

Facile Approach to Grafting of Poly(2-oxazoline) Brushes on Macroscopic Surfaces and Applications Thereof

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S Supporting Information

ABSTRACT: This study reports on a facile and versatile approach for modification of macroscopic surface via grafting of multifunctional poly(2-oxazoline) molecules in brush-like conformation. For this purpose, carboxyl-terminated poly(2-isopropyl-2-oxazoline) molecules have been synthesized by ring-opening cationic polymerization and subsequently grafted on underlined substrates by exploiting the "grafting to" approach. A systematic variation in thickness of the grafted poly(2-isopropyl-2-oxazoline) brushes has been demonstrated. Polymer-modified surfaces have been characterized by means of a number of analytical tools including ellipsometry, X-ray photoelectron spectroscopy, ultraviolet spectroscopy, attenuated total reflection infrared spectroscopy and atomic force microscopy. Interestingly, poly(2-isopropyl-2-oxazoline) molecules have been found to retain their physical properties even after grafting on macroscopic surfaces. Finally, fabricated polymer brushes have been used as platform for stabilization of inorganic nanoparticles on macroscopic surfaces.

KEYWORDS: *polymer brushes, poly(2-oxazoline), nanoparticles, surface modification, chemical grafting and cationic polymerization*

INTRODUCTION

In recent years, there has been an immense interest surrounding the modification of macroscopic surfaces in tailored fashion for making them suitable for a variety of cutting-edge technological applications.¹ Surface modification renders a suitable functionality to macroscopic surfaces for producing their affinity with external moieties such as inorganic nanoparticles (NPs) and biomolecules.² Because of the nanoscale size and high surface energy, inorganic NPs always tend to aggregate in bulk state, which limits their use in intended applications. Needless to mention that stabilization of NPs on macroscopic surfaces is motivated by the fact that it allows to access the higher surface area of NPs and hence improves the efficiency of the systems, where surface area is critical to their performance such as photocatalyst, nanosensors, gas sensors, photonics, adsorbents etc.³ Similarly, for most of the biomedical applications, biocompatibility and enhanced osteointegration of the macroscopic surfaces are desirable. These properties can be rendered to surfaces by modifying them with appropriate surface modifiers. Recently, a great deal of effort has been dedicated to the tailored modification of macroscopic surfaces or interfaces for immobilization of external moieties. The first protocol involves fabrication of self-assembled monolayer (SAM) by exploiting suitable molecules that can bind to a surface. The classical example of a SAM is the reaction of alkanethiols with a gold (Au) surface, first proposed by Allara and Nuzzo at Bell laboratories in 1983.⁴ Similarly, functionalization of solid substrates by self-assembling of silane compounds provides the possibility to tailor their surface properties in a controllable fashion.^{1a} Alternatively, polymer brushes have also been used to render a variety of functionalities and hence physical properties to macroscopic surfaces. Polymer brushes are the systems in

which polymer chains are grafted on the surfaces or interfaces by one chain end with an average distance between two anchoring points significantly smaller than the radius of gyration of similar polymer chains floating free in solution.⁵ This arrangement forces the polymer chains to stretch away from the surface because of segment–segment repulsions and to adopt an entropically unfavorable so-called "brushlike" conformation. Macroscopic surfaces grafted with polymer brushes have generated significant interest in a wide range of nanotechnological areas as well as in academic research.⁶ The use of polymer brushes offers not only a very promising mean to create new surface functionalities but also an effective way to tune the relevant surface properties such as wettability, adhesion, lubrication, friction or, for particles, colloidal stability, interesting for many applications.⁷ The factors influencing synthesis and properties of such layers have been the subject of numerous experimental and theoretical studies during the past few years.

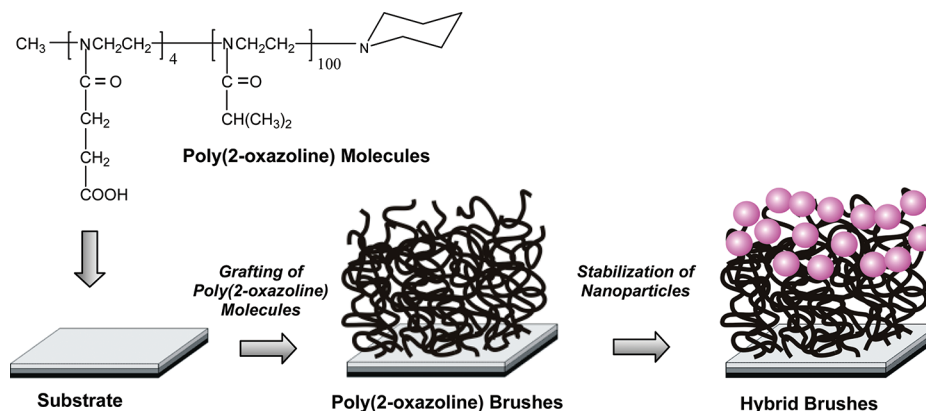
Recently, poly(2-oxazoline)s have attracted an immense interest of the researchers because of their biocompatibility, thermoresponsiveness with sharp transition, and easy modulation in transition temperature within a broad temperature window.⁸ A wide range of well-defined polymers with tailored properties have been synthesized by living cationic ring-opening polymerization.⁹ Despite the significant work done on tailored synthesis of poly(2-oxazoline) molecules in bulk, there exist only few reports on the preparation of poly(2-oxazoline) brushes on macroscopic surfaces.¹⁰ Taking the advantage of ease in modulation in properties of poly(2-oxazoline) by engineering

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Scheme 1. Schematic Presentation of the Fabrication of Poly(2-Oxazoline) Brushes and Stabilization of NPs Thereon



their chemical structure, a wide range of functionalities can be introduced onto the macroscopic surfaces by exploring their grafting behavior in brush conformation. The resulting brushes may offer a novel way of imparting the unique combination of thermal sensitivity and biocompatibility to macroscopic surfaces. The motivation of presented study is to develop a facile and versatile approach for chemical grafting of a stable and dense layer of the poly(2-oxazoline) molecules in brush conformation on macroscopic surfaces and explore their applications in stabilization of foreign moieties like inorganic NPs. To the best of our knowledge, for the first time, in this study, we report on the fabrication of the poly(2-isopropyl-2-oxazoline) brushes on macroscopic surfaces by employing the “grafting to” approach. The advantages offered by polymer brushes over conventional surface modification techniques such as self-assembled monolayers (SAM) include easy and controllable introduction of polymer chains with a high surface density, precise localization of the polymer chains on underlined surfaces, high stability and robustness of the grafted layers. Because of the presence of a plenty of polar functionalities, i.e., carbonyl groups in side chains and amino groups in back bones, poly(2-isopropyl-2-oxazoline) brushes are expected to offer a large number of the active binding sites¹¹ as compared to self-assembled monolayers for stabilization of foreign moieties.^{10d} Moreover, one can easily control the immobilized amount of the NPs/biomolecules by modulating the grafting density of the polymer brushes. Above all, polymer brushes offer a versatile mean to modify the surfaces/interfaces in a tailored fashion as this approach can be followed for grafting a variety of polymer molecules on a number of substrates.

As illustrated in Scheme 1, the employed protocol involves synthesis of a novel, well-defined and end functionalized poly(2-isopropyl-2-oxazoline) molecules by ring-opening cationic polymerization followed by their grafting on macroscopic surfaces in brushlike conformation. A controlled variation in thickness of grafted polymer brush layer has been demonstrated. Finally, application of fabricated poly(2-isopropyl-2-oxazoline) brushes has been demonstrated for stabilization of inorganic NPs such as gold (Au) on macroscopic surfaces. Au NPs are known to have excellent optical and catalytic properties, which render the wide applicability to presented system in a variety of potential areas such as in developing displays, catalysts, sensors and optical filters. Underlining the biocompatible nature of Au and poly(2-isopropyl-2-oxazoline) brushes, fabricated hybrid nanoassemblies can be promising material in separation of biomolecules.¹² Because of the easy fabrication,

plenty of functionalities along each grafted polymer chain and biocompatible nature, these brushes can also be exploited as surface modifiers for immobilization of functional components in biomedical applications such as in bio-implants.

EXPERIMENTAL SECTION

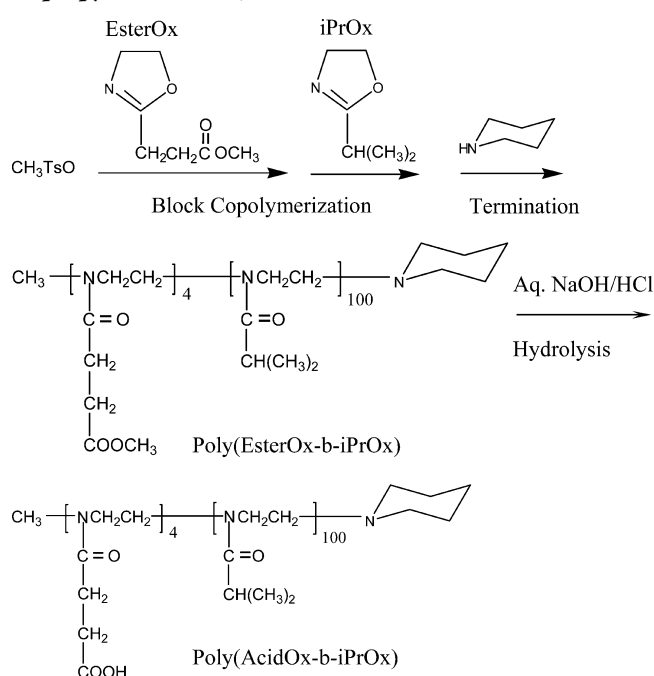
Materials. Methyl succinate chloride, 2-chloroethylamine hydrochloride, triethylamine, isobutyronitrile, cadmium acetate dihydrated, ethanolamine, calcium hydride, anhydrous sodium carbonate and sodium sulfate were purchased from Aldrich and used as received. Methyl p-toluene sulfonate and acetonitrile were also purchased from Aldrich and distilled twice from CaH_2 and stored under a dry nitrogen atmosphere. Hydrogen tetrachloroaurate ($HAuCl_4 \cdot 4H_2O$) and sodium borohydride ($NaBH_4$) were purchased from Aldrich and used without additional purification. Polyglycidyl methacrylate (PGMA) ($M_n = 17\,500\text{ g mol}^{-1}$) was purchased from Polymer Source, Inc. and used as received. Highly polished single-crystal silicon wafers of {100} orientation with ca. 1.5 nm thick native silicon oxide layers were purchased from Semiconductor Processing Co. and used as substrates. All the organic solvents were dried using standard methods before use. Millipore water was employed throughout the experiments.

Characterization Methods. Atomic force microscopy (AFM) studies were performed with a Dimension 3100 (Digital Instruments, Inc., Santa Barbara, CA) microscope. Tapping and contact modes were used to map the film morphology and thickness, respectively, in ambient conditions. XPS experiments were performed with an AXISULTRA spectrometer (Kratos Analytical, U.K.) equipped with a monochromatic $Al\ K\alpha$ X-ray source of 300 W at 20 mA. The survey and high-resolution spectra were recorded at analyzer's pass energy set value of 160 and 20 eV, respectively. All spectra were charge compensated using the C_{1s} component peak of the C 1s spectra at BE (binding energy) 285.00 eV as reference peak.¹³ Quantitative elemental compositions were determined from peak areas using experimentally obtained sensitivity factors and the spectrometer transmission function. UV-vis spectra were recorded with a Cary 50 spectrophotometer (Varian). Thickness of the grafted polymer brushes were measured at $\lambda = 632\text{ nm}$ and an incidence angle of 70° with a SENTECH SE-402 scanning microfocus ellipsometer equipped with an XY-positioning table for mapping of the sample surface. The measurements were performed for each sample after each step of the modification to use the measurements of the previous step as a reference for the simulation of ellipsometric data.¹⁴ The refractive indices used for the calculations were 3.858-i0.018, 1.4598, 1.525, 1.499 for silicon substrate, native silica layer, PGMA layer and poly(2-isopropyl-2-oxazoline) brushes, respectively. Molecular weights of synthesized polymers have been determined by size exclusion chromatography on HPLC-Pump, Series 1200 from Agilent Technologies coupled to ETA-2020 RI with Visco detector (Dr. Bures, DE) and a multi angle laser LS detector (DAWN, Wyatt Tech, USA). Column PL MIXED-C (Polymer Laboratories, UK) was used with THF as eluent at flow rate of 1.0 mL/min. The water contact angle measurements

were carried out at room temperature on “DSA-10” Krüss equipment with accuracy of 0.5°. ATR-FTIR (Attenuated Total Reflection Fourier Transform Infrared) measurements were performed on a spectrometer (IFS 55, BRUKER-Optics GmbH, Ettlingen, Germany) equipped with a special mirror setup (OPTISPEC, Zürich), a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector and a thermo stable in situ ATR double channel flow cell (IPF Dresden). The spectra were recorded using the SBSR (single beam sample reference) technique to ensure reproducible spectral background compensation at the measurements in aqueous environments.¹⁵ For this purpose, polymer brushes were grown on upper half of the silicon internal reflection element (Si-IRE) (Komlas GmbH, Berlin, Germany) plate and its lower half was used as reference. The resulting absorption spectra enable an accurate compensation of background absorptions and feature conveniently the flat baselines.

Synthesis of Carboxyl-Terminated Poly(2-isopropyl-2-oxazoline). A block copolymer of 2-(2-methoxycarbonylethyl)-2-oxazoline (esterOx) and 2-isopropyl-2-oxazoline (iPrOx) was synthesized as shown in scheme 2. The employed monomers iPrOx and esterOx were

Scheme 2. Synthesis of Carboxyl-Terminated Poly(2-isopropyl-2-oxazoline)



synthesized as reported elsewhere.^{9a,16} In a typical process, 0.65 g (4.14 mmol) of esterOx was added into a solution of 0.185 g (0.994 mmol) of methyl tosylate in 25 mL of acetonitrile under nitrogen atmosphere. The reaction mixture was heated at 75 °C for 3.5 h. Subsequently, 11.3 g (0.1 mol) of iPrOx was added into the reaction media at room temperature and allowed to stir at 75 °C for 42 h. The polymerization process was stopped by adding 0.17 g (1.99 mmol) piperidine at room temperature. A white colored product, poly(esterOx-b-iPrOx) block copolymer was precipitated from reaction mixture in diethyl ether and further purified by dissolving it into the chloroform and removing the solvent under reduced pressure. It should be noted here that polymerization of esterOx monomer has been confirmed by terminating the polymerization process after 3.5 h only with the addition of piperidine in a different set of the reaction and analyzing the resulting poly(esterOx) by NMR spectroscopy (data shown below).

In a subsequent step, poly(esterOx-b-iPrOx) was hydrolyzed into poly(acidOx-b-iPrOx).¹⁶ In a typical process, 0.1 M NaOH (20 mL) was added dropwise into the 5.35 g (0.5 mmol) poly(esterOx-b-iPrOx) copolymer dissolved in methanol (20 mL). Reaction mixture

was stirred at room temperature for 1 h and subsequently at 55 °C for additional 1.5 h. Methanol was then removed under reduced pressure and 20 mL of aq. HCl (0.1M) was added into the reaction media. After water was removed in vacuum, the obtained residue was dissolved in chloroform and the solution was dried under anhydrous sodium sulfate. Finally, solvent was removed under reduced pressure and obtained poly(acidOx-b-iPrOx) was used for fabrication of polymer brushes on macroscopic surfaces. In following discussion, poly(acidOx-b-iPrOx) copolymer has been referred as carboxyl-terminated poly(2-isopropyl-2-oxazoline).

Poly(EsterOx). NMR ^1H (CDCl_3) δ (ppm): 2.6 ($\text{OCCCH}_2\text{CH}_2\text{CO}$, esterOx), 3.5 (NCH_2CH_2 , esterOx), 3.7 (COCH_3) (esterOx).

First step. Poly(esterOx-b-iPrOx): yield, 9.71 g (75%); white colored powder; mol wt (M_n) 12 400; PDI, 1.41.

NMR ^1H (CDCl_3) δ (ppm): 1.11 (CH_3 , iPrOx) 2.6 ($\text{OCCCH}_2\text{CH}_2\text{CO}$, esterOx), 2.9 (CH , iPrOx), 3.5 (NCH_2CH_2 , iPrOx and esterOx), 3.6 (COCH_3) (esterOx).

NMR ^{13}C (CDCl_3) δ (ppm): 19.62 (CH_3 , iPrOx), 30.2 (CH , iPrOx), 43–48 (NCH_2CH_2 , iPrOx and esterOx), 51.58 (OCH_3 , esterOx), 171.9 ($\text{C}=\text{OCH}_2$, esterOx), 173.4 ($\text{C}=\text{O}(\text{OCH}_3)$, esterOx), 177.6–177.95 ($\text{C}=\text{O}$, iPrOx).

Second step. Poly(AcidOx-b-iPrOx): yield, 4.86 g (91%); white colored powder; mol wt (M_n), 10 700; PDI, 1.22

NMR ^1H (CDCl_3) δ (ppm): 1.11 (CH_3 , iPrOx) 2.6 ($\text{CH}_2\text{CH}_2\text{COO}$, acidOx), 2.9 (CH , iPrOx), 3.5 (NCH_2CH_2 , iPrOx and acidOx).

NMR ^{13}C (CDCl_3) δ (ppm): 19.62 (CH_3 , iPrOx), 30.2 (CH , iPrOx), 43–48 (NCH_2CH_2 , iPrOx and acidOx), 171.9 ($\text{C}=\text{OCH}_2$, acidOx), 173.4 ($\text{C}=\text{O}(\text{OH})$, acidOx), 177.6–177.95 ($\text{C}=\text{O}$, iPrOx).

Preparation of Poly(2-isopropyl-2-oxazoline) Brushes. Polymer brushes have been fabricated on silicon substrates by exploiting the “grafting to” method.¹⁷ Silicon wafers (2 cm × 1 cm) were used as underlined substrates, which were cleaned with dichloromethane in an ultrasonic bath for 45 min (15 min × 3) prior to their further modification. Subsequently, these substrates were stirred by means of in-house fabricated wafer holder in 1:1 mixture of 29% ammonium hydroxide and 30% hydrogen peroxide (**Warning:** This solution is extremely corrosive and should not be stored in tightly sealed containers due to evolution of gas) for 1.5 h and then rinsed several times with Millipore water. A thin layer of PGMA (ca. 2 nm) was deposited on substrate by spin-coating from a 0.02 w/w % solution in chloroform and annealed at 110 °C for 10 min. Subsequently, a thin film of carboxyl-functionalized poly(2-isopropyl-2-oxazoline) dissolved in chloroform was spin-coated and annealed at 150 °C for 16 h in a vacuum oven. To ensure the removal of unabsorbed polymer molecules from silicon substrates, we cleaned samples by Soxhlet extraction in chloroform for 4 h.

Stabilization of Nanoparticles on Poly(2-isopropyl-2-oxazoline) Brushes.¹¹ To stabilize the Au NPs on poly(2-isopropyl-2-oxazoline) brushes, we stirred samples in aqueous 5 mM HAuCl_4 solution for 2 hrs and subsequently treated with 1 mM NaBH_4 solution for 5 min in aqueous media. Finally, samples were cleaned several times with Millipore water, dried under argon, and used for characterization.

RESULTS AND DISCUSSION

The “grafting to” approach¹⁷ has been employed for the fabrication of homogeneously distributed poly(2-isopropyl-2-oxazoline) brushes on silicon substrates. The process involves chemisorptions of PGMA anchoring layer followed by grafting of carboxyl-functionalized poly(2-isopropyl-2-oxazoline) molecules on underlined substrate. It is well-known from literature that high reactivity of the epoxy groups of PGMA toward the hydroxyl groups of a variety of surfaces makes it a universal anchoring layer for grafting of polymer brushes.^{18,19} The chemical reaction between $-\text{COOH}$ groups of end-functionalized poly(2-isopropyl-2-oxazoline) molecules and epoxy units located in the “loops” and “tails” sections of the chemically attached PGMA layer leads to the chemical attachment of

poly(2-oxazoline) chains on silicon substrates in a brush-like conformation. Ellipsometry analysis of PGMA coated sample reveals thickness of the grafted layer as 2.5 ± 0.5 nm. Tapping mode AFM image of PGMA coated silicon wafer has been presented in the Supporting Information, Figure S1.

To show the grafting of PGMA and subsequently, poly(2-isopropyl-2-oxazoline) molecules on silicon substrate, samples have been analyzed by contact angle measurements. Figure 1

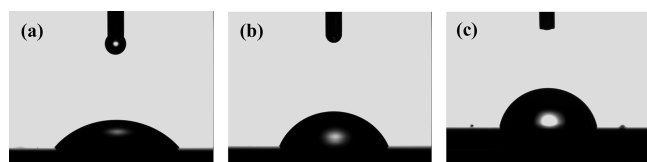


Figure 1. Static water contact angle measurements on (a) bare (b) PGMA coated and (c) PGMA and subsequently, poly(2-isopropyl-2-oxazoline) brushes modified silicon wafers.

reveals the photographs of the water droplet lying on substrate at every step of the grafting process of the polymer brush layer on silicon wafer. The static water contact angles have been found to consistently increase as $45 \pm 2^\circ$, $64 \pm 2^\circ$, and $70 \pm 2^\circ$ from bare silicon wafer, to PGMA anchoring layer and poly(2-isopropyl-2-oxazoline) brushes, respectively. The apparent

increase in hydrophobicity of samples from silicon wafer to poly(2-isopropyl-2-oxazoline) brushes can be attributed to the grafting of hydrophobic groups on the surfaces. It is noteworthy that in the case of poly(2-isopropyl-2-oxazoline) brushes pipe-ridine end groups introduces additional hydrophobic character to the polymer brush layer.

Figure 2a illustrates AFM image of poly(2-isopropyl-2-oxazoline) brushes grafted onto the silicon wafer. One can observe that these brushes have a carpet like morphology with smooth surfaces and homogeneous distribution on underlying substrate. The line scan shows root-mean-square (rms) roughness of 0.45 nm. In order to measure thickness of the grafted polymer brushes, AFM scratch test has been employed. For this purpose, a scratch has been made on polymer brush layer by a sharp knife and subsequently, sample has been scanned across the scratch in contact mode as shown in Figure 2b. Lower panel of this image reveals thickness of grafted layer as 12.5 nm in dry state.

A controlled variation in employed concentration of poly(2-isopropyl-2-oxazoline) solution in spin coating allowed us to modulate the thickness of resulting polymer brushes. Figure 3a illustrates variation in thickness of grafted polymer brushes from 4.5 to 12.5 nm with the change in concentration of polymer solution from 0.1 wt % to 4 wt %. As evident from Figure 3a, an increase in solution concentration beyond 2 wt %

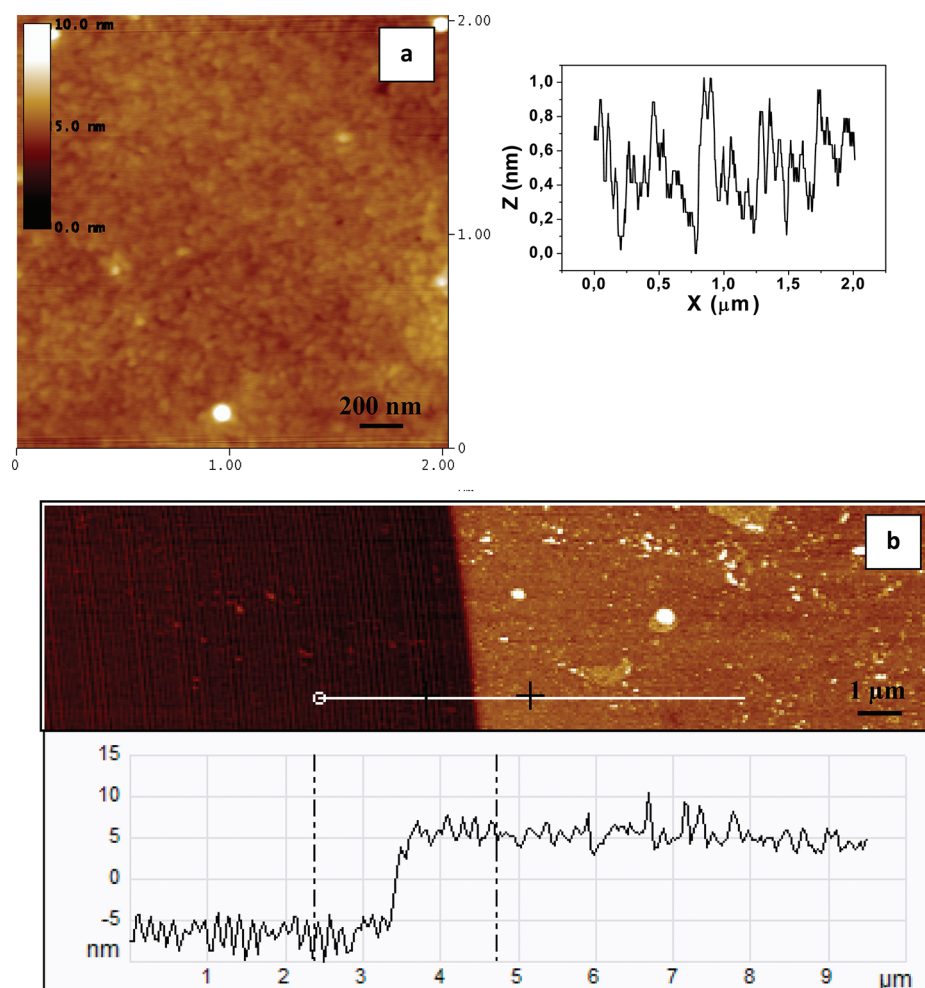


Figure 2. (a) Tapping mode AFM image (height: $2 \mu\text{m} \times 2 \mu\text{m}$) of poly(2-isopropyl-2-oxazoline) brushes grafted on macroscopic surfaces. (b) Contact mode AFM image of a scratch made on poly(2-isopropyl-2-oxazoline) brushes and line scan of this scratch revealing the polymer brush thickness as 12.5 nm.

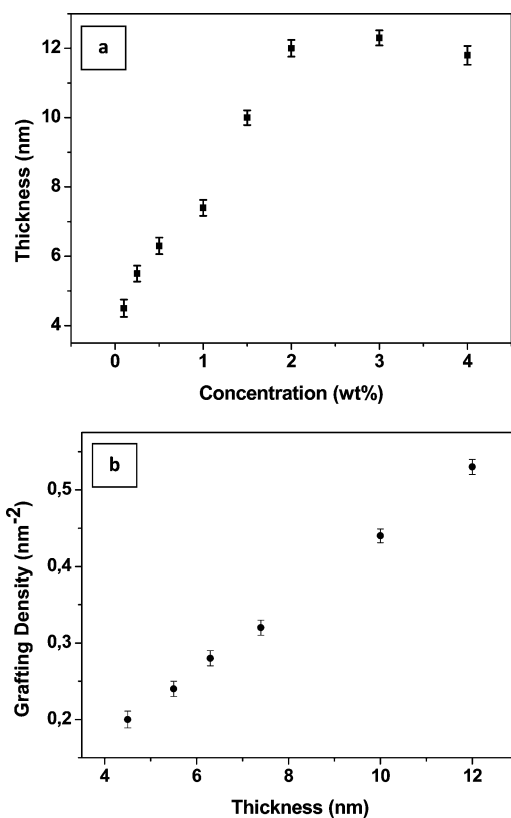


Figure 3. Modulation in thickness of grafted polymer brushes as a function of the employed concentration of poly(2-isopropyl-2-oxazoline) solution. (b) Calculated grafted densities of prepared poly(2-isopropyl-2-oxazoline) brushes as a function of the thickness.

has been found to hardly affect the thickness of grafted polymer brushes. It suggests that at this concentration, brushes acquire the maximum grafting density through “grafting to” approach. The grafting densities of polymer brushes have been calculated by $\sigma = 1/d_g^2$. Here d_g is the distance between two grafting sites, estimated from $d_g = M_n^{1/2} (N_A d \rho)^{-1/2}$, where M_n is number average molecular weight of polymer chains, N_A is Avogadro’s number, ρ is polymer density for poly(2-isopropyl-2-oxazoline) (~ 1.0 g/cm³), and d is dry state thickness of poly(2-isopropyl-2-oxazoline) brushes.¹⁸ Figure 3b illustrates calculated grafted densities as a function of the polymer brush thickness. These data reveal that employed approach offers an effective control over the grafting density of polymer brushes.

To exclude the fact that annealing of the sample at 150 °C during brush formation changes the chemical structure of the poly(2-isopropyl-2-oxazoline), samples have been characterized by surface analytical tools. Figure 4 shows an in situ ATR-FTIR spectrum of the poly(2-isopropyl-2-oxazoline) brush layer (dry state) grafted onto a silicon internal reflection element (Si-IRE). One can observe a characteristic peak at 1645 cm⁻¹, attributable to the amide band of poly(2-isopropyl-2-oxazoline) blocks of the employed polymer molecules. A whole range of ATR-FTIR spectrum of this sample is shown in Supporting Information, Figure S2, revealing all the expected bands from grafted polymer molecules. As mentioned above, poly(2-oxazoline) is well-known to show temperature responsive properties. ATR-FTIR spectroscopy has also been employed to study the temperature responsive behavior of fabricated poly(2-isopropyl-2-oxazoline) brushes in aqueous media at different temperatures and results are shown in Figure 4.

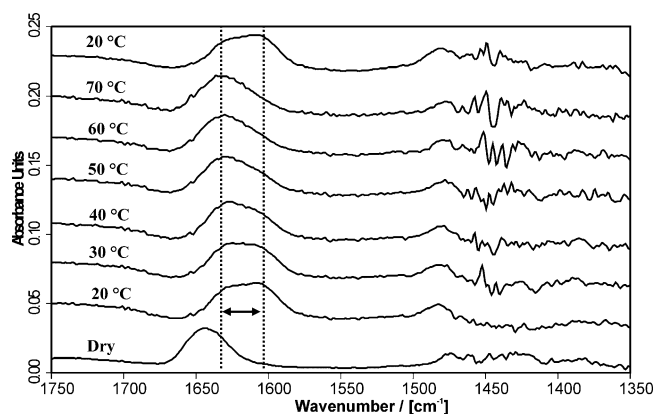


Figure 4. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra of the poly(2-isopropyl-2-oxazoline) brushes grafted on silicon substrate. The spectrum shown at the bottom has been scanned dry state, while others have been taken in aqueous state at indicated temperatures. The uppermost spectrum has been scanned in wet state at 20 °C after cooling the system from 70 °C.

First, when surrounding media of the polymer brushes is changed from dry to aqueous state at 20 °C, a significant shift in secondary amide position from 1644 to 1605 cm⁻¹ has been observed with the appearance of an additional shoulder at 1630 cm⁻¹. It can be attributed to the hydrogen bond interactions of grafted poly(2-isopropyl-2-oxazoline) molecules with water in hydrated state, which generally weakens the double bond character of the carbonyl groups leading to the downward shift in band position. When temperature of the aqueous media is increased from 20 to 70 °C at an interval of 10 °C, a clear shift in maximum of amide band has been seen from 1605 to 1635 cm⁻¹. An increase in temperature results in a loss of hydrogen bonding presumably due to the dehydration of the amide groups and hence results in upward shift of absorption band. Evidently, at elevated temperatures the hydrogen bonding is on a similar level as for the dry state. Interestingly, a reversible shift in amide band position can be seen in upper most scan in Figure 4 with the cooling of the system from 70 to 20 °C. The observed reversible thermo sensitive behavior of the poly(2-isopropyl-2-oxazoline) brushes can be attributed to the lower critical solution temperature phenomena of the poly(2-isopropyl-2-oxazoline) molecules in solution.⁸ These results reveal that fabricated polymer brushes show the temperature-sensitive properties, which can be interesting for biomedical applications in combination with their biocompatible nature.

Applicability of fabricated poly(2-isopropyl-2-oxazoline) brushes has been explored as surface modifiers for the stabilization of inorganic NPs. For this purpose, samples have been incubated into aqueous solution of HAuCl₄ for 2 h and subsequently treated with NaBH₄ solution. It is well-known from literature that carbonyl and amino groups readily complexes with electron deficient metal elements such as “Au” through the lone pairs of electron rich oxygen and nitrogen atoms.¹¹ In this study, presence of these groups along the grafted polymer chains has been exploited as binding sites for stabilization of Au NPs on underlined substrates. An interaction between immobilized NPs and functional groups of polymer brushes has been confirmed with XPS (see below). Figure 5a illustrates topographical AFM image of the poly(2-isopropyl-2-oxazoline) brushes immobilized with Au NPs. A comparison of this image with that of bare poly(2-isopropyl-2-oxazoline) brushes (shown in Figure 2a)

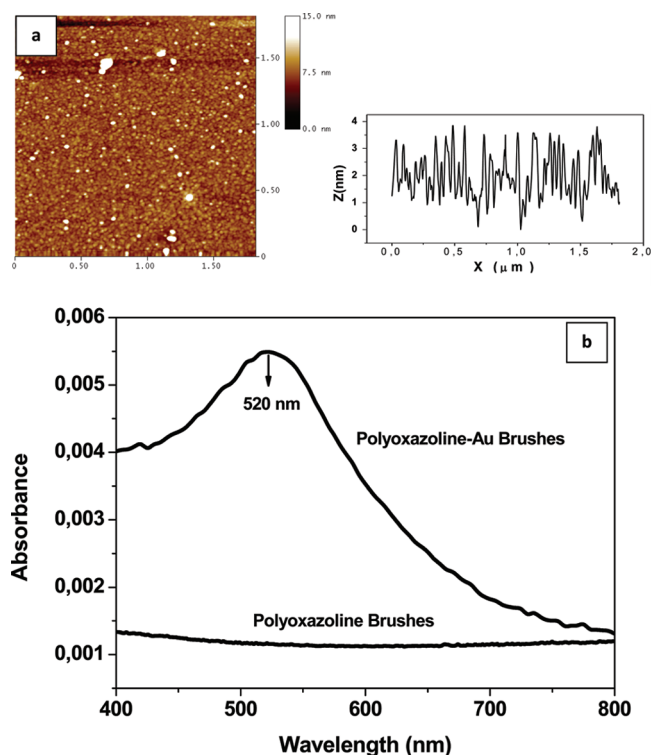


Figure 5. (a) AFM height image ($2 \mu\text{m} \times 2 \mu\text{m}$) and (b) UV-vis spectra of poly(2-isopropyl-2-oxazoline) brushes immobilized with Au NPs.

reveals that brushes have developed rough and pebbled morphology after the stabilization process. The rms roughness has been found to increase from 0.45 nm for bare brushes to 2.4 nm for Au NPs treated brushes. These results strongly confirm stabilization of inorganic NPs on modified macroscopic surfaces. The surface coverage (Φ) of Au NPs on polymer brushes has been found as $\sim 5\%$, which has been calculated by $100N\pi d^2/4A\%$; where d is diameter of NPs and N is the number of NPs in given area A . The number of NPs per area of the sample was counted by zooming a part of the AFM image. Authors believe that proposed approach can readily be used for stabilization of a variety of noble metal/metal oxide NPs on macroscopic surfaces.

To investigate optical properties of poly(2-isopropyl-2-oxazoline)-Au brushes, we have analyzed samples by UV-vis spectroscopy. For this purpose, poly(2-isopropyl-2-oxazoline)-Au nanoassemblies have been grafted onto quartz substrates. Figure 5b presents a UV-vis spectra of poly(2-isopropyl-2-oxazoline) brushes before and after the stabilization of Au NPs. Unlike the bare polymer brushes, presence of the characteristic plasmon resonance peak at 520 nm can be observed in the case of poly(2-isopropyl-2-oxazoline)-Au brushes, confirming the presence of Au NPs on modified surfaces.^{20,21} It is noteworthy that absence of absorption peak at 600 nm or higher wavelength excludes the aggregation of immobilized Au NPs on modified surfaces.^{22,23} These data demonstrate that poly(2-isopropyl-2-oxazoline) brushes can readily be exploited for a homogeneous immobilization of inorganic NPs on macroscopic surfaces. In our previous study,^{3d} we immobilized Au NPs on polystyrene brushes and found that variation in nature of solvent in surrounding media greatly affects the plasmon band position due to the swelling and deswelling of the polystyrene brushes. Similarly, Minko et al.²⁴ demonstrated modulation in plasmon band position of Au colloids immobilized on polymer

brushes. However, poly(2-oxazoline)s are well-known to show the temperature sensitivity but a temperature dependent variation in band position of immobilized Au NPs on poly(2-isopropyl-2-oxazoline) brushes could not be observed. It can be attributed to the small chain length of grafted molecules. It does not permit a significant change in interparticle distance of immobilized Au NPs, which is the driving force for the modulation of optical properties of immobilized NPs. However, ATR-FTIR analysis (as described above) clearly reveals that poly(2-oxazoline) maintain their temperature responsiveness even after grafting on surfaces. It is worth mentioning here that the motivation of this study is to modify the macroscopic surfaces by poly(2-oxazoline) brushes to use them as platform for immobilization of NPs or biomolecules by exploiting their unique properties. It is known from the literature that use of thin polymer brushes as surface modifier facilitates the uniform immobilization of the external moieties and control their aggregation on surfaces.²⁵

To further confirm the chemical structure of grafted molecules as poly(2-isopropyl-2-oxazoline), we have analyzed samples by XPS, and the results are shown in Figure 6a. One can observe a wide scan spectrum of the poly(2-isopropyl-2-oxazoline) brushes revealing the signals from different elements at characteristic positions. As shown in inset of Figure 6a, the C

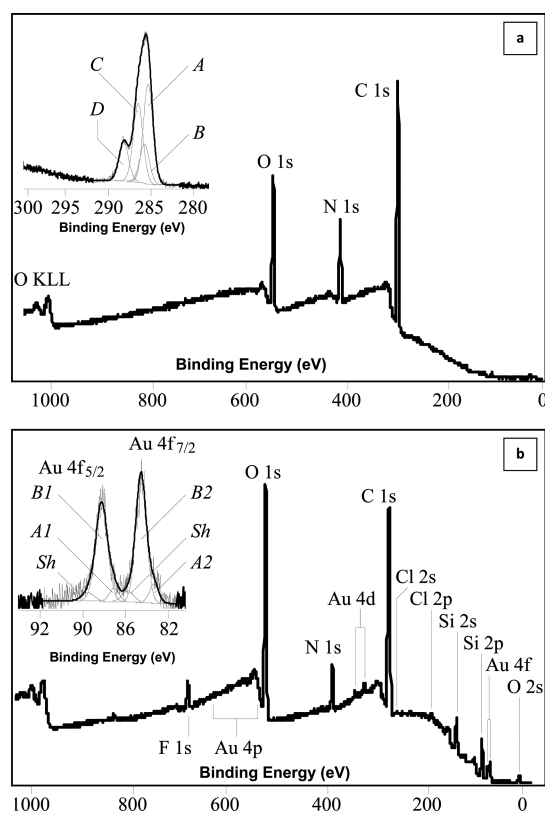


Figure 6. X-ray photoelectron spectroscopy analyses of poly(2-isopropyl-2-oxazoline) brushes (a) before and (b) after stabilization of Au NPs.

1s core level spectra can be deconvoluted into four component peaks (A, B, C, D) revealing the different binding states of the carbon atoms. Component peak A can be attributed to the methyl groups arising from saturated hydrocarbons surface contaminations. Component peak B represents carbon atoms in the α -position to the carbonyl carbon ($\underline{\text{C}}-\text{C}(\text{N})=\text{O}$).

Moreover, binding energy positions suggest that component peak C and peak D can be related to ($[\underline{C}-]_2N-C=O$) and ($[\underline{C}-]_2N-C=O$) moieties of the poly(2-isopropyl-2-oxazoline) molecules. The intensity ratios have been found in agreement with the stoichiometric ratio of the poly(2-isopropyl-2-oxazoline) molecule as $[B]:[C]:[D] = 1:2:1$, strongly indicating that grafted brush layer is composed of the poly(2-isopropyl-2-oxazoline) molecules. Figure 6b shows a wide scan XPS spectrum of polymer brushes immobilized with Au NPs. A closer look of these data reveals presence of the characteristic "Au" signals at relevant binding energies suggesting the stabilization of Au NPs on polymer brushes.²⁶ The atomic concentration of "Au" on the investigated substrates has been found as approximately 3.42%. A relatively higher intensity of "Si" peak in Figure 6b as compared to the Figure 6a may be attributed to the contamination of samples with traces of the silicon oxide species from substrate during in situ synthesis of Au NPs in the presence of $NaBH_4$ like strong reducing agents. Additionally, the immobilized Au NPs partly compress the polymer brushes, which can be evident by increased surface roughness of the brush layer after stabilization of Au NPs. As a result, photoelectrons of the silicon substrate also contribute to the wide-scan spectrum in Figure 6b, whereas the bare polymer brush layer in Figure 6a is thicker than the maximum information depth of the XPS method. Underlining the above facts, the amount of oxygen can also be expected to increase in the case of Au stabilized polymer brushes and hence their C, N, O ration seem to be different from bare polymer brushes. Inset in Figure 6b illustrates core level spectrum of "Au" revealing the XPS signature of the Au 4f doublet, attributable to Au NPs immobilized on poly(2-isopropyl-2-oxazoline) brushes. Each peak of this doublet can be deconvoluted into three component peaks as indicated by A, B, and Sh (Shake up peak). Appearance of the B1 and B2 peaks at 84 and 87.67 eV strongly confirms presence of the metallic "Au" NPs on polymer brushes. Moreover, presence of the smaller peaks A1 and A2 at the lower binding energy positions than B1 and B2 can be explained by the possible interactions of Au NPs with functional groups of grafted poly(2-isopropyl-2-oxazoline) molecules. Au NPs are known to interact strongly with the electron-rich nitrogen and oxygen atoms of the amide and carbonyl groups, respectively. The lone pair electrons of these elements are donated to the 4f orbitals of the Au atom resulting in complex formation. Such interaction between "Au" and amino or carbonyl functional groups have been reported in literature.^{11,12} Because the increased electron density on the "Au" atom through such electron transfers, binding energy of emitted photoelectrons is decreased and a slight shift toward lower binding energy is observed for component peaks A1 and A2.^{3b}

CONCLUSIONS

A facile approach for modification of macroscopic surfaces by means of a novel class of functional polymer brushes, namely poly(2-isopropyl-2-oxazoline) has been presented. An effective control on thickness of grafted polymer brush layer has been demonstrated. Application of fabricated polymer brushes in immobilization of external moieties such as NPs on macroscopic surfaces has been discussed. Because of the biocompatibility, temperature sensitivity, and affinity with inorganic nanoparticles, these brushes are expected to have a great potential in sensing, biomedical and catalytic applications. We believe that employed approach of surface modification can be

extended to a wide range of polymers to impart their fascinating properties to a variety of surfaces or interfaces.

ASSOCIATED CONTENT

Supporting Information

Tapping mode AFM image of PGMA coated silicon wafer and ATR-FTIR spectrum of poly(2-isopropyl-2-oxazoline) brushes. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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