Supporting Information for

Ion Pairing Effects in the Zwitterionic Ring Opening Polymerization of Valerolactone

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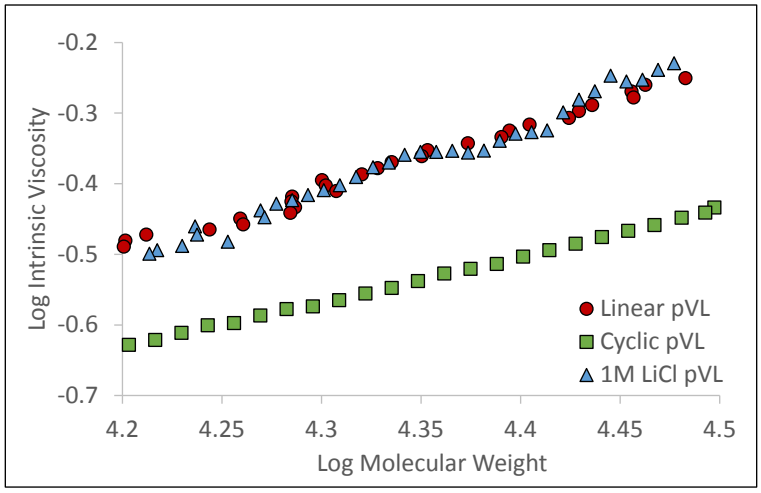

Figure S1. Mark-Houwink Plot of Intrinsic Viscosity (IV) as a function of log Molecular Weight for: Circles: Linear pVL synthesized using BnOH initiator, Squares: cyclic pVL synthesized in neat THF, and Crosses: Linear pVL synthesized in 1M LiCl in THF.

$\frac{\eta_{cyclic}}{\eta_{linear}} = 0.67$, $\frac{\eta_{cyclic}}{\eta_{LiCl}} = 0.66$

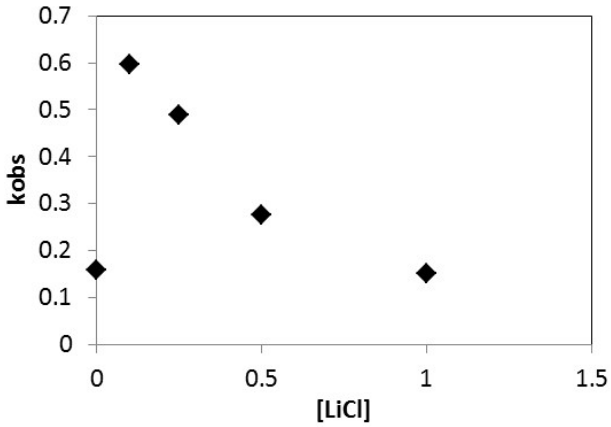

Figure S2. Plot of observed rate constant: k_{obs} (s^{-1}) versus [LiCl]. [VL]=1.0M, [NHC]=0.01M

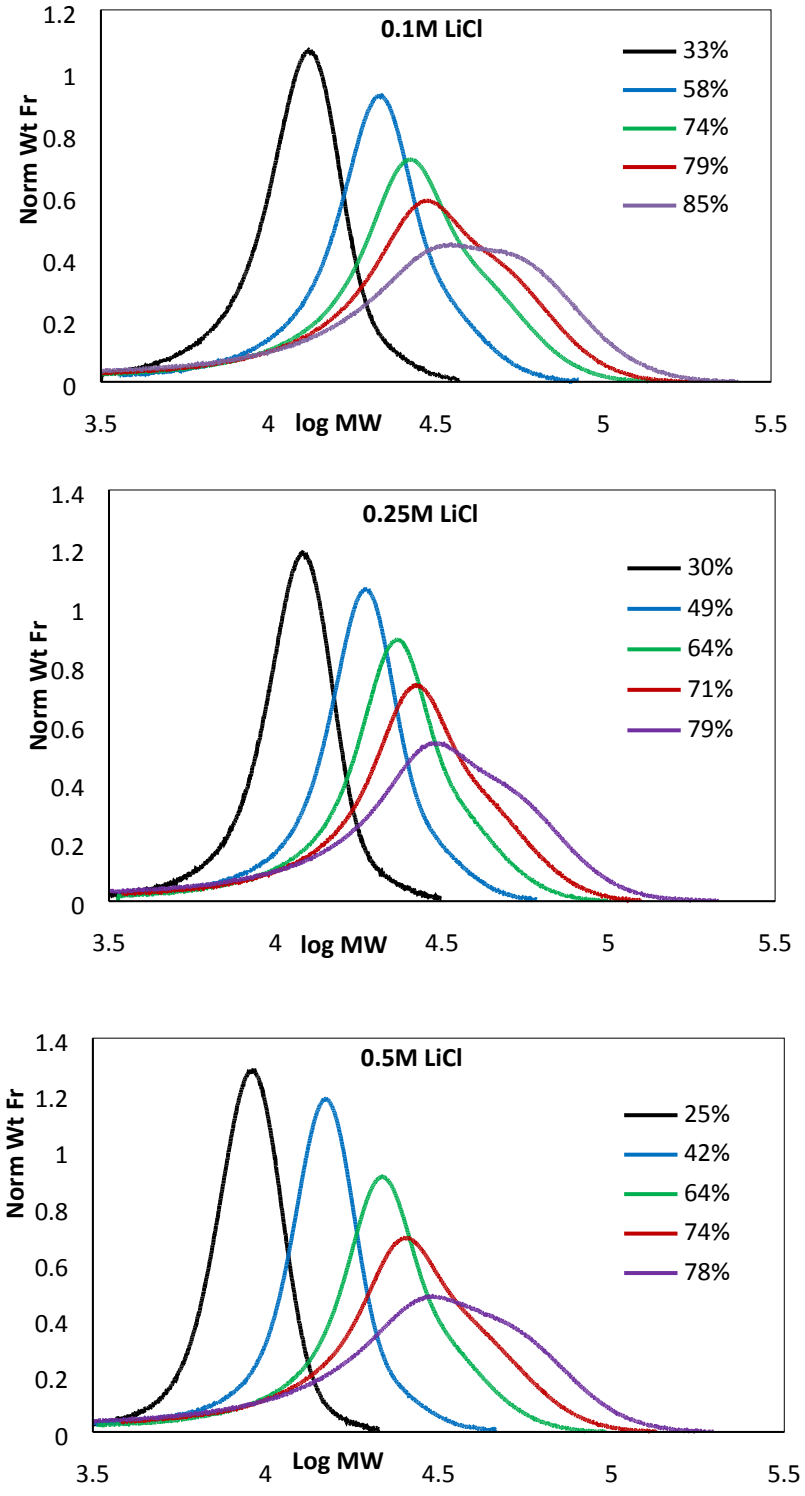

Figure S3. SEC characterization showing the molecular weight evolution of pVL samples at various [LiCl]. Percentage indicates monomer conversion. [VL]=1.0M, [NHC]=0.01M.

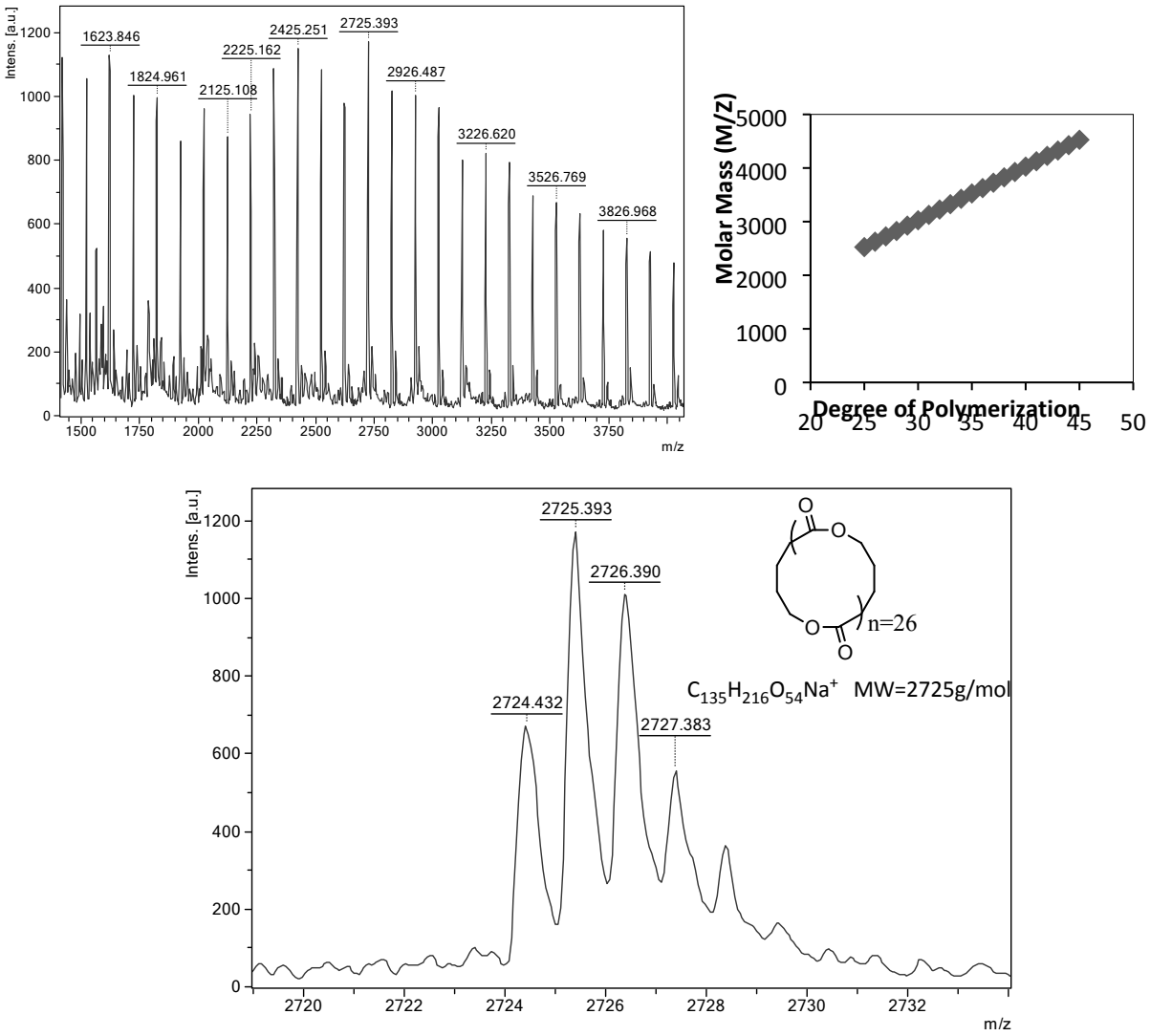

Figure S4. MALDI-TOF spectrum of cyclic poly(valerolactone) prepared in THF at 25°C at t=5min, 35% conversion. $[VL]_0$ = 1.0M, $[NHC]_0$ = 0.01M

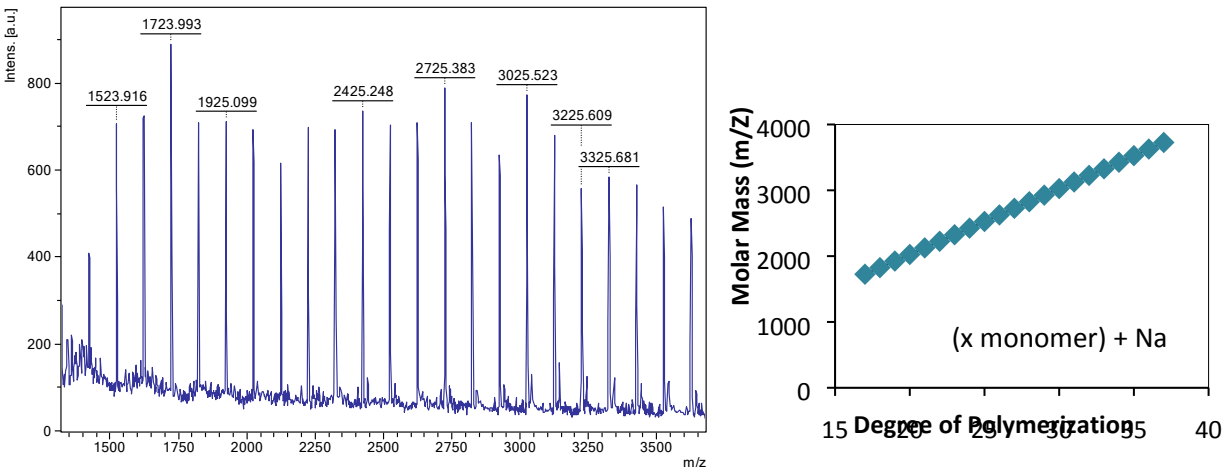

Figure S5. MALDI-TOF spectrum of cyclic poly(valerolactone) prepared in THF at 25°C at t=7min, 23% conversion. $[VL]_0 = 0.5M$, $[NHC]_0 = 0.0025M$

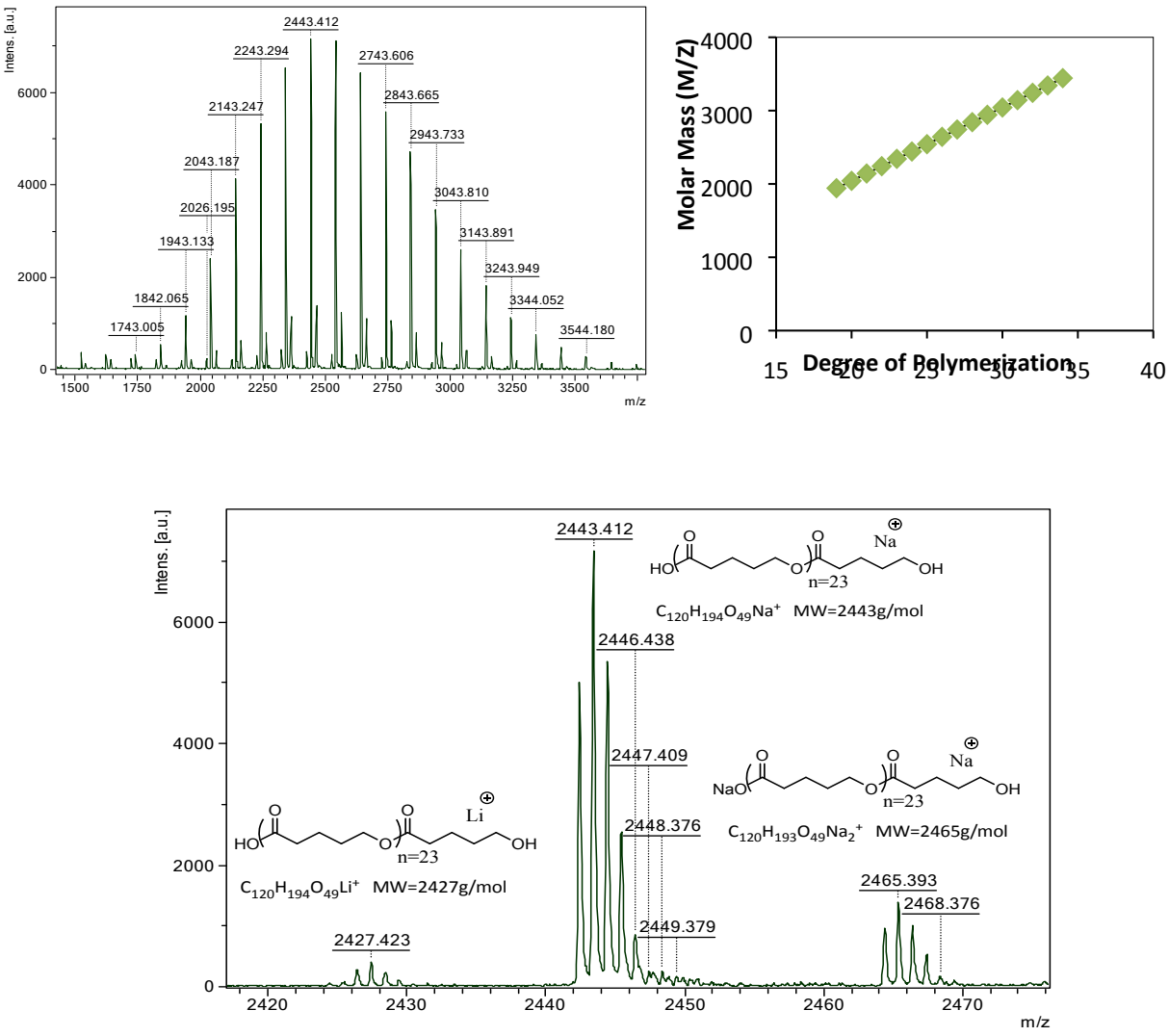

Figure S6. MALDI-TOF spectrum of linear poly(valerolactone) prepared in 1M LiCl in THF quenched at t=30s, 16% conversion. $[VL]_0$ = 1.0M, $[NHC]_0$ = 0.01M . M/z ~ 2427 corresponds to the lithium adduct of linear pVL. M/z ~ 2443 and 2465 correspond to sodium adducts of linear pVL.

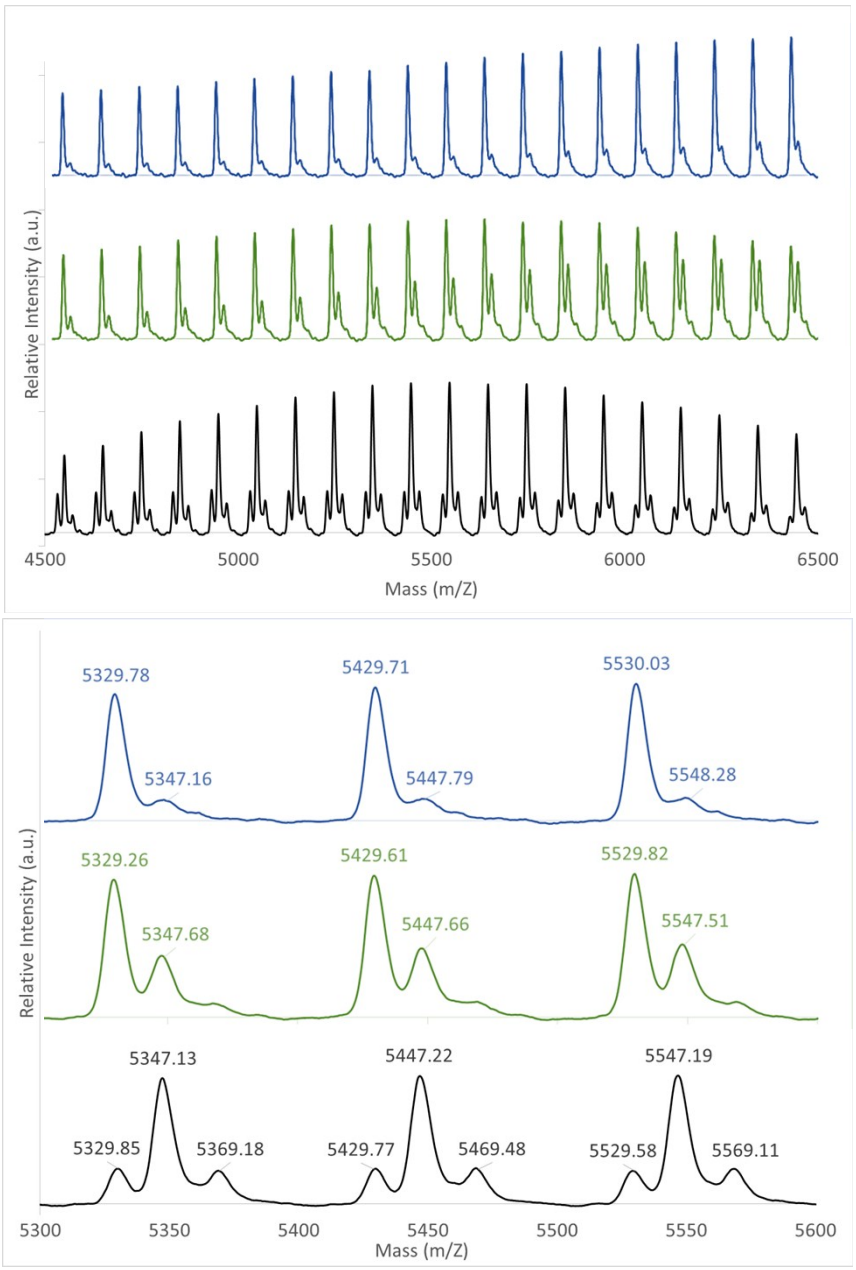

Figure S7. MALDI-TOF spectra of p(VL) prepared in THF at various [LiCl]. Samples were quenched at t=30s. From top to bottom: [LiCl]=0.1M (85% conversion), 0.25M (39% conversion), 0.5M (32% conversion). M/z ~ 5347 and 5369 correspond to linear polymer with H_2O endgroup and M/z ~ 5329 correspond to cyclic polymer.