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## APPENDIX A

### MONOMERS FOR GC ANALYSIS

#### 1. Calibration curve

##### 1.1 Calibration curve of styrene

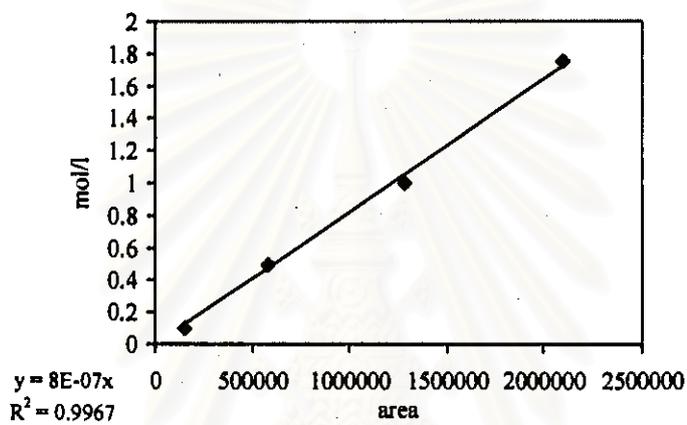


Figure A.1 Calibration curve of styrene

##### 1.2 Calibration curve of divinylbenzene

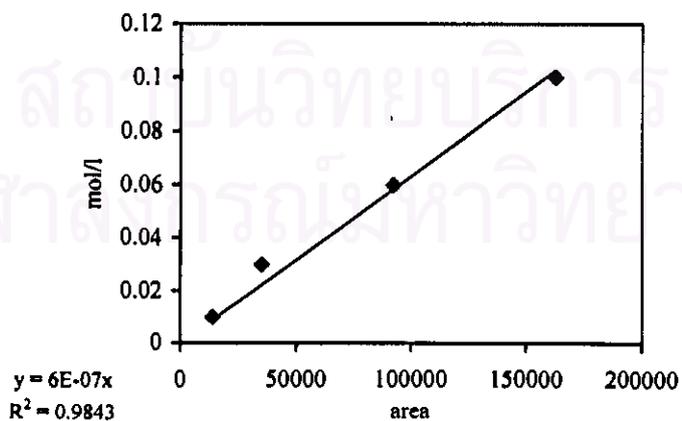


Figure A.2 Calibration curve of divinylbenzene

### 1.3 Calibration curve of ethylvinylbenzene

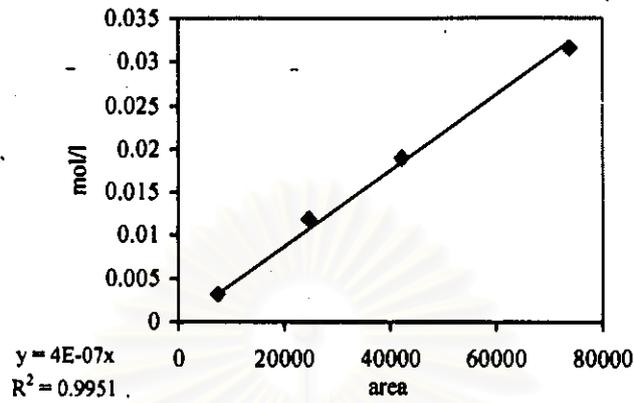


Figure A.3 Calibration curve of ethylvinylbenzene

The calibration equation can be expressed as:

$$C_i = R_i \times A_i \quad (\text{A.1})$$

where  $C_i$  = concentration of monomer  $i$

$R_i$  = detector response factor of monomer  $i$

$A_i$  = peak area of monomer  $i$

## 2. Determination of the contents of the monomers by GC technique

Table A.1  $R_i$  of the monomers

Monomer	Detector response factor
Styrene	$8 \times 10^{-7}$
Divinylbenzene	$6 \times 10^{-7}$
Ethylvinylbenzene	$4 \times 10^{-7}$

Sample chromatogram shown in Figure A.4 has retention times at 0.775 min (toluene); at 1.570 min (styrene); at 3.117 min. (ethylvinylbenzene); at 5.033 min (divinylbenzene).



Figure A.4 Chromatograms of the sampling solution after the completion of copolymerization

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## APPENDIX B

### PILOT SCALE REACTOR

#### 1. Batch reactor has 3 components as:

1.1 Reactor build from stainless steel 304 with an inside diameter of about 25 cm, 36 cm height and a capacity of 20 l. Bottom side was curved which 9 cm height and had tube with diameter of about 4 cm for transfer product. The cylindrical stainless steel reactor had a jacket, which contained the oil and heaters (No. 4) shown as No. 1 in Figure F.1. The heated oil in a jacket was measured by the thermocouple (No. 2), and heat was dissipated by gently bubbling air into the hot oil. An inside reactor had 4 buffer with 2 cm wide, 28 cm long (No. 5) and an inside temperature was measured by the thermocouple (No. 3).

1.2 Stirrer was turbine which build from stainless steel 304 with a diameter of about 14 cm, 3 cm height and 6 blades. An adjustable stirrer installed in a reactor was adjusted by variable drive motor (No. 6).

1.3 A cover was build from stainless steel 304 with a curve of about 9 cm height. A upper cover had a tube of adding mixture (No. 7) and a small tube for flow nitrogen (No. 8). At perimeter of cover had silicon gasket.

#### 2. Copolymerization

##### 2.1 Preparation of Aqueous Phase

Dissolve poly(vinyl alcohol) 0.09% by monomer weight was dissolved in distilled water, 8000 cm<sup>3</sup>, in a reactor. The monomer/water phase ratio throughout the experiments was fixed 1:7 wt/wt. The mixture was stirred by a stirrer at room temperature. Aqueous phase was prepared one day before experiments.

## 2.2 Preparation of Monomer Phase

The monomer solution phase contained styrene, divinylbenzene, benzoyl peroxide and organic solvent was charged into a reactor. A typical charge consisted styrene (92.5%), divinylbenzene (7.5%), benzoyl peroxide (0.5% by monomer weight) and organic solvent (100% by monomer weight).

The suspension experiments were made in a reactor with the dimensions and characteristics as shown in Figure B.1. The monomer solution phase containing styrene, divinylbenzene as a crosslinker, benzoyl peroxide as an initiator and toluene as an organic solution was added into a reactor with a rate of 90 cm<sup>3</sup>/min, which was stirred at an agitation speed of 240 rpm., while maintaining the reaction temperature at 70°C for 10 hour and the polymerization was carried out under a nitrogen atmosphere.

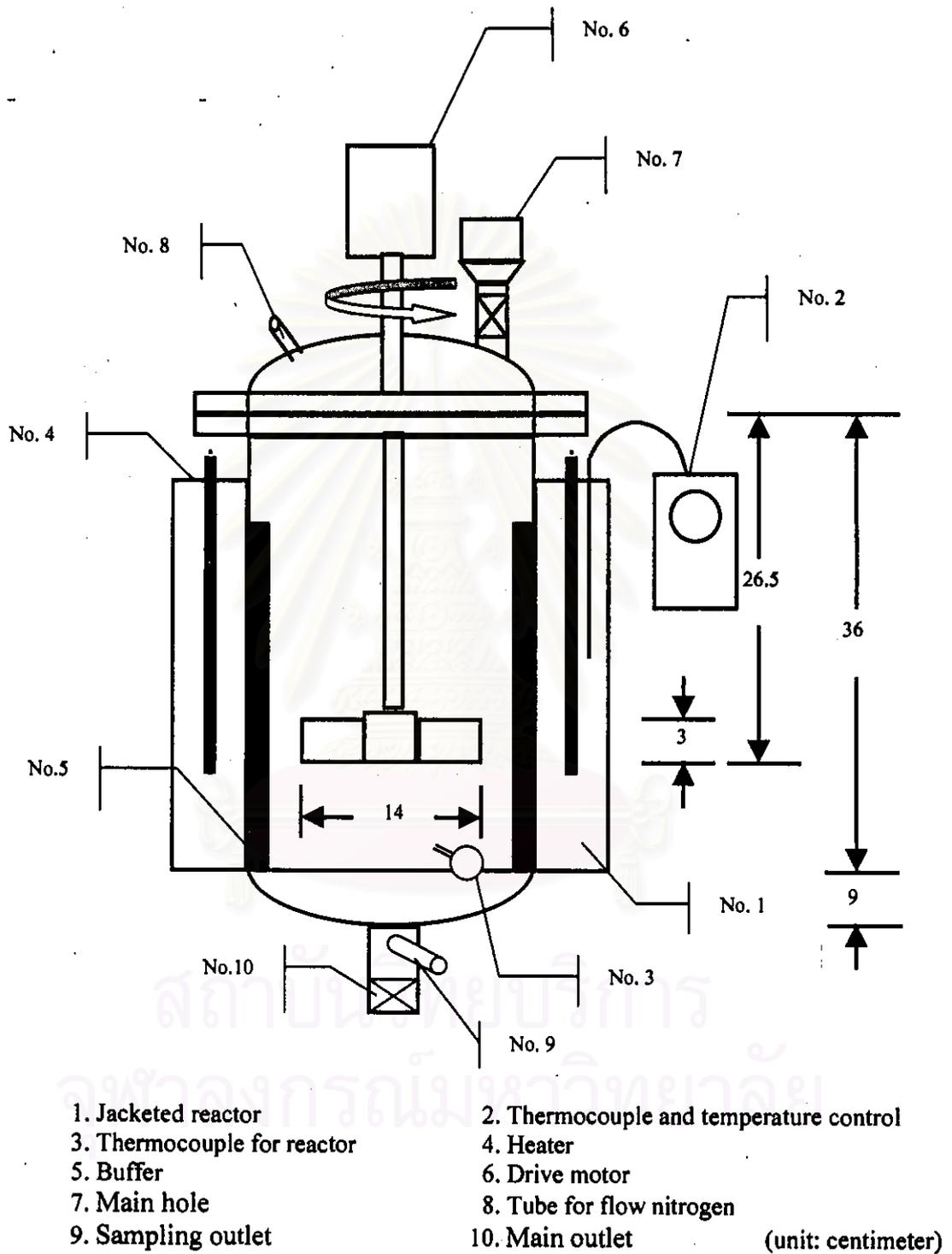


Figure B.1 Reactor for pilot scale.

## APPENDIX C

### CALCULATION OF THE DIFFUSION COEFFICIENT OF THE BEADS

#### C.1 Calculation of the diffusion coefficient of the beads

The diffusion coefficient of the imbibed bead can be calculated from

$$\tau = a^2 / D \quad (2.24)$$

where  $\tau$  is a characteristic swelling time  
 $a$  is the final radius of the fully swollen polymer.  
 $D$  is the diffusion coefficient of the swollen polymer in toluene

From Eq 2.24, The characteristic swelling time  $\tau$  can be obtained from the slope of the  $\ln(\Delta a_t / \Delta a_0)$  – time plot.

$$\ln(\Delta a_t / \Delta a_0) = \text{const.} - t / \tau \quad (2.25)$$

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 through out the entire swelling process

From the experiment, Sample B at 240 min, the slope of the  $\ln(\Delta a_t / \Delta a_0)$  – time plot is

0.0738. Thus,  $\tau = 13.5$  min

Since  $a = 1.07$  mm, thus,  $D = 0.084$  mm<sup>2</sup>/min

$= 1.49 \times 10^{-5}$  cm<sup>2</sup>/sec

Table C.1 Data for the calculation of the diffusion coefficient of the bead

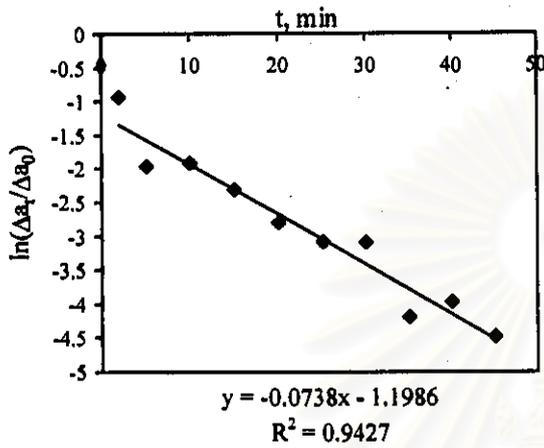
Sample	Time (min)	Bead radius (a, mm)	$\Delta at$ (mm)	$\ln(\Delta a_t/\Delta a_0)$
B at 240 min	0	0.41	-	-
	2	0.67	0.26	-0.9316
	5	0.76	0.09	-1.9650
	10	0.86	0.10	-1.9124
	15	0.93	0.07	-2.3179
	20	0.97	0.04	-2.8034
	25	1.00	0.03	-3.0910
	30	1.03	0.03	-3.0910
	35	1.04	0.01	-4.1897
	40	1.05	0.01	-3.9665
	45	1.06	0.01	-4.4773
50	1.07	0.02	-3.7842	
B (repeat) at 240 min	0	0.40	-	-
	2	0.66	0.26	-0.9373
	5	0.75	0.09	-1.9613
	10	0.85	0.10	-1.9087
	15	0.91	0.07	-2.3142
	20	0.95	0.04	-2.7997
	25	0.98	0.03	-3.0874
	30	1.01	0.03	-3.0874
	35	1.02	0.01	-4.1860
	40	1.04	0.01	-3.9628
	45	1.04	0.01	-4.4736
50	1.06	0.02	-3.7805	

Table C.1 Data for the calculation of the diffusion coefficient of the bead (continue)

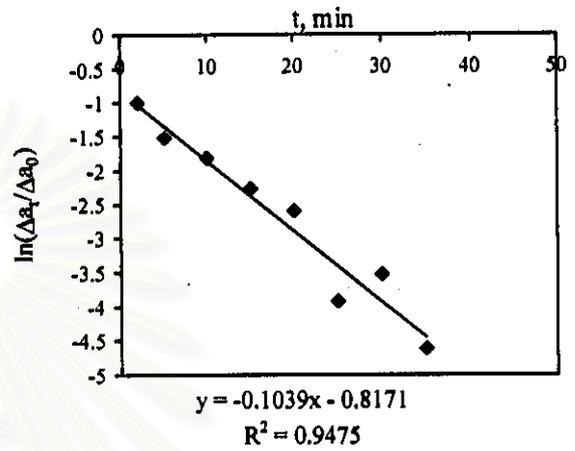
Sample	Time (min)	Bead radius (a, mm)	$\Delta at$ (mm)	$\ln(\Delta a_t/\Delta a_0)$
L at 240 min	0	0.41	-	-
	2	0.60	0.19	-0.9874
	5	0.71	0.11	-1.5115
	10	0.80	0.08	-1.8216
	15	0.85	0.05	-2.2736
	20	0.89	0.04	-2.6101
	25	0.90	0.01	-3.9318
	30	0.91	0.02	-3.5264
	35	0.92	0.01	-4.6250
	40	0.92	0.01	-4.6250
L (repeat) at 240 min	0	0.40	-	-
	2	0.59	0.19	-0.9955
	5	0.70	0.11	-1.5067
	10	0.78	0.08	-1.8168
	15	0.84	0.05	-2.2688
	20	0.87	0.04	-2.6053
	25	0.88	0.01	-3.9270
	30	0.90	0.02	-3.5216
	35	0.90	0.01	-4.6202
	40	0.91	0.01	-4.6202

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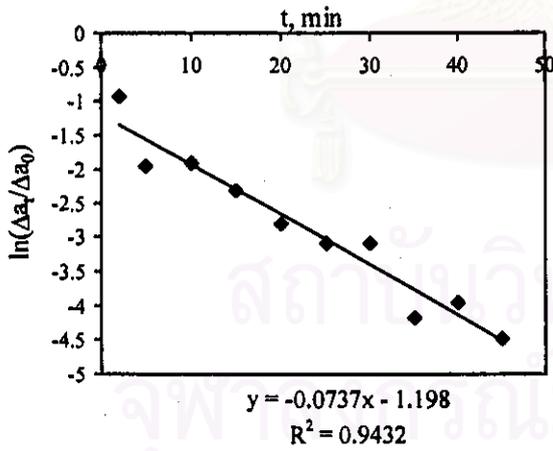
Variation of  $\ln(\Delta a_t/\Delta a_0)$  with swelling time.



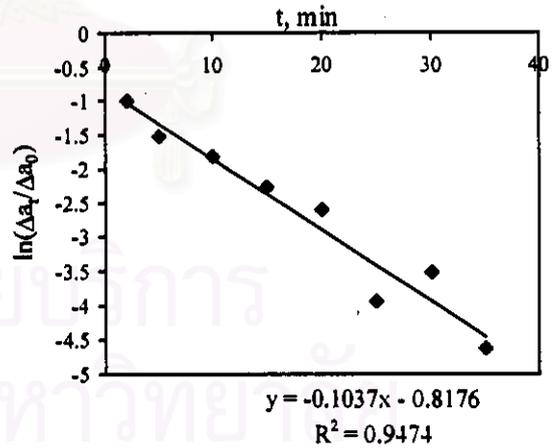
Sample B at 240 min



Sample L at 240 min



Sample B at 240 min  
(repeat)



Sample L at 240 min  
(repeat)

## VITA

Mr. Panomsak Chientachakul was born on April 24, 1974 in Bangkok, Thailand. He received his B. Sc. Degree in Chemical Technology from Faculty of Science, Chulalongkorn University in 1996 and he has been a graduate student in Chemical Technology from Graduate School, Chulalongkorn University in 1999.



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