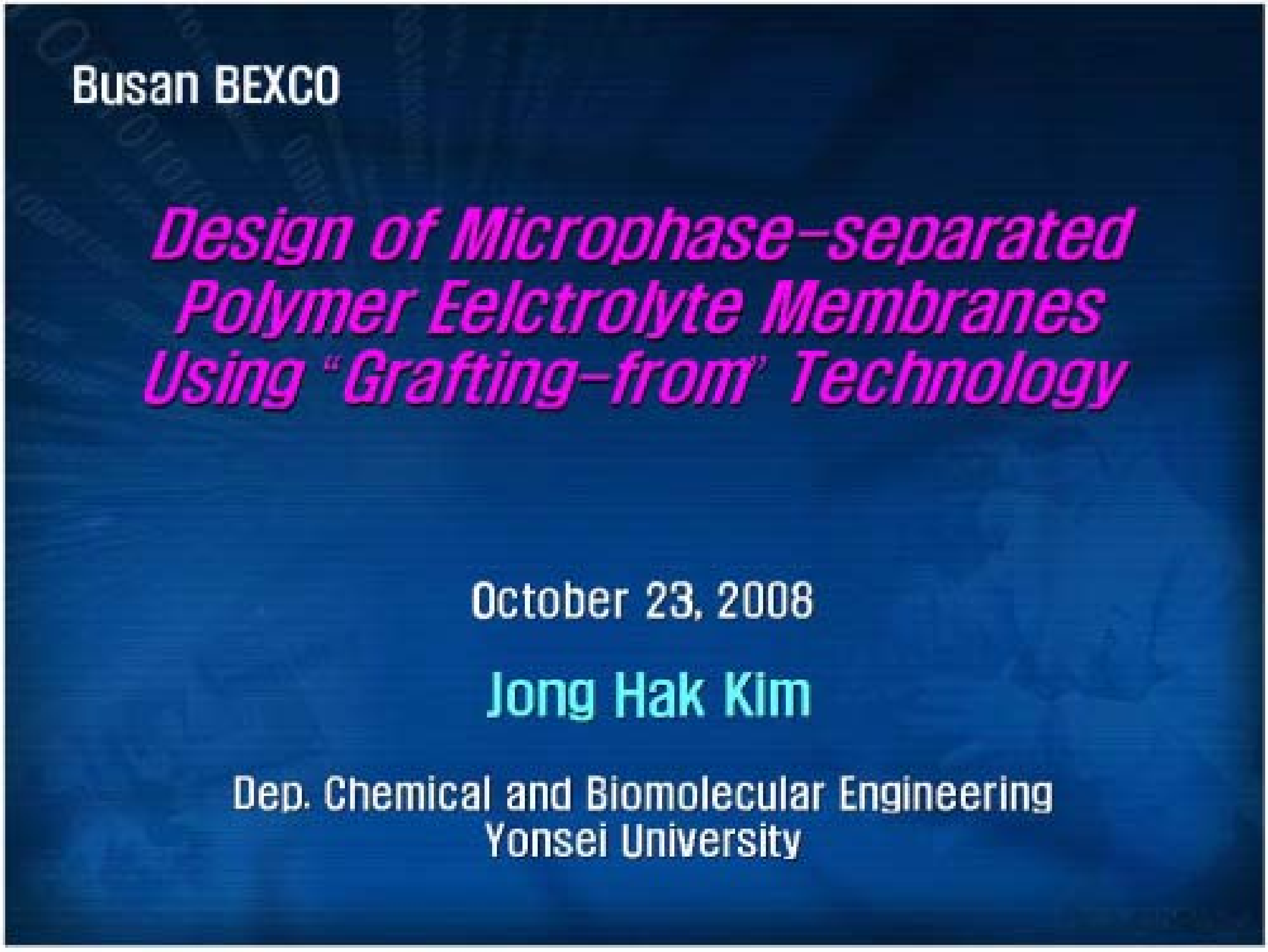
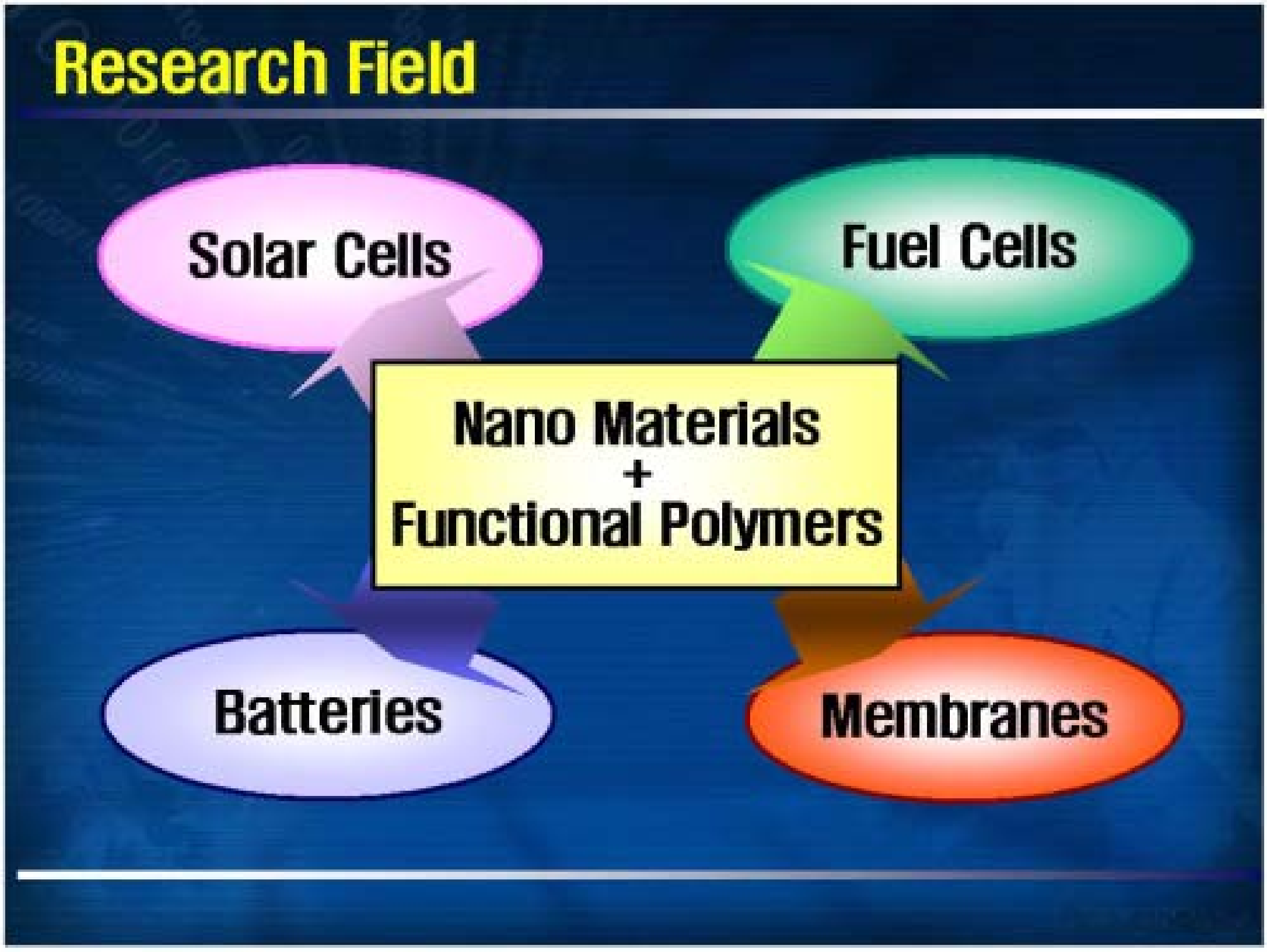
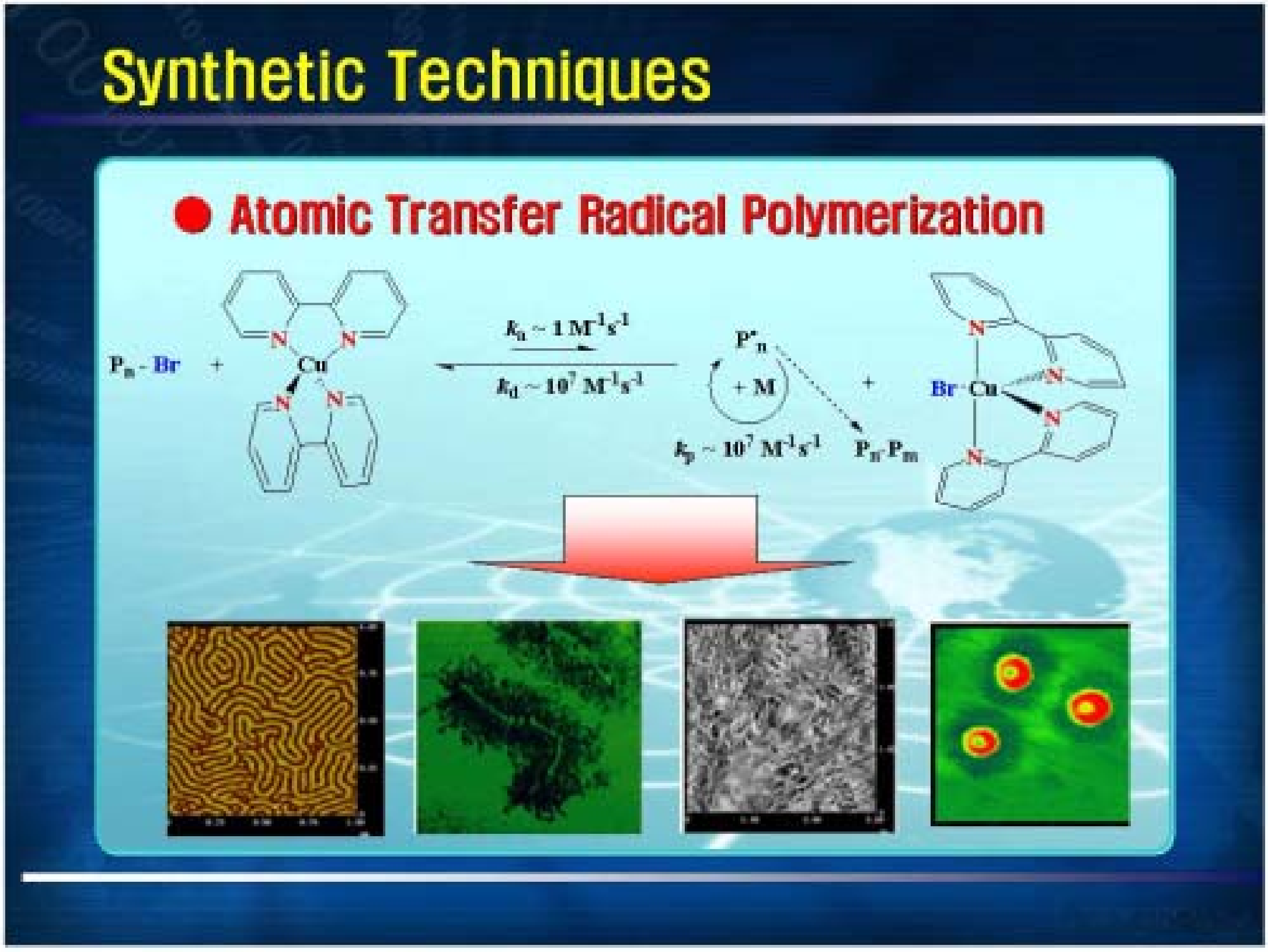
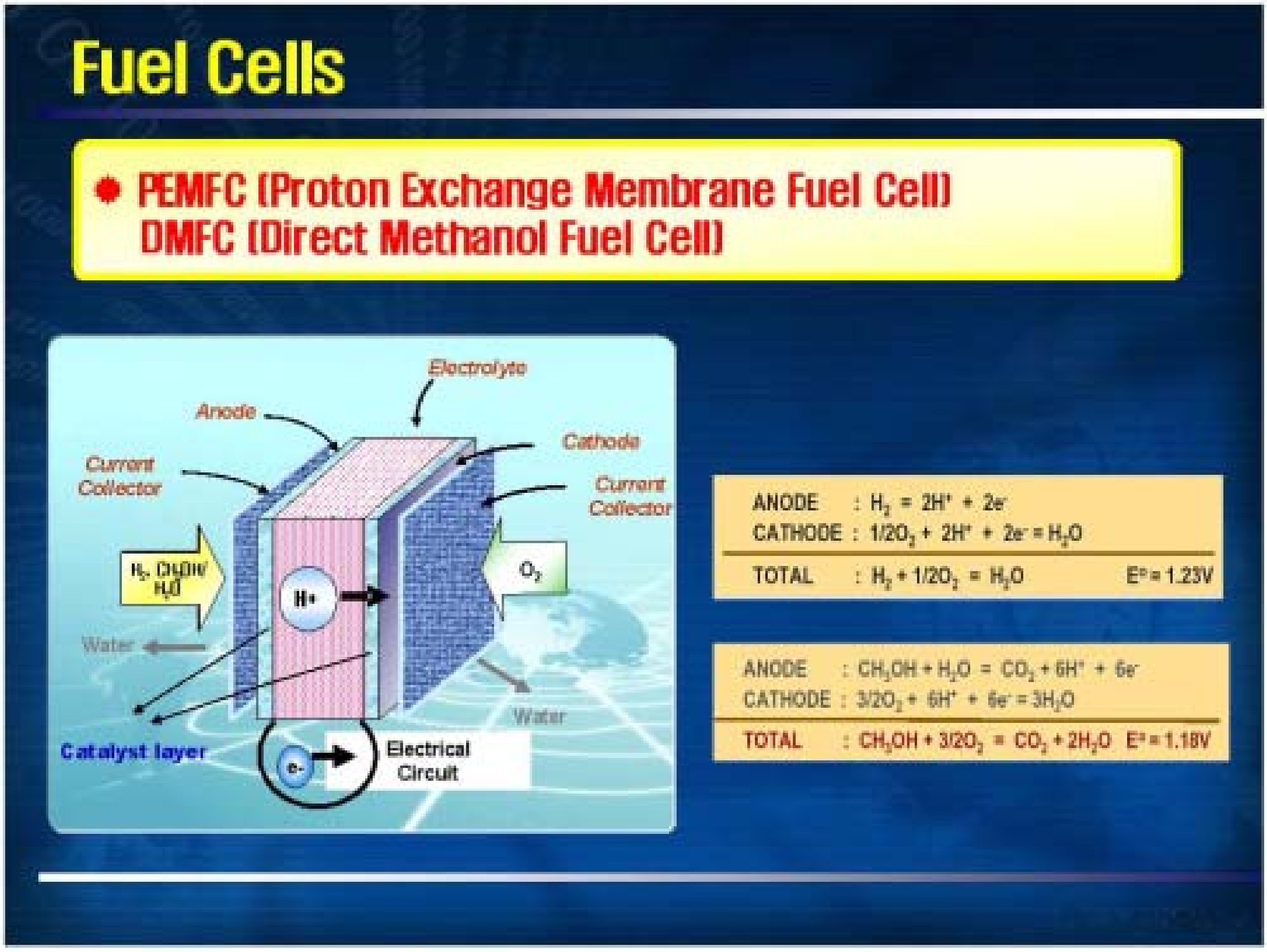
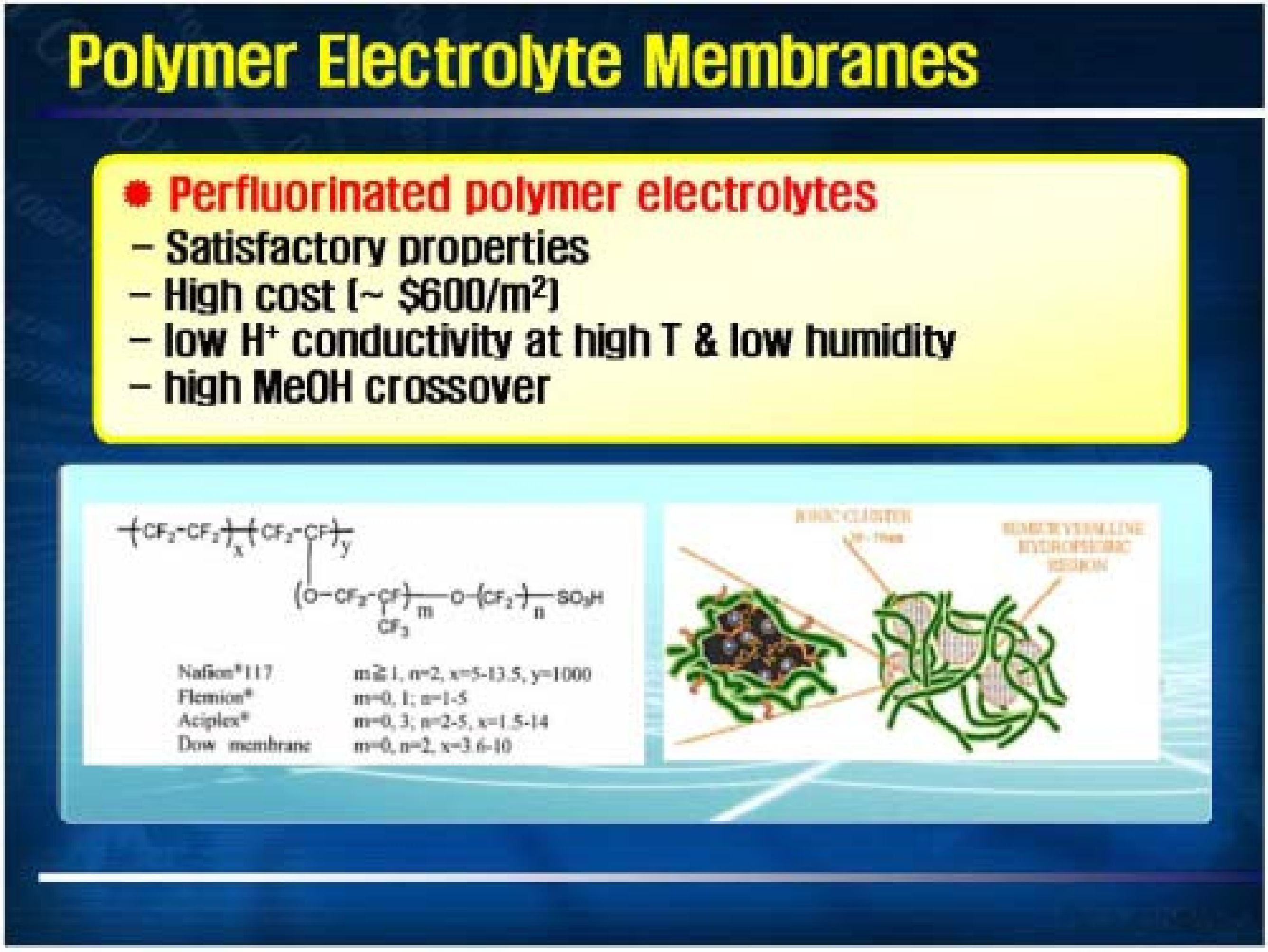
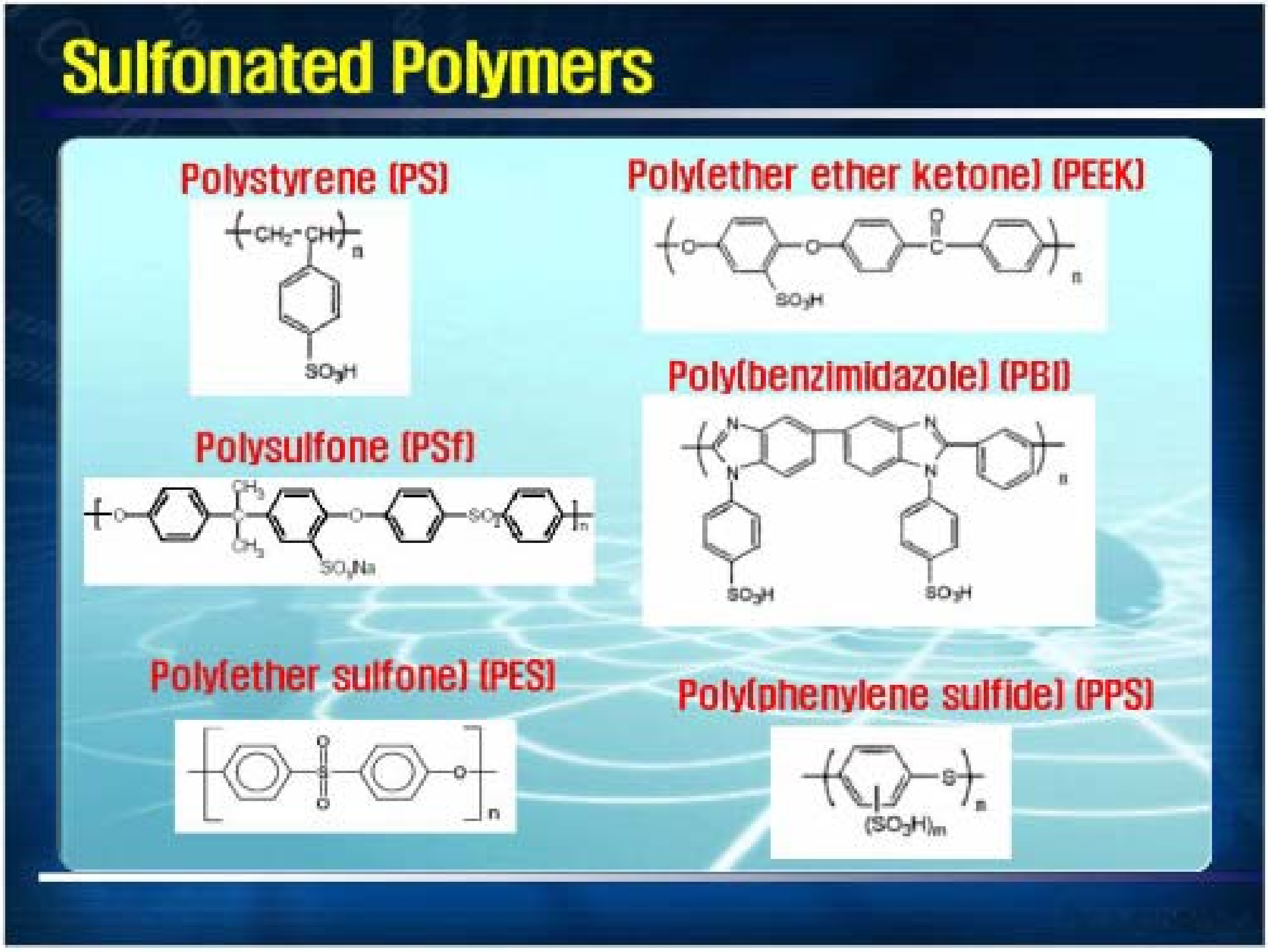

Busan BEXCO
Design of Microphase-separated Polymer Eelctrolyte Membranes Using "Grafting-from" Technology
October 23, 2008
Jong Hak Kim
Dep. Chemical and Biomolecular Engineering
Yonsei University

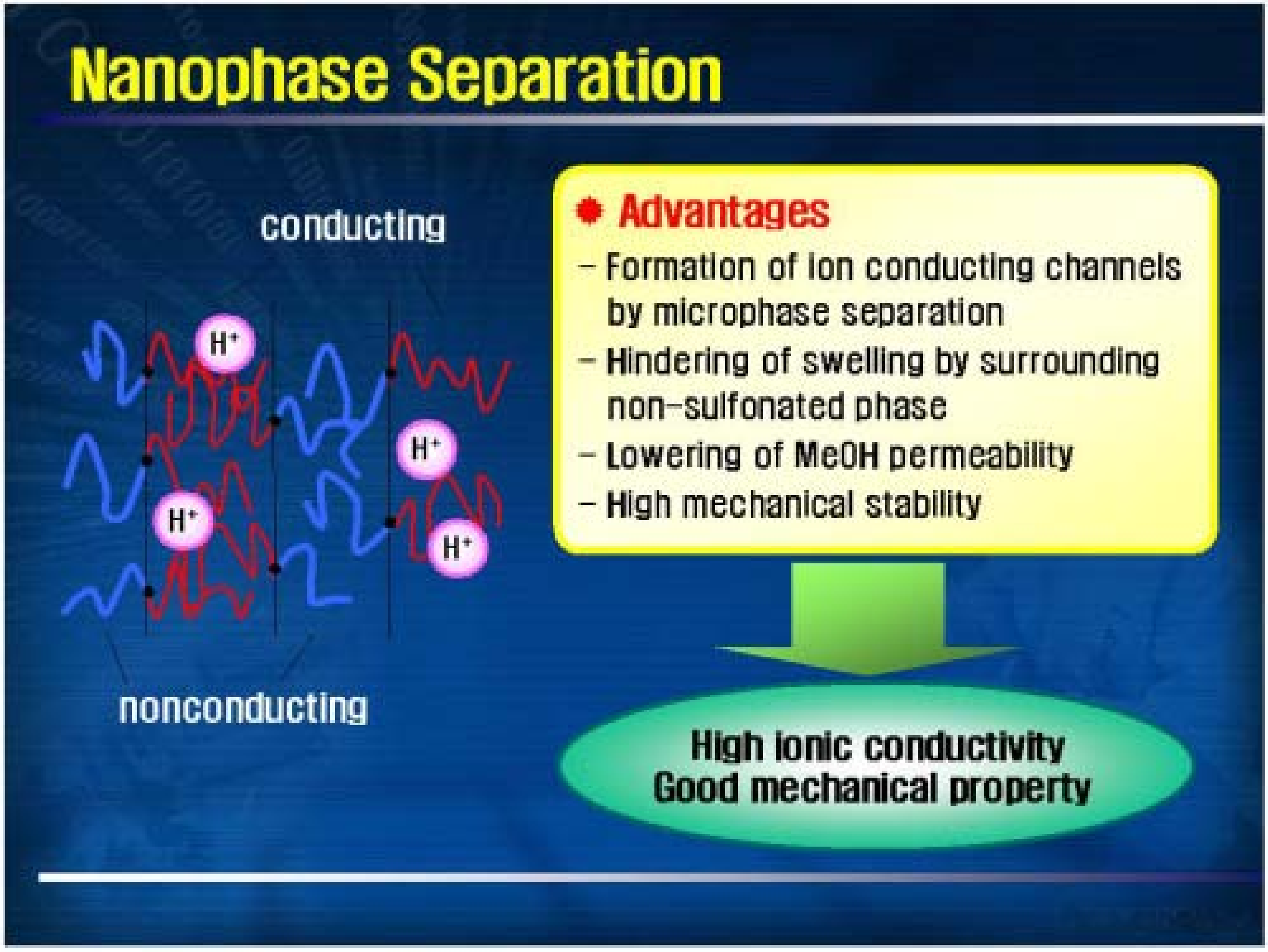

Research Field
Solar Cells
Fuel Cells
Nano Materials
+
Functional Polymers
Batteries
Membranes

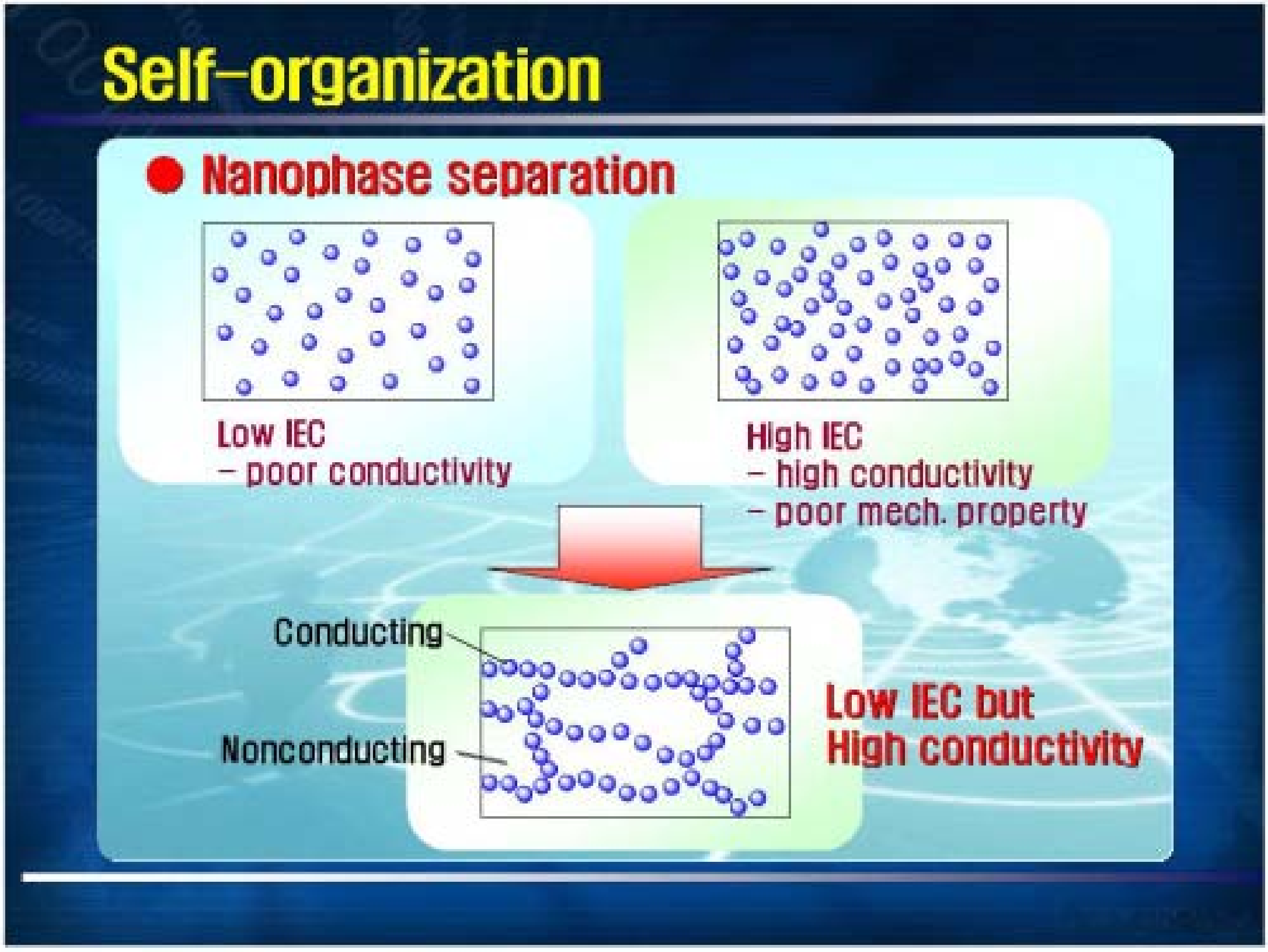

Synthetic Techniques
Atomic Transfer Radical Polymerization
P_n - Br
+
Cu
N
$k_a \sim 1\ M^{-1}s^{-1}$
$k_d \sim 10^7\ M^{-1}s^{-1}$
$P^{\bullet}_n$
+ M
$k_p \sim 10^7\ M^{-1}s^{-1}$
P_n-P_m
Br-Cu


Fuel Cells
PEMFC (Proton Exchange Membrane Fuel Cell)
DMFC (Direct Methanol Fuel Cell)
Electrolyte
Anode
Cathode
Current Collector
Current Collector
H_2, CH_3OH/ H_2O
O_2
H+
Water
Water
Catalyst layer
e-
Electrical Circuit
ANODE : H_2 = $2H^+$ + $2e^-$
CATHODE : $1/2O_2$ + $2H^+$ + $2e^-$ = H_2O
TOTAL : H_2 + $1/2O_2$ = H_2O E° = 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° = 1.18V


Polymer Electrolyte Membranes
Perfluorinated polymer electrolytes
– Satisfactory properties
– High cost (~ $600/m²)
– 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
IONIC CLUSTER


Sulfonated Polymers
Polystyrene (PS)
Poly(ether ether ketone) (PEEK)
Poly(benzimidazole) (PBI)
Polysulfone (PSf)
Poly(ether sulfone) (PES)
Poly(phenylene sulfide) (PPS)

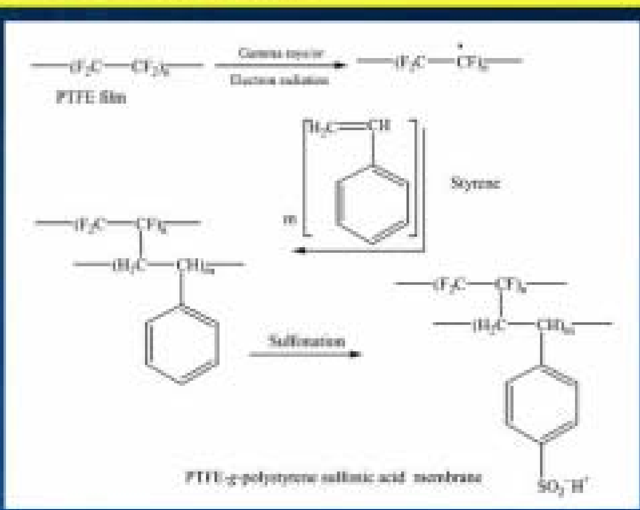

Nanophase Separation
conducting
H+
nonconducting
Advantages
- Formation of ion conducting channels by microphase separation
- Hindering of swelling by surrounding non-sulfonated phase
- Lowering of MeOH permeability
- High mechanical stability
High ionic conductivity
Good mechanical property


Self-organization
Nanophase separation
Low IEC
- poor conductivity
High IEC
- high conductivity
- poor mech. property
Conducting
Nonconducting
Low IEC but
High conductivity

Graft Copolymerization

Prog. Polym. Sci. 2004, 29, 499

Grafting of PS onto PTFE



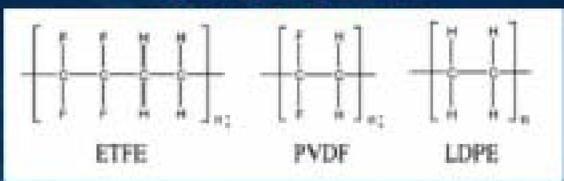
- Radiation (γ-ray, electron beam)
  - chain grafts are covalently attached to main chain

Graft Copolymer Electrolytes

J. Membr. Sci. 2005, 251, 121

Membrane Property

Base polymers



Basic grafting scheme

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

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

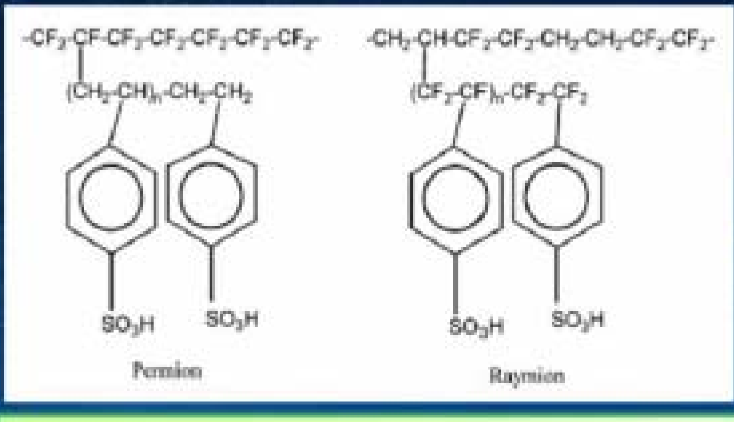
grafted co-polymer $\xrightarrow{\text{sulfonation}}$ solid polymer electrolyte

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	90	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

Commercial Graft Membranes

Commercial Membranes



J. Electrochem. Soc. 1998, 145, 780

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

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

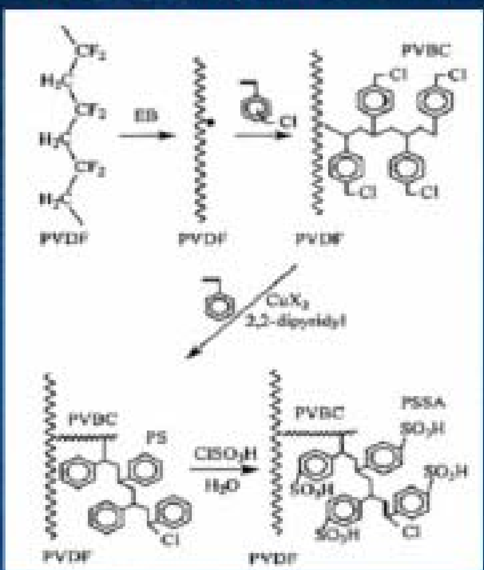
FEP: poly(tetrafluoroethylene-co-hexafluoropropylene)
PTFE: poly(tetrafluoro ethylene)
ETFE: poly(ethylene tetrafluoroethylene)

Living Graft copolymer

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

PVDF-g-PVBC-PS by ATRP

Electron-beam preirradiation grafting => ATRP



DOG (%)		IEC (meq/g)	Water Uptake (g/g)	Water Uptake for $N(H_2O)/N(SO_3H)$	Conductivity (mS/cm)
PVBC	PS				
17	24	1.0	0.44	13	NDᵃ
27	38	2.3	0.42	10	17
27	50	2.2	0.36	9	25
27	132	—	—	—	70

Promising materials for fuel cells !!!

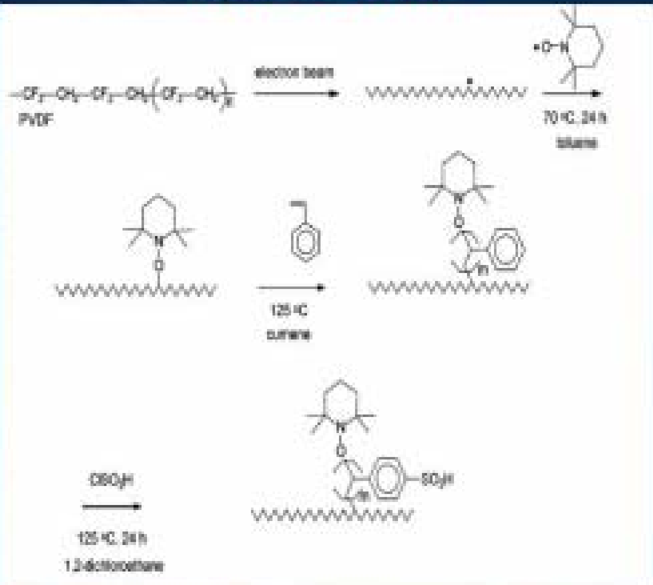
PVBC: poly(vinylbenzyl chloride)

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]	9[d]	1.14	0.19[e]	0.09[e]	26
34[c]	1[d]	2.04	0.62[e]	0.23[e]	21
59[c]	n.d.[b]	2.63	1.63[e]	0.96[e]	32
60[c]	102[d]	2.80	2.09[e]	1.16[e]	31
Nafion 105	50[f]		1.00[f]	0.51[f]	28[f]
Nafion 117	51[f]		0.89[f]	0.37[f]	23[f]

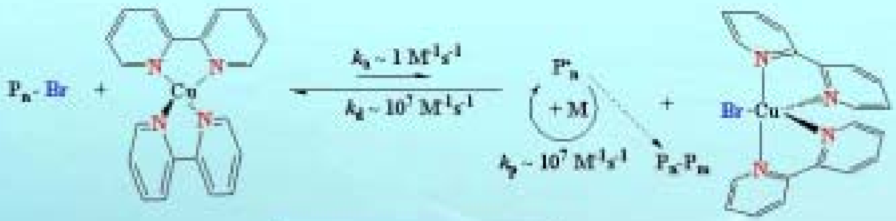
[a] Commercial Nafion 105 and 117 included for comparison.; TEMPO-grafting. [b] Not determined. [c] Conventional EB-grafting. [d] Ref 16. [e] Ref 8e. [f] Ref 17.

Preliminary H_2/O_2 fuel cell tests show promise for PEM

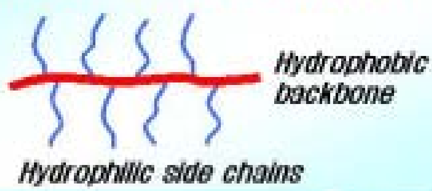
TEMPO: 2,2,6,6-tetramethylpiperidinyl-1-oxy, PSSA: poly(styrene sulfonic acid)

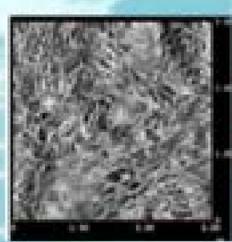
Our "Grafting from" Technology

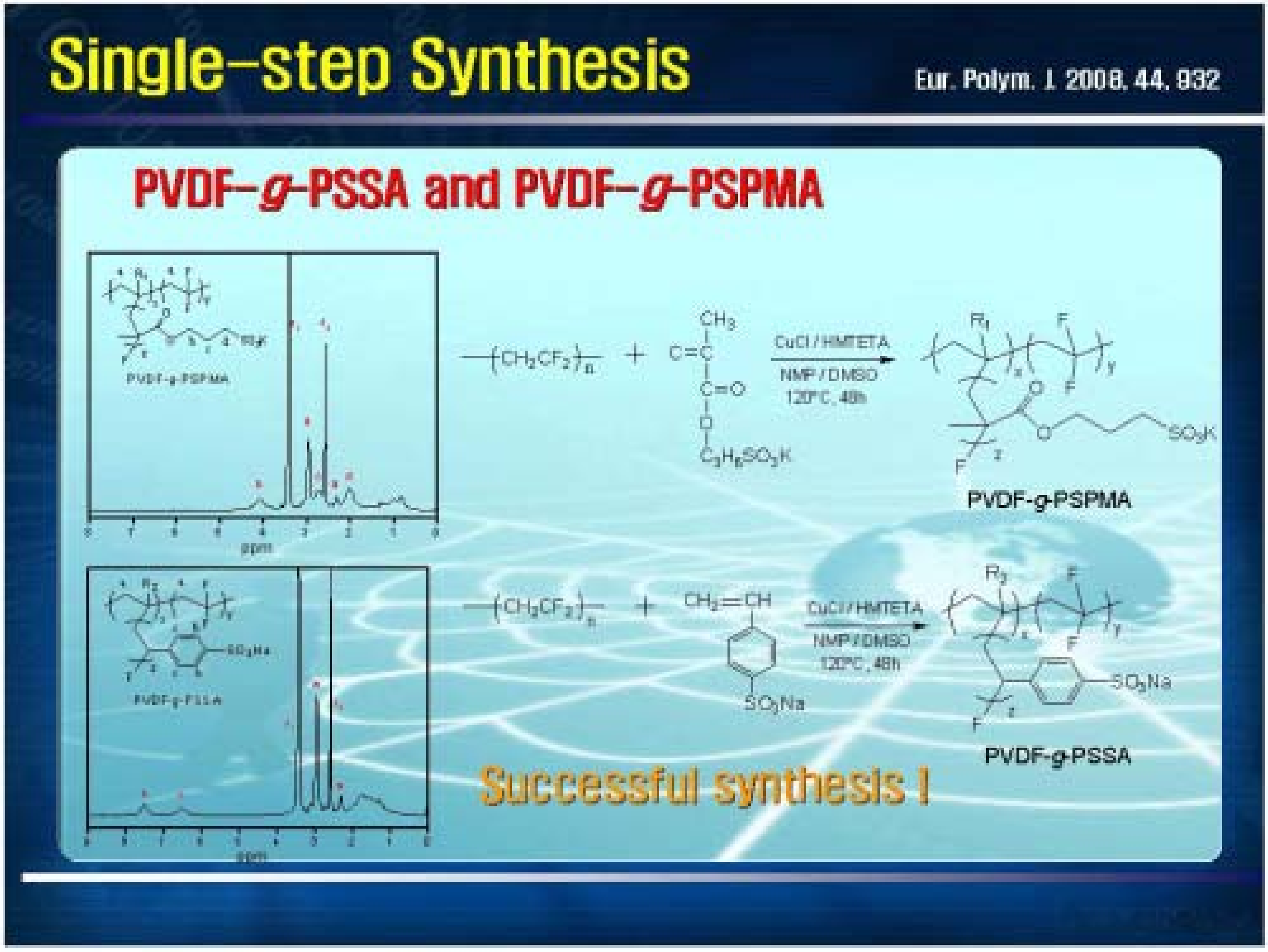
Atomic Transfer Radical Polymerization

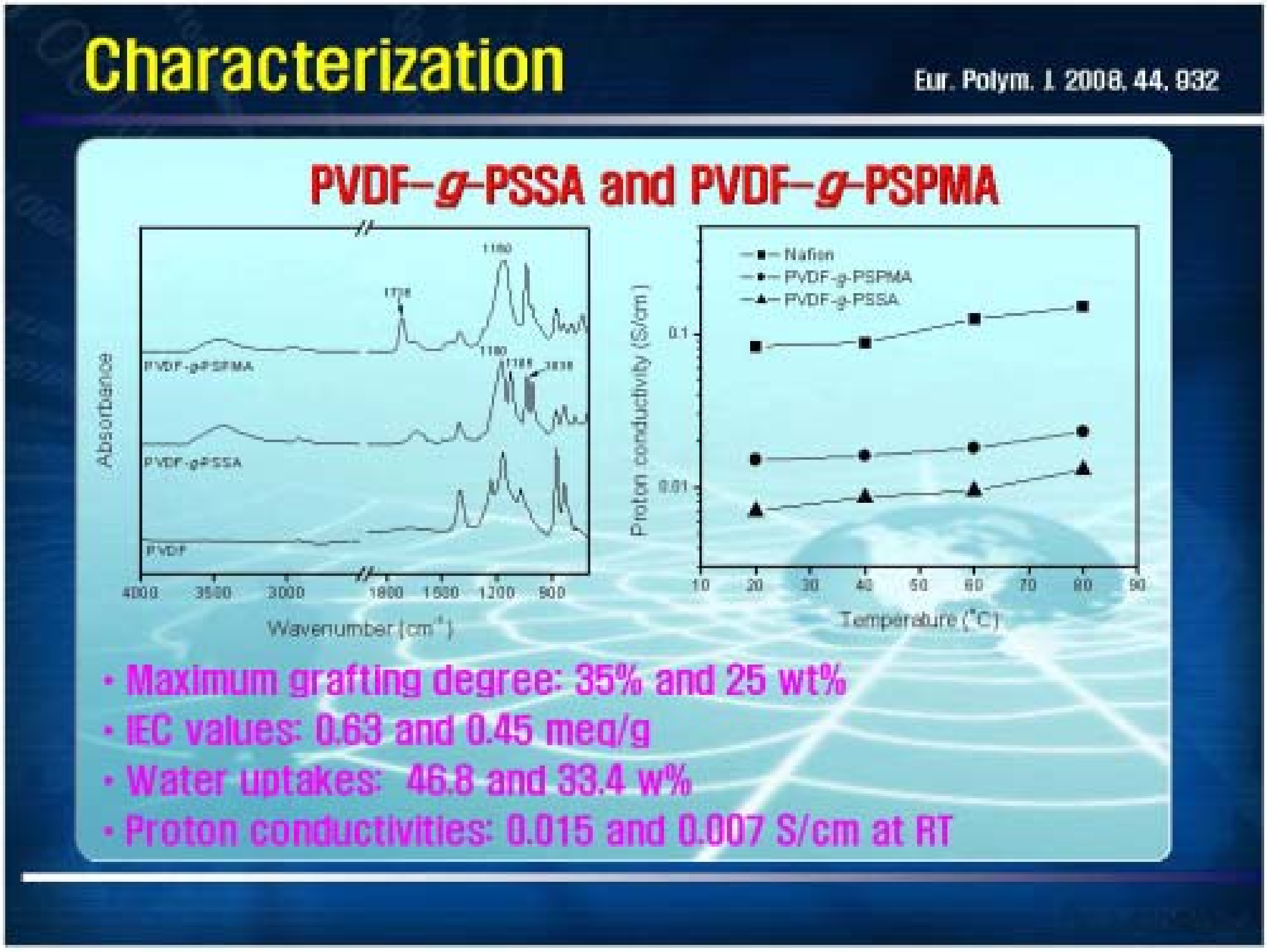


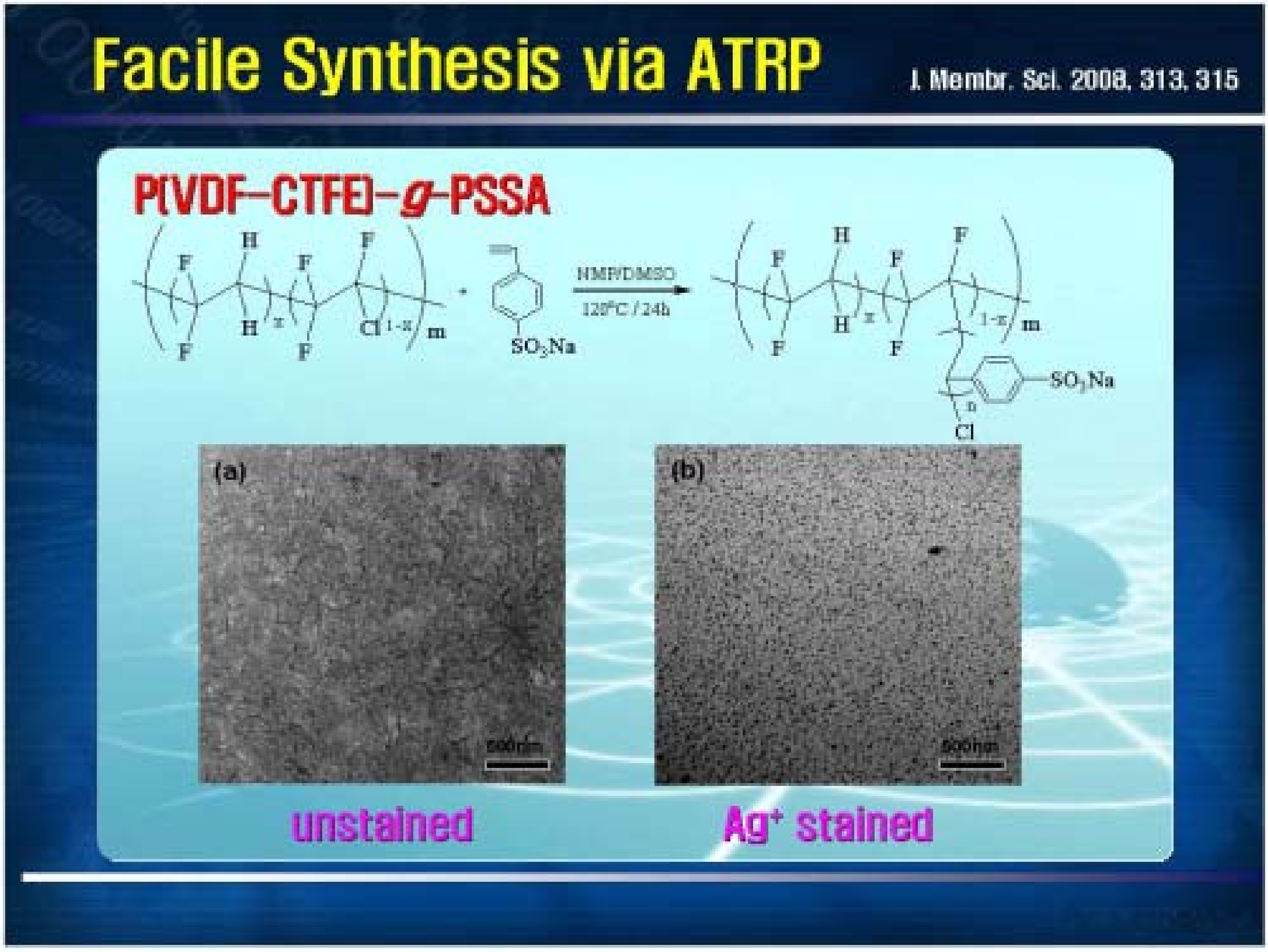
Amphiphilic comb copolymer

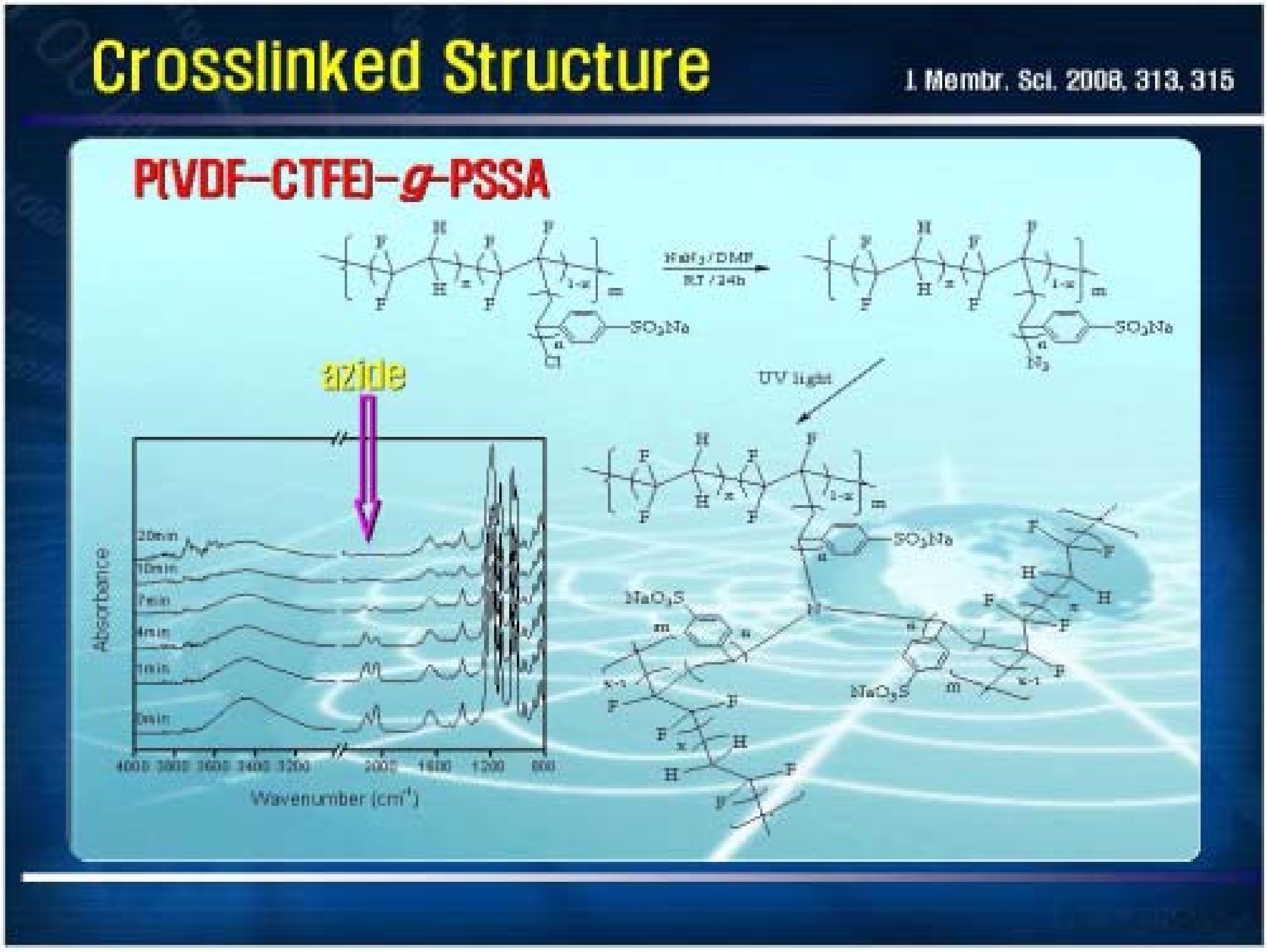





Single-step Synthesis
Eur. Polym. J. 2008, 44, 932
PVDF-*g*-PSSA and PVDF-*g*-PSPMA
PVDF-g-PSPMA
ppm
CuCl / HMTETA
NMP / DMSO
120°C, 48h
PVDF-*g*-PSPMA
PVDF-g-PSSA
CuCl / HMTETA
NMP / DMSO
120°C, 48h
PVDF-*g*-PSSA
Successful synthesis !


Characterization
Eur. Polym. J. 2008, 44, 932
PVDF-*g*-PSSA and PVDF-*g*-PSPMA
Absorbance
PVDF-g-PSPMA
PVDF-g-PSSA
PVDF
Wavenumber (cm⁻¹)
Nafion
PVDF-g-PSPMA
PVDF-g-PSSA
Proton conductivity (S/cm)
Temperature (°C)
• Maximum grafting degree: 35% and 25 wt%
• IEC values: 0.63 and 0.45 meq/g
• Water uptakes: 46.8 and 33.4 w%
• Proton conductivities: 0.015 and 0.007 S/cm at RT

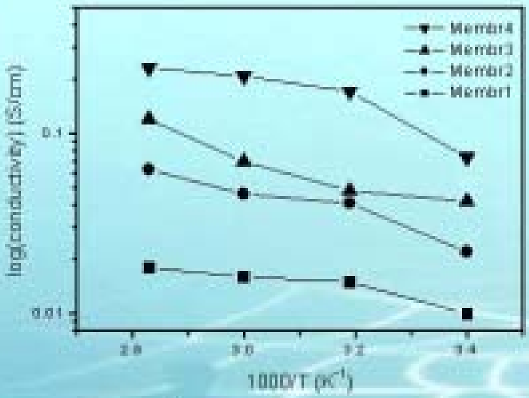

Facile Synthesis via ATRP
J. Membr. Sci. 2008, 313, 315
P(VDF-CTFE)-g-PSSA
NMP/DMSO
120°C / 24h
SO3Na
(a)
(b)
500nm
unstained
Ag+ stained

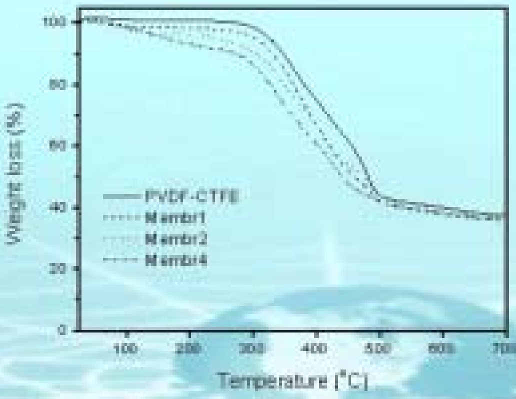

Crosslinked Structure
J. Membr. Sci. 2008, 313, 315
P(VDF-CTFE)-g-PSSA
NaN3 / DMF
RT / 24h
SO3Na
azide
UV light
20min
10min
7min
4min
1min
0min
Absorbance
Wavenumber (cm-1)

Membrane Properties

J. Membr. Sci. 2008, 313, 315

Crosslinked P(VDF–CTFE)-*g*-PSSA





Membrane	Proton Conductivity (S/cm)		Water Uptake (%)		Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
	20 °C	80 °C	20 °C	80 °C			
Membr4	0.074	0.231	300	430	21.1	357	20.3
Crosslinked Membr4	0.068	0.203	83	120	26.2	385	23.4

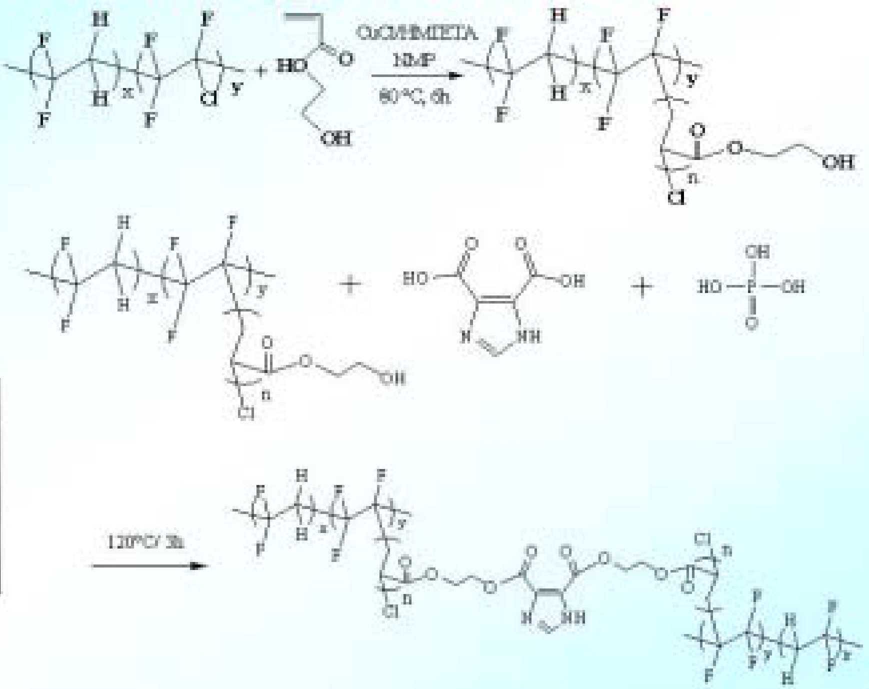
Anhydrous Membranes

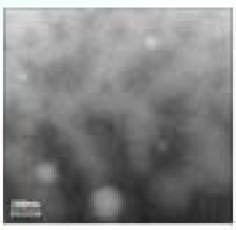
J. Membr. Sci. (in press)

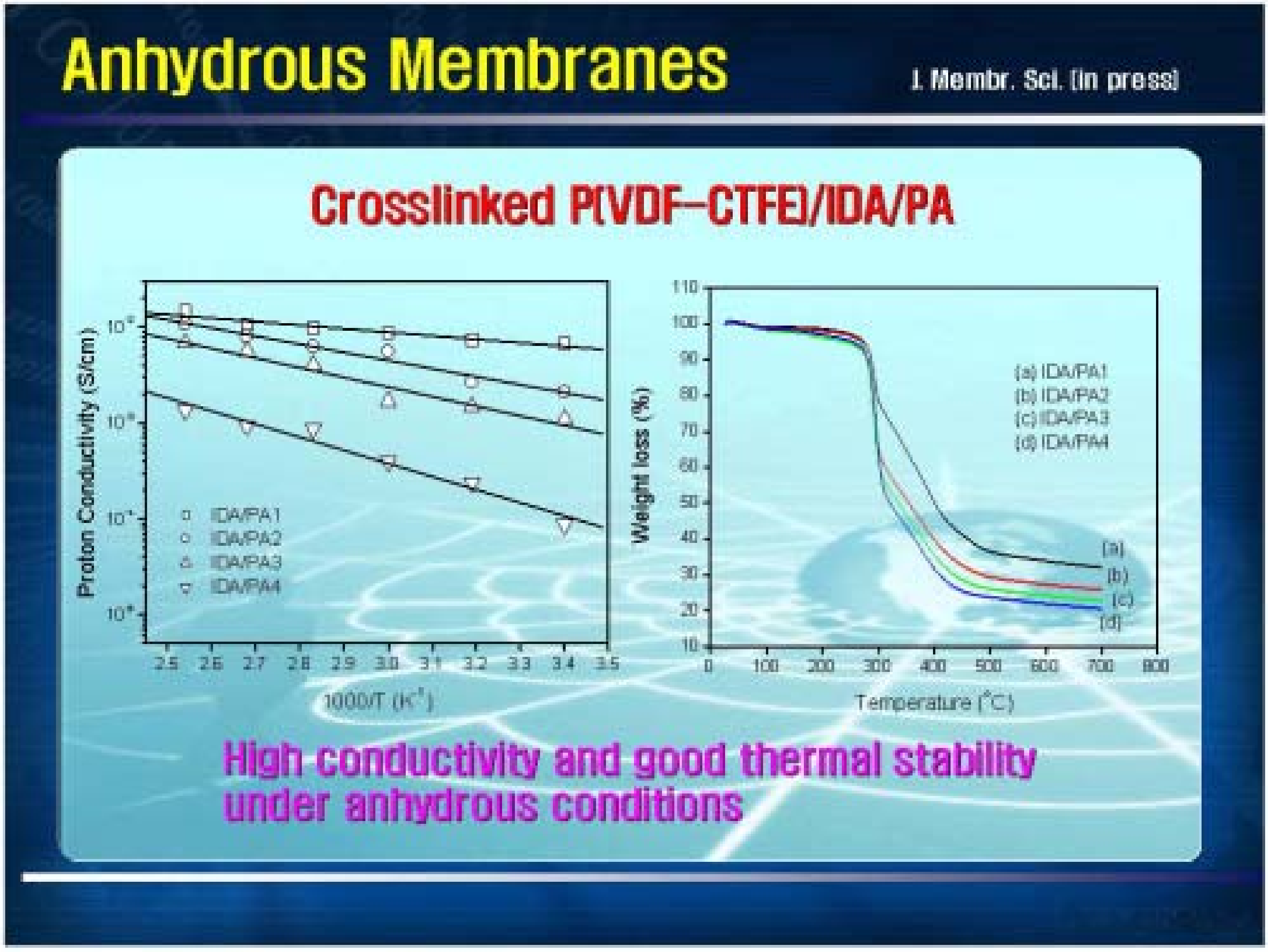
Crosslinked P(VDF–CTFE)/IDA/PA

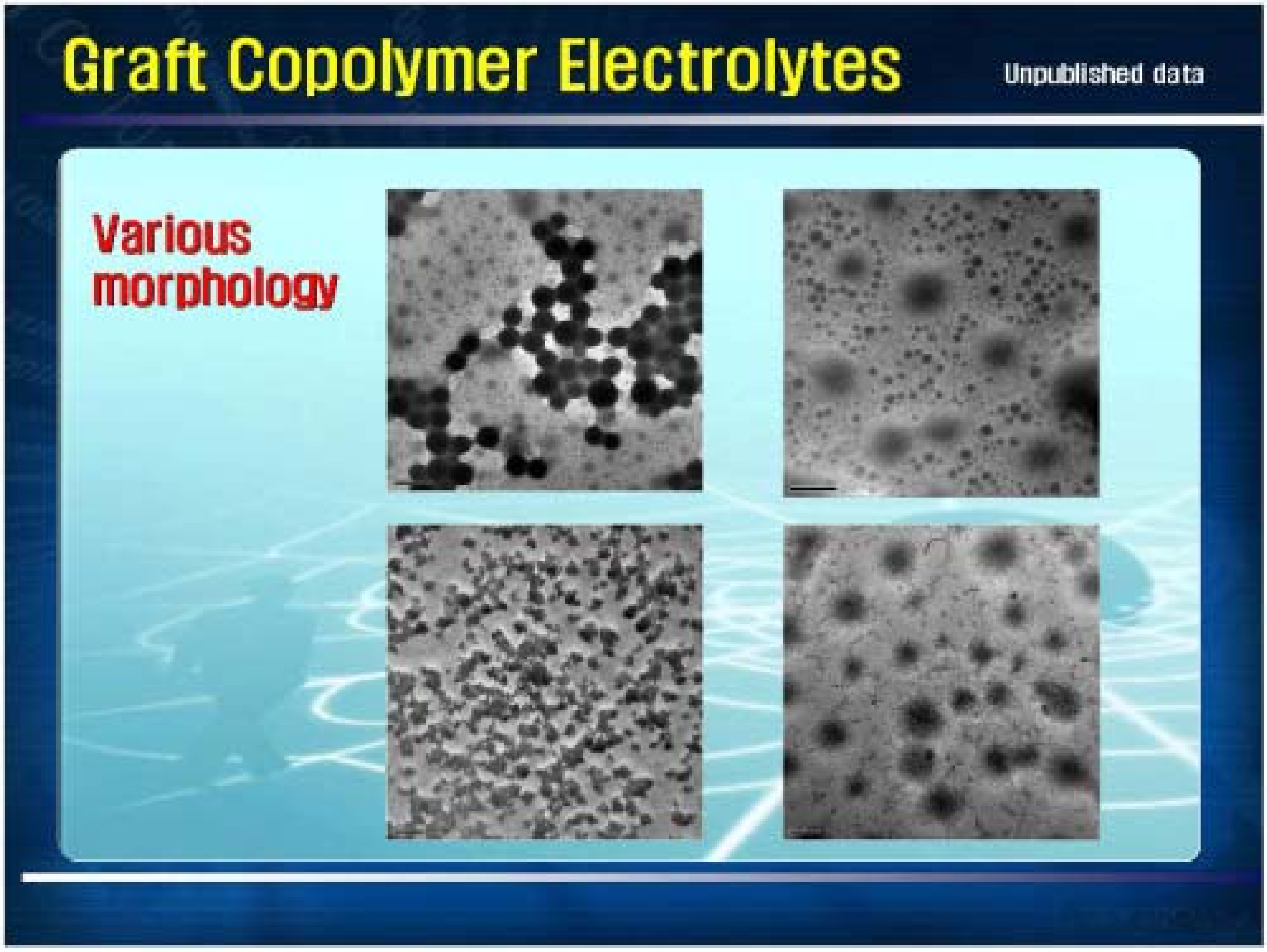
Step 1

Step 2






Anhydrous Membranes
J. Membr. Sci. (in press)
Crosslinked P(VDF–CTFE)/IDA/PA
Proton Conductivity (S/cm)
1000/T (K⁻¹)
IDA/PA1
IDA/PA2
IDA/PA3
IDA/PA4
Weight loss (%)
Temperature (°C)
(a) IDA/PA1
(b) IDA/PA2
(c) IDA/PA3
(d) IDA/PA4
High conductivity and good thermal stability
under anhydrous conditions


Graft Copolymer Electrolytes
Unpublished data
Various
morphology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• Korea Research Foundation (Basic Research Promotion)
Yonsei University