High Resolution Solid State ^{13}C NMR Spectroscopy of Polypropylene with Very High Syndiospecificity

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ABSTRACT: The high resolution solid state ^{13}C NMR spectra were observed for highly syndiotactic polypropylene samples with three kinds of crystalline forms, forms I, II, and III. The forms I and II are the most stable helical conformation, $(-TTGG-)_2$ and all trans planar zigzag conformation, respectively. The sample with the third new crystalline form, form III, was prepared by soaking the sample with form II in toluene at room temperature for two days. The conformation was proposed to be $(-T_6G_2T_2G_2-)$. This is based on the comparison of the observed spectrum with the calculated ones with ^{13}C NMR γ -effect for the candidates of the conformation. There are form I (23%) and amorphous component (11%) other than form III (66%) in the sample at 20°C. From the variable temperature NMR experiments of these three samples with predominantly forms I, II, and III, respectively, the transitions among different crystalline forms and amorphous component were discussed.

KEY WORDS Highly Syndiotactic Polypropylene / High Resolution Solid State ^{13}C NMR Spectroscopy / ^{13}C γ Shielding Effect / Crystalline and Amorphous Components / $(-T_6G_2T_2G_2-)$ Form of Syndiotactic Polypropylene /

Contrary to isotactic polypropylene (i-PP), syndiotactic polypropylene (s-PP) has received very little attention. This is due to the poor syndiospecificity of the earlier catalysts. However, in the last few years, new metallocene catalysts have been developed, which allow very high syndiospecificity.^{1,2} Thus, a detailed structural study of such a highly stereoregular s-PP will be necessary.

Two different crystalline forms^{3–7} of the chains have been reported for s-PP obtained by changing the preparations of s-PP samples. One form is called form I which consists of chains with $(-TTGG-)_2$ conformation, and another is form II with planar zigzag conformation. Form I is the most stable structure in s-PP, while form II undergoes a transition to form I above 50°C with increasing temperature.⁶ The structures of form I and of the sample after drawing have already been studied by Bunn *et al.*⁷ and Sozzani *et al.*^{8,9} by using solid-state ^{13}C NMR. These NMR spectra were interpreted in terms of preferred conformations and the γ -effect on the ^{13}C NMR chemical shift.^{10,11}

In this study, a sample with predominantly new crystalline form, form III, was obtained by special sample preparation. The ^{13}C CP/MAS NMR spectrum was significantly different from those of other forms, forms I and II. The differences in the spectra among three forms, I, II, and III were interpreted by taking into account of the preferred conformations and the ^{13}C NMR γ -effect. Then the conformation of the new crystalline form, form III, was proposed. Moreover, the transition among three crystalline forms and amorphous component was examined from the temperature-dependent ^{13}C CP/MAS NMR spectra of three samples and then the determination of the fraction of each form

by the spectral simulation.

EXPERIMENTAL

Materials

The averaged molecular weight of s-PP sample used here was $M_n = 7.0 \times 10^4$ and $M_w = 1.53 \times 10^5$ (by GPC). From the methyl region of the ^{13}C NMR spectrum in solution, the rrrr pentad distribution was determined as 0.93.¹² Sample A (form I) was prepared by annealing at 120°C for two days, and sample B (form II) was prepared by drawing the s-PP sample in ice-water immediately after melting.⁶ The crystalline forms of these samples were confirmed by IR. Further, sample C with a new crystalline form (form III) was prepared by soaking sample B in toluene at room temperature for two days.

NMR Spectroscopy

The high resolution solid state ^{13}C NMR (^{13}C CP/MAS) spectra were recorded at 100.4 MHz on a JEOL GX-400 spectrometer at 20°C. A 62.5 kHz r.f. field strength was used for the matching Hartmann-Hahn condition. Magic angle spinning (MAS) was carried out at a rate of 6.2 kHz. The cross-polarization (CP) contact time was 1 ms and 400 scans were acquired. The temperature-dependent ^{13}C CP/MAS experiments were carried out by changing the temperature from 40°C to 100°C at 10°C intervals. The methyl ^{13}C peak of hexamethylbenzene was used as an external reference at 17.3 ppm from tetramethylsilane (TMS). In order to obtain the spectra which were emphasized the mobile components in the samples, PSTMAS (pulse saturation magic angle spinning) method was also used.

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RESULTS AND DISCUSSION

 ^{13}C NMR Spectra of Forms I, II, and III

In previous X-ray diffraction studies,³⁻⁶ it has been shown that there are two kinds of molecular conformations of s-PP depending on the sample preparation. One type is form I, which consists of molecular chains with helical conformation, $(-TTGG-)_2$, and is the most thermodynamically stable crystalline form. The other type is form II, which consists of chains with an all trans planar zigzag conformation. Figure 1 (a) and (b) shows the ^{13}C CP/MAS NMR spectra of samples A and B at 20°C, respectively. In Figure 1(a), there are two peaks at 48.29 and 39.64 ppm in the methylene region. The difference in the chemical shifts is explained using the γ -effect. In the $(-TTGG-)_2$ conformation, the methylene carbons are placed at two different positions. In one site (39.64 ppm), they receive two γ -effects from two different methine carbons. In the other site (48.29 ppm), no γ -effect is received.

On the other hand, only one peak at 48.29 ppm is observed in the methylene region of sample B as shown in Figure 1(b). This indicates that the sample consists of a molecular chain with an all trans conformation where the methylene carbons receive no γ -effect. Difference in chemical shifts between samples A and B are also observed for methyl and methine peaks although the difference is small. The methyl carbon receives one γ -effect from a methine carbon in form I, but it receives two γ -effects in form II. In the case of methine carbon, it receives two γ -effects from two carbons in forms I and II. However, two carbons are methylene and methyl in form I, but two methyl's in form II.

Figure 1. ^{13}C CP/MAS NMR spectra of syndiotactic polypropylene at 20°C: (a) sample A, (b) sample B, and (c) sample C. The details of the experimental condition are described in the text.

Figure 1(c) shows the ^{13}C CP-MAS NMR spectrum of sample C with new crystalline form (form III) obtained in this study. It is apparent that this spectrum is different from those of samples A and B, and not a mixture of the two spectra. For example, a new methylene peak appears at 43.72 ppm between the two methylene peaks of form I. Thus, the form III is a conformation which is different from those of forms I and II.

Structure Determination of New Form III

Generally, chemical shift calculations based on the γ -effect on the ^{13}C NMR chemical shift and a rotational isomeric state model (RIS model) has successfully provided reasonable assignments of stereosequence-dependent peaks in ^{13}C NMR solution spectra of PPs¹³⁻¹⁹ and olefin copolymers.^{10,11} So, the conformation probabilities of dyad syndiotactic propylene units are calculated using the RIS model. The fraction of the preferred conformations, $TTTT$, $TTGG$, and $G'G'TT$ are 0.33, 0.21, and 0.21, respectively, and the other conformations were negligible. Apparently, the $TTTT$ conformation is formed in form II. On the other hand, $TTGG$ and $G'G'TT$ are formed in form I. By combination of these three preferred dyad syndiotactic sequences, longer propylene units than dyad were considered. From the calculation of conformation probability, it is reasonable to propose T_6G_2 in the case of tetrad monomer units, and $T_{10}G_2$, $T_6G_2T_2G_2$, and $T_4G_2T_4G'_2$ in hexad monomer units, respectively.

Figure 2 shows the stick spectra which are calculated by an additive contribution of γ -gauche effect for each gauche bond by assuming the preferred conformations predicted above. The stick spectra (a) and (b) represent the $-TTGG-$ (form I) and $-TTTT-$ (form II) conforma-

Figure 2. The ^{13}C NMR stick spectra of syndiotactic polypropylene predicted for the chains with preferred conformations. The chemical shift difference on the basis of the γ -effect is noted in the stick spectrum (e): γ_{CH} in the CH_2 region means the γ effect between CH and CH_2 carbons. γ_{CH_2} and γ_{CH_3} in the CH region mean γ effect between CH_2 and CH carbons, and that between CH_3 and CH carbons, respectively. $\gamma_{\text{CH}_2-\gamma_{\text{CH}_3}}$ is the difference between these two γ effect. γ_{CH} in the CH_3 region means γ effect between CH and CH_3 carbons.

tions, respectively, which agree with the observed spectra. Spectra (c), (d), (e), and (f) represent the spectra of s-PP with conformations, $-T_6G_2-$, $-T_{10}G_2-$, $-T_6G_2T_2G_2-$, and $-T_4G_2T_4G_2'-$, respectively. In these spectra, the character of the spectrum (e) agrees with the observed spectrum (Figure 1(c)) of sample C. In the methylene region, six methylene carbons are placed at three different positions in the $(-T_6G_2T_2G_2-)$ conformation. One methylene carbon receives two γ -effects from two different methine carbons and such a peak should appear at the highfield similar to the methylene peak at 39.64 ppm in form I. On the other hand, the peak assigned to three methylene carbons which receive no γ -effect should appear at the lowfield similar to the methylene peak at 48.29 ppm in forms I and II. The other two methylene carbons receive only one γ -effect from a methine carbon and the peak should appear between these two peaks. These predictions are in agreement with the observed methylene peak pattern of sample C (Figure 1(c)). The presence of the shoulder at the lowfield side of the main peak of the methine carbons, and two peaks at 22.25 ppm and 19.05 ppm with the intensity ratio of 2:1 in the methyl region, are also observed. Thus, the new crystalline form III of s-PP is concluded to be $(-T_6G_2T_2G_2-)$ conformation. The chemical shift difference among each peak in the methylene region is represented as $\gamma\text{CH}-\text{CH}_2$, the difference between two peaks in the methine region is $(\gamma\text{CH}_2-\text{CH})-(\gamma\text{CH}_3-\text{CH})$, and the difference between two peaks in the methyl region is $\gamma\text{CH}-\text{CH}_3$. The observed values in the spectrum of sample C were 4.3 ppm, 0.5 ppm, and 3.2 ppm, respectively.

Chatani *et al.*²⁰ reported a new structure of s-PP by X-ray structure analysis. The s-PP sample with planar zigzag form was exposed to benzene, toluene, or *p*-xylene vapor below 50°C for several days. Then, the X-ray fiber photograph was observed and only $(-T_6G_2T_2G_2-)$ model using the finally accepted unit cell gave a discrepancy factor of 18% for all the observed reflections. After refinement, the final discrepancy factor was 14%. Thus, the structure of form III determined with ^{13}C CP/MAS NMR here is in agreement with the structure reported by Chatani *et al.*

Fraction of Several Forms in Sample C

It is clear that there are another conformations other than form III in the sample C. The presence of small peak at 21.86 ppm in the methyl region and slightly larger intensity of the peak at 39.35 ppm in the methylene region than the expected intensity (the relative intensity of these peaks should be 1:2:3 for form III to lower field), indicate small amounts of form I are involved in the sample. In addition, in the PSTMAS NMR spectrum of sample C, an intensive peak at 20.35 ppm other than two peaks which are assigned to form III is observed in the methyl region (data not shown). This indicates that there is also amorphous component in the sample.

One of the merits of ^{13}C CP/MAS NMR in polymer structural analysis is relatively easy to determine the fraction when there are several kinds of structures in the sample. As mentioned above, the sample C contains forms III, I, and amorphous component although the content of the latter two components is low. Figure 3 shows the decomposition of the spectrum of sample C

Figure 3. Spectral simulation of ^{13}C CP/MAS NMR spectrum of sample C at 20°C. The fraction of forms III, I, and amorphous component was determined and summarized in Table I.

Table I. The fraction of forms III, I, and amorphous component in sample C determined from the peak simulation of the observed ^{13}C CP/MAS NMR spectrum at 20°C

	CH_2		CH		CH_3	
	Peak no. ^a	Fraction ^b	Peak no.	Fraction	Peak no.	Fraction
Form III	1	32.1 (3.0)	8	23.8 (1.0)	11	42.7 (1.8)
	4	21.4 (2.0)	9	42.3 (1.8)	14	24.0 (1.0)
	5	10.7 (1.0)				
Form I	2	12.5 (1.0)	10	22.6	12	22.5
	6	12.5 (1.0)				
Amorphous	3	10.8	7	11.3	13	10.8

^aThe peak no. is noted in Figure 3. ^bThe fraction is represented as % for each carbon region. () means relative peak ratio in form III or form I.

at 20°C by assuming the presence of forms III, I, and amorphous component. The chemical shift of each peak of form I in sample C is assumed to be the same as that of sample B (form I). Similarly, the methine and methylene carbon chemical shifts of s-PP in the amorphous region are assumed to be the same ones observed clearly in the spectra of the sample C at 100°C as mentioned below. The chemical shift of the methyl peak of amorphous component is assumed to be 20.35 ppm which is the central methyl peak in the PSTMAS NMR spectrum. These chemical shifts for amorphous component in the solid state NMR are in agreement with the random coil shifts of s-PP in solution. The agreement between the observed and simulated spectra is good. The fraction determined is summarized in Table I. The fractions are form III, 66%; form I, 23%; and amorphous component, 11%. These values are essentially the same among the methylene, methine, and methyl peaks used for the determination within experimental error. In addition, the relative peak ratio for forms III and I is also reproduced in the spectral

simulation, (prediction 3:2:1, observed 3:2:1) for form III in the methylene region, (prediction 1:2, observed 1:1.8) for form III in the methine region, (prediction 2:1, observed 1.8:1) for form III in the methyl region, and (prediction 1:1, observed 1:1) for form I in the methyl region. This indicates the validity of the assignment of form III.

Temperature Dependence of ^{13}C CP/MAS NMR Spectra

Figure 4 shows the ^{13}C CP/MAS NMR spectra of sample A with increasing temperature along with the stick spectrum of the random coil shift of s-PP in solution. Above 60°C, a new small peak becomes visible at lowfield of the methine peak of form I. With increasing temperature, this peak becomes sharper and the intensity increases. In addition, the methylene peak of 48.29 ppm at 40°C appears to shift highfield slightly, which is due to appearance of a new peak at higher field site of the methylene peak. The intensity of the latter peak increases with increasing temperature. Since the chemical shifts of these new peaks are close to those of s-PP observed in solution, these can be assigned to amorphous component. The spectral simulation of Figure 4 shows that the form I decreases gradually from 80% (40°C) to 70% (100°C). The remainder is amorphous conformation. After the NMR measurement at 100°C, the spectrum of sample A was observed at 40°C again. No significant change was observed between two spectra at 40°C, indicating that the transition from the crystalline form I to an amorphous structure is reversible.

By contrast, temperature dependences of the ^{13}C

Figure 4. ^{13}C CP/MAS NMR spectra of syndiotactic polypropylene of sample A as a function of temperature. I, form I; a, amorphous component.

CP/MAS NMR spectra of sample B are more complicated. As shown in Figure 5, the spectrum at 100°C are quite different from that at 40°C. Judging from the change in the spectral pattern, it is clear the structural transition from form II to coexistence of form I and amorphous component occurs with increasing temperature. Detailed analysis of the spectral change gives us the information on the aspect of the structural transition. A new sharp peak at 20.5 ppm which is assigned to amorphous component is clearly visible at lowfield of the methyl peak between 40–60°C. The methine peak shifts gradually to lowfield from 40°C to 60°C and a shoulder appears at the highfield side of the main peak in the methine region. Above 70°C, the peak is clearly splitted into a doublet. The lowfield peak is assigned to amorphous component and highfield one to form I. In methylene region, a small broad peak becomes visible at about 40 ppm above 60°C. These spectral changes clearly show the transition from form II to form I with increasing temperature. This transition has also been observed in the DSC thermograph.⁶ Figure 6 shows the plot of the fraction of forms II and I, and amorphous component determined by the spectral simulation of sample B against temperature. Form II decreases rapidly between 40°C and 80°C, and amorphous component increases gradually with increasing temperature. Form I increases between 40°C and 80°C, but slightly decrease between 80°C and 100°C. After the ^{13}C CP/MAS measurement at 100°C, the sample was observed at 40°C again. The spectrum is quite similar to that of form I at

Figure 5. ^{13}C CP/MAS NMR spectra of syndiotactic polypropylene of sample B as a function of temperature. II, form II; I, form I; a, amorphous component.

Figure 6. The plot of the fraction of forms II, I, and amorphous component determined by the spectral simulation of sample B against temperature.

Figure 8. The plot of the fraction of forms III, I, and amorphous component determined by the spectral simulation of sample C against temperature.

Figure 7. ^{13}C CP/MAS NMR spectra of syndiotactic polypropylene of sample C as a function of temperature. III, form III; I, form I; a, amorphous component.

40°C and therefore, with decreasing the temperature, a transition from an amorphous structure to form I also occurs. No more form II appears.

Figure 7 shows the ^{13}C CP/MAS NMR spectra of sample C with increasing temperature. The sample contains forms III, I and amorphous component at 20°C as mentioned above (Table I). The peaks characteristic to the form III, *i.e.*, one peak at 43.72 ppm in the methylene region, and two peaks at 21.86 ppm and 19.05 ppm in the methyl region, can be still observed at 90°C. This indicates that form III is still present at 90°C.

Above 60°C, the lowfield peak at 28.5 ppm which is assigned to amorphous component, can be observed clearly in the methine region. At 100°C, the spectrum becomes similar to that of sample B although the peaks from form I tend to be sharp in sample C. The fraction of forms III and I, and amorphous component is plotted against temperature (Figure 8). Form III decreases gradually and amorphous component increases gradually with increasing temperature. Form I increases above 80°C which is in contrast to the case of sample B (Figure 6).

Thus, the conformation of new crystalline form of s-PP was proposed from the comparison of the observed spectrum with the calculated ones with ^{13}C NMR γ -effect for the candidates of the conformation. Moreover, from the variable temperature NMR experiments of three kinds of samples with predominantly forms I, II, and III, respectively, the transitions among different crystalline forms and amorphous component were discussed. In this study, the minor chemical shift effects (<0.5 ppm), which may be produced by the crystal packing observed for the methylene and methyl peaks in the spectrum of annealed α -form of i-PP¹⁰ are neglected because the concept about ^{13}C γ -effect used for spectral assignment is applicable to only the single-chain conformation. The study about the influence of the crystal packing to the ^{13}C CP/MAS NMR spectra of PP is now in progress.

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