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# Supplementary Information

## Leveraging peptide-cellulose interactions to tailor the hierarchy and mechanics of peptide-polymer hybrids

Daseul Jang[a], Laura E. Beckett[a], Jong Keum[b], LaShanda T.J. Korley[a, c]

[a.] Department of Materials Science and Engineering, University of Delaware, 127 The Green, 201 Dupont Hall, Newark, Delaware, USA, 19716.

[b.] Center for Nanophase Materials Sciences and Neutron Scattering Division, Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, Tennessee, USA, 37830.

[c.] Department of Chemical and Biomolecular Engineering, University of Delaware, 150 Academy Street, Newark, Delaware, 19716.

* Corresponding author: lkorley@udel.edu

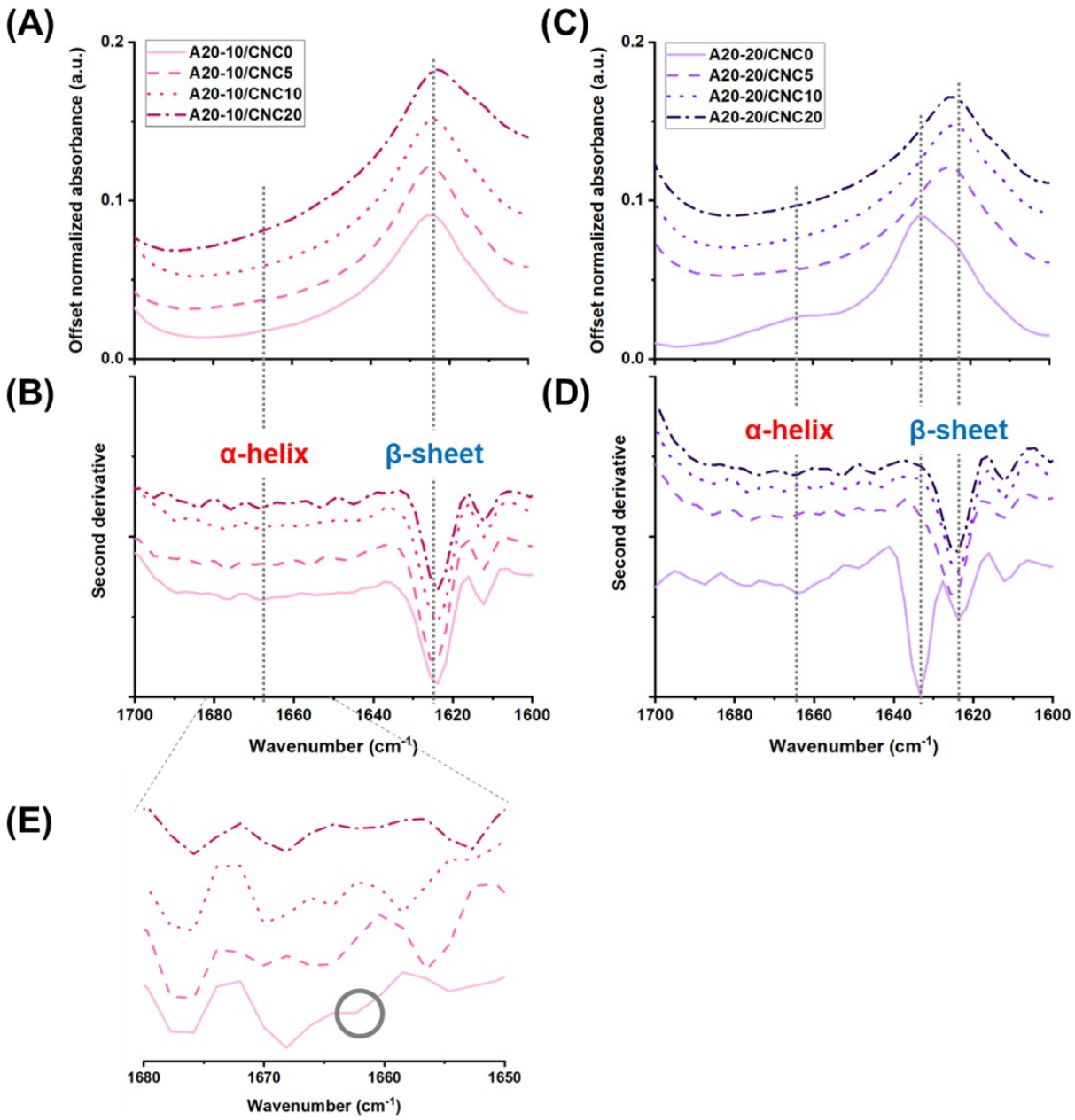
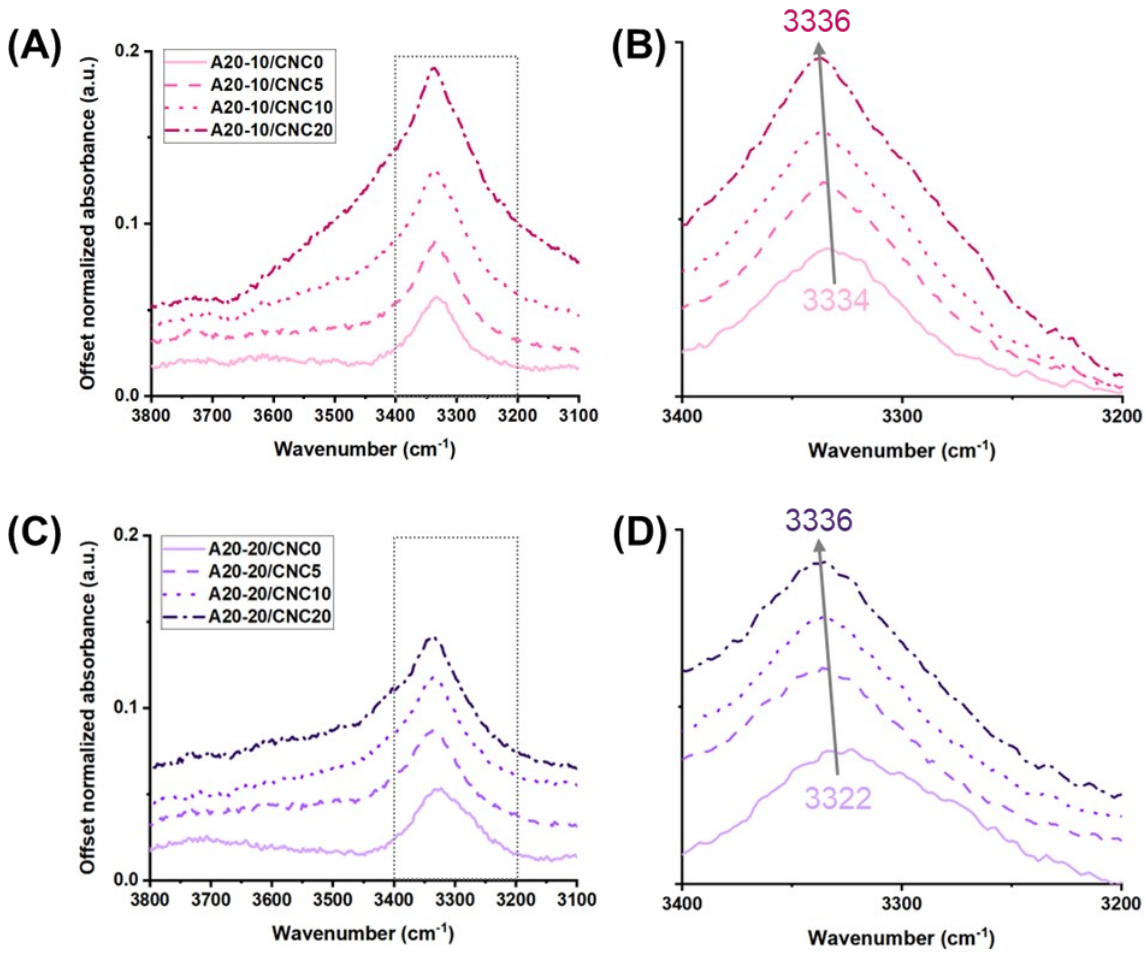


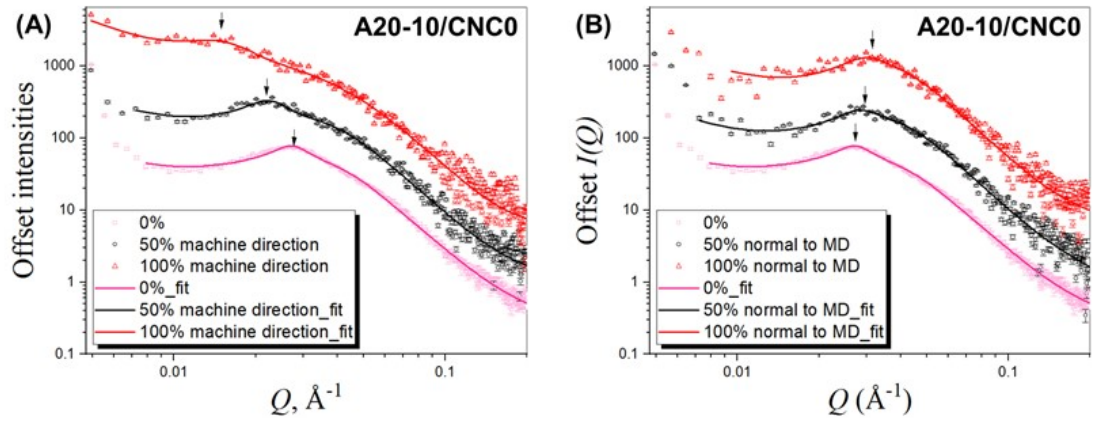

**Figure S1**. ATR-FTIR spectra of **(A)** A20-10/CNC and **(C)** A20-20/CNC in the amide I stretching region (1700-1600 $cm^{-1}$). The second derivative analysis of **(B)** A20-10/CNC and **(D)** A20-20/CNC used to determine the peptide secondary structure. **(E)** ATR-FTIR spectra of A20-10/CNC in the region of 1660-1670 $cm^{-1}$ to aid the visualization of the α-helical conformation. A gray-colored circle indicates the peak assigned to α-helices.



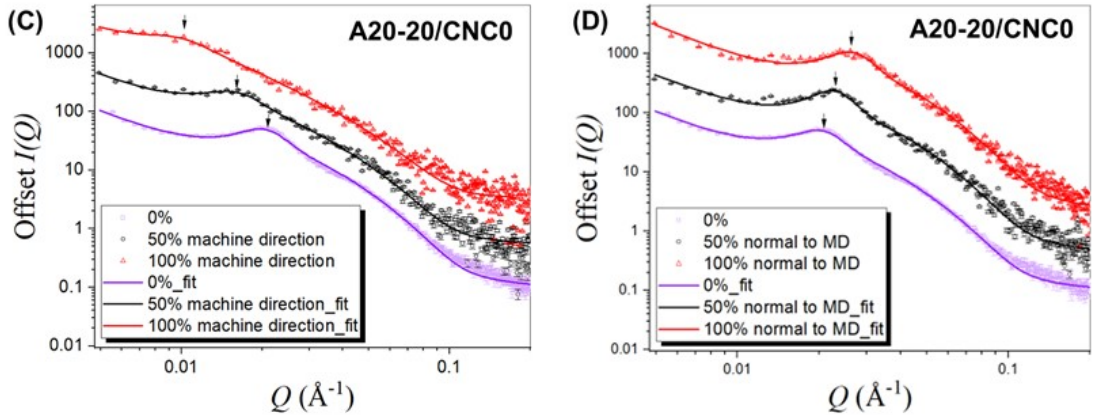

**(E)**

| | FWHM | | FWHM |
|---|---|---|---|
| **A20-10/CNC0** | 77 | **A20-20/CNC0** | 104 |
| **A20-10/CNC5** | 81 | **A20-20/CNC5** | 105 |
| **A20-10/CNC10** | 135 | **A20-20/CNC10** | 101 |
| **A20-10/CNC20** | 194 | **A20-20/CNC20** | 127 |

**Figure S2.** ATR-FTIR investigation of peptidic polyurea/cellulose nanocrystals (PPU/CNC) nanocomposites. (**(A)** and **(B):** A20-10/CNC; **(C)** and **(D)**: A20-20/CNC) in the N-H stretching region. **(B)** and **(D)** show the zoomed in region (3200-3400 $cm^{-1}$) of the PPU/CNC nanocomposites, highlighting that the peak position of the neat PPUs (3334 and 3322 $cm^{-1}$ for A20-10/CNC0 and A20-20/CNC0, respectively) shifted slightly toward a higher wavenumber when CNCs are added. **(E)** Table summarizing the full width at half maximum (FWHM) for the PPU matrices and the PPU/CNC nanocomposites.




| A20-10/CNC0 | | | | | |
|---|---|---|---|---|---|
| | 0% | 50% MD | 100% MD | 50% normal to MD | 100% normal to MD |
| Lamellar thickness (Å) | 33 | 32 | 29 | 32 | 30 |
| Polydispersity in thickness | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
| Long spacing (Å) | 216 | 253 | 318 | 206 | 186 |
| Polydispersity in long spacing | 0.3 | 0.3 | 0.4 | 0.3 | 0.3 |
| Long spacing of roughly ordered lamellae (Å) | 223 | 239 | 428 | 194 | 184 |




| A20-20/CNC0 | | | | | |
|---|---|---|---|---|---|
| | 0% | 50% MD | 100% MD | 50% normal to MD | 100% normal to MD |
| Lamellar thickness (Å) | 44 | 42 | 42 | 42 | 39 |
| Polydispersity in thickness | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
| Long spacing (Å) | 263 | 316 | 461 | 245 | 207 |
| Polydispersity in long spacing | 0.3 | 0.4 | 0.5 | 0.3 | 0.3 |

**Figure S3.** 1D SAXS scattering patterns (dot) and fitted scattering patterns (solid ) of the neat PPUs (A and B: A20-10/CNC0; C and D: A20-20/CNC0) as a function of strain (0, 50, and 100%) and stretching direction (parallel to the machine direction (A and C) and perpendicular to the machine direction (B and D)). Tables summarizing the lamellar thickness and long spacing calculated from model fits for A20-10/CNC0 and A20-20/CNC0.

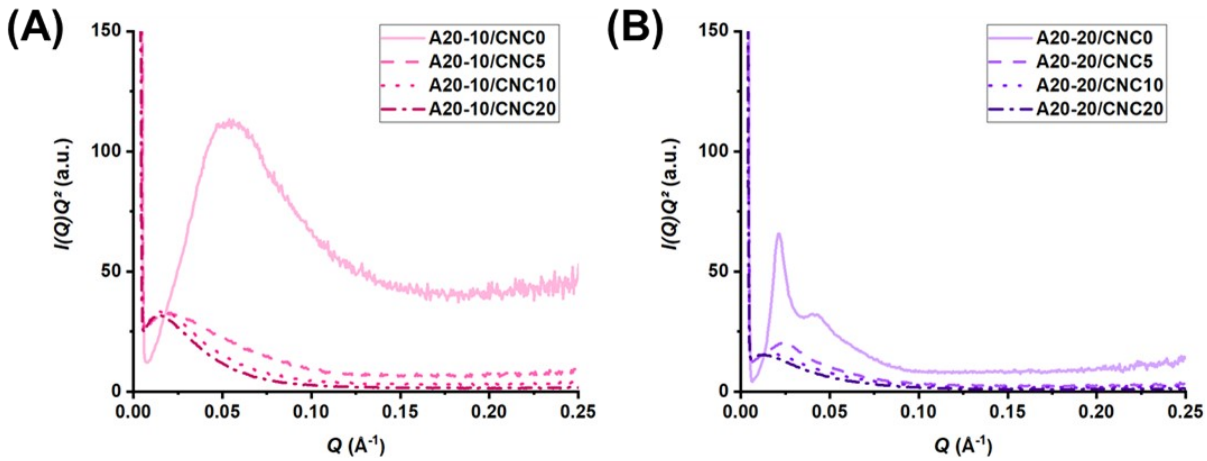



**Figure S4.** Lorentz-corrected SAXS patterns of the (A) A20-10/CNC and (B) A20-20/CNC series.

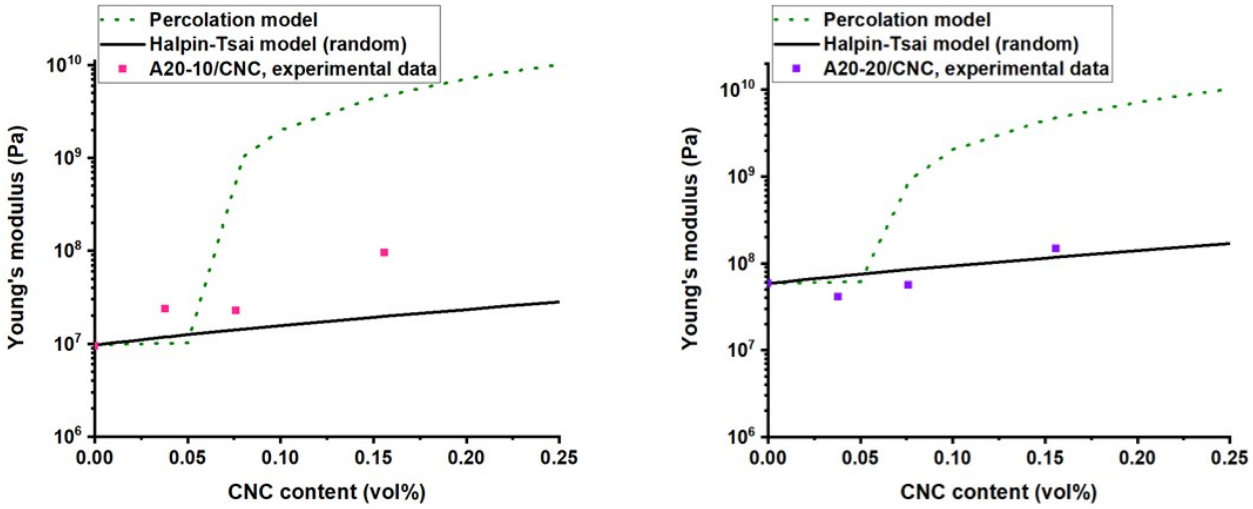



**Figure S5.** Experimental Young's moduli of A20-10/CNC and A20-20/CNC nanocomposites compared with the percolation model (green dot) and the Halpin-Tsai model for randomly-oriented CNCs (black solid line).

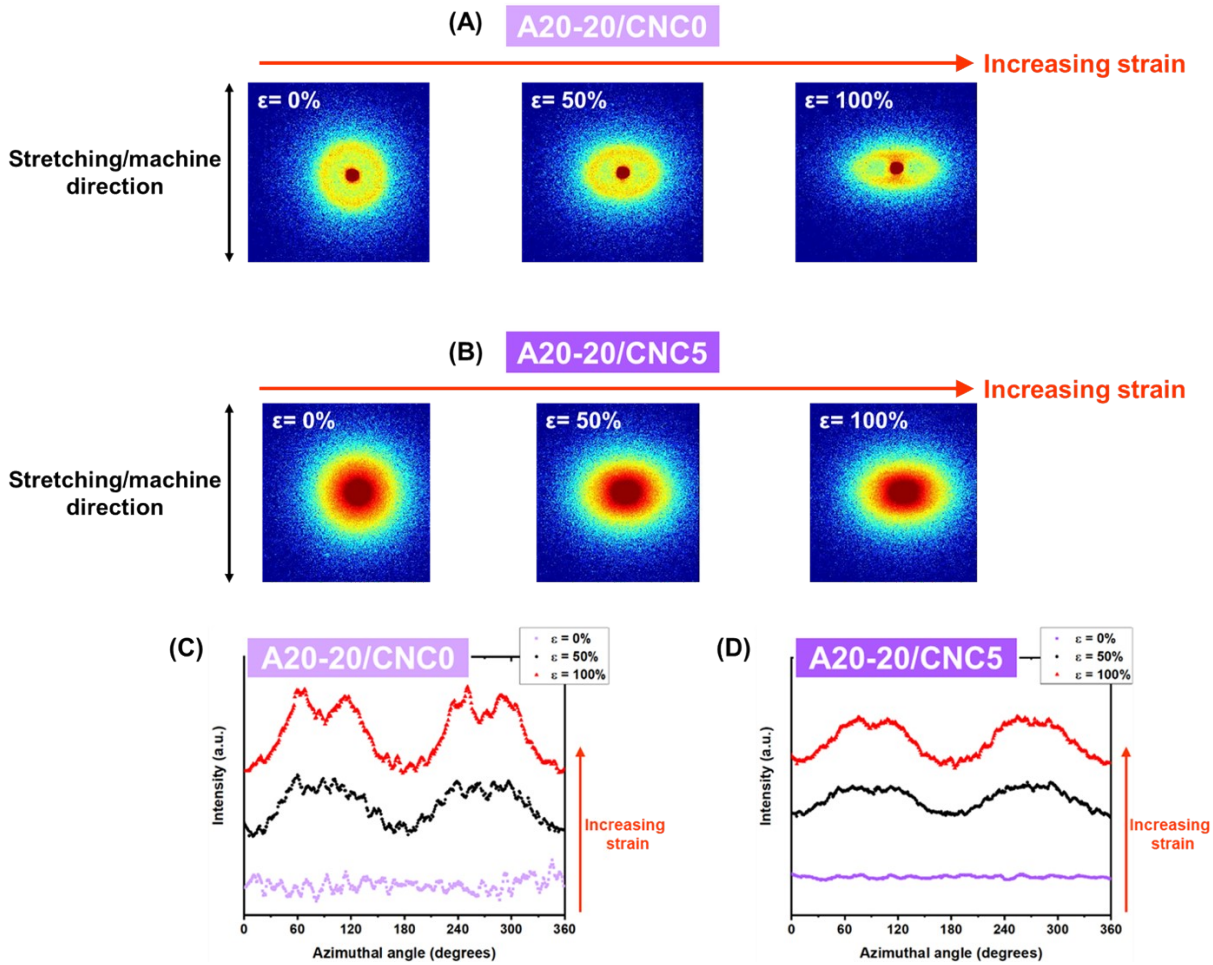



**Figure S6.** 2D SAXS patterns of (A) A20-20/CNC0 and (B) A20-20/CNC5 as a function of strain. Azimuthal profiles (centered at q = ~ 0.02 ± 0.005 Å-1) for (C) A20-20/CNC0 and (D) A20-20/CNC5 at 0, 50, and 100% strain.

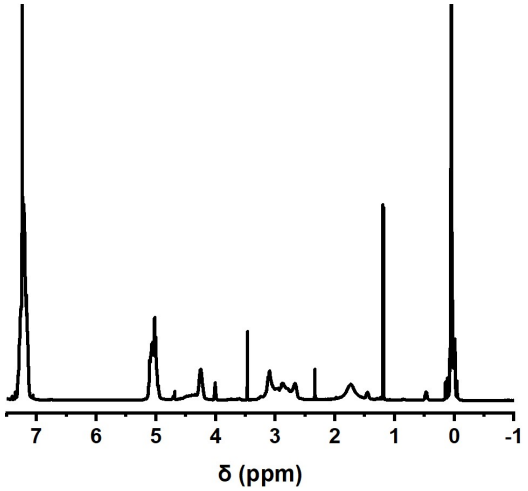



**Figure S7.** $^{1}$H-NMR spectrum of poly(β-benzyl-L-aspartate)-*b*-poly(dimethylsiloxane)-*b*-poly(β-benzyl-L-aspartate) (PBLA-*b*-PDMS-*b*-PBLA) triblock copolymers recorded in $CDCl_3$ (δ 7.26 ppm). The average repeat length of the PBLA block was calculated using the peak at δ = 5.15 ppm (80H, PBLA benzyl-) and the peak at δ = 0 ppm (240 H, PDMS methyl-).

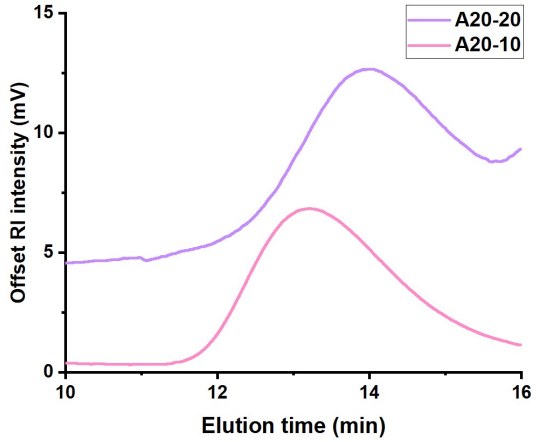



**Figure S8.** GPC traces of A20-10 and A20-20 used as the matrices. Tetrahydrofuran was used as the mobile phase and nine polystyrene standards (589 – 2,110,000 g/mol) were used to determine the relative molecular weight and dispersity.