

# Preparation of Microporous Particles of Isotactic Polypropylene via a Thermally Induced Phase Separation Method

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**ABSTRACT:** A new method for the preparation of microporous particles of isotactic polypropylene (IPP) using thermally induced phase separation (TIPS) was developed in this study, in which chloroform was used as a diluent and Span80 was used as a pore-forming agent. The morphology and properties of the microporous IPP particles thus produced were characterized with scanning electron microscopy, mercury intrusion porosimetry, and differential scanning calorimetry, and they were compared with IPP particles produced by a cryogenic pulverization

method. The results showed that IPP particles with a fully developed microporous structure, an average particle size between 50 and 120  $\mu\text{m}$ , and a specific area of about 5.19  $\text{m}^2/\text{g}$  can be obtained via the TIPS method under definite conditions. The influence of some factors on the size and porosity of IPP particles is discussed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 3050–3057, 2009

**Key words:** microstructure; ultrafine particle; phase separation; isotactic

## INTRODUCTION

Isotactic polypropylene (IPP) is a thermoplastic commodity polymer; however, its application is restricted by intrinsic disadvantages such as high crystallinity, low surface energy, and bad mechanical properties. For overcoming these problems and achieving desired properties, surface modification has been proved to be an efficient approach; examples include grafting functional groups of maleic anhydride, phenyl ethylene, methyl methacrylate, or hydroxymethyl acrylamide to the chain of IPP<sup>1–6</sup> and chlorinating IPP particles with chlorine in an aqueous-phase suspending system.<sup>7,8</sup> In these processes, IPP particles with a granular size of about 120–350  $\mu\text{m}$  are used, and they are generally produced via cryogenic pulverization of commercial IPP powder or granules. However, the IPP particles thus produced have limited porosity and specific area because the IPP particles are basically compact and solid in structure. To increase the porosity and specific area to facilitate the surface modification of the polymer, an ultrafine IPP powder with a microporous structure is highly desired.

With respect to the production of porous particles of polymers, there are two different approaches, that is, the chemical method and the physical method. Suspension polymerization,<sup>9–12</sup> the dynamic swelling method (DSM),<sup>13,14</sup> and alkali/acid treatment<sup>15</sup> are chemical methods. Suspension polymerization is a traditional method for the production of polymer microspheres, combining the polymerization of the monomer and pore formation of the polymer into one process. DSM uses a monodisperse polymer particle as a substrate and a monomer as a swelling agent, and when the monomer is polymerized in the particle, the porosity of the microspheres is increased accordingly. Alkali/acid treatment is a new method put forward by Okubo in the 1990s.<sup>15</sup> First, latex particles with a certain particle size are obtained through emulsion polymerization, and then they are turned into submicrometer latex particles containing acid or alkaline functional groups with a seed emulsion polymerization method. After a fractional acid and alkali treatment, porous submicrometer microspheres are produced. Among these methods, suspension polymerization has been commercially used for the production of polymers; however, the commercial IPP powder thus produced has only limited porosity and specific area, and the other two methods are still in the stage of research and development.

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In comparison with the chemical method, the physical method is much simpler because it starts with a commercial IPP polymer, and the controlling factors are related only to the dissolution and recrystallization of the polymer. The rapid expansion of supercritical solutions (RESS) technique<sup>16</sup> is a physical method. For the RESS process, a polymer is first dissolved in a supercritical solvent, forming a homogeneous solution, and then the solution is sprayed out through a nozzle of several micrometers into a chamber with reduced pressure for the rapid vaporization of the solvent. In the course of ejection, ultrafine particles with a uniform size are formed because of the strong mechanical disturbance and high degree of supersaturation of small droplets. Using this method, Matson et al.<sup>17</sup> successfully prepared IPP ultrafine particles with a microporous structure.<sup>17</sup> However, the RESS process does not seem practical because of its intensive capital and operation costs, the lower solubility of IPP in a supercritical liquid, and the high viscosity of the solution.

The thermally induced phase separation (TIPS) method is another physical method, and it is widely used in producing IPP microporous membranes and macroporous resins. The principle of TIPS is that many polymers with high crystallinity can be dissolved in some molecular solvents with a high boiling point at a higher temperature, and the polymers will separate from the solvent as the temperature decreases to a certain value; finally, polymer materials with a microporous structure can be obtained after the diluent is removed. The TIPS method aroused much interest as soon as it was put forward by Castro<sup>18</sup> in 1980. In the early 1990s, Kim and Lloyd<sup>19–25</sup> conducted a series of studies on the production of microporous membranes using TIPS. Recently, a macroporous IPP resin was developed by TIPS for the treatment of restaurant wastewater containing grease.

For the preparation of microporous IPP membranes with TIPS, the mass content of IPP in the solution is generally above 50% so that a continuous membrane phase with a certain mechanical strength can be obtained. This implies that if the content of IPP in the diluent is low enough, then fine IPP particles instead of a continuous membrane phase will be formed during the cooling process. Besides, the size and porosity of the particles can be controlled during the recrystallization process by the adjustment of some factors, such as the stirring strength, cooling rate, and pore-forming agent. Therefore, the TIPS method is suitable for the commercialized preparation of microporous IPP fine particles because it is just a physical process and the controlling processes are easier to implement.

The objective of this study was to develop a cost-effective method for the preparation of microporous IPP particles that can be operated under mild conditions, controlled easily, and applied to industrial manufacturing. Toward this aim, the TIPS method is possible, but no such attempt has been reported in the literature until now.

This article reports the experimental results regarding the preparation of microporous particles of IPP with the TIPS method with chloroform as the diluent and Span80 as the pore-forming agent. The microstructure and properties of the IPP particles produced under various conditions were characterized with scanning electron microscopy (SEM), mercury porosimetry, and differential scanning calorimetry (DSC) methods.

## EXPERIMENTAL

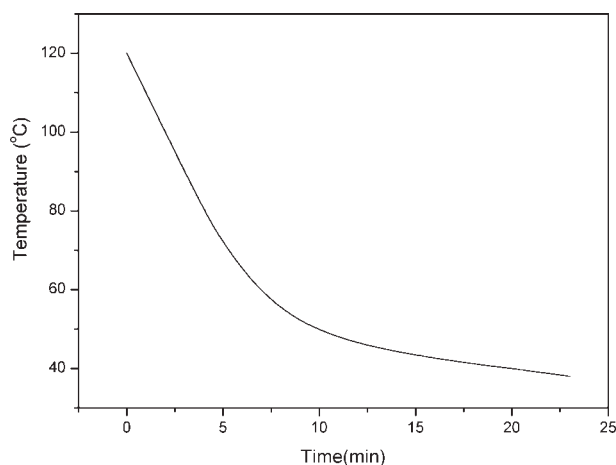
### Materials

IPP granules (563S; melt flow rate = 60 g/10 min) with a diameter of about 3 mm were supplied by Daelim Industrial (Jung-gu, Korea). Span80 was produced by the Tientsin No. 3 Reagent Factory (Tientsin, China). Analytical-grade chloroform was purchased from the Beijing Reagent Factory (Beijing, China).

### Preparation of the IPP microporous particles

The experimental apparatus was a 2-L stainless steel pressure reactor (WHFSK-2, Weihai, China) with a maximum working pressure and temperature of 9.8 MPa and 300°C, respectively, and the rotating speed of the paddle was tunable between 0 and 750 rpm. The temperature of the reactor was automatically controlled by an external electrical heating mantle, which could be taken down, and the reactor could be conveniently immersed into a cooling tank if necessary.

The experimental procedure was as follows. First, 20 g of IPP, 900 g of chloroform, and a definite amount of the pore-forming agent (Span80), if necessary, were added to the reactor. Second, the reactor was sealed and stirred at the speed of 100 rpm, and then the liquid was heated to 120°C and remained at a constant temperature for 2 h to guarantee that IPP was fully dissolved in chloroform, forming a homogeneous solution. Third, the reactor was immersed into a cooling water tank immediately after the electrical heating mantle was taken down. The temperature of the cooling water was kept at about 20°C by flowing tap water; as such, the system temperature could decrease to 70°C within 5 min and then gradually cool to room temperature. Fourth, the reactor was opened, and the IPP particles were separated



**Figure 1** Typical cooling curve of the polymer solution inside the reactor.

from chloroform with vacuum filtration. Finally, the wet particles of IPP were dried via vacuum vaporization at 50°C with a vacuum degree of 0.08 MPa, and microporous IPP particles were obtained.

The cooling rate of the IPP solution inside the reactor under typical operation conditions was measured and is shown in Figure 1.

To investigate the influence of pore-forming agent Span80 on the microstructure of IPP particles, five samples (E1–E5) were prepared with the TIPS method under the conditions listed in Table I. These samples were compared with a contrast sample (E0), which was an IPP powder prepared via cryogenic pulverization and sieving with an average particle size of 120 mesh.

### Morphology of the IPP particles

A scanning electron microscope is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample, producing signals that contain information about the sample's surface topography, composition, and other properties such as the electrical conductivity. In this experiment, the particle size, morphology, and microstructure for IPP samples E0–E5, as listed in Table I, were studied with SEM (S-250, Cambridge Instruments, Cambridge City, England) at the ambient temperature. The preparation of the samples and measurements can be simply described as follows. First, the microporous IPP was mounted on conductive tape. The IPP sample needed to be made conductive through the covering of the sample with a thin layer of a conductive material. This was done with a device called a sputter coater. The sputter coater used an electric field and argon gas. During the test, an

accelerating voltage of 20 kV irradiated the surface of IPP, and thus the picture of IPP was obtained.

### Porosity measurement of the IPP particles

The microstructure of the IPP samples with respect to the porosity, pore size distribution, and specific area was studied with the mercury porosimetry method because this method is applicable to porous materials with a pore size in the range of 3.7–58,000 nm. Measurements were performed from 0 to 400 kPa for the low pressure range and from 0.2 to 200 MPa for the high pressure range with mercury intrusion porosimetry (Pascal/140/240, Thermo Electron Corp., MA). The surface tension of mercury was assumed to be 480 mN/m, and the contact angle of mercury with the sodium chloride was assumed to be 140°.

### DSC analysis of the IPP particles

To measure the crystallinity of the IPP samples prepared under different conditions, DSC analysis was conducted with a PerkinElmer Pyris 1 power-compensation differential scanning calorimeter (MA). In the course of testing, each sample was heated from 40 to 200°C at the heating rate of 10°C/min under the protection of nitrogen flowing at the rate of 20 mL/min, and the thermogram was recorded for the first heating cycle.

## RESULTS AND DISCUSSION

### Selection of the diluent

The TIPS diluents, widely used in preparing microporous IPP membranes, virtually all have a high boiling point and/or are solid at the ambient temperature,<sup>22</sup> and the diluent needs to be removed from the membranes by extraction. In 2001, Yang and Perng<sup>26</sup> put forward an alternative TIPS diluent, camphene, a low-boiling-point solvent, which can be removed from a membrane directly by warming when the membrane preparation is over, and the volatilized solvent can be reclaimed by

**TABLE I**  
Preparation Conditions for Different IPP Samples

Sample	Mass ratio of IPP in the diluent (g of IPP/mL of diluent)	Diluent	Mass fraction of Span80 in the diluent (%)
E0	—	—	—
E1	1/30	Chloroform	0
E2	1/30	Chloroform	0.50
E3	1/30	Chloroform	0.75
E4	1/30	Chloroform	1.00
E5	1/30	Chloroform	1.25

TABLE II  
Pore Size Distributions and Specific Areas for Different IPP Particles

		Sample				
		E0	E2	E3	E4	E5
Specific area (m <sup>2</sup> /g)		0.02	0.42	2.53	5.19	5.73
Pore size	105–50	N/A	2.98%	1.56%	0.89%	0.76%
range(μm)	50–10	N/A	68.88%	3.20%	6.59%	1.97%
	10–5.0	N/A	28.14%	1.01%	6.41%	1.08%
	5.0–1.0	N/A	0.00%	2.70%	16.11%	10.95%
	1.0–0.5	N/A	0.00%	3.43%	17.45%	1.62%
	0.5–0.1	N/A	0.00%	19.62%	52.55%	4.86%
	0.1–0.01	N/A	0.00%	68.48%	0.00%	87.79%

condensation. Obviously, a low-boiling-point diluent is superior to a high-boiling-point one because the former can be removed easily from the polymer and recycled with lower separation cost. In this respect, we preferred a low-boiling-point organic solvent as the diluent in this research.

The IPP polymer, with its high crystallinity, is not soluble in any organic solvent at ambient temperature; however, it can be dissolved in some aromatic and halogenated hydrocarbons, such as benzene, chlorobenzene, dichloroethane, chloroform, and carbon tetrachloride, at a high temperature. Among these low-boiling-point solvents, chloroform is promising because of its low toxicity, nonflammability, and reasonable boiling point of 61.3°C. On the contrary, the remaining solvents have various disadvantages; for example, the benzene series of solvents and dichloroethane are flammable, explosive, and highly toxic, and carbon tetrachloride is an ozone-depleting substance being phased out by the Montreal protocol.

### Selection of the pore-forming agent

To control the microstructure of the IPP granule, a pore-forming agent is used to disturb the crystallization process, prevent the formation of compact IPP spherulites, and form the micropores of the IPP particles. A pore-forming agent is indeed a surfactant with an amphiphilic structure, which is adsorbed onto the IPP surface, forming a repulsive layer to prevent regular crystallization and make the IPP particles more stable against aggregation.

On the basis of the properties of the polymer and diluent involved, we chose Span80 as the pore-forming agent, considering the following facts:

1. Span80 can be well dissolved in chloroform and has the strongest lipophilicity of Span series surfactants because of its larger hydrophobic group.
2. Span80 is highly stable in the temperature range of the experiment (<120°C) because it is

commercially produced by the reaction of sorbitol and fatty acids at 260°C,<sup>27</sup> which is much higher than the operating temperature of this experiment.

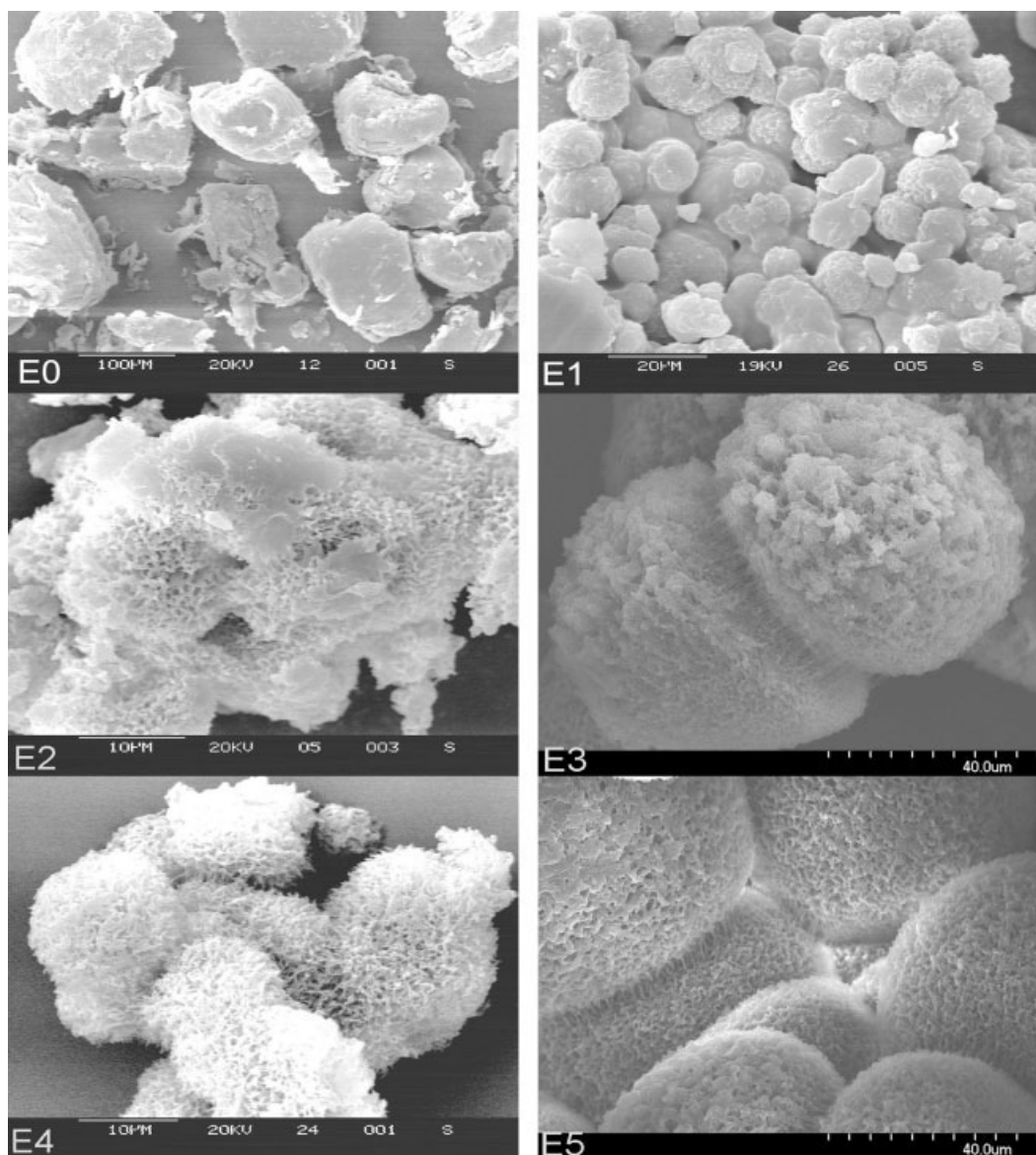
3. Span80 is a low-cost surfactant and is available commercially.
4. Span80 is nontoxic and environmentally benign and can be reclaimed easily.

### Microstructure and morphology of the IPP particles

As shown in the SEM photographs, the IPP particles produced by cryogenic pulverization were quite different from those produced by the TIPS method. By comparing samples E0 and E1, we found that the IPP particles produced by pulverization were irregular in shape, with their size in the range of 80–120 μm, whereas those produced by the TIPS method were generally aggregates of smaller particles of 10–20 μm with a smooth surface. This can mainly be attributed to the difference in the particle-forming mechanisms. Pulverization is an approach of “from top to bottom,” in which the IPP particles become smaller and smaller as a result of constant shear stress imposed by extrusion and collision of the rolling particles during the pulverization process. The irregular shape and surface defects of the particles are related to the randomness of the shear stress as well as the thermoplasticity of the IPP materials. On the contrary, the TIPS process is an approach of “from bottom to top,” in which the polymer is first precipitated as tiny nuclei and then grows into particles as the solution temperature decreases.

By comparing SEM photographs of E1–E5, we can see the influence of pore-forming agent Span80. Clearly, although the particle sizes of samples E1–E5 were virtually the same, being in the range of 10–30 μm for particulates and 50–120 μm for aggregates, the differences in their microstructures and porosities were remarkable. Sample E1, prepared in the absence of Span80, was completely nonporous, whereas samples E2–E5, prepared in the presence of





**Figure 2** SEM micrographs of IPP samples prepared under different conditions.

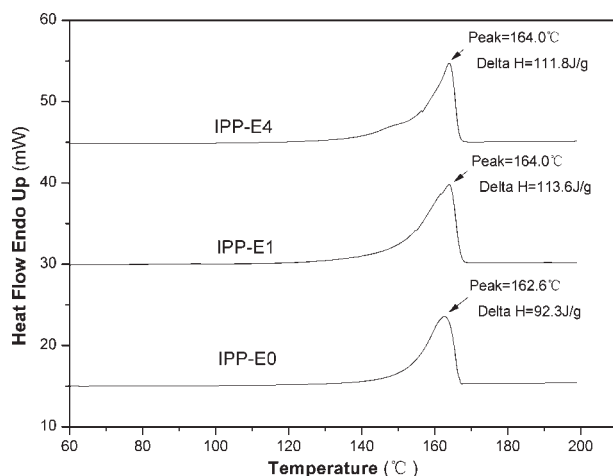
Span80, showed various porous structures, and the higher the concentration was of Span80 in the solution, the higher the porosity was of the IPP particles. Table II presents the pore size distributions and specific areas of samples E0 and E2–E5 from the mercury porosimetry analysis method.

As shown in Table II, the specific area of E0 was much lower than that of E2–E5. The pore size of E0 was too low to be detected with Pascal/140/240 mercury intrusion porosimetry, and this suggests that the IPP particles of E0 were solid rather than porous in structure. The specific area increased swiftly with the concentration of Span80 before 1.0%, that is, from  $0.42 \text{ m}^2/\text{g}$  for E2 to  $5.19 \text{ m}^2/\text{g}$  for E4, and then increased tardily or leveled off, that is, from  $5.19 \text{ m}^2/\text{g}$  for E4 to  $5.73 \text{ m}^2/\text{g}$  for E5. Moreover, as the concentration of Span80 increased, the

pore size distribution became wider, and a microporous structure was gradually formed inside the IPP particles. Therefore, it is appropriate to choose 1% as a suitable concentration of Span80 for the preparation of ultrafine IPP particles with a profuse microporous structure.

#### Crystallization of IPP in chloroform

The TIPS process can be deemed a recrystallization process, and hence the morphology and size of the IPP particles are highly dependent on the experimental conditions employed (e.g., the IPP content in the solution, the cooling rate of the solution, the strength of mechanical stirring, and the surfactants). As shown in Figure 2, all IPP particles prepared via the TIPS method were virtually spherical, with their



**Figure 3** DSC curves of IPP powder for samples E0, E1, and E4.

size ranging from several to tens of micrometers. This could be described by the folded-chain lamella model<sup>28</sup> and the spherulite model.<sup>29</sup> At a high temperature, the IPP polymer, dissolved in the solvent, is fully stretched; as the temperature decreases, the polymer chains begin to gather, forming some chain packets and lamellae with a band structure. The lamellae are the precursors of the crystal nucleus. As the crystal nucleus grows radially, the chloroform molecules between lamella are expelled constantly, and finally, the solid spherulites are formed, as shown by SEM of sample E1. The irregularity of the IPP particles in size and sphericity can be mainly attributed to the age difference of crystallization for different nuclei and the operating conditions, which are unfavorable for ideal crystallization (e.g., concentrated IPP in the solution, mechanical disturbance, and a rapid cooling rate).

When the crystallization process is finished and has settled for a period of time, the IPP particulates will be suspended in the upper layer of the solution because of its lower density versus chloroform. It has been found from our experimentation that the superposed layer is about 80% of the total volume. This suggests that a 1/30 mass ratio of IPP versus chloroform is suitable, and the maximum mass ratio is about 1/24; otherwise, the IPP particles will aggregate because of the intensive collision and adhesion of particles restricted by the limited space provided by chloroform. This deduction was verified by a supplementary experiment using the mass ratio of 1/20 for IPP, from which no clear chloroform layer was found and hard aggregates were detected.

### Crystallinity of the IPP particles

To investigate the crystallinity of the IPP particles prepared with the TIPS method, DSC analysis was

conducted for samples E1 and E4, which were compared with the contrast sample E0. The DSC results are shown in Figure 3. Figure 3 shows that the melting temperature of E1 and E4 was 164°C, which was slightly higher than that of sample E0, 162.6°C. This suggests that the crystallinity of IPP particles prepared by TIPS is higher than the crystallinity of IPP particles prepared by the cryogenic pulverization method because the melting temperature of a polymer increases with its crystallinity. This observation is further justified by the crystallinity, which was calculated with the following equation with the fusion enthalpy shown in Figure 3:

$$\text{Crystallinity (\%)} = \frac{\Delta H_f}{\Delta H_f^*} \times 100 \quad (1)$$

where  $\Delta H_f$  is the fusion enthalpy of IPP samples measured by DSC and  $\Delta H_f^*$  is the fusion enthalpy of an IPP crystal with 100% crystallinity, that is, 209 J/g.<sup>30</sup> The crystallinity values of samples E0, E1, and E4 were calculated to be 44.2, 54.3, and 53.5%, respectively.

### Effect of Span80 on the pore formation of IPP particles

As shown in Figure 2, there was a remarkable difference in the microstructure and morphology for samples E1–E5 prepared with the TIPS method under the same conditions except for the concentration of Span80. This suggests that the pore-forming agent, Span80, and its concentration play a determinant role in the microstructure and porosity of the IPP particles.

Span80, that is, sorbitan monooleate with CAS 1338-43-8, is a nonionic surfactant and is insoluble in water but soluble in organic solvents. It has an amphiphilic structure, that is, a hydrophilic group of hydroxyl at one end and a hydrophobic group of nonpolar alkyl at the other.

From a microscopic point of view, the presence of a surfactant in a chloroform solution can change the surface status of the IPP nucleus and interfere with the growth of the crystal and accordingly the final morphology and microstructure of IPP particles precipitating in a TIPS process. According to the crystallization process of IPP and the structural characteristics of Span80, a pore-forming mechanism is proposed in Figure 4.

Figure 4(a) shows the monolayer adsorption of Span80 onto the surface of the IPP lamella, a precursor of the IPP nucleus for crystallization, which originates from the high surface energy of the tiny lamella. The nonpolar alkyl end of Span80 is apt to be adsorbed onto the nonpolar surface of IPP, whereas the polar hydroxyl end extends to the polar

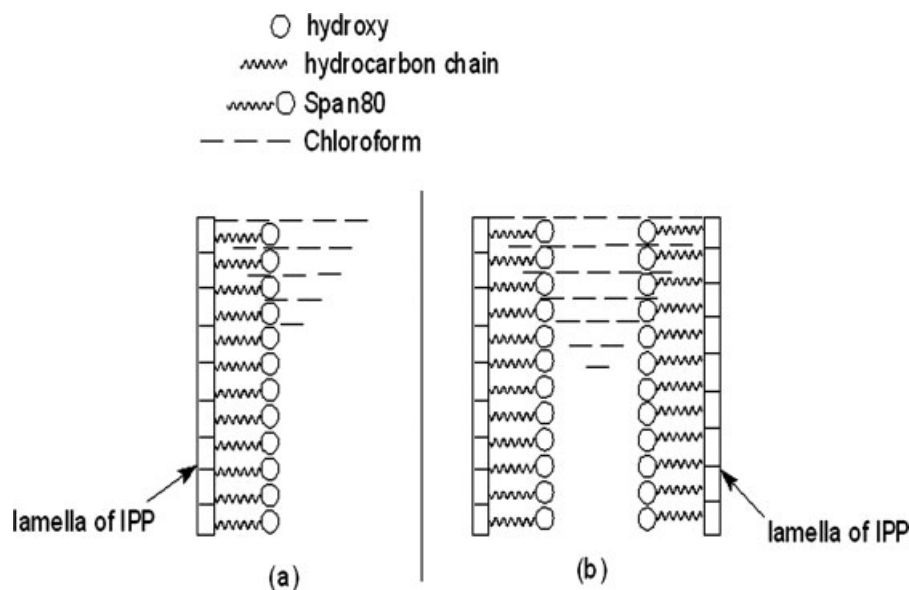


Figure 4 Adsorption of Span80 on the surface of the IPP lamella.

medium of chloroform in terms of the principle of “like dissolves like”. As the temperature decreases, the concentration of the lamellae increases, and the distance between lamellae becomes less and less, as shown in Figure 4(b); this leads to a crystallization process. In this process, the repulsive force between the like ends of the adsorption layer produces a steric hindrance effect for the regular growth of crystals and forms a porous structure because of the mechanical support of the adsorption layer.

Obviously, the fully developed microporous structure requires the presence of abundant lamellae with stable monolayer adsorption of the surfactant. This means that the concentration of Span80 in chloroform must reach a certain value to equilibrate the desorption of the surfactant and satisfy the need for the newly formed IPP lamellae during the crystallization process. Otherwise, if the concentration of Span80 is not high enough, the stable adsorbent layer will not be formed on the newly born surface of the lamellae, and the adjacent lamellae will adhere to one another, forming hard aggregates and lowering the porosity of the particles. This helps to explain the experimental observation that the porosity and specific area of IPP particles always increase with the concentration of Span80, as shown by SEM photographs of samples E1–E5.

## CONCLUSIONS

Microporous IPP particles with an average particle size between 50 and 120  $\mu\text{m}$  and a specific area of about 5.19  $\text{m}^2/\text{g}$  were successfully produced via the TIPS method with chloroform as the diluent and

Span80 as the pore-forming agent. The porosity and specific area of the IPP particles prepared via the TIPS method were much higher than those of IPP particles produced via the cryogenic pulverization method. The mass fraction of IPP versus chloroform has an important effect on the aggregation of particles. The pore-forming agent and its concentration have a determinant influence on the microstructure and porosity of the product. The TIPS method is potentially viable for the production of IPP particles used for efficient chemical surface modification for various purposes.

## References

- Jia, D.; Luo, Y.; Li, Y.; Lu, H.; Fu, W.; Cheung, W. L. *J Appl Polym Sci* 2000, 78, 2482.
- Rengarajan, R.; Vivic, M.; Lee, S. *J Appl Polym Sci* 1990, 39, 1783.
- Liu, C. S.; Wang, Q. *J Appl Polym Sci* 2000, 78, 2191.
- Vainio, T.; Hu, G. H.; Lamba, M.; Seppälä, J. V. *J Appl Polym Sci* 1996, 61, 843.
- Patel, A. C. P.; Brahmabhatt, R. B.; Rao, P. V. C.; Rao, K. V.; Devi, S. *Eur Polym J* 2000, 36, 2477.
- Pan, Y.; Ruan, J.; Zhou, D. *J Appl Polym Sci* 1997, 65, 1905.
- Kimura, T.; Takahashi, T.; Shimizu, K. U.S. Pat. 5,180,791 (1993).
- Akers, J.; James, B.; Leng, D. E.; Normand, R. J. U.S. Pat. 4,524,189 (1985).
- Leong, H. C.; Katz, M.; Cheng, C. H. U.S. Pat. 5,156,843 (1992).
- Kun, K. A.; Kunin, R. *J Polym Sci Part A-1: Polym Chem* 1968, 7, 2689.
- Cheng, C. M.; Vanderhoff, J. W.; El-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 1992, 30, 2129.
- Katz, M.; Cheng, C. H. U.S. Pat. 5,135,740 (1992).
- Okubo, M.; Ikegami, K.; Yamamoto, Y. *Colloid Polym Sci* 1989, 267, 193.

14. Ugelstad, J.; Mfutakamba, H. R.; Mørk, P. C.; Ellingsen, T.; Berge, A.; Schmid, R.; Holm, L.; Jørgedal, A.; Hansen, F. K.; Nustad, K. *J Polym Sci Polym Symp* 1985, 72, 225.
15. Okubo, M.; Mori, H.; Ito, A. *Colloid Polym Sci* 1999, 277, 598.
16. Oliveira, J. V.; Pinto, J. C.; Dariva, C. *Fluid Phase Equilib* 2005, 228, 381.
17. Matson, D. W.; Petersen, R. C.; Smith, R. D. *J Mater Sci* 1987, 22, 1919.
18. Castro, A. J. U.S. Pat. 4,247,498 (1980).
19. Lloyd, D. R.; Kinzer, K. E.; Tseng, H. S. *J Membr Sci* 1990, 52, 239.
20. Lloyd, D. R.; Kim, S. S.; Kinzer, K. E. *J Membr Sci* 1991, 64, 1.
21. Kim, S. S.; Lloyd, D. R. *J Membr Sci* 1991, 64, 13.
22. Lim, G. B. A.; Kim, S. S.; Ye, Q. H.; Wang, Y. F.; Lloyd, D. R. *J Membr Sci* 1991, 64, 31.
23. Kim, S. S.; Lim, G. B. A.; Alwattari, A. A.; Wang, Y. F.; Lloyd, D. R. *J Membr Sci* 1991, 64, 41.
24. Alwattari, A. A.; Lloyd, D. R. *J Membr Sci* 1991, 64, 55.
25. McGuire, K. S.; Lloyd, D. R.; Lim, G. B. A. *J Membr Sci* 1993, 79, 27.
26. Yang, M. C.; Perng, J. S. *J Membr Sci* 2001, 187, 13.
27. Brown, K. R. U.S. Pat. 2,322,820 (1943)
28. Keller, A. *Philos Mag* 1957, 2, 1171.
29. Norton, D. R.; Keller, A. *Polymer* 1985, 26, 704.
30. Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1999; p V/29.