

Swetha Karingal Veedu, Alvaro Quinteros Sedano, Jean-François Gohy, Evelyne van Ruymbeke, Charles-André Fustin

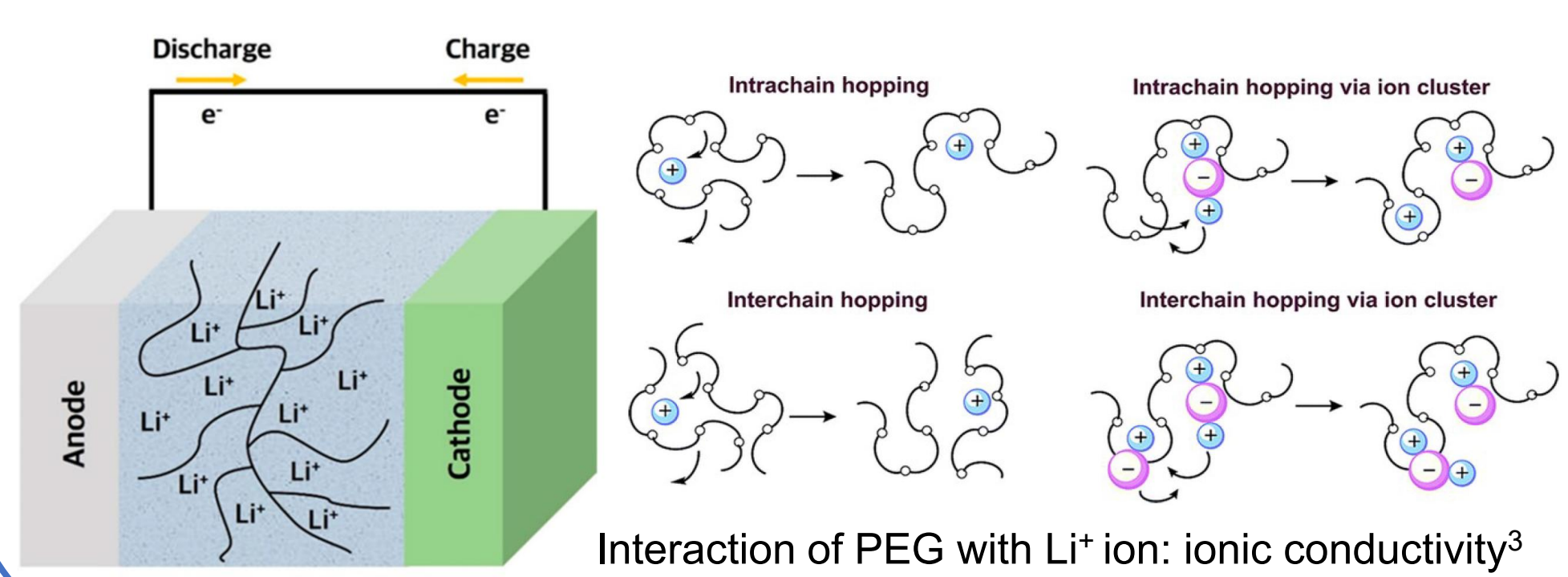
Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Place Pasteur 1, 1348 Ottignies-Louvain-la-Neuve, Belgium

swetha.karingal@uclouvain.be

## Introduction

Solid polymer electrolytes (SPEs) are promising for high energy density Li-metal batteries (LMBs), offering safety advantages over traditional liquid electrolytes<sup>1</sup>. Using chemically crosslinked networks to prepare SPEs is a widely accepted method to enhance mechanical properties and thermal stability, but which also has certain limitations. Vitrimers are a new class of crosslinked polymers that possess the ability to flow at high temperatures due to the presence of exchangeable covalent bonds<sup>2</sup>. The objective of this project is to comprehensively investigate the effective implementation of the vitrimer behavior to improve various properties of SPEs for LMBs. This involves synthesizing vitrimer-like SPE networks and optimizing their properties by modifying dynamic covalent bonds (DCBs) and network topology.

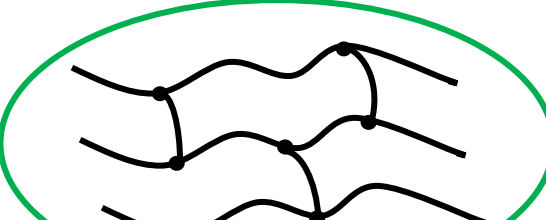
### Solid polymer electrolytes in Li-Metal batteries<sup>3</sup>



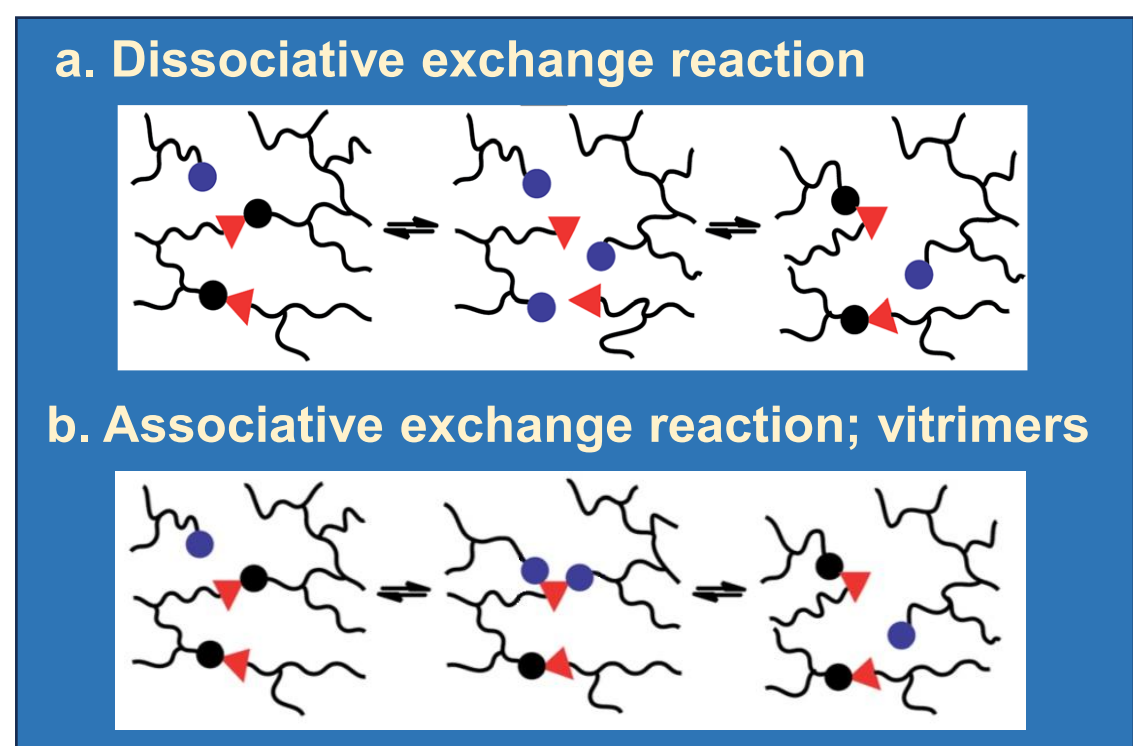
### Thermoplastic



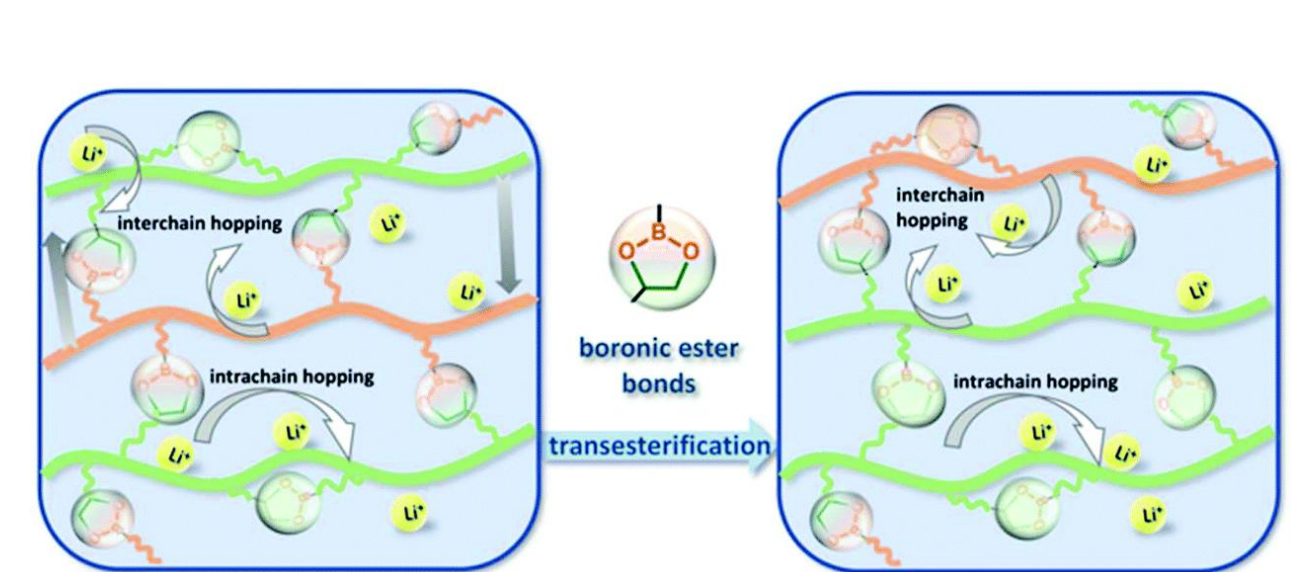
### Thermoset



### Covalent adaptable networks(CANs)<sup>4</sup>

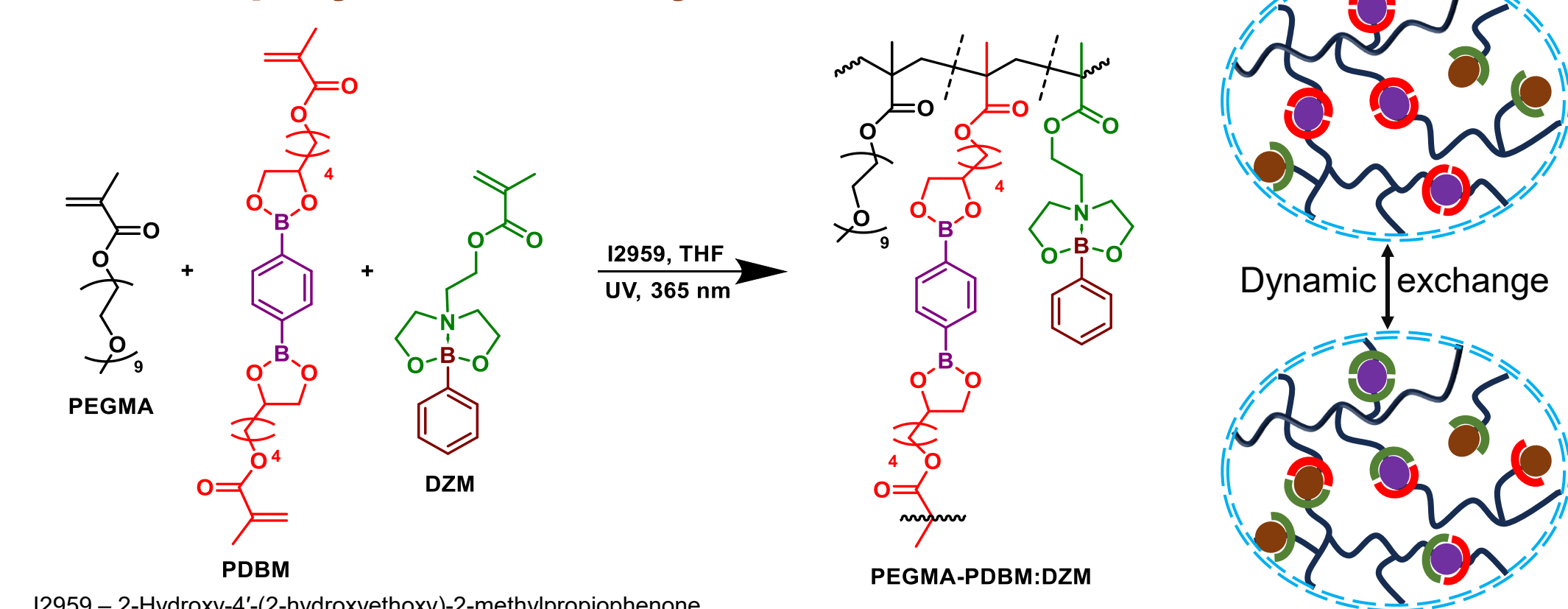


### Ion conduction & Dynamic behavior in SPEs<sup>5</sup>

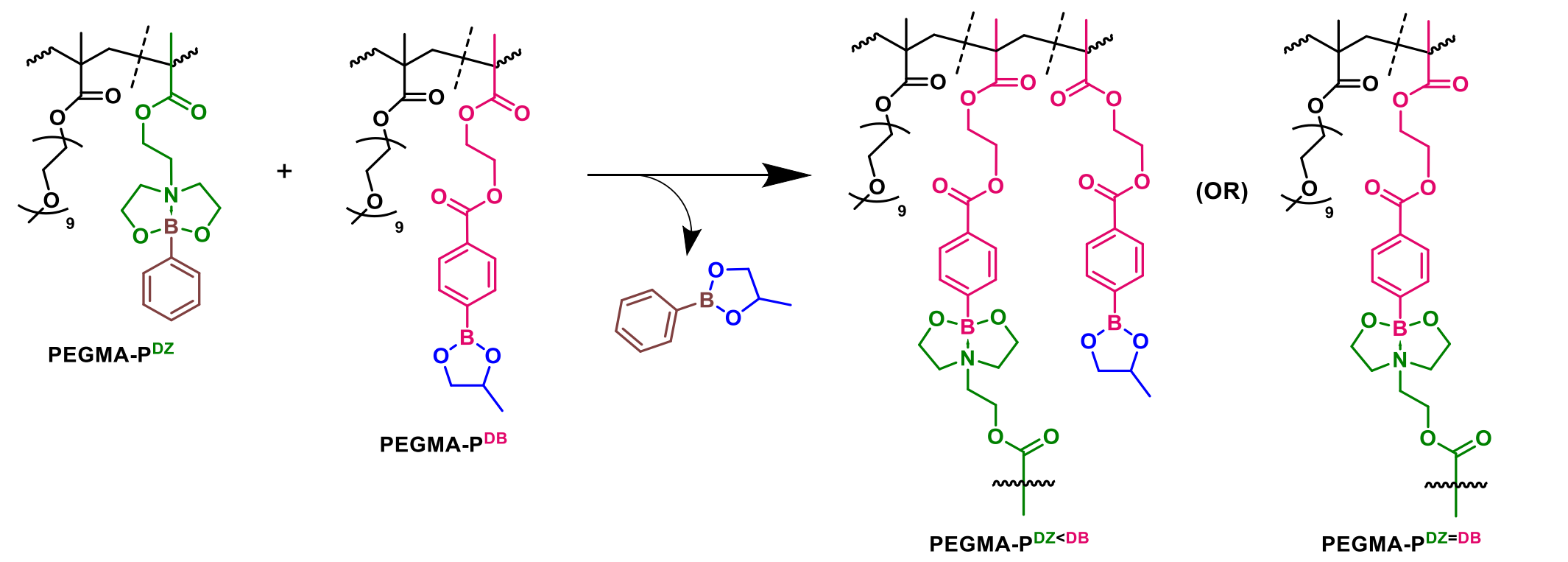


## Synthesis of Vitrimer

### A. Photopolymerized Polymer network



### B. Complementary polymer network

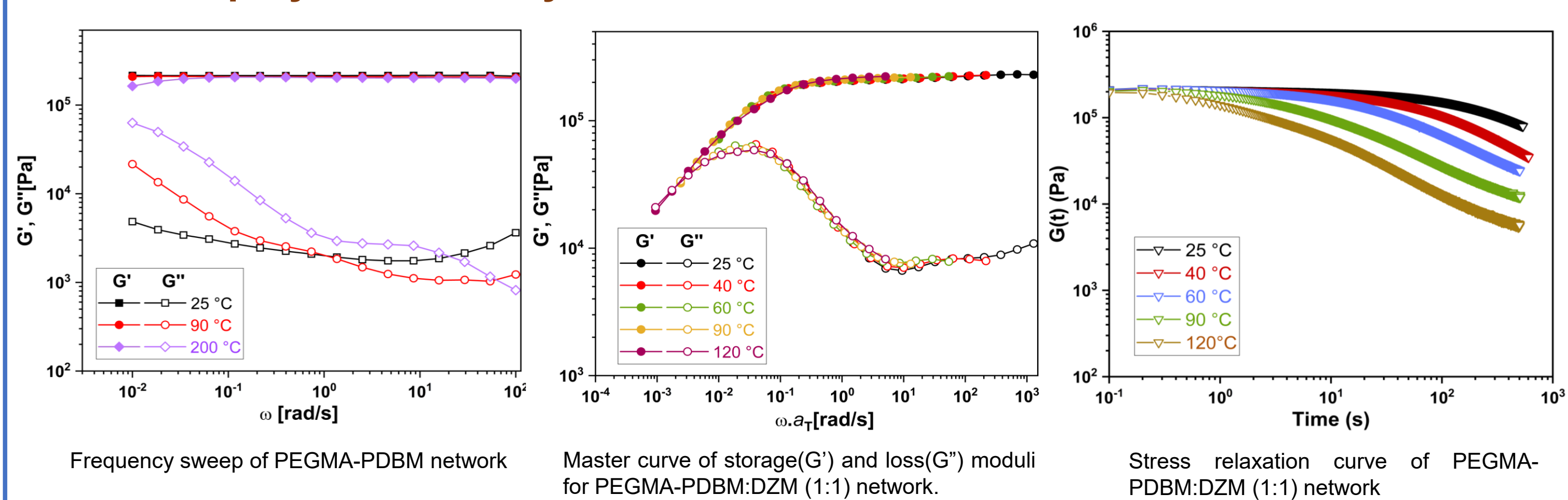


A. Vitrimer network synthesized using Dioxaborolane(PDBM) as the crosslinker and Dioxazaborocane (DZM) as the pendant groups. Two networks developed: (i) PEGMA-PDBM, and (ii) PEGMA-PDBM:DZM, DZM pendant groups enhance dynamics.

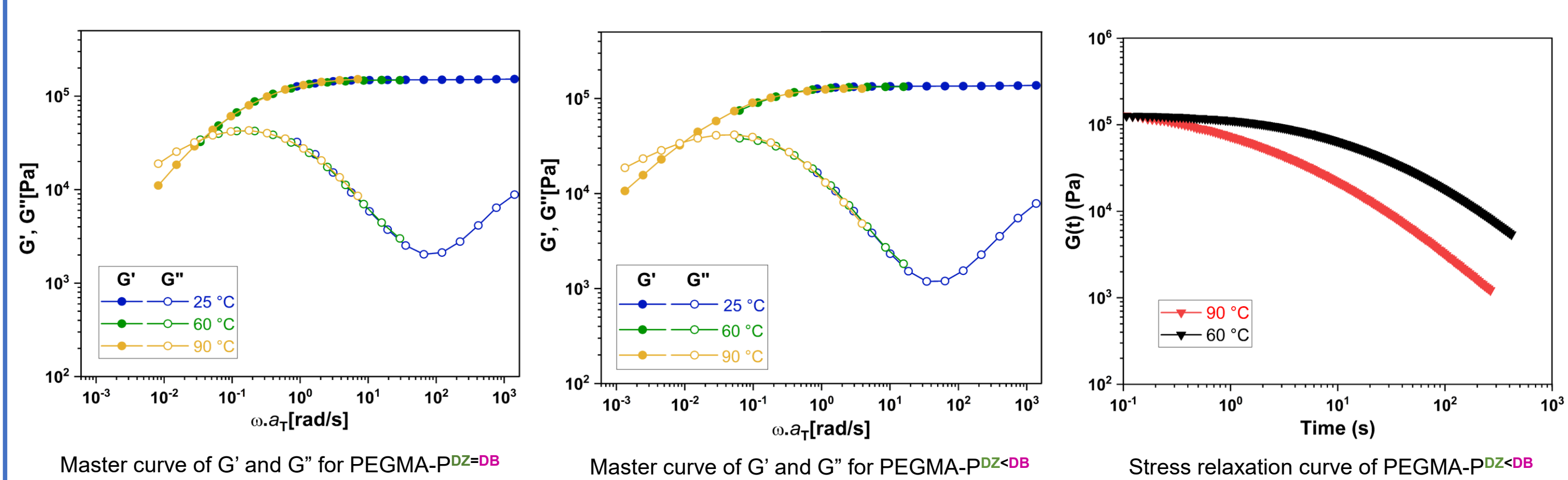
B. Vitrimer network synthesized by reacting two Copolymers bearing complementary boronic ester functions. In PEGMA-PDBM,  $n_{DB} = n_{PDB}$  and PEGMA-PDBM-DZM,  $n_{DB} = 2n_{PDB}$  (excess DB group).

## Characterization: Rheology

### A. Photopolymerized Polymer network



### B. Complementary polymer network

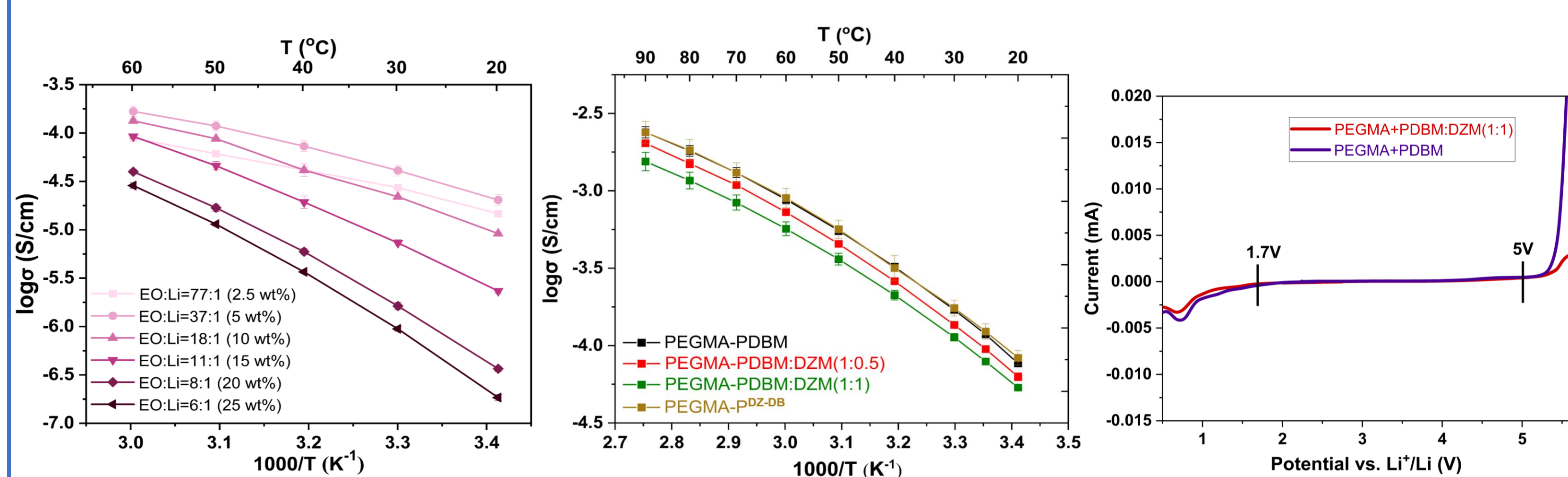


A. DZM speeds up the exchange dynamics  
Faster stress relaxation at higher temperature.

B. PEGMA-PDBM-DZM reaches crossover faster than PEGMA-PDBM  
Faster stress relaxation at higher temperature.

## Characterization of SPE: Electrochemical Performances, Self-healing test

### ❖Ionic conductivity & Electrochemical stability window

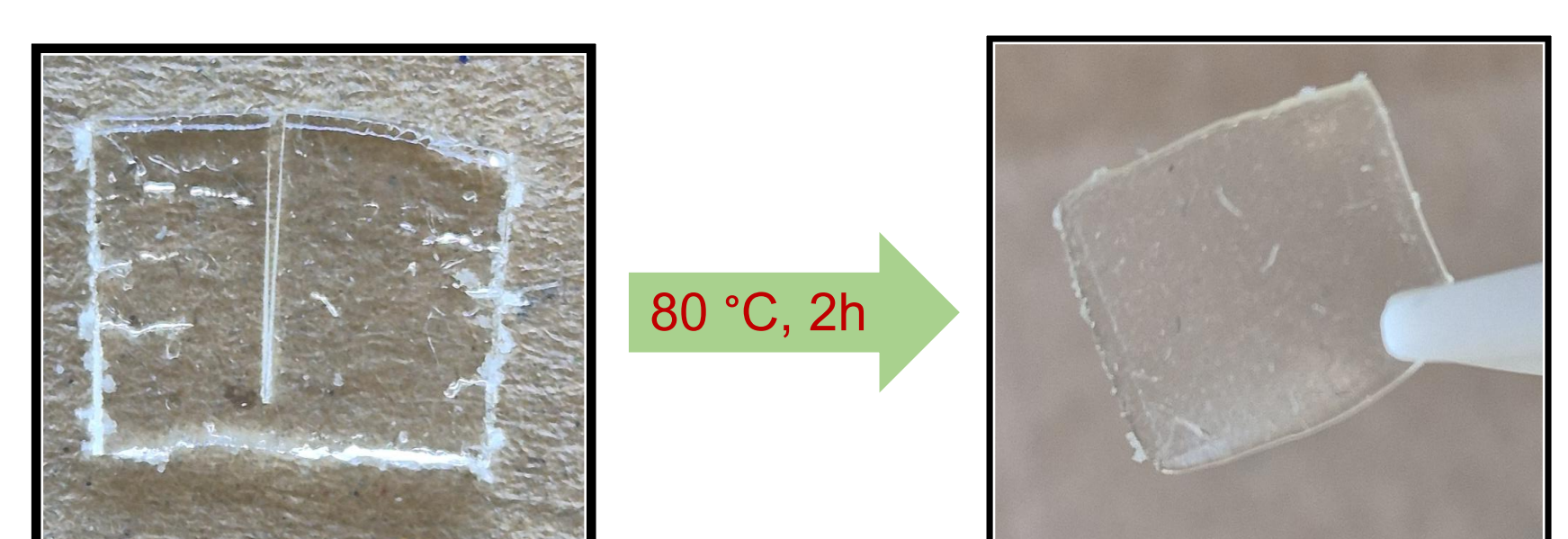


Ionic conductivity ( $\sigma$ ) of PEGMA homopolymer with different LiClO<sub>4</sub> concentrations in solid state

$\sigma$  of PEGMA-PDBM and PEGMA-PDBM:DZM=1:0.5 & 1:1 with LiClO<sub>4</sub>

Electrochemical stability window (ESW) of PEGMA-PDBM and PEGMA-PDBM:DZM=1:1

### ❖Self-healing test



- ✓ Ionic conductivity ( $\sigma$ ) of PEGMA homopolymer is higher at 5 wt% LiClO<sub>4</sub>
- ✓ Ionic conductivity of PEGMA-PDBM is slightly higher than that of PEGMA-PDBM:DZM.
- ✓ The Electrochemical stability window(ESW) for PEGMA-PDBM:DZM is from 1.7V to 5V.
- ✓ Self healing SPEs

## Conclusion

Vitrimer networks based on PEGMA and boronic esters were synthesized. The first network was directly obtained via photopolymerization using a difunctional dioxaborolane (PDBM) crosslinker and a dioxazaborocane (DZM) comonomer. The second network was formed by reacting two polymers bearing complementary boronic ester functionalities. The dynamic and electrochemical properties were evaluated by rheology and ionic conductivity tests. The dynamic behavior of the polymer network formed using a PDBM crosslinker is enhanced by the incorporation of a DZM pendant group with a dative N→B bond. The ESW suggests that a variety of cathodes can be used for further battery testing. In second network, PEGMA-PDBM-DZM (lower crosslinking density) has similar  $\sigma$  as that of PEGMA-PDBM network. A deeper understanding of the polymer networks will be achieved through DMA analysis, battery tests, and further rheology studies.

## References

- [1] W. Gu, F. Li, T. Liu, S. Gong, Q. Gao, J. Li, Z. Fang, *Adv. Sci.* **2022**, 9, e2103623
- [2] M. Hayashi, *Polymers* **2020**, 12.
- [3] Z. Xue, D. He, X. Xie, *J. Mater. Chem. A* **2015**, 3, 19218.
- [4] W. Denissen, J. M. Winne, F. E. Du Prez, *Chem. Sci.* **2016**, 7, 30.
- [5] S. Li, C. Zuo, Y. Zhang, J. Wang, H. Gan, S. Li, L. Yu, B. Zhou, Z. Xue, *Polymer Chemistry* **2020**, 11, 5893.

## Acknowledgement

This work is financed by the ARC project "INVITE" n° 22/27-125.