Nanofabrication of Block Copolymers of PDMS/Polyamide having Trichlorogermyl Pendant Using LbL Technique

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Summary: Block copolymers $[AB]_x$ type of aminopropyl-terminated poly(dimethylsiloxane) (NH_2-PDMS) and polyamides trichlorogermyl pendant group were prepared by a solution phase one pot polycondensation method. The prepared block copolymers were assembled with polyethylene-*alt*-(maleic) anhydride (PEMA) as multilayered thin film assembly through covalently linked Layer by Layer (LbL) technique using dipping method. The prepared thin films had thickness in the range of 15 to 20 nm as measured on an ellipsometer. In the systems where quartz was used as substrate, film growth after each deposition was monitored through UV-Vis spectrophotometer, which substantiated the multilayer film build-up. Atomic Force Microscopic (AFM) images showed homogeneous and robust film, which were strong enough to endure the force of 400 nN. As the block copolymers are thermally stable and have the capacity to absorb water, so their prepared robust ultra-thin films can show potential of thermally resistant nano thin films, protective hydrophilic coatings in addition to separation membranes.

Key words: Block copolymers, Nanofabrication, Layer by Layer technique, Thin films, Poly amide, PDMS.

Introduction

Rapidly growing needs of society stresses the importance of designing of new protective polymeric thin films and coatings for a sustainable development, because the surface of any object determines how it would interact with its surroundings. The protective thin films are deposited on solid substrates by various techniques such as thermal evaporation, chemical vapor deposition, sputtering, electro deposition, molecular beam epitaxy, adsorption from solution, Langmuir Blodgett (LB) techniques and self-assembly etc. However, Layer by Layer (LbL) technique introduced by Prof. Gero Decher and his coworkers in the early 90's has attracted enormous attention of scientists in fabrication of nanoscale hybrid films for advanced coatings and smart surfaces, for multiple application of materials [1, 2]. Thin films deposited by this technique readily employ electrostatic interactions and covalent bonds [2] while donor/acceptor interaction, hydrogen bonding, adsorption/drying, stereo-complex formation and specific recognition interaction can also participate alone or in synergistic combinations [3]. LbL has proved to be advantageous as it allows facile incorporation of functional materials, processing under ambient conditions [4], control over layer sequence and thickness control [1], besides offering a variety of choice for the shape and surface of substrate [5]. Recently, biological, metallic or oxidic nanoparticles, nano platelets, DNA, therapeutic compounds, and carbon nano tubes have been successfully incorporated with other components into LbL assembled films [6].

Usually layer pair thickness [3] varies from 1-100 nm and has found suitable for a variety of applications including membranes for direct methanol fuel cells [7], polymer catalytic electrodes [8], field effect transistors [9], anti-reflection coatings [10], and humidity sensors [11]. Although these are in nanometer scale, yet they influence the surface properties of underlying material thus controlling its direct interaction with surrounding environment [12].

PDMS containing block copolymer membranes have found applications as biomaterials, e.g. soft contact lenses and artificial corneas and lungs [13, 14]. In the present study, the aromatic polyamides being the oldest high temperature materials upon polymerization with soft PDMS have proved to be promising due to the integration of elastomeric properties in macromolecular materials [15].

Several membranes have been prepared by adopting the LbL technique for block copolymers that has proved to be an environment friendly approach in industries such as in gas separation, water purification and waste water treatment systems [16]. Thin films, coatings and membranes fabricated *via* emerging and attractive LbL technique has attained the special place in today's research not only due to its inherent beauty but with diverse applications in nanotechnology, drug delivery,

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sensors, membranes, paints, antifogging and detergent industry [17]. Currently fabrication of water resistant coatings and antifouling paints has attained attention due to their potential to protect objects against harsh environmental conditions [18]. LbL technique has proved to be a versatile nanofabrication approach for developing protective coatings [19], filtration membranes, functional coatings, tissue scaffolds, solar cells, and batteries [20].

In our previous study block copolymers having general formula $[(\text{-CO-R}'\text{-CO-HN-Ar-NH-CO-R}'\text{-CO})_x\text{NH(CH}_2)_3\text{-(Me}_2\text{SiO)y(CH}_2)_3\text{NH}_2]_n$, [n=18.00 to 1175.0] where $\text{R}'=\text{CH}_2\text{CH(CH}_2\text{GeCl}_3)$;$\text{CH}_2\text{CHGeCl}_3\text{CH}_2$;and $\text{Ar}=\text{-C}_6\text{H}_4$;$\text{-(o.CH}_3\text{C}_6\text{H}_4)_2$;$\text{-o.CH}_3\text{OC}_6\text{H}_4)_2$; -$(\text{o.CH}_3\text{C}_6\text{H}_4)$ were synthesized by a polycondensation reaction of polyamide having a pendant trichlorogermyl group and terminal acid chloride $\text{Cl(-CO-R}'\text{-CO–NHAr-NH-CO-R}'\text{-CO-)}_x\text{Cl}$ with aminopropyl-terminated polydimethylsiloxane $\text{H}_2\text{N(CH}_2)_3(\text{Me}_2\text{SiO})_y\text{-(CH}_2)_3\text{NH}_2$] [21]. Due to the existence of polar amide bonds and amide blocks containing GeCl_3, block copolymers absorb 5-9% moisture when dipped in water for 148 hours at room temperature. Glass transition temperature (T_g) of these block copolymers is in the range of 337.1 ºC to 393.3ºC hence their ability to tolerate high temperature stress. Due to the promising properties of these thermally stable block copolymers, it is envisioned that their fabrication into LbL multilayer thin films can have potential applications in industry, however, the commercially available PDMS has already been nanofabricated in LbL assemblies by our group [22].

Experimental

Block copolymers synthesized by a method reported by Gill *et al.* [21, 23]. Polyethyleneimine water free (PEI, M_W~25000), aminopropyl terminated poly(dimethylsiloxane) (PDMS M_W ~ 2500), aminopropyl terminated poly (dimethylsiloxane) (PDMS M_W~27000), Poly(ethylene-*alt*-maleic anhydride) (PEMA average M_W ~ 100,000-500,000) were purchased from Aldrich. HCl (37%), H_2SO_4 (95-97%), toluene (99.7%), tetrahydrofuran (THF) (99.7%) and methanol (99.9%) were obtained from Riedel de Haén and Sigma Aldrich, respectively. Silicon wafers were purchased from Poly-Labo, Strasbourg, France. Quartz microscope slides were obtained from UQG (optics) Ltd. Milton, Cambridge, England. All chemicals were used as purchased unless otherwise specified.

Block CoPolymers Synthesis

Synthesized Block copolymers [AB]x type, having PDMS and polyamides with trichlorogermyl pendant group were nanofabricated into multilayer, in order to achieve their unique properties down to nanoscale [23]. The physical and thermal properties of block copolymers employed for nanofabrication in this study are given in Table-1. The decomposition temperatures of block copolymers were determined through thermo gravimetric analysis (TGA).

Table-1: Physical and Thermal properties of Block copolymers

Polymer Code	**General Formula**	**Physical Appearance**	**Decomposition Temperature**
PA 1	***p*(*o*-TD-Cl_3GeFA/PDMS)**	**Dark brown gel**	**500 ˚C**
PA 2	***p*(DMPDA-Cl_3Ge FA/PDMS)**	**Brown gel**	**459 ˚C**
PA 3	***p*(APE-Cl_3Ge FA/PDMS)**	**Brown honey-like**	**432 ˚C**
PA 4	***p*(PDA-Cl_3Ge-MA/PDMS)**	**Beige gel**	**517 ˚C**
PA 5	***p*(o-DA -Cl_3Ge-MA/PDMS)**	**Dark brown gel**	**518 ˚C**
PA 6	***p*(PDA-Cl_3Ge-CA/PDMS)**	**Brown gel**	**501 ˚C**

LbL Nanofabrication of the Synthesized Block Copolymers

Dip coating method was employed for nanofabrication being a reliable method for fabricating uniform thin films; it is also preferable method due to the use of organic solvents [24]. Solution of block copolymers and PEMA were made in toluene and THF, respectively. Thickness of the cleaned silicon wafer substrate was measured using an ellipsometer. The substrate was dipped in PEI solution for 15 minutes, followed by rinsing in pure water and drying in pure nitrogen (N_2) gas. Thickness of the precursor PEI layer was measured with the help of an ellipsometer prior to the subsequent LbL deposition of polymers following the optimized time and concentrations reported earlier [23]. The substrate was dipped in PEMA solution for 30 minutes, followed by rinsing in three separate wash of THF and drying in N_2 gas. Subsequently, the substrate was then dipped in block copolymers solution for 50 minutes, rinsed using three separate wash of toluene. Whereas, the schematic depiction of thin film deposition *via* LbL technique is given in Fig. 1. After drying the film under a stream of N_2 gas, ellipsometric measurements were done to confirm the growth and increase in thickness of the layer pair. A typical prepared sample had 9-11 number of deposited polymer layer pairs, thus the film architecture was PEI (PEMA/block copolymer)$_n$. Silicon and quartz were used as substrates for this architecture. The films prepared onto quartz substrate were monitored with a UV-Vis spectrophotometer.

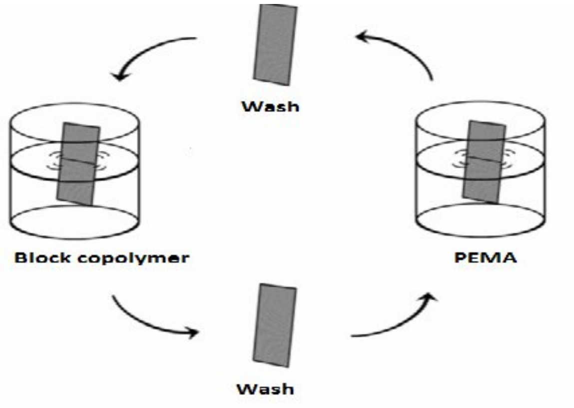


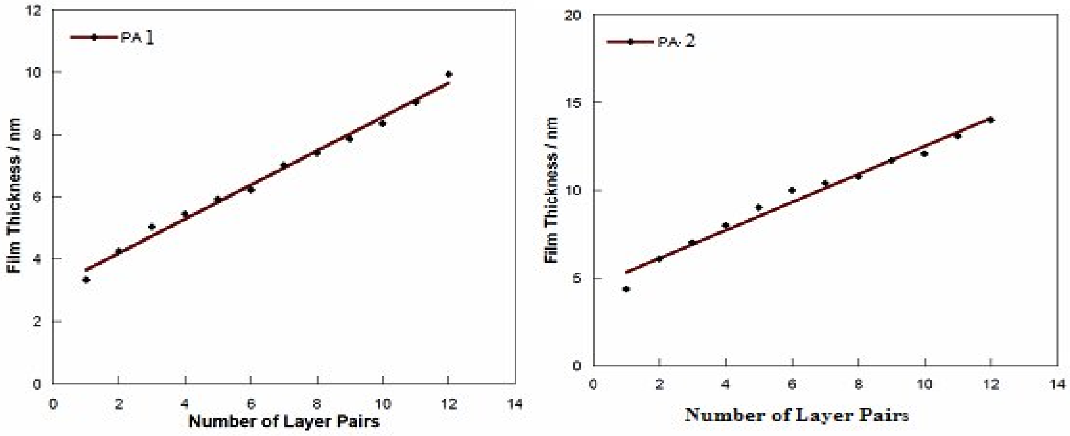
Fig. 1: General sequence of film deposition *via* Layer by Layer (LbL) technique.

Results and Discussion

The series of block copolymers prepared by the incorporation of rigid structural segments adjacent to the flexible Siloxanes units combines the advantageous properties of the parent polymers and develops the new properties like an increase in glass transition temperature and increase in the thermal stability etc. [15]. The glass transition temperature (T_g) of these block copolymers [25] are high and falls in the range of 250°C to 290°C indicating chain stiffness due to amide block [26]. Therefore these materials have potential for fabrication of mechanically strong and robust thin films with potential use for the environment and medical field. PDMS does not swell in water, but owing to the presence of polar amide linkage and $GeCl_3$ as pendant group in the amide block, the copolymers absorb moisture by weight, which make them hydrophilic [27].

Multilayer thin films of block copolymers were prepared on silicon and quartz substrate. The film thickness of each layer pair was measured on an ellipsometer. These block copolymers reported in our previous studies [21] were fabricated with PEMA to build layers having architecture PEI(PEMA/block copolymer)$_n$ where n being the number of layer pair. The pre-cleaned and activated substrates were immersed in aqueous solution of Polyethyleneimine (PEI) to provide the excess of amine groups to surface.

It was observed that thickness of film increases with the incremental increase in the layer pair, as assessed on an ellipsometer. It is seen from the Figs 2a and 2b, showing the LbL buildup of block copolymers PA 1 and PA 2, there is a regular increase in thickness of the deposited layer as a function of number of layer pairs. However, the thickness per layer pair was much less as compared to those of lower molecular weight PDMS as reported by Gill *et al.*, 2010 in which the average increase in thickness was ca. 1.5 nm. The linear increase in thickness is attributed to the covalent linkage between the end functionalized block copolymer with PEMA [22]. However, in the (PEMA/ block copolymer)$_n$ architecture the growth per layer pair was less due to high molecular weight of block copolymers having the pendant trichlorogermyl moiety attached with the bulky polyamide segment.

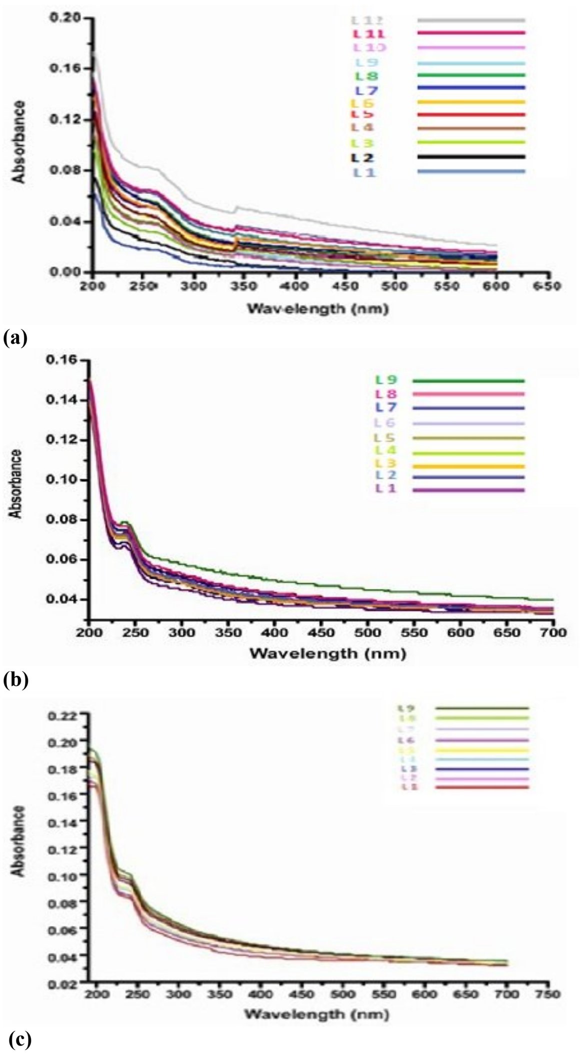


(a) (b)

Fig. 2: Ellipsometric measurement of LbL growth for block copolymer PA1 a) and PA2 (b).

Multilayer Build up Monitored via UV-Vis Spectroscopy

The amide segment of the block copolymers have UV active chromophores within the main chain, which made it possible to monitor the film buildup through UV-Vis spectrophotometer in the systems where quartz slides were used as substrates. The UV spectra were recorded after depositing the each layer pair. Due to the presence of UV active chromophores in the block copolymer PA1-PA6, the film growth was monitored by UV-Vis spectrophotometer. Absorption due to aromatic moiety of polyamide segment was observed at 248-258 nm as shown in the Fig. 3a, 3b and 3c. The increase in absorbance with the increase of the number of layer pairs on the quartz substrate suggested an increase in polymer concentration onto the substrate.



(a)

(b)

(c)

Fig.3: UV spectra of LbL of (a). PEI (PEMA/ PA4)$_{12}$, (b). PEI(PEMA/PA5)$_9$, (c). PEI(PEMA/ PA6)$_9$.

Atomic Force Microscopy (AFM)

AFM images were taken in contact mode with a Multimode Nanoscope IIIA Scanning Probe Microscope from Veeco (Santa Barbara, CA, USA). Deflection and height mode images were scanned simultaneously at a scan rate (between 2 and 4 Hz) with a resolution of 512 x 512 pixels. AFM studies (Fig. 4) of some selected samples were performed to show the surface topology and roughness. Several scans (scan rate 1.001 Hz) were performed over a given surface area. The AFM images were then further studied with the help of WSxM software107 to obtain the root mean square (RMS) roughness. The scan area is 5 x 5 micron in all the AFM images.

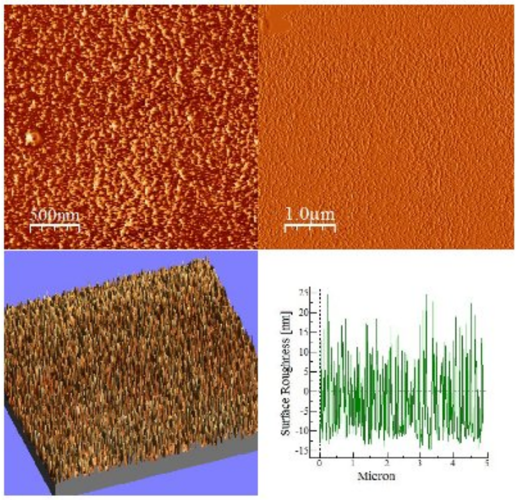


Fig. 4: AFM images of PEI(PEMA/PA3)$_6$ showing topology [the upper left is a 2-D image, upper right is derivative 2-D image, lower left is 3-D image and lower right is the surface profile of the given sample].

The topology shows homogeneous multilayer film formation. The RMS surface roughness is 9.2796 nm. A cantilever force of 400nN was used to study the inner morphology of the multilayers but due to the robustness of films, the polymer bulges from the sides as shown by the profile of the AFM image (Fig. 5).This resilient behavior is due to inherent flexibility of PDMS component of film. Similar trend was shown for thin films prepared by other block copolymers.

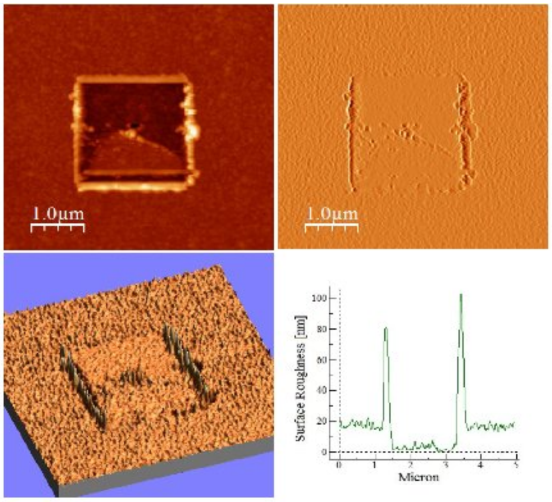


Fig. 5: AFM images of PEI(PEMA/PA 3)$_6$ showing topology of a sample PA 3 with cantilever force of 400nN [the upper left is a 2-D image, upper right is derivative 2-D image, lower left is 3-D image and lower right is the surface profile of the given sample].

Fig. 6 shows the AFM images of the films prepared using block copolymer PA-4. The concentrations of the polymer used were 10mg/mL with standard dipping times for both the polymers. A gel like surface morphology was observed.

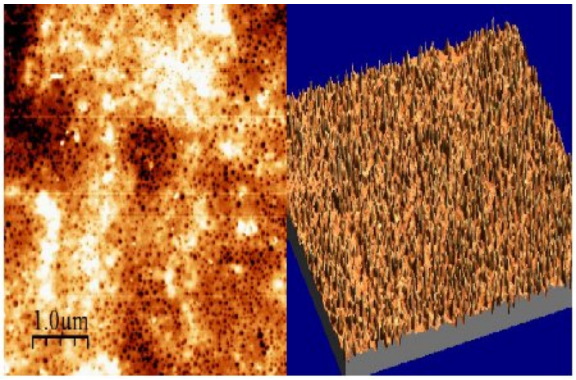


Fig. 6: AFM images of PEI(PEMA/PA4)$_6$ showing topology [the left image is a 2-D and right is the 3-D image].

Conclusion

As the decomposition temperature and the T_g of the block copolymers used for the LbL were 500 ˚C and 337.1 ˚C to 393.3˚C respectively, therefore, their successful fabrication into ultrathin film ensures the thermal resistance of thin films. Presence of hydrogen bonds gives extra stability, and polar sites enable them to absorb 5-9% moisture when dipped in water at room temperature. Prepared thin films shows toughness and linear growth in multilayer buildup with homogeneity as visible through the AFM images, ellipsometer and UV-Vis spectrophotometer results. Due to aromaticity in the backbone of the amide segment and bulky pendant group the growth per layer pair was less. Nevertheless the end functionalization of the two polymers guaranteed the film growth through alternate deposition of the polymer with covalent linkage. Due to these observed properties it is predicted that thin films have potential applications as thermally stable and separation membranes.

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