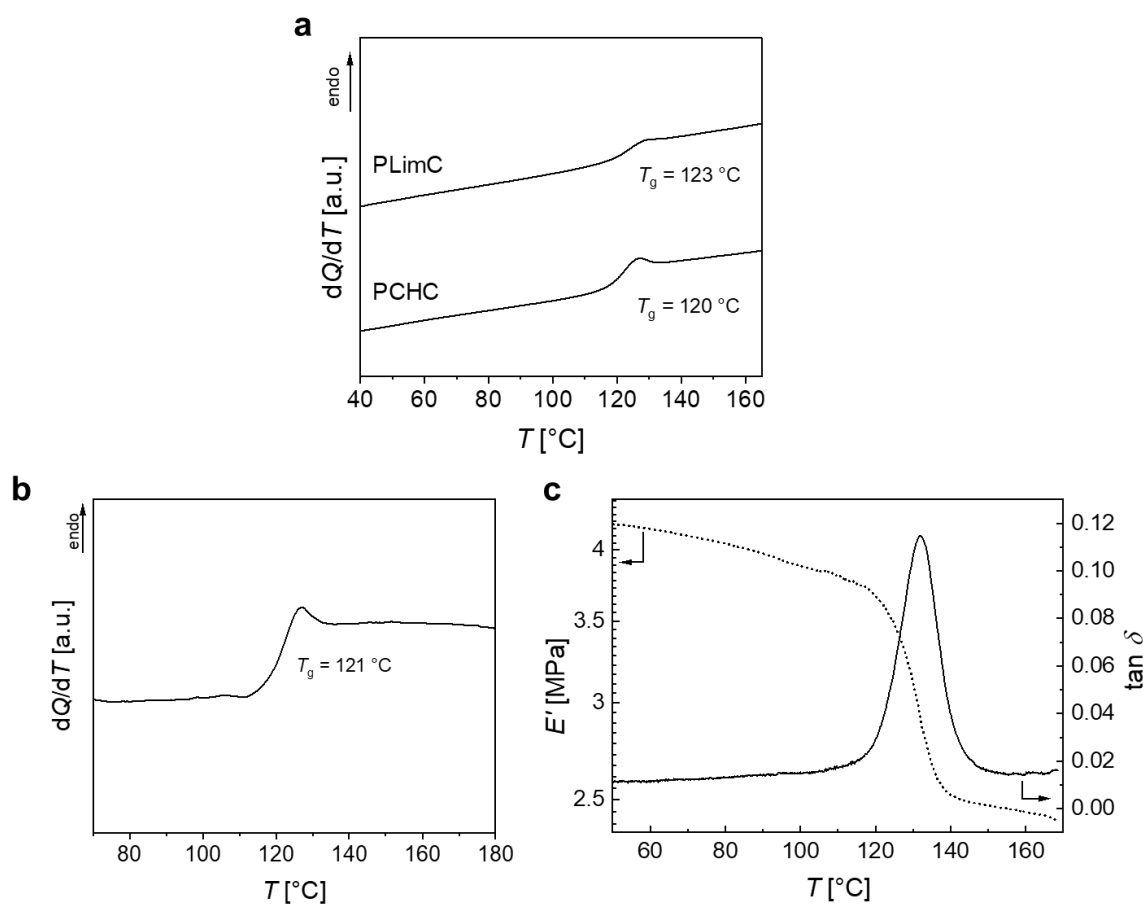
**Fig. S1**  $^1\text{H}$  NMR spectra of the synthesized PLimC-*b*-PCHC diblock copolymers (solvent  $\text{CDCl}_3$ ).



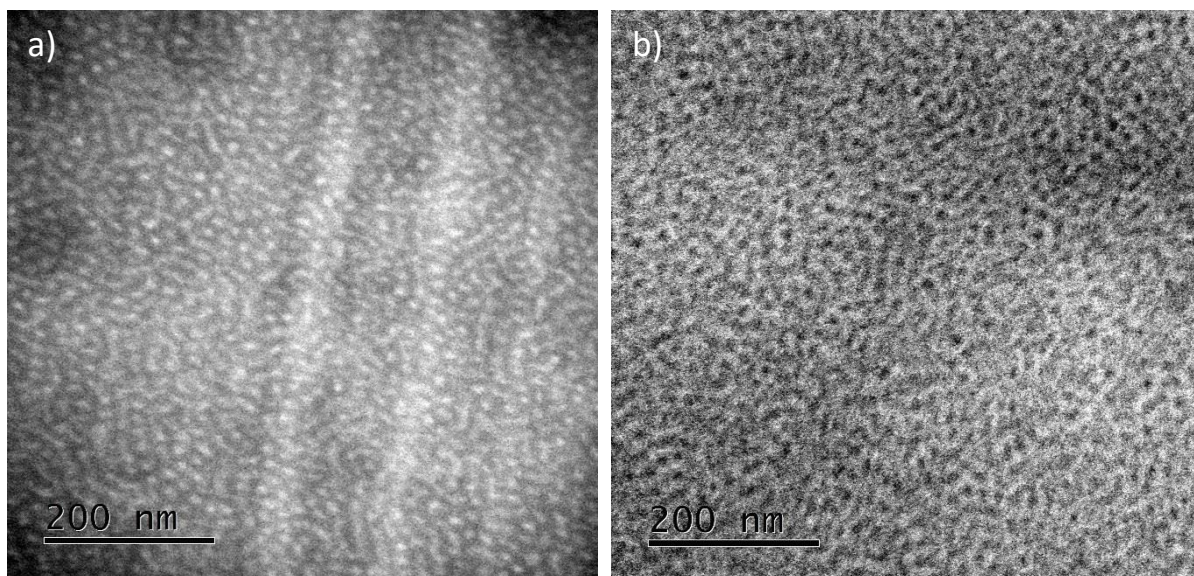
**Fig. S2**  $\text{CHCl}_3$ -GPC traces of a)  $\text{PLimC}_{93}\text{PCHC}_7^{32}$ , b)  $\text{PLimC}_{72}\text{PCHC}_{28}^{43}$ , c)  $\text{PLimC}_{67}\text{PCHC}_{33}^{21}$ , d)  $\text{PLimC}_{59}\text{PCHC}_{41}^{20}$ , e)  $\text{PLimC}_{36}\text{PCHC}_{64}^{75}$ , f)  $\text{PLimC}_{30}\text{PCHC}_{70}^{67}$ , g)  $\text{PLimC}_{23}\text{PCHC}_{77}^{65}$  and h)  $\text{PLimC}_{19}\text{PCHC}_{81}^{25}$ . The dashed traces correspond to the chromatograms of the respective precursor blocks (see Table 1, main text).



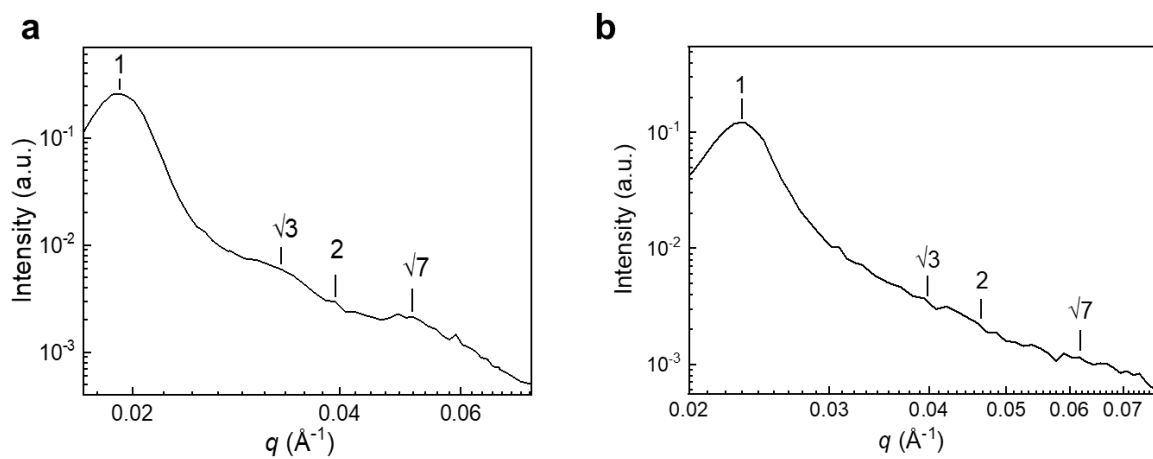
**Fig. S3** TGA traces of a) the homopolymers PLimC<sup>31</sup> and PCHC<sup>36</sup> and c) PLimC<sub>52</sub>PCHC<sub>48</sub><sup>121</sup>.



**Fig. S4** a) DSC traces of the homopolymers PLimC<sup>31</sup> and PCHC<sup>36</sup>. b) DSC and c) DMA traces of PLimC<sub>52</sub>PCHC<sub>48</sub><sup>121</sup>.

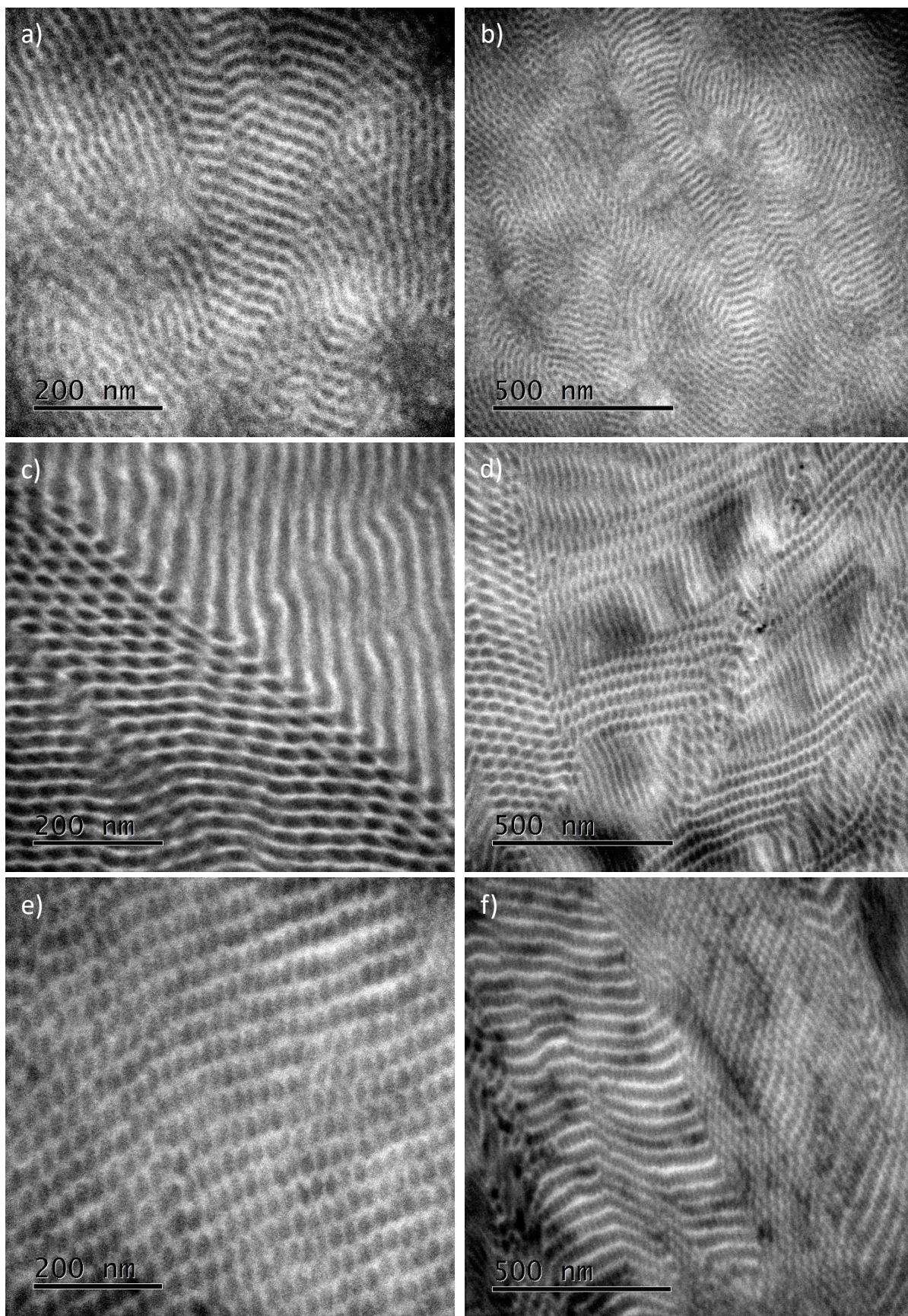


**Fig. S5** TEM micrographs of a) PLimC<sub>93</sub>PCHC<sub>7</sub><sup>32</sup> and b) PLimC<sub>19</sub>PCHC<sub>81</sub><sup>25</sup> (PLimC selectively stained with OsO<sub>4</sub> vapour).



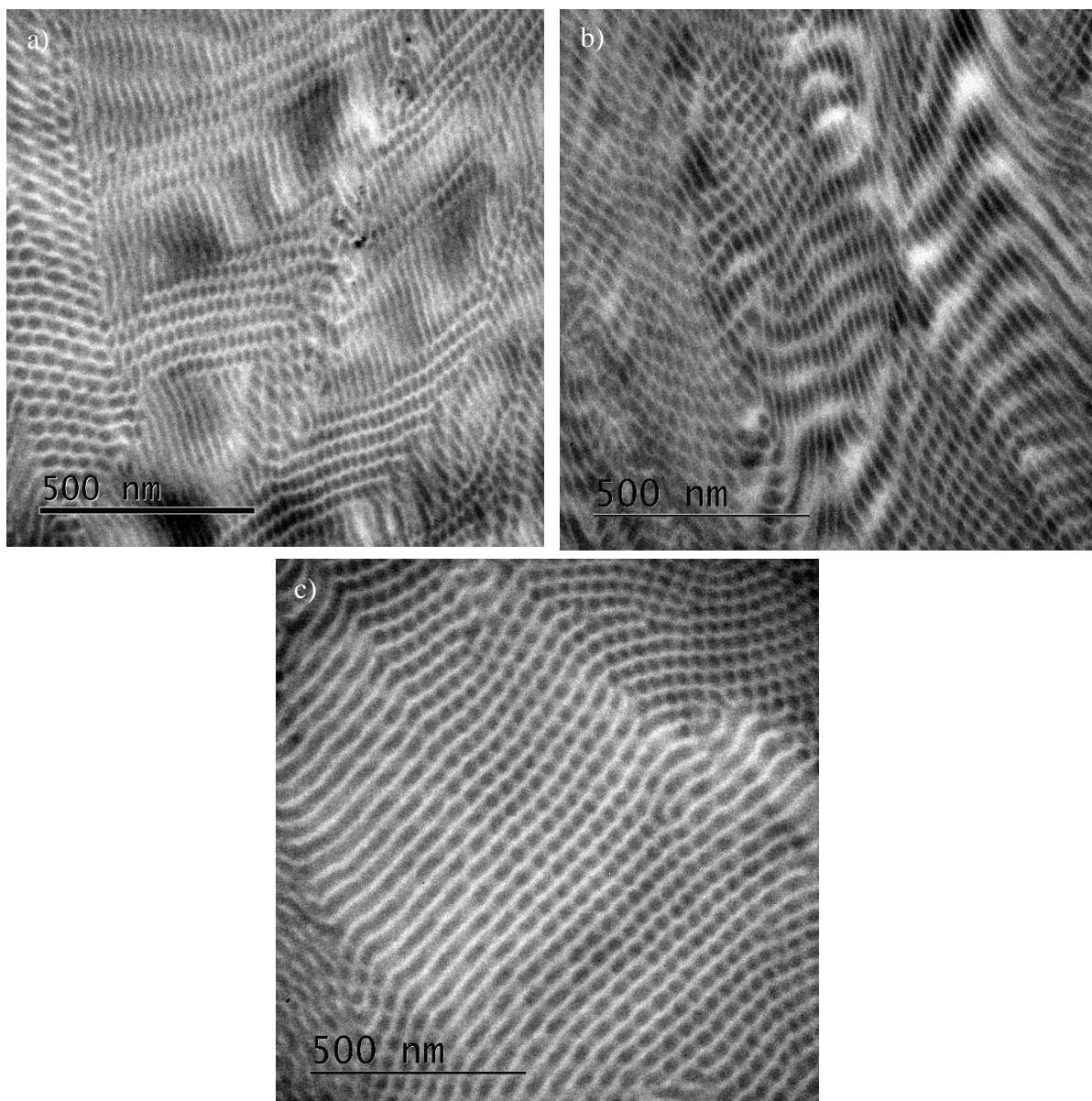
**Fig. S6** SAXS profiles of a) PLimC<sub>23</sub>PCHC<sub>77</sub><sup>65</sup> and b) PLimC<sub>72</sub>PCHC<sub>28</sub><sup>43</sup>.





**Fig. S7** TEM micrographs of PLimC<sub>67</sub>PCHC<sub>33</sub><sup>21</sup> (a, b), PLimC<sub>36</sub>PCHC<sub>64</sub><sup>75</sup> (c, d) and PLimC<sub>30</sub>PCHC<sub>70</sub><sup>67</sup> (e, f). PLimC is selectively stained with OsO<sub>4</sub> vapour.





**Fig. S8** a) Initial morphology of PLimC<sub>36</sub>PCHC<sub>64</sub><sup>75</sup>, b) morphology after thermal annealing at 150 °C for 2 days and c) 5 days under nitrogen atmosphere (PLimC selectively stained with OsO<sub>4</sub> vapour).

## References

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- 2 K. N. Gurudutt, S. Rao, P. Srinivas, *Flavour Fragr. J.* 1992, **7**, 343–345; O. Hauenstein, M. Reiter, S. Agarwal, B. Rieger, A. Greiner, *Green Chem.* 2016, **18**, 760-770.