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Towards High Molecular Weight Poly(bisphenol A carbonate) with Excellent Thermal Stability and Mechanical Properties by Solid-State Polymerization*

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Abstract Poly(bisphenol A carbonate) (BPA-PC) was post-polymerized by solid-state polymerization (SSP) after supercritical CO_2-induced crystallization in low molecular weight particles prepolymerized *via* melt transesterification reaction. The effects of the crystallization conditions on melting behavior and SSP of BPA-PC were investigated with differential scanning calorimetry (DSC), Ubbelohde viscosity method and gel permeation chromatography (GPC). The reaction kinetics of the SSP of crystallized prepolymers was studied as a function of reaction temperatures for various reaction periods. As a result, the viscosity average molecular weight of BPA-PC particles (2 mm) increased from 1.9×10^4 g/mol to 2.8×10^4 g/mol after SSP. More importantly, the significantly enhanced thermal stability and mechanical properties of solid-state polymerized BPA-PC, compared with those of melt transesterification polymerized BPA-PC with the same molecular weight, can be ascribed to the substantial avoidance of undergoing high temperature during polymerization. Our work provides a useful method to obtain practical product of BPA-PC with high quality and high molecular weight.

Keywords: Poly(bisphenol A carbonate); Solid-state polymerization; Supercritical CO_2-induced crystallization; High molecular weight; High quality.

INTRODUCTION

Poly(bisphenol A carbonate) (BPA-PC) is an important engineering thermoplastic that is extensively utilized in numerous commercial applications including optical recording, automotive, architecture, electronic and electrical, health and medical, and leisure and safety industries, primarily due to its excellent heat and impact resistance, unusual mechanical, electrical and optical properties[1]. As a consequence, commercial demand for BPA-PC is promptly increasing[2]. Currently, BPA-PC is synthesized industrially either by an interfacial phosgenation process or by a melt transesterification process. High molecular weight BPA-PC with excellent optical clarity and color can be obtained *via* interfacial polymerization. However, this process involves phosgene, a highly regulated toxic and hazardous chemical, and generates extremely large amounts of organic, aqueous and solid wastes, which can raise serious environmental risks. Melt transesterification process is a solvent-free, potentially phosgene-free alternative route to the manufacture of BPA-PC. Since the transesterification reaction is highly reversible[3], the chain extension and final molecular weight are strongly

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limited by condensate (phenol) removal from the reaction mass. The removal of phenol becomes more difficult due to the increasingly high melt viscosity as the molecular weight of the polymer increases. Increasing the reaction temperature to reduce melt viscosity often deteriorates polymer qualities for the reason that high temperature usually leads to side reactions, including crosslinking, chain branching and discoloration of the final product[4, 5]. Similar problems also occur in other melt polycondensation reactions of polyesters with high molecular weight such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). Hence developing more environmentally friendly and lower cost techniques to manufacture BPA-PC with high quality and high molecular weight has been proven highly significant[6].

Solid-state polymerization (SSP) is the very route to the preparation of BPA-PC with high quality and high molecular weight, which is a phosgene-free, solvent-free and environmentally benign alternative[7, 8]. Currently, SSP is mainly used in the manufacture of high molecular weight PET, PBT and nylon[9–13]. In a typical SSP process, the low molecular weight prepolymer synthesized by melt transesterification reaction is heated to a temperature above its glass transition temperature (T_g) to allow the end groups to be mobile enough to engage in chain growth reactions, but below its melting temperature (T_m) to make the growing polymer stay solid, without melting or sticking. A continuous flow of sweep fluid, an inert gas[8, 14] such as N_2 or supercritical carbon dioxide ($scCO_2$[8, 15]), through the particles or a vacuum is used to facilitate the removal of reaction byproduct[7]. In recent studies, it has been reported that BPA-PC with high quality and high molecular weight can be produced *via* SSP at relatively low temperatures of 165–240 °C[7, 8, 14]. Therefore, the deterioration of quality caused by high temperature and other drawbacks including the use of detrimental materials and the dispose of toxic wastes, can be prevented in the synthesis process of BPA-PC *via* SSP.

To operate above T_g and below T_m, crystallization prior to SSP is inevitable in the production process of BPA-PC. Otherwise, the amorphous prepolymer particles of virgin state would agglomerate and melt to a viscous mass. BPA-PC is a crystallizable polymer with a very slow rate of crystallization due to the low mobility of its rigid chains. Unlike PET, BPA-PC does not thermally crystallize, which suffers from long crystallization period (about 170 h at 190 °C[16]), low degree of crystallinity and large energy consumption. In solvent-induced crystallization, solvents commonly used (*e.g.*, acetone, methylene chloride) not only are very difficult to eliminate from the polymer after the course of crystallization but also have an undesirably harmful effect on environment. It was found that BPA-PC could crystallize when exposed to CO_2 at certain conditions[17], which was proven to be an environmentally benign and efficient alternative to the conventional methods mentioned above[17–19]. The absorbed $scCO_2$ can plasticize amorphous regions of polymers by decreasing T_g remarkably (down to 75 °C with $scCO_2$ at 8 MPa[20]) due to the increased free-volume fraction. Therefore, the ordinarily rigid chains have better mobility to rearrange into a more energetically favored state in $scCO_2$, leading to the induction and promotion of rapid crystallization at lower crystallization temperature (T_c) of polymers. Furthermore, $scCO_2$ could be easily removed from the polymer upon degassing from the reactor. Besides BPA-PC, similar researches have also been reported for polymers such as PET[21] and poly(phenylene sulfide) (PPS)[22].

Although a few researches have been carried out to develop and analyze the process of solid-state polymerization[23–25], the high quality including thermal stability and mechanical properties associated with the high molecular weight BPA-PC after SSP has never been reported previously to the best of our knowledge. For the practical use of BPA-PC by SSP, the performance of the final product is absolutely essential to be further explored. It is noted that the performance of BPA-PC *via* SSP is affected by prepolymer properties (prepolymer molecular weight, degree of crystallinity, particle size and catalyst concentration) and reaction conditions (temperature, time and pressure)[26]. In this research, to achieve BPA-PC with high quality, we attempt to explore the effects of $scCO_2$ temperature, pressure and time on the crystallization characteristics of low molecular weight BPA-PC particles in an effort to produce a material that can undergo SSP process, then to obtain the certain high molecular weight BPA-PC through regulating the experimental conditions of SSP process such as temperature and time. The melting behaviors of BPA-PC prepolymer, the molecular weights and their distributions of the polymers after SSP were investigated with differential scanning calorimetry (DSC), Ubbelohde viscosity method and gel permeation chromatography (GPC), respectively. In particular, the enhanced thermal stability and mechanical properties of the high molecular weight BPA-PC produced *via* SSP are also presented.

EXPERIMENTAL

Prepolymer Synthesis

Prepolymer was synthesized by melt transesterification reaction of diphenyl carbonate (DPC) and bisphenol A (BPA) with an initiator, and then cut into uniform sized particles about 13 mg in weight and 2 mm in size. The prepolymer had an initial viscosity average molecular weight (M_η) of 1.9 × 10^4 g/mol and polydispersity index (PDI) of 1.74, as determined by Ubbelohde viscosity method and GPC, respectively. There was no crystallinity observed in the prepolymer using DSC, indicating that no crystal nucleation in the polymer matrix was caused by the small amount of catalyst used in this process[14, 27, 28].

Supercritical CO_2-Induced Crystallization

The amorphous BPA-PC prepolymer particles were treated with $scCO_2$ to be rendered in a suitable morphology for SSP. This process involved placing prepolymer particles in a high pressure apparatus heated to the crystallization temperature (80, 100, 120 or 140 °C). CO_2 was added to the vessel (upon 5, 10, 15 or 20 MPa), and then vented at the end of the experiment. After crystallizing for certain time (2, 4, 6, 8 or 10 h), the semicrystalline polymer particles were collected. There was very little change in both M_η and PDI after crystallization as confirmed by Ubbelohde viscosity method and GPC, respectively. This indicated that chain extension did not occur during this process.

Solid-State Polymerization

The semicrystalline BPA-PC prepolymer particles were prepared and crystallized by the method described above, and then placed into an SSP reactor equipped with heating system, vacuum pump and a manometer. The reaction temperature was raised to 120 °C for 1 h to dehydrate the prepolymer, and then kept constant at 200, 210, 220, 230 or 240 °C for certain time (3, 6, 9 or 12 h) under a constant high vacuum (about 10 Pa), afterward allowed to be cooled to room temperature.

Characterization

The thermal analysis of the samples was conducted using a Perkin-Elmer pyris-1 DSC (USA), calibrated by indium, at a rate of 10 K/min from 50 °C to 300 °C in N_2 atmosphere. The mass of each tested sample was about 5 mg. T_m was measured from the maximum in the melting endotherm. The percent crystallinity (P) was calculated from enthalpy of fusion according to:

$$P = \frac{\Delta H_{\mathrm{f,sample}}}{\Delta H_{\mathrm{f}}^{0}} \tag{1}$$

where $\Delta H_{\mathrm{f,sample}}$ is the calibrated specific fusion heat of the sample by integrating area of the melting peak, and $\Delta H_{\mathrm{f}}^{0}$ is the fusion heat of the standard state of 100% crystalline BPA-PC, which has been determined to be 0.11 kJ/g[29].

Intrinsic viscosity $[\eta]$ measurements were performed using an Ubbelohde viscometer at 20 °C in the solvent of dichloromethane. The samples were completely dissolved in the above solvent at room temperature for several hours. Intrinsic viscosity was calculated after the Solomon-Ciuta equation[30]:

$$[\eta] = \frac{\sqrt{2\left[t/t_0 - \ln(t/t_0) - 1\right]}}{c} \tag{2}$$

where c, t and t_0 refer to the concentration of the solution, the flow time of the solution and the flow time of pure solvent, respectively. The viscosity average molecular weight (M_η) of the samples was calculated from intrinsic viscosity $[\eta]$ values, using the equation proposed by H·Schnell[4]:

$$[\eta] = 1.23\times10^{-4} M_\eta^{0.83} \tag{3}$$

The molecular weight distribution (MWD) of BPA-PC particles before and after SSP was determined using a Shimadzu GPC instrument with a tetrahydrofuran (THF) mobile phase and polystyrene standards for calibration. The oven temperature was 40 °C, and the flow rate of THF was 1.0 mL/min.

Thermogravimetric analysis (TGA) was conducted on a Q500 analyzer (TA Instruments) under N_2 atmosphere. Around 10 mg of the samples was heated from room temperature to 800 °C at a heating rate of 10 K/min for each test.

The tensile tests were carried out on an Instron 5567 universal testing machine with a crosshead speed of 10 mm/min at room temperature (23 °C). The Izod notched impact strength of the specimens was measured with a VJ-40 Izod machine according to ASTM D256-04. The fracture direction was vertical to the flow direction. All the values were calculated as the average of at least five specimens for each sample.

RESULTS AND DISCUSSION

Prepolymer Crystallization Induced by scCO₂

As shown in Fig. 1, the melting behaviors of BPA-PC prepolymers crystallized in $scCO_2$ at different temperatures, pressures and times, are characterized by double melting peaks. The double melting behavior results from the different thermal stabilities of two crystals in the sample[19]. However, these three parameters have different effects on the shifts of melting peaks during annealing in $scCO_2$. First, the lower melting peaks move to higher temperatures with increasing treatment temperature, indicating that the crystals melting at lower temperatures are thickened. Nevertheless, the higher melting peaks shift marginally in the melting isotherms and become sharp with increasing treatment temperature, which indicates that more crystals become uniform sized. Second, the melting peaks shift to higher temperatures with increasing pressure, but no obvious melting peak is observed under 5 and 10 MPa. These results show that the shift of melting peaks to higher T_m is connected with the increase in lamellar thickness or crystal size, which does not occur under low pressure. Third, the upward shift of T_{m1} of BPA-PC is also affected by increasing annealing time. For the samples treated for 2, 4, 6, 8, and 10 h (Fig. 1c), the lower melting peaks are at 183.6, 185.6, 186.5, 187.0, and 188.0 °C, respectively, while there is no detectable shift observed in the higher melting peaks. The slight increase in T_{m1} is attributed to the rejection of crystal defects and the smoothing of crystal folding surfaces with the increasing annealing time during isothermal crystallization[31, 32]. In addition, the surface energy is reduced by the increasing regularity in the chain conformation at crystal surface, which also results in a slight increase in T_{m1}[33].

It is easy to control the prepolymer crystallinity by adjusting crystallization conditions including temperature, pressure and crystallization period. The crystallinity of the prepolymers crystallized in $scCO_2$ at the crystallization conditions in Fig. 1 ranges from 7% to 17% and shows increasing trends with increasing crystallization temperature, pressure and time to various degrees. For example, crystallinity of −15% can be obtained under a moderate condition (100 °C, 15 MPa, and 6 h), and higher crystallinity are gained at higher temperatures or pressures, whereas no significant crystallinity change is observed with increasing crystallization period. At higher temperatures, the solubility of CO_2 decreases, while the mobility of polymer chains is enhanced. Schnitzler and Eggers[34] reported that, compared with the solubility influence, the positive temperature influence becomes dominant when the temperature of the CO_2-PC system is above 70 °C. This leads to a stronger sorption and swelling behavior of BPA-PC. Additionally, the CO_2 density increases with increasing CO_2 pressure, thus the volume fraction of CO_2 absorbed by the BPA-PC sample increases, which enhances the mobility of the chains and lowers T_g simultaneously. Therefore, it is kinetically favorable to transform the amorphous phase into a lower free-energy crystalline structure. However, it is well-known that high pressure itself also reduces the free-volume fraction and thus increases T_g of the BPA-PC sample. These two reverse processes might have a net effect according to the change of free volume[19].

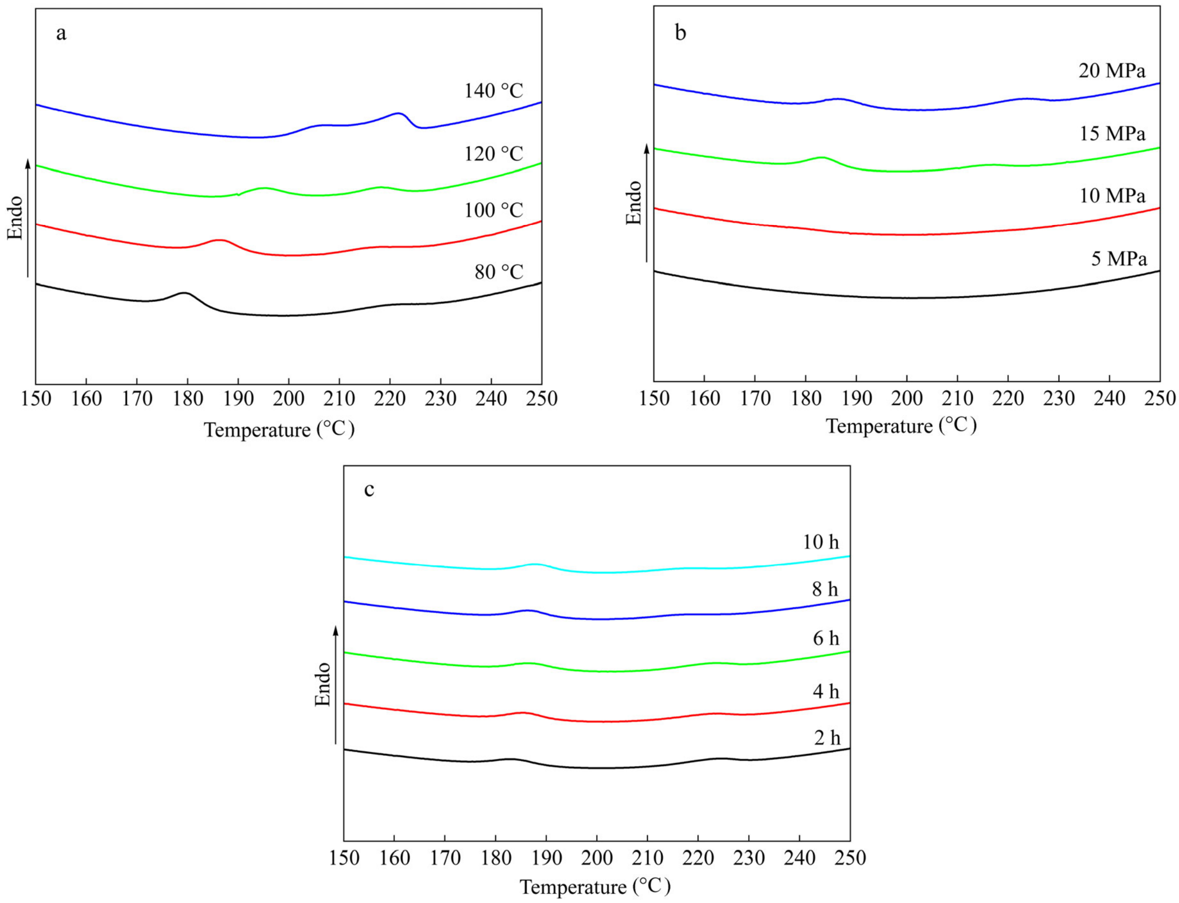

Fig. 1 Melting behavior of BPA-PC prepolymers crystallized in $scCO_2$ under the condition of (a) 15 MPa, 6 h and various temperatures indicated; (b) 100 °C, 6 h and various pressures indicated; (c) 100 °C, 15 MPa and various times indicated

Optimization of $scCO_2$-Induced Crystallization Conditions

A systematic study of the effect of $scCO_2$-induced crystallization conditions such as temperature, pressure and time on the SSP of BPA-PC was carried out. The intrinsic viscosities and their corresponding viscosity average molecular weights which can be calculated *via* Eq. (3) of BPA-PC under different $scCO_2$-induced crystallization conditions after SSP of 210 °C and 9 h under vacuum are listed in Table 1. As seen in Fig. 2 and Table 1, the highest intrinsic viscosity is obtained from the prepolymer with a medium crystallinity of ~15%, corresponding to the crystallization condition of 100 °C, 15 MPa and 6 h, after SSP of 210 °C and 9 h under vacuum. It is well-known that low crystallinity (such as ~7%) might not be adequate to keep the polymer particles structurally integral and rigid during SSP. However, high crystallinity does not always contribute to the SSP rate. The prepolymer crystallinity has two contradictory effects on the SSP rate. High prepolymer crystallinity can accelerate the SSP by increasing the effective concentrations of catalyst and reactive end groups that are rejected from the crystalline phase and migrate to the amorphous phase[12, 25]. On the other hand, high crystallinity might decrease the SSP rate by inhibiting the chain-end mobility and limiting byproduct diffusion throughout the polymer particles. Therefore, prepolymers of medium crystallinity, with faster end-group diffusion and chain extension than those of other crystallinities, are desirable to obtain high molecular weight BPA-PC by SSP. Accordingly, the crystallization condition of 100 °C, 15 MPa and 6 h was chosen as the optimum to produce prepolymers of medium crystallinity used in subsequent SSP process.

Table 1. Intrinsic viscosity and viscosity average molecular weight of BPA-PC under different $scCO_2$-induced crystallization conditions after SSP of 210 °C and 9 h under vacuum

Crystallization condition	Temperature (°C)				Pressure (MPa)				Time (h)				
	80	100	120	140	5	10	15	20	2	4	6	8	10
Intrinsic viscosity (dL/g)	0.54	0.59	0.53	0.52	0.55	0.57	0.59	0.55	0.53	0.55	0.59	0.56	0.55
M_η (× 10^4 g/mol)	2.5	2.8	2.4	2.3	2.5	2.6	2.8	2.5	2.4	2.5	2.8	2.6	2.5

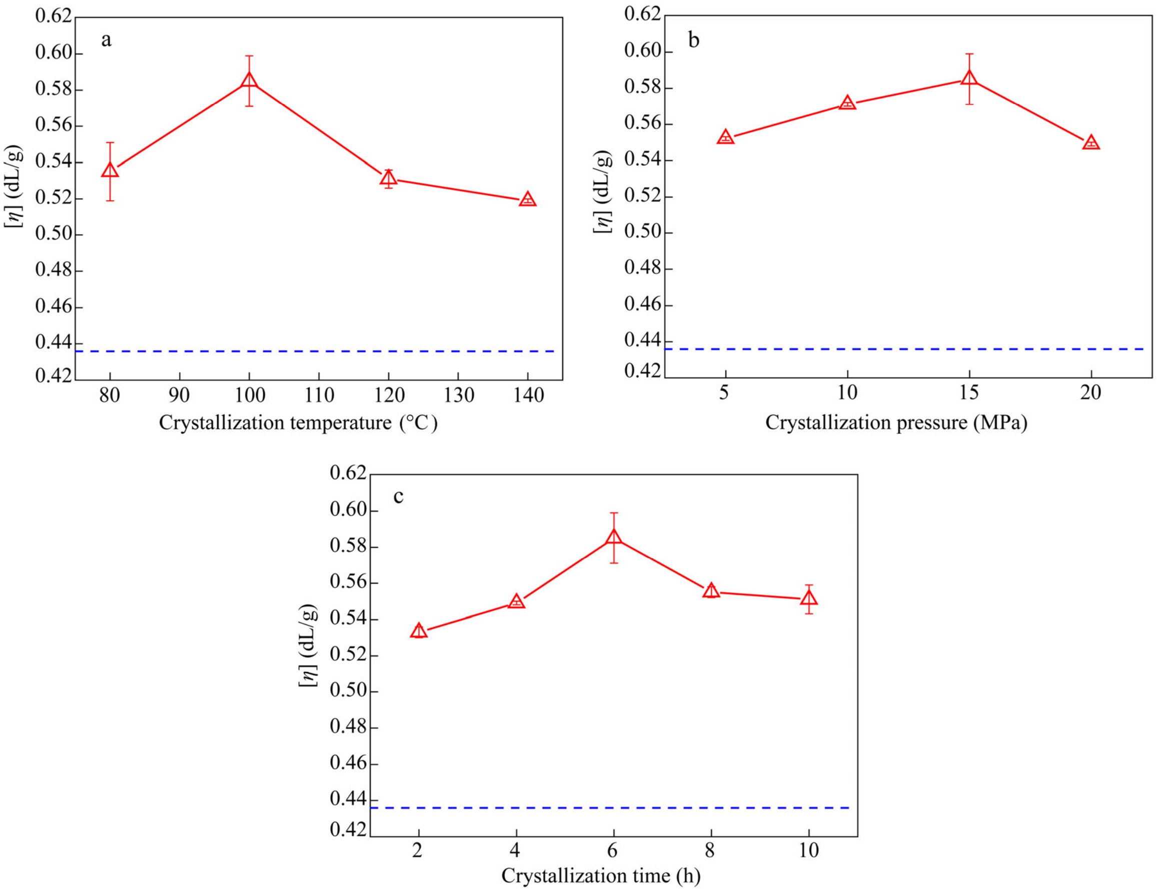

Fig. 2 Variation of intrinsic viscosity of BPA-PC with crystallization temperature (a), pressure (b) and time (c) of $scCO_2$-induced crystallization after SSP of 210 °C and 9 h under vacuum
The dash line in the bottom represents the initial intrinsic viscosity (0.43 dL/g) of prepolymer before SSP.

Reaction Kinetics of Solid-State Polymerization of BPA-PC

Initially, the amorphous BPA-PC prepolymer particles with a M_η of 1.9 × 10^4 g/mol were rendered 15% crystalline with a T_m of 221.6 °C in $scCO_2$. Figure 3 shows the effects of reaction temperature and time on the SSP of BPA-PC. The SSP process was allowed to run at various reaction temperatures from 200 °C to 220 °C for a specific period of time from 3 h to 12 h, and the corresponding M_η of samples obtained under the conditions mentioned above are presented in Table 2. At 210 and 220 °C, the intrinsic viscosity increases sharply during the previous 9 h of reaction and appears to decline afterwards. However, the intrinsic viscosity increases only marginally at 200 °C. This is probably because rapid end-group diffusion and chain extension could not be induced by the reaction temperature that is not high enough[26]. At each temperature, the intrinsic viscosity of the polymer synthesized for 9 h is higher than those of the polymers synthesized for other reaction periods. It can be seen that a greater degree of polymerization occurs at 210 °C and 9 h, where the intrinsic viscosity increases substantially from 0.43 dL/g to 0.59 dL/g, and the M_η increases from 1.9 × 10^4 g/mol to 2.8 × 10^4 g/mol accordingly. For the samples polymerized at 200 and 220 °C, the intrinsic viscosity maximizes to 0.465 and

0.534 dL/g, respectively. Additionally, it is disadvantageous to work at higher temperature or longer time because the side reactions that lead to chain degradation, catalyst activity reduction and color body formation should occur at and above 220 °C or 12 h. At 230 and 240 °C, the M_η increase merely to 2.3×10^4 g/mol and 2.2×10^4 g/mol after 9 h of SSP time, respectively, clearly inferior to that of the sample obtained at 210 °C. As a result, the SSP condition of 210 °C and 9 h was used to produce the final product of BPA-PC with high molecular weight for the following performance tests.

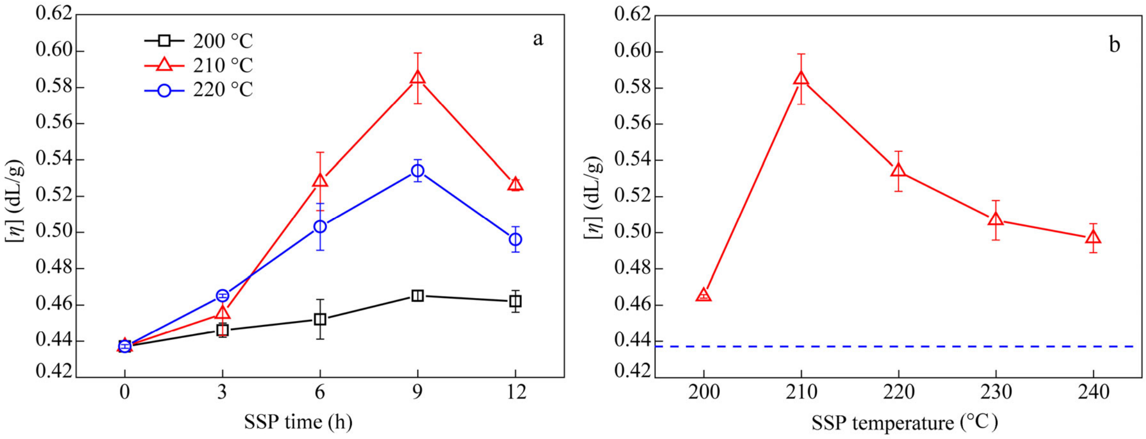

Fig. 3 Variation of intrinsic viscosity of solid-state polymerized BPA-PC with (a) SSP time at various temperatures of 200, 210 and 220 °C, and (b) SSP temperature for the reaction period of 9 h
The dash line in the bottom represents the initial intrinsic viscosity (0.43 dL/g) of prepolymer before SSP.

Table 2. Viscosity average molecular weight ($\times 10^4$ g/mol) of BPA-PC at different SSP temperatures

SSP time (h)	M_η ($\times 10^4$ g/mol)		
	T_{ssp} = 200 °C	T_{ssp} = 210 °C	T_{ssp} = 220 °C
0	1.9	1.9	1.9
3	1.9	2.0	2.0
6	2.0	2.5	2.3
9	2.0	2.8	2.4
12	2.0	2.4	2.2

Molecular weight distribution can directly reflect the degree of polymerization and degradation during SSP of BPA-PC, and can be tested by GPC. In Fig. 4, the polydispersity indexes of BPA-PC particles after SSP are shown as a function of time and temperature under the same reaction conditions stated above, and always maintain below 2.0. It is interesting to find that the plots in Fig. 4 exhibit the same variation trend as those in Fig. 3, indicating that polydispersity index increases with the increasing polymerization reaction degree. This is because the phenol diffusion from the surface is faster than that from the interior, leading to the formation of polymer chains with higher molecular weight on the surface of particles. However, polymer chains degrade after the polymerization reaction temperature and time reaching a certain degree, resulting in a decrease in polydispersity index.

Thermal Stability and Mechanical Properties of Solid-State Polymerized BPA-PC

Solid-state polymerization has been found to significantly increase the thermal stability of BPA-PC due to the restriction of polymer chains mobility affected by the high molecular weight. Improvement of the thermal stability of the sample named PC-1 was characterized by TGA. PC-1 was rendered 15% crystalline in $scCO_2$ under the condition of 100 °C, 15 MPa and 6 h, and its M_η increased from 1.9×10^4 g/mol to 2.8×10^4 g/mol after SSP of 210 °C and 9 h under vacuum. PC-2, synthesized by melt transesterification reaction, has the same molecular weight as the solid-state polymerized PC-1 as determined by Ubbelohde viscosity method. TGA curves for PC-1 before and after SSP as well as that of PC-2 are shown in Fig. 5. The thermal degradation temperature (T_d, at 5% weight loss) of PC-1 prepolymer occurs at 448 °C. It is very interesting to find that SSP causes a shift of T_d toward higher temperature (almost 30 K), that is, the T_d of PC-1 after SSP reaches 477 °C. More notably, the T_d of PC-1 after SSP is much higher than that of PC-2 (461 °C). In other words, the thermal stability of BPA-PC can be significantly improved after SSP. The enhanced resistance of degradation can be ascribed to the substantial increase in molecular weight as well as the avoidance of undergoing high temperature during polymerization.

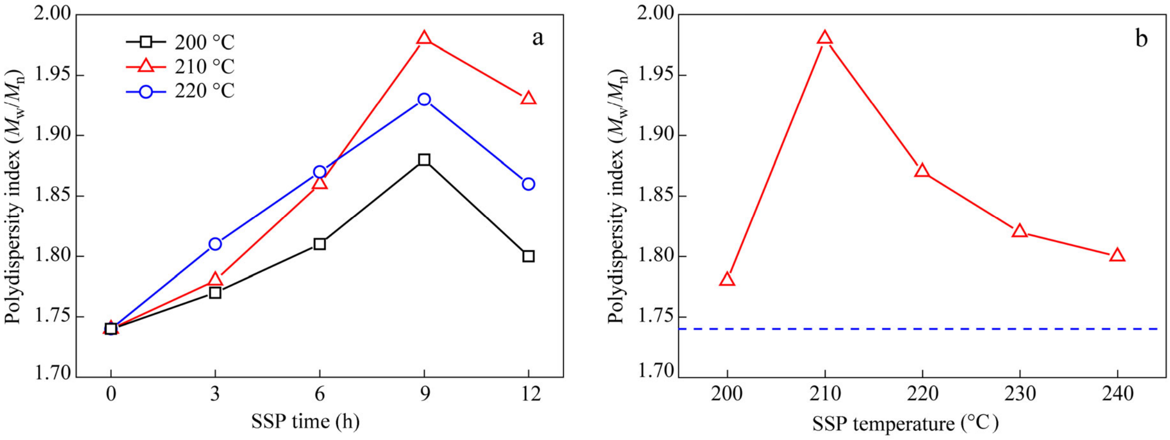

Fig. 4 Variation of polydispersity index of solid-state polymerized BPA-PC with (a) SSP time at various temperatures of 200, 210 and 220 °C, and (b) SSP temperature for the reaction period of 9 h
The dash line in the bottom represents the initial intrinsic viscosity (0.43 dL/g) of prepolymer before SSP.

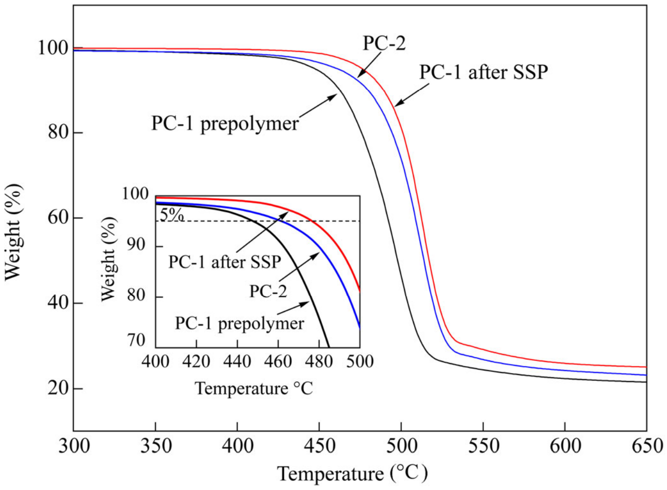

Fig. 5 Comparison of TGA thermograms of PC-1 prepolymer (1.9 × 10^4 g/mol), solid-state polymerized PC-1 (2.8 × 10^4 g/mol) and melt transesterification polymerized PC-2 (2.8 × 10^4 g/mol)
The TGA thermograms are partially enlarged in the inset, where a fuzzy area becomes more visible.

In order to investigate the effect of SSP on mechanical properties of BPA-PC, both tensile and impact tests were applied. Figure 6(a) shows the typical stress-strain curves of PC-1 before and after SSP as well as that of PC-2. Compared with PC-1 prepolymer and PC-2, solid-state polymerized PC-1 shows a remarkable increase in yield strength and elongation-at-break associated with increasing strain. The impact strength of the samples was calculated and plotted in Fig. 6(b). Obviously, the impact strength of PC-1 after SSP is much higher than those of PC-1 prepolymer and PC-2. Solid-state polymerization effectually improves the Young's modulus, tensile strength, elongation-at-break and impact strength, and the results are summarized in Table 3. As for PC-1, the elongation-at-break increases sharply from 38.98% ± 10.95% to 99.38% ± 9.98%, and the impact strength increases markedly from (22.05 ± 3.70) kJ/m^2 to (44.75 ± 3.30) kJ/m^2 after SSP, where more than 2.5-fold and 2-fold improvements have been achieved, respectively. The values of yield strength and Young's modulus of PC-1 after SSP are also enhanced to a certain extent. Clearly, the mechanical properties of PC-1 after SSP are superior to those of PC-2 to various degrees. In general, the mechanical properties of BPA-PC can be remarkably improved after SSP. The enhancements of mechanical properties arise from the same reason as that of the significantly improved thermal stability of BPA-PC, that is, the substantial increase in molecular weight as well as the avoidance of undergoing high temperature during polymerization.

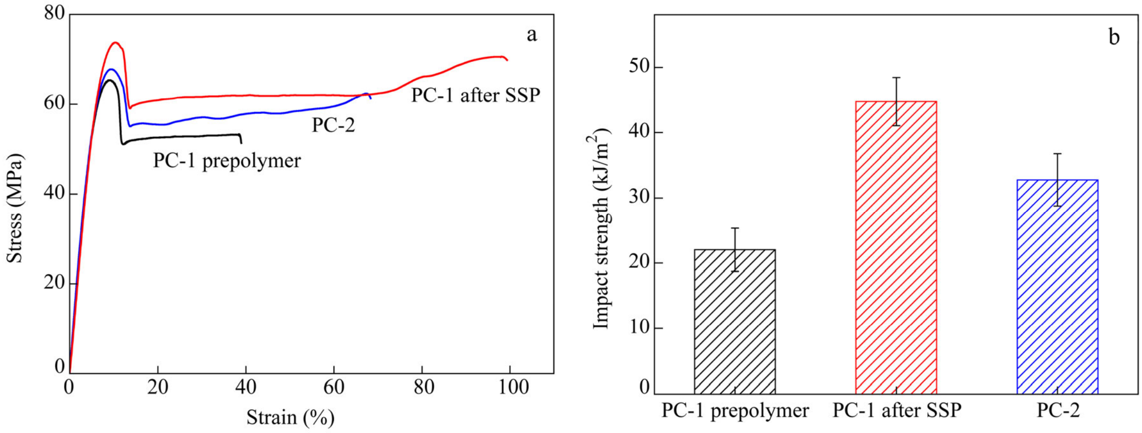

Fig. 6 Comparison of stress-strain curves (a) and impact strength (b) of PC-1 prepolymer (1.9 × 10^4 g/mol), solid-state polymerized PC-1 (2.8 × 10^4 g/mol) and melt transesterification polymerized PC-2 (2.8 × 10^4 g/mol)
The tensile and impact tests are carried out at room temperature

Table 3. Mechanical properties from tensile and impact tests of PC-1 prepolymer (1.9 × 10^4 g/mol), solid-state polymerized PC-1 (2.8 × 10^4 g/mol) and melt transesterification polymerized PC-2 (2.8 × 10^4 g/mol)

Sample	Young's modulus (MPa)	Yield strength (MPa)	Elongation-at-break (%)	Impact strength (kJ/m^2)
PC-1 prepolymer	1020 ± 16	65.4 ± 2	39.0 ± 11.0	22.1 ± 3.7
PC-1 after SSP	1280 ± 24	73.7 ± 2	99.4 ± 10.0	44.8 ± 3.3
PC-2	1247 ± 13	67.8 ± 3	68.4 ± 11.5	32.8 ± 4.2

It is worth mentioning that the BPA-PC sample maintained excellent transparency that could be applied to optical applications. Although the BPA-PC prepolymer crystallized in $scCO_2$ became opaque due to the limited crystallinity and foaming, the high molecular weight BPA-PC after SSP was heated when processed and then the crystals melted. Moreover, the discoloration of BPA-PC was avoided via SSP for the reason that the sample was polymerized without undergoing high temperature that leads to side reactions. As a result, the solid-state polymerization has little or no influence on the transparency of BPA-PC.

CONCLUSIONS

In summary, high molecular weight BPA-PC with excellent thermal stability and mechanical properties is successfully obtained *via* solid-state polymerization after supercritical CO_2-induced crystallization. The crystallization condition of 100 °C, 15 MPa and 6 h is chosen as the optimum to produce prepolymers of medium crystallinity (~15%) that have faster end-group diffusion and chain extension to obtain high molecular weight BPA-PC during subsequent SSP process. Especially, SSP of BPA-PC at the condition of 210 °C and 9 h under vacuum results in a high molecular weight (increased M_η from 1.9 × 10^4 g/mol to 2.8 × 10^4 g/mol) as well as a narrow molecular weight distribution (maintaining below 2.0). More notably, thermal stability and mechanical properties of BPA-PC are significantly improved after SSP, compared with those of melt transesterification polymerized BPA-PC with the same molecular weight, for the reason that the sample was polymerized without undergoing high temperature that leads to side reactions. Our work could provide guidance for obtaining the final product of BPA-PC with high quality and high molecular weight.

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