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Interfacial Molecular Structures of Polyelectrolyte Brush in Contact with Dry Nitrogen, Water Vapor, Liquid Water, and Aqueous Electrolyte Solution Studied by Sum Frequency Generation Spectroscopy

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Abstract: Interfacial structures of alkylated polyvinylpyridine (C*n*-PVP) brushes with various side chain lengths ($n = 2, 6, 12$) in dry nitrogen, water vapor, liquid water, and aqueous electrolyte solution were investigated by sum frequency generation (SFG) spectroscopy. The SFG spectra of the polymer brushes in the CH stretching region in dry nitrogen revealed that the conformational order of the side chain depended on the chain length. The conformational order of the polymer brush with hexyl, C6, side chain, was very high, and the side chain was almost in *all-trans* conformation with the tilt angle of methyl group being ca. 34° with respect to the surface normal. Significant contribution from CH stretching of methylene group was observed in the SFG spectra of the polymer brush with the shorter, ethyl, C2, or longer, decyl, C12, side chains. Relative intensity of CH stretching of methylene group to that of methyl group, that is, degrees of gauche defects, increased significantly upon in contact with water vapor at all the brushes, and essentially no CH stretching peaks were observed when the brushes were in contact with liquid water, showing almost completely disordered conformational structure. These conformation changes were very fast, suggesting that the changes were related to the orientation change of the side chains. SFG spectra of the brush/water interface in the OH stretching region were dominated by OH stretching vibration of ice-like water. The higher was the electrolyte concentration, the lower was the OH intensity, reflecting the reduction of the double layer thickness in solution of higher electrolyte concentration.

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1. Introduction

Polyelectrolyte is one of the most important materials in many fields including biological systems and material science. For examples, nucleic acids, one of the key materials in biological system, are polyelectrolytes with phosphate backbone. Polyelectrolytes are used for polymeric drugs,[1] antibacterial coatings[2] by protecting the surfaces of prostheses organs or catheters from adhesion of proteins, improvement of the stability of colloids,[3−5] and the formation of multilayers of nanoparticles.[6−9] It is also a very important component of polymer electrolyte membrane (PEM) fuel cell. As polyelectrolyte has hydrophilic and hydrophobic components, an interaction between polyelectrolyte and water plays a crucial role in controlling the structure and functions of various materials. One of the most important examples is a folding/unfolding process of a protein.

A polymer, which is grafted on a solid substrate, is called a "polymer brush", and in the case of polyelectrolyte, it is called a "polyelectrolyte brush". Polyelectrolyte brush recently has attracted much attention because of its wide variety of possible applications.[10−12] It is also considered to be a model system of a biological membrane. To understand the function of polyelectrolyte in general and polyelectrolyte brush in particular, it is essential to know molecular structures of polyelectrolyte surfaces under various environments. However, only bulk structures of polyelectrolytes have been investigated,[13−15] and almost no study on surface structure is available.[16]

Sum frequency generation (SFG) is a second-order nonlinear optical process, in which two photons of frequencies ω_1 and

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ω_2 generate one photon of sum frequency ($\omega_3 = \omega_1 + \omega_2$).[17,18] The second-order nonlinear processes including SFG are prohibited in media with inversion symmetry under the electric dipole approximation and allowed only at the interface between these media where the inversion symmetry is necessarily broken. By using visible light of fixed wavelength and tunable IR light as two input light sources, the SFG signal is resonantly enhanced when the energy of IR beam becomes equal to that of a vibrational state of surface species. Thus, SFG spectroscopy can be surface sensitive vibrational spectroscopy and, recently, has successfully been applied to investigate molecular structures of polymer surfaces and interfacial water at various interfaces.[19−25]

In this Article, we demonstrated the usefulness of SFG spectroscopy for the structural investigation of polymer brush in contact with various environments including liquid water by applying it to poly(4-vinyl-*N*-*n*-alkylpyridinium)bromide (alkyl = ethyl, hexyl, and dodecyl) polyelectrolyte brushes formed on a quartz surfaces, which have been reported to have an antibacterial function.[26] It was found that the conformational order of alkyl chains is very strongly affected by environment. Alkyl chains are in relatively high conformational order in dry nitrogen, gauche defects are introduced to alkyl chains upon contact with water vapor, and alkyl chains became totally disordered in liquid water. Structures of interfacial water of the brushes in contact with water vapor and liquid water were also investigated. Structural change was reversible and fast when the environment was changed between dry nitrogen and water vapor. Effects of chain length and ionic strength on the structure of water were also studied.

2. Experimental Section

Fused quartz prisms with hemicylindrical shape (IR grade, d = 25 mm, l = 25 mm, Pier Optics) were used as substrates to improve the sensitivity in SFG measurements.[27] Aminopropyltrimethoxysilane (APS), poly(4-vinylpyridine) (M_w = 160 000), and alkyllbromide were purchased from Aldrich. The other chemicals, ethanol, dry dichloromethane, 1,4-dibromobuthane, dry nitromethane, triethylamine, acetone, and methanol, were purchased from Wako. All chemicals were used without further purification.

The alkylated-PVP (C*n*-PVP) polymer brushes were constructed on the substrate using the quarterization reaction of PVP following the method B described in ref 28. Briefly, an amino terminated monolayer of APS was constructed on the fused quartz prism, which was oxidized in a boiling solution of concentrated H_2SO_4:H_2O_2 (3:1) for 1 h, then rinsed several times with Milli-Q water, by the silane coupling reaction.[29] The APS modified prism was immersed in a mixture of 4.5 mL of 1,4-dibromobutane, 45 mL of dry nitromethane, and 0.05 mL of triethylamine for 2 h at 60 °C to convert the terminal amino group to butyl ammonium bromide (C4Br). The substrate was then treated in a solution of 4.5 g of polyvinyl-pyridine in 45 mL of nitromethane/alkyl bromide (10:1, v/v) for 24 h at 75 °C to obtain a C*n*-PVP polymer brush. The substrate was rinsed with acetone and then with methanol. The yield of the N-alkylation was reported to be more than 96%.[30]

The SFG, IR, and ellipsometry measurements were carried out for the sample after each synthetic step to monitor the surface molecular structure.

The present SFG system was described in details elsewhere.[31,32] Briefly, the infrared (200 μJ@3000 cm^{-1}) and visible (100 μJ@532 nm) beams were incident from the cylindrical face and were overlapped at the flat face of the prism. A flow cell made of Teflon, which allowed one to change gases and liquids without affecting the sample position and optical alignment, was used for the SFG measurements. The polarization combination of s, s, and p for SFG, visible, and infrared light, respectively, was employed. This combination is sensitive only for the component of molecular vibrations normal to the surface at an isotropic interface.

SFG spectra were analyzed by using the following equation:[17,18]

$$I_{\mathrm{SFG}}(\omega) \propto \left|\sum_q \chi^{(2)}_{\mathrm{R},q} + \chi^{(2)}_{\mathrm{NR}}\right|^2 = \left|\sum_q \frac{A_q}{\omega - \omega_q + i\Gamma_q}\exp(i\theta_q) + \chi^{(2)}_{\mathrm{NR}}\right|^2 \qquad (1)$$

where ω is the infrared frequency, $\chi_{\mathrm{NR}}^{(2)}$ is the nonresonant contribution to the surface nonlinear susceptibility, and ω_q, A_q, θ_q, and Γ_q are the resonant frequency, transition amplitude, phase difference between resonant and nonresonant term, and homogeneous width of the qth vibrational mode, respectively.

All measurements were carried out at room temperature.

3. Results and Discussion

3.1. Interfacial Structure of C*n*-PVP Brush in Contact with Dry Nitrogen. Figure 1 shows the SFG spectra in the CH stretching region of (a) C2-PVP, (b) C6-PVP, and (c) C12-PVP covered quartz prism in contact with dry nitrogen. For a comparison, the result of quartz prism modified by octadecyltrichlorosilane (OTS) monolayer is also shown in Figure 1d. Open circles and solid lines represent experimental data points and fitting curves for eq 1, respectively. Several peaks were observed. Two peaks at 2862 and 2916 cm^{-1} were attributed to be due to CH symmetric stretching (d$^+$) and asymmetric stretching (d$^-$), respectively, of the methylene (CH_2) group. Three peaks at 2880, 2941, and 2968 cm^{-1} were assigned to CH symmetric stretching (r$^+$), Fermi resonance between r$^+$ and CH bending overtone (FR), and CH asymmetric stretching (r$^-$), respectively, of methyl (CH_3) group. A broad peak observed at around 3040 cm^{-1} was assigned to overlapped aromatic CH stretching vibrations of the pyridinium ring (ring CH).

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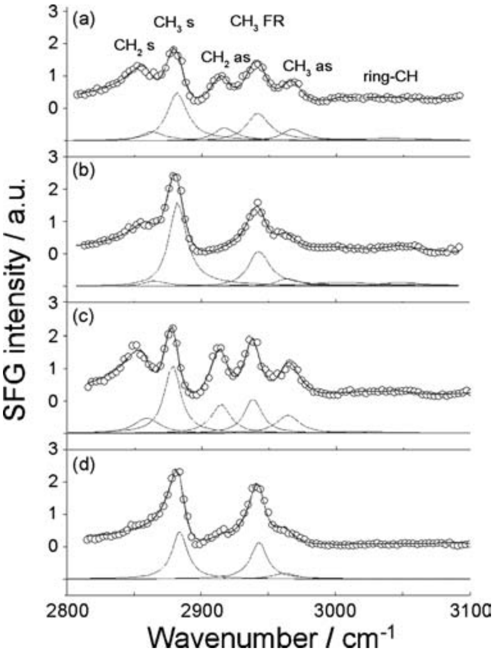

Figure 1. SFG spectra in the CH stretching region of (a) C2-PVP, (b) C6-PVP, (c) C12-PVP, and (d) OTS covered quartz prism in dry nitrogen.

The SFG spectrum of C6-PVP (Figure 1b) is similar to that of OTS (Figure 1d), and the peaks corresponding to CH$_2$ groups were very weak. As mentioned previously, SFG is inhibited in the centrosymmetric media. It is well-known that no methylene peak is observed at OTS-modified surface[33,34] when OTS is in *all-trans* conformation where the CH$_2$ group is in inversion symmetry and is, therefore, SFG inactive.[34] Thus, it can be concluded that the hexyl side chain of the C6-PVP polymer brush is also mainly in *all-trans* conformation without gauche defect where only the terminal CH$_3$ group is in noncentrosymmetry and contributes to the SFG spectrum.

The peaks corresponding to both CH$_2$ and CH$_3$ groups were clearly observed at C2-PVP and C12-PVP as shown in Figure 1a and c, respectively, but origins of CH$_2$ peaks of these two cases are different. Although it was mentioned above that the presence of SFG peaks due to CH stretching of CH$_2$ group means the presence of gauche defect, it is valid only for long alkyl chains. Clear observation of the peaks corresponding to the CH$_2$ groups C12-PVP (Figure 1c) indicates that dodecyl side chains of the C12-PVP polymer brush had certain degree of gauche defects in their conformation, where CH$_2$ is SFG active.[39] From the comparison with the result of C6-PVP, one can conclude too long of a side induces more gauche defects. In the case C2-PVP, however, the presence of the peak corresponding to CH$_2$ modes does not necessarily mean that the ethyl side chain is disordered because of a low symmetry of ethyl group.

The tilt angle of the methyl group can be calculated from the amplitude ratio of r$^-$/r$^+$ based on the procedure proposed by Hirose and his colleague.[35,36] By assuming an azimuthally isotropic interface, the ratio of the vibrational intensities of r$^+$ and r$^-$ can be approximated by

$$\left|\frac{\chi^{(2)}_{\mathrm{ssp,as}}}{\chi^{(2)}_{\mathrm{ssp,s}}}\right| = \left|\frac{A(\mathrm{r}^-)}{A(\mathrm{r}^+)}\right| \propto \left|\frac{\beta_{caa}}{\beta_{aac}} \times \frac{-2(\cos\theta - \cos^3\theta)}{(1+r)\cos\theta - (1-r)\cos^3\theta}\right| \qquad (2)$$

where θ is the angle between the main axis of the methyl group and the surface normal, β_{caa} and β_{aac} iare the nonzero components of second-order hyperpolarizability β, and r is the ratio of β_{ccc}/β_{aac}. The values of β_{caa}/β_{aac} and r are 0.25 and 4.21, respectively.[36] Tilt angles of methyl group with respect to surface normal of C2-, C6-, and C12-PVP polymer brushes deduced from eq 2 in dry nitrogen are 43°, 34°, and 51°, respectively, as summarized in Table 1 together with the observed intensity ratio, r$^-$/r$^+$.

3.2. Interfacial Structure of C*n*-PVP Brush in Contact with Water Vapor and in Liquid Water. After SFG spectra under dry nitrogen (Figure 1) were obtained, the effect of environment on the structures of the C*n*-PVP brush was examined by changing the media to be contacted with the brush. Figure 2 shows a series of SFG spectra of C6-PVP obtained sequentially in (a) dry nitrogen, (b) water vapor saturated nitrogen, (c) dry nitrogen after the removal of water vapor, (d) liquid water, and (e) dry nitrogen after the removal of water. The peaks due to CH$_2$ groups, which were very weak in dry nitrogen (Figures 1c and 2a), were clearly observed when the brush was in contact with water vapor saturated nitrogen (Figure 2b), indicating that a higher degree of gauche defects was introduced in the hexyl side chain with water vapor. At the same time, the intensity ratio between r$^-$ and r$^+$ drastically changed from 0.35 in dry nitrogen to 1.14 in water vapor saturated nitrogen, indicating the tilt angle of methyl group was changed from 34° in dry nitrogen to 70° in water vapor saturated nitrogen (Table 1). These results show that the significant conformation change was induced by being contacted with water vapor. This is reasonable because when the brush was in contact with water vapor, the hydrophilic hexyl ammonium group interacts with water, and the hydrophobic side chain is expected to orient to the bulk polymer chain.

SFG spectra of C2- and C12-PVP brushes and of OTS obtained in water vapor saturated nitrogen are shown in Figure 3. As observed for C6-PVP, SFG spectra of C2- (Figure 3a) and C12-PVP (Figure 3c) brushes also show the conformational change, although the change was less significant than that of C6-PVP. The relative intensity of CH$_2$ peaks to CH$_3$ peaks became larger, indicating the introduction of a higher degree of gauche defects, in contact with water vapor saturated nitrogen. The intensity ratio between r$^-$ and r$^+$, that is, tilt angle of methyl group, drastically changed as summarized in Table 1. On the contrary, the SFG spectrum of OTS in contact with water vapor saturated nitrogen (Figure 3d) was almost the same as that observed in dry nitrogen, showing no conformational change of OTS.

The SFG spectrum of C6-PVP after the removal of water vapor from the cell by flowing dry nitrogen gas (Figure 2c) was almost the same as the one shown in Figure 2a. Similar results were obtained for C2- and C12-PVP brushes. These results demonstrate that the structural change of C*n*-PVP induced by water vapor is reversible.

The SFG spectrum of C6-PVP in liquid water was completely different from those in nitrogen and in water vapor as shown in Figure 2d. There are no apparent peaks in the CH stretching

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Table 1. Amplitude Ratio, $A(r^-)/A(r^+)$, and Tilt Angle of the Methyl Group of C2-, C6-, and C12-PVP in Dry Nitrogen and in Water Vapor Saturated Nitrogen

	in dry nitrogen		in water vapor saturated nitrogen	
	$A(r^-)/A(r^+)$	tilt angle of methy group with respect to surface normal/deg	$A(r^-)/A(r^+)$	tilt angle of methy group with respect to surface normal/deg
C2-PVP	0.53	43	0.85	57
C6-PVP	0.35	34	1.14	70
C12-PVP	0.71	51	0.90	59

region except a small shoulder due to the ring CH modes, indicating the hexyl side chain became completely disordered. Figure 4 shows SFG spectra of C2- and C12-PVP brushes and of OTS obtained in water. Similar results were observed at C2- (Figure 4a) and C12-PVP (Figure 4c) brushes. Disappearance of the peaks may be due to the difference in Fresnel factors at quartz/nitrogen and quartz/water interfaces, but the presence of C−H peaks in the SFG spectrum of OTS shows that is not the case. Thus, C*n*-PVP took a totally random structure when they were in contact with liquid water. The shape of the SFG spectrum of OTS monolayer was not affected even in liquid water, demonstrating the very stable structure of the rigid OTS monolayer. The smaller peaks in water than those in nitrogen are due to the difference in Fresnel factors at quartz/nitrogen and quartz/water interfaces.

The SFG peaks in the CH stretching region were recovered after the removal of liquid water as shown for C6-PVP in Figure 2d but with higher relative intensity of CH_2 peaks to CH_3 peaks than in dry nitrogen, suggesting the incomplete removal of water. The SFG spectrum of C6-PVP initially obtained in dry nitrogen as shown in Figure 2a was obtained after the sample was dried by blowing heated dry nitrogen for long time, that is, more than 1 h. Thus, the structural change of the C*n*-PVP brush induced by contacting with liquid water was also reversible, but recovery was much slower than after contacting with water vapor.

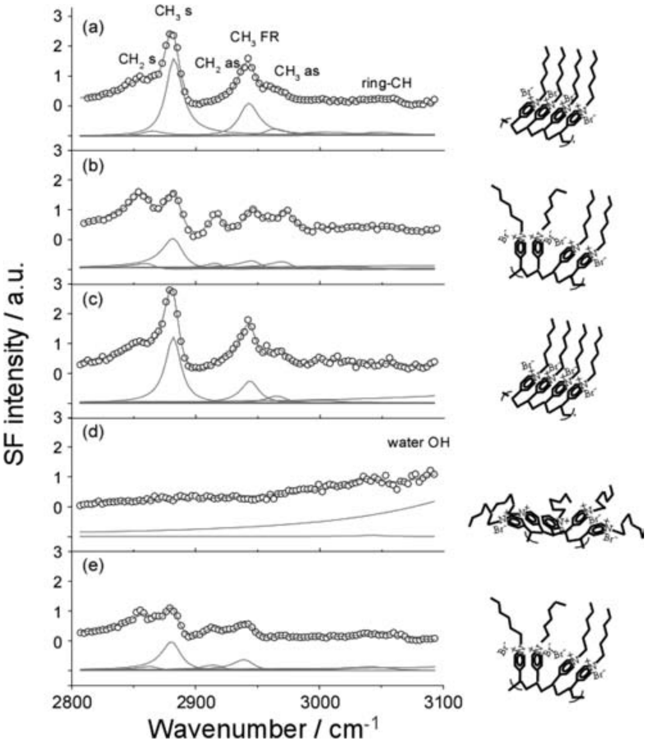

Figure 2. SFG spectra of C6-PVP in the CH stretching region in (a) dry nitrogen, (b) water vapor saturated nitrogen, (c) dry nitrogen after the removal of water vapor, (d) liquid water, and (e) dry nitrogen after the removal of water. Conformational structures of C6-PVP are schematically shown at right-hand side of each spectrum.

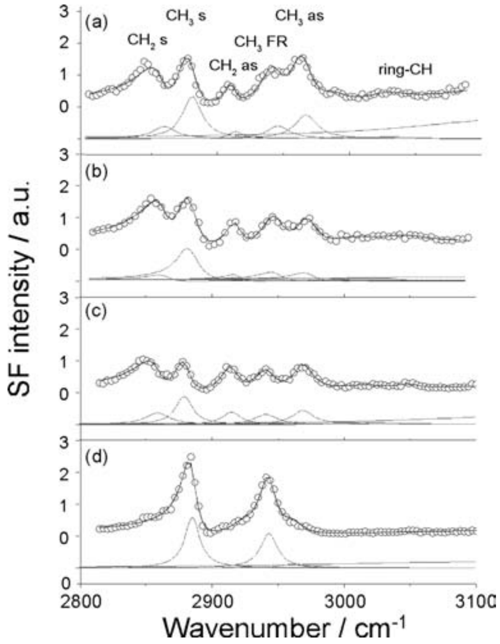

Figure 3. SFG spectra in the CH stretching region of (a) C2-PVP, (b) C6-PVP, (c) C12-PVP, and (d) OTS covered quartz prism in water vapor saturated nitrogen.

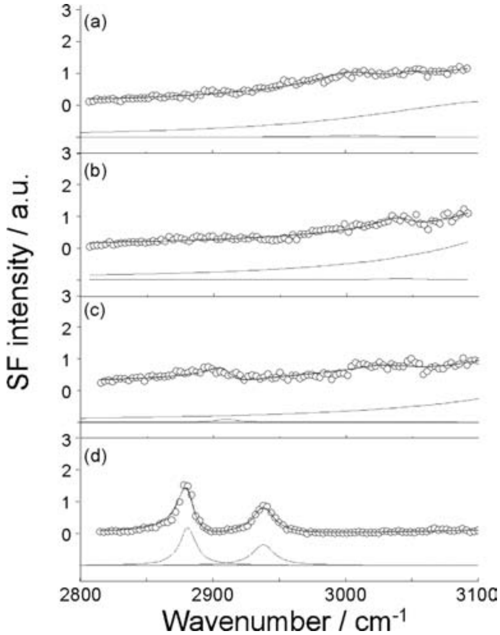

Figure 4. SFG spectra in the CH stretching region of (a) C2-PVP, (b) C6-PVP, (c) C12-PVP, and (d) OTS covered quartz prism in liquid water.

Similar SFG results were reported for uncharged poly(*n*-alkyl methacrylate) film with methyl, butyl, and octyl side chains before, during, and after contact.[37] Poly(*n*-octyl methacrylate) showed complete and irreversible structure change, poly(*n*-butyl methacrylate) showed reversible but incomplete structure change,

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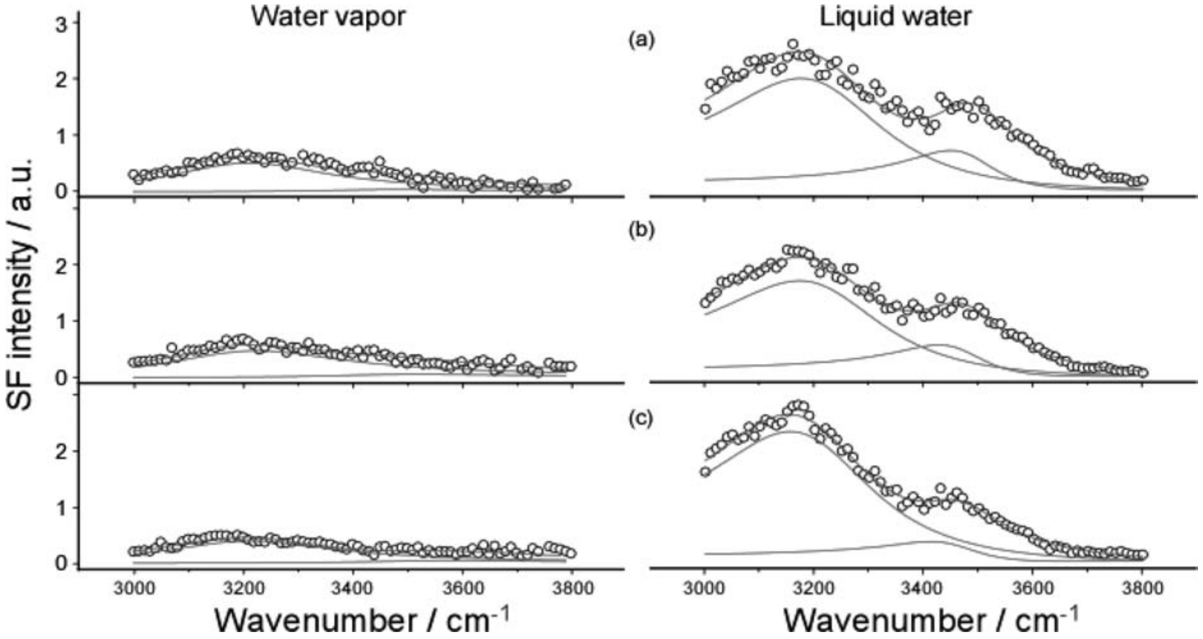

Figure 5. SFG spectra in the OH stretching region of (a) C2-PVP, (b) C6-PVP, and (c) C12-PVP covered quartz prism in contact with water vapor saturated nitrogen (left) and liquid water (right).

and poly(methyl methacrylate) did not show any structure change. The present result that even C2-PVP, the chain length of which is between methyl and butyl, showed the complete restructuring demonstrates that water interacts with the polyelectrolyte brush surfaces more strongly than with uncharged polymer surfaces.

3.3. Structure of Water at C*n*-PVP Brush/Water Vapor and C*n*-PVP Brush/Liquid Water Interfaces. SFG spectra of water in the OH stretching region are generally broad because of the strong coupling between the vibration of neighboring water molecules and Fermi resonance with the overtone of the HOH bending mode (ν_2)[38] and are featured by two major peaks at ca. 3200 and ca. 3400 cm^{-1}, which are known to be due to the symmetric OH stretching (ν_1) of tetrahedrally coordinated, that is, “ice-like”, water and the asymmetric OH stretching (ν_3) of more randomly arranged, that is, “liquid-like” water, respectively.[39−41]

Figure 5 shows SFG spectra in the OH stretching region of (a) C2-, (b) C6-, and (c) C12-PVP brushes in contact with water vapor saturated nitrogen (left panel) and liquid water (right panel). While no peak was observed in the OH stretching region when C*n*-PVP brushes were in contact with dry nitrogen (not shown), clear spectra in the OH stretching region were observed at all the surfaces in contact with the surfaces (left panel), showing that water was indeed adsorbed on the C*n*-PVP surfaces. In the SFG spectra, a broad band with a peak at ca. 3200 cm^{-1} due to the “ice-like” water was observed, but the peak at ca. 3400 cm^{-1} due to the “liquid-like” water was not apparent. This shows that adsorbed water is highly ordered. As we have already reported, the 3200 cm^{-1} peak dominates in the SFG spectrum obtained at the water/OTS-modified quartz interface because water at the hydrophobic surface tends to have highly ordered structure. Ordering of the interfacial water molecules at hydrophobic surface has also been observed at water/CCl_4 interface.[42] The intensity of the OH band at C12-PVP surface was much smaller than those of C6- and C2-PVP surfaces, possibly because the amount of adsorbed water on the C12-PVP surface was less due to higher hydrophobicity of the dodecyl side chain of C12-PVP.

On the other hand, both peaks at ca. 3200 cm^{-1} due to the “ice-like” water and at ca. 3400 cm^{-1} due to the “liquid-like” water were observed in the SFG spectra obtained in liquid water (right panel). The relative intensities of the 3200 cm^{-1} peak to the 3400 cm^{-1} peak are affected by the chain length of the side chain as 3.4, 3.6, and 5.9 for C2-, C6-, and C12-PVP, showing that the longer is the chain length, the higher is the relative intensity of the 3200 cm^{-1}, that is, “ice-like”, peak. This shows that a higher order of interfacial water is present at the C*n*-PVP brush with the longer side chain, reflecting the higher hydrophobicity of the brush surface. The reason only the 3200 cm^{-1} peak was observed in water vapor but both the 3200 cm^{-1} and the 3400 cm^{-1} peaks were observed in liquid water is that, while only adsorbed water contributes to the SFG spectrum in the former, both highly ordered water at the close vicinity of the brush surface and less ordered water, which is present next to the highly ordered water layer at the interface, contribute to the SFG spectrum in the latter.

3.4. Rate of the Structural Change of C6-PVP/Water Vapor Interfaces. To evaluate how fast the interfacial structure changes, time dependencies of the SFG intensities of C6-PVP with fixed IR frequency at 2880 and 3200 cm^{-1} were measured. Figure 6 shows the result obtained when the environment was changed in the following sequences. Each data point represents the average of SFG intensities obtained by 10 laser pulses, that is, 1 s. Initially, the cell was filled with dry nitrogen, and after 300 s, water vapor was introduced to the cell. Dry nitrogen was again introduced to the cell at 600 s from the beginning of the measurement at 300 s. As shown in Figure 6, intensities at 2880

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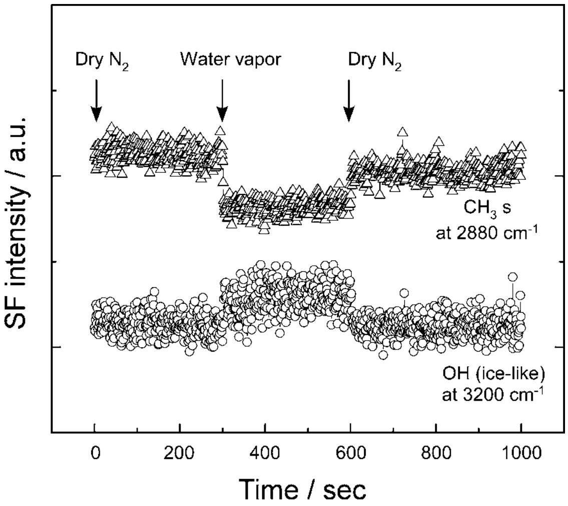

Figure 6. Time dependencies of the SFG intensities of C6-PVP with fixed IR frequency at (a) 2880 cm^{-1} and (b) 3054 cm^{-1} when the contact environment was changed between dry nitrogen and water saturated nitrogen at the time shown by arrows. Each data point corresponds to the SFG signals averaged for 10 laser pulses, that is, 1 s.

and 3200 cm^{-1} decreased and increased immediately after the introduction of water vapor, and they recovered quickly to the original values when dry nitrogen was introduced. These results show that the changes of both the brush conformation and the interfacial water structure were very fast and took place at the same rate. Similarly, very fast intensity changes were observed when liquid water was introduced, although the recovery after the replacement of liquid water by dry nitrogen was much slower. The rates of the change obtained here were probably determined by the rate of the replacement of the environment, and the actual rate of the structural change should be faster than observed. Thickness of the methyl-PVP brush was reported to be changed in the order of a minute when it contacted with the water vapor,[43] that is, much slower than the conformation change observed here, indicating that changes in the SFG spectra shown in Figure 2 and time dependence of the 2880 cm^{-1} peak shown in Figure 6 were dominated by the conformation change of alkyl side chain. The presence of the ring CH bands in the spectra obtained in water (Figure 4a−c) also indicates that the conformation of the main chains did not change much. This is reasonable because the polymer main chains were anchored to the solid surface at many points and, therefore, were not flexible to be affected by the environment change.

3.5. Effect of Ionic Strength on SFG Spectra in Electrolyte Solutions. Figure 7 shows SFG spectra in the OH stretching region of C6-PVP in solutions containing (a) 0, (b) 0.01, (c) 0.1, and (d) 0.5 M NaClO$_4$. It is clear that the higher is the ionic strength, the lower is the SFG intensity. The ionic strength-dependent SFG intensity shows that the C6-PVP brush indeed behaves as polyelectrolyte. Previous SFG studies of water structure on charged surfaces showed a similar trend.[27,44] When ionic strength becomes high, the thickness of the electric double layer at the solid/liquid interface becomes thin, leading to the smaller number of water molecules within the double layer, that is, lower SFG intensity. In the present case, the C*n*-PVP bromide polyelectrolyte brush dissociates to C*n*-PVP$^+$ and Br$^-$t, and the degree of the dissociation depends on ionic strength according to Gouy−Chapman theory.[45]

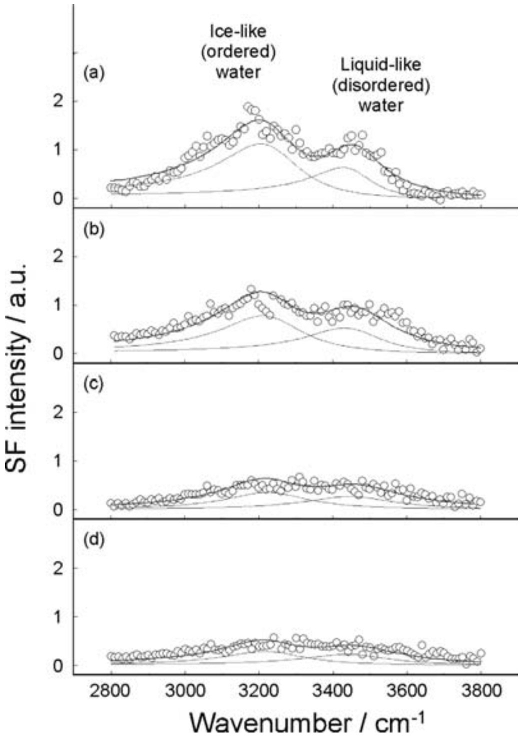

Figure 7. SFG spectra in the OH stretching region of C6-PVP covered quartz prism in aqueous solutions containing (a) 0, (b) 0.01, (c) 0.1, and (d) 0.5 M NaClO$_4$.

4. Conclusion

In summary, SFG measurements of C*n*-PVP ($n = 2$, 6, and 12) in dry nitrogen revealed that the conformational order of the side chain depended on the chain length. The highest conformational order was observed for the C6-PVP brush with C6 side chain being almost in *all-trans* conformation. A higher degree of gauche defect was introduced in contact with water vapor, and completely disordered structure was observed in liquid water. SFG spectra of the brush in contact with water vapor and liquid water in the OH stretching region were dominated by the OH stretching vibration of ice-like water, although some contribution of “liquid-like” water was observed in liquid water. It was clarified that the electric double layer was formed at the polyelectrolyte brush/aqueous solution interface induced by the electrolytic dissociation of C6-PVP bromide.

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