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Investigation of the structure of poly(vinyl alcohol)–iodine complex hydrogels prepared from the concentrated polymer solutions

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Abstract

The structure and dynamics of poly(vinyl alcohol) (PVA)–iodine complex hydrogels that were prepared from concentrated PVA solutions have been characterized by high-resolution solid-state ^{13}C NMR spectroscopy. The fully relaxed dipolar decoupling (DD)/MAS ^{13}C NMR spectrum indicates that the hydrogels contain at least two components, a highly mobile and broader components. The former is assigned to the soluble or well water-swollen PVA chains that are not closely associated with the PVA–iodine complexes, whereas the latter may be mainly ascribed to the aggregated PVA chains that are produced by the formation of the PVA–iodine complexes because no diffraction peaks due to the conventional PVA crystallites are observed by wide-angle X-ray diffractometry. Furthermore, ^{13}C spin-lattice relaxation time (T_{1C}) analyses reveal that the broader component is composed of the highly restricted component probably assignable to PVA molecular chain aggregates containing the PVA–iodine complexes and the less mobile component. As for the former component, their CH resonance line measured by the T_{1C}-filtering method is successfully resolved into 7 constituent lines by the least-squares curve fitting. The statistical analysis of the integrated intensities of the constituent lines thus obtained also reveals that the probability f_a for the formation of intramolecular hydrogen bonding in the successive two OH groups along each chain and another probability f_t of the *trans* conformation are, respectively, as high as 0.86 and 0.88. This fact indicates that the PVA molecular chain aggregates containing the PVA–iodine complexes should be composed of PVA segments with the *trans*-rich conformation and the PVA–iodine complexes therein may also be formed with these several *trans*-rich segments surrounding the rod-like polyiodine cores in agreement with the so-called aggregation model. Moreover, several new diffraction peaks that should be interpreted in terms of the hexagonal structure are observed for the PVA–iodine complex hydrogels in the low 2θ region in the wide-angle X-ray diffraction (WAXD) profile measured by a strong X-ray source at SPring-8. This suggests the necessity of more detailed WAXD characterization to propose a new structure model, which should be referred to as the hexagonal aggregation model, for the PVA–iodine complexes.

Keywords: Solid-state ^{13}C NMR; Wide-angle X-ray diffractometry; Poly(vinyl alcohol)–iodine complexes

1. Introduction

It is well known that iodine readily forms blue-colored complexes with specific polymers such as starch, nylon-6, poly(vinyl alcohol) (PVA) [1,2] and so on. Recently, PVA–iodine complexes have been paid much more attention for not only the reason that PVA is one of water-soluble and environmentally-friendly synthetic polymers [3,4], but also that PVA–iodine complexes are widely used for polarizing films in a practical application [5]. Therefore, the characterization of the structure of PVA–iodine complexes has been continued as an important research topic. Many researchers tried to establish the structure model for the PVA–iodine complexes. However, until now, the structure of PVA in the complexes is not well understood although there seems almost no dispute for the structure of iodine in the complexes as linear polyiodine ions such as I_3^- and I_5^-. Two structure models for the PVA–iodine complexes were proposed in 1965, the helix model [6] and the aggregation model [7]. In the helix model,

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a single PVA chain goes around a polyiodine helically, which is basically the same structure as that of starch–iodine complexes. In contrast, in the aggregation model, each polyiodine is surrounded by some parallel-oriented PVA chains. In addition, previous studies on the formation of the PVA–iodine complexes were mainly carried out either in the dilute solutions [8–11] or in the PVA films or fibers [3,12–15]. However, it is also very important to prepare the PVA–iodine complexes from concentrated PVA–iodine–KI aqueous solutions without effects of the presence of the conventional PVA crystallites and to simply characterize the structure and dynamics of the PVA–iodine complexes in the hydrogels by solid-state ^{13}C NMR spectroscopy.

In our previous studies [16–26], we have already established the systematic characterization method of the chain conformation and intra- and inter-molecular hydrogen bonding for different PVA samples by solid-state ^{13}C NMR spectroscopy. In particular, by assuming the random distribution of *trans* and *gauche* conformations along the PVA chains and the statistical formation of the intramolecular hydrogen bonds between appropriate adjacent OH groups without employing any crystal structure model, two sorts of probabilities could be successfully obtained for the distribution of the *trans* conformation and for the formation of the intramolecular hydrogen bonding [21–26]. In this paper, we apply the similar analytical method to the characterization of the structure and dynamics of the PVA–iodine complex hydrogels prepared from the concentrated PVA solutions. Wide-angle X-ray diffraction (WAXD) measurements are also performed for the hydrogels to briefly discuss a new structure model, which should be referred to as the hexagonal aggregation model, for the PVA–iodine complexes.

2. Experimental

2.1. Samples

The PVA sample used was kindly provided by Kuraray Co.: the degrees of polymerization and saponification were 1750 and 99.9%, respectively. The triad tacticities, which were determined at 50 °C in deuterated dimethyl sulfoxide (DMSO-d_6) by gated scalar decoupling ^{13}C NMR spectroscopy, are as follows: $mm = 0.23$, $mr = 0.50$, $rr = 0.27$. Iodine and potassium iodide of reagent grade were used as received from Nacarai Tesque without further purification. De-ionized water was used in all experiments.

The concentration of PVA and KI in each aqueous solution were 10% and 2%, respectively, and the molar ratio of KI and I_2 was 4:1 throughout this work. For solid-state ^{13}C NMR measurements, the concentration of PVA–iodine complexes was increased by soaking the hydrogels in a higher KI aqueous solution containing saturated I_2 for 4 days. The weight fraction of water in the hydrogels was decreased from 0.90 to 0.85 by this method.

2.2. ^{13}C NMR measurements

Solid-state ^{13}C NMR measurements were performed at room temperature on a Chemagnetics CMX-200 spectrometer operating at a static magnetic field of 4.7 T. ^{1}H and ^{13}C radio frequency field strengths $\gamma B_1/2\pi$ were 69.4 kHz for both CP and dipolar decoupling processes. The CP contact time was 0.8 ms and the recycle time after the acquisition of free induction decay (FID) was 7 s. Each sample was packed into a 7 mm cylinder-type MAS rotor with an O-ring seal [16,22–27]. The MAS rate was about 3.5 kHz. Totally, 400–600 FIDs were accumulated using 4K data points in the frequency range of 10 kHz. ^{13}C chemical shifts relative to tetramethylsilane (Me_4Si) were determined by using the CH_3 line at 17.36 ppm of hexamethylbenzene crystals as an external reference. The CPT1 pulse sequence [28] was used to measure ^{13}C spin-lattice relaxation times (T_{1C}s).

2.3. Wide-angle X-ray diffractometry

Wide-angle X-ray diffraction (WAXD) profiles were measured for the freeze-dried PVA–iodine hydrogels sample over the range of $2\theta = 5–38°$ at room temperature by Rigaku Rint 2000. Cu-Kα radiation was used as an X-ray source (40 kV, 300 mA). An aluminum foil was used to cover the PVA powder-like sample and to measure the WAXD profile for comparison. WAXD profiles were also measured for the PVA–iodine hydrogels without drying by a strong X-ray source ($\lambda = 1.2400$ Å) at beam line BL24UX in SPring-8.

3. Results and discussion

3.1. The formation of PVA–iodine complex hydrogels

A sort of phase diagram for the formation of PVA–iodine complex hydrogels, which is shown in Fig. 1, was prepared by naked-eye observations of the color change indicating the gel formation on cooling. Each PVA solution with a given KI/I_2 concentration was prepared by heating in a sealed glass tube at 120 °C for 1 h and then color changes were observed on cooling at room temperature. The color changed from yellow to greenish-yellow, green, bluish green, and finally to dark

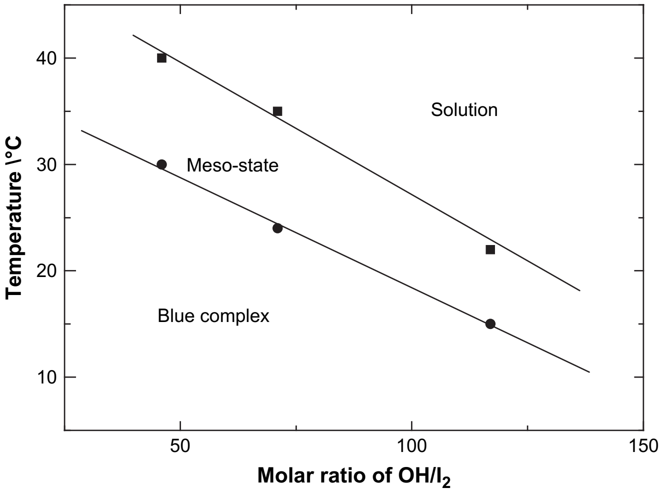

Fig. 1. Phase diagram for the formation of the PVA–iodine complex hydrogels.

blue, which corresponds to the color characteristic to stable PVA–iodine complexes. Such a successive color change indicates that the formation of PVA–iodine complexes from the homogeneous solution occurs gradually on cooling. The characteristic temperatures for the complex formation strongly depend on the iodine concentration, as seen in Fig. 1. Here, the meso-state indicates the transitional region where the color changes from yellow to dark blue. According to this phase diagram, the PVA–iodine complex hydrogels used in this work were prepared by cooling the PVA solution with a mole ratio of $OH/I_2 = 76.7$ from 120 °C to room temperature.

3.2. Characterization of the PVA–iodine complex hydrogels by solid-state ^{13}C NMR

To precisely characterize the structure and dynamics of the hydrogels by solid-state ^{13}C NMR spectroscopy, the concentration of the PVA–iodine complexes was increased by soaking the newly prepared hydrogels into a higher KI aqueous solution containing saturated I_2. The weight fraction of PVA in the hydrogels was increased from 0.10 to 0.15 by this method. Fig. 2(a) shows the CP/MAS ^{13}C NMR spectrum of the PVA–iodine hydrogels thus obtained, which was measured at room temperature without drying. As is well known, the CH resonance lines for various PVA solid samples split into three lines, I′, II′ and III′, which are mainly composed of the contributions from lines I, II and III for the crystalline component of PVA and the latter three lines are, respectively, assigned to the CH carbons associated with two, one and no intramolecular hydrogen bond(s) in the triad sequences with the planar zigzag conformation [16–26,29]. Similar three lines, I′, II′ and III′, are clearly observed in the PVA–iodine hydrogels and, moreover, an additional resonance line appears between line II′ and III′ in Fig. 2(a), which is ascribed to the contribution of a highly mobile component and assigned to the CH carbons in the *mr* triad sequences by the comparison with the lines observed in Fig. 2(b) described below [16,26,30].

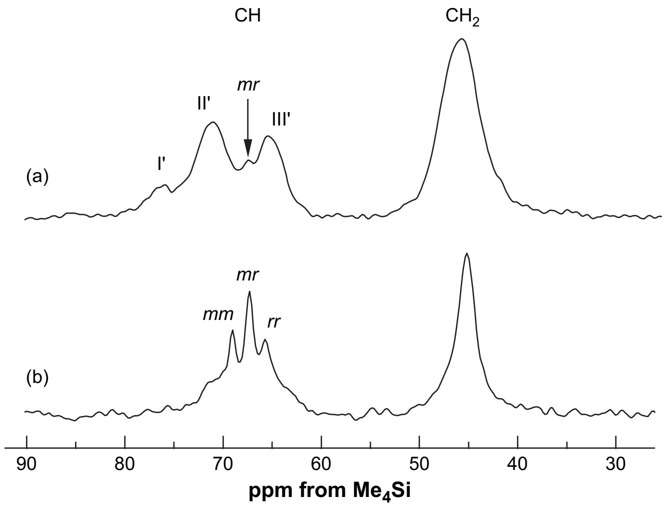

Fig. 2. High-resolution solid-state ^{13}C NMR spectra of the PVA–iodine hydrogels; (a) CP/MAS ^{13}C NMR spectrum; (b) fully relaxed DD/MAS ^{13}C NMR spectrum.

For further quantitative investigations of the PVA–iodine hydrogels, a fully relaxed dipolar decoupling (DD)/MAS ^{13}C NMR spectrum was also obtained by the $\pi/4$ single pulse, as shown in Fig. 2(b), by considering T_{1C}s of this sample described later in detail. A sharp triplet is clearly observed for the CH resonance line and it is assigned to the CH carbons in the *mm*, *mr* and *rr* triad sequences in the order of decreasing chemical shift value [31]. The T_{1C} of the triplet was also found to be as short as 0.089 s as described later. These facts indicate that a highly mobile component, which corresponds to the rubbery component in the hydrated PVA films [16,26,30], exists in the hydrogels, probably forming the soluble chains or highly water-swollen chains in the hydrogels that are not closely associated with PVA molecular chain aggregates produced as a result of the formation of the PVA–iodine complexes.

To estimate the mass fraction of the mobile component, the fully relaxed spectrum was resolved into two components, the mobile and broader components, by the subtraction method. In this case, each line of the mobile component was assumed to be described by a Lorentzian curve with an appropriate line width. These three Lorentzians were subtracted from the fully relaxed spectrum so as to obtain an undistorted resonance line that should be ascribed to the broader component. Such a subtraction could be successfully carried out as shown in Fig. 3. The broader component thus obtained should be composed of the molecular chain aggregates containing PVA–iodine complexes and the less mobile component as described below. Finally, the mass fraction of the mobile component was determined to be 0.60 by using the integrated intensities of the two components.

The ^{13}C spin-lattice relaxation process was also measured for the PVA–iodine complex hydrogels at room temperature. The CPT1 pulse sequence [28] was employed for the broader component, whereas the saturation recovery method modified

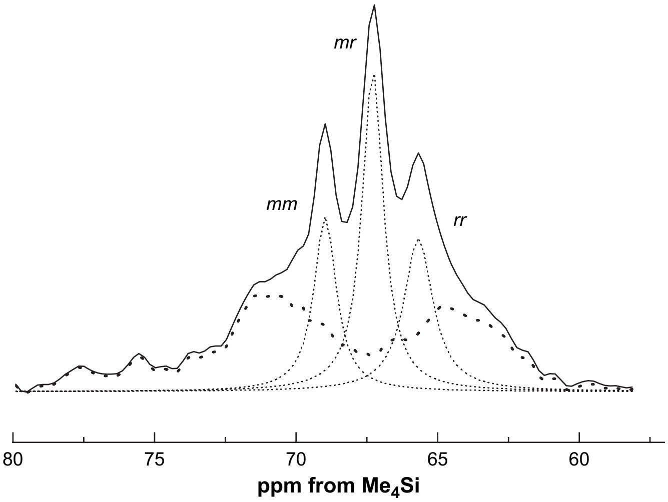

Fig. 3. The CH resonance line for the fully relaxed DD/MAS ^{13}C NMR spectrum of the PVA–iodine hydrogels; broken lines: Lorentzian lines describing the mobile component that should be assigned to the CH carbons in the *mm*, *mr* and *rr* units; dotted line: the spectrum obtained by the subtraction of the three Lorentzian lines from the observed line.

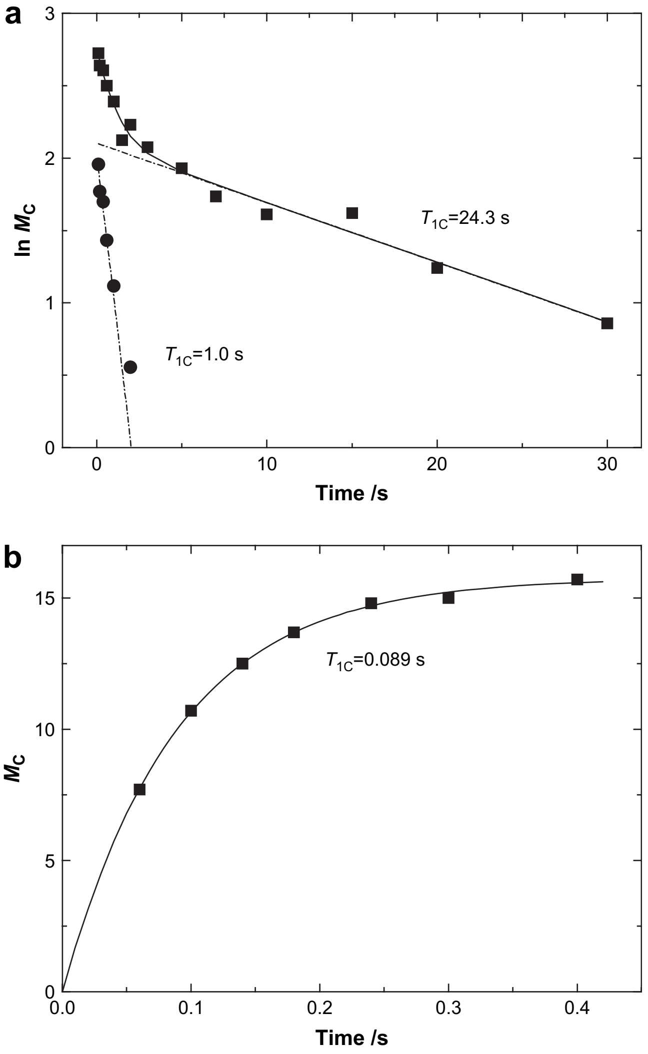

Fig. 4. ^{13}C spin-lattice relaxation behavior for the CH_2 carbons of the PVA–iodine hydrogels: (a) measured by the CPT1 pulse sequence; (b) measured by the modified saturation recovery method.

for solid-state measurements [32,33] was used for the narrow component because the CP method was not effective for this component as shown in Fig. 2. The peak intensities of the CH_2 resonance line obtained by the respective methods are plotted as a function of the delay time for the relaxation in Fig. 4. The least-squares fittings by a computer clearly reveal that there exist two components with T_{1C} values of 24.3 and 1.0 s for the broader component while the mobile component is composed of a single component having a T_{1C} value that is as short as 0.089 s. Other CH resonance lines were also found to contain similar three components and their T_{1C} values are listed in Table 1 together with the previous results for the dried and hydrated PVA films [16] for comparison. It is simply found that the T_{1C} values of the respective components evidently decrease with the increase of the content of water in the samples although the PVA chains forming the respective components are not the same in all samples. According to the previous assignment [16–20,23–26], the three components in the dried and hydrated PVA films are assigned to the crystalline, less mobile noncrystalline and mobile noncrystalline components in the order of decreasing T_{1C} values, respectively. In contrast, the component having the largest T_{1C} in the PVA–iodine hydrogels should be assigned to the PVA molecular chain aggregates produced as a result of the formation of the PVA–iodine complexes because no WAXD peaks due to the conventional PVA crystals were observed as described later. Such molecular chain aggregates, which may be mainly composed of the PVA–iodine complexes, are strongly restricted in molecular mobility although the restriction extent is not very high compared to that in the crystalline component in the dried or hydrated films. The less mobile component with $T_{1C} = 0.6–1.0$ s in the hydrogels may be the medium component undergoing the restriction in molecular mobility from the molecular chain aggregates containing the PVA–iodine complexes, whereas the corresponding component in the films is subjected to the similar influences from the crystallites. In addition, the component with the smallest T_{1C} in the hydrogels is really the mobile component having no restriction from the molecular chain aggregates, which corresponds to the rubbery component free from the restriction produced by the crystallites in the hydrated PVA films [16,26,30].

By using the difference in T_{1C}, the T_1-filtered CP/MAS ^{13}C NMR spectrum of the molecular chain aggregates containing the PVA–iodine complexes was selectively measured by the CPT1 pulse sequence [28]. Here, the relaxation delay time τ in the pulse sequence was set to 5 s, because the other two components fully disappear at $\tau = 5$ s. Fig. 5 shows the spectrum of the CH carbons as a thick solid curve thus obtained. This spectrum seems to contain similar constituent resonance lines observed for the crystalline and noncrystalline components in different PVA samples [22,24,25]. Therefore, this spectrum was resolved into the respective constituent lines

Table 1
^{13}C spin-lattice relaxation times (T_{1C}) of the respective resonance lines for PVA–iodine hydrogels, measured at room temperature

Samples	T_{1C} (s)			
	CH			CH_2
	I′	II′	III′	
PVA–iodine hydrogels	–[a]	24.4, 1.0, 0.16	16.4, 0.6, 0.18	24.3, 1.0, 0.089
Hydrated PVA films[b,c]	43.7, 8.5, 0.29	42.3, 5.5, 0.25	48.0, 5.5, 0.24	45.6, 6.4, 0.14
Dried PVA films[c]	60.0, 12.1, 1.1	65.0, 14.6, 1.2	62.0, 12.3, 2.2	65.0, 14.6, 1.3

[a] Not estimated because of the low signal/noise ratio.

[b] The water content is 0.18 g/g.

[c] Ref. [16].

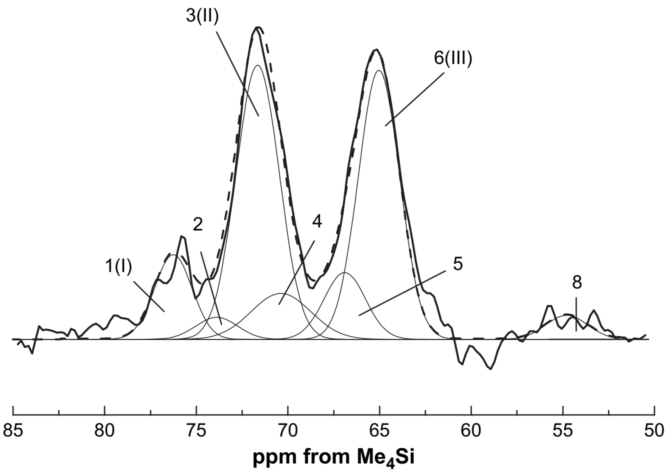

Fig. 5. Line shape analysis of the CH resonance line for the PVA molecular chain aggregates containing the PVA–iodine complexes observed as the largest T_{1C} component of the hydrogels. The dashed line indicates the composite curve of the constituent lines shown by thin solid lines.

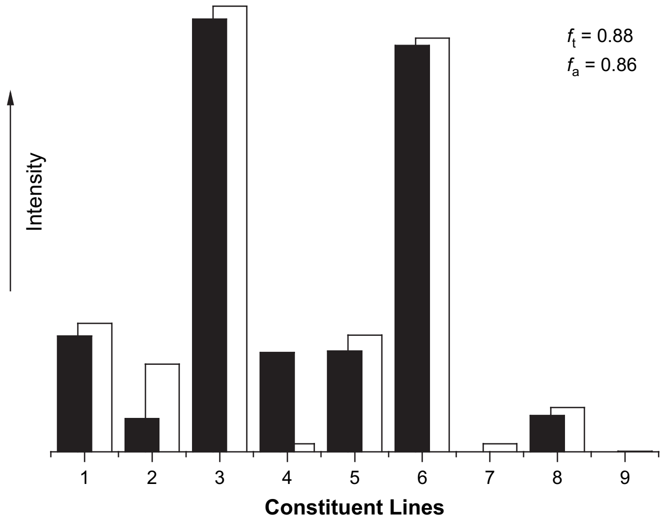

Fig. 6. Histograms for the experimental and calculated relative intensities of the 9 constituent lines for the CH resonance line of the PVA molecular chain aggregates containing the PVA–iodine complexes shown in Fig. 5.

by the method previously proposed [22]. In this method, totally 9 constituent lines with different chemical shifts were used, which were produced by considering the effects of the formation of intramolecular hydrogen bonding [16,22] and the γ-*gauche* effect [34] on the chemical shifts. Here, each constituent line is assumed to be described as a Gaussian curve. As is clearly seen in Fig. 5, the CH line is successfully resolved into 7 constituent lines by the least-squares curve fitting, the composite curve (broken line) being in good accord with the observed curve (thick solid line). Since lines 2, 4, 5 and 8 are associated with the *gauche* conformation, the existence of these lines indicates that some amount of the *gauche* conformation is also produced in the molecular chain aggregates.

To know the fraction of the *gauche* or *trans* conformation in the aggregates, the statistical analysis was performed for the integrated intensities of the respective constituent lines for the CH resonance line by using the equations previously derived [22]. In this case, it is assumed according to the previous evaluation [22,24,25] that almost no preferential partitioning of the *mm*, *mr* and *rr* sequences may occur for the different components like the cases of the A-PVA solid samples. Fig. 6 shows the experimental integrated intensities (solid histograms) for the constituent lines obtained by the lineshape analysis shown in Fig. 5 and the statistically calculated intensities (open histograms) that were obtained so as to fit the experimental intensities by the least-squares method by using the probability f_t for the formation of the *trans* conformation in the C–C bonds and the probability f_a for the formation of the intramolecular hydrogen bonding in the possible *m* or *r* units as adjustable parameters. The calculated intensities are in good accord with the experimental intensities for the PVA molecular chain aggregates except for line 4. The disagreement for line 4 may be due to the contribution from the folding parts of the PVA chains and such chain folding is not well described at high f_t values by the statistically random treatment although it is successfully applicable to other parts of the chains as described in detail in a previous publication [25]. Interestingly, the f_t and f_a values are found to be as high as 0.88 and 0.86, respectively. Moreover, the linewidths of the constituent lines associated with the *trans* conformation are much narrower than those for the noncrystalline component in the conventional PVA films [24], suggesting a considerably narrow distribution in structure for the molecular chain aggregates. These facts indicate that the aggregates should be mainly composed of rather extended PVA segments with the *trans*-rich conformation.

The initial mole ratio [OH]/[I$_2$] is 76.7 in this sample but this ratio will be greatly decreased in the molecular chain aggregates by the formation of PVA–iodine complexes containing rod-like I_3^- and I_5^- polyiodine ions. Nevertheless, it is plausible to assume that the aggregates may not only be composed of the PVA–iodine complexes but also *trans*-rich PVA chains additionally produced by the complex formation. Therefore, the PVA–iodine complexes or rod-like I_3^- and I_5^- ions themselves seem to be embedded in the *trans*-rich, rather extended PVA segments in the aggregates. This suggests that the aggregation model [7], in which each polyiodine ion is surrounded by some parallel-oriented PVA chains, is a better model for the PVA–iodine complexes than the helix model [6].

3.3. WAXD and a structure model

The WAXD profile was measured for the PVA–iodine hydrogels after freeze-drying to maintain the structure of PVA in the hydrogels, which is shown in Fig. 7(a). A broad diffraction peak is observed at $2\theta = \sim 21°$ together with three strong peaks at $2\theta = \sim 22°$, 26°, and 36°, which are all ascribed to KI crystals produced by drying. However, the diffraction peaks ascribed to the conventional PVA crystallites, which are shown in the profile of PVA powders in Fig. 7(b) for comparison, are not detected in the freeze-dried PVA–iodine hydrogels. This indicates that no conventional PVA crystallites are formed in

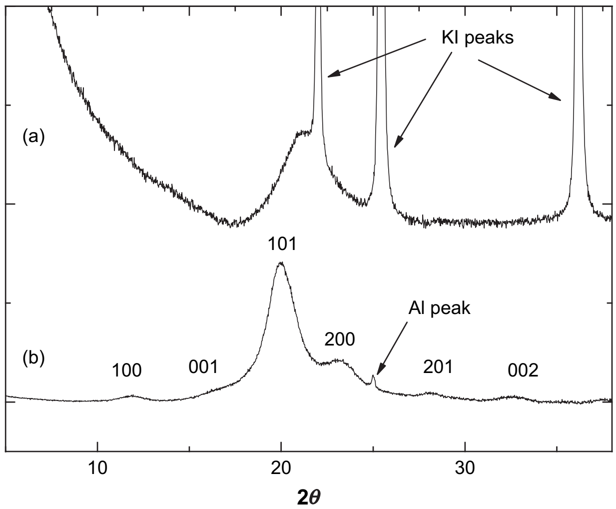

Fig. 7. WAXD profiles of different PVA samples: (a) freeze-dried PVA–iodine hydrogels; (b) PVA powders.

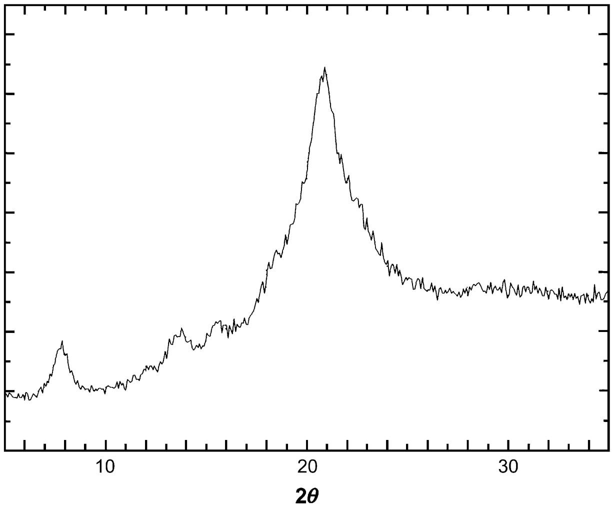

Fig. 8. WAXD profile of the PVA–iodine hydrogels obtained without drying by a strong X-ray source at SPring-8.

the original, water-containing hydrogels and the component with the largest T_{1C} shown in Figs. 4 and 5 should be simply assigned to the PVA molecular chain aggregates produced as a result of the formation of the PVA–iodine complexes in the hydrogels as already described above. In addition, the rather broad diffraction peak at $2\theta = \sim 21°$ seems to correspond to the peak that was observed for the PVA–iodine complexes in PVA films [12,13]. However, additional two peaks at $2\theta = \sim 6.5°$ and $2\theta = \sim 13.5°$ that were clearly detected for the PVA–iodine complexes in the films [12,13] are not observed for the freeze-dried PVA–iodine hydrogels as seen in Fig. 7. This fact suggests that the structure of PVA–iodine complexes in the hydrogels may be significantly different from the structure of the PVA–iodine complexes formed in the PVA films in the presence of the crystallites.

To obtain further information of the structure of the PVA–iodine complexes in hydrogels, WAXD measurements were carried out for the PVA–iodine hydrogels without drying by a strong X-ray source at SPring-8. The WAXD profile obtained is shown in Fig. 8. Several diffraction peaks in the low 2θ region are evidently observed in addition to the broad peak at $2\theta = \sim 21°$. These diffraction peaks newly observed in the low 2θ region are completely different from those previously observed for the PVA–iodine complexes formed in the PVA films except for the broad peak at $2\theta = \sim 21°$ [12,13]. The cause of the disagreement is not clear at present but the presence of the conventional PVA crystallites and, more seriously, drying of the samples may affect the structure of the PVA–iodine complexes that would be detected by WAXD. In fact, the diffraction peaks newly observed in the low 2θ region in Fig. 8 could not be detected for the same PVA–iodine sample after freeze-drying. Moreover, these diffraction peaks were again clearly confirmed by re-swelling the same sample with water.

Since more detailed experiments should be made to elucidate the effects of drying and the presence of the conventional PVA crystallites on the complex structure, we here simply calculated the interplanar spacing (d) for each diffraction peak including the large peak at 20.7° and found that the ratio of the reciprocal d value at $2\theta = 7.7°$, 13.5° and 20.7° is $1 : \sqrt{3} : \sqrt{7}$. This fact suggests that a hexagonal structure may be formed for the PVA–iodine complex hydrogels. If such a structure is formed, the peaks at $2\theta = 7.7°$, 13.5° and 20.7° can be assigned to the reflections from the (100)/(010) planes, (110) plane, and (120)/(210) planes, respectively. Nevertheless, the peak at $2\theta = 15.6°$ is not well assigned to the reflection from any plane parallel to the chain axis associated with the hexagonal structure at present. The thicknesses of the (100) and (120) planes are estimated to be 8.7 and 8.2 nm by the Scherrer equation [35]. It is, therefore, reasonable to assume a new structure model for the PVA–iodine complexes, probably referred to as the hexagonal aggregation model, in which PVA segments having the *trans*-rich conformation and polyiodine ions are hexagonally packed with each other. Here, one basic structure unit that is composed of one polyiodine ion and almost parallel 6 PVA segments surrounding the ion will correspond to the aggregation model previously proposed [7]. The real structural model will be proposed after more detailed WAXD characterization is made for uniaxially drawn PVA–iodine complex hydrogels as well as for the complexes formed in the films in the presence of water.

Acknowledgements

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