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

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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 Tg
- 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


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 \( T_g \); \( n_D = 1.4-1.5 \); \( T_d > 150°C \)
- Good processability to fibers, films and tapes
  \((M_n=2000-4000 \text{ g/mol})\)
- Photocrosslinkable (preferably acrylic and fluorinated resins)
- Homogenous network with good mechanical properties
Scheme 1: General scheme of fluoroacrylate synthesis

2.6. CTFE/VCA/hydroxy VE copolymers

2.6.1) Fluorooligomers: CTFE/VCA-based copolymers

Length limit of polymer

Chain-transfer agent or suitable solvent

Photocrosslinkable reactive functions

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.

<table>
<thead>
<tr>
<th>CTFE in monom. mixture (mol %)</th>
<th>CTFE\textsuperscript{a} in copolym (mol %)</th>
<th>Yield (wt %)</th>
<th>M\textsubscript{n}\textsuperscript{d} (g.mol\textsuperscript{-1})</th>
<th>PDI\textsuperscript{b}</th>
<th>T\textsubscript{g} (°C)</th>
<th>T\textsubscript{d10} (°C)</th>
<th>N\textsubscript{C-H}/cm\textsuperscript{3} (10\textsuperscript{-3})</th>
<th>n\textsubscript{D} (23°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>60.3</td>
<td>64.0</td>
<td>2800</td>
<td>2.2</td>
<td>70</td>
<td>274</td>
<td>5.4</td>
<td>1.4379</td>
</tr>
<tr>
<td>70</td>
<td>51.8</td>
<td>64.1</td>
<td>2500</td>
<td>2.0</td>
<td>90</td>
<td>295</td>
<td>8.4</td>
<td>1.4358</td>
</tr>
<tr>
<td>60</td>
<td>45.9</td>
<td>65.8</td>
<td>2250</td>
<td>2.5</td>
<td>100</td>
<td>289</td>
<td>11.5</td>
<td>1.4357</td>
</tr>
<tr>
<td>50</td>
<td>39.8</td>
<td>70.6</td>
<td>2000</td>
<td>2.5</td>
<td>110</td>
<td>246</td>
<td>14.8</td>
<td>1.4459</td>
</tr>
<tr>
<td>40</td>
<td>34.6</td>
<td>72.2</td>
<td>1800</td>
<td>2.0</td>
<td>120</td>
<td>254</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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

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

  - $N_{C-H}/cm^3$ ($n_D$ 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**
  - Tg of acrylated CTFE/VCA/HBVE compositions ~90°C
  - E – modulus: 1 GPa at 20°C; 50 MPa at 120°C
  - $T_{air}^{d10} \sim 200–220°C$

- **DSC analysis**
  - Tg of acrylated CTFE/VCA-CH$_2$OH compositions ~100–105°C
  - $T_{air}^{d10} \sim 230–240°C$
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.

Collaboration with Prof. Y. Okamoto and Dr. F. Mikes, Brooklyn Polytechnic, USA.
2.9.2. Co-polymerization of perfluorovinyl dioxolane (F-Ox) with different fluorinated comonomers $M_2$ (CTFE, PPVE, PMVE and VDF)

\[ n \text{F}_2\text{C}═\text{CXY} + m \text{F}_2\text{C}═\text{CF2} \xrightarrow{\text{TBPPi / 75°C}} \text{C}_4\text{F}_5\text{H}_5 \]

$X=Y=\text{H}$ (VDF)
$X=\text{F}, Y=\text{Cl}$ (CTFE)
$X=\text{F}, Y=\text{OCF}_3$ (PMVE)

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

<table>
<thead>
<tr>
<th>Run #</th>
<th>Monomer M2</th>
<th>Monomers in the feed (mol %)</th>
<th>Copolym. comps. by microanal. (mol %)</th>
<th>Copolym. comps. by NMR (mol %)</th>
<th>Conv (wt.%)</th>
<th>Tg (°C)</th>
<th>Td,10 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>F₂C=CFCl</td>
<td>20</td>
<td>35</td>
<td>37.4</td>
<td>63</td>
<td>105</td>
<td>322</td>
</tr>
<tr>
<td>2</td>
<td>F₂C=CFCl</td>
<td>40</td>
<td>62</td>
<td>61.5</td>
<td>70</td>
<td>148</td>
<td>354</td>
</tr>
<tr>
<td>3</td>
<td>F₂C=CFOC₃F₇</td>
<td>64</td>
<td>87.4</td>
<td>85.2</td>
<td>82</td>
<td>144</td>
<td>342</td>
</tr>
<tr>
<td>4</td>
<td>F₂C=CFOCF₃</td>
<td>21</td>
<td>50.7</td>
<td>52.8</td>
<td>74</td>
<td>154</td>
<td>359</td>
</tr>
<tr>
<td>5</td>
<td>F₂C=CH₂</td>
<td>14</td>
<td>38.2</td>
<td>37.8</td>
<td>65</td>
<td>108</td>
<td>370</td>
</tr>
<tr>
<td>6</td>
<td>F₂C=CH₂</td>
<td>35</td>
<td>58.4</td>
<td>57.9</td>
<td>67</td>
<td>138</td>
<td>356</td>
</tr>
</tbody>
</table>

nᵣ < 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 Tg were synthesized.

2. Successful acrylation of hydroxy functionalized cooligomers

3. Photocrosslinking → original cured fluoroacrylated materials of low n_D, high Tg & Td and good mechanical properties

4. Novel functionalized copolymers of CTFE with perfluorinated dioxolanes with excellent optical properties

Suitable for waveguides applications
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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, firefighting foams, pharmaceuticals, etc.

Traditional commercial fluorosurfactants:

Long fluorocarbon chain $C_6<\text{R}_F<C_{12}$ and their derivatives

Perfluorooctane sulphonate (PFOS)

Perfluooctanoic 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 $C_i \leq 4$

a) for $R_F \rightarrow (CF_3)_2CF$

b) for fluorinated monomer $\rightarrow CH_2=CH$ (TFP)

$nCH_2=CH_{CF_3} + (CF_3)_2CFI \rightarrow R_F - hydrophobic - I$

Degradation

Hydrophilic

Hydrophobic
Scheme 1: Straightforward strategies for the preparation of 3,3,3-trifluoropropene-based surfactants
### Table 1. Properties of synthesized fluorinated surfactants

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Appearance</th>
<th>% Fluoro alkyl</th>
<th>10% decomp. temperature ( ^\circ C )</th>
<th>Tg and melting point ( ^\circ C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>((CF_3)_2CF(TFP)(CH_2)_3SCH_2CO_2(PEO)CH_3)</td>
<td>yellow visc. liq.</td>
<td>24</td>
<td>200</td>
<td>Tg &lt; 0 ( ^\circ C )</td>
</tr>
<tr>
<td>((CF_3)_2CF(TFP)CH_2CH_2N^+C_5H_5,I^-)</td>
<td>yellow solid</td>
<td>45</td>
<td>250</td>
<td>145</td>
</tr>
<tr>
<td>((CF_3)_2CF(TFP)CH_2CH_2N^+(CH_3)_2,I^-)</td>
<td>yellow solid</td>
<td>47</td>
<td>230</td>
<td>175</td>
</tr>
</tbody>
</table>

a) TGA: Thermal Analyst Instrument 51; heating rate 10\( ^\circ C \)/min; temperature range of 30-580\( ^\circ C \); air flow of 60 mL/min  

b) DSC: Perkin-Elmer Pyris 1; heating rate 20\( ^\circ C \)/min.

G. Kostov et al. USP 0027349 (2007)
### Table 2. Chemical resistance and solubility of synthesized fluorinated surfactants

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Surfactant A</th>
<th>Surfactant B</th>
<th>Surfactant C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(1) Base-acid resistance</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>98 % H₂SO₄ 25 °C; 7 days</td>
<td>0.0</td>
<td>&lt;1.2</td>
<td>0.0</td>
</tr>
<tr>
<td>60% HNO₃ 25 °C; 7 days</td>
<td>-</td>
<td>&gt;40.0</td>
<td>&lt;20</td>
</tr>
<tr>
<td>37% HCl 25 °C; 7 days</td>
<td>0.0</td>
<td>&gt;15.0</td>
<td>0.0</td>
</tr>
<tr>
<td>40% NaOH 25 °C; 7 days</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td><strong>(2) Solubility in selected solvents</strong></td>
<td>Solubility (g/100mL)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water 25°C; 72 hrs</td>
<td>&gt;10</td>
<td>&gt;10</td>
<td>&gt;10</td>
</tr>
<tr>
<td>Methanol 25°C; 72 hrs</td>
<td>&gt;10</td>
<td>&gt;10</td>
<td>&gt;10</td>
</tr>
<tr>
<td>Diethyl ether 25°C; 72 hrs</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Benzene 25°C; 72 hrs</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Acetone 25°C; 72 hrs</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

**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.

Surfactant A – (CF₃)₂CF(TFP)(CH₂)₃SCH₂CO₂(PEO)CH₃; Surfactant B – (CF₃)₂CF(TFP)CH₂CH₂N⁺C₅H₅I⁻; Surfactant C – (CF₄)₂CF(TFP)CH₂CH₂N⁺(CH₃)₃I⁻.
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 Xa = SC(S)OEt).
Figure 3. Surface tensions and conductivities vs. concentration of poly(VDF-co-TFP)-b-oligo(VA) surfactant (black) compared to those of PFOA (white)
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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

<table>
<thead>
<tr>
<th>Hydrogenated membranes</th>
<th>Fluorinated membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td>☹ Poor thermostability</td>
<td>☺ Good thermostability</td>
</tr>
<tr>
<td>☹ Low hydrolytic stability</td>
<td>☺ Stability to hydrolysis and to acids</td>
</tr>
<tr>
<td>☹ Instability to Radiations</td>
<td>☺ Good durability</td>
</tr>
<tr>
<td>☹ Non-negligible solubility in used fuels</td>
<td>☺ Properties of super acide (-CF₂-SO₃H)</td>
</tr>
<tr>
<td></td>
<td>☺ Good resistance to oxidation</td>
</tr>
</tbody>
</table>
4.2.1. SULFONYLFLUORIDE COPOLYMERS

Perfluorinated ionomers

- Commercially available Nafion ionomer (DuPont)

\[ - (C_2F_4C_2F_2)_n - (C_2F_2C_2F) - \]
\[ \text{OCF}_2\text{CFOCF}_2\text{CF}_2 - \text{SO}_3^- \text{H} \]

EW = 1100, n = 6.6

- Clemson-produced sulphonyl imide ionomer

\[ - (C_2F_4C_2F_2)_n - (C_2F_2C_2F) - \]
\[ \text{OCF}_2\text{CFOCF}_2\text{CF}_2 - \text{SO}_2\text{NSO}_2\text{CF}_3 \]

EW = 1075, n = 5.0
EW = 1200, n = 6.3
EW = 1470, n = 9.0

D. DesMarteau
PEM fuel cells — Nafion®

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

4.2.2. OUR SULFOFLUORINATED MEMBRANES

• Synthesis of sulphonylfluorine co-monomer (CF₂=CFCF₂OCF₂CF₂SO₂F) –
• Du Pont technology
• Co-polymerization

\[ n\text{CF}_2=\text{CF}_2 + x\text{CF}_2=\text{CFCF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F} \rightarrow R(\text{CF}_2\text{CF}_2)_n-(\text{CF}_2\text{CF})_x\text{CF}_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F} \]

\[ r_{\text{TFE}} = 10.02 \pm 0.63 \]
\[ r_2 = 0.3 \pm 0.9 \]

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>TFE/PPOTESF mol ration in the feed</td>
<td>2.95</td>
</tr>
<tr>
<td>(-SO₂F) content in the copolymer :</td>
<td></td>
</tr>
<tr>
<td>IEC (meq/g)</td>
<td>0.39</td>
</tr>
<tr>
<td>m₂ (mol.%)</td>
<td>4.28</td>
</tr>
<tr>
<td>Copolymer yield (wt.%)</td>
<td>40.8</td>
</tr>
<tr>
<td>Melting temperature (°C)</td>
<td>–</td>
</tr>
<tr>
<td>Thermal stability (°C)</td>
<td>–</td>
</tr>
</tbody>
</table>
4.3. CTFE-based copolymers for electrolyte membranes

Synthesis of poly(CTFE-co-FMS) copolymers

SULPHONATION

PEMFC

Collaboration with Prof. Gouverneur, Oxford Univ.
4.4. CARBOXYL CONTAINING MEMBRANES

• Synthesis of carboxyl comonomer CF$_2$=CF-CO$_2$CH$_3$ (MTFP) –

• Asahi glass technology

• Co-polymerization

CF$_2$=CF$_2$ + CF$_2$=CF-CO$_2$CH$_3$ + CH$_2$=CH$_2$ /CH$_2$=CH(CH$_3$) copolymer

| mol % | 40 | 10 | 30 | 20 |

AR, meq/g – 1.2-2.9
R, ohm.cm$^2$ – 1.2-1.58
$\alpha_{hydr.}$, % - 73-99 %
T$_g$ < 25$^\circ$C

$T_d^{OCO}$, $^\circ$C > 360
$T_f^{OCO}$, $^\circ$C – 180–190
$\sigma$, MPa – 35–40
$\varepsilon$, % - 150–200

Application; chloro – alkaline electrolysis; PEMFC

J. Membrane Sci., 1992, 68, 133
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.”

Li et al., Chem. Mater. 2003, 15, 4896-4915

DOE Basic Energy Sciences Workshop on Hydrogen, Storage, Production, and Use
http://www.sc.doe.gov/bes/reports/files/NHE_rpt.pdf
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)

Industrial Partner: PSA Peugeot-Citroën 2006–2009
PROTON EXCHANGE MEMBRANES

1) Al Li H₄

2) OH SO₃Na

Eaton Catalyst

H⁺

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 25ºC as well as continuous operation at 120-150ºC
Membranes combining 2 conduction mechanisms

- Use both water ($T < 100^\circ C$) and heterocyclic network (high $T > 100^\circ C$) 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

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MEFI (F)
Chemtura (USA)
PSA Peugeot Citroën (F)

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Dr. B. Ameduri (IAM, ENSCM, F)
Prof. V. Gouverneur (Oxford Univ. GB)
THANK YOU FOR YOUR KIND ATTENTION!