

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Optimum Conditions for the Vapor Deposition Polymerization of Styrene Monomer

Preliminary studies were carried out to determine the optimum conditions for the vapor deposition polymerization of styrene monomer. The effects of substrate temperature, type of UV irradiation lamp and type of substrate temperature were studied.

4.1.1 Type of UV Irradiation Lamp

The energy during polymerization was studied in terms of substrate temperature. Two UV lamps of differing intensity, 9 W and 100 W, were used. From preliminary study, it was found that the lower intensity UV irradiation lamp (9 watts) did not induce any polymerization on the substrate. This may be due to the fact that the power and intensity of 9 W UV irradiation lamp was too low and inadequate to induce polymerization on the substrate. Thus high intensity lamp of 100 W was used in subsequent experiments.

4.1.2 Substrate Temperature

The power of UV light is realized to the polymerization activation energy. Two ranges of substrate temperature were studied ;

- the hot surface with the range of 25-50 °C,
- the cold surface with the range 0-10 °C.

The results are shown in Table 4.1.

Table 4.1 Observations of film deposition using 100 W UV irradiation lamp

No.	The Substrate Temperature (°C)	Temperature Controller	Observation
1	25-50	Heater	No condensation of monomer
2	10	Cold Ice	Some condensation of monomer, but no film deposition
3	0	Thermoelectric Cooling Plate	More condensation with some film deposition

* Flow Rate = 202 ml N₂/min, deposition time = 6 hours.

From the above table, it can be seen that the deposition of styrene monomer onto the substrate depends strongly on the temperature of substrate surface. No condensation was found on the hot surface whereas some condensation of styrene vapor was obtained with cold ice, but there was limitation on the life-time and temperature range of cold ice. To solve this problem a thermoelectric cooling plate was assembled. The 0 °C substrate surface was found to induce more condensation with some fixed film by 100 W UV irradiation.

4.1.3 The Type of Substrate

The deposition of styrene vapor on various types of substrate was studied. The results of visual observations are shown in Table 4.2.

Table 4.2 Observations of film deposition on various substrates

No.	Substrate type	Observations
1	Glass-slide	some deposition
2	Silicon wafer	some deposition
3	Quartz disk	some deposition
4	Aluminum	some deposition
5	KBr disk	some deposition

Conditions : flow rate = 123.0 ml N₂/min, deposition time 16 hrs.

substrate temperature 5 to -5 °C, without photoinitiator

irradiation source = 100 W UV lamp.

From the above results, it can be concluded that it is possible to deposit styrene monomer on the various types of substrates shown in Table 4.2. No visible difference in film deposition was found among the different substrates.

4.1.4 Confirmation of Polymerization

The optimum vapor deposited polystyrene thin film was characterized to verify the polymerization. At 0 °C substrate temperature, there was greater monomer condensation with some film deposition. Therefore, to confirm the polymerization reaction, the observed film on substrate was characterized by FTIR.

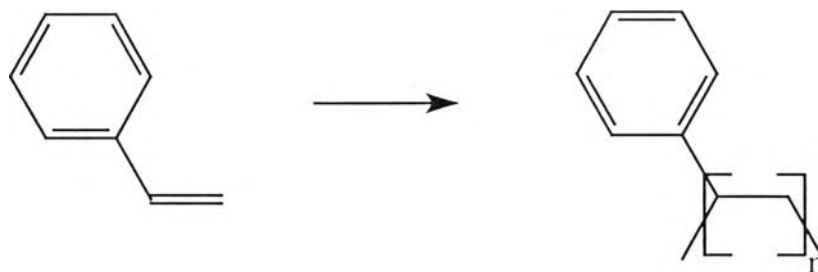


Figure 4.1 Polymerization reaction of styrene monomer.

During polymerization of styrene the double bond disappears while the benzene ring side group remains intact as shown in Figure 4.1.

Figure 4.2 shows the IR spectra of standard polystyrene, deposited film, and styrene monomer. It can be seen that the IR spectrum of deposited film (b) shows the absorption peak of $\text{-CH}_2\text{-}$ stretching of regular alkene at 2925 cm^{-1} while the absorption peak of =CH stretching of the vinyl group at 3082 cm^{-1} has disappeared when compared to spectrum of the monomer (c). Therefore, from the IR spectra, polymerization of styrene on the substrate surface was confirmed.

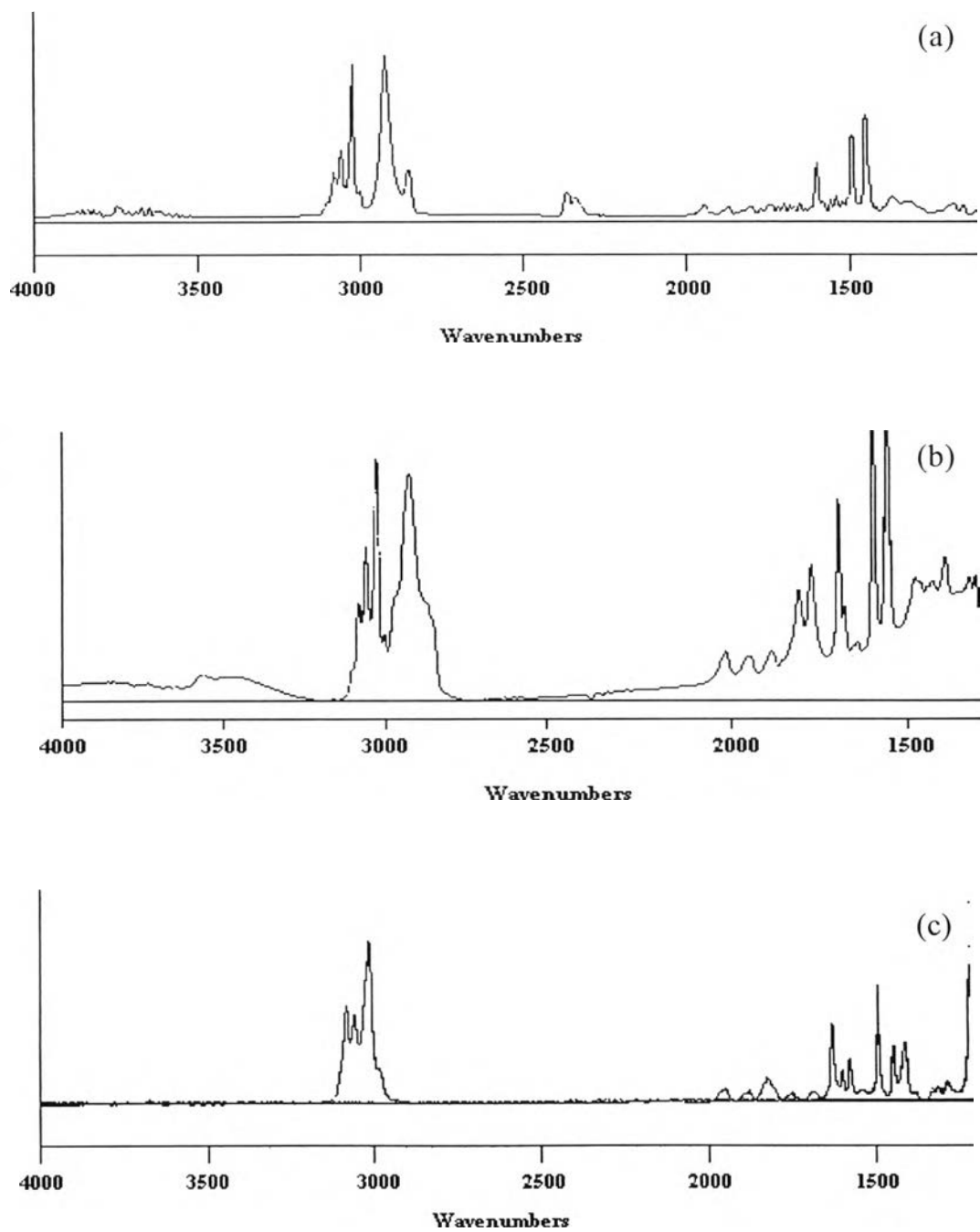


Figure 4.2 FT-IR spectrum of (a) standard polystyrene; (b) deposited film; (c) styrene monomer.

4.1.5 The Image of Deposited Film

A piece of dried deposited film on silicon wafer was analyzed by cross sectional scanning with electron microscope. The images obtained are shown in Figure 4.7. The thin deposited film can be seen clearly in both images.

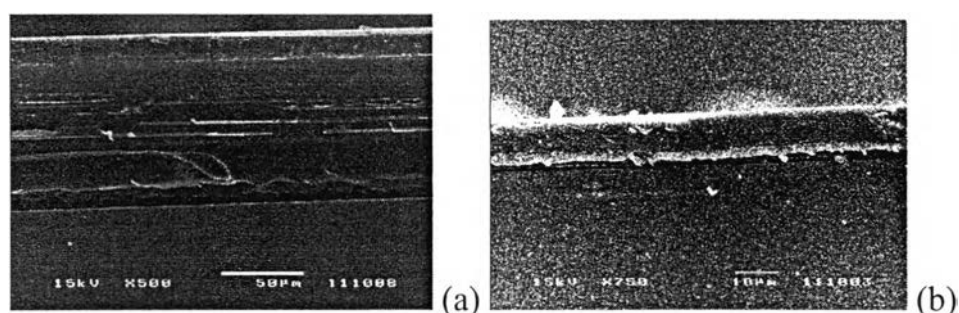
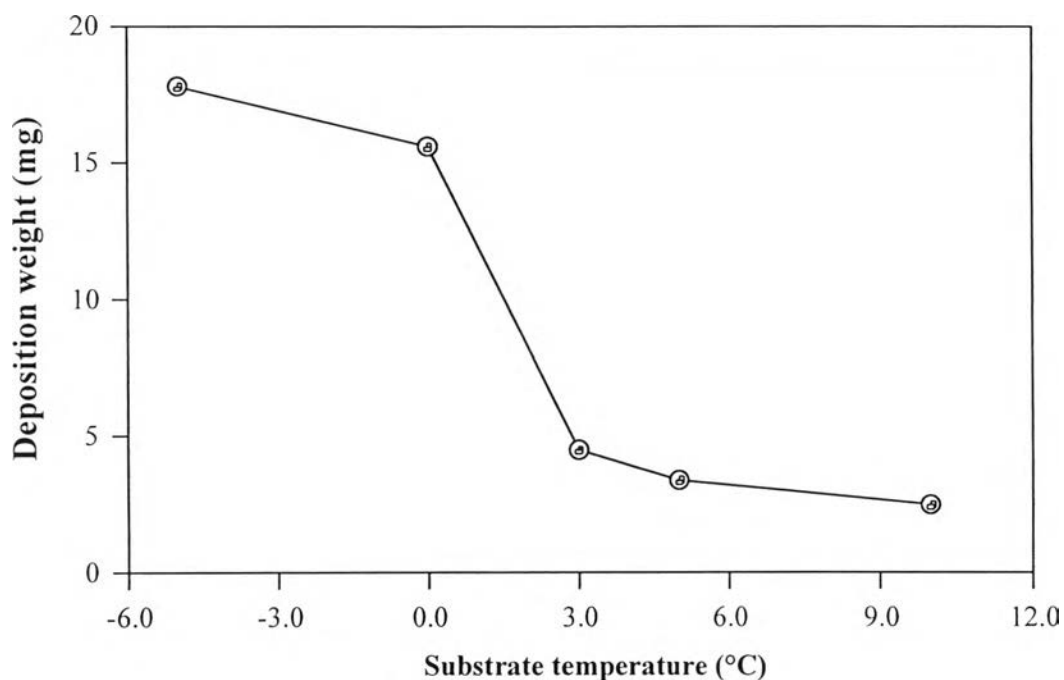


Figure 4.3 The scanning electron microimages of (a) 0 °C substrate temperature with 100 W lamp; (b) 3 °C substrate temperature with 100 W lamp

4.2 Effects of Deposition Conditions on the Deposition Weight

4.2.1 Effect of Substrate Temperature

The amount of deposited polymer was studied as a function of substrate temperature. The quartz disk was used as the substrate. The substrate temperature was varied from -5.0 °C to 10 °C and the results are shown in Figure 4.4.



Conditions : flow rate = 123.0 ml. N₂/min., deposition time = 8.0 hrs.
purging time = 3.0 hrs., no photoinitiator

Figure 4.4 Deposition weight plotted as a function of substrate temperature.

From Figure 4.4 it can be seen that lower substrate temperature induces more polymerization. This is probably because the monomer molecules have lower kinetic energy at low temperatures and stay on the substrate longer than in the case of hot surface. This leads to greater polymerization.

The deposition weight was found to increase gradually when substrate temperature was decreased from 10 °C to 3 °C. However, there is a sharp increase between 3 °C - 0 °C followed by a more gradual increase as the substrate temperature is decreased further.

It is postulated that the sharp increase may coincide with the formation of multi-layers of monomers after the monolayer deposition is completed.

4.2.2 Effect of the Amount of Photoinitiator

The selected photoinitiator was diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide. The quartz disk substrate was irradiated by 100 W UV irradiation lamp at 82.0 ml. N₂/min. flow rate, 8 hours deposition time and -5.0 °C substrate temperature. The change in deposition weight with change in the amount of photoinitiator is shown in Figure 4.5.

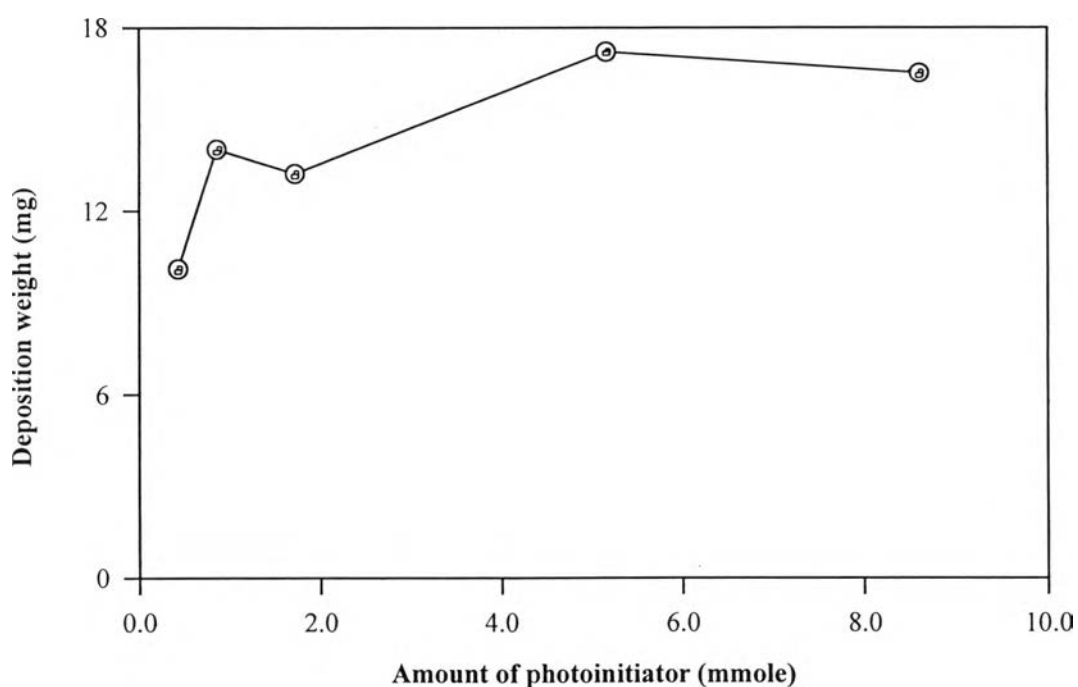


Figure 4.5 Deposition weight plotted as a function of amount of photoinitiator.

The amount of photoinitiator was varied from 0.430 to 8.612 mmole. The deposition weight is found to increase slightly with increasing amount of photoinitiator reaching a maximum at around 5 mmole as shown in Figure 4.5. This reveals that photoinitiator plays a decisive role in the polymerization and there is an optimum amount for maximum efficiency.

4.2.3 Effect of Deposition time

In this experiment, the quartz substrate was irradiated by 100 W UV lamp at 123.0 ml. N₂/min. flow rate, -5.0 °C substrate temperature, and 8.612 mmole of photoinitiator. The deposition time was varied from 4 to 24 hrs. The results are shown in Figure 4.6.

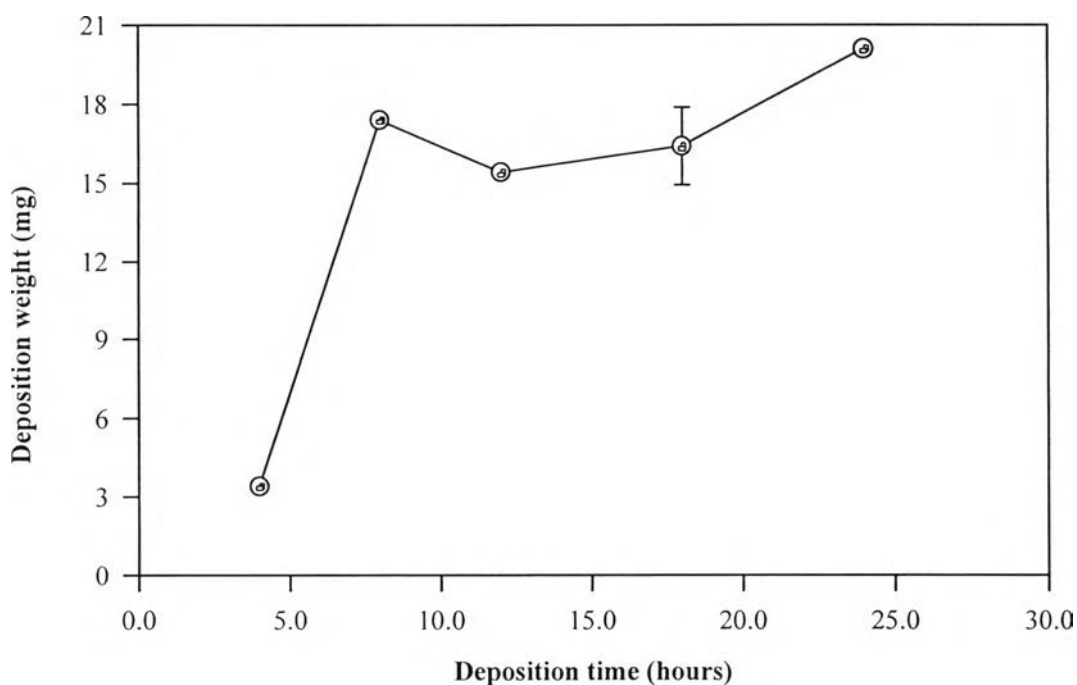


Figure 4.6 Deposition weight plotted as a function of deposition time.

Figure 4.6 shows that there is a sharp increase in deposition weight when the deposition time is increased from 4.0 to 8.0 hrs. The longer deposition time allows more monomers into the chamber with greater amount depositing on the substrate surface. However, after 8 hrs, the deposition weight tends to level off because then the surface becomes saturated.

4.2.4 Effect of Flow Rate

To study the effect of flow rate, the quartz disk was irradiated by 100 W UV irradiation lamp at $-5.0\text{ }^{\circ}\text{C}$ substrate temperature, with 8.612 mmole of photoinitiator and 8.0 hours deposition time. The flow rate was varied from 49.0 to 331.0 ml N_2/min . The results are shown in Figure 4.7. The deposition weight increases sharply as the flow rate is increased from 49.0 to 123.0 ml N_2/min . as shown in Figure 4.7. After this, there was only a slight increase in deposition weight as the flow rate was increased further.

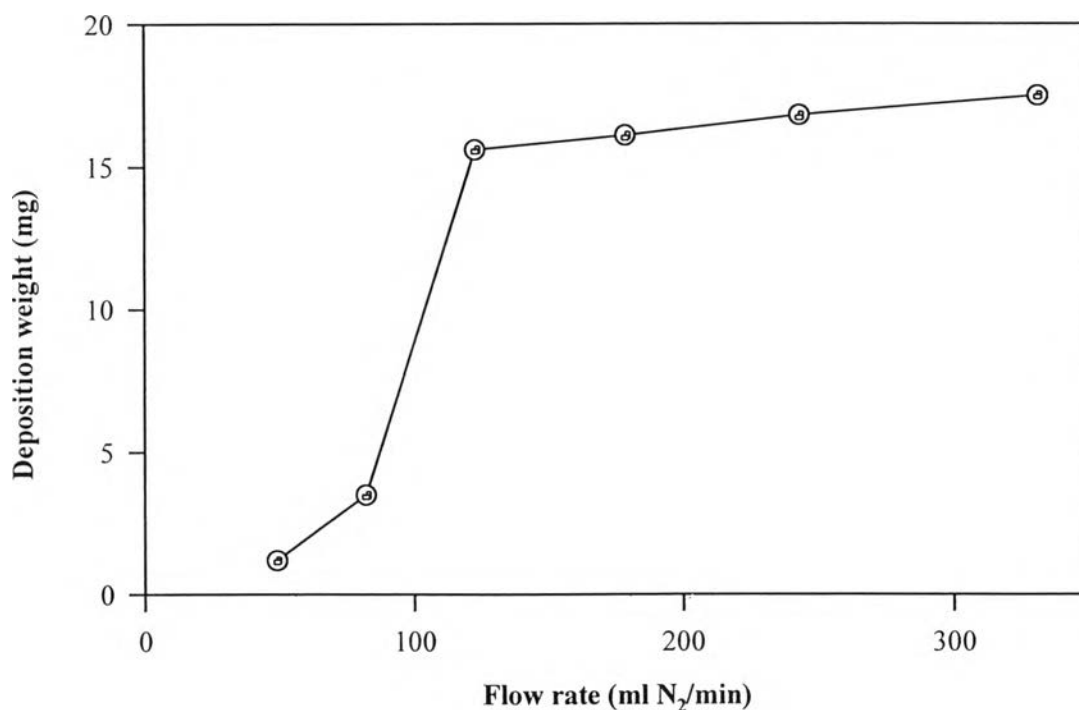
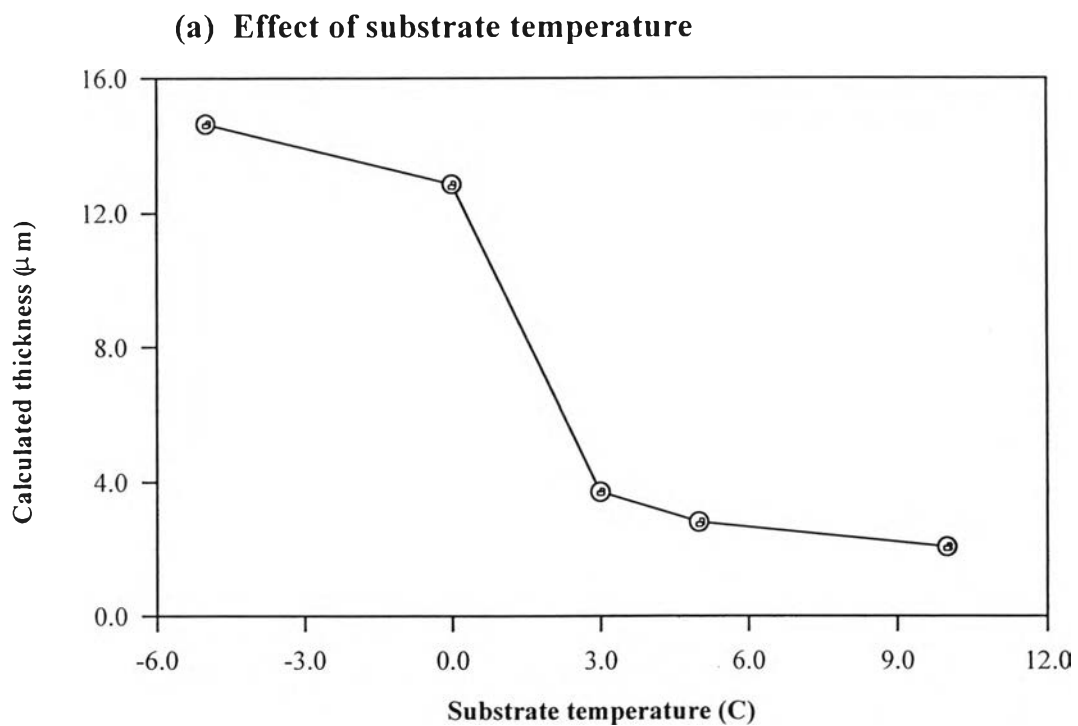


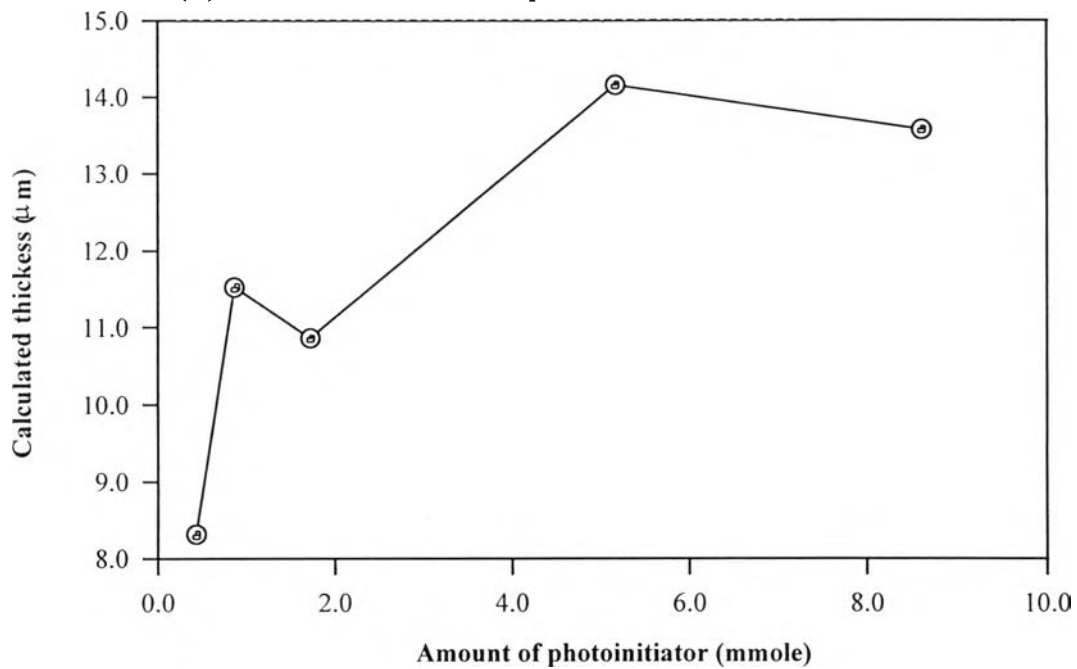
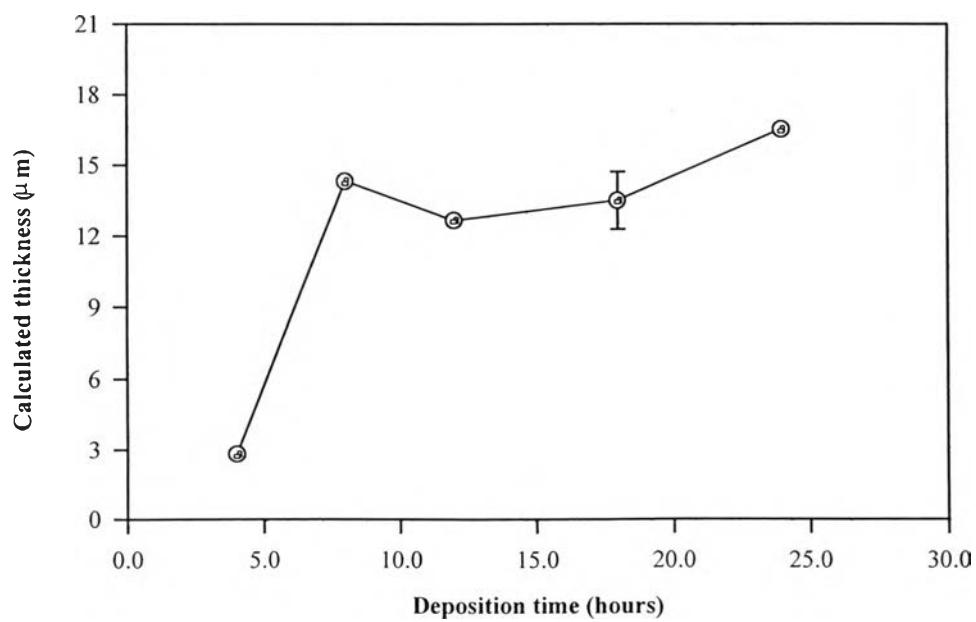
Figure 4.7 Deposition weight plotted as a function of flow rate

This indicates that above 100.0 ml N_2 / min there are no mass transfer limitations or monomer arrival limitations and that the rate of film deposition is governed by the rate of reaction.

4.3 Effect of Deposition Conditions on the Film Thickness

From the study of deposition weight, the estimated thickness can be derived (see Appendix I.2). Figure 4.8 (a-d) show the range of estimated thickness found in each experiment. The film thickness obtained in this work is found to range from 0.987 to 16.540 μm .



(b) Effect of amount of photoinitiator**(c) Effect of deposition time**

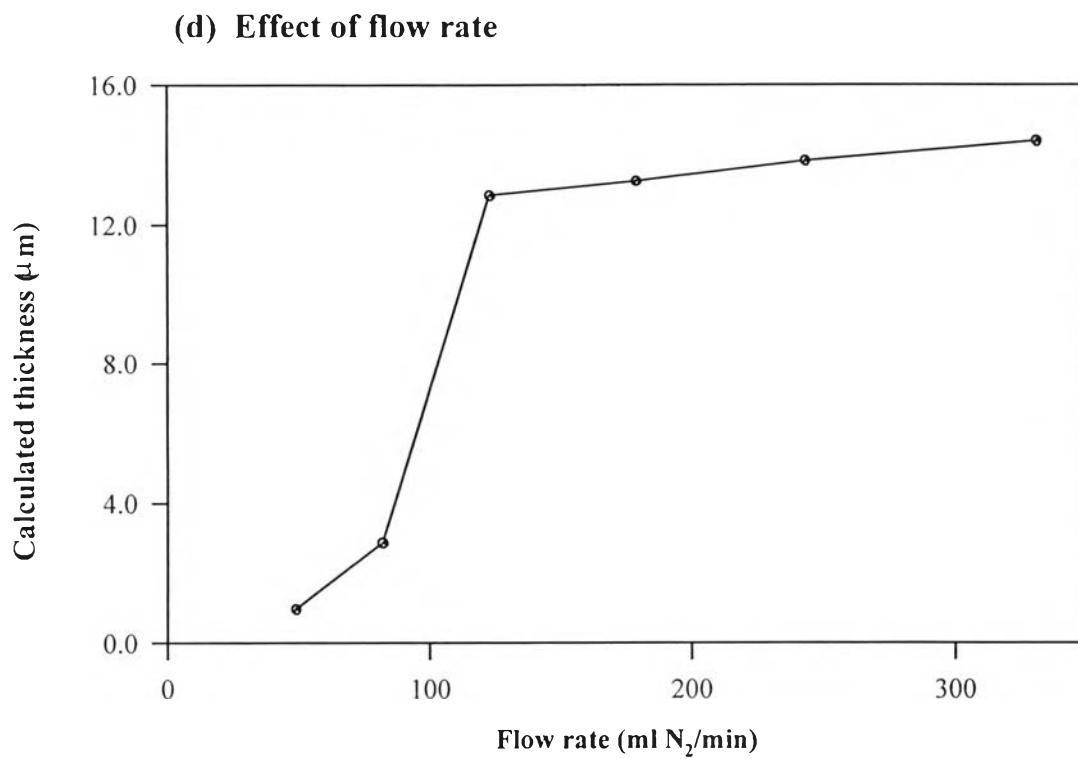


Figure 4.8 Calculated thickness plotted as a function of (a) substrate temperature; (b) amount of photoinitiator; (c) deposition time; (d) flow rate.

4.4 Effect of Deposition Conditions on Molecular Weight of the Deposited Film

The molecular weight was determined by GPC. In general, two peaks were observed at around 16 and 22 minutes respectively. The peak at 16 minutes was assigned as the polymer peak while the peak around 22 minutes was assigned as the monomer peak. Figure 4.9 gives a typical chromatogram obtained from one of the experiments.

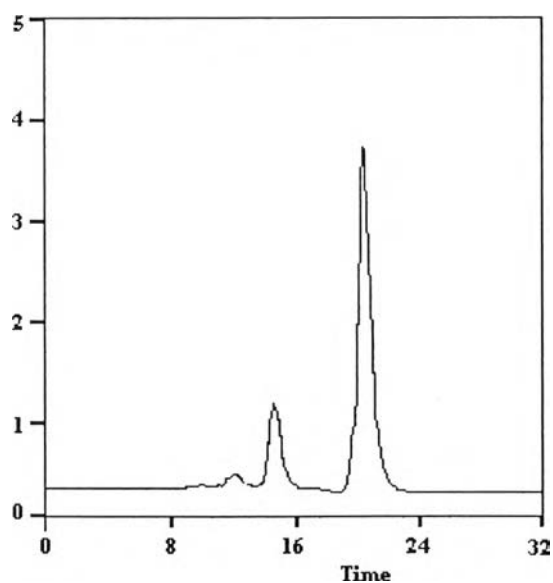
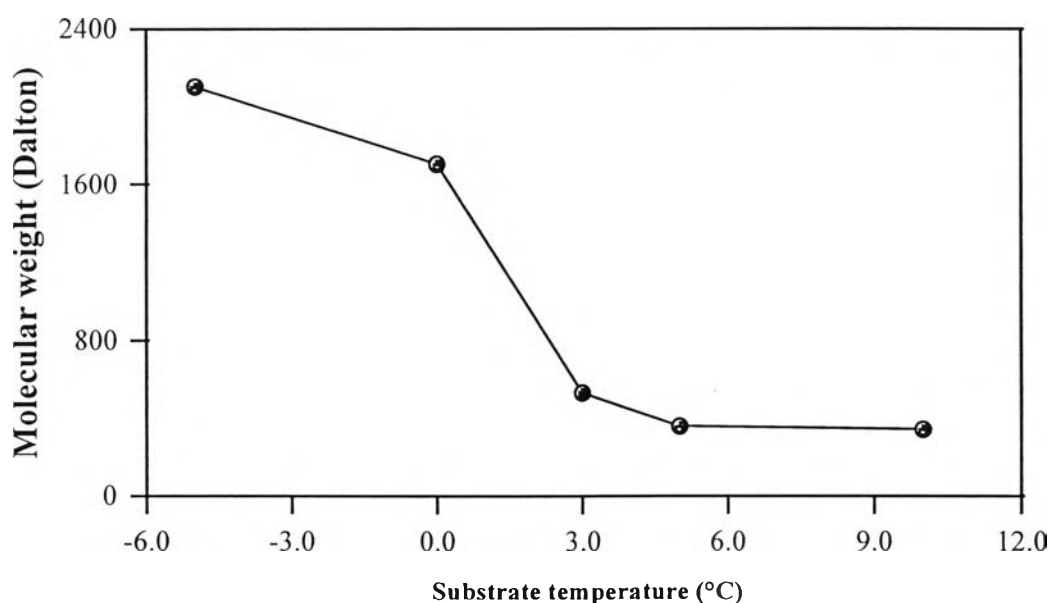


Figure 4.9 Typical chromatogram showing the polymer and monomer peaks at around 16 and 22 minutes.

4.4.1 Effect of Substrate Temperature

Figure 4.10 shows the variation of molecular weight with substrate temperature. It can be seen that the molecular weight is low and rather constant at the temperature above 5.0 °C. Sharp increase is observed as the substrate temperature is lowered from 5.0 to 0.0 °C. After 0 °C, the molecular weight continued to increase but with a slower rate to a maximum of 2300 at -5.0 °C. The results show that low substrate temperature is required for high molecular weight.

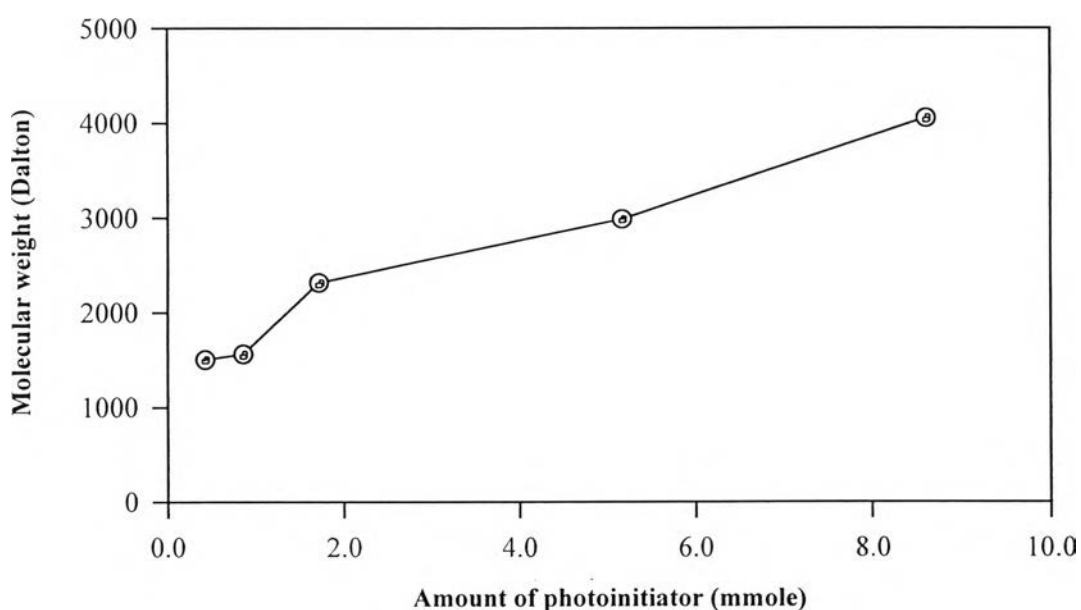


Conditions : flow rate = 123.0 ml. N₂/min., deposition time = 8.0 hrs.
purging time = 3.0 hrs., no photoinitiator

Figure 4.10 Effect of substrate temperature on molecular weight.

4.4.2 Effect of Amount of Photoinitiator

In Figure 4.11, molecular weight is plotted as a function of the amount of photoinitiator. Molecular weight was found to increase linearly with an increase in the amount of photoinitiator from 1500 to 4000.



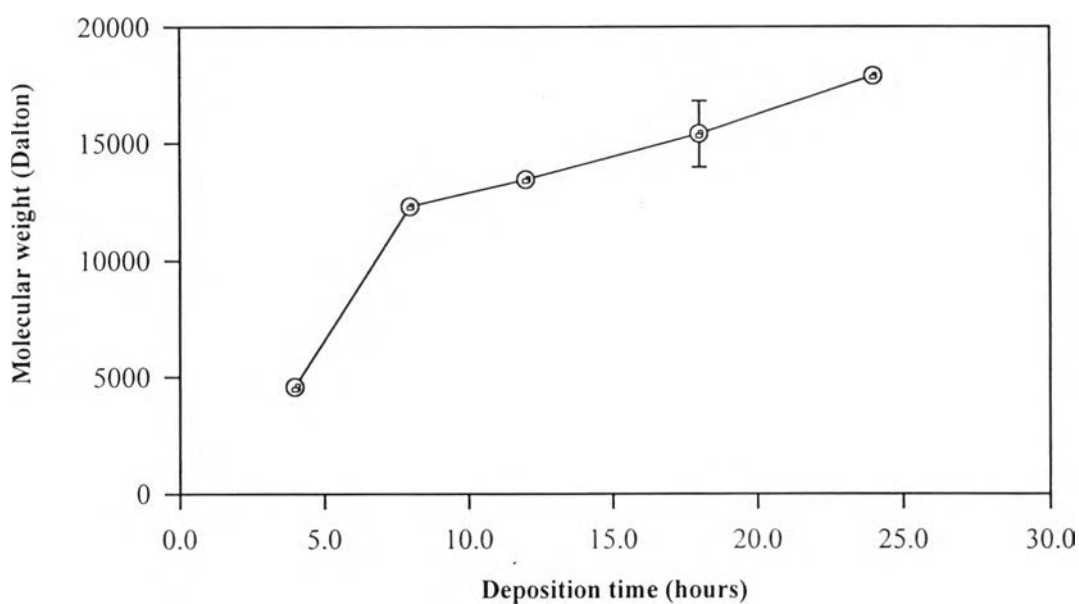
Conditions : flow rate = 82.0 ml. N₂/min., deposition time = 8.0 hrs.
purging time = 3.0 hrs., substrate temperature = -5.0 °C

Figure 4.11 Effect of amount of photoinitiator on molecular weight.

The increase in molecular weight with increase in the amount of photoinitiator is probably due to the immobility of free radicals on the substrate surface which inhibits termination of the radicals. The molecular weight is therefore found to increase proportional with the amount of initiator.

4.4.3 Effect of Deposition Time

In Figure 4.12, molecular weight is plotted as a function of deposition time. Molecular weight is found to increase with an increment of deposition time. The molecular weight increases sharply initially but after 10.0 hours, the increase in molecular weight is much slower.



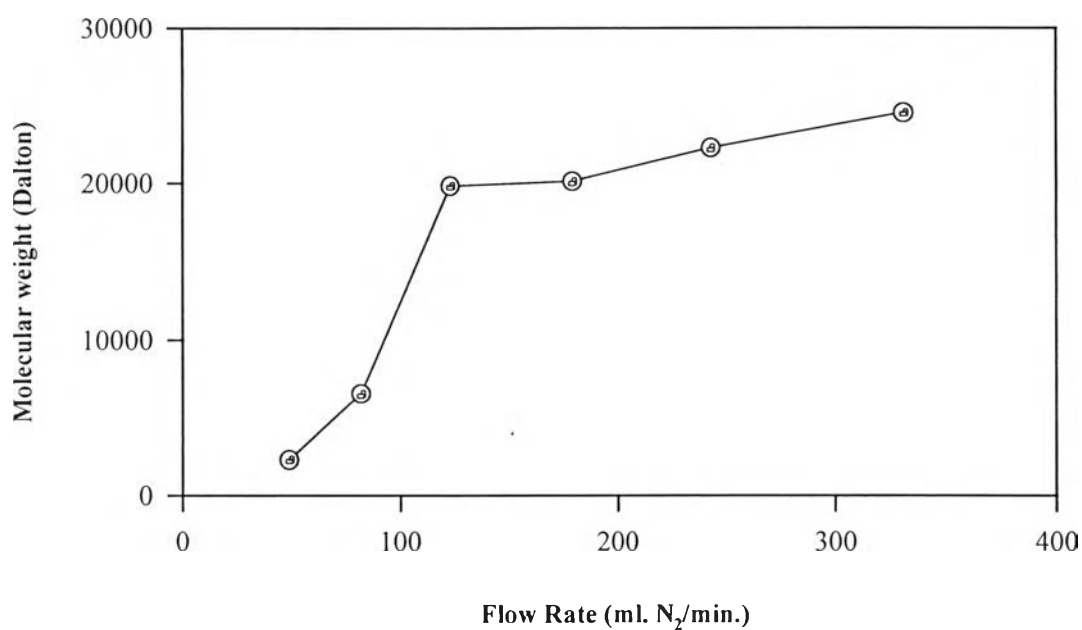
Conditions : flow rate = 123.0 ml. N₂/min., purging time = 3.0 hrs.
substrate temperature = -5.0 °C, photoinitiator = 8.612 mmole

Figure 4.12 Effect of deposition time on molecular weight.

With longer deposition time, more monomers are present in the reaction chamber leading to an increase in the molecular weight of deposited film. The increase is slower when the substrate surface becomes saturated.

4.4.4 The Effect of Flow Rate

In Figure 4.13, molecular weight is plotted as a function of flow rate. The molecular weight is found to increase sharply at the initial flow rate of 50-120 ml. N₂/min. But further increase in flow rate only induces gradual increase in molecular weight. The highest molecular weight obtained at 331 ml. N₂/min. flow rate is around 23,000.



Conditions : purging time = 3.0 hrs., substrate temperature = -5.0 °C
photoinitiator = 8.612 mmole, deposition time = 8.0 hrs.

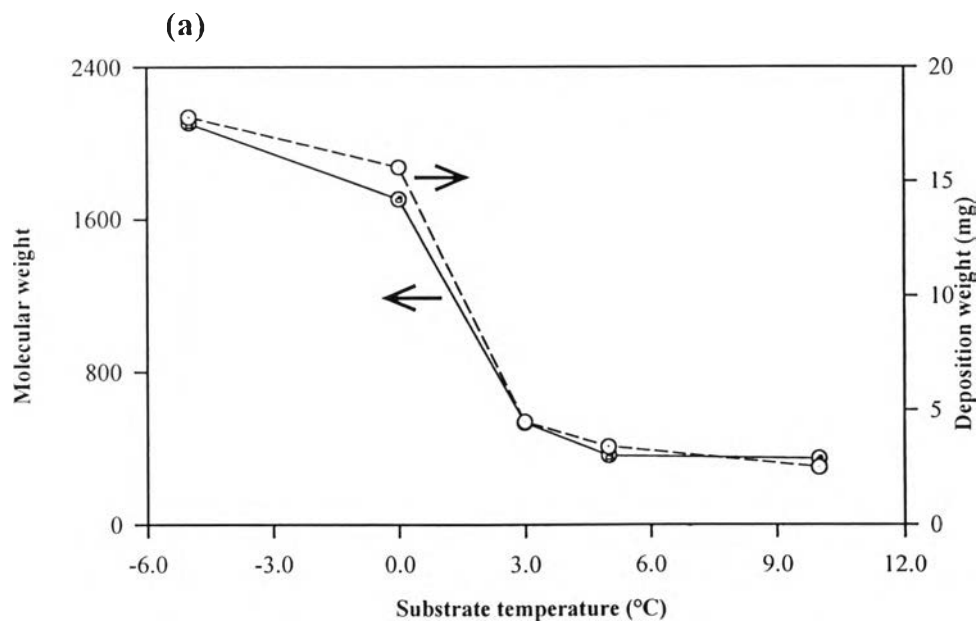
Figure 4.13 Effect of flow rate on molecular weight.

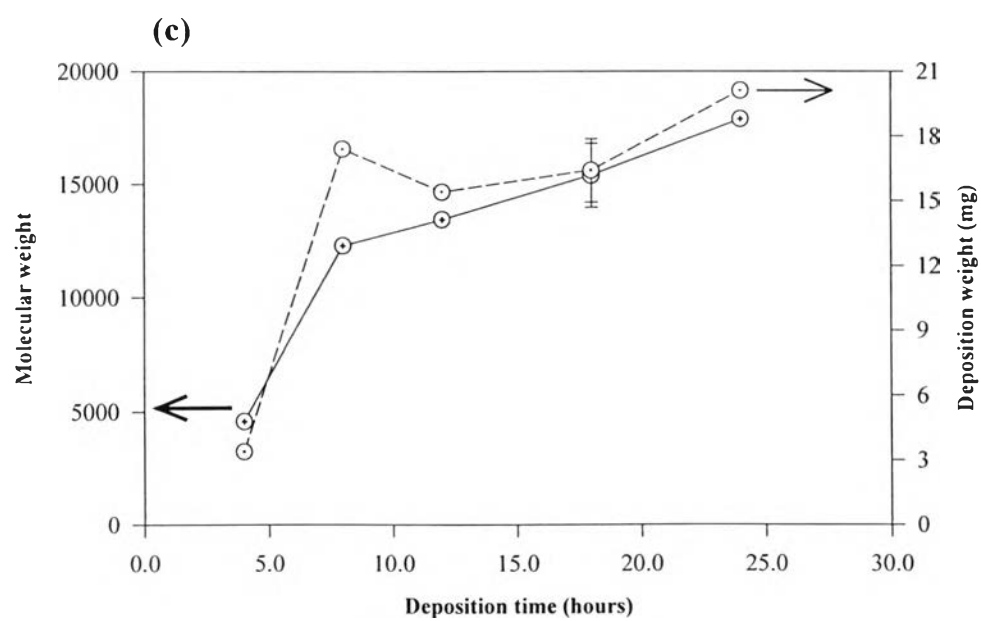
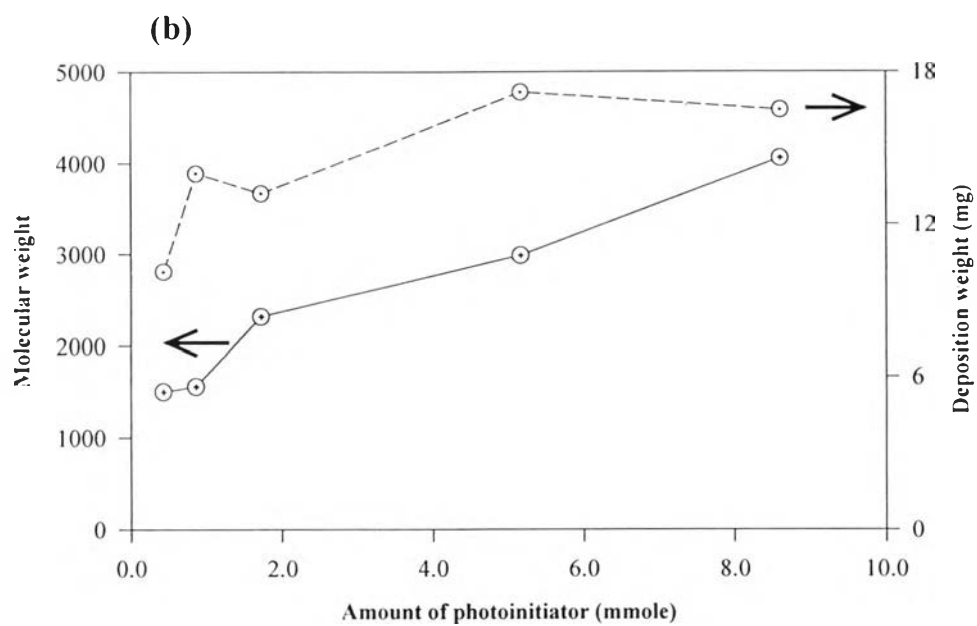
The increase in N₂ flow rate increases the rate of flow of monomer into the chamber. Therefore, at a fixed deposition time, more monomers are present in the chamber at higher flow rate leading to higher molecular weight. The increase is slowed down when the substrate surface

becomes saturated. The results show that there is an optimum flow rate for maximum yield.

4.5 Comparison between Deposition Weight and Molecular Weight

The deposition weight and molecular weight obtained from each experiment were plotted together in Figure 4.14 (a) - (d) to study their correlation.





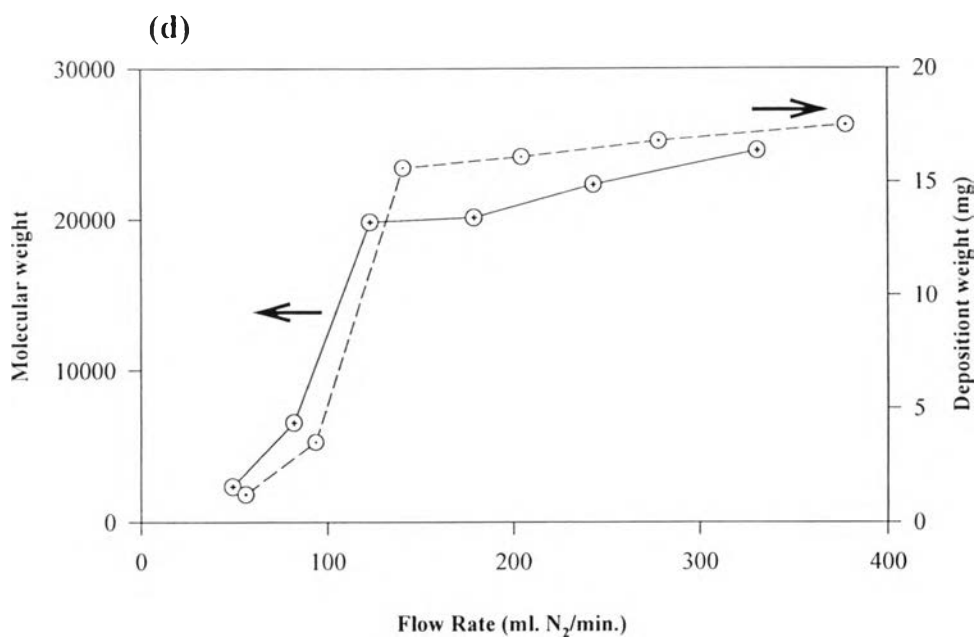


Figure 4.14 Molecular weight and deposition weight plotted as a function of (a) substrate temperature, (b) amount of photoinitiator, (c) deposition time, and (d) flow rate.

From the graphs, the change in deposition weight is found to correspond to the change in molecular weight which shows that polymerization increased with an increment of deposition weight. It is postulated that polymerization takes place with a 'live' polymer which continues to grow as the monomer is condensed on the surface. There is therefore a direct correlation between the molecular weight and the deposition weight.