Self-assembly of rigid polyelectrolytes as a mechanism for proton transport membrane formation

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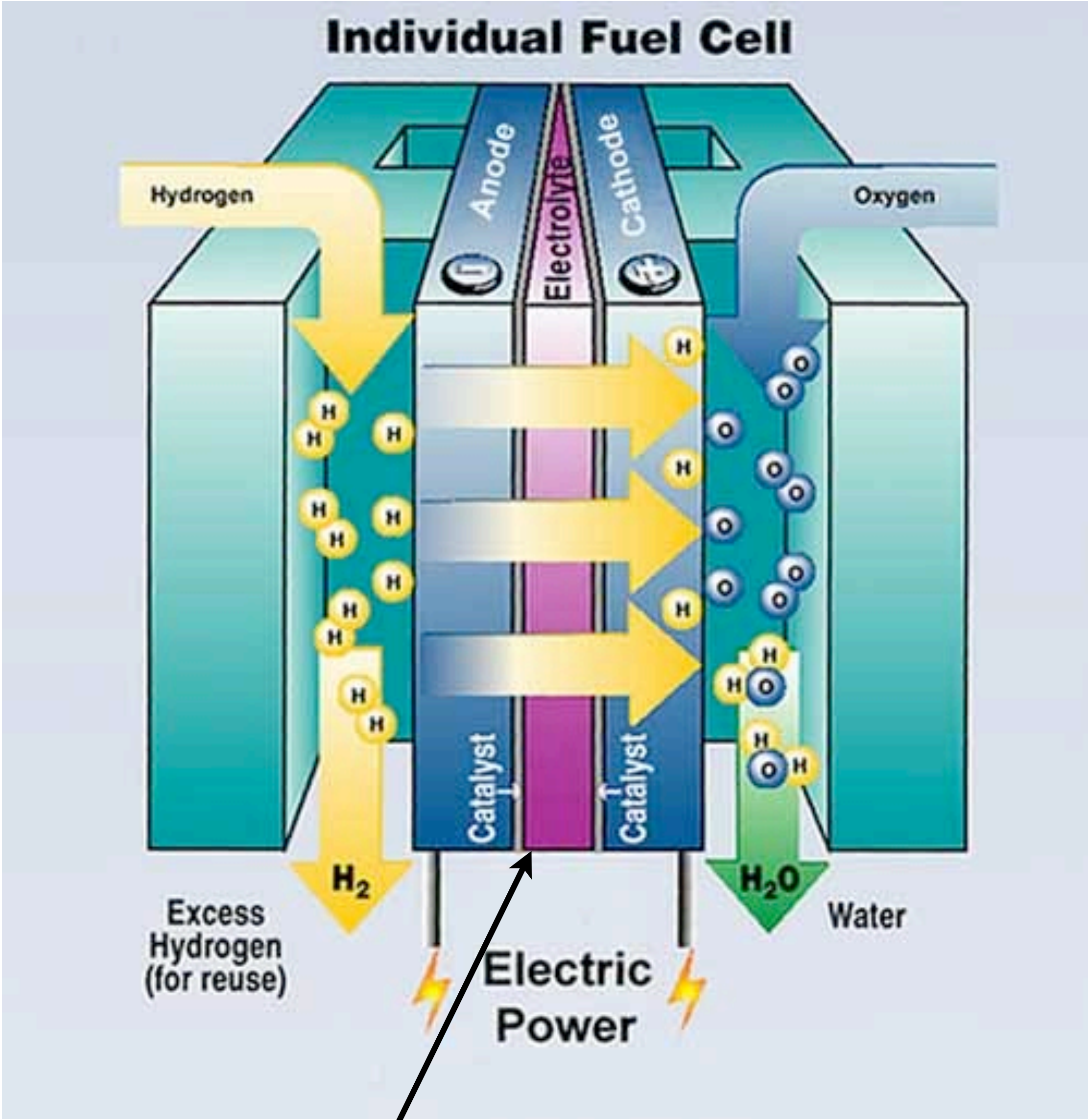


Polymer Electrolyte Membrane (PEM)

Polymer Electrolyte Membranes

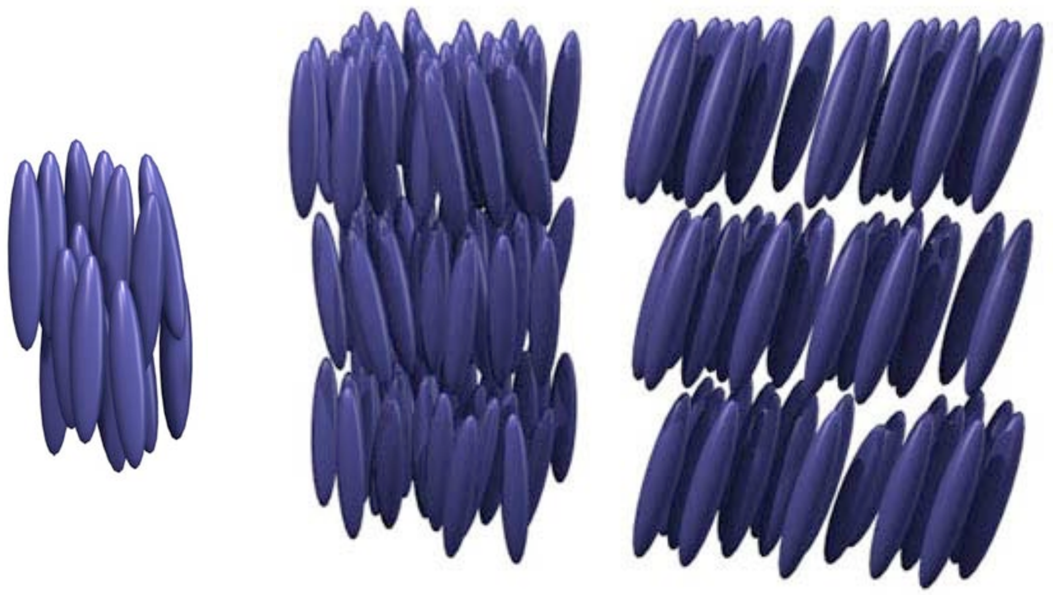
- The role of the polymer electrolyte is three-fold:
  - It separates the two electrodes and acts as an electronic insulator
  - It keeps the gases (hydrogen and oxygen) from mixing
  - It allows protons to be transported from the anode to the cathode

Polymer Electrolyte Membranes

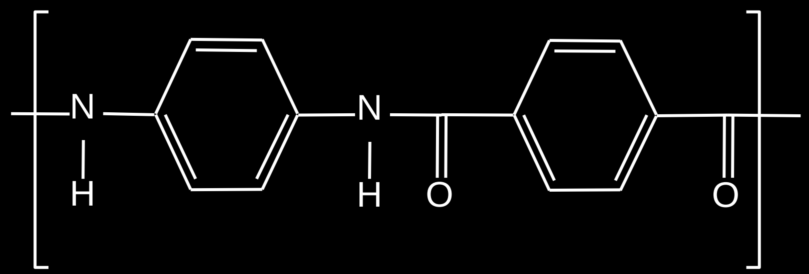
- Chemical and thermal stability
- Mechanical strength
- Molecular structure that promotes ion conduction

Designing Polymers

The self-organisation of liquid crystalline polymers (LCPs) can provide a way to tailor the molecular architecture and thus properties of a membrane...



Nematic Smectic A Smectic C



poly-paraphenylene terephthalamide

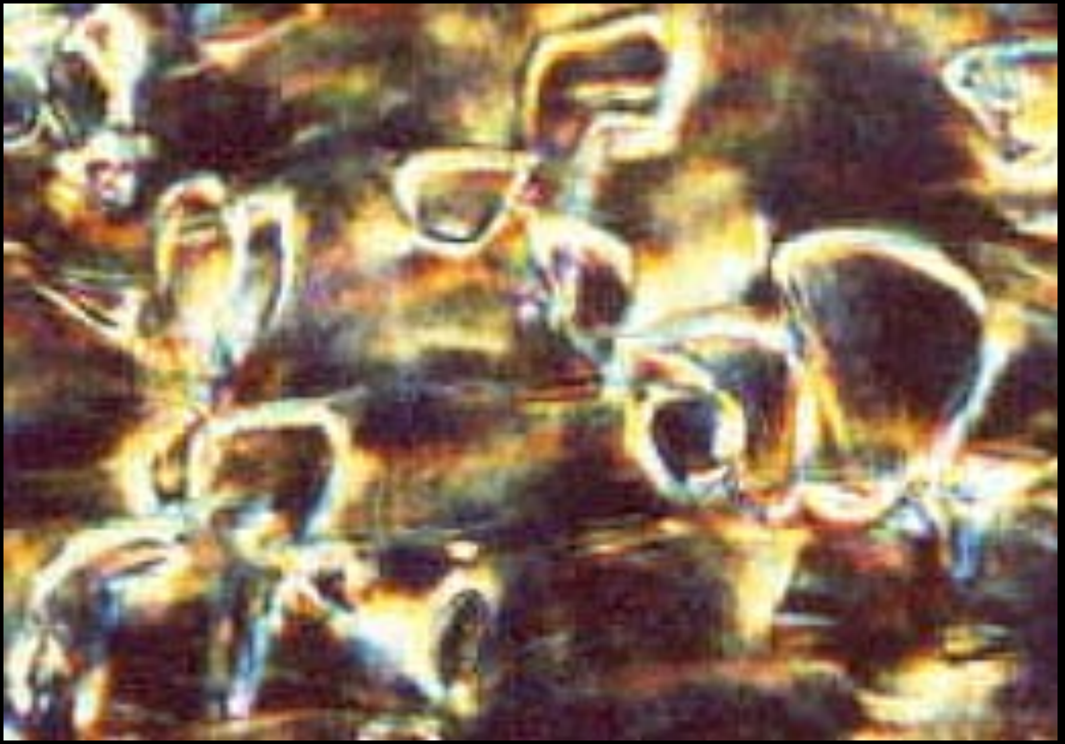
(PPTA)

Kevlar ®
or
Twaron ®

PPTA fibres processed in concentrated H_2SO_4 !

- Nematic phase in H_2SO_4 (8 to 20 wt/wt%)

- spontaneous alignment in H_2SO_4 translates into fibre (material) properties



Motivation :

Provide water solubility keeping Liquid Crystallinity

Method:

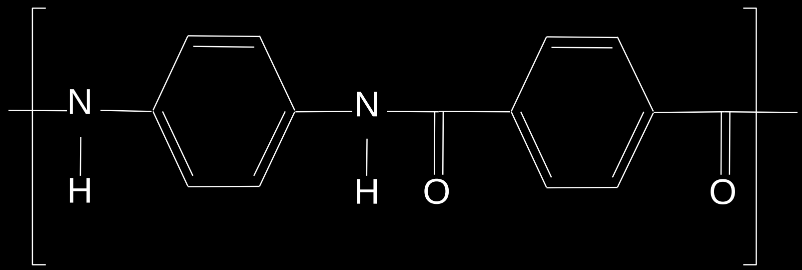
Introduction of electrostatic interactions

Strategy *(and talk structure)*

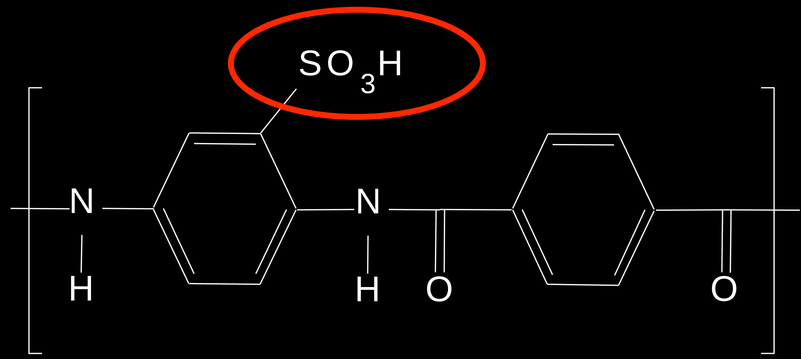
1. Solution LC Properties

2. Thin Films LC Properties

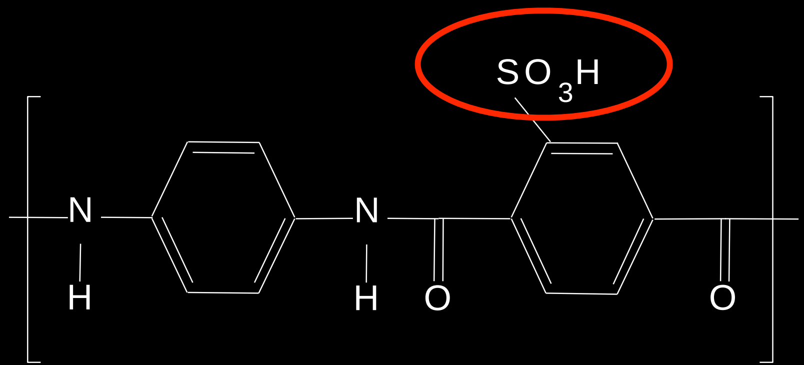
3. Proton conductivity



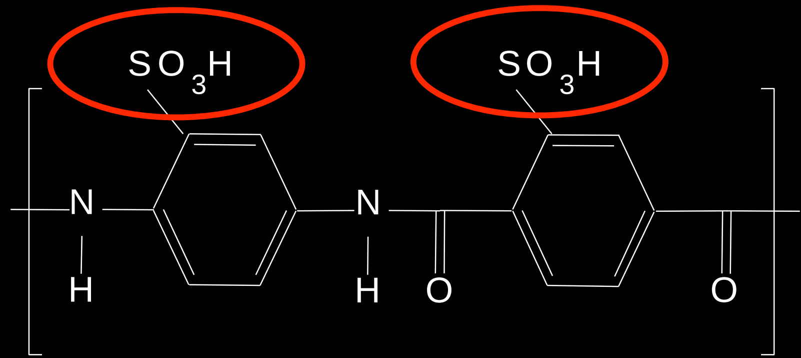
PPTA



Sulfo - PPTA

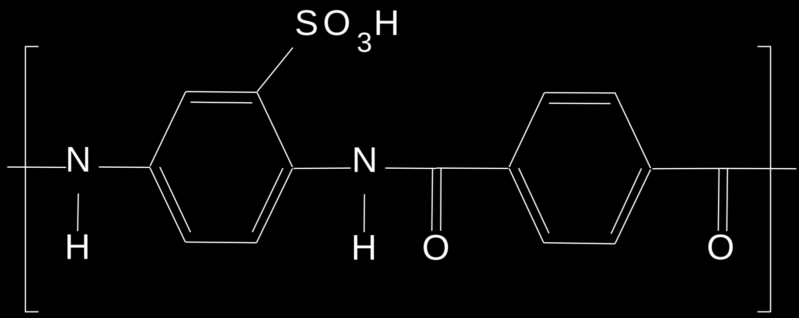


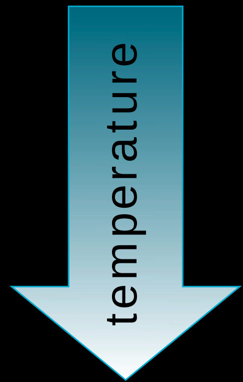
Sulfo"Invert" - PPTA



Sulfo^2 - PPTA

Sulfo - PPTA





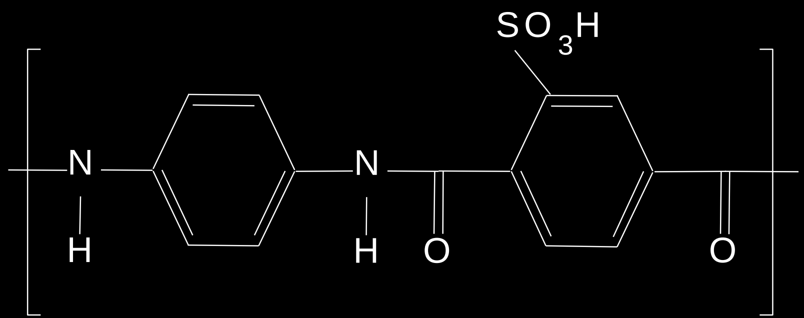
Sample preparation:

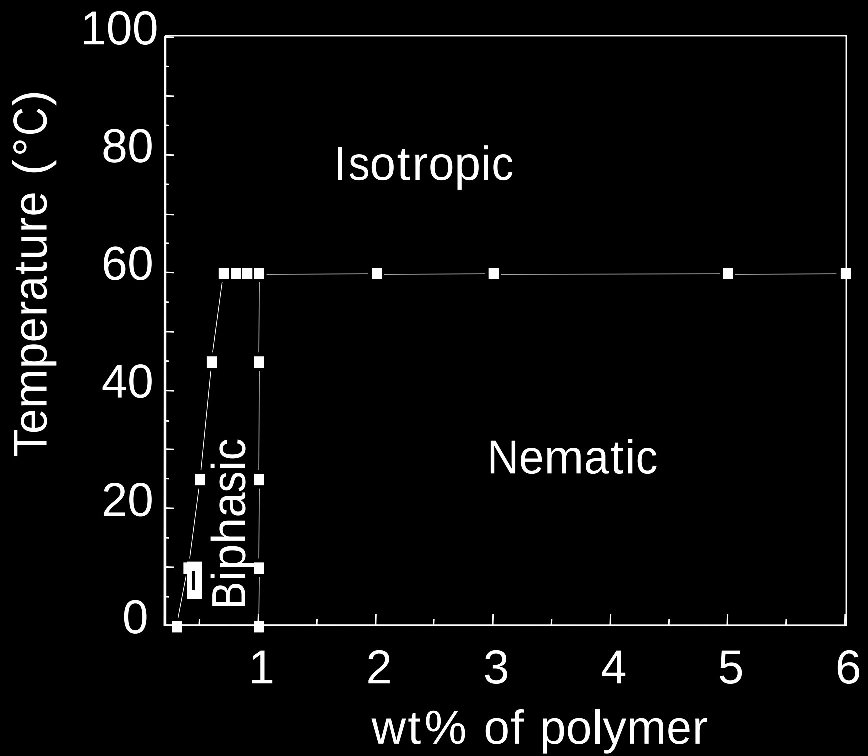
- Mw ~ 10.000 g.mol^{-1} (dp ~ 1.5)
- 1wt/wt% in deuterated water
- boiled at 100ºC in sealed tube for 15 minutes
- sonication bath at 60ºC for 2 hours

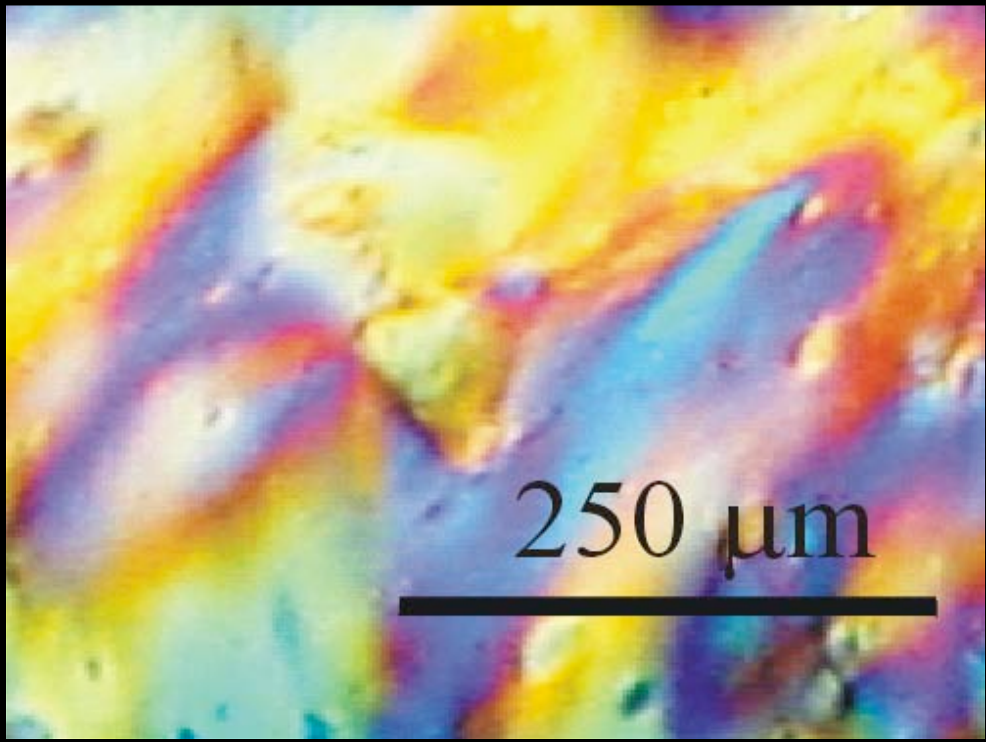
weak nematic gel
formed at very low concentrations

A Small-Angle Neutron Scattering Investigation of Rigid Polyelectrolytes under Shear., E. Mendes, S.Viale, O. Santin, M. Heinrich, S.J. Picken
J. Appl. Cryst. 36, 1000-1005 (2003)

Sulfo "Invert" PPTA



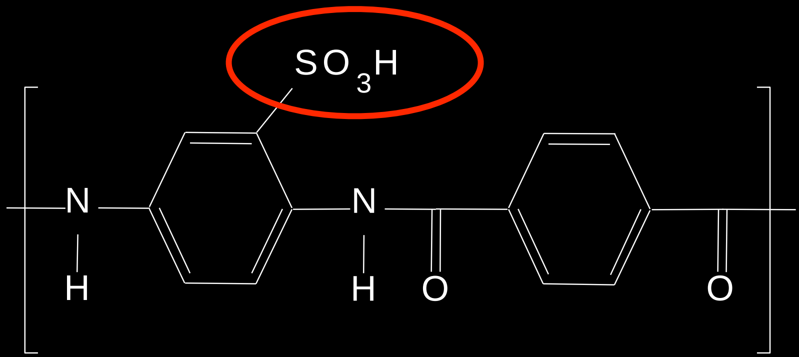




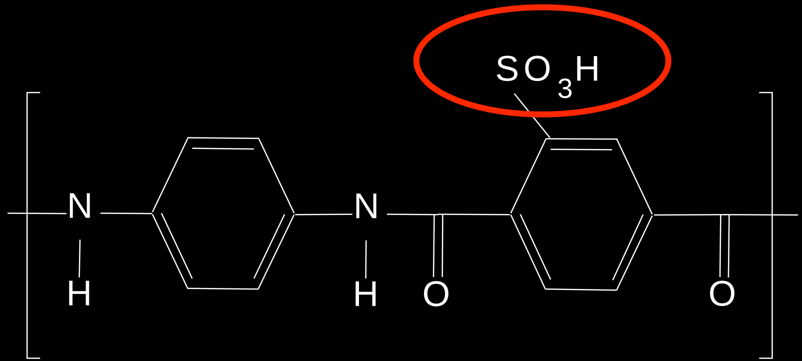
- M_W ~ 10.000 g.mol^{-1} (dp ~ 2)
- 0.3wt% of lithium as counterions

No Gel !

A Supramolecular Nematic Phase in Sulphonated Polyaramides
S. Viale, A S. Best, E. Mendes, W F. Jager, S. J. Picken
Chemical Communications, (14) 1596-1597 (2004)



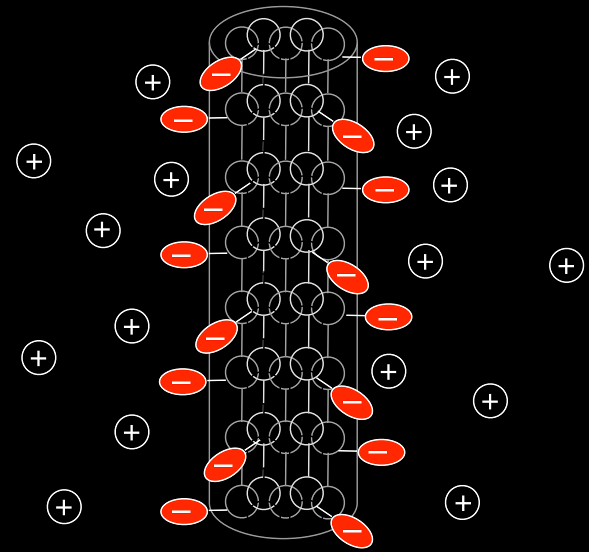
Sulfo - PPTA (Nematic Gel)
Weakly connected needle-like supramolecular aggregates



Sulfo"Invert" - PPTA- (LC Solutions)
Flowing supramolecular aggregates

Inspection of critical concentration
[$\Phi^* = 4d/L$] ~ 1%

with SANS peak position at Φ^*

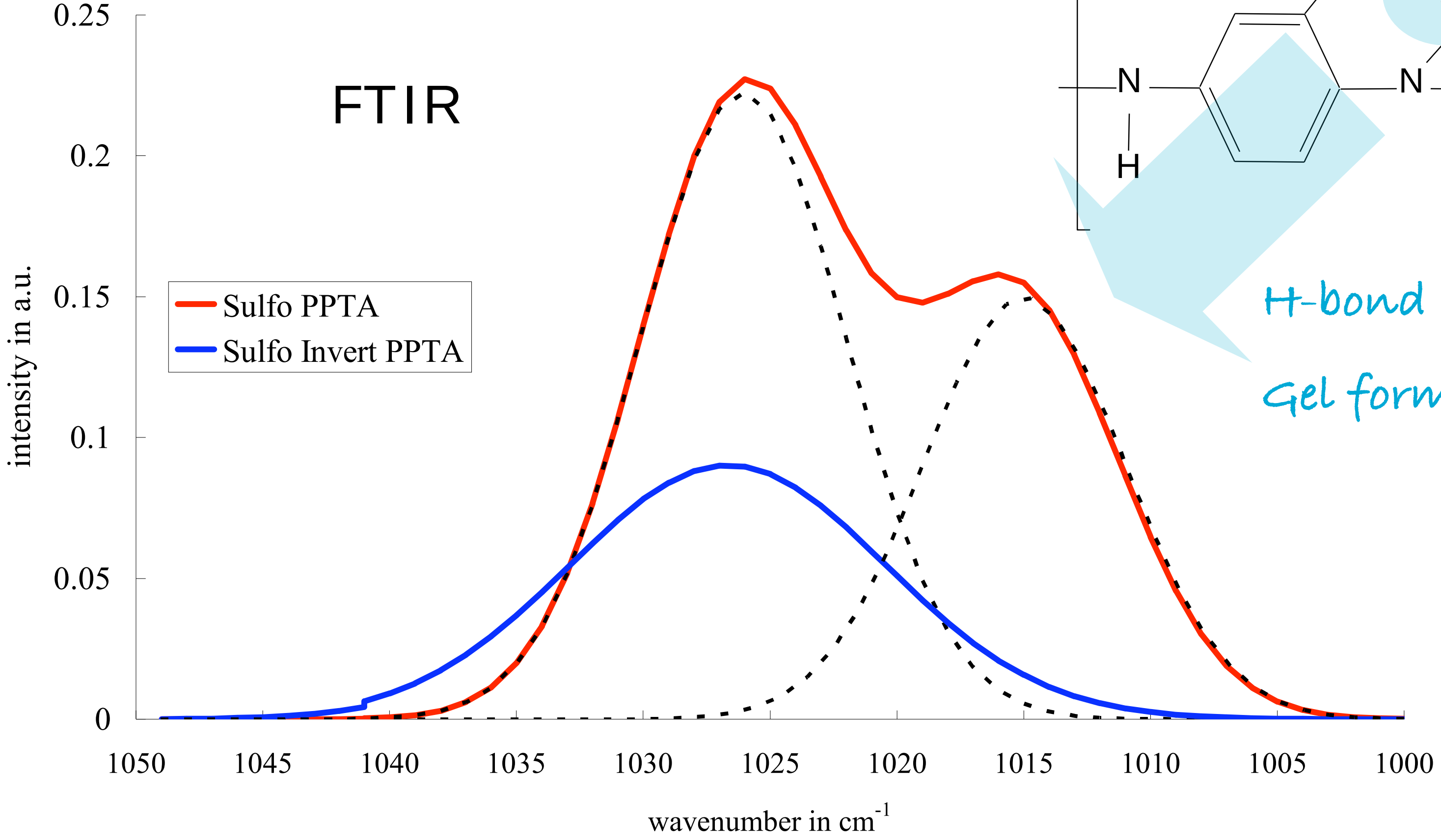


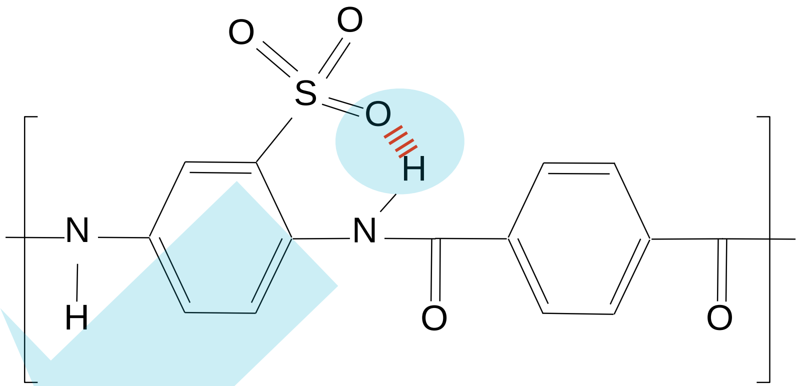
needle-like supramolecular aggregates
L/d ~ (8700Å / 22 Å)

5-7 molecules per cross section

Mechanism of gel formation:

Sulfo-PPTA vs. Sulfo "Invert" PPTA





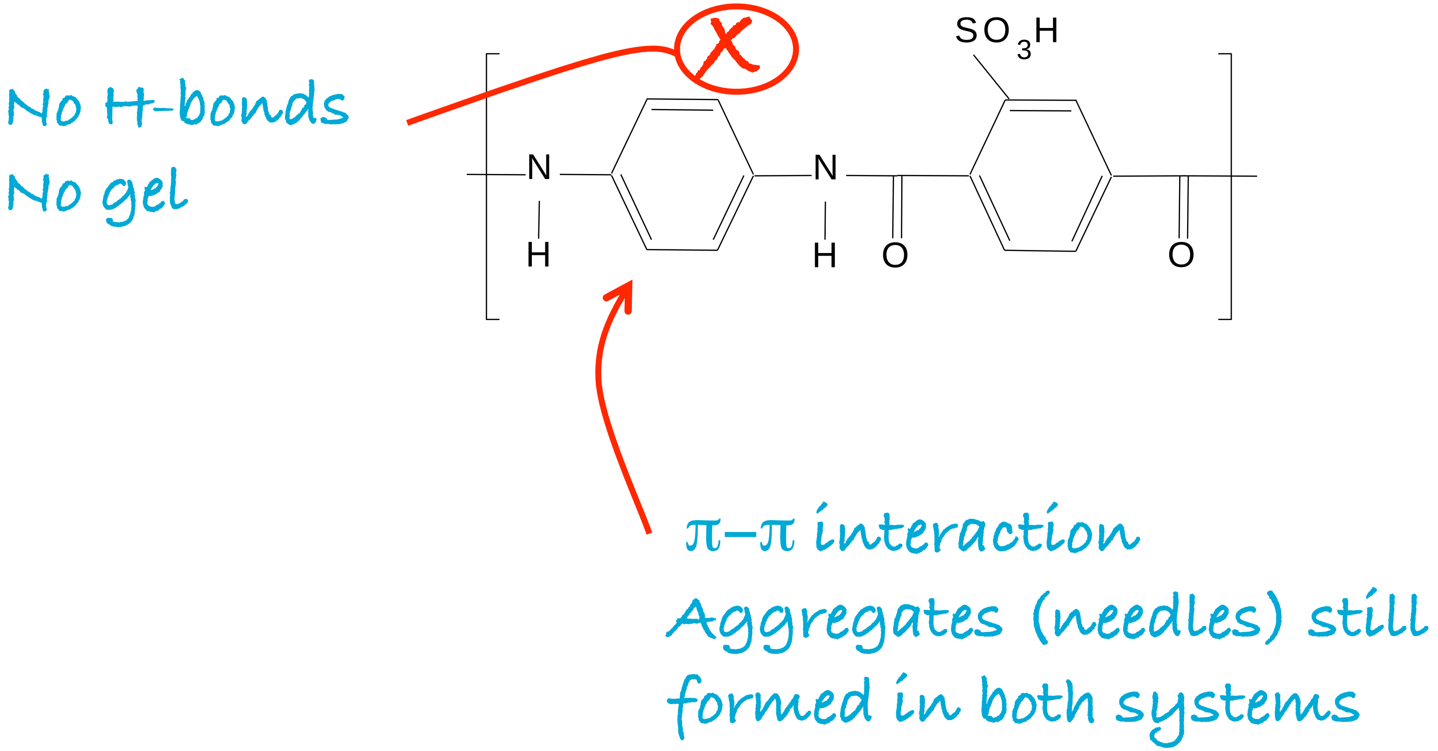
H-bond in Sulfo PPTA

Gel formation

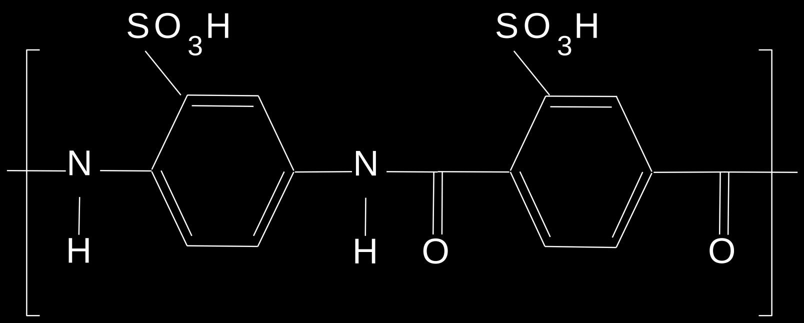
no H-bond in Sulfo "Invert" PPTA = No Gel

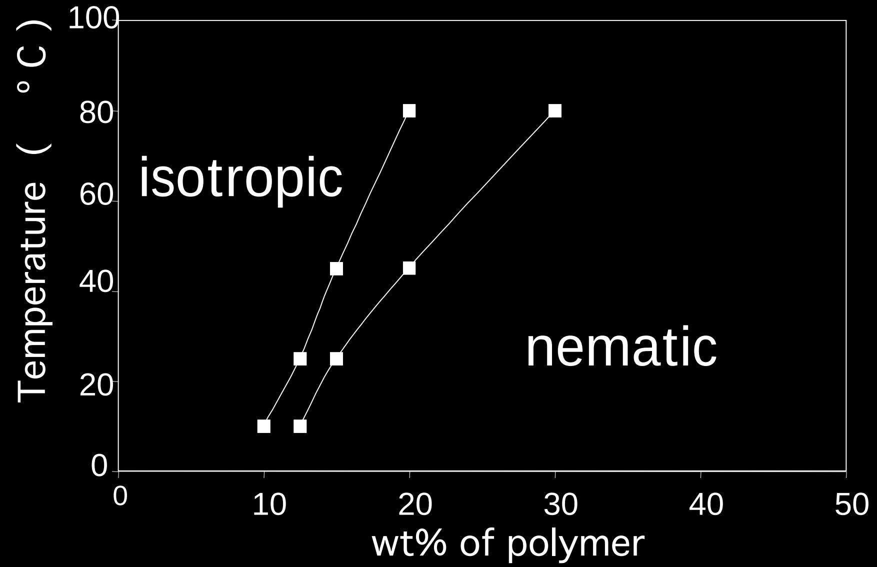
Mechanism of weak gel formation:

Sulfo-PPTA vs. Sulfo “Invert” PPTA



Sulfo² PPTA





Molecular Polyelectrolyte LC

- M_W ~ 15.000 g.mol^{-1} (dp ~ 2)
- 0.3wt% of lithium as counterions

1. Structure & Dynamics
of gels and solutions

Different interactions → Different structures → Different time-scales

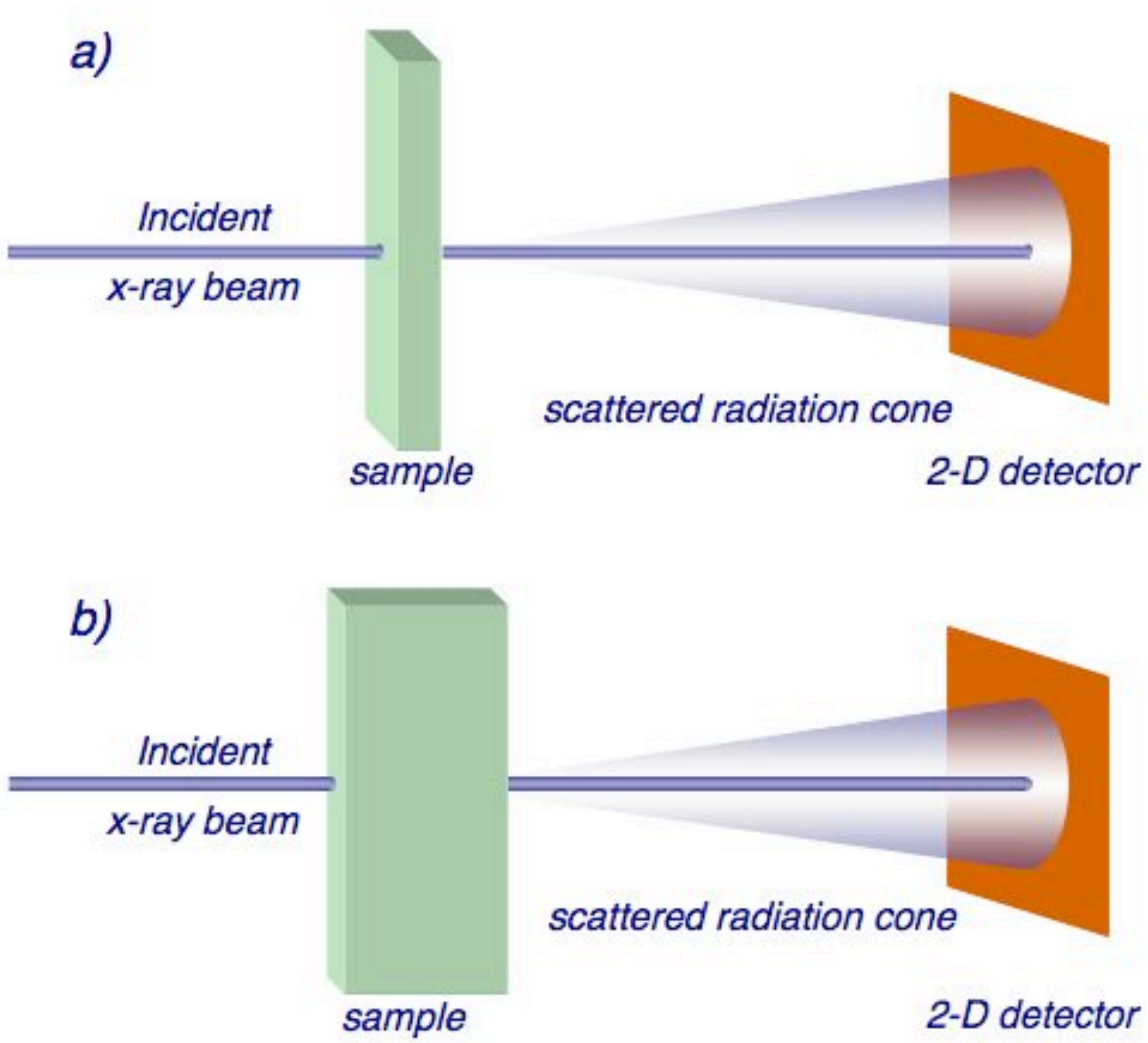
(details not shown today)

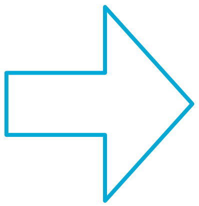
Casting

2. Thin Films

from S-PPTA and S-Inv-PPTA

Film Structure

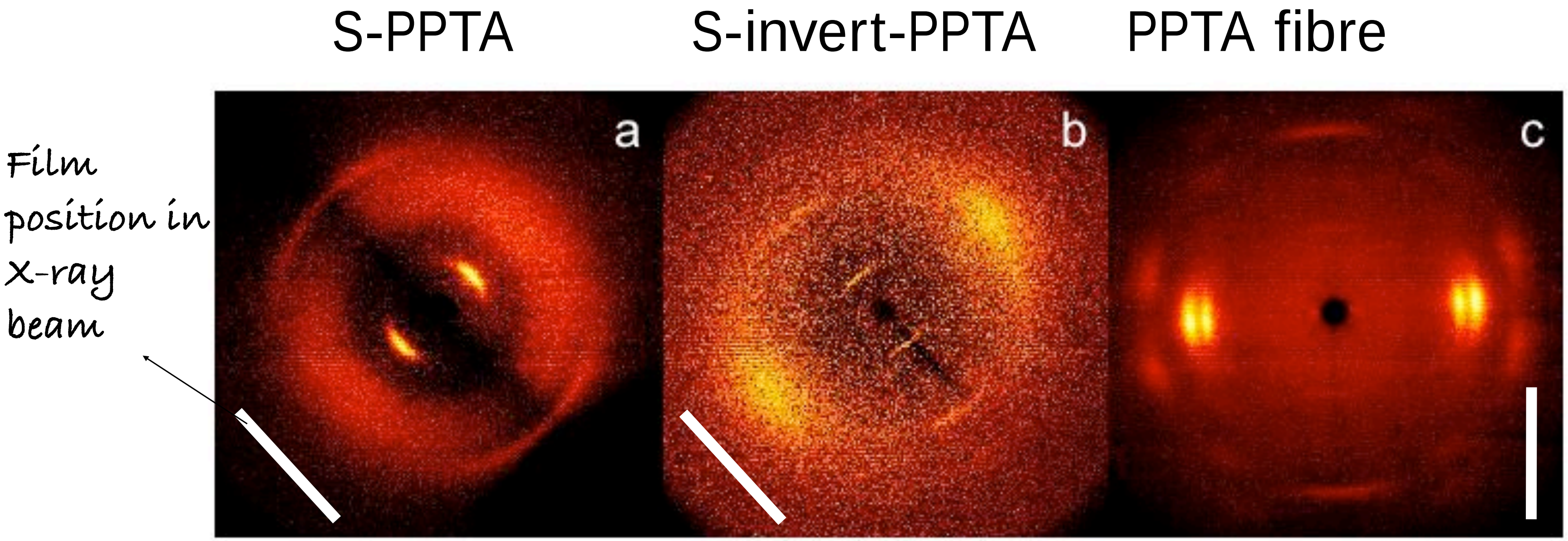




side view

Spontaneous Formation of Hierarchical Proton Conductive Structures in Sulfonated PPTA Copolymer Films, C. Sisbandini, H. A. Every, S. Viale, E. Mendes and S. J. Picken
Journal of Polymer Science B: Polymer Physics 45, 666-676 (2007)

Wide Angle X-ray Scattering



- Multiple scattering peaks observed in-plane of the film
- Similar to PPTA fibre
- Information about the polymer alignment

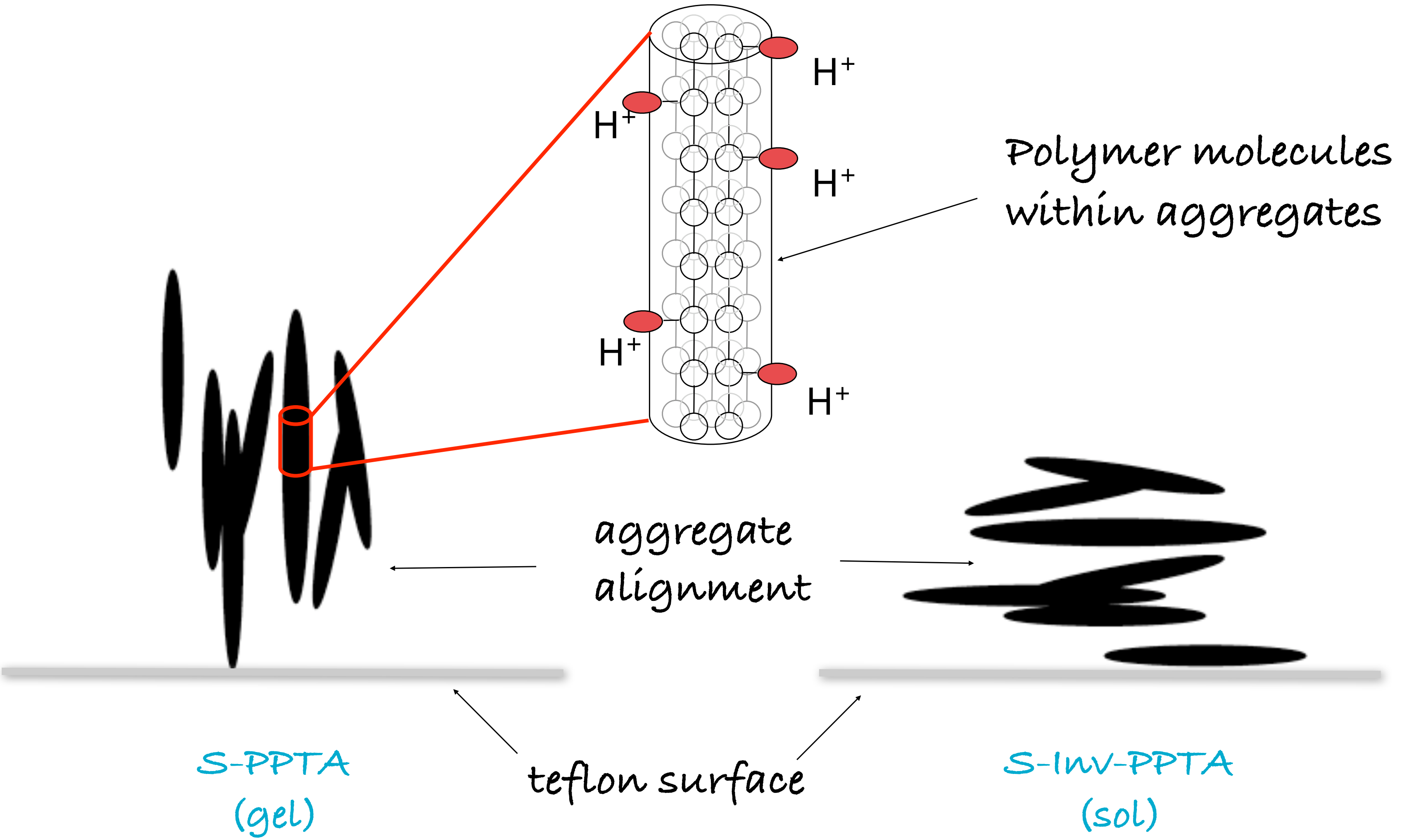
Ordered Structures in Proton Conducting Membranes from Supramolecular Liquid Crystal, H. A. Every, E. Mendes and S. J. Picken
J. Phys. Chem. B, 110 (47), 23729-23735 (2006)

Observations

- Similar peak positions observed for the sulfonated PPTA polymers
- Orientation of these peaks are rotated for S-invert-PPTA compared to S-PPTA
- Aggregate alignment
  - Planar for S-invert-PPTA
  - Homeotropic (perpendicular to film surface) for S-PPTA

surprise !

Homeotropic vs Planar Alignment



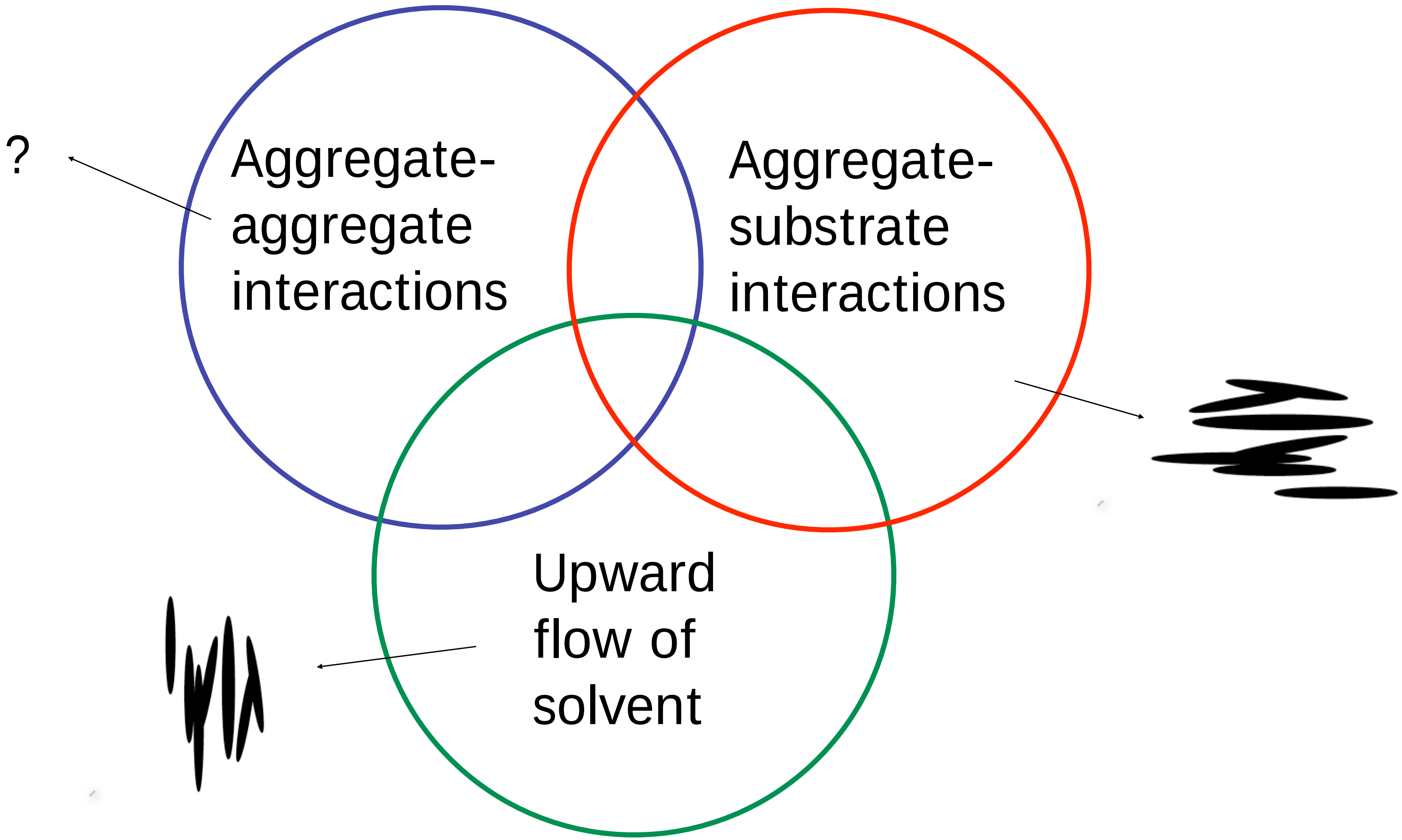
Physical Properties of Oriented Thin-Films Formed by the Electrostatic Complexation of Sulfonated Polyaramid, H. A. Every, L. V. van der Ham, S. J. Picken and E. Mendes, J. Phys. Chem. B, 112 (51), 16403-16408 (2008)

Since

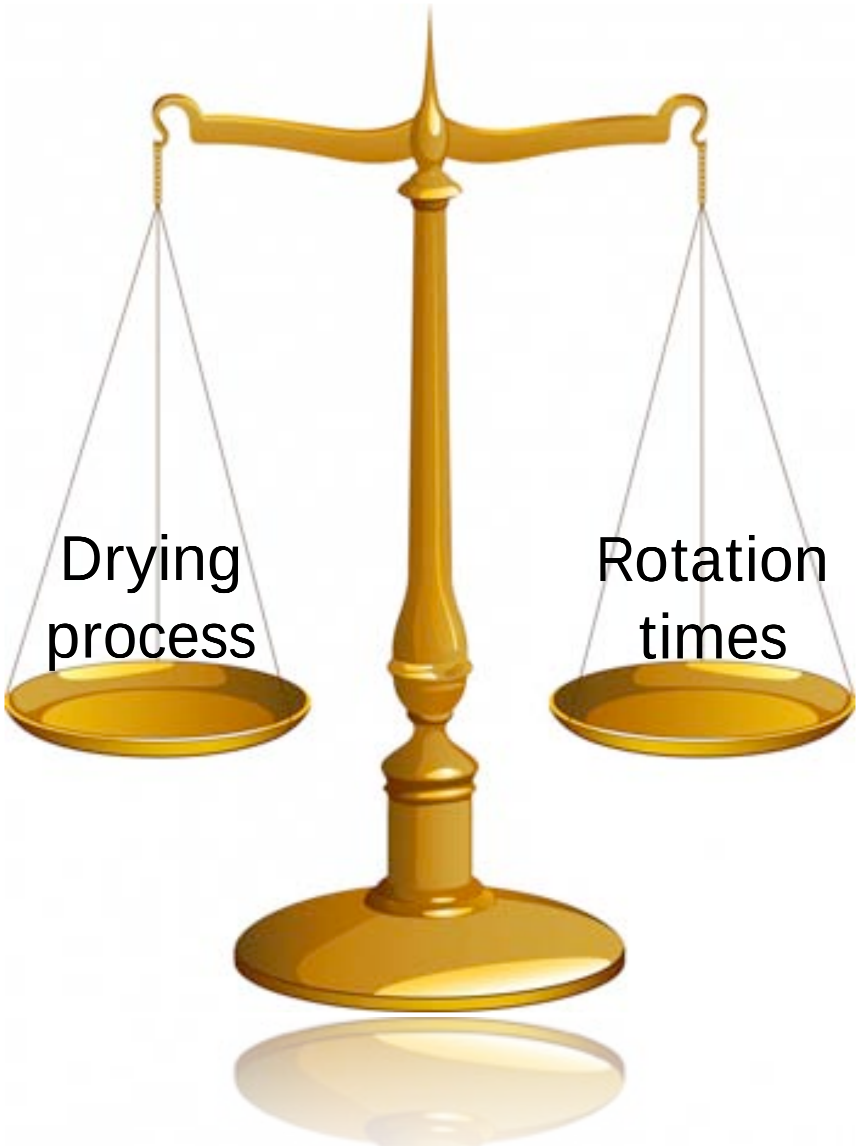
- S-PPTA and S-invert-PPTA are chemically identical
- Aggregate dimensions are similar for the same concentration

Why are the orientation in film different?

The Drying Process



Gel versus Free-flowing Solution



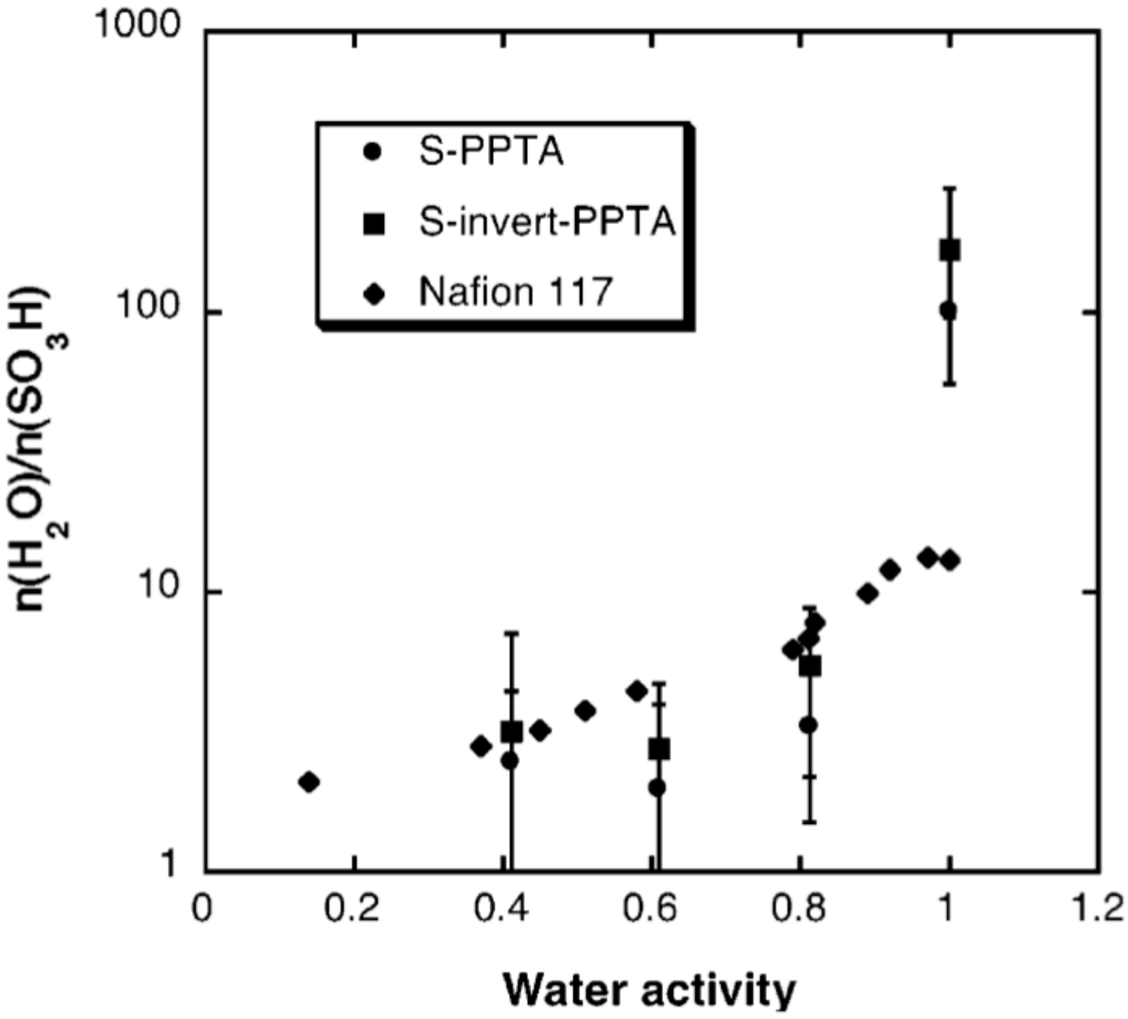
- S-PPTA is a weak gel
- S-invert-PPTA is easier-flowing solution
- Aggregate rotation time for S-PPTA >> S-invert-PPTA
- Balance between these factors affects final molecular orientation

A direct observation by XRD of reorientation in a supramolecular liquid crystal polymer induced by magnetic field, S. Viale, E. Mendes, S. J. Picken, Mol. Cryst. Liq. Cryst. 437, 1287-1296 (2005) how morphology determines

3. Conductivity

of S-PPTA and S-Inv-PPTA films?

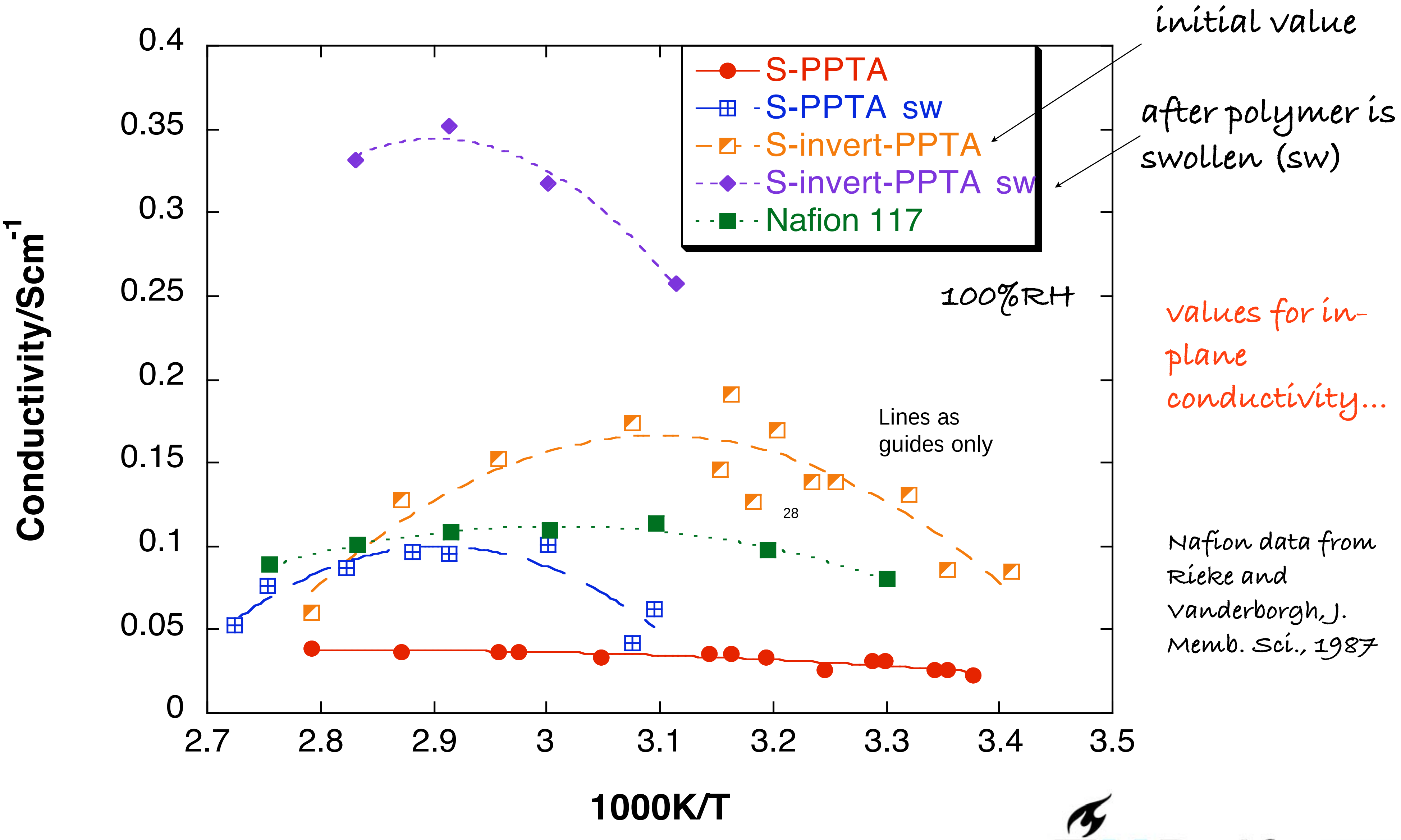
Water uptake



Water uptake (given as the ratio of water molecules per sulfonic acid group) as a function of water activity (relative humidity) for S-PPTA and S-invert-PPTA

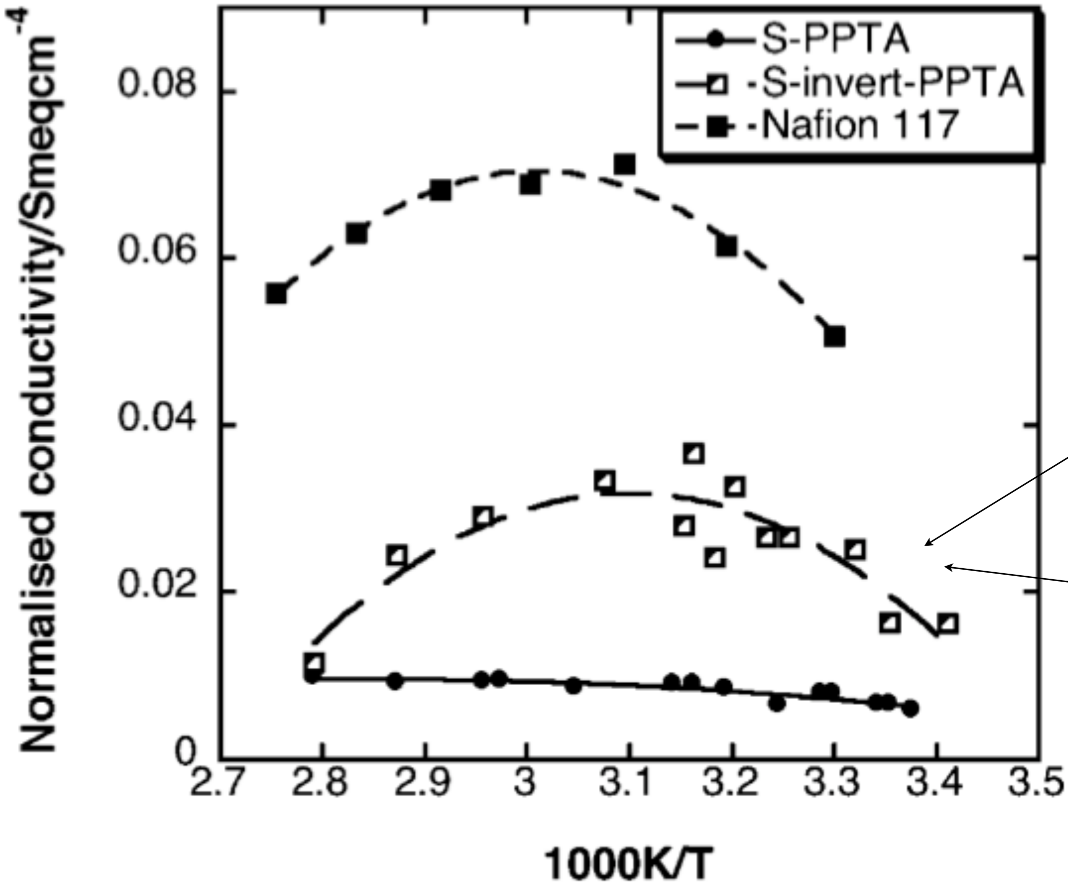
Nafion data from Rieke and Vanderborgh, J. Memb. Sci., 1987

Conductivity



Ordered Structures in Proton Conducting Membranes from Supramolecular Liquid Crystal, H. A. Every, E. Mendes and S. J. Picken
J. Phys. Chem. B, 110 (47), 23729-23735 (2006)

Conductivity



larger conductivity "in plane" due to membrane structure ?

S-Inv-PPTA aligned in plane !

Normalized conductivity with respect to the number of charge carriers per unit volume. Data for the sulfonated PPTA polymers in non-swollen state.

Conclusions

- Weak interaction between needle aggregates (gel) + different interactions during drying = homeotropic alignment
- Further understanding of interactions leads to control of Homeotropic alignment (various mechanisms and polymers possible here, waiting to be explored...)
- In-plane conductivity consistent with chain orientation Conductivity through the film still to be investigated

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W. Jager	NSM, (Delft)
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A. Lapp	
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O. Santin	University of Maringá (Brazil)

Dutch Polymer Institute for funding S.V. and H.E.

Conductivity measurements:

In-plane proton conductivities were measured with a Novacontrol Alpha Analyzer dielectric response analyzer. A standard windowpane system with indium electrodes was employed, allowing the samples to be exposed to an atmosphere of 100% relative humidity (vapor equilibrated). The measurements were performed over a temperature range of 26-90 °C and a frequency range of 1 MHz to 0.1 Hz.

TABLE 2: Theoretical and Experimental Ion Exchange Capacities for Sulfonated PPTA polymers

polymer	theoretical IEC/meqg^{-1}	experimental IEC/meqg^{-1}
S-PPTA	3.14	2.7 ± 0.1
S-invert-PPTA	3.14	3.6 ± 0.1
S^2-PPTA	5.02	4.9 ± 0.1
Nafion 117	0.91	-

ion exchange capacity (IEC)
which is defined as the number of ionic sites for a given molecular weight and is reported in milli-equivalents per gram.

values obtained by titration of aggregate solutions maximum usually attributed to evaporation of water above 50C, decreasing conductivity