Monosized macroporous resins with epoxy groups and their structure and gel chromatography properties

JIN Chao, YANG Yanguo, ZHAO Zhongzhang, YANG Shuming, TIAN xiulan & SU Tiansheng

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China
Correspondence should be addressed to Su Tiansheng

Abstract The monosized macroporous-polymer beads based on cross-linked poly(glycidyl methacrylate) have been synthesized by a new improving method——combining dispersion polymerization with swelling polymerization and polymeric solution porogens. The structure and gel chromatographic properties of the resins have been studied. The resins as matrix materials of various types of high performance liquid chromatography (HPLC) packings possess excellent separation properties

Keywords: cross-linked poly(glycidyl methacrylate) beads, monosized macroporous resins, HPLC packings.

Monosized macroporous polymer beads as special function materials have been seriously studied for a long time in polymer science and relevant application fields. This type of resins used as HPLC packings and their matrix materials possess excellent chromatographic properties especially favorable for improving column efficiency and permeability. In recent years, with progress of synthesized technology, some resins of this kind of physical structure, e.g. cross-linked polystyrene beads[1—3] and cross linked polymethacrylate beads[4,5], have been applied to different HPLC techniques in succession, thus leading to the rapid development of new packings.

This note presents the monosized macroporous polymer beads based on cross linked poly(glycidyl methacrylate). The resins were prepared by a new improving method——combining dispersion polymerization with swelling polymerization and polymeric solution porogens. The structure and gel chromatographic properties of the resins were studied.

1 Experimental

(i) Synthesis of resins

Materials: glycidyl methacrylate (GMA) as monomer, ethylene dimethacrylate (EDMA) as cross-linker, benzyl peroxide (BPO) as initiator, dibutyl phthalate (DBP) and cyclohexanol as diluents, polyvinyl alcohol (PVA) as stabilizer, sodium dodecyl sulfonate (SDS) as emulsifier. All materials were purified by normal methods.

Synthesis: The linear polymer seeds were polystyrene (PS) beads with monodisperse particle size which were prepared by dispersion polymerization in alcohol media. The PS seeds were swollen by emulsifying mixture of GMA, EDMA, BPO and diluents in an aqueous solution containing PVA and SDS at room temperature, usually not less than 6 h. Polymerization reaction was carried out in the aforesaid swelling system at 70℃, usually for 24 h. After being washed with water and extracted with toluene for the polymerization products, the copolymer beads of GMA-EDMA (called $P_{GMA/EDMA}$ resins) with monodisperse size and macroporous structure were obtained.

(ii) Characterization of resins. The particle size and surface morphology, specific surface area, pore distribution of the $P_{GMA/EDMA}$ resins were measured by scanning electron microscopy (SEM), BET and mercury instrusion method respectively. The pore structure of the resins was characterized by gel permeation chromatography (GPC) and SEM methods as well. The epoxy value of the resins was measured by perchloric acid titration method.

The $P_{GMA/EDMA}$ resins were packed in stainless steel columns by wet method with ethanol. The experiments of GPC were carried out in HPLC instrument (waters 6 000A pump, SPD-10A UV-Vis detector) with tetrahydrofuran (THF) as eluant, polystyrenes of standard molecular weight as sample, UV-254 nm detection at room temperature.

2 Results and discussion

(i) Synthetic method of resins. Generally, the seed-swelling polymerization is considered one of the most effective methods for the preparation of monosized polymer beads. The seeds used were monosized PS latex based on the emulsifier-free emulsion polymerization, which were swollen by small molecular compounds and then by mixtures of monomer and cross-linker. The swelling products were polymerized in aqueous solution containing stabilizer.

In this note, a new improving method was established including from dispersion polymerization to seed-swelling polymerization and polymeric solution porogens. The monosized linear PS beads with lower molecular weight were synthesized by the dispersion polymerization in organic media. In the linear PS beads, the constituents of molecular weight $<10^4$ were over 90 weight percentage, which were regulated by chain transfer agent in the polymerization process. The PS beads as seeds were swollen directly by emulsifying mixture of monomer, cross-linker, initiator and diluents in the aqueous solution containing stabilizer at the room temperature. After swelling, the polymerization reaction was carried out in the same solution system under heating and stirring conditions. The polymerization products were washed fully with water, and then extracted by organic solvents to remove the porogens which were polymer solution formed linear PS and diluents in swelling-polymerization process. This method is simple, efficient and suitable for the preparation of a series of $\mathrm{P_{GMA/EDMA}}$ resins with different monodisperse particles, macroporous structures and cross-linking densities (20%—70%). In comparison with the same kind of reports[4,5], this research has attained further development in both synthesized method and the structure index of synthesized products.

(ii) Control and characterization of resin particle. The particle diameter (*D*) of monosized resins synthesized is dependent on the particle diameter (*d*) of monosized seeds used and swelling multiple of seeds swollen by the organic phase including GMA, EDMA, BPO and diluents. As organic phase which is hard to dissolve in water will be fully absorbed by the seeds in effective swelling range, *D* can be calculated according to the formula below:

$$D \approx [(V+v)/v]^{1/3} d, \tag{1}$$

where V and v are the volume of organic phase and the seeds respectively, the value of $(V+v)/v$ is the swelling multiple. The experiments showed that by selecting the seeds in particle diameter of 2—7 μm, and controlling the swelling multiple within 40, a series of monosized $\mathrm{P_{GMA/EDMA}}$ resins in particle diameter of 5—20 μm can be obtained under the described polymerization conditions. The particle size and distribution of the resins were characterized by SEM. The particle dispersion coefficient (ε) was calculated by the following formula:

$$\varepsilon = \left[\sum_{i=1}^{n} (D_i - \bar{D})^2 \right]^{1/2} \Big/ \bar{D}, \tag{2}$$

where D_i and n were the particle diameter and the particle number of the resins determined, and $\bar{D}$ was the average particle diameter of n polymer beads. The results showed that a series of resins synthesized were monodisperse particle size in effective adjustable experiments range, and their ε were 1.5%—3%. An SEM picture of $\mathrm{P_{GMA/EDMA}}$ resin displayed directly the particle uniformity of this type of products (fig. 1(a)).

(iii) Control and characterization of resin pore. In the preparation process of $\mathrm{P_{GMA/EDMA}}$ resins, the linear process PS used was both the seeds of swelling polymerization and the polymer porogens. The main affecting factors for the macroporous structure of the resins were the molecular weight of PS contained in polymer beads and concentration of polymeric solution formed by PS and diluents. The experiments showed that the selective range of polymeric solution porogens was molecular weight less than 10^4 and PS concentration less than 30%. Adjusting material mixture ratio in the above-mentioned range, a series of $\mathrm{P_{GMA/EDMA}}$ resins with different porous structures including macroporous and supermacroporous structures could be obtained.

The pore distribution and pore morphological structure of $\mathrm{P_{GMA/EDMA}}$ resins were characterized by different methods including mercury intrusion, gel chromatography and SEM. Fig. 2 shows the pore

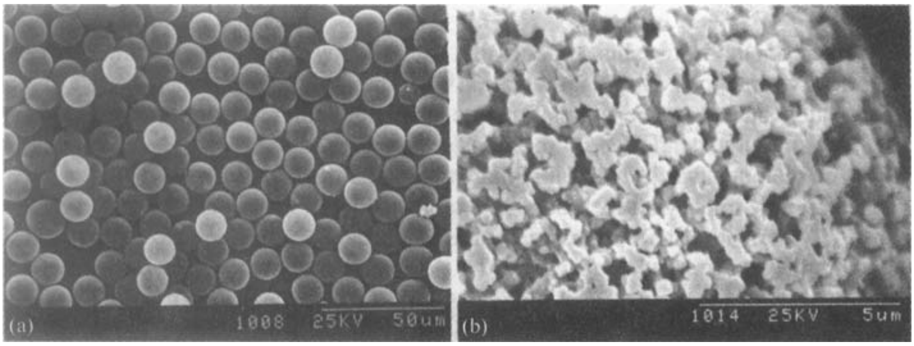

Fig. 1. SEM picture of $P_{\mathrm{GMA\ EDMA}}$ resins. (a) particle size and distribution of a resin; (b) morphological structure of a particle surface.

radius distribution of a dry state resin measured by mercury intrusion method. It was obvious that macroporous (>30 nm) and super-macroporous (>100 nm) structures were dominant within the porous beads. The macroporous and super-macroporous morphological structures on the resin particle surface could also be observed clearly by means of the SEM picture (fig. 1(b)). The specific surface area was mainly dependent on the porous structure of the resins, especially the microporous structure within the particle. Generally, the specific surface area will decrease with increasing of the pore diameter in the resins of the same pore volume. The specific surface area of different $P_{\mathrm{GMA\ EDMA}}$ resins were about 5 −80 $\mathrm{m^2/g}$ in range, which was measured by BET method.

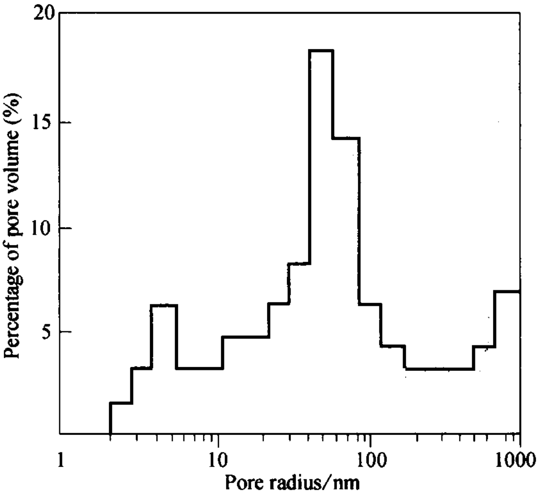

Fig. 2. Pore radius distribution of a $P_{\mathrm{GMA/EDMA}}$ resin (measured by mercury intrusion method).

(iv) Gel chromatographic properties of $P_{\mathrm{GMA/EDMA}}$ resins. The $P_{\mathrm{GMA/EDMA}}$ resins possess stronger hydrophobicity before chemical modifi-cation, so their properties can be characterized by GPC method in THF elution system and by using polymer as samples which does not react with epoxy groups. Fig. 3 shows the separation of some polystyrene standard samples with different molecular weights in a column packed $P_{\mathrm{GMA\ EDMA}}$ resins of 13 μm particle diameter. And we can obtain a good result on a shorter column and under highly flowing rate conditions. Fig. 4 shows the dependence of theoretical plate height (H) and column pressure (ΔP) on flow rate (F_c) by $P_{\mathrm{GMA/EDMA}}$ column. Judging from the H-F_c curve, under optimum flow rate conditions, the H value of two samples (toluene and polystyrene of molecular weight 9×10^3) were 40 and 80 μm respectively, and the corresponding reduced plate height ($h=H/D$) were 3 and 6 respectively. This is already a relatively high column efficiency for the porous polymer type of packings. Additionally, the operation pressure of the $P_{\mathrm{GMA/EDMA}}$ column, as shown in ΔP-F_c curve, was considerably low even under high flow rate conditions. Owing to the uniform particle size, good particle rigidity and macroporous structure, the resins possess high permeability, which was very favorable to the chromatographic applications.

According to polymer solution theory, in GPC method the relationship between molecular weight (M_W) of polystyrene standard samples and pore diameter (Φ[Å]) of column packings conforms to the following empirical formula[6]:

$$M_W = 2.25\,\Phi^{1.7}. \qquad (3)$$

So the pore distribution of column packing can be measured by the GPC calibration curve of the

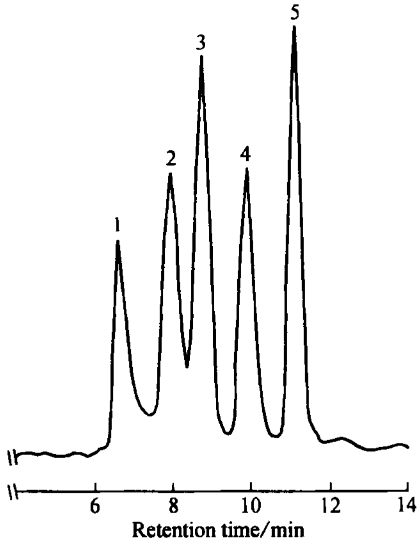

Fig. 3. GPC separation of some polystyrene standard samples on a $P_{GMA/EDMA}$ packed column. Column size: 8 mm I. D×300 mm; particle size of packing: 13 μm; eluent: THF; flow rate: 1.2 mL/min; detection: UV-254 nm; sample: 1, 1.8×10^6 (PS); 2, 2.33×10^5 (PS); 3, 5×10^4 (PS); 4, 8×10^2 (PS); 5, toluene.

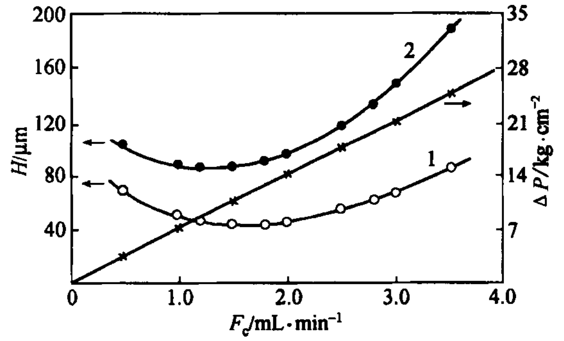

Fig. 4. Dependence of theoretical plate height (*H*) and column pressure (ΔP) on flow rate (F_c) on $P_{GMA/EDMA}$ packed column. (for chromatographic conditions see fig.3). Samples: 1, Toluene; 2, 8×10^2 (PS).

molecular weight-elution volume. The experiments showed that GPC exclusion limits of most $P_{GMA/EDMA}$ resins synthesized have already been over 1.8×10^6 polystyrene molecular weight, which illustrated that there were over 300 nm super-macroporous structures within the resin particles.

The $P_{GMA/EDMA}$ resins synthesized not only possess the above-mentioned physical structure, but good chemical reactivity as well because of a vast number of epoxy groups carried by the particles. The resins as matrix materials through chemical modification can be conveniently changed into various types of HPLC packings with high column efficiency, high permeability and different selectivity, for example, ion exchange HPLC packings carrying tertiary amino groups, quaternary ammonium groups, carboxyl groups and sulfonic acid groups; the reversed phase and hydrophobic interaction and gel filtration HPLC packings carrying alkyl groups, phenyl groups and hydroxyl groups respectively; the affinity HPLC packings carrying different affinity legends. The preliminary tests showed that most of the modified resins as new HPLC packings possess excellent chromatographic properties especially for the separation of biochemical substances.

Acknowledgements This work was supported by the National Natural Science Foundation of China (Grant Nos. 29575217 and 29635010).

References

1. Kulin, L. I., Flodin, P.,Ellingsen, T. et al., Monosized polymer particles in size-exclusion chromatography, J. Chromatogr., 1990, 514: 1.
2. Ellingsen, T., Aune, O., Ugelstad, J. et al., Monosized stationary phase for chromatography, J. chromatogr., 1990, 535: 147.
3. Wang, Q. C., Hosoya, K., Svec, F. et al., Polymeric porogens used in the preparation of novel monodis-persed macroporous polymeric separation media for high-performance liquid chromatography, Anal. Chem., 1992, 64: 1232.
4. Smigol,V.,Svec, F., Synthesis and properties of uniform beads based on macroporous copolymer glycidyl methylacrylate-ethylane dimethylacrylate: a way to improve separation media for HPLC, J. Appl. Polym. Sci., 1992, 46: 1439.
5. Smigol, V., Svec, F., Frechet, J. M. J., Novel uniformly sized polymeric stationary phase with hydrophilized large pores for direct injection HPLC determination of drugs in biological fluids, J. Liquid Chromatogr., 1994, 17: 891.
6. Halasz, I., Martin, K., Pore sizes of solids, Angew. Chem. Int. Ed. Engl., 1978, 17: 901.

(Received June 28, 1999)