SP1- Cooperation

Collaborative project

Collaborative project (generic)

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SEAFRONT

Synergistic Fouling Control Technologies

Deliverable 2.24: Synthesis of at least 24 (6x4) zwitterion-fluoropolymer conjugates

Delivery date: M33 ([month] 9th 2016)

Table of contents

Introduction

Deliverable 2.24 has been delivered 9 months later than initially scheduled (month 33 instead of month 24) upon decision of the EB of the Project, in order to give more time to complete the performance screening tests and better understand the value of these new prototypes.
Presently the performance tests on coating formulations including these zwitterionic-fluoropolymer conjugates are still ongoing, but the EB decided to release this Deliverable in any case.
The fluoropolymer segments of the conjugates are based on the perfluoropolyether (PFPE) backbone and the zwitterionic functionalities are both of the carboxybetainic and sulfobetainic types.
The zwitterion-fluoropolymer conjugates have been used as “additives” to paint formulations in the attempt to deliver a foul deterrence effect.
Deliverable 2.24 describes the synthesis of these materials prepared by Solvay Specialty Polymers (SSP) and by the University of Newcastle – School of Chemistry (UNEW-SCL), whereas the formulations into coating prototypes will be described in the public Deliverable 2.25.

Description of technology delivered

The number of prototypes initially scheduled (24) derives from the availability of 4 fluoropolymer intermediates and 6 zwitterionic intermediates which in principle could be combined together in all the possible combinations to provide 6x4 conjugates.
However, this simple assumption proved not to be feasible due to chemistry limitations, since the functionalities of the fluoropolymers (PFPE derivatives) and those of the zwitterionic intermediates demonstrated not to be compatible for chemical combination.
Therefore a different approach was followed, involving the build-up of the zwitterionic functionality by derivatization of the end groups present in the α and ω positions of the PFPE derivatives. Using this approach a considerable number of prototypes, exceeding the initial target of PFPE-zwitterionic compounds, were obtained by SSP and by UNEW-SCL.

The PFPE derivatives which have been used are α,ω-functionalized perfluoropolyethers, having the following general formula:

$$R_H\text{-}CF_2O(CF_2CF_2O)_p(CF_2O)_qCF_2\text{-}R_H \qquad [\ I\ ]$$

where R_H is a functional group (e.g. carboxylic ester, alcohol) and the average molecular weight of the PFPE backbone is typically 1,500 amu.
The PFPE functionalized oligomers are obtained by a proprietary technology of Solvay Specialty Polymers, which uses the photo-oxypolymerization of perfluoroolefins to build the perfluoropolyether backbone [(1)] .

In particular, the present PFPE derivatives are obtained by the photo-oxypolymerization of tetrafluoroethylene. The product obtained from this process is a peroxidic polymer, which is then submitted to chemical reduction to yield a key derivative intermediate, the PFPE di-acyl fluoride (DAF), from which other derivatives are obtained by using conventional organic chemistry applied to the functional chain ends.

The two bifunctional derivatives which were mostly used to prepare zwitterionic conjugates are the ester and the alcohol, whose formulae are reported below:

$CH_3CH_2OC(O)$-$CF_2O(CF_2CF_2O)_p(CF_2O)_qCF_2$-$COOCH_2CH_3$ **PFPE Di-ester**

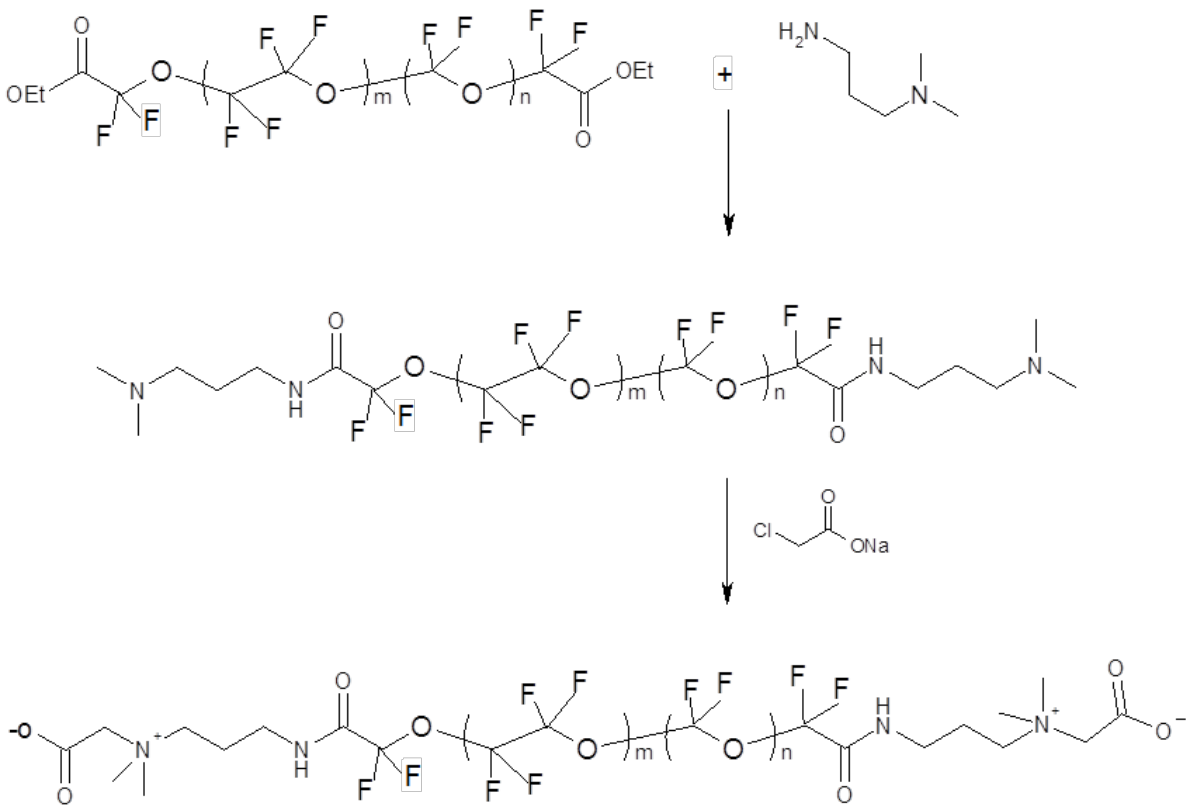
$HOCH_2$-$CF_2O(CF_2CF_2O)_p(CF_2O)_qCF_2$-$CH_2OH$ **PFPE Di-alcohol**

In the following paragraphs we will try to give an idea of the activities done on this task and the results obtained, by giving some examples of the synthetic pathways used to functionalize these two PFPE derivatives to get PFPE-zwitterionic conjugates.

Examples of prototypes synthesized

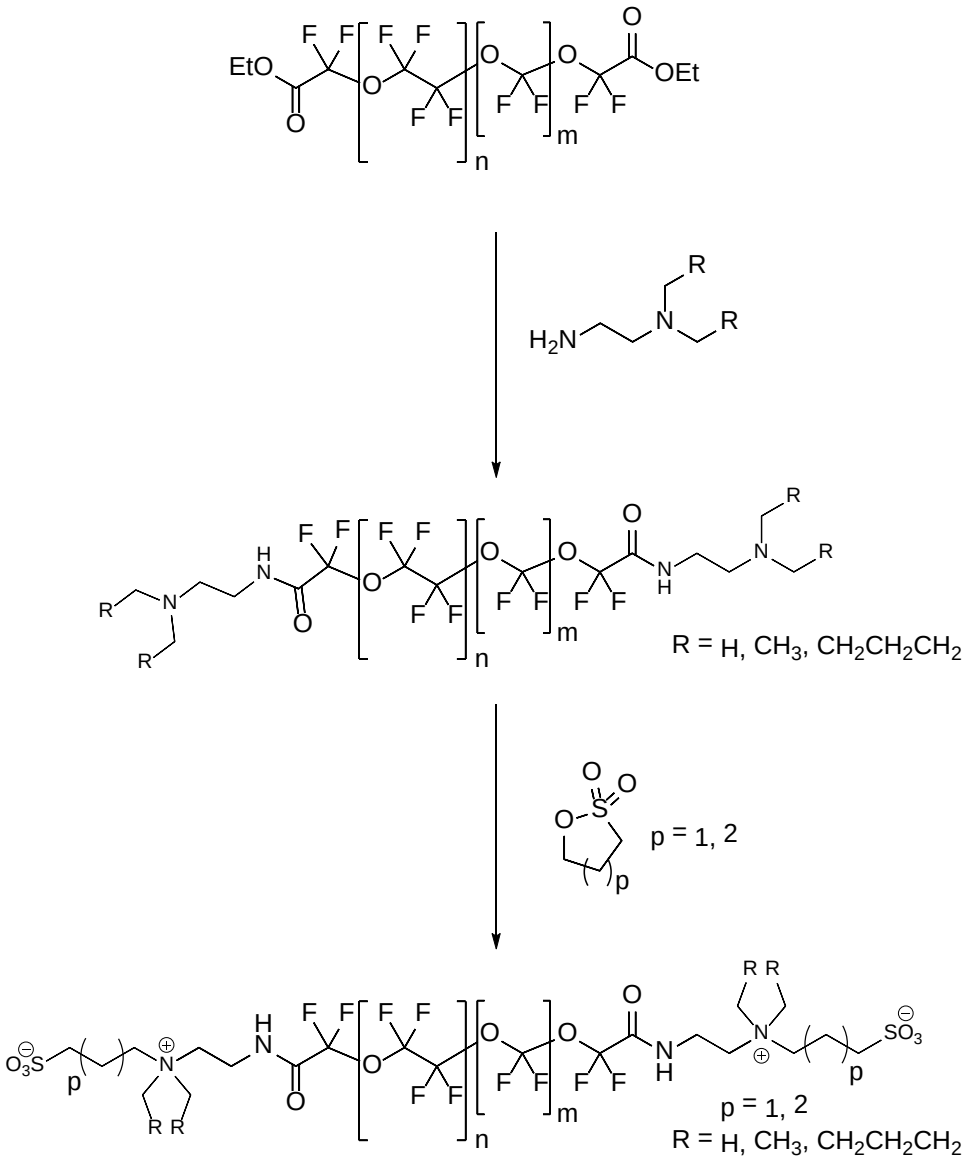
1) A first group of PFPE-zwitterionic conjugates prepared by SSP is based on the derivatization of the PFPE diester with an asymmetric diamine to get an amido-tertiary amine derivative which is further reacted with sodium chloroacetate to get the carboxybetainic derivative, as reported in the Scheme 1 below.
   The first step of reaction was performed without use of solvents at about 60°C and the conversion was monitored by IR spectroscopy (>95%); at the end the ethanol formed was distilled from the product. The second step of reaction was performed in conditions similar to those reported in the literature [(2)] , using a mixture ethanol/water (95:5) as solvent; the conversion was followed by ^{1}H-NMR (>95%) and the final product was carefully washed with water in order to remove the NaCl to form the zwitterionic moiety. The complete removal of the NaCl was checked by quantification of Na by ICP analysis. Two samples of this structure were prepared, starting from a PFPE diester with average molecular weight=1590.

Scheme 1: Synthesis of PFPE α,ω-di-(amido-carboxybetaine)



2) A second group of PFPE-zwitterionic conjugates prepared by UNEW-SCL is based on the derivatization of the PFPE di-ester with an asymmetric N^1,N^1-dialkyl diamine, followed by reaction with 1,3-propane sultone or 1,4-butane sultone to obtain PFPE α,ω-di-(amido-sulfobetaine) (Scheme 2). Different N^1,N^1-dialkyl diamines can be used in this procedure.
The first step was performed with 5 equivalent of three different N^1,N^1-dialkyl diamines under neat conditions at room temperature for at least 12 h, then washed with mixtures 1:1 of MeOH-H_2O and dried under vacuum. The reaction was studied by ^{1}H-NMR and IR spectroscopies and the results were consistent with a successful amidation reaction. These three amine-amide intermediates were soluble in MeOH, so the second step of reaction was done at reflux in MeOH either with 1,3-propane sultone or with 1,4-butane sultone for 24 h to obtain six different PFPE α,ω-di-(amido-sulfobetaines).

Scheme 2: Synthesis of PFPE *α,ω-di-(urethane-sulfobetaine).*



All samples display a colourless oil appearance and were characterized by ^{1}H-NMR spectroscopy.

Figure 1 shows the ^{1}H-NMR spectra of the starting PFPE di-ester, three amine-amide intermediates and N,N-dimethyl diamine, thus a proper comparison between signals allow a proper assignment of signals and confirmation of the structures.

Figure 1: 1H-NMR spectra of a) the starting PFPE di-ester, b)-d) three amine-amide intermediates and e) N,N-dimethyl diamine.

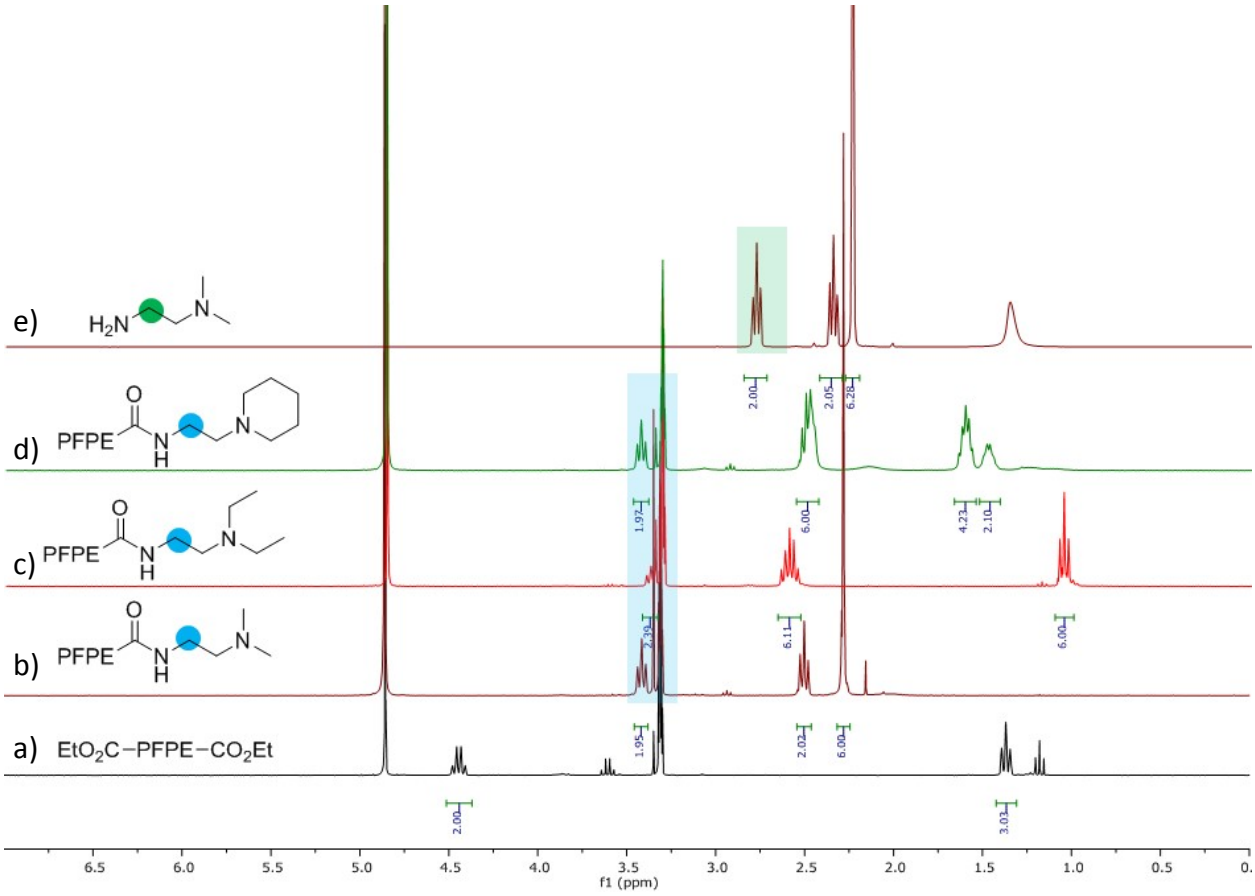
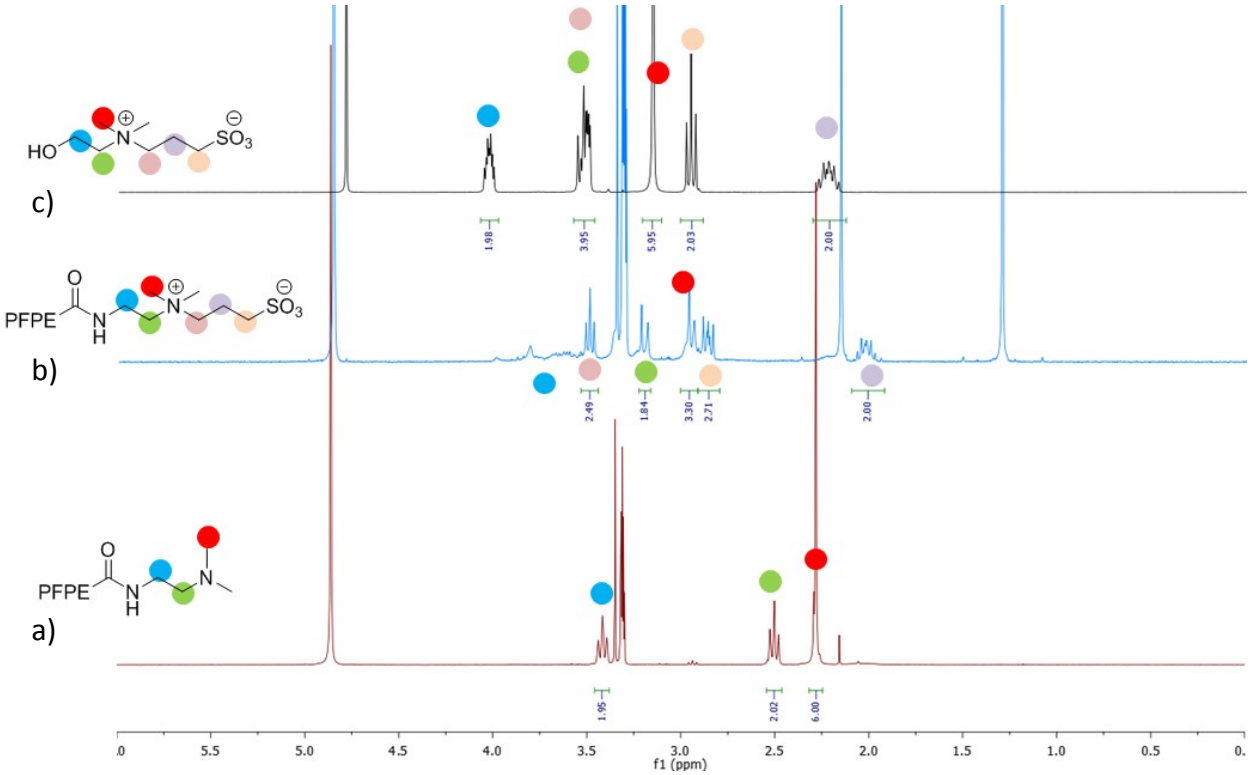


Figure 2 below shows the ^{1}H-NMR spectra of an amine-amide intermediate, a final PFPE α,ω-di-(amido-sulfobetaine) and a zwitterionic alcohol intermediate. The comparison of spectra allow to assign the signals and check the structure of the final zwitterionic compound.

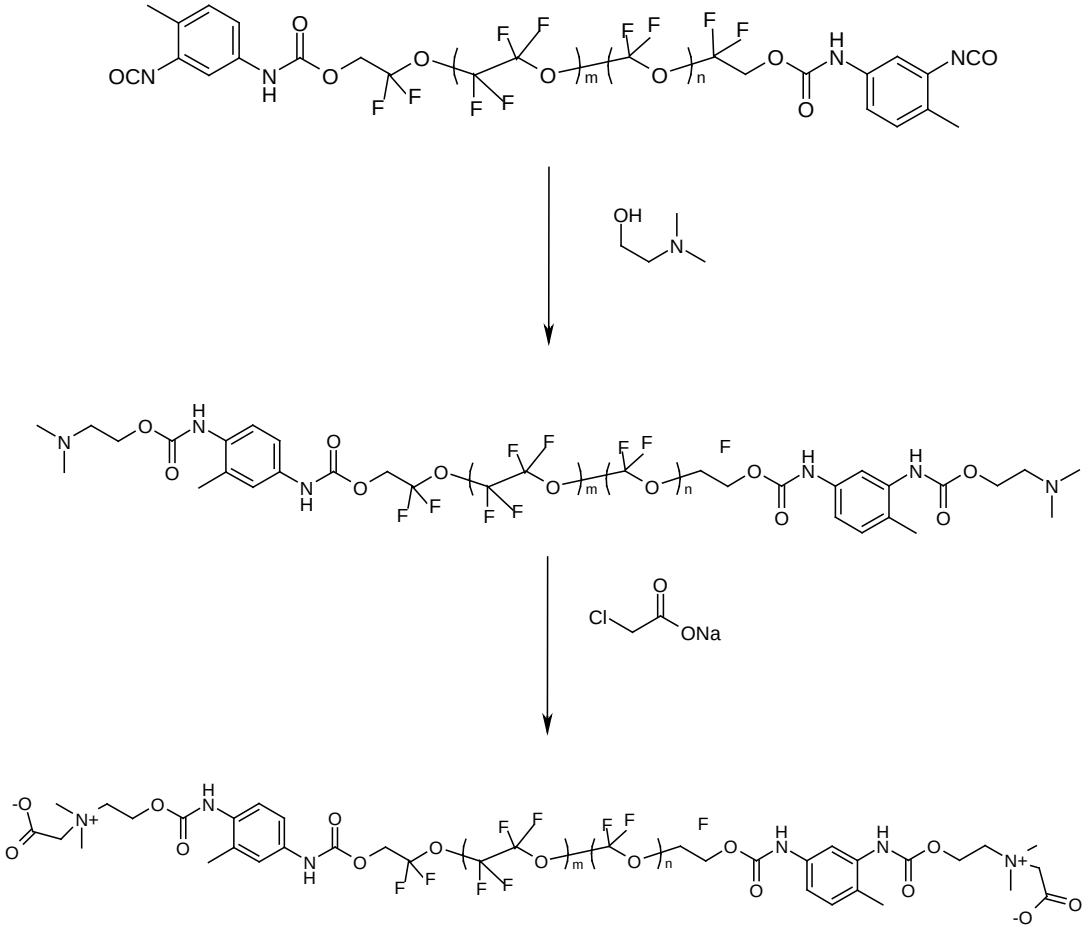
Figure 2: 1H-NMR spectra of a) an amine-amide intermediate, b) a final PFPE α,ω-di-(amido-sulfobetaine) and c) a zwitterionic alcohol intermediate.



These families of PFPE α,ω-di-(amido-sulfobetaine) could be obtained faster and easier than the PFPE α,ω-di-(urethane-sulfobetaine) compounds (see later), an observation which suggests this approach would be most amenable to scale-up.

3) A third group of PFPE-zwitterionic conjugates prepared by SSP is based on the derivatization of the PFPE di-alcohol, following a route similar to the pathway of the first group of prototypes, but using a urethane chemistry instead of an amide.
First the di-alcohol was reacted with toluene di-isocyanate (TDI) to get a PFPE di-isocyanate derivative, which was then reacted with an ethanol-tertiary amine, followed by reaction with sodium chloroacetate, according to the Scheme 3 below reported.

Scheme 3: Synthesis of PFPE α,ω-di-(urethane-carboxybetaine)

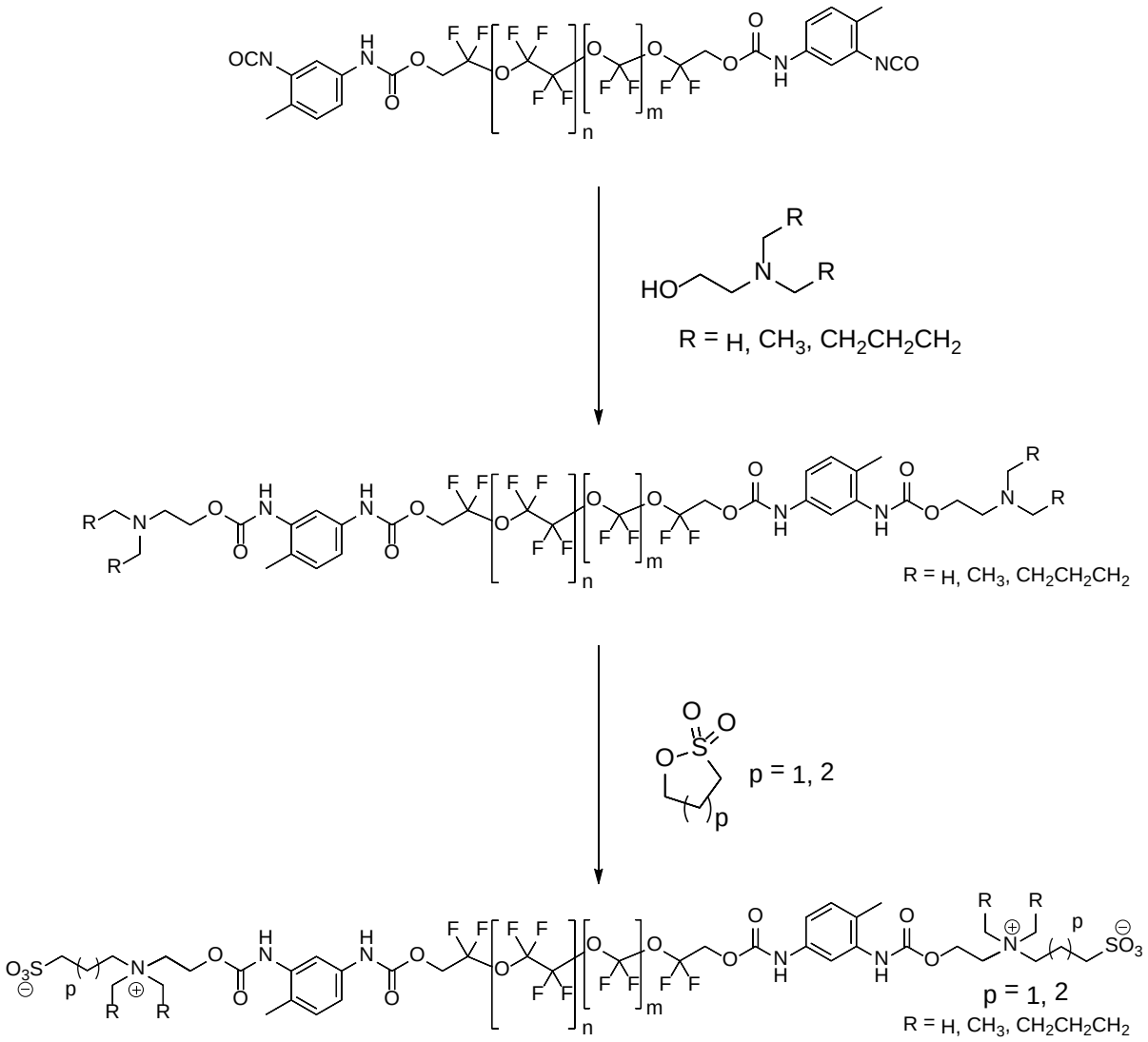


The starting material, PFPE di-isocyanate was easily prepared by reaction of the PFPE di-alcohol with excess toluene di-isocyanate (TDI), followed by removal of the unreacted TDI.
The first reaction step was performed in MEK catalysed by DBTDL and the conversion was monitored by IR (disappearance of the –NCO group); the second step of reaction with sodium chloroacetate was performed in conditions similar to the previous group of prototypes, except that in this case a partially fluorinated solvent (hexafluoroxylene) was also used in admixture with water in order to better solubilize the intermediate. The conversion was followed by ^{1}H-NMR (>95%) and the final product was carefully washed with water in order to remove the NaCl to form the zwitterionic moiety.
The final zwitterionic product is a solid, showing no solubility in water and slightly soluble in ethanol.

4) A fourth group of protoytpes was prepared by UNEW-SCL using a route similar to the previous group, but affording sulphobetaine conjugates instead of carboxybetaine. The

PFPE di-isocyanate derivative was reacted with a tertiary-amine alcohol, followed by reaction with 1,3-propane sultone or 1,4-butane sultone, according to Scheme 4 reported below. This procedure can be applied to different tertiary-amine alcohols.

Scheme 4: Synthesis of PFPE *α,ω-di-(urethane-sulfobetaine)*



The starting PFPE diisocyanate material was reacted with one equivalent of three different commercial amino alcohols under neat conditions at room temperature. The mixture was then washed several times with MeOH and the conversion was monitored by ^{1}H-NMR and IR spectroscopies (disappearance of signals according to the starting material and appearance of new signals corresponding the structure of these intermediates). These three PFPE-amine intermediates are soluble in trifluoroethanol, but not in MeOH or H_2O. The reaction of these intermediates with the two different sultones (1,3-propane sultone and 1,4-butane sultone) under reflux in trifluoroethanol allowed us to obtain six different PFPE α,ω-di-(urethane-sulfobetaine).

These zwitterion-fluoropolymer conjugates were characterized by ^{1}H-NMR spectroscopy by comparison with other zwitterionic intermediates. All have the appearance of a white high viscosity oil.

The Figure 3 shows the ^{1}H-NMR spectra of a PFPE-amine intermediate, a PFPE α,ω-di-(urethane-sulfobetaine) and a zwitterionic alcohol intermediate. The comparison between the spectra of alcohol zwitterionc structure and the final PFPE α,ω-di-(urethane-sulfobetaine) allow a verification and assignment of the signals according to the structure for the desired compound. Similar results and comparisons have been obtained with the other PFPE α,ω-di-(urethane-sulfobetaines).

Figure 3: Spectra of a) PFPE-amine intermediate, b) a PFPE α,ω-di-(urethane-sulfobetaine) and c) a zwitterionic alcohol intermediate.

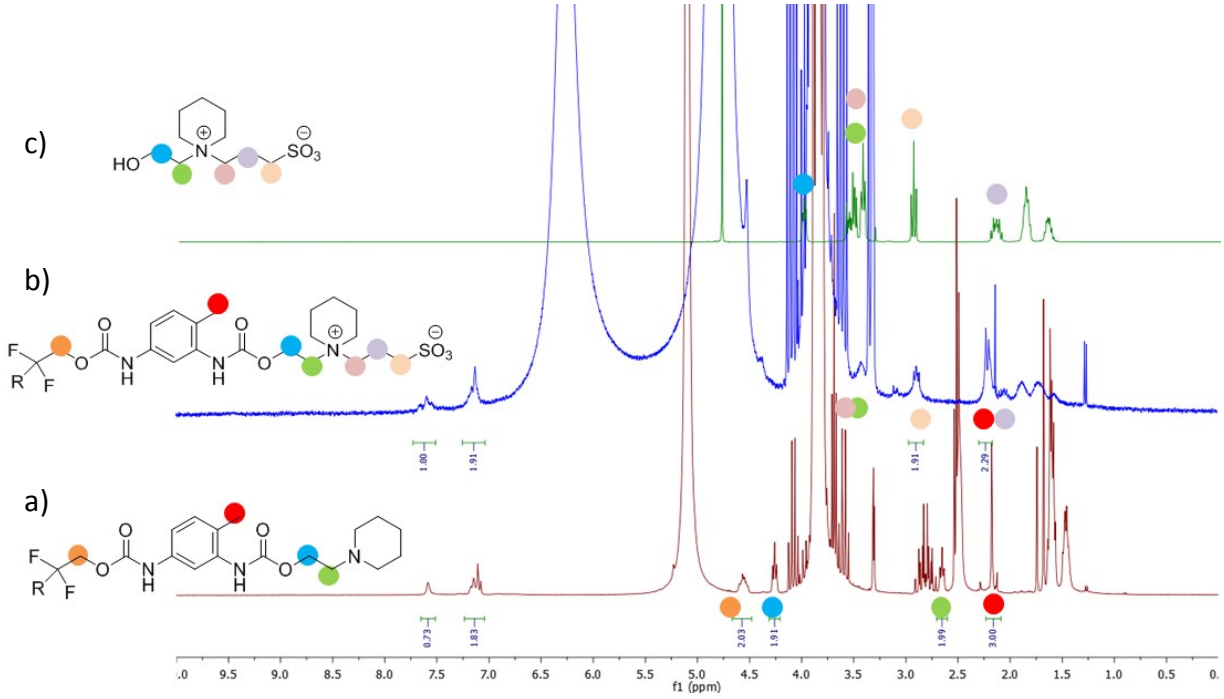
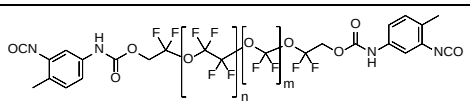
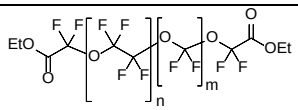
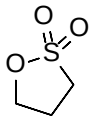
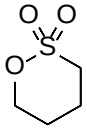
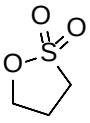
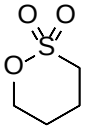
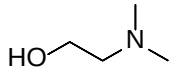
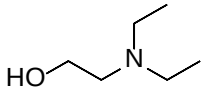
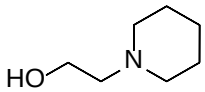
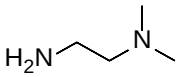
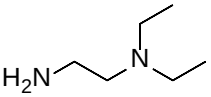
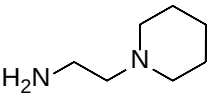


Chart 1 summarises the intermediates and compound used to obtained the 12 zwitterion-fluoropolymer conjugates by UNEW-SCL, described as second and fourth groups in the paragraphs above.

Chart 1 showing the different starting materials employed to obtain the 12 of zwitterion-fluoropolymer conjugates

				
				
	X	X		
	X	X		
	X	X		
			X	X
			X	X
			X	X

Conclusions

An overall number of 29 PFPE-zwitterionic conjugates have been synthesized by SSP and UNEW-SCL and delivered to International Paint for use as “additives” in paint formulations.
Such compounds were prepared mostly by direct functionalization of PFPE derivatives, mainly the PFPE α,ω-diester and the PFPE α,ω-dialcohol.
This report describes some examples of synthetic routes which have been used to build-up the zwitterionic functionality by chemical modification of the existing chain ends of the starting PFPE derivatives.

References

(1) *D. Sianesi et al., Organofluorine Chemistry: Principles and Commercial Applications, edited by R. E. Banks et al., Plenum Press, New York, 1994.*
(2) *Tim Coope et al.; J. Fluorine Chem. 161 (2014) 41-50*