Ion transport in self-assembled block copolymer electrolytes with different side chain chemistries

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Supporting Information

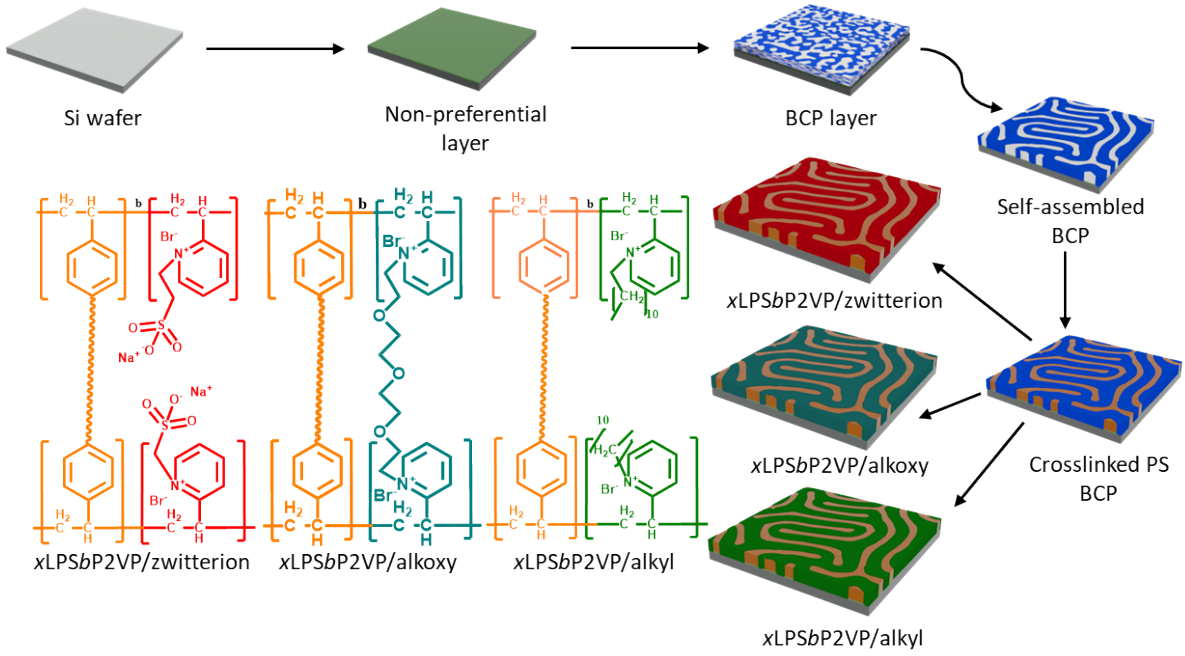

Figure S1. Schematic flow diagram depicting the preparation of the BCEs reported in this work and their chemical structures.

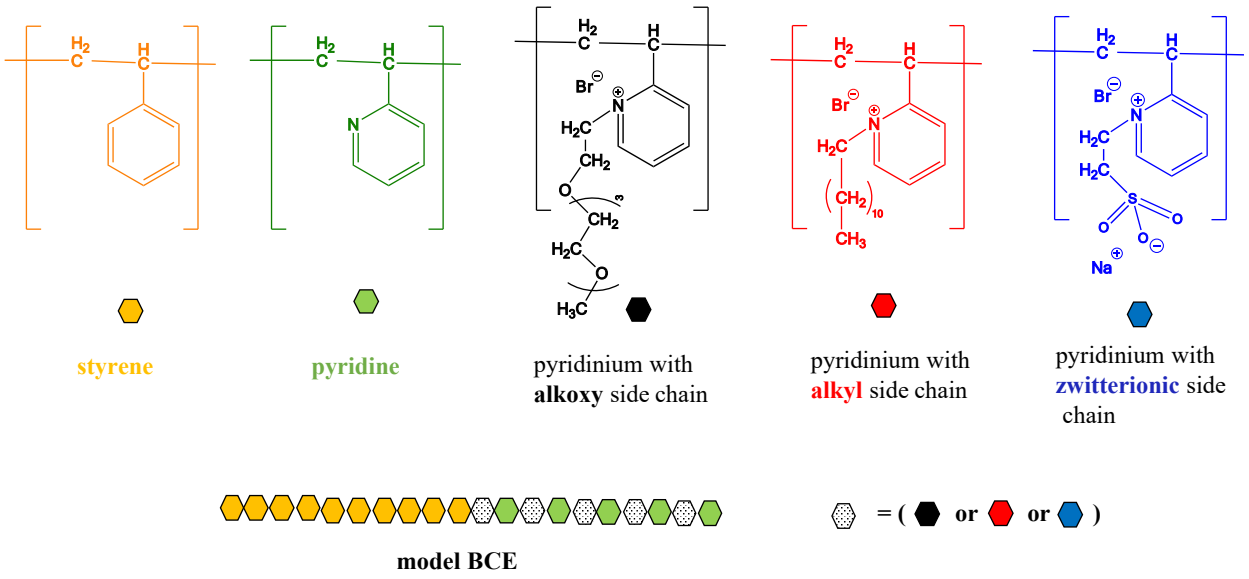

Figure S2. The structure of each monomer(top) and the representation of the three different BCE chains (bottom) that were simulated MD simulations. Yellow stands for styrene monomer; green stands for non-alkylated 2-vinylpyridine monomer; black stands for 2-vinylpyridinium with alkoxy side chain; red stands for 2-vinylpyridinium with alkyl side chain and blue stands for 2-vinylpyridinium monomer with zwitterionic side chain. Each pyridinium cation contains a bromide anion as the counterion.

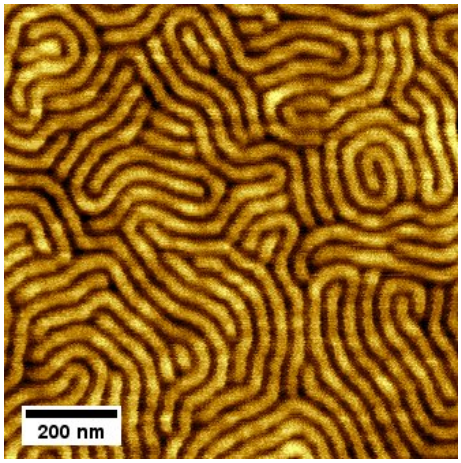

Figure S3. AFM image of self-assembled PS*b*P2VP with perpendicular lamellae microstructures.

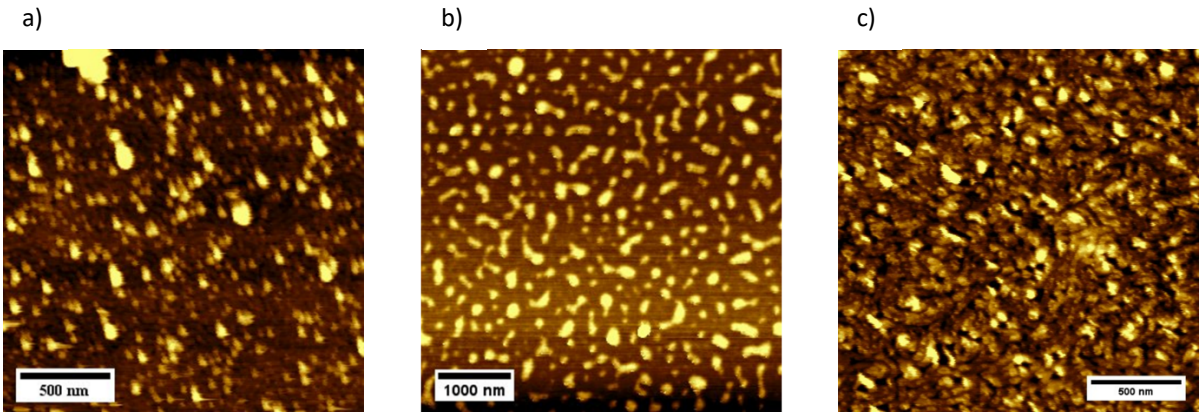

Figure S4. AFM images of a) PS*b*P2VP/zwitterion, b) PS*b*P2VP/alkoxy, and c) PS*b*P2VP/alkyl. The perpendicular lamella structures are lost when the Menshutkin reactions are performed without crosslinking the PS domain.

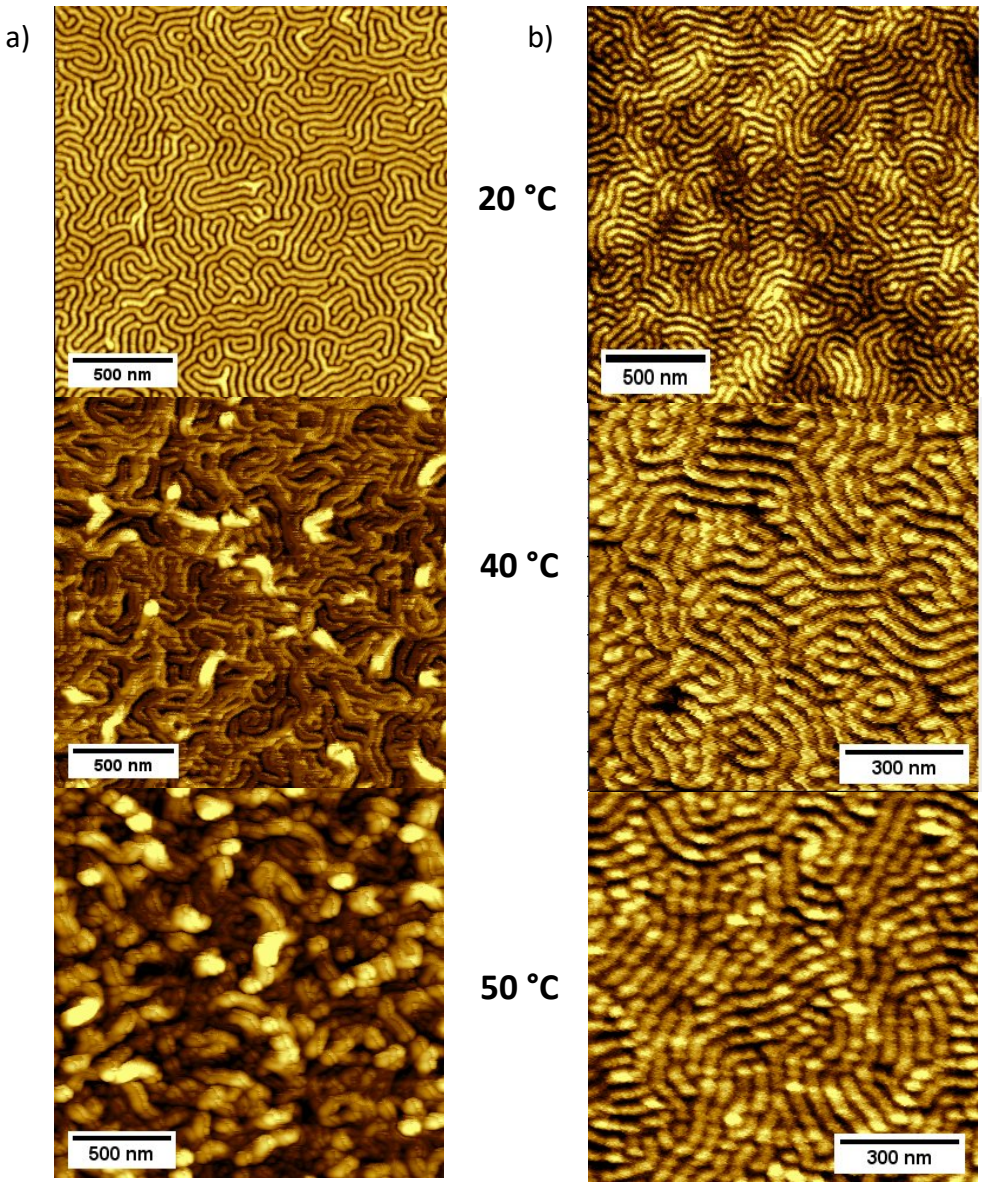

Figure S5. AFM images of a) PS*b*P2VP and b) *x*LPS*b*P2VP after being submerged in ethanol for 3 hrs at different temperatures.

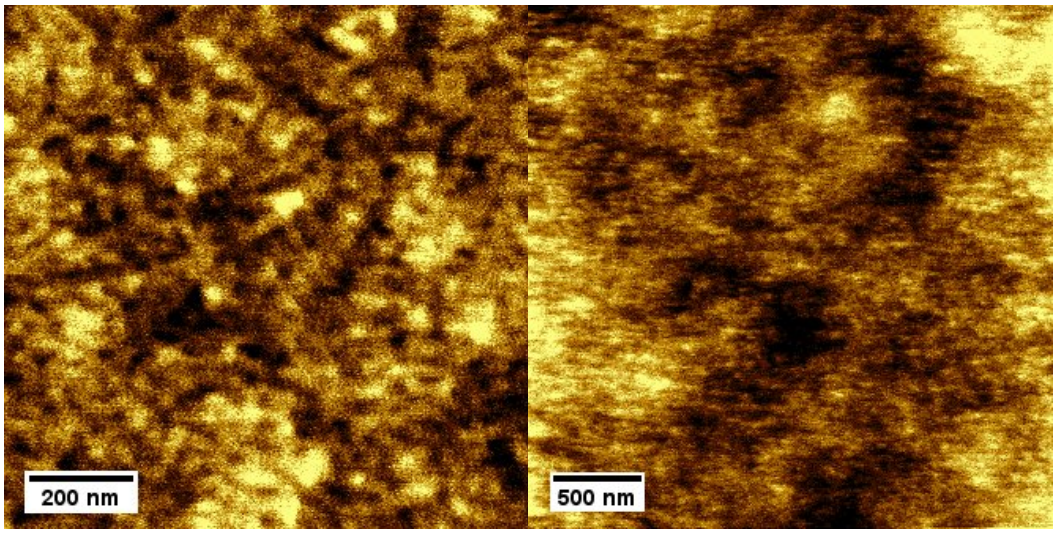

Figure S6. AFM images of *x*LPS*b*P2VP after being submerged in a 1-Br-PEG4 solution in ethanol for 15 mins at 20 °C.

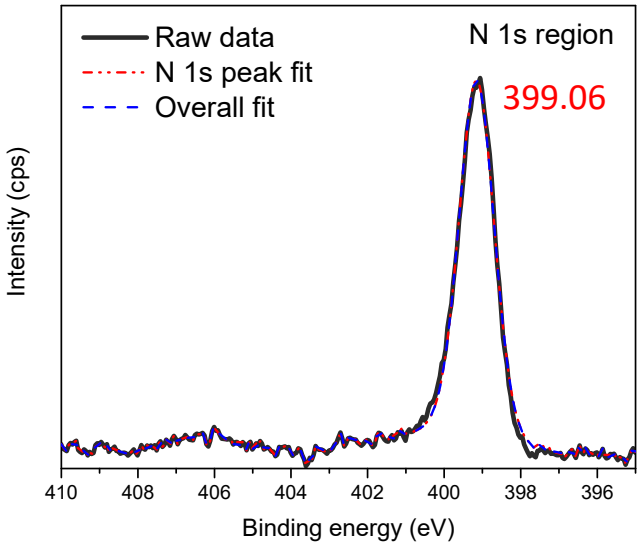

Figure S7. High resolution N 1s XPS spectrum of *x*LPS*b*P2VP.

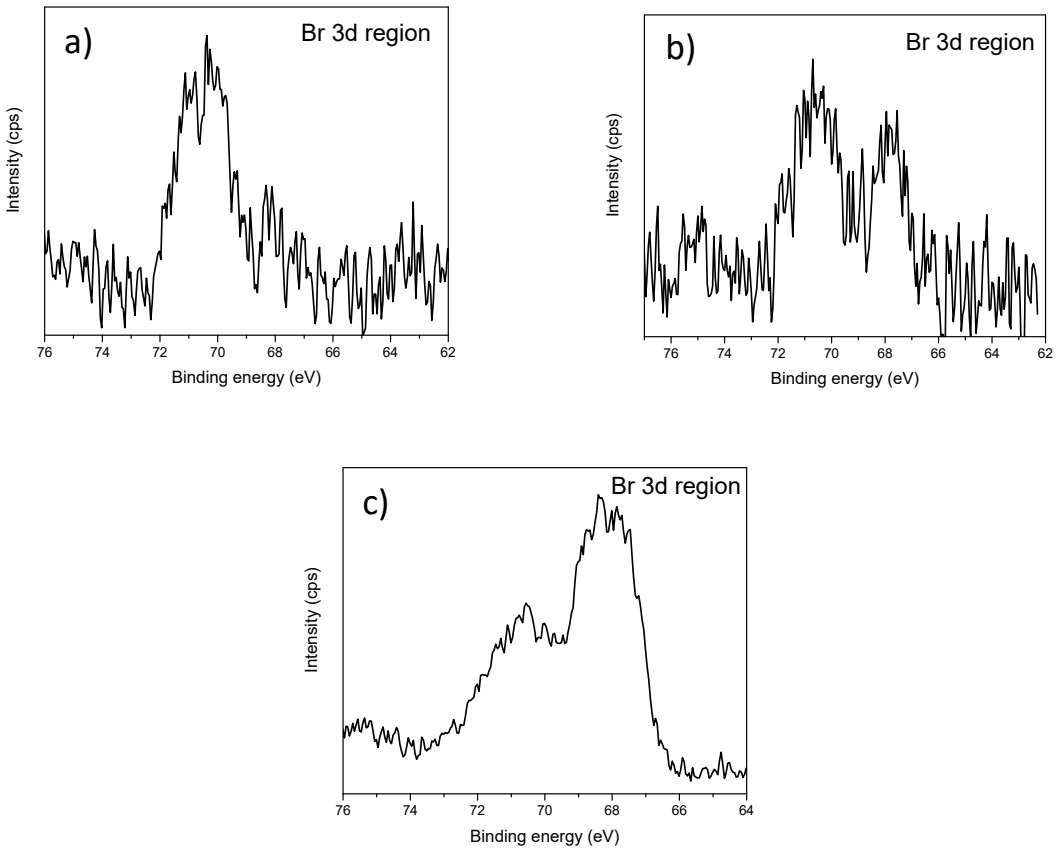

Figure S8. High resolution N 1s XPS spectra of a) *x*LPS*b*P2VP/zwitterion, b) *x*LPS*b*P2VP/alkoxy, and c) *x*LPS*b*P2VP/alkyl.

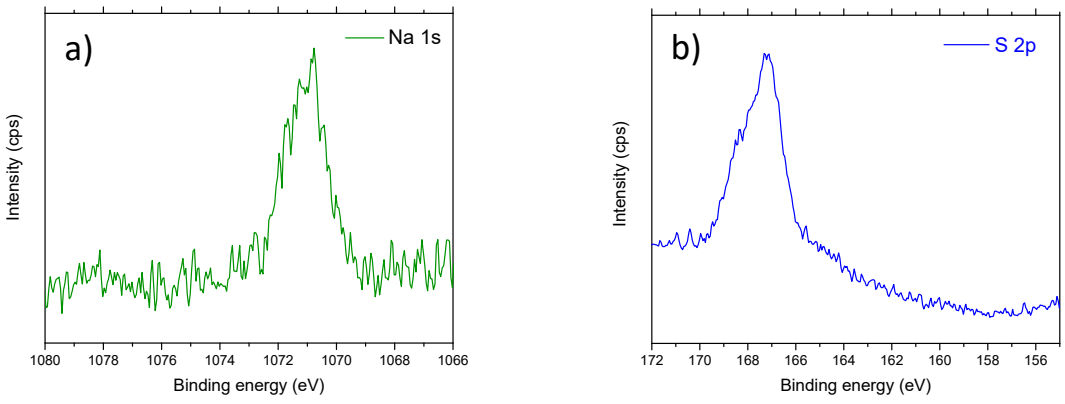

Figure S9. High resolution a) Na 1s and b) S 2p XPS spectra of *x*LPS*b*P2VP/zwitterion.

Molecular Dynamics Simulation setup

The Avogadro[1] software was used to generate the initial structures of the model BCEs with different side chains, and then the structures were optimized in the NVT (300 K) ensemble for 1 ns. With the help of the Packmol[2] software, the optimized BCE chains with the bromide counterions and water molecules were packed into a cubic simulation box length of around 75 Å. The SHAKE[3] algorithm was used to constrain the bond lengths and bond angles for the water molecules. Equilibration was carried out by first simulating each system for 30 ns in the NPT ensemble (temperature of 300 K and pressure of 1 atm) via the Nosé-Hoover thermostat and barostat, followed by 20 ns simulation in the NVT ensemble at a temperature of 300 K using the Nosé-Hoover thermostat. These were then used as initial configurations for the replica exchange molecular dynamics (REMD)[4] simulations that were then carried out with 16 replica systems equally distributed in temperature between 285 K to 360 K for 20 ns for each temperature for better sampling for structural data. In addition, 20 ns production runs in the NVT ensemble were carried out to obtain the dynamical properties like the diffusion coefficients of bromide ions and water molecules within the systems under study. Note that all electrostatic interactions in the simulations were calculated using the Ewald method, specifically PPPM[5]. The charges on the polymer were determined using the electrostatic potential grid-based method, CHELPG[6] around monomeric units.

Non equilibrium Simulations: Finally, to calculate the conductivity of the counterion within the novel BCEs, non-equilibrium MD simulations were performed by adding an electric field of 0.1 V $Å^{-1}$ in the z direction for 10 ns. Initially, the conductivity values for the zwitterion side chain system showed inconsistent values (very high negative value) for the cubic box simulation. Therefore, a new box dimension was considered for only conductivity calculations by replicating the initial box of each system (all three cases) in the directions of y and z so that the new system (1x2x2) times larger initial box using the LAMMPS replicate command. As before, equilibration was carried out. The resulting systems were subjected to an electric field of 0.1 V $Å^{-1}$ in the z direction for 10 ns. The ionic current was determined and from that the conductivity as was done previously by Li et al.[7]

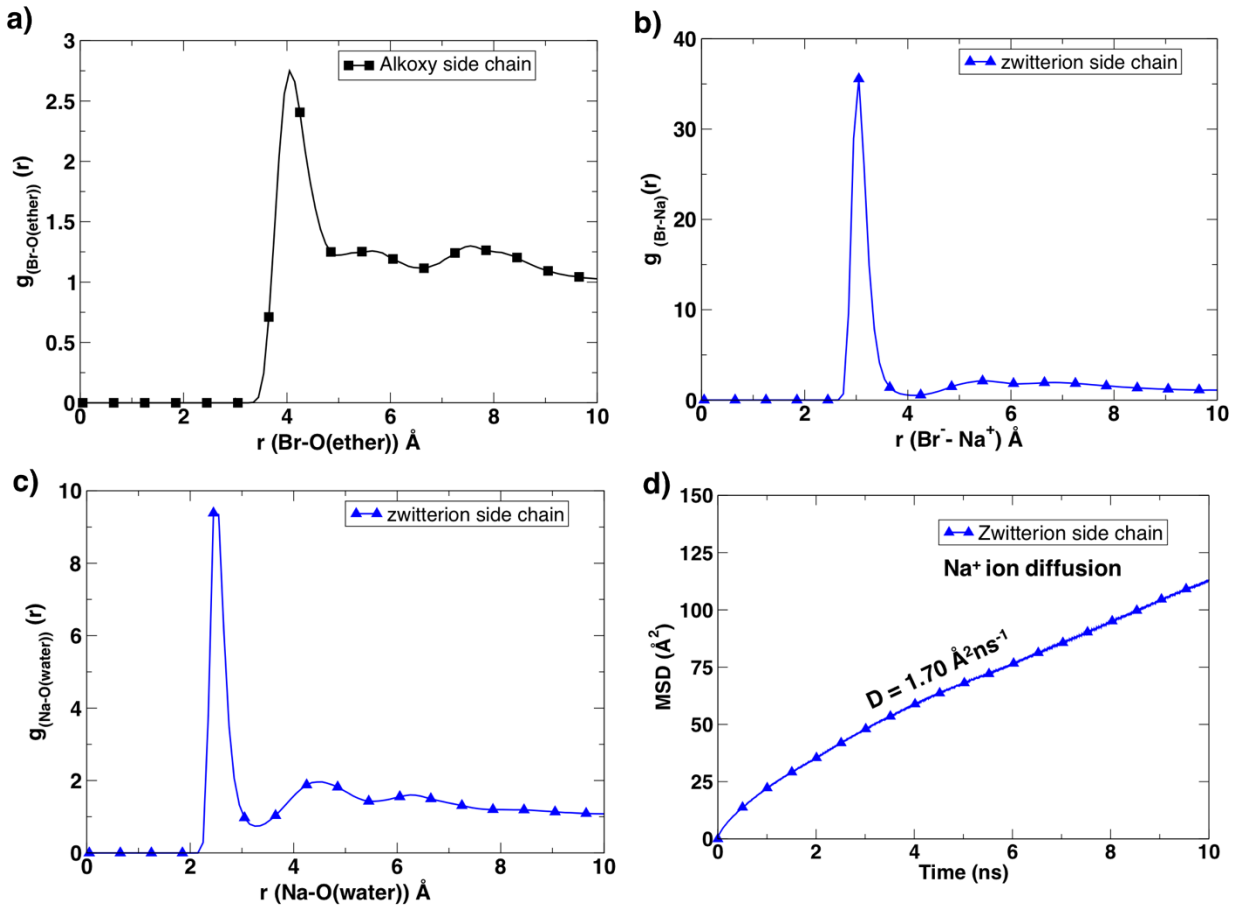

Figure S10. (a) The radial distribution function g(r) between the bromide ions and oxygens of the alkoxy side chain BCE system. **(b)** The radial distribution function g(r) between the bromide ions and sodium ions of the zwitterion side chain BCE system. **(c)** The radial distribution function g(r) between the sodium ions and water molecules of the zwitterion side chain BCE system. **(d)** Mean square displacement (MSD) versus time for the sodium ions in the zwitterion side chain BCE system. The diffusion constant is given by the slope of the line.

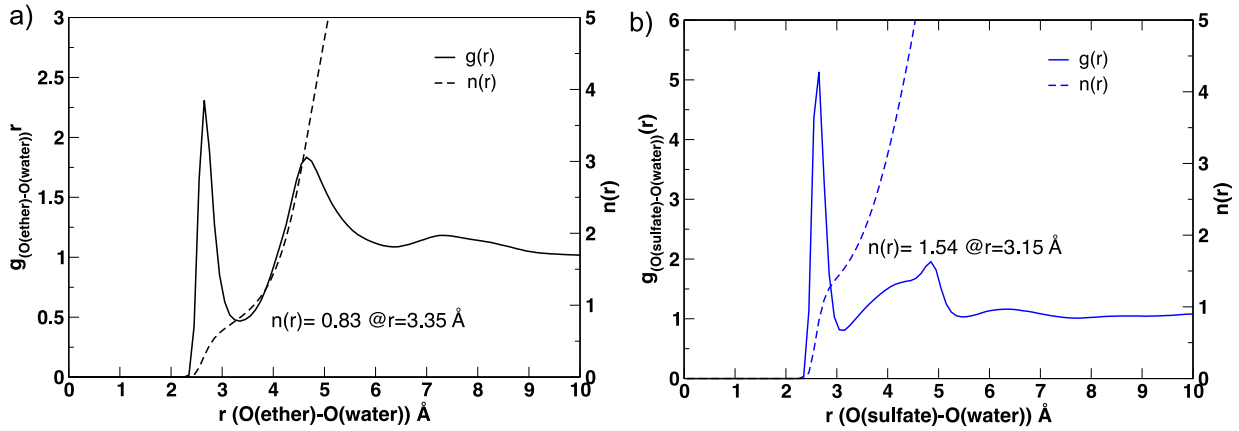

Figure S11. Radial distribution function, g(r), and the coordination number n(r) **a)** between ether oxygens and water oxygens in the alkoxy BCE system **b)** between sulfate oxygens and water oxygens in the zwitterionic BCE system.

Calculating IEC of the BCEs

$$IEC\left(\frac{mmol}{chain}\right) = \frac{mmol\ per\ chain\left(\frac{mmol}{chain}\right)}{Mn_{chain}\left(\frac{g}{chain}\right)} \quad \text{<S1>}$$

$$Mn_{chain}\left(\frac{g}{chain}\right) = Mn_{PS\ block}\left(\frac{g}{chain}\right) + Mn_{P2VP-SC\ block}\left(\frac{g}{chain}\right) \quad \text{<S2>}$$

$Mn_{PS\ block}\left(\frac{g}{chain}\right) = 40{,}500$; from Polymer Source Inc. (supplier)

$$Mn_{P2VP-SC\ block}\left(\frac{g}{chain}\right) = RUI \cdot MW_{RUI} + (RUC - RUI) \cdot MW_{RUC} \quad \text{<S3>}$$

RUI : # of repeat units with ionic groups

MW_{RUI} : Molecular weight of the repeat units with ionic groups

RUC : # of repeat units in the P2VP chain

$$RUC = Mn_{P2VP\ block}\left(\frac{g}{chain}\right)/MW_{2VP\ repeat\ unit}\ (g/mol) \quad \text{<S4>}$$

MW_{RUC} : Molecular weight of the 2-vinyl pyridine repeat unit = 105.14 g/mol

$Mn_{P2VP\ block}\left(\frac{g}{chain}\right) = 44{,}00$; from Polymer Source Inc. (supplier)

$$RUI = RUC \cdot f_{XPS}$$ <S5>

$f_{XPS} = \frac{I_{N\ 1s\ pyridinium}}{I_{N\ 1s\ pyridinium} + I_{N\ 1s\ pyridine}}$: from XPS data (I = integrated data from XPS)

$$MW_{RUI} = MW_{RUC} + MW_{SC}$$ <S6>

MW_{SC}: Molecular weight of the sidechain unit installed

For the alkyl sidechain (1-bromododecane), MW_{SC} = 249 g/mol

For the alkoxy sidechain (bromo-PEG3-bromo), MW_{SC} = 160 g/mol; *note: the MW of bromo-PEG3-bromo (320 g/mol) is divided by two as this reagent can alkylate two 2VP repeat units in the BCE

For the zwitterionic sidechain (bromo-ethyl sodium sulfonate), MW_{SC} = 211 g/mol

References

1. M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek and G. R. Hutchison, *J. Cheminformatics*, 2012, **4**.
2. L. Martínez, R. Andrade, E. G. Birgin and J. M. Martínez, *J. Comput. Chem.*, 2009, **30**, 2157–2164.
3. J.-P. Ryckaert, G. Ciccotti and H. J. Berendsen, *J. Comput. Phys.*, 1977, **23**, 327– 341.
4. Y. Sugita and Y. Okamoto, *Chem. Phy. Lett.*, 1999, **314**, 141-151.
5. R. Hockney and J. Eastwood, *CRC Press*, 1998.
6. C. M. Breneman and K. B. Wiberg, *J. Comput. Chem.*, 1990, **11**, 361-373.
7. K. Li, V. Subasinghege Don, C. S. Gupta, R. David and R. Kumar, *The Journal of Chemical Physics*, 2021, **154**, 184505.