
Review on Development of Polypropylene Manufacturing Process

Sumitomo Chemical Co., Ltd.
Process & Production Technology Center
Hideki SATO
Hiroyuki OGAWA

Polypropylene (PP) is a typical commodity plastic and has been widely used in many application fields including packaging films, industrial components and miscellaneous goods, due to its excellence in properties such as stiffness, heat resistance and processability in addition to light weight material density and also a relatively low price. The continued demands from the market for higher performances have stimulated, particularly in recent time, the improvement of PP manufacturing processes with newly created ideas. This review describes, mainly based on the information published in literature and patents, an outline of the development history of PP manufacturing processes and an introduction to recent progress, including our own technologies.

This paper is translated from R&D Report, "SUMITOMO KAGAKU", vol. 2009-II.

Introduction

Polypropylene (PP) has the physical characteristics of a low specific gravity, rigidity, heat resistance and superior workability. In addition, since it is comparatively low in cost, it is used in a variety of applications, such as films, industrial components for automobiles, furniture, etc., and miscellaneous goods. It has been more than 50 years since 1954, when G. Natta et al. of Italy were successful in synthesizing high molecular weight, highly crystalline PP,¹⁾ and the total worldwide demand for PP has currently reached an amount of approximately 47 million tons (prediction for 2008). However, replacement of other materials and resins is progressing even more, and moving forward, the forecast is for the highest growth rate among general purpose resins at an average of about 6% per year.²⁾

This flourishing of the PP market has been supported by the large improvements and simplification in the manufacturing process that had been accomplished with the leaps in catalyst performance. Furthermore, in addition to the characteristics of PP itself described above, the fact that there have been large improvements in the transparency and impact resistance at low temperatures through copolymerization with ethylene and other alpha olefins has probably been an important factor. With the increase in the level of requirements

for quality in recent years, a variety of ideas and contrivances have been integrated into the manufacturing process for PP. In this paper, we will give a summary of the changes and the current state of the PP manufacturing process based on information in the important patents and literature along with technologies developed by Sumitomo Chemical.

Changes in the PP Manufacturing Process

The PP manufacturing process is mainly made up of a raw material refining process, polymerization process, aftertreatment process and granulation process. The raw material refining process is the furthest upstream process and is a process for eliminating minute amounts of impurities that affect the process, such as water, oxygen, carbon monoxide, carbon dioxide, carbonyl sulfide and the like, from the propylene and other monomers as well as the solvents and other raw materials and auxiliary materials used. Moreover, this process may be set up at a raw material manufacturing plant positioned upstream of the PP manufacturing plant, but in either case, it is a fundamentally necessary process for stabilization of the overall process. The polymerization process is a process for polymerization that brings the propylene and, if necessary, ethylene and other monomers into contact with a catalyst having polymer-

ization activity. Most of the main industrial catalysts are in a granular shape. The main catalysts are mostly in the form of secondary or tertiary particles of several tens of μm that are aggregations of primary molecules having diameters of several hundred angstroms. The polymerization reaction occurs at the active points of the catalyst particles, and the PP that is formed precipitates out, and the catalyst splits into primary particles. However, there are few deviations in the shape of the catalyst, and this forms PP particles that resemble the original aggregated catalyst shape.³⁾ The aftertreatment process is a process for eliminating catalyst residue, the solvent and atactic polymers (AP: noncrystalline polymers where the methyl groups of propylene units are arranged irregularly on the chain), which are components that are unnecessary, from the PP particles obtained in the polymerization process. Of these, the operation for eliminating the catalyst is known as deashing.

In addition, when a solvent is used in the polymerization process, a process for recovering and purifying it is included. The granulation process is the furthest downstream process, and it is a process for melting and kneading additives and fillers into the PP particles that have undergone the after-processing and forming pellets.

In recent years, there are cases where large diameter PP particles are shipped directly without granulation through improvements in the catalyst performance, methods of stabilizer distribution, etc. However, this is limited to a few examples still, and it has not come to the point of completely eliminating the granulation process.⁴⁾ Moreover, storage, packaging and shipping, etc., are indispensable further downstream in commercial plants, but since they are not unique to PP manufacturing processes, we will not touch on them in this paper.

Of these processes, there have been particularly large improvements in simplifications for the aftertreatment process, such that they can be cited as a representative example of advances in chemical manufacturing processes. The PP manufacturing process can be divided into three generations, the first generation (deashing and AP removal), second-generation (non-deashing or non-solvent) and third-generation (non-deashing and non-AP removal) according to these advances in technology. In addition, classification can be done according to the polymerization method into solvent processes, bulk polymerization processes and vapor phase polymerization processes. Fig. 1 shows

the changes in the PP manufacturing processes arranged according to the processes required for the representative polymerization process for each generation. Moreover, the furthest upstream raw material refining process and the downstream granulation process, which are fundamentally required in all of these processes, are omitted in Fig. 1.

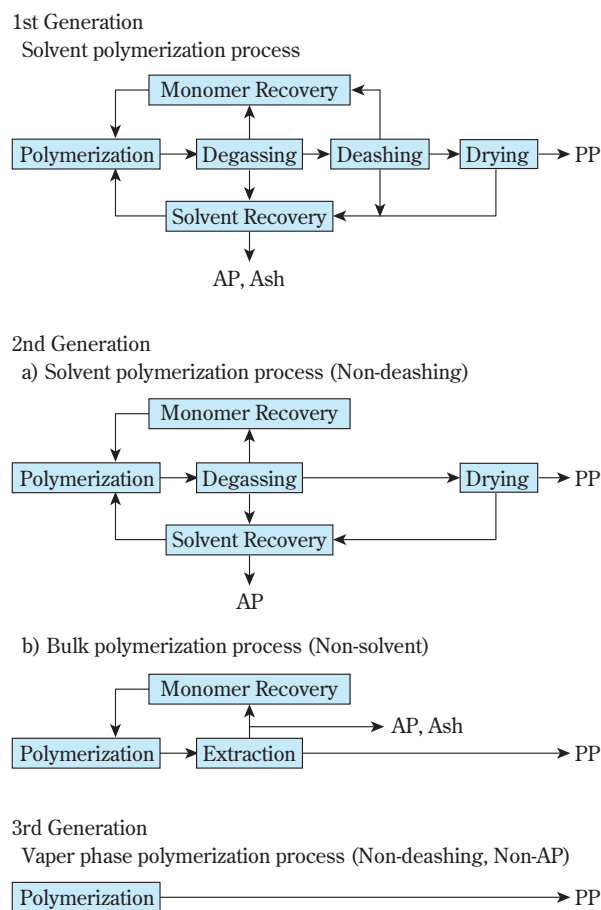


Fig. 1 Polypropylene manufacturing process

We will give a summary of these changes in PP manufacturing processes, using representative polymerization processes that Sumitomo Chemical has developed for each generation.

1. Solvent polymerization process

Since the PP particles are dispersed in the form of a slurry in the solvent with the solvent polymerization process, this is also called the slurry polymerization process, and it was a representative manufacturing process that was the main current in the first generation. Fig. 2 shows the first-generation solvent polymerization process developed by Sumitomo Chemical.⁵⁾ The Sumitomo Chemical solvent polymerization

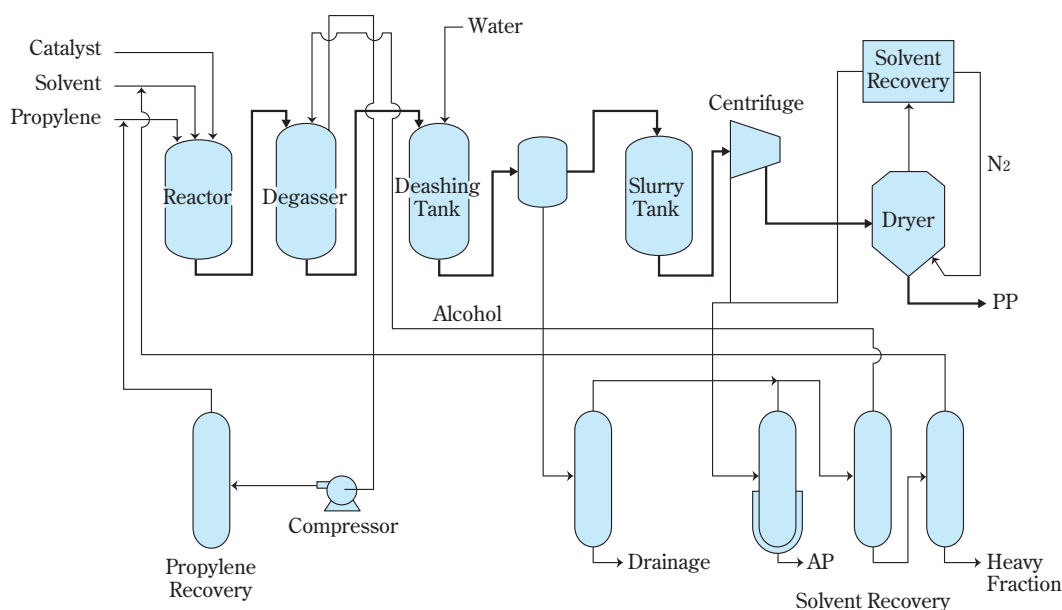


Fig. 2 Schematic flow diagram of Sumitomo's solvent polymerization process

process was one that initially introduced technology from the Italian company Montecatini, which was the first in the world to industrialize PP, but subsequently Sumitomo Chemical made a large number of technical improvements of its own and licensed them to a number of companies.

Solvent polymerization used an autoclave provided with an agitator for the reactor, and the conditions are a temperature of 50 to 80°C and pressure of approximately 1 MPa. It is carried out in the presence of hexane, heptane or another inert hydrocarbon solvent where polymerization inhibitors have been eliminated.

In the first generation, PP particles were obtained after going through separation and recovery of unreacted propylene, deashing (decomposition and elimination of the catalyst using alcohol), washing in water, centrifugal separation and drying for the aftertreatment processes. In addition, a process for separating the AP, which was produced as a secondary product at 10% of the amount polymerized was necessary at one time, and therefore, the AP was separated using its solubility in the polymerization solvent. Not only was this process complicated, but also the cost burden was large because of the separation and purification of the particularly large amount of alcohol and water used in deashing from the solvent that was recovered. Subsequently, in the second generation, the deashing process was omitted because of improvements in catalyst activity, and the large amounts of alcohol and water became unnecessary.

While the process was simplified in this manner, the omission of the process for eliminating secondary AP had to wait for the advent of superior catalysts that gave a high level of stereoregularity that made possible a reduction in the proportion of secondary AP generated in addition to increasing the polymerization activity.

2. Bulk polymerization process

The bulk polymerization process is also called the mass polymerization process, and solvents such as hexane and heptane are not used. It carries out polymerization in liquefied propylene. It aims at simplifying the process by also using the propylene monomer, which is the raw material, as the solvent.

Since no solvent other than the liquefied propylene is used, the energy costs for the steam, electricity, etc., required for recovering the solvent may be greatly reduced. The bulk polymerization process is a process that is representative of the second generation, but it coexisted with the first generation, and even now when the third generation is the main current, there are times when it is advantageous for the manufacture of propylene homopolymers. It plays a part in a variety of commercial process groups **Fig. 3** shows the second generation bulk polymerization process developed by Sumitomo Chemical, but if it is compared with the first generation solvent polymerization process (**Fig. 2**), we can see that it has been made much simpler. This Sumitomo Chemical process has been licensed to several companies, and has been evaluated highly.

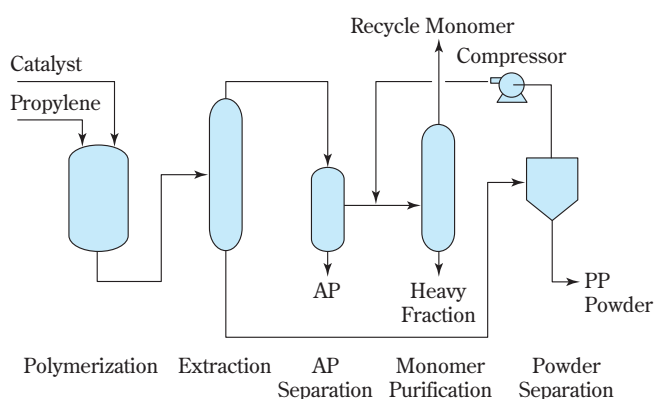


Fig. 3 Schematic flow diagram of Sumitomo's bulk polymerization process

It is characterized by the use of a continuous extraction tower that was developed by Sumitomo Chemical and has a special internal structure.⁵⁾ Furthermore, in addition to using a high performance catalyst that Sumitomo Chemical developed itself, we were successful in being the first in the world to greatly simplify deashing and the secondary AP elimination process by providing a countercurrent washing system that uses refined liquefied propylene.

The typical operating conditions for the bulk polymerization process are a temperature of 50 to 80°C and a pressure that is roughly the vapor pressure of propylene. It changes according to the temperature, but is in a range of 2 to 4 MPa. Since liquefied propylene, which is a monomer, is used for the solvent, the polymerization reaction is rapid, and the retention time is shortened. Since the volumetric efficiency is greatly improved, the reactor size for obtaining the same production capacity can be smaller than it was conventionally. However, even though there is high productivity, the heat elimination surface area is insufficient for removing the polymerization heat if the size of the device is reduced. Therefore, in the case of a stirred tank reactor, a special external heat exchanger that implements measures for preventing adherence of the polymer is used. On the other hand, loop reactors where the surface area for heat elimination can be increased relative to the reaction volume have become practical.

The bulk polymerization process is a process with many advantages like these, but it is not suitable for the manufacture of the polymers known as impact copolymers. Impact copolymers are a mixture of a propylene homopolymer component with a comparatively low molecular weight and a rubber component, which is an ethylene-propylene copolymer with a comparatively high

molecular weight. This has improved impact strength at low temperatures while at the same time maintaining the rigidity, which is one of the superior original characteristics of PP, as much as possible. It is mainly used in injection molding applications starting with automobile components. Industrially, it is obtained by polymerizing the latter following the polymerization of the former, and during continuous production, individual reactors are required for polymerization of each of the components. To polymerize the rubber component, the reaction composition must have a high ethylene concentration, but if ethylene is dissolved in the liquefied propylene to the point of obtaining the required ethylene concentration with bulk polymerization, the overall reaction pressure increases, so there have been almost no practical implementations. In addition, since the rubber component is dissolved in the liquefied propylene, there is a problem with the limitations for polymerization of the rubber component.

3. Vapor phase polymerization process

The vapor phase polymerization process falls under the category of bulk (mass) polymerization processes carried out only with monomers in the broad sense, but since polymerization is carried out in propylene gas rather than in liquefied propylene, it is handled as a process different from conventional bulk polymerization. It is positioned as a third-generation process, but the history is longer than expected, and the technology already existed when first generation processes were the main current. The vapor phase polymerization at that time was inferior in terms of quality because there was no process for separating the very many AP secondary products, and products were limited to special applications. However, with the subsequent complete elimination of deashing and AP removal operations because of the rapid improvement in catalyst performance, further simplifications were achieved in the process, and it achieved a position as the third generation process capable of manufacturing high performance products with diverse levels of quality. Fig. 4 shows the initial third-generation vapor phase polymerization process developed by Sumitomo Chemical for manufacturing impact copolymers.⁶⁾ Manufacturing impact copolymers requires at least two reactors, and a supply line for ethylene, which is a comonomer, is installed for the second stage reactor so that the rubber component can be polymerized. Moreover, manufacturing is fundamentally possible with one reactor for polymers other than impact

copolymers. The typical operating conditions are a temperature of 50 to 80°C and a pressure in the range of 1 to 2 MPa. Various types of reactors, such as stirred tanks and fluidized beds, have been developed by various companies, but while there are small differences in construction costs and variable costs, these are not determiners of the differences in the final product costs. The competition between makers can be said to be mainly in the area of product quality.⁷⁾ Along with the further improvements to the process, Sumitomo Chemical has made great strides on the quality front by commercializing a variety of polymer designs based on our own high performance catalyst technology.

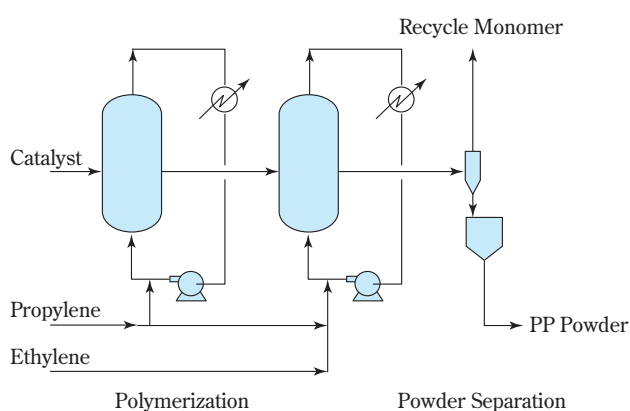


Fig. 4 Schematic flow diagram of Sumitomo's vapor phase polymerization process

Current Status of PP Manufacturing Processes

With the increase in the level of performance required for PP quality in recent years, a variety of ideas and contrivances have been integrated into the manufacturing process for PP. If we take a bird's eye view of the trends in process development that focus on these improvements in quality, all of them are pointing in one direction. In other words, while the configuration and conditions of the of the polymerization reaction are varied to diversify the molecular weight distribution and compositional distribution, attempts are being made to hold heterogeneousness of the polymer particle structure produced that tends to occur with this to a minimum.

There are roughly two directions for the specific methods. One is improvement of uniformity of the polymer particles produced using a circulation type reactor, and the other is improvement in the uniformity among polymer particles produced by using a reactor with a

narrow retention time distribution.

In the following, we will focus on the vapor phase polymerization process and review the patent and reference literature as well as the technology developed in recent years, inclusive of technology developed by Sumitomo Chemical, while focusing on the differences in reactor types and configurations aimed at improving the uniformity of polymer granular structures according to required performance.

1. Improvement in uniformity in particles using circulation type reactors

Improvement on the uniformity in the polymer particles produced is mainly aimed at controlling molecular weight distribution in many ways. In other words, since the physical characteristics such as the impact strength of molded products can be improved, a high molecular weight for the PP is desirable, but on the other hand, processing is difficult. Therefore, it is necessary to include a suitable amount of low molecular weight components for such improvements, and as a result, PP with a broad molecular weight distribution is desirable. This concept itself is not original, but to obtain PP with a broad molecular weight distribution, the molecular weight has been varied during a series of reactions in batch polymerization in the conventional process. Alternatively, a continuous polymerization method where multiple complete mixing reactors are set up with conditions that give different molecular weights are simply connected has been used. However, since the productivity of batch polymerization is very inferior, its use is limited to special applications, and it has not been widely disseminated. Since there is also a retention time distribution in the polymer particles produced with continuous polymerization, the molecular weight distribution varies with each particle. In addition, it is difficult to avoid uneven distribution of components with different molecular weights within single particles. **Fig. 5** shows conceptual diagrams of the polymer particle structures produced in these processes. As is shown in **Fig. 5** (a), the uneven distribution of the various components in the polymer particles produced is an important problem where defects (causing reductions in strength and problems with appearance) from poor melting and mixing called fisheyes arise in the forming process particularly when there is a large difference in the molecular weight between high molecular weight components and the low molecular weight components. To solve this problem, it is desirable to

Distribution of Composition/Molecular Weight	Distribution of Residence Time	Model Structure of Particle (Red-color portion indicates schematically a part polymerized in the second stage.)
(a) Perfect mixing type reactor	wide	
(b) Circulation type reactor (excluding impact co-polymer manufacturing)	narrow	
(c) Narrow residence time distribution type reactor (including batch type reactor)	narrow	

Fig. 5 Schematic structure of polymer particle produced by two polymerization zone type reactor

produce a polymer particle structure where the uniformity in the particles is improved as shown in Fig. 5 (b), and several measures for improvement have already been achieved.

In the following, we will introduce an example of the development of a circulation type reactor as one example of this. The reactor (called external circulation fluidized bed type reactor (1) in this paper) showing this concept in Fig. 6 can be thought of as an application of an external circulation fluidized bed connected to a fast fluid bed (riser part) and a moving bed (downcomer part) that are used in combustion furnaces and fluidized catalytic cracking (FCC) devices in a PP manufacturing reactor.^{8), 9)}

Since the gas flow rate in the riser part is high (0.8 to 5 m/s, particle terminal speed or greater), the coefficient of heat transfer is large (a 30% increase over a non-circulating fluidized bed). It is said that as a result there is a large improvement in the energy consumption.¹⁰⁾

However, the results on the quality of uniformity in the particles may be thought of as meriting more attention than these reductions in running costs. With this reactor, the PP particles and gas that are discharged from the riser part at high speeds are separated in the built-in cyclone separator. Liquefied propylene is supplied from the top part, and the PP particles can be forced down into the downcomer part after the concentration of hydrogen, which is the chain transfer agent for adjusting the molecular weight, is reduced by forming a gas barrier. Therefore, the low molecular weight components are polymerized in the riser part with a high hydrogen concentration and the high molecular

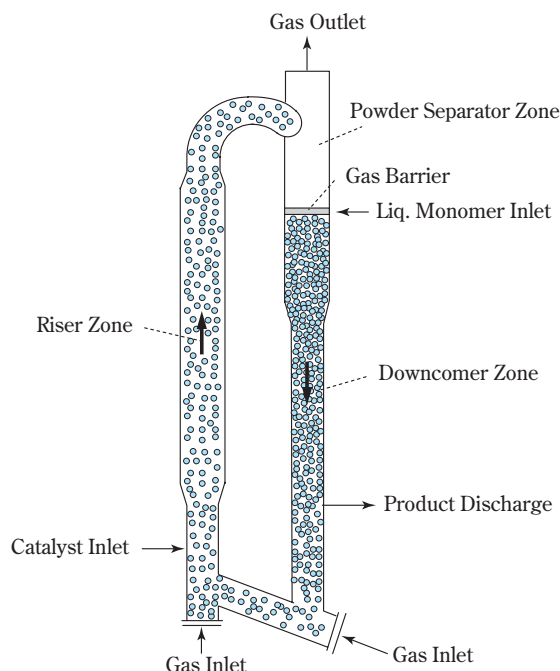


Fig. 6 “External circulation fluidized bed type reactor (1)”

weight components in the downcomer part with a low hydrogen concentration. The retention times in the riser part and downcomer part are short, and it is possible to make the content of components with different molecular weights uniform in the particles by carrying out circulation polymerization repeatedly without reverse mixing.^{10), 11)} Moreover, this process was originally configured to have a reactor where the riser part and downcomer part were independent,¹²⁾ but subsequently, this was improved to an integrated type with the loop shape described above. In addition, the external circulation fluidized bed type reactor (2) where an

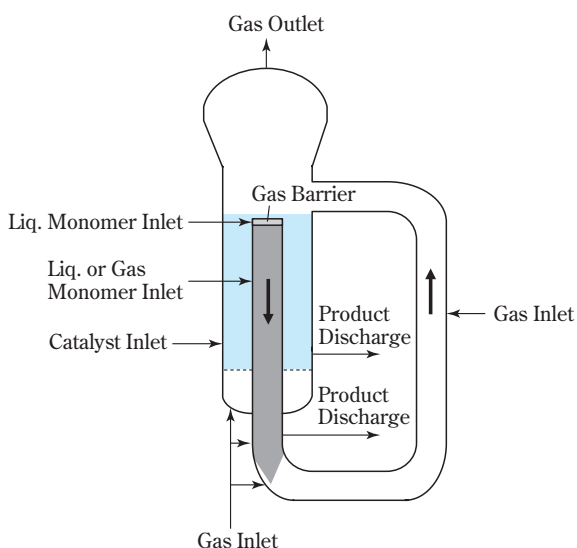


Fig. 7 “External circulation fluidized bed type reactor (2)”

external circulation function is configured for a conventional fluidized bed reactor as shown conceptually in Fig. 7 has been proposed.¹³⁾

We have discussed examples of applications of external circulation fluidized beds above, but several examples of internal circulation fluidized beds have been reported.¹⁴⁾ For example, as is shown conceptually in Fig. 8, an internal circulation fluidized bed type reactor that is given an internal circulation function with a moving bed provided in a conventional fluidized bed reactor has been proposed.¹⁵⁾ The fundamental thinking for improvements can be assumed to be the same as for the external circulation fluidized bed described above. It is possible to control uneven distribution of components with different molecular weights in the particles

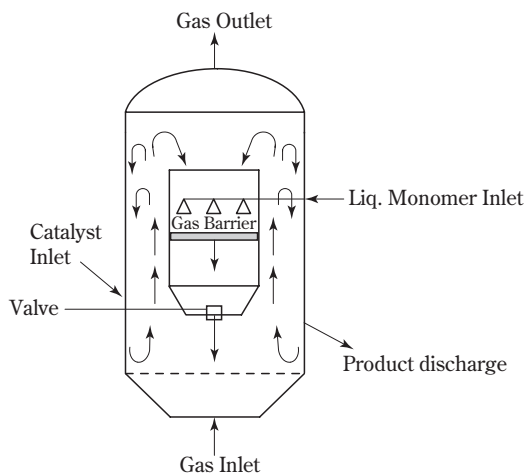


Fig. 8 “Internal circulation fluidized bed type reactor”

by supplying liquefied propylene to the uppermost part of the moving bed, forming a gas barrier and forming internal circulation. In particular, since it is possible to freely control the proportion of the retention time for the moving bed, which polymerizes the high molecular weight components, and the fluidized bed, which polymerizes the low molecular weight components, by independently controlling the amount of PP particles discharged by the moving bed, polymer designs with even more variety than with loop type external circulation reactors become possible.

These circulation type reactors can control the molecular weight distribution variously, but it is also possible to make various designs for the comonomer composition distribution by also controlling the comonomer concentration in each polymerization stage in the same manner. However, when impact copolymers are manufactured, the comonomers must be almost completely separated in the comonomer polymerization stage, and it is difficult to use a circulation type reactor by itself. Therefore, while improvements in the uneven distribution in the polymer particles produced are not achieved, the processes that will be discussed in the following aimed at producing polymer particle structures with improved uniformity among the particles like those shown in Fig. 5 (c) are being developed.

2. Improvements in uniformity among particles using narrow retention time distribution type reactors

For improvements in the uniformity among the polymer particles produced, we can expect greatly improved results in quality when both a propylene homopolymerization stage where the comonomers are almost completely separated, mainly as in the impact copolymers described above, and a polymerization stage where the composition differs greatly when the copolymerization stage has a high comonomer concentration are required. In the following, we will explain the reasons why a narrow retention time distribution type reactor is necessary, using the manufacture of impact copolymers as an example.

We have already discussed how continuous polymerization of impact copolymers requires polymerization of the comparatively low molecular weight propylene homopolymer component and rubber component, which is a comparatively high molecular weight ethylene-propylene copolymer, in separate reactors.

While ones with different configurations, such as mixing tank types and fluidized bed types are used for commercial production processes, the polymer particles are normally mixed into a state close to complete mixing in the reactors.¹⁶⁾ Therefore, in the two tank continuous process, which is the most simple for producing impact copolymers, the polymers produced in the end have a low mass ratio for the homopolymer component and the rubber component because of the retention time in each of the tanks, so they are mixed until it is high. If polymer particles with a high rubber component content are included, it invites dispersion problems during melting and mixing, and we have already said that it causes a lowering of quality where the appearance deteriorates and the impact resistance is lowered. The process has been improved with the goal of narrowing the retention time distribution particularly in the first stage to prevent a lowering of quality based on this mechanism.

A multi-tank device that increases the number of continuous reaction devices connected in series has been used to narrow the retention time distribution for manufacturing polymers with high quality from the concept above.

However, at the same time, there is an increasing demand for lowering costs along with increasing the PP performance, and there are limitations to the conventional method of just increasing the number of reactors. From this point of view, polymerization processes that can narrow the retention time distribution for the polymer particles with a smaller number of reactors are being developed. For example, a horizontal, mechanically stirred type reactor (1) like the one that shows this conceptually in Fig. 9 (a) has been developed.¹⁷⁾ This is one where the inside of the device is formed into multiple partitions by dividers, and reverse mixing of the particles cannot be completely controlled. While there is a range because of the retention time, it can narrow the retention time distribution to the same extent as one where 3 to 5 complete mixing reactors are arranged in series with only one reactor.¹⁸⁾

The horizontal, mechanically stirred type reactor (2) for which the concept is shown in Fig. 9 (b) can be said to be an improvement on the reactor described above with Fig. 9 (a). The dividers are installed at the top rather than at the bottom, so mixing of the gas in the gas phase part above is controlled, and the controllability of the molecular weight distribution and compositional distribution can be improved.¹⁹⁾ However, this

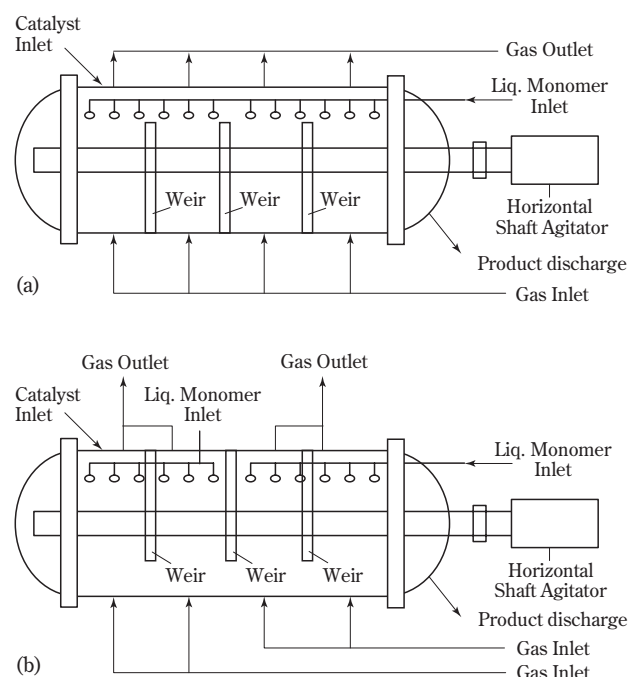


Fig. 9 “Horizontal, mechanically stirred type reactor (1) (2)”

horizontal, mechanically stirred type reactor has a problem with deflection because of gravitational force of the mixing shaft, so it is difficult to increase the scale. However, there has been success with increasing the size in recent years.²⁰⁾

On the other hand, there have been reports of forming multiple chambers vertically with fluidized beds, for which the scale can be increased comparatively easily.^{21)–24)} In particular, along with increasing the volume toward the bottom, which is the polymerization area, to make the retention time distribution at the various stages uniform, the multi-stage fluidized bed type reactor shown conceptually in Fig. 10 controls reverse mixing by forming a multi-stage device with dividers at each stage.²⁴⁾ These dividers are flat heat exchangers, and the polymerization heat is removed and the temperature made uniform at the various stages by providing a cooling jacket. Even though this device structure is extremely interesting, it is complicated, so we can assume that there will be difficulties. In addition, since the gas flow path becomes smaller as we go up the stages, the gas column velocity will be extremely fast at the upper stage, so we can assume that an individual gas discharge outlet must be provided for each stage.

In addition, since the particle diameter for the polymer particles produced differs according to the degree of particle growth, there have been reports of narrow-

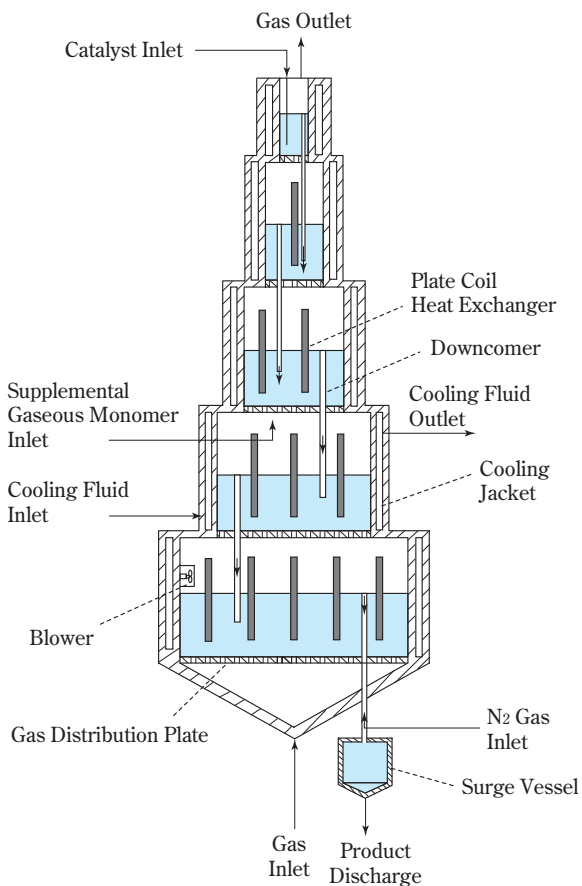


Fig. 10 “Multi-stage fluidized bed type reactor”

ing the retention time distribution using particle classification.^{25)–29)}

Among these, the example (called fluidized bed type reactor with particle segregation zone in this paper)²⁹⁾ developed by Sumitomo Chemical shown in **Fig. 11**, sets up one integrated into a conventional fluidized bed

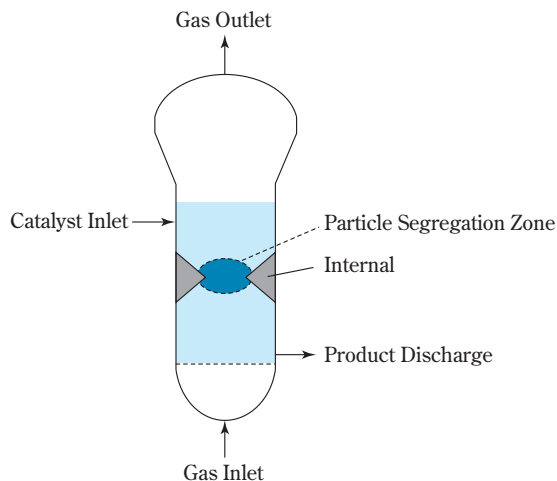


Fig. 11 “Fluidized bed type reactor with particle segregation zone”

type reactor and forms drum-like stages with different gas column velocities within the device. This is based on a unique concept where short paths for polymer particles that have not grown can be controlled by bending the particles using the differences in the gas column velocities. It has the important merit of making the modifications easy even with a conventional fluidized bed reactor that has already been built.

Besides ones that are modifications based on conventional devices such as the mixing tank types and fluidized bed types above, the tubular type reactor shown conceptually in **Fig. 12**, for example, has also been reported.³⁰⁾ This is a tubular type device where the ratio of the length of the device to the diameter is 100 or more, and even though there is solid-gas separation using a cyclone at fixed distances and a circulation gas

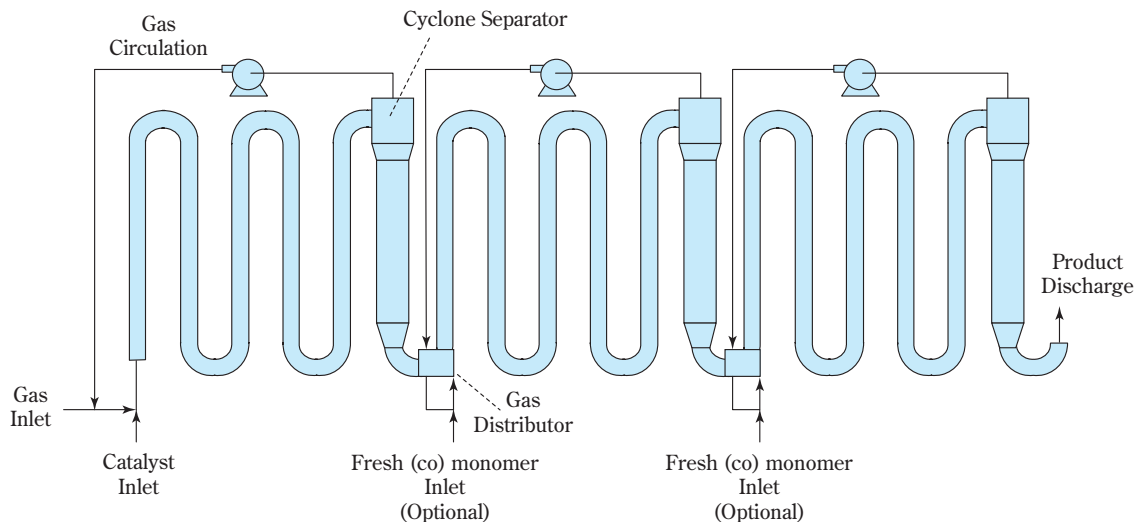


Fig. 12 “Tubular type reactor”

compressor, there is almost no reverse mixing, so the retention time distribution is extremely narrow. However, the fact that sufficient retention time cannot be assured with gas phase polymerization, which typically requires several hours, because the retention time is about 15 minutes even with a device length of 200 m is an important problem.

In addition, for example, we can also mention methods that use a moving bed type reactor developed by Sumitomo Chemical.^{31), 32)} This is a process that uses a non-circulating moving bed type reactor in the second or later stages after growing polymer particles to an extent that does not melt and clump because of problems with heat elimination. With this process configuration, it is thought that most of the retention time distribution arises in the second or later stages and sufficient retention time can be assured.

Conclusion

In this paper, we have given a review of the changes and current state of PP manufacturing processes, including technology developed by Sumitomo Chemical, based on information in patents and the literature. We mainly focused on the trends in process development aiming at improving quality in particular, but besides this, a variety of processes, such as many technical improvements aiming at stable operation and processes³³⁾ making high temperature polymerization possible by improving the polymer particle and monomer separation efficiency through operation in the supercritical range for propylene, have been developed. Even though a giant market has been formed for PP already, perfection of the manufacturing processes for it has not been completed. Further progress is desirable moving forward along with developing basic technology starting with catalysts and various types of peripheral technology to answer the demands from a market that will not fail.

At Sumitomo Chemical, we are thinking in terms of further polishing our own technology, which has been built up to this point and developing processes that provide products that are attractive to the market.

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PROFILE



Hideki SATO

Sumitomo Chemical Co., Ltd.
Process & Production Technology Center
Research Associate



Hiroyuki OGAWA

Sumitomo Chemical Co., Ltd.
Process & Production Technology Center
Senior Research Associate
(Present Post: Temporary Researcher)