Photoinduced Ring Opening Copolymerisation of Perfluoropolyalkylethers

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INTRODUCTION

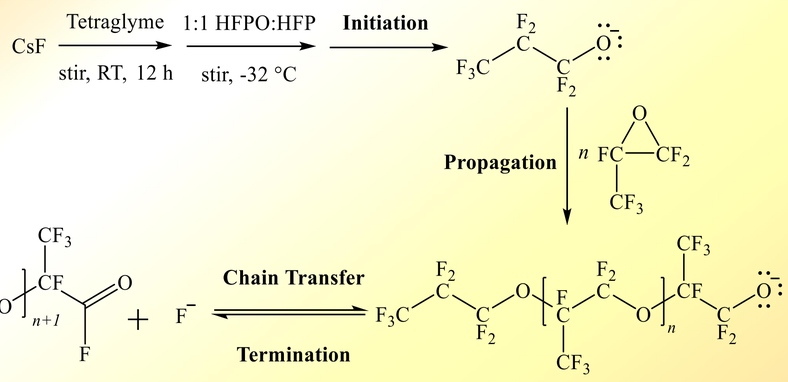
Perfluoropolyalkylethers (PFPAEs), based on structural units such as $-(CF_2O)-$, $-(CF_2CF_2O)-$, $-(CF_2CF_2CF_2O)-$ and $-(CF(CF_3)CF_2O)-$, represent a special class of fluoropolymers with remarkable properties (low glass transition temperature, high chemical and thermal inertness, low surface energy and refractive index, excellent ageing, weather and flame resistances)[1]. They can be a non-toxic alternative to the long perfluoroalkyl chains presently banned in many countries[2], and be used in many high technology areas such as aerospace, aeronautic (seals, gaskets), automotive industry, microelectronics, optics or even for antifouling and release coatings or textile treatment.

The purpose of our work is to synthesize new PFPAEs by anionic ring-opening polymerization of hexafluoropropoxide (HFPO) and functionalize them with different reactive groups. Here we describe the synthesis of PFPAE monofunctional alcohols ($HFPO_n$-MA) with different molecular weight and their use in photoinduced ring-opening polymerization of non-fluorinated diepoxides.

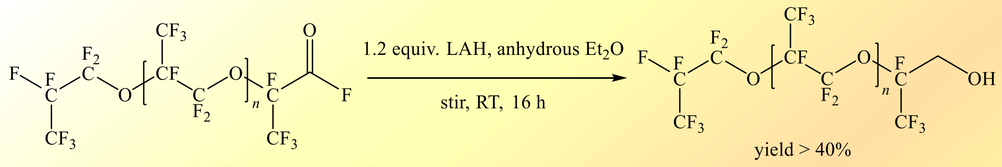
The bulk properties of the UV-cured copolymers were practically unaffected by the presence of the fluorinated comonomers when added in low amount (less than 5%wt), but their addition reflected on the surface properties, that were strongly modified.

SYNTHESIS OF $HFPO_n$-MA

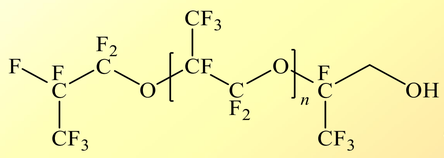
▶ ANIONIC RING-POLYMERIZATION OF HEXAFLUOROPROPYLENE OXIDE (HFPO)



▶ FUNCTIONALIZATION OF HFPO OLIGOMERS



▶ GENERAL PROPERTIES OF $HFPO_n$-MA

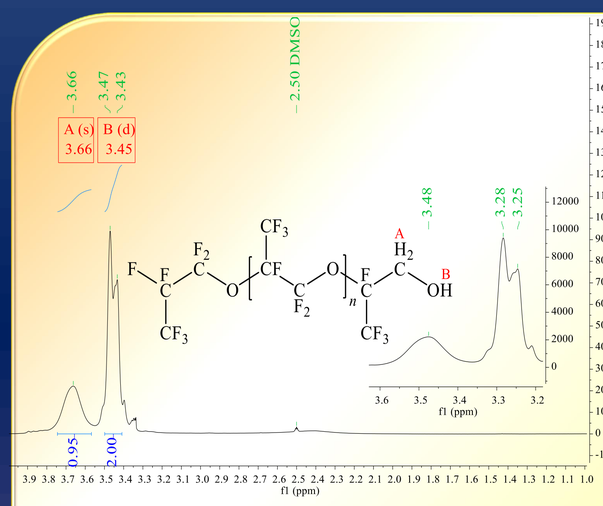


$n = 5$, $M_n = 1150$

$n = 10$, $M_n = 1810$

- Stability from -75 °C to 350 °C
- No formation of volatile products
- Excellent chemical stability

CHARACTERIZATION OF $HFPO_n$-MA



▶ ^{1}H-NMR (400 MHz, DMSO-d_6, 25 °C)

δ :

3.66 (*s*-broad, -CF(CF_3)CH_2O***H***, 1H)

3.45 (*d*, -CF(CF_3)C***H_2***O-, 2H, $^3J_{H\text{-}F}$ = 14.8 Hz)

▶ ^{19}F-NMR (400 MHz, BENZENE-d_6, 25 °C)

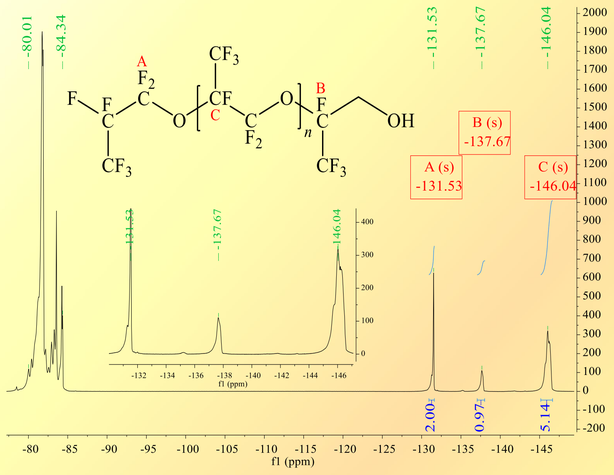
δ :

-146.04 (*q*, C***F***(CF_3) of repeat unit)

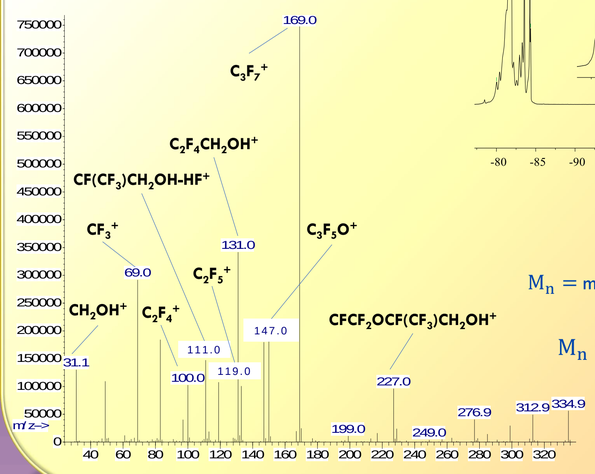
-137.67 (*ω* C***F***(CF_3))

-131.53 (*s*, α C***F***$_2$

-84.34 to **-80.01** (C***F***$_3$ and C***F***$_2$ of repeat unit)



▶ GC/MS (70 eV)



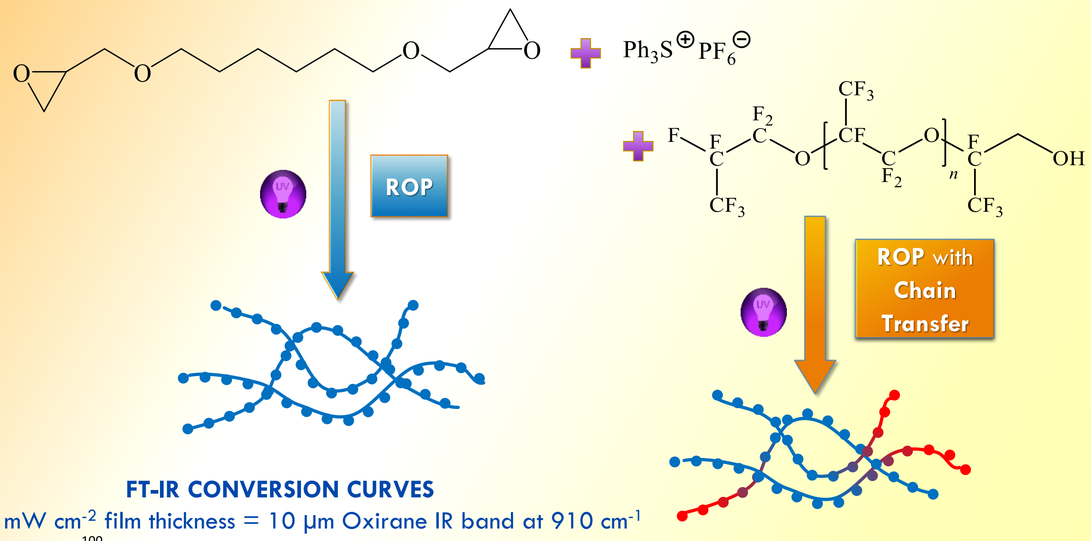
$$n = \int CF_{-145.41} = 5 \text{ (or } 10)$$

M_n = mass of α unit + $n \times$ mass of repeat unit + mass of ω unit

$M_n = 185 + n \times 166 + 131 = 1146$ $HFPO_5$–MA

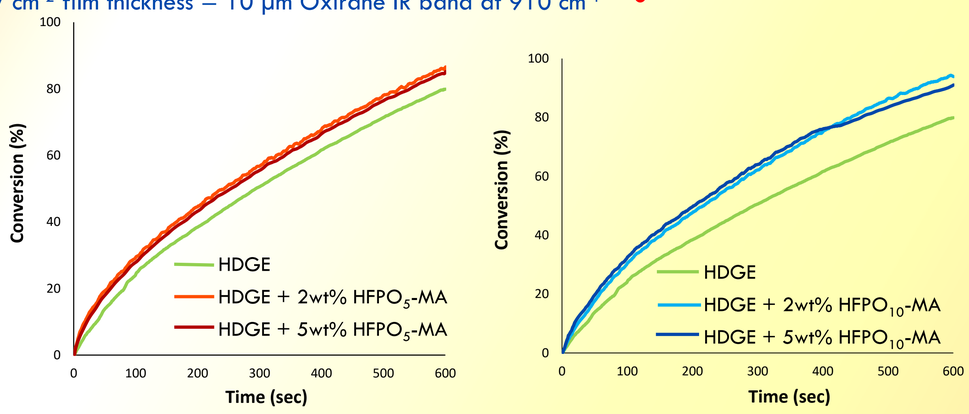
1810 $HFPO_{10}$–MA

PHOTOPOLYMERIZATION & CHARACTERIZATION

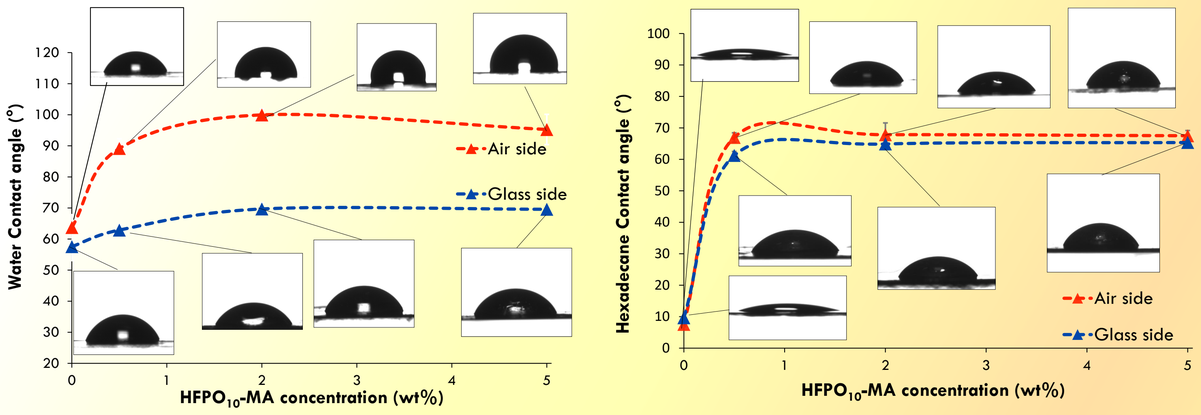


FT-IR CONVERSION CURVES

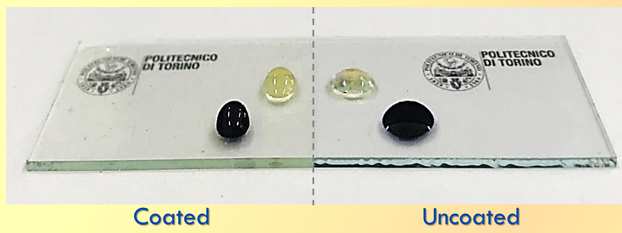
I = 300 mW cm^{-2} film thickness = 10 µm Oxirane IR band at 910 cm^{-1}

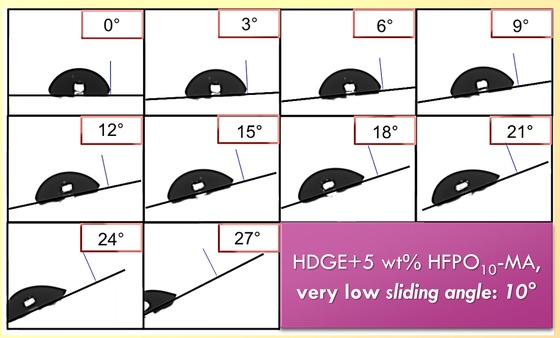


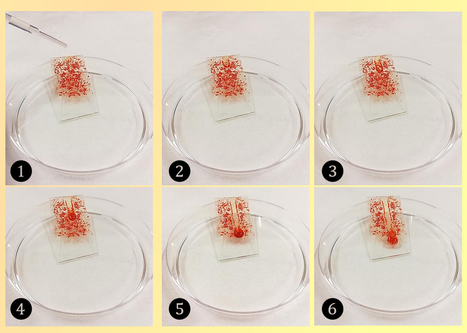
By adding the HFPO-MA, the reaction speeds up, the oxirane ring conversion is higher confirmed by photo-DSC.
Highly crosslinked polymeric networks are obtained whose gel percentage is higher than 92%



At the surface the HDGE polymer is modified by $HFPO_n$-MA:
air surfaces are made both hydrophobic and oleophobic, while glass surfaces are hydrophilic and oleophobic [3].
Air surfaces are oil and solvent repellent; they are self-cleaning.







ACKNOWLEDGMENTS

This project has received funding from the **Horizon 2020 European Union's Research and Innovation Program** under grant agreement No. 690917

MARIE CURIE ACTIONS

European Commission

REFERENCES

[1] R. Bongiovanni, A. Medici, A. Zompatori, S. Garavaglia, C. Tonelli Perfluoropolyether polymers by UV curing: Design, synthesis and characterization Polym. Int., vol. 61, no. 1, pp. 65–73, 2012.

[2]. Z.Wang, J.C. DeWitt, C.P.Higgins, I.T.Cousins A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs) Environ. Sci. Technol. vol. 51, pp.2508−2518, 2017.

[3] Y.Wang et al. Effect of end-groups on simultaneous hydrophilicity/oleophobicity and antifogging performance of nanometer thick PFPE films RCS Adv. vol.5, pp.. 30570- 30576, 2015.