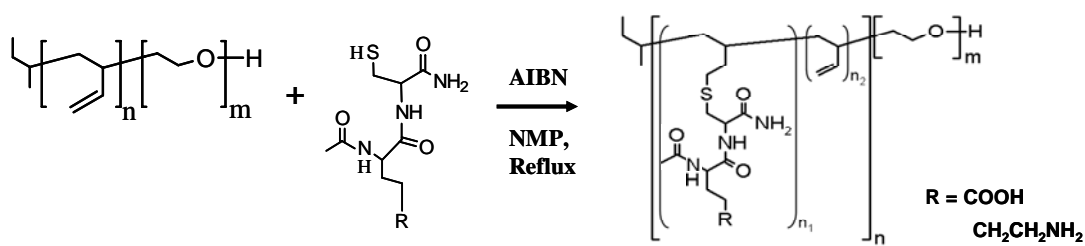# A Twist on Amphiphilicity Yields Sticky Supramolecular Cones

Xiaolin Li, Jennifer Haley, Helmut Schlaad, Rong Ju, Yan Geng ∗

Supporting Information

S1. Grafting Glu-Cys or Lys-Cys onto PBD_n-*b*-PEO_m.

The grafting procedure has been published elsewhere,[20] and briefly, the reaction flask containing the polymer PBD_n-*b*-PEO_m, dipeptide, and 2,2 azoisobutyronitrile (AIBN) was degassed for 30 minutes. Dry solvent, 1-methyl-2-pyrrolidinone (NMP) was then added. Molar ratio $[C=C]_0/[-SH]_0/[AIBN]_0 = 1:1.5:0.33$ was used to achieve a low grafting density of 30%. The resulting solution was heated to 70^oC and stirred for 48 hours under an argon atmosphere. AIBN was reinjected after 24 hours. After the reaction was complete, excess dipeptide was removed by dialysis. The product was freeze-dried and collected for ^{1}H NMR and Gel Permeation Chromatography (GPC) analysis.
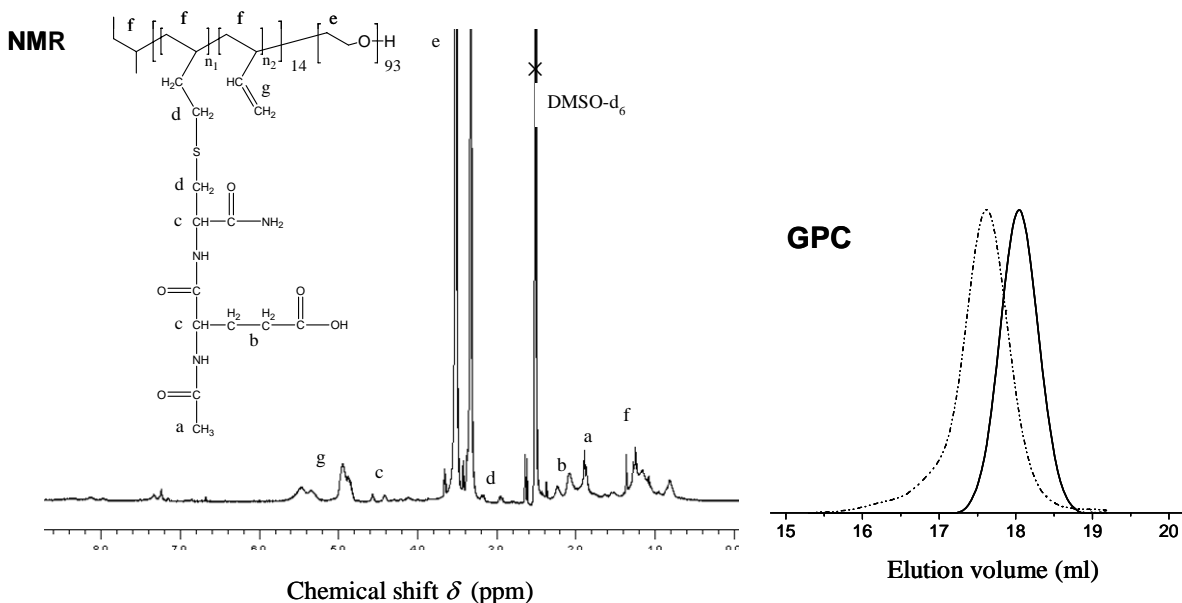
Using Glu-Cys grafted hybrid molecule as example, in ^{1}H NMR analysis, the characteristic signals of the grafted dipeptide were observed at $\delta = 1.9$ ppm (-**CH**$_3$, a), 2.1-2.3 ppm (-**CH**$_2$-**CH**$_2$-, b) and 4.4 – 4.6 (-CO-**CH**(R)-NH-, c); the signal of the thioether linkage -CH$_2$SCH$_2$- (d) arise at $\delta \sim 2.7$ and 2.9 ppm. Resonances at $\delta = 4.8$-5.6 ppm indicate that the conversion of PBD double bonds did not come to completion. The quantitative analysis of signal intensities relative to that of PEO at $\delta \sim 3.6$ ppm reveals that the hybrid molecule contains about four EC units and 10 unreacted butadiene units. GPC analysis using NMP as eluent showed single narrow peak for PBD$_{14}$-b-PEO$_{93}$ precursor (solid line) and the hybrid molecule with Glu-Cys grafts (dash line) respectively, indicating the narrow polydispersity of the PBD-b-PEG precursor has been preserved during the grafting process.

S2. Estimates of the aggregation number of peptide grafted PBD$_{14}$-*b*-PEO$_{93}$ conic nuclei and fully grown cones.

Assuming the core of the cones is largely made of the aggregated hydrophobic PBD polymer chains (as proposed in Scheme 1), aggregation number of the initial conic nuclei can be roughly estimated by $N = \dfrac{Mass}{M_n} \times N_A$, where N_A is the Avogadro constant, M_n is the molar mass of the PBD$_{14}$ polymer ($M_n \sim 756$ g/mol). The mass of the hydrophobic PBD conic core can be calculated as Mass $= V \times d$, where V is volume and d is density, which can be approximated by the bulk PBD polymer density (0.89 g/cm^3). The conic core volume V can then be calculated from TEM measurement, $V = 1/3 \ \pi \ r^2 \ h$. For a conic nucleate with $\sim$ 10nm height and 20° apex angle, $V = 1/3 \ \pi \ (10\text{nm} \times \tan(10°))^2 \times 10\text{nm} = 40 \ \text{nm}^3$ and the corresponding aggregation number is calculated to be $\sim$ 40 molecules. The aggregation number for a microns-long cone can be estimated in a similar fashion and calculated to be $\sim 10^5$.

S3. Hierarchical self-assembly of the 20% Glu-Cys grafted PBD$_{14}$-*b*-PEO$_{93}$ hybrid in water. (A) Supramolecular cone formation after one week, and (B) higher-order cone self-assembly at two weeks. (Scale bars: 5 μm)