

***Recent Advances in the Synthesis and
Properties of Functionalized
Fluoropolymers as Engineering Materials***

G.Kostov

*Department of Organic Chemical Technologies, Prof. As. Zlatarov University
of Burgas , Bulgaria; e-mail: gkostov@btu.bg*

VII National Conference on Chemistry, 26-29 May 2011, Sofia, Bulgaria

CONTENTS



1-Introduction. Objectives

2-Functionalized fluoropolymers for plastic optical fibres

3-Original fluorinated surfactants potentially non-bioaccumulable

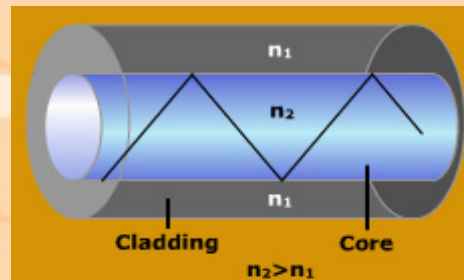
4-Functional fluoropolymers for fuel cell membranes

5-Conclusions and perspectives

1. FEATURES / BENEFITS / ADVANTAGES of F POLYMERS

LOW REFRACTIVE INDEX

- OPTICAL FIBRES AND COATINGS



LOW SURFACE ENERGY

- LUBRICITY, RELEASE

VERY LOW SURFACE TENSION

- SPECIALITY SURFACTANTS & FIRE FIGHTING AGENTS

VERY STRONG ORGANIC ACIDS

- CATALYSTS & PROTON EXCHANGE MEMBRANES



HIGH OIL, WATER AND SOIL REPELLENCY

- **TEXTILES, LEATHER, PAPER, WOOD, GLASS, CONCRETE, STONE, METALS PROTECTION**



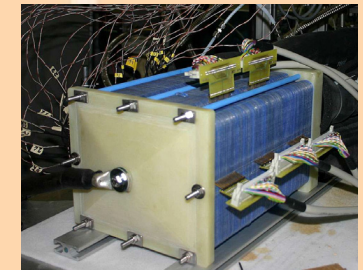
HIGH CHEMICAL, THERMAL, AND OXIDATIVE STABILITY

- **PROTECTIVE COATINGS**



INSULATION

- **WIRE AND CABLE INDUSTRIES**



CONTENTS



1-Introduction. Objectives

2-Functionalized fluoropolymers for plastic optical fibres

3-Original fluorinated surfactants potentially non-bioaccumulable.

4-Functional fluoropolymers for fuel cell membranes

5-Conclusions and perspectives

2.1. Advantages of polymer optical materials over conventional glasses

- **High optical transparency at transmission wavelengths**
- **Potential to tune their optical properties by tailoring the molecular structure**
- **Lightweight**
- **Flexibility even at large diameters**
- **Good processability**
- **Easy handling**
- **Low cost**

2.2.Applications of POWs

- **Short-haul communication links**
- **Data systems in aircrafts, automobiles**
- **Local area networks**
- **Inter- and intra- office network systems**

2.3.Disadvantages of POWs

- **POWs reveal optical losses much higher than silica**
PMMA (visible region) – 100 dB/km
Silica fibres – 0.3 dB/km
- **Transmission on short distances**
- **Develop partial crystallinity and low T_g**
- **Organic polymers are prone to oxidative degradation**

SOLUTION

Substitution of F (or D) atoms for H atoms

- low overtone band strength
- less scattering
- low n_D

Lower attenuation

Amorphous fluorinated polymers

Cytop™ (Asahi Glass)

Teflon® AF (Du Pont)

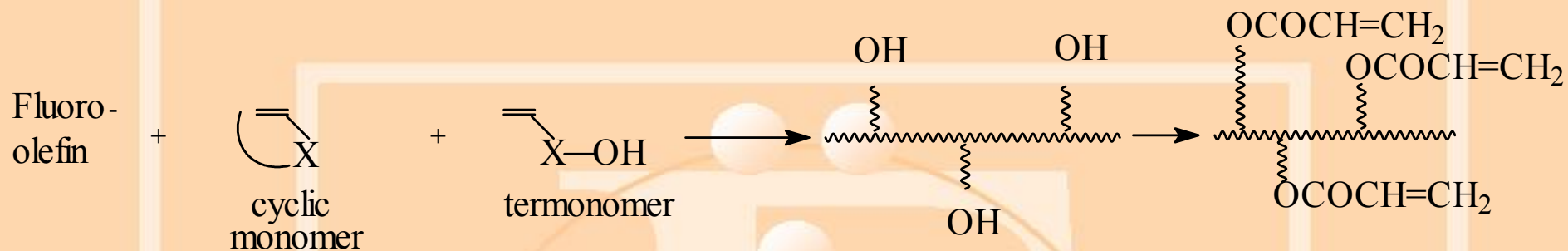
2.4. OBJECTIVES

- 1. Synthesis of novel amorphous hydroxy functional fluoropolymer resins and their acrylation. Photocrosslinking and optical materials**
- 2. New perfluorovinyl dioxolane monomers and copolymer and optical materials**

2.5. STRATEGY OF SYNTHESIS OF OPTICAL POLYMERS

Requirements for optical polymers

- **Optical transparency in the visible and NIR regions**
amorphous with high T_g ; n_D –1.4-1.5; $T_d >150^\circ\text{C}$
- **Good processability to fibers, films and tapes**
($M_n=2000-4000$ g/mol)
- **Photocrosslinkable (preferably acrylic and fluorinated resins)**
- **Homogenous network with good mechanical properties**



$\text{CF}_2=\text{CFCl}$ (CTFE)
 $\text{CF}_2=\text{CF}(\text{CF}_3)$ (HFP)



$\text{X}=\text{O}(\text{CH}_2)_n$
 $n=2$ or $n=4$

Vinylene carbonate

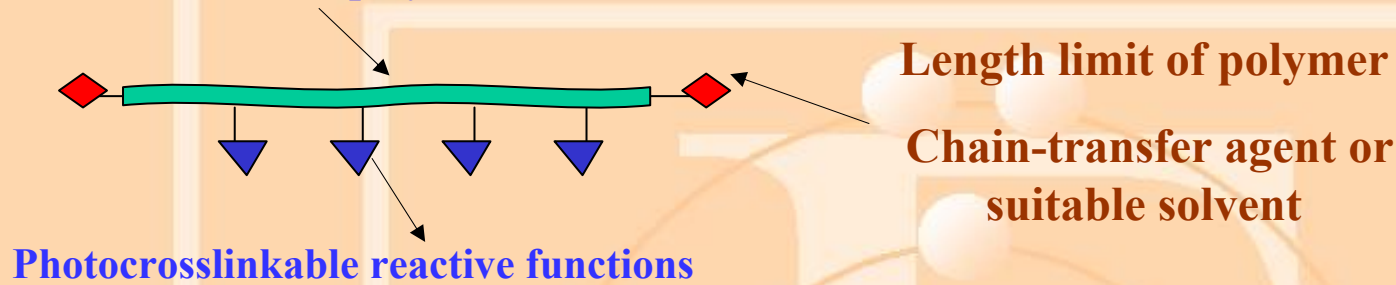
Scheme 1: General scheme of fluoroacrylate synthesis

Kostov, G. *et al.* EP 1479 702 A1(2005). (Assigned to Atofina)

Kostov, G.; Rousseau, A.; Boutevin, B.; Pascal, T. *Journal of Fluorine Chem.*, (2005), 126(2), 231-240.

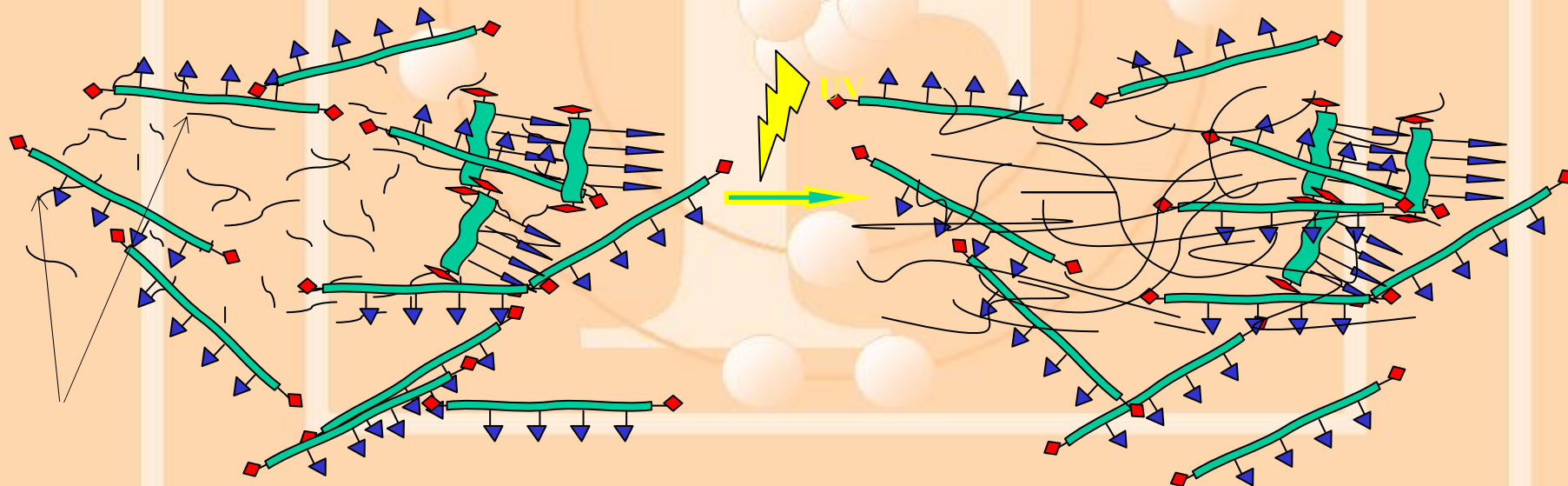
2.6. CTFE/VCA/hydroxy VE copolymers

2.6.1) Fluorooligomers: CTFE/VCA-based copolymers



Reactive diluents : fluorinated function monomers; precise adjustment of resins' refractive index

2) Photocrosslinking:



Reactive diluent(s)

Amorphous crosslinked network

Main characteristics of CTFE/VCA copolymers

Table 1: Selected monomer/copolymer compositions of CTFE/VCA copolymers and their main characteristics.

CTFE in monom. mixture (mol %)	CTFE^a in copolym (mol %)	Yield (wt %)	M_n^d (g.mol⁻¹)	PDI^b	T_g (°C)	T_{d10} (°C)	N_{C-H}/cm³ (10⁻³)	n_D (23°C)
80	60.3	64.0	2800	2.2	70	274	5.4	1.4379
70	51.8	64.1	2500	2.0	90	295	8.4	1.4358
60	45.9	65.8	2250	2.5	100	289	11.5	1.4357
50	39.8	70.6	2000	2.5	110	246	14.8	1.4459
40	34.6	72.2	1800	2.0	120	254	16.2	-

Solubility:

- Polar organic solvents : acetone, THF, EtOAc, DMF, DMSO
- Reactive diluents : HDDA, NVP, and the couple HDDA/ATRIFE

2.6.2. STUDY OF CTFE/VCA/HFP TERPOLYMERIZATION

➤ **Objective: to improve the solubility in reactive diluents and fluorine content in copolymers**

➤ **Reaction conditions:**

CTFE/VCA = 0.67 = const.

HFP in monomer mixture – from 5 to 20 mol.% (2.1 to 10 mol.% in copolymer composition – ^{19}F NMR

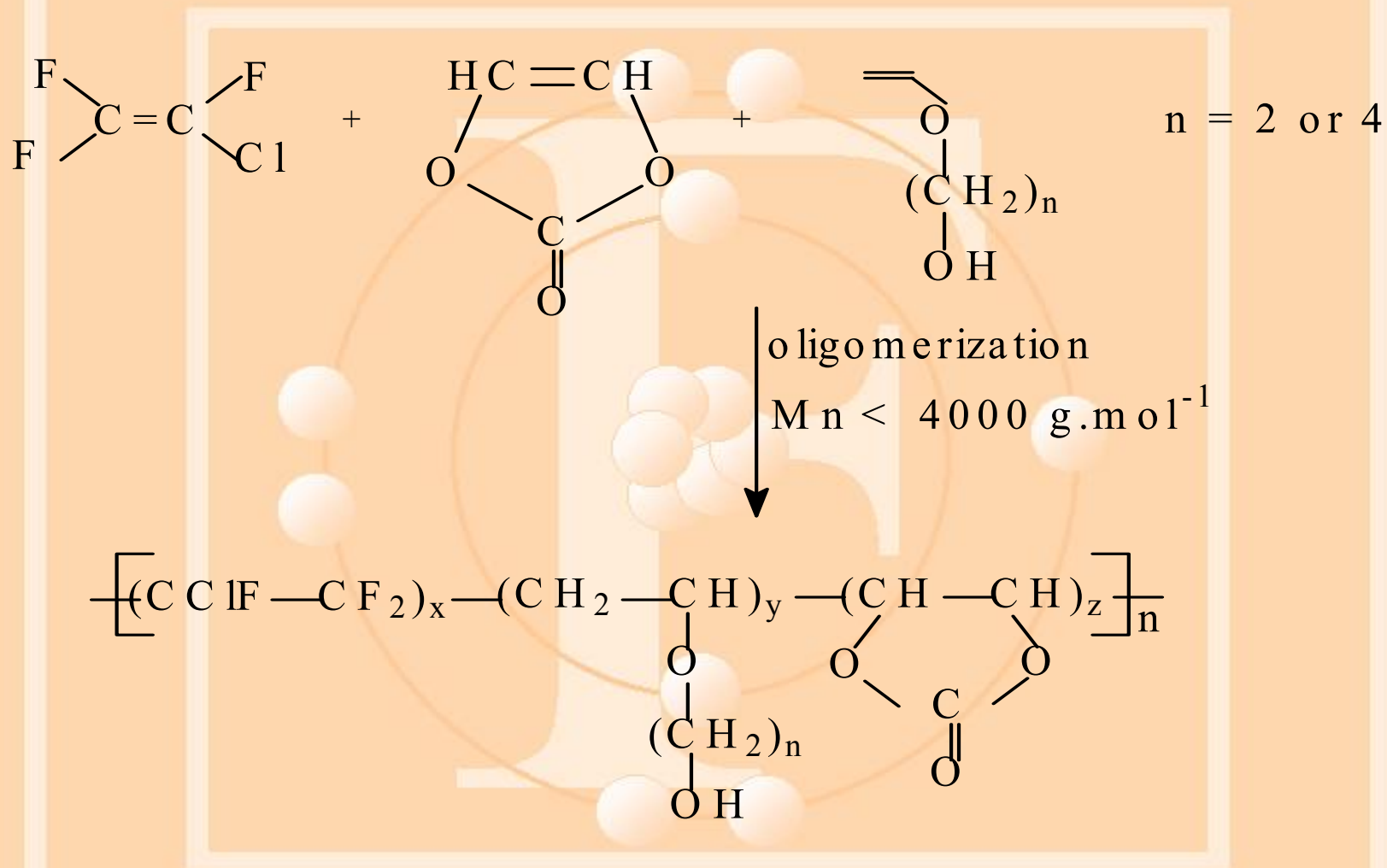
➤ **Characterization of CTFE/VCA/HFP terpolymers**

- solubility in reactive diluents

- $T_g \sim 120^\circ\text{C}; T_d \sim 250^\circ\text{C}$

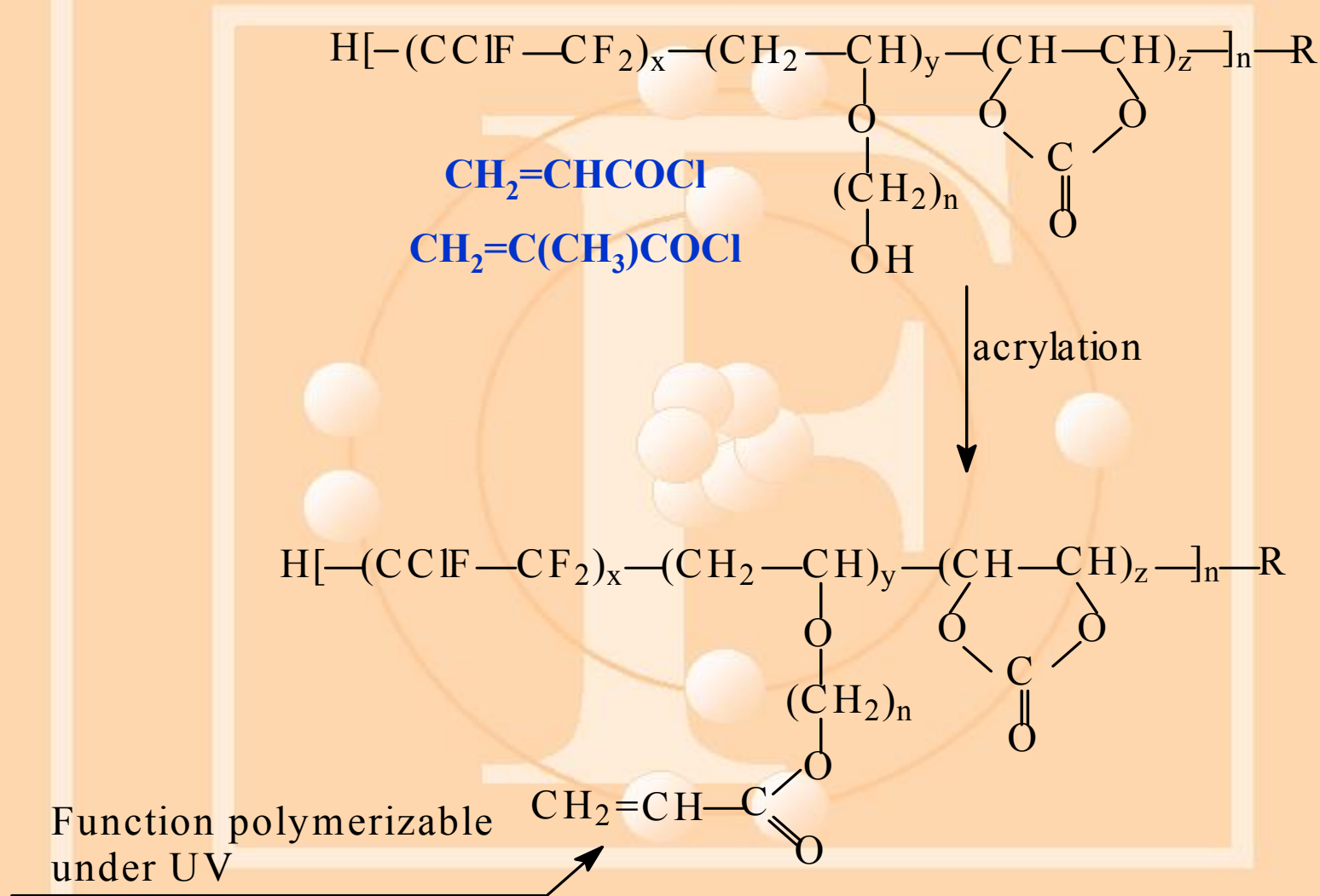
- $N_{\text{C-H}}/\text{cm}^3$ (n_D resp.)

2.6.3. SYNTHESIS OF CTFE/VCA/HYDROXY VINYL ETHER TERPOLYMERS



Scheme 3 : CTFE / VCA / hydroxy VE terpolymerization

2.7.ACRYLATION OF HYDROXY FUNCTIONALIZED CO-POLYMERS



Scheme 6 : Acrylation of -OH functionalized CTFE/VCA co-polymers

2.8. Characterization of UV-cured materials

➤ DMA analysis

T_g of acrylated CTFE/VCA/HBVE compositions ~90°C

E – modulus : 1 GPa at 20°C; 50 MPa at 120°C

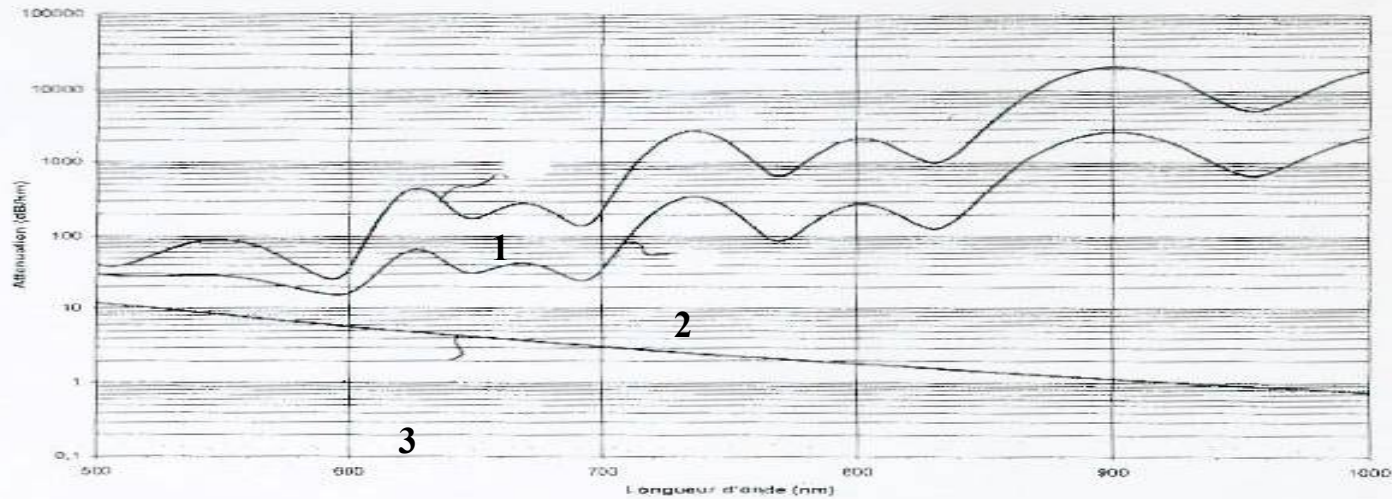
T_{d10}^{air} ~ 200–220°C

➤ DSC analysis

2

T_g of acrylated CTFE/VCA-CH₂OH compositions ~ 100–105°C

T_{d10}^{air} ~ 230–240°C



2.9. CTFE/Perfluorovinyl dioxolane co-polymers for optical fiber

2.9.1. Monomer synthesis

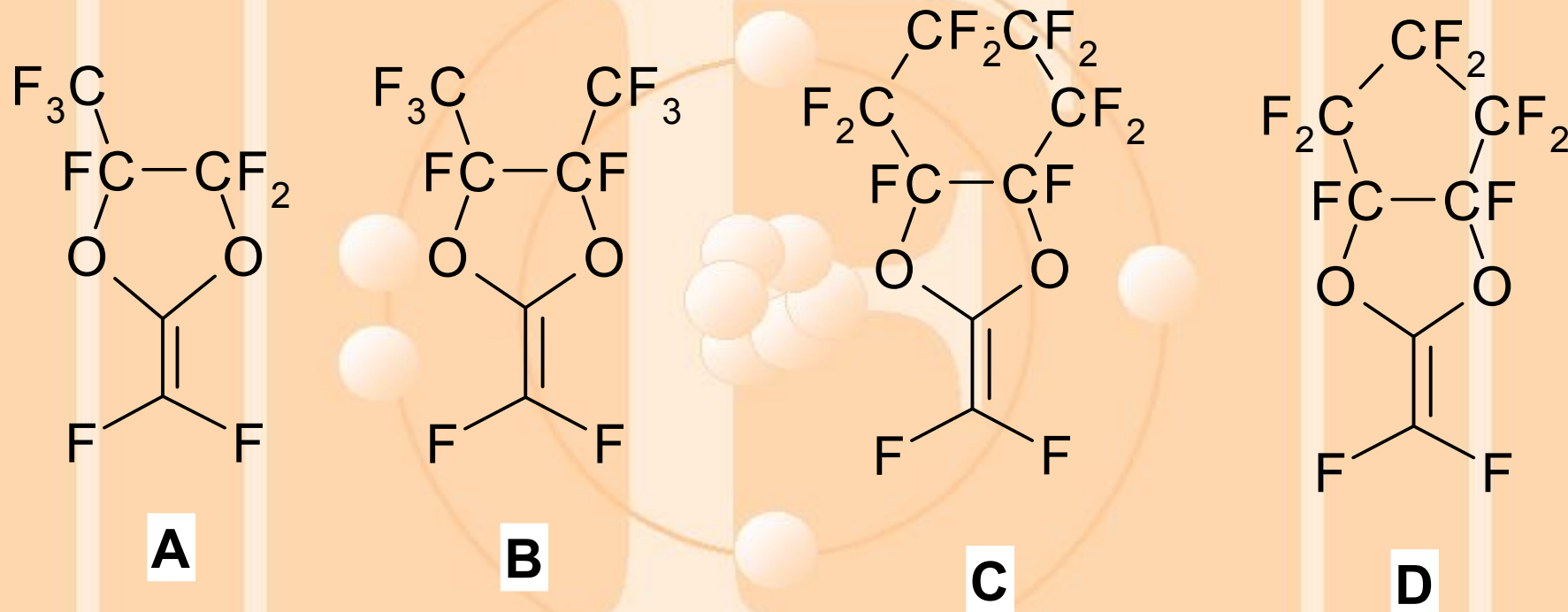
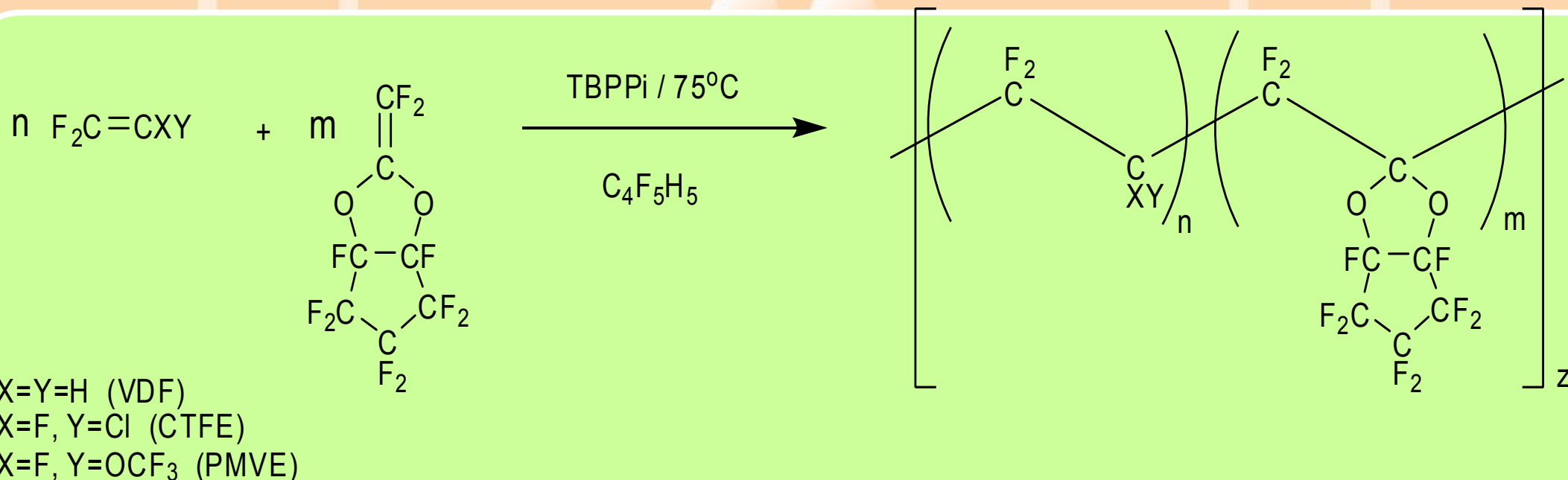


Figure 7. Chemical structures of substituted perfluoro-2-methylene-1,3-dioxolane derivatives.

2.9.2. Co-polymerization of perfluorovinyl dioxolane (F-Ox) with different fluorinated comonomers M₂ (CTFE, PPVE, PMVE and VDF)



Mikes, F., Teng, H., Kostov, G., Ameduri, B., Koike, Y., Okamoto, Y.,
Journal of Polym. Sci., Part A: Polymer Chemistry, 2009, 47, (23) 6571-
 6578.

Co-polymerization of perfluorovinyl dioxolane(F-Ox) with different fluorinated co-monomers M₂ (CTFE, PPVE, PMVE and VDF)

Run #	Monomer M ₂	Monomers in the feed (mol %)		Copolym. comps. by microanal. (mol.%)		Copolym. comps. by NMR (mol %)		Conv (wt.%)	T _g (°C)	T _{d,10} (°C)
		F-Ox	M ₂	F-Ox	M ₂	F-Ox	M ₂			
1	F ₂ C=CFCI	20	80	35	65	37.4	62.6	63	105	322
2	F ₂ C=CFCI	40	60	62	38	61.5	38.5	70	148	354
3	F ₂ C=CFOC ₃ F ₇	64	36	87.4	12.6	85.2	14.8	82	144	342
4	F ₂ C=CFOCF ₃	21	79	50.7	49.3	52.8	47.2	74	154	359
5	F ₂ C=CH ₂	14	86	38.2	61.8	37.8	62.2	65	108	370
6	F ₂ C=CH ₂	35	65	58.4	41.6	57.9	42.1	67	138	356

$$n_R < 1.35$$

2.10. CONCLUSIONS AND PERSPECTIVES

- 1. Binary (CTFE/VCA) and ternary (CTFE/VCA/HFP, CTFE/VCA/HVE) oligomers in good yield and high T_g were synthesized.**
- 2. Successful acrylation of hydroxy functionalized cooligomers**
- 3. Photocrosslinking → original cured fluoroacrylated materials of low n_D, high T_g & T_d and good mechanical properties**
- 4. Novel functionalized copolymers of CTFE with perfluorinated dioxolanes with excellent optical properties**



Suitable for waveguides applications

CONTENTS



1-Introduction. Objectives

2-Functionalized fluoropolymers for plastic optical fibres

3-Original fluorinated surfactants potentially non-bioaccumulable.

4-Functional fluoropolymers for fuel cell membranes

5-Conclusions and perspectives

3.1. Advantages of fluorinated surfactants

😊 Better surface active and better hydrophobic compared to hydrogenated analogues

😊 Lower interfacial tension and CMC

😊 Excellent chemical and thermal stability

😊 Oleophobicity: oil and fat repellants

😊 Useful in many industrial fields: paints, coatings, detergents, fire-fighting foams, pharmaceuticals, etc.

Traditional commercial fluorosurfactants :

Long fluorocarbon chain $C_6 < R_F < C_{12}$ } their derivatives

Perfluorooctane sulphonate (PFOS)

Perfluorooctanoic acid (PFOA)

3.2. DRAWBACKS OF FLUORINATED SURFACTANTS

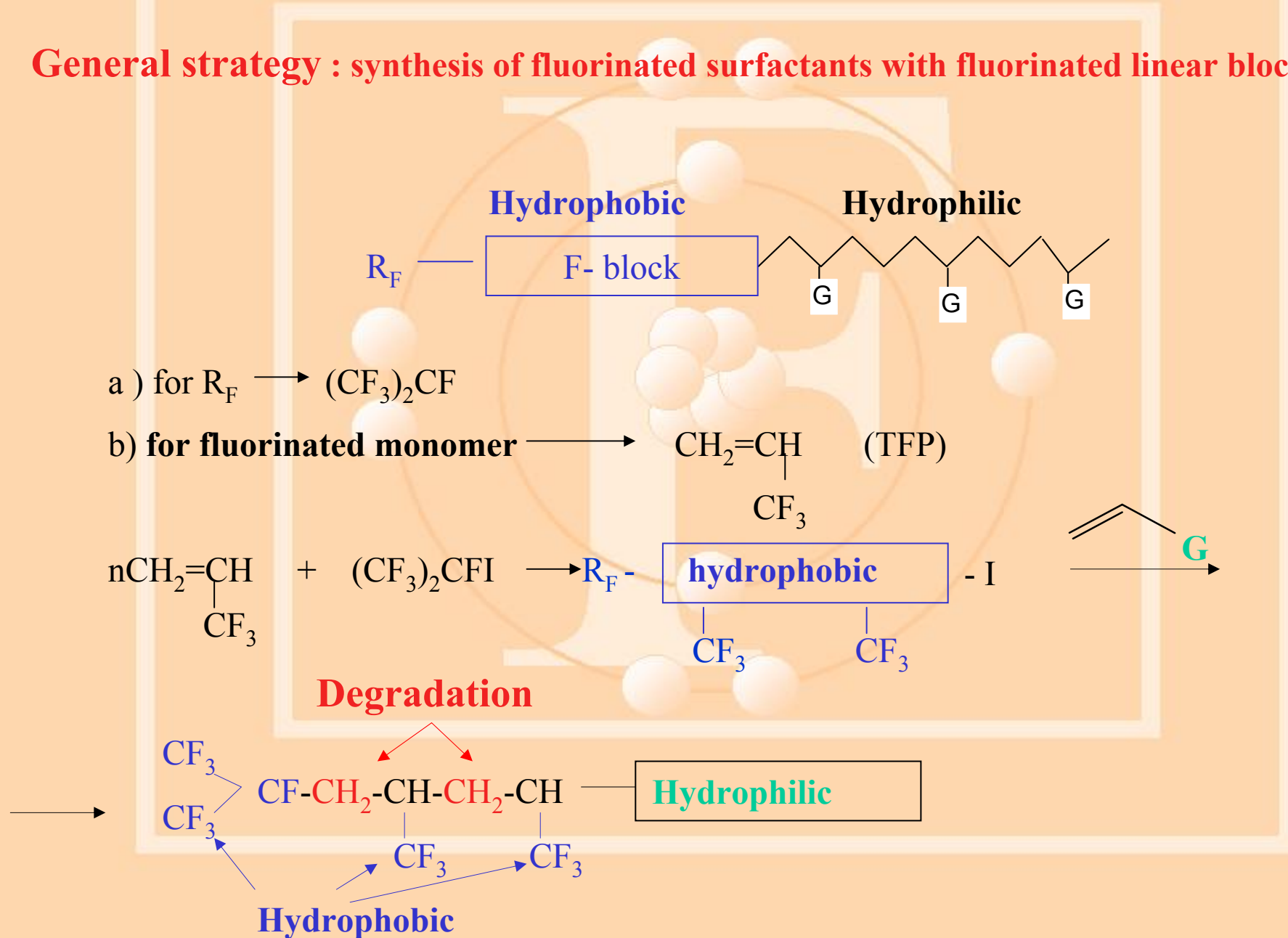
- ☹ **Bioaccumulable**
- ☹ **Toxic and persistent**
- ☹ **Wide-spread in the environment**

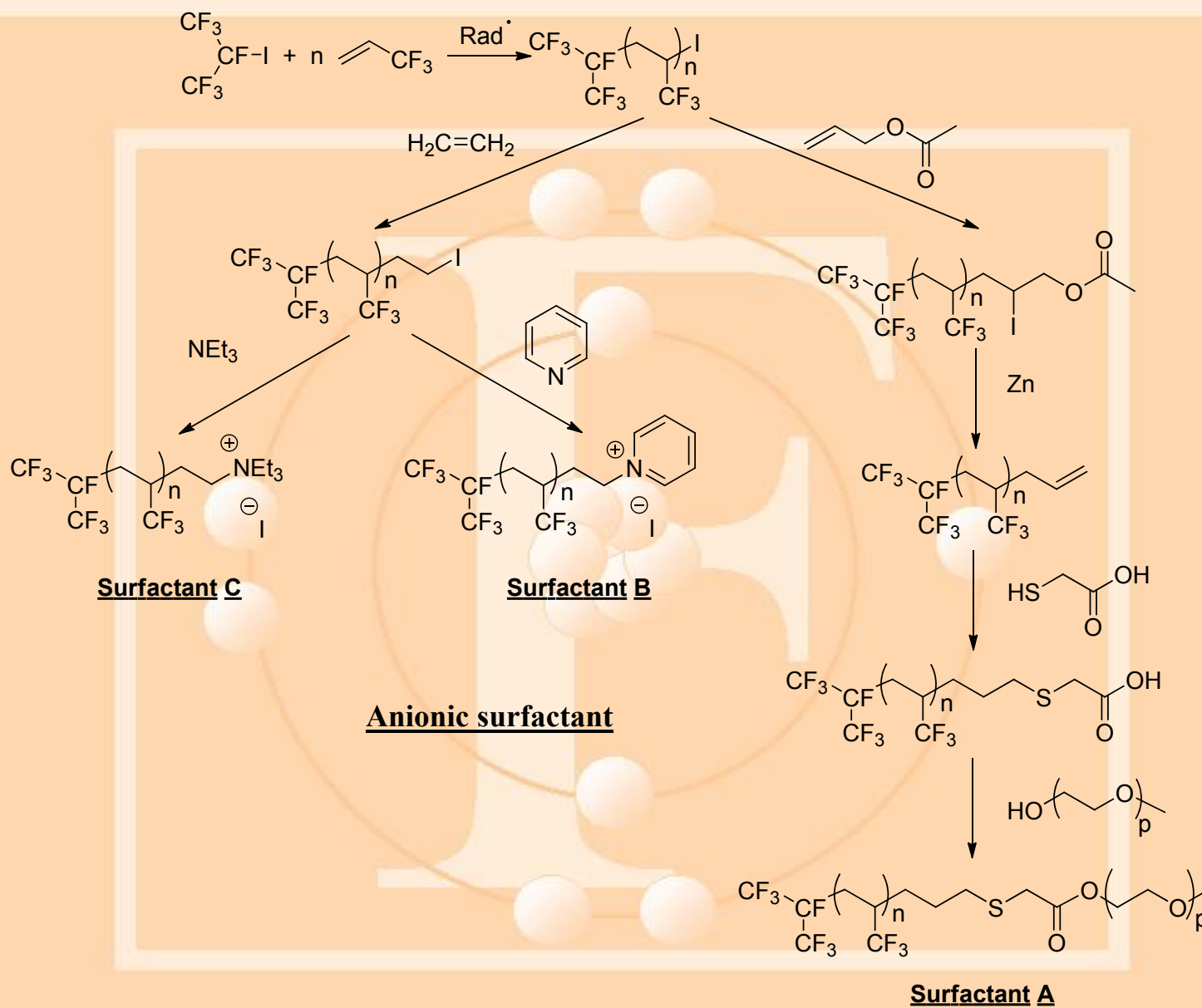
3M company suggested perfluorinated chain $\leq C_4$

- **Low bioconcentration factor**
- **Low toxicity**
- **Still high product performance**

3.3. Synthesis of different end products as fluorinated surfactants

General strategy : synthesis of fluorinated surfactants with fluorinated linear block $C_i \leq 4$





Scheme 1: Straightforward strategies for the preparation of 3,3,3-trifluoropropene-based surfactants

Table 1. Properties of synthesized fluorinated surfactants

Surfactant	Appearance	% Fluoro alkyl	10% decomp. temperature ^a (°C)	Tg and melting point ^b (°C)
$(CF_3)_2CF(TFP)(CH_2)_3SCH_2CO_2(PEO)CH_3$	yellow visc.liq.	24	200	Tg < 0 °C
$(CF_3)_2CF(TFP)CH_2CH_2N^+C_5H_5, I^-$	yellow solid	45	250	145
$(CF_3)_2CF(TFP)CH_2CH_2N^+(CH_3)_3, I^-$	yellow solid	47	230	175

- a) TGA : Thermal Analyst Instrument 51 ; heating rate 10°C/min; temperature range of 30-580°C; air flow of 60 mL/min
- b) DSC : Perkin-Elmer Pyris 1; heating rate 20°C/min.

G. Kostov *et al.* USP 0027349 (2007)

Table 2. Chemical resistance and solubility of synthesized fluorinated surfactants

Surfactant A – $(\text{CF}_3)_2\text{CF}(\text{TFP})(\text{CH}_2)_3\text{SCH}_2\text{CO}_2(\text{PEO})\text{CH}_3$; **Surfactant B** - $(\text{CF}_3)_2\text{CF}(\text{TFP})\text{CH}_2\text{CH}_2\text{N}^+\text{C}_5\text{H}_5\text{I}^-$; **Surfactant C** - $(\text{CF}_3)_2\text{CF}(\text{TFP})\text{CH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3\text{I}^-$.

Conditions		Weight losses (%)		
		Surfactant A	Surfactant B	Surfactant C
<u>(1) Base-acid resistance</u>				
98 % H ₂ SO ₄	25 °C; 7 days	0.0	<1.2	0.0
60% HNO ₃	25 °C; 7 days	-	>40.0	<20
37% HCl	25 °C; 7 days	0.0	>15.0	0.0
40% NaOH	25 °C; 7 days	0.0	0.0	0.0
<u>(2) Solubility in selected solvents</u>		<u>Solubility (g/100mL)</u>		
Water	25°C; 72 hrs	>10	>10	>10
Methanol	25°C; 72 hrs	>10	>10	>10
Diethyl ether	25°C; 72 hrs	<1	<1	<1
Benzene	25°C; 72 hrs	<2	<2	<2
Acetone	25°C; 72 hrs	<10	<10	<10

Conclusions:

The samples remained almost unaffected in 98 % H₂SO₄ and 40 % NaOH but not stable in 60 % HNO₃ at RT
Soluble in H₂O, CH₃OH but not in (C₂H₅)₂O and C₆H₆

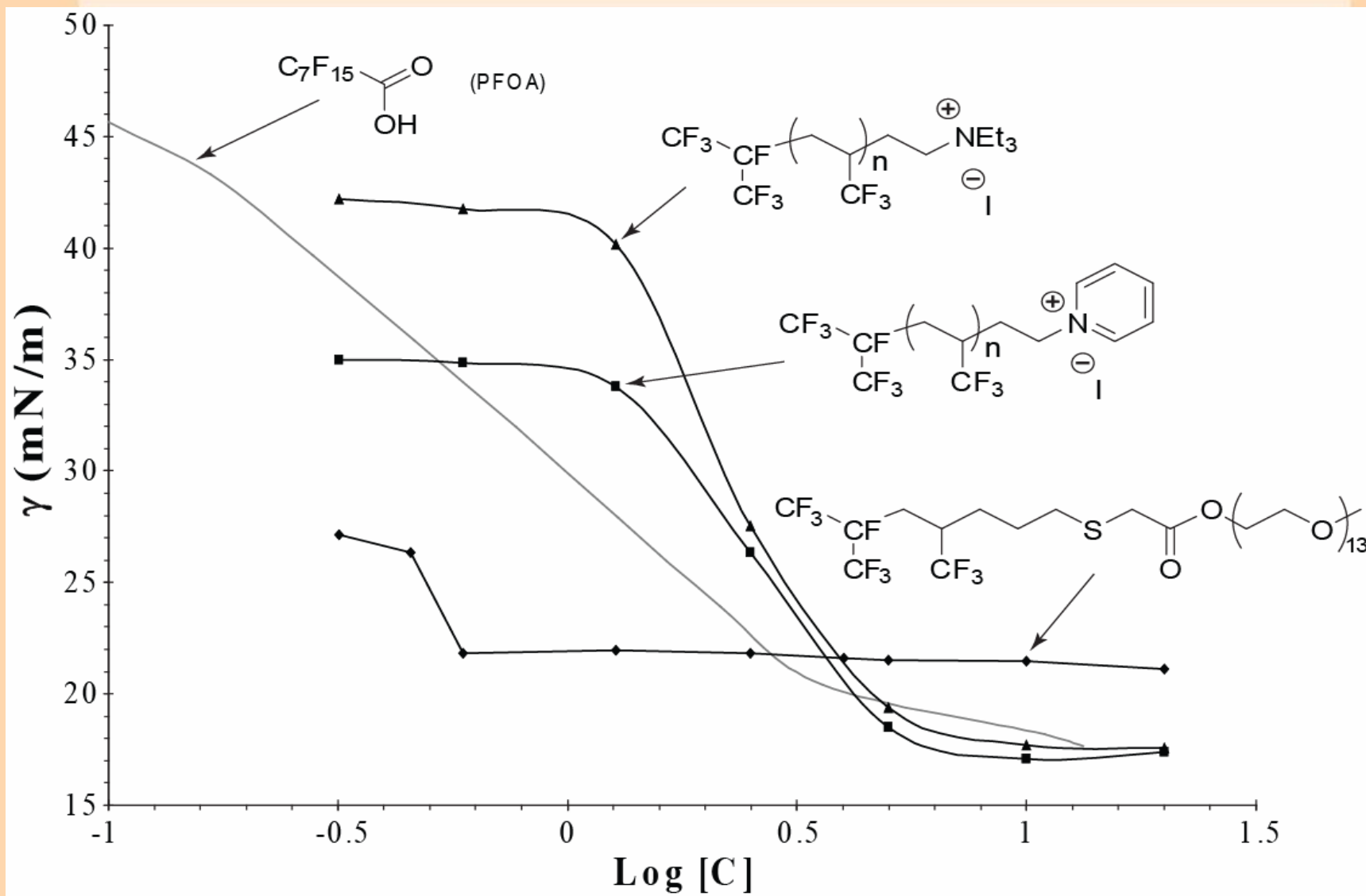
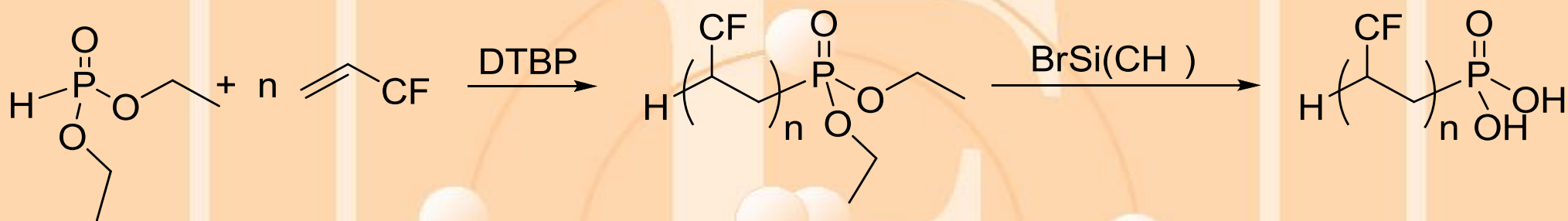


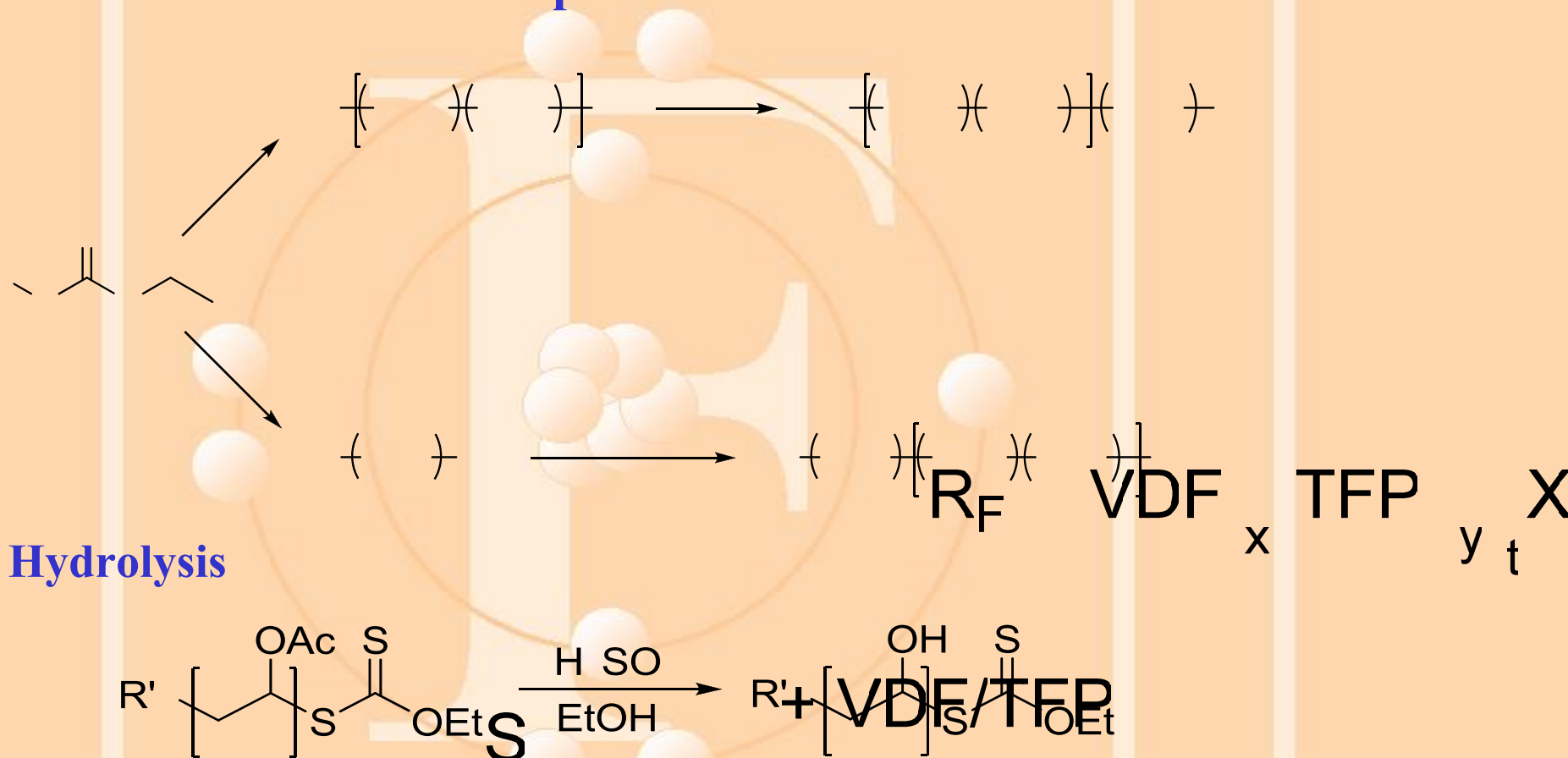
Figure 2: Surface tension versus the concentration of TFP-based surfactants compared to that of PFOA.

3.4. Phosphorous containing TFP surfactants



Scheme 2. Radical telomerization of 3,3,3-trifluoropropene (TFP) with diethyl hydrogenophosphonate followed by hydrolysis.

3. 5. Controlled radical copolymerization of VDF and TFP in the presence of xanthate



Scheme 4. Oligo(VDF-*co*-TFP)-*b*-oligo(VAc) block cooligomers obtained by MADIX technology, and their hydrolysis into fluorinated surfactants (where X_a = SC(S)OEt).

+ VAc

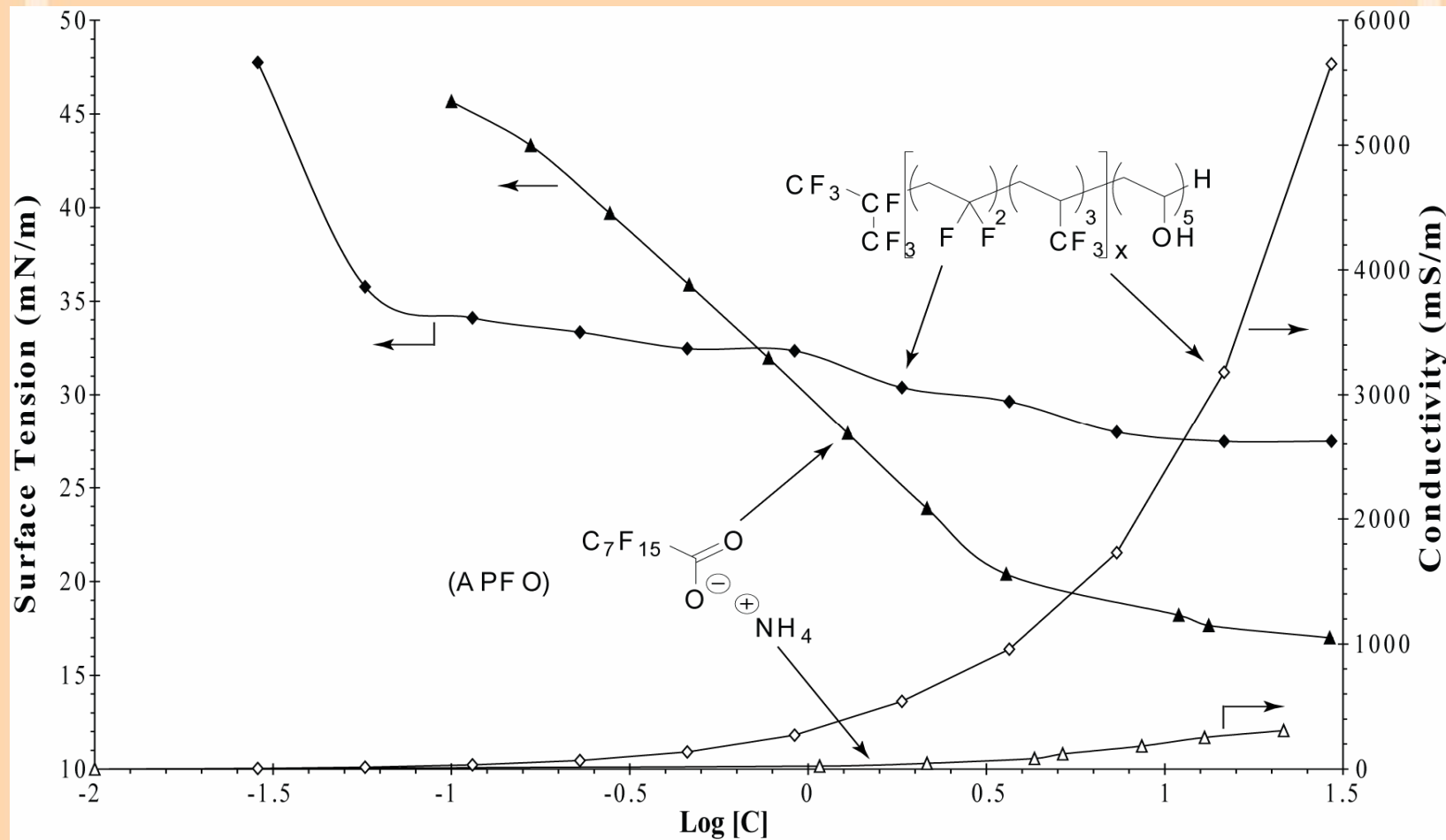


Figure 3. Surface tensions and conductimetries vs. concentration of poly(VDF-co-TFP)-b-oligo(VA) surfactant (black) compared to those of PFOA (white)

CONTENTS



1-Introduction. Objectives

2-Functionalized fluoropolymers for plastic optical fibres

**3-Original fluorinated Surfactants potentially
non-bioaccumulable**

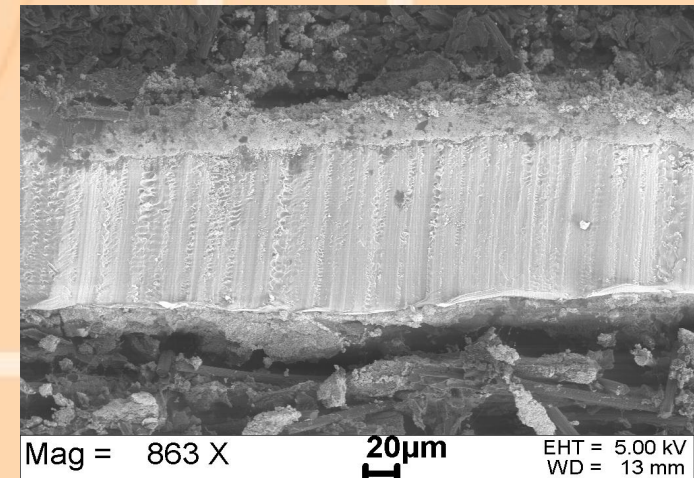
4-Functional fluoropolymers for fuel cell membranes

5-Conclusions and perspectives

4.1. FUEL CELL MEMBRANES

Main characteristics of the membrane

- To separate oxygen from hydrogen
- To insure a good protonic conductivity
- To be chemically, physically and mechanically stable in acid media and at high temperatures
- Reasonable cost/ applications
- No electronic conductivity



4. 2. Fluorinated ionomers for IE membranes

Hydrogenated membranes *versus* fluorinated membranes

Hydrogenated membranes

- ☹ Poor thermostability
- ☹ Low hydrolytic stability
- ☹ Instability to Radiations
- ☹ Non-negligible solubility in used fuels

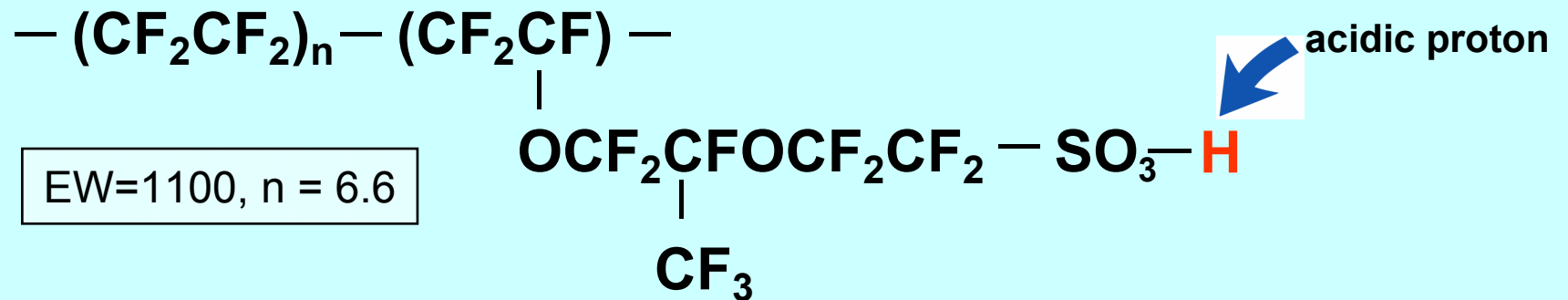
Fluorinated membranes

- ☺ Good thermal stability
- ☺ Stability to hydrolysis and to acids
- ☺ Good durability
- ☺ Properties of super acids ($-\text{CF}_2-\text{SO}_3\text{H}$)
- ☺ Good resistance to oxidation

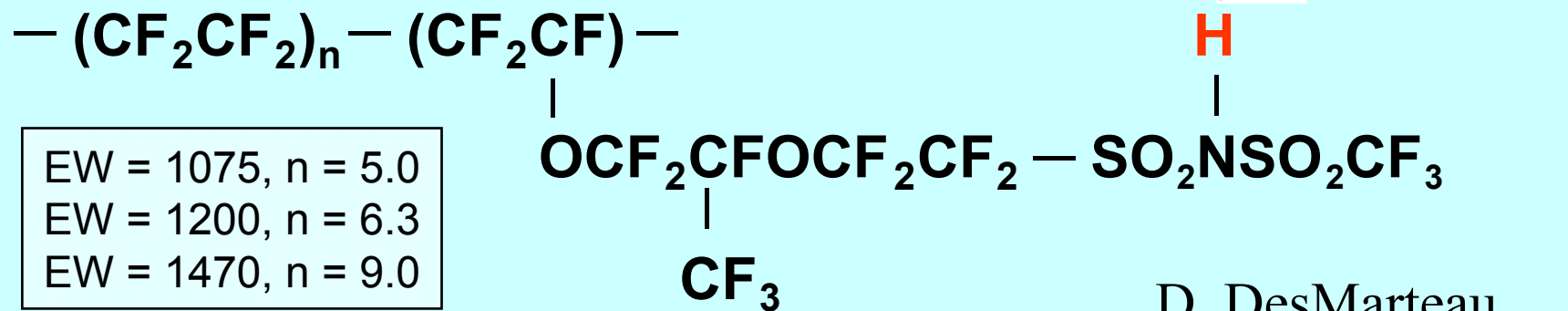
4.2.1. SULFONYLFLUORIDE COPOLYMERS

Perfluorinated ionomers

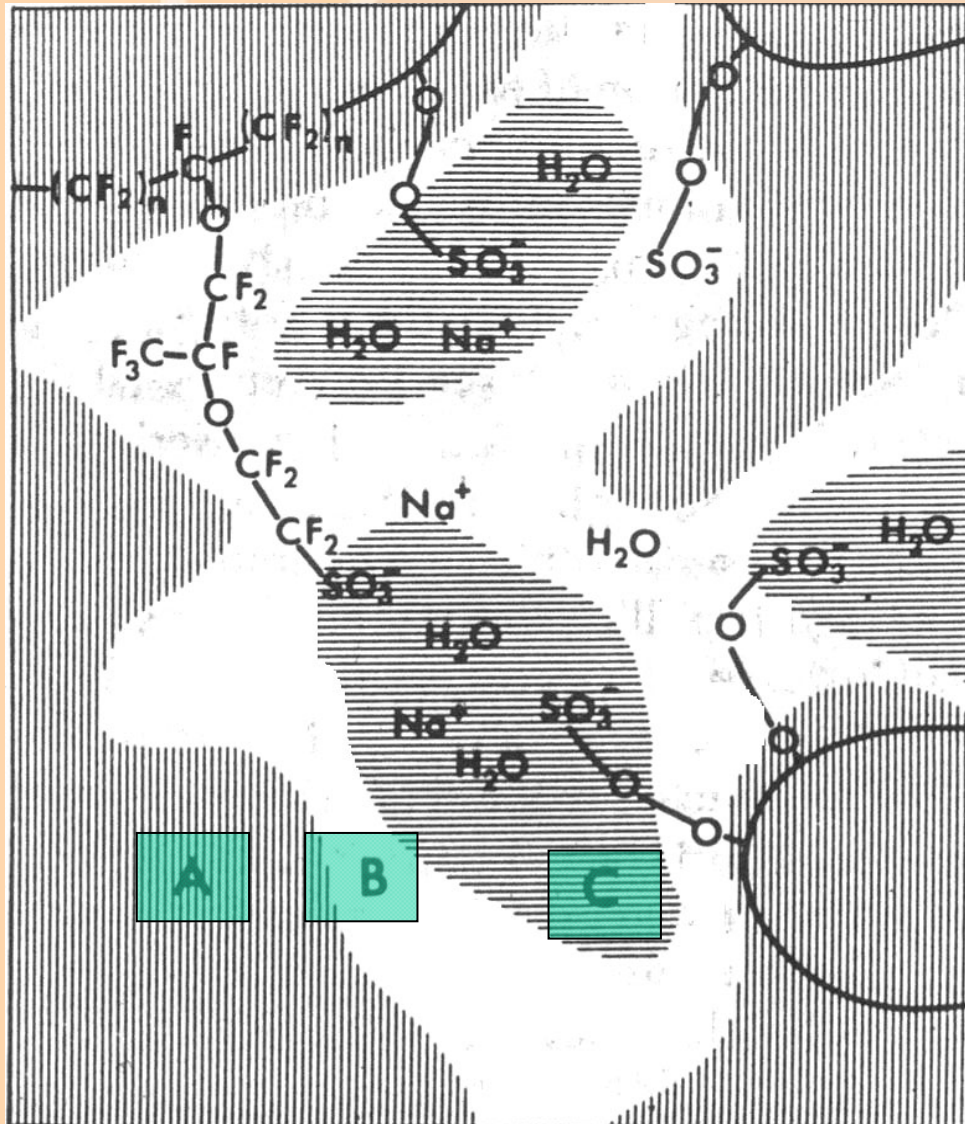
- Commercially available Nafion ionomer (DuPont)



- Clemson-produced sulphonyl imide ionomer



PEM fuel cells — Nafion[®]

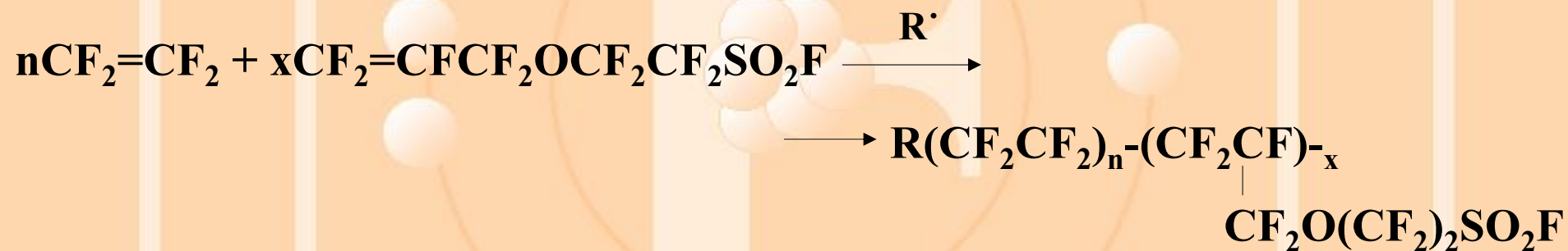


- A - fluorocarbon backbone
- B - interfacial zone
- C - ionic clusters

Yeo and Yeager, *Modern Aspects of Electrochemistry Vol 16*, Plenum Press, New York, 1985, p.437.

4.2.2. OUR SULFOFLUORINATED MEMBRANES

- **Synthesis of sulphonylfluorine co-monomer ($\text{CF}_2=\text{CFCF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$) –**
- **Du Pont technology**
- **Co-polymerization**



$$r_{\text{TFE}} = 10.02 \pm 0.63$$

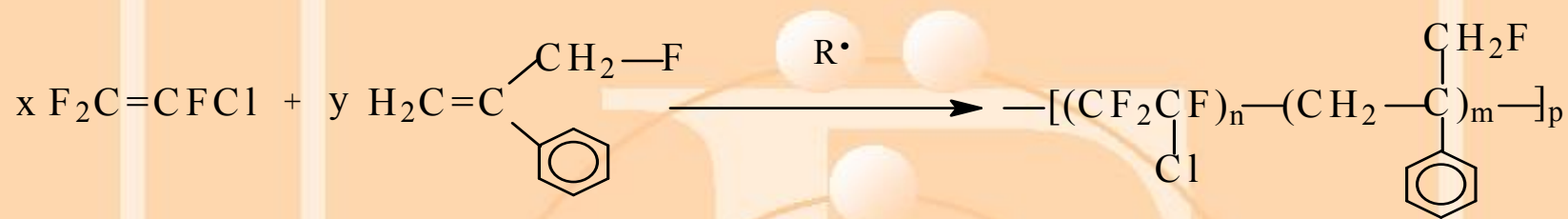
$$r_2 = 0.3 \pm 0.9$$

G. Kostov et al., J. Appl. Polym. Sci., 1993, 47, 735

Table 4.2.3. Copolymerization of TFE with PPOTESF in bulk

Parameters	Samples		
	1	2	3
TFE/PPOTESF mol ration in the feed	2.95	0.77	0.50
(-SO ₂ F) content in the copolymer :			
IEC (meq/g)	0.39	0.72	0.77
m ₂ (mol.%)	4.28	8.63	9.36
Copolymer yield (wt.%)	40.8	34.3	31.3
Melting temperature (°C)	–	282.3	287.3
Thermal stability (°C)	–	314.0	308.0

4.3. CTFE-based copolymers for electrolyte membranes



CTFE

FMS

1-(fluoromethyl)styrene

Synthesis of poly(CTFE-co-FMS) copolymers

SULPHONATION

PEMFC

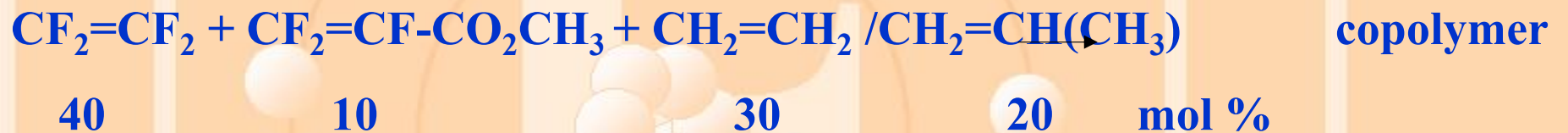


UNIVERSITY OF
OXFORD

Collaboration with Prof. Gouverneur, Oxford Univ.

4.4. CARBOXYL CONTAINING MEMBRANES

- Synthesis of carboxyl comonomer $\text{CF}_2=\text{CF}-\text{CO}_2\text{CH}_3$ (MTFP) –
- Asahi glass technology
- Co-polymerization



A_R , meq/g – 1.2-2.9

R , ohm.cm² – 1.2-1.58

$\alpha_{\text{hydr.}}$, % - 73-99 %

$T_g < 25^\circ\text{C}$

T_d^{OCO} , °C > 360

T_f^{OCO} , °C – 180–190

σ , MPa – 35–40

ε , % - 150–200

Application ; chloro – alkaline electrolysis ; PEMFC

Fuel cell challenges: high temp operation

- **DOE fuel cell cost target of \$30/kW**
 - Incremental advances are not adequate
 - High risk/high payoff basic research coupled with applied programs

“...a sophisticated set of guiding principles that are based on carefully designed and executed experimental and theoretical studies.”

Fuel cell cost

- Catalyst design
- Proton exchange membranes

High temperature operation
Tailored Nanostructures

- High temperature 120-200 °C
 - Eliminate complex water management systems
 - Decrease size of thermal management system
 - Reduction in quantity of Pt required (0.8 mg/cm² → 0.1 mg/cm²)

Drawbacks of sulphonated membranes

MeOH crossover

Cost (\$ 400-500 / m²)

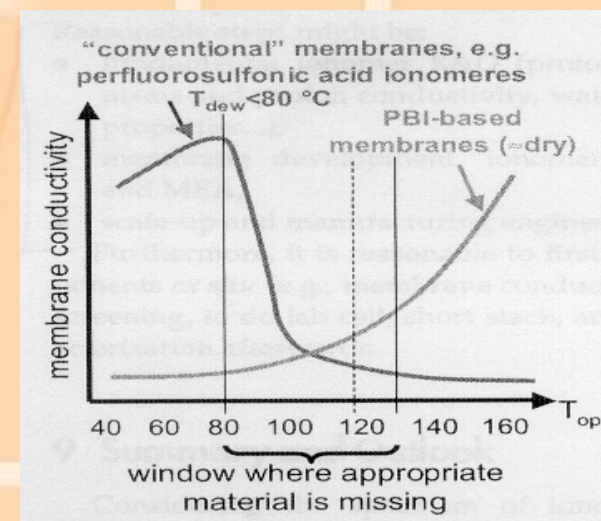
Drying from 80°C including poor performances



Search for intermediate and high temperature membranes

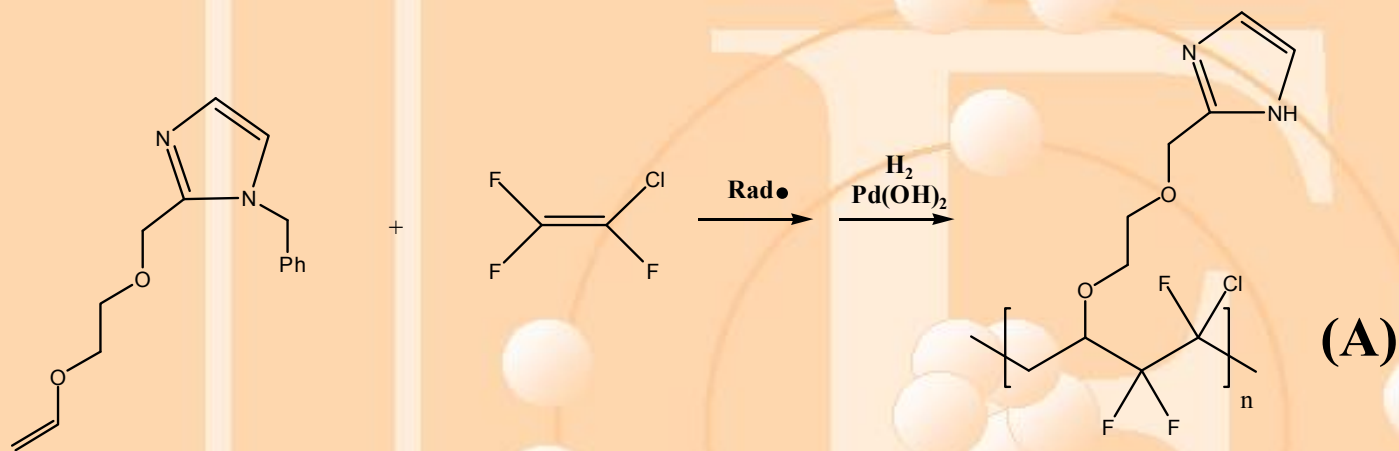
To replace H₂O by immobilized amphoteric solvents

Our choice: nitrogenous heterocycles

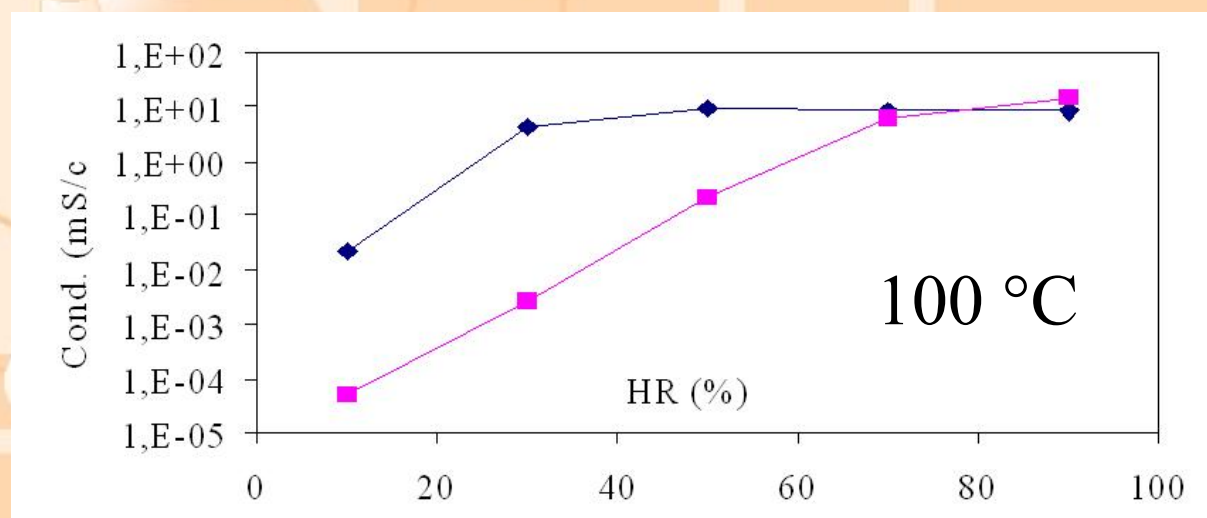


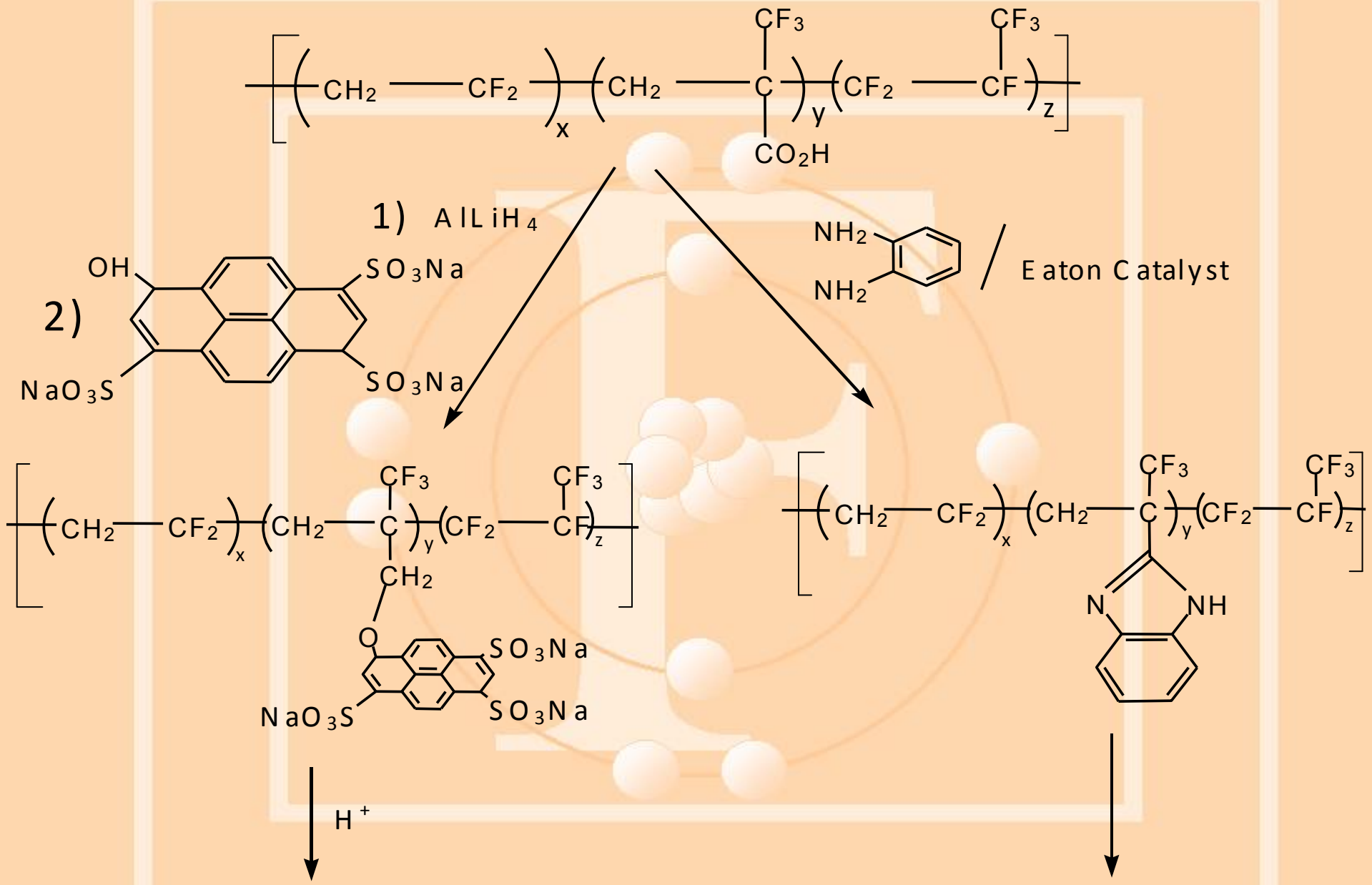
C. Weiser, Fuel Cells, 2004, 4, 245

4.5. Functional fluorinated co-polymers for quasi-anhydrous fuel cell membranes



IEC → 0.8 to 0.4
 Conductivity → ~ 10 mS.cm⁻¹
 (at 100 °C; 30 % RH)





PROTON EXCHANGE MEMBRANES

QUASI-ANHYDROUS MEMBRANES

Remaining challenges

- Find a useful balance between mechanical properties and glass transition temperature.
- Design membranes whose final structure enables proton conductivity suitable for fuel cell start up at 25°C as well as continuous operation at 120-150°C

Membranes combining 2 conduction mechanisms

- Use both water ($T < 100^{\circ}\text{C}$) and heterocyclic network (high $T > 100^{\circ}\text{C}$) as the proton conducting media.

Conclusions and perspectives

- **The new functionalized fluoropolymers are thermally stable up to 300°C with good dual conductivity.**
- **Efficient methods to mechanically stabilize the conductive films have to be developed.**
- **Exploratory experiments combining hydrated and anhydrous conducting domains are promising and will further be developed**

ACKNOWLEDGEMENTS

COMPANIES

Solvay (B)
Atofina (F)
MEFI (F)
Chemtura (USA)
PSA Peugeot Citroën (F)

ACADEMICS

Prof. B. Boutevin (IAM, ENSCM, F)
Dr. Al. Rousseau (INSA de Lyon, F)
Prof. Y. Okamoto (Brooklyn Polytechnic, US)
Dr. B. Ameduri (IAM, ENSCM, F)
Prof. V. Gouverneur (Oxford Univ. GB)



**THANK YOU FOR YOUR
KIND ATTENTION!**