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Revealing Surface Functionalities *via* Microwave for the para-Fluoro-Thiol Click Reaction

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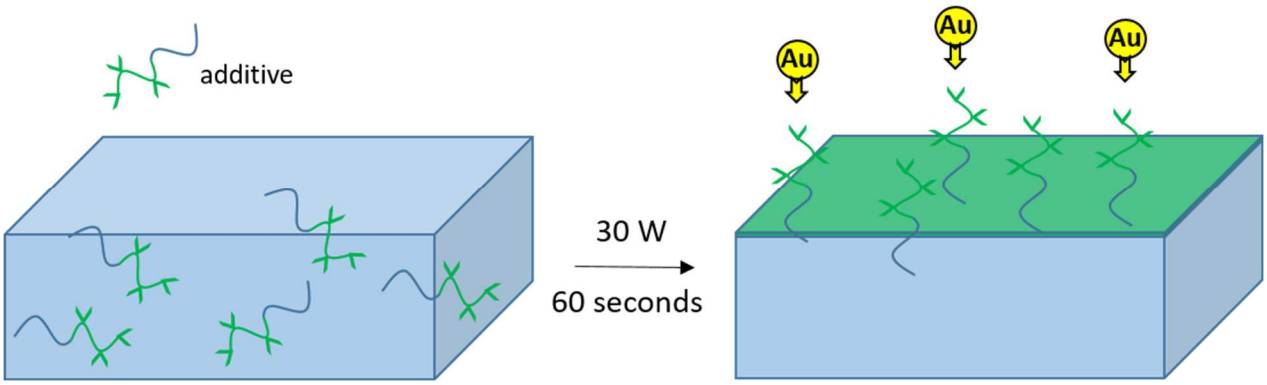


Abstract:

A fast and simple bottom-up methodology is reported to allow, thanks to a spontaneous phenomenon, the grafting of various materials on polymer substrates. In 60 seconds, the inert surface of polystyrene material is converted into a functional platform onto which organic molecules and metal particles can be anchored. A polystyrene (PS) matrix is blended with a small amount of a diblock copolymer additive engineered to both segregate at the material surface and be able to involve chemical reaction. Indeed, poly(penta fluorostyrene) (PSF) contains surface active fluorine atoms and the nucleophuge para-fluorine atom that allow nucleophilic substitution with thiols. Films of blend of PS matrix and PS-*b*-PSF additive are submitted to a microwave annealing to accelerate the spontaneous surface segregation of fluorine low surface energy atoms. XPS was performed to find that the optimal annealing condition was a treatment at 30 W during 60 seconds. With this procedure, a blend of 5 w% in additive can lead to a surface composed of 13 at% of fluorine atoms corresponding to 55 w% of diblock. The pentafluorostyrene units decorating the surface were used as anchors to immobilize gold nanoparticles *via* the para-fluoro-thiol click reaction.

Keywords: para-fluoro-thiol click reaction, surface segregation, diblock copolymer, microwave, gold nanoparticles.

1. Introduction

The control of surface composition and properties, such as wettability, adhesion, biocompatibility, friction and wear, is crucial to develop applications in electronics, water-treatment, energy and biomedical industries.[1-5]. Efficient "click chemistry" reactions have been developed for 30 years to graft surfaces with molecules, macromolecules, metal or inorganic nanoparticles.[6] Among them, Huisgen cycloaddition[7, 8], thiol-ene reaction[9], or Diels–Alder cycloadditions[10] are the most used. Recently, a new reaction has been investigated by the community: the nucleophilic aromatic substitution of para-fluorine atom of pentafluorophenyl moeities by a variety of nucleophiles, such as thiols, amines and alcohols.[11] The main limitation of these "click" methodologies is that the substrate must present surface reactive functions for the grafting to happen. Therefore, it is limited to a small range of materials.

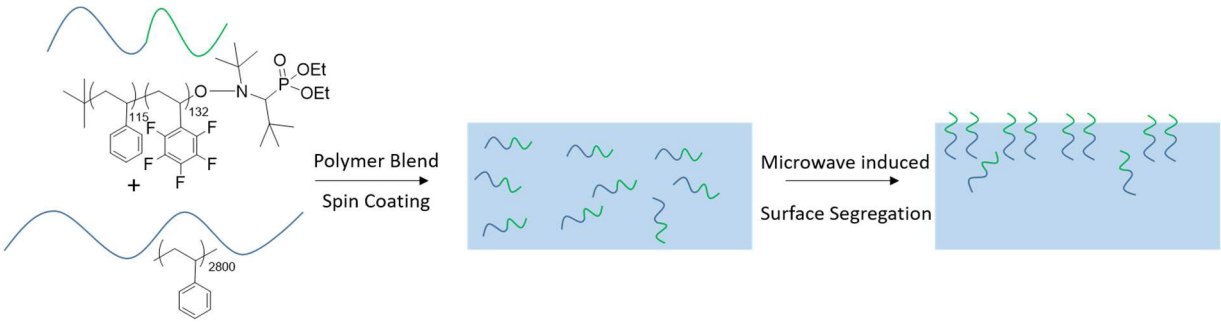
Polymers surface modification is a powerful tool in order to allow cheap inert materials to gain reactive surface functionalities. Surface segregation, a spontaneous phenomenon based on thermodynamics, is a "soft" way of modifying the external properties of a materials blend. It is directed by the equilibrium between the decrease of surface tension and the energy cost of segregation from the bulk, as governed by Gibbs adsorption isotherm.[12, 13] Therefore, in a polymer blend, a "surface field" drives the migration of the material with the lowest surface tension to the air interface. As a consequence, the phenomenon leads to significant modifications between the surface and the bulk composition and properties.[14-16] Surface segregation has been demonstrated in several polymeric systems[17-21], either in flat[22] or spherical[23] material and in dry (vacuum) or humid environment[24].

Even if surface segregation is a spontaneous phenomenon, the thermic properties of the blends components have a huge influence on the process kinetics. Blends of polystyrene (PS) and end-functionalized polystyrene, which glass transition temperatures (T_g) are around 100°C, would reach thermal equilibrium in the time scale of weeks at room temperature. A thermal annealing above T_g is required to reduce the segregation time to half a day.[25] Perhaps the most reported system is the blend of an end-fluorinated polystyrene additive (PS-F) in a PS matrix.[25-29] In the publications, the authors showed a strong fluorine surface enrichment and very hydrophobic films were produced. Indeed, the material surface energy is reduced by the segregation of fluorine atoms having a lower surface tension than the styrene repetitive units. In 1994, Affrossman *et al.* used PS-F/PS blend, they showed that an initial weight composition of 15/85, after a thermal annealing at 130°C for 24 hours, could lead to an enrichment in PS-F of 62 w%. Elman and coworkers proved by neutron reflectivity the segregation of deuterated PS-F in a hydrogenated polystyrene matrix.[25] Other studies were published [26, 28, 29], confirming the segregation of fluorinated polymers after annealing above *Tg* (from 110°C to 165°C) in the time scale of days (from 12h to 72 hrs).

Nowadays, energy is a vital challenge for mankind and many research studies are devoted to reduce its consumption. In this report, a rapid method is described to perform the fluorine surface enrichment in sixty seconds, thus dividing the annealing time by 1440 (1 day/1minute). Microwave-induced annealing is used to allow the surface segregation of a fluorinated additive in a polystyrene matrix. Recently, high ordered nano-phase segregation of block copolymers (BCP) were obtained by microwave annealing. A few minutes of irradiation were sufficient to organize polystyrene or poly(methyl methacrylate) based copolymer in lamellae, cylinders or

spheres.[30-33] Buriak *et al.* have proved that highly resistant silicon substrates (1-35 Ohms, doped by boron) can reach 200°C in a few seconds and serve as a hot pan to induce the nanosegregation of BCP. [34, 35] On the contrary, when glass substrates were used, no morphological modification was detected to a significant extent.

In this study, we used the ultra-fast annealing induced by the microwave irradiation to promote the surface segregation of a diblock copolymer, a polystyrene-*block*-poly(pentafluorostyrene) (PS-*b*-PFS) at the air/polymer interface (Scheme 1). The BCP additive, has been engineered to present a PS block compatible with the polystyrene matrix and a PFS block bearing 5 surface active fluorine atoms per repetitive monomer units, which can undergo the para-fluoro-thiol click reaction. To the best of our knowledge, nothing has been reported on the surface segregation of pentafluorostyrene-based copolymers. Contact angle (CA) measurement, X-ray photoelectron spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) analyses were carried out to demonstrate that a 60 seconds annealing is enough to enrich the surface of the blends with the BCP additive. Finally, the surface functionalization with gold nanoparticles GNPs was performed in two steps. Indeed, the successful nucleophilic substitution of the para fluorine atom with the thiol function of cysteine allows the immobilization of anchoring groups for GNPs surface docking. This proves the efficiency of surface segregation to create a functional platform from an inert substrate in a very short period of time and low energy consuming.



Scheme 1. Overview of the system studied in this report.

2. Results and Discussion

2.1. PS-*b*-PFS copolymer synthesis

The polystyrene-*block*-poly(pentafluorostyrene) (PS-*b*-PFS) was synthesized by Nitroxide Mediated Polymerization (NMP), a controlled radical polymerization based on the reversible trap of growing chains by nitroxide molecules (see in supporting information Scheme SI1).[36] The first step is the polymerization of styrene using the BlockBuilder® MA. Size exclusion chromatography was used to measure the molar mass of the polymer, Mn = 12 000 g.mol^{-1} (using conventional calibration with polystyrene sample), the average degree of polymerization DPn = 115 and its dispersity, $Đ$ = 1.27. After purification, the PS was used as macroinitiator to polymerize pentafluorostyrene and access the block copolymer additive. To ensure a sufficient mixing with the PS matrix and a high amount of fluorine moieties, we targeted a copolymer with a balanced composition, presenting the two blocks length equal. ^{1}H NMR was used to evaluate the ratio between PS and PFS molecular units and a DPn of 132 was calculated for the PFS block (Figure SI1). SEC analysis of the PS-*b*-PFS revealed a shift in the molar mass compared to the PS macroinitiator (Figure SI2), meaning the efficient chain extension of the PS first block with a PFS block. The copolymer dispersity $Đ$ and molar mass Mn were calculated to be 1.15 and 38 000 g.mol^{-1} respectively. Literature has shown that the segregation was best occurring when the additive had a smaller molar mass than the matrix, therefore we followed this requirement (PS matrix molar mass is 300,000 g.mol^{-1}).[22, 28] Differential Scanning Calorimetry was performed and only one glass transition temperature was detected at 107°C (Figure SI3) corresponding to the literature values of both PS and PFS homologue blocks.[37]

2.2. Surface segregation

2.2.1. Determination of suitable annealing conditions.

Films (thickness around 300 nm) were prepared onto silicon wafers by spin-coating from toluene solutions (4%) of a polymer blend composed of a PS matrix (Mn = 300 000 g.mol^{-1}, $Đ$ = 1.2) and the PS-*b*-PFS additive with a mass ratio 90/10. This first ratio was chosen to keep the additive content low and based on literature, which reports efficient segregation and surface properties evolution at 10% of additive.[17, 22, 26, 27] Such thick films were employed for two main reasons: 1) to avoid dewetting problems that appear in thin fluorine polymer films and 2) to separate the substrate/polymer and the polymer/air interfaces in order to reduce the number of competing interactions that can alter the surface segregation phenomenon.[13] Then, the films were introduced in a pressure resistant glass vial with air atmosphere (Figure SI4) and placed in the microwave oven. The optimal annealing

conditions were determined by applying different irradiation powers during different times. XPS was the technique of choice to investigate the presence and the amount of fluorine atoms at the surface of the polymer films. Figure 1 presents the Carbon spectra of the non-annealed film and films treated with microwave at various powers (10, 20, 30 and 40 Watts) during 60 seconds. Four major components are clearly observed: C=C from polystyrene rings (sp2, 284.5 eV), C–C from vinylic bonds of polystyrene (sp3, 285 eV), C–F from polypentafluorostyrene rings (288.5 eV) and the remaining 3 carbons of the pentafluorostyrene units 286.2 eV).[37, 38] The π–π* shake-up transitions of both polystyrene and polypentafluorostyrene are also observed at 291 eV and 293-296 eV, respectively. Quantitative analysis of the non-annealed film shows that the intensities ratio of the C=C (68.1 %) and C–C (23.5 %) components agrees with the composition of polystyrene (6:2). Note that the C-C component at 285 eV could also include aliphatic carbon from contamination. The polypentafluorostyrene is best fitted with two components (intensity ratio 5:3): 5 C–F bounds from the aromatic ring and the remaining 3 other carbons (those in the chain backbone) whose electrons are withdrawn by the fluorine atoms.[39]

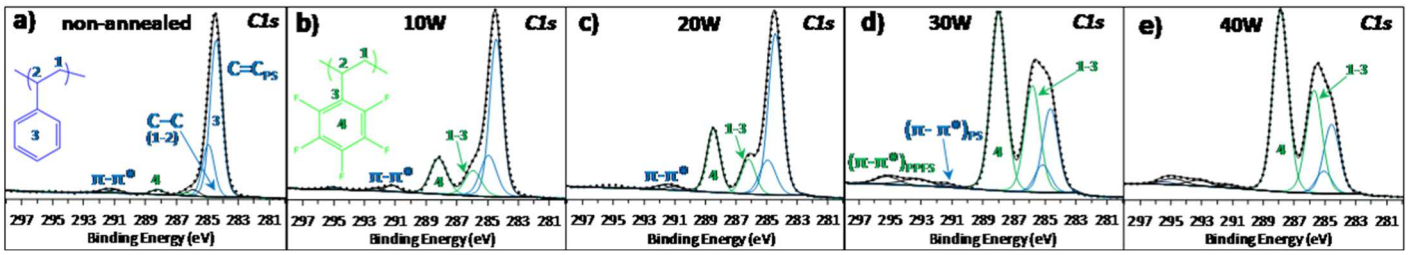


Figure 1. XPS carbon spectra of the a) non-annealed film and films treated with microwave at various powers: 10 b), 20 c), 30 d) and 40 W e) during 60 seconds.

As reported in Table 1, the intensity of fluorine increases along with the annealing power. A very significant increase is observed between the non-annealed sample (F: 3.8 %) and the sample annealed at 10 W, the minimum annealing power (F: 12.3 %). When the annealing power is increased from 10 W to 30 W, the intensity of the fluorine peak raises significantly to F: 26.8 % (Figure 1b-d). When the annealing power is increased beyond 30 W, no further rise of the fluorine is observed. Indeed, the amount of fluorine detected in the sample annealed at 40 W (F: 28.5 %, Figure 1e) is close to the one in the sample annealed at 30 W (Table 1). Also, when the samples

are annealed with different power conditions, from 10 W to 40 W, no additional components are observed by XPS analysis. Only the intensities of the same former components change or increase. This suggests that there is no chemical degradation of the sample under those various conditions.

Table 1. XPS quantification and characterization of the film components in function of the power (annealing time = 60 s).

Components	Position (eV)	FWHM (eV)	0 W[a] (%At.)	10 W (%At.)	20 W (%At.)	30 W (%At.)	40 W (%At.)
C=C	284.5	0.9	66.1	46.4	45.2	18.7	15.2
C–C	285	0.9	22.2	17.6	13.9	8.4	6.8
C–CF	286.2	1	2.1	8.7	8.9	16.7	17.8
C–F	288.5	0.9	3.2	11.9	14.9	25.6	28.8
π–π*	292	1.2	2.6	3.1	2	3.8	2.9
F–C	688.7	1.4	3.8	12.3	15.1	26.8	28.5

[a] Non-annealed sample

In order to save energy, 30 W was set as the optimum power to use in this study and the surface composition was followed during the annealing time from 0 to 210 seconds. Table 2 reports the carbon and fluorine surface content as measured by XPS (carbon spectra in Figure SI5). From 0 to 60 seconds microwave treatment, the fluorine surface content increases from 3.8 to 26.8%, and then stays stable to 25.9% for 90 s. Finally, when the annealing is longer, 120 seconds, the fluorine content slightly decreases to 21.1%. Although we could not observe a variation in the peaks shape in XPS, this decrease could come from a slight thermal degradation of the labile para-fluorine atoms at the interface with air.[35] This evolution in time corresponds to an increase of the temperature in the microwave vials. This leads consecutively to a more efficient surface segregation provided by a mobility rise and afterwards to a saturation at the surface. From these preliminaries experiments, a 60 s microwave treatment at 30 W was set for the rest of the study.

Table 2. XPS quantification and characterization of the film components in function of the annealing time (power = 30 W).

Components	Position (eV)	FWHM (eV)	0 second (% At.)	30 s (% At.)	60 s (% At.)	90 s (% At.)	120 s (% At.)

C=C	284.5	0.9	66.1	58.6	18.7	22.7	29.7
C–C	285	0.9	22.2	20.6	8.4	8.9	12.4
C–CF	286.1	1	2.1	3.4	16.7	13.3	13.4
C–F	288.5	0.9	3.2	6.1	25.6	21.5	19.2
π–π*	292	1.2	2.6	4.6	3.8	3.7	4.2
F–C	688.7	1.4	3.8	6.7	26.8	25.9	21.1

[a] Non-annealed sample

2.2.2. Variation of copolymer content in the blend

The blend composition was varied from 0 to 100 % of diblock copolymer to evaluate its influence on the surface wettability. Surface segregation was promoted *via* the microwave annealing and measurement of the contact angle with different liquids was performed to calculate the impact of the surface segregation on the surface tension values. In Figure 2a, the water contact angle is plotted against the copolymer content for the selected microwave treatment and, for comparison, the values of the non-annealed film are reported. First, the water contact angle raised when the copolymer content in the blend was increased, due to the augmentation of low surface energy fluorine atoms in the film. It is worth noting that the difference between the contact angles (CA) of a non-annealed pure PS film (90°) and the one of a pure PS-*b*-PFS film (101°C) is low. Nevertheless, after the microwave annealing, there is a clear increase in the water CA value for each composition of the blend except for the pure copolymer film. This is also in agreement with the surface segregation of the fluorinated segments observed by XPS. In the pure copolymer sample, the fluorine surface content before annealing must be sufficiently high to provide the surface with hydrophobic properties. The evolution of the contact angle with a non-polar solvent such as diiodomethane (Figure 2b) is more affected by the blend composition. Indeed, the difference between the pure polystyrene and the copolymer surface is 37° (respectively 29° and 66° after annealing). The same behavior has been observed between polyethylene and poly(tetrafluoroethylene) in which contact angle with diodomethane varied from 52 to 88°C when water contact angle changed only from 94 to 108°.[40] It can also be observed in Figure 2b that for every blend ratio above 5 % in additive, an increase of 20° is measured after the treatment of the film at 30 W during 60 seconds compared to the non-annealed sample. Oleophobic surfaces have largely been developed with polymer substrates and a common strategy is to functionalize micro-patterned surfaces with fluorine molecules.[41] Surface tension of the different polymer films was calculated by the OWRK method from the contact angle of three solvents, Water, Diiodomethane and Ethylene glycol (see experimental part and Table SI1 and SI2). Again, a strong influence of the surface segregation of the additive can be extracted from the values

reported in Figure 2c. For the blend with 5, 10 and 20 % in additive, the surface tension decreased by 4 to 8 $mN.m^{-1}$ after the microwave annealing. For comparison, the difference between polyethylene and poly(tetrafluoroethylene) surface tension is around 12 mN/m.[40]

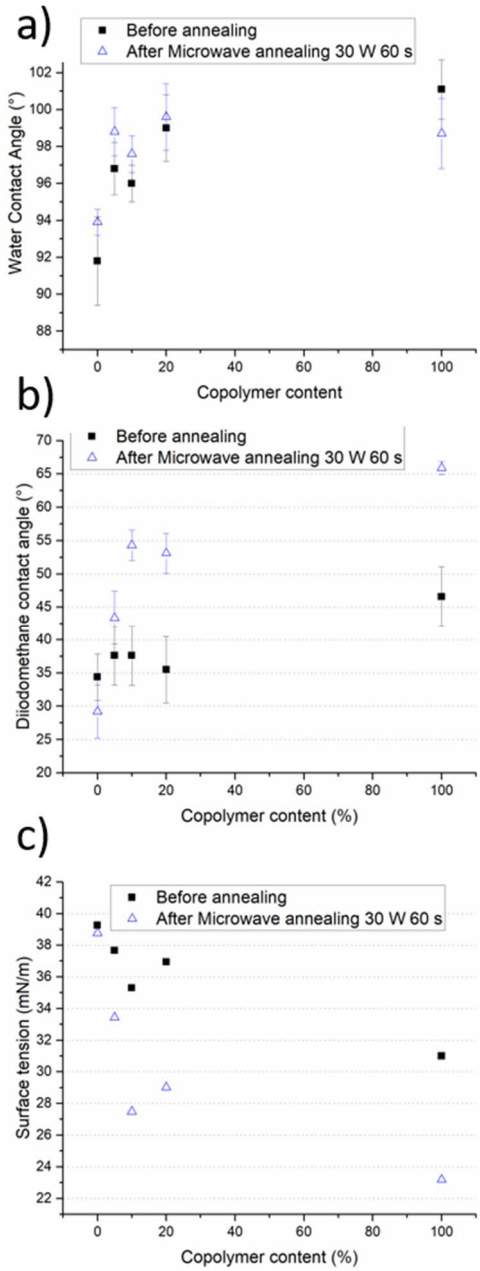


Figure 2. Evolution of the a) Water contact angle, b) Diiodomethane contact angle and c) surface tension of polymer blend composed of different matrix/additive ratios.

In order to understand these changes of wettability, the surface composition of these blends was analyzed by XPS (carbon spectra in Figure SI6 and surface composition in Table SI3). Figure 3 presents the overlay of the surface fluorine content of polymer film before and after annealing, with the theoretical content in the blend calculated from the matrix/additive ratio (calculation described in SI). The first observation is that the value of the fluorine surface content just after spin-coating is higher that the theoretical one. This means that surface segregation happened even during the evaporation process.[42] Indeed, the solvent allows chains to reorganize in order to minimize surface tension. This effect has already been observed by Affrossman *et al.* when they reported the study of a blend composed of a polystyrene matrix with a fluorine end-functional polystyrene.[27] Secondly, for all the blend compositions, the fluorine surface content increases after the microwave annealing promoting the migration of the copolymer. For example, when a blend of 5 w% in copolymer is used, the fluorine surface content is 2.1 % before annealing, and reaches 14 % after the 60 seconds treatment. This value corresponds to a surface enrichment as high as 55 w% in block copolymer. From a blend composed of 10 % of copolymer, a fluorine surface content similar to the one of a pure copolymer film was reached after annealing (around 25 %). Finally, the increase of the fluorine content for the pure PS-*b*-PFS film compared to the theory means that a reorganization in the upper layer occurs and leads to the surface orientation of the PFS block to the air.

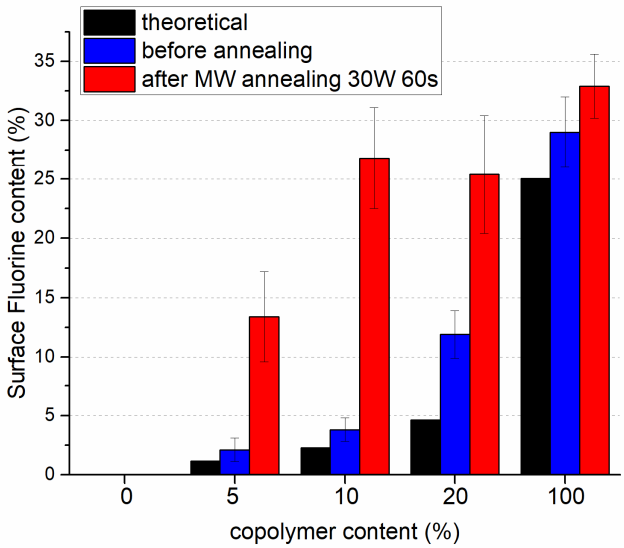


Figure 3. Comparison of the surface fluorine content determined by XPS before and after annealing for different polymer blends. The theoretical fluorine content in the blend is added, as calculated from the matrix/additive ratio.

2.2.3. Reversible segregation upon annealing in humid environment

Tanaka and Koberstein have shown in two different studies that immersing a polymer blend in a polar environment (water or ethylene glycol) could induce the adsorption of the more hydrophilic component at the surface.[12, 43] Using a polystyrene terminated by a fluorinated group, they proved the surface depletion of fluorine atoms after an annealing in saturated water vapor at 55 °C during 48 hours, resulting in the increase of the surface hydrophilicity. Indeed, the styrene unit being less hydrophobic than the fluorinated group, it migrated at the water/polymer interface. It has to be underlined that surface reorganization occurred in this case even in the glassy state. Following this finding, a sample composed of 10 % of diblock was first subject to treatment in dry atmosphere at 30 W during 60 s and analyzed by XPS to monitor the evolution of the surface composition. The fluorine surface content was around 30 % (see carbon spectra in Figure SI7 and surface composition in Table SI4). Then 0.5 mL of water was introduced at the bottom of the microwave vials, without changing the position of the samples (and the water does not touch the sample). Another annealing at 30W during 60 seconds was applied and some water vapor was observed in the vial at the end of the treatment. The fluorine surface content detected by XPS then decreased to 11%. The amount of fluorine for the sample annealed with water was still higher than before dry annealing (2.8 %) but lower than after the annealing in dry atmosphere (30 %). This strengthens previous findings in the literature in which research teams showed that annealing in water atmosphere could decrease the fluorine surface content of polystyrene blends. [12, 43, 44] Although the fluorine surface content didn't decrease to 0% after 60 seconds at 30 W, an appropriate annealing could lead to pure polystyrene surface. The objective of this study being surface functionalization from the fluorostyrene moieties, we did not further investigate this point.

2.2.4. Fluorine Depth Profile

In order to obtain more informations on the in-depth spatial distribution of fluorine within the copolymer film depending on the annealing conditions, ToF-SIMS depth profiles experiments (series of 30 cycles "analysis/sputtering" with 10 sec of etching per cycle) were performed on three different samples: a) the non-annealed film, b) the one after the microwave annealing in dry atmosphere (30W 60s) and c) the film after two

consecutive annealings, one in dry atmosphere followed by one in water vapor (2 times (30W, 60s)). Figure 4 presents the concentration depth-profile of C_2^- (in blue, representing the PS polymer matrix) and F^- (in green, representing the PFS block of the BCP additive) secondary ions over 220 seconds etching time obtained in negative polarity for the samples a), b) and c). The signal intensities were normalized relative to the total ion counts and adjusted to allow a better comparison between the three systems. In all cases, the C_2^- concentration increases with the etching while the F^- one decreases. However, for the annealing in dry atmosphere, the F^- signal decreases quickly at the beginning of the etching (the normalized intensity is equal to 0.07 after 5 cycles / 50 sec), while the F^- signal intensity remains much higher through all the sputtering for the non-annealing sample (the normalized intensity is equal to 0.48 after 50 sec and close to 0.4 at the end of the etching). For the sample c) with two consecutive annealing (one in dry atmosphere and one in water vapor), the fluorine signal mainly decreases during the five first cycles (the normalized intensity is equal to 0.16 after 50 sec) but with a lower slope comparing to sample b). Afterwards the intensity remains stable between 70 sec and 140 sec and then slightly increases to 0.2 until the end of the sputtering. A 3D image can be reconstructed for each system from the related depth profiles where the signal intensities of the considered secondary ions C_2^- and F^- are plotted over the analyzed area (600µm . 600µm = x and y dimensions) versus the etching time (the z axis, 220s). For a better visibility, the z axis is over-dimensioned compared to the other axes. Each species has a 3D distribution over the analyzed volume with one specific color (blue for C_2^- and green for F^-). The final 3D map corresponds to the overlay of the two species 3D distributions, to which a transparency factor is applied so that the two colors can be seen (the light blue color corresponds to areas where both ions C_2^- and F^- are present). When a color (corresponding to one species) is not appearing anymore on the image, it means the intensity of the related peak on the mass spectrum is too low to be plotted. Note that the sputtered depth has not been determined here; references samples of each polymer with precise thickness should have been analyzed using the same etching conditions to determine the sputtering ion yield of each compound. The 3D image related to the annealing in dry atmosphere b) clearly shows that fluorine species, characteristic of the PFS block, are mainly located at the upper part of the sample, which confirms the enrichment of the surface blend by the BCP additive and the depletion of the inner layers (bulk). For the non-annealed film a), even if the proportion of F^- is higher at the top surface than in the inner part of the blend, fluorine species are observed all over the analyzed volume, which confirms that BCP additive is present everywhere in the blend before annealing. Regarding the sample c), fluorine species are mainly located at the

surface of the blend but also over the entire analyzed volume, which reveals a fluorine migration from the top to the inner part of the blend induced by the second annealing in wet atmosphere. This preliminary experiment highlights the reversibility of the segregation process by changing the conditions of annealing.

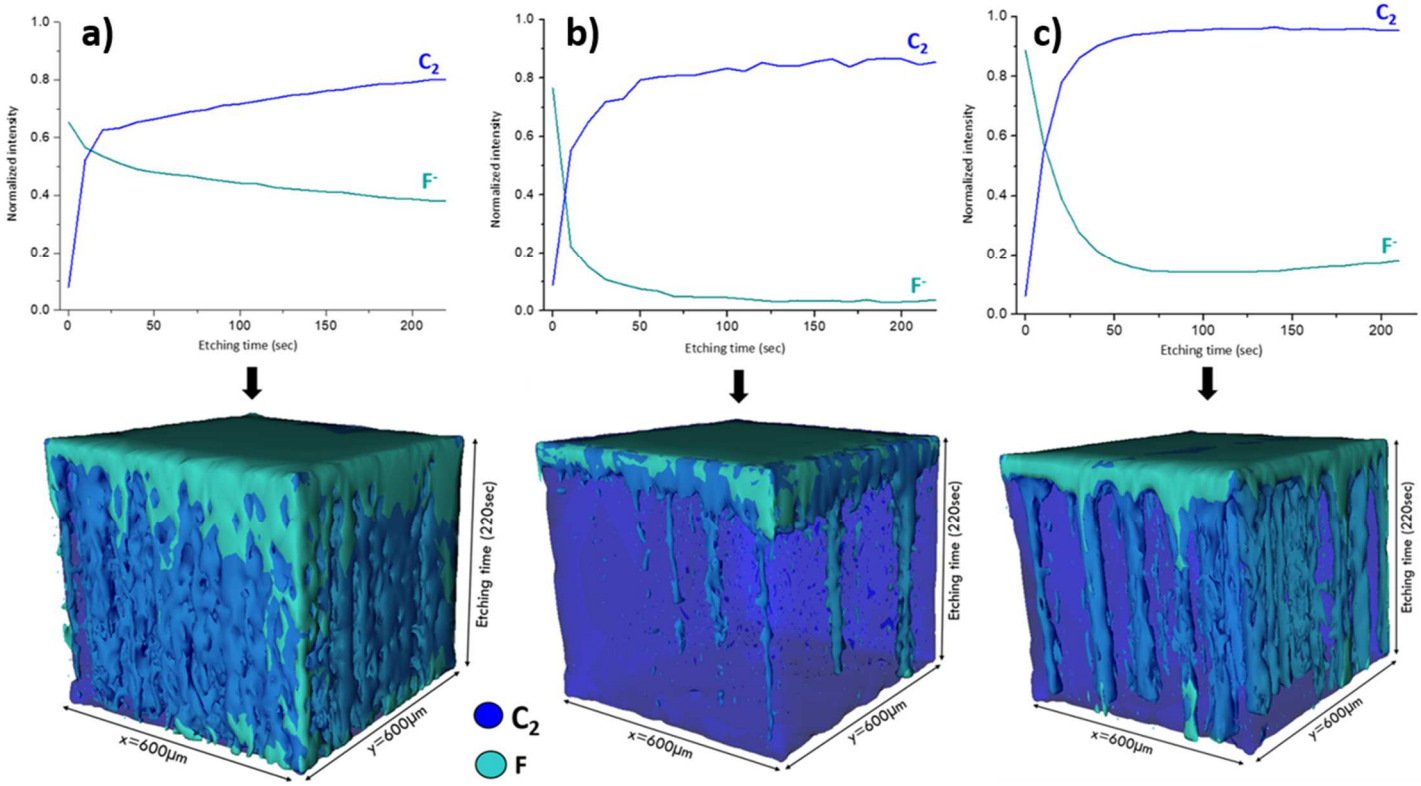


Figure 4. TOF-SIMS depth-profile experiments over 220s etching time of C_2^- (in blue) and F^- (in green) secondary ions in negative polarity and 3D images reconstruction from the depth-profiles showing the spatial distribution over 600 . 600µm^2 raster size and 220s etching time (for a better visibility, the z axis is over-dimensioned compared to the other axes) of C_2^- (in blue) and F^- (in green) at the surface of a polymer film from a blend of 10/90 in block copolymer/PS matrix a) before annealing, b) after a microwave annealing in air at 30W during 60s, c) after 2 successive microwave annealings at 30W during 60s, the first one in air and the second one in humid atmosphere.

2.3. Surface para-fluoro-thiol click reaction

In 2017, Delaittre *et al.* synthesized a statistical copolymer of N,N-dimethylacrylamide and pentafluorostyrene and studied its modification with thiols in water.[45] Following their experimental procedure, we studied the surface functionalization of the polystyrene film. For that purpose, a polymer blend composed of 10 w% of PS-

b-PFS was submitted to the microwave annealing to reveal the pentafluorostyrene moieties at the surface. Then, cysteine was grafted *via* thiol nucleophilic substitution of the para-fluorine atoms (Figure 5). XPS analysis of the annealed film grafted with cysteine revealed the presence of the anchored molecule at the surface of the sample, with nitrogen and sulfur atoms detection. The amount of fluorine measured by XPS after the modification decreased significantly (17.1 %, Table SI5) as compared with the film before the cysteine grafting (29.8 %). This is mainly due to the nucleophilic substitution of the para-fluorine atom. However, if only one fluorine (in para position) out of five in the repetitive unit is substituted by cysteine, then 24 % out of the initial 30 % of fluorine must remain at the surface. The extra 7 % (from 24 to 17 %) can either come from the presence of additional chemical elements at the surface of the film (sulfur, nitrogen) that naturally decreases the atomic composition of all element, or from a possible slight reorganization of the surface during the grafting reaction occurring in water (at room temperature), leading to a decrease in the PSF surface content. Therefore, it was not possible to investigate precisely the amount of fluorine that reacted with cysteine.

After the immobilization of gold nanoparticles *via* the cysteine anchors, no changes were observed by XPS in the chemical environments of the various elements. Only the grafted GNPs were clearly detected with a significant atomic contribution of 1.1 % (Table SI5).

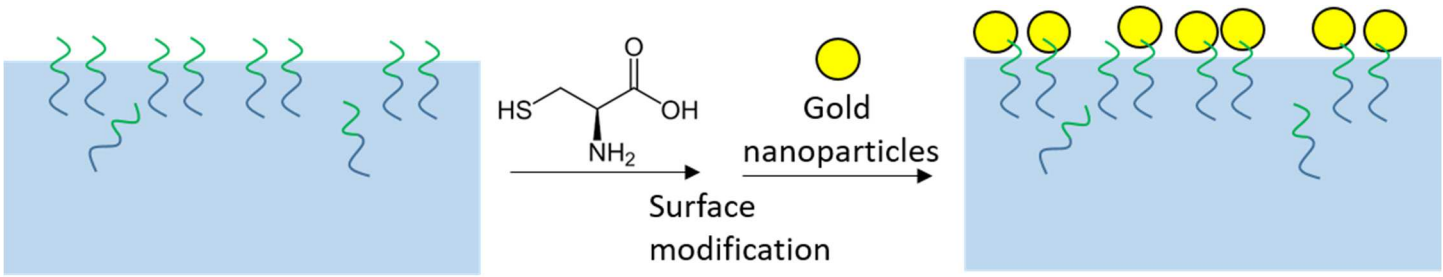


Figure 5: Gold nanoparticles grafting onto the pentafluorostyrene platform revealed by surface segregation

Atomic force microscopy was also used to assess the changes of the surface morphology before and after microwave annealing but also after GNPs grafting. In the PS-*b*-PFS block copolymer, the PS volume fraction is 0.4 and the AFM analysis of the pure diblock showed a nano-phase segregation with a mixture of *in-plane* and *out of plane* PS cylinders in a PFS matrix (see Figure SI8a). Figure 6a shows the image of the polymer blend with

10% of diblock before microwave treatment. The surface is mainly covered by polystyrene (in yellow) with small copolymer domains (corresponding to black domains). After microwave annealing, the surface covered by the copolymer largely increased and 200 nm domains appeared in which an *out-of-plane* cylindrical nano-structure can be observed (Figure 6b). Around these large domains, the homopolystyrene matrix is pierced by smaller copolymers areas. Obviously, the PS matrix does not swell the PS domain of the diblock due to its high molar mass (≈300 000 $g.mol^{-1}$) but there is a good compatibility between the macromolecules since no microphase segregation was observed. After the GNPs grafting, the films were imaged by AFM and SEM (Figure 6c and 6d respectively). With both techniques, a non-uniform gold pattern is observed, with a structure corresponding to the PS-*b*-PFS initial domains. Indeed, the PS phases being insensitive to nucleophilic substitution, the nanoparticles cannot be immobilized in these areas. It has to be underlined here, that the geometry of the grafting area (cylinders) is dependent of the diblock composition and therefore can be tuned by appropriate synthesis conditions. The average diameter of gold nanoparticles measured from AFM images (Figure 6-c) is 25 nm in good correlation with the UV-visible absorbance spectrum of the unbound particles showing a maximum at 523 nm (figure SI15).

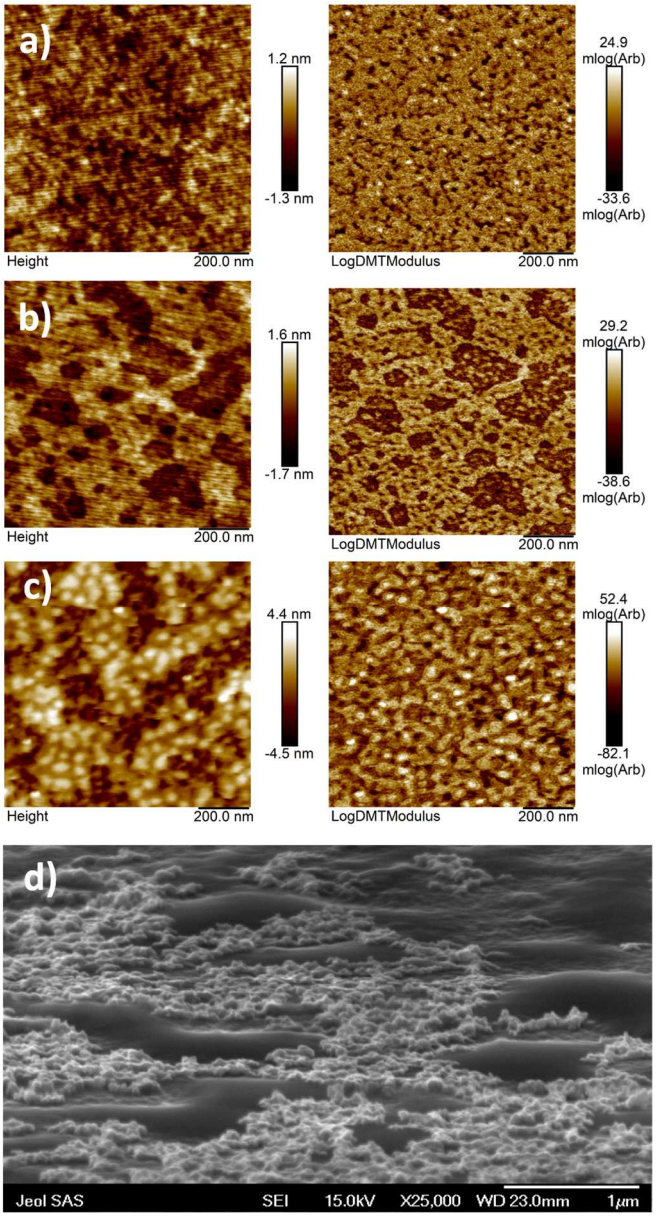


Figure 6. Images of the surface of a blend composed of 10% PS-*b*-PFS a) before any modification (AFM), b) after microwave annealing (AFM) c),d) after functionalization with Au NPs (AFM c, SEM d).

3. Conclusion

In summary, we demonstrated the efficiency of a microwave annealing to promote the surface segregation of a fluorinated additive, the PS-*b*-PFS, in a PS matrix. In 60 seconds, at a power of 30 W, the block copolymer enriches the surface and increases the hydrophobicity and oleophobicity of the film, without degradation of the matrix material. A blend of 10 w% in additive can lead to a surface composed of more than 20 % of fluorine atoms. ToF-SIMS, used to follow the in-depth spatial distribution of fluorine within the film, clearly showed that the surface was enriched in copolymer compared to the bulk of the film. This surface segregation phenomenon

is reversible. Indeed, when the same microwave annealing is performed under water vapor atmosphere, the low surface energy fluorine atoms hide in the bulk and a polystyrene surface is restored. Finally, it was proved that this time and energy reducing methodology is an efficient way to provide a functional platform for the immobilization of materials at the surface of, at the beginning, inert (PS) materials. Indeed, the PFS moieties can undergo nucleophilic substitution with thiol and have been used in this study to immobilize GNPs in the block copolymer domains. This methodology could be applied to a wide range of applications such as supported catalysis or bioadhesion.

4. METHODS

4.1. Experimental

Synthesis

PS-*b*-PFS diblock copolymer was synthesized in two steps using Nitroxide-Mediated Polymerization (NMP) as reported in supporting information (Scheme SI1). In the first step, styrene (120 mmol), the Blocbuilder® alkoxyamine (0.5 mmol) and the nitroxide radical (SG1 solution, 0.07 mmol, 15%) were added to a round bottom flask of 50 mL. The flask was sealed with a septum, put in an ice bath, degazed for fifteen minutes with nitrogen and immersed in an oil bath at 115 °C for 5h to reach 50 % of conversion (determined by ^{1}H NMR). The resulting viscous mixture of polystyrene (PS) and the styrene were precipitated twice in methanol to remove the remaining monomer, filtered and dried at room temperature under vacuum. In the last step, 300 mg of the dried powder of PS (0.025 mmol) were dissolved in 5 mL of dimethylformamide (DMF) overnight. After solubilizing PS-macroinitiator, the 50 mL round bottom flask was put in an ice bath. Then pentafluorostyrene (PFS) (7.5 mmol) and nitroxide radical (SG1 solution, 0.003 mmol, 15%) were added, the flask was sealed with a septum and the mixture was degassed for 15 minutes with nitrogen and immersed in an oil bath at 115 °C. After 3h, the reaction was stopped and the resulting block copolymer was precipitated twice in methanol, filtered, and dried at room temperature under vacuum. The resulting block copolymer (PS-*b*-PFS) was analyzed by ^{1}H NMR and size exclusion chromatography (SEC).

The homopolystyrene matrix is a commercial product from PSS-Polymer with a molar mass of Mn = 300 000 g.mol^{-1} and a Đ = 1.2.

Surface attachment of gold nanoparticles

The attachment of gold nanoparticles at the surface of the polymer blend with 10 % of diblock after microwave treatment was done through a nucleophilic substitution of the pentafluorostyrene with thiol groups from the cysteine. A 4 % toluene solution of polymer blend was spun cast on a silicon wafer substrate and annealed at 30 W during 60 s to allow the migration of the fluorine atoms at the surface of the film. The substrate was then dipped into 25 mL of a buffered solution (pH 12: NaOH: 35 mg + Na_2HPO_4:115.4 mg) containing cysteine (0.01M) for 7 hours at room temperature to allow the grafting of cysteine via thiol nucleophilic substitution of the para-fluorine atoms. Afterwards the film was thoroughly washed several times in buffered solutions (pH 12) to remove unbound cysteine, and finally washed twice in water to remove and avoid the formation of salt crystals during the drying process. During all these steps, we didn't observe any degradation of delamination of the films. The film was dried and analysis by XPS to observe the attachment of cysteine at the surface of the annealed film. A decrease was also observed in the water contact angle value of the film, from 98° to 72° before and after cysteine grafting respectively. In the last step, the cysteine-grafted film was dipped again into 25 mL of a buffered solution containing cysteine (0.01 M). Next 0.5 mL of a 50 mM of $HAuCl_4$ solution was added and mixed for 15 minutes before adding 2.5 mL of a $NaBH_4$ solution (0.01 M). After 2 hours, the color of the mixture became red due to the formation of gold nanoparticles stabilized by the fixation of cysteine at the surface of gold. This fixation occurs not only in solution but also at the film surface where cysteine molecules grafted on the film bound the surface of gold during the formation of the nanoparticles. The reaction was left over night at room temperature to complete the fixation of gold nanoparticles at the surface of the film. The film was washed successively in a buffered solution (pH 12) and in water several times to remove unbound nanoparticles and avoid the formation of salt crystals.

Thin films preparation

Toluene solutions of polymer blend were prepared at 4w% and spin-coated onto boron doped silicon substrates (TED PELLA – prod. n°16010, Orientation: <100>, Resistance: 1-30 Ohms Type: P (Boron doped)) at 1000 rpm to reach a thickness around 300 nm (measured by ellipsometry).

Microwave annealing

A CEM microwave was used on fixed mode at several powers for a controlled time. Microwave heating films were cast on substrate with a surface of 0,7 x 0,7 cm². The set-up used to submit the wafers to the microwave irradiation is described in supporting information (SI1). For the experiments in humid atmosphere, 0.5 mL of water is added in the microwave tube at the bottom without any contact with the film.

Characterization Techniques

All details about the characterization techniques can be found in supporting information.

Associated content

Supporting Information. Experimental details and additional characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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