

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Design and Construction of the Deposition Chamber

In this experiment, the deposition chamber was designed and constructed for preparing thin films of PMMA.

The important part of this system was the temperature controlled stage for substrate that had to be maintained at a suitable temperature. In the early work, the stage for substrate was designed to be hot surface by using a heater plate that was controlled by a temperature controller in the range of 0-399°C. Figure 4.1 shows the inner layout of the deposition chamber with hot substrate surface.

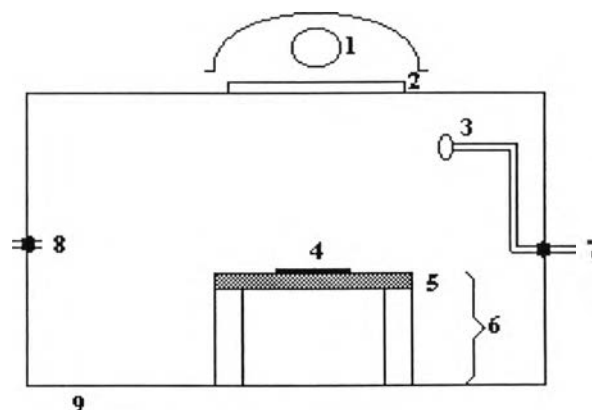


Figure 4.1 Inner layout of deposition chamber (hot surface system),
(1) Ultraviolet lamp; (2) Quartz window; (3) Manifold; (4) Substrate; (5) Heater; (6) Stage for substrate; (7) Gas feed to manifold; (8) Vent; (9) Chamber.

In this system the substrate temperature was heated up to the required temperature. The monomer was expected to go through the chamber and some of it would come into contact with the substrate and condense or absorb on it. The polymerization would then be initiated by 9 W UV lamp. Table 4.1 gives details of the parameters used in the experiments.

Table 4.1 Details of the parameters in the deposition on hot surface

Condition in the chamber	Atmospheric pressure(N ₂ atm)
N₂ flow rate (ml/min)	35 - 80ml/min*
Substrate temperature (°C)	25 - 50°C*
Temperature of water bath (°C)	55 °C
Irradiation time (hrs)	4 - 24 hrs*
Substrate	glass slide, quartz
Power of UV lamp (W)	9 Watts
The distance between substrate and UV lamp (mm)	100 mm

* Variation parameters

It was found that, with hot substrate surface, there was neither deposition nor polymerization of the monomer on the substrate, although a higher power UV lamp (100 W) was used and the deposition time was also increased. The distance between the substrate and UV lamp was decreased to 50 mm so that the substrate was nearer to the UV source.

These results showed that MMA monomer hardly deposited on the substrate at room temperature or higher. Thus, polymerization of PMMA was not possible when the monomer could not be condensed on the substrate.

A new system was therefore developed by changing the stage for substrate into a cold surface (Figure 4.2) using a thermoelectric cooling plate. The distance between substrate and UV source was also reduced. The 100 W UV lamp was again used to initiate the polymerization. Table 4.2 gives a summary of the results obtained by visual observation after the experimental conditions were modified.

Table 4.2 Results obtained on cold surface system

Irradiation time (hrs)	Substrate temperature (°C)	Deposition
4	20	none
4	10	low
4	5	medium
4	1	high
10	1	high
15	1	high
24	1	high

In the modified system, MMA was found to deposit on the substrate at substrate temperature below 10°C. However, after the irradiation and flowing of monomer were stopped and the substrate warmed up to room temperature, the deposited monomer was found to evaporate from the substrate. This shows that the polymerization did not occur and the unreacted monomers evaporated. The same results were obtained even when the deposition time was increased to 24 hrs, so it was possible that the 100 W UV source was not sufficient to initiate polymerization of MMA directly. Therefore a photoinitiator that

absorbs UV radiation that fits the radiation of the light source was used. The photoinitiator chosen was diphenyl(2,4,6-trimethyl- benzoyl)phosphine oxide. Figure 4.2 shows absorption spectrum of the initiator used compared to that of the radiation of the UV light source.

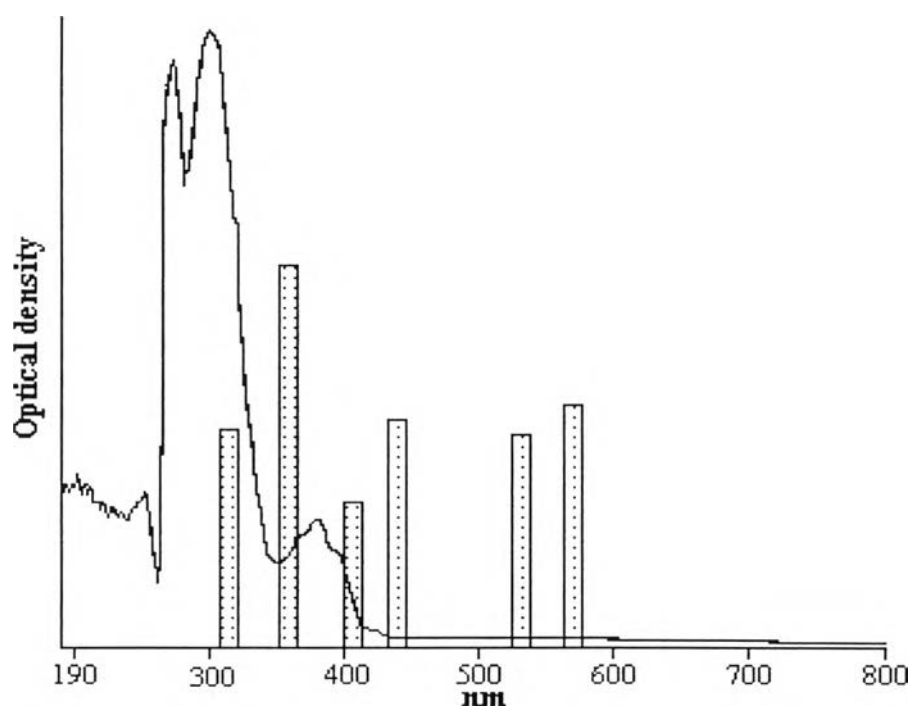


Figure 4.2 Absorption spectrum of diphenyl(2,4,6-trimethylbenzoyl) phosphineoxide which match the emission spectrum of the UV lamp.

The photolysis of this photoinitiator occurs by rupture of the $\text{-CO} = \text{PO-}$ bond. The phosphonyl radicals are highly reactive toward vinyl monomers.

To apply the initiator to the system, the substrate surface was coated with a solution of diphenyl(2,4,6-trimethylbenzoyl)phosphineoxide in chloroform (pale yellow solution) prior to deposition. It was found that a transparent thin film was formed on the cold surface after deposition of monomer. Table 4.3 gives details of the deposition conditions used in subsequent experiments, which yielded deposition of thin film of PMMA.

Table 4.3 Details of the parameters in the deposition on cold surface

Condition in the chamber	Atmospheric pressure(N ₂ atm)
N₂ flow rate (ml/min)	35 - 80ml/min*
Substrate temperature (°C)	5°C - 0°C *
Temperature of water bath (°C)	55 °C
Irradiation time (hrs)	2 - 6 hrs*
Substrate	quartz
Power of UV lamp (W)	100 Watts
The distance between substrate and UV lamp (mm)	50 mm

*Variable parameters

Since all the experiments were performed at ambient pressure, it was important to eliminate the problem of air inhibition by conducting the photopolymerization in an inert atmosphere such as N₂. Table 4.4 shows the effect of purging time of N₂ on polymerization. It can be seen that at least 3 hrs. purging time was required for initiating the polymerization. This clearly shows the importance of eliminating O₂ from the system.

Table 4.4 Effect of N₂ purging time on polymerization

Purging time (hrs.)	Polymerization
1	none
2	none
3	thin film on substrate
4	thin film on substrate

4.2 The Effect of Variable Parameters on the Deposition of PMMA

4.2.1 The Effect of % Photoinitiator

In this study, the concentration of photoinitiator solution used was varied from 0.5 - 2.5%. Figure 4.3 and 4.4 show the effect of concentration of photoinitiator on film thickness and molecular weight of the deposited film. The thickness and molecular weight of film increased with an increase in concentration of photoinitiator on the substrate. The thickness was found to increase from 4.9 to 104 μm . There was very little change in film thickness at concentration below 1% but the thickness increased sharply when the %photoinitiator was increased from 1-2%. There was however a slower increase after 2%. The results show that the photoinitiator is critical to the formation of thin film on the surface and the amount of film deposition depends on the concentration of the photoinitiator. In the case of molecular weight of the deposited film, it was found that there was a steady increase of MW from 213,839 to 371,346 when the % photoinitiator was increased from 0.5% to 2.5%. This shows that the photoinitiator has a direct influence on the molecular weight of the deposited film.

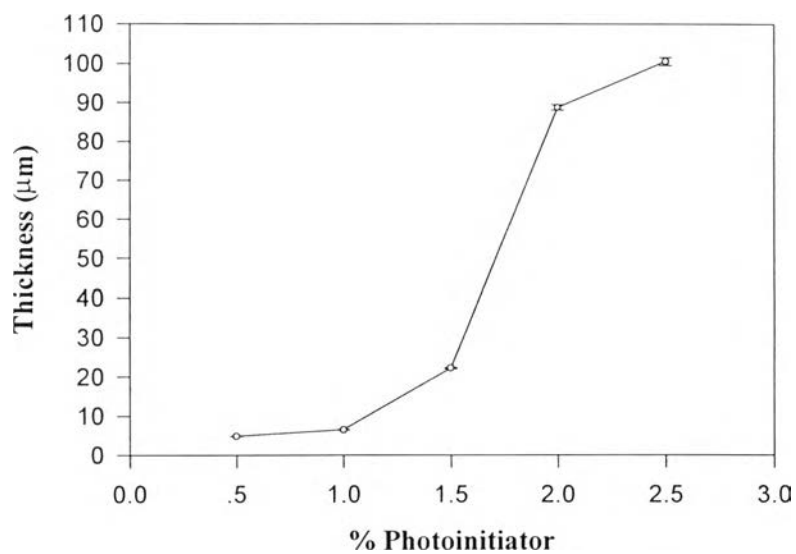


Figure 4.3 Effect of concentration of photoinitiator on film thickness
($D_t = 4$ hrs, $F_{N_2} = 110$ ml/min , $T_S = 268$ K).

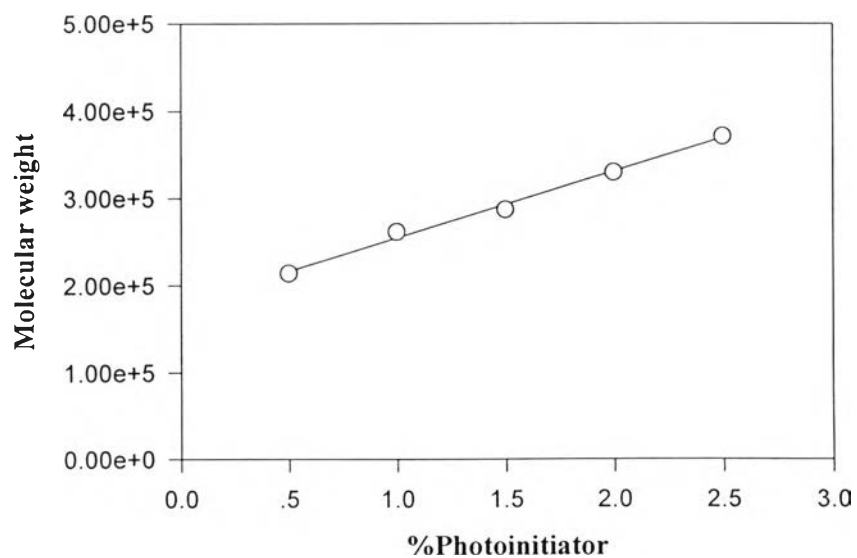


Figure 4.4 Effect of concentration of photoinitiator on molecular weight
of the deposited film ($D_t = 4$ hrs, $F_{N_2} = 110$ ml/min, $T_S = 268$ K).

4.2.2 The Effect of Deposition Time

In this experiment, the deposition time was varied from 2 to 10 hours. Figure 4.5 shows the effect of deposition time on film thickness. It was found that film thickness increased with increase in deposition time. The increase was greatest between 4 - 8 hours. The increase in deposition time allowed more monomers into the chamber and hence more deposition was achieved.

Figure 4.6 shows the effect of deposition time on molecular weight. The molecular weight is found to increase monotonously with deposition time from 150,000 to 450,000 throughout the whole range. With longer deposition time, the monomer has longer time to react, and more monomers are available for reaction, the molecular weight of the deposited film therefore increases with increase in deposition time. From the results it may be postulated that there are living polymers on the surface and that the initiator is capable of restarting chain growth of a polymer that has stopped growing. This leads to higher molecular weight with increase in deposition time.

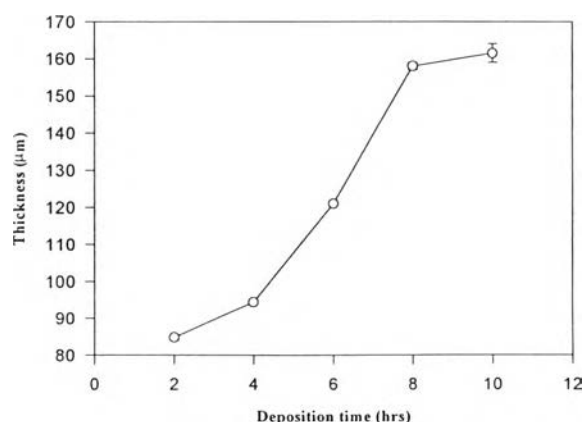


Figure 4.5 Effect of deposition time on film thickness

(% photoinitiator = 2.5, F_{N_2} = 90 ml/min, T_S = 268 K).

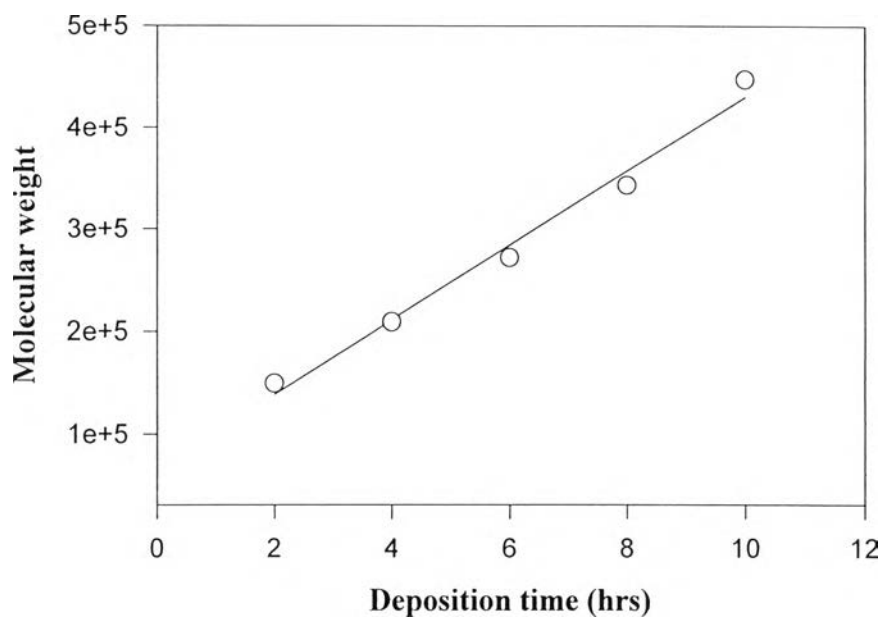
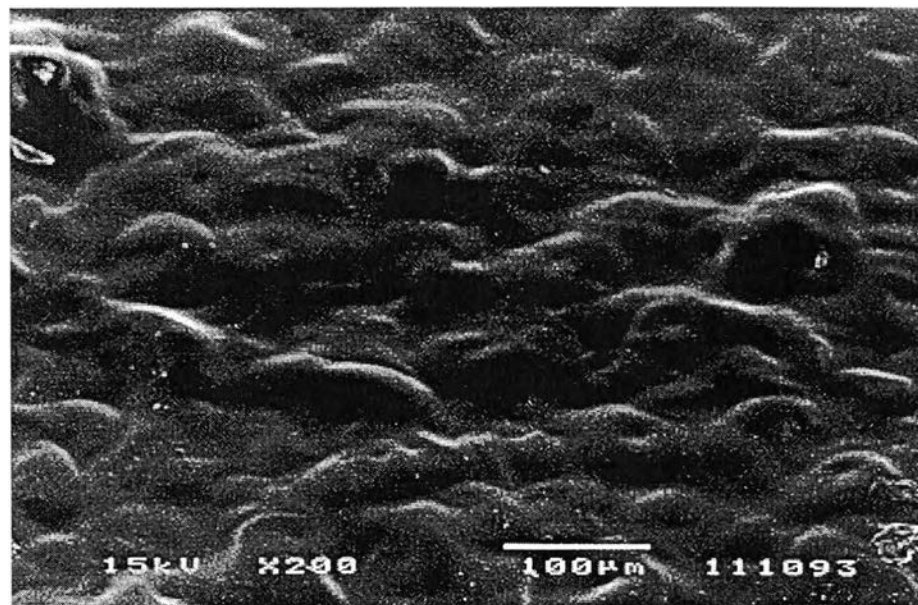
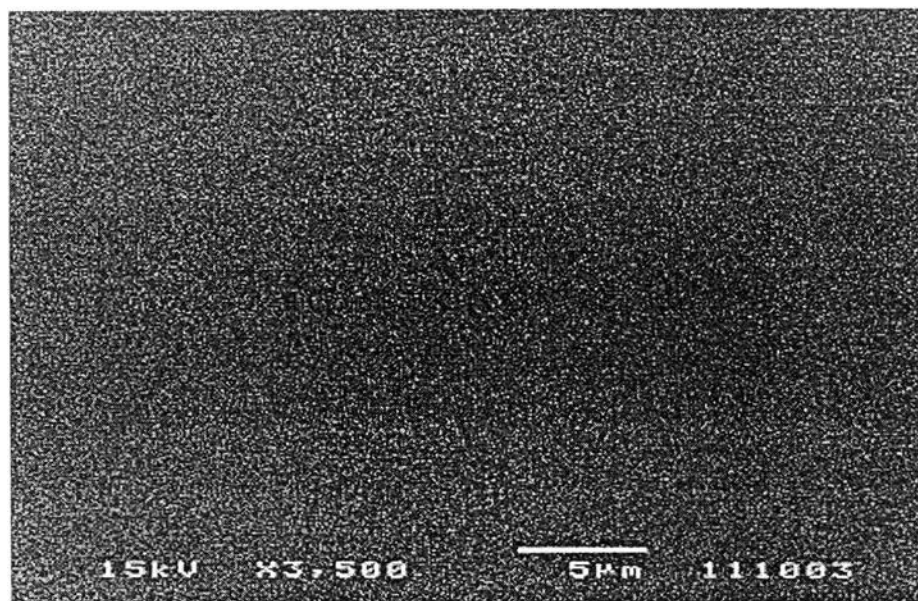


Figure 4.6 Effect of deposition time on molecular weight of the deposited film (% photoinitiator = 2.5, $F_{N_2} = 90$ ml/min, $T_s = 268$ K).

Figure 4.7 shows the surface characteristics of PMMA film at 2 and 4 hrs of deposition time. It can be seen by SEM that the surface is very rough with deposition time of 2 hrs. However with increase in the deposition time, the film becomes more uniform and transparent. This is may be due to the fact that at 2 hrs of deposition time, the system was not saturated with the MMA vapor, thus the incident rate of monomer and evaporation rate of unreacted monomer were not equal. This led to a very rough surface as shown in Figure 4.7a. As the deposition time was increased, the film became smooth because the system was saturated with the monomer vapor. (Figure 4.7b).



(a)



(b)

Figure 4.7 Surface of PMMA film at various deposition times
(a) Deposition time = 2 hrs; (b) Deposition time = 4 hrs
(%photoinitiator = 2.5%, F_{N_2} = 90 ml/min, T_S = 268 K).

4.2.3 The Effect of Irradiation Time

In this section, the disappearance of MMA monomer under the influence of ultraviolet radiation was studied. The 100 W UV lamp was used as the irradiation source and it was left on for up to 10 hours after switching off the monomer flow. It was found that, when monomer flow was stopped after 4 hours, the film thickness decreased when the irradiation time was increased (Figer 4.8). The result shows that very little polymerization takes place after the monomer flow is stopped and unreacted monomers evaporate from the surface. A decrease in film thickness is therefore observed.

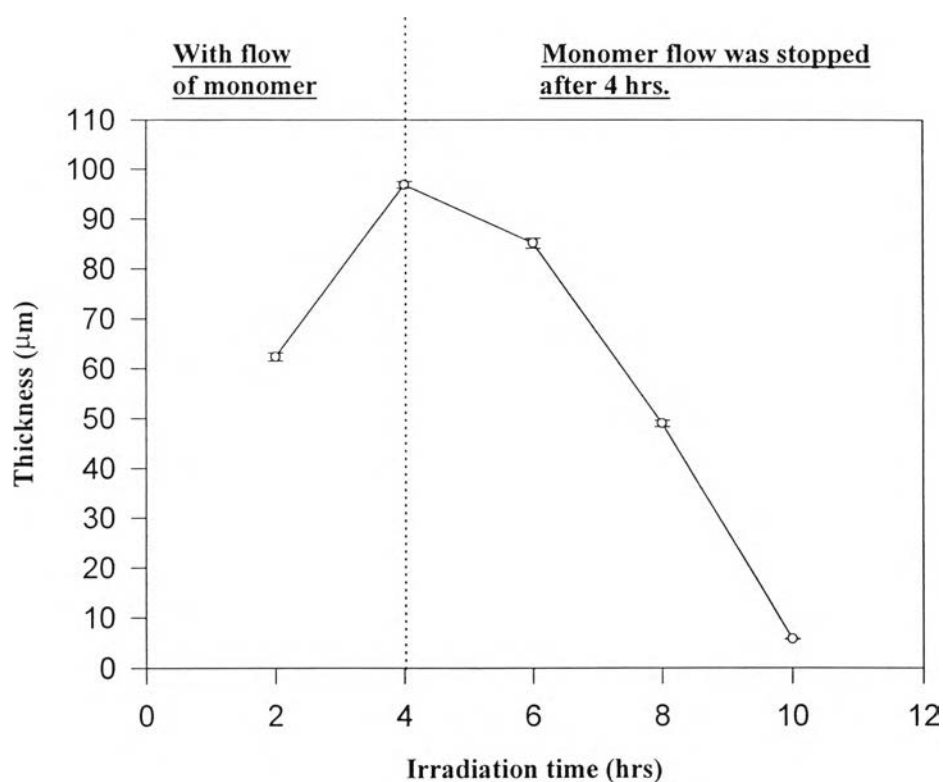


Figure 4.8 Effect of irradiation time on film thickness

(% photoinitiator = 2.5, $F_{N_2} = 110$ ml/min, $T_S = 268\text{K}$).

The evaporation of monomer is due to the excess heat generated by the UV lamp causing evaporation of the volatile monomers. Other worker has also observed similar effect with increase in irradiation time (Fouassier, 1993).

Figure 4.9 shows the IR spectra of deposited film at different irradiation times. The absorption peak at 1637 cm^{-1} assigned to C=C stretching was found to decrease markedly. At the irradiation time of 10 hrs the C=C stretching disappeared indicating the disappearance of monomer. The result confirmed that the increase in irradiation time led to a decrease in unreacted monomer.

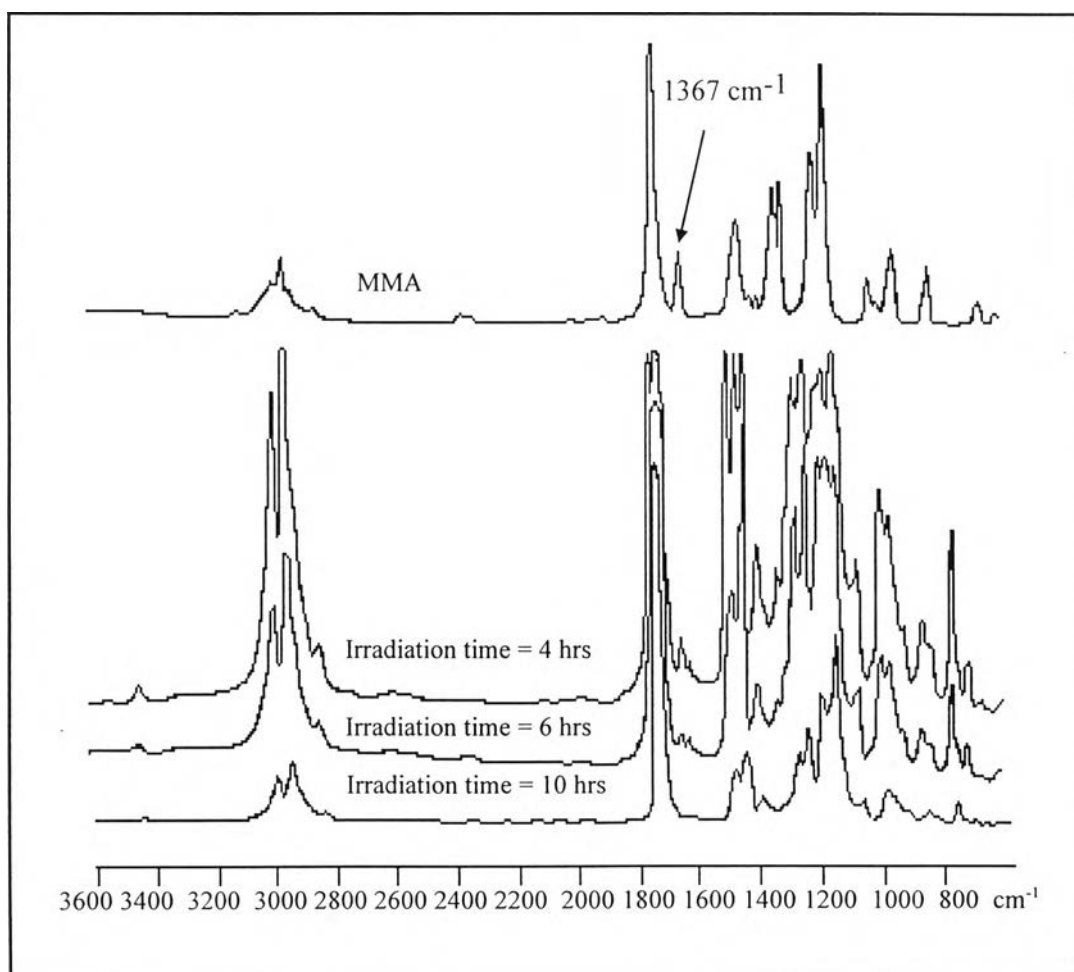


Figure 4.9 IR spectra of films deposited at various irradiation times.

4.2.4 The Effect of Substrate Temperature

The temperature of substrate has considerable effect on the formation of deposited film. At high substrate temperature, the number of adsorbed molecules is less than in the case of low substrate temperature. Hence for a fixed % photoinitiator, N_2 flow rate, and deposition time, the rate of film formation will be greater at low substrate temperature (Takasaki and Iijima,1991). This was confirmed in the present work.

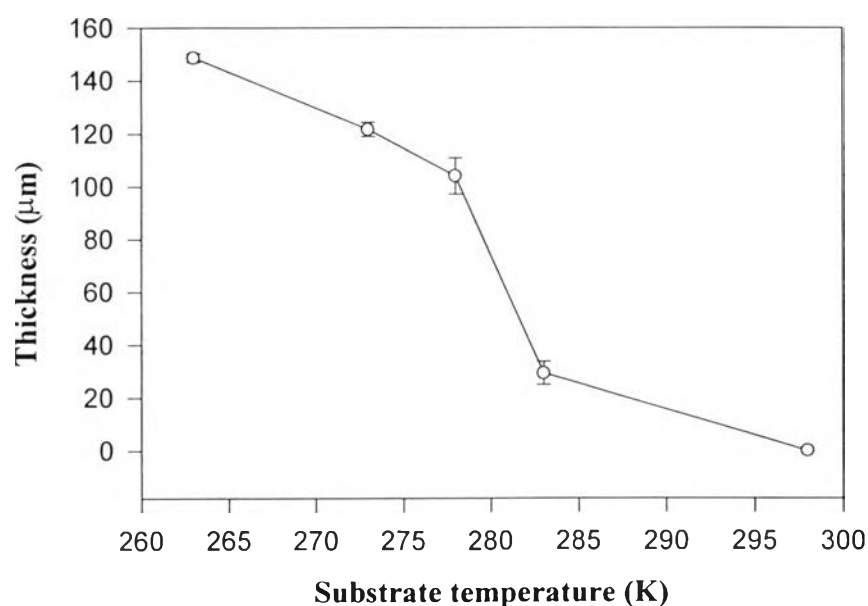


Figure 4.10 Effect of substrate temperature on film thickness
(% photoinitiator = 2.5, F_{N_2} = 110 ml/min, D_t = 4 hrs).

Figure 4.10 and 4.11 show the effect of substrate temperature on film thickness and molecular weight of the deposited film. The substrate temperature was varied from 263 K to 298 K. It was found that both the film thickness and molecular weight increased as substrate temperature decreased.

The results show that film deposition is more favorable at lower substrate temperature.

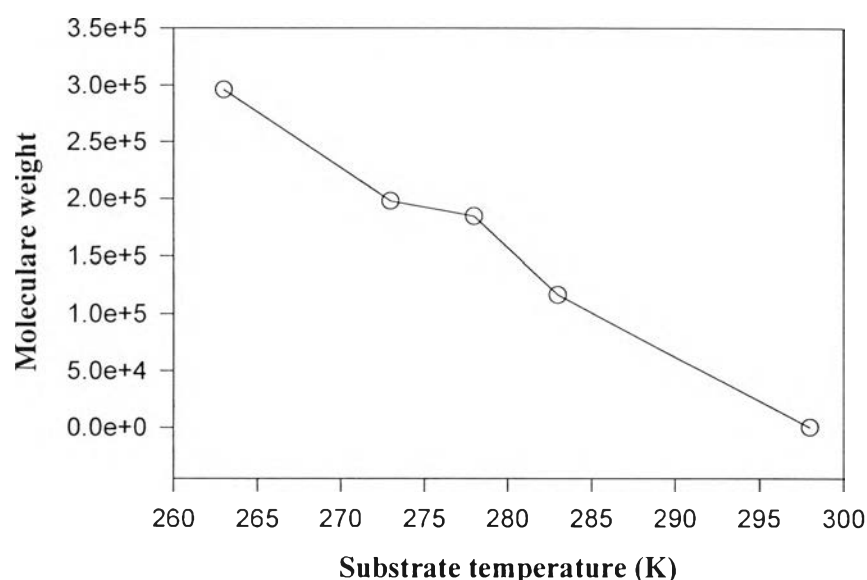
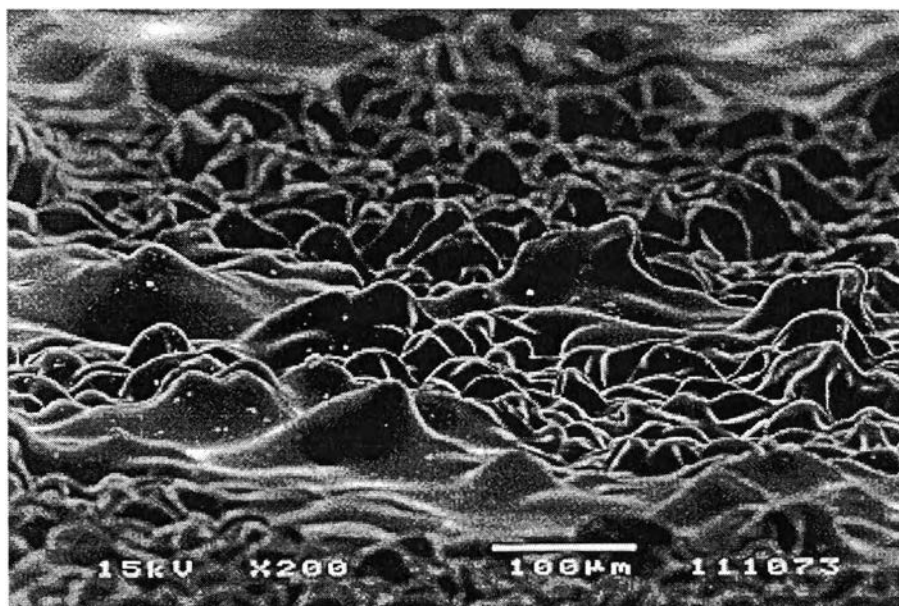
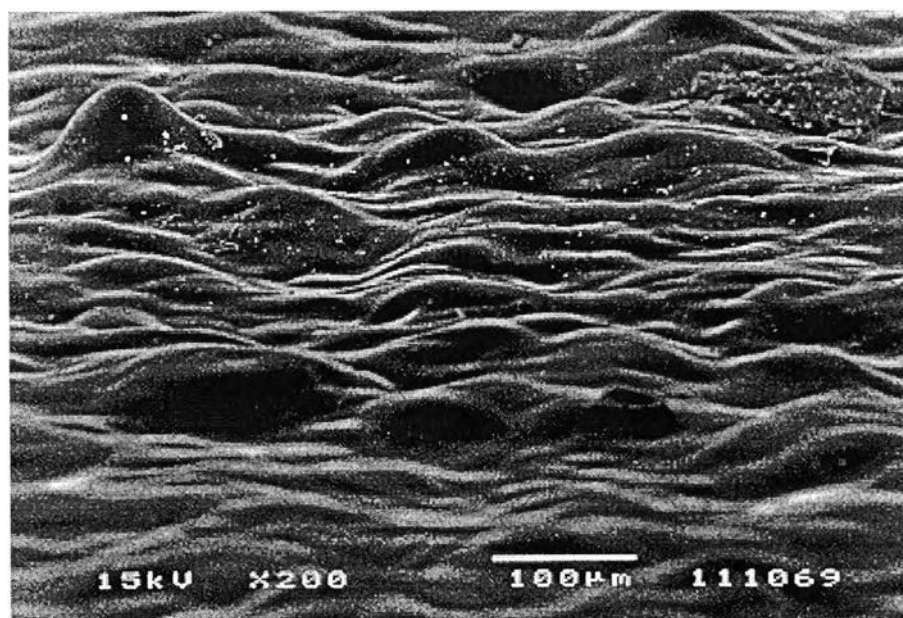


Figure 4.11 Effect of substrate temperature on molecular weight of deposited film (% photoinitiator = 2.5, $F_{N_2} = 110$ ml/min, $D_t = 4$ hrs).

Figure 4.12 shows the electron micrographs of the film surface at various substrate temperatures. It can be seen that at the substrate temperature of 283 K, the film surface was very rough indicating non-uniform monomer deposition. At substrate temperature of 273 K, the film became smoother, there were however a lot of porosities in the surface because some unreacted MMA monomers could still evaporate from the surface. At the substrate temperature of 263 K, the porosity disappeared and the surface became smooth because the MMA monomers hardly evaporated from the substrate resulting in an increase in molecular weight and film thickness. It can be concluded that deposition is more effective at low substrate temperatures.

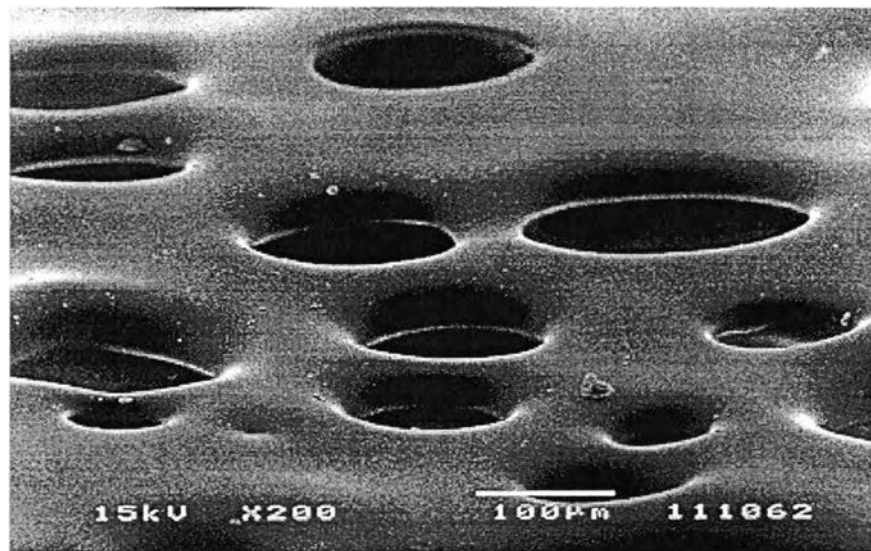


(a)

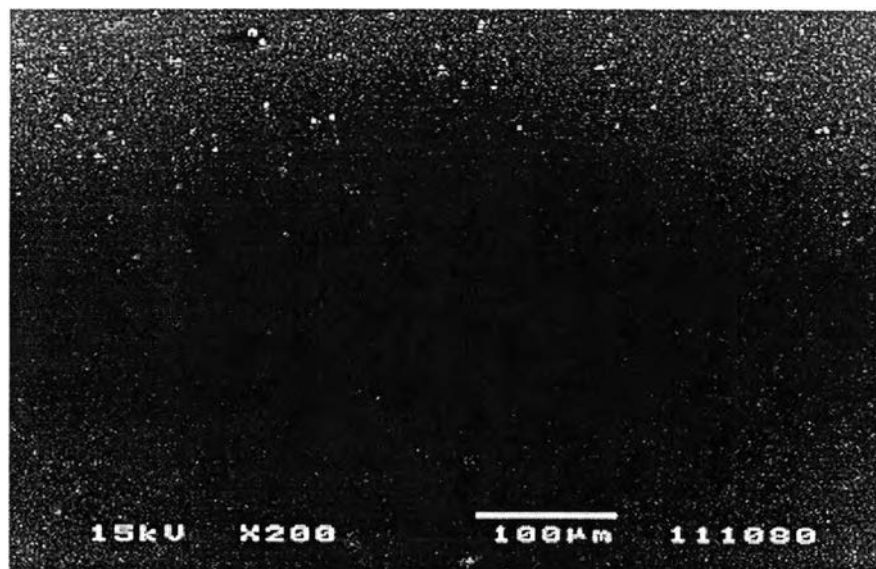


(b)

Figure 4.12 Change in the surface of PMMA film at various substrate temperatures (a) Substrate temperature 283 K; (b) Substrate temperature 278 K (% photoinitiator = 2.5, $F_{N_2} = 110$ ml/min, $D_t = 4$ hrs).



(c)



(d)

Figure 4.12 (continued) Change in the surface of PMMA film at various substrate temperature (c) Substrate temperature 273 K; (d) Substrate temperature 263 K (% photoinitiator = 2.5, $F_{N_2} = 110$ ml/min $D_t = 4$ hrs).

4.2.5 The Effect of N₂ Flow Rate

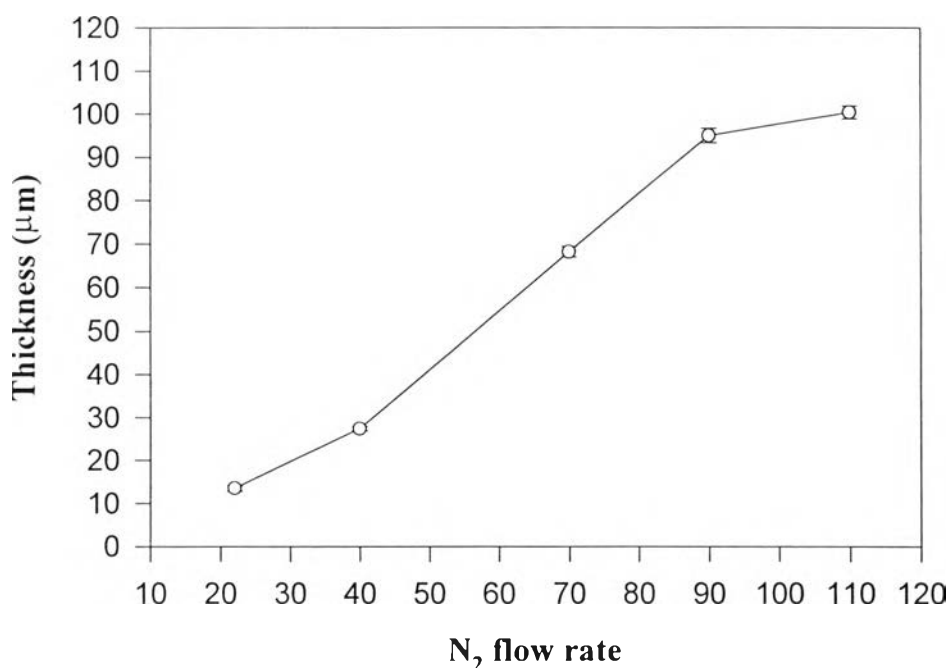


Figure 4.13 Effect of N₂ flow rate on film thickness

(% photoinitiator=2.5, $D_t = 4$ hrs $T_s = 268$ K).

The flow rate of N₂ through the liquid monomer determines the amount of monomer in the chamber. It was found that when the flow rate of N₂ increased, the film thickness and molecular weight also increased (Figures 4.13-4.14).

Figure 4.15 shows the electron micrographs of film surface at different N₂ flow rates. It can be seen that, at 22 ml/min of N₂ flow rate, the film surface is very rough with deep grooves while at N₂ flow rate of 40 ml/min, the surface becomes more transparent and smooth with shallow grooves (Figure 4.15(b)). At the N₂ flow rate of 70 ml/min the surface becomes even more smoother with no porosity. This can be explained that at

low N_2 flow rate, only a small amount of monomer is deposited on the surface resulting in a non-uniform deposition. At higher N_2 flow rate, the system is saturated with MMA vapor, so the porosities or grooves on the surface decrease and the film surface becomes smoother. This is accompanied by an increase in the molecular weight of PMMA as shown in Figure 4.14.

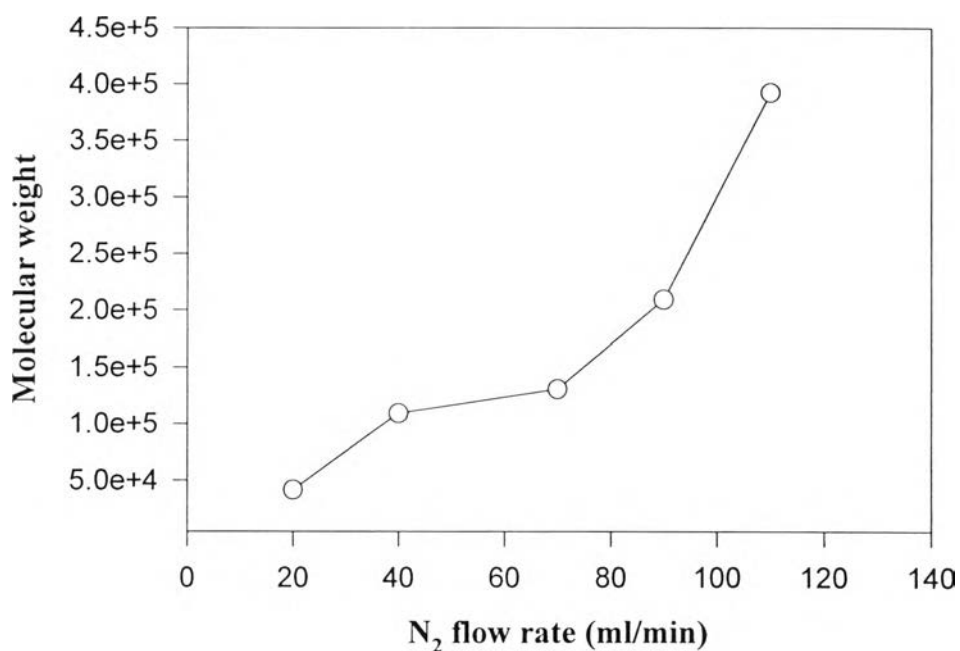
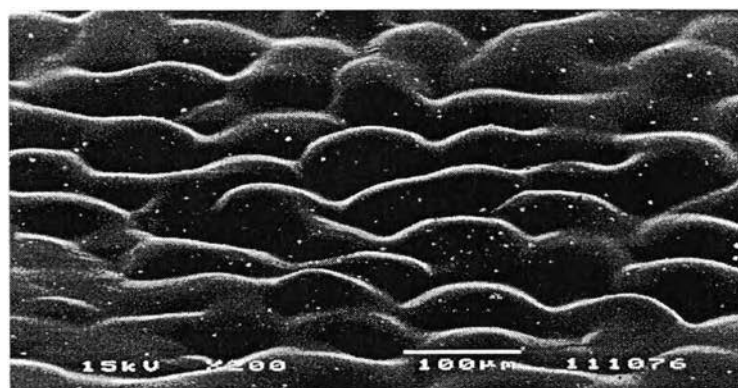
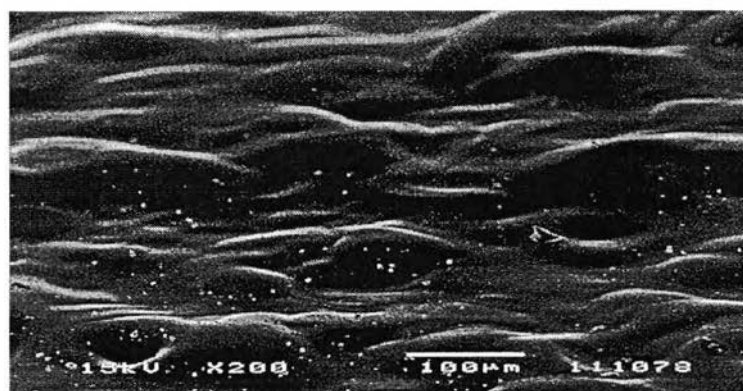


Figure 4.14 Effect of N_2 flow rate on molecular weight of deposited film (% photoinitiator = 2.5, $D_t = 4$ hrs, $T_S = 268$ K).



(a)



(b)



(c)

Figure 4.15 Film surface at various N₂ flow rates (a) N₂ flow rate 22 ml/min; (b) N₂ flow rate 40 ml/min; (c) N₂ flow rate 70 ml/min (% photoinitiator =2.5, D_t = 4 hrs, T_S = 268 K).