



CHAPTER IV

RESULTS and DISCUSSION

4.1 The optimum quantity of divinylbenzene crosslinking agent

The result of the first set of solubility test of imbibed beads synthesized with various concentrations of divinylbenzene as crosslinking agent was in Table 4.1.

TABLE 4.1

Effect of Crosslinking Agent on
the Solubility of Synthetic Beads

crosslinking agent(%)	solubility of beads in styrene monomer
0.05	dissolved
0.25	dissolved
0.3	non-dissolved

Before proceeding further to the next step of seeded suspension polymerization, where the polystyrene beads were brought to soak in the monomer solution until complete swelling and then to the further polymerization step, the synthetic beads must possess the principal property, that is they must not dissolve in the monomer solution but can only swell in the solution.

On the other hand, the objective of this study is to synthesize the imbibed beads with highly absorptive property. In order to get the best absorption property, the synthetic beads must not possess too excessive crosslinking sites inside the beads. In fact, the amount of crosslinking sites can be measured by determining the pore volume and the structure of the beads sample. Because the instrument for measuring the porosity was not available in Thailand, the samples were sent to Waters at Millipore for characterization of pore volume and structure for months. Therefore, the results from Table 4.1 can only represent the existence of the effect of crosslinking site on the solubility of beads in the monomer solution.

Then the optimum percentage of the crosslinking agent is its minimum amount inside the beads that make them maintain their spherical shape through the absorption period without breakage or deformation.

4.2 The optimum time for seeded suspension polymerization

The synthetic beads from section 4.1 were then brought to seeded suspension polymerization by soaking in excess monomer solution for 24 hours. Then the complete swelling beads were separated into two groups and brought to further polymerization at two different time and temperature schedules, that is

2B :- 70°C-2hr.+ 90°C-10hr. (12 hr.)

3B :- 70°C-2hr.+ 90°C-18hr. (20 hr.)

The results of both groups were shown below.

TABLE 4.2
Swelling of polystyrene crosslinked with
divinylbenzene, coded as 2B, in toluene

Run	Time (hr.)	ΔT (min)	Bead dia. (cm.)	Bead vol. ³ (cm ³)	$\Delta V/\Delta T$ (cm ³ /min) ³
2B	0.00		0.5347	0.0768	
	0.10	10	0.625	0.1226	0.00458
	0.30	20	0.6944	0.1682	0.00228
	1.00	30	0.75	0.2119	0.00146
	2.00	60	0.8333	0.2907	0.00131
	3.00	60	0.8819	0.3446	0.00090
	4.30	90	0.9722	0.4616	0.00135
	6.00	90	0.9792	0.4716	0.00011
	7.30	90	0.9861	0.4817	0.00011
	9.00	90	0.9931	0.4919	0.00011
	10.30	90	1.0277	0.5454	0.00059
	12.00	90	1.0277	0.5454	0

Swelling ratio = 7.1

TABLE 4.3

Swelling of polystyrene crosslinked with
divinylbenzene, coded as 3B, in toluene

Run	Time (hr.)	ΔT (min)	Bead dia. (cm.)	Bead vol. (cm ³)	$\Delta V/\Delta T$ (cm /min) ³
3B	0.00		0.5417	0.0798	
	0.10	10	0.6319	0.1268	0.0047
	0.30	20	0.6944	0.1682	0.0021
	1.00	30	0.7569	0.2178	0.0017
	2.00	60	0.8333	0.2907	0.0012
	3.00	60	0.8888	0.3528	0.0010
	4.30	90	0.9236	0.3958	0.00048
	6.00	90	0.9861	0.4817	0.00095
	7.30	90	1.0347	0.5565	0.00083
	8.20	50	break	-	-

Swelling ratio = 7

Table 4.2, 4.3 showed the absorption results of polystyrene beads in toluene by determining the beads diameter at different times. The beads from suspension polymerization were classified into two groups:

1. The first group was brought to the seeded suspension polymerization for 12 hours. However the size of the beads from the first seeded step was not

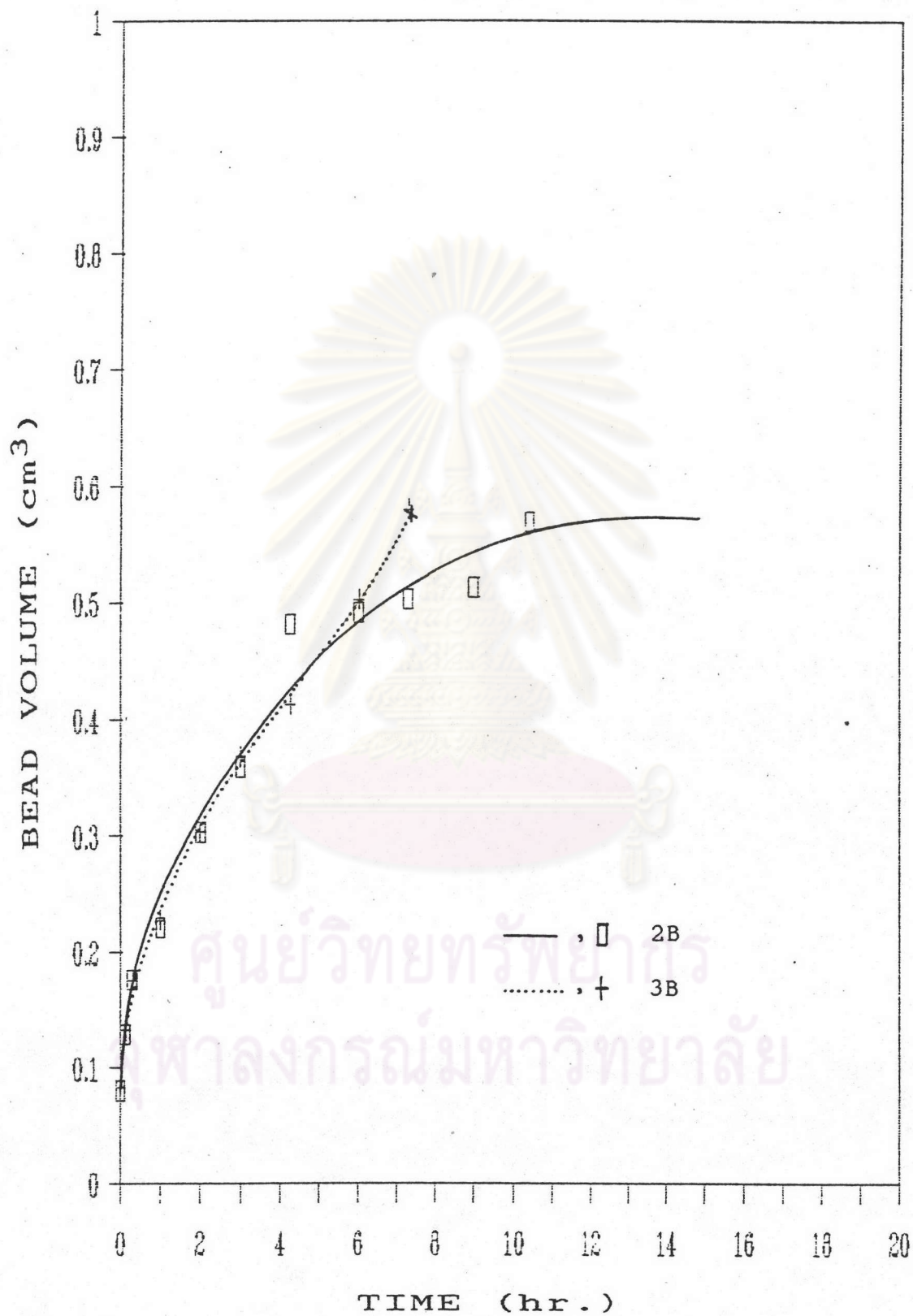


FIGURE 4.1 Variation of bead volumes with swollen time in toluene.

satisfied. Therefore, the seeded step was repeated again and the resulting bead size was determined to be about 3-5 mm. (2B)

2. The second group was brought to the seeded suspension step for 20 hours. Once again the beads size was too small. Therefore, the beads were brought through the seeded step again to get the satisfied size.(3B)

The absorption results from Table 4.2 and 4.3 were shown in graphs in Figure 4.1.

The rate of swelling of both groups, 2B and 3B, was shown to be approximately the same throughout the absorption period. However the result of the 3B group at time of 6 hours showed the higher rate of swelling, about 0.00095 greater than those of the 2B group (0.00011). In addition; at the time of 8 hours, the beads of the 3B group became deformed and torn from the edge of the sphere, presented accordingly in Figure 4.3, whereas there is no such deformation in the 2B beads and the size increased gradually and became constant at the time of 10 hours.

The swelling ratios of the beads of 2B and 3B were determined to be about 7.1 and 7 (before breakage), respectively. From Figure 4.1, both groups were shown to have a slightly different swelling ability at the 12 hr. or the 20 hr. and the beads being undergone the seeded suspension polymerization for 20 hr. became deformed after excessive swelling.

This result can be explained that too long

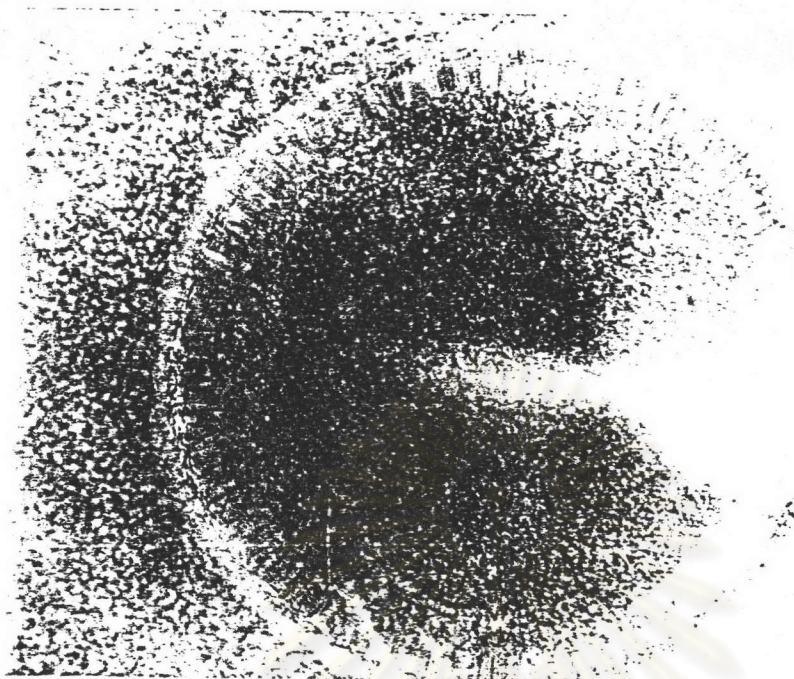


FIGURE 4.2 Optical Micrograph of the imbibed bead from 2B at full swelling stage under a magnification of 10.



FIGURE 4.3 Photomicrograph of the imbibed bead of the 3B group at fully swollen stage in toluene. The magnification was 10

the polymerization time will increase the excessive crosslinking sites inside the beads and make it rather rigid. Therefore, after excessive swelling in the solution, the beads expanded beyond its limit and became deformed, as shown in Figure 4.3.

4.3 The effect of time-temperature schedule for suspension polymerization

The time-temperature schedule in the suspension polymerization in the first period was changed from 70°C - 2 hr.+ 90°C - 4 hr. to 70°C - 4 hr.+ 90°C - 2 hr. with the same mixing speed at about 185 rpm. However, the second polymerization condition, 70°C - 4hr.+ 90°C - 2hr., failed because the polymer was melt and agglomerated around the stirrer. Therefore, the appropriate mixing speed must be sought for the second polymerization condition.

From Table 4.4, the proper mixing speed for the second condition is 220 rpm., which gave the largest bead size: at mesh size of 10-20, 41.27% were retained.

The synthetic beads from suspension polymerization using the second condition, 70°C - 4 hr.+ 90°C - 2 hr., came out soft and had larger size than those obtained from using the first condition, 70°C - 2hr.+ 90°C - 4hr. After the synthetic beads were dried and became rigid, they were brought to the further seeded suspension polymerization at 70°C - 4 hr.+ 90°C - 8 hr. (12 hr.).

TABLE 4.4

Effect of mixing speed on size distribution (wt.%)

Size distribution (mesh)	mixing speed (rpm.)			
	220	250	280	310
<10	2.3934%	1.4751%	-	-
10-20	41.2745%	35.7621%	28.1229%	14.6891%
20-30	34.5823%	39.0224%	47.4439%	50.1007%
30-40	18.4416%	21.4477%	21.2428%	31.6867%
>40	3.3082%	2.9303%	3.1897%	3.5232%

AT this time, the beads size came out satisfactorily large without further seeded step. The results of the toluene absorption were shown in Table 4.5 and Figure 4.4.

From Figure 4.4, it was found that the rate of absorption of the beads 5A increased significantly with the swelling ratio about 11.8. After comparing the swelling ratio of the beads 5A and the beads 2B in Figure 4.5, it was found that the beads 5A had the higher rate of absorption. This can be explained that the beads 5A did not undergo through the complete polymerization that is the crosslinking sites inside the beads were not too great, so it was a soft bead.

Consequently after swelling the beads in excess monomer solution for seeded suspension polymerization,

The beads could absorb more monomer and became satisfactorily large without further seeded step. In addition the crosslinking reaction inside the beads did not take place to an excessive extent. Therefore, the slightly crosslinked bead provided bead's flexibility

TABLE 4.5
Swelling of polystyrene crosslinked with
divinylbenzene in toluene (5A)

Run	Time (hr.)	ΔT (min)	Bead dia. (cm.)	Bead vol. (cm ³)	$\Delta V/\Delta T$ (cm /min) ³
5A	0.00	-	0.6667	0.1551	-
	0.15	15	0.7292	0.2030	0.0032
	1.00	45	0.8681	0.3425	0.0031
	2.00	60	1.0347	0.5801	0.0039
	3.00	60	1.0972	0.6916	0.0019
	6.00	180	1.2500	1.0227	0.0018
	7.30	90	1.2778	1.0924	0.00077
	9.30	120	1.3333	1.2411	0.0012
	10.30	60	1.3542	1.3002	0.00099
	14.00	210	1.4167	1.4887	0.00089
	17.30	210	1.4861	1.7185	0.0011
	20.00	150	1.5208	1.8418	0.00082
	23.00	180	1.5208	1.8418	0

swelling ratio = 11.8

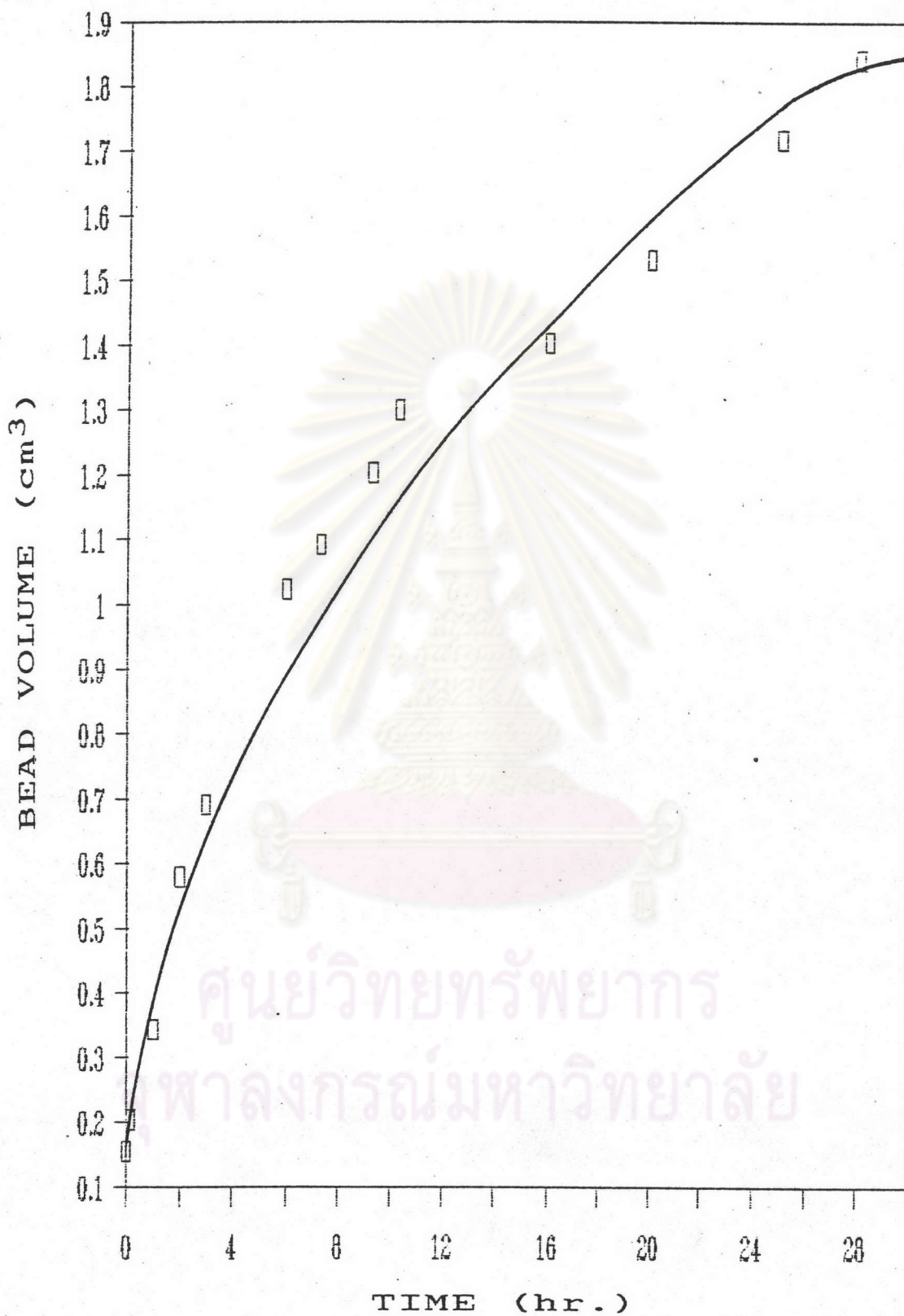


FIGURE 4.4 Absorption of the imbibed bead 5A in toluene.

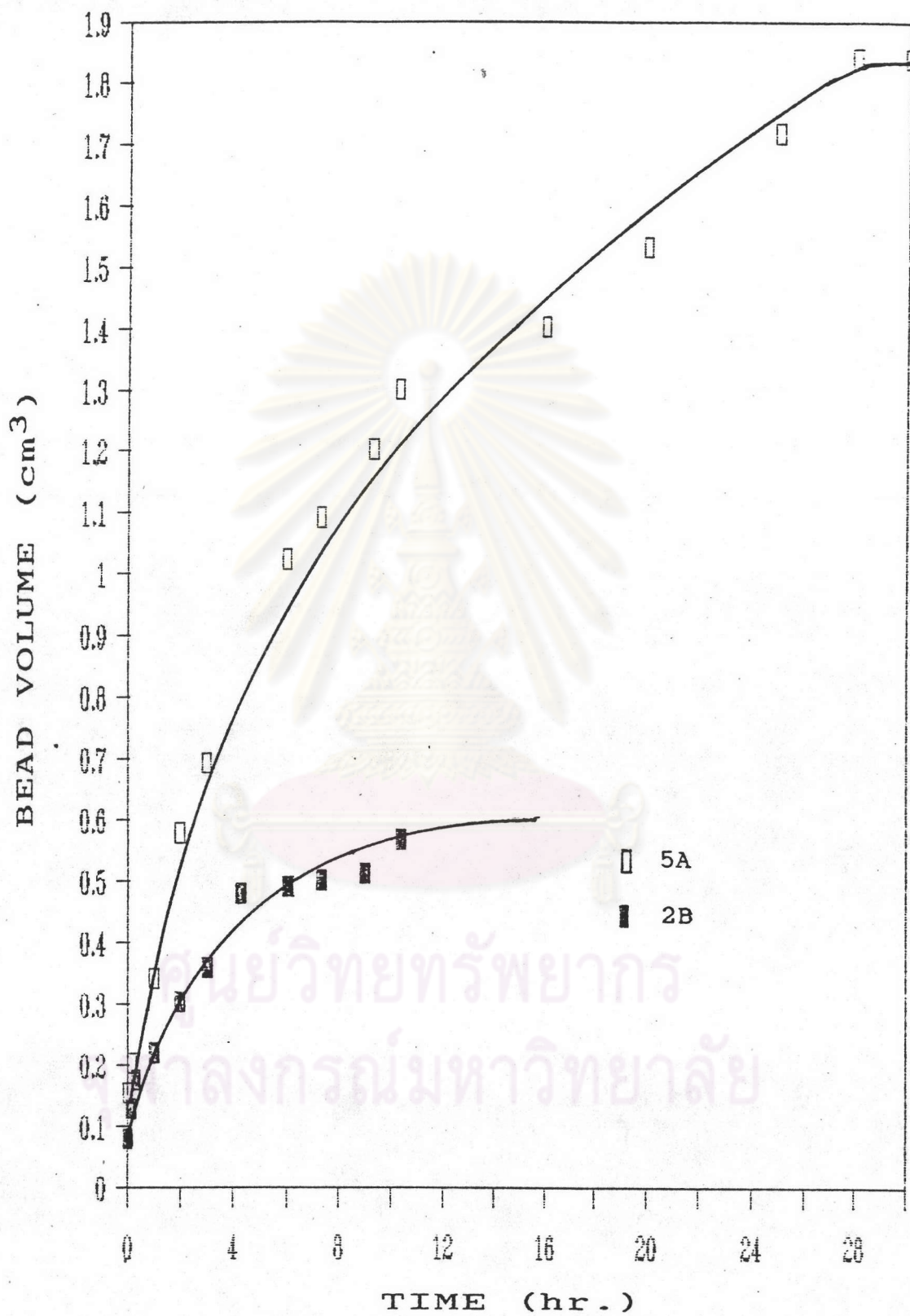


FIGURE 4.5 Comparative absorption of the imbibitor beads 2B and 5A in toluene

in expansion and swelling which permitted a higher absorption rate in toluene as shown in Figure 4.4.

4.4) The effect of suspending agent on bead size

In this study, two chemicals, HPMC and HPMC + HEC, were selected to determine the effect of the suspending agent on the bead size.

TABLE 4.6

The effect of suspending agent on bead size

bead size (mesh)	HPMC (wt.%)	HPMC + HEC (wt.%)
<10	-	2.3934
10-20	0.7326	41.2745
20-30	16.3705	34.5823
30-40	63.7100	18.4416
>40	19.1868	3.3082

From Table 4.6, when HPMC + HEC was used as suspending agent since the bead size gathered in the range of 10-20 mesh whereas the bead size resulting from only HPMC as suspending agent is in the range of 30-40 mesh. The surface tension and viscosity of both chemicals, HPMC and HEC, were shown in Table 4.7. Because HEC has a higher surface tension, the bead size obtained from the system containing HEC, will be larger than that using only HPMC alone. Although the viscosity of the HEC alone

Table 4.7

Comparison of HPMC and HEC aqueous solution (29,30)

Parameter	HPMC	HEC
surface tension (1%), (mN/m)	50-56	66.3
viscosity (2% sol.), (Pa S) (25 ^o C, 60 rpm.)	4*10 ⁶	1*10 ⁸

is two orders of magnitude greater than that of HPMC, the right proportion in weight percentages between the two suspending agents can be used to offset or counter balance the former's higher viscosity. Besides, other reaction conditions also contributed to its lower solution viscosity.

4.5 The effect of monomer phase volume fraction

Volume fraction of the monomer phase is one of the unique characteristics of suspension polymerization, as it is the center of the reaction site in terms of concentration and stability of the oleophilic phase. Table 4.8 shows the effect of monomer phase volume fraction on the bead formation and stability.

From Table 4.8, upon changing the ratios of monomer to water from 0.1 to 0.3 and 0.5, in spite of forming the larger beads, the bead formation did not succeed at all. They were coalesced.

TABLE 4.8

Effect of monomer phase volume fraction
on the formation of the bead

monomer phase volume fraction	property of the product
0.1	form bead
0.3	coalesced
0.5	coalesced

One possible explanation for the coalesced polymer may be due to the increasing of the monomer ratio inside the reaction vessel, a large number of monomer droplets were generated and distributed throughout the system, while the liquid medium responsible for the heat transfer was reduced. These caused the heat inside the vessel gradually accumulated to the point at which the droplets melt and agglomerated to the propeller of the mixing shaft.

4.6 Characterizations

4.6.1 Infrared Spectroscopy

In order to characterize the polystyrene bead and determine the crosslinking bond of divinylbenzene inside. The synthetic bead crosslinked with 0.3% divinylbenzene was analysed by Infrared spectroscopy, compared with standard polystyrene film, as shown in Figures 4.6 and 4.7.

PEAK THRESHOLD = 1.00 XT
 CM-1 XT

3847.00	79.595
3436.00	70.470
3103.00	75.075
3002.00	59.605
3000.00	51.925
3026.00	32.105
3002.00	60.505
2823.00	22.060
2851.00	51.060
1943.00	00.250
1071.00	90.425
1003.00	90.570
1735.00	03.010
1602.00	61.960
1504.00	02.905
1543.00	91.075
1494.00	30.365
1453.00	31.060
1374.00	00.520
1329.00	05.050
1274.00	07.740
1101.00	00.035
1155.00	00.945
1070.00	74.000
1029.00	00.105
901.00	00.705
965.00	00.445
907.00	04.450
841.00	94.755
757.00	37.320
699.00	3.175
621.00	03.505

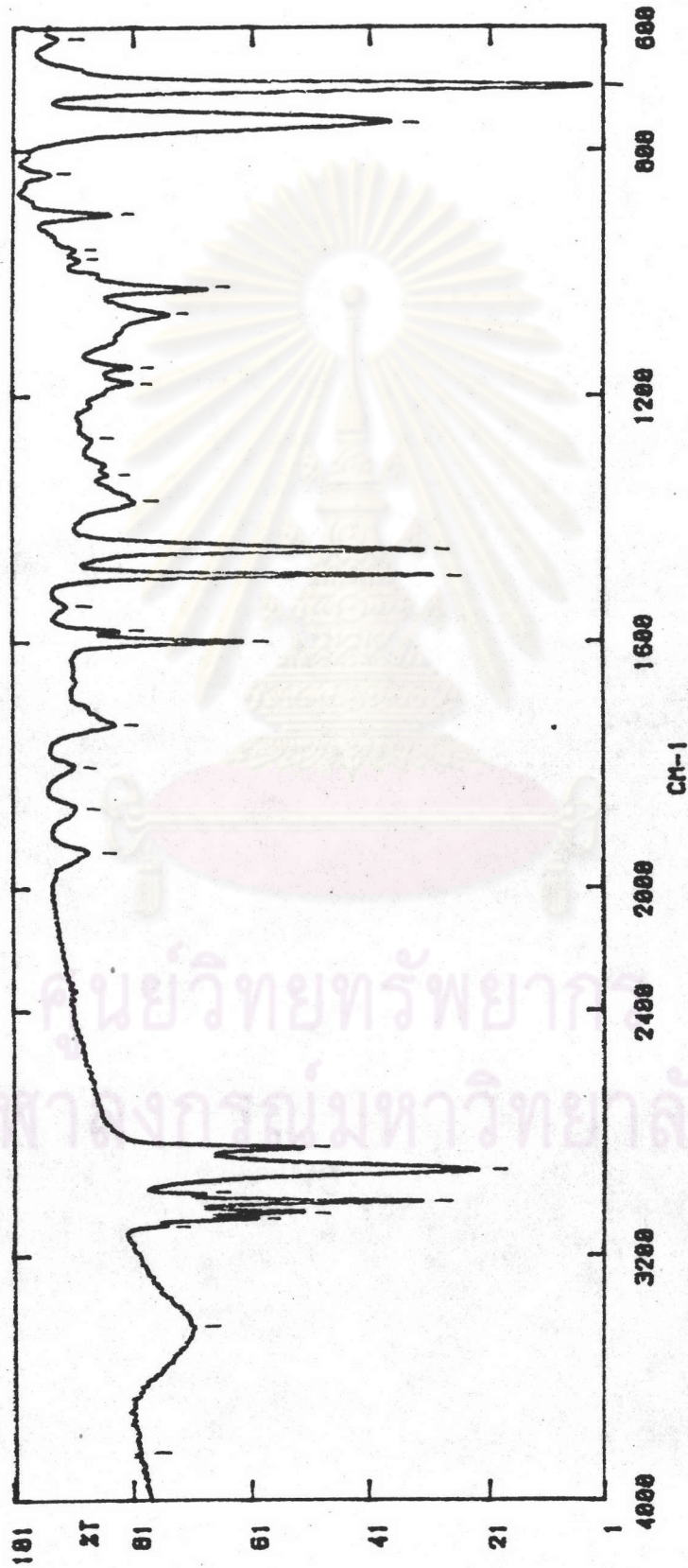


FIGURE 4.6 Infrared Spectroscopy of synthetic polystyrene imbibed bead.

PEAK THRESHOLD = 2.00 %T
CM-1

3103.00	68.090
3062.00	31.510
3060.00	20.430
3025.00	5.055
3002.00	51.450
2924.00	3.175
2850.00	31.475
2330.00	92.915
1943.00	75.930
1871.00	80.705
1803.00	79.945
1740.00	84.875
1667.00	86.415
1602.00	24.010
1584.00	60.630
1543.00	81.770
1494.00	3.175
1454.00	3.175
1372.00	59.305
1329.00	60.370
1182.00	67.330
1155.00	68.805
1070.00	61.430
1025.00	30.035
981.00	79.265
965.00	76.595
944.00	83.040
907.00	59.510
842.00	84.315
752.00	6.005
704.00	3.175
622.00	88.980

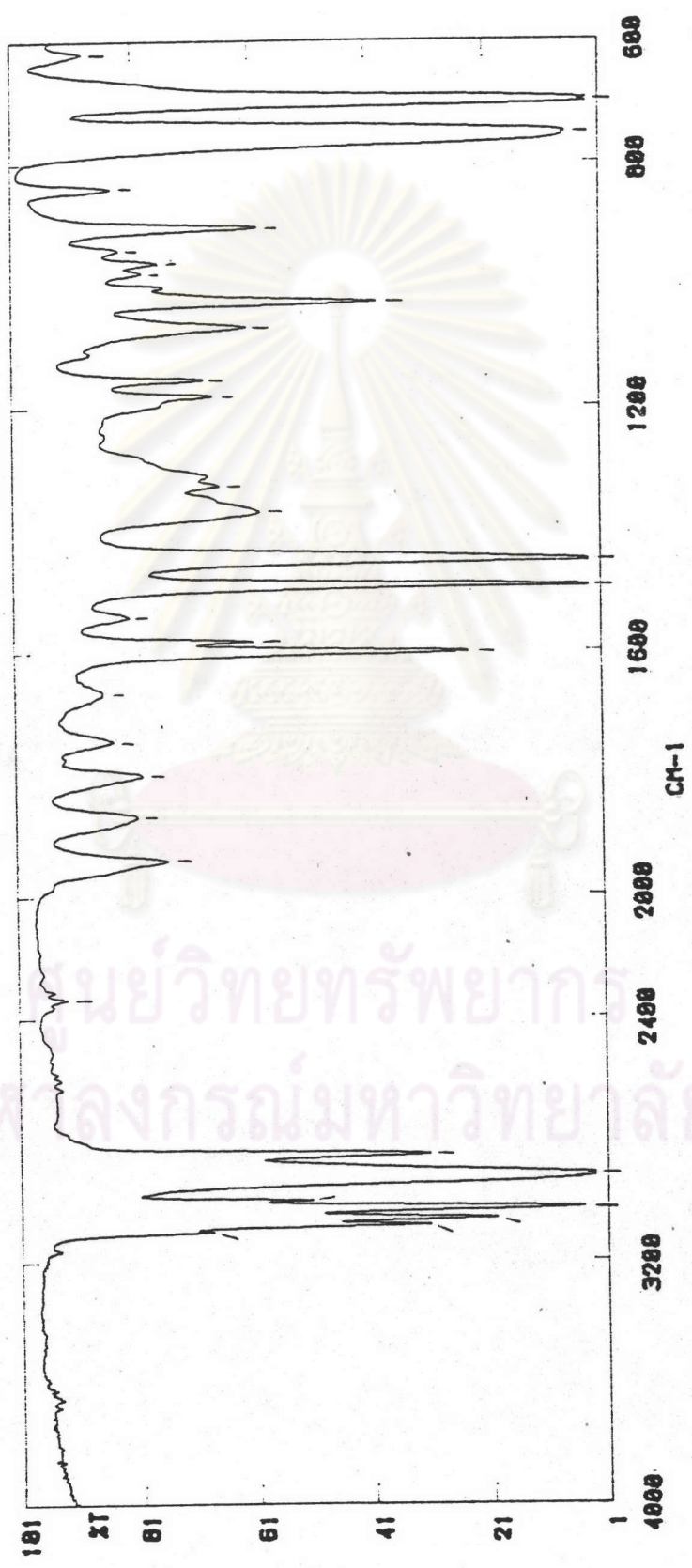


FIGURE 4.7 Infrared Spectroscopy of standard polystyrene film.

The results showed that the IR spectrum of both the synthetic bead and the standard polystyrene film were rather of the same pattern, as interpreted below. Figure 4.6 shows the following important peaks:

Wave number, cm^{-1}	Assignment
3060,3026	: =C-H group in aromatic ring
2923,2851	: saturated C-H stretching
1943,1871,1803,1735	: monosubstituted aromatic ring
1602,1584	: C=C stretching (aromatic ring breathing vibration)
1494,1453	: =C-H out of plane bending
757,699	: monosubstituted aromatic ring

Figure 4.7 shows the following significant peaks:

Wave number, cm^{-1}	Assignment
3060,3025	: =C-H group in aromatic ring
2924,2850	: saturated C-H stretching
1943,1871,1803,1746	: monosubstituted aromatic ring
1602,1584	: C=C stretching (aromatic ring breathing vibration)
1494,1454	: =C-H out of plane bending
757,704	: monosubstituted aromatic ring

From the spectrum interpretation, the synthetic beads was then characterized to be the polystyrene beads. To determine the crosslinking of divinylbenzene, the peak of p-disubstituted aromatic ring must be identified at $860-800 \text{ cm}^{-1}$. However, this region was generally interfered during thr IR experiment.

Therefore, the IR spectra of both the synthetic beads and the polystyrene film in this region cannot be discriminated from each other. In addition, the amount of divinylbenzene crosslinked in the beads is too small to affect the size of the p-disubstitution peak.

However, the synthetic beads were brought to soak in toluene which is the good solvent for polystyrene. It was found that the beads did not dissolve at all in toluene. Therefore, there must exist the crosslinking sites inside the synthetic beads.

4.6.2 BET

The BET method was used to measure the surface area of the porous bead. The surface area of the synthetic beads crosslinked with divinylbenzene was in the range 0.1-0.8 m²/g.

The beads was then brought to be analysed for the pore size ditribution by Water, Millipore Corporation. The results showed that the beads had a very small pore volume inside so it was likely characterized to be rather solid beads.

4.6.3 Scanning Electron Microscope

In addition, the beads were photographed by Scanning Electron Microscope to observe the surface appearance, can be seen in Figure 4.8 and 4.9, the following photomicrographs of the beads were taken with the magnifying ratios of 35 and 150.



FIGURE 4.8 Photomicrograph of the polystyrene bead crosslinked with divinylbenzene, magnifying ratio X 35.



FIGURE 4.9 Photomicrograph of the polystyrene bead crosslinked with divinylbenzene, magnifying ratio X 150.

From the photomicrographs, the surface of the beads was shown to be slightly porous. Therefore, this results support those from BET measurement and from Millipore's technique that the synthetic beads are slightly porous and have a small amount of surface area. The suggestions were given in Chapter 5.

4.7 Solvent sorption and desorption

4.7.1 Absorption

The absorption ability of the synthetic beads was tested by measuring the absorption amount of various solvents, as shown in Table 4.9 and Figures 4.10 and 4.11.

According to the hydrogen bond basis, the solvents used in this study can be divided into two categories:

1) Poorly hydrogen bond solvents: carbon tetrachloride, xylene, toluene, benzene, chloroform, 1,1,2 trichloroethane, and acrylonitrile.

2) moderately hydrogen bond solvents: amyl acetate, methyl methacrylate, tetrahydrofuran, methyl ethyl ketone, and acetone.

The results show that the swelling ratio of the imbibed bead in the poorly hydrogen bond solvent is higher than in the moderately hydrogen bond solvent. The highest swelling ratio in the poorly hydrogen bond group is 13.17 and the lowest ratio is 1.73. On the other hand, the highest swelling ratio in the moderately hydrogen bond group is 10.02 and the lowest

TABLE 4.9

The swelling ratio of synthetic bead in various solvent

Solvent	Solubility parameter [cal/cm] ^{3 1/2}	Swelling ratio
Carbon tetra- chloride	8.6 (p)	10.04
Xylene	8.8 (p)	11.06
Toluene	8.9 (p)	12
Benzene	9.2 (p)	12.28
Chloroform	9.3 (p)	13.17
1,1,2 Trichlo- roethane	9.6 (p)	11.54
Acrylonitrile	10.05 (p)	1.73
Amyl acetate	8.5 (m)	4.26
Methyl metha- crylate	8.8 (m)	8.49
Tetra hydro- furan	9.1 (m)	10.02
Methyl ethyl- ketone	9.3 (m)	3.16
Acetone	9.9 (m)	2.05

p : poorly hydrogen bond

m : moderately hydrogen bond

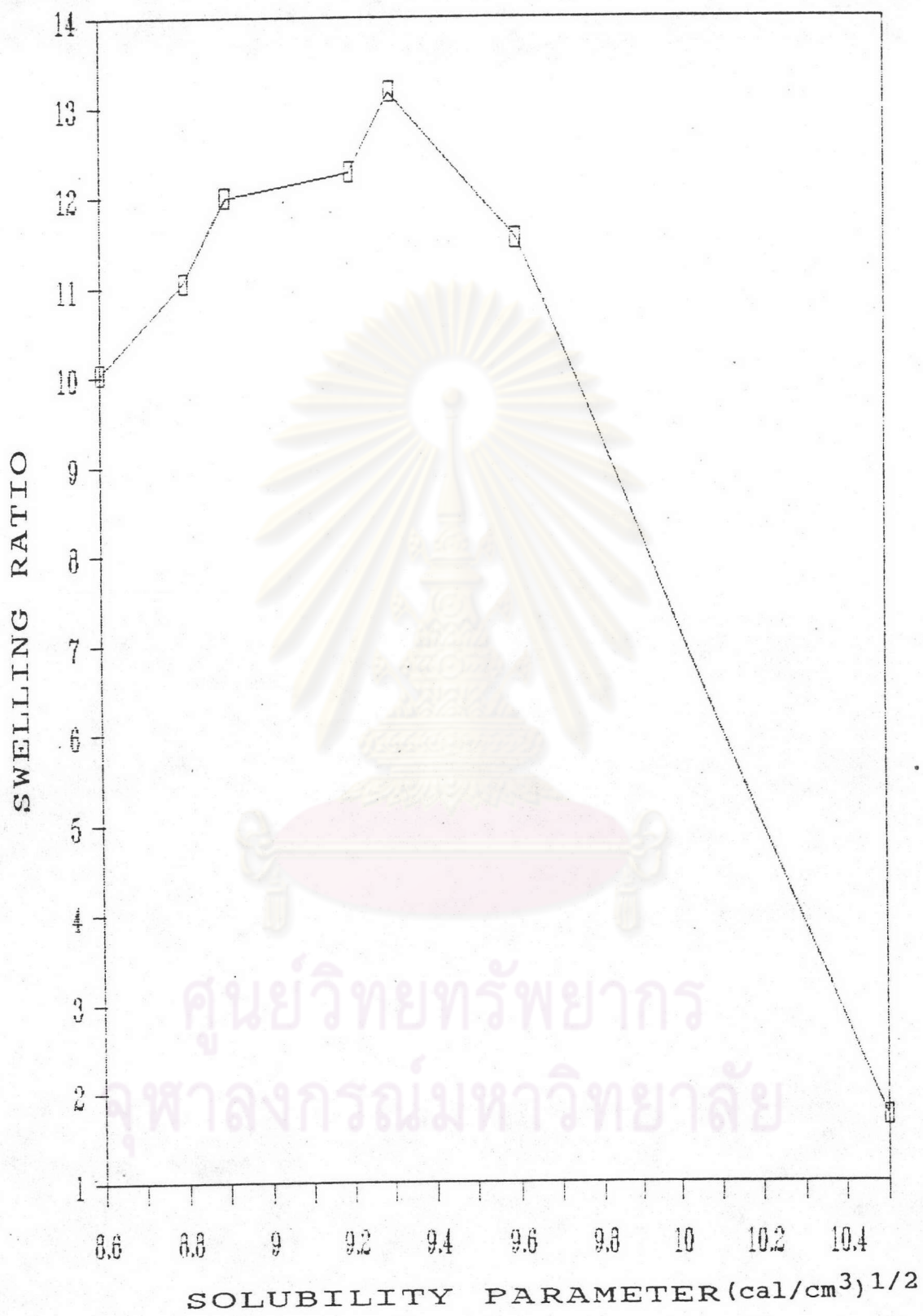


FIGURE 4.10 Comparative absorption of imbibed bead in poorly H-bond solvent.

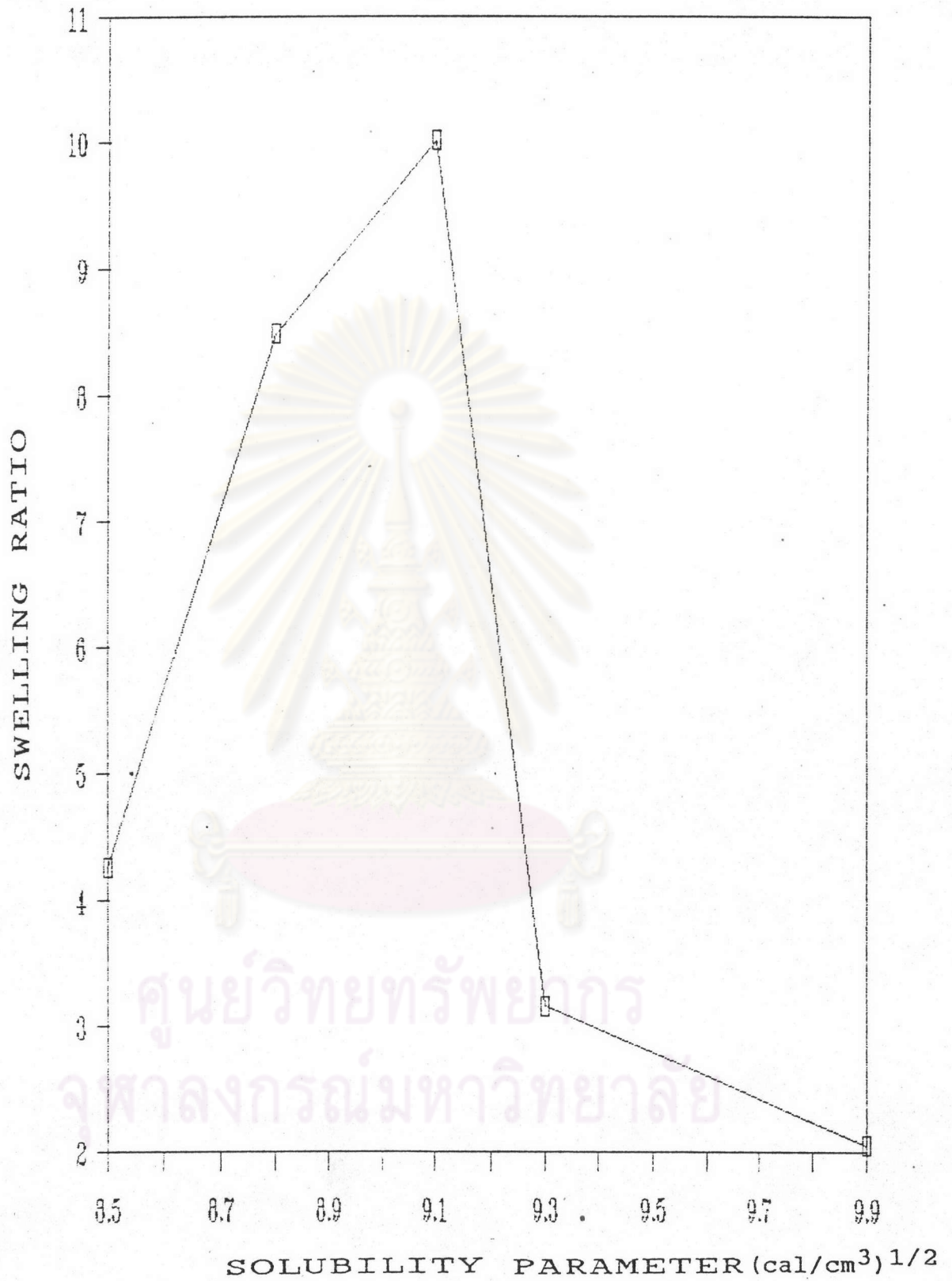


FIGURE 4.11 Comparative absorption of imbibed beads crosslinked with divinylbenzene with in moderately H-bond solvent.

ratio is 2.05. This can be explained that the nonpolar property of the styrene monomer causes the higher swelling of the polystyrene beads in the poorly hydrogen bond solvents.

From the swelling results, the solubility parameter of the polystyrene bead can be determined as follows. The swelling ratios in the poorly hydrogen bond solvents were plotted against solubility parameters, δ , as shown in Figure 4.10. The trend in the graph shows that the swelling ratio becomes highest in the range of $\delta = 8.6 - 9.6$ $[\text{cal}/\text{cm}^3]^{1/2}$ and decreases rapidly at solubility parameter = 10.5 $[\text{cal}/\text{cm}^3]^{1/2}$.

The solvent which possessed the high swelling ratio was then identified to be chloroform ($\delta = 9.3$ $[\text{cal}/\text{cm}^3]^{1/2}$) with the swelling ratio = 13.17. However, it cannot be concluded that the solubility parameter of the synthetic bead is exactly 9.3 $[\text{cal}/\text{cm}^3]^{1/2}$ because the highest swelling property in chloroform was resulted from both its nonpolarity and smaller molecular size. This information may give suggestion of small pore sizes inside the imbibed beads in relation to the BET and Millipore's determinations.

However, the solubility parameter of the polystyrene bead crosslinked with divinylbenzene was estimated accordingly to be in the range of $8.6 - 9.6$ $[\text{cal}/\text{cm}^3]^{1/2}$.

4.7.2 Desorption

After the polystyrene imbibed bead had been soaked in toluene, it was then brought to measure the desorption in a closed container, the desorption volume of which is shown in Figure 4.12

The synthetic bead showed the high desorption rate in the first fifteen minutes and the rate decreased gradually afterwards until the desorption amount became constant (97 %) after 23 hours.

4.8 Determination of Bead Density

The true density of the polystyrene bead was measured by Auto True Denser Model MAT-5000 and was reported to be about 1.05 g/cm^3 .

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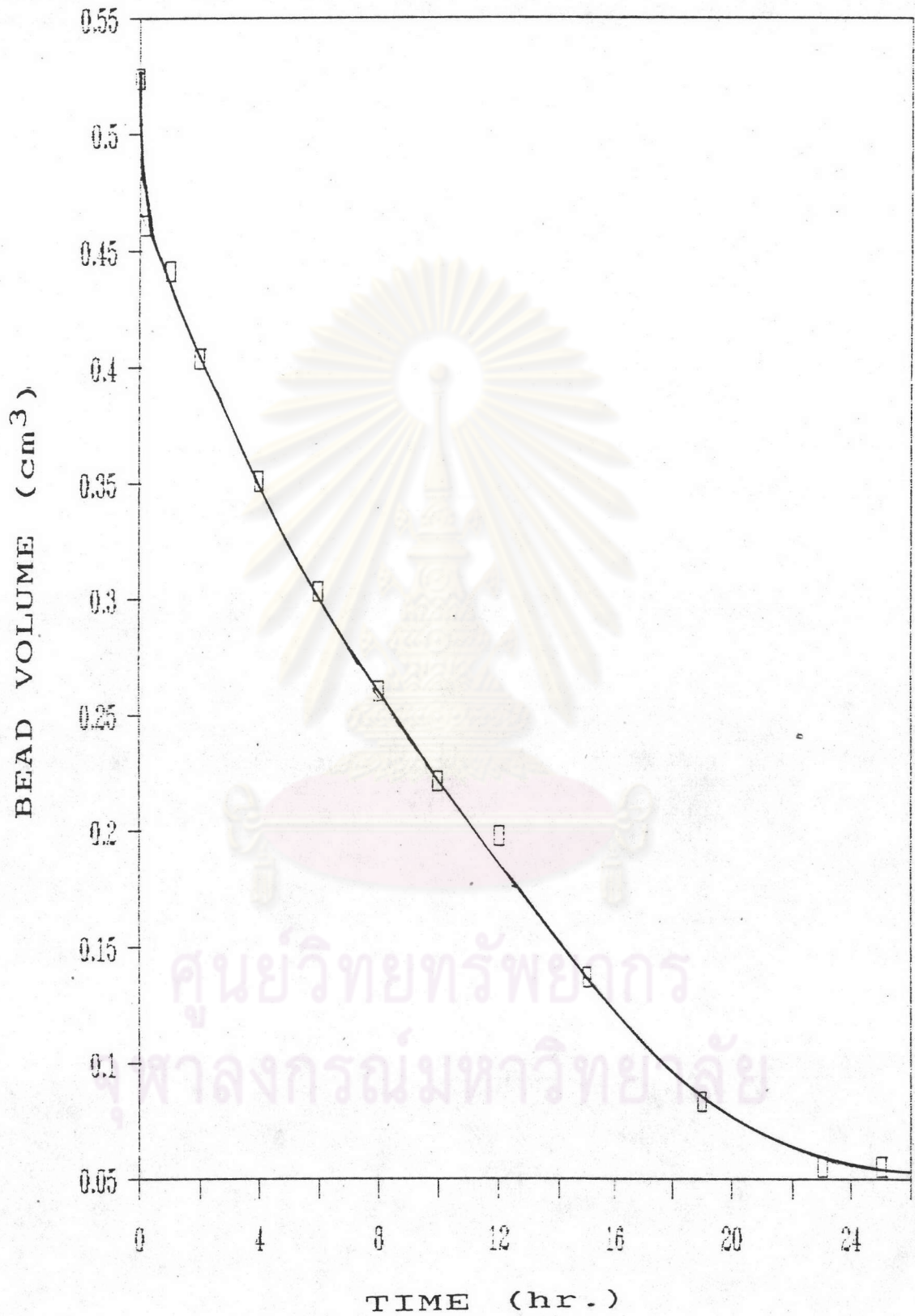


FIGURE 4.12 Desorption of imbiber bead..