

Figure S1: Heterogenic nature of the electrospun PCL and pseudorotaxane nanofibers. (i) Homogenous RA/neat PCL nanofibers, (ii) slight heterogeneity observed in RA/P-3 nanofibers, Heterogeneous nature of (iii) RA/P-6 and (iv) RA/P-12 nanofibers due to high elastic nature of the polymer solutions.

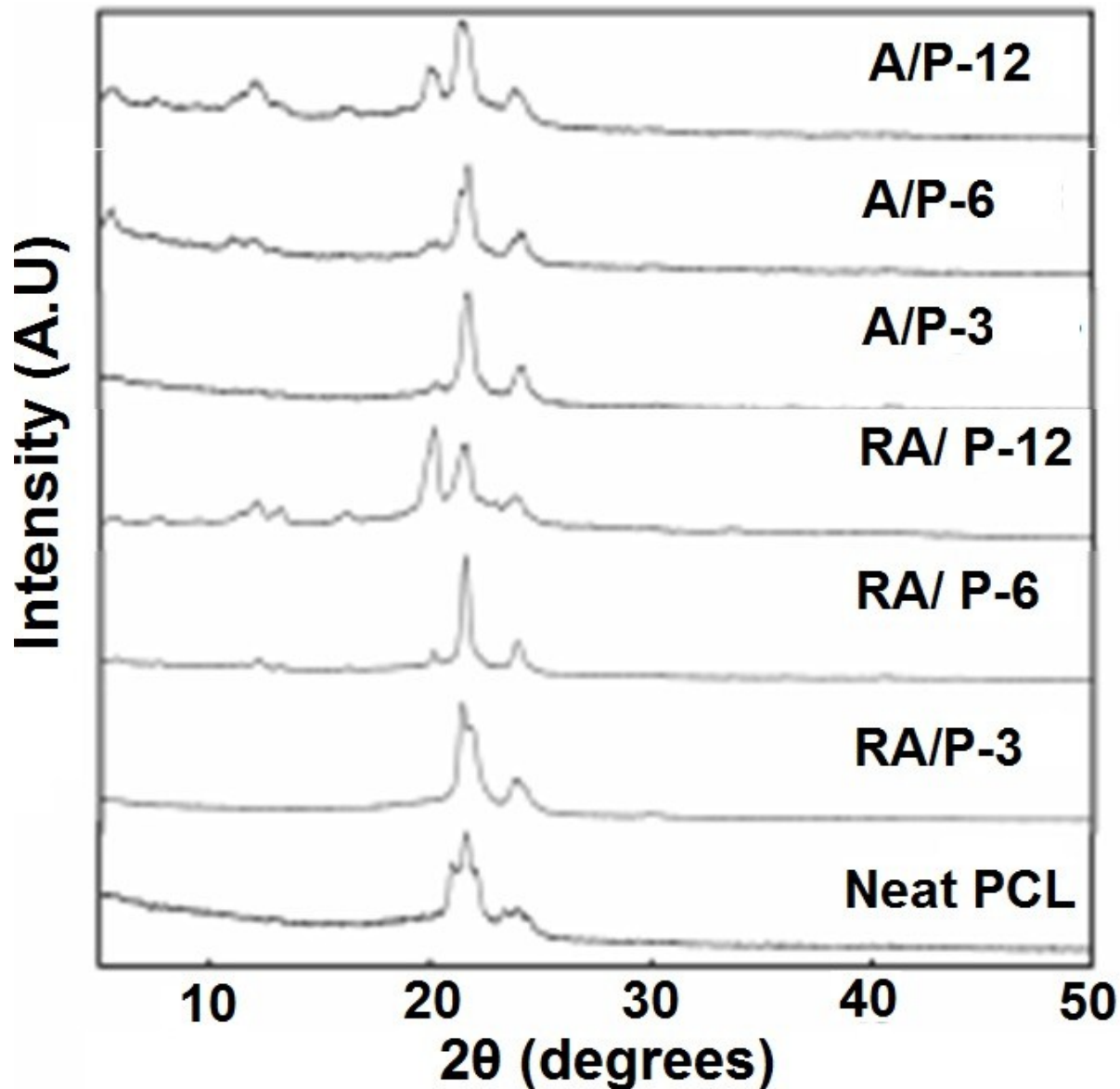


Figure S2: 1D-WAXD patterns of A- and RA- nanofibers of neat PCL and pseudorotaxanes. Neat PCL show crystal reflections at $2\theta = 22$ and 24° corresponding to (110) and (200) reflections respectively, while upon complexation with CDs, the pseudorotaxane show an additional peak at 20° corresponding to channel structure of the CDs. The intensity of this peak depends on the stoichiometric ratio between the CD:PCL, where pseudorotaxanes with larger coverages show this reflection with higher intensity (P-12>P-6>P-3).

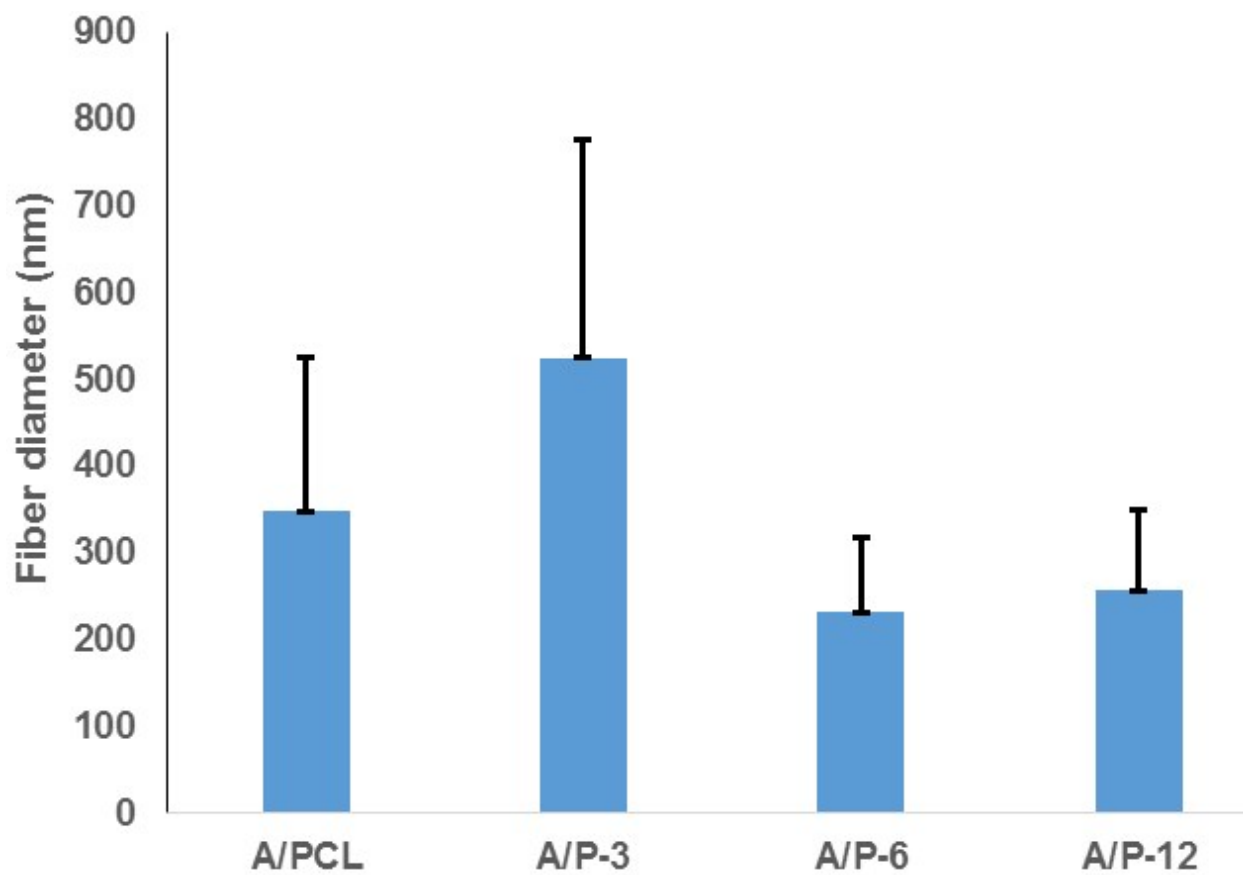


Figure S3: Fiber diameter values of A-nanofibers. A marked decrease in fiber diameter values of A/PCL is observed (compared to RA-nanofibers), while the diameter values of pseudorotaxanes especially higher stoichiometric ones do not show a marked decrease illustrating additional mechanical force do not cause extensive stretching of the jet.

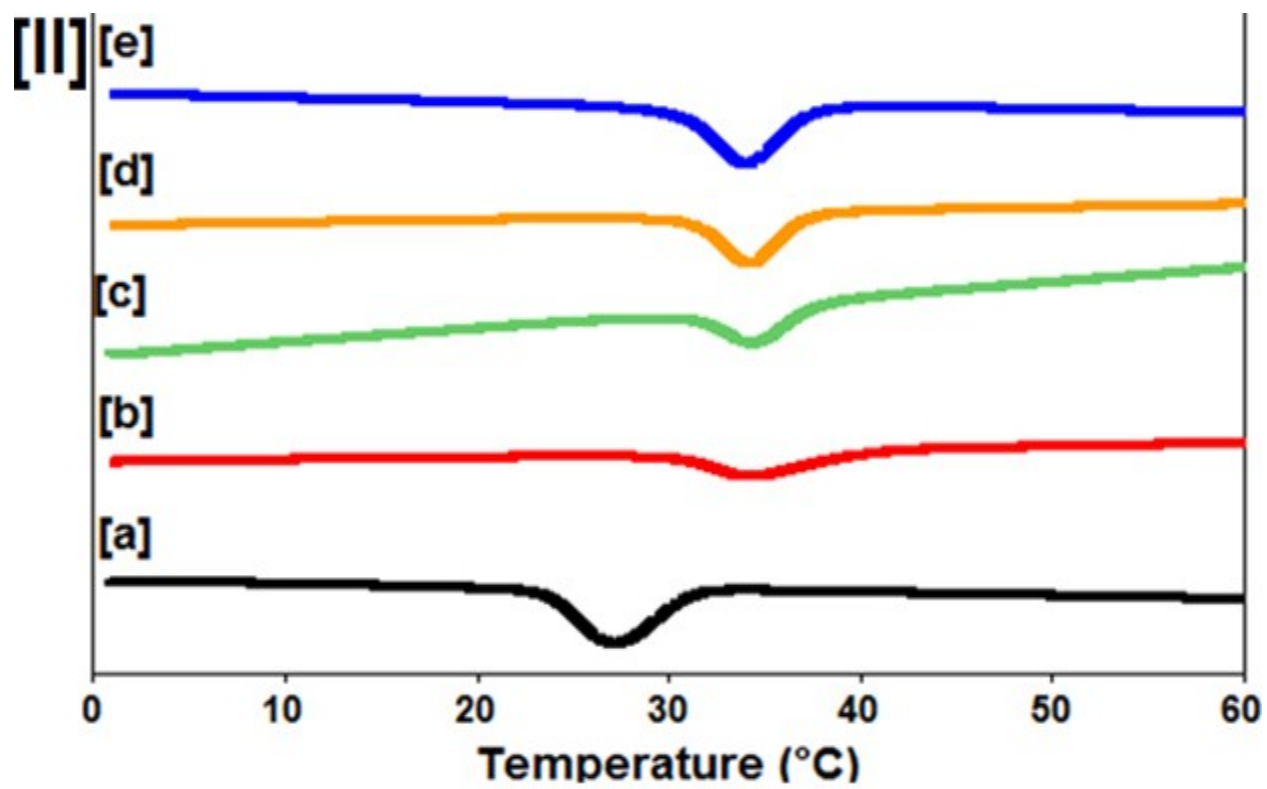
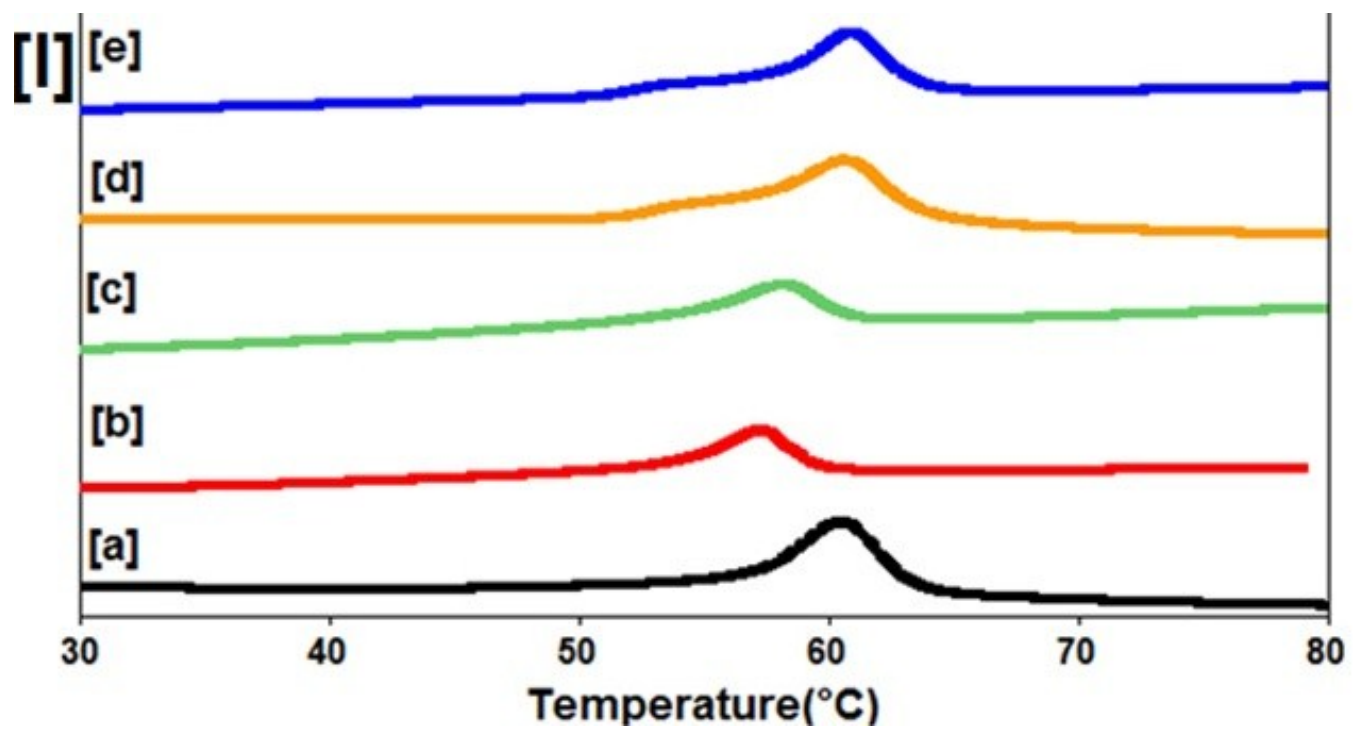


Figure S4. Thermal analyses of electrospun neat PCL and pseudorotaxanes electrospun from chloroform. (I) First melting cycle from 30 to 80 °C, at the rate of 20 °C/min. (II) First cooling cycle from 80 to 0 °C, at the rate of 20 °C/min (data is shown only from 60 °C). (a) Neat PCL, (b) Uncomplexed PCL/40% α -CD, (c) P-6 (CFM/DMF), (d) P-3 (CFM), (e) P-6 (CFM). Adapted with permission from ref [1]. Copyright American Chemical Society 2016.

References:

[1] Narayanan G, Aguda R, Hartman M, Chung C-C, Boy R, Gupta BS, et al. Fabrication and Characterization of Poly(ϵ -caprolactone)/ α -Cyclodextrin Pseudorotaxane Nanofibers. *Biomacromolecules*. 2016;17:271-9.