齐鲁工业大学
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Preparation of Carboxyl Modified PS-PGMA-DVB Microspheres

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羧基修饰 PS-PGMA-DVB 微球的制备

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CONTENTS

Abstract

Chromatography is an important part of analytical science and is one of the most important separation methods in the field of analytical chemistry. Chromatography is often used for the separation, enrichment and detection of target components in mixtures. The chromatographic stationary phase is a key substance for the separation of liquid chromatographic components. The chromatographic stationary phase will directly affect the separation efficiency and the accuracy of the detection data, so the research and discovery of new chromatographic packing materials are very important and necessary. Nowadays, chromatographic stationary phases can be divided into three major categories according to their matrix materials: inorganic matrices, organic matrices and composite materials. Due to the chemical stability of organic polymers, their development and research have been popular. In this thesis, poly(glycidyl methacrylate-divinylbenzene) (poly(GMA-DVB) microspheres were prepared by seeded swelling polymerization method, and then the carboxylated poly(glycidyl methacrylate-divinylbenzene) polymer microspheres stationary phases were prepared by chemical bonding using p-aminobenzoic acid as the carboxylation reagent. The synthesized stationary phases were characterized by scanning electron microscopy and Fourier transform infrared spectrometer.

Keywords: Stationary phase; High-performance liquid chromatography; Polymer microspheres

Abstract in Chinese

摘要

色谱技术是分析化学研究的一个重要分支，经常被用于分离，富集与检测混合物中的目标组分。色谱填料作为液相色谱柱中的重要成分，其填充物的存在会直接影响到色谱柱的分离效果以及测定结果的准确度。所以，新型的色谱填料的研制与开发一直都是一个重要的研究课题。可将色谱填料分为三大类：无机基质填料、有机基质填料、复合填料。由于有机聚合物的化学稳定性，其开发和研究受到了广泛的关注。本文采用分阶段种子溶胀法合成了聚甲基丙烯酸甘油酯-二乙烯基苯聚合物微球，采用对氨基苯甲酸为羧基化试剂，采用化学键合方法，合成了羧基修饰聚甲基丙烯酸缩水甘油酯-二乙烯基苯聚合物微球色谱固定相，并利用扫描电镜和傅里叶交换红外光谱分析了所制备的聚合物微球色谱填料。

关键词：色谱固定相 高效液相色谱 聚合物微球

1 Chapter 1 Introduction

1.1 Overview of High-Performance Liquid Chromatography

Chromatography is currently one of the most widely used analytical tools and is increasingly used in the environmental, biochemical and pharmaceutical fields[1]. Chromatography originated from experiments on the separation of phytochromes carried out by the Russian chemist Tswett but did not attract much attention because the findings were published in less well-known journals. It was not until the 1930s when the German biochemist Kuhn applied Tswett's method to isolate carotenoids and won the 1938 Nobel Prize in Chemistry, that chromatography was generally noticed by scientists[2,3]. Depending on the stationary phase and mobile phase status, chromatographic methods can be divided into different categories, and liquid chromatography is the most important component of all chromatographic techniques. It can be said that, unless the molecular weight of the compound is too large, other compounds can be analyzed by high-performance liquid chromatography[4].

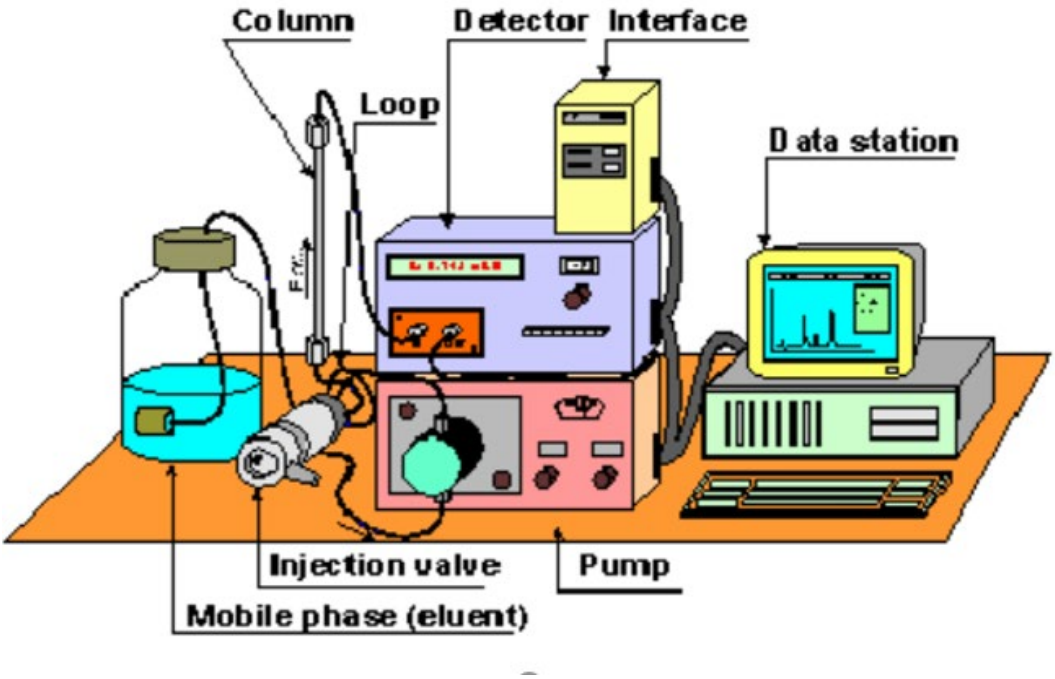

Figure 3.1 Schematic diagram of a modern high-performance liquid chromatography[5]

The structure of the modern high-performance liquid chromatography is shown in Figure 3.1, mainly composed of the high-pressure infusion system, injection system, column, detector and data processing system, 5 major systems, of which the column is the main component of the HPLC system, known as the "heart of chromatography". The flow of the HPLC system is summarized as follows: the separated sample is injected from the injection system, then brought into the column with the appropriate mobile phase, the different components are separated in the column and enter the detector in sequence, and finally, the data processing system acquires the chromatographic signal. [5,6]. Nowadays, high-performance liquid chromatography (HPLC) technology has made great progress, and even ultra-high performance liquid chromatography (UHPLC) technology has been developed [7].

1.2 HPLC Stationary Phase and Research Progress

The stationary phase has been regarded as the "heart" of chromatography, so the development of the stationary phase is one of the key factors affecting the development of chromatography. According to the physical morphology of the stationary phase, HPLC columns can be divided into packed columns and monolithic columns[8]. Packed columns mainly use micron-sized spherical particles as the stationary phase matrix and are filled into the HPLC column tube by a specific filling process [9]. The stationary phase matrix of the chromatography packed column can be divided into the inorganic matrix-based stationary phase and organic matrix-based stationary phase. Currently, the inorganic matrices used include silica gel, alumina, zirconia, etc[10]. The organic matrix is mainly organic polymer microspheres such as polystyrene and organic-inorganic hybrid microspheres [11]. Monolithic column matrix mainly includes inorganic silica, organic polymers and inorganic-organic hybrids and other monolithic materials [12].

The development of chromatographic stationary phase materials has gone through many important stages: initially, thin-shell packing was selected for high-performance liquid chromatography; then in the 1970s, with the discovery of high-pressure homogenization and column filling technology, particles with a particle size of less than 10μm

were commonly used as packing for chromatographic columns. Since the 1980s, HPLC stationary phase packing has made outstanding contributions to the progress of life science, making it gradually become a field of interest for researchers; after the 1990s, the field of biomedicine is developing more and more rapidly, therefore, various high-performance chromatographic stationary phases (including chiral columns) for pharmaceutical separation research are gradually appearing. Chromatographic stationary phases are further developing rapidly in the direction of solving environmental, pharmaceutical, etc[13,14]. Currently, chromatography researchers have developed thousands of different types of chromatographic stationary phases for different separation objects and separation modes [15]. Generally speaking, chromatographic instruments do not vary much, and the stationary phases are mainly selected according to the nature of the sample and the mobile phases are optimized to achieve the separation of different types of compounds, so the development of stationary phases is very rapid and the research on stationary phases is always evolving. At the same time, due to the development of science and technology, new analytical objects are emerging and the chromatographic techniques needed are constantly being improved, so it can be expected that the variety of liquid chromatography stationary phases will be very large [16].

1.3 Overview of Organic Polymer Microspheres

Polymer matrix stationary phases are mostly used with polymeric microspheres as the matrix. Compared with inorganic microsphere matrices, organic polymeric microsphere matrices have many advantages such as rich variety; easy chemical derivatization modification; wide pH tolerance range; strong loading capacity and high chromatographic capacity for separation samples and good compatibility for separation of biological macromolecules, so it has a broad application prospect in chromatography [17]. Staudinger and Heuer[18] first synthesized polystyrene-divinylbenzene (PS-DVB) organic polymer microspheres in 1934, and these polymer microspheres have attracted attention and modification studies since their appearance. The increase in the amount of cross-linking agent DVB makes the polymeric system exhibit a three-dimensional mesh-like three-dimensional structure.

Organic polymer microspheres with suitable cross-linkage (high mechanical strength, chemical stability, etc.) have been used for the preparation and application of high-performance liquid phase, size exclusion and ion chromatography stationary equivalents[19,20]. In addition to PS-DVB microspheres, polyethylene microspheres, polyacrylate microspheres, polystyrene microspheres and polymethacrylate microspheres are also used as stationary phase matrix for HPLC[21-23].

Polymeric microspheres are used in many fields such as agricultural science, industrial development, aerospace and the environment. Especially in recent years, the life sciences have developed rapidly and polymer microspheres are often used as the material of choice for immunoassays and tumour therapy due to their excellent biocompatibility and ease of modification. In addition, polymer microspheres are increasingly used as liquid chromatography fillers and ion chromatography fillers due to their easy to control particle size and high resistance to acids and bases[6].

1.4 Preparation of Polymeric Microspheres

At present, the preparation methods of organic polymer microspheres mainly include emulsion polymerization, suspension polymerization, dispersion polymerization, seed swelling polymerization and precipitation polymerization, etc [17].

（1） Emulsion polymerization method: It is the dispersion of monomers in water under the action of an emulsifier and then polymerization to obtain polymer microspheres. In the polymerization system of this method, water is usually used as a dispersant and sodium dodecyl sulfate is used as an emulsifier with initiators and monomers of different properties. Since the droplet particles after the formation of the emulsion are relatively small in size, the resulting polymer particles are also small in size [16]. The microspheres obtained by this method have good monodispersity, but the operation process is complicated and costly, and there is a large amount of emulsifier in the microspheres [17].

（2） Suspension polymerization method: the mechanism of the suspension polymerization method is generally one (or more) polymerizable monomers dispersed in the aqueous phase, through the drop addition of oil-soluble compounds to initiate polymerization, accompanied by vigorous mechanical stirring to make the monomer of the small liquid polymerization of free radicals [6]. The particle size of the microspheres produced by this method is between 10-1000um, with a wide particle size distribution, poor monodispersity, and stabilizer residues in the microspheres [17].

（3） Dispersion polymerization method：Dispersion polymerization method: The monomers are dissolved in the dispersion medium and then polymerized in the presence of dispersants after forming a stable dispersion system. This method avoids agglomeration between microspheres due to the addition of stabilizers in the reaction system, thus making it easy to prepare polymer microspheres with good monodispersity at the micron and submicron levels. For example, Tomomi Itoh et al [24] prepared polystyrene microspheres (0.5-2.1 μm) with narrow particle size distribution by dispersion polymerization. The particle size of microspheres made by this method is between 0.1-10 μm, with good monodispersity and fast polymerization, but dispersant will remain in the microspheres [25-27].

（4） Seed swelling polymerization method: First, the seed microspheres with small particle size and good monodispersity are prepared by using dispersion polymerization or emulsion polymerization; second, the seed microspheres are swollen in the reaction system by adding polymerization monomer, a cross-linking agent and pore-making agent; third, the swollen seed microspheres are polymerized by increasing the temperature, and the stabilizer is added to ensure that the final obtained microspheres with large particle size have good morphology[28]. According to the preparation process, the seed swelling method is generally divided into one-step swelling, two-step swelling and multi-step swelling methods.

2 Chapter 2 Experiment

2.1 Experimental reagents and instruments

Table 4.1 Experimental drugs

Reagent name	Specification	Manufacturer
2,2'-Azobis(2-methylpropionitrile)	Analytical purity	Shanghai Maclean Biochemical Technology Co., Ltd
Ethanol absolute	Analytical purity	Tianjin Fuyu Fine Chemical Co., Ltd
Styrene	Analytical purity	Sinopharm Chemical Reagent Co., Ltd
Dibutyl phthalate	Analytical purity	Tianjin Kemiou Chemical Reagent Co., Ltd.
Toluene	Analytical purity	Yantai Yuandong Fine Chemicals Co. Ltd
Sodium dodecyl sulfate（SDS）	Analytical purity	Sinopharm Chemical Reagent Co., Ltd
Glycidyl methacrylate	Analytical purity	Shanghai Aladdin Biochemical Technology Co., Ltd
Divinylbenzene（DVB）	Analytical purity	Anhui Zesheng Technology Co., LTD
Benzoyl peroxide（BPO）	Analytical purity	Tianjin Kemiou Chemical Reagent Co., Ltd.
Isopropyl alcohol	Analytical purity	Tianjin Fuyu Fine Chemical Co., Ltd
4-aminobenzoic acid	Analytical purity	Sinopharm Chemical Reagent Co., Ltd
Methanol	Analytical purity	Tianjin Fuyu Fine Chemical Co., Ltd

Table 4.2 Main Experimental Equipment

Equipment name	Model	Manufacturer
Vacuum Pump with Circulated Water System	SHZ-95B	Shanghai Jinfu Experimental Equipment Co., LTD
Scanning electron microscope（SEM）	Regulus 8220	Hitachi Limited
FTIR Spectroscopy	Nicolet™ iS50	Zhongchuan Electric Technology Co., LTD
Centrifuges	TG16-WS	Hunan Xiangyi Laboratory Instrument Development Co. LTD
Analytical Balance	FA1004	Shanghai Shunyu Hengping Scientific Instrument Co., LTD
Mechanical stirrer	JB90-SH	Shanghai Specimen model Factory
Digital thermostatic heating sets	ZNHW-II	Zhengzhou Ketai Experimental Equipment Co., LTD
Digital display thermostatic water baths	HH-2	Changzhou Deco Instrument Manufacturing Co., LTD
Vacuum drying oven	DZF-6020	Gongyi Yuhua Instrument Co. LTD

2.2 Pre-treatment of reagents

2.2.1 Purification of 2,2'-Azobis

First, a saturated solution of AIBN in anhydrous ethanol is prepared in an 80 °C water bath. After removal of insoluble impurities by filtration at atmospheric pressure, the filtrate was transferred to a conical flask and placed in a refrigerator at -10 °C for crystallization. After complete crystallisation (12 h in the refrigerator) the crystals are filtered using a vacuum filter. The filtered crystals were dried in a vacuum oven at 40 °C

for 12 h. After drying, the solids were transferred to a light-proof airtight container and stored in a refrigerator at 4 °C for storage.

2.3 Preparation of polystyrene microspheres

（1）1 g of polyvinylpyrrolidone was added to a 250 mL four-necked flask, 80 mL of anhydrous ethanol was added as a solvent, and the solution was then dissolved by sonication for 3 min. An electric stirring mechanism (heated by a heating jacket with a thermocouple) was installed with a reflux condenser.

（2）10 ml of styrene was added to the above flask as a monomer, followed by 0.44 g of AIBN as an initiator. The reaction is carried out under nitrogen protection and mechanical stirring (the glass tube introducing the nitrogen is inserted below the solution level and 1-2 bubbles per second are desirable) at a temperature of 70°C and 200-300 rpm for 24h.

（3）After completion of the 24-hour polymerisation reaction, the solution was first waited for the temperature to drop to room temperature; the mixture was then transferred to a centrifuge for separation by high-speed centrifugation (> 5000 rpm) and after completion of centrifugation, the solid was washed three times with ethanol, water and ethanol. The solids were then vacuum dried, weighed, sealed and set aside.

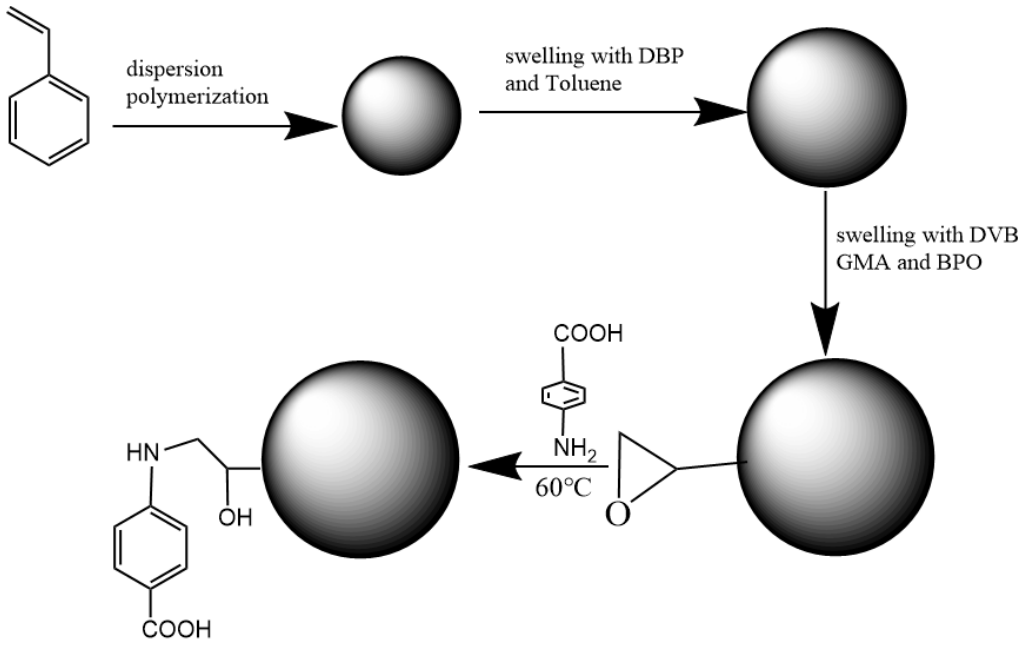

Figure 4.1 Schematic diagram of the preparation of carboxyl modified PS-PGMA-DVB microspheres

2.4 Preparation of PS-PGMA-DVB microspheres

（1）0.26 g of PS microspheres were added to a 250 mL four-neck flask with 10 mL of distilled water as a dispersant, the solution was then sonicated for 5 min and the dispersion was maintained with high speed stirring by an electric stirring mechanism fitted with a reflow condenser.

（2）1.2 mL of dibutyl phthalate and 1.2 mL of toluene were added to a 50 mL beaker and 20 mL of 0.375 wt% sodium dodecyl sulfate (SDS) solution was added to the beaker, which was then sonicated and then moved to the dispersion system in step (1) and swollen at 30 °C for 24 h with 300 rpm stirring.

（3）30 mL of 0.25 wt% SDS solution was added to a 50 mL beaker, then 0.6 mL of glycidyl methacrylate, 2 mL of divinylbenzene and 0.12 g of benzoyl peroxide were added to the beaker. The solution was then sonicated and added to the dispersion system

of step (1) and swollen at 30 °C and 300 rpm for 24 h; this step and the following required nitrogen protection.

（4）3.5 mL of a 10 wt% polyvinyl alcohol solution was added to the above flask and then the polymerisation reaction was carried out at 70 °C for 24 h. After the reaction was complete, the solution was naturally cooled to room temperature.

（5）After the solution was cooled to room temperature, the solution was transferred to a centrifuge for high-speed centrifugation. The centrifuged solid was washed three times with distilled water, and ethanol and then the solid was placed in a vacuum drying oven to dry, then weighed, sealed and set aside.

2.5 Preparation of BA-PS-PGMA-DVB microspheres

The carboxylation-modified glycidyl methacrylate-divinylbenzene polymer microspheres stationary phase was produced by direct reaction of glycidyl methacrylate-divinylbenzene polymer microspheres with p-aminobenzoic acid.

（1）3.0 g of PS-PGMA-DVB microspheres were added to a 250 mL 4-neck flask followed by 50 mL of isopropanol as a dispersant and sonicated for 3 min. 0.4 g of p-aminobenzoic acid was then added and mechanically stirred at 120 rpm for 5 h at room temperature.

（2）The reaction was carried out at 60 °C and 120 rpm with mechanical stirring for 24 h. At the end of the reaction, the reaction was cooled down to room temperature.

（3）After cooling to room temperature, the solution was transferred to a centrifuge for separation by high-speed centrifugation and the solids were washed three times with methanol, water and anhydrous ethanol and then transferred to a vacuum drying oven for drying. After drying the solid was weighed, sealed and set aside.

3 Chapter 3 Results and Discussion

3.1 FT-IR

The FT-IR spectra of polystyrene (PS) microspheres, polyglycidyl methacrylate-divinylbenzene (PS-PGMA-DVB) microspheres and carboxyl modified polyglycidyl methacrylate-divinylbenzene (BA-PS-PGMA-DVB) microspheres stationary phases between 500 and 4000 wave are shown as figure 5.1. The FTIR spectra indicate the following information:

The absorption peak near 3024 cm^{-1} can be attributed to the stretching vibration of the C-H bond; the absorption peak near 2919 cm^{-1} is the antisymmetric stretching vibration of methylene, these two peaks indicate that the first product is a PS microsphere; the absorption peak near 1722 cm^{-1} is the vibrational absorption peak of the C=O double bond in glycidyl methacrylate; the absorption peak near 1120 cm^{-1} is the stretching vibration absorption peak of O-C-O in the ester group; the absorption peak near 1078 cm^{-1} is the characteristic absorption of the epoxy group, and the absorption peaks near 1605 cm^{-1} and 1450 cm^{-1} are the characteristic absorption peaks of the benzene ring[5,17].

In comparison with FT-IR spectroscopy of the PS microspheres, the second product showed an increase in the number of peaks, mainly 1722 cm^{-1}, 1120 cm^{-1} and 1078 cm^{-1}, corresponding to the vibrational absorption peaks of the C=O double bond in the glycidyl methacrylate; the stretching vibrational absorption peak of the O-C-O in the ester group; and the characteristic absorption of the epoxy group, which could prove that the final product was PS-PGMA-DVB microspheres.

The variation in the peak position of the third product is mainly reflected in the absorption peaks near 1605 cm^{-1} and 1450 cm^{-1}, which are characteristic of the benzene ring, In addition, the carboxyl-modified glycidyl methacrylate-divinylbenzene microspheres showed enhanced absorption near 3431 cm^{-1} [5]compared to the glycidyl methacrylate-divinylbenzene microspheres, which can be attributed to the stretching vibration of the carboxyl group in the p-aminobenzoic acid. The results indicate that the preparation of

the glycidyl methacrylate-divinylbenzene microspheres was successful and that the p-aminobenzoic acid has been successfully bonded to the surface of the microspheres.

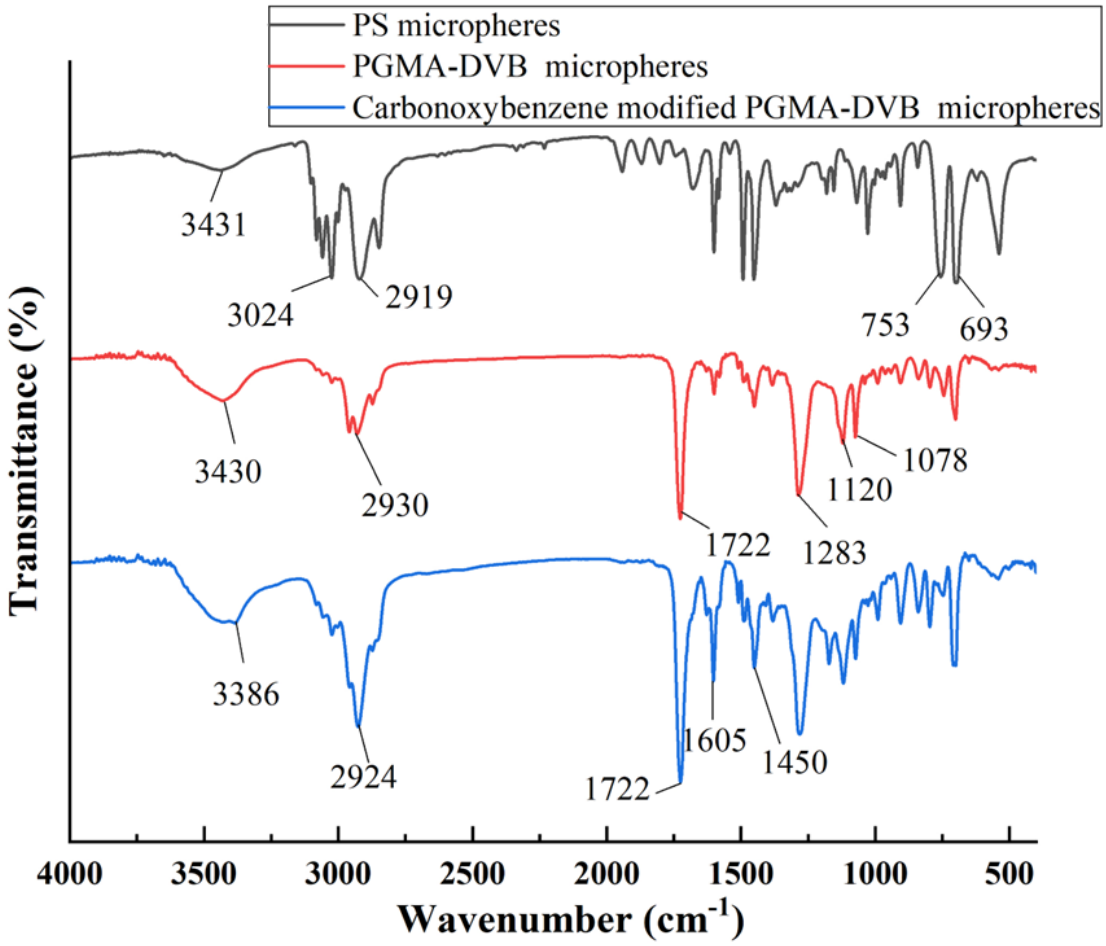

Figure 5.1 FT-IR spectroscopy of PS microspheres, PS-PGMA-DVB and BA-PS-PGMA-DVB microspheres

3.2 Scanning Electron Microscope

Two attempts were made in this experiment, the first dividing the 24h stirring into 12h plus 12h discontinuous stirring and the second for 24h continuous stirring. A scanning electron microscope was used to observe the morphology of polystyrene seed microspheres and poly(glycidyl methacrylate-divinylbenzene) microspheres, respectively.

The scanning electron microscope image of the product obtained by continuous stirring is shown in Figure 5.2, the results show that the polystyrene microspheres have good

spherical morphology and monodispersity, and that the particle size of the glycidyl methacrylate-divinylbenzene microspheres prepared by the seed swelling method is significantly larger, in addition to the obvious pores that can be seen on the surface of the glycidyl methacrylate-divinylbenzene microspheres.

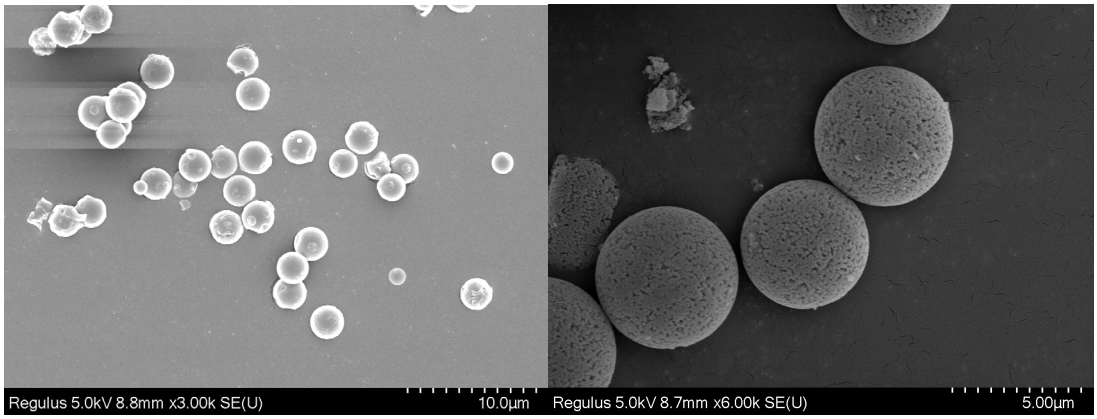

Figure 5.2 Scanning electron microscope image of PS and carboxyl modified PS-PGMA-DVB microspheres (continuous stirring)

The scanning electron microscope image of the product obtained by discontinuous stirring is shown in Figure 5.3. The pictures show that the surface of the discontinuously stirred product has more debris and the surface of the PS microspheres is not very smooth and there are more failed products that do not become microspheres.

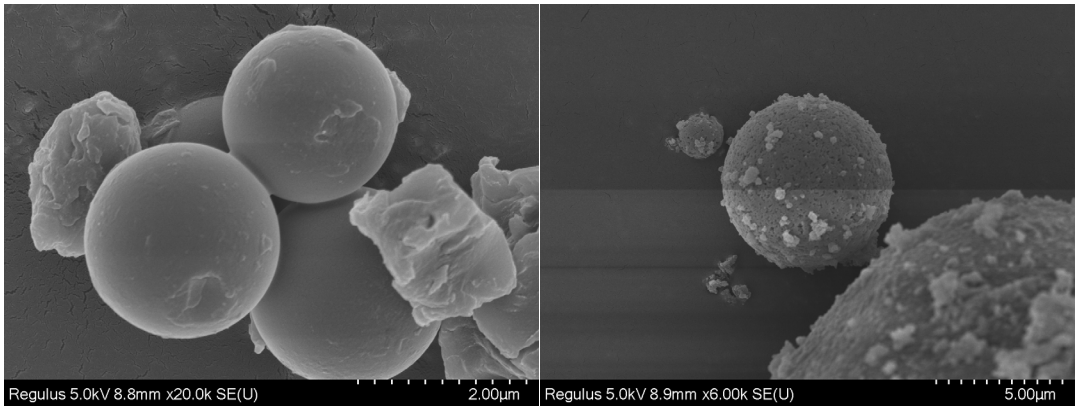

Figure 5.3 Scanning electron microscope image of PS and carboxyl modified PS-PGMA-DVB microspheres (discontinuous stirring)

4 Chapter 4 Conclusion

Chromatographic columns as an important component of high-performance liquid chromatography (HPLC), have been applied to various fields of analytical chemistry with the development of chromatographic techniques and analytical instruments, and therefore improving the performance of column packing has been a very important part of chromatographic research. In this thesis, the synthesis of PS microspheres is described in detail, and then the synthetic modification of PS microspheres is explored. Carboxyl modified poly(glycidyl methacrylate-divinylbenzene) microspheres were prepared by the seed swelling method and characterized by Fourier exchange infrared spectroscopy and scanning electron microscope. The preparation of carboxyl modified PS-PGMA-DVB microspheres was successful as shown by SEM and FTIR results

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