Fuel Cells – 2

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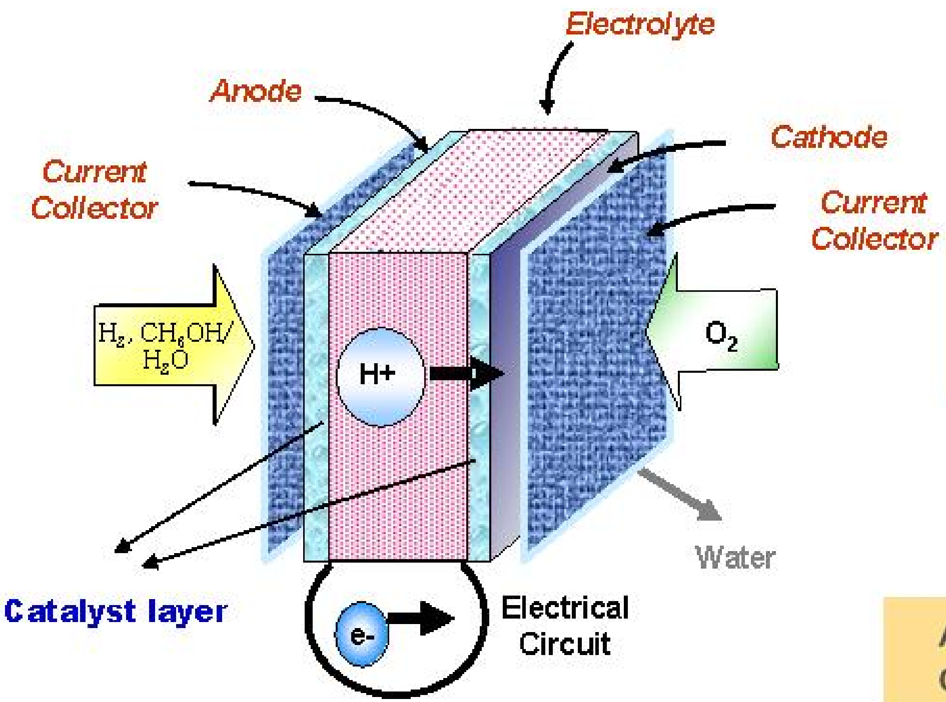
Recent Research Trends in Polymer Electrolyte Membranes

Fuel Cells

✹ **PEMFC (Proton Exchange Membrane Fuel Cell)**
DMFC (Direct Methanol Fuel Cell)



ANODE	: $H_2 = 2H^+ + 2e^-$	
CATHODE	: $1/2O_2 + 2H^+ + 2e^- = H_2O$	
TOTAL	: $H_2 + 1/2O_2 = H_2O$	$E^o = 1.23V$

ANODE	: $CH_3OH + H_2O = CO_2 + 6H^+ + 6e^-$	
CATHODE	: $3/2O_2 + 6H^+ + 6e^- = 3H_2O$	
TOTAL	: $CH_3OH + 3/2O_2 = CO_2 + 2H_2O$	$E^o = 1.18V$

Contents

✹ Overview of proton conducting membranes

- Structure, Synthesis
- Chemical properties
- Electrochemical properties
- Applications to fuel cell (DMFC, PEMFC)

✹ Membranes

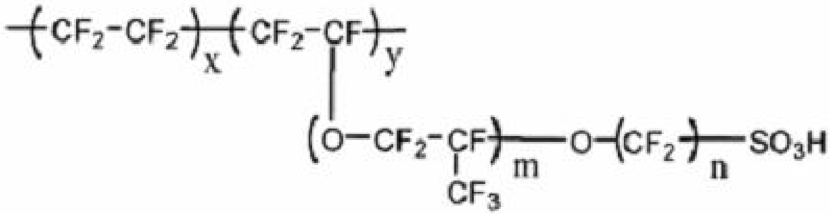
- Sulfonated aromatic polymers
- Alkylsulfonated aromatic polymers
- Acid-base polymer complexes
- Block copolymer electrolytes (BCE)
- Graft copolymer electrolytes (GCE)

Self-organizing !!!

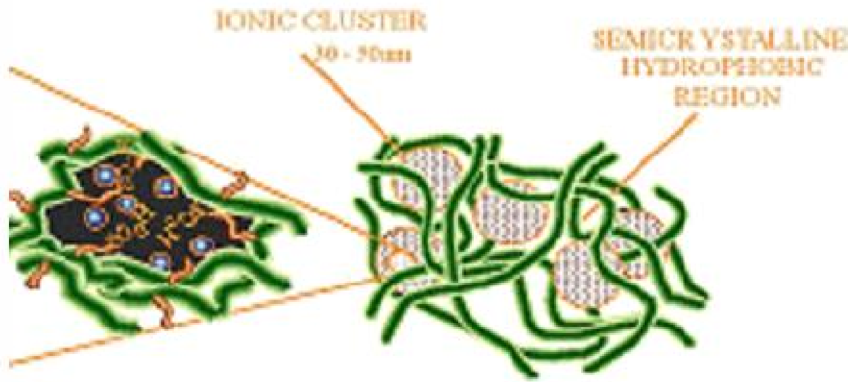
Background - 1

❋ Perfluorinated polymer electrolytes

- Satisfactory properties
- High cost (~ $600/m^2)
- low H^+ conductivity at high T & low humidity
- high MeOH crossover



Nafion®117	m≧1, n=2, x=5-13.5, y=1000
Flemion®	m=0, 1; n=1-5
Aciplex®	m=0, 3; n=2-5, x=1.5-14
Dow membrane	m=0, n=2, x=3.6-10



Background - 2

Features of Perfluorinated PEs

❋ **Aciplex, Dow membrane**

- Short side chain
- High ratio of SO_3H/CF_2
- High specific conductivity

❋ **GoreSelect membrane**

- Fine-mesh PTFE support impregnated with Nafion
- high mechanical stability ~10μm

PTFE: poly(tetra fluoro ethylene)

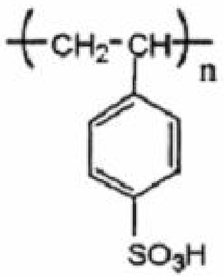
Background - 3

✹ Features of hydrocarbon polymers

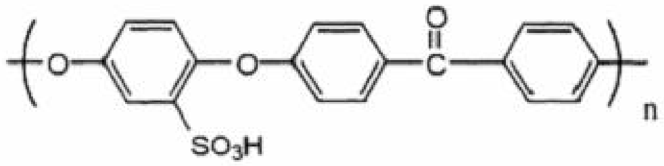
- Cheap !!!
- Low thermal/chemical stability
- Life-time can be improved by catalyst, assembly technology
- Contain polar group: high water uptake
- Decomposition can be depressed by molecular design
- easily recycled by conventional method

Sulfonated Aromatic Polymers

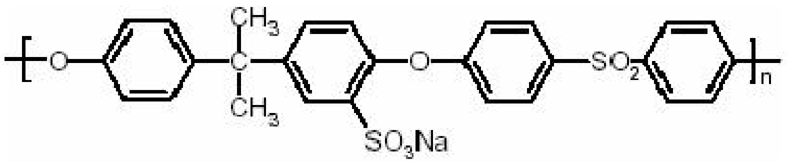
Poly(styrene) (PS)



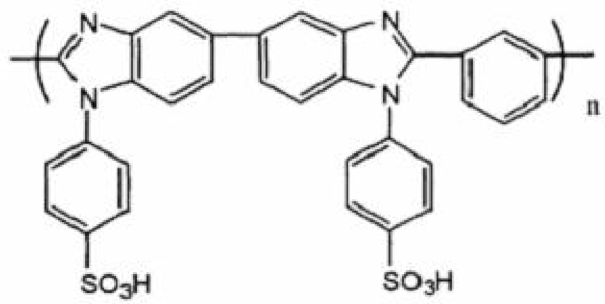
Poly(ether ether ketone) (PEEK)



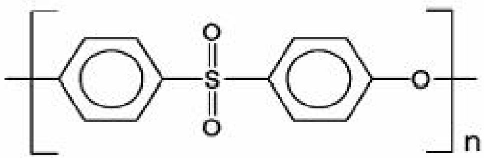
Polysulfone (PSf)



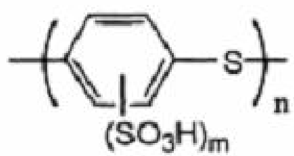
Poly(benz imidazole) (PBI)



Poly(ether sulfone) (PES)

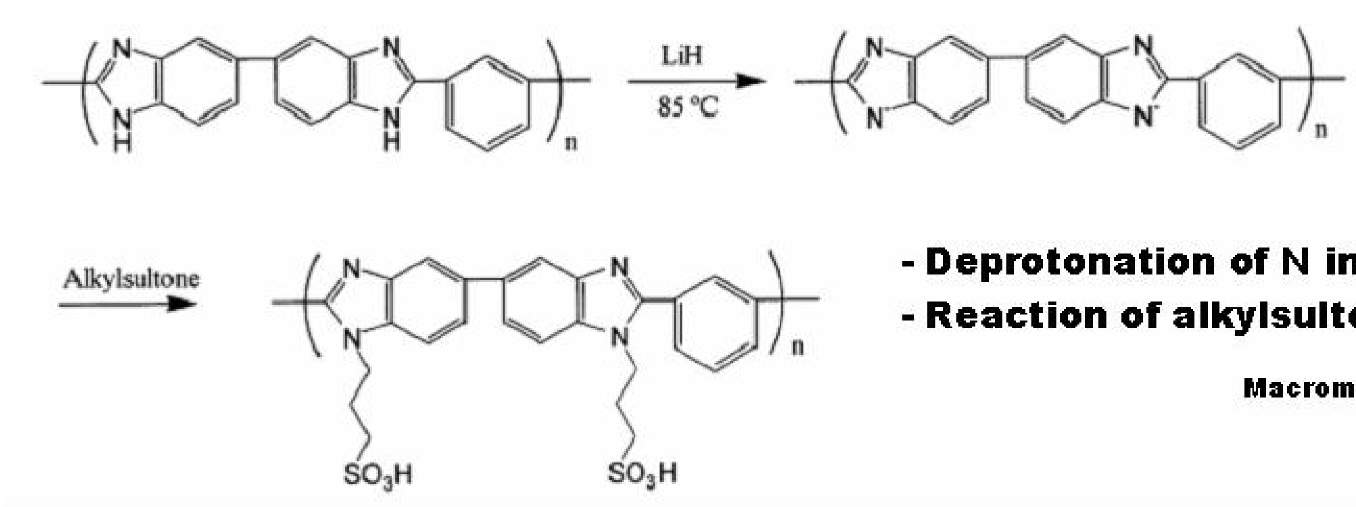


Poly(phenylene sulfide) (PPS)



Akylsulfonated Aromatic Polymers

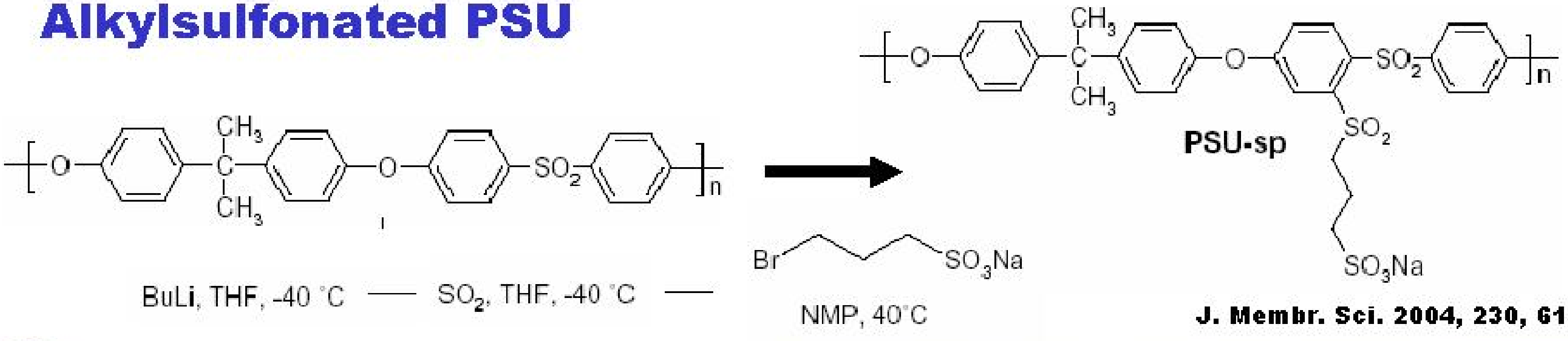
Alkylsulfonated PBI



- Deprotonation of N in BI ring
- Reaction of alkylsultone with PBI anion

Macromolecules 1993, 26, 5633.

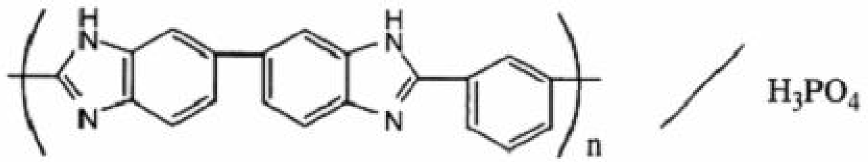
Alkylsulfonated PSU



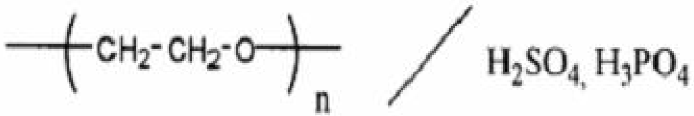
J. Membr. Sci. 2004, 230, 61.

Acid-Base Polymer Complexes

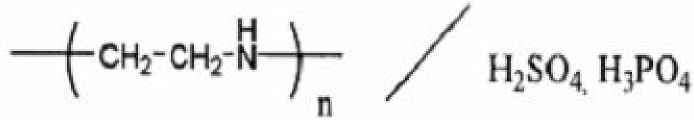
PBI/H_3PO_4



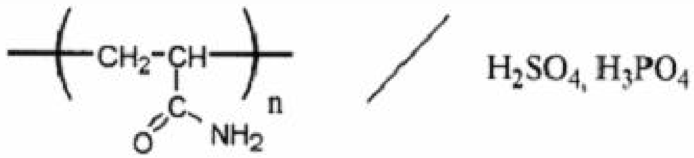
PEO/strong acid



PEI/strong acid



PAAM/strong acid

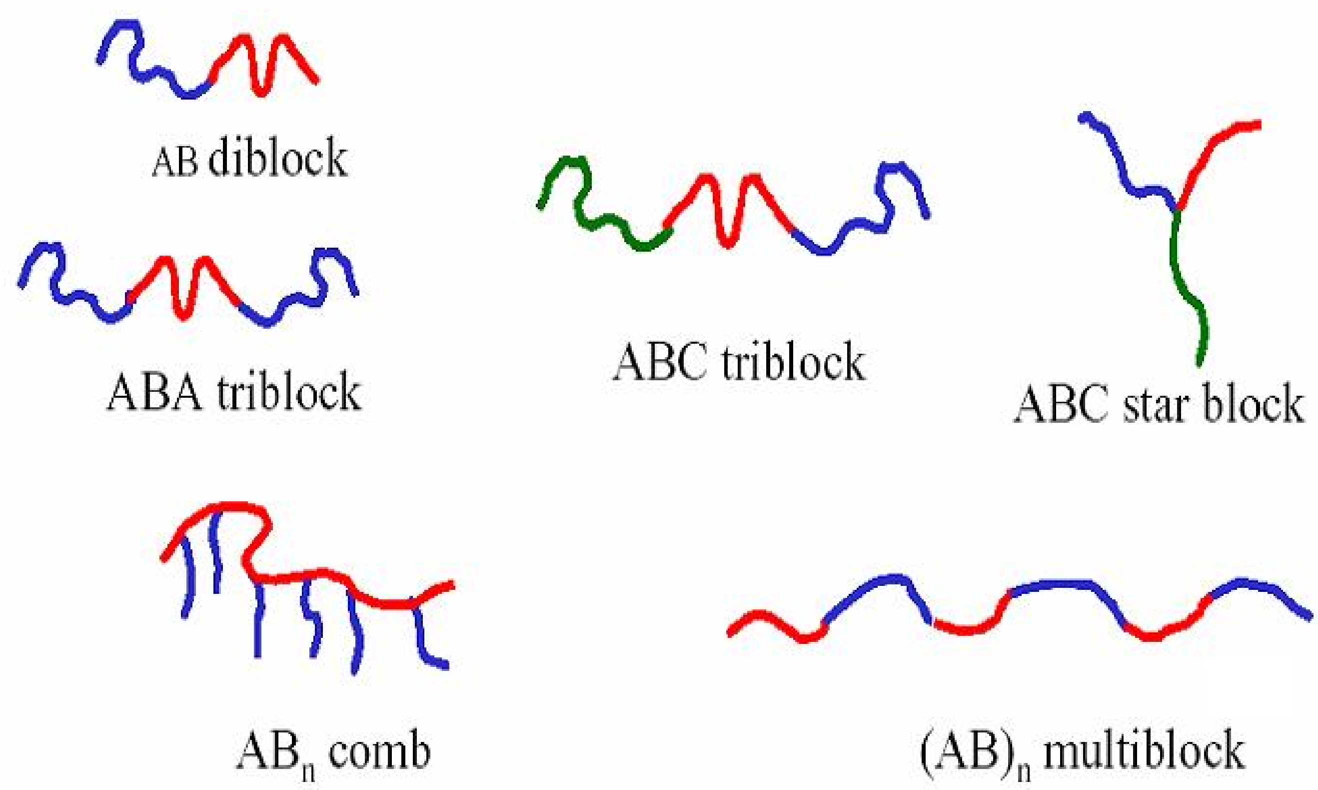


PVA/strong acid

PEO: poly(ethylene oxide), PEI: poly(ethylene imine)
PAAM: poly(acrylamide), PVA: poly(vinyl alchol)

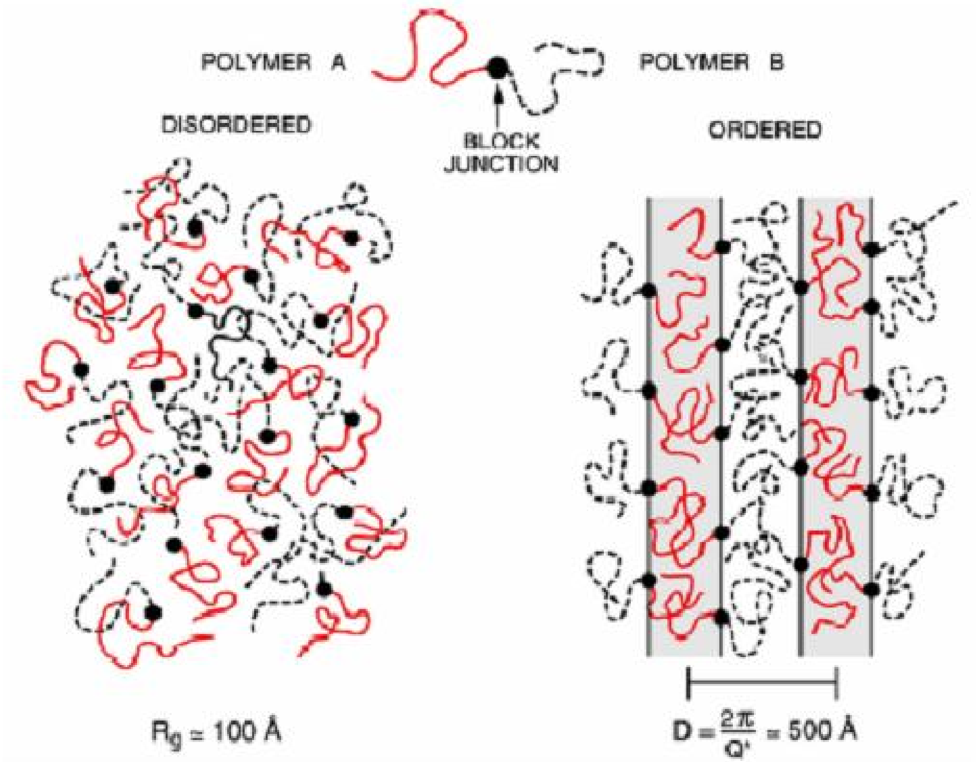
Block Copolymers

Types of Block copolymer



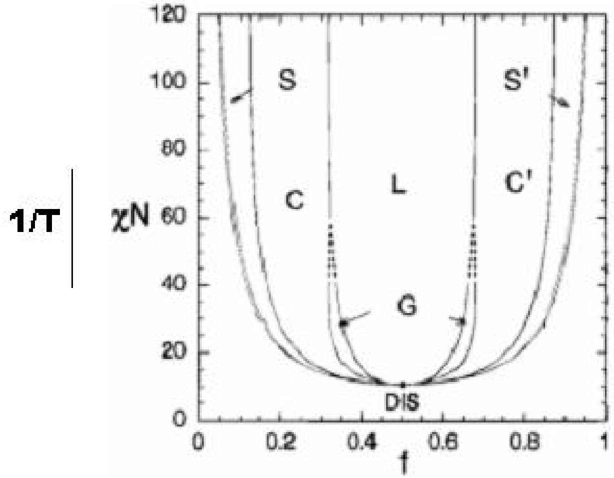
Block Copolymers

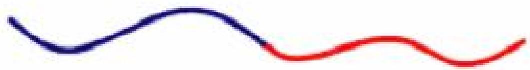
Phase separated morphology



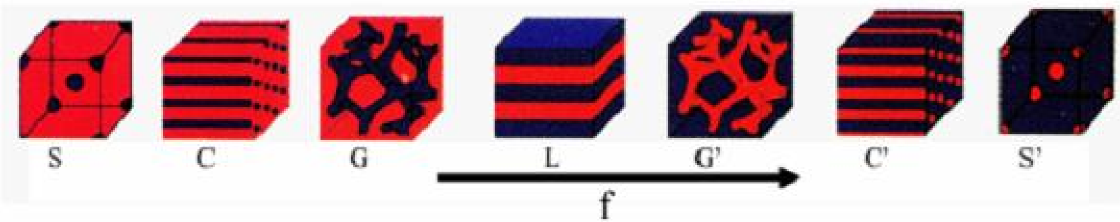
- Physical connection by covalent bond
- Immiscible pair: degree of segregation
- Order-disorder transition temperature (ODT)
- Self-assembly in nanometer length scales

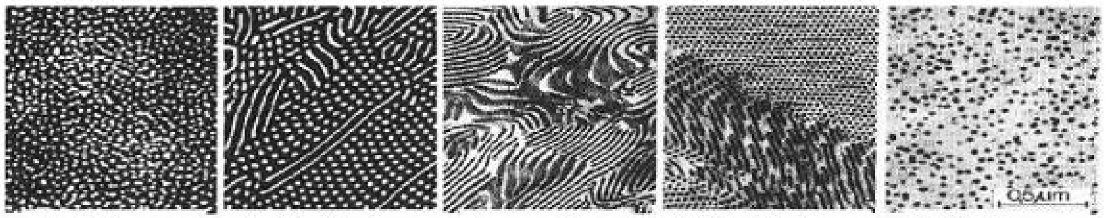
Phase Separated Morphology





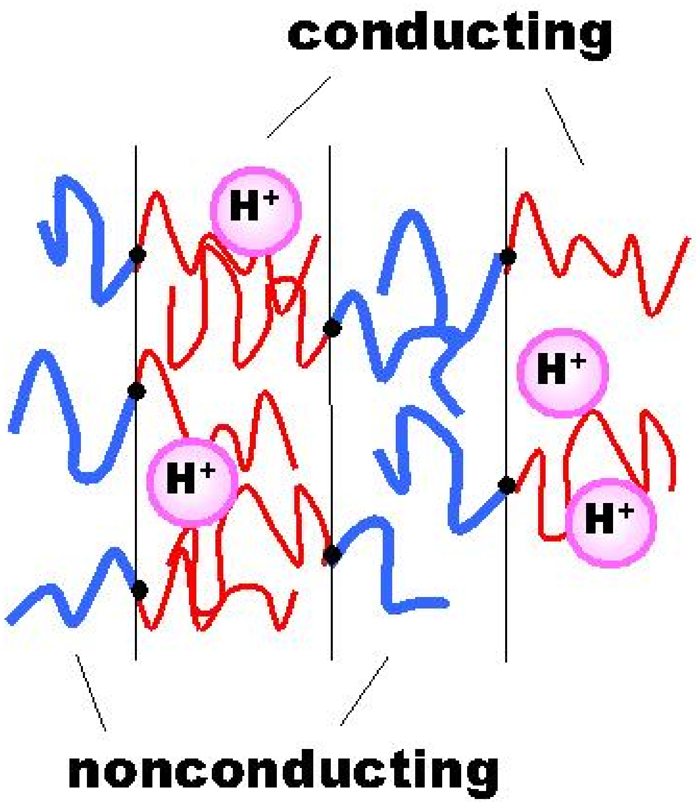
χ: interaction parameter
N: degree of polymerization
f: volume fraction





A Spheres	A Cylinders	Lamellae	B Cylinders	B Spheres
0-20% A	20-40% A	40-64% A	64-84% A	>84% A

Block Copolymer Electrolytes



✸ Advantages

- Formation of ion conducting channels by microphase separation
- Hindering of swelling by surrounding non-sulfonated phase
- Lowering of MeOH permeability
- High mechanical stability

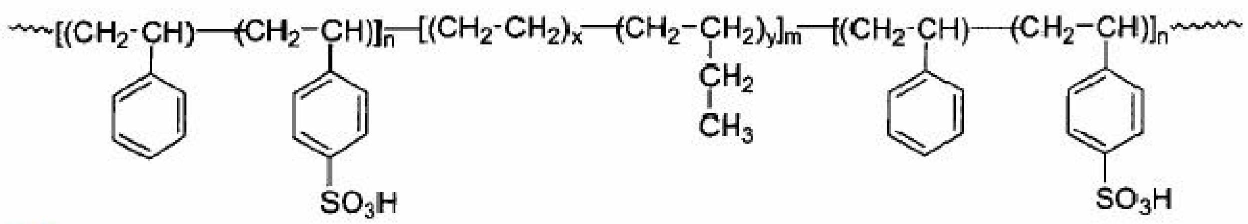
High ionic conductivity
Good mechanical property

Polystyrene-based BC (1)

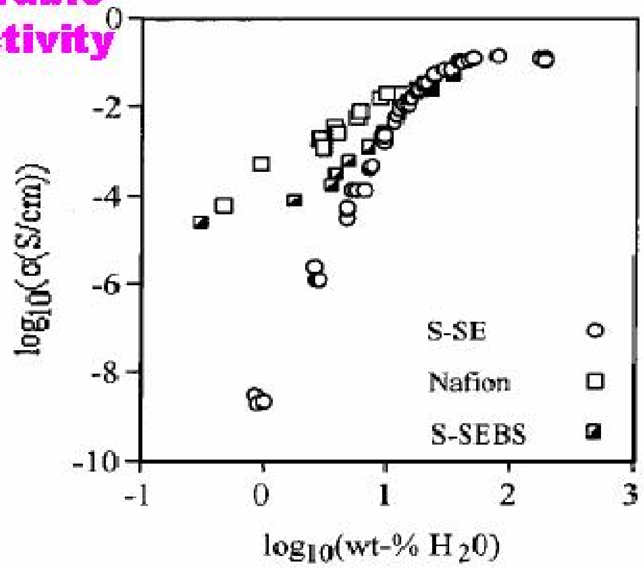
Macromolecules 2002, 35, 5916

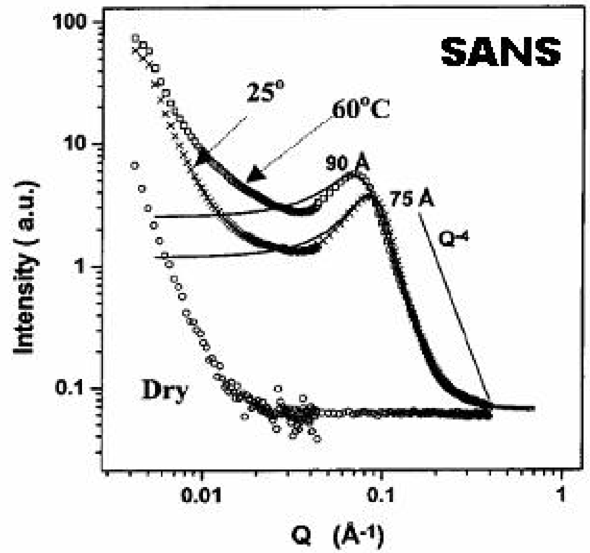
✸ Styrene-b-(ethylene-co-butylene)-b-styrene (SEBS)

- 0.1 S/cm, bicontinuous structure



Comparable conductivity





Interdomain distance

~ ion cluster

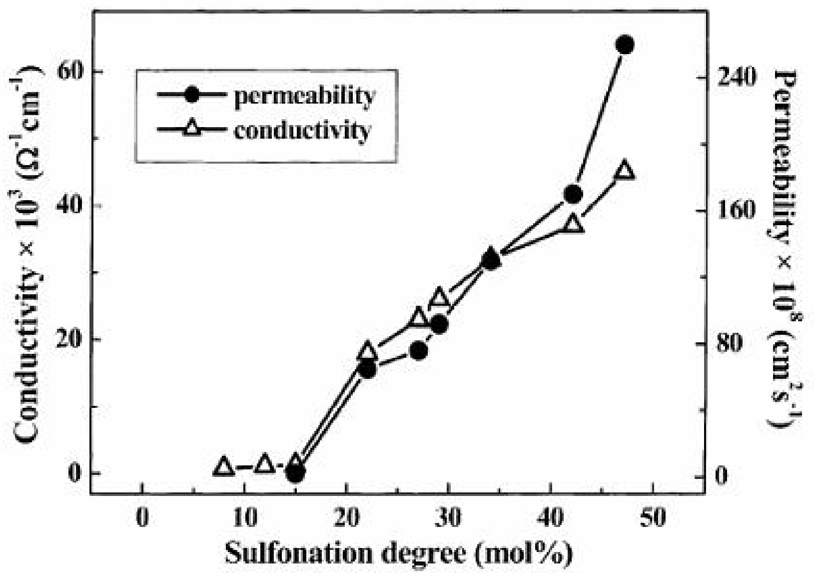
cf. Nafion ~5nm

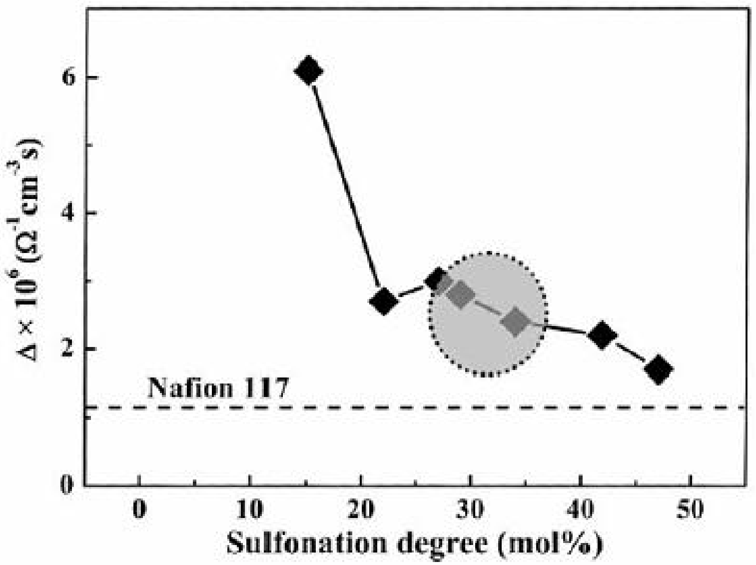
SANS: small angle neutron scattering

Polystyrene-based BC (2)

J. Memb. Sci. 2002, 207, 129.

❋ SEBS
- Comparable H^+ conductivity (~ 0.1S/cm)
- Lower MeOH crossover





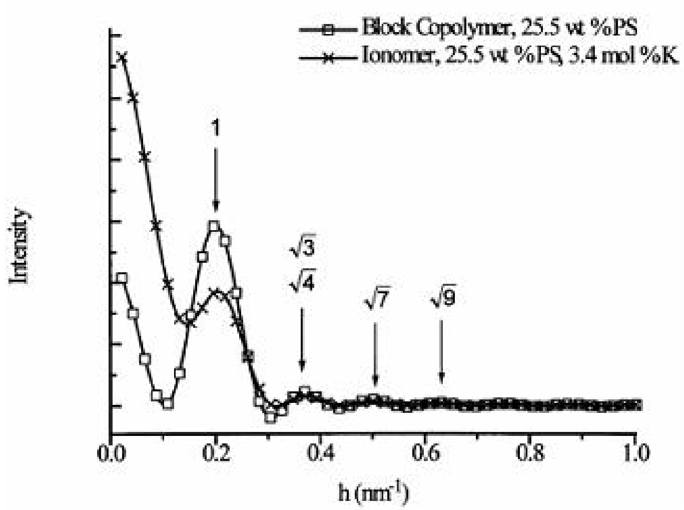
Δ: The ratio of conductivity to MeOH permeability

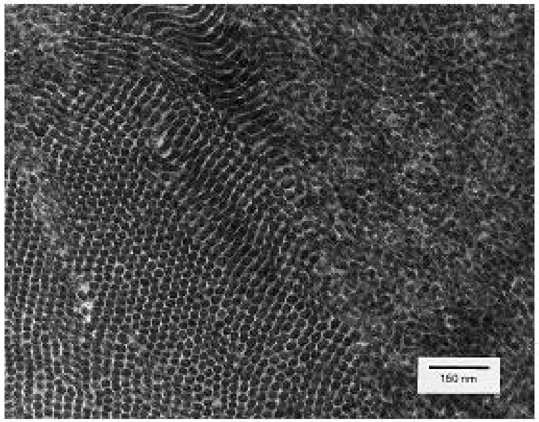
Polystyrene-based BC (3)

Polymer, 2000, 41, 3205

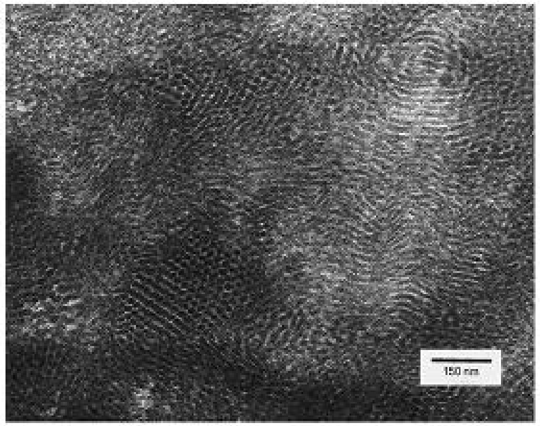
✸ Styrene-isobutylene-styrene

- hexagonally packed PS cylinder
- Upon increase of PS fraction, distance btn cylinders unchanged, cylinder diameter change





Block copolymer



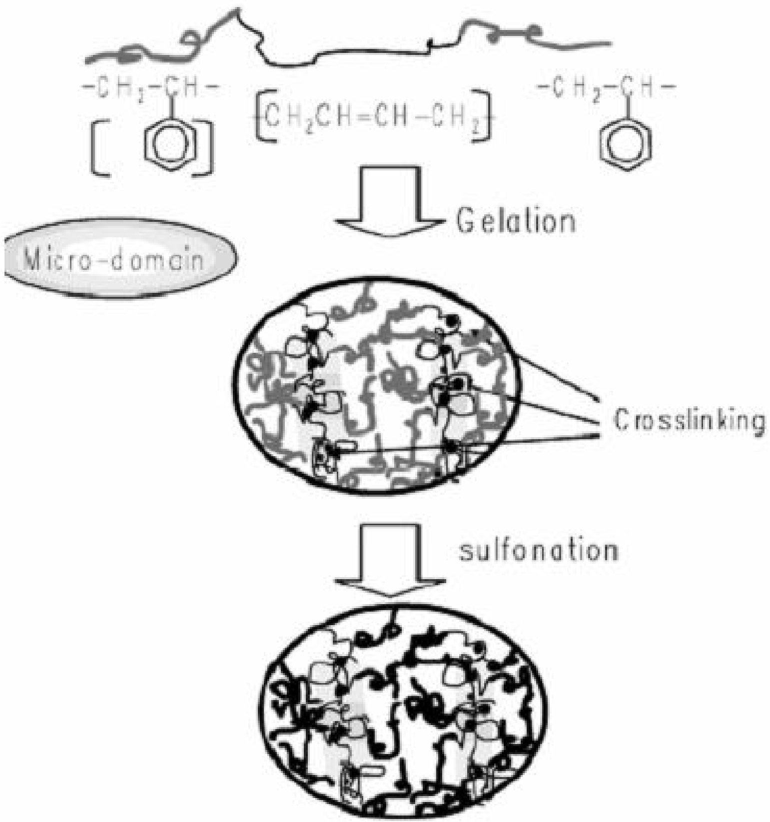
Ionomer

Polystyrene based BC (4)

Macromolecules 2003, 36, 3228

✹ Crosslinked SBS

- Structure fixation by UV crosslinking



Membrane properties

ID	proton conductivity (S/cm)	methanol permeability (cm²/s)	Φ
scSBS1	7.1×10^{-5}	*b*	
scSBS1.5	6.1×10^{-3}	*b*	
scSBS2	2.3×10^{-2}	8.1×10^{-8}	280 000
scSBR1	2.7×10^{-8}	*b*	
scSBR1.5	6.5×10^{-6}	*b*	
scSBR2	1.5×10^{-5}	*b*	
scSBR2.5	1.9×10^{-5}	7.4×10^{-8}	260
Nafion 117	6.3×10^{-2}	2.9×10^{-6}	22 000
sSEBS	3.8×10^{-2}	1.7×10^{-6}	22 000

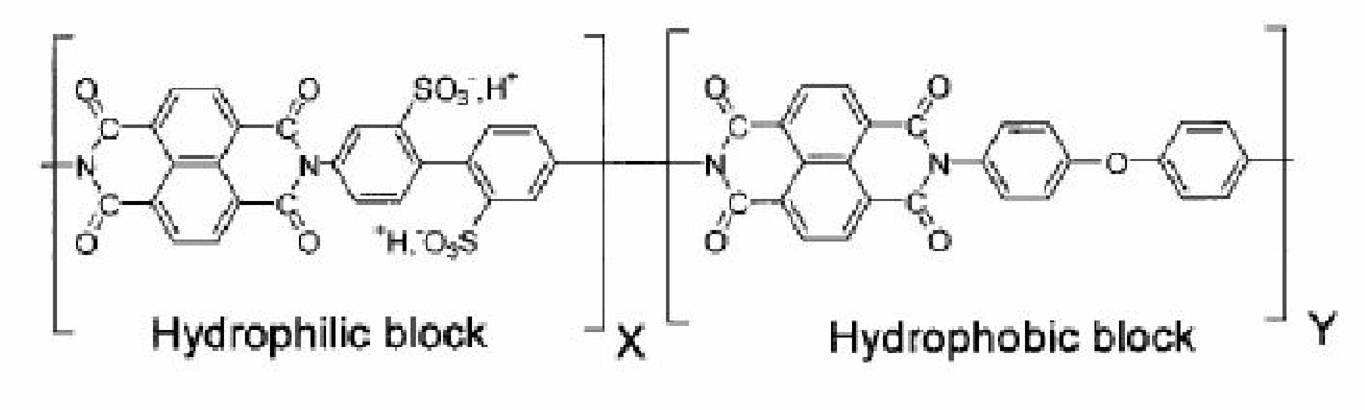
Φ: The ratio of conductivity to MeOH permeability

Polyimide (1)

Sep. Pur. Tech. 2001, 22, 681

✹ Block PI : successive step of polycondensation

- 1st step: 1,4,5,8-naphthalene tetracarboxylic dianhydride (NDTA) + 4,4'-diaminobiphenyl-2,2-disulfonic acid (BDSA)
- 2nd step: NDTA + 4,4'-oxydianiline (ODA)

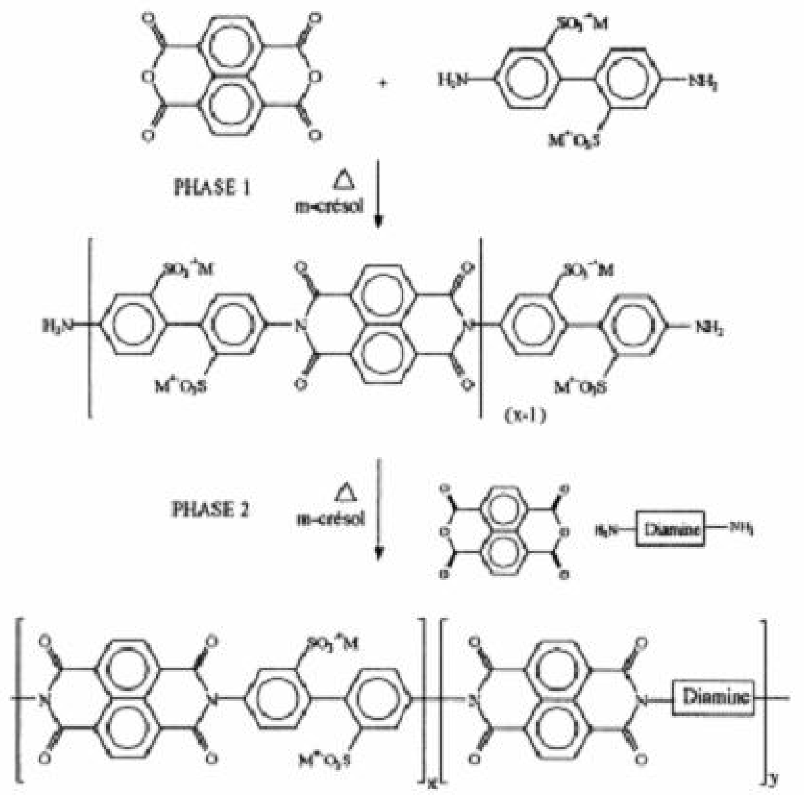


Polyimide (2)

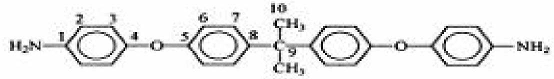
Polymer, 2001, 42, 359

✹ Block PI

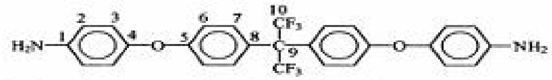
NDTA **BDSA**



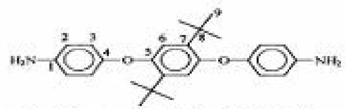
Aromatic diamines



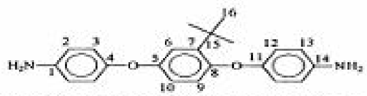
Bis[4-(aminophenoxy)4-phenyl]isopropylidene (pAPI)



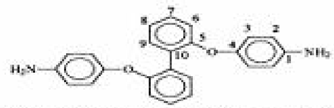
Bis[4-(aminophenoxy)4-phenyl]hexafluoroisopropylidene (pAPFI)



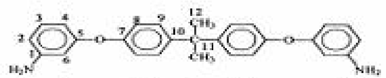
1,4-Bis-(4'-aminophenoxy)-2,5-tertiobutylbenzene (ADTB)



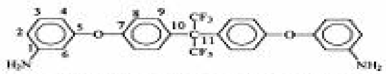
1,4-Bis-(4'-aminophenoxy)-2-tertiobutylbenzene (ATB)



2,2'-(4'-aminophenoxy)biphenyle (ABP)



Bis [3-(aminophenoxy)-4-phenyl]isopropylidene (mAPI)



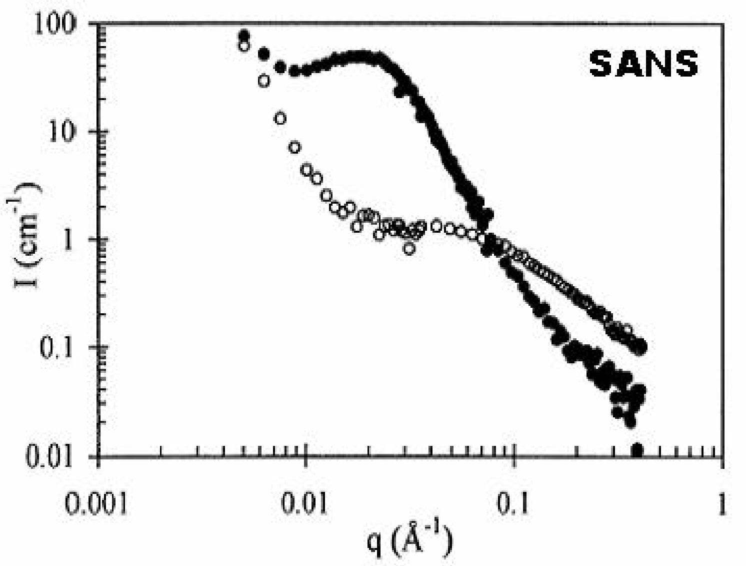
Bis [3-(aminophenoxy)-4-phenyl]hexafluoroisopropylidene (mAPFI)

Polyimide (3)

Polymer, 2001, 42, 359

✸ Property: Conductivity, morphology

Acronyms	IEC (meq g^{-1})	Water uptake	$\sigma \times 10^{-3}$ (S cm^{-1})
CH_3 5 20/80	0.63	13.5	0.32
CH_3 5 30/70	0.96	19.0	1.3
CH_3 5 40/60	1.30	27.0	6.5
CH_3 5 50/50	1.64	42.0	5.9
CF_3 5 20/80	0.56	14.0	0.40
CF_3 5 30/70	0.86	22.0	1.7
CF_3 5 40/60	1.17	31.0	4.6
CF_3 5 50/50	1.51	41.0	7.1
CF_3 5 60/40	1.86	46.5	8.3
*t*Bu 5 30/70	1.03	24.5	0.04
*t*Bu 5 40/60	1.38	45.5	3.1
*t*Bu 5 50/50	1.73	45.5	6.7



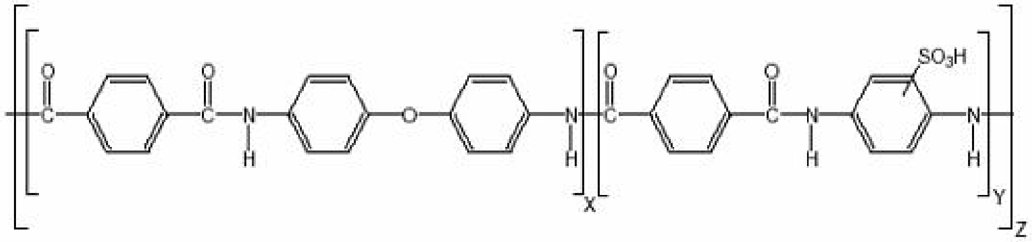
- **Low ionic conductivity ~ few mS/cm**
- **Presence of large ionic domains by SANS**

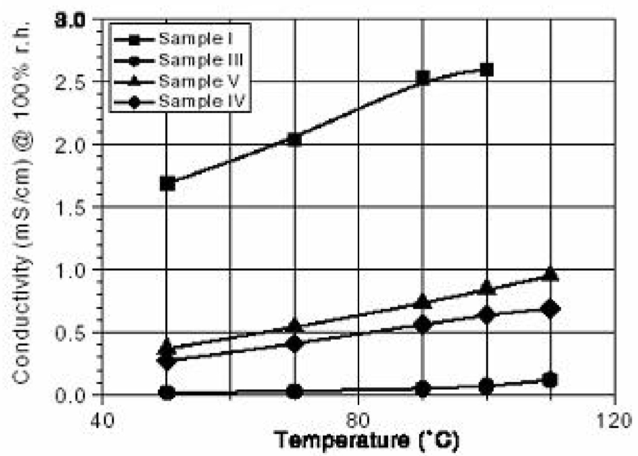
Polyaramides

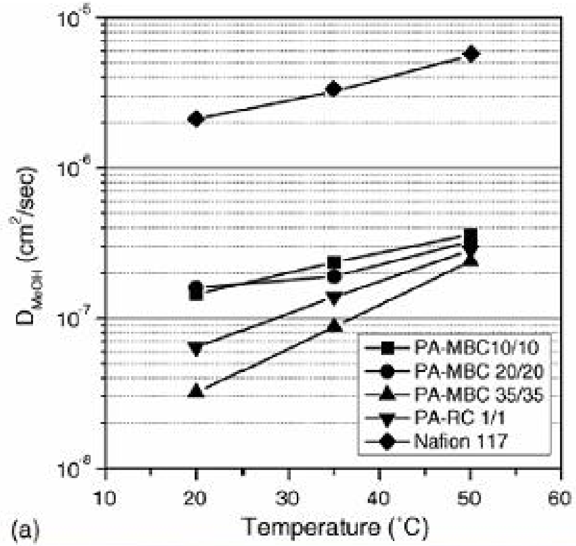
React. Funct. Polym. 2003, 57, 77

✹ Polyaramide

- Swelling is restricted by non-sulfonated domains
- not stable at high T (135 °C) due to desulfonation, hydrolytic cleavage of amide bonds.





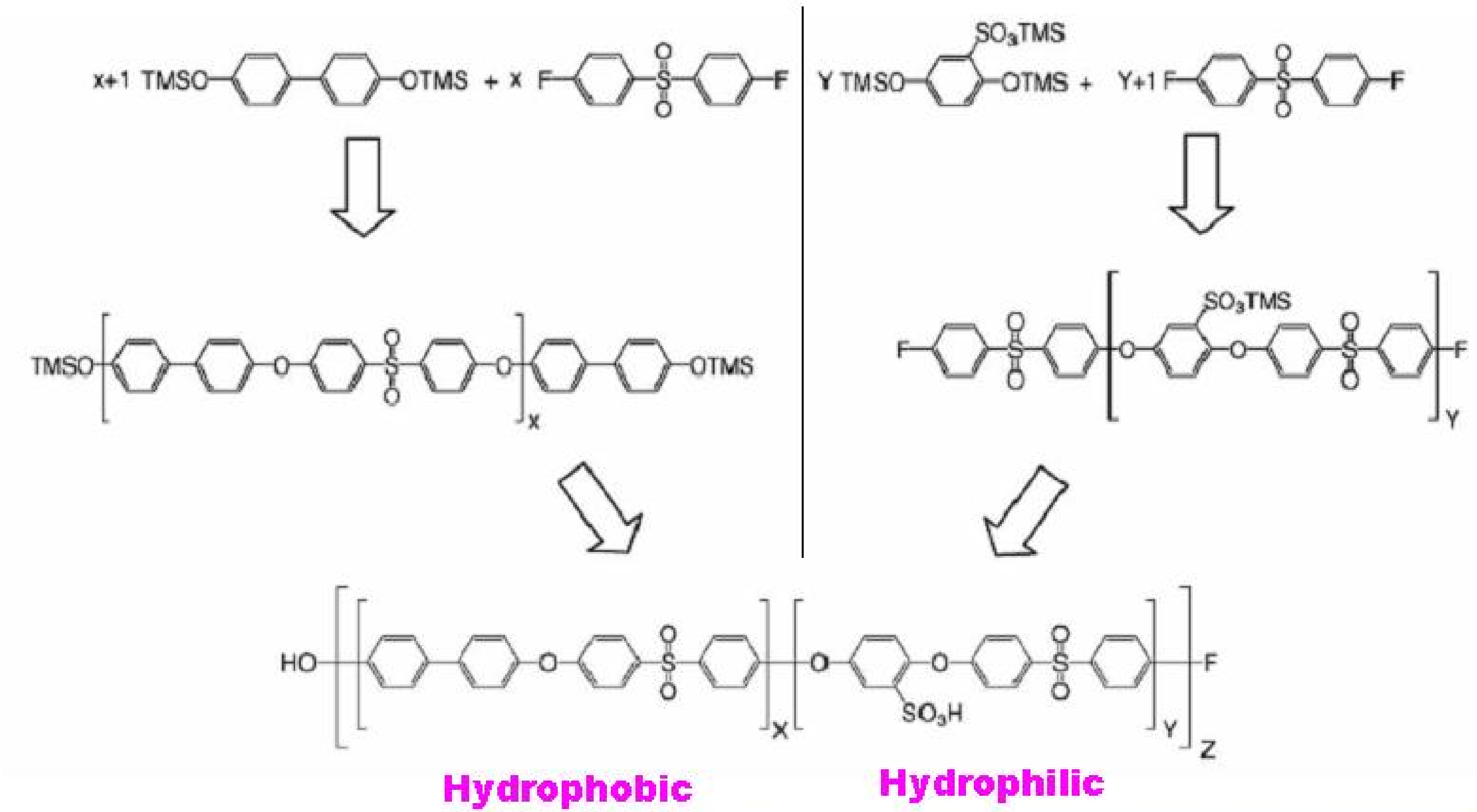


Poly(ether sulfone) (1)

Macromol. Symp. 2004, 210, 175

✸ Sulfonated BC

- Silyl method in NMP/K_2CO_3 at 150 °C



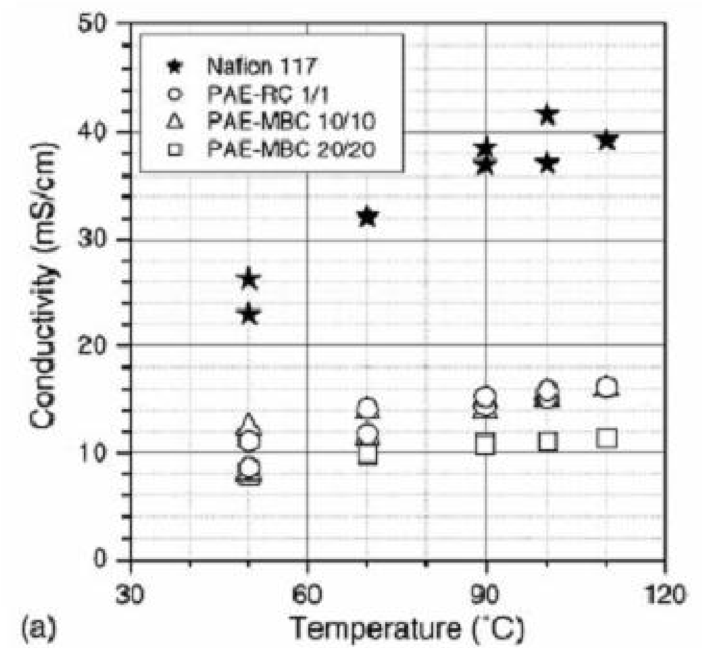
TMS: trimethylsilyl

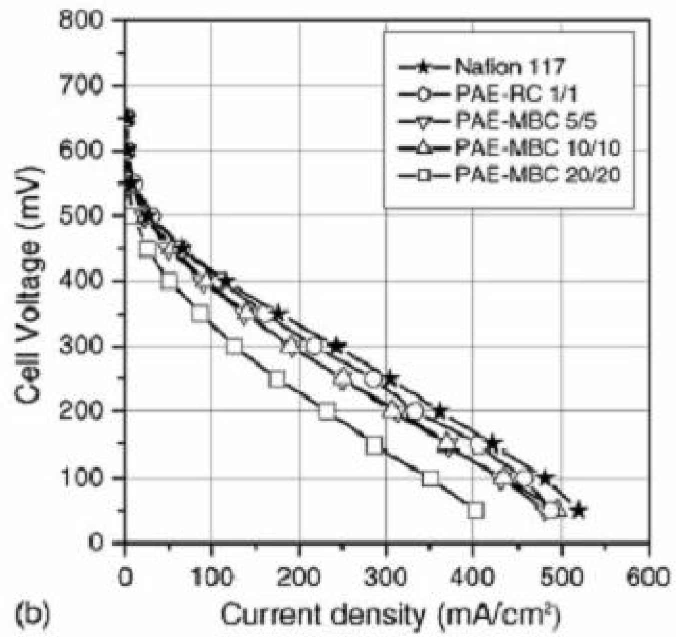
Poly(ether sulfone) (2)

Macromol. Symp. 2004, 210, 175

❋ Conductivity, DMFC performance

- lower conductivity, but comparable cell performance





Due to low MeOH crossover and lower thickness of membrane

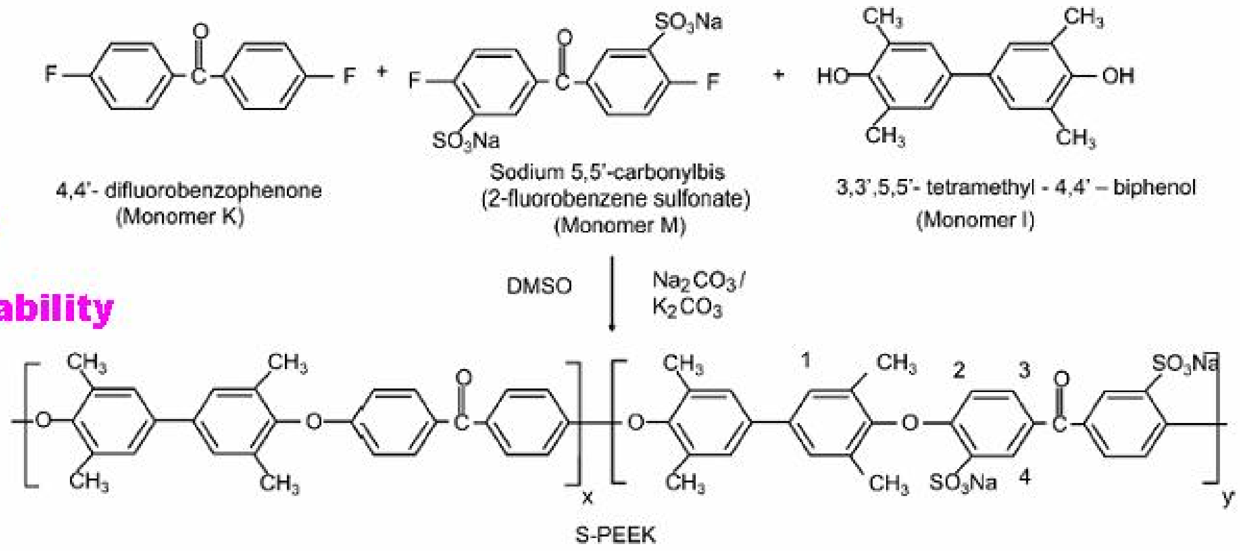
PEEK

J. Membr. Sci, 2004, 234, 75

✹ Nucleophilic aromatic substitution

high conductivity

low MeOH permeability



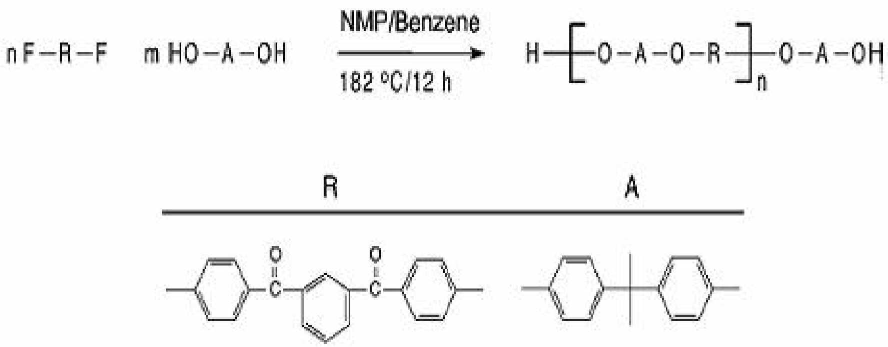
Property	S-PEEK-1	S-PEEK-2	S-PEEK-3	Nafion[b] 112	Nafion[b] 117
Degree of sulfonation (SO_3 per repeating unit)	0.4	0.8	1.2	1.0	1.0
Ion-exchange capacity (meq/g)	0.712	1.312	1.521	0.95	0.91
Water swelling (%)	13	37	54	34	38
Conductivity (S/cm) at 25 °C	0.024	0.038	0.070	0.082–0.100	0.10–0.16
Conductivity (S/cm) at 80 °C	0.033	0.067	0.134	0.07 at 90 °C	0.15–0.19 at 90 °C
MeOH diffusion coefficient (cm^2/s) at 25 °C	5×10^{-8}	3×10^{-7}	3×10^{-7}	–	2×10^{-6}
MeOH diffusion coefficient (cm^2/s) at 80 °C	3×10^{-7}	2×10^{-6}	6×10^{-6}	–	1.4×10^{-5}

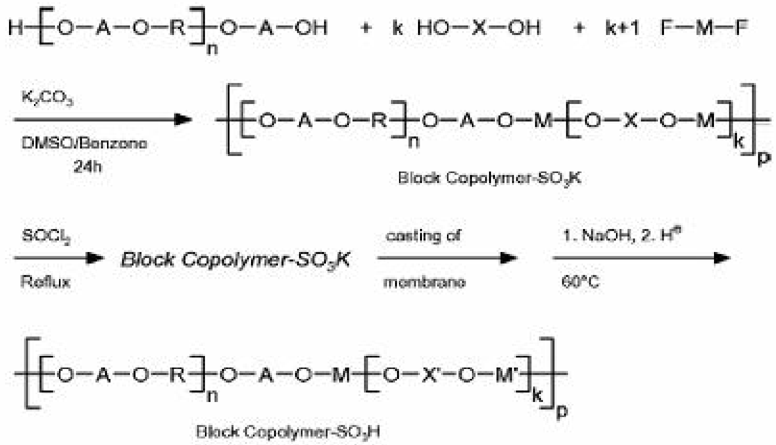
Block Copolymer Ionomer

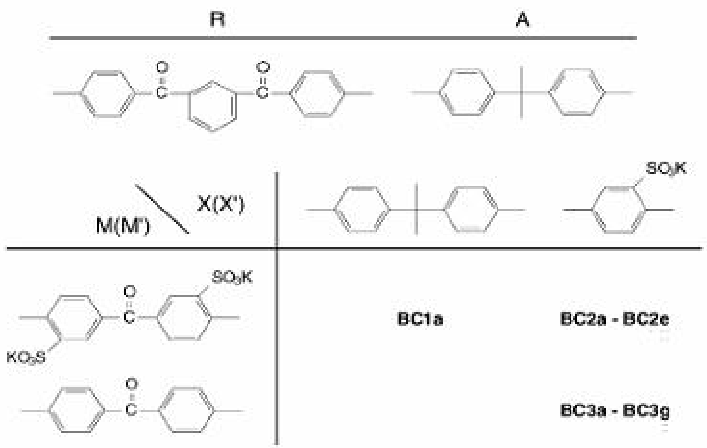
J. Membr. Sci. 2004, 245, 147

✹ Two-stage process: Nucleophilic substitution

End-functionalized hydrophobic blocks







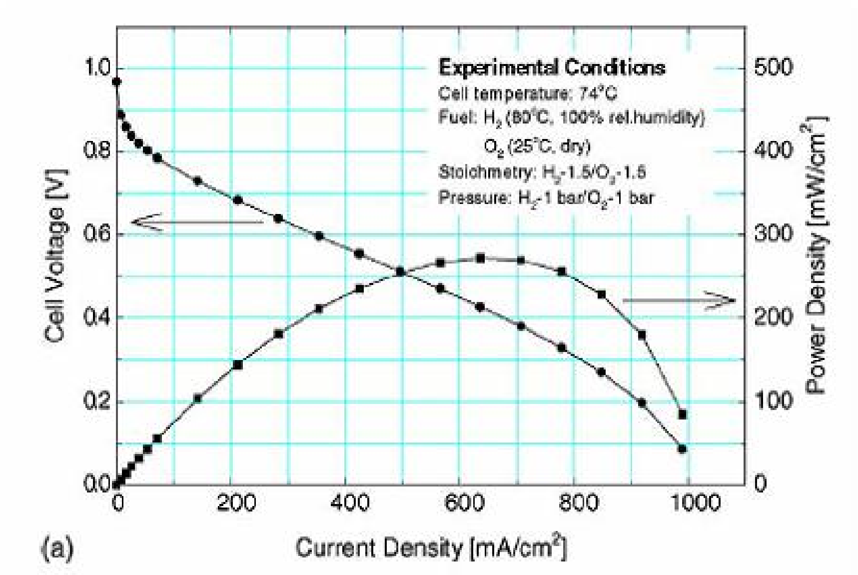
Phase separation leads to physical crosslinking

Block Copolymer Ionomer

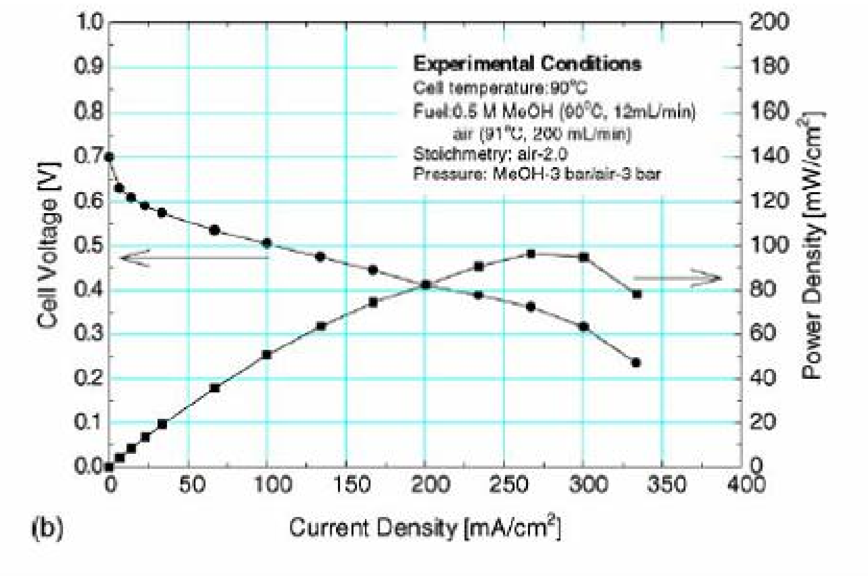
J. Membr. Sci. 2004, 245, 147

✹ Cell performance

PEMFC



DMFC



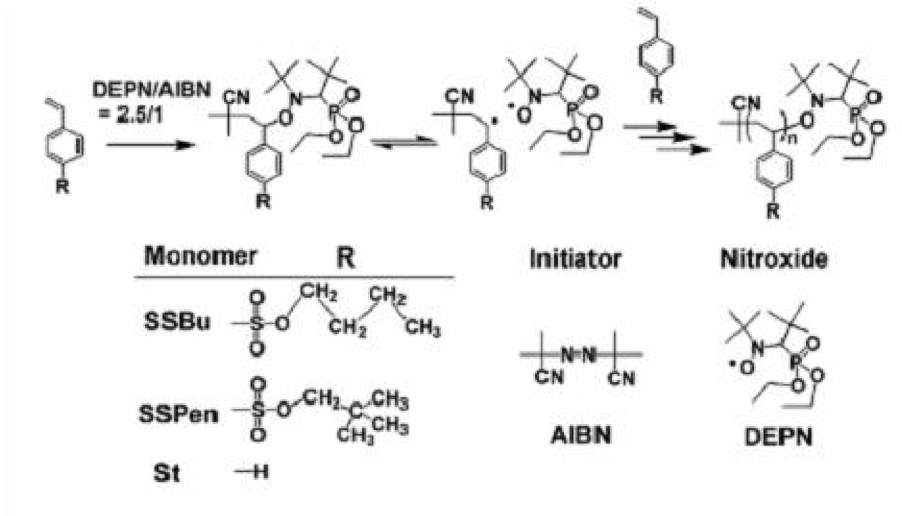
Good stability, acceptable performance during the operation

Nitroxide-mediated Living Radical

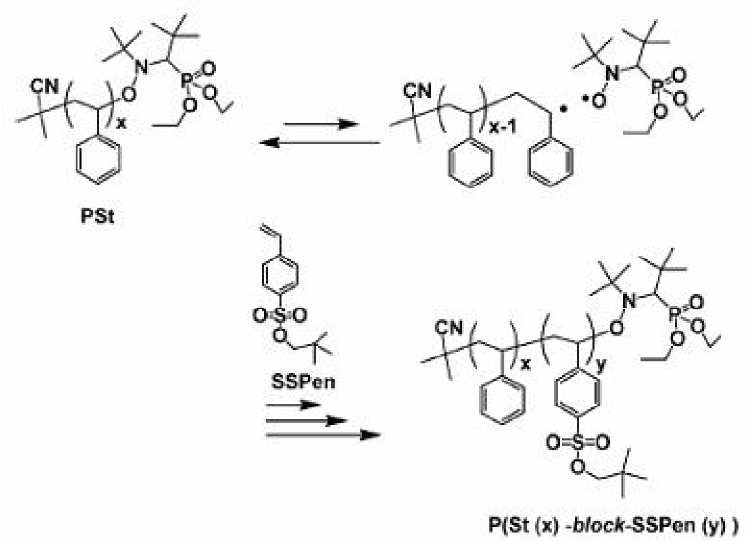
Polymer 2002, 43, 3155

✹ Styrene-b-styrenesulfonic acid

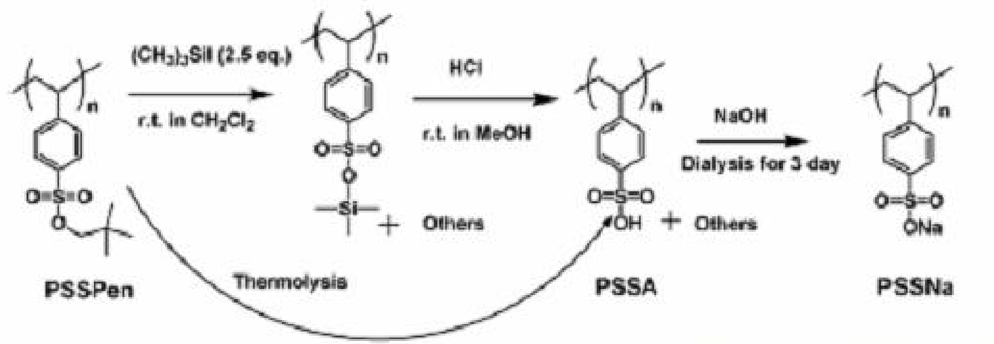
Polymerization of SSPEN or SSBu



Block copolymerization



Transformation to sulfonic acid



DEPN: 2,2,5,5-Tetramethyl-4-phosphono-3-azahexane-3-nitroxide

Break ???

Graft Copolymerization

- **Radiation (γ-ray, electron beam)**
  - chain grafts are covalently attached to main chain

- **Types of high energy radiations**

  1) Electromagnetic radiation
  - γ-ray, x-ray
    (Co-60; radioactive isotope, Cs-137; γ-ray source)

  2) Particulate radiation (charged particle)
  - electron, swift heavy ions
  - from accelerator

Simultaneous Irradiation Method

- **Polymer backbone is irradiated in the presence of monomer (vap. liq. bulk, solution)**
- **In air, N_2 or under vacuum**

Irradiation : $P \xrightarrow{\gamma\text{-rays}} P^{\cdot}$ (primary radicals)

Initiation : $P^{\cdot} + M \rightarrow PM^{\cdot}$ (graft chain)

Propagation : $PM^{\cdot} + nM \rightarrow PM^{\cdot}_{n+1}$ (graft growing chains)

Termination : $PM^{\cdot}_{n} + PM^{\cdot}_{m} \rightarrow PM_{n+m}$ (graft copolymer)

Deactivation

1) Mutual recombination

$$P^{\cdot} + P^{\cdot} \rightarrow PP \qquad \text{(recombination)}$$

P˙ : primary radical of polymer backbone

2) Homopolymerization

$$M \xrightarrow{\gamma\text{-rays}} M^{\cdot} \text{ (primary radicals)}$$

$$M^{\cdot} + nM \rightarrow M_n^{\cdot}$$

(homopolymer growing chains)

$$M_n^{\cdot} + M_m^{\cdot} \rightarrow M_{n+m} \qquad \text{(homopolymer)}$$

Pre-irradiation method

1) Irradiation of polymer to form active radical

2) Contact with monomer

- O_2 atmosphere

Formation of hydroperoxides

$$PH + O_2 \xrightarrow{\gamma\text{-rays}} POOH$$

Thermal decomposition $POOH \xrightarrow{\Delta} PO^{\cdot} + OH^{\cdot}$

Initiation $PO^{\cdot} + M \rightarrow POM^{\cdot}$

Propagation $POM^{\cdot} + nM \rightarrow POM^{\cdot}_{n+1}$

- Vac./inert atmosphere

$$PH \xrightarrow{\gamma\text{-rays}} P^{\cdot} + H^{\cdot}$$

$$P^{\cdot} + M \rightarrow PM^{\cdot}$$

Radiation-induced grafting

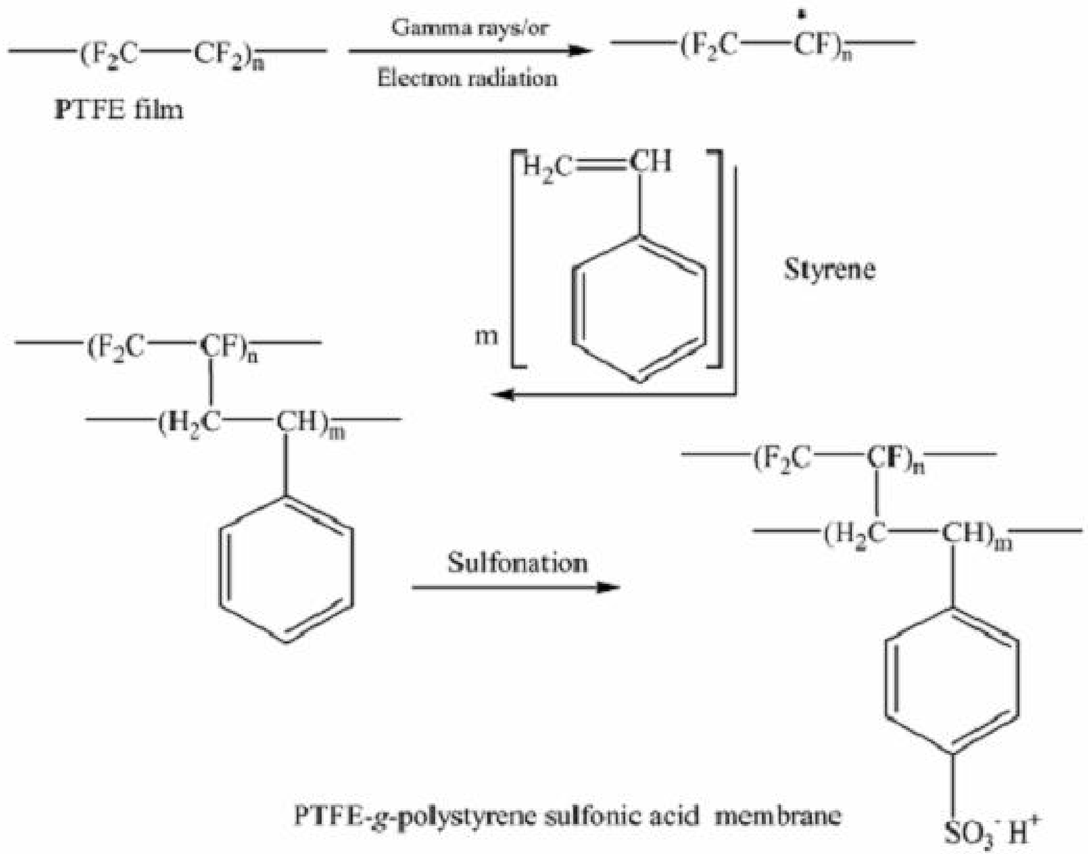
- **Broad, promising technique**

- **Reaction parameter:**
  - dose / dose rate
  - type or concentration of monomer
  - type of polymer film
  - type of additive
    (diluent, inhibitor, acid, x-agent)
  - temperature

Graft Copolymerization

Prog. Polym. Sci. 2004, 29, 499

✹ Grafting of PS onto PTFE

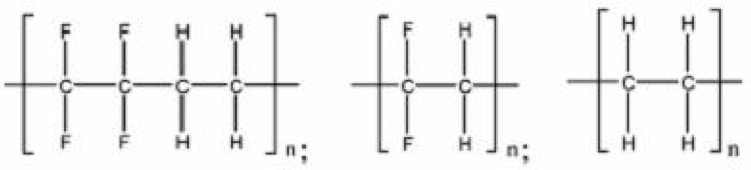


Graft Copolymer Electrolytes

J. Membr. Sci. 2005, 251, 121

✸ Membrane property

Base polymers



ETFE PVDF LDPE

Basic grafting scheme

base polymer $\xrightarrow{\gamma \text{ ray or e-beam}}$ activated polymer

activated polymer $\xrightarrow{\text{monomer+heat}}$ grafted co-polymer

grafted co-polymer $\xrightarrow{\text{sulfonation}}$ solid polymer electrolyte

Membrane no.	Base film	Nominal thickness (μm)	Wet thickness (μm)	DOG (%)	Area expansion rate (%)
Nafion® 117	Perfluoropolymer	170	224	–	44
3543P	PVDF	50	82	29	63.8
3544P	PVDF	50	94	36	82.8
3545P	PVDF	50	88	36	63.8
3547P	PVDF	50	80	14	25.4
3771P	PVDF	100	240	52	130
3900P	PVDF	50	80	28	67.8
3983P	PVDF	30	55	26	67.7
3986P	PVDF	30	58	34	96
3541P	ETFE	50	94	34	58.8
3842P	ETFE	68	90	27	63
3843P	ETFE	150	220	27	63.3
3898P	ETFE	50	98	26	63.5
3744P	LDPE	125	143	17	69
3746P	LDPE	125	–	7	25

ETFE: poly(ethylene tetrafluoroethylene, PVDF: poly(vinylidene fluoride)
LDPE: low density polyethylene

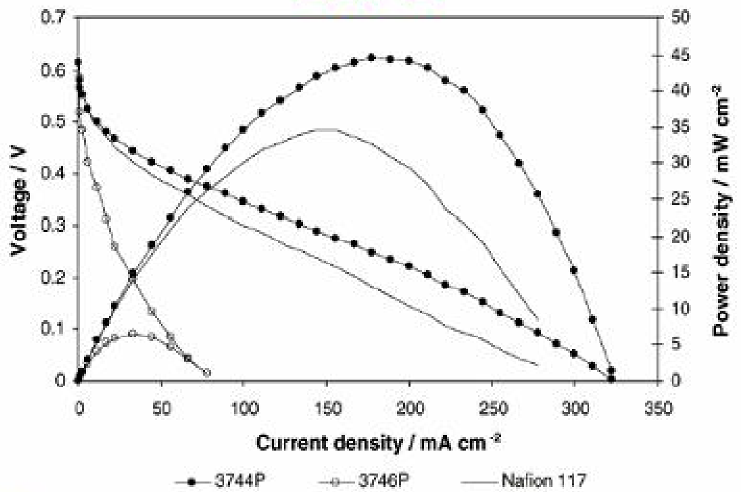
Graft Copolymer Electrolytes

J. Membr. Sci. 2005, 251, 121

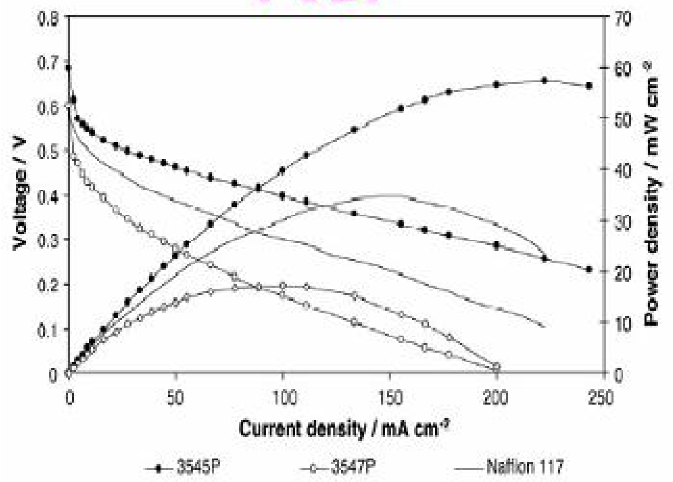
✸ Superior DMFC performance

Membrane no.	Diffusion coefficient ($cm^2\ s^{-1}$) × 10^6	Proton conductivity ($mS\ cm^{-1}$)	Membrane resistivity ($\Omega\ cm^2$)
Nafion® 117	3.42	42.51	0.53
3543P	1.5	101.52	0.08
3544P	1.72	135.71	0.07
3545P	1.35	62.23	0.14
3547P	0.73	9.55	0.83
3771P	2.92	177.56	0.13
3900P	1.54	59.62	0.14
3983P	1.0	43.08	0.13
3986P	1.07	35.62	0.16
3541P	1.43	69.66	0.13
3842P	1.92	74.65	0.12
3843P	2.02	80.35	0.27
3898P	1.47	82.31	0.12
3744P	1.3	61.06	0.23
3746P	–	–	–

LDPE



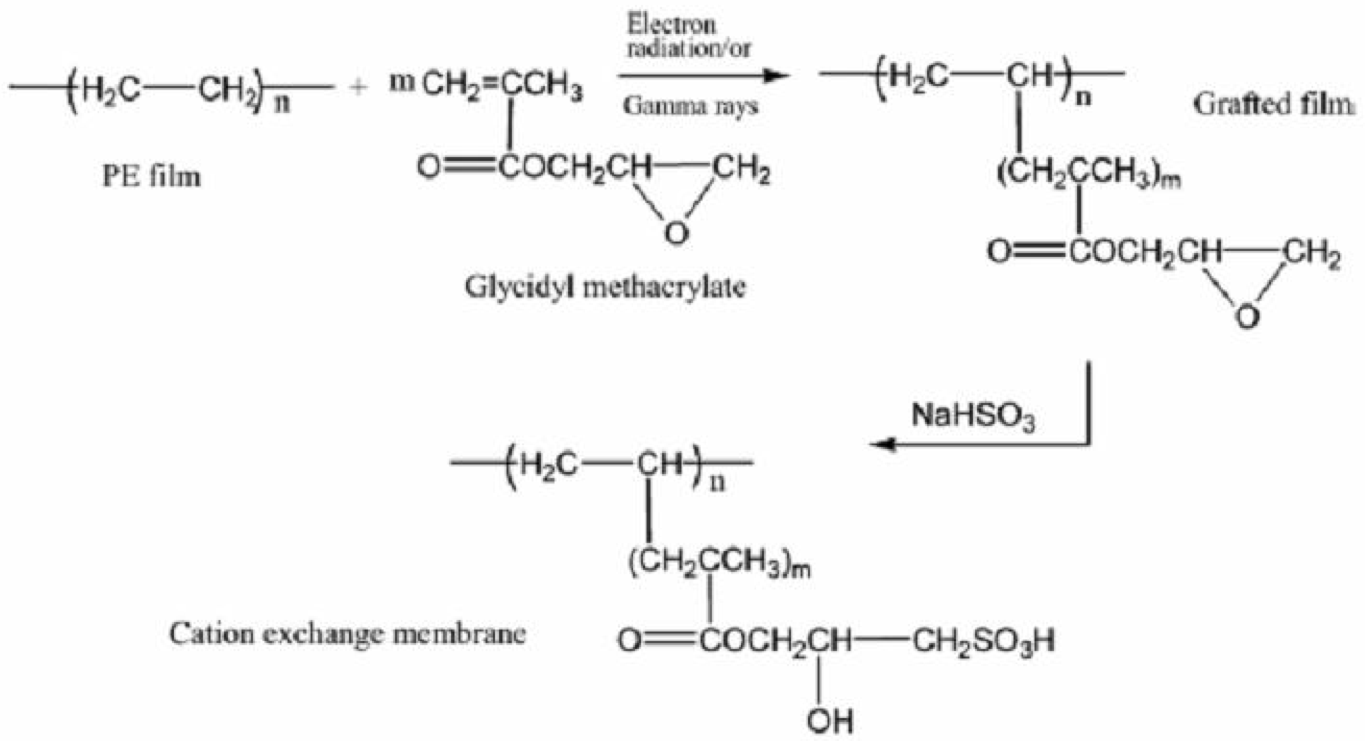
PVDF



Graft Copolymer Electrolytes

Prog. Polym. Sci. 2004, 29, 499
J. Electrochem. Soc, 1996, 143, 2795

✹ Grafting of GMA onto PE



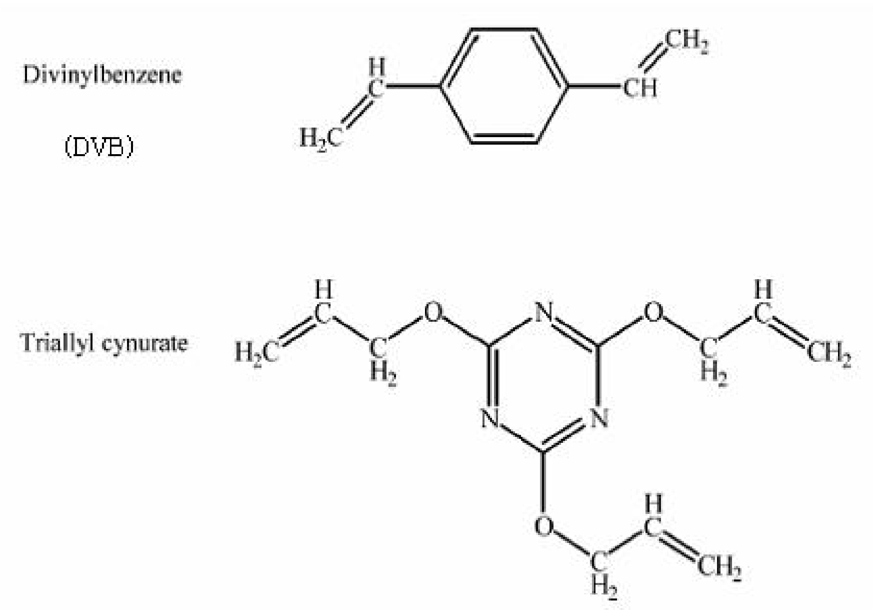
GMA: glycidyl methacrylate

Crosslinked Graft Copolymer

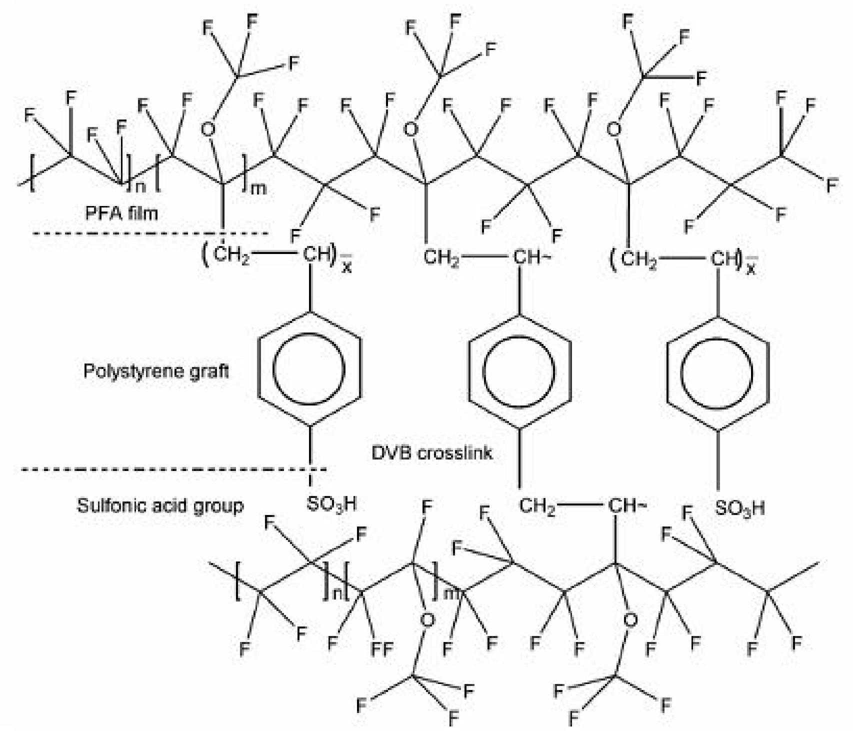
J. Membr. Sci. 2003, 216, 27

✵ Crosslinking with DVB

Crosslinking agent



PFA-g-PS/DVB-SO_3H Membrane



PFA: poly(tetrafluoroethylene-co-perfluorovinyl ether)

Crosslinked Graft Copolymer

J. Membr. Sci. 2003, 216, 27

Membrane properties

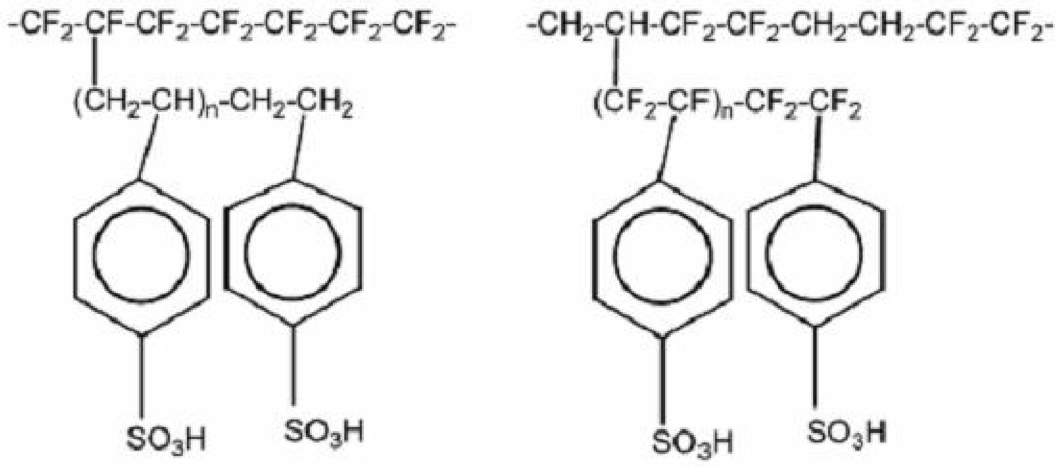
Membrane	Degree of grafting (wt.%)	DVB (vol.%)	Ion exchange capacity (mmol g^{-1})	Water uptake (wt.%)	Ionic conductivity (mS cm^{-1})	Thickness (μm)
PFA-g-PS-SO_3H	24.0	0	1.55	33	25.1	160
PFA-g-PS/DVB-SO_3H	24.0	2	1.62	24	15.9	155
PFA-g-PS/DVB-SO_3H	17.0	4	1.59	14	6.3	150
FEP-g-PS-SO_3H	14.8	0	0.98	–	89.3	78
FEP-g-PS/DVB-SO_3H	17.1	2	1.19	–	99.0	73
FEP-g-PS/DVB-SO_3H	18.8	4	1.16	–	69.0	101
FEP-g-PS/DVB-SO_3H	19.0	12[a]	1.26	21	27.8	171
ETFE-g-PS-SO_3H	32.0	0	2.13	45	190.0	Based on 50 μm
PVDF-g-PS-SO_3H	23.0	0	–	52	25.0	120
Nafion 117	–	–	0.91	19	59.2	180

- High conc. of DVB reduce water uptake and ionic conductivity

- Thermal stability (decomposition of SO3H) is not affected by crossliking

Commercial Graft Membranes

✹ Commercial Membranes



Permion

Raymion

- comparable performance with Nafion 117
- ~ 10,000h stability

J. Electrochem. Soc. 1998, 145, 780

- **Permion**: irradiation grafting of styrene onto FEP (or PTFE, ETFE)
- **Raymion**: pre-irradiation grafting of trifluorostyrene onto ETFE, followed by sulfonation

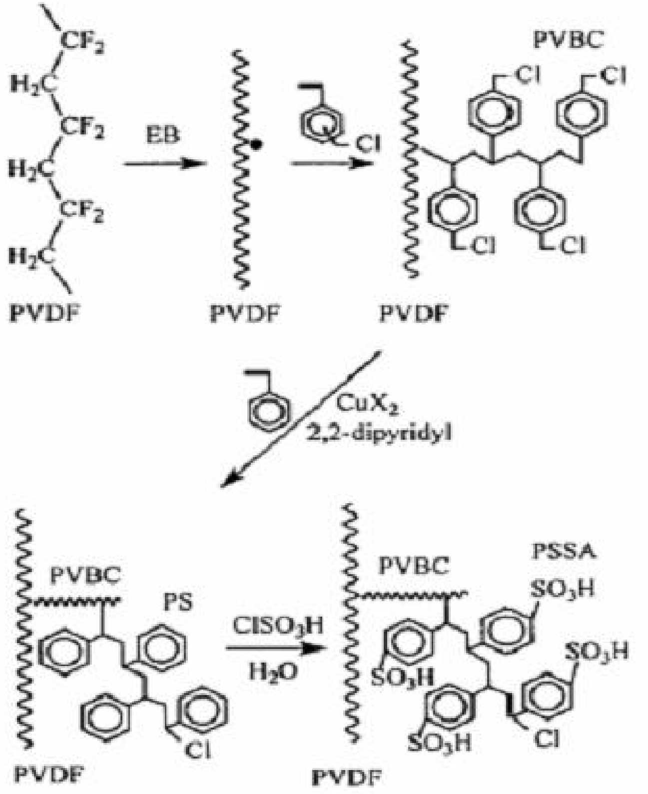
FEP: poly(tetrafluoroethylene-co-hexafluoropropylene)
PTFE: poly(tetrafluoro ethylene)
ETFE: poly(ethylene tetrafluoroethylene)

Living Graft copolymer

J. Poly. Sci. Poly. Phys. 2002, 40, 591

✹ PVDF-g-PVBC-PS by ATRP

Electron-beam preirradiation grafting => atomic transfer radical polymerization (ATRP)



DOG (%)		IEC	Water	Water Uptake for	Conductivity
PVBC	PS	(meq/g)	Uptake (g/g)	$N(H_2O)/N(SO_3H)$	(mS/cm)
17	24	1.9	0.44	13	ND[a]
27	38	2.3	0.42	10	17
27	50	2.2	0.36	9	25
27	132	—	—	—	70

Promising materials for fuel cells !!!

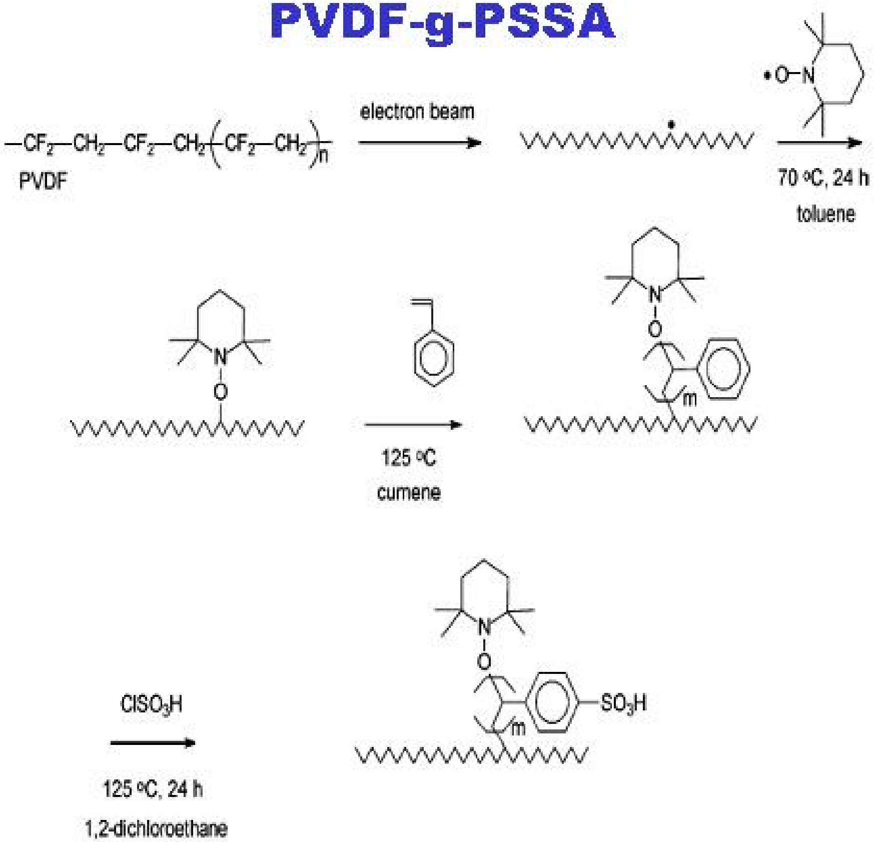
PVBC: poly(vinylbenzyl chloride)

Living Graft copolymer

Macromolecules 2004, 37, 9909

✺ TEMPO mediated polymerization

PVDF-g-PSSA



PS d.o.g. (%)	conductivity (mS/cm)	IEC_{theor} (meq/g)	IEC_{meas} (meq/g)	water uptake (g/g)	water uptake $N(H_2O)/N(SO_3H)$
14[a]	13	1.08	0.96	0.21	12
18[a]	33	1.31	1.11	0.27	14
20[a]	n.d.[b]	1.42	1.28	0.29	13
28[a]	40	1.80	1.67	0.40	14
40[a]	80	2.22	1.73	0.55	18
15[c]	0[d]	1.14	0.19[e]	0.09[e]	26
34[c]	1[d]	2.04	0.62[e]	0.23[e]	21
53[c]	n.d.[b]	2.63	1.63[e]	0.95[e]	32
60[c]	102[d]	2.80	2.08[e]	1.16[e]	31
Nafion 105	56[f]		1.00[f]	0.51[f]	28[f]
Nafion 117	51[f]		0.89[f]	0.37[f]	23[f]

[a] Commercial Nafion 105 and 117 included for comparison.; TEMPO-grafting. [b] Not determined. [c] Conventional EB-grafting. [d] Ref 16. [e] Ref 8e. [f] Ref 17.

Preliminary H_2/O_2 fuel cell tests show promise for PEM

TEMPO: 2,2,6,6-tetramethylpiperidinyl-1-oxy, PSSA: poly(styrene sulfonic acid)

Closing Remark