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NOTE

Influence of Cu(I)−Alkyne π-Complex Charge on the Step-by-Step Film Buildup through Sharpless Click Reaction

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ABSTRACT: Cu(I)-catalyzed azide−alkyne [3 + 2] cycloaddition is used to construct step-by-step covalent polymer or polyelectrolyte multilayers. The catalysis involves the formation of a transient, yet rather stable, positively charged Cu(I)/alkyne complex. We demonstrate that the formation of this complex has a strong influence on the multilayer buildup process. It favors, for example, the film buildup between neutral polymer bearing alkyne groups and polyanion bearing azide groups. In contrary, it disfavors the buildup of the same neutral polymer with polycations bearing azide groups. The constructions of other multilayer systems are investigated and discussed in the light of the electrostatic interactions between these positively charged Cu(I)/alkyne complexes and the polyelectrolytes.

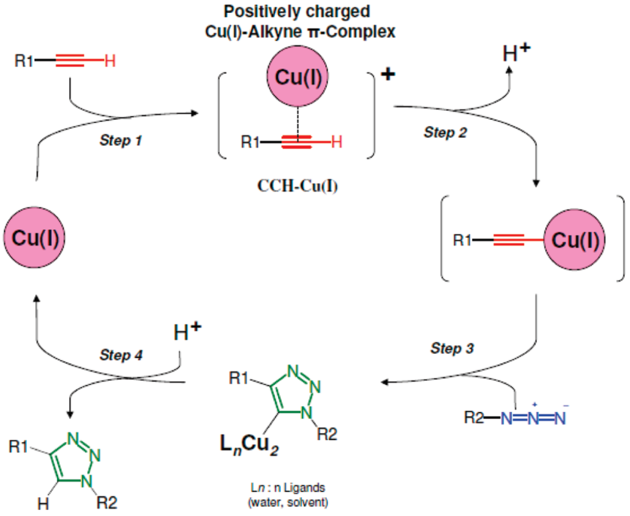
Introduction

The layer-by-layer (LbL) buildup of polymer films was introduced in 1991 by Decher et al.[1] First based on electrostatic interactions between polyanions and polycations,[2] it was later extended to polymers interacting through hydrogen bonds.[3] These films have anticipated applications in optical coatings, separation membranes, bioactive coatings, and many others.[4] However, these films suffer from their mechanical weakness. Besides architectures based on negatively charged mineral particles and polycations,[5] another strategy to overcome this weakness is to cross-link already formed polyelectrolyte multilayers.[6,7] Recently, the step-by-step formation of films with covalent bonds based on Cu(I)-catalyzed azide−alkyne [3 + 2] cycloaddition was proposed.[8]

The group of Caruso was the first to report about the LbL buildup of films entirely constituted of poly(acrylic acid) (PAA) functionalized with azide and alkyne groups,[9] a system also investigated by Tang et al.[10] Caruso et al. extended this buildup strategy to the development of capsules.[11] Bergbreiter et al. grew temperature-responsive films by sequential and covalent addition of poly(*N*-isopropylacrylamide) chains with grafted azide and alkyne groups,[12] and Hawker's group built assemblies from azide- and alkyne-terminated dendrimers.[13] In all of these cases, Cu(I) was generated in situ from Cu(II) in the presence of sodium ascorbate. Multilayer films can also be constructed on electrodes where Cu(I) is electrochemically generated in situ from Cu(II).[14]

Despite the growing interest for step-by-step film constructions using Sharpless click chemistry, there is little knowledge about the buildup mechanism and the parameters controlling it. This reaction relies on Cu(I) catalysis where the Cu(I) ion forms a π-complex with a triple bond (hereafter named CCH−Cu(I)), providing a positive entity (Scheme 1).[15,16] This complex has been isolated,[16] and its role as crucial intermediate in several catalytic mechanisms of chemical reactions has been established.[15b]

Scheme 1. General Outline of Species Involved in the Catalytic Cycle of Click Reaction between Azide and Alkyne Groups and Cu(I)[a]



[a] Cu(I)−alkyne π-complex is schematically represented.

When present along a polymer chain, π-complexes confer positive charges to the chain. Thus, electrostatic interactions can become important for step-by-step film constructions, an effect never reported up to now. Here we present the buildup of several films by using the Cu(I)-catalyzed azide−alkyne [3 + 2] reaction and modified polyelectrolytes or modified neutral polymers. We observed nonsymmetric effects on the film buildup between azide- and alkyne-bearing polymers. This is attributed to positive charges

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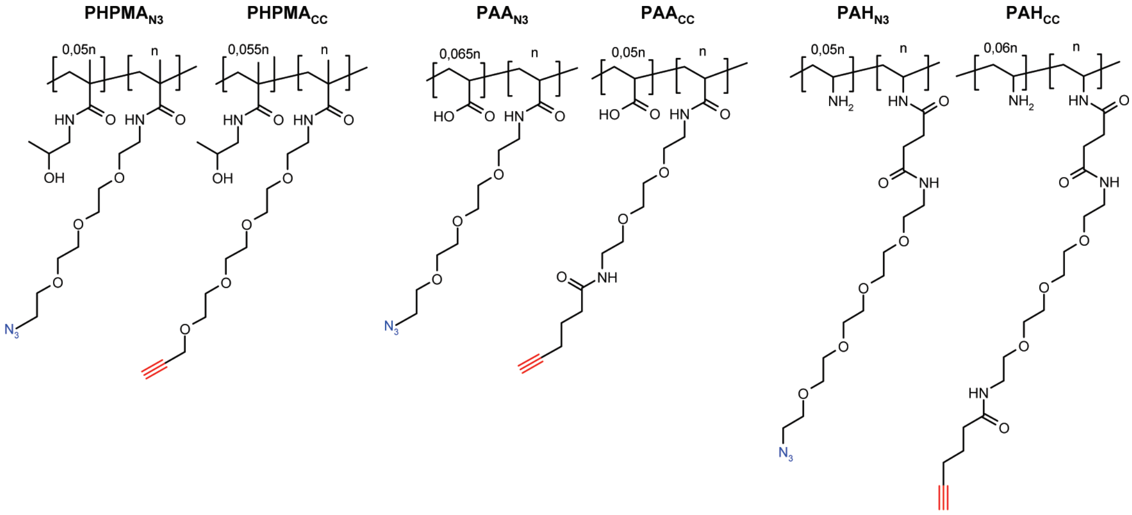
Scheme 2. Structures of Modified Polyelectrolytes PAA$_{\mathrm{N3}}$, PAA$_{\mathrm{C{\equiv}C}}$, PAH$_{\mathrm{N3}}$, and PAH$_{\mathrm{C{\equiv}C}}$ and Prepared Neutral Polymers PHPMA$_{\mathrm{N3}}$ and PHPMA$_{\mathrm{C{\equiv}C}}$[a]



[a] CC stands for alkyne group C≡C and N3 for azide group.

coming from Cu(I) π-complexes. Experiments allowed us to demonstrate the existence of these complexes during the click-chemistry-assisted step-by-step film buildup. The existence of these Cu(I)−alkyne π-complexes is of extreme importance for the buildup of "clicked" films and permits the rationalization of their buildup rate.

Experimental Section

Three polymer backbones, namely, PAA, poly(*N*-hydroxypropylmethacrylamide) (PHPMA), and poly(allylamine hydrochloride) (PAH) were functionalized with 6 ± 1% of azide or alkyne groups. These groups are linked to the polymer backbone through ethylene oxide $(\mathrm{EO})_n$ linkers ($n = 2$ or 4). The structures of the functionalized polymers are shown in Scheme 2.

All film constructions were investigated by quartz crystal microbalance (QCM; D300 from Q-Sense, Goteborg). The normalized frequency shifts, $\Delta f/\nu$, of the third, fifth, and seventh overtones were equal to 12%, and the dissipation was very small, typically on the order of 10^{-6}. (See Figure S-1 in the Supporting Information.) These are the conditions for the validity of the Sauerbrey relation.[17] For some typical buildup examples, we compared the thicknesses calculated from the data with the Sauerbrey's equation and the Voigt−Voinova model, and both are very close. (See Figure S-1 in Supporting Information.) This shows the reliability of the calculated thickness. We thus used the Sauerbrey relation to determine the film thicknesses. (See Supporting Information.)[17] Synthesis and characterization details about polymers and all experimental methods are given in the Supporting Information. A typical film buildup begins with the deposition of a PEI-(PSS/PAH)$_3$ precursor film to become insensitive to the substrate and to improve the reproducibility of our experiments (PEI: poly(ethylene imine); PSS: poly(styrene sulfonate)). Then, we deposited a PAA$_{\mathrm{N3}}$ or PAA$_{\mathrm{C{\equiv}C}}$ layer, which was anchored on the precursor film through electrostatic interactions. We continued with the step-by-step click buildup procedure. Either an alkyne- or an azide-functionalized polymer was brought in contact with the film for 5 or 20 min in the presence of a Cu(I) solution generated in situ from $\mathrm{CuSO_4}$ (0.36 mg/mL) and sodium ascorbate (8.8 mg/mL). After this deposition step, the polymer solution was replaced by a 10 mM sodium nitrate solution for 10 min to limit the click-reaction during the rinsing step. The sodium nitrate concentration of the rinsing solution was chosen to keep the ionic strength constant, and its replacement did not affect the QCM signal significantly (frequency shift smaller than 2 Hz). Then, the "complementary" polymer solution was brought in contact with the film under similar conditions. All experiments were performed at 25 °C and pH 4.

Table 1. Average and Standard Deviation of the Thickness Increments Derived from the Normalized Frequency Shift at 15 MHz (ν = 3) by using the Sauerbrey's Equation[a]

film constituents	thickness increment per bilayer (nm)
PAA$_{\mathrm{C{\equiv}C}}$/PAA$_{\mathrm{N3}}$	0.32 ± 0.09
PAA$_{\mathrm{N3}}$/PHPMA$_{\mathrm{C{\equiv}C}}$	11.4 ± 0.9
PAA$_{\mathrm{C{\equiv}C}}$/PHPMA$_{\mathrm{N3}}$	0.41 ± 0.09
PHPMA$_{\mathrm{C{\equiv}C}}$/PHPMA$_{\mathrm{N3}}$	1.18 ± 0.02
PAH$_{\mathrm{C{\equiv}C}}$/PAH$_{\mathrm{N3}}$	0
PAH$_{\mathrm{N3}}$/PHPMA$_{\mathrm{C{\equiv}C}}$	0.60 ± 0.05
PAH$_{\mathrm{C{\equiv}C}}$/PHPMA$_{\mathrm{N3}}$	0.36 ± 0.14

[a] In each case, three experiments were performed with a polymer adsorption time of 20 min.

Results and Discussion

The buildup was followed for the seven systems PAA$_{\mathrm{C{\equiv}C}}$/PAA$_{\mathrm{N3}}$, PAA$_{\mathrm{N3}}$/PHPMA$_{\mathrm{C{\equiv}C}}$, PAA$_{\mathrm{C{\equiv}C}}$/PHPMA$_{\mathrm{N3}}$, PHPMA$_{\mathrm{C{\equiv}C}}$/PHPMA$_{\mathrm{N3}}$, PAH$_{\mathrm{C{\equiv}C}}$/PAH$_{\mathrm{N3}}$, PAH$_{\mathrm{N3}}$/PHPMA$_{\mathrm{C{\equiv}C}}$, and PAH$_{\mathrm{C{\equiv}C}}$/PHPMA$_{\mathrm{N3}}$. Table 1 summarizes the thickness increments per bilayer for these systems. The graphic representation of the typical evolution of frequency shift for the buildup of each system is given in the Supporting Information (Figures S-2 to S-8).

In first approximation, all films grow linearly with the number of deposition steps, except the case of PAH$_{\mathrm{C{\equiv}C}}$/PAH$_{\mathrm{N3}}$, where no film construction is obtained. It appears that alkyne and azide groups do not play a symmetrical role in the film buildup.[18] Indeed, whereas the thickness increment is ~0.41 nm per bilayer for the PAA$_{\mathrm{C{\equiv}C}}$/PHPMA$_{\mathrm{N3}}$ system, it is ~11.4 nm per bilayer for the PAA$_{\mathrm{N3}}$/PHPMA$_{\mathrm{C{\equiv}C}}$ system. This huge difference can be attributed to the fact that PHPMA$_{\mathrm{C{\equiv}C}}$ becomes positively charged because of the formation of Cu(I)−alkyne π-complexes when it is brought into contact with Cu(I). The electrostatic interaction between CCH−Cu(I) distributed along the PHPMA chains and the carboxylic groups along the PAA chains favors the PHPMA/PAA electrostatic interactions and thus enhances the click reaction probability between the azide and alkyne groups.

By using modified PAH, the following buildup order of thickness increment is obtained: PAH$_{\mathrm{N3}}$/PHPMA$_{\mathrm{C{\equiv}C}}$ > PAH$_{\mathrm{C{\equiv}C}}$/PHPMA$_{\mathrm{N3}}$ > PAH$_{\mathrm{C{\equiv}C}}$/PAH$_{\mathrm{N3}}$. The formation of positively charged complexes along neutral PHPMA$_{\mathrm{C{\equiv}C}}$ chains should be

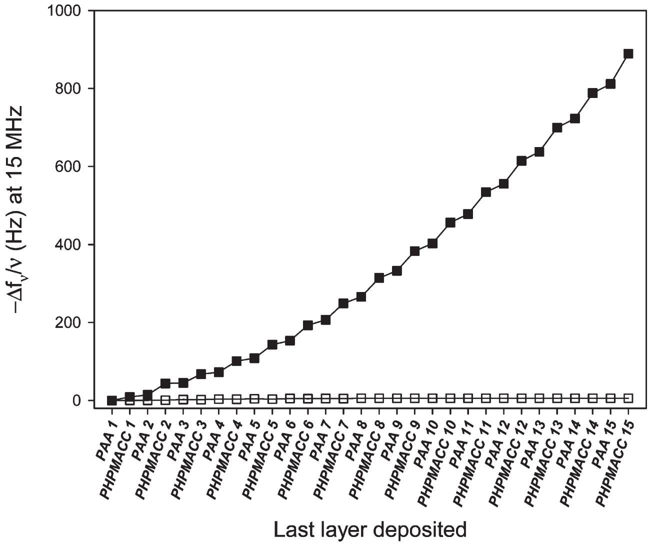


Figure 1. Evolution of the normalized frequency shift, measured at 15 MHz by QCM, of the PAA/PHPMA$_{C\equiv C}$ system as a function of adsorbed polymer layers performed, respectively, with sodium ascorbate (■) and without sodium ascorbate (□) at pH 4 with a polymer adsorption of 5 min.

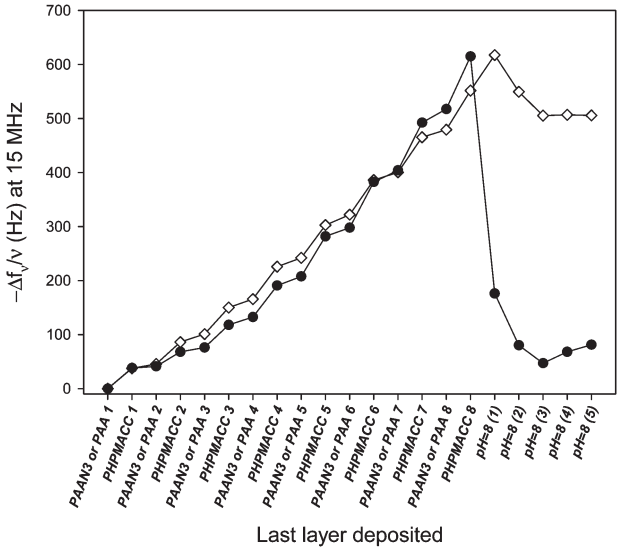


Figure 2. Evolution of the normalized frequency shift, measured at 15 MHz by QCM, of PAA$_{N3}$/PHPMA$_{C\equiv C}$ (◇) and PAA/PHPMA$_{C\equiv C}$ (●) as a function of adsorbed polymer layers. The buildup was performed at pH 4 with a polymer adsorption of 20 min. Five dissolution steps are performed at pH 8 with 10 mM of NaNO$_3$.

strongly favored compared with their formation along positively charged PAH$_{C\equiv C}$ chains. This could explain the weaker construction of PAH$_{C\equiv C}$/PHPMA$_{N3}$ compared with PAH$_{N3}$/PHPMA$_{C\equiv C}$. For PAH$_{N3}$/PAH$_{C\equiv C}$, strong electrostatic repulsion between PAH chains prevents the buildup of the film at pH 4 (the pH of the buildup) knowing that the pK_a of PAH is ~10.[19] Recently, Caruso's group has shown that the buildup of the click multilayers is pH-dependent, especially in the case of a system based on polycation.[20] The authors showed that by increasing the pH of the polycation solution, the buildup is better because of the reduction of electrostatic repulsion.

The less favorable buildup of PAH$_{N3}$/PHPMA$_{C\equiv C}$ compared with PAA$_{N3}$/PHPMA$_{C\equiv C}$ can also be explained by the repulsion between the CCH−Cu(I) complexes carried by PHPMA$_{C\equiv C}$ and the polycation PAH. One also observes the order PHPMA$_{C\equiv C}$/PHPMA$_{N3}$ > PAA$_{C\equiv C}$/PAA$_{N3}$ > PAH$_{C\equiv C}$/PAH$_{N3}$. The absence of electrostatic repulsions between PHPMA chains explains the better buildup of PHPMA$_{C\equiv C}$/PHPMA$_{N3}$ compared with PAA$_{C\equiv C}$/PAA$_{N3}$ and PAH$_{C\equiv C}$/PAH$_{N3}$ for which electrostatic repulsion between chains is present. Two reasons may explain the PAA$_{C\equiv C}$/PAA$_{N3}$ buildup compared with the absence of the PAH$_{C\equiv C}$/PAH$_{N3}$ buildup at pH 4: The charge density along the PAA chains, whose pK_a is ~4.5,[21] should be smaller than that along the PAH chains, leading to less electrostatic repulsion between the chains during the buildup, and the positively charged CCH−Cu(I) complexes should be stabilized along the negatively charged PAA chains. At first sight, this stabilization should favor the PAA$_{C\equiv C}$/PHPMA$_{N3}$ construction compared with PHPMA$_{C\equiv C}$/PHPMA$_{N3}$, yet the contrary is observed. This may be due to the intrachain interactions between these complexes and the PAA backbone, which tend to inhibit their reaction with the azide groups of the PHPMA chains.

To confirm the formation of the positively charged CCH−Cu(I) complexes on the polymer chains, a PHPMA$_{C\equiv C}$/PAA film was built in a Cu(II) solution in the presence and in the absence of sodium ascorbate. With this system, no click reaction could take place. The evolution of the normalized frequency shifts, measured by QCM, in both cases is given in Figure 1. In the absence of sodium ascorbate and thus of Cu(I), no film construction is observed, whereas in the presence of this reducer, the film construction takes place. This clearly confirms that the presence of Cu(I) is required for the in situ CCH−Cu(I) complex formation. Under such conditions, the film is held only through electrostatic interactions because no click reaction can take place. Moreover, the film buildup taking place over several hours also implies the long-term stability of the CCH−Cu(I) complexes.

Alkyne is a chemical function able to coordinate various transition metals,[22] and these complexes represent important intermediates in several chemical transformations.[23] Among them, the π-complex formed between carbon−carbon triple bond and silver ion Ag(I) has been well studied.[24] To validate the hypothesis of the presence of positively charged CCH−Cu(I) complexes further, we verified that PHPMA$_{C\equiv C}$/PAA films can also be built in the presence of Ag(I) ions instead of Cu(I), thus of CCH−Ag(I) π-complexes. A film construction is indeed observed with a thickness increment of 2.8 nm per bilayer. (See Figure S-9 in Supporting Information.)

Next, we verified that even if the construction is electrostatically assisted, click reaction takes place and confers mechanical strength to PAA$_{N3}$/PHPMA$_{C\equiv C}$ multilayers. At the end of such a film construction, we replaced the rinsing solution at pH 4 with a solution at pH 8 (Figure 2). After the buildup of eight PAA$_{N3}$/PHPMA$_{C\equiv C}$ bilayers, only one bilayer is lost after five rinsing steps at pH 8, whereas in the case of PAA/PHPMA$_{C\equiv C}$ film, the loss corresponds to seven bilayers. This confirms the film stability due to the presence of triazole groups linking PAA and PHPMA chains in the film. From this experiment, one can conclude that this construction is mainly driven by the electrostatic interaction between the positive Cu(I)−alkyne π-complexes on PHPMA and the carboxylic groups of PAA, and yet the click reaction takes place between the alkyne groups of PHPMA$_{C\equiv C}$ and the azide groups of PAA$_{N3}$ and confers mechanical stability to the film.

Conclusions

The step-by-step buildup through click reaction of polymer films does not require electrostatic interactions between the polymers. Yet, this type of interaction between CCH−Cu(I) complexes and the polymers can have important effects on the buildup process. It can favor the film buildup, as in the case of a neutral PHPMA polymer functionalized with alkyne groups interacting with a polyanion functionalized with azide groups. It can also disfavor the buildup as in the case of a neutral polymer functionalized with alkyne groups interacting with a polycation polymer functionalized with azide groups. This effect always superimposes to the conventional electrostatic interactions between polyelectrolyte chains. Finally, we highlighted that the positive Cu(I)−alkyne π-complex formed as intermediate during the catalytic cycle of click reaction has to be taken into account to understand film constructions and for the design of new multilayer films based on azide−alkyne click reaction.

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Supporting Information Available: Detailed synthesis of $\mathrm{PAH_{N3}}$, $\mathrm{PAH_{C\equiv C}}$, $\mathrm{PAA_{N3}}$, $\mathrm{PAA_{C\equiv C}}$, $\mathrm{PHPMA_{N3}}$, and $\mathrm{PHPMA_{C\equiv C}}$; polymer solutions and preparation of the films; build-up of $\mathrm{PHPMA_{N3}/PHPMA_{C\equiv C}}$ film: normalized frequency shift and dissipation versus time obtained by QCM and thickness evaluated by Sauerbrey's equation and Voigt−Voinova model; evolution of the normalized frequency shift for $\mathrm{PAH_{N3}/PHPMA_{C\equiv C}}$, $\mathrm{PAH_{C\equiv C}/PHPMA_{N3}}$, $\mathrm{PAH_{C\equiv C}/PAH_{N3}}$, $\mathrm{PHPMA_{C\equiv C}/PHPMA_{N3}}$, $\mathrm{PAA_{C\equiv C}/PAA_{N3}}$, $\mathrm{PAA_{N3}/PHPMA_{C\equiv C}}$, and $\mathrm{PAA_{C\equiv C}/PHPMA_{N3}}$ versus the last layer deposited; build-up of a $\mathrm{(PAA/PHPMA_{C\equiv C})_8}$ film in the presence of $\mathrm{AgNO_3}$ monitored by QCM. This material is available free of charge via the Internet at http://pubs.acs.org.

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