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The cooling crystallization processes of 1,2-diphenylethane in the MSMPR crystallizer

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ABSTRACT

1,2-Diphenylethane can be widely used in organic synthesis field because of its particular molecular structure. In order to gain high pure 1,2-diphenylethane, the mainly conventional purification method is vacuum distillation. However, the vacuum distillation exhausts excessive energy, needs heavy tower equipment, and it is not easy to achieve high pure product. To obtain high pure 1,2-diphenylethane, save money, and conserve energy, the cooling crystallization with ethanol is used to purify 1,2-diphenylethane. Firstly, the impact of crystallization temperature, crystal growing time, cooling rate, stirring speed, seed size, and seed weight on the cooling crystallization processes of 1,2-diphenylethane in ethanol were investigated. Then, the orthogonal experiment were also studied. It provides a reference for industrial cooling crystallization of 1,2-diphenylethane.

Keywords: 1,2-Diphenylethane; Cooling crystallization; MSMPR crystallizer; Ethanol; Solubility; Orthogonal experiment

1. Introduction

1,2-Diphenylethane ($C_{14}H_{14}$; Molecular Weight 182.26; Melting Point 52°C; Boiling Point 284°C; CAS Registry No. 103-29-7; Fig. 1) is well-known as an important aromatic chemical compound that can be considered a derivative of ethane in which one ethyl connects two benzene rings. 1,2-Diphenylethane has drawn tremendous attention from researchers working in organic synthesis field, especially, in modern drug synthesis field because of its particular molecular structure [1–3].

1,2-Diphenylethane is liable to undergo dehydrogenation, substitution, oxidation, and sulfonation reactions, etc. Thus, it is usually taken as an significant intermediate of organic synthesis. For example, it can be widely used for synthesizing the flame retardant 1,2-BIS(pentabromophenyl) ethane, fluorescent brightening agents, and forming the central core of some stilbenoid natural products and isoquinoline alkaloids, etc [4,5]. In the recent years, the chemical industry is starved of high pure 1,2-diphenylethane despite the lack of high pure product. In chemical industry, the purity of raw 1,2-diphenylethane is mostly below 98.5%. In order to purify the raw 1,2-diphenylethane, the mainly conventional purification method is vacuum distillation. However, the conventional vacuum distillation separation method of 1,2-diphenylethane is not absolutely perfect. For instance, the vacuum distillation exhausts excessive energy, needs heavy tower equipment, and it is not easy to achieve high pure product. To obtain high pure 1,2-diphenylethane, save money, and conserve energy, the cooling crystallization with ethanol is used to purify 1,2-diphenylethane. Ethanol as a cheap, accessible, and environmental friendly solvent, it can be easily used in the cooling crystallization processes of 1,2-diphenylethane. Until recently, few attempts have been done on cooling crystallization of 1,2-diphenylethane using ethanol. Hence it is quite essential to study the cooling crystallization processes of 1,2-diphenylethane with ethanol. Product, crystal growing rate, particle size distribution and mean size of particle

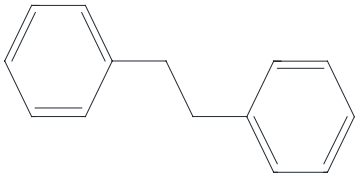

Fig. 1. Chemical structure of 1,2-diphenylethane.

group are the significant aspects during cooling crystallization of 1,2-diphenylethane. Therefore, the main emphasis of the researchers are placed on the product, crystal growing rate, particle size distribution and mean size of particle group. First of all, the solubilities of 1,2-diphenylethane in ethanol at different temperature were investigated. Then, the impact of several factors such as crystallization temperature, crystal growing time, cooling rate, stirring speed, seed size, and seed weight on crystallization processes of 1,2-diphenylethane were also studied. Finally, the orthogonal experiments of cooling crystallization were designed for the optimal scheme and the XRD analysis of material and product were also done. It can provide a reference for industrial cooling crystallization of 1,2-diphenylethane.

2. Experimental section

2.1. Materials and instruments

The materials and instruments are listed in Tables 1–2. 1,2-Diphenylethane (purity ≥ 99.9%) was purchased from Aladdin Chemistry Co., Ltd., (Shanghai, China) and ethanol (purity ≥ 99.7%) was obtained from Sinopharm Chemical Reagent Co., Ltd. The super thermostatic bath (accuracy: 0.01°C) was manufactured by Shanghai Fang Rui Instrument Co., Ltd., (China). The digital electric agitator was purchased from Changzhou Nuo Ji Instrument Co., Ltd., (China). The circulating water vacuum pump (maximal vacuum degree: 0.098 MPa) was supplied by Shanghai Hao Zhuang Instrument Co., Ltd., (China). The drying box (temperature range: RT+10~250°C) was given by Tianjin Test Instrument Co., Ltd., China. The standard test sieve (14~200 mesh) was produced by Zhejiang Shangyu City Dao Xu Zhang Xing Yarn Screen Factory, (China). The magnetic agitator (rotational speed range: 0~1,200 rpm) was purchased from Shanghai Modern Instrument Co., Ltd., China. The electronic analytical balance (accuracy: 0.1 mg) is from Shanghai Zan Wei Weighing Apparatus Co., Ltd., (China). The mixed suspension-mixed product-removal (MSMPR) crystallizer and jacketed vessel were self-products.

2.2. Measurement of solubility

The static equilibrium method [6–15] was adopted to measure the solubilities of 1,2-diphenylethane at the temperature range from 286.15 K to 298.15 K under atmospheric pressure in the ethanol. The schematic diagram of determining solubilities of 1,2-diphenylethane is shown in Fig. 2, which could be briefly described as follows. At the beginning, excess amount of 1,2-diphenylethane and 30 mL ethanol were added into the jacketed glass vessel with capacity of 100 mL. Between the inner and outer of walls of the vessel was filled by circulation coolant from a super thermostatic bath. The temperature was controlled by the super thermostatic bath and its fluctuation was within 0.01°C. Later, a magnetic stirred bar was put in the inner space of the jacketed glass vessel in order to accelerate dissolution of 1,2-diphenylethane. Then, a

Table 1
Details of the reagents used in the paper

Chemical name	CAS RN	Formula	MW	Mass fraction purity	Source
1,2-Diphenylethane	103-29-7	$C_{14}H_{14}$	182.26	≥99.9%	Aladdin Chemistry Co., Ltd., (Shanghai, China)
Ethanol	64-17-5	CH_3CH_2OH	46.07	≥99.7%	Sinopharm Chemical Reagent Co., Ltd.

Table 2
Details of the experiment instruments used in the paper

Instruments	Pattern	Producer
Super thermostatic bath	DC1006	Shanghai Fang Rui Instrument Co., Ltd., (China)
Digital electric agitator	EUMIX-R30	Changzhou Nuo Ji Instrument Co., Ltd., (China)
Circulating water vacuum pump	SHB-III	Shanghai Hao Zhuang Instrument Co., Ltd., (China)
Drying box	101-OAB	Tianjin Test Instrument Co., Ltd., (China)
Standard test sieve	Sieve mesh number: 14~200	Zhejiang Shangyu City Dao Xu Zhang Xing Yarn Screen Factory, (China)
MSMPR crystallizer	250 mL	Self-product
Magnetic agitator	JK-DMS-ProNI	Shanghai Modern Instrument Co., Ltd., (China)
Jacketed vessel	100 mL	Self-product
Electronic analytical balance	ZA22OR4	Shanghai Zan Wei Weighing Apparatus Co., Ltd., (China)

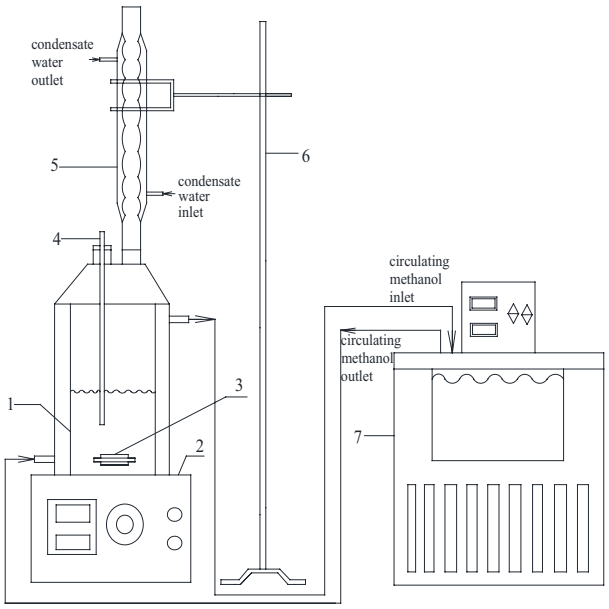

Fig. 2. Schematic diagram of determining solubility of 1,2-diphenylethane. (1) Jacketed vessel, (2) magnetic stirrer, (3) stir bar, (4) thermometer, (5) condenser, (6) iron support, (7) super thermostatic bath.

condenser was inserted in the hole which is in the top of the vessel for the sake of preventing evaporation of the solvent, and the thermometer was also inserted into the liquid for indicating the temperature of solution. When all the devices were set well, the experiment could be carried out and the stirring was kept for 12 h at the fixed temperature. Once the solid-liquid equilibrium was obtained, the magnetic stirrer was stopped and the system was kept static for 2 h to allow the undissolved particles to settle down. Followingly, the upper saturated solutions were drained by the dropper, passed through the sintered-glass filter and rapidly diverted into the ampoule. Finally, the 1,2-diphenylethane saturated solutions in the ampoule was absorbed by sampling probe for mass fraction analysis. The mass fraction was analyzed by Agilent Gas Chramotography (Agilent 7000D). The capillary column was HP-5 with the size of 30 m × 0.32 mm × 0.25 μm. The temperature of inlet was 280°C and the temperature of vaporizing chamber is 290°C. The temperature of connection tube was 280°C. The injection volume was 0.1 μL. The carrier gas was high pure nitrogen. All the experimental point at a certain temperature were repeated in parallel at least three times and the mean values were used to calculate the mole fraction solubility (x_1) expressed as follows.

$$x_1 = \frac{w_1 / M_1}{w_1 / M_1 + w_2 / M_2} \tag{1}$$

where w_1 and w_2 are the mass fraction of 1,2-diphenylethane and ethanol in the solution respectively, M_1 and M_2 are the molecular weight of 1,2-diphenylethane and ethanol respectively.

2.3. Cooling crystallization process

As shown in Fig. 3, the cooling crystallization equipment of 1,2-diphenylethane consisted of super thermostatic bath, MSMPR crystallizer, mechanical agitator, thermometer, motor, and iron support and so on. Initially, the super thermostatic bath was started and the required temperature was also set. When the required temperature was reached, 30 mL saturated solution was prepared immediately in the MSMPR crystallizer. Then, the seed crystals were added into the crystallizer, the mechanical agitator was started, and the cooling temperature was decreased at specific constant rate slowly until it was reached the certain temperature. Thirdly, the constant temperature was kept for several hours. After crystallization, the crystallized slurry was filtered by Buchner funnel at negative pressure and the crystals were washed twice by a little acetone. Finally, the crystals were dried for several hours at 35°C in the drying box.

2.4. Analysis of particle size

The particle size distribution of 1,2-diphenylethane were measured by Tyler Sieve Analysis Method [16]. The average size of particles between the two screens were calculated by arithmetic mean sieve mesh size of the lower and upper screens.

$$d_{pi} = \frac{d_{i-1} + d_i}{2} \tag{2}$$

where d_{pi} is the average size of particles between the two screens, d_{i-1}, d_i are the sieve mesh size of the upper and lower screen, respectively.

The mean size of particle group was calculated by the following equation.

$$\bar{d} = \sum d_{pi} x_i \tag{3}$$

where [Inline Equation] is the mean size of particle group, x_i was the mass fraction of particles in every classification area.

2.5. Crystal growing time and crystal growing rate

The crystal growing time t is defined as:

$$t = t_1 - t_2 \tag{4}$$

where t_1 is the time at which crystallization process is just over; t_2 is the time at which the cooling temperature is decreased to the constant temperature.

The crystal growth rate G is defined as:

$$G = \frac{\Delta m}{(t_1 - t_3)V} \tag{5}$$

where Δm is the mass difference between the product and seed, t_1 is the time at which crystallization process is just over, t_3 is the time at which the seed crystals were added into saturated solution, V is the volume of solution.

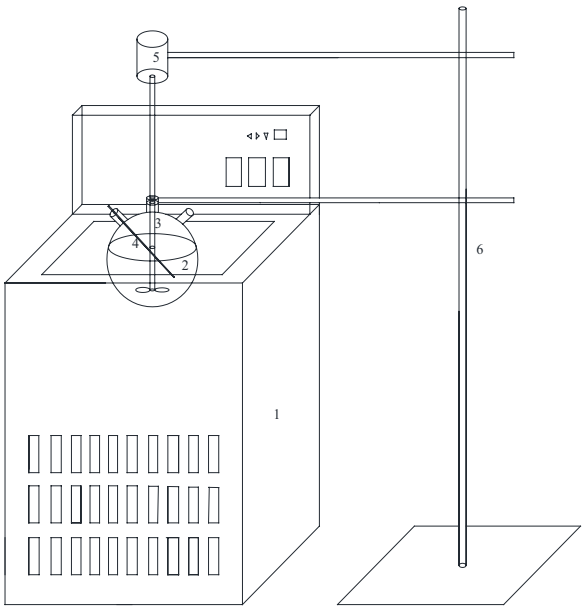

Fig. 3. The crystallization process of 1,2-diphenylethane. (1) Super thermostatic bath, (2) MSMPR crystallizer, (3) mechanical agitator, (4) thermometer, (5) motor, (6) iron support.

3. Results and discussion

3.1. Solubility data

The solubility data of 1,2-diphenylethane in pure ethanol from 286.15 K to 298.15 K (p = 101.3 k Pa) are listed in Table 3. T is the thermodynamic temperature, S is the mass solubility, x_1 is the mole fraction solubility. It can be seen that the mass solubility increases from 10.8316 g/(100 g C_2H_5OH) to 18.9312 g/(100g C_2H_5OH) with the temperature range from 286.15 to 298.15 K under atmospheric pressure. The temperature increases per Kelvin, the average increase of mass solubility of 1,2-diphenylethane is 0.675 g. At the same time, the mole fraction solubility increases from 0.0266 to 0.0457 with the temperature range from 286.15 to 298.15 K. The temperature increases per degree Kelvin, the average increase of mole fraction solubility of 1,2-diphenylethane is 0.0016. The solubility of 1,2-diphenylethane in ethanol is sensitive to the temperature and it indicates that the pure crystals of 1,2-diphenylethane can be easily separated from the over saturated solution through cooling crystallization.

Table 3
Solubility of 1,2-diphenylethane in pure ethanol from 286.15 to 298.15 K (p = 101.3 kPa)

T (K)	S (g/(100 g·C_2H_5OH))	10^2x_1
286.15	10.8316	2.66
287.15	11.4954	2.82
288.15	12.3278	3.02
289.15	12.8118	3.14
290.15	14.0333	3.43
291.15	14.4325	3.52
292.15	14.6633	3.57
293.15	14.8405	3.62
294.15	14.8903	3.63
295.15	14.9890	3.65
296.15	15.0865	3.67
297.15	17.5831	4.26
298.15	18.9312	4.57

3.2. Impact of crystallization temperature on 1,2-diphenylethane

The impact of crystallization temperature on 1,2-diphenylethane are presented in Fig. 4a–c. The experimental conditions are that the temperature of saturated solution is 25°C, the stirring speed is 150 rpm, the cooling rate is 0.5°C min^{-1}, the seed size is 1,015 μm, the mass of seed is 2.0 g, and the crystal growing time is 30 min. It can be clearly seen from Fig. 4a–c that the product of 1,2-diphenylethane decreases quickly from 4.49 to 3.74 g with increasing crystallization temperature from 7°C to 15°C. Meanwhile, the crystal growing rate of 1,2-diphenylethane gradually reduces from 75.54 to 69.44 kg m^{-3} h^{-1} with increasing crystallization temperature from 7°C to 15°C. The highest product and crystal growing rate of 1,2-diphenylethane are 4.49 g and 75.54 kg m^{-3} h^{-1} respectively at the crystallization temperature of 7°C. Furthermore, the particle size distribution of 1,2-diphenylethane are in the range from 116 to 1,015 μm and the crystals of 303–1,015 μm at different crystallization temperature account for more than 84.2% of the total products. At crystallization temperature of 7°C, the crystals of 303–1,015 μm occupy the largest proportion of 92.0%. The mean size of particle group keeps for 544–636 μm and the maximum mean size of particle group is 636 μm at the crystallization temperature of 11°C. In general, it is prone to gain higher product and higher crystal growing rate at the lower crystallization temperature while it is apt to get the larger crystals at the higher crystallization temperature.

The reason is that lower crystallization temperature means faster nucleation rate and higher crystal growing rate. Higher crystal growing rate devotes to high product, and faster nucleation rate leads to lots of small crystals and degrades the mean size of particle group. Consequently, the crystallization temperature plays important roles in the product, the crystal growing rate, the particle size distribution and the mean size of 1,2-diphenylethane particle group.

3.3. Impact of crystal growing time on 1,2-diphenylethane

The impact of crystal growing time on 1,2-diphenylethane are shown in Fig. 5a–c. The experimental conditions are that the temperature of saturated solution is 25°C, crystallization temperature is 7°C, the stirring speed is 150 rpm, the cooling rate is 0.5°C min^{-1}, the seed size is 603 μm, the mass of seed is 2.0 g. From Fig. 5a–c, it can be concluded that the product of 1,2-diphenylethane increases with crystal growing time slowly. The product rises from 4.46 to 4.57 g when the crystal growing time expands from 30 to 150 min. The lowest product is 4.46 g at crystal growing time of 30 min and the highest product is 4.57 g

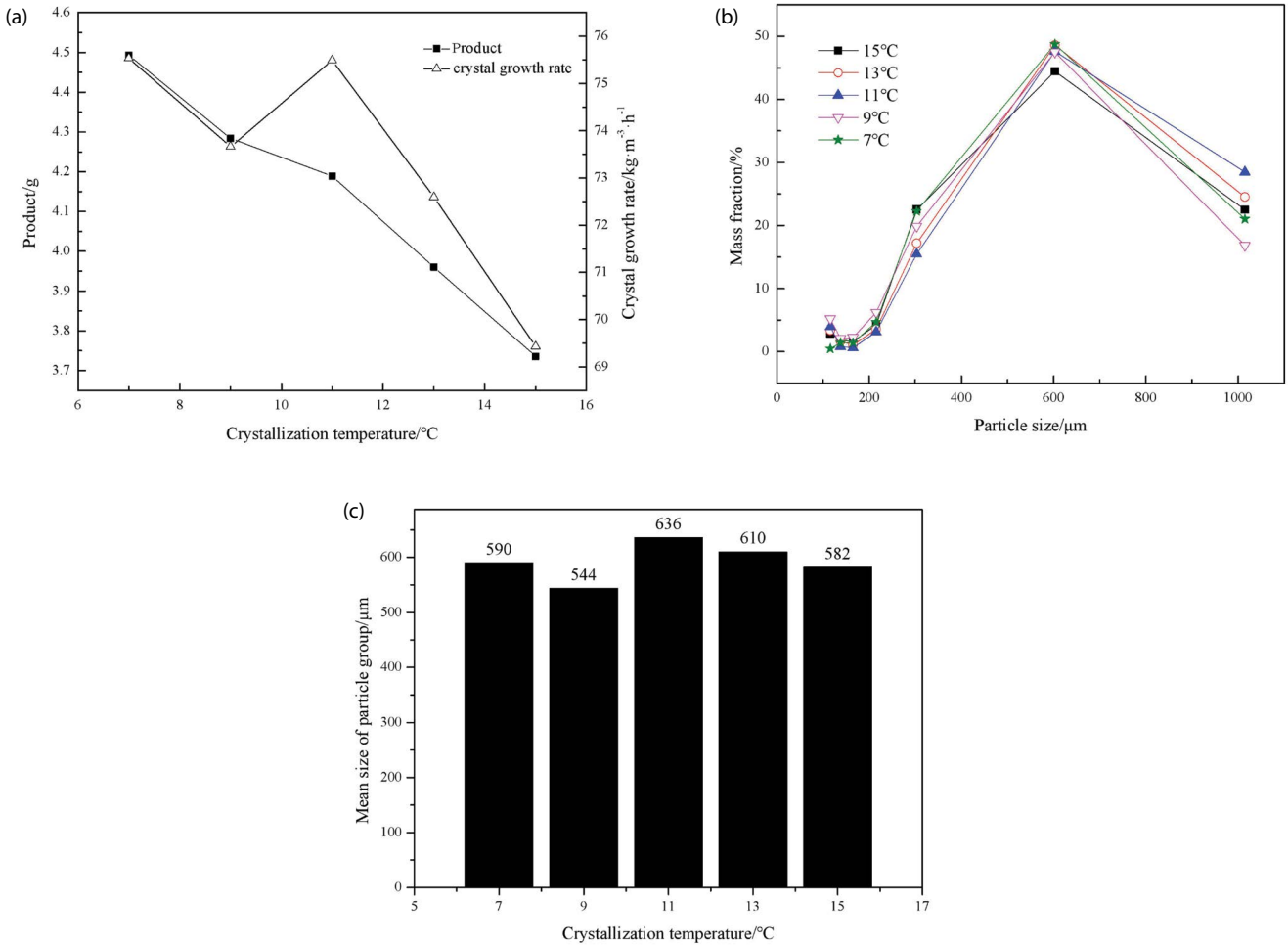

Fig. 4. Impact of crystallization temperature on (a) product and crystal growth rate, (b) particle size distribution, and (c) mean size of 1,2-diphenylethane.

at crystal growing time of 150 min. The crystal growing time goes up by 120 min and the product of 1,2-diphenylethane only increases by 0.11 g. Meanwhile, the crystal growing rate of 1,2-diphenylethane sharply falls from 74.58 to 27.66 kg m^{-3} h^{-1} with crystal growing time expanding 30 to 150 min. Moreover, the particle size distribution is very various according to different crystal growing time. The proportion of crystals of 303–1,015 μm exceeds 58.6% at different crystal growing time and the crystals of 303–1,015 μm occupy the largest proportion of 82.0% at crystal growing time of 60 min. Similarly, the mean size of particle group maintains 303–412 μm and the largest mean size of particle group reaches 412 μm at crystal growing time of 60 min. Generally, in shorter crystal growing time from 30 to 60 min, the higher product, higher crystal growing rate, and larger crystal size of 1,2-diphenylethane can be achieved. That is because when crystal growing time over 30 min, the oversaturation of solution becomes smaller and the increase of crystal is very small through expanding crystal growing time. It is at the cost of degrading the crystal growing rate. Consequently, the crystal growing time has a limited influence on the product of 1,2-diphenylethane but it has great influences on the crystal growing rate, the particle size distribution and the mean size of 1,2-diphenylethane particle group.

3.4. Impact of cooling rate on 1,2-diphenylethane

Fig. 6a–c illustrate the impact of cooling rate on 1,2-diphenylethane. The experimental conditions are that the temperature of saturated solution is 25°C, crystallization temperature is 7°C, the stirring speed is 150 rpm, the crystal growing time is 30 min, the seed size is 603 μm, the mass of seed is 2.0 g. It can be obviously found from Fig. 6a–c that the product of 1,2-diphenylethane climbs with cooling rate gradually at first and then it remains steady. When the cooling rate increases from 0.05 to 0.25°C min^{-1}, the product of 1,2-diphenylethane rises from 4.34 to 4.56 g and the highest product is 4.56 g at the cooling rate of 0.25°C min^{-1}. Meanwhile, the crystal growing rate of 1,2-diphenylethane has the similarly linear increase from 12.01 to 50.29 kg m^{-3} h^{-1} at the cooling rate from 0.05 to 0.25°C min^{-1}. In addition, the particle size distribution is diverse on the basis of different cooling rates. However, the crystals of 303–1,015 μm account for more than 76.6% of the total product and the crystals of 303–1,015 μm occupy the largest proportion of

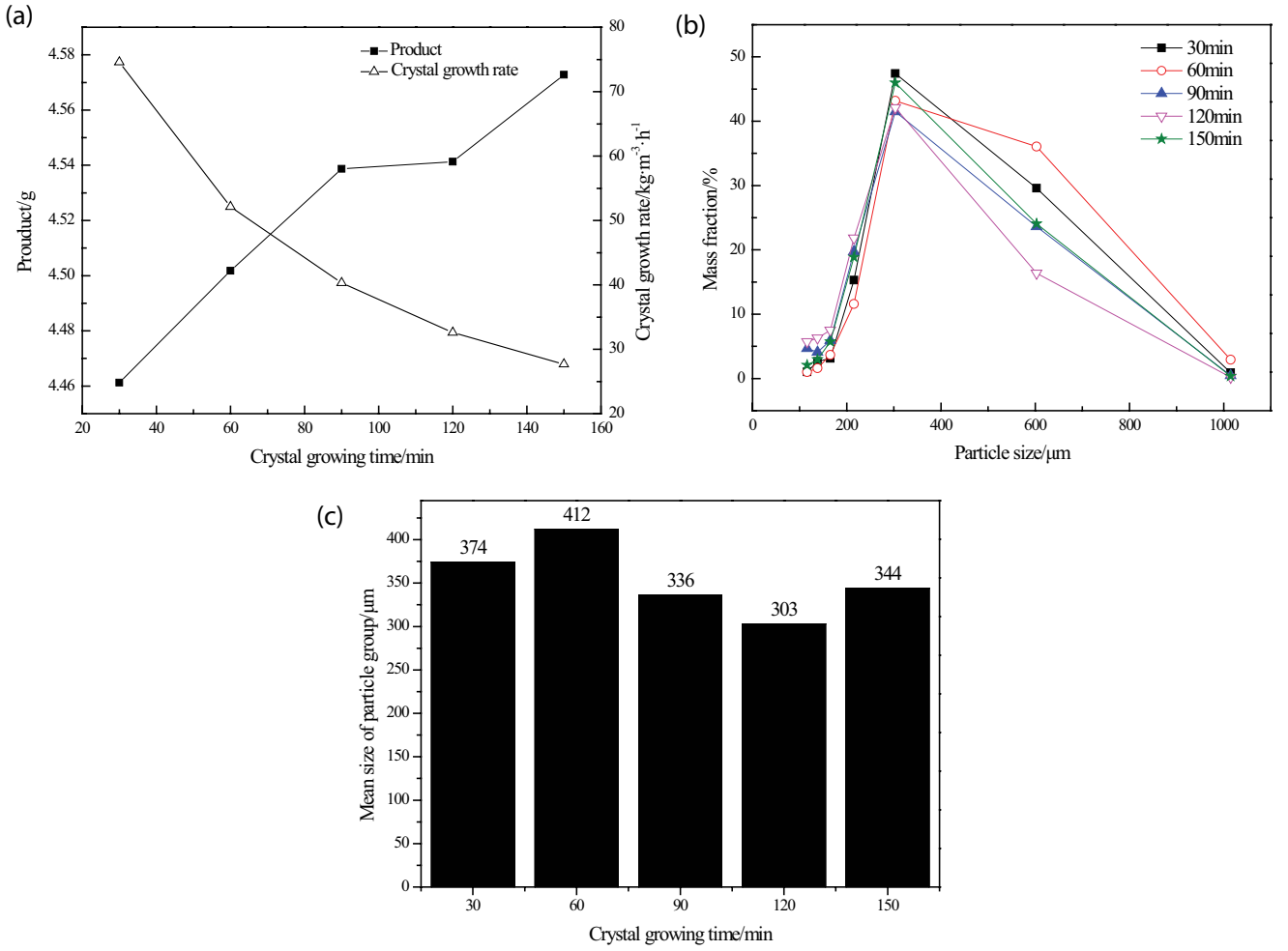

Fig. 5. Impact of crystal growing time on (a) product and crystal growth rate, (b) particle size distribution and (c) mean size of 1,2-diphenylethane.

86.5% at the cooling rate from 0.15°C min^{-1}. The mean size of particle group keeps for 383–494 μm and the maximum mean size of particle group is 494 μm at the cooling rate of 0.20°C min^{-1}. In general, at cooling rate of 0.20°C min^{-1}, it is prone to gain higher product, higher crystal growing rate, and larger crystal size. The reason is that higher cooling rate means that the oversaturation solution is easy to reach specific low temperature earlier and gain faster crystal growing rate. Consequently, the cooling rate plays a limited role in product but it plays vital roles in the crystal growing rate, the particle size distribution, and the mean size of 1,2-diphenylethane particle group.

3.5. Impact of stirring speed on 1,2-diphenylethane

The impact of stirring speed on 1,2-diphenylethane are depicted in Fig. 7a–c. The experimental conditions are that the temperature of saturated solution is 25°C, crystallization temperature is 7°C, the crystal growing time is 30 min, the cooling rate is 0.5°C min^{-1}, the seed size is 603 μm, the mass of seed is 2.0 g. Figs. 7a–7c indicate that the product of 1,2-diphenylethane rises slowly from 4.47 to 4.54 g with stirring speed from 90 to 210 rpm. The product of 1,2-diphenylethane only increases by 0.07 g when the stirring speed goes up by 120 rpm. Meanwhile, the crystal growing rate of 1,2-diphenylethane increases from 74.82 to 77.09 kg m^{-3} h^{-1} with the stirring speed from 90 to 210 rpm. Further, the particle size distribution has a small difference at the stirring speed range from 90 to 210 rpm. The crystals of 303–1,015 μm account for more than 83.4% of the total products and the crystals of 303–1,015 μm occupy the largest proportion of 91.3% at the stirring speed of 180 rpm. The mean size of particle group maintains 471–493 μm and the maximum mean size of particle group is 493 μm at the stirring speed of 150 rpm. In general, at the stirring speed of 150 rpm, the higher product, higher crystal growing rate, and larger crystal size have been realized. It is because that on the one hand, the higher stirring speed is in favour of crystals suspension in the mother liquor and it is good for mass transfer between crystal layer and mother liquor. On the other hand, the higher stirring speed is beneficial to the fragmentation of crystals and it can increase the probability of secondary nucleation. At the stirring speed of 150 rpm, the former occupies the leading

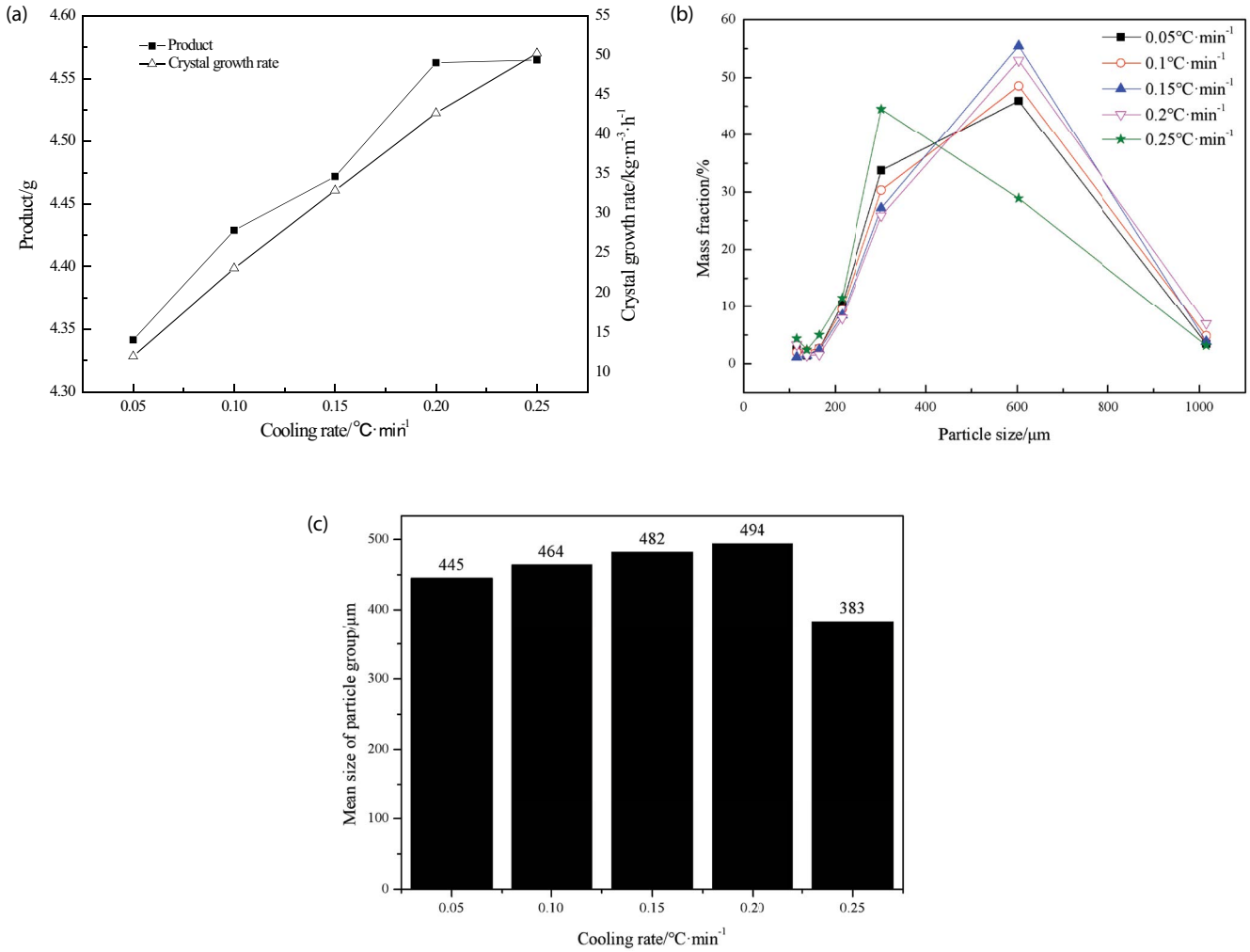

Fig. 6. Impact of cooling rate on (a) product and crystal growth rate, (b) particle size distribution and (c) mean size of 1,2-diphenylethane.

position. Consequently, the stirring speed plays limited roles in the product, the crystal growing rate, the particle size distribution, and the mean size of 1,2-diphenylethane.

3.6. Impact of seed size on 1,2-diphenylethane

The impact of seed size on 1,2-diphenylethane are presented in Fig. 8a–c. The experimental conditions are that the temperature of saturated solution is 25°C, crystallization temperature is 7°C, the crystal growing time is 30 min, the cooling rate is 0.5°C min^{-1}, the stirring speed is 150 rpm, the mass of seed is 2.0 g. As can be seen from Fig. 8a–c, the product of 1,2-diphenylethane increases with seed size firstly, then it decrease with seed size, and thirdly, it increases with seed size again. The lowest product of 1,2-diphenylethane is 4.48 g with the seed size of 165 μm and the highest product of 1,2-diphenylethane is 4.60 g with the seed size of 1,015 μm. The product only rises by 0.12 g when the seed size increases by 850 μm. Meanwhile, the crystal growing rate of 1,2-diphenylethane increases from75.03 to 78.93 kg m^{-3} h^{-1} with the seed size from 165 to 1,015 μm. It can be inferred that the seed size has limited influences on the product and the crystal growing rate of 1,2-diphenylethane. Moreover, the particle size distribution has very distinct differences due to different seed sizes. The crystals of 303–1,015 μm account for more than 66.5% of the total products. The highest proportion of crystals of 303–1,015 μm is 80.6% with the seed size of 603 μm. In general, the mean size of particle group increases gradually with seed size and it rises from 316 to 502 μm with the seed size from 165 to 1,015 μm. The

Table 4
The table of factors and levels of orthogonal experiment of product

Level	Factor *A*	Factor *B*	Factor *C*	Factor *D*
	T (°C)	*l* (μm)	*v* (°C min^{-1})	*n* (r min^{-1})
1	7	1015	0.25	120
2	10	603	0.20	150
3	13	303	0.15	180

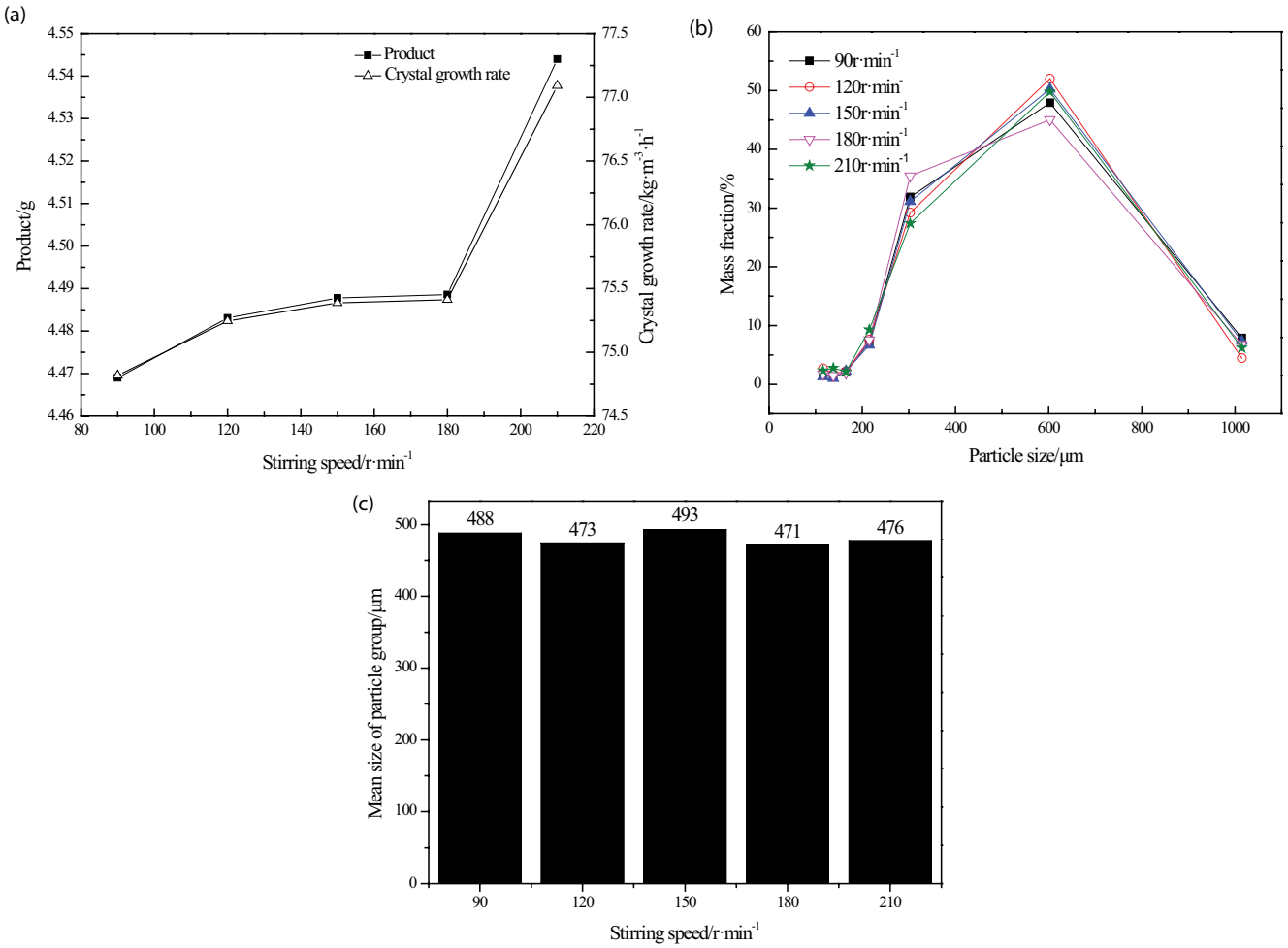

Fig. 7. Impact of stirring speed on (a) product and crystal growth rate, (b) particle size distribution and (c) mean size of 1,2-diphenylethane.

maximum mean size of particle group is 502 μm with the seed size of 1,015 μm. Therefore, the highest product, highest crystal growing rate, and largest crystal size have been realized with the seed size of 1,015 μm. Consequently, the seed size plays limited roles in the product and the crystal growing rate of 1,2-diphenylethane, but it has significant effects on the particle size distribution, and the mean size of 1,2-diphenylethane.

3.7. Impact of seed weight on 1,2-diphenylethane

Fig. 9a–c illustrate the impact of seed weight on 1,2-diphenylethane. The experimental conditions are that the temperature of saturated solution is 25°C, crystallization temperature is 7°C, the crystal growing time is 30 min, the cooling rate is 0.5°C min^{-1}, the stirring speed is 110 rpm, the seed size is 603 μm. It can be clearly seen from Fig. 9a–c that the product of 1,2-diphenylethane increase sharply from 3.58 g to 5.61 g with the seed weight increasing from 1.0 to 3.0 g. Meanwhile, firstly the crystal growing rate of 1,2-diphenylethane increases from78.05 to 82.56 kg m^{-3} h^{-1}, then decreases to 79.22 kg m^{-3} h^{-1}, and finally maintains about 79.20 kg m^{-3} h^{-1}. The highest crystal growing rate of 1,2-diphenylethane is 82.56 kg m^{-3} h^{-1} with the seed weight of 1.5 g. Furthermore, the particle size distribution differs from one seed weight to another and the crystals of 303–1,015 μm account for more than 58.7% of the total products. The proportion of crystals of 303–1,015 μm generally increases with seed weight, and the highest proportion of crystals of 303–1,015 μm is 88.2% when the seed weight reaches 2.0 g. The mean size of particle group increases with the seed weight at first and then decreases slightly with the seed weight. The mean size of particle group varies from 430 to 519 μm and the largest mean size of particle group is 519 μm with the seed weight of 2.5 g. Consequently, the seed weight plays big roles in the product, the crystal growing rate, the particle size distribution, and the mean size of 1,2-diphenylethane.

3.8. Orthogonal experiment

The table of factors and levels of orthogonal experiment of product are listed in Table 4. The four factors such as crystallization temperature (*A*), seed size (*B*), cooling rate

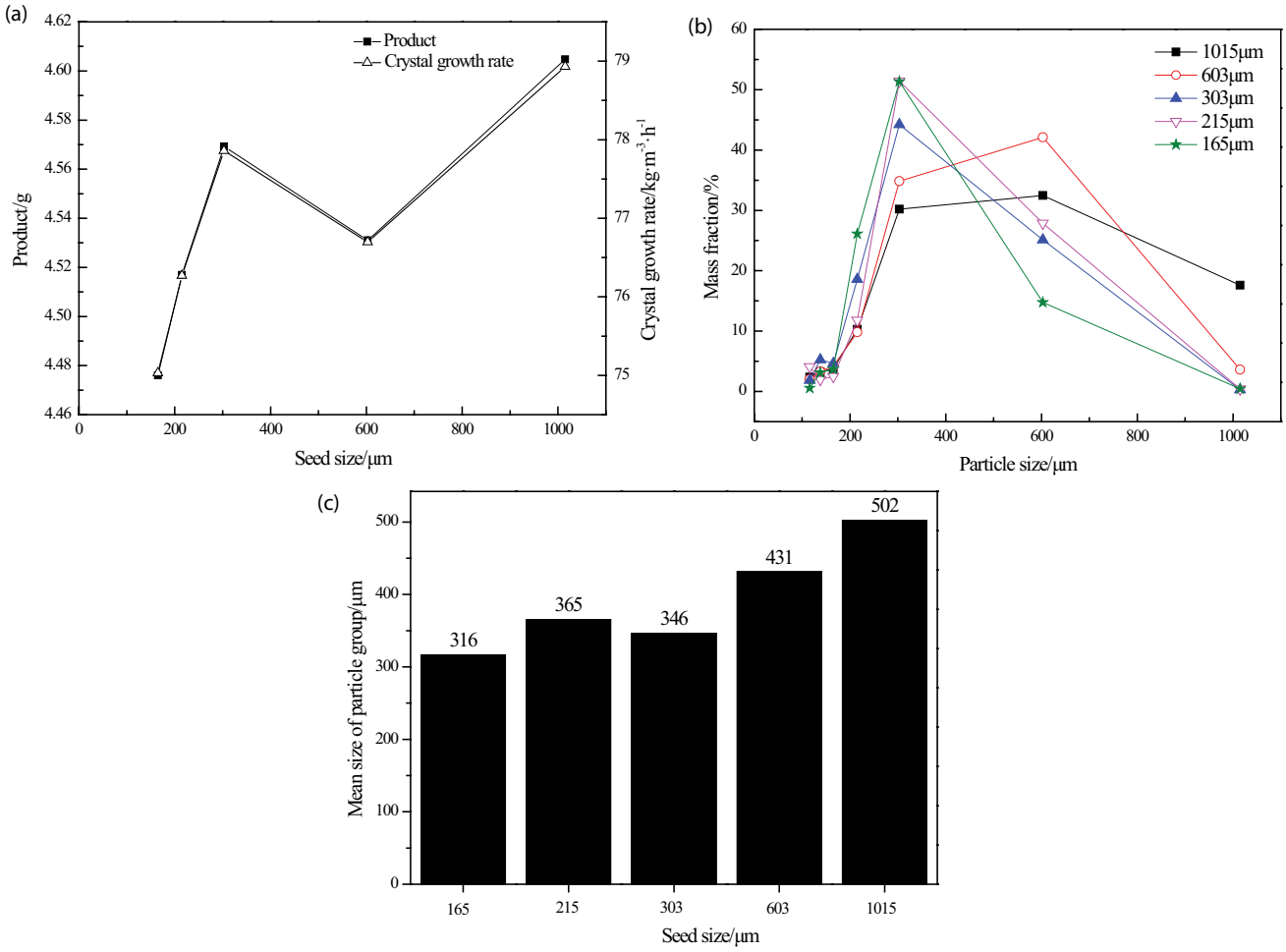

Fig. 8. Impact of seed size on (a) product and crystal growth rate, (b) particle size distribution and (c) mean size of 1,2-diphenylethane.

(*C*), stirring speed (*D*) are adopted and every factor are designed for three levels. The results of orthogonal experiment of product are listed in Table 5. It can be found that the optimal solution is $A_1B_1C_3D_1$. It also means that the optimal crystallization temperature is 7°C, the optimal seed size is 1,015 μm, the optimal cooling rate is 0.15°C min^{-1}and the optimal stirring speed is 120 rpm. The order of importance of factor is crystallization temperature > stirring speed > cooling rate > seed size.

3.9. XRD analysis

The X-ray power diffraction pattern of raw material of 1,2-diphenylethane and 1,2-diphenylethane recrystallized from the ethanol under different conditions are shown in Fig. 10. The curve a is the XRD profile of raw material of 1,2-diphenylethane and curve b, curve c, and curve d are the XRD profiles of 1,2-diphenylethane recrystals under different conditions respectively. It can be seen that the profile a is different from profile b, profile c, and profile d, that is, changes in the peak position and intensity. The profile a and profile b are similar and have no obvious changes. But the profile c, and profile d are quite different from profile a. The change of XRD profiles of 1,2-diphenylethane recrystals indicate that crystal structure have changed through cooling crystallization of 1,2-diphenylethane using ethanol.

3.10. DSC analysis

The DSC of raw material of 1,2-diphenylethane and 1,2-diphenylethane recrystallized from the ethanol under different conditions are shown in Fig. 11. The melting points of raw material of 1,2-diphenylethane and 1,2-diphenylethane recrystallized from the ethanol are in the range of 51.17–51.83°C. The melting point of recrystallized crystals of 1,2-diphenylethane are closer to melting point of pure 1,2-diphenylethane than that of raw material of 1,2-diphenylethane. It indicates that the purity of recrystallized crystals of 1,2-diphenylethane are improved.

4. Conclusions

In conclusions, 1,2-diphenylethane can be easily crystallized from the ethanol solution through cooling crystallization. The crystallization temperature and seed weight play significant roles in the product, crystal

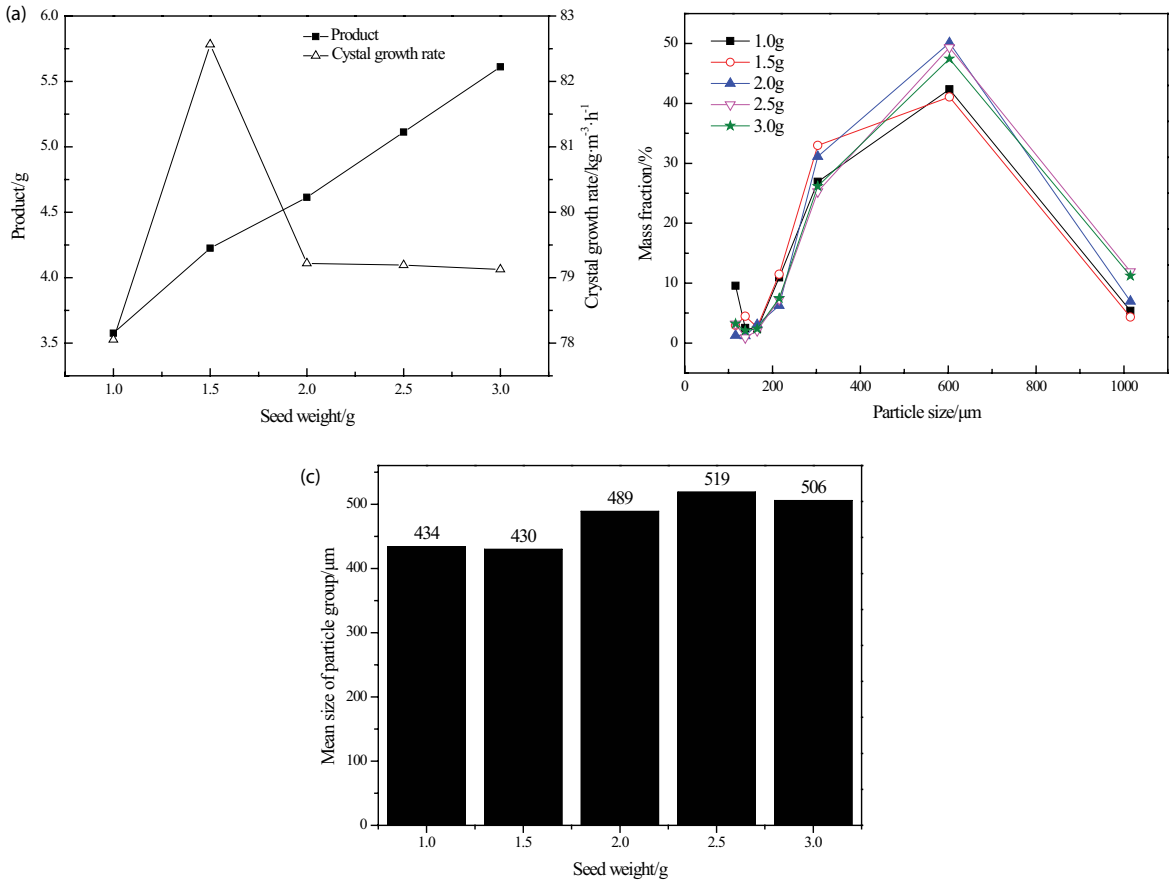

Fig. 9. Impact of seed weight on (a) product and crystal growth rate, (b) particle size distribution and (c) mean size of 1,2-diphenylethane.

Table 5
The results of orthogonal experiment of product

No.	Factors and levels				Product (g)
	A	*B*	*C*	*D*	
1	1	1	1	1	4.5831
2	1	2	2	2	4.5896
3	1	3	3	3	4.5443
4	2	1	2	3	4.2711
5	2	2	3	1	4.3176
6	2	3	1	2	4.2633
7	3	1	3	2	4.1423
8	3	2	1	3	4.0719
9	3	3	2	1	4.1118
K_1	13.717	12.997	12.918	13.013	
K_2	12.852	12.979	12.973	12.995	
K_3	12.326	12.919	13.004	12.887	
k_1	4.5723	4.3322	4.3060	4.3375	
k_2	4.2840	4.3263	4.3242	4.3317	
k_3	4.1087	4.3063	4.3347	4.2957	
R	0.4636	0.0259	0.0287	0.0418	
Order	$A > D > C > B$				
Optimal level	A_1	B_1	C_3	D_1	
Optimal solution	$A_1B_1C_3D_1$				

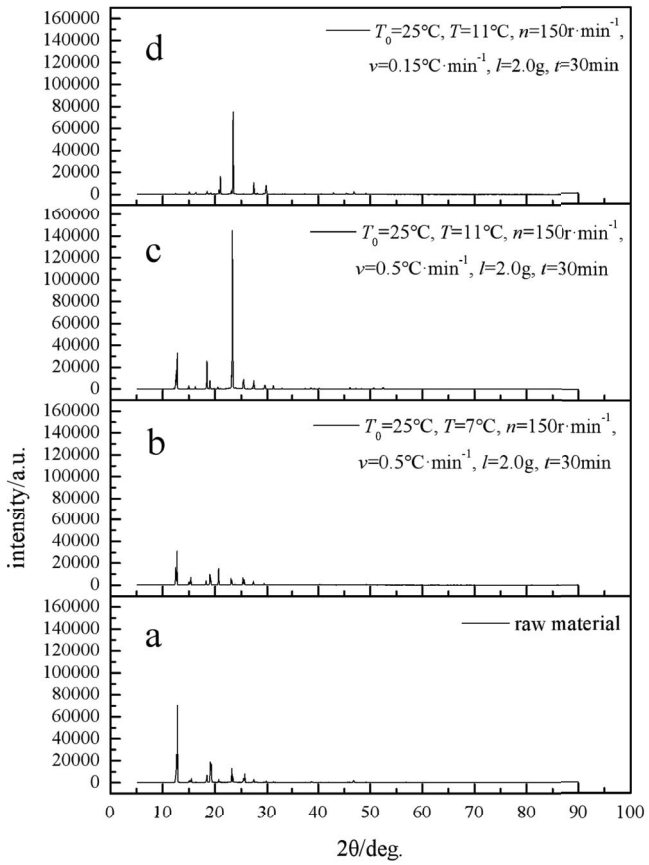

Fig. 10. X-ray power diffraction pattern of 1,2-diphenylethane.

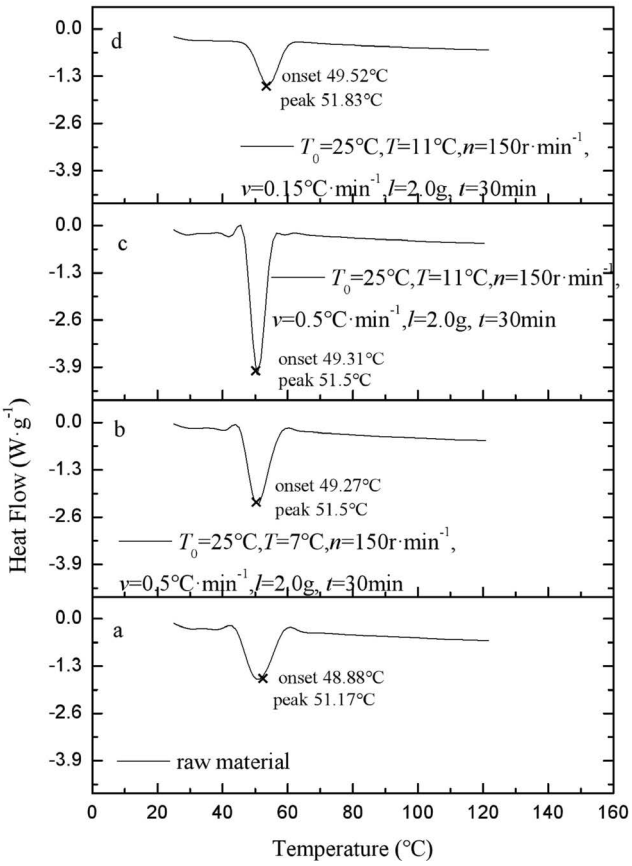

Fig. 11. DSC of 1,2-diphenylethane.

growing rate, particle size distribution, and mean size of 1,2-diphenylethane particle group. The stirring speed has limited influences on the product, the crystal growing rate, the particle size distribution, and the mean size of 1,2-diphenylethane particle group. The crystal growing time and cooling rate have limited effects on the product of 1,2-diphenylethane,but they have great influences on the crystal growing rate, the particle size distribution, and the mean size of 1,2-diphenylethane particle group. The seed size has limited influences on the product and the crystal growing rate, but it plays important roles in the particle size distribution and the mean size of 1,2-diphenylethane particle group. The optimal cooling crystallization condition is crystallization temperature of 7°C, seed size of 1,015 μm, cooling rate of 0.15°C min^{-1}, and stirring speed of 120 rpm.

Symbols

d_{i-1}	—	Sieve mesh size of the upper screen, μm
d_i	—	Sieve mesh size of the lower screen, μm
d_{pi}	—	Average size of particles between the two screens, μm
$\bar{d}$	—	Mean size of particle group, μm
G	—	Crystal growing rate, kg m^{-3} h^{-1}
k_i	—	Average of the experimental data
K_i	—	Sum of every experimental data
l	—	Seed size, μm
Δm	—	Mass difference between the product and seed, g
M_1	—	Molecular weight of 1,2-diphenylethane, g mol^{-1}
M_2	—	Molecular weight of ethanol, g mol^{-1}
n	—	Stirring speed, r min^{-1}
R	—	Difference between the maximum and minimum
S	—	Mass solubility, g (100g C_2H_5OH)$^{-1}$
t	—	Crystal growing time, min
t_1	—	Time at which crystallization process is just over, min
t_2	—	Time at which the cooling temperature is decreased to the constant temperature, min
t_3	—	Time at which the seed crystals were added into saturated solution, min
T	—	Thermodynamic temperature or the crystallization temperature, K or °C
v	—	Cooling rate, °C min^{-1}
V	—	Volume of solution, mL
w_1	—	Mass fraction of 1,2-diphenylethane in the solution
w_2	—	Mass fraction of ethanol in the solution
x_1	—	Mole fraction solubility
x_i	—	Mass fraction of particles in every classification area

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