Electronic Supplementary Material (ESI) for Soft Matter

The Synthetic Tuning of Clickable pH Responsive Cationic Polypeptides and Block Copolypeptides

Amanda C. Engler, Daniel K. Bonner, Hilda G. Buss, Eva Y. Cheung, Paula T. Hammond*

Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139
*Email: Hammond@mit.edu

Supplementary Information

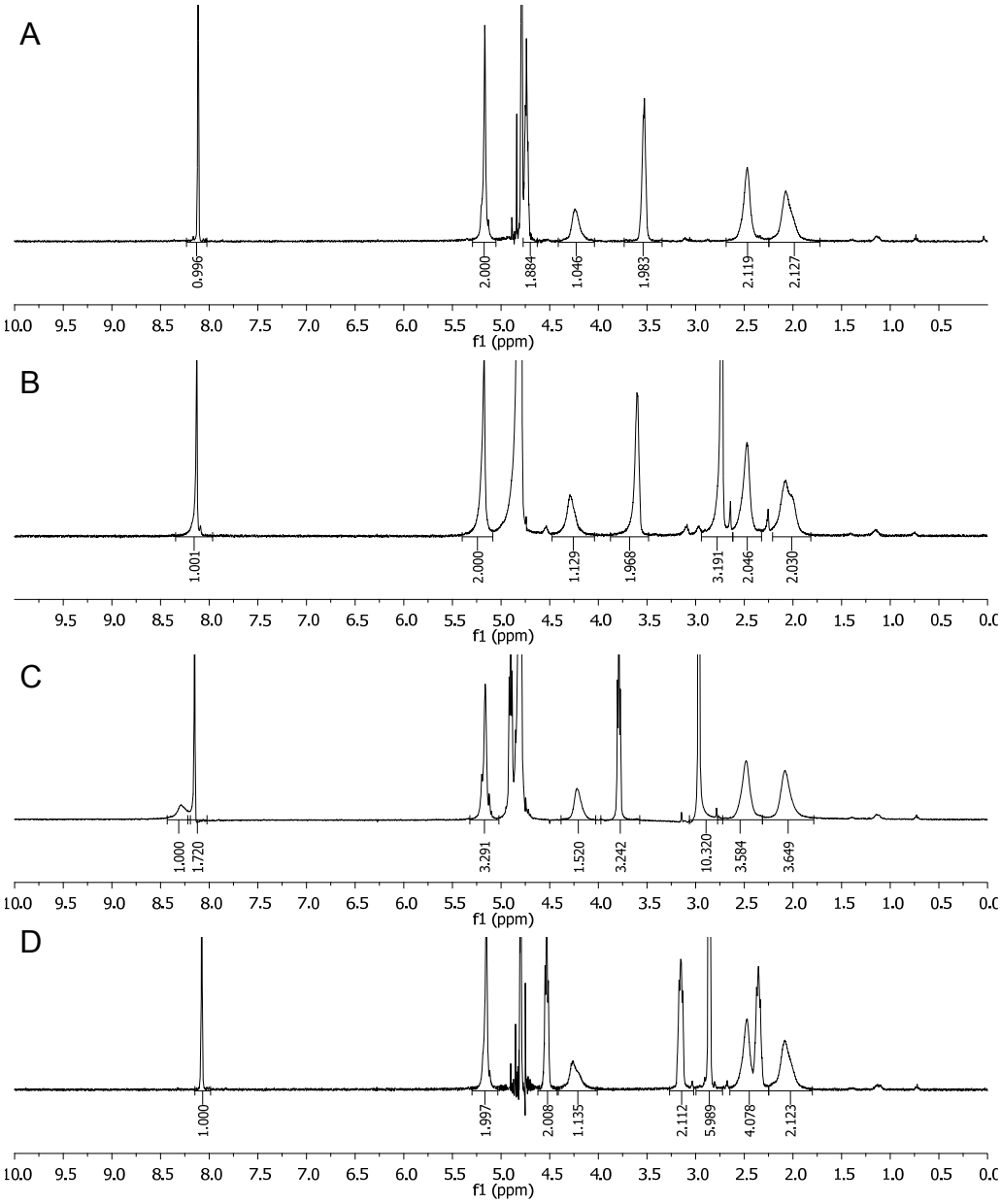

Figure 1. 1H NMR of PPLG (DP=75) functionalized with A) primary amine, B) secondary amine, C) dimethylethanamine, and D) dimethylpropanamine

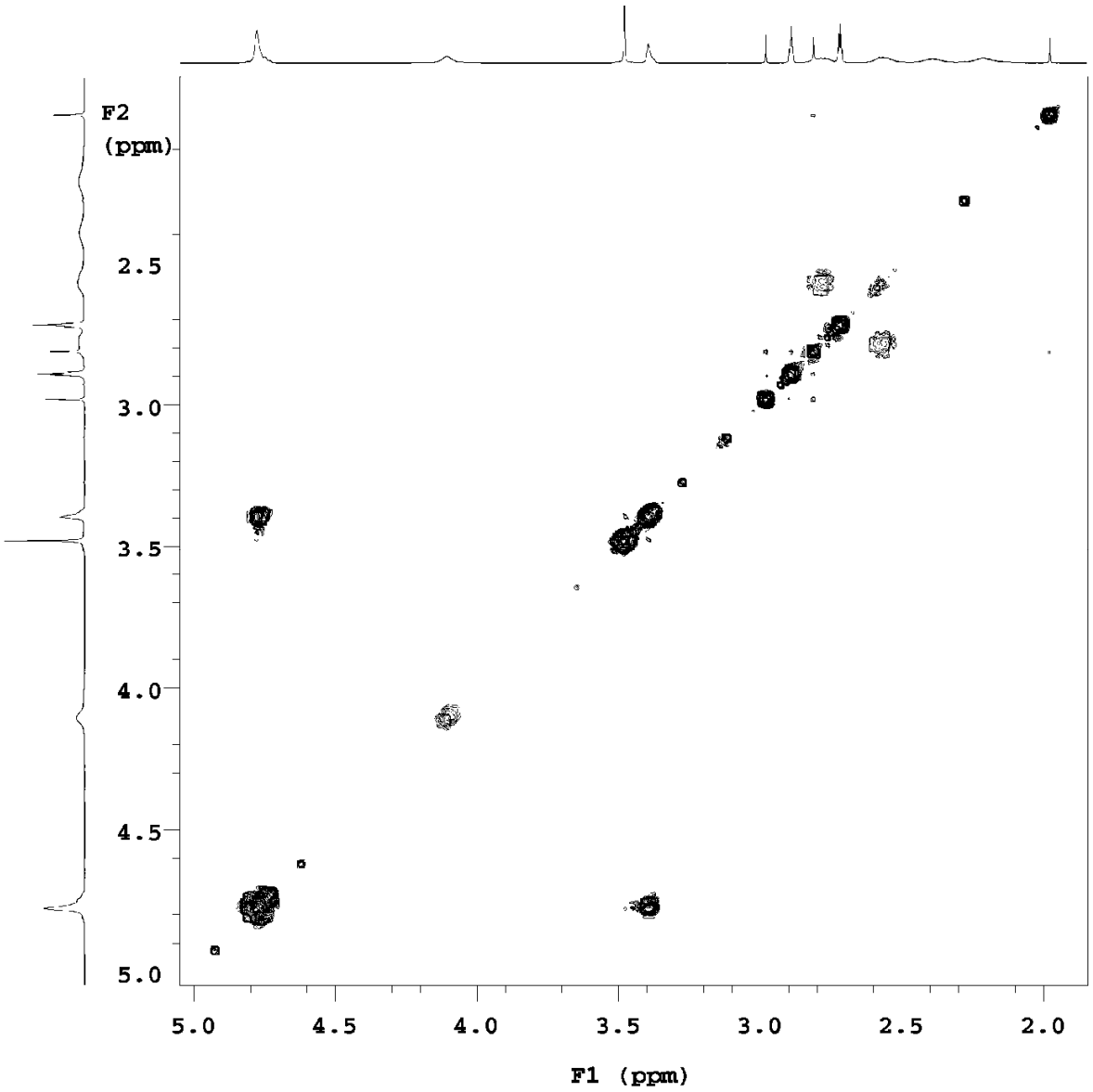

Figure 2. ^{1}H NMR of PPLG in DMF

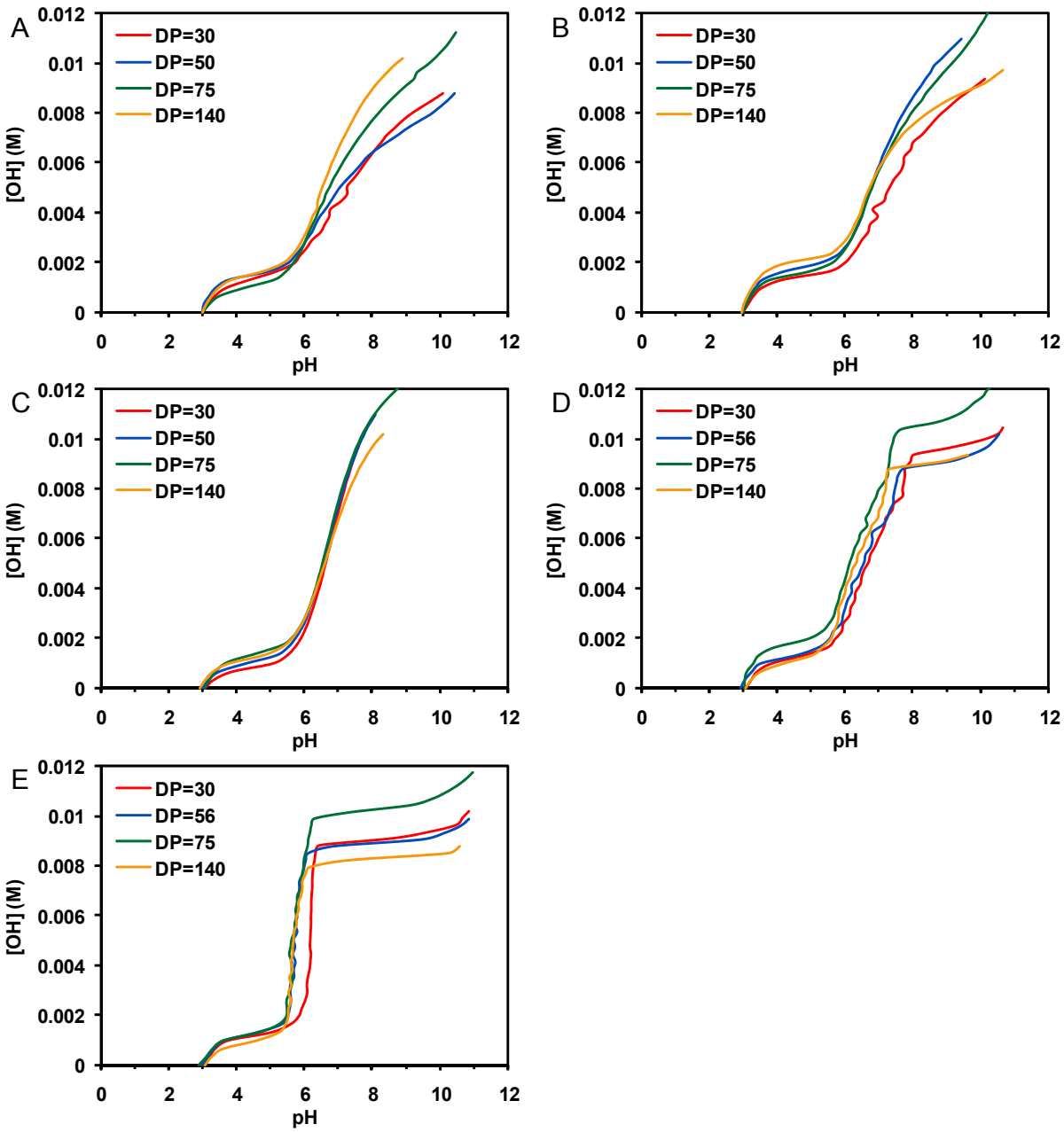

Figure 3. Titrations with increasing pH A) primary amine, B) secondary amine, C) dimethylethanamine, D) diethylamine, and E) diisopropylamine.

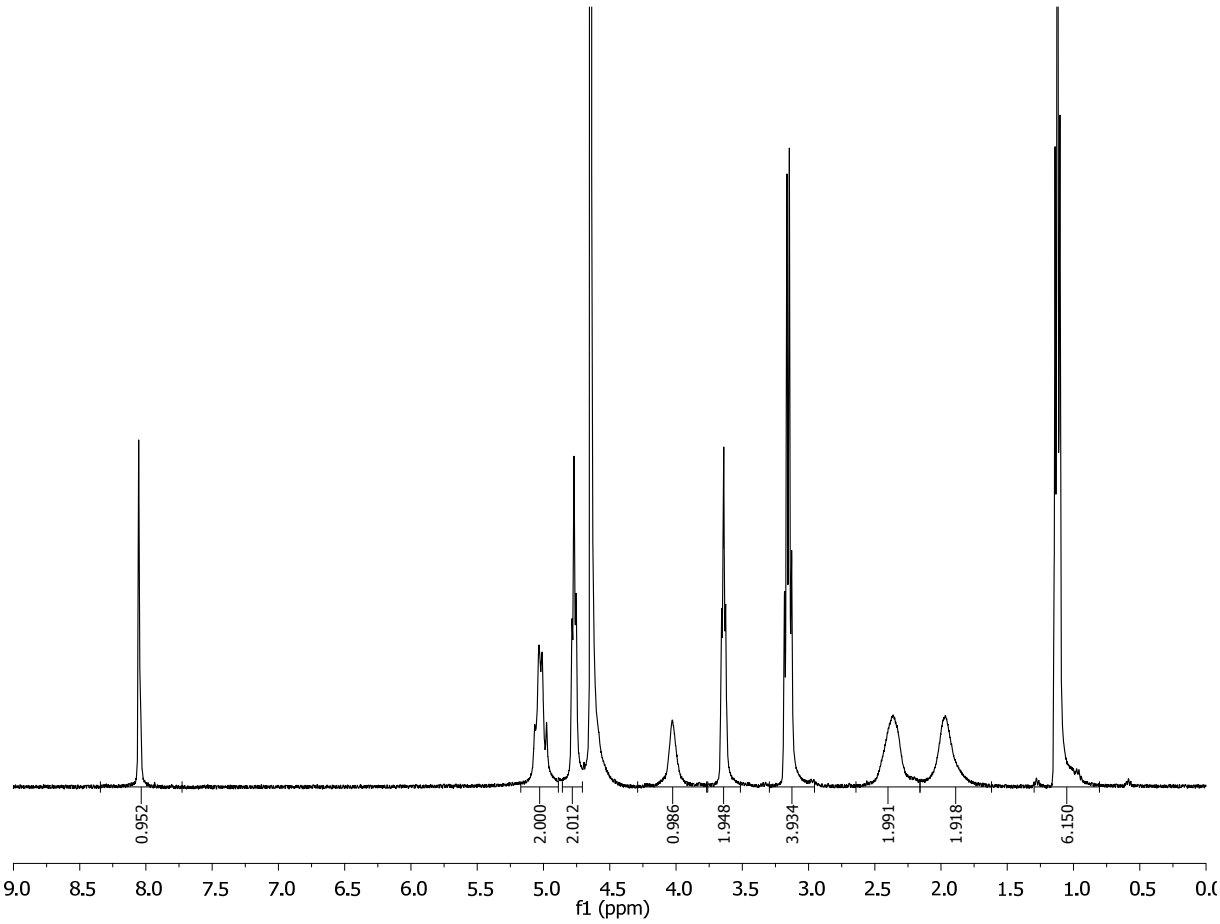

Figure 4. PPLG (DP=75) functionalized with diethylamine in D_2O after titration

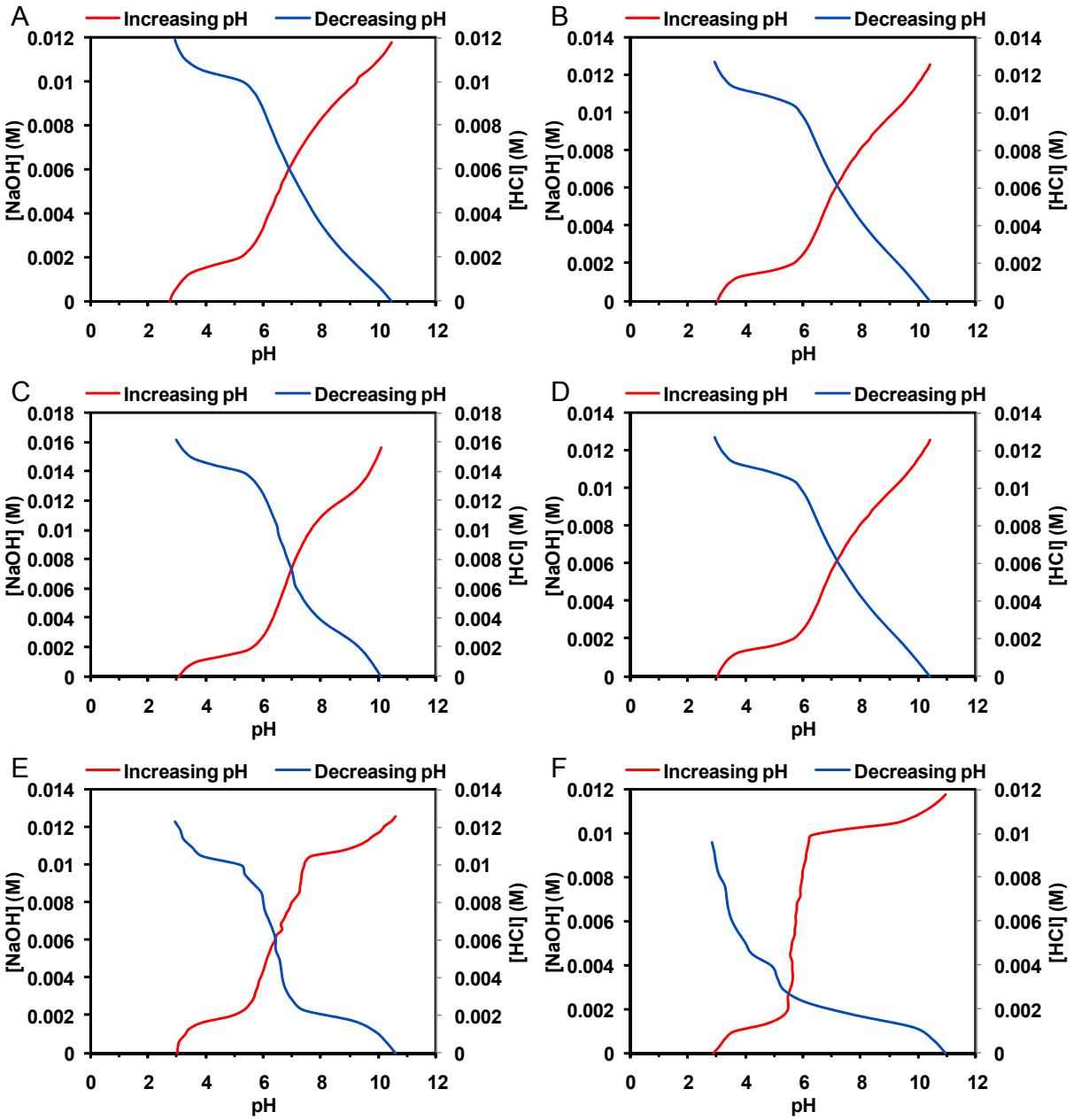

Figure 5. Titrations with increasing pH and decreasing pH for PPLG (DP=75) functionalized with A) primary amine, B) secondary amine, C) dimethylethanamine, D) dimethylpropanamine, E) diethylamine, and F) diisopropylamine.

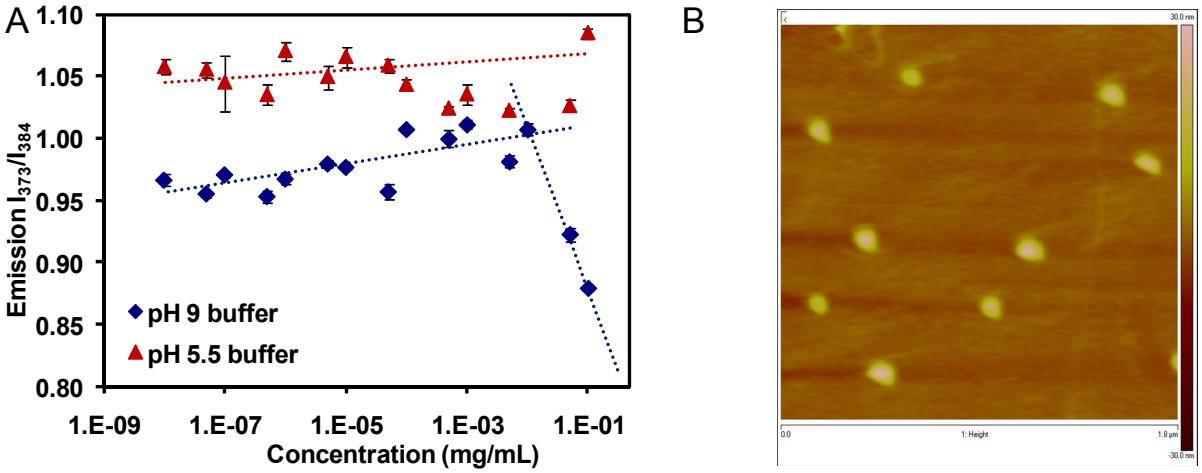

Figure 6. A) CMC determination by fluorometry using a pyrene probe for diethylamine substituted PEG-b-PPLG in pH 5.5 and 9 buffer and B) AFM image of diethylamine substituted PEG-b-PPLG at pH 9.21 and The AFM images are 2 by 2 μm.

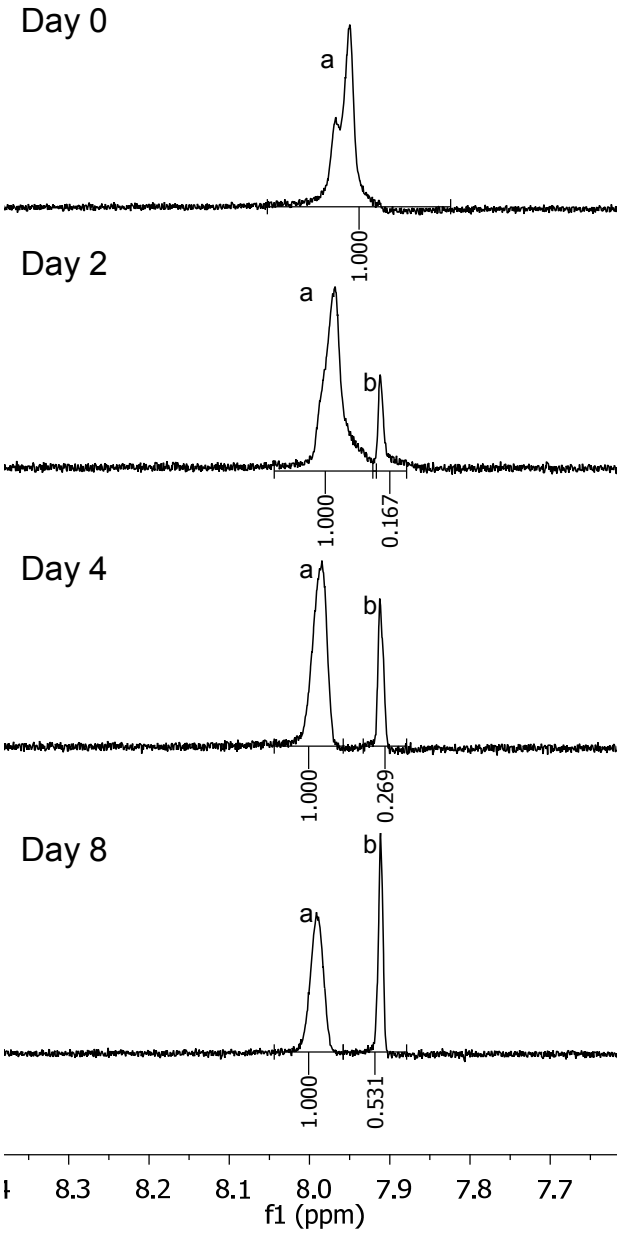

Figure 7. ^{1}H-NMR for PEG-b-PPLG functionalized with diethylamine hydrolyzed at pH 9 at various time points. The peak marked with a is from the triazole ring attached to the polymer by the ester linkage and the peak marked with b is from the triazole ring attached to the alcohol after the ester has been hydrolyzed.

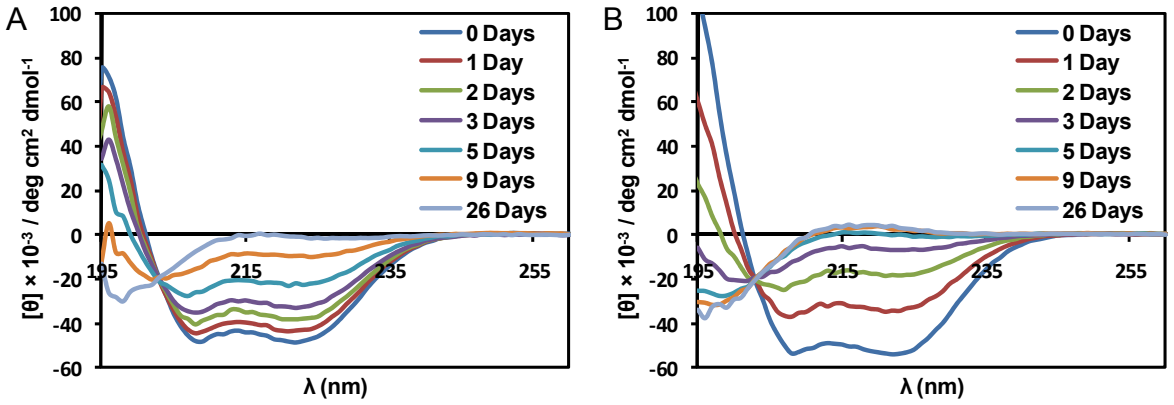

Figure 8. CD spectra of PPLG (DP=75) functionalized with secondary amine taken at various time points at A) pH 7.4 and B) pH 9.

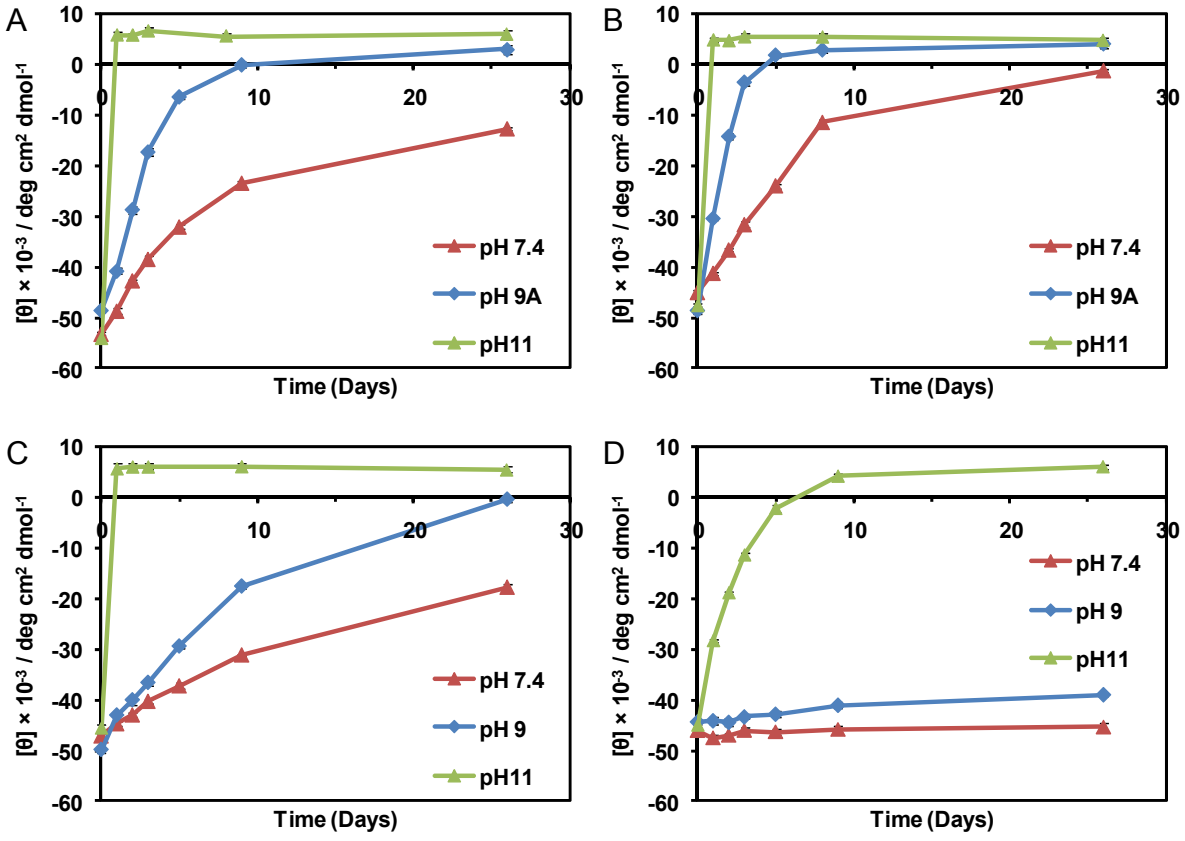

Figure 9. A) Value observed at 222nm at various pH values as a function of time for PPLG (DP=75) functionalized with primary amine, B) PPLG (DP=75) functionalized with dimethylpropanamine, C) PEG-b-PPLG functionalized with diethylamine, and D) PEG-b-PPLG functionalized with diisopropylamine.

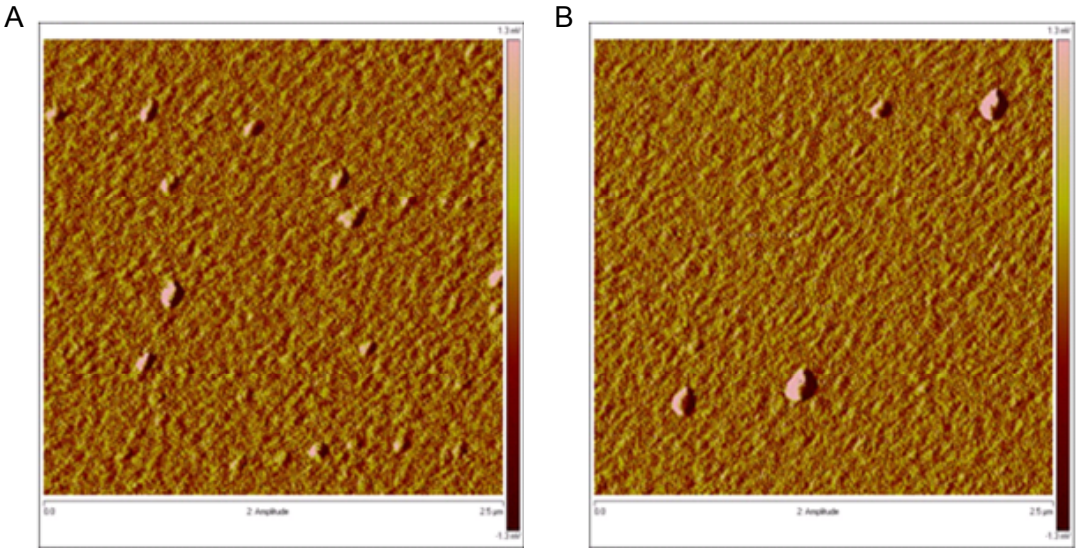

Figure 10. Amplitude AFM images (2.5 µm by 2.5 µm with a z scale of 1.5 nm) of polyplexes formed with dimethylethanamine PPLG with degree of polymerization of A) 75 and B) 140.