

Clicked into Place: Biomimetic Copolymer Adhesive for Covalent Conjugation of Functionalities

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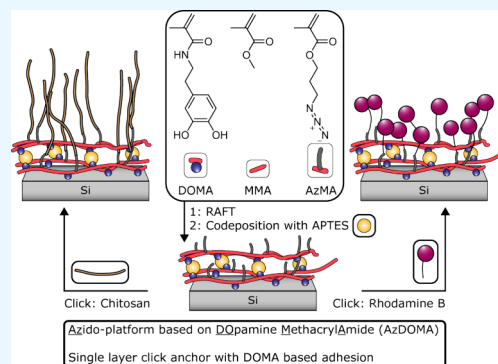


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ABSTRACT: Polydopamines (PDA) are a popular class of materials and promising candidates as adhesives for new fastening techniques. PDA layers can be formed on a wide range of substrates in various environments. Here, we present a novel method for functionalizing PDA-based copolymer films by using click chemistry. These copolymers adhere strongly to various surfaces and simultaneously have active groups that allow the attachment of functional groups. We discuss the coupling of two types of chitosan and a rhodamine B dye molecule to the alkyne groups of the copolymers by employing click reactions. Azidopropyl methacrylate (AzMA), methyl methacrylate (MMA), and dopamine methacrylamide (DOMA) are copolymerized and codeposited with (3-aminopropyl)triethoxysilane on silicon wafers, polyethylene (PE), and polytetrafluoroethylene (PTFE). AzMA provides the surfaces with azides for use in click reactions, MMA functions to control the polymer as a nonfunctional diluent, whereas DOMA provides adhesion, as well as cross-linking groups. After codeposition, the dyes are grafted to the copolymer to illustrate the ability of the films to link functional groups covalently. Fourier transform infrared spectroscopy confirms the successful click reaction in solution, and atomic force microscopy shows the surface morphologies following grafting. Fluorescence microscopy provides evidence of successful grafting. As an example of a possible application, layers exhibiting antifouling properties are prepared. Chitosan grafted to PE is tested for antifouling performance. These functionalized layers show nonspecific inhibition of protein adsorption. We find that chitosan can lower the adsorption of fluorescein-labeled bovine serum albumin (BSA) protein by more than 90% for the best performing fluorescein-labeled BSA protein and by more than 90% for the best-performing layer. These results demonstrate the viability of our PDA-based copolymers for surface functionalization through click chemistry grafting at challenging adhesion to surfaces.



INTRODUCTION

Polydopamines (PDAs) are a promising group of materials for tackling challenges in fastening.¹ PDA has found application as an adhesive for binding two surfaces together,^{2,3} but also for the formation of films,^{4–7} which can be functionalized^{8–10} or exhibit function.^{11–13} These catechol-based adhesives can be applied as a classical PDA film; however, the incorporation of catechols into polymer chains^{14–16} or hydrogels^{17,18} have also been utilized. These dopamine-based materials have found use, for example, on membranes for oil/water separation¹⁹ and titanium for antifouling in dental materials.²⁰

PDAs have been the subject of intensive research since the first discovery of their superior adhesive performance by Messersmith et al.²¹ in studies of the structure of mussel adhesive plaques. These mussel protein plaques contain considerable amounts of catechols and amines, also found in dopamine. Dopamine can be polymerized to form an adhesive layer on various substrates, from metals to polytetrafluoroethylene (PTFE) or polyethylene (PE).²¹ The same group also described the incorporation of dopamine into a copolymer to use as an adhesive coating on a micropillar surface.²²

Surface-initiated atom transfer radical polymerization (SI-ATRP) is a popular method for surface functionalization^{23–25}; however, they require the presence of initiator groups for polymerization. Alternatively, “grafting to” with click chemistry is a synthesis method through which complex materials can be readily and selectively coupled to surfaces in one reaction step.^{26–30} Thus, to widen the scope beyond SI-ATRP for which we have reported a platform earlier,³¹ we describe a PDA-like catechol-based system for functionalizing surfaces using click chemistry. Here, we use a monomer containing an azide group for click coupling.

As mentioned, dopamine methacrylamide (DOMA) is copolymerized with azidopropyl methacrylate (AzMA) and a methyl methacrylate (MMA) filler to obtain a material for

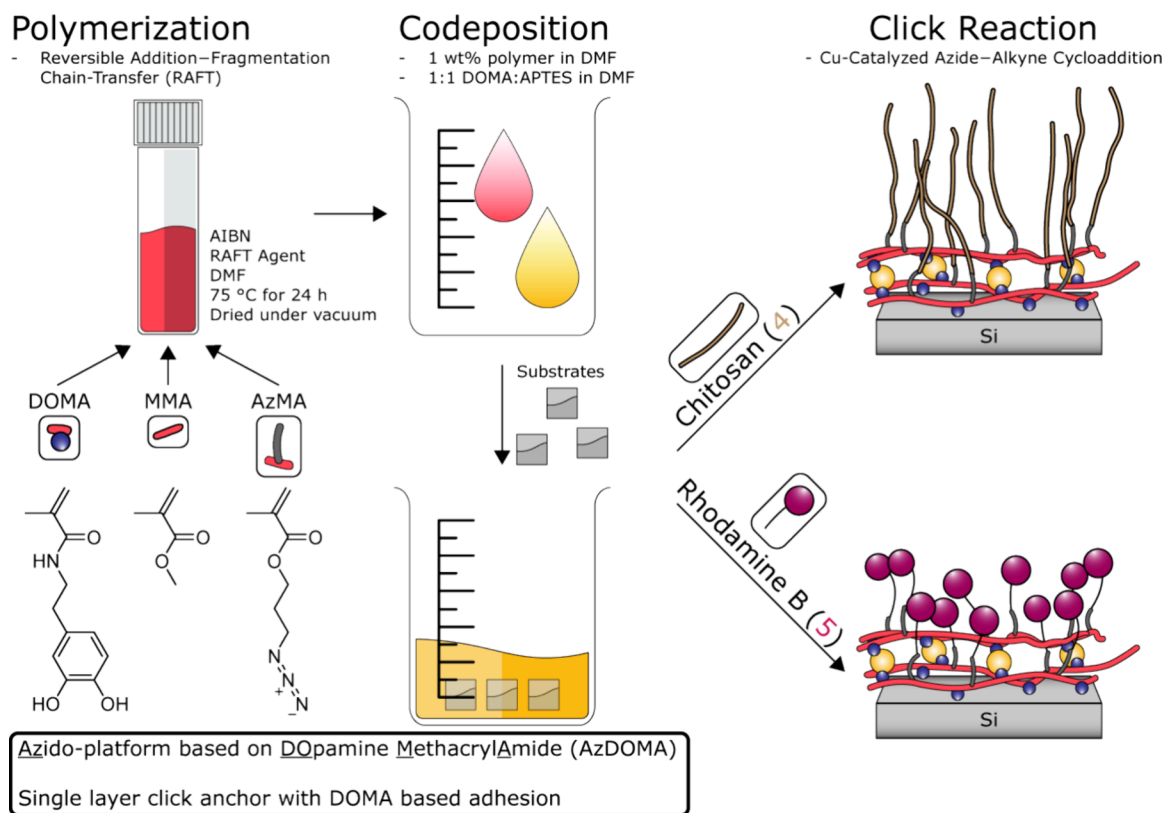
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Scheme 1. Schematic of the Application of Functionalities by a “Grafting to” Method Based on Click Chemistry^a

^aA copolymer is synthesized in RAFT polymerization using three monomers: adhesive DOMA, click-functional AzMA, and MMA for use as a neutral constituent for composition adjustment. This copolymer is applied to surfaces using codeposition in solution with APTES (yellow spheres) to provide improved cohesion. Functional groups are grafted to the surface through copper-catalyzed azide-alkyne cycloaddition (purple spheres), known as click reaction.

surface functionalization through click chemistry. These copolymers are applied using a codeposition method with (3-aminopropyl)triethoxysilane (APTES) to adjust the density of grafting sites on the surface as well as to engineer the layer thickness through cross-linking with catechol groups. The codeposition with APTES provides faster layer development and more stable layers through cross-linking the copolymer. A possible mechanism includes Michael-type addition,³² a reaction through which catechols can be modified.³³ The use of DOMA-containing copolymers works surprisingly well and renders the application of functional coatings based on a generic class of surface modifiers broadly applicable, containing various functional groups can be grafted to these surfaces, requiring only the presence of an alkyne triple bond, which is readily incorporated in DOMA-containing copolymers. We successfully adapted a method³⁴ used for the alkylation of rhodamine B and applied it to attach propargyl bromide to chitosan. Rhodamine B and chitosan are used to demonstrate the versatility of our PDA-based platform. The process of application to functionalization is shown in Scheme 1.

In the first step, the copolymer platform is synthesized by RAFT polymerization according to previously reported procedures.³¹ The copolymer is codeposited with APTES on the substrates. This provides a stable layer on the substrates, to which we introduce functionality through a click reaction. As mentioned, in the click reaction, either alkyne-functionalized rhodamine B dye or chitosan is grafted to the surface. The copolymer, dyes, and chitosan are characterized with ¹H NMR

and Fourier transform infrared (FTIR) measurements. After the test click reactions in solution, the silicon and PE substrates are functionalized and characterized by atomic force microscopy (AFM) and fluorescence microscopy. Finally, the chitosan layers are studied for antifouling performance by incubation in fluorescein-labeled bovine serum albumin protein solutions (BSA-FITC).

EXPERIMENTAL SECTION

Materials. (3-Aminopropyl)triethoxysilane (APTES, 99%), 2,2'-bipyridyl (Reagentplus, ≥ 99%), low *M_w* chitosan (50,000–190,000 Da), copper(I) bromide (CuBr, 97%), 4-cyano-4-(phenyl-carbonothioylthio)pentanoic acid (RAFT Agent, > 97%), dibenzyl ether (purum, 98%), dopamine HCl, fluorescein-labeled bovine serum albumin (BSA-FITC), methacrylic anhydride (94%), methacryloyl chloride (97%), methyl methacrylate (MMA, 99%), MgSO₄ (ACS Reagent, ≥ 97%), phosphor-buffered saline (PBS), polyethylene (HDPE, pellets, product code 547999), sodium bicarbonate (≥99.7%), sodium hydroxide (NaOH, ≥ 98%), sodium tetraborate decahydrate (≥99.5%), and sulfuric acid (ACS Reagent, 95%–97%) are bought from Sigma (Zwijndrecht, The Netherlands). CuBr is purified by cleaning 3× with acetic acid and subsequently 3× with ethanol. PBS solution is prepared by dissolving one tablet in 200 mL Milli-Q water. Ethyl Acetate (Analar Rectapur, 99.9%), *n*-hexane (GPR Rectapur, 98%), hydrochloric acid (35%), and methanol (GPR Rectapur, 100%) are purchased from VWR (Amster-

dam, The Netherlands). Azobisisobutyronitrile (AIBN), dimethylformamide (DMF, Emsure), and hydrogen peroxide (H_2O_2 , 30%) are obtained from Merck. AIBN is purified by recrystallization from methanol. Chitosan oligosaccharides (oligochitosan, 300–3000 Da), 3-chloro-1-propanol (>98.0%), dopamine HCl, and rhodamine B (>95.0%) are purchased from TCI Chemicals (Zwijndrecht, Belgium). Milli-Q water is acquired using a Milli-Q Advantage A10 purification system (Millipore, Billerica, MA, USA). Silicon wafers (100.0 \pm 0.5 mm diameter and 525 \pm 25 μm thickness, boron-doped with (100) orientation, 5–10 Ω cm, Okmetic, Finland) are obtained from the Nanolab of the MESA+ Institute of the University of Twente. HDPE square pieces are prepared by hot pressing HDPE pellets at 100 $^\circ\text{C}$ into larger flat substrates and cutting.

Azidopropyl Methacrylate (AzMA) Synthesis. Azidopropanol is synthesized according to published procedures.³⁵ The procedure for synthesizing azidopropyl methacrylate is adapted from Moon et al.³⁶ Briefly, 3.3 mL of TEA (23.7 mmol) is added to a solution of 2.0 g of azidopropanol (19.8 mmol) in 10 mL of dichloromethane and 0.1 g of MEHQ at room temperature. Next, 2.3 mL of methacryloyl chloride (23.7 mmol) is added dropwise at 0 $^\circ\text{C}$ in 10 min. This mixture is stirred at 0 $^\circ\text{C}$ for 1 h and then left to stir at room temperature for 24 h. The solution is washed with 10 vol% HCl, water, 10 wt % NaOH, and finally again with water. The resultant DCM solution is dried over MgSO_4 . MEHQ (0.1 g) is added to this solution and then dried at reduced pressure.

Copolymer Synthesis. The copolymerization protocol is adapted from our previous report, where 2-(2-bromoisobutyryloxy)ethyl methacrylate is replaced by AzMA. For the polymers used for the solution click reactions, the DOMA is replaced with an equivalent molar amount of MMA.

Codeposition. Two centimeters by 5 cm Si wafers (2 cm \times 5 cm) are cleaned using a 3:1 H_2SO_4 : H_2O_2 piranha solution for 30 min. *Take care when handling piranha as it can react violently with organic materials.* PE and PTFE substrates are cleaned by sonication in isopropanol for at least 30 min. One Si wafer and one PE substrate are added to a 50 mL Erlenmeyer flask. PTFE substrates are placed in a flask.

For both: 95 mg of AzDOMA (1 wt % total) is dissolved in 9 mL of DMF and 41 mg of APTES (0.19 mmol, 1:1 APTES:DOMA) is dissolved in 1 mL of DMF. The AzDOMA and APTES solutions are added to the flask containing the substrates. In the case of Si and PE, the flask is placed on a shaking table for 24 h, whereas the flask containing the PTFE substrates is stirred for 24 h. In both cases, the substrates are rinsed with copious amounts of water and acetone to remove and dissolve any unreacted copolymer and subsequently dried under nitrogen.

Rhodamine B and Chitosan Alkyne Coupling. The procedure for alkyne coupling is adapted from Schachtsneider et al.³⁴ Briefly, 2 g of rhodamine B (4.16 mmol), low M_w chitosan, or oligochitosan is added to 9 mL of DMF together with 1.62 g of K_2CO_3 (11.7 mmol) and 1.6 mL of propargyl bromide (80% in toluene, 16.7 mmol). The solution is stirred for 24 h at 60 $^\circ\text{C}$ after which it is precipitated in ethyl ether or water, for rhodamine B or either chitosan, respectively. The excess liquid is removed, and the product is dried under vacuum.

Click Reaction. The reaction is adapted from Wu and Gao.³⁷ Briefly, 0.1 g of rhodamine B-alkyne is added to 10 mL of DMF in a round-bottom flask and purged under nitrogen.

CuBr (16.64 mg, 0.12 mmol) and 0.05 g of AzMA-co-MMA when applicable and 24.6 μL of PMDETA (0.12 mmol) are added to a separate round-bottom flask and purged under nitrogen. After 20 min of purging, the contents of the first flask are added to the second flask to stir.

In the case of a reaction in solution, the solution is left to stir for 24 h under nitrogen overpressure and then precipitated in ethyl ether. The precipitate is dissolved in DCM and then reprecipitated in ethyl ether. The excess liquid is removed, and the powder is dried in vacuum at 40 $^\circ\text{C}$ overnight.

For surface modifications, three codeposited substrates are placed in an Erlenmeyer flask and purged for 20 min under nitrogen. Subsequently, the combined solution is added to the Erlenmeyer flask and left for 24 h under nitrogen overpressure. The substrates are then taken out, rinsed with copious amounts of water, followed by acetone, and dried under nitrogen.

AFM. AFM imaging is performed in Tapping Mode on a Multimode 8 AFM instrument operated with a JV vertical engage scanner and a NanoScope V controller (Bruker, Santa Barbara, CA, USA). Model NCH cantilevers (Nanoworld, Switzerland) are used with a spring constant of 42 N/m and a tip radius curvature of less than 8 nm. All AFM images are treated with the Flatten (0th order) and Plane Fit (1st order) calculations in the NanoScope Analysis 2.0 software.

FTIR Spectroscopy. Single-reflection FTIR spectra are obtained with a Bruker Alpha FTIR spectrometer equipped with a Platinum ATR single reflection crystal (Bruker Optic GmbH, Germany). Spectra were obtained between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1} at 64 scans.

Fluorescence Microscopy. An inverted Olympus IX71 fluorescence microscope (Olympus, Japan) is utilized. It is equipped with an IX2-RFAC reflector turret filter cube with excitation and emission wavelengths of 460–490 and 525 and 510–550 and 590 nm for biofouling and rhodamine fluorescence, respectively.

Antibiofouling Assessment. Two milligrams portion of BSA-FITC is dissolved in 20 mL of PBS solution to obtain a 0.1 mg mL^{-1} solution. Substrates are incubated in 2 mL solution for 3 h in the dark at 37 $^\circ\text{C}$. FITC is characterized using 460–490 nm excitation and 525 nm emission filter cube set. Images are processed using the ImageJ software, version 1.53e.

RESULTS AND DISCUSSION

To make functional surfaces using click chemistry from a polymer platform, two things are needed: an azide-containing (adhesive) copolymer and alkyne-coupled functional molecules. The copolymer is synthesized using our previously published method.³¹ Briefly, azidopropanol is synthesized according to the literature,³⁸ subsequently coupled to a methacrylate group.³⁶ This monomer is then used to synthesize the copolymer. The structure of this copolymer is shown in Scheme 2A.

The copolymers are functionalized using click chemistry according to the procedure from Wu and Gao.³⁷ First, to confirm the click functionality, an additional polymer without DOMA is prepared because DOMA will cross-link and precipitate in the presence of the copper catalyst used. The FTIR spectrum of the copolymer (Figure 1) shows the azide group at 2100 cm^{-1} as well as the groups corresponding to ester bonds in methacrylates at 1750, 1400, and 1300–1100 cm^{-1} .

Scheme 2. Chemical Structures of (A) the AzDOMA Random Copolymer and (B) the Alkyne-Functionalized Dye and Chitosan

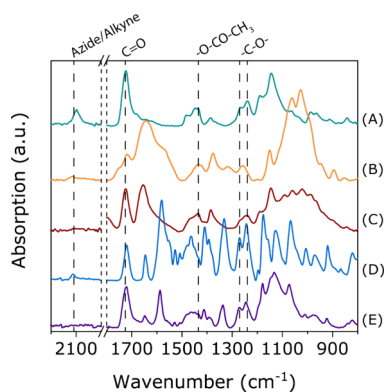
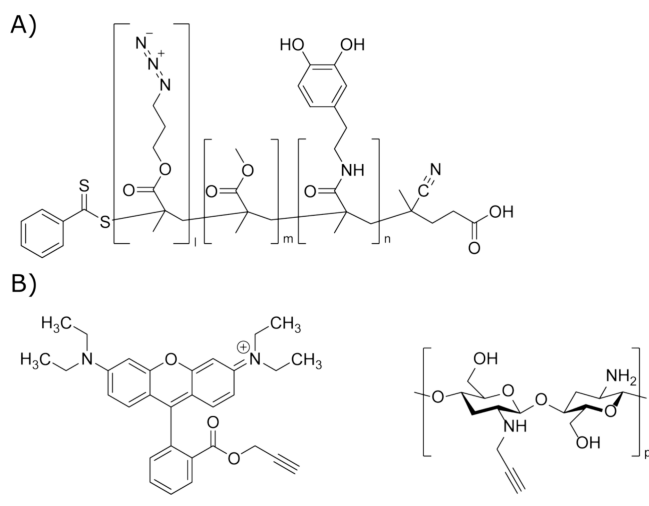


Figure 1. Cut out of the FTIR spectra of (top to bottom) the AzMA-copolymer without (A) DOMA, (B) alkyne-functionalized chitosan, (C) chitosan-clicked copolymer, (D) alkyne-functionalized dye, and (E) dye-clicked copolymer. The peaks around 2100 cm^{-1} in the spectra of the copolymer and functionalized chitosan/dye prove the presence of azide and alkyne functionalities, respectively. The full spectrum is given in the Supporting Information (Figure S1).

Rhodamine B and chitosan are coupled to propargyl bromide according to a procedure adapted from Schachtschneider et al.³⁴ The FTIR spectra of the products are shown in Figure 1 in spectra (B) and (D), for chitosan and rhodamine B, respectively. The spectra for both the chitosan and the dye also

show the presence of alkyne groups at around 2100 cm^{-1} as the azide group.

The FTIR spectra of the products of the click reactions are given in Figure 1 as well, that is, panels (C) and (E) for the chitosan and dye coupling reactions, respectively. Neither of these spectra show either the alkyne or the azide peak at $\sim 2100\text{ cm}^{-1}$ while showing spectra resembling a combination of the chitosan or dye with the copolymer. Specifically, the chitosan-clicked spectrum (Figure 1C) shows the broad peaks around 1600 and $1200\text{--}800\text{ cm}^{-1}$ of chitosan groups and the sharp peak at 1750 cm^{-1} for the polymer. In the dye-clicked spectrum (Figure 1E), several peaks are visible from 1650 to 1200 cm^{-1} of the dye (Figure 1D), whereas $1200\text{--}1000\text{ cm}^{-1}$ shows peaks of the copolymer. Based on the spectra, we conclude that the click reactions between chitosan and the copolymer and between the dye and the copolymer have been successfully performed. The next step is to apply these molecules to surfaces.

For surface functionalization, we chose Si and PE substrates. These materials are coated using codeposition with an APTES:AzDOMA (1:1) solution at 1 wt % AzDOMA in DMF. Subsequently, click reactions are carried out with the rhodamine dye and characterized using fluorescence microscopy. Representative photographs of the measurements are shown in Figure 2. In 2A, the usually smooth surface of Si wafers is coated by a rough red layer. The uneven surface is most likely caused by the shaking motion of the solution during application, which causes uneven deposition. However, the PE surface shown in 2B is uniformly red, and the apparent roughness is attributed to the roughness of the PE surface itself. The uniformity of the red color indicates that the layer is much more homogeneous than that on the Si substrate.

The surface functionalization is characterized again by using FTIR, given in Figure 3. The surface measurement in the bottom spectrum clearly shows the presence of AzDOMA on the surface. However, the dye does not show as strongly likely due to a lower rate of reaction as a result of diffusion toward and steric hindrance from the azide groups at the surface. Nonetheless, together with the fluorescence microscopy results and the striking lack of a peak at 2100 cm^{-1} , we clearly show the covalent binding of the dye to the surface. These results are compared to those of a third set of substrates, PTFE, as shown in Figure 4.

Figure 4 displays a PTFE substrate coated with AzDOMA and clicked with rhodamine B (4A), with a zoomed-in view using fluorescence microscopy on the right (4B). The pockmarks seen on the surfaces in 4B are most likely from

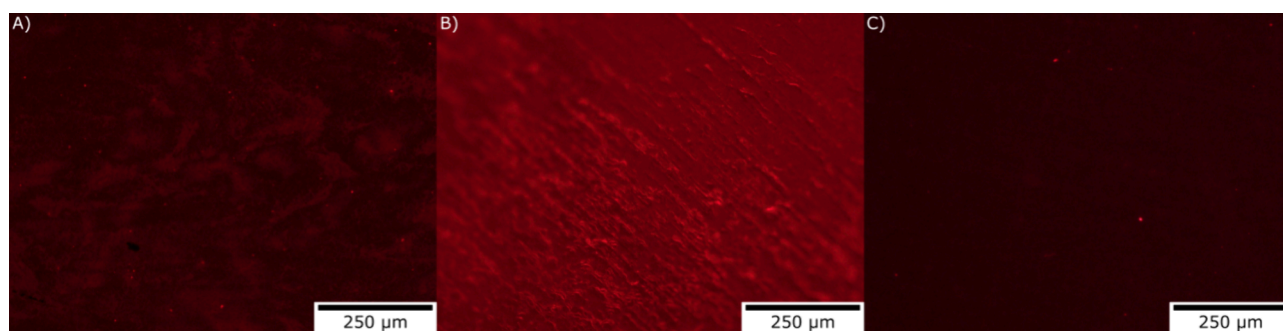


Figure 2. Fluorescence microscopy images of codeposited AzDOMA layers clicked with rhodamine B dye on (A) Si and (B) PE. (C) Image shows a PE surface without AzDOMA that was also added to the click reaction mixture for reference. Brightness increased by 33% for viewing purposes.

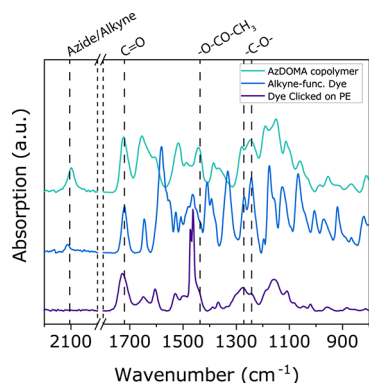


Figure 3. Cut out of the FTIR spectra of (top to bottom) the AzDOMA-copolymer, alkyne-functionalized dye, and dye-clicked copolymer on PE. The peaks around 2100 cm^{-1} in the spectra of the copolymer and functionalized dye prove the presence of azide and alkyne functionalities, respectively. The full spectra are given in the Supporting Information (Figure S2).

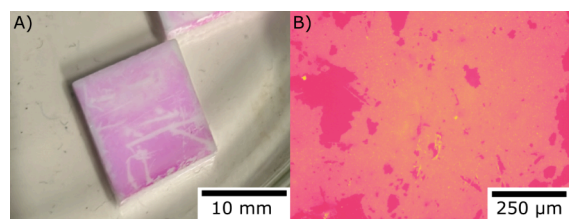


Figure 4. (A) Photograph of a PTFE coated with codeposited AzDOMA clicked with rhodamine B dye. (B) Fluorescence microscopy image of codeposited AzDOMA clicked with rhodamine B dye on a PTFE substrate. The darker pink spots correspond to the reflection of the bare substrate, whereas the salmon and yellow parts correspond to areas coated by the copolymer and dye.

the inherent surface roughness of the material itself. A strongly fluorescent layer can be seen, colored salmon to yellow at its most intense areas, compared to a more muted red of the Si and polyethylene substrates. Combining this information, our DOMA-based copolymer is used successfully to functionalize PTFE surfaces. This is an interesting result due to PTFE's low surface energy, which is not conducive to the adhesion of coatings. The coating of PE as well as PTFE show the versatile adhesive strength of mussel-based adhesion.

In the next case, we discuss rendering our coating layer antifouling by clicking chitosan groups. First, we discuss the surface morphology of the layers, as surface coverage with the antifouling component, chitosan, in this case, should be as

complete as possible. To this end, AFM is utilized to characterize the morphology after the click reaction. For completeness, we also characterized the dye-clicked surface. The corresponding AFM height maps are shown in Figure 5. Compared to smooth Si substrates (see Figure S3, Supporting Information), the codeposited layer in Figure 5A exhibits surface roughness over the entire surface. A similar surface is observed after dye coupling, most likely because the dye molecule is not very large compared to the polymer. However, when the chitosan is clicked, a significant difference is visible regarding the surface structure. The low M_w chitosan structure in 5C shows small spherical particles stuck to the surface. They are identified as collapsed chitosan chains, as they are not solvated. These particles, however, do not fill in the “valleys”, likely due to their size and steric hindrance. Instead, the surface looks like it maintained the roughness structure from the codeposited AzDOMA layer. The presence of these structures after a thorough washing indicates that the particles are not physisorbed. A similar morphology is seen in 5D, where these particles are still present but have become smaller due to the smaller chain length of oligochitosan (300–3000 Da) compared to the low M_w chitosan. We conclude here that the dye molecules and both varieties of chitosan can be covalently bound to surfaces using click chemistry. The layer thickness, as measured through step height values in AFM, is shown in Table 1.

Table 1. Step Height Values for the Codeposited Polymer Layers and Functionalities Grafted by Click Reactions^a

polymer	step height (nm)	σ (nm)
AzDOMA-APTES	52.9	3.1
AzDOMA-APTES + grafted rhodamine	107.6	49.0
AzDOMA-APTES + grafted low M_w chitosan	90.6	7.9
AzDOMA-APTES + grafted oligochitosan	113.6	20.0

^aStandard deviation values are also shown.

Following the imaging of the coatings functionalized with the clicked antifouling component, we describe their antifouling performance. We used BSA, labeled with fluorescent FITC (BSA-FITC). Samples are submerged in a BSA-FITC solution for 3 h at 37 °C. The substrates are then observed under a fluorescent microscope, where the intensity of the image is used to represent the coverage by the fluorescent protein. The fluorescence intensity values of the samples are normalized between uncoated PE and incubated, uncoated PE as the 0 and 100% reference points, respectively. The results, including the references, are shown in Figure 6.

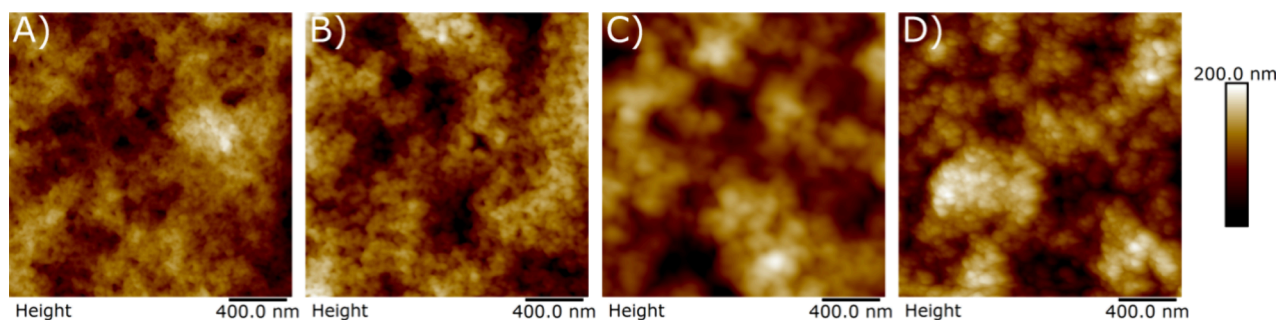


Figure 5. AFM tapping mode height images of (A) AzDOMA codeposited with APTES, (B) AzDOMA-APTES clicked with rhodamine dye, (C) AzDOMA-APTES clicked with low M_w chitosan, and (D) AzDOMA-APTES clicked with oligochitosan.

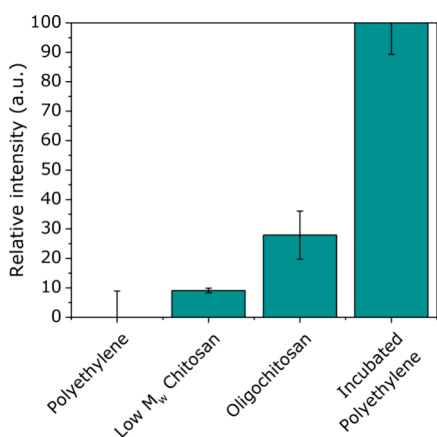


Figure 6. Relative intensity of the BSA-FITC fluorescence emission on chitosan-clicked PE substrates. The data points are normalized between uncoated PE and incubated, uncoated PE.

Here, we see the results from four different surfaces: unincubated PE, low M_w chitosan-clicked PE, oligochitosan-clicked PE, and incubated PE. The first and last cases are used for normalization. Both chitosan types drastically reduce fluorescent response intensity, indicating drastically reduced protein adsorption. The low M_w chitosan even reduces the protein adsorption by over 90%. These essential results provide striking evidence for a facile surface antifouling approach, as both chitosan-covered substrates reduce protein adsorption. However, the longer chains reduce fouling much more than the shorter oligo chains. There are two possible explanations for this observation: (A) Longer chains mean better coverage and thus less protein adsorption, or (B) it is related to different solubilities of the chitosan types. During synthesis, we observed that both chitosans form a suspension in DMF; however, the oligochitosan, when alkynized, dissolves in DMF, while on the contrary, the low M_w chitosan never fully dissolves. Potentially, the increased solubility of alkyne-oligochitosan means that it is alkynized to a further degree, and it is capable, in general, to react with multiple azides on the surface, leading to a loop-like structure on the surface, whereas the low M_w chitosan mainly takes the form of chains attached at only one end.

CONCLUSIONS

We describe the successful synthesis and application of terpolymers comprising dopamine for adhesion enhancement to various substrates and azide groups for subsequent coupling of functional groups by click chemistry. Substrates that we utilize include silicone oxide, PE, and PTFE. A coupling of rhodamine B dye is utilized to prove the functionalization concept, while chitosan is attached to render the surface antifouling. The reaction of the azides and alkynes in solution is confirmed using FTIR spectroscopy. Chitosan is used as a showcase where biofouling activity can be inhibited by more than 90%, depending on the chitosan chain length. The binding of smaller molecules, demonstrated with rhodamine B even on PTFE surfaces, can function as a platform for surface tagging, where the to-be-grafted molecule is decided on demand for security or identification purposes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c03428>.

Infrared spectra of the copolymers, alkyne functionalized dye, and dye clicked to PE; AFM image of clean Si-wafer substrate; NMR spectra of azidomethacrylate monomer and AzDOMA (PDF)

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Notes

The authors declare no competing financial interest.

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