Solid-State Polymerization of Bisphenol A Polycarbonate with a Spray-Crystallizing Method

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ABSTRACT: A novel crystallization method for the production of high-molecular-weight bisphenol A polycarbonate by solid-state polymerization is suggested. In this method, a low-molecular-weight polycarbonate prepolymer is dissolved in a solvent and then partially crystallized with a novel spray-crystallizing method to prepare crystallized polycarbonate particles having a very uniform and porous structure with a narrow melting region. As a result, during solid-state polymerization, the phenol byproduct can be easily removed from the polymerizing porous polycarbonate particles, and the polymerization rate is dramatically increased. In particular, the effects of the crystallization methods on secondary crystallization during solid-state polymerization and the melting behavior have been investigated with differential scanning calorimetry studies. The final product, a high-molecular-weight polycarbonate, displays a very narrow molecular weight distribution and uniform physical properties. A simultaneous process and an adequate reactor design for spray crystallization and solid-state polymerization are also suggested. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 883–889, 2009

Key words: crystal structures; crystallization; polycarbonates; solid-state polymerization

INTRODUCTION

Because of its excellent heat resistance, impact resistance, mechanical strength, and transparency, polycarbonate (PC) is widely used in the preparation of compact disks, transparent sheets, package wrapping, car bumpers, films for UV blockers, and many other new applications.[1] Accordingly, commercial demand for PC is rapidly increasing.[2] The conventional processes for the production of PC can be divided into interfacial polymerization using a phosgene and melt polymerization or solid-state polymerization (SSP) that does not use a phosgene. Compared with the interfacial polymerization process, the melt polymerization process, in which polymerization proceeds with starting monomers in their melt state, offers the advantages of requiring low initial capital and having fewer maintenance problems for long-term production periods because it does not use toxic materials. However, to produce high-molecular-weight PCs for injection and extrusion, a high-temperature, high-vacuum facility is needed because highly viscous melt reactants are treated, and thus the quality can easily deteriorate under certain abnormal conditions. Meanwhile, the SSP process, in which polymerization proceeds at a temperature lower than the melting temperature after the crystallization of low-molecular-weight PC prepolymers, does not use toxic materials, and the deterioration of quality can be avoided because the reaction occurs in a solid state at a lower temperature.

Many scientific and industrial studies have been carried out to develop and analyze the SSP process.[3–7] Crystallization is inevitable in SSP and highly affects the polymerization rate and the product quality. Many efforts have been made to develop and enhance the crystallization method of PC.[8–11] Early in 2000, DeSimone reported[10] that supercritical CO_2 induced the crystallization of PC and accelerated the polymerization rate during SSP because of the good solubility of the phenol in the sweeping supercritical CO_2. Many researchers also have tried to understand the diverse phenomena related to the crystallization and melting behavior of PC and have suggested related mechanisms.[12–15] Notably, Marand suggested a mechanism underlying the secondary crystallization and multiple-melting behavior of PC.[13]

In global chemical industries, two conventional methods for the crystallization and SSP of PC are widely applied: heat treatment and nonsolvent precipitation. In the SSP processes disclosed under U.S. Patent 4,948,871 and U.S. Patent 5,214,073, a semicrystalline PC, which can be polymerized in a solid-state manner, is prepared by the heat treatment of an amorphous PC prepolymer at its crystallization temperature over a long time or by its dissolution in a solvent and precipitation with a nonsolvent. In the process of crystallization by heat treatment, a very

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long period of more than 72 h is required, and the degree of crystallization is comparatively low. As such, it is difficult to prepare a semicrystalline PC that is suitable for SSP on a large scale. In the case of nonsolvent precipitation, two kinds of solvents, that is, a good solvent and a nonsolvent, are used sequentially. These solvents should be completely separated after crystallization, and the crystallized particles have a broad size distribution and melting region. Therefore, it is essential to develop a novel crystallization process for PCs that is suitable for SSP in which the size distribution, porosity, and thermal properties of semicrystalline PCs can be controlled.

In this article, in an effort to address the aforementioned problems, a novel spray-crystallizing method for the crystallization and SSP of PC is suggested. The crystallization and melting behaviors of PC particles crystallized by this method have been investigated with differential scanning calorimetry (DSC) studies, and the effects on the polymerization rate during SSP are discussed. Finally, the properties of high-molecular-weight PC produced after SSP are investigated with respect to the crystallization methods.

EXPERIMENTAL

Materials

A PC prepolymer was prepared by melt transesterification between bisphenol A (LG Chem, Ltd., Daejeon, Korea) and diphenyl carbonate (Sigma–Aldrich Co., St. Louis, USA). Diphenylcarbonate and bisphenol A were well mixed in a melt state in a ratio of 1.05 : 1 and then poured into a 3-L stirred-tank reactor under a nitrogen atmosphere. Lithium hydroxide (0.3 mol %) was added as a polymerization catalyst. The polymerization started with the agitation of the mixture under a reduced pressure of 250 mmHg at 180°C for 5 min, and then the reaction proceeded more under a reduced pressure of 1–4 mmHg at 230°C for 30 min. The weight-average molecular weight of the finally prepared PC prepolymer was 8400 g/mol.

Chloroform (Duksan Chemicals, Ansan, Korea) was used to dissolve the prepolymer, and methanol (Duksan Chemicals) was used to precipitate the crystallized prepolymer via a conventional nonsolvent precipitation method for comparison.

Methods

Crystallization of the PC prepolymers

An amorphous PC prepolymer prepared in advance was dissolved in a 2-L dissolution bath with chloroform as a solvent to yield a solution of 20% (w/w). With a spray-crystallizing method, the prepared solution was sprayed into the top of a drying chamber
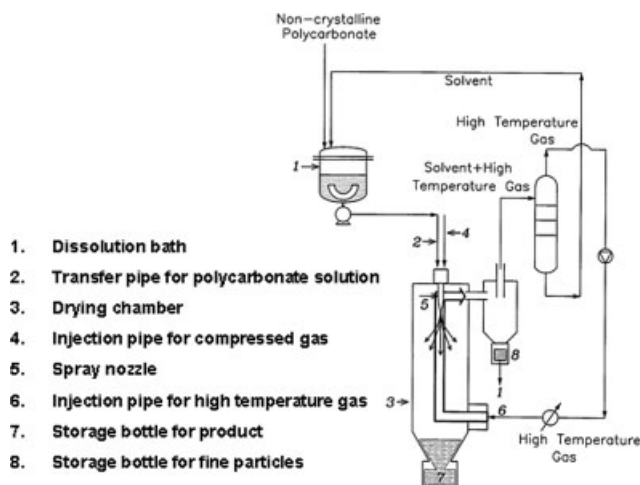
Figure 1 Schematic diagram of the spray-crystallizing equipment.

1. **Dissolution bath**
2. **Transfer pipe for polycarbonate solution**
3. **Drying chamber**
4. **Injection pipe for compressed gas**
5. **Spray nozzle**
6. **Injection pipe for high temperature gas**
7. **Storage bottle for product**
8. **Storage bottle for fine particles**

via a nozzle. High-temperature nitrogen at 120°C was simultaneously injected at a flow rate of 300 L/h to the lower portion of the drying chamber, as shown in Figure 1, to evaporate all of the solvent, thereby yielding a semicrystalline PC in the form of dried particles in the bottom portion of the drying chamber.

Both the evaporated solvent and high-temperature nitrogen in this procedure passed through a cyclone affixed to the side of the upper portion and were separated into a liquid-state solvent and gaseous-state nitrogen via a condenser. The solvent was then refluxed back into the dissolution bath, and nitrogen was refluxed into a heating chamber via a compressor. In the drying chamber, particles having a diameter of less than 80 μm, of which the crystallinity was lower than roughly 10%, could be obtained in a small amount. These particles were collected in the cyclone and refluxed into the dissolution bath. The crystallinity of the semicrystalline PC obtained from the lower portion of the drying chamber was observed with a differential scanning calorimeter (TA Instrument, Delaware, USA). A useful procedure for measuring the crystallinity by DSC involves drawing an arbitrary linear baseline from the first onset of melting to the last trace of crystallinity and determining the enthalpy of fusion from the area under this endotherm. The crystallinity could be calculated with the following equation:[10,16]

$$X_c = \Delta H_f(\text{Sample}) \times 100/\Delta H_0$$

where X_c is the crystallinity percentage; $\Delta H_f(\text{Sample})$ is the enthalpy of fusion measured in the melting region of the DSC thermogram of a semicrystalline PC; and ΔH_0 is the enthalpy of fusion of a crystalline phase, which is 26.2 cal/g for bisphenol A polycarbonate (BPA–PC).[17] The morphology and size of the particles

TABLE I
Sample Summary

Sample code	M_w of prepolymer	Crystallizing method	SSP time (h)	Phenol removal
8kSD-0	8400	Spray crystallization	0	—
8kSD-tN			5, 10, 15 (t)	N_2 purging
8kSD-tV				High vacuum
8kNP-0		Nonsolvent precipitation	0	—
8kNP-tN			5, 10, 15 (t)	N_2 purging
8kNP-tV				High vacuum

M_w = weight-average molecular weight.

were investigated with a scanning electron microscope (JEOL, Tokyo, Japan) and an image analyzer.

For comparison, the prepared solution was precipitated with methanol as a nonsolvent at a concentration of 200% of the prepared solution.

SSP of the crystallized prepolymers

The prepared semicrystalline PCs were poured into an SSP reactor, and an SSP reaction was conducted under an isothermal condition of 200°C while nitrogen was continuously injected at a speed of 3 L/min or under a very high vacuum condition without nitrogen purging. Sampling was done every 5 h, and the increase in the molecular weight was observed with gel permeation chromatography (Waters Co., Massachusetts, USA).

Details of all the samples are summarized in Table I.

RESULTS AND DISCUSSION

Morphology of the crystallized particles

Figure 2 shows the morphology of the crystallized PC particles prepared with the methods described

previously. The particle size and distribution are summarized in Table II.

In the spray-crystallizing method, the average diameter of the particles was 304 μm, and they showed a very uniform particle size. As such, an additional pulverization step for SSP was not required. In the case of the conventional nonsolvent precipitation method, the average diameter of the particles was 380 μm, and a large portion of the particles existed in the form of a lump with a diameter exceeding 1 mm; thus, pulverization was necessary for SSP. Consequently, the diameter of the pulverized particles was 200–600 μm.

The surface morphology of the particles crystallized by the spray-crystallizing method was very uniform and showed a porous structure. However, that of the particles crystallized by the conventional nonsolvent precipitation method was irregular and showed a less porous structure. In the spray-crystallizing method, the evaporation of the solvent from the particles was extremely fast, and a highly porous surface structure was formed. However, in the nonsolvent precipitation method, the particle surface
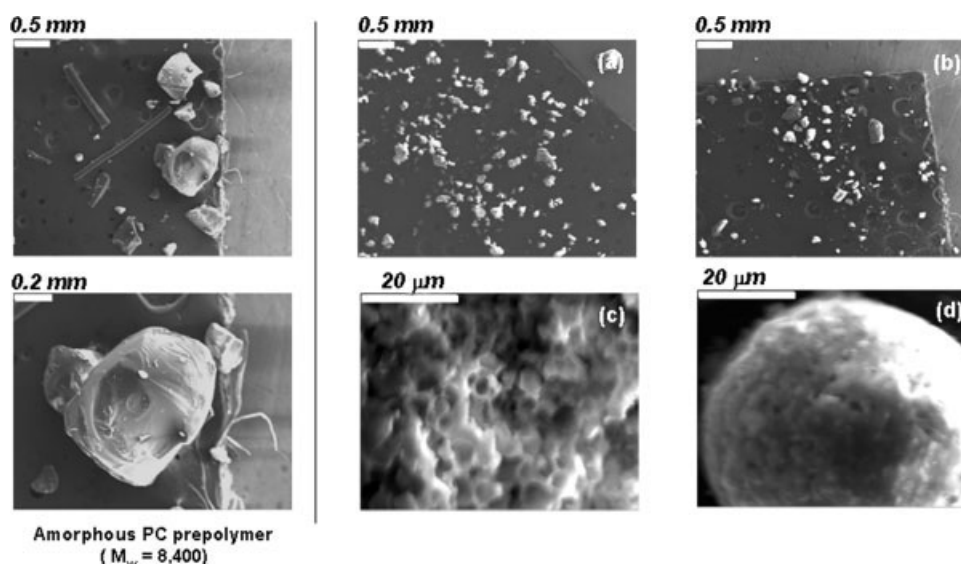

Figure 2 Surface morphology of the crystallized PC particles: (a) 8kSD-0 (low magnification), (b) pulverized 8kND-0 (low magnification), (c) 8kSD-0 (high magnification), and (d) pulverized 8kND-0 (high magnification).

TABLE II
Size and Distribution of Crystallized PC Particles

	Average size (μm)	Standard deviation (μm)	Size distribution (um)		
			D50	D70	D90
8kSD-0	304	51	312	380	400
8kNP-0 (pulverized)	380	120	398	467	580

was solidified more slowly because of slow dissolution of the solvent and the nonsolvent, and a less porous surface was formed finally.

Also, the size of the droplets sprayed from the nozzle in the spray-crystallizing method was very uniform; hence, in comparison with the conventional nonsolvent precipitation method, the particle size and the surface pore structure were very uniform.

DSC heating curves of the crystallized particles

Figure 3 and Table III show the thermal behavior of the crystallized particles, which was measured with DSC. The particles crystallized by the conventional nonsolvent precipitation method had a very broad melting temperature range, whereas the particles crystallized by the spray-crystallizing method had a very narrow range. In the conventional method, diverse PC crystal states could be formed from the core to the surface during the precipitation and crystallization of the PC particles because crystallization occurred with slow dissolution of the solvent and nonsolvent within the precipitating PC particles. As a result, the crystallized particles showed a broad melting temperature region. In contrast, in the case of the spray-crystallizing method, solvent evaporation proceeded very rapidly, and the size of the droplets and the crystalline state within the particles were both very uniform, regardless of the position within the particles.

Figure 3 and Table III show the effect of the temperature of the inlet N_2 gas on the melting behavior of the particles crystallized by the spray-crystallizing method. The melting temperature and the crystallinity increased as the temperature of the inlet N_2 gas was increased. With the spray-crystallizing method, crystallization occurred in a considerably higher
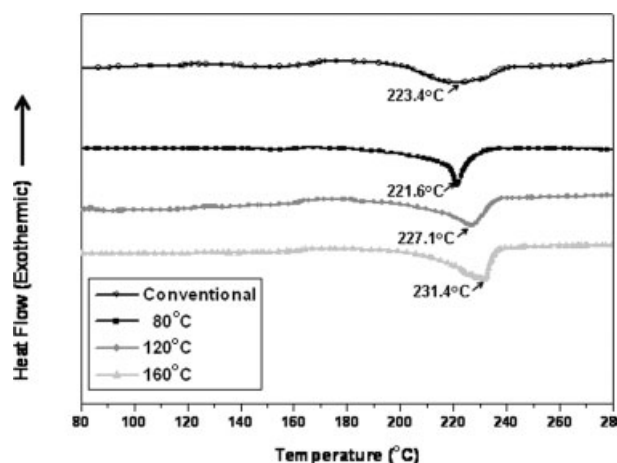

Figure 3 Effects of the crystallizing methods and N_2 temperature during spray crystallization on the melting behavior of crystallized PC particles (DSC curves).

temperature region in comparison with the nonsolvent precipitation method because the solvent evaporated rapidly, and the glass-transition temperature also rose quickly. As a result, increasing the temperature of the inlet N_2 gas was an effective means of increasing the crystallinity and the melting temperature.

Change in the crystalline state during SSP

Figure 4(a,b) and Table IV show the change in the crystalline state during SSP. Regardless of the crystallization method, the crystallinity and melting temperature increased as the SSP time was increased because the molecular weight of the growing PC crystals was increased, and the secondary crystallization occurred at an SSP temperature that corresponded to the crystallization temperature. However, only the particles crystallized by nonsolvent precipitation showed multiple-melting behavior. Generally, multiple-melting behavior can be explained by two mechanisms: (1) different crystal stability and (2) a melting–recrystallization–remelting process.[15,18–22] In 2001, Marand and coworkers[13,14] reported on the multiple-melting behavior of BPA–PC. They found a crossover phenomenon from secondary crystal formation at a low temperature to isothermal lamellar thickening at a high

TABLE III
Crystallization Temperature and Crystallinity

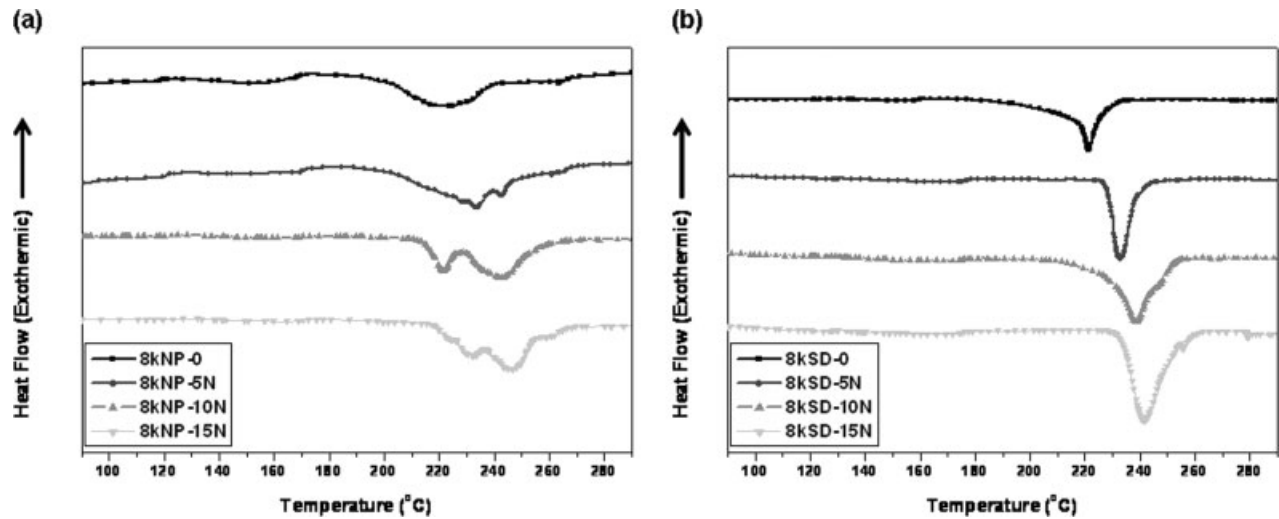| Sample code	Crystallizing method	Temperature of inlet gas (°C)	Melting temperature (°C)	X_c (%)
8kSD-0	Spray crystallization	80	221.2 ± 3.8	26.9 ± 1.8
		120	227.1 ± 2.1	27.8 ± 2.0
		160	231.4 ± 3.3	29.3 ± 1.1
8kNP-0	Nonsolvent precipitation	—	223.4 ± 6.8	26.1 ± 4.5

Figure 4 Change in the melting behavior during SSP (DSC curves).

temperature. In the results, as mentioned previously, the crystallization rate was relatively slow in the nonsolvent precipitation method, and it varied from the core to the surface as the solvent was dissolved with an external nonsolvent within the precipitating particles. As a result, the particles crystallized by the nonsolvent precipitation method had different crystal states and a broad melting region. During SSP, secondary crystallization of crystals with different states occurred, and they ultimately showed different secondary crystal states. In addition, the multiple-melting behavior of these crystals was observed by DSC analysis. Meanwhile, the crystallization rate was relatively fast in the spray crystallization, and the particles crystallized by the spray-crystallization method displayed a very uniform crystal state and a narrow melting region. As a result, although secondary crystallization also occurred, multiple-melting behavior was not observed. Furthermore, the particle size was larger and the particle distribution was very broad in the case of nonsolvent crystallization. As a result, the polymerization rate varied exten-

sively from the core to the surface within a particle and also between particles during SSP. Finally, the PC particles with a high molecular weight after SSP displayed multiple-melting behavior.

Increase in the molecular weight of PC during SSP

The effect of the crystallization method on the increase in the molecular weight of PC during SSP is shown in Figure 5. The molecular weight of the PC crystallized by conventional nonsolvent precipitation was increased as the SSP time was increased to 5 h, but the polymerization rate decelerated after 5 h. The final molecular weight of the PC crystallized by conventional nonsolvent precipitation reached only 28,420 g/mol after 15 h (Table V). Meanwhile, the molecular weight of the PC crystallized by spray crystallization increased steadily after 5 h and finally reached 41,924 g/mol after 15 h. The PC particles crystallized by the conventional method showed a

TABLE IV
Crystallization Temperature and Crystallinity

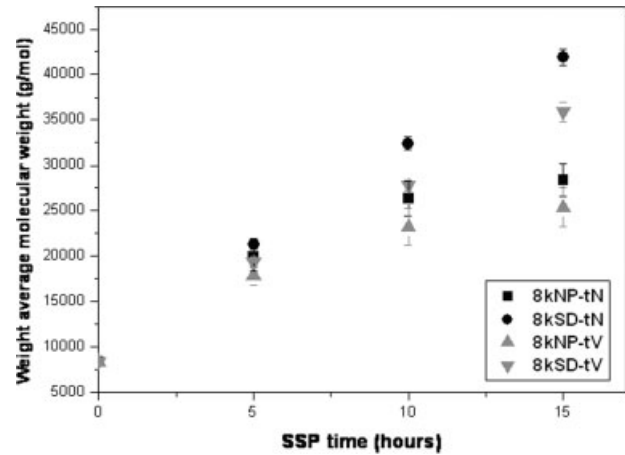| Sample code	Crystallizing method	Melting temperature (°C)	X_c (%)
8kNP-0	Nonsolvent	223.4	26.1
8kNP-5N	precipitation	233.6	30.0
		242.0	
8kNP-10N		221.4	38.7
		242.8	
8kNP-15N		221.0	41.3
		233.0	
		246.5	
8kSD-0	Spray	221.2	26.9
8kSD-5N	crystallization	232.9	40.0
8kSD-10N		241.8	46.4
8kSD-15N		245.1	48.1

Figure 5 Increase in the molecular weight during SSP.

TABLE V
Molecular Weights and PDIs

Sample code	Crystallizing method	M_w	PDI (M_w/M_n)
Prepolymer (8kNP-0 and 8kSD-0)	—	8,400	1.87
8kNP-5N	Nonsolvent precipitation	19,897	2.03
8kNP-10N		26,389	2.21
8kNP-15N		28,420	2.28
8kSD-5N	Spray crystallization	21,329	1.89
8kSD-10N		32,424	1.93
8kSD-15N		41,924	1.96

M_n = number-average molecular weight; M_w = weight-average molecular weight.

very broad size distribution; that is, there were a large number of large particles over 250 μm. In the case of the large particles, polymerization occurred only on the surface. In a previous study,[7] these authors reported the results of simulations and experiments concerning the effect of the particle size on the phenol diffusion rate and polymerization rate. When the particle size was greater than 250 μm, the phenol produced at the core could not be removed easily, and the polymerization rate at the core was very slow. In this study, the porosity of the surface was substantially higher in the spray-crystallized particles, and the phenol at the surface was more easily removed, in comparison with the nonsolvent-precipitated particles.

The polydispersity index (PDI) was increased by an increase in the molecular weight during SSP. The PDI of PC particles crystallized by the conventional method was considerably increased after 15 h of SSP in comparison with PC particles crystallized by the spray-crystallizing method. This indicates that there was a very large portion of unreacted parts in the large particles, possibly in the core region of the particles. In contrast, the increase in the PDI of the spray-crystallized PC particles was merely 4.8%, which was roughly one-quarter of that (i.e., 22.1%) obtained in the case of 8kNP-15N.

Figure 5 also shows the effect of the phenol removal method on the polymerization rate during SSP. The N_2-purging method was found to be more effective than the high-vacuum method because the partial aggregation that occurred in the latter during SSP was prevented in the N_2-purging method.

CONCLUSIONS

An amorphous PC prepolymer was crystallized for SSP by two crystallizing methods, a novel spray-crystallizing method and a nonsolvent precipitation method, and the effects of these methods were discussed. The spray-crystallized PC particles showed a

very narrow melting region and size distribution in comparison with the particles crystallized by the nonsolvent precipitation method. The effects of crystallization during SSP on the polymerization, the change in the crystallinity, and the melting behavior were investigated, and it was found that the spray-crystallizing method could provide a semicrystalline PC having a very stable and uniform crystal state. As a result, the SSP rate was faster and the molecular weight of the high-molecular-weight PC finally produced was more uniform in comparison with the conventional nonsolvent precipitation method. We also suggested a simultaneous method and related equipment to perform crystallization and SSP simultaneously in a single continuous SSP reactor (Fig. 6). In this method, the PC solution is sprayed from a top nozzle and then dried and crystallized as it descends to the bottom of the reactor. SSP is performed continuously as in a moving packed-bed reactor, and the final product is discharged by a screw discharger. Hot N_2
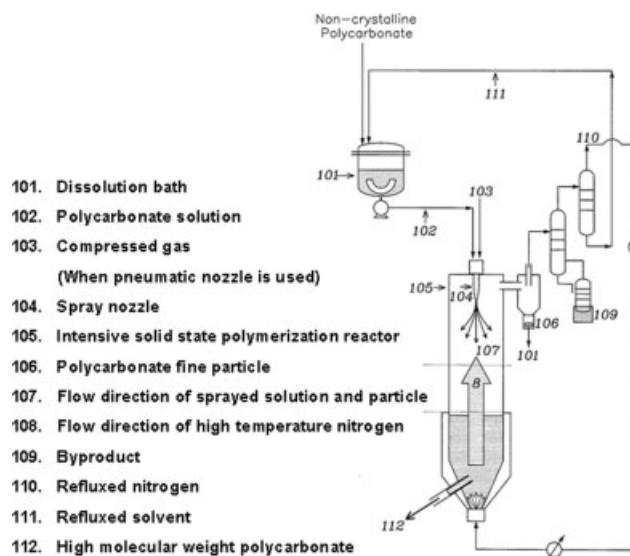

101. Dissolution bath
102. Polycarbonate solution
103. Compressed gas (When pneumatic nozzle is used)
104. Spray nozzle
105. Intensive solid state polymerization reactor
106. Polycarbonate fine particle
107. Flow direction of sprayed solution and particle
108. Flow direction of high temperature nitrogen
109. Byproduct
110. Refluxed nitrogen
111. Refluxed solvent
112. High molecular weight polycarbonate

Figure 6 Conceptual diagram of the rector for simultaneous crystallization and SSP.

gas is purged from the bottom, and it can remove the byproduct phenol and also evaporate the solvent. The simultaneous process and reactor are expected to be commercially useful in terms of the cost leadership of the process because the amount of equipment is reduced, the process is dramatically simplified, and the energy used for SSP can be directly reused for drying the crystallizing particles.

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