

## CHAPTER IV

### RESULT AND DISCUSSION

#### Optimum Quantity of the Suspending Agents and Buffer for Suspension Polymerization

The seed beads were prepared by the conventional suspension polymerization using HPMC and HEC as suspending agents and  $\text{NaHCO}_3$  as buffer. The appropriate condition for copolymerization was found by varying the composition of the suspending agents and  $\text{NaHCO}_3$  as listed in Table 3. The effect of the quantity of the suspending agent and  $\text{NaHCO}_3$  on suspension polymerization was studied. Table 6 gives the results of the polymer product formed.

**Table 6.** The effect of the suspending agents and  $\text{NaHCO}_3$  on suspension polymerization. Monomer phase: 0.3 % DVB. Temperature-time schedule: 70°C 4 hr; 90°C 5 hr.

HPMC (%wt)	HEC (% wt)	$\text{NaHCO}_3$ (% wt)	Polymer product
0.23-2.35	0.11-1.25	2-15	Coagulated polymer
2.53	1.32	13	Polymer beads
2.53	1.32	8	Coagulated polymer
3.02	1.91	24.64	Polymer powders

From Table 6, the seed beads were prepared by the conventional suspension polymerization. The monomer phase volume fraction was 0.075 which contained 0.3% divinylbenzene crosslinking agent and 0.3% benzoyl

peroxide. The composition of aqueous phase was 2.53% HPMC, 1.317% HEC and 13%  $\text{NaHCO}_3$  based on the monomer phase. The increased amount of  $\text{NaHCO}_3$  would increase the rate of dissolution of suspending agents. The rate of dissolution of the suspending agents was also increased about 10 to 120 times by raising the pH value (preferably pH 7.5 to 9) (27). Thus, the pH value of this aqueous solution was adjusted to about 8.

### Effect of Temperature-Time Schedule on Suspension Polymerization

From Table 6, at the aqueous phase composition of 2.53% HPMC, 1.32 % HEC and 13 %  $\text{NaHCO}_3$ , the seed bead could be formed. The effect of the temperature-time schedule on suspension polymerization was studied. Table 7 gives the results of polymer products form.

**Table 7.** The effect of temperature-time schedule on suspension polymerization. Monomer phase: 0.3 % DVB. Aqueous phase: 2.53 % HPMC, 1.32 % HEC and 13 %  $\text{NaHCO}_3$

Temperature-time schedule	Polymer product
70°C-3 hr + 90°C-3 hr	Coagulated polymer
70°C-4 hr + 90°C-2 hr	Soft and sticky beads
70°C-4 hr + 90°C-5 hr	Soft beads

During the early stage of the suspension polymerization at 70°C, the bulk monomer was sheared to elongate and break up into drops. After 3 hours, the temperature was changed to 90 °C, consequently, the polymer coagulated around the impeller. It can be attributed to the fact that (1) the more incompleated polymerized oligomers in the droplets, the more tackier the droplets, (2) an increase in temperature in a solution reduces the surface tension that decrease the droplet formation and enhance coagulation. To reduce

the unreacted monomer or incomplete oligomers in droplets, the reaction temperature was changed to 90 °C after 4 hours. Therefore, the appropriate temperature-time schedule was 70°C-4 hr + 90°C-5 hr. At this optimum condition, the yield of seed beads was 39.4 % and the average bead size was about 1.85 mm.

### Effect of Potassium 2,5-dihydroxybenzenesulfonate on Suspension Polymerization

In the previous experiment, which contained the monomer phase of 0.3% divinylbenzene, the seed beads obtained could be separated from the solution when they were soaked in the aqueous solution for 2 weeks. These seed beads were very soft and sticky. The divinylbenzene content in the monomer phase was thus increased to 1 %. The polymer formed was clustered and stuck to a big fused mass (no beads formation). This was attributed to the more rapid rise in viscosity of the dispersed phase due to the high polymerization rate. Therefore, the effect of potassium 2,5-dihydroxybenzenesulfonate on suspension polymerization was studied in order to reduce the coagulation. Table 8 shows the results of polymer products.

**Table 8.** The effect of potassium 2,5-dihydroxybenzenesulfonate on suspension polymerization. Monomer phase: 1 % DVB. Aqueous Phase: 2.53 % HPMC, 1.32 % HEC and 13 % NaHCO<sub>3</sub>

Hydroquinone (% based on monomer)	Polymer product
0 -0.05	Big fused mass
0.08-0.15	Coagulated polymer
0.16	Polymer beads
0.18	Coagulated polymer

The water-soluble inhibitor, potassium 2, 5-dihydroxybenzene sulfonate, was selected to kill the radicals escaping from the polymer particles. From Table 8, an appropriate amount of the inhibitor was 0.16 % based on the monomer. When the inhibitor was more than 0.16 %, the polymer coagulated, it might be possible to state that the fact that the potassium 2,5-dihydroxybenzenesulfonate might partition into the monomer-swollen particles and retarded the polymerization reaction. The effect of amount of divinylbenzene on the bead size was shown in Table 9.

**Table 9.** The comparison between the seed beads prepared by using 0.3% and 1 % divinylbenzene. Aqueous Phase: 2.53 % HPMC, 1.32 HEC and 13 % NaHCO<sub>3</sub>.

Parameter	Sample code: DVB0.3	DVB1
% DVB	0.03	1
% Hydroquinone	0	0.16
Bead size distribution (% wt)		
<0.42 mm	-	51.13
0.42-0.59 mm	-	20.15
0.59-0.84 mm	1.27	13.77
0.84-2 mm	23.91	14.58
>2 mm	74.82	-
Average size (mm)	1.85	0.62
% conversion	42.3	43.87
%yield	39.42	30
temperature-time schedule	70°C-4 hr + 90°C-5 hr	70°C-4 hr + 90°C-3 hr

From the system using 0.3% divinylbenzene as crosslinking agent, the average bead size was 1.85 mm resulted from the total 9 hour reaction time at two temperature levels. Unlike the above result, the average bead size prepared by using 1% divinylbenzene, an increase of the divinylbenzene concentration by a factor of 3.34 produced the beads of 0.62 mm with a shorter reaction time of total 7 hours at the same temperature levels. The divinylbenzene concentration would be consumed rapidly at the first temperature-time program. The decay of the radicals might be large at the beginning of the reaction and decreased gradually after 4 hours at 70°C. The increase in divinylbenzene concentration at the beginning induced a great number of short kinetic chain lengths to result in a relatively large number of low molecular weight beads. The increase in temperature at the later stage (90 °C) promoted those low molecular weight beads with short chain lengths to be polymerized to become the long chain length with the greater molecular weights.

From all experiments, the appropriate condition for the bead preparation are:

Aqueous phase: (volume fraction 0.925)

HPMC	2.53 %
HEC	1.32 %
NaHCO <sub>3</sub>	13.0 %
Hydroquinone	0.16 %

Monomer phase: (volume fraction 0.075)

Styrene	98.7 %
Divinylbenzene	1.0 %
Benzoyl peroxide	0.3 %

Temperature-time schedule: 70°C-4 hr + 90°C-3 hr

Using this appropriate condition, the effect of nitrogen flow rate and diluents, n-heptane and toluene, on bead size were studied.



## Properties of Beads: Effect of the Nitrogen Flow Rate and Diluents

There are three types of diluents used to prepare porous matrices(28) :

(a) By addition of a solvating diluent such as toluene and dichloro ethane to the polymerizing mixture. We propose to name this type of copolymers a PS type (porous by solvent)

(b) By addition of a nonsolvating diluent such as n-heptane and n-butyl alcohol, resulting in a PP type copolymer (porous by precipitator).

(c) By addition of linear polymer, e.g., polystyrene, which gives a PM type copolymer (porous by macromolecular material).

In this study, the styrene-divinylbenzene copolymer were prepared by using n-heptane and toluene as diluent. The properties of beads investigated were, bead size distribution, sorption and desorption, properties of pores, and surface and interior morphology.

### 1. Bead Size Distribution.

#### 1.1 Extent of bead sizes and their distribution

The polymer was prepared by varying the quantity of diluent and nitrogen flow rate, seed bead size distribution was shown in Tables 10 and 11. The bead sizes were sived into four classifications , e. g., <2 mm, 0.42-0.59 mm, 0.59-0.84 mm and 0.84-2.0 mm. The bead size distribution was reported in the percentage of the weight of the beads. Most of the bead sizes were in the range of 0.42-0.59 mm. To enlarge the bead size, the seed beads in range the of 0.42-0.59 mm were soaked in the monomer solution and were then repolymerized. Tables 12 and 13 show the size distribution of the large imbiber beads. The imbiber beads from one-step swelling polymerization were 2 times larger than the initial seed beads. It can be attributed to the fact that the absorbed monomer was desorbed, and become active enough to be then

repolymerized into the beads. Therefore, the large beads in the size range of 0.84-2 mm in diameter were prepared via seeded suspension polymerization. Since the beads can be swollen and repolymerized many times, the beads of any reasonably large sizes (1.2 mm) can be produced by this method. The bead size prepared via the conventional and seeded suspension polymerization gave a broad and narrow bead size distribution, respectively (Figure 4). The bead sizes prepared via seeded suspension polymerization were controlled by the size of the initial seed beads and crosslink density.

### 1.2 Effect of nitrogen flow rate

The bead sizes tend to be bigger 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, therefore, be obtained.

### 1.3 Effect of the diluents

The effect of toluene on the bead sizes: the bead sizes tend to be smaller in toluene with increasing its concentration. It may be attributed to that the polymer chains were disentangled in a good solvent such as toluene; the chains were stretch out to result in small excluded free volumes in the polymeric solution. The incoming polymeric radicals could, lowers, polymerized within the free volume available in the solution. It is, therefore, found the smaller beads in toluene diluent.

The effect of n-heptane on the bead sizes: the bead sizes tend to be larger in n-heptane with increasing its concentration. The polymer chains folded and entangled in n-heptane, a poor solvent for poly(styrene-co-divinylbenzene), to allow a large excluded free volume in this polymeric solution. Unlike the toluene diluent, the beads were become larger.

**Table 10.** Effect of nitrogen flow rate and toluene on bead properties in suspension polymerization

	C-T0/N1	C-T1/N1	C-T2/N1	C-T3/N1	C-T0/N2	C-T1/N2	C-T2/N2	C-T3/N2	C-T0/N3	C-T1/N3	C-T2/N3	C-T3/N3
N <sub>2</sub> flow rate (cm <sup>3</sup> /min)	11	11	11	11	16	16	16	16	21	21	21	21
% toluene	0	0.4	0.8	1.6	0	0.4	0.8	1.6	0	0.4	0.8	16
% conversion	43.87	56.72	39.73	49.72	47.58	38.54	30.71	51.64	57.06	51.96	38.87	39.06
%yield	30	23.19	36.74	31.09	29.09	30.71	16.48	14.4	37	35.19	34.21	31.26
Bead size distribution ( % wt)												
<0.42 mm	51.13	39.06	29.12	25.12	19.48	17.52	37.16	41.98	20.49	49.12	48.46	27.88
0.42-0.59 mm	20.15	23.98	21.44	38.48	25.98	32.29	27.93	25.8	40.07	38.42	31.18	25.82
0.59-0.84 mm	13.77	19.35	15.87	8.02	12.48	17.04	7.3	13.71	16.44	8.33	10.51	17.55
0.84-2.0 mm	14.58	17.59	33.46	17.62	42.24	33.14	27.59	18.5	22.99	4.13	9.83	28.74
Average size (mm)	0.62	0.67	0.82	0.61	0.9	0.83	0.75	0.66	0.86	0.52	0.58	0.78
Swelling ratio	10.43	10.06	10.75	10.29	10.02	7.26	8	9.11	8	6.43	11.39	16.35
Density (g/cm <sup>3</sup> )	0.9623	0.9379	0.963	0.9333	1.0969	1.0	1.0529	1.0326	.93	0.9621	0.9174	0.9502



**Table 11. Effect of nitrogen flow rate and n-heptane on bead properties in suspension polymerization**

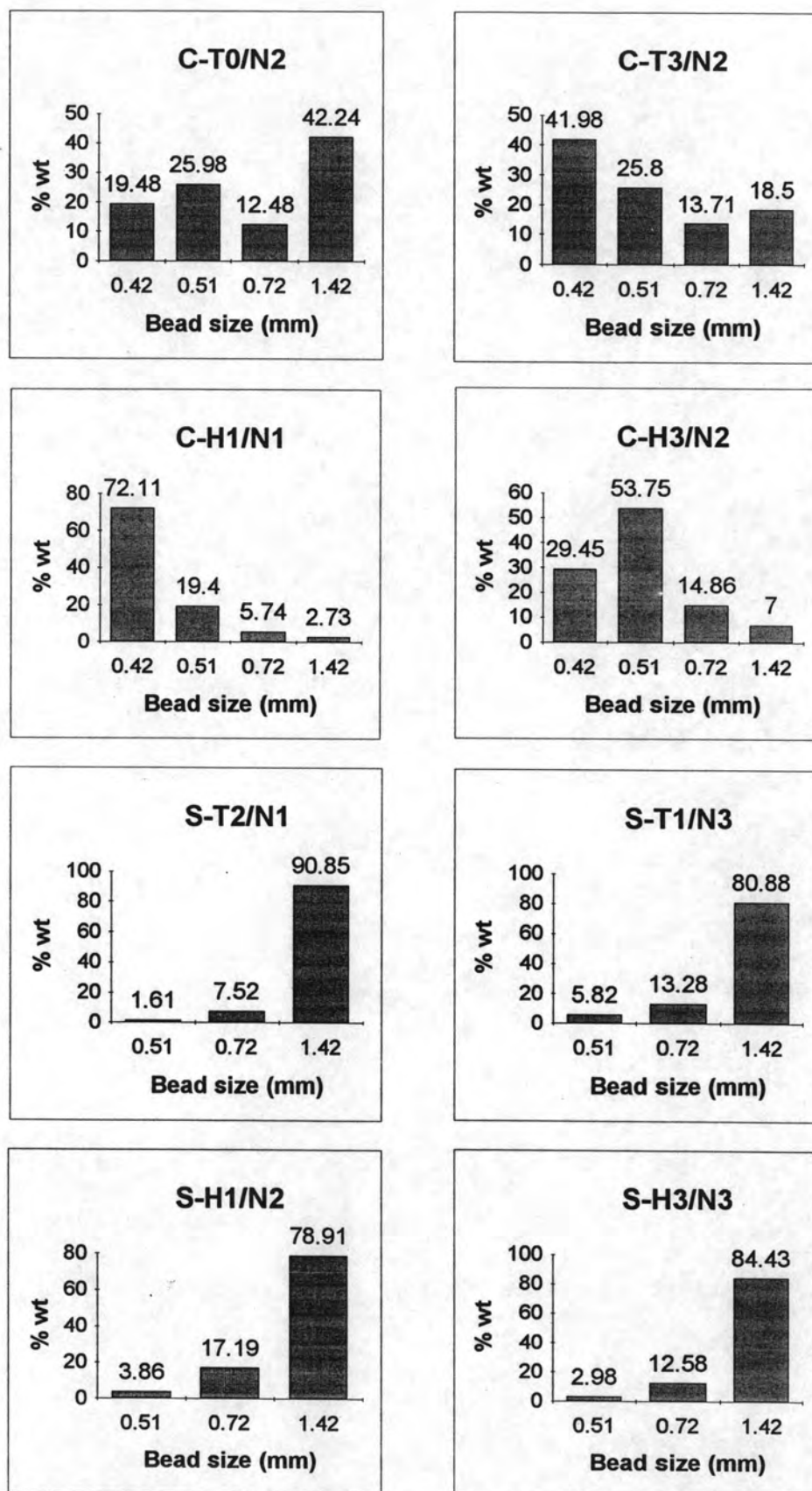
Parameter	C-T0/N1	C-H1/N1	C-H2/N1	C-H3/N1	C-T0/N2	C-H1/N2	C-H2/N2	C-H3/N2	C-T0/N3	C-H1/N3	C-H2/N3	C-H3/N3
N <sub>2</sub> flow rate (cm <sup>3</sup> /min)	11	11	11	11	16	16	16	16	21	21	21	21
% Heptane	0	3.14	9.41	15.67	0	3.14	9.41	15.67	0	3.14	9.41	15.67
% conversion	43.87	36.34	32.75	38.06	47.58	43.71	30.88	48.54	57.06	35	62.51	51.84
%yield	30	27.77	28.38	32.57	29.09	21.81	16.78	17.57	37	25	21.65	53.3
Bead size distribution ( % wt)												
<0.42 mm	51.13	72.11	44.37	46.46	19.48	35.29	28.9	29.45	20.49	35.67	28.01	68.95
0.42-0.59 mm	20.15	19.4	32.18	20.4	25.98	34.25	36.06	53.57	40.07	19.03	23.96	25.08
0.59-0.84 mm	13.77	5.74	9.57	10.75	12.48	12.91	15.1	14.86	16.44	12.45	13.37	5.4
0.84-2.0 mm	14.58	2.73	13.87	22.38	42.24	17.53	19.82	7	22.99	32.82	30.64	0.63
Average size (mm)	0.62	0.48	0.61	0.69	0.9	0.66	0.69	0.6	0.86	0.8	0.77	0.46
Swelling ratio	10.45	13.44	11.17	7.63	10.27	19.81	15.63	14.03	8	14.83	10.1	8.83
Density (g/cm <sup>3</sup> )	0.9623	0.9666	0.9475	0.9275	1.0969	1.028	0.9666	0.9526	0.9301	0.9814	0.9701	1.0027

**Table 12.** Effect of nitrogen flow rate and toluene on bead properties in seeded suspension polymerization

Parameter	S-T0/N1	S-T1/N1	S-T2/N1	S-T3/N1	S-T0/N2	S-T1/N2	S-T2/N2	S-T3/N2	S-T0/N3	S-T1/N3	S-T2/N3	S-T3/N3
N <sub>2</sub> flow rate (cm <sup>3</sup> /min)	11	11	11	11	16	16	16	16	21	21	21	21
% toluene	0	0.4	0.8	1.6	0	0.4	0.8	1.6	0	0.4	0.8	16
%yield	80.86	73.24	72.05	61.16	83.06	67.61	48.71	20.85	88.9	56.48	55.54	97.92
Bead size distribution ( % wt)												
0.42-0.59 mm	4.37	1.61	1.61	1.82	1.29	6.53	6.11	19.4	0	5.82	4.92	5.51
0.59-0.84 mm	16.91	25.67	7.52	28.47	7.76	18.89	16.4	50	11.45	13.28	21.44	21.26
0.84-2.0 mm	78.53	72.7	90.85	61.69	90.94	74.57	77.74	30.6	88.55	80.88	73.55	73.22
Average size (mm)	1.26	1.22	1.35	1.09	1.36	1.23	1.25	0.89	1.34	1.27	1.22	1.22
Swelling ratio	4.95	7.7	9.08	9.57	4.87	6.13	6.84	8	4.43	4.84	5.64	6.66
Density (g/cm <sup>3</sup> )	0.9477	0.9557	0.9832	1.0	1.0164	0.9604	1.0744	0.9467	0.9661	0.9443	0.949	0.946

**Table 13.** Effect of nitrogen flow rate and n-heptane on bead properties in seeded suspension polymerization

Parameter	S-T0/N1	S-H1/N1	S-H2/N1	S-H3/N1	S-T0/N2	S-H1/N2	S-H2/N2	S-H3/N2	S-T0/N3	S-H1/N3	S-H2/N3	S-H3/N3
N <sub>2</sub> flow rate (cm <sup>3</sup> /min)	11	11	11	11	16	16	16	16	21	21	21	21
% Heptane	0	3.14	9.41	15.67	0	3.14	9.41	15.67	0	3.14	9.41	15.67
% yield	80.86	63.67	75.94	17.1	83.06	69.07	44.89	64.93	88.9	47.83	59.93	60
Bead size distribution (% wt)												
0.42-0.59 mm	4.37	17.54	9.73	0	1.29	3.86	6.15	18.25	0	2.59	6.78	2.98
0.59-0.84 mm	16.91	47.96	44.96	22.65	7.76	17.19	20.55	49.21	11.45	14.08	22.44	12.58
0.84-2.0 mm	78.53	34.55	45.3	73.61	90.94	78.91	73.28	32.52	88.55	83.31	70.76	84.43
Average size (mm)	1.26	0.92	1.01	1.21	1.35	1.26	1.22	0.91	1.34	1.3	1.2	1.3
Swelling ratio	4.95	8.63	8.16	4.13	4.8	10.54	6.86	12.7	4.43	7.44	5.66	4.75
Density (g/cm <sup>3</sup> )	0.9477	0.9576	0.9626	0.9225	1.0164	0.9581	1.0444	1.0273	0.9661	1.0456	0.9736	1.286



**Figure 4** Bead size distribution of the seed and the final seeded beads prepared under the effects of diluents and nitrogen flow rate



## 2. Sorption

The sorption of the imbibed beads in toluene which has a total solubility parameter of  $18.2 \text{ (MPa)}^{1/2}$  was determined based on an increase in bead size upon swelling in good solvents. Appendix B shows the increase in bead diameter and volume with swelling time.

Figures 5-8 show the variation of bead volume with swelling time. The curves comprise three stages: (I) an initial stage of the high sorption rate can be easily observed because the solubility parameter of toluene closes to that of the styrene-divinylbenzene copolymers ( $18.6 \text{ (MPa)}^{1/2}$ , (22)) and its chemical structure is similar to the styrene-divinylbenzene copolymer structure.; (ii) a second stage of the slow sorption rate is due to the sorption into the pore inclusive of pore structure and dimension.; and (iii) a third stage of the plateau value because of the absorption saturation.

Figures 5 and 6 show the increasing of bead volume with swelling time for the seed beads prepared by using toluene and n-heptane, respectively, as diluent. The initial stage of sorption was about 10 min, the bead volume increased rapidly since the network began to expand by absorbing the surrounding solvent. Finally, the swollen bead reached a stationary state in equilibrium with the surrounding solvent within 50 min. The ranges of toluene sorption rate and diffusion coefficient (see Appendix C) of the seed bead was  $0.1\text{-}0.17 \text{ mm}^3/\text{min}$  and  $0.68 \times 10^{-3}\text{-}1.64 \times 10^{-3} \text{ cm}^2/\text{min}$ , respectively. These properties depend upon the bead diameter and bead morphology. Degree of crosslink is considered as an important controlling factor of the rate of solvent sorption and the bead morphology such as pore distribution.

Figures 7 and 8 show the increase in bead volume with swelling time for the large imbibed beads prepared by using toluene and n-heptane, respectively, as diluent. From these curves, the initial stage of sorption was about 25 min, and the equilibrium was reached within 2 hr. The ranges of



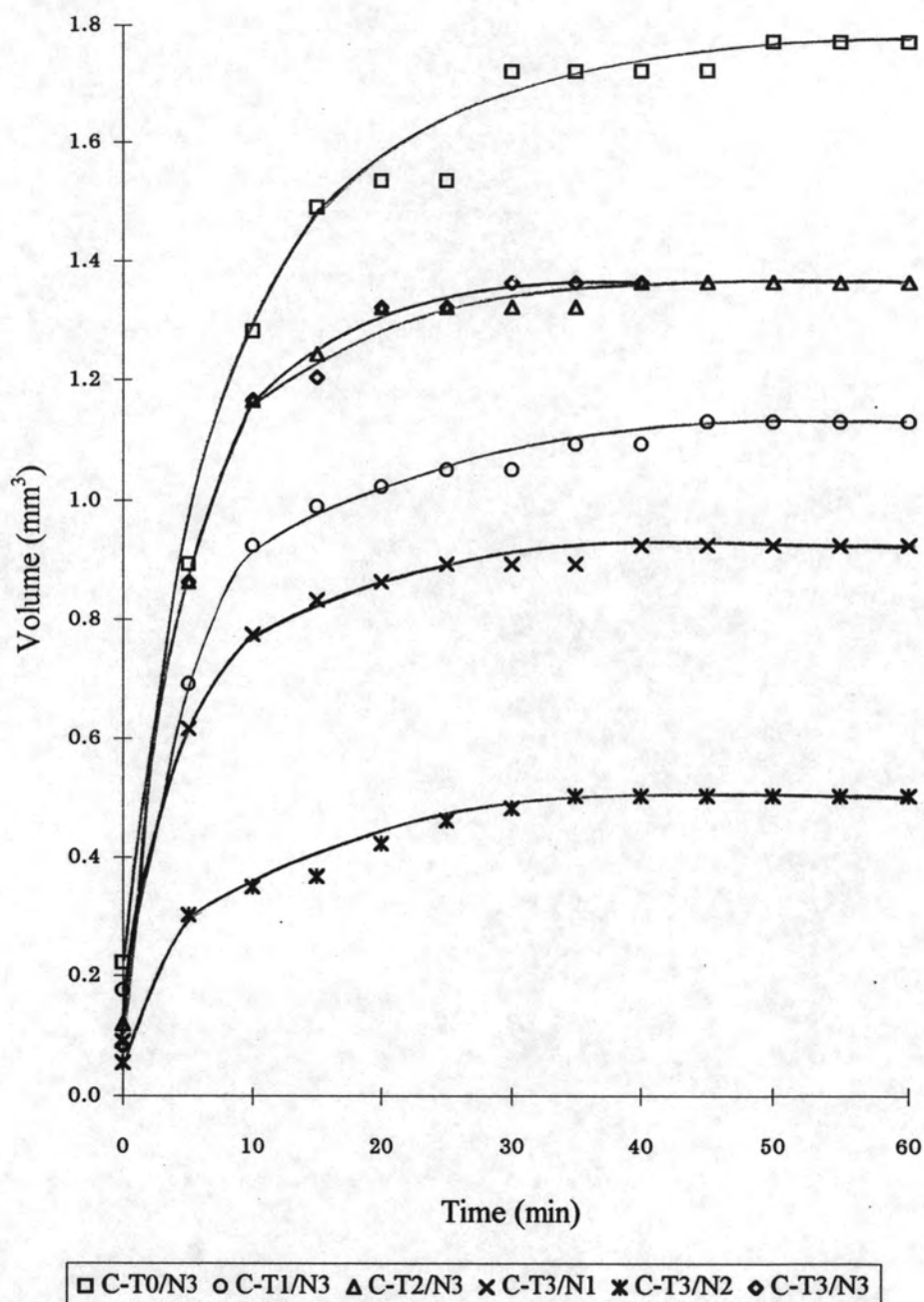
toluene sorption rate and diffusion coefficient (see Appendix C) of these imbiber beads were  $0.25\text{-}0.61\text{ mm}^3/\text{min}$  and  $0.93\times 10^{-3}\text{-}2.39\times 10^{-3}\text{ cm}^2/\text{min}$ , respectively. The toluene sorption rate and diffusion coefficient of these beads increased due to the increase of bead diameter. The duration of sorption time of the large beads was longer than that of the seed beads due to the higher crosslink.

The change of the swelling ratio of imbiber bead with time is also plotted as shown in Figure 9. The swelling ratio characteristic is similar to that of the bead volume.

Figure 10 shows the effect of toluene on the swelling ratio of beads. It can be found that the swelling ratio of the beads increased with increasing the amount of toluene at the same nitrogen flow rate. The bead prepared by using 1.6 % toluene and nitrogen flow rate of  $11\text{ cm}^3/\text{min}$  yielded the swelling ratio of 9.19. The swelling ratio was probably controlled by the close solubility of the styrene-divinylbenzene beads to toluene resulting from a slight crosslink.

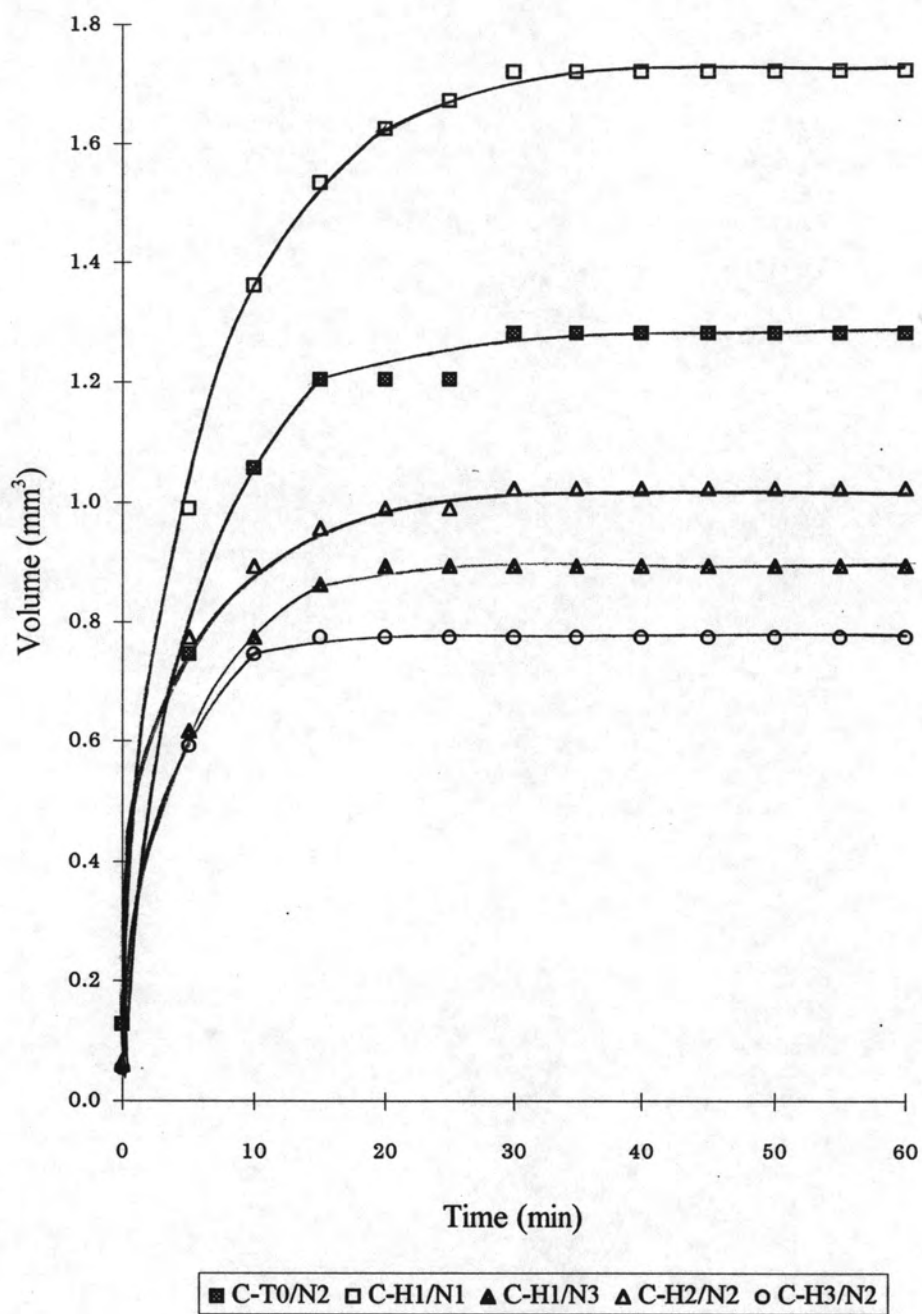
Figure 11 shows the effect of n-heptane on the swelling ratio of beads. It can be found that the swelling ratio of the beads decreased with increasing the amount of n-heptane at the same nitrogen flow rate. The bead prepared by using 3.14 % n-heptane at nitrogen flow rate of  $21\text{ cm}^3/\text{min}$  yielded the swelling ratio of 14.84. The n-heptane is the poor solvent for the imbiber beads that constrained the chains of the imbiber bead, which is suspected to give a better pore characteristic.

Figure 12 shows the effect of nitrogen flow rate on the swelling ratio at any amount of toluene levels. The swelling ratio 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.



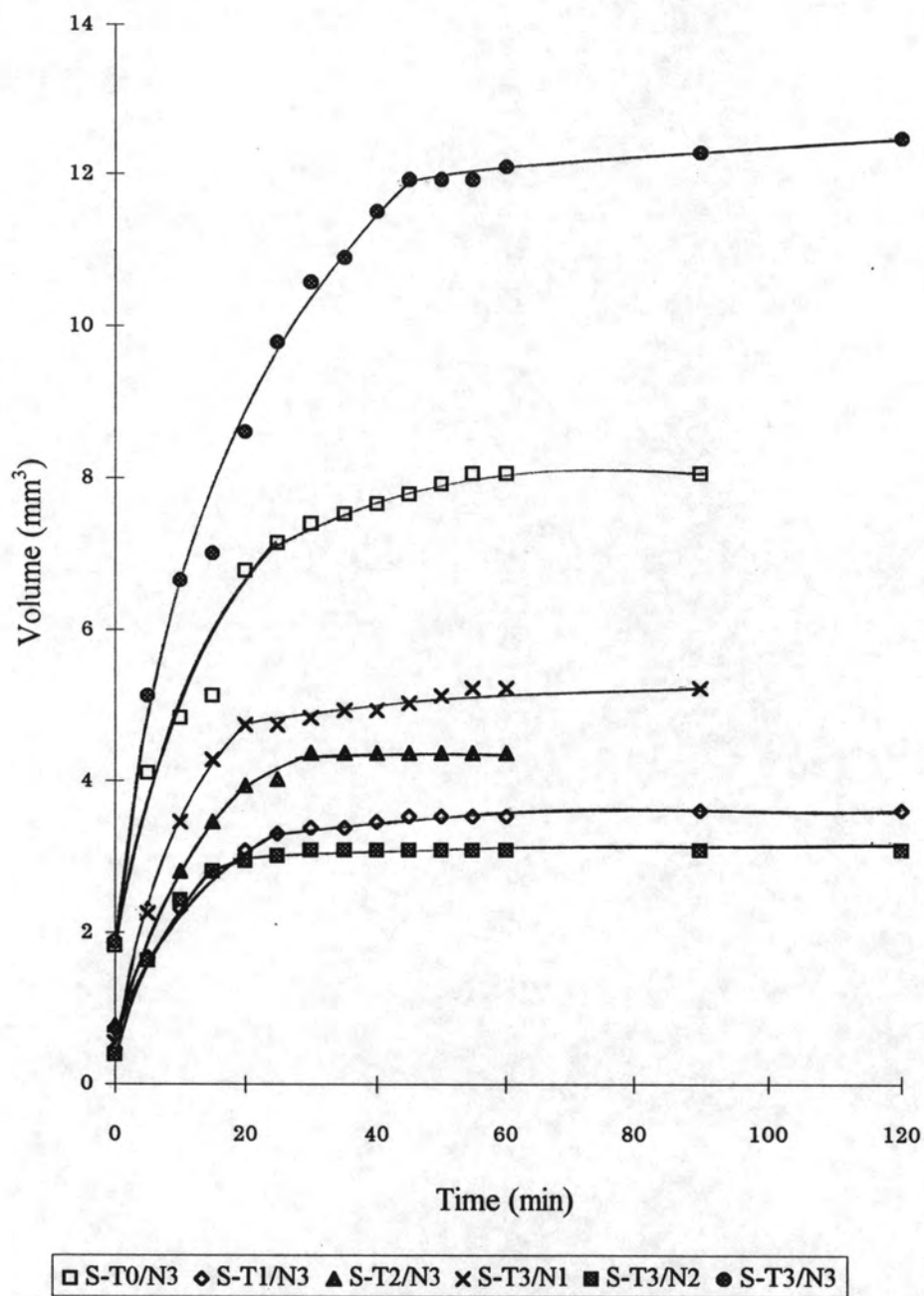
**Figure 5** Variation of seed bead volume with sorption time.

Seed beads were prepared by using toluene as diluent



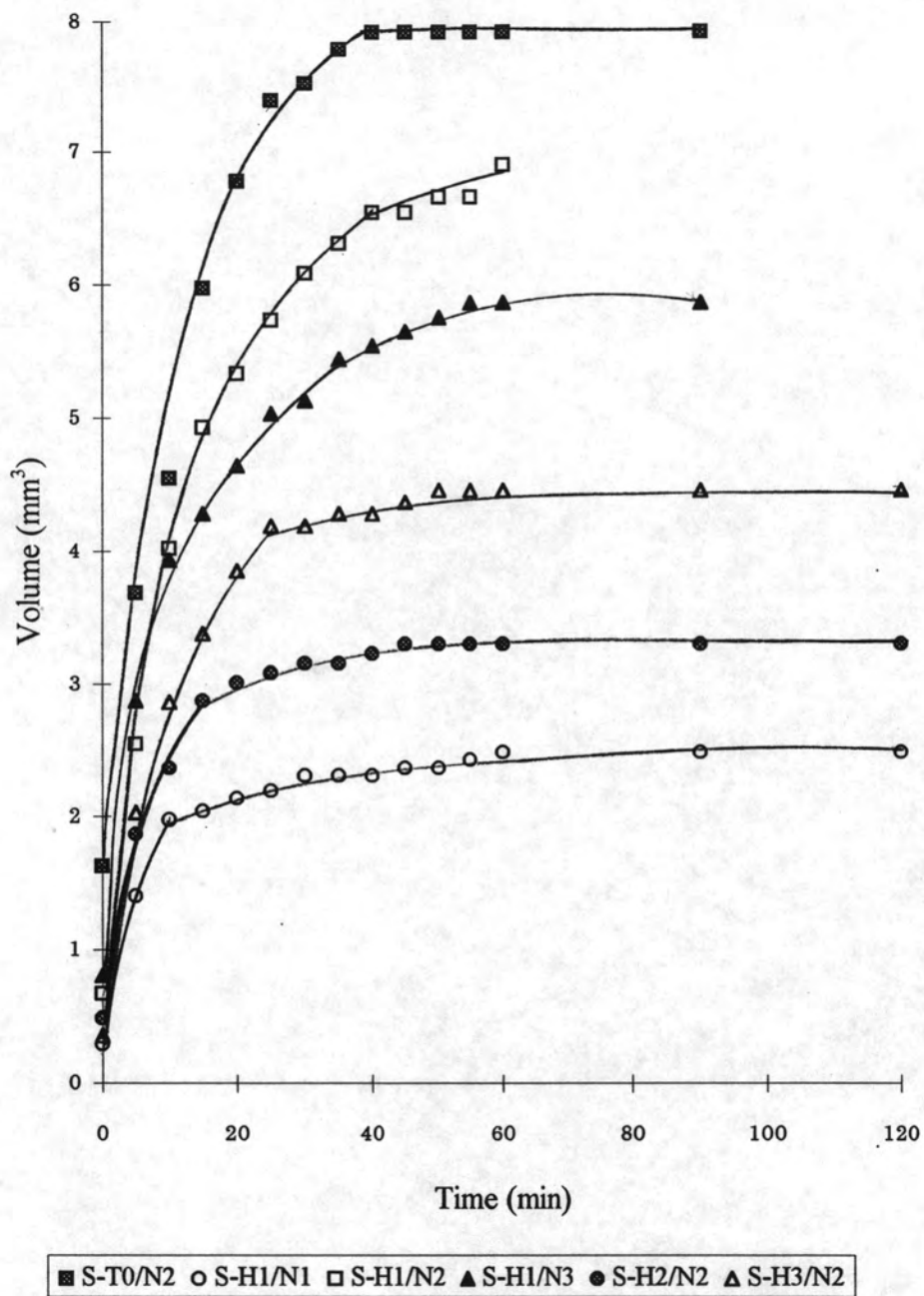
**Figure 6** Variation of seed bead volume with sorption time.

Seed beads were prepared by using n-heptane as diluent.



**Figure 7** Variation of the large imbibed bead volume with sorption time.

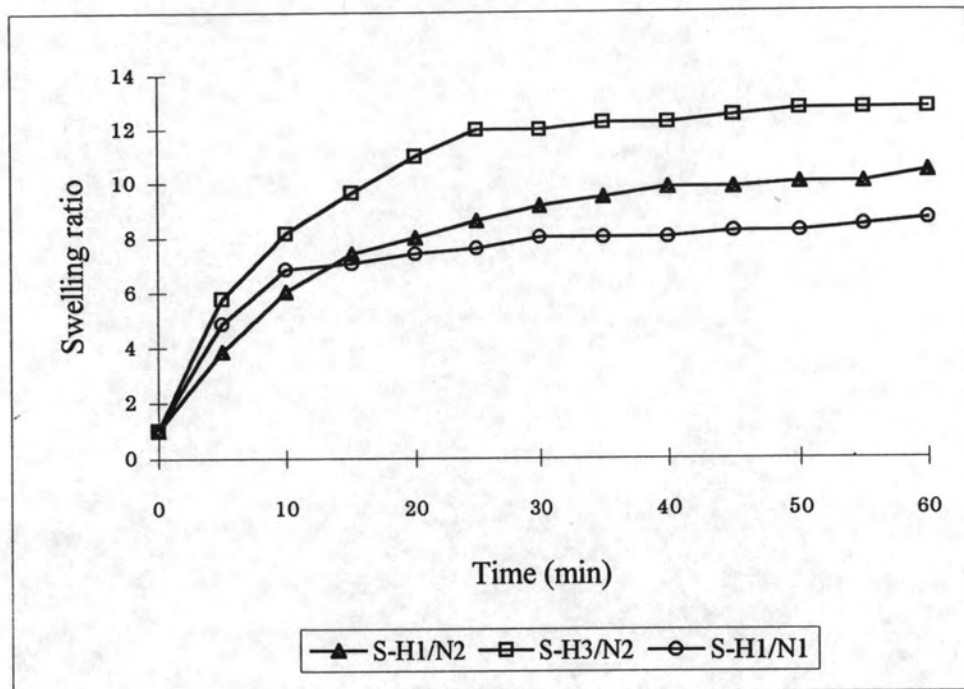
Beads were prepared by using toluene as diluent.



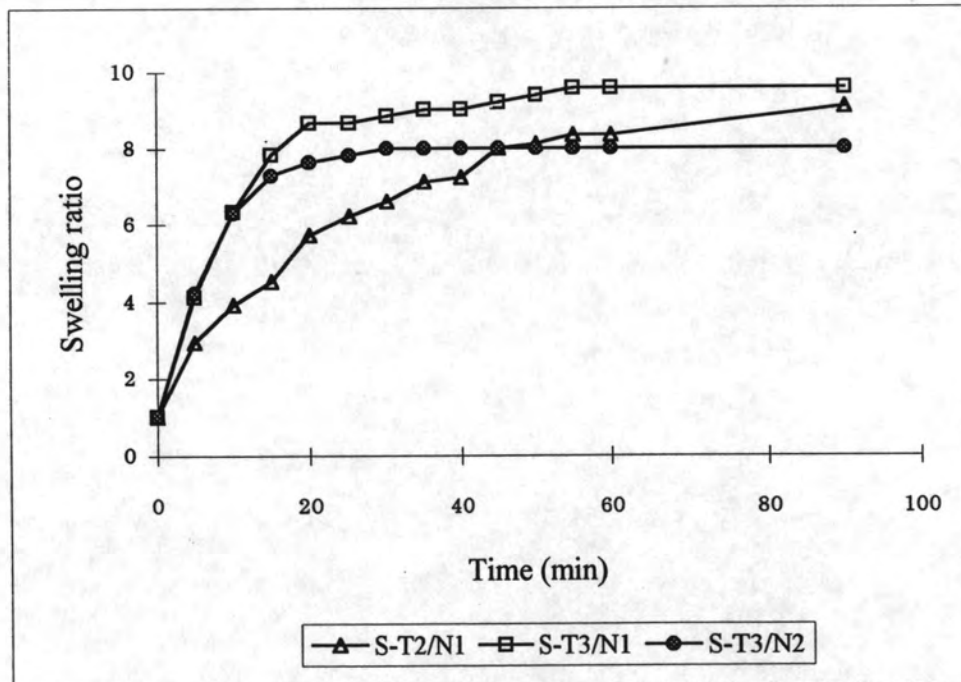
**Figure 8** Variation of the large imbibed bead volume with sorption time.

Beads were prepared by using n-heptane as diluent.



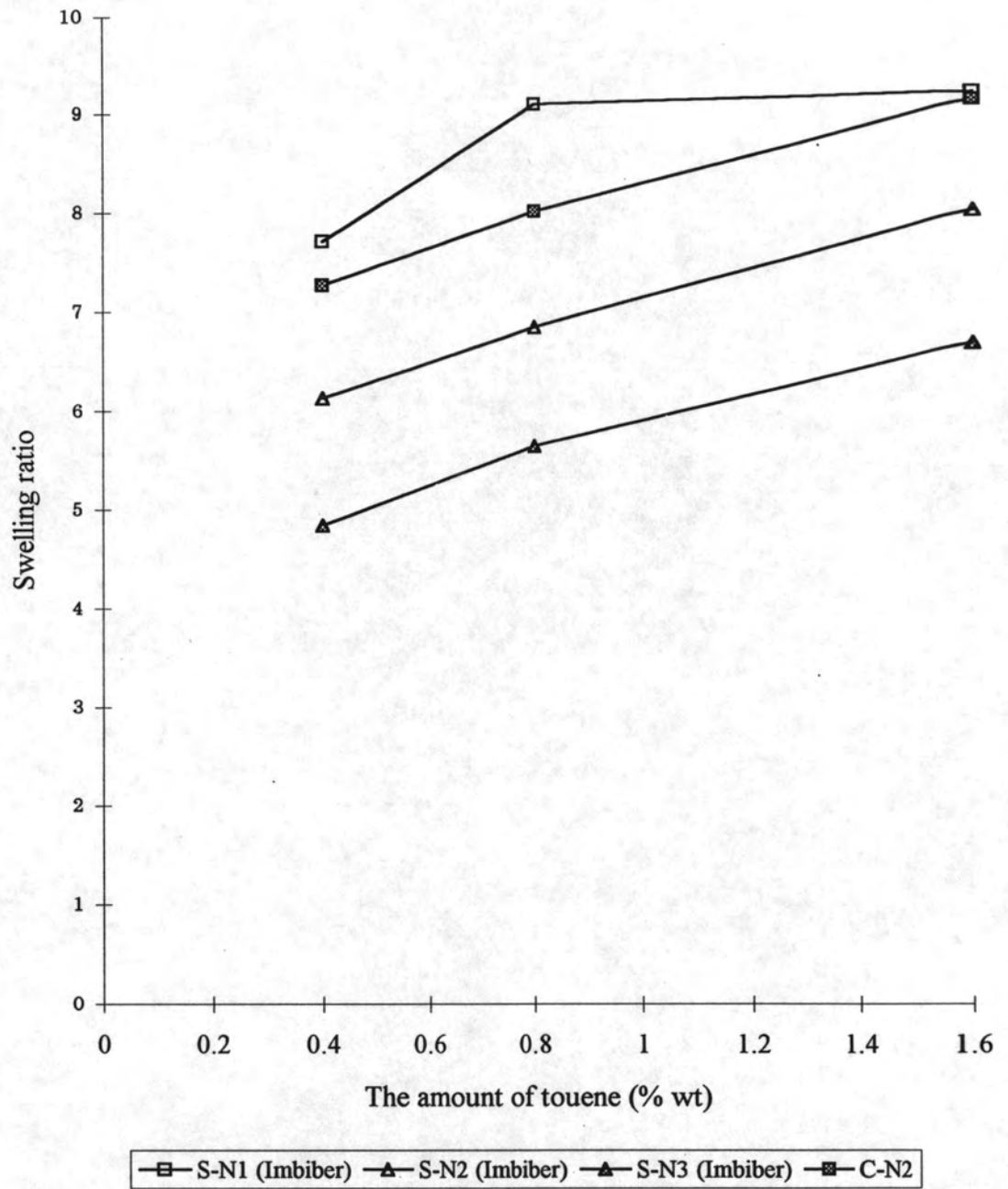


(a)



(b)

**Figure 9** The relationship between swelling ratio and swelling time  
 (a) Beads were prepared by using n-heptane as diluent.  
 (b) Beads were prepared by using toluene as diluent.



**Figure 10** Effect of touene on the swelling ratio of beads.

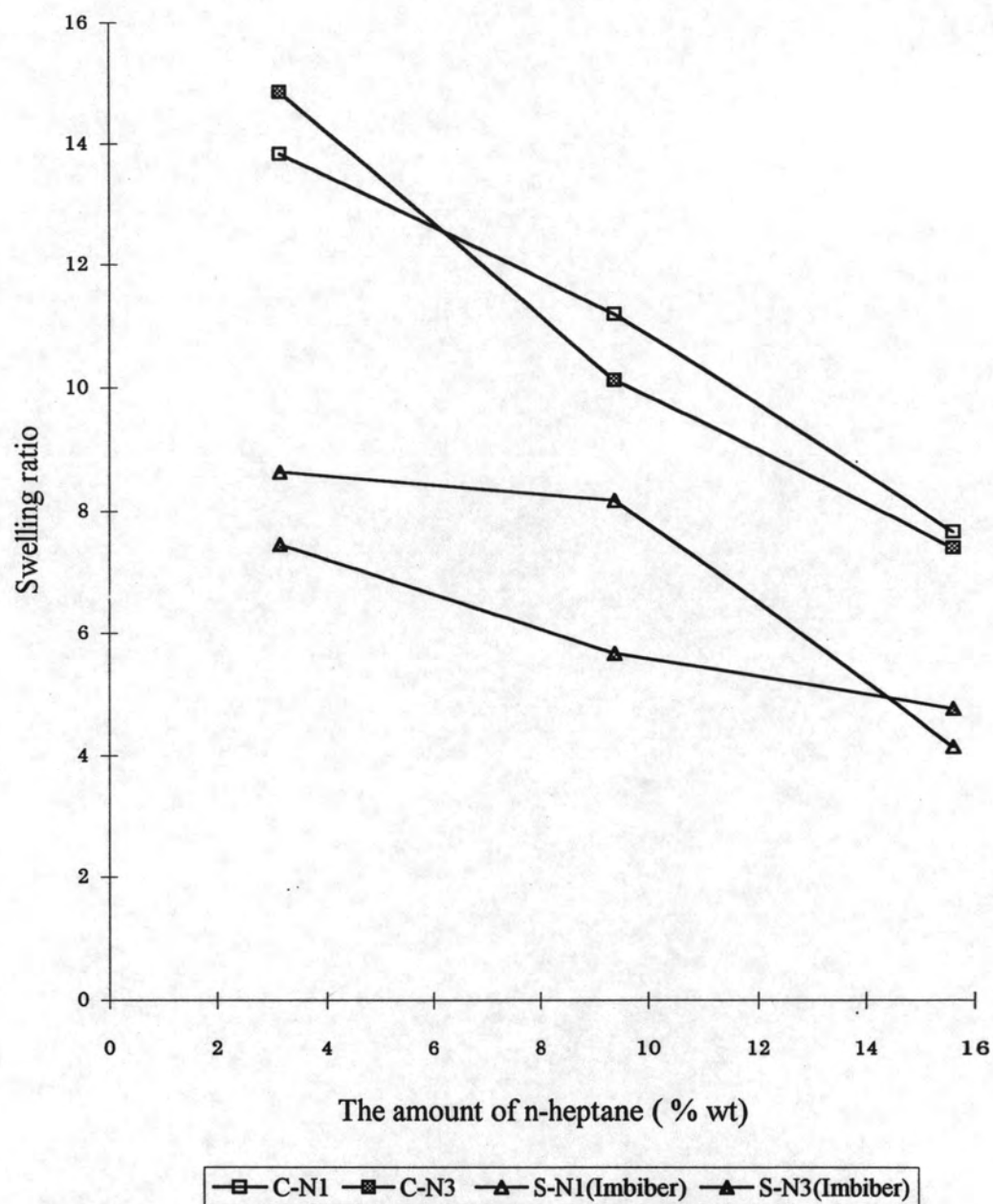
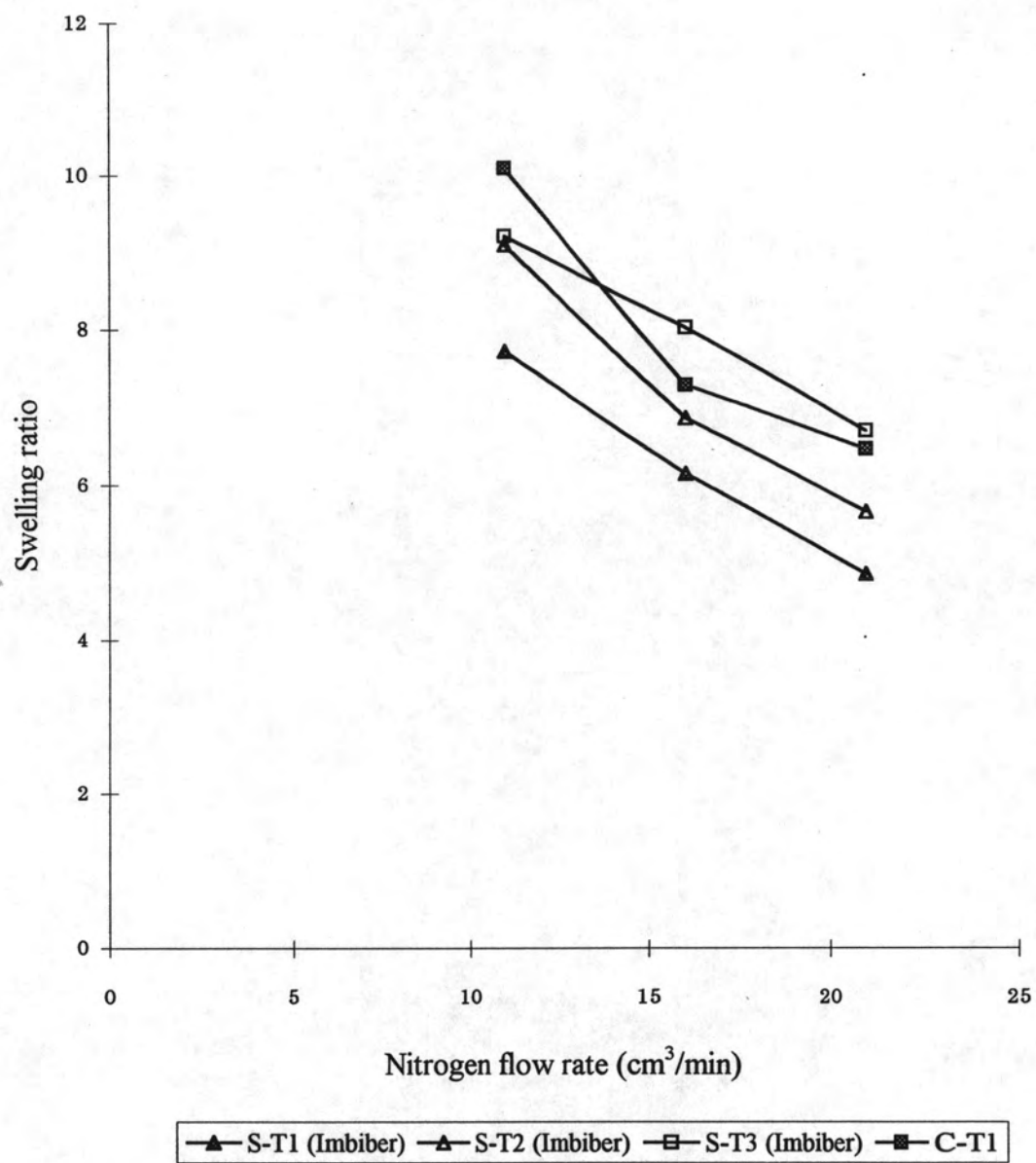


Figure 11 Effect of n-heptane on the swelling ratio of beads.



**Figure 12** Effect of nitrogen flow rate on the swelling ratio of beads.

Bead prepared by using toluene as diluent.

### 3. Desorption

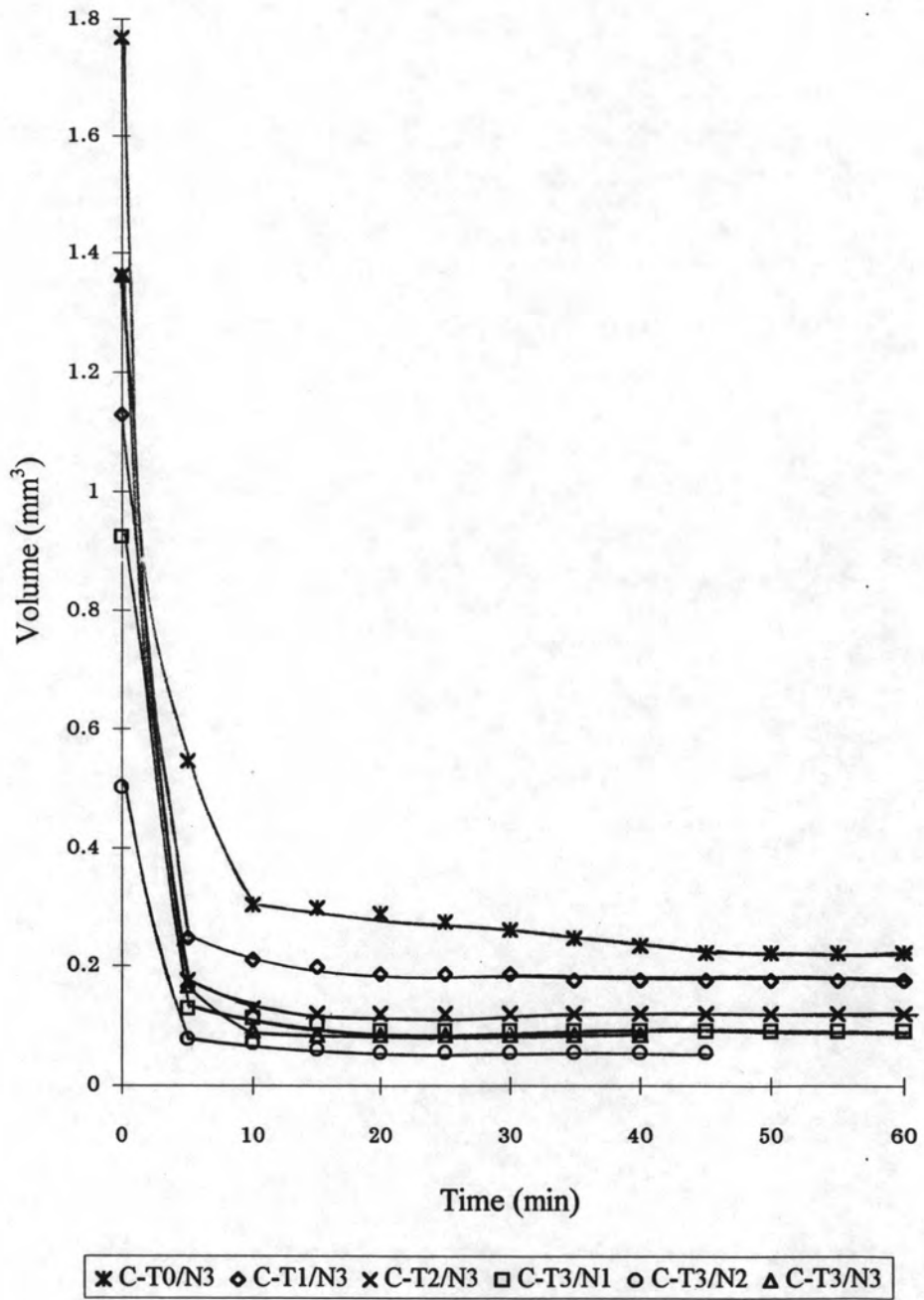
When a swollen bead was placed on the filter paper, the solvent diffused into the filter paper, an absorbing substrate with porous structure. It may be possible that the interaction between solvent and the substrate is higher than the interaction between the solvent and the polymer network. Appendix B shows the bead diameter and volume upon desorption at different times.

Figures 16-15 show the variation of swollen bead volume with time. These curves can be divided into three stages : (I) an initial stage of the high desorption rate. Since the cellulosic substrate is high absorptive (ii) a stage of slow desorption rate and (iii) a third stage of no solvent loss (plateau) or a very low, undetectable desorption rate due to the relatively high vapor pressure of toluene (3.8 kPa). All these beads retained their spherical morphology during and after the desorption process.

Figures 13 and 14 show the decreasing of the swollen bead volume with time for the seed beads prepared by using toluene and n-heptane, respectively, as diluent. The initial stage of desorption was about 5 min, and then the swollen bead lost all solvent within 50 min after the start of desorption process. The range of desorption rate of these seed beads was 0.09-0.28 mm<sup>3</sup>/min.

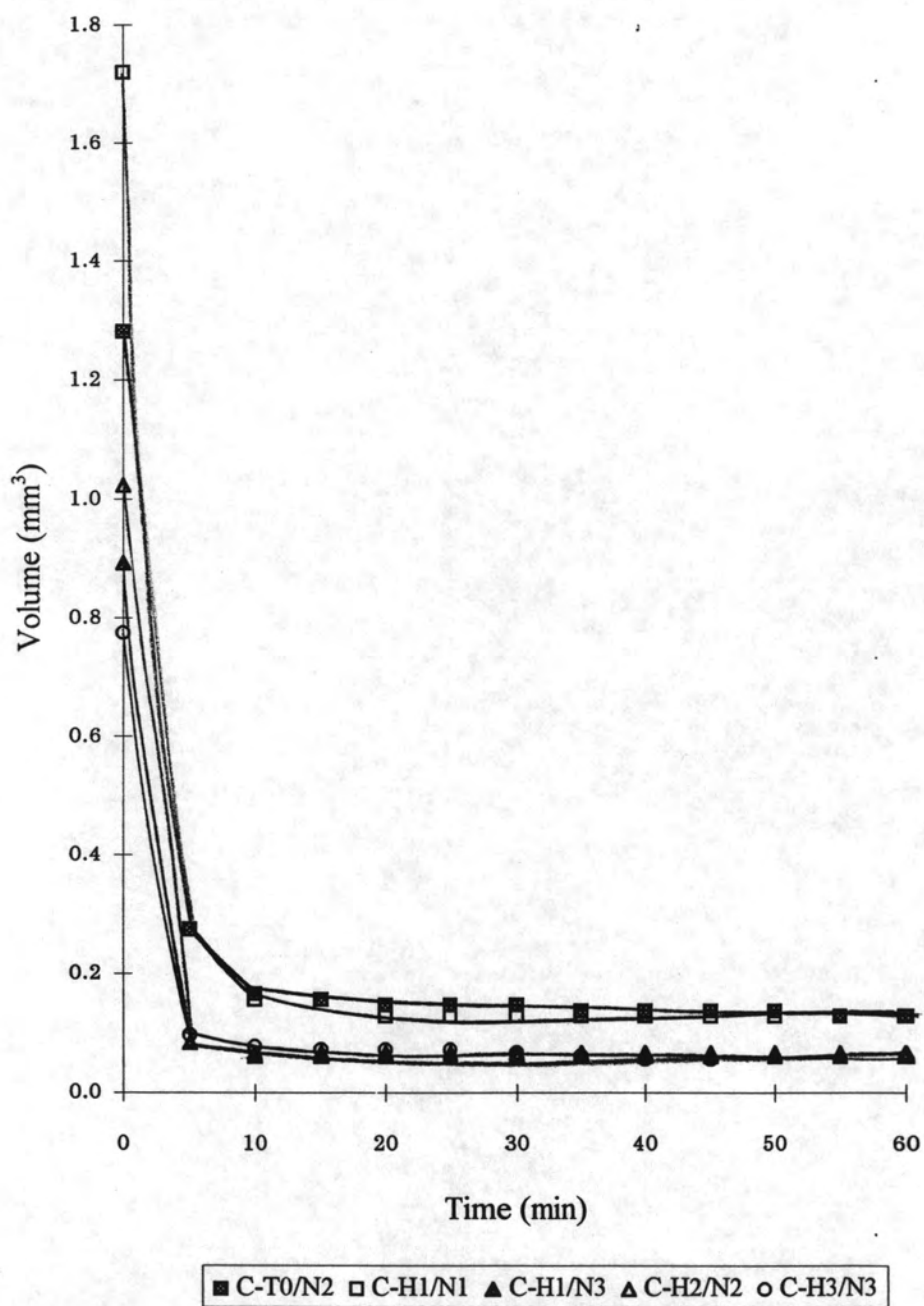
Figures 15 and 16, show the decreasing of the swollen bead volume with time for the large imbibed beads which were prepared by using toluene and n-heptane, respectively, as diluent. The initial stage of desorption curve was about 15 min, and then the swollen bead lost all its solvent within 90 min after starting the desorption process. The range of desorption rate of these seed beads was 0.31-0.75 mm<sup>3</sup>/min. The duration of desorption time of the large beads was longer than that of the seed beads due to the higher crosslink and the polymer beads retained the solvent within the chain.





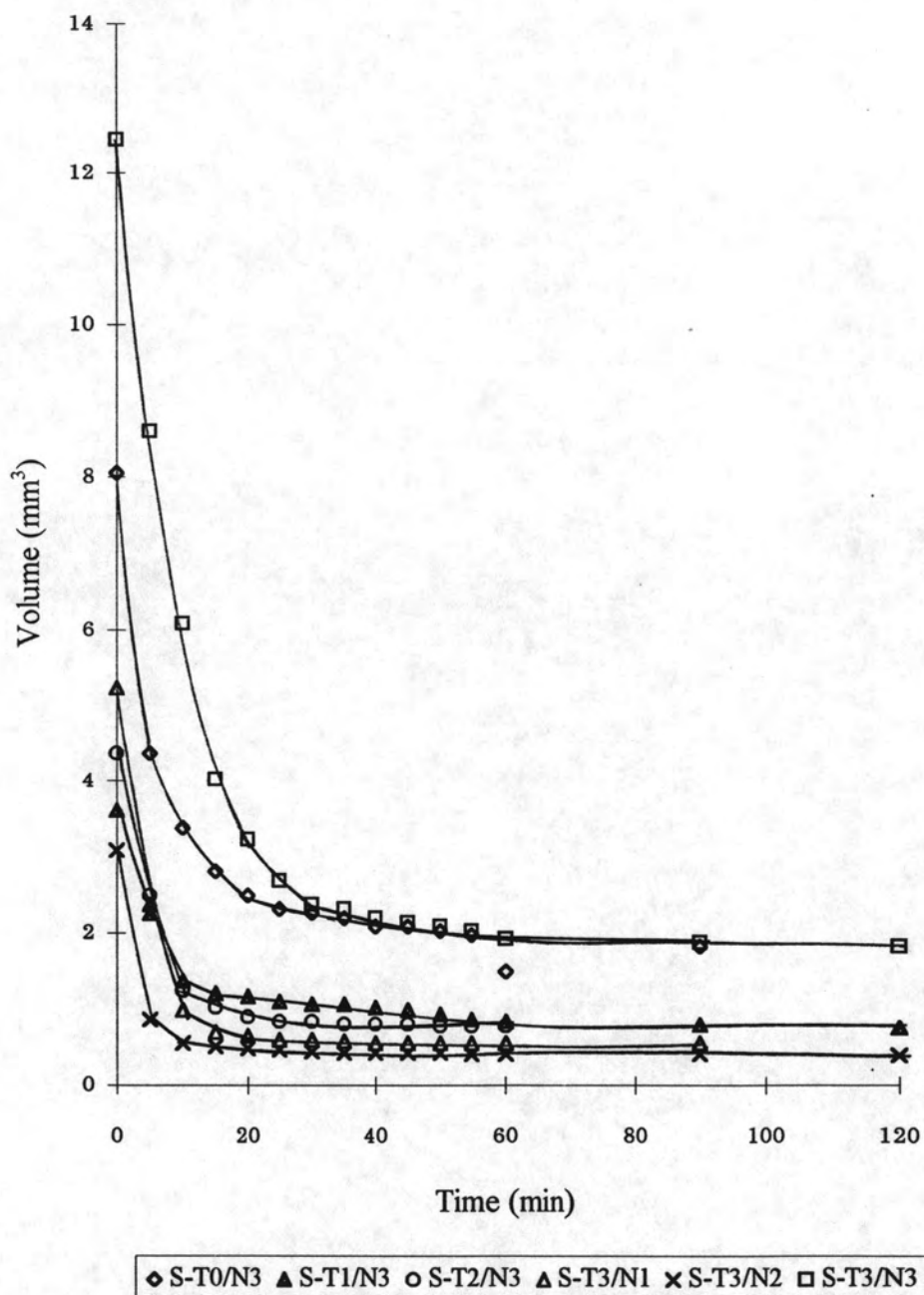
**Figure 13** Variation of seed bead volume with desorption time.

Seed bead were prepared by using toluene as diluent.



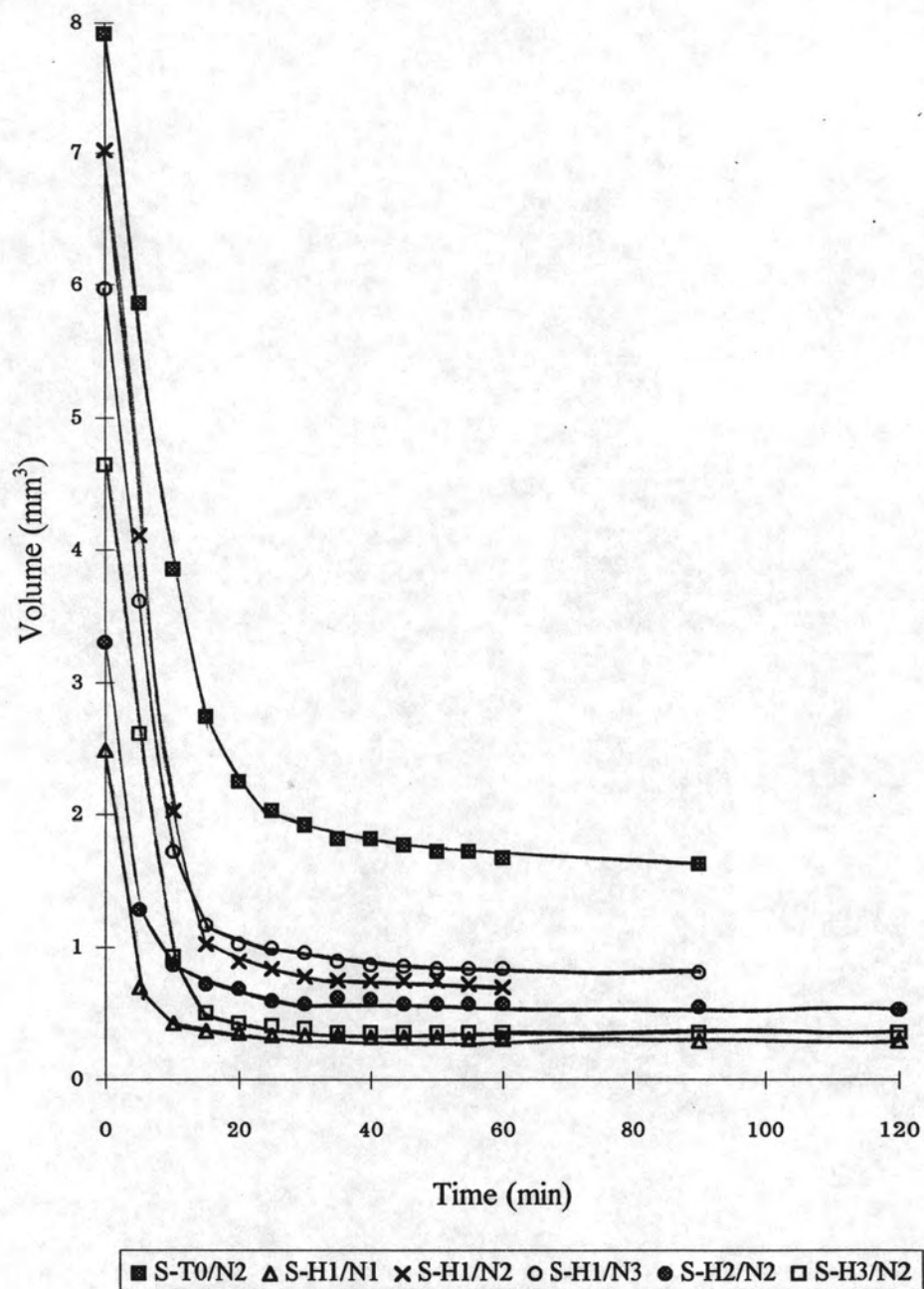
**Figure 14** Variation of the seed bead volume with desorption time.

Seed beads were prepared by using n-heptane as diluent.



**Figure 15** Variation of the large imbibed bead volume with desorption time.

Beads were prepared by using toluene as diluent.



**Figure 16** Variation of the large imbibed bead volume with desorption time.

Beads were prepared by using n-heptane as diluent.

#### 4. Density of the Beads

The density of styrene-divinylbenzene beads was determined by the density-gradient technique and the principle of this method was described (ASTM D-1505) in Appendix A. Table 8-11 also show the values of density of seeds and large imbibed beads. The densities of seed and large beads were about 0.9174 -1.0524 and 0.9225-1.0456 g/cm<sup>3</sup>, respectively. Therefore, some of the beads could float on the water. When these beads were used to get rid of the waste solvent and oil spill by rapid absorption, they could be easily separated from the water.

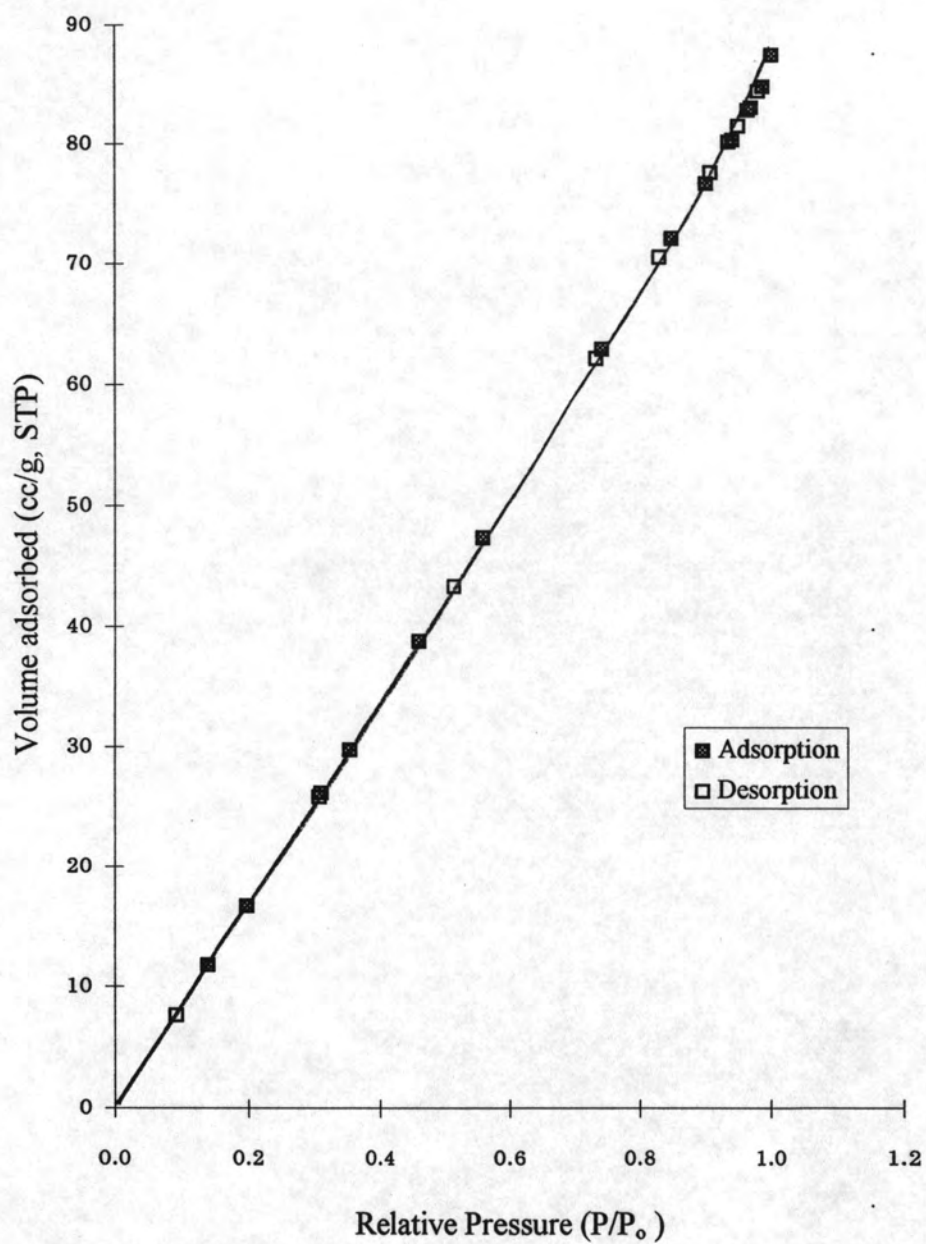
#### 5. Properties of Pore

The properties of pore were determined from the BET isotherm of sorption and desorption of nitrogen. The BET isotherms of sorption and desorption of nitrogen of the imbibed beads were of the type III of nonporous material as shown in Figure 17. The pore properties of the bead were shown in Table 14.

##### 5.1 Effect of the nitrogen flow rate

The optimum of nitrogen flow rate for bead preparation was 21 cm<sup>3</sup>/min since the bead obtained had the high specific surface area and pore volume. It may be possible to state that the aggressive flow rate of nitrogen gas disrupted the pore formation that induced the close pore formation (see Figures 34 and 35).





**Figure 17** Isotherm plot of nitrogen sorption and desorption: large imbiber bead  
(C-T2/N3)

**Table 14** Properties of the pores of the styrene-divinylbenzene copolymer

Parameter	C-H2/N2	C-H1/N3	S-H1/N3	C-T2/N3	S-T2/N3	C-T3/N3
N <sub>2</sub> flow rate (cm <sup>3</sup> /min)	16	21	21	21	21	21
% n-heptane	9.41	3.14	3.14	-	-	-
% touene	-	-	-	0.8	0.8	1.6
Specific surface area (m <sup>2</sup> /g)	139.874	138.961	137.762	155.03	156.372	2.709
Pore volume (ml/g)	0.1179	0.1167	0.1153	0.1308	0.1308	0.0021
Average pore diameter (Å)	33.59	33.59	33.49	33.76	33.29	30.36
Pore volume, ml/g, in pore size range <sup>a</sup>						
20-200	0.1681	0.1672	0.1649	0.1864	0.1868	0.001
>200	0.0106	0.0102	0.0102	0.0121	0.0114	0.0005
Surface area, m <sup>2</sup> /g, in pore size range <sup>a</sup>						
20-200	178.63	177.684	175.397	198	198.591	1.326
>200	1.422	1.370	1.367	1.618	1.527	0.059
Density (g/cm <sup>3</sup> )	0.9667	0.9745	0.9701	0.9174	0.949	0.9502

<sup>a</sup> From the BET measurement, no repeat of micropores was given.

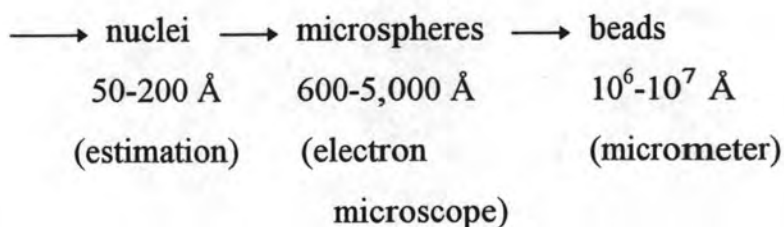
### 5.2 Effect of diluents

The conventional definition of porosity based on the mechanism of pore structure formation was given as follow (29)

agglomeration of

polymer chains

dimensions



(a) Gel porosity: exists only in the swollen state of a macromolecular network, e.g., an ion exchange matrix swollen in water or a crosslinked matrix swollen in an organic solvent.

(b) Macroporosity : due to the pores among the microspheres and their agglomerations.

(c) Microporosity: due to the pores present within the microspheres, among the nuclei and their agglomerations.

In the analysis of the pore structure of porous materials, a convenient classification based on the pore width (30): (a) micropores have widths of up to 20 Å, (b) mesopores have widths in the range 20-500 Å, and (c) macropores have widths greater than 500 Å.

When the diluent solvating power changes, the main differences on the porous structure formation are the critical concentrations for polymer precipitated polymer to agglomerate in microspheres and the entanglement degree of nuclear and internuclear chains (22). In presence of a bad solvent , the precipitated polymer tends to agglomerate rapidly to form large microspheres, consequently, the diluent distributes preferentially among the microsphere agglomerates to form big pores. On the other hand, in the presence of a solvating diluent, the diluent small the nuclear chains become less entangled. The low tendency of nuclei to agglomerate favours the formation of longer and less entangled internuclear chains. The microspheres are rather small and the pore forms are small.

In this study, the seed bead (C-T2/N3) and large imbibed bead (S-T2/N3) prepared by using 0.8% toluene as diluent and 21 cm<sup>3</sup>/min of nitrogen flow rate gave the maximum pore volume and specific surface area that were about 0.13 ml/g and 156.37 m<sup>2</sup>/g, respectively. The average diameter of the above-mentioned pores that was prepared by using toluene and n-heptane as diluent was about 33 Å (mesopore) (30). The average pore sizes prepared by using a good and a poor solvent (toluene and n-heptane,

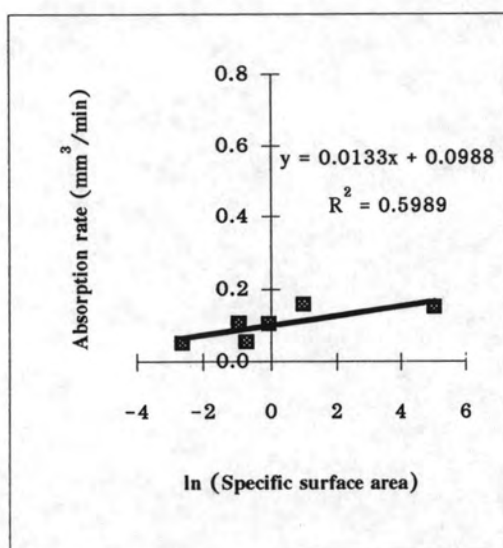
respectively ) cannot impose a significant effect. It is anticipated that such a finding could possibly be strongly effected by the concentration of divinylbenzene, the speeds of agitation and nitrogen flow rate. On the view of the divinylbenzene concentration, a crosslink density of the divinylbenzene could be a vital attribute to the pore formation accelerated by the fast diffusion of the radicals and divinylbenzene to copolymerize with polystyrene to result in a similar pore size average in both diluents.

### 5.3 Effect of pore properties on the sorption and desorption

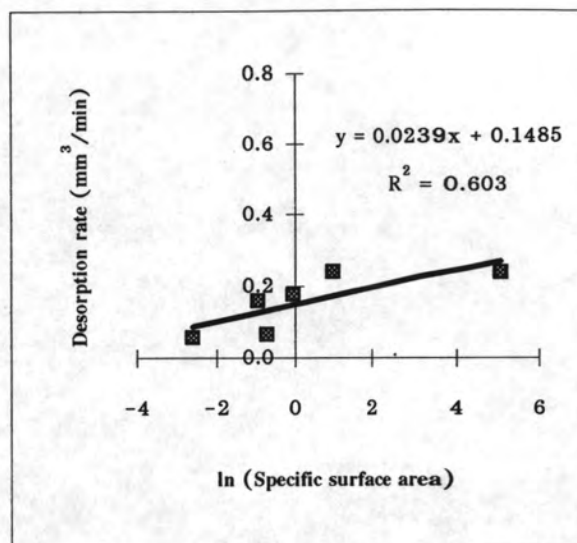
For the imbibed beads, the absorption and desorption rate decreased with increasing the specific surface area (figures 18 c-d and 19 c-d). However, the absorption and desorption rate increased with increasing the average pore diameter ( figures 20 c-d and 21 c-d).

## 6. Cycle of Solvent Sorption and Desorption

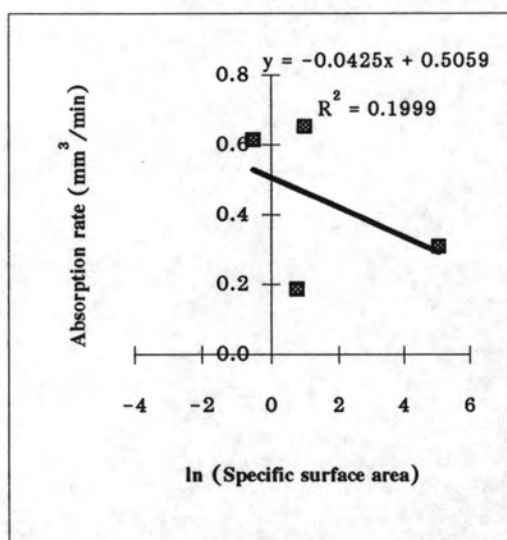
The beads could be used to absorb and desorb toluene for many cycles. The repeated sorption and desorption behavior of the second and third cycles were also the same as the first cycle as shown in Figures 22 and 23. The difference of volume between first cycle sorption and second cycle sorption may be possible to state that (1) the network of the beads was changed and (2) the homopolymer was dissolved. During sorption and desorption the seed and large bead still remained spherical throughout the cycles; they did not collapse, after repeated uses. The seed and large beads could be applied to absorb and desorb the waste solvents and oil.



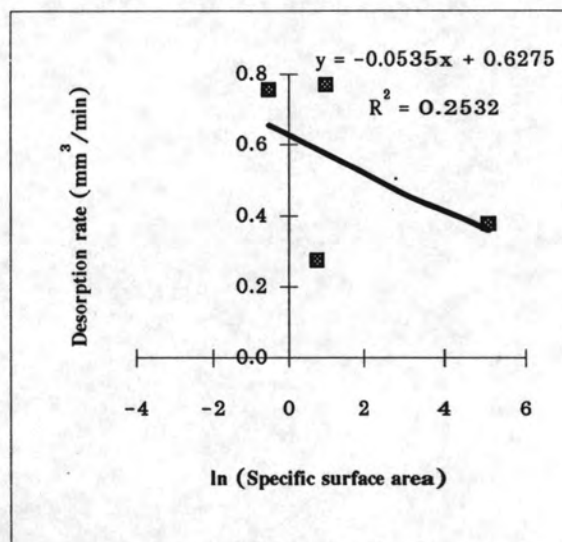
(a) Seed beads



(b) Seed beads



(c) Imbiber beads

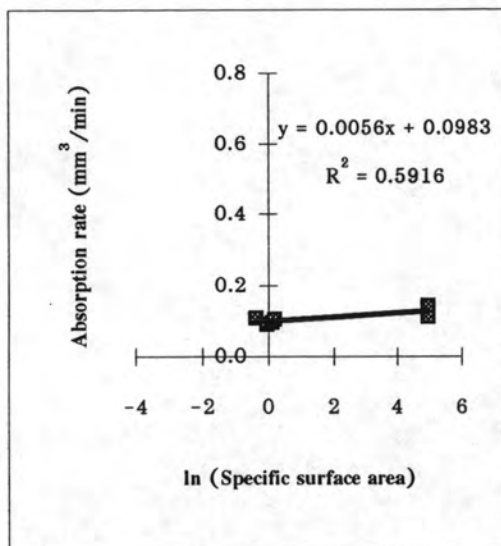


(d) Imbiber beads

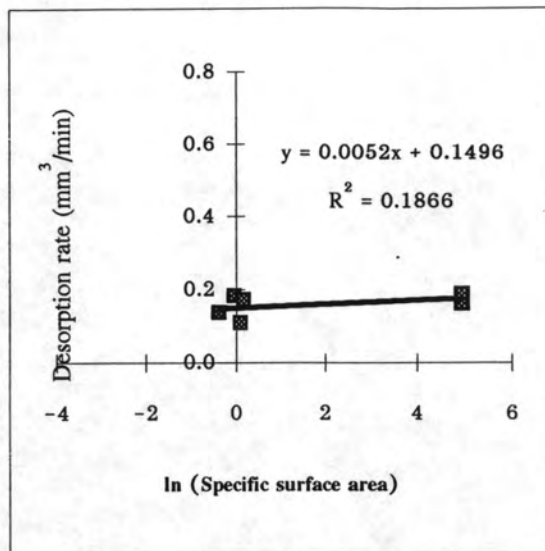
**Figure 18** Specific surface area vs. absorption and desorption rate

The beads were prepared under the effects of nitrogen flow rate and toluene as diluent

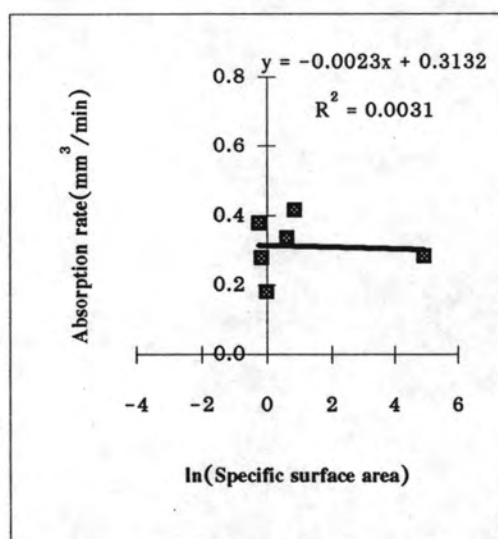




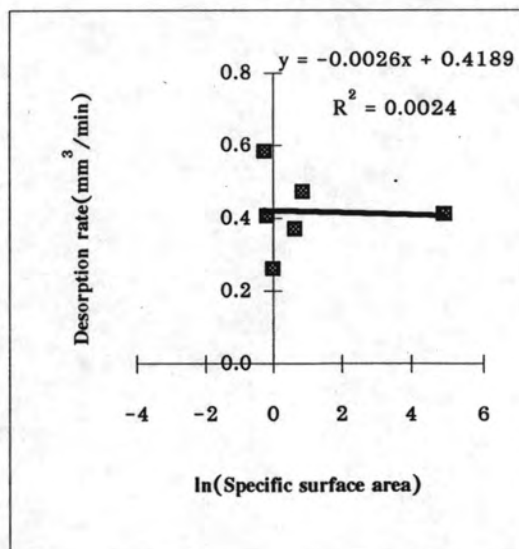
(a) Seed beads



(b) Seed beads



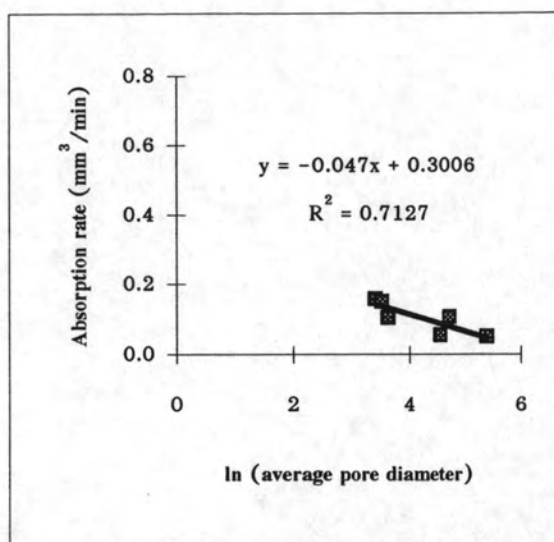
(c) Imbiber beads



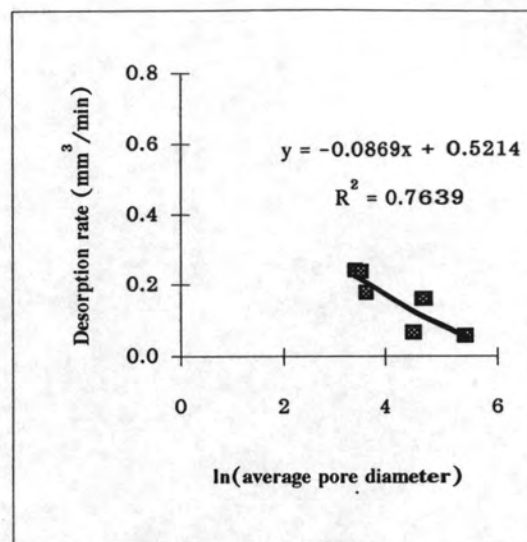
(d) Imbiber beads

**Figure 19** Specific surface area vs. absorption and desorption rate

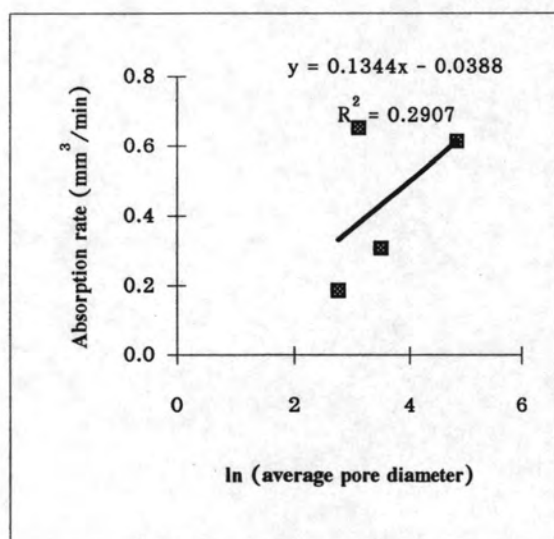
The beads were prepared under the effects of nitrogen flow rate and n-heptane as diluent



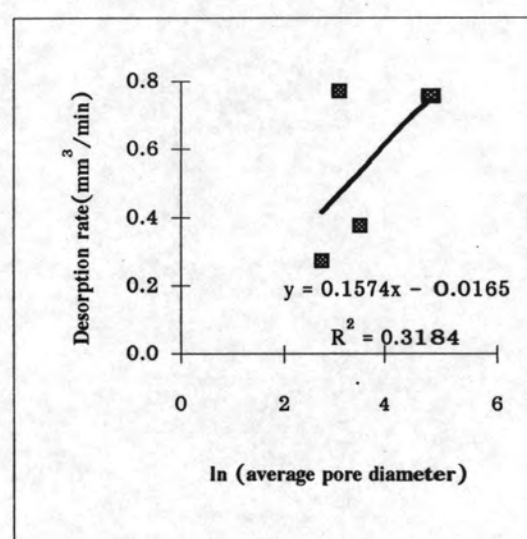
(a) Seed beads



(b) Seed beads



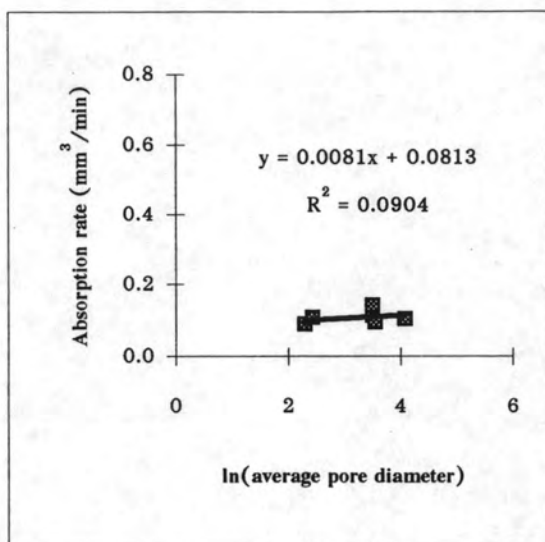
(c) Imbiber beads



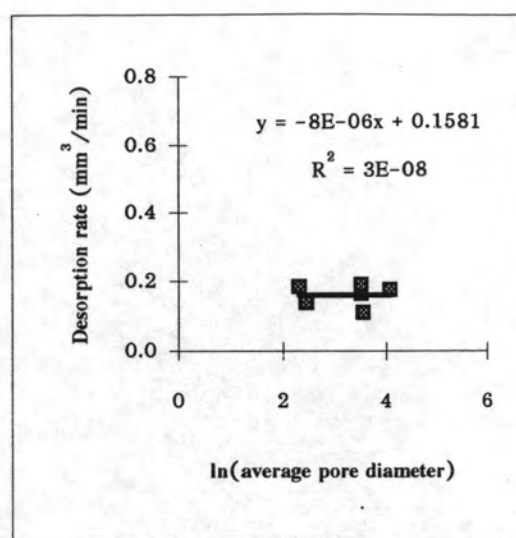
(d) Imbiber beads

**Figure20** Average pore diameter vs. absorption and desorption rate

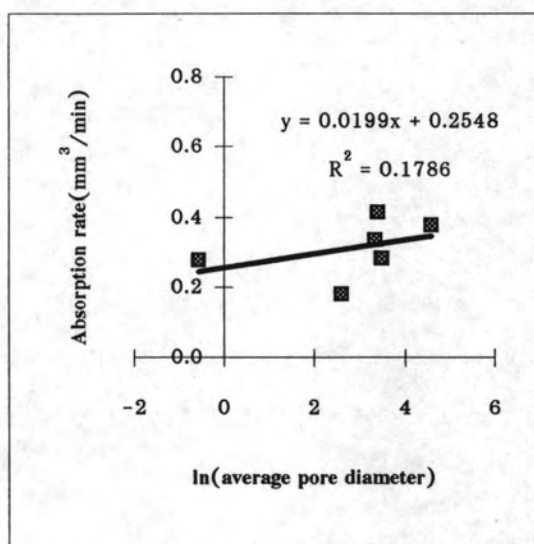
The beads were prepared under the effects of nitrogen flow rate and toluene as diluent



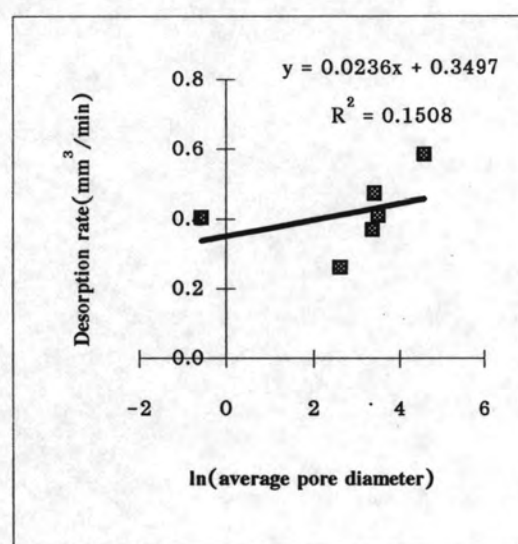
(a) Seed beads



(b) Seed beads



(c) Imbiber beads



(d) Imbiber beads

**Figure21** Average pore diameter vs. absorption and desorption rate

The beads were prepared under the effects of nitrogen flow rate and n-heptane as diluent

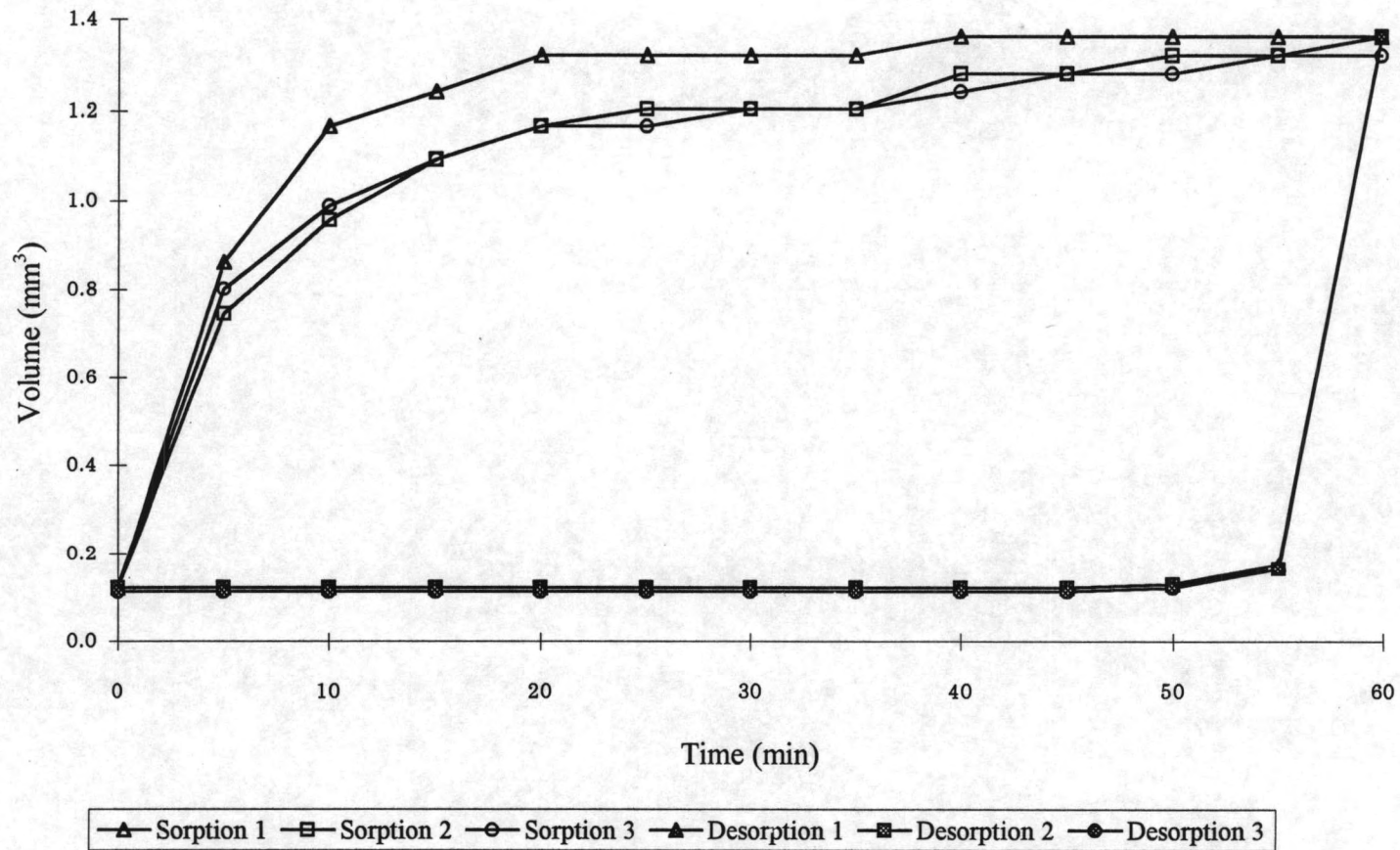


Figure 22 Variation of bead volume with time: seed bead C-T2/N3

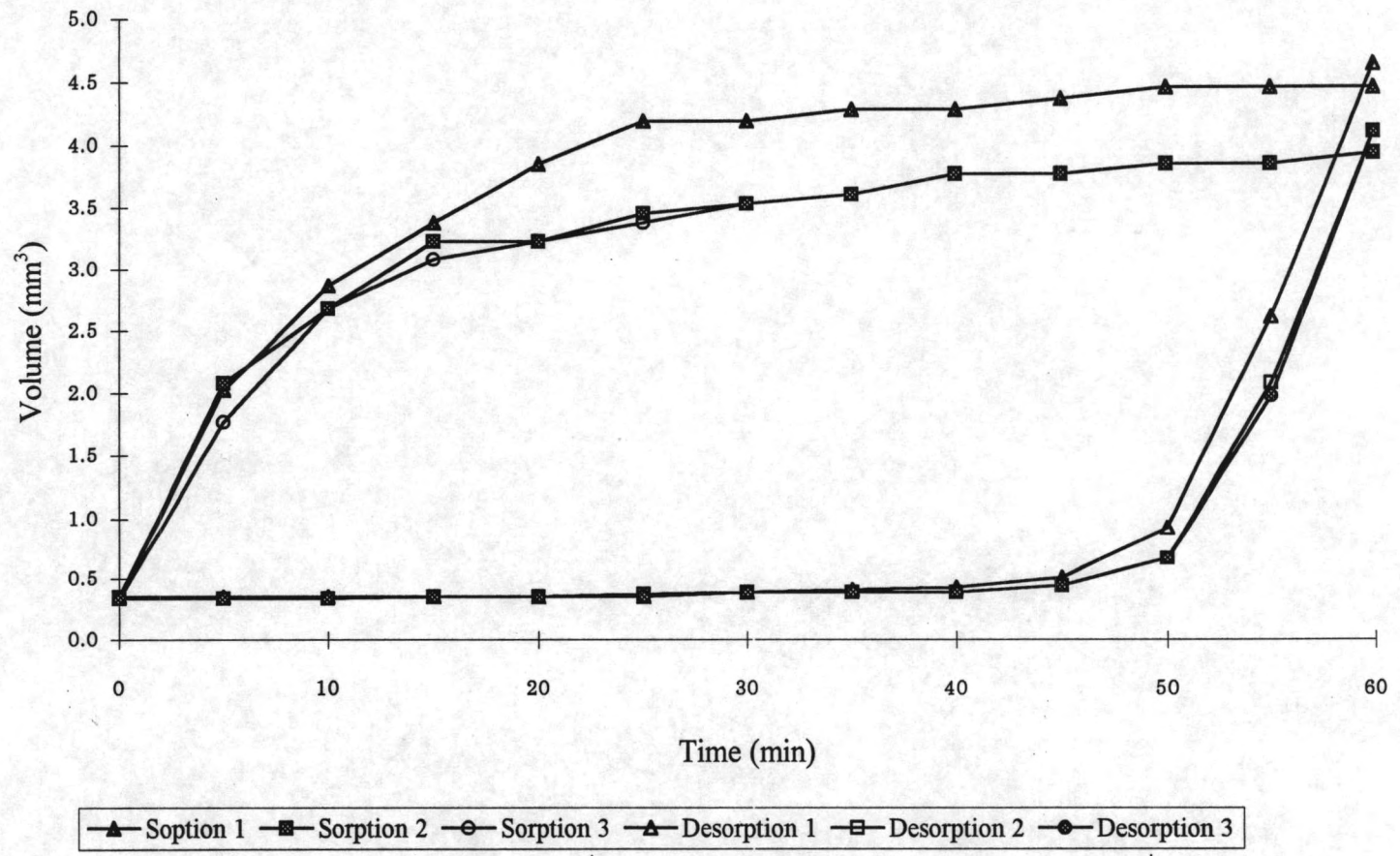


Figure 23 Variation of bead volume with time: large imbibed bead S-H3/N2



## 7. Diffusion Coefficient

The diffusion coefficient (D) could be calculated from Eq. 2 and 3 in Chapter II as follows.

$$\tau = a^2 / D \quad (2)$$

where  $a$  is the final radius of the fully swollen gel.

$\tau$  is the characteristic swelling time

$$\ln (\Delta a_t / \Delta a_0) = \text{const.} \cdot -t / \tau \quad (3)$$

where  $\Delta a_t$  is the difference between the size at time  $t$  and that at saturation swelling

$\Delta a_0$  is the total change in radius throughout the entire swelling process

The characteristic swelling time  $\tau$  could be obtained from the slope of the  $\ln (\Delta a_t / \Delta a_0)$  - time plot. The ranges of the diffusion coefficient of the seed bead and large beads prepared by using toluene as diluent were  $0.68 \times 10^{-3}$  -  $0.87 \times 10^{-3}$  and  $0.93 \times 10^{-3}$  -  $2.39 \times 10^{-3}$   $\text{cm}^2/\text{min}$ , respectively (Table 15). The ranges of the diffusion coefficient of the seed bead and large beads prepared by using n-heptane as diluent were  $1.02 \times 10^{-3}$  -  $1.41 \times 10^{-3}$  and  $0.99 \times 10^{-3}$  -  $2.21 \times 10^{-3}$   $\text{cm}^2/\text{min}$ , respectively (Table 16).

**Table 15.** The diffuse coefficient of the seed and large beads which were prepared by using toluene as diluent.

Sample code	N <sub>2</sub> flow rate (cm <sup>3</sup> /min)	Toluene (% wt)	Swelling ratio	$\tau$ (min)	Diffusion coefficient (cm <sup>2</sup> /min) x10 <sup>3</sup>
C-T0/N1	11	0	10.45	4.1	1.64
C-T0/N3	21	0	8	4.47	1.26
C-T3/N1	11	1.6	10.29	4.22	0.87
C-T3/N3	21	1.6	16.36	6.97	0.68
S-T0/N1	11	0	4.95	9.84	1.57
S-T0/N2	16	0	4.8	8.64	1.77
S-T0/N3	21	0	4.43	10.5	1.47
S-T1/N1	11	0.4	7.7	4.92	2.39
S-T1/N2	16	0.4	6.13	8.64	1.87
S-T1/N3	21	0.4	4.84	9.71	0.93
S-T2/N1	11	0.8	9.08	11.9	1.91
S-T2/N2	16	0.8	6.84	5.47	1.51
S-T2/N3	21	0.8	5.64	6.71	1.53
S-T3/N1	11	1.6	9.19	7.03	1.65
S-T3/N2	16	1.6	8	5.32	1.53
S-T3/N3	21	1.6	6.67	11.7	1.77

**Table 16.** The diffuse coefficient of the seed and large beads which were prepared by using n-heptane as diluent.

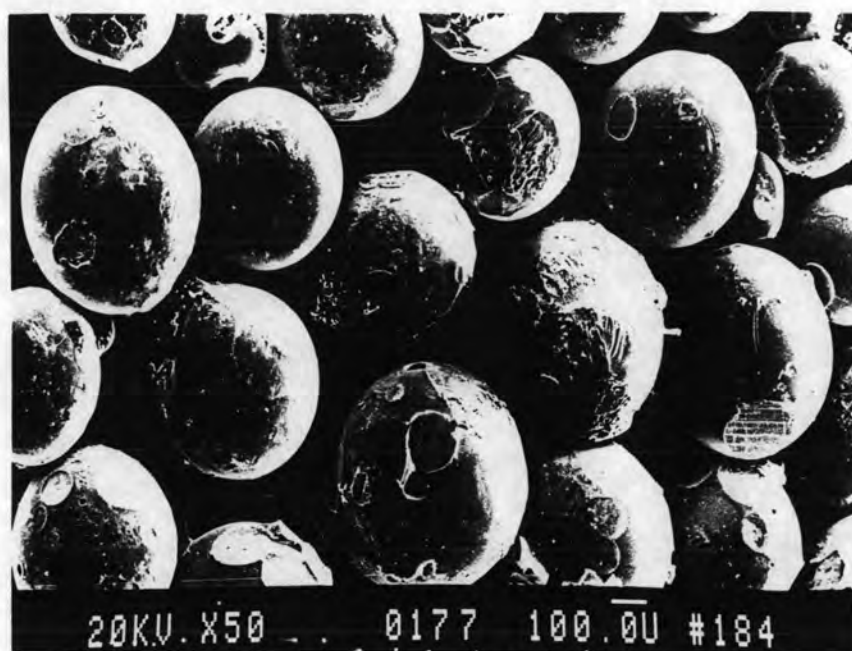
Sample code	N <sub>2</sub> flow rate (cm <sup>3</sup> /min)	n-Heptane (% wt)	Swelling ratio	$\tau$ (min)	Diffusion coefficient (cm <sup>2</sup> /min) x10 <sup>3</sup>
C-H1/N1	11	3.14	13.82	5.4	1.02
C-H3/N1	11	15.67	7.63	5.26	1.41
S-H1/N1	11	3.14	5.36	5.36	1.32
S-H1/N2	16	3.14	6.25	6.25	2.21
S-H1/N3	21	3.14	11.82	11.8	1.07
S-H2/N1	11	9.41	5.6	5.8	2.0
S-H2/N2	16	9.41	5.63	5.63	1.52
S-H2/N3	21	9.41	6.98	6.98	1.34
S-H3/N1	11	15.67	6.6	6.6	1.24
S-H3/N2	16	15.67	8.49	8.49	1.23
S-H3/N3	21	15.67	6.54	6.53	0.99

## 8. Morphology of the Surface and Interior of the Beads

Morphologies of the surface and interior of the beads were observed by SEM.

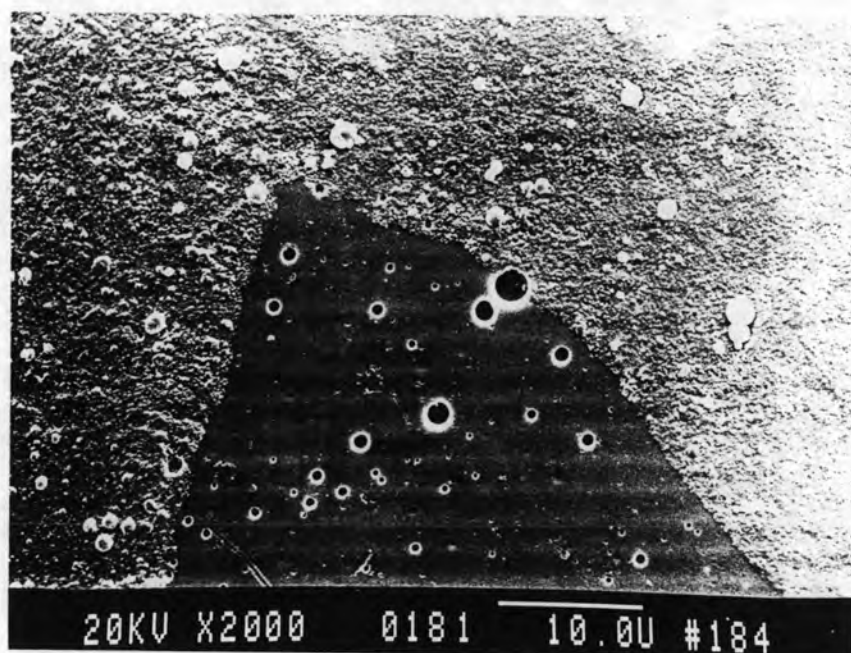
Figures 24-27 show the electron micrographs of the surface and interior of the seed bead prepared by using toluene as diluent. The seed bead surface was not smooth because of the solvent effect. Some of the beads had a flat side due to the collision of the beads during polymerization. The pore sizes were very small, since some pores were destroyed when the beads were cut. Figures 28-30, show the surface and interior of the seed bead which were prepared by using n-heptane as diluent. The seed bead surface was very smooth and the pore sizes were very small, so these pores could not be seen at the low magnification of SEM. The interior morphology of these beads showed both large and small pore sizes.

Figures 31-35, show the electron micrographs of the surface and interior of the large bead prepared by using toluene as diluent. The large bead surface was very rough. The rough pores gave the high surface area. The interior of the beads had many pores. Figures 36-40, show the surface and interior of the seed bead prepared by using n-heptane as diluent. The seed bead surfaces were very smooth. Most of the pores were on the surface.



**Figure 24** SEM micrograph of the surface of the seed beads (C-T2/N3)

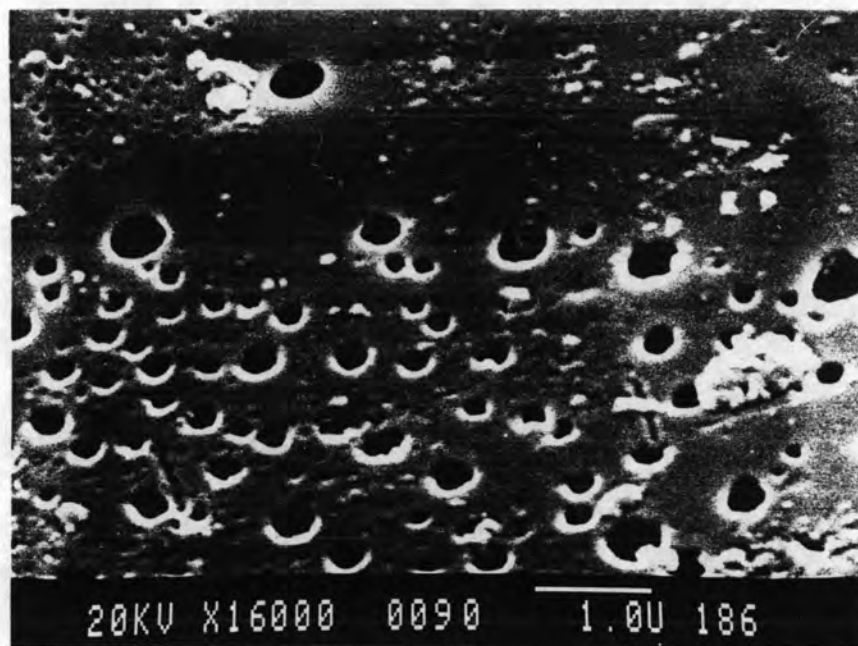
Diluent: toluene



**Figure 25** SEM micrograph of the surface of the seed beads (C-T2/N3)

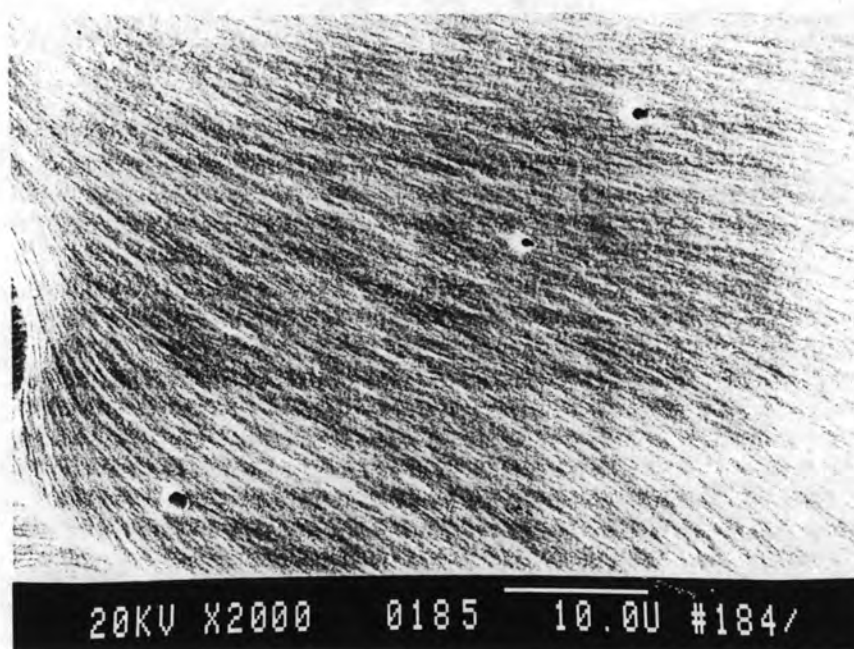
Diluent: toluene





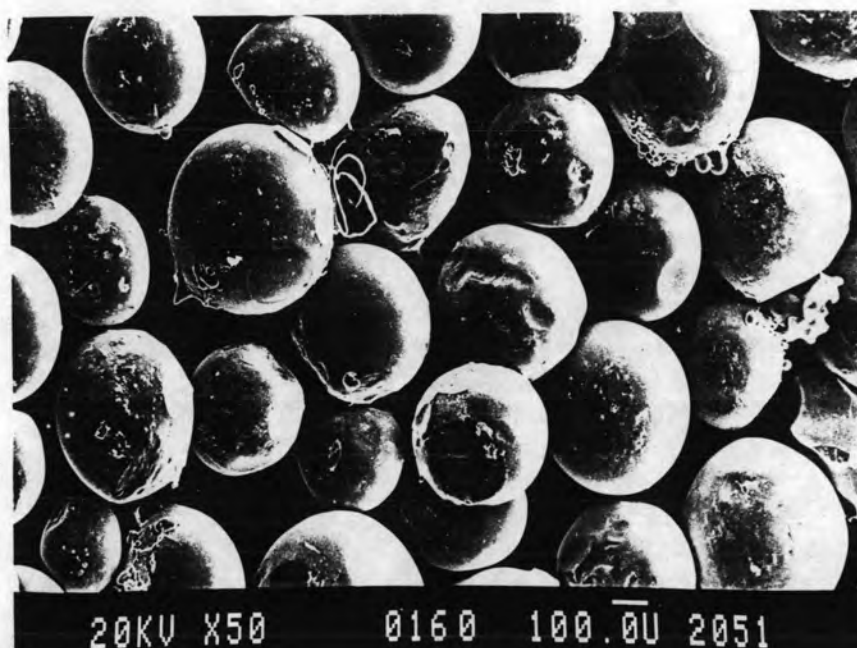
**Figure 26** SEM micrograph of the surface of the seed beads (C-T1/N1)

Diluent: toluene

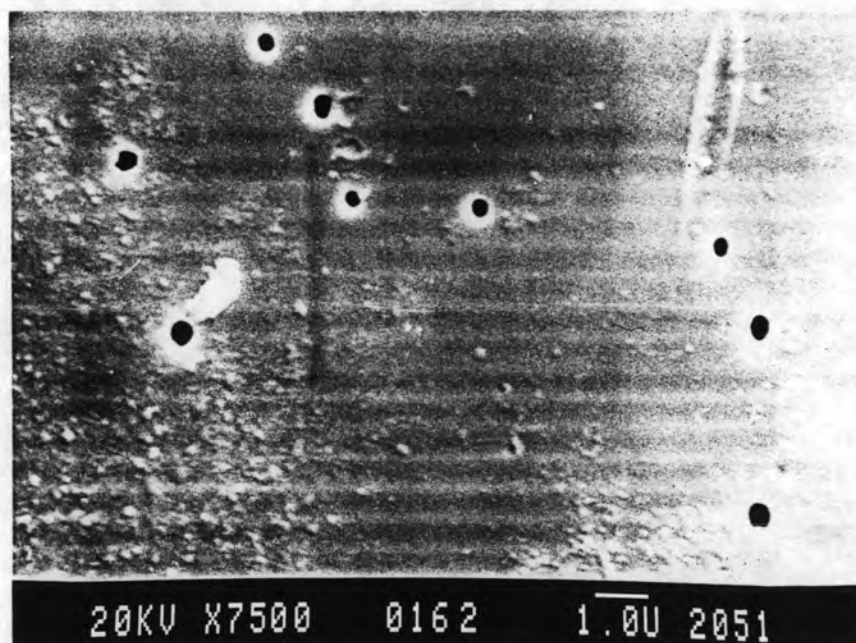


**Figure 27** SEM micrograph of the interior structure of the seed beads

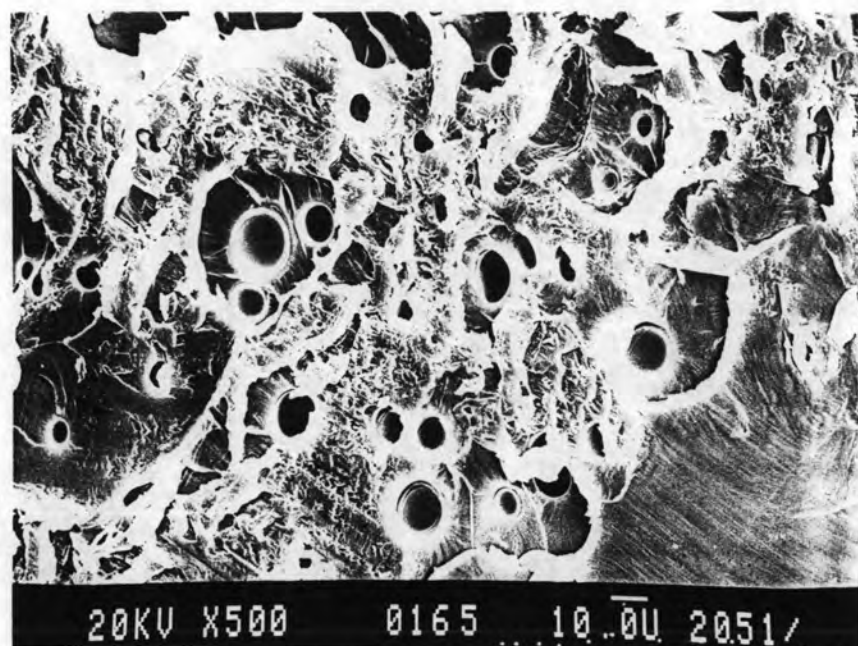
(C-T2/N3) Diluent: toluene



**Figure 28** SEM micrograph of the surface of the seed beads (C-H<sub>2</sub>/N<sub>2</sub>)  
Diluent: n-heptane



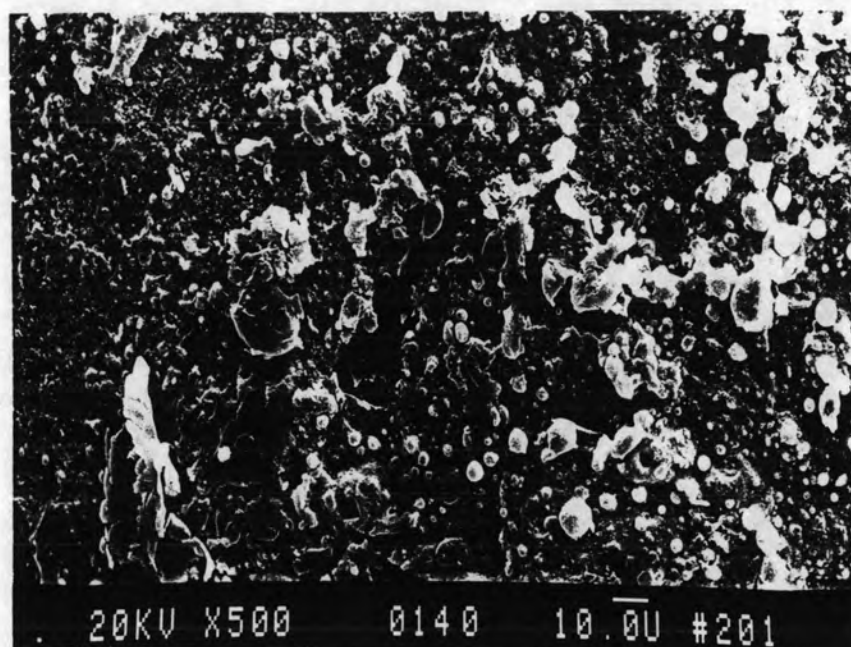
**Figure 29** SEM micrograph of the surface of the seed beads (C-H<sub>2</sub>/N<sub>2</sub>)  
Diluent: n-heptane



**Figure 30** SEM micrograph of the interior structure of the seed beads (C-H2/N2) Diluent: n-heptane



**Figure 31** SEM micrograph of the surface of the large beads (S-T2/N3) Diluent: toluene

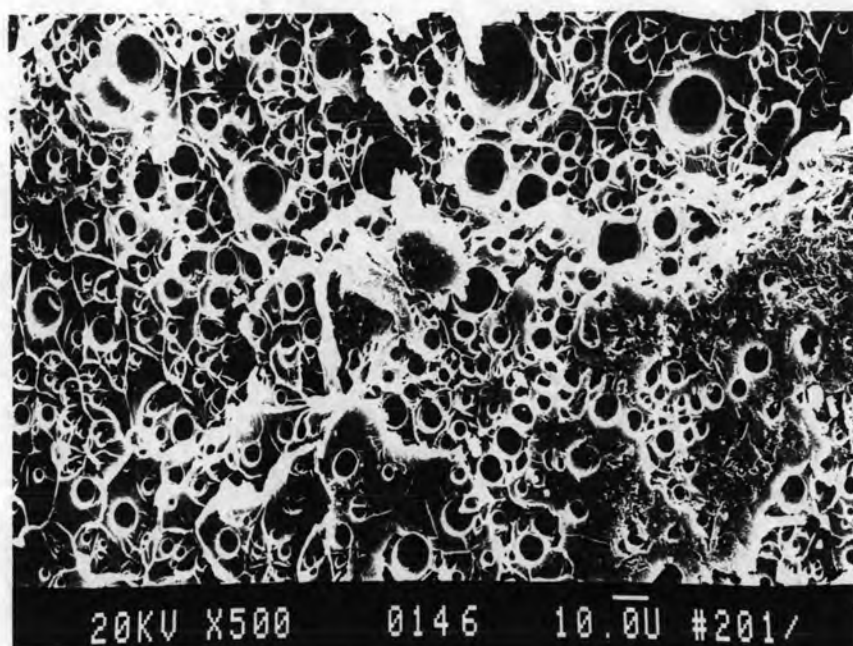


**Figure 32** SEM micrograph of the surface of the large beads (S-T2/N3)  
Diluent: toluene

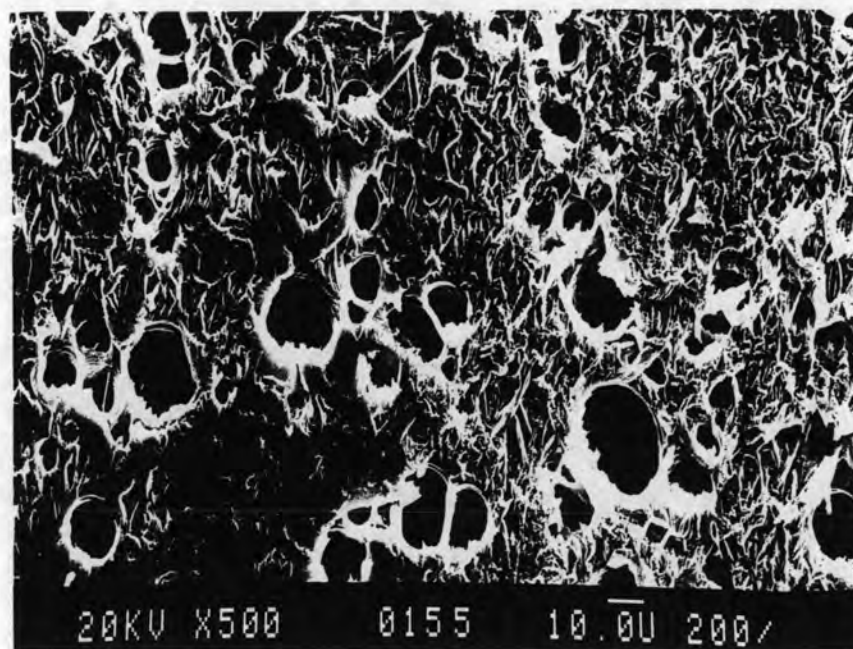


**Figure 33** SEM micrograph of the pore on the surface of the large beads  
(S-T2/N3) Diluent: toluene





**Figure 34** SEM micrograph of the interior structure of the large beads (S-T2/N3) Diluent: toluene

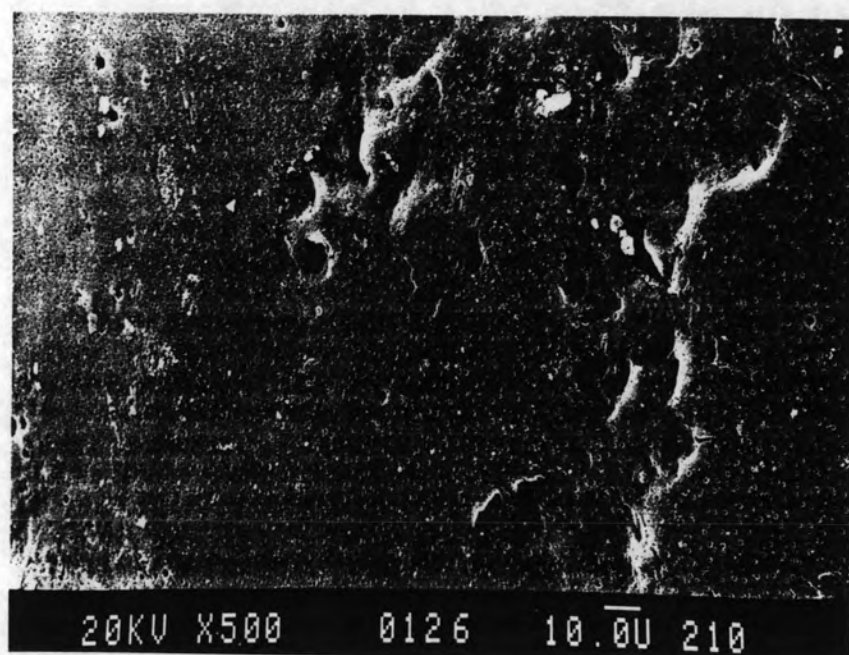


**Figure 35** SEM micrograph of the interior structure of the large beads (S-T3/N3) Diluent: toluene

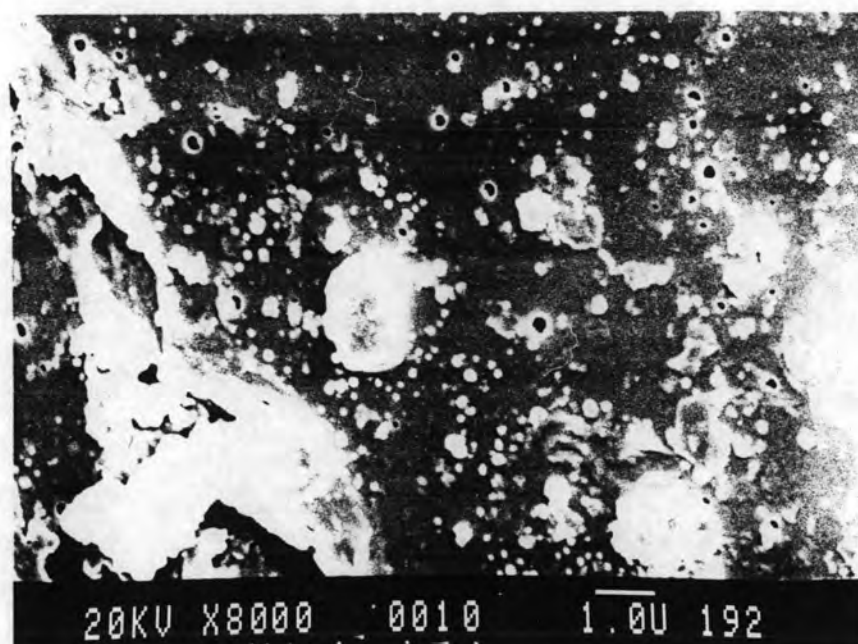




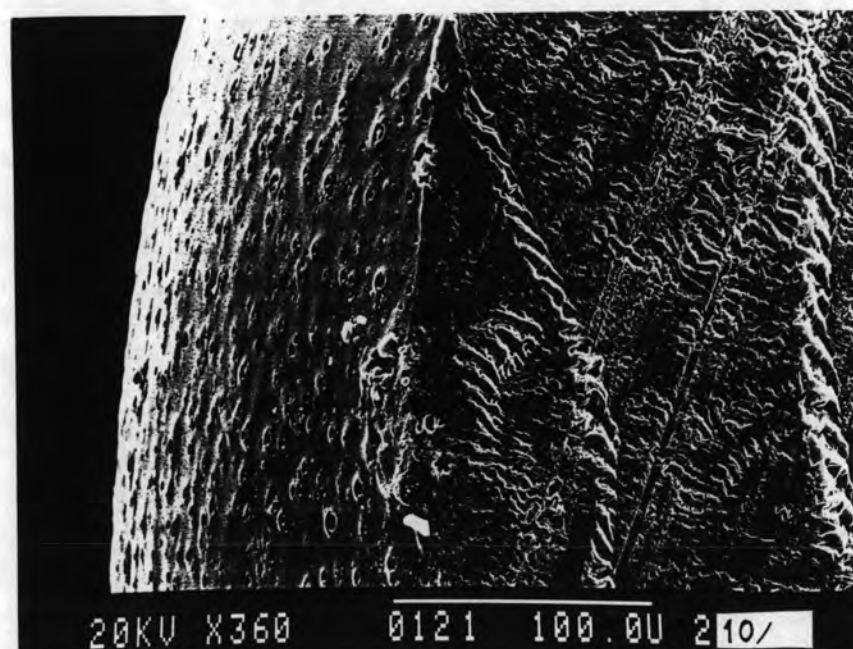
**Figure 36** SEM micrograph of the surface of the large beads (S-H1/N3)  
Diluent: n-heptane



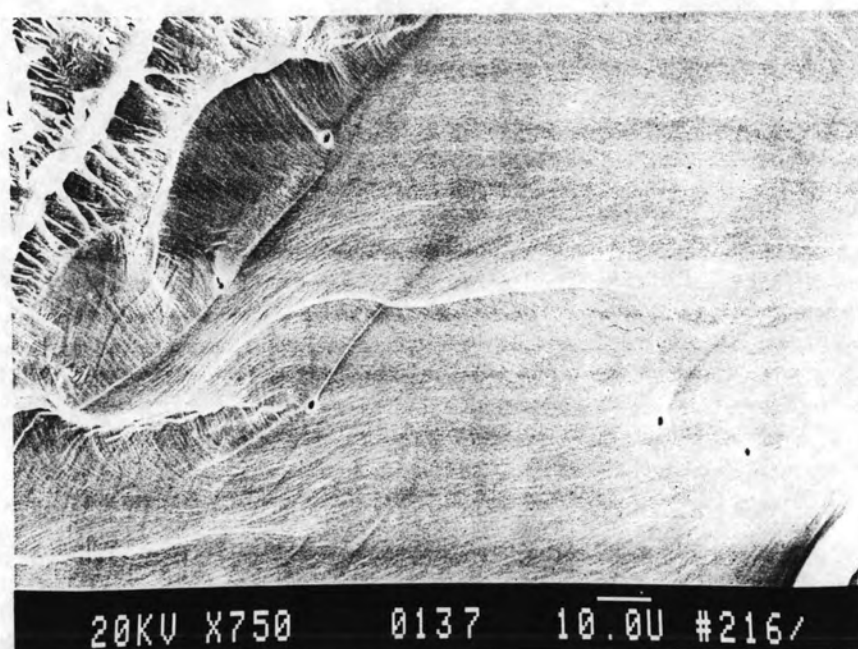
**Figure 37** SEM micrograph of the surface of the large beads (S-H1/N2)  
Diluent: n-heptane



**Figure 38** SEM micrograph of the surface of the large beads (S-H1/N1)  
Diluent: n-heptane



**Figure 39** SEM micrograph of the interior structure of the large beads  
(S-H1/N2) Diluent: n-heptane



**Figure 40** SEM micrograph of the interior structure of the large beads  
(S-H1/N3) Diluent: n-heptane