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Electronic Supplementary Information (ESI)

Self-assembly of a silicon-containing side-chain liquid crystalline block copolymer in bulk and in thin film: kinetic pathway of cylinder to sphere transition

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Fig. S1 Schematic illustration of the chain conformations of the block copolymer as casted, in temperature range $T_g < T < T_{LC-iso}$ and above T_{LC-iso} .



Fig. S2 Cross-section SEM image of a PDMS-*b*-P(4CNB11C)MA BCP thin film on silicon substrates after annealing at 120 °C. The cross-section shows a closepacked arrangement of bright spots corresponding to cross-sections of the PDMS cylinders as well as lines corresponding to the lengths of the cylinders.



Fig. S3 The 3D model (left) of the cyanobiphenyl group of P(4CNB11C)MA and the bond lengths (right) of the molecule after energy minimization within ChemBio 3D Ultra software, from which the length of the cyanobiphenyl group was calculated as C(1)- $N(14)=1.4023+1.3873*1/2*2+1.5014+1.4038+1.4113*1/2*2+1.4328+1.1606=9.6995 \approx 9.7$ Å.



Fig. S4 SEM image of morphology of the drop-cast thick thin film of PDMS-*b*-P(4CNB11C)MA BCP on silicon after annealing at 120 °C.



Fig. S5 SEM images of oxidized PDMS patterns from the as-cast thin films of PDMS-*b*-P(4CNB11C)MA BCP.



Fig. S6 Schematic illustration of the $\chi_{eff}N$ value location in the phase diagram when annealed at different temperatures.