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APPENDIX A

Experimental results obtained from DSC technique including the heat of homopolymerizations of styrene and MMA with the variation of AIBN concentration show in Tables A.1 and A.2, respectively. Those with the variation of polymerization temperatures are given in Tables A.3 and A.4, respectively. Plots of styrene conversion against time relevant to the data shown in Table A.1 and A.2 show in Figure A.1 and A.2, respectively similar plots to Figure A.1 and A.2, Figure A.3 and A.4 are the plots of results relevant to Table A.2 and A.4, respectively. The slopes of the plots obtained from the linear-regression method are the value of dx/dt .

The heat of polymerization of the copolymerization of styrene and MMA with the variation of comonomer compositions using 1.0%w/w AIBN at 60°C is given in Table A.5 and the plot of comonomer conversion against time shows in Figure A.5.

Table A.1 The heat of polymerization of styrene at 80°C using various AIBN concentrations.

Initiator concentration (%w/w)							
0.5		1.0		1.5		2.0	
Time (min.)	Heat (J/g)	Time (min.)	Heat (J/g)	Time (min.)	Heat (J/g)	Time (min.)	Heat (J/g)
0.0	0	0.0	0	0.0	0.000	0.0	0.000
4.5	31.384	4.5	34.732	5.0	49.906	4.5	47.051
9.1	56.324	9.1	66.554	10.0	90.450	9.1	86.172
13.6	76.677	13.6	94.490	15.0	127.133	13.6	124.334
18.2	98.016	18.2	120.338	20.0	164.154	18.2	160.349
22.7	118.048	22.7	144.865	25.0	198.696	22.7	194.021
27.3	136.944	27.3	167.917	30.0	230.337	27.2	224.915
31.8	153.490	31.8	189.512	35.0	259.247	31.8	255.447
36.4	170.125	36.4	210.195	40.0	287.602	36.3	284.536
40.9	185.870	40.9	230.040	45.0	315.535	40.9	310.848
45.5	200.685	45.5	249.485	50.0	341.232	45.4	335.011
50.0	215.571	50.0	269.517	75.0	461.325	49.9	359.613
75.0	290.233	75.0	360.349	100.0	574.796	75.0	484.226
100.0	350.974	100.0	438.727	125.0	712.244	100.0	651.851
125.0	401.813	125.0	523.100	150.0	722.787	125.0	675.735
150.0	447.134	150.0	643.473			150.0	678.287
175.0	491.153	175.0	660.269				
200.0	541.782						
225.0	609.013						
250.0	646.005						
275.0	655.254						
300.0	657.910						
$\Delta H_I = 658 \text{ J/g}$ $\Delta H_R = 3.29 \text{ J/g}$		$\Delta H_I = 660 \text{ J/g}$ $\Delta H_R = 15.2 \text{ J/g}$		$\Delta H_I = 723 \text{ J/g}$ $\Delta H_R = 15.9 \text{ J/g}$		$\Delta H_I = 678 \text{ J/g}$ $\Delta H_R = 13.8 \text{ J/g}$	

Table A.2 The heat of polymerization of styrene using 1.0%w/w AIBN at various polymerization temperatures.

Polymerization temperature (°C)									
60		70		75		80		85	
Time (min.)	Heat (J/g)	Time (min.)	Heat (J/g)	Time (min.)	Heat (J/g)	Time (min.)	Heat (J/g)	Time (min.)	Heat (J/g)
0.0	0.000	0.0	0.000	0.0	0.000	0.0	0.000	0.0	0.000
9.1	10.596	5.0	20.835	5.0	24.231	4.5	34.732	4.5	51.130
18.2	19.381	10.0	39.444	10.0	44.146	9.1	66.554	9.1	94.698
27.3	28.316	15.0	58.054	15.0	63.248	13.6	94.490	13.6	136.599
36.4	36.760	20.0	75.895	20.0	80.086	18.2	120.338	18.2	172.060
45.5	45.978	25.0	92.018	25.0	98.519	22.7	144.865	22.7	205.812
54.5	55.105	30.0	107.309	30.0	115.845	27.3	167.917	27.3	234.876
63.6	63.944	35.0	121.429	35.0	132.337	31.8	189.512	31.8	263.396
72.7	72.704	40.0	136.334	40.0	148.602	36.4	210.195	36.4	290.082
81.8	80.755	45.0	150.316	45.0	163.766	40.9	230.040	40.9	314.792
90.9	88.745	50.0	166.465	50.0	179.493	45.5	249.485	45.5	337.926
100.0	95.219	100.0	297.021	75.0	250.089	50.0	269.517	50.0	358.866
150.0	132.633	150.0	407.152	100.0	308.733	75.0	360.349	75.0	462.503
200.0	165.195	200.0	508.579	125.0	365.953	100.0	438.727	100.0	553.679
250.0	196.354	250.0	671.575	150.0	427.210	125.0	523.100	125.0	661.111
300.0	226.538	300.0	721.595	175.0	503.283	150.0	643.473	150.0	673.927
350.0	256.679	350.0	728.468	200.0	618.500	175.0	660.269		
400.0	290.864	360.0	729.104	225.0	633.469				
450.0	333.085			240.0	635.656				
500.0	409.805								
550.0	501.703								
600.0	506.852								
$\Delta H_1 = 507 \text{ J/g}$ $\Delta H_R = 44.9 \text{ J/g}$		$\Delta H_1 = 729 \text{ J/g}$ $\Delta H_R = 25.1 \text{ J/g}$		$\Delta H_1 = 636 \text{ J/g}$ $\Delta H_R = 23.4 \text{ J/g}$		$\Delta H_1 = 660 \text{ J/g}$ $\Delta H_R = 15.2 \text{ J/g}$		$\Delta H_1 = 674 \text{ J/g}$ $\Delta H_R = 9.18 \text{ J/g}$	

Table A.3 The heat of polymerization of MMA at 80°C using various AIBN concentrations.

Initiation concentration (%w/w)							
0.5		1.0		1.5		2.0	
Time (min.)	Heat (J/g)	Time (min.)	Heat (J/g)	Time (min.)	Heat (J/g)	Time (min.)	Heat (J/g)
0.0	0.000	0.0	0.000	0.0	0.000	0.0	0.000
0.9	7.713	0.9	11.099	0.9	21.123	0.9	22.309
1.8	19.298	1.8	27.576	1.8	41.073	1.8	44.674
2.7	30.856	2.7	42.248	2.7	59.855	2.7	66.538
3.6	41.860	3.6	56.732	3.6	78.910	3.6	87.893
4.6	52.224	4.6	70.948	4.6	97.342	4.6	110.096
5.4	62.242	5.4	85.796	5.4	116.198	5.4	130.215
6.4	73.122	6.4	100.396	6.4	133.881	6.4	150.160
7.3	83.471	7.3	113.112	7.3	151.936	7.3	169.326
8.2	93.687	8.2	126.686	8.2	168.480	8.2	189.446
9.1	104.211	9.1	139.736	9.1	186.816	9.1	210.887
10.0	113.799	10.0	152.076	10.0	204.496	10.0	234.439
12.5	128.253	12.5	188.337	12.5	261.377	12.5	320.222
15.0	155.190	15.0	229.346	15.0	417.677	15.0	525.316
17.5	182.239	17.5	298.868	17.5	527.577	17.5	534.414
20.0	214.855	20.0	495.430	20.0	533.034	20.0	538.725
22.5	273.804	22.5	509.866	22.5	538.562		
25.0	450.148	25.0	514.012	25.0	542.628		
27.5	496.663						
30.0	499.523						
$\Delta H_I = 500 \text{ J/g}$ $\Delta H_R = 35.2 \text{ J/g}$		$\Delta H_I = 514 \text{ J/g}$ $\Delta H_R = 28.4 \text{ J/g}$		$\Delta H_I = 543 \text{ J/g}$ $\Delta H_R = 28.9 \text{ J/g}$		$\Delta H_I = 539 \text{ J/g}$ $\Delta H_R = 29.3 \text{ J/g}$	

Table A.4 The heat of polymerization of MMA using 1.0%w/w AIBN at various polymerization temperatures.

Polymerization temperature (°C)									
60		70		75		80		85	
Time (min)	Heat (J/g)	Time (min.)	Heat (J/g)	Time (min)	Heat (J/g)	Time (min)	Heat (J/g)	Time (min)	Heat (J/g)
0	0.000	0.0	0.000	0.0	0.000	0.0	0.000	0	0.000
2.5	3.862	0.9	2.301	1.0	8.851	0.9	11.099	0.5	12.271
5.0	10.403	1.8	6.351	2.0	20.996	1.8	27.576	1.0	25.555
7.5	19.928	2.7	12.898	3.0	32.947	2.7	42.248	1.5	37.134
10.0	30.483	3.6	20.682	4.0	44.974	3.6	56.732	2.0	49.859
12.5	40.801	4.5	27.221	5.0	56.728	4.5	70.948	2.5	61.633
15.0	50.558	5.5	34.154	6.0	68.489	5.5	85.796	3.0	73.540
17.5	59.699	6.4	40.989	7.0	80.063	6.4	100.396	3.5	85.575
20.0	73.241	7.3	47.707	8.0	91.160	7.3	113.112	4.0	96.485
25.0	90.669	8.2	54.401	9.0	102.192	8.2	126.686	6.0	142.395
30.0	107.909	9.1	60.569	10.0	112.917	9.1	139.736	8.0	184.754
35.0	124.488	10.0	66.004	15.0	167.286	10.0	152.076	10.0	232.452
40.0	140.007	15.0	99.253	20.0	223.702	12.5	188.337	12.0	322.755
45.0	156.989	20.0	132.999	25.0	331.170	15.0	229.346	14.0	492.091
50.0	175.442	25.0	167.498	30.0	533.402	17.5	298.868	16.0	499.617
55.0	196.796	30.0	215.577	35.0	542.919	20.0	495.430	18.0	503.072
60.0	223.977	35.0	371.808	40.0	547.021	22.5	509.866		
65.0	275.298	40.0	486.709			25.0	514.012		
70.0	385.264	45.0	493.880						
75.0	478.037	50.0	496.608						
80.0	498.135								
85.0	501.172								
90.0	502.257								
$\Delta H_1 = 502 \text{ J/g}$		$\Delta H_1 = 497 \text{ J/g}$		$\Delta H_1 = 547 \text{ J/g}$		$\Delta H_1 = 514 \text{ J/g}$		$\Delta H_1 = 503 \text{ J/g}$	
$\Delta H_R = 63.7 \text{ J/g}$		$\Delta H_R = 41.0 \text{ J/g}$		$\Delta H_R = 36.2 \text{ J/g}$		$\Delta H_R = 28.4 \text{ J/g}$		$\Delta H_R = 23.2 \text{ J/g}$	

Table A.5 The heat of copolymerization of styrene and MMA using 1.0%w/w AIBN at 60°C with various comonomer compositions.

Comonomer composition (mole fraction of styrene)					
0.2		0.4		0.6	
Time (min)	Heat (J/g)	Time (min)	Heat (J/g)	Time (min)	Heat (J/g)
0.0	0.000	0.0	0.000	0.0	0.000
5.0	3.225	5.0	2.238	5.0	2.332
10.0	7.624	10.0	4.446	10.0	4.059
15.0	10.713	15.0	6.282	15.0	5.392
20.0	12.917	20.0	7.959	20.0	6.434
25.0	15.067	25.0	9.498	25.0	7.440
50.0	24.767	50.0	14.876	50.0	10.706
75.0	33.702	75.0	18.506	75.0	12.012
100.0	44.614	100.0	21.058	100.0	12.685
125.0	63.289	125.0	22.979	125.0	12.856
150.0	89.529	150.0	24.724	150.0	12.754
175.0	123.836	175.0	26.842	175.0	14.078
200.0	190.484	200.0	29.470	200.0	16.049
225.0	394.222	225.0	34.435	225.0	18.728
250.0	398.353	250.0	43.770	250.0	22.357
		275.0	60.820	275.0	27.358
		300.0	91.618	300.0	33.558
		325.0	158.328	325.0	41.934
		350.0	283.223	350.0	52.508
		375.0	289.552	375.0	66.902
		400.0	288.494	400.0	88.416
				425.0	119.562
				450.0	175.030
				475.0	253.583
				500.0	270.446
				525.0	271.049
				550.0	270.974
$\Delta H_I = 398 \text{ J/g}$ $\Delta H_R = 42.2 \text{ J/g}$		$\Delta H_I = 288 \text{ J/g}$ $\Delta H_R = 39.7 \text{ J/g}$		$\Delta H_I = 271 \text{ J/g}$ $\Delta H_R = 43.7 \text{ J/g}$	

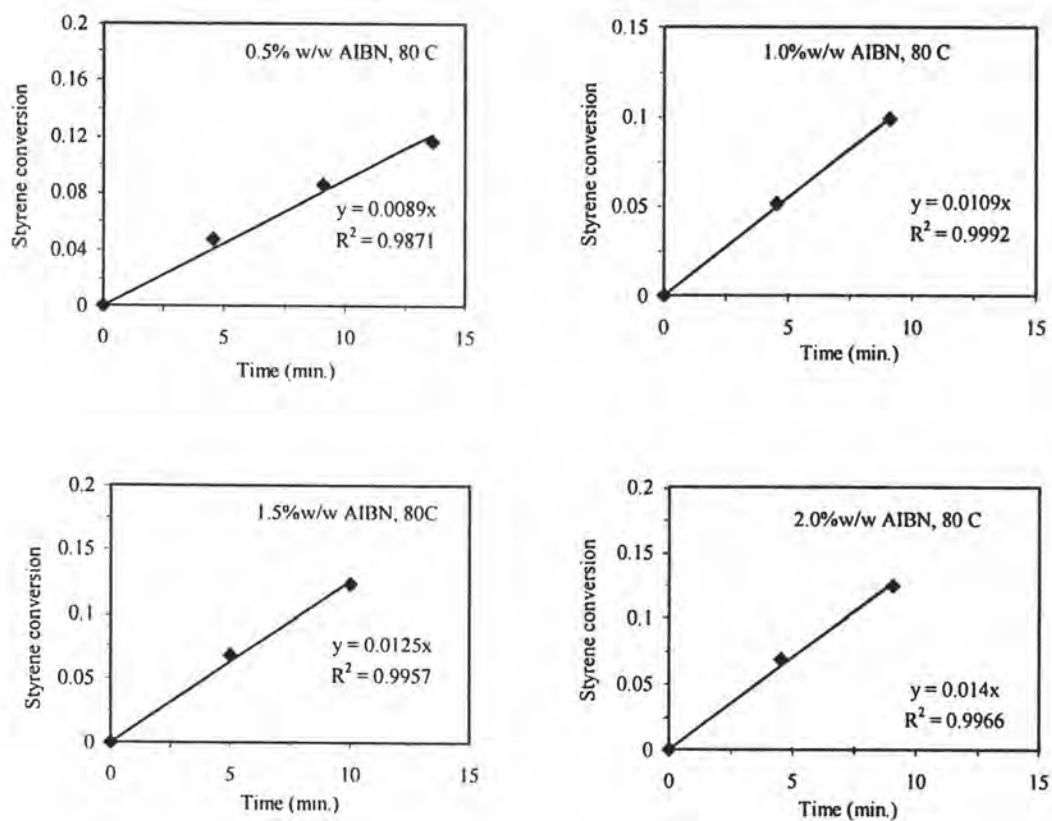


Figure A.1 Plots of styrene conversion against time of the polymerization of styrene using various amounts of AIBN at 80°C. The styrene conversion used was around 10%.

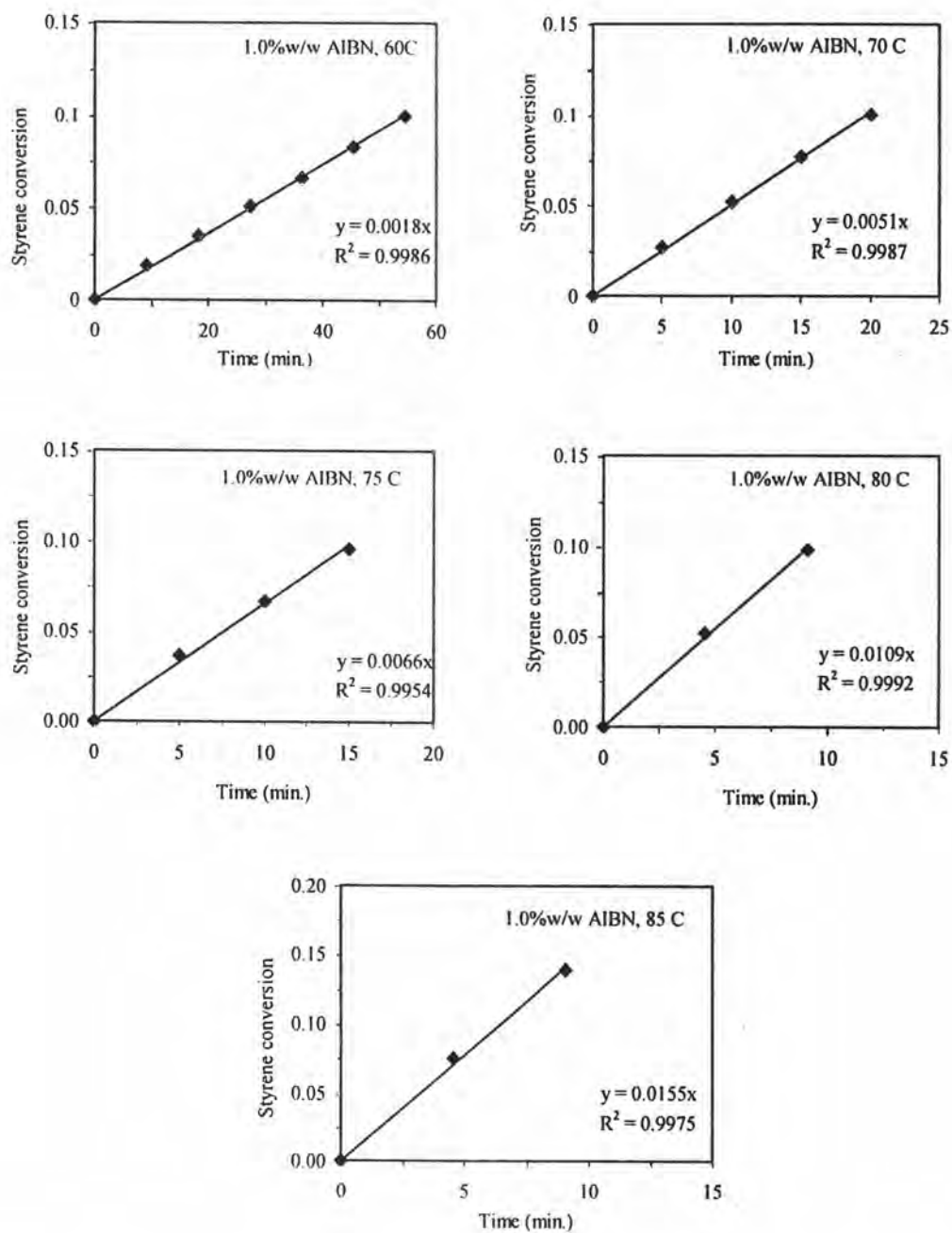


Figure A.2 Plots of styrene conversion against time of the polymerization of styrene using 1.0%w/w styrene at various polymerization temperatures. The styrene conversion used was around 10%.

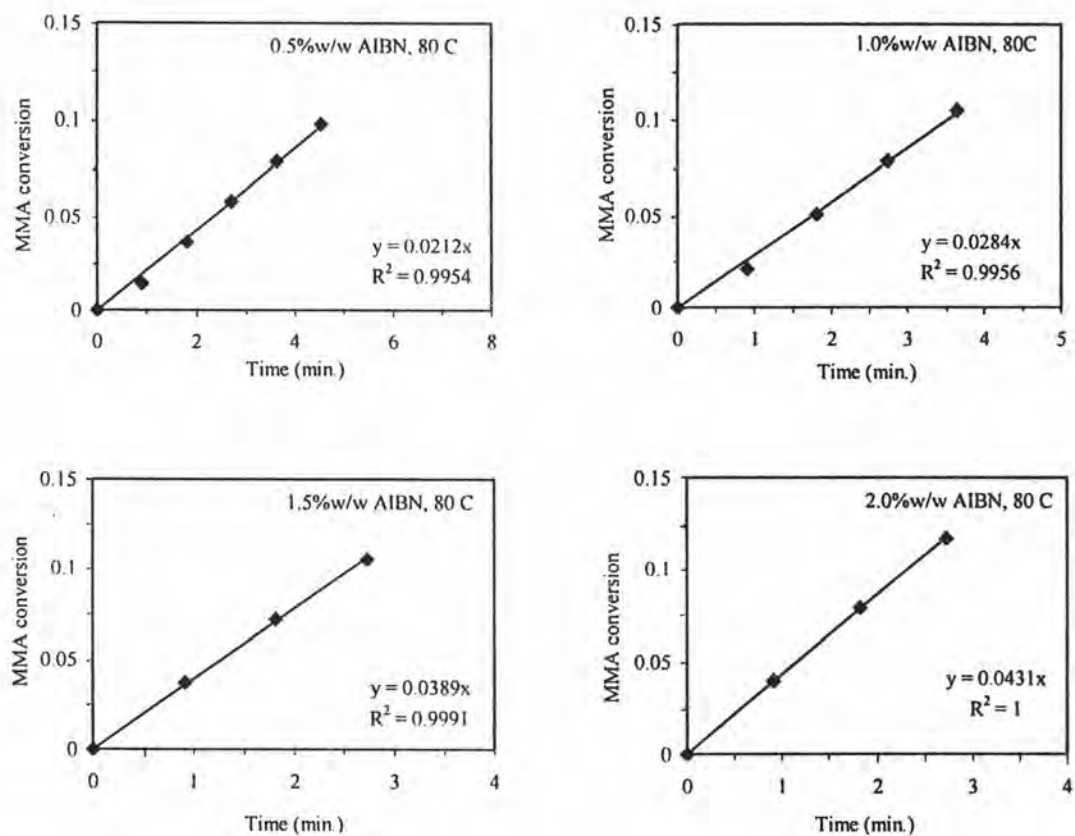


Figure A.3 Plots of MMA conversion against time of the polymerization of MMA using various amounts AIBN at 80°C. The MMA conversion used was around 10%.

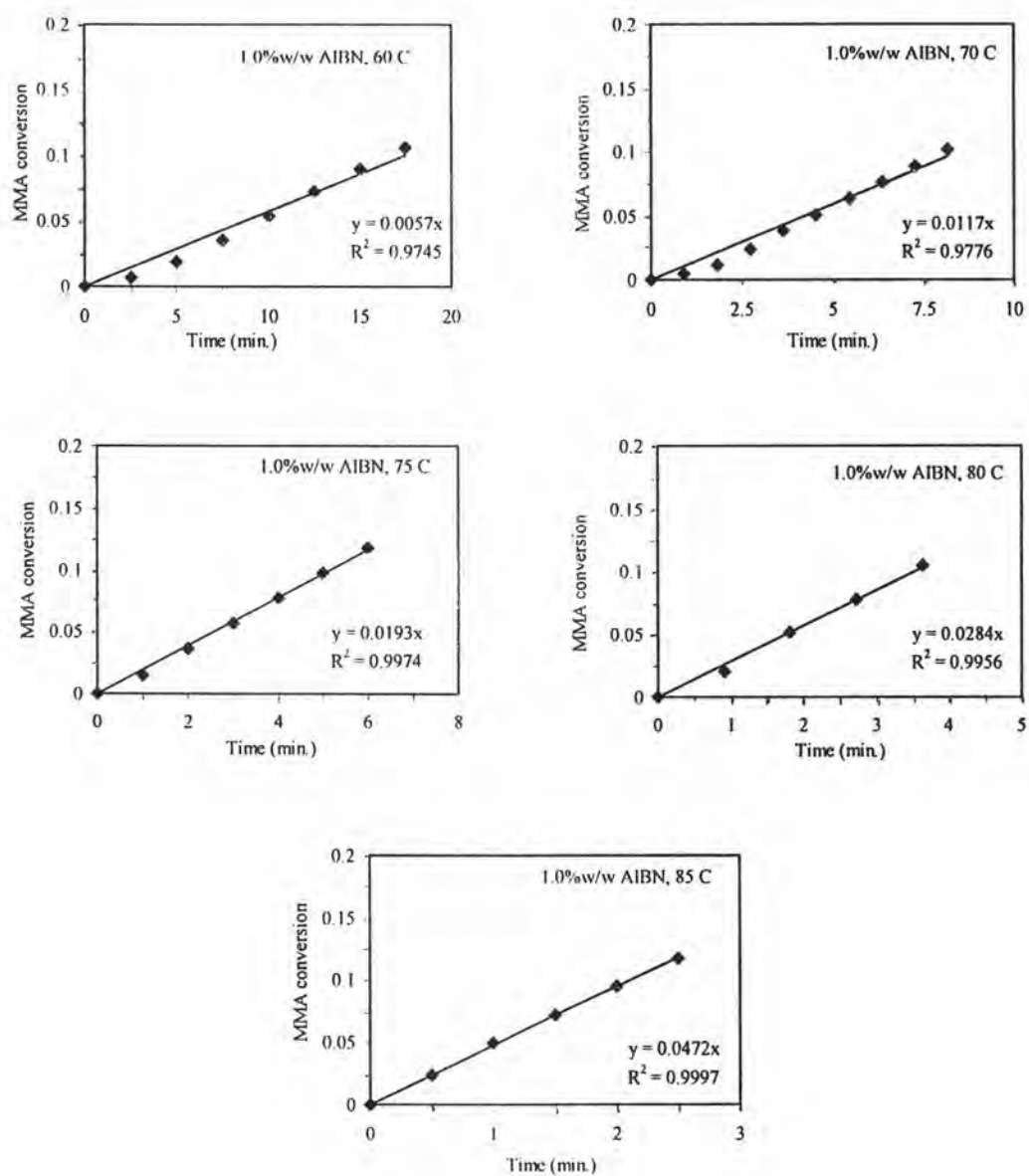


Figure A.4 Plots of MMA conversion against time of the polymerization of MMA using 1.0%w/w AIBN at various polymerization temperatures. The MMA conversion used was around 10%.

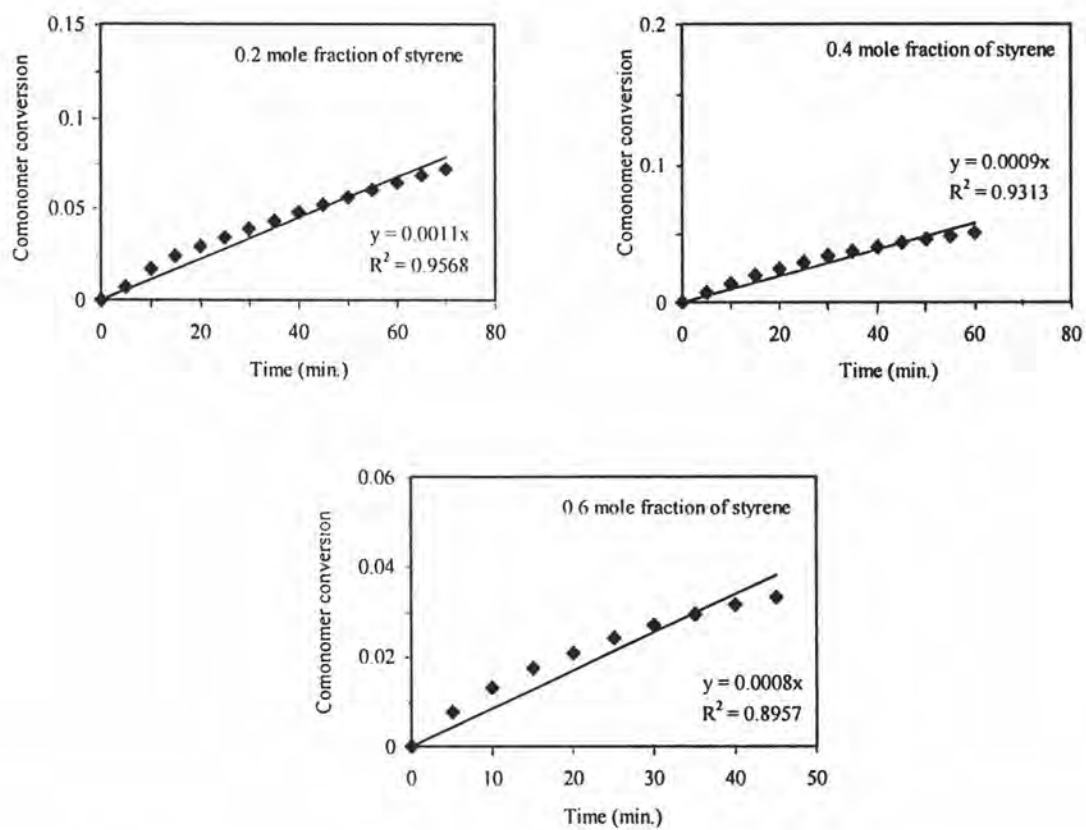


Figure A.5 Plots of comonomer conversion against time of the copolymerization of styrene and MMA using 1.0%w/w AIBN at 60°C. The comonomer conversion used was around 10%.

APPENDIX B

The reactivity ratio of styrene and MMA (r_1 and r_2) shown in Table 4.10 was assumed to pursue diffusion-controlled termination. Thus, Eq. (2.41) was used for the determination.

$$k_p = \frac{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}{\frac{r_1 f_1}{k_{11}} + \frac{r_2 f_2}{k_{22}}} \quad (2.41)$$

Since each pair of the reactivity ratio obtained were calculated from two sets of Eq. (2.41), two values of k_p obtained from the copolymerization with the particular comonomer compositions were selected. For instance, one pair of reactivity ratio values was calculated using the following values.

$$\begin{aligned} k_{11} &= 218 \text{ L}\cdot\text{mol}^{-1}\text{s}^{-1}, & k_{22} &= 680 \text{ L}\cdot\text{mol}^{-1}\text{s}^{-1}, \\ k_p &= 689 \text{ L}\cdot\text{mol}^{-1}\text{s}^{-1}, & f_1 &= 0.188, & f_2 &= 0.812 & \text{(a)} \\ k_p &= 625 \text{ L}\cdot\text{mol}^{-1}\text{s}^{-1}, & f_1 &= 0.382, & f_2 &= 0.618 & \text{(b)} \end{aligned}$$

Substitution of the values in (a) and (b) into (2.41) yield Eq.(c) and (d), respectively.

$$0.5587r_1 + 0.1637r_2 = 0.3053 \quad \text{(c)}$$

$$0.9491r_1 + 0.1861r_2 = 0.4722 \quad \text{(d)}$$

Solving Eq.(c) and (d) by mathematical method gave $r_1 = 0.40$ and $r_2 = 0.50$.

VITA

Naporn Santisampan was born on January 31, 1972 in Bangkok, Thailand. She received a Bachelor degree of Science in Chemistry, Chiang Mai University in March, 1993. She has joined the Thai Petrochemical Industry Public Co.,Ltd. as a scientist in Research & Development Department since November, 1993. She pursued a postgraduate studies in polymer science, the part time program of Petrochemitry and Polymer Science, Graduate School, Chulalongkorn University in 1996 and finished in April 1998.