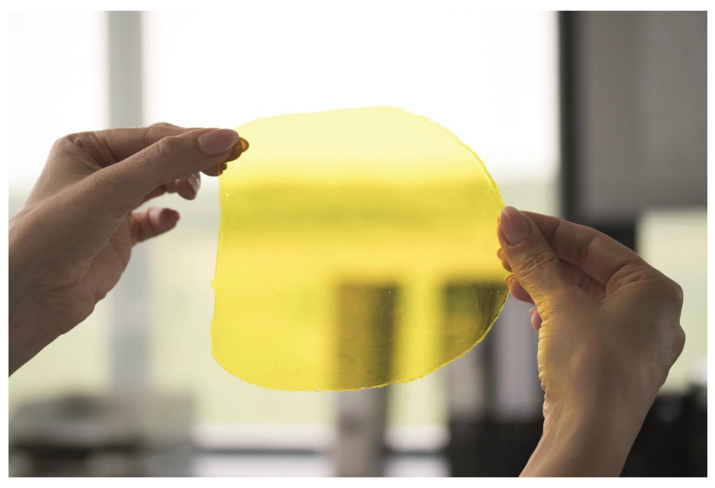
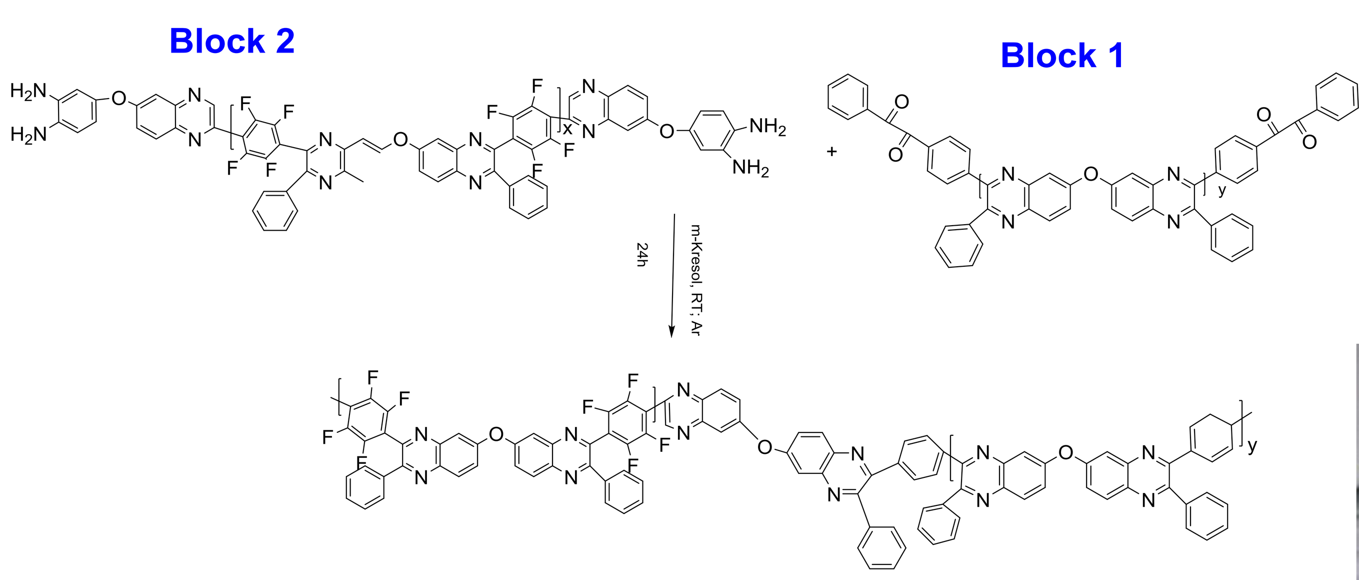
Fraunhofer IAP



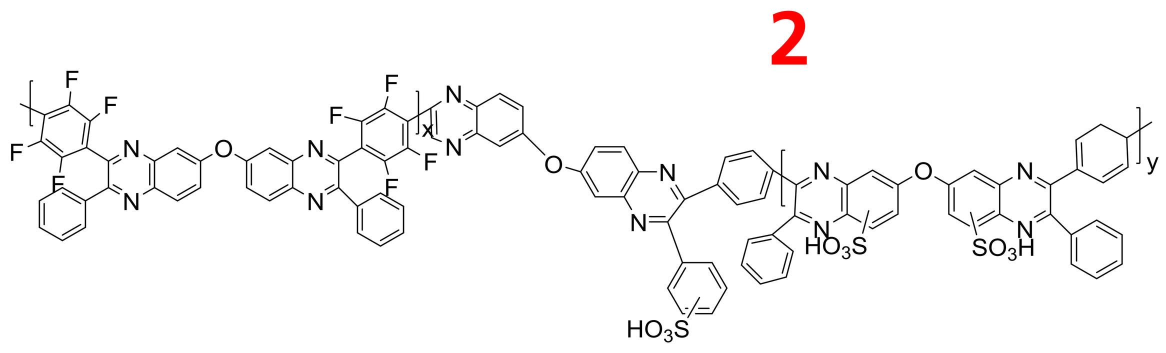
Proton-Conductive Block Copolyphenylquinoxalines Ionomers for Fuel Cells and Electrolysis

S. Janietz, H. Krüger, T. Brening
Fraunhofer-Institute for Applied Polymer Research IAP, Geiselbergstr. 69, 14476 Potsdam
Contact: silvia.janietz@iap.fraunhofer.de

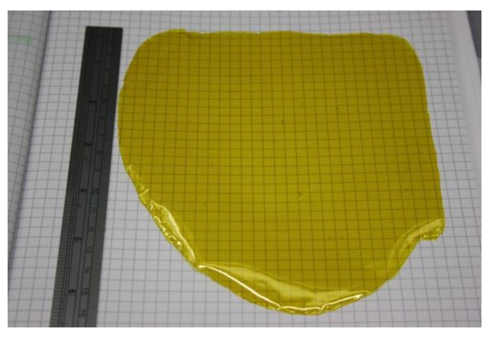
1

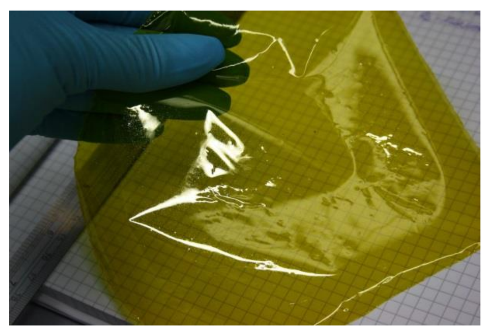


2



3

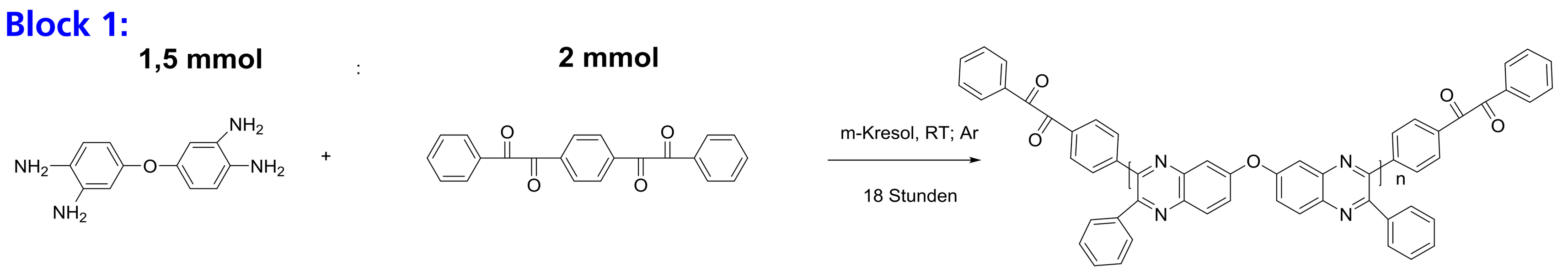




Task: Currently, perfluorinated polymers such as Nafion® are the state of the art materials because of their good physical and chemical stability along with high proton conductivity under a wide range of relative humidity at moderate operation temperatures. However their shortcomings such as high cost and high methanol permeation property, and the disposal of waste limit their application. Recently, introduction of aromatic hydrocarbon block copolymers based on to PEMs has been considered as a strategy to overcome the weak points.

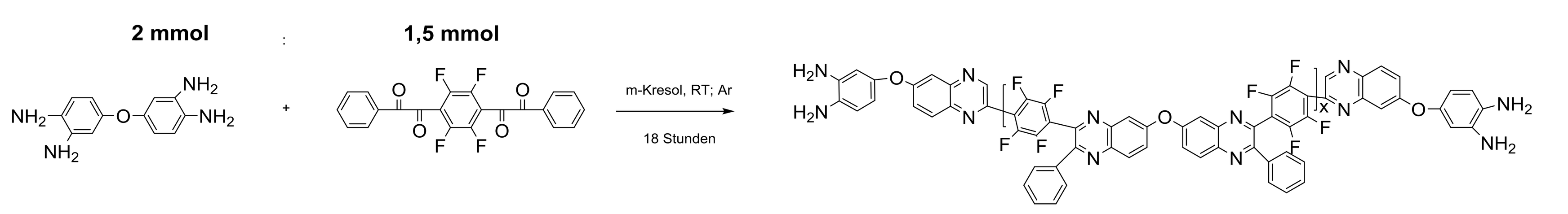
Synthesis: Poly(phenylquinoxalines) are a family of aromatic condensation polymers known for their outstanding thermal and chemical stability. Based on this polymer class new sulfonated block copolyphenylquinoxalines with hydrophilic and hydrophobic segments have been developed. The block copolymers were synthesized via polycondensation reactions of 3,3`-4,4`tetraaminodiphenylether and two different tetraketones.

Block 1:



GPC: M_w 3100g/mol ; M_n 2000 g/mol
4-3 monomer units

Block 2: hydrophob



GPC: M_w 6000 g/mol ; M_n 1900 g/mol
9-3 monomer units

Polycondensation of the two blocks see Figure 1

Polymerisation attempt	Yield g	[%]	molecular weight M_n [g/mol]	M_w [g/mol]
BT12/5	4,1	96	31.900	326.300
BT12/7	10,0	82	34.400	315.300

Sulfonation reactions (see Figure 2)

- Optimisation of sulfonic acid content ⟷ solubility/ processing
  - Sulfonation reactions are carried out in sulfuric acid / oleum mixture 4:1 at 125°C and for 27 hours
  - Sulfonated block copolyphenylquinoxalines with sulfur content between 7,5% and 3% are good soluble in DMAc and can be processed to membranes
  - Ion exchange capacities between 1,42 mmol/g and 2,35 mmol/g were determined (S-content)

Thermal characterization of the sulfonated block copolyphenyl-quinoxalines (SBPPQ)

TGA: weight loss of SBPPQ at 450°C under N_2 was 15 -17%
DSC: below 100°C desorption of water and above 350°C a desulfonation reaction took place

→ SBPPQ are thermal stable

Processing of membranes: The membranes were prepared through doctor blading from 10 to 20 % DMAC-solutions, thicknesses in the range between 40 -50µm; areas of 13 x 16 cm (see Fig. 3)

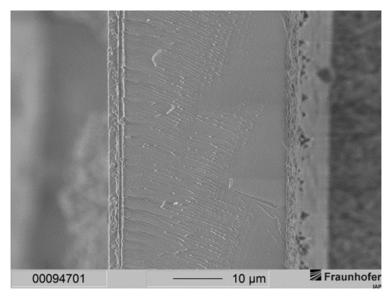
Mechanical characterization

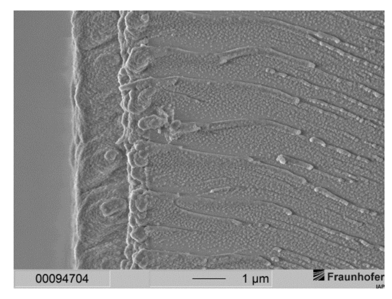
Sample Nr.	Tensile strength [MPa]	Strain at failure [%]	Stiffness [MPa]
BT13/4	146	8,43	4882

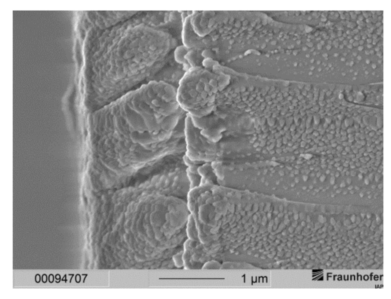
Oxydation stability (at RT in Fenton`s reagenz; 3% H_2O_2 with 2ppm $FeSO_4$ x $7H_2O$)

Membrane	2h	4h	6h	comment
FumasepF-10120	98,8%	98,5%	98,2%	color has changed, flexibility of the foil reduced
Membran 60 from BT13/4a; 7,5%S	99,4%	97,9%	95,2%	color has changed, but not brittle

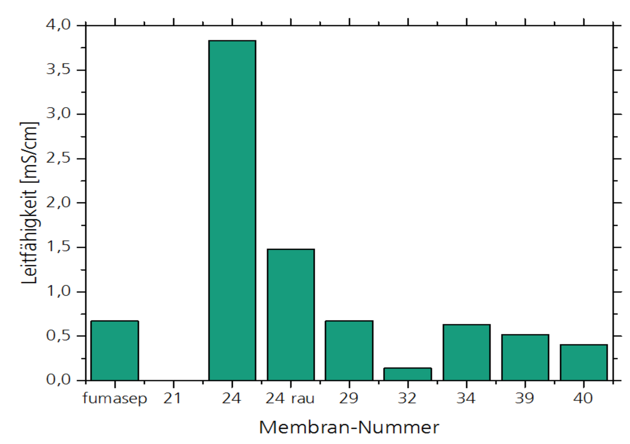
Characterization of membranes: Fig. 5; SEM images; store the membrane in water for 24h, cryo cross section







pathways for the water transportation through the membrane



Determination of the proton conductivity by impedance spectroscopy at r.t.

→ Proton conductivity comparable or higher as Nafion® membrane

Acknowledgement

The work shown was gratefully funded by the Fraunhofer Gesellschaft e.V. within the E-Strom project. We also thank Dr. Reinholdt and Dr. Schulz from the Fraunhofer ISC in Würzburg / Germany for SEM images and proton conductivity measurements.

[1] Patent application:102017208805.2; S. Janietz, H. Krüger, T. Brening