Supporting Information

Effect of Polymer Topology on Microstructure, Segmental Dynamics, and Ionic Conductivity in PEO/PMMA Based Solid Polymer Electrolytes

Recep Bakar,[1] Saeid Darvishi,[2] Tianyu Li,[3] Mertcan Han,[4] Umut Aydemir,[5,6] Sedat Nizamoglu,[4,7] Kunlun Hong,[8] Erkan Senses[2*]

[1]*Department of Material Science and Engineering, Koç University, Sariyer, Istanbul 34450, Turkey*

[2]*Department of Chemical and Biological Engineering, Koç University, Sariyer, Istanbul 34450, Turkey*

[3]*Department of Materials Science and Engineering, The University of Tennessee Knoxville, TN 37996, United States*

[4]*Department of Electrical and Electronics Engineering, Koç University, Sariyer, Istanbul 34450, Turkey*

[5]*Department of Chemistry, Koç University, Sariyer, Istanbul 34450, Turkey*

[6]*Koç University Boron and Advanced Materials Application and Research Center, Sariyer, Istanbul 34450, Turkey*

[7]*Department of Biomedical Science and Engineering, Koç University, Istanbul 34450, Turkey*

[8]*Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States*

*Corresponding author: esenses@ku.edu.tr
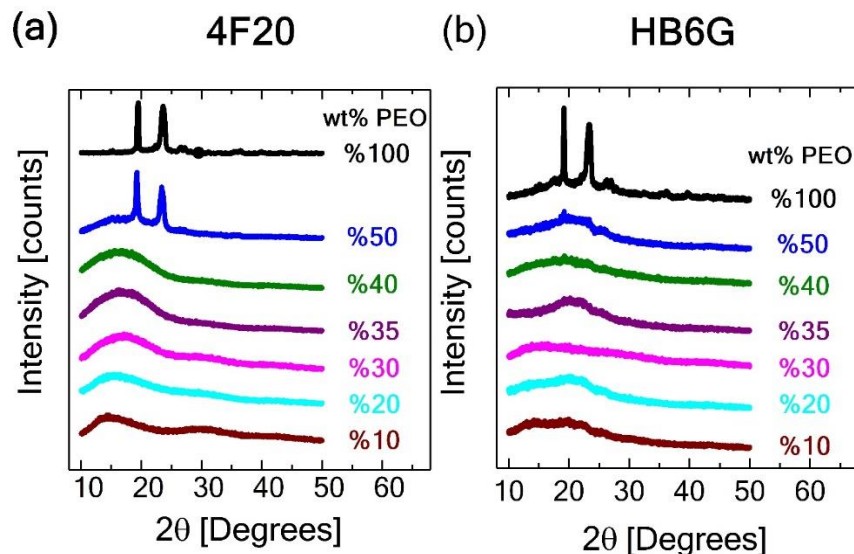
X-ray diffraction Analysis (XRD):

(a) 4F20   (b) HB6G

Figure S1. XRD results for PEO/PMMA blends in different PEO wt% concentrations and with various PEO topologies (a) 4-arms, (b) HB6G.

Calculation of the crystallization (%) in the PEO/PMMA blends

To estimate the degree of neat PEO crystallinity for different polymer structures along with the effect of number of arms and arm molecular weight on the crystallization, we used the following equation $X_c = \left(\frac{\Delta H_m}{\Delta H_c * f_{PEO}}\right) * 100$, where f_{PEO} is the weight fraction of PEO in the polymer blend, ΔH_m is the melting enthalpy of the sample, and ΔH_c is the melting enthalpy of completely crystalline PEO, which is 196.4 J/g.[1]

Table S1. Melting enthalpies and degree of crystallizations of various PEO architectures over different weight fraction of PEO in blends with PMMA.

Sample	wt% of PEO	Melting enthalpy	Crystallinity
		ΔH_m, J/g	X_c, %
L20	100.00	143.74	73.19
	75.00	88.00	44.91
	50.00	55.48	28.25
	40.00	17.67	9.00
	35.00	4.45	2.26
4F20	100.00	125.00	63.65
	75.00	46.26	23.55
	50.00	10.90	5.55
8F20	100.00	120.00	61.10
	75.00	76.00	38.10
	50.00	40.00	20.24
	40.00	0.96	0.49
HB6G	100.00	61.13	31.12
	75.00	37.04	18.86
	50.00	14.73	7.50
	40.00	7.11	3.62
	35.00	2.02	1.03

Modulated differential scanning calorimetry (MDSC)

Table S2. Glass transition temperatures with entire peak widths at half-maximum height

(ΔT_g) for neat PEO with various architectures in the blends with PMMA.

Sample	Neat PEO	
	Tg,eff, K	ΔTg, K
L20	221.76	10.62
4F20	220.49	9.49
8F20	222.69	10.56
HB6G	232.84	13.41
BB	215.68	9.99

Lodge-McLeish Self-concentration Model

T$_g$ for each component in the blend could be also estimated via the effective volume fraction

of each component, ϕ_{eff}, determined by the Eq. 1,[2]

$$\phi_{eff} = \phi_s + (1 + \phi_s)\phi \qquad (S1)$$

where ϕ_s is the self-concentration (volume fraction) of the polymer due to chain connectivity

effects and ϕ is the bulk blend composition. Self-concentration, ϕ_s, is also based on the

appropriate volume surrounding the polymer segment under consideration. Even though it is

usually to be on the order of the Kuhn length cubed (l_k^3), it can be changed by a multiplicative

constant of order unity, as the choice of $V = l_k^3$ is arbitrary.[3] Then the self-concentration, ϕ_s,

is estimated using the Eq. 2,[2]

$$\phi_s = \frac{C_\infty M_0}{k\rho N_{av} V} \qquad (S2)$$

where C_∞ is the characteristic ratio, M_0 is the repeat unit molar mass, N_{av} is the Avogadro number, ρ is the density of the polymer and k is the number of backbone bonds per repeat unit. The model associates the average local concentration of each component with a local glass temperature given by the Eq. 3,[2]

$$T_{g,eff} = T_g(\phi)|_{\phi=\phi_{eff}} \tag{S3}$$

In other words, the effective glass temperature, $T_{g,eff}$, is calculated from the macroscopic $T_g(\phi)$, however, evaluated at ϕ_{eff}. For the macroscopic composition dependence of the glass transition temperature, the well-known Fox equation was used but with the effective concentration, ϕ_{eff}, for each component.
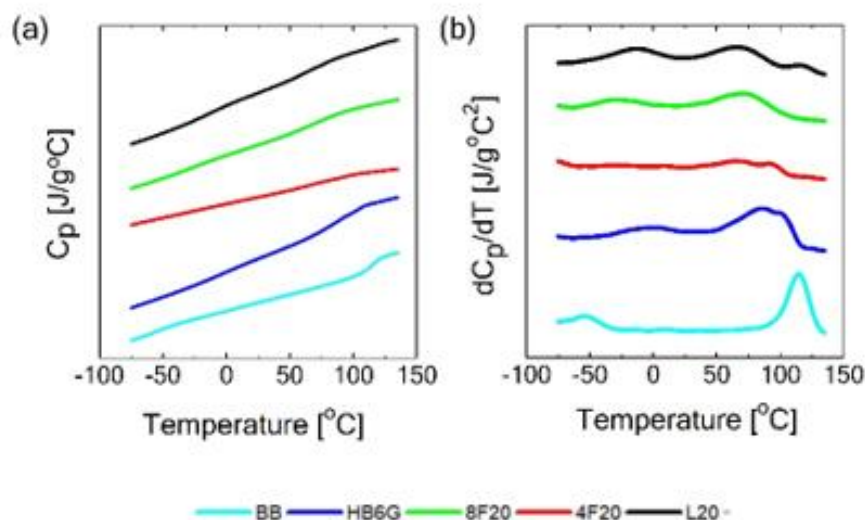

Figure S2. The dependence of the reversible heat flow (a) and its derivative with respect to temperature (b) for PEO/PMMA/LiTFSI based polymer electrolytes with regards to various PEO topologies including linear, 4-arms, 8-arms, hyperbranched and bottle brush.

Electrochemical Impedance Spectroscopy (EIS):

The ionic conductivity (σ) of the PEO/PMMA blend electrolytes was calculated using the

equation S4[4]:

$$\sigma = \frac{l}{R_b A} \tag{S4}$$

where l is the polymer electrolyte thickness, A accounts for the area of the SPE and R_b is the bulk resistance. The bulk resistance was obtained from the complex impedance plot shown by Figure S3 below.
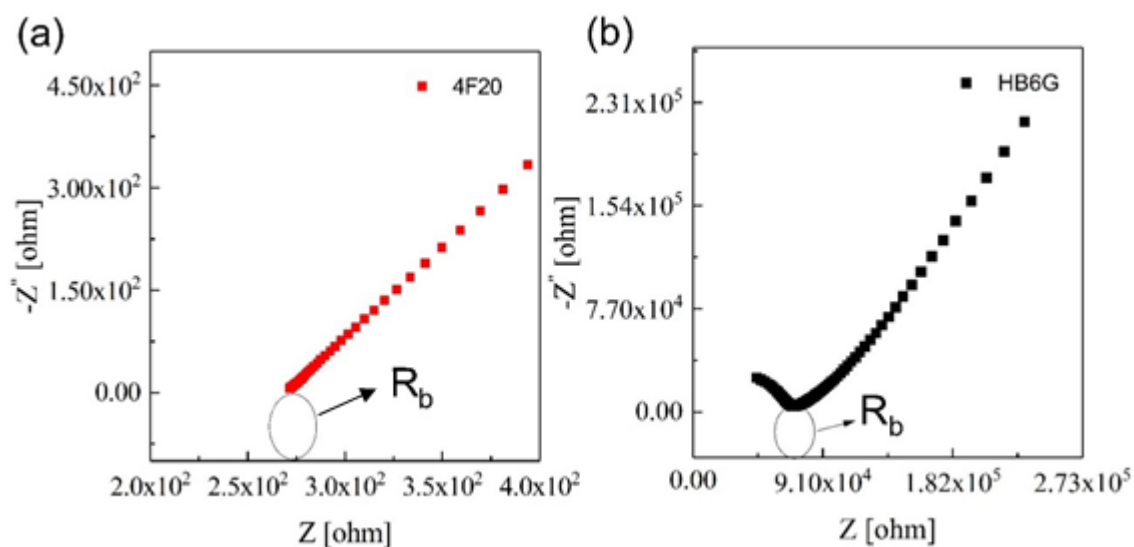

Figure S3. Example of Nyquist plots at 60°C used in the ionic conductivity calculations for the PEO blend electrolytes containing %50 4F20 (a) and HB6G PEO (b)
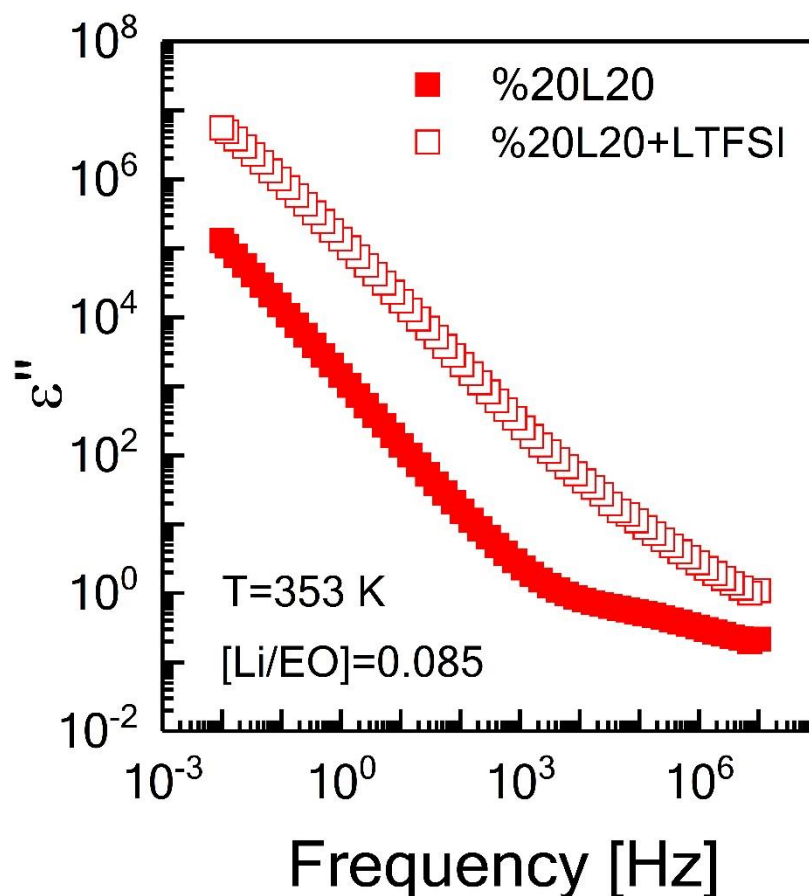
Broadband Dielectric Spectroscopy (BDS):

Figure S4. The frequency dependence of the dielectric loss (ε") data at 353 K for 20wt%

linear PEO/PMMA blend with (open) and without (filled) salt.

<div align="center">

References

</div>

1.   Yap, Y. L.; You, A. H.; Teo, L. L., Preparation and characterization studies of

PMMA–PEO-blend solid polymer electrolytes with SiO2 filler and plasticizer for lithium ion

battery. *Ionics* **2019,** *25* (7), 3087-3098.

2.   Lodge, T. P.; McLeish, T. C. B., Self-Concentrations and Effective Glass Transition

Temperatures in Polymer Blends. *Macromolecules* **2000,** *33* (14), 5278-5284.

3.   He, Y.; Lutz, T. R.; Ediger, M. D., Segmental and terminal dynamics in miscible

polymer mixtures: Tests of the Lodge–McLeish model. *The Journal of Chemical Physics* **2003,** *119* (18), 9956-9965.

4.   Vijayakumar, E.; Subramania, A.; Fei, Z.; Dyson, P. J., High-performance dye-sensitized solar cell based on an electrospun poly(vinylidene fluoride-co-hexafluoropropylene)/cobalt sulfide nanocomposite membrane electrolyte. *RSC Advances* **2015,** *5* (64), 52026-52032.