

Considerations on Detailed Analysis and Particle Growth in High Impact Polypropylene Particles

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ABSTRACT: Detailed analysis of the dispersion of ethylene and propylene copolymer components in high-impact polypropylene particles was performed by the morphological observation, pore volume analysis, and microscopic Fourier transform infrared spectroscopy of SPring-8. The results of the morphological observation and pore volume distribution suggest that copolymer components were formed in particles in such a manner as to fill the gaps of fine homopolypropylene particles. The results of the analysis by microscopic Fourier transform infrared spectroscopy were that the distribution of the amount of ethylene in the particles was homogeneous and indicated that copolymer

components were dispersed uniformly within the particles. Moreover, spots with high amounts of ethylene were formed on the particle surface, and when voids existed within the particle, spots with high amounts of ethylene were also formed on the void surface. The structure of the copolymer components existing locally on the surface was practically similar to the structure of the copolymer components within the particles. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 632–638, 2011

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INTRODUCTION

Polypropylene has advantages of high rigidity, light weight, and high recyclability. In view of these advantages, it is the most popularly used plastic in the world. The annual demand for polypropylene is in excess of 40 million tons. Polypropylene can be classified into three types: homopolypropylene, random polypropylene, and high-impact polypropylene (hiPP). Isotactic polypropylene (iPP), with its high crystallinity and excellent rigidity, is mainly used as homopolypropylene. It is used in injection-molding products and high-heat-resistant sheets. Polypropylene random copolymer is a copolymer consisting of propylene and a small amount of ethylene. It is a material combining appropriate strength and impact strength and is used in high-performance films and so on. hiPP is a material wherein copolymer components of ethylene and propylene, which are rubber components, are finely dispersed in a crystalline iPP matrix. Its features include an excellent balance of

rigidity and impact strength. For this reason, this material is widely used in home electric appliances and in injection-molding parts for the automotive industry, such as bumper and interior materials in cars.

When homopolypropylene and copolymer components are physically mixed, the dispersion of the copolymer components becomes nonuniform, and adequate mechanical balance is not obtained. Thus, hiPP is manufactured by so-called *reactor blending*; after the polymerization of homopolypropylene, it is moved to the next reactor, and the ethylene–polypropylene copolymer reaction is made to occur continuously. It is known that some problems, such as agglomeration and sticking to the reactor, occur during the copolymerization process, so controlling the shape of particles and controlling their properties are important topics. However, research related to hiPP particles is very meager, and understanding of hiPP particles is inadequate.

Kakugo¹ reported that the polypropylene particle structure in iPP was formed by mesoparticles (called *polymer globules*, with a size of about 1 μm), with each consisting of a group of several primary particles. On the basis of this structure, Debling and Ray² proposed models for the growth of grains in which copolymer components in the copolymerization process occupy the gaps between the primary

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particles and the mesoparticles of iPP. They performed morphological observations and line analysis of the rough ethylene distribution from the powder surface to the internal part by microscopic Fourier transform infrared (FTIR) spectroscopy, but because the detailed distribution of the powder is not fully understood, the analysis was probably inadequate. Cecchin et al.,³ MacKenna et al.,⁴ Urdampilleta et al.,⁵ and others reported on the space in the hiPP particles, the size of the mesoparticles, and the conditions of the particle surface in the copolymerization process through morphological observations with scanning electron microscopy (SEM) at low magnification and by pore volume analysis with the mercury press-in method. However, the dispersion state of the copolymer components in the microarea is not fully understood. Moreover, room for improvement also remains because the results of the mercury press-in method probably did not reflect the pore conditions accurately because pressure was applied on a sample that included soft components such as copolymer. Thus, in practice, it is difficult to say that analysis related to the particle growth mechanism of hiPP until now has been adequate.

Accordingly, clarifying the dispersion state of the copolymer components in iPP in a microarea and the pore volume with a method that does not apply pressure and clarifying the distribution of the amount of ethylene in the iPP whole particle would help to determine the particle growth mechanism of hiPP more accurately and would be very convenient for controlling the properties, such as adhesion, of the particles. The distribution of the copolymer components in hiPP particles and considerations related to the copolymer reactions and the growth mechanism of the hiPP particles are reported here in detail.

EXPERIMENTAL

Preparation of the solid catalyst

For the preparation of the solid catalyst, silicon tetrachloride, dinormal butyl phthalate, and titanium tetrachloride were dropped into a heptane slurry of magnesium diethoxide in a reactor replaced with inert gas sequentially and brought into contact at 110°C. The supernatant was removed and washed with heptane by decantation. Next, titanium tetrachloride was again charged and brought into contact at 110°C, the supernatant was removed and washed with heptane by decantation, and a heptane slurry of the solid catalyst was obtained.

Triethyl aluminum (TEA) and dicyclopentyl dimethoxysilane (DCPDMS) were brought into contact with the solid catalyst heptane slurry, and a small amount of propylene was introduced in the reactor

and polymerized thereafter. TEA and DCPDMS were removed by washing with heptane and separated, and catalyst A was prepared.

Polymerization of hiPP

Homopolypropylene particles (30 g) were placed in a stainless steel autoclave with a stirrer, and the charging tube was replaced with nitrogen. Hydrogen (0.6 MPa) was charged, and propylene was introduced so that the total pressure became 2.8 MPa. Next, TEA, DCPDMS, and catalyst A were charged sequentially into the autoclave through the charging tube, and homopolymerization started. During polymerization, propylene was supplied continuously so that the pressure remained constant. Subsequently, the pressure was released once, hydrogen at 0.1 MPa was charged, and a gaseous mixture of ethylene and propylene at a ratio of 1 : 1 was introduced such that the total pressure became 1.0 MPa. The gaseous mixture was supplied continuously so that the pressure remained constant during copolymerization. After copolymerization, hiPP powder was dried for 4 h at reduced pressure at 80°C.

SEM observation

Ruthenium tetroxide, which can stain amorphous components, was used to stain the particle surface and section, and SEM (made by JEOL, Ltd., Tokyo, Japan) observations were performed. Particle sections were cut out at -80°C with an ultramicrotome.

Measurement of the pore volume distribution

With a Shimadzu ASAP 2010 (Kyoto, Japan), the pore volume was measured by the nitrogen gas adsorption method. With this method, we made use of the measurements at -200°C, that is, below the glass-transition temperature of the copolymer component.

FTIR measurement

We obtained the sample for microscopic FTIR analysis by slicing a section about 100 μm thick from the central part of the hiPP particles using a knife and observing it under the microscope. Next, the sample was analyzed with microscopic FTIR placed in the infrared beam line of a SPring-8 synchrotron radiation facility (Sayo-Gun, Hyogo, Japan). Because the intensity of infrared radiation of this analyzing apparatus is high, and it has excellent spatial resolution, it is ideal for speedy section analysis over a wide range with high spatial resolution.⁶ The measurement of the whole sample or part thereof was carried out at 50-μm steps. The distribution of

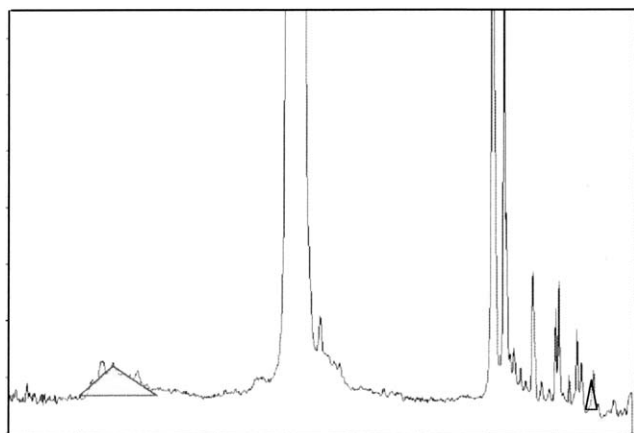


Figure 1 FTIR spectrum of hiPP.

ethylene component in the particles was mapped with an absorption of 721 cm^{-1} , called the *ethylene band*, as shown in Figure 1. Because the sample had irregular thickness, we corrected the amount of ethylene by dividing the ethylene band area by the absorption area near the $4000\text{--}4500\text{ cm}^{-1}$ range. The absorption near $4000\text{--}4500\text{ cm}^{-1}$ expressed the thickness of the sample, so it was called *thickness band*.⁷

RESULTS AND DISCUSSION

Morphology of the particle cross section and surface

Figure 2 shows the SEM image of the particle cross section cut out with an ultramicrotome. The light-colored parts are the parts stained by ruthenium tetroxide. Pores were observed in iPP that were on the order of micrometers. The polymer parts were considered to be divided into different sizes of several micrometers within the particle, which may have been represented by units of mesoparticles made up of several primary particles or groups of multiple particles. In case of hiPP, even when the amount of the copolymer components was small

(hiPP1), the copolymer components existed in mesh form.

As the amount of the copolymer increased, the mesh structure became finer, and the width of the mesh also expanded (hiPP2). The mesh structure may have indicated that the copolymer components were filled between mesoparticles. At several locations, rather large stained areas existed (as shown by arrows in the figure). These areas indicated copolymer components that occupied holes on the order of micrometers seen in homopolypropylene.

Figure 3 shows the particle surface stained by ruthenium tetroxide and observed through the SEM. Figure 3(a) shows iPP with no copolymer component, Figure 3(b) shows an hiPP particle containing 18 wt % copolymer components, and Figure 3(c) shows an hiPP particle containing 37 wt % copolymer components. The light-colored part is the part stained by ruthenium; it indicates the existence of the copolymer component. As shown in this figure, a small amount of the copolymer component existed on the surface when the content of the copolymer component in the particles was comparatively low. When the content of the copolymer component became high, the amount of the copolymer component on the surface increased significantly.

Pore volume

Figure 4 shows the changes in the pore volume in the particles corresponding to the content of the copolymer component studied by the nitrogen gas adsorption method. As shown in this figure, the pore volume decreased when the content of the copolymer component increased, and when the copolymer component exceeded 20 wt %, the pore volume practically decreased to one-tenth. Because the pore diameters were in the 2–100-nm range, it was difficult to observe them with SEM by this method. These pores practically disappeared when the copolymer component percentage exceeded 20 wt %.

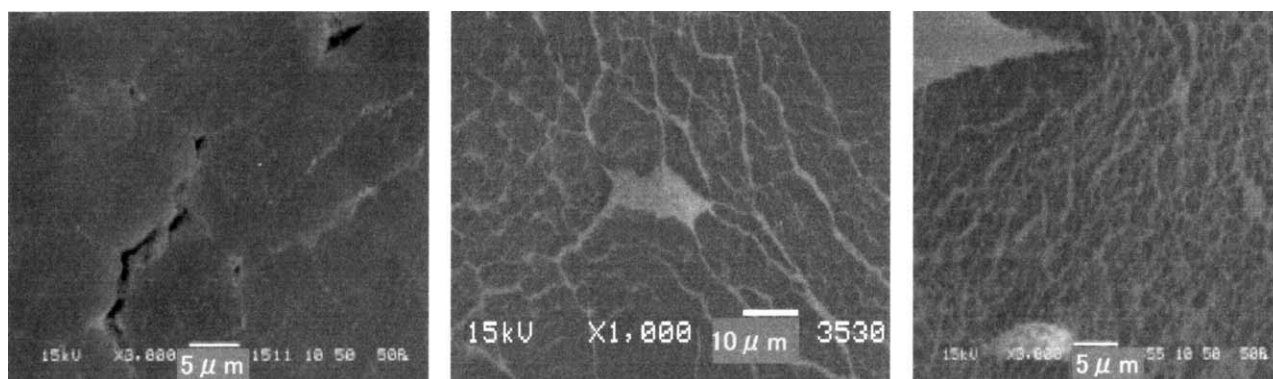


Figure 2 SEM photographs of the cross section stained with ruthenium tetroxide.

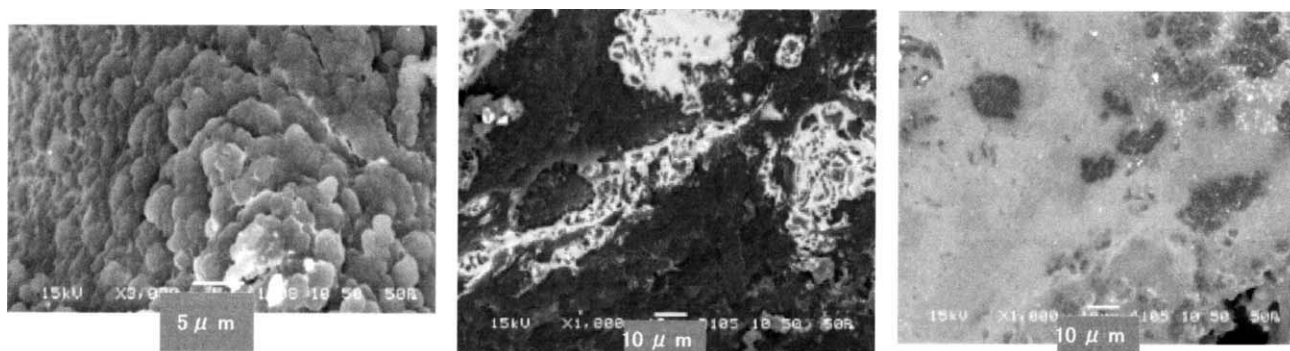


Figure 3 SEM photographs of the particle surface stained with ruthenium tetroxide.

Distribution of the amount of ethylene

Figure 5 shows the results of the analysis of ethylene distribution studied by microscopic FTIR spectroscopy placed in the infrared beam line of the SPring-8 synchrotron radiation facility. These specimens included particles with 18, 37, and 60 wt % copolymer components. The upper figures show optical photographs of the samples, whereas the lower figures show the distribution of the amount of ethylene of the part surrounded by yellow lines in the online photographs. The colors in the online figure indicate the amount of ethylene. The larger the numerical values were, the higher the ethylene amount was; that is, the larger the amount of the copolymer components was. As shown in these figures, regardless of the copolymer component amount within the particles, there was no gradient in the amount of ethylene, and the distribution was homogeneous. On the other hand, spots with high ethylene amounts formed near the surface. When the amount of the copolymer component increased, this trend became stronger.

Figure 6 relates to a typical particle used in the studies and shows the results of the measurement of a particle with internal voids. Figure 6(a,c) shows particles with comparatively low copolymer amounts of 13 wt %, whereas Figures 6(b,d) shows the results of particles in which the amount of the copolymer was 50%. Figure 6(a,b) shows optical photographs, whereas Figure 6(c,d) shows results of the FTIR analysis of almost the same region as in the photographs. From the results of imaging of the distribution of amount of ethylene, we observed that spots with high ethylene amounts formed near the surface and that the distribution of the amount of ethylene was uniform in the polymer region. These trends were the same as those of the particle shown in Figure 5, but characteristically, locations with high ethylene intensity were formed near the internal surface of the voids.

Amorphous components and crystalline polyethylene are known to exist in the copolymer formed in

hiPP. This crystalline polyethylene is considered to be formed from the reduced parts of active sites. At spots with high amounts of ethylene, such structures are likely to be formed selectively. Because amorphous and crystalline ethylene indicate different absorptions by wave numbers in infrared absorption, the difference appears on the infrared spectrum and can be distinguished. Figure 7 shows the distribution of the amount of ethylene on the surface of a typical particle with internal voids. Parts I and II, surrounded by four corners in the figure, indicate typical areas where the amount of ethylene was high on the surface of internal voids and the particle surface, whereas part III indicates an area with an average amount of ethylene within the polymer area of the grain. The FTIR spectra charts I–III show the FTIR spectrum near the ethylene band ($680\text{--}760\text{ cm}^{-1}$) and the results of curve-fitting analysis at the parts surrounded by four corners I–III in the figure.

The assignment of waveform analysis⁷ near the ethylene band is shown in the FTIR spectrum diagram I. Crystalline ethylene shows absorptions at 720 and 730 cm^{-1} , whereas amorphous ethylene is known to show absorption at 722 cm^{-1} . The structure called *isolated ethylene*, containing one ethylene unit in a propylene chain, shows absorption at 735

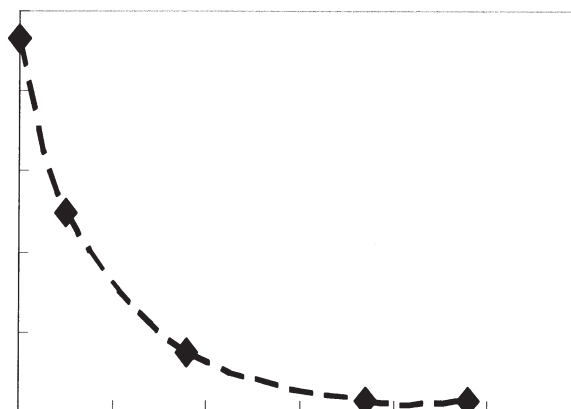


Figure 4 Change in the pore volume in the particle due to the copolymer content.

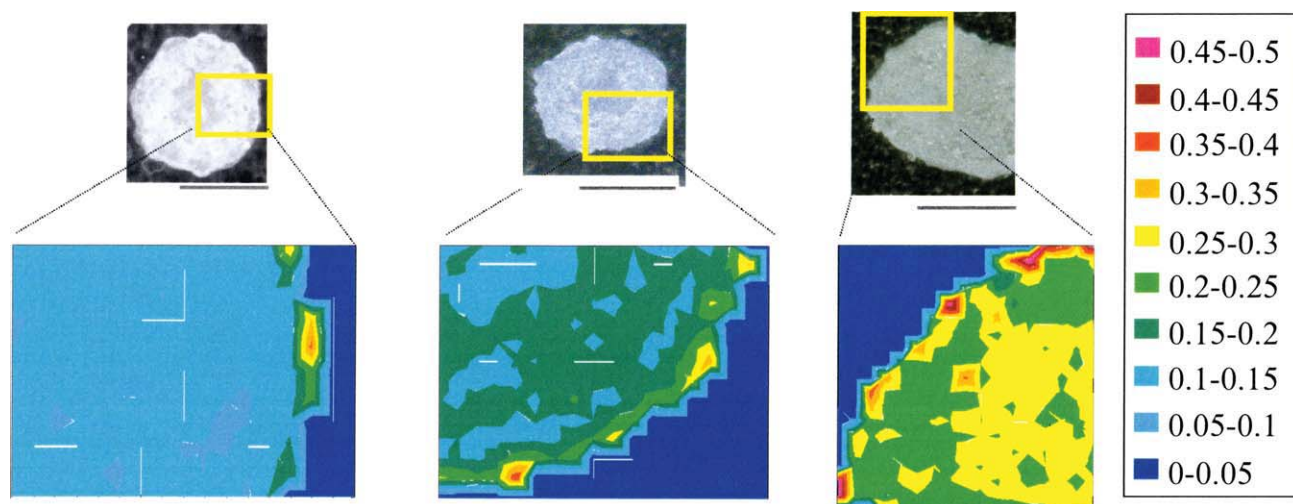


Figure 5 Images of the distribution of ethylene in the hiPP particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cm^{-1} . If the strength of each absorption comprising the ethylene band differs, the shape of the entire spectrum changes, and the difference can be detected better by curve-fitting analysis. Comparing the spectral diagrams I–III, we saw that the shape of the spectrum at each location was similar, and even if amounts of crystalline polyethylene and amorphous ethylene were compared from the curve-fitting analysis results, the component ratios were practically the same. This suggests that the structure of the copolymer component at each location was similar.

Particle growth mechanism

From the results of the detailed analysis obtained in this study (SEM observations, pore volume, and

microscopic FTIR), we presumed that the particle growth model proposed by Debling and Ray,² as shown in Figure 8, was the most ideal model.

Part I in the figure expresses the typical mesoparticle (globule) model; it was composed of primary particles of polypropylene. Because the active sites of polymerization are considered to exist on the surface of the primary particle, when copolymerization progressed from this state, the copolymer components generated at the active sites on the primary particle proceeded initially to fill the spaces between the primary particles in a mesoparticle (part II in the figure). As the reaction progressed further, the copolymer components could no longer be accommodated in the mesoparticle, and they filled up the spaces between the mesoparticles (see part III in the figure).

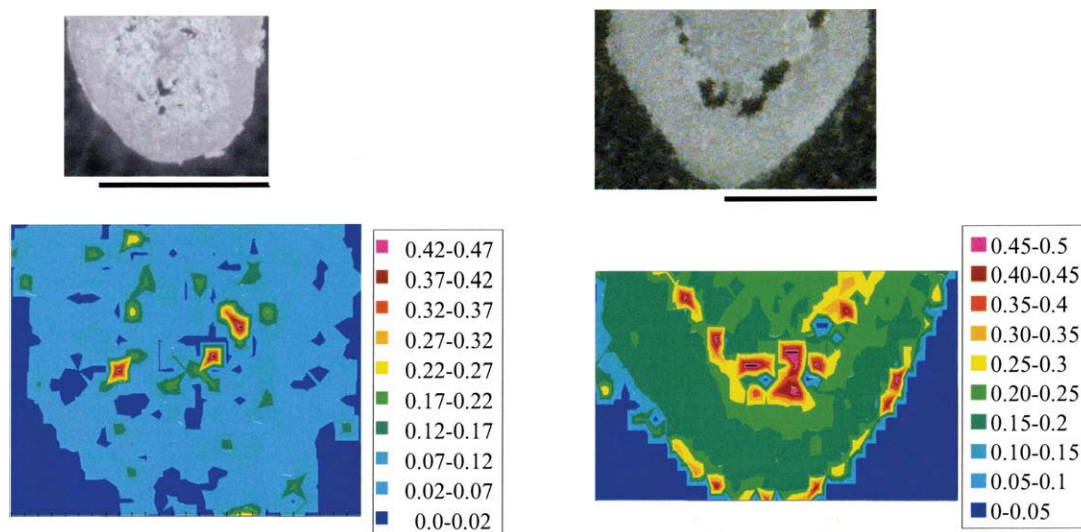


Figure 6 Images of the distribution of ethylene in the hiPP particles with internal voids. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

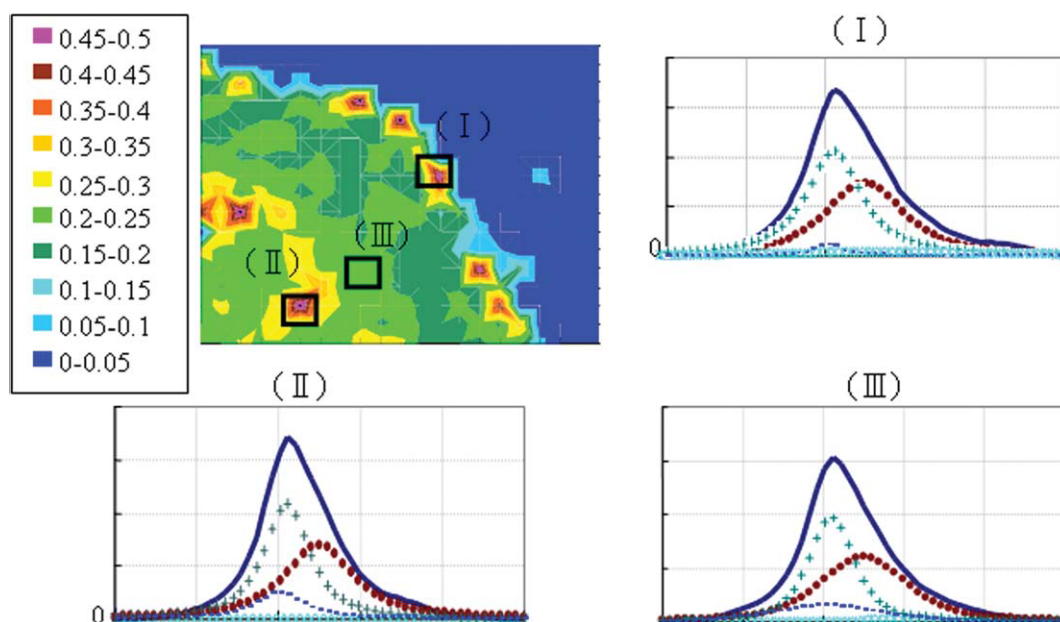


Figure 7 Infrared spectra of spots with different amounts of ethylene and results of the curve-fitting analysis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Primary particles were on the order of submicrometers. The size of the gaps between the primary particles was on the order of nanometers. Although observation by SEM was difficult, the reduction in the pore volume observed by the gas adsorption method (Fig. 4) indicated that pores in the mesoparticle were most likely filled by copolymer components during copolymerization. The mesh structure in the hiPP particles observed by SEM (Fig. 3) reflected the state of the copolymer components that could not enter the mesoparticle filling up the spaces between the mesoparticles. Moreover, in particles with a large amount of the copolymer components, the width of the mesh between mesoparticles seemed to have increased. This suggested that the copolymer components not only entered the spaces between particles but also expanded the spaces and generated cracks.

The results of the analysis of the amount of ethylene by FTIR (Figs. 5 and 6) indicated that no concentration gradient was observed from the surface toward the internal parts, although the content of the copolymer components in the composition within the particles was high. This means that the monomer concentration within the particles was practically the same as on the surface, even when copolymerization progressed. If the copolymer content increased and the spaces within the hiPP particles were closed completely by copolymer, because monomer would not have been able to diffuse into the internal parts of the particles rapidly, the concentration gradient of the monomer occurred in the particles. This suggests that even if the amount of polymer in the hiPP par-

ticles increased, the spaces within the particles may have remained, to which the monomer could diffuse.

From the SEM observation of the particle surface, we observed that the amount of the copolymer components of the particle surface increased steeply when the content of the copolymer components exceeded a certain value. When active sites existed on the surface, the amount of the copolymer components on the particle surface was considered to correspond to the content of the copolymer components. This suggests that the copolymer components on the particle surface were not formed on the surface. We presumed that the portions of high amounts of ethylene on the surface were formed by the pushing up of the copolymer components generated within the particles near the surface to the surface. In case of a particle having voids in the powder, spots with a high amount of ethylene were formed on the internal surface with similar structure to that on the surface. This suggests that similar to

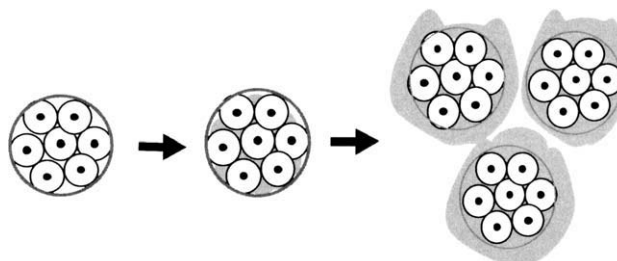


Figure 8 Growth model of the hiPP particles proposed by Debling and Ray.²

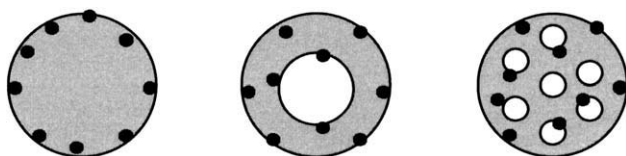


Figure 9 Images of the dispersion of the copolymer spots by the particle morphology.

the powder surface, spots with high amounts of ethylene were formed by the copolymer formed near the surface of the voids and were flowing out in the direction of the internal surface.

Proposal for an appropriate morphology of the hiPP particles

In the practical view of manufacturing hiPP, an appropriate morphology of hiPP particles for the stable production of hiPP was considered. Spots with high amounts of ethylene on the surface of the particles were thought to accelerate the adhesion of particles because of a high adhesiveness of the copolymer component. This phenomenon may cause some problems, such as agglomeration and sticking, in commercial plants. As described previously, spots with high amounts of ethylene were formed on the internal surface in the case of a particle having voids in the powder. We presumed that the morphology having voids in the inside of particles was effective for decreasing the formation of spots with high amounts of ethylene on the surface of the particles. Therefore, an hiPP particle having many small voids inside would be an appropriate morphology of hiPP particles, as shown in Figure 9.

As it is well known that the morphology of solid catalysts will influence in the morphology of the polymer particles strongly,¹ we think that it is possi-

ble to make hiPP particles with many small voids inside by the improvement of the solid catalyst.

CONCLUSIONS

Detailed analyses of hiPP particles were carried out by morphological observations, pore volume analysis, and microscopic FTIR spectroscopy. Copolymer components were dispersed in the space between the primary particles and mesoparticles of iPP. The distribution of ethylene in hiPP particles was practically homogeneous from the surface to the internal part of the particles. Spots with high amounts of ethylene were formed on the surface of the particles. In the case of the particles having internal voids, spots with high amounts of ethylene were also formed on the internal surface of the void. Furthermore, crystalline ethylene was not formed selectively, even at spots with high amounts of ethylene. These results strongly support the particle growth model proposed by Debling and Ray.² We concluded that Debling and Ray's particle growth model was the most appropriate model for expressing the hiPP particle growth.

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