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# Synthesis of monodisperse macroreticular styrene–divinylbenzene gel particles by a single-step swelling and polymerization method

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## Abstract

Monodisperse styrene–divinylbenzene gel beads in the range of 4.1–7.5  $\mu\text{m}$  were prepared via a single-step swelling and polymerization method. The seed particles prepared by dispersion polymerization exhibited good absorption of the monomer phase. The resulting gel beads were evaluated as packing materials for gel permeation chromatographic columns. The pressure resistance of gel beads prepared with a volume ratio of diluent to monomers of unity was higher than 120  $\text{kg}/\text{cm}^2$ , and it decreased with the relative amount of diluent. The pore size tended to decrease with decrease in the swelling ratio of the seed polymer. The median pore size in a swollen state was controllable in the range 30–550  $\text{\AA}$ .

## 1. Introduction

Monodisperse macroreticular styrene–divinylbenzene (St–DVB) copolymer beads having a micrometre-order diameters are in strong demand in a wide range of industrial fields, such as for gel permeation chromatographic (GPC) column packing materials, precursors for ion-exchange resins and solid polymeric catalysts.

Ugelstad et al. [1] developed a technique for the preparation of uniformly sized beads which he termed “activated multi-step swelling and polymerization”. This method has been applied to the preparation of monodisperse porous

styrene–divinylbenzene copolymer beads for the packing materials [2–5]. This method is an excellent one, but seems rather complex, since at least two-steps are needed in swelling process, i.e., the first step for the seed particles to be activated by the absorption of a water-insoluble compound, such as 1-chlorododecane and in some cases by the initial absorption of an accelerator such as acetone, and a subsequent step for the absorption of styrene, divinylbenzene and diluent.

This paper describes the preparation of monodisperse macroreticular St–DVB beads by seed polymerization involving only a single-step swelling process. The beads thus prepared were packed into chromatographic columns and their properties were assessed. The sizes of the par-

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ticles and pores are discussed in relation to the preparation conditions.

## 2. Experimental

### 2.1. Materials

Reagent-grade styrene and divinylbenzene, containing ca. 45% of ethylvinylbenzene, were obtained from Tokyo Kasei (Tokyo, Japan) and were used after distillation under reduced pressure. Other materials were used without further purification.

### 2.2. Dispersion polymerization

Monodisperse polystyrene seed particles were prepared by dispersion polymerization of styrene in ethanol or a mixture of ethanol and water under a nitrogen atmosphere using azobis(isobutyronitrile) (AIBN) as an initiator and poly(vinylpyrrolidone) and bis(2-ethylhexyl) ester of sodium sulfosuccinic acid as stabilizers according to the method reported by Paine et al. [6]. After a centrifugal purification, the purified seed particles were dispersed in water containing poly(vinyl alcohol) (PVA) (0.6%) with a particle content of 0.1 g/ml. Table 1 lists the preparation conditions and characteristics of the seed particles.

### 2.3. Seed polymerization

In a 500-ml flask fitted with a mechanical stirrer were placed various amounts of seed dispersion and 50 ml of water containing 0.6% (w/w) of PVA, and the mixture was stirred

slowly. A 30 g amount of a mixture of St, DVB, toluene containing 5% (w/w) (based on the organic phase) of isoamyl alcohol and 2% (w/w) (based on the total monomer) of 2,2'-azobis(2,4-dimethylvaleronitrile) (ADVN) initiator were emulsified in 300 ml water containing 0.25% (w/w) of sodium *n*-dodecyl sulfate and 0.6% (w/w) of PVA with an ultrasonic disrupter (UD-200; TOMY, Tokyo, Japan) until the particle size of the oil drops became at most 0.5  $\mu\text{m}$ . The mass ratio of St to DVB was 3:7 and the ratio of toluene to total monomer varied from 1.0 to 2.0. The mass ratio of the organic phase to the seed particles varied from 5 to 100. Then, one third portion of the emulsion was added dropwise to the dispersion of the seed particles, with stirring, over 15 min. The second and third one-third portions of the emulsion were added after 1-h intervals in the same way. The mixture was stirred for 24–48 h at room temperature so that all the emulsified organic phase was absorbed by the polymer seeds. The temperature was then increased to 70°C and polymerization was carried out for 10 h. The resulting gel beads were washed successively with hot water, acetone and tetrahydrofuran (THF) 2–4 times, followed by drying in vacuo.

### 2.4. Characterization of gel beads

Gel beads (8 g) dispersed in 50 ml of THF were packed into a stainless-steel column (30 cm  $\times$  7.6 mm I.D.) by a high-pressure slurry method to obtain a GPC column. The GPC calibration graph of polystyrene standards (Shodex) was obtained using THF as an eluent (0.5 ml/min) with a JASCO (Tokyo, Japan) PU 800 pump and a JASCO Model 880 UV detector

Table 1  
Preparation conditions and characteristics of seed particles

Seed No.	Styrene (g)	Ethanol (ml)	Water (ml)	Diameter ( $\mu\text{m}$ )	$M_n/10^4$	$M_w/10^4$	$M_w/M_n$
1	27	180	20	1.7	3.0	27.9	9.2
2	27	200	0	3.0	2.6	9.2	3.5

Polymerization temperature, 70°C; polymerization time, 20 h; initiator, AIBN, 0.27 g (1%, w/w, based on styrene).

(254 nm). The number of theoretical plates was determined from the benzene peak. The standard sample concentration was 0.1% (w/w) and 5  $\mu$ l of sample were injected through a Rheodyne (Cotati, CA, USA) Model 7125 loop injector. The particle size and surface morphology of beads were investigated by scanning electron microscopy (JSM-35CF; JEOL, Tokyo, Japan).

### 3. Results and discussion

#### 3.1. Preparation of monodisperse beads

St-DVB beads were prepared by seed polymerization using polystyrene seed obtained by dispersion polymerization. Table 2 gives preparation conditions and characteristics of the beads. The mass ratio of the absorbed organic phase to the original seed particles (swelling

ratio) was varied from 5 to 200. Fig. 1a and b show the scanning electron micrographs of gels 1-1 and 1-2, respectively, which indicate that irregularly shaped beads were obtained when the swelling ratio was less than 10. With a swelling ratio of 5, the beads became hollow when collapsed. Beads with a swelling ratio of 10 became spheres with navels. It is likely that there was some heterogeneity in the swollen droplets due to the high polystyrene concentration (20% or 10%) which caused the irregularity of beads in the polymerization process. At swelling ratios above 20, regular spherical beads were obtained and their size was essentially monodisperse. Fig. 1c and d show the scanning electron micrographs of a gel with a swelling ratio of 200 and indicate that the beads were uniform in size and had a macroporous structure.

It is noteworthy that the swelling ratio could be increased up to 200 times in this experiment.

Table 2  
Preparation conditions for styrene-divinylbenzene copolymer beads and characteristics of GPC columns

Toluene/monomers ratio	Gel	Seed		Oil/seed	Diameter ( $\mu$ m)	F.R. <sup>a</sup> (ml/min)	M.P. <sup>b</sup> (kg/cm <sup>2</sup> )	N <sup>c</sup> ( $\times 10^3$ )	V <sub>p</sub> /V <sub>t</sub> <sup>d</sup>	D <sub>50</sub> <sup>e</sup> ( $\text{\AA}$ )
		Mass (g)	Type							
1.0	1-1	6.0	2	5	n.d. <sup>f</sup>	—	—	—	—	—
	1-2	3.0	2	10	n.d. <sup>f</sup>	—	—	—	—	—
	1-3	1.5	2	20	6.4	4.5	125	8.2	0.44	552
	1-4	1.2	2	25	7.0	10.0	125	8.8	0.41	179
	1-5	1.0	2	30	7.3	6.0	122	11.9	0.43	112
	1-6	0.75	2	40	7.4	8.0	128	11.6	0.42	57
	1-7-2	0.60	2	50	7.5	7.6	124	10.7	0.41	46
	1-7-1	0.60	1	50	4.2	1.6	131	8.8	0.41	45
	1-8	0.30	1	100	4.6	3.3	130	15.8	0.39	30
1-9	0.15	1	200	5.0	4.6	123	12.7	0.38	32	
1.5	2-1	0.60	1	50	4.1	2.0	54	15.0	0.46	65
	2-2	0.30	1	100	4.5	1.5	76	12.0	0.46	42
2.0	3-1	0.60	1	50	4.1	0.9	25	9.4	0.52	91
	3-2	0.30	1	100	4.4	0.8	20	8.8	0.53	72

Polymerization temperature, 70°C; polymerization time, 10 h; total amount of organic phase, 30 g; styrene/divinylbenzene ratio, 3:7; initiator, ADVN (2 mass-% based on monomers).

<sup>a</sup> Final flow-rate in packing procedure.

<sup>b</sup> Maximum pressure in packing procedure.

<sup>c</sup> Number of theoretical plates (in 30-cm).

<sup>d</sup> Ratio of pore volume to total volume of column.

<sup>e</sup> Median pore size of gel in a swollen state.

<sup>f</sup> Not determined.

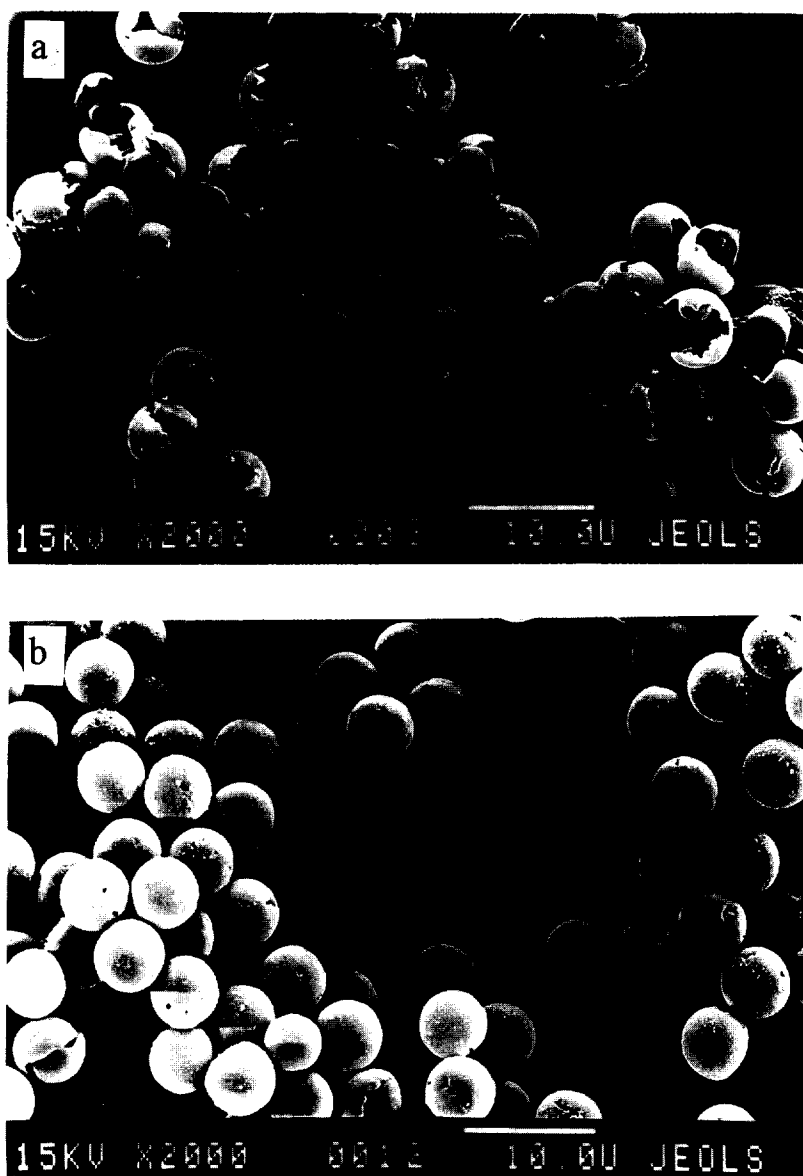


Fig. 1. Scanning electron micrographs of styrene-divinylbenzene gel beads. (a) Gel 1-1 ( $\times 2000$ ); (b) gel 1-2 ( $\times 2000$ ); (c) gel 1-9 ( $\times 2000$ ); (d) gel 1-9 ( $\times 10\,000$ ).

In contrast, Šmigol et al. [7] reported that the swelling ability of “non-activated” latex particles did not exceed 70-fold when emulsifier-free emulsion latex was used as the seed. The difference in swelling ability can be attributed to the method used for the preparation of seed particles. It has been reported that particles pre-

pared by dispersion polymerization contain a small amount of grafted polymer on the polymeric stabilizer, in our case case poly-(vinylpyrrolidone) [8]. The presence of the graft polymer can be considered to increase the absorption ability without “activating” the seed particles. Polymer beads prepared by dispersion

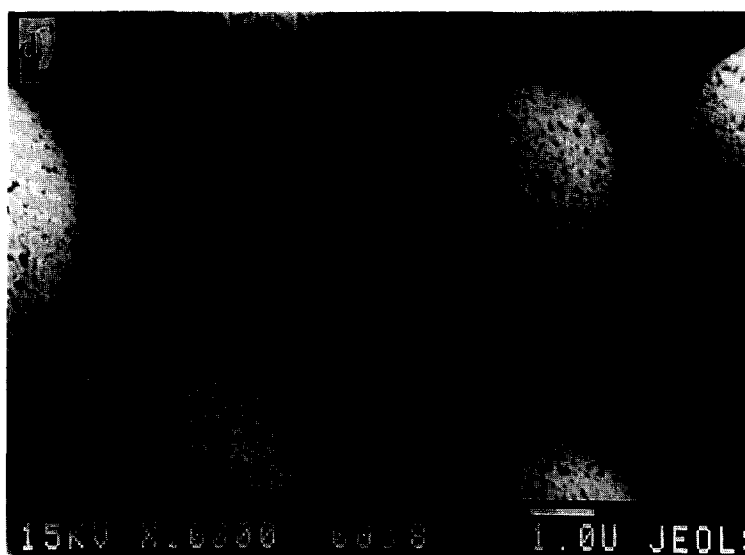


Fig. 1. (Contd.)

polymerization have the additional advantage that the diameter of the beads can be easily controlled in the range 1–10  $\mu\text{m}$  [6,8–10].

### 3.2. Characteristics of GPC column

Table 2 also gives the packing conditions and characteristics of GPC columns. The maximum pressure represents the final pressure in the packing procedure. When the amount of toluene

was equal to that of monomers, each gel had a pressure resistance higher than 120  $\text{kg}/\text{cm}^2$ . On the other hand, gels prepared using toluene in amounts 1.5 and 2 times that of the monomer had pressure limits around 60 and 20  $\text{kg}/\text{cm}^2$ , respectively. Hence the pressure limit decreased with an increase in the relative amount of diluent. It appears that the preferred ratio of toluene to the monomer is 1:5 with respect to pressure resistance. The number of theoretical

plates (NTP) was more than 8000 for a 30-cm length. Fig. 2 shows the chromatograms of a mixture of polystyrene standards, styrene oligomers and benzene using column 1-8. A fairly good separation was obtained.

Fig. 3 shows the calibration graphs for columns with the synthesized gel beads. It is clear that the exclusion limit decreased as the swelling ratio increased, although the value of the exclusion limit could not be determined because the molecular mass of the polystyrene standard was less than  $3.04 \cdot 10^6$ . There was a shift in the region of linearity in the fractionation curves, from higher to lower molecular masses. This correlated with an increasing swelling ratio and decreasing pore diameter (Table 2). Together with the exclusion limit, this indicates that a gel with a low swelling ratio is suitable for GPC of

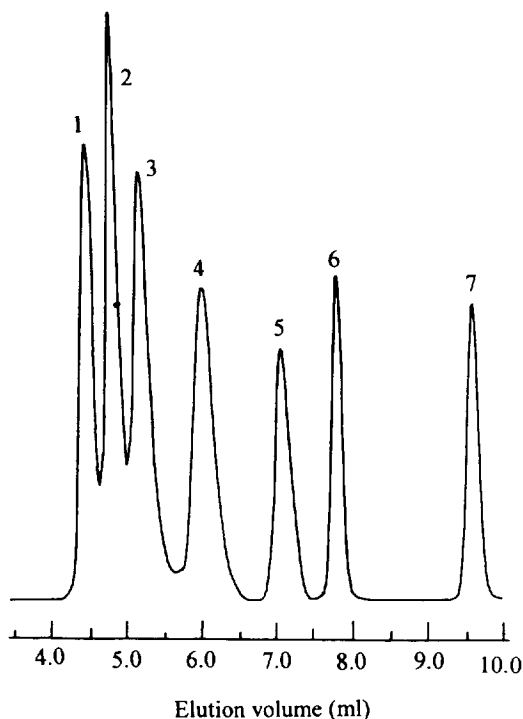


Fig. 2. Chromatogram of polystyrene standards and benzene obtained with column 1-8. Sample, polystyrene standards [ $M_r = 1.13 \cdot 10^6$  (1),  $1.56 \cdot 10^5$  (2),  $2.85 \cdot 10^4$  (3),  $3.25 \cdot 10^3$  (4)], styrene oligomers [ $M_r = 681$  (5), 265 (6)] and benzene (7). Flow-rate, 0.5 ml/min (THF).

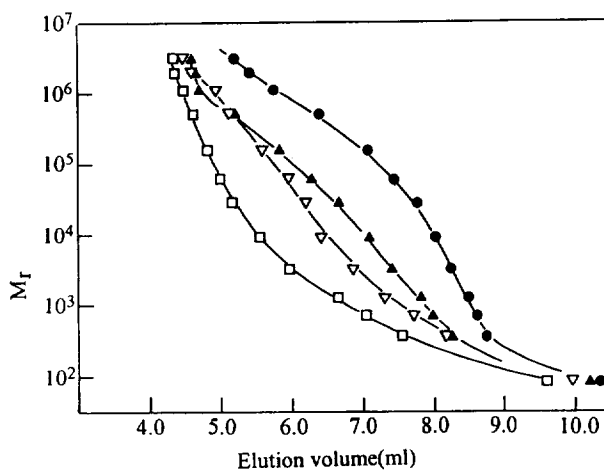


Fig. 3. Calibration graphs for columns packed with prepared styrene-divinylbenzene gel beads. ● = Gel 1-3; ▲ = gel 1-5; ▽ = gel 1-7-1; □ = gel 1-8. Column, 30 cm  $\times$  7.6 mm I.D.; eluent, THF (0.5 ml/min). Sample: polystyrene standards ( $M_r = 3.04 \cdot 10^6$ ,  $1.95 \cdot 10^6$ ,  $1.13 \cdot 10^6$ ,  $5.01 \cdot 10^5$ ,  $1.56 \cdot 10^5$ ,  $6.60 \cdot 10^4$ ,  $2.85 \cdot 10^4$ ,  $9.24 \cdot 10^3$ ,  $3.25 \cdot 10^3$ ,  $1.32 \cdot 10^3$ ), styrene oligomers [ $M_r = 681$  (6-mer), 577 (5-mer), 369 (3-mer), 265 (2-mer)] and benzene.

high-molecular mass compounds and a gel with a high swelling ratio for GPC of low-molecular mass compounds.

Clear exclusion limits could not be determined owing to the lack of suitable standards. However, the void volume ( $V_0$ ) of columns could be estimated by extrapolating the curves in Fig. 3, which generally became steep around 4.4–4.5 ml. We estimated the ratio  $V_0/V_t = 0.33$  (where the total column volume  $V_t = 13.61$  ml). When monodisperse beads are regularly closest-packed into a column, they occupy 0.74 of total volume, if the particle size is small enough for the wall effect to be negligible. Therefore, the lowest theoretical value of the void volume is about 0.26 of the total volume, which in practice is not attained. Indeed, a ratio of  $V_0$  to  $V_t$  of 0.35 has been reported for monodisperse beads of  $5 \mu\text{m}$  [2]. Our results correspond to this value. The pore volume ( $V_p$ ) is defined as the difference between the elution volume of benzene and the void volume ( $V_0$ ). The ratio of  $V_p$  to  $V_t$ , which influences the resolution of the column, is given

in Table 2. This value varied from 0.39 to 0.44 for gels which were prepared with the same amount of toluene as monomers. The ratio increased to 0.46 or 0.52 as the amount of toluene increased for the gels prepared with a 1.5- or 2.0-fold excess of toluene, respectively.

In the application of polymeric beads as packing materials in HPLC columns, they are used in a swollen state. Therefore, it is important to evaluate the pore size and its distribution in a swollen state. They are often determined from the calibration graph for GPC using the empirical relationship between the dimension and molecular mass of polystyrene in an eluent (THF) [11]:

$$D(\text{\AA}) = 0.62(M_r)^{0.59}$$

where  $M_r$  is the molecular mass of polystyrene. The median pore size ( $D_{50}$ ) was determined from Fig. 3 and the molecular mass of the polystyrene eluted at the centre between  $V_0$  and the benzene peak was used for  $M_r$ . The values of  $D_{50}$  are given in the last column of Table 2.  $D_{50}$  increased with increase in the toluene fraction in the organic phase.

The effect of the type of seed particles on the shape of the calibration graphs curves is shown in Fig. 4. The difference between the calibration graphs for columns packed with gels 1-7-1 and 1-7-2 lies in the high-molecular mass region, which indicates that the large pore distributions of both types of gels are different. Both gel beads were prepared at a swelling ratio of 50. The difference decreased with increase in swelling ratio. As shown in Table 1, the mass-average molecular mass of seed 1 is much higher than that of seed 2, and its molecular mass distribution is wider. It is likely that the difference in pore structure is due to this difference in molecular mass and its distribution for the seed particles. Cheng et al. [12] also reported that the average pore size increases with increasing molecular mass of the seed polymer, and a broad pore size distribution is obtained using a seed polymer with a broad molecular mass distribution.

In Fig. 5, the median pore size is plotted

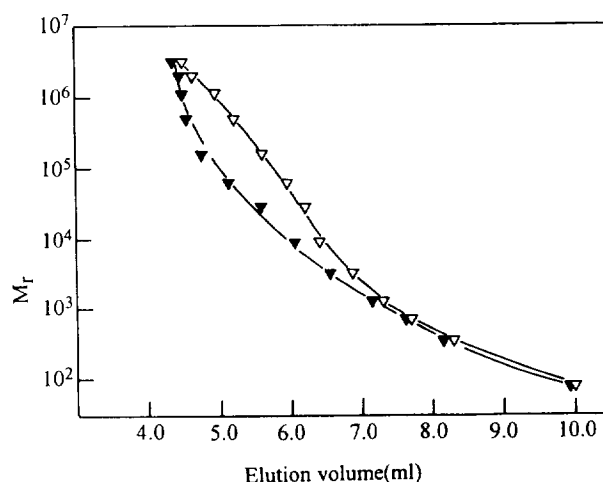


Fig. 4. Effect of types of seeds on calibration graphs.  $\nabla$  = Gel 1-7-1;  $\blacktriangledown$  = gel 1-7-2. Column, 30 cm  $\times$  7.6 mm I.D.; eluent, THF (0.5 ml/min).

against swelling ratio. The pore size decreased with increasing swelling ratio, and became almost constant when the swelling ratio reached 100. Moreover, it increased slightly with the relative amount of diluent. Thus, the median pore size can be controlled in the range from 30 to 550  $\text{\AA}$  by the amount of absorbed organic phase.

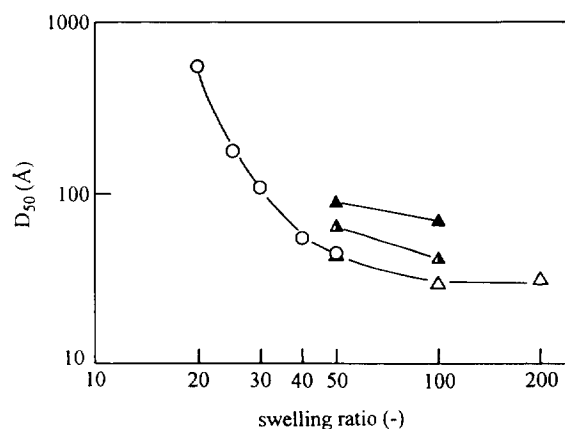


Fig. 5. Relationship between pore size and the swelling ratio.  $\circ$  = Seed 2;  $\triangle$  = seed 1. Toluene/monomers = ( $\circ$ ) 1.0, ( $\triangle$ ) 1.5 and ( $\blacktriangle$ ) 2.0.

#### 4. Conclusions

A single-step swelling and polymerization method provided monodisperse macroreticular styrene–divinylbenzene gel beads even if the amount of absorbed organic phase was 200 times that of the seed particles. This is due to the high absorption ability of seed polymers prepared by dispersion polymerization. GPC columns packed with the prepared gel beads showed good properties, e.g., low void volume and relatively high number of theoretical plates. The median pore size ranged from 30 to 550 Å, which was dependent on the ratio of absorbed organic phase to seed particles. Packing materials that are suitable for polymer samples with a variety of molecular masses can be prepared using this method.

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