

CHAPTER V

CONCLUSION AND SUGGESTIONS

Conclusion

This study on synthesis of styrene-divinylbenzene copolymer beads has reached its goals in providing information on the influencing factors that affect on the properties of the imbibed beads. The effect of such influential parameters such as diluents, inhibitor and nitrogen flow rate were studied. The properties of imbibed beads such as solvent sorption and desorption, pore size, specific surface area, and pore volume were obtained by several analytical techniques. The findings can be concluded as follows:

1. Appropriate condition for the preparation of the polystyrene imbibed beads crosslinked with divinylbenzene could be drawn as follows.

Aqueous phase: HPMC	2.53 %
HEC	1.32 %
NaHCO ₃	13.0 %
Hydroquinone	0.16 %

Monomer phase: (0.075 % of monomer phase volume fraction)

Styrene	98.7 %
Divinylbenzene	1.0 %
Benzoyl peroxide	0.3 %

Temperature-time schedule:

For the conventional polymerization; 70°C-4 hr+90°C-3hr.

For the seeded polymerization; 70°C-4 hr+90°C-3hr.

1.1 Divinylbenzene was used as the crosslinking agent in the synthesis of polystyrene imbibed beads due to its bifunctionality. The crosslinking agent helps stabilize and maintain the dimension of the imbibed beads during solvent sorption and desorption because of its crosslinking network.

1.2 To the suspension containing 1% divinylbenzene, hydroquinone was added to the reaction mixture to kill the radicals escaping from the polymer particles to control the extent of crosslinking, and the size of the beads. For the reaction time was 7 hours, the average seed beads size was 0.65 mm.

2. Properties of the beads

The effects of nitrogen flow rate and diluents, toluene and n-heptane, on bead preparation were studied. The properties of beads could be shown as follows:

2.1 Bead size distribution: the seed beads were in the size range of 0.42-0.59 mm, while the large imbibed beads were in the size range of 0.8-2.0 mm.

(a) The effect of nitrogen flow rate on bead size: the bead sizes tend to increase with increasing the nitrogen flow rate. The increasing flow rate of nitrogen gas brought in more initiators and monomers to react, the large bead sizes could be obtained.

(b) The effect of toluene on the bead size: the bead sizes tend to be decreased with increasing the amount of toluene.

(c) The effect of the n-heptane on the bead size: the bead sizes tend to be increased with increasing the amount of n-heptane.

2.2 Sorption: the seed beads and large beads could completely absorb toluene within 50 min and 2 hours, respectively. The seed beads prepared by using 1.6 % toluene and nitrogen flow rate of 21 cm³/min yielded the maximum sorption at 16.4 times its own dimension. The large imbibed beads prepared by using 15.6 % n-heptane and nitrogen flow rate of 16 cm³/min

yielded the maximum sorption at 11 times its own dimension. The low swelling ratio of the large beads can be attributed to the fact that the absorbed monomer was polymerized in the seed beads from which a higher crosslink density was increased.

(a) The effect of toluene on the swelling ratio: the swelling ratio of the beads increased with increasing the amount of toluene at the same nitrogen flow rate. This swelling ratio was probably controlled by the close solubility of the styrene-divinylbenzene beads to toluene resulting in slight crosslink.

(b) The effect of n-heptane on swelling ratio: the swelling ratio of the beads decreased with increasing the amount of n-heptane. The n-heptane is the poor solvent for the imbibed beads which constrained the chains of the imbibed bead, which is suspected to give a better pore characteristic.

(c) The effect of nitrogen flow rate on swelling ratio: the swelling ratio of the beads decreased with increasing nitrogen flow rate for the beads prepared by using toluene as diluent. The increasing flow rate of nitrogen gas brought in more initiator and monomers to react from which high crosslinking could occur.

2.3 Desorption: the seed beads and large beads were completely desorbed within 50 min and 90 min, respectively. Solvent-bead interaction was claimed to be responsible for the rate.

3. Density of the beads: the density of the beads were determined by the density-gradient technique. The density of the seed beads and large beads were about 0.9174-1.0524 and 0.9925-1.0456 g/cm³. These beads can certainly float on water surface if they were used for removal of spilled oil.

4. Properties of pore: the average diameter of pores about 33.5 Å (mesopore). The seed beads and large imbibed beads prepared by using 0.8 % toluene as diluent and 21 cm³/min of nitrogen flow rate gave the maximum pore volume and specific surface area which were about 0.13 ml/g and 155.02

m^2/g , respectively. The seed beads and large imbibed beads prepared by using 3.14 % n-heptane as diluent and $21 \text{ cm}^3/\text{min}$ of nitrogen flow rate gave the maximum pore volume and specific surface area which were about 0.12 ml/g and $137.76 \text{ m}^2/\text{g}$, respectively. The excluded free volume is probably the plausible cause of the mesopore formation.

5. The seed beads and large imbibed beads could be used to absorb and desorb toluene for repeated cycles. The sorption and desorption behavior of the second and third cycles were also the same as the first cycle.

6. Diffusion coefficient: the diffusion coefficient range of the seed bead and large beads prepared by using toluene as diluent were 0.68×10^{-3} - 0.87×10^{-3} and 0.93×10^{-3} - $2.39 \times 10^{-3} \text{ cm}^2/\text{min}$, respectively. The diffusion coefficient range of the seed bead and large beads prepared by using n-heptane as diluent were 1.02×10^{-3} - 1.41×10^{-3} and 0.99×10^{-3} - $2.21 \times 10^{-3} \text{ cm}^2/\text{min}$, respectively. There are no differences in diffusion coefficient of seed beads and large beads prepared in either good or poor solvent for the beads.

Suggestions

1. Using mixtures of good and bad solvents in the synthesis. Usually, good solvents produce structures with small pores while bad solvents produce structures with large pores. Structures with intermediate pore sizes can be obtained using mixtures of good and bad solvents.

2. Using various divinylbenzene contents. It was possible to prepare porous copolymers with low divinylbenzene contents, when a large amount of diluent was employed.

3. Using Soxhlet method to remove low molecular weight diluents. The temperature should be low to prevent the excessive crosslink.