

Supporting Information

Role of Solvation Site Segmental Dynamics on Ion Transport in Ethylene-Oxide based

Side-Chain Polymer Electrolytes

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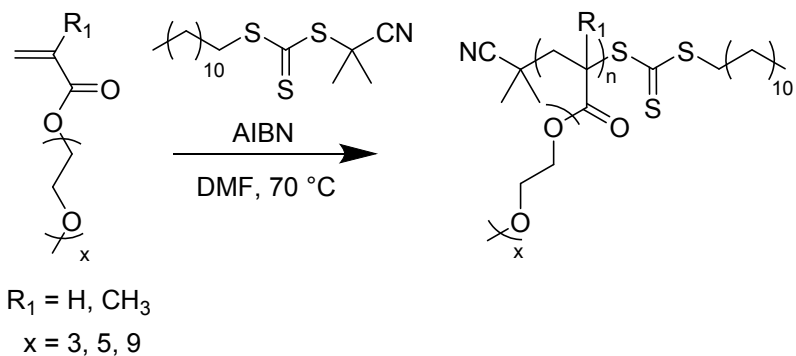
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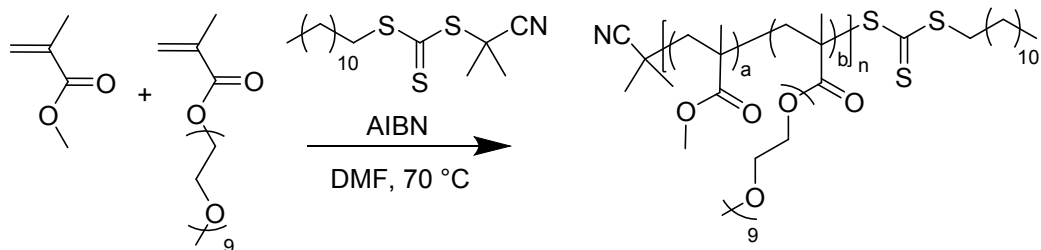
Contents:

1. RAFT Polymerization reaction schemes
2. GPC data
3. Raw Li⁺ ion MSD vs. time data
4. DSC thermograms and VTF fitting parameters
5. Solvation site connectivity as a function of x_{EO}
6. Radial Distribution Functions
7. Full FTIR spectra
8. Raman data and estimates of free ion fraction
9. NMR of POEM_{9-*r*}-PMMA random copolymer
10. Field Parameters for MD Simulations
11. Molecular Dynamics Simulation Protocols
12. Simulated Fictive Temperatures

1. RAFT Polymerization reaction schemes



Scheme S1 – General reaction scheme for RAFT polymerization of homopolymer POEM_x and POEA₉



Scheme S2 – Reaction scheme for copolymerization of OEM₉ and MMA

2. GPC Data

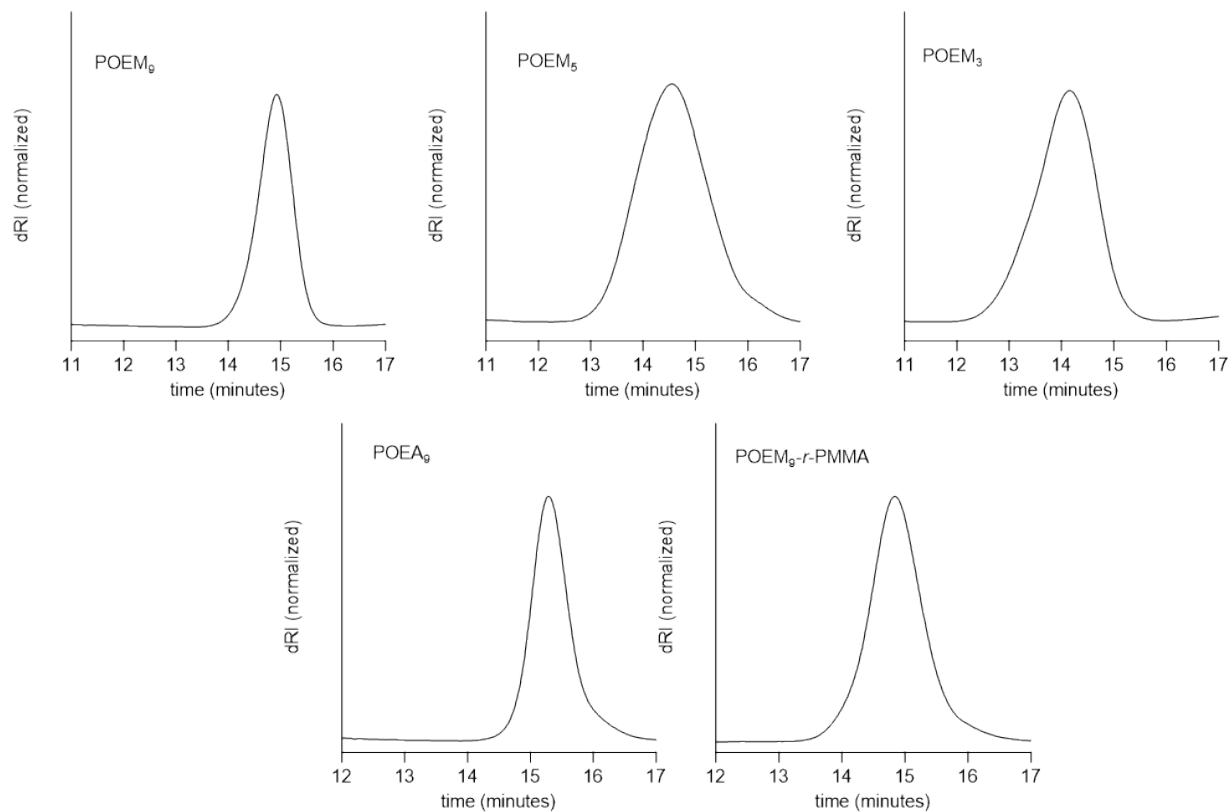


Fig. S1 – Differential refractive index (dRI) vs. elution time data taken from GPC-MALS measurements of synthesized polymers in THF. Molecular weight and dispersity are taken from these data assuming a differential refractive index of $dn/dc = 0.073 \text{ mL g}^{-1}$.

3. Raw Li^+ ion mean-squared displacement (MSD) data

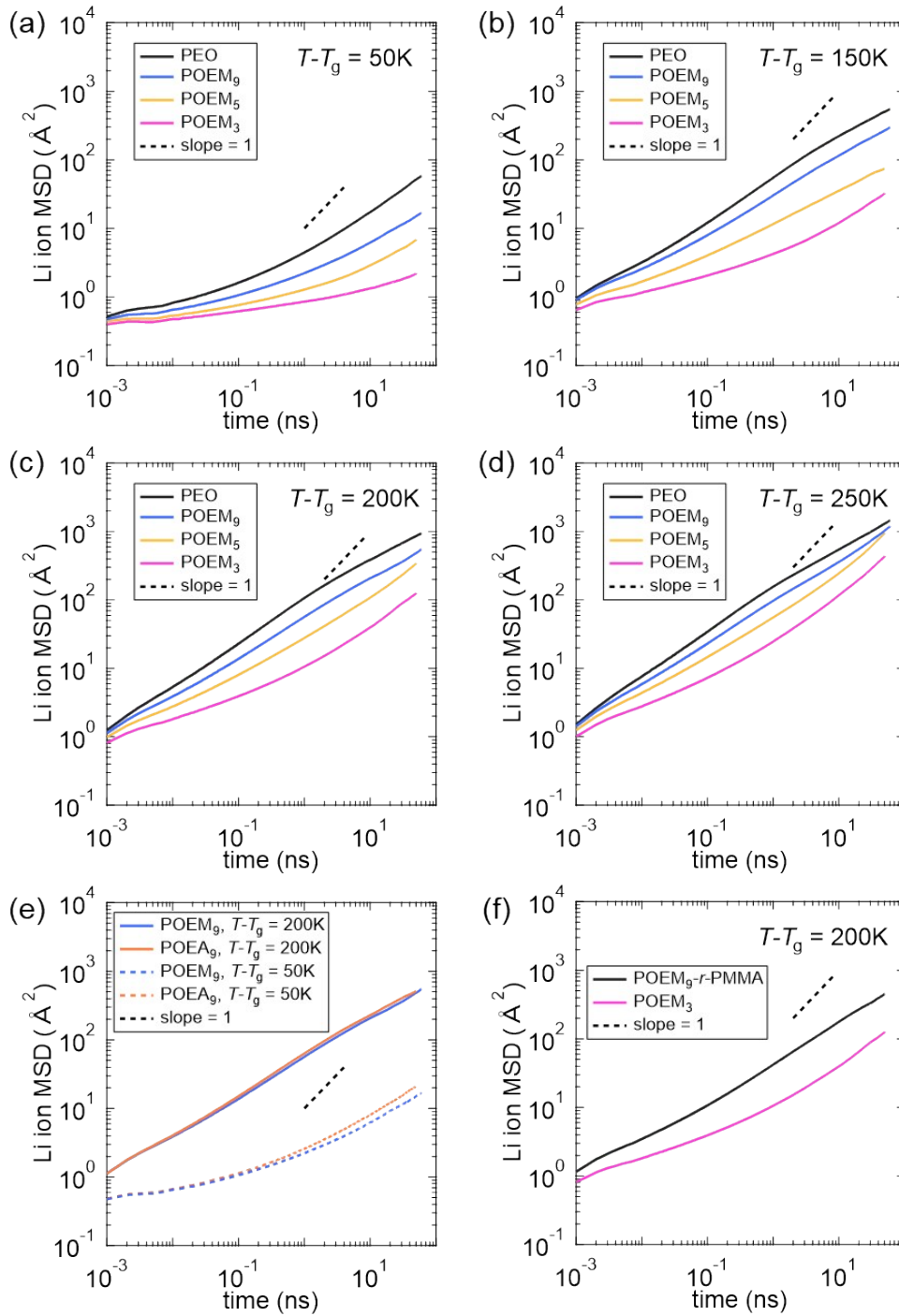


Fig. S2 – Li^+ ion MSD data in (a) PEO, (b) POEM₉, (c) POEM₅, (d) POEM₃, (e) POEA₉ and (f) POEM₉-r-PMMA used to calculate MSD ratios in Fig. 3, Fig. 6, and Fig. 7 of the text.

4. DSC thermograms and VTF fitting parameters

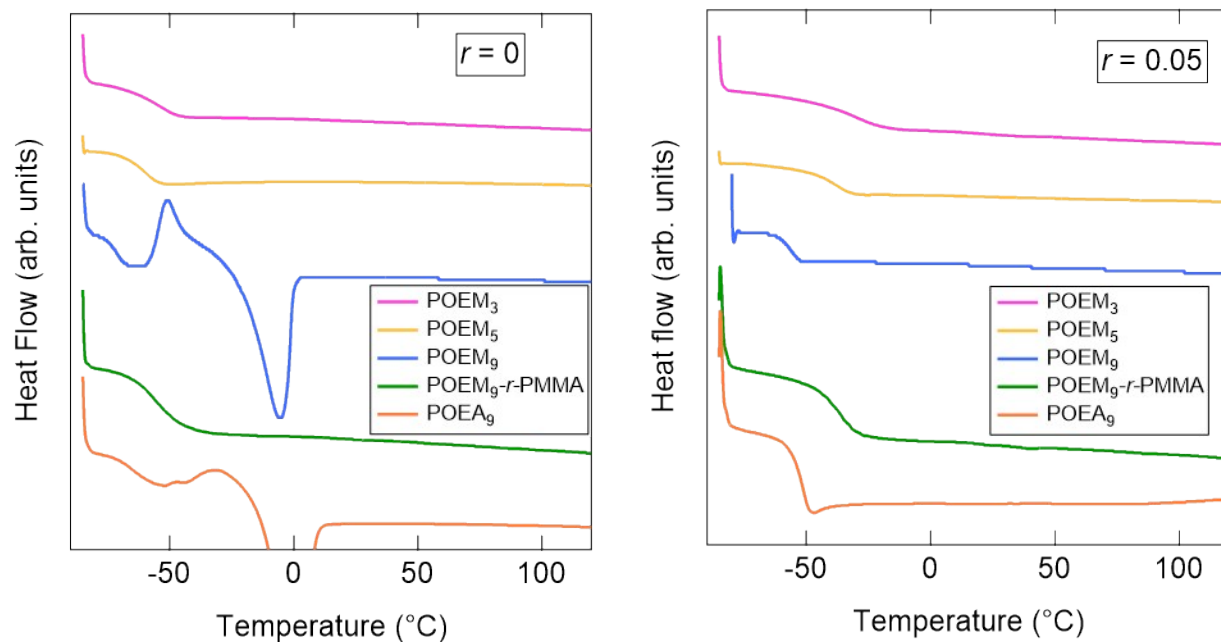


Fig. S3 – DSC thermograms of neat and $r = 0.05$ samples. These curves represent the third heating cycle, and T_g is taken as the midpoint in the inflection in the heat flow rate.

Table S1. VTF Fit Parameters for $r = 0.05$ Electrolytes

Material	A (S cm ⁻¹)	E_a (J mol ⁻¹)	T_0 (K)
PEO	0.0581	3784	228.2
POEM ₉	0.262	8754	186.6
POEM ₅	0.317	11890	176.4
POEM ₃	0.204	11986	189.0

5. Solvation site connectivity as a function of x_{EO}

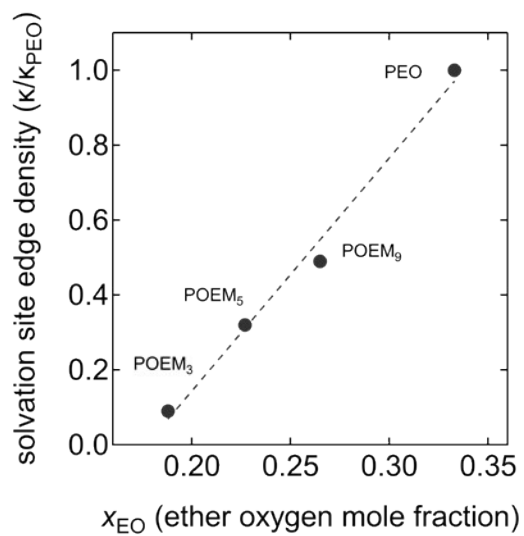


Fig. S4 – Normalized solvation site edge density (κ/κ_{PEO}) as a function of ether oxygen mole fraction. x_{EO} is defined as the ratio of ether oxygens in a repeat unit to the total number of atoms (not including hydrogens).

6. Radial Distribution Functions

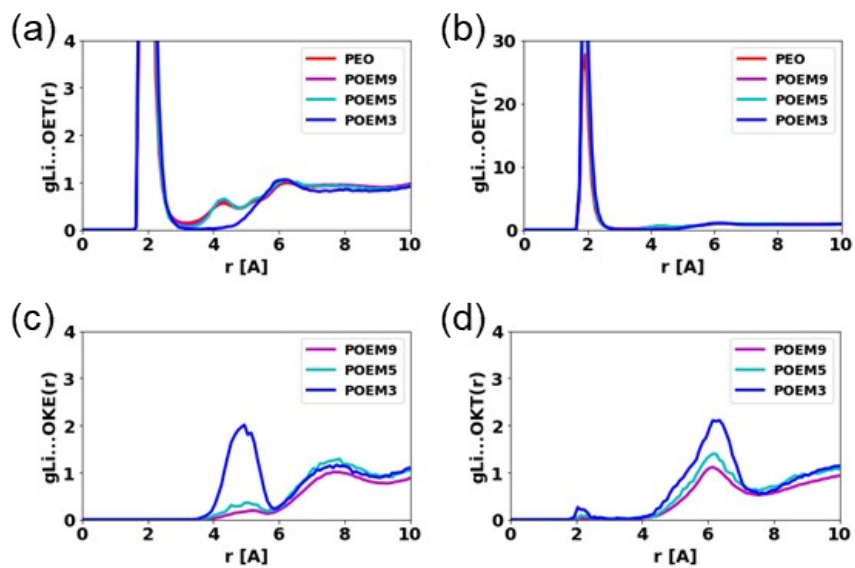


Fig. S5 – Radial distribution functions (RDF) between Li ion and oxygen atoms in PEO and POEM_x at 150K above T_g. The Li-OET RDF are shown both in full scale (a) and in zoomed scale (b). The Li-OKE RDFs (c) and Li-OKT RDFs (d) are computed for POEM_x only. Note that the RDFs are normalized by the concentration of each oxygen type, so the relative heights of the peaks do not necessarily relate to the composition.

7. Full FTIR spectra

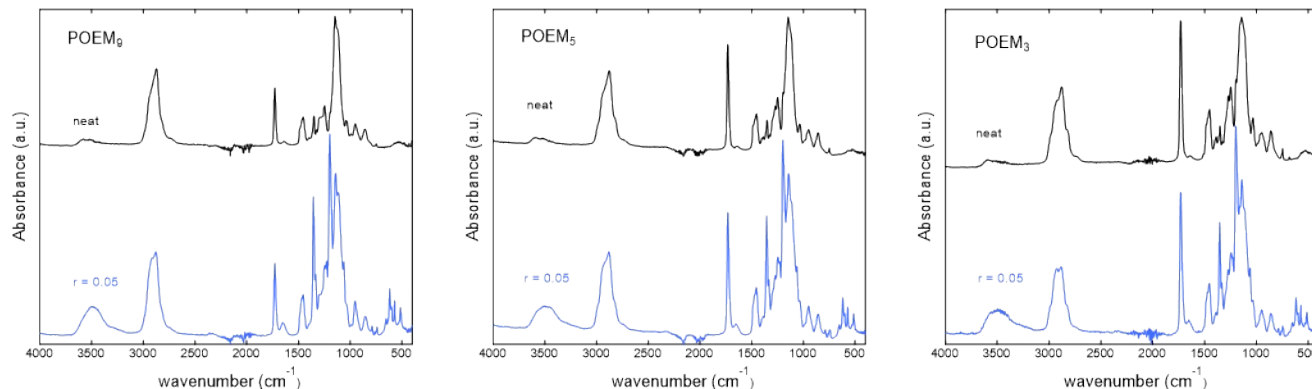


Fig. S6 – Full ATR-FTIR spectra of POEM₉, POEM₅, and POEM₃, both neat and at $r = 0.05$.

8. Raman data and estimates of free ion fraction

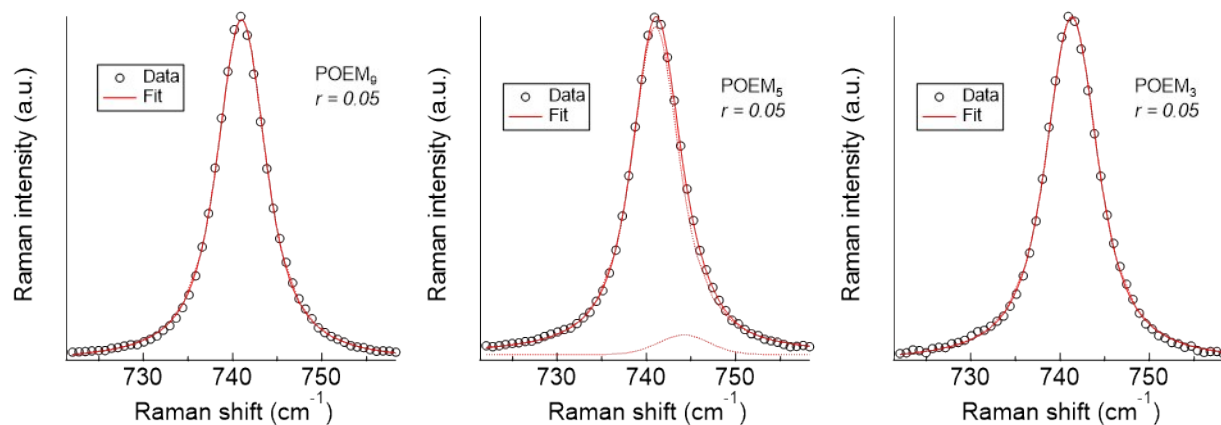


Fig. S7 – Raman spectra and fits for POEM₉, POEM₅ and POEM₃ $r = 0.05$ electrolytes. Black open circles represent the raw data, dotted red lines are fits to individual peaks at 741 cm⁻¹ (free TFSI) and 744 cm⁻¹ (associated TFSI), and solid red lines are the combined fit. Raman data is fit to two Voigt peaks, which converge in the case of POEM₉ and POEM₃. The free ion fraction is taken from the area fraction under the 741 cm⁻¹ peak.

9. NMR of POEM₉-*r*-PMMA random copolymer

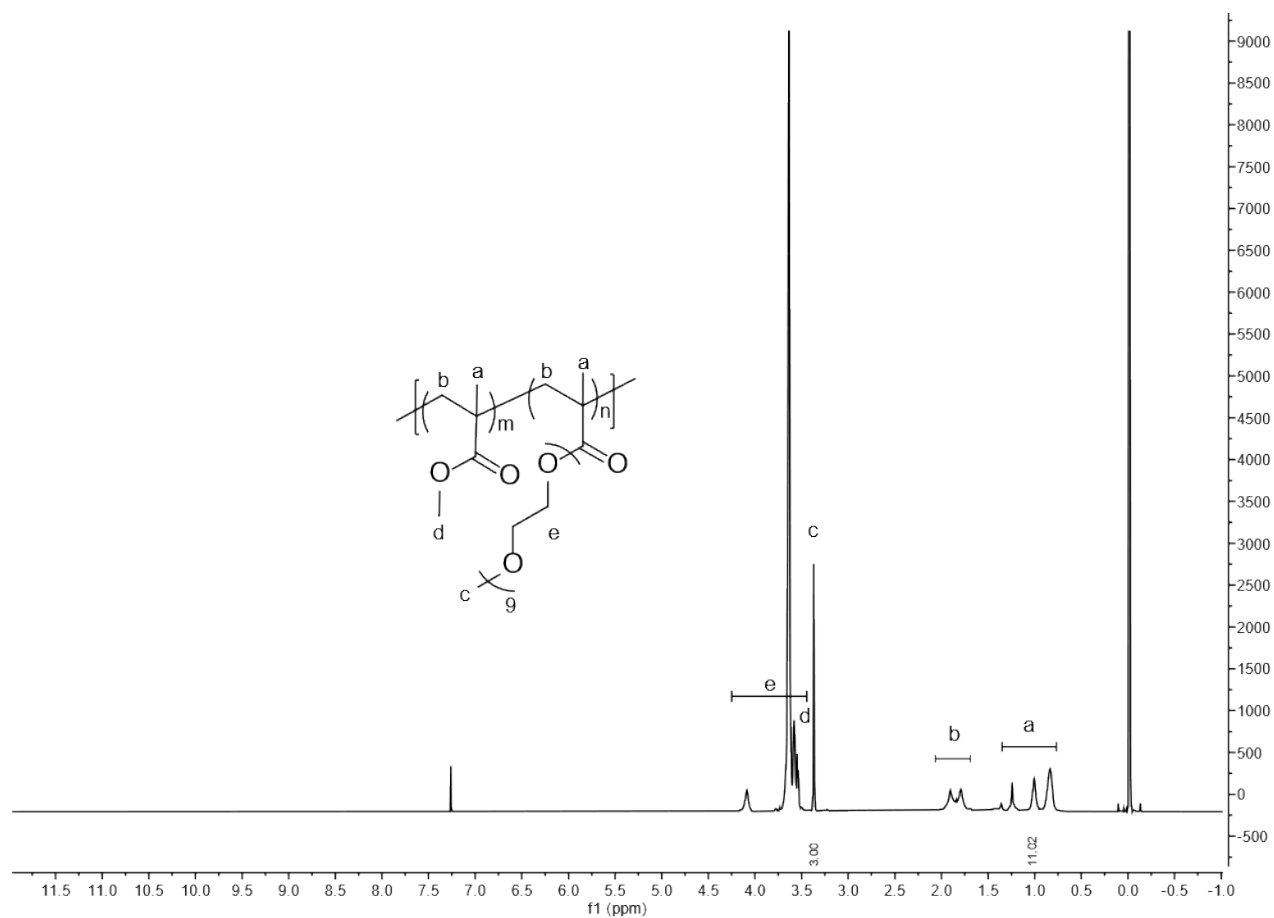


Fig. S8 – ¹H-NMR spectra of POEM₉-*r*-PMMA in CDCl₃. The ratio of peak integrals for the ether side-chain end methyl group (c, δ = 3.38 ppm) to the methacrylate backbone methyl group (a, δ = 0.7 – 1.5 ppm) was used to determine the mol fraction of POEM₉ in the copolymer. $I_c/I_a = 0.273 = x_{\text{POEM}_9}$.

10. Force Field Parameters for MD Simulations

In this study, the TraPPE-UA force field¹⁻³ is used for all inter- and intramolecular interactions between polymer atoms. Instead of rigid bonds used in TraPPE-UA force field, the generalized CHARMM bonding parameters are used⁴. Parameters for the lithium cation are adapted from a previous simulation study⁵. Fig. S9 provides reference labels for the different atom types in polymer for assigning the appropriate force field parameters.

10.1 United Atom Model: Terminal Groups, Tacticity, and Atom Type Assignments

For PEO and POEM simulation cells, a single, long polymer chain with approximately 10,000 interaction sites is used. The use of single, long polymer chain has been adopted in other simulation studies for SPEs to eliminate the co-diffusion of Li⁺ ion with polymer chain⁶. The degree of polymerization and approximate molecular weights for simulated chains are listed below. For PEO, the termini at both ends are methoxyl end groups as noted in (OET-CE3) in Fig. S9. For POEM_x and POEM_{9-r}-PMMA, the terminal at either end is a CH₃ that is connected to a CT interaction site. For POEA₉, the terminal at either end is a CH₃ that is connected to a C1 interaction site. POEM_x in this study are atactic. When generating the atactic POEM_x chains, the stereochemistry of each chiral center is randomly chosen as S or R with equal probability. In order for the random copolymer POEM_{9-r}-PMMA to mimic the oxygen content of POEM₃, each monomer is randomly chosen as POEM₉ or PMMA with 1/3 and 2/3 probabilities, respectively. The stereochemistry of POEM₉ monomers in the random copolymer is also randomly chosen as S or R with equal probability.

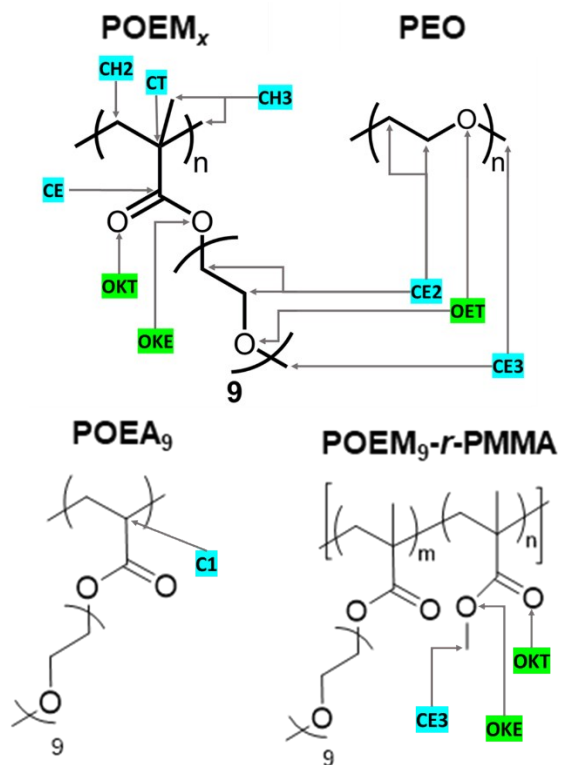


Fig. S9 – Reference labels for atom types in force field parameters.

Table S2. Molecular weight of simulated polymer chains

Material	N	M_n (g mol ⁻¹)
PEO	3333	147000
POEM ₉	300	149000
POEM ₅	455	146000
POEM ₃	625	145000
POEA ₉	300	145000
POEM ₉ -r-PMMA	620	140000

10.2 Non-bonded Interaction Parameters

The nonbonded interactions includes Lennard-Jones interactions and Coulombic interactions. For united atoms i and j , their nonbonded interaction is:

$$u_{nb}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}, \quad (1)$$

where r_{ij} is the separation distance between atoms i and j , σ_{ij} is the Lennard-Jones diameter, ϵ_{ij} is the Lennard-Jones interaction strength, ϵ_0 is the vacuum permittivity. q_i and q_j are the partial charges of atoms i and j .

Unlike LJ interactions are computed with Lorentz-Berthelot mixing rules. For 1-2, 1-3, and 1-4 bonded interaction sites, the Lennard-Jones interactions are turned off. Coulomb interactions are turned off for 1-2 and 1-3 bonded interaction sites and scaled to 0.5 for 1-4 bonded interactions. The non-bonded interaction parameters are listed in Table S3.

Table S3. Bonding potential parameters for polymer atoms

atom	m (amu)	σ_{ii} (Å)	$\frac{kcal}{\epsilon_{ii} (mol)}$	$q (e)$
CE2	14.027	3.950	0.091411	0.25
CE3	15.035	3.750	0.194746	0.25
OET	15.999	2.850	0.109296	-0.50
CH2	14.027	3.950	0.091411	0.00
CH3	15.035	3.750	0.194746	0.00
CT	12.011	6.400	0.000994	0.05
C1	13.019	4.680	0.019870	0.05
CE	12.011	3.820	0.079488	0.55
OKT	15.999	3.050	0.156989	-0.45
OKE	15.999	2.800	0.109296	-0.40

10.3 Bonding Potential Parameters

1-2 bonded united atoms interact via a harmonic bonding potential in the form:

$$u_{bond}(r_{ij}) = k_{bond}(r_{ij} - r_{ij}^{(0)})^2, \quad (2)$$

Where r_{ij} is the separation distance between atoms i and j , k_{bond} is the force constant and $r_{ij}^{(0)}$ is the equilibrium bond length. The bonding interaction parameters are listed in Table S4.

Table S4. Bonding potential parameters for polymer atoms

bond	k_{bond} ($\frac{kcal}{mol \cdot \text{\AA}^2}$)	$r_{ij}^{(0)}$ (\AA)	bond	k_{bond} ($\frac{kcal}{mol \cdot \text{\AA}^2}$)	$r_{ij}^{(0)}$ (\AA)
CE2-CE2	225.0	1.54	CE2-OKE	360.0	1.41
CE2-OET	360.0	1.41	CE-CT	200.0	1.52
CE3-OET	360.0	1.41	CE-C1	200.0	1.52
CH3-CT	225.0	1.54	CE-OKT	360.0	1.20
CH2-CT	225.0	1.54	CE-OKE	360.0	1.34
CH3-C1	225.0	1.54	CE3-OKE	360.0	1.34
CH2-C1	225.0	1.54	CH2-CH2	225.0	1.54

10.4 Bending Potential Parameters

1-2-3 bonded united atoms interact via a harmonic bending potential in the form:

$$u_{bend}(\theta_{ijk}) = k_{bend}(\theta_{ijk} - \theta_{ijk}^{(0)})^2, \quad (3)$$

Where k_{bend} is the force constant, θ_{ijk} is the angle between united atoms i , j , and k , and $\theta_{ijk}^{(0)}$ is the equilibrium angle. The bending interaction parameters are listed in Table S5.

Table S5. Bending potential parameters for polymer atoms

bend	k_{bend} ($\frac{kcal}{mol \cdot rad^2}$)	$\theta_{ijk}^{(0)}$ (Å)	bend	k_{bend} ($\frac{kcal}{mol \cdot rad^2}$)	$\theta_{ijk}^{(0)}$ (Å)
CE2-OET-CE2	60.0136	112.0	OKT-CE2-CE2	49.9782	112.0
CE2-OET-CE3	60.0136	112.0	CH2-CT-CE	62.1000	109.5
CE2-CE2-OET	49.9782	112.0	CT-CE-OKT	62.1000	125.0
CH2-CT-CH2	62.1000	109.5	CT-CE-OKE	70.1483	110.0
CH3-CT-CH2	62.1000	109.5	CH3-CT-CE	62.1000	109.5
CT-CH2-CT	62.1000	114.0	CH3-CT-CH3	62.1000	109.5
CH2-C1-CH2	62.1000	109.5	CH2-C1-CE	62.1000	109.5
CH3-C1-CH2	62.1000	109.5	C1-CE-OKT	62.1000	125.0
C1-CH2-C1	62.1000	114.0	C1-CE-OKE	70.1483	110.0
CE-OKE-CE2	62.1000	115.0	CH3-C1-CE	62.1000	109.5
CE-OKE-CE3	62.1000	115.0	CH3-C1-CH3	62.1000	109.5
OKT-CE-OKE	62.1000	125.0	OKE-CE2-CE2	49.9782	112.0

10.5 Torsional Potential Parameters

The torsional potentials for 1-2-3-4 bonded united atoms take the form:

$$u_{tors}(\phi_{ijkl}) = \frac{K_1}{2}[1 + \cos(\phi_{ijkl})] + \frac{K_2}{2}[1 - \cos(2\phi_{ijkl})] + \frac{K_3}{2}[1 + \cos(3\phi_{ijkl})] + \frac{K_4}{2}[1 - \cos(4\phi_{ijkl})], \quad (3)$$

Where c_1 , c_2 , and c_3 are coefficients and ϕ_{ijkl} is the dihedral angle defined by atoms i , j , k , and l . The torsional interaction parameters are listed in Table S6.

Table S6. Torsional potential parameters for polymer atoms

torsion	$\frac{kcal}{K_1 (mol)}$	$\frac{kcal}{K_2 (mol)}$	$\frac{kcal}{K_3 (mol)}$	$\frac{kcal}{K_4 (mol)}$
OKE-CE2-CE2-OET	1.888000	-1.888000	0.000000	0.000000
OET-CE2-CE2-OET	1.888000	-1.888000	0.000000	0.000000
CE2-CE2-OET-CE2	2.882840	-0.650809	2.218510	0.000000
CE2-CE2-OET-CE3	2.882840	-0.650809	2.218510	0.000000
CH3-CT-CH2-CT	0.000000	0.000000	1.833350	0.000000
CH2-CT-CH2-CT	0.000000	0.000000	1.833350	0.000000
CT-CH2-CT-CE	0.000000	0.000000	1.833350	0.000000
CH3-CT-CE-OKT	-0.919280	0.229880	-0.609280	0.000000
CH2-CT-CE-OKT	-0.919280	0.229880	-0.609280	0.000000
CH3-CT-CE-OKE	0.915310	0.216840	0.609670	0.000000
CH2-CT-CE-OKE	0.915310	0.216840	0.609670	0.000000
CT-CE-OKE-CE2	9.689610	7.678560	1.387070	0.000000
CH3-C1-CH2-C1	0.000000	0.000000	1.833350	0.000000
CH2-C1-CH2-C1	0.000000	0.000000	1.833350	0.000000
C1-CH2-C1-CE	0.000000	0.000000	1.833350	0.000000
CH3-C1-CE-OKT	-0.919280	0.229880	-0.609280	0.000000
CH2-C1-CE-OKT	-0.919280	0.229880	-0.609280	0.000000
CH3-C1-CE-OKE	0.915310	0.216840	0.609670	0.000000
CH2-C1-CE-OKE	0.915310	0.216840	0.609670	0.000000
C1-CE-OKE-CE2	9.689610	7.678560	1.387070	0.000000
CT-CE-OKE-CE3	9.689610	7.678560	1.387070	0.000000
CE-OKE-CE2-CE2	-2.988080	2.142010	-0.087834	0.203768
OKT-CE-OKE-CE3	-9.669740	7.376500	-1.045270	0.000000
OKT-CE-OKE-CE2	-9.669740	7.376500	-1.045270	0.000000

11. Molecular Dynamics Simulation Protocols

To prepare the starting configuration, a single polymer chain with approximately 10,000 interaction sites is initiated in a large box. To equilibrate the initial configuration, the polymer chain is first relaxed under NVT ensemble at 500K for 30 ns. Then a 20 ns NPT equilibration at 500K and 1 bar is performed to ensure the density does not drift. The process of introduction of Li ions is as follows: TFSI ions are introduced at random positions in the equilibrated neat polymer at the designated ratio of $r = 0.05 = [\text{LiTFSI}]/[\text{EO}]$. To remove any steric clashes in the simulation cell, the system is relaxed under NVE ensemble for 10,000 steps, where the maximum displacement of an atom is limited to 0.1 Å per step. The system is subsequently equilibrated for 15 ns under NPT at 400 K and 1 bar.

To perform simulation at each temperature, the salt-doped polymer is equilibrated at the designated temperature under NPT for 10ns. Then the system is further equilibrated for 10ns under NVT ensemble. At the beginning of this NVT equilibration, the box size is scaled to reflect the ensemble average density during at the last 3 ns of NPT equilibration. Then, the trajectory for analysis is collected from a 100-ns production simulation under NVT ensemble.

12. Simulated Fictive Temperatures

Fictive temperature (T_f) is used as a proxy for T_g that can be estimated from simulation. The simulated T_g referred to in the text is in fact the fictive temperature. To determine T_f the polymer is cooled from 400K to 100K at a cooling rate of 10K/ns at 1 bar under NPT ensemble. The density is plotted as a function of temperature. Two linear segments are fitted to for the glass and liquid region respectively. The T_f is determined as the intercept of the extrapolated linear fit lines. This procedure to calculate T_f is sensitive to the fitting range of the two segments. Therefore, the end points of the fitting segments are systematically sampled in the following manner. The starting point of the glassy segment was fixed at 50 K, while the end point of the glassy segment was randomly sampled between 180K and 200K. Similarly, the starting point of the liquid segment was fixed at 400K, whereas the end point of the liquid segment was sampled between 300K and 320K. The fitting intervals for the glassy segment and the liquid segment are randomly drawn within the sampling interval defined above, the intersections between which yield a set of T_f values. Only T_f values that fall between the end points of fitting segments are kept. The T_f calculation described above was repeated for another independent sample. For each sample, combinations of glassy and liquid fitting ranges are generated 10,000 times. The mean and standard deviation of the set of T_f values collected from both samples are reported. Table S7 lists the average and uncertainty of T_f obtained using the protocol described above. Fig. S10 includes the cooling curve and the distribution of resulting T_f values collected.

Table S7. Simulated fictive temperatures for polymers studied.

Material	T_f
PEO	262 ± 3 K
POEM ₉	250 ± 2 K
POEM ₅	246 ± 2 K
POEM ₃	252 ± 3 K
POEA ₉	245 ± 2 K
POEM ₉ -r-PMMA	259 ± 2 K

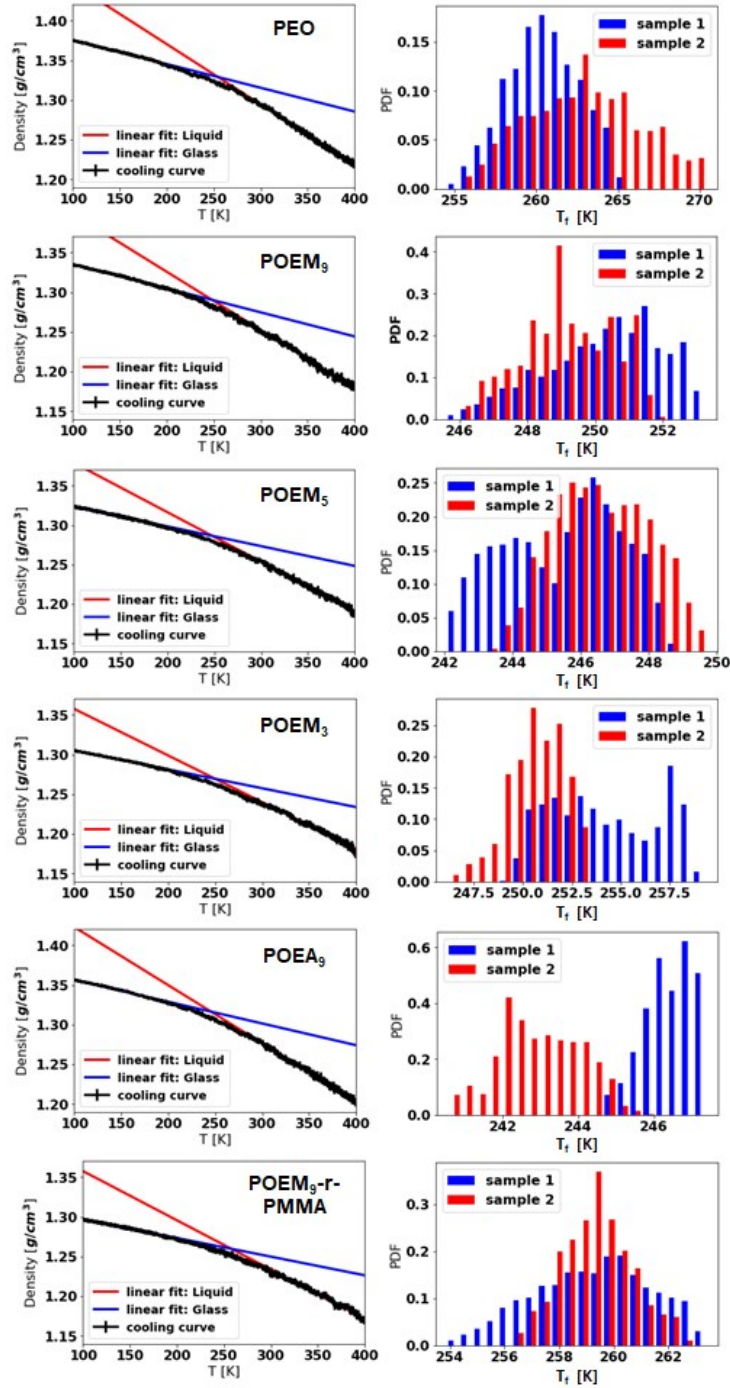


Fig. S10 – Fictive temperatures (T_f) in simulations at $r = 0.05$. (a) Representative density as a function of temperature. Example fitting lines for liquid and glassy regions are shown in red and blue, respectively. The fitting range for the example linear fits are [100K,200K] for the glassy

region and [300K,400K] for the liquid region. (b) Normalized histograms of collected T_f values. Histograms from different samples are plotted in different colors.

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