Structural Characterization of Polyallene in the Solid State As Studied by Variable-Temperature High-Resolution ^{13}C NMR Spectroscopy

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ABSTRACT: High-resolution ^{13}C NMR spectra of polyallenes in the solid state were measured over the temperature range from room temperature to 100 °C by means of the variable-temperture cross polarization/magic angle spinning NMR and pulse saturation transfer/magic angle spinning NMR techniques. It was shown that the ^{13}C resonance lines of the noncrystalline, orthorhombic, monoclinic, and paracrystalline forms are chemically shifted from one another. On the basis of these peak assignments, the structural change was studied over the course of the temperature change.

Introduction

The structure of polymers in the solid state, which describes how the polymers are formed, is very important in understanding their physical properties. X-ray diffraction is a direct method for studying the structure of solid polymers. However, when polymers contain several structural phases, it is sometimes difficult to study them by X-ray diffraction alone. On the other hand, solid-state high-resolution ^{13}C NMR has proved to be a very useful tool to probe the higher order structure and dynamics of polymers in the solid state.[1-4] The NMR chemical shift can give information about the magnetic environment of any specified nucleus, which comes from any specified structure, and so can detect the differences among the crystallographic forms of a solid polymer.[5-9] Further, recent technological development has made it possible to do variable-temperature (VT) high-resolution solid-state NMR experiments, and so NMR has become a very useful method for investigating the structures and dynamics of solid polymers over the course of temperature change.[10-13]

Polyallene $[(-CH_2C(=CH_2)-)_n]$ assumes four types of crystallographic forms: orthorhombic, monoclinic, paracrystalline, and noncrystalline forms, as reported by X-ray diffraction study, and they are transformed into each other by heat treatment.[14] In the orthorhombic and monoclinic forms, the chain conformation are the same 2/1 helix.[14-16] In order to obtain information about the interchain interaction through the observation of the ^{13}C NMR chemical shift, this polymer is very convenient.

In this work, we observe high-resolution ^{13}C NMR spectra of polyallenes in the solid state as a function of temperture by means of ^{13}C cross polarization/magic angle spinning (CP/MAS) NMR and pulse saturation transfer (PST)/MAS NMR[19] and clarify the effect of crystallographic forms on the ^{13}C chemical shift of the main-chain and the side-chain carbons. The process of transition among the four types of crystallographic forms by heat treatment is discussed.

Experimental Section

Materials. Polyallene was prepared by Ziegler-type catalysis.[17] Sample A was synthesized as follows. Purified toluene (180 mL) was transferred into a flask equipped with a magnetic stirrer and an allene inlet and outlet under a nitrogen atmosphere. Allene gas was bubbled into the solvent throughout this experiment. After the solvent was saturated, 0.15 mL of $VOCl_3$ was added. The solution changed from colorless to dark red. Then 4.16 mL of triisobutylaluminum was added, and the solution became cherry red. Polymerization began immediately and a bulky white polymer appeared. After a suitable time interval, 150 mL of ethanol was added, and the polymer was then collected by filtration. The polymer was then repeatedly washed with 10% ethanolic HCl, ethanol, water, and acetone and dried.

Sample B was prepared in the same way as sample A, but the experimental scale was 1/3. After polymerization, the polyallene was transferred into a flask with *o*-dichlorobenzene and was refluxed. It became partly transparent and was collected by filtration and dried. This sample, designated B, was brittle.

Sample C was prepared by recrystallization of sample A as follows. A 0.1% w/v *o*-dichlorobenzene solution of sample A was kept at 108 °C for 2 h and was slowly cooled at a rate of 7 °C/h to 83 °C. The recrystallized polyallene was collected by filtration and then dried.

Polyallene has three kinds of carbon groups: CH_2, $CH_2=$, and $>C=$. Their ^{13}C signals appear at 17-54, 104-122, and 130-153 ppm, respectively.[18] Figure 1 shows the 125.7-MHz high-resolution ^{13}C NMR spectrum of polyallene (sample A) in a 1% w/v *o*-dichlorobenzene/dimethyl-d_6 sulfoxide solution at 120 °C. In the spectrum, three single peaks, besides that of the solvent, appear at 41.3, 112.7, and 143.8 ppm. Assignments of peaks for the CH_2, $CH_2=$, and $>CH=$ carbons are straightforward from reference data. From these results, the sample prepared was identified as pure polyallene.

In the DSC thermogram, sample A clearly exhibits a broad intense peak over the temperature range ~100-124 °C. This may be due to the melting of the sample. The temperatures obtained here agree approximately with those of Tadokoro.[14]

Measurements. ^{13}C NMR spectra of polyallenes were measured as a function of temperature with a JEOL JNM GSX 270 NMR (67.5 MHz) spectrometer with a VT CP/MAS accessory. Contact times were 2, 5, and 10 ms. Repetition times were 5 and 15 s. The sample was contained in a cylindrical ceramic rotor. The rotor was spun at ca. 4 kHz. The spectral width was 27 kHz, and 8 K data points were used. The number of accumulations was 600-1000. ^{13}C chemical shifts were calibrated indirectly from adamantane at high field (29.5 ppm) relative to TMS (tetramethylsilane). Spectra were also measured with a VT PST/MAS[19] accessory. In the PST/MAS method, ^{13}C magnetizations are obtained by a direct ^{13}C 90° single pulse and are enhanced by a nuclear Overhauser effect (NOE) from the saturated protons (the pulse sequence is shown in Figure 2). The PST/MAS

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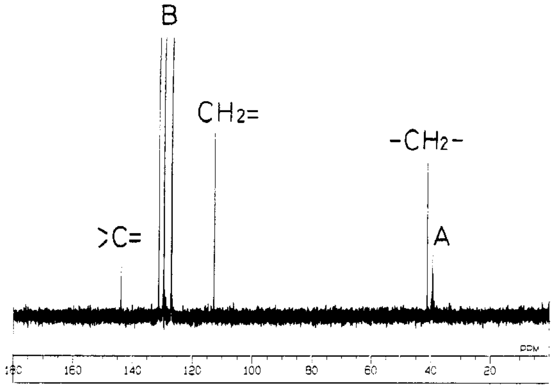

Figure 1. 125.7-MHz ^{13}C NMR spectrum of polyallene (sample A) in 1% w/v *o*-dichlorobenzene/dimethyl-d_6 sulfoxide solution at 120 °C. A, dimethyl-d_6 sulfoxide; B, *o*-dichlorobenzene.

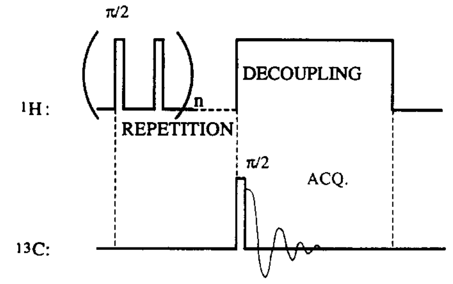

Figure 2. Schematic representation of a pulse sequence in the pulse saturation transfer method.

technique enhances peak intensities for mobile carbons. Repetition time was 5 s. The number of accumulations was 350–850. The other conditions were the same as in the ^{13}C CP/MAS NMR experiments.

High-resolution ^{13}C NMR spectra of polyallene in 1% w/v *o*-dichlorobenzene/dimethyl-d_6 sulfoxide solution were obtained at 120 °C with a JEOL JNM GSX 500 NMR (125.7 MHz) spectrometer with a VT accessory. The spectral width was 7 kHz and 32 K data points were obtained. The number of accumulations was 224. ^{13}C chemical shifts were calibrated indirectly through the central peak (39.5 ppm) of dimethyl-d_6 sulfoxide relative to TMS.

X-ray diffraction measurements were carried out in a glass capillary on a Rotaflex apparatus (Rigaku Denki Co.), using Cu Kα beams generated at 40 kV and 90 mA. The exposure time was 15 min.

The DSC measurements were performed with a Perkin-Elmer DSC calorimeter.

Results and Discussion

Figure 3 shows ^{13}C CP/MAS NMR spectra of polyallenes (samples A–C) in the solid state at room temperature, where SSB indicates spinning sidebands. Each carbon peak in the spectrum (a) is expanded as shown in the spectrum (b). The peaks for the carbon groups can be readily assigned on the basis of the solution-state ^{13}C NMR spectrum. As shown in spectrum A(b) for sample A, each carbon signal is clearly split into two peaks M and O. We conclude that they arise from two types of structures in the sample. On the other hand, in spectrum B(b) for sample B, the ^{13}C signal for each carbon is a single peak. We believe that they arise from one type of structure in this sample and that they correspond to peak O in sample A. In spectrum C(b), the ^{13}C signal for the >C= carbon group is split into two peaks that correspond to peaks M and O in sample A; the ^{13}C signals for the CH_2 and CH_2= carbon groups do not split into two peaks but have shoulders at the same chemical shift positions of peaks M of sample A. We thus conclude that sample C consists mainly of two types of structures as in sample A. The ^{13}C NMR chemical shifts of the assigned peaks are listed in Table I.

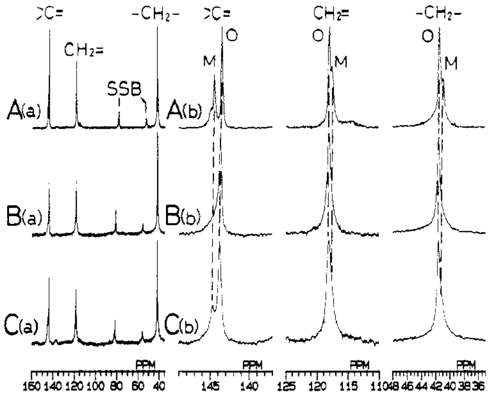

Figure 3. 67.5-MHz ^{13}C CP/MAS NMR spectra of polyallenes in the solid state. Spectra a: (A) sample A (contact time = 10 ms, repetition time = 15 s); (B) sample B (contact time = 2 ms, repetition time = 5 s); (C) sample C (contact time = 5 ms, repetition time = 5 s). Spectra b: Each signal for the carbon groups in spectra A–C is expanded. O, orthorhombic form; M, monoclinic form.

Table I
Observed ^{13}C NMR Chemical Shifts (δ) of Polyallene in the Solid State at Room Temperature

	>C=		CH_2=		CH_2	
sample	M[a]	O[b]	O	M	O	M
A	144.4	143.4	118.0	117.5	41.3	40.9
B	*c*	143.6	118.1	*c*	41.5	*c*
C	144.6	143.6	118.1	*c*	41.5	*c*

[a] Monoclinic form. [b] Orthorhombic form. [c] Not identified.

To clarify the origin of the peaks M and O, we attempted to determine the crystal structure for samples B and C by X-ray diffraction. We obtained several concentric circles in the X-ray photographs. From these, the distances between the neighboring atomic planes were determined. For convenience, the distances between the neighboring atomic planes for the orthorhombic and monoclinic forms were calculated from the crystal lattices obtained by Tadokoro et al.[14] Comparing the values of distances obtained in this work with the reference values, we found that the structure for sample B is predominantly orthorhombic while that for sample C consists of a major orthorhombic form and a minor monoclinic form.

From these results, peaks O and M can be assigned to the orthorhombic and monoclinic forms, respectively. The >C= carbon in the orthorhombic form appears at higher field than that in the monoclinic form, but the CH_2= and CH_2 carbons in the orthorhombic form appear at lower field. The ^{13}C chemical shift differences for the >C=, CH_2=, and CH_2 carbon groups between the orthorhombic and monoclinic forms are about 1.0, 0.5, and 0.4 ppm, respectively. These significant differences arise from a local difference in the interchain interactions between the orthorhombic and monoclinic forms in which the conformations are the same 2/1 helix. The difference of 0.4–1.0 ppm is comparable to the effect of crystal structure of polyethylene in the orthorhombic and monoclinic forms (about 1.4 ppm) in which the conformations are the same all-trans zigzag.[8,9]

As described in the Introduction, polyallene assumes orthorhombic, monoclinic, paracrystalline, and noncrystalline structures upon heat treatment. To elucidate the transformations of these structures and the thermal stability of polyallene we employed VT ^{13}C CP/MAS and

Table II
Observed ^{13}C NMR Chemical Shifts (δ) of Polyallene in the Solid State as a Function of Temperature[g]

T/°C	>C=				CH$_2$=				CH$_2$			
	N[a]	M[b]	O[c]	P[d]	O	M	N	P	N	O	M	P
room temp	—[e]	144.5	143.5	—	117.9	—	114.7	—	—	41.4	41.1	—
	(144.9)	(—)	(—)	(—)	(—)	(117.2)	(114.6)	(—)	(42.2)	(41.6)	(—)	(—)
55	—	144.5	143.6	—	118.1	—	114.7	—	42.5	41.4	41.1	—
	(145.2)	(144.7)	(143.9)	(—)	(117.8)	(117.4)	(114.7)	(—)	(42.5)	(41.5)	(—)	(—)
60	—	144.6	143.7	—	118.0	—	114.7	—	42.5	41.5	41.1	—
	(145.2)	(—)	(144.0)	(—)	(117.9)	(117.4)	(114.6)	(—)	(42.7)	(41.4)	(—)	(—)
70	145.1	144.2	143.8	143.3[f]	118.0	—	114.6	—	42.8	41.5	41.1	—
	(145.3)	(—)	(—)	(—)	(—)	(117.5)	(114.6)	(—)	(42.9)	(41.5)	(41.0)	(—)
80	145.3	144.7	143.8	—	118.2	117.6	114.7	—	43.0	41.5	41.2[f]	—
	(145.4)	(—)	(—)	(—)	(—)	(—)	(114.6)	(—)	(43.0)	(—)	(—)	(—)
100	145.4	—	—	—	—	—	114.5	—	43.1	—	—	—
	(145.5)	(—)	(—)	(—)	(—)	(—)	(114.6)	(—)	(43.1)	(—)	(—)	(—)

[a] Noncrystalline form. [b] Monoclinic form. [c] Orthorhombic form. [d] Paracrystalline form. [e] Not identified. [f] For shoulder peak. [g] Values in parentheses were determined by the PST/MAS technique; unparenthesized values were determined by the CP/MAS technique.

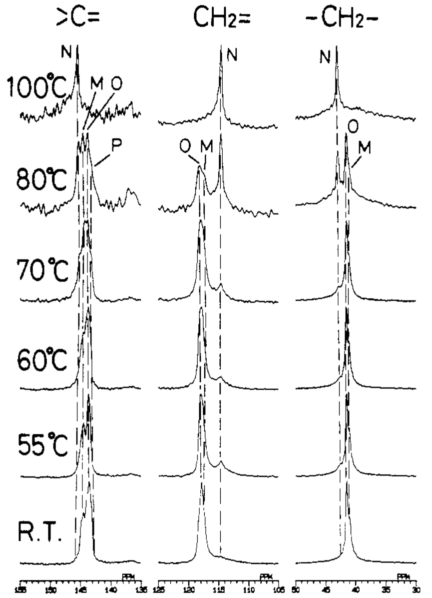

Figure 4. 67.5-MHz ^{13}C CP/MAS NMR spectra of polyallene (sample A) as a function of temperature (contact time = 2 ms, repetition time = 5 s). O, orthorhombic form; M, monoclinic form; N, noncrystalline form; P, paracrystalline form.

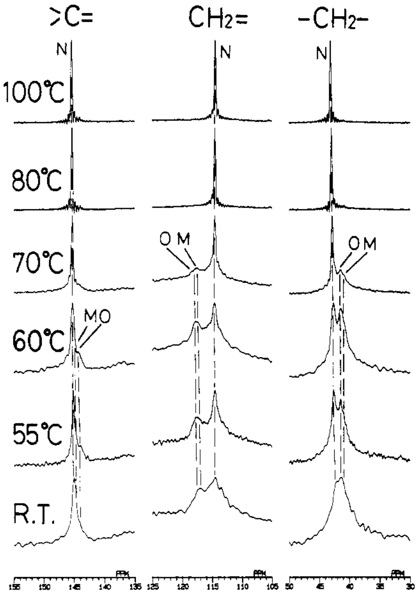

Figure 5. 67.5-MHz ^{13}C PST/MAS NMR spectra of polyallene (sample A) as a function of temperature (contact time = 2 ms, repetition time = 5 s). O, orthorhombic form; M, monoclinic form; N, noncrystalline form; P, paracrystalline form.

PST/MAS experiments. We note that the PST/MAS technique in contrast with the CP/MAS technique enhances the peak intensity for carbons in the noncrystalline state, which undergo relatively rapid reorientation. Figures 4 and 5 show VT ^{13}C CP/MAS and VT ^{13}C PST/MAS NMR spectra, respectively, of polyallene (sample A) in the solid state at temperatures from room temperature to 100 °C (Table II). The spectral pattern changes considerably as the temperature is increased. At 100 °C, each ^{13}C signal becomes a sharp single peak in both the CP/MAS and PST/MAS NMR experiments. These signals are designated N. In the CP/MAS spectrum at room temperature, peak N is very weak, but in the PST/MAS spectrum it is intense and sharp. This means that the carbons contributing to peak N are undergoing reltively faster reorientation compared with the carbons contributing to the other peaks. Therefore, peak N is assigned to the noncrystalline component. The experimental finding that the melting point of sample A appears at 100–120 °C supports this assignment. It is also found that the intensity of peak M, which is assigned to the monoclinic form, increases from room temperature to 80 °C.

If we look at the ^{13}C signal for the >C= carbon in the CP/MAS spectrum at 70 and 80 °C carefully, a new peak P appears as a shoulder at the highest field. The appearance of this peak at high temperature shows that the carbons contributing to it are in a stable state at high temperature as compared with the monoclinic and orthorhombic forms. This peak disappears at 100 °C.

From X-ray diffraction, it is known that a paracrystalline component exists in addition to the monoclinic, orthorhombic, and noncrystalline components. In this structure, polymer chains are parallel to each other, although the relative spatial positions between the chains along the chain axis are random, and also the positions or the orientations of the chains on the projection perpendicular to the chain axis have some degree of randomness. The polymer chains in the paracrystalline state can undergo reorientation faster than in the orthorhombic or monoclinic states but slower than in the noncrystalline state. From these observations we draw the following conclusions concerning the transformation between the four crystallographic states of polyallene. The paracrystalline component transforms from the monoclinic and orthorhombic forms as the temperture is increased. Upon further high-temperature treatment, it transforms to the noncrystalline form. From these observations we assigned peak P to the paracrystalline component. As an example, Figure 6 shows the deconvolution of the observed ^{13}C CP/

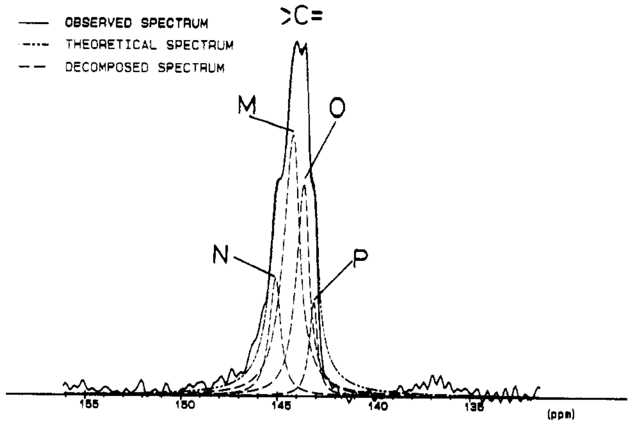

Figure 6. Deconvolution of the observed ^{13}C CP/MAS NMR spectrum of polyallene (sample A) at 70 °C by computer fitting. N, noncrystalline component (145.2 ppm); M, monoclinic component (144.4 ppm); O, orthorhombic component (143.8 ppm); P, paracrystalline component (143.2 ppm).

MAS spectrum of polyallene at 70 °C with a Lorentzian function by computer fitting.

From the above results, the following can be concluded. Through the observation of VT ^{13}C CP/MAS and PST/MAS NMR spectra of polyallene in the solid state as a function of temperature, we can identify the existence of the monoclinic, orthorhombic, paracrystalline, and noncrystalline components. The observed ^{13}C peaks were assigned to these components. It was also found that the paracrystalline structure is stable at high temperature.

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Registry No. Polyallene (homopolymer), 24979-93-9.