Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

Structure and dynamics of dynamic covalent cross-linked PEOs and PEO/$LiPF_6$ electrolyte: A coarse-grained simulation study

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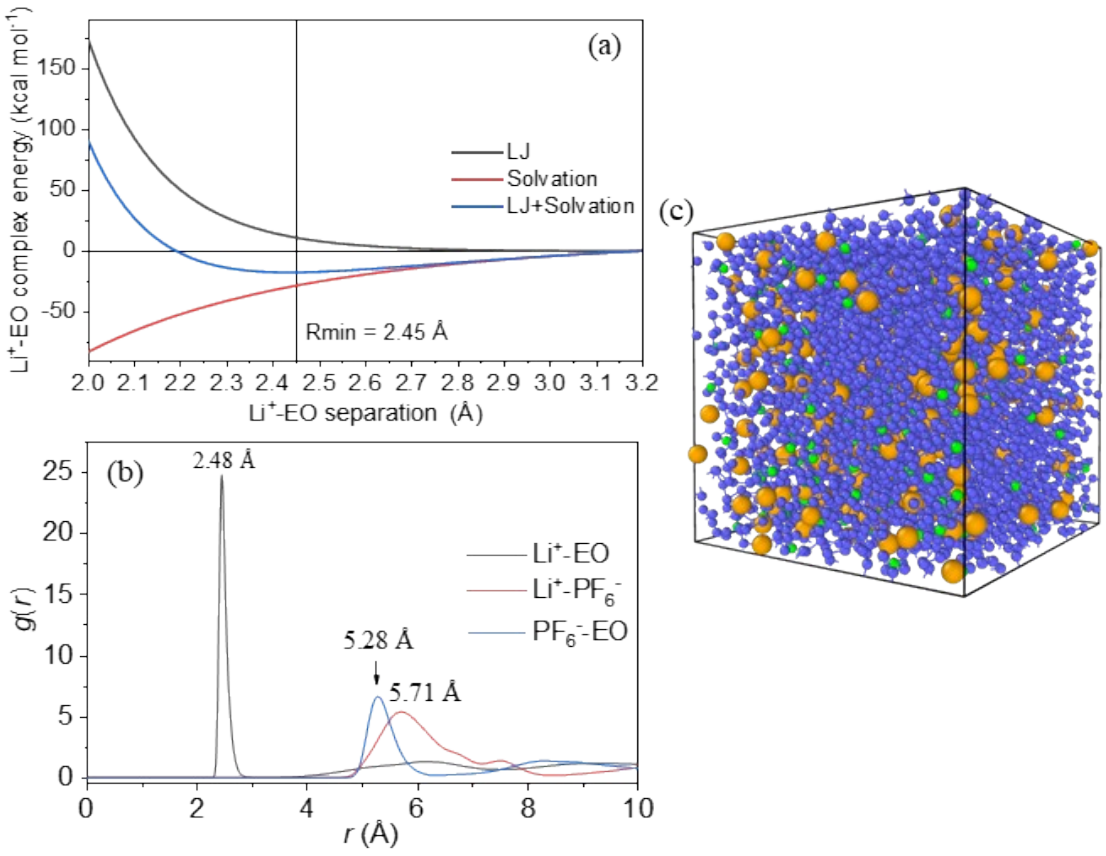

Figure S1. (a) The hybrid Li^+-EO pairwise potential energies as a function of Li^+-EO separation with $S_{EO\text{-}+} = 34\epsilon$. (b) Radial distribution functions (RDFs) for PEO_{16}-$LiPF_6$. (c) A snapshot of the simulation box to demonstrate the distribution of Li^+ (Green) and PF_6^- (Khaki) in PEO_{16}-$LiPF_6$.

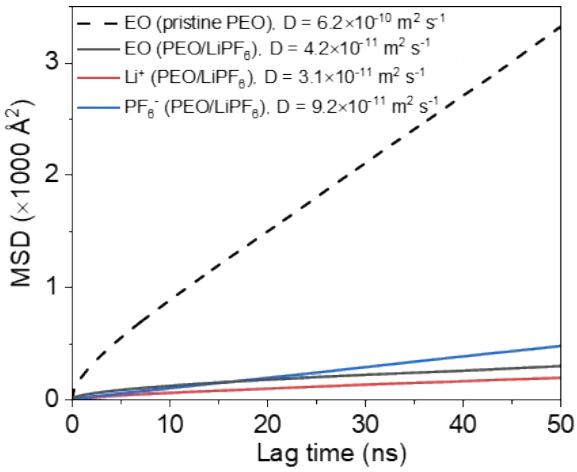

Figure S2. Mean-squared displacements (MSDs) for linear PEO and PEO_{16}-$LiPF_6$. MSDs were calculated from the following expression:[1]

$$MSD = \left\langle \frac{1}{N}\sum_{i=1}^{N} |r_i(t) - r_i(0)|^2 \right\rangle \qquad (1)$$

where N is the number of particles the MSD is calculated over and $\boldsymbol{r}_i(t)$ is the coordinate of particle i at time t, while < > represents ensemble averaging.

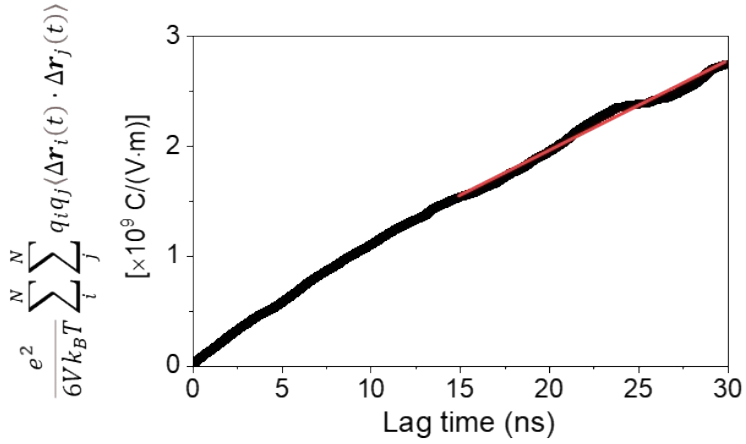

Figure S3. The collective displacement ($\frac{e^2}{6Vk_BT}\sum_i^N\sum_j^N q_iq_j\langle\Delta r_i(t)\cdot\Delta r_j(t)\rangle$) of ions for PEO_{16}-$LiPF_6$ used to calculate ionic conductivity (λ). λ was calculated from the equilibrium dynamics using the following relation:[2]

$$\lambda = \frac{e^2}{6Vk_BT}\lim_{t\to\infty}\frac{d}{dt}\sum_i^N\sum_j^N q_iq_j\langle\Delta r_i(t)\cdot\Delta r_j(t)\rangle \qquad (2)$$

where e is the electron charge ($1.6022\times10^{-19}C$), V is the volume of the simulation box, k_B is Boltzmann's constant (8.6173×10^{-5} eV K^{-1}), T is the temperature (353 K), t is time, q_i and q_j are the charges over ions i and j in electrons, $\Delta\boldsymbol{r}_i(t)$ is the displacement of ion i during time t, the summation

is performed over all ions, N is the number of cations plus anions, and < > denotes the ensemble average.

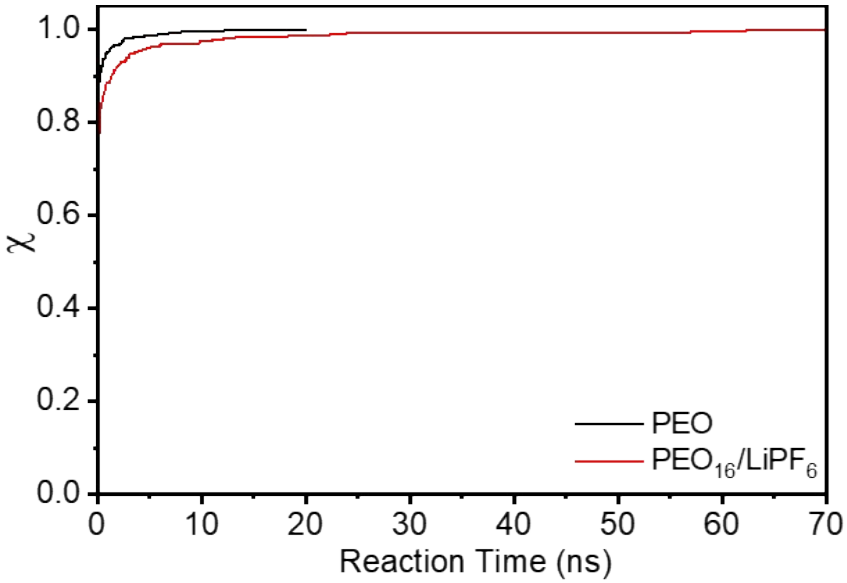

Figure S4. The fractional conversion (χ) as a function of reaction time for the preparation of dynamic covalent cross-linked PEO and PEO_{16}-$LiPF_6$ electrolyte at 353 K with $E_a = 0.1\epsilon$.

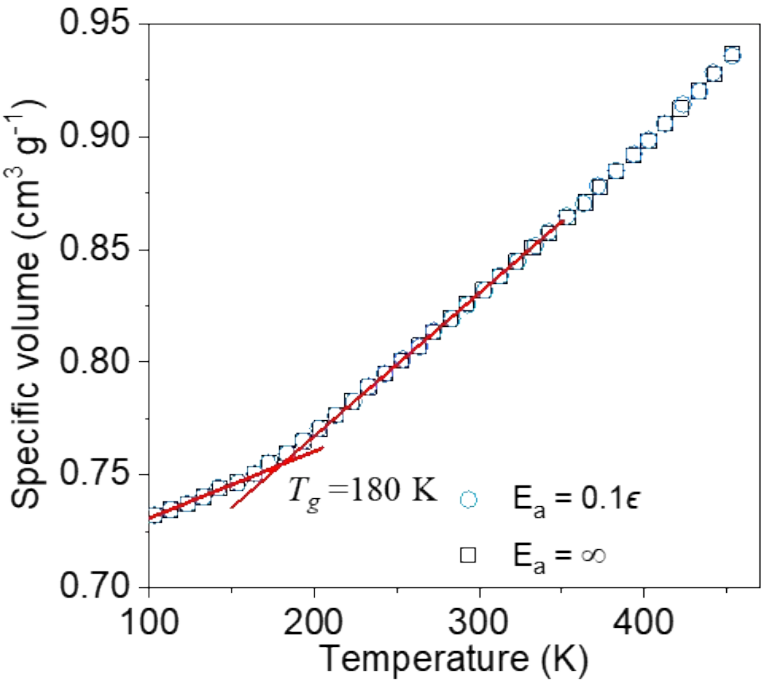

Figure S5. The time-average specific volume of cross-linked PEOs as a function of temperature to determine the glass transition temperature (T_g) by finding the point of intersection of the fitted lines in the rubbery and glassy regions.[3]

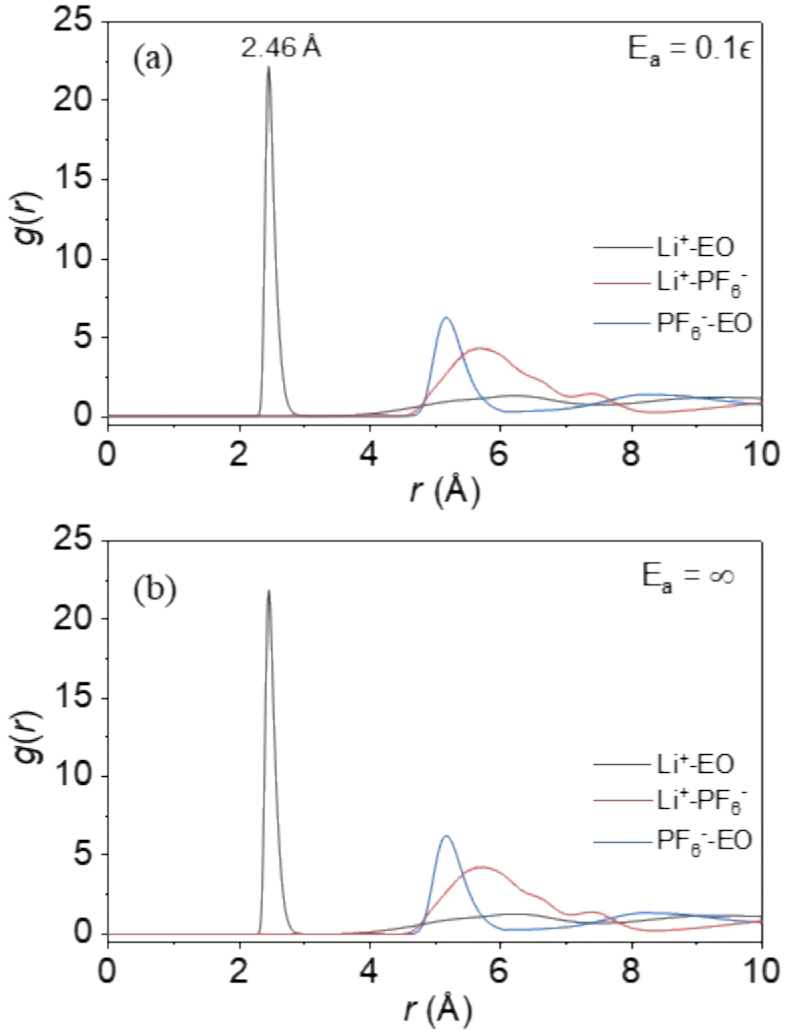

Figure S6. RDFs for cross-linked PEO_{16}-$LiPF_6$ electrolytes.

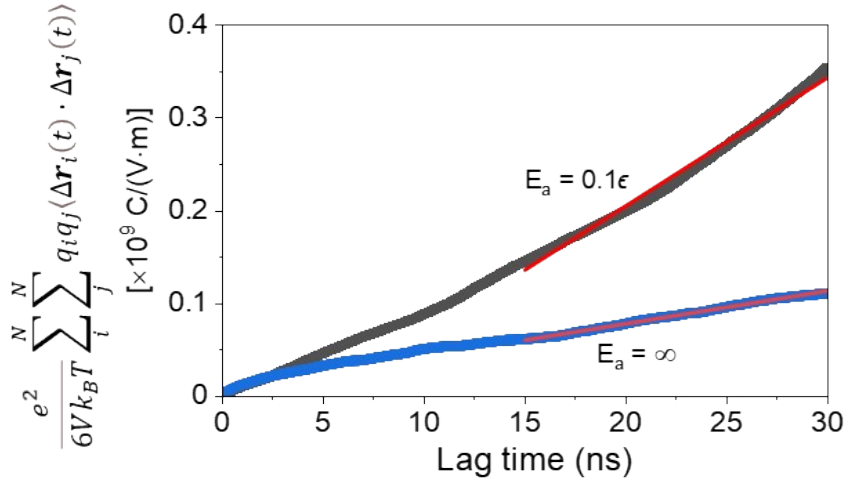

Figure S7. The collective displacement ($\frac{e^2}{6Vk_BT}\sum_i^N\sum_j^N q_iq_j\langle\Delta r_i(t)\cdot\Delta r_j(t)\rangle$) of ions for cross-linked PEO_{16}-$LiPF_6$ electrolytes to calculate ionic conductivity.

References:

[1] E. J. Maginn, R. A. Messerly, D. J. Carlson, D. R. Roe and J. R. Elliot, Living J. Comp. Mol. Sci. **1** (1), 6324 (2018).

[2] O. Borodin and G. D. Smith, J. Phys. Chem. B **113** (6), 1763-1776 (2009).

[3] F. Khabaz and R. Khare, *J. Phys. Chem. B*, **119** (44), 14261-14269 (2015).