Structure, Composition, and Vibrational Property of Iodine-Doped Polyvinyl Alcohol Studied by Temperature-Dependent I K-Edge Extended X-Ray-Absorption Fine Structure

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The temperature dependence of the I K-edge extended X-ray absorption fine-structure (EXAFS) spectra of a highly oriented iodine-containing polyvinyl alcohol (I-PVA) film was investigated in order to reveal any local structures around I. It was firstly demonstrated that an analysis of the EXAFS amplitude, which is associated with the Debye–Waller factor (mean square relative displacement) provides information concerning the composition ratio of the dopant species. In the present high-contrast I–PVA film it was found that a significant amount (64%) of isolated I^- is present, and that the polyiodine species, which contributes to a high polarization property of I–PVA for ultraviolet and visible light, consists of 21% I_3^- and 15% I_5^-, without containing neutral I_2.

A stretched film of iodine-doped polyvinyl alcohol (I–PVA) is widely known as being a high-quality polarizer in the ultraviolet (UV) and visible regions.[1)] Photoabsorption in the UV-visible region exhibits a highly polarized nature; the absorption coefficient for the stretched direction was found to be by far greater than that for the perpendicular direction over a wide range of 250—800 nm. The polarized absorption bands were ascribed to the valence electronic transitions allowed for the direction of the molecular axis of the polyiodide species, which are found to be oriented along the stretched direction.

Many investigations have been carried out in order to clarify the dopant species and the local structure around the iodine. Polarized Raman spectroscopic studies[2)—5)] have elucidated that there exist I_3^- and I_5^- anions which are highly oriented toward the stretched direction, although no quantitative composition analysis of each ployiodine species has been conducted. By means of Mössbauer spectroscopy,[6)] it was found that iodine is in the three states of $I^{-0.5}$, $I^{-0.25}$, and $I^{\delta-}$, implying the absence of neutral I_2 species. A detailed intensity analysis clarified that in a stretched film the ratio of I^-, I_3^-, and I_5^- is 0.00 : 0.28 : 0.72, while in an unstretched film the ratio is 0.14 : 0.56 : 0.30. X-ray diffraction studies[7)—9)] were also carried out and revealed the structure of crystalline parts, though a larger part of the films is in the amorphous state. Polyiodide anions were found to locate between two PVA chains, the hydroxyl groups of which face each other. There remain, however, several ambiguities and controversies concerning the local structure of I–PVA films. Although the local structure is significantly dependent on the conditions of the sample preparations, it is strongly desired to reveal the dopant species: whether there no isolated I^- ions remain in a stretched film, how much I_3^- or I_5^- is present in the film, and so forth.

Extended X-ray absorption fine-structure (EXAFS) spectroscopy has been extensively applied to structural studies of non-crystalline materials. There have been published several EXAFS studies concerning dopant structures in polyacetylene; Oyanagi et al.[10)] investigated Br-doped polyacetylene, and elucidated the existence of polybromide anions in polyacetylene. In the present study, we measured and analyzed the I K-edge EXAFS spectra of I–PVA in order to investigate the local structure around the I atoms. We focused our attention on identifying the dopant species, which are possibly I^-, I_2, I_3^-, I_5^- or larger polyanions. Another aspect of the present study was to carry out a more explicit analysis of the mean square relative displacements (MSRD) given in the EXAFS analysis. MSRD is an important structural parameter which describes the vibrational properties for a pair of absorbing and scattering atoms; we have already performed many temperature-dependent EXAFS studies in order to elucidate any vibrational softening of the surface chemical bonds in small metal clusters[11)] and on well-defined surfaces.[12)] In the present study, we analyzed the temperature dependence of the MSRD of gaseous I_2 and $[(C_5H_5)_2Fe]I_3$, taking into account of all the possible normal stretching modes, and compared them to the vibrational frequencies given by the Raman spectra. We subsequently applied this analysis to the I–PVA system and considered the vibrational properties by which the dopant species are possibly identified and quantitized.

Experimental

Highly oriented I-containing PVA films with a high-contrast quality (Arisawa KN-18242T, labeled as a high-contrast film hereafter) were employed in the EXAFS experiments. The amount of iodine was estimated based on the I K-edge X-ray absorption intensity described below to be 8×10^{-5} g cm^{-2} in one sheet of the film. Using a density of 1.3 g cm^{-3} and a thickness of 30 μm, the iodine concentration was determined to be 2 wt%, namely, 0.007 in one unit of PVA ($-CH_2CH(OH)-$).

The UV-visible spectra were recorded using a Hitachi U-3500 spectrometer. In order to evaluate the polarization factor of the I–PVA film, two sheets of the films were used, the stretched directions of which were either parallel or perpendicular to each other. Since the present I–PVA film was too thick to obtain the absorption coefficient in the parallel direction, we prepared an I–PVA film with a smaller concentration of iodine; the UV-visible spectrum of an unstretched film was also taken in order to obtain a better spectral understanding. To identify polyiodide anions in the I–PVA film, the Raman spectrum of the high-contrast film was recorded using an Ar^+ laser line (514.5 nm) as the excitation light.

The EXAFS measurements were performed using the vertical wiggler hard X-ray station BL-14A of the Photon Factory in National Laboratory for High Energy Physics.[13)] I K-edge EXAFS spectra (32650—33950 eV) were taken using a Si(553) double-crystal monochromator with the transmission mode. The intensities of the incident and transmitted X-rays were measured with ionization chambers located before and after the sample. About 200 heaped sheets (ca. 30 mm in thickness including any coating materials) of the I–PVA films were required in order to obtain sufficient I K-edge absorption intensities. The polarization dependence was investigated by placing the stretched direction parallel and perpendicular to the electric-field vector of the X-rays. The measurement temperatures (T) were 77 and 300 K. For low-temperature measurements the sample was put directly in a bottle filled with liquid nitrogen in order to keep it at a uniform temperature. For reference spectra, we measured the I K-edge EXAFS of gaseous I_2 at 423, 473, 523, and 573 K, a hexane solution of I_2 at 300 K and $[(C_5H_5)_2Fe]I_3$ at 50 and 300 K. A closed-cycle cryostat was used for a low-temperature measurement of $[(C_5H_5)_2Fe]I_3$.

Results and Discussion

Results of Raman and UV-Visible Spectra. Figure 1 shows the Raman spectrum of a high-contrast I–PVA film. The Raman line at 109 cm^{-1}can be assigned to a symmetric stretching mode of I_3^- and that at 157 cm^{-1} to a symmetric stretching of I_5^- according to the literature.[2—5)] The other two lines at ca. 210 and ca. 310 cm^{-1} are due to overtones of the stretching modes of I_3^- and I_5^-. These results imply the coexistence of polyiodide anions of I_3^- and I_5^- in the film. Moreover, no evidence can be found for the presence of polyiodide anions larger than I_5^-.

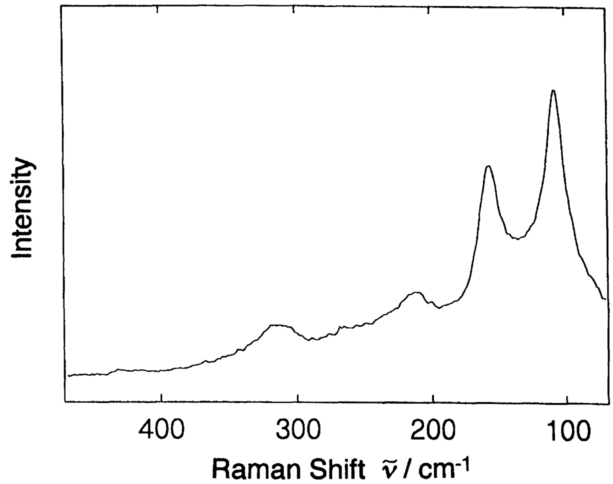

Fig. 1. A Raman spectrum of the high-contrast I–PVA film. The lines appearing at 109 and 157 cm^{-1} are ascribed to the symmetric stretching modes of I_3^- and I_5^-, respectively, and those at 210 and ca. 310 cm^{-1} are recognized as their overtones.

Figure 2 gives the UV-visible spectrum of an unstretched I–PVA film prepared by ourselves. The five absorption peaks have been tentatively assigned to I^- (210 nm), I_5^- (300 nm), I_3^- (350 nm), I_3^- (480 nm) and I_5^- (600 nm).[14)] Although the high-contrast film (stretched) shows absorption bands that are too strong, and only a broad band can be seen in the range of 300—750 nm in the parallel direction, we can conclude that the broad band of the high-contrast film originates from a

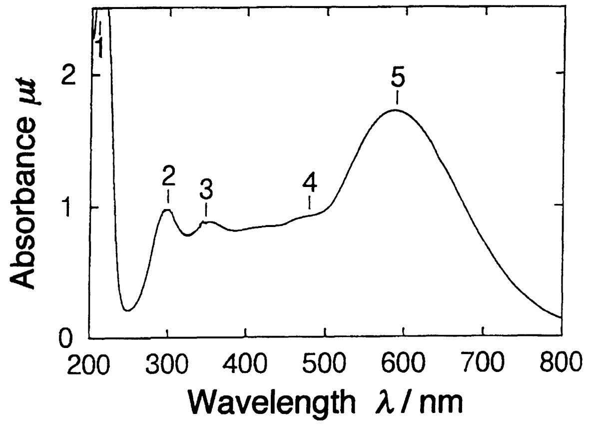

Fig. 2. UV-visible spectra of the unstretched I–PVA film prepared by ourselves. Five absorption bands 1—5 can be seen, and peak 1 has been assigned to I^-, peaks 3 and 4 to I_3^-, and peaks 2 and 5 to I_5^-.

superposition of the absorptions of I_3^- and I_5^-, this being consistent with the Raman results. Moreover, much more intense absorption was observed at 210 nm in the present high-contrast I–PVA film, implying that there exist a considerable amount of isolated I^- anions. Figure 3 shows the transmittance (T) and the linear polarization factor (V) of the high-contrast I–PVA film in the UV-visible range, which were obtained using two sheets of the film. T and V are equivalent to $(T_{/\!/}+T_{\perp})/2$ and $(T_{/\!/}-T_{\perp})/(T_{/\!/}+T_{\perp})$, respectively, where $T_{/\!/}$ and $T_{\perp}$ are, respectively, the transmittances in the parallel and perpendicular directions. For a wide range of wavelengths (300—750 nm) we can find a high linear polarization factor close to 100% and a considerable transmittance of 30—40%, thus confirming the high quality of the present I–PVA film as a polarizer.

Analysis of EXAFS. The extraction of the EXAFS oscillation functions ($\chi(k)$; k is the photoelectron wave number) was performed according to a well-established procedures: pre- and post-edge background subtraction and subsequent normalization using the edge jump and reported absorption coefficients.[15,16] Figure 4 shows $\chi(k)$ of the I–PVA film at 300 K where the electric field vector is parallel (//) and perpendicular ($\perp$) to the stretched direction. It is apparent that the // spectrum exhibits a strong EXAFS oscillation due to I–I coordination, while the $\perp$ spectrum gives almost no EXAFS signals. This implies that the I–I bond is highly oriented toward the stretched direction.

After multiplied by k^2, the EXAFS oscillation functions ($\Delta k=2.2$—11.0 Å^{-1}) were Fourier transformed into r space. Here, the Hanning window function with a width of 0.05 Å^{-1} was employed for both end sides of $\chi(k)$. Figure 5 shows the Fourier transforms for the // and $\perp$ spectra of the I–PVA film as well as those for the I_2 solution and $[(C_5H_5)_2Fe]I_3$. The features appearing at ca. 1 Å originate from a poor background subtraction to obtain $\chi(k)$. These peaks, however, did not affect the true signals observed at a distance greater than 2 Å, judging from the following curve-fitting analyses. The first nearest neighbor (n.n.) shell at around 2—3 Å can be immediately ascribed to the 1st n.n. I–I coordinations for all of the transforms. The contribution is split into two, even in the case of the I_2 solution (ca. 1.8 and ca. 2.4 Å) with a unique I–I distance. This effect is well known for a heavy-atom scatterer, and is caused by an abrupt change in the backscattering phase shift and amplitude at around ca. 6 Å in the case of iodine. As expected from Fig. 4, the magnitude of the Fourier transforms for the 1st n.n. I–I shell is much more intense in the // spectrum than in the $\perp$ one. Furthermore, the peak-top distance (ca. 2.6 Å) for the // spectrum is located more closely to that of $[(C_5H_5)_2Fe]I_3$ (ca. 2.6 Å), and not to the I_2 one (ca. 2.4 Å), indicating that the chemical state of the polyiodine species in the film is not neutral I_2, but polyiodide anions like I_3^- in $[(C_5H_5)_2Fe]I_3$. Although in the case of polyiodide anions the second n.n. I–I shells within the polyanions should be enhanced due to a multiple-scattering focusing effect of the central I atom, these shells were not observed, even in the reference material of $[(C_5H_5)_2Fe]I_3$. This might originate not only due to the rather long I–I distance (ca. 5.8 Å) for the second n.n. shell, but also due to the low-energy resolution of the monochromator because of the high photon energies of I K-edge spectra.

In order to obtain structural parameters, such as an

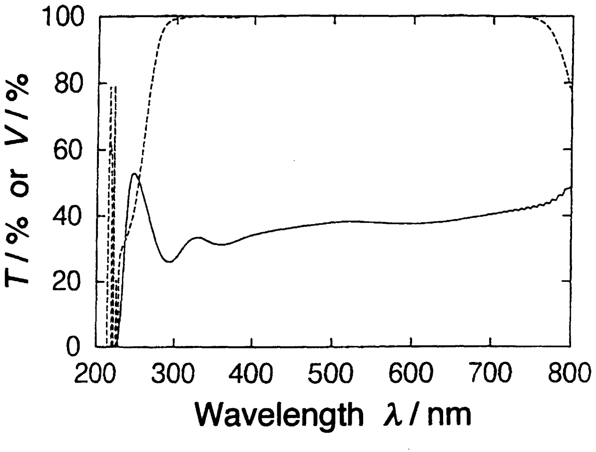

Fig. 3. Averaged transmittance T (solid line) and a linear polarization factor V (dashed) of the high-contrast I–PVA film in the UV-visible range.

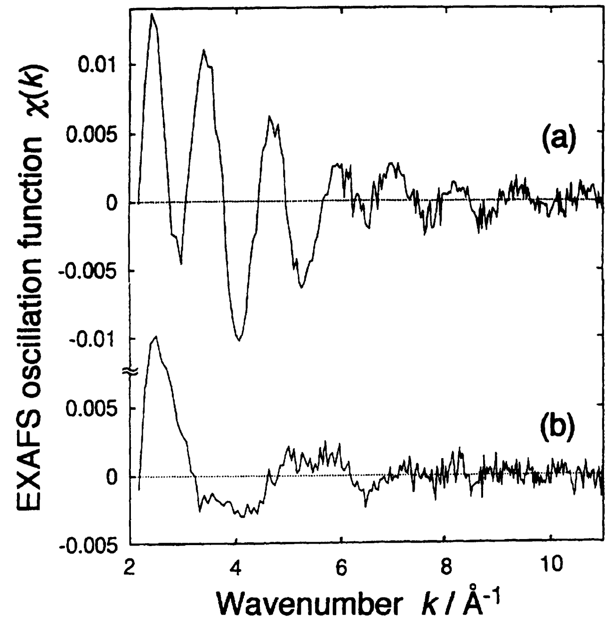

Fig. 4. I K-edge EXAFS oscillation function $\chi(k)$ of the high-contrast I–PVA film with the electric field vector (a) parallel (//) and (b) perpendicular ($\perp$) to the stretched direction. In the // spectrum a strong oscillation can be seen which is attributed to the 1st n.n. I–I coordination, while almost no EXAFS oscillation is observable in the $\perp$ spectrum. This implies that polyiodide species are well oriented to the stretched direction in the present I–PVA film.

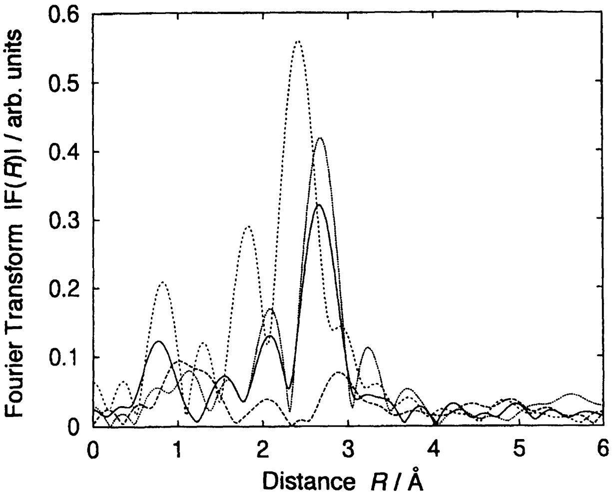

Fig. 5. Fourier transforms $|F(R)|$ of the k^2-weighted EXAFS oscillation functions $k^2\cdot\chi(k)$ of the high-contrast I-PVA film (solid line: the // spectrum, long-dashed line: the $\perp$ spectrum), $[(C_5H_5)_2Fe]I_3$ (dotted) and hexane solution of I_2 (short-dashed). As expected from Fig. 4, no I–I contribution can be seen in the $\perp$ spectrum. The peak position of the 1st n.n. I–I shell in the // spectrum is closer to that of $[(C_5H_5)_2Fe]I_3$ and not to that of the I_2 solution.

effective coordination number (N^*), an interatomic distance (R) and MSRD C_2 (EXAFS Debye–Waller factor), a curve-fitting analysis was performed after Fourier filtering the 1st n.n. I–I shell and a subsequent inverse Fourier transformation. A single-shell EXAFS function can be given within the plane-wave and single-scattering scheme as[15]

$$\chi(k)=\frac{N^*F(k)}{kR^2}\exp\left[-2C_2k^2\right]\sin\left[2kR+\phi(k)-\frac{4}{3}C_3k^3\right], \quad (1)$$

where $F(k)$ and $\phi(k)$ are the backscattering amplitude and the total phase shift, respectively. For simplicity, amplitude reduction factors both for the intrinsic and extrinsic origins are implicitly included in $F(k)$. In all of the present analyses a mean cubic relative displacement (C_3) in Eq. 1, which expresses the asymmetry of the distribution function, was found to be negligibly small. For the K-edge EXAFS spectra, since p-symmetric waves are emitted from the absorber, the effective coordination number (N^*) is given as[15]

$$N^*=3\sum_{i=1}^{N}\cos^2\delta_i, \quad (2)$$

where N is the real coordination number, δ_i the angle between the electric field vector and the bond direction, and the summation runs through all of the equivalent bonds of interest. In the case of random orientation of the sample, N^* is immediately found to be equal to the real coordination number (N).

The reference spectrum of a hexane solution of I_2 at 300 K was used as an empirical standard (N=1, R=2.67 Å) to obtain $F(k)$ and $\phi(k)$. Here, the I–I distance was assumed to be equal to the value of gaseous I_2. The I–I distance obtained for $[(C_5H_5)_2Fe]I_3$ is 2.92±0.02 Å for both 50 and 300 K, which shows excellent agreement with the X-ray data of 2.93±0.02 Å;[17] this implies a high accuracy of the present analysis. The I–I distance of the I–PVA film at 77 K was determined to be 2.89±0.02 Å, which is close to that of $[(C_5H_5)_2Fe]I_3$, but not to the I_2, exemplifying the existence of polyiodide anions. This conclusion is consistent with the Raman and UV-visible results. The effective coordination number was given as 1.55±0.20 for the // spectrum of the I–PVA film, which is discussed later.

The temperature dependence was subsequently analyzed using each lowest-temperature spectrum as a reference. With Eq. 1, the difference of C_2 between temperatures T_1 and T_2, ($\Delta C_2(T_1,T_2)$), can be evaluated[15] using

$$\frac{\chi(k,T_2)}{\chi(k,T_1)}=\exp\left[-2\Delta C_2(T_1,T_2)k^2\right], \quad (3)$$

where the small temperature dependence of R is neglected for simplicity. The resultant value of ΔC_2 (50 K, 300 K) of $[(C_5H_5)_2Fe]I_3$ is $(0.246\pm0.025)\times10^{-2}$ Å^2 and that of I-PVA (the // spectra) is $(0.447\pm0.045)\times10^{-2}$ Å^2. We measured several temperature points for gaseous I_2; the resulting values are ΔC_2 (423 K, 473 K)$=(0.039\pm0.004)\times10^{-2}$ Å^2, ΔC_2 (423 K, 523 K)$=(0.106\pm0.011)\times10^{-2}$ Å^2, ΔC_2 (423 K, 573 K)$=(0.140\pm0.014)\times10^{-2}$ Å^2. These results are used in the following section.

Analysis of Intramolecular Vibrations. The analysis of MSRD C_2 of polyatomic systems determined by EXAFS has been carried out within the harmonic approximation by several authors.[18,19] In the present polyiodide systems the harmonic approximation can be applied because of the previous finding of a negligible contribution of the anharmonic term (C_3) in the EXAFS analysis. In general, the mean-square relative displacement (σ_{0j}^2; where subscripts 0 and j mean absorber and scatterer, respectively) can be given as[15]

$$\sigma_{0j}^2=\sum_n\left(\hat{r}_j\cdot e_{jn}-\hat{r}_j\cdot e_{0n}\right)^2\frac{\hbar}{2\omega_n}\coth\left(\frac{\hbar\omega_n}{2k_BT}\right), \quad (4)$$

where $\hat{r}_j$ is a unit vector directed to the j-th atom with respect to the absorber (the 0th atom), k_B the Boltzmann constant and $\hbar$ Planck's constant divided by 2π, e_{jn}, and ω_n^2 are, respectively, the eigenvector and eigenvalue of the eigenequation such that[15]

$$\mathsf{V}e_n=\omega_n^2\mathsf{T}e_n, \quad (5)$$

where $\mathsf{T}=(T_{ij})$ and $\mathsf{V}=(V_{ij})$ are the matrices defined by

$$T_{ij}=m_i\delta_{ij} \text{ and } V_{ij}=\frac{\partial^2V}{\partial u_i\partial u_j}, \quad (6)$$

where u_i is the displacement of atom i.

It is straightforward to apply the formulae to the present system. Since the polyiodide anions are linearly coordinated, we can introduce some simplifications without approximations. The bending vibrational modes of linear molecules do not contribute to σ_{0j}^2 because of an orthogonality between $\hat{r}_j$ and e_{jn} (or e_{0n}). This allows a scalar expression of Eq. 4. Using the same mass number for all of the atoms, the averaged MSRD C_2, which is given by taking the average for all the possible 0–j pairs, and directly corresponds to the experimentally obtained value, can be expressed as

$$C_2=\sum_n\sum_{i=1}^{N_a-1}\frac{\hbar}{2(N_a-1)m\omega_n}(\varepsilon_{in}-\varepsilon_{i+1,n})^2\coth\left(\frac{\hbar\omega_n}{2k_BT}\right),\tag{7}$$

where ε_{in} is given by $\varepsilon_{in}=\sqrt{m}e_{in}$ (m is the mass of the atoms) and N is the number of atoms. Moreover, if we assume that the distances and force constants between n.n. coordinations are all equal and that all of the force constants, except for the n.n. coordination, can be neglected, the formula can be further simplified as

$$C_2=\sum_{n=1}^{N_a-1}\frac{\hbar}{(N_a-1)m\omega_n}\left(1-\cos\frac{n\pi}{N_a}\right)^2\coth\left(\frac{\hbar\omega_n}{2k_BT}\right)\tag{8}$$

and

$$\omega_n=2\sqrt{\frac{\alpha}{m}}\sin\left(\frac{n\pi}{2N_a}\right),\tag{9}$$

where α is the n.n. force constant.

The analysis of gaseous I_2 is straightforward using the temperature dependence of C_2; the averaged value of ω obtained to be 198±25 cm^{-1}, which agrees fairly well with the Raman data of 215 cm^{-1}.[20] An analysis of I_3^- in $[(C_5H_5)_2Fe]I_3$ can be similarly performed; the obtained value of α is 6.8 eV $Å^{-2}$, which gives $\omega_1=$ 121±15 cm^{-1} (symmetric stretching) and $\omega_2=$209±25 cm^{-1} (asymmetric stretching). The former is Raman active and is in agreement with the Raman data of 107 cm^{-1}.[21]

In an analysis of I–PVA, however, the above simple model given by Eq. 8 was found to be less reliable. When we calculated C_2 using the present Raman data and Eqs. 8 and 9, we obtained ΔC_2 (77 K, 300 K)=0.293×10^{-2} $Å^2$, assuming that all of the polyiodide anions consist of I_3^-, and that ΔC_2 (77 K, 300 K)=0.387×10^{-2} $Å^2$ in the case of I_5^- anions. Both values are noticeably smaller than the EXAFS result of 0.447×10^{-2} $Å^2$, implying a breakdown of the simple model. We had thus better apply and alternative model. Nour et al.[22] have already proposed a more complicated potential for understanding the infrared and Raman spectra of I_5^- in $[C_6H_3(COOH)_3\cdot H_2O]_{10}H^+I_5^-$. The off-diagonal terms are taken into account in the potential, which is given as

$$V=\frac{1}{2}\sum_{i=1}^{4}\alpha_i(u_i-u_{i+1})^2+\sum_{i=1}^{3}\alpha_{i,i+1}(u_i-u_{i+1})(u_{i+1}-u_{i+2}),\tag{10}$$

where $\alpha_1=\alpha_4$, $\alpha_2=\alpha_3$, and $\alpha_{12}=\alpha_{34}$. Using the values of ω_1 and ω_2 given by Nour et al.[22] and ω_3 given by the present Raman measurement, one can determine the force constants as being $\alpha_1=\alpha_4=7.5$ eV $Å^{-2}$, $\alpha_2=\alpha_3=3.7$ eV $Å^{-2}$, $\alpha_{12}=\alpha_{34}=2.6$ eV $Å^{-2}$, and $\alpha_{23}=1.6$ eV $Å^{-2}$, and the vibrational frequencies as being $\omega_1=75$ cm^{-1}, $\omega_2=90$ cm^{-1}, $\omega_3=157$ cm^{-1}, and $\omega_4=157$ cm^{-1}. These results yield ΔC_2 (77 K, 300 K)=0.634×10^{-2} $Å^2$. Recalling the Raman and UV-visible results, which reveal the coexistence of I_3^- and I_5^- anions in the I–PVA film, it is quite reasonable that the experimentally obtained ΔC_2 (77 K, 300 K)=$(0.447\pm0.045)\times10^{-2}$ $Å^2$ is located between the values of I_3^- (0.293×10^{-2} $Å^2$) and I_5^- (0.634×10^{-2} $Å^2$).

Estimation of the Composition of Iodine Species. As a consequence of the previous sections, the present I–PVA film was found to contain I^-, I_3^-, and I_5^-. The experimental ΔC_2 value can be expressed as the linear combination of a I_3^- and I_5^- concentrations. We can first evaluate the composition ratio, $c=[I_3^-]/([I_3^-]+[I_5^-])$, using

$$\Delta C_2^{\mathrm{obsd}}\cong\frac{cN_1\Delta C_{2,1}^{\mathrm{calcd}}+(1-c)N_2\Delta C_{2,2}^{\mathrm{calcd}}}{cN_1+(1-c)N_2},\tag{11}$$

where $N_1=1.33$ and $N_2=1.60$ are the coordination numbers of colinear I_3^- and I_5^- species, respectively, and $\Delta C_{2,1}^{\mathrm{calcd}}$ and $\Delta C_{2,2}^{\mathrm{calcd}}$ are the calculated ΔC_2 of I_3^- and I_5^-. Regarding the validity of Eq. 11 two assumptions have been employed: First, the interatomic distances in the two species are not quite different from each other; second, both polyiodide anions are similarly aligned to the strectched direction. Since we have found only a negligible distance devation between the I–PVA film and $[Fe(C_5H_5)_2]_2I_3$, the I–I distance of the I_5^- anion in the I–PVA film should be close to those of the I_3^- anion in the I–PVA film as well as $[Fe(C_5H_5)_2]_2I_3$, implying the reasonableness of the first assumption. The second assumption is also justified because of the high orientation of polyiodide anions demonstrated by the EXAFS and UV-visible spectra. The ratio $[I_3^-]:[I_5^-]$ is consequently calculated as 0.59 : 0.41.

Moreover, by assuming perfect orientation, the real coordination number should be 0.52, using the value of the obtained effective coordination number of 1.55. The real coordination numbers of I_3^- and I_5^- are respectively 1.33 and 1.60, indicating the presence of a considerable number of isolated I^- anions in the present I–PVA film. Using the previously-obtained ratio of $[I_3^-]:[I_5^-]$ one can conclusively calculate the ratio $[I^-]:[I_3^-]:[I_5^-]$ as 0.64 : 0.21 : 0.15. In the present estimation of the composition ratios, we neglected the structural and/or thermal disorder, which cannot be described within Gaussian distribution functions. Since we found no asymmetric contributions in the analysis, the above assumption seems to be reasonable for the most part. Moreover, the UV-visible spectrum shows the presence of a significant amount of isolated I^- anions. The absorbance of the present I–PVA film at 210 nm (the absorption is characteristic of isolated I^-) can be estimated from the total iodine concentration of 8×10^{-5} g cm^{-3} and the known absorption coefficient of 16500 mol^{-1} cm^{-1}.[23] The obtained value of 6.7 is not contradictory with the present UV-visible spectrum, which gave absorption that was too strong to measure (the absorbance of more than 4). On the other hand, the assumption of perfect orientation of the polyiodide anions can be justified within an error bar of ca. 10% based on the excellent polarization dependence of the EXAFS and the UV-visible spectra; the final error bar for the composition ratios was estimated to be less than ca. 20%.

The thus-obtained composition ratio is essentially different from the value given by the Mössbauer measurement ($[I^-]:[I_3^-]:[I_5^-]$=0.00 : 0.28 : 0.72) for a stretched I–PVA film.[6] This is probably because of different sample-preparation procedures. In a high-contrast film excess amounts of I^- anions were introduced in order to increase the concentration of I_3^-, which shows strong absorptions at around 300—500 nm along the stretched direction, and is thus important for a good polarizer. This leads to the presence of considerable amounts of I^- in the I–PVA film. We suppose that in the sample preparation for a Mössbauer measurement a smaller I^- concentration during iodine dosage resulted in a smaller amount of isolated I^- and a larger amount of I_5^-.

Conclusions

The I K-edge EXAFS spectra of an I-doped PVA film was investigated in order to clarify the chemical states of iodine with the help of UV-visible and Raman spectra. The I-PVA film was found to contain isolated I^- and polyiodide anions as I_3^- and I_5^-. These findings are consistent with the UV-visible and Raman data, and from the Raman spectrum no evidence can be seen for the presence of larger polyiodide anions.

Through temperature and polarization-dependent measurements of the EXAFS spectra, an apparent coordination number and a vibrational amplitude for the 1st n.n. I–I bond was obtained; this provides a successful estimation of the composition ratio, $[I^-]:[I_3^-]:[I_5^-]$, of 0.64 : 0.21 : 0.15. A schematic picture of the present I–PVA film can conclusively be depicted as in Fig. 6.

The coexistence of I_3^- and I_5^- anions may allow the present film to be used as a high-quality polarizer over the wide range of 300—750 nm, since both anions effectively absorb UV-visible light complementarily. Although the obtained composition ratio does not seem to be a universal parameter, and may vary significantly, depending on the sample-preparation procedure, the present estimation will be quite useful for understanding the performance of the I–PVA film as a polarizer, and will also be helpful for further improvements.

Finally, we would like to emphasize the usefulness of the vibrational analysis of the EXAFS spectra, which has consequently enabled us to estimate the composition ratio of the iodine species.

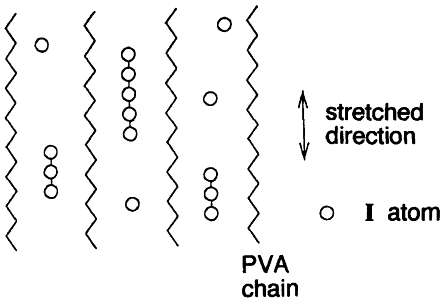

Fig. 6. Schematic picture of I–PVA. Polyiodide anions as I_3^- and I_5^- are oriented along the PVA chain, and considerable amounts of isolated I^- anions remain in the film.

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