

PREPARATION OF GPC PACKED POLYMER BEADS BY A SPG MEMBRANE EMULSIFIER

YASUO HATATE*¹⁾, YOSHIMITSU UEMURA*¹⁾,
KAZUYA IJICHI*¹⁾, YOSHIO KATO*²⁾ AND TADASHI
HANO*³⁾

*Dept. of Appli. Chem. & Chem. Eng., Kagoshima University,
Kagoshima 890*

YOSHINA BABA*⁴⁾ AND YOSHINOBU KAWANO*⁴⁾
Dept. of Materials Science, Miyazaki University, Miyazaki 889-21

Key word: Polymer Beads, SPG Membrane, GPC, Styrene, Divinyl Benzene, Suspension Polymerization

Monodispersed porous polystyrene beads crosslinked with divinylbenzene were prepared by in situ polymerization. For this objective, the preparation of uniform oil microdroplets in water was successfully achieved by using a Shirasu Porous Glass (SPG) membrane emulsifier (POEM[®] from Reika Kogyo Co. Ltd.). Separation abilities for a gel permeation chromatograph (GPC) column were discussed with polymer microbeads obtained by changing key experimental factors such as the pore sizes of the SPG membrane and diluents. Consequently, it was evident from gel permeation chromatography that the porous beads prepared by SPG emulsification can be used for the effective separation of a molecular weight range of 10^2 to 10^6 .

Introduction

High speed liquid chromatography plays an important role in high speed quantitative analysis. In this analysis, gel permeation chromatography (GPC) is essential to the determination of molecular weight distribution of polymers. Polymer beads packed in a GPC column are determinant for separation performance, so the porous gel microbeads should possess characteristics such as strength against mechanical stress, uniform pore size and uniform particle size (Takeuchi and Mori, 1967).

Suspension and/or seed polymerizations have been adopted for the production of microbeads. However, severe classification is necessary to clear the above demands due to the broad size distribution of microbeads produced from droplets with the broad size distribution via the conventional suspension polymerization. So, the conventional method is disadvantageous in terms of low yield and high cost. On the other hand, seed polymerization enables the preparation of uniform polymer particles (Moroishi *et al.*, 1986). However, controlling pore size distribution in the particles is impossible in spite of the complicate preparation process.

To overcome this situation, an inorganic material, Sirasu Porous Glass (SPG), seems to be promising because uniform droplets can be produced as an O/W emulsion through uniform pores of a SPG membrane (Nakashima and Kuroki, 1981, Nakashima and Shimizu, 1993).

In the present work, SPG membrane emulsification was employed to efficiently prepare uniform porous particles of 5-10 μm (Omi *et al.*, 1994). An organic solution

including styrene monomer was dispersed to make an O/W emulsion through a SPG membrane, and in situ polymerization proceeded in the organic droplets to produce polystyrene beads of uniform size. The characteristics of packed beads for a GPC column were discussed by using polymer beads prepared under various experimental conditions.

1. Experimental

Reagent Styrene, divinylbenzene and 2, 2'-azobis isobutyronitrile were used as monomer, crosslinking agent and initiator, respectively. These reagents were mixed together with a solvent or solvents such as dodecane, isooctane and toluene to prepare the dispersed phase. Polyvinyl alcohol (PVA, DP = 500, 88% hydrolysis) aqueous solution including sodium dodecyl benzene sulfonate (DBSNa) or sodium dodecyl sulfonate (SDS) as surfactant was used as the continuous phase.

Apparatus Figure 1 shows a schematic diagram of a membrane emulsifier (POEM[®], Reika Kogyo Co. Ltd.). Symbol A in the figure shows a fully wetted SPG tube of 0.7 mm thickness, 10.0 mm outer diameter and 100 mm length, which was used as a membrane. Six kinds of SPG tube with $d_p = 0.3 \sim 3.3 \mu\text{m}$ were used. The continuous phase (water phase, B) was circulated downward in the tube by vibrating cone C in the figure. The organic phase was pressurized from D to the outside portion of the SPG tube at 300-700 kPa gauge, and passed through the pores of the SPG membrane into the continuous phase to make monodispersed O/W emulsion. The O/W emulsion prepared was transferred into a 500 ml round type separable flask shown in Fig. 2. The suspension polymerization was

*1) Received on November 28, 1994. Correspondence concerning this article should be addressed to Y. Hatate

*2) Y. KATO is now with Div. of Gel Production, Toso Co. Ltd.

*3) T. HANO is now with Dept. of Appli. Chem., Oita University

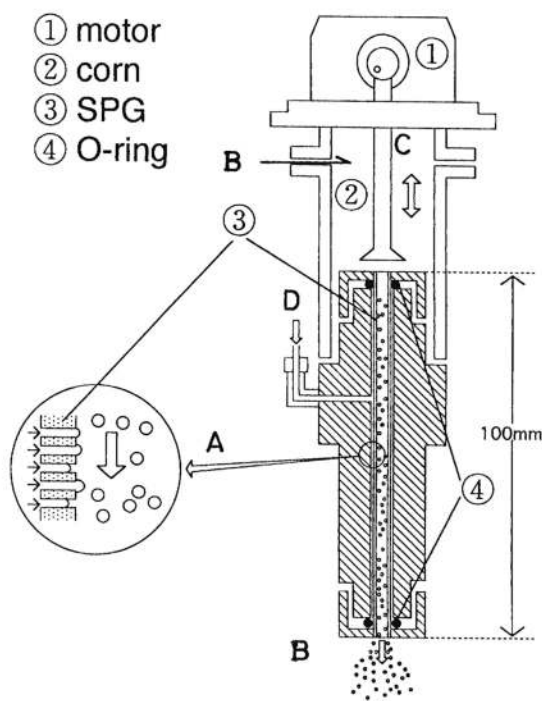


Fig. 1 Schematic diagram of SPG membrane emulsifier

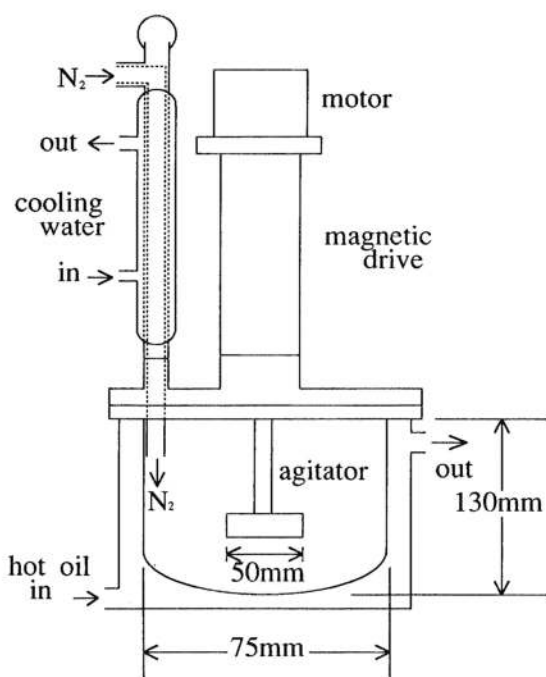


Fig. 2 Schematic diagram of polymerization reactor

carried out for 21.6 ks at 150 rpm in the reactor. Polystyrene microbeads formed were washed with methanol and water, and dried in a vacuum. Size distributions of the beads were determined by direct measurements of microphotographs. Separation characteristics of the beads were investigated with elution curves of several standard polystyrene samples ranging from 10^3 to 10^6 in molecular weight by packing the beads

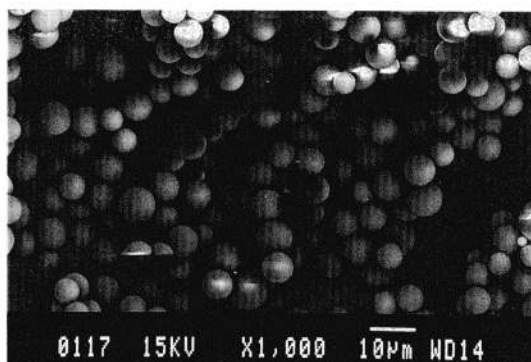


Fig. 3 Representative photograph of polystyrene GPC beads $d_B = 5.85 \mu\text{m}$, variance = 0.24 [-] ($d_p = 1.1 \mu\text{m}$, $C_M = 3 \text{ kmol/m}^3$, $\gamma = 1$ [-], $\beta = 2$ [-], $C_I = 0.2 \text{ kmol/m}^3$, $T_R = 353 \text{ K}$, Surfactant = SDS, Solvent = Toluene)

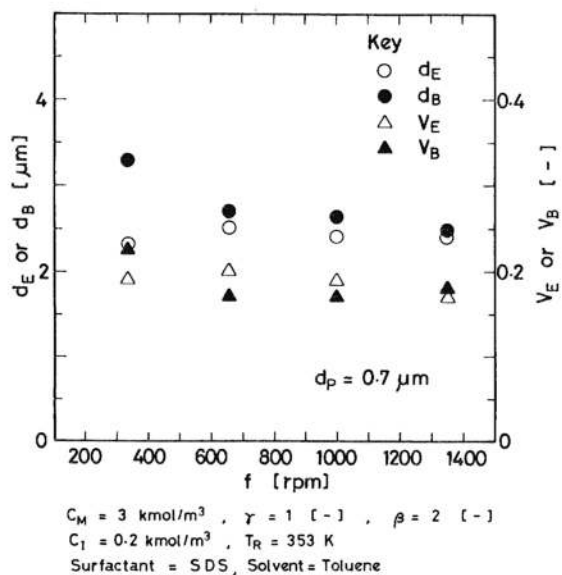


Fig. 4 Effect of vibration frequency on diameter and variance for emulsion droplets and bead particles

prepared into a GPC column. The standard conditions for preparation of GPC beads is as follows; $C_M = 3 \text{ kmol/m}^3$, $\gamma = 1$ [-], $\beta = 2$ [-], $C_I = 0.2 \text{ kmol/m}^3$, and $T_R = 353 \text{ K}$.

Results and Discussion Figure 3 shows a representative SEM photograph of crosslinked polystyrene microbeads. It is obvious from the figure that almost uniform beads were prepared by the SPG membrane emulsifier POEM[®]. So, it is concluded that no classification of particles is necessary, although classification is absolutely essential to obtain uniform beads for the ordinary process. The effect of frequency of the vibration cone on the average size of beads and its variance was investigated as shown in Fig. 4 because the circulating velocity of the continuous phase in the SPG tube would be affected by the vibration of the cone. The organic droplets through SPG pores would grow too large by small shearing stress at low circulating velocities. Average sizes become almost constant above 600 rpm frequency and their variances (=

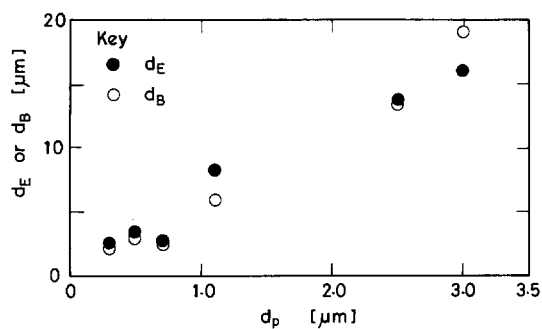
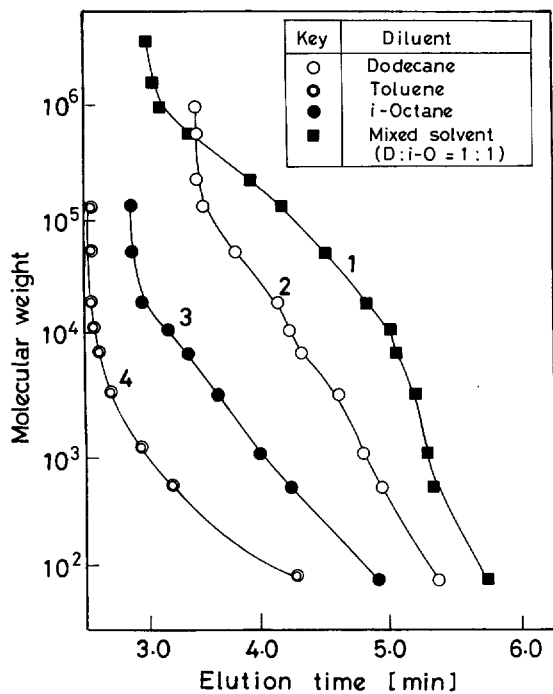


Fig. 5 Effect of SPG membrane pore size on diameter for emulsion droplets and bead particles



Conditions :

Column size : 6.0 mm ID x 15 cm
 Flow rate : 0.6 ml/min
 Eluent : THF
 Sample : Polystyrene stds.
 $C_M = 3 \text{ kmol/m}^3$, $\gamma = 1 [-]$, $\beta = 2 [-]$
 $C_I = 0.2 \text{ kmol/m}^3$, $T_R = 353 \text{ K}$

Fig. 6 Effect of co-solvent in polymerization on GPC elution curve

standard deviation/average size) are about 0.2, showing the comparatively high uniformity of beads size. Figure 5 shows the relation between bead size and pore size of the SPG membrane. It is evident from this figure that bead sizes were about 5 times that of pore size below $3.5 \mu\text{m}$ of pore size. Co-existent solvent with monomer during polymerization, such as dodecane, isooctane, toluene and a 1:1 mixture of dodecane and isooctane is regarded to play an important role in GPC separation ability. Figure 6 shows GPC elution curves for 6 - $9 \mu\text{m}$ beads prepared under several co-existent solvents at DVB/St = 1.2 and 2.9 mol/l of initial styrene concentration. Different exclusive limiting molecular weights were observed for different

Table 1 Column assessment of beads prepared

| Beads No. | diluent | d_B [μm] | TP/column | ΔP [kPa] | As |
|-----------|---------------|-------------------------|-----------|------------------|------|
| 1 | mixed solvent | 7.50 | 4840 | 300 | 2.24 |
| 2 | dodecane | 6.12 | 4425 | 200 | 1.92 |
| 3 | i-octane | 8.97 | 4740 | 400 | 1.57 |
| 4 | toluene | 6.84 | 2760 | 100 | 0.27 |

Mixed solvent is 1:1 mixture of dodecane and i-octane.

As is asymmetric factor of elution peak.

As = 1 indicate symmetry. As < 1 or > 1 indicate leading or tailing peak, respectively.

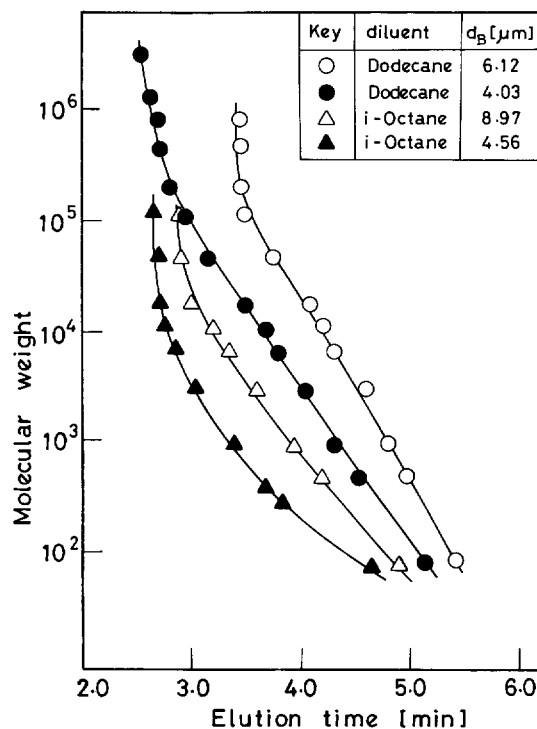


Fig. 7 Effect of diameter of packed particles on GPC elution curve

co-existent solvents, that is, $8 \times 10^5 - 10^2$ (dodecane and isooctane), $10^5 - 10^2$ (dodecane), $2 \times 10^4 - 10^2$ (isooctane) and $10^4 - 10^2$ (toluene), respectively. It is obvious from the figure that toluene is not suitable as a co-existent solvent and the mixed solvent of dodecane and isooctane is the best. Generally speaking, solvents inducing microphase separation seem to be suitable as a co-existent solvents, which act to form broad micropore size distributions achieving separation of 10^2 to 10^6 of molecular weight (based on polystyrene standards). Table 1 shows the theoretical plate number for each bead using a test sample of $0.3 \mu\text{l}$ THF solution containing 0.1 wt% benzene. The packing condition of the beads is as follows; column size = 6.0 mm (ID) \times 15 cm (L), mobile phase = THF, flow rate = 1.0 ml/min, detector = UV 254 nm and temperature = 298 K. Good column performance is obvious from the table, except for toluene diluent beads. Bead size also seems to be a key factor in GPC separation ability. Figure 7 shows the effect of bead size on GPC elution curves for each diluent.

It is evident from the figure that the separable range

of molecular weights was almost the same for isooctane diluent beads in the range of $d_B = 4 - 9 \mu\text{m}$, however a wider separable range was observed in the column of smaller beads for dodecane diluent.

Although laborious adjustments are needed to control the bead size by the conventional method, easy control of bead size is possible by adopting a SPG tube with suitable membrane pore size as mentioned above.

Conclusion

A new preparation method of GPC packed column polymer beads was developed through monodisperse O/W emulsification by use of a SPG membrane emulsifier POEM®. 3 - 10 μm microporous polystyrene beads crosslinked with divinylbenzene were prepared to investigate the GPC separation ability.

The following results were obtained;

- (1) Monodispersed beads of desired size ranging from 1.5 to 10 μm could be easily made by adjusting pore size of the SPG membrane of POEM®. No classification of raw products (beads) is needed, so it is possible to lower the production cost of GPC packed column beads.
- (2) Separation ability of the beads was significantly affected by diluent during polymerization. A mixed solvent of dodecane and isooctane was most superior of all, achieving the separation ability of 10^2 to 10^6 of molecular weight.
- (3) Almost no effect of bead size on the separation ability was observed in the range of $d_p = 4 - 9 \mu\text{m}$ for isooctane

diluent beads, however a wider separable range was observed in the column of smaller beads for dodecane diluent.

Nomenclature

| | | |
|----------|--|------------------------|
| C_I | = initiator concentration | [kmol/m ³] |
| C_M | = styrene monomer concentration | [kmol/m ³] |
| d_B | = average diameter of beads | [μm] |
| d_E | = average diameter of oil droplets | [μm] |
| d_p | = pore diameter of SPG membrane | [μm] |
| f | = frequency of vibration cone | [min ⁻¹] |
| T_R | = reaction temperature | [K] |
| V_B | = variance of bead diameter (= standard deviation/ d_B) | [-] |
| V_E | = variance of droplet diameter (= standard deviation/ d_E) | [-] |
| β | = volume ratio of styrene and divinylbenzene to solvent | [-] |
| γ | = mole ratio of divinylbenzene to styrene | [-] |

Literature cited

- Moroishi, Y., T. Asano, I. Sakai and I. So; "Solvent - resistant uniform diameter microparticles," *Jpn. Tokkyo Koho JP61*, **225**, p.208 (1986)
- Nakashima, T. and Y. Kuroki; "Effects of Composition and Heat Treatment on the Phase Separation of Na₂O-B₂O₃-SiO₂-Al₂O₃-CaO Glass Prepared from Volcanic Ashes," *Nippon Kagaku Kaishi*, **8**, 1231-1238 (1981)
- Nakashima, T. and M. Shimizu; "Preparation of Monodispersed O/W Emulsion by Porous Glass Membrane," *Kagaku Kogaku Ronbunshu*, **19**, 984-990 (1993)
- Omi, S., K. Katami, A. Yamamoto and M. Iso; "Synthesis of Polymeric Microspheres Employing SPG Emulsification Technique," *J. Applied Polym. Sci.*, **51**, 1-11 (1994)
- Takeuchi, T. and S. Mori; "Gel permeation Chromatography," P.30, Maruzen, Tokyo (1967)