

Vibrational and Impedance Spectroscopic Analysis of Semi- Interpenetrating Polymer Networks as Solid Polymer Electrolytes

(Supporting Information)

Nimai Bar, Pratyay Basak and Yoed Tsur**

* Corresponding author Yoed Tsur, Associate Professor, Wolfson faculty of Chemical Engineering, *Technion*-Israel Institute of Technology, Haifa, 3200003, Israel, Email: tsur@technion.ac.il

*Corresponding author Pratyay Basak, Senior Scientist & Assistant Professor, Nanomaterials Laboratory, Inorganic & Physical Chemistry Division, Council of Scientific and Industrial Research-Indian Institute of Chemical Technology (CSIR-IICT), Hyderabad, 500 007, India, Phone: +91-40-27193225, Fax: +91-2716-0921. Email: pratyay@iict.res.in

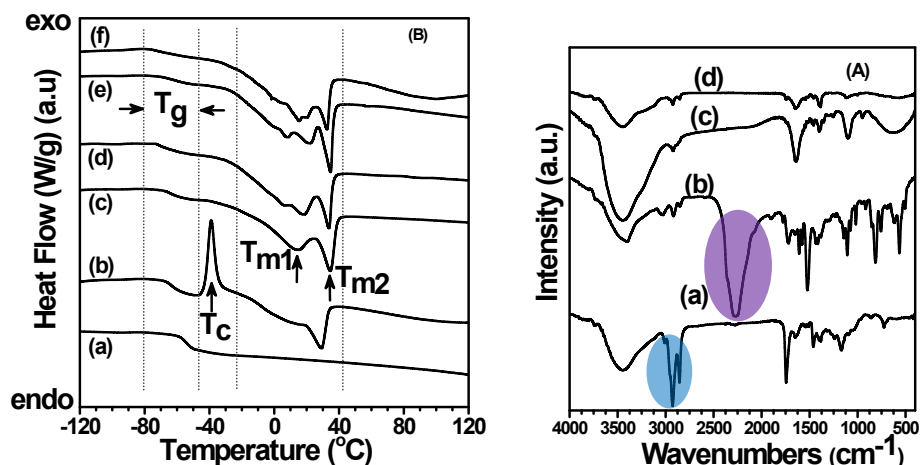


Figure SI-1: Right: the *mid*-FTIR stack plots of (a) pure castor oil (CO), (b) 4-4 diphenylmethane diisocyanate (MDI), (c) polyethylene glycol (d) PEO-PU network. The blue colored circle disappeared and violet colored circle appeared after oven curing at 80 °C for 48 hours. **Left:** typical DSC thermograms for the PEO-PU/PEGDME semi-IPN matrices with LiClO₄ as the electrolyte: (a) EO/Li=10, (b) EO/Li=20, (c) EO/Li=30, (d) EO/Li=60, (e) EO/Li=80 and (f) EO/Li=100, data from *J. Phys. Chem. C* **2014**, *118*, 159–174.

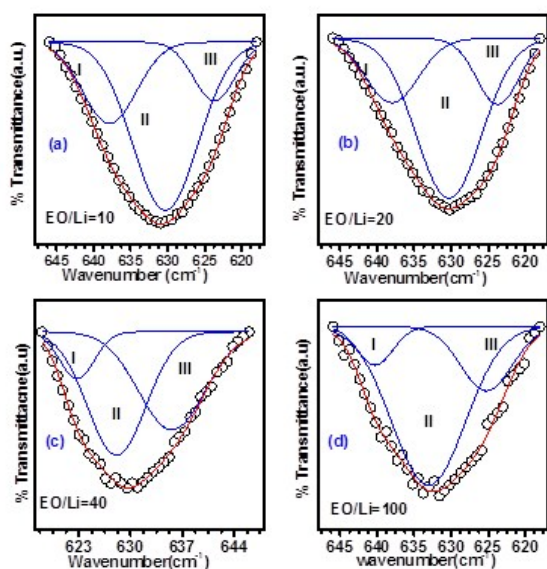


Figure-SI-2: Deconvolution FT-IR spectra in perchlorate anion ($-\text{ClO}_4^-$) stretching zone of the semi-IPN solid polymer electrolytes matrix containing different salt concentrations (EO/Li= 10, 20, 40 and 100).

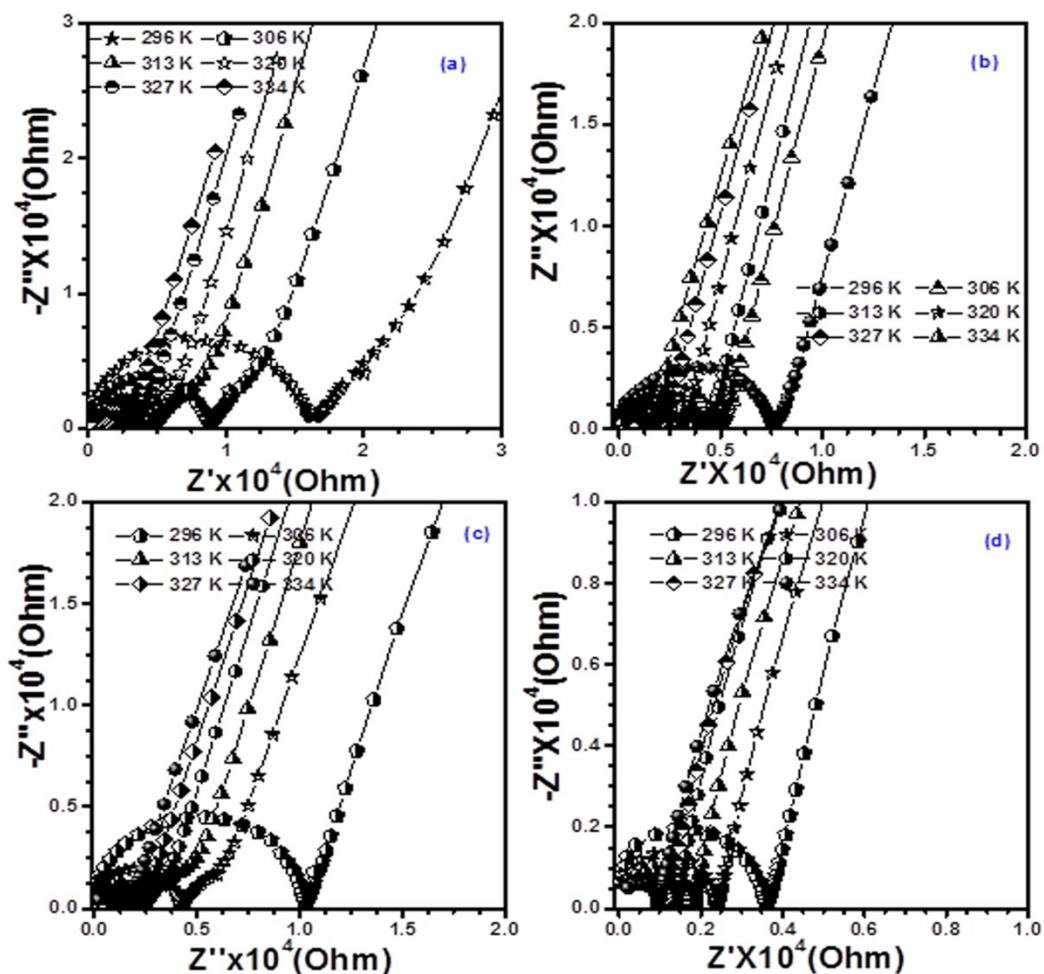


Figure-SI-3: Nyquist plots at different temperature of the solid polymer electrolytes at various temperatures. (a) PEO-PU/PEGDME: LiClO₄ (60/40). (b) PEO-PU/PEGDME: LiClO₄ (50/50) at EO/Li ratio 30. (c) PEO-PU/PEGDME: LiClO₄ (40/60) at EO/Li ratio 30. (d) PEO-PU/PEGDME: LiClO₄ (30/70) at EO/Li ratio 30.

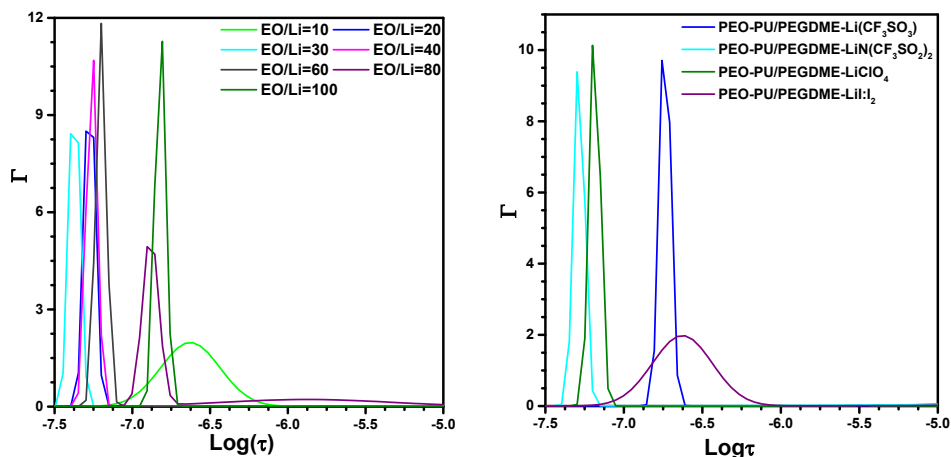


Figure-SI-4: DFRT plots for: (a) polymer electrolytes loaded with various concentrations of lithium perchlorate (LiClO_4) salt. (b) polymer electrolytes incorporated with different anion containing lithium salts

Table-SI-1: the ionic conductivity (σ), glass transition temperature (T_g), percentage of crystallinity ($\% \chi$), free and contact ions pairs for the solid polymer electrolytes composed of many salt concentrations; 10, 20, 30, 40, 60, 80, and 100.

Sample name EO/Li	Conductivity (σ) $\times 10^{-3}$ (S/cm)	Glass Transition Temperature(T_g)	% Crystallinity (χ)	Free ion 623 cm^{-1}	Ion pairs 632 cm^{-1}
10	0.06	-54	--	13	62
20	0.3	-63.6	14.7	37	63
30	0.43	-65	24.1	43	57
40	0.2	-68.2	32.3	38	62
60	0.12	-69.2	33.1	28	72
80	0.09	-70.1	34.6	30	70
100	0.07	-71.8	35.2	20	71

Ionic conductivity (σ), glass transition temperature (T_g) and percentage of crystallinity ($\% \chi$) data from *J. Phys. Chem. C* **2014**, *118*, 159–174.

Table-SI-2: FT-IR - deconvolution in the ether stretching regime (1180-1000 cm^{-1}), peak positions and individual peak areas for the semi-IPN matrix burdened with different salt concentration.

Sample	Individual peak positions (cm^{-1}) and peak areas (%)								
EO/Li	1025	1035	1074	1094	1106	1118	1136	1148	1162
10	0.83	7.13	13.14	12.35	1.11	45.46	3.84	15.68	0.43
20	1.29	3.58	6.14	14.97	2.52	49.10	7.6	11.49	3.27
30	1.23	5.26	7.17	33.10	1.61	14.37	26.7	11.34	0.43
40	1.41	4.30	17.39	7.85	8.61	34.36	14.04	11.12	0.54
60	1.41	4.47	18.52	7.85	9.31	34.67	10.03	13.12	0.58
80	1.53	5.15	16.11	15.80	21.58	28.39	9.21	1.93	0.29
100	1.12	3.72	8.97	12.42	23.72	35.63	8.82	8.66	0.095

Table-SI-3. FT-IR - deconvolution in the carbonyl stretching zones (1760-1560 cm^{-1}) peak positions and individual peak areas for the semi-IPN matrix loaded with different salt concentrations.

Sample	Individual peak positions (cm^{-1}) with peak areas (%)									
EO/Li	1581	1590	1601	1621	1640	1659	1679	1706	1726	1750
10	0.78	2.64	9.14	19.36	19.56	14.07	17.87	4.42	7.49	4.64
20	0.72	2.99	8.08	23.56	23.12	15.22	13.35	7.21	4.02	1.69
30	0.80	3.07	7.89	32.34	23.62	11.09	11.10	7.67	3.60	1.17
40	0.43	1.86	5.97	15.45	25.56	6.91	22.7	10.76	6.26	4.09
60	0.79	4.48	9.21	15.23	17.39	9.43	14.1	8.73	12.93	7.66
80	0.52	2.31	6.79	12.52	12.57	9.79	24.49	15.62	10.32	5.06
100	0.39	2.46	7.62	18.95	17.06	21.15	11.17	11.67	6.37	3.34

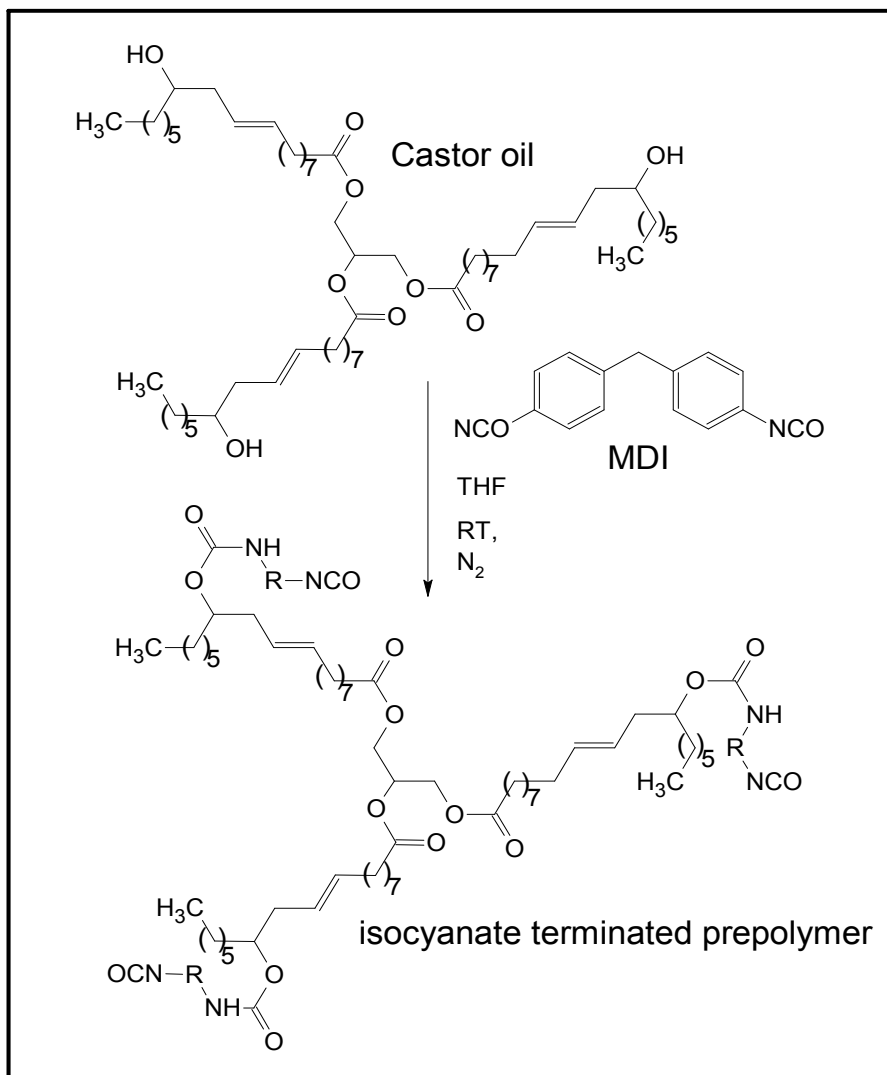
Table-SI-4: EIS analyzed by ISGP – the HF peak position, normalized area and resistance for the PEO-PU/PEGDME semi-IPN solid polymer electrolyte matrix loaded with different salt concentrations, different Li-salts and polymeric compositions.

Sample name	EO/Li	$\log\tau$	A	$R_p(\Omega)$	$R_b=A*R_p(\Omega)$
PEO-PU/PEGDME(60/40): LiClO ₄	30	-5.8584	0.9371	17529	16426
PEO-PU/PEGDME(50/50): LiClO ₄	30	-5.956	0.9772	7639	7464
PEO-PU/PEGDME(40/60): LiClO ₄	30	-6.4173	0.9599	6355	6100
PEO-PU/PEGDME(30/70): LiClO ₄	30	-7.3727	0.9330	583	543
PEO-PU/PEGDME(30/70): LiI ₂	10	-6.4854	0.9445	3534	3337
PEO-PU/PEGDME(30/70): LiN(CF ₃ SO ₂) ₂	10	-6.7378	0.9792	2346	2297
PEO-PU/PEGDME(30/70): Li(CF ₃ SO ₃)	10	-6.5847	0.9363	2680	2623
PEO-PU/PEGDME(30/70): LiClO ₄	10	-6.6274	0.9749	2880	2819
PEO-PU/PEGDME(30/70): LiClO ₄	20	-7.2726	0.9276	771	715
PEO-PU/PEGDME(30/70): LiClO ₄	30	-7.3727	0.9630	583	561
PEO-PU/PEGDME(30/70): LiClO ₄	40	-7.2605	0.9592	893	856
PEO-PU/PEGDME(30/70): LiClO ₄	60	-7.2014	0.9905	976	966
PEO-PU/PEGDME(30/70): LiClO ₄	80	-7.0822	0.9475	1224	1159
PEO-PU/PEGDME(30/70): LiClO ₄	100	-6.9234	1.0302	1746	1798

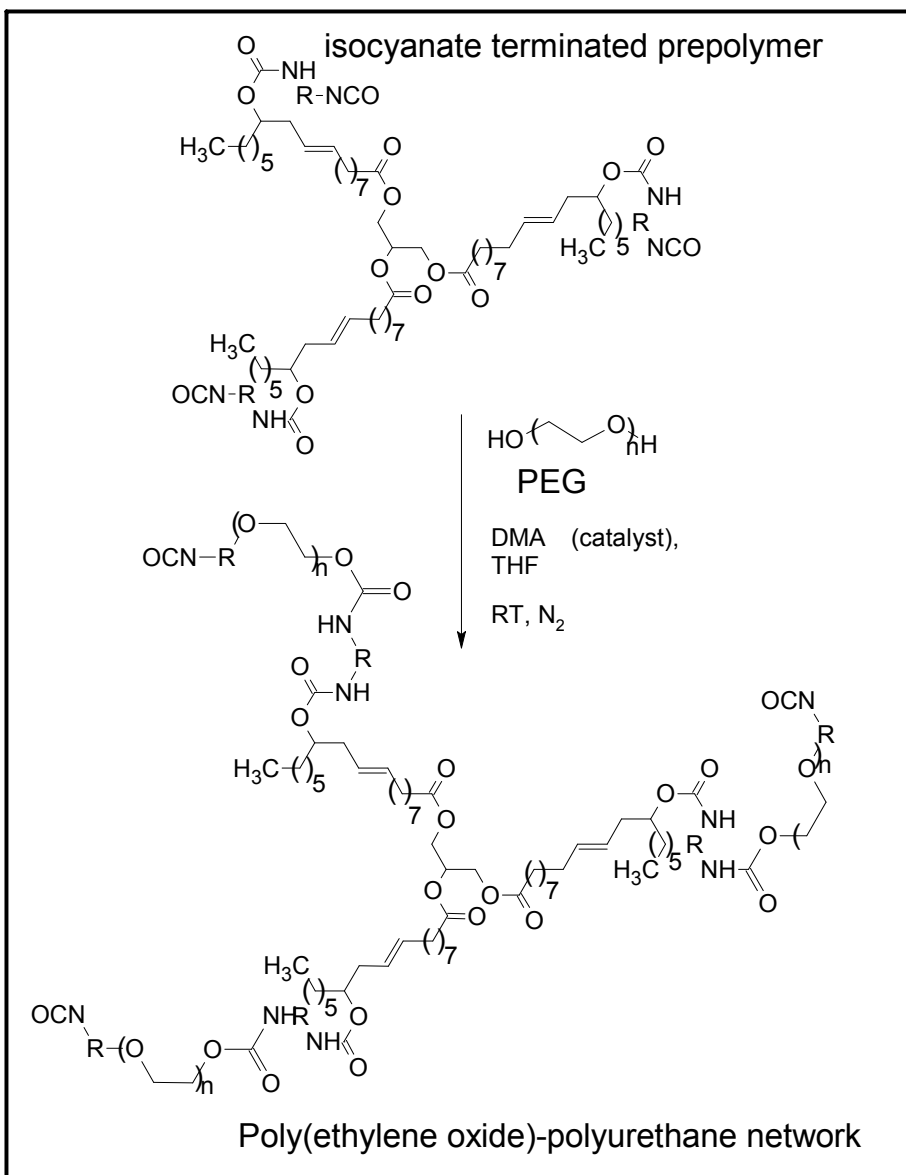
Table-SI-5: ISGP results of semi-IPN solid polymer electrolytes and parameters from ISGP; relaxation time ($\log\tau$), peak area (A) and resistance (R) values are summarized at various temperatures and compositions of the SPEs.

Sample Name	T(K)	Log τ	A	$R_p(\Omega)$	$R=A*R_p(\Omega)$
PEO-PU/PEGDME(60/40)-LiClO ₄	296	-5.8584	0.9371	17529	16426
	306	-6.0917	0.9507	9666	9189
	313	-6.2989	0.9719	4689	4557
	320	-6.4771	0.9754	3415	3330
	327	-6.6636	0.9617	2176	2092
	334	-6.8161	0.9227	1621	1495
PEO-PU/PEGDME(50/50)-LiClO ₄	296	-5.956	0.9772	7639	7464
	306	-6.1874	0.9660	4867	4701
	313	-6.391	0.9764	4061	3965
	320	-6.5428	0.9829	2927	2876
	327	-6.6999	0.9793	2109	2065
	334	-6.849	0.9793	1551	1518
PEO-PU/PEGDME(40/60)-LiClO ₄	296	-6.4173	0.9599	6355	6100
	306	-6.6224	0.9588	3690	3537
	313	-6.8067	0.9715	1982	1925
	320	-6.9458	1.0165	1446	1460
	327	-7.0861	0.9242	1085	1002
	334	-7.2027	0.9822	827	812

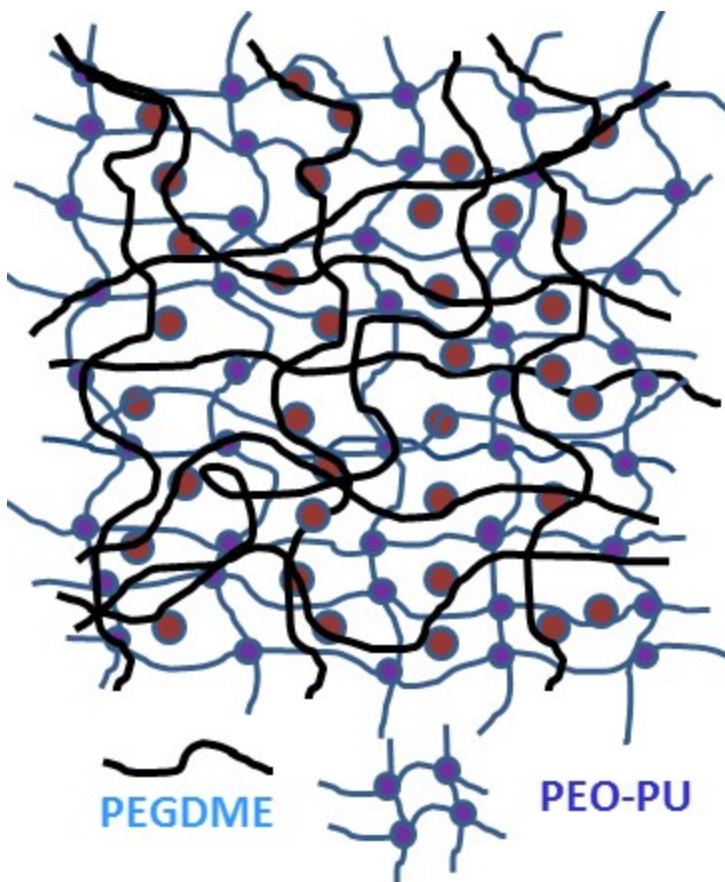
Synthetic scheme for the semi-IPN electrolytes



Scheme 1. Reaction of castor oil and diphenylmethane-4-4'-diisocyanate to give an isocyanate-terminated prepolymer network in the first step of the reaction.



Scheme 2. Reaction of isocyanate-terminated prepolymer with poly(ethylene glycol) to form poly(ethylene glycol)-polyurethane networks



Scheme 3. A schematic representation of Li-ion solvation in PEO-PU/PEGDME solid polymer electrolytes matrix.