ACS APPLIED MATERIALS & INTERFACES

Research Article

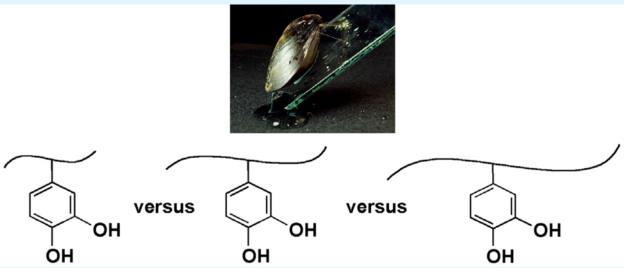
www.acsami.org

Molecular Weight Effects upon the Adhesive Bonding of a Mussel Mimetic Polymer

Courtney L. Jenkins,[†] Heather J. Meredith,[‡] and Jonathan J. Wilker*[,†,‡]

[†]Department of Chemistry and [‡]School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907, United States

Supporting Information



ABSTRACT: Characterization of marine biological adhesives are teaching us how nature makes materials and providing new ideas for synthetic systems. One of the most widely studied adhering animals is the marine mussel. This mollusk bonds to wet rocks by producing an adhesive from cross-linked proteins. Several laboratories are now making synthetic mimics of mussel adhesive proteins, with 3,4-dihydroxyphenylalanine (DOPA) or similar molecules pendant from polymer chains. In select cases, appreciable bulk bonding results, with strengths as high as commercial glues. Polymer molecular weight is amongst several parameters that need to be examined in order to both understand biomimetic adhesion as well as to maximize performance. Experiments presented here explore how the bulk adhesion of a mussel mimetic polymer varies as a function of molecular weight. Systematic structure−function studies were carried out both with and without the presence of an oxidative cross-linker. Without cross-linking, higher molecular weights generally afforded higher adhesion. When a $[N(C_4H_9)_4](IO_4)$ cross-linker was added, adhesion peaked at molecular weights of ~50 000−65 000 g/mol. These data help to illustrate how changes to the balance of cohesion versus adhesion influence bulk bonding. Mussel adhesive plaques achieve this balance by incorporating several proteins with molecular weights ranging from 6000 to 110 000 g/mol. To mimic these varied proteins we made a blend of polymers containing a range of molecular weights. Interestingly, this blend adhered more strongly than any of the individual polymers when cross-linked with $[N(C_4H_9)_4](IO_4)$. These results are helping us to both understand the origins of biological materials as well as design high performance polymers.

KEYWORDS: *molecular weight, adhesion, mussels, catechol, biomimetic, DOPA, polymer, adhesive*

■ INTRODUCTION

Mimics of Mussel Adhesives. We can learn a great deal about materials design when looking to the seas. Marine organisms such as mussels, oysters, barnacles, and sandcastle worms all use specialized adhesives in order to affix themselves to wet surfaces. Most synthetic glues, by contrast, fail at wet bonding. Perhaps the most well studied bioadhesive is that produced by marine mussels (Figure 1). This adhesive is comprised of several proteins, each containing the 3,4-dihydroxyphenylalanine (DOPA) amino acid for cross-linking and curing.[1−4]

Shellfish have become the inspiration for many biomimetic polymers, which place the cross-linking chemistry of mussels into polypeptides,[5−7] polyamides,[8] polyacrylates,[9−14] polyethylene glycols,[15−20] polyurethanes,[21] and polystyrenes.[22−27] Incorporation of DOPA chemistry into synthetic polymers is now being pursued by dozens of laboratories.[28−30] Consequently, we seek to determine the most important factors that give rise to the strongest adhesion possible.

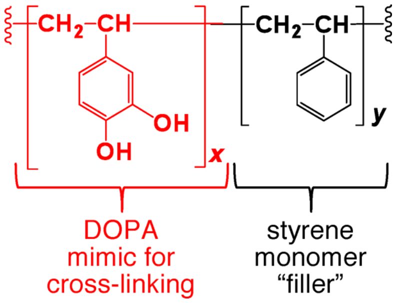
Several DOPA containing proteins are combined by the animal's foot to generate an adhesive plaque.[31,32] Each of these mussel foot proteins (Mfps) is tailored to play a specific role. The lower molecular weight proteins, Mfp-3 at ~6000 g/mol, Mfp-5 at ~9000 g/mol, and Mfp-6 at ~11 000 g/mol,[32] are at the interface of the substrate and the plaque.[33] Presumably, these low molecular weight proteins are bringing about wettability. Intermediate molecular weight proteins, Mfp-2 at ~45 000 g/mol and Mfp-4 at ~90 000 g/mol, compose the bulk portion of the plaque.[32] The highest molecular weight protein, Mfp-1 at ~110 000 g/mol, provides a protective coating for a high strength exterior.[31,32] These six proteins come together to form one assembly able to adhere to nearly any surface.

Any given synthetic polymer mimic may be called upon to reproduce the function of the six different proteins produced by mussels. With a wide range of molecular weights found for mussel adhesive proteins (~6000 g/mol to ~110 000 g/mol),[32] it is difficult to predict which single polymer chain length will yield the strongest adhesion. For the studies described herein, we used poly[(3,4-dihydroxystyrene)-*co*-styrene] (Scheme 1).[22] In terms of chemical functionalities, this system may be the simplest of all the mussel adhesive mimics, thus making it a good subject to investigate the relationship between molecular structure and macroscopic function. In a prior study, we

Received: March 15, 2013
Accepted: May 13, 2013
Published: May 13, 2013

Figure 1. Photograph of a marine mussel clinging to a glass sheet with adhesive plaques.

Scheme 1. Poly[(3,4-dihydroxystyrene)-*co*-styrene], A Functional Mimic of Mussel Adhesive Proteins



determined that a polymer composition of ∼33 mol % 3,4-dihydroxystyrene and ∼67 mol % styrene yielded the strongest bonding, comparable to the adhesion strength of a commercial cyanoacrylate (Krazy Glue).[34] At this time, we do not know how the molecular weight of a mussel mimetic polymer will impact adhesion. Here we seek to determine which, if any, molecular weight may provide the strongest bulk bonding for a biomimetic copolymer system.

Molecular Weight and Adhesion. Adhesive materials are generated from a variety of synthetic polymers including epoxies, poly(urethanes), poly(vinyl acetates), and cyanoacrylates. Although those materials are in wide use for both industrial manufacturing and biomedical repairs, higher bond strengths are often in demand. Several parameters have been examined extensively to enhance adhesion; however, the effect of the molecular weight on bulk adhesion has not been explored in great detail and offers opportunities to improve performance.[35−37]

Molecular weight impacts polymer properties including the glass transition temperature (T_g), melting temperature (T_m), stiffness, strength, viscoelasticity, toughness, and viscosity.[38−40] Increases in molecular weights provide additional chain entanglements and reduced free volumes, causing restricted movement of the chains, subsequently raising the T_g, T_m, and viscosity.[38,39] Other properties that can be altered with molecular weight include strength, tackiness, and toughness, each increasing with higher molecular weights.[36,38,41] Crazing and wetting decrease with lower molecular weights.[38] Chain entanglement, interdiffusion, and interfacial interactions, all of which are affected by molecular weight, also affect polymer adhesion.[36,41,42]

Prior studies have examined the influence of polymer molecular weight upon adhesion. Typically, however, only a relatively narrow range of molecular weights have been studied within a single polymer family.[5,36,41,43−46] For appreciable bulk bonding to be present, a minimum of 5000 g/mol appears necessary.[47] However, an optimal molecular weight for the highest bond strength remains unknown. Most likely, differences between the many classes of polymeric adhesives and varied testing methods prevent us from finding a single, ideal molecular weight.

Poly(vinyl alcohol),[48,49] epoxidized natural rubber,[43−45] and poly(isobutylene)[50] have each been explored with regard to the influence of molecular weight upon adhesion. An intermediate molecular weight was found to yield the strongest bonds with each polymer.[43−45,48−50] For poly(vinyl alcohol) blends, the tensile strength peaked at a molecular weight of ∼100 000 g/mol.[48,49] The peel strength of epoxidized natural rubber was maximized at a lower molecular weight of 39 000−68 000 g/mol.[43−45] In the case of poly(isobutylene), the molecular weight providing the best shear strength was much higher, at ∼700 000 g/mol, whereas the tack strength decreased when the molecular weight increased.[50] Work with other polymeric systems such as poly(dimethylsiloxanes), however, has noted that stronger adhesion corresponds directly to higher molecular weights.[36,41,46]

In general, a balance between wettability and strength is required to achieve the strongest bonding possible.[43−45] Adhesive failure modes also vary with molecular weight. Below the optimum molecular weight for adhesion, failure was cohesive, indicating that a higher strength, higher molecular weight polymer may enhance bonding.[44] Above the peak molecular weight, however, failure was mostly adhesive, likely due to lower wettability preventing the polymer from interacting well with the surface.[44]

Lower molecular weight polymers, or even monomers and oligomers, can allow for more interactions with a surface due to high mobility. The resulting wettability provides many contact points between the polymer and surface.[41] This mobility also enables flow, aiding in the dissipation of energy when a bond is being stressed. High surface wetting is necessary for contact between the polymer and substrate prior to bond setting.[51] Such wettability from low molecular weights, however, comes at the expense of cohesion. To overcome surface wetting problems with high molecular weight polymers, testing can be carried out near the T_g, thus enhancing mobility for improved surface interactions.[41,52] Once attached to a surface, higher molecular weight polymers can provide strong cohesive interactions to help resist bond failure.[41] Higher molecular weights also provide a route for dissipating energy when the bond is under strain. Chain entanglements and elongation prior to breaking may aid high strength bonding with high molecular weight polymers.[41,46]

Additional polymer−polymer interactions including hydrogen bonds or other types of cross-links may influence the interplay between molecular weight and adhesion. The degree of cross-linking can be coupled to polymer molecular weight, influencing both the bulk and surface interactions.[36,41,46] For example, in the epoxidized natural rubber system, the presence of hydrogen bonding motifs yields optimized adhesion at lower molecular weights.[35−43] An analogous trend can be accomplished by cross-linking the polymer, effectively increasing the molecular weights.[38] Cross-linking decreases the number of free polymer chain ends, observed with poly(dimethylsiloxanes).[37,41,46] A greater extent of cross-linking resulted in reduced poly(dimethylsiloxane) wetting and thus decreased adhesion.[41,52] Results presented below investigate how molecular weight dictates the adhesion of a biomimetic polymer system, both with and without cross-linking agents.

■ EXPERIMENTAL SECTION

Materials. Chemicals and solvents were purchased from Sigma Aldrich. Tetrabutylammonium periodate $[N(C_4H_9)_4](IO_4)$ was made following a literature procedure[53] and confirmed by ultraviolet−visible absorption spectroscopy, ^1H NMR spectroscopy, and melting point determinations. A sheet of aluminum 6061-T6 was purchased from Farmer's Copper and cut into adherends (8.9 cm × 1.3 cm). These substrates were cleaned following the ASTM D2651-01 standard method.[54]

Polymer Synthesis. The biomimetic polymers were synthesized following a procedure from our laboratory described previously.[34] Briefly, an anionic polymerization was conducted by copolymerizing styrene and 3,4-dimethoxystyrene with *n*-BuLi initiator to form poly[(3,4-dimethoxystyrene)-*co*-styrene]. A typical synthesis included 5.8 mL (51 mmol) of styrene, 5.3 mL (35 mmol) of 3,4-dimethoxystyrene, 0.45 mL of *n*-BuLi, 2.5 M in hexanes, (1.1 mmol), and 80 mL of anhydrous toluene solvent. The polymer was deprotected to form poly[(3,4-dihydroxystyrene)-*co*-styrene] using BBr_3, 1 M in hexanes.[34] The reaction was quenched with methanol, and then the polymer solution was precipitated and washed with a solution of 1% (v/v) HCl in water. The polymer was dried by rotary evaporation, yielding a light brown solid.

Polymer Characterization. To confirm the structure and determine the catechol content of each poly[(3,4-dimethoxy styrene)-*co*-styrene] derivative, ^1H NMR spectra were recorded on a Varian Inova-300 MHz spectrometer. Gel permeation chromatography (GPC) was run in THF on a Polymer Laboratories PL-GPC20 to provide the molecular weights and polydispersity indices (PDIs). A previous study from our laboratory showed optimized adhesion of poly[(3,4-dihydroxystyrene)-*co*-styrene] at a 33% 3,4-dihydroxystyrene and 67% styrene monomer content.[34] Consequently, we targeted ~33% 3,4-dihydroxystyrene content for the polymers used in this study.

Adhesion Studies. Bulk lap shear adhesion bonding was carried out with a modified version of the ASTM D1002 standard method.[22,55] Poly[(3,4-dihydroxystyrene)-*co*-styrene] was dissolved at 0.300 g/mL in 1:1 acetone:dichloromethane. Then 22.5 μL of this polymer solution was spread onto each aluminum adherend. When used, a tetrabutylammonium periodate $[N(C_4H_9)_4](IO_4)$ cross-linker solution was prepared by dissolving 0.341 g of $[N(C_4H_9)_4](IO_4)$ into 1.00 mL of 1:1 acetone:dichloromethane for a typical experiment. A 1:3 $[N(C_4H_9)_4](IO_4)$:3,4-dihydroxystyrene molar ratio was chosen for cross-linking to mimic the ratio of iron:DOPA proposed to be present in mussel adhesive plaques.[2,3,56] This ratio has yielded some of the strongest adhesion observed with any synthetic polymer mimic of mussel adhesive proteins and made for an obvious choice here.[34] Prior studies have varied periodate:catechol ratios; however, the effects examined were with regard to gelation rather than adhesion.[57,58]

The $[N(C_4H_9)_4](IO_4)$ solution (15.0 μL) was added to the polymer solution on one of the adherends before they were overlapped at 1.20 cm × 1.20 cm. Adherends were allowed to set for 1 h at room temperature before heating at 55 °C for 22 h, followed by an additional 1 h of cooling at room temperature. Lap shear bond strengths were quantified at a loading rate of 2 mm/min using an Instron 5544 Materials Testing System with a 2000 N load cell. Maximum force was divided by the overlap area to determine the adhesion strength of each polymer (Supporting Information Figure S1). Conditions for testing were chosen to be consistent with previous studies with this polymer system.[22,23,26,34] Subsequent, minor modifications have been made to the experimental setup including an ASTM D2651-01 method for adherend cleaning[54] and the machining of an alternate testing bracket (Supporting Information Figure S1). Consequently, adhesion data presented here may vary slightly from work reported previously. The ASTM cleaning method includes degreasing the substrates in trichloroethylene followed by washes in hot base and acid baths. Additional washes and scraping had to be employed to remove the insoluble, cross-linked polymers. Each data point is the average of at least 10 samples, and error bars show the 90% confidence intervals.

■ RESULTS AND DISCUSSION

Polymer Synthesis. Polymers with a variety of molecular weights were made by altering the *n*-BuLi:monomer ratio during synthesis. The *n*-BuLi:monomer ratios were varied from 0.7 to 5.7 mol %. A family of 10 polymers was prepared ranging from number average molecular weights (M_n) of 22 000 to 84 000 g/mol and weight average molecular weights (M_w) of 27 000 to 105 000 g/mol. The synthesis of higher molecular weights was attempted without success. Table 1 provides details on the specifics of each polymer. The characterization data in Table 1 are shown for the protected intermediate poly[(3,4-dimethoxystyrene)-*co*-styrene)] due to visibility of the methoxy peaks in ^1H NMR spectra to provide composition data and to prevent adhesion to the high surface area GPC column. We targeted ~33 mol % 3,4-dihydroxystyrene to be in each polymer owing to prior results showing strong adhesion.[34] The polymers made here displayed final 3,4-dihydroxystyrene contents within a range of 27−34 mol %. Representative ^1H NMR spectra of poly[(3,4-dihydroxystyrene)-*co*-styrene)] are provided in the Supporting Information. Figures S2 and S3 are the polymer before and after cross-linking with $[N(C_4H_9)_4](IO_4)$, respectively. Typical yields were ~75%. A relatively narrow range of polydispersities (PDIs) were found at 1.2 to 1.5.

Table 1. Synthesis and Characterization Data for Poly[(3,4-dimethoxystyrene)-*co*-styrene] Copolymers

final styrene content (%)	final 3,4-dimethoxystyrene content (%)	M_n (g/mol)	M_w (g/mol)	PDI
69	31	22 000	27 000	1.2
70	30	30 000	41 000	1.4
66	34	35 000	48 000	1.4
73	27	37 000	54 000	1.5
70	30	40 000	50 000	1.2
69	31	50 000	65 000	1.3
73	27	57 000	79 000	1.4
71	29	61 000	92 000	1.5

Adhesion and Molecular Weight. Adhesion was measured for each polymer in Table 1. Lap shear bonding with aluminum was chosen to provide a common substrate bonded together in a standard configuration. These selections also facilitate direct comparisons with prior results.[22,23,26,34] Supporting Information Figure S1 shows a typical force-versus-extension curve obtained during an adhesion test. The sharp break at failure is indicative of brittle fracture. Maximum adhesion strength data are presented in Figures 2 and 3 and work of adhesion data are in Supporting Information Table S1.

Molecular weight imparted a strong influence upon the adhesion of this biomimetic system. Adhesion increased directly with molecular weight in the M_n and M_w ranges of ~20 000 to ~100 000 g/mol examined here. These data appear to agree with prior reports with other polymer systems in that higher

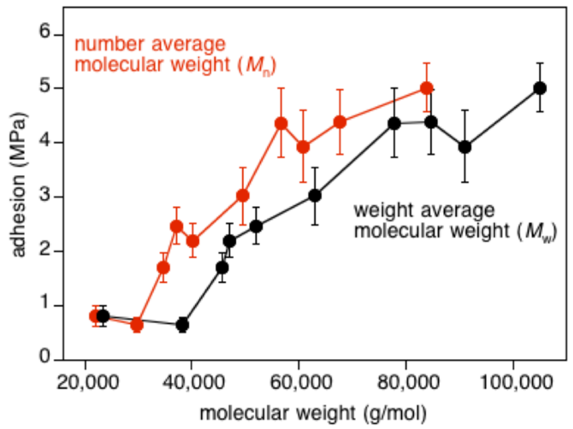


Figure 2. Effect of molecular weight upon adhesion for poly[(3,4-dihydroxystyrene)-*co*-styrene]. The number average molecular weight (M_n) is shown in red and the weight average molecular weight (M_w) is depicted in black. Adhesion testing was conducted in shear on aluminum substrates.

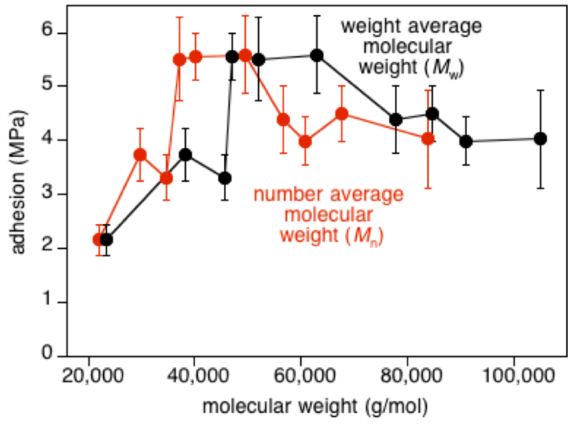


Figure 3. Effect of molecular weight upon adhesion for poly[(3,4-dihydroxystyrene)-*co*-styrene] when cross-linked with $[N(C_4H_9)_4](IO_4)$. The number average molecular weight (M_n) is shown in red and the weight average molecular weight (M_w) is depicted in black. Adhesion testing was conducted in shear on aluminum substrates.

molecular weight polymers can provide greater cohesive polymer—polymer interactions. With the polymer alone, the cohesion—adhesion balance appears to lie more toward adhesion at lower molecular weights. Higher molecular weights introduce more cohesion, more interpenetration, and consequently, greater bulk adhesive performance. To provide a point of reference, the maximum adhesion seen in Figrue 3, at ~6 MPa, approaches the ~7 MPa performance measured for ethylcyanoacrylate, Krazy Glue, when tested under similar conditions.[34]

The influence of polymer molecular weight upon adhesion changes dramatically with introduction of the oxidative cross-linker tetrabutylammonium periodate. Figure 3 shows that the maximum adhesion for the cross-linked polymers is found at intermediate chain lengths. Peak adhesion of ~5.5 MPa occurred in the ranges of $M_n \approx 37\,000-50\,000$ g/mol and $M_w \approx 50\,000-65\,000$ g/mol.

Cross-linking provides an effective means of increasing polymer chain lengths. Oxidative cross-linking of catechol-containing molecules proceeds via one electron oxidation to seminquinones, two electron oxidation to quinones, or a combinaton thereof.[59,60] Subsequent Michael addition, with nucleophiles adding to the oxidized species, brings about covalent cross-links. In the case of poly[(3,4-dihydroxystyrene)-*co*-styrene], phenolic oxygens are the only obvious nucleophile present in the polymers for such reactions. Cross-linking may be a result of oxidized 3,4-dihydroxystyrene, in the form of semiquinones and/or quinones, coupling with aromatic hydroxyl groups.

Polymer—polymer and polymer—surface interactions change as a result of cross-linking. The copolymers described here became insoluble after cross-linking. Various organic solvents, hot acid, and hot base were all used to attempt dissolution without significant success. Extraction of cross-linked polymers with THF, followed by examination with gel permeation chromatography, showed only low concentrations of small fragments. The molecular weight observed ($M_w < 5000$ g/mol) was lower than that of the starting polymer ($M_w = 27\,000$ g/mol). Extraction of a cross-linked polymer with DMSO-d_6 and investigation by ^{1}H NMR spectroscopy found prominent tetrabutylammonium resonances from $[N(C_4H_9)_4(IO_4)]$ as well as lower intensity polymer signals (Supporting Information Figure S3). Cross-linked polymeric solids were also subjected to solid state matrix assisted laser desoprtion and ionization mass spectrometry without obtaining any appreciable signals. Consequently, we can surmise that cross-linking increases molecular weights at least to the point of insolubility. However, the insoluble nature of this system precludes us from providing specific details on molecular weights after cross-linking.

In terms of the adhesive—cohesive balance, cross-linking appears to show where the optimum resides. Below $M_n \approx 37\,000$ g/mol ($M_w \approx 50\,000$ g/mol) there is not sufficient cohesive bonding to yield the strongest bulk adhesion possible. Going beyond $M_n \approx 50\,000$ g/mol ($M_w \approx 65\,000$ g/mol), the added cohesion comes at the expense of surface adhesive interactions and bulk bonding suffers.

The polymers, both with and without $[N(C_4H_9)_4](IO_4)$ cross-linking, gave the least bulk adhesion when molecular weights were low. Typically, low molecular weights allow for higher surface wetting. However, this effect may not be relevant here, given that the polymers were dissolved in solvent prior to application onto the substrates. Heating then evaporated away this solvent. Dissolution allows high surface wetting regardless of the polymer molecular weight.

Comparisons to Other Polymers. The data in Figure 2 for poly[(3,4-dihydroxystyrene)-*co*-styrene], alone, indicate behavior similar to poly(dimethylsiloxanes) in that bulk adhesion increases directly with molecular weight.[36,41,46] We can imagine that, with both poly(dimethylsiloxane) and our biomimetic system, there may well be a point at which adhesion drops with molecular weights higher than those accessible synthetically. When poly[(3,4-dihydroxystyrene)-*co*-styrene] was cross-linked, the behavior became similar to both epoxidized natural rubber and poly(vinyl alcohol) for which there was a peak molecular weight corresponding to maximum bulk adhesion. With epoxidized natural rubber, hydrogen bonding motifs enhance polymer interactions and, consequently, lower molecular weights can give rise to appreciable adhesion.[43−45] Even without $[N(C_4H_9)_4](IO_4)$ cross-linking, hydrogen bonding between pendent catechol groups may be part of the poly[(3,4-dihydroxystyrene)-*co*-styrene] copolymers.

Perspectives from Marine Biology. Given that mussel adhesive proteins are known to be cross-linked extensively, the most appropriate comparisons to make here may be with our cross-linked polymers (Figure 3). The optimized adhesion of cross-linked poly[(3,4-dihydroxystyrene)-*co*-styrene] at $M_n \approx$ 37 000 to 50 000 g/mol ($M_w \approx$ 50 000 to 65 000 g/mol) is similar to the molecular weight of the Mfp-2 at ~45 000 g/mol.[32] This protein happens to be the most abundant constituent of mussel plaques.[31] However, it is possible that these similarities are coincidence. Poly[(3,4-dihydroxystyrene)-*co*-styrene] is a single polymer doing the job of six proteins of quite varied molecular weights. Perhaps it is not surprising that the best adhesion for cross-linked poly[(3,4-dihydroxystyrene)-*co*-styrene] was found to reside between the molecular weight extremes of Mfp-3 at ~6000 g/mol and Mfp-1 at ~110 000 g/mol.

When considering the range of protein molecular weights in mussel plaques, we wondered if there may be some benefit conferred by the mixture. Consequently, we prepared 1:1:1 blends by weight of three poly[(3,4-dihydroxystyrene)-*co*-styrene] polymers with M_w's of 27 000, 54 000, and 105 000 g/mol. This range spans that of our shortest polymer to our longest polymer and contains one in the middle.

Bulk adhesion was measured for this blend of three polymers both with and without $[N(C_4H_9)_4](IO_4)$ cross-linking. Data are provided in Table 2. For the polymer blend alone, adhesion at 2.9 ± 0.6 MPa appeared to be a simple average of the three constituents with the 27 000 g/mol polymer at 0.8 ± 0.2 MPa, 54 000 g/mol at 2.5 ± 0.3 MPa, and 105 000 g/mol at 5.0 ± 0.4 MPa. The story changed significantly with cross-linking. The polymer blend cross-linked with $[N(C_4H_9)_4](IO_4)$ adhered at 7.8 ± 0.7 MPa. Such adhesion is stronger than what was found for the individual polymers when cross-linked, with the 27 000 g/mol polymer adhering at 2.2 ± 0.3 MPa, 54 000 g/mol at 5.5 ± 0.8 MPa, and 105 000 g/mol at 4.0 ± 0.9 MPa. This unexpected result may help us to understand why mussel plaques are comprised of a mixture of proteins with molecular weights of such a wide range.

Table 2. Adhesion Data for Individual Polymers Compared to a Blend of the Same Polymers

M_n (g/mol)	M_w (g/mol)	polymer adhesion (MPa)	polymer + $(IO_4)^-$ adhesion (MPa)
22 000	27 000	0.8 ± 0.2	2.2 ± 0.3
37 000	54 000	2.5 ± 0.3	5.5 ± 0.8
84 000	105 000	5.0 ± 0.4	4.0 ± 0.9
blend	**blend**	**2.9 ± 0.6**	**7.8 ± 0.7**

In the case of our experiments, the different polymers are deposited from a homogeneous solution, rather than being spatially separated in an arrangement analogous to how mussels create their adhesive plaques. Nonetheless, each synthetic polymer may bring a unique property to the system. The lowest molecular weight polymer could reside at the surface providing adhesive bonding. An intermediate molecular weight polymer may be improving cohesive bonding. The highest molecular weight polymer then brings about an initial, high strength network. Mobility of the lower molecular weight species allows for interpenetration and formation of a network. Incorporation of cross-linking is then likely to lock this network together, forming covalent bonds and, effectively, increasing molecular weights. Increasing polydispersity is known to improve adhesive strengths when tested in shear.[50] Ultimately, the blend of multiple molecular weights may allow each component to fulfill different rolls of adhesive and cohesive bonding, much like the various mussel adhesive proteins.

CONCLUSIONS

Data presented here show that molecular weight has a major impact on the bulk adhesion of a polymer system mimicking the DOPA-containing proteins produced by mussels. Results differed when the polymer was examined alone versus with an added cross-linker. The strongest bonding for cross-linked polymers was observed at molecular weights roughly corresponding to the middle range of protein molecular weights used by mussels. Interestingly, a blend of polymers with differing molecular weights adhered stronger than any of the individual components contained within. Perhaps this enhanced bonding with a polymer blend helps to explain why mussels use such a wide range of molecular weights when building their adhesive plaques. Systematic studies like those presented here are helping us to understand the evolution of biological materials and how to use such insights when designing high performance materials.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Image of a lap shear test, a typical force-versus-extension curve, ^{1}H NMR spectra of poly[(3,4-dihydroxystyrene)-*co*-styrene)] before and after cross-linking, and work of adhesion data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: wilker@purdue.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We appreciate support for this work provided by the Office of Naval Research. We would also like to thank Cristina Matos-Peréz, Allison Mattes, and James White for many helpful discussions and assistance with syntheses.

REFERENCES

(1) Waite, J. H. *Integr. Comp. Biol.* **2002**, *42*, 1172−1180.
(2) Wilker, J. J. *Curr. Opin. Chem. Biol.* **2010**, *14*, 276−283.
(3) Wilker, J. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 8076−8078.
(4) Waite, J. H.; Andersen, N. H.; Jewhurst, S.; Sun, C. J. *J. Adhes.* **2005**, *81*, 297−317.
(5) Yu, M. E.; Deming, T. J. *Macromolecules* **1998**, *31*, 4739−4745.
(6) Wang, J.; Liu, C. S.; Lu, X.; Yin, M. *Biomaterials* **2007**, *28*, 3456−3468.
(7) Saxer, S.; Portmann, C.; Tosatti, S.; Gademann, K.; Zurcher, S.; Textor, M. *Macromolecules* **2010**, *43*, 1050−1060.
(8) Li, L.; Li, Y.; Luo, X. F.; Deng, J. P.; Yang, W. T. *React. Funct. Polym.* **2010**, *70*, 938−943.
(9) Wang, J. J.; Tahir, M. N.; Kappl, M.; Tremel, W.; Metz, N.; Barz, M.; Theato, P.; Butt, H. J. *Adv. Mater.* **2008**, *20*, 3872−3876.
(10) Gao, C. L.; Li, G. Z.; Xue, H.; Yang, W.; Zhang, F. B.; Jiang, S. Y. *Biomaterials* **2010**, *31*, 1486−1492.
(11) Chung, H. Y.; Glass, P.; Pothen, J. M.; Sitti, M.; Washburn, N. R. *Biomacromolecules* **2011**, *12*, 342−347.
(12) Kaur, S.; Weerasekare, G. M.; Stewart, R. J. *ACS Appl. Mater. Inter.* **2011**, *3*, 941−944.
(13) Shao, H.; Bachus, K. N.; Stewart, R. J. *Macromol. Biosci.* **2009**, *9*, 464−471.

(14) Stepuk, A.; Halter, J. G.; Schaetz, A.; Grass, R. N.; Stark, W. J. *Chem. Commun.* **2012**, *48*, 6238−6240.

(15) Malisova, B.; Tosatti, S.; Textor, M.; Gademann, K.; Zurcher, S. *Langmuir* **2010**, *26*, 4018−4026.

(16) Yuan, S. J.; Wan, D.; Liang, B.; Pehkonen, S. O.; Ting, Y. P.; Neoh, K. G.; Kang, E. T. *Langmuir* **2011**, *27*, 2761−2774.

(17) Lee, H.; Lee, K. D.; Pyo, K. B.; Park, S. Y.; Lee, H. *Langmuir* **2010**, *26*, 3790−3793.

(18) Murphy, J. L.; Vollenweider, L.; Xu, F. M.; Lee, B. P. *Biomacromolecules* **2010**, *11*, 2976−2984.

(19) Brubaker, C. E.; Kissler, H.; Wang, L. J.; Kaufman, D. B.; Messersmith, P. B. *Biomaterials* **2010**, *31*, 420−427.

(20) Lee, B. P.; Chao, C. Y.; Nunalee, F. N.; Motan, E.; Shull, K. R.; Messersmith, P. B. *Macromolecules* **2006**, *39*, 1740−1748.

(21) Sun, P. Y.; Tian, L. Y.; Zheng, Z.; Wang, X. L. *Acta. Polym. Sin.* **2009**, 803−808.

(22) Westwood, G.; Horton, T. N.; Wilker, J. J. *Macromolecules* **2007**, *40*, 3960−3964.

(23) White, J. D.; Wilker, J. J. *Macromolecules* **2011**, *44*, 5085−5088.

(24) Yang, Z.; Pelton, R. *Macromol. Rapid Commun.* **1998**, *19*, 241−246.

(25) Pan, X. D.; Qin, Z. Q.; Yan, Y. Y.; Sadhukhan, P. *Polymer* **2010**, *51*, 3453−3461.

(26) Matos-Peréz, C. R.; Wilker, J. J. *Macromolecules* **2012**, *45*, 6634−6639.

(27) Cristescu, R.; Mihailescu, I. N.; Stamatin, I.; Doraiswamy, A.; Narayan, R. J.; Westwood, G.; Wilker, J. J.; Stafslien, S.; Chisholm, B.; Chrisey, D. B. *Appl. Surf. Sci.* **2009**, *255*, 5496−5498.

(28) Sedó, J.; Saiz-Poseu, J.; Busqué, F.; Ruiz-Molina, D. *Adv. Mater.* **2013**, *25*, 653−701.

(29) Faure, E.; Falentin-Daudré, C.; Jérôme, C.; Lyskawa, J.; Fournier, D.; Woisel, P.; Detrembleur, C. *Prog. Polym. Sci.* **2013**, *38*, 236−270.

(30) Moulay, S. *C. R. Chim.* **2009**, *12*, 577−601.

(31) Silverman, H. G.; Roberto, F. F. *Mar. Biotechnol.* **2007**, *9*, 661−681.

(32) Lin, Q.; Gourdon, D.; Sun, C. J.; Holten-Andersen, N.; Anderson, T. H.; Waite, J. H.; Israelachvili, J. N. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 3782−3786.

(33) Zhao, H.; Waite, J. H. *J. Biol. Chem.* **2006**, *281*, 26150−26158.

(34) Matos-Peréz, C. R.; White, J. D.; Wilker, J. J. *J. Am. Chem. Soc.* **2012**, *134*, 9498−9505.

(35) Pizzi, A. In *Wood Adhesives: Chemistry and Technology*, 2nd ed.; Pizzi, A., Ed.; Marcel Dekker, Inc.: New York, New York, 1989.

(36) Choi, G. Y.; Zurawsky, W.; Ulman, A. *Langmuir* **1999**, *15*, 8447−8450.

(37) Deruelle, M.; Leger, L.; Tirrell, M. *Macromolecules* **1995**, *28*, 7419−7428.

(38) Nielsen, L. E.; Landel, R. F. In *Mechanical Properties of Polymers and Composites*, 2nd ed.; Faulker, L. L., Ed.; Marcel Dekker: New York, 1994.

(39) Gowariker, V. R.; Viswanathan, N. V.; Sridhar, J. In *Polymer Science*, 1st ed.; New Age International Ltd.: New Delhi, India, 1986.

(40) Mark, J.; Ngai, K.; Graessley, W.; Mandelkern, L.; Samulski, E.; Koeing, J.; Wignall, G. In *Physical Properties of Polymers*, 3rd ed.; University Press: Cambridge, UK, 2004.

(41) Galliano, A.; Bistac, S.; Schultz, J. *J. Colloid Interface Sci.* **2003**, *265*, 372−379.

(42) Hon, D. N. S. In *Analysis of Adhesives*; Taylor & Francis Group, LLC: 2003.

(43) Khan, I.; Poh, B. T. *J. Appl. Polym. Sci.* **2011**, *120*, 2641−2647.

(44) Khan, I.; Poh, B. T. *J. Polym. Environ.* **2012**, *20*, 132−141.

(45) Poh, B. T.; Yong, A. T. *J. Adhesion.* **2009**, *85*, 435−446.

(46) Shanahan, M. E. R.; Michel, F. *Int. J. Adhes. Adhes.* **1991**, *11*, 170−176.

(47) Pizzi, A.; Mittal, K. L. In *Handbook of Adhesive Technology*, 2nd ed.; Pizzi, A., Mittal, K. L., Eds; Marcel Dekker: New York, 2003.

(48) Ali, S. S.; Tang, X. Z.; Alavi, S.; Faubion, J. *J. Agric. Food. Chem.* **2011**, *59*, 12384−12395.

(49) Elizondo, N. J.; Sobral, P. J. A.; Menegalli, F. C. *Carbohydr. Polym.* **2009**, *75*, 592−598.

(50) Krenceski, M. A.; Johnson, J. F. *Polym. Eng. Sci.* **1989**, *29*, 36−43.

(51) Shanahan, M. E. R.; Carre, A. *Langmuir* **1995**, *11*, 1396−1402.

(52) Galliano, A.; Bistac, S.; Schultz, J. *J. Adhes.* **2003**, *79*, 973−991.

(53) Santaniello, E.; Manzocchi, A.; Farachi, C. *Synthesis* **1980**, 563−565.

(54) ASTM International. *Standard D2651: Preparation of Metal Surfaces for Adhesive Bonding*; West Conshohocken, PA, 2008.

(55) ASTM International. *Standard D1002: Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading (Metal-to-Metal)*; West Conshohocken, PA, 2010.

(56) Sever, M. J.; Weisser, J. T.; Monahan, J.; Srinivasan, S.; Wilker, J. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 448−450.

(57) Lee, B. P.; Dalsin, J. L.; Messersmith, P. B. *Biomacromolecules* **2002**, *3*, 1038.

(58) Shao, H.; Weerasekare, G. M; Stewart, R. J. *J. Biomed. Mater. Res., Part A* **2011**, *97A*, 46−51.

(59) Deming, T. J. *Curr. Opin. Chem. Biol.* **1999**, *3*, 100−105.

(60) Rzepecki, L. M.; Waite, J. H. In *Bioorganic Marine Chemistry*; Scheuer, P. J., Eds; Springer-Verlag: Berlin, 1991.