Electronic Supplementary Material (ESI) for Polymer Chemistry

Electronic Supplementary Information

VUV grafting process: An efficient tool for 3D bulk patterning of polymer sheets.

Cécile Baudin[a], Jean-Philippe Renault[b], Stéphane Esnouf[b], Serge Palacin[a]
and Thomas Berthelot[a]*

[a] *SPCSI Chemistry of Surfaces and Interfaces Group, CEA, IRAMIS*
F-91191, Gif-sur-Yvette, France E-mail: thomas.berthelot@cea.fr

[b] *CEA, IRAMIS, UMR 3299 CNRS/CEA SIS2M Interdisciplinary Group of Molecular Systems and Material, Laboratoire de Radiolyse, F-91191, Gif-sur-Yvette, France.*

Table of Contents

General Experimental Section

1. Materials and reagents

Hydrophobic poly(vinylidene fluoride) sheets (β PVDF, SOLEF, 9µm thick) were purified by Soxhlet extraction in toluene and dried at 50°C under vacuum. The PVDF sheets were sliced into rectangular strips about 4 cm x 1.5 cm in size and then stored in nitrogen atmosphere. Acrylic acid (AA) (Fluka) was distilled under reduced pressure and stored in a nitrogen atmosphere at 4°C. Styrene (Aldrich) was used as received. MilliQ water was used throughout the study. Polyethylene (PE), Polyethylene terephthalate (PET) sheets, Fluorinated ethylene propylene (FEP) sheets (25 µm thick) were purchased from Goodfellow and used as received. TEM copper grids (regular grids with center mask and solid border, grid sizes 200 mesh and 1000 mesh, 125 µm and 25 µm pitch respectively) were purchased from Sigma Aldrich. UV fused silica USAF 1951 resolution targets (thickness: 1 mm; dimensions: 2x2 inch; surface accuracy (λ): 2; surface quality: 40-20; transmittance at 172 nm: more than 90%) were purchased from Edmund Optics; the positive targets were chrome pattern, and clear background; the negative target were clear pattern and chrome background.

2. VUV irradiation

A pulsed tubular Xe_2*-excimer lamp based on dielectric-barrier discharge (XERADEX^{TM}, Radium Lampenwerk, Wipperfuerth, Germany; electrical power: 20W; diameter: 4 cm; length: 12 cm; λ_{exc}: 172 ± 12 nm; radiant power: 8 W; exitance : 50 mW cm^{-2}) was used as radiation source. β PVDF, PE and PET irradiations were carried out under nitrogen atmosphere. The samples were fixed at a distance of 7.2 cm from the lamp, and irradiated on one side for 5, 10, 15, 20, 30, 60, 120 and 180 minutes. To measure the VUV fluence, we devised an indirect actinometric method based on the two reactions depicted below on **Scheme S1**.

3. Indirect actinometric method used for measuring the VUV fluence

At 172 nm, the quantum yield of water photolysis is $\Phi = 0{,}41(7) \pm 0{,}03$ [22]. The yield of the second reaction is 5% with respect to the amount of HO° produced [23]. The photon fluence is thus determined by the quantification of the amount of 7-hydroxycoumarin produced by fluorescence. HPLC was used to check that no additional products were observed besides hydroxycoumarins. In a typical experiment, 200 µl (hold in a well of a fluorescence 96 well microplate) of 10^{-4} M aqueous solution of coumarin are irradiated in aerated conditions for increasing times up to ten minutes. The fluorescence emission spectra of the as formed 7-hydroxycoumarin (emission maximum at 456 nm) is recorded on a Gemini XPS microplate reader using an excitation wavelength of 332nm and quantified using reference solutions containing 10^{-4} M coumarin and known concentrations of 7-hydroxycoumarin in the 10^{-8} 10^{-6} M range. For the geometry used in the polymer irradiations, the measured production of 7-hydroxycoumarin was 10^{-9} mol.cm^{-2}.min^{-1}, which gives a fluence of 0.6 mW.cm^{-2}. The fluorescence quantification of 7-hydroxycoumarin production allows also a cm scale mapping of the lamp fluence using a microplate reader. We choose the most homogenous zone to carry on the polymer irradiations. It is noteworthy that getting an equivalent production of HO° radical in the light absorption layer (with an absorption coefficient of about 500 cm^{-1} at 172 nm, we considered that light was totally absorbed in 30µm [24]) requires a dose rate of 25 kGy/min.

4. VUV-induced Polymerization

Within ca. two hours after irradiation, the irradiated sheets were immersed into a tube containing the previously degassed aqueous acrylic acid (AA) solution. After one hour at 60 °C, the sheet was removed from the solution and submitted to ultrasonic treatment in water for 15 min. The sheets were then Soxhlet-extracted with water for 12 hours to discard ungrafted PAA and dried under high vacuum at 50°C until constant weight. The grafting yield Y (wt%) was determined gravimetrically according to the following **formula 3**:

$$(3)\ Y(wt\%)=((m_f-m_i)x100)/m_i$$

where m_f and m_i are the weights of the grafted and initial sheet, respectively.

5. Patterned VUV-induced Polymerization

Two different types of masks were used to create 3D bulk patterns into polymer sheets (PVDF or FEP): i) stencil-like masks as TEM copper grids with 25 and 125 µm pitch and ii) optical masks as UV fused silica USAF 1951 resolution targets (positive and negative targets). After 30 min of VUV irradiation under N_2 atmosphere, the resulting sheets were immersed either in a degassed aqueous acrylic acid (AA) solution, or in a degassed pure styrene solution [25]. After 25 min at 60 °C, all the polymer sheets were removed from the different solutions and submitted to ultrasonic treatment in appropriate solvents for 15 min (water for acrylic acid or toluene for styrene).

6. ESR characterization

The ESR experiments were carried out at room temperature on a X band (ν= 9.85 GHz) EMX Bruker ESR spectrometer using a 100kHz field modulation, 1 gauss of amplitude modulation and an applied microwave power of 1 mW. The spectra were obtained by sweeping the static magnetic field (from 327.5 to 337.5 mT) and by recording the first derivative of the absorption spectrum. The irradiated PVDF sheets were kept under nitrogen during the ESR analysis except otherwise stated. A double integration of the ESR signal was performed and the corresponding concentration was calculated from a reference sample of hydroxy-TEMPO mixed with polypropylene powder. A maximum error of 10% has been considered

7. Infrared spectroscopy

FTIR spectra of the polymer sheets were carried out with a Nicolet Magna-IR^{TM} 750 spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector. The spectra were recorded in an Attenuated Total Reflectance mode (ATR) using a diamond-crystal with single reflection. Spectra were collected by cumulating 512 scans at a resolution of 2 cm^{-1} using H_2O and CO_2 correction.

8. UV-vis spectroscopy

A Perkin Elmer Lambda 650 spectrometer was used to measure the absorbance of VUV-irradiated sheets. The β pristine PVDF sheet was used as reference sample.

9. Optical microscopy

An Olympus BX-61 microscope was used to perform micrographs of the resulting 3D bulk patterns on PVDF and FEP sheets.

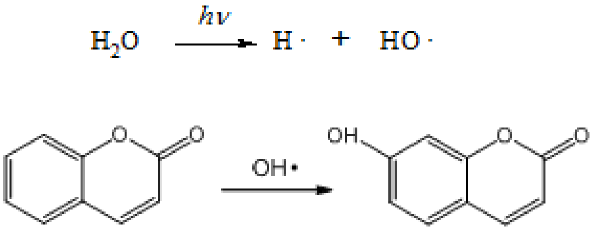
For some micrographs, the samples were immersed in a solution of aqueous $CuSO_4$ (0.1 M)/NH_3 (0.6 M) for 2 h. Micrographs of the front and the back sides of the 3D bulk patterns on polymer film were recorded by top sample lighting.

One 3D bulk patterns sample was cut by cryofracture in liquid nitrogen. Then the resulting sample was clamped between two microscope slides and observed by optical microscopy.

10. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

Scanning electron microscopy was carried out with a Philips apparatus equipped with a LaB6 tip and coupled with an X-ray detector (PGT-Princeton Gamma) and a PRISM Digital spectrometer. The samples were immersed in a potassium hydroxide solution 0.05M to exchange the carboxylic protons by potassium ions [26]. Then the sheets were embedded in

EPON resin before being cut by a Leica microtome. The cut edge was coated with Au using a sputtering device and analysed.



Scheme S1. Indirect actinometric method used for measuring the VUV fluence.

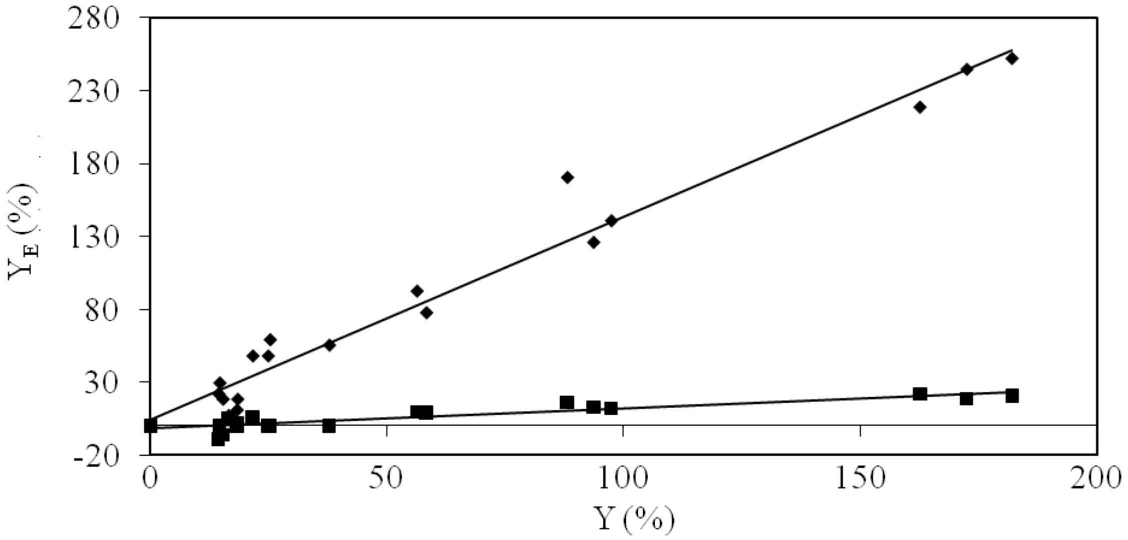


Figure S1. Thickness (♦) and surface (■) variations (%) *vs* grafting yield (Experimental conditions: VUV irradiation time 30 minutes, [Mohr's salt]=0.25 wt%, 60°C for 1 h). The grafting yields correspond to the data of figure 1.

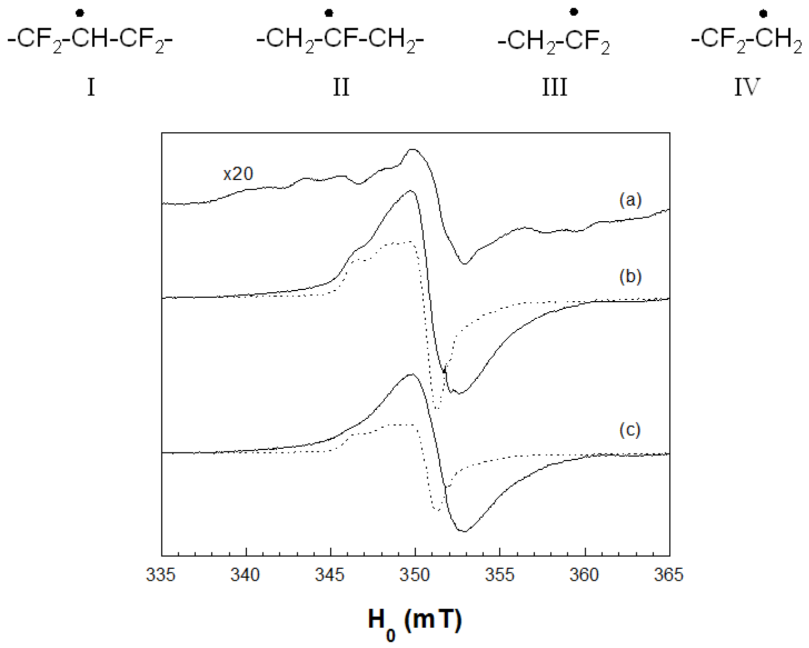


Figure S2. a) ESR spectra of γ-irradiated β-PVDF at a dose of 51,6 kGy, b) ESR spectra of VUV irradiated β-PVDF for 30 minutes under nitrogen (–) immediately after irradiation, (- -) exposed to air 150 minutes, c) decomposition of b) into (–) singlet and (- -) peroxy radicals contributions.

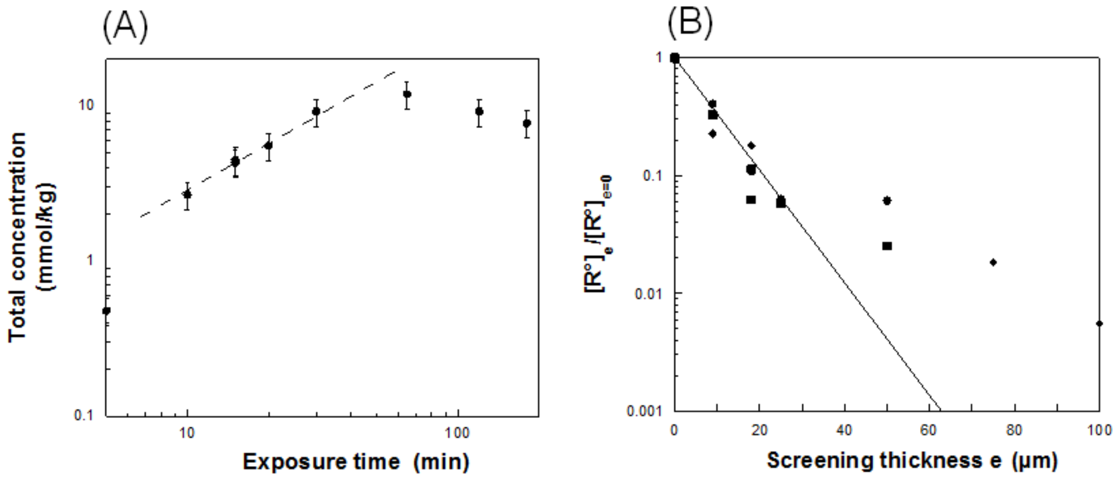


Figure S3. (A) Evolution of the total concentration of radicals (polyenyle and peroxy) with the exposure time. (B) Variation of the total concentration of radicals with the thickness of the PVDF sheet interposed between the VUV lamp and the β-PVDF film. Different exposure times were used, the concentration was divided by the concentration measured with no attenuation.

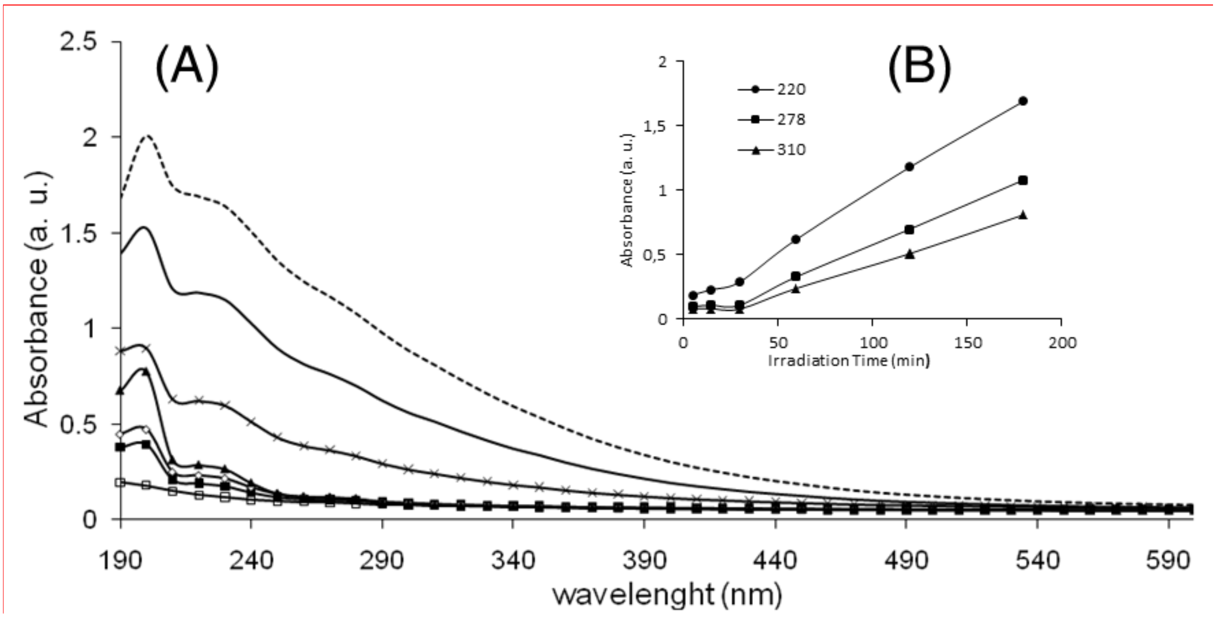
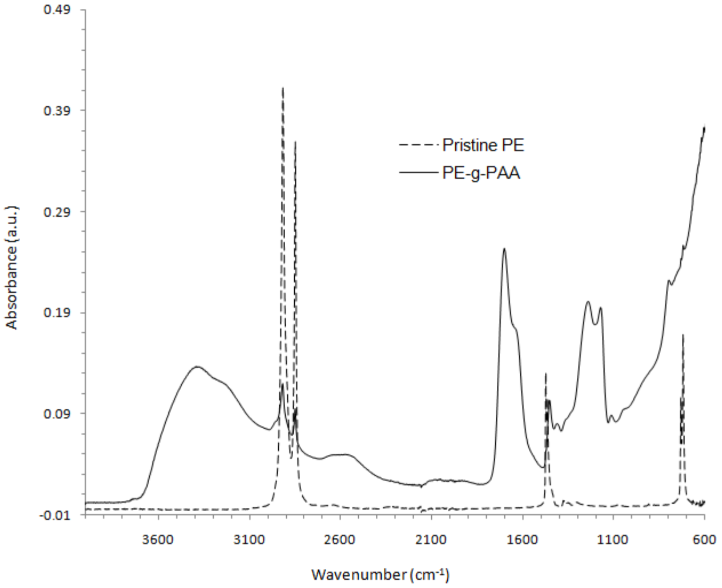


Figure S4.(A) UV absorption spectra of pristine PVDF sheets (□) and after 5 minutes (■), 15 minutes (◊), 30 minutes (▲), 1h (×), 2h (—) and 3h (…) VUV-irradiation times, respectively. (B) UV absorbance values *vs* irradiation times for 220, 276 and 310 nm absorption bands of polyenyls (-(CF=CH)$_n$-CH-) corresponding to n=2, 3 and 4.

A)



B)

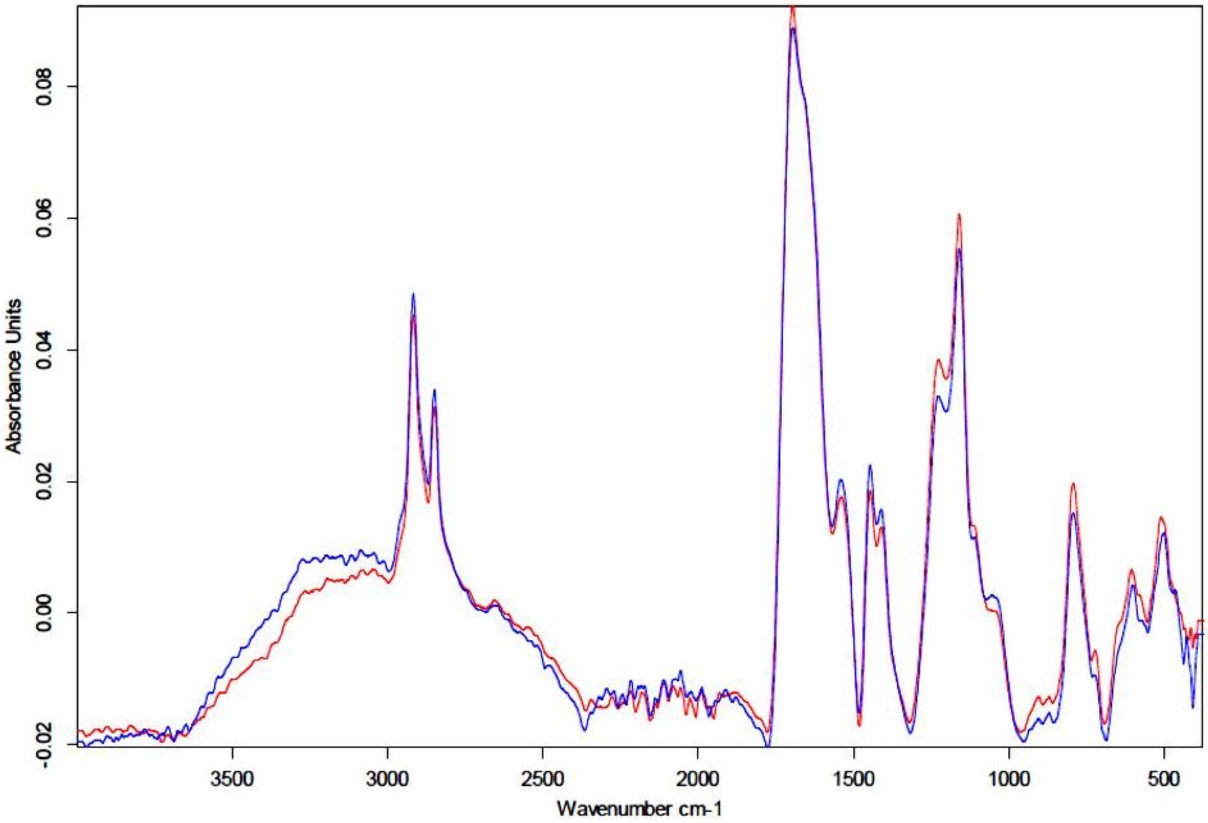
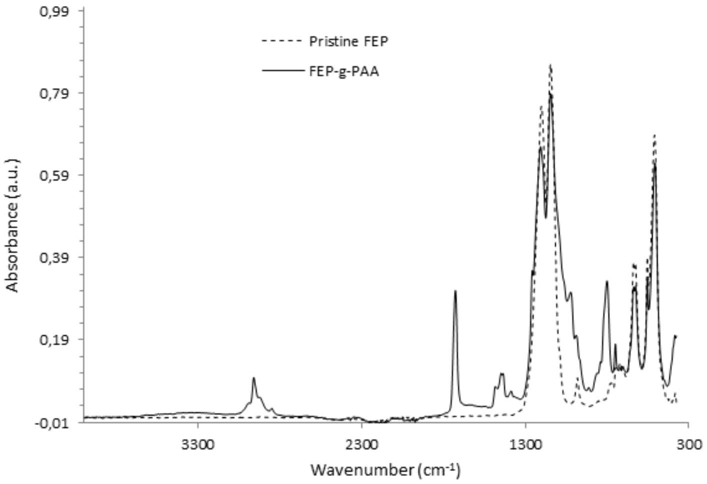


Figure S5. FTIR ATR spectra PE-*g*-PAA copolymers (20 min VUV Irradiation, grafting conditions: 60°C, 1h with [AA] = 80 vol % in water, [Mohr's salt] = 0.25 wt %). A) ATR FTIR spectra of pristine PE and PE-*g*-PAA. B) ATR FTIR spectra of the two different sides of PE-*g*-PAA film.

A)



B)

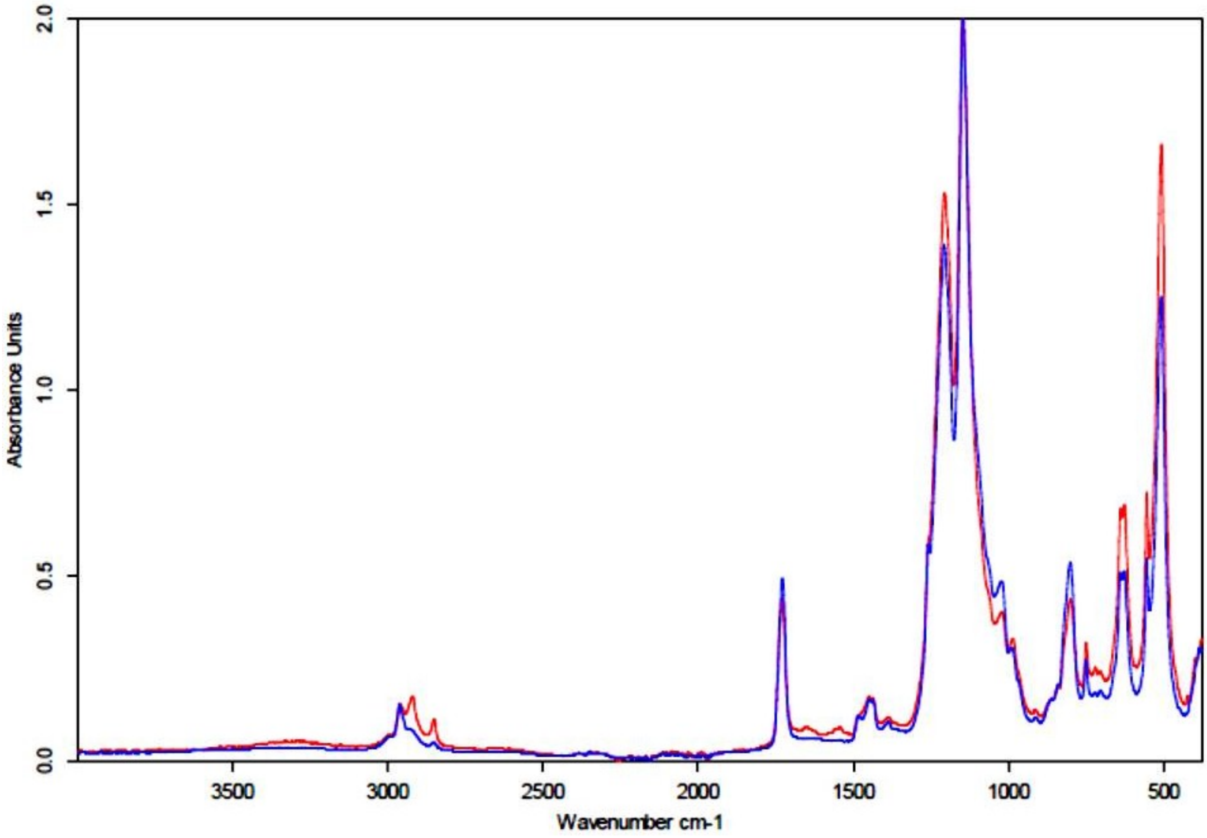
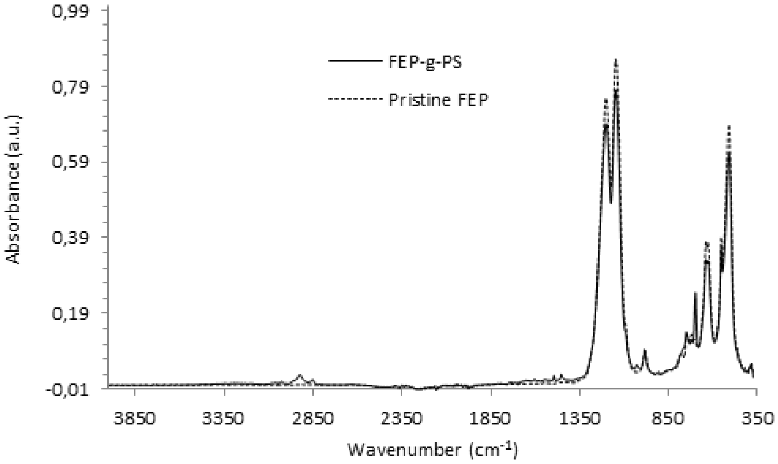


Figure S6. FTIR ATR spectra FEP-*g*-PAA copolymers (20 min VUV Irradiation, grafting conditions: 60°C, 1h with [AA] = 80 vol % in water, [Mohr's salt] = 0.25 wt %). A) ATR

FTIR spectra of pristine FEP and FEP-*g*-PAA. B) ATR FTIR spectra of the two different sides of FEP-*g*-PAA film.

A)



B)

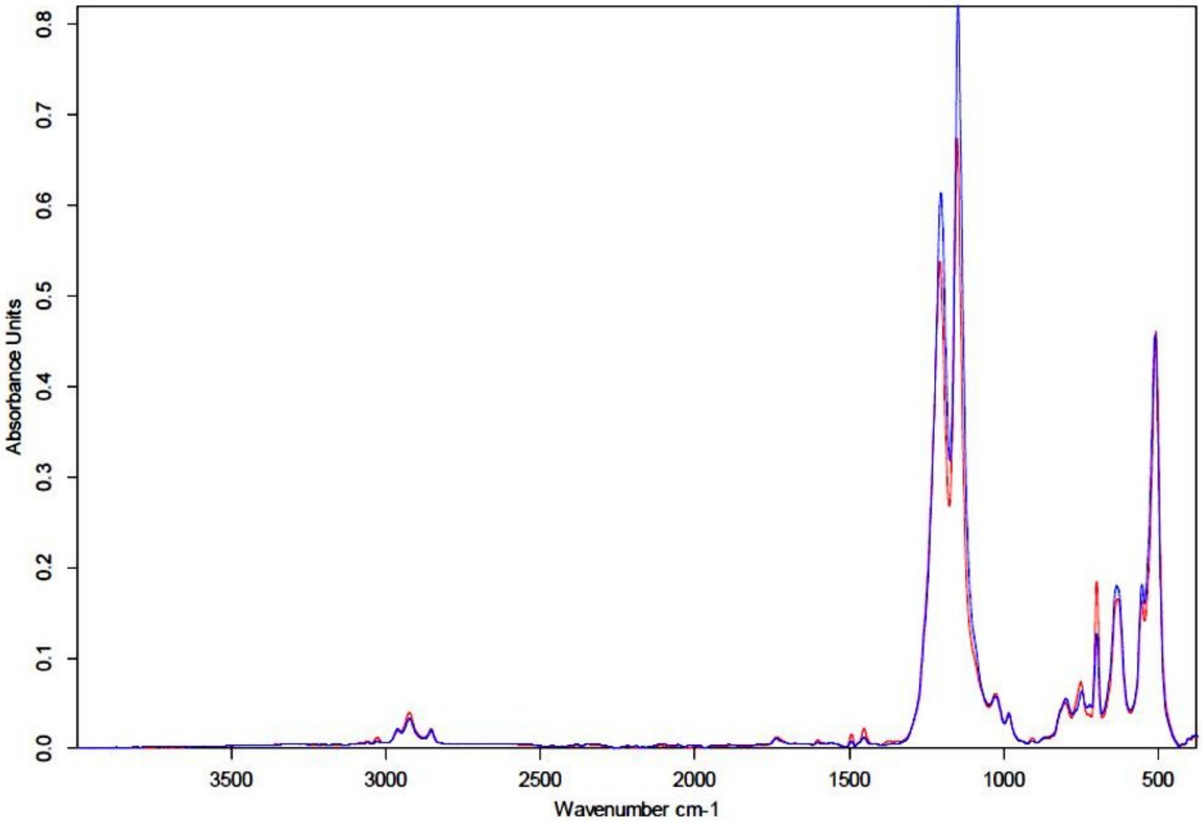
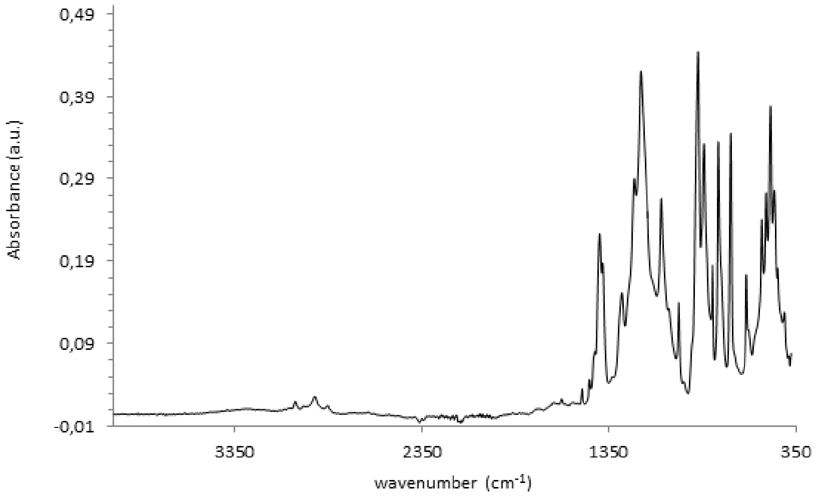


Figure S7. FTIR ATR spectra FEP-*g*-PS copolymers (20 min VUV Irradiation, grafting conditions: 60°C, 1h with pure styrene). %). A) ATR FTIR spectra of pristine FEP and FEP-*g*-PS. B) ATR FTIR spectra of the two different sides of FEP-*g*-PS film.

A)



B)

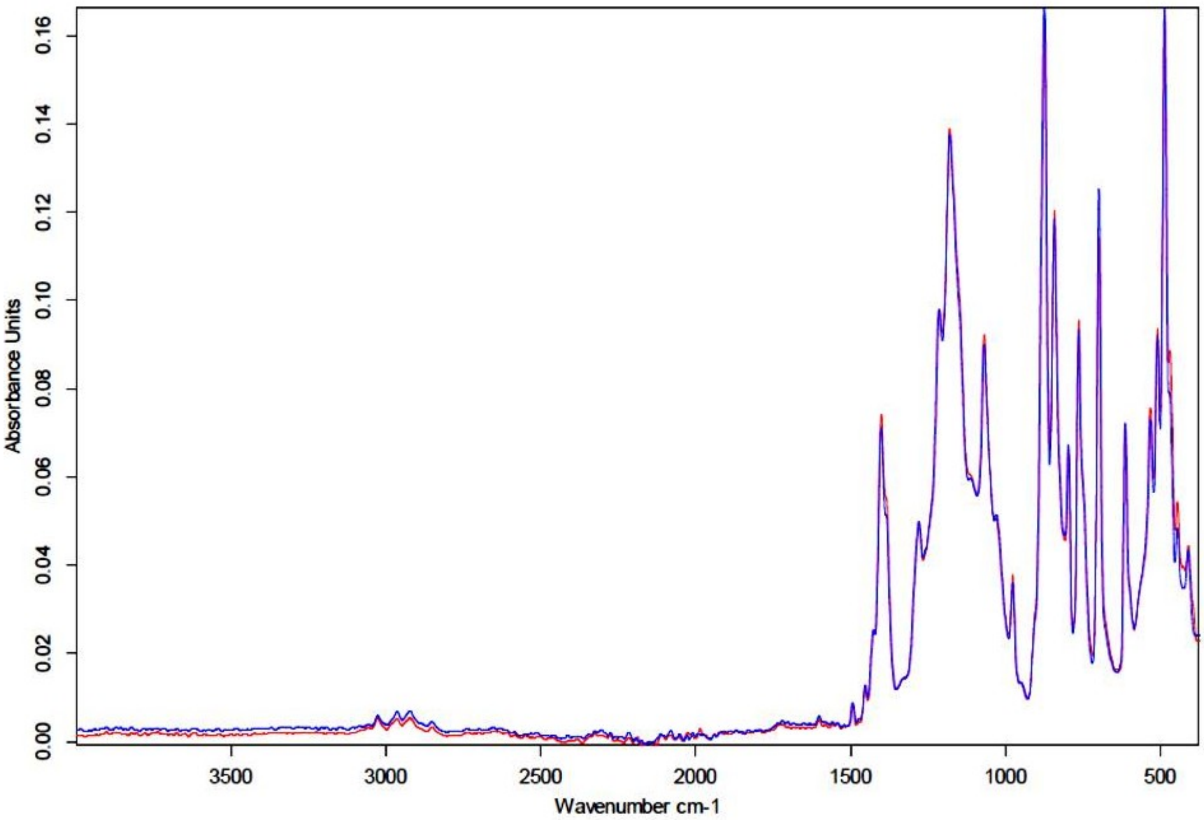


Figure S8. FTIR ATR spectra PVDF-*g*-PS copolymers (20 min VUV Irradiation, grafting conditions: 60°C, 1h with pure styrene). A) ATR FTIR spectra of PVDF-*g*-PS. B) ATR FTIR spectra of the two different sides of PVDF-*g*-PS film.

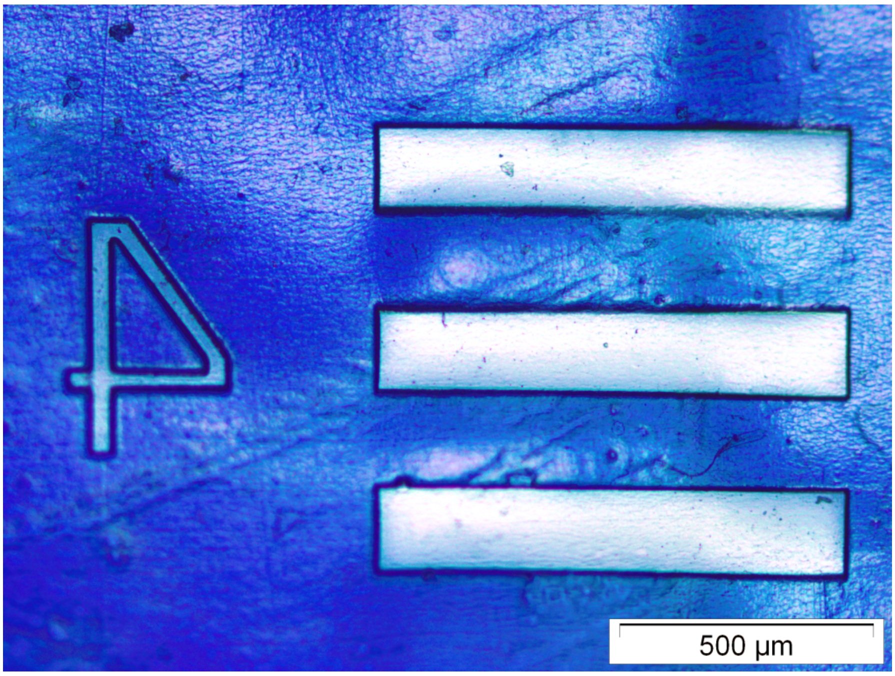


Figure S9. Optical micrograph of the back side of PVDF-*g*-PAA-Cu^{2+} obtained with a positive fused silica USAF 1951 resolution target.

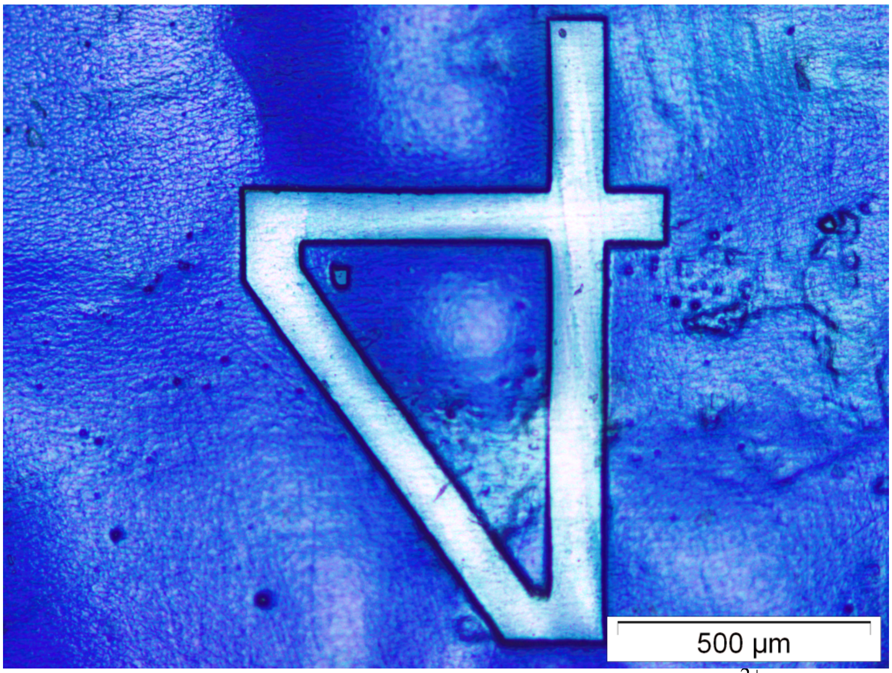


Figure S10. Optical micrograph of the front side of PVDF-*g*-PAA-Cu^{2+} obtained with a positive fused silica USAF 1951 resolution target.

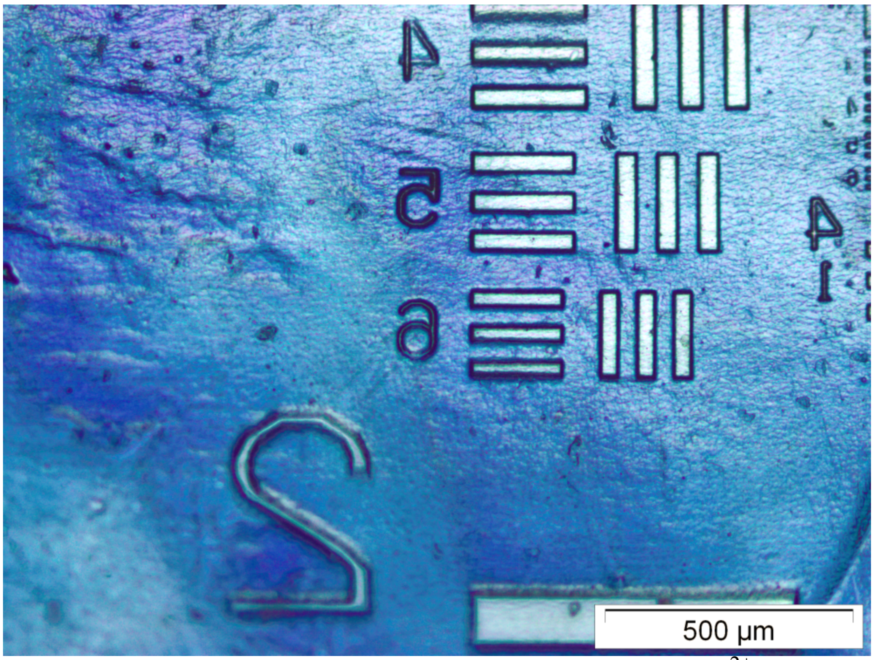


Figure S11. Optical micrograph of the back side of PVDF-*g*-PAA-Cu^{2+} obtained with a positive fused silica USAF 1951 resolution target.

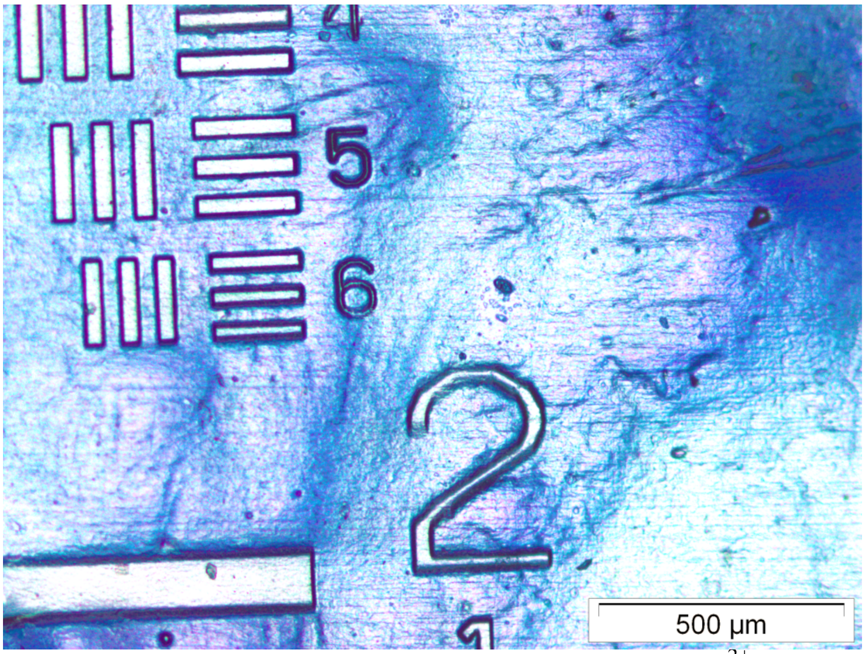


Figure S12. Optical micrograph of the front side of PVDF-*g*-PAA-Cu^{2+} obtained with a positive fused silica USAF 1951 resolution target.

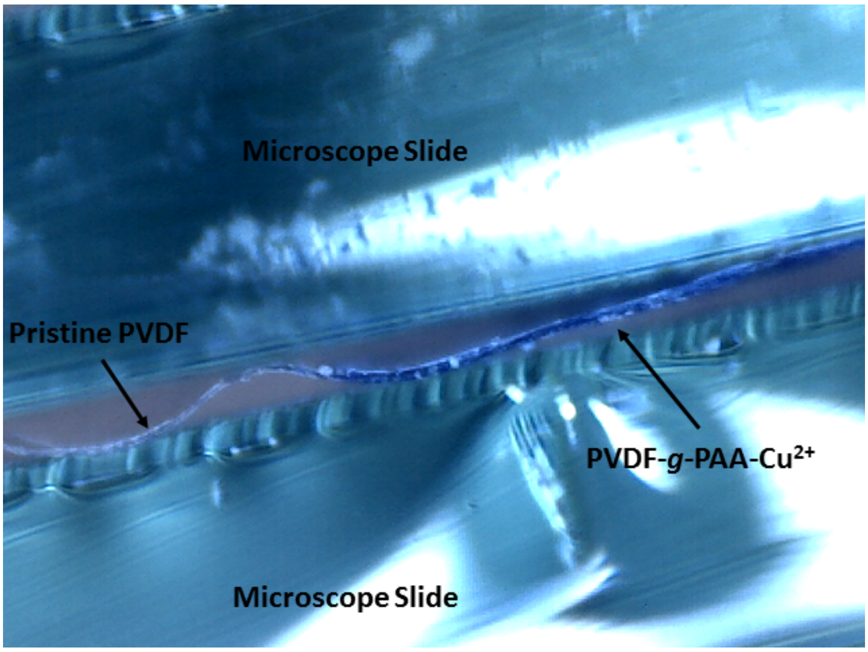


Figure S13. Optical micrograph of the thickness of cut patterned PVDF-*g*-PAA-Cu^{2+} film obtained with a positive fused silica USAF 1951 resolution target.