Induction heating for surface triggering styrene polymerization

1. Introduction

Titanium and its alloys present high interests for technological applications due to their high resistance corrosion, mechanical properties and biocompatibility [1-5]. For example, titanium is largely used as orthopedic metallic implant [6]. In addition, TiO_2 layers on Ti possess a wide variety of functional properties in self-cleaning [7,8], photocatalysis [9], gas sensing [10,11], solar energy conversion [12] and wettability [13].

In combination with those remarkable characteristics, some Ti applications require specific surface properties that can be imparted with suitable surface functionalizations of the TiO_2 oxide layer. Creating a thin and adherent polymeric layer is one of the common ways to achieve such a surface modification. This kind of polymeric layers can be obtained via surface-initiated atom transfer radical polymerization (ATRP). Nowadays, a wide variety of materials have been reported as suitable substrates for surface-initiated ATRP: glass, metals, metal oxides, etc. [14-20]. ATRP takes place through a reversible redox reaction involving a transition metal catalyst which is oxidized as the polymer is converted from the dormant state to the radical active state. The mechanism involves the transfer of a halogen atom from an initiator to the metal catalyst yielding an active radical initiator, which can then lead to the monomer polymerization.

ATRP surface-initiation can be carried out if the polymerization initiator is grafted on the surface to functionalize. The tendency of organophosphonic acids to form monolayers on metal oxide surfaces [21-24] and their important resistance to homocondensation and hydrolysis [25] make them interesting candidates for TiO_2 surface functionalizations. Therefore, the grafting of phosphonic acid compounds on titanium is a topic of great interest that has already been widely studied [26-35]. As the phosphonic acid function is able to strongly bind TiO_2 surfaces, it can be used as an anchoring group to graft an ATRP initiator in order to do surface-initiated ATRP polymerization.

Heating the system during ATRP polymerization facilitates the radical formation and prevents the deactivation of the radical by back transfer of the halogen from the metal catalyst to organic radical species [36,37]. To the best of our knowledge, ATRP studies published so far in the literature always mention a conventional heating method. More specifically, conventional heating methods are used in published studies about polymer brush formation on TiO_2 by ATRP [38-40]. Nevertheless, a new promising way to heat conductive pieces exists: induction heating. Induction heating is a heating method for conducting materials allowing to heat a substrate directly and contactless. It is based on Faraday's law of electromagnetic induction and Joule's law. Faraday's law states that any change in the magnetic environment of a solenoid will cause an electromotive force (emf) to be induced in the solenoid. Reciprocally, any change of emf in a solenoid will cause a magnetic field to be induced in the environment of this solenoid. Thus, when an alternating current flows through a solenoid, the periodic current variation leads to the appearance of an alternating magnetic field (with the same frequency than the alternating current). If a metallic piece is placed in this alternating magnetic field (i.e. inside the solenoid), induced alternating eddy currents will appear in it, mainly below the surface (due to the so-called "skin effect" which is an intrinsic property of alternating currents). According to Joule's law (which states that when current flows in an electrical resistance some energy is dissipated in the conductor as heat) the eddy currents induced in the piece of metal placed in the solenoid will cause a temperature increase of this piece of metal [41]. As far as we know this heating technique has never been used in the frame of ATRP polymerization studies.

The aim of the present work is to study the efficiency of induction heating vs. conventional heating for surface-initiated ATRP of styrene on titanium substrates modified with a 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid monolayer, which is our ATRP initiator. Indeed, the ATRP polymerization being surface-initiated (with a grafted initiator), we found interesting to investigate the impact of surface-initiated heating and to compare it to a complete system heating configuration. First, we synthesized and grafted the 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid on titanium substrates. Then, ATRP of styrene was carried out using two different ways of heating: conventional and induction heating. The different steps of this work are schematically summarized in Fig. 1.

2. Material and methods

2.1. Chemicals

Titanium substrates (sheet of 1.0 mm thickness, 99.6+%) were purchased from Advent Research Materials Ltd.

All reagents used for the synthesis of the 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid were purchased from Aldrich Chemical Co.: 10-bromo-1-undecanol (98%), 3,4-dihydro-2H-pyra- ne (97%), *p*-toluenesulfonic acid (98%), triethyl phosphate (98%), pyridinium-p-toluene-sulfonate (98%), 2-bromoisobutyryl-bro- mide (98%), pyridine (97%) dried on CaH_2, bromotrimethylsilane (97%), anhydrous anisole (99.7%), dichloromethane, petroleum ether, diethylether, ethyl acetate, methanol, acetonitrile, acetone, ethanol, absolute ethanol (>99.8%) and anhydrous tetrahydrofuran. All these chemicals were used without any further purification.

Reagents for the polymerization were also purchased from Aldrich Chemical Co. and purified before use: copper (I) bromide (98%) was purified according to a method described elsewhere [42], N,N,N,N,N-pentamethyldiethylenetriamine (PMDETA, 99%) was distilled and styrene (99%) dried with NaH before being distilled.

2.2. Synthesis of the 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid

Synthesis of the 11-(2-bromoisobutyrate)-undecyl-1-phos- phonic acid has been reported previously elsewhere [20]. The same conditions were used in this work to synthesize this initiator of polymerization with an overall yield of 30%.

2.3. Substrates preparations

The substrates are rectangular-shaped (10 x 20 mm^2) coupons of titanium. They are mechanically polished down to 9 im using grit silicon carbide papers and diamond paste then etched down to 0.02 im using a mixture of colloidal silica polishing suspen- sion/H_2O_2 (4/1, v/v). The polishing is carried out on a Buehler Phoenix 4000 instrument. At the end of the polishing steps, the metal coupons are cleaned by sonication 15 min in ethanol and blown dry under a nitrogen flow. Just before modification, the substrates are cleaned again by sonication during 15 min in ethanol and subjected to a UV/O_3 treatment of 30 min.

The 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid mono- layer is then formed by immersing the samples in a 1 mM solution of the molecule in absolute ethanol during 24 h at room temperature in the dark. They are then rinsed copiously with ethanol, cleaned by sonication 15 min in the same solvent, blown dry under a nitrogen flow and directly characterized.

ATRP was carried out according the following procedure: Cu(I)Br, anisole and styrene are added to a reaction flask sealed with a rubber septum. The reaction mixture is deaerated five times by freeze-pump-back-filling with argon. PMDETA (used as a ligant to ensure solubilization of Cu(I)Br) is added to the mixture with a syringe. Reagents concentrations used for this reaction mixture are: 3.9 M for styrene, 25 mM for PMDETA and 15 mM for Cu(I)Br. Then, either the mixture is heated by conventional heating or the titanium substrate itself is heated by induction heating. In the conventional heating pathway, the mixture is stirred and heated to 90 °C. Once this temperature is reached, the modified titanium substrates are immersed in the mixture for 1 h. For the induction heating pathway the modified titanium substrate is immersed in the mixture at room temperature. The induction heating of the modified titanium substrate itself is then initiated. It was performed with an Ambrell EasyHeat induction heating system with a power output of 110 A and a frequency of 198 kHz. The used solenoid is composed of seven spires with an internal diameter of 9 cm. The heating was realized by applying sequences of heating pulses (120 s) followed by cooling periods (180 s) during 1 h. The temperature curve of the induction heating of titanium immersed in ani- sole (acquired with a K-type thermocouple soldered on the titanium surface) is shown in Fig. 2. Note that the temperature measurement is impossible during the induction heating pulses because of the appearance of eddy currents in the thermocouple wires.

It appears that the temperature increases progressively at the beginning, reaching 95 °C at the end of the first induction heating pulse, 127 °C at the end of the second one and 140 °C at the end of the third one. The maximum reached temperature then get stabilized after four sequences at 144 °C. The surface temperature decreases from 144 °C to 106 °C during the cooling periods. After

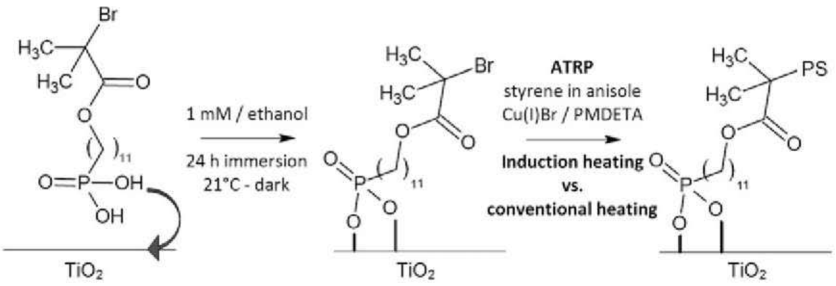

Fig. 1. Schematic of the titanium substrate modification methodology used in this work.

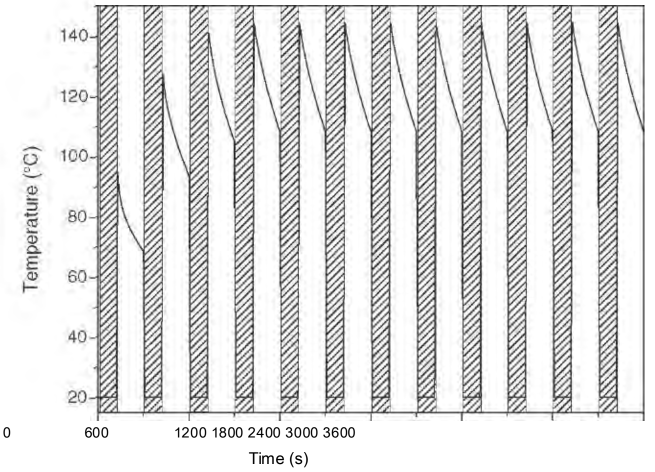

Fig. 2. Evolution of the temperature at the surface of a titanium coupon (10 x 20 mm) immersed into 20 mL of anisole during the induction heating profile (repeated sequence: 120 s heating pulse-180 s cooling period). Induction heating pulses are represented by hatched areas.

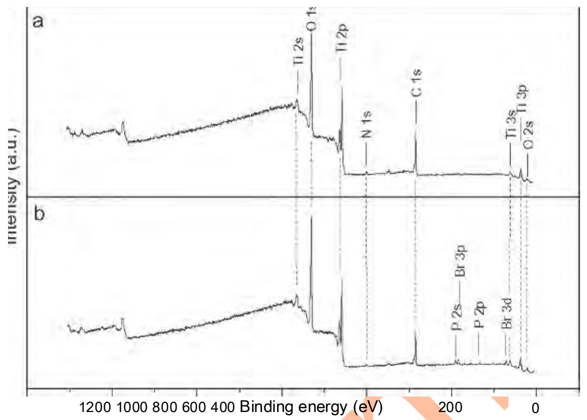

Fig. 3. XPS survey spectra of a bare polished Ti substrate (a) and a Ti substrate modified by immersion 24 h in a 1mM 11-(2-bromoisobutyrate)-undecyl-1- phosphonic acid solution (in absolute ethanol) at room temperature in the dark (b).

the polymerization, the coated substrates are cleaned by sonication 15 min in methanol and rinsed copiously with methanol and then dichloromethane in order to remove the untethered polystyrene.

Each surface modification has been repeated at least three times for each characterization method used in this work in order to ascertain the reproducibility of the results presented here.

2.4. Substrates characterizations

The modified substrates were characterized by X-ray photoelectron spectroscopy (XPS), attenuated total reflectance spectroscopy (ATR), scanning electron microscope (SEM) and static contact angle measurements.

XPS is used to study the elemental composition of the modified substrates. The spectra have been acquired with a SSX-100 spectrometer using a monochromatized X-ray Al Ka radiation (1486.6 eV), the photoemitted electrons being collected at 35° takeoff angle. Nominal resolution was measured as full width at half-maximum of 1.0-1.5 eV for core levels and survey spectra, respectively. The binding energy of core levels was calibrated against the C 1s binding energy set at 285.0 eV, an energy characteristic of alkyl moieties. The peaks were analyzed using mixed Gaussian-Lorentzian curves (80% of Gaussian character).

SEM studies were performed using a JEOL 7500 F microscope with an acceleration voltage of 20 kV.

ATR data were collected to assess the presence of polystyrene on titanium surfaces. They were acquired on a Brucker Equinox 55-PMA37 equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector and a germanium crystal. All spectra are the average of 120 scans at a spectral resolution of 2 cm^{1}.

Static contact angle measurements were carried out using a DIGIDROP (GBX Surface Science Technology) contact angle goniometer at room temperature and at ambient atmosphere. A syringe was used to dispense 2.5 iL of probe droplets of milli-Q water to the sample surface.

3. Results and discussion

3.1. Grafting of the 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid

After the 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid grafting on titanium as described in the experimental section,

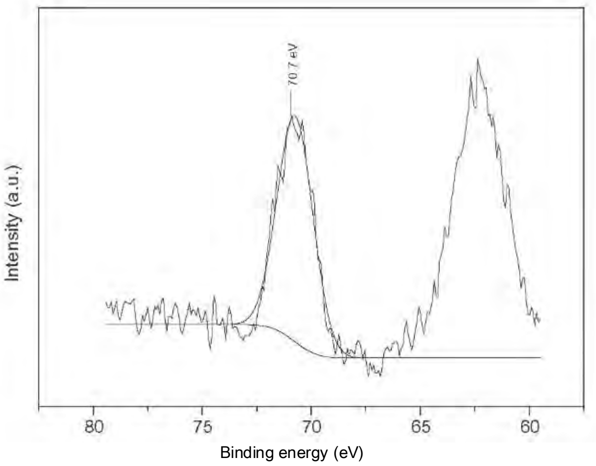

Fig. 4. XPS Br 3d core level spectrum of a Ti substrate modified by immersion 24 h in a 1 mM 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid solution (in absolute ethanol) at room temperature in the dark.

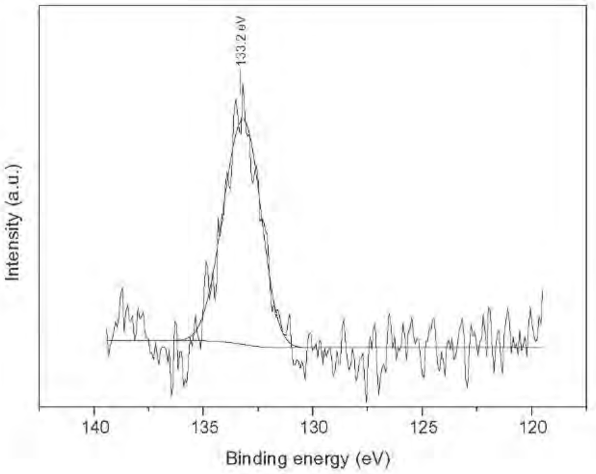

Fig. 5. XPS P 2p core level spectrum of a Ti substrate modified by immersion 24 h in a 1 mM 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid solution (in absolute ethanol) at room temperature in the dark.

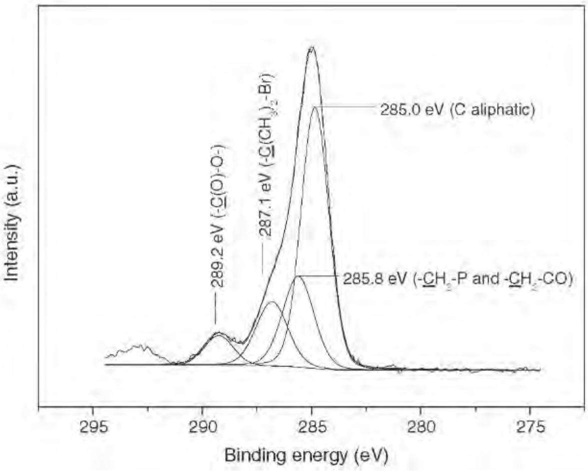

Fig. 6. XPS C 1s core level of a Ti substrate modified by immersion 24 h in a 1 mM 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid solution (in absolute ethanol) at room temperature in the dark.

substrates were first characterized by static contact angle. The grafting leads to increase of the contact angle from 45.7° ± 0.3° for bare titanium substrates to 86.1° ±0.3° for the modified ones. This increased hydrophobicity due to the grafting of the 11-(2-bro- moisobutyrate)-undecyl-1-phosphonic acid is in good correlation with previous studies [20,43].

These modified substrates were also systematically characterized by XPS Fig. 3 shows representative XPS survey spectra of titanium substrates before and after the grafting of the initiator.

We can point out the presence of the P 2s, P 2p, Br 3p and Br 3d core levels photoelectrons peaks on modified substrates while they are not present on the spectra of unmodified substrates. This confirms the presence of the grafted molecule on the titanium surface. Br 3d and P 2p core levels XPS high resolution spectra are presented at Figs. 4 and 5, respectively.

Table 1

Contact angles of milli-Q water droplets deposited on bare Ti substrates, Ti substrates modified with 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid (=initiator) and modified Ti substrates after ATRP polymerization of styrene (=PS) with conventional or induction heating.

Substrates	Contact angles (°)
Bare Ti	45.7 ± 0.3
Ti-initiator	86.1 ± 0.3
Ti-initiator-PS (conventional heating)	64.4 ± 0.9
Ti-initiator-PS (induction heating)	92.0 ± 0.7

The bromine (Br 3d core level) and phosphorus (P 2p core level) peaks are centered at a binding energy of 70.7 eV and 133.2 eV, respectively. These energies are characteristic of the bromine and phosphorus constitutive of the grafted molecule. Fig. 6 shows an analysis of the C 1s core level in four peaks centered at 285.0 eV ($C_{aliphatic}$), 285.8 eV (-CH_2-P and -CH_2-CO), 287.1 eV (-£(^3)2- Br) and 289.2 eV (-C(O)-O-), each of them characteristic of the different carbon species present in the grafted molecule.

3.2. ATRP polymerization of styrene with conventional and induction heating

After the ATRP polymerization of styrene on titanium substrates modified by 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid, the substrates were characterized by static contact angle, SEM, ATR and XPS. All the measured contact angles values are summarized in Table 1.

A radically different hydrophilicity of the surface can be noticed after styrene polymerization with respect to the heating method used during the ATRP process. Using a conventional heating method lead to a more hydrophilic surface (64.4° ± 0.9°) than using induction heating which leads to a much more hydrophobic surface (92.0° ±0.7°). A value of 95° ±1° has been observed in the literature for the ATRP of styrene during 24 h with a

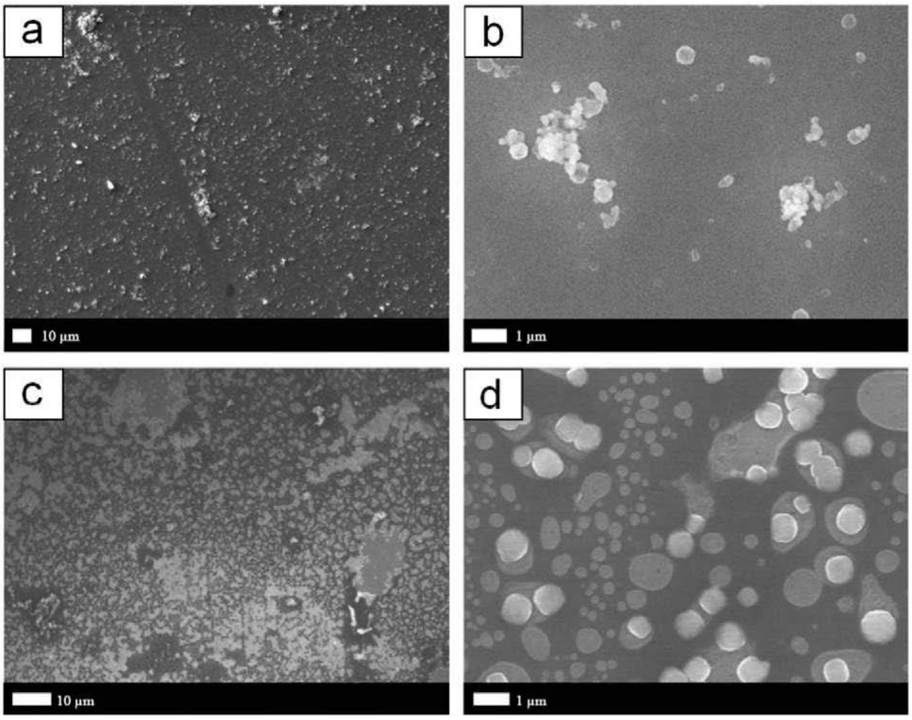

Fig. 7. SEM pictures of the polystyrene layer formed by ATRP with conventional heating (a and b) and with induction heating (c and d) on titanium substrates modified with 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid.

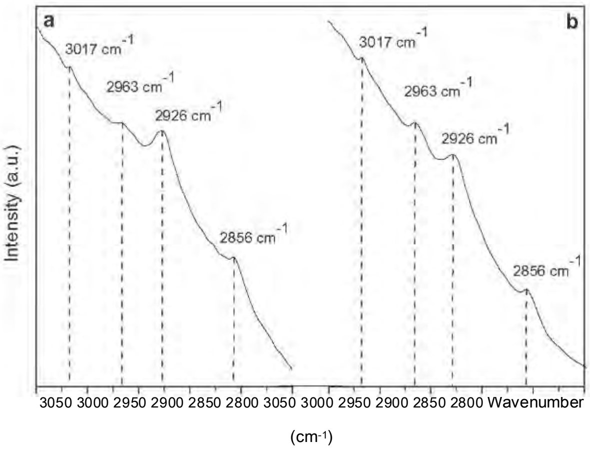

Fig. 8. ATR spectra of the polystyrene layer formed by ATRP with conventional heating (a) and with induction heating (b) on titanium substrates modified with 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid.

conventional heating at 90 °C [20,44-47]. In other words, using induction heating allows us to obtain hydrophobicity properties similar to the one obtained after a 24 h ATRP with conventional heating in only 1 h.

In order to characterize the morphology of the polymer layers formed with these two different heating conditions, the treated samples were observed by SEM. Representative pictures are presented in Fig. 7.

We can observe that the polystyrene grows with a spherical morphology. Note that these spheres have a larger overall diameter when the polystyrene is formed under induction heating conditions. Moreover, with induction heating conditions, the formed polystyrene layer is much denser than the one obtained with conventional heating conditions.

These substrates were also characterized by ATR. The obtained spectra (Fig. 8) reveal absorption bands at 2856, 2926 and 2963 cm^{-1} corresponding to the symmetric stretching of CH_2 groups, asymmetric stretching of CH_2 groups and symmetric stretching of CH_3 groups, respectively. Furthermore the band at 3017 cm^{-1} is attributed to the aromatic C-H stretching. These values are in agreement with reported polystyrene reference infrared spectra [48].

Table 2
C 1s/Ti 2p ratios calculated on basis of the XPS analysis of titanium substrates modified with polystyrene formed by ATRP polymerization with different heating conditions.

	C 1s/Ti 2p
Conventional heating	4.84
Induction heating	55.60

Regarding the results presented up to now, it appears that the induction heating is more efficient than the conventional heating for the ATRP of styrene. In order to confirm these observations, XPS analyses were carried out. The corresponding survey spectra are presented in Fig. 9.

It clearly appears that the C 1s core level peak is more intense in the case of induction heating. Moreover, the Ti 2p core level photo- electrons peak from the substrate is more attenuated when induction heating is used supporting our previous observations i.e. that the formed polymer layer is thicker and with a higher coverage with induction heating than with a conventional heating. The calculated C 1s/Ti 2p ratios (whereas "C 1s" represents the normalized area of the C 1s photoelectrons peak and "Ti 2p" represents the normalized area of the Ti 2p photoelectrons peak) are compared in Table 2.

It appears that induction heating leads to a C 1s/Ti 2p ratio more than 10 times higher than the one obtained with conventional heating. This fact testifies again that a larger quantity of polystyrene is formed in 1 h with induction heating than with conventional heating. We can also notice the presence of a N 1s core level peak in the case of a polystyrene layer formed under conventional heating conditions. This can be explained by the presence of remaining PMDETA on the surface, which is not visible with the induction heating pathway. In both cases however, Cu 2p, Cu 3p and Cu 3s core level photoelectrons peaks are present indicating that some copper from Cu(I)Br used as a catalyst for the ATR polymerization is entrapped in the polystyrene layer and/or strongly physisorbed on it.

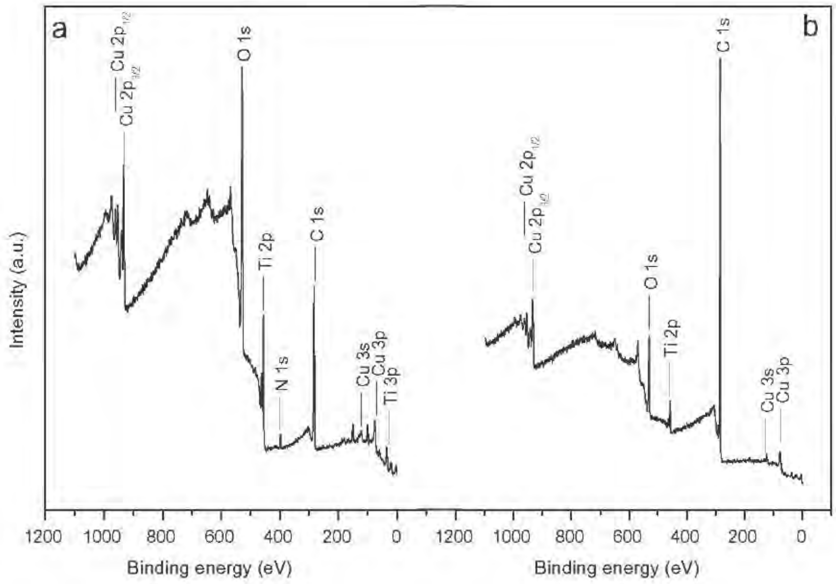

Fig. 9. XPS survey spectra of the polystyrene layer formed by ATRP with conventional heating (a) and with induction heating (b) on titanium substrates modified with 11-(2-bromoisobutyrate)-undecyl-1-phosphonic acid.