The Effects of Chemical Substitution and Polymerization on the pK_a Values of Sulfonic Acids

Haitao Dong,[†] Hongbo Du,[†] Sumith Ranil Wickramasinghe,[‡] and Xianghong Qian*,[†]

Department of Mechanical Engineering, Colorado State University, Fort Collins, Colorado 80523-1374, and Department of Chemical and Biological Engineering, Colorado State University, Fort Collins, Colorado 80523-1370

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The effects of ring substitution on the pK_a value of benzenesulfonic acid (BSA) were investigated using a combined quantum mechanical and classical approach. Ring substitution with strong electron-withdrawing elements such as F, Cl, and Br is found to enhance the acidity of the BSA. More importantly, ring substitution with $-NO_2$ groups which form an extended conjugated π-system with the benzene ring exhibits the strongest enhancement of the acidity. The effects of polymerization on the styrenesulfonic acid (SSA) were also investigated by solving the classical Poisson−Boltzmann equation. It is found that polymerization significantly decreases the acidity of SSA due to the alteration of the electrostatic environment surrounding the acid group upon polymerization. The average pK_a value converges to 2.9 from the corresponding monomer value of −0.53 at a degree of polymerization of 8−12. These results shed significant light on how to design sulfonic-acid-based solid acid catalysts to achieve desired catalytic properties.

1. Introduction

Solid acid catalysts have found a wide range of applications in organic synthesis and green chemistry.[1−3] Due to their heterogeneous nature, applying solid acid catalysts can improve the overall efficiency of the synthesis because they are easier to be separated from the reaction media, resulting in a higher percentage of catalyst reuse, lower impact on environment, and less reactor corrosion than the traditional inorganic acids.[4] The carriers of solid acid catalysts are usually amorphous inert materials, such as mesoporous silica, on which organic acid groups are anchored through covalent bonding.[4−8]

In organic synthesis, strong acids are widely used as catalysts in alkylation, acylation, hydrolysis, isomerization, etc.[2,9] To increase the acid strength of the solid acid catalysts, the organic acids can be modified by chemical substitution. In particular, substitution with halides such as F and Cl with strong electronegativity has been shown to effectively increase the acid strength of the organic acids to the range of inorganic acids. Trifluoromethanesulfonic acid, for instance, has an enhanced acid strength that is comparable to H_2SO_4 acid.[10] In the present work, we study the acid strength of benzenesulfonic acid (BSA) influenced by the various chemical substitutions on the benzene ring. We used *ab initio* quantum chemical methods to calculate the free energy changes of the ionization process of the sulfonic acid group in BSA with and without a variety of chemical substitutions. The details of the thermodynamic cycle and the quantum chemical calculations are given in the Methodology section.

The most widely used commercial solid acid catalyst, Nafion, is a polymeric perfluoroalanesulfonic acid.[11] Nafion can also be attached onto the surface of mesoporous silica in order to increase its surface area. It has been reported that the Nafion attached on mesoporous silica exhibits a significant enhancement of its catalytic activity.[12−14] However, the acid strength of this solid acid catalyst is not exactly known. Nafion's pK_a value is expected to be different from its corresponding monomer value because the electrostatic environment surrounding the acid groups is changed due to spatial correlations of these groups and polymerization. Forsyth et al. showed that two carboxyl groups in a protein can have very different pK_a values of 2 and 9, indicating significant changes in their environment.[15] Mbaraka et al. also reported a pK_a dependence on the spatial locations of the acid groups in an experimental study of organosulfonic acid groups absorbed on amorphous silica surface.[16] The pK_a dependence is attributed to the cooperativity of neighboring acid sites.

In the present work, we attempt to study the change of pK_a values of the sulfonic acid groups in styrenesulfonic acid (SSA) oligomers as a function of the degree of polymerization (DP). After polymerization, the microscopic environment surrounding the sulfonic acid groups will be different. Since the dielectric constants of water and the polymer are drastically different, the presence of the other organic residues surrounding the sulfonic acid groups will change the electrostatic interactions between the charged groups. In addition, polymerization will modify the *van der Waals* interaction and potentially the hydrogen bonding interaction as well. Therefore, the free energy change of the ionizing process is expected to be different, leading to a shift in its pK_a value. We apply the classical continuum dielectric model based on the Poisson−Boltzmann equation (PBE) to calculate the pK_a values of SSA oligomers with DP varying from 2 to 12. In order to take into account the variation in the oligomer conformational structures, the multiconformation continuum electrostatics (MCCE) package developed by Gunner's group is used.[17,18] It incorporates a PBE solver (DelPhi code[19]) with the molecular mechanics force field and Monte Carlo sampling to generate a reliable distribution of conformational structures. The solvent in our calculations is treated implicitly; i.e., the solvation structures around the acid groups are not explicitly considered. The solvent responds to the charge

* Corresponding author. E-mail: xhqian@engr.colostate.edu.
[†] Department of Mechanical Engineering.
[‡] Department of Chemical and Biological Engineering.

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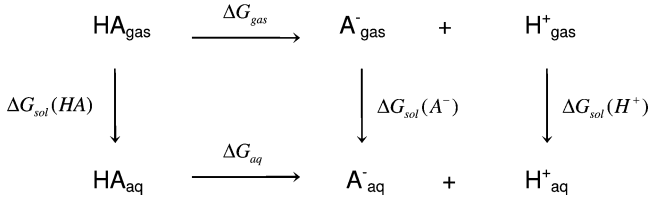
SCHEME 1: Thermodynamic Cycle for Determining the Free Energy Change for Proton Dissociation and the pK_a Value of Acid HA



distribution as a whole, based on a proper dielectric constant. The charges on the atoms of the SSA oligomers are obtained using *ab initio* molecular dynamics simulations with CPMD.[20] The computational details including the use of MCCE code and the calculations of atomic charges are presented in the Methodology section.

2. Methodology

2.1. Thermodynamic Cycles for Acids with Chemical Substitution. The pK_a value of an acid group is determined from the free energy change of the ionization process in the aqueous solution. However, this quantity is very difficult to calculate directly. Therefore, the following thermodynamic cycle (Scheme 1) is used to separate the total free energy change into contributions from the gas phase and the solvation process.

The gas phase free energies for the acid and its conjugate base can be calculated by accurate electronic structure methods. For the solvation free energies, the polarizable continuum model (PCM) has been used for a number of small organic acids and bases.[21] It was used here for calculating the solvation free energies of the monomeric organosulfonic acids. Due to a proton's relative small size and large charge, the error in its calculated solvation free energy is expected to be large. Instead, the experimental solvation free energy of −264.0 kcal/mol was used in the pK_a calculations here.[22] It should be noted that this value accounts for 1.9 kcal/mol of difference in free energy due to changing the gas phase standard state of 1 atm to the solution standard state of 1 mol/L. The pK_a value of the acid HA is determined using the following formula.

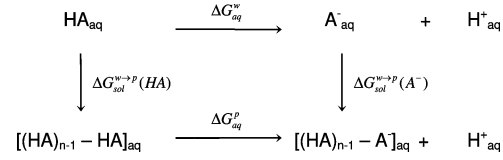
$$\mathrm{p}K_a = \frac{1}{2.303RT}(\Delta G_{gas} - \Delta G_{sol}(\mathrm{HA}) + \Delta G_{sol}(\mathrm{A}^-) + \Delta G_{sol}(\mathrm{H}^+)) \quad (1)$$

Chemical substitution is known to influence pK_a values. Trifluoromethansulfonic acid, for instance, has a pK_a value comparable to that of pure sulfuric acid because of the strong electronegativity of the substituted fluorine.[10] The shift in the pK_a values can be conveniently calculated by comparing two thermodynamic cycles, one for an acid without substitution (HA) and the other with substitution (HB):

$$\Delta\mathrm{p}K_a = \mathrm{p}K_a(\mathrm{HB}) - \mathrm{p}K_a(\mathrm{HA}) = \frac{1}{2.303RT}(\Delta\Delta G_{gas}(\mathrm{HA} \rightarrow \mathrm{HB}) - \Delta\Delta G_{sol}(\mathrm{HA} \rightarrow \mathrm{HB}) + \Delta\Delta G_{sol}(\mathrm{A}^- \rightarrow \mathrm{B}^-)) \quad (2)$$

The pK_a values determined using the free energy difference of the two proton dissociation processes is expected to be more accurate because the errors involved in the calculated gas phase free energies as well as solvation free energies can be partially canceled out. Moreover, the solvation free energies of a proton are exactly the same in the two cycles, and thus are canceled completely. This eliminates the errors that may be embedded in the experimental measurements of proton solvation energy.

SCHEME 2: Thermodynamic Cycle for Determining the pK_a Values of Short Oligomers of Styrenesulfonic Acid



2.2. Gas Phase Free Energy. The complete basis set (CBS) quantum model chemistry developed by Petersson et al. can be used to calculate gas phase free energy accurately.[23−25] However, it is not suitable in this work because of the large number of atoms in the substituted BSA molecules. Instead, the less computationally demanding DFT based B3LYP functional was used to calculate the gas phase free energies. We have previously shown that the errors involved in B3LYP/6-31+G(d) are approximately constant compared to CBS-QB3 for small carboxylic acids.[26] We expect this feature to be retained for BSA and its substituted species. Moreover, the errors in the calculated pK_a values can be further reduced by using eq 2 because the errors are expected to be similar in magnitude for similar molecular structures.

2.3. Solvation Free Energy. Tomasi's polarizable continuum model (PCM) is one of the most commonly used and reliable solvation models.[27] It treats the solvent as a continuum medium with an appropriate dielectric constant polarized by the charges and multipole distributions on the solute molecules. In our calculations, the conductor-like PCM (CPCM) was used to calculate solvation free energies.[28] It has been shown that this model can accurately predict solvation free energies for carboxylic acids and their conjugate bases.[29,30] Moreover, Liptak et al. have reported that this model combined with the CBS-QB3 method is able to accurately predict pK_a values for 20 phenols with standard deviations of less than 0.4 pK_a units.[31] In our calculations, the gas phase structures of the acids optimized at the HF/6-31+G(d) level and the UAHF atomic radii[32] were used to build the solutes. Studies have shown that the structures optimized at a high level of theory/basis sets or with solvent do not necessarily give more accurate solvation free energies.[33] In our recent paper, the predicted pK_a values using the same methods for small carboxylic acids are within 1.3 pK_a units from their corresponding experimental values.[26] This high level of accuracy is due to a partial cancellation of errors among the gas phase free energies as well as the solvation free energies.

2.4. Thermodynamic Cycle for Polymeric Acids. Large molecular systems like polymeric organosulfonic acids are beyond the capabilities of the *ab initio* electronic structure methods. To predict the pK_a value of a sulfonic acid group in a polymer, one can treat the ionizing acid group as the solute, and calculate the electrostatic interaction energy with the rest of the polymer using an implicit method; i.e., the rest of the polymer acts like a part of the solvent with a unique dielectric constant. The shift in pK_a values due to the polymerization can be obtained from the thermodynamic cycle shown in Scheme 2 and eq 3.

$$\Delta pK_a^{w\rightarrow p} = \frac{1}{2.303RT}(\Delta G_{sol}^{w\rightarrow p}(A^-) - \Delta G_{sol}^{w\rightarrow p}(HA)) \quad (3)$$

The pK_a values of the monomeric sulfonic acids (or ΔG_{aq}^{w}) can be obtained from calculations or experimental measurements. The differences in the solvation free energies, $\Delta G_{sol}^{w\rightarrow p}$, can be calculated from appropriate solvation models.

2.5. Classical Reaction Field Energy. The thermodynamic cycle in Scheme 2 greatly simplifies the calculation of pK_a for polymeric organic acids. However, so far, it remains difficult to use *ab initio* electronic structure methods to determine solvent effects, which now include interactions between different parts of the polymer. We instead used a classical continuum dielectric model for the solvation free energies. This model is based on the Poisson−Boltzmann equation (PBE)

$$\nabla\cdot\varepsilon(\vec{r})\nabla\varphi(\vec{r}) = -4\pi\rho_0(\vec{r}) - 4\pi\sum_\lambda q_\lambda\rho_\lambda \exp[-\beta q_\lambda\varphi(\vec{r})] \quad (4)$$

where the mean electrostatic potential at a position $\vec{r}$ due to the charges in the system, $\varphi(\vec{r})$, is approximated by the Boltzmann distribution $\exp[-\beta q_\lambda\varphi(\vec{r})]$. In eq 4, $\varepsilon(\vec{r})$ is the position dependent dielectric constant, ρ_0 the charge distribution of the solute, and q_λ and ρ_λ the charge and concentration of the λth species in the solvent, respectively. The PBE has been used widely to calculate the electrostatic properties of macromolecular systems.[34−36] In particular, proteins are highly charged macromolecules and their electrostatic features are crucial to many biological processes. It has been shown that PBE can accurately describe the electrostatic environment of proteins, reflected in a number of pK_a calculations.[17,37−40]

Under the PBE frame, the Coulombic system is divided into a solute region and a structureless solvent region (may have multiple dielectric regions). The solvation free energy of the solute (e.g., the ionizable sulfonic acid group as in the present study) is a sum of contributions from the electrostatic interactions including the interactions between the solute and the induced charges in the solute−solvent interface (the reaction field energy), and the interactions due to the presence of external fields and salts in the solvent (not considered in the present study).

$$\Delta G_{sol} = \sum_j q_j\varphi_{coul}(\vec{r}_j) + \sum_j q_j\varphi_{react}(\vec{r}_j) + \sum_j q_j\varphi_{solv}(\vec{r}_j) \quad (5)$$

More comprehensive discussions on using eqs 4 and 5 can be found elsewhere.[19] In our calculations, the PBE is used for both the neutral molecule and for the ionized acid group (the conjugate base), respectively. The difference in the solvation free energies is used to calculation the pK_a changes. Currently, we are only interested in the intrinsic pK_a values, i.e., when all other ionizable groups are at their neutral states with only one positive charge on the entire polymer. Therefore, the differences in the solvation energies involving the interactions between the targeted ionizable sulfonic acid group and other ionized sulfonic acid groups in the SSA oligomers are not considered.

2.6. Calculation Details. To study the influence of chemical substitution on pK_a values, benzenesulfonic acid (BSA) was used as the starting acid. Ring substitutions at various positions with −F, −Cl, −Br, −OH, and −NO_2 were investigated. The structures of BSA and its conjugate base were first optimized in the gas phase at the B3LYP/6-31+G(d) level. The gas phase free energies of these species were given by frequency calculations at the same level/basis set. The HF/6-31G+(d) optimized gas phase structures were used to calculate the solvation free energies with the CPCM model at HF/6-31+G(d). For all chemical substitutions investigated, six variations in the substitution positions were selected. These variations include three single substitutions at the 2-, 3-, and 4-position; two double substitutions at the 2,6- and 3,5-positions; and one triple substitution, at the 2,4,6-position, all shown in Figure 1. The procedure of calculating the gas phase and solvation free energies for these substituted neutral acids and their corresponding conjugate bases is the same as that of the starting BSA acid. All of the quantum chemical calculations were carried out using the Gaussian 03 package.[41]

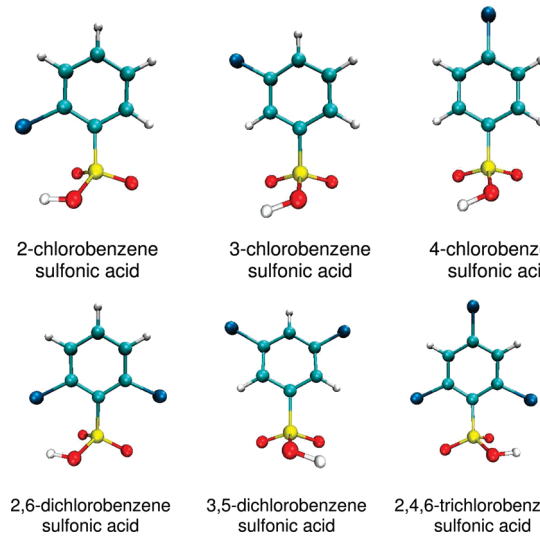


Figure 1. Schematic structures of various ring substitutions of benzenesulfonic acids (BSAs) with Cl. The other elements in the substitution studies are F, Br, OH, and NO_2 groups.

To study the effect of polymerization on pK_a values, styrenesulfonic acid (SSA) was used as the monomer acid in which the C=C bond allows the polymerization to occur. The PBE of the SSA oligomers was solved numerically using the Delphi code.[19] It utilizes a finite-deferential method and is capable of treating multiple solvent media with different dielectric constants as well as multivalent salts. In order to take into account the different conformations in the oligomers, the multiconformation continuum electrostatics (MCCE) program developed by Gunner's group is used.[17,18] This program is built on the Delphi code. In the MCCE calculations, the structures and atomic charges of SSA oligomers with degrees of polymerization (DP) of 2−6, 8, and 12 were obtained by using the Car−Parrinello molecular dynamics (CPMD) simulations.[42] The BLYP functional was used for the valence electrons,[43] while the interactions between these electrons with the "frozen cores" were described by the Goedecker pseudopotentials.[44] The energy cutoff was 70 Ry. The fictitious mass of electrons was 800 amu, and the time step was 0.125 fs. The MD was carried out using NVT at 300 K, and this temperature was kept with a Nose−Hoover chain thermostat.[45] The equilibrium structures were obtained from a 1 ps simulation run followed by another 1 ps simulation to calculate the EPS charges (shown in the Tables SI-1 and 2 of the Supporting Information).[46] Because of the large size of the 6-, 8-, and 12-mers and the large number of negatively charged anions, the charges were not calculated for these neutral

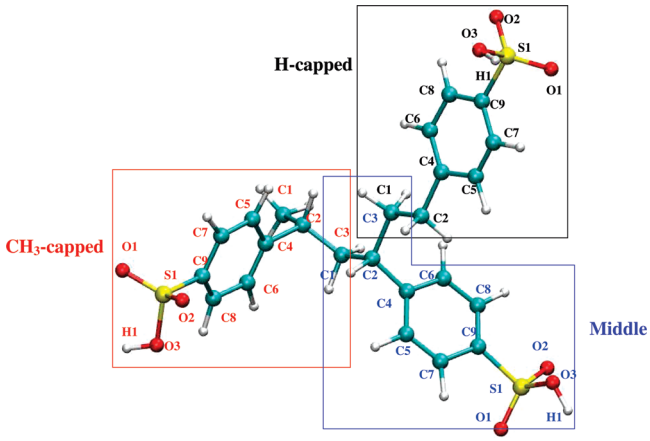


Figure 2. Three residues on the styrenesulfonic acid trimer used in the MCCE calculation. Note the backbone CH_2 groups are shared between neighboring residues. The scheme is the same for other SSA oligomers, with one CH_3-capped end residue, one H-capped end residue, and the rest middle residues.

oligomers and their conjugate bases. Instead, the charges from the 5-mer were used.

In MCCE, each SSA oligomer is divided into three different residues: CH_3-capped, H-capped, and middle residues, as shown in Figure 2. Their pK_a shifts with respect to the monomer value were determined by calculating solvation free energy differences between these residues and the corresponding monomer. The charges on the hydrogen atoms are merged onto the neighboring carbon atoms, except for the ionizing proton. The radii for C (sp^3), C (sp^2), O, S, and H are 2.00, 1.70, 1.40, 1.85, and 1.00 Å, respectively. In the residues, the benzenesulfonic acid group was allowed to rotate around the C2−C4 bond to three sp^3 carbon covalent positions. Three thousand Monte Carlo samplings were used. The solvent is a mixture of water and the rest of the organic molecule with dielectric constants ε of 80 and 3 for water and oligomers, respectively.

3. Results and Discussion

3.1. Effects of Chemical Substitution on pK_a. The pK_a values of organic acids are affected by chemical substitution of the H atoms by other elements. After the proton on the acid group dissociates, the negative charge on the anion can be stabilized by substituted elements with a strong electron withdrawing ability, favoring the formation of the anion and thus lowering the pK_a value of the substituted organic acid. In this work, we used benzenesulfonic acid as an unsubstituted starting acid. It is a strong acid with a pK_a value of −2.7.[47] The H atoms on the ring structure can be substituted by various other elements, potentially modifying its pK_a value.

Following the calculation procedure described in the Methodology section, the gas phase free energy changes and solvation free energies of the acids and their corresponding conjugate bases are listed in Tables 1 and 2, respectively. The B3LYP/6-31+G(d) method was used to determine the gas phase free energies. It should be noted that the DFT-derived gas phase free energies may be associated with a large amount of error.[48] In our previous study on carboxylic acids, this method gave results that are comparable (with a correction) to the accurate but computationally more demanding CBS-QB3 model.[26] We expect the high accuracy of this method based on our treatment can be retained for the organosulfonic acids. In fact, the enthalpy change for proton dissociation of BSA in the gas phase is 311.4 kcal/mol by B3LYP/6-31+G(d), in good agreement with experimental value of 310.2 ± 6.7 kcal/mol.[49]

For solvation free energies, the CPCM model at HF/6-31+G(d) was used on the gas phase structures of acids and anions optimized at HF/6-31+G(d). However, it is interesting to notice that the solvation free energies of the −OH substituted BSA/anions show a large variation depending on the positions substituted, e.g., substitutions at the 3,5-positions are about 12 kcal/mol lower than substitutions at the 2- or 2,6-positions. Nonetheless, the same solvation model was used in our study of carboxylic acids and predicted solvation free energies that compare well with available experimental results.[26] Due to the lack of experimental solvation energy data for organosulfonic acids, the accuracy of this model is hard to assess for systems investigated here. We expect the errors in the pK_a calculations to be reduced, since only the differences in gas phase free energies and solvation free energies are used.

The calculated pK_a shifts from BSA of a series of chemically substituted BSA are listed in Table 3, and the pK_a values are plotted in Figure 3. These pK_a values were obtained by adding the calculated pK_a shifts to the experimental pK_a value of the unsubstituted BSA with pK_a(HB) = pK_a(HA) + ΔpK_a(HA = BSA, HB = substituted BSA), where pK_a(HA) = −2.7. Three halide elements at six substitution positions increase the acidity of BSA due to their strong electron withdrawing ability. Moreover, −F, −Cl, and −Br give very similar pK_a shifts at all of the substitution positions investigated. The pK_a shifts due to −Br substitution are slightly smaller than those by −F and −Cl at all of the positions studied except at the 2- and 2,6-positions. Even though the electronegativity of F is 4.0, much higher than that of Cl (3.0) and Br (2.8),[50] its effects on the pK_a values are similar to those of Cl and Br.

The pK_a shift due to ring substitution by halides shows a strong dependence on the positions substituted. Among the three singly substituted BSAs, substitution at the 2-position (*ortho*) yields the lowest pK_a values, whereas substitution at the 4-position (*para*) gives the highest. With the 2-position being the nearest to the sulfonic acid group, the electron-drawing ability of the halides is the most pronounced. This is also true for the doubly substituted BSAs. At the two *ortho* positions (2,6-), the pK_a shifts are lower than those at the two *meta* positions (3,5-) for all of the halide groups. The triply substituted BSAs at the 2,4,6-positions show similar pK_a shifts as the 2,6-substituted BSAs, indicating that the substitutions at the *ortho* positions dominate the effects on pK_a values.

The effects of ring substitutions by −OH and $-NO_2$ groups on the pK_a values of BSA also show an interesting trend. The electron withdrawing ability of the hydroxyl group is very pronounced at the *ortho* positions. The pK_a values of 2- and 2,6-OH substituted BSA are even lower than those substituted by the halides. However, at the 3- and 4-positions, −OH substitution shows an opposite effect, as the pK_a values of substitutions at these positions are higher than that of the original BSA value. Substitutions at 3,5-positions give a pK_a value close to that of BSA. Substitutions at the 2,4,6-positions again give negative pK_a shifts because they involve two *ortho* positions. Substitution by $-NO_2$ gives the lowest pK_a values at every position among all studied elements due to the large π-conjugate system formed between the benzene ring and the $-NO_2$ group(s). For the three singly $-NO_2$ substituted BSA's, the values of pK_a shifts are not as spread as seen in the halide and −OH substituted BSAs due to the delocalization of the π-conjugate system. As the number of the $-NO_2$ substitutions increases, the pK_a value becomes more negative. The pK_a value of 2,4,6-nitro BSA reaches −9.76, showing that the sulfonic acid group has a very high tendency to release a proton in

TABLE 1: Free Energy Changes for Proton Dissociation in the Gas Phase for Benzenesulfonic Acid (BSA) and Various Other Ring Substituted Acids by B3LYP/6-31+G(d)

		free energy changes for proton dissociation in the gas phase (kcal/mol)				
BSA		311.54				
substitute element		F	Cl	Br	OH	NO_2
position	2-	310.23	309.61	309.36	303.60	307.78
	3-	307.50	306.77	306.95	310.19	301.05
	4-	308.32	306.99	307.35	312.32	299.30
	2,6-	308.04	306.77	306.60	296.55	295.70
	3,5-	303.48	302.31	302.69	309.93	291.60
	2,4,6-	304.75	304.45	303.37	297.09	284.03

TABLE 2: Solvation Free Energies of Benzenesulfonic Acid (BSA) and Ring Substituted BSAs and Their Conjugate Anions by the CPCM Model at HF/6-31+G(d)

		solvation free energies of the neutral species (kcal/mol)				
BSA		−12.12				
substitute element/group		F	Cl	Br	OH	NO_2
position	2-	−11.31	−9.74	−9.46	−11.90	−9.22
	3-	−12.59	−11.54	−11.74	−17.76	−13.90
	4-	−12.51	−11.58	−11.78	−18.44	−13.76
	2,6-	−12.01	−9.36	−8.81	−12.10	−14.15
	3,5-	−12.20	−10.27	−10.59	−23.48	−15.17
	2,4,6-	−11.63	−7.47	−6.96	−17.26	−17.05
		solvation free energies of the anions (kcal/mol)				
BSA conjugate anion		−61.94				
substitute element/group		F	Cl	Br	OH	NO_2
position	2-	−61.69	−59.80	−59.47	−57.14	−58.85
	3-	−59.34	−57.77	−57.71	−65.87	−56.00
	4-	−59.60	−57.68	−57.56	−68.08	−54.46
	2,6-	−61.81	−58.00	−57.14	−53.03	−56.68
	3,5-	−56.14	−53.22	−53.23	−71.87	−50.18
	2,4,6-	−58.32	−52.88	−52.01	−58.09	−48.99

TABLE 3: Calculated pK_a Shifts of Ring Substituted Benzenesulfonic Acids (BSAs)

substitute element/group		calculated pK_a shifts				
		F	Cl	Br	OH	NO_2
position	2-	−1.38	−1.59	−1.74	−2.46	−2.62
	3-	−0.71	−0.87	−0.54	0.26	−2.03
	4-	−0.36	−0.61	−0.11	0.70	−2.29
	2,6-	−2.55	−2.64	−2.53	−4.39	−6.27
	3,5-	−1.60	−1.73	−1.23	−0.14	−3.77
	2,4,6-	−2.68	−3.06	−2.49	−4.01	−7.06
BSA exp. pK_a		−2.7 (ref 47)				

aqueous solution. In the optimized *ortho* −OH and $-NO_2$ substituted structures, direct intramolecular hydrogen bonds are formed between the substituted groups and the sulfonic acid group. The formation of hydrogen bonds will alter the proton dissociation free energy of the sulfonic acid group. It is also possible that water molecules can be involved in the formation of hydrogen bonds with these substituted groups. In the latter case, an explicit inclusion of water molecules would be necessary in calculating the solvation free energies involving the *ortho* substitutions. This point will be explored in our future studies.

3.2. Effects of Polymerization on pK_a. The acidity constants, pK_a, of the ionizing sulfonic acid groups in the organosulfonic acid polymers are expected to be different from their corresponding monomer values because the electrostatic environments surrounding the sulfonic acid groups are modified upon polymerization. To study the effects of polymerization on pK_a values, we chose styrenesulfonic acid (SSA) as the monomeric acid because of its ability to polymerize. The calculation details using MCCE code can be found in the Methodology section. Our previous experience has shown that the MCCE calculated pK_a values agree well with the pK_a values determined using the *ab initio* quantum chemical method for the dimer and trimer of methacrylic acid (MAA).[51] For the MAA dimer, the differences are less than 0.8 pK_a units, while, for the trimer, the mean absolute deviation is 0.90 units between the two methods. This agreement indicates that the classical continuum dielectric model can nicely describe the amount of perturbation to the electrostatic environment around the acid groups due to polymerization. It however should be noted that the agreement is not accidental. An implicit solvation model is used to calculate the solvation free energy for both the classical PBE and the *ab initio* polarizable continuum model (PCM).

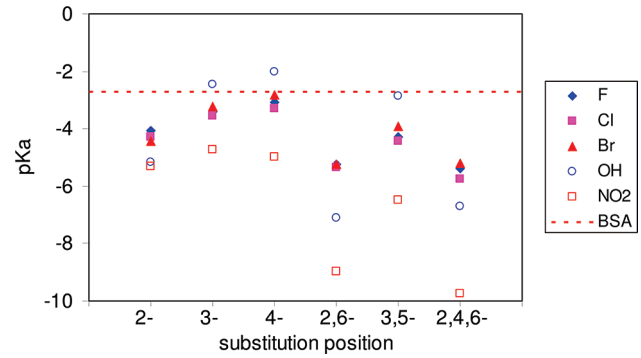


Figure 3. Calculated pK_a values of ring substituted benzenesulfonic acids (BSAs).

TABLE 4: Calculated pK_a Values of Styrenesulfonic Acid (SSA) Oligomers with Degree of Polymerization (DP) Ranging from 2 to 12

	pK_a		
	CH_3-capped	H-capped	mid (average)
monomer	exp. pK_a = −0.53 (ref 53)		
dimer	0.26	0.62	
trimer	0.39	0.29	0.78
4-mer	1.32	1.02	1.06
5-mer	1.59	1.60	2.05
6-mer	1.73	1.94	2.78
8-mer	3.11	1.73	2.61
12-mer	1.93	1.65	2.93

Although it is difficult to assess the accuracy of the classical continuum dielectric model for the SSA oligomers due to the lack of available experimental data, the purpose of this study is to investigate the effects of polymerization on pK_a, which can be illustrated by the relative change in pK_a value as a function of degree of polymerization (DP) given by the MCCE calculations. The experimental pK_a value of polymeric methacrylic acid is 7.3, an increase of over 2 pK_a units over its corresponding monomer value of 4.65.[52] Our previous MCCE calculations of MAA oligomers quantitatively predicted this pK_a increase, indicating the reliability of the method.[51]

Table 4 lists the calculated pK_a values for the SSA oligomers with DPs ranging from 2−12. The results are plotted in Figure 4. Since the experimental value for monomeric styrenesulfonic acid (ethyl-benzene sulfonic acid) is not available in the literature, the experimental pK_a value (−0.53) of toluenesulfonic acid (TSA, i.e., methyl-benzene sulfonic acid) is used as a reference pK_a value,[53] onto which the MCCE-calculated pK_a shifts for SAA oligomers are added. TSA has a similar structure to ethyl-benzene sulfonic acid, which is one of the residues used in the MCCE calculations. Depending on the positions in the polymer chain, there are three different residues that include the ionizing acid group: CH_3-capped, H-capped, and middle residues. Their pK_a values are listed separately in Table 4. For the 4-mer and longer oligomers, there are multiple middle residues. Listed are the average pK_a values for the middle residues.

The pK_a values of the sulfonic acid groups in SSA oligomers all show a positive shift compared to the monomer value of −0.53. The dimer has pK_a values of 0.26 for the CH_3-capped residue and 0.62 for the H-capped residue, respectively, without the middle residue. For the trimer, the pK_a values are 0.39 and 0.29 for the two end residues and 0.78 for the middle residue, respectively. This almost one pK_a unit increase for the dimer and trimer indicates the significant influence of polymerization upon pK_a values. The pK_a values increase as the DP value increases up to the 6-mer, where the values are 1.73, 1.94, and 2.78, respectively, for the three different types of residues, respectively. This over 2 pK_a units increase over the monomer value suggests that the electrostatic environments around the ionizing acid groups have changed significantly. Further increase in the DP value has no obvious effect on pK_a values. The pK_a values of the 8- and 12-mer remain more or less the same as the 6-mer (except for the 8-mer's CH_3-capped residue with a pK_a value of 3.11). Figure 4 shows the pK_a values averaged over the middle residues (light blue triangles) converge to 2.9, slightly higher than the converged value over all residues (blue diamonds). This converged pK_a value of 2.9 for the averaged middle residues would be an appropriate estimate for the SSA polymers because the middle residues dominate the long chain polymers.

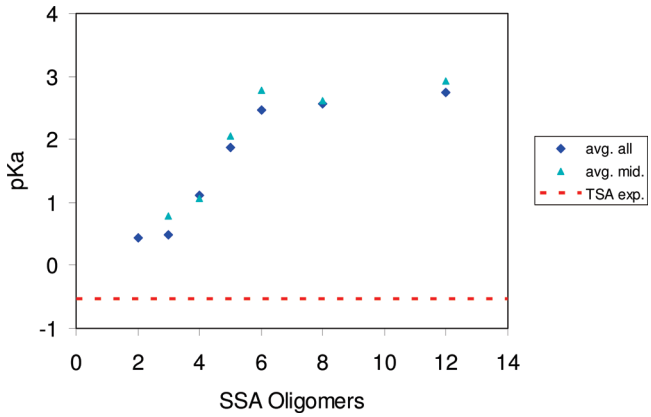


Figure 4. Calculated pK_a values for oligomers of styrenesulfonic acid (SSA) with DP values ranging from 2 to 12.

The trend that the pK_a values increase with the increase of DP value and converge rapidly is similar to the results observed for methacylic acid oligomers. It is also interesting to examine the spatial variations of pK_a values along the SSA oligomers. The pK_a values of the dimer predicted by the MCCE calculations show that the CH_3-capped sulfonic acid group is slightly more acidic than the H-capped group. However, the pK_a values of the two end residues in the trimer show that the H-capped group is slightly more acidic than the CH_3-capped group. By examining the pK_a values of the longer oligomers, the acidities of the two end residues are not significantly different, as the mean absolute deviation between the two is only 0.38 pK_a units. The MCCE results for the trimer, on the other hand, show that the middle residue has a higher pK_a value than the two end residues. The same trend can be seen for most of the longer oligomers. For instance, the average pK_a value for the middle residues in the 5-mer is 2.05, which is higher than both the CH_3-capped (1.59) and H-capped residue (1.60). For the 6-mer and 12-mer, the middle residues are also less acidic than the two end residues. For the 4-mer and 8-mer, the middle residues are less acidic than the H-capped residues but more acidic than the CH_3-capped residues. The pK_a difference between the middle residues and the H-capped residues becomes larger as the chain grows longer. In the 4-mer, the middle residues are only slightly less acidic than the H-capped residue. In the 12-mer, the difference between the two pK_a values becomes more than 1 pK_a unit. This variation in pK_a values along the polymer chain indicates that the electrostatic environment surrounding each ionizing residue could be different depending on their relative positions and the conformation of the polymers.

It has previously been shown that the MCCE-derived pK_a values for the MAA oligomers agree well with experimental data and the results from more accurate *ab initio* quantum chemical methods. This indicates that the continuum dielectric model based on the PBE is able to capture the essence of the electrostatic properties of an ionizing process. Even though the important solvation structures of water are not explicitly included in the PBE, the interactions between the ionizing groups with their environment can be approximated using a mean-field approach. Georgescu et al. have reported that the MCCE calculations have a remarkable accuracy in predicting pK_a values for proteins. For 166 ionizable groups in 12 proteins tested, the mean square deviation of the calculated pK_a values from their experimental values is only 0.83 pK_a units.[39] Our MCCE results on the SSA oligomers are expected to have a similar accuracy.

It should be kept in mind, however, the conformational structures and the atomic charges of the SSA oligomers in our calculations were obtained from the gas phase. These may not reflect the true conformation and charge distribution of the oligomer in water. In this work, the oligomers adopt a fully extended chain conformation. Other conformational structures that may cause different perturbation to the interaction between the ionizing groups and their environment were not included. Also, only the intrinsic acidity constant of the ionizing group (where other acid groups are in their neutral states) was considered in the present study. The more complex multiple ionization constants which involve interactions between various neutral and charged groups were not studied.

4. Conclusions

The effects of chemical substitution on the pK_a values of organosulfonic acids have been studied from calculating the free energy changes associated with the ionization process in water. A thermodynamic cycle was used to partition the total free energy change in water into changes in the gas phase free energy and solvation free energy. These quantities were calculated by using *ab initio* quantum chemical methods. By comparing the gas phase free energies at the B3LYP/6-31+G(d) level and the CPCM solvation free energies at HF/6-31+G(d) level for the acids with and without chemical substitution, the relative changes in pK_a values were obtained.

Ring substitution by the halides F, Cl, and Br increases the acidity of BSA due to their strong electronegativity. The three halides have more or less the same effect, since the pK_a decrease in magnitude is almost the same. Ring substitution by the −OH group has a stronger effect in lowering the pK_a value at the 2-(*ortho*) position due likely to the formation of intramolecular hydrogen bonds in the corresponding conjugated base. However, substitutions at the 3- and 4-positions show a slight increase in pK_a values. Ring substitution by NO_2 has the strongest effect on reducing the pK_a value among all of the elements and groups studied. This is due to the increase in π-conjugation with each $-NO_2$ substitution. The negatively charged anion becomes more stable as the charge is distributed in a larger π-system to increase the acidity of the system.

The pK_a values depend on where the positions of the ring substitution occur. For three single ring substitutions, the 2-(*ortho*) position gives the lowest pK_a value (highest acidity), while the 3- (*meta*) and 4- (*para*) positions are less effective in increasing the acidity of the BSA. For double ring substitutions, the pK_a value at the 2,6-position is lower than that at the 3,5-position. Substitution at the 2,4,6-position gives the lowest pK_a value among all studied positions.The effects of polymerization on the pK_a values of styrenesulfonic acid were studied using the classical continuum dielectric model solving the Poisson−Boltzmann equation. Our results show that polymerization increases the pK_a values and thus reduces the acidity of the acid groups. The average pK_a value of the SSA dimer has a significant increase over that of the monomer value. The pK_a value increases sharply as the DP value increases to up to 6, after which the pK_a value converges. A converged average pK_a value of 2.9 is reached when the DP is 12. This pK_a value can be used as an estimate for the average pK_a values of SSA polymers. The decrease in acidity of polymeric SSA has significant implications on the application of the organosulfonic acid-based solid acid catalysts. The monomeric pK_a values of the organosulfonic acids may not be used to approximate the actual acidity of the catalysts. The polymeric acids could be significantly weaker than the corresponding monomer acids. However, this decrease in acidity can be offset by chemical substitution of electron-withdrawing or π-conjugation groups on the benzene ring, as demonstrated in this study. Our results indicate that it is possible to manipulate the acidity of polymeric solid acids via chemical substitutions and controlling the degree of polymerization.

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Supporting Information Available: Tables showing atomic charges for the neutral residues and anions of styrenesulfonic acid oligomers given by the CPMD calculations and atomic charges of the styrenesulfonic acid monomer given by the CPMD BLYP functional and Gaussian B3LYP/6-31+G(d) calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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