

Preparation of monodisperse poly(styrene-co-divinylbenzene) microspheres by vibration dispersion method

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(Received 1 January 2015 • accepted 12 May 2015)

Abstract—Monodisperse micron-size poly(styrene-co-divinylbenzene) (PST-DVB) microspheres were successfully prepared by vibration dispersion. A vibrator was used to generate a controlled vibration to jet from a single nozzle of 200 μm to produce uniform droplets. The effects of variations in selected process parameters upon the droplets formation and the diameter of the microspheres were investigated. It was demonstrated that changes in the velocity of oil phase, drive frequency and destabilization amplitude have significant effects on the formation of uniform droplets and the average diameter of the microspheres. Rational polynomial regression equations of the above parameters were established. Based on these equations, we could calculate the operation conditions to produce uniform droplets with the desirable diameter.

Keywords: Monodisperse, Poly(Styrene-co-divinylbenzene), Vibration Dispersion Method, Droplets, Drop Size

INTRODUCTION

Micron-size poly(styrene-co-divinylbenzene) (PST-DVB) particles with hydrophobic structure are one of the most important kinds of organic polymeric monolithic columns [1]. Since PST-DVB particles have various advantages in mechanical strength and chemical stability [2], they are widely applied to the separation and purification of drugs, immunology, active carriers, chromatographic packing, etc. Up to now, PST-DVB particles have been indispensable to the national economy as a class of functional polymeric materials [3-7].

Several methods to prepare PST-DVB microspheres, including emulsion polymerization, suspension polymerization, seed polymerization and dispersion polymerization, have been developed [8-12]. It has been reported that large microspheres with narrow size distribution demonstrate many edges, such as high separation resolution, low performance pressure and low costs [13,14]. Only the method of suspension polymerization can be utilized to fabricate this kind of microsphere [15]. However, the microspheres prepared with suspension polymerization are unsuitable for further application because of the wide size distribution of the microspheres, which result from mechanical stirring in the reactor. Recently, polymer spheres fabricated through the approach of an emulsifier-free emulsion polymerization have controlled size and clean surface; however, the particle size of these spheres is of nanometer scale [16]. Various polymerization techniques have been used to overcome the limitation of broad size distribution in traditional suspension polymerization [17,18]. A method of spraying suspension polymerization was developed to fabricate microspheres with a narrow size distribution, but the size of the microspheres was difficult to

predict [19]. Ogino et al. [20] prepared uniform PST-DVB beads via the method of single step swelling polymerization. However, it is hard to do chemical modification of these microspheres. Kim et al. successfully prepared monodisperse micro-sized polystyrene particles by seeded polymerization using reactive macrosurfactants. However, it cost more than one day to prepare monodisperse particles in one experiment. [21]. Uniform-sized polymeric beads with diameters in excess of 1 mm were prepared by free radical polymerization in an ascension process through a heated column, whereas the injection of droplets into the column must be very slow, which is time-consuming and difficult to control. Furthermore, high concentration of PVA had to be employed to avoid contact among polymerizing spheres [22]. Monodisperse polystyrene particles having average diameters ranging from 0.5 to 3 mm were prepared with the method of ice-particle jet, but the method was restricted to the condition of gas-liquid phase [23]. Recently, the approach of two-phase microspheres flows is a popular method to prepare uniform microspheres, while the diameters of microspheres obtained by this method are less than 100 μm [24,25].

We exploited the method of vibration dispersion to prepare monodisperse PST-DVB microspheres. A vibrator was used to generate a controlled vibration to jet from a single nozzle to produce the disturbances to control jet breakup. By regulating the frequency of the vibration, breakup could be well controlled to fabricate uniform droplets. Next, these uniform droplets were polymerized in a reactor, where a circulating fluidization was utilized to avoid the coalescence and breakage of the droplets in the process of polymerization. The generational rate of droplets was related to the frequency. The parameters on the method of vibration dispersion included density, viscosity and interfacial tension of stream. These parameters have been discussed in Rayleigh theory [26] and Weber equation. In this work, we investigated the effect of the parameters involving the velocity of stream, drive frequency and destabilization amplitude on the formation of uniform droplets and the average

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diameter of PST-DVB beads. By studying the relationships of the three factors, we can obtain exactly the operation conditions to produce PST-DVB particles with the desirable diameter.

EXPERIMENTAL

1. Materials

Styrene (ST, Kewei New Material Technology Co. Ltd., Tianjin, China) was purified by reduced pressure distillation. Divinylbenzene (DVB, 55.0 wt%, Aladdin Shanghai Co. Ltd., China) was washed by 5.0 wt% solution of sodium hydroxide and deionizer water. Polyvinyl alcohol (PVA, degree of polymerization 1700, degree of hydrolysis 88.5%) was also provided by Aladdin Shanghai Co. Ltd., China. Benzoyl peroxide (BPO) was from Kewei New Material Technology Co. Ltd., Tianjin, China.

2. Apparatus

A schematic of the vibration dispersion polymerization process is shown in Fig. 1. A single nozzle with pore size of 200 μm was installed at the bottom of the polymerization reactor, connected with the vibrator under the reactor. The oil phase was fed into the nozzle actuated by a syringe pump. The aqueous phase was circulated from the top to the bottom of the reactor, and the temperature of the aqueous phase was maintained at 80 $^{\circ}\text{C}$ by a heat exchanger. The velocity of oil phase was monitored by a flow meter.

3. Characterization

The diameters and size distribution of microspheres were measured with a particle size analyzer (Mastersizer-2000, Malvern Instruments, UK). The images of the oil phase stream and the generation of droplets were obtained using a digital single lens reflex (DSLR, D80, Nikon, Tokyo, Japan). The morphologies of the final micro-

spheres were determined with a scanning electron microscopy (SEM, S-4800, Hitachi, Tokyo, Japan).

RESULTS AND DISCUSSION

1. Properties of Vibration Dispersion Polymerization

The formation of uniform droplets must pass through three different stages. First, the oil phase was injected into the nozzle by a syringe pump. Second, the oil jet discharged from the nozzle at laminar flow condition tended to break into short lengths. Finally, the jet was dispersed to monodisperse spherical droplets by a controlled and uniform vibration to the nozzle, and then the droplets entered into the reactor. Because the temperature of the aqueous phase is higher than the decomposition temperature of initiator (BPO), the polymerization started while the droplets were generated. Consequently, the vibration conditions and the flow rate of the oil phase through the nozzle were investigated as crucial factors in the formation of monodisperse droplets.

2. Influence of Velocity of Oil Phase

The key to obtaining uniform PST-DVB microspheres by the method of vibration dispersion is that the liquid jet can be broken up into monodisperse droplets. With the velocity of oil phase increased, the jet expresses four states, respectively: dripping, smooth flow, wavy flow and spray stream [27]. According to the theory of McCarthy, only applying a steady excitation to smooth flow can obtain effectively uniform droplets. Interfacial tension plays a major role in breaking up the jet when the jet is in the state of smooth flow. Because of interfacial tension, the jet has a potential to be broken up into uniform droplets while a certain vibration is applied to the smooth flow [28,29].

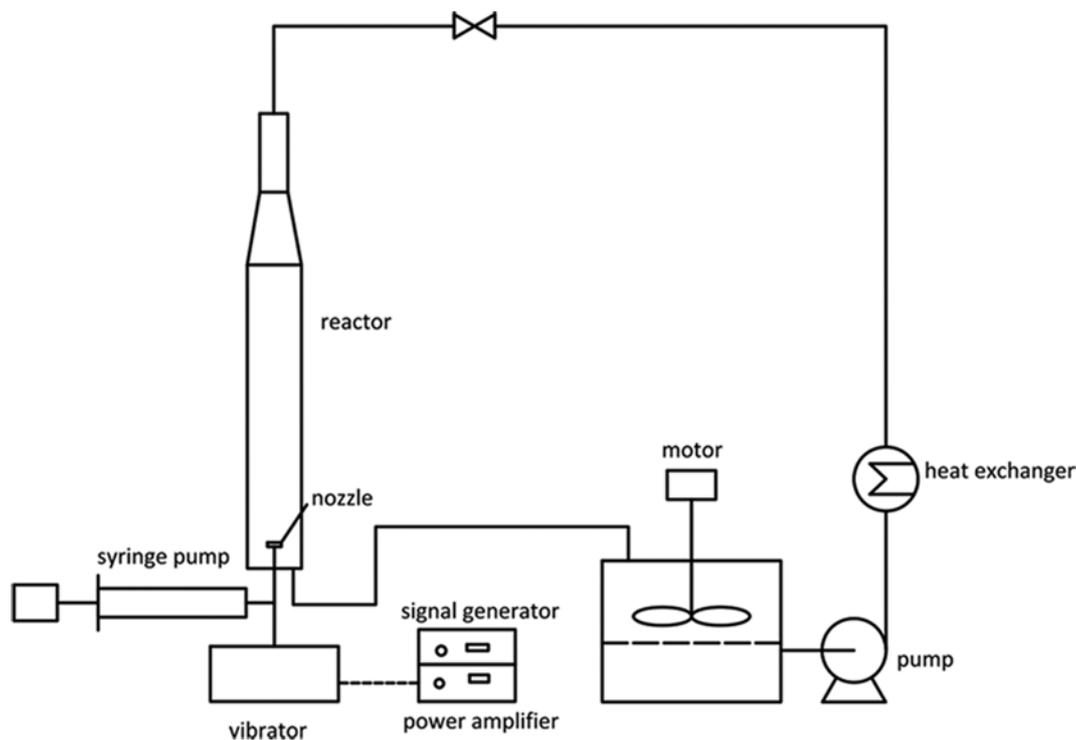


Fig. 1. A schematic representation of the vibration dispersion polymerization process.

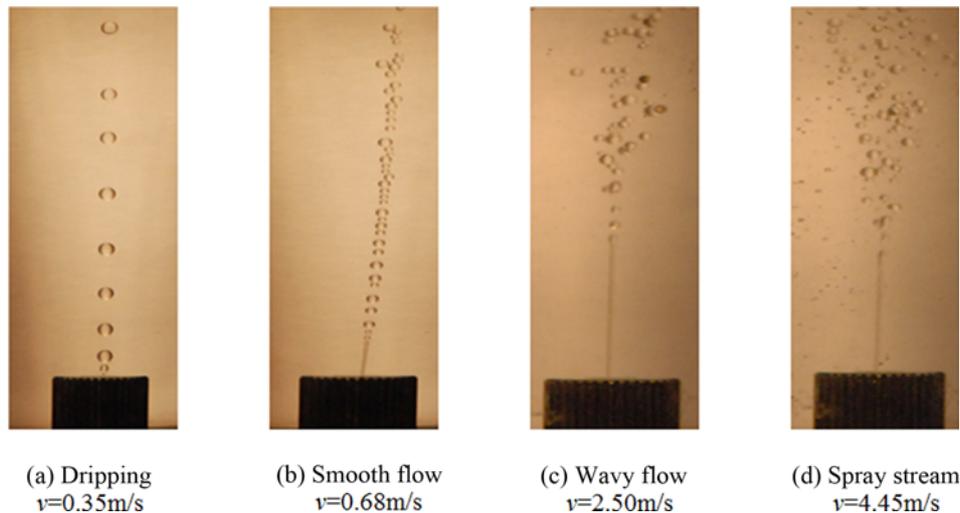


Fig. 2. The state of jet as a function of velocity of oil phase for a 200 μm nozzle without vibration.

As shown in Fig. 2, the range of velocity of oil phase was investigated to determine the state of the smooth flow for a given 200 μm nozzle without vibration. When the velocity of the oil solution (v) was 0.35 m/s, the jet was in the state of dripping. In this state, the jet could be dispersed to droplets, but the numbers of droplets were too small, as shown in Fig. 2(a). On the contrary, as shown in Fig. 2(c) and 2(d) the jet was only dispersed to droplets with a broad size distribution when the rate was too fast. In Fig. 2(b), it can be noticed that the ideal monodisperse microspheres could be fabricated while the jet was in the state of smooth flow at the range of the velocity from 0.55 m/s to 1.60 m/s.

3. Excitation System: Influence of Amplitude

The jet was dispersed to the droplets of different forms with the increase of the amplitude of the vibrator. To elucidate the influence of amplitude on the formation of droplet, a series of studies were conducted. The excitation frequency was held constant at 150 Hz, and the amplitude was varied. The results are summarized in Fig. 3. At a given velocity of oil phase (0.83 m/s), an amplitude threshold exists for the formation of uniform droplets. In Fig. 3(a), the

jet was broken into uneven droplets at the 0.3 mm applied amplitude. The monodisperse droplets were prepared at the range of the amplitude from 0.7 mm to 4.7 mm, as shown in Fig. 3(b), 3(c) and 3(d), respectively. Moreover, the number of droplets and the diameter of droplets remained steady, namely, the jet was stable. On the other hand, from Fig. 3(e), higher amplitude (>4.7 mm) produced small droplets among the main droplets, which led to the deterioration of uniformity. Amplitude is one of the most important parameters in the liquid-liquid vibration dispersion method, providing the energy that requires breaking up the jet to droplets. Uniform droplets can be obtained with suitable amplitude.

The effect of frequency on the marginal of amplitude was also investigated. The findings from these experiments are plotted in Fig. 4, which demonstrate the range of obtained values. We defined A_{m-l} as the lower margin of amplitude at which stable jet breakup began; A_{m-u} was defined as the upper margin of amplitude. As the frequency kept increasing, A_{m-l} and A_{m-u} increased first then started to drop, as shown in Fig. 4. It seemed that the effect of frequency on A_{m-u} was more significant than on A_{m-l} . Only the range enclosed

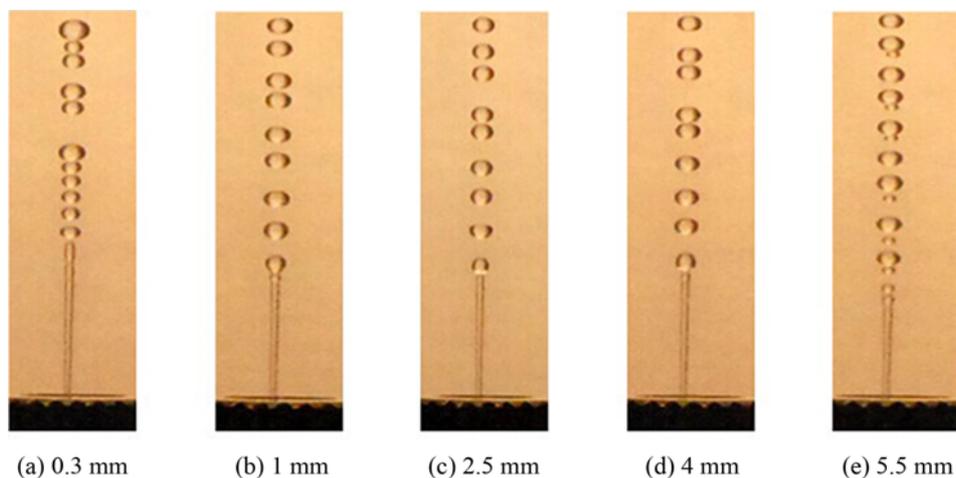


Fig. 3. Droplet generation as a function of amplitude for a frequency=150 Hz and a jet velocity of 0.83 m/s.

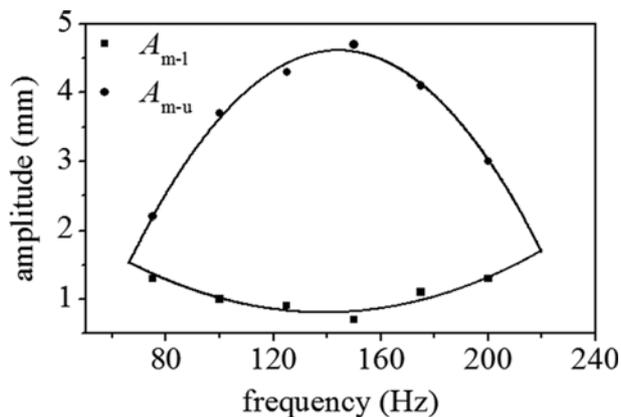


Fig. 4. Excitation amplitude as a function of frequency.

by these two para-curves can obtain uniform droplets. Furthermore, the relationship between A_m and frequency f could be fitted well by polynomial curve and the fitting equations as follows:

$$A_{m-u} = -5.92 + 0.15f - 6.08 \times 10^{-4} f^2 \quad (1)$$

$$A_{m-l} = 3.47 - 0.04f + 1.38 \times 10^{-4} f^2 \quad (2)$$

By combining Eq. (1) with Eq. (2), it was easy to get the range of frequency that can produce uniform droplets from 67 Hz to 234 Hz. Furthermore, the widest frequency bandwidth was 3.8 mm when the frequency came to 143 Hz. The two numbers were in good agreement with experimental values (40 mm, 150 Hz).

4. Excitation System: Influence of Frequency

In these experiments, the velocity of oil phase was held constant at 1.09 m/s, while the amplitude was kept at 3.0 mm. Fig. 5 reveals that the droplet behavior was strongly influenced by the excitation frequency. The breakup was random at 45 Hz, where a frequency for droplet separation could not be specified. Based on Armster theory [30], it was easy to produce small droplets between main droplets. When the frequency increased to 70 Hz, the breakup became regular and monodisperse droplets could be obtained. Furthermore, the regular breakup lasted to 320 Hz. This means that there existed a 250 Hz (70 to 320 Hz) frequency range where uni-

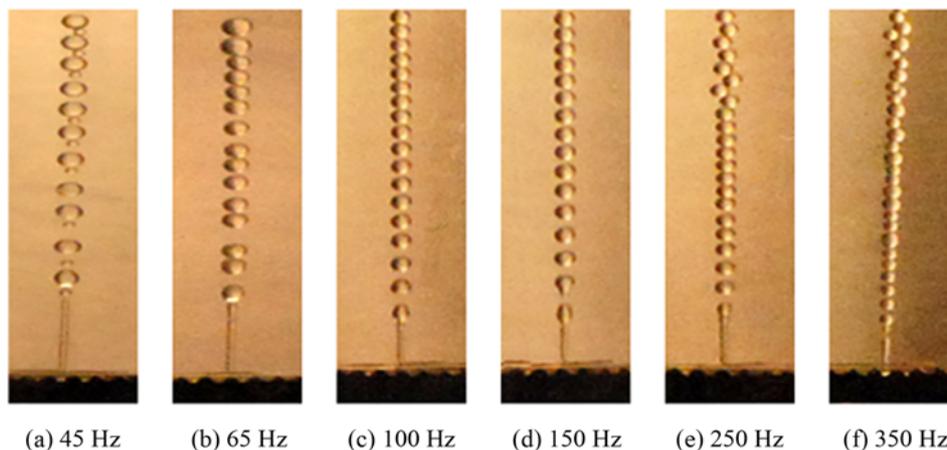


Fig. 5. Droplet generation as a function of frequency for a velocity=1.09 m/s and an amplitude of 3 mm.

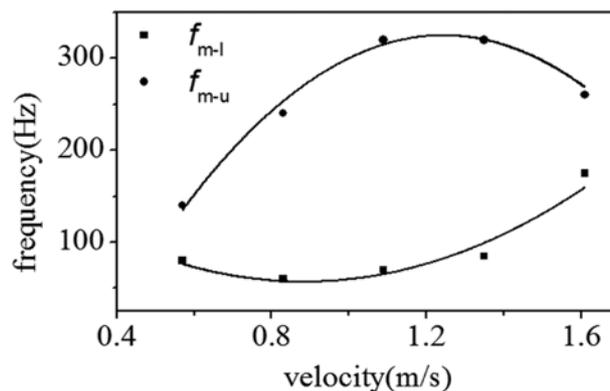


Fig. 6. Excitation frequency as a function of velocity.

form droplets were obtained for a 200 μm nozzle at 1.09 m/s. But the main droplets started merging at 350 Hz, which caused wide size distribution of droplets. It was obvious that the number of droplets increased at high frequency, which shortened the distance between main droplets. Consequently, it affected the generation of droplets.

Studies on the same jet moving at different velocities were also performed. The data are shown in Fig. 6. Here, f_{m-l} and f_{m-u} were used as notations for the starting and ending frequencies of the uniform droplets regime, respectively. As Fig. 6 shows, the variation of the frequency range with velocity was nonlinear for a given jet. As the velocity kept increasing, the frequency range where uniform droplets obtained increased first then started to decrease. The widest frequency bandwidth occurred when the velocity was 1.09 m/s. It is obvious that f_m and the velocity oil solution v could be fitted well by polynomial curve and the fitting equations as follows:

$$f_{m-l} = 209.19 - 344.26v + 194.74v^2 \quad (3)$$

$$f_{m-u} = -322.19 + 1040.63v - 418.42v^2 \quad (4)$$

The size of the droplets generated in any periodic stream can be determined from the driving frequency, the jet diameter, and the velocity of the oil solution. The ultimate frequency f yields the total volume flow rate of liquid as $(4/3) \pi d^3 f$, which equals the flow rate

through the jet orifice, i.e., $v\pi r^2$. Equating the two flow rates and assuming that f_{m-l} and f_{m-u} are the lower and upper bands of the regular breakup regime, $d_1 = \sqrt[3]{3vr^2/4f_{m-l}}$ and $d_2 = \sqrt[3]{3vr^2/4f_{m-u}}$ are the smallest and largest uniform droplets that can be produced at the given physical jet conditions. What's more, we can obtain uniform droplets with diameters we expect and acquire the operating conditions (f, v, A). The specific method is described by

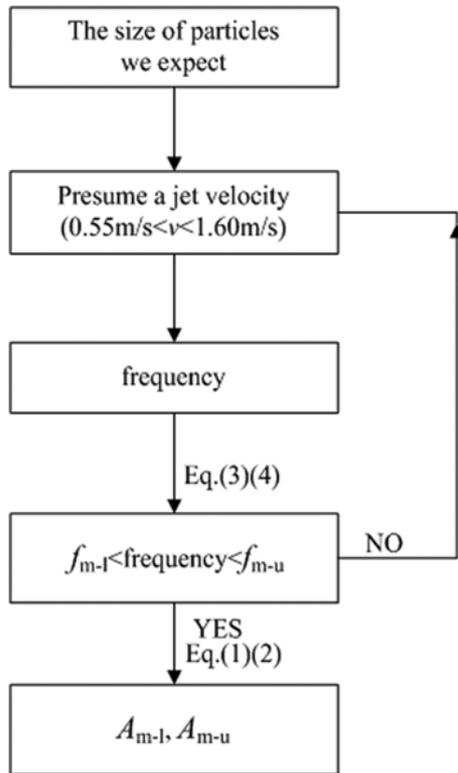


Fig. 7. Operating conditions to get desirable uniform droplets.

Table 1. Experimental data according to three factors and three levels of CCD

Run	Factor1 A: f (Hz)	Factor2 B: v (m/s)	Factor3 C: A (mm)	Response R1: d_m (mm)
1	150	1.35	4	0.651
2	150	1.09	4	0.602
3	150	1.09	3	0.598
4	100	1.35	5	0.735
5	100	0.83	5	0.632
6	200	1.35	5	0.585
7	150	1.09	5	0.600
8	100	1.09	4	0.496
9	200	0.83	3	0.500
10	200	1.35	3	0.592
11	150	0.83	4	0.549
12	100	1.35	5	0.732
13	100	0.83	3	0.633
14	200	0.83	5	0.498
15	200	1.09	4	0.543

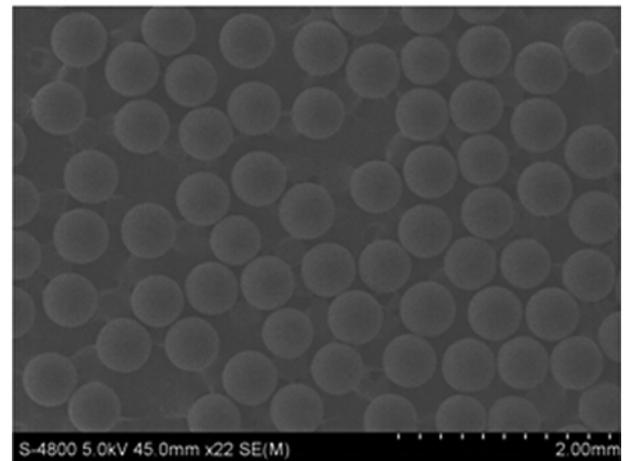
Fig. 7.

5. Parameters Affecting the Diameter of PST-DVB Particles

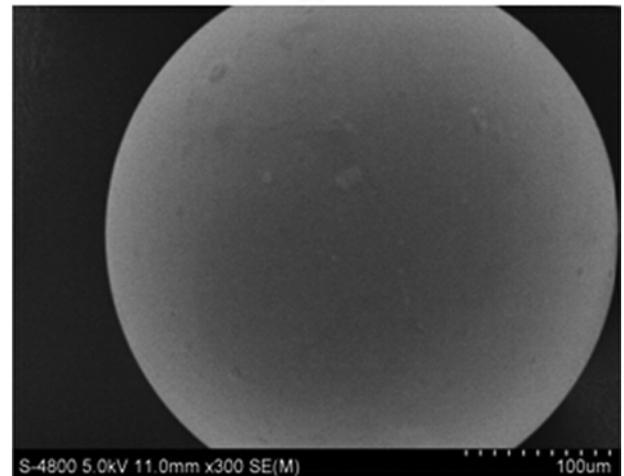
Response surface methodology (RSM) offered statistical design of experimental tools such as central composite design (CCD), which

Table 2. Results of ANOVA

Response	R1	
Source	F-value	P-value (Prob>F)
Model	566.92	<0.0001
A-f	3244.38	<0.0001
B-v	1793.63	<0.0001
C-A	0.090	0.7705
AB	4.80	0.0533
AC	0.021	0.8868
BC	0.19	0.6706
A ²	24.60	0.0006
B ²	28.06	0.0003
C ²	0.74	0.4089



(a)



(b)

Fig. 8. (a) SEM micrographs of overall appearance and (b) outer surface of PST-DVB microspheres.

were often used to optimize process performance. The regression equation of R1 was as follows:

$$R_1 = 0.71112 - 3.95237 \times 10^{-3} f + 0.60881 v + 7.88829 \times 10^{-3} A + 5.76923 \times 10^{-4} f v - 5 \times 10^{-6} f A - 2.88462 \times 10^{-3} v A + 5.06031 \times 10^6 f^2 - 0.19988 v^2 - 5.49615 \times 10^{-4} A^2 \quad (5)$$

Results of ANOVA are listed in Table 1. It was found from Table 2 that the model F -value of 566.92 implied the model was important and the average diameter could be predicted by RSM. Values of 'Prob> F ' less than 0.0500 indicated that model terms were significant. In this case A , B , A^2 , and B^2 were significant model terms. Values greater than 0.1000 indicated that the model terms were not significant. Although it was demonstrated that v , f had higher impact on average diameter, the values of amplitude had a very small effect on diameter of the microspheres.

Average particle diameter and particle distribution of the PST-DVB microspheres are important for certain applications. Fig. 8 shows the SEM images of the overall appearance and outer surface of PST-DVB microspheres prepared by vibration dispersion method. In Fig. 8(a) the PST-DVB microspheres have a narrow size distribution. As shown in Fig. 8(b), a smooth spherical structure can be observed from the SEM images of PST-DVB microspheres. The results verified that the experimental recipe used in the present work was suitable for preparing microspheres with smooth surface. Microspheres were prepared under the condition that frequency was 150 Hz with amplitude of 3.0 mm at the 0.83 m/s. Particle size analysis as shown in Fig. 9 indicates that microspheres were monodisperse with a mean diameter of 549 μm , which is in agreement with theoretical diameter of 550 μm . The geometrical standard deviation $\delta = 0.057$ was also determined. The value of δ is smaller than that of the microspheres obtained by conventional suspension polymerization. The result demonstrates that the size distribution of the microspheres meets the qualification of monodisperse.

CONCLUSION

PST-DVB microspheres were prepared with the method of vibration dispersion. Compared with conventional polymerization, this method could prepare large microspheres with narrow size distribution. The jet can be dispersed to uniform droplets by adjusting various control parameters such as frequency, amplitude and the

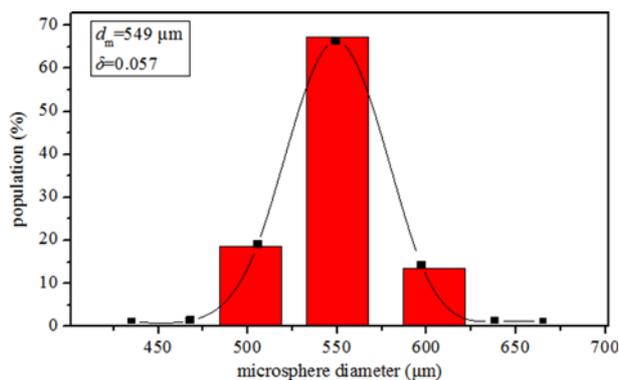


Fig. 9. Size distribution curve of PST-DVB microspheres.

velocity of oil phase. In addition, conditions required for obtaining the desired particles can be confirmed through polynomial fitting equations on frequency and the marginal of amplitude, the velocity of oil phase and the marginal of frequency. The method of vibration dispersion is convenient and effective to prepare monodisperse microspheres for various applications.

ACKNOWLEDGEMENT

We are grateful for the financial support from the National Natural Science Foundation of China (Grant No.51103098) and Tianjin Research Program of Application Foundation and Advanced Technology (Grant No. 13JCQNJC3100).

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