

CHAPTER III

EXPERIMENTAL

Chemicals

1. Styrene ($C_6H_5CH=CH_2$, St) 99.6 % purity containing 10-15 ppm of tert-butylcatechol : Siam Resin
2. Divinylbenzene ($C_6H_4(CH=CH_2)_2$, DVB) 70-85 % purity having 0.1 % of tert-butylcatechol : Fluka
3. n-Heptane (C_7H_{16}), AR grade : Carlo Ebra
4. Methanol (CH_3OH), Commercial grade : Riede-deHaën
5. Toluene (C_7H_8), AR grade : Mallinckrodt
6. Benzoyl peroxide ($C_{14}H_{10}O_3$) : Merck
7. Potassium 2,5-dihydroxybenzenesulfonate ($C_6H_5KO_5S$; HQ) : Fluka
8. Hydroxy ethyl cellulose (HEC) : Union Carbide
Cellosize® QP5200H
9. Hydroxy propyl methyl cellulose (HPMC) : Dow Chemical
Methacel® K15MS
10. Sodium bicarbonate ($NaHCO_3$) : BDH
11. Sodium hydroxide (NaOH) : Eka Kemi
12. Sodium sulfate (Na_2SO_4) : Carlo Ebra

Glassware

1. 5-Necked flask, 500 cm³
2. Liebig condenser
3. Nitrogen gas tube
4. and other general laboratory glassware

Equipment

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|--|-----------------------------|
| 1. Brunauer Emmett and Teller Sorptometer (BET Sorptometer) | : Micromeritic
ASAP 2000 |
| 2. Flowmeter | : Supelco |
| 3. Four-bladed impeller | |
| 4. Heating mantle | : Horst |
| 5. Mechanical stirrer | : Ika-Werk RW 20 |
| 6. Scanning electron microscope (SEM) | : Jeol JSM-35CF |
| 7. Stereomicroscope coupling with Luzex-F software programme of Nireco QJ 8500 | : Olympus SZH 10 |

Procedures

1. Purification of Chemicals

1.1 Removal of the inhibitor : The monomer and 10% NaOH solution were poured in a separatory funnel and the mixture was shaken vigorously. The red aqueous phase was drained off. The same procedure was repeated until the aqueous solution turned colourless. The monomer was then washed with distilled water until the litmus paper did not change its original colour. Then the monomer was dried with anhydrous Na₂SO₄.

1.2 Distillation :

(a) The dried monomer was distilled in presence of CuCl_2 . The distilled monomer was stored in a refrigerator.

(b) Methanol, commercial grade, was purified by distillation prior to use.

2. Synthesis of Styrene-Divinylbenzene Copolymer

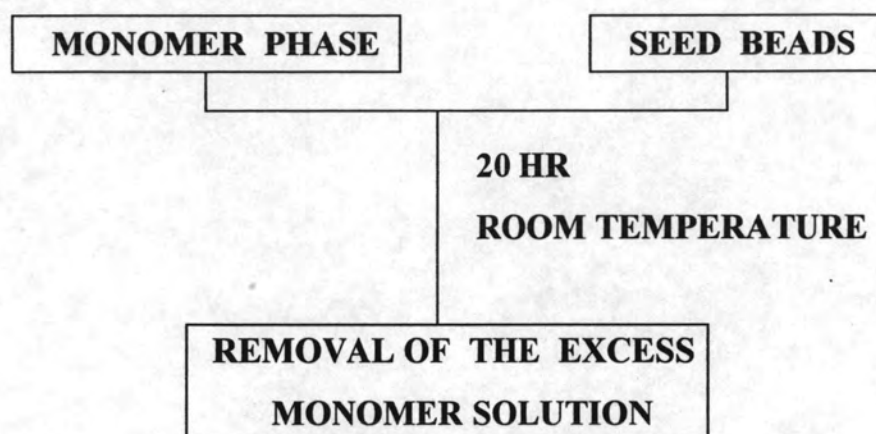
2.1 Conventional Suspension Polymerization

The styrene-divinylbenzene copolymer was prepared by suspension copolymerization. The procedure of conventional- and seeded-suspension polymerizations were summarized as shown in Figure 1 and 2. The equipment set-up was shown in Figure 3.

The solution of the suspending agents was prepared and charged into a 500 cm^3 reaction flask. The monomer solution phase contained styrene monomer, divinylbenzene as a crosslinker, benzoyl peroxide as an initiator and organic solvent was added to the flask at an agitation speed of 250 rpm. Polymerization was carried out at the desired temperature-time schedule under a nitrogen atmosphere. The seed beads of small size were obtained.

In order to find an appropriate condition for copolymerization, a series of reaction mixtures was set up by varying the composition of the suspending agents, NaHCO_3 and temperature-time schedule as shown in Table 3. The effects of the inhibitor, nitrogen flow rate, toluene and n-heptane on suspension polymerization were studied. Table 4 gives a typical polymerization recipe.

I. SWELLING STEP



II. SEEDED SUSPENSION POLYMERIZATION

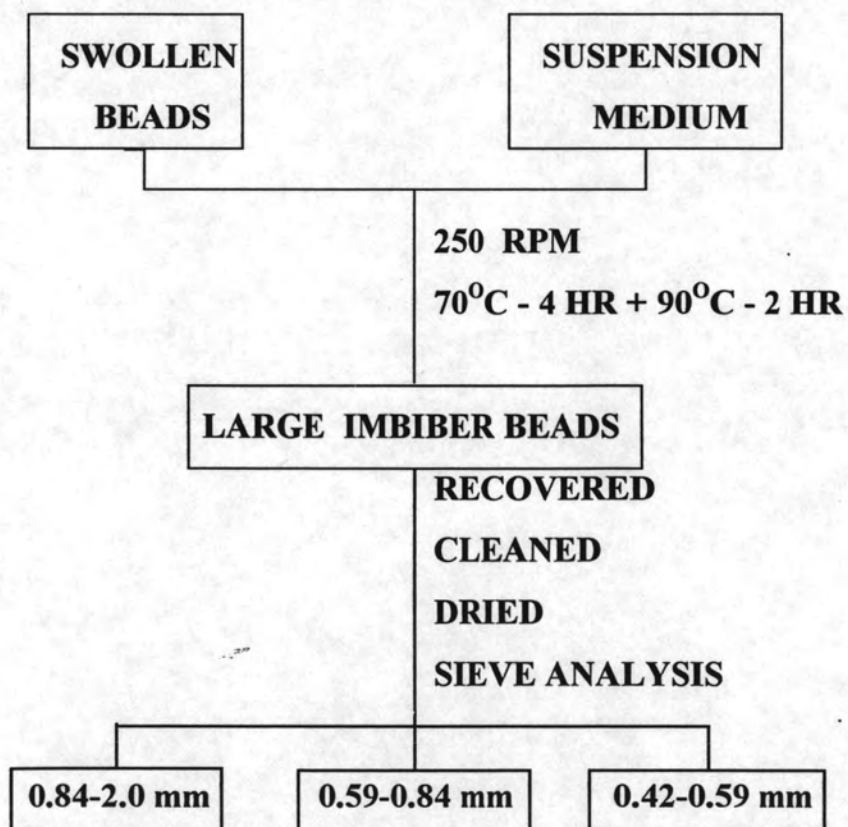


Figure 2. Diagram of seeded suspension polymerization

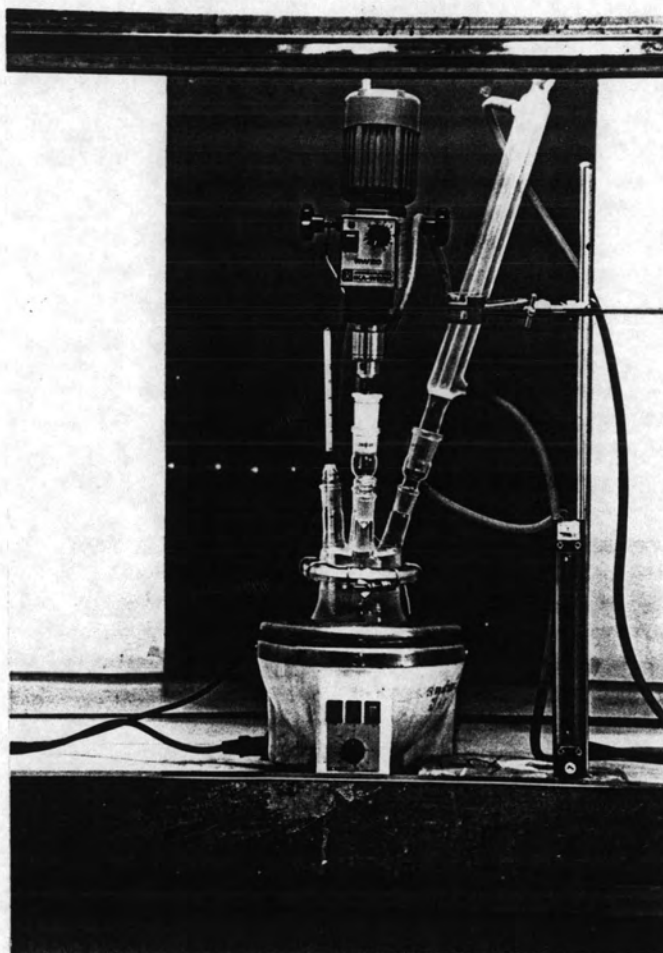


Figure 3 The equipment set-up for suspension polymerization.

2.2 Seeded Suspension Polymerization

The seed beads of styrene-divinylbenzene copolymer were cleaned and dried. These beads were sieved into fractions of a narrow size distribution. The sieved seed beads were swollen in the monomer solution, which was prepared with the same composition from which the seed beads were received. Swelling of seed beads was carried out at room temperature in a closed container for 20 hr. The swollen beads were strained on a sieve to separate the excess monomer and were then dispersed in the suspending medium with agitation. Polymerization was carried out at 70°C-4hr+90°C-2hr.

After the polymerization, the polymer beads were washed with water, soaked in methanol for 24 hr and then dried at 50°C under vacuum.

Characterization

The polymer beads were subjected to various instrumental analyses as below.

1. Particle Size Analyses

The seed beads were brought to the analysis of the particle size distribution. The wire gauze of different mesh sizes was stacked over one another varying from 2 mm at the upper stack to 0.84 mm, 0.59 mm and 0.42 mm at the lower stacks, respectively. All the beads were first filled in at the top of the stack. The smaller beads will be separated from the larger ones that passed through the upper gauze to the lower gauzes for further separation, whereas the larger ones will be retained on the upper wire gauze. The results of the bead size distribution were reported in percent weight.

2. Scanning Electron Microscope (SEM): To observe the surface, interior morphology including porosity of the beads, the beads were prepared conventionally for SEM measurement.

3. Brunauer, Emmett and Teller Sorptometer (BET): To determine the specific surface area, pore volume and pore size of the beads. The beads were weighted about 0.3 g and were degas at 50°C under vacuum within 3 hours. Then the beads were analyzed at -196 °C in the BET.

4. Determination of Bead Density : The detemination of the density of beads by using the density-gradient technique followed ASTM D1505 test method was described in Appendix A.

5. Solvent Sorption and Desorption by imbiber beads

One imbiber bead was placed in a mini petri dish (1.5x 1 cm) to immerse and swell in the excess solvent. Time zero was the time when the bead was placed into the bulk solvent and the measurement of swelling kinetics was started, consequently. The bead remained spherical throughtout the entire process and the variation in diameter was measured as function of time by the stereomicroscope coupling with a Luzex-F software program. The diameter of bead could be measured by clicking three points on the edge of the bead. The circle around the bead and the bead diameter were shown. The accuracy of the bead diameter measured from this method was 0.00001 mm.

For desorption kinetics measurements, a fully swollen bead was placed on a piece of the filter paper substrate (38.5 cm²) in a petri dish (1.5 x 10 cm). It was covered to reduce evaporation and keep out of contaminating particles. Again, the bead remained spherical and the variation of diameter was measured as a function of time by the same stereomicroscope and computer software.

All experiment conditions and the coding of the samples were shown in Table 5. The coding of samples is as follows. The first letter is the type of the polymerization technique; the second letter is the type of the diluent and the number is the level of the amount of diluent; the third letter refers to nitrogen and the number is the level of nitrogen flow rate.

Table 5. The coding of samples

Sample no.	Sample code	Conventional suspension polymerization		
		Solvent	%wt	N ₂ flow rate (cm ³ /min)
1	C-T0/N1	-	-	11
2	C-T0/N2	-	-	16
3	C-T0/N3	-	-	21
4	C-T1/N1	Toluene	0.4	11
5	C-T1/N2	Toluene	0.4	16
6	C-T1/N3	Toluene	0.4	21
7	C-T2/N1	Toluene	0.8	11
8	C-T2/N2	Toluene	0.8	16
9	C-T2/N3	Toluene	0.8	21
10	C-T3/N1	Toluene	1.6	11
11	C-T3/N2	Toluene	1.6	16
12	C-T3/N3	Toluene	1.6	21
13	C-H1/N1	Heptane	3.14	11
14	C-H1/N2	Heptane	3.14	16
15	C-H1/N3	Heptane	3.14	21
16	C-H2/N1	Heptane	9.41	11
17	C-H2/N2	Heptane	9.41	16
18	C-H2/N3	Heptane	9.41	21
19	C-H3/N1	Heptane	15.67	11
20	C-H3/N2	Heptane	15.67	16
21	C-H3/N3	Heptane	15.67	21

Table 5. The coding of samples (continued)

Sample no.	Sample code	Seeded suspension polymerization		
		Solvent	%wt	N ₂ flow rate (cm ³ /min)
22	S-T0/N1	-	-	11
23	S-T0/N2	-	-	16
24	S-T0/N3	-	-	21
25	S-T1/N1	Toluene	0.4	11
26	S-T1/N2	Toluene	0.4	16
27	S-T1/N3	Toluene	0.4	21
28	S-T2/N1	Toluene	0.8	11
29	S-T2/N2	Toluene	0.8	16
30	S-T2/N3	Toluene	0.8	21
31	S-T3/N1	Toluene	1.6	11
32	S-T3/N2	Toluene	1.6	16
33	S-T3/N3	Toluene	1.6	21
34	S-H1/N1	Heptane	3.14	11
35	S-H1/N2	Heptane	3.14	16
36	S-H1/N3	Heptane	3.14	21
37	S-H2/N1	Heptane	9.41	11
38	S-H2/N2	Heptane	9.41	16
39	S-H2/N3	Heptane	9.41	21
40	S-H3/N1	Heptane	15.67	11
41	S-H3/N2	Heptane	15.67	16
42	S-H3/N3	Heptane	15.67	21

Note: C and S = conventional and seeded suspension polymerization, respectively, H = n-heptane, T = toluene, numbers 1, 2 and 3 = low, medium and high level