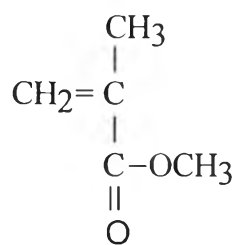


CHAPTER III EXPERIMENTAL SECTION

3.1 Materials

Methyl methacrylate (MMA) was used as monomer in this work. It was purchased from Fluka Chemica Co.,Ltd. The properties of MMA are listed in Figure 3.1.

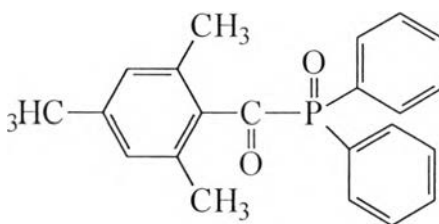


MMA

MW	: 100.11	Refractive index, n_D^{25}	: 1.4120
Boiling point	: 101 °C	Vapor pressure (mbar)	: 42.720
Melting point	: -48 °C	Heat of vaporization	: 0.36 kJ/g
Density	: 0.939 g/cm ³ (25 °C)	Heat of polymerization	: 57.7 kJ/mol

Figure 3.1 Chemical structure and properties of MMA.

A new type of photoinitiator that absorbs light relatively strongly between 350 and 400 nm, diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide, was purchased from Aldrich Co., Ltd. This photoinitiator shows negligible yellowing in resulting film.



MW	: 348.35
Melting point	: 88-92 °C

Figure 3.2 Chemical structure and some properties of the photoinitiator.

Quartz (4mm thick, 25mm long and wide) and glass slides (3 mm thick, 35 mm long and 25 mm wide, from Shanghai Machinery Corporation) were used for substrates.

Tetrahydrofuran (THF, AR grade) was purchased from Lab-Scan and used as the mobile phase for GPC.

N₂ was used as carrier gas. It was provided from Paxair. Before mixing with the vaporized monomers, the N₂ carrier gas was metered through flow meter to the desired amount at room temperature.

High Intensity-Long Wavelength UV Lamp. The specifications of the lamp are :

Wavelength	: 365 nm
Intensity	: 21,7000mW/cm ² at 2" and 8900mW/cm ² at 10"
Wattage	: 100 watts

3.2 Instruments

3.2.1 Fourier Transform Infrared Spectrometer (FTIR)

The BIO-RAD FTS45A Fourier Transform Infrared (FTIR) spectrometer was used to observe the polymerization and IR spectra of deposited film. The FTIR was carried out in a transmission mode with a resolution of 8 cm^{-1} , 16 number of scan per sample.

3.2.2 UV/Vis Spectrophotometer (UV/Vis)

The Perkin Elmer Lambda-16 UV-Vis spectrophotometer was used to determine the absorption spectra of photoinitiator to confirm that the absorption spectra of photoinitiator was in the range of emission of 100 W UV lamp.

3.2.3 Scanning Electron Microscope (SEM)

SEM digitized photographs were obtained from JEOL 5200-2AE (MP 15152001), with a magnification range of 35-200,000 times. The film surface and the film thickness of PMMA were studied using accelerated voltage of 15 kV by 150-3500 magnification.

3.2.4 Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography was performed on a Water Associates Model 150, a viscosity detector and refractive index detector (RI) are used. PL gel 10 mm MIXED-B column was used with molecular weight resolving range 500-10,000,000. Injection size was 50-125 ml of 0.3% solution with an elution rate of 22ml/min. Tetrahydrofuran (AR grade) from Lab-Scal was used as the mobile phase. The molecular weight distribution of the PMMA film was measured relative to linear monodisperse polystyrene standards.

3.3 Experimental Procedures

3.3.1 The Construction of the Thin Film Deposition Chamber.

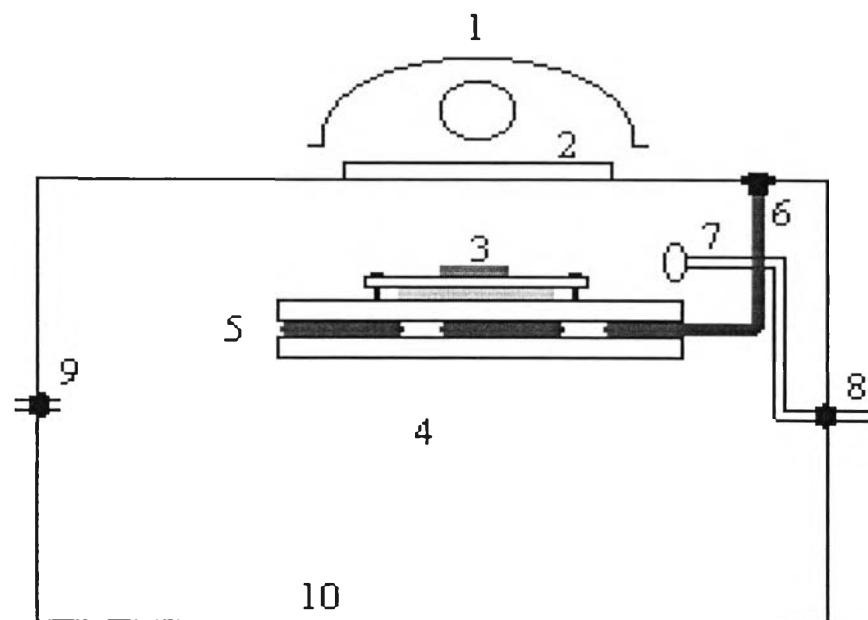


Figure 3.3 Inner layout of thin film deposition chamber, (1) Ultraviolet lamp; (2) Quartz window; (3) Substrate; (4) Stainless steel plate; (5) Cooling plate; (6) Water cooling system; (7) Manifold; (8) To manifold; (9) Vent; (10) Chamber.

Figure 3.3 shows the inner layout of thin film deposition chamber. The chamber is made of stainless steel. The dimensions are 150 mm in height and width, and 300 mm in length. The upper part which is covered with quartz window can be removed to introduce the substrates for deposition.

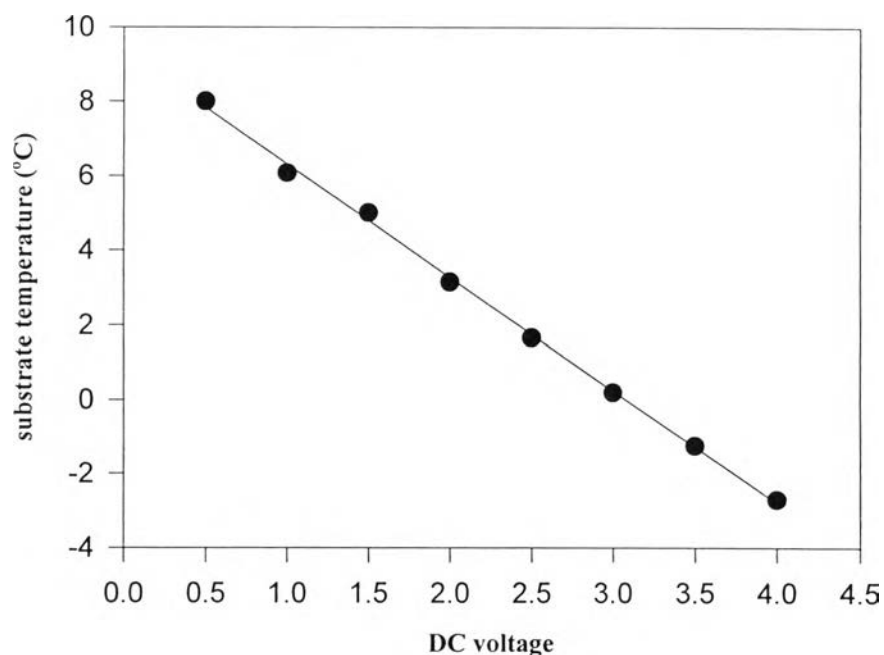


Figure 3.4 Relationship between temperature of stainless steel plate and DC voltage power supply.

In the chamber there is a fixed stage for placing the substrate on top and with a cooling plate underneath. The substrate can be cooled to the desired temperature by adjusting the DC voltage power supply (Figure 3.4). Water cooling system consisting of a couple of aluminium plates covering the copper coil was used to remove heat from the cooling plate. The manifold was 8 mm in diameter and 50 mm in length and was situated at about 50 mm from the substrate. The UV-lamp was located above the quartz window 50 mm from the substrate. Figure 3.5 shows the complete the system layout.

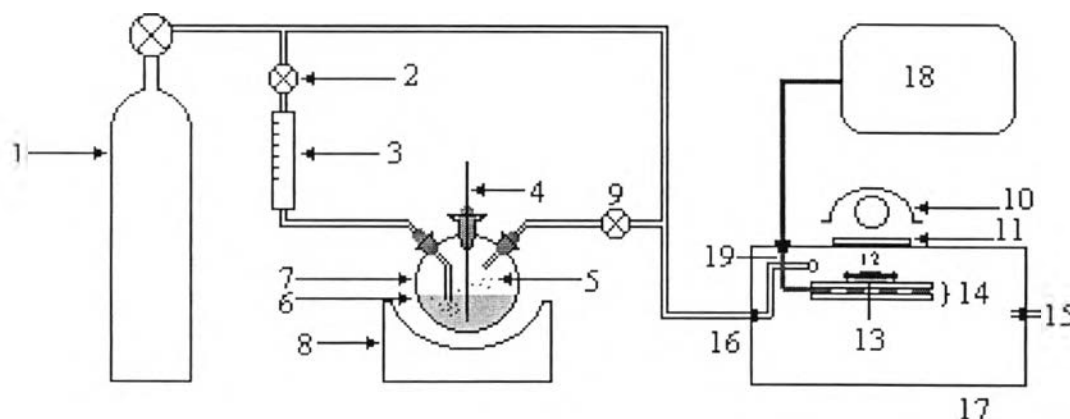


Figure 3.5 Schematic diagram of the thin film deposition system, (1) N_2 ; (2) Needle valve; (3) Flow meter; (4) Thermometer; (5) Vapor of monomer; (6) Liquid monomer; (7) Three neck round bottle; (8) Water bath; (9) Needle valve; (10) UV lamp; (11) Quartz window; (12) Substrate; (13) Cooling plate; (14) Water cooling system; (15) Vent; (16) To manifold; (17) Chamber; (18) Water cooling bath.

3.3.2 Sample preparation

3.3.2.1 *Monomer preparation.* MMA monomer readily polymerizes through free radicals, thus it is usually stored in the presence of an inhibitor. It is important to remove the inhibitor in advance as follows:

a) Washing to remove inhibitor : the inhibitor is usually an aromatic such as hydroquinone or t-butylpyrocatechol. It can be removed by washing the monomer with 10% aqueous NaOH. An equal amount of the basic solution and the monomer were placed in a separatory funnel and mixed by tumbling. The heavier aqueous phase was drained off. The procedure

was repeated until the resulting liquid was clear. The monomer was then washed with distilled water until it was neutral to litmus paper.

b) Drying : a drying agent anhydrous Na_2SO_4 was added to the monomer (100 g/l) with occasional tumbling, drying was completed in about half an hour.

3.3.2.2 *Substrate preparation.* Both quartz and glass slide were washed by cleaning solution and distilled water. Before deposition, both substrates were coated with a solution of photoinitiator in chloroform in the concentration range of 0.5 to 2.5 % (w/v) and dried in air for 30 minutes.

3.3.2.3 *Deposition procedures.* A schematic of the deposition chamber is shown in Figure 3.5. The substrate (one quartz and one glass slide) was placed on the stage located in the chamber. The chamber was then closed by the quartz window. The N_2 was purged through the chamber at room temperature for 3 hours to eliminate the moisture, dirt and air inhibitor. After purging, N_2 was passed through the liquid monomer in order to carry the monomer vapor into the chamber. The flow rate of N_2 through monomer determines the concentration of monomer in the gas mixture. After switching on the UV lamp, the mixture of MMA monomer and N_2 (flow rate of 22 to 110 ml/min) was let into the chamber. The monomer deposited on the substrate surface was cooled by the cooling plate. Finally, the polymerization took place on substrate surface via UV irradiation.

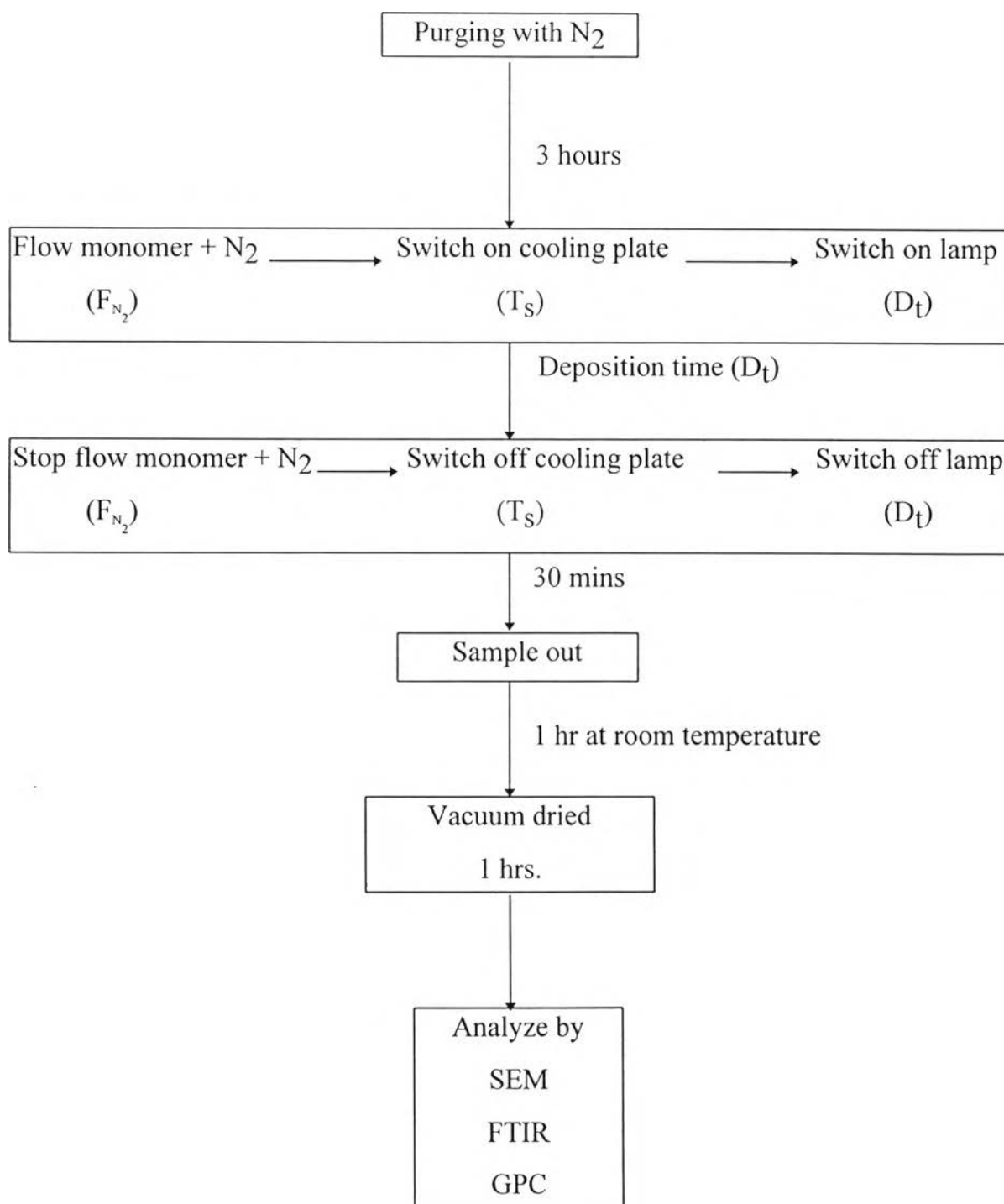


Figure 3.6 Flow chart of experiment procedures.

The conditions used in this work are shown in the Table 3.1 and 3.2.

Table 3.1 Fixed parameters for film deposition

Fixed Parameters	Fixed values
The distance between UV-lamp and substrate	50 mm
N ₂ purging time	3 hours.
Power of UV-lamp	100 watts
Temperature of water bath	55°C
Type of substrate	quartz and glass slide
Photoinitiator/solvent	Diphenyl (2,4,6-trimethyl-benzoyl) phosphine oxide /Tetrahydrofuran
Volume of photoinitiator solution (0.5% - 2.5%)	0.2 ml for quartz 0.3 ml for glass slide

Table 3.2 Variable parameters in film deposition

Variable parameters	Range
Percent photoinitiator (%Ph)	0.5 - 2.5% (w/v)
Deposition time (D_t)	2 - 10 hrs
Exposure time (E_t)	2 - 10 hrs
Substrate temperature (T_S)	298 - 263 K
Flow rate (F_{N_2})	22 - 110 ml/min

3.4 Sample Characterization

3.4.1 Fourier Transform Infrared Spectrometer (FTIR)

The PMMA film obtained from the experiments was peeled from the substrates and characterized by FTIR. The characteristic peaks for PMMA were shown in Table 3.3.

Table 3.3 Corresponding wavenumbers for IR peaks of PMMA

Absorption peak	Wavenumber cm-1
C=O	1735
C-O	1300-1000
C-H	3000-2800
C=C	1680-1560

3.4.2 Scanning Electron Microscope (SEM)

The PMMA film obtained on the glass slide substrate was cut into a small piece ($5 \times 5 \times 1 \text{ mm}^3$) for SEM observation. The cross-section of the sample was used to determine the thickness and the surface of films was also characterized by SEM with the magnification range of 100-3500.

3.4.3 Gel Permeation Chromatography (GPC)

Tetrahydrofuran (AR grade) was used as the solvent for dissolving the PMMA film. This solution was filtered by using PTFE filter membrane pore size $0.2 \mu\text{m}$ before injected into the GPC.