CARISMA 2012
3rd Carisma International Conference
on Medium and High Temperature
Proton Exchange Membrane Fuel Cells

Copenhagen,
3 – 5 September 2012

Aromatic Polyethers for High Temperature Polymer Electrolyte Membrane Fuel Cells (HT-PEMFCs) operating above 180°C

A. K. Andreopoulou[1,2]; *C. Morfopoulou[1,2]*; *I. Kalamaras[1]*; *M. K. Daletou[1]*; *K. D. Papadimitriou[2,3]*; *S. G. Neophytides[1,3]*; *J. K. Kallitsis[1,2,3]*

1. Institute of Chemical Engineering Sciences, FORTH/ICE-HT, Patras 26504, Greece
2. Department of Chemistry, University of Patras, 26500 Patras, Greece
3. Advent Technologies S. A., Patras Science Park, 26504, Patras, Greece

Advanced Polymers & Hybrid Nanomaterials Research Lab

ICEHT/FORTH University of Patras Advent

outline

- high temperature polymer electrolyte membrane fuel cells (HT PEMFCs)
- pyridine based aromatic polyethers for HT PEMFCs
- side chain functionalized copolymers
- cross-linking of aromatic polyethers: chemistry & properties
- HT PEMFCs performance based on cross-linked membranes

HT PEMFCs

Membrane Requirements :

- High Ionic Conductivity
- Electrical Insulator
- Chemical & Oxidative Stability
- Mechanical & Thermal Integrity
- Low Gas Permeability
- Low Production Cost

HT *vs* LT PEMFCs :

Kinetics of both electrode reactions are enhanced resulting in higher catalytic activity

CO tolerance of the catalyst is dramatically increased

- 10-20 ppm at 80 °C
- 1000 ppm at 130 °C
- 30000 ppm at 200 °C

NO NEED FOR HIGH PURITY H_2

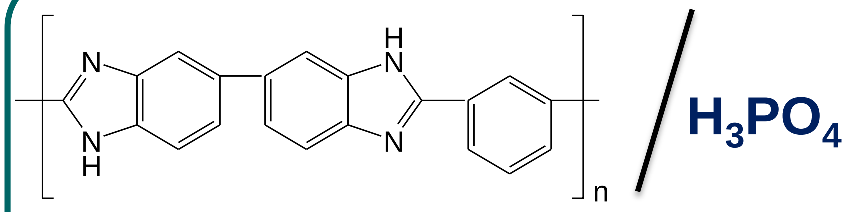
The Complexity of the system is reduced

- No need for humidification of the feed gases
- Simplified cooling system
- Effective heat recovery

THE OVERALL PROCEDURE IS DRASTICALLY SIMPLIFIED

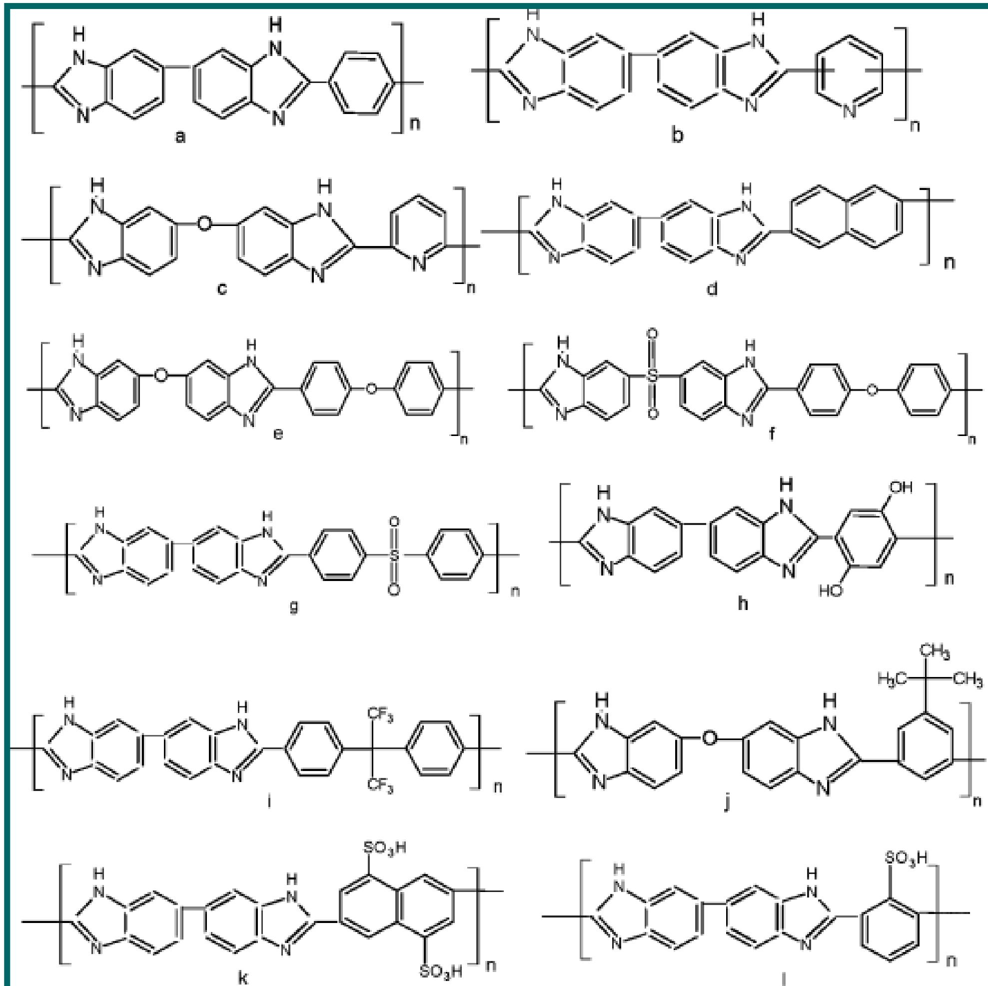
HT PEMFCs

(PBI - Polybenzimidazole)



- High thermal stability (Td=500ºC)
- High Tg(~440°C)
- High ionic conductivity

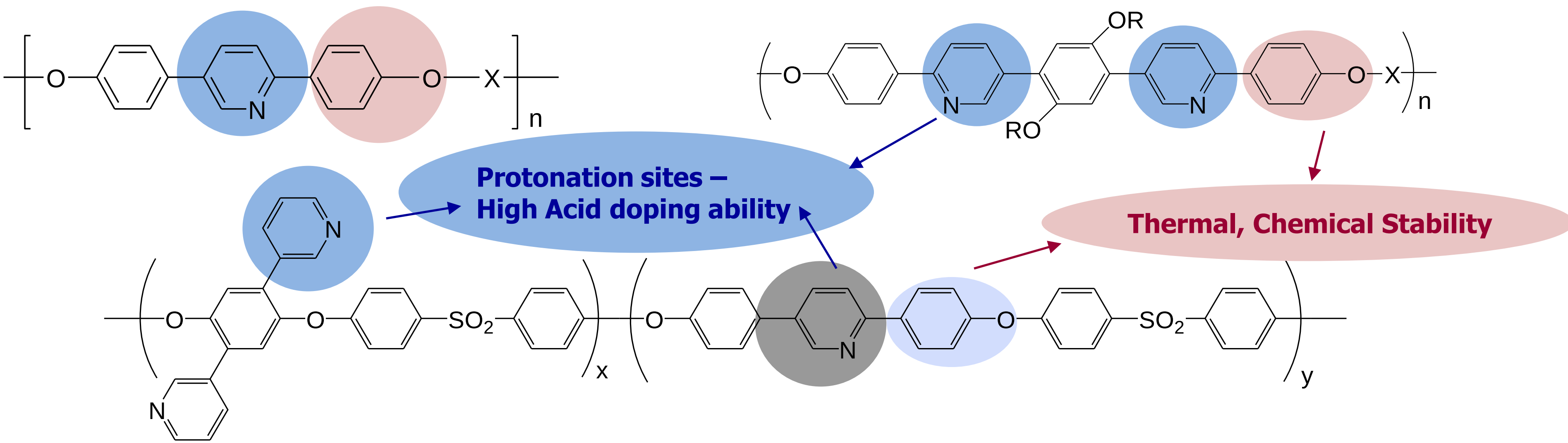
Modified PBIs



Qingfeng, L., Jensen, J. O., Savinell, R.F., Bjerrum, N. J. Progress in Polymer Science 34 (2009) p.p. 449–477

Aromatic Polyethers bearing Pyridine Groups

Route to Design and Synthesis of Novel Polymers



Structural Characteristics

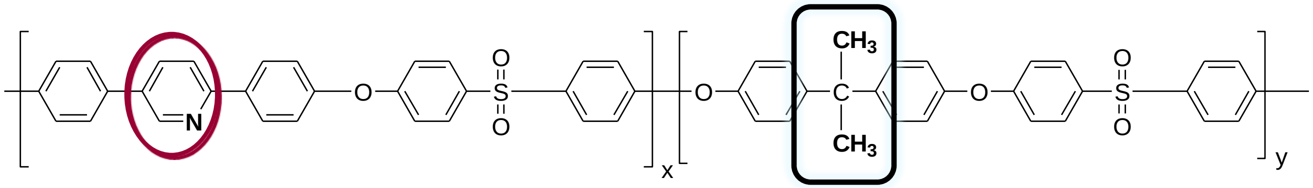
Aromatic Polyether
- High Thermal Stability
- High Chemical Stability

Pyridine Polar Group
- H^+ Acceptor site
- Hydrogen Bond site

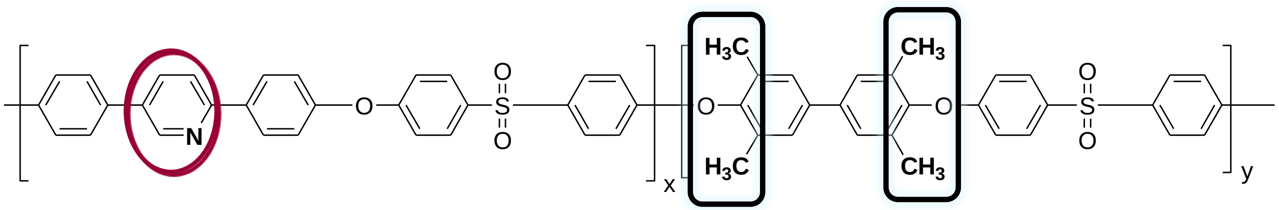
- **Monomer Preparation**
- **Polymerization via polycondensation**
- **Characterization via H-NMR, GPC, DMA, TGA, FT-iR, Tensile testing**
- **Selection of the best membranes for MEA construction and testing**

J. K. Kallitsis, M. Geormezi, S. Neophytides, Polymer International, 58, 1226–1233, (2009)

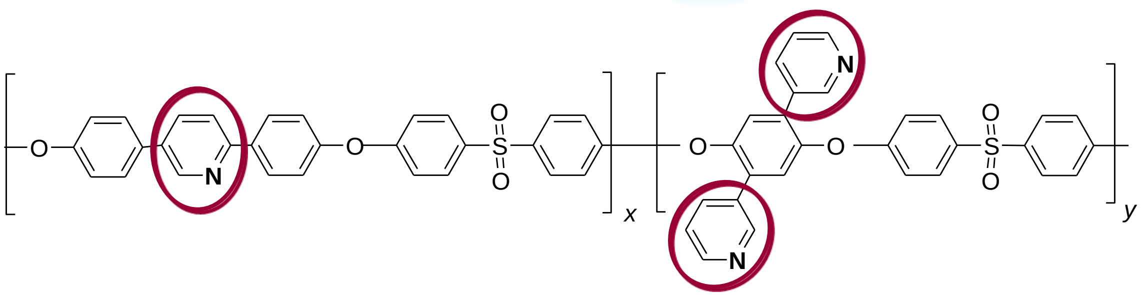
Copolymers of Aromatic Polyethers Bearing Pyridine &/or Methyl Groups



PPycoPSF



TMPySF



3-dPPycoSF

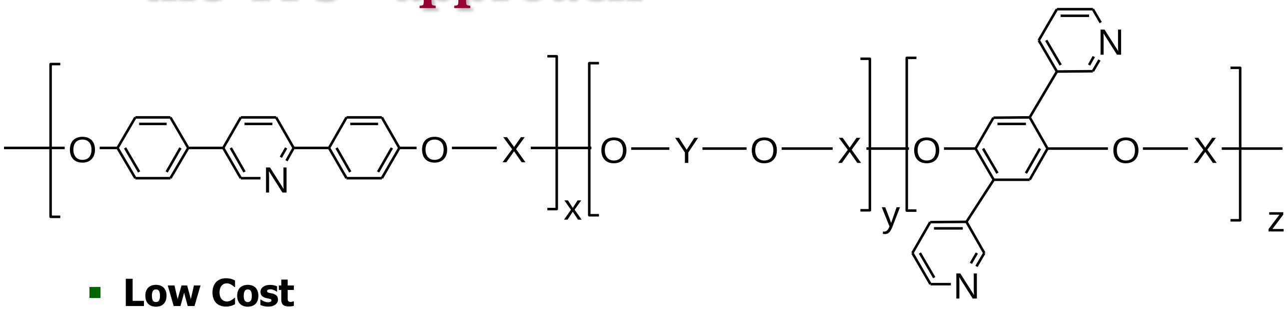
- Diversity of the macromolecular structures
- Excellent Solubility Properties independent of MWs
- High MWs Polymers and copolymers
- Excellent Thermal & Mechanical properties

- High Oxidative Stability
- High & controllable doping ability in strong acids (H_3PO_4)
- High ionic conductivity of the doped membranes

N.Gourdoupi, A.K. Andreopoulou, V. Deimede, J.K. Kallitsis *Chem.Mater*., *15,* 5044, 2003
E.K. Pefkianakis, V. Deimede, M.K. Daletou, N. Gourdoupi, J.K. Kallitsis Macromol. Rapid Commun., 26, 1724, 2005
M. Geormezi, Ch. Chochos, N. Gourdoupi, J.K. Kallitsis, S. Neophytides Journal of Power Sources 196 (2011) 9382– 9390

Advent Technologies

the TPS® approach

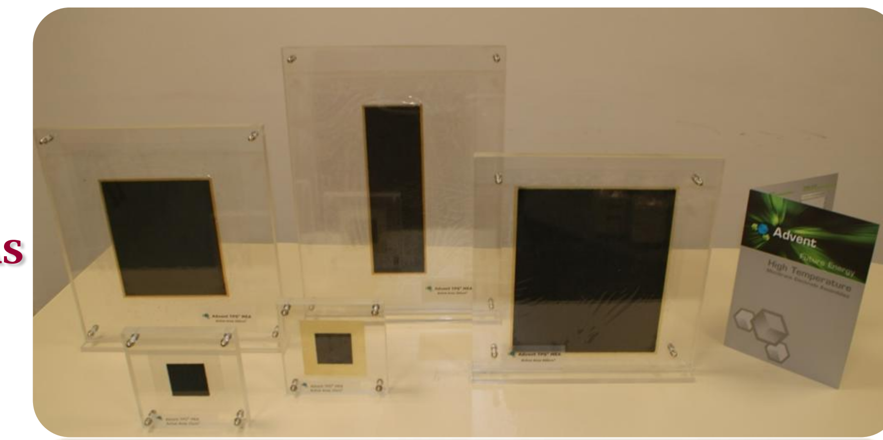


Polymer

Membrane

- Low Cost
- Large scale manufacturing
- Durable, stable

Advent TPS® High Temperature MEAs



Currently Advent develops fully integrated HT-PEMFC systems for electricity generation, also combined with water electrolysers, MeOH or LPG reformers

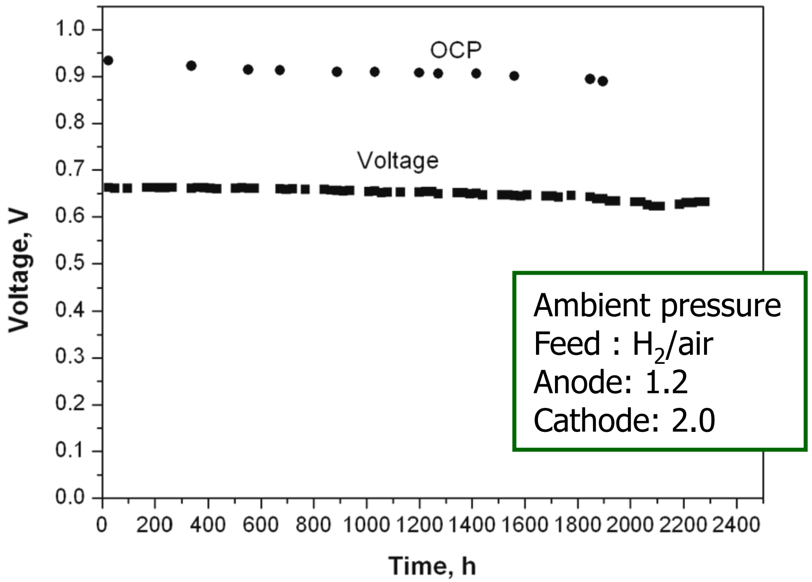
Issued patents:

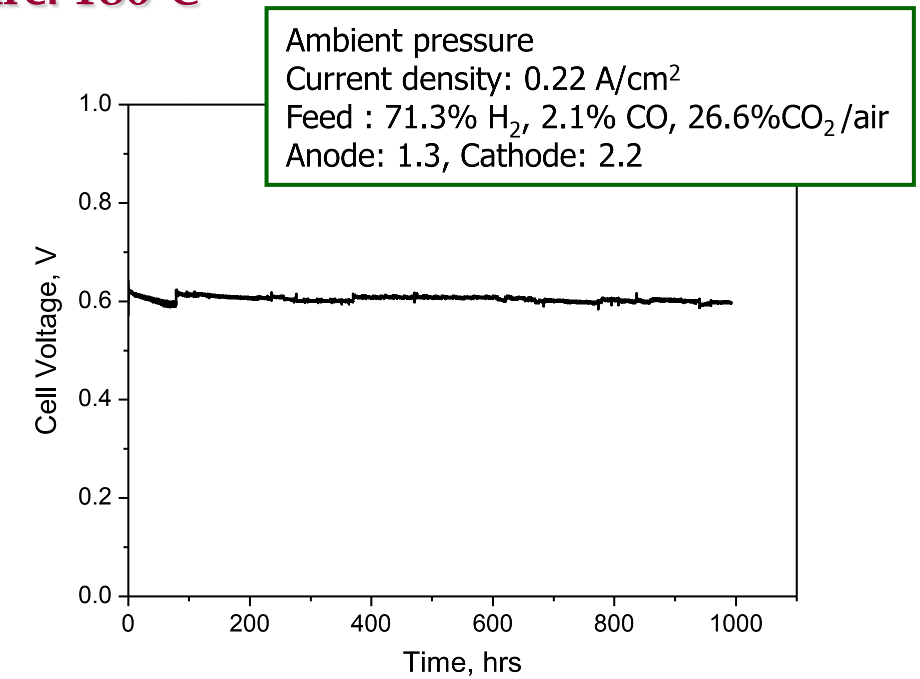
US 7,786,244	31/08/2010
US 7,842,733	30/11/2010
US 7,754,843	31/07/2010
EP 2,134,768	15/09/2010
US 7,842,734	30/11/2010
US 7,842,775	30/11/2010

Advent

Available lifetime data-New generation Advent TPS® MEA

Temperature: 180°C





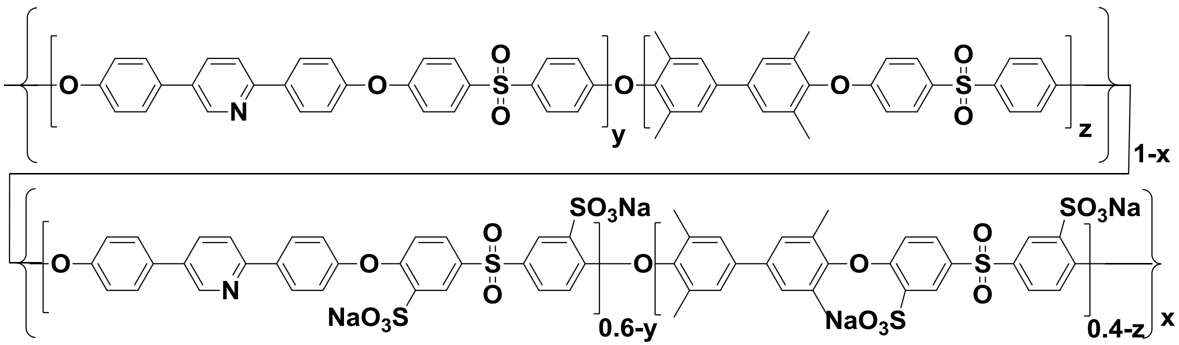
- Operation temperature: 150°C-200°C
- High carbon monoxide tolerance
- Long term stability with small voltage drop
- Endurance under differential pressure
- No need for humidified gases
- Zero degradation under cycling operating conditions
- Easier to mass production due to favorable membrane properties

Advent

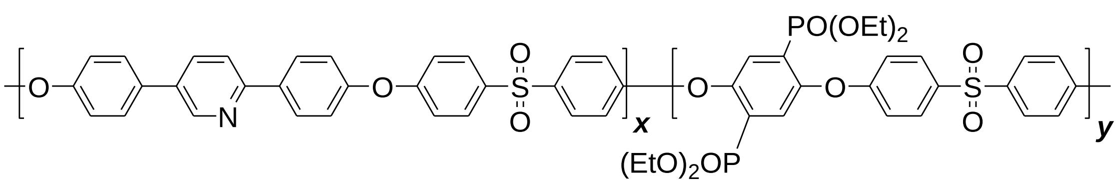
Functional side groups

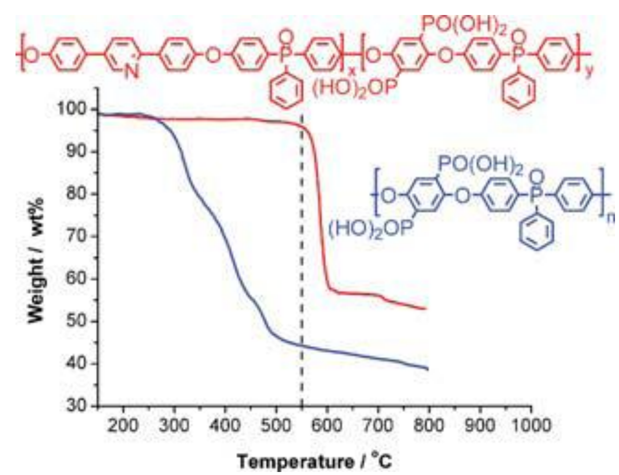
great versatility of the synthetic route

Sulfonated copolymers



Phosphonate ester or phosphonic acid side groups





acid–base interactions between the pyridine and the side phosphonic acid groups, with no weight loss up to 550° C

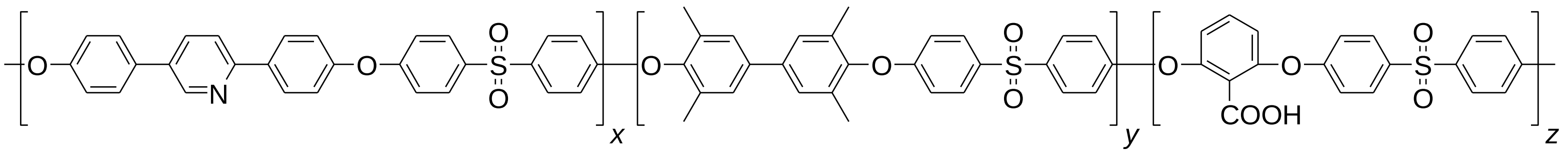
I. Kalamaras, M. K. Daletou, V. G. Gregoriou, J. K. Kallitsis, FUEL CELLS 11, 2011, No. 6, 921–931

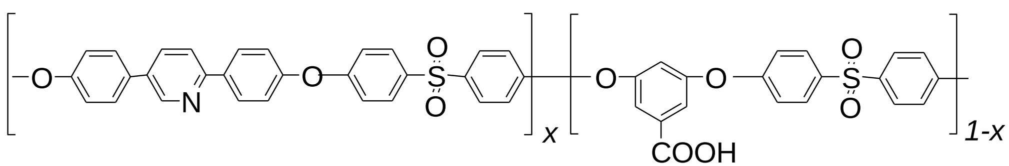
K. Papadimitriou, A. Andreopoulou, J. Kallitsis, Journal of Polymer Science, Part A, 48, 2817-2827, (2010)

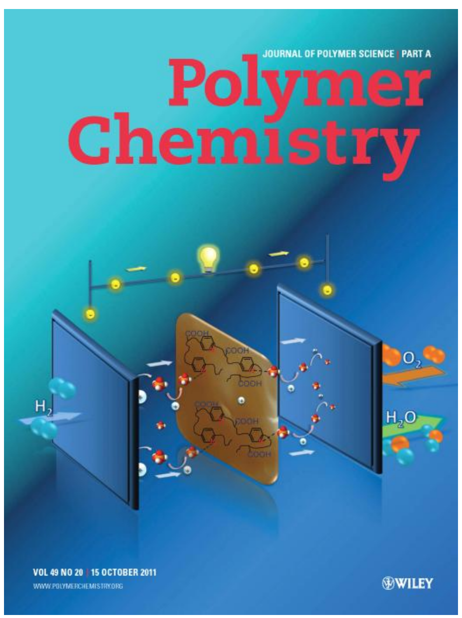
Functional side groups

great versatility of the synthetic route

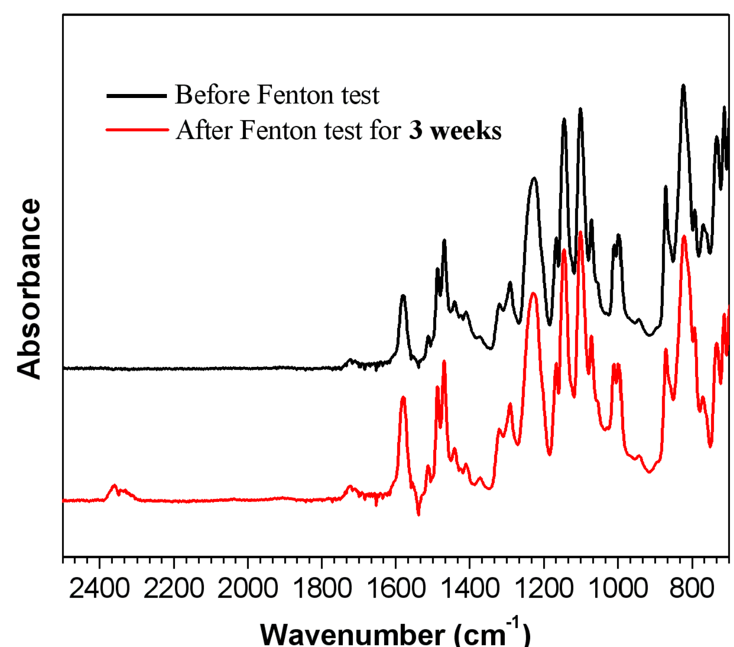
Carboxylic acid side groups







FTIR spectra:
no changes in the chemical structure



C. Morfopoulou, K. Andreopoulou, J. Kallitsis, J. Polym Sci. Part A: Polym. Chem., 2011, 49, 4325.

Covalently Crosslinked Membranes

Increasing the fuel cells **operation temperature above 180^oC and even up to 220^oC** offers several distinct advantages:

- Increased conductivity of the H_3PO_4 doped membranes at lower doping levels.
- Increased tolerance of the catalytic layers to contaminants, most importantly CO and sulfur species, due to their weaker chemisorption on the catalyst surface. Thus reformates of lower purity can be adequately used as fuel, reducing the cost for H_2 purification.
- Better heat management and heat utilization.
- Efficient combination with other electrochemical devices e.g. a methanol or LPG reformers.

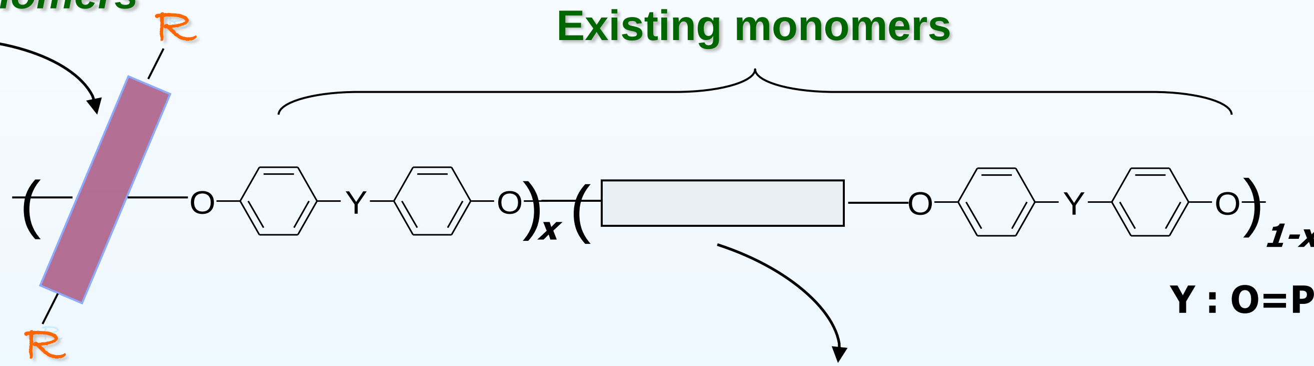
Chemically Cross-linked PEMs present superior stability

- ✓ **Increase in operating temperature**
- ✓ **Increase in mechanical & chemical stability**

Linear aromatic polyethers containing side cross-linkable units

New diol monomers

Existing monomers



Y : O=P-Ph, SO_2

pyridine and/or methyl bearing monomers

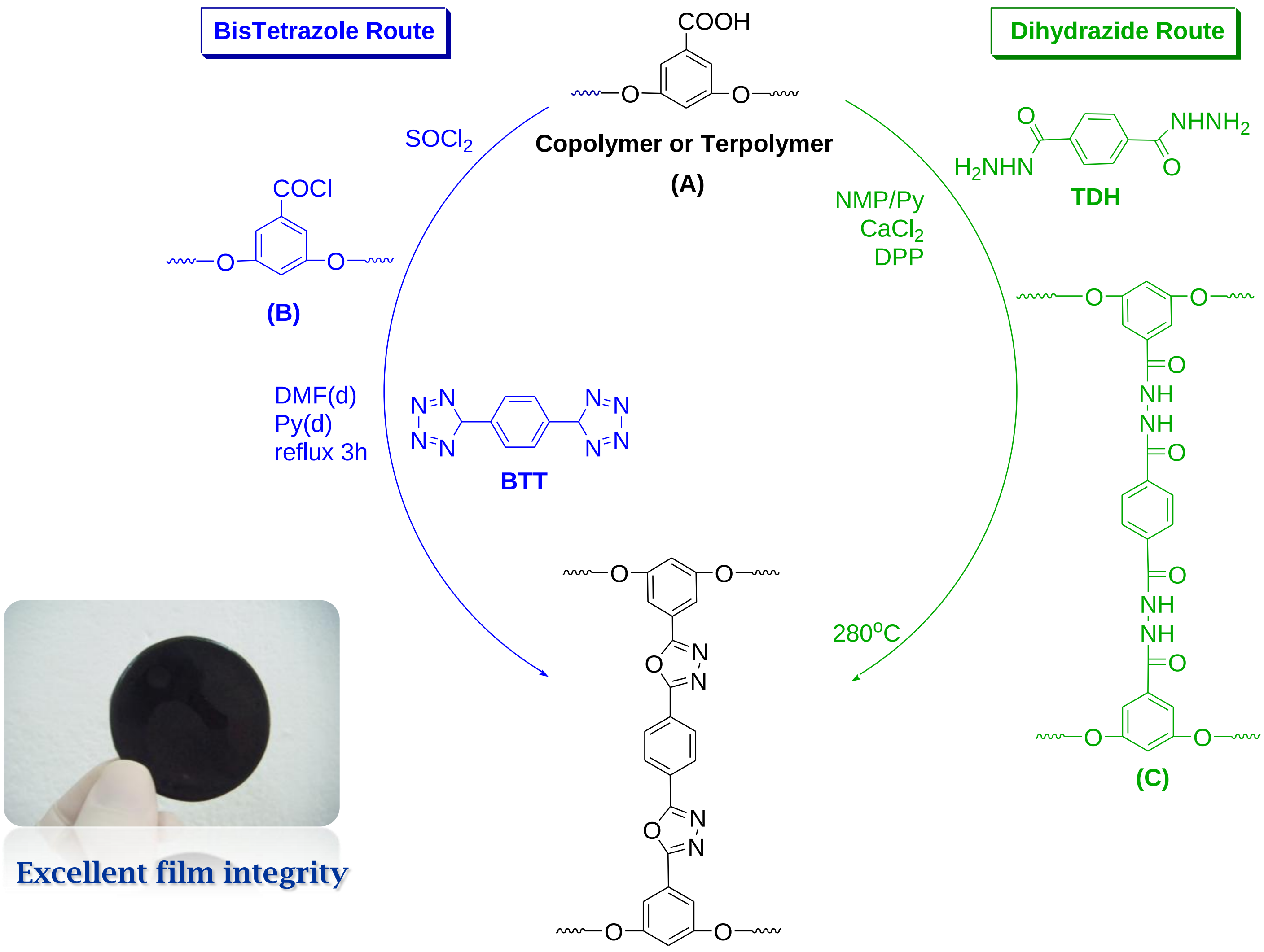
R = Crosslinking Sites

- carboxylic units
- double bonds
- triple bonds

Characterization of the resulting crosllinked membranes :

- thermal and mechanical analysis
- evaluation of their phosphoric acid uptake
- HT PEMFC performance.

Cross-linking through side carboxylic acids



1,3,4-Oxadiazole Bridges

Excellent film integrity

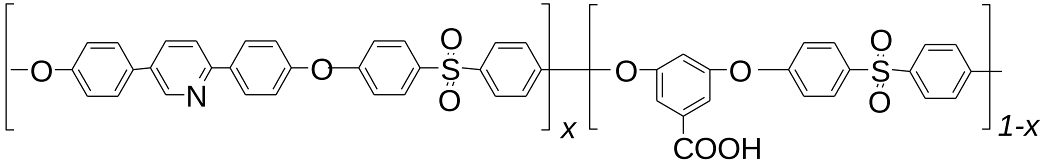
Good film integrity

▪C. Morfopoulou, A.K. Andreopoulou, M.K.Daletou, S.G.Neophytides, J.K.Kallitsis Submitted 2012
▪Andreopoulou, A.; Voege, A.; Paloukis, F.; Morfopoulou, C.; Papadimitriou, K.; Neophytides, S.; Kallitsis, J.; Daletou, M.; Kalamaras, J. U.S. Pat. Appl. Publ. (2012), US 20120202129 A1 20120809.

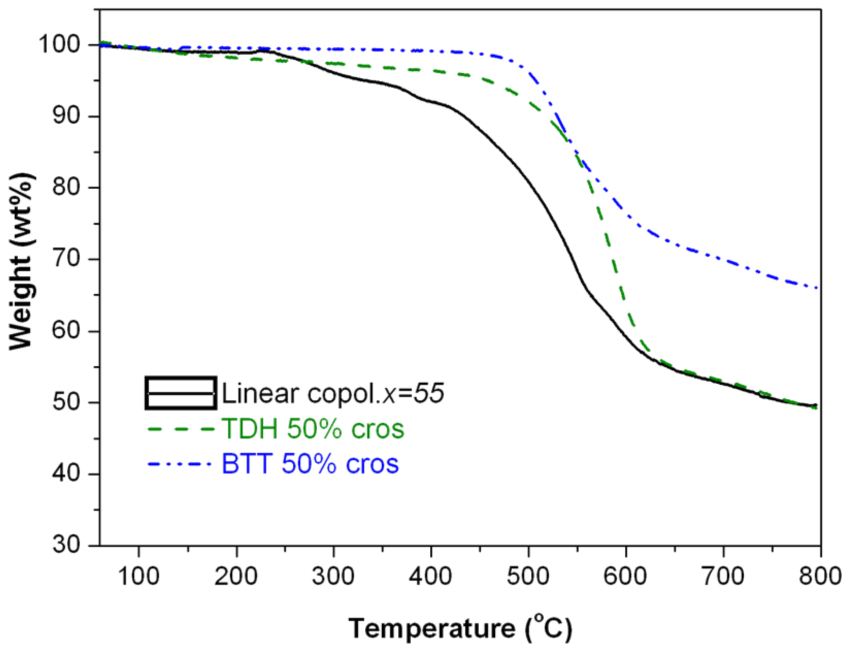
Cross-linking through side carboxylic acids

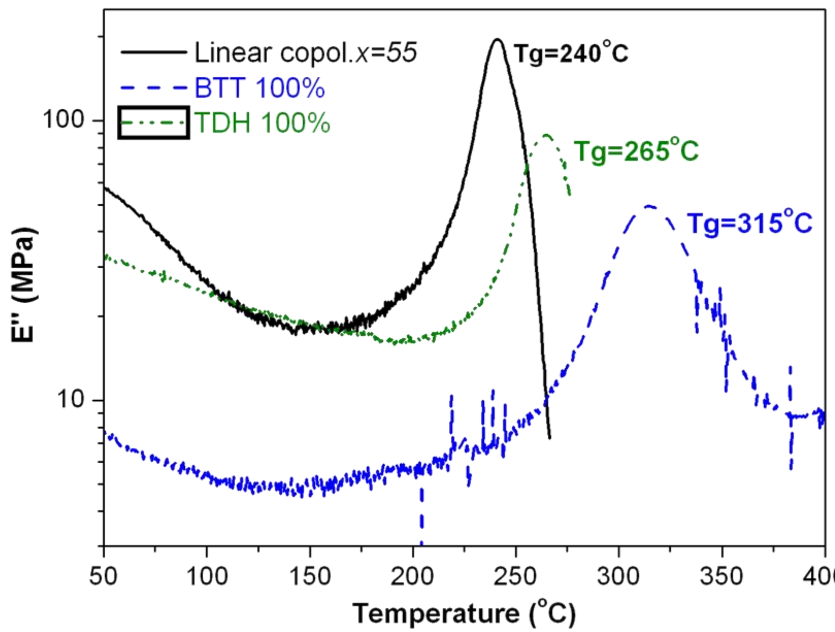
Comparison of the two methods:

- **through bistetrazole (BTT)**
- **through dihydrazide (TDH)**



x=55



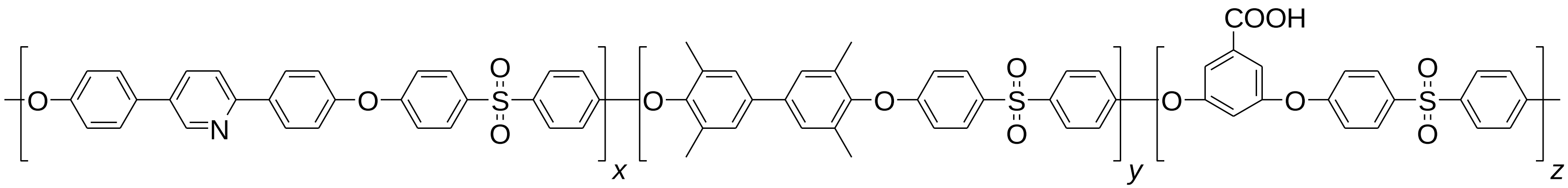


C. Morfopoulou, A. Andreopoulou, M. Daletou, S. G. Neophytides, J. K. Kallitsis, SUBMITTED 2012

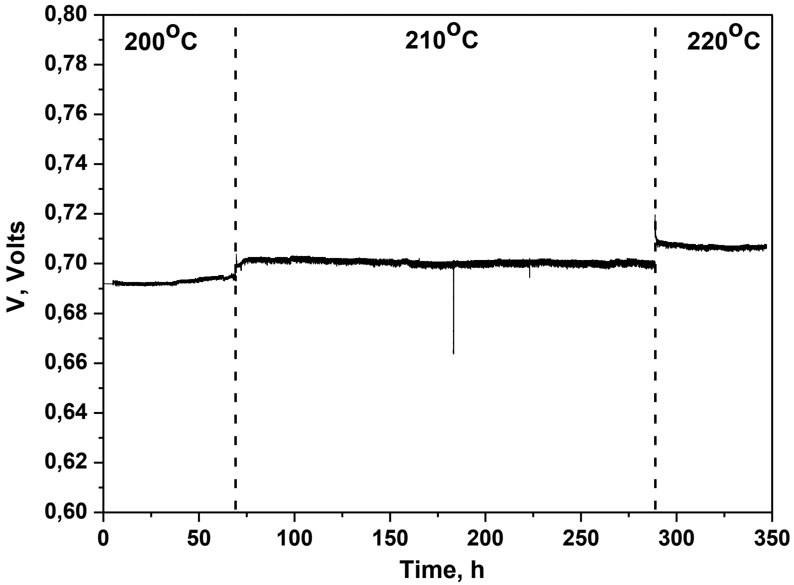
Cross-linking through side carboxylic acids

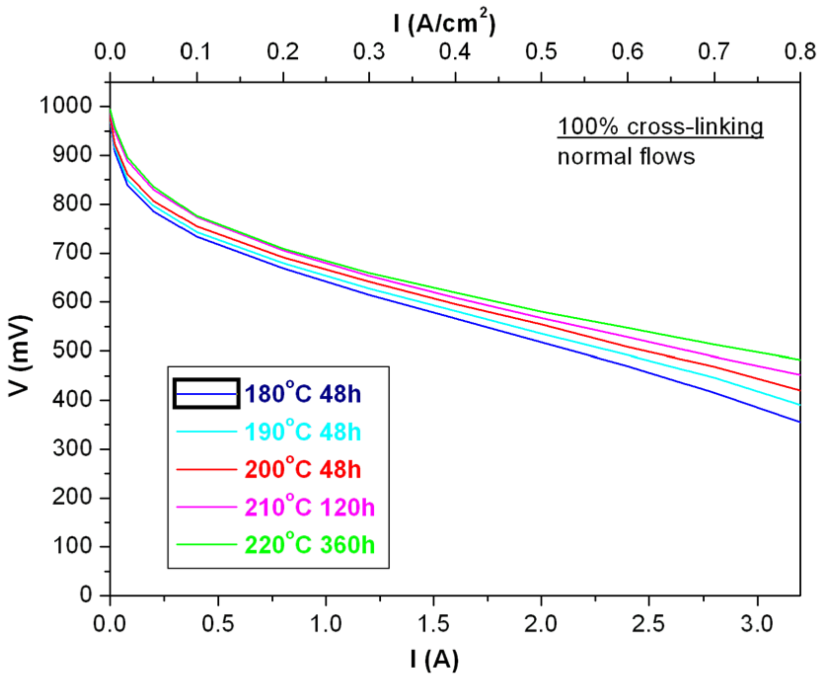
using bistetrazole (BTT) as the crosslinking agent

x=70, y=20, z=10



cell potential vs time @ $0.2A/cm^2$



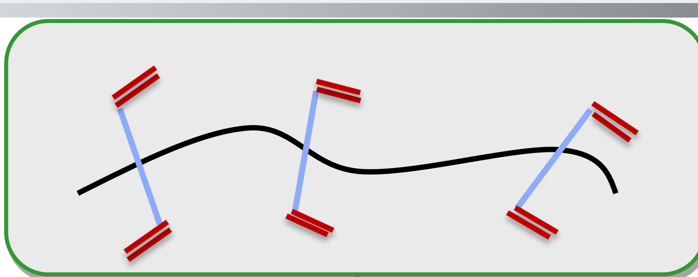


Feed: H_2 (λ=1.2)/O_2 (λ=2)

MEA active area	4 cm^2
Membrane	**100% cross-linked**
Doping	210 %
Thickness	175μm

C. Morfopoulou, A. Andreopoulou, M. Daletou, S. G. Neophytides, J. K. Kallitsis, SUBMITTED 2012

Cross-linking through side double bonds

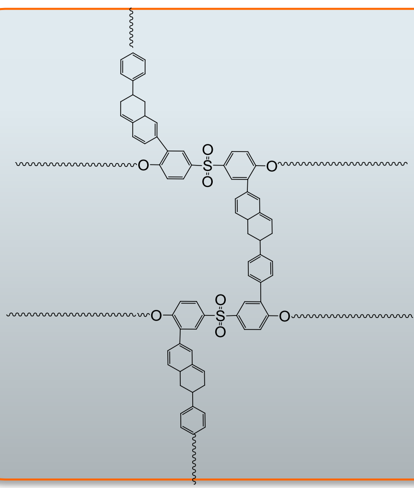


(1)

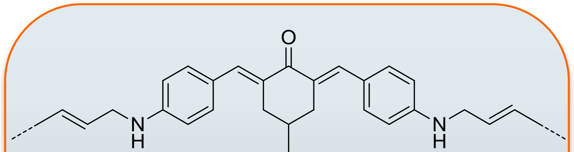
(2)

(3)

Thermal Cross-linking



Cross-linking through *bisazide*

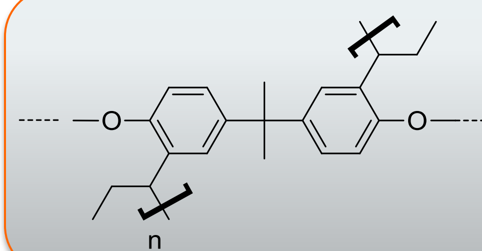


Amines

and

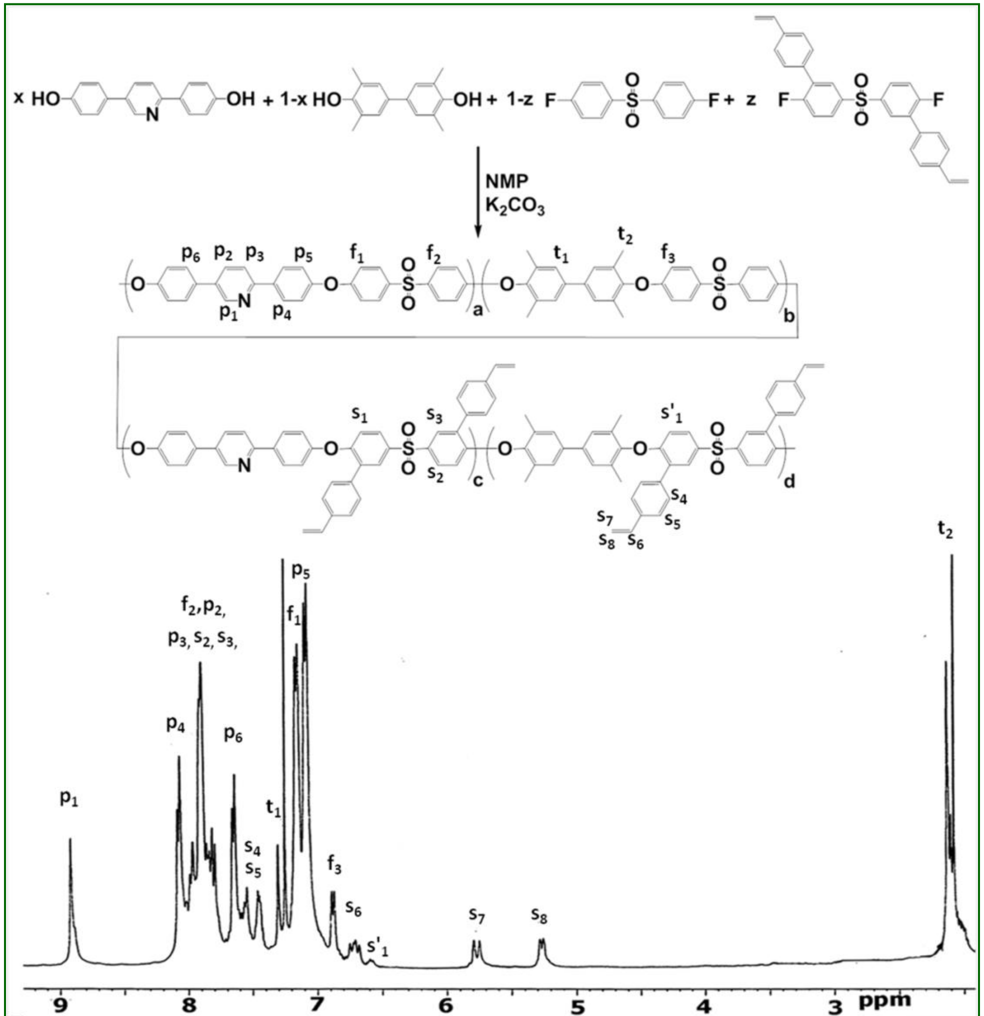
Aziridines

H_3PO_4 Cross-linking through cationic polymerization



- K. D. Papadimitriou, F. Paloukis, S. G. Neophytides, J. K. Kallitsis, *Macromolecules,* 44 (12), 2011,pp 4942–4951
- I. Kalamaras, M.K.Daletou, S.G.Neophytides, J.K.Kallitsis *J. Membr. Sci.* 415–416, (2012), pp 42–50
- K. D. Papadimitriou, M. Geormezi, S. G. Neophytides, J. K. Kallitsis Submitted, 2012
- Andreopoulou, A.; Voege, A.; Paloukis, F.; Morfopoulou, C.; Papadimitriou, K.; Neophytides, S.; Kallitsis, J.; Daletou, M.; Kalamaras, J. U.S. Pat. Appl. Publ. (2012), US 20120202129 A1 20120809.

Thermal Cross-linking of double bonds



PPy(x)T(y)STF(z)S(w)

Copolymer	Mn	Mw	I
PPy(100)STF(20)S(80)	12000	20000	1.7
PPy(80)T(20)STF(20)S(80)	10000	18000	1.8
PPy(75)T(25)STF(20)S (80)	9000	14000	1.6
PPy(75)T(25)STF(15)S(85)	13000	25000	1.9
PPy(60)T(40)STF(7.5)S(92.5)	13000	21000	1.6
PPy(60)T(40)STF(10)S(90)	9000	14000	1.6
PPy(60)T(40)STF(15)S(85)	21000	36000	1.7
PPy(60)T(40)STF(20)S(80)	13000	22000	1.7

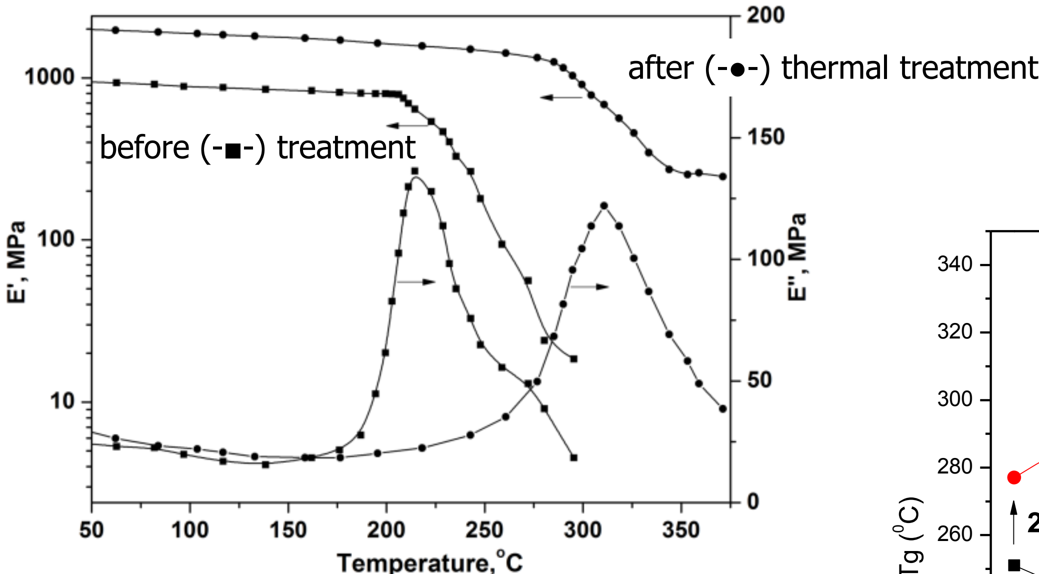
Pyridine diol = **Py** content
(x) =60-100

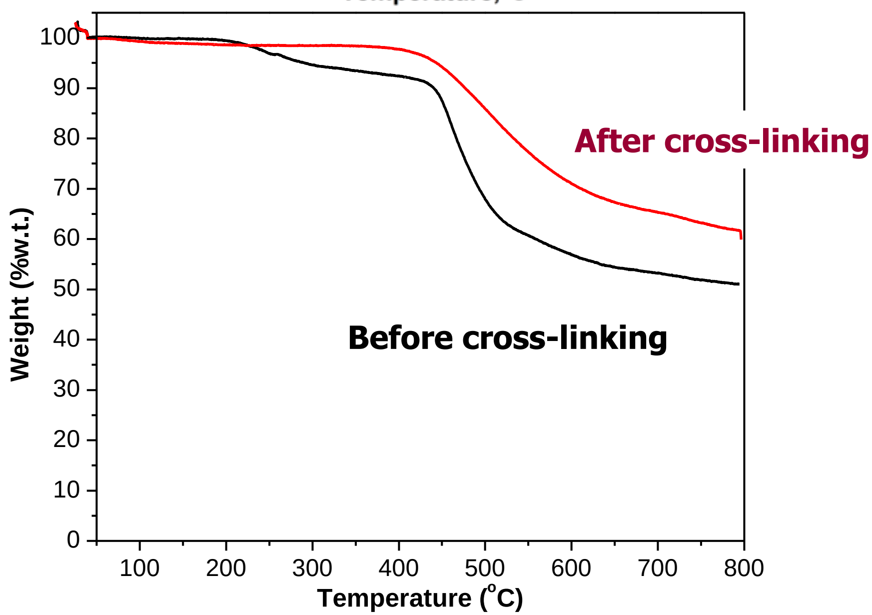
3,3′-bis(4-vinylbenzene)-4,4′-difluorodiphenyl sulfone =
STF content
(z) = 7.5-20%

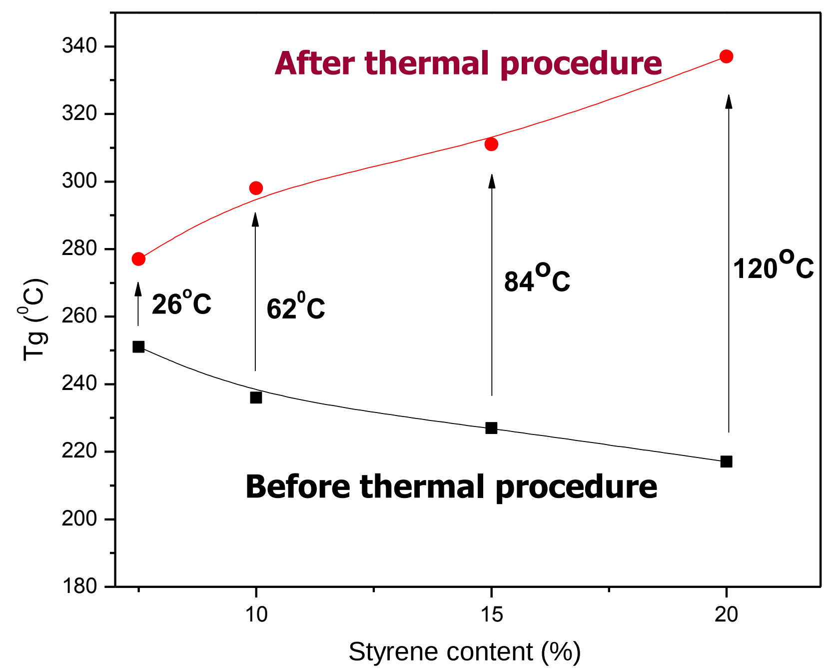
I. Kalamaras, M.K.Daletou, S.G.Neophytides, J.K.Kallitsis *J. Membr. Sci.* 415–416, (2012), pp 42–50

Thermal Cross-linking of double bonds

PPy(60)T(40)STF(15)S(85)



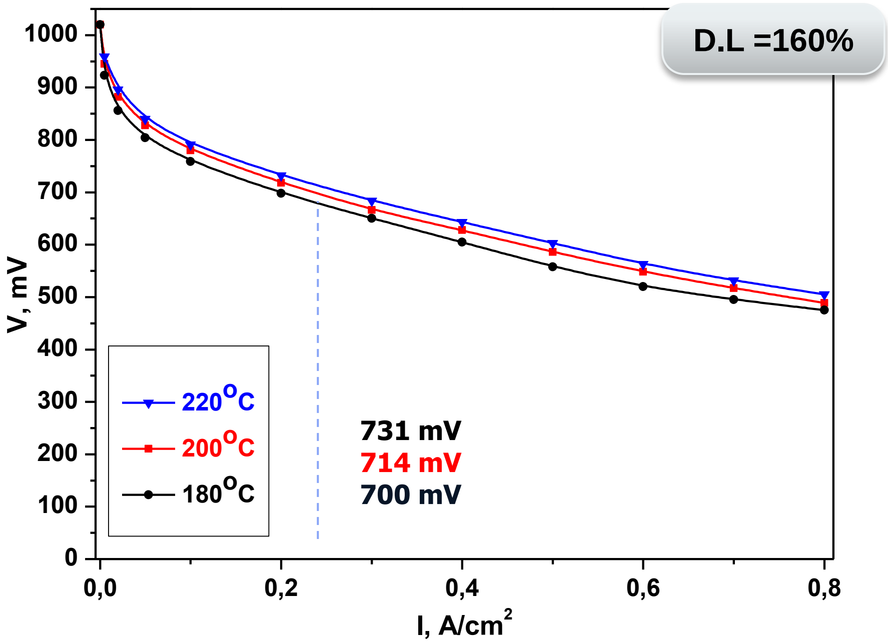


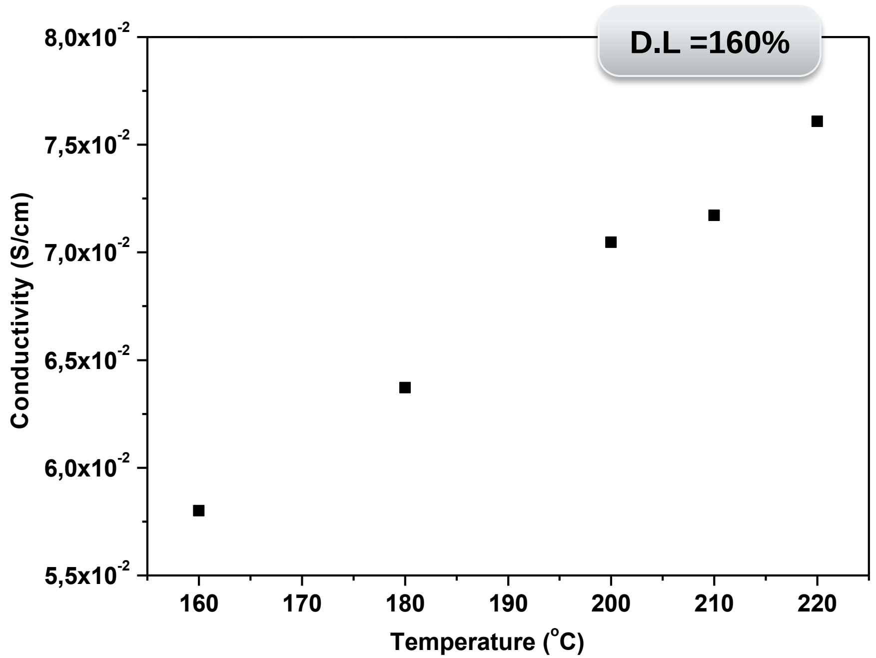


I. Kalamaras, M.K.Daletou, S.G.Neophytides, J.K.Kallitsis
J. Membr. Sci. 415–416, (2012), pp 42–50

Thermal Cross-linking of double bonds

Cross-linked **PPy(60)T(40)STF(15)S(85)**
Doping level: 160% wt
Membrane thickness:110μm

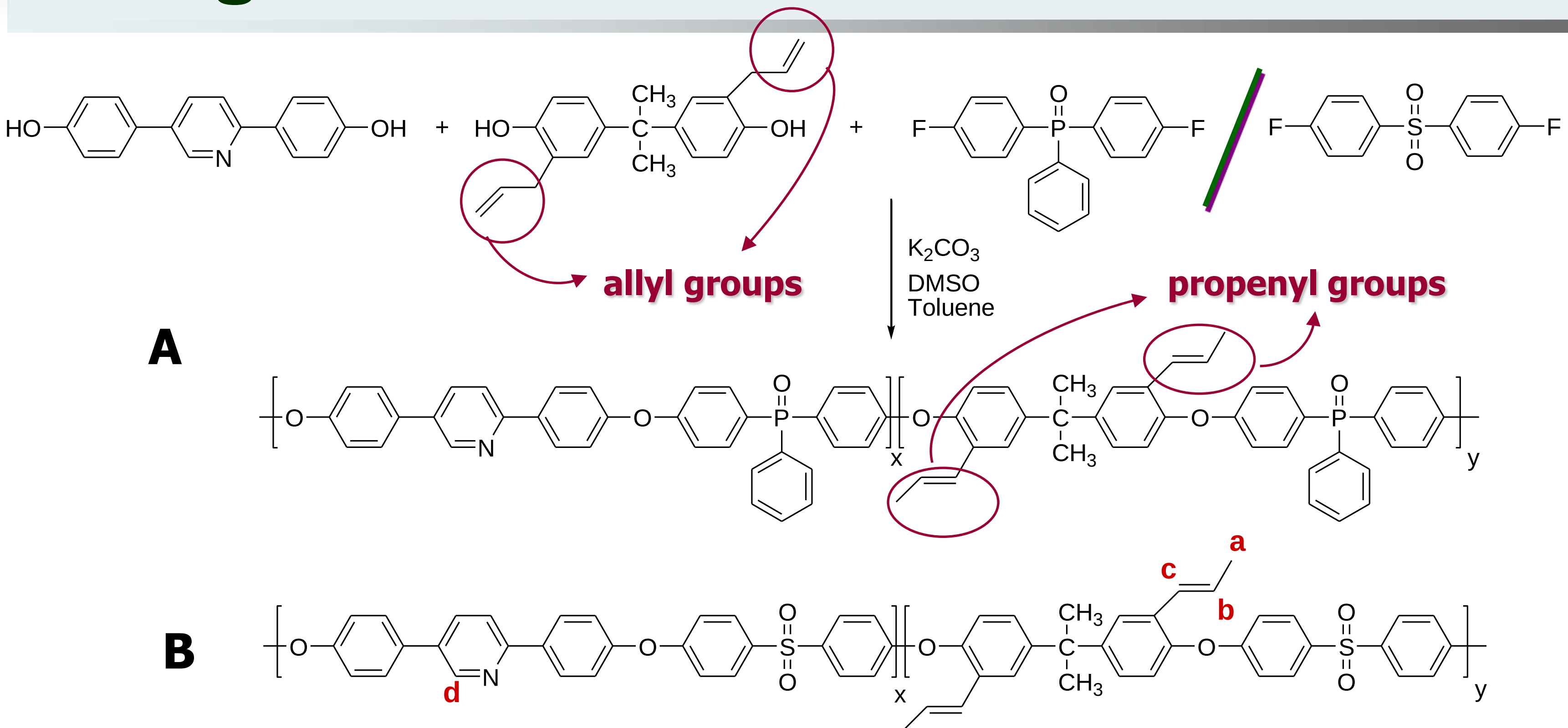




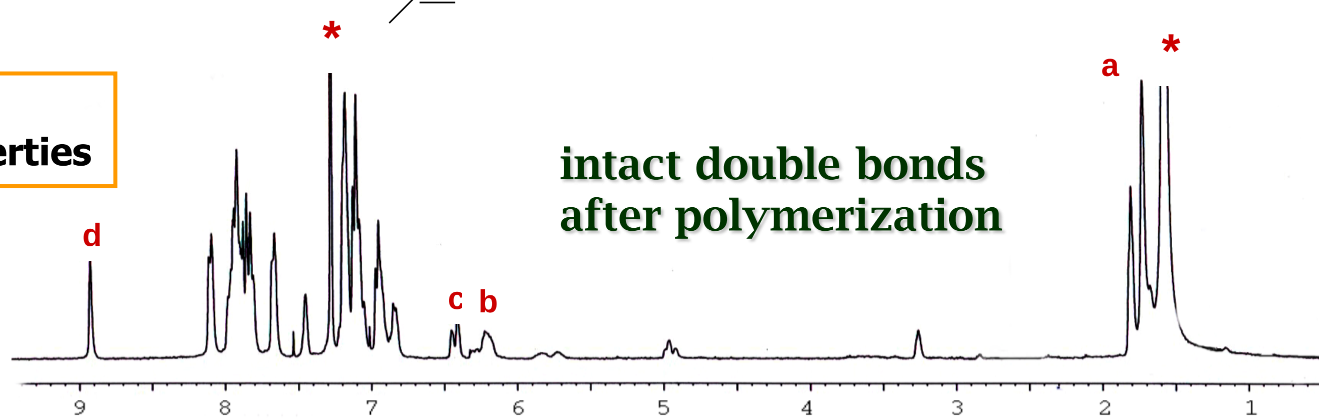
Feed: H_2 (λ=1.2)/O_2 (λ=2)

- I. Kalamaras, M.K.Daletou, S.G.Neophytides, J.K.Kallitsis J. Membr. Sci. 415–416, (2012), pp 42–50
- Andreopoulou, A.; Voege, A.; Paloukis, F.; Morfopoulou, C.; Papadimitriou, K.; Neophytides, S.; Kallitsis, J.; Daletou, M.; Kalamaras, J. U.S. Pat. Appl. Publ. (2012), US 20120202129 A1 20120809.

Cross-linking of double bonds through a bisazide



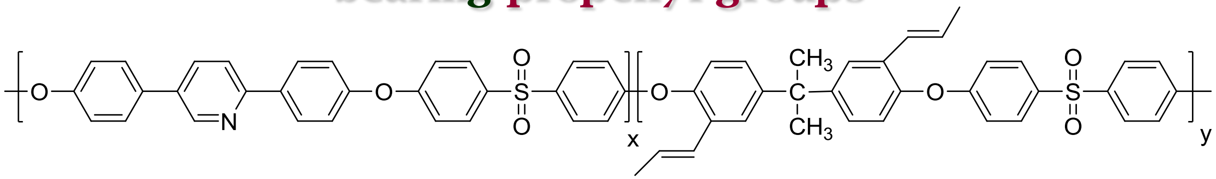
- ✓ **High molecular weights**
- ✓ **Excellent film forming properties**



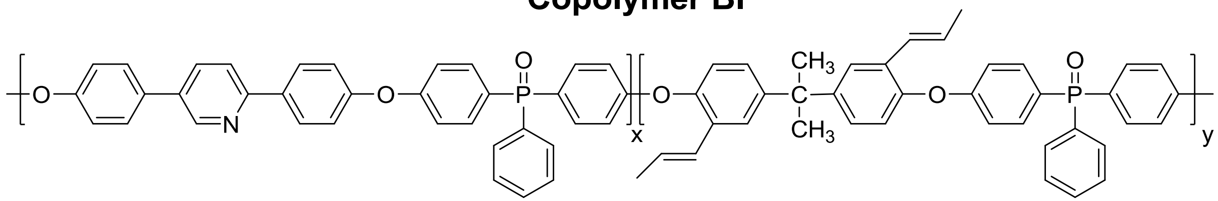
K. D. Papadimitriou, F. Paloukis, S. G. Neophytides, J. K. Kallitsis, *Macromolecules,* 44 (12), 2011,pp 4942–4951

Cross-linking of double bonds through a bisazide

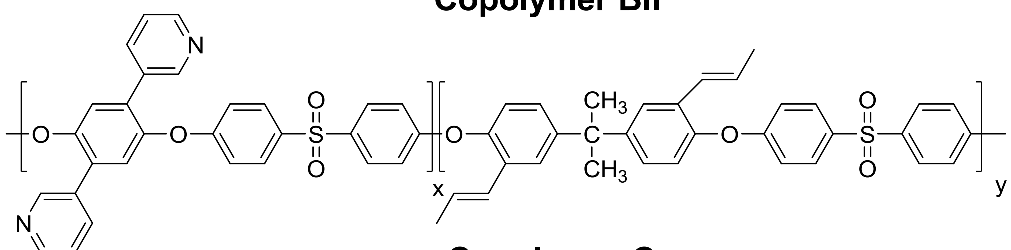
Library of prepared Side Chain Unsaturated Aromatic Polyethers bearing propenyl groups



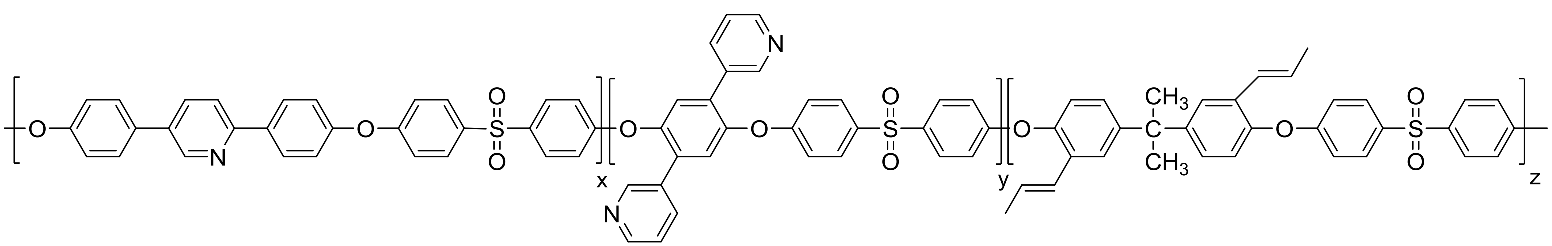
Copolymer BI



Copolymer BII



Copolymer C

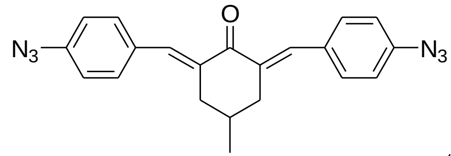


Terpolymer B

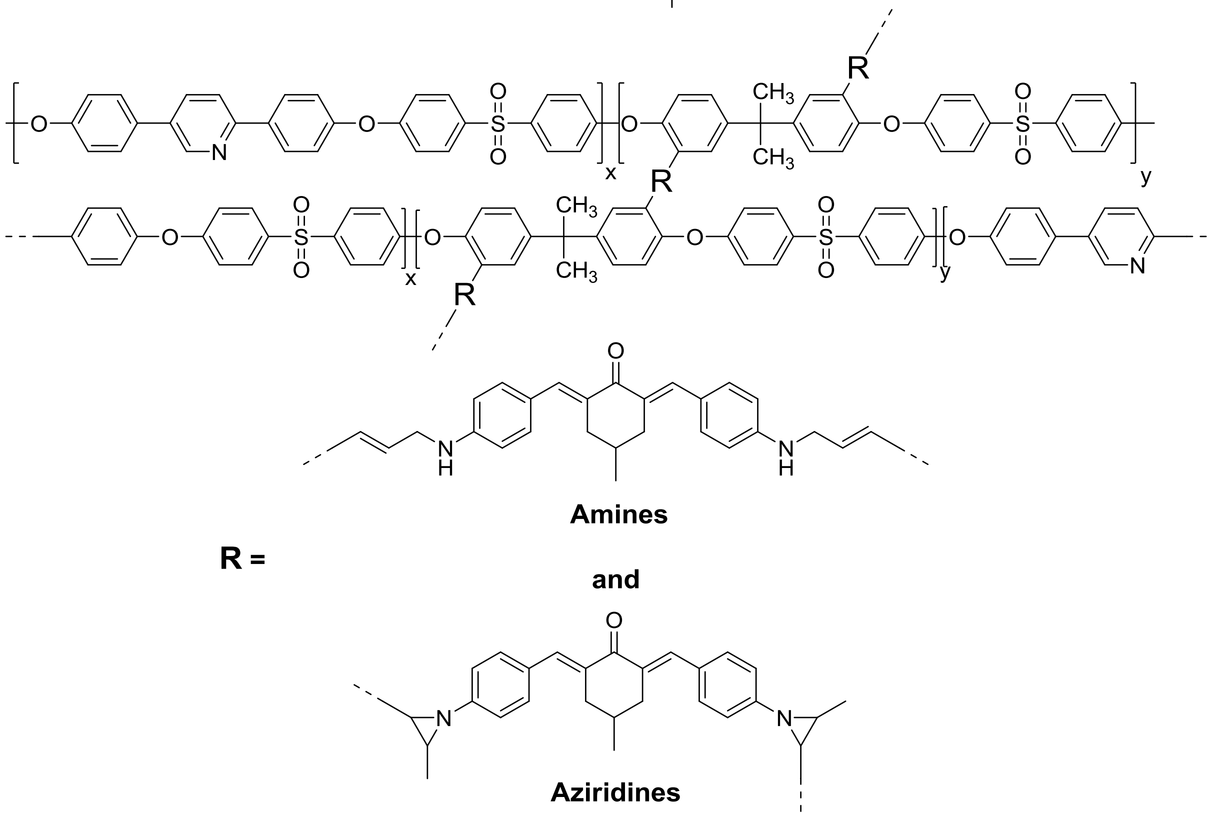
K. D. Papadimitriou, F. Paloukis, S. G. Neophytides, J. K. Kallitsis, *Macromolecules,* 44 (12), 2011,pp 4942–4951

Cross-linking of double bonds through a bisazide

Crosslinking agent :



Bisazide



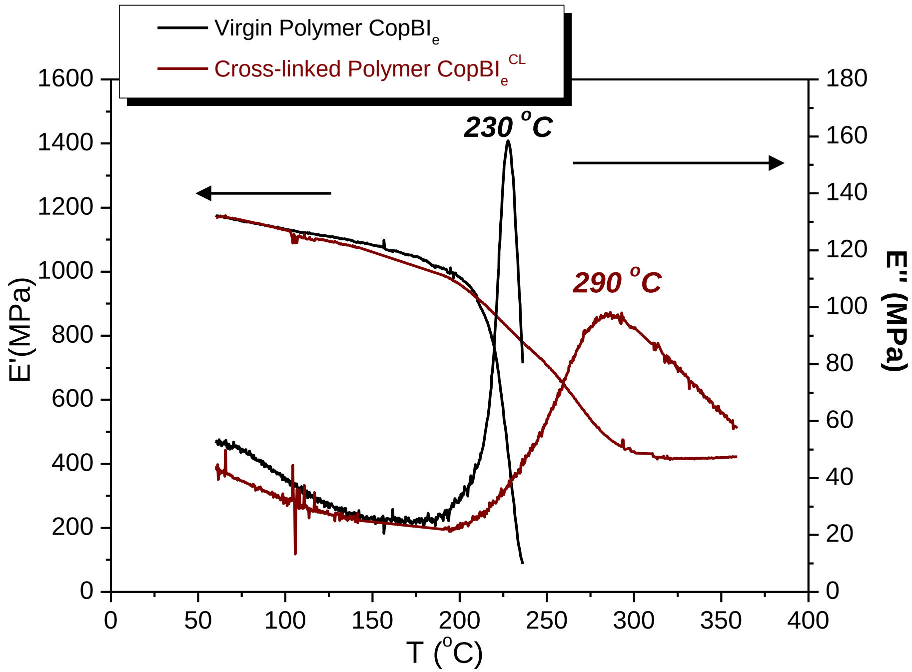
Cross-Linked Polymer

▪K. D. Papadimitriou, F. Paloukis, S. G. Neophytides, J. K. Kallitsis, Macromolecules, 44 (12), 2011,pp 4942–4951

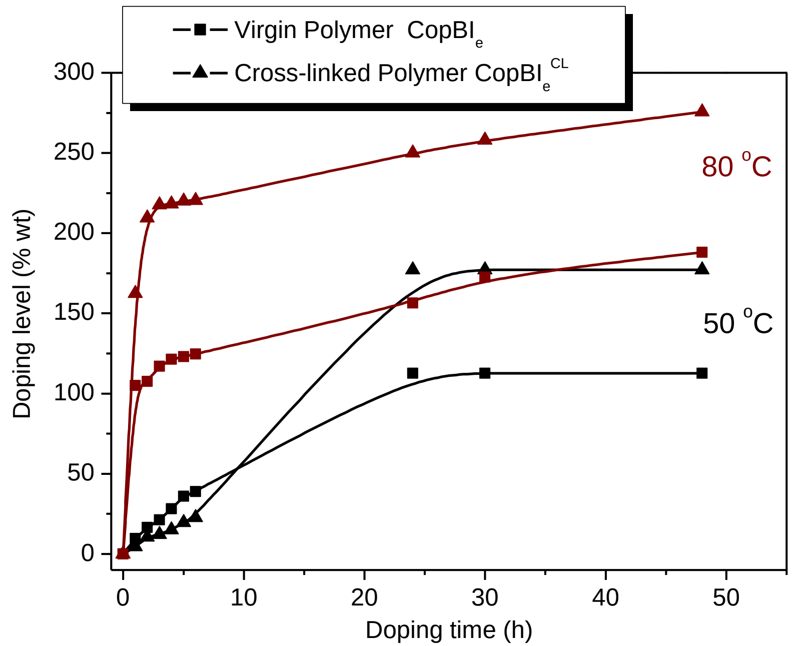
▪Andreopoulou, A.; Voege, A.; Paloukis, F.; Morfopoulou, C.; Papadimitriou, K.; Neophytides, S.; Kallitsis, J.; Daletou, M.; Kalamaras, J. U.S. Pat. Appl. Publ. (2012), US 20120202129 A1 20120809.

Cross-linking of double bonds through a bisazide

Example of DMA curves between a cross-linked membrane and its virgin analogue



Characteristic example of the doping ability between a cross-linked membrane and its virgin analogue



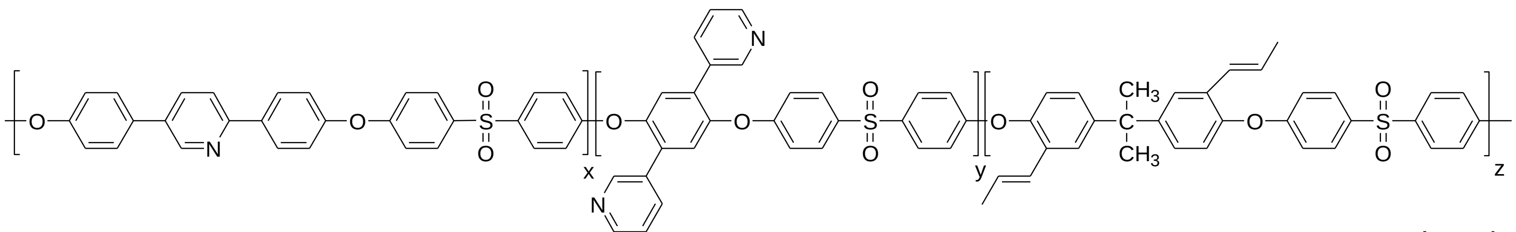
- High doping levels
- Higher doping ability of the cross-linked membranes due to the formation of the aziridines and amines

K. D. Papadimitriou, F. Paloukis, S. G. Neophytides, J. K. Kallitsis, *Macromolecules,* 44 (12), 2011,pp 4942–4951

Cross-linking of double bonds through a bisazide

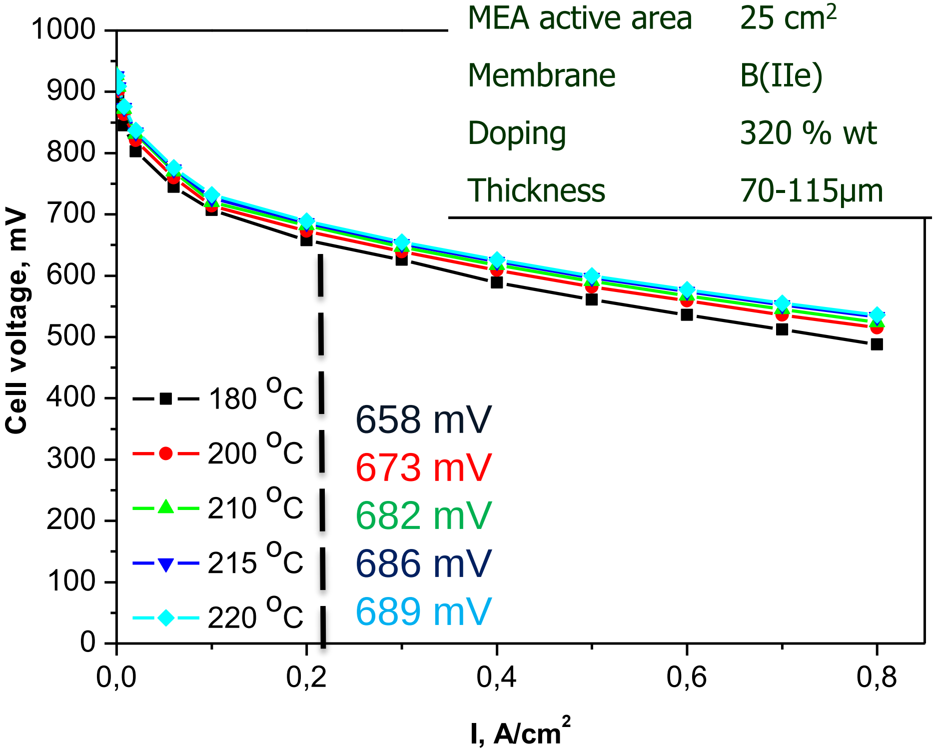
Electrochemical Characterization:

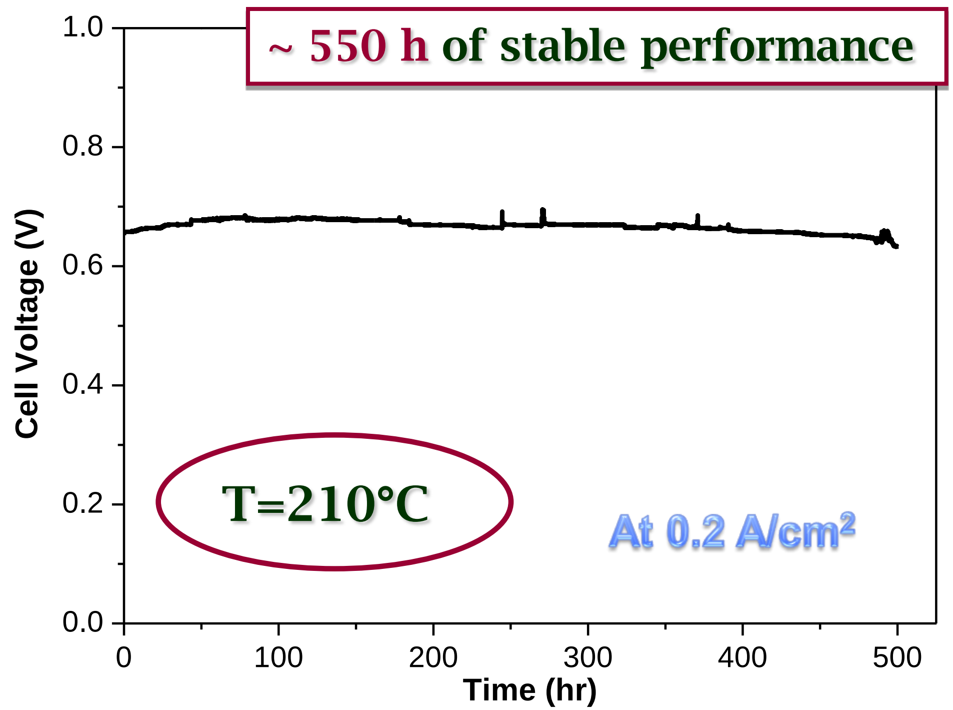
I-V Curves and Long -Term Durability Test of the Cross-linked with **Bisazide** **TerpolB5^{CL}**



Feed: H_2/Air normal flows

MEA active area	25 cm^2
Membrane	B(IIe)
Doping	320 % wt
Thickness	70-115μm

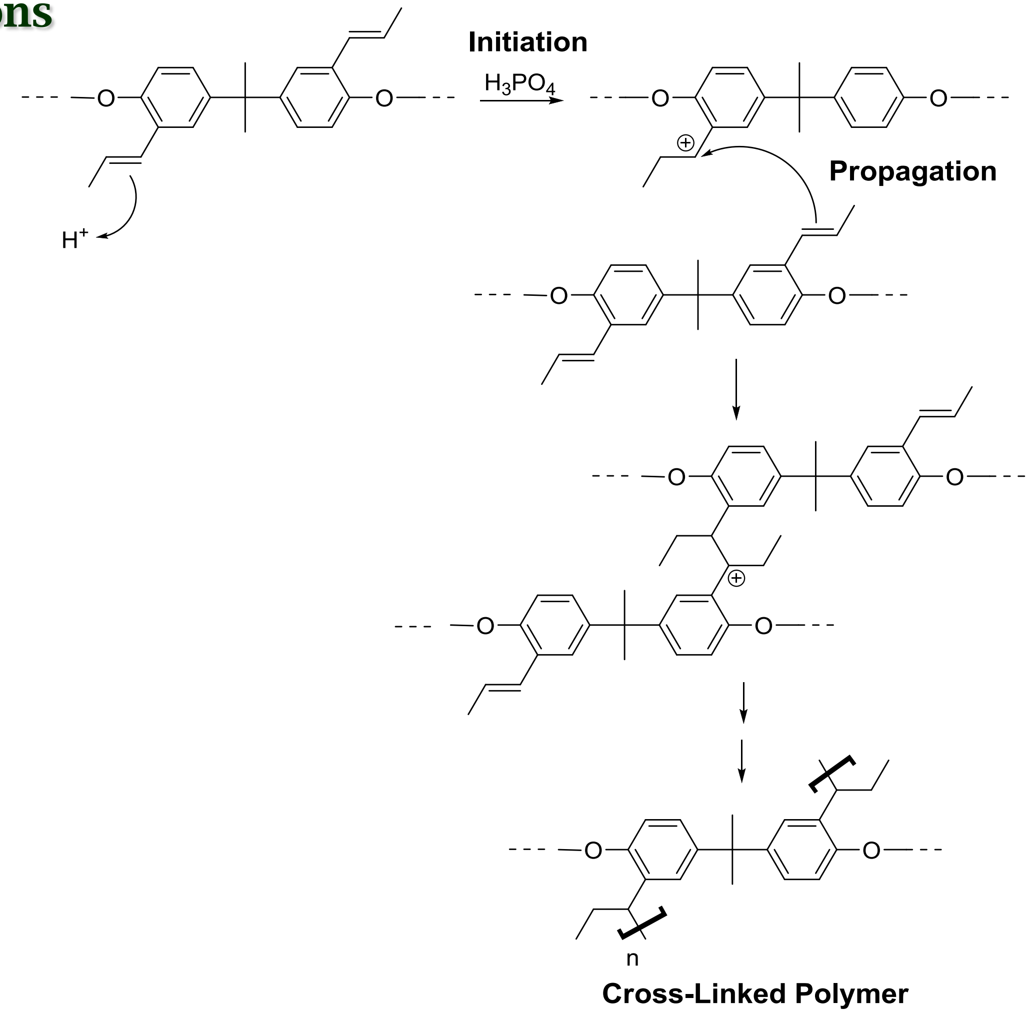




Andreopoulou, A.; Voege, A.; Paloukis, F.; Morfopoulou, C.; Papadimitriou, K.; Neophytides, S.; Kallitsis, J.; Daletou, M.; Kalamaras, J.
U.S. Pat. Appl. Publ. (2012), US 20120202129 A1 20120809.

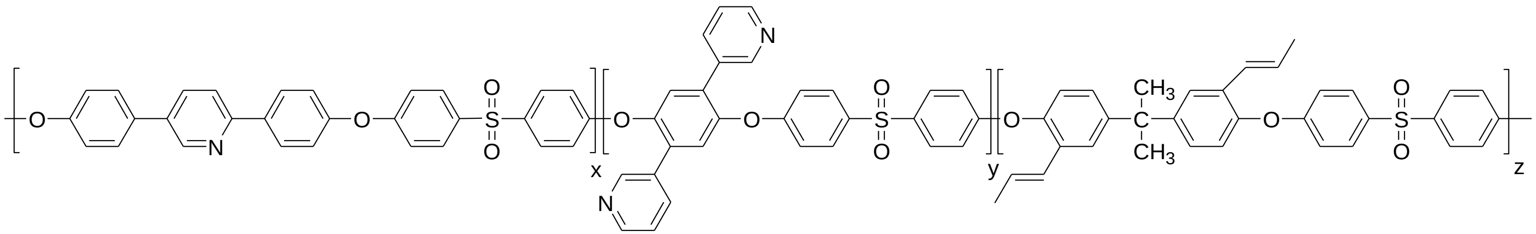
H_3PO_4 Cross-linking of double bonds

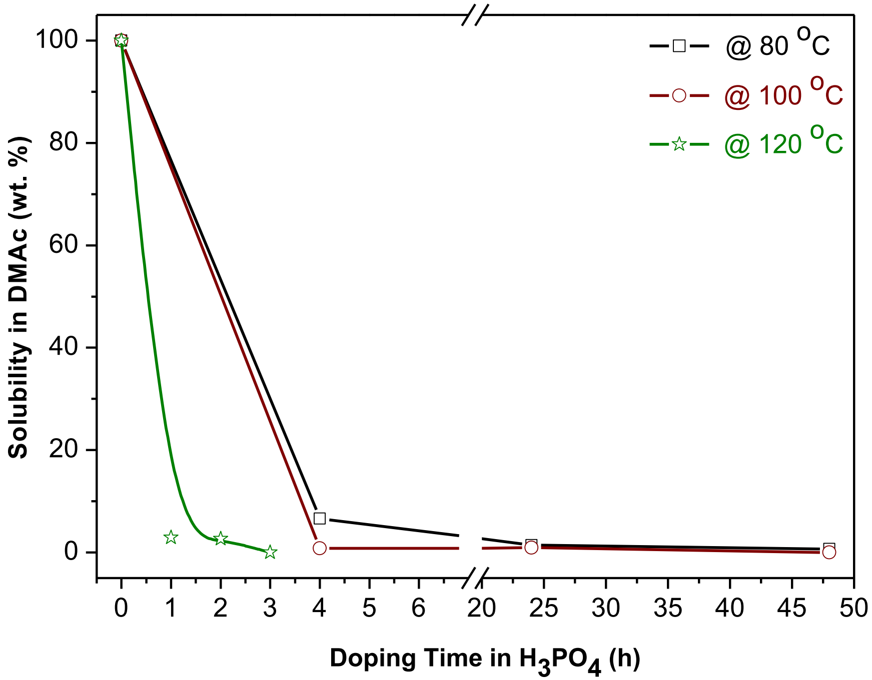
through a “cationic polymerization” like mechanism of repetitive alkylation reactions



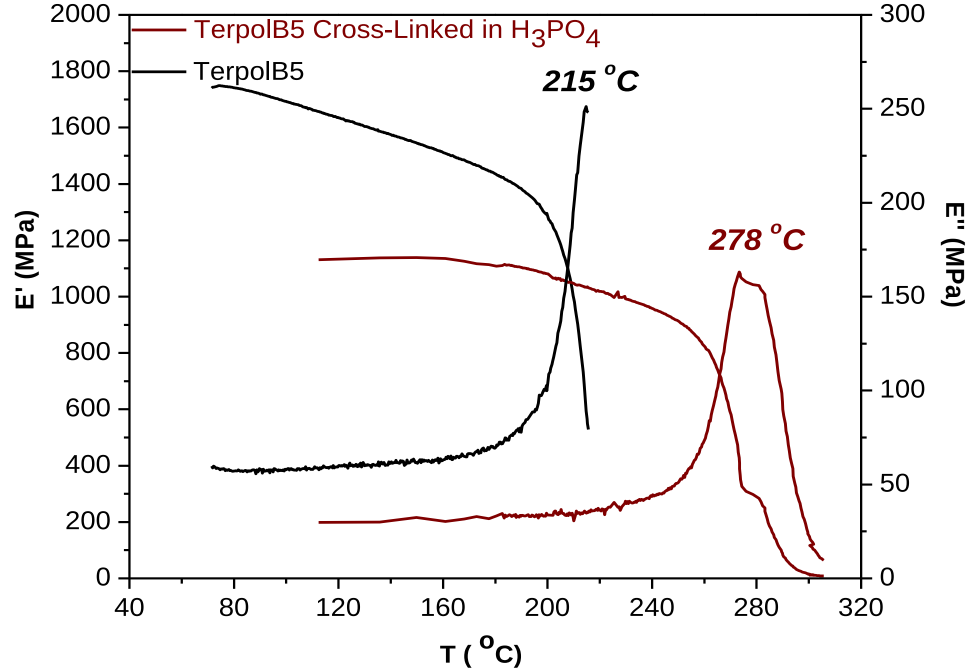
- K. D. Papadimitriou, M. Geormezi, S. G. Neophytides, J. K. Kallitsis Submitted, 2012
- Andreopoulou, A.; Voege, A.; Paloukis, F.; Morfopoulou, C.; Papadimitriou, K.; Neophytides, S.; Kallitsis, J.; Daletou, M.; Kalamaras, J. U.S. Pat. Appl. Publ. (2012), US 20120202129 A1 20120809.

H_3PO_4 Cross-linking of double bonds





Solubility dependence in DMAc after 6 hours at 60 °C versus the doping time in H_3PO_4 at different temperatures for the cross-linked terpolymer

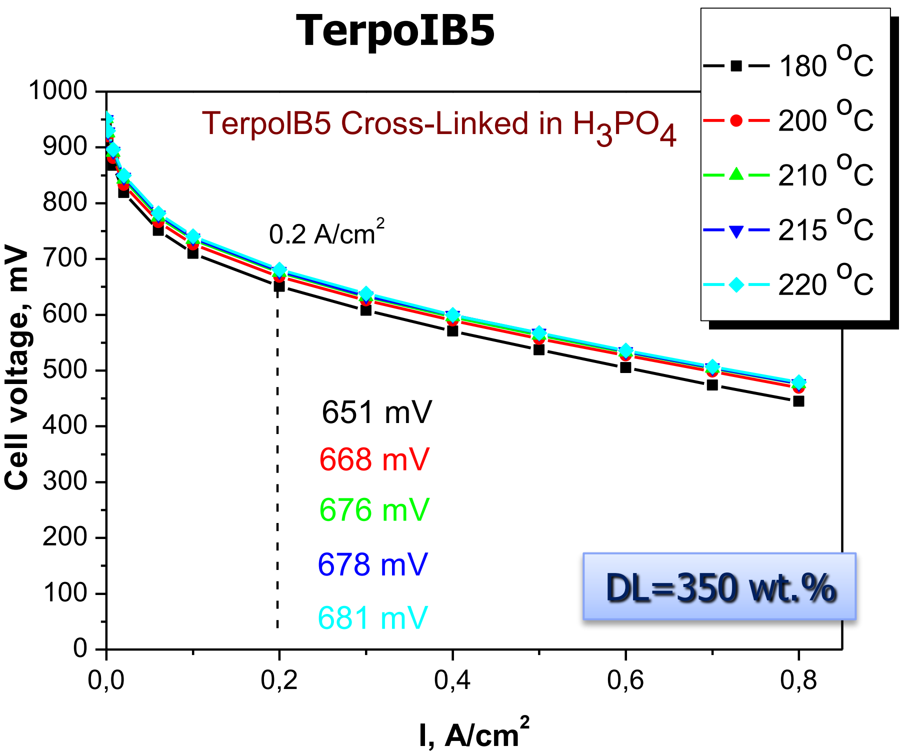


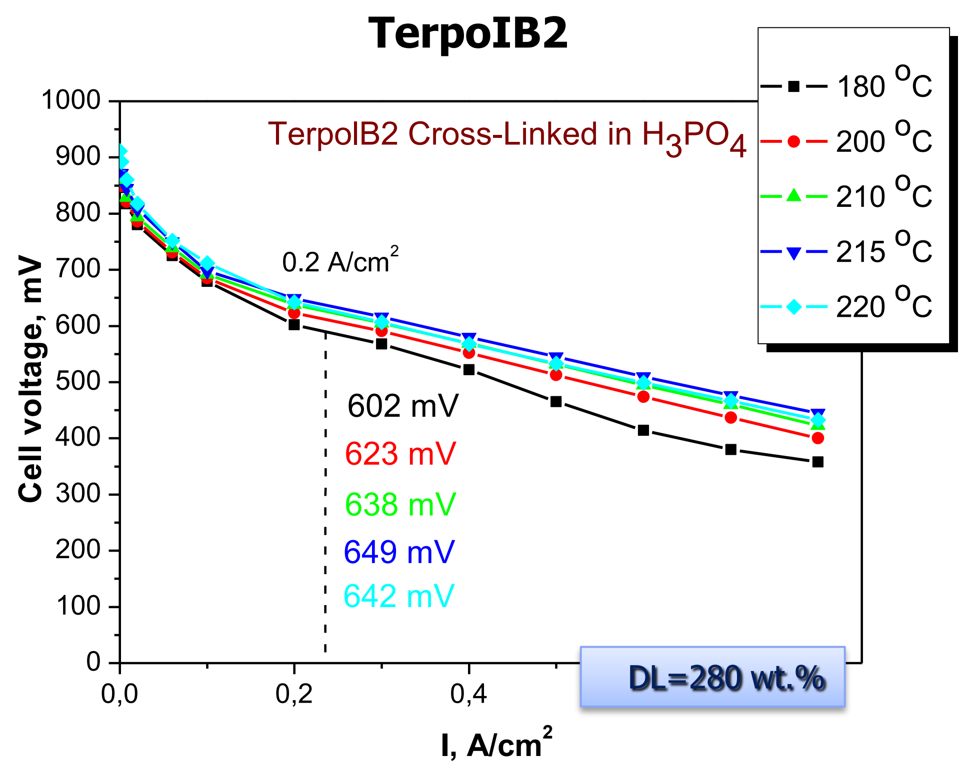
DMA curves of the cross-linked in acid and the virgin terpolymer

Andreopoulou, A.; Voege, A.; Paloukis, F.; Morfopoulou, C.; Papadimitriou, K.; Neophytides, S.; Kallitsis, J.; Daletou, M.; Kalamaras, J. U.S. Pat. Appl. Publ. (2012), US 20120202129 A1 20120809.

H_3PO_4 Cross-linking of double bonds

Electrochemical Characterization
I-V Curves





Feed: H_2/Air normal flows

Andreopoulou, A.; Voege, A.; Paloukis, F.; Morfopoulou, C.; Papadimitriou, K.; Neophytides, S.; Kallitsis, J.; Daletou, M.; Kalamaras, J.
U.S. Pat. Appl. Publ. (2012), US 20120202129 A1 20120809.

Conclusions

- **High Temperature Fuel Cell Operation offers certain advantages to Fuel Cell Technology and expands the range of the current applications.**
- **New copolymers bearing side crosslinkable carboxy or double bonds and pyridine units were successfully Crosslinked providing** membranes with **higher T_g values** and phosphoric acid **doping ability** compared to the neat polymers.
- Preliminary fuel cell tests in temperatures between 180-220^{o}C showed **very good performances**
- **Long term durability** measurements showed stable performance **for 550h** at **T=210^{o}C** for the crosslinked terpolymers bearing double bonds.

Acknowledgements

University of Patras

Prof. J. K. Kallitsis

Dr. K. Papadimitriou

Dr. I. Kalamaras

Ch. Morfopoulou

Advent

Dr. N. Gourdoupi

Dr. M. Geormezi

Dr N. Triantafyllopoulos

MS. E.Theodorakopoulou

MS. G. Paloubis

FORTH/ICE-HT

Dr. Stylianos Neophytides

Research Director

Dr M. Daletou

Dr G. Avgouropoulos

New Energy World JU

fuel cells & hydrogen for sustainability

Financial Support from European Commission

- IRAFC FCH-JU 245202 (2010-2012) *"Development of an Internal Reforming Alcohol High Temperature PEM Fuel Cell Stack"*
- DEMMEA FCH-JU 245156 (2010-2012) *"Understanding the Degradation Mechanisms of Membrane-Electrode-Assembly for High Temperature PEMFCs and Optimization of the Individual Components"*

Thank you for your attention !