Chem Soc Rev

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Journal:	*Chemical Society Reviews*
Manuscript ID:	CS-REV-11-2014-000378.R1
Article Type:	Review Article
Date Submitted by the Author:	25-Feb-2015
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Controlled Decoration of Surface with Macromolecules: Polymerization on Self-assembled Monolayer (SAM) †

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Received (in XXX, XXX) Xth XXXXXXXXX 201X, Accepted Xth XXXXXXXXX 201X
First published on the web Xth XXXXXXXXX 201X
DOI: 10.1039/b000000x

Polymer functionalized surfaces are important components for various sensors, solar cells and molecular electronic devices. In this context, use of self-assembled monolayer (SAM) formation and subsequent reactions on the surface has attracted lot of interests for its stability, reliability and excellent control over orientation of functional groups. The chemical reactions to be employed on SAM must ensure an effective functional group conversion while the reaction condition must be mild enough to retain the structural integrity. This synthetic constraint has no universal solution; specific strategies such as “graft from”, “graft to”, “graft through” or “direct” immobilization approaches are employed depending on the nature of the substrate, polymer and its area of applications. We have reviewed current developments of methodology of immobilization of polymer in the first part of the article. Special emphasis has been given on the merits and demerits of certain methods. Another issue concerns utility – demonstrated or preceived - of conjugated or non conjugated macromolecules anchored on functionally decorated SAM in the areas of material science and biotechnology. In the last part of the review article, we looked at the collective research efforts towards SAM-based polymer devices and identified major pointers of progress (236 references).

1. Introduction

Designer surfaces decorated with specific macromolecules are of wide interest for their possible applications ranging from material science[1] to chemical biology.[2] For example, several research groups across the globe showed that polymer coated/functionalized surface can play an important role in solar cell device fabrication.[3, 4] Nonbiofouling and protein repulsion properties of those surfaces have been studied for several decades[5, 6] Simple techniques such as spin coating, chemial vapour deposition, laser ablation, Langmuir-Blodgett (LB) film formation, plasma deposition and electrochemical reactions have been extensively used to prepare polymer-coated surfaces.[7] These techniques offer fairly thin films of polymer on almost any surfaces. However, lack of stability, durability, reproducibility or control over thickness are the main drawbacks associated with the above mentioned methods.

In ordet to overcome some of the problems associated with the above methods, current research trends are increasingly directed towards utilization of self-assembled monolayer (SAM) formation technique. In this case, suitably functionalized long chain organic molecules are spontaneously assembled on surfaces to form densely packed monolayer anchored by covalent-like interactions. Since the molecules are attached to surface by strong interaction, it is extremely stable and the physisorbed or unreacted molecles can be washed out easily after SAM formation or any further reaction on it. Moreover, control over the orientation of the molecules, near molecular precision of thickness and requirement of ultralow quantity of the precious molecules made it very useful for the development of devices in the form of chip. For example, densely packed, uniform brushes showed a higher capacitance compared to the spin-coated dielectrics in organic field-effect transistors.[8]

Operational simplicity is the added advantage for its rapid study in laboratory scale.

SAM can be formed on various surfaces, if molecules with suitable functional groups are chosen. For example, long chain thiols spontaneously assemble to gold surfaces due to strong Au-S interactions. Similarly, siloxane molecules form SAM on silicon, glass, quartz and indium tin oxide (ITO) surface. Phosphonate SAMs on ITO surfaces are particularly useful for photovoltaic device fabrication. The specific surface and the molecules are chosen based on the area of application and ease of availablity of substrates. Each SAMs with various surfaces and substrates have some merits and demerits. Several review articles have highlighted various aspects of SAM on different surfaces.[9-11] Application aspects of SAM have been highlighted by Vijayamohanan and others.[12] Applications of the polymer functionalized surfaces were reviewed by Klok[13] and later by Azzaroni and others.[14] In a recent review, we discussed methods of immobilization of biological molecules and their applications as biosensors.[15] In that article, we had discussed only about the immobilization biological macromolecules and its application in biosensor field. In the current review article, we have highlighted the recent developments on functionalization of surfaces with polymeric molecules in general, after SAM formation. The discussion is mainly restricted to silicon-related surfaces (silicon wafer, silica gel, glass, quartz), ITO surfaces and gold surfaces due to the availability of exhaustive literature in the area. A few examples of other surfaces like graphenes, fullerenes, carbon nanotubes have been discussed to identify broader scopes in the related research area.

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Professor Asit Baran Mandal is Director of CSIR-CLRI since 2006 and Distinguish Professor of AcSIR. He received Doctoral degree from Jadavpur University, Calcutta. He Represented Indian Science community in countries like Canada, USA, UK, Germany, Singapore, Italy, Ethiopia, China, Japan, Spain, Australia, Turkey, Mexico etc. He is FASc(1995), FNAE(2013) from India and FRSC (UK)(1996). He is a recipient of several awards like the Rev.Fr.L.M. Yeddanapally Memorial Award(1993), CSIR Technology Award(2006, 2007, 2011), green technology award(2011), NRDC technology award(2012) etc. He served as editorial board member for Proc.Ind.Acad.Sci. and Int.J.Surf.Sci.Tech. He has ~360 papers in reputed journals and 28 patents.

One of the most straight forward ways to functionalize a surface with polymers is "direct" immobilization method. In this case, polymers can be immobilized directly on a given surface by synthesizing α,ω-difunctional chains where one functional end (with suitable surface-binding moiety) can be utilized for attachment on the surface, while the other end is attached to the specific polymers. However, the synthetic routes must necessarily be unique for each type of polymer chains and synthetic challenges for such functional polymers can be formadible, if the polymer part features a sensitive functional group.

An alternate approach is "graft to" approach, where a polymer is grafted to the functional group at the exposed terminus of preformed SAM. A handful of reviews highlighted the recent advancement of "graft to" methods of polymerization.[16] The method is very straightforward experimentally, however, steric repulsions between polymer chains prohibit the formation of dense polymeric assembly. Instead of stretched polymer chains assembled perpendicular to the surfaces, it collapses to form mushroom or pancake like structure.[17-19] Moreover, it is very difficult to immobilize polymers with high molecular weight since the reaction between polymer end-group and the complementary group on the surface becomes less efficient with increasing molecular weight.

A more useful and well studied approach is "graft from" approach where a dense layer of polymer is grown from the SAM with initiator at the exposed terminus using controlled polymerization techniques.[20] In this case, distance between the neighbouring grafting point is small and hence, steric repulsion leads to stretching of chains with the formation of a brush type conformation of tethered chains. Since the method offers a dense layer with good control over thickness, this methodology is used most widely for surface functionalization with polymers in nanoscale. Several review articles have specifically addressed the broad scope of this type of methodology. Almost a decade ago, Huck, Li and others[21, 22] and recently Dubois, Locklin[1, 20] reviewed various aspects of functionalization of surfaces through self-assembled monolayer and "graft from" polymerization.

An intermediate approach is "grafting through" polymerization method where solution polymerization is performed in the presence of a surface functionalized with groups reacted in polymerization.[23] It often has the advantages of simplicity with "graft to" method but with improved performances in terms of grafting density.[24, 25] Recently, we showed that "graft through" click polymerization is an efficient process for surface functionalization through SAM.[26] Fig. 1 depicts the schematic representation of "graft to", "graft from", "graft through", "direct" method of immobilization.

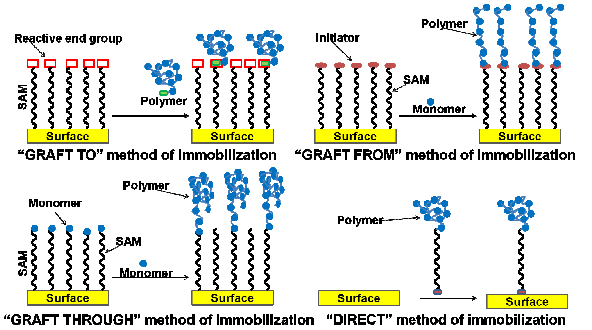


Fig 1 Schematic representation of "graft to" "grafting from", "graft through" and "direct" method of immobilization.

Each of the above mentioned methods have their own advantages and disadvantages in the view of their practical applications. The entire research area itself is an emerging and rapidly growing field. In this review article, we have highlighted some of their developments, merits, demeririts and challenges associated with various methodologies.

The other issue concerns utility – demonstrated or perceived – of conjugated or non conjugated macromolecules anchored on functionally decorated SAM in the specific area of photovoltaics[27-29] and sensing.[30] It has direct implication for the development of devices in the form of a chip. Since the last decade there have been hundreds of papers that addressed immobilization methods of macromolecules on functionally tailored SAM and their application in device fabrication or other fields. Although the research groups are spread out in many continents across the globe, the practical, easily adaptable, universally applicable and defect free techniques remain scarce yet. The main objective of this review is to look at the collective research efforts towards the methodology development (via "graft from", "graft to", "graft through", "direct") and application of SAM-based polymer functionalized surfaces. We also have attempted to idendify major pointers of progress and challenges associated with it.

Very recently supramolecular self-assembly has drawn significant interests for the bottom-up construction of nanostructures using small molecules, biological molecules and curved surfaces. In a recent review article, Busseron *et al* highlighted their formation and uses as functional nanomaterials.[31] In this review article, we have mainly restricted our discussion on growing or immobilization of polymers on self-assembled monolayer (SAM) on selected flat surfaces.

1.1. Characterization

One particular challenge in this field of research is related to the characterization of grafted polymers since many of the common techniques applicable to solution polymerization (such as solution NMR, gel permiable chromatography) can not be used on surfaces directly. Moreover, for an ultrathin layer of polymer, total amount of materials is small and hence it is impossible to get complete molecular picture by using only one or two characterization techniques. In the case of solution polymerization, gel permeable chromatography (GPC) is a commonly used technique to determine the molecular weight distribution of polymers. Since it can not be used directly on the surfaces, several research groups indirectly concluded the molecular weight distribution of the polymers on the surfaces by parallaly performing the polymerization in solution under same condition.[32, 33] However, it was noted by some research groups[25] that polymerization on surfaces may not be directly correlated with solution polymerization. Prucker and Ruhe have demonstrated that surface attachment leads to a slight decrease in the radical efficiency of the initiator.[34] Genzer and others employed Monte Carlo simulation to investigate simultaneous controlled radical polymerization in solution and from a flat surface and concluded: "the assumption that the molecular weight of surface-initiated polymers is equal to that of polymers grown in bulk, invoked often in determining the grafting density of surface bound polymers, is generally invalid".[35] On several occasions molecular weight and its distribution of the surface-attached polymers was determined by detaching the polymers from the surfaces after polymerization, followed by GPC study of the polymers in solution. For example, Caykara et al reported the leaching out of polymer brush (66 nm thickness) from silicon surface by soft etching method (soft etching bath: 20 wt % HF, 40 wt % H_2O, 25 wt % K_2CO_3, 8 wt.% KOH, and 9 wt.% Na_2SO_4) and deduced the leached polymer molecular weight by GPC.[36] Alkyl thiolate based SAM polymers can be detached from the gold surface by treatment with iodine or electrochemical desorption.[37]

Another important characterization method to study the growth of polymers from the surface is: ellipsometry study. In this case, a plane polarized laser beam is reflected by the substrate and thin polymer films resulting in a change of phase and amplitude. Hence, the thickness of the film can be calculated by comparing the changes in phase and amplitude. With time, the ellipsometric film thickness increases initially at the beginning and reaches a saturation point after several hours or days for different polymerization methods. Analysis of the data can precisely highlight the growth rate of the polymers on the surface or the controlled/living nature of the plymerization methods.

The quartz crystal microbalance (QCM) is one of the most useful and powerful tools for studying polymer SAM because it can detect very small changes in mass, usually in the range of nanograms.[38] QCM is also useful to monitor *in situ* the conformation changes of surface tethered polymer chains (swelling, collapse).[39, 40]

Various microscopic techniques are frequently used to study the morphology, density or distribution of the polymer films on the surfaces. For example, atomic force microscope (AFM)[41] and scanning tunneling microscope (STM) help to directly visualize thin polymeric film in molecular resolution. In both the cases, a fine tip of atomic dimension is used which measures the force between the tip and surface in AFM or tip and electron density in STM. These techniques are also useful in studying the efficiency of various polymerization techniques as well as minute change of conformation.

The other useful microscopic methods to study the fuctionalized surfaces in nanoscale are scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In SEM, an image is generated with the help of secondary electrons to provide an impression in three dimensions. TEM produces two dimensional image through an ultrathin slice of specimen. These techniques are particularly useful to study the defects after polymerization on surfaces.

Various spectroscopic methods are useful for understanding the chemical composition of the polymer SAM and to monitor the fate of a functional group after a chemical reaction. However, since the amount in the monolayer is small and bound to the surfaces, often certain common techniques can not be used directly for the monolayers. For example, infrared (IR) spectroscopy can be used to unambiguously identify common functional groups present on SAMs. A specific grazing-angle reflection-absorption infrared spectroscopy can be used conveniently for studying surface polymers where incoming light is reflected under a large angle of incidence (grazing angle reflection configuration). For example, SAMs on silicon surfaces are characterized by transmission IR under Brewster angle.

Another very important spectroscopic technique, used frequently to study the immobilized polymers on surfaces is X-ray photoelectron spectroscopy (XPS). The method is very useful for the determination of elemental composition of the substrate as well as identify any change in elemental state after reaction. In this case, irradiation of the sample with monochromatic X-rays result in the emission of core electrons of different nuclei. Binding energy of the specific core electrons on an element can be calculated to determine the elemental composition and oxidation state of the element.

UV-vis absorption and fluorescence spectroscopies are the basic techniques to obtain the preliminary structural informations such as prsence of extended conjugation, aromatic moiety, packing of SAM, etc. In some cases, success of the polymerization reactions can also be judged from the UV-vis spectroscopy by observing the appearance of new peaks or the shifting of the peaks.

Specific electrochemical techniques such as cyclic voltammetry (CV), amperometry and impedance measusrements can be conviniently used to study the bound polymers with electrochemically active groups. These methods can be particularly used for sensor applications by electrochemically observing any event of binding to the functionalized surface. The methods are inexpensive and easy to operate, and hence very attractive to design devices in the form of a chip.

Last, but not least, contact angle measurement is very simple, effective and inexpensive method to monitor the change of structural composition of the grafted polymer. Since the contact angle (water) is high for hydrophobic layer and low for hydrophilic layer, any change in polarity of the functionalized surface can be easily observed by the contact angle measurement. It is partcularly useful to obtain preliminary information of polymerization reaction on SAM.

2. Chemical modification of surfaces before polymerization: Self-assembled Monolayer (SAM) formation

In most of the cases (except direct immobilization), prior functionalization of surfaces with SAM is necessary as the polymer is either grown from SAM ("graft from" method) or anchored to SAM ("graft to" method). For "graft through" method, the SAM of the monomer is formed on surface before performing the polymerization reaction. Furthermore, covalent immobilization of polymers to SAM or growing of polymers from SAM would depend on the chemical functionality to be exploited in each of them and it is imperative that SAMs are functionally tailored according to the reaction identified for each of the specific purposes. For example, in the case of "graft from" polymerization method, a SAM of initiator is formed on surface, whereas in the case of "graft to" method a SAM with reactive end group is formed that can be used for anchoring purpose.

To form SAM of initiator group (for "graft from" polymerization), a long chain alkyl thiol (for gold surface) or siloxane/chlorosilane (for silicon/glass/ITO surface) with suitable end functional group such as 2-bromoisobutrate (for atom transfer radical polymerization), dithioester (for reversible addition fragmentation chain transfer polymerization), 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) (for nitroxide mediated polymerization) is spontaneous assembled under suitable condition. However, α,ω-difunctional chain with thiol/siloxane at one end and a sensitive initiating group at the other end may not be trivial to synthesize. In such cases, post assembly chemical modification is very useful. For example, ruthenium bases Grubbs' type catalyst was anchored on alkene functionalized SAM to grow polymer via ring opening metathesis polymerization route (*vide infra*). Similarly, reversible addition fragmentation chain transfer (RAFT) polymerization can also be performed by converting surface-immobilized conventional free radical initiator into RAFT initiator in situ by adding suitable compounds such as dithioester, dithiocarbonate, trithiocarbonate. In a few cases, hydroxyl functionalized SAM was converted to atom transfer radical polymerization (ATRP) initiating group by the esterification reaction.[42] In surface initiated anionic polymerization, SAM of a bromoaromatic compound is formed on the surface first, which can be converted to anionic initiating group by using butyl lithium or other suitable reagent.[43] Similarly, for surface initiated cationic polymerization, activation of the end group of SAM with $TiCl_4$ or other substrate is necessary to initiate the polymerization. For surface initiated Kumada type polycondensation, prior formation of SAM with bromoaromatic terminal end group is necessary to initiate the catalytic polymerization.[44]

Prior formation of SAM with suitable reactive end functional group is needed to immobilize already prepared polymer by "graft to" method. Yan's group has extensively studied the formation of SAM with end functional aromatic azide group to anchor different polymers by photoirradiation (*vide infra*). Gopalan and others formed SAM of azido trimethoxysilane on silicon surface to immobilize alkyne functionalized polymers by "click" chemistry approach.[45] Another way of using "click" chemistry approach is to form SAM with protected alkyne end group.

SAM with epoxy end group is useful to directly immobilize carbxylic acid bearing polymers.[46] Those polymers can also be anchored to amine functionalized SAM after activation.[47]

In the case of "graft through" click polymerization, a monolayer of the monomer is formed on the surface before starting the polymerization reactions. Hence monolayer bearing azide group is useful for "graft through" click polymerization.[26] A monolayer of bromoaromatic end group is useful for "graft through" Ni(0)-mediated polycondensation.[48] Ruhe and others prepared the SAM of 3-methacryloylpropyl trimethoxysilane (MPS) on silicon surface to perform "graft through" ATRP reaction.[49]

3. Functionalizaion of surfaces with poymers via SAM: methodology

For decades, several mehods have been developed to create polymer functionalized surfaces via SAM formations. All the methods can be classified into four main categories based on the process of attachment: (i) immobilization of already prepared polymers to the end group of SAM, known as "graft to" method, (ii) growing of polymers from end group initiator of SAM, known as "graft from" method, (iii) an intermediate "graft through" approach where a monomer is attached to surface and (iv) "direct" immobilization of suitably functionalized polymers on surface via the formation of SAM. Choice of suitable method is important in designing devices since density and orientaion of polymers often affect the device performances. For "graft to" method of immobilization, covalent bond formation is preferred because of stability, however, non covalent interactions were occassionally used for operational simplicity.[50]

3.1 "Graft to" method of immobilization

It is one of the simplest approaches to functionalize surfaces with wide ranges of polymers. In this case, both SAM and polymers are synthesized first with suitable functional groups. The immobilization step is then performed usually in mild conditions. Anchoring polymer chains to surfaces using a ''grafting to'' approach was proven to be an effective strategy for creating highly functional interfaces.[51] The process is extremely versatile since many of the traditional C-C or C-N bond forming reactions can be conveniently applied to immobilize a wide range of polymers. Most common reactions are "click" reaction between azide-functionalized SAM and alkyne functionalized polymers and *vece versa*, insertion of nitrene (SAM) into C-H bond of adjacent polymer chains, Diels-Alder reaction, coupling reaction between acid functionalized polymers and amine functionalized SAM or vice versa, reactions between epoxy groups and acid groups of polymers etc.

Ruhe *et al* reported the grafting of polystyrene (PS), poly (dimethyl acrylamide) (PDMAA), poly (heptadecaflurodecyl acrylamide) (PHFDA) polymers to phenyl sulphonyl azide functionalized surface by thermal or photo activation reaction. In this case, an intermediate highly reactive nitrene moiety is generated which inserts into C-H bonds (Fig. 2). The polymer functionalized surfaces are smooth, homogeneous with very low surface roughness. The film thickness depends on temperature (120-180^{0}C), time and molecular weight of the polymers.[52]

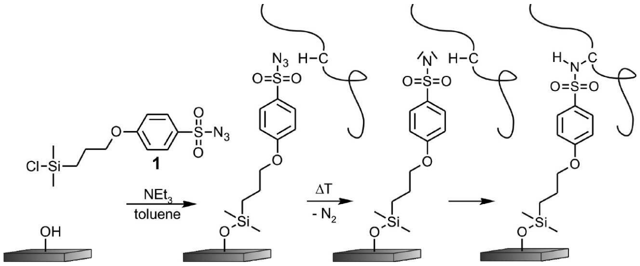


Fig 2 Attachment of polymers to SAM of sulfonyl azide (Reprinted with permission from (G. K. Raghuraman, K. Schuh, O. Prucker, J. Ruehe, *Langmuir,* 2010, **26**, 769). Copyright (2010) "American Chemical Society."

Yan's group has demonstrated that aromatic azide functionalized surface is useful to immobilize certain polymers such as polystyrene with a spatial and topographical control (Fig. 3).[53] In this case, a photolysis was performed on the surface anchored azide functional groups to transform into a highly reactive singlet nitrene intermediate, which in turn inserts into the C-H bond of the adjacent polymer chains. The process is versatile due to the chemical reactivity of nitrenes, which can covalently bound to a myriad of molecules and materials.[53]

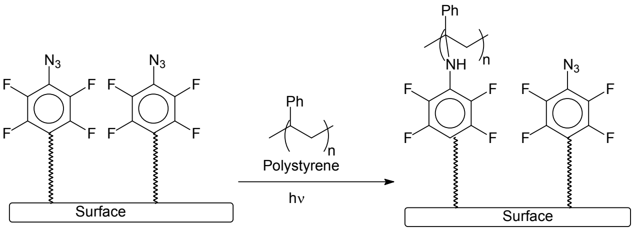


Fig 3 Photo-induced covalent immobilization of polystyrene on azide functionalized SAM

They have further demonstrated that for photochemically initiated immobilization of polymers, surface and interface properties are valuable in controlling the yield and efficiency of the polymerization. It was observed that dilution of the photolinker resulted in a gradual decrease in thickness of the immobilized film. Different film thickness and morphologies were obtained by adjusting the density of the photoactive groups on the surface. The functional group on the non-photoactive molecule can be chosen, depending on the material to be immobilized, to create a chemically compatible surface for increased immobilization yield and efficiency.[54]

Yan's group further showed that thermal activation of aromatic nitrenes can also be performed to immobilize polymers to SAM on silicon surfaces. By this method, patterned polymer films could also be fabricated. The thickness could be controlled by the type and molecular weight of the polymer.[55]

The C-H insertion method using an azide functionalized surface was also used to covalently immobilize a chemically inert polypropylene using both photoirradiation and activation by heating. The surface immobilized polymer thickness can be increased with increasing the reaction time and molecular weight of the polymers. Moreover, immobilization by the UV irradiation provide lower thickness compared to the thermal grafting method.[56]

The methodology was extended for micropatterning of different polymers like polystyrene (PS), poly(ethylene oxide) (PEO), poly(2-ethyl-2-oxazoline) (PEOX), poly(methyl methacrylate) (PMMA), poly(vinyl acetate) (PVAc) by photochemical activation (Fig. 4). Further, the polymer bound surface was treated with protein conjugated fluorescein-doped silica nanoparticles (FSNPs). After treatment with FSNP-labeled Concanavalin A (FSNP-Con A) the neutral hydrophilic polymers (PEO, PEOX) developed a strong fluorescence, because of FSNP Con A was efficiently adsorbed on this polymers. The weak hydrophobic polymers (PS, PMMA & PVAc) developed weak fluorescence because of lower adsorption.[57]

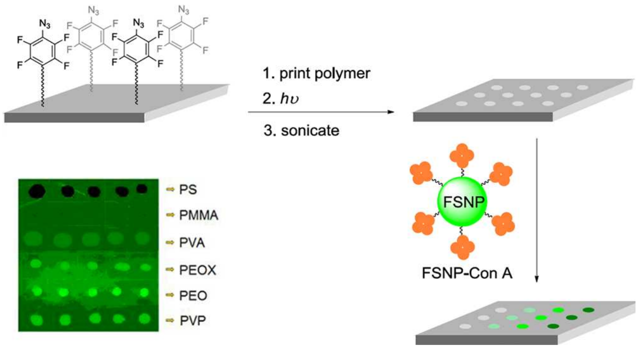


Fig 4 Arrays of different polymer functionalized surfaces, immobilization using azide functionalized surface followed by treatment with fluorescein-doped silica nanoparticles (FSNPs). Reprinted with permission from (H. Wang, Q. Tong, M. Yan, *Anal. Chem.,* 2013, **85**, 23). Copyright (2013) American Chemical Society."

Nitrene reactions are also useful for the immobilization of single polymers on surfaces also. Recently, in a concept note, Yan highlighted various aspects of photochemical immobilization of single polymers on perfluoroazide functionalized surfaces.[58, 59] He noted that the surface immobilized single polymers have unique properties that differ from either the bulk polymers or single polymer in solution. In a review article, Furukawa has described another important approach to immobilize single polymer by using polysilanes.[60]

Azide functionalized surfaces can also be conveniently used to immobilize polymers by "click" reaction. High yield and moderate reaction conditions of those types of reactions made it particularly attractive to apply for surface-based reactions recently. For example, Gopalan and others reported the immobilization of regioregular ethynyl-terminated poly(3-hexylthiophene) (P3HT) to an azide functionalized self-assembled monolayer (SAM) on a silica surface (Fig. 5). Those types of thiophene polymers are important for molecular electronic devices.[61, 62] The grafting of P3HT brushes was studied as a function of "click" reaction time; it was observed that the growth of the brushes was governed by a diffusion controlled process.[45]

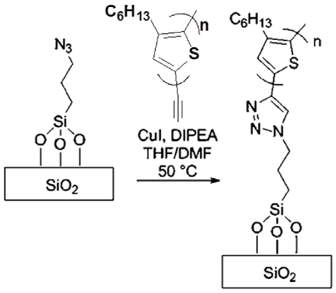


Fig 5 Immobilization of poly(3-hexylthiophene) on azide SAM by "click" reaction using CuI/N,N-diisopropylethylamine (DIPEA) in tetrahydrofuran (THF)/dimethylformamide (DMF) solvent. Adapted from Ref. 45 with permission from The Royal Society of Chemistry.

In an alternative way, alkyne functionalized surface was used for "click" reaction to immobilize azide functionalized polymers. For example, Azarroni and others reported the synthesis of different polymers end-functionalized with azide group and then immobilized to SAM on silicon substrate by the "click" reaction (Fig. 6). However, this method provided low grafting density because of steric hindrance of already grafted polymers.[51]

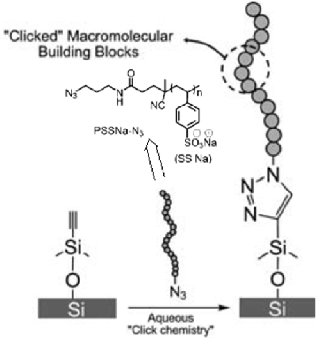


Fig 6 Immobilization of azide functionalized polyelectrolytes on alkyne terminated SAM. Reproduced from Ref. 51 with permission from The Royal Society of Chemistry.

Z. D. Cheng and others reported regiospecific "click" reaction on fullerene (C_{60}) surface to obtain shape amphiphiles with precisely defined surface chemistry and molecular topology.[63] In this case, micellar morphologies were observed from their self-assembly with a mixture of 1,4-dioxane and DMF as the common solvent and water.

Ostaci *et al* employed Cu(1)-catalyzed click reaction to graft polyethylene glycol (PEG), polymethylmethacrylate (PMMA), polystyrene (PS) SAM on silicon surface (Fig. 7). The resulting 1,4-substituted 1,2,3,-triazole linkage is thermally very stable and relatively inert to hydrolysis, oxidation, and reduction. The "click" chemistry based grafting procedure does not affect the chemical nature of precursor molecules and proceeds under mild condition. The scanning probe microscope (SPM) images showed the presence of a globular like morphology with spherical structures. The surface morphology of the brushes is strongly influenced by the polymer weight fraction in the grafting solution.[64]

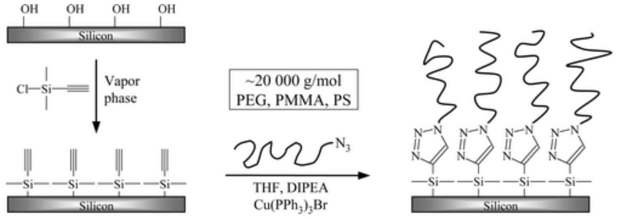


Fig 7 Immobilization of polyethylene glycol, polymethylmethacrylate and polystyrene on alkyne functionalized surface by "click" reaction. Reprinted with permission from (R.-V. Ostaci, D. Damiron, S. Capponi, G. Vignaud, L. Leger, Y. Grohens, E. Drockenmuller, *Langmuir,* 2008, **24**, 2732.). Copyright (2008) American Chemical Society.

Later, detail study of grafting of poly (ethylene glycol) brushes to silicon substrate using Cu (I)-catalyzed azide-alkyne "click" reaction was performed by the same group. They found that significant time dependent polymer grafting process proceeds between 24h and 72h. The grafted PEG layer thickness is only slightly improved by increasing the grafting reaction time from 24 h (4.9 nm) to 72 h (5.6 nm). With the increase of surface grafting, roughness decreased (4.4 nm, 1.9 nm and 1.3 nm for 12 h, 24 h, 48 h and 72 h respectively).[65]

Thiol-ene "click" reaction is an useful method to immobilize alkene functionalized polymer directly to thiol functionalized surfaces. The grafting can take place in a matter of minutes under UV-irradiation, without photoinitiator.[66]

Although "click" reaction is very efficient, orthogonal and modular technique, the synthesis of azide or alkyne functionalized polymers is often not trivial. A more widely synthesized polymers are carboxylic acid functionalized polymers. Those polymers can be easily immobilized to epoxy or amine functionalized SAM. For example, acrylic acid or vinylpyridine-based polymers can be immobilized on electrode surface by employing the reaction between epoxy functional group on surface and carboxylic acid end groups on the polymer resulting in the the formation of ester linkage. Depending on the solution pH, the two polymers could be protonated or deprotonated resulting in their different charges.[46]

When mixed epoxy and hydroxyl functionalized surfaces are used, binary brushes of two polymers can be synthesized by immobilization of carboxylic acid functionalized PS and poly (2-vinylpyridine) polymers (Fig. 8). Those binary brushes on surfaces are important to study the switching behavior by exposing to different solvents. Hence, two different lateral morphologies were identified - dimple (round clusters) after toluene exposure and ripple (elongated domains) after ethanol exposure. In this case, upon exposure of the sample to toluene, the top of the layer is preferentially occupied by polystyrene, while in ethanol and water (pH=3.0) the surface is dominated by PVP. The grafted polymer surface thickness was much smaller compared to "graft from" method, because of diffusion limitation of the grafting. The contact angle data clearly showed that a top layer of the binary brush switches from hydrophobic to a hydrophilic energetic state, upon exposure to selective solvents.[67]

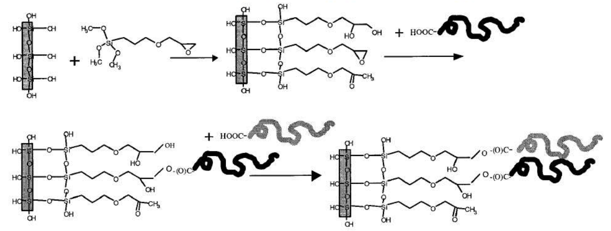


Fig 8 Immobilization of carboxylic acid functionalized polymers on epoxy and hydroxyl functionalized mixed SAM. Reprinted with permission from (S. Minko, S. Patil, V. Datsyuk, F. Simon, K. J. Eichhorn, M. Motornov, D. Usov, I. Tokarev, M. Stamm, *Langmuir,* 2002, **18**, 289. Copyright (2002) American Chemical Society.

However, when carboxylic acid functionalized polymers are directly used to immobilize on epoxy functionalized SAM, grafting density is low, particularly for high molecular weight polymers since slow diffusion of entangled chains and the reactive end becomes kinetically trapped within the limited distance from the surface.[68] Moreover, carboxylic acid functionalized polymers are not directly immobilized to amine terminated SAM because of low reactivity. Hence, carboxylic acid functionalized polymer is often converted to N-hydroxysuccinimide (NHS) ester or carbonate. For example, Yuan *et al* converted carboxylic acid functionalized dual responsive copolymer to NHS-ester by DCC coupling.[69] The NHS-functionalized polymer was then immobilized to amine functionalized surface under mild condition (Fig. 9).

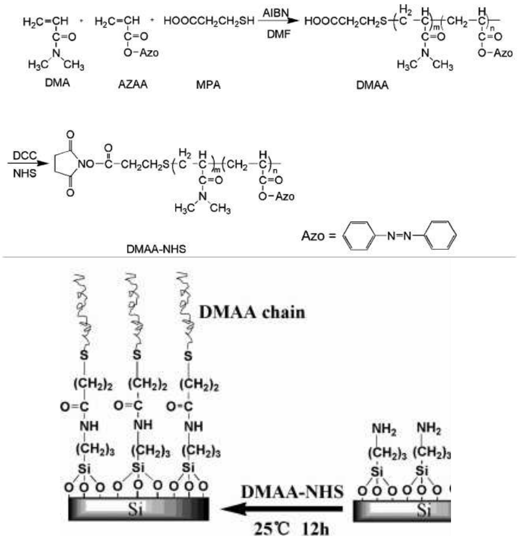


Fig 9 Synthesis of NHS-functionalized polymers followed by its immobilization on amine functioanlized surface. Reprinted with permission from (W. F. Yuan, G. Y. Jiang, J. X. Wang, G. J. Wang, Y. L. Song, L. Jiang, *Macromolecules,* 2006, **39**, 1300). Copyright (2006) American Chemical Society.

This kind of coupling reaction is also useful to immobilize an important PEG-based polymers to study cell resistant properties.[47]

Similarly, biomimetic phosphorylcholine (PC) functionalized polymer was immobilized on functionalized silicon surface by aminolysis reaction with carbonate functional group (Fig. 10). The thickness of the PC-functionalized film was found to be about 40 Å, same as calculated length of a molecule stretched out with four carbonyl carbons for each phosphorous.[70]

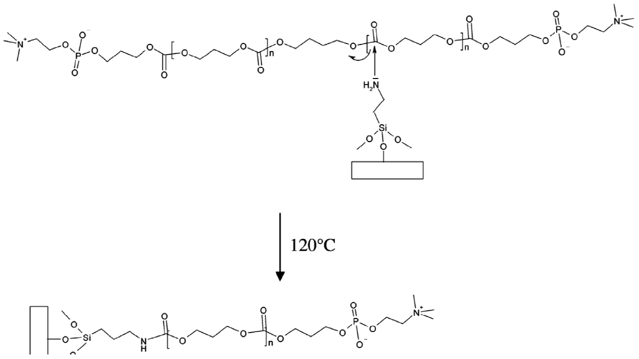


Fig 10 Immobilization of phosphorylcholine-based polymer on amine functionalized surface. Reprinted with permission from (E. M. E. Kristensen, F. Nederberg, H. Rensmo, T. Bowden, J. Hilborn, H. Siegbahn, *Langmuir,* 2006, **22**, 9651). Copyright (2006) American Chemical Society."

Nagel *et al* reported the immobilization of ferrocene-based polymers by the reaction between anchored amine functional groups and epoxy functional groups on polymer. The polymer on surface enabled electrical communication between the co-factor pyrroloquinoline quinine of soluble glucose dehydrogenase and the electrode for sensitive detection of this enzyme.[71]

Orthogonal, mild reactions such as Diels-Alder or hetero Diels-Alder reactions can be used to immobilize diene or dienophile functionalized polymers. For example, Kowollik and others reported the immobilization of cyclopentadienyl end-capped poly(3-hexylthiophene) (P3HT-cp) through covalent bond formation by Diels–Alder ligation (Fig. 11). One advantage is that the process occurs without the need of catalyst.[72]

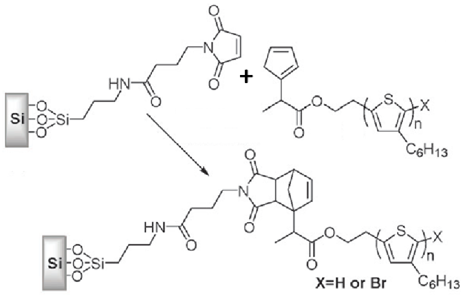


Fig 11 Diels-Alder reaction to immobilize thiophene polymers on surface. Adapted from Ref. 72 with permission from The Royal Society of Chemistry

Sulfur-based polymers can also be immobilized on surface via hetero Diels-Alder reaction (HAD). Nebhani and others used the electron deficiency of C=S bond to facilitate the HDA cycloaddition.[73]

Gooding and others employed the stepwise construction of PEG layers onto a non oxidized silicon surface. For this, hydrosilylation reaction was performed with 1,8-nonadiyne to form acetylene terminated surface, which was further functionalized with amine group by Cu (I) catalyzed click reaction. The amine terminated layer was then further conjugated with PEG to produce an antifouling surface (Fig. 12).[74]

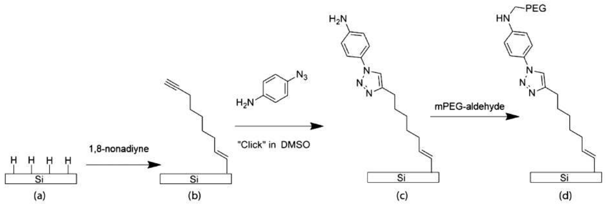


Fig 12 Click reaction to functionalize surface with amine group followed by reaction with aldehyde terminated methoxypolyethylene glycol (mPEG). Reprinted with permission from (B. S. Favel, M. Jasieniak, L. Velleman, S. Ciampi, E. Luais, J. R. Peterson, H. J. Griesser, J. G. Shapter, J. J. Gooding, *Langmuir,* 2013, **29**, 8355). Copyright (2013) American Chemical Society.

Although “graft to” method has the advantage of operational simplicity some fundamental drawbacks are also associated with it. For example, the grafting density is limited by thermodynamic and kinetic factors while surface coverage is limited by the volume of the polymer chain in its coiled state.[75]

3.2 “Graft from” polymerization for surface functionalization

This is the most popular and widely used approach to prepare polymer-functionalized designer surfaces with high grafting density and controlled thickness.[21] In this case, an initiator is attached to the surface first to form SAM. Polymer is then grown from the initiator group by exposing to solutions containing monomers and catalysts. Cationic polymerization, anionic polymerization, ring opening polymerization (ROP), ring opening metathesis polymerization (ROMP), nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer polymerization (RAFT) are the methods to grow the polymers from surfaces. Judicial choice of polymerization method is important to have better control over brush density, thickness, polydispersity and compositions. The ease of performing reactions and availability of reactive sites are also important criteria. ROMP is one example of “graft from” polymerization reaction which became “easy to perform” after the discovery of a series of Grubbs’ type ruthenium-based catalysts. However, the monomers are limited to those containing strained ring systems. Another attractive route is surface-initiated anionic or cationic polymerizations due to wider ranges of available monomers. The controlled/living nature of those types of polymerization is another advantage to fine tune the composition of the surface-bound well-defined polymers with low polydispersity. However, those reactions are extremely sensitive in nature, require specific glass wares, rigorous purification of the materials and a long reaction time. A more preferred method is various controlled radical polymerization reaction such as ATRP, RAFT and NMP polymerization. Those techniques are reliable, easy to perform and provide polymers with high grafting density and sufficient thickness. In a series of important experiments Ruhe et al has demonstrated that after the immobilization to surface, the efficiency of initiator may decrease.[34] However, it can still allow the formation of polymers with a high graft density because; during the polymerization process a low molecular weight compound is replaced by a high molecular weight polymer.

In the following section we will discuss about various aspects of different “graft from” polymerization reactions.

3.2.1 Atom transfer radical polymerization from SAM

It is one of the extremely versatile and robust techniques to grow polymer from the surface. In this case, a SAM with reactive halide end functional group is formed on the surface followed by its exposure to a solution of styrenes, acrylates, acrylamides based monomers, Cu (I) catalyst and ligands. In the initiating step, a formal homolytic cleavage of carbon-halogen bond occurs to generate a carbon-centered radical facilitated by single electron transfer from transition metal complex to the halogen atom. This leads to generation of oxidized metal complex. Chain propagation can take place from the attack of reactive radical species to the monomer. As the oxidized metal complex can reconvert the propagating radical chain to the corresponding halogen-capped dormant species, the process of this type of polymerization is farely controlled. Even a better control can be achieved by adding sacrificial initiator or deactivating Cu (II) species.[76, 77]

Within a few years of discovery of solution ATRP process by Matyjaszewski and others,[78] the ATRP from curved surface was reported by Huang and Wirth.[79] A year later, Fukuda and others reported first ATRP reaction from SAM on plannar silicon surface.[77] In the beginning of the last decade, Huck and others achieved a significant breakthrough in the synthesis of polyelectrolyte brushes of controlled thickness and density, by employing ATRP reaction to produce triblock copolymer brushes composed of cationic, anionic and neutral segments.[80] Very recently we have demonstrated “grfat from” ATRP polymerization can be conveniently performed on functionalized single walled carbon nanotube.[81]

Locklin and others prepared N-hydroxysuccinimide functionalized high density polymers and copolymers on surfaces using ATRP (Fig. 13). A high grafting density of 25.7 mmol/cm^2 was observed for a 50 nm thick layer. N-hydroxysuccinimide functional group is useful for the further attachment of functional groups or biomolecules on surfaces.[82]

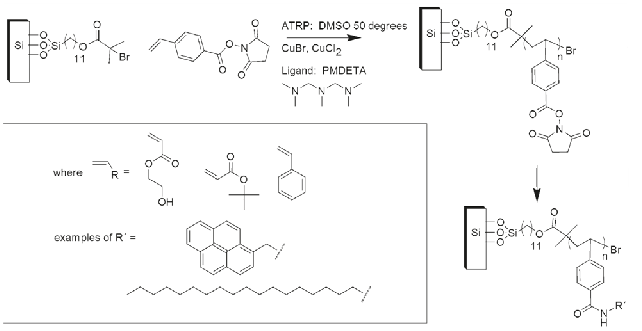


Fig 13 Surface-initiated atom transfer radical polymerization (ATRP) to grow homopolymer from the surfaces followed by aminolysis. Reprinted with permission from (S. V. Orski, K. H. Fries, G. R. Sheppard, J. Locklin, *Langmuir,* 2010, **26**, 2136). Copyright (2010) American Chemical Society.

Fang and others also reported the controlled high grafting of polystyrene (82 wt %) on to the graphene nanosheets by diazonium addition /ATRP.[83] Polystyrene nanocomposites with high molecular weight (M_n= 60000) showed significant mechanical enhancements of tensile strength and Young’s modulus.

Recently we reported the use of bromide functionalized single walled carbon nanotube (SWCNT-Br) initiator to obtain polymethylmethacrylate (PMMA)-g- SWCNT through controlled radical polymerization techniques (CRP).[84] Even without the use of additional sacrificial initiator, the polymerization was well-controlled. We also reported the covalent functionalization of SWCNTS by other polymers such as polyurethanes by radical polymerization.[84]

Kikuchi et al later demonstrated that a well defined cationic polymer brush on surface could be obtained employing copper-catalyzed ATRP of 2-(methacryloxy)ethyltrimethylammonium chloride (MTAC) in a fluorinated solvent 2,2,2-trifluoroethanol (TFE). They have also found that the addition of a small amount of isopropyl alcohol reduced the polymerization rate and produced the polymer with predictable molecular weight and narrower molecular weight distribution.[85] Huck and others also successfully synthesized gold nanoparticles inside polyelectrolyte brushes.[86]

Koylu and Carter reported synthesis of cleavable stimuli responsive polymer relying on acid-sensitive polymer brush through ATRP reaction and cleaving selectively by treatment with a p-toluenesulfonic acid / dioxane solution. Removal of the grafted layer was achieved by treatment with acidic solution, the cleaved PS chains were collected and analyzed by GPC, NMR etc. This strategy was useful for the comparison of the molecular weight of the free polymer to polymer brushes later cleaved from the photopolymer film. It was determined that the molecular weight of the polymer brushes was higher than the free polymer. This suggested that it cannot be universally assumed that the kinetics of surface brush growth and solution polymerization are the same when using a free initiator during the reaction.[87]

Pei et al reported the synthesis of poly ionic liquid polymer (poly [1-(4-vinylbenzyl)-3-butyl imidazolium hexafluorophosphate] (PVBIm-PF6)) on silicon surface through SI-ATRP. The (PVBIm-PF6) surface polymer brushes (Fig. 14) showed reversible switching between hydrophilicity (contact angle 41^0) and hydrophobicity (contact angle 95^0) by exchanging their counterions.[88]

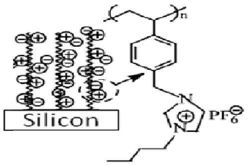


Fig 14 Poly (ionic liquid) brushes on surfaces on surfaces prepared via surface-initiated ATRP reaction. Reprinted with permission from (X. He, W. Yang, X. Pei, *Macromolecules,* 2008, **41**, 4615). Copyright (2008) American Chemical Society.

Brushes of poly[2-(1-butylimidazolium-3-yl) ethyl methacrylate hexafluorophosphate] ($PBIMH-PF_6^-$)[89] and oligoethylene glycol functionalized surface was also prepared using similar strategy by different research groups.[90] These methods provided fairly dense surface coverage althogh control over the thickness of the polymer layer and uniformity of surface coverage over the large area was challenging.

Effect of initiator density on polymer brush thickness for aqueous medium ATRP reaction on surfaces was studied by Huck and others. They concluded that the initiator density at the start of the polymerization determines the ultimate "footprint" and hence grafting density of polymer in polymer brushes. They clearly observed that on increasing the initiator density, thickness of the polymer brushes increased proportionately. However, there was no clear maximum initiator density. [91]

Enhancement of rate of polymerization was observed when surface-initiated ATRP reaction was performed under aqueous environment.[92]

Baker and others observed the enhancement of control over the polymer films prepared by graft from ATRP reaction could be achieved by the variation of the areal density of the immobilized initiators (Fig. 15). They have clearly demonstrated that when the fraction of the surface by initiator decreased below 5% of a monomer, the thickness of the polymer films dropped dramatically because of the increase of the area per polymer chain.[93]

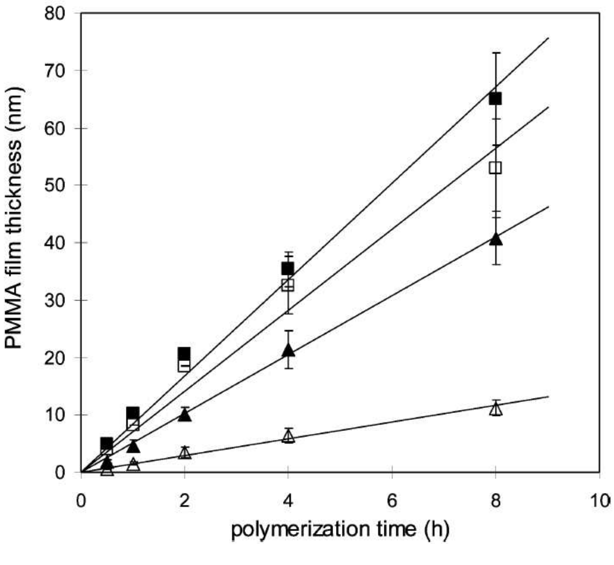


Fig 15 Evolution of the ellipsometric brush thickness with time for the polymerization of MMA (methyl methacrylate) from diluted initiator monolayers on Au substrates at 28 °C. (□, 100% 2-bromopropionyl bromide (2-BPB); ■, 50% 2-BPB; ▲, 5% 2-BPB; Δ, 1% 2-BPB). Reprinted with permission from (X Z. Bao, M. L. Bruening, G. L. Baker, *Macromolecules,* 2006, **39**, 5251.). Copyright (2006) American Chemical Society.

Recently, cross-linking phenomenon among the polymer chains was introduced to obtain a more uniform and homogeneous surface coverage over a large areas (Fig. 16). Cross-linking was also responsible for the film to be cycled between swollen and dry state with change in thickness from 140 nm to 340 nm.[94]

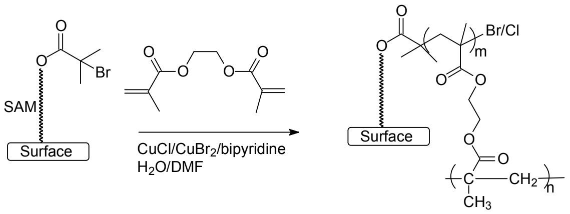


Fig 16 "Graft from" ATRP for the growing of cross-linked copolymers

Cross linking with silane was also used (Fig. 17) to form an unusually stable polymer layer of N-vinylpyrrolidone. In this case, the thermal stability can go up to 130 °C for 3h. The thermal stability also allows post polymerization at elevated temperature. The polymer functionalized surface was successfully used to minimize non specific adsorption of certain proteins.[95]

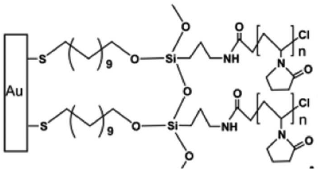


Fig 17 Silane cross-linked polymers grown from the surface using surface-initiated ATRP reaction . Reprinted with permission from (X. Liu, K. Sun, Z. Wu, J. Lu, B. Song, W. Tong, X. Shi, H. Chen, *Langmuir,* 2012, **28**, 9451). Copyright (2012) American Chemical Society.

Mixed self-assembled monolayer can be used to perform ATRP reaction from surfaces (Fig. 18)[96] to improve the efficacy. It was useful to control the lateral density of the polymer brush on surface. Lateral packing as well as morphology could also be controlled by initiator concentration, which is important for controlling the binding behavior of protein on the polymer functionalized surfaces.[97]

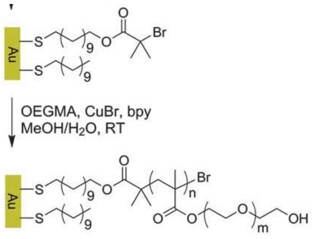


Fig 18 Surface initiated ATRP reaction from mixed SAM. Reproduced from Ref. 97 with permission from The Royal Society of Chemistry

Huang and others reported the well controlled grafting of poly(N-vinylpyrrolidone) (PVP) on to silicon surface by SI-ATRP using 1,4-dioxane/water mixtures as solvents, N-vinylpyrrolidone (NVP) and CuCl/5,7,7,12,14,14-hexamethyl-

1,4,8,11 tetraazacyclotetradecane (Me_6TATD) as a catalyst (Fig. 19). Film thickness varied from 1.66 to 33.56 nm, depending on the time duration of polymerization. PVP functionalized surfaces showed excellent biocompatibility while offering a reduced amount of protein adsorption.[98]

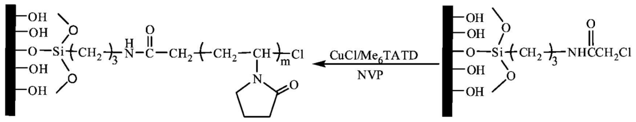


Fig 19 Surface initiated ATRP to prepare poly(N-vinylpyrrolidone) modified surface. Reprinted with permission from (Z. Wu, H. Chen, X. Liu, Y. Zhang, D. Li, H. Huang, *Langmuir,* 2009, **25**, 2900). Copyright (2009) American Chemical Society.

Fu and others used the combination of ATRP and "click" reaction in one pot to grow redox-active ferrocene-based polymers (Fig. 20). The simultaneous nature of both the reactions was proved by kinetic study. The redox responsive property of the surface was demonstrated in the reversible loading and unloading of β-cyclodextrine via host-guest interaction.[99]

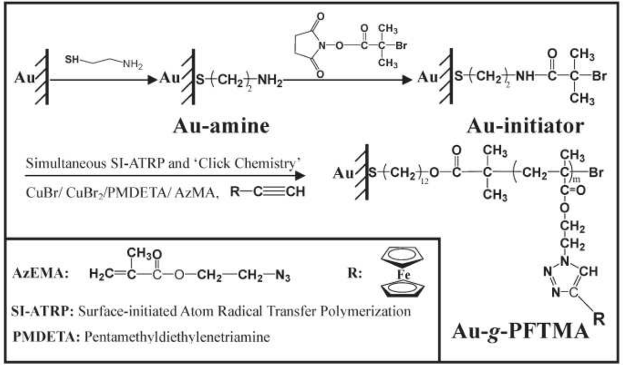


Fig 20 Simultaneous ATRP and "click" reaction from the surface. Reprinted with permission from (L. Q. Xu, D. Wan, H. F. Gong, K.-G. Neoh, E.-T. Kang, G. D. Fu, *Langmuir,* 2010, **26**, 15376.). Copyright (2010) American Chemical Society.

Recently, diazonium-based compounds were used to immobilize initiator on surfaces. In this case, by varying the initiator density on the surface the solvent content in the PMMA layer is shown to vary from 15% to 94%.[42]

Pyun et al demonstrated that by adding sacrificial initiator (Fig. 21) like ethyl 2-bromoisobutyrate in solution, chain length of polymer brushes could be controlled for ATRP reaction on ITO surfaces. The cyclic voltammetric (CV) study of homopolymer brushes established a linear correlation of molar mass with free linear polymers surface coverage. The success of controlled polymerization was further confirmed by atomic force microscopic (AFM) studies.[100]

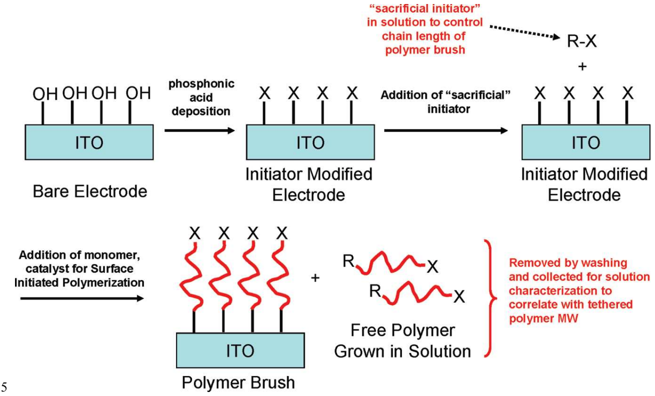


Fig 21 The role of sacrificial initiator for surface-initiated ATRP reaction. Reprinted with permission from (B. Y. Kim, E. L. Ratcliff, N. R. Armstrong, T. Kowalewski, J. Pyun, *Langmuir,* 2010, **26**, 2083.). Copyright (2010) American Chemical Society.

The ATRP can also be used to prepare diblock copolymers. For example, Boyes *et al* synthesized diblock copolymer brush PS-*b*-poly(*tert*-butyl acrylate) (P(*t*-BA)) on silicon wafer surface through SI-ATRP (Fig. 22). The surface diblock copolymers have a solvent sensitive nature and were used for the synthesis of inorganic nanoparticles by reduction of the treated PAA. The SAM was reduced by addition of H_2 gas that caused the surface morphology change from smooth and featureless to having definite surface features.[101]

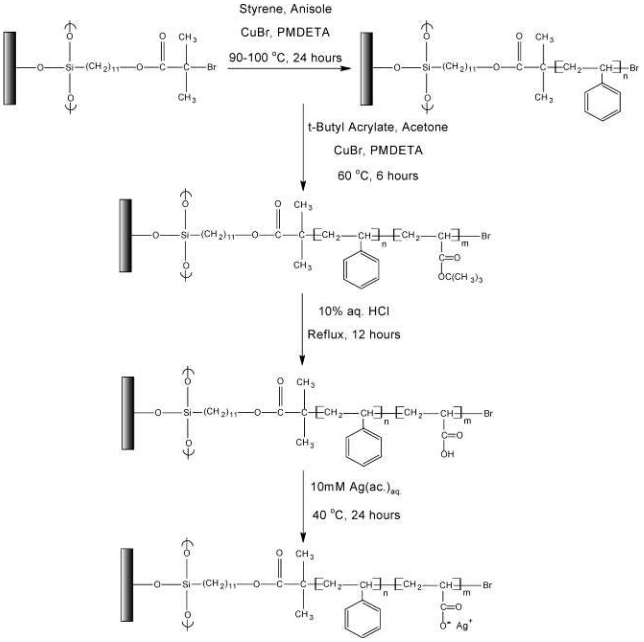


Fig 22 Surface-initiated ATRP reaction to grow styrene-block-methacrylic acid copolymer. Reprinted with permission from (S. G. Boyes, B. Akgun, W. J. Brittain, M. D. Foster, *Macromolecules,* 2003, **36**, 9539.). Copyright (2003) American Chemical Society.

Triblock copolymers composed of two hydrophilic poly(2-hydroxyethyl methacrylate) blocks and a hydrophobic poly(*n*-butyl methacrylate) middle parts were also synthesized using similar strategy. Polarization modulation infrared reflection absorption spectroscopy revealed an increase of the chain tilt toward gold surface during growth of the individual blocks.[102]

ATRP was used to immobilize liquid crystalline polymer brushes on silicon surface.[103] In this case, the special feature of the surface films essentially unchanged by dipping in organic solvents like chloroform and tetrahydrofuran. Moreover, in a marked contrast from the behavior of the spin cast film, the surface thin film did not show any dewetting in the isotropic state.[104] ATRP reaction can also be used for the rapid synthesis of carboxylic acid functionalized polymer brushes.[105]

Locklin *et al* immobilized photoswitchable spiropyran (SP)-based polymers (Fig. 23). Since the method involved "graft from" approach, the number of functional groups present on the surface could be greatly enhanced through the 3D arrangement of tethered polymer chains. This was useful to amplify the responsive nature of the surfaces.[106]

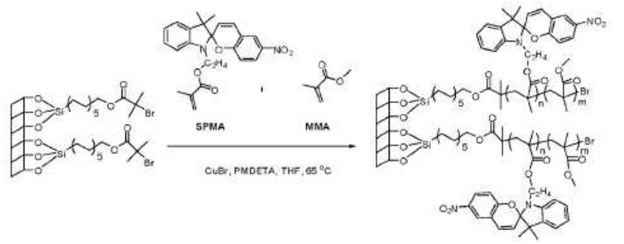


Fig 23 Growing of spiropyran-based polymers from surface using surface-initiated ATRP reaction. Reproduced from Ref. 106 with permission from The Royal Society of Chemistry

Binary polymer brush was prepared via two-step reverse ATRP on silicon surfaces by Matyjaszewski *et al* (Fig. 24). The surface polymer preparation is a two step process. The grafting density of the polymer brushes can be controlled through temperature and time of decomposition, enabling the tethered initiator required for the sequential polymerization. It could be increased by lowering the temperature of the initiation stage or using more active Cu(II)/ ligand catalyst.[107]

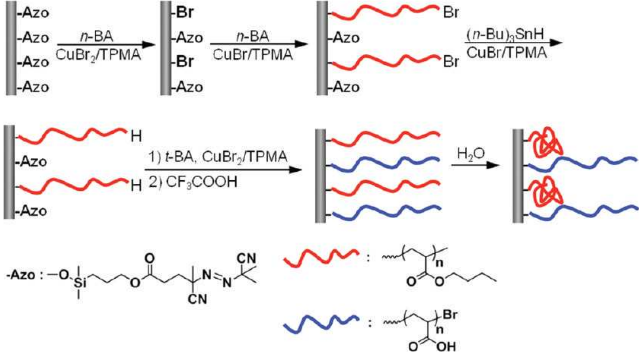


Fig 24 Reverse ATRP reaction to prepare bynary polymer brushes on surface. Reprinted with permission from (P. Ye, H. Dong, M. Zhong, K. Matyjaszewski, *Macromolecules,* 2011, **44**, 2253). Copyright (2011) American Chemical Society.

Klok and others reported the development of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) and poly(ethylene glycol) methacrylate (PEGMA) based hydrolytically degradable co-polymer brushes from silicon substrate by atom transfer radical copolymerization (SI-ATRcoP). The surface thickness could be controlled by reducing reaction time and adjusting the BMDO concentration. The polymer thin film was relatively stable under neutral and mild base condition (pH-9), and labile under acidic condition at pH 3-5.[108]

Sequential ATRP reaction was performed on self-assembled monolayer of a bromoisobutyrate initiator to tether triblock copolymer brushes of styrene and methyl acrylate (Fig. 25). The tethered triblock copolymer brushes exhibited reversible change in surface properties upon treatment with different solvents.[32]

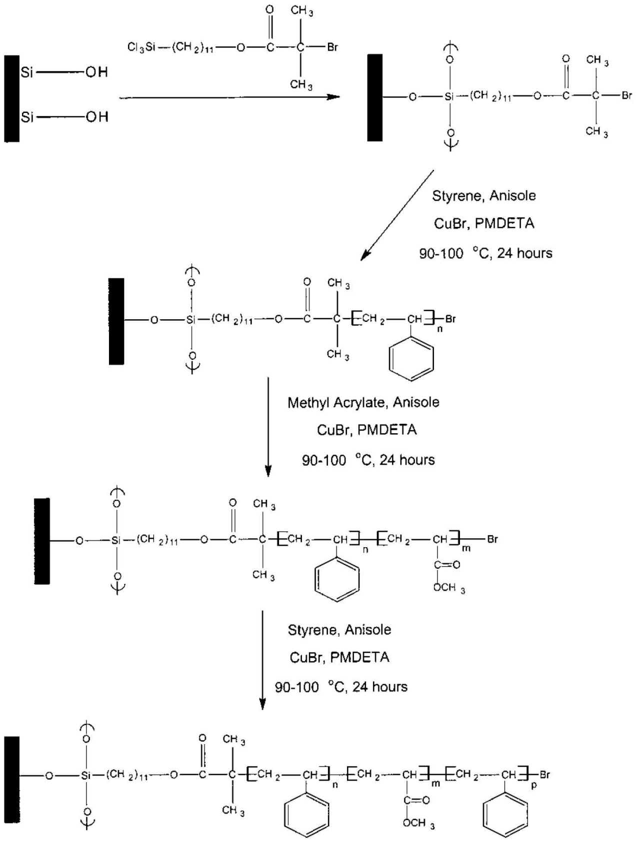


Fig 25 Surface-initiated sequential ATRP reaction to grow triblock copolymers from surface. Reprinted with permission from (S. G. Boyes, W. J. Brittain, X. Weng, S. Z. D. Cheng, *Macromolecules,* 2002, **35**, 4960.).Copyright (2002). American Chemical Society.

A combination of ATRP and RAFT polymerization technique was used by Boyes and others to synthesize stimuli responsive surface diblock polymers such as poly(styrene) (PSty)-*b*-PSty, PSty-*b*-poly(acrylic acid), PSty-*b*-poly(*N*-isopropylacrylamide), and poly(methyl acrylate)-*b*-poly(*N,N*-(dimethylamino)ethyl acrylate) (Fig. 26). This is the first example of the formation of well-defined PAA diblock copolymer brushes without the use of postpolymerization modification. Moreover, the surface diblock copolymers showed rearrangement capabilities in response to solvent changes.[109]

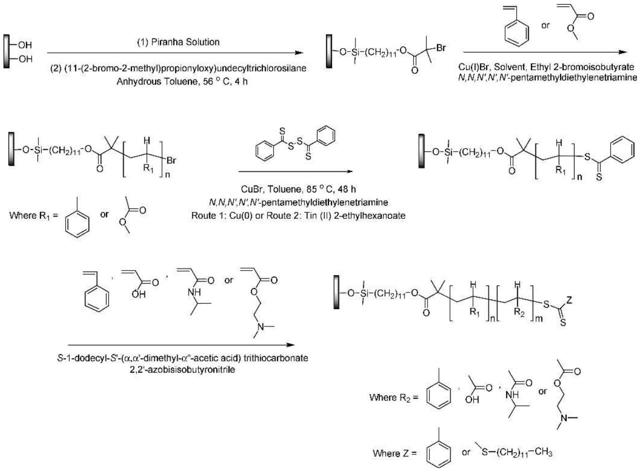


Fig 26 Sequential ATRP and RAFT reaction to grow block copolymers from surface. Reprinted with permission from (M. A. Rowe, B. A. G. Hammer, S. G. Boyes, *Macromolecules,* 2008, **41**, 4147).Copyright (2008). American Chemical Society."

Sequential ATRP and RAFT reaction is also useful to perform resist-free micropattern of binary polymer brushes in silicon surface (Fig. 27).[110] In this case, the ATRP initiator was first micropatterned onto Si (100) surface via UV-induced hydrosilylation through a photo-mask. The RAFT initiator was then coupled with unhydrosilylated region to grow the RAFT polymers forming micropattern of polymers.

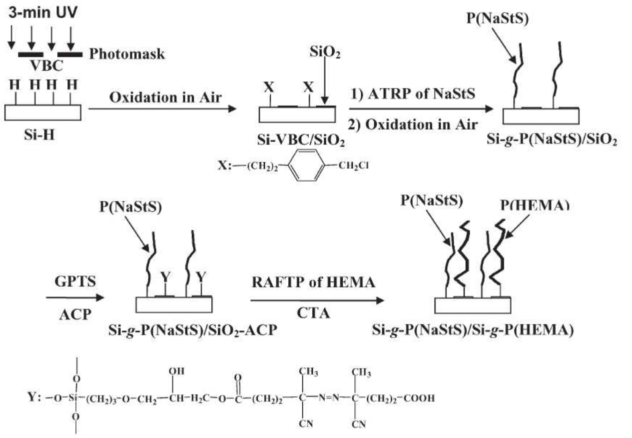


Fig 27 Strategy for resist-free micropatterning of surfaces using sequential ATRP and RAFT reaction in presence of chain transfer agent (CTA). Reproduced from Ref. 110 with permission from The Royal Society of Chemistry.

Zuilhof and others presented a novel surface engineering approach by combining photochemical grafting and ATRP reaction to anchor zwitterionic polymers on the surface (Fig. 28). The SI-ATRP zwitterionic polymer brush exhibited very good antifouling properties. The highly versatile top or post fictionalization of the zwitterionic polymer brush was achieved by a strain-promoted alkyne−azide cycloaddition ("click") reaction.[111]

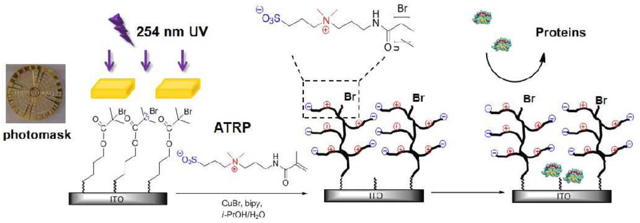


Fig 28 Combination of photochemical grafting and ATRP reaction to anchor zwitterionic polymers on surfaces. Reprinted with permission from (Y. Li, M. Giesbers, M. Gerth, H. Zuilhof, *Langmuir,* 2012, **28**, 12509). Copyright (2012). American Chemical Society.

Combination of UV-assisted imprint lithography and surface initiated ATRP was also used for nanostructured patterning of surfaces.[112]

Walters *et al* compared the efficacies of two types of living radical polymerization such as ATRP and single electron transfer (SET) for different methacrylate polymers. They also studied the effect of solvent, catalyst/ligand system and temperature on success of polymerization. They concluded that SET was more promising for achieving comparable polymer layer thickness at lower reaction temperature and shorter reaction times.[113]

One drawback of conventional ATRP reaction on surface is the presence of residual catalytic copper-containing organometallic species after reaction, that may be detrimental for biological applications. Recently ARGET (activators regenerated by electron transfer) version of ATRP reaction has been developed to reduce the required amount of copper to the level of a few ppm.[114]

3.2.2 Nitroxide-mediated polymerization (NMP) reaction on surfaces

Surface-initiated nitroxide-mediated polymerization reaction is an useful technique to prepare styrene-based polymers without using metal-based catalysts. In this case, a suitable initiator is attached to the surface (Fig. 29) so that reversible activation/deactivation of growing polymer chains can occure by a nitroxide free radical. First NMP-based "graft from" polymerization was reported by Hawker and others who immobilized alkoxamine based initiator on silicon surface to grow styrene polymers from it.[33] The method particularly allowed accurate control of molecular weight and thickness of the brush while maintaining low polydispersity. The "living" nature of the allowed sequential polymerization to prepare block copolymer brushes. The addition of free, sacrificial initiator in solution helps improving the efficacy of polymerization. However, it leads to the formation of free non-surface attached polymers needing final rigorous washing steps.

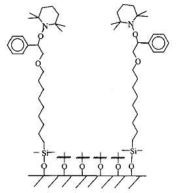


Fig 29 Initiator functionalized SAM for nitroxy mediated polymerization (NMP). Reprinted with permission from (M. Husseman, E. E. Malmstrom, M. McNamara, M. Mate, D. Mecerreyes, D. G. Benoit, J. L. Hedrick, P. Mansky, E. Huang, T. P. Russell, C. J. Hawker, *Macromolecules,* 1999, **32**, 1424). Copyright (1999) American Chemical Society.

Biocompatible oligo(ethylene glycol) containing polymer brushes were prepared by Ober *et al* on silicon oxide surface using nitroxide mediated polymerization (NMP) (Fig. 30). Cell adhesion studies showed that oligoethylene glycol (OEG)-containing polymer brushes effectively served in preventing nonspecific adhesion.[115]

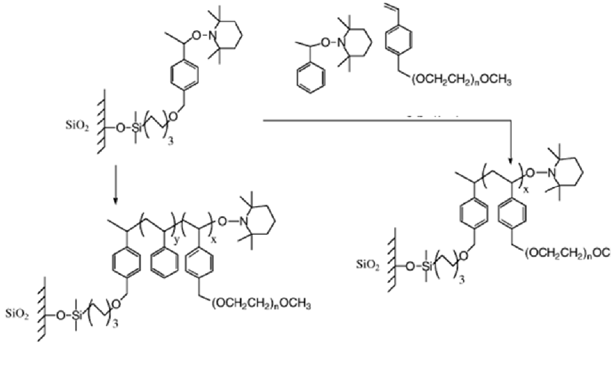


Fig 30 "Graft from" NMP polymerization to prepare homopolymer and copolymer functionalized surface. Reprinted with permission from (L. Andruzzi, W. Senaratne, A. Hexemer, E. D. Sheets, B. Ilic, E. J. Kramer,

B. Baird, C. K. Ober, *Langmuir,* 2005, **21**, 2495). Copyright (2005.). American Chemical Society.

Carter et al reported the nitroxide-mediated controlled “living” free radical polymerization (NM-LFRP) on silicon surface of styrene-d_8 to form polymer brushes on surface (Fig. 31). They were also able to compare different substarte cleaning methods, silane coupling agent treatments and their effect on polymer brush growth.[116]

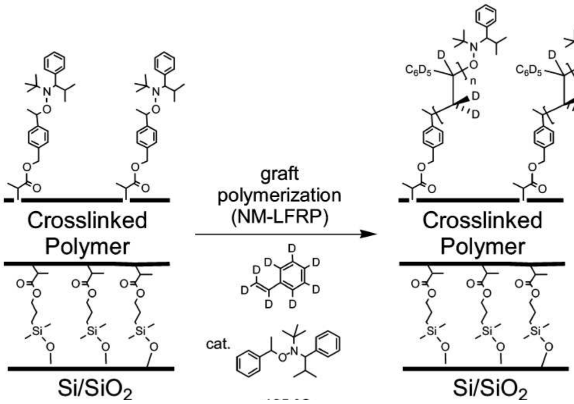


Fig 31 Surface-initiated NMP reaction to prepare polymer brushes. Reprinted with permission from (M. Beinhoff, J. Frommer, K. R. Carter, *Chem. Mater.,* 2006, **18**, 3425). Copyright (2006) American Chemical Society.

Ober and others prepared styrene-based homopolymer and diblock copolymer brushes bearing semifluorinated alkyl side groups on silicon surfaces using surface initiated NMP method. They concluded from their results that “after grafting the first block onto the surface the nitroxide-end capped polymer chains were able to polymerize second block in a “living” fashion and the stretched brush so formed was dense enough that the outermost block in all cases completely covers the surface.[117]

Later, Andruzi *et al* prepared biocompatible polymer brushes by immobilizing oligoethyline glycol containing styrenic polymers using the same NMP polymerization technique.[115] NMP method is also useful for the site selective surface-initiated polymerization.[118] Devaux and others showed that NMP polymerization can provide polystyrene brushes with high grafting density and stretching. They also performed a direct comparison of molecular weight and polydispersity between surface and bulk polymers by degrafting of the brushes into a toluene/HF solution.[119]

Nitroxide mediated polymerization (NMP) was useful to fabricate oligo N-isopropylacrylamide (oligoNIPAM) brushes (an important responsive polymers; *vide infra*) with amine end-groups. For example, Caykara and others prepared biofunctional oligoNIPAM brushes using NMP polymerization in the presence of cystamine chain transfer agent. AFM, XPS, FTIR, water-contact angle measurements were useful to characterize the polymer functionalized surface.[120]

One main drawback for NMP polymerization is the requirement of relatively high reaction temperature, which may cause problems for certain sensitive monomers. Moreover, NMP polymerization is useful mostly for styrenic monomers, hence limiting the scopes and versatility of the polymerization processes.

3.2.3 Reversible addition-fragmentation chain transfer (RAFT) polymerization

This is the most versatile technique to prepare polymers brushes with specific end functional groups since it tolerates a range of sensitive functional groups. In this case, a SAM of conventional free radical initiator (like azo initiator group) is formed on the surface followed by keeping under a solution of monomers (styrene, methacrylate, methacrylamide etc) and chain transfer agent (dithioester) to grow the polymer from surface. For example, Baum and others prepared polymer brushes of methacrylate, methacrylamide and styrene from azo functionalized silicon wafer[121] in the presence of a chain transfer agent (2-phenylprop-2-yl dithiobenzoate) (Fig. 32). Radical transfer between growing chains, either those in solution or those on a surface provides the necessary control over polymerization while capping of growing chains by dithioesters provide the “living” characteristics. In this case, a small amount of untethered radical initiator is required to scavange impurites for preventing quick termination of chain growth. For methacrylate and styrene polymers, both M_n and PDI were comparable for “free” polymer and cleaved polymer.

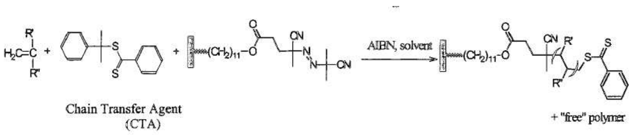


Fig 32 Surface-initiated RAFT polymerization by immobilizing azo-initiator on surface**.** Reprinted with permission from (M. Baum, W. J. Brittain, *Macromolecules,* 2002, **35**, 610). Copyright (2002) American Chemical Society.

In an alternative approach, a chain transfer agent is immobilized on the surface first;[122] then immersed into a solution of monomer and radical initiator (Fig. 33). For example, dithiobenzoate- or trithiocarbonate-derivatized silicon wafers were used to prepare a varieties of polymer brushes.[123-126] In most cases, film thicknesses correlated well with experimental molecular weights of free polymer chains. Further, Boyes and others noted the versatile nature of RAFT polymerization on surfaces “while ATRP is a very powerful technique for the synthesis of polymer brushes, it has some limitations, particularly in regards to the polymerization of highly functional monomers. RAFT polymerization is a much more versatile controlled living radical polymerization (CLRP) technique with regards to the polymerization of functional monomers compared to ATRP.”[123]

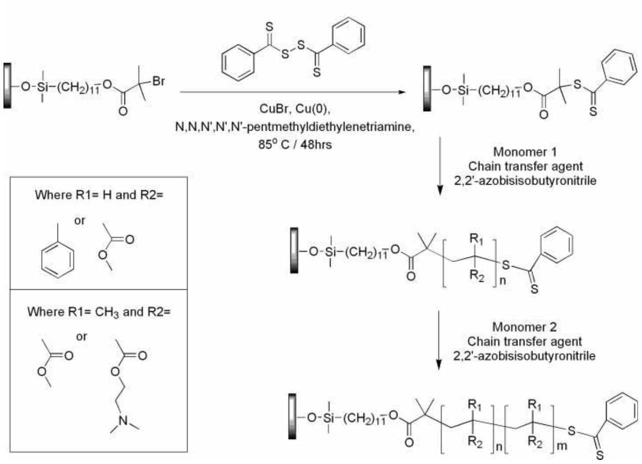


Fig 33 “Graft from” RAFT polymerization by immobilizing chain transfer agent on the surface. Reprinted with permission from (M. D. Rowe-Konopacki, S. G. Boyes, *Macromolecules,* 2007, **40**, 879). Copyright (2007) American Chemical Society.

Caykara *et al* reported the synthesis of cationic poly[(ar-vinylbenzyl)trimethylammonium chloride] by RAFT reaction for quantitative DNA immobilization. In this case, the addition of free RAFT agent was necessary to control molecular weight growth from the surface. Further, sacrificial RAFT agent was added to characterize and confirm the formation of well-defined polymer by facilitating the formation of free polymer in solution. A variation of molecular weight (M_n) from 10500 to 43000 with low PDI of 1.1-1.2 was observed for the free polymer, depending on reaction time.[127]

Kang et al reported controlled growth of block copolymer brushes of methacrylate polymers by RAFT polymerization on silicon wafer surface. The time-of-flight secondary-ion mass spectrometry (ToF-SIMS) was used for understanding the orthogonal surface chemistry or spatial ordering of the block sequence in the grafted PDMAEMA-*b*-PHEMA and PDMAEMA-*b*-PMMA copolymers on the surface.[128]

Later, the same group reported the fabrication of tunable mixed charged copolymer brush consisting of negatively charged carboxylic acid monomer (4-vinylbenzoic acid, VBA) and positively charged quaternary amine monomer ((ar-vinylbenzyl) trimethylammonium chloride) (VBTAC) through RAFT mediated polymerization from 4-cyanopentanoic acid dithiobenzoate (CPAD), immobilized on silicon surface. The VBA and VBTAC RAFT copolymer properties can be readily varied by changing pH. This particular property can be employed to regulate the adsorption of charged biomacromolecules such as DNA and proteins.[129]

Polymer brush with pendent glucosylurea group was prepared on glass surface using RAFT polymerization. The surface polymer brushes applicable in non-specific adsorption of protein and cell adhesion test.[130]

Li et al reported the effect of rate retardation on immobilized RAFT graft polymers on silicon surface mediated by three types of RAFT agent and two types of monomers (styrene & butyl acrylate). It was found that type of monomer, structure of RAFT agent, and local RAFT concentration on the surface have dramatic influences on the thickness of grafted polymer layer. The grafting polymerization with more severe rate retardation effect yielded thinner polymer films on the silicon wafer.[124]

Pattern et al demonstrated that use of microwave irradiation for radical polymerization can influence the growth of polymer from surface. The irradiation can cause up to a 39-fold increase in brush thickness at reduced reaction times for a range of monomer types like acrylamides, acrylates, methacrylates, and styrenes.[131]

Hydrogen-terminated silicon substrate could also be used to immobilize amine terminated small molecule that was useful for grafting initiator of RAFT polymerization. A cationic polymer was finally grown with grafting density as high as 0.93 chains / nm^2.[132]

Theato et al reported the functionalization and patterning of poly pentafluorophenyl (PFP) acrylate esters active polymer brush by surface-initiated RAFT (S-RAFT) using the surface-immobilized chain transfer agent (S-CTA) anchored onto the silicon substrates. The patterning was achieved using a lithography technique.[133]

Compared to most of the radical polymerization techniques, RAFT polymerization is slower. Moreover, preparation of the suitable RAFT agent may require multistep synthetic procedure.

3.2.4 Ring opening metathesis polymerization (ROMP)

This method allows the growing of well-defined polymer brushes from surface with appreciable thickness in very short time using strained cyclic monomers like functionalized norbornenes. The method became particularly popular following the discovery of Grubbs’ type catalysts. Several years back we showed that Grubbs’ type catalyst is useful to perform cross-metathesis on SAM of gold nanoparticles.[134] In the case of surface-initiated ROMP, ruthenium alkylidene is first immobilized on a surface by post functionalization of SAM, which is then immersed in a solution containing norbornene monomers. In the last decade, Whitesides’ group prepared a 90 nm thick polymer brushes within 30 minutes of reaction time by employing the surface initiated ROMP. The technique allowed the preparation of block copolymer also by incorporating another monomer sequentially.[135] Later, Grubbs and others produced a thick film in the dimensions of micrometer using ROMP on silicon surface.[136]

Choi et al performed ROMP using Grubbs 3rd generation catalyst to grow diblock copolymers from surfaces in a controlled way (Fig. 34). The strategy is useful for endo isomers also to provide a thickness value of more than 200 nm for second diblock polymers.[137]

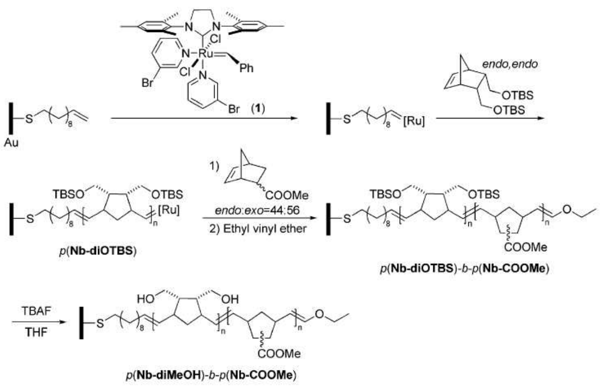


Fig 34 Ring Opening Metathesis Polymerization (ROMP) from surface-immobilized ruthenium based catalyst. Reprinted with permission from (B. Kong, J. K. Lee, I. S. Choi, *Langmuir,* 2007, **23**, 6761). Copyright (2007) American Chemical Society.

Immobilized Grubbs type catalyst was recently used to perform ring opening metathesis polymerization of partially fluorinated norbornene substrates (Fig. 35). Interestingly, thickness could be tuned from a few nanometers to several micrometers by changing the monomer concentrations. Because of the presence of fluorinated substrates on the surface, the films exhibit hydrophobic as well as oleophobic surface properties and provide effective barriers to the diffusion of aqueous ions.[138]

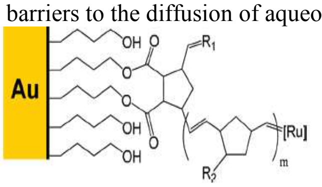


Fig 35 Surface-immobilized Grubbs type catalyst to perform ring opening metathesis polymerization. Reprinted with permission from (C. J. Faulkner, R. E. Fischer, G. K. Jennings, *Macromolecules,* 2010, **43**, 1203). Copyright (2010) American Chemical Society.

Later, Jennings and others reported the enhancement of rate of the polymerization can be achieved by combining with other SIP technique. Hence, ATRP can be used to grow a macroinitiator and surface initiated ROMP can be used to produce final coating.[139]

Samanta and Locklin reported the preparation of photochromic spiropyran-based polymer brush formation by surface-initiated ROMP (SI-ROMP) (Fig. 36). Final brush thickness could be controlled by varying the concentration of catalyst and monomer, as well as reaction temperature. These densely packed and highly smooth polymer films were successfully used as surfaces with switchable color and wettability using light as the external stimulus.[140]

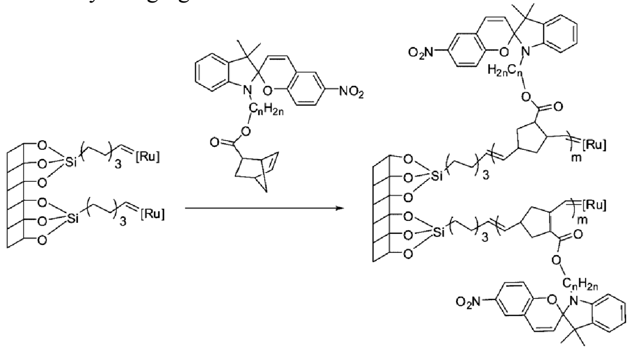


Fig 36 Preparation of photochromic spiropyran-based polymer brushes by surface-initiated ROMP. Reprinted with permission from (S. Samanta, J. Locklin, *Langmuir,* 2008, **24**, 9558). Copyright (2008) American Chemical Society.

The ROMP was also used for the formation of densely packed narborane with poly(*p*-phenylene ethynylene) (PPE) derivatives on silicon surfaces (Fig. 37). The advantage of "graft from" polymerization over spin casting method was clearly shown by higher chemical stability and emission quantum yield. However, in this case, surface polymer chains aligned parallel to surface. The AFM analysis of surface polymers showed a heterogeneous coverage of the polymers with periodicity in thickness to reflect the formation of the islands.[141]

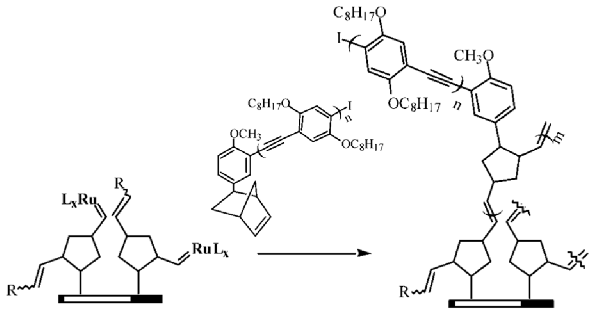


Fig 37 Densely packed narborane with poly(*p*-phenylene ethynylene) (PPE) derivatives on silicon surfaces prepared by "graft from" ROMP. Reprinted with permission from (J. H. Moon, T. M. Swager, *Macromolecules,* 2002, **35**, 6086). Copyright (2002) American Chemical Society.

Naijie Zhang *et al* reported functionalization of fullerenes with norbornene moiety via Ring Opening Metathesis Polymerization (ROMP).[142] In this case, high molecular weight C_{60}- polymers (Mn= 103360) were obtained with ability of well-controlled film formation from chloroform solution. Later Frechet et al used ROMP reaction to obtain polymer functionalized with short inter-fullerene distances.[143] In this case fullerene content of the polymer is high indicating its usefulness in photovoltaic devices. Recently Emrick and others reported covalently cross linking of fullerenes by 3-hexylthiophene-based polymers. A moderate hole and electron mobilities were observed by field effect transistor transfer measurements.[144] The fullerene-based compounds such as fulleropyrrolidine systems can be used as effective interlayers in photovoltaic cells to tailor electrodes for raising solar cell efficiency.[145]

Surface initiated ring opening metathesis polymerization (SI-ROMP) of low strain cyclooctadiene (COD) was reported for the first time by Chen and others (Fig. 38). In this case, vapor phase polymerization was performed to minimize chain transfer by reducing polymer chain mobility at vapour/solid interface. The surface grafted polybutadiene (PBd) thin film thickness was controlled by reaction time and reached 40 nm after 7 hours. However, prior attachment of a norbornyl-containing silane and a Grubbs catalyst to silicon substrates were necessary to carry out the polymerization effectively.[146]

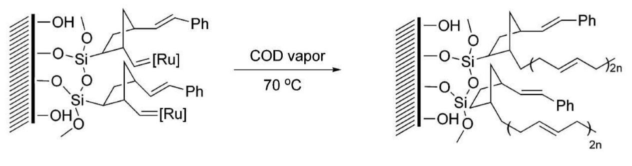


Fig 38 Vapour phase ROMP from surfaces of the monomers with unstrained ring system. Reprinted with permission from (J. Feng, S. S. Stoddart, K. A. Weerakoon, W. Chen, *Langmuir,* 2007, **23**, 1004). Copyright (2007) American Chemical Society.

Later Lerum, Chen and others showed that vapour-phase ROMP could be used for the polymerization of several other low strained cyclic olefins such as cyclopentene, 1,4-cyclohexadiene, cycloheptene, 1,3,5,7-cyclooctatetraene, cyclododecene etc.[147]

One main drawback of surface initiated ROMP reaction is: the unavailability of number of monomers with strained ring systems. Moreover, maintaining specific orientation in the thick polymer layer is also challenging.

3.2.4 "Living" Anionic polymerization from SAM

This technique was used by a few research groups to prepare well defined polymer brushes of low thickness. The "living" nature is particularly advantageous to prepare block copolymers by the sequential addition of monomers. In general, anion is generated on aromatic or benzylic carbon first which then participate in the polymerization of styrene type monomers. For example, the research group of Ulman prepared SAM of biphenyllithium moieties on gold substrate to initiate anionic polymerization of styrene (Fig. 39). Although the polymer brush on surface was smooth and homogeneous, it provided a low thickness value of only 18±0.2 nm. The authors also calculated grafting density (approximately 7-8 chains/R_g^2) and polymerization degree (N = 382), using mean-field theory. Polarized external reflection (ER) FTIR spectra of the grafted layer confirmed highly stretched preferentially oriented polystyrene chains.[43]

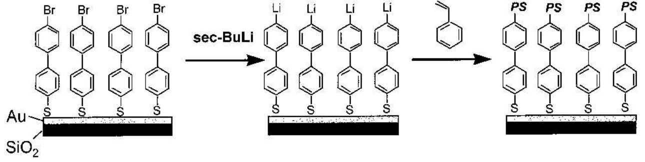


Fig 39 Surface initiated anionic polymerization to prepare polystyrene functionalized surface. Reprinted with permission from (R. Jordan, A. Ulman, J. F. Kang, M. H. Rafailovich, J. Sokolov, *J. Am. Chem. Soc.,* 1999, **121**, 1016). Copyright (1999) American Chemical Society.

Advincula and others described the preparation of styrene, isoprene and butadiene based homo & copolymers by employing living anionic surface-initiated polymerization (LASIP) on silicon and gold surface (Fig. 40). The surface polymer morphology is of unique shape. It was postulated that these morphologies were determined by grafting densities, molecular weight and wetting of the polymer.[148]

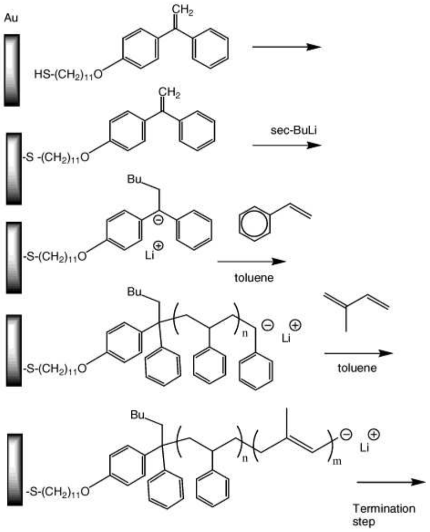


Fig 40 Preparation of homopolymers and copolymer brushes on surface using "graft from" anionic polymerization. Reprinted with permission from (R. Advincula, Q. G. Zhou, M. Park, S. G. Wang, J. Mays, G. Sakellariou, S. Pispas, N. Hadjichristidis, *Langmuir,* 2002, **18**, 8672). Copyright (2002) American Chemical Society.

Diblock copolymer brush on oxide surfaces was also prepared using anionic polymerization from 1,1-diphenylethylene monolayer (Fig. 41). *n*-Butyllithium was used to create the necessary anion initiating group on surface. To prepare the copolymer brush, the researchers converted hydroxyl-terminated poly(isoprene) brushes to the corresponding alkoxide and used to initiate ethylene oxide polymerization.[149]

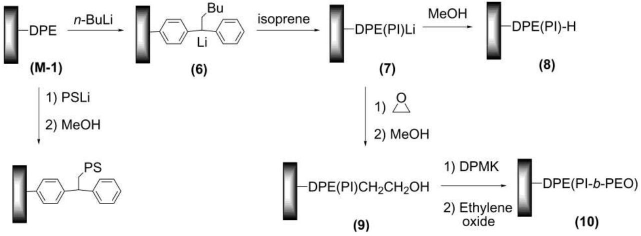


Fig 41 Surface-bound lithiated anionic initator to prepare ethylene oxide polymerization. Reprinted with permission from (R. P. Quirk, R. T. Mathers, T. Cregger, M. D. Foster, *Macromolecules,* 2002, **35**, 9964). Copyright (2002) American Chemical Society.

Alkoxy terminated SAM was also used to grow glycidol polymer at the elevated temperature (Fig. 42). Optimization of reaction conditions and reinitiation of cycles produced polyglycidol brushes of up to 70 nm thickness. The structure and degree of branching of the polymer were elucidated from ^{13}C NMR of the cleaved polymer.[150]

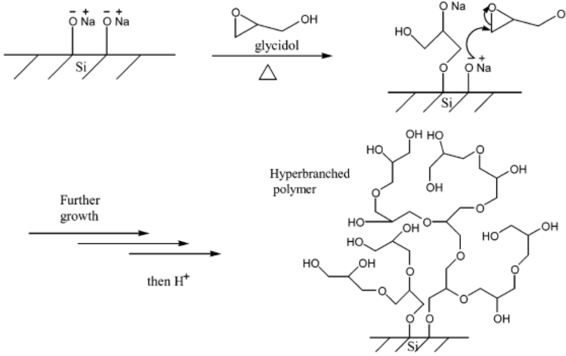


Fig 42 Alkoxy terminated SAM for the preparation of polyglycidol brush on surfaces. Reprinted with permission from (M. Khan, W. T. S. Huck, *Macromolecules,* 2003, **36**, 5088). Copyright (2003) American Chemical Society.

Quirk and Mathers performed living anionic polymerization of isoprenes by initiating polymerization from surface-bound 1,1-diphenylethylene with *n*-butyllithium. However the thickness was very low possibly due to unwanted quenching of the anions.[151]

There is only limited number of examples of surface initiated anionic polymerization because of the requirement of sophisticated experimental set up for its extreme sensitivity. Long reaction time, low value of final surface polymer thickness and restricted monomer functionality are also the reasons behind its unpopularity.

3.2.5 Cationic polymerization from SAM

Compared to other "living" polymerization techniques, surface-initiated cationic polymerization has been rarely used by the researchers. In the beginning of the last decade, Brittain and others described the synthesis of polystyrene brushes on silicon-based substrates by surface-initiated cationic polymerization. Hence, carbocationic initiators, 2-(4-(11-triethoxysilylundecyl)phenyl-2-methoxypropane and their corresponding SAM was prepared first. Growth of polystyrene brushes was then successfully achieved with the help of $TiCl_4$. Solvent polarity, additive and $TiCl_4$ concentrations are main factors that influence polystyrene thickness. The authors also immobilized deuterium based initiator to understand the percentage of conversion and found only 7% conversion under typical carbocationic polymerization condition.[152]

Ulman and others demonstrated that a SAM of trifluoromethane sulfonate can be used to initiate the living cationic ring-opening polymerization of 2-ethyl-2-oxazoline (Fig. 43). The method provided an ultrathin layer (~10 nm) with uniform thickness[153]

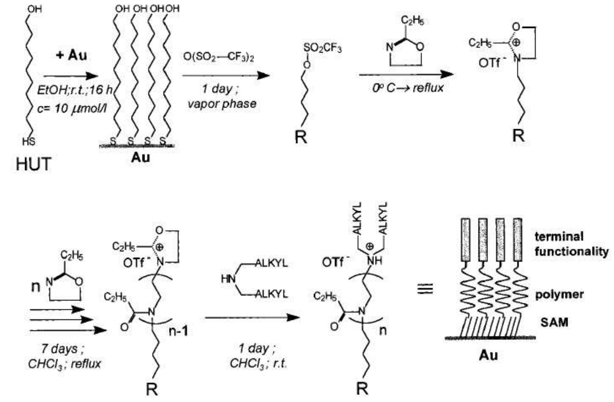


Fig 43 Living cationic polymerization from trifluoromethane sulfonate based SAM. Reprinted with permission from (R. Jordan, A. Ulman, *J.*

Am. Chem. Soc., 1998, **120**, 243). Copyright (1998) American Chemical Society.

Like other ionic polymerization, the main drawback of surface-initiated cationic polymerization is its poor efficacy leading to low value of thickness of polymer films. Moreover, number of substrates for cationic polymerization is very limited and needs special skill to successfully perform the polymerization on surfaces.

3.2.6 Metal-mediated catalyst transfer polycondensation

This is one of the most promising techniques to produce covalently bound thin films of conjugated polymers. In this case, surface is first functionalized with aryl halide group which is then undergone oxidative addition of a transition metal complex to obtain the surface-bound external initiator. Subsequent polymerization using a monomer provides polymer brushes with appreciable thickness. Initially, Senkovskyy and others produced grafted polymers using this technique.[154] Later Khanduyeva *et al* group successfully prepared cross-linked film of polystyrene-*g*-P3HT using nickel based catalyst transfer polycondensation or Kumada catalyst-transfer polycondensation.[155] In a feature article, Locklin et al particularly highlighted the recent developments on Kumada catalyst-transfer polycondensation.[20] Locklin and others further reported surface-initiated Kumada catalyst-transfer polycondensation (SI–KCTP) from gold surfaces to generate an ultrathin polymer layer of thickness 10-42 nm with globular morphology. However, after the polymerization, a small amount of polymer was also observed in solution.

This type of competitive polymerization in solution was an obvious drawback which might cause unwanted consumption of costly monomers.[44]

The same group further demonstrated the unsubstituted and alkoxy substituted polyphenylene brushes can be prepared on silicon substrate by surface-initiated Kumada-type catalyst-transfer polycondensation (SI-KCTP) using bis-(cyclooctadiene)nickel(0) ($Ni(COD)_2$) and 1,2-bis(diphenylphosphino)ethane (dppe) (Fig. 44). The surface polymer morphology was dependent on polymer side chains and steric bulkiness. The conjugated surface polymer thickness might go up to 30 nm. The authors pointed out that "this technique enjoys considerable advantages over electrochemical methods for the formation of surface-bound conjugated polymers due to the more controlled nature of chain transfer coupling polycondensation as opposed to electrochemical oxidation, the ability to form undoped polymers, and the applicability of the technique to the formation of polymer films on nonconducting substrates."[156]

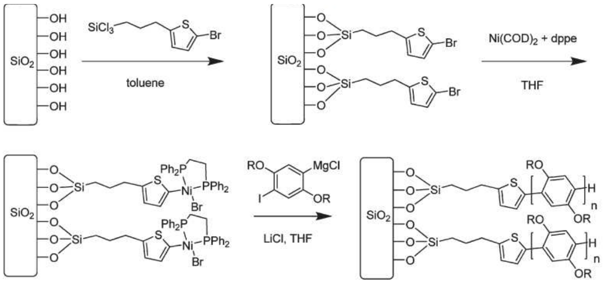


Fig 44 Nickel-based surface initiated Kumada catalyst transfer polycondensation. Reprinted with permission from (N. Marshall, S. K. Sontag, J. Locklin, *Macromolecules,* 2010, **43**, 2137). Copyright (2010) American Chemical Society.

Side chain substituted well defined conjugated thiophene based polySAM on silicon wafer and ITO surface was prepared by employing Ni (0) mediated Kumada catalyst-transfer polycondensation (KCTP). The modified surface film thickness varied between 40 to 65 nm.[157]

Patton et al described the synthesis of homo-, block, and clickable co-polypeptide brushes from low surface area substrates using nickel-mediated SIP of α-amino acid N-carboxyanhydrides. Hence poly(N-carbobenzyloxy-L-lysine), poly(g-benzyl-L-glutamate) and poly(S-tert-butylmercapto-L-cysteine) brushes from the respective N-carboxyanhydrides (NCAs) monomers were successfully prepared. Obviously, the end functionalized Ni species played a mediating role during chain extension or post polymerization to block co polypeptieds.[158]

Palladium-mediated surface-initiated Kumada catalyst transfer polycondensation is an excellent method to functionalize surfaces with thiophene-based conjugated polymers in near perpendicular orientation and controlled thickness (Fig. 45). The anisotropy and degree of orientation can be confirmed by using polarized UV-Vis spectroscopy. The palladium initiator density can be measured using cyclic voltammetry and a ferrocene-capping agent, where surface density was found to be 55% ($1.1 x 10^{14}$ molecules per cm^2). [159]

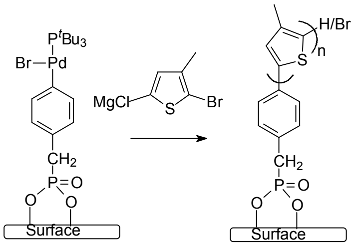


Fig 45 Palladium-mediated surface-initiated Kumada catalyst transfer polycondensation

Although "graft from" metal mediated polycondensation reactions have gained a significant attention only in recent years, its practical implementation starting with the preparation of an aryl halide monolayer is still challenging. For example, binding of and initiator to the surfaces with good surface coverage is difficult to achieve in one step.

3.2.7 Other "graft from" polymerization methods

Enzymatic "graft from" ring opening polymerization was used by Choi and others to immobilize biodegradable polyesters on surfaces.[160] A combination of directed deposition of functionalized areas of SAM and consecutive surface initiated polymerization is helpful for the preparation of amplified patterned surface.[161] Li et al reported the synthesis of homopolymers and diblock copolymers via surface-initiated reverse iodine transfer polymerization technique (Fig. 46). Narrow molecular weight distribution, linear kenetic plot and linear plot of molecular weight versus monomer conversion indicated a controlled and living nature of polymerization.[162]

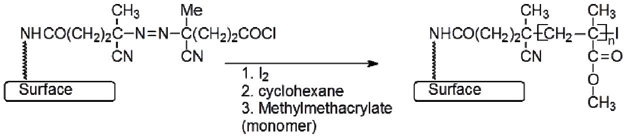


Fig 46 Reverse iodine transfer polymerization from surface

Tsujii and others reported synthesis and immobilization of an organotellurium based chain transfer agent (CTA) on silicon wafers and silica nanoparticles (SiNPs) and performed surface-initiated organotellurium-mediated living radical polymerization (SI-TERP) (Fig. 47) from the immobilized chain transfer agent using a variety of monomers, such as styrene, MMA, BA, NIPAM, NVC, and NVP. Surface polymer brush thickness will be decreased after grafting. The surface polymer brush was characterized by predictable number-average molecular weights (close to the theoretical values) and low polydispersity indices. Atomic force microscopy and transmission electron microscopy analyses of the concentrated polymer brushes (CPBs) revealed the highly stretched and anisotropic structure of the grafted polymer.[163]

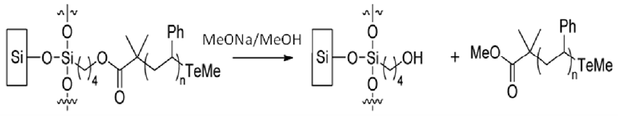


Fig 47 Surface initiated organotellurium-mediated living radical polymerization to prepare styrene-based polymer. Adapted with permission from (S. Yamago, Y. Yahata, K. Nakanishi, S. Konishi, E. Kayahara, A. Nomura, A. Goto, Y. Tsujii, *Macromolecules,* 2013, **46**, 6777). Copyright (2013) American Chemical Society.

Zapotoczny and others successfully applied self-templating approach to synthesize conjugated polymer brush on surfaces (Fig. 48). For this, terminal alkyne functionalized acrylate polymers were immobilized on surface using photopolymerization under UV irradiation. Side groups were then polymerized using Rh-catalyze reaction. Those types of conjugated systems are highly conductive after appropriate doping.[164]

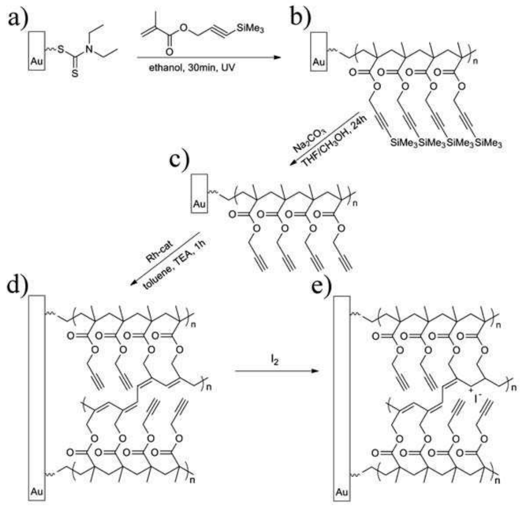


Fig 48 Self-templating approach to prepare conjugated polymer brushes on surface. Reproduced from Ref. 164 with permission from The Royal Society of Chemistry

Very recently, surface-initiated N-carboxyanhydride ring-opening polymerization (NCA-ROP)/vapour deposition polymerization has attracted significant attention for the preparation of biocompatible polypeptide films.[165, 166]

Most of the "graft from" methods are powerful techniques for the immobilization of polymers in the form of brush considering high surface density with stretched chain orientation. However, those methods are limited to chain growth polymerization and often requires difficult step of initiator immobilization on surfaces. Often it requires separate steps of initiator immobilization and the polymerization reaction. Further, synthesis of polymers can be better controlled in solution as compared to the polymerization on the surface.[167]

3.3 "Graft through" method of immobilization

The "graft through" polymerization method is an intermediate method of "graft from" and "graft to" polymerization that involves simply performing a solution polymerization in the presence of a surface functionalized with reacting groups which react in the polymerization. The advantage of this method is its operational simplicity like a one-pot synthesis and immobilization of the polymer. In this method, high grafting densities of polymer can be obtained provided with suitable reaction conditions.

Ruhe et al reported the growth of styrene polymer from styrene and methacrylate functionalized surface (Fig. 49) by radical polymerization method. It was found that the formation of the polymer layer levels off at rather low monomer and initiator conversion, and films of 15 nm thickness are formed. Further, the concentration of initiator has little influence on the thickness. A model was developed to explained above phenomenon.[23]

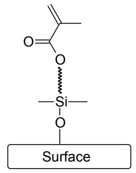
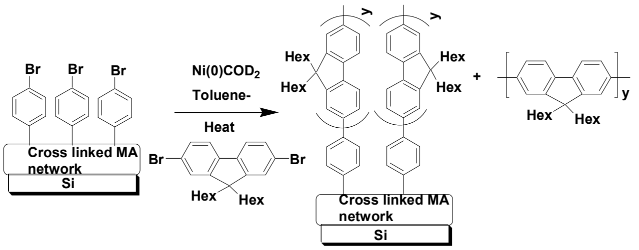


Fig 49 Methacrylate functionalized surface to prepare polymethacrylate brush by "graft through" method of polymerization

Carter and others reported one of the first examples of functional surface brush growth polymerization method employing Ni (0) mediated condensation polymerization (Fig. 50). Further, nanocontact molding was used to prepare patterned functional surfaces. The optical fluorescence behavior of the surface functionalized polymer properties was similar to that spin coated polyfluorene (PF) surface. The patterned surface also provided photo luminasance under exposure of UV-irradiation (long & short wave length).[25]



Hex = Hexyl, COD=1,3-cyclooctadiene, MA = methacrylate

Fig 50 Ni(0)-mediated "graft through" polymerization from surface which can be used to prepare patterned surface. Adapted with permission from (M. Beinhoff, A. T. Appapillai, L. D. Underwood, J. E. Frommer, K. R. Carter, *Langmuir,* 2006, **22**, 2411). Copyright (2006) American Chemical Society.

Later, strategy was slightly modified to achieve better control in growth of the film. The total film thickness (siloxane-grafted polymer) was 98 nm, indicating an increase of about 68 nm due to growth of the PF layer on the surface.[48] Patterning of the surface with poly (9, 9-dihexyl fluorine) using microwave irradiation was achieved to reduce the reaction time.[168]

Transition metal catalyzed polymerization of substituted acetylenes provides functional surfaces with extended conjugated molecules (Fig. 51). These reactions follow step kinetics and proceed through a metathesis-like addition reaction involving an active metal carbene species. The polyacetylene brushes also present unsaturated functionality as the end group, that is useful for further modification.[169]

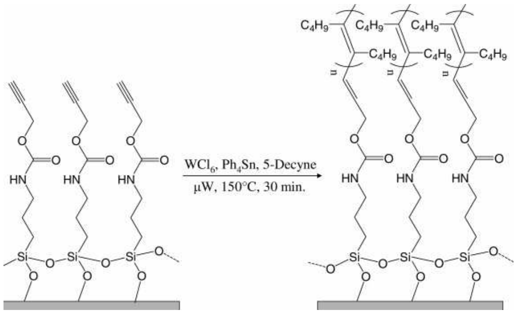


Fig 51 “Graft through” transition metal mediated polymerization of substituted acetylenes. Reprinted with permission from (S. B. Jhaveri, K. R. Carter, *Langmuir,* 2007, **23**, 8288). Copyright (2007) American Chemical Society.

Poly 3-methyl thiophene (P3MT) polymer film was synthesized on ITO electrode using “graft through” catalyst transfer polycondensation (Fig. 52). Polymer film thickness was controlled from 30 to 265 nm by varying the solution monomer concentration. A tunable work function further confirmed its potential use as organic electronic material.[170]

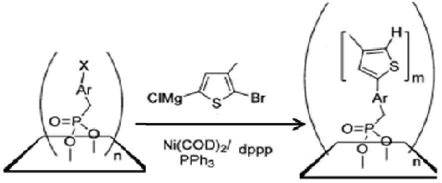


Fig 52 “Graft through” catalyst transfer polycondensation to prepare P3MT polymer film. Reprinted with permission from (N. Doubina, J. L. Jenkins, S. A. Paniagua, K. A. Mazzio, G. A. MacDonald, A. K. Y. Jen, N. R. Armstrong, S. R. Marder, C. K. Luscombe, *Langmuir,* 2012, **28**, 1900). Copyright (2012) American Chemical Society.

Recently we performed “graft through” click polymerization to incorporate various polytriazoles under mild conditions(Fig. 53). The band gap calculation revealed its semiconjugating nature while atomic force microscopy and ellipsometry revealed its high degree of polymerization.[26]

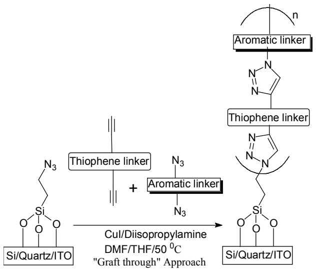


Fig 53 “Graft through” click polymerization to prepare polytriazole on surface. Reproduced from Ref. 26 with permission from The Royal Society of Chemistry

3.4 Direct methods of immobilization

This is the most straight forward method to functionalize surfaces with suitable polymers. In this case, a polymer with suitable end group is prepared first which is then used to form SAM on a suitable surface. Park *et al* reported synthesis of the copolymers of Poly(n-hexylisocyanate)-*b*-poly[3-(trimethoxysilyl) propyl methacrylate] ($PHIC_m$-*b*-$PTMSM_n$) by living anionic polymerization and ATRP method. The polymers were self assembled directly onto silicon to form polymeric self assembled mono layers (PSAMs). The rod like PSAMs exhibited nematic liquid crystalline monolayer parallel to one another.

The PSAMs prepared by “direct” immobilization method exhibited a low grafting density, solvent sensitivity, reactivity toward additional surface-functionalizing reagents, the ability to form a mixed SAM with a nanoscopic pattern, and rapid photopatternability. The simple processing conditions for “direct” immobilization method to prepare a uniform nanometer-thick PSAM (Fig. 54), are advantageous in comparison with the conditions required by other methods.[171]

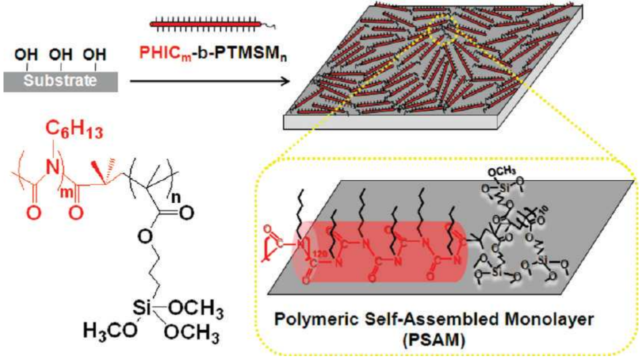


Fig 54 Direct grafting method to immobilize methacrylate polymer on surface. Reprinted with permission from (M. Han, M. S. Rahman, J.-S. Lee, D. Khim, D.-Y. Kim, J.-W. Park, *Chem. Mater.,* 2011, **23**, 3517). Copyright (2011) American Chemical Society.

Poly (2-oxazoline) brushes have been grafted directly on silicon surface by interaction with carboxylate functional group (Fig. 55). The polymer had been synthesized by ring opening cationic polymerization. An effective control on thickness of grafted polymer brush layer has been demonstrated.[172]

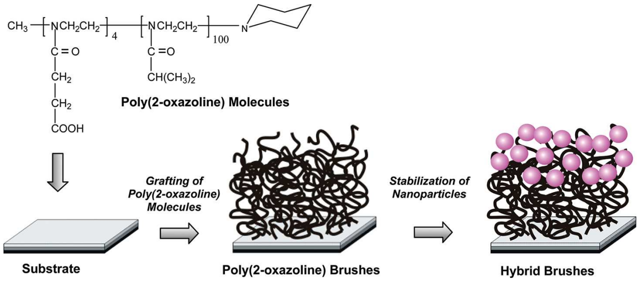


Fig 55 Direct grafting of poly(2-oxazoline) on silicon surface. Reprinted with permission from (M. Agrawal, J. Carlos Rueda, P. Uhlmann, M. Mueller, F. Simon, M. Stamm, *ACS Appl. Mater. Interfaces,* 2012, **4**, 1357). Copyright (2012) American Chemical Society.

Nano- and micropattering of polymer brushes were also employed by direct grafting using triethoxysilane polymers.[173]

Dual functional copolymer with “bio-reactive” and “bio-inert” moieties had been directly grafted to silica surface with trimethoxysilane group (Fig. 56). The polymer contained polyethylene glycol (PEG) part (bio-inert), which was responsible to prevent non specific protein adsorption, as well as N-hydrxysuccinimide part (bio-reactive) which was responsible for protein immobilization.[174]

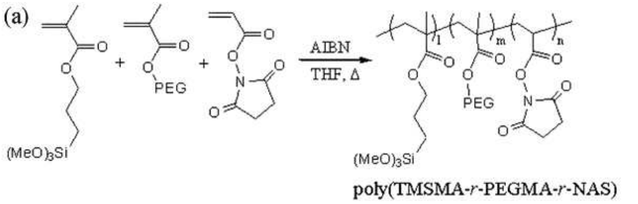


Fig 56 Preparation of trimethoxysilane functionalized copolymers for direct grafting to silicon surface. Poly(TMSMA-*r*-PEGMA-*r*-NAS): random copolymers of poly(ethylene glycol) methyl ether methacrylate (PEGMA), 3-(trimethoxysilyl)propyl methacrylate (TMSMA), and *N*-

acryloxysuccinimide (NAS). Reprinted with permission from (S. Park, K.-B. Lee, I. S. Choi, R. Langer, S. Jon, *Langmuir,* 2007, **23**, 10902). Copyright (2007) American Chemical Society.

Direct covalent attachment strategy was also employed to immobilize ABC type triblock copolymers containing glassy and rubbery segments. The surface properties of the thin film could be reversibly altered by the appropriate solvent exposure.[175]

Sayed *et al* reported immobilization of thiol-functionalized polystyrene (PS-SH) on the gold surface directly to control the surface aggregation structure of polymer thin film. The PS–SH was prepared by living anionic polymerization technique. The polymer thickness on surface varies depending on the polymer solution concentration. However, continuous and homogeneous structure of the polymer film was obtained, irrespective of the polymer concentration.[176]

Tajima *et al* demonstrated that poly(3-butylthiophene) (P3BT) can form a SAM on a gold surface directly (Fig. 57). Unlike the spin-coated polymers, which showed an edge-on orientation, the SAM layer showed an end-on orientation. This particular orientation is important for the enhancement of hole mobility of a molecular electronics devices.[177]

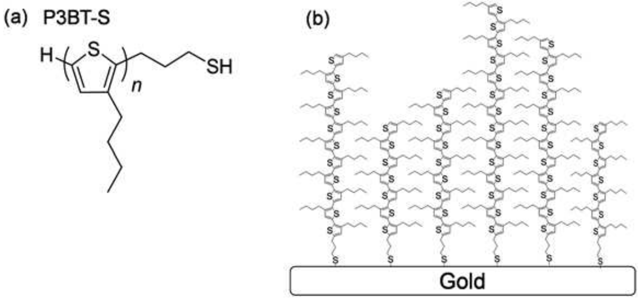


Fig 57 Thiol functionalized poly(3-butylthiophene) (a) and direct immobilization on gold surface (b). Reproduced from Ref. 177 with permission from The Royal Society of Chemistry)

McCormic *et al* reported the preparation of polymers bearing dithioester end groups by RAFT polymerization technique. The subsequent reduction of dithioester end groups to thiols allows direct anchoring of polymers on gold surface (Fig. 58).[178]

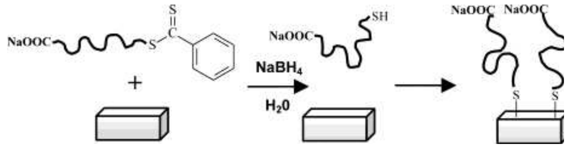


Fig 58 Thioester group bearing polymer and subsequent immobilization to gold surface after reduction. Reprinted with permission from (B. S. Sumerlin, A. B. Lowe, P. A. Stroud, P. Zhang, M. W. Urban, C. L. McCormick, *Langmuir,* 2003, **19**, 5559). Copyright (2003) American Chemical Society.

McCullough *et al* successfully synthesized soluble regioregular polyalkylthiophenes bearing thiol-terminated side chains by post polymerization (stille coupling) that was patterned on gold coated glass substrates through capillary force lithography technique (Fig. 59).[179]

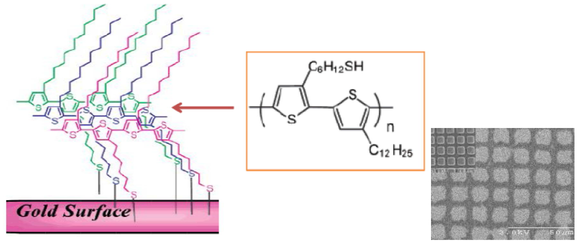


Fig 59 Patterning of regioregular polyalkylthiophenes bearing an end thiol groups by direct immobilization on gold surface. Reprinted with permission from (L. Zhai, D. W. Laird, R. D. McCullough, *Langmuir,* 2003, **19**, 6492). Copyright (2003) American Chemical Society

Protein resistant surfaces have been fabricated by direct immobilization of poly (ethylene glycol) based polymer through pendent thioether group (Fig. 60) on gold surface. The polymeric monolayer could be formed from water-based as well as toluene-based copolymer solution. Water-based solution provided a higher surface coverage and dense surface coverage.[180]

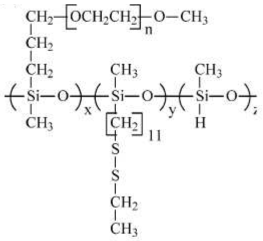


Fig 60 Disulfide bearing polymer for direct immobilization and patterning on gold surface. Reprinted with permission from (C. Zhou, V. K. Khlestkin, D. Braeken, K. De Keersmaecker, W. Laureyn, Y. Engelborghs, G. Borghs, *Langmuir,* 2005, **21**, 5988). Copyright (2005) American Chemical Society.

Direct method of immobilization is very straightforward, but synthesis of polymers with anchorable end groups is not always trivial. Moreover, formation of dense polymeric layer using this method is challenging because of the preferred coiled conformation of polymers in normal state. However, higher conformational entropy of immobilized macromolecules, due to reduced steric crowding may facilitate response to external stimuli such as solvent, pH, or temperature.

4. Applications

4.1 Responsive surfaces

A polymer functionalized surface is called responsive when it undergoes change in chemical composition, architecture, conformation or physical properties in response to external stimuli such as solvent, temperature, pH, and ions. Those responsive surfaces are important to design smart surfaces. For example, external stimuli responsive surface offers the possibility for the development of intelligent devices such as controllable separation system, bioanalytical devices etc.[181, 182] Chen and others showed that thermoresponsive fluidic devices can be used as an extractor of DNA molecules from a specimen of human blood through temperature tuning.[183] Recently we have shown that poly(NIPAM) can be immobilized on leather surface to improve its properties.[184] Various applications of responsive surfaces in biotechnology have been reviewed by Mendes.[185]

One of the most popular polymers used for preparing responsive surfaces is poly(N-isopropylacrylamide) (poly(NIPAM)). It changes hydrophilic to hydrophobic and vice versa in aqueous environment at the temperature close to physiological temperature (32 °C). The specific temperature is called lower critical solution temperature (LCST). The phenomenon can be explained by considering the breaking of hydrogen bonding between amide groups of poly(NIPAM) followed by replacing with intramolecular hydrogen bonding among themselves above LCST. If poly(NIPAM) is immobilized on surface, a change in the thickness of the polymer layer, water contact angle, stiffness is observed at around LCST, due to the change of conformation of the polymer brushes.

Yin *et al* reported novel highly dense temperature responsive polyNIPAM polymer brush (Fig. 61), synthesized by the combination of the self-assembly of a monolayer of dendritic photoinitiator and surface-initiated photo-polymerization (SIP). The surface polymer brush property was characterized by the coil-to-globule transition in low to high temperature. The surface polymer brush thickness could be controlled by changing UV-irradiation time.[186]

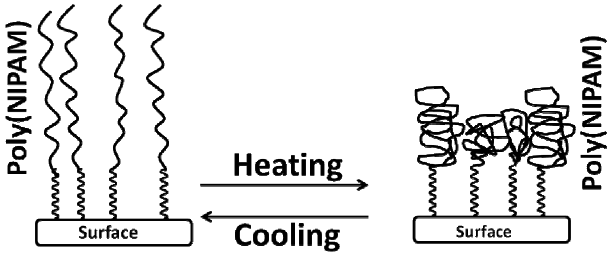


Fig 61 Thermoresponsive poly(NIPAM) functionalized surface

Yameen and others showed that the volume flow through poly(NIPAM) brushes increases above LCST.[187] Azzaroni et al studied the potentiality of PNIPAM brushes as thermoresponsive barrier. They have shown clearly that swollen PNIPAM brushes below LCST dramatically decrease ionic transport through nanopores with a reduced effective cross-section (Fig. 62).[188]

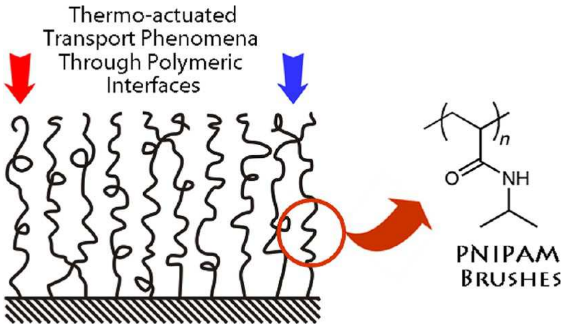


Fig 62 Responsive surface with tunable ionic transport. Reprinted with permission from (T. Alonso Garcia, C. A. Gervasi, M. J. Rodriguez Presa, J. Irigoyen Otamendi, S. E. Moya, O. Azzaroni, *J. Phys. Chem. C.,* 2012, **116**, 13944). Copyright (2012) American Chemical Society.

Zauscher et al reported the nanopatterned surface of temperature responsive polymer poly (NIPAM). The reversible, stimulus-responsive conformational height change of the patterned polymer brushes was demonstrated by repeated cycling in water and water/methanol mixtures. The surface is of potential application in bio-nanotechnology where polymeric actuators may manipulate the transport, separation, and detection of biomolecules.[189]

A 60 nm thick temperature responsive poly(NIPAM) film was formed by Wang and others on glass surface. The authors commented that these kind of glasses have potential applications as environmentally switchable materials, temperature sensitive optical valve under water engineering and other "smart windows".[190]

Aoyagi and others designed temperature-responsive glycopolymer brushes to facilitate selective adhesion and collection of hepatocytes. For example, the brush surfaces facilitate the adhesion of HepG2 cells at 37 ºC under nonserum condition, whereas no adhesion was observed for NIH-3T3 fibroblasts. However, when the temperature was decreased to 25 ºC, almost all the HepG2 cells detached from the block copolymer brush (Fig. 63).[191]

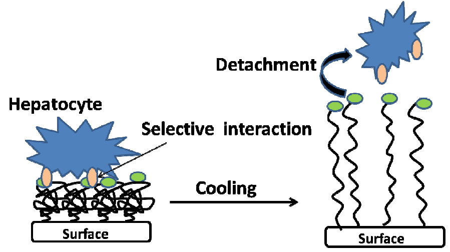


Fig 63 Design of responsive surface to facilitate selective adhesion and collection of hepatocytes

Yu et al showed that thermoresponsive poly(NIPAM) functionalized surfaces could be used as protein-repellent also.[192]

Terminally functionalized poly (N-isopropylacrylamide) brush grafted glass surfaces were used for temperature-controlled cell adhesion/detachment. By using the thermoresponsive nature of the surface, the specific adhesion temperatures of bovine carotid artery endothelial cells (BAECs) on the surface was successfully controlled. BAECs were initiated to adhere on the thermoresponsive surfaces at 31 ºC, while their adhesion was significantly suppressed at 25 ºC (Fig. 64).[193]

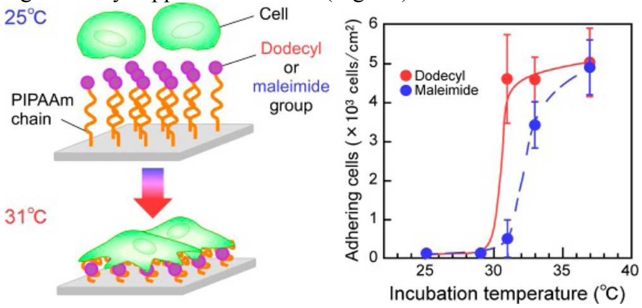


Fig 64 Poly(NIPAM) functionalized glass surface for temperature controlled cell adhesion/detachment. Reprinted with permission from (N. Matsuzaka, M. Nakayama, H. Takahashi, M. Yamato, A. Kikuchi, T. Okano, *Biomacromolecules,* 2013, **14**, 3164). Copyright (2013) American Chemical Society."

Genzer and others reported anchoring of responsive poly(acrylamide) (PAAm) with gradual variation of grafting density. They demonstrated that using the grafting density gradient geometry, the mushroom-to-brush transition can be accessed on a single sample.[194]

Choi *et al* demonstrated that the efficiency of thermally controlled cell adhesion on poly(NIPAM) brushes are determined by protein adsorption mechanism (Fig. 65) on surfaces. They showed that at an average molecular weight of 30 kDa, the robust protein adsorption to polymer brushes impairs rapid cell release below the lower critical solution temperature. Those findings demonstrated the impact of protein adsorption mechanisms, surface chemistry, and polymer properties on thermally controlled cell capture and release.[195]

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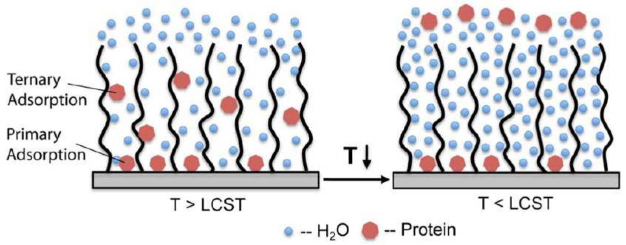

Fig 65 Temperature controlled cell adhesion from thermoresponsive NIPAM polymer brushes. Reprinted with permission from (S. Choi, B.-C. Choi, C. Xue, D. Leckband, *Biomacromolecules,* 2013, **14**, 92). Copyright (2013) American Chemical Society.

Chen et al showed that PNIPAM grafted silicon surface is useful as a medium to extract human genome DNA molecule from biological specimen. Further, temperature induced DNA capture and release from the surface was demonstrated by exploiting variable adhesion force on the surface. This is envisaged to be useful for the detection of breast cancer recurrence DNA.[196]

It has been shown recently that the Poly (NIPAM) is moderately cytotoxic[197] at 37 ºC. Random copolymers of 2-(2-methoxyethoxy) ethyl methacrylate (MEO_2MA)- oligo(ethylene glycol) methacrylate (OEGMA) are a new class of thermo responsive polymers which have adjustable LCST in water with co-monomer composition variation.[198] The poly(OEGMA-co-MEO_2MA)-modified gold surfaces can be switched from cell-attractive to cell repellent by the change of temperature from 37 to 25 °C. This behavior is also reversible and successive cycle of this temperature responsive property can be repeated.[199]

pH responsive surfaces can show reversible swelling and collapse of polymer brushes and important to develop actuators or to allow pH controlled transport / adsorption. Klok and others developed tunable pH responsive surfaces by immobilizing poly(methacrylic acid) followed by post functionalization with amine compounds.[200]

Zhao *et al* prepared gas-controlled switchable surface that was useful for reversible capture and release of proteins. In contrast to adding acid or base for pH change, using carbon dioxide or nitrogen as trigger helped cycle switching without the accumulation of salt.[201]

Solvent responsive brushes were prepared by immobilizing two different types of polymers on surfaces. Upon treatment with different solvents, the tethered triblock copolymer of styrene and methacrylate brushes exhibited reversible change in surface properties.[32] Ionov and others reported the development of mixed polymer brushes with the property of locking of switching. In this case, the wetting behaviour can be locked in hydrophobic state which can be further unlocked via treatment of proper "unlocking" solvent.[202]

A photoresponsive polymer functionalized surface was prepared by anchoring a photolabile group that is poised for cleavage upon UV light, thereby switching the surface wettability from hydrophobic to hydrophilic.[203]

Choi et al prepared poly pentafluorophenyl acrylate (PPFPA) brush by RAFT polymerization on silicon wafer that could be subsequently converted with amino-spirospyrans resulting in reversible light responsive polymer brush films.[133]

Miyahara et al studied in Poly(NIPAAm-Co-AECPBA) based SAM on gold surface to design glucose responsive polymer brush. The newly synthesized and reversible Poly(NIPAAm-Co-AECPBA) SAM electrode offered good response and enhancement compared to cross linked or gel coupled surface. This polymer on surface was capable of undergoing reversible glucose-dependent change in hydration at room temperature allowing design of Gate-modified Field Effect Transistor.[204] Zauscher and others demonstrated that poly(NIPAM)-co-poly(acrylic acid)-(3-aminophenyl-boronic acid) brushes can be used as microcantiliver based detection of glucose at physiologically relevant concentrations.[205]

Katz and others designed signal-responsive interface by grafting poly(4-vinyl pyridine) (P4VP), functionalized with Os-complex redox unit on indium tin oxide surface for bioelectronic applications. The material was used for reversible activation of bioelectrocatalytic process.[206]

Azzaroni and others reported the preparation of light responsive brush using photoremovable group 4,5-dimethoxy-2-nitrobenzyl (NVOC) (Fig. 66). The brush is neutral and hydrophobic due to the presence of aromatic chromophore. Upon irradiation, NVOC group is removed and polyanionic chain is generated. Further, the brush can be swelled or collapsed by the variation of pH.[207]

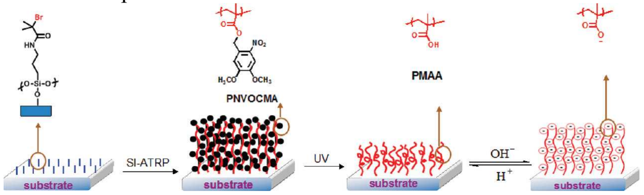

Fig 66 Light sensitive brush using photocleavable group. Reprinted with permission from (J. Cui, N. Thi-Huong, M. Ceolin, R. Berger, O. Azzaroni, A. del Campo, *Macromolecules,* 2012, **45**, 3213). Copyright (2012) American Chemical Society.

Fang *et al* reported stimulus-responsive fluorescence behavior from conjugated polymer (CP)-based surfaces. The reversible nature of florescence emission and quenching was observed by changing the solvent. In poor solvents the films undergo coil conformation causing aggregation-induced fluorescence quenching effect. In good solvents the side chains tend to be swollen and adopt extended or loose coil structure to regain fluorescence.[208]

A dual responsive surface can be prepared from a mixture of two or more monomers (block-co-polymer) with distinct properties. A dual responsive surface, triggerable by light and pH, was prepared by Campo and others by immobilizing photocleavable acrylate polymer. In this case, the presence of ionisable groups induce a photo-triggered swelling response.[209]

Dual responsive (solvent and temperature) polymer functionalized surface was prepared by immobilization of poly(NIPAM)-block-polystyrene on silicon surface. This diblock copolymer grafted surface could resist non-specific protein adsorption and facilitate cell adhesion at the appropriate temperature.[210]

Minko *et al* described the synthesis of adaptive and switchable surfaces/thin polymer films fabricated from two incompatible carboxyl-terminated polymers chemically grafted to Si substrates. The surface film offered switching properties like from hydrophilic to hydrophobic or from smooth to rough upon the external stimuli (solvent, temperature).[211]

Song et al developed dual temperature and light responsive surfaces exhibiting tunable wettability by immobilizing copolymer brush containing azobenzene moiety and dimethylaminoethyl methacrylate. Because of the presence of azobenzene groups in surface polymer brush, structural configuration changes from normal *trans* to more polar *cis* configuration upon UV irradiation causing the change in wettability property.[69]

A triple responsive poly(NIPAM)-co-acrylic acid functionalized surface was prepared by Lee and others (Fig. 67) that showed reversible electrochemical switching independently or simultaneously by temperature, ionic strength and pH.[212]

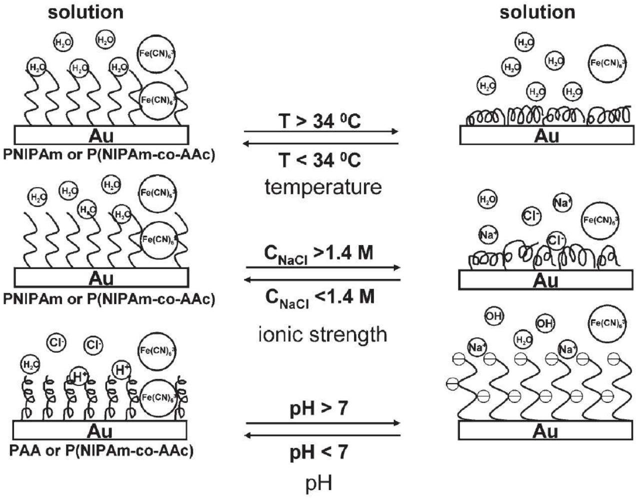

Fig 67 Ttriple responsive surface triggered by temperature, ionic strength, pH. Reproduced from Ref. 212 with permission from The Royal Society of Chemistry.

4.2 Molecular electronics

A few years back, Zotti and others reviewed the monolayers and multilayers of conjugated polymers as nanosized electronic components.[29] You *et al* reported the fabrication of Poly(3-methylthiophene) (P3MT) on ITO surface through covalent bond using (SI-KCTP). Those covalently bound layers offer superior stability in air, water and organic solvents. The surface-bound P3MT layers (Fig. 68) successfully served as the hole-transport layer for solution-processed bulk heterojunction polymer solar cells.[213]

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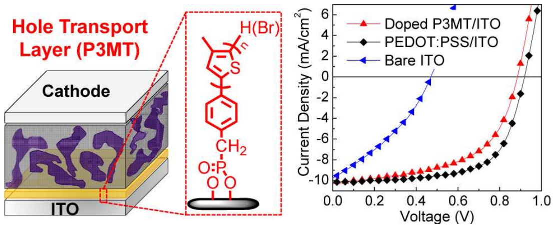

Fig 68 Polythiophene brush as hole transporting layer. Reprinted with permission from (L. Yang, S. K. Sontag, T. W. LaJoie, W. Li, N. E. Huddleston, J. Locklin, W. You, *ACS Appl. Mater. Interfaces,* 2012, **4**, 5069). Copyright (2012) American Chemical Society.

Advincula *et al* demonstrated the growth of highly conjugated polyvinylcarbazole (PVK) from ITO electrode surface (Fig. 69). The covalently linked PVK allowed forming device preparation without solubility problems. PVK surface polymer can act as a hole-transporting layer and the polyfluorene copolymer can be easily spin coated on top of the grafted PVK, resulting in the improvement of electro luminance behaviour .[214]

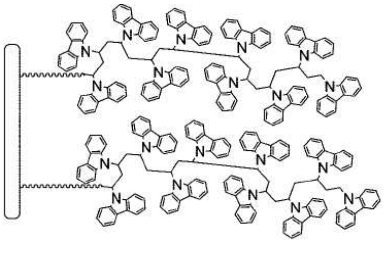

Fig 69 Polyvinylcarbazole brush on ITO surface to use as hole transporting layer. Reprinted with permission from (T. M. Fulghum, P. Taranekar, R. C. Advincula, *Macromolecules,* 2008, **41**, 5681). Copyright (2008) American Chemical Society.

Kilbey et al observed that regioregular poly (3-hexylthiophene) brushes immobilized on ITO surfaces can be used as anode buffer layer-an important component for organic photovoltaic cell fabrication. The authors studied current-voltage characterization and noted "the potential of these novel nanostructured buffer layers to replace the PEDOT:PSS buffer layer typically applied in traditional P3HT-PCBM solar cells.[3] Gopalan and others studied saturation hole mobility for P3HT brushes measured in an FET structure (Fig. 70), which was $5X10^{-5}$ $cm^2\ V\ s^{-1}$, which is comparable to hole mobilities in FETs with monolayer thick dip-coated P3HT.[45]

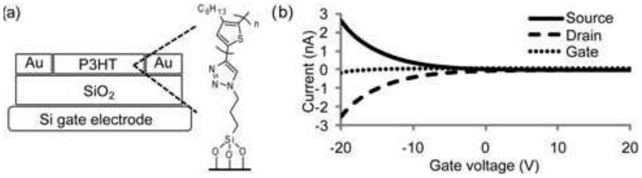

Fig 70 Poly(3-hexylthiophene) brush for FET device fabrication (a) and charge-transfer characteristic curves of P3HT brushes (b). Reproduced from Ref. 45 with permission from The Royal Society of Chemistry.

It was further shown that end-functionalized poly(3-butylthiophene) with a thiol group can be used to form self-assembled monolayer that can change the backbone orientation of spin-coated polymers from an edge-on to an end-on orientation. An appreciable amount of hole mobility for the substrate indicated in organic devices that require vertical charge transportation.[177]

4.2 Biotechnological applications

Polymer functionalized surfaces are useful for various biological applications such as designing protein resistant, nonfouling and antibiotic surface. In a recent review article, Chen and others discussed the exploring of new interfacial biological phenomenon by combining surface topography with polymer chemistry.[215] One of the most studied applications of polymer functionalized surfaces is designing protein resistant surfaces. It is particularly important for the fabrication of antibody microarrays with relaxed requirements for intermediate washing steps. Specifically, it was proven that lowering non-specific binding during the interrogation of protein microarrays can lead to significantly lowered limits of detections (LODs).[216]

Effective prevention of nonspecific protein adsorption from real-world complex media such as blood plasma is crucial for in vivo diagnostics. Jiang and others developed zwitterionic poly(carboxybetaine acrylamide)(polyCBAA) grafted surface that was used for sensitive and specific protein detection in undiluted blood plasma using a sensitive surface Plasmon resonance (SPR) sensor. Further, because of the significant reduction of nonspecific protein adsorption, it was possible to monitor the kinetics of antibody-antigen interactions in undiluted blood plasma.[217]

The antifouling surface properties were investigated in detail by observing the adsorption of human serum albumin (HSA) and lysozyme (Lys) onto PEG functionalized surface from phosphate buffer solutions. X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS), in combination with principal component analysis (PCA) were useful methods for the detail study of protein fouling. The results revealed no fouling of albumin onto PEG coatings (Fig. 71) whereas the smaller protein lysozyme adsorbed to a very low extent.[74]

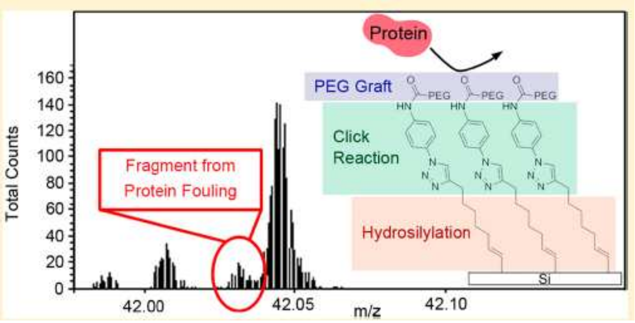

Fig 71 Polyethylene glycol functionalized surface as protein repellent. Reprinted with permission from (B. S. Favel, M. Jasieniak, L. Velleman, S. Ciampi, E. Luais, J. R. Peterson, H. J. Griesser, J. G. Shapter, J. J. Gooding, *Langmuir,* 2013, **29**, 8355). Copyright (2013) American Chemical Society.

Yan et al reported the formation of patterned surface by the covalent immobilization of various molecular weights of Poly (2-ethyl-2-oxazoline) (PEOX) and showed that the extent of non-specific protein adsorption is dependent on the molecular weight of immobilized polymer. Thus, the fluorescence imaging and ellipsometry studies showed that the largest amount of BSA adsorbed on lower molecular weight of PEOX (5000) and the smallest on highest molecular weight of PEOX (500000). The kinetic analysis of BSA adsorption by surface plasmon resonance imaging (SPRI) showed that PEOX 5000 exhibited the fastest association rate and the slowest dissociation rate whereas PEOX 500000 had the slowest association rate and the fastest dissociation rate.[218] Cai and others showed that Oligo(ethylene glycol) functionalized surfaces are important to design bioinert substrates.[219]

Jordan and others demonstrated that tailored poly(2-oxazoline) polymer brushes on surfaces are useful to control protein adsoreption and cell adhesion.[220]

Schouten and others synthesized densely packed polyacrylamide (PAAm) brush on silicon wafer and evaluated for fouling by two bacterial strains and a yeast strain. A strong reduction in microbial adhesion was seen on PAAm brush-coated surfaces for all strains. A high reduction (70-92%) in microbial adhesion to the surface-grafted PAAm brush was observed, as compared with untreated silicon surfaces.[221]

Other nonfouling moieties such as ethylene glycol, phosphobetaine, and sulfobetaine lacks the immobilization capability.[5] Surface immobilized poly (quaternary ammonium) brushes showed to have antibacterial properties.[222] Ramstedt et al studied simultaneously the antibacterial and cytotoxic effect of surfaces with sulfonate brushes containing silver salt. The authors found a specific concentration range where silver could be used to kill the bacteria without harmful effect on mammalian cells.[223]

Jiang *et al* further reported that zwitterinic polymers such as sulfobetaine methacrylate polymer, carboxybetaine methacrylate polymers, grafted to surface, exhibit high resistance to nonspecific protein adsorption from human serum and plasma.[224] Jiang and others further showed that protein adsorption from blood serum and plasma onto poly(sulfobetaine)-grafted surface is dependent on the film thickness.[225]

Emmenegger and others studied the interaction of blood plasma with various antifouling surfaces and observed that plasma deposition can be completely prevented by zwitterionic carboxybetaine poly(CBMA) brushes. However, polymer with other zwitterionic groups, poly(SBMA), and poly(PCMA) did not prevent plasma deposition, but prevented the adsorption of main plasma proteins HAS, IgG, Fbg, and lysozyme from single-protein solutions.[226]

Liu *et al* demonstrated that polyacrylamide functionalized surfaces are useful as ultralow fouling to resist protein adsorption, cell adhesion, and bacterial attachment. With the optimal film thickness, the adsorption amount of all three single proteins on polyacrylamide-grafted surface was about 3 pg/mm^2 (Fig. 72).[227]

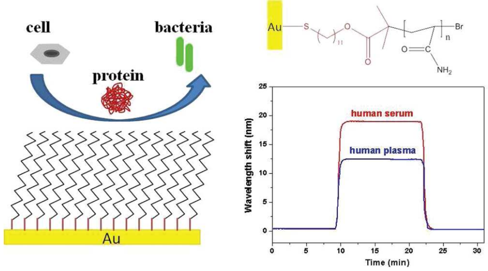

Fig 72 Study of interaction of blood plasma on zwitterionic polymer brushes. Reprinted with permission from (Q. Liu, A. Singh, R. Lalani, L. Liu, *Biomacromolecules,* 2012, **13**, 1086). Copyright (2012) American Chemical Society.

Antibacterial and antifouling polymer brushes on surface was prepared using 2-(methoxyethoxy)ethyl methacrylate and hydroxyl-terminated oligo(ethylene glycol) methacrylate which was subsequently functionalized by a natural antibacterial peptide, magainin I, via an oriented chemical grafting on hydroxyl group. The modified surface was antibacterial for gram positive bacteria such as *L. ivanovii* and *B. cereus.*[228] Ramstedt and others observed that poly(3-sulfonylmethacrylate) can also have potential antibacterial applications.[229]

Wooley *et al* reported hyperbranched fluoropolymer (HBFP) and different weight percentages (14, 29, 45, and 55%) of poly(ethylene glycol) (PEG) functionalized glass slides provided enhanced ability to inhibit protein adsorption and marine organism settlement. The surface antifouling and fouling performance of hyper branched (HBFP-PEG) composites coatings were evaluated by adsorption of green fouling alga *Ulva* zoospore settlement.[230]

Inner wall of silicon-glass microreactors were functionalized with poly(methacrylic acid) to immobilize the lipase from *Candida Rugosa*. All enzyme molecules in the brush layer exhibited similar activity as in solution. However, depending on the requirements, the biocatalytic activity can be tuned. The surface may evolve as a new platform for studying the activity of enzymes and for performing biocatalysis.[231]

Peptide functionalized poly(2-hydroxyethyl methacrylate-*co*-2-(methacryloyloxy)ethyl phosphate) brushes can be used as osteoconductive surface to modify bone implant materials.[232]

ITO electrode functionalized with poly(4-vinylpyridine) and Os (4,4'-dimethoxy-2,2'-bipyridine) has been utilized by Katz and others to prepare biochemically controlled bioelectrocatalytic interface. The design should be useful to allow biochemical processing of complex information.[233]

Functionalized surfaces with poly(maleic anhydride)-based comb-copolymer can be used to facilitate stretching, aligning, and imaging of dsDNA chains. Since the stretching can be obtained for relatively large droplet size (millimetres range), it does not require small volume spotting machine. This may be useful in the understanding of life's fundamental building blocks.[234]

5 Conclusion

From the above discussion it is clear that utilization of self assembled monolayer formation technique is important for the controlled decoration of surfaces with macromolecules where the electron transfer studies through mixed SAMs of thiophenol and thioctic acid and the electrochemical rectification behaviors at the electrode (metal) surface modified with poly (acrylic acid) and decanethiol have already been demonstrated in the recent past.[235, 236]. Various techniques such as “graft from”, “graft to” or “graft through” methods have been developed, although each of the method has its own advantages and disadvantages. Judicious choice of methodology is important to retain the structural integrity of the substrates, obtain desired grafting density and optimize the layer thickness. The polymer functionalized surfaces can be used as component in smart material, sensor, solar cell, molecular electronic and biomedical systems. Antibacterial and antifouling surface is only one prominent, commercially viable example of such an application. Much of the current research is focused on the development of commercially viable devices utilizing those materials.

Acknowledgement

Financial support from CSIR network project NWP54 is gratefully acknowledged. The authors acknowledge partial funding from CSIR-ZERIS (WP21) and DST (SR/FT/CS-104/2009).

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†*Electronic Supplementary Information (ESI) available: [table for different immobilization methods and applications with references]. See DOI: 10.1039/b000000x*

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