Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplemental Information

Synthesis & Characterization of Anion Exchange Membranes Based on Hydrogenated Poly(Norbornene)

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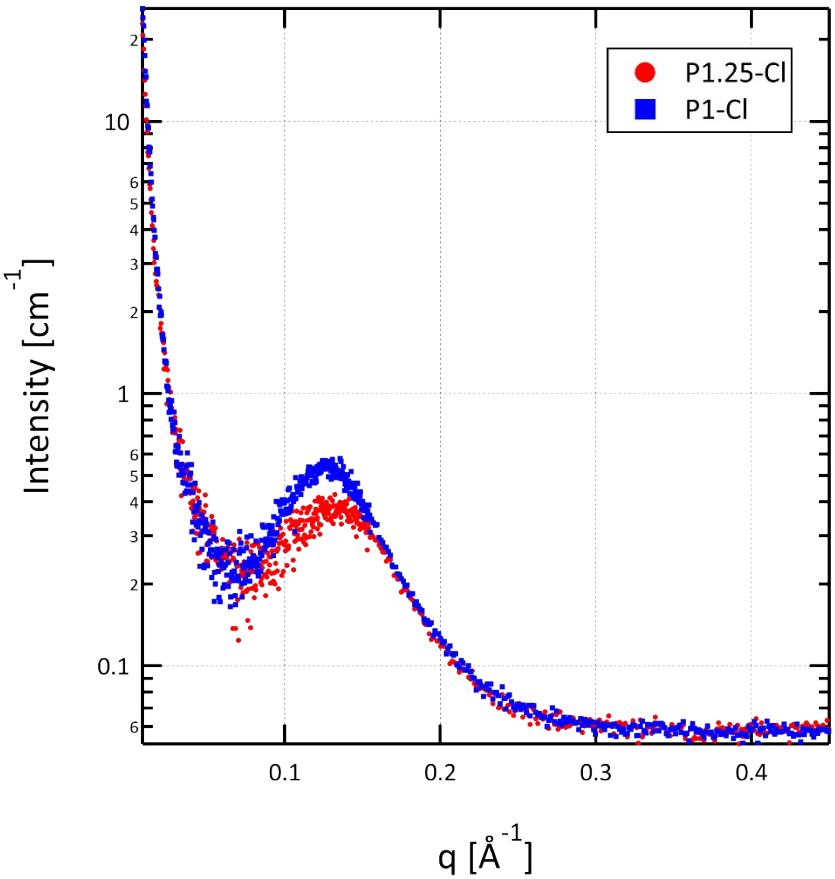


Figure S1. SAXS data for both samples in the Cl^- form. The low angle data are noisy due to weak scattering. Data are on an absolute scale.

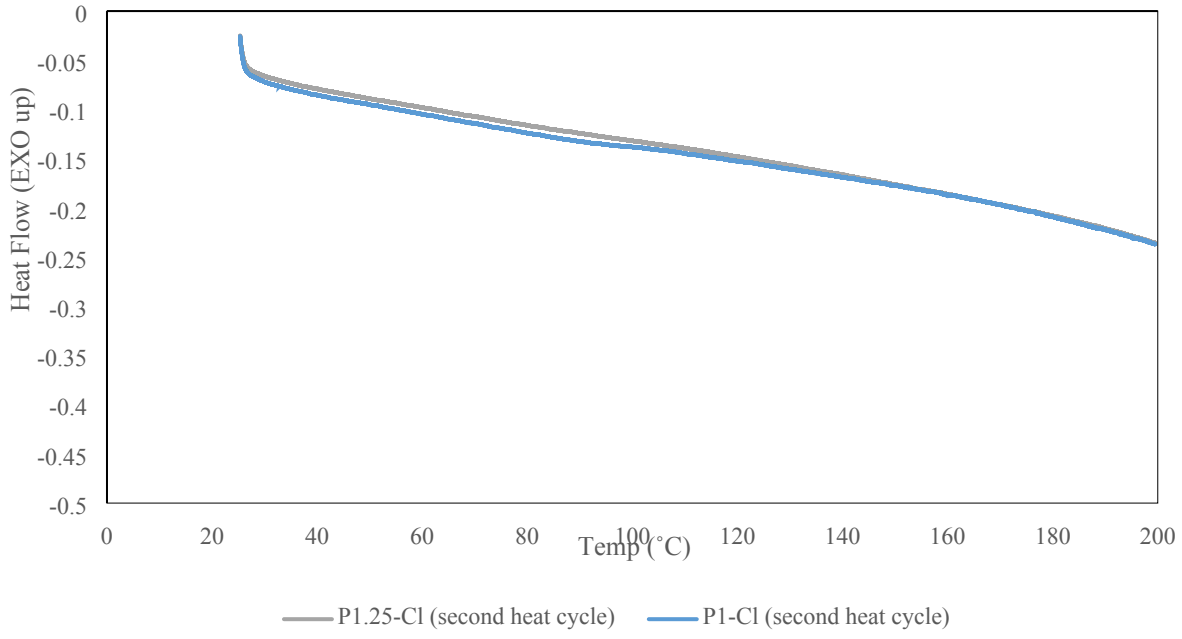
Small-angle X-ray scattering (SAXS) data for both cation-containing hydrogenated poly(norbornene) samples were fit using the "Kinning-Thomas" model.[1] This model combines the form factor for a hard

sphere with a structure factor derived by Percus and Yevick for objects on a liquid-like lattice. Yarusso and Cooper, as well as Winey and co-workers, have successfully used this model for ionic-aggregates in charged polymers.[2-4] The model returns a scaling factor (K), the aggregate radius (R_p), the aggregate volume (V_p), and the radius of closest approach (R_p). The reader is referred to the above citations for more detailed information. The core-to-core correlation distance of the particles is given by $d^* = 2\pi/q^*$, where q^* is the center of the primary peak in the scattering pattern.

Sample	R_p (Å)	V_p (Å^3)	R_{CA} (Å)	d* (Å)
P1-Cl	14.8 +- 2.7	20100 +- 6900	21.1 +- 1.3	49.8
P1.25-Cl	14.8 +- 2.5	18700 +_ 9300	19.6 +- 1.8	48.1

Table S1 – Fitting results for Kinning-Thomas model, including the correlation length, for a morphology of spherical ionic aggregates.

Dynamic scanning calorimetry (DSC) analysis of the samples was performed to determine if any crystalline domains were present. Alternating heating/cooling cycles were run from 25 °C to 200 °C at 1 ° C/min on 3–4 mg samples of each sample using a TA Instruments Discover Series (DSC).



Solution studies:

For 1 L of 1 mol L^{-1} NaOH and 0.1 mol L^{-1} BTMA solutions,

$1\ mol_{-OH}$

$0.1\ mol_{BTMA}$

$$1\ L_{H20} \times \frac{1000\ mL}{1\ L} \times \frac{1\ g}{1\ mL} \times \frac{1\ mol}{18\ g} = 55.56\ mol_{H2O}$$

Total moles: $1\ mol_{-OH} + 0.1\ mol_{BTMA} + 55.56\ mol_{H2O} = 56.65\ mol_{total}$

Mol%:

$$mol\%_{-OH} = \frac{1\ mol_{-OH}}{56.65\ mol_{total}} = 0.018\ mol\%_{-OH}$$

$$mol\%_{BTMA} = \frac{0.1\ mol_{BMTA}}{56.65\ mol_{total}} = 0.0018\ mol\%_{BTMA}$$

In swollen polymer film:

$$\frac{1\ meq}{g} IEC = \frac{0.001\ mol_{-OH}}{g_{poly}}\ or\ \frac{0.001\ mol_{BTMA}}{g_{poly}}\ or\ \frac{0.002\ mol_{ions}}{g_{poly}}\ or\ \frac{0.001\ mol_{ion\ pairs}}{g_{poly}}$$

$$mol_{-OH} = \frac{0.001\ mol_{-OH}}{g_{poly}} \times 1\ g_{poly} = 0.001\ mol_{-OH}$$

$$mol_{BTMA} = \frac{0.001\ mol_{BTMA}}{g_{poly}} \times 1\ g_{poly} = 0.001\ mol_{BTMA}$$

If there is 1 gram of swollen polymer, then there is 0.4 g water in the polymer.

$$0.4\ g_{H20} \times \frac{1\ mol_{H20}}{18.0\ g_{H20}} = 0.0222\ mol_{H20}$$

$$mol_{total} = 0.0222\ mol_{H20} + 0.001\ mol_{-OH} + 0.001\ mol_{BTMA} = 0.02422\ mol_{total}$$

$$mol\%_{-OH} = \frac{0.001\ mol_{-OH}}{0.02422\ mol_{total}} = 0.041\ mol\%_{-OH}$$

$$mol\%_{BTMA} = \frac{0.001\ mol_{BMTA}}{0.02422\ mol_{total}} = 0.041\ mol\%_{BTMA}$$

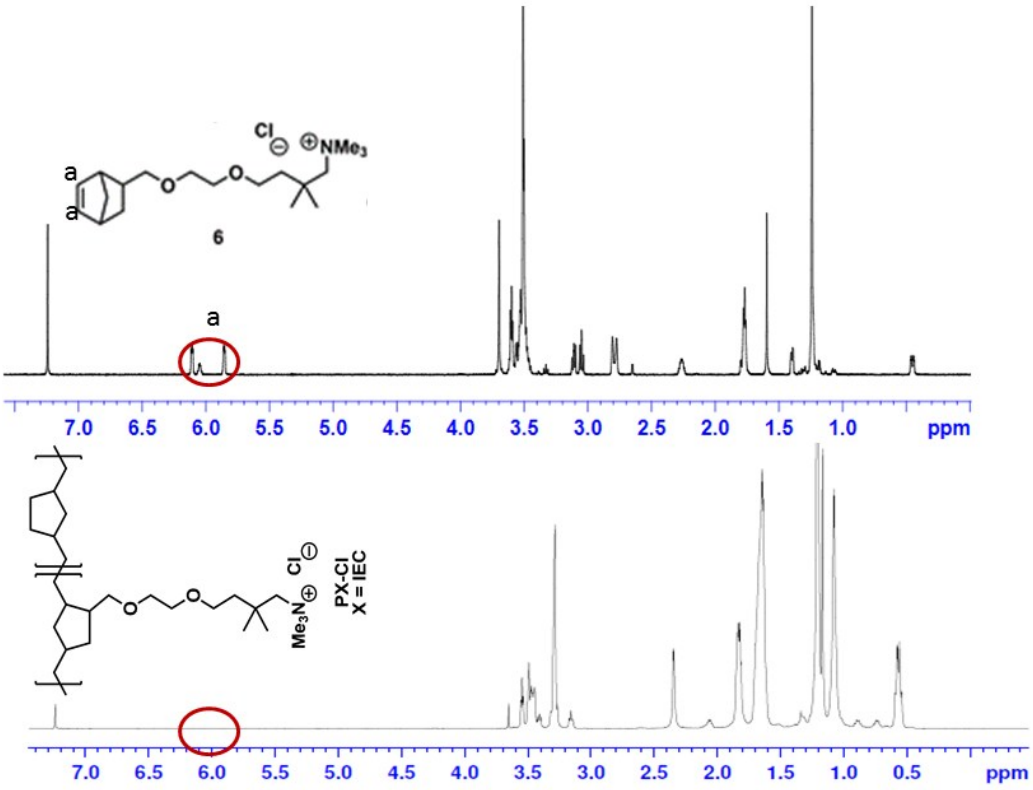


Figure S2. 1H-NMR spectra of monomer (6) (upper) and P1 (lower). The peaks inside of the red circle on the upper spectra indicate the vinyl peaks of the norbornene group for monomer (6). Multiple peaks arise from the endo and exo isomers of monomer (6). The lack of peaks in the red circle for the lower spectra indicates no unreacted monomer present in P1.

References

1. Kinning, D. J.; Thomas, E. L., Hard-Sphere Interactions Between Spherical Domains in Diblock Copolymers. *Macromolecules* **1984,** *17*, 1712-1718.
2. Zhou, N. C.; Chan, C. D.; Winey, K. I., Reconciling STEM and X-ray scattering data to determine the nanoscale ionic aggregate morphology in sulfonated polystyrene ionomers. *Macromolecules* **2008,** *41* (16), 6134-6140.
3. Yarusso, D. J.; Cooper, S. L., Microstructure of Ionomers - Interpretation of Small-Angle X-Ray-Scattering Data. *Macromolecules* **1983,** *16* (12), 1871-1880.
4. Yarusso, D. J.; Cooper, S. L., Analysis of Saxs Data from Ionomer Systems. *Polymer* **1985,** *26* (3), 371-378.