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APPENDICES

APPENDIX A

Data of Absorption and Desorption in Toluene:Isooctane Solvent of the Copolymer Beads.

Table A-1 Absorption and desorption of polymer bead of poly(methyl methacrylate)/

polystyrene (Run PMMA/PS: 1st)

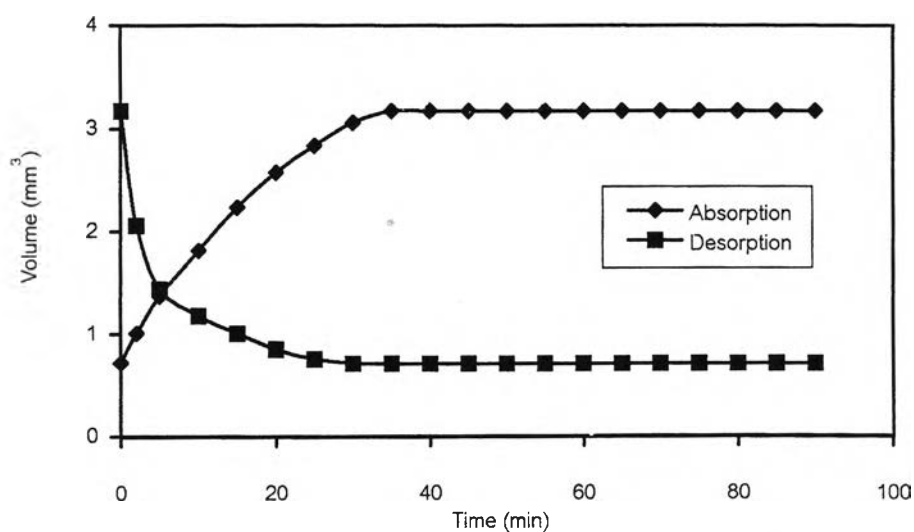| Time (min)	Absorption			Desorption		
	Bead Dia. (mm)	Bead Vol. (mm^3)	$\Delta V/\Delta T$ (mm^3/min)	Bead Dia. (mm)	Bead Vol. (mm^3)	$\Delta V/\Delta T$ (mm^3/min)
0	1.1111	0.7184	0.1455	1.8222	3.1681	-0.5558
2	1.2444	1.0094	0.1202	1.5778	2.0565	-0.2066
5	1.3778	1.3698	0.0875	1.4000	1.4368	-0.0513
10	1.5111	1.8072	0.0857	1.3111	1.1801	-0.0342
15	1.6222	2.2359	0.0675	1.2444	1.0091	-0.0307
20	1.7000	2.5732	0.0521	1.1777	0.8554	-0.0186
25	1.7556	2.8338	0.0441	1.1333	0.7622	-0.0088
30	1.8000	3.0545	0.0229	1.1111	0.7182	0.0000
35	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
40	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
45	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
50	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
55	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
60	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
65	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
70	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
75	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
80	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
85	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
90	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000

Figure A-1 Variation of polymer bead volume with time (Run PMMA/PS: 1st)

Table A-2 Absorption and desorption of polymer bead of poly(methyl methacrylate)/

polystyrene (Run PMMA/PS: 2nd)

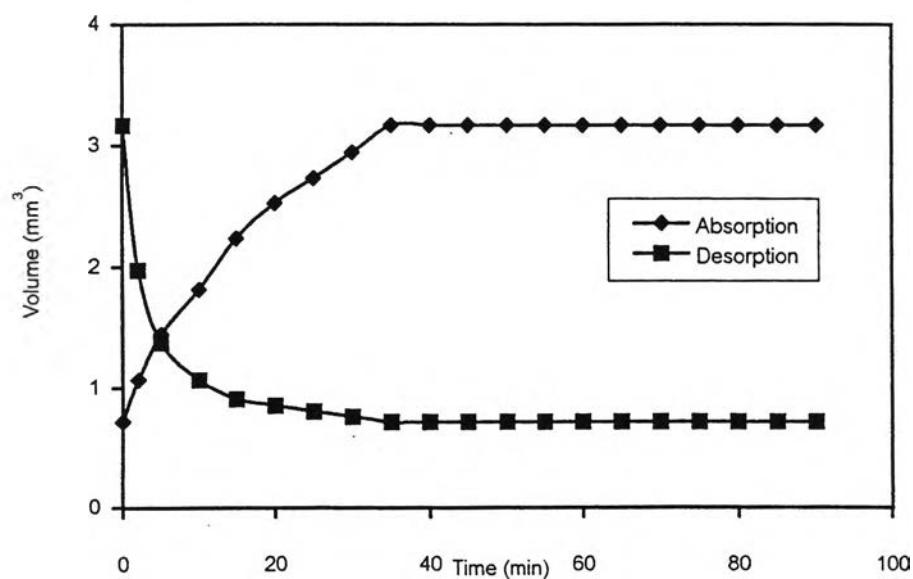| Time	Absorption			Desorption		
(min)	Bead Dia. (mm)	Bead Vol. (mm^3)	$\Delta V/\Delta T$ (mm^3/min)	Bead Dia. (mm)	Bead Vol. (mm^3)	$\Delta V/\Delta T$ (mm^3/min)
0	1.1111	0.7184	0.1730	1.8222	3.1681	-0.5986
2	1.2667	1.0644	0.1242	1.5556	1.9709	-0.2005
5	1.4000	1.4372	0.0740	1.3776	1.3694	-0.0610
10	1.5111	1.8072	0.0857	1.2667	1.0641	-0.0319
15	1.6222	2.2359	0.0574	1.2000	0.9048	-0.0099
20	1.6889	2.5231	0.0409	1.1778	0.8554	-0.0095
25	1.7333	2.7275	0.0431	1.1556	0.8079	-0.0091
30	1.7778	2.9428	0.0452	1.1333	0.7622	-0.0088
35	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
40	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
45	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
50	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
55	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
60	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
65	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
70	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
75	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
80	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
85	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
90	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000

Figure A-2 Variation of polymer bead volume with time (Run PMMA/PS: 2nd)

Table A-3 Absorption and desorption of polymer bead of poly(methyl methacrylate)/

polystyrene (Run PMMA/PS: 3rd)

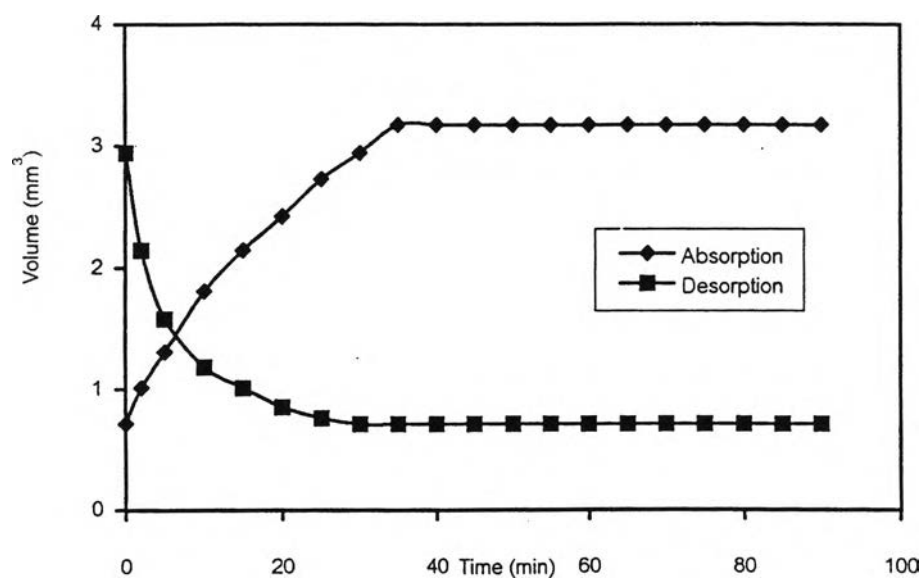| Time	Absorption			Desorption		
(min)	Bead Dia. (mm)	Bead Vol. (mm^3)	$\Delta V/\Delta T$ (mm^3/min)	Bead Dia. (mm)	Bead Vol. (mm^3)	$\Delta V/\Delta T$ (mm^3/min)
0	1.1111	0.7184	0.1455	1.7778	2.9419	-0.3986
2	1.2444	1.0094	0.0984	1.6000	2.1447	-0.1889
5	1.3556	1.3046	0.1005	1.4444	1.5780	-0.0796
10	1.5111	1.8072	0.0676	1.3111	1.1801	-0.0342
15	1.6000	2.1453	0.0559	1.2444	1.0091	-0.0307
20	1.6667	2.4248	0.0605	1.1778	0.8554	-0.0186
25	1.7333	2.7275	0.0431	1.1333	0.7622	-0.0088
30	1.7778	2.9428	0.0452	1.1111	0.7182	0.0000
35	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
40	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
45	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
50	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
55	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
60	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
65	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
70	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
75	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
80	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
85	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000
90	1.8222	3.1690	0.0000	1.1111	0.7182	0.0000

Figure A-3 Variation of polymer bead volume with time (Run PMMA/PS: 3rd)

Table A-4 Absorption and desorption of polymer bead of poly(methyl acrylate)/polystyrene

(Run PMA/PS: 1st)

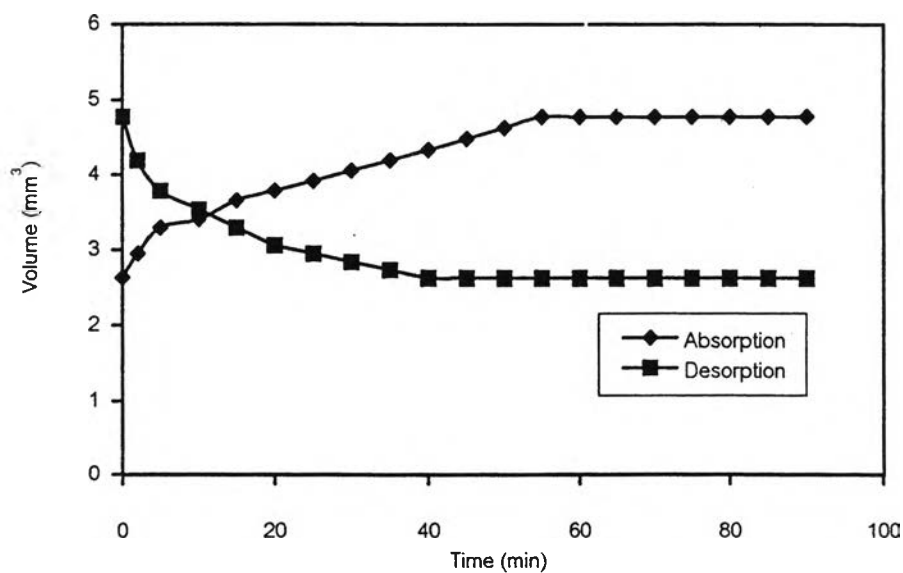| Time	Absorption			Desorption		
(min)	Bead Dia. (mm)	Bead Vol. (mm^3)	$\Delta V/\Delta T$ (mm^3/min)	Bead Dia. (mm)	Bead Vol. (mm^3)	$\Delta V/\Delta T$ (mm^3/min)
0	1.7111	2.6240	0.1594	2.0889	4.7739	-0.2919
2	1.7778	2.9428	0.1145	2.0000	4.1900	-0.1351
5	1.8444	3.2864	0.0240	1.9333	3.7848	-0.0510
10	1.8666	3.4064	0.0499	1.8889	3.5298	-0.0487
15	1.9111	3.6558	0.0258	1.8444	3.2864	-0.0464
20	1.9333	3.7848	0.0264	1.8000	3.0545	-0.0223
25	1.9556	3.9169	0.0270	1.7778	2.9428	-0.0218
30	1.9778	4.0519	0.0276	1.7556	2.8338	-0.0213
35	2.0000	4.1900	0.0282	1.7333	2.7275	-0.0207
40	2.0222	4.3312	0.0289	1.7111	2.6240	0.0000
45	2.0444	4.4756	0.0295	1.7111	2.6240	0.0000
50	2.0667	4.6231	0.0301	1.7111	2.6240	0.0000
55	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
60	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
65	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
70	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
75	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
80	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
85	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
90	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000

Figure A-4 Variation of polymer bead volume with time (Run PMA/PS: 1st)

Table A-5 Absorption and desorption of polymer bead of poly(methyl acrylate)/polystyrene

(Run PMA/PS: 2nd)

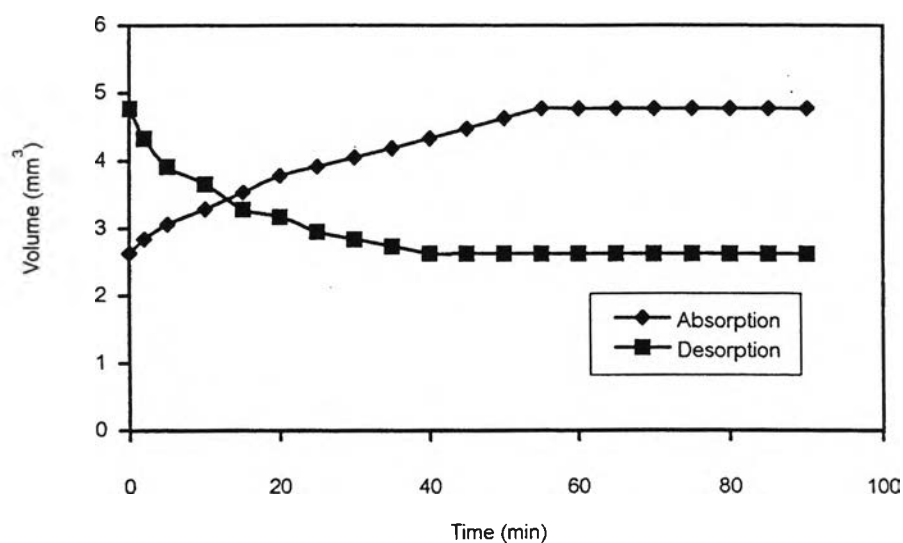| Time	Absorption			Desorption		
(min)	Bead Dia. (mm)	Bead Vol. (mm^3)	$\Delta V/\Delta T$ (mm^3/min)	Bead Dia. (mm)	Bead Vol. (mm^3)	$\Delta V/\Delta T$ (mm^3/min)
0	1.7111	2.6240	0.1049	2.0889	4.7739	-0.2213
2	1.7556	2.8338	0.0736	2.0222	4.3312	-0.1381
5	1.8000	3.0545	0.0464	1.9556	3.9169	-0.0522
10	1.8444	3.2864	0.0487	1.9111	3.6558	-0.0739
15	1.8889	3.5298	0.0510	1.8444	3.2864	-0.0235
20	1.9333	3.7848	0.0264	1.8222	3.1690	-0.0452
25	1.9556	3.9169	0.0270	1.7778	2.9428	-0.0218
30	1.9778	4.0519	0.0276	1.7556	2.8338	-0.0213
35	2.0000	4.1900	0.0282	1.7333	2.7275	-0.0207
40	2.0222	4.3312	0.0289	1.7111	2.6240	0.0000
45	2.0444	4.4756	0.0295	1.7111	2.6240	0.0000
50	2.0667	4.6231	0.0301	1.7111	2.6240	0.0000
55	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
60	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
65	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
70	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
75	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
80	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
85	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
90	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000

Figure A-5 Variation of polymer bead volume with time (Run PMA/PS: 2nd)

Table A-6 Absorption and desorption of polymer bead of poly(methyl acrylate)/polystyrene

(Run PMA/PS: 3rd)

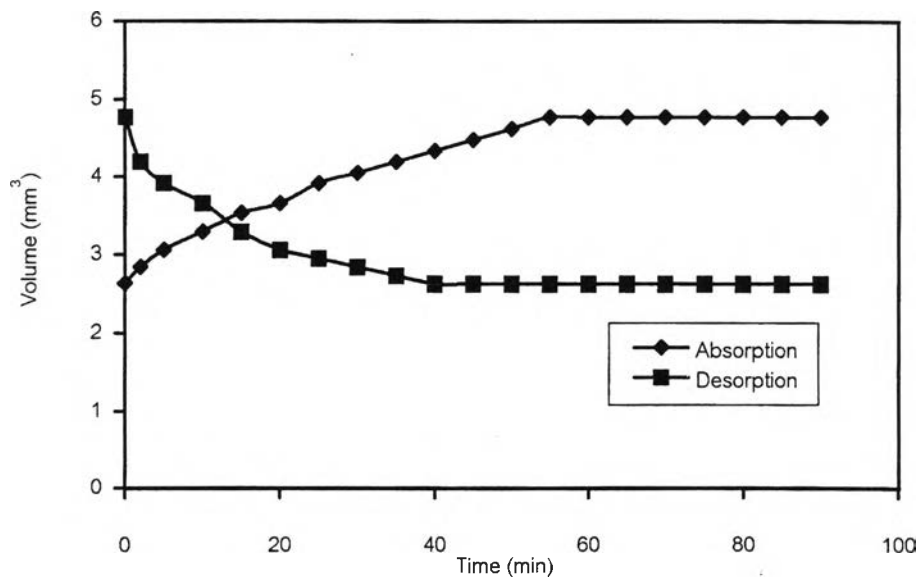| Time (min)	Absorption			Desorption		
	Bead Dia. (mm)	Bead Vol. (mm^3)	$\Delta V/\Delta T$ (mm^3/min)	Bead Dia. (mm)	Bead Vol. (mm^3)	$\Delta V/\Delta T$ (mm^3/min)
0	1.7111	2.6240	0.1049	2.0889	4.7739	-0.2919
2	1.7556	2.8338	0.0736	2.0000	4.1900	-0.0910
5	1.8000	3.0545	0.0464	1.9556	3.9169	-0.0522
10	1.8444	3.2864	0.0487	1.9111	3.6558	-0.0739
15	1.8889	3.5298	0.0252	1.8444	3.2864	-0.0464
20	1.9111	3.6558	0.0522	1.8000	3.0545	-0.0223
25	1.9556	3.9169	0.0270	1.7778	2.9428	-0.0218
30	1.9778	4.0519	0.0276	1.7556	2.8338	-0.0213
35	2.0000	4.1900	0.0282	1.7333	2.7275	-0.0207
40	2.0222	4.3312	0.0289	1.7111	2.6240	0.0000
45	2.0444	4.4756	0.0295	1.7111	2.6240	0.0000
50	2.0667	4.6231	0.0301	1.7111	2.6240	0.0000
55	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
60	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
65	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
70	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
75	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
80	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
85	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000
90	2.0889	4.7739	0.0000	1.7111	2.6240	0.0000

Figure A-6 Variation of polymer bead volume with time (Run PMA/PS: 3rd)

Table A-7 Absorption and desorption of polymer bead of poly(2-ethylhexyl acrylate)/polystyrene

(Run P(2-EHA)/PS: 1st)

| Time (min)	Absorption			Desorption		
	Bead Dia. (mm)	Bead Vol. (mm^3)	$\Delta V/\Delta T$ (mm^3/min)	Bead Dia. (mm)	Bead Vol. (mm^3)	$\Delta V/\Delta T$ (mm^3/min)
0	2.5556	8.7414	1.9430	3.9333	31.8625	-2.7894
2	2.8889	12.6275	0.9361	3.6889	26.2837	-2.2971
5	3.0889	15.4359	0.6393	3.3333	19.3925	-0.7251
10	3.2889	18.6325	0.4718	3.1111	15.7668	-0.3883
15	3.4222	20.9917	0.5092	2.9778	13.8254	-0.3550
20	3.5553	23.5377	0.3629	2.8445	12.0502	-0.2975
25	3.6444	25.3522	0.4781	2.7222	10.5625	-0.1759
30	3.7556	27.7427	0.1993	2.6444	9.6828	-0.1888
35	3.8000	28.7392	0.2040	2.5556	8.7389	0.0000
40	3.8444	29.7593	0.1038	2.5556	8.7389	0.0000
45	3.8667	30.2786	0.1050	2.5556	8.7389	0.0000
50	3.8889	30.8036	0.1062	2.5556	8.7389	0.0000
55	3.9111	31.3346	0.1074	2.5556	8.7389	0.0000
60	3.9333	31.8717	0.0000	2.5556	8.7389	0.0000
65	3.9333	31.8717	0.0000	2.5556	8.7389	0.0000
70	3.9333	31.8717	0.0000	2.5556	8.7389	0.0000
75	3.9333	31.8717	0.0000	2.5556	8.7389	0.0000
80	3.9333	31.8717	0.0000	2.5556	8.7389	0.0000
85	3.9333	31.8717	0.0000	2.5556	8.7389	0.0000
90	3.9333	31.8717	0.0000	2.5555	8.7389	0.0000
100	3.9333	31.8717	0.0000	2.5556	8.7389	0.0000
110	3.9333	31.8717	0.0000	2.5556	8.7389	0.0000
120	3.9333	31.8717	0.0000	2.5556	8.7389	0.0000
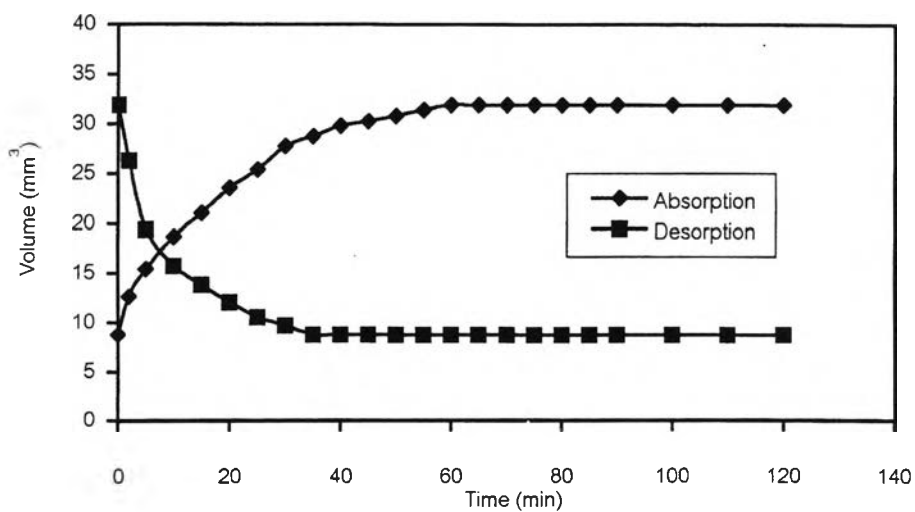
Figure A-7 Variation of polymer bead volume with time (Run P(2-EHA)/PS: 1st)

APPENDIX B

The calculation of the diffusion coefficient of solvents absorbed and desorbed in the core/shell beads.

The diffusion coefficient of core/shell beads can be calculated from equation (B-1)

$$\tau = a^2/D \qquad \text{(B-1)}$$

where τ is a characteristic swelling time

a is the final radius of the fully swollen gel

D is the diffusion coefficient of the gel in the liquid

From the equation (B-2), the characteristic swelling time τ can be obtained from the slope of the ln $(\Delta a_t / \Delta a_0)$ – time plot.

$$\ln (\Delta a_t / \Delta a_0) = \text{const.} - t / \tau \qquad \text{(B-2)}$$

where Δa_t is the difference between the size (radius) at time t and that at the saturation swelling

Δa_0 is the total change in radius throughout the entire swelling process

From the experiment, the core/shell bead of poly(methyl methacrylate)/polystyrene by one-stage suspension polymerization, as Run PMMA/PS for the first cycle was plotted. The slope of the ln $(\Delta a_t / \Delta a_0)$ – time plot is –0.0523. Thus,

$$\tau = 19.12 \text{ minutes}$$

Since a = 0.911 mm, thus D = 0.0434 mm^{2}min^{-1}

Table B-1 Data for the calculation of the diffusion coefficient of solvents absorbed and desorbed in the core/shell beads.
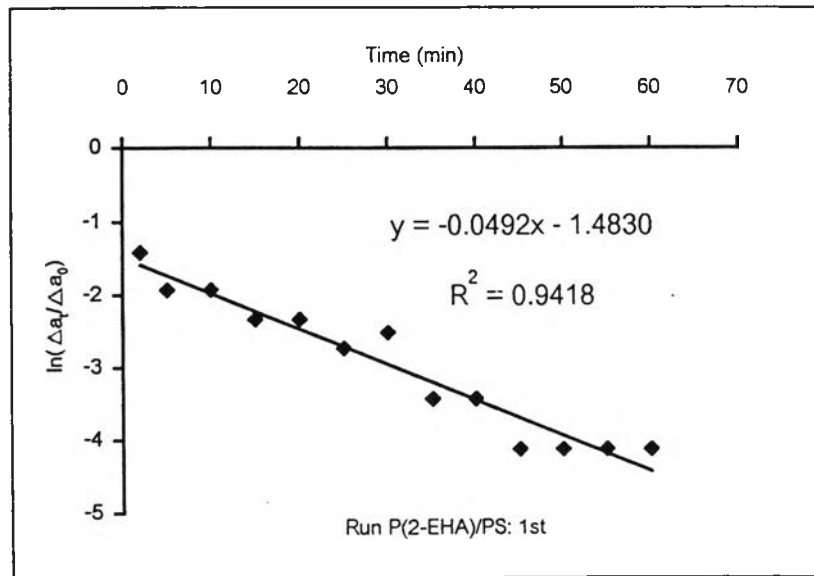
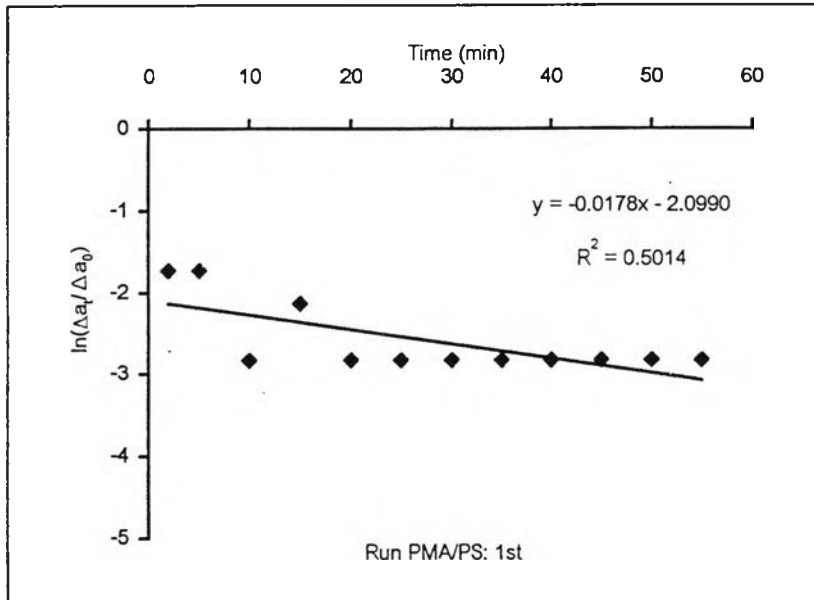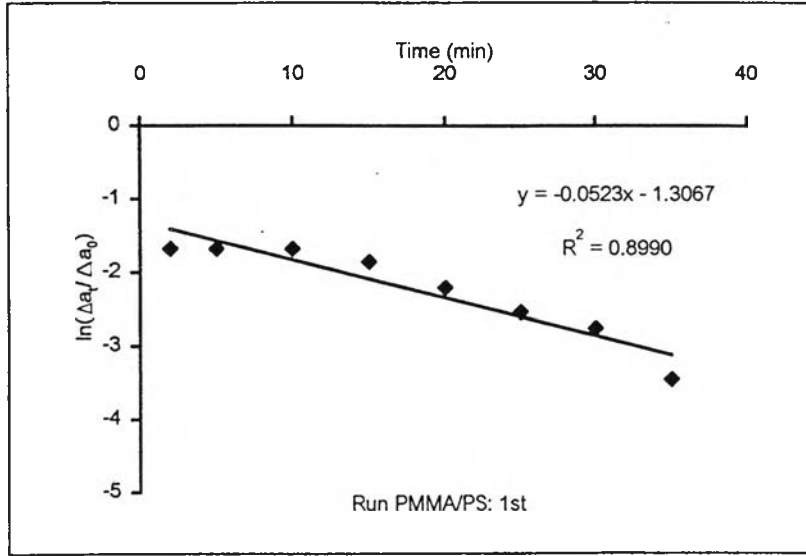| Runs	Time (min)	Bead Radius (a, mm)	Δa_t (mm)	$\ln (\Delta a_t / \Delta a_0)$
PMMA/PS: 1st	0	0.55555	-	-
	2	0.62222	0.06665	-1.6740
	5	0.68889	0.06667	-1.6740
	10	0.75555	0.06665	-1.6740
	15	0.81111	0.05555	-1.8563
	20	0.85000	0.03889	-2.2129
	25	0.87778	0.02778	-2.5494
	30	0.90000	0.02222	-2.7727
	35	0.91111	0.01111	-3.4658
PMMA/PS: 2nd	0	0.55555	-	-
	2	063335	0.07778	-1.5198
	5	0.70000	0.06666	-1.6740
	10	0.75555	0.05555	-1.8563
	15	0.81111	0.05555	-1.8563
	20	0.84445	0.03333	-2.3671
	25	0.86665	0.02222	-2.7725
	30	0.88889	0.02222	-2.7225
	35	0.91111	0.02222	-2.7725
PMMA/PS: 3rd	0	0.55555	-	-
	2	0.62222	0.06667	-1.6740
	5	0.67778	0.05556	-1.8562
	10	0.75555	0.07777	-1.5199
	15	0.80000	0.04444	-2.0794
	20	0.83335	0.03333	-2.3671
	25	0.86665	0.03333	-2.3671
	30	0.88889	0.02222	-2.7725
	35	0.91111	0.02222	-2.7725

Table B-1 (Continued)

Runs	Time (min)	Bead Radius (a, mm)	Δa_t (mm)	$\ln(\Delta a_t / \Delta a_0)$
PMA/PS: 1st	0	0.85555	-	-
	2	0.88889	0.03335	-1.7346
	5	0.92222	0.03333	-1.7347
	10	0.93331	0.01109	-2.8351
	15	0.95555	0.02225	-2.1391
	20	0.96665	0.01111	-2.8333
	25	0.97778	0.01111	-2.8333
	30	0.98889	0.01111	-2.8333
	35	1.00000	0.01111	-2.8333
	40	1.01111	0.01111	-2.8333
	45	1.02222	0.01111	-2.8333
	50	1.03335	0.01111	-2.8333
	55	1.04445	0.01111	-2.8333
PMA/PS: 2nd	0	0.85555	-	-
	2	0.87778	0.02225	-2.1399
	5	0.90000	0.02222	-2.1402
	10	0.92222	0.02222	-2.1402
	15	0.94445	0.02225	-2.1399
	20	0.96665	0.02222	-2.1402
	25	0.97778	0.01111	-2.8333
	30	0.98889	0.01111	-2.8333
	35	1.00000	0.01111	-2.8333
	40	1.01111	0.01111	-2.8333
	45	1.02222	0.01111	-2.8333
	50	1.03335	0.01111	-2.8333
	55	1.04445	0.01111	-2.8333

Table B-1 (Continued)

Runs	Time (min)	Bead Radius (a, mm)	Δa_t (mm)	$\ln(\Delta a_t / \Delta a_0)$
PMA/PS: 3rd	0	0.85555	-	-
	2	0.87778	0.02222	-2.1399
	5	0.90000	0.02222	-2.1402
	10	0.92222	0.02222	-2.1402
	15	0.94445	0.02222	-2.1399
	20	0.95555	0.01111	-2.8333
	25	0.97778	0.02222	-2.1399
	30	0.98889	0.01111	-2.8333
	35	1.00000	0.01111	-2.8333
	40	1.01111	0.01111	-2.8333
	45	1.02222	0.01111	-2.8333
	50	1.03335	0.01111	-2.8333
	55	1.04445	0.01111	-2.8333
P(2-EHA)/PS: 1st	0	1.27778	-	-
	2	1.44445	0.16665	-1.4191
	5	1.54445	0.10000	-1.9299
	10	1.64445	0.10000	-1.2929
	15	1.71111	0.06665	-2.3354
	20	1.77766	0.06665	-2.3370
	25	1.82222	0.04455	-2.7383
	30	1.87778	0.05556	-2.5176
	35	1.90000	0.02222	-3.4341
	40	1.92222	0.02222	-3.4341
	45	1.93335	0.01111	-4.1268
	50	1.94445	0.01111	-4.1272
	55	1.95555	0.01111	-4.1272
	60	1.96665	0.01111	-4.1272

Run PMMA/PS: 1st

$y = -0.0523x - 1.3067$

$R^2 = 0.8990$

Run PMA/PS: 1st

$y = -0.0178x - 2.0990$

$R^2 = 0.5014$

Run P(2-EHA)/PS: 1st

$y = -0.0492x - 1.4830$

$R^2 = 0.9418$

Run PMMA/PS: 2nd

Run PMA/PS: 2nd

Run PMMA/PS: 3rd

$y = -0.0374x - 1.5129$

$R^2 = 0.8697$

Run PMA/PS: 3rd

$y = -0.0163x - 2.0948$

$R^2 = 0.6537$
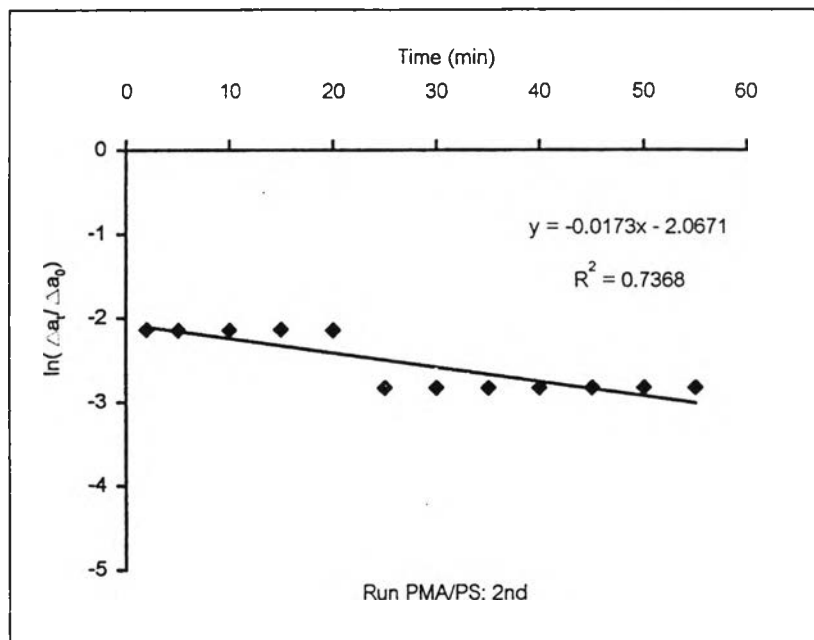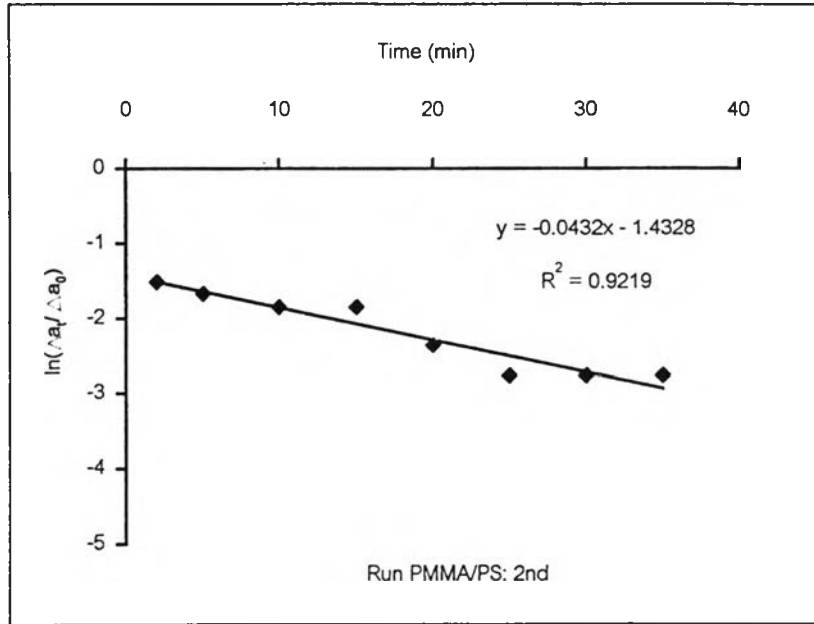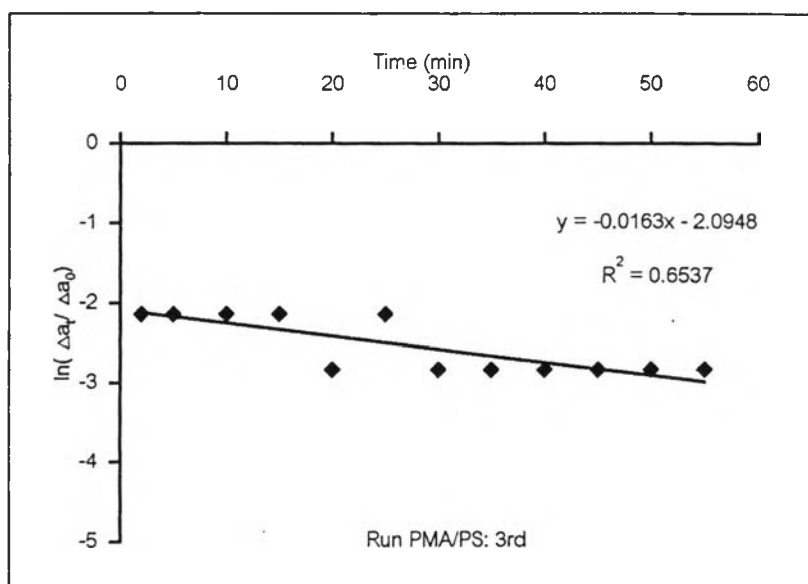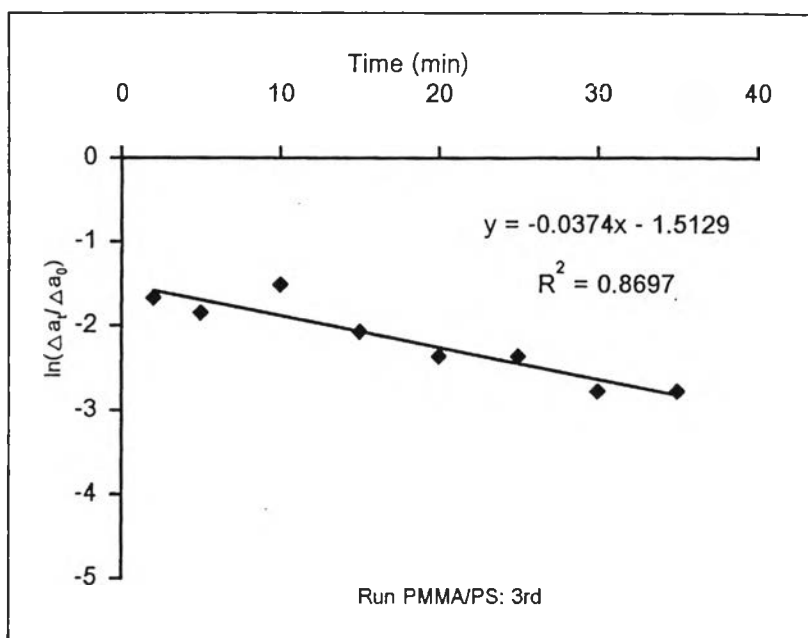
VITA

Mr. Pranut Akkarakittimongkol was born on July 31, 1974, in Phrae, Thailand. He received his Bechelor's degree of Science in Industrial Chemistry from the Faculty of Science, Chiang Mai University in 1996. He pursued the Master's Degree in Polymer Science, in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 1997 and finished his study in 2000.