(Accepted February 7, 1997)

Spectroscopic Study of Ethylene Vinyl Alcohol Copolymer and Poly(vinyl alcohol)

Weigang Xu, Shigeo Asai, and Masao Sumita

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152, Japan.

Abstract : The assignments of FTIR and Raman spectra of poly(vinyl alcohol) (PVOH) and four ethylene vinyl alcohol (EVOH) copolymers 72, 59, 44, and 32mole% of ethylene group, has been performed by *in-situ* measurements and deconvolution analysis. By comparing with the spectra of high-density polyethylene, the bands in the region of $1000\sim1200\text{cm}^{-1}$ was classified into the C-C and C-O stretching vibrations. It was found that the C-C stretching vibration of PVOH and EVOH copolymers is affected significantly by disordered distribution of hydroxy group and crystallinity.

1. Introduction

The FTIR and Raman spectra of polyethylene (PE) (1,3) and poly(vinyl alcohol) (PVOH) (4,5) have been studied for many years. On the other hand, ethylene vinyl alcohol copolymer (EVOH) can not be understood well. Matsumoto et al. firstly reported the IR spectra of EVOH copolymers in the whole range of hydroxyl group concentration without showing assignments(6). Recently, Cooney et al. reported the Raman spectrum of EVOH copolymer and gave the assignments by using deuteration for EVOH32 (68 mole percent of hydroxyl group) copolymer(7), but not for the copolymers in the whole range of hydroxyl group concentration. The most interesting was the spectra in the region of $1000\sim1200\text{cm}^{-1}$. The bands in this region for PE were attributed to the C-C stretching vibrations, and those for PVOH were attributed to hydrogen bonded C-O stretching vibration. Therefore, in the case of EVOH copolymers, these bands should be overlapped seriously.

Even for PVOH, several different assignments still existed. It was difficult to complete the assignments only from IR spectrum of PVOH because some bands were inactive or weakly active in IR spectrum.

In the present study, FTIR, Raman and the *in-situ* measurements were carried out. The derivative and Fourier self-deconvolution spectra were used to discriminate peaks from overlapping bands and broad shoulders. The assignments of EVOH copolymers and PVOH were systematically investigated. In addition, the spectra of EVOH copolymers in the whole range of hydroxyl group concentration were measured to study the effect of hydroxyl group on C-C stretching vibration, and the effect of hydrogen bond on the C-O stretching vibration.

2. Experimental

2.1 Sample Preparation

Four kinds of EVOH copolymer with 72, 59, 44, 32 mole percent of ethylene group were labelled as EVOH72, EVOH59, EVOH44 and EVOH32 respectively. The pellets of the copolymers were kindly supplied by Kuraray Co. Ltd. High density polyethylene (HDPE) was a commercial product from Japan Oil Chemical Co. The HDPE and EVOH pellets were pressed into thin films by heating to 20°C above their melting points in a hot press, and then quenched in ice water.

For PVOH film, the 5 wt% aqueous solution of PVOH

was prepared by dissolving powder (Wako Chemical Co. Ltd.) in water at 100°C for 2 hours, then cast on a PMMA plate and dried at 25°C for 5 days.

2.2 Raman Spectroscopy

Raman spectra were examined by an NR-1800 Laser Raman Spectrophotometer, Japan Spectroscopic Co., Ltd. with a triple monochromator. The specimen was excited by a Coherent Innova 70 Argon ion laser in the 514.8 nm wavelength. The Raman scattering light was collected in back scattering geometry. The spectral slit width was 2 cm⁻¹.

In-situ Raman spectra during heating were obtained by loading a Mettler FP82HT hot stage (Mettler instrument AG) into the Raman instrument.

2.3 FTIR Spectroscopy

FTIR spectra were obtained by a JIR-6000 Fourier Transform Infrared Spectrometer, JEOL. Ltd., at a

resolution of 1 cm⁻¹.

In-situ FTIR spectra during heating were obtained by loading the Mettler FP82HT hot stage into microscopy system of FTIR instrument.

The accumulation numbers were more than 1000 scans in order to achieve sufficiently high signal to noise ratio for derivative calculation and Fourier self-deconvolution. The fourth order derivative and self-deconvolution spectra were mainly used for band detection. After the wavenumbers of overlapped spectra were located, the spectrum profiles were simulated by the least squared fitting method using Lorentzian and Gaussian line shape model.

Fig.1 shows the data analysis procedure to recognize peak and estimate integral intensity of FTIR band for EVOH59 copolymer.

3. Results and Discussion

The Raman spectra of PVOH, HDPE and EVOH copolymers in the region of 1000~1200 cm⁻¹ are shown in Fig.2(a). The FTIR spectra in the region of 800~1200 cm⁻¹ are shown in Fig.2(b). The bands recognized from fourth order derivative spectra are illustrated in Fig.3.

3.1 The C-C stretching vibration

The similarity of main-chain among HDPE, PVOH and EVOH copolymer results in the spectral similarity. Therefore, the C-C stretching vibration for PVOH and EVOH copolymers could be assigned by comparison with that in HDPE whose spectra has definite assignment already.

3.1.1 The C-C stretching vibration of HDPE

The vibrational spectrum of PE was most well studied among the polymers. The factor group analysis was successful to identify the normal modes for both infrared and Raman spectra.

In the region of 1000~1200 cm⁻¹ of Raman spectrum, 1131 cm⁻¹ and 1064 cm⁻¹ bands for HDPE are strongly active, and assigned to A_g symmetric and B_{1g} asymmetric C-C stretching vibrations respectively(2) (Table 1). According to the principle of mutual exclusion under the Born's cyclic boundary condition for polymers, the both bands are only active in Raman spectrum but inactive in IR spectrum. As the long sequence with trans conformation is not infinitely long, the bands are weakly active(3) in IR spectrum as shown

Fig. 1 The data analysis procedure to recognize peak and estimate integral intensity of FTIR spectra for EVOH59 copolymer. The bottom part: Fourier self-deconvolution spectrum. The middle part: second and forth order derivative spectra by Savitzky-Golay method. The top part: the experimental data was fitted by least square method to provide the integral intensity of the band.

Fig. 2 (a) The Raman spectra of PVOH, HDPE and EVOH copolymers in the region of $1000\sim1200\text{cm}^{-1}$.
(b) The FTIR spectra of PVOH, HDPE and EVOH copolymers in the region of $800\sim1200\text{cm}^{-1}$.

Fig. 3 The FTIR and Raman band shift of PVOH, HDPE and EVOH copolymers. The data were recognized from derivative curve.

in Fig.2(b).

The both C-C stretching vibrations were originated

Table 1 The assignments of Raman and IR spectra for HDPE and PVOH in literatures[1-5]. vvw : very very weak; vs : very strong; s : strong.

		C-C stretching vibration (cm^{-1})		C-O stretching vibration (cm^{-1})
		A _R symmetric mode	B _{IR} asymmetric mode	
HDPE	IR	1131 vvw	1064 vvw	
	Raman	1131 vs	1064 vs	
PVOH	IR	1144 s		1096 s
	Raman	1147 s	1072 s	1094 s

from long trans sequence in crystalline phase. Therefore, both bands of Raman spectrum disappear above the melting point while a new broad band at 1080cm^{-1} increases that was originated from disorder conformation. This property was applied to estimate the crystallinity and interphase between amorphous and crystalline phase proposed by Strobl[8].

3.1.2 The C-C stretching vibration of PVOH

Compared with HDPE, the assignments of PVOH were rather confused in literatures. The 1144cm^{-1} band of infrared spectrum was firstly assigned to C-O-C

stretching vibration by Krimm[1], then was assigned to C-C stretching vibration by Tadokoro[2]. The remained problem was that both the symmetric and asymmetric vibrations should be found in comparison with HDPE, and 1144cm^{-1} band should be assigned to one of them. The assignment proposed by Tadokoro should be proved directly via experiments. It seems that FTIR measurement is a suitable method to clarify the problem.

The 1144cm^{-1} was crystalline band. It decreased in swollen or melting state, and increased during annealing, which was used to characterize the crystallinity of PVOH proposed by Peppas[9].

3.1.3 The C-C stretching vibration of EVOH copolymers

Few research about EVOH copolymers was reported. Only the spectrum of EVOH32 copolymer was reported by Cooney et al.[7] recently. Compared with their results, the much more bands as shown in Fig.3 were found from the derivative spectra in the present experiment.

The band shifts of symmetric C-C stretching vibrations with variation of the concentration of hydroxyl group in the region of $1130\sim 1150\text{cm}^{-1}$ were observed clearly in both Fig.4. The band shifted 13cm^{-1}

Fig. 4 The crystalline sensitivity band shifts of FTIR and Raman spectra at $1130\sim 1150\text{cm}^{-1}$ for PVOH, HDPE and EVOH copolymers. The three regions were separated according the WAXD results[6,13].

from 1131cm^{-1} of HDPE to 1144cm^{-1} of PVOH in FTIR spectrum.

The band of asymmetric C-C stretching vibration in the region of $1060\sim 1070\text{cm}^{-1}$ was also active in FTIR spectrum. The band was so weak that it only showed a shoulder except for EVOH72 specimen. But the band can be clearly discriminated in the fourth derivative and Fourier self-deconvolution spectra as shown in Fig.1. The band in IR spectra of PVOH shifted 4cm^{-1} to 1068cm^{-1} comparing with the band of PE. The shift of asymmetric C-C stretching band was smaller than that of symmetric one in the whole range of hydroxyl group concentration. It was of interest that the band was also found for PVOH.

According to the continuous shift as shown in Fig.4, the $1131\sim 1147\text{cm}^{-1}$ band of FTIR and Raman spectra can be assigned to symmetric C-C stretching vibration coupled with C-O stretching vibration in crystalline phase, which firstly confirmed the assignment proposed by Tadokoro[2] with direct experimental proof.

The $1064\sim 1072\text{cm}^{-1}$ band of both IR and Raman spectra for EVOH copolymers and PVOH can be assigned to asymmetric C-C stretching vibration in crystalline phase.

The $1110\sim 1130\text{cm}^{-1}$ band can be assigned to C-C stretching vibration coupled with C-O stretching vibration in amorphous phase for both IR[10] and Raman spectra.

3.1.4 The effect of disordered distribution of hydroxyl group on the C-C stretching vibration

The difference between PVOH and EVOH copolymers is mainly in the distribution of hydroxyl group. Hydroxyl group in EVOH copolymers was randomly distributed. Such disordered sequence destroyed the homogeneous C-C stretching vibration of the chain. The principle of mutual exclusion was invalid in EVOH copolymers accordingly. This may be the reason that the C-C stretching vibration was active in both Raman and IR spectra for the EVOH copolymers. Therefore, for the EVOH copolymers, the asymmetric C-C stretching vibration of IR spectra as shown in Fig.2(b) was also strongly active.

3.1.5 The effect of crystallite on the C-C stretching vibration

Both FTIR and Raman bands in the $1131\sim 1147\text{cm}^{-1}$

and $1064\sim 1072\text{cm}^{-1}$ region were sensitive to crystallinity for PVOH, HDPE and EVOH copolymers. The bands disappeared above the melting point as shown in Fig.5, Fig.6, and Fig.7. The bands were attributed to long sequence with trans conformation in crystalline phase accordingly.

Fig.6(a) showed the *in-situ* FTIR spectra of PVOH when the swollen specimen was heated from room temperature to melting point. The 1124cm^{-1} band in IR spectrum for PVOH was hardly observed. In the second derivative FTIR spectra, the band can be clearly observed as illustrated in Fig.6(b). The behavior in Raman spectrum was the same as that in IR spectrum. After annealing, the 1124cm^{-1} band decreased and the 1144cm^{-1} band increased. The sum of integrated intensity of them kept constant after annealing treatment[11]. Therefore, the 1124cm^{-1} band can be assigned to the same mode as 1144cm^{-1} band in amorphous phase for IR spectra[10].

The EVOH copolymers can crystallize in the whole range of hydroxyl group concentration[12]. For the EVOH32 and EVOH44 copolymers, the crystallinity

Fig. 5 The *in-situ* Raman spectra of the EVOH72 and EVOH59 copolymer at 20°C (Room temperature) and melting state. The melting points of EVOH72 and EVOH59 are 110°C and 140°C, respectively.

Fig. 6 (a) The *in-situ* FTIR spectrum of PVOH. The original film was in swollen state. The specimen was heated from 20°C to 220°C in Mettler hot stage. (b) The second derivative of *in-situ* FTIR spectrum, the arrows mark both of the C-C stretching bands.

Fig. 7 (a) The *in-situ* spectrum of FTIR EVOH59 copolymer. The specimen was heated from 20 °C to 220°C, then cooled to 20°C in Mettler hot stage. (b) The second derivative *in-situ* FTIR spectrum of EVOH59 copolymers, the arrows mark both of the C-C stretching bands.

was much lower than that of HDPE and PVOH. Therefore, the amorphous band at 1124cm^{-1} was clearly observed in IR spectra as illustrated in Fig.2(b). For EVOH59 copolymer as shown in Fig.7 (a), the 1124cm^{-1} band became a shoulder of the 1134cm^{-1} crystalline band. For EVOH72 copolymer, the 1124cm^{-1} band was weak and can not be observed except in simulation.

The second order derivative FTIR spectra of PVOH and EVOH59 copolymer in melting point were illustrated in Fig.6(b) and 7b. It was clearly observed that the 1124cm^{-1} band remained, whereas the bands in $1131\sim 1147\text{cm}^{-1}$ and $1064\sim 1072\text{cm}^{-1}$ disappeared above their melting points, which proved that the assignments of symmetric and asymmetric C-C stretching vibrations in crystalline phase for PVOH and EVOH copolymers were reasonable.

In the Raman spectra of EVOH copolymers, a shoulder was found at 1124cm^{-1} , but can not be clearly observed like that of PVOH.

According to WAXD analysis[13], the EVOH copolymers have three different types of crystalline unit in the whole range of hydroxyl group concentration, orthorhombic for 0~20% mole percentage of hydroxyl group (PE model), pseudo-hexagonal for 20~60% (EVOH model) and monoclinic for 60~100% (PVOH model). The spectra in crystalline phase depend on not only local chain conformation but also packing. As shown in Fig.4, the shifts of spectra both in FTIR and Raman seem to correspond the three ranges. It may infer that the symmetric C-C stretching band is affected by crystal structure. The band shift decreases slowly in monoclinic range following the increase of hydroxyl group concentration, and decreases sharply in pseudo-hexagonal range, but almost no change in orthorhombic range.

3.2 The C-O stretching vibration

3.2.1 The C-O stretching vibration of PVOH

For PVOH, the 1096cm^{-1} band of FTIR spectrum was assigned to the C-O stretching vibration in general. In solid state, the concentration of hydrogen bonded C-O bond was more than 90% according to near infrared (NIR) research[13]. Hence the 1096cm^{-1} band should be assigned to the hydrogen bonded C-O stretching vibration. The unsolved problem was how to find the location of free C-O vibration and how the hydrogen

Fig. 8 The FTIR spectrum in the region of C-O stretching vibrations, and its second and fourth order derivative spectra. The specimen in three states, original (bottom), swollen (top) and annealed (middle) was examined. The 1096cm^{-1} band in FTIR can be clearly separated into two bands in fourth derivative spectra.

bond affects the C-O vibration.

3.2.2 The effect of hydrogen bond on C-O stretching vibration of PVOH by swelling and annealing treatment

The location of the C-O vibration band was quite scattering in literatures[12,14]. The variations were in a wide range of $1085\sim 1100\text{cm}^{-1}$ wavenumber. This was typical behavior of a band bonded by hydrogen bond. Fig.8 illustrates FTIR bands for the original, swollen and annealing PVOH specimens. The band was at 1094cm^{-1} in original specimen, 1090cm^{-1} in swollen specimen and 1097cm^{-1} in annealed specimen.

From the second and fourth derivative spectra, the 1096cm^{-1} band was found to split into 1100cm^{-1} and 1086cm^{-1} bands as shown in Fig.8, which was in agreement to the dichroism measurement[14]. It was well known that O-H stretching vibration has three kinds of modes, a free, an intermolecular hydrogen bonded and an intramolecular hydrogen bonded band

[15]. The intermolecular hydrogen bonded O-H stretching vibration shifted to lower wavenumber than intramolecular hydrogen bonded one[16]. By reference to O-H stretching vibration, the 1086cm^{-1} band can be assigned to intramolecular hydrogen bonded C-O stretching vibration and the 1100cm^{-1} band to intermolecular hydrogen bonded C-O stretching vibration.

Thus, the observed band was actually the combination of intramolecular hydrogen bonded C-O stretching vibration and intermolecular bonded one. The shift of the observed band can be explained successfully by the ratio of them. For swollen specimen, the water molecule may break the intermolecular hydrogen bond. The intensity of 1086cm^{-1} band increased because the concentration of intramolecular hydrogen bond increased[17]. The observed band shifted to 1090cm^{-1} accordingly. For annealed specimen, the intensity of 1086cm^{-1} band decreased because the intramolecular hydrogen bond decreased with increasing intermolecular hydrogen bond. The observed band shifted to 1097cm^{-1} accordingly.

3.2.3 The assignment of C-O stretching vibration of EVOH copolymers

Both intra- and intermolecular bonded bands can be observed in derivative FTIR spectrum of EVOH copolymers. The 1100cm^{-1} and 1086cm^{-1} bands seemed to shift slightly to low frequency with the decrease of hydroxyl group concentration. Therefore, the assignments of EVOH copolymers were the same as that of PVOH.

In the Raman spectra as illustrated in Fig.2(a), the clearly observed band for PVOH at 1096cm^{-1} can also be assigned by hydrogen bonded C-O stretching vibration, which did not split into two bands because the C-O band in Raman spectrum was weaker than that of C-C stretching band. For EVOH32 copolymer, the band was only a weak shoulder. For EVOH44, 59, 72 copolymers, the band seemed to be overlapped with the 1080cm^{-1} band that was assigned to amorphous C-C stretching vibration in the case of PE. The intensity of the band for EVOH copolymers was higher than that for HDPE due to the low crystallinity. Similarly to the HDPE, the 1080cm^{-1} band in EVOH59 and EVOH72 copolymers can be observed as a major band at their melting points as illustrated in Fig.5. So the band with

broad line width for EVOH copolymers in Raman spectra can be assigned to C-C stretching vibration in amorphous phase, while the 1094cm^{-1} band for PVOH was still assigned to hydrogen bonded C-O stretching band.

3.2.4 Free C-O stretching vibration and free C-O index

In isopropyl alcohol[18], the C-O stretching band normally located at 1130cm^{-1} . But the band disappeared in dilute solution while a new peak was observed at 1060cm^{-1} . The shift was about 70cm^{-1} between two bands. The 1060cm^{-1} band was assigned to free C-O band while the 1130cm^{-1} band to hydrogen bonded C-O band. Unfortunately, the PVOH can not be dissolved in such solvents, e.g. CCl_4 and CS_2 . In fact, the EVOH copolymers was the most suitable specimens with low dilute concentration of hydroxyl group. The ethylene group can screen the intramolecular and intermolecular hydrogen bond. It was found that the 1020cm^{-1} band increased to very large extent with the decrease of hydroxyl group as illustrated in Fig.2(b). The band can be assigned to free C-O stretching vibration in EVOH copolymers accordingly. In the derivative spectrum of PVOH, the band was also found.

For the PVOH treated with formaldehyde[19], it is well known that a strong absorbance band at the 1020cm^{-1} was assigned to the C-O stretching vibration in the $-\text{O}-\text{CH}_2-\text{O}-$ group. The formaldehyde deduces the concentration of bonded C-O group. The assignment of free C-O stretching vibration in the present research is in agreement with that of C-O stretching vibration in the $-\text{O}-\text{CH}_2-\text{O}-$ group by formaldehyde.

By the curve fitting of the least squared method, the integrated intensity ratio between free and hydrogen bonded C-O band, defined as free C-O index, could be estimated as following:

$$I_{\text{free}} = A_{\text{free}} / (A_{\text{inter.}} + A_{\text{intra.}})$$

I_{free} is the free C-O index; A_{free} , $A_{\text{inter.}}$, $A_{\text{intra.}}$ are the resolved integrated absorbance of free, intramolecular hydrogen bonded and intermolecular hydrogen bonded C-O stretching vibration respectively as shown in Fig.1. The results are presented in Fig.9. The index from the present study was larger than that from NIR study[13], but had same trend. The results from the both studies showed that the concentration of the free bond had rather high in the case of EVOH72 copolymer. The

Fig. 9 The integrated intensity ratio between free C-O band and hydrogen bonded C-O band, free C-O index. The solid circles were estimated from O-H bands in the NIR spectrum measured by K. Akahane et al. as a reference[10].

1120cm^{-1} band for EVOH72 copolymer was clearly observed accordingly.

Although the 1045cm^{-1} band was observed as a weak shoulder in the whole range of hydroxyl group concentration of EVOH copolymers and PVOH, the band was clearly observed in derivative FTIR. The band can be assigned to the stretching vibration of hydrogen bonded primary C-O band in branch structure.

4. Conclusion

An attempt has been made to systematically recognize the bands of FTIR and Raman spectra for PVOH and EVOH copolymers by means of *in-situ* measurements and deconvolution analysis. By comparing the spectra of HDPE, the bands in the region of $1000\sim 1200\text{cm}^{-1}$ can be classified into C-C stretching vibrations and C-O stretching vibrations.

The assignment of symmetric C-C stretching vibration for PVOH was confirmed experimentally and the asymmetric C-C stretching vibration was found firstly. For PVOH and EVOH copolymers, the C-C stretching vibration was affected significantly by disordered distribution of hydroxyl group and

Table 2 The assignments of the bands in the region of $1000\sim 1200\text{cm}^{-1}$ from both literature[12] and present work.

Wavenumber (cm^{-1})	Krimm	Tadokoro	Dunn	Pritchard	present work
1131~1147	$\nu(\text{COC})$	$\nu(\text{CC})_{\text{crys.}}$	$\nu(\text{CO})_{\text{bonded}}$	$\nu(\text{CC}+\text{CO})$	$\nu_{\text{s}}(\text{CC}+\text{CO})_{\text{crys.}}$
1110~1131	—	$\nu(\text{CC})_{\text{amor.}}$	—	—	$\nu_{\text{s}}(\text{CC}+\text{CO})_{\text{amor.}}$
1060~1070	—	—	—	—	$\nu_{\text{as}}(\text{CC}+\text{CO})_{\text{crys.}}$
1090~1100	$\nu(\text{CO})$	$\nu(\text{CO})$	$\nu(\text{CO})_{\text{free}}$	$\delta(\text{CO}+\text{OH})$	$\nu(\text{CO}+\text{HO})_{\text{intermolecular hydrogen bond}}$
1080~1090	$\nu(\text{CO})$			—	$\nu(\text{CO}+\text{HO})_{\text{intramolecular hydrogen bond}}$
1010~1025	—	—	—	—	$\nu(\text{CO})_{\text{free}}$
1040~1050	—	—	—	—	$\nu(\text{CO})_{\text{primary}}$

crystallinity. The C-O stretching vibration was affected by hydrogen bond, and was firstly classified into intermolecular hydrogen bonded C-O, intramolecular hydrogen bonded C-O and free C-O stretching vibration. The free C-O index was used to characterize the concentration of hydrogen bond quantitatively.

The assignments in the region of $1000\sim 1200\text{cm}^{-1}$ were firstly clarified in the present study. The assignments in both literatures[12] and present work were listed in Table 2.

References

1. S.Krimm, C.Y. Liang, and G.B.B.M. Sutherland, *J. Chem. Phys.*, **25** (3), 549 (1956).
2. H. Tadokoro, The Structure of Macromolecule, Chapter 5. P.187-351 (1976).
3. M.J. Gall and P.J. Hendra, *Spectrochimica Acta*, **28A**, 1485 (1972).
4. H.Tadokoro, S. Seki, I. Nitta and K. Osaki, *J. Chem. Soc. Jap.*, **78** (7), 1061 (1957).
5. S.Krimm, C.Y. Liang, and G.B.B.M. Sutherland, *J. Polym. Sci.*, **22**, 227 (1956).
6. T. Matsumoto, K. Nakamae, H. Oka, and S. Kawarai, *Sen'i Gakkaishi*, **30** (8), T- 391 (1974).
7. T.F.Cooney, L. Wang, S.K. Sharma, R.W. Gauldie, and A.J. Montana, *J. Polym. Sci., Polym. Phys. Ed.*, **32**, 1163 (1994).
8. G. R. Strobl, and W. Hagedorn, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1181 (1978).
9. N. A. Peppas, *Makromol. Chem.*, **178**, 595 (1977).
10. K. Imai, J. Ukita, and M.Matsumoto, *Kobunshi Kagaku*, **16**, 597 (1959).
11. H. Tadokoro, *J. Ind. Chem. Jap.*, **59**, 731 (1956).
12. C.A. Finch, Polyvinyl Alcohol Development, J. Wiley & Sons Ltd, No.10, A.S. Dunn, Spectroscopic Properties of Polyvinyl Alcohol (1992).
13. T. Akahane, Y. Kazusa, and H. Nakayasu, *Kobunshi Ronbunshu*, **37** (5), 383 (1980).
14. V.N. Lebedeva, G.I. Distler, and Y.I. Kortukova, *Vysokomol. Soyed.* **A9** (10), 2076 (1967).
15. S. Hu, F. Horii, and H. Odani, *Bull. Inst. Chem. Res.*, Kyoto Univ., **69** (2), 165 (1991).
16. M.M. Coleman, X. Yang, H. Zhang, and P.C. Painter, *J. Macromol. Sci.-Phys.*, **B32** (3), 295 (1993).
17. F. Horii, S. Hu, T. Ito, H. Odani, and R. Kitamura, *Polymer*, **33** (11), 2299 (1992).
18. Y. Nishino, J. Ukita, and T. Kominami, *J. Ind. Chem. Jap.*, **58** (2), 159 (1955).
19. S. Kanbara, The Solid Structure of Polymers, Kyouritu P.203, (1965).