Localized and structured growth of polymer brushes using ink jet printing approach

Tarek Ali Azouaou[1], *Justin* Lemarchand[1], *Vincent* Noël[1], *Giorgio* Mattana[1], *Philippe* Decorse[1] and *Christian* Perruchot[1*]

[1] Université Paris Cité, CNRS, ITODYS, F-75013 Paris, France

Abstract. Inkjet printing (IJP) technique has been used for the deposition of silica nanoparticles with controlled position and shape onto flexible polyethylene naphthalate (PEN) substrate. The printed silica areas have been chemically functionalized with a silane molecule bearing an ATRP initiator group. Surface-initiated atom transfer radical polymerisation (SI-ATRP) methodology has been betrothed to grow polymer brushes onto the silica printed areas. X-ray photoelectron spectroscopy (XPS) has been used after each step of functionalisation in order to determine the elemental surface composition. In addition, IJP has been used to design specific pattern at 250 micrometer scale. By combining maskless IJP technic and XPS line-scan mode, this work clearly demonstrates that the position and the pattern shape of printed areas can be controlled on demand, and that, structurally polymer brushes are only generated onto the functionalised silica printed areas.

Introduction

Surface modification of conducting or insulating substrates by polymer brushes has become a powerful approach to tailor on demand either the chemical or physical properties of material interfaces [1]. To ensure long-term stability and durability of the properties, each polymer brush must be covalently tethered by one chain-end to the substrate surface. Among the various approaches to graft polymers onto surface substrate, surface-initiated controlled radical polymerisation (SI-CRP) has demonstrated to be very powerful and allows great advances for surface engineering. Indeed, polymer brushes have several applications, mainly in the fields of stimuli-responsive surfaces (pH-, thermo- sensitive), biofouling surfaces, bio-compatible surfaces, bio-sensing surfaces, wetting / non-wetting surfaces [2-3]. SI-CRP approach is mostly employed as a result of its relative simple experimental setup, using mild temperature conditions, high tolerance towards a large variety of functional monomers and is also compatible with aqueous or green chemistry media. In addition, good control of the thickness of the top layer polymer can be obtained, with a high grafting density. However, all SI-CRP strategies need pre-treatment of the surface substrate with specific functional group that can initiate the polymerisation reaction to process. Among the grafting from strategies, surface-initiated atoms transfer radical polymerisation (SI-ATRP) has been widely used since halogenated initiator moieties can be easily grafted onto the surface substrate [4-5]. SI-ATRP allows the growing of polymer brushes on various organic, inorganic, metallic or semi-conducting substrates [6]. Grafting of the initiator group is obtained by chemical or electro-chemical treatment by dipping the substrate into a solution containing a bi-functional molecule (i.e. molecule containing a reactive anchoring group on one end and an ATRP-initiator group at the other end). The entire surface of the substrate is then covered by the ARTP-initiator moieties and the polymer brushes grow from the complete treated surface. Consequently, there is no control of the position or shape of the polymer area onto the substrate surface.

In the recent years, inkjet printing (IJP) technique has attracted considerable attention since easy functionalisation of planar and flexible substrate can be obtained using commercially available inks formulation containing either inorganic (i.e. silica) or metallic (i.e. copper, silver, gold) nanoparticles suspension in aqueous media [7]. IJP is very a versatile and adjustable technique since the position, the shape and the dimension (from ~100µm up to centimeter length) of the printed area can be easily controlled via dedicated PC software. IJP is a fully digital and non-contact technique, but more importantly, it is a maskless technique. In addition, IJP is performed at ambient conditions and do not require large volumes of ink. Using IJP technique, the dimension of the printed area fill the gap between the fully treated-surface using conventional chemical, electrochemical or physical (plasma, CVD, PVD) approaches and functionalisation of nanometer-size area scales using lithography (photo- or electro-) or micro-electrochemistry techniques [8].

In this work, inkjet printing technique has been used for the deposition of nanoparticles of silica (i.e. *NP*-silica) with controlled position and shape onto flexible

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* Corresponding author: christian.perruchot@u-paris.fr

polyethylene naphthalate (PEN) substrate. A silane molecule, functionalised with a halogenated ATRP end-group, is then covalently grafted onto the silica printed areas. Finally, SI-ATRP procedure, using different methacrylate monomers, has been used to grow polymer brushes onto the silica printed areas. X-ray photoelectron spectroscopy (XPS) has been used to control the modifications of the elemental surface composition after each chemical treatment of the substrate, and to confirm the growth of polymer brushes onto the printed areas. In addition, onto patterned surface, XPS line-scan mode allows to reconstruct the surface composition.

Experimental

Ink jet printing:
Poly(ethylene) naphthalate (PEN Teonex® Q65HA) flexible and transparent substrate was purchased from Putz Folien (Germany). Fumed NP-silica (Sigma) was used to formulate the ink suspension (1% wt / vol in ethanol-water 90-10 vol / vol). Areas functionalised by silica were inkjet-printed using a Fujifilm Dimatix Materials Printer DMP-2850 [9], directly on the PEN substrate. The ejected volume of the dropped ink was 10 pL and the drop spacing was set at 10 μm. The printer platen temperature was maintained at 40°C during printing, to promote rapid evaporation of solvent and reduce the 'coffee-ring' edge effect. Finally, the printed pattern areas were thermally sintered in an oven at 180°C during one hour.

ATRP initiator:
3-(2-bromoisobutyramido) propyltriethoxysilane (chemical structure in Figure 1a) has been synthesized according to literature [10]. The silane functionalized with the ARTP initiator was grafted by immersing the PEN-silica substrate in a water/ethanol solution (80 / 20 vol. by vol.) containing 1% silane molecule for 6 hours. The resulting functionalized substrate was carefully and abundantly rinsed with ethanol to remove all excess of unreacted silane, then air-dried overnight at room temperature (RT). The silane end group acts as anchoring species to silica printed area whereas the halogenated end groups serve as initiator for the ARTP process in order to grow the polymer brushes.
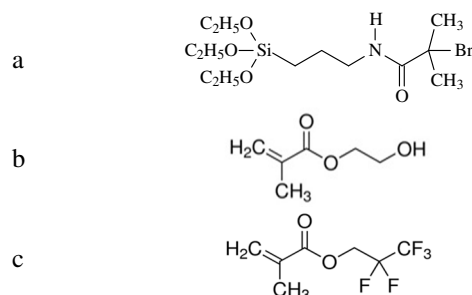
ATRP Chemicals and procedure:
Copper bromide (CuBr) catalyst, pentamethyldiethyl triamine (PMDETA) ligand and methacrylate monomers (hydroxyethyl methacrylate (HEMA) and pentafluoropropyl methacrylate (PFPMA)) were purchased from Sigma Aldrich and used without further purification. The chemical structure of HEMA and PFPMA monomers are presented in Figures 1b and 1c respectively.

In a typical polymerisation procedure, the functionalised initiator grafted onto silica printed area was immersed into argon-degassed acetonitrile solution (6 ml) containing CuBr catalyst (100 mg, 0.68 mmol) PMDETA ligand (150 μL, 0.68 mmol) and methacrylate monomer (1.66 mL for HEMA or 2.32 ml for PFPMA). The catalyst / ligand / monomer were set at 1 / 1/ 20

molar ratio for all experiments. The reaction polymerisation was moderately stirred overnight at RT. The resulting material was carefully rinsed with acetonitrile to remove all non-grafted catalyst/ligand and monomer species. The polymer brushes grafted onto the silica printed area were vacuum-dried prior to XPS analysis. The sample notation is as follows:
PEN-SiO₂-Init-pHEMA (for HEMA monomer) or PEN-SiO₂-Init-pPFPMA (for PFPMA monomer).

Fig. 1: Chemical structure of (a) silane bearing ATRP initiator, (b) HEMA and (c) PFPMA molecules
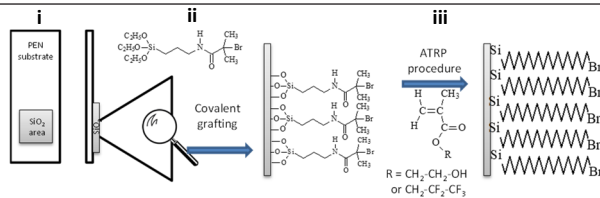
XPS Characterization:
XPS analysis were performed on a K Alpha⁺ spectrometer (ThermoFisher), equipped with a monochromated X-Ray Source (AlKα, 1486.6 eV). An X-ray spot size of 400 μm was used. The hemispherical analyzer was operated in CAE (Constant Analyzer Energy) mode, with a pass-energy of 100 eV and a step of 1 eV for the acquisition of survey spectra, while a pass-energy of 40 eV and a step of 0.1 eV were used for the acquisition of high resolution spectra. The spectra were recorded and data processing was performed with Advantage© software (V 5.99 from ThermoFisher). The elemental surface compositions were calculated by determining the area of each element of interest with a Shirley type background subtraction and using the Scofield sensitivity factors of the spectrometer. The spectra were calibrated against the C_{1s} main peak component C-C/C-H set at 285.0 eV.

Results and discussion

Inkjet printed areas are digitally controlled via appropriate software, but more importantly, IJP is a maskless technique. Thus the position and the pattern, with shape and dimension varying from *ca* 100 μm lateral resolutions up to centimeter scale, of the printed area can be controlled on demand.

In a preliminary experiment, IJP was used for the deposition of silica on 0.5 * 0.5 mm² areas onto the PEN substrate.

Figure 2 summarizes the stepwise strategy used to grow polymer brushes onto the PEN substrate. The three steps are (i) surface modification of PEN substrate by inkjet printing of silica patterns, (ii) grafting the silane functionalised with the ATRP initiator and (iii) the growth of the polymer brushes using ATRP procedure.

Fig. 2: General scheme summarizing the stepwise strategy used for surface modification of PEN substrate by (i) inkjet printing of silica pattern (0.5 * 0.5 mm²), (ii) grafting the silane functionalised with the ATRP initiator and (iii) the growth of the polymer brushes using ATRP procedure.

XPS was used to monitor the changes in the surface chemical composition of the PEN substrate after each functionalization step [11]. Figure 3 displays the survey spectra of bare PEN substrate (Fig. 3a), silica inkjet-printed area (Fig. 3b), silica chemically functionalized with the silane bearing the ARTP initiator (Fig. 3c), and after the growth of polymer brushes using HEMA (Fig. 3d) or PFPMA (Fig. 3e) monomer by ATRP procedure.
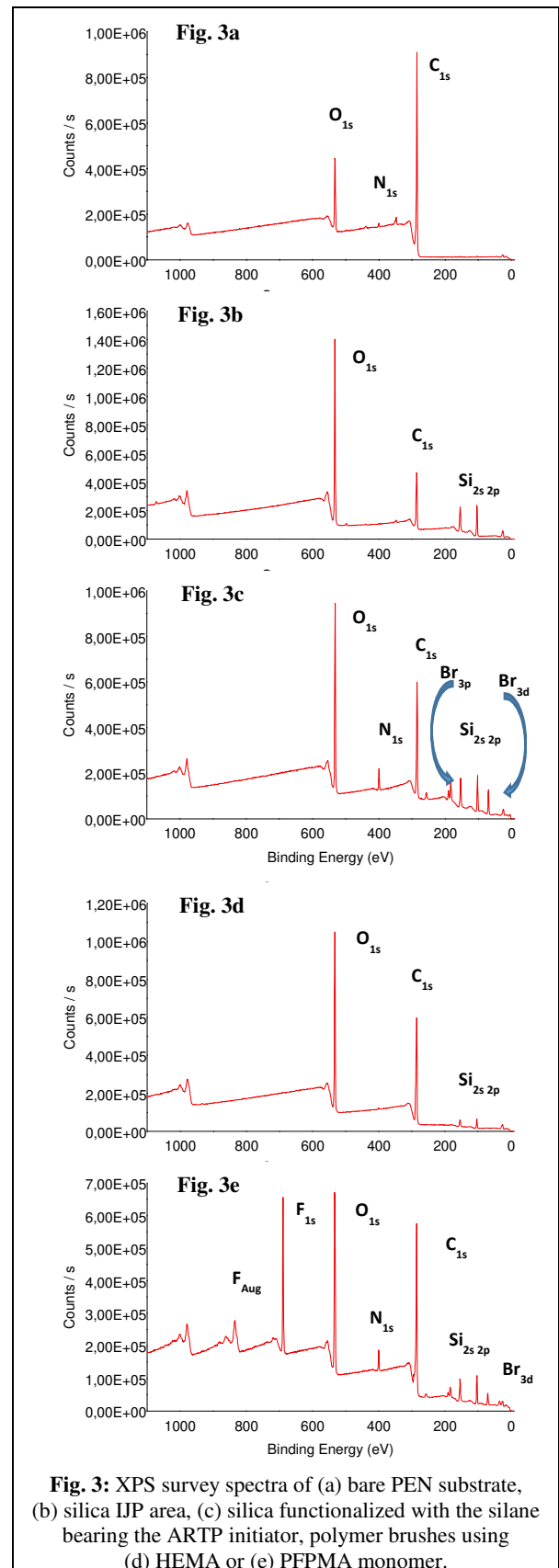
For bare PEN substrate (Fig. 3a), carbon C_{1s} (285 eV) and oxygen O_{1s} (532 eV) peaks are clearly detected, as expected. Adventitious nitrogen N_{1s} (400 eV) and calcium Ca_{2p} (349 eV) peaks are weakly detected.

After IJP of a silica layer (Fig. 3b), the relative intensity of carbon C_{1s} peak is decreasing whereas the relative intensity of oxygen O_{1s} peak is increasing (oxygen arising from PEN substrate and silica top layer). Additional peaks of silicon Si_{2p} (102 eV) and Si_{2s} (153 eV) are clearly detected. These latter peaks are characteristic of the silica deposited surface layer.

Chemical grafting of the silane bearing ATRP initiator (Fig. 3c) is clearly evidenced by the detection of nitrogen N_{1s} (~400 eV) and bromine Br_{3d} (~70 eV) - Br_{3p} (182-190 eV) doublet peaks respectively. These elements are unambiguous markers and clearly demonstrate the effective grafting of the ATRP initiator groups onto the silica layer. Silane derivatives are molecules known to react easily towards hydroxyl surface groups present on metallic, oxide or inorganic (alumina, silica) surfaces [12].

Using the ATRP procedure with methacrylate monomer, polymer brushes are generated onto the silica areas. In the case of HEMA monomer (Fig 3d), carbon C_{1s} and oxygen O_{1s} peaks are clearly observed, whereas the relative intensities of silicon Si_{2p} and Si_{2s} peaks considerably decrease. Nitrogen N_{1s} signal is almost not detected. These observations clearly demonstrate that the outermost pHEMA brushes mask the underlying silica layer, inducing a significant decrease of the silicon and nitrogen peaks intensity [13].

When PFPMA monomer is used to grow polymer brushes, in addition to carbon C_{1s} and oxygen O_{1s} peaks, silicon Si_{2p} and Si_{2s}, nitrogen N_{1s} and bromine Br_{3d} signals are still detected, but with lower intensities when compared to Figure 3c. However additional peaks assigned to fluorine F_{1s} (~689 eV) and F_{Auger} (~835 eV) are clearly detected. Fluorine is an unambiguous elemental marker of PFPMA monomer (5 fluorine atoms per monomer unit). Thus the detection of fluorine peaks are a direct confirmation that polymer brushes are grafted onto the silica layer.

Fig. 3: XPS survey spectra of (a) bare PEN substrate, (b) silica IJP area, (c) silica functionalized with the silane bearing the ARTP initiator, polymer brushes using (d) HEMA or (e) PFPMA monomer.

The surface elemental compositions as determined by XPS of the PEN substrate after each step of functionalization are reported in Table 1.
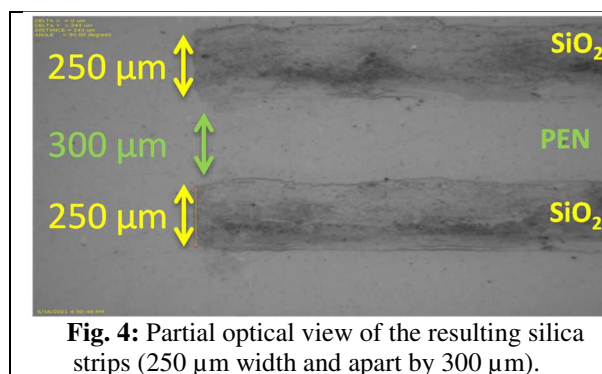
Element (%) Sample	C	N	O	Si	Br	F

Raw PEN	83.5	1.1	15.0	0.4	---	---
PEN-SiO₂	36.7	0.1	44.5	18.7	---	---
PEN-SiO₂-Init	47.1	4.8	31.4	14.4	2.4	---
PEN-SiO₂-Init-p(HEMA)	63.1	0.4	31.7	4.8	< 0.1	---
PEN-SiO₂-Init-p(PFPMA)	55.1	3.3	22.4	7.3	0.9	11.0

Table 1: Surface elemental compositions as determined by XPS.

When compared to bare PEN substrate, the deposition of a thin silica layer by IJP onto the PEN substrate induced a significant decrease of the carbon content, and an increase of the oxygen and silicon contents as expected. The PEN substrate is partially masked by the top silica layer. Grafting of the silane bearing the ATRP initiator group is evidenced by the increase of the nitrogen and bromine contents. XPS analyses clearly demonstrate that polymer brushes are present at the outermost surface of the silica layer. Indeed, the significant decrease of nitrogen and silicon contents (for HEMA monomer) and the specific detection of fluorine peaks (for PFPMA monomer) are unambiguous proof that the ATRP initiator is still active after chemical grafting and that it can engender the growth of polymer brushes via SI-ATRP procedure. The outermost polymer brushes thus mask the underlying PEN-silica substrate [14].

In order to push even further the lateral resolution of the IJP technique, four strips of silica, having a width of 250 µm and apart by 300 µm, have been patterned onto the PEN substrate. Figure 4 presents an optical view (partial view recorded from the Dimatix printer camera) of the resulting silica bands deposited by IJP.
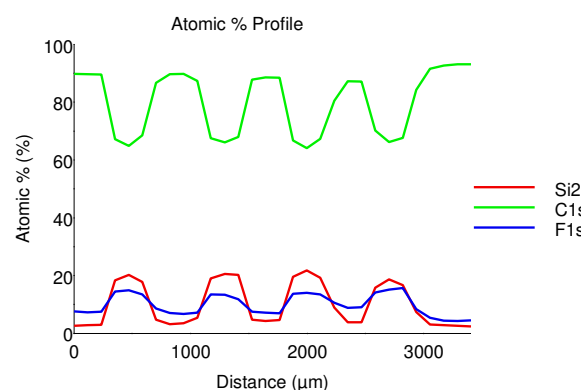

Fig. 4: Partial optical view of the resulting silica strips (250 µm width and apart by 300 µm).

As previously described, similar protocols have been employed in order to (i) graft the silane functionalized ARTP-initiator and (ii) to growth polymer brushes with PFPMA monomer using ATRP procedure, onto this patterned PEN-Silica surface.

The resulting patterned material has been characterized by XPS using the line-scan mode. The diameter of the X-ray source was set at 100 µm and the step size was fixed at 50 µm. The line-scan analysis was performed perpendicularly to the silica strips pattern. Figure 5 presents the reconstructed carbon, silicon and fluorine contents as determined by scan-line mode analysis.

Fig. 5: Plot of the reconstructed carbon, silicon and fluorine contents as determined by scan-line mode analysis.

The scan line mode analysis clearly shows a "square wave" form. The carbon rich areas mainly arise from the uncoated PEN substrate, whereas the silicon rich areas are a direct evidence of the silica bands deposited by IJP. Silicon exhibits four maximum plateau values corresponding to the four printed silica regions. It is important to note that carbon and silicon rich areas are opposed, demonstrating that the top silica printed layer partially mask the underlying PEN substrate. The width of the maximum silicon plateau contents is approximately 250 µm, in good agreement with the width of the silica printed areas. In addition, fluorine is used as a unique elemental marker of the PFPMA polymer brushes. It is worth noticing that the shape of the fluorine content matches that of the silicon one. This observation clearly demonstrates that polymer brushes are mainly present onto the silica regions, as expected. This scan line analysis demonstrates that silica bands can be printed onto the PEN substrate and that after chemical treatment via the silane containing the ATRP initiator group, the growth of polymers brushes can be localised on the desired position with specific shape.

Conclusion

Inkjet printing technology has been used to print silica areas onto flexible PEN substrate. The silica was subsequently chemically modified with a silane molecule bearing an ATRP initiator. Then, the initiator groups are active to generated polymer brushes via SI-ATRP process on the treated areas. These results demonstrate that structurally and controlled design, of various shape and dimension, can be easily generated by inkjet printing technique. The physico-chemical surface properties of the resulting material are thus governed by the specific properties of the polymer brushes. Work is currently in progress in order to lower the dimension of the printed silica zones, to extend this approach to others flexible insulating (i.e. Kapton ®, polyethylene imine) or conductive (ITO coated PET) substrate and to pattern the substrate with more complex shapes. In addition, using others (meth)acrylate monomers bearing specific lateral group, polymer brushes exhibiting specific

chemical properties will be generated only on the desired position. Thus the resulting material will exhibit specific properties only on the structurally and localised printed areas.

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