Solid-State CP/MAS ^{13}C NMR Study of Cellulose Polymorphs

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ABSTRACT: Highly crystalline cellulose samples, which also have a high purity of crystal form, were used or prepared as models of cellulose polymorphs, cellulose I, III_I, IV_I, II, III_{II}, and IV_{II}, for solid-state ^{13}C NMR and X-ray diffraction analyses. Differences between cellulose I, II, and III in the ^{13}C NMR spectra appear at the chemical shifts of C6 in the anhydroglucose units; they have signals at 65.5–66.2, 63.5–64.1, and 62.1–62.8 ppm, respectively. Cellulose IV has a doublet signal for C4 at 83.6–84.6 ppm and a signal for C6 at 63.3–63.8 ppm, which is identical with that of cellulose II. Thus the mechanisms for the formation of cellulose polymorphs are primarily ascribed to some conformational and/or environmental transformations of C4 and C6. So-called cellulose IV_I is likely to be a mixture of cellulose I and real cellulose IV_I. The differences between cellulose III_I and III_{II} were not detected clearly at the chemical shifts of C4 and C6 but at the chemical shift of C1 and the signal pattern of C2, C3, and C5.

Introduction

It is well-known that cellulose has four polymorphs, cellulose I, II, III, and IV, which are distinguishable by X-ray diffraction. Cellulose I is the crystal form of native cellulose. Cellulose II is generally formed in regenerated cellulose or mercerized cellulose. Cellulose III is prepared by treatment of cellulose with liquid ammonia or organic amines followed by removal of the chemicals. Cellulose IV_I is prepared only from cellulose III_I by, for example, heat treatment in glycerol at 260 °C. Cellulose IV_{II} is obtained from both cellulose II and III_{II} by thermal treatment.[1]

The reversibility and the irreversibility of transformation of cellulose polymorphs involving cellulose I and II have been reported by Hayashi et al.[2,3] Namely, the transformations between cellulose I, III_I, and IV_I (cellulose I family) and also those between cellulose II, III_{II}, and IV_{II} (cellulose II family) are reversible by chemical or thermal treatments, although the cellulose II family once formed from the cellulose I family returns no longer to the cellulose I family. Gardiner and Sarko[4] report that cellulose IV_I and IV_{II} have identical unit cell size but may have different polarity of cellulose chains, *parallel* for cellulose IV_I and *antiparallel* for cellulose IV_{II}.

Many structural analyses have been carried out by using X-ray diffraction and the subsequent calculation techniques of the packing energy and conformations, electron diffraction, infrared spectroscopy, Raman spectroscopy, and others, in order to elucidate the transformation mechanisms of the above cellulose polymorphs and families. Two categories of hypotheses to explain the above phenomena have been proposed. One is the idea that the difference of the polarity of cellulose chains between the two families[4-8] causes those phenomena. Another is that some conformational differences of cellulose chains between them are the primary reasons for those phenomena and that the chain polarities are the same.[2,3,9,10] However, many questions about structural analyses of cellulose including the above phenomena still remain unsolved.[11]

Recently, high-resolution CP/MAS (cross polarization/magic angle sample spinning) ^{13}C NMR has provided much interesting and significant information about solid-state structure of cellulose, and the interpretation of the spectral patterns has been extensively discussed.[12-24] CP/MAS ^{13}C NMR spectra of cellulose I and II revealed the chemical shifts of C6 to be different.[12-17] Horii et al. have proposed the hypothesis that this is due to the conformations of the hydroxyl group of C6 in anhydroglucose units, t-g for cellulose I and g-t for cellulose II and amorphous cellulose.[18,20]

CP/MAS ^{13}C NMR measurements of cellulose III and IV were reported by Fyfe et al.[17] and Hayashi et al.[2] However, since those samples did not have sufficient crystallinity and purity of crystal forms, the spectra seemed to be mixed with not only amorphous but also other polymorphs. Thus it was difficult to detect a clear difference between cellulose polymorphs from the broad peaks in those spectra.

In this paper, therefore, cellulose samples having both high crystallinity and high purity of the crystal forms have been prepared for the first time. These model samples for cellulose polymorphs have been analyzed by X-ray diffraction and solid-state ^{13}C NMR in order to elucidate the mechanisms of the transformations of the crystal forms.

Experimental Section

Original Cellulose Samples. Ramie and microcrystalline cellulose powder (Avicel, Asahi Chemical Co. Ltd.) were used as cellulose I samples.

Preparation of Cellulose II.[13] Twenty grams of microcrystalline cellulose powder was first dissolved in the mixture of 187 mL of 85% phosphoric acid and 7.3 mL of water at room temperature for 6 weeks. The cellulose solution was then poured into 583 mL of water to regenerate cellulose II. The precipitate was collected by repetition of washing with water followed by centrifugation and freeze-drying. This cellulose II sample was used for the preparation of cellulose III_{II} and IV_{II} as described below. Celllose II having much higher crystallinity was obtained as precipitates from the supernatant of the above mixture of water and phosphoric acid by the addition of a equal volume of methanol.

Preparation of Cellulose III. A cellulose I or II sample was soaked in liquid ammonia at −33 °C for several hours, according to the conventional method for the preparation of cellulose III.[25] The reaction product was obtained by evaporation of liquid ammonia at room temperature under atmospheric pressure. Another

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Table I
Degrees of Polymorization of Cellulose Samples

cryst form	sample or preparation method	DPv
1. cellulose I	ramie	1012
2. cellulose I	microcrystalline cellulose powder	138
3. cellulose III_I	1 treated with liquid NH_3 at −33 °C	1012
4. cellulose III_I	1 treated with liquid NH_3 at 140 °C	690
5. cellulose III_I	2 treated with liquid NH_3 at −33 °C	130
6. cellulose III_I	2 treated with liquid NH_3 at 140 °C	130
7. cellulose IV_I	4 treated with glycerol at 260 °C	62
8. cellulose IV_I	5 treated with glycerol at 260 °C	65
9. cellulose II	regenerated cellulose prepared from 2 in H_2O	15
10. cellulose II	regenerated cellulose prepared from 2 in MeOH	6
11. cellulose II	mercerized ramie	911
12. cellulose III_{II}	9 treated with liquid NH_3 at −33 °C	17
13. cellulose III_{II}	9 treated with liquid NH_3 at 140 °C	16
14. cellulose III_{II}	11 treated with liquid NH_3 at −33 °C	927
15. cellulose III_{II}	11 treated with liquid NH_3 at 140 °C	460
16. cellulose IV_{II}	9 treated in water at 190 °C	21

method[26] is the following. The cellulose I or II sample was first soaked in liquid ammonia at −33 °C in a stainless steel pressure vessel. The vessel was maintained at room temperature for 2 days and then heated to 140 °C (over the critical temperature of ammonia = 132.5 °C) for 1 h. Ammonia was removed at this temperature by loosening the screw cap of the pressure vessel.

Preparation of Cellulose IV. For the preparation of cellulose IV_I, high-crystallinity or low-crystallinity cellulose III_I was first soaked in glycerol for 3 days at room temperature. Fresh glycerol was exchanged three times during the soaking. Then the sample in glycerol was heated in the pressure vessel at 260 °C for 0.5 h.[27] After cooling to room temperature, the product was washed with water and acetone successively and dried in vacuo. The yields were 80–85%. Cellulose IV_{II} was prepared from the cellulose II sample by heating in water at 190 °C for 2 h.[28] After cooling to room temperature, the product was washed with water and acetone successively and dried in vacuo. The yield was 55%.

Viscosity Measurements. Intrinsic viscosities of cellulose samples were measured using 0.5 mol of Cuen (copper ethylenediamine solution) and a capillary-type viscometer.[29] Degrees of polymerization of cellulose (DPv) were calculated from the intrinsic viscosity according to the following formula:[30]

$$DPv^{0.905} = 0.75[\eta] \quad (1)$$

X-ray Diffractions. X-ray diffraction patterns of cellulose samples were recorded on a JEOL JDX-5B diffractometer equipped with the reflection-type goniometer and the pulse-height discriminator (PHD) system, using Ni-filtered Cu Kα radiation. Radiation conditions were 40 kV and 35 mA, and the scanning rate was 0.5° of 2θ per a minute.

NMR Measurements. Solid-state ^{13}C NMR spectra were recorded on a JEOL JNM-GX270 spectrometer (magnetic field = 6.34 T; ^{13}C frequency = 67.8 MHz) with a CP/MAS unit at room temperature. The spinning rate and the contact time were 3.6–3.8 kHz and 2 ms, respectively. A bullet type Kel-F rotor contained about 300 mg of a sample. Recycle time of pulse was 5 s. The spectrum was accumulated 80–100 times. The signal of the CH of adamantane was used as an external reference to determine chemical shifts.

Results and Discussion

Preparation of Highly Crystalline Cellulose I and II. Cellulose samples used in this work and their degrees of polymerization (DPv) are shown in Table I. In native cellulose samples, algal and bacterial celluloses are known to have higher crystallinity than ramie and microcrystalline cellulose powder. However, solid-state ^{13}C NMR studies on native celluloses have revealed that native celluloses consist of two different spectrum patterns, cellulose I_α and I_β, which correspond to the main component of the former and the latter samples, respectively.[13-15,24] In this study, cellulose I_β rich samples were used as the model of native cellulose in higher plants.

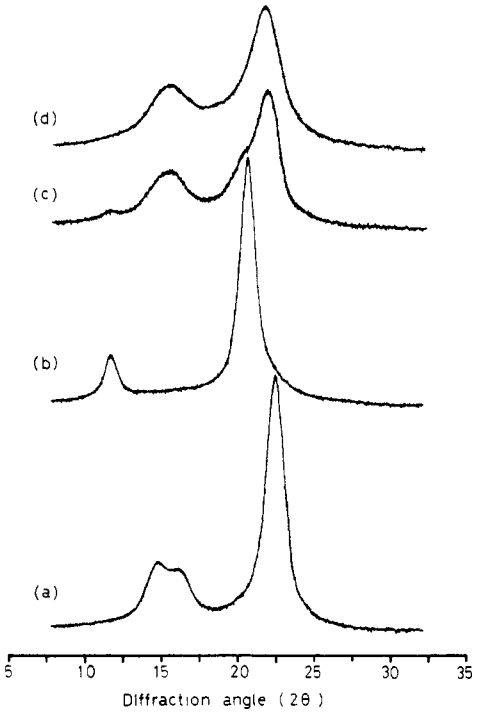

Figure 1. X-ray diffraction patterns of the cellulose I family: (a) ramie cellulose I; (b) cellulose III_I prepared from ramie; (c) cellulose IV_I prepared from (b) in this figure; (d) cellulose IV_I prepared from the sample 5 in Table I.

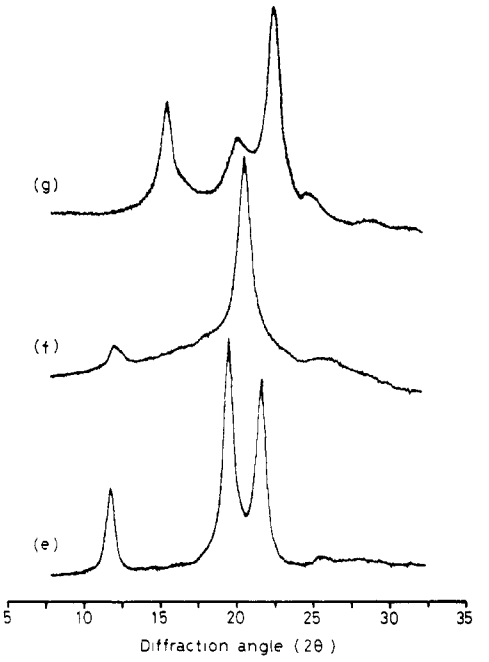

Figure 2. X-ray diffraction patterns of the cellulose II family: (e) cellulose II; (f) cellulose III_{II}; (g) cellulose IV_{II}.

Since the crystallinities of cellulose II in mercerized and regenerated celluloses are not so high, a low molecular weight regenerated cellulose sample was used as the model of cellulose II (Figure 2e). The cellulose II sample regenerated by the addition of methanol (no. 10 in Table I) has a DPv of 6; it is a cellulose oligomer. Cellulose oligomers have been reported as good models of cellulose II for X-ray diffractions and solid-state ^{13}C NMR studies.[19,31]

Preparation of Highly Crystalline Cellulose III_I and III_{II}. As shown in Figure 1b, highly crystalline cellulose III_I was obtained from ramie by the method reported by Yatsu et al.[26] Although the preparation condition of highly crystalline cellulose III from ramie was very severe,

Table II
Peak Positions in X-ray Diffractograms and Diffraction Planes of Cellulose Polymorphs

	diffraction angle 2θ, deg			
polymorph	1$\bar{1}$0	110	020	012
cellulose I	14.8	16.3	22.6	
cellulose II	12.1	19.8	22.0	
cellulose III_I	11.7	20.7	20.7	
cellulose III_{II}	12.1	20.6	20.6	
cellulose IV_I	15.6	15.6	22.2	
cellulose IV_{II}	15.6	15.6	22.5	20.2

as described in the Experimental Section, the infrared spectrum and the meridional X-ray diffraction pattern of the flat-film fiber photograph of this cellulose III did not show cellulose III_{II} but only cellulose III_I.[2]

Highly crystalline cellulose III_{II} has been prepared from the low molecular weight and highly crystalline cellulose II sample by treatment with liquid ammonia at 140 °C under high pressure (Figure 2f). Mercerized ramie did not transform to a more highly crystalline cellulose III_{II} than the above sample, probably because of the relatively lower crystallinity of mercerized ramie. After treatment of the cellulose II with liquid ammonia at −33 °C, these samples showed almost amorphous X-ray diffraction patterns. The DPv's of cellulose III prepared from relatively low molecular weight celluloses or prepared by the treatment with liquid ammonia at −33 °C were almost identical with those of the sample before the treatments, whereas in the case of ramie and mercerized ramie, the treatment at 140 °C brought about a decrease in the DPv.

Thus cellulose I or II sample having higher crystallinity can transform to higher crystallinity cellulose III.

Preparation of Highly Crystalline Cellulose IV_I and IV_{II}. Relatively highly crystalline cellulose IV_I can be prepared from cellulose III_I by the presoaking in glycerol followed by heating in glycerol at 260 °C.[27] This treatment was applied to four cellulose III_I samples in Table I. As shown in Figure 1, highly crystalline cellulose III_I prepared from ramie did not transform to cellulose IV completely, and the peaks due to cellulose III were still detected. On the other hand, the low-crystallinity cellulose III_I prepared from microcrystalline cellulose powder by the treatment with liquid ammonia at −33 °C seems to contain relatively pure cellulose IV. Many attempts to prepare highly crystalline cellulose IV_I made it clear that the cellulose III_I with the lower molecular weight and lower crystallinity transforms to a relatively higher crystallinity cellulose IV_I, although the crystallinity is far less than that of the other cellulose polymorphs (Figures 1 and 2). As shown in Table I, cellulose IV_I samples prepared from both ramie cellulose III_I and microcrystalline cellulose III_I have almost identical DPv's, and this result indicates that cellulose IV_I has a leveling-off DPv around 60–65.

High-crystallinity cellulose IV_{II} has been prepared from high-crystallinity and low molecular weight cellulose II by heating in water at 190 °C. Relatively low molecular weight regions of cellulose II may be lost by degradation and dissolution during the hydrothermal treatment to cause a slight increase in DPv.

The results of the preparation of cellulose IV_I and IV_{II} indicate that the higher crystallinity cellulose IV can be prepared from the lower molecular weight cellulose III_I or II by thermal treatments and that the crystallinity of the original sample does not always run parallel with the crystallinity of the transformed cellulose IV.

Peak positions of each X-ray diffraction pattern and their assignments to reflection planes are shown in Table II.

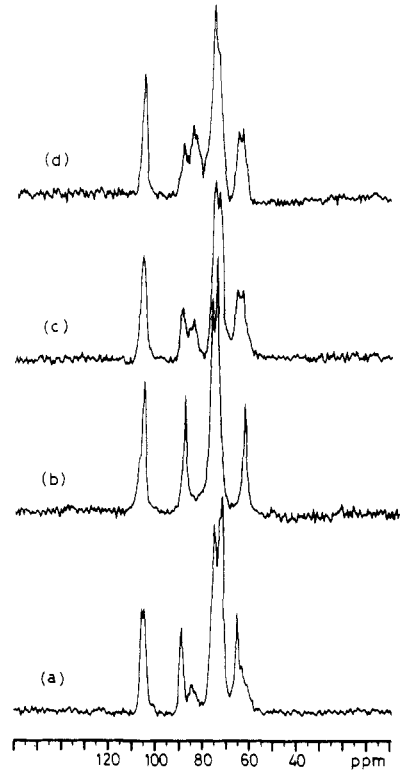

Figure 3. Solid-state ^{13}C NMR spectra of the cellulose I family: (a) ramie cellulose I; (b) cellulose III_I prepared from ramie; (c) cellulose IV_I in Figure 1c; (d) cellulose IV_I in Figure 1d.

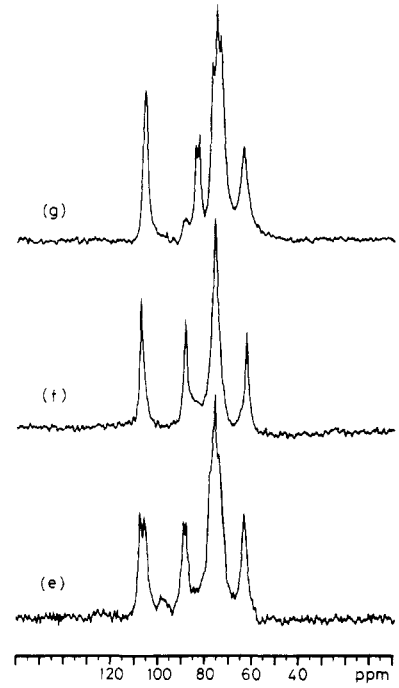

Figure 4. Solid-state ^{13}C NMR spectra of the cellulose II family: (e) cellulose II; (f) cellulose III_{II}; (g) cellulose IV_{II}.

Solid-State ^{13}C NMR Spectra of Cellulose I and II. These spectra were shown in Figures 3a and 4e, respectively. Signal patterns of these cellulose polymorphs were almost identical with those reported so far.[12-18,20] A clear difference between them is the signal position of C6, 65.7 ppm for cellulose I and 63.7 ppm for cellulose II. The shoulder signal around 64 ppm and the small broad signal around 84 ppm in ramie are known to arise from the C6 and C4 carbons in the amorphous region, respectively. The small signal around 98 ppm in the spectrum of highly

Table III
^{13}C Chemical Shifts of Crystalline Celluloses

polymorph	^{13}C chem shifts, ppm		
	C1	C4	C6
cellulose I	105.3–106.0	89.1–89.8	65.5–66.2
cellulose II	105.8–106.3	88.7–88.8	63.5–64.1
cellulose III_I	105.3–105.6	88.1–88.3	62.5–62.7
cellulose III_{II}	106.7–106.8	88.0	62.1–62.8
cellulose IV_I	105.6	83.6–84.4	63.3–63.8
cellulose IV_{II}	105.5	83.5–84.6	63.7
amorphous	ca. 105	ca. 84	ca. 63

crystalline cellulose II is assigned to the α-type anomeric C1 carbon of the reducing end glucose residue in the cellulose oligomers.

Solid-State ^{13}C NMR Spectra of Cellulose III_I and III_{II}. The solid-state ^{13}C NMR spectrum of highly crystalline cellulose III_I prepared from algal cellulose, whose main crystal pattern is cellulose I_α, has been already reported by Atalla.[32] As shown in Figure 3b, highly crystalline cellulose III_I has also been prepared from ramie, which mainly consists of cellulose I_β, and shows the ^{13}C NMR pattern identical with that prepared from algal cellulose. The spectrum of highly crystalline cellulose III_{II} (Figure 4f) has been obtained from high-crystallinity and low molecular weight cellulose II.

Both cellulose III_I and III_{II} have almost identical signal patterns at C4 and C6; namely, these carbons show single resonances at 88.0–88.3 and 62.1–62.8 ppm, respectively. The difference between cellulose III_I and III_{II} is evidenced at C1: 105.3–105.6 ppm for III_I and 106.7–106.8 ppm for III_{II}. Different patterns were also found around 70–80 ppm arising from C2, C3, and C5; cellulose III_{II} shows a single broad signal, whereas the signal for III_I is split.

Solid-State ^{13}C NMR Spectra of Cellulose IV_I and IV_{II}. Solid-state ^{13}C NMR spectrum of highly crystalline cellulose IV_{II} has been obtained as shown in Figure 4g. This pattern has several unique characteristics, compared with others. First of all, a sharp doublet resonances for C4 appeared at 83.6 and 84.4 ppm; these positions are almost identical with that of C4 in amorphous cellulose. However, judging from the high crystallinity of this cellulose IV_{II} sample as shown in the X-ray diffraction pattern (Figure 2g), the sharp doublet resonances are apparently assigned to crystalline C4. Single resonances for C1 and C6 appeared at 105.5 and 63.7 ppm, respectively, and the latter was slightly broad. The resonances due to C2, C3, and C5 display maxima at 73.8, 74.8, and 77.0 ppm.

On the other hand, as described in the third section, since the crystallinities of the cellulose IV_I samples were not so high, they showed complicated patterns, especially at C4 and C6 in Figure 3c,d. Two resonances for C6 appeared at 63.7 and 65.7 ppm, and two relatively broad resonances for C4 appeared at approximately 89 and 84 ppm in these spectra. However, it is difficult to interpret these complicated and unresolved ^{13}C NMR patterns as the typical pattern of cellulose IV_I.

As described previously, the C6 signals at 65.7 and 63.7 ppm in these spectra are identical with those for cellulose I and IV_{II} or II, respectively. The signals around 84 and 89 ppm for C4 appeared at the same positions as those in the spectra of cellulose IV_{II} or amorphous cellulose and cellulose I, II, or III, respectively. Although the slight cellulose III peaks were detected in the X-ray diffraction pattern of the sample, Figure 1c, the resonances due to this residual cellulose III were not distinguishable because of the overlap with other signals. When the X-ray diffraction patterns of these two cellulose IV_I samples are considered in connection with the corresponding solid-state ^{13}C NMR spectra, it is found that the C4 signal at about 84 ppm increases and simultaneously the 89 ppm signal decreases upon increasing the crystallinity and purity of cellulose IV_I. The X-ray diffraction pattern of the sample in Figure 1d shows that this so-called cellulose IV_I sample includes neither cellulose II nor III. However, it is likely that this broad cellulose IV_I pattern consists of a mixture of cellulose I and IV. Furthermore, it is well-known that cellulose I reappears from cellulose IV_I by acid hydrolysis.[2,3] In this case, however, it is possible to consider that the residual cellulose I in the so-called cellulose IV_I samples reappears by the removal of cellulose IV, which is more susceptible to acid hydrolysis than cellulose I in the mixture. Therefore, all these X-ray, ^{13}C NMR, and chemical data indicate that the so-called cellulose IV_I is a mixture of cellulose I and IV. Namely, the thermal treatment of cellulose III_I brings about the partial transformation to cellulose IV_I together with the partial returning to cellulose I. Atalla[9] has also reported from the data of Raman spectra that cellulose IV_I is a mixture containing cellulose I.

Thus in view of the likelihood that the cellulose IV_I samples used in this work are crystallographically impure and may contain cellulose I, the chemical shifts of C4 and C6 of cellulose IV_I and IV_{II} may be similar. The chemical shift of C4 around 84 ppm is probably the signature of cellulose IV, which sets it apart from the spectra of the celluloses, I, II, and III.

Cellulose Polymorphs and Families. X-ray diffractions and solid-state ^{13}C NMR of highly crystalline and pure cellulose polymorphs have revealed that the difference between cellulose I, II, III, and IV appears at the chemical shifts of C4 and C6, irrespectively of I and II families. The chemical shifts of these cellulose polymorphs are summarized in Table III. Some conformational transformations[33] or crystalline packing influences of C4 and C6 in anhydroglucose units are likely to cause these chemical shift differences between cellulose polymorphs, together with the transformations of X-ray diffraction patterns.

As for the cellulose I and II families, cellulose III_I and III_{II} have different ^{13}C NMR resonance shapes corresponding to C1 and the patterns for C2, C3, and C5. However, since so-called cellulose IV_I has not only relatively low crystallinity but also a structure mixed with cellulose I, clear differences between cellulose IV_I and IV_{II} cannot be discussed. Further studies on cellulose IV_I, including the preparation of pure cellulose IV_I, are required to elucidate the true difference between cellulose IV_I and IV_{II} polymorphs.

Registry No. Cellulose, 9004-34-6.

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Growth of Polypropylene Particles in Heterogeneous Ziegler–Natta Polymerization

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ABSTRACT: Nascent polypropylene particles prepared with δ-$TiCl_3$ catalyst systems have been examined by small-angle X-ray scattering, wide-angle X-ray diffraction, and electron microscopy. The catalyst crystallites which disperse at the initial stage of polymerization uniformly within the polymer particles retain their initial size during the course of polymerization. As the polymerization proceeds, the 0.2–0.35-μm primary polymer particles become visible under an electron microscope, and their size increases in proportion to the cube root of the polymer yield.

Introduction

In a previous paper we examined the architecture of nascent polypropylene particles prepared with heterogeneous Ziegler–Natta catalysts by transmission electron microscopy using a newly developed staining method.[1] The nascent polymer particles are made up of primary polymer particles which contain one or sometimes a few catalyst crystallites at the individual cores. The sizes of the catalyst crystallites within the primary polymer particles are in good agreement with that of the original catalyst crystallites. The primary polymer particles, 0.2–0.35 μm in diameter, are much smaller than the polymer globules observed on the surfaces of the nascent polymer particles, about 1 μm in diameter, which have so far been accepted as the primary polymer particles.[2] Such a difference in size suggests that several tens of the primary polymer particles probably constitute each of the polymer globules, i.e., secondary polymer particles. From these findings, we concluded that the nascent polymer particles may have a tertiary structure.

In olefin polymerization with the $TiCl_3$ catalysts it is observed in an electron microscope that the original catalyst particles disintegrate immediately into basic particles.[3,4] Hock reported that such basic particles retain their shapes during the course of polymerization.[3] On the other hand, Buls et al. reported that these basic particles break down further into smaller units.[4] Our previous observation of the nascent polymer particles indicated that the catalyst crystallites keep their initial shapes even at higher polymer yields.[1]

In the present work, we have examined the microstructure of the nascent polypropylene particles widely differing in polymer yield by using small-angle X-ray scattering (SAXS), wide-angle X-ray diffraction (WAXD), and electron microscopy to understand the growth mechanism of polymer particles during polymerization. From these observation we have concluded that the catalyst crystallites retain their sizes in the course of the polymerization and the primary polymer particles grow with the proceeding of polymerization.

Table I
Characteristics of Catalysts

catalyst	av particle size,[a] μm	crystallite size,[b] Å	polymerization activity,[e] g of polym/g of catal
δ-$TiCl_3$(I)	19	108,[c] 185[d]	1100
δ-$TiCl_3$(II)	18	75,[c] 75[d]	4500

[a] Determined by a sedimentograph with decaline as the disperse medium. [b] Determined with WAXD. [c] D_{300}, length of the primary catalyst crystallites normal to the (300) plane. [d] D_{003}, length of the primary catalyst crystallites normal to the (003) plane. [e] Polymerization was cararied out at 65 °C for 2 h in liquefied propylene.

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