

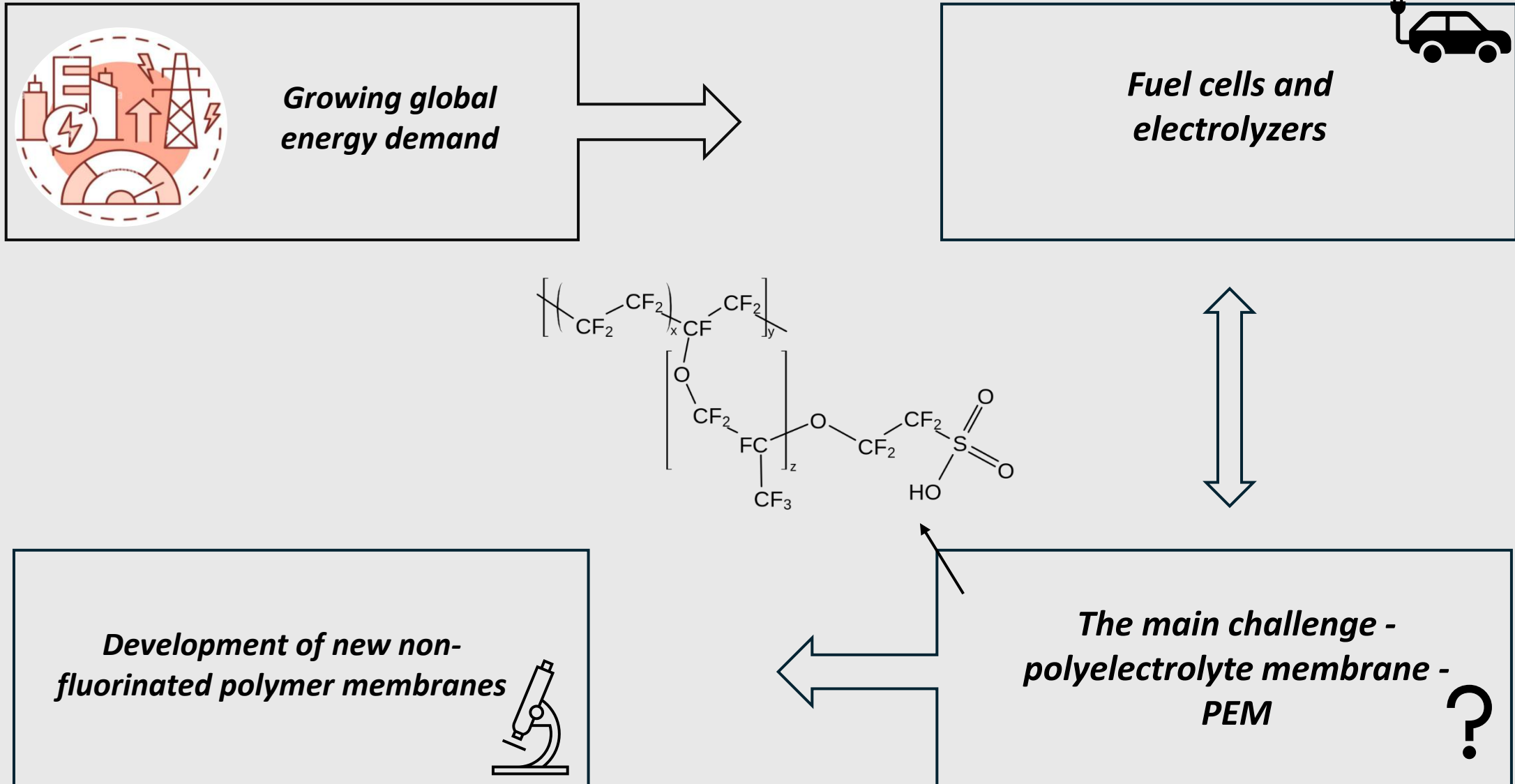
Balancing Mechanical Properties and Chemical Stability in Sulfonated Poly(Phenylene Sulfone)s

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- **Relevance**



Proton Exchange Membranes: PFSA vs Hydrocarbons

High Proton Conductivity

Low Gas Permeability

Low Cost

Mechanical &
Thermochemical Stability

Minimal Swelling

An Ideal PEM



Standard PFSA Membranes (Nafion)



High Cost & Synthesis



High Water Drag



Thermal Limitations



Sulfonated Hydrocarbon Alternatives (sPPS)



Economical: Lower manufacturing costs



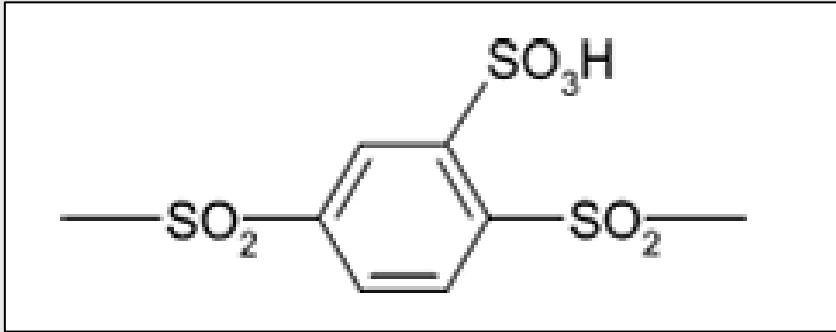
Reduced Crossover: Low fuel permeability



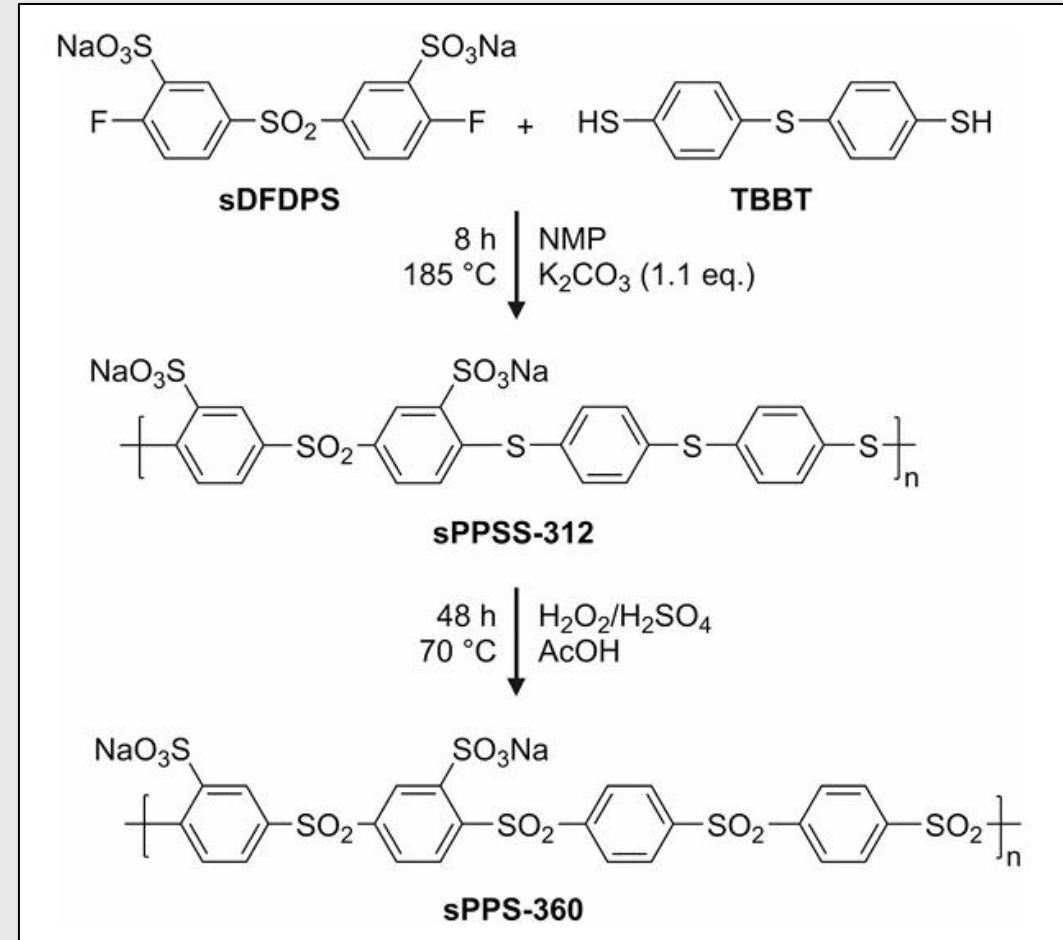
High Durability

Proton Exchange Membranes: PFSA vs Hydrocarbon Alternatives

Strong Electron-Withdrawing Sulfone ($-\text{SO}_2-$) $\rightarrow$ $\left\{ \begin{array}{l} \downarrow \text{Aromatic Ring Density} \rightarrow \uparrow \text{Hydrolytic Stability} \\ \uparrow \text{Acid Strength} (\downarrow \text{p}K_a) \rightarrow \uparrow \text{Proton Dissociation at Low RH} \end{array} \right.$



Structural Advantages of Sulfonated Poly(phenylene sulfone)s (sPPS)



Project Objective

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- *Obtaining microblock fragments by Fidell-Crafts synthesis*
- Checking the purity of monomers

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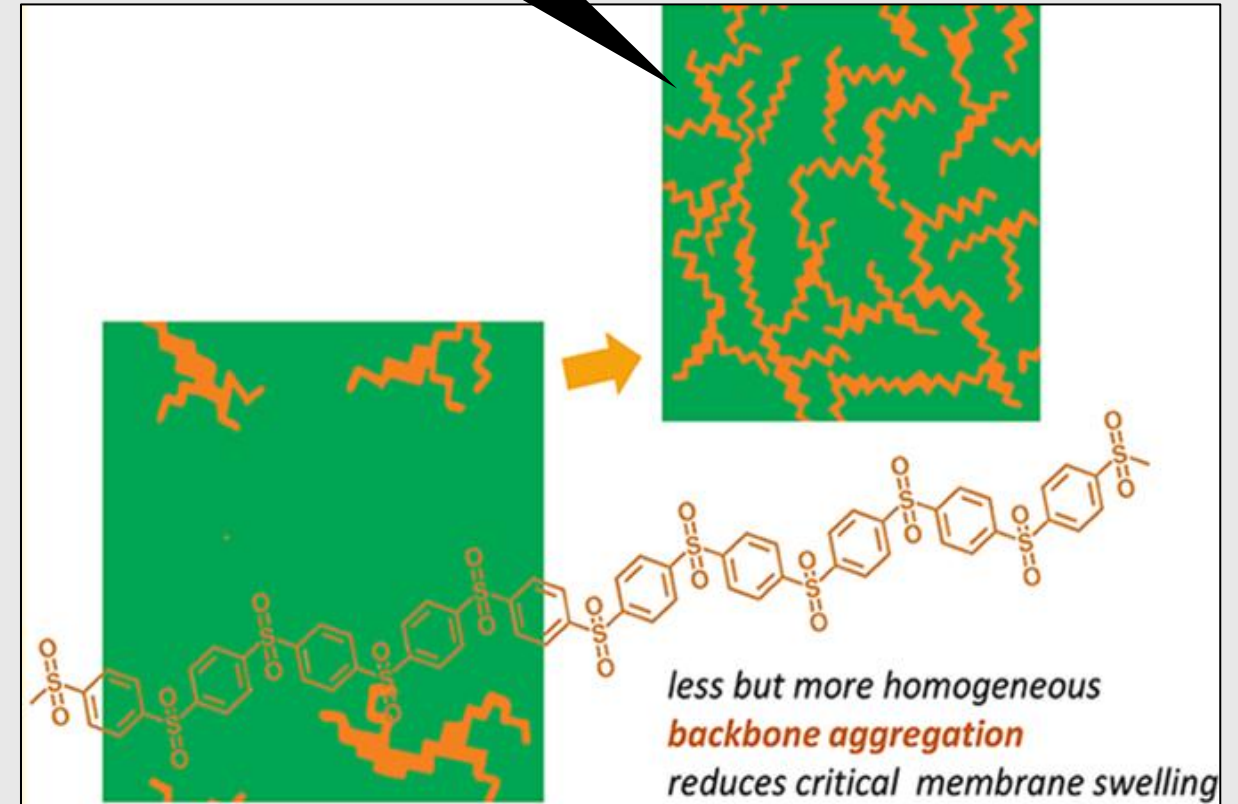
- polymer synthesis
- thermal crosslinking
- analysis of the targeted membrane properties

The PEM Dilemma: IEC vs Mechanical Stability

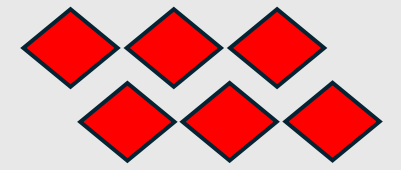
High Ionic Content ($\uparrow$ IEC) $\xrightarrow{\text{Excessive Hydration}}$ $\uparrow$ Water Uptake & Swelling $\rightarrow$ Mechanical Failure

Multiblock Copolymers:

- **Benefit:** Nano-phase-separated domains $\rightarrow$ **High Proton Conductivity**
- **Drawbacks:**
 - Multi-step synthesis
 - Complex phase-segregation control
 - **Result:** Major processing challenges



Microblock Strategy: Sequence-Controlled PEMs

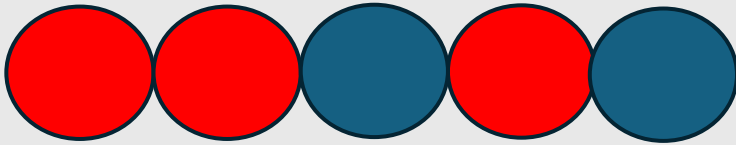


Sequence Engineering via Pre-Assembled Monomers

[Hydrophobic Fragment] — [Hydrophilic Domain] — [Hydrophobic Fragment]

• Random Sulfonation (Standard):

– [Sulfonated] – [Sulfonated] – [Non-Sulfonated] – [Sulfonated] – [Non-Sulfonated] –



Intermolecular Packing

- Extended hydrophobic fragments align & pack tightly
- Strong π – π stacking & van der Waals forces established
- Serves as **physical crosslinks**

Microblock

- Shorter block lengths
- Nano-phase separation is suppressed
- Continuous ionic channels are restricted

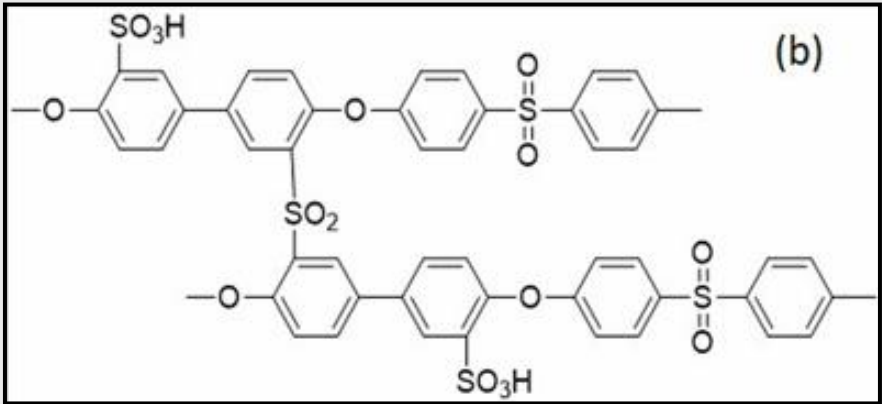
• Microblock-Controlled Sequence:

–[Non-Sulfonated Block] – [Sulfonated Segment] – [Non-Sulfonated Block] ---



The Thermal Crosslinking Mechanism

Solid Polymer Film $\xrightarrow{\Delta T \text{ (Elevated Temperature)}}$ Interchain Sulfone / Covalent Linkages



[Un-crosslinked Chains]

~~~~~ SO<sub>3</sub>H ~~~~~

~~~~~ SO<sub>3</sub>H ~~~~~

(High swelling)

[Thermally Crosslinked Network]

~~~~~ SO<sub>3</sub>H ~~~~~

Heat  
| (Covalent Bond)

~~~~~ SO<sub>3</sub>H ~~~~~

(Restricted mobility, compact)

Covalent Interchain Links $\rightarrow$ $\downarrow$ Conformational Freedom $\rightarrow$ $\left\{ \begin{array}{l} \downarrow \text{Water Uptake \& Swelling} \\ \uparrow \text{Mechanical Strength \& Stability} \end{array} \right.$

The Dual Functional Requirement

Thermal Crosslinking Activation $\Leftrightarrow$ Reaction Pair Required: $\left\{ \begin{array}{l} 1. \text{ Thermally Labile} - \text{SO}_3\text{H Groups} \\ 2. \text{ Electron-Rich Aromatic Rings} \end{array} \right.$

Standard sPPS Backbone $\xrightarrow{\text{Strongly Withdrawing } -\text{SO}_2- \text{ Groups}}$ Electron-Deficient Phenyl Rings



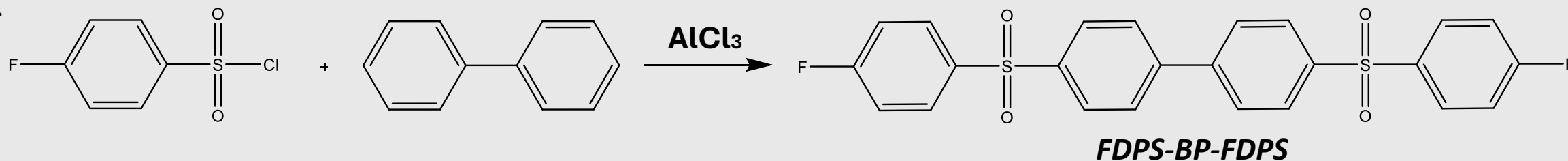
Lacks BOTH Reactive Groups $\rightarrow$ Incapable of Direct Thermal Crosslinking



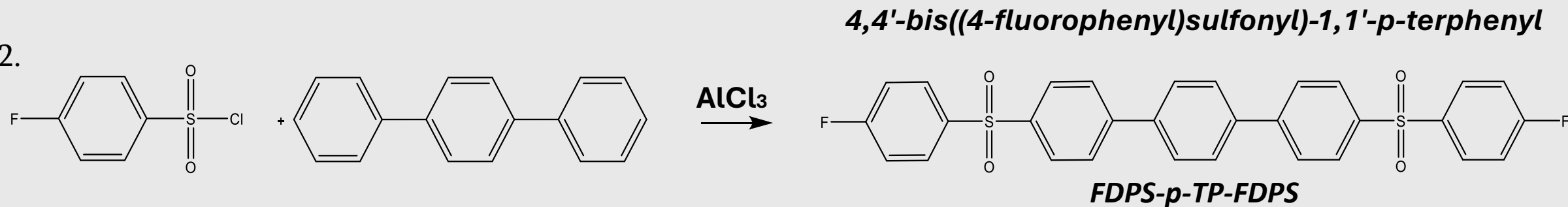
Strategy: Targeted introduction of active moieties into sPPS backbone $\rightarrow$ Enables Thermal Crosslinking

Monomers

1.



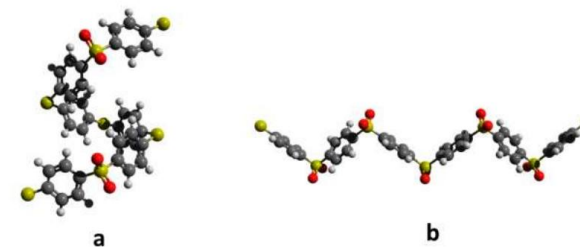
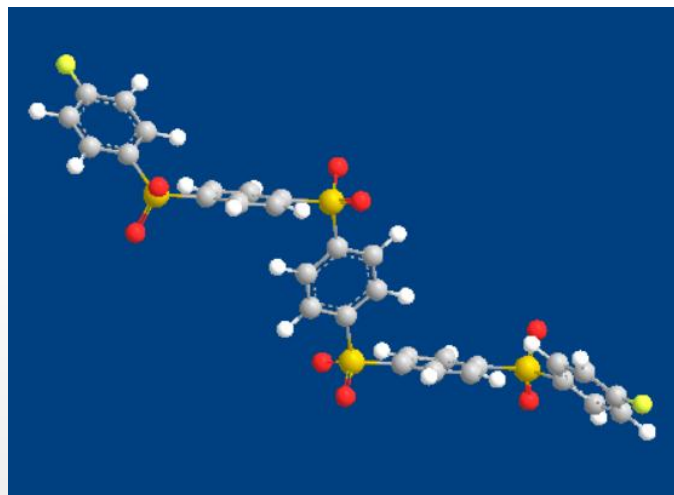
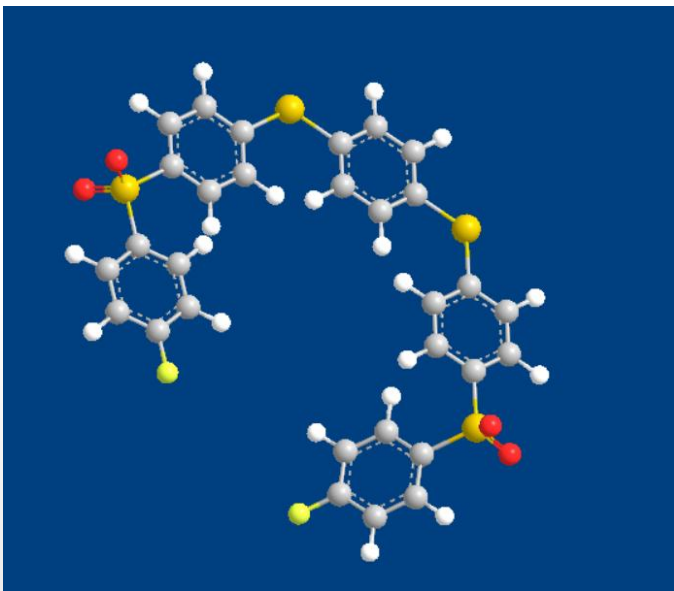
2.



[1] [2].N. David E. Knox (Matawan, „Sulfonated aromatic poly(arylene ether) ion exchange polymers“. United States 5081306, 14 jan 1994.

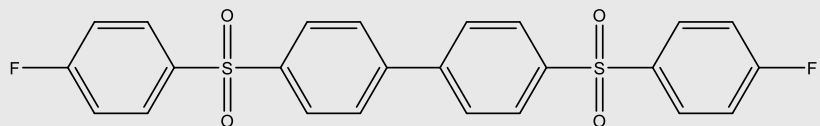
N.Dumbadze - Synthesis and Characterization of Novel Ion-Conducting Highly Sulfonated Poly(phenylene sulfone)s for Electrochemical Application, PhD, Agricultural University of Georgia Tbilisi, 2025.

'open book' structure



Description/ purity

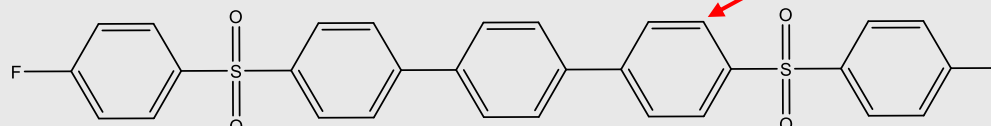
FDPS-BP-FDPS



- *Washing - with HCl, deionized water, MeOH*
- $T = 266.6 - 267.4\text{ }^{\circ}\text{C}$
- yield 62%

ortho-substitution

FDPS-p-TP-FDPS

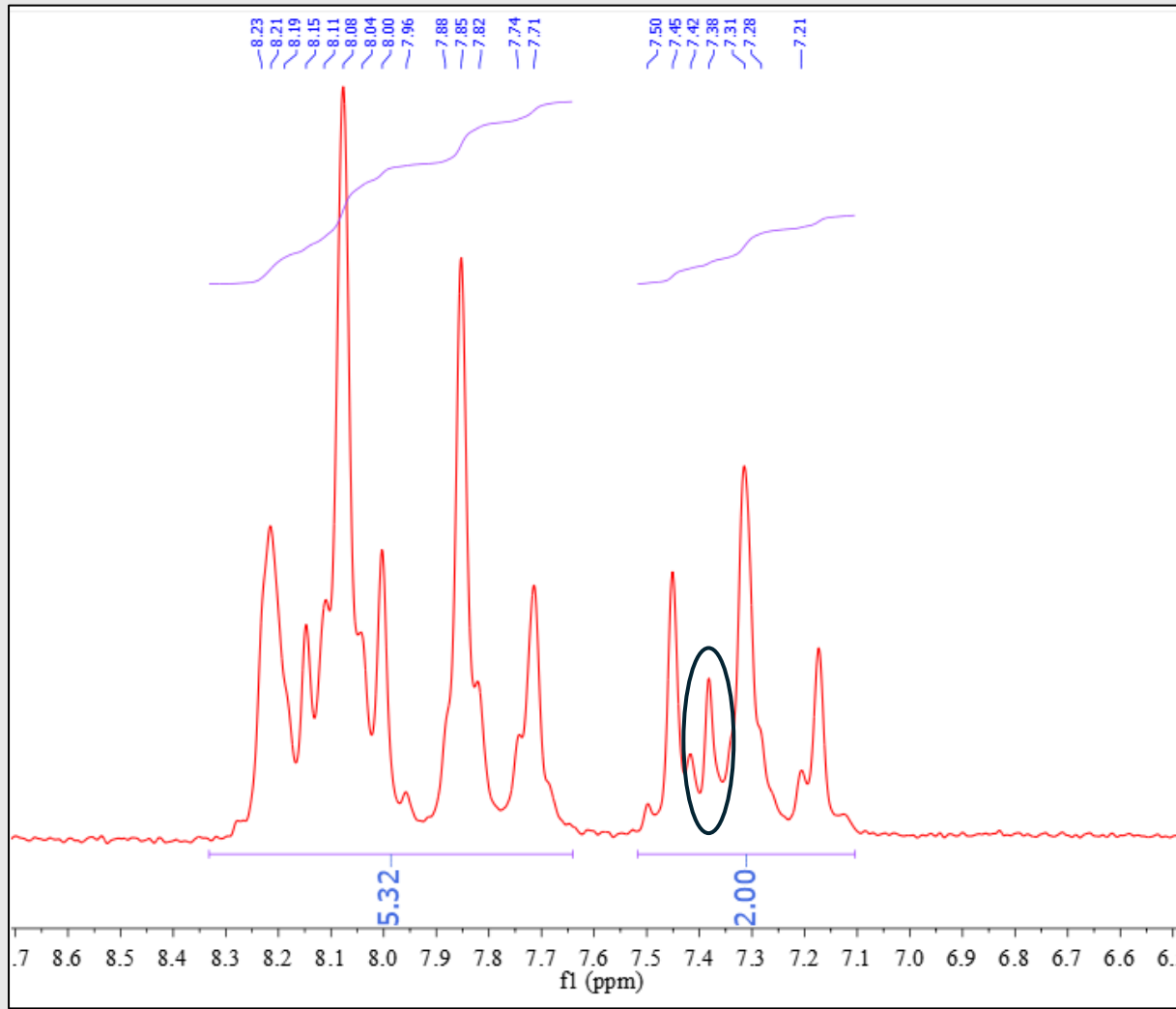


| solvent | Acetone | NMP | Chloroform | Acetonitrile | DMAc | DMSO | DMF |
|------------|---------|-----|------------|--------------|------|------|-----|
| Solubility | - | + | - | - | - | + | + |

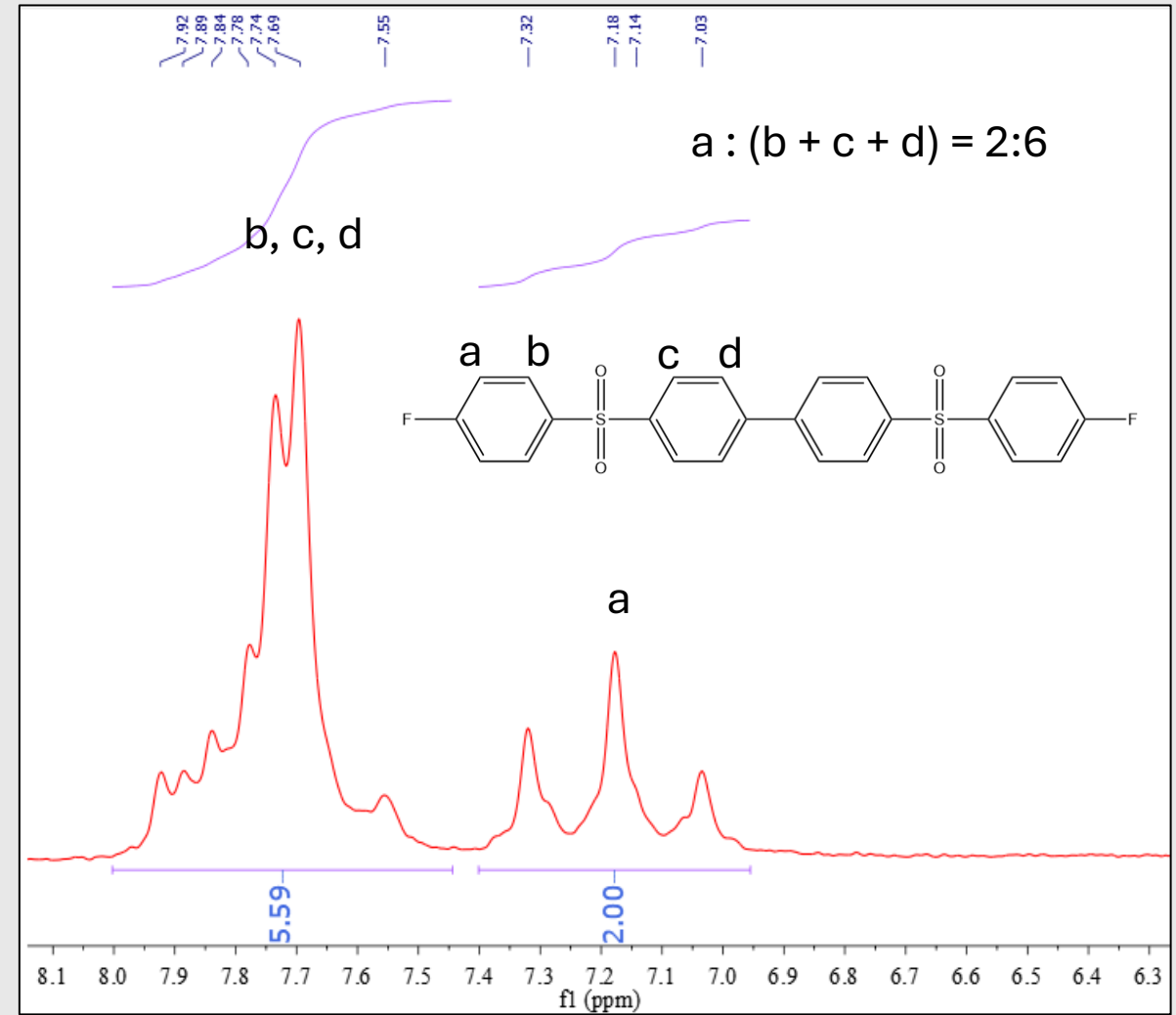
Solubility of FDPS-p-TP-FDPS in various solvents

- **Washing in a Soxhlet apparatus**
- **Purity check by thin layer chromatography**
- **Yield 73.5%**

NMR spectrum

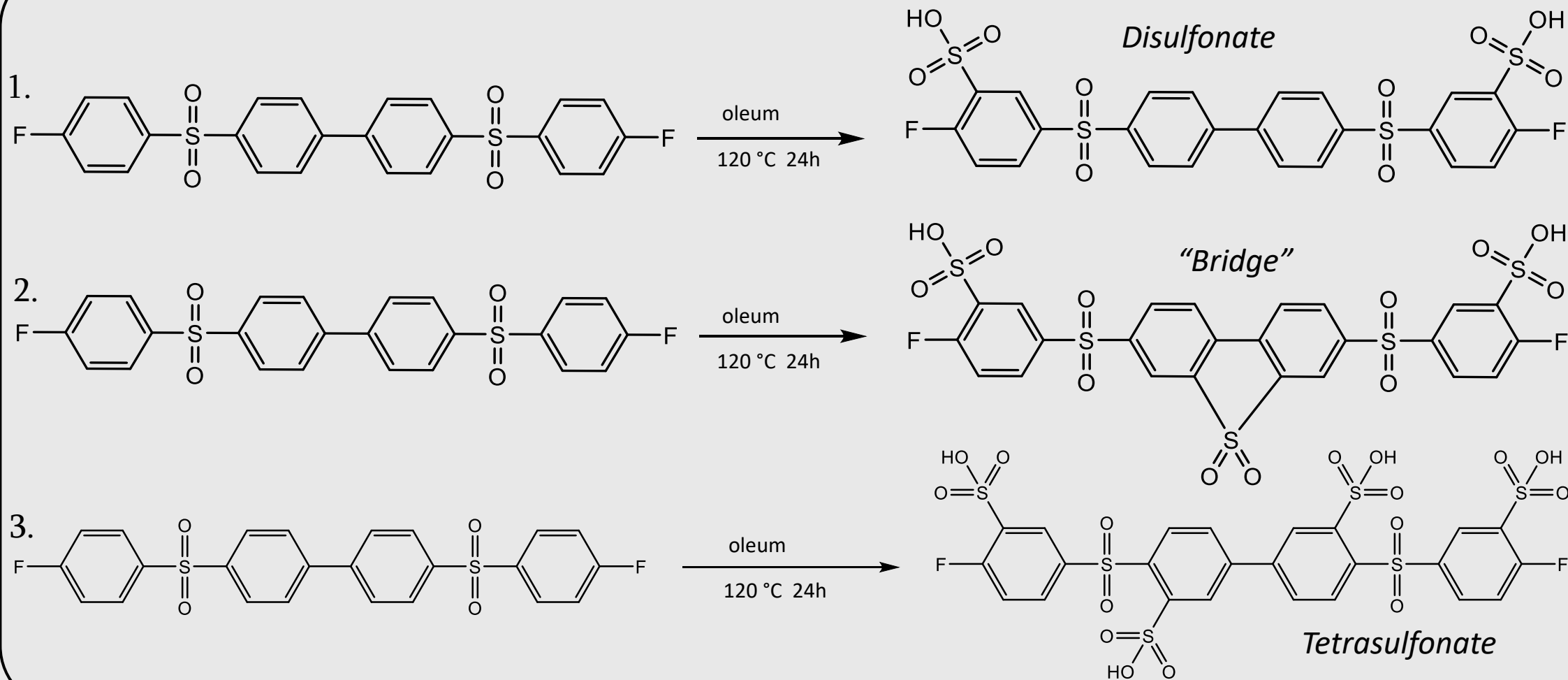


¹H NMR spectrum of FDPS-BP-FDPS after recrystallization from chloroform (CDH₃)



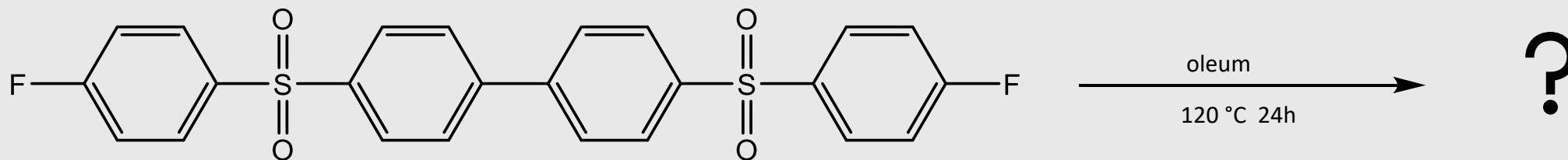
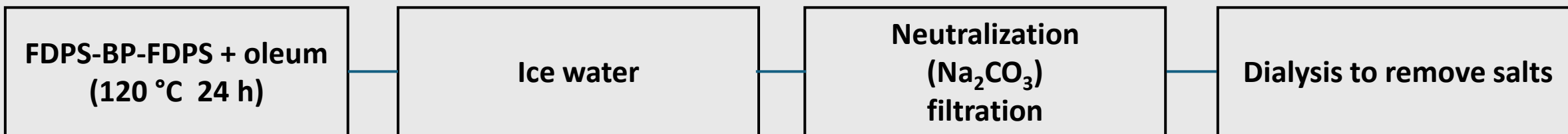
¹H NMR spectrum of FDPS-BP-FDPS after recrystallization from toluene (DMSO – d₆)

sulfonation

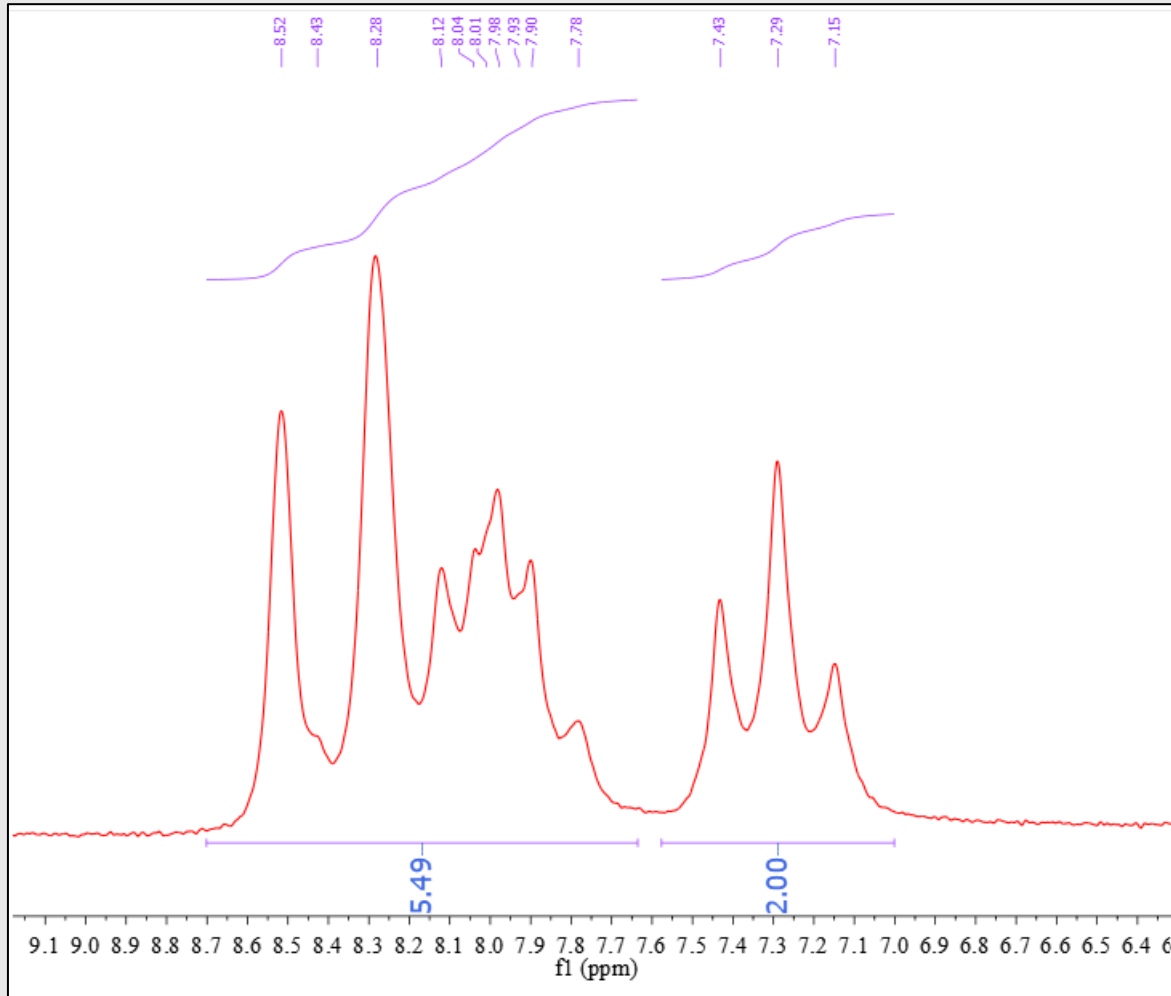


The synthetic route

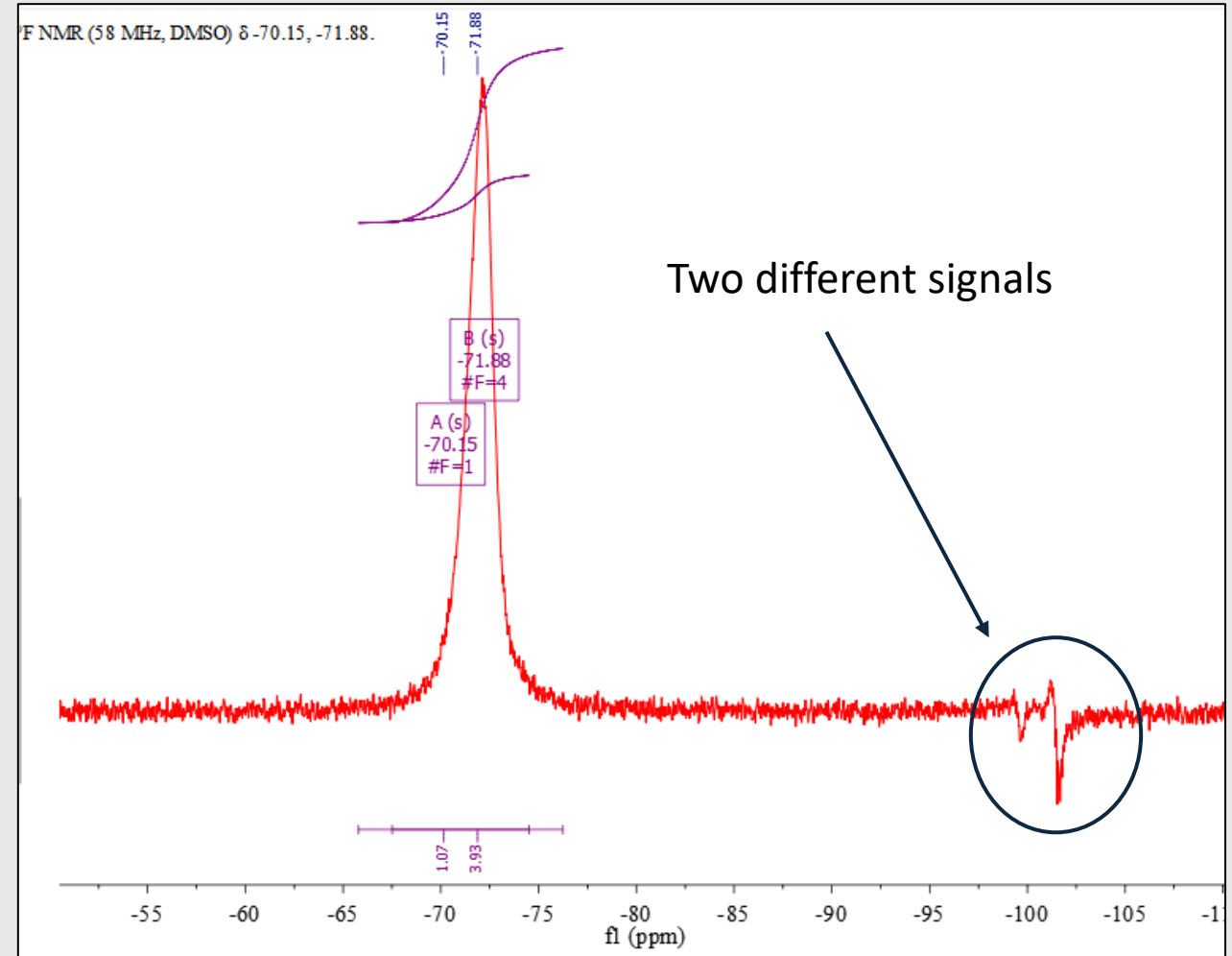
obtaining the sulfonated FDPS-BP-FDPS product



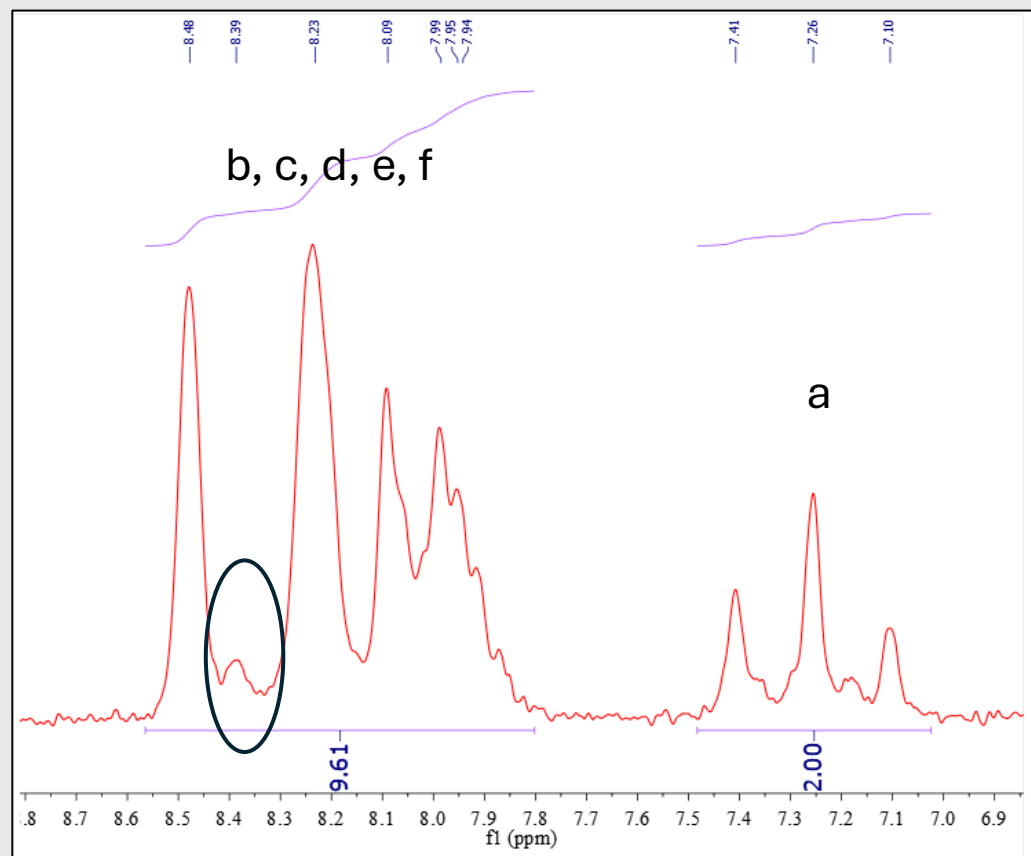
NMR spectrum



^1H NMR spectrum of sulfated FDPS-BP-FDPS (DMSO- d_6) #1



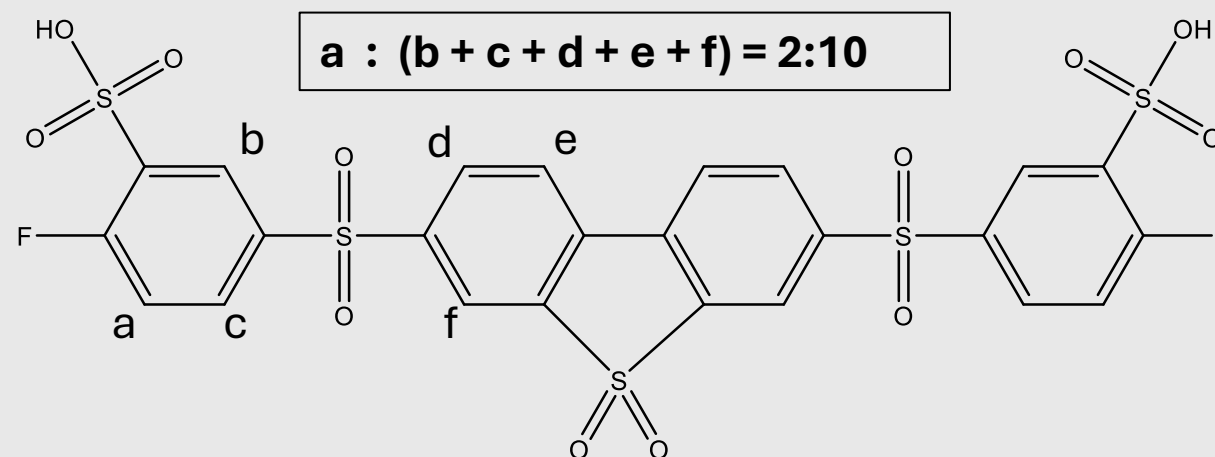
^{19}F NMR spectrum of FDPS-BP-FDPS

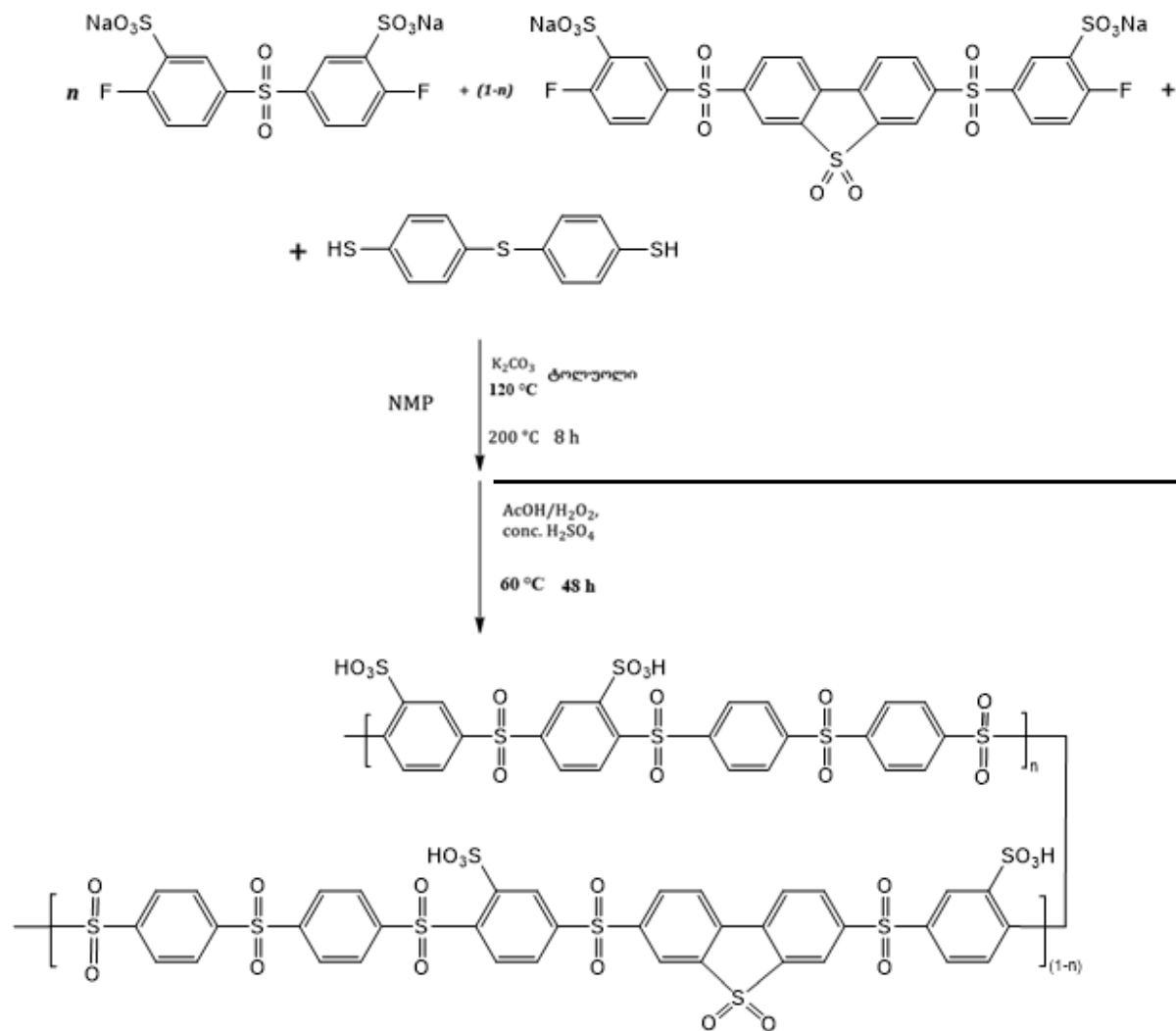


^1H NMR spectrum of bridged sulfated FDPS-BP-FDPS (DMSO- d_6) #2

| solvent | Toluene | Ethyl acetate | i-PrOH | Acetonitrile | DMAc | Methanol | Ethanol |
|------------|---------|---------------|--------|--------------|------|----------|---------|
| solubility | — | — | — | — | + | + | — |

Solubility of bridged sulfated FDPS-BP-FDPS in various solvents

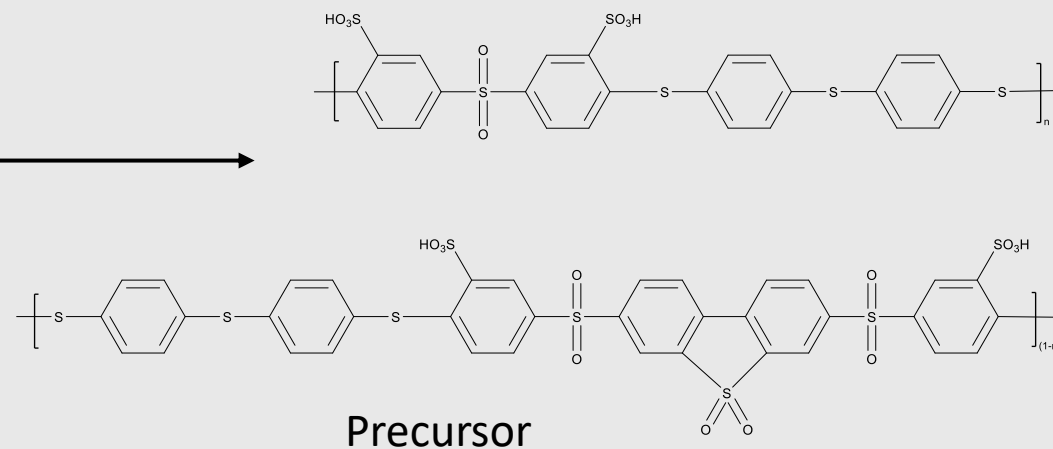




Synthesis scheme of sPPS-400-p-TP-XXL

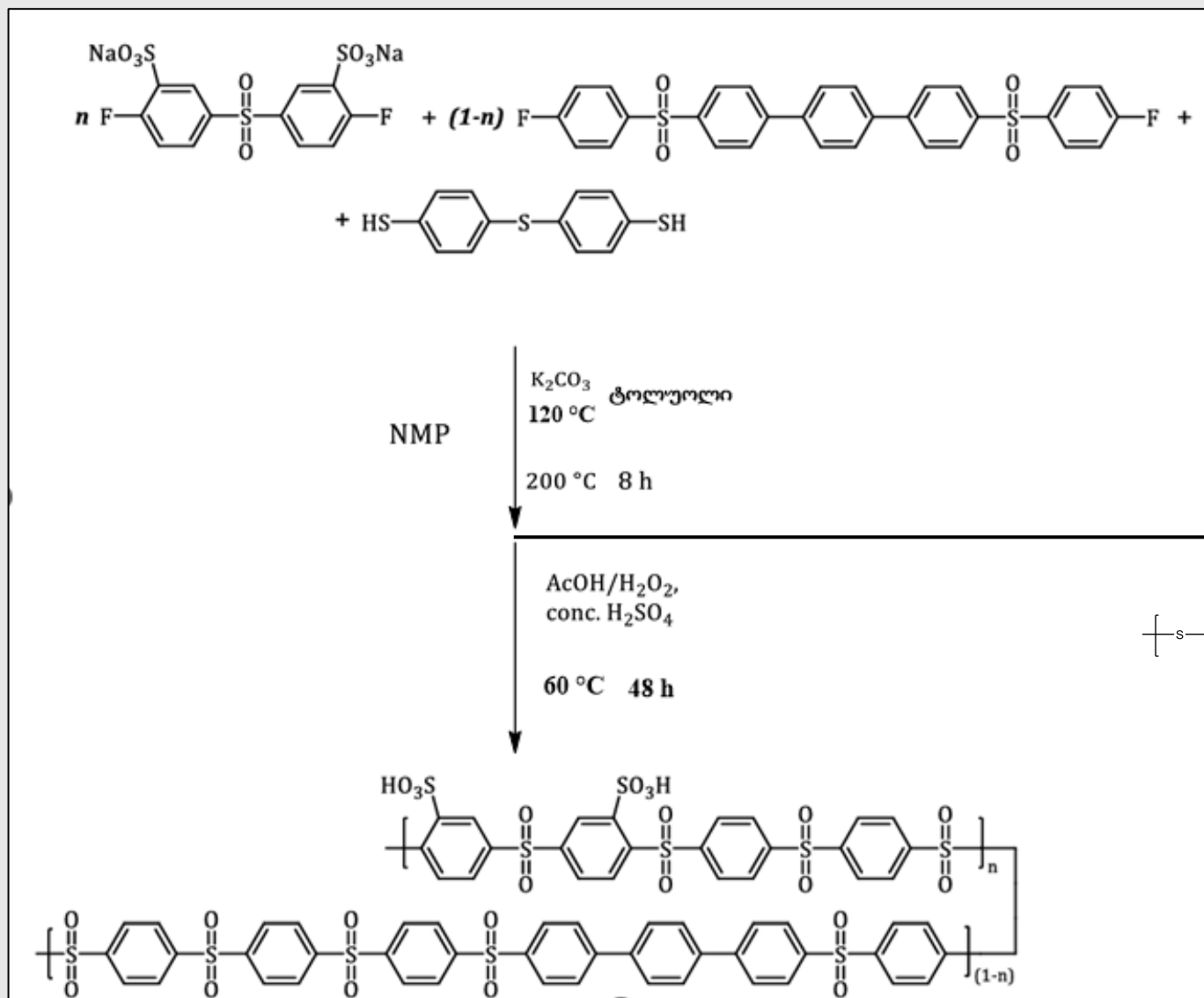
$EW = 400$ $n = 0.5319$ $(1-n) = 0.4681$

Theoretically calculated ion exchange capacity (IEC) - 2.5 mmol·eq./g.



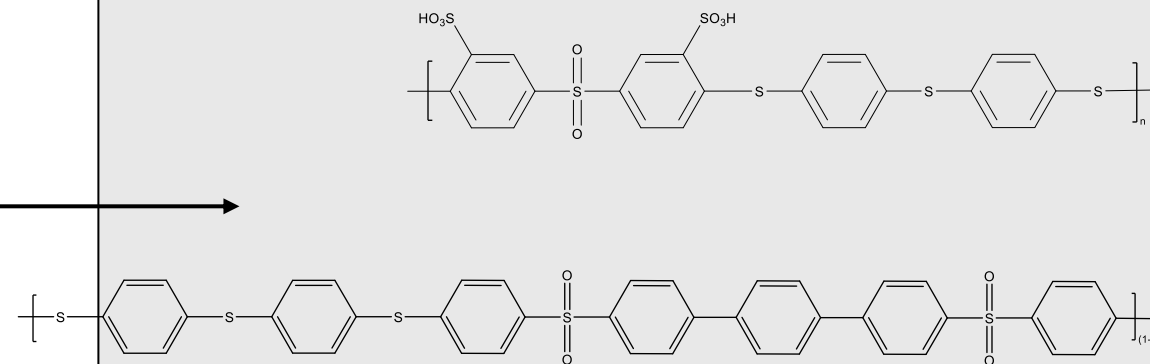
- The practical ion-exchange capacity was determined via titration

Polymers



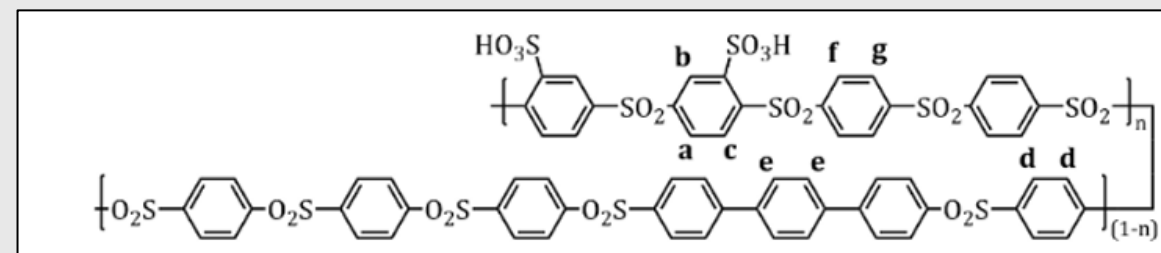
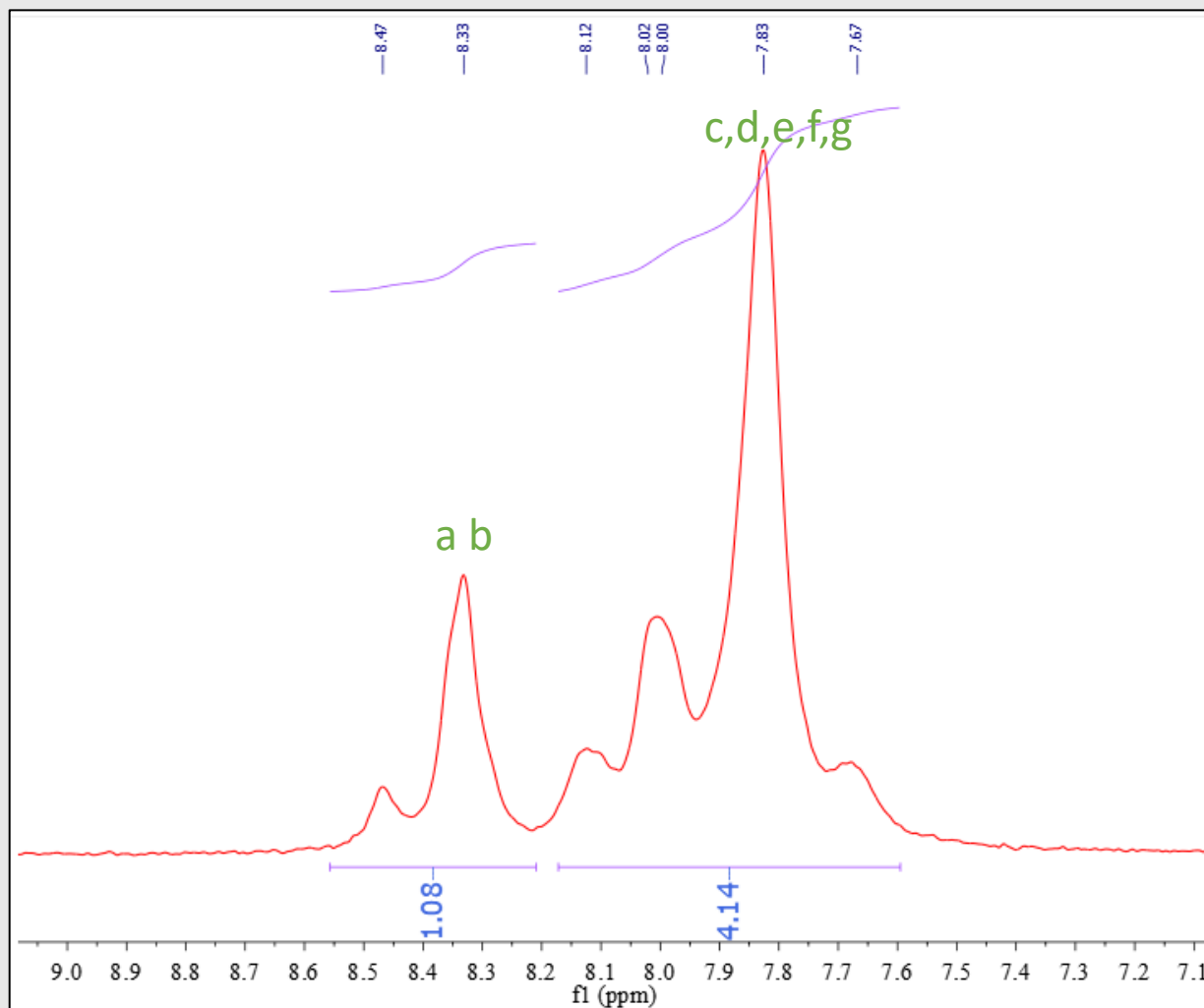
Synthesis scheme of sPPS-400-p-TP XXL

EW = 400 $n = 0.915$ $(1-n) = 0.085$



Precursor

NMR spectrum



***^1H NMR spectrum of sPPS-400-p-TP-XXL
(DMSO- d_6)***

- The practical ion-exchange capacity was determined via titration

Summary data

Summary data of sPPS-400-sBP-XXL

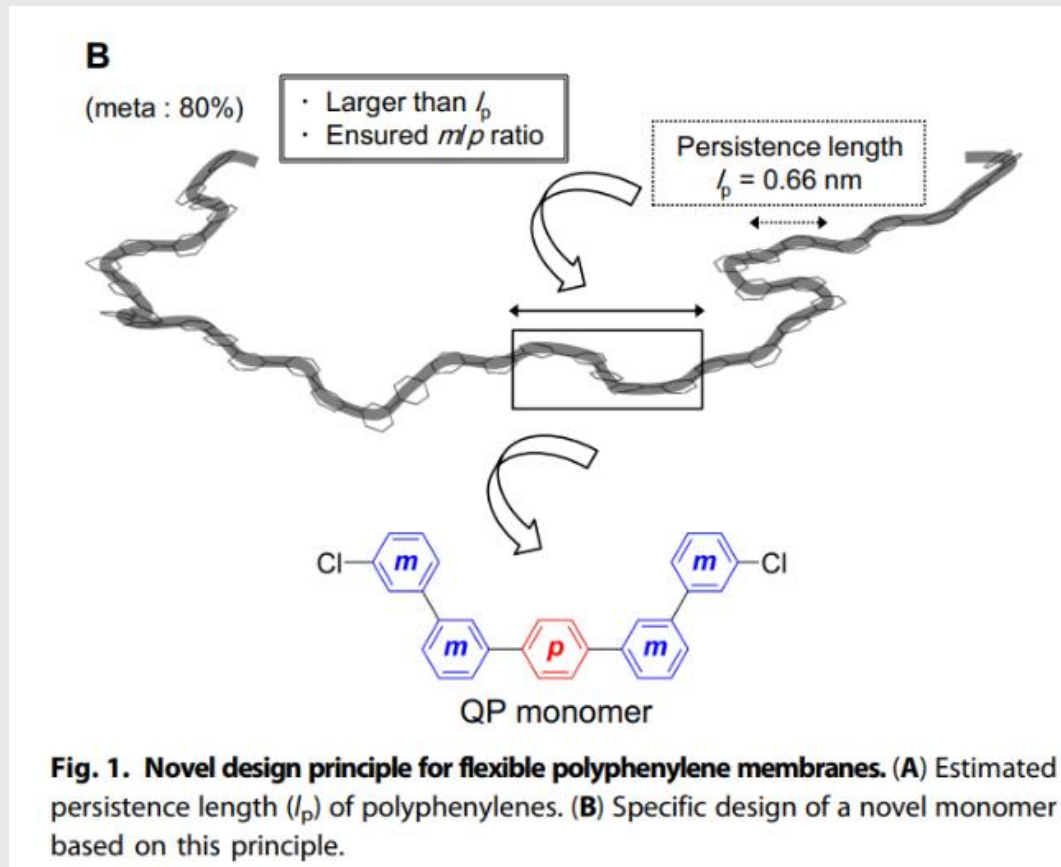
| Sample | IEC
(Theoretical) | IEC
(Practical) | Film
forming
ability | η_{int}
After
oxidation |
|----------------------|----------------------|--------------------|----------------------------|------------------------------------|
| sPPS-400-sBP-
XXL | 2.5 | 2.36 | x | 0.33 |

Summary data of sPPS-400-p-TP-XXL

| Sample | IEC
(Theoretical) | IEC
(Practical) | Film
forming
ability | λ_p
(80°C) | η_{int}
unoxidised | η_{int}
After oxidation |
|-----------------------|----------------------|--------------------|----------------------------|-----------------------|----------------------------|---------------------------------|
| sPPS-400-p-TP-
XXL | 2.5 | 2.38 | √ | 36.20 | 1.36 | 1.45 |

All-Aromatic Backbone $\xrightarrow{\text{Strong C-C Bonds}}$ Exceptional Thermal & Fenton Oxidative Stability

180° Poly(*p*-phenylene) Alignment $\rightarrow$ Rigid Rod Conformation $\rightarrow$ $\left\{ \begin{array}{l} \text{No Chain Entanglement} \\ \text{Extreme Mechanical Brittleness} \\ \text{Membrane Cracking Under Stress} \end{array} \right.$



• Outlook

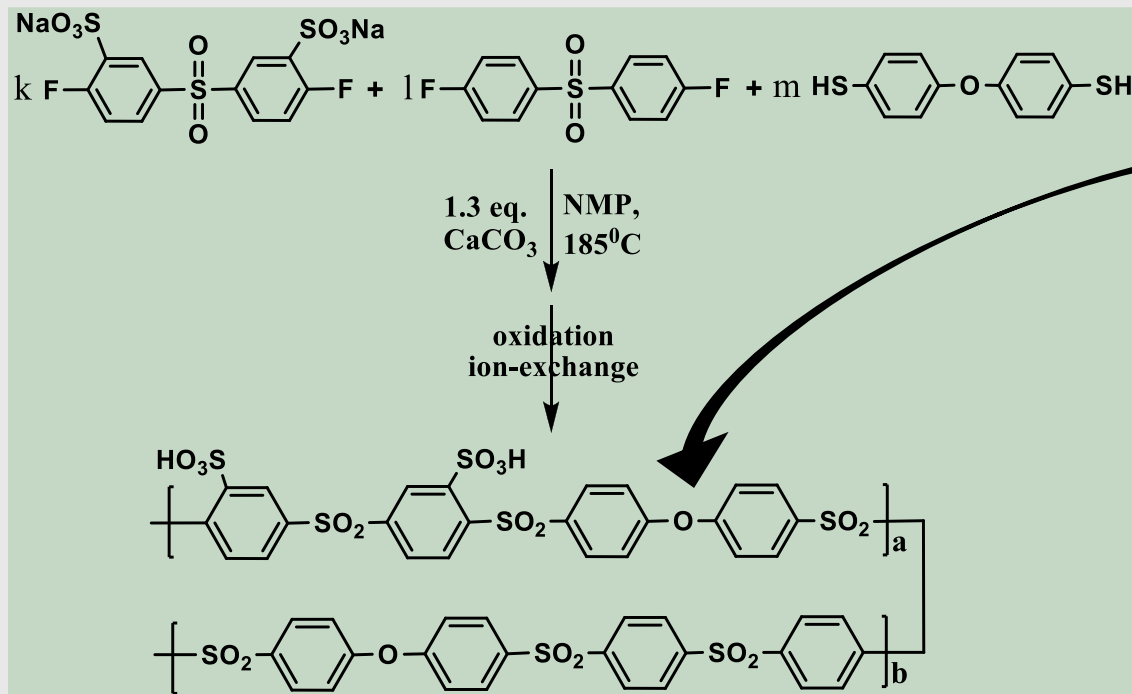
J.Miyake: "Design of flexible polyphenylene proton-conducting membrane for next-generation fuel cells"

Persistence Length (l_p) $\equiv$ Distance required for polymer backbone to bend 90°

- **High l_p (e.g Poly(*p*-phenylene), $l_p \rightarrow \infty$):** Rigid rod behavior $\rightarrow$ Unentangled & brittle
- **Low l_p (e.g Polyethylene, $l_p \approx 0.7$ nm):** Flexible coil behavior $\rightarrow$ High chain entanglement & tough film

1. Dithiol Route: Incorporate Dithiol Units $\rightarrow$ Modulate Main-Chain Geometry & Reduce l_p

2. Oxythiol Route: Introduce Flexible Ether/Oxythiol Linkages $\rightarrow$ $\begin{cases} \uparrow \text{Chain Conformational Freedom} \\ \uparrow \text{Dry-State Mechanical Stability} \end{cases}$



Ether/oxythiol Linkages

• **Outlook**

Conclusions

conclusions

- **microblock monomer strategy** is an effective tool for sequence control in sPPS backbones..

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- Synthesized and confirmed the structures of two microblock precursors (FDPS-BP-FDPS and FDPS-*p*-TP-FDPS) via ^1H and ^{19}F NMR

conclusions

microblock monomer strategy is an effective tool for sequence control in sPPS backbones.

- Synthesized and confirmed the structures of two microblock precursors (FDPS-BP-FDPS and FDPS-*p*-TP-FDPS) via ^1H and ^{19}F NMR

- Demonstrated that trace monomer impurities directly limit polymer molecular weight, resulting in poor film-forming ability

conclusions

- **microblock monomer strategy** is an effective tool for sequence control in sPPS backbones.

- Synthesized and confirmed the structures of two microblock precursors (FDPS-BP-FDPS and FDPS-*p*-TP-FDPS) via ^1H and ^{19}F NMR

- Demonstrated that trace monomer impurities directly limit polymer molecular weight, resulting in poor film-forming ability

- Initiated polymer backbone modifications using dithiol and oxythiol linkages to reduce persistence length (l_p)

Thank you
for your attention

