

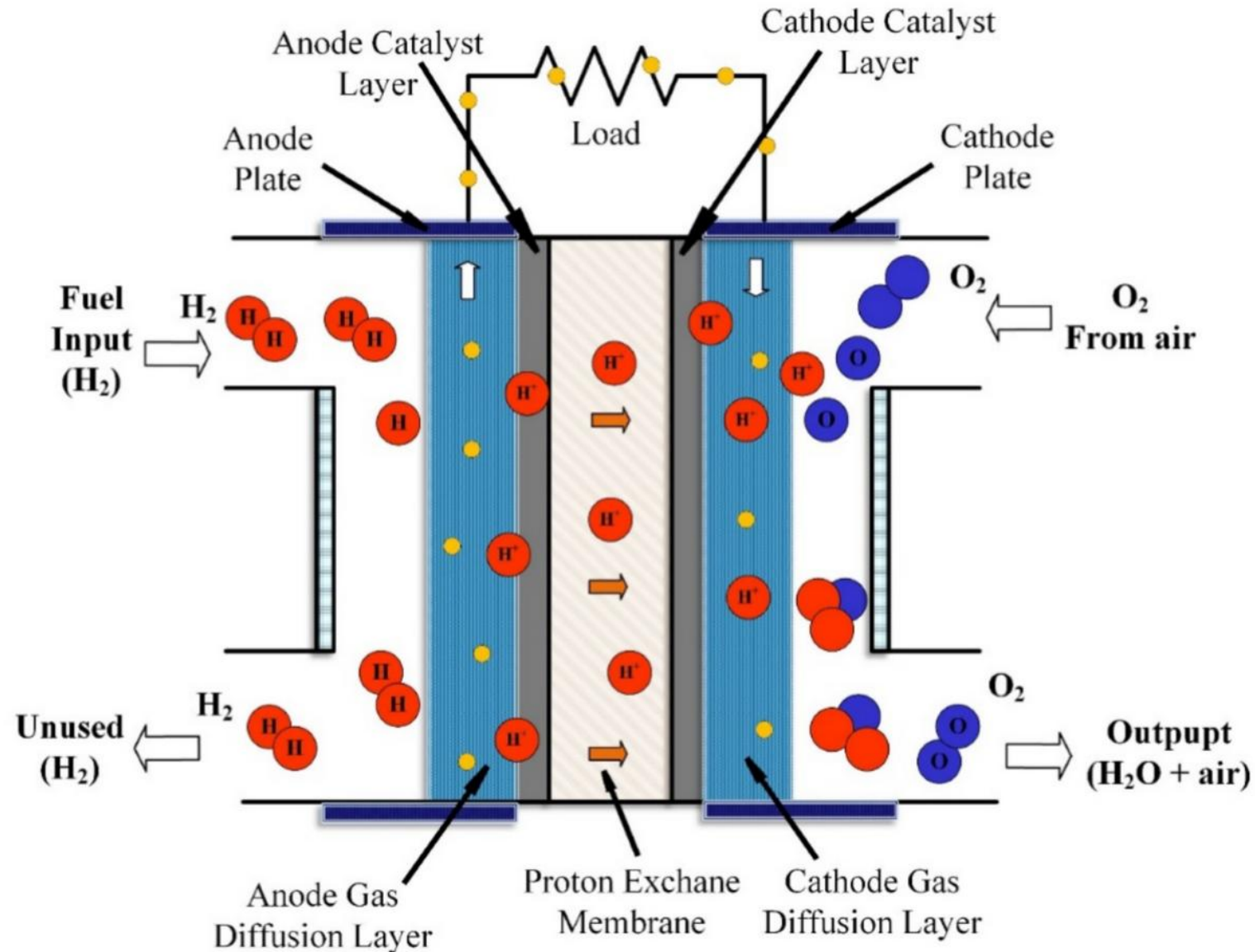


sPPS/PBI-O Blends as Polymer Electrolytes: The "Snake-in-a-Cage" Effect

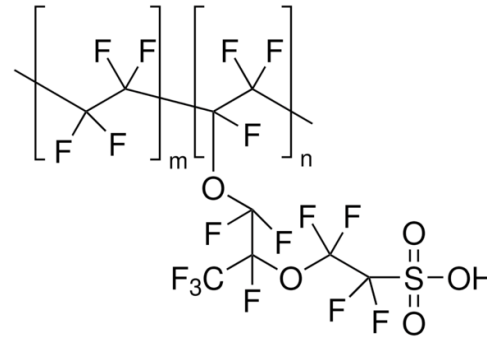
Elene Lezhava

Scientific Supervisor
Prof. Giorgi Titvinidze

- Development of clean, efficient, and alternative energy technologies



- Hydrogen enables excess renewable electricity to be stored and later converted back into electricity when needed ²



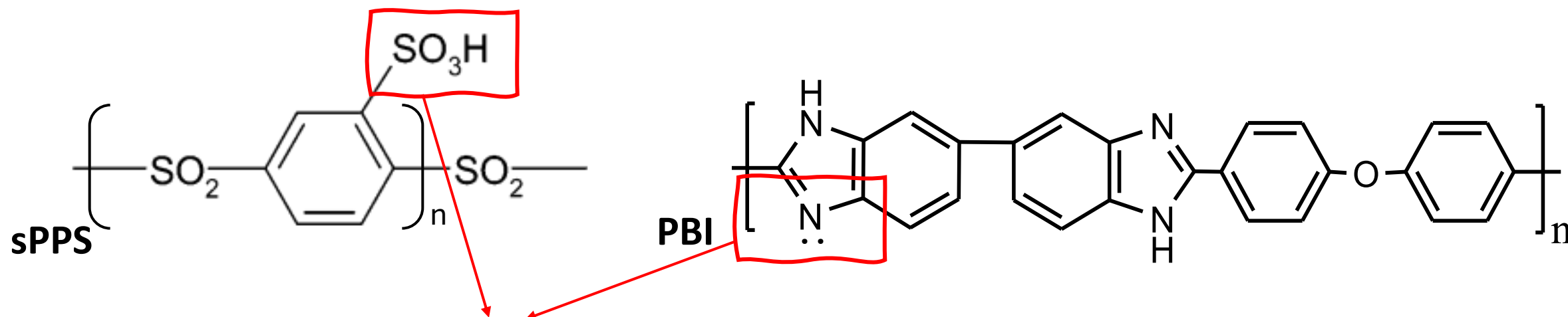
- **Potential environmental impact of fluorinated compounds and increasing regulatory restrictions in recent years**
- **High production cost**
- **Deterioration of properties under high-temperature and low-humidity conditions**



□ Poly(phenylene sulfones)

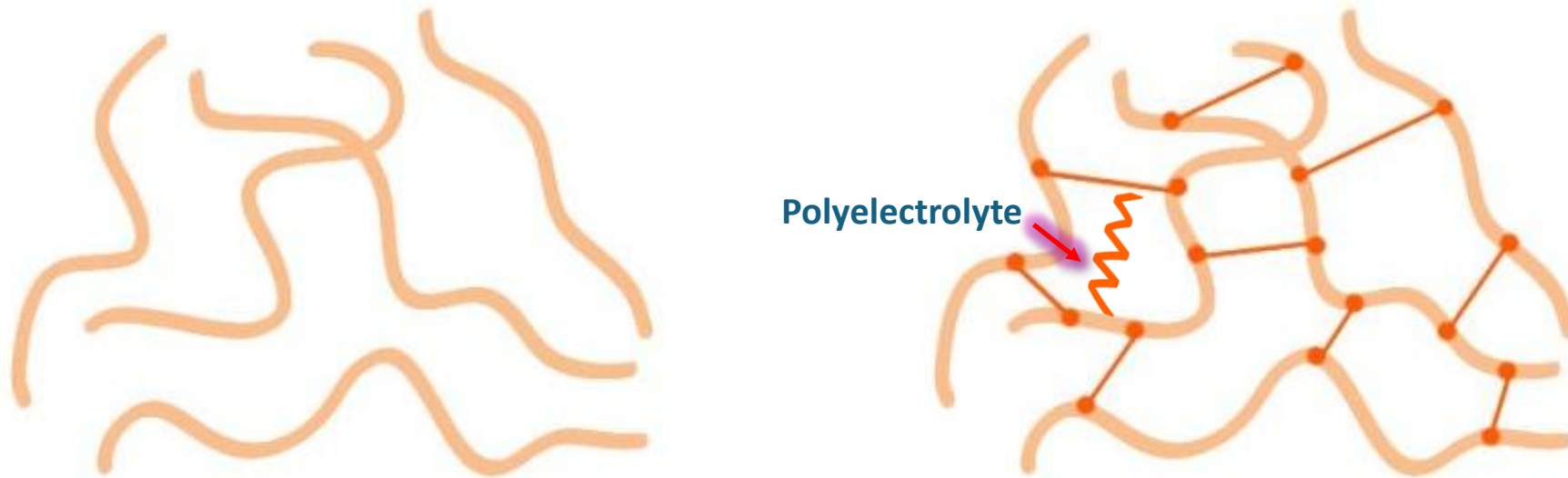
□ sPPS/PBI Polymer Blends

- high proton conductivity
- Its strong affinity for water make it difficult to use in stable membrane systems.
- high stability
- excellent film-forming ability



- Ionic interactions are established between the components
- Under conditions of high humidity, water molecules can weaken ionic interactions, which may lead to the leaching of sPPS

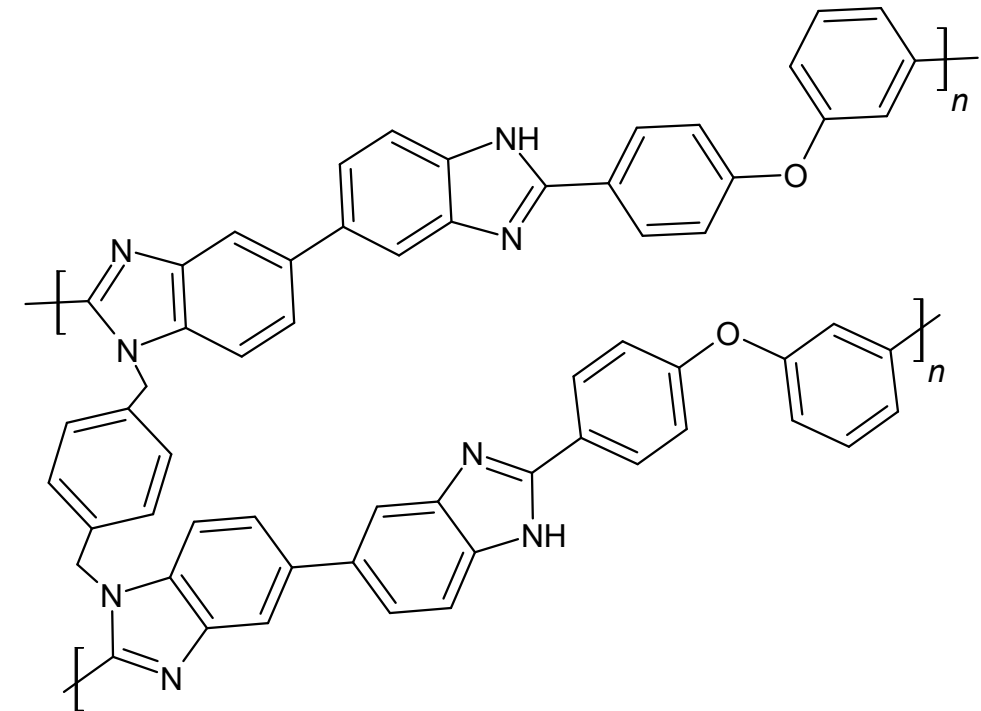
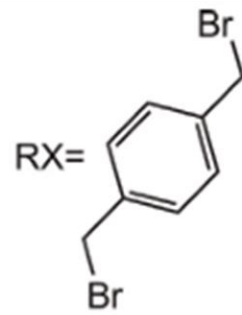
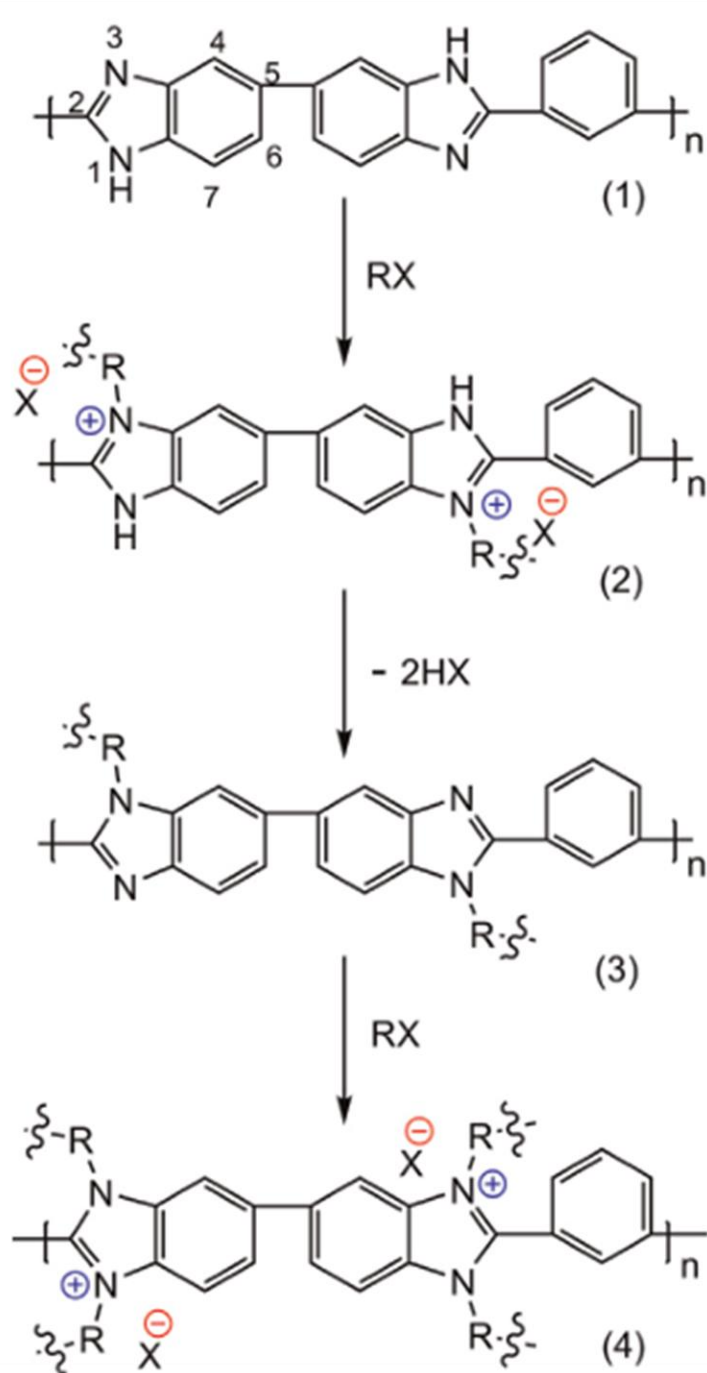
Formation of Additional Covalent Bonds within the PBI Matrix



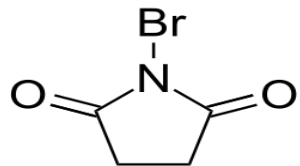
“Snake-in-a-Cage” effect

Covalent Crosslinking of Poly(benzimidazole)

- ❑ For the crosslinking of PBI, an electrophilic crosslinking agent was selected:
- ❑ 1,4-Bis(bromomethyl)benzene

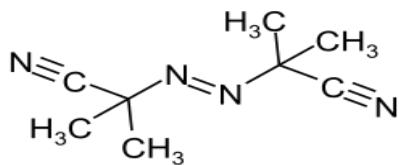


Scheme of Covalent Crosslinking of PBI



N-bromosuccinimide
(brominating agent)

azobisisobutyronitrile (radical
initiator)



Synthesis of 1,4-Bis(bromomethyl)benzene

p-Xylene

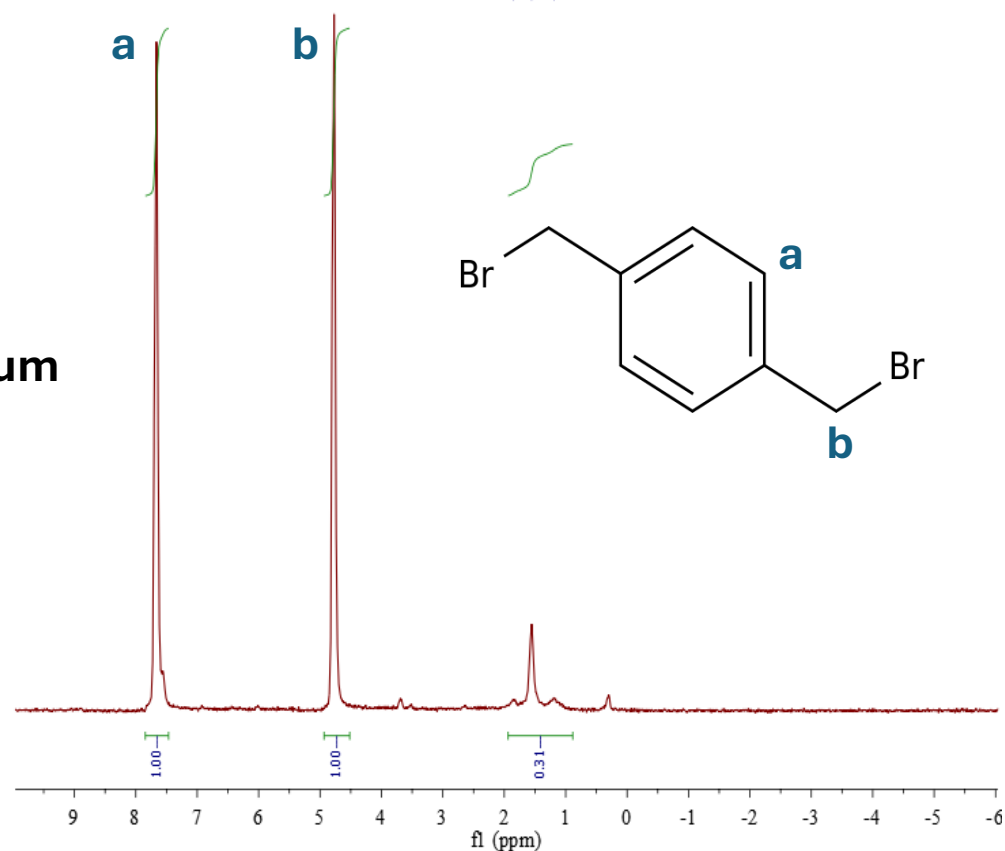
NBS

AIBN

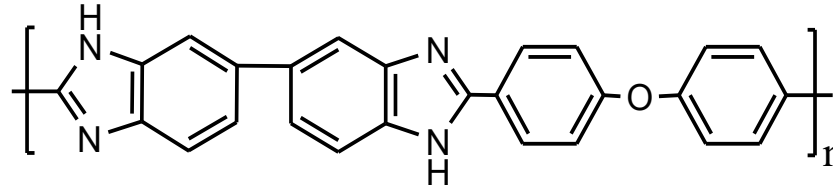
acetonitrile
(solvent)



^1H NMR spectrum



Evaluation of Covalent Crosslinking of Pure PBI



Pre-casting crosslinking

- Crosslinking agent added before membrane formation 2% and 5% crosslinking agent relative to polymer mass

Post-casting crosslinking

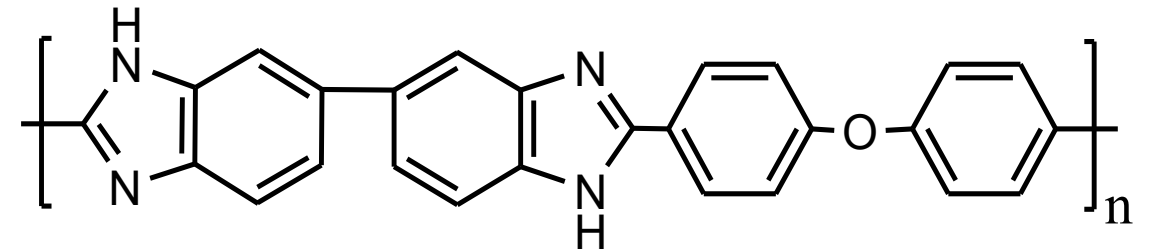
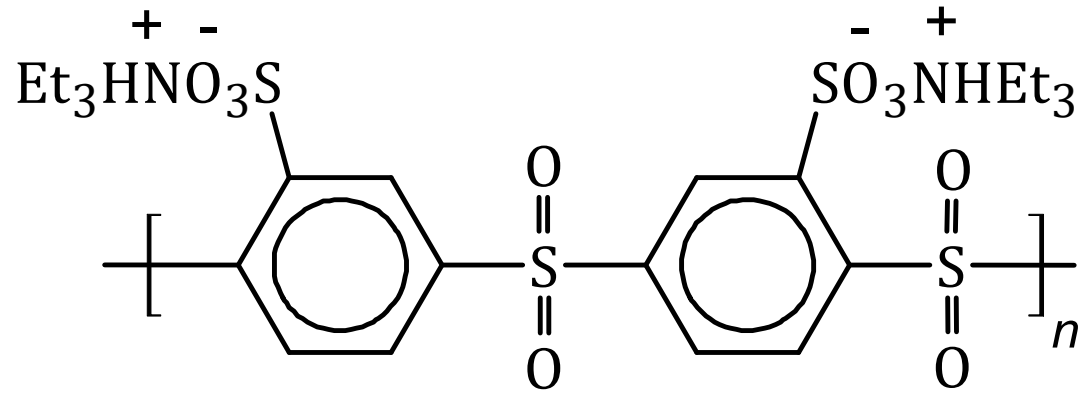
- Treatment with a 1% p-xylylene dibromide solution

After 48 h treatment in DMSO at 100°C:

With 2% p-xylylene dibromide: 0.6% mass loss
With 5% crosslinking agent: no mass loss detected

- **The membranes showed good mechanical stability and completely maintained their structural integrity after prolonged treatment in DMSO, indicating the formation of a covalent network**

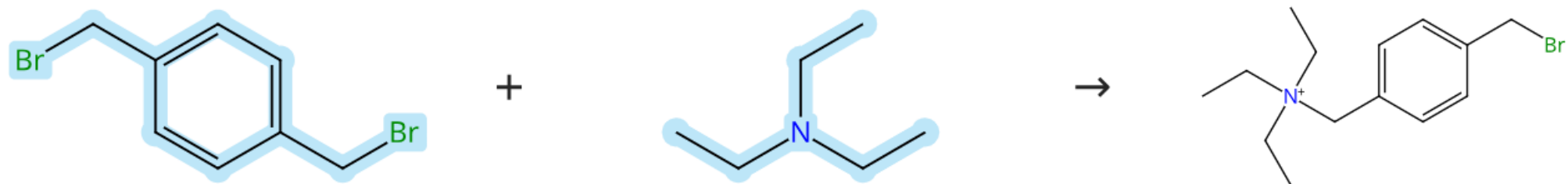
Preparation of the Initial Polymer Blend



- Opaque membrane that rapidly dissolves in DMSO
- No covalent network was formed

sPPS-260/PBI-O Polymer Blend- 80%/20%

- ❑ The neutralizing agent, triethylamine, participates in a side reaction with p-xylylene dibromide.

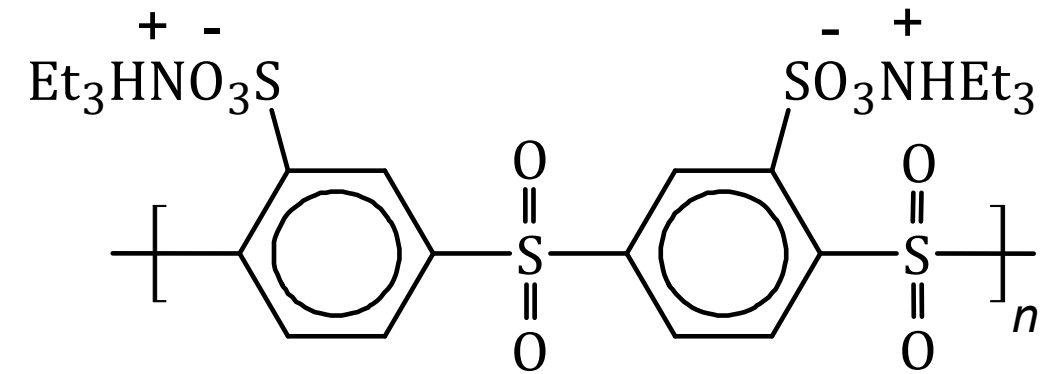
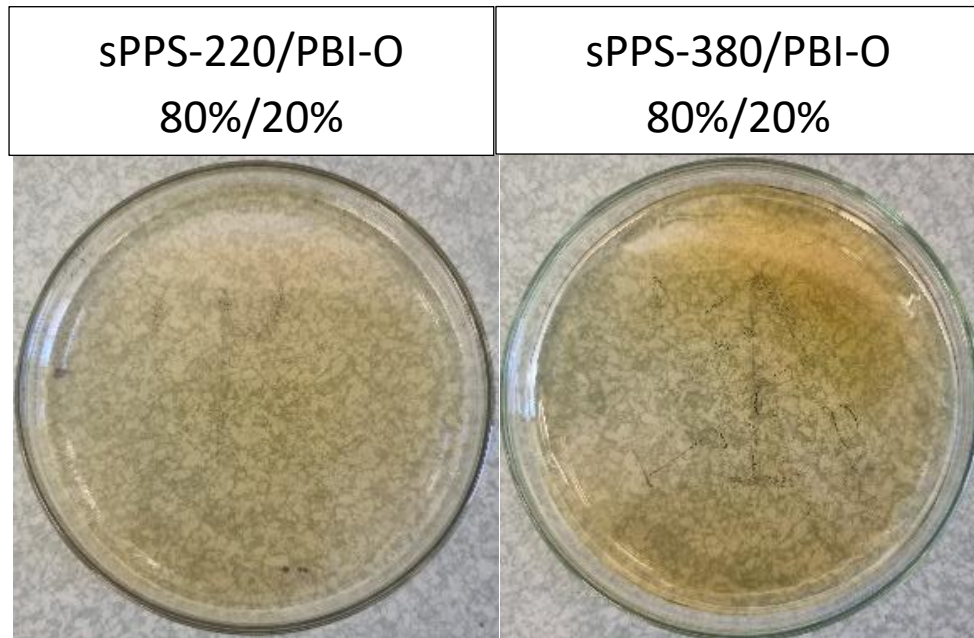


The crosslinking agent is partially consumed before reacting with the PBI chains.

Formation of side products, which causes the film to become opaque.

Alternative approaches:

- ❑ Post-crosslinking of the formed sPPS/PBI membrane
- ❑ conversion of the functional groups ($-\text{SO}_3\text{H}$) of sPPS into the Li^+ or Na^+ form



High chemical stability: The membranes did not dissolve in DMSO, even at temperatures close to its boiling point. **However, upon addition of triethylamine, the films dissolved rapidly.**



Disruption of ionic interactions

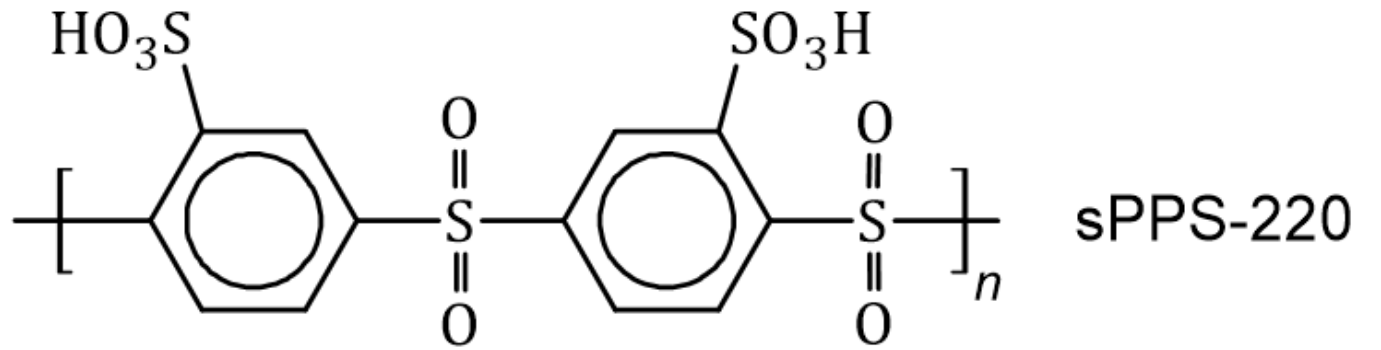
Covalent Crosslinking of Polymer Blends

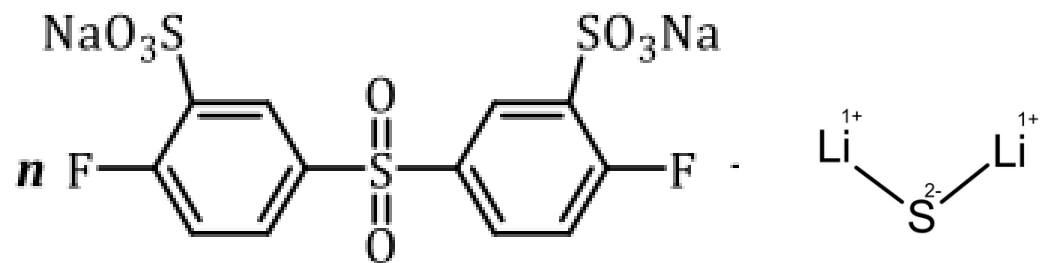
Treatment with **1,4-bis(bromomethyl)benzene** in acetonitrile in a thermostatic oven until the solvent evaporated → the resulting membranes **did not exhibit sufficient stability**.

The membranes were treated with a **dibromide solution at elevated temperature for 8 hours**.

A **covalently crosslinked PBI-O network** was formed **partially in the sPPS-220/PBI-O blend** and **effectively in the sPPS-380/PBI-O blend**.

Optimization of sPPS-220 Synthesis

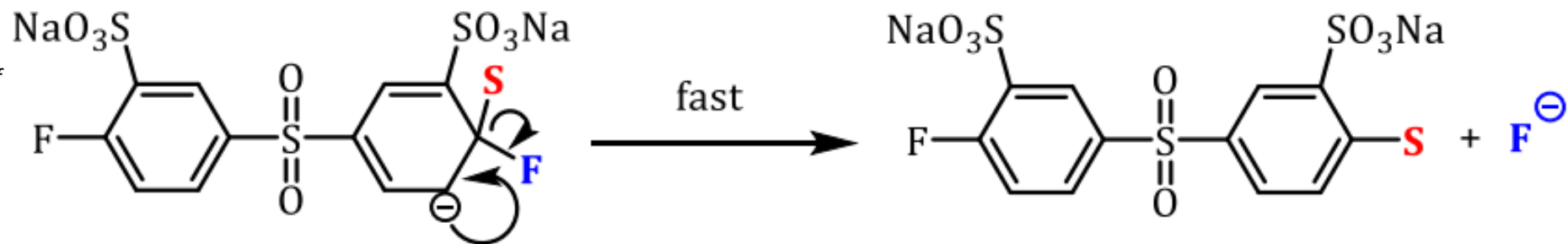
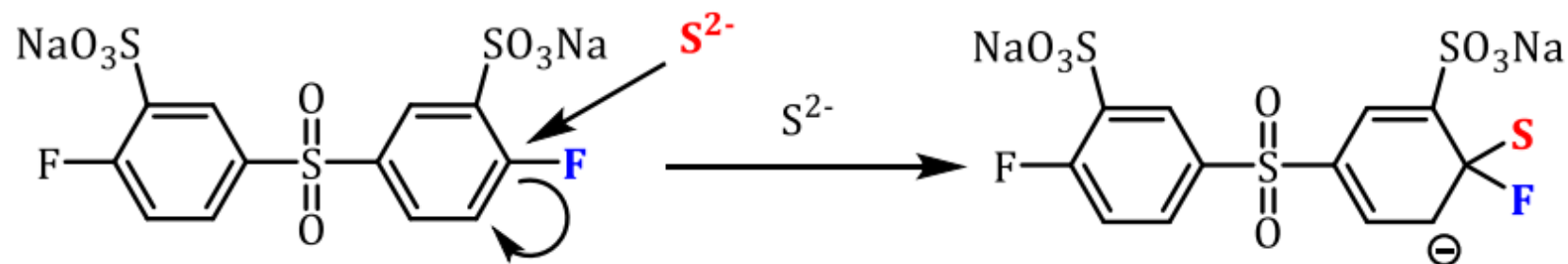




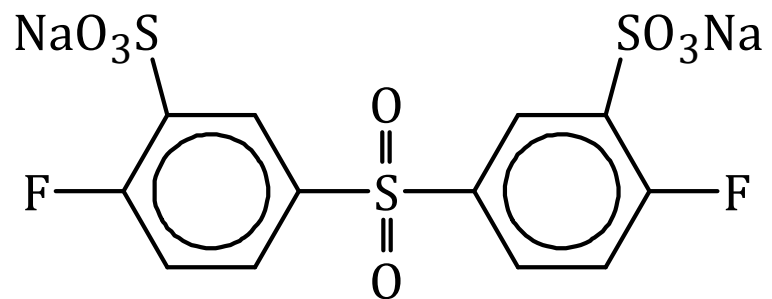
SDFDPS

Synthesis of sPPS-220

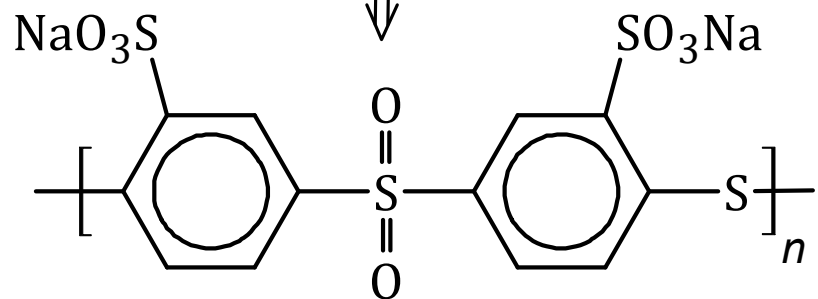
Lithium sulfide-based polycondensation route



Synthesis and Characterization of Novel Ion-Conducting Highly Sulfonated Poly(phenylene sulfone)s for Electrochemical Application. Nodar Dumbadze

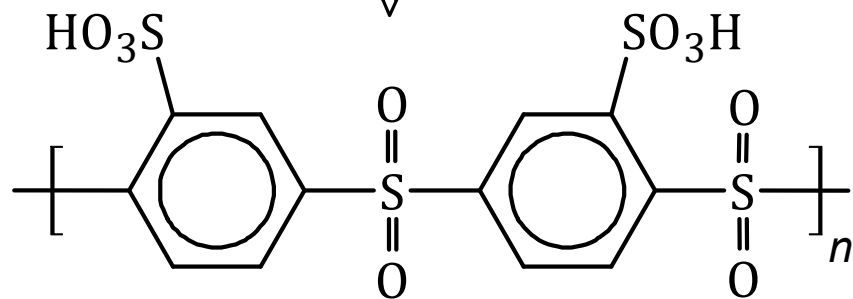


Li_2S



sPPSS-204

H_2O_2



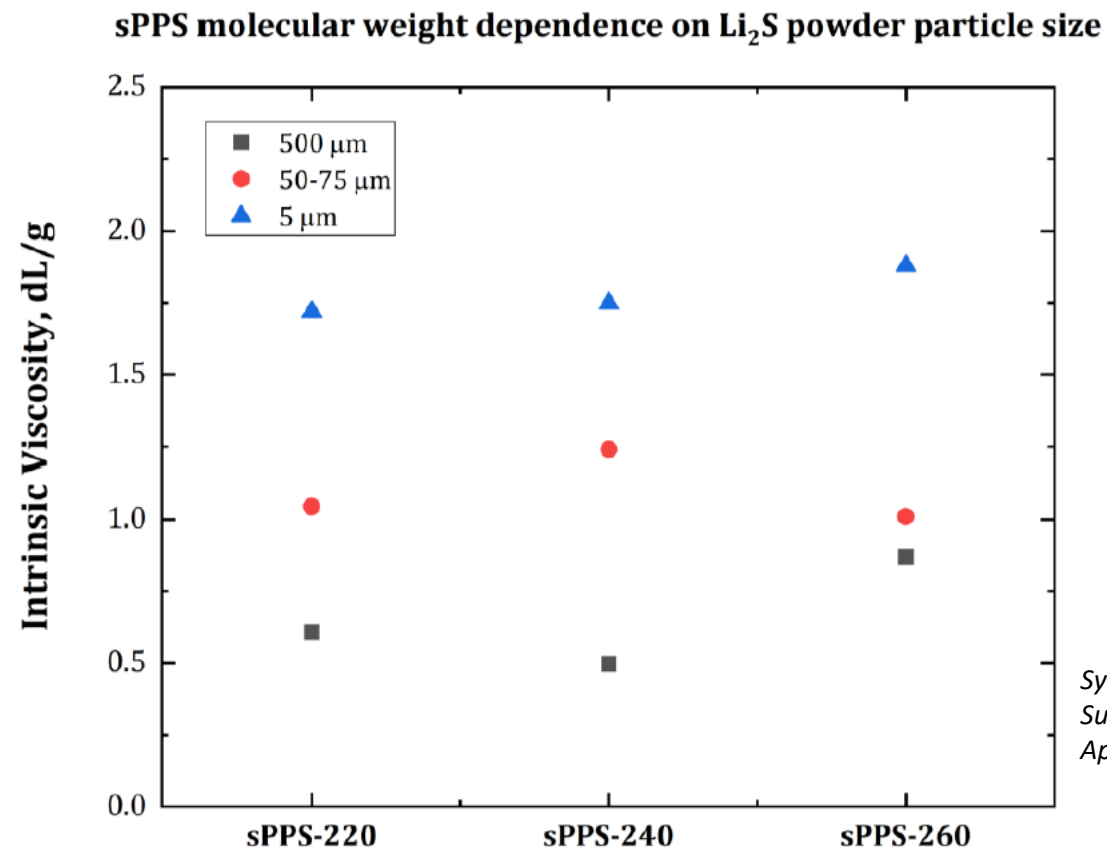
sPPS-220

Synthesis of sulfonated poly(phenylene sulfone) sPPS-220
from sulfonated poly(phenylene sulfide) sPPSS-204

Two-step synthesis

The main challenge of the standard synthetic method

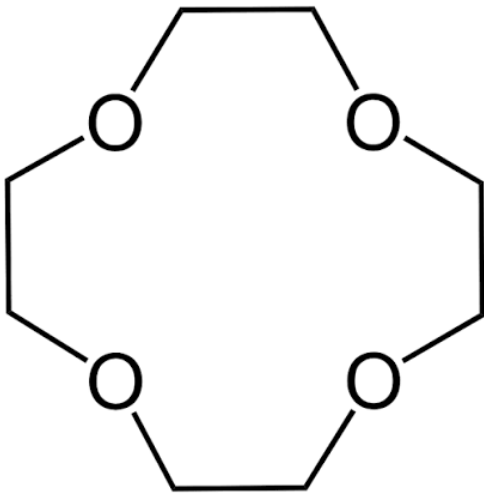
- ❑ the limited solubility of Li_2S in N-methyl-2-pyrrolidone (NMP), which is traditionally used as the polycondensation solvent.
- ❑ **As a result, the reaction proceeds under heterogeneous conditions.**



Synthesis and Characterization of Novel Ion-Conducting Highly Sulfonated Poly(phenylene sulfone)s for Electrochemical Application. Nodar Dumbadze

Graph showing the dependence of sPPS molecular weight on the particle size of lithium sulfide

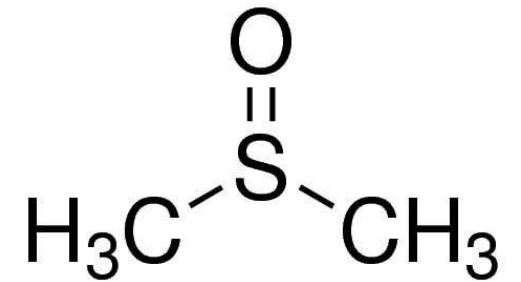
- ❑ To address this problem, coordinating agents can be used to promote the solvation of lithium ions (Li^+) and reduce the ionic interaction between Li^+ and S^{2-}



12-Crown-4



Diglyme



dimethyl sulfoxide

Improving Li_2S Reactivity through the Effect of DMSO

Solvent systems

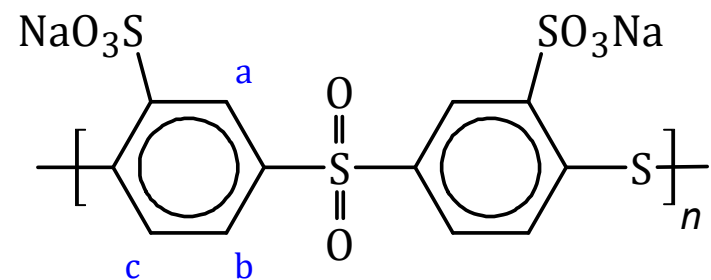
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graph TD; A[Solvent systems] --> B[DMSO]; A --> C[NMP/DMSO]; B --> D[Reactions were carried out at different temperatures (100°C, 120°C, and 140°C)]; C --> E[The DMSO content was 5 and 10 vol%.];
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DMSO

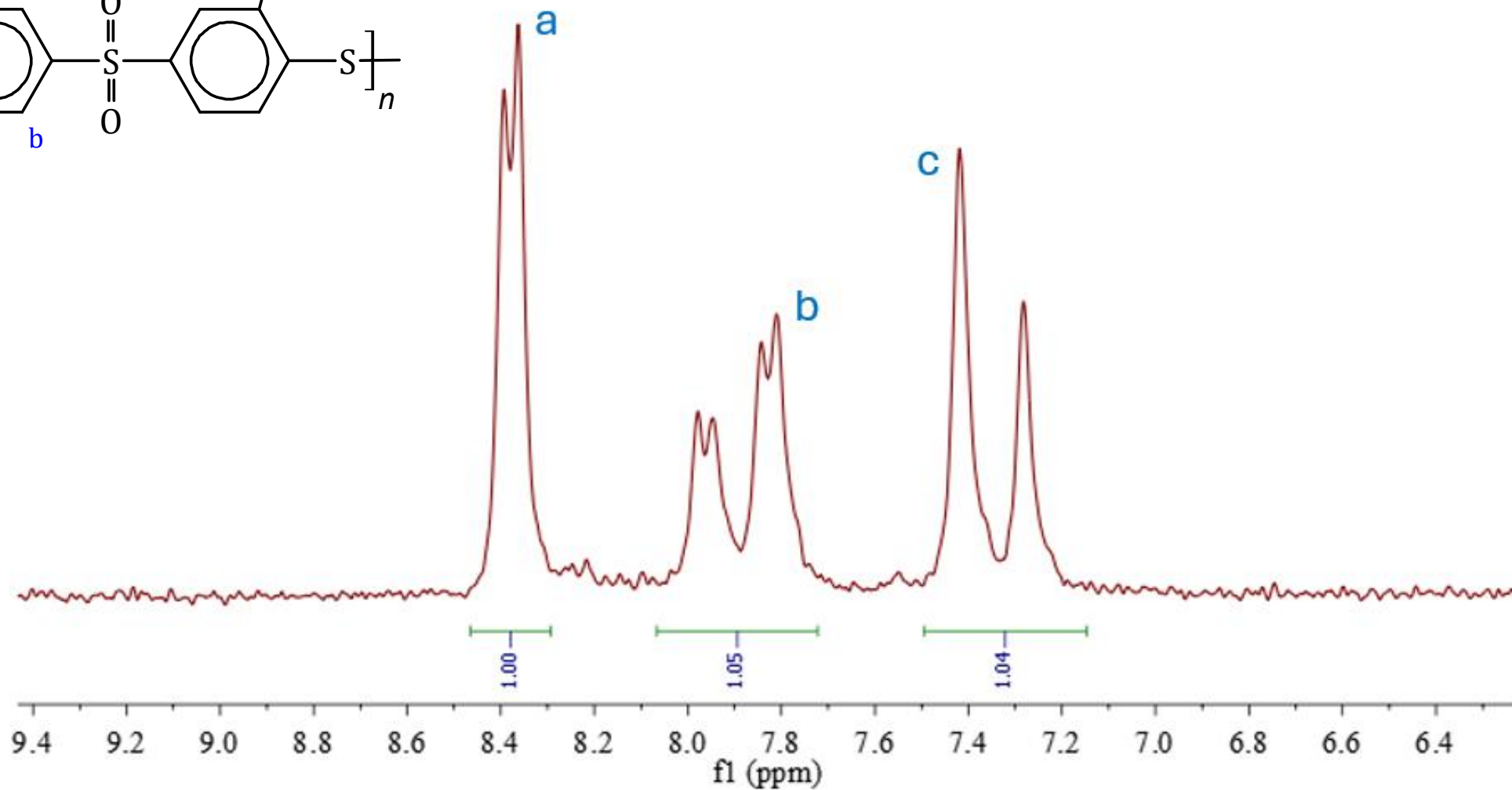
Reactions were carried out at different temperatures (100°C, 120°C, and 140°C)

NMP/DMSO

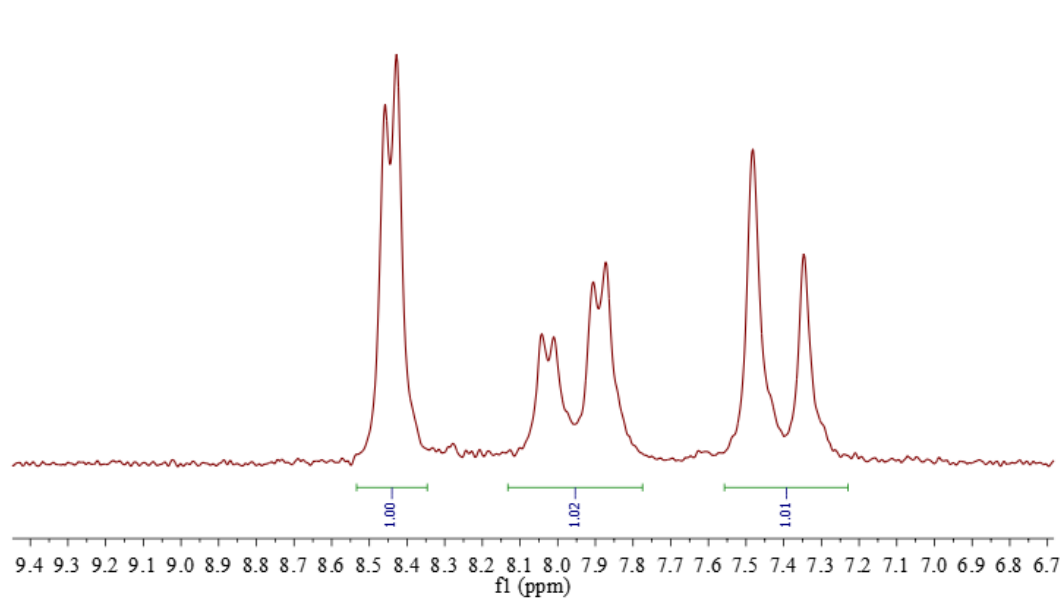
The DMSO content was 5 and 10 vol%.



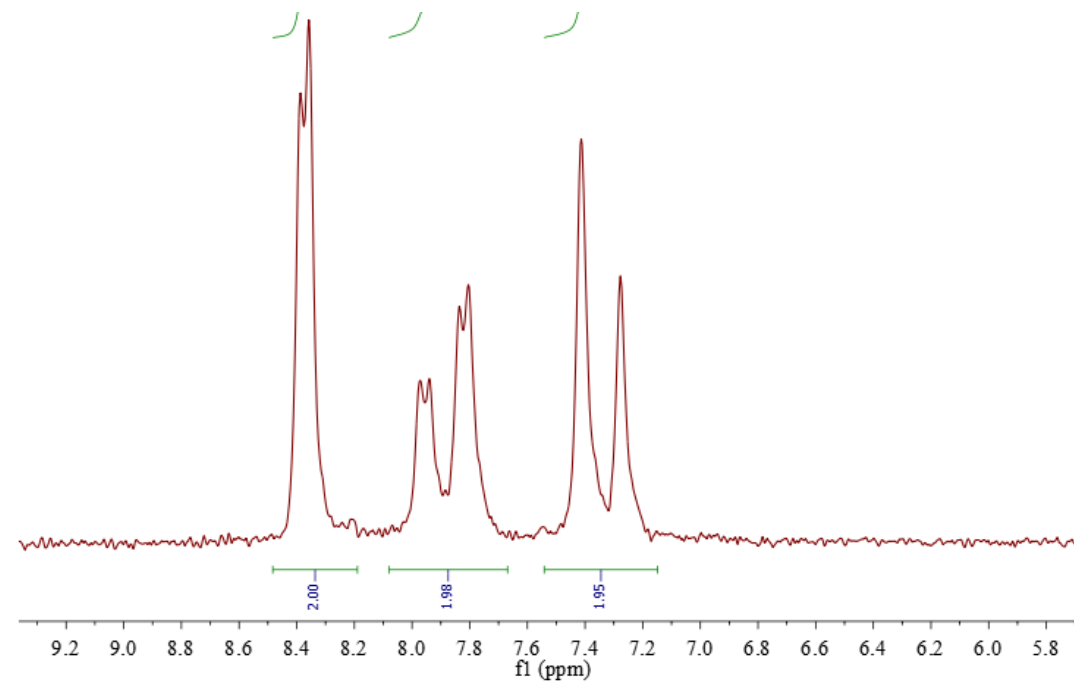
^1H NMR spectrum of sPPSS-204 synthesized at 100°C



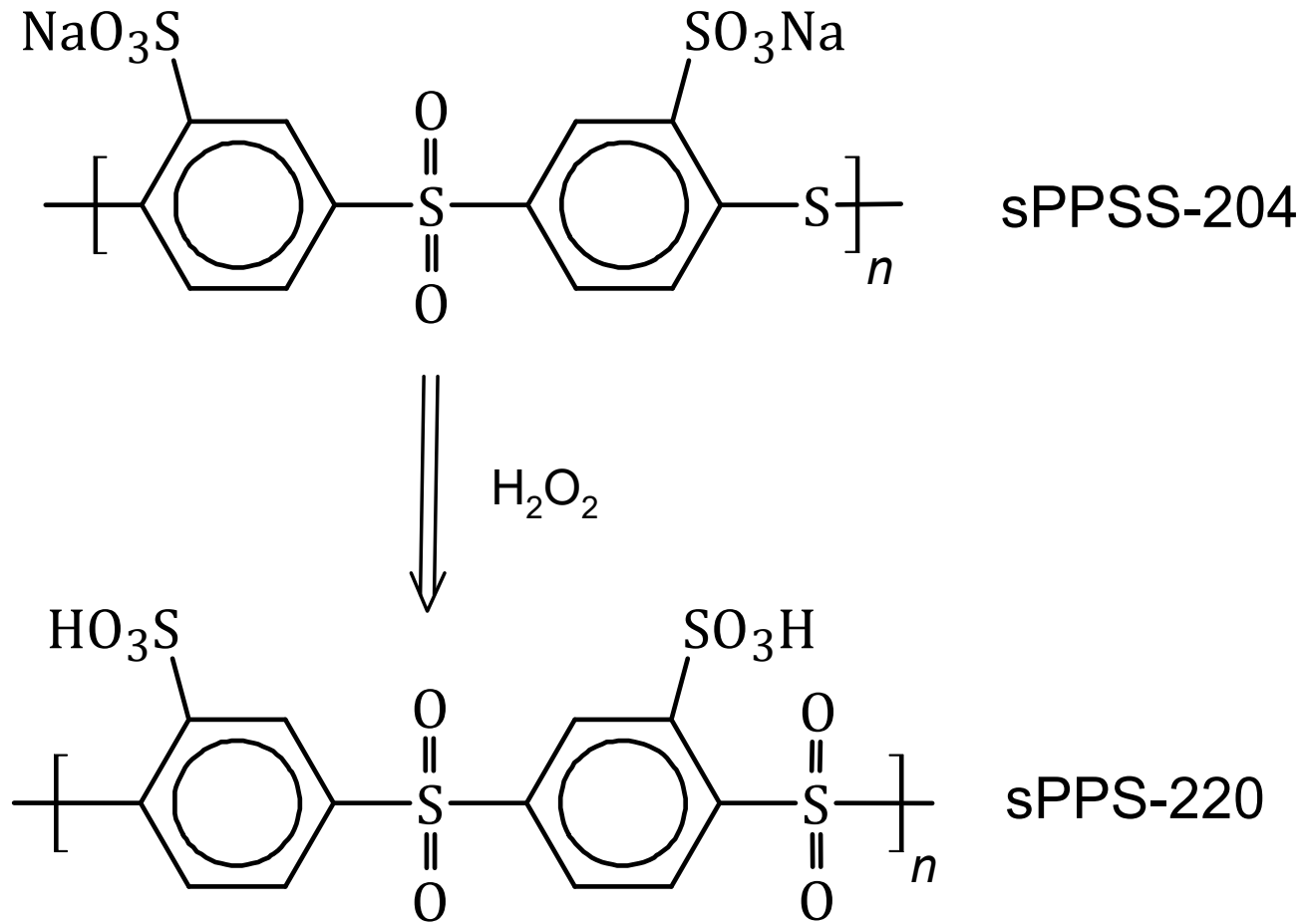
^1H NMR spectrum of sPPSS-204 synthesized at 120°C

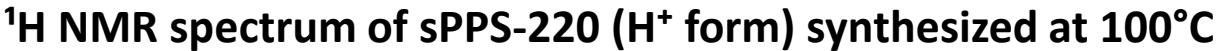


^1H NMR spectrum of sPPSS-204 synthesized at 140°C

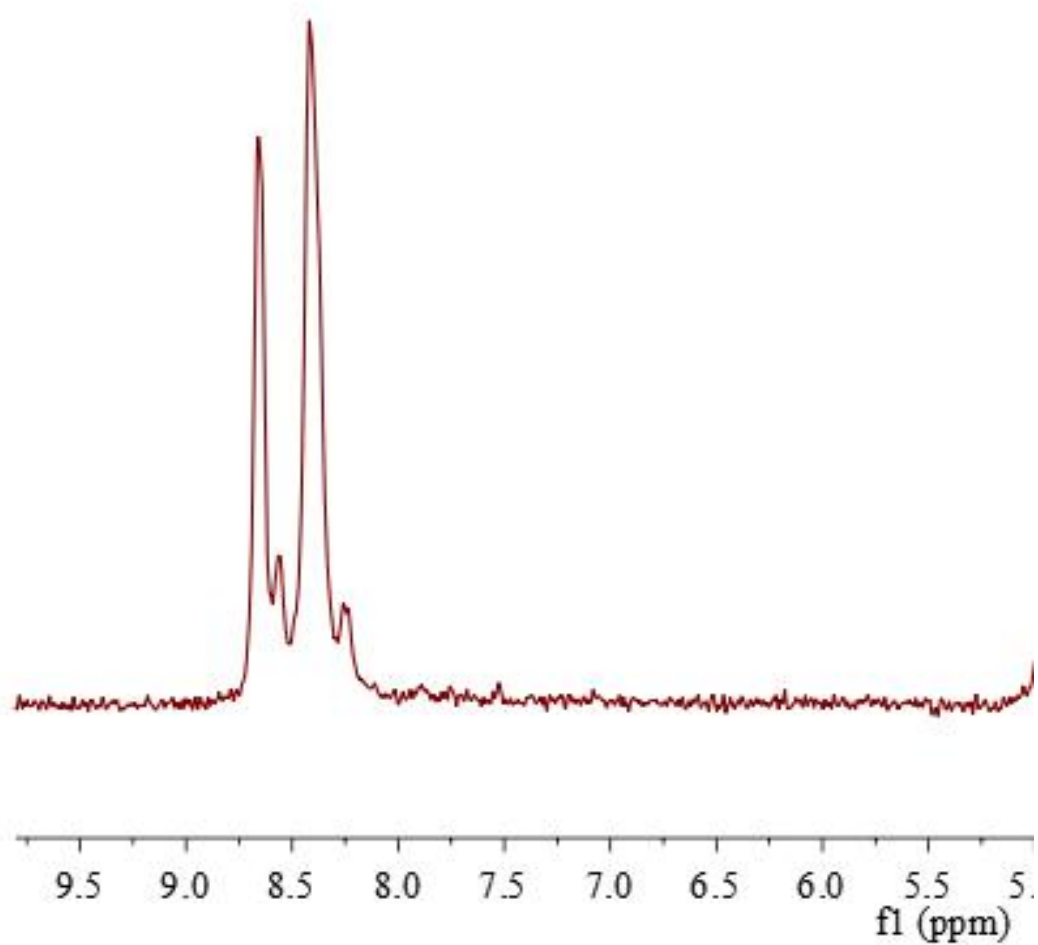


Oxidation of sPPSS-204

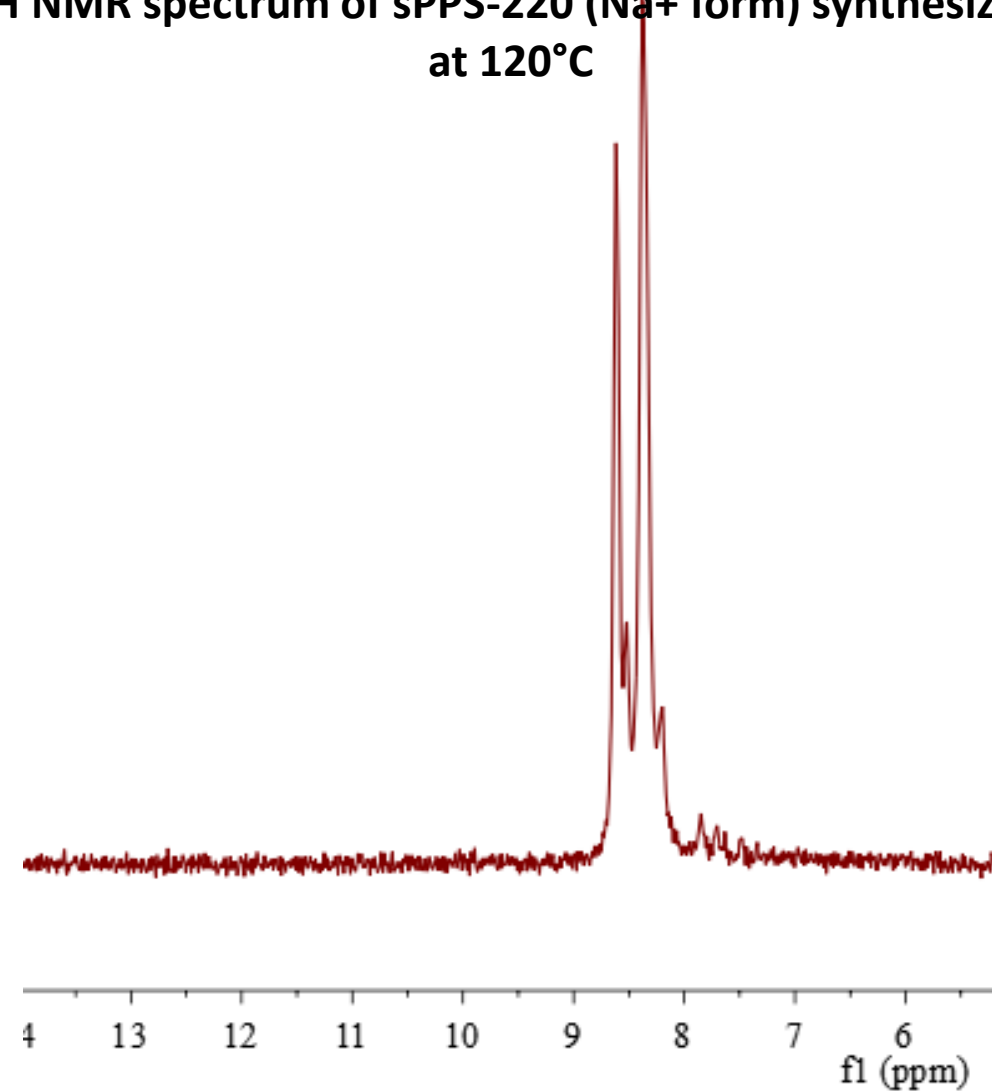




**^1H NMR spectrum of sPPS-220 (Na⁺ form)
synthesized at 140°C**



**^1H NMR spectrum of sPPS-220 (Na⁺ form) synthesized
at 120°C**



Determination of viscosity coefficients

Synthesis temperature	η_{int} Before oxidation	η_{int} after oxidation
100°C	0.41	0.42
120°C	0.48	0.50
140°C	0.58	0.62

Conclusion

- In the present study, strategies for the structural stabilization of sPPS/PBI-based proton-conducting membranes through covalent crosslinking were developed.
- The crosslinking agent 1,4-bis(bromomethyl)benzene was synthesized, and its high purity was confirmed by ^1H NMR spectroscopy. PBI-O crosslinking using p-xylene dibromide was performed by both pre-crosslinking and post-crosslinking methods. The pre-crosslinking approach proved to be particularly effective. It was established that the use of triethylamine in sPPS/PBI-O polymer blends inhibits covalent crosslinking due to competing reactions.
- It was established that the properties of membranes prepared from polymer blends are strongly influenced by the type and molecular characteristics of sPPS. The covalently crosslinked sPPS-380/PBI-O system exhibited the highest stability, maintaining its structural integrity under exposure to a strong solvent and thermal treatment. For the first time, DMSO was successfully used as a solvent for the synthesis of sPPS-220. The reactions were carried out at relatively low temperatures (100°C , 120°C , and 140°C), and no side reactions were observed.

Thank you

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- [11] Atanasov, V., Buerger, M., Wohlfarth, A., Schuster, M., Kreuer, K., & Maier, J. (2011). Highly sulfonated poly(phenylene sulfones): optimization of the polymerization conditions. *Polymer Bulletin*, 68(2), 317–326. <https://doi.org/10.1007/s00289-011-0539-3>