RECENT ADVANCES OF FUNCTIONAL FLUORINE-CONTAINING COPOLYMERS: SYNTHESIS, PROPERTIES AND APPLICATIONS

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ABSTRACT

Selected aspects of our research on the synthesis, properties and applications of functionalized fluoropolymers in different areas will be presented.

Novel fluorinated copolymers for optical fibres and waveguides. We have investigated new thermoplastic fluoroacrylated copolymers, synthesized by radical copolymerization of fluoroalkene(s) with five-membered cyclic carbonate and a third monomer or transfer agent. The reaction of hydroxy functionalized copolymers with different acrylating agents results in fluoroacrylated resins with good solubility in reactive diluents. In the presence of photoinitiator(s), they were crosslinked under UV-radiation in order to obtain optical waveguides. The synthesis of original perfluorovinyl dioxolane and its radical copolymerization with different fluorinated alkenes, such as vinylidene fluoride (VDF), perfluoromethyl and perfluoropropyl vinyl ethers and chlorotrifluorethylene (CTFE) are presented. The thermal properties (Tg > 130 °C and Td > 300 °C), refractive indexes (n_D < 1.35) could determine their application as good candidates for optical waveguides materials.

Fluoropolymers for non-bioaccumulable surfactants Original fluorinated surfactants based on 3,3,3-trifluoropropene (TFP) as alternatives to perfluorooctanoic acid (PFOA) were synthesized straightforward in three to five steps in good overall yields. All surfactants showed good inertness to bases and acids, and satisfactory surface properties. The synthesis of poly(vinylidene fluoride-co-3,3,3-trifluoropropene)-b-oligo(vinyl alcohol) block copolymers by sequential controlled radical copolymerization of these fluoroalkenes in the presence of xanthate, and their use as original surfactants are presented. The hydrolysis of poly(VAc) sequences into oligo(vinyl alcohol) led to original water soluble surfactants, the surface tension of which was comparable to that of perfluorooctanoic acid.

Novel poly(VDF-co-PMVA) diacrylate copolymers for micro fluid devices. The synthesis of poly(VDF-co-perfluoromethyl vinyl ether (PMVE) based diacrylates is described. Two major approaches are applied to obtain poly(VDF-co-PMVE) based diols as a precursors for acrylates. Acrylation of diols is reported using various acrylating agents. UV curing of C2 and C3 acrylates is reported. The potential application as micro fluid device was discussed.

Functionalized fluoropolymers for fuel cell membrances. Vinylidene fluoride based copolymers were synthesized by iodine transfer controlled radical polymerization with hexafluoropropene (HFP) and α-trifluoromethacrylic acid (TFMA). The terpolymers were functionalized by chemical modification with heterocyclic benzimidazoles using Eaton's catalyst or with aromatic sulphoacides by Mitsunobu reaction. The main properties of the membranes synthesized were also investigated.

Fluoropolymers for nanocomposite materials. Poly(VDF-*ter*-TFMA-*ter* HFP) copolymers were applied to the preparation of the corresponding fluorinated polymers/silica nanocomposites by the sol-gel reactions with tetraethoxysilane and silica nanoparticles under alkaline and acidic conditions, respectively. Interestingly, poly(VDF-*ter*-TFMA-*ter*-HFP) copolymers/silica nanocomposites, which were prepared under alkaline conditions, were found to exhibit no weight loss behavior even after calcination at 800 °C.

Key words: *functionalized fluorinated copolymers, synthesis, properties, optical waveguides, surfactants, fuel cells membranes, fluoroelastomers, nanocomposites.*

Introduction

Fluorinated functional polymers [1-2] exhibit remarkable properties (thermal and oxidative stabilities, chemical inertness, low refractive index, good surface properties, etc) that enable them to find numerous applications in high tech fields: aerospace, energy, automotive industries, optics, microelectronics, and engineering.

Novel fluorinated copolymers for optical fibres and waveguide[3]. Our objectives in this work were to synthesize copolymers containing fluorinated and five-membered cyclic monomers, including a third monomer or transfer agent, both containing OH groups susceptible to be used for grafting of acrylic monomers. In the presence of reactive diluents and photoinitiator these fluoroacrylated resins can be photocrosslinked under UV-radiation in order to obtain materials for optical waveguides. The main characteristics and properties of these materials were also studied. In the other case, cyclic perfluorinated comonomers with commercialized flioroolefins were used to obtain novel amorphous copolymers with excellent properties for optical waveguides.

Fluoropolymers for non-bioaccumulable surfactants. Fluorosurfactants are involved in more than 200 applications including detergents, firefighting foams, coatings, cosmetics, emulsifiers, adhesives, electroplating, antifogging, and antistatic agents [4] However, recent studies directed by the U.S. Environmental Protection Agency (EPA) [5] showed that these surfactants are bioaccumulable [4,6-7] (due to the too stable perfluorinated chain), toxic, and persistent,[8-9] and that decreasing their production by as much as 95% was scheduled by the end of 2010, followed by definitive stop of their production by 2015. The purpose of this report is to show that it is possible to obtain cationic, anionic and non-ionic surfactants by simple and efficient modifications of fluorinated telomers obtained by iodine transfer polymerization. The concept is illustrated using the telomerization of 3,3,3-trifluoropropene and their modifications in 2-4 steps to obtain the various types of surfactants.

Novel poly(VDF-co-PMVA) diacrylate copolymers for micro fluid devices. In contrast with perfluorinated compounds, hydrofluorinated molecules can be degraded by first, elimination of HF, yielding a double bond that can be oxidized and cleaved[10]. This degradation can be advantageously achieved by the methylene and methyne group brought by each TFP unit. The hydrophilic counterpart can be brought by a polar group or, even better, by a polar block. Recently DeSimone et al. showed the possible application of crosslinked perfluoropolyethers (PFPEs) networks as a replacement of poly(dimethylsiloxane) (PDMS) in microfluidic devices [10]. Such PFPEs networks are based on UV-curing of PFPEs bearing methacrylic moiety, which is accessible from corresponding α,ω-diols and 2-isocyanoethyl methacrylate[10-11]. That is why we have focused our attention to fluorinated α,ω-diols and fluorinated (di)acrylates for microfluid devices.

Functionalized fluoropolymers for fuel cell membrances The objective of this presentation deals with the syntheses of new generations of original membranes prepared from aromatic and aliphatic fluorinated copolymers incorporating fluoromonomers such as vinylidene fluoride, hexafluoropropene, and an aromatic fluorinated monomer functionalized by a sulfonic acid, or α-trifluoromethacrylic acid.

Fluoropolymers for nanocomposite materials. Iodine transfer polymerization (ITP) has been chosen since this is a suitable technique able to control the polymerization of fluorinated olefins. However few fluoropolymer/nanofilelrs blends composites have been produced and recently Sawada's group has been able to encapsulate (or to blend diamonds or silica with Rf-(AA)Rf triblock cooligomers). No similar work involving copolymers based on vinylidene fluoride has already been acheievd. Hence, the objectives of our research concern the preparation of stable nanocomposite from mixing nano silica with poly(VDF-*ter*-TFMA-*ter*-HFP) copolymers.

2. EXPERIMENTAL

2.1. Materials

Chlorotrifluoroethylene, C_2F_3Cl, CTFE (98%) and hexafluoropropene, C_3F_6, HFP (98%) were kindly supplied from Atofina. 1,3-dioxol-2-one, vinylene carbonate, VCA (98%) of BASF was distilled before use. The initiators used were tert-butyl peroxypivalate, (Luperox 11M75) and bis(4-tert-butylcyclohexyl) peroxydicarbonate (Perkadox 16S). 1,4-butanediol vinyl ether, $CH_2=CH-O(CH_2)_4OH$ (HBVE) and ethylene glycol vinyl ether, $CH_2=CH-O(CH_2)_2OH$ (EGVE) were used after distillation. Acrylating agents used acryloyl chloride, $CH_2=CHCOCl$, methacrylolyl chloride, $CH_2=C(CH_3)COCl$, acrylic acid, $CH_2=CHCO_2H$, methacrylic anhydride, $[CH_2=C(CH_3)CO]_2O$, were also distilled. 3,3,3-Trifluoropropene ($CH_2=CH-CF_3$, TFP) and 2-iodoperfluoropropane ((CF_3)$_2$CF-I), and perfluorooctanoic acid (C_7F_{15}-COOH, PFOA) were kindly supplied by Great Lakes Chemical Corporation, now Chemtura (West Lafayette, USA). All other chemicals were used as received from the suppliers

2.2. Reaction procedures

2.2.1. Polymerization

The copolymerization of fluoroolefins with comonomers (from 0/100 to 100/0 mol %) was carried out in autoclave-inox of 300 and 500 cm^3 at 80 ± 3°C during 4 -8 hrs. Perkadox 16S or Luperox 11M75 (preferably) from 0.1 to 5.5 mol % vs. monomers (ΣM) were used as initiators; Different solvents were employed depending on the monomers used. Both batch and semi-flow (preferably) operations of the copolymerization were used.

2.3. Measurements

FT-IR spectra were recorded on a Nicolet Nexus FTIR spectrometer with an accuracy of band of ± 2 cm^{-1}. ^1H, ^{13}C NMR spectra were recorded respectively on BRUKER AC 200, 400 and WP 250 spectrometers with TMS as the reference for proton. ^{19}F NMR spectra were recorded on BRUKER AC 200 with CFCl$_3$ as the reference. All spectra were measured in acetone d$_6$ solutions and the chemical shifts (δ) are given in ppm.

The microanalysis (C, H and O) of copolymer synthesized were measured in the Laboratoire de Mesures Physiques, CNRS, Université Montpellier II, France.

The surface tension of the various surfactants was measured at different concentrations to assess the critical micellar concentration (CMC) of the surfactant in water at 25 °C. The surface tension was determined with a Spectra-Physics Tensiometer DCAT21 using the Wihlemy platemethod.

Differential scanning calorimetry analyses, DSC, were performed under nitrogen with a Perkin Elmer Pyris 1 DSC apparatus, calibrated with indium. All the samples were heated from 50°C to 200°C or/and from –130°C to 80°C (calibration with n-octane and octadecane) at 20°C/min; Dynamical mechanical analysis (DMA) was performed with a Perkin Elmer DMA 7 calibrated with hexane and indium. All samples were run at 5°C.min^{-1} and 1 Hz from –130°C to 250°C. Thermogravimetric analyses, TGA, were performed on a TGA 51 Instruments Thermal Analyst 2000 apparatus at a heating rate of 10°C/min from 30 to 700°C. Size Exclusion Chromatography, SEC, was performed on a spectra Physics apparatus with two PL gel columns (5 μm particles size, 300 mm length, one with 50 Å and one with 100 Å pores size) and one Styragel HR2 column (7.8 mm internal diameter x 300 mm length). The detection was achieved with a SP8430 differential refractometer. The eluent was THF and the flow rate was 0.8 ml/min. Refractive indices were obtained from 1.6 mm thick samples using an Abbe refractometer.

3. RESULTS AND DISCUSSIONS

3.1 Strategy of synthesis of optical polymers

The copolymers for optical applications require optical transparency which means to be amorphous as the crystallinity increases the loss of light through scattering. They have to be

thermally stable over 85°C with a high Tg (Tg > 100°C), colourless and transparent in the visible and NIR regions. Furthermore, they have to be photocrosslinkable, preferably acrylic and fluorinated resins with refractive index 1.4-1.5 and gradient index stability up to 130-150°C. To obtain compositions with good processability to fibers or films, the molecular weight of copolymers synthesized have to be in the range of 2000-3000 g/mol, i.e. in the range of oligomers. The end optical materials with crosslinked structure have to be also amorphous, homogeneous with good mechanical properties.

Hence, the general scheme of the synthesis of such type of fluoroacrylated oligomers can be written as follows :
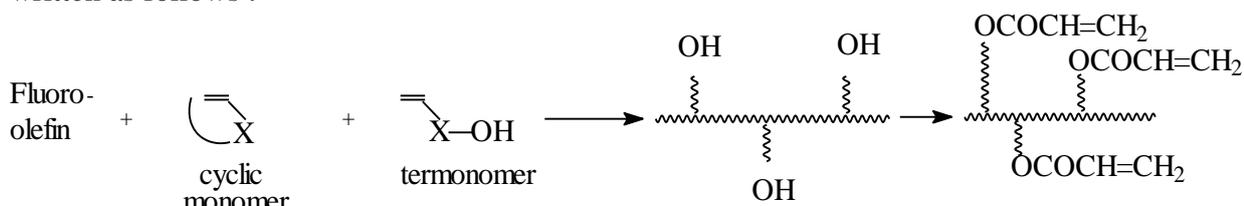

Scheme 1. General scheme of fluoroacrylate synthesis

Binary CTFE/VCA and ternary CTFE/VCA/Hydroxy vinyl ether (VE up to 20 mol %) copolymers were synthesized by radical copolymerization with a good yield (> 50 wt %), molecular weight in the range of 2 500 g/mol and Tg > 80°C. The alcohol function of vinyl ether monomers has to be protected before and deprotected after polymerization. Silylation is a suitable reaction for this purpose. Incorporation of fluorine atoms in the chemical structure of oligomers enhances the thermostability and reduces both the optical losses (decreasing of N_{C-H}/cm^3) and the water absorption. CH_3OH ($R_o = [MeOH]_o / [\Sigma M]_o > 1$) can be used as an effective transfer agent to reduce the molecular weight and to functionalize the basic CTFE/VCA oligomer with OH - terminal groups. Acrylation of –OH functionalized CTFE/VCA binary and hydroxy VE ternary oligomers with different acrylating agents (preferably acryloyl and methacryloyl chlorides) was successfully carried out. The acrylated fluorooligomers have good solubility in polar and halogenated solvents, methanol and mono- and bifunctional acrylated diluents but lower Tgs.

Compositions of fluoroacrylated resins with reactive diluents and photoinitiator were prepared and found to have good homogeneity, transparency and low refractive indeces, suitable for processing of films, fibers and rods. These formulations can be readily cured under UV-radiation to obtain solid amorphous, transparent materials with good thermal and mechanical properties, high Tg (> 100°C), suitable for optical waveguides applications [3].

3.2. Fluoropolymers for non-bioaccumulable surfactants

The overall paths for the syntheses of these surfactants is described in Scheme 1. From the radical telomerization of 3,3,3-trifluoropropene (TFP), several surfactants can be obtained (anionic, cationic and non-ionic) in satisfactory yields (50 % overall yields from i-C_3F_7I). The initial step is the telomerization of 3,3,3-trifluoropropene (TFP) in the presence of perfluoroalkyl iodides (($CF_3)_2CFI$) that was reported in patents assigned to Great Lakes [12-13] and by Kostov et al [14]. The telomerization in bulk as that initiated by organic peroxides such as di*tert*-butylperoxide led to TFP telomers in high yields (>80 %). The degree of polymerization (DP_n = n in ($CF_3)_2CF$-(TFP)$_n$-I) could be tuned by the initial molar ratio [TFP]$_0$/[(($CF_3)_2CFI]_0$). The nucleophilic substitution of R_F-(TFP)$_x$-CH_2-CH_2-I by either triethylamine (NEt_3) or pyridine (C_5H_5N) at room temperature or at 40°C, respectively, led to cationic surfactants bearing ammonium groups (Scheme 1) in satisfactory yield (> 75 %) with a slight dehydroiodination. These mild experimental conditions avoid any dehydroiodination
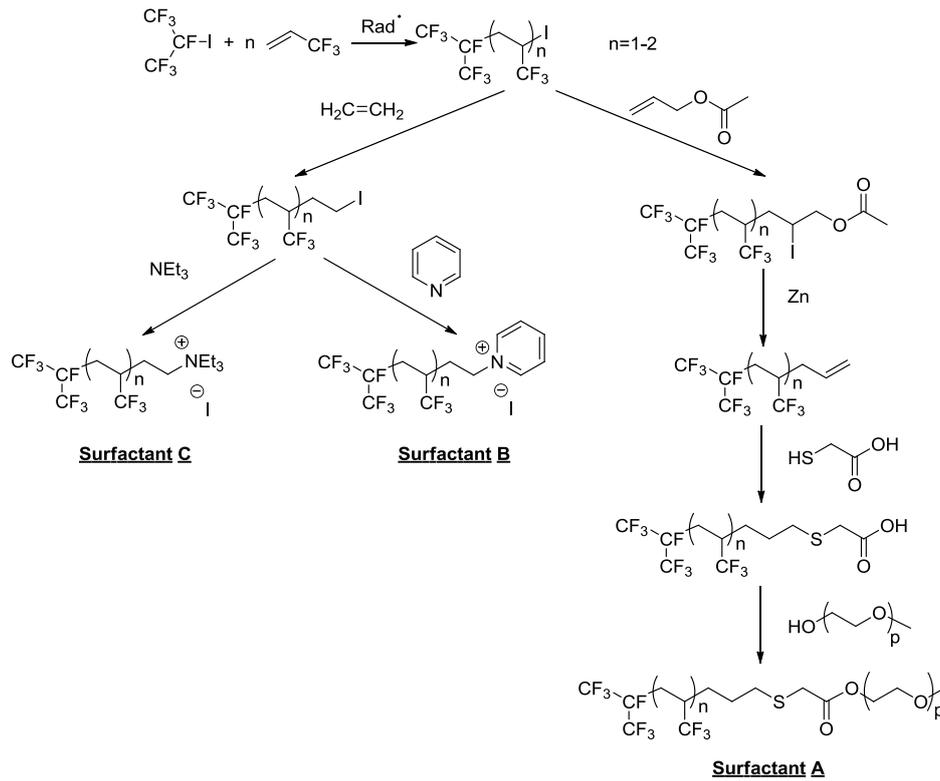
Scheme 1: Straightforward strategies for the preparation of 3,3,3-trifluoropropene-based cationic and non-ionic surfactants
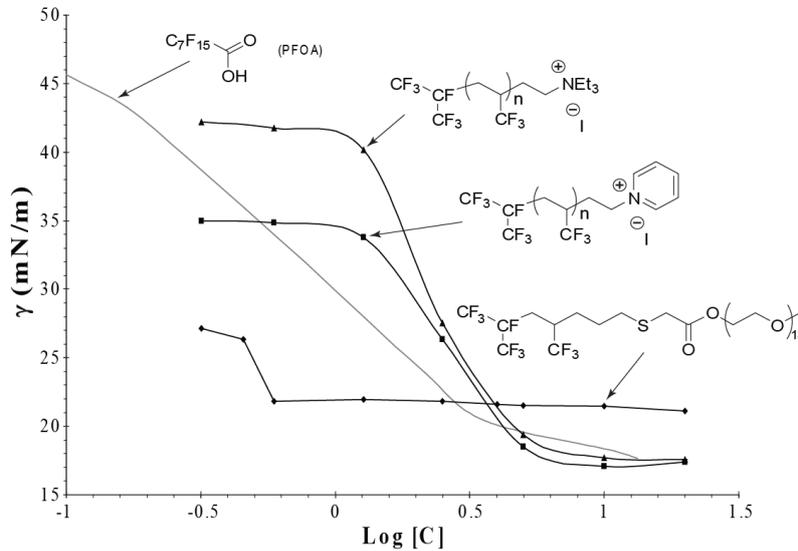

Figure 1: Surface tension versus the concentration of TFP-based surfactants compared to that of PFOA.

Surface tensions of the various surfactants were assessed at different concentrations to determine the critical micellar concentration (CMC) of the surfactants in water at 25 °C. The results are displayed in Figure 1, and the CMC values were found to be 0.06, 4.1, 3.2, and 3.0 g.L^{-1} for surfactants A, B, C, and PFOA, respectively. It can be seen that both cationic surfactants (B, C) behave like PFOA while the non ionic surfactant (A) has a higher surface tension but a lower CMC[15] Only very few xanthates bearing a fluorinated R$_F$ leaving group, have been synthesized yet[16]. A new fluorinated xanthate has been prepared for further use as chain transfer agent to

control the radical copolymerization of TFP and VDF. This process, named macromolecular design via interchange of xanthate (MADIX) is also a successful means for the controlled radical copolymerization of vinyl acetate (VAc)[17-18]. Hence, a second block of poly(VAc) was inserted. In the final step, the poly(VAc) block of the copolymer was transformed into poly(vinyl alcohol) via acid hydrolysis to achieve a poly(VDF-*co*-TFP)-*b*-poly(VAc)-Xa amphiphilic block copolymer. The reverse path was investigated as well leading to poly(VAc)-*b*-poly(VDF-*co*-TFP)-Xa diblock copolymer. Both strategies are summarized in Scheme 3[19-20]:
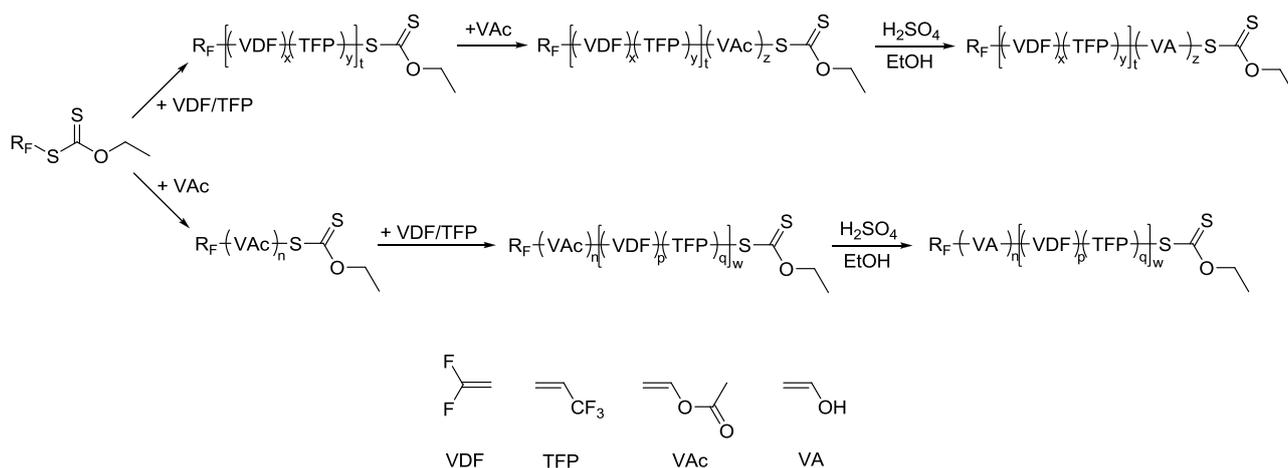
Scheme 3. Strategies for the preparation of amphiphilic block copolymers.

### 3.3. Novel poly(VDF-co-PMVA) diacrylate copolymers for micro fluid devices

Original networks based on poly(VDF-co-PMVE) copolymers were achieved from the UV activated photopolymerization of telechelic diacrylates, containing either two carbon atoms (diacrylate C2) or three carbon atoms (diacrylate C3) as a spacer between the ester group and the poly(VDF-co-PMVE) polymer chain. Scheme 4 shows two synthetic pathways towards crosslinked networks of above mentioned diacrylates. Telechelic diiodo poly(VDF-co-PMVE)copolymer was successfully ethylene end-capped in *t*-buthanol using TBPPi as initiator of radical chain transfer reaction. Subsequent two steps of hydrolysis and reesterification to obtain corresponding C2 diol were optimized. Optimal reaction conditions for hydrolysis were found to be at a DMF/H_2O ratio of 5 with a reaction temperature of 120 °C for 14 hours. Optimal reaction conditions for reesterification were found to be simple heating at 65 °C under Claisen condenser with MeOH in the presence of acid (H_2SO_4 or *p*-TsOH) until MeOH started to distill. Unfortunately we werent able to eliminate the coloring of diols during the reaction with DMF/H_2O. . This is a consequence of sideway reactions as dehydrofluorination. The C3 diols were successfully prepared by radical addition of telechelic diiodo poly(VDF-co-PMVE)copolymer onto allyl alcohol in the presence of AIBN in CH_3CN. Subsequently iodine atoms on fluorinated bis (iodohydrine)intermediate were reduced using Bu_3SnH with AIBN. The acrylation reaction was also optimized. Best results were obtained, when acryloyl chloride and PVPP were used for both C2 and C3 diols. Networks of C2 or C3 diacrylates were prepared by UV crosslinking [21].
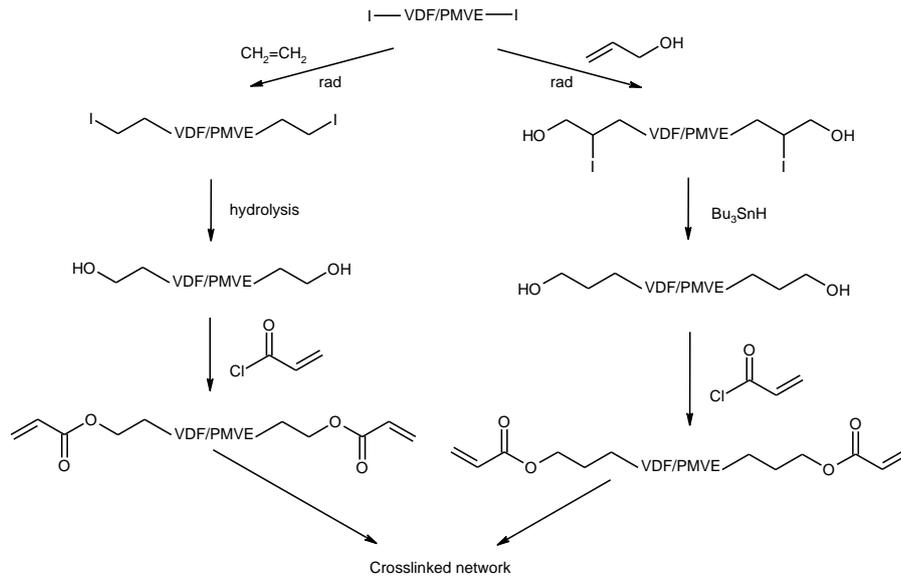
Scheme 4. Various strategies to synthesize photocrosslinkable telechelic diacrylates containing C2 or C3 spacers

3.4. Functionalized fluoropolymers for fuel cell membrances

The objective of this presentation deals with the syntheses of new generations of original membranes prepared from aromatic (Scheme 5) and aliphatic fluorinated (Scheme 6) copolymers incorporating fluoromonomers such as vinylidene fluoride (VDF, $F_2C=CH_2$), hexafluoropropene (HFP, $F_2C=CFCF_3$), and an aromatic fluorinated monomer functionalized by a sulfonic acid, or α-trifluoromethacrylic acid (TFMA) according to the following reactions :
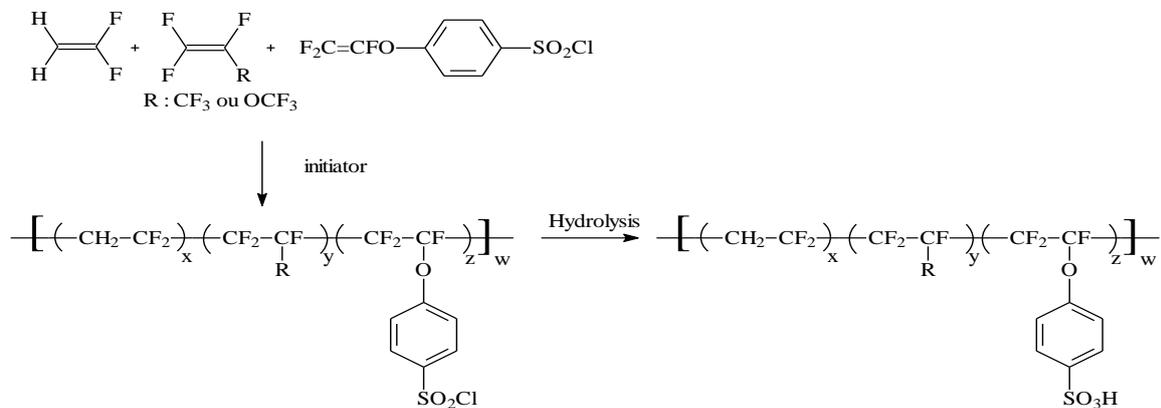
Scheme 5: Radical terpolymerization of vinylidene fluoride (VDF) with hexafluoropropene (HFP) and trifluorovinyl oxy paraphenyl sulfonyl chloride, precursors of original fuel cell membranes:
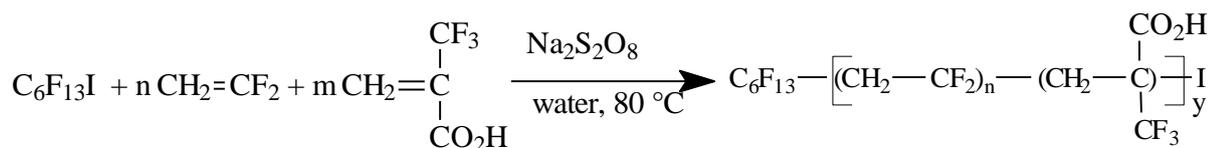

Scheme 6: Iodine transfer copolymerization of VDF with α-trifluoromethacrylic acid (TFMA)

Further work has recently been investigated on the use of other sulfonated synthons (such as (or tris(sodium sulfonate) dies) to graft onto these poly(VDF-ter-MAF-ter-HFP) terpolymers [22] However, perfluorosulfonic polymers suffer from three limitations (methanol crossover, high cost and loss of performance from ca. 85 °C since the membrane start to dry). Beside, Kreuer [23] and then, Jannash [24]'s groups have pioneered novel concepts where H_2O is replaced by an amphiteric immobilized solvent; i.e. a system which exhibits a donor-acceptor behavior. These teams used nitrogeneous heterocycles as suitable candidates for amphoteric solvents and our choice is benzimidazole function which has the property to enable proton conduction. This new challenge should allow us to prepare fluorinated membranes which keep certain conductivity at T > 120 °C since it is known that nowadays requirements for car industry and for stationary are such that the membrane could bear severe conditions for 5,500 hrs [25-26] and 40,000 hrs, respectively. This is why a second chemical modification of the carboxylic acid side groups of the initial copolymers was successfully achieved by condensation (on the presence of Eaton catalyst) with benzene orthodiamine [27]. These modified copolymer show better thermostability than the initial ones and are potential candidates as original sulfonic and quasi-anhydrous membranes.

3.5. Fluoropolymers for nanocomposite materials

As shown in Scheme 1, we succeeded in preparing poly(VDF-*co*-TFMA/HFP copolymer/silica composites in 17 ~ 24 % isolated yields under alkaline or acidic conditions. These fluorinated silica composites thus obtained were found to exhibit a good dispersibility and stability not only in water but also in methanol, ethanol and tetrahydrofuran. Thus, we have measured the size of these fluorinated composites in methanol by the use of DLS at 25 °C. These composites are nanometer size-controlled (23.7 ~ 137 ± 1.5 ~ 23 nm) fine particles. The size of each composite was found to increase effectively by the nanocomposite reactions compared to the parent silica nanoparticles (11 nm), indicating that core (silica nanoparticle)/corona (fluorinated copolymer)-type nanoparticles should be smoothly produced by the sol-gel reactions in Scheme 7. In order to clarify the properties of these new poly(VDF-*co*-TFMA) copolymer/silica composites, we have tested these nanocomposites for the thermal stability by the use of thermogravimetric analyses (TGA), in which the weight loss of these nanocomposites was measured by raising the temperatures around 800 °C at a 10 °C/min heating ratio under air atmospheric conditions [28].
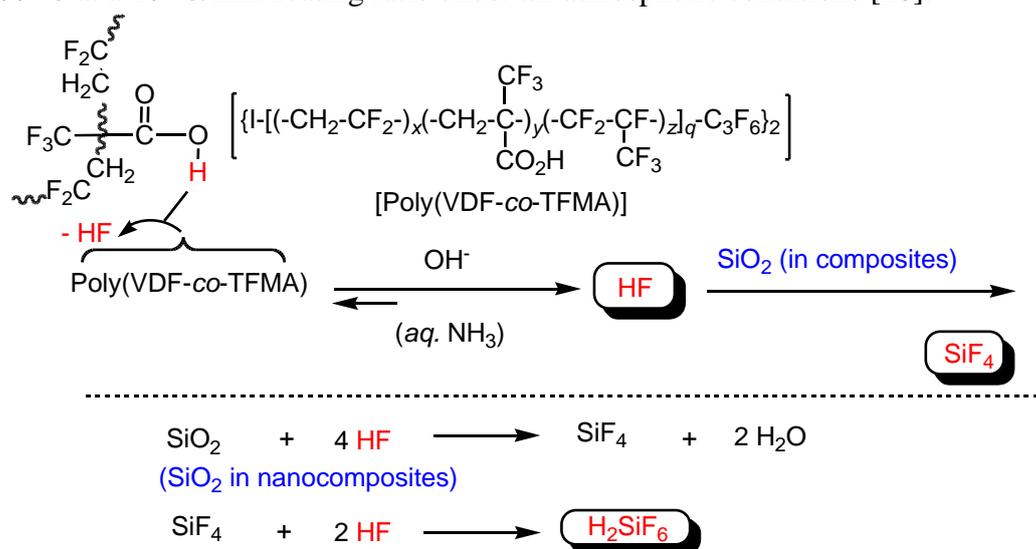
Scheme 2 Plausible mechanism for the formation of hexafluorosilicic acid

4. CONCLUSIONS

Compositions of fluoroacrylated resins with reactive diluents and photoinitiator were prepared and found to have good homogeneity, transparency and low refractive indeces, suitable for processing of films, fibers and rods. These formulations can be readily cured under UV-radiation to obtain solid amorphous, transparent materials with good thermal and mechanical properties, high Tg (> 100°C), suitable for optical waveguides applications. The synthesis of original perfluorovinyl dioxolane and its radical copolymerization with different fluorinated alkenes are presented. The thermal properties (Tg > 130 °C and Td > 300 °C), refractive indexes (n_D < 1.35) could determine their application as good candidates for optical waveguides materials.

Original 3,3,3-trifluoropropene telomers have been synthesized under radical conditions and were modified into hydrogenofluorosurfactants by simple chemistry in high overall yields. Their physicochemical properties showed good inertness to bases and acids. Their surface tensions were assessed and show interesting CMC values similar to that of PFOA. Also surfactants based on vinylidene fluoride with alternating C-H and C-F bonds (which may act as degradation sites), and also containing both TFP and VDF units appear as excellent alternatives to perfluorinated chains. New fluorinated block copolymers based on poly(VDF-*co*-TFP), and oligo(vinyl alcohol) sequences were synthesized by controlled radical polymerization in the presence of a fluorinated xanthate.The final product showed a good solubility in water, and exhibit comparable surface tension than that of ammonium perfluorooctaonate (APFO).

Telechelic diiodo poly(VDF-co-PMVE)copolymer was successfully ethylene end-capped in *t*-buthanol using TBPPi as initiator of radical chain transfer reaction. Subsequent two steps of hydrolysis and reesterification to obtain corresponding C2 diol were optimized. The C3 diols were successfully prepared by radical addition of telechelic diiodo poly(VDF-co-PMVE)copolymer onto allyl alcohol in the presence of AIBN in CH_3CN. Subsequently iodine atoms on fluorinated bis (iodohydrine) intermediate were reduced using Bu_3SnH with AIBN. The acrylation reaction was also optimized. Best results were obtained, when acryloyl chloride and PVPP were used for both C2 and C3 diols. Networks of C2 or C3 diacrylates were prepared by UV crosslinking.

The radical copolymerization (and terpolymerization) of VDF and TFMA (and HFP) was successfully achieved in emulsion in good yields without any surfactant. Interestingly, the obtained emulsions were stable for several months leading to monodispersed particles sizes of ca. 100 nm. Then, successful chemical modifications of the carboxylic acid side groups of the resulting copolymers were successfully achieved in two different ways: by reduction and etherification with sulfonic acid paraphenol or by condensation (on the presence of Eaton catalyst) with benzene orthodiamine. These modified copolymers with improved thermostability than the initial ones and are valuable candidates as original sulfonic and especially quasi-anhydrous membranes.

Poly(VDF-*ter*-TFMA-ter-HFP) terpolymers were applied to the preparation of the fluorinated copolymer/silica nanocomposites under alkaline and acidic conditions, respectively. More interestingly, these fluorinated nanocomposites, which were prepared under alkaline conditions, were found to exhibit no weight loss behavior at 800 ^{o}C, although the corresponding fluorinated nanocomposites, which were prepared under acidic conditions, exhibited a clear weigh loss behavior.

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