

**Investigating the Correlation of Segmental Dynamics, Free Volume Characteristics and Ionic Conductivity in Poly(Ethylene Oxide) Based Electrolyte: A Broadband Dielectric and Positron Annihilation Spectroscopy Study**

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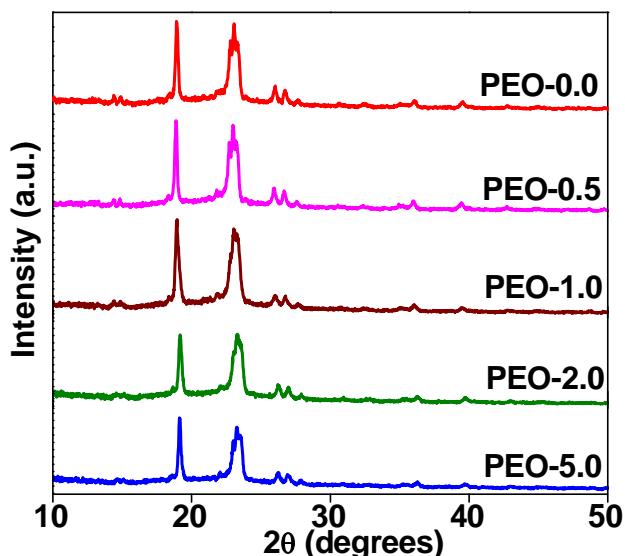
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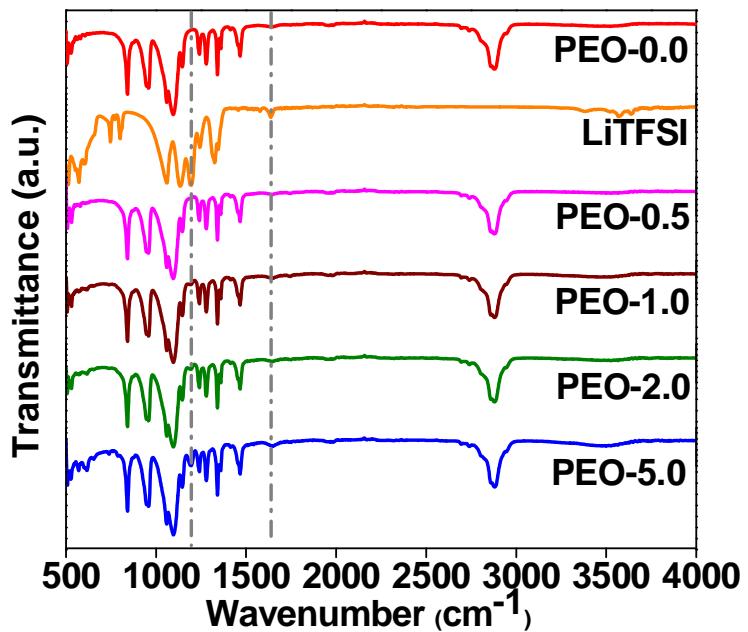
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**1. X-ray diffraction measurement of PEO- $x$ LiTFSI electrolytes:**



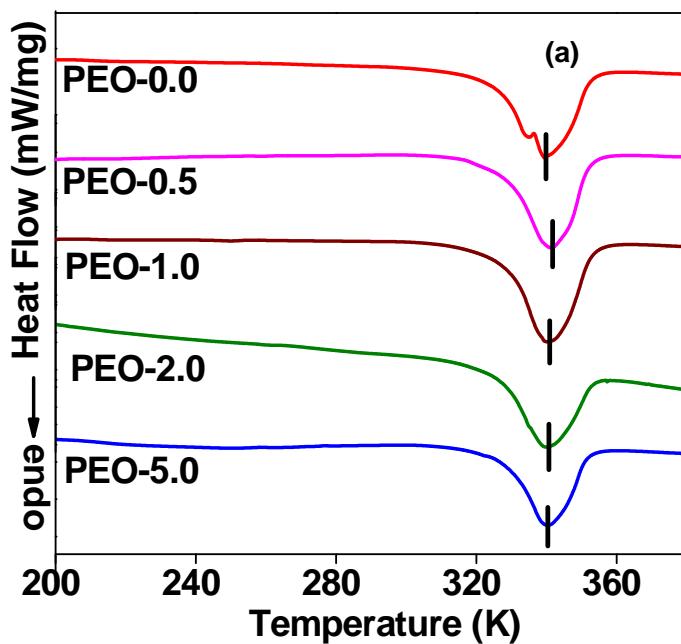
**Figure S1:** XRD patterns of pristine PEO and PEO-LiTFSI electrolytes.

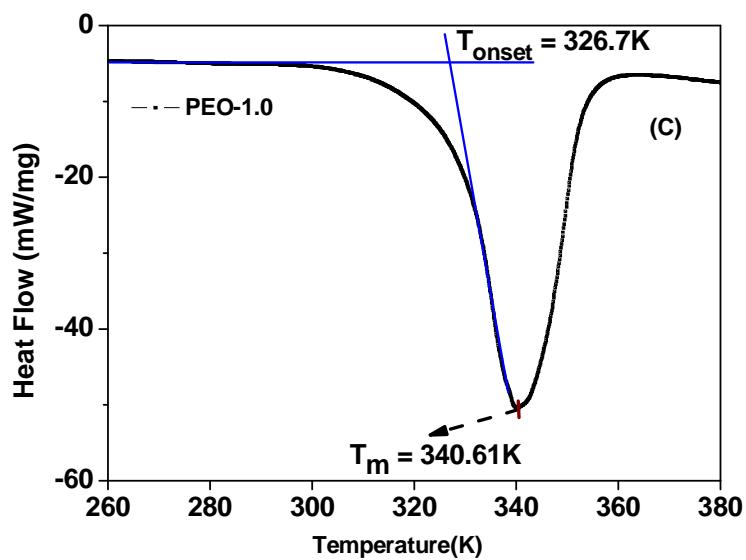
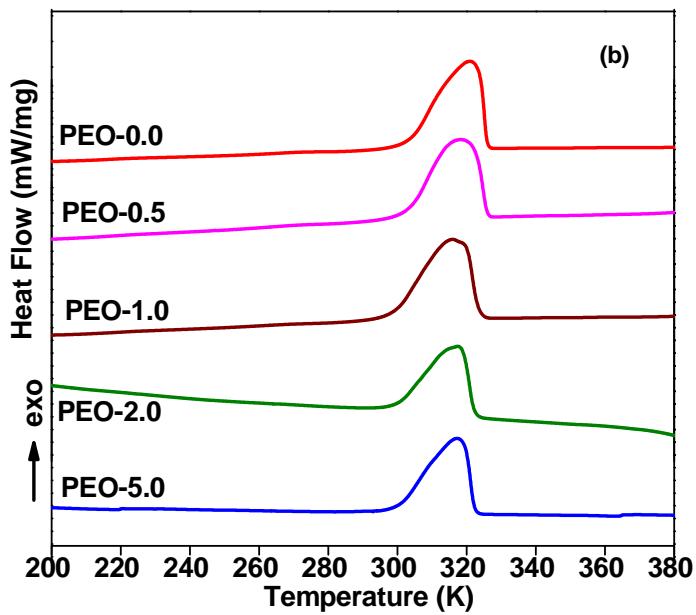
**2. FTIR spectra of PEO-LiTFSI electrolytes:**



**Figure S2:** FTIR spectra of pristine PEO and PEO-LiTFSI electrolytes. Vertical dotted lines show the peaks corresponding to salt in the electrolytes.

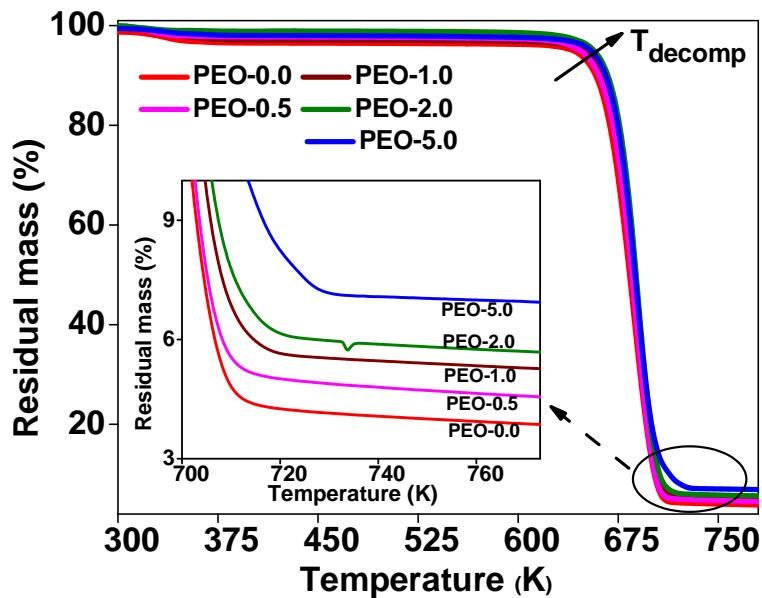
**3. Differential Scanning Calorimetry (DSC) measurements of PEO-LiTFSI electrolytes:**





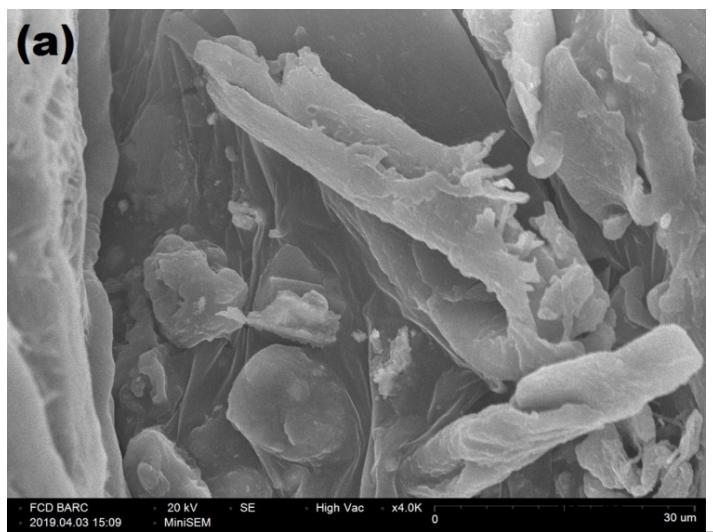
**Figure S3:** (a) DSC thermograms from the heating cycles of pristine PEO and PEO-LiTFSI electrolytes. Small vertical bars denote melting temperature of the PEO crystallites. (b) DSC thermograms (cooling cycle) of pristine PEO and PEO-LiTFSI electrolytes. (c) Onset of melting for PEO-1.0 as intersection of baseline with tangent drawn from point of highest slope. Melting temperature taken as endothermic peak minima as shown.

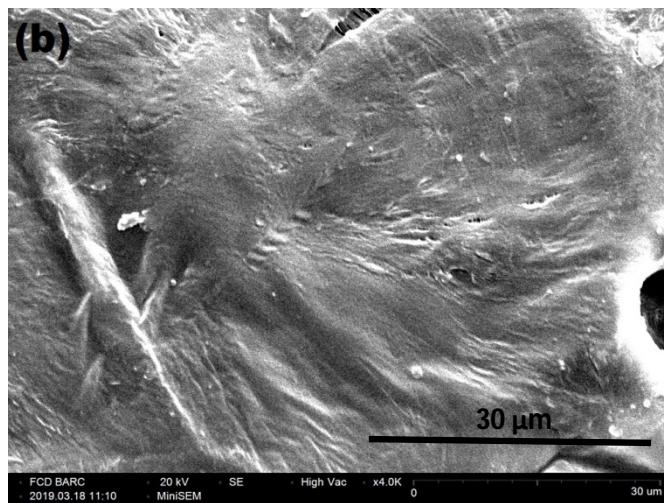
#### 4. Thermal Gravimetric Analysis (TGA) measurements:



**Figure S4:** TGA curve of PEO-LiTFSI electrolytes. Inset shows the enlarged view from the high temperature region.

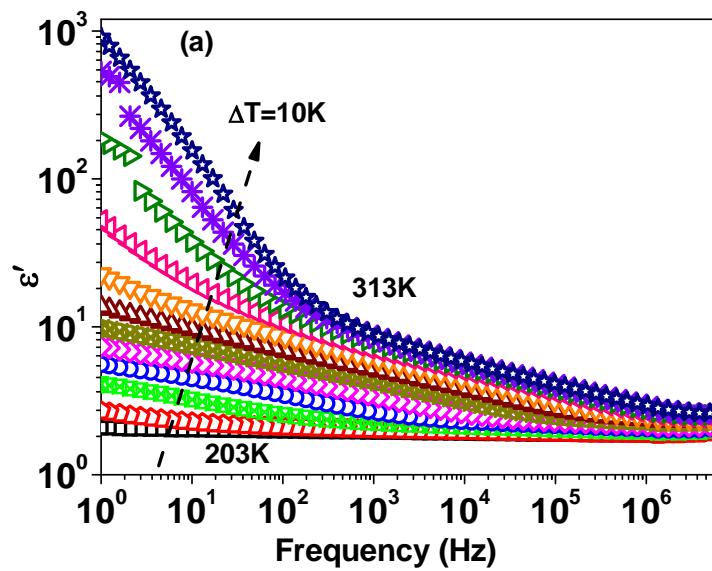
#### 5. Characterization by Scanning Electron Microscopy (SEM)

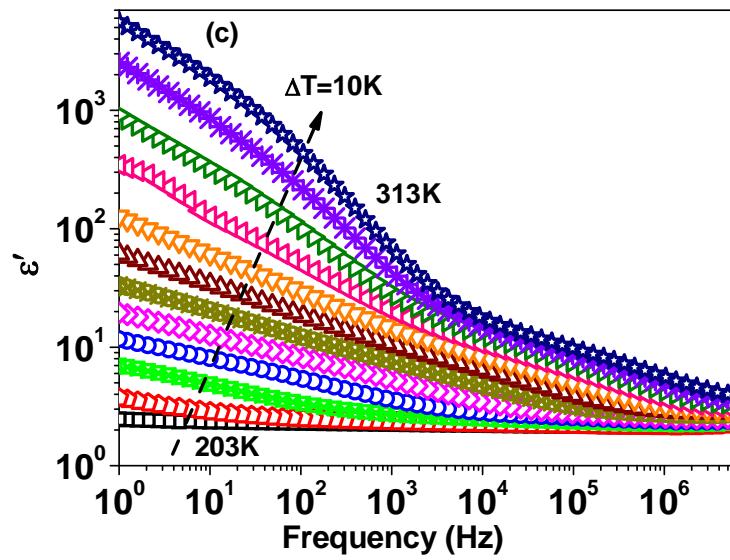
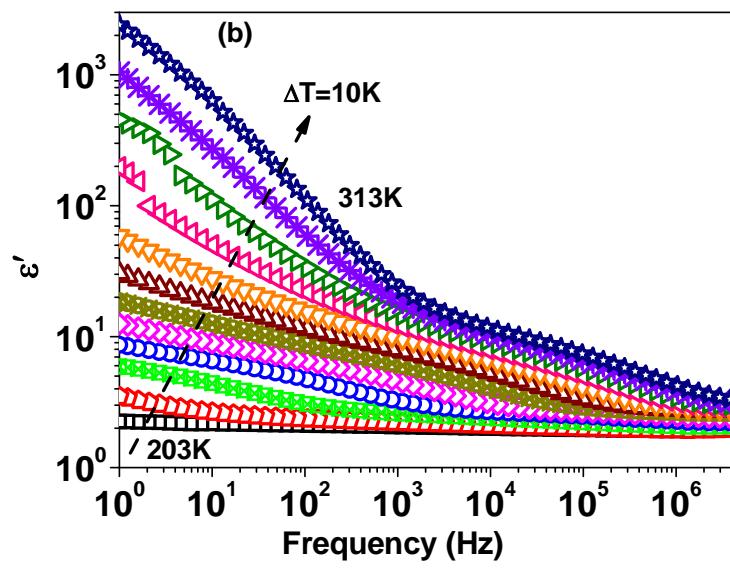


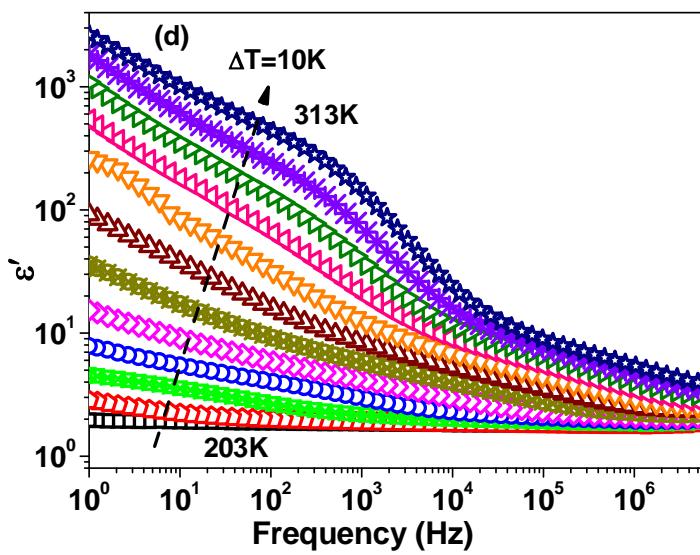


**Figure S5:** Scanning Electron Microscope (SEM) images of fractured surface of (a) pristine PEO and (b) PEO-5.0

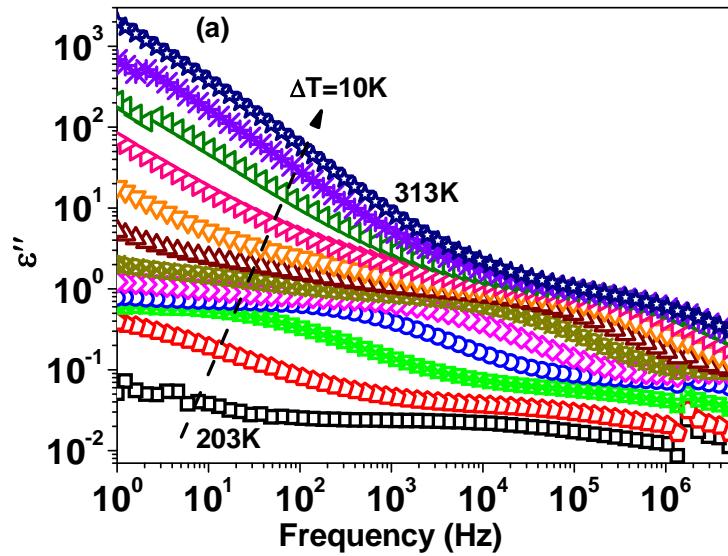
## 6. Broadband Dielectric Spectroscopy (BDS)

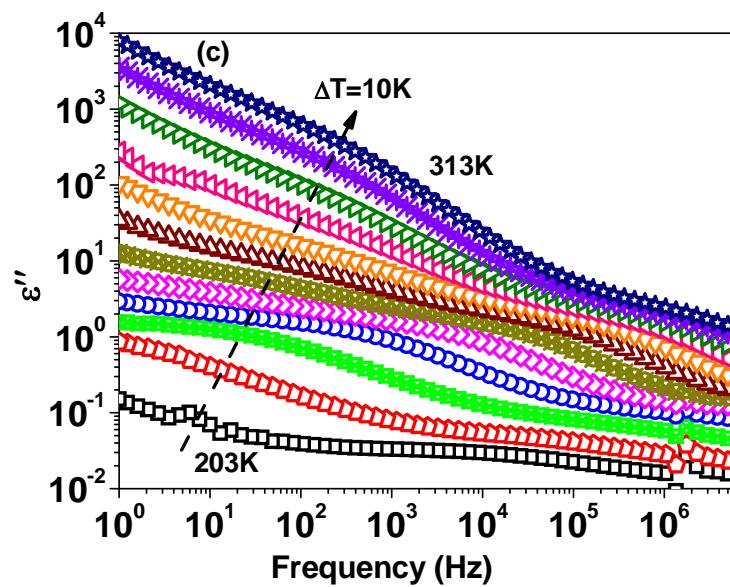
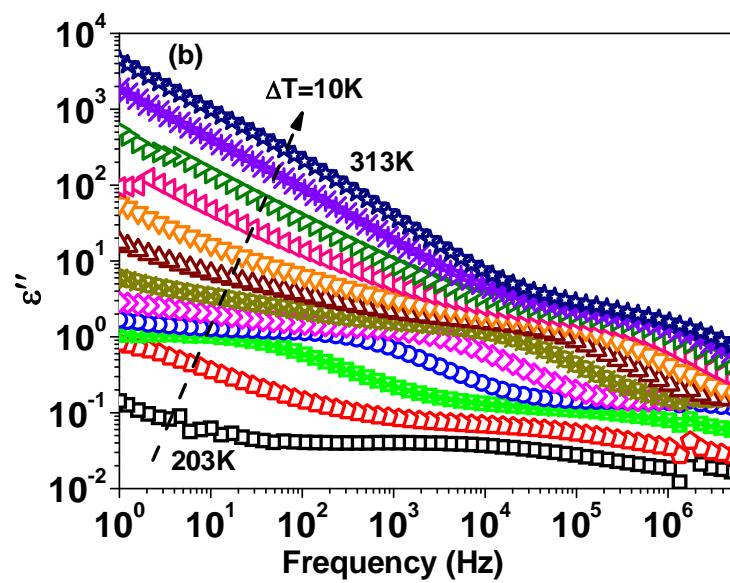


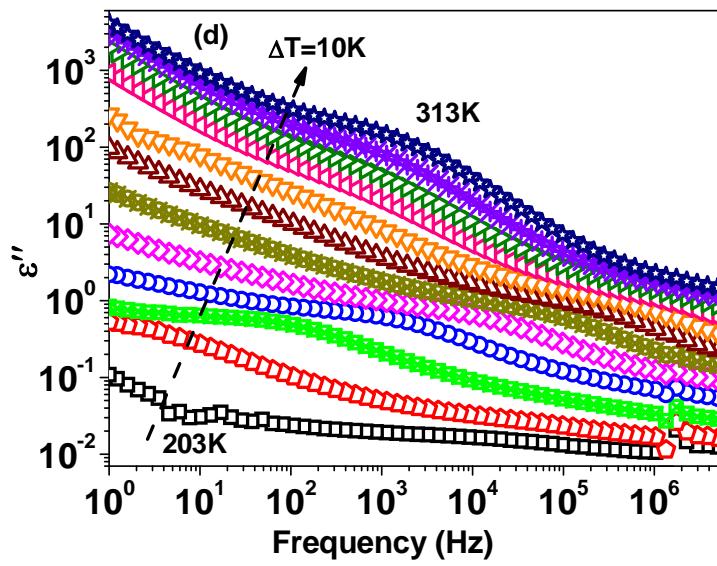




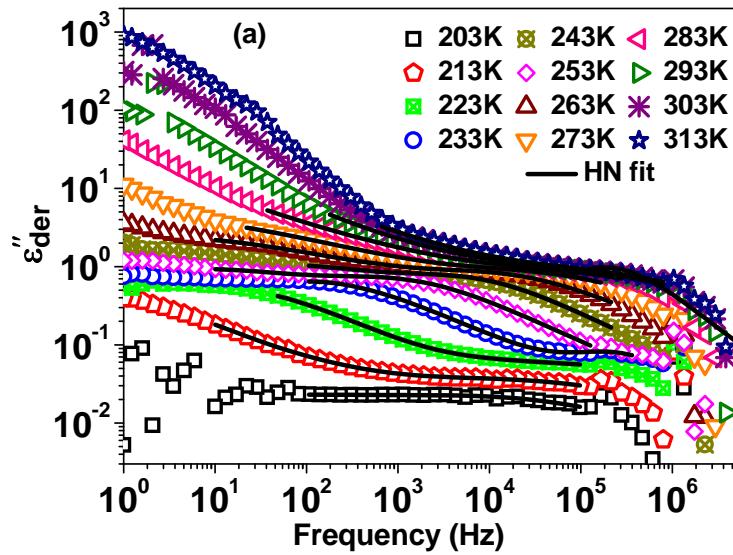
**Figure S6:** Real part( $\epsilon'$ ) of the complex permittivity of (a) PEO-0.0 (b) PEO-0.5 (c) PEO-2.0 (d) PEO-5.0 electrolytes.

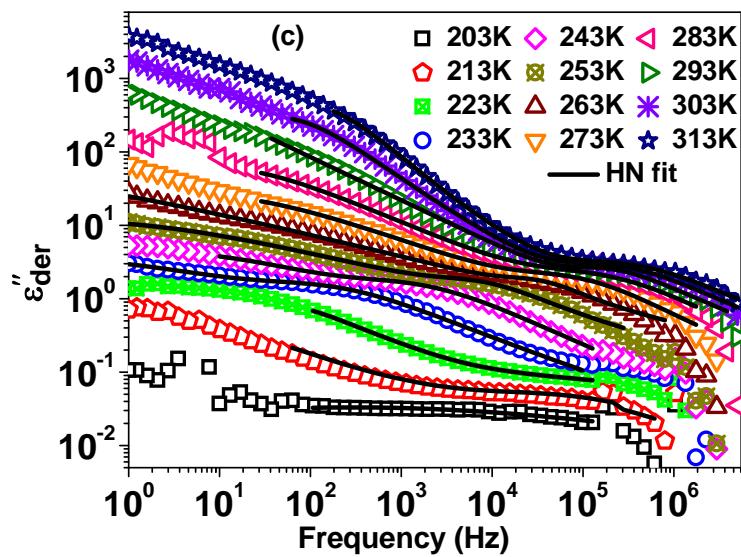
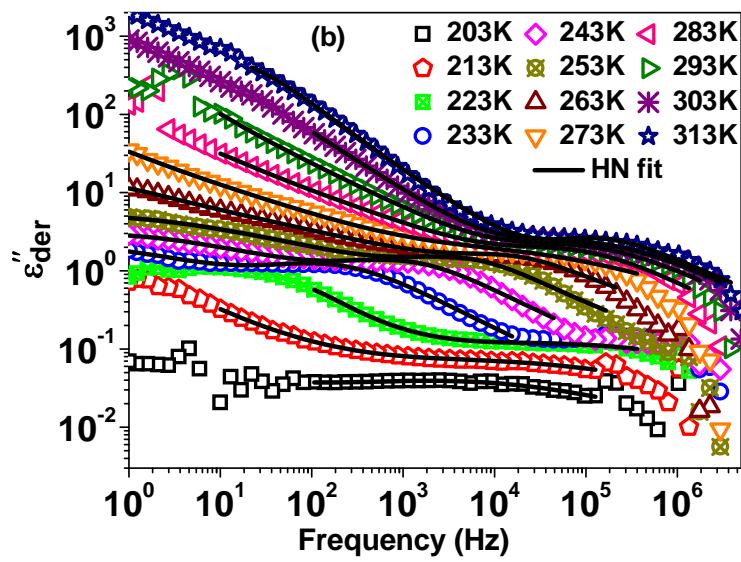


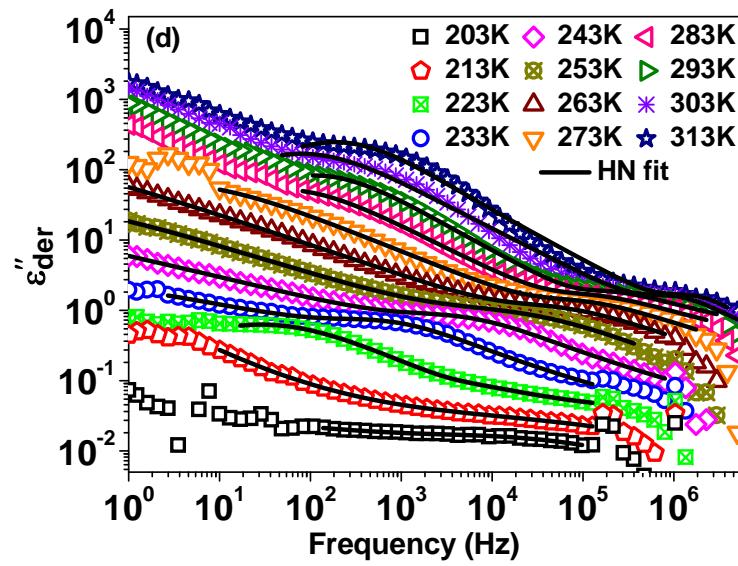




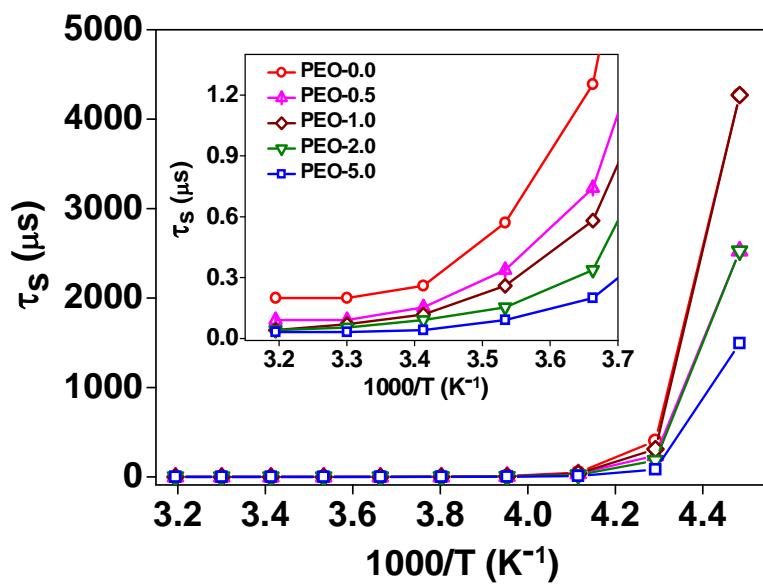
**Figure S7:** Imaginary part( $\epsilon''$ ) of the complex permittivity of (a) PEO-0.0 (b) PEO-0.5 (c) PEO-2.0 (d) PEO-5.0 electrolytes.



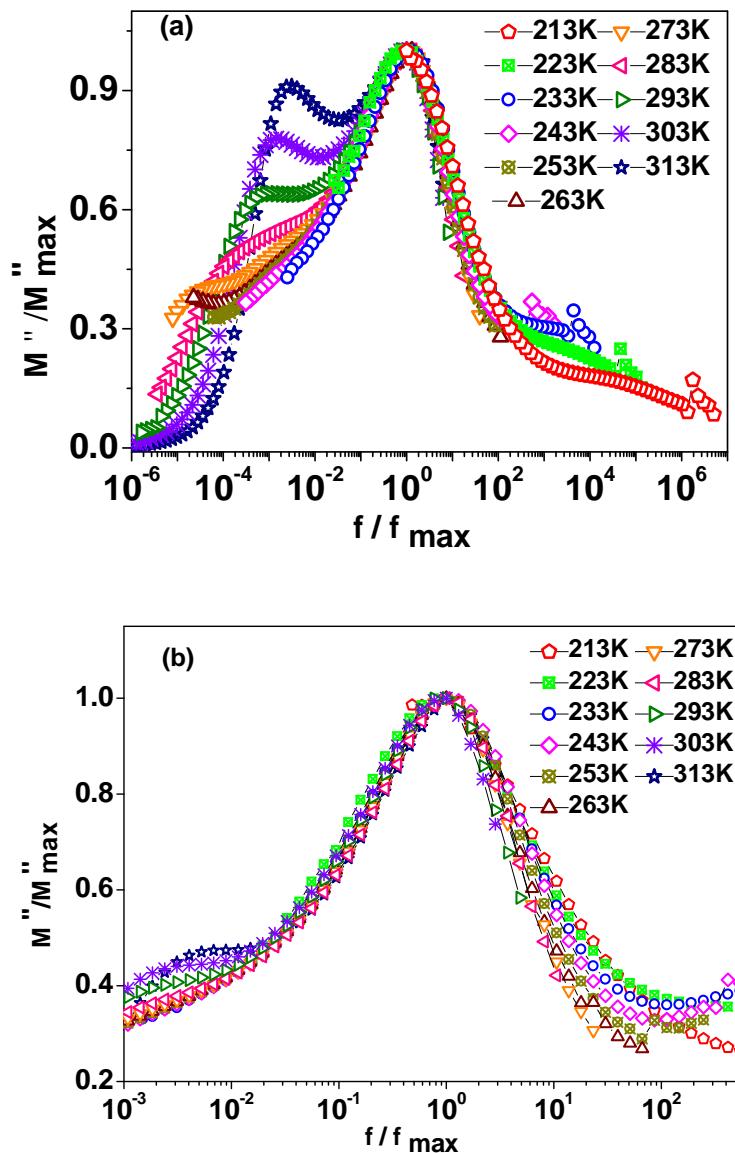


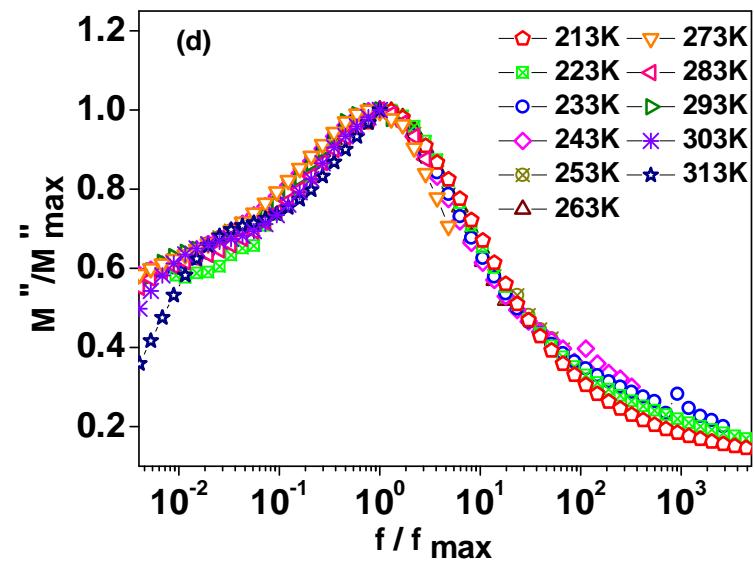
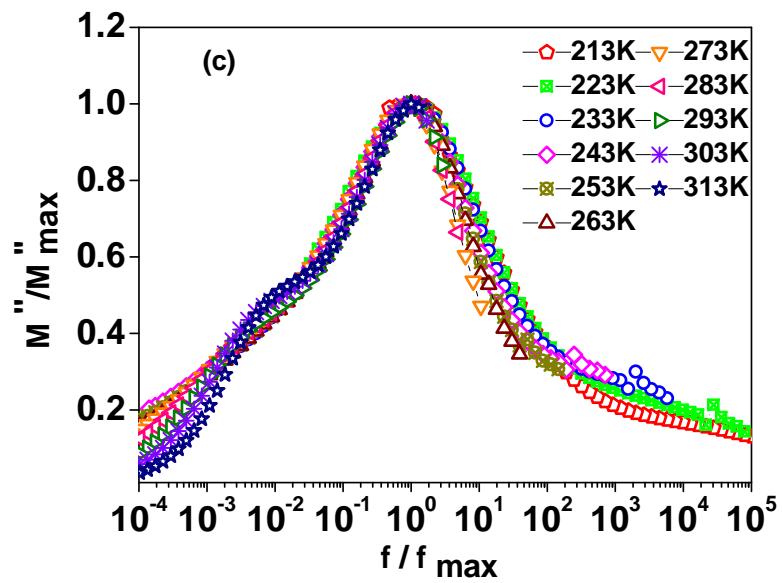


**Figure S8:** dc conduction free dielectric permittivity of (a) PEO-0.0 (b) PEO-0.5 (c) PEO-2.0 (d) PEO-5.0 electrolytes

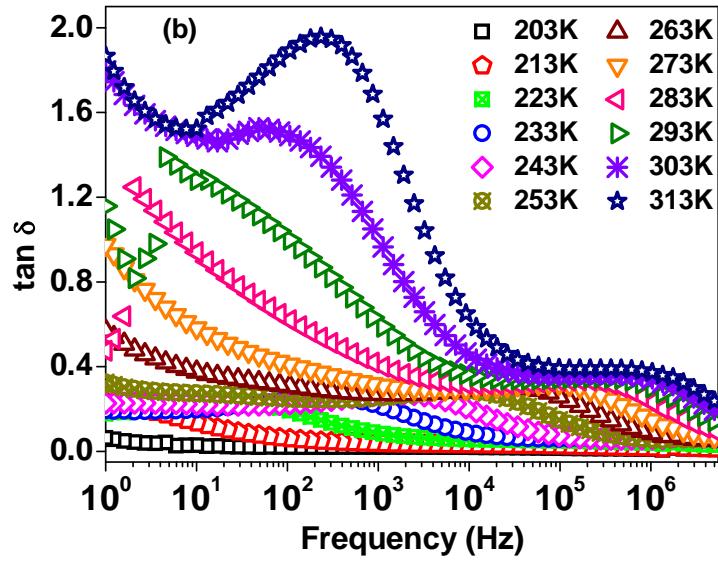
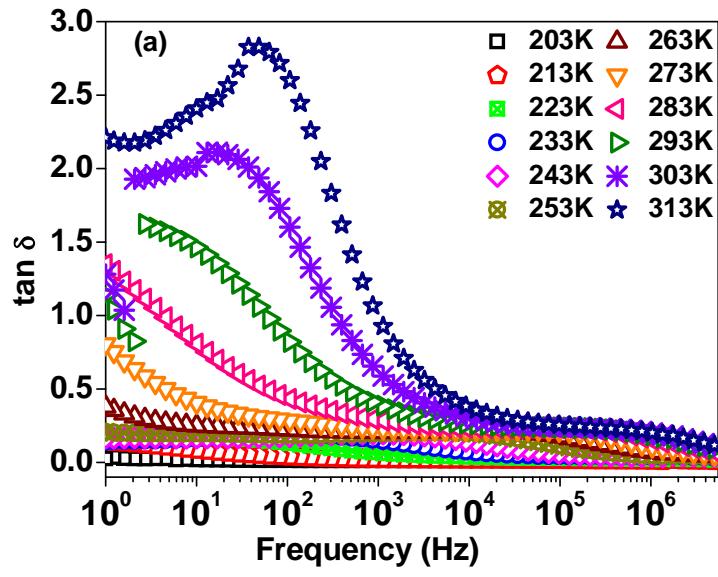


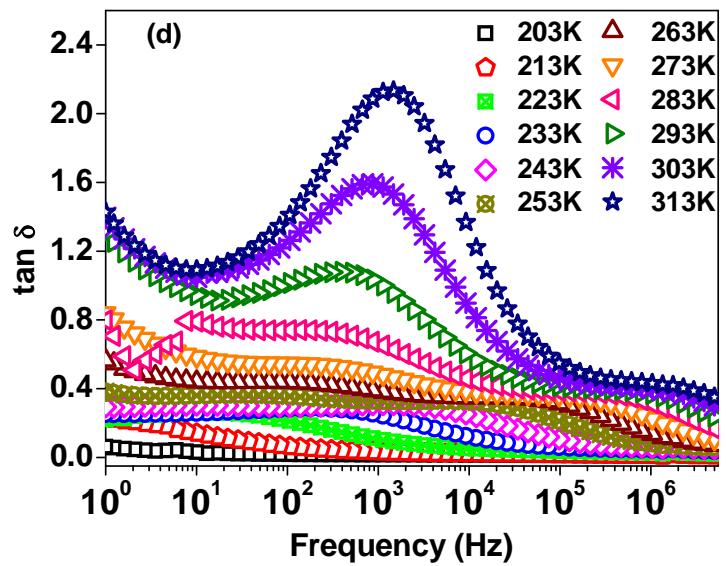
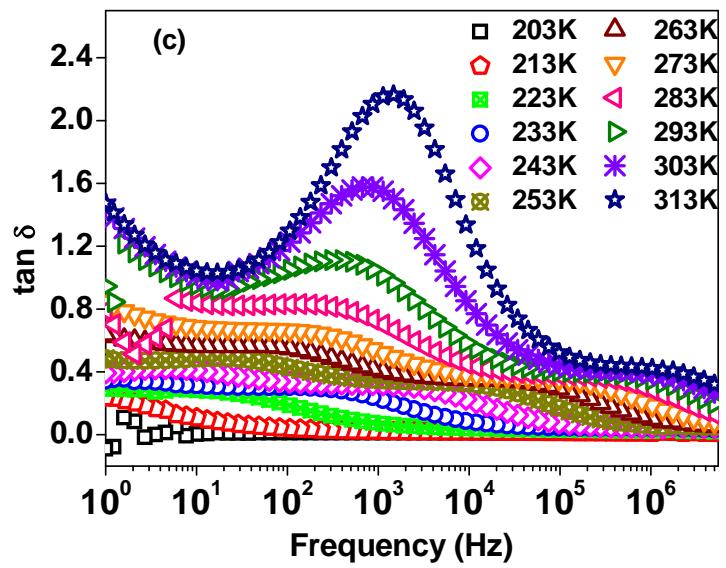
**Figure S9:** Segmental relaxation times with temperature in PEO-LiTFSI electrolytes. Inset shows the variation in relaxation time in higher temperature region.

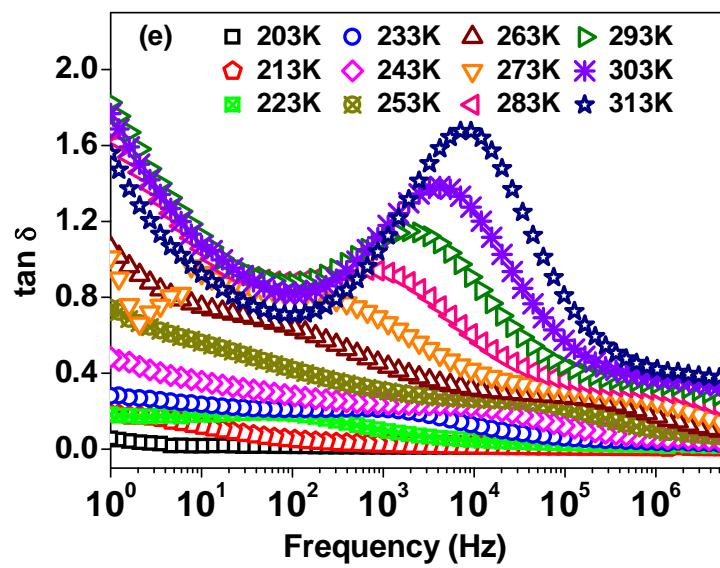




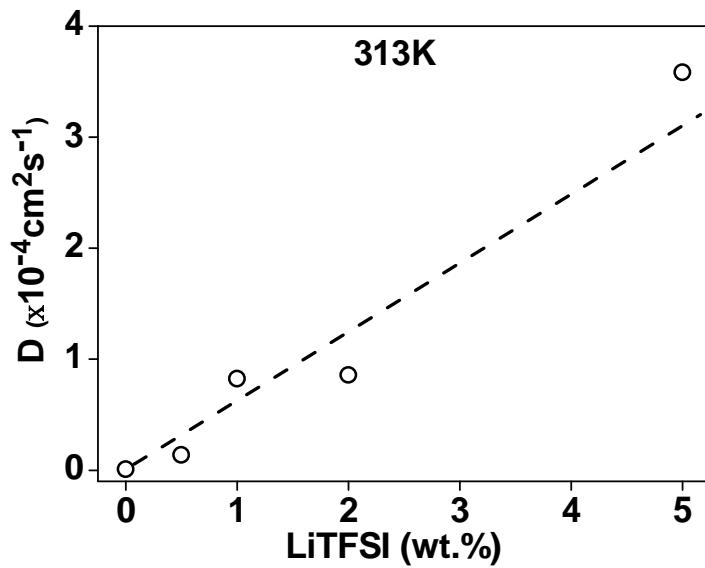
**Figure S10:** Master curve by maxima normalization technique (a) PEO-0.0 (b) PEO-0.5 (c) PEO-2.0 (d) PEO-5.0 electrolytes. Master curve could not be formed for pure PEO through maxima normalization technique.







**Figure S11:** Loss tangent spectrum of (a) PEO-0.0 (b) PEO-0.5 (c) PEO-1.0 (d) PEO-2.0 (e) PEO-5.0 electrolytes.



**Figure S12:** Ion diffusivity,  $D$  ( $\text{cm}^2 \text{s}^{-1}$ ) of the electrolytes at 313K. The dashed line is the eye guide.