

CHAPTER III

EXPERIMENTAL

3.1 Material

3.1.1 Chemical reagent

- 1,1,1-tris(4-hydroxyphenyl)ethane 99% purify (CAS No. 27955-94-8) was supplied by Sigma–Aldrich
- 2,3,4,5,6-Pentafluorostyrene 99% purify (CAS No. 653-34-9) was supplied by Sigma–Aldrich
- 4,4'-(hexafluoroisopropylidene)diphenol 99% purify (CAS No. 1478-61-1) was supplied by Sigma–Aldrich
- Dichlorodiphenylsilane 97%purify (CAS No. 80-10-4) was supplied by Sigma–Aldrich
- Calcium hydride 93% purify (CAS No. 7789-78-8) was supplied by Acros
- Cesium fluoride 99% purify (CAS No. 13400-13-0) was supplied by Carlo
- 4-dimethylamino pyridine > 97.0 % purify (CAS No. 1822-51-1) was supplied by Sigma–Aldrich
- Tetrabutylammoniumbromide was supplied by Acros

3.1.2 Solvents

- *N,N*-Dimethylacetamide (DMAc), analytical grade, was supplied by RCI Labscan Limited.
- Diethyl ether, lab–grade, was supplied by RCI Labscan Limited.
- Triethylamine, lab–grade, was supplied by RCI Labscan Limited.
- Ethyl acetate, commercial grade, was supplied by RCI Labscan Limited.
- Hexane, commercial grade, was supplied by Italmar (THAILAND) Co., Ltd.
- Tetrahydrofuran, HPLC grade, was supplied by RCI Labscan Limited.

- Dichloromethane, commercial grade, was supplied by Italmar (THAILAND) Co., Ltd.

3.1.3 Plastic pellet

- Polycarbonate was supplied by Chimei Co., Ltd grade wonderlite PC 110, Melt flow index of PC is 10g/10min.
- Poly(methyl methacrylate) (PMMA) was supplied by Diap Co., Ltd grade Acrypet MD. Melt flow index is 5.7g/10min.

3.1.4 Other chemicals

- Argon gas
- Hydrochloric acid, analytical grade, was supplied by RCI Labscan Limited.
- Anhydrous magnesium sulfate was supplied by Asia Pacific Specialty Chemicals Limited.
- Silica gel 60 particle size 63-200UM (70-230 MESH) was supplied by Merk.

3.2 **Equipment**

- Nicolet Fourier Transform Infrared (FT-IR) Spectrometer
- Bruker 400 Mz Model Ultrahield Nuclear Magnetic Resonance (NMR)
- SHIMADZU Gel Permeation Chromatography (GPC)
- TA Instruments TGA 2950
- DSC822 METTLER
- CEAST Capillary Rheometer
- Leica DMXDP Optical Microscope (OM)
- JSM-6400 Model Scanning Electron Microscope (SEM)
- Lloyd Universal Tensile Testing Machine
- LED He-Ne Ligth Source (633 nm)
- TEK Oscilloscope with light detector (24 V)

3.2 Methodology

3.3.1 Preparation of Cladding Materials

All materials used in reaction need completely dried. *N,N*-Dimethylacetamide (DMAc) and dimethylformamide (DMF) were dried by distillation over calcium hydride and stored over activated 4 Å molecular sieves. Hexane and ethyl acetate were distilled before used. THF was dried and distilled over Na-benzophenone. Triethylamine (Et₃N) was stored over potassium hydroxide pellet. Glassware was dried at 120 °C for 12 hours before using.

3.3.1.1 Synthesis of 1,1-Bis(4-hydroxyphenyl)ethyl-1-phenyl 2,3,5,6-tetrafluorostyrol ether (BHPFS)

The cross-linkable bisphenol (BHPFS) was synthesized following by Yinghau Qi's report. 1,1,1-Tris(4-hydroxyphenyl)ethane (10.5 g, 0.034 mol) and 2,3,4,5,6-pentafluorostyrene (5.2 g, 0.027 mol) were dissolved in *N,N*-dimethylacetamide (DMAc) (40 ml); it was dried over calcium hydride and distilled and stored over activated 4 Å molecular sieves, in present of calcium hydride (2.1 g, 0.05 mol) and cesium fluoride (0.20 g, 1.32 mmol) at 80°C under argon gas in the dark for 18 h. Then the mixture was filtered. 0.5 N, 300 ml HCl was add into the solution. Then the solution was extracted with diethyl ether (150 ml) three times and washed diethyl ether phase with distilled water until neutral. It was then dried over anhydrous magnesium sulfate, and evaporated with rotary evaporator. The obtained crude product was purified by column chromatography. The overall reaction is shown in Figure 3.1.

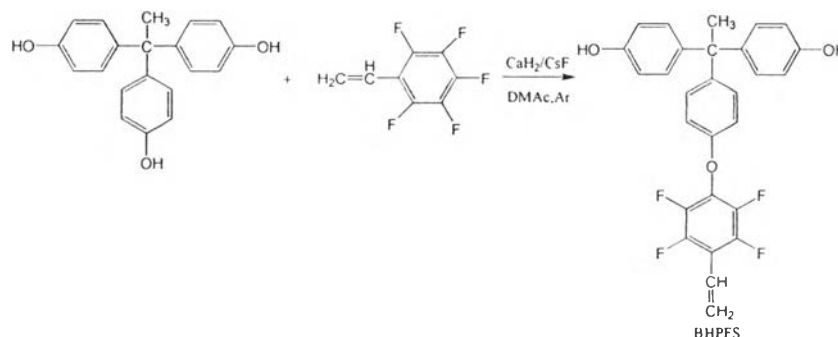


Figure 3.1 Synthesis of Cross-Linkable bisphenol (BHPFS) (Qi, *et al.*, 2005).

3.3.1.2 Synthesis of poly(arylene silyl ether) (PASE)

There are various conditions in this work, all attempts to substitute dichlorodiphenylsilane with diphenol monomers. Table 5.1 shows the conditions using in this work.

Table 5.1 The synthesized PASE conditions

condition	catalyst	temperature	solvent	time
1	TBAB	room temp.	toluene	48
2	CaH ₂	80 °C	DMF	48
3	Et ₃ N	room temp.	DMF	72
4	Et ₃ N, DMAP	room temp.	THF	24

PASE was synthesized from the reaction of BHPFS (25 mol% of diphenol), 4,4'-(hexafluoroisopropylidene) diphenol (6F-BPA) and dichlorodiphenylsilane (CPS) as shown in Figure 3.2.

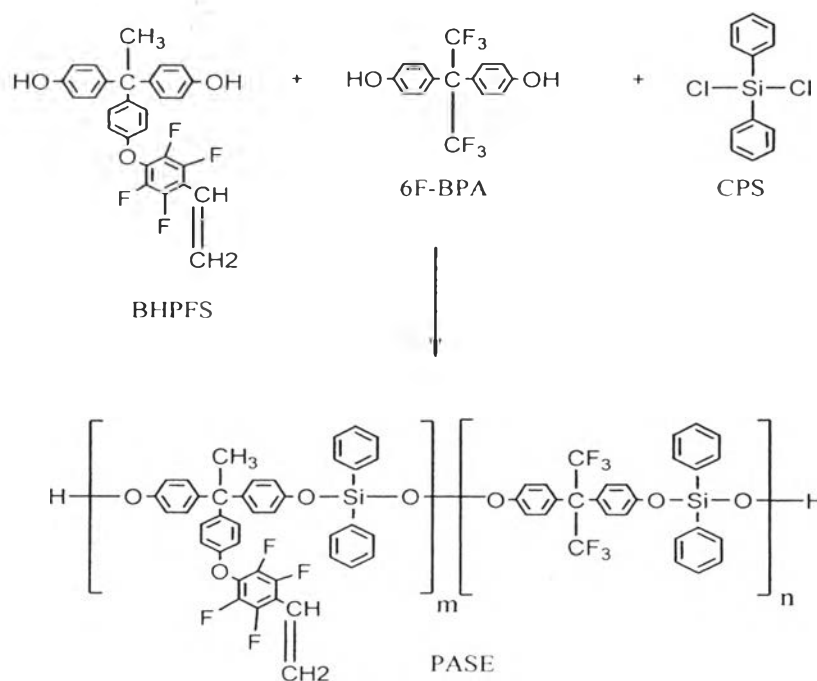


Figure 3.2 Synthesis of poly(arylene silyl ether) (PASE).

First condition, tetrabutylammonium bromide (TBAB) was used as a catalyst. BHPFS (0.1199 g, 0.25 mmol) and 6F-BPA (0.2534 g, 0.75 mmol) and TBAB (0.4835 g, 1.25 mmol) were dissolved in 5 ml toluene. The mixture was stirred under argon gas for 1 h. CPS (0.2532 g, 1 mmol) was dropped by keeping in argon atmosphere. The reaction was stirred at room temperature for 48 h. The complete disappearance of 6F-BPA by TLC (hexane / dichloromethane / EtOAc, 3:1:1) in the solution was observed and precipitate was occurred. The precipitate was filtered and washed three times with toluene and followed by small amount of dichloromethane. The solid part was recrystallized in mixed solvent of hexane and dichloromethane, and then white crystal was filtered and washed with small amount of dichloromethane.

Second condition, the catalyst was calcium hydride (CaH_2). BHPFS (0.1200 g, 0.25 mmol) and 6F-BPA (0.2522 g, 0.75 mmol) were dissolved in 9 ml dried *N,N*-dimethylformamide (DMF). The mixture was stirred under argon gas for 1 h. CPS (0.2532 g, 1 mmol) was dropped by keeping in argon atmosphere. The reaction was stirred at 80 °C for 48 h. The mixture was then rinsed into iced-water (20 ml) and extracted three times with dichloromethane. The organic phase was dried over anhydrous MgSO_4 , filtered, and solvent removed by rotary evaporation.

Third condition, triethylamine (Et_3N) was used as a catalyst. BHPFS (0.2780 g, 0.5 mmol) and 6F-BPA (0.6150 g, 1.5 mmol) were dissolved in 15 ml dimethylformamide (DMF). The mixture was then stirred under argon gas. Triethylamine (Et_3N) (5 ml) was then added. CPS (0.253 g, 1 mmol) was dropped by keeping in argon atmosphere. The reaction was stirred at room temperature for 72 h. Then 50 ml 10% HCl was added into the solution and extracted three times with dichloromethane. The dichloromethane phase was washed with distilled water until neutral. The organic phase was dried over MgSO_4 , filtered, and solvent removed by rotary evaporation.

The last condition, Et_3N and 4-dimethylamino pyridine (DMAP) were used as a catalyst and accelerating agent respectively. In three necks round bottom flask, BHPFS (0.6000g, 1.25 mmol) and 6F-BPA (1.2609 g, 3.75 mmol) were added, followed by calculation of 15 ml of tetrahydrofuran (THF). The mixture was then stirred under argon gas. By syringe addition, the reaction flask was charged

with 5.56 ml (40 mmol) of Et₃N and CPS. Mole ratios of CPS were varied at diphenol:CPS equal to 2:1, 1:1, 1:1.25, 1:2 and 1:3. Precipitation occurred, and the reaction mixture was stirred for 1 h. A catalytic amount of DMAP, 10 mole percent (61 mg, 0.5 mmol) was then added and the reaction was stirred at room temperature for 24 h. The mixture was filtered to remove the precipitates and washed them with THF, and solvent removed by rotary evaporation.

3.3.1.3 *Blending of PASE and PMMA*

10%, 20% and 25% by weight of PASE (8.3, 25 and 20 g) were mixed with PMMA (75, 75 and 60 g., respectively) in Barbender Mixer N50 with Oil bath circulation T300 B at 175 ° C, 60 rpm of rotor speed for 20 minutes.

3.3.2. Characterization of Cladding Materials

3.3.2.1 *Chemical Structure and Molecular Weight*

FT-IR spectra of BHPFS and PASE were obtained by using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 400-4000 cm⁻¹ with 64 scans at a resolution 4 cm⁻¹. KBr Technique was applied in the preparation of powder samples. All H¹-NMR spectra were conducted on a Bruker 400 MHz NMR spectrometer in CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal reference.

The molecular weights of polymers were determined by gel permeation chromatography (GPC) using a Waters HPLC columns styragel[®] HR 6E THF 7.8x300 mm. coupled with RID-10A SHIMADZU refractive index detector. 0.25% wt/v of samples was filtered with syringe filter diameter 13 mm. PTFE 0.45 μm. of Vertical Chromatography Co., Ltd. before using

3.3.2.2 *Thermal Properties*

DSC analyses were carried out using a Perkin-Elmer DSC 822 instrument. BHPFS was first heat from 30°C to 300 ° C, cooled down from 300°C to 30°C and then reheated to 300°C at 5°C/min heating rate under N₂ atmosphere with a flow rate of 10 ml/min. PASE was measured at -30 ° C to 300 ° C. The study of curing temperature of BHPFS and PASE were performed in DSC at 30-300 ° C. 0.1% of dicumyl peroxide (DCP) was mixed in the material as an initiator.

TG-DTA curves were collected on a Perkin-Elmer Pyris Diamond TG/DTA instrument. The samples was loaded on the platinum pan and heated from 30°C to 700 ° C at 10°C/min heating rate under N₂ atmosphere with a flow rate of 100 ml/min.

3.3.2.3 Morphology

Morphology of PASE/PMMA blends was determined by JSM-6400 Model Scanning Electron Microscope (SEM). The samples were cracked under liquid nitrogen and coated by platinum.

3.3.2.4 Rheology property

Rheology property of core and cladding materials was studied with capillary rheometer (CEAST-5000) at 225 – 250 °C, 10-10,000 s⁻¹ shear rate and die diameter 1 mm with ¼ L/D.

3.3.3 Co-extrusion optical fiber

The PASE/PMMA blended and PMMA were dried at 80 °C for 12 hours and PC pellet was dried at 120 °C for 5 hours before co-extruding. Co-extruder consists of single screw extruder and melt- spinning using a same die (Figure 3.3). The diameter of single screw die which is used to form core part is 1 mm. The circular sheath die have 0.7 mm width. The single screw has 19 mm. diameter, 500 mm. length and 2:1 compression ratio. A barrel diameter of melt- spinning is 2.2 cm and the length is 15 cm. Piston speed is varied; 10, 20 and 24.5 mm/min. The rotor has cross section area equal to 56.768 cm². The die model is shown in appendix A.

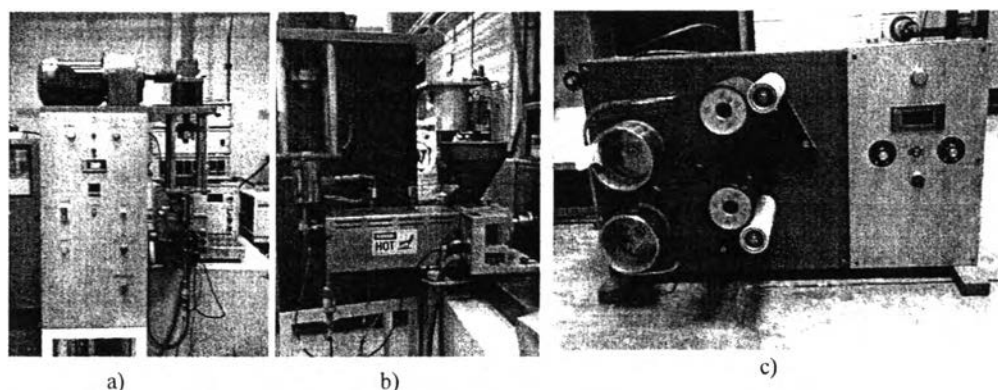


Figure 3.1 (a) Front view, (b) side view of co-extruder and (c) rotor.

3.3.4 Characterization of Optical Fiber

Optical and mechanical properties of the fibers were studied following below:

3.3.4.1 *Diameter and Morphology*

The Leica DMXDP optical microscope (OM) was used to determine diameters of core and cladding thickness of optical fiber at the magnification of 4x and 20x. The morphology of fibers was studied by using the JSM-6400 Model scanning electron microscope. The specimens were coated with platinum under vacuum to make them electrically conductive.

3.3.4.2 *Mechanical Properties*

The tensile strength of fiber at 5% elongation and the elongation at break were estimated by LLOYD universal tensile testing machine with 100 mm/min crosshead speed, 2.5 kN load cell with 5 cm gauge length.

3.3.4.3 *optical properties*

The fiber attenuation, numerical aperture (NA), bending loss and operating temperature were measured by using 633 nm light source and TEK Oscilloscope with light detector (fig. 3.4) having maximum responsibility at 20 V.

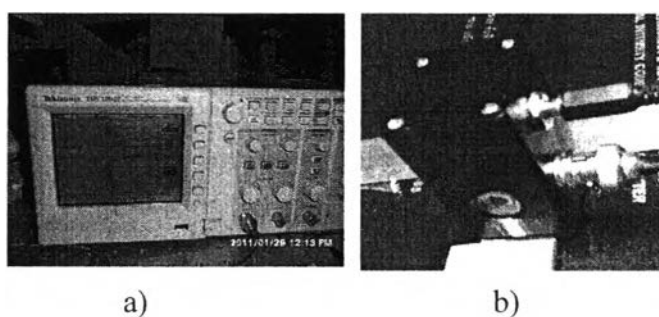


Figure 3.4 The picture of a) TEK Oscilloscope, and b) light detector.

a. Attenuation

Attenuation or optical loss was characterized by cut-back method; the experimental set-up is shown below. The 80 cm length fiber was measured the power output (P_o) first. Then the fiber was cut to 50 cm and measured the power output (P_i). An experiment set up was shown in the figure 3.5. Since the

detector transforms the light to voltage (V) so the attenuation can calculate from the relationship between power and voltage following the equation as shown below.

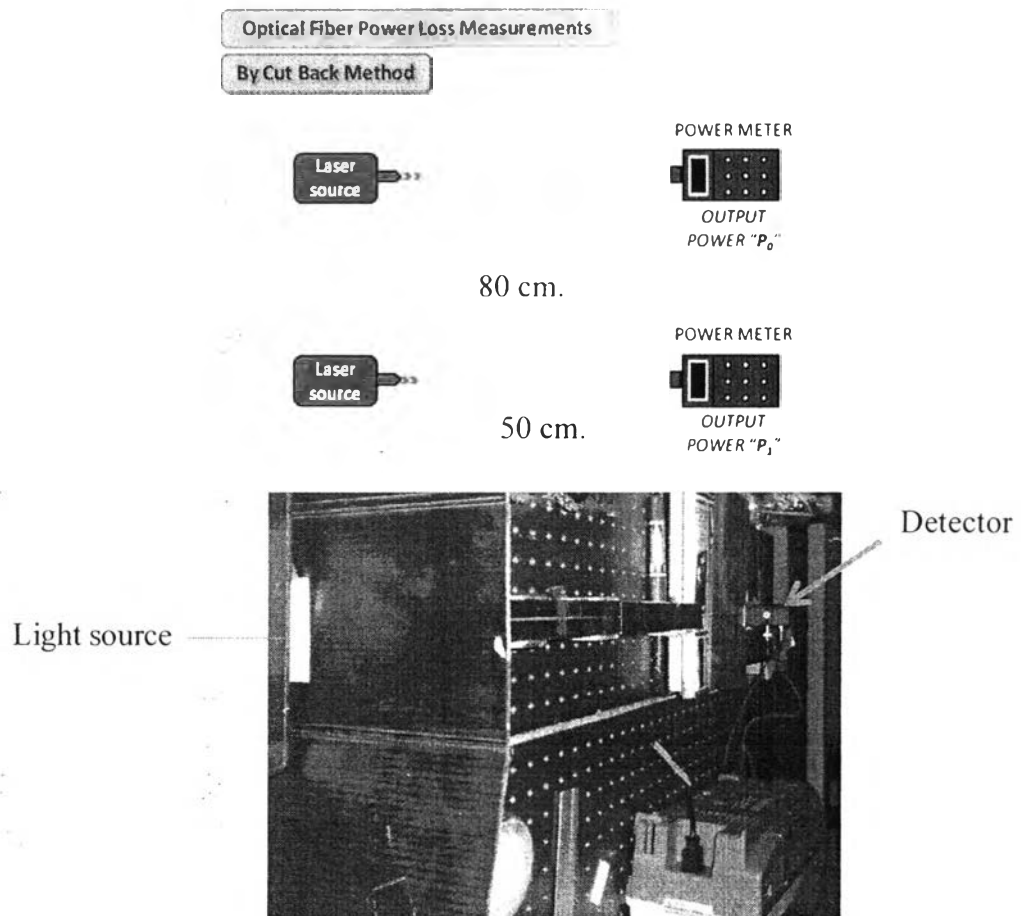


Figure 3.2 Attenuation experimental set-up.

$$\text{attenuation coefficient } (\alpha) = \frac{10}{L-x} \cdot \log \left(\frac{P_0}{P_1} \right)$$

$$P = IV; \quad I = \frac{V}{R} \quad \therefore P = \frac{V^2}{R}$$

$$\text{Attenuation coefficient} = \frac{20}{L-x} \cdot \log \frac{V_o}{V_i} \quad \text{Equation (1)}$$

b. Numerical Aperture

The red light shone through a 50 cm length fiber. A distance between the detector and the end of fiber is 1 cm. then changing the detector position

on a left and a right side until the voltage output is zero and determining the distance from the left to the right. The experimental set-up and the calculation are shown below;

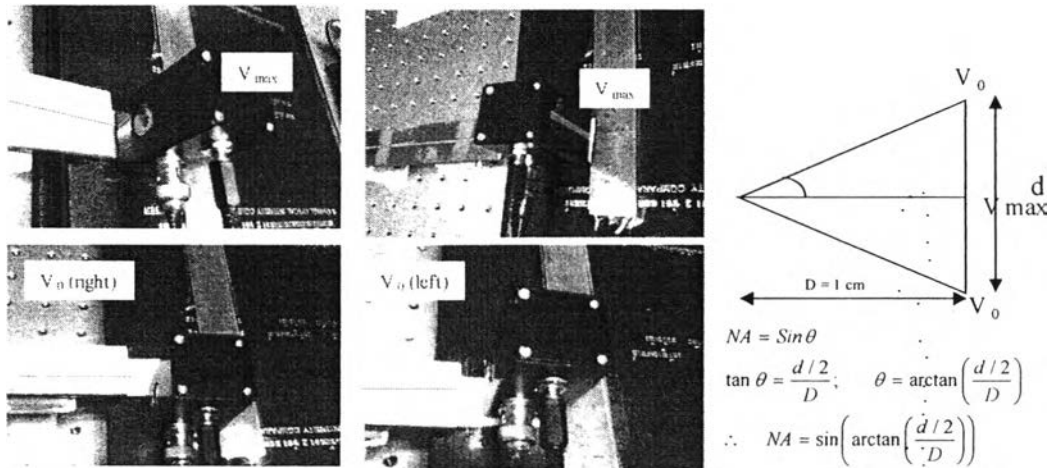


Figure 3.6 Numerical aperture experimental set-up.

c. Bending Loss

A 30 cm length fiber was measured power output (P_{straight}) first. Then the fiber was bended beginning from the biggest radius to the smallest; 10, 7.7 and 5.8 cm. The power output (P_{bend}) in each diameter was reported and calculated as equation (2).

$$\text{Optical loss} = 10 \cdot \log \frac{V_{\text{bend}}^2}{V_{\text{straight}}^2} \quad \text{Equation (2)}$$

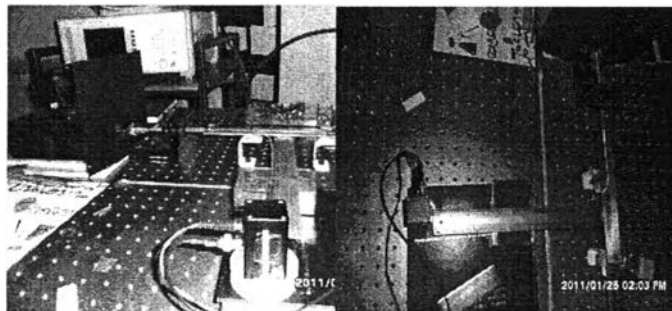


Figure 3.7 Bending loss experimental set-up.

d. Operating Temperature

20 cm. length fibers was measured power output at room temperature (25 ° C) first and then increases the temperature until the power loss reduced. The temperature in which the power loss reduced 10% is the operating temperature. The hot steel was used as a heating source and the experimental set-up is in Figure 3.8. Thermocouple and thermometer was used for measuring the temperature.

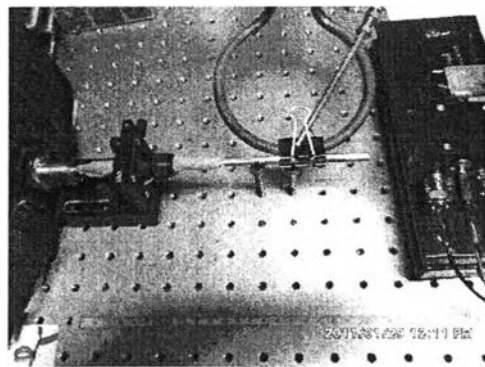


Figure 3.8 Maximum operating temperature experimental set-up.