

Surface Hydration and Antifouling Activity of Zwitterionic Polymers

Zhan Chen*

Cite This: *Langmuir* 2022, 38, 4483–4489

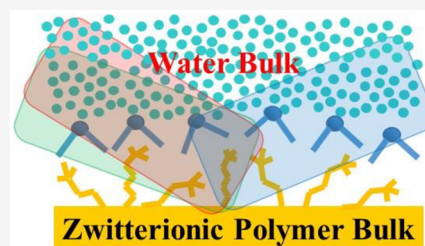
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: It is believed that the strong surface hydration of zwitterionic polymers leads to excellent antifouling properties. This Perspective presents the recent developments in studies on such surface hydration in situ using sum frequency generation (SFG) vibrational spectroscopy. SFG research provides direct molecular level evidence that zwitterionic polymers have strong surface hydration, which prevents protein adsorption and marine animal attachment. The salt effect and protein interaction on surface hydration of zwitterionic polymers have also been examined using SFG. Possible future research directions on surface hydration of new zwitterionic polymers including zwitterionic hydrogels, copolymers, and mixed charged polymers are discussed. It is also important to combine experimental SFG studies with computer simulations to further elucidate the surface hydration to understand antifouling mechanisms.



INTRODUCTION

Antifouling polymers play important roles in a variety of applications such as biomedical implants, drug delivery, membranes for separation, coatings used in the marine environment, etc. Polymers containing poly(ethylene glycol) (PEG) components exhibit excellent antifouling activities and have been widely researched and utilized.¹ Recently, zwitterionic polymers have been developed into powerful antifouling materials with advantages over PEG-containing polymers.^{2–4} Zwitterionic materials have positive and negative charges next to each other, exhibiting an overall charge neutral property. It is widely believed that the excellent antifouling performance of zwitterionic polymers is due to the strong surface hydration, which prevents other molecules from displacing surface bound water to stick to the surface. However, the report on direct observation of the surface hydrated zwitterionic polymers is limited, because of the lack of appropriate tools that can probe the solid/liquid interface in situ.

We have applied a nonlinear optical spectroscopic technique—sum frequency generation (SFG) vibrational spectroscopy—to investigate interfacial water behavior at the zwitterionic polymer/water or zwitterionic polymer/aqueous solution interfaces in situ.^{5–10} Such in situ studies provide direct spectroscopic observation of the strong surface hydration of zwitterionic polymers at the molecular level. SFG is a second-order nonlinear optical spectroscopic technique, which can probe surfaces and buried interfaces including solid/liquid interfaces in situ in real time at the molecular level with a submonolayer interface specificity.^{11–14} SFG theory, instrumentation, experimental procedures, and data analysis methodology have been extensively published^{11–14} and will not be repeated in this Perspective.

STRONG HYDRATION AND SALT EFFECT ON HYDRATION OF ZWITTERIONIC POLYMER SURFACES

SFG has been extensively applied to study interfacial water behavior at various water surfaces and buried water interfaces.^{15–17} We have used SFG to study interfacial water behavior of interfaces between water and a variety of zwitterionic polymers including poly(carboxybetaine acrylamide)s (pCBAA)s with one (pCBAA1) and two (pCBAA2) carbon atoms between the positively charged quaternary amine and the negatively charged carboxyl groups, and poly(sulfobetaine methacrylate) (pSBMA).^{5–10} Figure 1 shows the molecular formulas of pCBAA1, pCBAA2, and pSBMA. The common features of the SFG spectra collected from the interfaces between these zwitterionic polymers and water include strong water O–H stretching signals and the domination of the strongly hydrogen-bonded O–H stretching signal centered below 3200 cm⁻¹, showing the strong surface hydration of zwitterionic polymers (Figure 1).^{5–10}

The strong surface hydration of a zwitterionic polymer is related to its antifouling activity. SFG studies showed strong surface hydration of pCBAA1 and pCBAA2 at pH of 7 or higher, while the surface hydration substantially decreased at lower pHs (Figure 1).⁶ This was well-correlated to the reported results that protein adsorption has a tendency to increase at low pH values

Received: March 1, 2022

Published: April 5, 2022



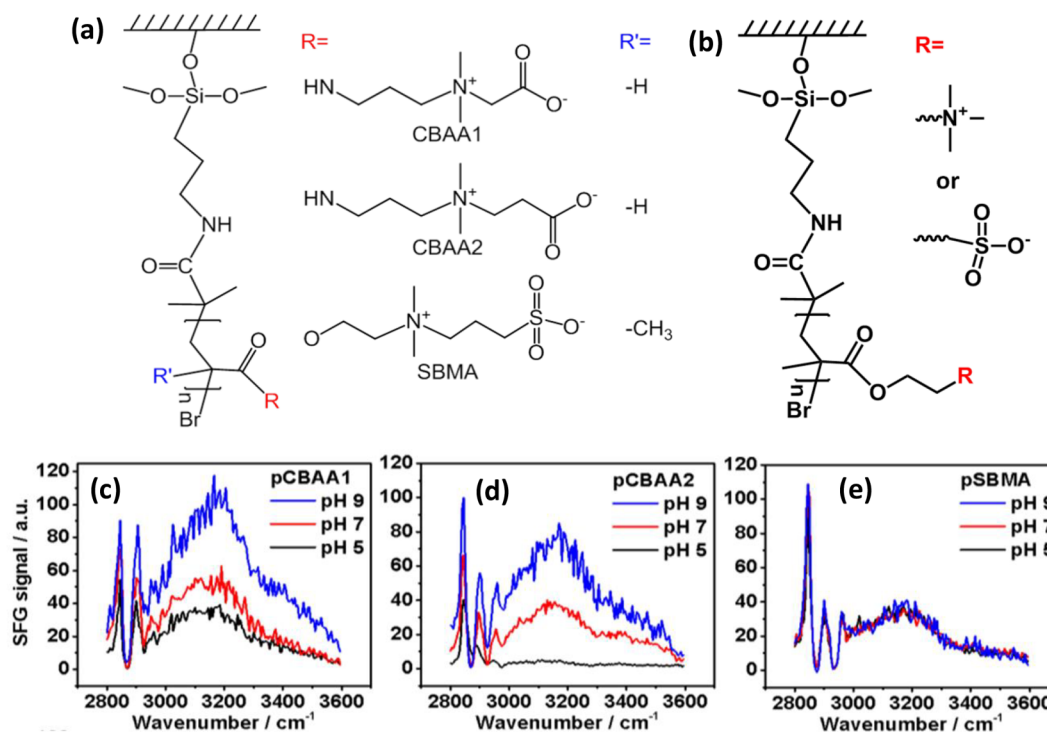


Figure 1. (a) Molecular formulas for pCBAA1, pCBAA2, and pSBMA. (b) Molecular structure of the mixed charged polymer. SFG spectra collected from interfaces between various solutions and (c) pCBAA1, (d) pCBAA2, as well as (e) pSBMA at different pH values. Solutions of pH 5, 7, and 9 are HCl solution, water, and NaOH solution, respectively. [Panel (a) has been reproduced with permission from ref 8. Copyright 2015, American Chemical Society, Washington, DC. Panel (b) has been reproduced with permission from ref 22. Copyright 2018, American Chemical Society, Washington, DC. Panels (c), (d) and (e) have been reproduced with permission from ref 6. Copyright 2014, American Chemical Society, Washington, DC.]

for pCBAA1 and pCBAA2.¹⁸ SFG results also indicated that surface hydration of pSBMA does not change between pH 5 and pH 9 (Figure 1),⁶ which matches well with the bacteria attachment data, showing similarly low amounts of bacteria attachment on pSBMA in this pH range.¹⁹

Because of the strong surface hydration, proteins such as bovine serum albumin (BSA), fibrinogen, and lysozyme could not disrupt the surface hydration layer on pSBMA at the polymer/protein solution interfaces, evidenced by similar SFG water spectra collected from the pSBMA/water and the pSBMA/protein solution interfaces.⁷ This is different from antifouling polymers containing PEG components, where proteins can interact with the polymer surface hydration layer (shown by varied SFG water signals in the SFG spectra collected from the polymer/water and polymer/protein solution interfaces).⁷ SFG water signals detected from the PEG containing polymer/protein solution interfaces can be recovered to that detected from the polymer/water interface after the polymer was removed from the protein solutions and washed by water.⁷ Therefore, likely zwitterionic pSBMA has a stronger surface hydration, in comparison to the PEG containing polymers, leading to a better antifouling performance of pSBMA.

Because of the strong surface hydration, marine animals, such as mussels, avoid staying on pSBMA surfaces, even after we bound these mussels to the pSBMA surfaces with rubber bands.²⁰ Small amounts of mussels remained on pSBMA (forced by rubber bands) could generate mussel adhesives strongly adhering to the surface, which were difficult to be removed.²⁰ Therefore, the antifouling property of zwitterionic polymers is determined by whether foulants want to remain on their surfaces

or not, not by how strong the foulants stick to the surfaces. Because of the strong surface hydration, foulants do not want to remain on the zwitterionic polymer surface, leading to the excellent antifouling activity of zwitterionic polymers.

Superb antifouling properties are required for polymers used as biomedical implants, marine coatings, and drug delivery materials. For such applications, antifouling polymers will be used in solutions with high concentrations of salts. For example, the ionic strength of seawater is ~ 0.6 M. High salt concentration in solution may reduce the zwitterionic surface hydration, influencing the antifouling performance of zwitterionic polymers.

SFG studies showed that salt molecules in the solution greatly reduced water O–H stretching signal at the zwitterionic polymer/salt solution interfaces, compared to that at the zwitterionic polymer/water interfaces.⁶ This was observed from a variety of zwitterionic polymers including pCBAA1, pCBAA2, and pSBMA.⁶ The ions in the salt solution could screen the charges on the zwitterionic polymer surface, reducing the surface hydration. The strong hydration of a zwitterionic polymer (e.g., pCBAA or pSBMA) is mainly due to the strong hydration of negatively charged groups on the polymer surface.²¹ Metal cations in the salt solution could interact strongly with these negative charges on the zwitterionic polymer surface to reduce the surface hydration.

Our recent SFG studies showed that a newly designed zwitterionic polymer—poly(trimethylamine N-oxide) (pTMAO)—could effectively resist the salt effect on surface hydration.¹⁰ The molecular formula of pTMAO is shown in Figure 2. For other zwitterionic polymer materials such as

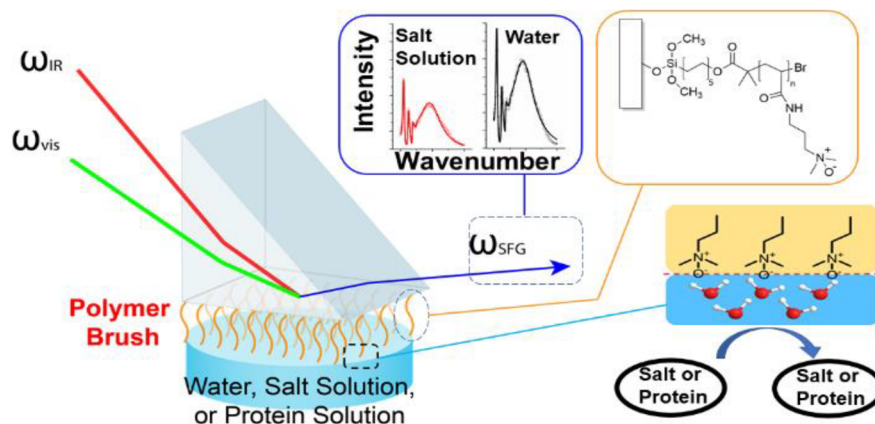


Figure 2. (Left) SFG sample geometry used to study the pTMAO/water interface or the pTMAO/solution interface. (Right, top left) Representative SFG spectra collected from interfaces. Red represents the pTMAO/0.5 M NaCl solution interface; black represents the pTMAO/water interface. (Right, top right) Molecular formula of pTMAO. The repeating unit of TMAO is represented by n . (Right, bottom right) Schematic showing the interface between pTMAO and water or solutions. [Reproduced with permission from ref 10. Copyright 2021, American Chemical Society, Washington, DC.]

pCBAs and pSBMA, SFG water signals collected from the salt solution (e.g., 0.2 or 0.5 M NaCl solution) interface decreased substantially.^{6,22} Differently, SFG results indicated that substantial SFG water signals could still be observed from the pTMAO/0.5 M NaCl solution interface (Figure 2) or the pTMAO/seawater interface (Figure 3).¹⁰ The strong hydration of pTMAO ensures its excellent antifouling activity in salt solutions and in seawater. SFG spectra collected from the pTMAO/seawater interface and pTMAO/protein solution (in seawater) interfaces are the same, showing that protein molecules (BSA, fibrinogen, lysozyme) could not disrupt the surface hydration of pTMAO in seawater (Figure 3).¹⁰

Computer simulation was used to investigate interfaces between pTMAO and water, salt solutions, and protein solutions.¹⁰ It was found that the water structures are not very different at the pTMAO/water and pTMAO/0.6 M NaCl solution interfaces, well correlated to the SFG data. pTMAO has a unique character, compared to other zwitterionic polymers. That is, in pTMAO, the distance between the positive (N^+) and negative (O^-) charges is much shorter (with only one chemical bond). The simulation study reveals that such a short distance between the positive and negative charges on pTMAO enables stronger hydrogen bonds between O^- and water, and also enables repulsion between N^+ and Na^+ , leading to strong resistance against salt disruption on polymer surface hydration.¹⁰

Molecular dynamics simulations have also been used to study protein adsorption on pTMAO surface in 0.6 M NaCl solution, using lysozyme as an example.¹⁰ It was found previously by simulations that lysozyme molecules could be easily adsorbed onto all the surfaces studied such as azobenzene brush surfaces, graphene, gold crystal, and polyethylene. It was completely different on a pTMAO surface. During the simulated time period of 190 ns, the lysozyme protein could come close to the pTMAO surface, but then went away from the surface, demonstrating the excellent antifouling performance of pTMAO (Figure 3). Because of the strong hydration on the pTMAO surface, the protein displayed large translational and rotational mobility on the pTMAO surface.¹⁰ On other surfaces, because of the lack of strong surface hydration, the lysozyme molecules do not have such mobility, leading to the adsorption on these surfaces. The simulation results could be well-

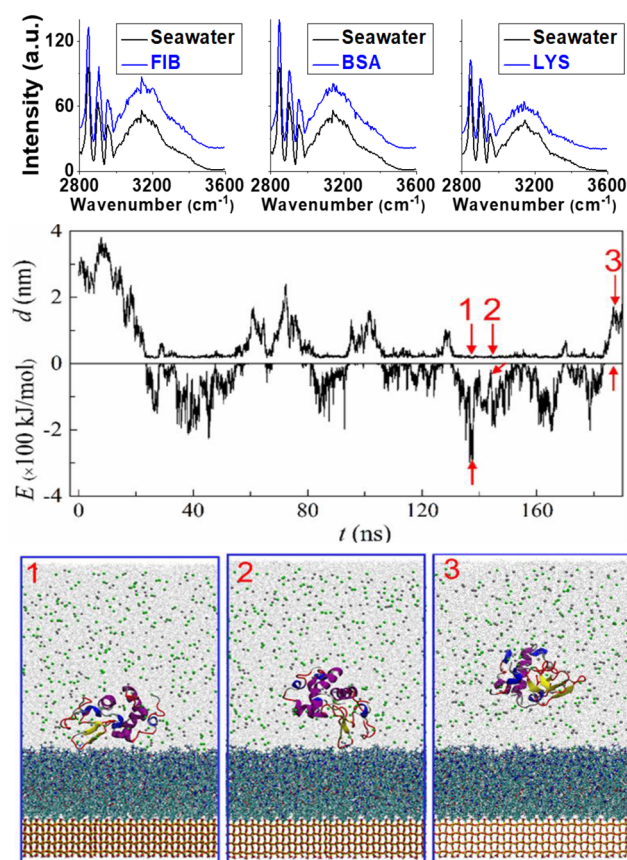


Figure 3. (Top) SFG spectra collected from the pTMAO/seawater interfaces and pTMAO/protein solution (in seawater—offset by 20 in intensity) interfaces. (Middle, top) Minimum distance (d) and (down) total interaction energy (E) between lysozyme (LYS) protein and surface atoms as a function of time (t). Bottom: Protein's pTMAO surface attaching-bumping events: (1) side-on landing, (2) end-on landing, and (3) bumping away. [Reproduced with permission from ref 10. Copyright 2021, American Chemical Society, Washington, DC.]

correlated to the SFG studies on pTMAO/protein solution (in seawater) interfaces, providing further understanding on the origins of such SFG results.¹⁰

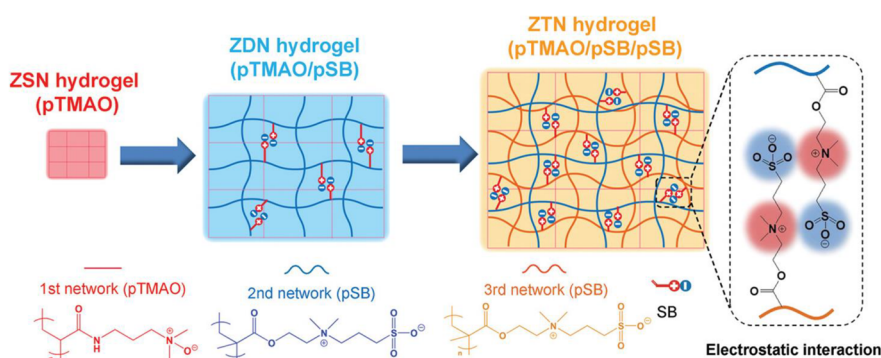


Figure 4. Schematic for preparation of the pTMAO/poly(sulfobetaine) (pSB)/pSB zwitterionic triple-network (ZTN) hydrogel with strong electrostatic interaction and network entanglement. [Legend: ZSN, zwitterionic single network; ZDN, zwitterionic double network. Reproduced with permission from ref 26. Copyright 2021, John Wiley and Sons.]

MOVING FORWARD

Surface Hydration of Newly Developed Zwitterionic Polymer Materials: Zwitterionic Hydrogel. As discussed above, strong surface hydration of zwitterionic polymers plays significant roles in determining the excellent antifouling performance of these materials. Hydrogels are cross-linked hydrophilic polymer networks that can retain great amounts of water (sometimes more than 90%). Hydrogels have been widely researched for use in many biomedical-related applications such as biomedical implants, wound care, drug delivery because of their unique properties such as biocompatibility, tunable mechanical properties, and excellent permeability. Zwitterionic hydrogel materials have been extensively investigated which combine the excellent properties of zwitterionic polymers and hydrogels.^{23,24}

One shortcoming of some of the hydrogels is the lack of mechanical strength. Jiang et al. developed a zwitterionic hydrogel material with excellent mechanical properties as a high-strength zwitterionic elastomer.²⁵ In such a study, two weak zwitterionic hydrogels were integrated into an elastomer-like high-strength pure zwitterionic hydrogel via a “swelling” and “locking” mechanism. Such a material demonstrated both excellent biocompatibility and strong mechanical strength.²⁵ Recently, the same group developed a high-strength and nonfouling zwitterionic triple-network hydrogel involving pTMAO in saline environments (Figure 4), which demonstrated excellent antifouling performance and better mechanical strengths, compared to the double-network hydrogel.²⁶

To fully understand the structure–property relationship between these newly developed zwitterionic hydrogels, it is necessary to characterize the interfacial structures and interfacial hydration of these materials. We demonstrated the feasibility to apply SFG to study interfacial hydration and protein interactions of hydrogels including a zwitterionic hydrogel.²⁷ The future study of interfacial hydration/interfacial interaction of new zwitterionic hydrogels with excellent mechanical strength is needed, which will provide fundamental understanding on the interfacial properties of these excellent materials, aiding in the design, development, and optimization of zwitterionic hydrogels with superb interfacial and mechanical characteristics.

Surface Hydration of Newly Developed Zwitterionic Polymer Materials: Copolymers Containing Zwitterionic Components. A copolymer is a polymer that contains two or more different types of monomers, which can achieve desired properties that cannot be achieved by homopolymers. Copolymers with zwitterionic materials have been developed,

for example, for membrane coatings and antifouling materials.^{28,29} The use of zwitterionic component in a copolymer is aimed to facilitate the copolymer antifouling performance (due to the strong surface hydration). In order to understand the surface structure–function relationship, it is necessary to probe interfacial structure and interfacial hydration of such copolymers. Such studies will provide detailed fundamental knowledge on how the copolymer interfacial properties and structures are dependent on the types of copolymer components and ratios of different components, providing guidance on the rational design of copolymers containing zwitterionic components with desired functions.

Surface Hydration of Newly Developed Zwitterionic Polymer Materials: Mixed-Charged Polymers. Zwitterionic polymers have excellent antifouling activities, because of their strong surface hydration with strong interactions between surfaces charges and interfacial water molecules. A variety of zwitterionic polymers such as pCBAs, pSBMA, and pTMAO have been developed and researched. The syntheses of these zwitterionic polymers are not straightforward and sometimes can be quite challenging. Similar strong surface hydration to zwitterionic polymer can be achieved using a mixed charged material, a material with mixed positive and negative charges.¹⁹ The difference between a zwitterionic polymer and a mixed charged polymer is that, in a mixed charged polymer, the positively charged group and the negatively charged group do not need to be directly next to each other. Such a mixed charged polymer is usually easier to synthesize with lower cost. It is worth mentioning that the BSA surface has a mixed charge property: The BSA surface has a similar amount of many more negatively charged K and positively charged E amino acids than other protein molecules.³⁰ Such a large number of K and E components (with similar amounts of E and K components) lead to the strong hydration of BSA surface,³⁰ enabling the antifouling activity.

We have studied surface hydration of mixed charged polymers with positively charged (with quaternary amine) and negatively charged (with sulfonate) groups with different bulk mixing ratios using SFG and tested their antifouling activities against protein adsorption using surface plasmon resonance (SPR).²² SPR results demonstrated that the 1:1 mixed charged polymer exhibited much better antifouling performance than mixed charged polymers with more negatively charged or positively charged groups in the material.²² This is related to the fact that the 1:1 mixed charged polymer has stronger surface hydration than other mixed charged polymers. Strong SFG interfacial

water signals were detected from the 1:1 mixed charged polymer/water interface, dominated by the strongly hydrogen bonded water signals centered at $\sim 3200\text{ cm}^{-1}$. For other mixed charged polymers, it was found that the interfacial water on the polymer/water interface either has a low ordering structure or contains a substantial amount of weakly hydrogen-bonded water species.²² It was also found that the protein molecules such as BSA and fibrinogen could not disrupt the surface hydration layer of the 1:1 mixed charged polymer, because of the strong surface hydration, shown by similar SFG spectra collected from the polymer/water and polymer/protein solution interfaces.²²

Because of the easy synthesis and lower cost, and with similar antifouling activity as the zwitterionic polymers, mixed charged polymers have great potentials for use in many applications as antifouling polymer materials. A variety of combinations of the positively charged and negatively charged groups can be introduced in such materials, leading to the development of antifouling materials with unique as well as tunable properties. Their interfacial structures and surface hydration should be probed systematically.

Combining Experimental Studies and Computer Simulations. Our SFG studies showed strong hydration on zwitterionic polymer surfaces.⁵ Normally, SFG water spectra are quite broad and interfacial water molecules can have different interfacial interactions. Computer simulations can provide additional details about interfacial water behavior at the atomistic level, providing further knowledge on surface hydration.¹⁰ Detailed interfacial water structure and hydrogen bonding strength, molecular interactions between the negatively charged groups or the positively charged groups of the zwitterionic polymer and water molecules at the interface, various interfacial interaction energies, and effects of ions on water structures at zwitterionic polymer/salt solution interfaces can be examined by computer simulations. The simulated results can be compared to the SFG data to validate SFG results and provide detailed interpretation of SFG data. SFG and simulation studies on surface hydrations of various zwitterionic polymers should be performed to understand their similar and different characters for antifouling applications. Furthermore, computer simulations on interactions between zwitterionic polymers and biological systems such as proteins could lead to further understanding on the effect of surface hydration on such interactions, and the molecular mechanisms of antifouling activities of zwitterionic polymers.

SFG Studies on Zwitterionic Polymers beyond Protein Adsorption. Protein adsorption serves as a good model test for antifouling activity study. The real environments where the antifouling materials are used can be much more complex, compared to protein solutions. For biomedical applications, zwitterionic materials may directly contact with blood, which contains many different components. For coatings used in a marine environment, they directly interact with marine animals. Therefore, it is necessary to conduct studies (e.g., SFG studies) in more-complicated “real” environments.

We have applied SFG to study interfaces between different polymers and adhesives generated by live mussels.²⁰ It was found that mussels dehydrated the “fouling” polymer surfaces then deposited adhesives on the dehydrated polymer surfaces. For a zwitterionic polymer surface that is strongly hydrated, it is difficult to dehydrate the surface; therefore, mussels do not want to remain on such a surface, even after a rubber band was used to tie the mussel onto the surface.

In the future, we should study zwitterionic polymers in more-complex “real” environments to understand surface hydration and the effects of various factors on surface hydration with SFG, as well as its relationship to antifouling. For zwitterionic polymers targeted for biomedical applications, SFG should be applied to study interactions between various zwitterionic polymers and different cells, tissues, or whole blood. For zwitterionic polymers designed for use as antifouling coatings in marine environment, SFG could be used to study surface hydration and interfacial interaction between zwitterionic polymers and live marine animals other than mussels such as barnacles, oysters, etc. The zwitterionic polymer surface hydration in contact with different marine animals will be compared, which will lead to an understanding of the general rules of zwitterionic polymer antifouling.

SUMMARY

In this Perspective, our SFG results on zwitterionic polymer surface hydration were presented. It was found that surfaces of all the zwitterionic polymers studied including pCBAA, pSBMA, and pTAMO exhibit strong hydration in aqueous environments. The strong surface hydration prevents protein adsorption and ensures the excellent antifouling performance. Ions in the salt solution may reduce the zwitterionic polymer surface hydration to influence the antifouling activity. The short distance between the negatively charged and positively charged groups, such as those in pTMAO, could effectively prevent the ion disruption on the surface hydration, leading to the excellent antifouling behavior in seawater.

SFG is a powerful nonlinear optical spectroscopy, which can be applied to study solid/liquid interfaces in situ in real time at the molecular level. Many SFG studies have been applied to examine model water interfaces. We have demonstrated the feasibility of applying SFG to study complex interfaces such as the zwitterionic polymer/mussel adhesive plaque (deposited by live mussel) interface. It is expected in the future that SFG will be applied to study more-complicated “real” zwitterionic polymer interfaces such as those involving cells, blood, or live marine animals. Such studies could provide important real-world knowledge regarding zwitterionic polymer hydration and zwitterionic polymer interfacial interactions, which may not be able to be deduced from model water interface studies. The future combination of SFG and computer simulation studies will validate the simulation results experimentally and provide detailed and atomistic level interpretations of experimental results. The studies on new zwitterionic polymers such as zwitterionic hydrogels, zwitterionic copolymers, and mixed charged polymers will lead to the fundamental understanding on the structure (including surface structure/surface hydration)–function relationships of advanced zwitterionic polymer materials, helping the design and development of multifunctional zwitterionic materials.

AUTHOR INFORMATION

Corresponding Author

Zhan Chen – Departments of Chemistry and Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, United States;  orcid.org/0000-0001-8687-8348; Email: zhanc@umich.edu

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.langmuir.2c00512>

Notes

The author declares no competing financial interest.

Biography



Professor Zhan Chen is a Michael D. Morris Collegiate Professor of Chemistry, Macromolecular Science and Engineering, Biophysics, and Applied Physics at the University of Michigan. He received his B.S. degree in Chemistry from Peking University, M.S. degree in Physics from Chinese Academy of Sciences, Ph.D. degree in Chemistry from the University of California at Berkeley, and he did his postdoctoral research at Lawrence Berkeley National Laboratory. He worked at the University of Michigan as an assistant professor (2000–2005) and as an associate professor with tenure (2005–2009); he was promoted to a full professor with tenure in 2009. His research is focused on understanding molecular structures of polymers and biological molecules at interfaces using advanced spectroscopic methods.

ACKNOWLEDGMENTS

The author acknowledges the support from the Office of Naval Research (No. N00014-20-1-2234) and the University of Michigan. The author also thanks Prof. Shaoyi Jiang (Cornell University) and Prof. Tao Wei (Howard University) for extensive discussions on the research related to zwitterionic polymers.

REFERENCES

- (1) Ma, H.; Hyun, J.; Stiller, P.; Chilkoti, A. "Non-fouling" Oligo(ethylene glycol)-Functionalized Polymer Brushes Synthesized by Surface-Initiated Atom Transfer Radical Polymerization. *Adv. Mater.* **2004**, *16* (4), 338–341.
- (2) Schlenoff, J. B. Zwitteration: Coating Surfaces with Zwitterionic Functionality to Reduce Nonspecific Adsorption. *Langmuir* **2014**, *30* (32), 9625–9636.
- (3) Zhang, Z.; Chao, T.; Chen, S.; Jiang, S. Superlow Fouling Sulfobetaine and Carboxybetaine Polymers on Glass Slides. *Langmuir* **2006**, *22* (24), 10072–10077.
- (4) Ladd, J.; Zhang, Z.; Chen, S.; Hower, J. C.; Jiang, S. Zwitterionic Polymers Exhibiting High Resistance to Nonspecific Protein Adsorption from Human Serum and Plasma. *Biomacromolecules* **2008**, *9* (5), 1357–1361.
- (5) Leng, C.; Sun, S.; Zhang, K.; Jiang, S.; Chen, Z. Molecular Level Studies on Interfacial Hydration of Zwitterionic and Other Antifouling Polymers in Situ. *Acta Biomater.* **2016**, *40*, 6–15.
- (6) Leng, C.; Han, X.; Shao, Q.; Zhu, Y.; Li, Y.; Jiang, S.; Chen, Z. In Situ Probing of the Surface Hydration of Zwitterionic Polymer Brushes: Structural and Environmental Effects. *J. Phys. Chem. C* **2014**, *118* (29), 15840–15845.
- (7) Leng, C.; Hung, H.-C.; Sun, S.; Wang, D.; Li, Y.; Jiang, S.; Chen, Z. Probing the Surface Hydration of Nonfouling Zwitterionic and PEG Materials in Contact with Proteins. *ACS Appl. Mater. Interfaces* **2015**, *7* (30), 16881–16888.
- (8) Leng, C.; Hung, H.-C.; Sieggreen, O. A.; Li, Y.; Jiang, S.; Chen, Z. Probing the Surface Hydration of Nonfouling Zwitterionic and Poly(ethylene glycol) Materials with Isotopic Dilution Spectroscopy. *J. Phys. Chem. C* **2015**, *119* (16), 8775–8780.
- (9) Han, X.; Leng, C.; Shao, Q.; Jiang, S.; Chen, Z. Absolute Orientations of Water Molecules at Zwitterionic Polymer Interfaces and Interfacial Dynamics after Salt Exposure. *Langmuir* **2019**, *35* (5), 1327–1334.
- (10) Huang, H.; Zhang, C.; Crisci, R.; Lu, T.; Hung, H.-C.; Sajib, M. S. J.; Sarker, P.; Ma, J.; Wei, T.; Jiang, S.; Chen, Z. Strong Surface Hydration and Salt Resistant Mechanism of a New Nonfouling Zwitterionic Polymer Based on Protein Stabilizer TMAO. *J. Am. Chem. Soc.* **2021**, *143* (40), 16786–16795.
- (11) Tian, C. S.; Shen, Y. R. Recent progress on sum-frequency spectroscopy. *Surf. Sci. Rep.* **2014**, *69* (2–3), 105–131.
- (12) Chen, Z.; Shen, Y. R.; Somorjai, G. A. Studies of polymer surfaces by sum frequency generation vibrational spectroscopy. *Annu. Rev. Phys. Chem.* **2002**, *53*, 437–465.
- (13) Guo, W.; Lu, T.; Gandhi, Z.; Chen, Z. Probing Orientations and Conformations of Peptides and Proteins at Buried Interfaces. *J. Phys. Chem. Lett.* **2021**, *12* (41), 10144–10155.
- (14) Lu, X.; Zhang, C.; Ulrich, N.; Xiao, M.; Ma, Y.-H.; Chen, Z. Studying Polymer Surfaces and Interfaces with Sum Frequency Generation Vibrational Spectroscopy. *Anal. Chem.* **2017**, *89* (1), 466–489.
- (15) Tian, C. S.; Shen, Y. R. Sum-frequency vibrational spectroscopic studies of water/vapor interfaces. *Chem. Phys. Lett.* **2009**, *470* (1–3), 1–6.
- (16) Backus, E. H. G.; Schaefer, J.; Bonn, M. Probing the Mineral-Water Interface with Nonlinear Optical Spectroscopy. *Angew. Chem. Inter. Ed.* **2021**, *60* (19), 10482–10501.
- (17) Nihonyanagi, S.; Yamaguchi, S.; Tahara, T. Ultrafast Dynamics at Water Interfaces Studied by Vibrational Sum Frequency Generation Spectroscopy. *Chem. Rev.* **2017**, *117* (16), 10665–10693.
- (18) Zhang, Z.; Vaisocherová, H.; Cheng, G.; Yang, W.; Xue, H.; Jiang, S. Nonfouling Behavior of Polycarboxybetaine-Grafted Surfaces: Structural and Environmental Effects. *Biomacromolecules* **2008**, *9* (10), 2686–2692.
- (19) Mi, L.; Bernards, M. T.; Cheng, G.; Yu, Q.; Jiang, S. pH responsive properties of non-fouling mixed-charge polymer brushes based on quaternary amine and carboxylic acid monomers. *Biomaterials* **2010**, *31* (10), 2919–2925.
- (20) Del Grosso, C. A.; Leng, C.; Zhang, K.; Hung, H.-C.; Jiang, S.; Chen, Z.; Wilker, J. J. Surface Hydration for Antifouling and Bioadhesion. *Chem. Sci.* **2020**, *11* (38), 10367–10377.
- (21) Shao, Q.; He, Y.; White, A. D.; Jiang, S. Difference in Hydration between Carboxybetaine and Sulfobetaine. *J. Phys. Chem. B* **2010**, *114* (49), 16625–16631.
- (22) Leng, C.; Huang, H.; Zhang, K.; Hung, H.-C.; Xu, Y.; Li, Y.; Jiang, S.; Chen, Z. Effect of Surface Hydration on Antifouling Properties of Mixed Charged Polymers. *Langmuir* **2018**, *34* (22), 6538–6545.
- (23) Liu, S.; Tang, J.; Ji, F.; Lin, W.; Chen, S. Recent Advances in Zwitterionic Hydrogels: Preparation, Property, and Biomedical Application. *Gels* **2022**, *8* (1), 46.
- (24) Zhang, Y.; Liu, Y.; Ren, B.; Zhang, D.; Xie, S.; Chang, Y.; Yang, J.; Wu, J.; Xu, L.; Zheng, J. Fundamentals and applications of zwitterionic antifouling polymers. *J. Phys. D: Appl. Phys.* **2019**, *52* (40), 403001.
- (25) Dong, D.; Tsao, C.; Hung, H.-C.; Yao, F.; Tang, C.; Niu, L.; Ma, J.; MacArthur, J.; Sinclair, A.; Wu, K.; Jain, P.; Hansen, M. R.; Ly, D.; Tang, S. G.; Luu, T. M.; Jain, P.; Jiang, S. High-strength and fibrous capsule-resistant zwitterionic elastomers. *Sci. Adv.* **2021**, *7* (1), eabc5442.
- (26) Li, X.; Tang, C.; Liu, D.; Yuan, Z.; Hung, H. C.; Luozhong, S.; Gu, W.; Wu, K.; Jiang, S. High-Strength and Nonfouling Zwitterionic Triple-Network Hydrogel in Saline Environments. *Adv. Mater.* **2021**, *33* (39), 2102479.
- (27) Zhang, C.; Parada, G. A.; Zhao, X.; Chen, Z. Probing Surface Hydration and Molecular Structure of Zwitterionic and Polyacrylamide Hydrogels. *Langmuir* **2019**, *35* (41), 13292–13300.

(28) Bengani, P.; Kou, Y.; Asatekin, A. Zwitterionic copolymer self-assembly for fouling resistant, high flux membrane with size-based small molecule selectivity. *J. Membr. Sci.* **2015**, *493*, 755–765.

(29) Koschitzki, F.; Wanka, R.; Sobota, L.; Gardner, H.; Hunsucker, K. Z.; Swain, G. W.; Rosenhahn, A. Amphiphilic Zwitterionic Acrylate/Methacrylate Copolymers for Marine Fouling-Release Coatings. *Langmuir* **2021**, *37* (18), 5591–5600.

(30) Zhang, K.; Huang, H.; Hung, H.-C.; Leng, C.; Wei, S.; Crisci, R.; Jiang, S.; Chen, Z. Strong Hydration at the Poly(ethylene glycol) Brush/Albumin Solution Interface. *Langmuir* **2020**, *36* (8), 2030–2036.

Recommended by ACS

Effects of Amphiphilic Polypeptoid Side Chains on Polymer Surface Chemistry and Hydrophilicity

Mikayla E. Barry, Rachel A. Segalman, *et al.*

JANUARY 28, 2022
ACS APPLIED MATERIALS & INTERFACES

READ 

Cross-Linking Highly Lubricious Phosphocholinated Polymer Brushes: Effect on Surface Interactions and Frictional Behavior

Noa Iuster, Jacob Klein, *et al.*

SEPTEMBER 01, 2017
MACROMOLECULES

READ 

Mapping the Interfacial Chemistry and Structure of Partially Fluorinated Bottlebrush Polymers and Their Linear Analogues

Azhad U. Chowdhury, Benjamin Doughty, *et al.*

DECEMBER 29, 2020
LANGMUIR

READ 

Control of Polymer Brush Morphology, Rheology, and Protein Repulsion by Hydrogen Bond Complexation

John Andersson, Andreas Dahlin, *et al.*

APRIL 14, 2021
LANGMUIR

READ 

Get More Suggestions >