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# Synthesis and reactivity of a fluorinated *N*-alkylmaleimide towards free-radical grafting and polymerization reactions

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### Abstract

A new fluorinated *N*-alkylmaleimide, *N*-(2-pentadecafluoro-*n*-octanoyloxy)-ethyl)maleimide (FOMI), was synthesized from perfluorooctyl carboxylic acid (FOCA) by reaction of the furan adduct of maleic anhydride (MAH) with ethanolamine and esterification of the resulting alcohol-imide. The reactivity of FOMI in free-radical reactions such as copolymerization with butyl vinyl ether (BVE) and grafting onto olefin copolymers (OCP) was investigated. Copolymerization with 2/1 molar excess BVE yields a copolymer with 63 mol% FOMI in moderate conversion, indicating that homopropagation of the maleimide prevails over comonomer alternation. The thermal stability of FOMI is quite poor, with onset of the pyrolytic loss of the *N*-perfluoroalkylcarboxyethyl moiety just above 100 °C, similarly to that of FOCA. This restricts the possibilities for direct melt functionalization of OCP with FOMI. To bypass this limitation three distinct approaches were preliminarly investigated. These were respectively based on either direct grafting of FOMI at low temperature, or reaction of a MAH-grafted polyolefin with a low molecular weight amine or amino-terminated oligomer bearing the perfluoroheptyl group. A functionalization degree FD = 2% was achieved by solution grafting of a linear very low density polyethylene (VLDPE) with FOMI and Perkadox 16 as the freeradical initiator. The relatively high grafting efficiency was attributed to the growth of some oligomeric FOMI grafts onto the OCP. The alternative routes of post-modification of VLDPE-*g*-MAH by imidization with an amidoamine obtained by amidation of FOCA with a diamine or an amino-terminated FOMI/BVE oligomer, respectively, were also preliminarly investigated. © 2003 Elsevier B.V. All rights reserved.

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# 1. Introduction

It is well known that the replacement of hydrogen with fluorine atoms improves the chemical, thermal and photochemical stability of polymeric materials. Moreover, the presence of even a small fraction of fluorinated groups or co-monomers can result in dramatic reduction of surface energy, particularly when the polymeric structure, the physico-chemical properties of the material and the type of fabrication, contribute to magnify this effect. This is well documented in the literature, and heterophasic multilayered thin films, coatings with microphase-segregated or gradient composition or, more commonly, with a macroscopically homogeneous composition but a molecularly thin highly fluorinated layer at the air–polymer interface can be obtained as the result of self-assembling of highly fluorinated components, thermodynamically driven phase segregation, or

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simply selective enrichment of fluorinated groups at the interface. While such behavior is easily obtained and understood with relatively sophisticated polymeric structures, such as block copolymers, and a number of studies have described the self-assembling into crystal-like domains of long linear perfluorinated molecules in monolayers or even at the polymer-air interface of relatively highly fluorinated copolymers with perfluorinated side chains (typically linear  $C_8$  or longer), more flexible and economically viable approaches are still needed and explored with the aim of obtaining materials with useful additional properties for a number of applications. Thus a high optical purity, toughness, chemical stability, photoinduced crosslinking or cleavage behavior are needed in optical applications such as waveguides and photolithography; good adhesion, photochemical stability and/or soilrelease behavior are required for protective coatings or waterrepellent finishing of masonry, textile, paper, leather and other materials; scratch and mar resistance, long-term stability of the polymer surface against molecular reorganization leading to unwanted increase of surface energy are required for antifouling applications.

Our research activity at the University of Pisa, started about 10 years ago, was prompted by the increasing awareness of the need of new products for the preservation of our country's rich cultural heritage. Indeed most products commonly employed as protective coatings or consolidants for deteriorated objects, particularly stone and masonry surfaces exposed to severe environmental hazard and accelerated decay in polluted areas, are commercially available only because they were developed for more profitable applications, and can hardly be considered the most suitable for the specific requirements of the preservation of works of art. Our early activity was therefore mainly focused at the synthesis and testing of relatively simple copolymers of fluorinated alkyl (meth)acrylates (FA), which can be polymerized by simple free-radical process and can be applied as solutions in common (not fluorinated) organic solvents, giving efficient and durable water repellent protective coatings for natural stones of different composition and morphology.

While an appreciable improvement of hydrophobic and photodegradation behavior of acrylic-based copolymers was usually observed as the result of the introduction of FA it was immediately clear that better control on the structure, amount and local distribution of fluorinated groups throughout the macromolecule was needed in order to significantly improve the above properties. In addition, solubility, adhesion to the substrate and interfacial properties in general were observed to be strongly dependent on the (co)polymer composition and structure. The polymerization of both commercial and newly synthesized FA with unfluorinated ones and with other unsaturated comonomers, particularly vinyl ethers VE, was therefore studied in detail.

# 1.1. Reactive characteristics of partially fluorinated vinyl monomers

The presence of fluorine can dramatically affect the chemical reactivity of vinyl derivatives, particularly when fluorine substitution occurs at or close to the polymerizable vinyl group.

With the main objective of developing a simple and versatile process for the preparation of fluorinated macromolecular compounds for diverse applications, the main focus being on protective coatings, the reactivity of a series of fluorinated vinyl monomers in free-radical and ionic polymerization was investigated.

Different material properties and performances in coating and related thin film applications were expected from controlled introduction of fluorinated groups through the use of variously fluorinated comonomers and, if required, controlled polymerization processes. Both homogeneous and dispersed phase polymerization processes were considered, one of the goals being the development of environmentally friendly, highly durable and performing coating materials, possibly obtained with a moderate degree of fluorination which makes the material less costly and thus more appealing for industrial applications.

In particular the free-radical copolymerization of two classes of FA was investigated. The first includes acrylic (or methacrylic) esters containing fluorine only in the alkoxy moiety, with at least one unfluorinated carbon next to the ester group (structure **a** of Scheme 1); the reactivity of type **a** monomer is similar to that of their unfluorinated analogs [1,2]. The second class includes fluorovinyl (structures **b** and c) and fluoroalkyl-substituted (structure d) acrylates, including those fluorinated both at the double bond and in the side chain (structure e). The electronic polarization due to the presence of F next to the double bond affects the reactivity of monomers **b**-**e** [2,3] by increasing electrophilicity and therefore affinity towards electron-rich, nucleophilic monomers such as, e.g. VE, vinyl esters and  $\alpha$ -olefins.

# 1.2. Synthesis of acrylic-based copolymers by free-radical polymerization

Copolymerization of type a acrylates with unfluorinated ones proceeds smoothly and in good yields to give substantially random copolymers with easily predictable properties (e.g. glass transition temperature  $T_g$ , solubility, surface energy); on the other hand, efficient incorporation of different nucleophilic comonomers, such as VE, can be better achieved with the more electrophilic type **b**-e acrylates. In fact, while the negatively polarized double bond of VE precludes their homopolymerization under free-radical conditions, the same feature makes them well suited to produce alternating or quasi-alternating copolymer sequences with FA, since the latter can form with VE charge transfer complexes or polarized adducts. The tendency of type a acrylates to build alternating comonomers sequences and the efficiency of VE incorporation depend both on the nature of the VE (the bulkier, the better [4]) and, to a larger extent, on





the magnitude of the electronic perturbation of the acrylic group, that is, on the structure of the fluoroalkyl moiety and its distance from the ester group. In particular, the reactivity is not significantly affected when the perfluoroalkyl group is spaced apart from the ester oxygen by at least a C<sub>2</sub> unfluorinated spacer; in this case an equimolar feed of FA and butyl vinyl ether (BVE) yields copolymers with over 85 mol% acrylic units, whereas as much as 32 mol% BVE incorporation is obtained in the same conditions with HFIMA (**a**,  $R = CF_3, x = 1, n = 1$ ) [2,5]. Combining the data collected for copolymerization of primary VE with different types of FA, the tendency to build alternating structures, including perfectly alternating ones as in HFIFA (**e**,  $R = CF_3, x = 1$ , n = 1) is in the order reported in Scheme 2.

Appropriate selection of comonomers and composition allows therefore to *independently* modify the copolymer structure and properties (average fluorine content,  $T_g$ , etc.). In addition, monomers such as MTFMA, hardly homopolymerizable by free-radical mechanism, can be converted in good yields into quasi-alternating copolymers with VE under the same conditions [3]. When the comonomer distribution becomes increasingly alternating, the physicochemical properties of the copolymer can no longer be predicted and must be experimentally determined. This was specifically investigated, particularly in connection with the photodegradative behavior and the surface properties of thin films of these materials, as discussed later.

# *1.3. Ionic polymerization of fluorinated acrylates and vinyl ethers*

The anionic polymerization of type  $\mathbf{a}$  FA can be performed, as expected, with similar results as of their unfluorinated analogs; appropriate selection of the reaction conditions can lead to polymers with different tacticity [6].

The reactivity of perfluorooctylethyl vinyl ether (FOEVE) was investigated under both free-radical and carbocationic polymerization conditions. Preliminary results from our laboratory on bulk free-radical copolymerization with electrophilic monomers (diethyl maleate, DEM, and butyl methacrylate) confirmed the negligible influence of the perfluoroalkyl moiety when spaced apart by a dimethylene from the polymerizable group [7]. In fact a mixture of FOEVE, BVE and DEM gave a terpolymer with alternating structure (that is, with a 50 mol% total content of the vinyl ethers, alternating with the remaining 50 mol% DEM units)

that was unexpectedly enriched in the fluorinated VE to the expense of BVE with respect to the feed composition, as if its nucleophilic character were enhanced rather than reduced by the presence of the fluorinated substituent, thus promoting its preferential copolymerization with DEM.

The cationic polymerization of FOEVE under controlled/ living conditions was also investigated, since a living polymerization process can allow the synthesis of block copolymers and other interesting macromolecular structures. Due to the negligible solubility of FOEVE in unfluorinated solvents, the controlled/living cationic polymerization of BVE in 1,1,2-trichloro trifluoroethane was initially studied and shown to occur at T = 0 °C with the initiating system based on EtAlCl<sub>2</sub>, 1-butoxyethyl-acetate and 1,4-dioxane [8]. The fluorinated solvent slows down the polymerization and lowers the blocking activity (that is, the capacity of the living macrocation of further chain growth upon addition of a second comonomer) at high monomer conversions. Unfortunately, when the homopolymerization of FOEVE was tested under the same conditions proved successful for BVE, only negligible conversions were obtained, while a conventional initiator such as BF3-OEt2 was highly effective in the same solvent. This was a clear indication of the extreme sensitivity of the selected initiating system to the nature of both solvent and monomer.

### 1.4. Surface properties

The surface properties and surface dynamics of thin films of the above described acrylic-based copolymers, prepared by solution casting, spin coating and Langmuir–Blodgett (LB) technique have been studied by means of static and dynamic contact angle using both the sessile drop and the Wilhelmy balance methods [9,10]. In addition, their permeability to water and the dynamics of surface restructuring, conducive to significant variations of the surface energy of the films, were investigated by the attenuated total reflection (ATR) technique, revealing the strong dependence of film swelling on its surface composition and structural order [11].

Comparing the properties of spin coated and LB films, it was shown how the structural order, more than the average chemical composition, can affect the wetting behavior of a hydrophobic polymer by dictating the chemical composition and homogeneity of the outermost molecular layer, which ultimately determines the surface properties. In contrast to the spin coated films, nearly isotropic and with a surface fluorine content only slightly higher than in the bulk, the LB films are intrinsically anisotropic, with alternation of layers of hydrophilic unfluorinated main chains and hydrophobic fluorinated side chains. This anisotropy can produce apparently contradictory results, such as a higher water swelling of the more highly fluorinated copolymers when the construction of the LB film causes the perfluorinated side chains to be oriented inward and thus effectively buried inside the film.

A more extensive study on a series of copolymers of FOEMA, FHEFA, HFIFA, HFIMA and IFA highlighted the strong contribution of the terminal CF<sub>3</sub> groups in increasing both static ( $\theta$ ) and advancing ( $\theta_a$ ) contact angle with water [9], well beyond their weighed contribution to the average fluorine content in the copolymer (%F). On the contrary, a better correlation was observed between %F and the receding contact angle,  $\theta_r$ , as expected from its sensitivity to the low-surface energy microdomains. An increase of  $T_{g}$ and a moderate crosslinking (obtained by introducing the reactive comonomer 3-trimethoxysilylpropyl methacrylate, TSPMA), both affecting the segmental mobility of the macromolecular chain, improve the film stability against surface restructuring on wetting. As a general rule  $\theta_r$ , rather than  $\theta_{a}$ , is related to the protection efficiency of the film, since it reflects the swelling behavior of the wet film surface. In fact  $\theta_r$  was shown to be more strictly connected to the true equilibrium contact angle as measured by a modified Wilhelmy plate method, where an applied vibration allows relaxation of kinetic instabilities during the contact angle measurement under static conditions [12].

### 1.5. Photodegradation behavior

The photodegradation processes taking place on representative fluorinated copolymers and on selected unfluorinated analogs were studied by Chiantore and coworkers at the University of Turin, by means of accelerated photoaging under strictly controlled conditions, using a fluorescent xenon lamp to mimic solar irradiation. Chromatographic and spectroscopic techniques were used to monitor the chemical evolution during up to 2000 h of irradiation [13–16].

The first results regarding homo- and copolymers of type **a** fluoroalkyl acrylates and methacrylates with unfluorinated ones confirmed the expected high stability of fluoro-containing homopolymers and of the fluorinated co-units of the copolymers [13–15]. Unfortunately, while a methacrylic polymer with solely fluorinated side chains would grant excellent stability, its application possibilities are quite limited and copolymerization with simply unfluorinated or otherwise functional comonomers is usually necessary to improve adhesion, solubility, etc. The overall stability of type **a** FA copolymers was observed to be generally controlled by the reactivity of the unfluorinated co-units, which may be schematically divided in two classes on the basis of their main effect on the mechanism of photooxidation.

Those having long or branched side alkyl chains follow a common degradation pathway which mainly produces extensive cross linking, promoted by radicals generated on the flexible side groups; gel formation is the most apparent consequence of the photooxidative processes for this class of copolymers. On the contrary, in the presence of methyl acrylate (MA) units the oxidation occurs primarily starting from the main chain tertiary carbon position, inducing scission reactions in the macromolecules.

The most effective  $T_g$ -lowering vinyl comonomers that is those providing a macromolecular main chain with enhanced conformational flexibility, are characterized by either long plasticizing side chains or by less sterically hindered vinyl groups as in acrylates [7]. Incidentally, these comonomers are also particularly sensitive to photooxidative conditions. As in the case of MA copolymers, also for those with VE crosslinking is no longer the main degradation pathway [17]. Both TFEMA/BVE and MTFMA/BVE undergo extensive photooxidation, with development of new carbonyl containing functional groups and onset of chain scission processes controlled by the reactivity of the VE units [16]. Fluorine atoms are in such structures too far from the weak tertiary C-H of the VE to provide long-term stabilization of the polymer, although the kinetics of the overall photodegradation process is usually slowed down. Aside from the different effects on molecular weight distribution and gel formation, the structural changes caused by photooxidation of these copolymers are quite similar, consisting in the formation of hydroxyl-bearing groups through the typical mechanism of hydrocarbon oxidation, and of lactone groups.

Two representative cases of the evolution of molecular weight distribution as the consequence of chain scission and crosslinking processes, respectively, are shown in Fig. 1. One can see from Fig. 1a that at the beginning of the degradation the molecular weight distribution of FOEMA/ BA (BA: butyl acrylate) broadens on the higher molecular weight (lower retention volume) side, indicating chain extension. At longer degradation times, when gel formation is no longer negligible, the normalized curves are only representative of the soluble fractions remaining in the samples. In the case of TFEMA/BVE negligible gel formation and fast reduction of molecular weight clearly indicate that chain scission is the prevailing photodegradation process.

The introduction of fluorine atoms in  $\alpha$ -position of the acrylic monomer effectively reduces the oxidation reactions taking place on adjacent VE units. However, a detailed study carried out on HFIFA/BVE and EDFMA/BVE copolymers showed that their degradation is not suppressed, although the structural changes revealed by FT-IR analysis are quite different in comparison with the previous cases [18]. As an alternative approach, an alkyl isopropenyl ether was used in place of the VE, thus suppressing the reactivity associated with the main chain tertiary carbon. In any case the structural regularity achievable by copolymerization of VE with  $\alpha$ - or



Fig. 1. Normalized SEC analyses of fluorinated copolymers subjected to up to 1500 h accelerated photoaging: (a) FOEMA/BA; (b) TFEMA/BVE.

 $\beta$ -fluorinated acrylates is a useful tool to improve the chemical and photochemical stability of these materials.

# 1.6. Fluorinated acrylic-based copolymers as protective coating materials for stone

The performances of a series of copolymers of type **a**-e fluorinated acrylates, containing up to four different fluorinated and unfluorinated comonomers to adapt their properties to the specific application, have been tested over the years by various laboratories in Florence, Venice and Milan, aiming at developing new protective coating materials for the safeguard of cultural heritage [1,2,5,19-24]. The fundamental requirements for a protective coating when the substrate is a porous one, such as a natural stone, are water repellence, preservation of the substrate permeability to water vapor, good optical properties (i.e. negligible shortand long-term modification of color and gloss upon application), chemical and photochemical stability and inertness towards the stone substrate, also related to the required reversibility of the treatment [25]. The protective properties of the selected fluorinated copolymers were compared with those of representative acrylic (Paraloid<sup>TM</sup> B72) and siloxane-based commercial products widely employed in this field. Techniques such as static and dynamic contact angle measurement, determination of capillary water absorption and permeability, colorimetry and monitoring of the above parameters upon accelerated photoaging were routinely carried out on treated stones of different composition and porosity (from 1 to 40%), and particularly on carbonatic ones. Special attention was devoted to the comparative evaluation of fluorinated and unfluorinated copolymer analogs. Systematic variations of structural features such as the length of fluorinated side chain (FOEMA and TFEMA), mole fraction of fluorinated co-units, side chain branching (HFIMA and HFIFA), replacement of acrylate with VE comonomers, main chain fluorination (FHEFA and HFIFA),

were screened in order to single out those affecting most the relevant application properties of the coating.

As an example, copolymers of TFEMA and FOEMA with dodecyl methacrylate (DMA), methyl acrylate (MA) and BVE, with comparable average F content, were tested to assess the role of side chains of various length and of the unfluorinated comonomer [20]. A FOEMA/DMA copolymer with 28 wt.% F (about 30 mol% FOEMA units) was the most effective in lowering capillary water absorption at shorter wetting times (<24 h), whereas TFEMA/MA and, particularly, TFEMA/BVE perform better than FOEMA/ DMA at times exceeding 48 h. This behavior can be understood in terms of local reorganization of the coating material at the polymer-water interface. In the case of the TFEMA copolymers, containing a much higher (about 70%) mole fraction of fluorinated units, the CF<sub>3</sub> groups are more likely to be homogeneously distributed in the bulk of the polymer with little enrichment at the polymer-air interface; therefore, the good but not outstanding performance of the coating at short contact times is balanced by a fair and long-lasting water repellency. The very high initial hydrophobicity of the FOEMA copolymer is due to self-segregation and organization of the perfluorooctyl side chains in semicrystalline domains at the polymer-air interface; such structure is quickly destroyed when air is replaced by water and the interfacial energy is raised, favoring a thermodynamically driven surface restructuring where the fluorinated groups are replaced by less hydrophobic ones. Any water repellent efficacy is quickly lost also by the unfluorinated materials, even those performing well at shorter times such as EMA/BVE.

The most durable hydrophobic protection was provided by TFEMA/BVE; this was ascribed to the combined effects of  $T_g$ , lower than that of TFEMA/MA and possibly allowing the deposition of a more uniform coating, and to the lower polarity of the VE unit, resulting in a reduced water sensitivity of the coating. However, TFEMA/BVE loses its efficacy after photoaging, as the consequence of the very poor photochemical stability of this latter copolymer [16].

Less systematic data are available for copolymers of type b-e FA. Among them, copolymers of EDFMA and HFIFA with BVE were compared with Lumiflon<sup>TM</sup> LF200 (Asahi), an alternating CTFE/VE copolymer (CTFE: chlorotrifluoroethylene). Preliminary results [19] have confirmed the expected superior photooxidative stability of the CTFE/ VE copolymer, which undergoes fast crosslinking due to the presence of reactive groups in the side chain, but remains structurally unaltered as opposed to most FA/VE copolymers. This coating material performs well also in terms of protective behavior, which is comparable at short times with that of the highly water repellent TFEMA/BVE and slightly better than HFIFA/BVE at longer contact times. The performance and surface properties (contact angle with water) of Lumiflon was almost unaffected by 1500 h of photoaging. A similar behavior was also observed on some substrates when using self-crosslinkable fluorinated acrylic terpolymers containing the reactive trialkoxysilyl group in the side chain, with the general structure [26]:



1.7. Water-borne multifunctional polymers for improved coating adhesion and self-crosslinking

Prompted by the interesting results obtained by our reactive terpolymers as protective coatings on stone, a research project aimed at the development of new waterborne fluorinated polymer dispersions bearing reactive groups was commenced. Reactive or otherwise functional groups are generally required in order to stabilize the colloidal dispersion prepared by emulsion polymerization processes, or when controlled particle size and particle size distribution (affecting penetration into porous networks), high performances in terms of film formation behavior, film mechanical strength and adhesivity, are needed for the final application. However, control of the polymerization can be critical when a high degree of fluorination (which makes the polymer hydro- and oleophobic) or the introduction of hydrolytically unstable alkoxysilane groups, conducive to condensation products through sol-gel type reactions, depress the colloidal stability of the latex.

A fluorinated acrylic latex based on the general structure reported in Fig. 2, prepared by simple batch emulsion polymerization, was comparatively evaluated with two other commercial fluorinated acrylic-based latexes as water- and oil-repellent finish for textiles [27,28]. As a further development of this research activity, better controlled procedures based on starved-feed semi-continuous emulsion polymerization process are being developed, aiming at the preparation of hybrid nanostructured polymer particles with selective fluorination (e.g. in the shell of a core-shell structure) and controlled conversion of the silane groups [29].

#### 1.8. Nanotechnology applications

Fluorinated polymers are increasingly considered as materials in electronic and optoelectronic applications, such as data storage, microlithography and other techniques requiring high optical purity, control of refractive index, selective sensitivity to ultra-low wavelength irradiation.

Uniform Langmuir–Blodgett (LB) films of poly(2,2,3, 3,3-pentafluoropropyl methacrylate) (PPFPMA), that is the same material previously tested as protective coating [1], were deposited at low surface pressure using the Langmuir–Schaefer (LS, a variation of LB) technique, yielding from ultra-thin to relatively thick uniform layers [30]. The quality of monolayer was good enough to allow its use for the development of nanostructured materials. The LB films were found to be sensitive to electron beams, allowing nanowriting by positive patterning produced on low-dose irradiation. At higher irradiation doses, negative pattern associated with film crosslinking could also be produced. The main advantage provided by PPFPMA with respect to unfluorinated acrylic homopolymers is the improved deposition quality, and thus better quality of the nanoscripture.

# 1.9. Polyolefin fluorination through free-radical grafting of fluorinated molecules

In the present report is described the synthesis of a new fluorinated *N*-alkylmaleimide from a perfluoroalkyl carboxylic acid readily available as industrial electrofluorination product, and its reactivity towards free-radical reactions such as copolymerization with vinyl ethers (VE) and grafting onto polyolefins. The alternative two-step grafting and functional modification of polyolefins by means of low molecular weight or oligomeric fluorinated compounds based on the perfluorocarboxylic acid precursor will also be briefly discussed.

Maleimide and bis-maleimide derivatives are useful building blocks and crosslinking agents for highly thermostable polymers and networks. Differently from maleic anhydride (MAH), maleimide homopolymerization in the presence of free-radical initiators can be a significant pathway for monomer consumption [31,32]. High molecular weight products are easily obtained by copolymerization



Fig. 2. General structure of multicomponent fluorinated latex polymers.

with electron-rich monomers (e.g. VE). These latter are usually characterized by close to alternating comonomer sequences, although with a less regular structure if compared with MAH copolymers due to the not negligible maleimide homopropagation. The alternating copolymerization of maleimides has long been the subject of mechanistic studies [33,34] and even recently new features related to the extremely high reactivity of such system have been devised, e.g. in photoinitiated copolymerization [35].

Most maleimides studied as monomers in free-radical grafting or copolymerization reactions are N-aryl derivatives, seemingly due to the relatively easy synthesis and excellent thermal stability of the resulting succinimide repeat units. N-arylmaleimides show a stronger tendency towards formation of alternating copolymer structures with respect to the N-alkyl derivatives [36,37], although strictly alternating copolymers are hardly obtained even in the presence of fluorinated substituents [38,39] and are best achieved by functional conversion of alternating precursors such as poly(maleic anhydride-alt-ethylene), e.g. with an amine [40,41]. The presence of the aromatic groups imparts a higher conformational rigidity, that is higher  $T_{g}$ , and increased photochemical sensitivity with respect to the aliphatic analog. These can be undesired features if the monomer has to be employed in the formulation of a coating for outdoor applications where colorlessness and, more generally, interaction with UV-Vis light can be critical parameters. As opposed to the aromatic maleimides, only a limited number of papers report on the synthesis and use of N-alkylmaleimide as monomers or reagents in free-radical processes, and only one, to our knowledge, deals with a fluorinated N-alkylmaleimide [42]. These latter are potentially interesting building blocks for new polymeric materials with applications as protective coatings for valuable surfaces, such as in the preservation of works of art and waterproofing of historic buildings, or in optics and electronic applications [43]. In addition they can be used as fluorinating agents for polyolefins through free-radical grafting, which was shown to be an efficient method of direct melt functionalization of high density polyethylene (HDPE) with a fluoroalkyl substituted N-arylmaleimide [44]. Freeradical grafting should be a viable route also for reactions in

solution, although no examples are reported with a maleimide derivative as the monomer. A procedure frequently found involves the post-modification of maleated polyolefins with an amine or amine-terminated macromolecule [45,46]. However, such approach is likely to lead to lower grafting yields, and therefore to less efficient use of the aminofunctional derivative.

This can be a major concern when the functional reagent is a costly one, such as a highly fluorinated molecule, which is also expected to be poorly miscible with a hydrocarbon matrix. On the other hand, fluorination of polyolefins can result in new materials with novel surface properties, such as ultra-low friction coefficient and oil repellence, as well as improved compatibility with fluorinated thermoplastic and elastomeric polymers.

We have therefore synthesized *N*-(2-pentadecafluoro-*n*-octanoyloxy)-ethyl)maleimide (FOMI) in order to study its behavior in free-radical copolymerization and grafting reactions.

### 2. Results and discussion

The fluorinated N-alkylmaleimide derivative N-(2-pentadecafluoro-n-octanoyloxy)-ethyl) maleimide (FOMI) was synthesized by way of the intermediate 3,6-oxy-(1,2,3,6tetrahydro)phtalic anhydride (1), the adduct of maleic anhydride (MAH) and furan that is easily obtained by simple Diels Alder addition reaction. The adduct is stable at the relatively high temperatures generally required to carry out the cyclization of a *N*-alkylmaleamic acid to the respective imide (see Scheme 3), thus allowing to substantially increase the yield of imidation of maleic anhydride with an aliphatic amine. Indeed the latter is usually very low in the direct imidation of MAH, due to the moderate but not negligible reactivity of the MAH C=C and the consequent formation of polymerization products. In fact, previous attempts to prepare the imide by direct condensation of the maleamic acid obtained from MAH and ethanolamine under relatively mild conditions were unsuccessful. A first attempt carried out in the presence of catalytic H<sub>2</sub>SO<sub>4</sub> at room temperature for several days gave negligible yields, in poor agreement with a





previous report maintaining a 51% conversion [47]; a second attempt run in heterophase with aqueous phosphoric acid in refluxing xylene solution, according to the method adopted by Kita et al. [48] for isopropylamine, led to the formation of insoluble polymerization products.

The synthesis through the intermediate 1 proceeds smoothly, although in moderate yields due to the selective reactivity of the endo-isomer of the adduct 1. Indeed the latter was obtained as a 2/1 exo/endo mixture (Scheme 4), the main product being the thermodynamically favored exo isomer due to steric compression that promotes fast isomerization of the kinetically favored endo isomer. Aminolysis of 1 with stoichiometric ethanolamine, carried out in the presence of an initial excess of ethanolamine in order to prevent competitive alcoholysis of the anhydride, gave the maleamic acid (2), which underwent dehydration-cyclization by mild thermal treatment in refluxing ethanol. The same reaction led to unidentified polymerization products when carried out at higher temperature using 2-methoxyethanol as the solvent, due to retro-Diels Alder cleavage of the protecting group on the maleic C=C bond. Isolation of pure N-(2'hydroxyethyl)-(3,6-endoxy-1,2,3,6-tetrahydro)phtalimide (3) from the crude product was achieved with best results by way of chromatographic separation (about 23% yield, in addition to some 10% uncondensed amic acid precursor). Simple reprecipitation from ethanol at T = -25 °C afforded the same product but in lower yield (about 15%). Both products corresponded to the pure exo isomer. The moderate overall yield was at least partially due to some unavoidable retro-Diels Alder and polymerization side reactions.

The imide-alcohol (3) then underwent concurrent retro-Diels Alder [49] and esterification reaction with pentadecafluoro-*n*-octanoic acid [50] under mild conditions with an inorganic catalyst (sodium bisulfate) and upon azeotropic



Scheme 4.

water removal, yielding the *N*-(2-(pentadecafluoro-*n*-octanoyloxy)-ethyl)maleimide (**4**) (FOMI). Unexpectedly, the fluorinated *N*-alkylmaleimide thermal stability is quite poor, and similar to that of the perfluorocarboxylic acid precursor, as shown by the thermal degradation curve of Fig. 3 where the onset of the first pyrolytic step is observed just above 100 °C. This initial degradation, associated with loss of the *N*-perfluoroalkylcarboxyethyl moiety, is followed by complete volatilization of the residue at temperatures above 400 °C.

The reactivity of the fluorinated maleimide as a monomer in free-radical graft- and copolymerization reactions was then investigated.

#### 2.1. Copolymerization with butyl vinyl ether (BVE)

The reactivity of FOMI was firstly tested in copolymerization reactions with VE. A single experiment was carried out, using a large molar excess of BVE (FOMI/BVE = 32/68) in order to favor its incorporation in the copolymer structure, that is through growth of alternating comonomer sequences. The resulting FOMI/BVE = 63/37 copolymer composition, as determined from the <sup>1</sup>H NMR resonances at 4.7–4.3 and 1.0–0.7 ppm, respectively, indicates that homopropagation of the maleimide prevails over comonomer alternation, although the low conversion (overall = 39%; FOMI = 49%) and low molecular weight of the resulting copolymer  $(M_n = 11,000 \text{ g/mol}, M_w/M_n = 1.45 \text{ by SEC})$  suggest also a low homopropagation efficiency in these conditions.

#### 2.2. Graft reactions on olefin copolymers (OCP)

The poor thermal stability of the fluorinated compound suggested to avoid using it for direct polyolefin grafting in the melt, since the method usually requires temperatures that exceed the melting temperature of polyethylene (and thus of most olefin copolymers), that is well above the stability range of pure FOMI. However, solution grafting of polyolefins in the presence of free-radical initiators can be successfully achieved with MAH and other poorly homopropagating disubstituted olefins [51]. In order to generate a sufficiently high concentration of free radicals at a temperature well within the stability range of FOMI, grafting



Fig. 3. Pyrolytic weight loss curve of FOMI. Extrapolated onset of first stage:  $157 \,^{\circ}$ C; residue at 300  $^{\circ}$ C: 15.9%.

reactions were performed in benzene at T = 70 °C with Perkadox<sup>TM</sup>16 as the initiator (half life  $t_{1/2} = 20$  min at T = 70 °C). The reactivity of two different olefin copolymers (OCP), a linear very low density polyethylene (VLDPE, a copolymer of ethylene and 1-octene) and an ethylene–propylene copolymer (EPM), were preliminarly tested with MAH as the grafting monomer.

Similar polyolefin/monomer molar ratios were fed to the reaction solutions in both MAH and FOMI grafting experiments, corresponding to a 1/1 polyolefin/FOMI weight ratio (see Table 1). Such a high concentration of grafting monomer was employed with the aim of maximizing the functionalization degree (FD), according to previous unpublished results from our laboratory, and thus allow a quantitative determination of the grafting efficiency by means of spectroscopic techniques (IR, NMR); in fact, differently from the products of grafting with MAH, the titration method could not be used for the polyolefin-FOMI adduct. A relatively high monomer-to-initiator molar ratio and minimum amount of solvent were used in order to minimize cross linking and radical transfer side reactions, leading to gel formation and increased fraction of ungrafted material, respectively. The polymers grafted with MAH were exctracted with acetone to remove low molecular weight by-products and unreacted monomer, then with toluene to separate the soluble fraction from any gel-like material deriving from crosslinking reactions competitive with the grafting process. VLDPE-g-FOMI was redissolved in *n*-hexane and chloroform after the acetone extraction, to

Table 1							
Free-radical	grafting	of maleic	derivatives	onto	olefin	copolymers	(OCP)

Sample <sup>a</sup>	OCP/monomer <sup>b</sup> (mole ratio)	Monomer/initiator (mole ratio)	FD <sup>c</sup> (%)
VLDPE-g-MAH	10.3	10	0.51
EPM-g-MAH	14.7	10	0.35
VLDPE-g-FOMI	11.4	5	2.00

<sup>a</sup> Grafting reaction of maleic monomer (MAH or FOMI) in benzene solution; initiator Perkadox 16, T = 70 °C, 3 h.

<sup>b</sup> Average MW of OCP repeat units is used, based on copolymer composition.

<sup>c</sup> Functionalization degree (moles of grafted succinic derivative per 100 olefin repeat units) as determined by titration (MAH) or <sup>1</sup>H NMR (FOMI).

exclude the possibility of thermal decomposition of the maleimide derivative in hot toluene.

In the grafting reactions with MAH, the VLDPE solution was comparatively less viscous than that of EPM, the latter becoming increasingly more viscous during the reaction due to the larger fraction of crosslinked material formed. In addition to favor gel formation, with less than 50% extractable polymer, the soluble fraction of EPM-g-MAH had a FD = 0.35%, lower than that of VLDPE-g-MAH (0.51%) and corresponding to a scant 2.5% conversion of the olefin (see Table 2). The following grafting experiment with FOMI was carried out only on VLDPE, since the EPM sample was shown to be more prone to crosslinking in the reaction conditions adopted.

The grafting reaction with FOMI, leading to the succinimidyl derivative VLDPE-*g*-FOMI (Scheme 5), proceeded with apparently lower overall conversion due to the larger olefin/OCP weight ratio, but actually gave about the same fraction of soluble graft copolymer (82 against 87% with MAH, see % gel in Table 2). The significantly higher FD can not be ascribed to the amount of initiator and thus of grafting sites, but rather to the probable growth of some oligomeric FOMI grafts, as expected when using a homopropagating maleimide instead of MAH. A moderate decrease of molecular weight in VLDPE-*g*-FOMI (see Table 3) is indicative of free-radical induced chain scission reactions competing with radical coupling and crosslinking processes leading to gel formation. However, no detailed analysis was made in order to further elucidate the actual mechanisms involved.

As an alternative approach to the above described polyolefin fluorination through free-radical grafting of FOMI,

Table 2

Free-radical grafting of activated olefins (MAH and FOMI) onto olefin copolymers (unless stated, values are given in mg)

Run	Conversion <sup>a</sup> (%)	Soluble fraction	OCP		Olefin		olefin	OCP
			Feed	Soluble fraction	Feed	Soluble fraction	Conversion (%)	% as gel
VLDPE-g-MAH	73	367	420	363	83	4	4.5	13
EPM-g-MAH	37	184	412	182	85	2	2.5	56
VLDPE-g-FOMI	40	88	110	72	110	16	15	18

<sup>a</sup> Soluble polymer fraction with respect to the total amount of OCP and grafting olefin.



Table 3 SEC analyses of VLDPE and graft-VLDPE

Sample	$M_{\rm n}~({\rm g/mol})$	$M_{\rm w}$ (g/mol)	$M_{\rm w}/M_{\rm n}$
VLDPE	91000	228000	2.5
VLDPE-g-FOMI	69000	180000	2.6

two synthetic pathways to chemical modification of functional MAH-grafted polyolefins (OCP-g-MAH) by means of aminolysis of the succinyl anhydride groups with formation of fluorinated maleimide grafts were considered, as shown in Scheme 6. These are: (i) reaction with an amidoamine derivative (**5**) of the perfluorinated carboxylic acid precursor; (ii) reaction with an amino-terminated FOMI copolymer (**6**).

The amidoamine (5) was synthesized by treatment of the fluorinated acid with oxalyl chloride in dry toluene at RT, followed by reaction of the resulting acyl chloride with a large excess of hexamethylenediamine. Unfortunately, the resulting fluorinated amidoamine was insoluble in all common unfluorinated organic solvents, making unpractical its use as a fluorinated modifier of OCP-g-MAH through reaction in solution at moderately high temperature. Melt functionalization was deemed unsuitable due to the expected thermal instability of the fluorinated amide.

A preliminary test of co-oligomerization with aminofunctional initiator was carried out to explore the feasibility of the route based on grafting of an amino-terminated FOMI oligomer (6) onto OCP-g-MAH. BVE was copolymerized with diethyl maleate (DEM), a disubstituted olefin expected to display a reactivity similar to that of a maleimide in freeradical copolymerization, using an aminofunctional diazocompound (2,2'-azobisisobutirroamidine hydrochloride, AIBA) as the initiator and thiol (aminoethanthiol hydrochloride, AET) as a chain transfer agent, in order to maximize the amount of NH<sub>2</sub>-terminated oligomeric products. The results, summarized in Table 4, indicate a quite poor control of the polymerization process, giving oligomeric products in low yield and with a less than quantitative degree of chain end functionalization (EFD). The addition of AET



Scheme	6.
Scheme	υ.

Table 4 Copolymerization of DEM and BVE in the presence of aminofunctional initiator and transfer agent

Run	AET (mol%)	Conversion <sup>a</sup> (%)	Composition <sup>b</sup> (DEM/BVE/AIBA)	$M_{\rm n}$ (g/mol)	$M_{\rm w}/M_{\rm n}$	Amidine end groups (% of chains) <sup>c</sup>
DEM/BVE1	-	39	15/7/1	2100	1.7	66
DEM/BVE2	2.5	24	3/0.5/1	700	2.8	36
DEM/BVE3	5.1	15	4.5/1.5/1	900	2.1	56

<sup>a</sup> Overall comonomer conversion (the contribution of chain end moieties from AIBA or AET is here neglected, thus the conversion can be slightly overestimated).

<sup>b</sup> Molar composition as determined by <sup>1</sup>H NMR; the fraction of aminoethylsulfide end groups from AET could not be evaluated.

<sup>c</sup> From the  $M_{\text{ncale}}/M_{\text{nexp}}$  ratio, where  $M_{\text{ncale}}$  is calculated from the copolymer molar composition, in the hypothesis that each macromolecule carries an amidine chain end from the initiator, and  $M_{\text{nexp}}$  is the experimental SEC value. Here the  $-NH_2$  end groups from AET are not included.

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as a chain transfer agent, while not granting a higher EFD, causes a further reduction of monomer conversion and an unexpected increase in polydispersity, in addition to lower the MW as expected. Due to these discouraging results, the analogous copolymerization with DEM replaced by more precious FOMI was not performed.

### 3. Concluding remarks

Following the main line of the research project aimed at producing fluorinated polymeric materials with different content and structural distribution of fluorine in the macromolecules, the grafting of long perfluoroalkyl chain ( $C_7F_{15}$ ) onto polyolefins was attempted. Maleic derivatives are suitable to give this grafting reaction initiated by free radicals produced in situ. For this reason a N-substituted maleimide was selected, as this molecule combines the grafting capacity of the maleic double bond with the versatility offered by the substituent on the N atom. In the present case three distinct approaches were preliminarly investigated for the grafting of the perfluoroalkyl chain onto ethylene/1-alkene copolymers. These were respectively based on either direct grafting of a N-substituted fluorinated maleimide (FOMI), or reaction of a MAH-grafted polyolefin with a low molecular weight amine or amino-terminated oligomer bearing the perfluoroheptyl group. The former approach was limited by the low thermal stability of FOMI, and could be successfully performed only in solution. The latter approaches offer on the other hand much higher versatility, and even if further optimization is needed, they can be considered as feasible procedures for the modification of polyolefins by free-radical addition of fluorinated molecules.

# 4. Experimental

### 4.1. General experimental procedures

Pentadecafluoro-n-octanoic acid (98%, trade name RM-258, a gift from Miteni S.p.A.), absolute ethanol (Carlo Erba, 99.8%), oxalyl chloride (Aldrich), aminoethanthiol hydrochloride (AET, Fluka) and 4,4'-tert-butylcyclohexyl peroxydicarbonate (Perkadox<sup>TM</sup> 16, Akzo) were used as received. Azobis-1,1-dimethyl-2-propionitrile ( $\alpha, \alpha'$ -azobisisobutirronitrile, AIBN, Akzo) and 2,2'-azobisisobutirroamidine hydrochloride (AIBA, Akzo) were recrystallized from ethanol; maleic anhydride (Carlo Erba) was recrystallized from anhydrous benzene. 1,6-Diaminohexane (Fluka) and diethyl maleate (Aldrich) were vacuum distilled (0.2 mmHg) and stored under nitrogen. Benzene (Carlo Erba) and butyl vinyl ether (BVE, Fluka) were distilled after refluxing over Na/K alloy. Dimethylformamide was fractionally distilled after refluxing over KOH. Poly(etheneco-propene) rubber (EPR CO-038 from Enichem Elastomers, 30 mol% of C<sub>3</sub> co-units) and low density polyethylene

(VLDPE Engage<sup>TM</sup> 8150 from Du Pont Dow Elastomers, 24 mol% of C<sub>8</sub> co-units) were purified by 8 h soxhlet extraction with acetone. Etanolamine (Aldrich) was distilled from KOH under inert atmosphere. Furan (Fluka) was distilled from Na. Tetrahydrofuran (Fluka) was twice distilled from Na and LiAlH<sub>4</sub>, respectively.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded from CDCl<sub>3</sub> or DMSO-d<sub>6</sub> solutions with a Varian Gemini 200 spectrometer operating at 200 and 50.29 MHz, respectively, using the solvent as an internal reference. <sup>19</sup>F NMR spectra were recorded on a Varian VxR-300 spectrometer operating at 282.2 MHz, using CFCl<sub>3</sub> as an external reference. FT-IR spectra were recorded either from KBr pellets or from films cast from CHCl<sub>3</sub> solutions of the polymers on KBr disks, using a Perkin Elmer 1330 instrument. A Reichert Polyvar polarizing microscope with Mettler FP52 hot plate was used for melting points determination. Thermogravimetric analysis (TGA) was performed with a Mettler TG50 thermobalance and Mettler TC11 processor, using dry nitrogen purge and a scan rate of 10 °C/min. Molecular weights were determined by size exclusion chromatography (SEC) from 5 g/l chloroform solutions, using a Perkin Elmer Mod. 2/2 pump with Rheodyne 7161 injector, two PL GEL Mixed C columns, a Jasco 830 RI differential refractometer and a Perkin Elmer LC-75 spectrophotometric detector, operating at 1 ml/min. A set of polystyrene standards ( $M_w$  2.1, 9.0, 19, 83 and 233 kDa) was used for calibration.

# 4.2. Determination of the functionalization degree (FD) of MAH-grafted polyolefins

The degree of functionalization (FD), defined as the moles of grafted MAH per 100 polyolefin monomer units, was determined by titration as previously described [52]. The procedure followed for VLDPE-*g*-MAH is reported here as a representative example.

A 500 ml flask fitted with reflux condenser and oil bath was loaded with VLDPE-g-MAH (0.229 g), 150 ml toluene and 100 ml of a 85/15 v/v *n*-butanol/water solution). The mixture was stirred 1 h at 77 °C until complete dissolution of the polymer, then purged 15 min with nitrogen. The solution was titrated with 1.20 ml of 0.0388N KOH in butanol (previously standardized against 0.0510N *p*-toluensulfonic acid) using thymol blue as an indicator; after adding an additional 2 ml KOH solution the mixture was back-titrated with 1.25 ml of 0.0597N aqueous HCl (standardized against the KOH titration solution). FD is calculated as the mean of direct and back titration (0.50 and 0.53%, respectively).

# 4.3. Synthesis of N-(2-(pentadecafluoro-n-octanoyloxy)ethyl) maleimide (FOMI) (4)

### 4.3.1. 3,6-Oxy-(1,2,3,6-tetrahydro)phtalic anhydride (1)

In a 250 ml three-necked flask with magnetic stirrer and reflux condenser containing 9.80 g (0.100 mol) of maleic anhydride dissolved in 100 ml of anhydrous benzene, were

added under dry nitrogen with a dropping funnel 6.81 g (0.100 mol) of freshly distilled furan. After 2 h stirring at room temperature a precipitate had formed; stirring was maintained for another 24 h, the solid filtered off under dry nitrogen and washed with anhydrous benzene. The resulting white crystals were a 2/1 exo/endo mixture of the title compound (15.65 g, 94% yield); mp 124-125 °C (lit. 125 °C) [53]. IR (KBr pellet): v 3098, 3067, 3035, 2995 (C–H); 1860 (broad,  $v_{as}$  C=O); 1795 (broad,  $v_{svm}$  C=O) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, T = 50 °C):  $\delta$  7.45 (2H, dd,  $J_1 = J_2 = 1,5$  Hz, O-CH endo), 7.00 (2H, s, =CH endo), 6.55 (2H, dd, J = 1,5 Hz, =CH exo), 6.40 (2H, dd, J = 1,5 Hz, -CH-C-O endo), 5.45 (2H, dd, J = 1,5 Hz, -O-CH exo), 3.15 (2H, s, -CH-C-O exo) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, T = 50 °C):  $\delta$  169.8 (C=O), 136.9 (=CH exo), 136.4 (=CH endo), 109.4 (O-CH endo), 82.2 (O-CH exo), 48.7 (CH-C-O) ppm.

# 4.3.2. N-(2'-hydroxyethyl)-3,6-endoxy-1,2,3,6tetrahydrophtalimide (**3**)

To a 100 ml two-necked flask with magnetic stirrer and reflux condenser containing 1.84 g (0.030 mol) ethanolamine and 50 ml absolute ethanol, was added 1 (4.98 g, 0.030 mol) under nitrogen in little portions during 1 h. The suspension was stirred 18 h at room temperature, then refluxed 5 h in ethanol. The resulting limpid colorless solution was divided in two fractions: the first was reduced to about 20 vol.% at the rotary evaporator, left overnight at -25 °C and the obtained precipitate filtered off, washed with absolute ethanol and vacuum-dried (yield 15%); the second evaporated under reduced pressure and purified by silica gel chromatography with 5/4 methanol/ethyl acetate as the eluent (yield 23%). Both procedures gave the same white crystalline product as pure exo-isomer. mp 124-125 °C (decomposition). IR (KBr pellet): v 3480 (O-H); 3098, 3035, 3000, 2970, 2936, 2892 (C–H); 1766 (*v*<sub>as</sub> C=O); 1692 (*v*<sub>sym</sub> C=O), 1436, 1402, 1332, 1166, 1056, 1014, 876 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.5 (2H, d, *J* = 1, 5 Hz, =CH), 5.25 (2H, d, *J* = 1, 5 Hz, -O-CH), 3.75-3.60 (4H, m, N-CH<sub>2</sub>-CH<sub>2</sub>), 2.9 (2H, s, CH-C=O), 2.7-2.1 (1H, broad, –OH) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  176.7 (C=O), 136.4 (=CH), 80.9 (O-CH), 60.0 (CH<sub>2</sub>-OH), 47.4 (CH–C=O), 41.6 (N–CH<sub>2</sub>) ppm.

# 4.3.3. N-(2-(pentadecafluoro-n-octanoyloxy)ethyl)maleimide (FOMI) (4)

A 250 ml three-necked flask equipped with magnetic stirrer and Dean Stark apparatus was loaded with pentadecafluoro-*n*-octanoic acid (2.07 g, 0.005 mol), **3** (0.81 g, 3.8 mmol), sodium bisulfate monohydrate (0.058 g, 0.42 mmol) and 100 ml of dry benzene. The mixture was refluxed 24 h while removing the azeotropic water and monitoring the conversion by NMR. After roto-evaporation of the remaining solvent, purification of the raw solid by flash chromatography with 3/2 ethyl acetate/*n*-hexane elution gave 0.73 g of a white crystalline product (yield 35%): mp 80–81 °C. IR (KBr): v 3110, 2960, 1776 (v<sub>as</sub> C=O), 1710 ( $v_{sym}$  C=O), 1448, 1410, 1328, 1260, 1204, 1142, 1090, 1024, 928, 804, 696 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.73 (2H, s, =CH), 4.52 (2H, t, J = 5.5 Hz, CH<sub>2</sub>-O-C=O), 3.90 (2H, t, J = 5.5 Hz, N-CH<sub>2</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  170 (C=O), 134.4 (=CH), 130–105 (m, -(CF<sub>2</sub>)<sub>6</sub>-CF<sub>3</sub>), 64.9 (O-CH<sub>2</sub>), 36.0 (N-CH<sub>2</sub>) ppm. <sup>19</sup>F NMR (CDCl<sub>3</sub>) [54]: -81.3 (3F, t, CF<sub>3</sub>), -118.8 (2F, d, -CF<sub>2</sub>-C=O), -122.2, -122.5, -123.1, -123.2 (8F, s, -(C<u>F<sub>2</sub>)<sub>4</sub>-CF<sub>2</sub>-CF<sub>3</sub>), -126.6 (2F, s, -CE<sub>2</sub>-CF<sub>3</sub>) ppm.</u>

### 4.4. Polyolefin grafting reactions

# 4.4.1. Solution grafting of MAH onto VLDPE (VLDPE-g-MAH)

VLDPE (0.420 g, approximately 8.7 mmol of olefin co-units) was introduced under inert atmosphere in a 100 ml schlenk containing MAH (0.083 g, 0.84 mmol) in 10 ml dry benzene. The mixture was stirred at 50 °C until complete dissolution of the polymer, then cooled down at room temperature before adding with a syringe a solution of Perkadox 16 (0.032 g, 0.084 mmol) in 6 ml of benzene. The clear and fluid solution was then stirred 3 h at 70 °C, becoming viscous and cloudy after the first 20 min. The polymer was recovered by precipitation in acetone, then extracted in soxhlet first with acetone to remove unreacted low MW compounds, then with toluene. The toluenic solution was evaporated to give 0.37 g of VLDPE-g-MAH (73% yield). IR (film on KBr): v 2922, 2856 (C-H), 1776 (v as C=O), 1724 (v<sub>svm</sub> C=O), 1460, 1364, 1260, 1090, 1028 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  3.7–3.6 (broad, CH–C=O), 3.3–2.6 (broad, CH<sub>2</sub>– C=O), 2.2-1.9 (broad, CH VLDPE), 1.25 (broad, CH<sub>2</sub> VLDPE), 0.9–0.8 (t, CH<sub>3</sub> VLDPE) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>) [55]: δ 170.5 (C=O, graft-MAH), 38.8 (CH g-MAH), 37.2 (main chain -CH-), 34.6 (CH<sub>2</sub>, g-MAH), 33.8 (main chain -CH<sub>2</sub>-CH-), 33.5 (side chain *n*-pentyl-CH<sub>2</sub>), 31.7 (side chain CH<sub>2</sub>-Bu), 29.9 (CH<sub>2</sub>-Pr), 29.5 (main chain -<u>C</u>H<sub>2</sub>-CH<sub>2</sub>-), 26.5 (CH<sub>2</sub>-Et), 22.5 (CH<sub>2</sub>-Me), 13.9 (CH<sub>3</sub>) ppm.

# 4.4.2. Solution grafting of FOMI onto VLDPE (VLDPE-g-FOMI)

Following the same procedure described for VLDPE-g-MAH, FOMI (0.110 g, 0.20 mmol) and VLDPE (0.110 g) were dissolved in 3 ml dry benzene; the reaction was carried out upon addition of Perkadox 16 (0.015 g, 0.04 mmol) in 2 ml benzene; after approximately an hour the solution, initially fluid and limpid, had become viscous and whitish. The polymer was precipitated and extracted with acetone, then separated from the insoluble fraction by soxhlet extraction first with *n*-hexane then with chloroform. The unified extracts gave 0.088 g (40%) of succinimide-graft copolymer. IR (film on KBr): v 2960, 2922, 2854 (C-H), 1786, 1710 (C=O), 1462, 1402, 1336, 1256, 1210, 1146, 1092,  $1024, 802 \text{ cm}^{-1}$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.6–4.4 (2H, CH<sub>2</sub>–O), 4.1 (H, CH-C=O), 3.95-3.75 (2H, N-CH<sub>2</sub>), 2.3 (2H, CH<sub>2</sub>-C=O), 2.1-1.5 (main chain CH), 1.4-1.1 (16H, CH<sub>2</sub> VLDPE), 1.0-0.7 (3H, CH<sub>3</sub>) ppm.

#### 4.4.3. Poly(FOMI-co-BVE)

A 10 ml test tube with magnetic stirrer was charged with FOMI (0.162 g, 0.30 mmol), BVE (0.062 g, 0.62 mmol), AIBN (5.0 mg, 0.03 mmol, 3.3 mol% with respect to the total amount of comonomers) and 1 ml THF, the solution was freeze-pump-thaw degassed and heated 60 h at 65 °C. The copolymer was precipitated in 50 ml methanol, filtered off and washed repeatedly with *n*-hexane, leaving 0.088 g (39% yield) of product. IR (film on KBr): v 2964-2878 (C-H), 1784, 1706 (C=O), 1400, 1334, 1240, 1208, 1148, 1088, 1020, 802 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.6–4.4 (2H, CH2-O-C=O), 4.1-3.6 (2H, N-CH2), 3.6-2.4 (3H, -CH-O-CH<sub>2</sub>-), 2.4-1.7 (2H, -CH-CH- imide units), 1.7-1.5 (2H, main chain -CH<sub>2</sub>-), 1.5-1.1 (4H, CH<sub>2</sub>-CH<sub>2</sub>-Me), 1.0-0.6 (3H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 178.0 (C=O), 130-100 (perfluorinated carbons), 73-70 (O- CH), 69-68 (-CH-O- CH2), 66-63 (- CH2-O-C=O), 51-48 (main chain -CH<sub>2</sub>-), 38-36 (N-CH<sub>2</sub>), 34-32 (-CH-CH- imide units), 32-31 (-CH<sub>2</sub>-Et), 19.1 (-CH<sub>2</sub>-Me), 13.7 (-CH<sub>3</sub>) ppm.

# 4.4.4. Poly(DEM-co-BVE)

All polymerizations were carried out in DMF at 70 °C during 24 h, using the same comonomers-to initiator ratio (50/50 BVE/DEM, 1.1 mol% AIBA). In a typical run DEM (1.72 g, 10 mmol), BVE (1.0 g, 10 mmol), AIBA (60 mg, 0.22 mmol), and AES (56 mg, 0.49 mmol) were introduced into a 50 ml test tube with 8 ml DMF, freeze-pump-thaw degassed and polymerized 24 h at 70 °C under magnetic stirring. The final product was taken up with diethyl ether, extracted sequentially with water, 0.1 N HCl, 0.5 M NaHCO<sub>3</sub> and H<sub>2</sub>O, the ethereal phase was then dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent and unreacted DEM by vacuum heating to 70 °C/0.2 mmHg afforded 0.66 g (24%) of polymeric product. The copolymer composition was calculated from the <sup>1</sup>H NMR resonances centered at 6.8 (AIBA chain end), 4.1 (DEM units) and 0.85 (BVE units) ppm, while the average fraction of AIBA-terminated chains was calculated from the average composition and the number average molecular weight, as determined by SEC. IR (film): v 3638–3442 (NH<sub>2</sub>, NH), 2982, 2962, 2938, 2908, 2874 (C-H), 1728 (C=O), 1466, 1448, 1370, 1298, 1260, 1226, 1176, 1156, 1096, 1034, 980, 860, 798 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.8 (-C(=NH)-NH<sub>2</sub> from AIBA chain ends), 4.4–3.8 (2H, -COO-CH<sub>2</sub>), 3.6–3.0 (3H, -CH-O-CH<sub>2</sub>-), 3.0-2.1 (6H, main chain -CH-CH- from DEM, -S-CH<sub>2</sub>- CH<sub>2</sub>-NH<sub>2</sub>), 2.0-1.6 (main chain -CH<sub>2</sub>-), 1.4-1.1 (10H,  $-COO-CH_2-C\bar{C}_3$ ,  $-O-C\bar{C}_2-C\bar{C}_2-CH_2-Me$ ,  $-CH_3$ from AIBA chain ends), 0.9-0.7 (3H, -CH<sub>3</sub> from BVE) ppm.

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