

## Electronic Supporting Information

### Critical role of ion exchange conditions on the properties of network ionic polymers

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## Experimental Methods

### Materials

1,4-dibromobutane (99%), 1,5-dibromopentane (97%), 1,6-dibromohexane (98%), 1,7-dibromopentane (97%), bis(trifluoromethylsulfonyl)imide lithium salt (LiTFSI, 99.95%) were purchased from Sigma Aldrich and used without further purification. Methanol (MeOH, HPLC grade) was purchased from Fisher Scientific and used without further purification. Tris(2-dimethylaminoethyl)amine (Me<sub>6</sub>TREN, 99+%) was purchased from Alfa Aesar and used without further purification.

### Synthesis of network materials

#### *Synthesis of Br<sup>-</sup> network ionic polymer with different linker length (Cx = 4-7)*

The synthesis was reported previously by our group<sup>1</sup>. Dibromo specie (3 equivalence, 1.44 mmol) and Me<sub>6</sub>TREN (2 equivalence, 0.96 mmol) were measured and mixed in a 5 mL glass vial. The error of the mass measurement is lower than 0.1 wt% to make sure high conversion to the network structure. Note that 1,4-dibromobutane reacts with Me<sub>6</sub>TREN rapidly, thus, faster transfer and measurement is required before the mixture turns into solid-like polymer. The reaction mixture was well mixed by a Vortexer followed by a water bath sonicator. The reaction vessel is made by two a 6.35 cm by 6.35 cm glass slides with Kapton tape as a spacer. Vacuum grease was applied to the top of the Kapton tape to make sure the reaction is airtight. After adding 350  $\mu$ L of mixture to the center of the glass slide, the second glass was placed on the top. Air bubbles were eliminated by apply pressure on the glass slides. The reaction vessel was heated at 80 °C for 16 h with a 2 kg weight placed at the top. The products

from this reaction were opaque and white networks which were carefully peeled off from the glass slide with razor to avoid cracking.

#### *Ion exchange of ionic polymer networks*

Br<sup>-</sup> ionic networks were exposed in air for 24 h, before ion exchange, which allows the networks to be soften by absorbing water from the atmosphere. Such procedure avoids sudden volume expansion which induces cracking during ion exchange. 1:1.5, 1:3 and 1:10 mole ratio of salt solutions (with respect to the theoretical Br<sup>-</sup> in the ionic networks assuming complete reaction) were prepared using LiTFSI and 50 mL MeOH. The networks were then submerged into the salt solutions in petri dishes with Teflon<sup>®</sup> covering bottom and small stir bars which stir at 150 rpm. At each time point a small piece of the sample was cut and removed from the salt solution. Additionally, washes with pure MeOH were performed to remove the excess salts in/on the networks. After washing the networks for several times (typically 4-5 times) with 1 hour interval between washes, the sample was allowed to sit in MeOH overnight as a final wash. Once the conductivity of the final wash solution is equal to pure MeOH (around 1.0  $\mu\text{S}/\text{cm}$  in our case), the wash was considered as completed. After the removal of excess salts, the network was dried in vacuum oven at 100 °C for 12 h to remove MeOH and moisture. All of the samples were then stored in the glovebox which was filled with Ar before further testing.

### **Characterization of network ionic polymers**

#### *Conductivity measurements*

The ionic conductivity of the samples was measured using Bio-Logic CESH sample holder and Bio-Logic SP300 potentiostat with continuous nitrogen flow. Inside of the glove box, the 5 mm diameter network sample was placed in between two stainless-steel electrodes with one layer of

Kapton (40  $\mu\text{m}$ ) as the spacer to prevent shortage. The sample was then loaded into the sample holder. After the sample holder was taken out from the glove box, it was immediately connected to the nitrogen tube. The sample was then heated to 363 K and allowed to cool to 323 K with 10 K interval. One hour equilibration time at each temperature point was implemented before the impedance measurement. The impedance data was processed to make a plot of real ( $\sigma'$ ) and imaginary ( $\sigma''$ ) conductivities versus frequency. The network ionic conductivity was taken as the real conductivity where the conductivity loss ( $\tan\delta = \sigma'/\sigma''$ ) is at maximum.

#### *Thermal characterization*

All DSC samples were packed in T-Zero pans and sealed in the glove box to minimize the influence of moisture. The Tgs of the network were measured using a DSC (Q2500, TA instruments) from -20  $^{\circ}\text{C}$  to 80  $^{\circ}\text{C}$  at a heating/cooling rate of 10 $^{\circ}\text{C}/\text{min}$ . The halfpoint of  $\Delta C_p$  during the second heating curve was used to determine the Tgs of the samples.

The thermal stability of the network was measured using a TGA (Q50, TA instruments) from 20  $^{\circ}\text{C}$  to 600  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ . Degradation temperature is defined as the temperature where 5 wt.% of sample is lost.

The water uptake of the network was measured firstly by placing network in the air for 48 h while recording the surrounding humidity (40%  $\pm$  10% RH) or immersing into DI water for 48 h and then a TGA (Q50, TA instruments) was used to monitor the weight lost at 120  $^{\circ}\text{C}$  until mass lost reached equilibrium. The lost wt.% is defined as the water uptake.

#### *Ion exchange characterization*

Elemental analysis was used to determine the ion exchange extent of the network. The samples were packed in the glove box filled with Argon to minimize the moisture during transfer. The samples were then submitted to microanalysis lab in School of Chemical Sciences

and tested using Thermo Scientific Orion Ion Selective Electrodes for fluoride and bromide content. The HCN test was conducted using Exeter Analytical CE 440 in the same facility.

## Figures and Table

Table S1. Elemental analysis of aliquots of networks during ion exchange

Time (min)	Br wt. % residual					
	C4 3 equiv.	C5 3 equiv.	C6 3 equiv.	C7 3 equiv.	C7 1.5 equiv.	C7 10 equiv.
0	43.25	41.67	40.2	38.83	38.83	38.83
10	17.48	16.92	10.92	7.99	6.96	3.56
20	13.43	10.71	9.05	4.1	5.62	3.52
30	11.68	8.19	7.62	2.96	3.67	2.09
40	9.51	7.03	5.74	2.94	4.18	2.19
50	8.43	6.68	5.52	2.94	3.38	1.2
60	7.34	6.84	3.91	1.96	3.38	0.92
120	5.15	5.78	2.81	1.44	3.44	0.66
180	4.71	5.7	1.91	1.2	3.5	0.62
360	4.13	4.33	1.8	1.16	4.07	0.52
540	4.4	5.08	1.68	1.18	3.66	0.75
720	4.58	4.81	----	1.87	3.67	0.71
1440	4.31	4.77	1.73	1.86	3.65	0.47
2880*	2.79±0.14	1.74±0.12	1.72±0.09	1.51±0.17	3.65±0.02	0.47±0.19

\*Average of three separately prepared samples with standard error of the mean

### Ion exchange extent calculation:

$$\frac{(1 - \text{mol}\%) \times \text{MW of Br}}{(1 - \text{mol}\%) \times \text{MW of Br network} + \text{mol}\% \times \text{MW of TFSI network}} = \text{Br wt}\% \quad (\text{eq.1})$$

MW of C4 network with Br anion = 184.75 g/mol

MW of C4 network with TFSI anion = 384.992 g/mol

MW of C5 network with Br anion = 191.763 g/mol

MW of C5 network with TFSI anion = 392.005 g/mol

MW of C6 network with Br anion = 198.776 g/mol

MW of C6 network with TFSI anion = 399.018 g/mol

MW of C7 network with Br anion = 205.789 g/mol

MW of C7 network with TFSI anion = 406.032 g/mol

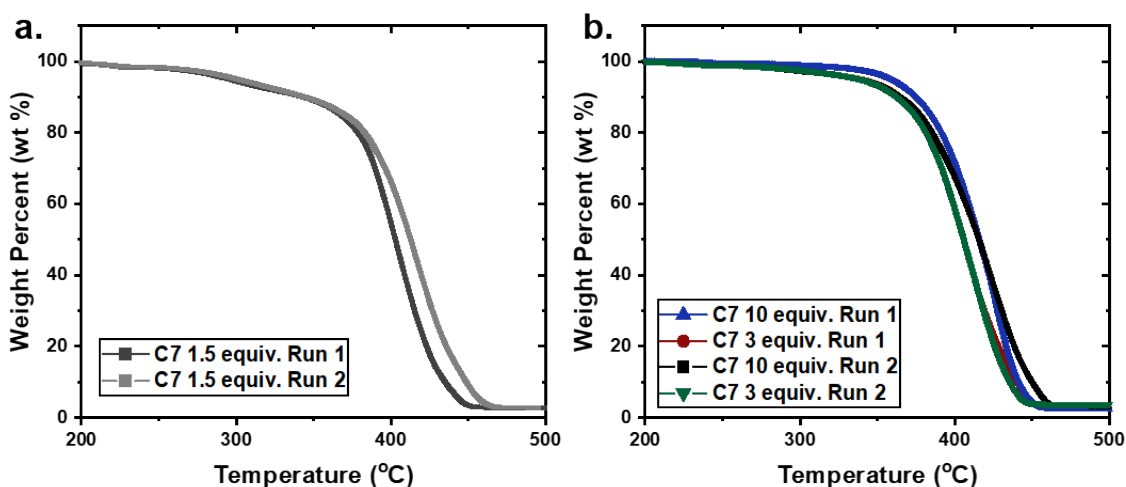


Figure S1. a. Two TGA runs of C7 1.5 equiv. ion exchanged sample both showing a two-steps degradation with an initial step starting at around 260 °C. b. TGA runs of C7 3 and 10 equiv. ion exchanged networks all showing single step degradation around 350 °C.

## References

1. C. Shen, Q. Zhao, C.M. Evans, Ion specific, odd–even glass transition temperatures and conductivities in precise network polymerized ionic liquids, *Molecular Systems Design & Engineering*. **2019**, 4, 332–341