Structural and Dynamic Study of Ethylene−Vinyl Alcohol Copolymer Gels by ^{1}H Pulse NMR and Solid-State ^{13}C NMR

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ABSTRACT: ^{1}H pulse NMR and solid-state ^{13}C NMR spectra of ethylene−vinyl alcohol copolymer (EVOH) gels were measured as a function of ethylene content, and furthermore, the ^{13}C spin−lattice relaxation times (T_1) and the ^{1}H spin−spin relaxation times (T_2) have been measured, to elucidate the structure and dynamics of the mobile and immobile regions in the gels. From the ^{1}H pulse NMR experimental results, it is found that the ^{1}H T_2 signal is mainly composed of two or three kinds of components with different molecular motions. The long T_2 component is assigned to correspond to the mobile region, which comes from the un-cross-linked region, the short T_2 component corresponds to the immobile region, which comes from the cross-linked region, and the intermediate T_2 component corresponds to the intermediate region between the mobile and immobile regions, which comes from the vicinity of the cross-linked region in the EVOH gel. Furthermore, from the solid state ^{13}C NMR experimental results, it is found that the formation of hydrogen bonds between the hydroxyl groups in vinyl alcohol parts of EVOH copolymers with high vinyl alcohol fraction and the formation of hydrophobic interactions between the methylene groups in ethylene parts of EVOH copolymers with high ethylene fraction contributes to its gel formation.

Introduction

It is known that poly(vinyl alcohol) (PVA) in aqueous solution,[1] in dimethyl sulfoxide (DMSO) solution,[2] and in water/DMSO mixtures[3−5] forms gel by undergoing freeze−thaw cycles which lead to formation of hydrogen bonds between the PVA interchains.[1] From high-resolution solid-state ^{13}C NMR experiments on PVA gels,[6,7] it has been elucidated that there exist two kinds of the regions in the gel with different molecular motions and furthermore that the CH carbon in the slow motion region splits into three signals such as in solid PVA,[8,9] which come from the CH carbons with two hydrogen bonds, one hydrogen bond, and no hydrogen bond. Further, in addition to these studies, structure and dynamics of PVA gel system have been elucidated in details by means of ^{1}H pulse NMR and high-resolution solid-state ^{13}C NMR and the dynamic viscoelasticity method.[10−12]

In this work, we are concerned with (ethylene (E)−vinyl alcohol (V)) (EVOH) copolymer gels with a wide range of ethylene contents, in which the V units often form intra- and intermolecular hydrogen bonds with themselves like PVA, and on the other hand, the E units interact hydrophobically with themselves like polyethylene. From such a situation, it can be expected that the copolymers forms gel with the formation of intermolecular hydrogen bonds between the V units and/or hydrophobic interactions between the E units by undergoing freeze−thaw cycles such as in the case of PVA. For this, it can be expected that physical properties of the copolymer gels are very different from PVA gel.

In previous work,[13] we have studied structure and dynamics of EVOH copolymers with a wide range of ethylene contents in the solid state by means of high-resolution solid-state ^{13}C NMR methods. It has been elucidated that the copolymers in the solid state are mainly composed of two regions with relatively fast and slow molecular motions which come from the mobile and immobile regions, respectively, and their fractions are changed with an increase in ethylene content and that the structure and dynamics are closely related to formation of hydrogen bonds between the V units and to hydrophobic interactions between the E units.

In this work, on the basis of knowledge of structure and dynamics of the EVOH copolymers in the solution state[14] and in the solid state,[13,15,16] we aim to prepare EVOH gels by having the reaction undergoing freeze−thaw cycles such as in the preparation of PVA gel and to elucidate structure and dynamics of EVOH copolymers in the gel state with a wide range of ethylene contents by means of ^{1}H pulse NMR and high-resolution solid-state ^{13}C NMR, and, further, to clarify the mechanism of gel formation.

Experimental Section

Materials. EVOH copolymers with ethylene contents of 5, 10, 27, 32, 55, and 74% were used in this work and were obtained from Kuraray Co., Ltd. The microstructures of these EVOH copolymers were already characterized by solution ^{13}C NMR as reported previously.[13]

The gel was prepared from EVOH/dimethyl sulfoxide (DMSO) solution by repeating freeze−thaw cycles three times, where the solution was frozen at − 20 °C for 20 h and then melted at 20 °C and kept for 4 h. The obtained gels were soft. Furthermore, to obtain hard gels, a mixture of DMSO and water as solvent was used.

High-Resolution Solid-State ^{13}C NMR and ^{1}H Pulse NMR Measurements. High-resolution solid-state ^{13}C CP/MAS (cross polarization/magic angle spinning)[17] and ^{13}C PST/MAS (pulse saturation transfer/magic angle spinning)[23] NMR spectra were measured by a JEOL GSX-270 NMR spectrom-

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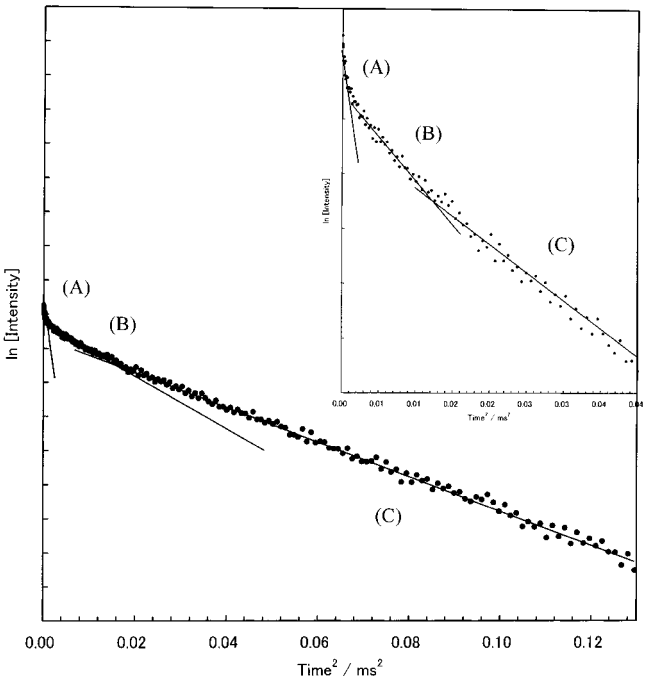

Figure 1. Typical ^{1}H T_2 curves of EVOH gels with ethylene contents of 32% obtained by solid echo ^{1}H pulse NMR method at room temperature.

eter operating at 67.8 MHz. In the CP method, enhancement of the ^{13}C magnetization is effective for the relatively immobile region in solids and, on the other hand, in the PST method the nuclear Overhauser effect (NOE) enhances the ^{13}C magnetization for the mobile region. The ^{13}C T_1 (spin−lattice relaxation time) value was determined by the Torchia pulse sequence.[18] The $\pi/2$ pulse widths for ^{1}H and ^{13}C nuclei are 4.8 and 4.9 μs, respectively. The contact time is 2 ms, and the repetition time is 5 s. The spectral width was 27 kHz and 8 k data points were taken. The spectra were accumulated 8500−150 000 times to achieve a reasonable signal-to-noise ratio. The MAS rotor was spun at 3.5−3.8 kHz. A cylinder-type rotor with a rubber O-ring is used to prevent the evaporation of solvent in the gel during the experiments. The measurement temperature range was from 0 to 45 °C as indicated by the calibration temperature.[19] The ^{13}C chemical shifts were calibrated indirectly through the upfield peak (29.5 ppm) of adamantane relative to tetramethylsilane (TMS).

^{1}H pulse NMR measurements were carried out with a Bruker Minispec PC20 spectrometer operating at 20 MHz. The solid-echo method[20,21] was used for the ^{1}H T_2 (spin−spin relaxation time) measurements. The decomposition of the obtained ^{1}H T_2 signal into three kind of the components with different molecular motion was carried out with the nonlinear least-squares method by an NEC PC9801 microcomputer. All of the T_2 decays obtained in this experiment were decomposed by three T_2 components carefully with reasonable experimental errors. The experimental errors for T_2 and the fraction of three T_2 components are less than 10%.

Results and Discussion

Solid-Echo ^{1}H NMR Spectral Analysis of EVOH Gels and the Dynamics Structure. A typical ^{1}H T_2 signal of EVOH gel with high ethylene content of 32% as obtained by ^{1}H solid echo method is shown in Figure 1. The ^{1}H T_2 value is determined from the slope of the plot of ln M against time t^2, where M is the amplitude of the spin echo signal and the T_2 signal is assumed to be the Gaussian decay in the spectral analysis. According to the BPP (Bloembergen−Purcell−Pound) theory for NMR relaxation,[22] T_2 decreases continuously as the correlation time τ in molecular motion is increased. This

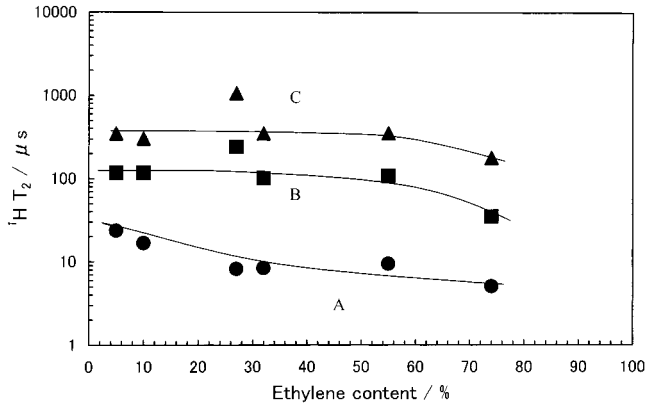

Figure 2. Plots of ^{1}H T_2 of EVOH gels against ethylene content, as determined by solid-echo ^{1}H pulse NMR method at room temperature.

means that shorter T_2 corresponds to slower molecular motion. Thus, T_2 can give dynamical information about the gels through the BPP theory. As seen from Figure 1A, it is apparent that the ^{1}H T_2 curve is composed of three kinds of components, such as the short T_2 component corresponding to the immobile region (region A), the intermediate T_2 component corresponding to the interfacial region (region B), which exists between the mobile and immobile regions, and the long T_2 component corresponding to the mobile region (region C). By aid of computer-fitting, the ^{1}H T_2 value was obtained from the T_2 signal with a small experimental error. The result is the same as that of PVA gel.[10] It can be said that the short T_2 component corresponding to the immobile region comes from the cross-linked region in the EVOH gels, the long T_2 component corresponding to the mobile region comes from the non-cross-linked region, and the intermediate T_2 component with the intermediate mobility comes from the vicinity of the cross-linked region.

The ^{1}H T_2 values determined for the individual regions were plotted against the ethylene content as shown in Figure 2. It is found that the ^{1}H T_2 values for the immobile, mobile, and intermediate regions are gradually decreased with an increase in ethylene content. The increase of the ethylene content in EVOH samples in the gel state leads to a reduction in molecular motion for the individual regions.

Figure 3 shows the fraction of each of the immobile, mobile, and intermediate regions with different molecular motions as a function of ethylene content. In the ethylene content range less than 55%, the fractions of three kinds of regions, the immobile, mobile, and intermediate regions, with different mobilities are almost independent of ethylene content. In the ethylene content range larger than 55%, the fractions of the mobile region is largely decreased with an increase in ethylene content. On the other hand, the fractions of the intermediate and immobile regions are largely increased with an increase in ethylene content. Their fractions are close to each other. This means that the fraction of the cross-linked region as formed by an addition of hydrophobic interaction between the ethylene parts to hydrogen bonds between the vinyl alcohol units is increased with an increase in ethylene content. From such a situation, the molecular motion for all of the three regions are more restrained with an increase in ethylene content.

^{13}C CP/MAS NMR Spectral Analysis of EVOH Gels and the Dynamics Structure. In the CP method,

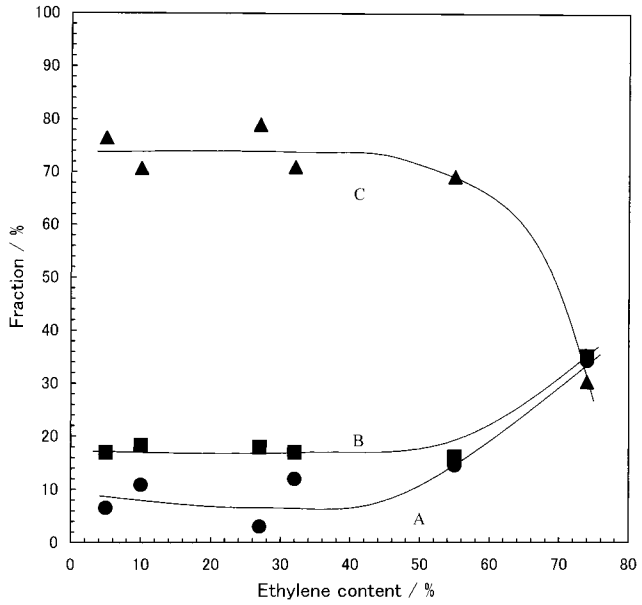

Figure 3. Plots of the fractions of the three kind of the regions of EVOH gels with different molecular motions against the ethylene content at room temperature.

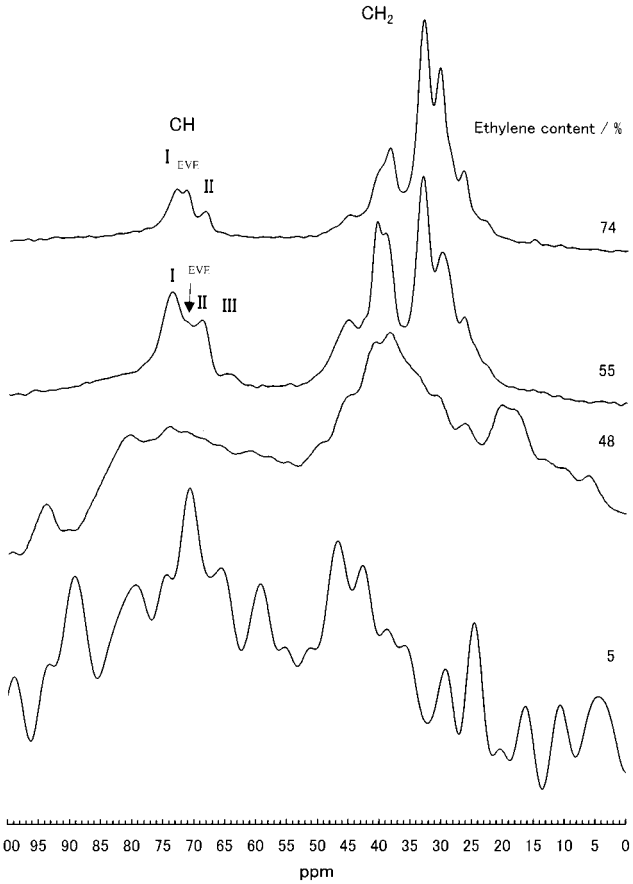

Figure 4. 67.8 MHz ^{13}C CP/MAS NMR spectra of EVOH gel as a function of ethylene content at room temperature.

enhancement of the ^{13}C magnetization is effective for the relatively immobile regions such as solids, but is greatly reduced for the mobile regions such as gels. For this, it is expected that ^{13}C CP/MAS NMR gives us dynamic information about gels in an addition to structural information about the structure. ^{13}C CP/MAS NMR spectra of EVOH gel samples with a wide range of ethylene contents from 5 to 74% at room temperature are shown in Figure 4. Only the intense background signal in the ^{13}C CP/MAS spectra of EVOH gels with low ethylene contents from 5 to 48% appears under the present measurement condition. This is due to the following reasons. At the present measurement temperature, the gels are very soft and so the mobility of EVOH network chains becomes high. This leads to a large reduction of the CP efficiency. Thus, the background signal which comes from the polymer materials used in an NMR probe appears intensely in the spectrum. The ^{13}C CP/MAS spectra of EVOH samples with high ethylene contents of 55 and 74% were obtained with a reasonable signal-to-noise ratio. It is found that the spectral patterns for the CH carbon of the V units and for the CH_2 carbon of the E and V units are greatly changed by varying the ethylene content. To obtain the sufficient CP efficiency for the immobile component of EVOH gels with low ethylene content, ^{13}C CP/MAS NMR spectra of EVOH gel with an ethylene content of 5% were measured with repetition time of 5 s by changing the contact time in the range from 100 to 2000 μs (not shown). At long contact time, the noncrystalline region, which is undergoing slow molecular motion, can be often observed. However, it is found that the CP efficiency is not enough apparently.

The ^{13}C PST/MAS NMR spectrum of EVOH gel with ethylene content of 5% was shown in Figure 5B. This spectrum is very similar to the solution-state ^{13}C NMR spectrum of EVOH like the case of PVA gel.[6,7] In the spectrum, the mm, mr, and rr triad peaks for the CH carbon (in the 65−69 ppm region), and the m and r diad peaks for the CH_2 carbon (in 45−48 ppm region) of V units in EVOH appear clearly. It can be said that the V units in the high mobile region are observed by the PST/MAS NMR. On the other hand, ^{13}C CP/MAS NMR spectrum of its gel was measured under different conditions of the contact time of 1000 μs, the repetition time of 3 s and the accumulation number of 150 000 from the measurement condition used for the observed ^{13}C CP/MAS NMR spectra as shown in Figure 4 (see Figure 5A). In this spectrum, peaks I, II, and III for the CH carbon of V units, which come from the immobile region, and the mr peak of the triad peaks (as appeared in the 65−69 ppm region) for the CH carbon, which comes from the mobile region, appear clearly as shown in Figure 5A. On the other hand, EVOH gel samples with higher ethylene content become very hard, and thus ^{13}C CP/MAS NMR spectra of EVOH gels with ethylene contents of 55 and 74% appear more clearly with a reasonable signal-to-noise ratio even at room temperature (not shown in the figure) because the gels are very hard and so their molecular motion is greatly restrained. This does not conflict with the pulse ^{1}H NMR results as shown in Figures 2 and 3, in which the ^{1}H T_2 value of EVOH gels is decreased with ethylene content and the fractions of the mobile and intermediate regions (corresponding to the cross-linked and non-cross-linked regions, respectively) in EVOH gels with ethylene contents larger than 55% are increased.

Next, we are concerned with temperature-variable of ^{13}C CP/MAS NMR spectra of EVOH gels to obtain further dynamic information on the gels. ^{13}C CP/MAS NMR spectra of EVOH gels with an ethylene content of 32% at 0 and 23 °C are shown in Figure 6. The ^{13}C CP/MAS NMR spectrum at 23 °C has a very low signal-to-noise ratio, and thus the intense background signal appears as a whole as shown in Figure 6B. This means

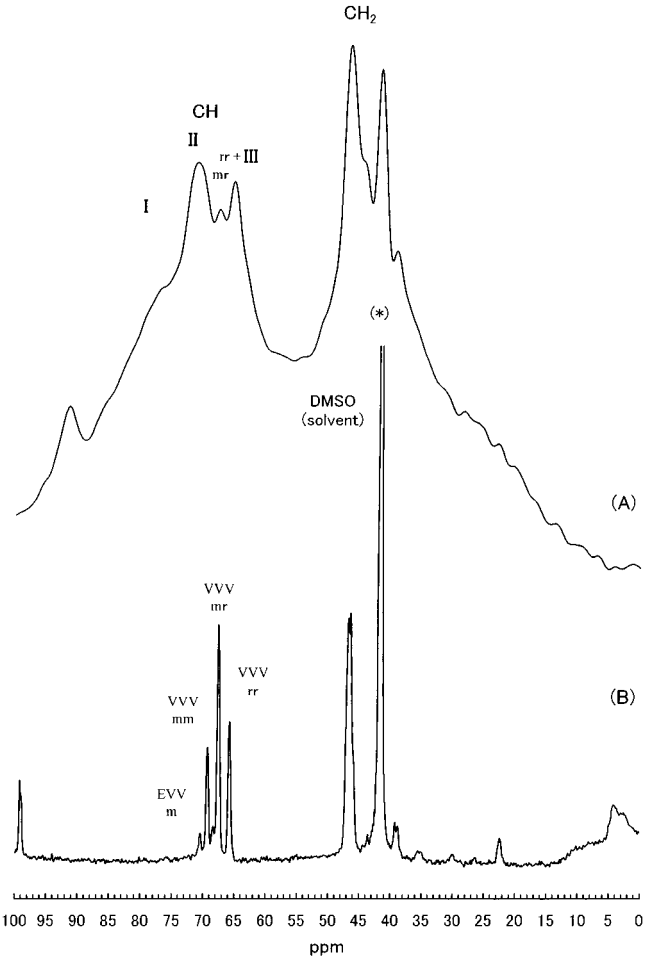

Figure 5. 67.8 MHz ^{13}C NMR spectra of EVOH gel with an ethylene content of 5% at room temperature: (A) CP/MAS NMR spectrum and (B) PST/MAS NMR spectrum.

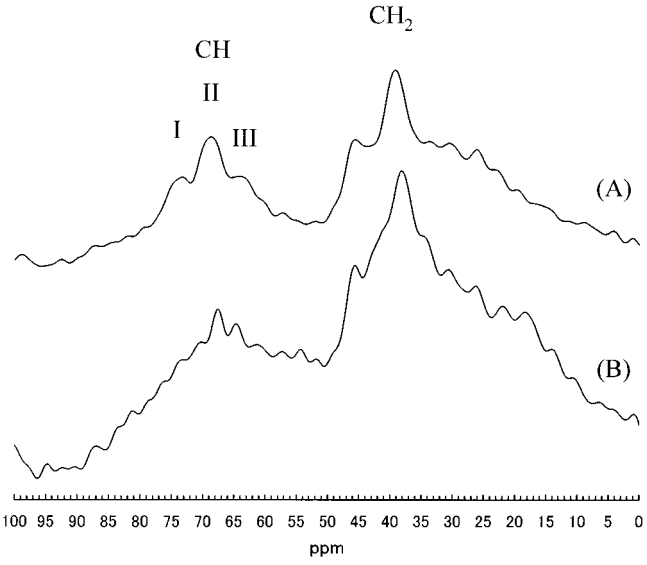

Figure 6. 67.8 MHz ^{13}C CP/MAS NMR spectra of EVOH gel with an ethylene content of 32% at 0 (A) and 23 °C (B).

that the CP efficiency of the gels becomes insufficient by undergoing fast molecular motion at 23 °C, where these gel samples are very soft, and thus its mobility is high. As temperature is decreased, the individual peaks in the spectrum (A) at 0 °C appear more clearly compared with those in the spectrum (B) at 23 °C. This is due to an increase in the CP efficiency by reduction

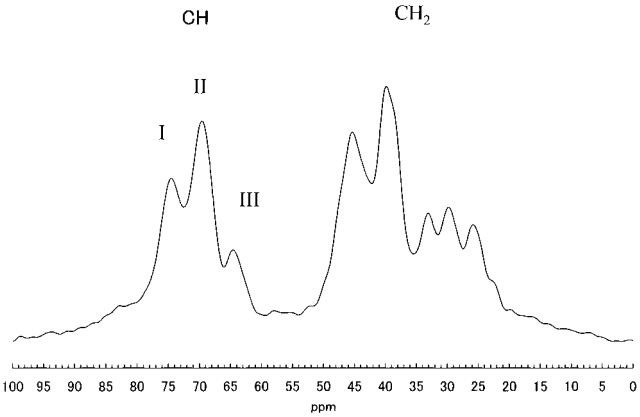

Figure 7. 67.8 MHz ^{13}C CP/MAS NMR spectra of EVOH gel in a mixture of DMSO and H_2O with a volume ratio of 60/40 at room temperature, where the ethylene content of EVOH is 32%.

of molecular motion at low temperature. The three peaks, I, II, and III, for the CH carbon of the V units appear like the ^{13}C CP/MAS NMR spectra of solid EVOH samples. Furthermore, the EVOH copolymer gel prepared by using a mixture of DMSO and water as solvent is relatively harder compared with one prepared by using DMSO as solvent. This is due to the reason that the intermolecular affinity between EVOH and mixture solvent of DMSO and water becomes much lower compared with that between EVOH and DMSO solvent, and then the hydrophobic and/or hydrophilic interactions between polymer chains are enhanced. Thus, the EVOH copolymer with the ethylene content of 32% as prepared by using a mixture of DMSO and water as solvent becomes relatively hard. This leads to the point that the ^{13}C CP/MAS NMR spectrum of the EVOH gel is well resolved with a reasonable signal-to-noise ratio like solid EVOH as shown in Figure 7. All of peaks in these spectra can be assigned in the same way as already assigned in PVA gel[6] and solid EVOH[13] as below.

Figures 8 and 9 show partially relaxed ^{13}C spectra of EVOH gel with the ethylene contents of 5 and 74%, respectively, as a function of the delay time by using the Torchia pulse sequence in order to determine ^{13}C T_1. In the ^{13}C T_1 experiments, the mobile region with a short T_1 value near the T_1 minimum in the slow motion region disappears at the shorter delay time. Further, the immobile region with a long T_1 value remains at the longer delay time.

Next, we are concerned with details of the spectral analysis. The spectral assignment was made according to the previous assignments on solid EVOH samples.[13] The assignment of the ^{13}C peaks of the CH carbon was made. First, Terao et al.[8] found that in solid PVA the CH signal splits into three peaks (peaks I, II, and III) of which the chemical shift differences are much larger as compared with the case of the three splitting CH peaks of PVA in solution. The splitting of the latter comes from the microtacticity. They assigned that such a large chemical shift difference comes from the formation of hydrogen bonds between the hydroxyl groups. In our previous works,[6,7] it was first found that the CH signal of PVA gels with high polymer concentration splits into three peaks such as in the case of solid PVA, and that with low polymer concentration there appear three splitting peaks such as in the PVA solution by microtacticity in the peaks I, II, and III region. In

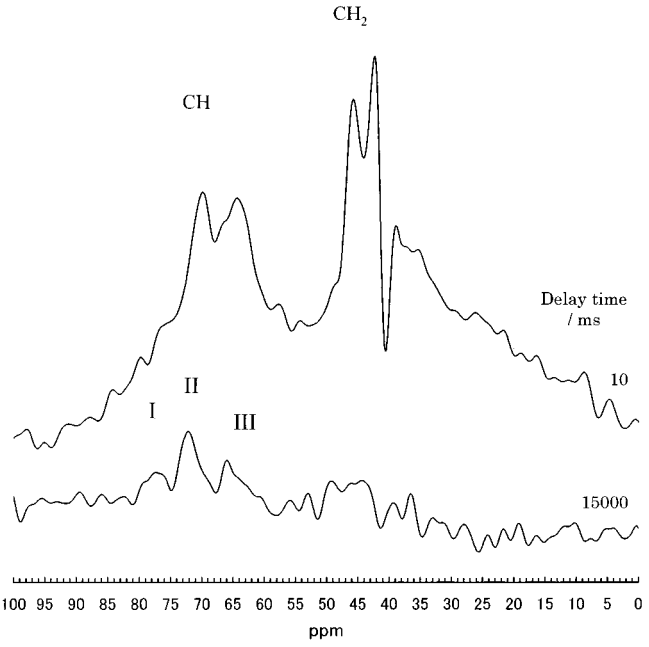

Figure 8. Partially relaxed 67.8 MHz ^{13}C NMR spectra of EVOH gel as a function of the delay time by using the Torchia method at room temperature, where the ethylene content of EVOH is 5%.

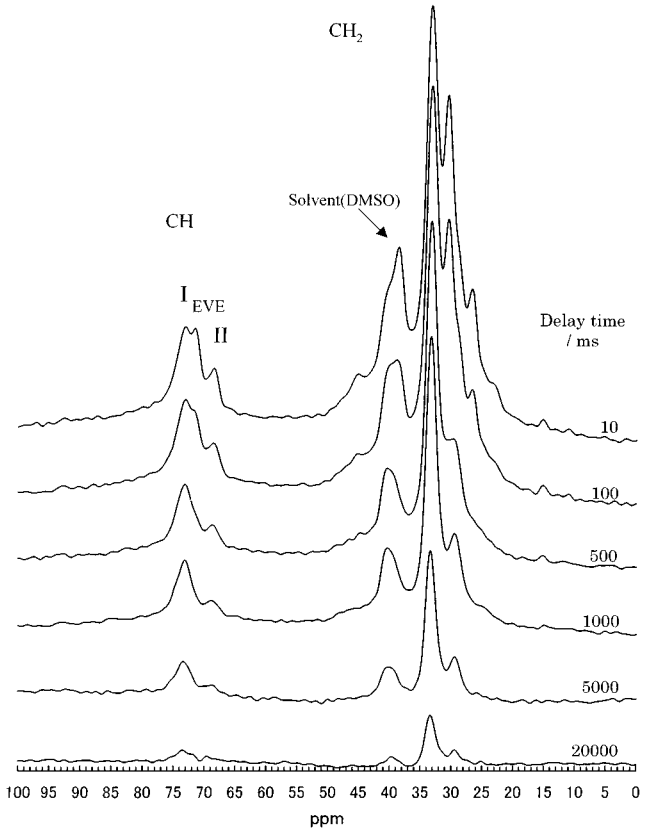

Figure 9. Partially relaxed 67.8 MHz ^{13}C NMR spectra of EVOH gel as a function of the delay time by using the Torchia method at room temperature, where the ethylene content of EVOH is 74%.

isotactic PVA gel, peak I appears intensely at a lower field by about 8 ppm as compared with the chemical shift position of the mm triad peak in PVA solution. Their chemical shift difference is very large as compared with the solvent effect. Therefore, we think that it is natural to assign peaks I, II, and III by two, one, and zero hydrogen bonds. Then, the chemical shift positions of peaks I, II, and III appearing in EVOH copolymer gels are the same as those of PVA gels. Thus, the assignment of peaks I, II, and III appearing in EVOH copolymer gels is based on that of PVA gels. The assignment of the three peaks I, II, and III of the CH carbon in EVOH gel with low ethylene content as appearing at about 77, 71, and 65 ppm, respectively, can be made according to the assignment of the CH peaks in PVA gel,[6] where peak I comes from the formation of two intramolecular or intermolecular hydrogen bonds, peak II from the formation of one intramolecular or intermolecular hydrogen bond, and peak III from no hydrogen bond (Figures 8 and 5A). On the other hand, in EVOH gel samples with high ethylene content, the ^{13}C chemical shift positions of peaks I and II are different from those in EVOH gel samples with low ethylene content. This is due to appearance of new configurational arrangements due to the large amount of the ethylene units in the copolymers. From such a situation, according to the previous assignment,[13] it is observed that peak I comes from the CH carbon of the V unit in the EVE sequence as the major contribution in addition to two intramolecular or intermolecular hydrogen-bonded CH carbon of the V units as the minor contribution, and peak II from one intramolecular or intermolecular hydrogen-bonded CH carbon of the central V unit in VVV sequences as the minor contribution (Figures 4 and 9). Furthermore, by analyzing the partially relaxed spectra of EVOH gel (with the ethylene content of 5%) by using the Torchia method, as shown in Figure 8, it was found that each of three CH peaks I, II, and III in EVOH gel remains even at a longer delay time (=15000 ms). This arises from the fact that peaks I, II, and III in the EVOH gel are "frozen in molecular motion" on the NMR time scale, because these three peaks comes from cross-linking region in the gel. The EVOH sample used in this work has the distribution of meso and racemic sequences being random. Therefore, the vinyl alcohol units forming two intramolecular or intermolecular hydrogen bonds (peak I), one intramolecular or intermolecular hydrogen-bond (peak II), and no hydrogen bond (peak III) from CH are made by a random distribution of meso and racemic sequences. Thus, peaks I, peak II, and peak III have the same T_1 values in the cross-linking region. From the results of EVOH gels and PVA/H_2O gels,[6] peak III has a long T_1 because it arises from a species "frozen in molecular motion".

Furthermore, we are concerned with the peak assignment of the CH_2 carbon in EVOH gel with high ethylene content (Figure 9). The CH_2 peaks at 33 and 30 ppm come from the asterisked central CH_2 carbons in both of the $-CH_2-CH_2-CH_2$*-CH_2-CH_2- unit and $-CH_2-CH_2-CH_2$*-CH_2-CH_2- units without and with fast exchange between the trans and gauche conformations, respectively. The CH_2 peak at 30 ppm decays fastly at shorter delay time compared with CH_2 peak at 33 ppm. This arises from the fact that the CH_2 carbons of the ethylene units with the trans zigzag conformation in the crystalline region, which appear at 33 ppm, are frozen in molecular motion on the NMR time scale, and on the other hand the CH_2 carbons in the noncrystalline region, which appear at 30 ppm, are undergoing fast exchange between the trans and gauche conformations at room temperature. Thus, the peak for the CH_2 carbons in the crystalline region remains even at a longer delay time.

From such a situation, in EVOH samples with high ethylene content, the gel may be formed by the crystalline region formed by hydrophobic interaction between the ethylene units of EVOH.

Finally, it is concluded that changes in structure and dynamics of EVOH gel samples were characterized as a function of the ethylene content by ^{1}H pulse NMR and high-resolution solid-state ^{13}C NMR, and the formation of the EVOH gel was explained by the formation of the cross-linking by the formation of intermolecular hydrogen bonds between the vinyl alcohol parts and the crystalline region formed by the hydrophobic interaction between the ethylene parts.

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