

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

3.1.1 Chemicals

3.1.1.1 Styrene Monomer. Styrene was purchased from Fuka Chemika Co.,Ltd. in analytical grade with bp.=142-146 °C and M.W.=104.15. Normally, an inhibitor is added to the styrene monomer to prevent self-polymerization. Therefore, the added inhibitor [4-*tert*-butylcatechol] was removed prior to use (Section 3.3.1).

3.2.2.2 Sodium Hydroxide and Sodium Sulfate. Sodium hydroxide, 97% assay, M.W.=40.00, was purchased from UNIVAR Co.,Ltd. Anhydrous sodium sulfate, 99% assay, M.W.=142.04, was purchased from ANALAR Co.,Ltd.

3.1.1.3 Photoinitiator. Photoinitiator is a kind of compound consisting of an electron donor and an acceptor to initiate polymerization of monomer. Photoinitiator must be chosen to match the radiation from the light source. Two types of different UV irradiation sources (see 3.2.1.5) were used in this research, therefore the photoinitiators also consisted of two types. The first type used with low intensity UV lamp was 1-hydroxycyclohexyl phenyl ketone with λ_{\max} at 240 nm [analytical grade, M.W.204.27, bp.175 °C and mp.47-50 °C from Aldrich Co.,Ltd.]. The second type used with high intensity UV lamp was diphenyl(2,4,6-trimethyl-benzoyl) phosphine oxide with λ_{\max} at 365 nm [analytical grade, M.W.=348.35 and mp.=88-92 C from Aldrich Co.,Ltd.].

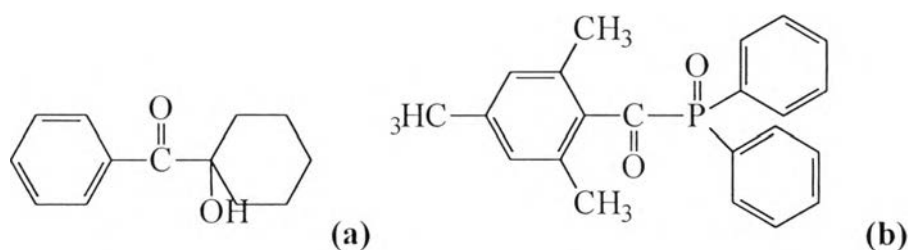


Figure 3.1 Structures of photoinitiators (a) 1-Hydroxycyclohexyl phenyl ketone; (b) Diphenyl(2,4,6-trimethyl-benzoyl) phosphine oxide.

3.1.1.4 *Chloroform (CHCl₃)*. Chloroform, analytical grade, was purchased from J.T. Baker Co.,Ltd.

3.1.1.5 *Tetrahydrofuran(THF)*. THF, [99.8% assay, M.W.72.11, bp.66.0 °C], was purchased from LAB SCAN Co.,Ltd.

3.1.1.5 *Ultra High Pure Nitrogen Gas* Nitrogen gas in Ultra High Pure grade (UHP; purity99.999%) was obtained from TIG and Praxair Co.,Ltd.

3.1.2 Substrates

3.1.2.1 *Glass Slide*. Styrene monomer was firstly deposited on a 25.4x76.2x1 mm glass-slide. Deposited polystyrene film on glass-slide can be characterized directly by Attenuated Total Reflection (ATR) of Fourier Transform Spectroscopy technique.

3.1.2.2 *Silicon Wafer*. Microelectronic device depositions are based on silicon wafer support. Therefore, the studies of deposition of thin-film of polystyrene on silicon wafer are also of interest. A set of flat-type silicon wafer with p-type doped from Monsanto Co.,Ltd. was used. Due to the FTIR transparent property of silicon wafer, the deposited film on silicon wafer support can be characterized directly by FTIR transmission.

3.1.2.3 Aluminum Plate. Since metals are parts of microelectronic structure and the porous surface of metal support can accommodate the deposited molecule to form a film, therefore metal surface was also used in this study. Aluminum plate in commercial grade was used as a metal surface in this research.

3.1.2.4 Quartz Disk. A quartz disk 3.8 cm in diameter and 0.5 cm in thickness was used in this study.

3.1.2.5 Potassium Bromide (KBr) Disk. Potassium bromide crystal disk, which is FTIR transparent window, was also used in this work.

3.2 Vapor Deposition Polymerization System

3.2.1 Vapor Deposition Polymerization System Construction

3.2.1.1 General Layout. The vapor deposition polymerization chamber was designed and constructed as a box with 150x150x300 mm dimensions. Since oxygen is the main inhibitor in free-radical polymerization, therefore purging the whole system by inert gas, such as UHP nitrogen, is important. Moreover, UHP nitrogen was also used as the carrier gas to carry the styrene vapor into the chamber. The styrene vapor was generated by heating styrene monomer up to 40 °C in a water-bath. Thus, the inlet part was designed to support two sources of inlet gas, i.e. UHP nitrogen, and mixture of UHP nitrogen and styrene vapor. The inlet gas was spread horizontally onto the substrate surface by a manifold.

The manifold is a T-way tube with many small holes mounted inside the chamber at the end of the inlet tube. It was used to spray the inlet gases onto the substrate. The incident styrene molecules on substrate

were polymerized by exposition to an external UV irradiation source through a quartz window in a vertical position.

The top part of the VDP chamber, the mask, was mounted with a piece of quartz window (103x103x5 mm) which is UV transparent. The mask could be taken off to replace the substrate on the substrate holder.

The substrate was placed inside the chamber perpendicular to the UV irradiation source situated above the quartz window. The irradiation path length was defined as the distance from the substrate surface to the quartz window.

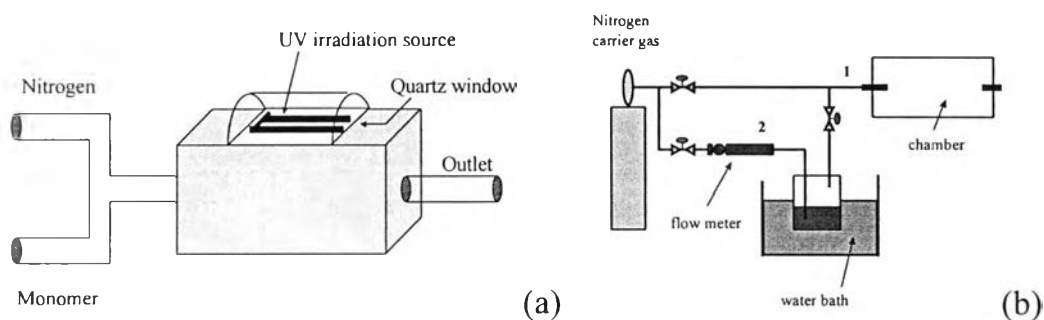


Figure 3.2 General layout of the vapor deposition chamber (a) The external connection; (b) Gas flow diagram.

3.2.1.2 The Flow Rate Meter. To study the effect of flow rate of styrene vapor on deposition rate of PS thin-film, two flow rate meters corresponding to two ranges [11-399 ml.N₂/min and 39-331 ml.N₂/min from ColePalmer Co.,Ltd.] were installed in the gas flow lines.

3.2.1.3 Substrate Heating Device Installation. To study the effect of high temperature substrate surface, a 800-watt heater with 10x12.5 dimensions was attached to the substrate holder. A temperature controller and a K-type thermocouple accessories with 0-399 °C temperature range [from

Shinko Co.,Ltd.] were mounted to the surface of substrate holder to control and monitor the temperature of the heater.

Due to the high power of 800-watt substrate holder, the electric current is also high (~4 ampere) with the 220 VAC. Therefore an 8 ampere solid state relay device was installed in the electrical line. Finally, the heating plate substrate holder was adjusted to 5 cm irradiation path length.

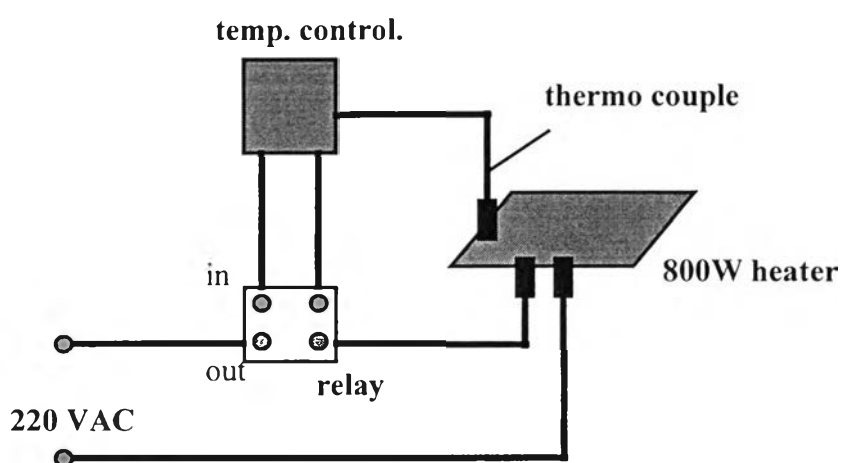


Figure 3.3 Set up diagram of the electrical supplier for a 800W heater.

3.2.1.4 Cooling Device Installation.

- *Cold Ice* Cold ice is the package of re-refrigerated substance which generates a cold substrate temperature at 10 °C at the surface for at most 10 hours. In this research the cold ice was packed in the 14.5x15x4.5 mm aluminum box which was also connected to a thermocouple to monitor the substrate temperature. To set up the box of cold ice, all accessories for 800 W heater has to be removed. The set of cold ice device was installed to give a 5 cm irradiation path length.

- *Thermoelectric Cooling Plate* Due to the limitation of substrate temperature and cooling life-time of cold ice, the use of electronic cooling device was needed. A thermoelectric cooling plate is a sandwich of many diodes between a couple of opposite ceramic plates. The different temperatures between the opposite ceramic plates are generated after introducing the direct current voltage to all diodes. The upper plate is cold while the lower plate becomes hot. Thermoelectric cooling plate was purchased in Z-MAX model with 16 VDC from Tellurex Co.,Ltd. It replaced the cold ice box inside the chamber to give lower substrate temperatures.

The direct current in 16VDC supplier consisted of a vari a.c. transformer [3.5 ampere of 240/240 VAC, 0.98 KVA, from Staco Energy Product. Co.], a transformer [5 ampere of 220/16VAC], a bridge rectifier diode [4 ampere of 220/20 volts] and a capacitor [4700 MF of 25VDC]. All devices were assembled as shown in Figure 3.4.

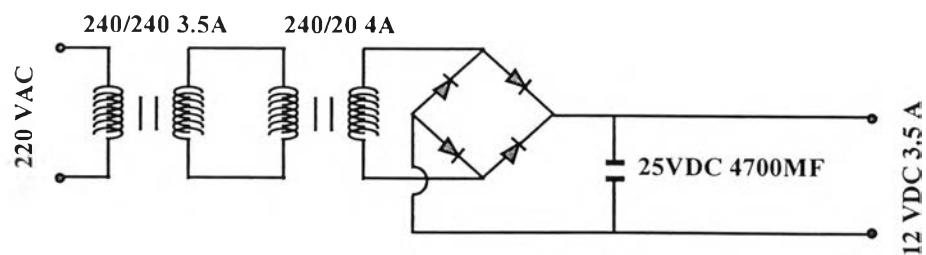


Figure 3.4 Electrical assembly of the direct current voltage supplier for the thermoelectric cooling plate.

Owing to the heat from the lower plate of the thermoelectric cooling device, a water cooling coil was needed underneath the lower plate. The cooling coil system consisted of a couple of aluminum strip plates and a 4-loop copper coil which were assembled as in Figure 3.5.

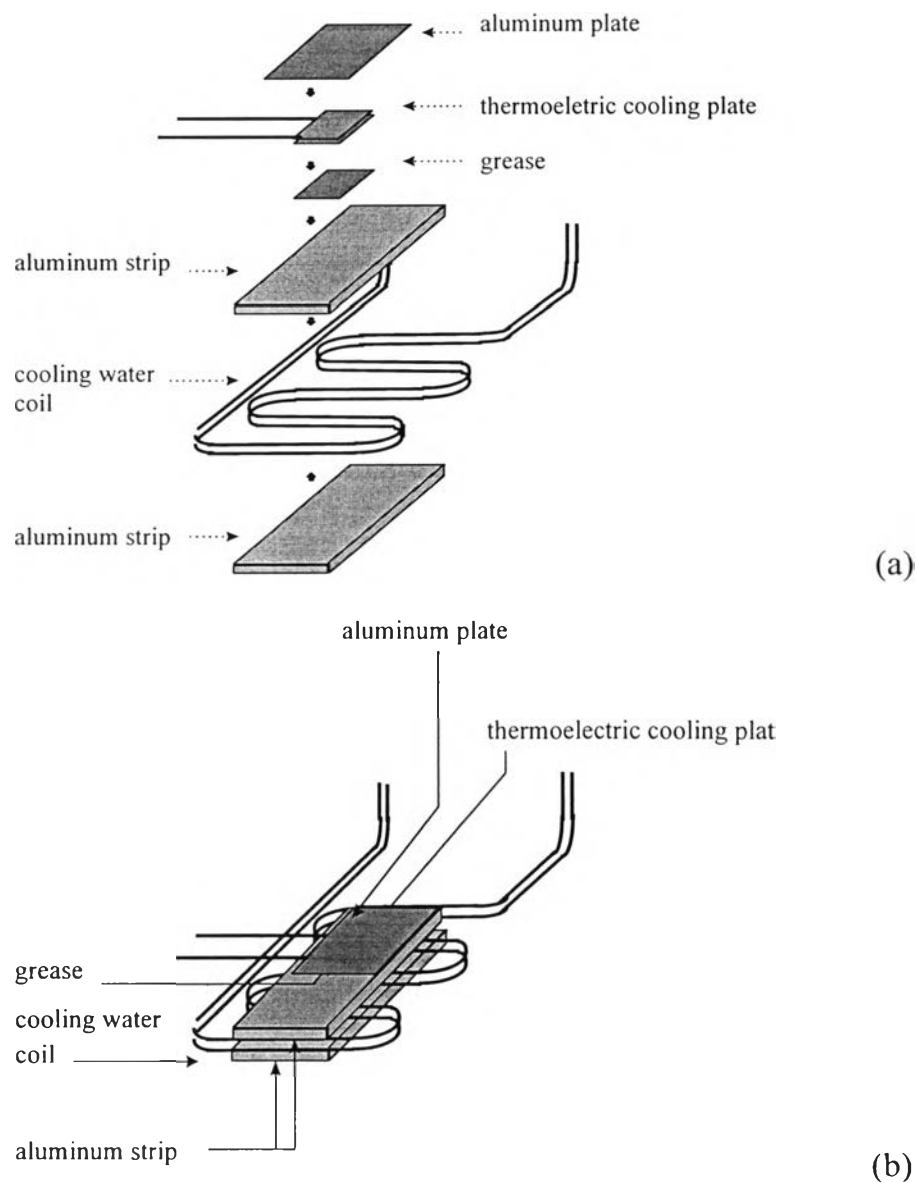


Figure 3.5 The set up of water cooling coil for thermoelectric cooling plate device (a) the layer-by-layer assembling; (b) the final assembly.

3.2.1.5 *Ultraviolet Irradiation Source.* Two UV lamps were used as the UV irradiation source. The first lamp was low intensity with a low-pressure mercury lamp [9 watts TUV-PLS, UV-C at 2.5 watts with $\lambda_{\max}=254$ nm purchased from Phillips Co.,Ltd.]. The second lamp was of higher intensity with a high-pressure mercury lamp [100 watts, UV-A with $8900 \mu\text{W}/\text{cm}^2$ at 10", and $\lambda_{\max}=365$ nm from Cole Palmer Co.,Ltd.].

3.2.2. System Assembling

1) The set of sample holder was installed inside the chamber as in Figure 3.6.

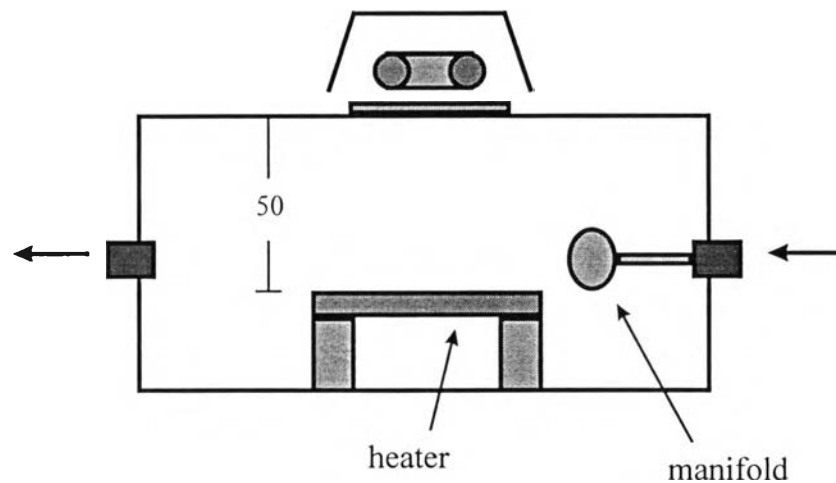


Figure 3.6 Internal assembly of substrate holder.

2) The control panel (Figure 3.7) consisted of

- A flow rate meter and its control valve.
- A set of temperature controller which is already connected to its thermocouple.
- Connecting gas flow tube (0.5 mm ϕ teflon tube).

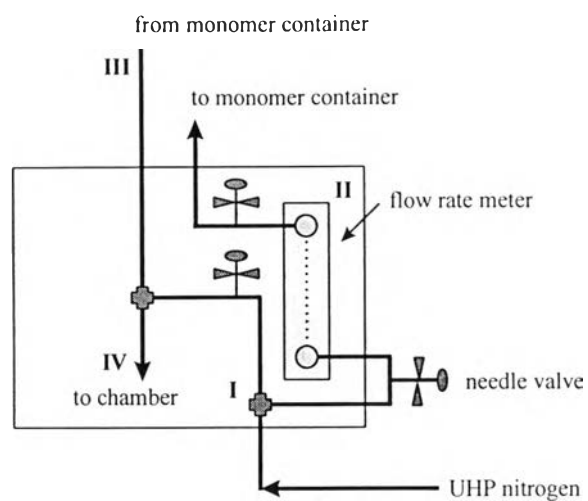


Figure 3.7 Schematic of gas flow connections at the back of the control panel.

3) The chamber was installed in front of the control panel on the left hand side (Figure 3.8).

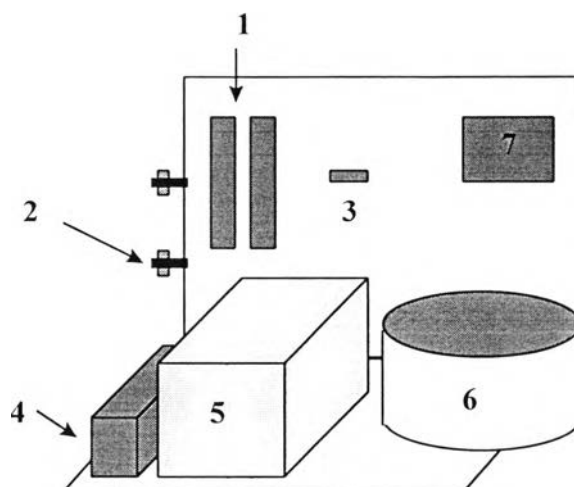


Figure 3.8 Layout of vapor deposition polymerization system;
 (1) Flow rate meters; (2) control valve for flow rate meter; (3) valve for nitrogen purging line; (4) electrical supplier box; (5) vapor deposition polymerization chamber; (6) water-bath and monomer container; (7) a set of temperature controller and thermocouple.

4) The electrical wire of sample holder was connected to the external electrical supplier.

5) The thermocouple wire was inserted into chamber and attached to the substrate holder surface.

6) The chamber was closed by the cover mask.

7) The water bath together with a set of monomer container (a three-neck round bottom flask with its adapter) was placed in front of the control panel at the right hand side.

8) The gas regulator was connected at the releasing valve of the UHP nitrogen gas tank.

9) The gas tube was connected at the output of gas regulator to the input I (Figure 3.7).

10) The output II (Figure 3.7) was connected to the input of monomer container adapter by a 2/8" teflon tube.

11) The output of the monomer container was connected back to the input III (Figure 3.7) by a 2/8" teflon tube.

12) The output IV (Figure 3.7) was connected to the input of vapor deposition polymerization chamber by a 2/8" teflon tube.

13) The input gases, either pure UHP nitrogen or mixture of UHP nitrogen and styrene monomer, were sprayed by a manifold.

14) Finally, the output of vapor deposition polymerization chamber was connected to outside atmosphere.

The whole set up of the vapor deposition polymerization system is shown in Figures 3.9, 3.10, 3.11, and 3.12

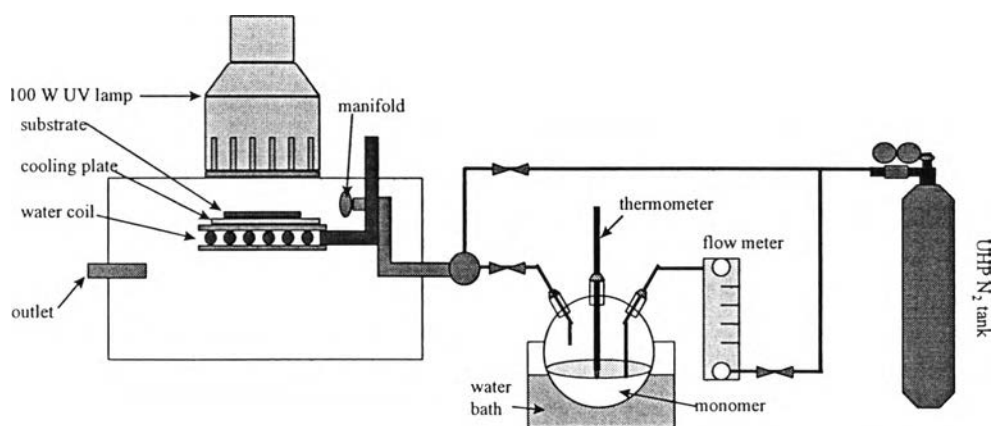


Figure 3.9 Schematic diagram of vapor deposition polymerization chamber with the thermoelectric cooling plate system.

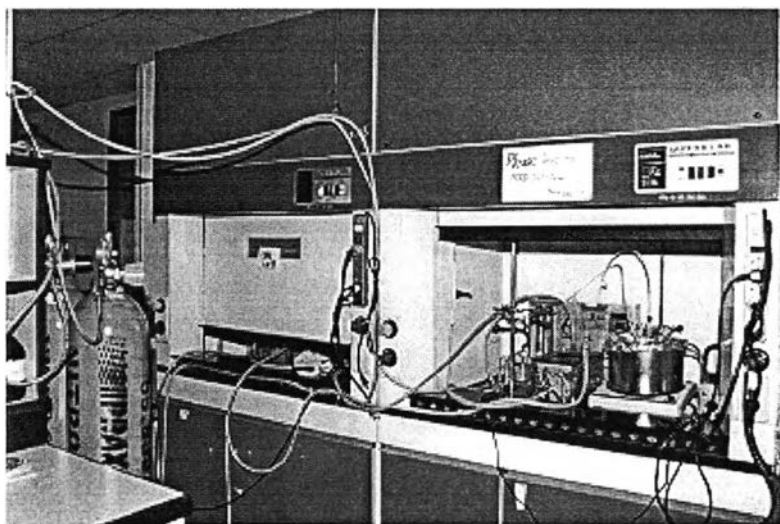


Figure 3.10 Vapor deposition polymerization system layout.

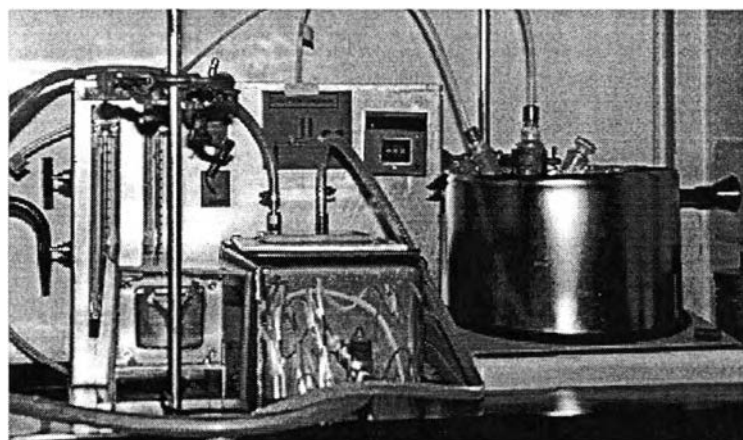


Figure 3.11 External connection of the vapor deposition polymerization chamber.

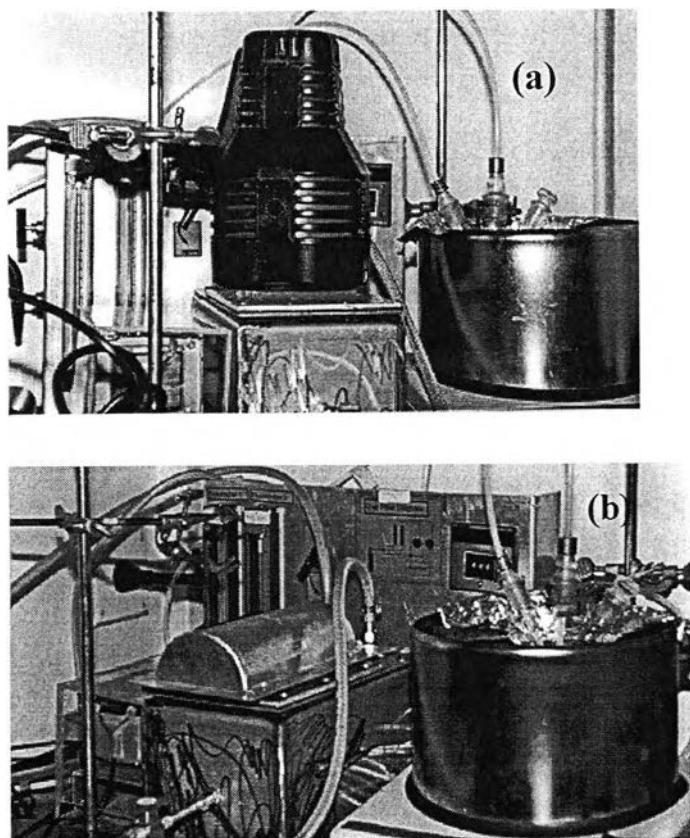


Figure 3.12 Installation of (a) 100 watts ;(b) 9 watts UV irradiation lamp.

3.3 Deposition Procedures

3.3.1 Monomer Preparation

Styrene monomer was first washed with 10% aqueous NaOH using roughly equal parts of the basic solution and the monomer. The mixture was then placed in a separatory funnel and mixed by tumbling. The heavier aqueous phase was drained off. The procedure was repeated once or twice until the liquid was clear. The monomer was then washed by distilled water until litmus paper showed that all the base was removed. Anhydrous Na₂SO₄ a drying agent, was added to the monomer (100g/l) with occasional tumbling. The drying was completed in about half an hour.

3.3.2 General Procedure for Vapor Deposition

1) The air/oxygen which was the main inhibitor for free-radical polymerization was flushed out by purging the UHP nitrogen through the manifold at 150 ml.N₂/min for 3 hours. The monomer in the container was heated up to 40 °C by water bath.

2) The purging line was closed and the control valve was connected to the flow rate meter. The flow rate of UHP nitrogen gas was adjusted.

3) The UV irradiation lamp installed on top of the quartz window plate was switched on.

4) The deposition line, and the flow of monomer were maintained for 10 minutes for the steady state conditions. The UV lamp was switched off, and the deposited film was taken for characterization.

3.4 Characterization Instruments

3.4.1 Fourier Transform Infrared Spectrophotometer (FTIR)

Styrene monomer is an ethylene molecule with one of the hydrogens replaced by a benzene ring. After polymerization the double bond becomes a single bond. Therefore the deposited film can be characterized by the stretching and bending peaks of alkane, alkene and aromatic functional groups using an FTIR spectrometer which in this case was a BIO-RAD FTS45A Fourier Transform Infrared Spectrophotometer at 8 cm^{-1} resolution and 16 numbers of scans per sample.

3.4.2 Gel Permeation Chromatography (GPC)

To characterize the molecular weight of deposited film, all films were dissolved in THF and analyzed by Perkin-Elmer/Waters Styragel HR5E column with refractive index (Perkin-Elmer series 200) detector.

3.4.3 Scanning Electron Microscope (SEM)

A JOEL 5200 2AE(MP52001) Scanning Electron Microscope with magnification range of 35-20,00 times was used to characterize the deposited film.

3.5 Determination of Deposition Weight

Deposited substrate was left in desiccator for one hour to evaporate the unreacted monomer. The deposition weight was calculated from the difference in the weight of substrate before and after dissolution in THF.

3.6 Estimation of Film Thickness

The estimated thickness of polymer film was based on a smooth surface assumption. The estimated thickness was derived according to Appendix I.2.