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Role of boric acid in the formation of poly(vinyl alcohol)–iodine complexes in undrawn films

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ABSTRACT

The role of boric acid in the formation of poly(vinyl alcohol) (PVA)–iodine complexes in undrawn films has been investigated by using wide-angle X-ray diffraction (WAXD) and high-resolution solid-state ^{13}C NMR spectroscopy. From UV–vis absorption spectroscopy, it is confirmed that boric acid is necessary for the formation of the complexes in films that are treated with I_2/KI aqueous solutions at relatively low I_2 concentrations. The WAXD profiles indicate that, irrespective of the presence of iodine, crystallite sizes perpendicular to the chain axis become smaller by the addition of boric acid in the swelling media. Moreover, small crystallites and surficial parts of larger crystallites may be partially dissolved in the swelling process with water and boric acid suppresses the re-crystallization in the drying process with or without iodine. The ^{13}C spin–lattice relaxation time analysis reveals that there exist two components called the mobile and the less mobile components in the films and the latter component, which contains the complexes and the crystalline component, is increased in the fraction by the presence of boric acid. The evaluation of the CH resonance line shows that some of the intermolecular hydrogen bonds are broken by boric acid, which increases the intramolecular hydrogen bonds. The CH_2 lineshape analysis also reveals that the *gauche* fraction is appreciably increased in the less mobile component by the addition of boric acid. These facts suggest that boric acid may promote the formation of PVA–iodine complexes particularly in the surficial areas of the crystallites probably by reducing the molecular mobility of the PVA chains by causing cross-linking among them.

1. Introduction

Poly(vinyl alcohol) (PVA) has a broad range of industrial applications, for example, in fibers, films, coatings, and adhesives [1]. In particular, PVA films have been used as high-quality polarizers because of their ability to form PVA–iodine complexes [2,3] and their dichromatic performance in the film microstructure. The polarizer is usually prepared by soaking PVA films in iodine (I_2)–potassium iodide (KI) aqueous solution with boric acid and subsequently drawing them to obtain high uniaxial orientation ratios.

Since the formulation of the blue color reaction in the 1920s, many researchers have attempted to establish the structural model for PVA–iodine complexes: Zwick et al. proposed the so-called helix model in which a polyiodide ion was surrounded by a helical PVA chain [4]. In contrast, Tebelv et al. suggested an aggregation model composed of some parallel-oriented PVA chains [5]. By studying of syndiotactic PVA, Matsuzawa et al. proposed that the complexes are produced by the incorporation of polyiodides into aggregates of the syndiotactic sequences [6]. Yang and Horii proposed the hexagonal aggregation model by high-resolution solid-state ^{13}C NMR analyses of PVA–iodine complex gels prepared from concentrated PVA aqueous solutions [7].

Miyasaka et al. proposed a more detailed model, based on their experimental results of the PVA films soaked in I_2/KI solutions. In their model, complexes formed in the noncrystalline phase have such a structure that a linear polyiodide I_3^- or I_5^- ion is surrounded by four syndiotactic PVA segments having an extended chain conformation [8]. They also proposed another model associated with the crystalline phase in the case of the high iodine concentrations [9].

Although several studies have been conducted on PVA–iodine complexes [10–12], there still remain many discrepancies among the previously proposed structural models. It is known that there are three steps in the preparation of a PVA polarizer containing PVA–iodine complexes: soaking the films in the I_2/KI aqueous solution, uniaxially drawing them, and adding boric acid. However, few studies have been conducted on PVA–iodine complexes in the presence of boric acid in the soaking media. Since cross-linking

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occurs between PVA and boric acid [13–16], a phenomenological interpretation of the role of boric acid may be that the PVA–iodine complexes will be stabilized by cross-linking with boric acid [4,17]. However, there is no systematic investigation to confirm the role of boric acid in the stabilization of the PVA–iodine or determine its previously unknown role in stabilization. It is, therefore, very important to understand the effect of boric acid on the formation of the PVA–iodine complexes by also considering other important factors related to the preparation of the PVA polarizer.

The purpose of this study is to elucidate the actual role of boric acid in the formation of the complexes. To this end, the structural analyses are carried out mainly by the wide-angle X-ray diffractometry (WAXD) and high-resolution solid-state ^{13}C NMR spectroscopy of undrawn PVA films prepared by soaking in different aqueous solutions containing compounds that closely affect the formation of the complexes.

2. Experimental

2.1. Samples

Commercially available PVA films having a thickness of 75 μm, produced by Kuraray Co. Ltd., were used in this study. The degrees of polymerization and saponification were 2400 and greater than 99 mol%, respectively. I_2, KI, and boric acid of reagent grade were used as received from Wako Chemicals.

2.2. Treatment of the PVA films

Three types of undrawn PVA films were prepared by treatment with different aqueous solutions. The concentrations of components in the respective solutions are $[I_2] = 0.04$ wt%/[KI] = 4 wt%, [KI] = 4 wt%/$[B(OH)_3] = 4$ wt%, and $[I_2] = 0.04$ wt%/[KI] = 4 wt%/$[B(OH)_3] = 4$ wt% and their solution codes are represented as I_2/KI, KI/$B(OH)_3$, and I_2/KI/$B(OH)_3$ in this paper, respectively. The films were pre-swollen in distilled water at 30 °C for 30 s and then soaked in the respective aqueous solutions at 30 °C for 150 s. Water-swollen films were also prepared in a similar manner as reference films. Finally, for subsequent experiments, all the films were dried in an oven at 50 °C for 4 min under a normal pressure. The codes of the films thus obtained are summarized in Table 1.

2.3. Ultraviolet and visible (UV–vis) absorption spectra

The UV–vis absorption spectra of the films were recorded in a wavelength range of 200–900 nm by a Shimazu UV-2500PC having a light-path length of 1 cm.

2.4. Wide-angle X-ray diffraction (WAXD) measurements

WAXD patterns were measured at room temperature over the range $2\theta = 5$–40° by a 2D-PSPC on a Bruker D8 DISCOVER. The X-ray source was Ni-filtered Cu Kα radiation that was generated at 40 kV and 110 mA and monochromatized with a graphite monochromator. WAXD profiles were obtained by scanning the intensities along the equatorial axis on the WAXD patterns. In the measurements of never-dried PVA films after treatment with different aqueous solutions, the respective films were covered with aluminum foils having a thickness of 7 μm to protect them from drying.

Table 1
PVA films prepared by soaking in different aqueous solutions.

Sample code	Solution code	Solution composition/wt%		
		I_2	KI	$B(OH)_3$
FW	W	0	0	0
FIK	I_2/KI	0.04	4.0	0
FKB	KI/$B(OH)_3$	0	4.0	4.0
FIKB	I_2/KI/$B(OH)_3$	0.04	4.0	4.0

2.5. High-resolution solid-state ^{13}C NMR spectroscopy

Cross-polarization/magic angle spinning (CP/MAS) ^{13}C NMR spectroscopy was carried out at room temperature on a Chemagnetics CMX-200 operating at a static magnetic field of 4.7 T. The ^{1}H radio frequency field strength $\gamma B_1/2\pi$ was 60 kHz in the CP and dipolar decoupling processes. Here, γ is the gyromagnetic ratio and B_1 is the amplitude of the rotating magnetic field. The CP contact time and MAS rate were set to 0.8 s and 3.5 kHz, respectively. Each sample was dried in a vacuum oven at 50 °C for 2 days to remove residual water, packed into a 7 mm cylinder-type MAS rotor, and dried at 50 °C for 1 day. Here, the MAS rotor with an O-ring seal [7,18–21], was used to keep the samples dry during the NMR measurements.

^{13}C chemical shifts relative to tetramethylsilane ($(CH_3)_4Si$) were determined by the CH_3 line at 17.36 ppm of hexamethylbenzene crystals as an external reference. The CPT1 pulse sequence was used to measure ^{13}C spin–lattice relaxation times (T_{1C}) [22].

3. Results

3.1. UV–vis absorption spectrum

Fig. 1 shows the UV–vis absorption spectra of the PVA films soaked in different aqueous solutions.

In the spectrum of FIKB, five absorption peaks appear at approximately 200, 290, 360, 470, and 600 nm, which are assigned to the I^-, I_3^-, $I_2 \cdot I_3^-$, I_3^-, and I_5^- ions, respectively. The first three peaks were confirmed by the experiment on PVA dissolved in I_2/KI solution [23], and the last two peaks are attributed to the formation of the PVA–iodine complexes [24–26]. The spectra of the films (FIK and FKB) soaked in I_2/KI and KI/$B(OH)_3$ aqueous solutions show no peaks at approximately 470 and 600 nm, clearly indicating that boric acid is necessary for the formation of the PVA–iodine complexes in I_2/KI solutions. This is one of the most important

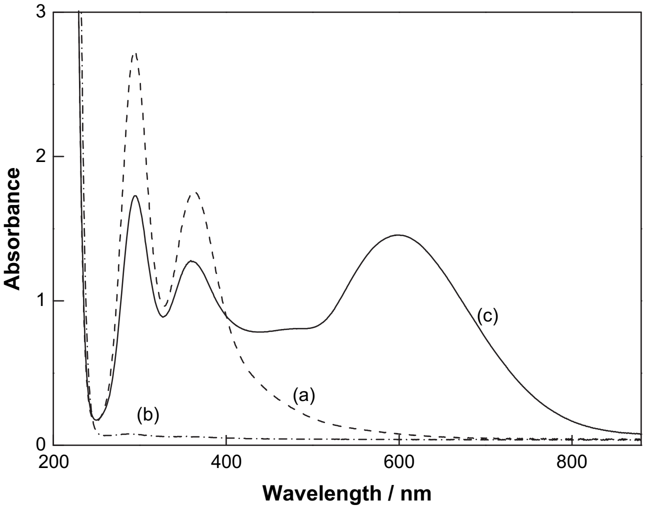

Fig. 1. UV–vis absorption spectra of PVA films soaked in different solutions: (a) FIK, (b) FKB, and (c) FIKB.

conditions required for the formation of the complexes in the films at relatively low I_2 concentrations because the complexes are actually formed in concentrated PVA/I_2/KI solutions even without the presence of boric acid [7].

3.2. WAXD profiles

Fig. 2 shows the WAXD profiles of the films that were soaked in different solutions and then dried.

The diffraction peaks around $2\theta = 11°$, 20° and 23° are assigned to the (100), (10)/(110), and (200) planes of the PVA crystals [27]. The FIK spectrum shows almost the same profile as that of the FW spectrum, indicating that the PVA crystallites are not affected by the addition of I_2 and KI to the swelling medium. In contrast, each peak of FKB and FIKB (I_2/KI/$B(OH)_3$), which were treated with media containing boric acid, becomes broader than those of FW and FIK. Such broadening indicates that the crystallite sizes perpendicular to the chain axis may become smaller by the addition of boric acid in the swelling media.

In order to elucidate the effect of boric acid in the swelling media on the crystallinity, the WAXD profiles of the PVA films without drying after the treatments with different solutions, were also measured, as shown in Fig. 3. The atomic scattering factor of the B atom is sufficiently lower than the factors of carbon and oxygen. Moreover, the concentration of boric acid is as low as about 10 mol% against monomer units of PVA. Therefore, the effect of boric acid on the WAXD intensity is negligibly small under our experimental conditions. FW and FIK show weak and broad diffraction peaks; therefore, the broad diffraction from water is also observed at approximately 26°. Since the corresponding dried films show larger and narrower peaks after drying, as observed in Fig. 2, partial dissolution and re-crystallization of the crystallites occur during the swelling and drying processes, respectively. That is, small crystallites and surficial parts of larger crystallites may be preferentially dissolved and re-crystallized in these processes.

In contrast, such significant differences in the intensity and width cannot be observed between the undried and dried films (FKB and FIKB) that were treated in the media containing boric acid. This indicates that re-crystallization during the drying process may be suppressed by cross-linking with boric acid irrespective of the addition of I_2.

In addition, it should be noted here that the diffraction intensities are much higher for FKB and FIKB than for FW and FIK as seen in Fig. 3. Since experimental conditions affecting the diffraction intensities are not appreciably different for these samples, this cause may be that boric acid also suppresses further partial dissolution during the treatments with aqueous solutions containing boric acid after pre-swelling while it occurs without boric acid for FW and FIK.

3.3. CP/MAS ^{13}C NMR spectra

Fig. 4 shows the CP/MAS ^{13}C NMR spectra of the PVA films dried after soaking in different aqueous solutions. It is well known that the CH resonance lines of these samples also split into three lines, lines I′, II′, and III′, which are mainly composed of contributions from lines I, II, and III in the spectra of the crystalline component. These latter three lines are assigned to the CH carbons that are associated with two, one, and no intramolecular hydrogen bond(s), respectively, in the triad sequences with the all-*trans* conformation

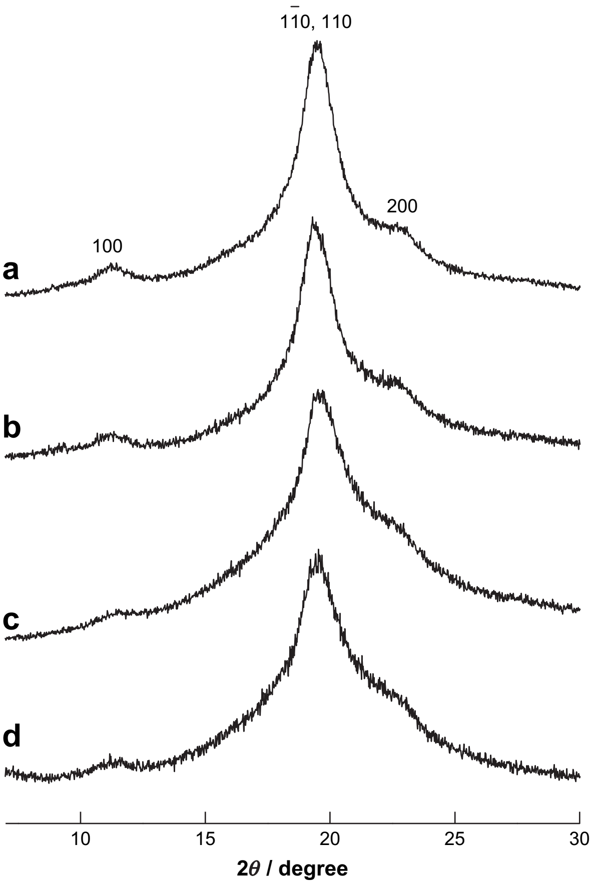

Fig. 2. WAXD profiles of PVA films soaked in different solutions: (a) FW, (b) FIK, (c) FKB, and (d) FIKB.

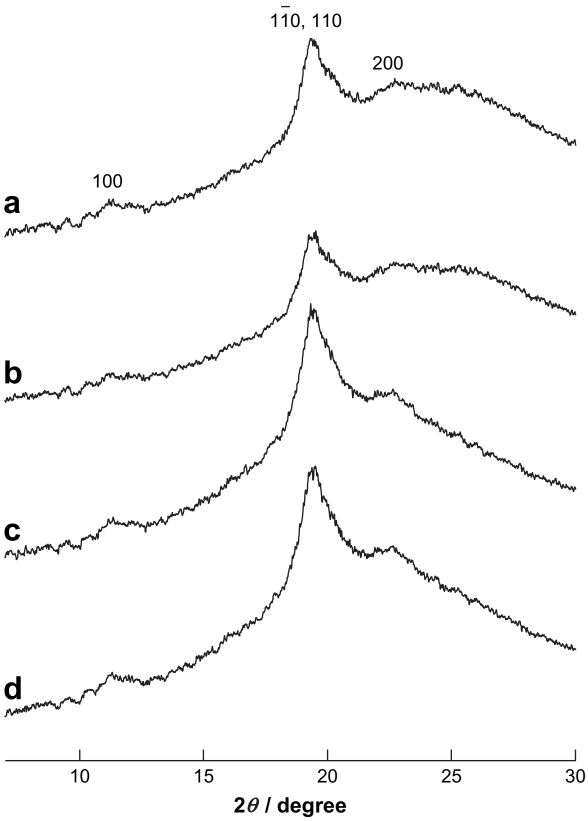

Fig. 3. WAXD profiles of never-dried PVA films soaked in different solutions: (a) FW, (b) FIK, (c) FKB, and (d) FIKB.

for PVA [7,18–21]. In the case of dried solid PVA, the CP signal intensity depends mainly on the mole fraction of each component at room temperature, which is fully below T_g, because molecular motion is highly restricted in both noncrystalline and crystalline regions [18]. The relative intensities of line III′ for FKB and FIKB, which are soaked in the solutions containing boric acid, are appreciably reduced as compared to those of FW and FIK, primarily because of the increase in the intensity for line II′. Moreover, a slightly broader tailing of the CH_2 resonance line is observed at the upfield side for FKB and FIKB.

3.4. ^{13}C spin–lattice relaxation times

In order to obtain detailed information on components having different chain mobilities in the films, the T_{1C} relaxation behavior of these samples was measured at room temperature using the CPT1 pulse sequence [22]. Logarithmic peak intensities of the CH and CH_2 resonance lines were plotted against the decay time τ of the longitudinal relaxation for each sample. Fig. 5 shows two examples of the plots for line II′ for FW and FIKB.

In this figure, the solid circles indicate the experimental points. The least-square fittings using a computer clearly reveal that both decays can be satisfactorily described as a linear combination of two exponentials having different T_{1C} values. While the smaller T_{1C} component can be assigned to the noncrystalline component, the larger T_{1C} component cannot simply be ascribed to the crystalline component because this component contains some amount of *gauche* conformation, which is discussed later. In this study, therefore, the smaller and larger T_{1C} components should be termed as the mobile and less mobile components, respectively. Two similar components were obtained in the other lines for different films, and their T_{1C} values are summarized in Table 2.

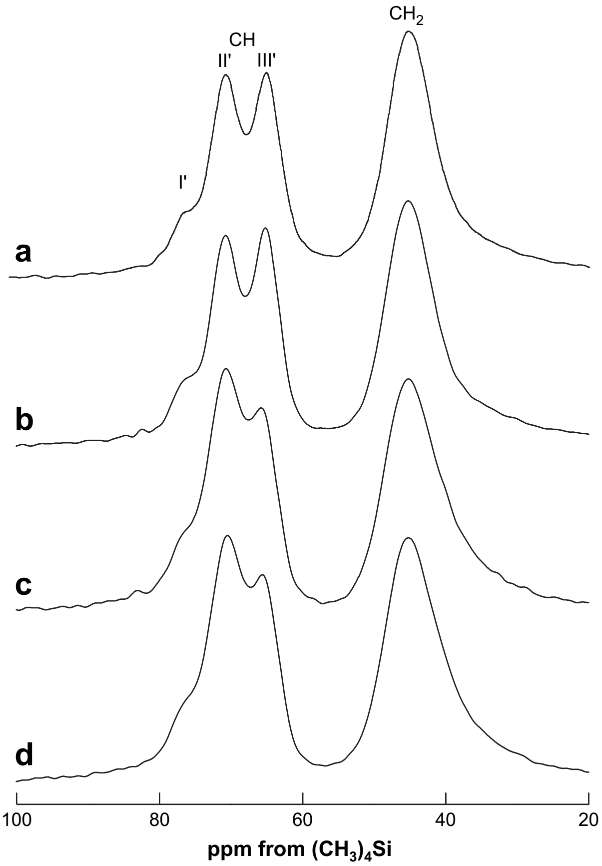

Fig. 4. CP/MAS ^{13}C NMR spectra of PVA films soaked in different solutions: (a) FW, (b) FIK, (c) FKB, and (d) FIKB.

The fraction of the less mobile component, which was obtained from the peak intensity by the T_{1C} analysis, is also shown for each sample as a simple reference. Significant increases in the T_{1C} values are observed for both the components in the films treated with IK, KB, or IKB, suggesting the reduction in the chain mobility due to the existence of boric acid or iodine in the soaking media. In particular, the T_{1C} value of line II′ for FIKB is the largest, suggesting the occurrence of some specific interaction in this part, probably with boric acid and PVA–iodine complexes. The apparent fractions of the less mobile component, which were estimated from the peak intensities by the T_{1C} analysis, are also appreciably increased by the addition of boric acid regardless of the addition of I_2 as seen for FKB and FIKB. Such increases are not attributed to the increase in the degree of crystallization because no significant changes were recognized in the WAXD profiles of FKB and FIKB. This fact also indicates that the larger T_{1C} component contains the noncrystalline component that is highly restricted in chain mobility.

3.5. Spectra of the less mobile and mobile components

As shown in Table 2, the difference between the T_{1C} values of the less mobile and mobile components is sufficiently large to

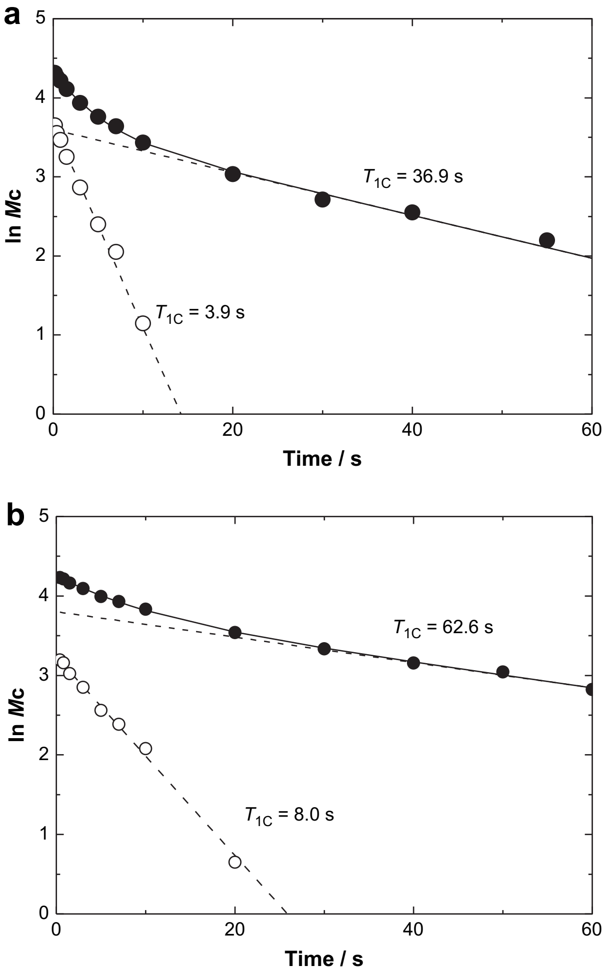

Fig. 5. ^{13}C spin–lattice relaxation behavior for line II′ for films soaked in different solutions: (a) FW and (b) FIKB.

Table 2
^{13}C spin-lattice relaxation times (T_{1C}) of PVA films soaked in different solutions.

Sample	T_{1C}/s							
	CH						CH_2	
	I′		II′		III′			
FW	33.5 (0.49)	4.2	36.9 (0.48)	3.9	44.5 (0.46)	4.9	36.6 (0.52)	2.9
FIK	41.6 (0.58)	4.4	43.0 (0.59)	5.5	49.3 (0.59)	6.5	49.2 (0.52)	5.3
FKB	–[a]	–[a]	48.1 (0.73)	3.6	52.0 (0.73)	5.5	47.8 (0.69)	4.8
FIKB	–[a]	–[a]	62.6 (0.64)	8.0	49.6 (0.77)	4.5	48.1 (0.71)	4.8

The values in parentheses are the fractions of the components of the larger T_{1C} values.
[a] Not estimated because of low spectral resolution.

separately record the spectra of these components by techniques that have been previously reported [7,18–21]. Figs. 6 and 7 show the CP/MAS ^{13}C NMR spectra of the less mobile and mobile components, respectively, recorded for the films soaked in different solutions. Here, the former spectra were measured at $\tau = 50$ s by the CPT1 pulse sequence [22] and the latter spectra were obtained by subtracting the former spectra from the corresponding CP/MAS spectra that are shown in Fig. 4. Lines I_L–III_L and I_M–III_M are, respectively, shown for the three peaks of the CH resonance lines in the spectra of the less mobile and mobile components simply to discriminate among these peaks. There is no significant difference between the spectra of the less mobile components of FW and FIK. This indicates that iodine ions I^-, I_3^-, and $I_2{\cdot}I_3^-$ do not appreciably affect the hydrogen bonds in the less mobile component, including the crystalline component, of FIK. In contrast, line III_M of the mobile component, which is mainly attributed to the CH carbons associated with intermolecular hydrogen bonding, is smaller than that of FW, as shown in Fig. 7, suggesting possible breaks in the intermolecular hydrogen bonding by iodine in the mobile component. In the cases of the films (FKB and FIKB) treated with aqueous solutions containing boric acid, the relative intensities of line II_L in the less mobile component are more enhanced than those of FW and FIK. Further, the upfield tailing of the CH_2 resonance line is more prominent in the case of FKB and FIKB. These results may be due to some effect of boric acid on the structure of the less mobile component, which will be evaluated below by conducting the lineshape analysis of the CH_2 resonance lines for all samples used here.

3.6. Lineshape analysis of the CH_2 resonance lines

The broad upfield tailing of the CH_2 resonance lines observed in Fig. 6 is attributed to the so-called γ-*gauche* effect induced by the introduction of the *gauche* conformations to the component [28]. When the downfield shift of this effect is assumed to be 5.2 ppm, two lines appear at $\delta_t - 5.2$ and $\delta_t - 10.4$ ppm due to the existence of

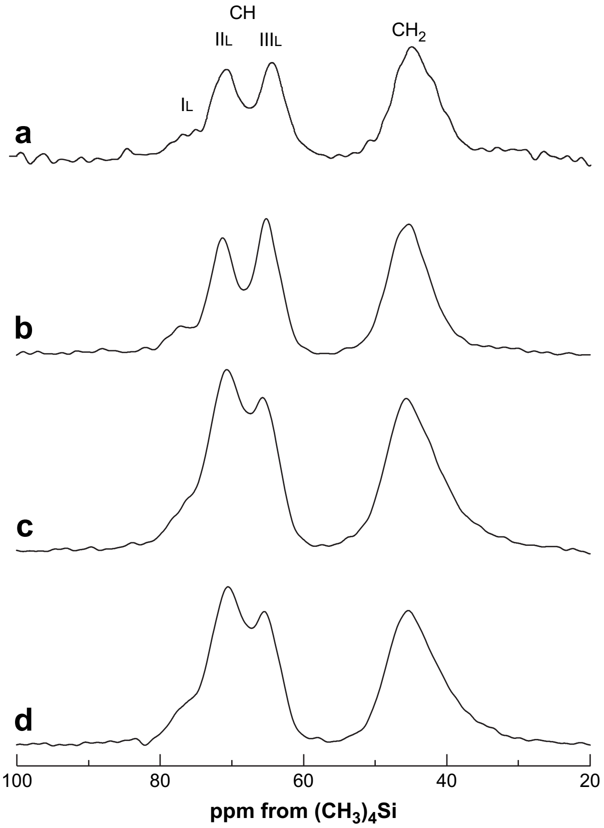

Fig. 6. CP/MAS ^{13}C NMR spectra of less mobile components, selectively recorded for different films soaked in different solutions: (a) FW, (b) FIK, (c) FKB, and (d) FIKB.

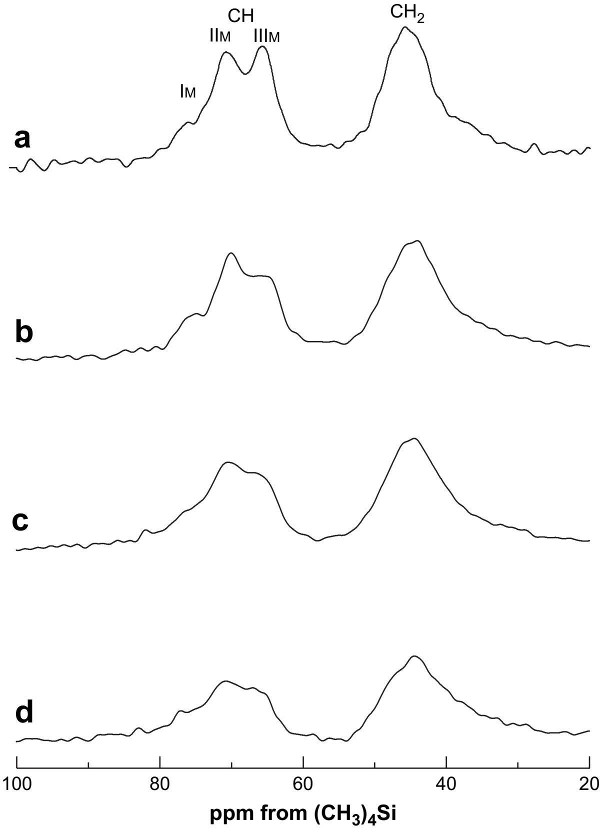

Fig. 7. CP/MAS ^{13}C NMR spectra of mobile components, selectively recorded for different films soaked in different solutions: (a) FW, (b) FIK, (c) FKB, and (d) FIKB.

one and two γ-carbon(s), respectively, at the *gauche* position along each chain [19,29]. Here, δ_t denotes the chemical shift of the CH_2 carbons in the all-*trans* sequences without the γ-*gauche* effect. By considering these resonance lines, the CH_2 lines of the less mobile and mobile components of different PVA films effectively resolve into three Gaussian contributions, lines 1–3 in the order of decreasing chemical shift. The results of the Gaussian contributions of the less mobile components of FW and FKIB are shown in Fig. 8 as representative examples. The fractions (f_t) of the *trans* conformation thus obtained for different components of the PVA films soaked in different solutions are summarized in Table 3. We observe that the f_t value of the less mobile component of FW is as low as 0.93 although this value is 1.0 for the crystalline component of PVA.

This indicates that the less mobile component of FW should be composed of not only the crystalline component with the all-*trans* conformation but also conformationally disordered sequences containing the *gauche* conformations. Such a structure may be formed by the insufficient phase separation into crystalline and noncrystalline phases induced during the preparation of the films. Un-annealed PVA films prepared by casting from the aqueous solution were also found to contain the less mobile component; however, this component completely transformed into a crystalline component after annealing at 180 °C, probably as a result of the improvement over the phase separation into the crystalline and noncrystalline phases [29].

Table 3
Fractions (f_t) of the *trans* conformation for different components of PVA films soaked in different solutions.

Sample	f_t	
	Less mobile component	Mobile component
FW	0.93	0.80
FIK	0.93	0.81
FKB	0.83	0.80
FIKB	0.83	0.80

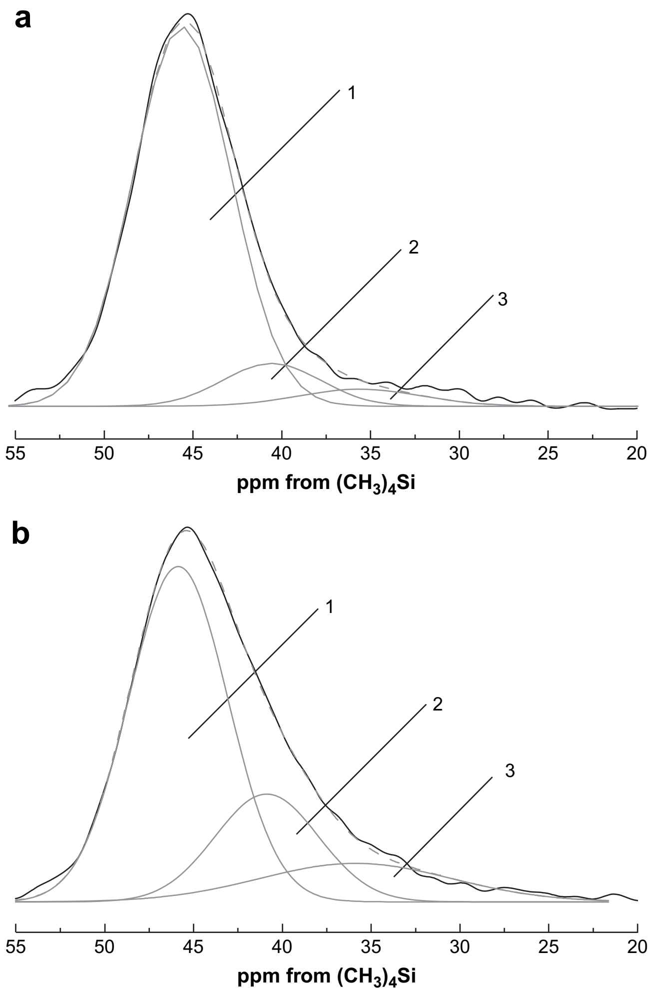

Fig. 8. Lineshape analyses of less mobile components of CH_2 resonance lines for the PVA films soaked in different solutions: (a) FW and (b) FIKB.

The f_t values of the less mobile and mobile components do not appear to change even by treatment with an aqueous solution not containing boric acid, as observed for FIK in Table 3; however, the f_t value of the less mobile component appreciably decrease to 0.83 for FKB and FIKB. This fact suggests that more disordered components containing higher *gauche* contents may be produced as less mobile components when the film is soaked in an aqueous solution containing boric acid although no significant change appears in the mobile components.

4. Discussion

Our discussion mainly focuses on the role of boric acid in the process of soaking the PVA films in aqueous iodine solutions.

The first step is the pre-swelling of the films in water. As shown by the WAXD profiles of FW in Figs. 2 and 3, partial dissolution of the smaller crystallites and the surficial parts of the larger crystallites occurs when the films are pre-soaked in water. The insufficient phase separation into the crystalline and noncrystalline phases may induce such partial dissolution in the un-annealed PVA films. In fact, WAXD profiles revealed no occurrence of significant partial dissolution by pre-swelling with water for the PVA films annealed at 180 °C for 30 min, suggesting the improvement of the phase separation by annealing [30].

After pre-swelling in the water, the films are soaked in the I_2/KI aqueous solution with or without boric acid and dried at 50 °C in an oven. Boric acid is found to suppress the re-crystallization of the dissolved PVA chains during the drying process irrespective of the presence of iodine. However, the PVA–iodine complexes were formed only when boric acid was present in the soaking media. The CP/MAS ^{13}C NMR measurements revealed that the chain mobility of the less mobile component, which contains the crystalline and noncrystalline components having molecular mobility similar to those of the crystalline component, is significantly restricted by boric acid, and its fraction also appears to increase considerably. Additionally, some amount of intermolecular hydrogen bonding of this component is broken by water; therefore, intramolecular hydrogen bonds are formed in appropriate sequences together with cross-linking with boric acid.

When boric acid diffuses into the area formed by partial dissolution, cross-linking occurs among the PVA chains as the cases of PVA solutions [13–16]. Such cross-linking appears to suppress the re-crystallization of the PVA chains during the drying process irrespective of the presence of iodine. In the presence of iodine along with boric acid, the PVA–iodine complexes are formed probably owing to the cross-linking by boric acid and resulting reduction in molecular mobility of PVA chains as indicated by the T_{1C} measurements. In contrast, when the concentration of iodine in the PVA solution is high, PVA–iodine complexes are formed even in the absence of boric acid [7]. Therefore, some effect of the concentration of iodine in the PVA solution may appear by the cross-linking with boric acid, which may be preferable for the formation of PVA–iodine complexes. In particular, such an effect will be more pronounced in PVA chains that are partially dissolved in the surficial areas of the crystallites by the pre-swelling with water. Moreover, the PVA–iodine complexes thus formed may be highly oriented on the surface of the crystallites. The reduction in the molecular mobility of the PVA chains by cross-linking may also promote the formation of PVA–iodine complexes in the surficial areas of the crystallites. This assumption is supported by a previous finding that PVA–iodine complexes can be formed only at low temperatures [26].

In a previous study, the solid-state ^{13}C NMR analysis revealed that PVA–iodine complexes are composed of PVA segments having *trans*-rich conformations probably surrounding the I_3^- and I_5^- ions in the gels prepared from concentrated PVA solutions [7]. In this study, such *trans*-rich segments may be preferably produced from the partially dissolved chains in the surficial areas of the crystallites under the condition of soaking of the PVA films. By considering this point of view, partially dissolved chains appear capable of fulfilling the requirements for forming PVA–iodine complexes. However, it is too early to propose the structure model among boric acid, iodine, and PVA. We will propose a new structure model in our next paper for the drawn PVA films since similar characterization reveals that the oriented noncrystalline chains also produced by the suppression of drawing-induced crystallization through cross-linking with boric acid contribute to the formation of the PVA–iodine complexes.

5. Conclusions

The role of boric acid in the formation of PVA–iodine complexes in PVA films was investigated mainly by WAXD and solid-state ^{13}C NMR spectroscopy, and the following conclusions were obtained:

(1) Boric acid is necessary for the formation of PVA–iodine complexes in undrawn films when they are treated with I_2/KI aqueous solutions at relatively low I_2 concentrations.
(2) Boric acid suppresses the re-crystallization of the PVA chains in the drying process and the reduction in the molecular mobility of the PVA chains, probably due to cross-linking among PVA chains which are produced by the partial dissolution of smaller crystallites and the surficial parts of larger crystallites when the films are pre-swollen with water.
(3) Boric acid may promote the formation of PVA–iodine complexes, particularly in the surficial areas of crystallites, which are produced by partial dissolution in the pre-swelling process with water, probably by reducing the molecular mobility of the PVA chains by causing cross-linking among them.

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