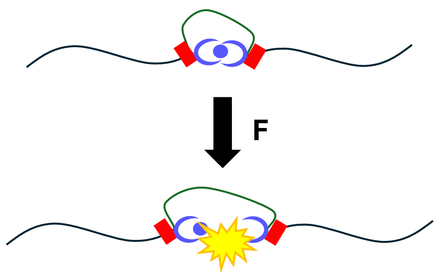
DEVELOPMENT OF POLYMER NETWORKS CONTAINING TETHERED WEAK BONDS

Charlène Breton[(1)], Danish Equbal[(1)], Thomas Hooper[(2)], Dimitrios Sakellariou[(2)], Charles-André Fustin[(1)]

1) UCLouvain, Institute of Condensed Matter and Nanoscience - Bio and Soft Matter division (IMCN-BSMA), Louvain-la-Neuve, Belgium
2) KULeuven, Membrane Separations, Adsorption, Catalysis, and Spectroscopy for Sustainable Solutions (cMACS), Leuven, Belgium

For many years, polymers were built exclusively from strong bonds. Nowadays, a new class of polymer network containing weak bonds is rising. While giving interesting properties to the network such as self-healing, facilitated recycling or higher toughness, weak bonds have major drawbacks, such as lower mechanical strength, bad shape persistence, creep, or fatigue due to an overall lower strength and faster dynamic. Therefore, it is of interest to introduce the concepts of **sacrificial bonds** and **hidden length** to limit those drawbacks. These concepts are inspired from biological materials such as nacre, bones or mollusks' byssus, known for their stiffness, strength and toughness with self-repair capacity[(1)]. Sacrificial bonds are defined as bonds that rupture before strong bonds failure under deformation, while the hidden length is characterized by the length difference between the folded and unfolded portion of the polymer, or the length released after weak bond breakage[(3)].



Energy dissipation

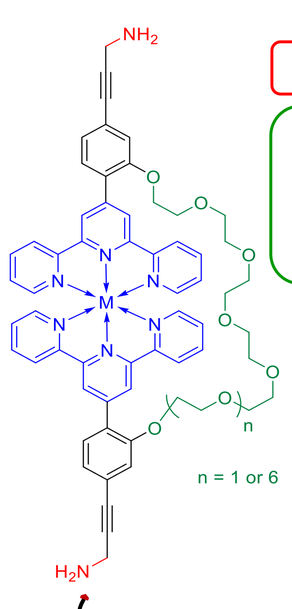
In this work, our aim is to give a **quantitative understanding of the impact of inserting tethered weak bonds into polymeric materials on the macroscopic properties**.

DESIGN & SYNTHESIS → CHEMICAL CHARACTERIZATION → STRUCTURAL CHARCATERIZATION → VISCOELASTIC PROPERTIES → MACROSCOPIC PROPERTIES

DESIGN & SYNTHESIS

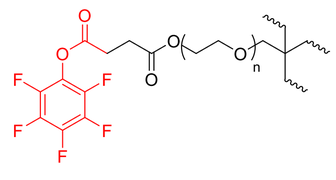
Metal-Ligand bond:
- Lifetime and strength tuning (Fe^{2+}; Ni^{2+}; Co^{2+}; Cu^{2+}; Zn^{2+})
- Stimuli responsive (*Temperature; pH; Redox*)
- Spontaneous reformation

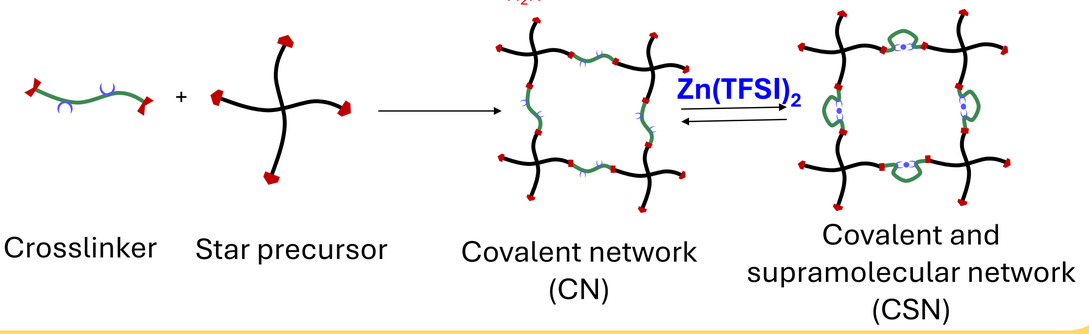
Model network:
20 kg.mol^{-1} 4-arm PEG star
15 wt% in propylene carbonate



Functional group

Poly(ethylene glycol) tether:
Tuning of the length (6 or 12 units)

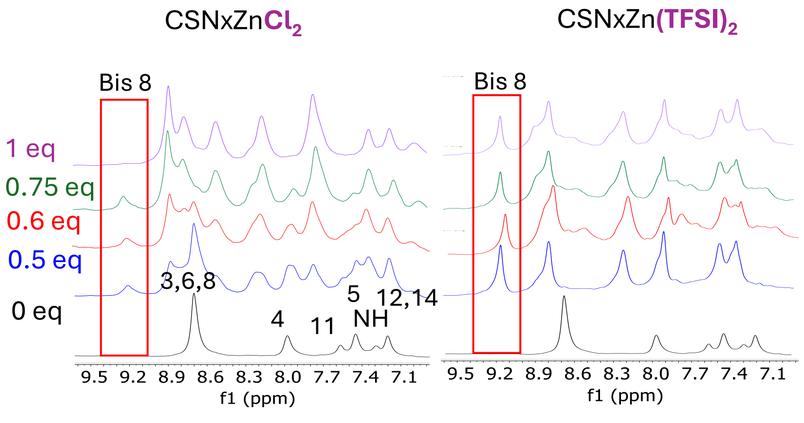


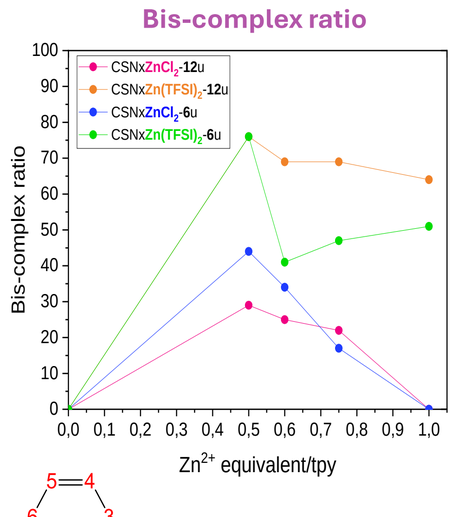


Crosslinker | Star precursor | Covalent network (CN) | Covalent and supramolecular network (CSN)

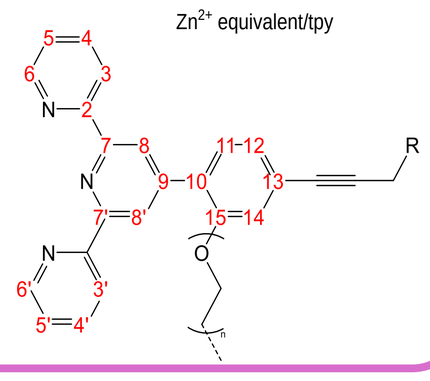
CHEMICAL CHARACTERIZATION

Metal ion diffusion and counter-ion influence:





- Strong influence of the counter-ion on the bis-complex stability: $Zn(TFSI)_2$ forms stable complexes;
- 0.5 eq of Zn^{2+} is the optimum amount to reach the highest proportion of bis-complexes.



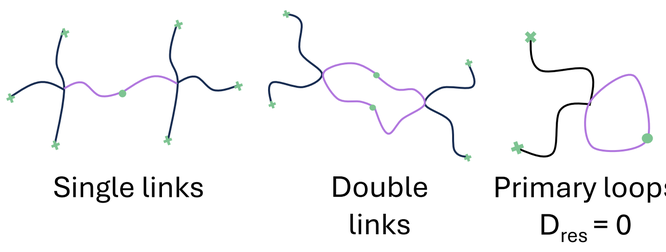
STRUCTURAL CHARCATERIZATION

DQ NMR: Gives information on the **local dynamic order of the polymer backbone**.

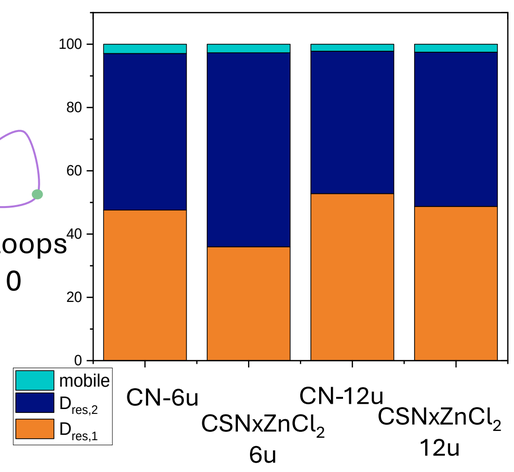
✓ Information on mesh size:
- 2 D_{res} ⇔ 2 mesh sizes, Similar D_{res} values ⇔ Similar mesh sizes;
- No drastic change of mesh size: Complexation between neighboring terpyridines.

	CN-6u	CSNxZnCl$_2$-6u	CN-12u	CSNxZnCl$_2$-12u
$D_{res,1}/2\pi$ (Hz)	166	200	136	145
$D_{res,2}/2\pi$ (Hz)	45	53	29	37
$D_{res,1}/D_{res,2}$	4,3	4,3	5,3	4,2

✓ Information on defects:
- 3 possible connections:



Single links | Double links | Primary loops $D_{res} = 0$

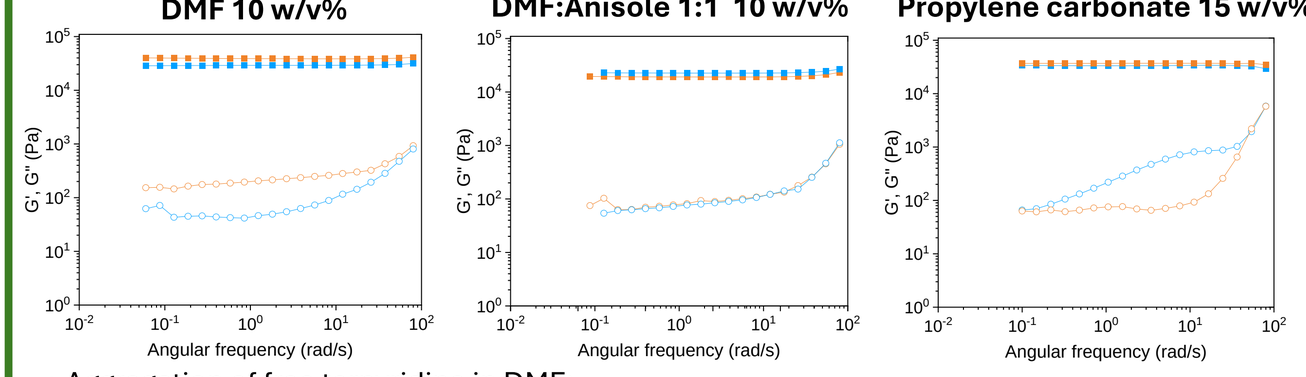


- $D_{res,1}$ → Single links
- $D_{res,2}$ → Double links
- Low ratio of **primary loops**

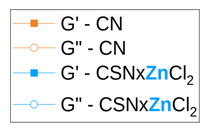
No change of network architecture while introducing ions.

VISCOELASTIC PROPERTIES

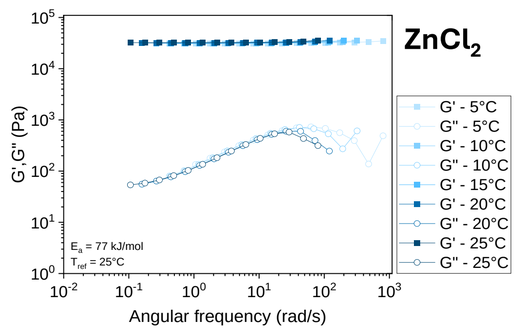
Solvent influence:

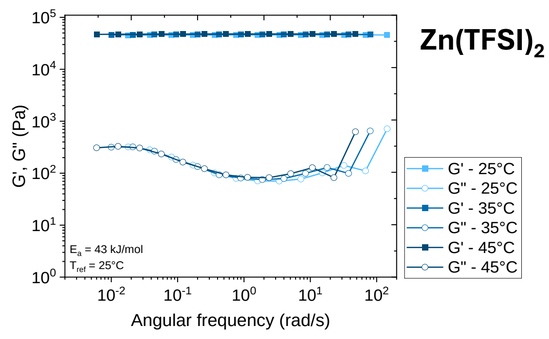


- Aggregation of free terpyridine in DMF;
- DMF acts as complexing solvent competing with the formation of bis-complexes.

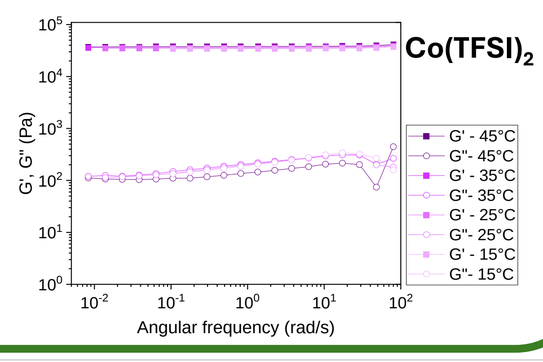


Counter-ion and metal ion influences:

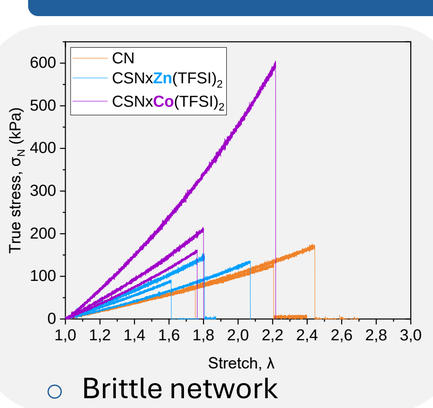




- Cl^- act as competitive ligand;
- $TFSI^-$ forms more stable complexes than Cl^-: delay of the relaxation time;
- Co^{2+} forms more stable complexes compared to Zn^{2+}.



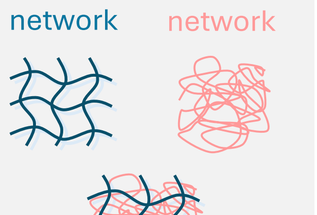
MACROSCOPIC PROPERTIES



- Brittle network

Embedded network strategy

Macroscopic crack propagation delayed



Double network

CONCLUSION

Model networks, based on a 4-arm star precursor, containing tethered terpyridines as sacrificial bonds, were successfully synthesized. In depth characterization at different length scales, from the chemical structure to macroscopic properties, was carried on. We highlighted the dynamic behavior of the sacrificial bond and the influence of different parameters. We confirmed that the network architecture is not affected by the dynamics of the complex. As prepared gels are soft and brittle, complicating the mechanical characterization. An embedding network strategy will be used next to get in depth knowledge on energy dissipation upon tensile stress and bond recovery.

References

(1) Zhou, X., Guo, B., Zhang, L. & Hu, G.-H. Chem. Soc. Rev. **46**, 6301–6329 (2017).

(2) Ducrot, E., Chen, Y., Bulters, M., Sijbesma, R. P. & Creton, C. Science **344**, 186–189 (2014).

(3) Nakajima, T. Polym. J. **49**, 477–485 (2017).

(4) Creton, C. Macromolecules **50**, 8297–8316 (2017).

Acknowledgement

This project (40007519) has received funding from the FWO and F.R.S.-FNRS under the Excellence of Science (EOS) program, grant 40007519.