Microstructures in Poly(vinyl alcohol-*co*-crotonic acid) Studied by ^{1}H NMR and ^{13}C NMR

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ABSTRACT: Microstructural analysis was carried out on a copolymer of vinyl alcohol and a small amount of crotonic acid. ^{1}H NMR spectroscopy at 90 MHz and ^{13}C NMR spectroscopy at 125.76 MHz were used to examine the various kinds of γ-lactone structures formed in the copolymer. The ^{13}C NMR spectra were useful for the trace characterization of irregular structures, e.g., 1,2-glycol linkages and short branches, in the poly(vinyl alcohol) sequence.

Introduction

Usually poly(vinyl alcohol) (PVA) is prepared by radical polymerization of vinyl acetate (VAc) followed by saponification of poly(vinyl acetate) (PVAc).[1] Chemical and physical properties of PVA are strongly influenced by the degree of polymerization as well as the degree of saponification. Molecular polarity, characteristic of PVA, can be much improved by copolymerizing VAc with a small amount of vinyl compound containing a carboxyl group. The carboxyl group in the copolymer may react with the neighboring hydroxyl group to form a lactone structure.[2,3] Matsumoto[2] and Maruhashi et al.[4] estimated the lactone content in various kinds of copolymers on the basis of data from conductometric titration and infrared spectroscopy, respectively. Nevertheless, the lactone structure and trace amounts of irregular structures in poly(vinyl alcohol-*co*-crotonic acid) (PVA–CA) have never been directly observed.

In the present work, VAc was copolymerized with crotonic acid (CA), and the resulting copolymer (PVAc–CA) was saponified in the presence of methanol. ^{1}H NMR and ^{13}C NMR spectra of PVA–CA were measured to examine not only the lactone structure formed by the intramolecular reaction of the carboxyl group with the hydroxyl group but also the irregular structures arising from 1,2-glycol bonding and short branching in the course of chain propagation of VAc. Although the structural behavior of the methyl group in the CA unit was sensitively reflected in the 90-MHz ^{1}H NMR spectra, it was difficult to discriminate the proton signals of irregular structures from those of the PVA sequence. Hence, quantitative analysis of PVA–CA was carried out through 125.76-MHz ^{13}C NMR spectra. The latter method was very powerful in structural elucidation of trace constituents in the polymer even at contents less than 0.1 mol %.

Experimental Section

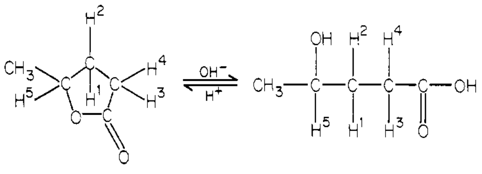
VAc and CA, manufactured by Wako Pure Chemical Industries Ltd., were copolymerized in acetone at a prescribed molar ratio in the presence of the radical initiator α,α′-azobis(isobutyronitrile). In order to replace the acetyl group in the resulting copolymer by the hydroxyl group, saponification was performed in methanol at 40 °C by adding sodium methoxide catalyst. PVA, used for reference, was produced in a conventional manner at Kuraray Co., Ltd. γ-Valerolactone, obtained from Nakarai Chemicals Ltd., was used to aid the spectral analysis. NMR samples were prepared by dissolving γ-valerolactone, PVA, or PVA–CA in spectroscopic grade deuterium oxide (E. Merck, Japan) at a concentration of 5.0, 13.0, or 13.0 wt %, respectively. Tetramethylsilane was used as a standard for calibration of both the ^{1}H NMR and the ^{13}C NMR spectra.

^{1}H NMR spectra of γ-valerolactone and PVA–CA were recorded on a Varian EM390 NMR spectrometer at 90 MHz. ^{13}C NMR spectra of PVA were measured with a JEOL FX-200 NMR spectrometer at 50.15 MHz under the following conditions: data points, 16.4K; spectral width, 10.0 kHz; pulse width, 20 μs; pulse interval, 2 s; number of scans 25 300. ^{13}C NMR spectra of PVA–CA were observed with a Bruker WM-500 NMR spectrometer at 125.76 MHz under the following conditions: data points, 32K; spectral width, 29.4 kHz; pulse width, 40 μs; pulse interval, 2 s; number of scans, 30 200.

Results and Discussion

^{1}H NMR Study on Lactone Formation. It is widely known for a number of carboxylic acids having the hydroxyl group that lactone is formed as a result of the intramolecular reaction of the carboxyl group with the hydroxyl group. However, a lactone structure for the copolymer of vinyl alcohol and olefinic acid has never been directly observed. Prior to the structural investigation of PVA–CA, tautomerism between γ-valerolactone and γ-hydroxyvaleric acid was examined as a model for the PVA–CA case.

The 90-MHz ^{1}H NMR spectrum of γ-valerolactone dissolved in deuterium oxide varied with the concentration of sodium hydroxide as shown in Figure 1. For convenience, protons of the compounds were numbered as



γ-valerolactone

On the basis of the results of spin simulation for the ^{1}H NMR signals of γ-valerolactone, values of chemical shifts (ν) and spin–spin coupling constants (J) were determined as follows: $\nu(CH_3) = 1.40$, $\nu(H^1) = 1.83$, $\nu(H^2) = 2.35$, $\nu(H^3) = 2.56$, $\nu(H^4) = 2.56$, $\nu(H^5) = 4.80$ ppm; $J(CH_3\text{–}H^5) = 6.3$, $J(H^1\text{–}H^2) = -12.0$, $J(H^1\text{–}H^3) = 9.0$, $J(H^1\text{–}H^4) = 9.0$, $J(H^1\text{–}H^5) = 6.8$, $J(H^2\text{–}H^3) = 7.8$, $J(H^2\text{–}H^4) = 7.8$, $J(H^2\text{–}H^5) = 7.8$, $J(H^3\text{–}H^5) = 0$, $J(H^4\text{–}H^5) = 0$ Hz.[5] On addition of sodium hydroxide to the deuterium oxide solution of γ-valerolactone, ^{1}H NMR signals of γ-hydroxyvaleric acid appeared, with a signal reduction of γ-valerolactone. Simulated values for the chemical shifts and the spin–spin coupling constants of the proton signals of γ-hydroxyvaleric acid were as follows: $\nu(CH_3) = 1.16$, $\nu(H^1) = 1.69$, $\nu(H^2) = 1.72$, $\nu(H^3) = 2.20$, $\nu(H^4) = 2.25$, $\nu(H^5) = 3.80$ ppm; $J(CH_3\text{–}H^5) = 6.3$, $J(H^1\text{–}H^2) = -12.0$, $J(H^1\text{–}H^3) = 7.8$, $J(H^1\text{–}H^4) = 7.8$, $J(H^1\text{–}H^5) = 6.3$, $J(H^2\text{–}H^3) = 7.8$, $J(H^2\text{–}H^4) = 7.8$, $J(H^2\text{–}H^5) = 6.3$, $J(H^3\text{–}H^4) = -12.0$, $J(H^3\text{–}H^5) = 0$, $J(H^4\text{–}H^5) = 0$ Hz. It was noted that all proton signals of γ-valerolactone shifted toward lower frequency because of ring opening and that the original spectrum was restored by the addition of hydrochloric acid, leading to ring formation. These results supported the observation that a reversible interconversion took place between γ-valerolactone and γ-hydroxyvaleric acid and that this depended upon the solution conditions.

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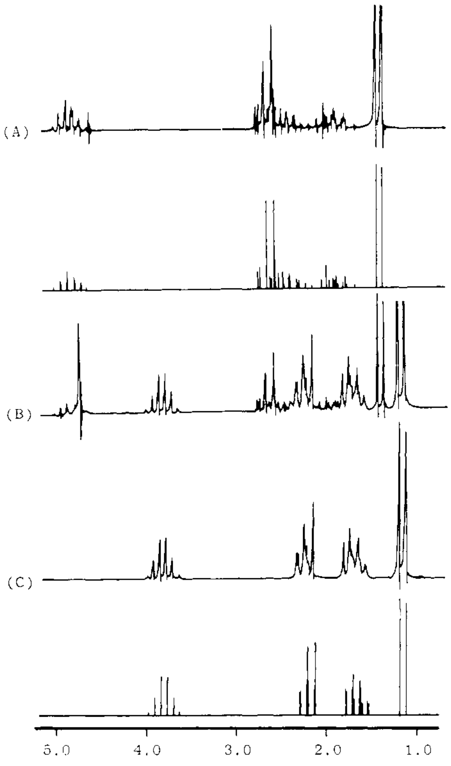


Figure 1. 90-MHz ^{1}H NMR spectra of (A) γ-valerolactone in pure solution, (B) γ-valerolactone and γ-hydroxyvaleric acid in the presence of equimolar sodium hydroxide, and (C) γ-hydroxyvaleric acid in the presence of excess sodium hydroxide measured in deuterium oxide at 27 °C. Simulated spectra for γ-valerolactone and γ-hydroxyvaleric acid are shown below the spectra of (A) and (C), respectively.

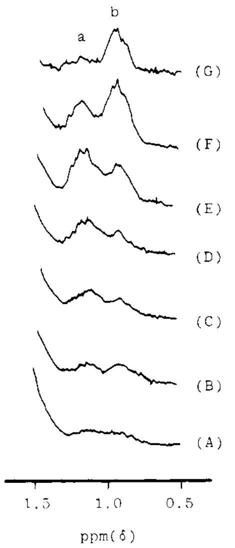


Figure 2. 90-MHz ^{1}H NMR spectra of methyl groups in PVA-CA with prepared CA contents of (A) 3.7, (B) 4.7, (C) 6.5, (D) 7.0, (E) 11.1, (F) 12.8, and (G) 18.8 mol % measured in deuterium oxide at 27 °C.

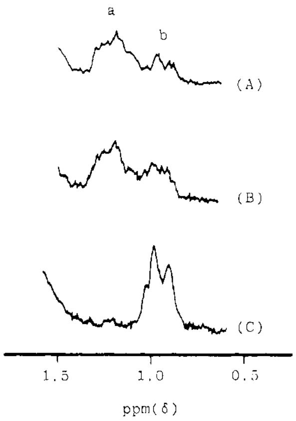


Figure 3. 90-MHz ^{1}H NMR spectra of methyl groups in PVA-CA with the prepared CA content of 11.1 mol % (A) in the presence of excess hydrochloric acid, (B) in pure solution, and (C) in the presence of excess sodium hydroxide measured in a 1/1 (v/v) mixture of deuterium oxide and dimethyl-d_6 sulfoxide at 80 °C.

Figure 2 illustrates that the methyl signals of PVA-CA dissolved in deuterium oxide fall into two groups, one appearing at 0.92 ppm and the other at 1.16 ppm in the ^{1}H NMR spectrum. With increasing CA content in PVA-CA, the group with the lower frequency (a) increased in intensity, accompanied by a decrease in intensity of the group with the higher frequency (b). When sodium hydroxide was added to a deuterium oxide solution of PVA-CA with a fixed CA content, group b was converted into group a as can be seen from Figure 3, while an opposite phenomenon occurred on addition of hydrochloric acid rather than sodium hydroxide. By analogy with the tautomerism between γ-valerolactone and γ-hydroxyvaleric acid, these results indicate that the carboxyl and the hydroxyl groups in PVA-CA undergo an intramolecular reaction to form the lactone structure and that the reaction is promoted in the presence of hydrochloric acid and reversed in the presence of sodium hydroxide. Thus, group a is assigned to methyl protons in the open form and group b to those in the closed form.

The lactone structure in PVA-CA is not always uniform because of heterogeneous arrangements of the monomeric units as well as unsymmetrical configurations of the functional groups. However, the most probable structure is presumably γ-lactone, according to the general rule that γ-lactone with a five-membered ring is much more stable than β-lactone with a four-membered ring and δ-lactone with a six-membered ring.[6] Fine structure on the ^{1}H NMR signals of the groups a and b suggests that several kinds of configurations of the functional groups are present in both the open and the closed forms.

^{13}C NMR Study on Lactone Formation. Irregular structures in the PVA sequence such as 1,2-glycol linkages and short branches are generally so few in number that it is almost impossible to observe them by 90-MHz ^{1}H NMR spectroscopy. In order to study these microstructures as well as the lactone structure, ^{13}C NMR spectra of PVA-CA were measured at 125.76 MHz, which is at present the highest frequency available for measurement, corresponding to 500 MHz for ^{1}H NMR.

From the values of reactivity ratios of VAc and CA, $R_{VAc} = 0.3$ and $R_{CA} = 0.01$, determined by Ham,[7] the product of the reactivity ratios is calculated at $R_{VAc}R_{CA} = 0.003$, much less than unity. Therefore, the propagation probability of the monomer CA to the CA terminal of the polymer chain would be negligibly small during the copolymerization of VAc and CA. When the CA content in PVA-CA is relatively small, it is reasonable to neglect the CA-CA bonding compared with the CA-VA bonding. A VA-CA-VA sequence contains four asymmetric carbon nuclei, so there are 16 kinds of triad sequences, classifiable into two groups in the following manner. According to the Fischer projection, the symbols E and T are used to denote erythro and threo combinations of the methyl and the carboxyl groups in the CA unit, respectively. The symbols e and t indicate erythro and threo combinations of the methyl, the carboxyl, and the hydroxyl groups between the neighboring CA and VA units, respectively. The direction

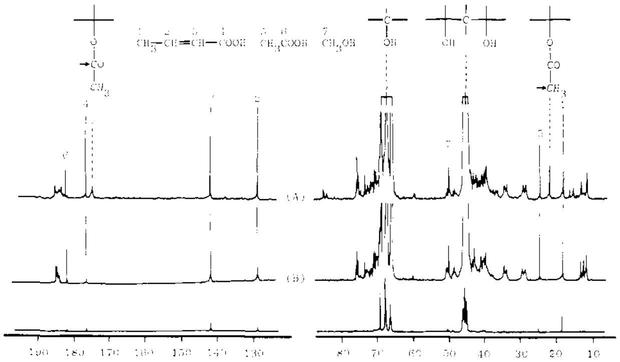


Figure 4. 125.76-MHz ^{13}C NMR spectra of PVA–CA with a prepared CA content of 5.0 mol % (A) in pure solution and (B) in the presence of excess sodium hydroxide measured in deuterium oxide at 27 °C and expanded 16 times in height. The original spectrum for (B) is shown at the bottom of the figure.

of the CA unit is designated by an arrow, while that of the VA unit is fixed as shown by the chemical formulas, ignoring a slight irregularity in the propagation of VAc.

group I $—CH_2CH(OH)CH(CH_3)CH(COOH)CH_2CH(OH)—$

$e\overrightarrow{E}e,\quad e\overrightarrow{E}t,\quad t\overrightarrow{E}e,\quad t\overrightarrow{E}t$

$e\overrightarrow{T}e,\quad e\overrightarrow{T}t,\quad t\overrightarrow{T}e,\quad t\overrightarrow{T}t$

group II $—CH_2CH(OH)CH(COOH)CH(CH_3)CH_2CH(OH)—$

$e\overleftarrow{E}e,\quad e\overleftarrow{E}t,\quad t\overleftarrow{E}e,\quad t\overleftarrow{E}t$

$e\overleftarrow{T}e,\quad e\overleftarrow{T}t,\quad t\overleftarrow{T}e,\quad t\overleftarrow{T}t$

It is noteworthy that the triad sequences in group I form γ-lactone alone, whereas those in group II form β- and δ-lactones. Since it seems reasonable even in PVA-CA to assume that γ-lactone is much more stable than β- and δ-lactones, eight kinds of sequences in group I are treated as actual precursors of lactones. Each of the sequences can form two kinds of γ-lactones containing a methyl group inside or outside the lactone ring, and accordingly the γ-lactone in PVA–CA may have 16 kinds of configurations.

As shown in Figure 4, various kinds of polymer structures were observed in the 125.76-MHz ^{13}C NMR spectra of PVA–CA with a prepared CA content of 5.0 mol %. It was indicated from the extremely sharp signals in Figure 4 that CA, acetic acid, and methanol were mixed with PVA–CA. Signals of PVA–CA appearing in the frequency ranges 11.0–22.0, 28.0–47.5, 65.0–88.0, and 174.5–187.5 ppm could be roughly grouped into methyl, methylene, methine, and carbonyl carbon signals, respectively. Two sets of large peaks in the 44.5–46.0- and 66.0–69.0-ppm ranges were, respectively, consistent with methylene and methine carbon signals of PVA, which had been measured at frequencies lower than 125.76 MHz.[8] Signals at 21.9 and 174.8 ppm, converted into signals of acetic acid in the presence of sodium hydroxide, were assigned to methyl and carbonyl carbons in the acetyl group, respectively, arising from incompleteness in saponification of PVAc–CA.

The complicated line shapes of the small signals can be seen more clearly in the expanded spectra shown in Figures 5 and 6. Since signals related to CA units and γ-lactones were not observed in the 50.15-MHz ^{13}C NMR spectrum of PVA as shown in Figure 7, they could be easily discriminated from signals due to the PVA sequence. All the carbon signals of the γ-lactones disappeared on addition of sodium hydroxide, so they were assignable as depicted in Figure 5A. At least eight kinds of signals attributable to methyl carbons in γ-lactones appeared at 12.4, 13.8, 14.3, 14.6, 15.2, 15.4, 16.0, and 16.2 ppm, and four of them located on the higher frequency side were relatively large in peak area. Three pairs of signals at 36.3 and 36.7 ppm, 84.2 and 85.1 ppm, and 185.5 and 185.9 ppm were assigned to γ-lactone carbons, i.e., β or β′ carbons containing a methyl group, γ carbons forming an ester bond, and carbonyl carbons, respectively. α-Carbon signals of γ-lactones might be buried in the methylene carbon signals of the PVA sequence.

Signals of methyl carbons in CA units, open forms of lactones, were observed at 11.0–13.5 ppm. A signal that

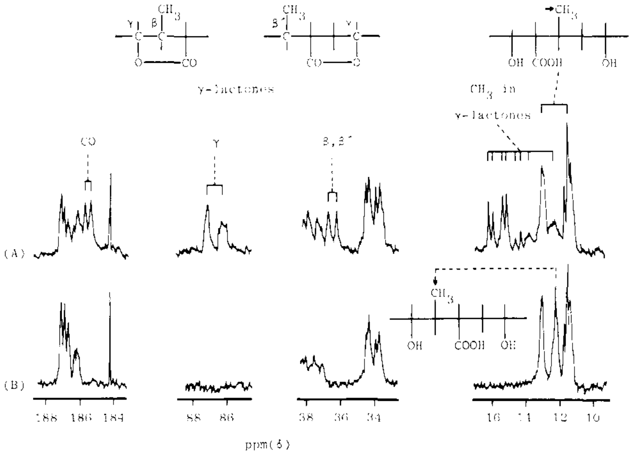


Figure 5. 125.76-MHz ^{13}C NMR spectra of PVA–CA with a prepared CA content of 5.0 mol % (A) in pure solution and (B) in the presence of excess sodium hydroxide indicating signals related to lactone formation in the spectra shown in Figure 4.

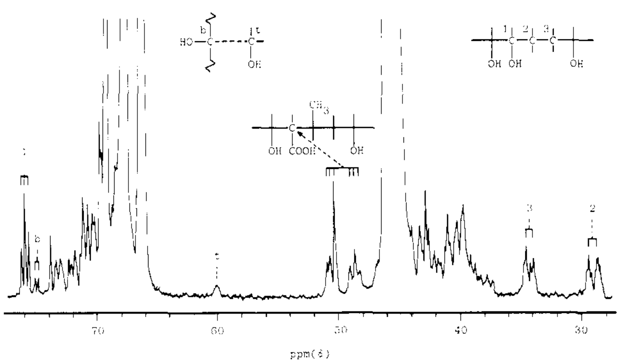


Figure 6. 125.76-MHz ^{13}C NMR spectrum of PVA–CA with a prepared CA content of 5.0 mol % in the presence of excess sodium hydroxide indicating methylene and methine carbon signals in the spectrum shown in Figure 4B.

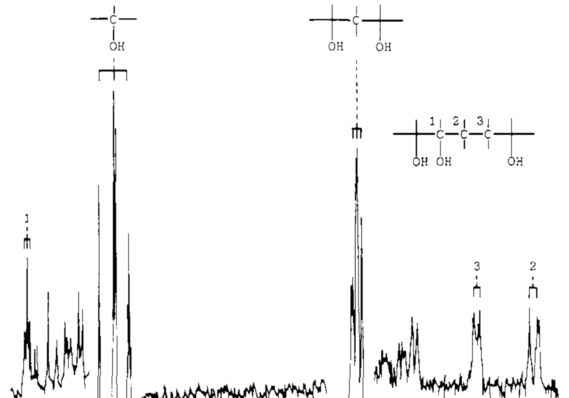
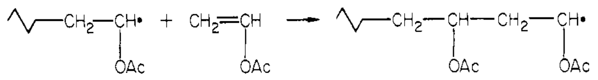


Figure 7. 50.15-MHz ^{13}C NMR spectrum of PVA measured in deuterium oxide at 27 °C.

appeared at 12.4 ppm on addition of sodium hydroxide was assigned to a methyl carbon in CA units belonging to group I. Peak areas of signals at 11.3, 11.6, 11.8, 13.0, 48.0, 48.4, 48.8, 50.1, 50.4, and 50.6 ppm were only slightly affected by the presence of sodium hydroxide. The sum of the peak areas of the former four signals was nearly equal to that of the latter six signals, excluding an overlapped signal of methanol at 50.1 ppm. The chemical shift value for the α carbon in CA units belonging to group II was calculated at ca. 54 ppm,[10] though somewhat uncertain in precision. Hence, the signals at 11.3, 11.6, 11.8, and 13.0 ppm and those at 48.0, 48.4, 48.8, 50.1, 50.4, and 50.6 ppm were, respectively, assigned to methyl carbons and α carbons in the CA units belonging to group II. Five to six kinds of signals at 186.1–187.2 ppm were assignable to carbonyl carbons in CA units, but it was difficult to distinguish between groups I and II. A synthesis of model compounds for PVA–CA is planned, so as to perform a more precise study of the lactone structure.

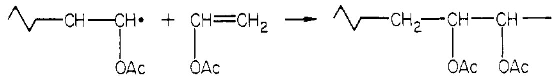
^{13}C NMR Study on Irregular Structures. VAc undergoes predominantly head-to-tail addition polymerization to produce PVAc with a normal chain structure, while small amounts of irregular structures are occasionally generated in the polymer as a result of a head-to-head addition followed by a tail-to-tail addition of VAc.[9]

head-to-tail addition



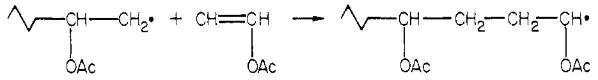
$$\sim\!\!\sim CH_2-\underset{OAc}{CH}\cdot + CH_2{=}\underset{OAc}{CH} \rightarrow \sim\!\!\sim CH_2-\underset{OAc}{CH}-CH_2-\underset{OAc}{CH}\cdot$$

head-to-head addition



$$\sim\!\!\sim CH-\underset{OAc}{CH}\cdot + \underset{OAc}{CH}{=}CH_2 \rightarrow \sim\!\!\sim CH_2-\underset{OAc}{CH}-\underset{OAc}{CH}-CH_2\cdot$$

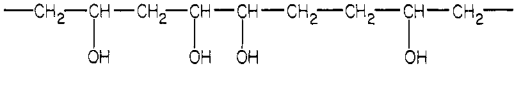
tail-to-tail addition



$$\sim\!\!\sim \underset{OAc}{CH}-CH_2\cdot + CH{=}\underset{OAc}{CH} \rightarrow \sim\!\!\sim \underset{OAc}{CH}-CH_2-CH_2-\underset{OAc}{CH}\cdot$$

Through the saponification of the acetyl group, the normal part of PVAc is converted into PVA with a regular structure composed of a series of 1,3-glycol units, and a few 1,2-glycol linkages as well as 1,4-glycol linkages are formed in PVA from the irregular parts of PVAc. Although the 1,2-glycol linkage in PVA was assayed by means of a periodic acid method,[9] none of the nondestructive methods has been successfully applied to the structural analysis.

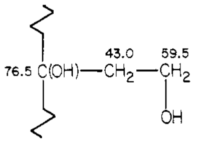
In a similar manner, the 1,2-glycol linkage would be formed in PVA–CA prepared by the alcoholysis of PVAc–CA. According to the method of Levy and Nelson,[10] chemical shift values for the ^{13}C NMR signals relating to the 1,2-glycol structure were calculated in ppm as follows.



$$-\overset{45.7}{CH_2}-\underset{OH}{\overset{66.4}{CH}}-\overset{42.4}{CH_2}-\underset{OH}{\overset{75.0}{CH}}-\underset{OH}{\overset{78.1}{CH}}-\overset{30.5}{CH_2}-\overset{34.7}{CH_2}-\underset{OH}{\overset{69.0}{CH}}-\overset{46.1}{CH_2}-$$

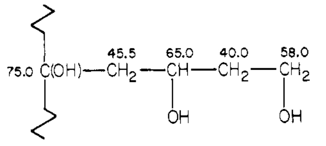
The calculated values of chemical shifts were in fair agreement with the observed ones, so the ^{13}C NMR signals were assigned as illustrated in Figure 6. Similar results were obtained from the 50.15-MHz ^{13}C NMR spectrum of PVA shown in Figure 7, supporting the above assignments. Splitting of the carbon signals could be attributed to the conformational effect of bonds surrounding the 1,2-glycol linkage.

With respect to PVA, branching in a polymer chain is one of the longstanding questions. It has been generally accepted that two kinds of branches, short and long, are present in the polymer chain of PVAc and that saponification of PVAc has no effect on the former but removes the latter formed on the acetyl group.[12] On the basis of a back-biting mechanism proposed by Roedel,[11] the short branch in PVA may take either of the following structures designated by B_1 and B_2. The structure B_1 corresponds to a monomer unit of vinyl alcohol; the structure B_2 is a dimer.



$$\overset{76.5}{C}(OH)-\overset{43.0}{CH_2}-\underset{OH}{\overset{59.5}{CH_2}}$$

B_1



$$\overset{75.0}{C}(OH)-\overset{45.5}{CH_2}-\underset{OH}{\overset{65.0}{CH}}-\overset{40.0}{CH_2}-\underset{OH}{\overset{58.0}{CH_2}}$$

B_2

Observing a ^{1}H NMR signal attributable to the α-methylene protons in a β-hydroxyethyl group, Adelman and Ferguson regarded the structure of the short branch in PVA as B_1.[12] On the contrary, Nozakura et al. supported B_2 by comparing the ^{1}H NMR signal with that of a model compound.[13] ^{13}C NMR signals due to short branches have never been detected because of their paucity.[13]

Chemical shift values of model compounds for B_1 and B_2 measured at 25 MHz[8a,13b] are given in ppm in the chemical formulas of B_1 and B_2, respectively. As shown in Figure 6, two kinds of small signals were observed at 60.0 and 75.0 ppm in the 125.76-MHz ^{13}C NMR spectrum of PVA–CA. By comparison of the chemical shift values with those of the model compounds, the singlet signal at 60.0 ppm and the doublet signal at 75.0 ppm were assigned to the terminal methylene carbon and the carbon located at the branch point, respectively. However, carbon signals of the short branch other than those two were not discriminated from a number of complex signals attributable to the PVA sequence and a variety of CA units. Therefore, it is impossible to determine the definite structure of the short branch unless the ^{13}C NMR spectrum of PVA is also measured at 125.76 MHz.

Composition of PVA–CA. The ^{1}H NMR method is an excellent method for the quantitative analysis of copolymers. When Fourier transform ^{13}C NMR spectroscopy is used to determine the copolymer composition, special care has to be devoted to the spin–lattice relaxation time (T_1) and the nuclear Overhauser enhancement (NOE).[10] There are two reasons, long T_1 and variable NOE, for loss of correlation between the number of carbon nuclei comprising a peak and the integrated peak area. When T_1 is close to the pulse interval, even small differences in T_1 values among the different nuclei will lead to significant differences in peak areas. The NOE is usually complete for all protonated carbons in molecules containing more than a few carbons, indicating the dominance of dipole–dipole spin–lattice relaxation.

Both 90-MHz ^{1}H NMR and 125.76-MHz ^{13}C NMR spectra were utilized in the quantitative analysis of PVA–CA prepared from 95.0 mol % of VAc and 5.0 mol % of CA. In the 90-MHz ^{1}H NMR spectrum, where it was difficult to distinguish proton signals of the irregular structures from those of the PVA sequence, the copolymer composition was assayed from peak areas of the methylene protons in the VA unit and the methyl protons in the CA, γ-lactone, and VAc units as follows: VA units forming the PVA sequence, the 1,2-glycol linkage, and the short branch, 94.2 mol %; CA units, 2.8 mol %; γ-lactone units, 1.3 mol %; VAc units, 1.7 mol %. In order to avoid problems related to T_1 and NOE, the 125.76-MHz ^{13}C NMR spectrum was measured at relatively long pulse intervals (2 s), and the copolymer composition was assayed from peak areas of the protonated carbons, i.e., the methylene carbons in PVA sequences, 1,2-glycol linkages, and short branches and the methyl carbons in CA, γ-lactone, and VAc units,

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as follows: VA units forming the PVA sequence, 92.0 mol %; 1,2-glycol linkages, 2.0 mol %; short branches, 0.4 mol %; CA units, 2.8 mol %; γ-lactone units, 1.4 mol %; VAc units, 1.4 mol%. Thus, the results from the 125.76-MHz ^{13}C NMR spectrum agreed with those from the 90-MHz ^{1}H NMR spectrum within experimental error.

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Structural Studies of Poly(ethylenimine). 2. Double-Stranded Helical Chains in the Anhydrate

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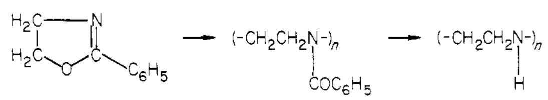
ABSTRACT: X-ray structural analysis of linear poly(ethylenimine) in the anhydrous state revealed that the polymer chains exist as double-stranded helices, distinct from the fully extended form in the sesquihydrate and the dihydrate. One molecular chain in the anhydrate takes practically a 5/1 helical form (five monomeric units per turn) with an identity period of 0.958 nm, and a pair of chains possessing the same helical sense forms a double strand with a relative rotation of 180° about the chain axis at the same level. The formation of the double-stranded helices in the anhydrate is ascribable to N–H···N hydrogen bonding between the two polymer chains in the double strand. The crystals of the anhydrate are orthorhombic, with cell dimensions a = 2.98 nm, b = 1.72 nm, and c (fiber axis) = 0.479 nm. The space group is D_{2h}^{24}-$Fddd$, and there are 40 monomeric units (8 strands) in the unit cell. The observed fiber period of 0.479 nm, which is half the length of the identity period of the 5/1 helix, is interpreted in terms of statistical dispositions of the strands; two diffuse layer lines interpreted by doubling the fiber period are well explained by this statistical structure. In more detail, the period estimated from the intervals of the diffuse layer lines is not exactly twice the fiber period; a 69/14 helical chain (4.93 monomeric units per turn) may be a better approximation, and probably the double strand has no periodicity. The large unit cell is interpreted in terms of hexagonal-like closest packing of the right-handed and left-handed strands. The X-ray diffraction study also revealed that a reversible transformation between the double-stranded helical chains and the extended chains on absorption of water vapor and dehydration is attained in the solid state, with retention of the orientation of the chain axis.

Linear poly(ethylenimine) (PEI) is remarkably hygroscopic; it exists as one of several hydrates or their mixture in air. In a previous paper,[1] we reported the crystal structures of two hydrates of PEI, viz., the sesquihydrate $(-CH_2CH_2NH-\cdot 1.5H_2O)_n$ and the dihydrate $(-CH_2CH_2NH-\cdot 2H_2O)_n$. The NH groups of PEI can behave as both proton donors and proton acceptors for hydrogen bonding, and, in fact, all of the NH groups in both hydrates participate in N–H···O and N···H–O hydrogen bonding with water, irrespective of the difference in their EI to water mole ratio. Therefore, the structure of the anhydrate and especially the behavior of the NH groups in the anhydrous state are of much interest. However, besides the hygroscopic feature, the low molecular weight PEI used in the previous study has made it difficult to prepare a uniaxially oriented specimen of the anhydrate, which is indispensable for the X-ray structure analysis. Recently, a high molecular weight PEI enabled us to prepare uniaxially oriented samples of the anhydrate by dehydration of uniaxially oriented samples of the hydrates, and X-ray structure analysis of the anhydrate revealed that the polymer chains exist as double-stranded helices.

Experimental Section

The sample used in this study was obtained from 2-phenyl-2-oxazoline, and the molecular weight was estimated to be about



1 × 10^5. The details of the synthesis and polymer characterization will be reported elsewhere.[2] The original PEI sample was melted and dehydrated at about 100 °C in vacuo and was subjected to quenching in dry ice/methanol followed by stretching about five times. The sample thus obtained was highly oriented but tended

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