Supporting Information

Amino Acid Vinyl Esters: A New Monomer Palette for Degradable Polycationic Materials

Glen B. Thomas, Corinne E. Lipscomb, Mahesh K. Mahanthappa*

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706 (USA)

* Corresponding Author: mahesh@chem.wisc.edu

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**Figure S1.** Boc-deprotection of (a) poly(Boc-glycine vinyl ester) (P(BGVE)-1; top) to the cationic (b) poly(vinyl ammonium glycinate trifluoroacetate) (P(VGly•CF₃COOH); bottom) using CF₃COOH at 60°C.

**Figure S2.** SEC traces of P(VAc-co-BVVE)-3 (left) and P(VAc-co-BPVE)-1 (right) using refractive index detection demonstrate unimodal molecular weight distributions of random copolymers.
Figure S3. Mayo-Lewis plot of $1/N_{\text{total}}$ versus $[\text{BGVE}]/[\text{M}]_{\text{total}}$ based on P(VAc-co-BGVE) samples 1-5 (from Table 1) demonstrating a near linear relationship, suggestive of the fact that chain transfer to BGVE monomer contributes the observed trend of decreasing degree of polymerization ($N_{\text{total}}$) with increasing [BGVE] in the copolymerization feed. The error bars in this plot derived from the estimated 10 % error in the values of $1/N_{\text{total}}$ that were derived from absolute copolymer molecular weights determined by size exclusion chromatography with triple detection.

From the Mayo-Lewis equation and the plot shown in Figure S3, we find that:

$$\frac{1}{v_{\text{tr}}} = \frac{1}{v} + C_{BGVE} \frac{[\text{BGVE}]}{[\text{M}]_{\text{total}}}$$

(Equation S1)

where $v_{\text{tr}}$ is the kinetic chain length when chain transfer is operative, $v$ is the kinetic chain length in the absence of any chain transfer events, $C_{BGVE} = 0.021$ is the chain transfer constant for BGVE, and $[\text{M}]_{\text{total}}$ is the total monomer concentration in the polymerization.
**Figure S4.** SEC traces of poly(vinyl acetate-co-Boc valine vinyl ester) \( \text{P(VAc-co-BVVE)-2} \) and poly(vinyl acetate-co-vinyl trifluoroacetamidovalinate) \( \text{P(VAc-co-VTFAcVal)-2} \) using viscometric detection demonstrate preservation of a unimodal molecular weight distribution after \( \text{CF}_3\text{COOH Boc-deprotection and subsequent trifluoroacetylation.} \)

**Figure S5.** SEC traces of poly(vinyl acetate-co-Boc valine vinyl ester) \( \text{P(VAc-co-BVVE)-2} \) and poly(vinyl trifluoroacetate-co-vinyl trifluoroacetamidovalinate) \( \text{P(VTFAc-co-VTFAcVal)-2} \) using viscometric detection demonstrate preservation of a unimodal molecular weight distribution after \( \text{HCl(aq) deprotection/hydrolysis and subsequent trifluoroacetylation.} \)