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Fluorinated Polymeric Multilayers by Off-Stoichiometric Thiol-Ene Photopolymerization

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This article reports the synthesis of a novel perfluoropolyalkylether (PFPAE) vinylether monomer and its use as a comonomer in the thiol-ene photopolymerization of a trifunctional thiol together with a trifunctional vinylether. The crosslinked copolymers are obtained in the form of few mm thick layers and characterized. By changing the thiol/ene ratio, the polymers are optimized to tailor their surface composition and obtain adhesion between two thick layers despite the presence of the fluorinated monomer. The final bilayered structures are adhesive, and appeared chemically resistant, with good dimensional stability: therefore, these fluorinated thiol–ene based copolymers are likely to be of interest for applications based on layer-by-layer processes, such as additive manufacturing and microfluidics.

1. Introduction

The thiol–ene photopolymerization, which is based on the addition of a thiol containing -SH groups to a monomer with an –ene functional group (i.e., a carbon double bond), offers both the advantages of click reactions and the benefits of the spatiotemporal controlled photoinduced processes.[1,2] The reaction is very fast and easily takes place in the presence of oxygen or water, eventually without the use of a photoinitiator. Due to a unique step-growth polymerization mechanism, the molecular-weight evolution in thiol–ene systems occurs slowly, delaying gelation: polymers obtained are homogenous networks characterized by low shrinkage stress and good thermomechanical properties.[3,4]

UV-curable thiol–ene systems typically consist in perfectly balanced stoichiometric mixtures, ideally containing the same equivalents of thiol and ene functionalities.[5,6] However, the use of thiol–ene off-stoichiometric formulations, i.e., mixtures characterized by an excess of one of the two functional groups, allows to realized polymeric networks having remaining reactive sites. By changing the degree of off stoichiometry, it is possible to control the density of unreacted groups present at the surface of the cured networks: this leads to the production of polymers suitable for further modification to get tunable properties and showing strong adhesion to metal and glass substrates. Off-Stoichiometry Thiol-Ene (OSTE) polymers allow post functionalization, e.g. the covalent attachment of hydrophilic and/or biological sensing molecules[7,8] and enzymes.[9] In applications where the adhesion among layers is essential, namely additive manufacturing and microfluidics fabrication, the presence of reactive groups at the surface of OSTE networks can be exploited to form covalent bonds and avoid adhesive failure among layers.[10–12]

In synthesizing a thiol-ene network, also changing average functionality has a profound effect on properties. In particular the addition of a monothiol comonomer to a polyfunctional thiol not only leads to a decrease in the concentration of functional units that serve as crosslinkers but also enhances termination, excluding some of the arms of the polythiol from extending to an infinite gel.[13] As there is a drastic decrease in the crosslinking density, the polymers show low Tg and low Young modulus, thus facilitating adhesion.

Following these guidelines, we exploited off-stoichiometric thiol-ene chemistry to promote adhesion of fluorinated photopolymers that are well known for their very low surface energy, thus inherently non adhesive,[14] while exhibiting interesting properties such as excellent thermal and chemical resistance.[15] Ternary off stoichiometric thiol–ene–ene systems were photopolymerised, formed by hydrogenated thiol and vinyl ether resins and a newly synthesized monofunctional fluorinated vinyl

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ether comonomer (present at the 25 w/w% of the hydrogenated –ene counterpart), where the fluorinated chain is a perfluoropolyalkylether (PFPAE) based on a hexafluoropropylene oxide structural unit.[16] PFPAE is a highly fluorinated building block imparting interesting properties to materials such as low friction, low glass transition temperature, very low refractive index. It has found relevant applications in high tech fields such as polymeric electrolytes for batteries,[17] microfluidic and lab-on-a-chip devices:[18,19] however, the low adhesion makes the joining and assembling of parts difficult and common rubber adhesives do not work, as they are not able to even wet the surface of the products.[20] Moreover, fluorinated polymers can be of interest in vat polymerization which is the process behind several 3D printing techniques, namely stereolithography: the good adhesion among layers is crucial for successful fabrications.[21]

The present paper investigates the photopolymerization kinetics of a novel fluorinated thiol–ene system to optimize the curing process and tailor the polymer surface composition by changing the stoichiometry. It shows that multilayered fluorinated structures can be fabricated obtaining good interfacial adhesion between the different layers.

2. Experimental Section

2.1. Synthesis of the PFPAE-DEGVE

2.1.1. Materials

Hexafluoropropylene oxide (HFPO) was generously supplied by Chemours, USA; cesium fluoride and tetraethylene glycol dimethyl ether were purchased from Sigma–Aldrich, Canada. Methoxyperfluorobutane (Novec™ HFE-7100) was purchased from 3M, USA.

1,1,1,3,3-Pentafluorobutane (PFB) was purchased from Alfa Caesar, USA; di(ethylene glycol) monovinyl ether (DEGVE), 4-dimethylaminopyridine (DMAP), and all other chemicals were purchased from Sigma–Aldrich, Canada. Triethylamine (Et_3N), PFB, and dichloromethane (DCM) were dried for 48 h over preconditioned 3 Å molecular sieves (20% w/v); all other chemicals were used as received.

2.1.2. Procedure

HFPO anionic ring-opening polymerization was conducted according to the following synthetic procedure[22,23] obtaining a monofunctional PFPAE acyl fluoride. In details: in a nitrogen-purged glovebox, dry CsF (1 equiv., 10 mmol, 1.52 g) was added to an Ace glass reactor tube and dissolved in 5 mL of anhydrous tetraglyme by stirring for 30 min at room temperature. Then, 10 mL of anhydrous HFE-7100 were added, while gaseous HFPO (1 equiv., 10 mmol, 1.66 g) was weighed into a reservoir cylinder. The CsF/tetraglyme/HFE-7100 mixture was cooled at $T = -32$ °C, HFPO was slowly introduced into the reactor through a calibrated metering/condensing equipment: the slurry was allowed to dissolve for 12 h at −32 °C under vigorous stirring. Additional monomer (7 equiv., 0.07 mol, 11.61 g) was added again to the mixture kept at −32 °C. The mixture was warmed up to 0 °C, stirred for at least 1. The salt precipitated on the bottom of the reactor tube was removed as well as the tetraglyme, which slowly separated from the oligomer without stirring.

The monofunctional PFPAE acyl fluoride $M_n = 1380$ g mol^{-1} (20 g, 14.47 mmol, 10 mL) was dissolved in 50 mL of dried PFB, added to a 500 mL 3-necked round-bottomed flask and cooled at 0 °C. A mixture of triethylamine (2.2 mL, 15.93 mmol, 1.1 equiv.), DMAP (53.1 mg, 0.43 mmol, 3 wt.%), and di(ethylene glycol) monovinyl ether (21.75 mL, 15.93 mmol, 1.1 equiv.) in 50 mL of dry 40:60 DCM:PFB solution, was added, dropwise, to the PFPAE acyl fluoride/PFB solution, at 0 °C, under continuous stirring. After 30 min, the ice bath was removed, and the reaction mixture was let to stir at room temperature during 12 h. Due to the high moisture-sensitivity of PFPAE acyl fluoride, all the operations were performed in a glovebox or under inert atmosphere. The reaction was followed by thin layer chromatography (TLC) and stopped in ≈12 h; powdered iodine was used as TLC stain and a 5:95 ethyl acetate/pentane solution as eluent. The conversion of the acyl fluoride into the corresponding vinyl ether was checked by the appearance of orange-brown spots on light yellow background, located between the baseline of the TLC plate and the eluent. The reaction mixture was purified by flash chromatography (5:95 ethyl acetate/pentane solution was used as eluent) obtaining ~80% isolated yield of pure product (transparent oil).

The structure of the PFPAE-DEGVE was confirmed by ^{1}H-NMR, ^{19}F-NMR, ^{13}C-NMR, GC-MS, and MALDI-ToF-MS (see Figures S1–S6 in Supporting Information).

The MW of the product was estimated by ^{19}F-NMR (See Supporting Information).

2.2. Thiol-ene Photoinduced Photopolymerization

2.2.1. Materials

Synthesized PFPAE-DEGVE, trimethylolpropane trivinyl ether (TVE, kindly provided by BASF, Germany), and trimethylolpropane tris-(3-mercaptopropionate) (TRIS, purchased by Sigma–Aldrich, Italy) were used as comonomers. The chemical structures of the products are in **Figure 1**. 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur 1173 by BASF, Germany) was used as radical photoinitiator.

2.2.2. Procedure

PFPAE-DEGVE was copolymerized with TVE and TRIS, with 1 wt.% of photoinitiator: compositions are in **Table 1**. They were prepared by mixing different amounts of TRIS with the ene components, i.e., a mixture of PFPAE-DEGVE and TVE at a fixed weight ratio of 1:4 (3.6 mol%), corresponding to the maximum solubility of the fluoromonomer in TVE. Thiol/ene ratios were 1:1 or off-stoichiometry, i.e., 2:1 and 0.5:1.

The conversion χ of the photopolymerization reaction was monitored by Fourier Transform-Infra Red (FT-IR) spectroscopic analysis, in transmission mode and in Attenuated Total Reflectance (ATR) mode. Trasmission FT-IR spectroscopic analyses were performed in real time using a Nicolet iS50 FT-IR

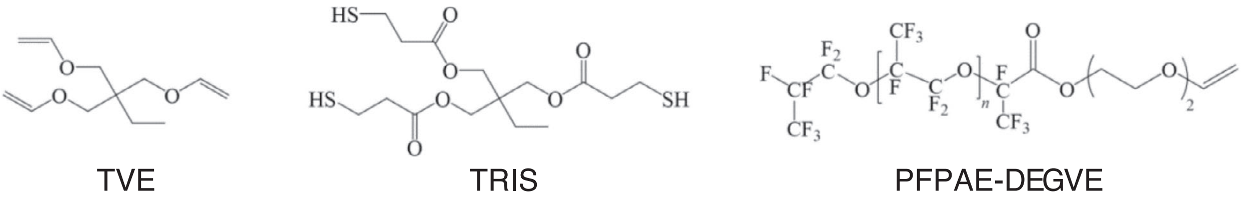


Figure 1. Chemical structure of the employed comonomers.

spectrometer (Thermo Fisher Scientific): simultaneously with the FT-IR scan acquisition, thin films (i.e., ≈10 µm on a Si wafer as substrate) of the reactive comonomers mixtures were irradiated with an UV mercury-xenon Lightningcure LC8 lamp (Hamamatsu), provided of an optical fiber, having an intensity equal to 7.5 mW cm^{-2} on the sample surface. Light intensity was measured with a UV Power Puck II digital radiometer.

Polymerization conversion χ was followed by monitoring the decrease of the absorbance of the vinyl ether groups of TVE at 1615 cm^{-1} and PFPAE-DEGVE at 1640 cm^{-1}, and of the TRIS thiol groups at 2570 cm^{-1} as a function of the irradiation time. Conversion was estimated according to the following equation:

$$\chi = 1 - \frac{A_t}{A_0} \qquad (1)$$

where A_t is the absorbance of a specific reactive group at time t and A_0 is the absorbance at t = 0. The derivative of the first order of the functional group conversion ($d\chi/dt$) was calculated in order to study the rate of photopolymerization of the reactive mixtures. The experimental data were then fitted with a polynomial expression of the third order.

FT-IR spectra were also recorded in ATR mode, employing a Nicolet Smart iTX accessory equipped with an ATR diamond crystal, to check the monomer-to-polymer conversion of thick samples (layer thickness ~ 1 mm), cured in silicone molds by using an UV mercury-xenon Lightningcure LC8 lamp (Hamamatsu), provided of an optical fiber, with a light intensity of 7.5 mW cm^{-2} for 10 s of irradiation. ATR FT-IR spectra were recorded on both sides of the layer, i.e., on the surface in contact with the mold during the photocuring, and on the air side, i.e., the surface exposed to the air during the photocuring.

2.3. Fabrication of Bilayers

Fluorinated thiol–ene copolymers were employed to fabricate bilayers using sequential photopolymerization steps. First, the formulation was poured into a 2 cm × 1.5 cm × 0.25 cm PDMS mold. The mold, partially filled, was irradiated in air for 10 s through an optic fiber connected with a UV mercury-xenon Lightningcure LC8 lamp (Hamamatsu). The light intensity (i.e., 7.5 mW cm^{-2}) was measured with a UV Power Puck II digital radiometer. Then, the fresh formulation was added on the surface of the cured layer and was exposed to UV light, with the same conditions as the first layer (intensity = 7.5 mW cm^{-2}, time = 10 s).

2.4. Polymer Characterization

Dynamic mechanical analyses (DMTA) were performed using a TT-DMA (Triton Technology Ltd) instrument at a frequency of 1 Hz in tensile configuration: the scans were carried out with a heating rate of 3 °C min^{-1} from –100 °C up to the temperature at which the rubbery state was reached (i.e., 50 °C). The size of the specimens was ≈20 mm × 10 mm × 1 mm. The T_g values were estimated by the maximum of the loss factor, tan (δ), curve.

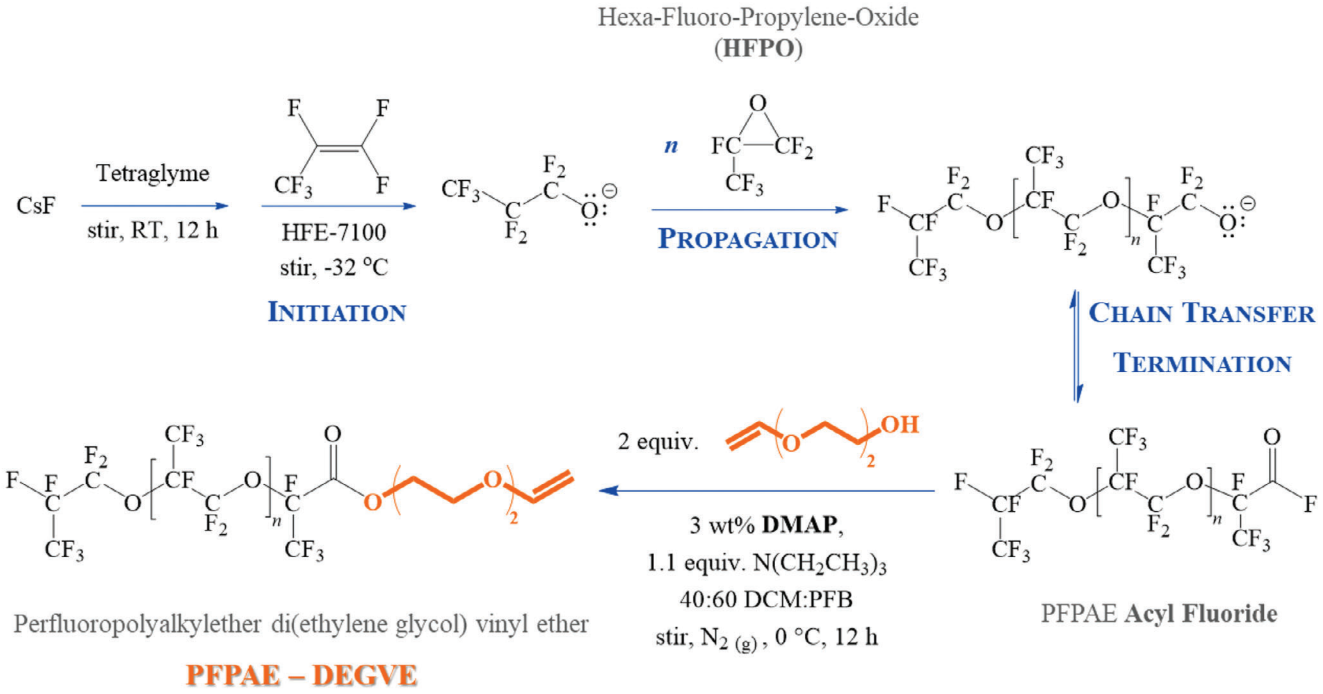
Chemical resistance and dimensional stability of the photocured copolymers were evaluated by swelling tests. Different bilayer samples were immersed in several solvents and weighed at different soaking time to evaluate the swelling trend. Swelling percentage was calculated through the following equation:

$$\text{Swelling } \% = \frac{W_t - W_0}{W_0} \times 100 \qquad (2)$$

where W_t is the weight of the material after soaking in a solvent for time t (measured immediately after removing the sample from the solvent) and W_0 is the original weight of the material.

Table 1. Composition of the thiol-ene photocurable formulations with different thiol/ene ratios.

SH:C = C ratio	PFPAE-DEGVE MW = 1502; C = C equivalent = 1502 (functionality = 1)	TVE MW = 212; C = C equivalent = 71 (functionality = 3)	TRIS MW = 399; -SH equivalent = 133 (functionality = 3)
0.5	1.5 g 1 mmol 12 w/w%	6.0 g 28 mmol 45 w/w%	5.7 g 14 mmol 43 w/w%
1	1.5 g 1 mmol 8 w/w%	6.0 g 28 mmol 32 w/w%	11.4 g 29 mmol 60 w/w%
2	1.5 g 1 mmol 5 w/w%	6.0 g 28 mmol 20 w/w%	22.8 g 57 mmol 75 w/w%



Scheme 1. PFPAE-DEGVE synthesis: Anionic ring-opening polymerization of HFPO and functionalization of the resulting fluorinated acyl fluoride with a di(ethylene glycol) vinyl ether.

The adhesion between the photocured layers was evaluated by visual inspection and manual bending of the bilayer specimens after the photopolymerization reaction and after 24 h of water immersion at RT.

Static contact angle measurements were performed on both side of the copolymers, namely the substrate side (i.e., the surface of the polymerizing mixture in contact with the mold) and the air side (i.e., the surface of the polymerizing mixture exposed to air), using a FTA 1000C instrument, equipped with a video camera and image analyzer, at room temperature with the sessile drop technique. At least three measurements were performed on each sample and the values averaged. The probe liquid was water, whose surface tension is 72.1 mN m^{-1}.

The bilayer samples were examined with the use of an optical microscope (Olympus BX53 M).

3. Results and Discussion

3.1. Synthesis of the Fluorinated Monofunctional Vinylether Monomer PFPAE-DEGVE

A novel fluorinated vinyl ether monomer was synthesized (PFPAE-DEGVE): PFPAE-DEGVE structure is characterized by a perfluoropolyether chain (PFPAE) obtained by anionic polymerization of hexafluoropropylene oxide (HFPO), a diethylene glycol spacer (DEG) connected to the PFPAE moiety with an ester group, and a vinyl ether end group (VE). The pathway followed to synthesize PFPAE-DEGVE is made of few steps as shown in **Scheme 1** and described in the Experimental Section.

First, in the presence of an alkoxide as anionic initiator obtained from HFE, HFPO was polymerized, obtaining a fluorinated oligomer ended by an acyl fluoride, after chain transfer termination. The degree of polymerization was n≈6.4, and the number average molecular weight was 1380 g mol^{-1}. The acyl fluoride was made reacted with DEGVE through its hydroxy group, obtaining an ester. PFPAE-DEGVE was obtained in good yield (i.e., > 83% of isolated product) and, thanks to the purification by flash chromatography purity was very good (see ^{13}C-NMR, ^{19}F-NMR and ^{1}H-NMR spectra, GC-MS, and Maldi TOF spectra in SI).[22] The product appears as a transparent oil. The MW, estimated by ^{19}F-NMR (see SI), is 1502 g mol^{-1}.

3.2. Photopolymerization of Thiol-ene-Fluorinated ene Systems

PFPAE-DEGVE was used as a fluorinated monofunctional comonomer in the photopolymerization of a thiol-ene system, made of a hydrogenated trivinylether (TVE) and a trifunctional thiol (TRIS) (see structures in Figure 1). The thiol/ene ratio was either stoichiometric (1:1 ratio between the -SH groups and the ene functionality) or off-stoichiometric. In the off-stoichiometric thiol-ene systems (OSTE), there was either an excess of thiol groups (2:1 thiol/ene ratio) or an excess of vinylether groups (0.5:1 thiol/ene ratio), while the PFPAE-DEGVE content was maintained 3.6 mol%, with respect to TVE: this concentration corresponds to the maximum solubility of the fluoromonomer in TVE. The composition of the monomers was detailed in Table 1 of the Experimental section.

The photopolymerization conversion of the reactive groups was monitored by real time FT-IR:[24] the curves of the conversion χ of the different reactive groups are plotted in **Figure 2**, showing the decrease of the C=C double bonds of the TVE and

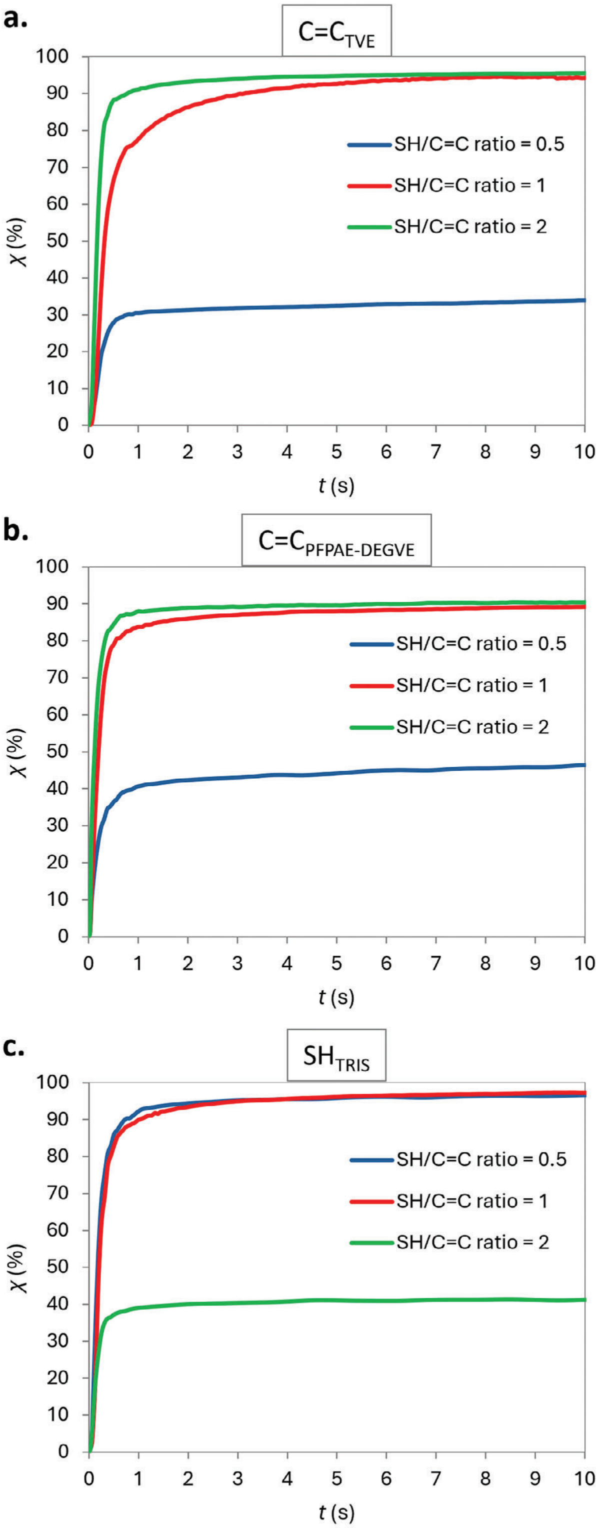
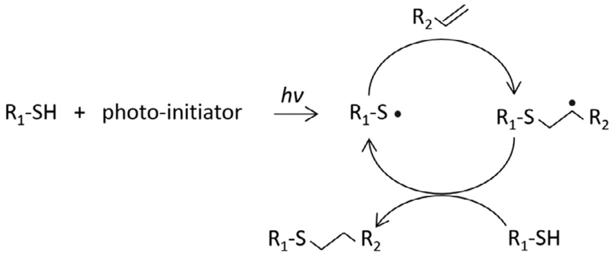


Figure 2. Real time FT-IR conversion χ curves as a function of irradiation time t of the copolymers having thiol/ene molar ratios of 0.5, 1, and 2. a) conversion of TVE double bonds (1615 cm^{-1}); b) conversion of PFPAE-DEGVE double bonds (1640 cm^{-1}); c) conversion of thiol groups (2750 cm^{-1}).



Scheme 2. Ideal step-growth polymerization mechanism of thiol-ene systems: propagation and chain transfer reactions continuously cycle proceeding at equal rates.

of the fluorinated monomer, together with the reduction of the -SH groups upon irradiation.

As it can be observed in Figure 2, the double bonds and the thiol functional groups react instantaneously when exposed to UV-light. The vinyl ether functionalities of TVE (Figure 2a), in both the stoichiometric formulation as well as the one having an excess of thiol groups, show quantitative conversion in less than 1 s, although exposed to a low intense irradiation (i.e., 7.5 mW cm^{-2}). When the vinyl functionalities are twice the thiols (thiol/ene molar ratio = 0.5), the double bonds conversion reaches a value ≈35%; the C = C groups in excess remain unreacted.

Monitoring the concentration of the double bonds of the fluorinated vinyl ether PFPAE-DEGVE (Figure 2b), similar results are obtained: the conversion χ of the unsaturation is 98% (even higher than TVE) when the thiol/ene ratio is either 1 or 2, the χ value is ≈41% when the thiol/ene ratio = 0.5. Thus, the PFPAE-DEGVE comonomer has a reactivity even higher than the hydrogenated TVE. It is reported for other light-mediated thiol–ene radical reactions that electron-rich vinyl ethers react more rapidly than electron-poor ones:[6] here, despite the presence of fluorine, reactivity is maintained. This means that the long-fluorinated chain does not lower the electron density of the functional group: it suggests that its electron withdrawing character has no effect and this can be due to the presence of the ethylene oxide spacer.

The thiol conversion χ versus irradiation time is reported in Figure 2c: χ reaches 100% when the thiols are either in stoichiometric amount or half the double bonds concentration. When the -SH groups are in excess (2:1 ratio) their conversion is ≈41%. Comparing equistoichiometric formulations (thiol/ene ratio = 1), the conversion of the double bonds and that of the thiol groups (reported in Figure 2) have very similar trends, thus confirming that in the step-growth photo-induced polymerization of the investigated systems, the propagation and the chain transfer steps proceed at equal rates, continuously cycling (**Scheme 2**). The reaction thus follows a step-growth polymerization chemistry, and there is no homopolymerization of the vinyl ether double bonds.[25] The polymerization under investigation is clearly representative of a true step growth polymerization with nearly equivalent consumption of the two functional groups.

A summary of the final conversions χ is reported in **Table 2**: the data confirm that the limiting reactant always reaches almost complete conversion, while the conversion of the group in excess is always less than 50%.

Table 2. Final conversion values by real time FT-IR (UV-light intensity of 7.5 mW cm^{-2}, irradiation time of 10 s), and gel point values for the UV curable formulations with different [SH]/[C = C] ratios.

[SH]/[C = C]	Functional group	Final conversion %	Experimental Gel point
0.5	TVE double bonds	33.8	19
	PFPAE-DEGVE double bonds	46.3	12
	Thiol	96.6	32
1	TVE double bonds	94.3	37
	PFPAE-DEGVE double bonds	89.3	32
	Thiol	97.2	35
2	TVE double bonds	95.5	31
	PFPAE-DEGVE double bonds	90.4	30
	Thiol	41.2	18

Polymerization rates (dχ/dt) can be estimated through the first derivative of the conversion data: they are plotted in **Figure 3** as a function of the conversion χ. Rates are found similar for both thiols and enes and dependent on the functional groups concentrations: as reported in the literature thiol-vinyl ether systems have roughly equivalent ratios of propagation to chain transfer kinetic parameters and polymerization rates scale roughly with the same order in both thiol and ene functional group concentrations.[6,25]

As expected, being the system multifunctional a tridimensional network is built, thus the polymerization at first speeds up, then reaches a maximum after which the rate slowly goes to zero. The maximum of the curing curves is conventionally interpreted as the gel point of the curable systems, when the reaction becomes diffusion dependent. Gel points are reported in Table 2.

As the glass transition of the polymers are lower than the reaction temperature (see next section), the reaction easily proceeds also after reaching the gel point: as discussed above, final conversions are almost quantitative (unless the monomer is in excess).

3.3. Characterization of the Photopolymers

The copolymers were casted in PDMS molds: 1 mm thick layers were obtained and characterized by ATR FT-IR spectroscopy. Typical spectra before and after irradiation are reported in **Figure 4**.

As highlighted by the colored bars in the spectra before irradiation of Figure 4a,b, the thiol groups are detectable at 2570 cm^{-1}, at 1620 cm^{-1} there this the absorption of the TVE double bonds, while the PFPAE-DEGVE stretching appears as a shoulder at a higher wavenumber, the C—S bond stretching mode is assigned to the band at 1140 cm^{-1}. After irradiation, the conversions of the double bonds and of the thiol groups were evaluated examining the spectra recorded on the air side of the samples (i.e., the side in contact with air during the irradiation). The conversions were found very similar to those recorded for thinner films in real time FT-IR (in transmission mode, see Figure 2). At the end of the ir-

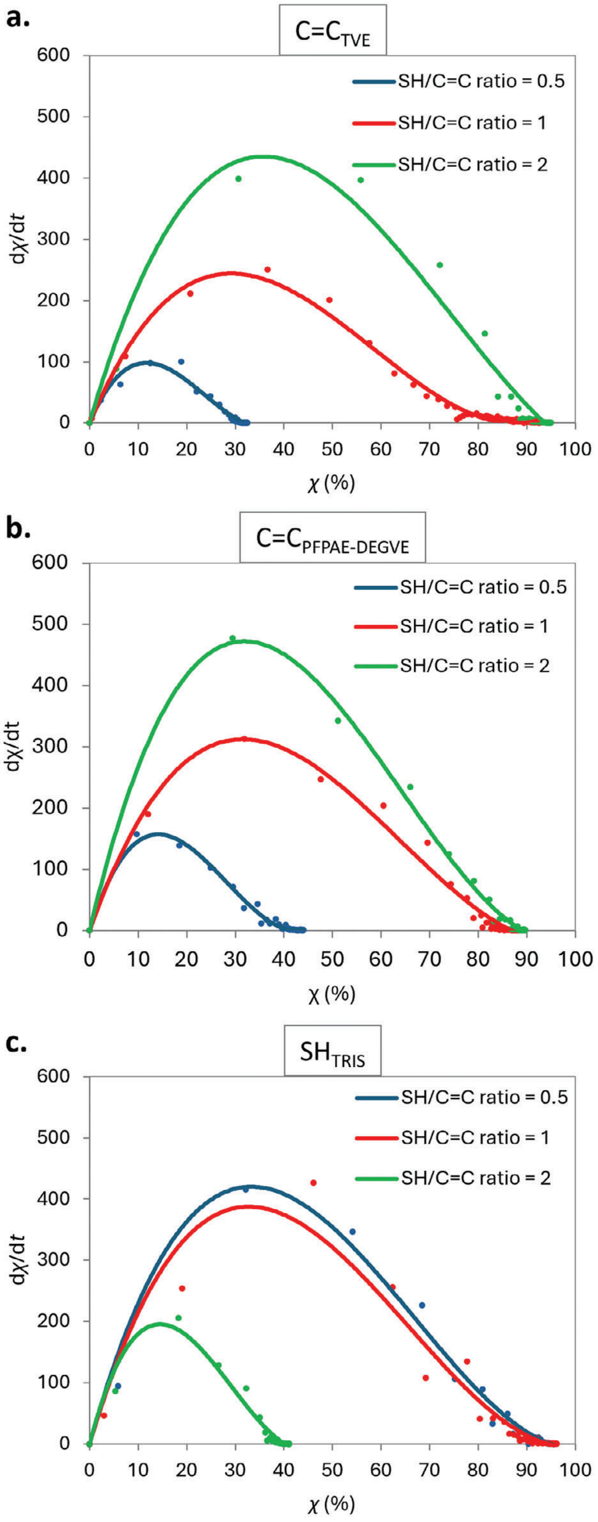


Figure 3. Rate of conversion was calculated using the kinetics data obtained by FT-IR analysis. a) conversion of TVE double bonds; b) conversion of PFPAE-DEGVE double bonds; c) conversion of thiol groups.

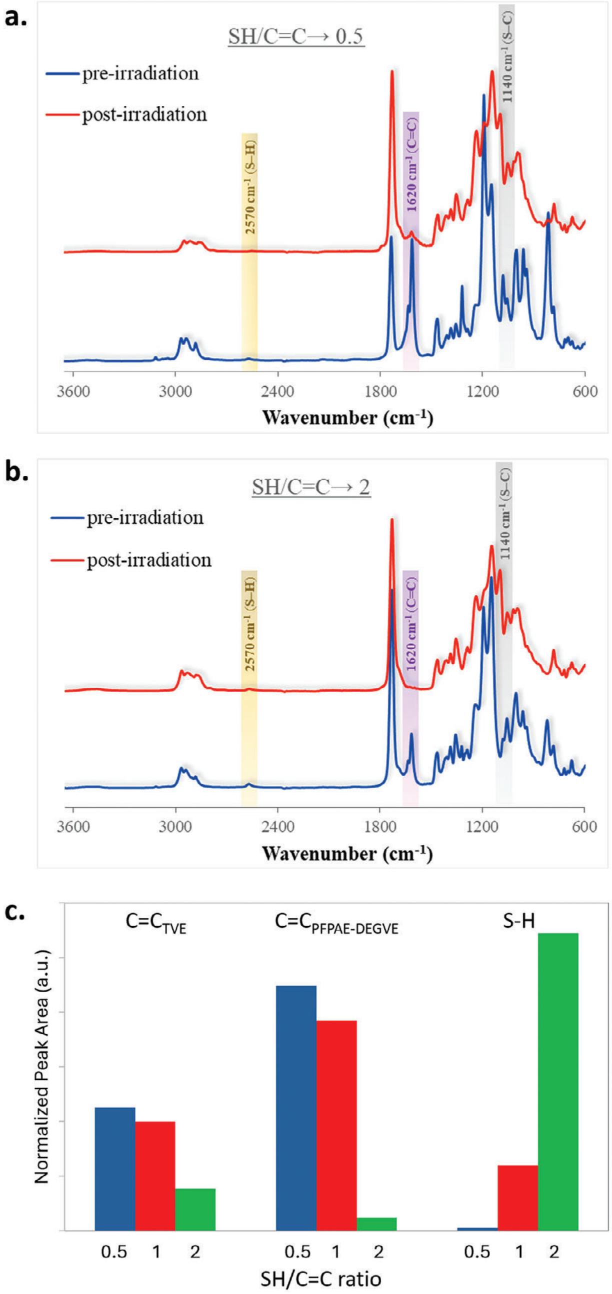


Figure 4. ATR FT-IR spectroscopic analyses. a) and b) spectra of the copolymers having a thiol/ene molar ratio of 0.5 a) and of 2 b), before and after irradiation (UV-light intensity of 7.5 mW cm^{-2}, irradiation time of 10 s). c) surface concentration of ene and thiol groups as a function of SH/C = C molar ratios after irradiation (UV-light intensity of 7.5 mW cm^{-2}, irradiation time of 10 s).

radiation, as expected, the surface concentration of the unreacted C = C unsaturation and of the unreacted -SH groups depend on the thiol/ene ratios. The surface amounts of reactive groups, estimated by ATR FT-IR analyses, are plotted versus the thiol/ene ratio in Figure 4c. The surface of the OSTE networks having a thiol/ene molar ratio of 0.5 maintains unreacted vinyl groups, in particular the fluorinated vinyl groups are twice the TVE double bonds: in fact, they are preferentially enriching the polymer surface as will be discussed below. When the thiol/ene molar ratio was 2, the surface contains a low amount of double bonds and is characterized by a strong presence of unreacted thiols. For the stoichiometrically balanced system, few reactive groups are detectable at the copolymer surface. In conclusion, the data clearly suggest that the surface chemistry of the OSTE polymers is easily controlled by the initial thiol/ene ratio.

Table 3. Static water contact angle (WCA) of both air and mold side of the fluorinated copolymers.

SH/C = C ratio	WCA – air side [°]	WCA – mold side [°]
0.5	79.4 ± 0.7	80.6 ± 0.6
1	80.5 ± 2.8	81.1 ± 2.3
2	79.4 ± 1.5	81.1 ± 2.4

Static water contact angle (WCA) measurements were performed on both surfaces (i.e., air side and mold side) of the UV-cured networks to evaluate their wettability with water. The data collected in **Table 3** suggest that both the external surfaces of the photocured copolymers are enriched in PFPAE: in fact, values are higher than the homologous polymer without PFPAE-DEGVE, for which the contact angle is ≅ 36°. Both surfaces are nearly hydrophobic: as reported in previous works,[22,23] fluorinated comonomers tend to migrate toward the interphase with an apolar medium and in our case both the upper surface (in contact with air) and the substrate of the PDMS mold are apolar. However, the water repellency reached by PFPAE copolymers described elsewhere is higher than the hydrophobicity exhibited by the fluorinated thiol–ene copolymers investigated in this work (WCA > 90 °). In the former cases, the copolymers were photocured in form of thin films (thickness of ~300 µm) onto a polar substrate (i.e., glass): therefore, the PFPAE component has preferentially migrated toward the less polar surfaces (i.e., air side), greatly improving the hydrophobicity of this surface.[26,27]

All the fluorinated thiol–ene networks were characterized by DMTA to evaluate their morphological phases and phase transitions. They all exhibit a glass-rubber transition at T≈-60 °C which can be due to the fluorinated chains; at higher temperatures there is a second glass transition which changes as a function of the SH/C = C ratio. The stoichiometric network has a Tg = 8 °C, while the values for the off-stoichiometric systems are +2 and −9 °C when the ene or the thiol is the excess reactant, respectively. Therefore, the networks prepared exhibit a clear phase separation: they have a soft phase formed by the mobile fluorinated PFPAE chains and a harder phase due to the hydrogenated moieties.[28] Indeed, all polymers are rubbery at room temperature. The off-stoichiometric polymers have a lower Tg as expected: unconverted functional groups cause the decrease of the crosslinking density of the networks and reduction of the elastically effective chains.

3.4. Preparation of Bilayers

In **Figure 5**, a schematic illustration of the steps followed to fabricate a bilayer structure is shown. First, the off-stoichiometric

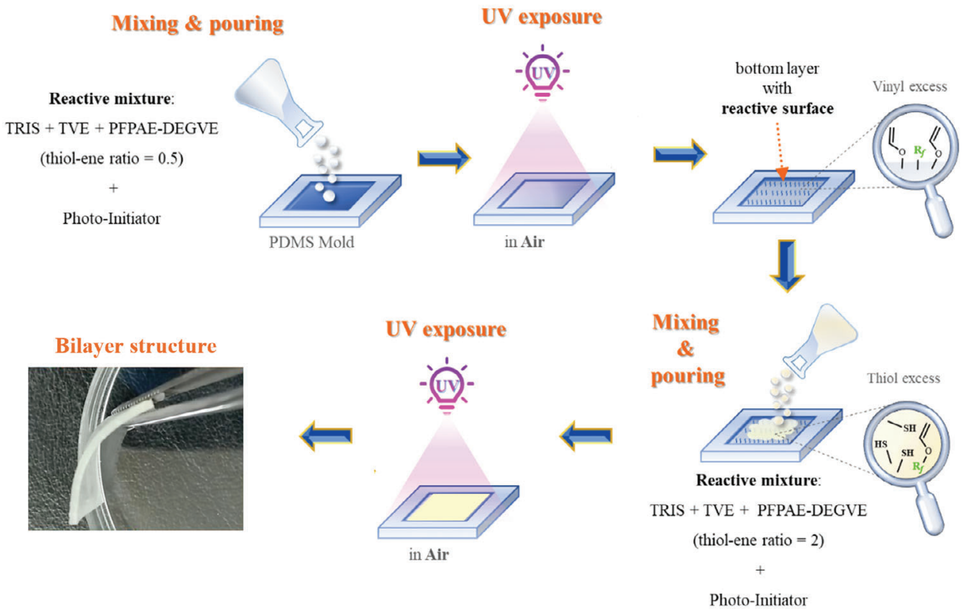


Figure 5. Schematic representation of the steps followed to realize the bilayer structures.

formulation with an excess of vinylether groups was poured to partially fill the PDMS mold; then it was irradiated to assure complete curing. After curing the first layer, the off-stoichiometric formulation having an excess of thiol groups was added on the surface of the layer previously cured: the second layer was exposed to UV light and cured. Since this method takes inspiration from additive manufacturing process, it can be considered a layer-by-layer process.

The bilayered samples when obtained by overlapping a polymer with a thiol/ene molar ratio of 0.5 (i.e., an excess of vinylether) and a polymer with a thiol–ene molar ratio of 2 (thiol content twice the double bonds equivalents), exhibited good interfacial adhesion (**Figure** 6b). Even after 24 h immersion in water the adhesion was highly satisfactory (Figure 6c). This is particularly interesting considering the low-adhesion exhibited by fluoropolymers and is explained taking into account the surface compositions of the polymers as identified by ATR analyses (Figure 3): the first layer has unreacted double bonds, which are able to react with the system forming to second layer where there is an excess of thiols. Thus, during irradiation of the second layer, besides the formation of a network, there is the covalent bonding of the two layers through the -SH and the ene groups. The same results were obtained inverting the order of the layer-by-layer process, i.e., forming a bottom layer with a thiol/ene ratio = 2, and a top layer with thiol/ene ratio = 0.5.

On the contrary overlapping stoichiometric systems which showed no unreacted groups at the surface after crosslinking (as assessed by ATR-FTIR – see Figure 4c), there is a dramatic layer delamination during demolding (see Figure 6a): this indicates no adhesion due to the absence of chemical bonding at the interface.

To assess the chemical resistance and the dimensional stability of the fluorinated bilayers, several swelling tests were performed in different solvents (**Figure** 7). The swelling percentage was calculated after different periods of immersion.

The fluorinated thiol–ene bilayer showed good chemical resistance toward all the solvents tested. First, in any solvent, no

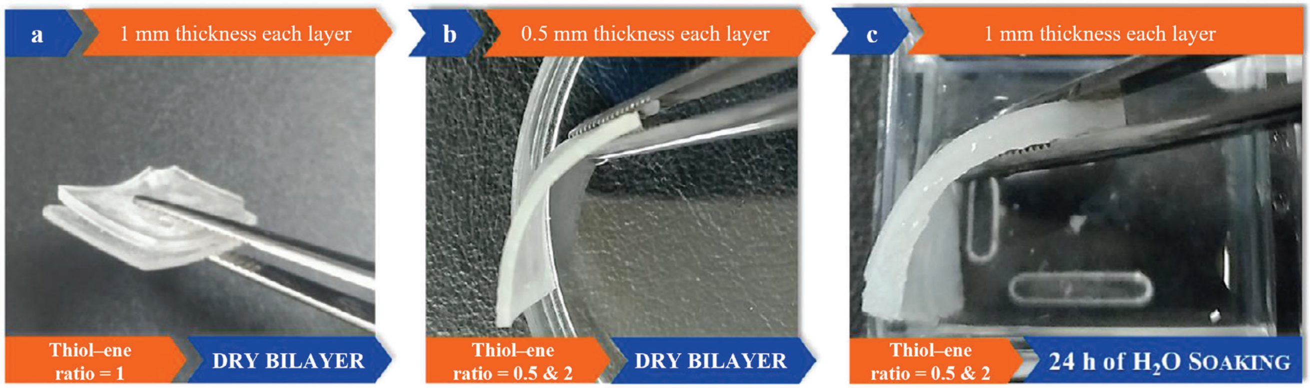


Figure 6. Fluorinated bilayer structures: a) when using stoichiometric polymers no adhesion; b) when combining the off-stoichiometry polymers good adhesion after the photopolymerization reaction c) adhesion is maintained after 24 h of water immersion at RT.

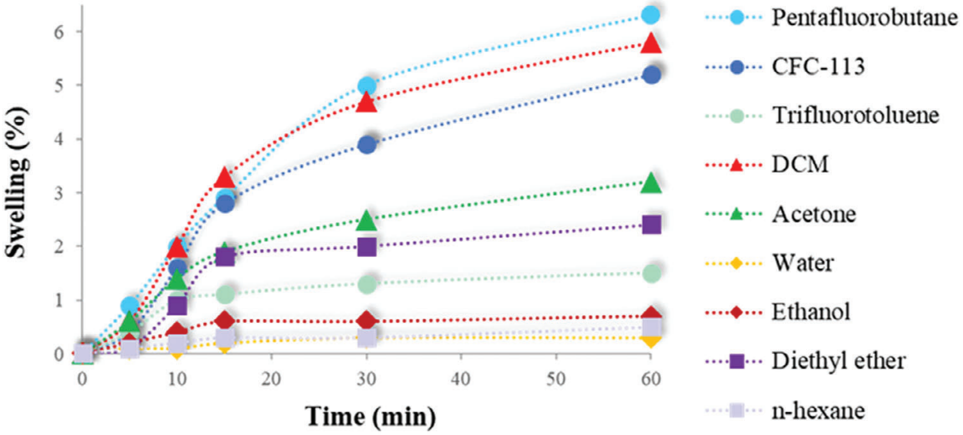


Figure 7. Swelling percentage of fluorinated bilayer samples (realized with off-stoichiometric thiol–ene formulations) after immersion in different solvents.

adhesion failure between the joined layers was noticed (by visual inspection) after the swelling test despite the presence of fluorine. The swelling of the cured copolymers, performed over 1 h, was nearly zero in polar protic solvents such as water and ethanol, as well as in hydrocarbons (hexane). In acetone and diethyl ether swelling reached 3%. Exposing the bilayers to fluorinated solvents, swelling was very low indeed and did not exceed 6% by weight. In summary, the fluorinated OSTE copolymers have excellent properties of adhesion and very limited swelling: this makes them suitable for 3D-printing and microfluidics.[29]

4. Conclusion

In this work, a novel PFPAE vinyl ether monomer was synthesized and used as special monofunctional comonomer in a thiol–ene system. The step-growth photopolymerization was monitored in real time by FTIR and the conversion of each reactive group was determined as a function of the thiol/ene ratio. Varying the stoichiometry of the thiol/ene ratio enabled to tune the surface composition of the polymer: non reacted functionalities, either -SH or double bonds, were present at the polymer surfaces. All polymers, independently of the stoichiometry, showed biphasicity, with a Tg at ≈-60 °C related to the PFPAE phase and a second Tg, related to the hydrogenated network, below room temperature. Preparing bilayers, excellent adhesion between the different cured layers was achieved when a polymer with a thiol excess and a polymer with an ene excess were combined. It is important to underline that adhesion was obtained in the presence of a low energy surface component such as the PFPAE- DEGVE comonomer. Even upon treatment with different solvents, the bilayer showed no adhesion failure: the chemical resistance was good as well as the dimensional stability, while swelling was low.

Therefore, the fluorinated copolymers described can be potentially exploited in several fields where layer-by-layer processing is needed, namely 3D-printing and microfluidics: the fluorinated thiol-ene layers can be tailored to show low Tg and have different surface chemistry. This is relevant not only to improve adhesion, as shown in this work, but also for post functionalization of the surfaces, while keeping the same bulk composition.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

adhesion, multilayers, Perfluoropolyalkylethers, thiol-ene, UV-curing

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