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Molecular insights into the hydration of zwitterionic polymers†

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Preventing ice formation and accumulation on solid surfaces has been a great challenge to address for various engineering and technological applications. Recently, the new development of zwitterionic polymer coatings attracted a lot of attention due to their excellent anti-icing performance (*i.e.*, effectively reducing ice formation and adhesion), making them ideal material candidates for anti-icing coating applications. In this study, we employ density functional theory (DFT) to explore the hydration behaviors of two representative zwitterionic polymers, *i.e.*, poly(sulfobetaine-methacrylate) (polySB) and poly(2-methacryloxyethyl-phosphorylcholine) (polyMPC). Through detailed bonding analysis by crystal orbital Hamilton populations (COHP), our results indicate strong interaction and covalent-nature bonds between the hydrogen atoms in water molecules and polymers' oxygen atoms of the anionic group of the polymer. Electron partial density of states (PDOS), Bader charge analysis, and energy calculations further demonstrate the physical and chemical nature of the water-polymer bonds. Interestingly, our modeling results also reveal that the addition of more water molecules will decrease the bonding stability of the bond between adsorbed water molecules to the polymer. Such induced bond instability, along with the polymer's hydrophilic character, suggests that continuous association and dissociation of bonded water molecules serve as the key mechanism which explains the inhibition of water clustering of the hydration layer. Our findings provide valuable insights into the physiochemical nature of water-polymer interaction by unveiling the molecular mechanism of hydration behavior, paving the way for design of next-generation anti-icing materials.

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Design, System, Application

Zwitterionic polymers have emerged as a promising material for anti-icing applications. However, a lack of fundamental understanding of the interfacial hydration mechanism of these polymers has hindered their design and optimization for improved anti-icing performance. To address this issue, we conducted an atomistic modeling study based on density functional theory (DFT) to investigate how the charge distribution and specific zwitterionic units (*i.e.*, phosphorylcholine and sulfobetaine groups) impact the hydration behaviors of zwitterionic polymers. Our results reveal that the anionic group of the polymer chain plays a crucial role in governing the strength of interaction with water molecules, which ultimately affects the ice formation energy. Specifically, we found that the more negatively charged the anionic group, the stronger the anti-icing effect it will have. These findings highlight the critical role of the zwitterionic unit in the water-polymer interaction and suggest a materials-by-design approach to engineer anti-icing polymers through molecular design.

Introduction

In a harsh and cold environment, ice is a significant problem for many engineering applications, ranging from aircraft,¹ ships,² trains, power lines,³ to renewable systems,⁴ which can

cause significant damage and lead to great economic losses. An efficient, environmental, and economical solution to the icing issue is essential. As early as 1946, there have been growing efforts to prevent water icing on surfaces by using ice-phobic, superhydrophobic, and anti-icing coatings.⁵ Up to date, many approaches and strategies have been proposed to develop and optimize efficient and durable anti-icing coatings that can inhibit the formation, propagation, and adhesion of ice.⁶ To reduce ice adhesion, various methods have been employed; for instance, aqueous or organic lubricant coatings have demonstrated relatively good anti-icing performance.^{7,8} Additionally, coatings with wetting properties,^{9,10} charges, and ions have been used to inhibit

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To improve the effectiveness of zwitterionic polymers in antifouling and anti-icing applications, an in-depth understanding of the molecular level interactions between zwitterionic polymers and water is required. To bridge this knowledge gap, in this study, we employ atomistic modeling approach based on density functional theory (DFT) to conduct a thorough examination of the fundamental interactions between zwitterionic polymers and water at the molecular and electronic levels, for the first time. DFT is a powerful computational tool that is capable of accurately calculating weak interactions and predicting the electronic structure of adsorbates and adsorbents, which is crucial for

understanding the adsorption process. By comparing two representative zwitterionic polymers, polysulfobetaine (polySB) and polyphosphorylcholine (polyMPC), as potential anti-icing coating polymers, we aim to gain in-depth insights into the hydration process and provide a physical and chemical understanding of the water–polymer interaction at a fundamental molecular level, which is needed to develop an extension of structure–property relationships for materials by design.

Methods

As previously mentioned, polySB and polyMPC demonstrated remarkable resistance to icing and fouling, as shown in experiments.¹⁷ Structurally, they possess a reversed charge distribution, with polySB having an anionic terminal group and polyMPC having a cationic terminal group. Additionally, they have distinct anionic groups, phosphorylcholine in polyMPC and sulfobetaine in polySB. Hence, in this study, we selected these two zwitterionic polymers to gain insights into designing effective anti-icing coatings. For both studied polymers, polySB and polyMPC, we use periodic structure models of one “short” chain with four monomers surrounded by vacuum to avoid any possible interactions between periodic replicas. The atomic structure of the 3D periodic models of polySB and polyMPC are shown in Fig. 1. Then, water molecules are incrementally added to the simulation cell to simulate polymer hydration with different water

content. All dry and wet models are fully optimized to the ground structure before hydration and bonding analysis. The Vienna *ab initio* Simulation Package (VASP)^{30–32} is used to perform non-spin-polarized planewave DFT calculations, where the core and valence electrons are described using the projector-augmented wave (PAW)^{33,34} and the generalized-gradient approximation in the Perdew–Burke–Ernzerhof (PBE) form is used to describe electron exchange and correlation.³⁵ The Kohn–Sham equations are used to improve the accuracy of self-consistent density functional theory (DFT) calculations. The theoretical single-electron Kohn–Sham equation can be expressed as

$$(-\hbar^2/2m\nabla^2 + v[\{\vec{R}_I\}, \vec{r}, \rho(\vec{r})])\phi_i^{\text{KS}}(\{\vec{R}_I\}, \vec{r}) = \varepsilon_i(\{\vec{R}_I\})\phi_i^{\text{KS}}(\{\vec{R}_I\}, \vec{r}) \quad (1)$$

where first term corresponds to kinetic energy T and uses symbol of gradient $\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$. In the eqn (1), we find a set of one-electron orbital's $\phi_i^{\text{KS}}(\{\vec{R}_I\}, \vec{r})$ and their energies ε_i . The orbitals are combined with orbital occupation function f_i for constructing the total density of electrons (ρ) that is composed out of pairs of orbitals with coinciding indices

$$\rho(\vec{r}) = \sum_i f_i \phi_i^{\text{KS}*}(\vec{r}) \phi_i^{\text{KS}}(\vec{r}) \quad (2)$$

Total density determines the potential as following

$$v[\vec{r}, \rho] = \delta/\delta\rho[E^{\text{tot}}[\rho] - T[\rho]] \quad (3)$$

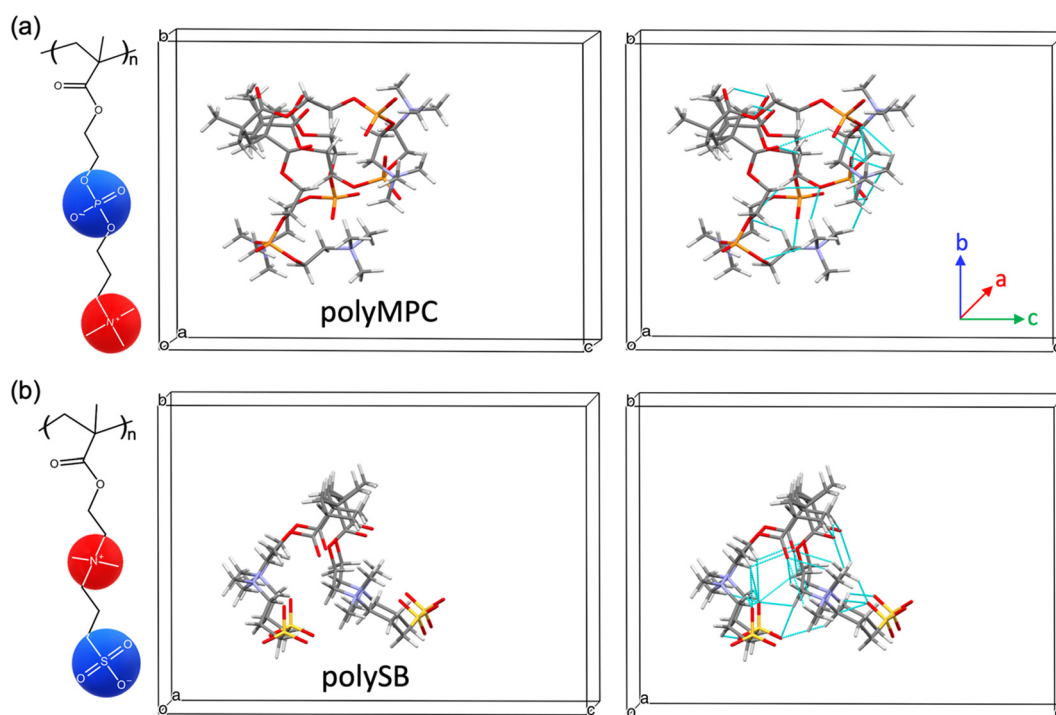


Fig. 1 Ground polymer structures with 4 monomers for (a) polyMPC and (b) polySB. The left and right simulation cells show the optimized configurations of models with and without visualization of hydrogen bonds, respectively. Dashed cyan line represents hydrogen bonds. Red, yellow, orange, purple, gray, and white atoms are oxygen, sulfur, phosphorus, nitrogen, carbon, and hydrogen, respectively.



Dispersion interactions are considered by applying Grimme's PBE-D₃ corrections with Becke-Johnson damping function.³⁶ The kinetic energy cutoff is set to 400 eV and the Gaussian smearing of 0.03 eV is used for Brillouin-zone integrations. Atomic positions are optimized using the conjugate-gradient method with energy and force tolerance of 10⁻⁶ eV and 0.01 eV Å⁻¹, respectively. The electron density of states (DOS) is a measure of the number of states within a specific energy range. It is used to analyze the electronic structure of a system. The definition of DOS is

$$n(\varepsilon) = \sum_i \delta(\varepsilon - \varepsilon_i) \quad (4)$$

where the Dirac delta function is approximated using a Gaussian function of finite width. Then, the Bader method is used to perform partial charges analysis of all atoms in the calculated ground structures.^{37–40}

To provide a detailed picture of the nature of the bonding between water and polymer, we carry out charge density and chemical bonding analyses by calculating the crystal orbital Hamilton population (COHP)⁴¹ using the Local Orbital Basis Suite Toward Electronic-Structure Reconstruction (LOBSTER) code.⁴² To examine interaction strength, water adsorption energies are calculated using the following equation: $\Delta E_{\text{Ads}} = (E_{\text{surf}+\text{H}_2\text{O}} - E_{\text{surf}} - E_{\text{H}_2\text{O}})/n$, where $E_{\text{surf}+\text{H}_2\text{O}}$ is the energy of the wet surface, E_{surf} is the energy of the initial dry surface, $E_{\text{H}_2\text{O}}$ is the energy of a free water molecule, and n is the number of

water molecules per simulation cell. Furthermore, to include the temperature effect, the Gibbs free energy⁴³ is calculated according to the following equation: $\Delta G = (\Delta H - T\Delta S)/n$, where ΔS is the difference of entropy between the adsorption state of hydrogen and gas phase, ΔH is the change in enthalpy, and T is temperature. If water adsorption is a spontaneous reaction, then ΔG will be negative.

Results and discussion

Electronic structure of zwitterionic polymers

We first examine the atomic and electronic properties of the ground structure of dry zwitterionic polymers, as depicted in Fig. 1. As expected, the simulated ground structures of polySB and polyMPC have “physical” crosslinking in the form of hydrogen bonds between their side chains due to the strong dipole–dipole interaction between their anionic and cationic groups, as shown in the right simulation cells in Fig. 1. PolyMPC has more crumpled ground structure and longer side chains than polySB, which has more straight side chains. However, polySB has a larger number of hydrogen bonds within its side chains, with an average bond length of 2.38 Å, while in polyMPC it is 2.42 Å. Since atomic charges play an important role in the interaction of charged groups, we use Bader charge analysis to calculate the charge of the main atoms in the anionic and cationic groups. The Bader electron population of the atom ($Q_{\text{A}}^{\text{Bader}}$) is calculated as the

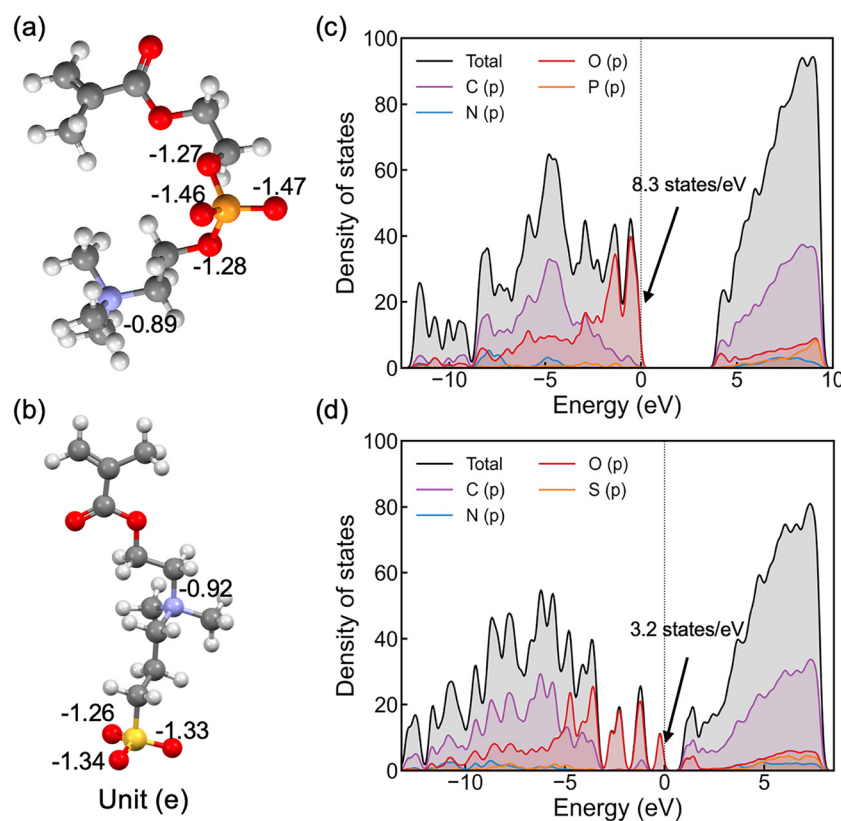
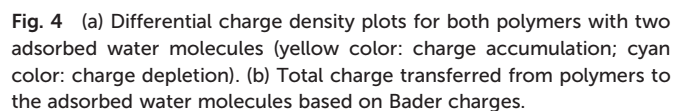


Fig. 2 Calculated average Bader atomic charges for (a) polyMPC and (b) polySB. Partial density of states of (c) polyMPC and (d) polySB, where the Fermi level is marked as vertical dotted lines at zero energy.



Furthermore, Fig. 5a and b shows that the $\text{O}_{\text{poly}}\text{-H}_{\text{water}}$ bond in polyMPC is stronger than in polySB, which is consistent with the shorter $\text{O}_{\text{poly}}\text{-H}_{\text{water}}$ bond length of 1.68 Å in polyMPC compared to 1.84 Å in polySB, as well as the greater charge transferred to the adsorbed water molecules from polyMPC than from polySB. Interestingly, in Fig. 5b, we observe that the increase in water content, which results in a thicker hydration layer, leads to a decrease in the strength of the $\text{O}_{\text{poly}}\text{-H}_{\text{water}}$ bond of the closest water molecule to the polymer. Such weakening of the $\text{O}_{\text{poly}}\text{-H}_{\text{water}}$ bond is also evident in the depression of the -COHP bonding states in Fig. 5c and d.



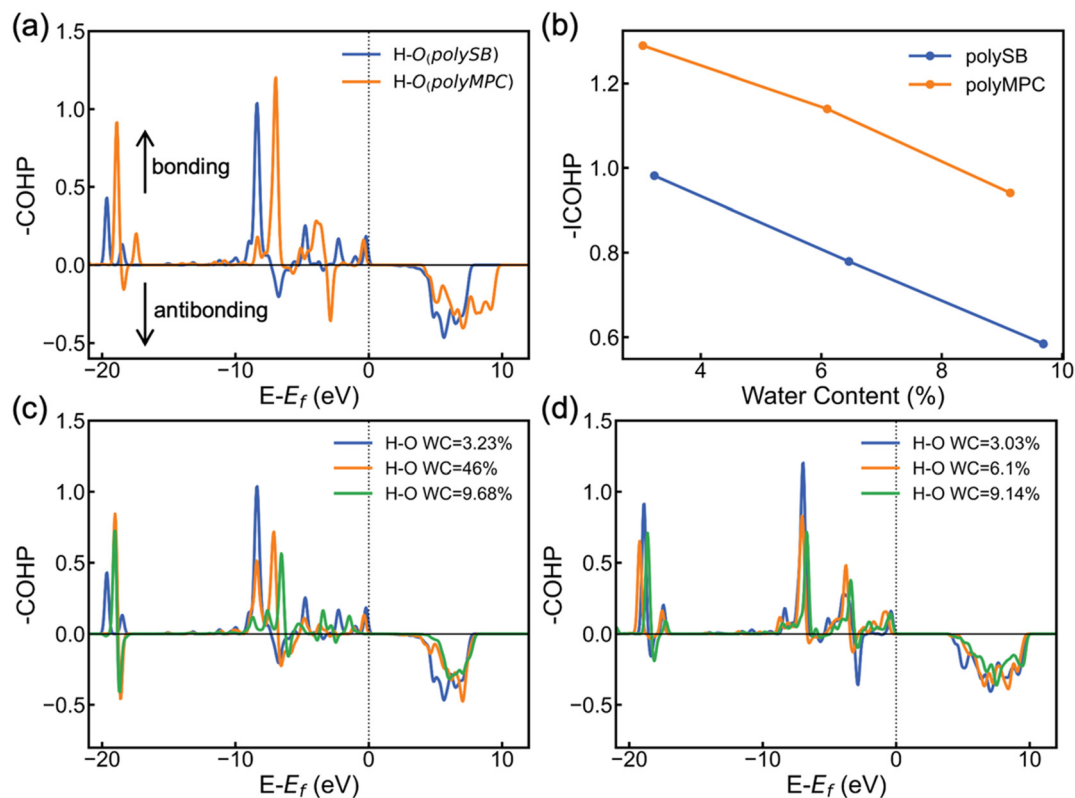


Fig. 5 (a) Crystal orbital Hamilton population (COHP) of the bond between hydrogen atom of the adsorbed H₂O and the nearest oxygen of polySB and polyMPC at WC = 3.23% and 3.03%, respectively. (b) Integrated COHP (ICOHP) vs. water content, calculated COHP for the bond between hydrogen atom of adsorbed H₂O and nearest oxygen atom of the polySB (c) and polyMPC (d) at different WC.

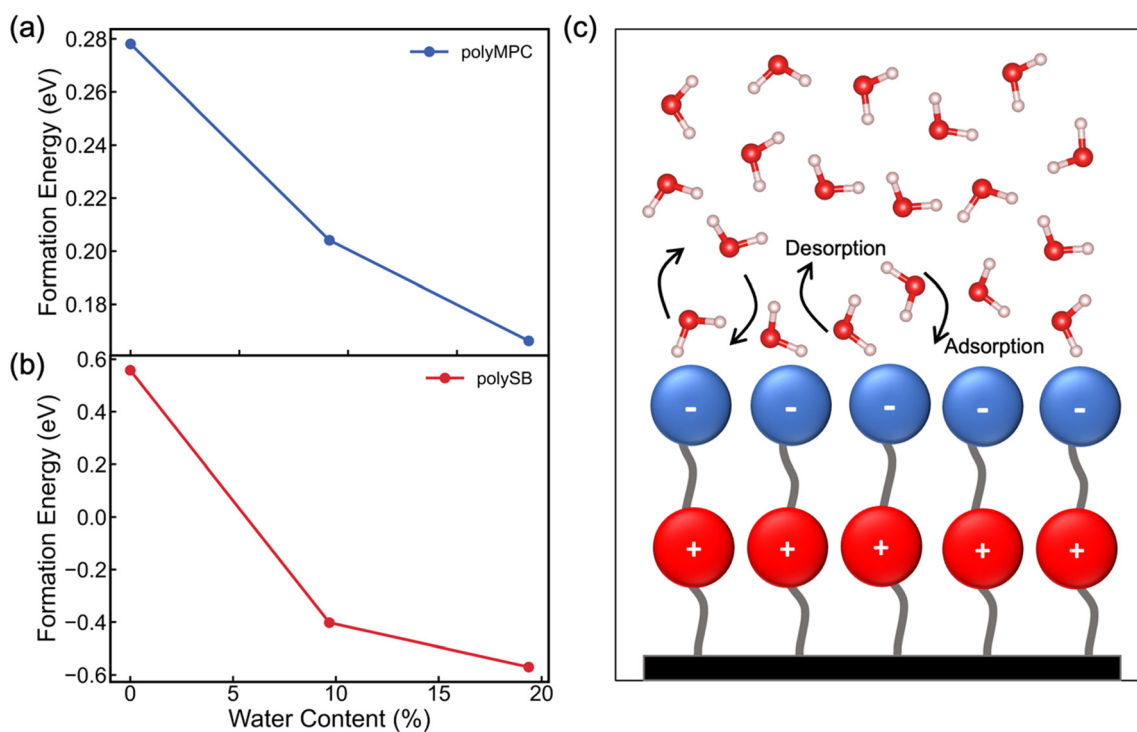


Fig. 6 Calculated formation energy for small ice cluster of the farther water molecules from the surface of (a) polyMPC and (b) polySB vs. WC of the hydration layer. (c) A schematic illustration showing the expected dynamic of polySB hydration layer.



We next evaluate the formation energy (E_{form}) to further test the hypothesis that the strongly bonded dynamic hydration layer will not likely freeze as informed from our above analysis. In our simulation, E_{form} is calculated from the energy difference of four H_2O molecules forming a small ice cluster on polymer relative to the same number of adsorbed liquid like water molecules: $E_{\text{form}} = E_{4\text{H}_2\text{O}}^{\text{ice}} - E_{4\text{H}_2\text{O}}^{\text{liquid}}$, where $E_{4\text{H}_2\text{O}}^{\text{liquid}}$ is the total energy of the polymer with four adsorbed water molecules and $E_{4\text{H}_2\text{O}}^{\text{ice}}$ is the total energy of the system with adsorbed ice cluster. Ground structures of adsorbed ice cluster are shown in Fig. S5.† The calculated clustering formation energies are +0.28 eV for polyMPC and +0.58 eV for polySB, in the absence of water, as shown in Fig. 6a and b. This result indicates that there is repulsion between the interacting components, making the tightly adsorbed ice clusters right on polymers is energetically unfavorable and unstable.

We further calculate the formation energy needed for small ice clustering on hydrated polymer surface, in the present of hydration layer with water content of approximately 9.5% and 19.5%. The resulting formation energy of the cluster (shown in Fig. 6a and b) significantly decreases on both wet polymers, but remains positive on polyMPC, suggesting that a thicker layer of water molecules needs to be present on the surface of polyMPC before ice formation. These results help to explain the experimental observation that the delayed ice nucleation or formation and the low ice adhesion on polySB, which is likely due to the presence of a non-freezable hydration layer.¹⁷ The similar observation was found with poly(ethylene glycol),⁵⁰ which reduces ice adhesion due to hydrogen-bonded water molecules on the surface that do not freeze and serve as a self-lubricating interfacial layer. Based on our simulation results, it is expected that it will take longer time and more water to form ice on polyMPC compared to polySB and that polyMPC will have much lower ice adhesion strength due to a thick water-lubricating interfacial layer. Our findings suggest polyMPC is an excellent candidate for anti-icing coating applications outperforming polySB. Additionally, the previously indicated bond instability (Fig. 5b) along with the superhydrophilic nature of the polymers suggest that the nearest layer of adsorbed water molecules on the polymer surface has dynamically bond forming and breaking, as illustrated in Fig. 6c. This dynamic hydration layer acts as a non-freezing hydration lubricant, which has been suggested by Yu *et al.*,¹⁸ who observed similar hydration lubricant on the hydrophilic segment made of strongly bonded water molecules through hydrogen bonds, which forms non-freezable adsorbed water molecules. Built upon our modeling framework established in this study, in the future, it is worth testing a larger number of polymers having diverse chemical structures to further understand the relationship between the anti-icing properties and their molecular characteristics of zwitterionic polymers.

Conclusion

In this study, we investigate the intermolecular interactions between water molecules and two representative superhydrophilic zwitterionic polymers using DFT. We find that polyMPC and polySB have different atomic structures and electronic properties, leading to contrast hydration behaviors associated with interactions with water. Particularly, polyMPC has a more crumpled ground structure, a stronger total dipole moment, and more occupied states at the Fermi level compared to polySB. Detailed bonding analyses demonstrate that the bond between water and polyMPC is stronger compared to polySB, with polyMPC exhibiting more charge transfer to tightly adsorbed water molecules. The partial covalent nature of the polymer–water bond is further confirmed by COHP chemical bonding analysis. The tightly bonded first layer of adsorbed water molecules, known as the hydration layer, does not freeze and acts as a self-lubricating interfacial layer. These characteristics explain the observed delay of ice formation on zwitterionic polymers with relatively low ice adhesion. Our findings suggest that the strong interaction between water and polyMPC make it a promising candidate for anti-icing applications. Our work provides valuable insights into the hydration mechanism of zwitterionic polymers at a fundamental level, paving the way for establishing a materials-by-design strategy for high-performance anti-icing polymers.

Author contributions

W. X. supervised and coordinated all aspects of the project. S. A. T. performed all the calculations and analysis. Both authors contributed to the writing of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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