Novel perfluoropolyalkylethers (PFPAEs): from synthesis to applications

Summary

This dissertation presents the research work I carried out during my PhD in the framework of the H2020-MSCA-RISE-2015 project "PhotoFluo". The aim of the work is the synthesis of novel perfluoropolyalkylether (PFPAE) monomers having epoxy and vinyl ether functionalities, and their use in photoinduced polymerization processes with the aim of obtaining photocured fluorinated networks exploitable as engineering materials. The main motivation for this research is the great relevance presented by PFPAEs in terms of harmlessness while assuring the same, or often even improved, performances of many fluoroalkylic polymers. Being non-persistent and non-bioaccumulable in the environment, PFPAEs represent one of the most promising safe alternatives to polymers having a fluoroalkylic chain -C_8F_{19}, which were banned worldwide by different environmental-protection organizations since the late 2000s.

Up to now, only (meth)acrylic structures of the kind *(meth)acr*–Rh–PFPAE–Rh–*(meth)acr* have been proposed in photopolymerization, having –(CF_2O)–, –(CF_2CF_2O)–, –($CF_2CF_2CF_2O$)– and –($CF(CF_3)CF_2O$)– as PFPAE structural unit in a restricted range of length, and with Rh typically containing a variable urethane group. Therefore, the photopolymerization (or curing) was limited to radical processes and no report on ionic photopolymerization of PFPAE monomers is available. The design of new PFPAE monomers is therefore promising for further exploiting photopolymerization and, in general, for innovating present applications. Besides introducing new reactive functionalities, tailoring the entire monomer structure varying the PFPAE building block and the hydrogenated chain Rh can permit the tuning of the reactivity and of the properties of the final polymers obtained by photopolymerization.

Therefore, in the present work the first goal is the synthesis of new PFPAE building blocks and their chain extension with Rh chains to obtain different structures with OH functionalities as end groups. Then these precursors are functionalized with photopolymerizable groups G to obtain telechelic monomers (G–Rh–PFPAE–Rh–G) with epoxy or vinyl ether functionalities. For all new monomers, the polymerization conditions are studied, and the polymers obtained are fully characterized also in view of demonstrating their potential

applications in industry, in particular in the fields of coatings, optical devices, electrolytic membranes. Copolymerizations of the PFPAEs monomers with commercially available hydrogenated homologues are also investigated, as it is a way for changing the structure of the cured materials and tuning their properties. A challenge of the research is the selective tailoring of the surface properties of photocured copolymers by employing the PFPAE monomers in small amount, relying on surface segregation phenomena.

The manuscript is organized as follows. The first part of the thesis is focused into the world of the fluorinated materials and their application in our daily life. The dramatic toxicity issues caused by the uncontrolled employment of different classes of fluoropolymers is highlighted, and the actions adopted to limit their use and to ban their production are plentifully discussed. Thus, the non-toxic PFPAEs are introduced and described in terms of safety, synthesis, properties, applications, and global market.

After that, the curing technique chosen to polymerize the synthesized PFPAE monomers is described: photoinduced polymerization is considered environmentally friendly because solventless. Moreover, it rapidly occurs at room temperature through the irradiation of a light of a certain wavelength, enabling great time and energy savings with respect to the traditional polymerization techniques. Advantages and drawbacks compared to other polymerization processes, suitable photosensitive monomers, and main applications of the photopolymerization are also described.

The last part of the thesis is dedicated to the experimental work I carried out and includes the synthesis on novel PFPAE starting oligomers, their functionalization with various photocurable end-groups (i.e., alcohol, epoxide, and vinyl ether functionalities), the employment of the photoreactive PFPAEs in photoinduced polymerization processes, and the comprehensive characterization of the photocured PFPAE networks properties. Finally, on the basis of their properties, the obtained fluorinated photocured materials are proposed for various applications: as self-cleaning/anti-stain coatings, for the fabrication of micropatterned multilayer structures (by photolithography), as polymer electrolytes for lithium-ion batteries, and for the fabrication of optical waveguide devices.