Dynamic gelified polymer electrolytes for electrochemical storage

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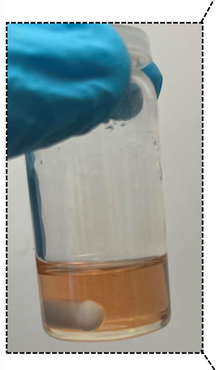
OBJECTIVE

This work aims to develop a gelified semi-interpenetrating network combining an epoxy-acid vitrimer network and an ion conducting polymer electrolyte (PLiMTFSI), with the aim of achieving improved mechanical and electrochemical performance.

SYNTHETIC PATHWAY



Vitrimer precursor

PEG(COOH)2 Mw=600 g/mol — 71,3 wt%

PEGDGE Mw=500 g/mol — 10,7 wt%

TGpAP Mw=277 g/mol — 18 wt%

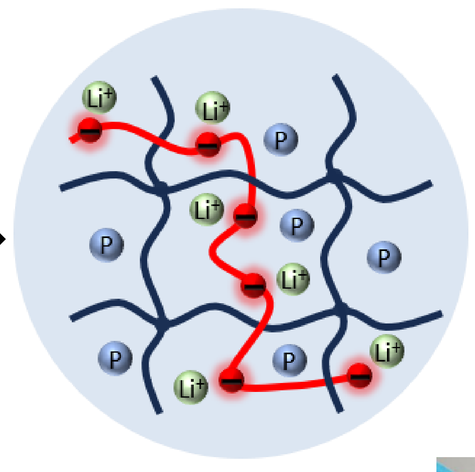
TBD Mw=139 g/mol — 5 %$_{mol}$/[COOH]

MLiTFSI Mw=346 g/mol

PEG500 Mw=500 g/mol

1) 80 °C, 2h

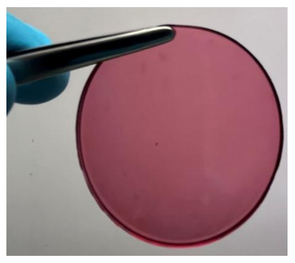
2) 150 °C, 4h



- PMLiTFSI
- Vitrimer network
- Ion pair
- Plasticizer

❖ **Composition of semi-interpenetrating polymer networks:**

Sample name	PEG500 (wt%)	Vitrimer precursor (wt%)	MLiTFSI (wt%)	AIBN
S_{010}	0	100	0	0
S_{163}	10	60	30	2%$_{mol}$ / [MLiTFSI]
S_{253}	20	50	30	

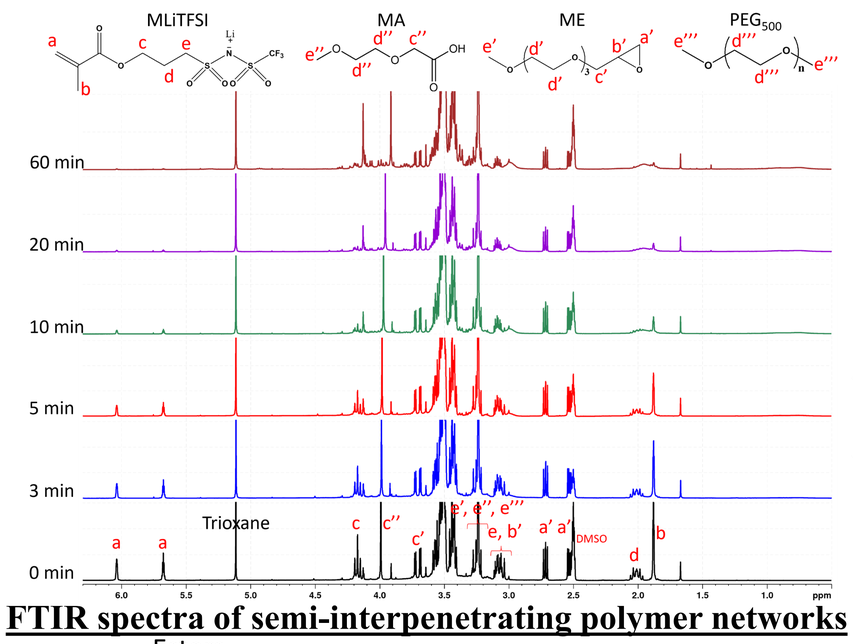


Diameter = 45 mm
Thickness = 1 mm

RESULTS

Kinetic Study of MLiTFSI Polymerization in the Presence of Vitrimer Precursors at 80 °C

❖ Evolution of ^{1}H NMR spectra (DMSO-d_6) with polymerization time of K4



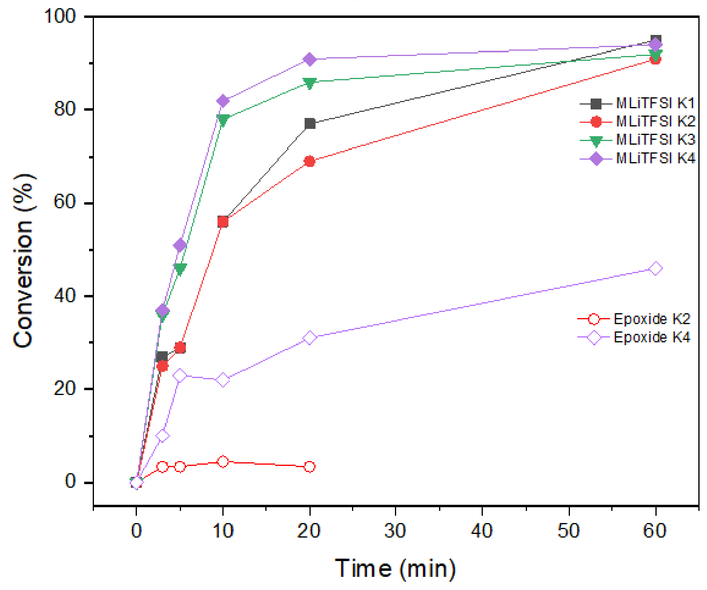
❖ Kinetic formulation of MLiTFSI polymerization

	MLiTFSI	ME	MA	AIBN
K1	[0.87]	-	-	2%$_{mol}$
K2	[0.87]	[1.43]	-	
K3	[0.87]	-	[1.43]	
K4	[0.87]	[1.43]	[1.43]	

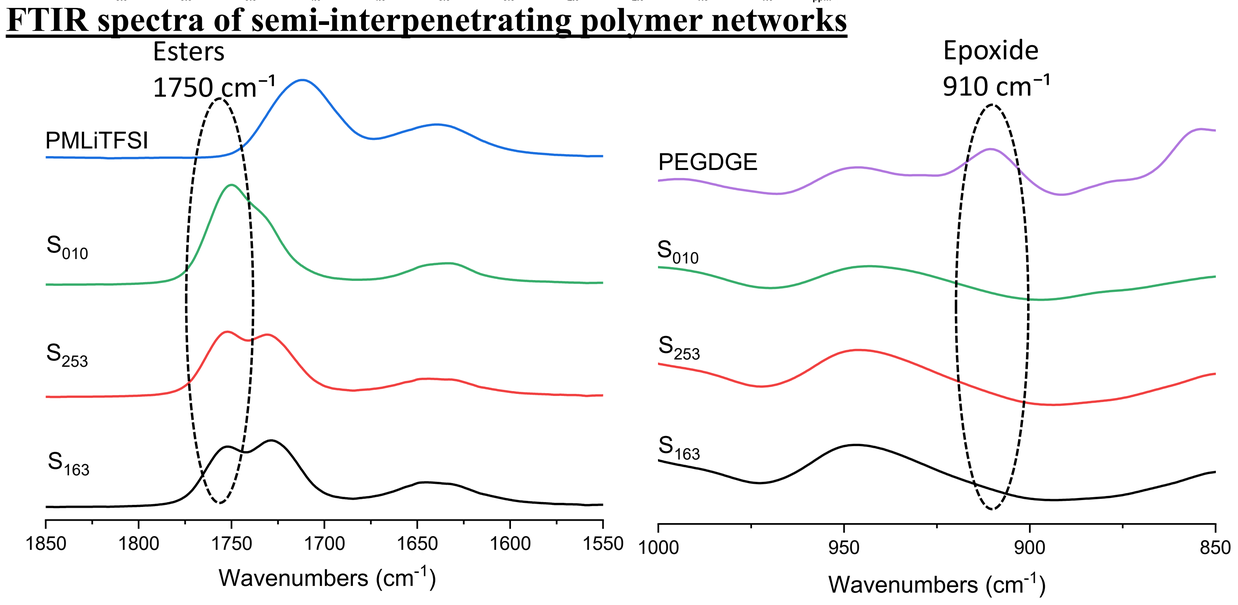
✓ The epoxide and the acid have no influence on the polymerization of MLiTFSI.

✓ Over 90% conversion of MLiFSI at 80 °C.

❖ Evolution of MLiTFSI and Epoxy conversions with time



FTIR spectra of semi-interpenetrating polymer networks



✓ Disappearance of epoxy at 910 cm^{-1} and carboxylic acid at 1726 cm^{-1}

✓ Appearance of esters at 1750 cm^{-1}

Physical and ion conducting properties

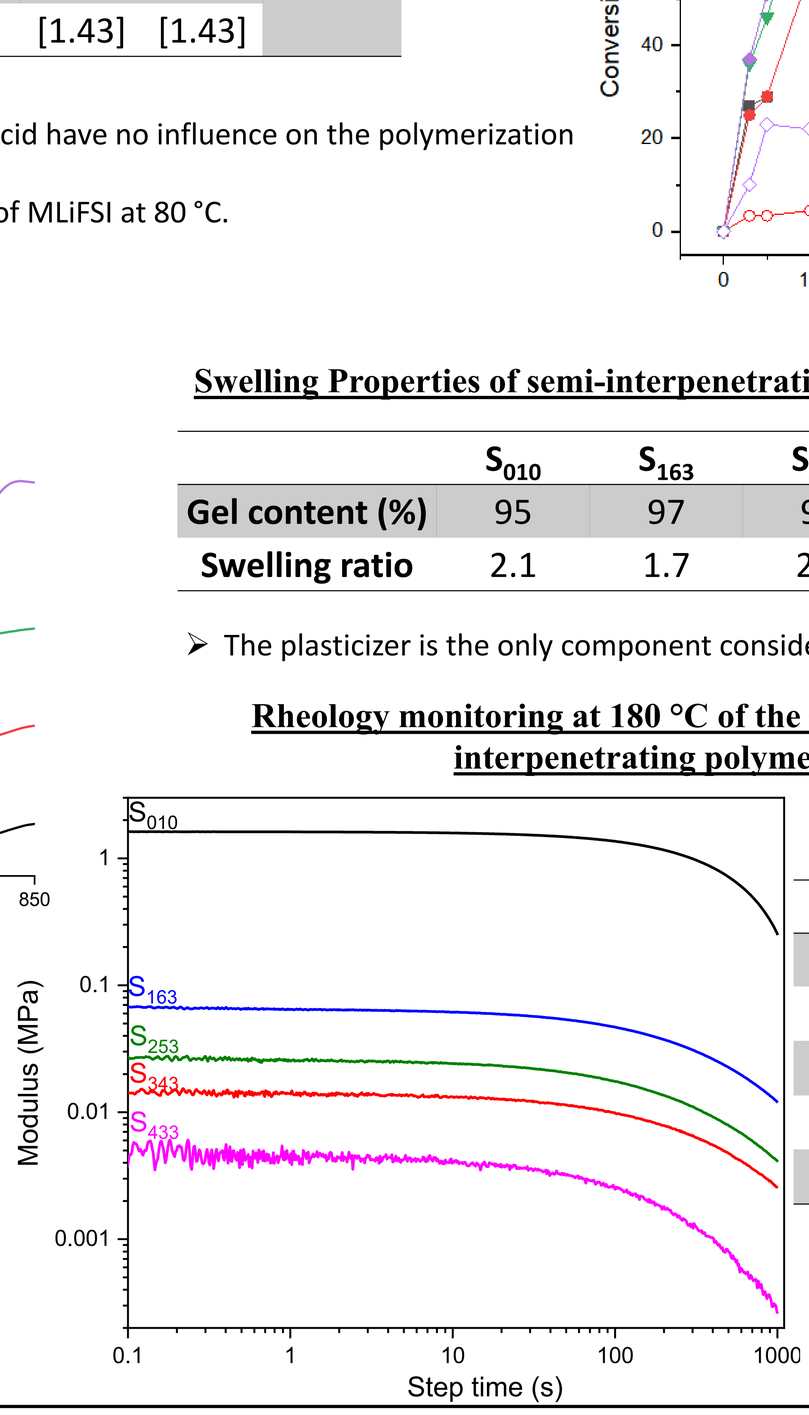
	S_{010}	S_{163}	S_{253}	S_{343}	S_{433}
T_g [°C]	- 37	- 18	- 22	- 30	- 48
G_N [MPa]	1.60	0.06	0.02	0.01	0.004
σ [S/Cm]	-	1.1 x10^{-5}	1.9 x10^{-5}	3.3 x10^{-5}	4.5 x10^{-5}

Swelling Properties of semi-interpenetrating polymer networks in THF

	S_{010}	S_{163}	S_{253}	S_{343}	S_{433}
Gel content (%)	95	97	96	99	99
Swelling ratio	2.1	1.7	2.0	1.4	1.7

➢ The plasticizer is the only component considered extractable in the solvent

Rheology monitoring at 180 °C of the stress relaxation of semi-interpenetrating polymer networks



	t_{gel} (s)	$t_{relaxation}$ (s)
S_{010}	600	180
S_{163}	440	220
S_{253}	350	250
S_{343}	420	420
S_{433}	200	500

CONCLUSION

In summary, a dynamic gelified semi-interpenetrating network was successfully developed by combining an epoxy-acid vitrimer with the single-ion conducting polymer PLiMTFSI. FTIR, swelling, and rheology confirmed the formation and dynamic behavior of the network, while the resulting materials exhibited ionic conductivity on the order of 10^{-5} S/cm at 60 °C, comparable to values reported for analogous single-ion systems