Application of Concentrated Emulsion Polymerization for Preparation of Ion-Exchange Chromatography Columns

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ABSTRACT: Concentrated inverse emulsion polymerization was used for making chromatography columns [based on crosslinked polystyrene divinylbenzene (PS–DVB)] with pore sizes less than 10 μm. For application of these columns in ion-exchange chromatography, the sulfonation process was performed by concentrated sulfuric acid. According to X-ray fluorescence analysis and ASTM D2187-94 standard test method, the total capacity of resins (sulfonated PS–DVB) increased with increasing time. To obtain high-capacity resins, the sulfonation process was carried out over two steps. The optimum sulfonation time for the first and second sulfonation steps was 24 and 48 h, respectively. By increasing the DVB content, the capacity of resins passed through a maximum; thus the optimum amount of DVB, as crosslink-ing agent in the sulfonation process, was 22.5%. The structure of columns was analyzed by scanning electron microscopy (SEM). SEM evaluations showed that the porous structure of PS–DVB resin was maintained intact after the sulfonation steps. According to DSC–thermal gravimetry thermograms, it was confirmed that the residual monomer concentration after polymerization process was negligible. Also, the PS–DVB resins exhibit thermal stability up to 300°C and this quantity would increase with increasing amount of DVB weight percentage. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2973–2979, 2004

Key words: inverse emulsion polymerization; ion exchangers; styrene; sulfonated PS–DVB; latices

INTRODUCTION

Concentrated emulsion polymerization has been used for preparing precursors for latices of homopolymers, copolymers, and tough polymers. They have also been used to prepare conductive polymers, composites, composite membranes, microsponge molecular reservoirs, polymer-supported quaternary onium salts, polymer-supported palladium complexes, and quaternary onium salt polymer-supported enzymes or cells. In contrast to the conventional emulsions, concentrated emulsions have a large volume fraction of dispersed phase, greater than 0.74 and as large as 0.99.[1–10] It has a pastelike appearance and behavior. When the volume fraction of the continuous phase is sufficiently small, the dispersed phase is composed of polyhedral cells separated by thin films of continuous phase. The concentrated emulsions are prepared by dropwise addition of the dispersed phase to a small amount of a continuous phase containing a surfactant. As well established, experimental observations have indicated that the phase in which the surfactant is soluble constitutes the continuous phase of an emulsion. The adsorption of surfactant on the interface between the two media of the emulsion is responsible for its kinetic stability. The concentrated emulsions have attracted our attention as a possible pathway for polymerization for a number of reasons:

1. The ordered organization of surfactant molecules at the interface between the two media may organize the monomers in its vicinity and thus accelerate the rate of conversion.
2. Because of the presence of the surfactant layer, the reduced mobility inside the cells could generate an earlier gel effect, which would lead to the delay in the bimolecular termination reaction. Hence, the higher molecular weight is expected to be higher if the polymerization occurs in a concentrated emulsion than in bulk.
3. The polymerized system maintains the structure of the emulsion precursor.
4. A better control of the size of latices can be made by controlling the size of the cells of concentrated emulsion, using suitable surfactants, ionic strengths, and pH values. Hence the splitting of a bulk system into a large number of small, independent cells may have favorable effects. In addition, a concentrated emulsion can be polymerized to generate either latices, a porous medium, or a composite.

The aim of this research work was to prepare chromatography columns by using the concentrated emulsion polymerization technique. Also this kind of polymerization is used especially for making ion-ex-

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TABLE I
Applied Formulations for Preparation of Resins with Different DVB Content

Sample	St (g)	DVB (g)	Span80 (g)	AIBN (g)	Cummene hydroperoxide (g)	Water (g)
DVB 2.07%	12.06	0.25	1.34	0.07	0.07	62
DVB 5.2%	9.3	0.485	1.07	0.07	0.07	49
DVB 7.08%	12.415	0.88	1.32	0.07	0.07	67
DVB 9.73%	14.49	1.41	1.56	0.07	0.07	64
DVB 16%	10.75	1.72	1.34	0.07	0.07	63
DVB 20%	13.29	2.67	1.6	0.07	0.07	64
DVB 30%	13.95	4.21	1.81	0.07	0.07	73
DVB 36.7%	9.68	3.56	1.66	0.07	0.07	67
DVB 50%	10.70	10.70	2.14	0.07	0.07	85

change chromatography columns. The so-called columns are applicable for separation of different compounds such as inorganic cations and anions, amino acids, proteins, peptides, phenols, vitamins, amines, and organic acids and bases.[11]

EXPERIMENTAL

Materials

The following chemicals were used:

- Styrene (monomer; Merck, Darmstadt, Germany)
- Divinyl benzene (crosslinking agent; Merck)
- Span 80 (emulsifier; Merck)

The following chemicals were used for ion-exchange capacity determination of sulfonated crosslinked polystyrene divinylbenzene (PS–DVB) resins:

AIBN (Fluka, Buchs, Switzerland)

Cummene hydroperoxide (initiator; Aldrich, Milwaukee, WI)

Sulfuric acid [95–97% (w/w), sulfonating agent; Merck]

Phosphor pentoxide (catalyst for sulfonation step; Merck)

Dichloroethane (solvent; Merck)

Hydrochloric acid (Merck)

Sodium chloride (Merck)

Sodium hydroxide (Merck)

Apparatus

Thermal analysis [DSC–thermal gravimetry (TG)] of resins was carried out on an STA 625 analyzer (Polymer Labs, Poole, UK) in N_2 at a heating rate of 10°C/min to measure thermal stability and residual monomer concentration of the produced resins. X-ray fluorescence (XRF) measurements were performed using an energy-dispersive XRF spectrometer (Microanaly-
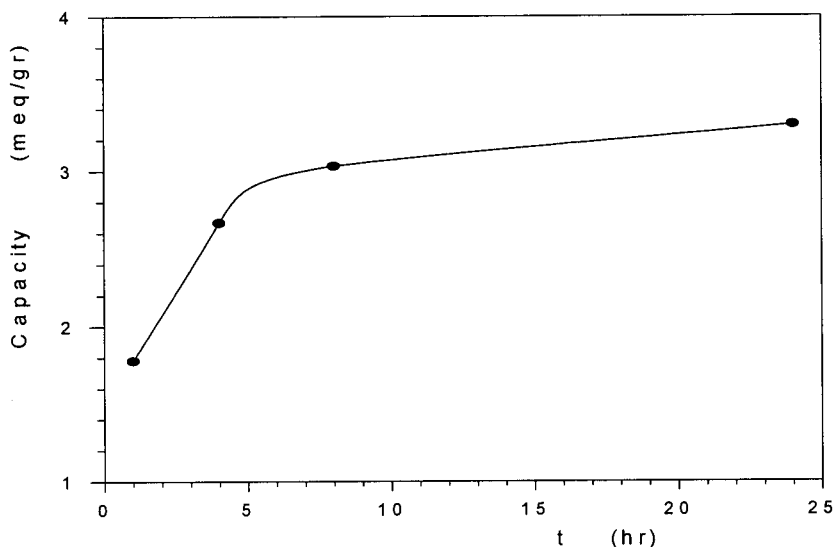

Figure 1 Variation of ion-exchange capacity with time in sulfonated PS–36.7%DVB (first sulfonation step).

TABLE II
X-ray Florescence Characteristics of
Sulfonated PS–37.5%DVB

Content	Time (h)			
	1	4	8	24
Sulfur, %	<1.4722	<1.5102	2.3723	2.6491
Ferrous, %	386 ppm	416 ppm	531 ppm	158 ppm
Total	0.0386	0.0416	2.7022	2.3881

sis Group, model XR 300, Oxford Instruments, Oxford, UK) according to ASTM D2187-94 standard test method, which was used to determine the degree of sulfonation and capacity of the sulfonated resin. The porous structure of PS–DVB resins was studied using a scanning electron microscope (SEM; Cambridge Model S 360, Cambridge, UK).

Procedure for preparation of concentrated emulsion

A 250-cm^3 three-neck round-bottom flask was filled with a magnetic stirrer and thermometer. To prepare an inverse emulsion of water in monomer solution, the flask was initially charged with styrene, divinylbenzene, emulsifier, and initiators. Then double-distilled water was added dropwise to this solution, with continuous stirring. The concentrated emulsion containing 84% dispersed phase was prepared and transferred into glass tubes by means of vacuum. The packed tubes were closed and polymerization was performed in the oven for 48 h at 50°C. Then the water phase or dispersed phase of the PS–DVB resin was removed from the oven according to the following steps:

- 10 h at 70°C
- 5 h at 80°C
- 5 h at 105°C
- 5 h at 140°C

Applied formulations are listed in Table I.

Ion-exchange capacity measurements

The capacity of sulfonated PS–DVB resins was measured according to the ASTM D2187-94 standard test method.[12] The sulfonated resins were dried in an oven for 16 h at 105°C. A weighed portion (W) of dried sulfonated PS–DVB resin was charged into an Erlenmeyer flask equipped with stirrer, containing 0.1N sodium hydroxide in 50% (w/w) sodium chloride solution in water. The reaction mixture was kept under these conditions for 16 h, and its capacity was determined by titration with 0.1N hydrochloric acid in the presence of phenolphthalein as indicator. The capacity of resin was calculated in term of milliequivalents per gram according to the following equation:

$$C = \frac{V \times 0.1 - V_a \times 0.1}{W}$$

where W is the weighed portion of sample (g), V_a is the volume of acid consumed (cm^3), C is the capacity of resin (meq/g), and V is the volume of the aliquot portion of solution (cm^3).

Sulfonation process

The packed columns containing different amounts of DVB were washed with dichloroethane under vacuum
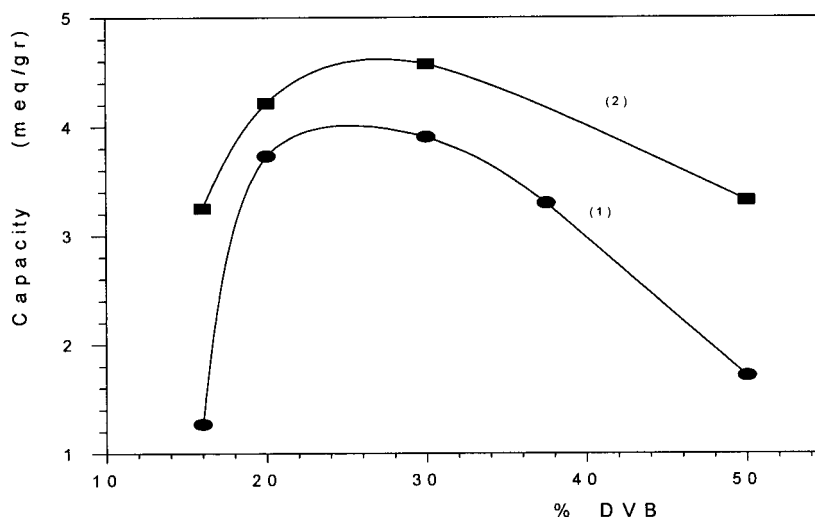

Figure 2 Capacity variations of sulfonated PS–DVB resin with various DVB content: (1) first step of sulfonation; (2) second step of sulfonation.
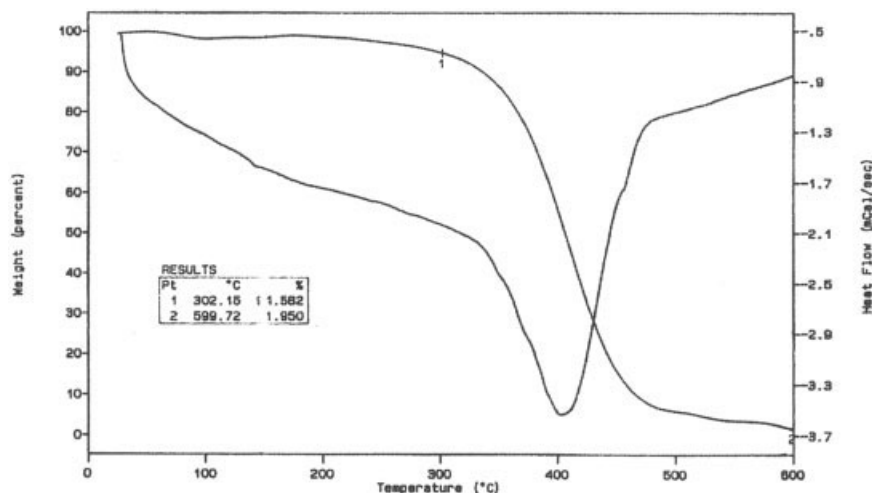
Figure 3 DSC–TG thermogram of PS–20%DVB, in N_2, at a heating rate of 10°C/min.

at room temperature to remove the emulsifier and cause swelling of the PS–DVB resin.

After 2 h, the concentrated sulfuric acid (H_2SO_4– 5%P_2O_5 solution) was passed through the column.[13–15] To close the packed columns, two rubber septums were placed on the top and bottom of tubes. The sulfonation step was carried out by placing the tubes in an oven and kept for the required time at 50°C. The columns were washed carefully with 80, 50, and 25% (w/w) sulfuric acid, respectively, and then with distilled water to remove traces of sulfuric acid.[15] Finally, distilled water was passed through the columns until the drained water had a pH of 6. The columns were subsequently dried for 1 week at 70°C and then for 24 h at 100°C, respectively.

RESULTS AND DISCUSSION

To choose the optimum sulfonation time and determine the role of crosslink density in the sulfonation process, first PS–DVB resins with various DVB content were prepared, and then the sulfonation step was carried out using a typical method, mentioned above. Experimental observations show that working with resins containing DVB content less than 16% is not suitable for the sulfonation step because of poor mechanical properties of the resin structure.

On the other hand, the flow rate of sulfuric acid through the column would decrease, because of swelling, which leads to small pore sizes of resins. Therefore, because of the tough resin structure, the resin would shrink and emerge through the tube. This kind of resins can be used in reverse chromatography.[16,17] To avoid these problems, we focused our attention on preparing resins with higher DVB content.

The sulfonation step was carried out on a PS– 36.7%DVB resin. As may be seen in Figure 1, the capacity of sulfonated resin increases with time and finally reaches a constant amount after 8 h. So in this stage, the optimum sulfonation time was selected to
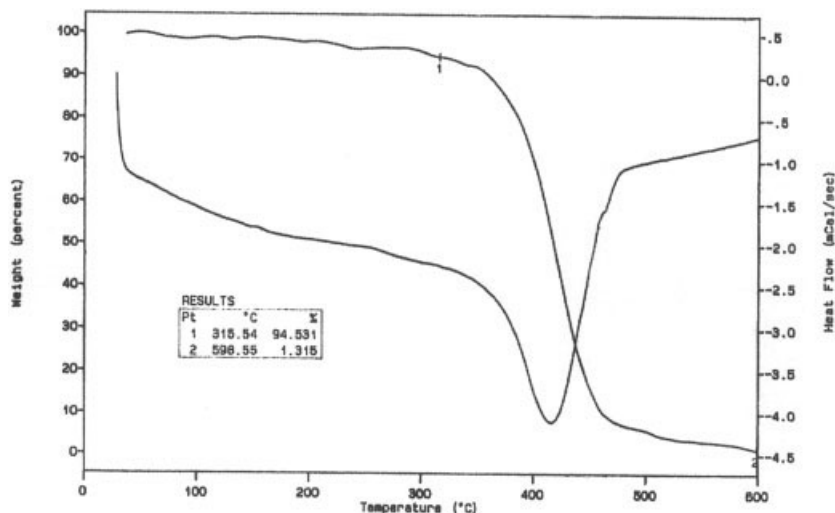

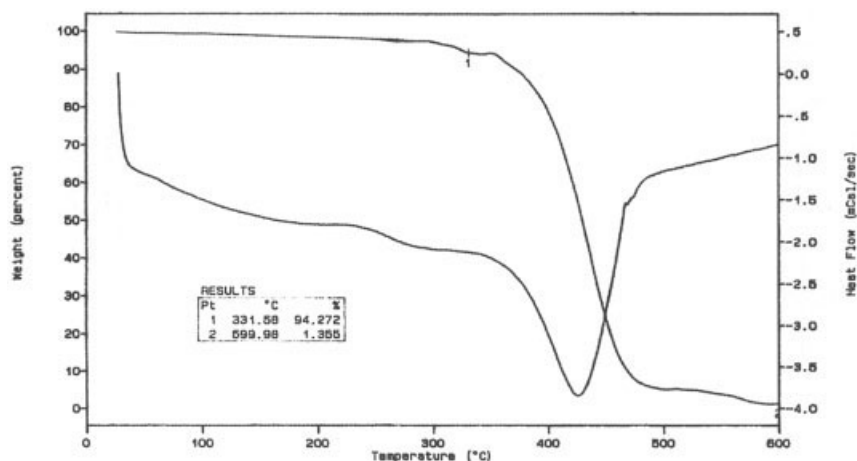**Figure 4** DSC–TG thermogram of PS–30%DVB, in N_2, at heating rate of 10°C/min.

Figure 5 DSC–TG thermogram of PS–50%DVB, in N_2, at a heating rate of 10°C/min.

be 24 h. XRF results show that the degree of sulfonation would increase with time. As the results (Table II) show, the instrument can detect the sulfur content of sulfonated resins during 8- and 24-h sulfonation, but it is not detectable after 1 and 4 h.

The role of DVB as crosslinking agent was studied in the sulfonation process (Fig. 2). A plot of capacity versus %DVB indicates that the degree of sulfonation increases with increasing %DVB of resins (Fig. 2), until a maximum point at 22.5%DVB content, beyond which the degree of sulfonation decreases with increasing DVB content, in which the polystyrene chains have freedom and ability to change their conformations easily. In this case when two phases—the PS–DVB resin and polar sulfuric acid—come into contact with each other, they tend to repel each other because of high surface tension at the interface between the two phases. Therefore to achieve a high-capacity resin, the sulfonation time should be more than 24 h. By increasing the DVB content, the resin structure would be less tough and so conformational changes of poly-

meric chains are more difficult. As a result, the contact of PS–DVB and sulfuric acid would improve and, finally, capacity of the resin would increase. Also in the case of high DVB content, the degree of sulfonation decreases because of reduction in suitable and accessible sites for the sulfonation process. To evaluate the sulfonation process, the sulfonated PS–DVB was washed with distilled water and dried. Then the second sulfonation step was carried out. As seen in Figure 2, the degree of sulfonation in the second sulfonation step has increased and capacity behavior is like that of the first sulfonation step. The resin capacities had higher values in the second sulfonation step than those in the first sulfonation step. The higher-capacity values in the second sulfonation step are attributed to the following reasons:

- The second sulfonation step was performed at 48 h.
- After the first sulfonation step, the resin had a more polar structure and surface tension at the
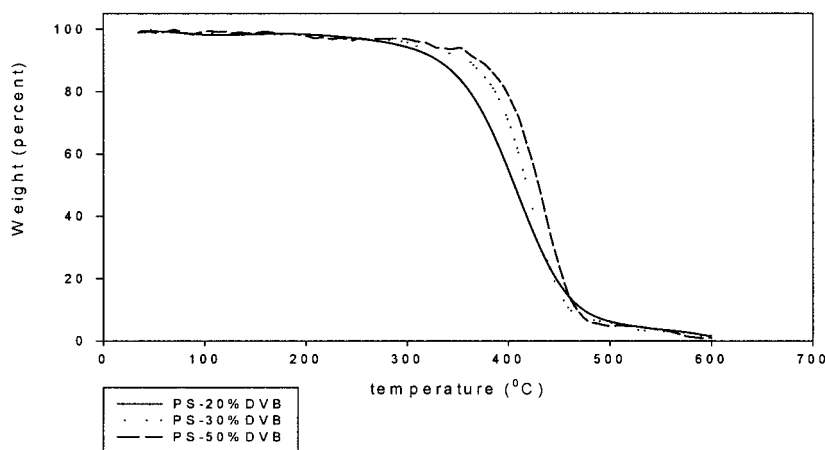

Figure 6 TG thermogram of PS–DVB resin versus temperature, in N_2, at a heating rate of 10°C/min.

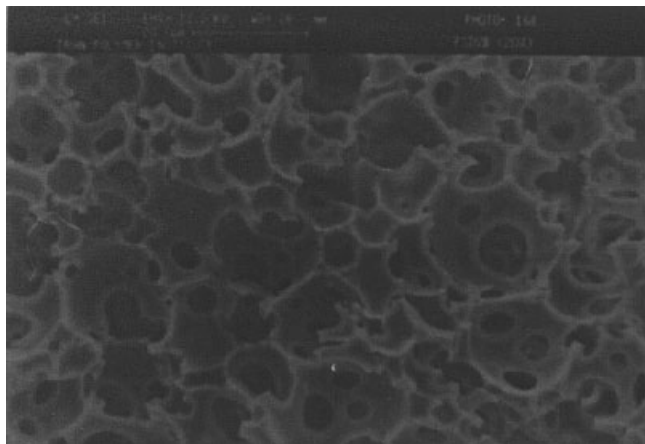**Figure 7** SEM micrograph of PS–20%DVB at ×1000 magnification.

Figure 9 SEM micrograph of PS–50%DVB at ×1000 magnification.

interface between acid and resin was reduced. Therefore the contact between two phases was thereby increased, leading to later facile sulfonation and higher capacity.

- Formation of ionic clusters is another factor affecting the capacity, causing it to decrease. In other words, by increasing the degree of sulfonation, the electrostatic forces in the resin became appreciable. As the degree of sulfonation increased, the negative charges on the polymeric chains as well as the electrostatic repulsion forces increased, thereby causing the rate of diffusion to decrease and finally stopping the sulfonation reaction.

Thermal analysis

Because the sulfonated PS–DVB resins are used for column chromatography, these resins should have specific characteristics such as high thermal stability, negligible residual monomer, and porous structure.
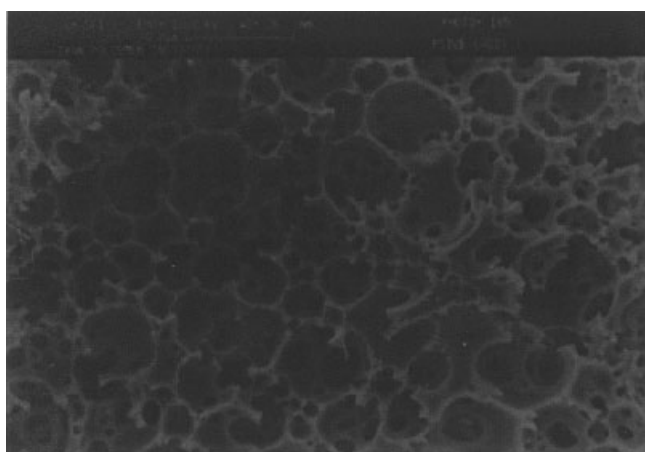
Various methods were used to study thermal analysis: differential scanning calorimetry (DSC) and thermal gravimetry (TG) were used to determine the thermal stability and residual monomer content. It may be seen from Figures 3–6 that there is no weight loss attributed to heating to decomposition temperature. Also, there was no exothermic peak in the DSC thermogram up to the decomposition temperature. Therefore, the residual monomer content in synthesized resins is negligible, and thermal stability of resins is up to about 300°C. It is to be noted that the small deviation from linearity in the TG thermogram is attributed to the presence of solvent and water in resin and instrumental error (buoyancy forces, etc.).

SEM analysis

We studied the porous structure of PS–DVB resins before and after the sulfonation step by SEM. On the basis of microscopic observations, it is concluded that:
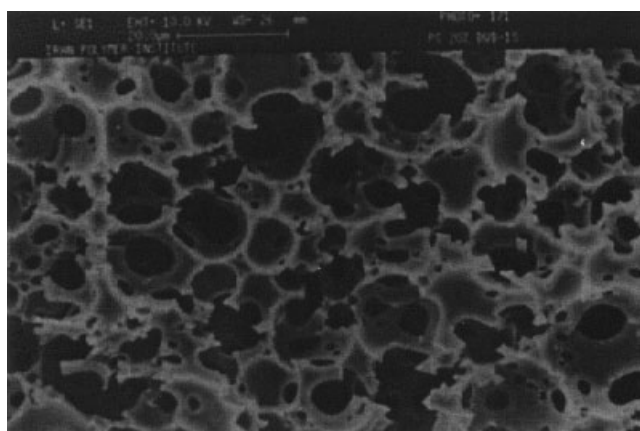

Figure 8 SEM micrograph of PS–30%DVB at ×1000 magnification.

Figure 10 SEM micrograph of PS–20%DVB at ×1000 magnification (after the first sulfonation step).

- The prepared resins have a porous structure with pore sizes less than 10 μm.
- The presence of large pores in the resin are representative of dispersed-phase particles, which are removed during the drying process. Also, the small pores on sidewalls of the dispersed phase are attributed to water vapor pressure.
- During and after the sulfonation process, the porous structure of resins was preserved (Figs. 7–12).

CONCLUSIONS

In this article, the concentrated emulsion was prepared by dropwise addition of double-distilled water to a solution containing styrene, divinyl benzene, emulsifier, and initiators. Then the continuous phase of prepared emulsion (i.e., monomer) was polymerized to generate PS–DVB resin. The PS–DVB resin was sulfonated after completion of the concentrated emulsion polymerization by concentrated sulfuric acid; during this step, the sulfonated PS–DVB resin was produced.

Results of SEM, DSC–TG, and XRF analyses, used to evaluate the produced resins, can be summarized as follows:

- Concentrated emulsion polymerization can be used to make porous columns with pore sizes less than 10 μm.
- According to XRF analysis and ASTM D2187-94 standard test method, the optimum sulfonation time is 24 h (first sulfonation step).
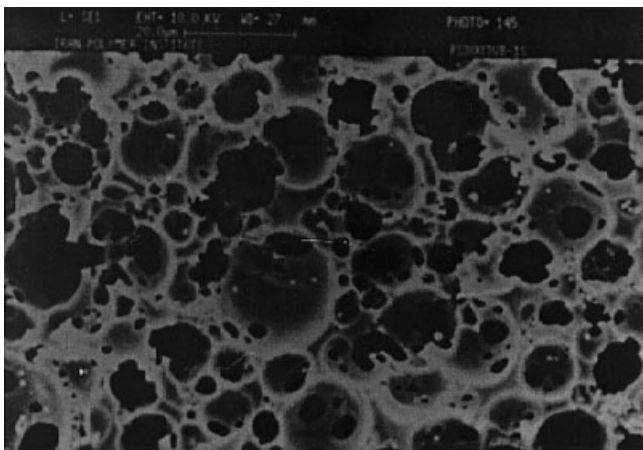

Figure 11 SEM micrograph of PS–30%DVB at ×1000 magnification (after the first sulfonation step).

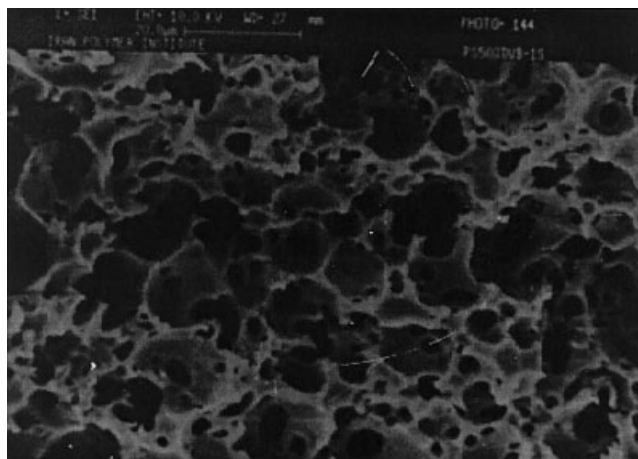**Figure 12** SEM micrograph of PS–50%DVB at ×1000 magnification (after the first sulfonation step).

- The optimum PS/DVB ratio for the sulfonation step is 77.5/22.5.
- After sulfonation processes the PS–DVB resin porous structure is preserved.
- According to DSC–TG thermograms, the thermal stability of synthesized resin is about 300°C and would increase with increasing DVB concentration.
- The DSC–TG analysis shows that residual monomer concentration is negligible.

References

1. Lissant, K. J. J Colloid Interface Sci 1966, 22, 492.
2. Lissant, K. J.; Mayhan, K. G. J Colloid Interface Sci 1972, 42, 201.
3. Lissant, K. J.; Peace, B. W.; Wu, S. H.; Mayhan, K. G. J Colloid Interface Sci 1974, 47, 416.
4. Princen, H. M.; Aronson, M. D.; Moser, J. C. J Colloid Interface Sci 1980, 75, 246.
5. (a) Princen, H. M. J Colloid Interface Sci 1985, 91, 160; (b) Princen, H. M. J Colloid Interface Sci 1983, 105, 50.
6. Princen, H. M.; Kiss, A. D. J Colloid Interface Sci 1986, 112, 427.
7. Kraynick, A. M.; Hansen, M. G. J Rheol 1986, 30, 409.
8. Ruckenstein, E.; Ebert, G.; Platz, G. J Colloid Interface Sci 1989, 133, 432.
9. Bhakta, A.; Ruckenstein, E. Langmuir 1995, 11, 1486.
10. Bhakta, A.; Ruckenstein, E. Langmuir 1995, 11, 4642.
11. Hancock, W. S. CRC Handbook of HPLC for the Separation of Amino Acids, Peptides and Proteins, Vol. II; CRC Press: Boca Raton, FL, 1984; pp. 23–43, 287–300, 357.
12. ASTM D2187-94. Annu Book ASTM Stand 1994, Vol. 11.02.
13. Djalilian, M. Sulfonation of Styrene Divinylbenzene; Iran Polymer Institute: Tehran, Iran, 1995.
14. Vink, H. Makromol Chem 1981, 182, 279.
15. Kucera, F.; Jancar, J. Polym Eng Sci 1998, 38, 783.
16. Clarke, J. T. U.S. Pat. 2,731,411, 1956.
17. Ahuja, S. Chromatography and Separation Chemistry: Advancements and Developments; American Chemical Society: Washington, DC, 1986; p. 83.