

Published in final edited form as:

*J Am Chem Soc.* 2012 June 6; 134(22): 9498–9505. doi:10.1021/ja303369p.

## Polymer Composition and Substrate Influences on the Adhesive Bonding of a Biomimetic, Cross-Linking Polymer

Cristina R. Matos-Pérez<sup>1</sup>, James D. White<sup>1</sup>, and Jonathan J. Wilker<sup>1,2,\*</sup>

<sup>1</sup>Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907-2084, USA

<sup>2</sup>School of Materials Engineering, Purdue University, Neil Armstrong Hall of Engineering, 701 West Stadium Avenue, West Lafayette, IN 47907-2045, USA

### Abstract

Hierarchical biological materials such as bone, sea shells, and marine bioadhesives are providing inspiration for the assembly of synthetic molecules into complex structures. The adhesive system of marine mussels has been the focus of much attention in recent years. Several catechol-containing polymers are being developed to mimic the cross-linking of proteins containing 3,4-dihydroxyphenylalanine (DOPA) used by shellfish for sticking to rocks. Many of these biomimetic polymer systems have been shown to form surface coatings or hydrogels, however bulk adhesion is demonstrated less often. Developing adhesives requires addressing design issues including finding a good balance between cohesive and adhesive bonding interactions. Despite the growing number of mussel mimicking polymers, there has been little effort to generate structure-property relations and gain insights on what chemical traits give rise to the best glues. In this report, we examined the simplest of these biomimetic polymers, poly[(3,4-dihydroxystyrene)-*co*-styrene]. Pendant catechol groups (i.e., 3,4-dihydroxystyrene) were distributed throughout a polystyrene backbone. Several polymer derivatives were prepared, each with a different 3,4-dihydroxystyrene content. Bulk adhesion testing showed where the optimal middle ground of cohesive and adhesive bonding resides. Adhesive performance was benchmarked against commercial glues as well as the genuine material produced by live mussels. In the best case, bonding was similar to cyanoacrylate “Krazy” or “Super” glue. Performance was also examined using low (e.g., plastics) and high (e.g., metals, wood) energy surfaces. Adhesive bonding of poly[(3,4-dihydroxystyrene)-*co*-styrene] may be the strongest of reported mussel protein mimics. These insights should help us to design future biomimetic systems, thereby bringing us closer to development of bone cements, dental composites, and surgical glues.

### INTRODUCTION

Adhesives play a prominent role in everyday life, being used in several industries including aerospace, automobile manufacturing, housing construction, wood products, packaging, and labeling.<sup>1,2</sup> Worldwide revenue generated by adhesives topped \$40 billion in 2010.<sup>3</sup> New roles for specialty adhesives will be found once we can develop the materials in demand for applications including surgical adhesives, orthopedic cements, and dental glues. Marine biology can provide inspiration for the design of such materials. The natural adhesive system of marine mussels is receiving growing interest in the context of biomimetics. These shellfish affix themselves to wet rocks by assembling a cross-linked matrix of proteins.<sup>4,5</sup> Essential to the cross-linking chemistry of these proteins is the 3,4-dihydroxyphenylalanine (DOPA) residue.<sup>4,5</sup> Several proteins have been isolated from mussel adhesive plaques, each

\*To whom correspondence should be addressed. wilker@purdue.edu.

with DOPA comprising between 3% and 30% of the total amino acid content.<sup>4,5</sup> A mechanism we have proposed for the formation of mussel adhesive involves  $\text{Fe}^{3+}$  templating DOPA residues followed by redox chemistry to generate radicals.<sup>6–13</sup> Reactivity of these radicals may bring about protein-protein coupling for cohesive bonding within the bulk material and protein-substrate linkages for surface adhesive bonding.<sup>12,13</sup> Alternatively or perhaps complementary is direct binding of DOPA to high energy surfaces via metal chelation,<sup>14–18</sup> individual metal-ligand bonds,<sup>16,19</sup> non-specific adsorption,<sup>18</sup> or hydrogen bonding.<sup>18,20</sup> Oxidative<sup>21,22</sup> and enzymatic<sup>21–23</sup> cross-linking may also be involved.

Incorporating DOPA and analogous reactive groups such as catechol (i.e. 1,2-dihydroxybenzene) into polymers is being pursued for a variety of applications. This field is expanding rapidly, especially in the last 5 years, with many laboratories contributing.<sup>24</sup> Mussel mimetic polymers are being generated from polypeptides,<sup>25–27</sup> polyamides,<sup>28</sup> polyacrylates,<sup>17,29–35</sup> polyethylene glycols,<sup>36–52</sup> polystyrenes,<sup>53–59</sup> and polyurethanes.<sup>60</sup> These polymers are enabling the development of imaging agents,<sup>48</sup> nanoparticle shells,<sup>44,48,61</sup> elastomers,<sup>30,33,59</sup> resins,<sup>58,62</sup> coacervates,<sup>31</sup> hydrogels,<sup>36–38,42,43</sup> surface treatments,<sup>27,40,49,52</sup> antibacterial coverings,<sup>51,63</sup> and antifouling coatings.<sup>34,35,45–47,50,51</sup> A subset have shown the ability to bond two substrates together.<sup>25,26,29–33,36–42,53,54,60</sup>

Whereas a coating only requires adhesive bonding to the surface of interest, bulk glues also need the presence of cohesive forces. These cohesive interactions are required to form the majority of the material and reach between substrates to yield a functional glue. Too much cohesion, however, will result in a hardened material without significant affinity for a surface. Likewise, too much adhesive bonding will come at the expense of cohesion and the bulk material will not exist. This balance of cohesion and adhesion can be elusive, with no way to predict where an optimal interplay may reside.

Despite the growing number of synthetic systems mimicking aspects of mussel adhesive proteins, there have been few detailed and systematic insights to illustrate which aspects of the polymers give rise to the greatest bulk adhesion. In particular, performance enhancements will arise from understanding how the polymer composition dictates function. In other words: How much pendant catechol should a polymer contain in order to achieve the strongest bulk bonding? Consequently, we embarked upon a structure-property study in which the relative contributions of cohesion and adhesion could be changed systematically by altering the polymer composition. The resulting insights will show where one might find the highest performing biomimetic material.

In an effort to gain straightforward chemical insights and also to keep future scale up in mind, our mimics of mussel adhesive proteins are kept as simple as possible. The DOPA amino acid can be stripped down to only a catechol group pendant from a polymerizable olefin, hence the choice of 3,4-dihydroxystyrene (Figure 1). To minimize structural and thermal perturbations to the host polymer resulting from this monomer, polystyrene was chosen to represent a protein backbone (Figure 1). Styrene is commercially available and easy to polymerize on large scales. A further advantage for these studies is that polystyrene, alone, does not exhibit any appreciable bonding capability.<sup>53</sup> The target copolymers are thus poly[(3,4-dihydroxystyrene)-*co*-styrene], shown in Figure 1.

Copolymers were prepared by a two step synthetic route developed in our laboratory previously.<sup>53</sup> We have also made cationic versions of these cross-linking polymers.<sup>54</sup> Polymerization of styrene and 3,4-dimethoxystyrene yielded polymers for which the ratio of monomers in the final polymers was generally a reflection of the starting feed.<sup>53</sup> The styrene and 3,4-dihydroxystyrene monomers distribute throughout the copolymer statistically or randomly, thereby providing a suitable model for how DOPA residues are located within

mussel adhesive proteins.<sup>53</sup> The relatively simple synthesis allows access to large quantities of polymer, up to ~20 grams per reaction in an academic laboratory. Our initial effort with poly[(3,4-dihydroxystyrene)-*co*-styrene] found lap shear bulk adhesion at up to  $1.2 \pm 0.5$  MegaPascals (MPa).<sup>53</sup> Over 1 MPa (~145 pounds per square inch or PSI) can be considered in the realm of high strength bonding and, once achieved, will enable development of applications in several fields.<sup>1,2</sup> Of course, even stronger bonding is often desired.

Several factors influence the performance of an adhesive including the substrate type, surface preparation (e.g., roughness), cure conditions (e.g., temperature, time, humidity), solvent, concentration, and viscosity.<sup>2</sup> Beyond such formulation issues, an appealing chemical aspect to explore is that of polymer composition. By varying the ratio of 3,4-dihydroxystyrene:styrene within poly[(3,4-dihydroxystyrene)-*co*-styrene], we can gain access to a family of adhesive copolymers with varied degrees of cross-linking. This type of systematic study has not been carried out in detail with any other mussel mimetic polymer system. Bonding performance described below was examined on an array of low to high energy surfaces: poly(tetrafluoroethylene) (Teflon), poly(vinyl chloride) (PVC), polished aluminum, sanded steel, and wood. Polymer composition turns out to be a major factor dictating bonding performance. This study presents the synthesis, characterization, and bulk-adhesion of several polymers. We are excited to report that the strongest bonding of these polymers displays adhesion on par with commercial products such as “Krazy” or “Super” glues, albeit with very different adhesion chemistry.

## EXPERIMENTAL SECTION

Styrene and 3,4-dimethoxystyrene monomers were purchased and purified with alumina columns for removal of polymerization inhibitors. Details are provided in our earlier report.<sup>53</sup> Solvents were commercial anhydrous grade. A Varian Inova-300 MHz spectrometer was used to collect NMR spectra. Gel permeation chromatography (GPC) data were obtained using a Polymer Laboratories PL-GPC20 system and THF eluent. Polystyrene GPC standards (Varian, Inc.) were used for instrument calibration. Differential scanning calorimetry (DSC) data were obtained with a TA Instruments DSCQ2000.

### Synthesis of Poly[(3,4-dimethoxystyrene)-*co*-styrene] Copolymers

In a typical polymerization 2.86 mL (24.9 mmol) of styrene and 3.70 mL (25.0 mmol) of 3,4-dimethoxystyrene were added to a round bottom flask with 30 mL of anhydrous toluene. The reaction was cooled to  $-78\text{ }^{\circ}\text{C}$  and, after 10 min, 0.17 mL of *n*-butyllithium was added drop-wise. The solution turned orange, was stirred under an argon atmosphere for 8 h at  $-78\text{ }^{\circ}\text{C}$ , and then allowed to warm to room temperature for an additional 12 h of reaction. Polymerization was quenched by addition ~1 mL methanol. Further addition of ~100 mL cold ( $-20\text{ }^{\circ}\text{C}$ ) methanol precipitated the polymer. After isolation by filtering and drying under vacuum, at least three rounds of dissolution in chloroform (~15 mL) and precipitation with methanol (~100 mL) were used to remove unreacted monomers. Yield of poly[(3,4-dimethoxystyrene)<sub>33</sub>-*co*-styrene<sub>67</sub>] was 4.4 g, 33 mmol, 66%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.6–2.3 ppm (broad, polymer backbone), 3.4–3.8 ppm (broad, methoxy peaks), 6.0–7.4 ppm (broad, aromatic).

### Synthesis of Poly[(3,4-dihydroxystyrene)-*co*-styrene]

Treatment with BBr<sub>3</sub> and an acidic work up yielded the catechol-containing polymers according to our previous methods.<sup>53</sup> A typical deprotection was accomplished by dissolving poly[(3,4-dimethoxystyrene)<sub>33</sub>-*co*-styrene<sub>67</sub>] (4.4 g, 33 mmol) in 50.0 mL of anhydrous dichloromethane (DCM) under an argon atmosphere. The reaction was cooled to  $0\text{ }^{\circ}\text{C}$  and, after 10 min, BBr<sub>3</sub> (1.2 mL, 13 mmol) was added dropwise over 10 min. The

solution was warmed up to room temperature and stirred overnight (~12 h). The polymer was treated with 1% HCl followed by an aqueous work up to obtain poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>] (3.6 g, 27 mmol, 82%). Loss of the <sup>1</sup>H NMR methoxy peaks indicated complete deprotection. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.6–2.3 ppm (broad, polymer backbone) and 6.0–7.4 ppm (broad, aromatic).

## Adhesion Studies

Substrates for lap shear testing were prepared by cutting each material into rectangular pieces, 8.89 cm long by 1.25 cm wide. A centered hole of 0.64 cm diameter was drilled into each adherend 2.22 cm from one end. Aluminum was 0.318 cm thick, type 6061 T6, and mirror polished with Mibro #3 and Mibro #5 polish followed by washing with hexanes, ethanol, acetone, then deionized water, 30 min each, and air dried overnight. The steel adherends, 0.318 cm thick, were sanded with 50 grit sandpaper prior to testing and then washed with ethanol, acetone, and hexanes. Poly(vinyl chloride) (PVC, 0.318 cm thick) and poly(tetrafluoroethylene) (Teflon, 0.318 cm thick) were obtained from Ridout Plastics (San Diego, CA).

Red oak was purchased at a local hardware store and, after cutting to 1.27 cm thick, had a surface roughness approximately equivalent to sanding with 220 grit sandpaper. The wood adherends were cut and adhesion strength measured parallel to the wood grain, running along the 8.89 cm edge of the adherend. Water loss from these wood substrates may have occurred during the adhesive cure. Massing of several oak adherends before versus after a typical cure treatment of 1 h at room temperature, 22 h at 55 °C, and 1 h at room temperature revealed an average 4.12% decrease (e.g., 10.1 g to 9.68 g).

Lap shear adhesion measurements were conducted on an Instron 5544 Materials Testing System equipped with a 2,000 Newton load cell. Copolymer solutions in 1:1 acetone/dichloromethane (0.3 g/mL, 22.5 μL) were added to each adherend. Then 15 μL of cross-linking solution (or solvent when not adding the cross-linker) were added to deliver 0.33 equivalents of cross-linker per catechol group. The adherends were overlapped at 1.25 × 1.25 cm in a lap shear configuration (Figure 2). Each assembly was allowed to cure for 1 h at room temperature, 22 h at 55 °C and then 1 h cooling at room temperature.

Figure 2 shows a representative extension-versus-force plot used for quantifying adhesion. The early region of the trace is flat while the crosshead moves up to begin loading the sample. Once the bond begins to be stressed, a rise is seen until the sudden drop, indicating bond breakage. Adherends were pulled apart at a rate of 2 mm/min. The maximum bonding force in Newtons was recorded. Final adhesive force in MPa was obtained by dividing the maximum load at failure, in Newtons, by the measured area of adhesive overlap in m<sup>2</sup>. For the polymer composition studies in Figure 3, each sample was tested a minimum of 20 times, averaged, and reported with error bars showing ± one standard deviation. The comparisons to commercial adhesives in Tables 2 and 3 were each tested a minimum of 10 times, averaged, and reported with error bars showing ± one standard deviation. Tensile adhesion tests were carried out in an analogous manner using aluminum rods of 1 cm diameter.

## RESULTS AND DISCUSSION

### Polymer Synthesis and Characterization

Nine polymers of varied composition were prepared in order to examine the influence of catechol cross-linking chemistry upon adhesion strength. According to <sup>1</sup>H NMR spectroscopy, the 3,4-dimethoxystyrene content of each final polymer was similar to that placed in the feed. Table 1 provides mole percent data for each monomer in the feed versus

that found in the isolated polymers. For targeting low catechol polymers (e.g., <15%), the 3,4-dimethoxystyrene monomer content in the final polymer was a reflection of that in the starting feed. When targeting higher catechol derivatives, the monomer ratio in feed needed to include a little more 3,4-dimethoxystyrene than the catechol mole percent desired for the final polymer (Table 1).

The last three entries of Table 1 serve to illustrate the variability observed when repeating a given synthesis. With 50% or 51% of the 3,4-dimethoxystyrene monomer in the feed, polymers were obtained with between 26% and 42% incorporation. This inconsistency may be related to water content of the liquid monomer. The 3,4-dimethoxystyrene was column purified prior to each polymerization reaction. We observed that higher incorporation often resulted when the time between purification and polymerization was minimized.

Gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) were also carried out in order to further characterize the isolated copolymers. Given the cross-linking and adhesive nature of these polymers, GPC and DSC data were most easily obtained from the protected poly[(3,4-dimethoxystyrene)-*co*-styrene] species. This approach prevented both adhesion onto the high surface area GPC column and cross-linking during the high temperature DSC experiment. The GPC data, shown in Table 1, provided molecular weight distributions for the copolymers. Anionic polymerization yielded consistent number average molecular weights in the range of ~32,000–58,000 for each derivative. Use of a 1:35 ratio of *n*-BuLi initiator:monomers for all polymerizations helped keep molecular weights similar. Polydispersity indices all fell between 1.2 and 1.5. Anionic polymerization was used here to achieve low PDI values. Radical polymerizations may also be suitable for the synthesis of poly[(3,4-dihydroxystyrene)-*co*-styrene]. When preparing cationic derivatives, nitroxide-mediated radical polymerization worked well.<sup>54</sup>

Differential scanning calorimetry indicated that the glass transition temperatures ( $T_g$ ) shifted lower with increasing 3,4-dimethoxystyrene in the polymer and less styrene. Table 1 shows a  $T_g = 106\text{ }^{\circ}\text{C}$  for a 100% polystyrene. Introduction of 3,4-dimethoxystyrene dropped the  $T_g$  values, gradually, down toward  $60\text{ }^{\circ}\text{C}$  for the 42% 3,4-dimethoxystyrene, 58% styrene copolymer. The methoxy groups of 3,4-dimethoxystyrene may disrupt polymer order, thus resulting in these decreased  $T_g$  values relative to 100% polystyrene.<sup>64</sup> Each poly[(3,4-dimethoxystyrene)-*co*-styrene] derivative showed a  $T_g$  below that of 100% polystyrene ( $T_g = 106\text{ }^{\circ}\text{C}$ ) and above that of 100% poly(3,4-dimethoxystyrene), found earlier to be  $T_g = 53\text{ }^{\circ}\text{C}$ .<sup>53</sup> For every polymer only one transition temperature was observed. These single thermal events indicate a statistical or random copolymer in which the 3,4-dimethoxystyrene monomers are distributed throughout the host polystyrene chain.<sup>65</sup> By contrast, multiple thermal events would have indicated segregated phases or blocks.<sup>65</sup>

Thermogravimetric analysis (TGA,  $5\text{ }^{\circ}\text{C}/\text{min}$ ) of a typical deprotected polymer showed 7.5% mass loss between  $\sim 50\text{ }^{\circ}\text{C}$  and  $\sim 200\text{ }^{\circ}\text{C}$ . When the same polymer was examined by TGA after being subjected to the conditions used for adhesion experiments (DCM/acetone solvent, 1 h room temperature, 22 h at  $55\text{ }^{\circ}\text{C}$ , 1 h room temperature), 8.2% mass loss was noted. This result indicates that a great deal of additional solvent does not appear to persist within the polymer after curing. Generally speaking, this synthetic approach provides control over the polymer composition, molecular weight, and distribution of pendant catechol groups throughout the polymer chain.

### Bulk Adhesion Strengths

Cross-linking can often enhance the adhesive bonding of polymers. Too much cross-linking, however, may be counterproductive and generate a hardened material without the ability to bond surfaces well. Practically speaking, there is no easy way to predict where this “sweet



spot” of optimal cross-linking resides. Consequently, we prepared the family of copolymers shown in Table 1, each with varied pendant catechol content to bring about different degrees of cross-linking.

General insights on the bulk adhesive bonding of these polymers were gained by measuring the lap shear adhesion of mirror polished aluminum (Figure 2). Lap shear bonding is the most widely used general method for quantifying adhesion.<sup>1,2</sup> Although standard deviations may appear to be large, other adhesion configurations such as tensile or peel tend to be worse. Aluminum is a high energy surface and a common substrate for the aviation and automotive industries.<sup>2</sup> We mirror polished the aluminum to make the adhesion more challenging.

Adhesion of each polymer was examined both with and without the addition of a cross-linking agent. Iron-induced,<sup>6–13</sup> simple oxidative,<sup>21,22</sup> and enzymatic<sup>22,23</sup> cross-linking have been proposed to be used by marine mussels when producing their adhesive plaques. Our prior studies with DOPA-containing proteins showed that adhesion could be increased with  $\text{Fe}^{3+}$ .<sup>66</sup> Addition of iron may have enhanced adhesion of poly[(3,4-dihydroxystyrene)-*co*-styrene]<sup>53</sup> and a DOPA-containing protein<sup>67</sup> somewhat, but the effects were minimal. Periodate,  $(\text{IO}_4)^-$ , is a strong oxidant and did lead to stronger adhesion than  $\text{Fe}^{3+}$  when cross-linking poly[(3,4-dihydroxystyrene)-*co*-styrene].<sup>53</sup> Mussels do not have access to reagents such as  $(\text{IO}_4)^-$ . Nonetheless, the goal here is to achieve strong adhesion, hence the choice of  $(\text{IO}_4)^-$  for cross-linking. Periodate has been used to induce cross-linking in DOPA-containing peptides<sup>23</sup> and synthetic polymers containing DOPA.<sup>25</sup> The tetrabutylammonium salt of  $(\text{IO}_4)^-$  was used here for solubility in the same organic solvents as the catechol-containing copolymers. When the copolymers were cross-linked, a 3:1 catechol: $(\text{IO}_4)^-$  ratio was employed. This ratio preserves that of DOPA:Fe proposed to exist in  $\text{Fe}(\text{DOPA})_3$  complexes within mussel adhesive plaques and threads.<sup>10,12,13,68,69</sup>

Bulk adhesion strength was measured for each of the poly[(3,4-dihydroxystyrene)-*co*-styrene] variants. Figure 3 plots adhesion as a function of the mole percent pendant catechol monomer in each polymer. At 0% catechol, the 100% polystyrene exhibited very little bonding at  $0.6 \pm 0.3$  MPa. Every catechol-containing polymer showed more adhesion than 100% polystyrene, ranging from only slightly more with the 5% catechol polymer at  $0.8 \pm 0.3$  MPa to ~3 MPa for the 33% catechol and higher copolymers. In general, increasing the catechol content brought about increased adhesion up to the point of ~33%. Further addition of catechol into the polymers did not enhance adhesion. Perhaps catechol in the range of 33% maximized adhesion without reaching into the range of too much cross-linking being a detriment to function.

Reactions of the copolymers with  $(\text{IO}_4)^-$  often brought about significant increases in adhesion. Data in Figure 3 show that, up to 33% catechol, every polymer bonded more strongly with  $(\text{IO}_4)^-$  relative to the analogous polymer alone. With 5% catechol, for example, adhesion of the polymer alone at  $0.8 \pm 0.3$  MPa jumped several-fold to  $3 \pm 1$  MPa with  $(\text{IO}_4)^-$ . Beyond 33% catechol, however, adhesion dropped in a conspicuous fashion. Adhesion of  $(\text{IO}_4)^-$  with 100% polystyrene was negligible, at  $0.1 \pm 0.1$  MPa.

These data indicate that the “sweet spot” for optimal adhesion resides at the cross-linked polymer of ~33% catechol and ~67% styrene. When the catechol content goes over ~33% and  $(\text{IO}_4)^-$  is added, adhesion suffers. Most likely, too much cross-linking is biasing the system toward extra cohesion within the bulk material at the expense of surface adhesive attachment. With less catechol than ~33%, not enough cross-linking is available and bulk adhesion has not been maximized.

In our first report of poly[(3,4-dihydroxystyrene)-*co*-styrene] copolymers, the maximum adhesion determined from a 3.4% catechol copolymer with (IO<sub>4</sub>)<sup>−</sup> was 0.9 MPa.<sup>53</sup> Data presented here show that significant improvements can be made to adhesive performance from a systematic study of polymer composition. Relative to 100% polystyrene at 0.6 ± 0.3 MPa or 0.1 ± 0.1 MPa with (IO<sub>4</sub>)<sup>−</sup>, incorporation of mussel mimetic chemistry brought about adhesion to this polymer that, otherwise, does not display any strong bonding properties.

### Comparison of Polymer Catechol Content to DOPA in Mussel Adhesive Proteins

Several DOPA-containing mussel foot proteins (“Mfp’s”) have been isolated from the adhesive plaques of this shellfish. The DOPA content of each protein can vary with several factors, the most prominent of which is the time of year. That said, of all the amino acids in each protein, DOPA comprises roughly 10–15% of Mfp-1,<sup>70</sup> 2–4% of Mfp-2,<sup>71</sup> 25% of Mfp-3,<sup>72</sup> 5% of Mfp-4,<sup>73</sup> 30% of Mfp-5,<sup>74</sup> and 3.5% of Mfp-6.<sup>74</sup> Mussel adhesive plaques are constructed from a hierarchy of proteins. Contacting the surface directly are Mfp-3,<sup>72</sup> Mfp-5,<sup>74</sup> and Mfp-6.<sup>74</sup> A protective coating over the whole plaque is comprised of Mfp-1.<sup>75</sup> The bulk adhesive plaque, above the surface and below the coating, is Mfp-2<sup>71</sup> and Mfp-4.<sup>73</sup> Our most strongly adhering biomimetic copolymer contains the equivalent of ~33% DOPA. This value most closely resembles Mfp-3 (~25% DOPA) and Mfp-5 (~30% DOPA). In mussel plaques, these two proteins may only be needed to provide adhesive interactions with the surface. The other proteins are available for cohesion. Compared to DOPA proteins, poly[(3,4-dihydroxystyrene)-*co*-styrene] is a seemingly simpler system, but one that must bring about both cohesion and adhesion. Prior to seeing the data in Figure 3, we could not have looked at the protein sequences and predicted the polymer composition giving rise to the strongest bonding.

### Comparisons to Commercial Glues

At 7 ± 1 MPa, the maximum adhesion of cross-linked poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>] on aluminum is quite appreciable. We sought to benchmark this performance against established commercial adhesives under identical conditions. The substrate, quantity of glue, and cure conditions (e.g., time and temperature) were held constant. Three of the most common classes of adhesives were chosen for comparison: a poly(vinyl acetate) white glue (PVA, Elmer’s), an ethylcyanoacrylate (“Krazy” glue), and a two part epoxy. Results are shown in Table 2. We are excited to report that cross-linked poly[(3,4-dihydroxystyrene)-*co*-styrene] bonds aluminum more strongly than white glue and as strongly as a cyanoacrylate “Krazy” glue, although epoxy adhered the most. Interestingly, even though poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>] adheres comparably to cyanoacrylate, the chemistry differs dramatically. Cyanoacrylate adhesives are applied to surfaces in the form of a flowing monomer followed by polymerization. By contrast, the biomimetic adhesive is deposited onto the substrate already polymerized and is then cross-linked. Whereas cyanoacrylate does not have any specific chemistry for binding surfaces, the catechol groups of poly[(3,4-dihydroxystyrene)-*co*-styrene] can bring about both this needed surface adhesion as well as cross-linking within the bulk.

### Adhesion On Different Substrates

Of the myriad parameters influencing adhesion, the very substrate onto which the material bonds may be one of the most significant. Substrates can range from low energy plastics to high energy metals. The surfaces can be smooth or rough. Generally speaking, roughened surfaces of high energy tend to be the easiest for strong adhesion, allowing both chemical interactions and mechanical interlocking between the glue and the surface. Smooth plastics are, classically, the most challenging substrates for adhesion. Once the strongest adhering variant of poly[(3,4-dihydroxystyrene)-*co*-styrene] was identified for bonding polished

aluminum (Figure 3), performance was assessed on other substrates. In addition to aluminum, Teflon (poly(tetrafluoroethylene)), polyvinyl chloride (PVC), sanded steel, and red oak adherends were machined for these studies. These substrates provide a range of surface energies, roughness, and industrial applications. Pairs of each substrate were joined together using poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>], both with and without (IO<sub>4</sub>)<sup>-</sup> cross-linking, as well as with three commercial glues.

Data provided in Table 3 show how each adhesive performed on the different surfaces. After the experiments of Table 2 with aluminum, the substrate was changed to sanded steel. Here poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>] performed comparably to white glue, but the cyanoacrylate and epoxy were strongest. Interestingly, on sanded steel the biomimetic copolymer displayed similar adhesion strength both alone and when cross-linked with (IO<sub>4</sub>)<sup>-</sup>. Here we may be seeing an effect from Fe<sup>3+</sup> of the steel surface introducing cross-linking chemistry to the polymers and enhancing bulk bonding. For PVC, performance of poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>] with periodate was so strong that the substrate, itself, failed prior to the adhesive joint. Likewise, the cyanoacrylate also broke PVC and outperformed both white glue and epoxy. When periodate was left out of the formulation, poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>] joined Teflon as strongly as epoxy and more strongly than white glue but not to the same degree as cyanoacrylate.

Oak provided the strongest bonding for poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>] when cross-linked, at  $10 \pm 1$  MPa. Both white glue and epoxy were weaker, although the cyanoacrylate appeared to be the strongest. The porous nature of wood may allow for penetration and mechanical interlocking, thereby explaining the high adhesion for poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>]. This result prompted us to measure the adhesion of a commercial wood glue (Titebond II, Franklin International) under identical conditions. Interestingly, poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>] appears to have performed similarly to the purchased wood glue at  $9 \pm 2$  MPa.

These commercial adhesives have benefitted from decades of industrial formulation studies in which parameters such cure conditions, concentration, added filler, viscosity, and addition of adhesion promoters have all been examined. By contrast, poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>] is a relative newborn and, within the scope of this academic study, already performs comparably to commercial products. Ideally, an adhesive should be tailored for a target substrate. The poly[(3,4-dihydroxystyrene)-*co*-styrene] with the strongest bulk adhesion on aluminum is not necessarily the best polymer for other substrates. Beyond changing polymers for each surface, a detailed series of formulation efforts may enhance performance even further.

### Comparisons to Other Biomimetic Adhesive Polymers

We wished to place the performance of poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>] system within the expanding scope of other polymeric mussel protein mimics. Many of these new systems are being used most often to generate coatings<sup>27,34,35,40,45–47,49–52,63</sup> or hydrogels,<sup>36–38,42,43</sup> among several other end goals, and some have shown adhesion.<sup>25,26,29–33,36–42,53,54,60</sup> Direct comparisons of adhesive performance are difficult to make given how many variables are present including test methods, substrate composition, surface preparation methods, solvents, viscosity, cure time, cure temperature, and the presence or absence of water, among several other conditions. Some of the stronger mussel mimics reported are a polyurethane at 5.2 MPa,<sup>60</sup> polypeptides bonding up to 4.7 MPa,<sup>25</sup> and a poly(ethylene glycol)/polyacrylate at 1.2 MPa.<sup>29</sup> Fusion proteins have been expressed and modified to contain DOPA.<sup>76,77</sup> These representations of mussel proteins can adhere up to 4 MPa.<sup>67,78</sup> The data in Table 3 indicate that poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>] is the strongest bonding synthetic mimic of mussel adhesive tested to date.



Maximum adhesion was at  $10 \pm 1$  MPa for the cross-linked polymer joining wood. Polished aluminum, sanded steel, and PVC were adhered at greater than 5.7 MPa, also stronger than that reported for other biomimetic adhesives.

### Adhesion Strength of Synthetic Mimics Compared to Plaques from Live Mussels

Recently we developed a method for quantifying adhesive performance of the glue produced by live mussels.<sup>79</sup> On aluminum these shellfish adhere at  $0.3 \pm 0.1$  MPa.<sup>79</sup> The byssal adhesive system of mussels is comprised of plaques contacting the surface and threads connecting each plaque to the animal's soft inner body (Figure 1). Tensile measurements were required to obtain accurate adhesion data for the byssus. We were curious to see how the performance of our biomimetic polymers compared to the "real" material produced by mussels.

The polymer lap shear data from above (c.f., Table 3) cannot be compared directly to tensile measurements. In a lap shear test, the substrates are overlapped and force is applied parallel to the adhesive bond (Figure 2). Tensile testing is an end-to-end butt joint and the applied force is perpendicular to the glue. Consequently, we gathered tensile adhesive data for poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>] on aluminum rods. Pairs of tensile substrates were bonded together using 13.5 mg of dissolved poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>] and (IO<sub>4</sub>)<sup>-</sup> over the 1 cm diameter overlap area. Testing revealed that the polymeric adhesive was so strong that not all of the joined substrates could be broken within the 2,000 Newton capacity of our materials testing system. Some bonded substrates pairs did separate and provided a lower limit of 9 MPa for poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>] on aluminum in tensile mode. The biomimetic system appears to bond with significantly greater force than the natural material after which the polymer was designed. Although we may be trying to make the strongest possible glue, mussels need only adhere as strongly as their environmental conditions dictate. Indeed, if these shellfish were affixed to rocks any more strongly, detachment forces exerted by waves or predators might pull on the byssus to the point of damaging the soft, internal tissues to which the threads connect (Figure 1).

### CONCLUSIONS

With their ability to remain affixed to rocks in the turbulent intertidal zone it is no wonder that mussels have inspired so much research. Here we have presented a structure-property study on the simplest mimic of mussel adhesive. Several copolymers were synthesized, characterized, and examined for adhesive properties. A systematic approach was taken in order to determine the polymer composition giving rise to the greatest bulk adhesion. With the cross-linking and surface bonding chemistries present in these copolymers, the strongest adhesive is likely to provide a balance between cohesive and adhesive bonding. Adhesion was quantified on substrates ranging from low energy, smooth plastics to high energy, roughened metal. Performance was benchmarked against common commercial glues as well as the native material produced by live mussels. Adhesive performance of the biomimetic polymer was comparable, and in some cases better, than commercial products and the plaques of living shellfish. Relative to other mussel mimetic polymers, poly[(3,4-dihydroxystyrene)-*co*-styrene], appears to be the strongest bulk adhesive. These comparisons, although interesting, are difficult to make directly, given the broad variations in conditions. Overall, these results help attest to the value of using blueprints from biology when designing new materials. Such a biomimetic approach may aid development of the adhesives needed for industrial or biomedical applications including wood glues without toxic formaldehyde, surgical reattachment of soft tissues, and cements for connecting metal implants to bone.

## Acknowledgments

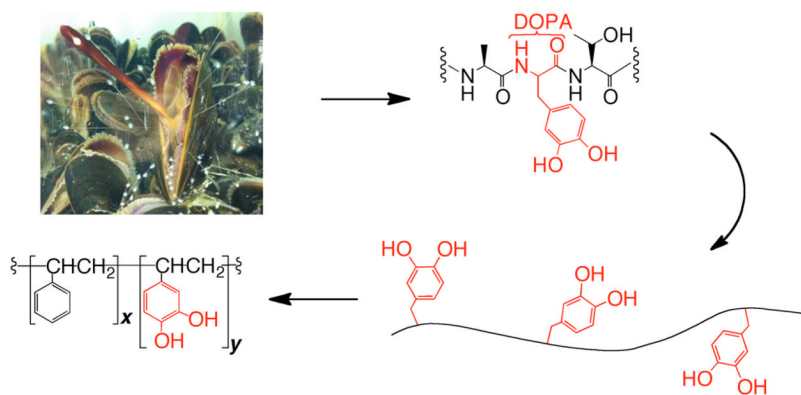
This work was supported by the Office of Naval Research, the National Science Foundation, and a Ruth L. Kirschstein National Research Service Award from the National Institute of Health to C.R.M-P. We thank Harold McCarron and Jeffrey Youngblood for insightful discussions, Kaumba Sakavuyi and Matt Walters for obtaining DSC data, Allison Mattes for assistance with GPC analysis, and Courtney Jenkins and Heather Meredith for help collecting the commercial adhesion data.

## References

1. Pocius, AV. An Introduction. 2. Carl Hanser Verlag; Munich: 2002. Adhesion and Adhesives Technology.
2. Petrie, EM. Handbook of Adhesives and Sealants. McGraw Hill; New York: 2007.
3. Croson ME. Adhesives and Sealants Industry. 2011; 18:17–18.
4. Waite JH. Integr Comp Biol. 2002; 42:1172–1180. [PubMed: 21680402]
5. Sagert, J.; Sun, C.; Waite, JH. Biological Adhesives. Smith, AM.; Callow, JA., editors. Springer-Verlag; Berlin: 2006. p. 125-143.
6. Hight LM, Wilker JJ. J Materials Sci. 2007; 42:8934–8942.
7. Loizou E, Weisser JT, Dundigalla A, Porcar L, Schmidt G, Wilker JJ. Macromol Biosci. 2006; 6:711–718. [PubMed: 16967473]
8. Monahan J, Wilker JJ. Chem Comm. 2003:1672–1673. [PubMed: 12877496]
9. Monahan J, Wilker JJ. Langmuir. 2004; 20:3724–3729. [PubMed: 15875406]
10. Sever MJ, Weisser JT, Monahan J, Srinivasan S, Wilker JJ. Angew Chem Int Ed. 2004; 43:448–450.
11. Weisser JT, Nilges MJ, Sever MJ, Wilker JJ. Inorg Chem. 2006; 45:7736–7747. [PubMed: 16961365]
12. Wilker JJ. Curr Op Chem Biol. 2010; 14:276–283.
13. Wilker JJ. Angew Chem Int Ed. 2010; 49:8076–8078.
14. Lee H, Scherer NF, Messersmith PB. Proc Natl Acad Sci USA. 2006; 103:12999–13003. [PubMed: 16920796]
15. Ooka AA, Garrell RL. Biopolymers (Biospectroscopy). 2000; 57:92–102. [PubMed: 10766960]
16. Jankovic IA, Saponjic ZV, Comor MI, Nedeljkovic JM. J Phys Chem C. 2009; 113:12645–12652.
17. Wang JJ, Tahir MN, Kappl M, Tremel W, Metz N, Barz M, Theato P, Butt HJ. Adv Mat. 2008; 20:3872–3876.
18. Lana-Villarreal T, Rodes A, Perez JM, Gomez R. J Am Chem Soc. 2005; 127:12601–12611. [PubMed: 16144408]
19. McBride MB, Wesselink LG. Environ Sci Technol. 1988; 22:703–708.
20. Mian SA, Saha LC, Jang J, Wang L, Gao X, Nagase S. J Phys Chem C. 2010; 114:20793–20800.
21. Fant C, Sott K, Elwing H, Hook F. Biofouling. 2000; 16:119–132.
22. Suci PA, Geesey GG. J Colloid Interface Sci. 2000; 230:340–348. [PubMed: 11017742]
23. Burzio LA, Waite JH. Biochemistry. 2000; 39:11147–11153. [PubMed: 10998254]
24. Moulay S. Comptes Rendus Chimie. 2009; 12:577–601.
25. Yu M, Deming TJ. Macromolecules. 1998; 31:4739–4745. [PubMed: 9680407]
26. Wang J, Liu C, Lu X, Yin M. Biomaterials. 2007; 28:3456–3468. [PubMed: 17475323]
27. Saxer S, Portmann C, Tosatti S, Gademann K, Zurcher S, Textor M. Macromolecules. 2010; 43:1050–1060.
28. Li L, Li Y, Luo XF, Deng JP, Yang WT. Reactive Functional Polymers. 2010; 70:938–943.
29. Sarbjit K, Weerasekare GM, Stewart RJ. ACS Appl Mater Interfaces. 2011; 3:941–944.
30. Glass P, Chung HY, Washburn NR. Langmuir. 2009; 25:6607–6612. [PubMed: 19456091]
31. Shao H, Bachus KN, Stewart RJ. Macromol Biosci. 2009; 9:464–471. [PubMed: 19040222]
32. Shao H, Stewart RJ. Adv Mat. 2010; 22:729–733.

33. Chung HY, Glass P, Pothan JM, Sitti M, Washburn NR. *Biomacromolecules*. 2011; 12:342–347. [PubMed: 21182292]
34. Gao CL, Li GZ, Xue H, Yang W, Zhang FB, Jiang SY. *Biomaterials*. 2010; 31:1486–1492. [PubMed: 19962753]
35. Li GZ, Xue H, Cheng G, Chen SF, Zhang FB, Jiang SY. *J Phys Chem B*. 2008; 112:15269–15274. [PubMed: 18989905]
36. Hu B, Messersmith PB. *Orthod Craniofacial Res*. 2005; 8:145–149.
37. Lee BP, Chao CY, Nunalee FN, Motan E, Shull KR, Messersmith PB. *Macromolecules*. 2006; 39:1740–1748.
38. Burke SA, Ritter-Jones M, Lee BP, Messersmith PB. *Biomed Mat*. 2007; 2:203–210.
39. Brubaker CE, Kissler H, Wang L-J, Kaufman DB, Messersmith PB. *Biomaterials*. 2010; 31:420–427. [PubMed: 19811819]
40. Murphy JL, Vollenweider L, Xu FM, Lee BP. *Biomacromolecules*. 2010; 11:2976–2984.
41. Brodie M, Vollenweider L, Murphy JL, Xu FM, Lyman A, Lew WD, Lee BP. *Biomed Mat*. 2011; 6:015014.
42. Ryu JH, Lee Y, Kong WH, Kim TG, Park TG, Lee H. *Biomacromolecules*. 2011; 12:2653–2659. [PubMed: 21599012]
43. Holten-Andersen N, Harrington MJ, Birkedal H, Lee BP, Messersmith PB, Lee KYC, Waite JJ. *Proc Natl Acad Sci USA*. 2011; 108:2651–2655. [PubMed: 21278337]
44. Black KCL, Liu ZQ, Messersmith PB. *Chem of Mater*. 2011; 23:1130–1135. [PubMed: 21666825]
45. Finlay AS, Dalsin J, Callow M, Callow JA, Messersmith PB. *Biofouling*. 2006; 22:391–399. [PubMed: 17178572]
46. Dalsin JL, Lin LJ, Tosatti S, Voros J, Textor M, Messersmith PB. *Langmuir*. 2005; 21:640–646. [PubMed: 15641834]
47. Lee H, Lee KD, Pyo KB, Park SY, Lee H. *Langmuir*. 2010; 26:3790–3793. [PubMed: 20148541]
48. Bae KH, Kim YB, Lee Y, Hwang J, Park H, Park TG. *Bioconjugate Chem*. 2010; 21:505–512.
49. Chawla K, Lee S, Lee BP, Dalsin JL, Messersmith PB, Spencer ND. *J Biomed Mater Res A*. 2009; 90A:742–749. [PubMed: 18570317]
50. Pechey A, Elwood CN, Wignall GR, Dalsin JL, Lee BP, Vanjecek M, Welch I, Ko R, Razvi H, Cadieux PA. *J Urology*. 2009; 182:1628–1636.
51. Yuan S, Wan D, Liang B, Pehkonen SO, Ting YP, Neoh KG, Kang ET. *Langmuir*. 2011; 27:2761–2774.
52. Malisova B, Tosatti S, Textor M, Gademann K, Zurcher S. *Langmuir*. 2010; 26:4018–4026. [PubMed: 20146501]
53. Westwood G, Horton TN, Wilker JJ. *Macromolecules*. 2007; 40:3960–3964.
54. White JD, Wilker JJ. *Macromolecules*. 2011; 44:5085–5088.
55. Yang Z, Pelton R. *Macromol Rapid Commun*. 1998; 19:241–246.
56. Daly WH, Moulay S. *J Polymer Sci*. 1986; 74:227–242.
57. Cristescu R, Mihailescu IN, Stamatina I, Doraiswamy A, Narayan R, Westwood G, Wilker JJ, Stafslin S, Chisholm B, Chrisey DB. *Applied Surface Sci*. 2009; 255:5496–5498.
58. Bernard J, Branger C, Beurroies I, Denoyel R, Margaillan A. *Reactive Functional Polymers*. 2012; 72:98–106.
59. Pan XD, Qin ZQ, Yan YY, Sadhukhan O. *Polymer*. 2010; 51:3453–3461.
60. Peiyu S, Liying T, Zhen Z, Xinling W. *Acta Polymerica Sinica*. 2009:803–808.
61. Adkins CT, Dobish JN, Brown CS, Mayrhoen B, Hamilton SK, Udoji F, Radford K, Yankeelov TE, Gore JC, Harth E. *Polymer Chem*. 2012; 3:390–398.
62. Kaneko D, Wang SQ, Matsumoto K, Kinugawa S, Yasaki K, Chi DH, Kaneko T. *Polymer J*. 2011; 43:855–858.
63. Han H, Wu J, Avery CW, Mizutani M, Jiang X, Kamigaito M, Chen Z, Xi C, Kuroda K. *Langmuir*. 2011; 27:4010–4019. [PubMed: 21391641]
64. Li C-H, Chang T-C. *Eur Polymer J*. 1991; 27:35–39.
65. Zhang H, Hong K, Mays JW. *Macromolecules*. 2002; 25:5738–5741.

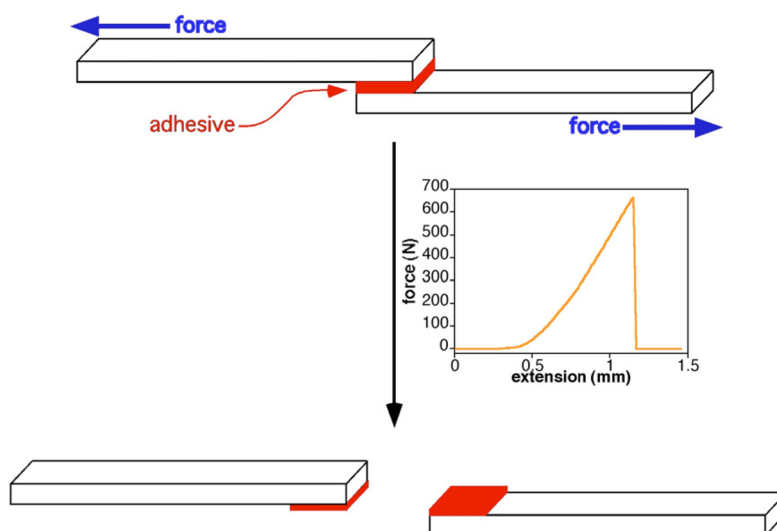
66. Doraiswamy A, Dunaway TM, Wilker JJ, Narayan RJ. *J Biomed Materials Res B: Applied Mat.* 2009; 89B:28–35.
67. Cha HJ, Hwang DS, Lim S, White JD, Matos-Pérez CR, Wilker JJ. *Biofouling.* 2009; 25:99–107.
68. Zeng H, Hwang DS, Israelachvili JN, Waite JH. *Proc Natl Acad Sci USA.* 2010; 107:12850–12853. [PubMed: 20615994]
69. Harrington MJ, Masic A, Holten-Andersen N, Waite JH, Fratzl P. *Science.* 2010; 328:216–220. [PubMed: 20203014]
70. Sun C, Waite JH. *J Biol Chem.* 2005; 280:39332–39336. [PubMed: 16166079]
71. Rzepecki LM, Waite JH. *Mol Mar Biol Biotech.* 1995; 4:313–322.
72. Papov VV, Diamond TV, Biemann K, Waite JH. *J Biol Chem.* 1995; 270:20183–20192. [PubMed: 7650037]
73. Vreeland V, Waite JH, Epstein L. *J Phycol.* 1998; 34:1–8.
74. Zhao H, Waite HH. *J Biol Chem.* 2006; 281:26150–26158. [PubMed: 16844688]
75. Rzepecki LM, Hansen KM, Waite JH. *Biol Bull.* 1992; 183:123–137.
76. Hwang DS, Gim Y, Cha HJ. *Biotechnol Prog.* 2005; 21:965–970. [PubMed: 15932281]
77. Hwang DS, Gim Y, Yoo HJ, Cha HJ. *Biomaterials.* 2007; 28:3560–3568. [PubMed: 17507090]
78. Lim S, Choi YS, Kang DG, Song YH, Cha HJ. *Biomaterials.* 2010; 31:3715–3722. [PubMed: 20144475]
79. Burkett JR, Wojtas JL, Cloud JL, Wilker JJJ. *Adhesion.* 2009; 85:601–615.



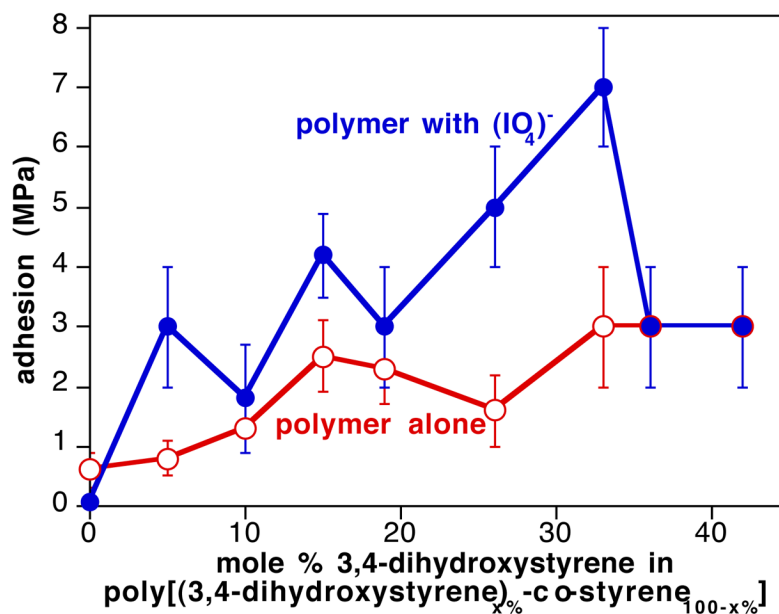
**Figure 1.**

Mussel adhesive is comprised of DOPA-containing proteins. These proteins are mimicked with synthetic polymers by placing pendant catechol groups along a polymer chain. One of the simplest possible mimics is poly[(3,4-dihydroxystyrene)-*co*-styrene] in which polystyrene represents the protein backbone and DOPA is represented by 3,4-dihydroxystyrene.





**Figure 2.** Lap shear bonding. Polymer glues are placed between two substrates and pulled to failure. Maximum adhesion is indicated by the peak of the extension (in mm) versus force (in Newtons) plot.



**Figure 3.** Adhesion strength as a function of the pendant catechol content in a series of poly[(3,4-dihydroxystyrene)-*co*-styrene] copolymers. Performance of the polymer alone (in red) and cross-linked with periodate (in blue) are shown. Adhesive bonding is in a lap shear configuration with aluminum substrates.

**Table 1**

Characterization data for poly[(3,4-dimethoxystyrene)-*co*-styrene] copolymers.

feed	polymer observed							
	3,4-dimethoxystyrene	styrene	3,4-dimethoxystyrene	styrene	$M_n$	$M_w$	PDI	$T_g$ (°C)
0%		100%	0%	100%	32,300	38,400	1.2	106
5%		95%	5%	95%	37,500	48,800	1.3	103
9%		91%	10%	90%	39,800	50,000	1.2	100
15%		85%	15%	85%	40,700	48,700	1.2	93
22%		78%	19%	81%	40,900	54,500	1.3	97
50%		50%	26%	74%	49,600	65,800	1.3	67
50%		50%	33%	67%	57,500	84,200	1.5	62
51%		49%	42%	58%	50,575	61,700	1.2	60

**Table 2**

Adhesive performance of poly[(3,4-dihydroxystyrene)<sub>33%</sub>-*co*-styrene<sub>67%</sub>] copolymer compared to commercial glues. Bonding was carried out on aluminum substrates in a lap shear configuration.

adhesive	adhesion strength (MPa)
poly(vinyl acetate) (PVA, white glue, Elmer's)	4 ± 1
ethylcyanoacrylate ("Krazy" glue)	7 ± 1
epoxy (Loctite)	11 ± 2
biomimetic polymer alone	3 ± 1
biomimetic polymer with (IO <sub>4</sub> ) <sup>-</sup>	7 ± 1

**Table 3**

Lap shear adhesive bonding, in MPa, for poly[(3,4-dihydroxystyrene)<sub>33%</sub>-co-styrene<sub>67%</sub>] and commercial glues on different substrates.

	poly(tetrafluoroethylene) (Teflon)	poly(vinyl chloride) (PVC)	polished aluminum	sanded steel	red oak
biomimetic polymer alone	0.7 ± 0.2	0.9 ± 0.1	4 ± 1	6 ± 2	5.1 ± 0.9
biomimetic polymer and (IO <sub>4</sub> ) <sup>-</sup>	0.4 ± 0.1	> 5.7 <sup>a)</sup>	7 ± 1	5 ± 1	10 ± 1
poly(vinyl acetate) (PVA, Elmer's)	0.36 ± 0.04	0.5 ± 0.1	4 ± 1	5.5 ± 0.9	5 ± 2
cianoacrylate "Krazy" glue	1.5 ± 0.3	> 5.7 <sup>a)</sup>	7 ± 1	10 ± 2	> 10 <sup>b)</sup>
epoxy (Loctite)	0.7 ± 0.1	3.8 ± 0.7	11 ± 2	9 ± 1	4 ± 2

<sup>a)</sup> substrate failed while adhesive bond remained intact

<sup>b)</sup> exceeded range of the instrument