

Hierarchical Self-Assembly of a Biomimetic Diblock Copolypeptoid into Homochiral Super Helices

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Representative MALDI and HPLC trace of a typical polypeptoid

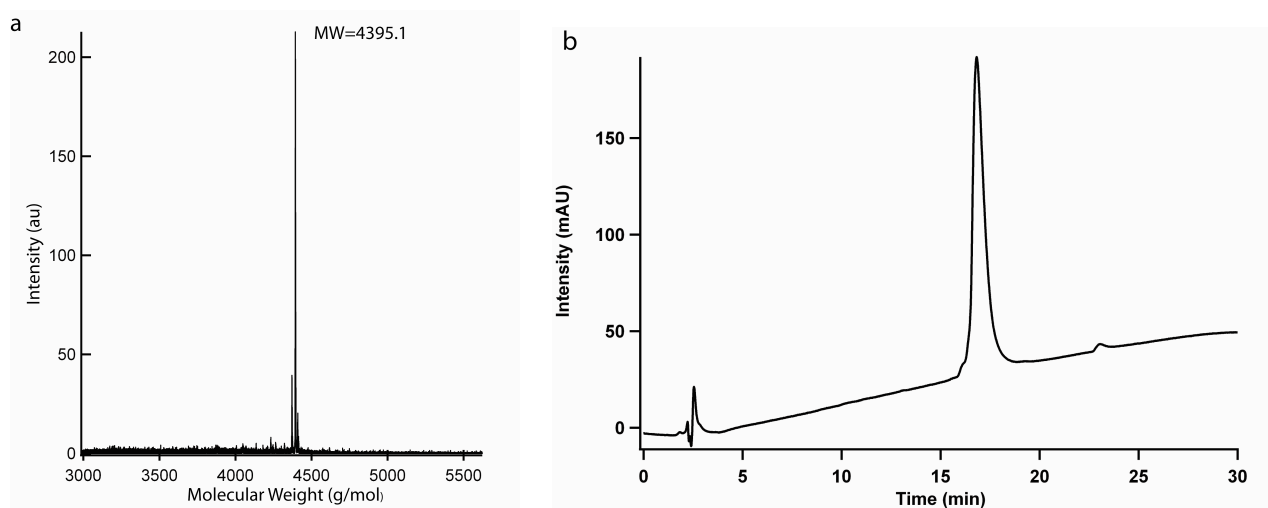


Figure S1: A typical MALDI mass spectrum (a) of $pNpe_{15}Nce_{15}$ showing the molecular weight to be 4372.1. The observed molecular weight is increased by 23 due to sodium from the matrix used. The second image (b) is a typical analytical reverse-phase HPLC trace demonstrating the purity of the polymer after purification.

Quantification of self-assembly yield

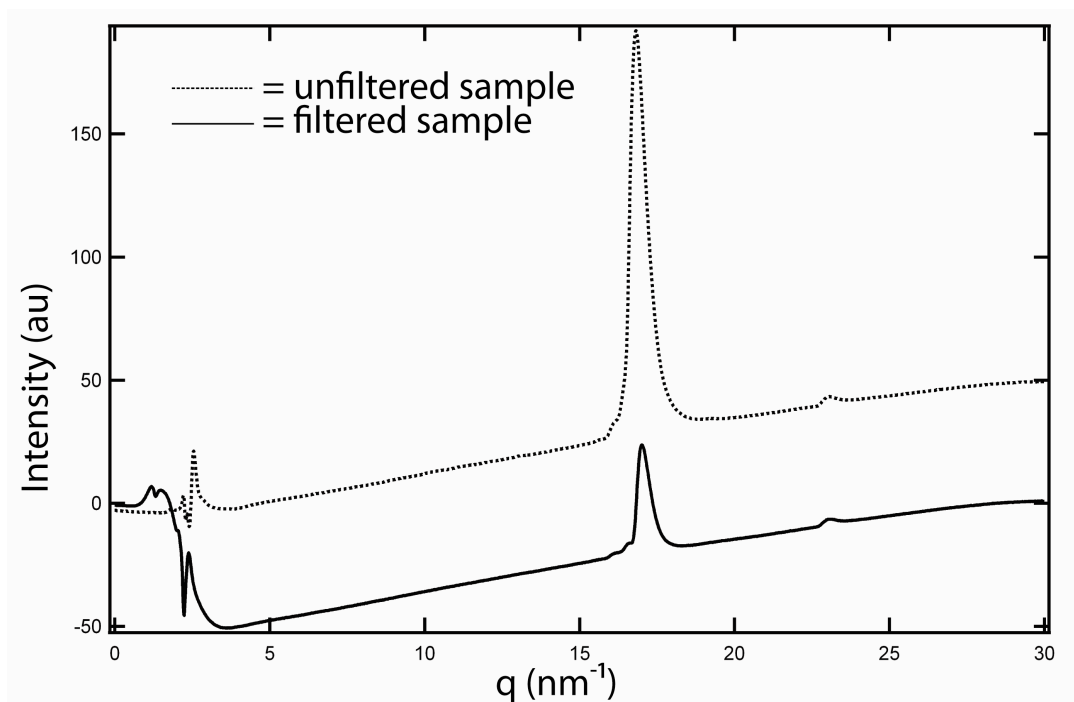


Figure S2: After 1 week a self-assembly solution was divided in half with one half going through a 100K Pall centrifugal filter and one half remaining unfiltered. The HPLC traces of a one week old self assembly solution before filtering and after filtering are shown above. After filtering, the area of the peak in HPLC has shrunk by 83% indicating that 83% of the peptoid material was participating in a self assembled structure larger than 100K which would be true of any sheets or helices.

Base titration of $p\text{Npe}_{15}\text{Nce}_{15}$

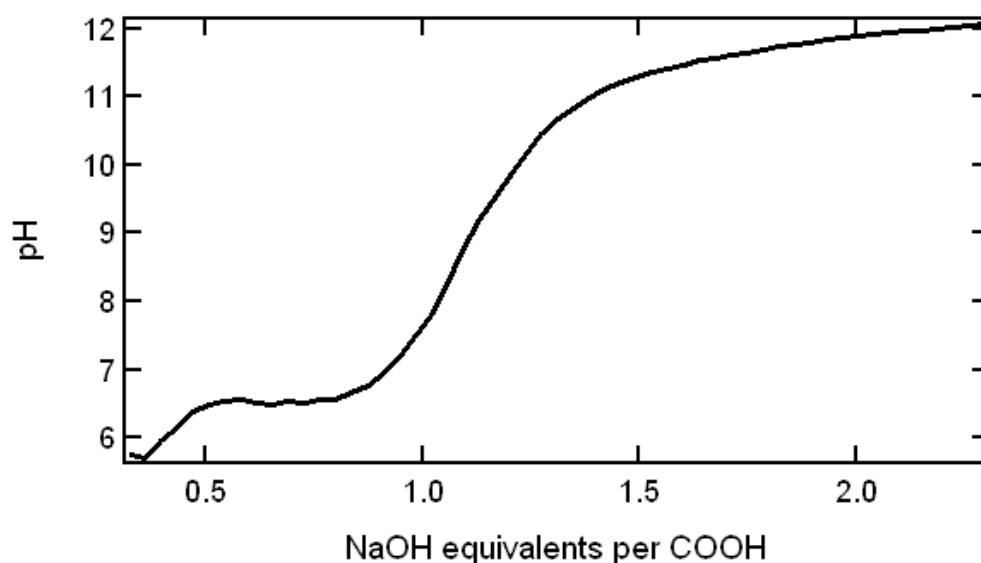


Figure S3: Sodium hydroxide was added in a dropwise fashion to a stirring aqueous solution of $p\text{Npe}_{15}\text{Nce}_{15}$. The pH was continually monitored using a Fisher Scientific AB15 pH meter. The titration curve is shown with the x-axis converted to molar equivalents of OH^- groups per carboxylic acid group. A plateau appears at pH 6.5 when 0.5 equivalents of NaOH have been added per carboxylate group. This is followed by a sharp increase in pH starting close to 1.0 equivalent. This increase indicates that 100% of the carboxylic acid groups are deprotonated and any additional NaOH simply raises the pH of the solution. The self-assembly solutions are mixed at pH 6.8 using 0.5 equivalents of sodium hydroxide.

X-ray scattering of solid and liquid samples of $pNpe_{15}Nce_{15}$

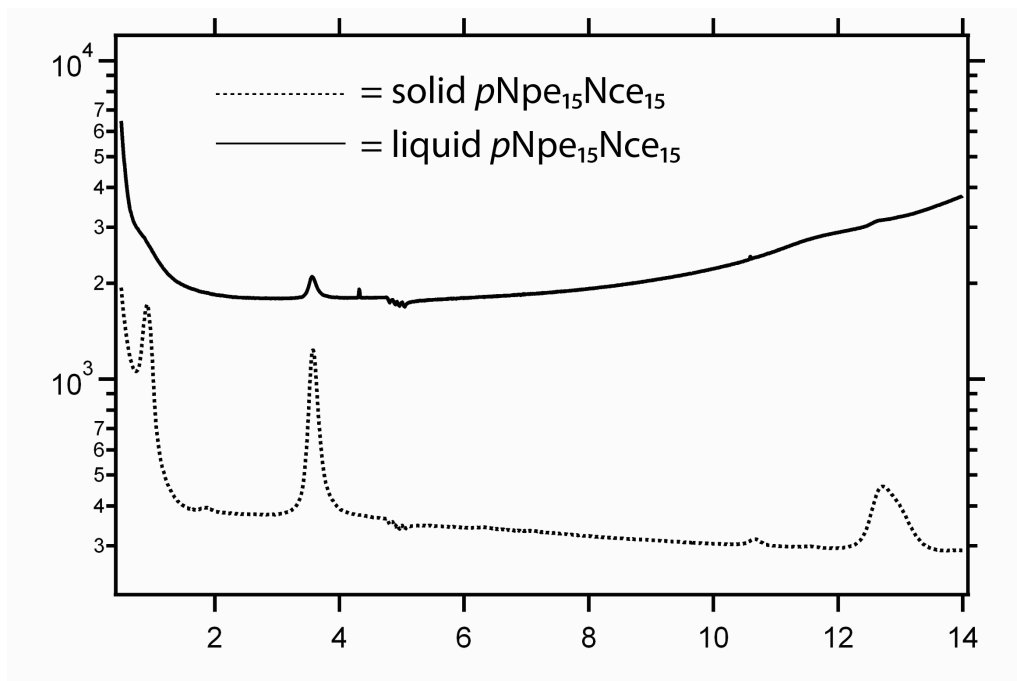


Figure S4: X-ray scattering was performed on both solid and liquid samples of $pNpe_{15}Nce_{15}$. The solid samples were obtained by evaporation of a self-assembled peptoid solution. This solid sample was then placed in the x-ray beam. For the liquid sample, the self-assembly solution was concentrated 10-fold by evaporation and then drawn up into a capillary sample tube for shooting. The two methods for scattering gave peaks in the same locations but the liquid sample scattering was significantly weaker in intensity. Therefore all data in the main body of this report were taken from solid samples.

Differential scanning calorimetry of $pNpp_{15}$ and $pNpe_{15}$

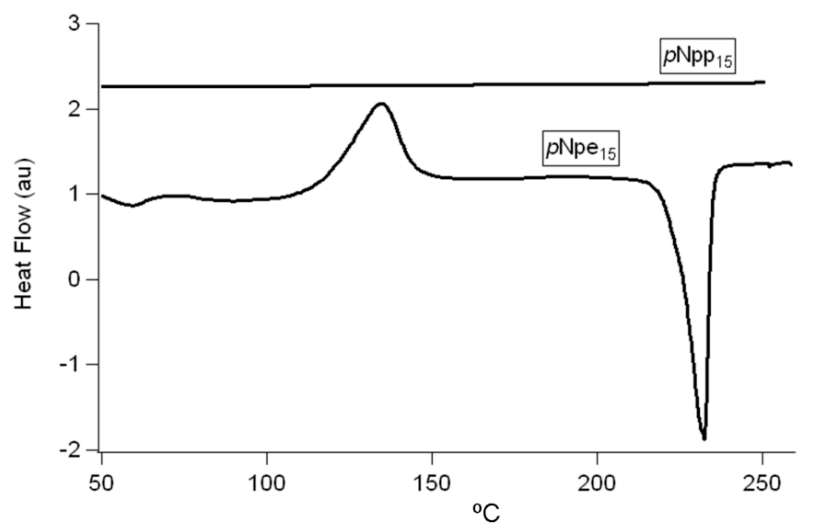


Figure S5: The self-assembled super helix resulting from a diblock of $pNpp_{15}Nce_{15}$ was found not to have any internal crystalline structure. The x-ray scattering trace for this structure is shown in the main body of this publication. It is hypothesized that the longer side chain length of the phenylpropyl group prevents the molecule from crystallizing. Differential scanning calorimetry data supports this hypothesis. The traces for the homopolymers of phenylpropyl, $pNpp_{15}$ and phenethyl, $pNpe_{15}$ show very different melting behavior¹. $pNpe_{15}$ has a clear melting and crystallization transition while $pNpp_{15}$ shows no melting transition before degradation around 250°C. This lack of crystallization in the solid state seems to be repeated in the solution state assembly as evidenced by the lack of interchain crystallization peaks within the x-ray scattering patterns for the super helix structure. Interestingly, this lack of crystallization does not seem to inhibit helix formation.

1. Rosales, A. M.; Murnen, H. K.; Zuckermann, R. N.; Segalman, R. A., Control of Crystallization and Melting Behavior in Sequence Specific Polypeptoids *Macromolecules* **43**, 5627-5636 (2010).

Gallery of SEM and TEM images of $pNpe_{15}Nce_{15}$ superhelices

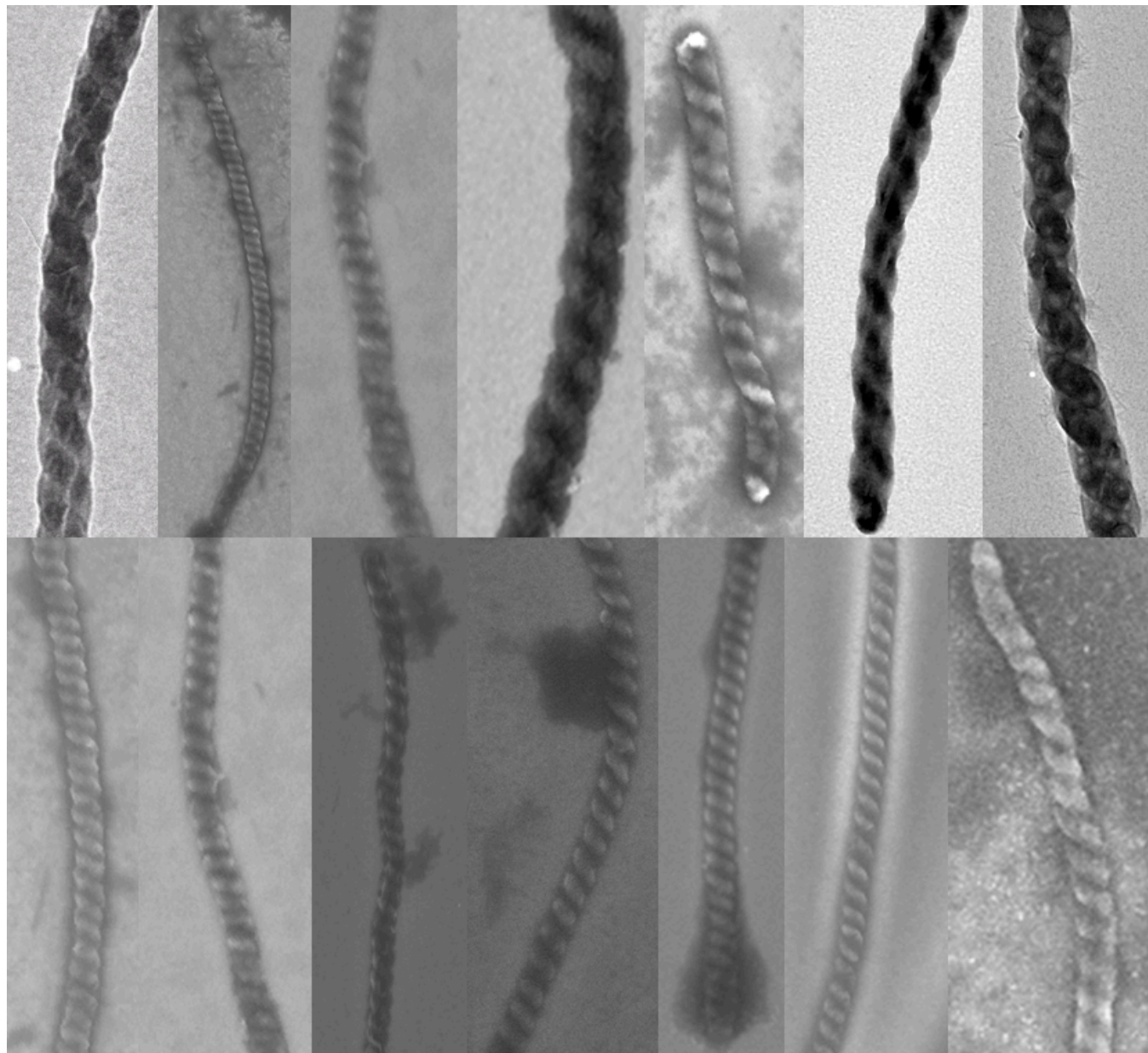


Figure S7: The image gallery above shows 15 helices aligned in a vertical direction such that it is possible to see their handedness. All of the helices are left handed, meaning that the pitch tilted up and to the left in the TEM and SEM images. The superhelix diameters are remarkably uniform, ranging from 612-620 nm.

Circular dichroism spectroscopy of $pNpe_{15}Nce_{15}$ superhelices

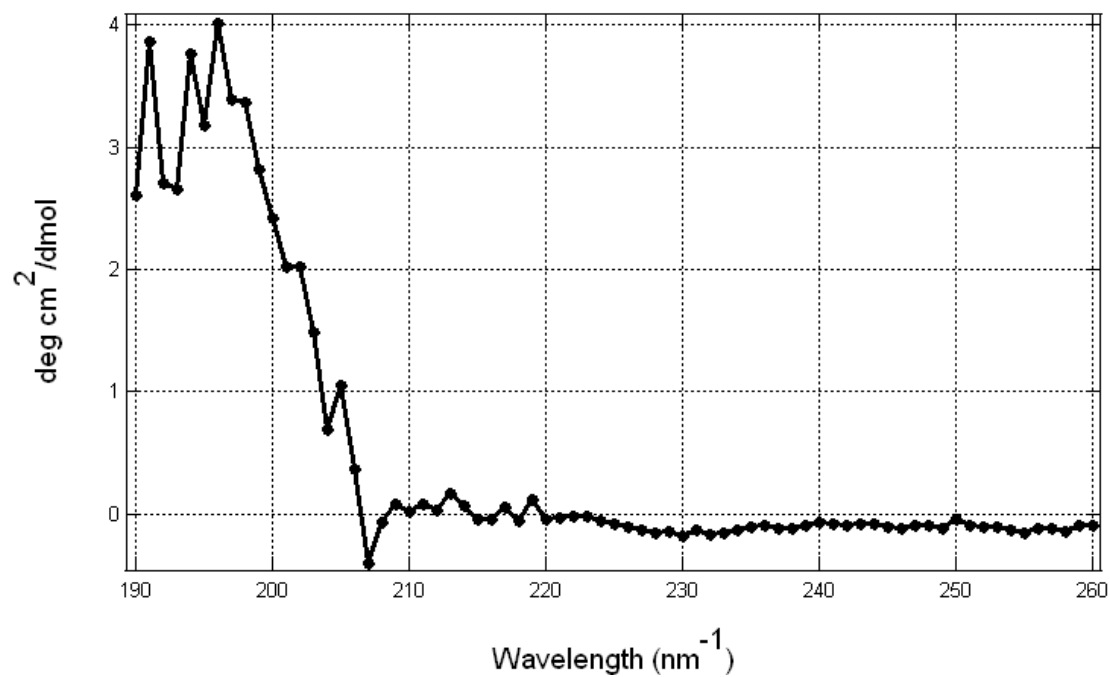


Figure S8: Circular dichroism was performed on a 300 μ M solution of $pNpe_{15}Nce_{15}$ superhelices to confirm the lack of chirality on a molecular level. As expected no rotation of light was seen, indicating a lack of molecular chirality.