methyl radicals with ethylene.[13] The very small fraction of ethyl branches for which there is ^{13}C evidence may be introduced *via* the extension of the Roedel mechanism described by Willbourn;[1] this must now be regarded as a reaction of very low probability. The possibility of occurrence of significant proportions of tetrafunctional branches, proposed by some authors, can be excluded.

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(13) A. S. Gordon and J. R. McNesby, *J. Chem. Phys.*, **31**, 853 (1959); **33**, 1882 (1960).

Tacticity of Poly(vinyl alcohol) Studied by Nuclear Magnetic Resonance of Hydroxyl Protons

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ABSTRACT: The high-resolution nmr spectrum of the hydroxyl protons in poly(vinyl alcohol) dissolved in dimethyl sulfoxide shows three well-separated triad peaks with spin–spin splitting. These hydroxyl peaks can be assigned to isotactic, heterotactic, and syndiotactic triads with increasing field strength. This assignment is ascertained by dimer and trimer model compounds as well as polymers with known stereoregularities. An interesting variation of coupling constants J(H–O–C–H) with configurational structures is observed.

The accurate determination of tacticity in poly(vinyl alcohol) (PVA) has been difficult and troublesome. Formerly it was investigated by X-ray diffraction[1] and infrared spectroscopy.[1-3] Dyad and triad tacticities were studied[4-7] by methylene and methine nmr spectra, respectively, but the overlapping of peaks is so severe, especially for the methine portion, that a quantitative determination has been difficult. On the other hand, it was disclosed that acetoxyl protons in poly(viny lacetate)[5,8-11] derived from PVA are rather useful to the triad tacticity study although overlap still remains.

Little attention has been paid to the nmr spectra of the hydroxyl protons in PVA. This neglect seems natural because heavy water was usually selected as the solvent and the hydroxyl protons and deuterons necessarily exchange between PVA hydroxyl groups and water so rapidly that hydroxyl protons under different environments cannot be discriminated by their nmr spectra.

There is another good solvent for PVA, dimethyl sulfoxide (DMSO), which turned out to give the key to a useful investigation of the hydroxyl protons in this polymer. In DMSO solution, the hydroxyl proton resonance of PVA shows three well-resolved triad peaks with spin–spin splitting. It has been well known that spin–spin splitting of hydroxyl peaks in some alcohols can be observed in DMSO solution.[12] The solvation of DMSO molecules to hydroxyl protons reduces the rate of proton exchange sufficiently to permit such an observation.

In order to assign and interpret the triad peaks of PVA, the model compounds meso and racemic pentane-2,4-diol, and isotactic, heterotactic, and syndiotactic heptane-2,4,6-triol were also investigated. (The former is abbreviated diol and the latter triol in the following discussions.) The nmr spectra of the diol[13-16] and triol[15] were published previously, but the splitting of the hydroxyl lines was not reported, even though various solvents including DMSO were used. This is probably because impurities such as water and traces of acid in the solution gave rise to rapid proton exchange.

Experimental Section

Materials. Four samples of PVA which were different in stereoregularity were used. Sample I is commercially produced PVA (Kuraray Co.), which was prepared by hydrolysis of radical polymerized poly(vinyl acetate). Samples II and III were derived from poly(vinyl *tert*-butyl ether) prepared by cationic polymerization. Polymerization of vinyl *tert*-butyl ether was carried out at -78° with $BF_3O(C_2H_5)_2$ as catalyst in toluene (sample II) and in methylene chloride (sample III). From poly(vinyl *tert*-butyl ether), PVA was derived by way of poly(vinyl acetate). Vinyl *tert*-butyl ether was synthesized from vinyl benzyl ether by an ether exchange reaction. Sample IV was derived from poly(vinyl trimethylsilyl ether), polymerized with $FeCl_3$ as catalyst in nitro-

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(1) K. Fujii, T. Mochizuki, S. Imoto, J. Ukida, and M. Matsumoto, *J. Polym. Sci., Part A*, **2**, 2327 (1964).

(2) S. Krimm, C. Y. Liang, and G. B. B. M. Sutherland, *J. Polym. Sci.*, **22**, 227 (1956).

(3) H. Tadokoro, *Bull. Chem. Soc. Jap.*, **32**, 1334 (1959).

(4) V. J. Bargon, K. H. Hellwege, and U. Johnsen, *Makromol. Chem.*, **85**, 291 (1965).

(5) K. C. Ramey and N. D. Field, *J. Polym. Sci., Part B*, **3**, 63 (1965); **3**, 69 (1965).

(6) A. Danno and N. Hayakawa, *Bull. Chem. Soc. Jap.*, **35**, 1748 (1962).

(7) W. C. Tincher, *Makromol. Chem.*, **85**, 46 (1965).

(8) F. A. Bovey, E. W. Anderson, D. C. Douglass, and J. A. Manson, *J. Chem. Phys.*, **39**, 1199 (1963).

(9) K. C. Ramey and D. C. Lini, *J. Polym. Sci., Part B*, **5**, 39 (1967).

(10) K. Fujii, Y. Fujiwara, and S. Fujiwara, *Makromol. Chem.*, **89**, 278 (1965).

(11) S. Murahashi, S. Nozakura, M. Sumi, H. Yuki, and K. Hatada, *J. Polym. Sci., Part B*, **4**, 65 (1966).

(12) O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, **86**, 1256 (1964).

(13) Y. Fujiwara, S. Fujiwara, and K. Fujii, *J. Polym. Sci., Part A-1*, **4**, 257 (1966).

(14) P. E. McMahon and W. C. Tincher, *J. Mol. Spectrosc.*, **15**, 180 (1965).

(15) S. Fujiwara, Y. Fujiwara, K. Fujii, and T. Fukuroi, *ibid.*, **19**, 294 (1966).

(16) T. Fukuroi, Y. Fujiwara, S. Fujiwara, and K. Fujii, *Anal. Chem.*, **40**, 879 (1968).

TABLE I
TRIAD TACTICITIES OF PVA PREPARED UNDER VARIOUS CONDITIONS

Sample no.	Monomer	Solvent	Catalyst	Tacticity[a] I	H	S
I	Vinyl acetate	Methanol	(Radical initiator)	$21._3$	$49._4$	$29._3$
II	Vinyl *tert*-butyl ether	Toluene	$BF_3O(C_2H_5)_2$	$49._7$	$38._8$	$11._5$
III	Vinyl *tert*-butyl ether	Methylene chloride	$BF_3O(C_2H_5)_2$	$18._6$	$50._0$	$31._4$
IV	Vinyl trimethylsilyl ether	Nitroethane	$FeCl_3$	$16._2$	$45._1$	$38._7$

[a] Abbreviations: I; isotactic; H, heterotactic; S, syndiotactic.

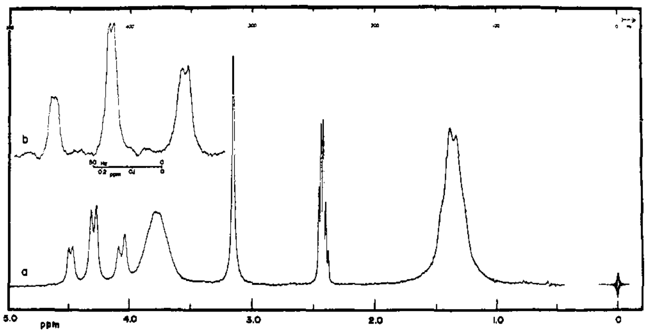

Figure 1. (a) Nmr spectrum (100 MHz) of poly(vinyl alcohol) in dimethyl-d_6 sulfoxide at 50°. (b) Hydroxyl proton spectrum (220 MHz) of poly(vinyl alcohol) at 42°.

ethane at −78°.[17,18] Soaking of poly(vinyl trimethylsilyl ether) in methanol led to precipitation of PVA.[18] Vinyl trimethylsilyl ether was prepared by the reaction of mercury diacetoaldehyde and trimethylchlorosilane.[19]

Sample I is known to be essentially atactic, while samples II, III, and IV were reported[18] to be highly isotactic, slightly syndiotactic, and highly syndiotactic, respectively.

Meso and racemic isomers of pentane-2,4-diol were prepared by hydrolysis of their formal derivatives, separated by gas chromatography. Heptane-2,4,6-triol was synthesized by hydrogenation of diacetylacetone and was separated into three isomers by means of elution chromatography.[20] All model compounds were purified by vacuum distillation.

Method. DMSO-d_6, which is more desirable than DMSO because of its less intense signal, was used as solvent for PVA and its model compounds throughout the present work. In order to observe the PVA hydroxyl proton signal clearly, care must be taken in preparing samples. At the first stage of this research work, broad signals were frequently observed which obscured the spectra to the extent that the various hydroxyl peaks could not be resolved.

Drying conditions and concentration of the samples are factors of critical importance. Small amounts of water contained in PVA could be removed by evaporating the DMSO solution of the polymer *in vacuo* at 40°, leaving a film; 15 mg of this film was dissolved in 0.5 ml of warm, carefully dried, commercial DMSO-d_6. Higher concentrations of samples or water impurity frequently broadens the signals. Hexamethyldisiloxane (HMDS) was used as an internal reference. Nondeuterated DMSO is convenient as an internal lock signal when observing the hydroxyl proton spectrum.

Nmr measurements were carried out over a temperature range of 20–100°. Throughout this range the hydroxyl splitting could be observed. Increasing temperature causes the resonance peaks to move upfield and to overlap with the methine resonance band. For determining triad tacticity, room-temperature measurements are sufficient, although 50° was arbitrarily selected in this paper. Samples of model compounds were similarly prepared and studied.

Most nmr spectra were obtained with a Varian HA-100 spectrometer, equipped with variable-temperature and spin-decoupling units, operating at 100 MHz; a few spectra were obtained with Varian A-60D and HR-220 spectrometers at 60 and 220 MHz, respectively.

Results

PVA. Figure 1a shows the 100 MHz spectrum of PVA (sample I) at 50°. The internal reference HMDS signal is observed as a symmetrical wiggle at 0 ppm. Downfield from HMDS, there appear resonances assigned to methylene (1.37 ppm from HMDS), partially deuterated DMSO in the solvent (2.45 ppm), water (3.16 ppm) which remains as an impurity in the sample and solvent, methine (3.82 ppm), and hydroxyl (4.10, 4.33, and 4.52 ppm) protons.

The three hydroxyl resonance lines are split into doublets. This splitting is ascribed to spin–spin coupling with the methine protons, as demonstrated by the field strength independency of the splittings (measured at 60, 100, and 220 MHz) and by the spin-decoupling method. The 220-MHz spectrum of the hydroxyl protons is shown in Figure 1b.

In Figure 2 are shown the 100-MHz hydroxyl proton spectra of other samples of PVA (samples II–IV) snthesized under different stereoregulating conditions. Sample II (Figure 2a), which is known to be highly isotactic, shows a very prominent peak at lowest field. In contrast, samples III and IV (Figure 2b and 2c, respectively), which were both believed to be predominantly syndiotactic, show the same three peaks, but the peak at the highest field is more prominent. Therefore, the three hydroxyl lines can be assigned to isotactic (mm, according to the nomenclature of Bovey, *et al.*[21]), heterotactic (mr), and syndiotactic (rr) triad configurations with increasing field strength. Table I indicates the quantitative triad probabilities obtained from the area intensities of resonance lines. It is shown that the PVA commercially produced by radical polymerization is slightly syndiotactic, and sample IV is not as syndiotactic as determined previously by the spectrum of the corresponding poly(vinyl acetate).[18]

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(17) I. W. Bassi, G. Dall'Asta, U. Campigli, and E. Strepparola, *Makromol. Chem.*, **60**, 202 (1963); S. Murahashi, S. Nozakura, and M. Sumi, *J. Polym. Sci., Part B*, **3**, 245 (1965).

(18) K. Shibatani, M. Nakamura, and Y. Oyanagi, *Kobunshi Kagaku*, **26**, 118 (1969).

(19) A. N. Nesmeyanov, I. F. Lutsenko, and V. A. Brattsev, *Dokl. Akad. Nauk SSSR*, **128**, 551 (1959).

(20) K. Fujii, *J. Polym. Sci., Part B*, **3**, 375 (1965).

(21) F. A. Bovey, *Pure Appl. Chem.*, **15**, 349 (1967); H. L. Frisch, C. L. Mallows, and F. A. Bovey, *J. Chem. Phys.*, **45**, 1565 (1966).

TABLE II
THE CHEMICAL SHIFTS OF THE HYDROXYL PROTONS AND THE COUPLING CONSTANTS J(H–O–C–H) FOR PVA AND ITS MODEL COMPOUNDS[a,b]

	Chemical shift (—OH), ppm from HMDS					J(H–O–C–H), Hz				
	I	H	S	m end	r end	I	H	S	m end	r end
PVA	4.52	4.33	4.10			3.1	4.3	5.3		
Triol i	4.52			4.37		3.8			4.1	
h		4.33		4.36	4.17		4.7		4.0	5.0
s			4.15		4.18			5.6		4.9
Diol m				4.35					4.1	
r					4.14					4.9

[a] In dimethyl-d_6 sulfoxide at 50°. [b] Abbreviations: I, H, and S denote isotactic, heterotactic, and syndiotactic triads, respectively, while i, h, and s denote isotactic, heterotactic, and syndiotactic isomers of triol, respectively; m, meso; r, racemic.

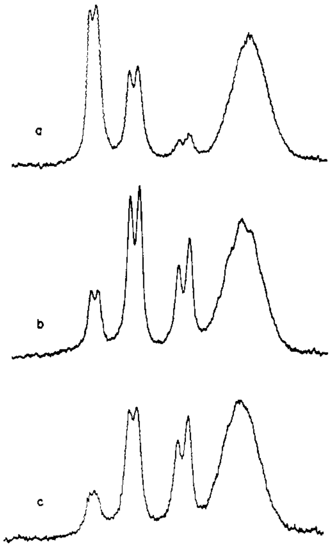

Figure 2. Hydroxyl proton spectra (100 MHz) of poly(vinyl alcohol) synthesized under different conditions: (a) highly isotactic (sample II), (b) slightly syndiotactic (sample III), moderately syndiotactic (sample IV).

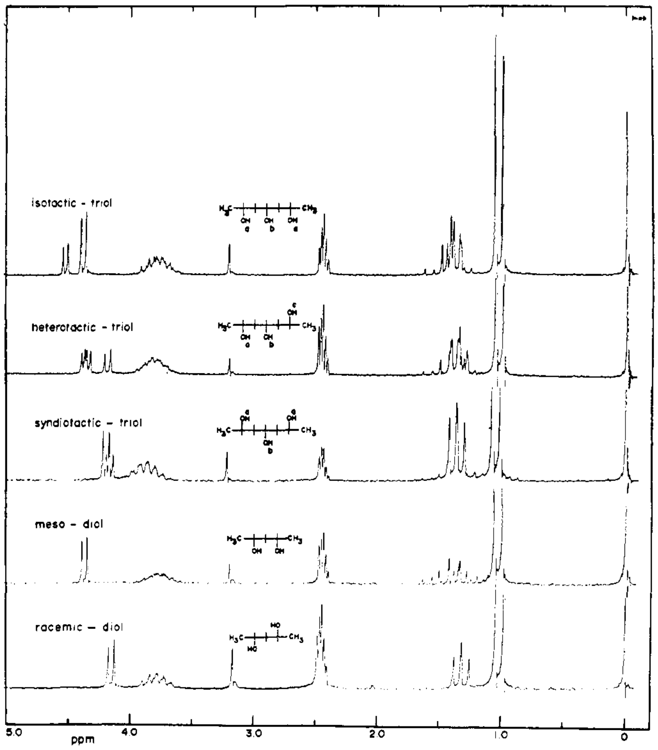

Figure 3. Nmr spectra (100 MHz) of isotactic, heterotactic, and syndiotactic heptane-2,4,6-triol, and of meso and racemic pentane-2,4-diol in dimethyl-d_6 sulfoxide at 50°.

The coupling constants measured from the splittings of the hydroxyl doublets are not the same but differ according to the triad configurations. They are 3.1, 4.3, and 5.3 Hz for isotactic, heterotactic, and syndiotactic triads, respectively.

Model Compounds. Figure 3 shows the 100-MHz spectra of five model compounds. In every spectrum, the hydroxyl resonance appears at lowest field with spin–spin splitting.

The hydroxyl proton resonance of the meso diol splits to a doublet by coupling with methine protons. The methine resonance shows a complicated fine structure. This is interpreted as the A part of the $ABKLX_3$ seven-spin system instead of $AKLX_3$,[22] B being the hydroxyl proton. On the other hand, the methine part of the racemic diol spectrum is simpler, with seven apparent peaks corresponding to the equivalence of two methylene protons (K and L). The hydroxyl doublet of the racemic diol is located at higher field and has a coupling constant larger than that of the meso diol (Table II).

In the cases of the isotactic and syndiotactic triols, the hydroxyl resonance consists of two doublets whose intensities are 1:2. The stronger doublet should be assigned to the terminal hydroxyl protons (a in Figure 3), and the weaker corresponds to the central one. The three hydroxyl protons in the heterotactic triol are different in environment, and hence three doublets with equal intensity are seen in Figure 3. In this case, the assignment cannot be determined from their intensities. But they can reasonably be assigned, with increasing field strength, to the terminal proton of the meso side (a in Figure 3), the central (b), and the terminal one of the racemic side (c), by comparing chemical shifts and coupling constants with those of other isomers. That is to say, the doublets at lowest and highest fields are similar, in nmr parameters, to the terminal protons of the isotactic and syndiotactic triol, respectively. The coupling constant between the central hydroxyl and the methine protons increases in the order of isotactic (3.8 Hz), heterotactic (4.7 Hz), and syndiotactic (5.6 Hz) triols, showing a trend consistent with PVA. All the chemical shifts and coupling constants J(H–O–C–H) at 50° are given in Table II. This temperature was selected simply because the mutual overlap of peaks was smallest.

Discussion

Chemical Shift and Assignment. The chemical shift differences between neighboring triad peaks are so large, about

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(22) Y. Fujiwara and S. Fujiwara, *Bull. Chem. Soc. Jap.*, 37, 1005 (1964).

0.2 ppm, that there is little overlap at 100 MHz. Hence this method provides an easy and accurate determination of the triad sequences in PVA.

The chemical shift differences of these triad peaks are certainly large even in comparison with ^{1}H nmr spectra of other kinds of vinyl and related polymers: the difference between isotactic and syndiotactic peaks is 0.45 ppm for the hydroxyl protons in PVA, while it is 0.21 ppm for the methyl in poly(methyl methacrylate),[23] 0.29 ppm for the methine in poly(styrene),[24] and 0.04 ppm for the acetoxyl in poly(vinyl acetate).[10] In spite of this large separation, there appears no further fine structure to be expected due to higher *n*-ads than triad, say pentad. This is also the case for the 220-MHz nmr spectrum (Figure 1).

Table II indicates that the chemical shifts of the central hydroxyl protons of the triols give good agreement with those of the corresponding peaks in PVA spectra. This confirms the above assignments for PVA. At the same time, such an excellent agreement between polymer and trimer models means that the chemical shifts of hydroxyl protons are mainly determined by triad configurations and are hardly affected by longer range configurations. This is consistent with the fact that microtacticity such as pentad could not be resolved even with measurements at 220 MHz. Therefore, one need not worry about the possibility of unexpected overlaps of microtactic structure, as has been shown in the methylene spectrum of poly(vinyl chloride).[25] However, to determine higher order microtacticity, it is necessary to adopt another method, for example, ^{13}C nmr.

Accuracy and Precision. Because the triad peaks are well resolved and further microtactic structure is absent, the triad tacticity in PVA chain can be determined fairly accurately. In practice, the tacticity values obtained from peak area measurements are probably accurate to within ±2% in absolute value. This error is mainly caused by uncertainty of the base line and boundary lines among the three resonance peaks. However, the precision of relative tacticity can be made within ±0.5% by adopting common base and boundary lines.

Coupling Constant. The vicinal coupling constants *J*(H–O–C–H) are unequal among different configurations in both polymer and model compounds, showing a common trend. This result can be explained in terms of molecular structure, considering the following factors.

(1) Conformation of the Chain Skeleton. Conformational analyses of the main chain have been investigated for dimer and trimer models of vinyl polymers,[14,16,24,26–30] particularly through the temperature dependence of the vicinal coupling constant between methine and methylene protons. For pentane-2,4-diol, Fukuroi, *et al.*,[16] reported that TG (=GT) and TT forms are preferred for meso diol, and TT, GG, and $T\bar{G}$ (=$\bar{G}T$) forms for racemic diol. These respective conformers must exert a different influence upon the environments of hydroxyl groups.

(2) Hydrogen Bonding. The TT and $T\bar{G}$ (=$\bar{G}T$) conformations mentioned above for meso and racemic diols, respectively, were ascribed to the stabilization by intramolecular hydrogen bonding.[16] The formation of hydrogen bonding probably affects the properties of the hydroxyl group, especially its bonding and conformation.

(3) Conformation of the Hydroxyl Group. The dependence of vicinal coupling constant on dihedral angle is now well known.[31] The present differences in *J*(H–O–C–H) may be attributable to the average location of the dihedral angle formed by H–O–C–H, which is imposed probably by the formation of a hydrogen bond with the neighboring hydroxyl group. Recently, some kinds of alcohols were found to have exceptionally small or large values of *J*(H–O–C–H), which seem to arise from intramolecular hydrogen bonding.[32]

(4) Solvent Effects. Remarkable solvent effects on the conformations of diols have been reported.[16] Intermolecular interaction, especially hydrogen bonding with solvent molecules, must be taken into consideration.

Details of these discussions and related data will be published in a subsequent paper.[33]

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(23) H. L. Frisch, C. L. Mallows, F. Heatley, and F. A. Bovey, *Macromolecules*, **1**, 533 (1968); R. C. Ferguson, *ibid.*, **2**, 237 (1969).

(24) F. A. Bovey, F. P. Hood III, E. W. Anderson, and L. C. Snyder, *J. Chem. Phys.*, **42**, 3900 (1965).

(25) F. Heatley and F. A. Bovey, *Macromolecules*, **2**, 241 (1969).

(26) Y. Abe, M. Tasumi, T. Shimanouchi, S. Saitoh, and R. Chujo, *J. Polym. Sci., Part A-1*, **4**, 1413 (1966).

(27) D. Doskočilová, J. Štokr, B. Schneider, H. Pivcová, M. Kolínský; J. Petránek, and D. Lím, *J. Polym. Sci., Part C*, **No. 16**, 215 (1967).

(28) D. Doskočilová, S. Sýkora, H. Pivcová, B. Obereigner, and D. Lím, *ibid.*, **No. 23**, 365 (1968).

(29) B. Schneider, J. Štokr, D. Doskočilová, S. Sýkora, J. Jakeš, and M. Kolínský, *ibid.*, **No. 22**, 1073 (1969).

(30) H. Pivcová, M. Kolínský, D. Lím, and B. Schneider, *ibid.*, **No. 22**, 1093 (1969).

(31) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(32) N. L. Bauld and Y. S. Rim, *J. Org. Chem.*, **33**, 1303 (1968); R. D. Stolow and A. A. Gallo, *Tetrahedron Lett.*, **29**, 3331 (1968); R. R. Fraser, M. Kaufman, P. Morand, and G. Govil, *Can. J. Chem.*, **47**, 403 (1969); G. A. Neville and D. V. C. Awang, *Org. Magn. Resonance*, **2**, 341 (1970).

(33) NOTE ADDED IN PROOF. After this article had been submitted, a similar work was published in *J. Polym. Sci., Part B*, **10**, 385 (1972), by J. R. Demember, H. C. Haas, and R. L. McDonald. They had independently studied the tacticity of PVA (polymer but not model compounds) by nmr of the hydroxyl protons.