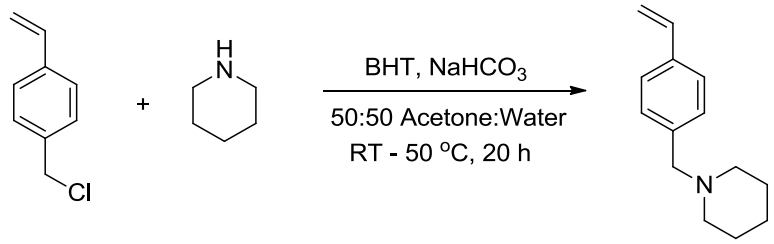
Synthesis of 4-vinylbenzyl piperidine



$NaHCO_3$ (5.02 g, 59.7 mmol) was added to 100 mL of a binary mixture of water/acetone (1:1 v:v) in a 250-mL two-necked, round-bottomed flask equipped with an addition funnel and reflux condenser. To this mixture, piperidine (16.96 g, 199.2 mmol) was added and stirred until completely dissolved. At room temperature, 4-vinylbenzyl chloride (7.61 g, 49.8 mmol) was added drop-wise, and the solution was subsequently heated to 50 ^{o}C and stirred for 20 h. Following the reaction, the remaining solid salt was filtered and discarded, and acetone was removed under reduced pressure (0.5 mmHg) at 23 ^{o}C. The remaining solution was diluted with 500 mL of diethyl ether, and washed with 50 mL of ultrapure water 6 times. The organic phase was then washed with 100 mL of 2.0 M HCl 3 times, saving the aqueous washes. Then, 200 mL of 4.0 M NaOH was added to the acid washes, producing a cloudy heterogeneous solution. This mixture was extracted with 50 mL of diethyl ether 3 times, the organic phase was dried over anhydrous sodium sulfate, and the ether was removed under reduced pressure (0.5 mmHg) at 23 ^{o}C. 4-vinylbenzyl piperidine (4-VBP) was isolated as a clear liquid upon distillation from calcium hydride and dibutyl magnesium (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, δ): 1.5 (2H, m, piperidine protons), 1.6 (4H, m, piperidine protons), 2.4 (4H, m, piperidine protons), 3.52 (2H, d, -CH_2-N), 5.25 (1H, d, vinyl proton), 5.60 (lH, d, vinyl proton), 6.60 (lH, dd, vinyl proton), 7.2-7.8 (4H, m, aromatic protons). Mass Spectrometry: Theoretical, m/z 201.1517; Experimental, m/z 201.1521. Boiling point: 236-239 ^{o}C (760 mmHg).

In situ FTIR monitoring the anionic polymerization of 4-vinylbenzyl piperidine

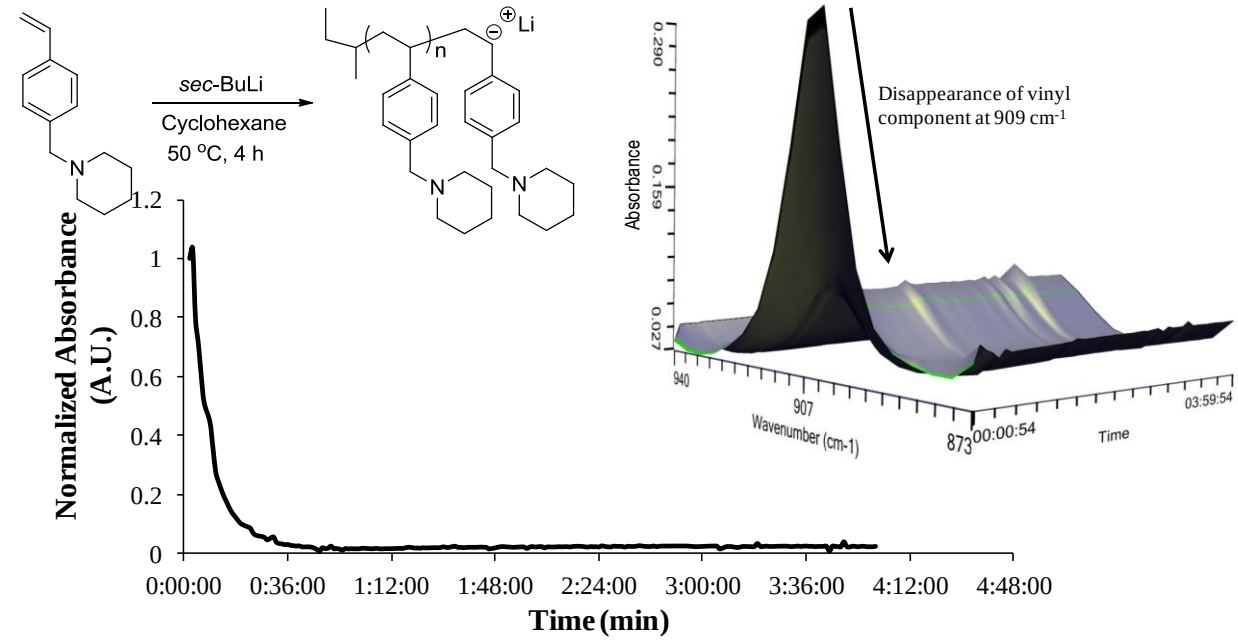


Figure S1 In situ FTIR monitoring 4-VBP vinyl concentration disappearance at 909 cm^{1} over time in a 3D waterfall plot and 2D normalized plot.

^{1}H NMR monitoring post-polymerization alkylation

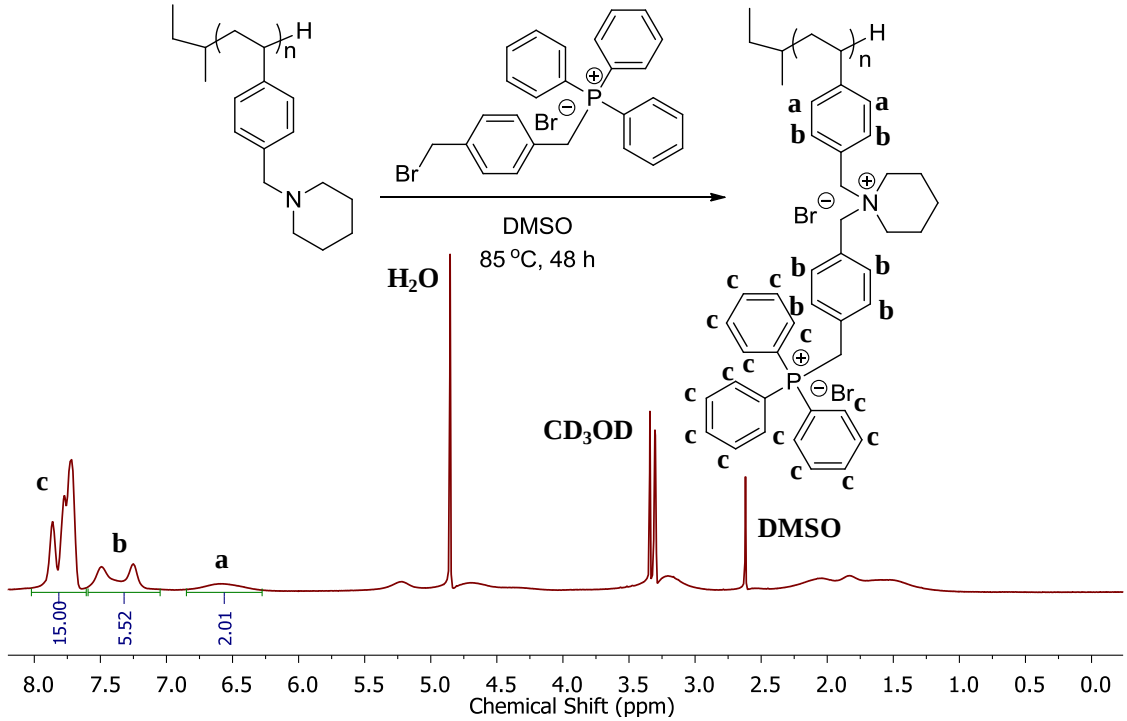


Figure S2 ^{1}H NMR characterization of poly(4-TPhPVBP)-Br aliquot sample at time, t = 48 h. Aromatic protons confirm quantitative alkylation.