

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Kinetics of Thermal-initiated Free Radical Bulk Homopolymerizations of Styrene and Methyl methacrylate

##### 4.1.1 Effect of the initiator concentration on the initial rate of polymerization

Herein Section 4.1 the term “polymerization” refers to the isothermally free radical bulk homopolymerization at specific temperature typically at 80°C unless otherwise stated. Typically 1.0%w/w AIBN was employed as the thermal labile initiator. Typical DSC thermograms of the polymerizations of styrene and MMA are shown in Figures 4.1 and 4.2, respectively. There are three distinct stages include a-b : the induction period and onset of the polymerization, b-c : gel effect shown the rapid increase of heat evolved which represents the progress of polymerization, and c-d : the glass or vitrification effect dependent upon the reaction temperature. The induction period was caused by oxygen inhibition of the polymerization, and this was also observed by Armitage, P.D., et al [10]. Even though the polymerization carried out under nitrogen atmosphere, trace amount of oxygen might exist in the reaction medium due to its existence in the monomer used.

The DSC thermograms of the polymerizations of styrene and MMA using various initiator concentrations are shown in Figures 4.3 and 4.4, respectively. The higher initiator concentration employed in the polymerization exhibited the markedly sharp exotherm and the short polymerization period to complete. This implied that the rate of polymerization depended upon the concentration of initiator used.

The residual styrene and MMA were measured calorimetrically followed the method described in Section 3.2.3, Chapter 3 and the typical DSC thermograms obtained are shown in Figures 4.5 and 4.6 respectively. The exotherm peak following

the glass transition of polystyrene was observed in Figure 4.5, but it was not found in the case of polymerization of MMA. Styrene and MMA conversion at the particular time were determined by using Eq. (2.46) and their plots with various AIBN concentrations show respectively in Figures 4.7 and 4.8. The values of heat of the isothermal polymerization ( $\Delta H_I$ ), heat of the polymerization of the residual monomer ( $\Delta H_R$ ), total heat of the polymerization ( $\Delta H_P$ ) and total styrene and MMA conversion at 80°C are given in Table 4.1. The gel effect was observed clearly in the polymerization of MMA while it seemed not to occur in that of styrene within the reaction time of 5 Hrs. The higher the initiator concentration used in the polymerization resulted in the faster the gel effect, which caused by the higher increasing viscosity of polymerizing mixture relative to the decrease of the rate of diffusion control termination. The polymerization rate decreased due to the formation of a glassy polymerizing medium so that the residual monomer hardly propagated.

Values of the heat of polymerization were calculated from the total area under the polymerization exotherm. These values were in good agreement with the work of Ebdon, J.R. and Hunt, B.J. [13] who reported the values of 50.4-58.8 kJ/mol for the styrene polymerization. Malavasic, T. et al. [9] and Armitage, P.D. et al. [10] reported respectively the values of 52.9-54.6 and 52.0-55.6 kJ/mol for the polymerization of MMA. Differences of the reported values from those found in this study might be due to the calibration of the instrument. The DSC furnace was calibrated by melting indium standard material, i.e., its heat of fusion has been known. This process required a short period compared to the time used for the polymerization reactions especially in the case of the styrene polymerization. Accordingly, the heat measured from the polymerization of styrene differed greatly from the literature values than those of MMA polymerization which required the shorter polymerization period.

Values of the total styrene and MMA conversions are presented in Table 4.1. It is noted that the conversions were less than 100% due to the vitrification effect.

In addition, the styrene and MMA conversions after completion of the DSC experiments were also measured using GC technique for comparison of the reliability of the results determined from DSC. The results are given in Table 4.2.

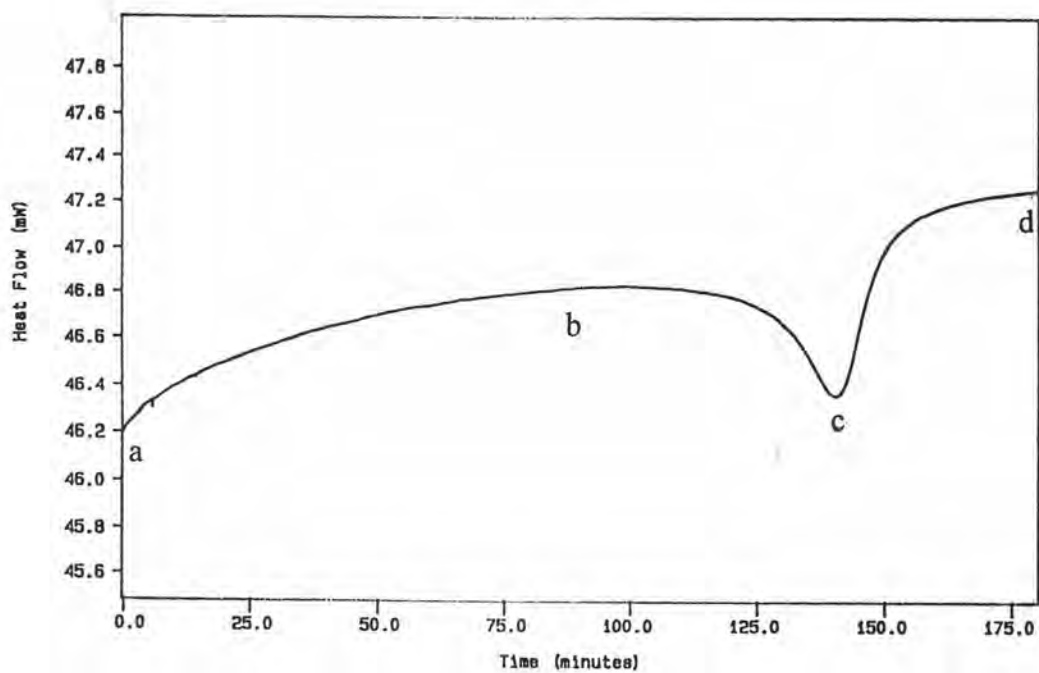
Values of the styrene and MMA conversions are apparently similar to those obtained from DSC technique. This implies that DSC technique should be reliable to employ for the study of the kinetics of the polymerization.

**Table 4.1**  $\Delta H_I$ ,  $\Delta H_R$ ,  $\Delta H_P$  and total styrene or MMA conversions of isothermal free radical bulk homopolymerization of styrene and MMA at 80°C using various AIBN concentrations.

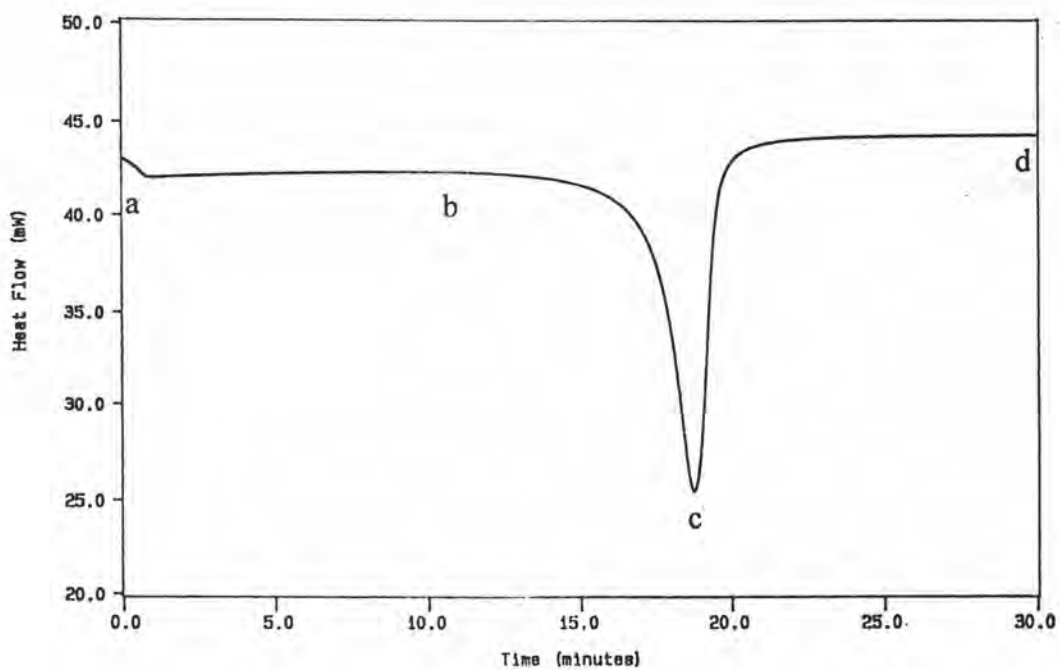
Monomer	AIBN (%w/w)	$\Delta H_I$ (J/g)	$\Delta H_R$ (J/g)	$\Delta H_P$ (kJ/mol)	Total monomer conversion (%)
Styrene	0.5	658	3.29	68.8	99.5
	1.0	660	15.2	70.2	97.7
	1.5	723	15.9	76.8	97.8
	2.0	678	13.8	72.0	98.0
MMA	0.5	500	35.2	53.5	93.4
	1.0	514	28.4	54.2	94.8
	1.5	543	28.9	57.2	94.9
	2.0	539	29.3	56.8	94.8

**Table 4.2** Residual monomer and the total monomer conversion of the polymerizations of styrene and MMA using various AIBN concentrations at 80°C. Comparison of the values as obtained by the techniques of DSC and GC.

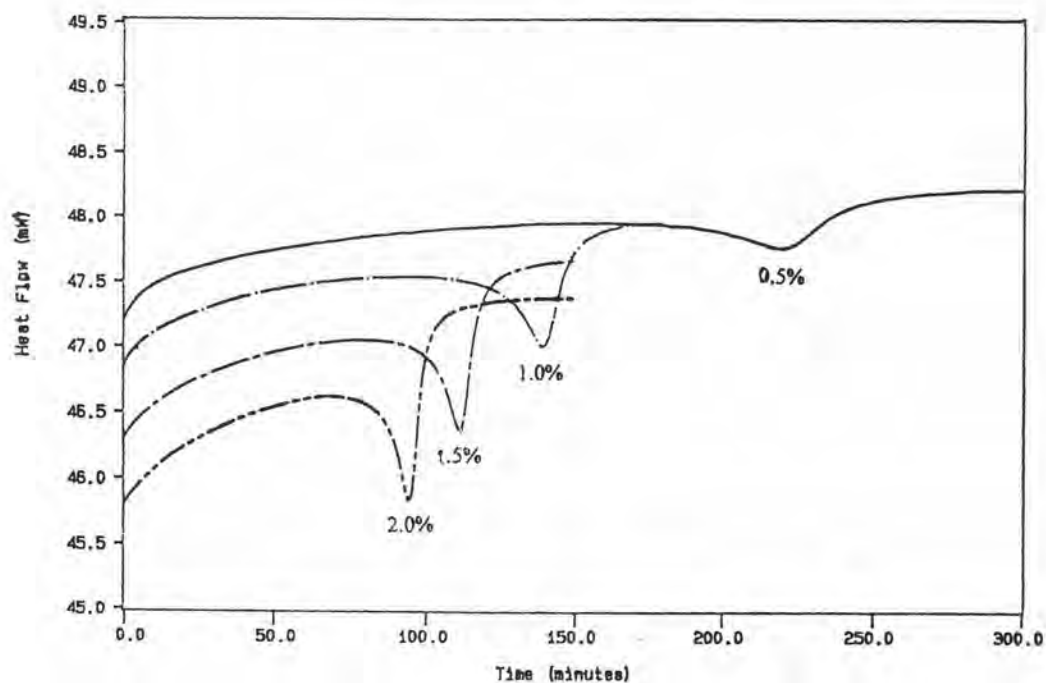
Monomer	AIBN (%w/w)	GC technique		DSC technique
		Residual monomer content (%)	Total monomer conversion (%)	Total monomer conversion (%)
Styrene	0.5	3.94	96.1	99.5
	1.0	3.58	96.4	97.7
	1.5	2.15	97.8	97.8
	2.0	2.27	97.7	98.0
MMA	0.5	5.27	94.7	93.4
	1.0	3.76	96.2	94.8
	1.5	2.93	97.1	94.9
	2.0	2.34	97.7	94.8



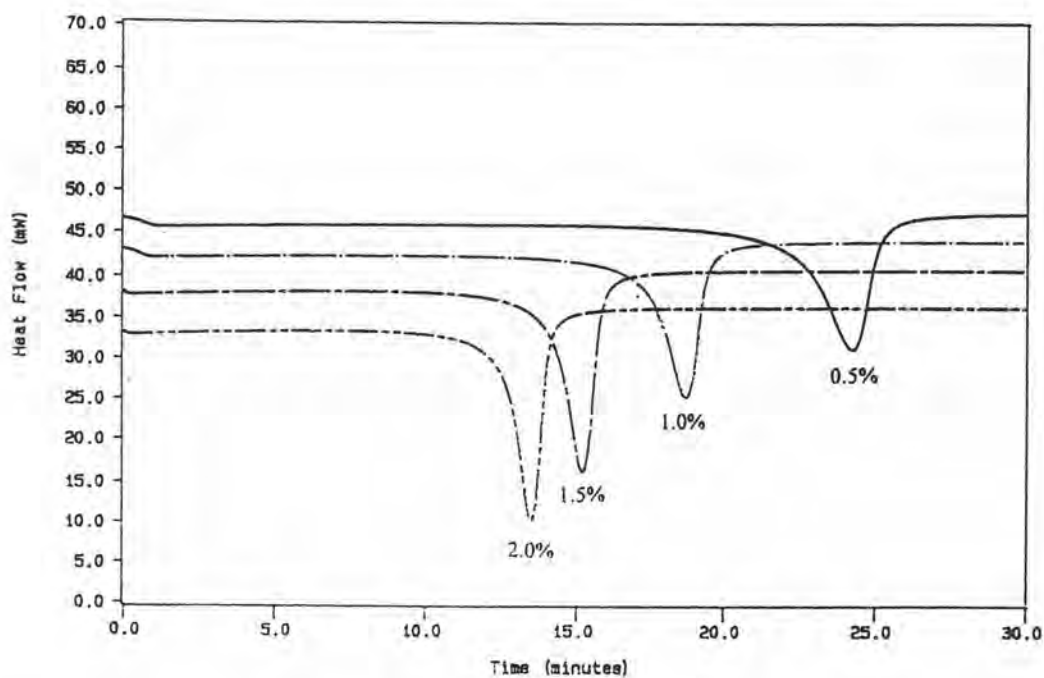
**Figure 4.1** A typical DSC thermogram of the thermal-initiated free radical bulk homopolymerization of styrene at 80°C using 1.0%w/w AIBN.



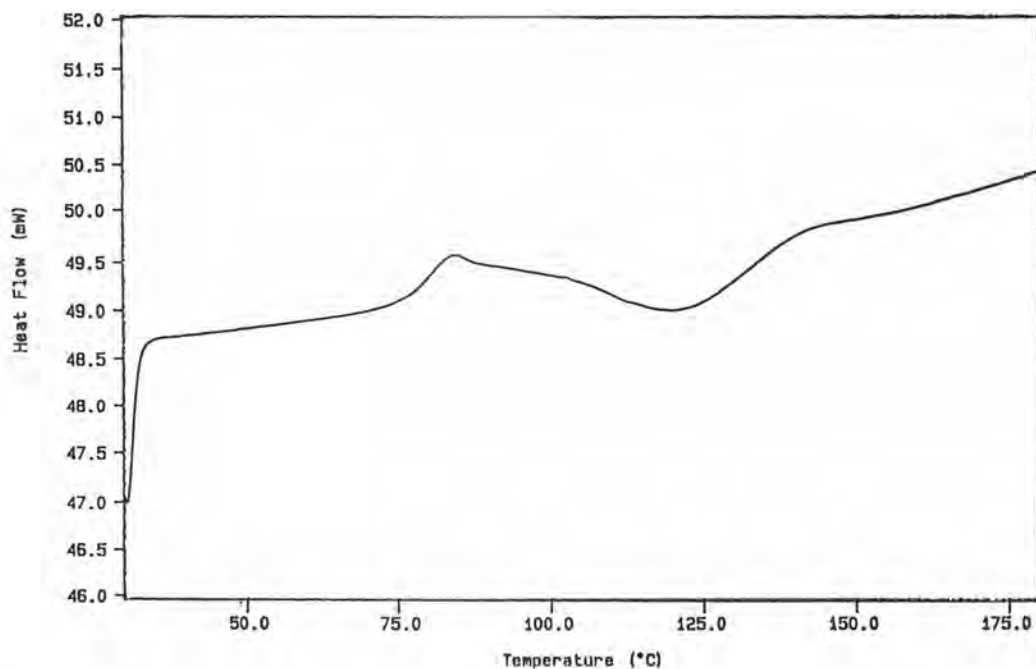
**Figure 4.2** A typical DSC thermogram of the thermal-initiated free radical bulk homopolymerization of MMA at 80°C using 1.0%w/w AIBN.



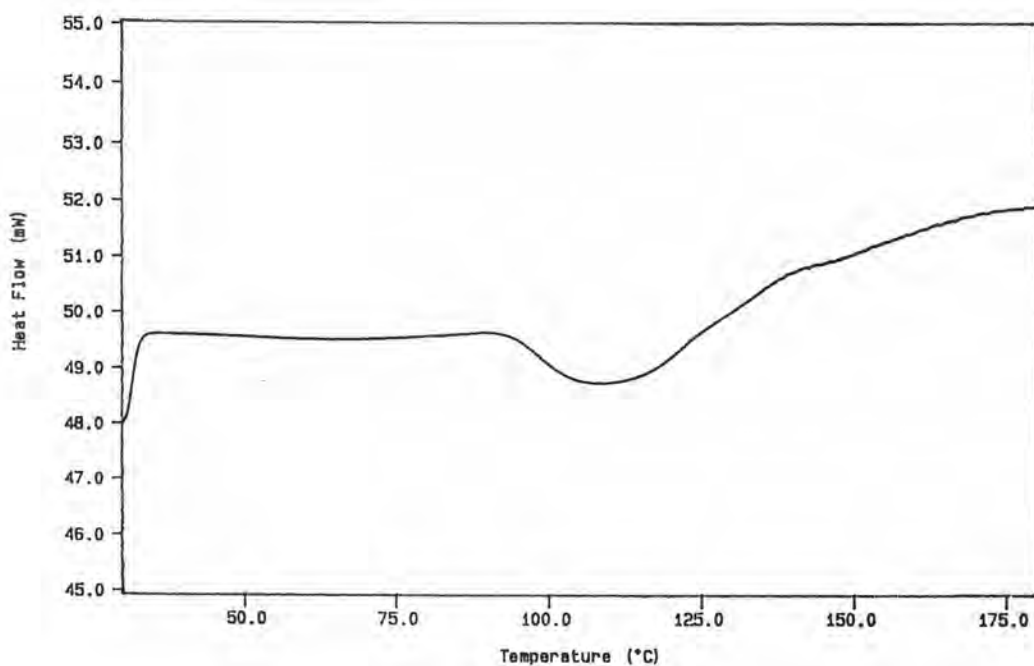
**Figure 4.3** Overlaid DSC thermograms of the thermal-initiated free radical bulk homopolymerization of styrene at 80°C using various AIBN concentrations.



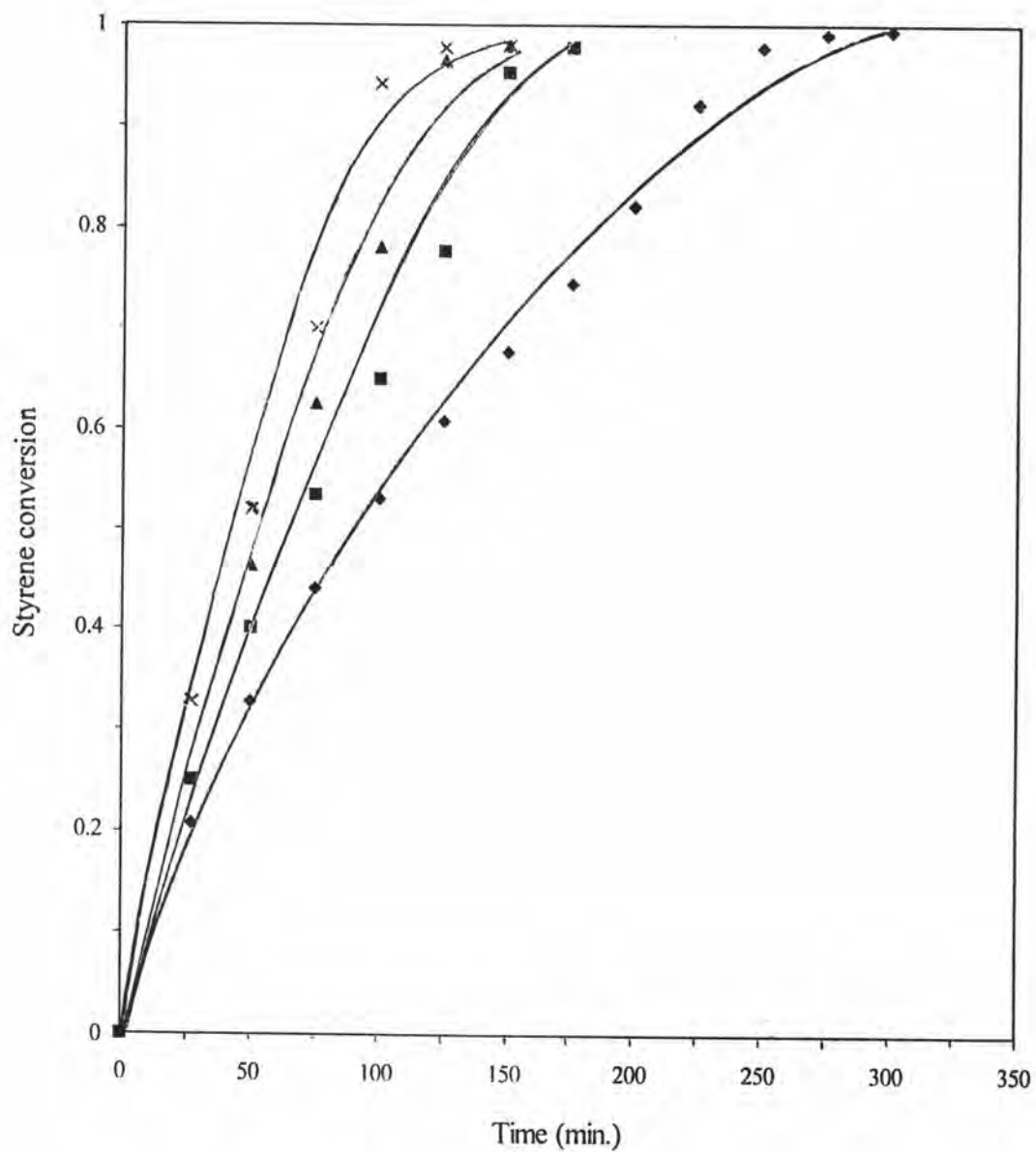
**Figure 4.4** Overlaid DSC thermograms of the thermal-initiated free radical bulk homopolymerization of MMA at 80°C using various AIBN concentrations.



**Figure 4.5** A typical DSC thermogram of the residual styrene after the isothermal free radical bulk homopolymerization at 80°C using 1.0%w/w AIBN.

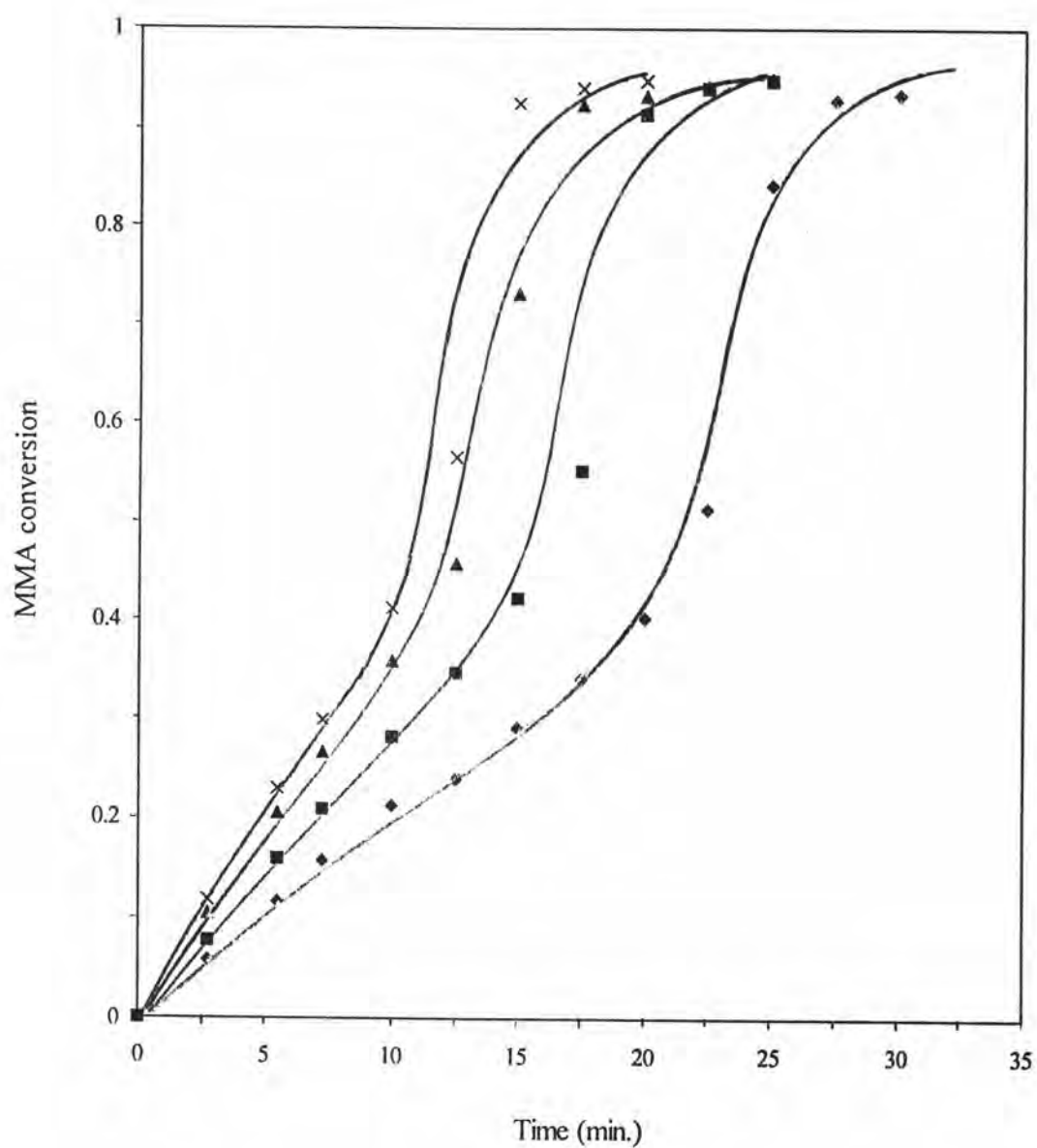


**Figure 4.6** A typical DSC thermogram of the residual MMA after the isothermal free radical bulk homopolymerization at 80°C using 1.0%w/w AIBN.



**Figure 4.7** Plot of conversion versus time for styrene polymerization at 80 °C using various AIBN concentrations : ♦, 0.5%; ■, 1.0%; ▲, 1.5%; ×, 2.0%w/w.





**Figure 4.8** Plot of conversion versus time for MMA polymerization at 80°C using various AIBN concentrations : ◆, 0.5%; ■, 1.0%; ▲, 1.5%; ✕, 2.0%w/w.

#### 4.1.2 Determination of the reaction order with respect to initiator concentration

The overall initial rates of the polymerizations of styrene and MMA and the overall initial rate constants are given in Table 4.3. The former values are calculated from Eq.(2.48) and the latter evaluated from the slope (dx/dt) of the plot of the particular monomer conversion against time. The value of slope under 10% of the particular monomer conversion was evaluated using the linear-regression method (see Appendix A). Then it was further calculated following Eq. (4.1) to obtain the overall initial rate constant.

$$k_{ov} = \frac{(dx/dt)}{[I]_0^{1/2}} \quad (4.1)$$

where  $k_{ov}$  is the overall initial rate constant.

The initial rate of polymerization  $R_{p,0}$  obtained increased with the increase of AIBN concentration. However, the dependence of the initiator concentration on the rate of polymerization was evaluated based on Eq. (4.2).

$$R_p = k_p(fk_d/k_t)^{1/2}[M][I]^{1/2} \quad (4.2)$$

In theory, the rate of polymerization  $R_p$  depends on the square root of initiator concentration or the order of polymerization with respect to the initiator concentration is 0.5. The order of the polymerizations of styrene and MMA could be evaluated experimentally from the slopes of the plot of  $\ln(R_{p,0})$  against  $\ln([AIBN])$ . Figures 4.9 and 4.10 show such the plot in the case of styrene and MMA polymerizations, respectively .

The reaction orders of the polymerizations of styrene and MMA with respect to the initiator concentration were 0.33 and 0.53, respectively, compared to the theoretical value of 0.5. This discrepancy of those values from the theory might be due to the decrease of the initiator efficiency  $f$  that occurred especially when it had high concentration rendering the primary AIBN radicals (2-cyano-2-propyl radicals)

obtained from the dissociation of initiator undergone the primary termination by two possible pathways including (a) the termination between the propagating radicals with the primary radicals and (b) the reaction between the radicals with each other. In addition, AIBN radicals might react with each other to give tetramethylsuccinodinitrile and dimethyl-N-(2-cyano-2-isopropyl)ketenimine [1].

**Table 4.3** The overall initial rate constants ( $k_{ov}$ ) and the initial rates of the polymerizations of styrene and MMA ( $R_{p,0}$ ) using various amounts of AIBN at 80 °C.

Monomer	AIBN (%w/w)	$k_{ov} \times 10^4$ ( $L^{1/2}mol^{-1/2}s^{-1}$ )	$R_{p,0} \times 10^3$ ( $mol-L^{-1}s^{-1}$ )
Styrene	0.5	8.81	1.29
	1.0	7.76	1.58
	1.5	7.21	1.81
	2.0	7.06	2.03
MMA	0.5	20.8	3.32
	1.0	19.6	4.45
	1.5	22.1	6.09
	2.0	21.2	6.75

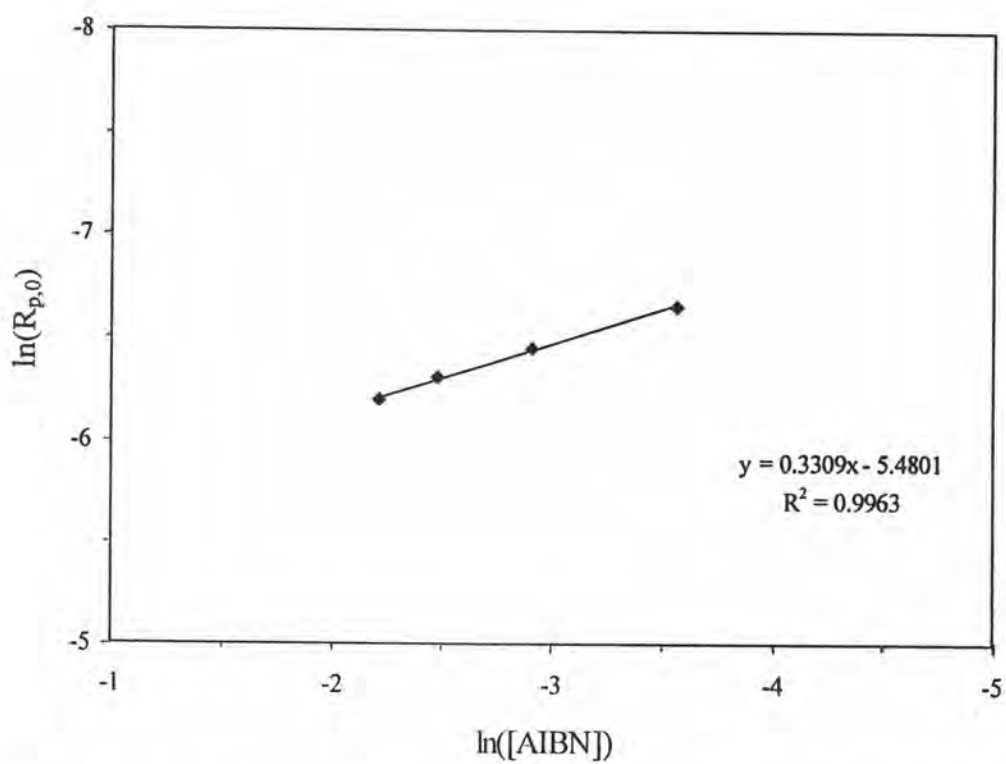


Figure 4.9 The plot of  $\ln(R_{p,0})$  against  $\ln([AIBN])$  of styrene polymerization at 80°C.

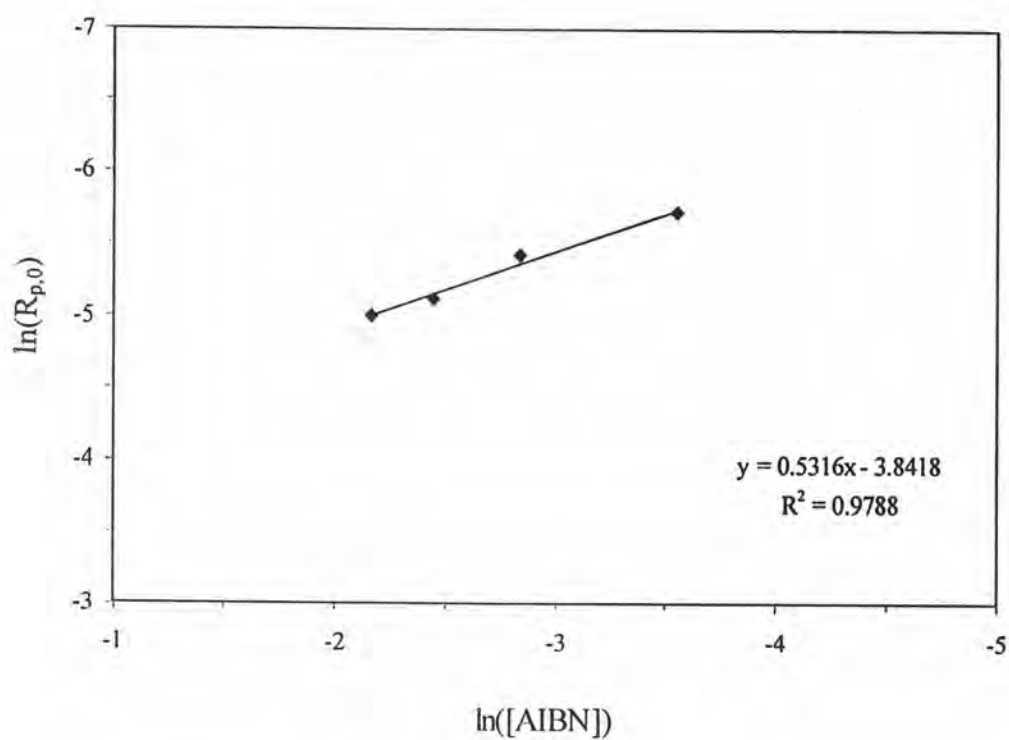


Figure 4.10 The plot of  $\ln(R_{p,0})$  against  $\ln([AIBN])$  of MMA polymerization at 80°C.

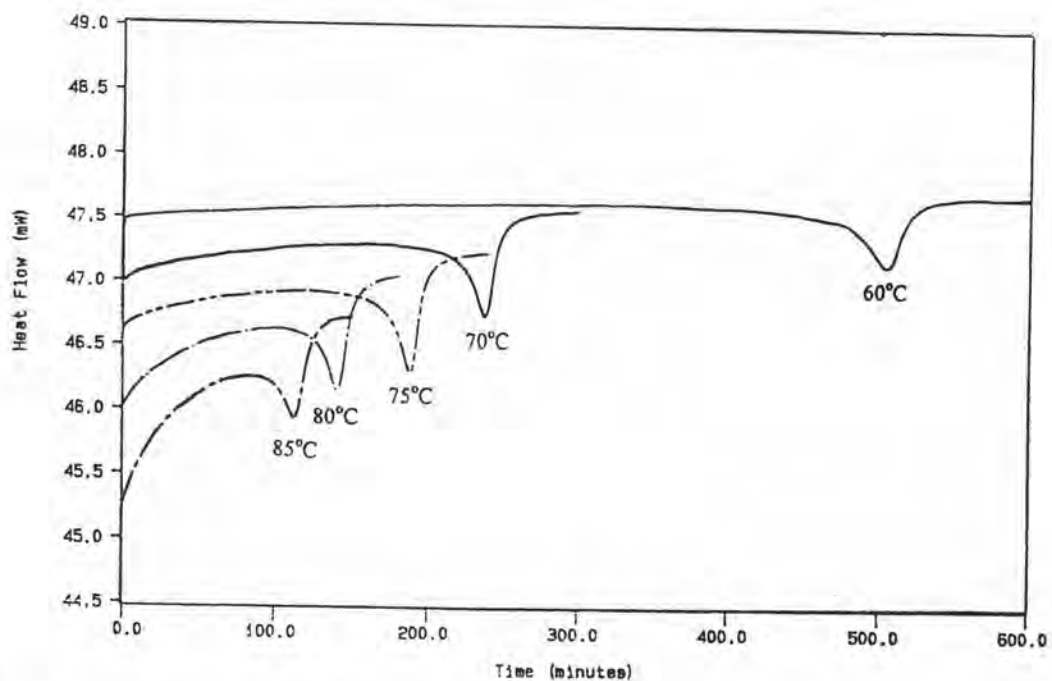
### 4.1.3 Effect of polymerization temperature on the initial rate of polymerization

Overlaid DSC thermograms of the polymerizations of styrene and MMA at the various temperatures (60, 70, 75, 80 and 85°C) are shown in Figures 4.11 and 4.12. The decrement of the polymerization time was achieved when the higher polymerization temperature was used. The monomer conversions at the particular time and at the specified reaction temperature were also calculated using Eq. (2.46). Values of  $\Delta H_i$ ,  $\Delta H_R$ ,  $\Delta H_p$ , and total styrene and MMA conversions are given in Table 4.4. The plot of the styrene and MMA conversion against time at various polymerization temperatures exhibits in Figures 4.13 and 4.14, respectively. For the styrene polymerization, the gel effect was also observed only when the polymerization was carried out at 60°C. In contrast, the gel effect was observed in all polymerizations of MMA and dominantly at the higher polymerization temperature.

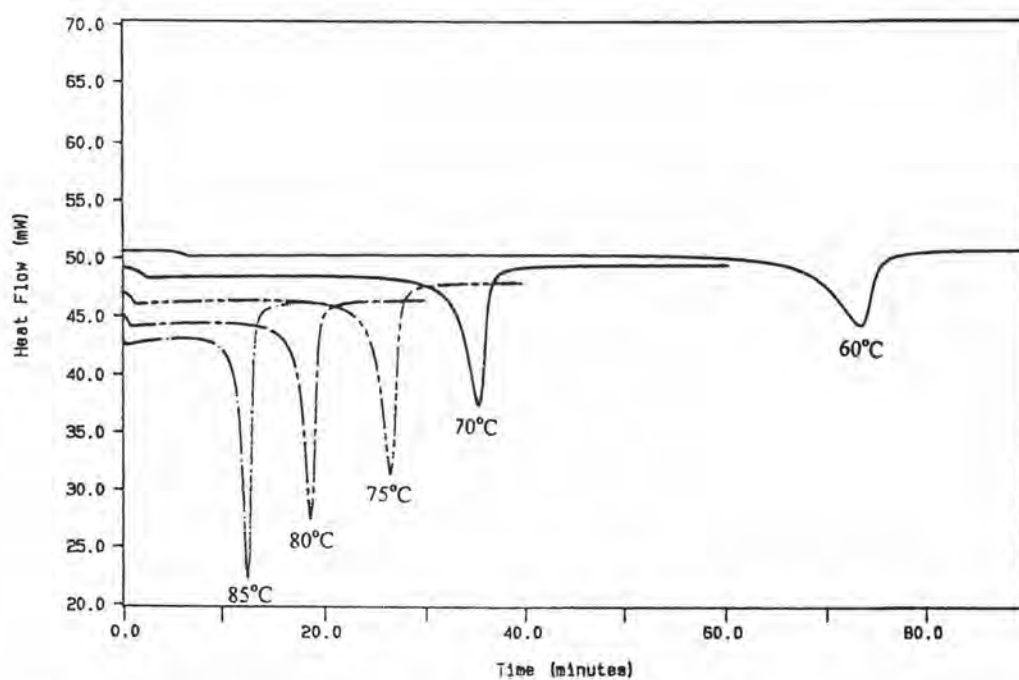
The extremely low value of  $\Delta H_p$  at low polymerization temperature (60°C) might be due to the loss of heat during the measurement as discussed previously. The polymerization of this batch was carried out at 60°C for 10 Hrs. However, the values of  $\Delta H_p$  at the other temperature were closed to each other but could not relate to the polymerization temperature. The styrene and MMA conversions increased with the increase of polymerization temperature but were less than 100% due to the vitrification effect.

**Table 4.4** Styrene and MMA conversions at various polymerization temperatures

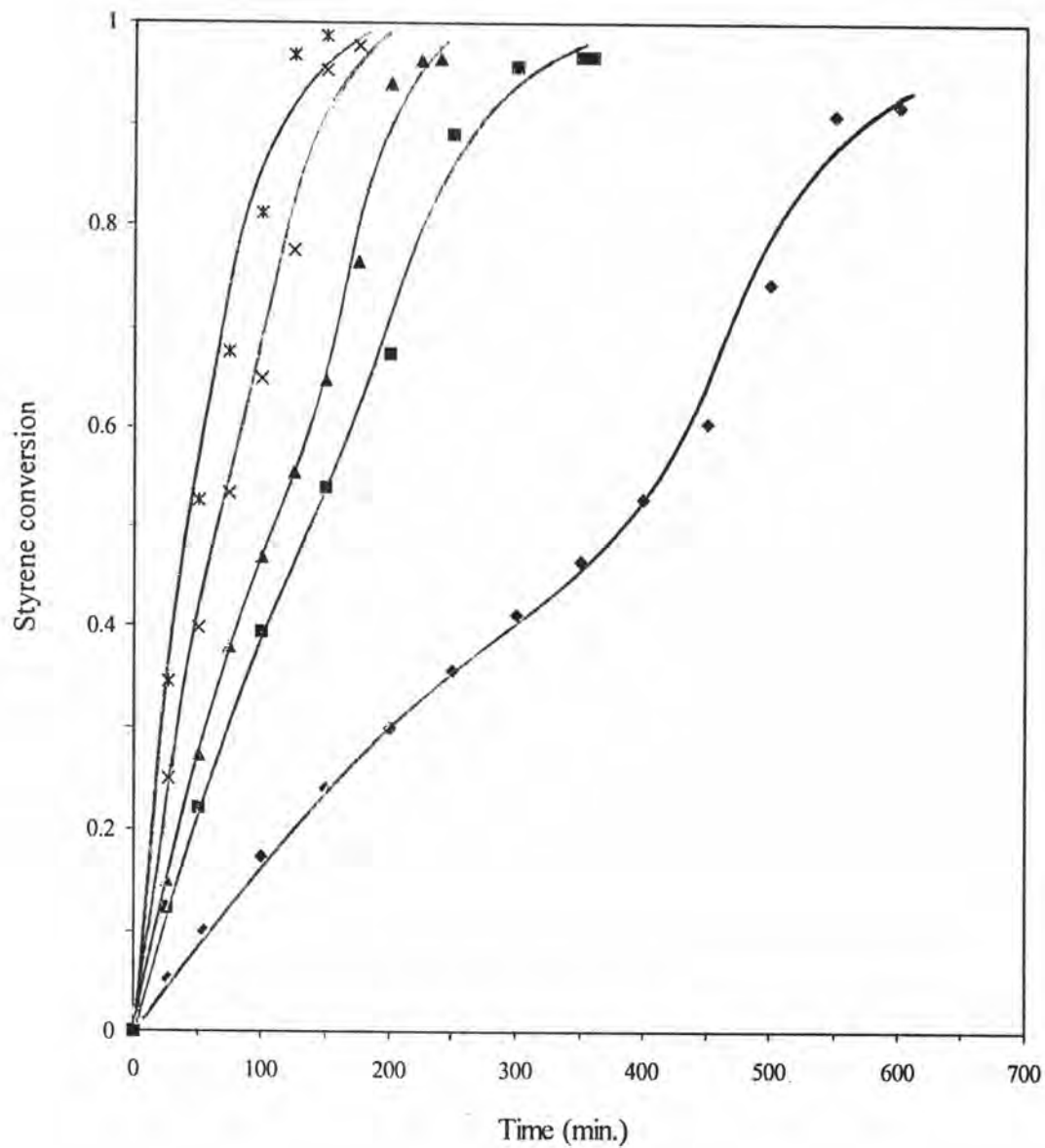
Monomer	Temperature (°C)	$\Delta H_I$ (J/g)	$\Delta H_R$ (J/g)	$\Delta H_p$ (kJ/mol)	Total monomer conversion (%)
Styrene	60	507	44.9	57.4	91.9
	70	729	25.1	78.4	96.7
	75	636	23.4	68.6	96.4
	80	660	15.2	70.2	97.8
	85	674	9.18	71.0	98.6
MMA	60	502	63.7	56.6	88.7
	70	497	41.0	53.8	92.4
	75	547	36.2	58.3	93.8
	80	514	28.4	54.2	94.8
	85	503	23.2	52.6	95.6



**Figure 4.11** Overlaid DSC thermograms of the thermal-initiated free radical bulk homopolymerization of styrene at various polymerization temperatures. 1.0%w/w AIBN was used as the initiator.

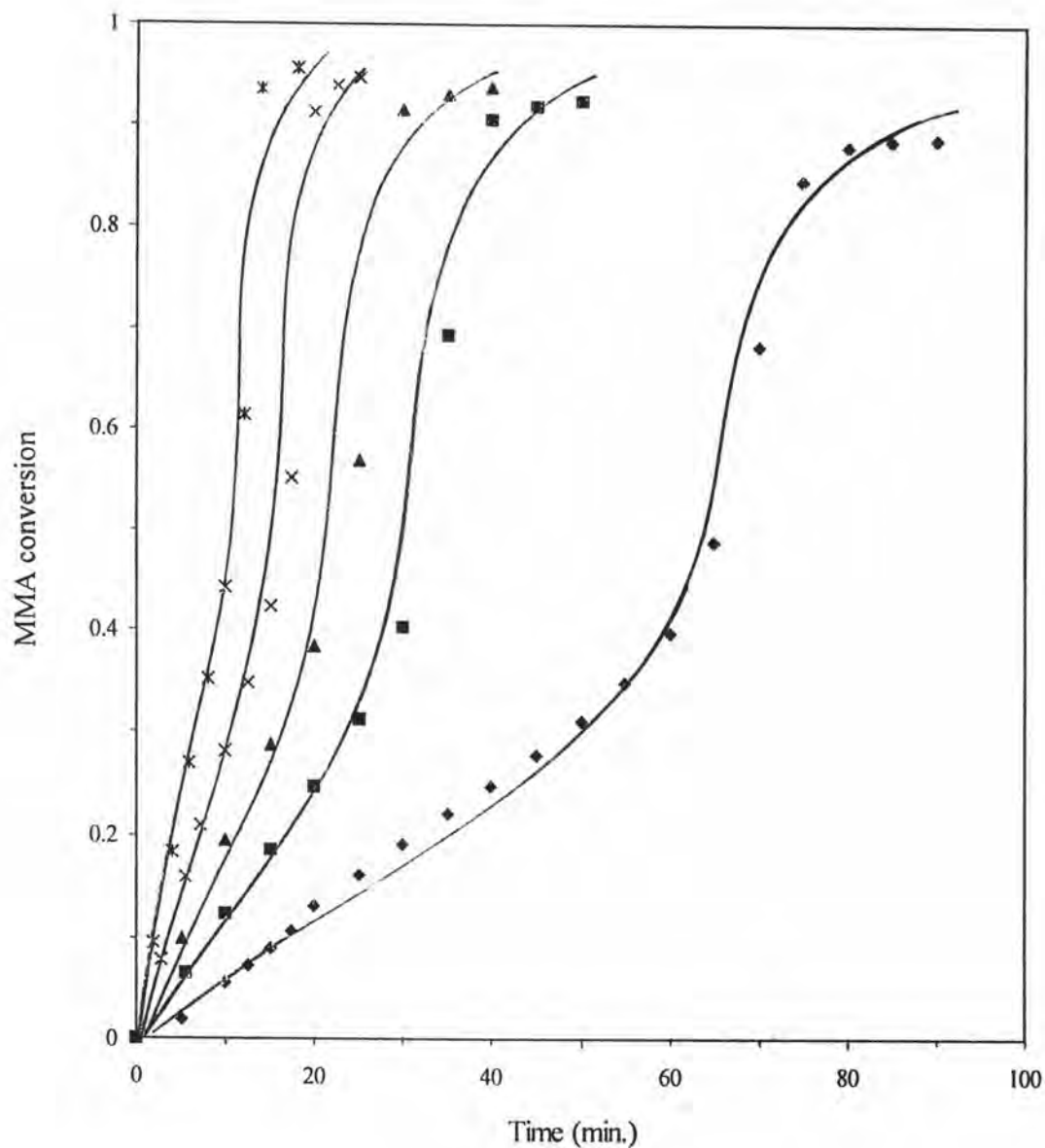


**Figure 4.12** Overlaid DSC thermograms of the thermal-initiated free radical bulk homopolymerization of MMA at various polymerization temperatures. 1.0%w/w AIBN was used as the initiator.



**Figure 4.13** Plot of conversion versus time for styrene polymerization using 1.0% w/w AIBN at the various polymerization temperatures : ♦, 60°C; ■, 70°C; ▲, 75°C; ×, 80°C; \*, 85°C.





**Figure 4.14** Plot of conversion versus time for MMA polymerization using 1.0%w/w AIBN at the various polymerization temperatures : ♦, 60°C; ■, 70°C; ▲, 75 °C; ✕, 80 °C, \*, 85 °C.

#### 4.1.4 Determination of activation energy for polymerization

The monomer conversion at the particular time, the overall initial rates and the overall initial rate constants of the polymerizations at each temperature were calculated using Eq. (2.46), (2.48) and (4.1), respectively. Moreover, the initial propagation rate constant ( $k_p$ ) was also evaluated using Eq. (4.3).

$$k_p = \frac{dx/dt}{(fk_d[I]/k_t)^{1/2}} \quad (4.3)$$

The values of the kinetic parameters used in Eq. (4.3) are taken from the literatures which are listed here in Table 4.5. Combining the data obtained from DSC measurement and the kinetic parameters shown in Table 4.5 yields the results as shown in Table 4.6.

The results shown in Table 4.6 were in good accordance with those predicted from the theory in that the increase of the reaction temperature results in the increase of the rate of polymerization.

The overall activation energy ( $E_a$ ) and the frequency factor ( $A$ ) of the polymerization could be evaluated from the Arrhenius equation,

$$\ln k = \ln A - \frac{E_a}{RT} \quad (4.4)$$

The slope and the intercept of the plot of  $\ln(\text{overall initial rate constant})$  against the polymerization time are the activation energy and frequency factor, respectively. The Arrhenius plot of the polymerization of styrene is shown in Figure 4.15 and that of MMA in Figure 4.16.

The evaluated values of  $E_a$  and  $A$  of the polymerization of styrene were 85.0 kJ/mol and  $2.84 \times 10^9 \text{ L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$ , respectively. They are higher than those cited in literatures. Rim, P.B., et al. [15] reported the values of  $E_a$  and  $A$  equal to 70.56 kJ/mol and  $2.71 \times 10^6 \text{ s}^{-1}$ . Ebdon, J.R., et al. [13] and Flory, P.J. [6] reported the value  $E_a$  of were of 79.8 and 92.4 kJ/mol, respectively.

Values of  $E_a$  and  $A$  of the polymerization of MMA were evaluated respectively to be 83.6 kJ/mol and  $4.88 \times 10^9 \text{ L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$ , which were relatively higher than the previous published values reported by Armitage, P.D., et al. [10] and Malavasic, T., et al. [9] the values of  $E_a$  and  $A$  to be 84.9 and  $5.30 \times 10^9$ , and 76.8 kJ/mol and  $4.9 \times 10^8 \text{ L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$ , respectively.

**Table 4.5** Values of the kinetic parameters used for the determination of  $k_p$ .

Substances	Parameters	Symbol	Value	Reference
AIBN	Efficiency of initiator	$f$	0.57	[19]
	Activation energy	$E_a$	112.29 kJ/mol	[20]
	Frequency factor	$A$	$8.232 \times 10^{12} \text{ s}^{-1}$	
Styrene	Activation energy for termination	$E_{a,t}$	10.1 kJ/mol	[21]
	Frequency factor for termination	$A_t$	$1.300 \times 10^9 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	
MMA	ln rate constant for termination	$\ln k_t$	$24.91 - 2536/T$	[18]

**Table 4.6** Values of the initial rate of the polymerization of styrene and MMA ( $R_{p,0}$ ), the overall initial rate constant ( $k_{ov}$ ), and the initial propagation rate constant ( $k_p$ ) at various polymerization temperatures. 1.0%w/w AIBN was employed as the initiator.

Monomer	Temperature (°C)	$k_{ov} \times 10^4$ ( $L^{1/2}mol^{-1/2}s^{-1}$ )	$R_{p,0} \times 10^4$ ( $mol-L^{-1}s^{-1}$ )	$k_p \times 10^{-2}$ ( $L-mol^{-1}s^{-1}$ )
Styrene	60	1.27	2.61	2.18
	70	3.58	7.40	3.60
	75	4.65	9.57	3.62
	80	7.76	15.8	4.70
	85	10.9	22.4	5.19
MMA	60	3.95	8.93	6.80
	70	8.13	18.3	8.18
	75	13.4	30.3	10.4
	80	19.6	44.5	11.9
	85	33.0	74.0	15.7

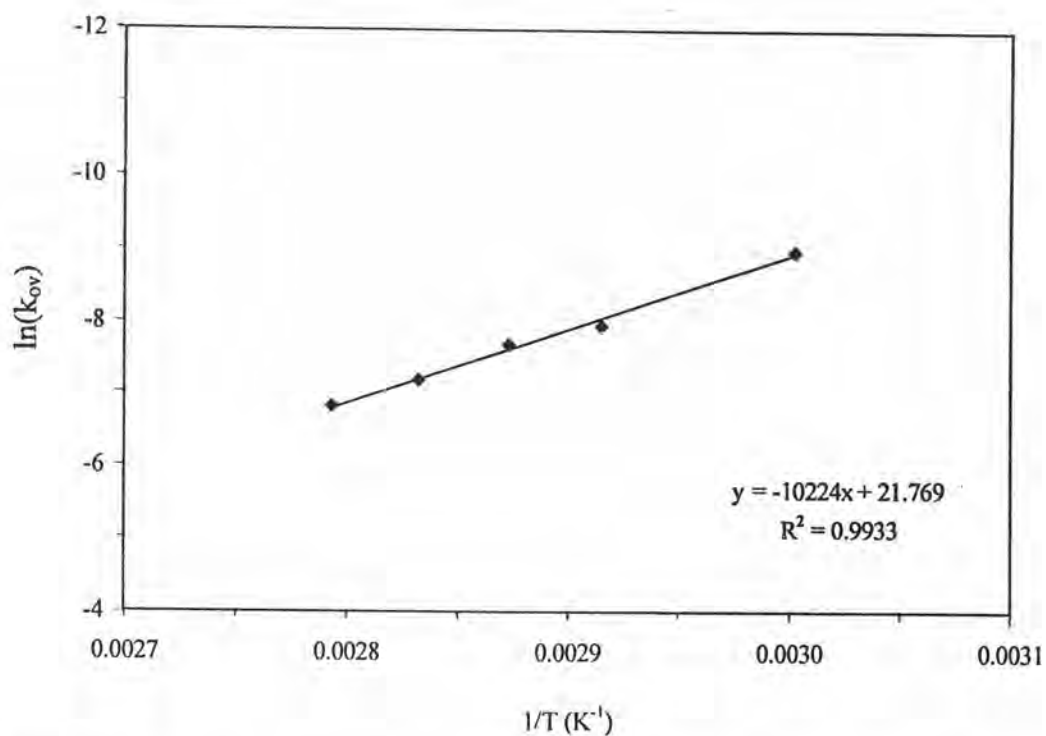


Figure 4.15 The Arrhenius plot for the polymerization of styrene using 1.0%w/w AIBN.

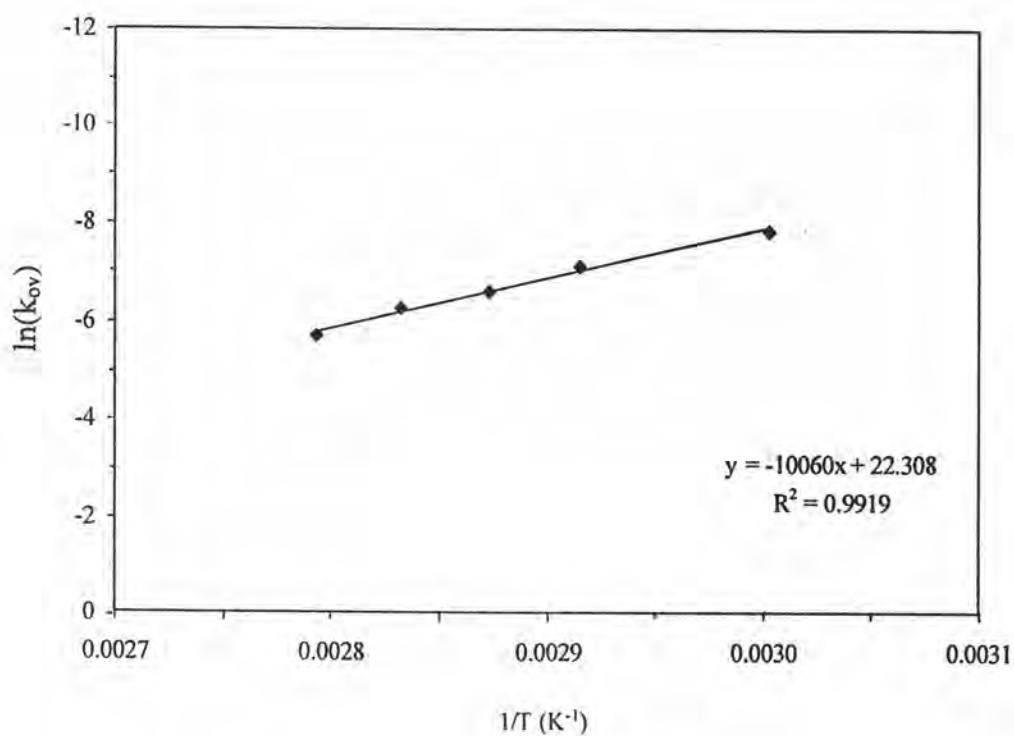


Figure 4.16 The Arrhenius plot for the polymerization of MMA using 1.0%w/w AIBN.

## 4.2 Kinetics of Thermal-initiated Free Radical Bulk Copolymerization of Styrene and Methyl methacrylate

### 4.2.1 Effect of feed monomer composition on the initial rate of copolymerization

The term "copolymerization" here refers to the isothermally free radical bulk copolymerization at 60°C using 1.0%w/w AIBN initiator. Typical DSC thermograms of the copolymerization of styrene and MMA with various feed monomer compositions are shown in Figures 4.17 - 4.18. Overlaid thermograms are shown in Figure 4.19. The thermal behaviour of each comonomer composition, for instance, the polymerization behaviour of the feed monomer composition with high mole fraction of MMA was closed to that of MMA homopolymerization. The increase of MMA mole fraction in the comonomer composition from 0.4 to 0.8 shortened the polymerization time.

Typical DSC thermogram of the residual comonomers after the copolymerization of styrene and MMA is shown in Figure 4.20. The exothermic characters of both styrene and MMA were observed as well as the glass transition of the copolymer formed. The values of  $\Delta H_I$ ,  $\Delta H_R$ ,  $\Delta H_p$  and the total monomer conversion are given in Table 4.7. The values of total heat of polymerization and the total comonomer conversion increased with the increase of MMA mole fraction in the feed monomer composition. In comparison to those evaluated from the homopolymerization of MMA, it was apparently that the increase of styrene mole fraction in the feed monomer compositions behaved as a retarder for the copolymerization which its conversion would not reach 100%. The plot of comonomer conversion versus time is shown in Figure 4.21. The behaviour of gel effect was observed in all copolymerizations. This implies that MMA should be dominantly affected on the copolymerization.

The residual comonomer of the copolymerized mixture were also measured by GC technique. The analysis results are presented in Table 4.8.

The total monomer conversion obtained from two different methods (DSC and GC) were slightly different. Possible postulation of the discrepancy of those values might be due to the adsorption of the residual comonomers on the surface of the polymer formed. Further experiments are needed to prove the earlier statement.

The overall initial rate constants ( $k_{ov}$ ) and the overall initial rates ( $R_{p,0}$ ) were determined followed Eq. (4.1) and (2.48). The initial propagation rate constant was evaluated from Eq. (4.5). The determined values are given in Table 4.9. The value of  $k_{i(12)}$  as reported by Chen et al. [22] was  $8.42 \times 10^8 \text{ mol-L}^{-1}\text{s}^{-1}$ .

$$k_p = \frac{(dx/dt)}{(fk_d[I]/k_{i(12)})^{1/2}} \quad (4.5)$$

The dependence of the initial rate on the feed monomer composition was also investigated which is shown in Figure 4.22. The small adding of styrene in the feed monomer composition resulted in the obvious decrease of the rate of copolymerization. This was also found previously by Khan, H.U. and Wadehra, B.M.L. [14]. The cause might be the difference of the polarity of the styrene and MMA.

**Table 4.7** Values of  $\Delta H_I$ ,  $\Delta H_R$ ,  $\Delta H_p$  and the total monomer conversion of the copolymerization of styrene and MMA with various comonomer compositions using 1.0%w/w AIBN at 60°C.

Mole fraction of styrene	$\Delta H_I$ (J/g)	$\Delta H_R$ (J/g)	$\Delta H_p$ (J/g)	Total comonomer conversion (%)
0.2	398	42.2	440	90.4
0.4	288	39.7	328	87.9
0.6	271	43.7	315	86.1

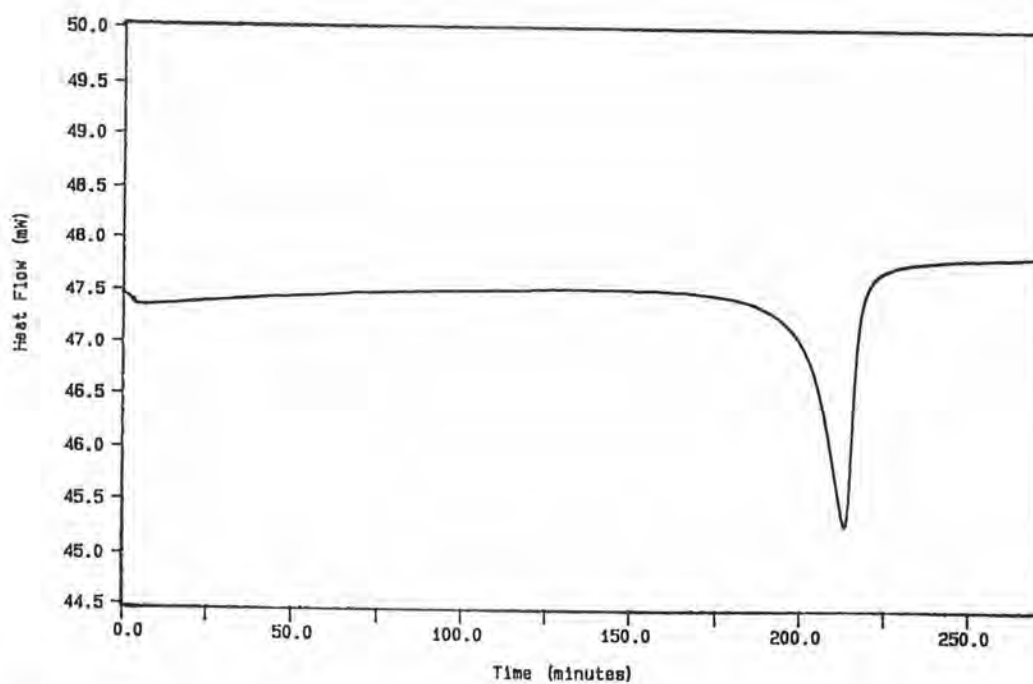
**Table 4.8** Residual comonomer of the copolymerization of styrene and MMA with various comonomer compositions using 1.0%w/w AIBN at 60°C.

Mole fraction of styrene	GC			DSC
	Residual MMA (%)	Residual styrene (%)	Total monomer conversion (%)	Total monomer conversion (%)
0.2	6.04	0.64	93.3	90.4
0.4	3.08	1.58	95.3	87.9
0.6	3.54	0.93	95.5	86.1

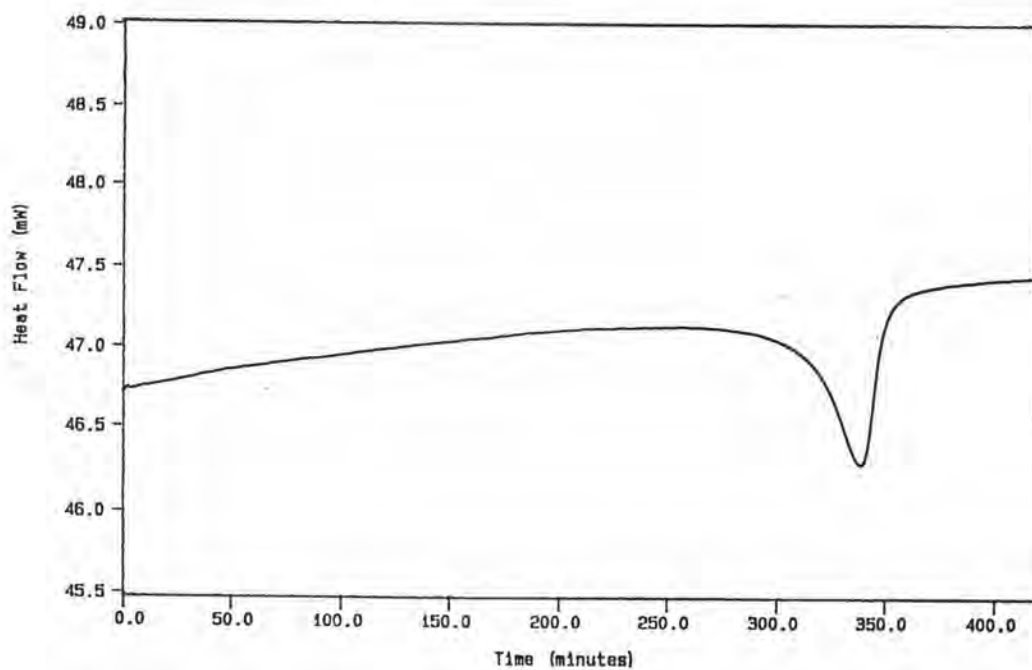
**Table 4.9** Values of the overall initial rate constants ( $k_{ov}$ ), the overall initial rates ( $R_{p,0}$ ) and the initial propagation rate constants ( $k_p$ ) of the copolymerization of styrene and MMA with various comonomer compositions using 1.0%w/w AIBN at 60°C.

Mole fraction of styrene	$k_{ov} \times 10^5$ ( $L^{1/2}mol^{-1/2}s^{-1}$ )	$R_{p,0} \times 10^4$ ( $mol-L^{-1}s^{-1}$ )	$k_p \times 10^{-2}$ ( $L-mol^{-1}s^{-1}$ )
0.2	7.69	1.70	6.89
0.4	7.02	1.52	6.25
0.6	5.64	1.20	4.98

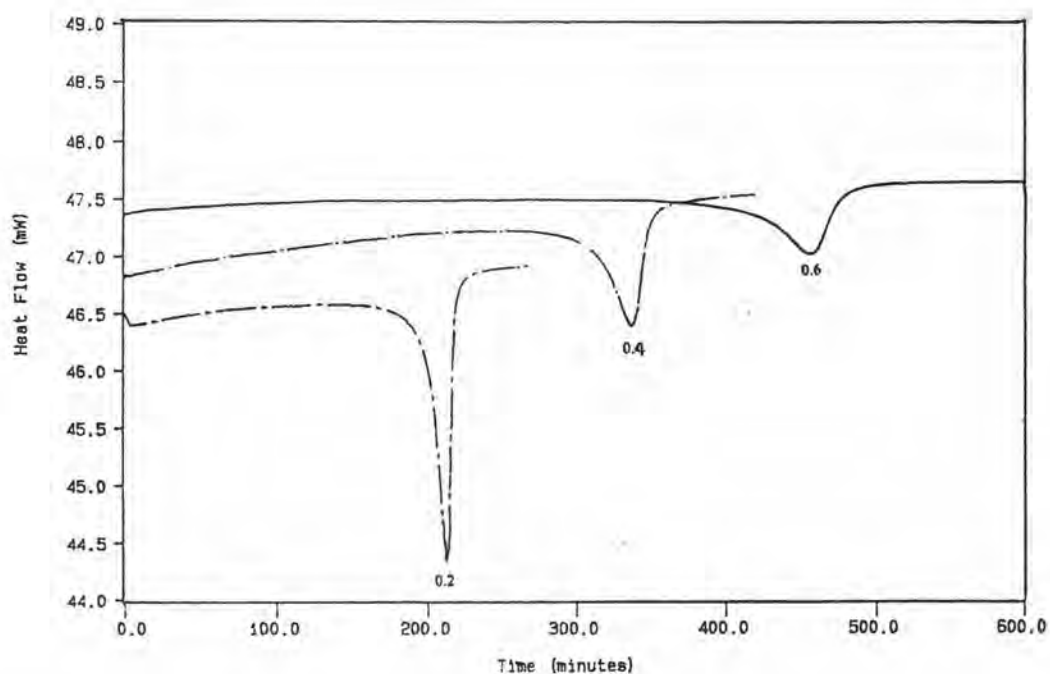




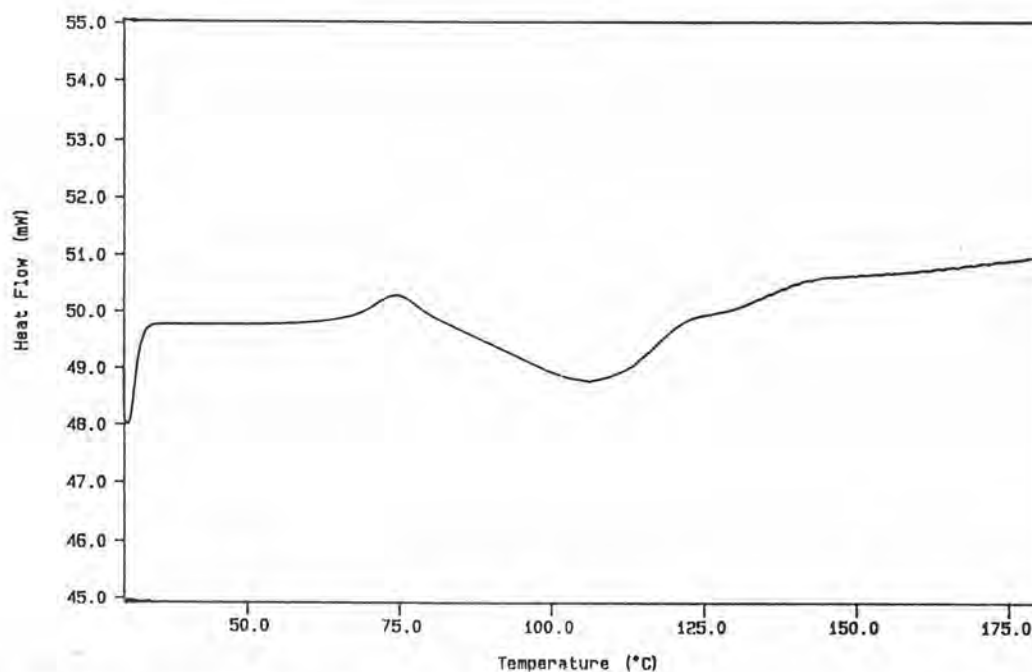
**Figure 4.17** A typical DSC thermogram of the copolymerization of styrene and MMA at 60°C with 0.2 mole fraction of styrene. 1.0%w/w AIBN was used as the initiator.



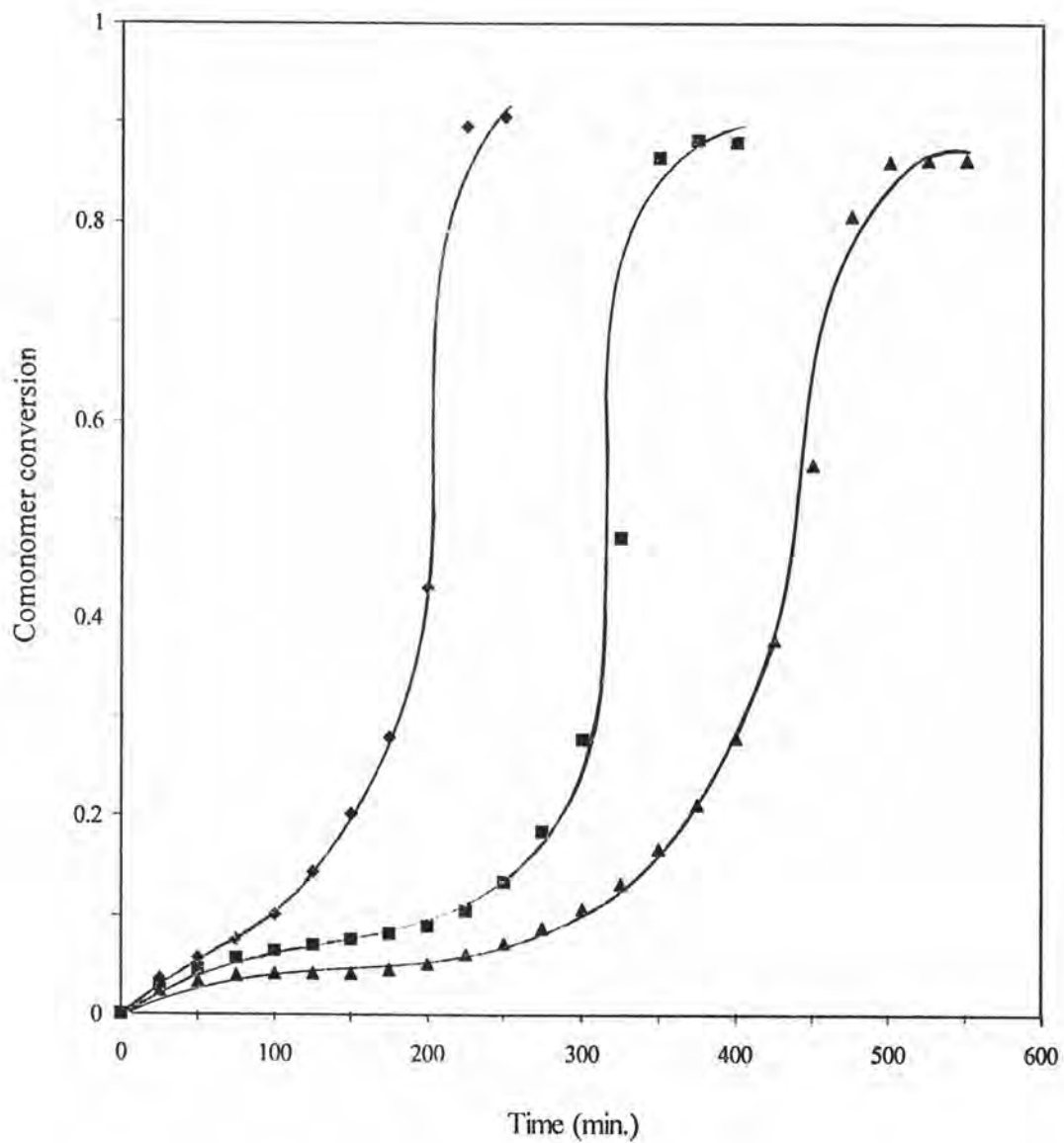
**Figure 4.18** A typical DSC thermogram of the copolymerization of styrene and MMA at 60°C with 0.4 mole fraction of styrene. 1.0%w/w AIBN was used as the initiator.



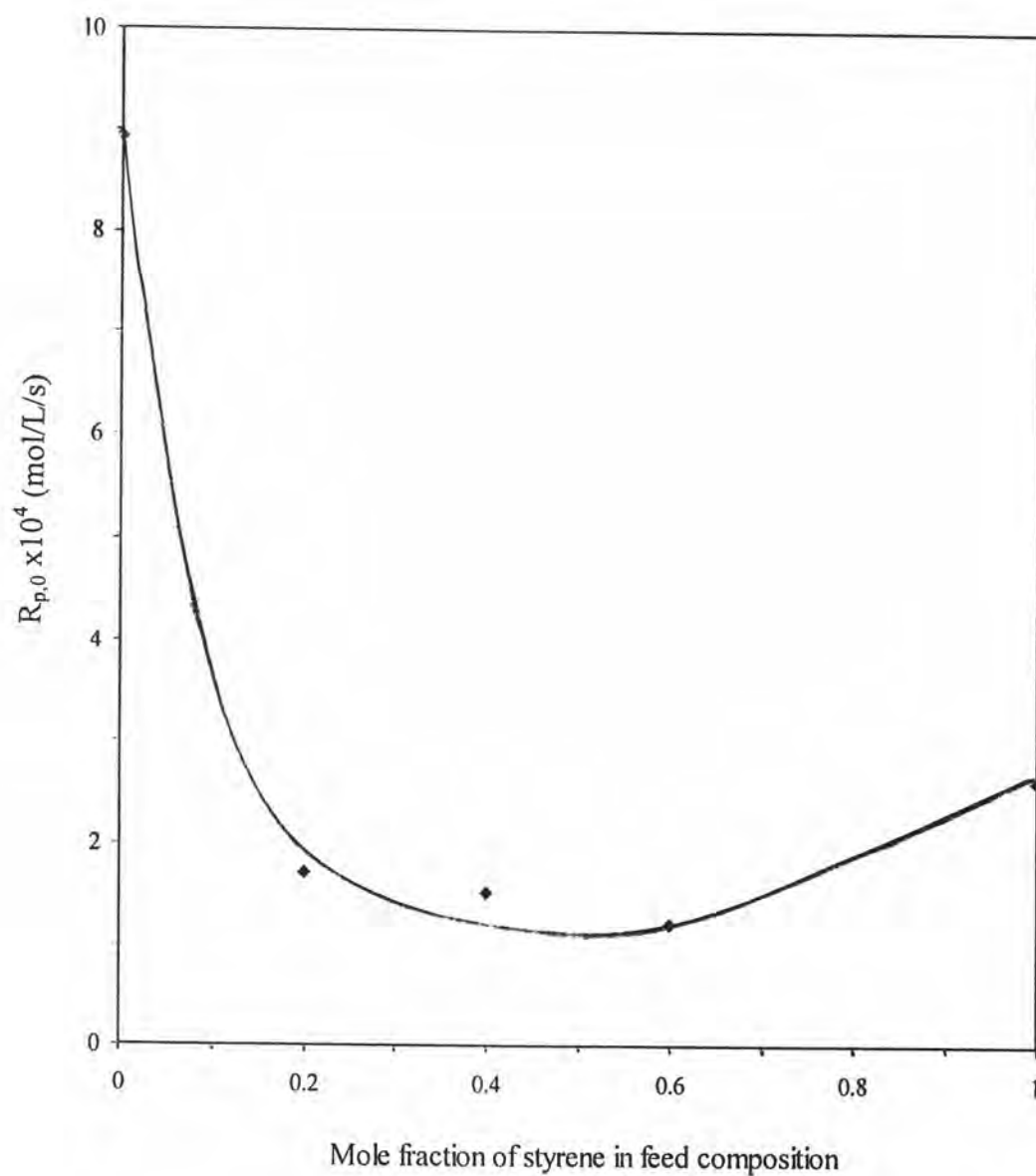
**Figure 4.19** Overlaid DSC thermograms of the copolymerization of styrene and MMA at 60°C with the variation of mole fraction of styrene in the feed monomer composition. 1.0% w/w AIBN was used as the initiator.



**Figure 4.20** A typical DSC thermogram of the residual comonomers after the isothermal copolymerization of styrene and MMA (0.4 mole fraction of styrene) at 60°C using 1.0%w/w AIBN.



**Figure 4.21** Plot of the comonomer conversion versus time of the copolymerization of styrene and MMA using 1.0%w/w AIBN at 60°C with the variation of mole fraction of styrene : ♦, 0.2 ; ■, 0.4 ; ▲, 0.6.



**Figure 4.22** Plot of the initial rate versus mole fraction of styrene in copolymerization at 60°C.

### 4.3 Determination of the Monomer Reactivity Ratio of Styrene and MMA

The reactivity ratio of styrene and MMA obtained based on the definition that it is a ratio of the rate constant for the homopolymerization to the cross-propagation. The homopolymerization rate constants ( $k_{11}$  and  $k_{22}$ ) were the previously determined values of  $k_p$  of homopolymerizations of styrene and MMA. While the value of  $k_{12}$  and  $k_{21}$  could not be directly evaluated from the copolymerization. However, according to the expression of  $k_p$  presented in Eq. (2.41), the values of  $r_1$  and  $r_2$  could be calculated using  $k_p$  from the two sets of Eq. (2.41). Since the values of  $k_p$  shown in Table 4.9 were obtained from the copolymerization of three various comonomer feed compositions, each particular pair of  $k_p$  could give one set of the monomer reactivity ratios. In theory, the monomer reactivity ratio of each comonomer pair should be identity; however, in this study the obtained values of  $r_1$  and  $r_2$  (see Table 4.10) were found not to be. Two values of  $k_p$  were obtained from two batches of polymerizations with different feed comonomer compositions.

**Table 4.10** Values of initial propagation rate constants ( $k_p$ ) used for the determination of reactivity ratios of styrene ( $r_1$ ) and MMA ( $r_2$ ). ( $k_{11} = 218 \text{ L}\cdot\text{mol}^{-1}\text{s}^{-1}$  and  $k_{22} = 680 \text{ L}\cdot\text{mol}^{-1}\text{s}^{-1}$ ).

Two values of $k_p$ used ( $\times 10^{-2}$ , $\text{L}\cdot\text{mol}^{-1}\text{s}^{-1}$ )	Monomer reactivity ratios	
	$r_1$	$r_2$
6.89, 6.25	0.40	0.50
6.25, 4.98	0.48	0.08
6.89, 4.98	0.45	0.34
	0.52 <sup>(1)</sup>	0.46 <sup>(1)</sup>

Note : (1) These values are obtained from literature [18 ].

The values obtained of the monomer reactivity ratio of styrene ( $r_1$ ) were closed to each other and slightly differed from the literature reported value of 0.52. While those of MMA ( $r_2$ ) was much different not only from each other but also from the literature reported value of 0.46. It was also observed that the markedly different value of  $r_2$  (0.08) was from the calculation of the value of  $k_p$  that obtained from the copolymerization with the lower MMA mole fraction. Since it was quite clearly observed from the plot of the comonomer conversion against time that MMA affected dominantly on the copolymerization. The decrease of MMA content might cause the reaction controlled by styrene. It is apparent that the polymerization of styrene required the longer polymerization time than that of MMA which may lead to a possible error as described previously, so that the reactivity of MMA related to styrene should be hardly measured. However, the differences of monomer reactivity ratios determined from this study against those reported in other literatures might be due to the following cause. The conventional method required the analysis of the copolymer compositions or the feed comonomer compositions and then the values of  $r$  were evaluated using one of the methods mentioned in Chapter 2, mostly by the graphical method [23], therefore, all of the experimental data were accounted for such the determination. In contrast to this study, only two sets of data were required for the evaluation.