

CHAPTER V

CONCLUSION AND SUGGESTION FOR FURTHER WORK

5.1 Conclusion

Differential scanning calorimetric technique was employed to study the kinetics of thermal-initiated free radical homopolymerization of styrene and MMA in the presence of AIBN initiator. The total heat of polymerization or the total peak area for 100% of monomer conversion was evaluated from the addition of the total peak area of the exothermic curve obtained from the isothermal and the dynamic (temperature scan) conditions. The monomer conversion at the particular time was evaluated from the ratio of the partial peak area at reaction time to the total peak area. Some kinetic parameters of the homopolymerizations of styrene and MMA using 0.5 to 2.0%w/w AIBN at 80°C and those using 1.0%w/w AIBN at 60-85°C are summarized in Table 5.1. Gas chromatography was employed to confirm the DSC technique. The data obtained from both techniques were not much different. The relative error of two methods were in the ranges of 0.01-3.58%.

The reaction order of the polymerization of styrene and MMA with respect to the initiator concentration are 0.33 and 0.53, respectively. The activation energy and frequency factor of the polymerization of styrene and MMA were 85.0 kJ/mol and $2.84 \times 10^9 \text{ L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$, and 83.6 kJ/mol and $4.88 \times 10^9 \text{ L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$, respectively.

DSC technique was also applied to study the kinetics of thermal-initiated free radical copolymerization of styrene and MMA at 60°C with the comonomer composition in the ranges of 0.2 to 0.6 mole fraction of styrene. The kinetic parameters found in this study are given in Table 5.2.

Table 5.1 Kinetic parameters of the thermal-initiated free radical homopolymerization of styrene and MMA.

Monomer	[I] (%w/w)	Temperature (°C)	$k_{ov} \times 10^4$ ($L^{1/2}mol^{-1/2}s^{-1}$)	$R_{p,0} \times 10^3$ ($mol-L^{-1}s^{-1}$)	$k_p \times 10^{-2}$ ($L-mol^{-1}s^{-1}$)
Styrene	0.5	80	8.81	1.29	-
	1.0	80	7.76	1.58	-
	1.5	80	7.21	1.81	-
	2.0	80	7.06	2.03	-
	1.0	60	1.27	0.261	2.18
	1.0	70	3.58	0.740	3.60
	1.0	75	4.65	0.957	3.62
	1.0	80	7.76	1.58	4.70
	1.0	85	10.9	2.24	5.19
MMA	0.5	80	20.8	3.32	-
	1.0	80	19.6	4.45	-
	1.5	80	22.1	6.09	-
	2.0	80	21.2	6.75	-
	1.0	60	3.95	0.893	6.80
	1.0	70	8.13	1.83	8.18
	1.0	75	13.4	3.03	10.4
	1.0	80	19.6	4.45	11.9
	1.0	85	33.0	7.40	15.7

Table 5.2 Kinetic parameters of thermal-initiated free radical copolymerization of styrene and MMA at 60°C using 1.0%w/w AIBN. The ranges of styrene in the mole fraction of comonomer composition were from 0.2 to 0.6 mole.

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

The total comonomer conversion were also comparatively measured by those mentioned techniques, i.e. DSC and GC. The results obtained from both techniques were slightly different within the relative error of 2.24-9.10%.

The dependence of the rate of copolymerization on the comonomer composition was that the rate of copolymerization was lower than that of homopolymerization and the adding of small amount of styrene in the comonomer mixture depressed the rate.

The monomer reactivity ratio of styrene and MMA determined from the different values of k_p are that, the reactivity ratio of styrene (r_1) was in the ranges of 0.40 - 0.48 and that of MMA (r_2) in the ranges of 0.08 - 0.50.

5.2 Suggestion for further work

There are some interesting points required for further studies prior to achieve the conclusion whether DSC technique is appropriate to apply as a new method for determination of the monomer reactivity ratios or not. The suggestions for further work are of the following topics:

- 1) The kinetic studies of the copolymerization of styrene and MMA by following these parameters.
 - a) The variation of the comonomer compositions in the other range such as 0.1, 0.3, 0.5, 0.7 and 0.9 mole ratio of styrene : to compare the reactivity ratios obtained for those values reported here.
 - b) The variation of the polymerization temperature : to investigate the effect of temperature on the reactivity ratios.
- 2) Study on the other pairs of monomer which require a short polymerization time : to reduce the error that may cause by the instrument due to a long operating period.