

Supplementary Information

for

**Styrenic DABCO Salt-Containing Monomers for the Synthesis
of Novel Charged Polymers**

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Materials. *n*-Butyl acrylate (*n*BA, 99+%) was purchased from Aldrich and passed through neutral alumina columns before use. α,α' -Azobis-(isobutyronitrile) (AIBN, Fluka, 99%) was recrystallized from methanol twice. 1-bromoethane (98+%), 1-bromobutane (98+%), 1-bromohexane (98+%), 1-bromododecane (98+%), and 1-bromohexadecane (98+) were purchased from Alfa Aesar and used without further purification. DABCO (99+%), 4-vinyl benzyl chloride (4VBCl, 99%), 2,6-di-*tert*-butyl-4-methylphenol (BHT, 99%), triethylamine (TEA, 99+), sodium tetrafluoroborate (NaBF₄, 98%), and bis(trifluoromethane)sulfonimide lithium (Li-Tf₂N) were purchased from Aldrich and used without further purification. Ethyl acetate (EtOAc, HPLC grade), chloroform (CHCl₃, HPLC grade), acetone (HPLC grade), methanol (MeOH, HPLC grade), *N,N*-dimethylsulfoxide (DMSO, HPLC grade) and *N,N*-dimethylformamide (DMF, HPLC grade) were obtained from Spectrum and used as received.

Analytical Methods. ¹H NMR and ¹³C NMR spectroscopy was conducted on a Varian Unity 400 at 400 MHz in deuterated DMSO, deuterated MeOD, or CDCl₃. Thermogravimetric analysis

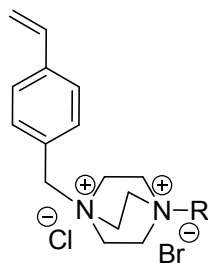
(TGA) was performed on a TA Instruments Q500 TGA with heating ramps from ambient to 600 °C at 10 °C/min. Thermal degradation temperatures (T_d) corresponded to 5% weight-loss. Differential scanning calorimetry (DSC) provided heat/cool/heat cycles with a heating rate of 10 °C/min and cooling rate of 10 °C/min on a TA instruments Q1000 DSC. DSC experiments used a nitrogen flush of 50 mL/min. DSC calibration utilized indium (mp = 156.60 °C) and zinc (mp = 419.47 °C) standards. The midpoint of the transition in the second heating ramp determined glass transition temperatures (T_g). Dynamic mechanical analysis (DMA) utilized a TA Instruments Q800 Dynamic Mechanical Analyzer in tension mode at a frequency of 1 Hz, oscillatory amplitude of 15 μ m, and a static force of 0.01 N. The temperature ramp was 3 °C/min. The peak maxima of tan delta curves determined T_g values.

Synthesis of *N*-4VinylBenzyl-*N'*-alkyl DABCO BrCl (VBDC_xBrCl) monomers. In a representative DABCO salt-containing monomer synthesis (Scheme 1), DABCO (5.6 g, 50.0 mmol) and 1-bromohexane (6.3 mL, 45.0 mmol) were dissolved in 100 mL of ethyl acetate and stirred overnight. White suspension was filtered, washed with ethyl acetate, and dried *in vacuo* at room temperature. The mono-alkylated DABCO intermediate was used without further purification. Alkylated DABCO (12.2 g, 44.1 mmol), 4VBCl (7.4 g, 48.5 mmol), and BHT (0.14 g) were dissolved in 100 mL acetonitrile and stirred overnight. The white suspension was filtered, washed with acetonitrile, and dried *in vacuo* at room temperature to give a white solid (13.9 g, 72% yield). BHT was removed during the filtration. ¹H NMR (400 MHz, *d*₆-DMSO, Figure S1): 7.65-7.57 (m, 4H, H_{a+b}), 6.81 (dd, 1H, $J_1 = 10.9$ Hz, $J_2 = 17.6$ Hz, H_c), 5.98 (d, 1H, $J = 17.6$ Hz, H_d), 5.39 (d, 1H, $J = 10.9$ Hz, H_e), 4.96 (s, 2H, H_f), 3.94 (s, 12H, H_g), 3.52 (m, 2H, H_h), 1.65 (m, 2H, H_i), 1.27 (s, 6H, H_j), 0.86 (s, 3H, H_m). ¹³C NMR (100 MHz, *d*₆-DMSO): 139.76, 136.18, 133.83, 127.17, 126.40, 116.95, 66.09, 63.76, 50.74, 50.49, 31.00, 25.62, 22.23,

21.67, 14.24. HRMS (ESI+): m/z calculated for $[\text{VBDC}_x\text{Br}^+]$ 393.1900 g/mol; found 393.1897 g/mol.

Synthesis of DABCO Salt-Containing Homopolymers and Copolymers. A typical homopolymerization was conducted as follows (Scheme 2,3). VBDC_6BrCl (2.0 g, 5.0 mmol), AIBN (8.2 mg, 0.05 mmol), DMSO (4.0 mL), and MeOH (2.0 mL) were added to a 100 mL, round-bottomed flask equipped with magnetic stirrer. The solution was purged with nitrogen for 20 min and stirred at 65 °C for 24 h. The resulting solution was dialyzed against MeOH and dried *in vacuo* to obtain a brittle clear solid of (2.4 g, 87% yield). ^1H NMR spectroscopy confirmed the structure of poly(VBDC_6BrCl) (Figure S3). A typical copolymerization was conducted as follows: *nBA* (2.0 g, 15.6 mmol), AIBN (2.8 mg, 0.017 mmol), VBDC_6BrCl (0.669 g, 1.6 mmol) and DMSO-DMF mixture (10.7 g) were added to a round-bottomed flask equipped with magnetic stirrer. The solution was purged with argon for 20 min and stirred at 65 °C for 24 h. The resulting solution was precipitated into a MeOH- H_2O mixture. The precipitate was collected and dried *in vacuo* to obtain an solid of (2.4 g, 90% yield). Calculation based on the ^1H NMR spectrum of poly($\text{VBDC}_6\text{BrCl-co-nBA}$) showed 11.5 mol% incorporation of VBDC_6BrCl (Figure S4).

SEC analysis was unable to produce reliable molecular weight information of ion-containing copolymers. Dynamic light scattering showed aggregate formations for all poly(VBDC_xBrCl)s, poly($\text{VBDC}_x\text{BrCl-co-nBA}$)s, and poly(VBTEACl-co-nBA)s in various SEC solvents. However, all polymerizations were conducted with 0.1 mol% AIBN in DMF-DMSO mixture with 20 wt% solids, and stirred at 65 °C for 24 h. Polymerization conditions generally dominate the molecular weight in conventional free radical polymerizations, even with ionic monomer presence.¹⁻⁴



Scheme S1. N-4-Vinylbenzyl-N'-alkyl DABCO-BrCl (VBDC_xBrCl) monomer library.

Table S1. Mass spectroscopy, NMR, yield, yellowing temperature, and solubility in water of VBDC_xBrCl monomer library.

R	Mono-alkylated DABCO salt NMR	VBDC _x BrCl NMR	VBDC _x BrCl m/z* Observed (g/mol)	VBDC _x BrCl m/z* Predicted (g/mol)	Yield (%)	Transition* (°C)	Solubility in H ₂ O
C2	√	√	337.1274	337.1274	97	223.4	Y
C4	√	√	365.1592	365.1587	92	216.2	Y
C6	√	√	393.1897	393.1900	72	203.9	Y
C12	√	√	477.2848	477.2839	50	189	N
C14	√	√	505.3152	505.3152	82	191	N
C16	√	√	533.3444	533.3465	63	189	N

* HRMS ESI+ m/z calculated for [VBDC_xBr⁺]

*Transition: Yellowing of solid powder. No melting.

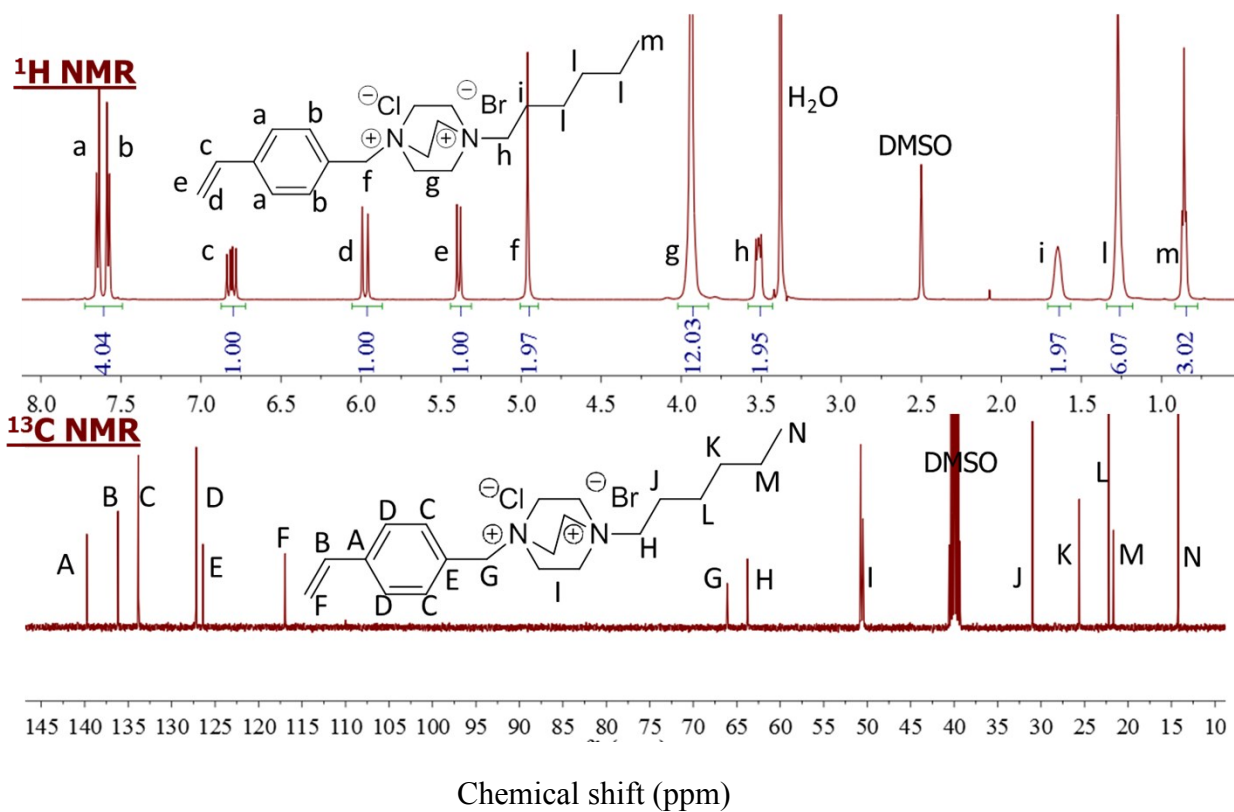


Figure S1. ¹H NMR and ¹³C NMR spectra of VBDC₆BrCl.

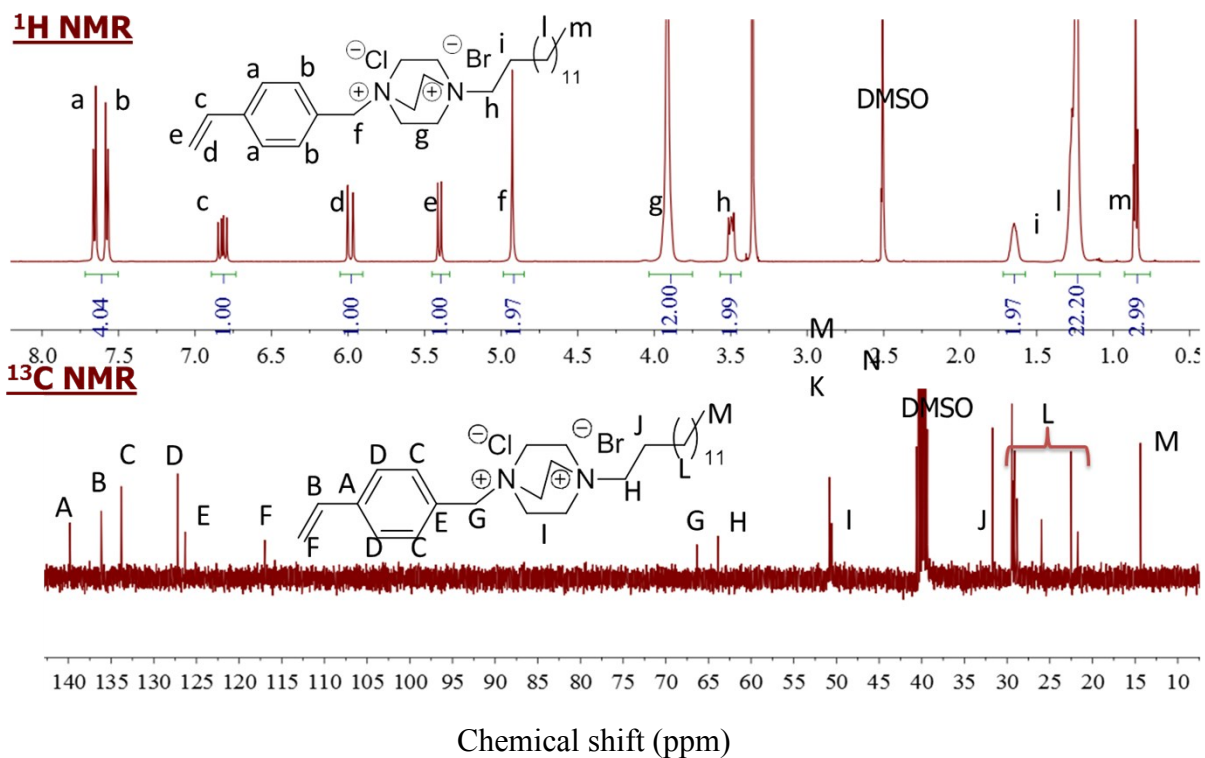


Figure S2. ^1H NMR and ^{13}C NMR spectra of VBDC₁₄BrCl.

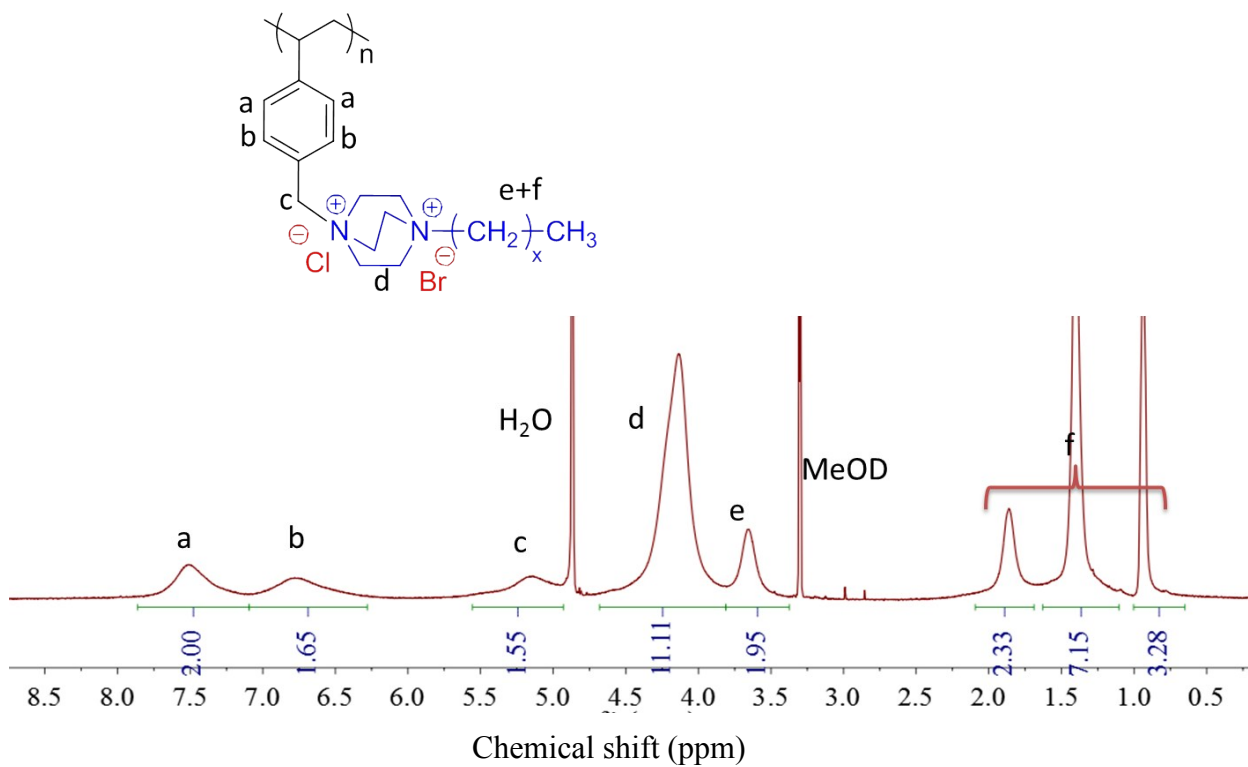
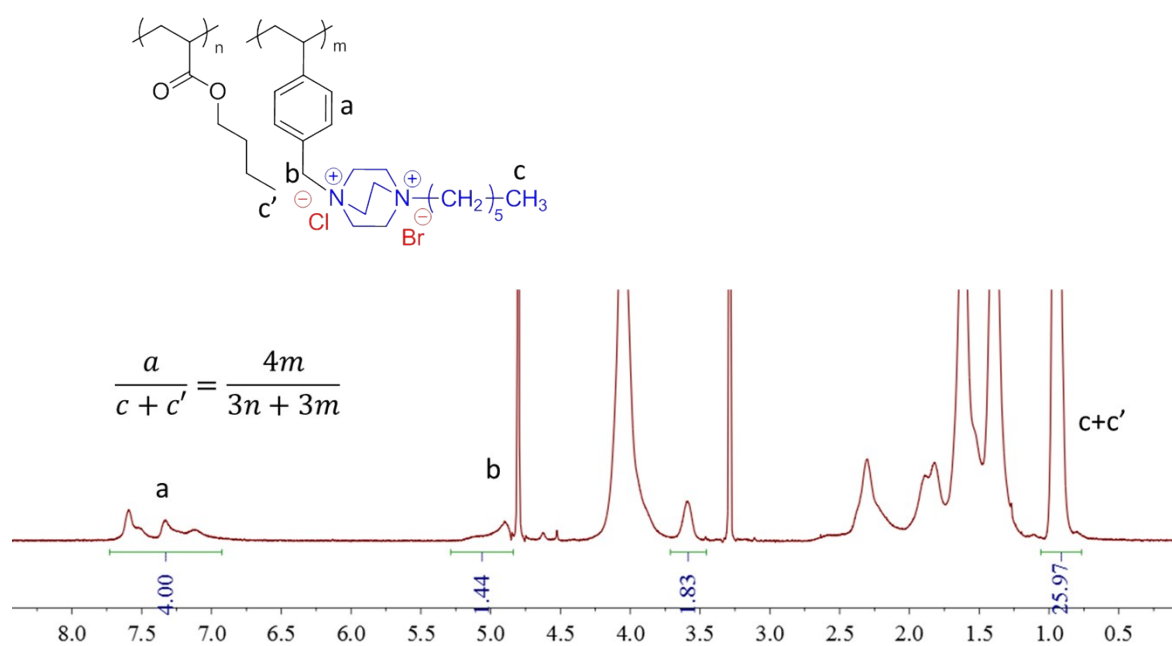
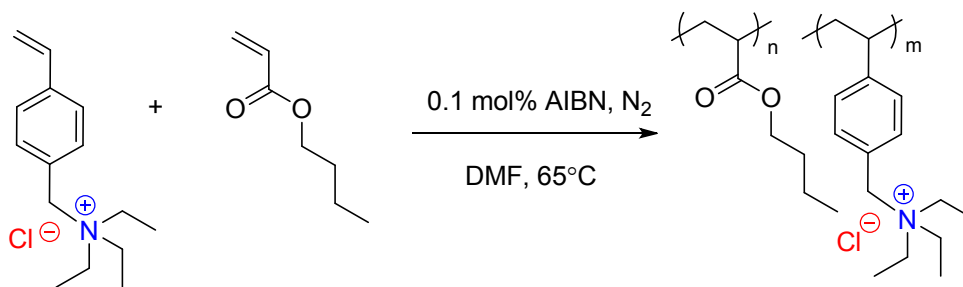


Figure S3. ^1H NMR spectrum of poly(VBDC₆BrCl).



Chemical shift (ppm)

Figure S4. ^1H NMR spectrum of poly(VBDC₆BrCl-*co*-*n*BA) with 12 mol% VBDC₆BrCl.



Scheme S2. Synthesis of poly(VBTEACl-*co*-*n*BA). Triethyl-(4-vinylbenzyl) ammonium chloride (VBTEACl)

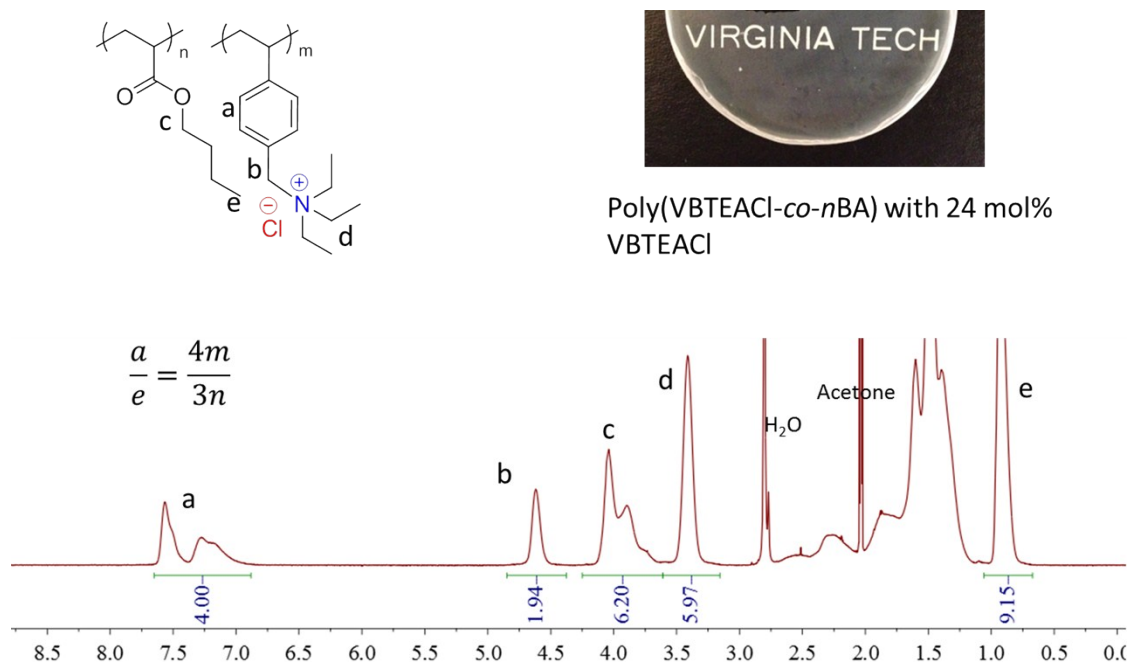


Figure S5. ^1H NMR spectrum and the solution-cast film of poly(VBTEACl-*co*-*n*BA) with 24 mol% VBTEACl.

Table S2. Ionic monomer in feed and in polymer for poly(VBTEACl-*co*-*n*BA)s.

Poly(VBTEACl- <i>co-n</i> BA)		
Feed mol%	Observed mol%	Observed wt%
3	3	6
9	11	19
17	24	39
33	48	64

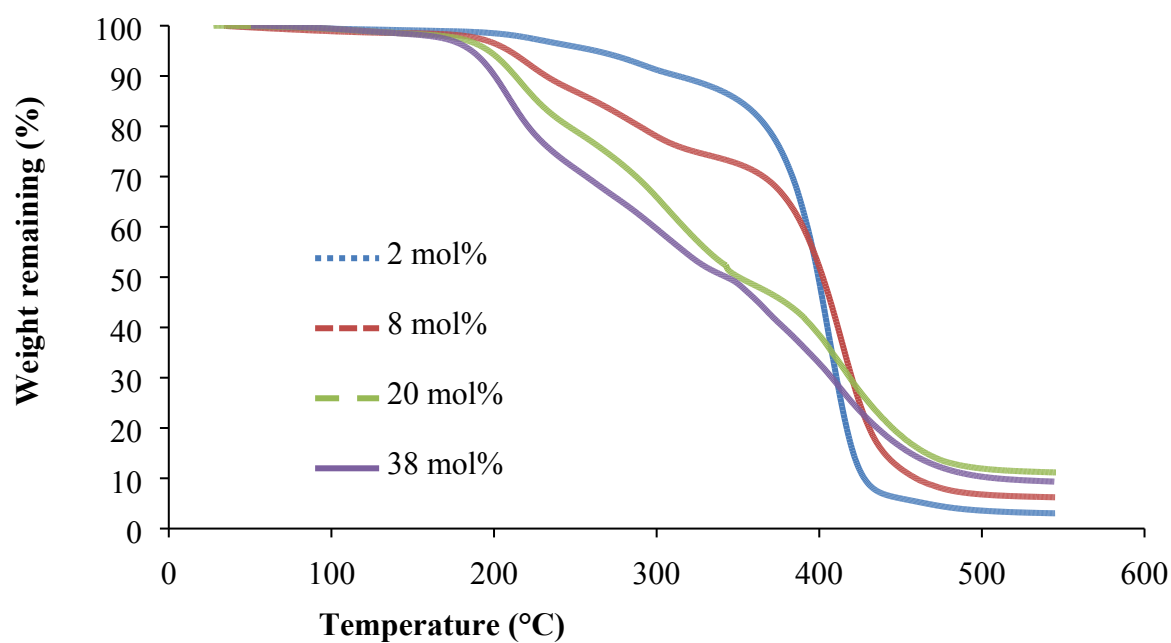
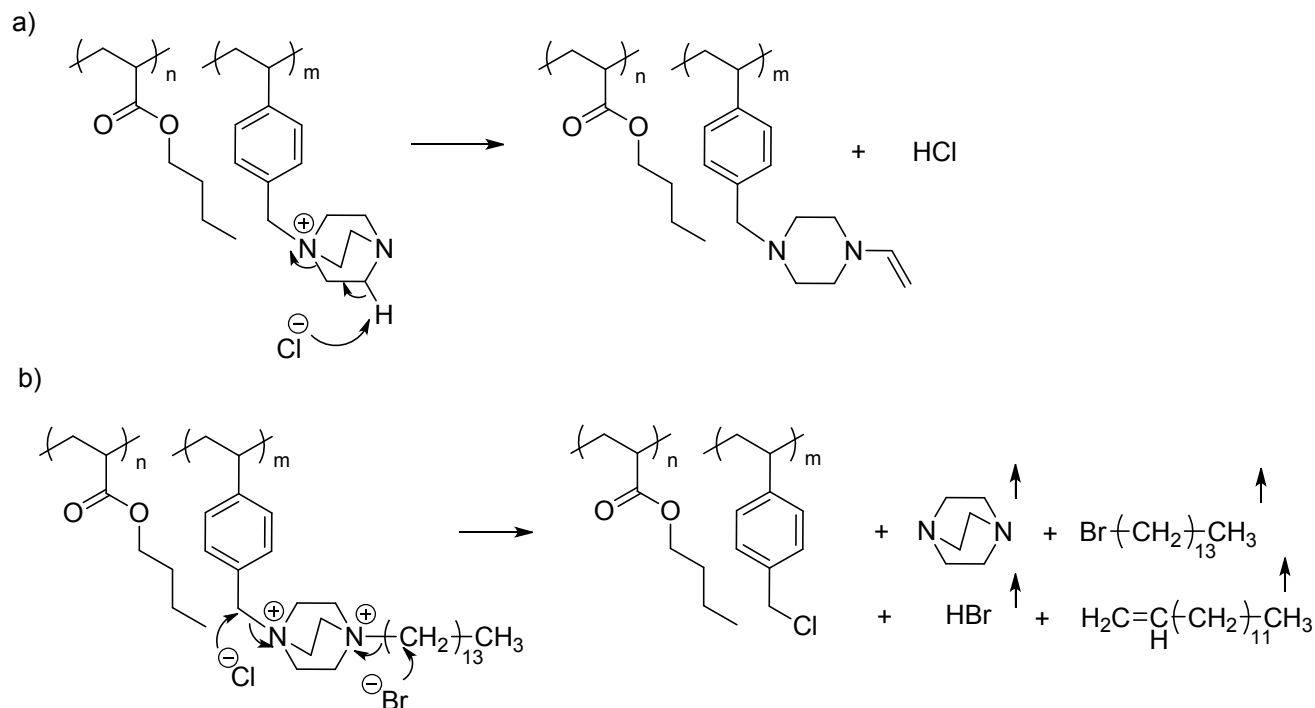


Figure S6. TGA traces of poly(VBDC₁₄BrCl-*co-n*BA)s with varying ionic monomer concentrations.



Scheme S3. (a) Proposed dequaternization of the benzyl-substituted ammonium through Hofmann elimination of poly(VBDC₆BrCl-*co*-*n*BA)s. (b) Thermal degradation of poly(VBDC₁₄BrCl-*co*-*n*BA)s through a nucleophilic substitution mechanism for the benzyl-substituted ammonium.

Table S3. 5 wt% loss temperatures and correlation of first weight-loss step of poly(VBDC₁₄BrCl-*co*-*n*BA)s to a nucleophilic substitution degradation pathway.

VBDC ₁₄ BrCl mol%	T _d (°C) 5 wt%	Observed weight-loss 1 st step (%)	Theoretical weight-loss 1 st step Nu(%)	Theoretical weight-loss 1 st step Hoffman (%)
2	262	8	6	4
8	209	24	21	16
20	197	43	40	30

38	186	60	56	41
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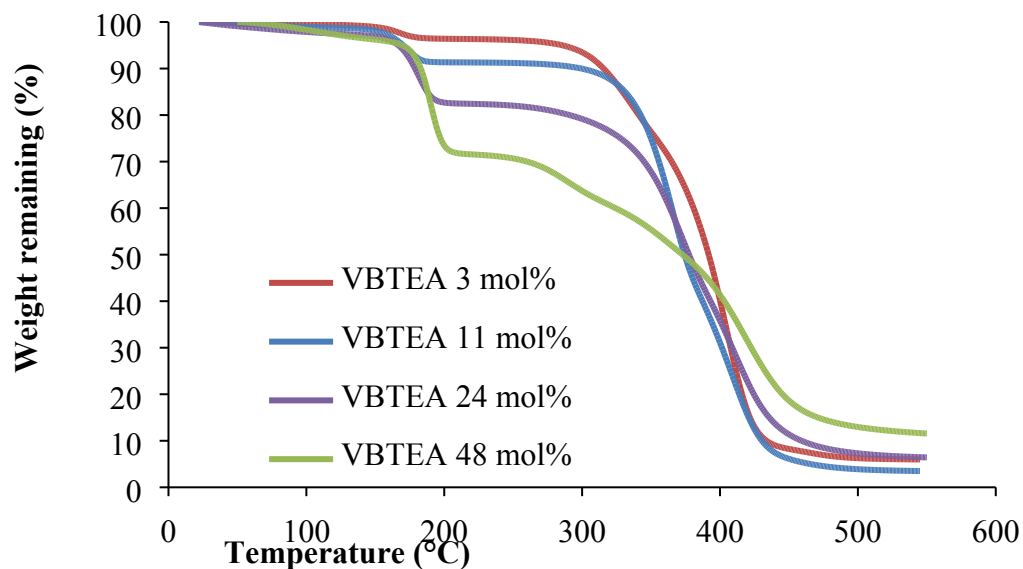
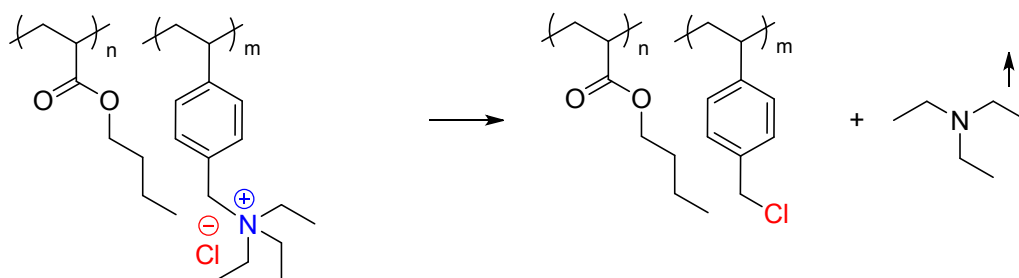


Figure S7. TGA traces of poly(VBTEACl-*co*-*n*BA)s with varying ionic monomer concentrations.



Scheme S4. Thermal degradation of poly(VBTEACl-*co*-*n*BA) through a nucleophilic substitution mechanism.

Table S4. 5 wt% loss temperatures and correlation of first weight-loss step of poly(VBTEACl-*co*-*n*BA)s to a nucleophilic substitution degradation pathway.

VBTEACl mol%	T _d (°C) 5 wt%	Observed weight-loss 1 st step (%)	Theoretical weight-loss 1 st step
3	286	3	2
11	170	8	8
24	167	14	14
48	170	25	26
100 ⁵	200	41	40

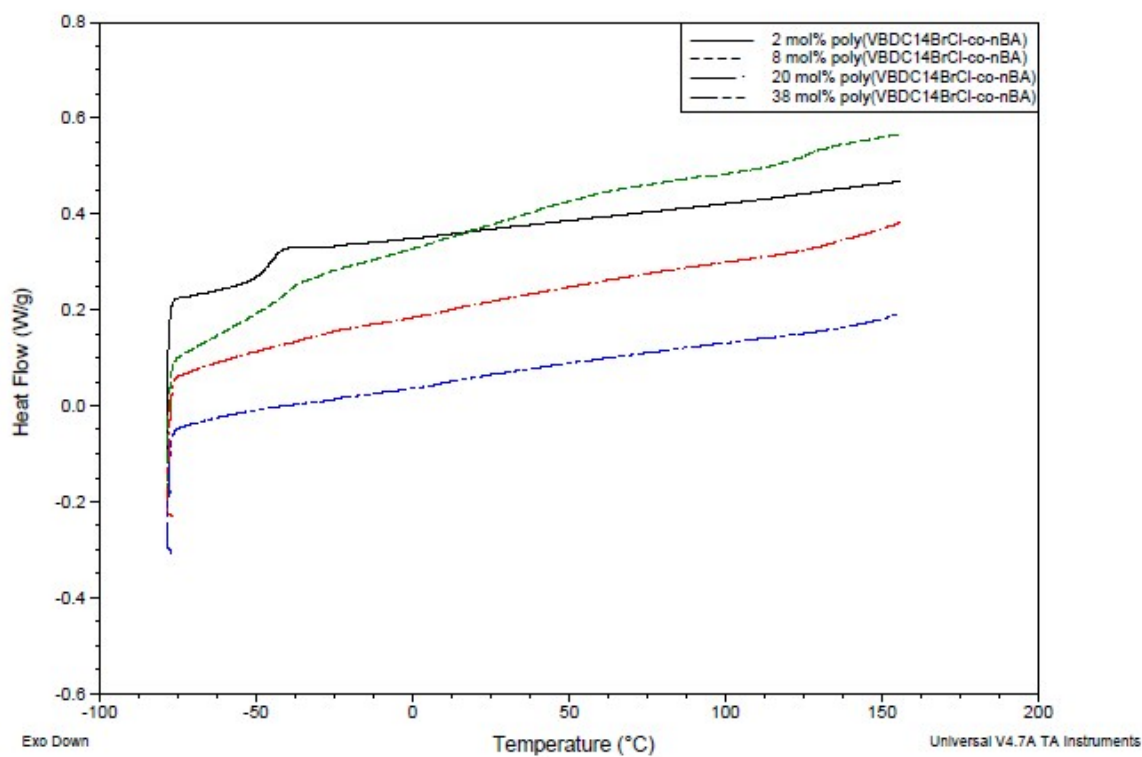


Figure S8. DSC second heating ramps of poly(VBDC₁₄BrCl-co-nBA)s with varying ionic monomer concentrations.

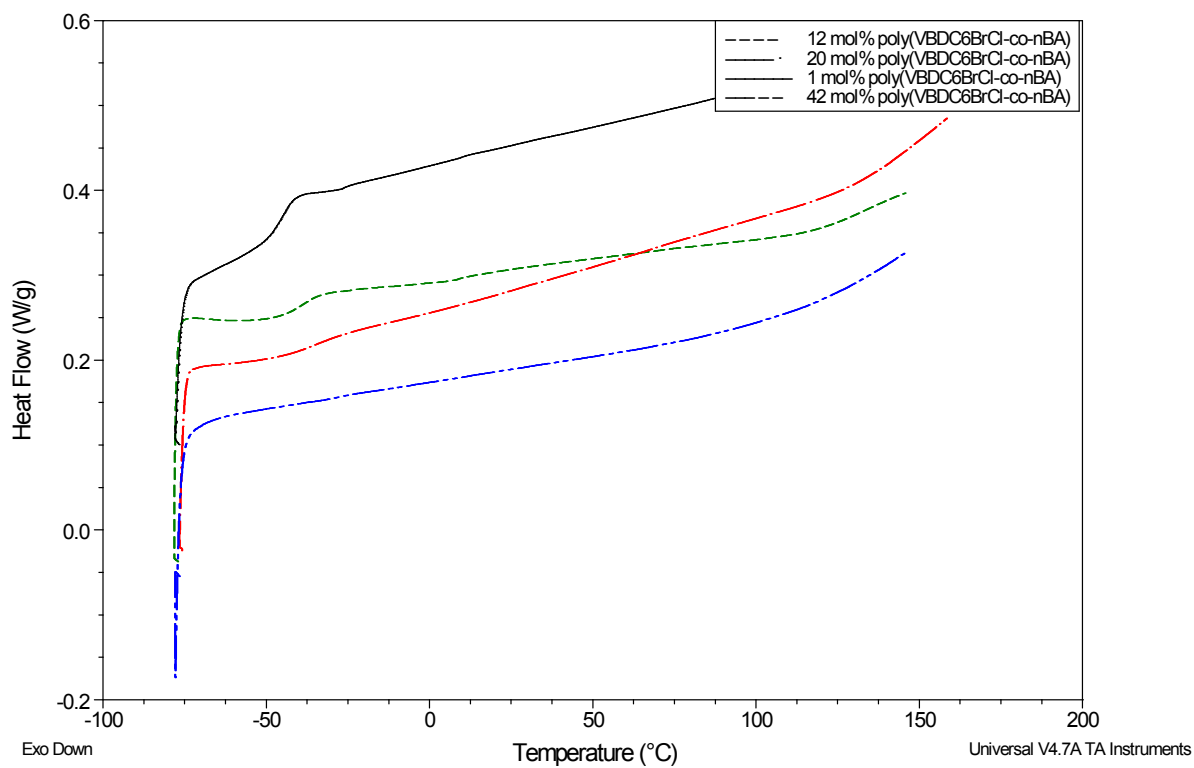


Figure S9. DSC second heating ramps of poly(VBDC₆BrCl-co-nBA)s with varying ionic monomer concentrations.

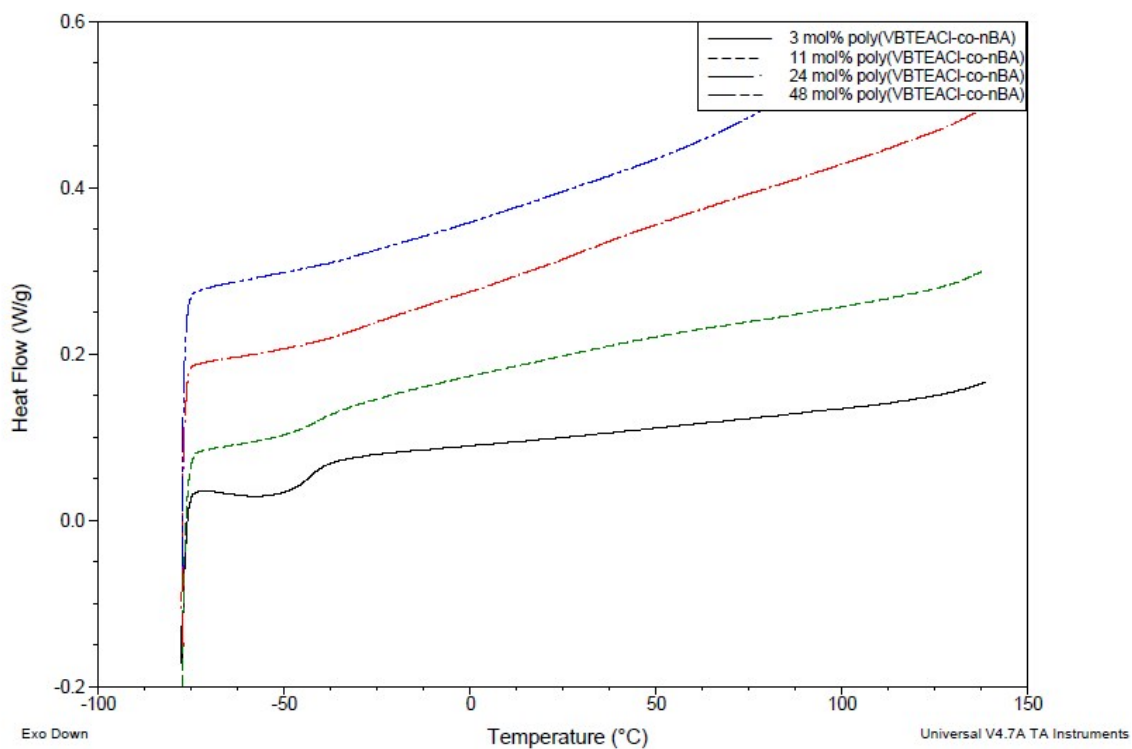


Figure S10. DSC second heating ramps of poly(VBTEACl-*co-n*BA)s with varying ionic monomer concentrations.

Table S5. T_g values of poly(VBDC₁₄BrCl-*co-n*BA)s, poly(VBDC₆BrCl-*co-n*BA)s, poly(VBTEACl-*co-n*BA)s with varying ionic monomer concentrations. ND: not observed.

Poly(VBDC ₆ BrCl- <i>co-n</i> BA)		Poly(VBDC ₁₄ BrCl- <i>co-n</i> BA)		Poly(VBTEACl- <i>co-n</i> BA)	
Ionic monomer mol%	T_g (°C)	Ionic monomer mol%	T_g (°C)	Ionic monomer mol%	T_g (°C)
1	-45	2	-45	3	-44
12	-39	8	-40	11	-42
20	-35	20	ND	24	-36
42	ND	38	ND	48	ND

References

- 1 S. Cheng, M. Zhang, N. Dixit, R. B. Moore and T. E. Long, *Macromolecules*, 2012, **45**, 805.
- 2 S. Cheng, M. Zhang, T. Wu, S. T. Hemp, B. D. Mather, R. B. Moore and T. E. Long, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 166.
- 3 J. A. Pojman, J. Willis, D. Fortenberry, V. Ilyashenko and A. M. Khan, *J. Polym. Sci., Part A: Polym. Chem.*, 1995, **33**, 643.
- 4 M. Gauthier, T. Carrozzella and G. Snell, *J. Polym. Sci., Part B: Polym. Phys.*, 2002, **40**, 2303.
- 5 S. T. Hemp, M. Q. Zhang, M. H. Allen, S. J. Cheng, R. B. Moore and T. E. Long, *Macromol. Chem. Phys.*, 2013, **214**, 2099.