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THE STUDY OF MICROSTRUCTURES OF POLY(VINYL ALCOHOL) BY NMR

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The study of microstructures of poly(vinyl alcohol) by NMR

ABSTRACT: The microstructures of various poly(vinyl alcohol) samples have been studied by ^1H and ^{13}C -NMR techniques. Spectra taken in a mixed solvent ($\text{d}_6\text{-DMSO}^\dagger$ and D_2O) show marked changes with changing the ratio $\text{d}_6\text{-DMSO}$ to D_2O , which may be due to conformation changes. The concentration of 1,2-glycol linkages has been determined quantitatively in the ^1H -NMR spectrum. Weak features, arising from endgroups formed by the chain transfer reactions to monomer or polymer, have been identified in the spectrum. One of the major endgroups has been determined to exist in the γ -lactone form under the acidic condition, while in the carboxylic acid sodium salt form under the alkaline condition. No free carboxylic acid group has been detected. The short chain branches consisting of two monomer units (butyl branches) have been also estimated. Other structural irregularities, polyene structures which arising from the heat treatment, were analyzed by a two-dimensional NMR(COSY) method.

INTRODUCTION

Usually poly(vinyl alcohol) is prepared by radical polymerization of vinyl acetate followed by saponification of poly(vinyl acetate) (ref.1). Chemical and physical properties of poly(vinyl alcohol) are strongly influenced by the degree of polymerization as well as the degree of saponification. Moreover it has been clear that the microstructures of the polymer chain may be an important factor to determine their properties (ref.2-4). As shown in Fig. 1, there are many kinds of microstructures in poly(vinyl alcohol), the objectives being the determination of tacticity and detection of irregular structures such as end groups, short branches, polyene structure and reversed monomer sequences. NMR is the most powerful method available for characterizing microstructures of polymer. In this paper, the results of ^1H and ^{13}C -NMR study on the microstructures of poly(vinyl alcohol) are presented.

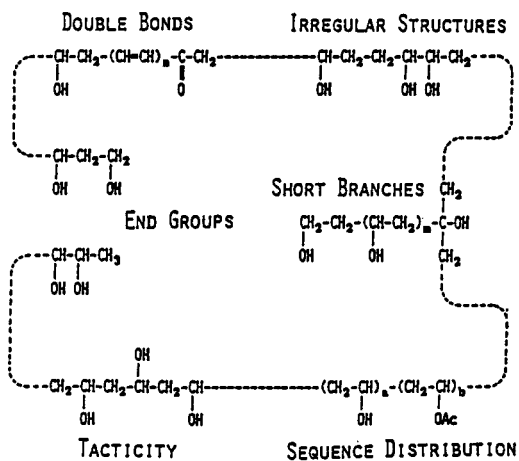


Fig. 1

Microstructures of poly(vinyl alcohol).

EXPERIMENTAL

Materials

PVA-A,B (PVA-117, 103, Kuraray Co.) and PVA-C (#17-99, Shanxi Vinylon Co., Shanxi, China) are commercially available samples, which were prepared by hydrolysis of radical polymerized poly(vinyl acetate) (PVAc). PVA-D and E were derivatives of PVAc synthesized from vinyl acetate, VAc, in an alcohol solution. PVA-D was obtained in methanol at -78°C in the presence of triethylborane, and PVA-E in ethanol at 200°C without an initiator. PVA-F was derived from PVAc, which was polymerized at 60°C on addition of a small

$^\dagger \text{d}_6\text{-DMSO} = (\text{CD}_3)_2\text{SO}$

amount of acetaldehyde as a chain transfer agent. 2,3-Hexanediol, 2,5-Hexanediol, and threo- and erythro-1,3,4-hexanetriol were used as model compounds of neighboring 1,2-glycol structure. They were synthesized in our laboratory or were purchased, if available.

Measurements

The 400 and 500 MHz ^1H -NMR spectra were obtained at 60°C with JEOL JNM-GX400 and JNM-GX500 spectrometers. Sample concentration was 5%(w/v) in perdeuteriated dimethyl sulfoxide (d_6 -DMSO) or D_2O , which provides the internal lock signal. Approximately 256 - 10000 free induction decays were accumulated using a pulse width of 4 μs (corresponding to a flip angle of 45°), a pulse interval of 5.0 s, and spectral width of 8000-10000 Hz. Homonuclear 2D correlated spectroscopy (COSY) was performed by using the standard sequence $\text{D}-90^\circ - \tau_1 - 45^\circ - \text{FID}$ (ref.5). The delay time (D) was set to 1.5s. The first 90° pulse causes each proton to precess at its initial frequency during τ_1 . The second 45° pulse causes magnetization exchange between protons that are J -coupled to each other. The initial data matrix was 3500Hz (1K data point) in both dimensions, and digital resolution after zero-filling was 3.5 Hz/point. A sine-bell filtering function was used in both dimensions. The 100 and 125 MHz ^{13}C -NMR spectra were obtained with JNM-GX400 and JNM-GX500. The sample concentration was 10%(w/v) in d_6 -DMSO and/or D_2O . The spectra were recorded at 80°C , using pulse widths of 10 μs (pulse angle 45°) and pulse intervals of 3.0 s. Spectra were obtained after accumulation of 5000 - 20000 scans. Tetramethylsilane, TMS, was added as an internal standard to the d_6 -DMSO solution, and sodium 3-trimethylsilylpropionate, TSP, to the D_2O solution. In performing quantitative ^{13}C -NMR measurements, one must take into account differences in Nuclear Overhauser effect (NOE) and spin-lattice relaxation times (T_1). Neither T_1 nor NOE value has been determined, but one additional ^{13}C -NMR experiment was performed on PVA with a much longer delay time (10s) and gating off the decoupler to remove the NOE. The results were identical with those obtained by ^{13}C -NMR with the standard method.

TACTICITY

Regarding ^1H -NMR spectra, a number of workers (ref. 6-8) showed that when $\text{DMSO}-d_6$ is used as a solvent, three distinct hydroxyl proton resonance, corresponding to triad sequences, can be observed. ^{13}C -NMR spectra of PVA samples were taken at 22.6 and 67.9 MHz in $\text{DMSO}-d_6$ solution by Wu and Sheer (ref.9). They concluded that the methine carbon atom resonance was interpreted in terms of pentads. Ovenall (ref.10) has reported an investigation on the microstructure of atactic and highly isotactic poly(vinyl alcohol) samples by 100 MHz ^{13}C -NMR. The resolution enhanced spectra were well resolved at the heptad and hexad tacticity sequences. We have reported (ref. 11) the ^{13}C -NMR spectra of PVA dissolved in D_2O and $\text{DMSO}-d_6$ at 100MHz. Fig.2 illustrates variations of the methylene carbon atom resonances of PVA-A when the solvent ratio D_2O to $\text{DMSO}-d_6$ is changed. With increasing $\text{DMSO}-d_6$ content, the peaks due to three m-centered tetrads shift upfield. Considering the non hydrogen atom γ -gauche interaction reported by Tonelli (ref.12), we concluded that some conformation changes have occurred in the polymer solution.

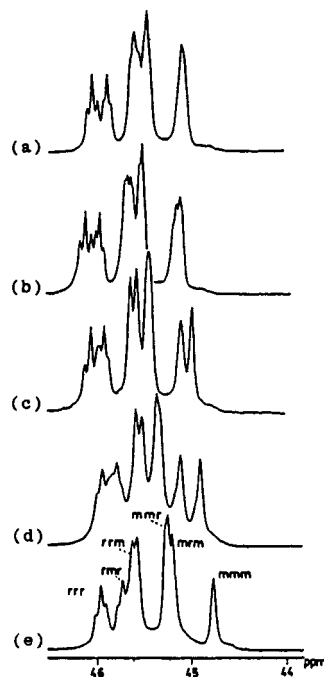


Fig. 2

Solvent effects on 100 MHz ^{13}C -NMR spectra of PVA-A at 80°C ; $\text{D}_2\text{O}/\text{DMSO}-d_6$ (vol/vol)

- (a) D_2O only
- (b) 3/1
- (c) 1/1
- (d) 1/3
- (e) $\text{DMSO}-d_6$ only.

1,2 GLYCOL LINKAGES

The determination of 1,2-glycol linkages in PVA is important because such an irregular bonding produces serious undesirable effects on the properties of PVA, such as thermal deterioration and reduction of mechanical properties. The chemical assay method (ref.13) has usually been adopted for this determination, but some new method of nondestructive determination has long been sought. The 400 MHz $^1\text{H-NMR}$ spectrum of PVA-A dissolved in DMSO-d_6 is shown in Fig. 3, where the hydroxyl proton signals were removed from the observable range by adding a few drops of trifluoroacetic acid (TFA) to the solution. Since the signals related to the 1,2-glycol linkages, which appeared in the chemical shift regions 0.8-1.3 and 3.0-3.8 ppm, were very small, the partly expanded spectra are also shown in the figure. Using the results from the proton chemical shifts of some model compounds, we could assign all the CH resonances of PVA relating to the 1,2-1,4-glycol and terminal 1,2-glycol structures as depicted in Fig.3. The 100 MHz $^{13}\text{C-NMR}$ signals corresponding to the 1,2-glycol linkages are small in intensity for all samples. The signals were enhanced as shown in Fig. 4 for PVA-E. Signal assignment was made according to the data of the previous papers (ref.14). Splitting of the carbon signals in the figure may suggest the presence of some configuration effect which is produced by the surrounding atoms on the 1,2-glycol linkage. By the signal intensity measurements, the contents of the 1,2-glycol units located at the terminal and the inner positions of a polymer chain were evaluated and are listed in Table 1. The sum of the values for PVA-A approximately agrees with the total value of the 1,2-glycol linkage determined by the chemical assay method with periodic acid titration.

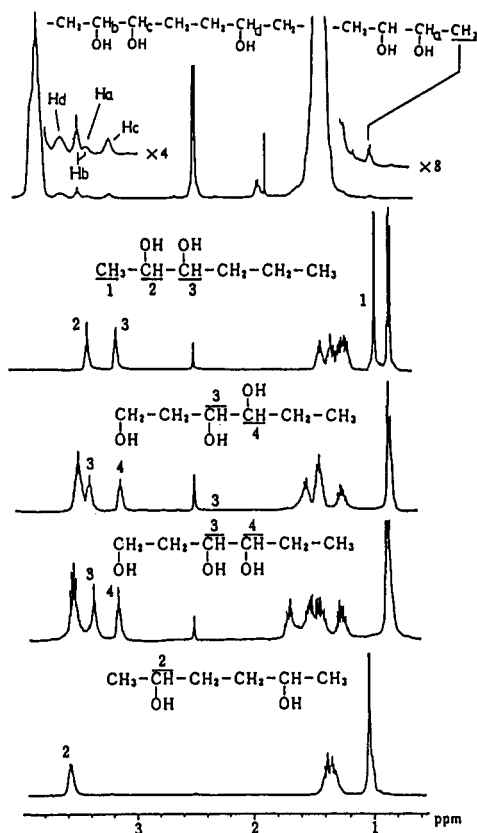


Fig. 3 400 MHz $^1\text{H-NMR}$ spectra of PVA-A and its model compounds of irregular structure in PVA.

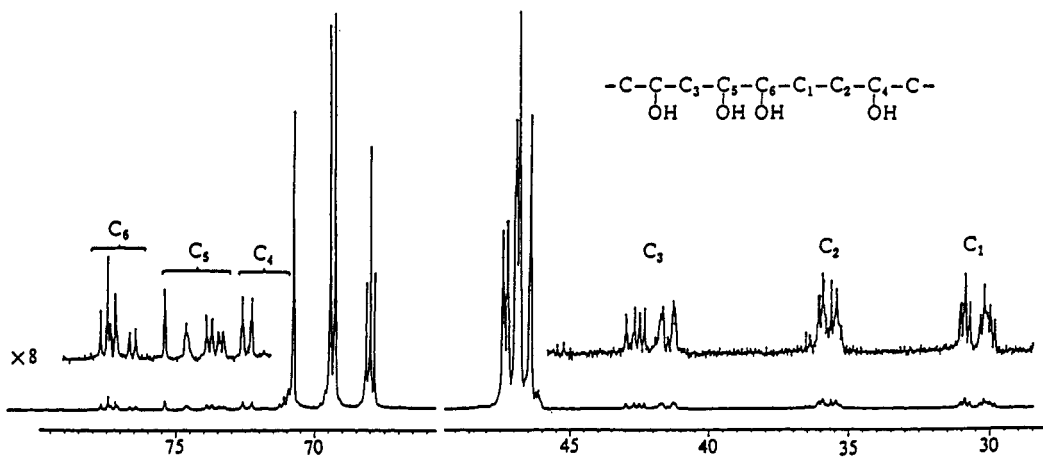


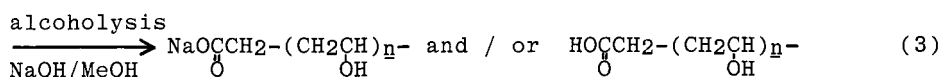
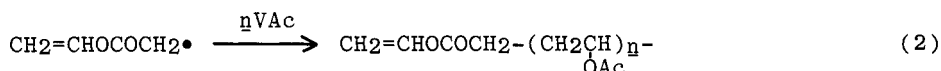
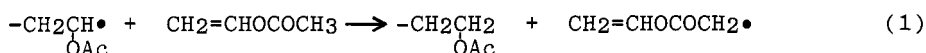
Fig 4 100 MHz $^{13}\text{C-NMR}$ spectra of PVA-E in D_2O , increased amplitude showing only 1,2-glycol linkage.

TABLE 1 Contents of the 1,2-glycol units per 100 monomer units

Sample	inner positions	terminal	Total
P V A - A	1.61	0.06	1.68
P V A - C	1.64	0.06	1.70
P V A - D	0.67	0.03	0.70
P V A - E	2.60	0.50	3.10

END GROUPS

Chain transfer reaction is predominantly occurred in vinyl acetate polymerization. Consequently, various kinds of end groups exist in PVA (ref.15). The major end groups are HOCH₂CH₂- and CH₃CH(OH)CH(OH)CH₂-. Other major end groups arising from the chain transfer reaction to monomer or polymer were investigated by ¹H-NMR. Chain transfer to the terminal acetyl methyl group of VAc would lead to an end group which is a vinyl acetate ester (eqs(1)-(2))



and alcoholysis would convert it to a carboxylic acid end group and/or a carboxylic acid sodium salt end group (eq.(3)). 500MHz ¹H-NMR spectra of PVA-A dissolved in deuterium oxide are shown in Fig. 5. When HCl was added to D₂O solution of PVA, the peak resonanced at about 2.3ppm disappeared, and the groups Ha and Hb increased in intensity. An opposite phenomenon occurred on addition of NaOH. These results and our previous data(ref.14) indicate that the carboxyl and the hydroxyl groups in PVA undergo an intramolecular reaction to form the γ -lactone structure and that the reaction is promoted in the presence of hydrochloric acid and reversed in the presence of sodium hydroxide. Thus, the peaks Ha and Hb are assigned to methylene protons in the closed form and the peak at 2.3ppm is assigned to those in the open form as pointed in the figure. 500MHz ¹H-NMR spectrum of PVA-A dissolved in DMSO-d₆ at 60°C is shown in Fig.6. No carboxylic acid proton was observed.

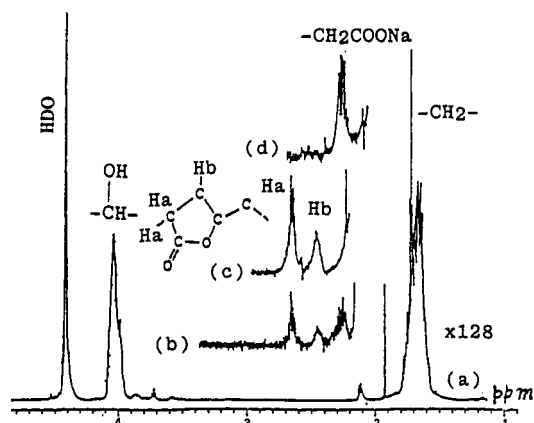


Fig. 5 500 MHz ¹H-NMR spectra of PVA in D₂O at 60°C (a) normal spectrum; (b) same, increased amplitude; (c) in the presence of excess DCl; and (d) in the presence of excess NaOH.

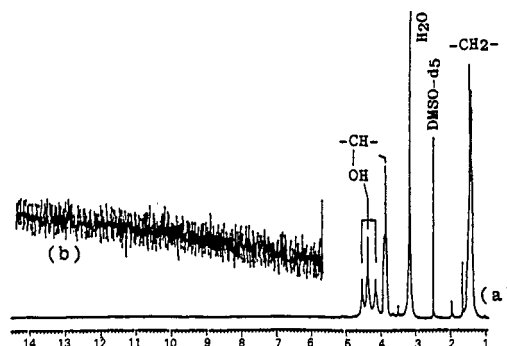


Fig. 6 500 MHz ¹H-NMR spectra of PVA in DMSO-d₆ at 60°C (a) normal spectrum; (b) same, increased amplitude.

calculated that PVA-A, -B and -C had about 0.000, 0.027 and 0.013 B2 endgroups/100 repeat units, respectively. It may be said that the concentration of short branches in PVA depends on the conversion in VAc polymerization reaction.

POLYENE STRUCTURE

Treatment of PVA with heat results in the formation of conjugated polyene structures. Consequently PVA is colored yellow. The conjugated polyene structure has usually been studied by UV spectrum(ref.21). 2D-NMR experiments were performed on the sample with thermal treatment to determine the polyene fine structure. The 500MHz ^1H -NMR spectrum of PVA-F treated with heat at 150°C for 4 h in air atmosphere dissolved in DMSO-d_6 is shown in Fig. 8. Observed resonances in the region 6.0–7.3ppm can be assigned to the polyene structure. Since these signals were very small, the partly expanded spectra is also shown in Fig. 9. These resonances are extremely complex due to the occurrence of resonance lines corresponding to many different lengths of conjugated bonds sequence in a small chemical shift of the spectra. In spite of this complexity, several conjugated sequence assignments can be made unambiguously through application of COSY. COSY gives correlation maps showing the connectivity of spin-spin coupled protons. COSY spectra will thus give information on the connectivity of protons with scalar coupling along the conjugated bonds. Fig.10 shows the 500MHz COSY spectrum of PVA-F at 80°C dissolved in DMSO-d_6 . The F2 axis(horizontal) represents the ^1H -NMR spectrum of PVA as shown in Fig.10. In the case of triene($n=3$), in which n indicates the conjugation sequence of $-(\text{CH}=\text{CH})_3-$, starting from the H-1 signal at 6.08ppm, a unique transverse connectivity with H-2 at 7.21ppm is then possible. Hence H-2 is correlated with H-3. From H-3 on, the same mechanism reveals connectivities with H-4, H-5 and H-6. Fig.10 also showed other kinds of connectivities with monoene($n=1$) and diene($n=2$) structures.

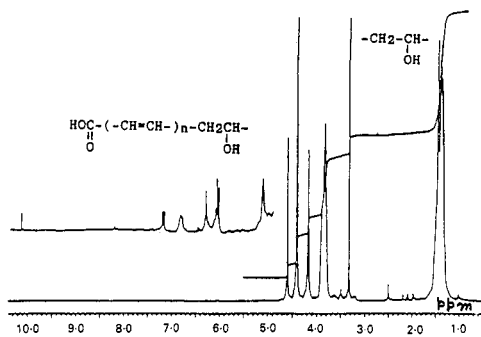


Fig. 8 500 MHz ^1H -NMR spectra of PVA-F treated with heat (150°C *4 h) in air atmosphere in DMSO-d_6 at 60°C .

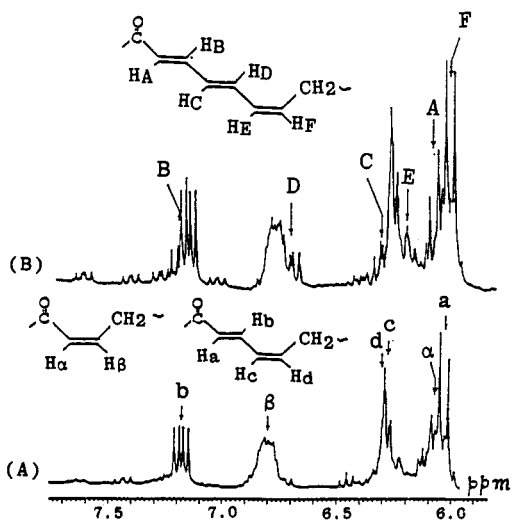


Fig. 9 The olefinic region of the ^1H -NMR spectra of PVA-F treated with heat in DMSO-d_6 at 60°C (A) 150°C *4 h in air; (B) 150°C *4 h in vacuum.

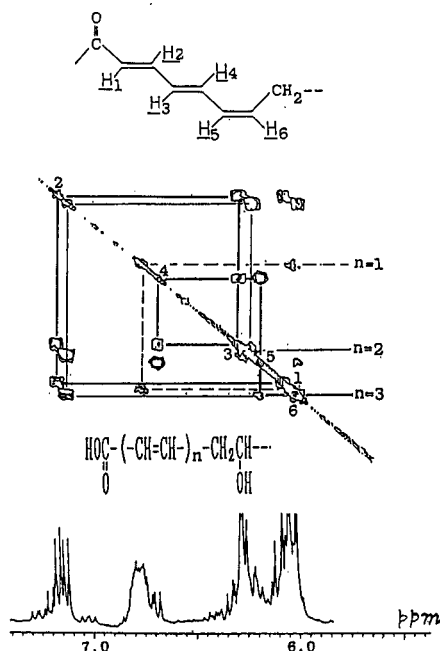


Fig. 10 500 MHz ^1H COSY spectra of PVA-F treated with heat (150°C *4 h) in vacuum atmosphere in DMSO-d_6 at 60°C .

From analyzing the 2-D COSY spectrum, we found that three kinds of conjugated sequences were contained in the polymer. 500MHz 1D ^1H -NMR spectrum was utilized in the quantitative analysis of PVA-F treated with heat. The concentration of n -polyenes; $-(\text{CH}=\text{CH})_n$ was as follows: monoene($n=1$), 0.137mol%; diene($n=2$), 0.083mol%; triene($n=3$), less than 0.01mol%.

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