

Influence of Degree of Crystallinity and Syndiotacticity on Infrared Spectra of Solid PVA

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ABSTRACT: The influence of the degree of crystallinity and the syndiotacticity on the 1145, 1095, and 916 cm^{-1} bands was studied. The intensity of the 1145 cm^{-1} band increased with increasing syndiotacticity at a low degree of crystallinity and with an increasing degree of crystallinity for a sample with syndiotacticity. The intensity of 1095 cm^{-1} band increased with increasing syndiotacticity at a fixed degree of crystallinity and was independent of the degree of crystallinity for a sample. The intermolecular hydrogen bonds were found to play an important role. The differences of the relations between the absorbance ratio D_{1145}/D_{1095} and the degree of crystallinity with syndiotacticity were explained. The extent of the decrease of the intensity of 916 cm^{-1} band with an increasing degree of crystallinity increased with decreasing syndiotacticity. The predominant introduction of syndiotactic sequences in the crystals was assumed in the lower syndiotacticity. The improved equation between the syndiotactic diad content in percent [s -(diad) %] and the absorbance ratio D_{916}/D_{849} was established as s -(diad) % = $71.1 \times (D_{916}/D_{849})^{0.327}$ for the films heated at 50°C with use of a syndiotactic diad content obtained from NMR spectra. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1291–1298, 2001

Key words: poly(vinyl alcohol); infrared spectroscopy; NMR; syndiotactic; degree of crystallization

INTRODUCTION

The participation of crystals in solid commercial poly(vinyl alcohol) (A-PVA) for the infrared absorption band at 1145 cm^{-1} was found in 1948¹ and further investigated in detail around 1955.^{2–4} This band was then assigned to the CC stretching vibration in the crystals,^{5,6} which was coupled with CO stretching^{4,7} or the OCC symmetric stretching vibration,⁸ assigned to the skeletal vibration of the atactic or syndiotactic part by Mu-

rahashi et al. in 1962.⁹ The band at 1096 cm^{-1} was, on the other hand, assigned to the CO stretching vibration^{10,11} or the OCC antisymmetric stretching vibration.⁸ In 1994, both bands had been reported to be due to the crystallinity through an investigation with Raman spectra.¹¹ An equation was represented in 1955 between the degree of crystallinity and the absorbance ratio (D_{1145}/D_{1096}) for A-PVA.² In 1966, the dependency of the ratio D_{1145}/D_{1096} on the heat-treatment temperature as a measure of the crystallinity was reported to be different from the syndiotacticity, that is, the racemic diad content (r).¹² Both bands are therefore to be reconsidered and the equations in accordance with tacticity are required to determine the degree of crystallinity.

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The intensities of the infrared absorption band at 916 cm^{-1} of the solid PVAs assumed to be syndiotactic were found in 1963 to be higher than were those of commercial and isotactic PVAs and the absorbance ratio D_{916}/D_{849} was shown to be suitable as the measure of the tacticity. The ratio was also found to decrease with an increasing heat-treatment temperature.¹³ This fact has remained unexplained. Sumi et al. established a relation between *s*-(diad) % and D_{916}/D_{849} as *s*-(diad) % = $72.4(D_{916}/D_{849})^{0.43}$ (Sumi's equation) with use of the *r* content determined by nuclear magnetic resonance spectroscopy (NMR) for poly(vinyl acetate) at 100 MHz.¹⁴ Recently, this relation was found to give rather lower values than the true ones for PVAs with *r* % lower than 58% by using the *r* content determined by higher-resolution NMR instruments for PVA. A new equation was applied for the wide range of syndiotacticity that is required. This article reports on the investigations of the problems mentioned above.

EXPERIMENTAL

Samples

The samples of different syndiotacticities shown in Table I were used. The sample S53.0PVA is a commercial PVA NH26 (Nippon Gosei). S57.8PVA was prepared from poly(vinyl trifluoroacetate) obtained through bulk polymerization at 60°C using benzoyl peroxide as an initiator.¹⁵ The S61.0PVA derived from vinyl pivalate was kindly supplied by the Kuraray Co. The sample has a 1,2-glycol linkage content around 1.7 mol %

higher than that of the 1.0 mol % of S57.8PVA.¹⁶ S62.7PVA and S63.8PVA were prepared from poly(vinyl trifluoroacetate) obtained through photo-induced polymerization at -75°C using 2,2'-azobis-2,4-dimethyl valeronitrile¹⁷ and at -78°C using benzophenone-tetrahydrofuran,¹⁸ respectively. The degrees of polymerization (DPs) were estimated from the intrinsic viscosities determined for the acetylated PVAs using benzene as a solvent at 30°C. The equation $[\eta] = 8.91 \times 10^{-3} DP^{0.62}$ was used.¹⁹ The triad contents were determined from the intensities of the methine carbon of 125 MHz ^{13}C -NMR spectra taken at 80°C in DMSO- d_6 using a Bruker-DRX-500 NMR spectrometer.²⁰ The *s*-(diad) % was estimated as *s*-(diad) % = $S + (1/2)H$ (*S*: syndiotactic triad percent; *H*: heterotactic triad percent) with the assumption of a simple Markofian process for polymerization.

Films and Heat Treatment

Films were prepared by casting the aqueous solutions at room temperature. The samples, except S53.0PVA, were dissolved in water at 120–130°C. The thickness of the films was around 10 μm . The films were heated at 50, 120, 160, and 180°C for 5 min in an oven to prepare films of different degrees of crystallinity.

Degrees of Crystallinity

The degrees of crystallinity were determined from the density using the equation²¹

$$1/d = X/1.345 + (1 - X)/1.269$$

Table I Samples Used

| Sample | Monomer | Polymerization | DP | NMR Triad | | | NMR Diad |
|-----------------------|---------|---------------------------|------|---------------|---------------|---------------|--------------|
| | | | | <i>mm</i> (%) | <i>mr</i> (%) | <i>rr</i> (%) | <i>r</i> (%) |
| S63.8 PVA | VTFA | BP, -78°C | 1150 | 13.3 | 45.9 | 40.8 | 63.8 |
| S62.7PVA | VTFA | V-65, -75°C | 1590 | 15.0 | 44.7 | 40.3 | 62.7 |
| S61.0PVA ^a | VPI | | 1640 | 14.7 | 48.7 | 36.6 | 61.0 |
| S57.8PVA | VTFA | BPO, 60°C | 3340 | 17.7 | 49.0 | 33.3 | 57.8 |
| S53.0PVA ^b | VAc | | 2600 | 22.6 | 48.8 | 28.6 | 53.0 |

VTFA: vinyl trifluoroacetate; VPI: vinyl pivalate; VAc: vinyl acetate; BP: benzophenone; V-65: 2,2'-azobis-2,4-dimethyl valeronitrile; BPO: benzoyl peroxide; *m*: meso; *r*: racemi.

^a Kuraray Co., Ltd.

^b Nippon Synthetic Chemical Industry Co., Ltd.

where d is the density of the film, and X , the degree of crystallinity. The density was determined by a flotation method using a benzene-carbon tetrachloride system.

Infrared Spectra

Infrared spectra of the films were taken with a Nippon Bunko FTIR spectrometer FTIR-7000.

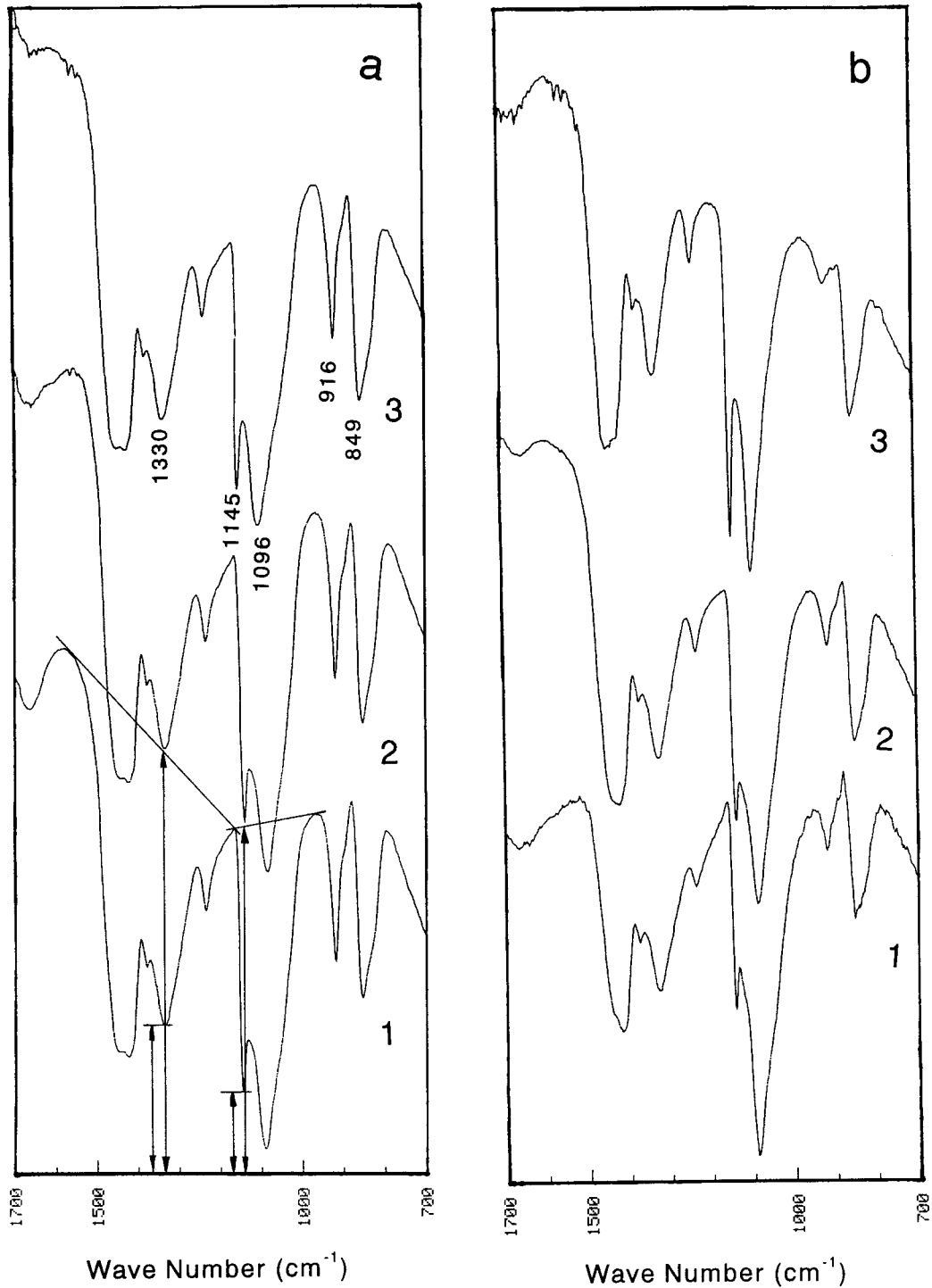


Figure 1 Infrared spectra of PVA films heated at three temperatures: (a) S64.0PVA, (1) untreated, (2) 120°C, (3) 180°C; (b) S53.0PVA, (1) untreated, (2) 120°C, (3) 180°C.

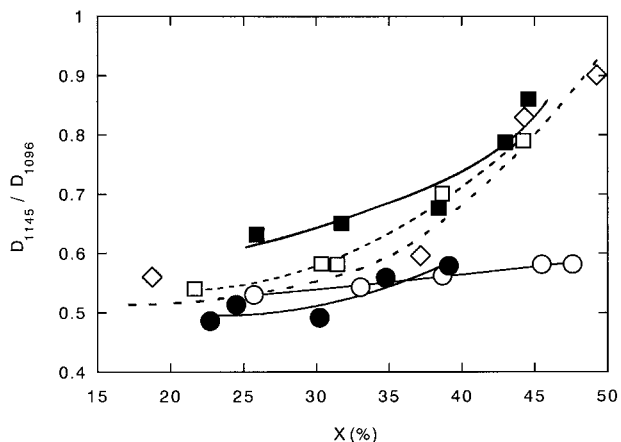


Figure 2 D_{1145}/D_{1096} against degree of crystallinity: (○) S63.8PVA; (●) S62.7PVA; (□) S61.0PVA; (■) S57.8PVA; (◇) S53.5PVA.

RESULTS AND DISCUSSION

Figure 1(a,b) shows IR spectra of the different heat-treated samples for two kinds of PVA of different tacticities. The intensities of the 1145 and 916 cm^{-1} bands are seen to change in accordance with the heating, that is, with the crystallinity in each PVA and with the tacticity in each draw ratio as reported previously.^{2,3,13,22} Detailed discussions are given below: First, the 1145 cm^{-1} band and, second, the 916 cm^{-1} band are described.

Figure 2 shows the dependency of D_{1145}/D_{1096} on the crystallinity for five kinds of samples. The baselines used for the determination of those absorbances are shown in the figure. The ratios increase steeply with the degree of crystallinity for the samples S53.0, S57.8, and S61.0PVA, whereas the increase is slow with the degree of crystallinity for samples S62.7 and S63.8PVA of higher syndiotacticities. The dependency of S53.0PVA is naturally identical with that reported previously.^{2,3} The curves for samples S57.8 and S61.0PVA are not so different from that for sample S53.0PVA. The similar behavior of S57.8PVA with that of S53.0PVA was reported previously.^{12,23} In S61PVA, the presence of a larger amount of 1,2-glycol linkages is considered to be due to its behavior.

Figures 3 and 4 show the dependency of D_{1145} and D_{1096} on the degree of crystallinity. Both absorbances are normalized to the band 1330 cm^{-1} to correct the differences in the film thickness. The band is of the mixed CH and OH bending modes and is insensitive for tacticity and crystal-

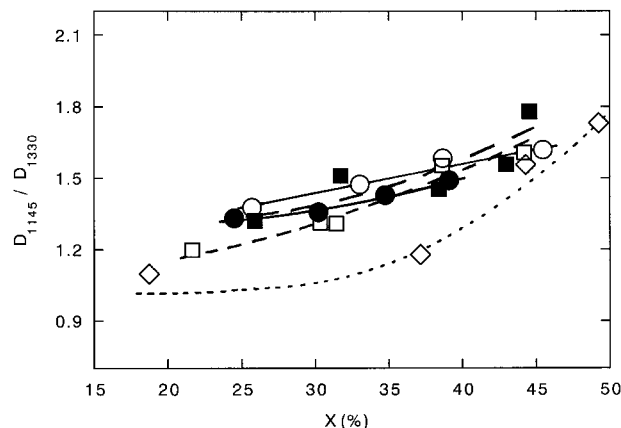


Figure 3 D_{1145}/D_{1330} against degree of crystallinity: (○) S63.8PVA; (●) S62.7PVA; (□) S61.0PVA; (■) S57.8PVA; (◇) S53.0PVA.

linity. D_{1145} depends clearly on the degree of crystallinity, whereas it depends on the syndiotacticity only at a low degree of crystallinity, although the differences are not so clear. D_{1096} increases with increasing syndiotacticity at a fixed degree of crystallinity and is independent of the degree of crystallinity. These facts are considered to be due to the crystalline structure of the PVA crystals. Recent investigations have revealed the inner structure of the crystals to be composed of intra- and intermolecular hydrogen bonds. The temperatures above which the X-ray scattering intensity at the 100 plane²⁴ and elastic modulus²⁵ decrease, increase with increasing syndiotacticity. This suggests that the intermolecular hydrogen bonds increase with increasing syndiotacticity.

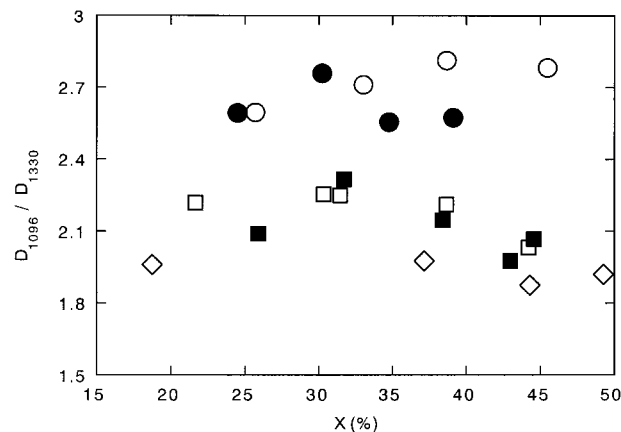


Figure 4 D_{1096}/D_{1330} against degree of crystallinity: (○) S63.8PVA; (●) S62.7PVA; (□) S61.0PVA; (■) S57.8PVA; (◇) S53.0PVA.

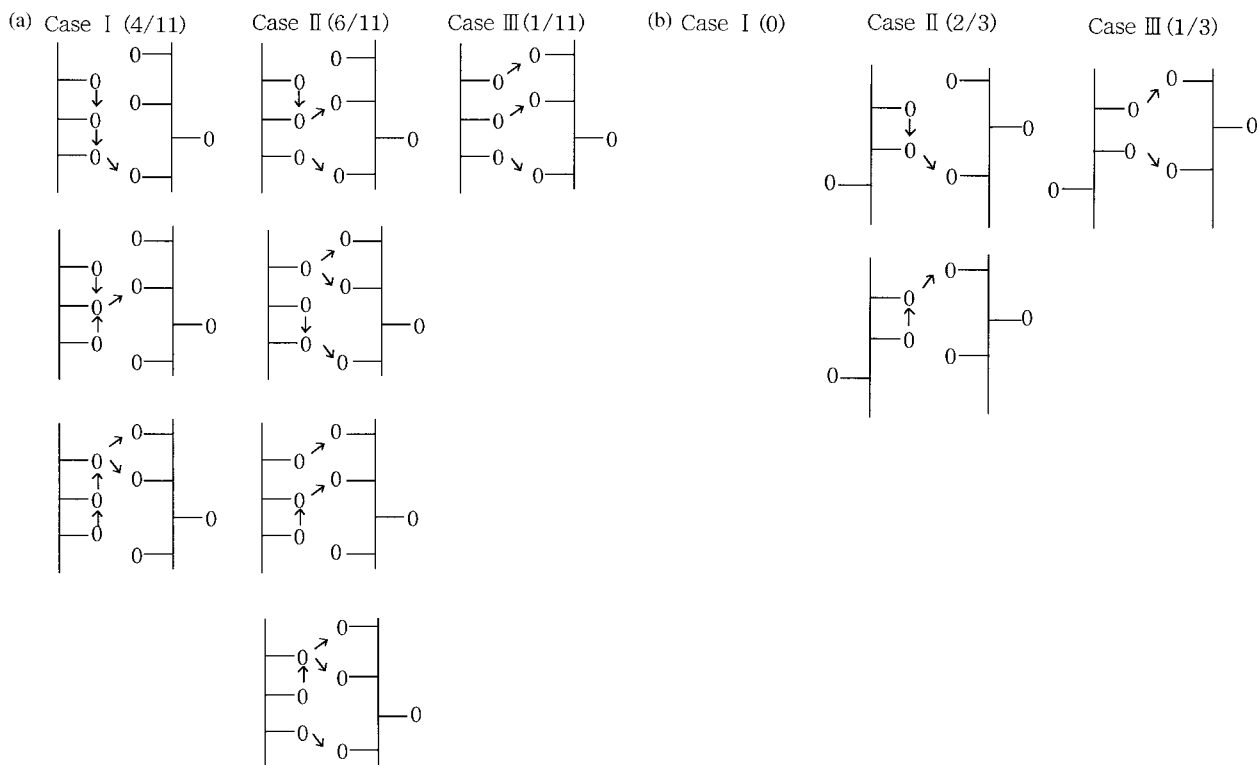


Figure 5 Intra- and intermolecular hydrogen bonds²⁸: (a) for mm - mrr pair; (b) for mr - rr pair.

In ^{13}C -NMR spectra in the solid state, the absorption due to methine carbon is split into three peaks in accordance with the carbons with the hydroxyl oxygens with two intra-(I), one intra-(II), and one inter-(III) hydrogen bonds.^{26,27} A theoretical estimation of the carbons in the crystal for PVA with different tacticities was carried out assuming possible sequence pairs.²⁸ Two examples of the pairs are shown in Figure 5. The amounts of I, II, and III carbons in the crystals were separated using ^{13}C spin-lattice relaxation

analyses.²⁷ The observed amounts are approximately identical with the theoretical values as shown in Table II. The probability of the intermolecular hydrogen bonds of case I, II, and III carbons are 1/3, 1/3–1/2, and 1. Thus, the amounts of intermolecular hydrogen bonds for the samples shown in Table II are estimated as shown in Table III. In the estimation, a sample is assumed to have (each integrated fraction shown in Table II times 100) mol carbons for cases I, II, and III.

Table II Calculated Fractions and Integrated Fractions of Cases I, II, and III for the Crystalline and Noncrystalline Spectra of PVA Samples

| Sample | Calculated Fraction | | | Integrated Fraction | | |
|----------------|---------------------|-------|-------|---------------------|-------|-------|
| | I | II | III | I | II | III |
| Crystalline | | | | | | |
| <i>s</i> -PVA | 0.119 | 0.471 | 0.410 | 0.064 | 0.350 | 0.586 |
| <i>a</i> -PVA | 0.146 | 0.499 | 0.355 | 0.109 | 0.457 | 0.434 |
| <i>i</i> -PVA | 0.369 | 0.460 | 0.171 | 0.386 | 0.351 | 0.263 |
| Noncrystalline | | | | | | |
| <i>a</i> -PVA | | | | 0.170 | 0.493 | 0.337 |

Table III Amounts of Intermolecular Hydrogen Bond of Samples of Different Syndiotacticities in Moles

| Sample | I | II | III | I + II + III |
|----------------|------|---------------------------------------|------|---------------------------------------|
| Crystalline | | | | |
| <i>s</i> -PVA | 2.1 | 17.5 ^a (11.7) ^b | 58.6 | 78.2 ^a (72.4) ^b |
| <i>a</i> -PVA | 3.6 | 22.9 (15.3) | 43.4 | 69.9 (62.3) |
| <i>i</i> -PVA | 12.9 | 17.6 (1.7) | 26.3 | 56.8 (50.9) |
| Noncrystalline | | | | |
| <i>a</i> -PVA | 5.7 | 24.7 (16.5) | 33.7 | 64.1 (55.9) |

^a In the case of probability of 1/2.^b In the case of probability of 1/3.

The 1145 cm⁻¹ band is considered to be assigned to the OCC symmetric stretching vibration deduced by the analysis of the factor group.⁸ The dependence of the band on the syndiotacticity at a low degree of crystallinity suggests that the band is concerned with the intermolecular hydrogen bonds due to the syndiotactic sequences in the crystals. In A-PVA, the intermolecular hydrogen bondings are introduced predominantly with heating to lead to an identical intensity with those of the PVAs of higher syndiotacticity. The predominant introduction of syndiotactic sequences into crystals was found through ¹³C spin-lattice relaxation analysis as shown in Table II (integrated fractions of case III carbon for crystalline and noncrystalline parts are 0.434 and 0.337, respectively)²⁶ and also was deduced from the behavior of the 916 cm⁻¹ band with the degree of crystallinity as described below. However, there is a report in which the independence of the band with the hydrogen bonds is described on the basis of the slight shift of the band on deuteration. Further investigation is required. The 1096 cm⁻¹ band is considered to be assigned to the OCC antisymmetric stretching vibration.⁸ The present investigation shows that the band increases with increasing syndiotacticity. The band is considered to be due to the contribution from the intermolecular hydrogen bonds since the amount of the bond increases with increasing syndiotacticity as is shown in Table II. The band also is contributed to by the amorphous parts since this band is independent of the degree of crystallinity.

The curves shown in Figure 2 are understood by the behavior of both bands with the degree of crystallinity and syndiotacticity, that is, the D_{1145}/D_{1095} 's of S53.8 and S57.8PVA are larger than those of S63.0 and S64.0PVA at a fixed degree of crystallinity since the D_{1095} 's for the

former are lower than those for the latter. The linear relationship was found in 1955 between D_{1095}/D_{1145} and an inverse degree of crystallinity by Nagai et al.² The dependencies of D_{1095}/D_{1145} on the inverse degree of crystallinity are shown in Figure 6 for five samples. The linear relationships are approximately established for five samples although the intercepts and slopes have different tacticity and the points for the samples S57.8 and S61.0PVA are scattered. The slope decreases with increasing syndiotacticity. The relation for S53.0PVA is nearly identical with that by Nagai et al. The points shown in Figures 2–5 are scattered. The estimation of the absorbances by a curve separation will give more correct values.

Figure 7 shows the apparent *s*-(diad) % estimated from the equation by Sumi et al.¹⁴ [IR-*s*-(diad) %] against the degree of crystallinity. The IR-*s*-(diad) % depends on the degree of crystallin-

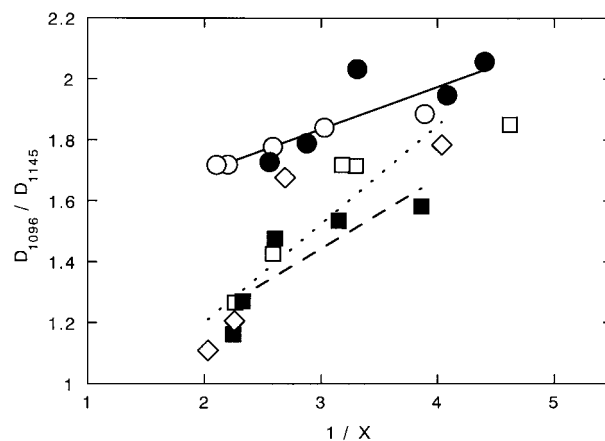


Figure 6 D_{1095}/D_{1145} against $1/X$: (○) S63.8PVA; (●) S62.7PVA; (□) S61.0PVA; (■) S57.8PVA; (◇) S53.0PVA. (—; ○, ●) $y = 1.42 + 0.14/X$; (- - -; ■) $y = 0.75 + 0.23/X$; (· · ·; ◇) $y = 0.55 + 0.32/X$.

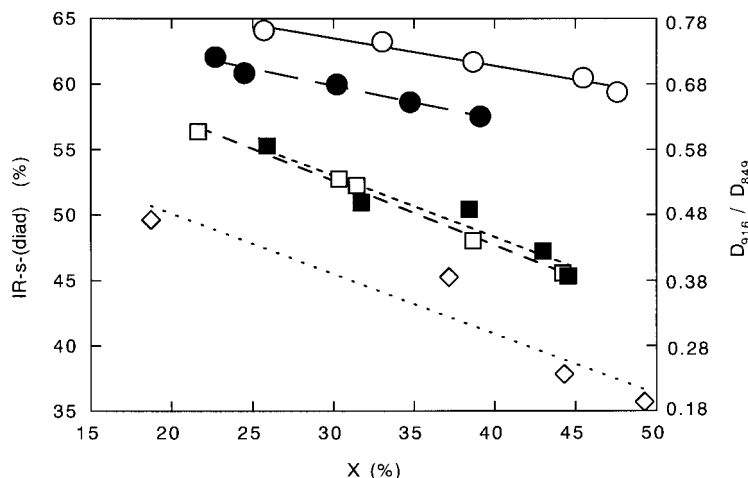


Figure 7 IR-s-(diad) % and D_{916}/D_{849} against degree of crystallinity: (○) S63.8PVA; (●) S62.7PVA; (□) S61.0PVA; (■) S57.8PVA; (◇) S53.0PVA.

ity and syndiotacticity. The slope of a straight line in Figure 6 decreases with increasing syndiotacticity. The 916-cm^{-1} band was assigned to the methylene rocking motion⁸ or the skeletal motion.²⁸ The band is suggested to be due to the amorphous parts and to decrease in intensity in accordance with the introduction of syndiotactic sequences in the crystals. The larger slope in the samples of lower syndiotacticity is concerned with the predominant introduction of syndiotactic sequences in the crystals as described above. In the samples with higher syndiotacticity, S63.8PVA

and S64.0PVA, no predominant introduction of syndiotactic sequences occurs. The Sumi equation is considered to be improved with the D_{916}/D_{849} 's determined for the samples with an identical degree of crystallinity since it depends on the degree of crystallinity and, with use of an accurate *s*-(diad) %, determined by higher-resolution NMR spectroscopy. The samples heat-treated at 50°C , the degrees of crystallinity of which were in the range of 35–38 %, were used. Figure 8 shows the logarithmic plot of the *s*-(diad) % (NMR-s-(diad) %) against D_{916}/D_{849} . The equation

$$s\text{-(diad)\%} = 71.1 \times (D_{916}/D_{849})^{0.327}$$

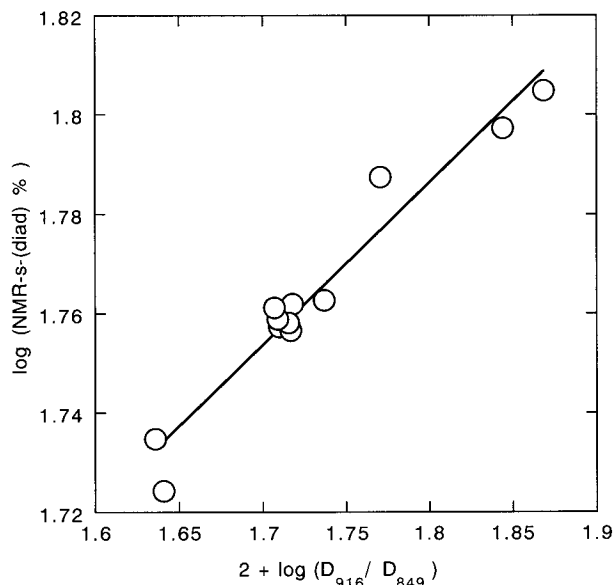


Figure 8 Log-log plots of NMR-s-(diad) % against D_{916}/D_{849} .

was established.

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REFERENCES

1. Elliot, A.; Ambrose, E. J.; Temple, R. B. *J Chem Phys* 1948, 16, 877.
2. Nagai, E.; Mima, S.; Kuribayashi, S.; Sagane, N. *Kobunshi Kagaku* 1955, 12, 199; Nagai, E.; Kuribayashi, S. *Kobunshi Kagaku* 1955, 12, 22.
3. Tadokoro, H.; Seki, S.; Nitta, I. *Bull Chem Soc Jpn* 28, 559, 1955; *J Chem Phys* 1955, 23, 1331.
4. Nishino, Y.; Ukita, J.; Kominami, T. *J Chem Soc Jpn Ind Soc* 1955, 58, 159.
5. Tadokoro, H.; Seki, S.; Nitta, N. *J Polym Sci* 1956, 22, 563.

6. Tadokoro, H. *Bull Chem Soc Jpn* 1959, 32, 1334.
7. Nagai, E.; Kuribayashi, S. *Kobunshi Kagaku* 1955, 12, 368.
8. Ling, C. Y.; Pearson, F. G. *J Polym Sci* 1959, 35, 303.
9. Murahashi, S.; Yuki, H.; Sano, T.; Yonemura, U.; Tadokoro, H.; Chatani, Y. *J Polym Sci* 1962, 62, S77.
10. Krimm, S.; Liang, C. Y.; Sutherland, G. B. B. M. *J Polym Sci* 1956, 22, 227.
11. Cooney, T. F.; Wang, L.; Sharma, S. K.; Gandie, R. W.; Monta, A. J. *J Polym Sci B Polym Phys* 1994, 32, 1163.
12. Sumi, M.; Matsumura, K.; Ohno, R.; Nozakura, S.; Murahashi, S. *Kobunshi Kagaku* 1966, 23, 605.
13. Fujii, K.; Ukida, J. *Makromol Chem* 1963, 65, 74.
14. Murahashi, S.; Nozakura, S.; Sumi, M.; Yuki, H.; Hatada, K. *Kobunshi Kagaku* 1966, 23, 605.
15. Haas, H. C.; Emerson, E. S.; Schuler, N. W. *J Polym Sci* 1956, 22, 291.
16. Yamaura, K.; Matsuzawa, S.; Go, Y. *Kobunshi Kagaku* 1969, 26, 265.
17. Matsuzawa, S.; Yamaura, K.; Noguchi, H.; Hayashi, H. *Makromol Chem* 1973, 165, 217.
18. Matsuzawa, S.; Yamaura, K.; Yamada, S.; Shinke, Y.; Nakano, Y.; Koike, Y. *J Polym Sci* 1988, 35, 391.
19. Nakajima, A. *Kobunshi Kagaku* 1949, 6, 451.
20. Wu, T. K.; Ovenall, D. W. *Macromolecules* 1973, 6, 582.
21. Sakurada, I.; Nukushina, Y.; Sone, Y. *Kobunshi Kagaku* 1955, 12, 506.
22. Sumi, M.; Matsumura, K.; Ohno, R.; Nozakura, S.; Murahashi, S. *Kobunshi Kagaku* 1967, 4, 606.
23. Bohn, C. R.; Schaeffgen, J. R.; Statton, W. O. *J Polym Sci* 1961, 55, 531.
24. Nagura, M.; Matstuzawa, S.; Yamaura, K.; Ishikawa, H. *Polym J* 1982, 14, 69.
25. Nakamae, K.; Nishimoto, K.; Okubo, H.; Matsuzawa, S.; Yamaura, K. *Polymer* 1992, 33, 2581.
26. Terao, T.; Maeda, S.; Saika, A. *Macromolecules* 1983, 16, 1535.
27. Horii, F.; Hu, S.-H.; Itoh, T.; Odani, H.; Kitamaru, R.; Matsuzawa, S.; Yamaura, K. *Polymer* 1992, 33, 2299.
28. Hu, S.-H.; Horii, F.; Odani, H. *Bull Inst Chem Res Kyoto Univ* 1991, 69, 165.