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"Click" polymerization on a self-assembled monolayer: a convenient approach to functionalize various surfaces with polytriazoles†

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"Click" polymerization reaction has been performed on the functional self-assembled monolayer to incorporate polytriazoles. Ellipsometric and atomic force microscopic studies indicated a high degree of polymerization and fairly dense surface coverage. Band gap calculation revealed the possibility of its use as a semiconducting material.

In recent years, Cu(I) catalyzed "click" reaction has attracted a great deal of attention because of its application in polymer synthesis,[1,2] surface functionalization,[3,4] nanotechnology[5,6] *etc.* The reaction requires mild conditions, is compatible with a large number of sensitive functional groups and produces an important triazole moiety.[7] Recently Rowan and others reviewed the use of triazoles and polytriazoles as a building block for the construction of functional materials.[8] Polytriazole compounds are particularly attractive because of their unique structural features[9–12] that can be useful in molecular electronics and solar cell applications. For example, Tsuji, Fujihara and others used polytriazole compounds for the generation of insulated molecular wires (IMWs).[13] Mirkin and others demonstrated that triazole-based molecular wires can be formed *in situ* for the construction of molecular transport junctions.[14] Recently Lee and others reported the use of phenothiazine-based "click" polymers for dye-sensitized solar cell applications.[15] Immobilization of those types of polymers on different surfaces is an integral part of research[16] for the development of molecular electronic devices[17] and solar cell materials in the form of a chip.

The polymeric compounds can be immobilized on the surface by simple physical adsorption methods like spin coating,[9] vacuum deposition, Langmuir–Blodget film formation *etc.* However, those techniques tend to afford arrays of immobilized macromolecules which are less defined, less precise and more fragile. For better reproducibility, durability and precision, polymeric compounds can be attached to surfaces through an organized monomolecular layer with defined orientation,[18] such as a self-assembled monolayer (SAM).[19,20] In this case, suitably functionalized, straight chain aliphatic molecules can be spontaneously assembled[21] on metal or glass or indium tin oxide (ITO) surfaces to form stable covalent bonds between its terminal functionality and the activated metal, metal oxide or silicate. The exposed end of a SAM can then be utilized to immobilize polymeric compounds *via* strong non-covalent interaction or covalent bond formation. For example, Rotello and others utilized multipoint non-covalent interactions on an end functionalized SAM to immobilize polystyrene.[22] Gopalan and others utilized "click" reaction on an azide-functionalized surface to immobilize polythiophene compounds.[23] In this case only a single triazole unit was incorporated. Recently Mirkin[14] and Nesterov[24] showed separately that stepwise "click" reaction can be performed to immobilize multiple triazole units on a functionalized monolayer. The process is labour intensive and time consuming if one wants to generate a moderate number of triazole units unless iterative immersing–washing steps are automated.[24]

In this paper we report a clear cut demonstration that "click" polymerization can be conveniently performed on an azide-functionalized SAM using a "graft through" approach[25,26] (an approach of polymerization where solution polymerization is performed in the presence of a surface functionalized with groups that react in the polymerization) for polytriazole incorporation. To the best of our knowledge, this is the first example of "click" polymerization on a functionalized surface in a one step reaction set up. The development is also significant because polytriazoles have been anchored to the surface through a SAM where strong bonding between the surface and molecules exists.[27]

Scheme 1 depicts the polymerization reaction on an azide functionalized silicon surface **1** using two monomers 2,5-diethynylthiophene **(1)** and 4,4′-oxybis(azidobenzene) (**2**).

We studied and standardized the polymerization reaction on the silicon surface first because of the convenience of characterization using IR spectroscopic techniques. However we extended the approach to other surfaces like quartz and ITO under similar reaction conditions.

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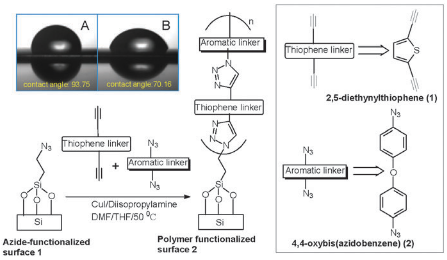

Scheme 1 "Click" polymerization reaction on a functionalized silicon surface using a "graft through" approach. Inset: picture of water droplets on surfaces to measure contact angle: left side-azide functionalized surface, right side: polymer functionalized surface.

First, the azide functionalized silicon surface was prepared according to a literature procedure.[23] In brief, a silicon wafer cleaned with piranha solution was treated with 3-azidopropyltrimethoxysilane in toluene at 90 °C for 2 hours to form the azide-terminated SAM on silicon. The unreacted physisorbed azide molecules were removed from the surface by repeated sonication in fresh toluene. The contact angle measurement revealed the hydrophobic nature of the surface (contact angle = 93.75°: Scheme 1, the inset picture, left). The presence of the azide group was confirmed by the appearance of a sharp peak in IR spectra at 2100 cm^{-1} (Fig. 1A, red curve).

Polymerization was then performed on the azide functionalized silicon surface using 2,5-diethynylthiophene and 4,4′-oxybis-(azidobenzene) in the presence of copper(I) as catalyst. Our initial attempt to use copper sulphate and sodium ascorbate as the catalyst system did not yield the desired result. However, clear proof of polymerization on the surface was obtained (infrared spectroscopy, ellipsometry, X-ray photoelectron spectroscopy, atomic force microscopy – *vide infra*) when the reaction was performed in the presence of Cu(I)I/diisopropylamine as the catalyst system in a DMF–THF solvent mixture at 50 °C for 72 h. Copious precipitation along with sharp increase in viscosity is indicative of competitive polymerization in solution. However, this type of competitive polymerization is common for the "graft through" approach of immobilization.[25] Hence, we washed the surface thoroughly and repetitively with fresh toluene, acetone, water, dimethyl sulfoxide and ethanol in a sonicator to remove the physisorbed polymer or unreacted materials. The competitive solution polymerization may be minimized by changing the concentration of the monomers used. Moreover, a control experiment was performed at room temperature using the same surface, azides and alkynes in the absence of catalyst that did not yield the polymer functionalized surface as confirmed by IR spectroscopic and other studies.

Interestingly, after polymerization, the contact angle of the polymer-functionalized surface decreased to 70.18° (Scheme 1 inset picture: right) indicating diminished hydrophobicity. This may be due to the presence of a polar functional group like thiophene. Fig. 1A and B show the IR spectra of the silicon surface after the azide functionalization (black curve) and polymerization (red curve), respectively. In IR spectra, sharp decrease in peak intensity at 2100 cm^{-1} was observed indicating the maximum consumption of azide groups during the polymerization reaction. Appearance of strong peaks at 2800–2900 cm^{-1} due to the C–H stretching frequency further confirms the successful implementation of "click" polymerization on the surface. Ellipsometric thickness measurements indicated the thickness of the polymer functionalized layer as 25–26 nm indicating moderate to high degree of polymerization. The thickness is higher than that of the reported polythiophenes incorporated by the "graft to" approach.[23] However, a similar high value of thickness was observed by Grande *et al.* in the "graft through" approach of RAFT polymerization.[26] A much lower value of film thickness of 11.9 nm was observed by ellipsometry when the polymerization reaction was performed for 24 hours. Fig. 1B shows the UV-vis spectra of the quartz surface after azide-functionalization (black curve) and polymerization (red curve), respectively. For the polymerized surface, a new peak appeared at 321 nm indicating the presence of an aromatic ring or a conjugated π-electron system. The band gap calculated from the absorption edge was found to be 2.54 eV, indicating that the material may fall in the category of semiconductors.

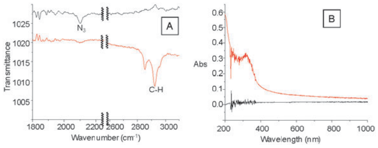

Fig. 1 Spectroscopic studies of azide-functionalized (black) and polymer functionalized surfaces (red curve). (A) IR spectra on functionalized silicon surfaces; (B) UV-vis spectra on functionalized quartz surfaces.

Both surfaces were also characterized by using X-ray photoelectron spectroscopy (Fig. 2A: black curve – azide functionalized surface; red curve – polymer functionalized surface). Appearance of peaks at 402.0 and 406.0 eV corresponds to N(1s) of differently charged nitrogen species of the azide group (Fig. 2A inset: black curve) on the azide functionalized silicon surface. The disappearance of the peak at 406.0 eV and broadening of the peak at 402 eV after "click" reaction indicated that most of the azide functionality has been consumed to form the "click" product[23,28,29] (Fig. 2A inset: red curve for the N(1s) region). The attenuation of peaks for Si(2s), Si(2p) and O(1s) and appearance of new peaks for S(2s) and S(2p) further confirmed the success of "click" polymerization reaction (Fig. 2A red curve). No peak for copper was observed in XPS after polymerization, indicating the catalytic nature of the metal. Moreover, when a control experiment was performed on a chloro terminated SAM (instead of azide terminated) on silicon using the same monomers and catalyst systems, no peak for S(2s) or 2p was observed in the XPS for the silicon surface (Fig. S2, ESI†) after washing, indicating that no polymerization took place on the surface in the absence of azides.

Fig. 2B and C show the atomic force microscope (AFM) pictures of the azide functionalized silicon surface and the surface

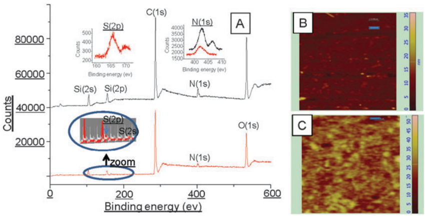

Fig. 2 (A) XPS survey scan of azide functionalized (black curve) and polymer functionalized silicon surfaces. Insets: multiplex-scan spectra for the S(2p) and N(1s) region. (B) and (C) AFM pictures of azide and polymer functionalized surface respectively. Scale bar = 500 nm.

after polymerization reaction, respectively. The cross section profiles are provided in Fig. S1, ESI.† For the azide functionalized surface (Fig. 2B), several small islands throughout the surface were observed. Those types of islands were observed by other authors[23] and attributed to the formation of siloxane aggregates in solution.[30] Moreover, the azide-containing trialkoxysilane used to modify the surface is well known to produce polymerized regions of the siloxane upon reaction with a surface. Hence, the resulting thickness is greater than that of a monolayer and the resulting surface is not as uniform as the underlying support. The polymerization resulted in a fairly dense coverage of the surface (Fig. 2C) with roughness (rms) value of 5.2 nm, determined using Nova software from an area of 9 μm × 9 μm and a sample amount of 53 592.

We extended the polymerization method on other surfaces such as indium tin oxide (ITO) which is one of the most useful materials for device fabrication. Self-assembled monolayers of azides on ITO were formed using a procedure in the literature[31] and "click" polymerization was performed using 2,5-diethynylthiophene and 4,4′-oxybis(azidobenzene) using copper(I) as catalyst as described for functionalized silicon surfaces (*vide supra*). XPS spectra indicated the appearance of signals for S(2p) (Fig. S3A, ESI†) after polymerization and the SEM micrograph indicated fairly dense surface coverage after polymerization (Fig. S3B, ESI†). Cyclic voltammetry (CV) of the polymer functionalized ITO surface was performed using Ag/AgCl as the electrode to understand its usability as semiconducting material (Fig. S4, ESI†). From CV, the HOMO and LUMO of the surface growth polymer were determined by using the equations:[32] HOMO $= -(\varphi_{\mathrm{ox}} + 4.71)$ and LUMO $= -(\varphi_{\mathrm{red}} + 4.71)$. In the case of the oxidation peak the process was observed at 1.42 V corresponding to the HOMO value of −6.13 eV. In the case of reduction the peak was observed at −1.18 V corresponding to the LUMO level of −3.52 eV. Thus the band gap (HOMO–LUMO gap) was calculated to be 2.52 eV, which indicates the possibility of its use as semiconducting material. UV-vis spectra indicated a similar band gap (*vide supra*). This is also in agreement with the observation of others that triazole polymers can be used as semiconducting material.[24]

In summary, we demonstrated that a "graft through" approach can be utilized to perform "click" polymerization on a functionalized SAM on different surfaces. The process is very convenient, needs only a one-step reaction set up and affords the anchoring of polytriazoles on the surface *via* a SAM by strong bonding. It is mild, compatible with a large number of sensitive functional groups and affords polymers containing conjugated systems like triazoles and thiophenes with high density on the surface. Such chemistry should permit rapid immobilization of various oligothiophenes and other conjugated systems along with multiple triazole units simultaneously. Adaptation of this strategy to decorate surfaces by the attachment of different kinds of conjugated, non-conjugated and semi-conjugated polymeric systems and suitable biological systems for device fabrication is currently being pursued in our laboratory.

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