Electronic Supplementary Material (ESI) for Polymer Chemistry

Peptide-based Lipid Mimetics with Tunable Core Properties via Thiol-Alkyne Chemistry

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Supplemental Information

The following data are provided in support of this manuscript: Figure S1 presents quantitative ^{13}C NMR for the thiol-yne conjugation to form $Chol_2PBLG_{11}$ and $POSS_2PBLG_{11}$, Figure S2 presents angle-dependent DLS decay rate data to verify Brownian diffusion of spherical particles and to calculate D_{app}, Figure S3 shows DMF GPC traces for two samples, Figure S4 shows the kinetics associated with a pH jump in terms of scattered intensity and Figure S5 shows how

^{13}C NMR. Bis-addition resonances show up at ~ 44 and 35 ppm for thiol carbon from Chol, 45 and 37 ppm for thiol carbon from POSS. Unfortunately, peaks associated with cholesterol show up in this region as well. For POSS-addition, 2 carbons from POSS show up around 35 ppm. For mono-addition at C(1), the alkene carbons would appear at 134 and 117, which is interfered with by aromatic carbons from benzyl protecting group of the polypeptide. For mono-addition at C(2), peaks would be present at 153 (next to thio ether) and 97 ppm. For no additions (un-reacted peptide) peaks would be present at ~ 68 and 80 ppm. Furthermore, when referring back to ^{1}H NMR, two additions would show up at ~ 2.8 and 3.4 ppm as well as the methylene next to amide on the end group shifting from 3.9 to 3.5. If mono-addition was present, there would be no shift in the methylene (we see it disappear) and protons associated with the alkene would be present at ~ 6.3 and 5.4 ppm (we do not observe that). For mono-addition at C(2), methylene

stays at 3.9 and protons on end are present at ~ 5 ppm (no indication of this). From these facts, it appears that we have no presence of mono-addition in either conjugate.

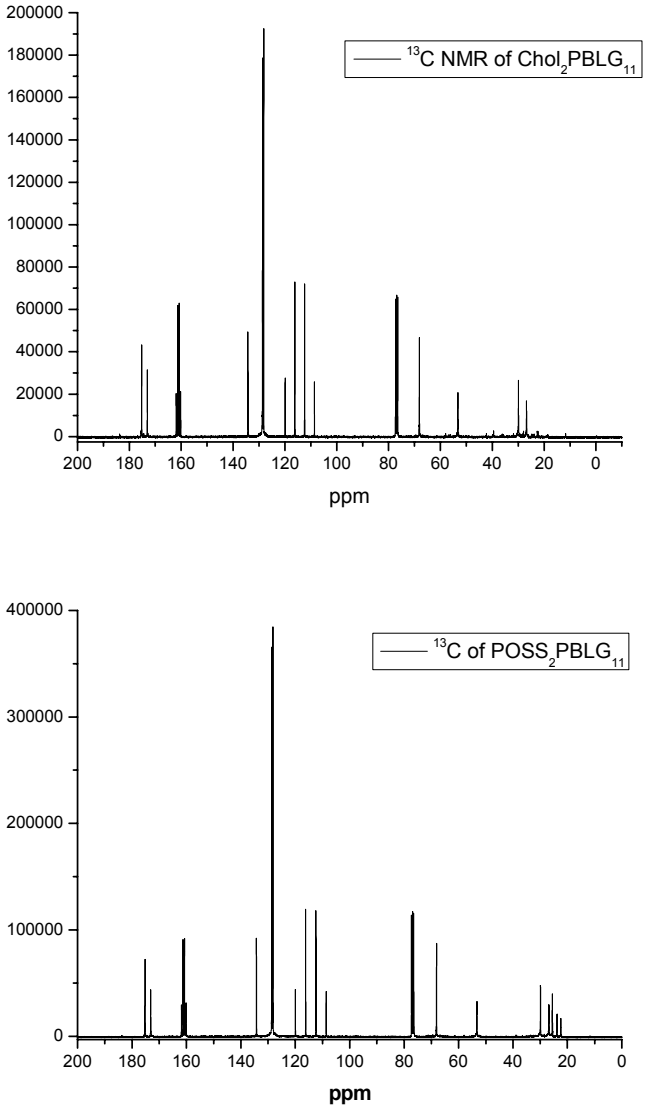

Figure S1. Quantitative ^{13}C NMR for conjugates $Chol_2PE_{11}$ (top) and $POSS_2PE_{11}$ (bottom.) From these spectra, and comparing with ^{1}H NMR in the main manuscript, there do not appear to be any mono-addition products, or unreacted peptide.

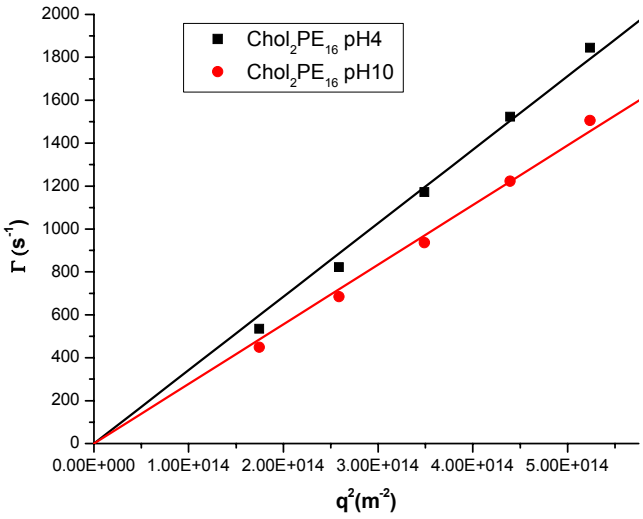

Figure S2. Γ vs. q^2 plot for $Chol_2PE_{16}$ in DI H_2O (0.025 wt%) at pH 4 and 10. Linearity in these plots, as well as the intercept through the origin suggests Brownian diffusion of spherical, monodisperse particles.

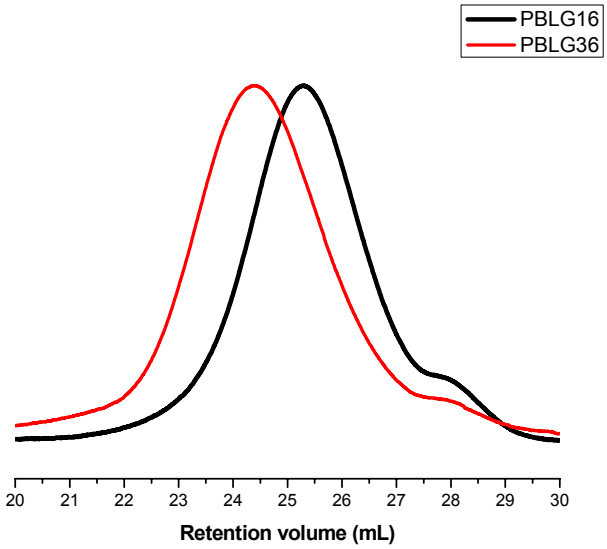

Figure S3. DMF Traces of acetylene-terminated PBLG polypeptides. PDIs were on the order of 1.2-1.4, typical for ROP of NCAs. The small shoulder at high elution volumes is an indication of termination events in a diminutive amount of low molecular weight peptides which are eventually removed by dialysis.

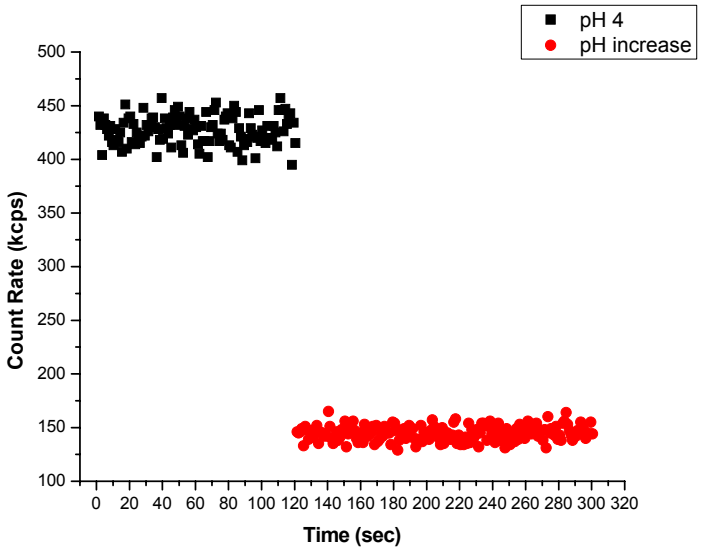

Figure S4. Kinetics of the morphology transition for ODT_2PE_{16} vesicles with pH. In this experiment, the scattering intensity is measured as a function of time. At low pH, the intensity is high. Since we know from DLS that this is a smaller aggregate, the high intensity is a result of increased chain packing at the vesicle interface. At about 120 seconds, an aliquot of NaOH solution is added, the sample is shaken and placed back in the scattering assembly. The dramatic decrease in scattering intensity occurs over the ca. 10 sec required for the pH jump. After the experiment, the final pH was measured to be around 8. DLS data taken before and after the pH perturbation yield R_h values consistent with the observed pH responsiveness in Figure 3.

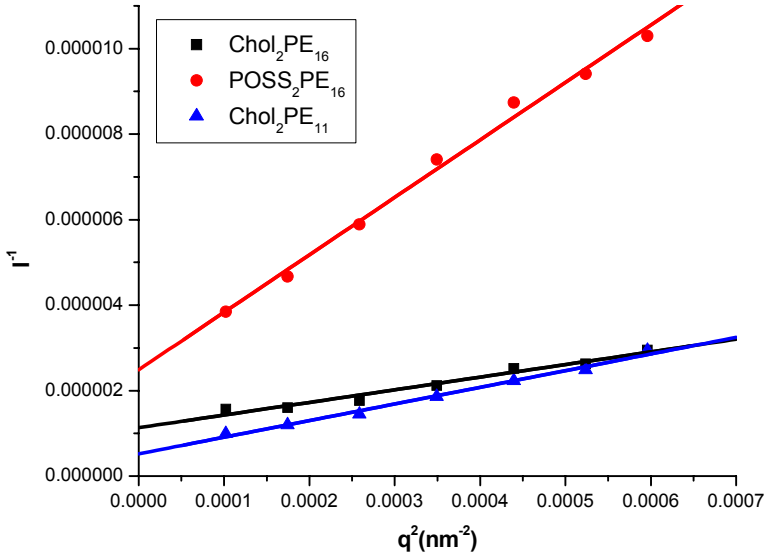

Figure S5. Inverse scattering intensity versus q^2 for $Chol_2PE_{16}$ (black squares), $POSS_2PE_{16}$ (red circles), and $Chol_2PE_{11}$ (blue triangles). This plot illustrates the difference in effective aggregation number (N_{agg}) for the three samples. The Chol-based amphiphiles have much higher scattering intensities (evidenced by smaller I^{-1} values) leading to a larger effective aggregate M_w ($M_w \sim 1/y\text{-int}$). There is little discrepancy in the R_g values of $POSS_2PE_{16}$ and $Chol_2PE_{16}$, thus this plot demonstrates that the Chol-based amphiphiles are of the highest order/chain density at the vesicle interface.