PhD in Materials Science and Technology

Research Title: Synthesis of highly fluorinated crosslinked polymers: investigation of the structure-properties relationships and development of new products

Funded by	Politecnico di Torino

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Context of the research activity	Fluoropolymers have had a profound effect on all aspects of industry since their discovery1. The fluorine element shows strong electronegativity, a small Van der Waals radius (1.32 Å), low polarizability, and a strong C-F bond therefore when it replaces hydrogen in a polymer structure, it drastically modifies its main properties, guaranteeing high thermal, chemical, ageing and weather resistances, unique inertness, resistance to oxidation and hydrolytic decompositions, low flammability, low refractive index, low dielectric constants, low moisture absorption, and low surface energy (oil and water repellency). Fluoropolymers are already used in many high technologies areas: automotive industries (ca. 300 g of fluoropolymers per car, including fluids for transmission and components of fuel cells and Lithium batteries), aerospace (use of elastomers as seals, gaskets, O-rings for tanks of liquid hydrogen or hydrazine in boosters of space shuttles), chemical plants (pipes and coatings, high performance membranes), microelectronics and optics (core and cladding of optical fibers), textile treatment, building (paints resistant to UV and to graffiti, especially for the Cultural Heritage), antifouling and release coatings, biomaterials, applications. The main structural units present in fluoropolymers are fluoroalkylic, while interesting structural units are –(CF2O)–, –(CF2CF2O)–, –(CF2CF2CF2O)– and –(CF(CF3)CF2O)–: the perfluoropolyalkylether chains one can obtain are highly inert, do not crystallize and show Tgs much lower than fluoroalkylic. They find various applications such as elastomers, lubricants, pump fluids, and heat transfer fluids under very severe conditions. As fluoroalkylic they show very low surface tension but have the advantage not being bioaccumulative like perfluoroalkylchains

	which caused concerns and the banning in different applications. Among the polymerization methods, photopolymerization is very attractive: i) the polymer formation is fast (no more than a few minutes compared to hours requested by thermal processes); ii) the process can be conducted in bulk and therefore is solvent free; iii) the process is carried out at room temperature and consumes low amount of energy; iv) the process permits spatial resolution, as it mainly occurs in the illuminated areas. Moreover, there is a wide range of controlling parameters to tailor the properties of the final polymer: besides the type of photoinitiator, monomer structures, number and type of reactive functional groups, also the type of irradiation and rate, the atmosphere in which the polymerization is conducted can influence the polymer properties. Triggered by a radiation with the aid of a photoinitiator, either radicals or ions are formed, a chain reaction follows with an ionic or a radical mechanism, and consumes the monomer, usually at the liquid state, creating the polymer. When the photopolymerization takes place with multifunctional monomers, the products are crosslinked. Originally, the process was limited to the field of coatings, inks, and adhesives due to limited penetration of light, while nowadays many other applications are emerging benefiting of this ecofriendly process. The first perfluoropolyalkylether structures properly designed to be reactive in photopolymerization was reported by the supervisor. Up to now, only acrylic structures of this kind G–Rh–PFPAE–Rh–G or PFPAE- Rh –G have been proposed in a limited range of structures (in particular the choice of the length of the fluorinated chain is limited).

Objectives	**The aim of this project is the preparation of new polymers based on perfluoropolyether macromonomers, by means of photopolymerization processes in view of innovating the applications of fluoropolymers and extending the use of photopolymerization processes.** **A complete investigation of the structure-properties relationships will also be conducted.** **The research work develops in three main steps:** **A. the preparation of new fluoromonomers** **B. the photopolymerization of the new monomers** **C. the full characterization of the obtained polymers to investigate structure-properties relationships and identify materials suitable for selected applications.** The synthetic activities of step A will give us a portfolio of monomers suitable for radical and cationic processes of polymerization. Once the monomers are available, their reactivity in photopolymerization will be tested (step B). For all new

	monomers, the polymerization conditions have to be studied. Copolymerizations of the PFPAEs monomers with commercially available hydrogenated homologues will also be investigated, as it is a way for changing structures and tuning properties. Among the many goals of a chemical modification, a challenge is the tailoring of the surface properties of photopolymers by photocopolymerization of hydrophobic monomers (as PFPAEs monomers) with common hydrogenated monomers: compositional gradient along the sample depth can be obtained relying on surface segregation phenomena rising from differences between comonomers in terms of surface tension, diffusion, reactivity (for example, gradient materials can be prepared where one surface is selectively enriched of the PFPAE monomer and exhibit properties different from the bulk and from the other surfaces) . A complete characterization of photopolymers will allow establishing structure-properties relationships. Among the new structures developed, we expect to select suitable materials for applications and turning into innovative products. Polymers whose properties are adequate will be used for preparing simple prototypes and tested at a lab scale in view of real applications. As the POLITO team has experience in photolithography and microfluidic devices using photopolymers, examples of prototypes the PhD student could develop are: - patterned coatings for antifouling applications;- a simple microfluidic device. The project is linked to an academic exchange program of the European Union(Research and Innovation Staff Exchange) coordinated by the Politecnico di Torino.

Skills and competencies for the development of the activity	Preferred degrees of the applicants are M.SC. IN CHEMICAL ENGINEERING, MATERIALS ENGINEERING, CHEMISTRY, MATERIALS SCIENCE, BIOTECHNOLOGY. Preferred background of the applicants should be in the area of chemistry, polymer chemistry and polymer science.