

# Clarification of Cross-Linkage Structure in Boric Acid Doped Poly(vinyl alcohol) and Its Model Compound As Studied by an Organized Combination of X-ray Single-Crystal Structure Analysis, Raman Spectroscopy, and Density Functional Theoretical Calculation

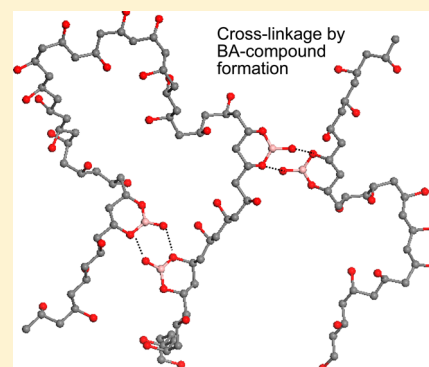
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## S Supporting Information

**ABSTRACT:** When boric acid (BA) is added to poly(vinyl alcohol) (PVA), a chemical reaction occurs to form the cross-linkages between the amorphous PVA chains. The local structural change caused by this reaction has been clarified concretely from the microscopic level on the basis of the X-ray-analyzed crystal structure, Raman spectra, and *ab initio* density functional theory using a model compound produced by the reaction between pentanediol (PENT) and boric acid (PENT–BA). The PENT–BA compound was found to take the TT and TG conformations in the methylene segmental parts depending on the stereoregularity of the PENT molecule itself, *meso* and *racemo* configurations, respectively. These two conformations give the Raman bands at the different positions. By comparison of the Raman spectra between the PVA–BA and PENT–BA model compounds, the local structures of PVA chains connected to BA molecules have been derived concretely: the syndiotactic PVA parts in the amorphous region form the TG-type ring structure with the 3-coordinate boron atom, where T and G are trans and gauche conformers, respectively. On the other hand, the isotactic PVA part takes the TT conformation when it forms a ring with boron atom. The thus-created rings are hydrogen-bonded to form a dimer, which plays a role as cross-linkage between the neighboring PVA chain segments in the amorphous region.



## ■ INTRODUCTION

Poly(vinyl alcohol) (PVA)–iodine complex is a typical optical polarizer used for liquid-crystal displays, sunglasses, polarization microscopes, and so on.<sup>1,2</sup> In the actual manufacture of polarizer, boric acid (B(OH)<sub>3</sub>, BA) is added to PVA film so that the iodine complex becomes thermally more stable and the optical and mechanical properties are greatly improved.<sup>3–6</sup> In this way, the addition of BA is indispensable for the actual usage of polarizer, but the concrete role of BA has not yet been clarified well. The PVA chains were speculated to be linked with BA to form the covalently bonded ring compound.<sup>7,8</sup> But there are various types of ring structure as illustrated in Figure 1.<sup>9–11</sup> For example, in Figure 1b the PVA chain is connected with 4-coordinate boron atom, which was reported to be formed when PVA was mixed with an aqueous borax solution.<sup>11</sup> In the case of Figure 1c, the PVA chain is linked with 3-coordinate boron atom. Figure 1d,e shows the cross-linked structures between the two neighboring PVA chains via the 4-coordinate boron atoms. However, it is difficult to determine which structure model is the most appropriate for the description of the local structure of PVA–BA the compound.

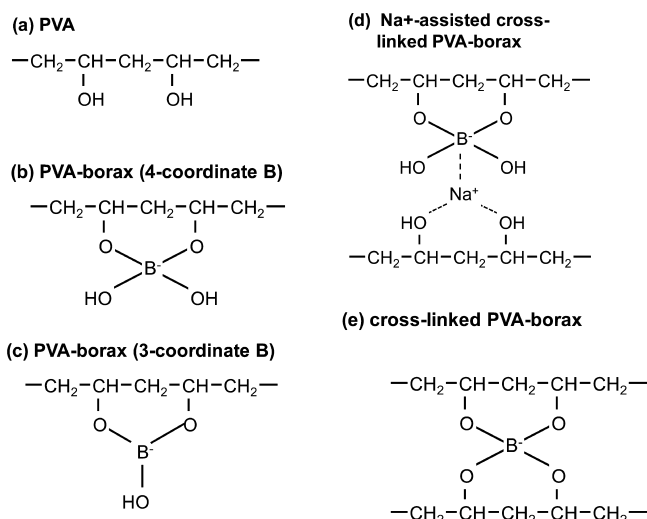
The usage of a model compound should be useful for this purpose. On the basis of the X-ray diffraction method,

Kuribayashi et al. reported the crystal structure of the BA compound with pentanediol (CH<sub>3</sub>–CH(OH)–CH<sub>2</sub>–CH(OH)–CH<sub>3</sub>, PENT) as a model of the PVA–BA system,<sup>12</sup> in which a boron atom forms the 3-coordinate structure with PENT molecule as shown in Figure 2c. This structure had been used without any doubt for a long time in the discussion of PVA–BA cross-linkages. However, we must notice here that the PENT compound with BA exists in the two kinds of polymorph: the monoclinic and orthorhombic forms,<sup>12–15</sup> among which the monoclinic-type crystal was analyzed by Kuribayashi et al. as mentioned above.<sup>12</sup> No X-ray structure analysis had been conducted for the orthorhombic-type crystal. If the linkage mode between PENT and BA molecules is different between the orthorhombic and monoclinic forms, then the structural uniqueness used as the most plausible local structure model of PVA–BA compound system is lost, and it becomes unreliable to adapt the linkage mode proposed by Kuribayashi et al. as it is. We need first of all to clarify the structure of the PENT–BA linkage part in the orthorhombic

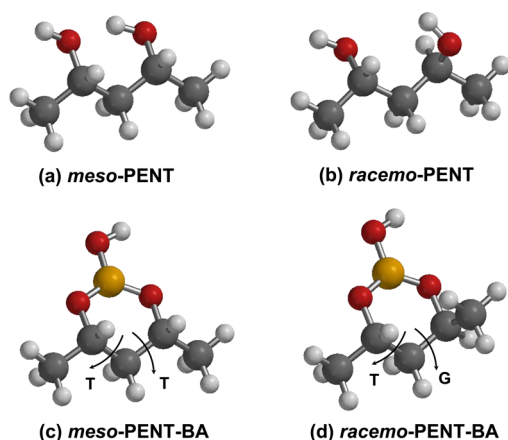
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**Figure 1.** Possible chemical structures of PVA–boric acid compound proposed in the literature.



**Figure 2.** Molecular structures of PENT and PENT–BA compounds: (a) *meso*-PENT, (b) *racemo*-PENT, (c) *meso*-PENT–BA compound, and (d) *racemo*-PENT–BA compound. The *racemo*-PENT molecule in the BA compound takes a TG conformation.

form and compare the structure between these two crystal forms. Then, for the first time, we may be able to discuss the local structure of the cross-linked part of the PVA–BA system with definite guarantee. In the first half of this paper, therefore, the X-ray structure analysis of the orthorhombic crystal form of PENT–BA compound will be reported to compare with that of the monoclinic-type crystal form.

At that stage, however, we have to ask again the direct applicability of the bonding mode found in the PENT–BA compound to the PVA–BA system without any doubt. If the X-ray structure analysis of the PVA–BA compound can be made successfully, then it will reveal the structure of the cross-linkage part. However, the cross-linkages are formed in the amorphous region of PVA–BA compound, and the X-ray diffraction signals are so broad and ambiguous making it actually impossible to know the local structure of PVA–BA linkage parts through the X-ray structure analysis. In such a sense, the usage of Raman spectral data might be rather useful for extracting the concrete local structure of the PVA–BA cross-linkage part. For this purpose, therefore, the correlation must be known at first between the Raman spectral data and the X-ray-analyzed structure of the PENT–BA model compound. The normal-

mode calculation will be useful in the assignment of the observed Raman peaks to the concrete structure. The second stage is to compare the Raman spectra measured for PVA–BA compound with that of the PENT–BA model compound, from which the local structure in the PVA–BA compound may be derived easily and reasonably.

In the present paper, therefore, we will report at first the crystal structure analysis of PENT–BA model compound, and second we will relate this structure to the Raman signals. On the basis of these information, the local structure of PVA–BA compound will be derived through the comparison of Raman spectra with that of the PENT–BA model compound. As mentioned above, the addition of BA to the PVA sample is important for the industrial manufacture of more mechanically and thermally tough polarizer. The clarification of the local cross-linked structure of PVA–BA will be helpful for the interpretation of the role of BA in the formation of PVA–iodine polarizer. For this purpose, the structure analysis must be made about the iodine complex of PVA, PVA–BVA, and the corresponding model compounds (PENT–iodine and PENT–BA–iodine complexes). But the structure analyses of these complexes have not yet been made successfully. Therefore, in the present paper, only the local structures of PVA–BA and PENT–BA will be discussed, and the study of a role in the iodine complex formation will be reported in a future report.

## EXPERIMENTAL SECTION

**Samples.** Pure *meso*-PENT could not be obtained commercially. So we purchased the mixture of *racemo*-PENT and *meso*-PENT from Wako Chemicals Co., Japan, the purity of which was 99%. The mixture of *racemo*- and *meso*-PENT was melted at 85 °C and mixed with BA powder. Cooling of this mixture down to room temperature gave a mixture of single crystals and sherbet-like substance. As known from the X-ray structure analysis to be described in a later section, these single crystals were of the orthorhombic-type crystal modification of *meso*-PENT–BA compound, different from the monoclinic-type crystal modification reported by Kuribayashi et al.<sup>12</sup> The sherbet-like substance was the *racemo*-PENT–BA compound, which was found to be crystallized below −40 °C. Unfortunately, a single crystal of this *racemo*-PENT–BA compound could not be obtained successfully in the present study. As another way, pure *racemo*-PENT was purchased from Wako Chemicals Co., which we tried to crystallize from the solution but the single crystal could not be obtained because of the same reason as mentioned above. PVA powder was supplied by Kuraray Co. Ltd., Japan. The degree of polymerization was 1700. Addition of a boric acid (BA) aqueous solution of 5 wt % concentration into PVA aqueous solution of 7.5 wt % concentration gave the precipitation of white gel of PVA–BA complex.

**Measurements.** X-ray structure analysis was performed for the orthorhombic-type *meso*-PENT–BA single crystal. The crystal was mounted on the goniometer head of an X-ray generator (Rigaku R-axis Rapid II). A graphite-monochromatized Mo K $\alpha$  line was used as an incident beam. The oscillation method was applied where the angle  $\omega$  was scanned with the oscillation range  $\Delta\omega$  5° at different  $\chi$  and  $\phi$  angles. The X-ray exposure time was 30 s for 1 frame of 2D X-ray diffraction pattern. The 10 700 reflections in total were collected from the 40 frames. The  $R_{\text{merge}}$  or the degree of agreement among the equivalent  $hkl$  reflections was 0.033.

Raman spectra were measured with a back-scattering mode using a Japan Spectroscopic Co. NRS-2100 spectrometer with an incident laser beam of 532 nm as an excitation light source. The resolution power was  $2.0\text{ cm}^{-1}$ .

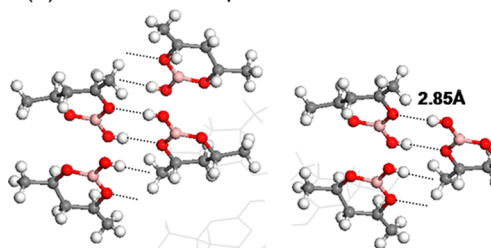
**X-ray Structure Analysis.** The crystal structure analysis was carried out by using a software Crystal Structure (Rigaku). The direct method was applied to find out the initial models necessary for the refinement of crystal structure by using an SIR92 software developed by Altomare et al.<sup>16</sup> Least-squares refinement was made on the basis of the full matrix method by using the quantity  $\sum w(|F_o|^2 - |F_c|^2)$  as a minimized function with weight  $w = 1$ . The reflections satisfying the data of  $|F_o| > 4\sigma(|F_o|)$  were used in the least-squares refinement of the structure model, where  $|F_o|$  and  $\sigma(|F_o|)$  were the observed structure factor and its standard deviation, respectively. The absorption correction for the observed intensity was made in the structural refinement. The reliability of the final structure was indicated by the reliability factors,  $R$  and  $R_w$  which are defined in the following equations:  $R = \sum ||F_o|^2 - |F_c|^2| / \sum |F_o|^2$  and  $R_w = [\sum (w||F_o|^2 - |F_c|^2|^2) / \sum w(|F_o|^2)^2]^{1/2}$ . In these equations,  $|F_c|^2$  is the square of the calculated structure factor and the summation was made over the observed  $hkl$  reflections. The weight  $w$  was 1.

**Quantum Chemical Calculation of Raman Spectra.** Quantum chemical calculation of Raman spectra was performed for a dimer of PENT–BA compounds using Gaussian03 (Gaussian Inc., USA), where density functional theory was applied with a functional B3LYP and basis function of 6-31G+ + (d, p). The structure model was optimized starting from the structure obtained by X-ray analysis. The vibrational frequency calculation was performed using a Hessian matrix.

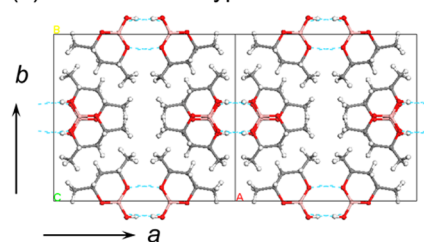
## RESULTS AND DISCUSSION

**1. Crystal Structure of the PENT–BA Compound.** As mentioned above, *meso*-PENT gives the two kinds of polymorphic crystals when it reacts with BA molecules. Kuribayashi et al. analyzed the monoclinic-type crystal structure, the unit cell parameters of which are  $a = 15.36 \pm 0.06\text{ Å}$ ,  $b = 13.53 \pm 0.02\text{ Å}$ ,  $c = 7.68 \pm 0.06\text{ Å}$ , and  $\beta = 113.3^\circ$  with the space group symmetry  $C2/c$ .<sup>12</sup> They prepared the monoclinic-type single crystals through the complicated processes starting from the mixture of *meso*-PENT with borax, where the 4-coordinate boron atom was reduced to 3-coordinate boron structure. In the present study, the *meso*-PENT was mixed directly with BA to get the orthorhombic-type crystal. The X-ray structure analysis revealed the unit cell parameters of  $a = 14.303 \pm 0.010\text{ Å}$ ,  $b = 13.119 \pm 0.009\text{ Å}$ , and  $c = 7.702 \pm 0.005\text{ Å}$ , and the space group was  $Pbcn$ . The crystal structures are shown in Figure 3. The atomic fractional coordinates, the anisotropic temperature factors, and the molecular geometries are shown in Table 1. The details of the structure analysis are shown in the Supporting Information. As shown in Figure 3, the two oxygen atoms of a PENT molecule are connected to the boron atom with the covalent bonds. Another oxygen atom is sticking out as the B–OH group. Thus, the boron atom was found to possess three chemical bonds with oxygen atoms or the 3-coordination structure, which is the same as the case of the monoclinic-type crystal form analyzed by Kuribayashi et al. The two PENT–BA molecules are connected by the intermolecular hydrogen bonds to form a dimer. However, the packing mode of these dimers inside the unit cell is different between the orthorhombic and monoclinic types as shown in Figure 3.

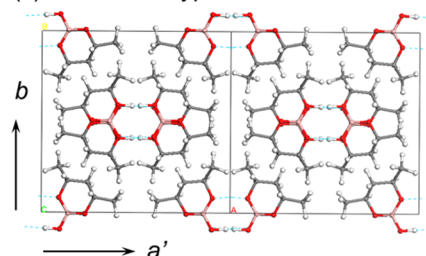
(a) PENT–BA Compound



(b) Orthorhombic-type



(c) Monoclinic-type



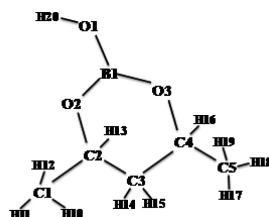
**Figure 3.** Crystal structures of the *meso*-PENT–BA complex: (a) molecular aggregation state, (b) the crystal structure of orthorhombic type revealed in the present study, and (c) the crystal structure of monoclinic type reported by Kuribayashi et al.<sup>12</sup>

**2. Raman Spectra of the Pentanediol/Boric Acid Compound.** The Raman spectra of *meso*-PENT and *meso*-PENT–BA compounds are shown in Figure 4 in the frequency region of  $550\text{--}900\text{ cm}^{-1}$ . The Raman spectra of *racemo* species are shown in Figure 5. As seen from these figures, the spectra are different between *meso*- and *racemo*-PENTs and also between PENTs and their BA compounds, making it possible to identify the compounds by the spectra. To assign these Raman bands, the molecular orbital calculation was performed for these species. In this case, we adopted the dimer shown in Figure 3 as an initial model, which was optimized energetically before the calculation of the vibrational spectra. As shown in Figures 4 and 5, the thus-calculated Raman spectra are in relatively good agreement with the experimental data in the position and relative intensity of the peaks. In Figure 4, the *meso*-PENT exists in a liquid state at room temperature, and so the molecules may take the statistically random form between the *trans* (T) and *gauche* (G) forms. In fact, the observed Raman spectrum is an overlap of the spectra calculated for the *trans–trans* (TT) and *trans–gauche* (TG) conformational models. The PENT molecules in the *meso*-PENT–BA compound take the TT form as known from the X-ray structure analysis. Correspondingly, the Raman spectra calculated for the TT form of *meso*-PENT–BA compound reproduce the observed spectra well. The vibrational modes of some peaks are shown in Figure 6 for PENT and *meso*-PENT–BA complexes.

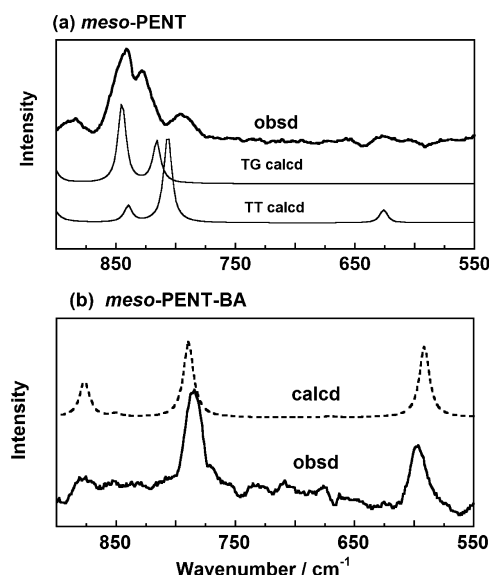
**Table 1. (a) Atomic Fractional Coordinates and Thermal Parameters of Orthorhombic-Type *meso*-PENT–BA Compound, and (b) Molecular Geometries of PENT–BA Compound<sup>a</sup>**

(a) Atomic Fractional Coordinates and Thermal Parameters of Orthorhombic-Type <i>meso</i> -PENT–BA Compound						
atoms	<i>x</i>		<i>y</i>		<i>z</i>	<i>U</i> <sub>iso</sub>
O(1)	0.0987(4)		0.5976(3)		0.5472(10)	0.104(2)
O(2)	0.0940(3)		0.4203(3)		0.5396(7)	0.099(2)
O(3)	0.2342(3)		0.5112(3)		0.6007(7)	0.111(2)
C(1)	0.0918(6)		0.2453(6)		0.527(2)	0.217(5)
C(2)	0.1412(6)		0.3217(6)		0.550(2)	0.202(6)
C(3)	0.2404(6)		0.3345(6)		0.5454(15)	0.143(4)
C(4)	0.2853(5)		0.4173(7)		0.6226(15)	0.147(4)
C(5)	0.3840(5)		0.4348(6)		0.6000(13)	0.160(4)
B(1)	0.1422(6)		0.5074(8)		0.5611(12)	0.082(3)
H(10)	0.0609		0.2228		0.6289	0.260
H(11)	0.1309		0.1924		0.4841	0.260
H(12)	0.0466		0.2624		0.4409	0.260
H(13)	0.1391		0.3169		0.6729	0.242
H(14)	0.2527		0.3435		0.4252	0.171
H(15)	0.2685		0.2729		0.5841	0.171
H(16)	0.2794		0.4022		0.7428	0.176
H(17)	0.3988		0.4254		0.4808	0.193
H(18)	0.4214		0.3905		0.6686	0.192
H(19)	0.3961		0.5034		0.6320	0.192
H(20)	0.047(3)		0.593(4)		0.530(9)	0.06(2)
(b) Molecular Geometries of PENT–BA Compound						
bond (Å)		angle (deg)		dihedral angle (deg)		
O1–B1	1.341	O1–B1–O2	120.14	O1–B1–O2–C2	178.40	
O2–B1	1.344	O1–B1–O3	115.92	O1–B1–O3–C4	178.31	
O3–B1	1.351	O2–B1–O3	123.93	C1–C2–O2–B1	−179.33	
O2–C2	1.461	B1–O2–C2	120.57	C1–C2–C3–C4	−160.77	
O3–C4	1.442	B1–O3–C4	119.22	C5–C4–O3–B1	158.82	
C1–C2	1.239	O2–C2–C3	110.69	C5–C4–C3–C2	−172.95	
C2–C3	1.429	O3–C4–C3	112.46			
C3–C4	1.395	C1–C2–C3	131.12			
C4–C5	1.441	C2–C3–C4	122.55			
		C3–C4–C5	121.58			

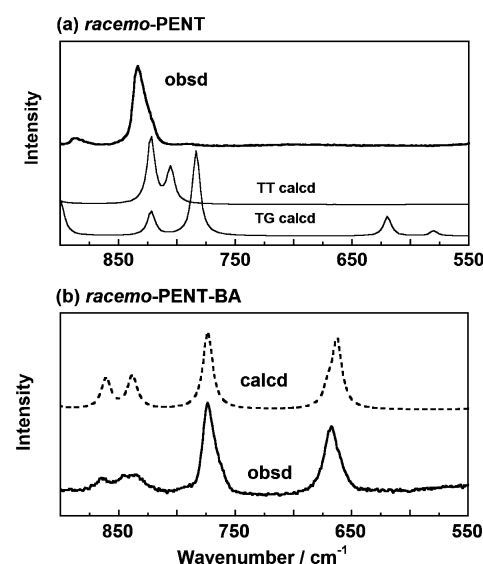
<sup>a</sup>Numbering of atoms is as below.



Not only the *meso*-PENT but also the *racemo*-PENT forms a compound with BA molecules. We have challenged to get the single crystals of *racemo*-PENT and *racemo*-PENT–BA from the solutions without any success. Then the molecular conformations were estimated on the basis of Raman spectral data given in Figure 5. The Raman spectra were calculated for the two possible models of *racemo*-PENT, i.e., TT and TG conformers. As compared in Figure 5, the agreement with the



**Figure 4.** Raman spectra of *meso*-PENT and its BA compound in comparison with the calculated spectra. The *meso*-PENT is found to consist of TT and TG forms in the liquid state at room temperature, while it takes TT form in the BA compound (refer to Figure 2c).

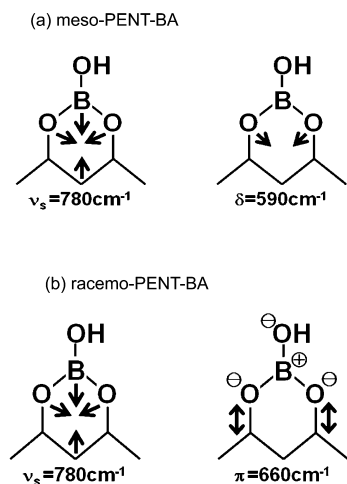


**Figure 5.** Raman spectra of *racemo*-PENT and its BA compound in comparison with the calculated spectra, where the *racemo*-PENT is found to take a TT conformation as known from the good correspondence of the calculated spectrum, while it takes TG form in the BA compound (refer to Figure 2d).

observed spectrum is better for the TT model in the frequency regions of 750–850 and 550–650 cm<sup>–1</sup>.

Now let us see the structure of *racemo*-PENT–BA. As pointed out in the previous section, the *meso*-PENT molecule takes a TT structure about the central two C–C skeletal bonds. In the case of *racemo*-PENT, the chain conformation in PENT–BA should take TG structure in order to form a pair of B–O–C linkages between *racemo*-PENT and BA molecules as shown in Figure 2d. This TG structure of the *racemo*-PENT molecule was energetically optimized to give the calculated Raman spectra in good agreement with the observed data, as reproduced in Figure 5b.



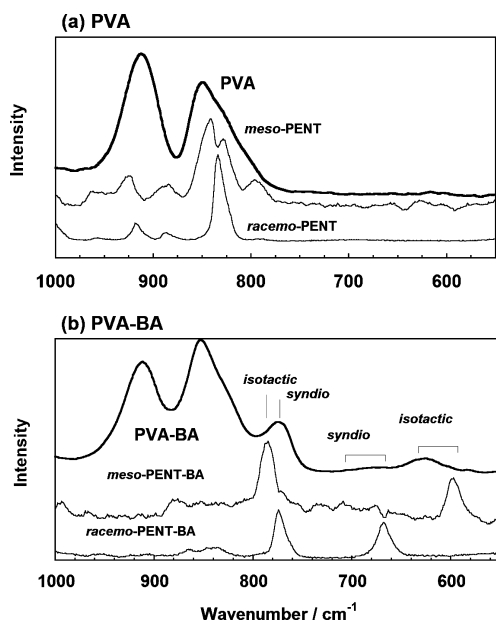


**Figure 6.** Vibrational modes corresponding to the Raman bands observed for the *meso*- and *racemo*-PENT-BA compounds shown in Figure 3.

In this way, when the PENT molecule reacts with BA and the ring structure is created with the BO-C linkages, the PENT molecule takes the TT and TG conformers depending on the *meso*- and *racemo*-optical isomers, respectively. As discussed in the preceding section, PENT molecule reacts with BA so that the two hydroxyl groups of BA can form a pair of BO-C linkages through the dehydration reaction. This information may be helpful for the deduction of the local structural change occurring in the reaction of PVA chains with BA as will be discussed in the next section.

### 3. Raman Spectra of the PVA/Boric Acid Compound.

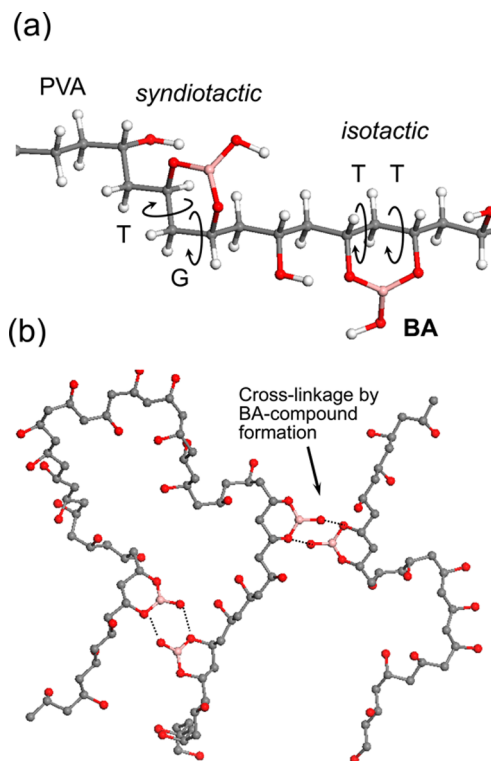
The Raman spectra measured for PVA and PVA-BA mixture are shown in Figure 7. The Raman spectrum of PVA may be approximated to consist of the spectra of *meso*- and *racemo*-PENT compounds, because the syndiotactic and isotactic sequences in atactic PVA chain correspond to *racemo* and *meso* forms, respectively. In fact, as seen in Figure 7a, the Raman



**Figure 7.** Raman spectra of PVA and its BA compound in comparison with those of the model compounds.

spectrum of PVA is coincident well with the overlapping of the spectra of *meso*- and *racemo*-PENT in the frequency region of 500–1000  $\text{cm}^{-1}$ . In this frequency region, the PVA shows the two strong bands at 910 and 850  $\text{cm}^{-1}$ , which are assigned to the C–O stretching and  $\text{CH}_2$  rocking mode, respectively.<sup>17</sup> Once the PVA sample was treated with BA, some new bands were detected to appear. For example, the new band at 630  $\text{cm}^{-1}$  may correspond to the 590  $\text{cm}^{-1}$  band observed for *meso*-PENT-BA, which is the borate ring mode including the CC bonds of TT conformation of *meso*-PENT molecule (see Figure 6a). In other words, the 630  $\text{cm}^{-1}$  Raman band of PVA-BA can be assigned to the BA compound formed on the isotactic (or *meso*) PVA segmental part. The 680  $\text{cm}^{-1}$  band is assigned to the borate ring mode of the CC bonds of TG type as seen in *racemo*-PENT molecule (Figure 6b). This band may be assigned to the BA compound of the syndiotactic (*racemo*) PVA chain part. The 780  $\text{cm}^{-1}$  band of PVA-BA corresponds to the overlap of the bands of *meso* and *racemo* compounds. The strong 850 and 918  $\text{cm}^{-1}$  bands are originated from the PVA itself.

These Raman spectral analyses allow us to derive the local structures as illustrated schematically in Figure 8. The



**Figure 8.** (a) Ring formations in the local parts of the PVA chain and (b) an illustration of the cross-linkage structure in the PVA amorphous chains.

syndiotactic PVA chain parts may form the ring structure of TG conformation with BA, and the isotactic PVA parts form the ring structure of TT conformation, as seen in Figure 8a. These rings are connected to each other through the hydrogen bonds and form dimers (see Figure 8b), which play a role as the cross-linkages between the neighboring PVA chains and can be predicted to give more tough property to PVA sample and PVA polarizer.

## ■ CONCLUSIONS

The X-ray structure analysis was performed for the *meso*-PENT–BA compound of orthorhombic type, clarifying the ring structure between PENT and BA molecules. The ring structure itself was found to be essentially the same between the orthorhombic and monoclinic forms. The PENT molecule takes two types of configuration, *meso* and *racemo* type. Depending on such a configuration, the molecular conformations (TT and TG) and the corresponding Raman bands of PENT were found remarkably different from each other. By comparing the Raman spectral data between PENT and PVA, the local structures of the PVA–BA parts existing in the amorphous region were derived concretely. An important point to be noticed is that the syndiotactic and isotactic monomer sequences in PVA chains take the conformations of TG and TT forms, respectively, as illustrated in Figure 8. As a result, the neighboring PVA chains in the amorphous region are cross-linked together via the formation of dimeric ring structure with the 3-coordinate boron atoms. These cross-linkages are considered to stabilize the PVA film and also the PVA–iodine complex in the polarizer.

So far, the PVA film had been known empirically to form the cross-linkages by addition of BA. However, we need to emphasize the uniqueness of the present study in such a point that the detailed and concrete structure of cross-linkage parts has been derived as illustrated in Figure 8 on the basis of the X-ray and Raman spectral data collected for the PENT–BA and PVA systems. The next problem to be solved is the reason why the PVA–iodine complex is stabilized when the cross-linkages are formed through the PVA–BA complexes.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The cif file of the X-ray crystal structure analysis of the orthorhombic form of *meso*-PENT–BA compound. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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