

Structure Controlling and Adsorption Application of Polyethersulfone Porous Microspheres Prepared *via* Electrospraying

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Abstract The focus of this work is to control the structure of electrosprayed polymer microspheres and then study the effect of different structures on the microspheres' adsorption properties. Scanning electron microscopy (SEM) coupled with image analysis software was employed to evaluate the size distributions and the structure of microspheres. According to the observation and analysis results, two types of polyethersulfone (PES) porous microspheres (perfect sphere-shaped and collapsed) were prepared *via* electrospraying technology by adjusting the solvent and polymer molecular weight. The porous PES microspheres can remove bisphenol A (BPA) from its aqueous solution effectively. Compared with collapsed microspheres, the rough microspheres had much higher specific surface area and better mobility in the BPA aqueous solution, so it showed a better adsorption capacity than that of collapsed microspheres. The solvent evaporation rate and the occurrence rate of phase separation significantly affect the structure and morphology of microspheres.

Keywords: Electrospraying; Polyethersulfones microspheres; Structure; Endocrine disruptors; Adsorption.

INTRODUCTION

Polymer microspheres are widely used in many fields, such as microstorage, microreactor, microseparator, microstructural unit^[1–4], *etc.* It has been known that the polymer microspheres can be produced with several common technologies including interfacial polymerization^[5, 6], emulsion and suspension polymerization^[7, 8], interfacial precipitation^[9, 10], supercritical fluid processes^[11], electrospraying^[12] and so on. Among these methods, electrospraying is an alternative and advanced technology for preparing polymer microspheres. It is a method based on electrohydrodynamic technology for preparing microspheres by using polymer as raw materials^[13] and can be considered as one of the special cases of electrospinning. Generally, when either a concentrated solution of a polymer or solutions of a high-molecular-weight polymer are electrospinning, the jet will be continuous and make a bending and whipping movement, so random arranged fibers are obtained. If either a dilute solution of a polymer or solutions of a low-molecular-weight polymer are electrospinning, it is common to obtain electrosprayed microspheres with the break of jet^[14]. Compared with other methods for preparing polymer microspheres, there are several advantages of electrospraying: relative ease of setup, open-atmosphere operation without a sophisticated chamber, high production efficiency due to the direction of microspheres onto the collector under an electric field, and well dispersed microspheres due to self-repellence resulting from the electric charges on the microspheres^[15].

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The structure of electrosprayed microspheres can directly affect their final applications. So it is significant to control the processing conditions to get expected structure. Achieving this goal often depends on the solution properties (solution viscosity, surface tension, molecular weight of the polymer, *etc.*), processing parameters (applied voltage, solution feeding rate, tip-to-collector distance, *etc.*) and the environment conditions (temperature, humidity, *etc.*)^[16]. By changing the above factors, polymer microspheres with various morphologies can be obtained. For example, our group has produced microspheres of three structures (perfect sphere-shaped, red blood cell-shaped and Chinese lantern-shaped) *via* the addition of poly(ethylene glycol) and poly(vinyl alcohol) in our earlier studies^[17].

Nowadays, the widespread use of endocrine disruptors such as bisphenol A (BPA) around the world has led to serious environmental problems. Endocrine disruptors can influence internal secretion and destroy the balance in the endocrine system even at low dose exposures^[18]. Therefore, it is very necessary to remove endocrine disruptors. Some methods of removing endocrine disruptors have been reported in the literature. For example, carbonaceous^[19], clays materials^[20], hydrophobic porous polymer membranes^[21], hydrophobic porous polymer particles^[22], UV-irradiated DNA matrices^[23], *etc.*, could selectively remove endocrine disruptors. Polymer microspheres prepared by electrospraying with diameters ranging from a few nanometers to micrometers could also remove endocrine disruptors effectively, because of their large specific surface area due to the small diameters and the porous structure.

In this study, porous polyethersulfone (PES) microspheres were prepared *via* electrospraying technique. The effects of solvent properties and molecular weight on the morphology and size of porous microspheres were investigated. The porous microspheres were then used for adsorbing endocrine disruptors from their aqueous solution, and the adsorption capacity and efficiency of PES porous microspheres with different structures were compared.

EXPERIMENTAL

Materials

PES₁ (Ultrason E 6020P) with an intrinsic viscosity of 0.40 dL/g in dimethyl sulfoxide (DMSO) at 303.2 K was purchased from BASF Chemical Co. (Germany) and the molecular weight of PES₁ is 50000 g/mol. PES₂ with an intrinsic viscosity of 0.34 dL/g in DMSO at 303.2 K was purchased from Gharda Co. (India) and the molecular weight of PES₂ is 40000 g/mol. Bisphenol A was purchased from Changlian Chemical Co. (China). Solvents used in this study (*N*-methyl-2-pyrrolidone (NMP), DMSO, *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAc)) are purchased from Kelong Chemical Co. (China). All the chemicals are of analytical grade and are used without further purification unless otherwise described.

Preparation of Microspheres

PES was dissolved in solvent at 70 °C for 4 h until it became a homogeneous solution. For preparing microspheres, the solution was placed in a 50 mL syringe, to which a capillary tip of 0.5 mm inner diameter was attached. The positive electrode of high-voltage power supply was connected to the capillary tip. A direct current high voltage-generator (ZGF Chuan Gao Electro-tech Inc, China) was used to provide a voltage of 10 kV. The grounded electrode was connected to a metallic collector immersed in a water bath. The distance between the tip and the collector was maintained at 6 cm and the flow rate was constant 1 mL/h. The spraying stream is broken up after moving a certain distance, and then microspheres are collected in the water bath.

Turbidity Titration Experiments

Deionized water was used as precipitator. The concentration of PES solutions used in the titration experiment were 0.08 g/mL. The deionized water was added into the PES solution dropwise until the white precipitate emerged and it didn't disappear during shaking the solution for a long time. Keep a record of deionized water consumption when turbidity point emerged.

Scanning Electron Microscopy of Microspheres

The morphology of microspheres was observed with scanning electron microscopy (SEM and EDS Inspector F, FEI Company, all operation at an accelerating voltage of 20 kV). The samples were coated by an E-1045 ion sputter coater with Au/Pd to reduce charging. The diameters of microspheres were measured using PS-CS3 image analysis software; In order to have statistical significance, more than 200 microspheres were measured per sample. The shell density was measured by the drainage method.

Adsorption Experiments

BPA was dissolved in ethanol and then diluted with deionized water. The adsorption experiments were carried out as following: a certain amount of microspheres was dispersed into 10 mL BPA solution at 20 °C with initial concentration of 300 μmol/L. The BPA concentrations at certain time intervals were detected by a UV-Vis spectrophotometer UV-2310 II (Shanghai TECHCOMP, Shanghai, China) at the wavelength of 276 nm. The removal ratio and adsorbed capacity of microspheres were calculated as following:

$$R_t = \frac{c_0 - c_t}{c_0} \times 100\% \quad (1)$$

$$Q_t = \frac{(c_0 - c_t) \cdot V}{m} \quad (2)$$

where R_t (%) is the removal ratio of BPA by microspheres at time t ; c_0 is the initial concentration of BPA solutions (μmol/L); c_t is the concentration at time t (μmol/L); Q_t is the adsorbed BPA amount per gram of microspheres at time t (μmol/g); V is the volume of BPA solution used in the experiment (L); and m is the weight of microspheres (g).

RESULTS AND DISCUSSION

The Structure Control of Microspheres

Effect of solvents on structure of microspheres

The structure of microspheres produced by electrospraying showed a great dependence on the solvent used in the electrosprayed solution. In order to study the internal nanostructures of microspheres, an effective method^[24] was used to cut the microspheres. Figure 1 shows porous surface and inner morphology SEM images of electrosprayed microspheres made by electrospraying PES solutions with different solvents. As shown in Fig. 1, at a given polymer concentrations of 0.08 g/mL and same electrospraying processing parameters, different morphology particles were obtained. When NMP was used as solvent in the solution, a great deal of irregular shaped microspheres (Fig. 1a) was fabricated. While the solvent was DMSO, the porous microspheres with a collapsed (red blood cell-shaped^[25]) surface morphology (Fig. 1c) were prepared. Using DMAc and DMF solvents resulted in spherical shape microspheres (Figs. 1e and 1g). However, the surface of microspheres prepared by PES₁/DMAc solution has holes (Fig. 1e). From the high-magnification SEM images and the cross-section images of different microspheres (Figs. 1b, 1d, 1f and 1h), these microspheres all showed porous structure and the microspheres electrosprayed by PES₁/DMAc solution had a big hole in the cross-section.

Solution concentration is another factor affecting the structure of microspheres. Therefore, changing the electrosprayed solution concentration can control the structure effectively. According to the above analysis, it can be deduced that while there are still some defect, the microspheres showed a good roundness when DMF and DMAc were selected as solvent. As shown in Fig. 2, increasing the solution concentration of PES₁/DMAc, the microspheres obtained still maintained a good roundness and the number of the hole on their surface reduced. When the electrosprayed solution was 0.12 g/mL, the hole on the microspheres surface disappeared. However, when the concentration increased to 0.13 g/mL, microspheres along with some nanofibers were produced. And further increasing in the concentration will lead to more nanofibers obtained. Therefore, the optimum solution concentration of PES₁/DMAc to prepare microspheres is 0.12 g/mL.

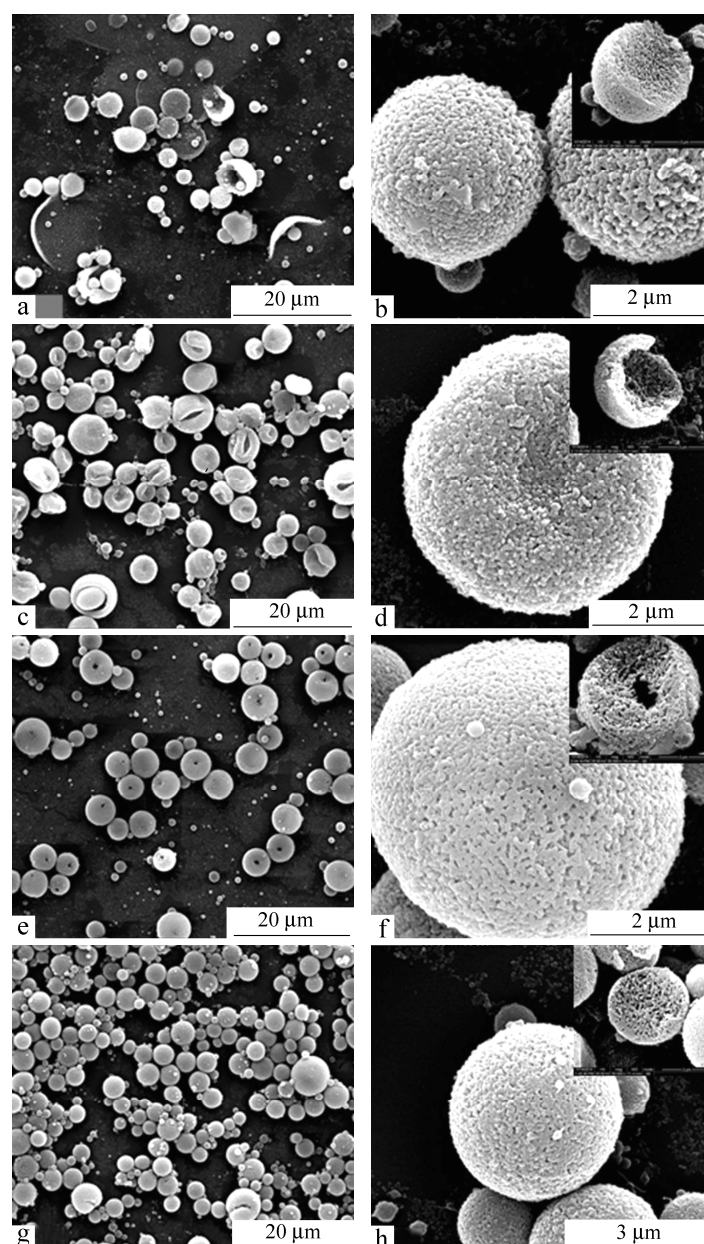


Fig. 1 Porous surface and inner morphology SEM images of microspheres obtained from PES₁ solution with the same concentration (0.08 g/mL) but different solvents: (a) and (b) PES₁/NMP solutions, (c) and (d) PES₁/DMSO solutions, (e) and (f) PES₁/DMAc solutions and (g) and (h) PES₁/DMF solutions

When the electrosprayed solution was PES₁/DMF, the preparation process was much easier to be controlled with the increase of solution concentration. The electrosprayed microsphere produced by these solutions always kept a good roundness (Fig. 3). Similarly to PES₁/DMAc solution, there were still some nanofibers as byproduct when the concentration is higher than a certain value. According to the SEM images shown in Fig. 3, the optimum solution concentration of PES₁/DMF to produce microspheres is 0.10 g/mL. The optimum concentrations of PES₁ and PES₂ in different solvents were studied, the results are shown in Table 1. Meanwhile, the diameter of electrosprayed microspheres by using DMAc is relatively smaller than that by using other solvents and all of them are ranged from 1.78 μm to 3.34 μm (as shown in Table 1).

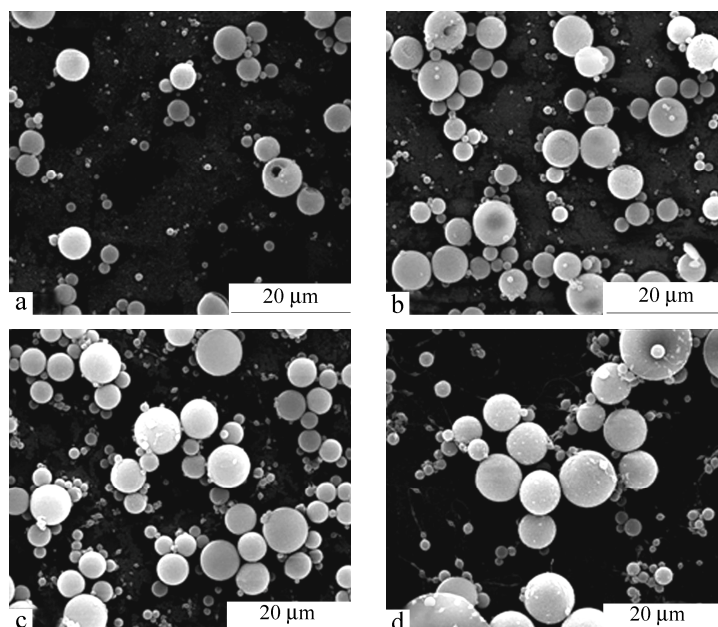


Fig. 2 SEM images of porous microspheres obtained from PES₁/DMAc solutions with different concentrations: (a) 0.10 g/mL, (b) 0.12 g/mL, (c) 0.13 g/mL and (d) 0.15 g/mL

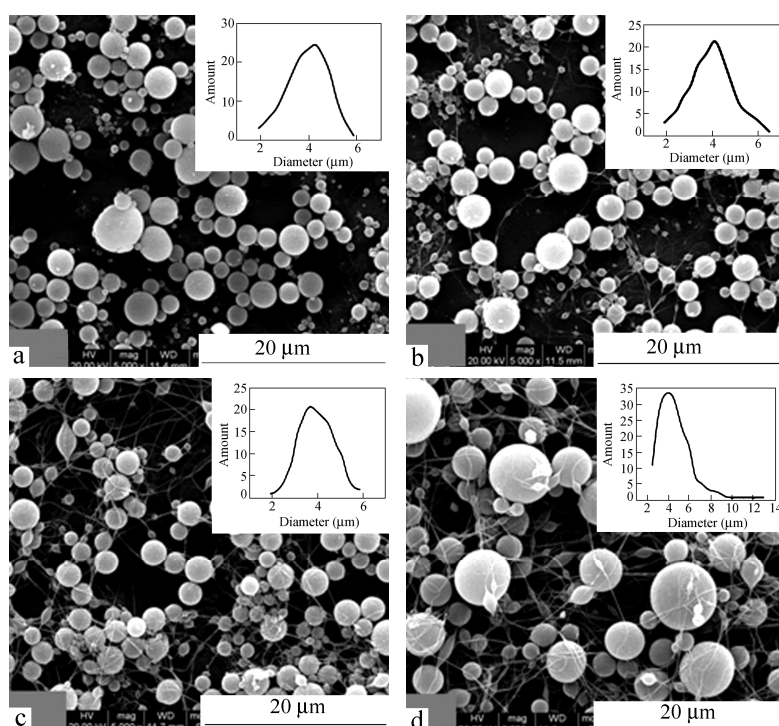


Fig. 3 SEM images of porous microspheres obtained from PES₁/DMF solutions with different concentrations: (a) 0.10 g/mL, (b) 0.12 g/mL, (c) 0.14 g/mL and (d) 0.15 g/mL. The insets top of each SEM images are the diameter distribution of the microspheres respectively.

Table 1. Diameter of microspheres

	Mean diameter (μm)	Standard deviation (μm)
PES ₁ /DMSO (0.08 g/mL)	3.34	1.69
PES ₁ /DMAc (0.12 g/mL)	1.78	0.84
PES ₁ /DMF (0.10 g/mL)	2.71	1.19
PES ₂ /DMSO (0.11 g/mL)	2.89	1.82

Effect of polymer molecular weight on the structure of microspheres

The polymer itself played a decisive role in the property of polymer solution, so surely has a significant impact on the structure of microspheres. Comparing Fig. 1(b) with Fig. 4(a), it can be found that the structure of electrosprayed microspheres is quite different when different molecular weight PES samples were used as raw materials although the solution concentration was the same (0.08 g/mL PES/DMSO). The microspheres produced by PES₂/DMSO solution have some large sunken holes whereas there is no hole but some degree of collapse for microspheres prepared by the solution of PES₁/DMSO. Certainly, for PES₂/DMSO solution, increasing its concentration, the structure of microspheres will become good and when the solution concentration increased to 0.11 g/mL, the microspheres with good roundness can be obtained.

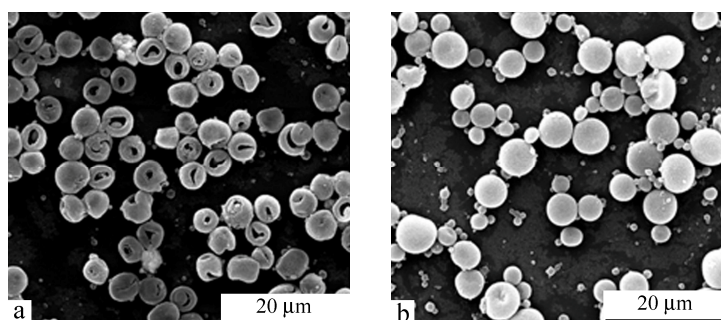


Fig. 4 SEM images of electrosprayed porous microspheres obtained from PES₂/DMSO solutions with different concentrations: (a) 0.08 g/mL and (b) 0.11 g/mL

The forming mechanism of different structure microspheres

In order to further investigate the effect of solvent and polymer molecular weight on the structure of microspheres, it is necessary to study the formation mechanism, as shown in Fig. 5. The formation process of electrosprayed microspheres can be divided into two steps. The first step is electrospraying which was accompanied with rapid evaporation of solvent while the second step is the figuration of microspheres in coagulation bath with the help of phase separation. Therefore, the solvent evaporation rate and occurrence rate of phase separation will significantly affect the structure and morphology of microspheres. During the electrospraying process, the surface of microspheres will pre-cured with the rapid solvent evaporation. In this case, under the same conditions, the lower the boiling point of solvent, the more volatile the solvent and thereby the higher the solution concentration of the electrosprayed droplets before coagulation. A higher concentration is very important to maintain the roundness of microspheres. As shown in Fig. 6(a), the boiling point of DMF is the lowest, therefore, the roundness of microspheres produced by PES₁/DMF solutions is the best. With the increase of boiling point of solvent used in this paper, the roundness of microspheres becomes worse. These results revealed that low boiling point solvent is helpful for the formation of microspheres with good roundness indeed. When the droplets sprayed into the coagulation bath, the occurrence rate of phase separation determined the final structure of microspheres. The lower the solvent's cloud point (Fig. 6b), the sooner the occurrence of phase separation and the better the roundness of microspheres (Fig. 1h). The schematic diagram of PES microspheres formation mechanism was shown in Fig. 5. When the high boiling point solvent and high cloud point solvent was used, the collapsed microspheres were obtained, on the contrary perfect sphere-shaped microspheres would be prepared.

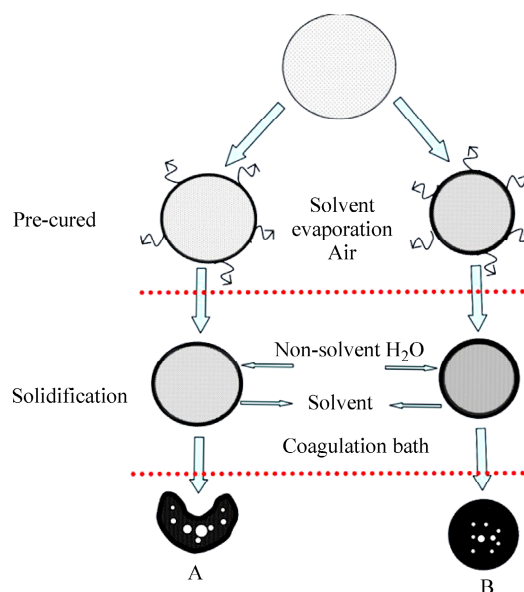


Fig. 5 The schematic diagram of PES microspheres formation mechanism for different solvents: (A) high boiling point and high cloud point solvent and (B) low boiling point and low cloud point solvent

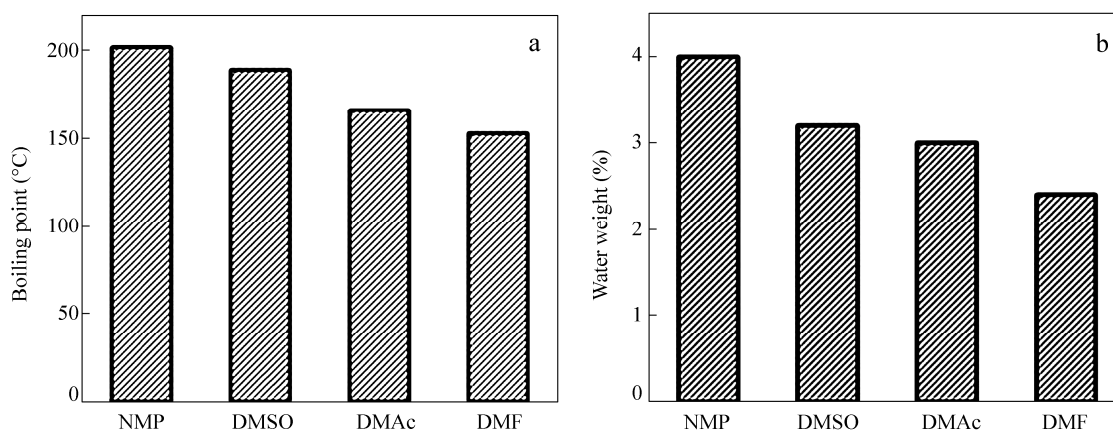


Fig. 6 (a) the boiling points of four solvents; (b) the water weight precent of PES₁ solution with the concentrations of 0.08 g/mL when the turbidity point appears

Meanwhile, the roundness of smaller microspheres is better than that of the bigger ones, because the smaller microspheres were faster solidified and were more difficult to become collapsed shaped ones. As can be seen in Table 1, the average diameters of microspheres produced with the using of DMAc and DMF are 1.78 μm and 2.71 μm , respectively, whose roundness is much better than that of DMSO (average diameter of microspheres is 3.34 μm).

Table 2. Properties of PES₁ and PES₂

	Contact angle	Turbidity titration (%)
PES ₁	72.8	3.2
PES ₂	77.7	2.8

Additionally, the molecular weight and hydrophobic property of polymer also can affect the structure of microspheres when the same solvent was used. For example, the roundness of microspheres produced by PES₂/DMSO solution is better than that of PES₁/DMSO solution with the same solution concentration because the hydrophobicity of PES₂ is stronger than that of PES₁. However, as shown in Fig. 4(a), the roundness of

microspheres produced by PES₂ is good but their surface has many holes, which is mainly due to the lower molecular weight of PES₂. It will result into a weaker entanglement of polymer molecular chains and thereby leading to a hole structure. In this case, increasing the electrospayed solution concentration can prepare microspheres with good roundness (Fig. 4b).

Adsorption of BPA with Microspheres

The porous electrospayed microspheres have a very high specific surface area (shown in Fig. 7) and they can be used to remove endocrine disruptors from their aqueous solutions. In this study, the adsorption properties of different PES microspheres to endocrine disruptor BPA were investigated. As shown in Fig. 8, the adsorption capacity of round microspheres prepared by different solvents and different molecular weight polymers is comparatively higher than that of microspheres with a certain degree collapse. Compared with collapsed microspheres, there is a much higher specific surface area and a better mobility in the BPA aqueous solution for round microspheres, so they showed a better adsorption capacity than that of collapsed microspheres. The adsorption capacity of round microspheres prepared by different solvents and different molecular weight polymers has some difference because of the different pore sizes and specific surface areas of round microspheres (as shown in Table 3). The high specific surface area results in a better adsorption capacity. Among them the microspheres prepared by 0.12 g/mL PES₁/DMAc with a minimum size (1.78 μm) and maximum specific surface area (15.82 m^2/g) has a maximum adsorption capacity to BPA (55.33 $\mu\text{mol}/\text{g}$).

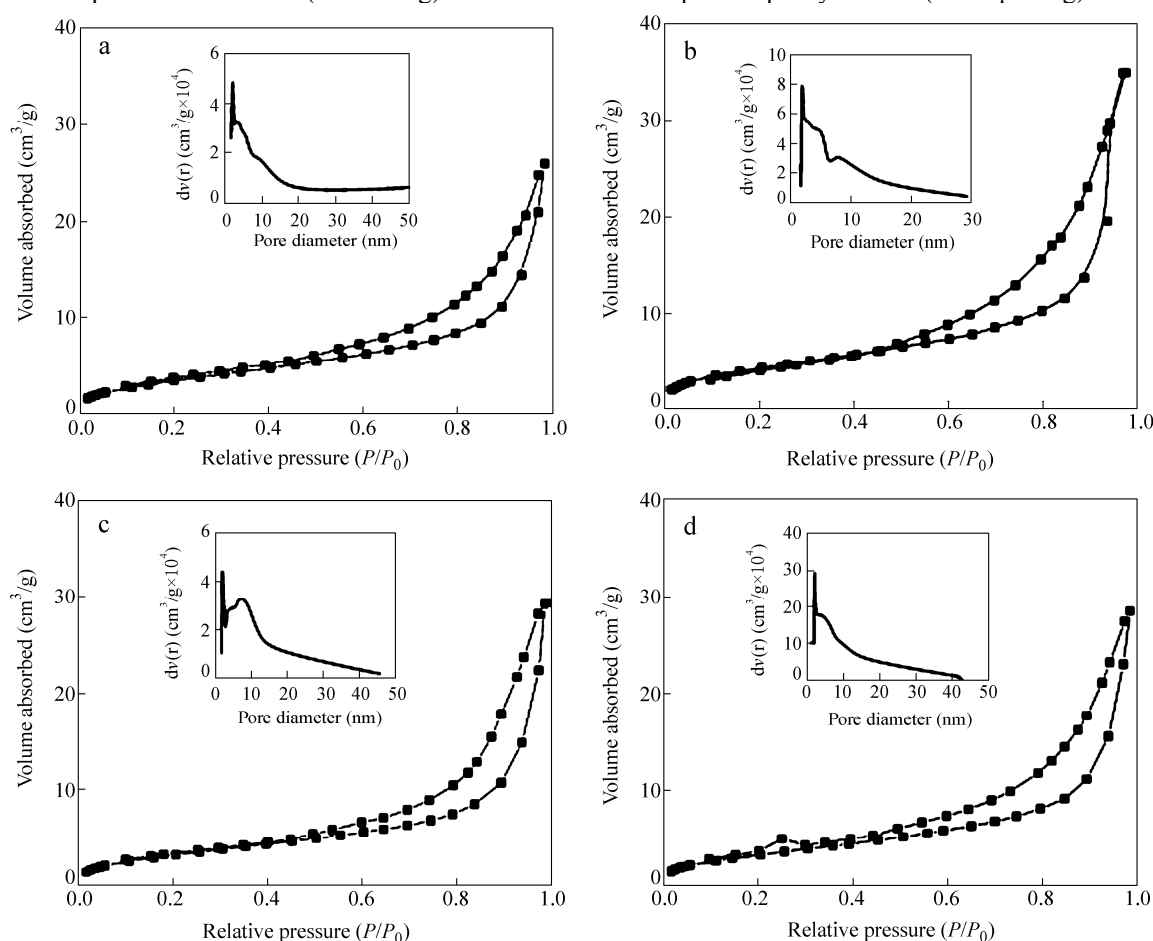


Fig. 7 Nitrogen adsorption-desorption isotherms and pore size distribution (inset) of microspheres electrospayed with different solutions: (a) 0.10 g/mL PES₁/DMF, (b) 0.12 g/mL PES₁/DMF, (c) 0.08 g/mL PES₁/DMSO and (d) 0.11 g/mL PES₂/DMSO

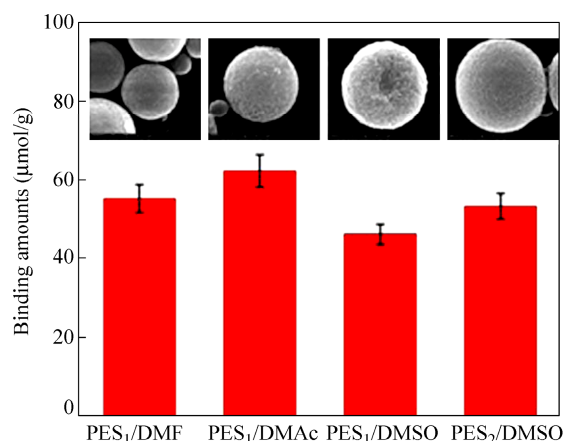


Fig. 8 The binding amounts per unit mass of the electrospayed PES microspheres of different structures in BPA aqueous solutions

Table 3. Pore size and specific surface area of microspheres

	Pore size (nm)	Specific surface area (m ² /g)
PES ₁ /DMSO (0.08 g/mL)	6.199	12.93
PES ₁ /DMAc (0.12 g/mL)	6.833	15.82
PES ₁ /DMF (0.10 g/mL)	7.568	11.94
PES ₂ /DMSO (0.11 g/mL)	7.290	12.08

CONCLUSIONS

Porous PES microspheres with high specific surface area were prepared by electrospaying. The effect of solvent and molecular weight on the structure of microspheres was investigated. By using different solvent and controlling the exchange rate of solvent and non-solvent, two different structures of PES porous microspheres were produced. Lower boiling point solvent is helpful for the formation of microspheres with good roundness. Increasing the molecular weight of PES can prepare better round microspheres. The porous PES microspheres can remove BPA from it aqueous solution effectively. Compared with collapsed microspheres, there is a better adsorption capacity for round microspheres. For the round microspheres, the microspheres produced by PES₁/DMF solutions have the best adsorption capacity, the binding amount to BPA can reach to 55.33 μmol/g.

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