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Assembly of Ultrathin Polymer Multilayer Films by Click Chemistry

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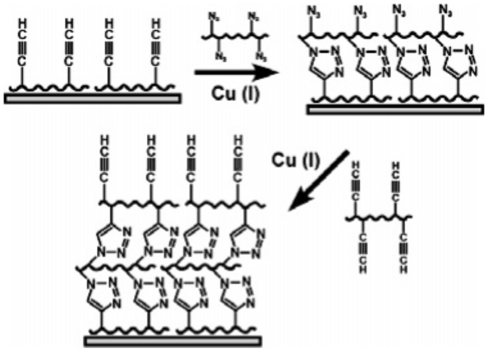
Layer-by-layer (LbL) assembly is a versatile technique for fabricating tailored thin films of diverse composition.[1,2] The majority of work has focused on the assembly of polyelectrolyte (PE) films by either electrostatic[2,3] or hydrogen bonding[4,5] interactions. More recent work has reported polymer multilayer assembly facilitated by covalent bonding.[6,7] Covalently bound films offer the advantage of higher stability due to the cross-linked polymer networks and are not susceptible to disassembly under varying solution conditions (e.g., salt, pH), as is typically observed for a range of electrostatically coupled and H-bonded films.[8,9] Herein, we report a highly efficient and generalizable method based on click chemistry to construct LbL polymer films.

Click chemistry refers to a set of covalent reactions with high reaction yields that can be performed under extremely mild conditions. The most well documented click reaction is the Cu^I-catalyzed variant of the Huisgen 1,3-dipolar cycloaddition of azides and alkynes to form 1,2,3-triazoles.[10,11] To date, click chemistry has been used in a broad range of applications, including functionalizing biological molecules,[12] solubilizing carbon nanotubes,[13] and synthesizing dendrimers.[14] The combination of click chemistry and LbL assembly offers a number of significant advantages. First, the reaction proceeds with high yields in mild conditions, and it is particularly efficient in water. Second, the triazole linkages have excellent physicochemical properties and are extremely stable to hydrolysis, oxidation, or reduction.[11] Third, it is applicable to a wide range of materials, from polymers and proteins to nanoparticles, dye molecules, and biological systems. Finally, this method can be used to assemble single component films, which is not possible using conventional LbL assembly.

In this communication, we report the LbL assembly of poly(acrylic acid) multilayer films using click chemistry. To our knowledge, this is the first time LbL multilayer assembly has been constructed from essentially the same PE. We demonstrate that this technique provides a simple and general method for the assembly of PE films of controlled thickness and that the click moiety provides stable cross-links within the films.

Poly(acrylic acid) with either azide (PAA-Az) or alkyne functionality (PAA-Alk) was synthesized using living radical polymerization (see Supporting Information). NMR analysis showed that PAA-Az (M_w 86 000) and PAA-Alk (M_w 61 000) contained ~16 and ~14% functional groups, respectively, for cross-linking. Infrared spectroscopy showed the characteristic azide peak at 2100 cm^{-1} for PAA-Az and a fingerprint weak alkyne peak at 2120 cm^{-1} for PAA-Alk (data not shown), confirming functionalization of the polymers. These polymers were then LbL assembled with Cu^1 as a catalyst (Scheme 1).

Scheme 1. LbL Assembly of Polymer Films Using Click Chemistry



LbL assembly was performed by sequentially exposing the substrates (quartz, silicon, or gold) to PAA-Az and PAA-Alk solutions containing copper sulfate and sodium ascorbate for 20 min, with water rinsing after deposition of each layer.[15] The dipping solutions were prepared from the following stock solutions: (a) PAA-Az (0.83 mg mL^{-1}), (b) PAA-Alk (0.83 mg mL^{-1}), (c) MilliQ water (pH 3.5), (d) copper sulfate (0.36 mg mL^{-1}), and (e) sodium ascorbate (0.88 mg mL^{-1}). The pH of each solution was adjusted to 3.5 using 0.1 M HCl. Polymer dipping solutions were made up in a constant volume ratio of 3(a or b):1(d):1(e). The aqueous wash solutions were made up in a similar ratio, however, using solution (c) in place of (a) or (b). To prevent oxidation of the copper, new copper stock solutions were prepared after deposition of each PAA-Az/PAA-Alk bilayer.

LbL assembly of the PAA-Az/PAA-Alk multilayers was first monitored by UV−vis spectroscopy (Figure 1). Linear growth of the film was observed by monitoring the peak at 240 nm, which corresponds to the complex formation between copper and the PAA.[16] A control system of PAA without click groups, used for comparison, showed a plateau in absorbance after only two bilayers, indicating that the click groups are essential for the deposition of consecutive PAA layers and the formation of PAA multilayers. The formation of triazole linkages in the multilayers was confirmed by X-ray photoelecton spectroscopy (a peak at 400 eV was observed which has been commonly assigned to triazole functionality[17]).

The films were further characterized by reflection−absorption Fourier transform infrared spectroscopy (RAS−FTIR). The carboxylic acid peak at ~1730 cm^{-1} from the PAA multilayers was used to monitor the film buildup on a gold surface (Figure 2). The film absorbance increases regularly with bilayer number, in accordance with the UV−vis data (Figure 1). A five-bilayer film was then used to demonstrate the stability of such films to pH cycling (Figure 2 inset). The peak at 1730 cm^{-1} could be reversibly switched between protonated and deprotonated forms by immersion of the film in solutions of alternating pH (3.5 and 9.5). The peak height at pH 3.5 remained essentially constant, indicating negligible polymer desorption during the cycling experiments. This result provides further evidence that the film is constructed using covalent interactions, as PAA-containing films assembled using hydrogen bonding interactions would disassemble under these basic conditions.[8] The films were also found to be stable in a range of organic solvents (ethanol, acetone, and dimethylformamide). The film stability is attributed to the triazole cross-links.

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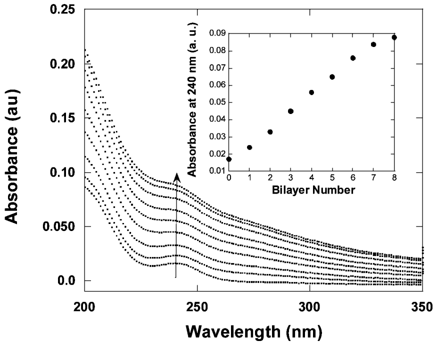

Figure 1. UV−vis absorption spectra for (PAA-Az/PAA-Alk) multilayer films assembled on quartz with increasing bilayer number. The arrow indicates increasing bilayer number. Inset: Absorbance as a function of bilayer number monitored at 240 nm.

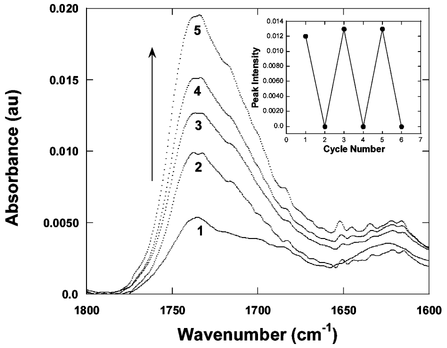

Figure 2. RAS−FTIR absorption spectra of (PAA-Az/PAA-Alk) multilayer films assembled on gold substrates with increasing bilayer number. The arrow indicates increasing bilayer number (bottom to top: bilayers 1, 2, 3, 4, and 5). Inset: Reversible change in the RAS−FTIR peak at 1730 cm^{-1} with a change in pH (pH 3.5 even cycle number; pH 9 odd cycle number) for (PAA-Az/PAA-Alk)$_5$. The peak height is given as zero as it disappears into the bulk spectra at basic pH and is too low to assign.

The thicknesses of air-dried PAA-Az/PAA-Alk multilayer films (four and eight bilayers) assembled on poly(ethyleneimine) (PEI)-coated silicon were determined by spectroscopic ellipsometry (see Supporting Information). The initial PAA-Az layer was adsorbed using electrostatic interactions. Film thicknesses of 25 ± 6 and 38 ± 4 nm were calculated for the four- and eight-bilayer systems, respectively. Taking into account the thickness of the PAA-Az prelayers (4 nm), we obtain PAA-Az/PAA-Alk average bilayer thicknesses of approximately 4.6 nm.

The morphology of the air-dried click PAA multilayer films was examined by atomic force microscopy (AFM). This composition is significantly different than previous multilayer films, and consequently, comparison is difficult. We do note, however, that the surface topology has similarities with those seen for hydrogen-bonded PAA/poly(4-vinylpyridine) LbL systems.[18] The surface roughnesses over $5 \times 5\ \mu m^2$ are approximately 4 and 6 nm for the four- and eight-bilayer films, respectively. These are higher than those reported for PAA/poly(allylamine hydrochloride) films, which have a surface roughness of about 2 when assembled at pH 3.5.[19] However, PAA/poly(*N*-isopropylacrylamide) films assembled by hydrogen bonding have been reported with surface roughnesses of between 5 and 8 nm measured over $1 \times 1\ \mu m^2$.[20] We also determined the thickness of the films by scratching the surface and measuring the step increment with the AFM. Thickness values (for films including the PEI/PAA-Az prelayers) consistent with those measured by ellipsometry were obtained: 22 ± 4 and 43 ± 7 nm for the four- and eight-bilayer films, respectively.

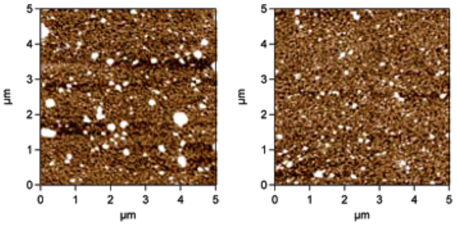

Figure 3. AFM images of the click PAA multilayer films assembled on silicon (a) (PAA-Alk-PAA-Az)$_4$ (*z* scale of 10 nm) and (b) (PAA-Alk-PAA-Az)$_8$ (*z* scale of 25 nm).

In summary, we have demonstrated a new approach to prepare LbL films by using click chemistry. Using this technique, PAA layers can be sequentially deposited based on covalent interactions under mild aqueous conditions. The formation of these single-component PAA films cannot be achieved using conventional LbL assembly. In addition, these films offer additional stability due to the extremely stable triazole linkages formed. This method provides a general technique to significantly increase the suite of thin films that can be fabricated using the LbL technique. It offers particular appeal for systems that cannot be fabricated using traditional LbL assembly, such as noncharged, non-H-bonding polymers. Further, it is particularly well suited to biological systems. Currently, we are extending this approach to prepare tailored click multilayer films and capsules of various materials.

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Supporting Information Available: Synthetic details of monomers and polymers used and experimental methods and techniques. This material is available free of charge via the Internet at http://pubs.acs.org.

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