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Notes

Structural Study of Poly(vinyl alcohol) in the Gel State by High-Resolution Solid-State ^{13}C NMR Spectroscopy

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Introduction

It is well-known that poly(vinyl alcohol) (PVA) in aqueous solution forms a gel by undergoing freeze−thaw cycles. It has been suggested that the cause of the gel formation may be due to the formation of intermolecular hydrogen bonds.[1] However, it is not clear.

It has been demonstrated that high-resolution solid-state NMR spectroscopy is a useful means to obtain information about the structure of solid polymers.[2] This may suggest that high-resolution solid-state NMR spectroscopy will provide structural information about the immobile component of polymer gels together with the mobile component.

From such a situation, we aim to measure high-resolution solid-state ^{13}C NMR spectra of a PVA gel and to elucidate the structure of the immobile component of the gel. Further, we will discuss the cause of the gel formation.

Experimental Section

Materials. The sample of PVA used in this study is provided by Kuraray Co., Ltd. The degree of polymerization and the degree of saponification of PVA are 1700 and 99.9%, respectively. The fractions of mm, mr, and rr triads evaluated from the ^{13}C NMR spectrum of PVA in deuterated dimethyl sulfoxide (DMSO) solution are 0.29, 0.44, and 0.27, respectively, where m and r indicate meso and racemic diads, respectively.

PVA Gel Preparation. A PVA sample was dissolved in deuterated water. The polymer concentration was 9% (w/w). The PVA gel was prepared from this solution by repeating freeze−thaw cycles four times (frozen at −20 °C for 20 h and then melted at 25 °C and kept at 25 °C for 4 h). PVA gel samples with different polymer concentrations were prepared by evaporating water.

Measurements. High-resolution solid-state ^{13}C CP/MAS (cross polarization/magic angle spinning) and ^{13}C PST/MAS (pulse saturation transfer/magic angle spinning) NMR spectra were measured by a JEOL GSX-270 NMR spectrometer operating at 67.8 MHz. In the CP method, enhancement of ^{13}C magnetization is effective for solids, and on the other hand, in the PST method,[3] the nuclear Overhauser effect (NOE) enhances ^{13}C magnetization in mobile components such as gels. The PVA gel sample was contained in a cylinder-type rotor with a rubber O-ring. The use of an O-ring prevents loss of water from the gel during the high-speed spinning of the rotor. The $\pi/2$ pulse widths for ^{1}H and ^{13}C nuclei were 4.5 and 4.6 μs, respectively. The contact time was 2 ms, and the repetition time was 5 s. The spectral width was 27 kHz and 8k data points were taken. Spectra were accumulated 200−10 000 times to achieve a reasonable signal-to-noise ratio. The rotor was spun at 3.8−4 kHz. The ^{13}C chemical shifts were calibrated indirectly through the adamantane upfield peak (29.5 ppm) relative to tetramethylsilane (TMS).

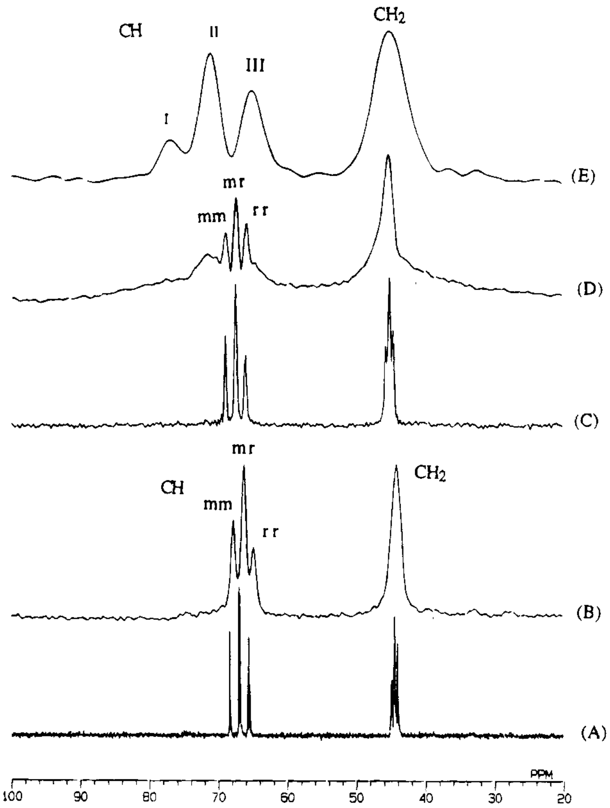

Figure 1. ^{13}C NMR spectra of PVA in the solution, gel, and solid states, as measured by some NMR methods. Solution-state NMR method: (A) in PVA/D_2O solution and (B) in the gel state. Solid-state NMR method: in the gel state (C) [PST/MAS] and (D) [CP/MAS], and in the solid state (E) [CP/MAS].

Solution-state ^{13}C NMR spectra were measured by a JEOL GSX-500 NMR spectrometer operating at 125 MHz. A PVA gel was contained in an NMR tube with a diameter of 10 mm and a small amount of deuterated water was added for a deuterium lock.

Results and Discussion

Solution-state and solid-state ^{13}C NMR spectra of the PVA gel are shown in Figure 1 together with the solution-state ^{13}C NMR spectrum of PVA in D_2O solution and the solid-state ^{13}C NMR spectrum of PVA in the solid state. In the solution-state ^{13}C NMR spectrum of PVA aqueous solution (Figure 1A), each of the ^{13}C signals for the CH_2 and CH carbons splits into multiplet peaks due to stereochemical configuration. The three splitting peaks for the CH carbon are assigned to mm, mr, and rr triads from downfield,[4] and further, each of the triad peaks splits into pentad peaks, where m and r indicate meso and racemic diads, respectively. The

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Table 1. Relative ^{13}C Peak Intensities for the CH Carbons in PVA

samples	peak I	peak II	peak III	mm	mr	rr
PVA gel polymer concn % (w/w)						
9.1	0.05	0.33	0.27	0.09	0.17	0.09
11.8	0.07	0.36	0.33	0.05	0.11	0.08
13.8	0.09	0.36	0.35	0.04	0.10	0.06
35.0	0.09	0.50	0.41			
PVA (solid)	0.14	0.49	0.37			
PVA (solution, at −50 °C)	0.05	0.27	0.68			

(peak I to rr: peak fraction)

splitting peaks for the CH_2 carbon come from tetrad configurations. In the solution-state ^{13}C NMR spectrum of the PVA gel, as shown in Figure 1B, the ^{13}C signal for the CH carbon splits into three peaks due to triad configurations in the case of PVA solution, and the ^{13}C signal for the CH_2 carbon becomes a broad peak. The ^{13}C PST/MAS NMR spectrum of the PVA gel, as shown in Figure 1C, is very similar to the solution-state ^{13}C NMR spectrum of the PVA gel (Figure 1B). This means that only the mobile component of the PVA gel is observed in both of the spectra.

In the ^{13}C CP/MAS NMR spectrum of PVA in the solid state, the ^{13}C signal for the CH carbon with three splitting peaks is observed as shown in Figure 1E. The chemical shift difference between these peaks is considerably larger than the splitting due to stereochemical configuration. Terao et al.[5] explained such a splitting by the number of intramolecular hydrogen bonds with neighboring hydroxyl groups. The most downfield peak (peak I), the central peak (peak II), and the most upfield peak (peak III) come from the CH carbons forming two hydrogen bonds, one hydrogen bond, and no hydrogen bonds with the hydroxyl group, respectively. This becomes reference data for understanding ^{13}C CP/MAS NMR spectra of the PVA gel as shown below.

In the ^{13}C CP/MAS spectrum of the PVA gel (Figure 1D), the CH signal is composed of both the three splitting peaks corresponding to the triad configurations and the three splitting peaks as in the ^{13}C CP/MAS spectrum of solid PVA. This means that both the immobile and mobile components of PVA gel are observed.

In order to clarify such a situation, ^{13}C CP/MAS experiments on PVA gels with different polymer concentrations were carried out. Water in a PVA gel sample prepared by freeze−thaw cycles was gradually taken out by evaporation. By this procedure, four kinds of PVA gel samples with different polymer concentrations were prepared, where the polymer concentrations are 9.1, 11.8, 13.8, and 35.0% (w/w). The relative peak intensities for the ^{13}C spectra of four kinds of PVA gel samples and solid PVA are shown in Table 1. As shown in Figure 2 and Table 1, as the water fraction of the PVA gel is decreased, the intensities of the three splitting peaks due to stereochemical configurations are decreased and the intensities of the three peaks (I−III) are increased . In sample D, of high polymer concentration, the three peaks due to stereochemical configurations completely disappear. On the basis of the Terao's assignment for solid PVA, peaks I, II, and III may be assigned to the CH carbons with two (intermolecular or intramolecular) hydrogen bonds, one (intermolecular or intramolecular) hydrogen bond, and no hydrogen bonds, respectively. The ^{13}C CP/MAS NMR spectrum of sample D is very similar to that of solid PVA except the intensity of peak III in the former is somewhat larger than that in the latter. These experimental results show that as the water fraction is decreased, the fraction of the immobile component of the PVA gel is increased and the amount of CH carbons with no hydrogen bonds in sample D is somewhat larger than that in solid PVA.

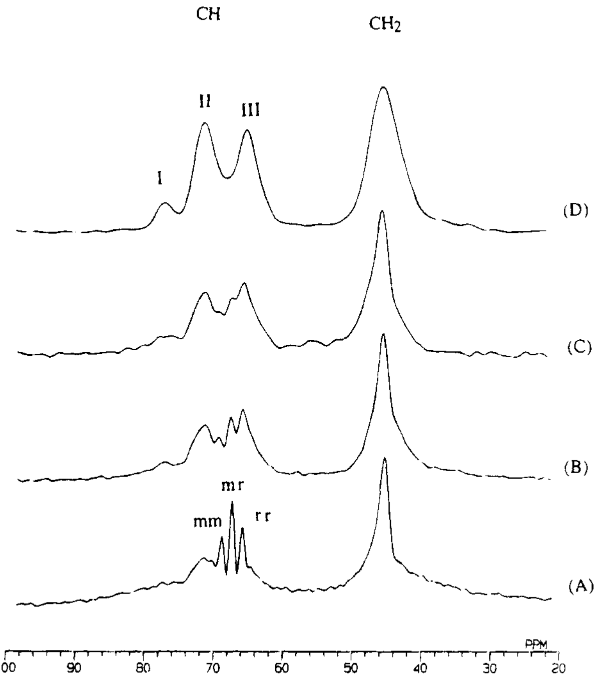

Figure 2. 67.8 MHz ^{13}C CP/MAS NMR spectra of PVA in the gel state: (A) original gel A prepared by freeze−thaw cycles; (B)−(D) gels B, C, and D prepared by vaporizing water from gel A. The polymer concentrations of samples A−D are 9.1, 11.8, 13.8, and 35.0% (w/w), respectively.

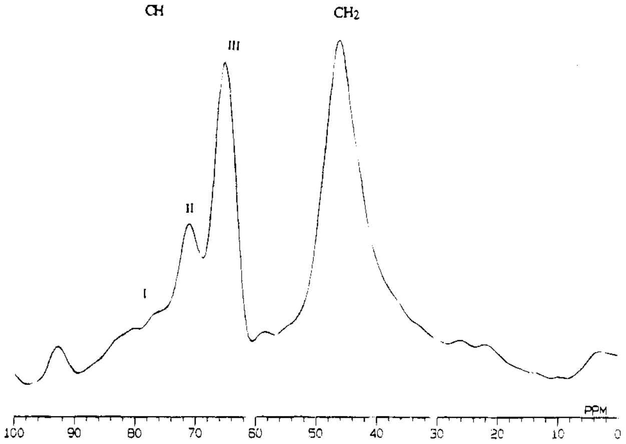

Figure 3. 67.8 MHz ^{13}C CP/MAS NMR spectrum of PVA gel at −50 °C.

Next, we are concerned with the structure of PVA solutions at low temperatures in order to clarify the mechanism of gel formation by freeze−thaw cycles. The observed ^{13}C CP/MAS spectrum of PVA solution was measured at −50 °C in going from room temperature to −50 °C (Figure 3). The three peaks which come from the splittings by stereochemical configurations completely disappear. Instead, peaks I, II, and III appear. In PVA solution at −50 °C, some hydroxyl groups form hydrogen bonds as in the PVA gel and so the cross-linked structure is formed. This means that the gel formation is induced in going from room temperature to −50 °C. From these experimental findings, it can be said that the procedure of freeze−thaw cycles leads to an increase in the amount of cross-linked structure by hydrogen bonding.

Finally, we can conclude as follows. Hydrogen-bonding plays an important role for the formation of the PVA gel through the formation of cross-linkings between interchains. In the PVA gel, there exist the CH carbons forming only one hydrogen bond at low polymer concentrations, but at high polymer concentrations there are two types of CH carbons forming two hydrogen bonds and one hydrogen bond. The ratio of the number of CH carbons forming two hydrogen bonds to that forming one hydrogen bond is 9:50 for the PVA gel at high polymer concentrations and 14:49 for solid PVA. It can be said that high-resolution solid-state NMR is a very useful means for elucidating the structure of the PVA gel.

References and Notes

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