The covalent grafting of polymers to the solid surface

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Introduction

Polymers that generally have found countless number of applications as the designing materials; have also appeared to be useful in the area of nanotechnology. For the latter, a crucial approach becomes a molecular scale, which is an attribute of many modern devices in organic electronics, medicine, transplantology, sensors [1]. For these devices identity and purity of chemical structures is of a fundamental importance. This however may be a specific problem in case of any polymeric structure. A concept of the polymer brushes existing in the literature for several years addresses the needs of nanotechnology, since it assumes a creation of well defined polymeric systems on a molecular scale. To achieve the defined polymer structure a role of the substrate in the ordering of the attached molecules is of a great importance, therefore the oriented single crystal surfaces are used in some applications. Also a manner the polymer is attached to the solid surface needs to be defined. Practically only the formation of a strong covalent bonding between the polymer chain and the surface atoms of the substrate is acceptable, which is known as the grafting process [2,3]. The grafting procedures described here are based on the known methods of the living polymerization that are especially useful for the controlled surface process like Atom transfer radical polymerization (ATRP), ring-opening metathesis polymerization (ROMP), ionic polymerization. In addition, a brief review is presented in the area of the organic self assembled monolayers (SAM), which are frequently used as the structure initiating the growth of the polymer chain from the substrate surface.

Surface modification via covalently attached molecules

Surface modification has been known for many years in numerous applications of systems, in which solid phase interacts with gaseous or solution species. In many cases formation of the covalent linkage with the surface atoms is crucial and therefore classical methods like spin-coating or vapor deposition cannot be applied or appear to be less effective. The choice of the modification method strongly depends on the substrate type, which generally can be divided into: carbon, semiconductor (frequently represented by silicon) or metal. Here, we shortly discuss methods that have been used in the modification of these substrates prior to a further polymerization.

The spontaneous process in which organic molecules bind to the solid surface forming a single layer, generally known as Self-Assembled Monolayers (SAM) [4], is recently probably the most studied in the literature method of the surface modification. The formation of SAM is attractive due to its simplicity, low costs and relatively mild conditions required. Compounds, like thiols, halogenosilanes, alkoxysilanes, carboxylic acids, disulfides, selenols etc., posses a specific property of spontaneous chemisorption on the appropriate substrates to form the covalent linkage between the organic species and the surface. The chemical properties of the monolayer may be varied by the molecule terminating group. A full control of the film structure, which includes a mixed composition and tunable coverage, is relatively easily attainable. The structure of the mixed monolayer is determined by several factors; generally it is believed to be a function of thermodynamic properties of the system [5]. In the typical SAM formation process a monolayer is created, however, the formation of well defined multilayers is also possible in so called layer- by-layer procedure that employs interactions between terminating groups of the attached molecules.

The main drawback of this surface modification method is a limited number of substrates that can be modified via SAMs; these are mainly noble metals (like gold), oxides (like indium tin oxide (ITO)) and silicon. The strength of the bonding depends on the system used, e.g. for silanes/oxides and alkenes/silicon the linkage is relatively strong, whereas in case of the thiol/industrial metals system the linkage formed is relatively weak and can be easily broken under severe conditions, like elevated temperature, exposition to some solvents, etc.

The electrografting of diazonium salts that has been proposed in 1992 as an universal and very useful method of electrochemical modification of different conductive surfaces, appeared to overcome the mentioned limitations for the monolayer formation, although this process is not spontaneous [6]. Reduction of these salts has been widely investigated due to the possibility of covering the surfaces of carbon, semiconductors and metals with the monolayer of numerous organic compounds. This is a cathodic electrode process, in which radical generation is accompanied with the evolution of nitrogen. As a result, the aromatic moiety of diazonium salt binds to the surface according to scheme shown in Figure 1.
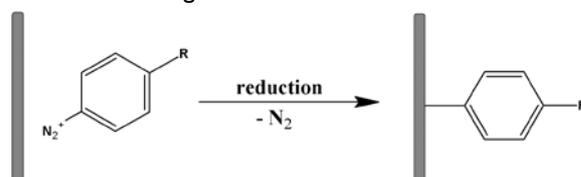

Fig. 1. Electrochemical reduction of diazonium salts – general scheme

Since rather gentle conditions of the reduction are required, especially low cathodic overvoltage, many easily-oxidized metals (Fe, Cu etc.,) may be modified on industrial scale. Moreover, a wide selection of molecules can be immobilized via the electrochemical reduction of a corresponding diazonium salt. The last can be easy synthesized starting from the respective aromatic amine.

Recently several groups have reported on the spontaneous grafting of the diazonium salts without the electrochemical induction. Such chemisorption was observed on carbon, semiconductor and metal substrates [7]. A neutral medium can also be applied that is more favorable in case of many substrates being sensitive to harsh conditions. It is believed that such a spontaneous process also leads to the formation of the covalent linkage, however the mechanism of the process is still not clear.

The silicon surface modifications usually find their analogy in the organosilanes reactions. Many ways exist to initiate the surface process, like thermal, electrochemical or photochemical, in which as a result either Si-C or Si-O bonds are formed [8]. It was shown by Basal and coworkers that chlorinated Si(111)-H surface can further react with Grignard reagent (in the substitution reaction) to form modified silicon surface according to the scheme shown in Figure 2 [9]. Many methods of chlorination were proposed, eg. with benzene solution of PCl_5.

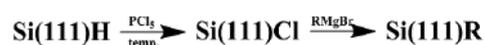$$Si(111)H \xrightarrow[\text{temp.}]{PCl_5} Si(111)Cl \xrightarrow{RMgB_r} Si(111)R$$

Fig. 2. Silicon surface modification with Grignard reagent – general

Later, it was found by Boukherroub and coworkers that hydrogen terminated silicon surface can directly react with Grignard reagent yielding a modified surface with similar chemical, spectroscopic and electrochemical properties [10].

Modified surfaces have been investigated by means of variety of special methods, which can be divided into two groups: first, in which surface is observed directly like in case of AFM or STM, and the second, in which an indirect evidence of organic layer formation is collected based on a signal from specific surface functional groups, like in case of electrochemical and spectroscopic methods. Few of them, including UVVis, FT IR, AFM etc,. can currently be applied *in situ* during the modification. The most common techniques useful in the surface studies are listed in the Table 1.

Table 1

Methods used for the modified surface investigations

Type	Technique
Electrochemical	Cyclic Voltammetry, Impedance Measurements;
Spectroscopic	X-ray photoelectron Spectroscopy, UVVis and IR Spectroscopy, Quartz Crystal Microbalance, Surface Enhanced Raman Spectroscopy, Scanning Tunneling Microscopy, Atomic Force Microscopy;
Physical	Contact Angle, Wettabillity;

Atom Transfer Radical Polymerization

Atom transfer radical polymerization (ATRP) has been a widely employed method for the formation of the polymer brushes [11]. In the process shown schematically in Figure 3, the carbon-carbon bond is created with the transition metal acting as a catalyst. Matyjaszewski and Wang were first who described in 1995 the ATRP process [12]. Nowadays, their invention is commonly used for the polymerization of vinyl monomers and yields polymers of low polydispersivity, which in turn can be employed as a macroinitiators in the copolymers' formation.
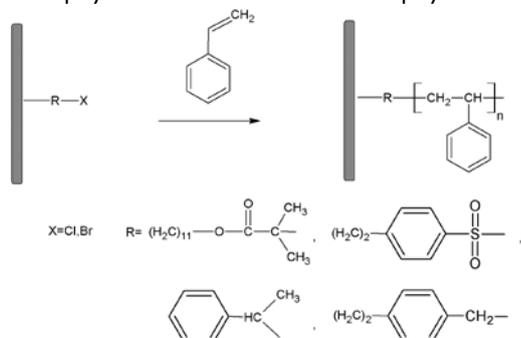
Fig. 3. Surface-initiated ATRP – general scheme

Due to its features, ATRP has gained much attention as a polymerization technique also in the surface-initiated polymerization. One of the first examples of the surface-initiated ATRP is the polymerization of methyl methacrylate described by Fukuda and co-workers in 1998 [13]. In their work, the initiator, 2-(4-Chlorosulfonylphenyl) ethyl trimethoxysilane (CTS) was deposited on the silicon surface using the Langmuir-Blodgett technique. The graft polymerization was carried out from the solution containing diphenyl ether, CuBr, dHbipy, MMA, and p-toluenesulfonyl chloride. The poly(methyl methacrylate) film of very narrow polydispersity and the thickness equal to 80 nm was formed in less than 12 hours. Those observations have caused further development of the technique. The paper published in 2001 by Jones and Huck described the formation of thick polymer brushes (PMMA, PGMA) via the surface – initiated ATRP performed in aqueous medium at room temperature [14]. Those two conditions are of great importance, since the temperature sensitive substrates can be used. Besides, the side reactions, like e.g. thermal cross-linking, trans-estrification, elimination reactions, are less likely to occur. The addition of water greatly enhanced the rate of polymer brush growth, still keeping a high control over the process. As a result, the 35 nm thick PMMA layers were formed in only 35 min.

Lately, Pinson and co-workers have described the process of the polymer grafting by ATRP from metallic surfaces [15]. They prepared poly(methyl methacrylate), poly(n-butyl acrylate) and polystyrene brushes on iron electrodes, which were previously modified by electrochemical reduction of aryl diazonium salts. The grafted layer was used as an effective ATRP initiator for the vinyl monomers' polymerization. Iron was chosen because of its wide range of applications as an industrial metal, and on the other side, to demonstrate the protective properties against corrosion which are exhibited by the hydrophobic polymer brushes.

The ATRP process can be applied not only for the modification of planar surfaces but also for colloidal supports. In 1998 Huang and Wirth showed that living polyacrylamide thin film can be grown from a benzyl chloride SAM on silica gel [16]. Due to the fact that the ATRP is a controlled process, polymer films formed on nanoporous silica leave the pores intact and the modified silica gel can be used in size exclusion chromatography, e.g. for the separation of proteins.

Ionic polymerization

Ionic polymerization can occur via two different mechanisms, anionic or cationic. In the anionic case the chain elongation occurs on anionic centers. Hydrocarbons (styrene, butadiene, isoprene), polar compounds (methacrylates, acrylates) and heterocyclic compounds can undergo the anionic polymerization. Vinyl monomers and heterocyclic compounds can polymerized via cationic mechanism, in which carbenium cations or oxonium ions respectively, are the active centers. The course of both reactions is shown in Figure 4 and 5.
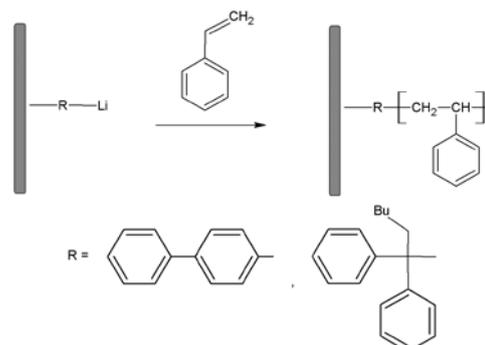
Fig. 4. Surface-initiated anionic polymerization – general scheme

Anionic polymerization of vinyl monomers, due to its living nature and absence of side reactions, results in linear polymers with very low polydispersity. This makes it an attractive way for the synthesis of well defined polymer brushes [11]. In 1998, Jordan and co-workers described the anionic polymerization as a preparation method of dense polymer brushes on planar gold surfaces [2]. The polymerization of styrene was initiated by SAM of biphenyllithium moiety. The obtained polymeric film of high stability and high grafting density exhibited an extremely smooth, homogeneous surface with a roughness of 0,3 – 0,5 nm. These excellent properties of the polymer layer could be obtained in a very slow process, since the reaction time required for the formation of 18 nm thick film reached of three days. Similar route was described by Advincula and co-workers for gold and silica substrates, which were modified with alkylthiol and alkylsilane precursor, respectively [17]. The initiator was activated by n-BuLi. Also in this experiment, the formation of 16 nm thick film required several days. The living nature of surface-initiated anionic polymerization was proved by sequential addition of monomers, which resulted in the formation of block copolymer brushes.

Quite new application of anionic surface-initiated polymerization has been demonstrated by Sakellariou and co-workers, who grafted polymer to the multiwalled carbon nanotubes [18]. They were able to form high-molecular-weight polymers (poly(ethylene oxide) and

polystyrene) in a controlled manner without destruction of the carbon nanotubes' structure. The substrate was functionalized by the covalent attachment of initiator moieties through Diels-Alder cycloaddition. As a result, polymer grafted nanocomposites containing a high percentage of hairy polymer were obtained.
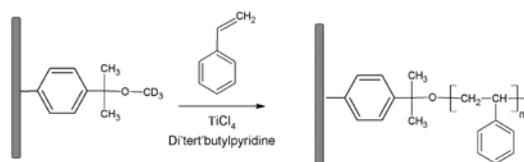

Fig. 5. Surface-initiated cationic polymerization – general scheme

Synthesis of polymer brushes by means of cationic surface-initiated polymerization method is only briefly described in the literature. Also for that route the long time process seems to be a most challenging problem. Jordan and Ulman have investigated the cationic polymerization of 2-substituted 2-oxazoline that was initiated at SAM on a gold surface [19]. The resulting product, a linear poly(N-acylethylenimine) appeared to be of a low polydispersity and high stability. In addition, it has tailorable properties, making possible to control its hydrophilicity and crystallinity. Also here, the reaction time was very long, of the order of 7 days. Zhao and Brittain demonstrated that time of the polymerization may be shortened drastically if the process is carried out at temperature reduced to -78°C. They obtained 30 nm thick polymer film of polystyrene within one hour. It is believed that at these conditions a suppression of chain transfer reactions helps in the film formation [20].

In a study by Dronavajjala and co-workers an innovative cationic surface-initiated polymerization method was described [3]. The efficient and highly controlled growth of polymer brushes was performed when the gold substrate was covered with cationic palladium organometallic complex on cyano-terminated alkanethiol SAM. The anchoring of Pd complex to the substrate was achieved by a simple ligand exchange reaction between the complex and the tail group of SAM. That effective surface modification method allowed to complete polymerization at room temperature in relatively short time of several hours.

Ring-Opening Metathesis Polymerization

The surface-initiated ring-opening metathesis polymerization (SI-ROMP) has been studied intensively for the last few years. The idea of the process is shown in Figure 6. ROMP itself is a type of olefin metathesis polymerization with a relief of the ring strain in the cyclic olefins, mainly norbornene derivatives, as a driving force. ROMP is also an example of a living polymerization with transition metals' complexes, typically Ru, Re, W, or Mo in a role of initiators [21]. Polymers synthesized via this type of polymerization have good electrical properties, therefore they may be employed in polymeric electronic devices, when grafted on a conductive substrate [11].
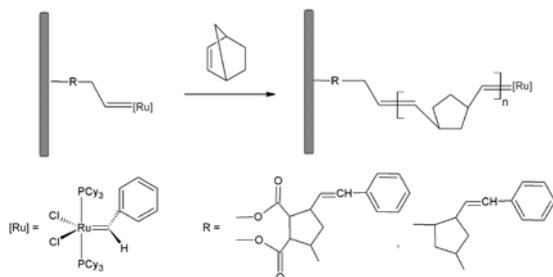

Fig. 6. Surface-initiated ROMP – general scheme

The polymer brushes obtained via surface-initiated ROMP were described for the first time in 1998 by Weck and co-workers [21]. The authors have synthesized a kind of "molecular wire" that consist a conjugated chain terminated with thiol group on one side and cyclic alken on the other side. That molecule was used as an initiating unit

for the ROMP process in a presence of ruthenium initiator after its immobilization as SAM on the gold surface. To avoid a possible polymerization between the adjacent initiating units, an addition of dodecanethiol was used in the SAM-formation step. The resulting mixed monolayer has led to a well-defined polymeric structure attached to the gold substrate. Although the procedure allows forming only a short-chain polymeric material, this work has demonstrated that ROMP can be used as a surface-initiated polymerization method.

Two years later Kim and co-workers reported on another ROMP process at room temperature offering a high degree of control over a surface polymerization [22]. The three-step procedure was employed starting from formation of SAM on silicon attached norbornenyl groups followed by ruthenium catalyst attachment to the substrate using these groups, and final polymerization of the added monomer. The authors have found that the thickness of the polymeric film can be controlled by the monomer concentration and polymerization time. This procedure was used in microcontact printing technique to obtain a patterned polymeric film on the silicon surface.

The silicone surface has also been modified by Lewis and coworkers [23]. In this three-step procedure a coupling of a linker to a chlorinated silicon surface was carried out in a Grignard reaction, then the ruthenium catalyst was bond to the surface via an olefin-cross metathesis reaction, and finally a growth of the polymer film occurred after the nornbornene monomer addition. The obtained surfaces are believed to find their application in the production of novel metal-insulator-semiconductor devices, and in the inhibition of surface corrosion processes.

An interesting, new application of surface-initiated ROMP was proposed by Faulkner and co-workers, who have produced the hydrophobic coatings on the carbon paper electrodes [24]. The carbon paper electrodes are commonly used as the gas diffusion layers in the proton exchange membrane fuel cells. The role of the electrode is to enable the oxygen transport to the catalyst layer and to remove water from the catalyst region. Previously, the hydrophobic coatings were prepared using CF_4, CHF_3 or PTFE, however the procedures have employed a highly specialized equipment or led to sealing of small pores, respectively. The new idea is to prepare flourocarbon-rich films via surface-initiated ROMP of 5-(perfluorohexyl)norbornene (NBF6). The resulting coating exhibits hydrophobic and oleophobic properties and effectively acts as a barrier for the diffusion of aqueous ions to the conductive carbon fibers. According to Faulkner and co-workers, this approach could be applied to surface-initiated ROMP of other norbornenyl derivatives and to different porous supports.

Electrochemical polymerization

The most common method applied in the synthesis of the conducting polymers is the electropolymerization that typically starts from the oxidized form of monomers generated at the electrode surface. In the anodic process many of easily-oxidizable metals cannot be used as substrates, since their oxidation occurs at lower potential than that for the monomer oxidation. Besides, the oxide formation may lower a quality of the obtained surface-polymer structure. A possible solution is a previous inactivation of the substrate surface toward its oxidation. In the literature such inactivation is usually achieved by means of SAMs formation. Polyaniline film has been widely studied as a model conjugated polymer on many substrates, including gold and Indium-Tin Oxide (ITO) electrodes. In the first case, 4-aminothiophenol (4-ATP) has been used as a polymerization precursor in the process shown in Figure 7.

Fig. 7. Electrochemical oxidation of 4-aminothiophenol confined to the surface

Lukkari and coworkers have studied the properties of 4-ATP monolayer in acidic medium [25]. In their work the irreversible oxidation peak at the potential of 0.80 V was associated to the oxidation of the amine group terminating the monolayer. The process results in the surface radical cation formation (Fig.7) that initiates further polymerization, which apparently occurs at the potential lower than the oxidation of the bulk aniline. Therefore, the polymer film is facilitated to grow directly on the SAM, the polymerization starting on unoccupied electrode surface is less likely. The mechanism of the preferred aniline polymerization of on SAM studied in 1997 has revealed a spontaneous replacement of the terminal imine group by quinonoid-type oxygen, which is inactive towards further polymerization in the acidic environment [25]. Even though, other groups [26] have reported successful electrochemical polymerization on 4-ATP modified gold electrode. They found a relation between the electrical conductivity of the polyaniline film vs. mole fraction of 4-ATP in the SAM containing immobilized n-decanethiol [27].

Alkoxysilane type of SAMs has been also widely applied in surface modifications. That attempt was made by Cruz-Silva and coworkers for the growth of polyaniline film on ITO electrode modified with N-phenyl-γ-aminopropyl trimethoxysilane (PAPTS) [28]. Some works have reported on other than polyaniline films attached to SAMs. An example is the ω-pyrrolyl undecanethiol - modified gold electrode used for the polypyrrole formation in microcontact printing described by Grace and Pandian [29].

Literature

1. Senaratne W., Andruzzi L., Ober Ch.K.: *Self-Assembled Monolayers and Polymer Brushes in Biotechnology: Current Applications and Future Perspectives.* Biomacromolecules 2005, **6,** 2427.
2. Jordan R., Ulman A., Kang J., Rafailovich M., and Sokolov J.: *Surface-Initiated Anionic Polymerization of Styrene by Means of Self-Assembled Monolayers.* J. Am. Chem. Soc. 1999, **121,** 1016-1022.
3. Dronavajjala K.D., Rajagopalan R., Uppili S., Sen A., Allara D.L., Foley H.C.: *A simple Technigue to Grow Polymer Brushes Rusing In Situ Surface Ligation of an Organometallic Initiator*, J.Am.Chem.Soc. 2006, **128,** 13040-13041.
4. Nuzzo, R.G.; Allara, D.L.: *Adsorption of bifunctional organic disulfides on gold surfaces.* J. Am. Chem. Soc. 1983, **105,** 4481-4483.
5. Hayes W.A., Kim H., Yue X., Perry S.S.; Shannon C.: *Nanometer-Scale Patterning of Surfaces Using Self-Assembly Chemistry. 2. Preparation, Characterization, and Electrochemical Behavior of Two-Component Organothiol Monolayers on Gold Surfaces* Langmuir. 1997, **13,** 2511-2518.
6. Pinson J., Podvorica F.: *Attachment of organic layers to conductive or semiconductive surfaces by reduction of diazonium salts.* Chem.Soc.Rev. 2005 **34,** 429-439.
7. Adenier A., Cabet-Deliry E., Chausse A., Griveau S., Mercier F., Pinson J., Vautrin-Ul Ch.: Chem. Mater. 2005, **17,** 491-501.
8. Wayner D.D.M., Wolkow R.A : *Organic modification of hydrogen terminated silicon surfaces.* J. Chem. Soc., Perkin Trans. 2002, **2,** 23-34.
9. Bansal A., Li X., Lauerman I., Lewis N.S.: *Alkylation of Si Surfaces Using a Two-Step Halogenation/Grignard Route.* J. Am. Chem. Soc. 1996, **118,** 7225-7226.
10. Boukherroub R., Bensebaa F., Morin S., Wayner D.D.M.: *New Synthetic Routes to Alkyl Monolayers on the Si(111) Surface.* Langmuir 1999, **15,** 3831-3835.
11. Edmondson S., Osborne V., Huck W.: *Polymer brushes via surface-initiated polymerizations.* Chem. Soc. Rev. 2004, **33,** 14–22.
12. Matyjaszewski K., Wang J.S.: *Controlled/"Living" Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complex.* J. Am. Soc. 1995, **117,** 5614-5615.
13. Ejaz M., Yamamoto S., Ohno K., Tsujii Y., Fukuda T: *Controlled Graft Polymerization of Methyl Methacrylate on Silicon Substrate by the Combined Use of the Langmuir−Blodgett and Atom Transfer Radical Polymerization Techniques.* Macromolecules, 1998, **31,** 17, 5934-5936.
14. Jones D. and Huck W.: *Controlled Surface-Initiated Polymerizations in Aqueous Media.* Adv. Mater. 2001, **13,** 1256-1259.
15. Matrab T., Chehimi M., Perruchot C., Adenier A., Guillez A., Save M., Charleux B., Cabet- Deliry E., Pinson J.: *Novel Approach for Metallic Surface-Initiated Atom Transfer Radical Polymerization Using Electrografted Initiators Based on Aryl Diazonium Salts.* Langmuir 2005, **21,** 4686-4694.
16. Huang X., Wirth M.J.: *Surface-Initiated Radical Polymerization on Porous Silica.* Anal. Chem. 1997, **69,** 4577-4580.
17. Advincula R., Zhou Q., Park M., Wang S., Mays J., Sakellariou G., Pispas S., Hadjichristidis N.: *Polymer Brushes by Living Anionic Surface Initiated Polymerization on Flat Silicon (SiOx) and Gold Surfaces: Homopolymers and Block Copolymers.* Langmuir 2002, **18,** 8672-8684.
18. Sakellariou G., Ji H., Mays J., Baskaran D.: *Enhanced Polymer Grafting from Multiwalled Carbon Nanotubes through Living Anionic Surface-Initiated Polymerization.* Chem.Mater. 2008, **20,** 6217–6230.
19. Jordan R., Ulman A.: *Surface Initiated Living Cationic Polymerization of 2-Oxazolines.* J. Am. Chem. Soc. 1998, **120,** 2, 243-247.
20. Zhao B., Brittain W.: *Synthesis of Polystyrene Brushes on Silicate Substrates via Carbocationic Polymerization from Self-Assembled Monolayers.* Macromolecules 2000, **33,** 342-348.
21. Weck M., Jackiw J., Rossi R., Weiss P., Grubbs R.: *Ring-Opening Metathesis Polymerization from Surfaces.* J. Am. Chem. Soc. 1999, **121,** 4088-4089.
22. Kim. N., Jeon N., Choi I., Takami S., Harada Y., Finnie K., Girolami G., Nuzzo R., Whitesides G., Laibinis.: *Surface-Initiated Ring-Opening Metathesis Polymerization on Si/SiO₂.* Macromolecules 2000, **33,** 2793-2795.
23. Juang A., Scherman O., Grubbs R., Lewis N.: *Formation of Covalently Attached Polymer Overlayers on Si(111) Surfaces Using Ring-Opening Metathesis Polymerization Methods.* Langmuir 2001, **17,** 1321-1323.
24. Faulkner C., Payne A., Jenings K.: *Surface-initiated ring-opening metathesis polymerization of 5-(perfluorohexyl)norbornene on carbon paper electrodes.* Journal of Colloid and Interface Science 2010, **351,** 248–253.
25. Lukkari J., Kleemola K., Meretoja M., Ollonqvist T., Kankare J.: *Electrochemical Post-Self-Assembly Transformation of 4-Aminothiophenol Monolayers on Gold Electrodes.* Langmuir 1998, **14,** 1705-1715.
26. Jiao L-s., Wang Z., Niu L., Shen J., Sou T-y., Dong S-j., Ivaska A.: *In situ electrochemical SERS studies on electrodeposition of aniline on 4-ATP/Au surface.* J.Solid State Electrochem. 2006,**10,** 86-893.
27. Abaci S., Shannon C.: *The influence of decanethiol/4-aminothiophenol mixed monolayers on the electrodeposition of polyaniline thin films.* Electrochimica Acta 2005, **50,** 2967-2973.
28. Cruz-Silva R., Nicho M.E., Resendiz M.C., Agarwal V., Castillon F.F., Farfas M.H: *Electrochemical polymerization of an aniline-terminated self-assembled monolayer on indium tin oxide electrodes and its effect on polyaniline electrodeposition.* Thin Solid Films 2008, **516,** 4793-4802.
29. Grace A.N., Pandian K.: *Selective growth of polypyrrole on ω-pyrrolyl undecanethiol monolayer patterned gold surface using microcontact printing technique.* Current Science 2003, **85,** 374-378.

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