CHAPTER IV
SYNTHESIS OF POLY(ARYLENE SILYL ETHER)

4.1 Abstract

A new cladding, Poly(arylene sillyl ether) was synthesized. Hydroxyl-terminated monomers, cross-linkable BHPFS and 4,4'-(hexafluoroiso- propylidene) diphenol (6F-BPA), were polymerized using diphenyldichlorosilane as a coupling agent. TBAB, CaH_2 or Et_3N were use as base catalysts, the reaction having TBAB as a catalyst was not successful and the reaction having CaH_2 or Et_3N as a catalyst provided low molecular weight polymers; 4,056 and 4,699 respectively. Poly(arylene silyl ether)s which have $M_w = 37,443$ with $M_n/M_w = 1.69$ are achieved by using Et_3N and dimethylamino pyridine (DMAP) co-catalyst at ratio diphenol:silane equal to 1:1.25. The other ratios; 2:1, 1:1, 1:2 and 1:3, have lower molecular weights.

4.2 Introduction

POF used for data communications are made mostly of polymethyl methacrlylate (PMMA) and perfluorinated (PF) polymer material. General aliphatic polymer has high absorption loss due to carbon–hydrogen stretching vibration. Fluoropolymers have been developed to be used as cladding materials because C-F bonds do not absorb visible light. Moreover, fluoropolymer can provide a good mechanical, chemical and thermal resistance to the core. Fluorine containing polymers are of great interest for use in optical applications because they have unique properties and high temperature performance. They have excellent thermal and chemical stability, low dielectric constant and low refractive index.

Silicon containing polymers have attractive characteristics such as good transparency and flexibility. The polymers with silicon in the main chain have attracted the attention as high performance materials. Poly(siloxane)s with excellent low temperature flexibility and high temperature stability (Minegishi, S., et al. 1995). Yamamoto T. and coworkers (1998) produce plastic optical fiber having a silane-crosslink structure as a cladding material. In 1982, Clarke R. studied an optical fiber

core and a cross-linked polyfluorosiloxane cladding having a fluorine content. The use of polyfluorosiloxane cladding produces a waveguide having a high numerical aperture and excessive microbending light loss are incurred along the waveguide. Silylethers can be synthesised directly from the reaction of inexpensive commercially available dichlorosilanes with alcohols (Marco M. M., *et al*, 2007). Since silicon-halide bonds are highly reactive, they are readily attracked by variety of nucleophile, facilitating mild reaction conditions. However, all silyl ether s are susceptible to slow hydrolysis, a reaction which kinetically is dependent upon the nature of substituent (Church, A.C., *et al.*, 2001)

The purposes of this chapter are to synthesize and characterize poly(arylene silyl ether) to be a cladding material.

4.3 Experiment

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

First BHPFS monomer 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 dreied over calcium hydride and disstilled, 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 was evaporated with rotary evaporator. The obtained crude product was purified by column chromatography.

There are various catalysts used to substitute dichlorodiphenylsilane with diphenol monomers. Tetrabutylammonium bromide (TBAB), calcium hydride (CaH_2), triethylamine (Et_3N) and 4-dimethylamino pyridine (DMAP) were used in this work.

First condition, 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 stir at 80 $^\circ$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 add 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 calnulation 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 Et_3N 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.

The chemical structure of the synthesized materials was characterized by Nicolet FT-IR spectrometer and Bruker 400 MHz model ultrahield NMR. SHIMADZU GPC was used to determine the molecular weight. Thermal properties were characterized by TA Instruments TGA 2950 and DSC822 METTLER (10 °C/min).

4.4 Result and discussion

4.4.1 Synthesis and Structural Characterization

4.4.1.1Synthesis of Cross-linkable Bisphenol (BHPFS) Monomer

Spots of crude product in thin layer chromatography (TLC) with 40% ethyl acetate in hexane as a mobile phase system were visualizing in UV and saturated I_2 gas. The crude product has three fractions. After the crude product was purified by column chromatography at gradient eluent (8%, 13% and 18% ethyl acetate in hexane), white powder of cross-linkable bisphenol (BHPFS) was obtained (62.84% yleid) (Fig. 4.1). The chemical structure was characterized by FT-IR and ^{1}H-NMR. FT-IR (KBr), wavenumber (cm^{-1}) Fig. 4.2; 3311 cm^{-1} broad (O-H), 3061 cm^{-1}and 3023 cm^{-1} (=CH str. of aromatic), 1606 cm^{-1} and 975 cm^{-1}(asym. C-F str.), 1502, 1485 cm^{-1} (C=C), 1215, 1172 cm^{-1} (C-O-C) (Qi Y., *et.al.*, 2005). H^1-NMR (400 MHz, CDCl$_3$, TMS) Fig. 4.3; δ 7.05 (d, 2H, H_5), 6.09 (d, 4H, H_2), 6.85 (d, 2H, H_4), 6.77 (d, 4H, H_3), 6.65 (dd, 1H, H_6), 6.10 (d, 1H, H_7), 5.70 (d,1H, H_7), 4.70 (s, 2H, *O-H*)

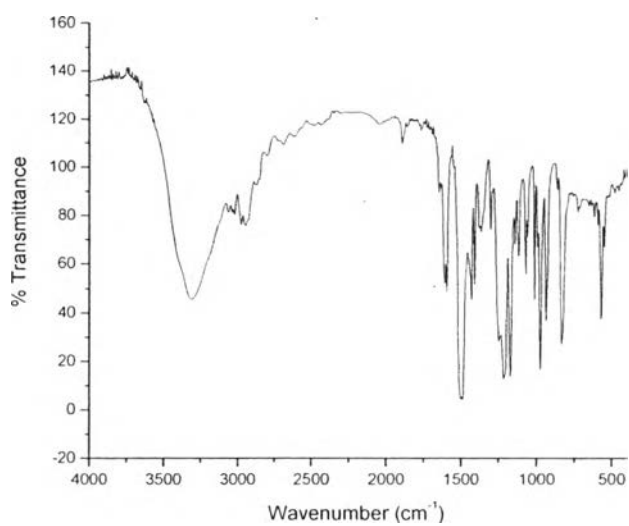**Figure 4.1** Pictures of BHPFS.
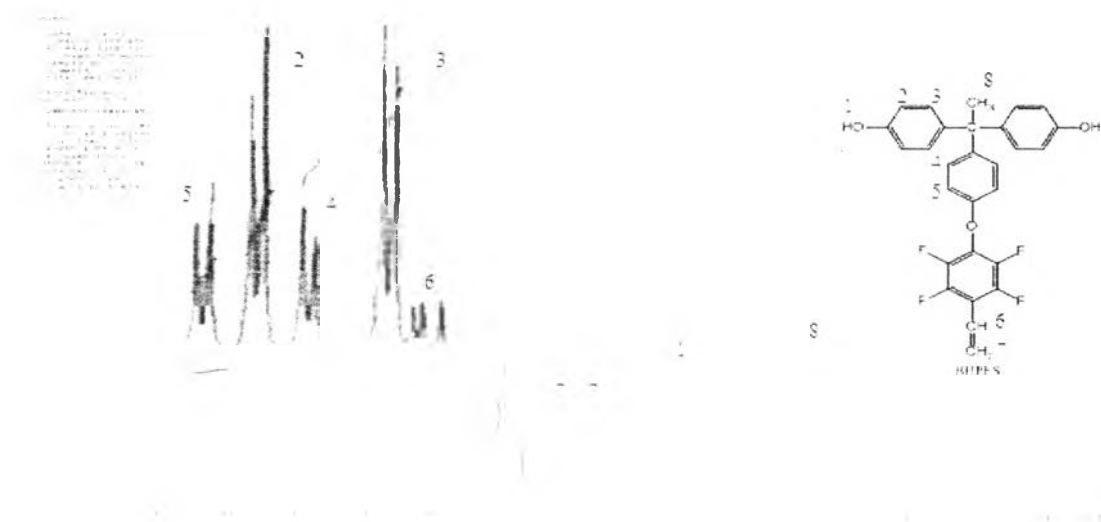

Figure 4.2 FT-IR spectrum of BHPFS structure.

Figure 4.3 ^{1}H-NMR spectrum of BHPFS.

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

According to the first condition that used TBAB as a catalyst, the chemical structure of crystal product was characterized by ^{1}H-NMR. The result is not a required product. From the ^{1}H-NMR spectrum show chemical shifts of 6F-BPA monomer and TBAB catalyst, however chemical shift of O-H of 6F-BPA disappear. This indicates that tetrabutylamonium can form ionic salt with 6F-BPA (Starks C. M., *et al.*, 1994). ^{1}H-NMR (400 MHz, CDCl$_3$, TMS) Fig. 4.4; δ 7.18 (d, 4H, H_1), 6.945 (d, 4H, H_2), 3.30 (t, 8H, N-CH_2), 1.70 (m, 8H, -CH_2-), 1.70 (q, 8H, -CH_2-CH$_3$), 0.97 (t, 12H, CH_3)
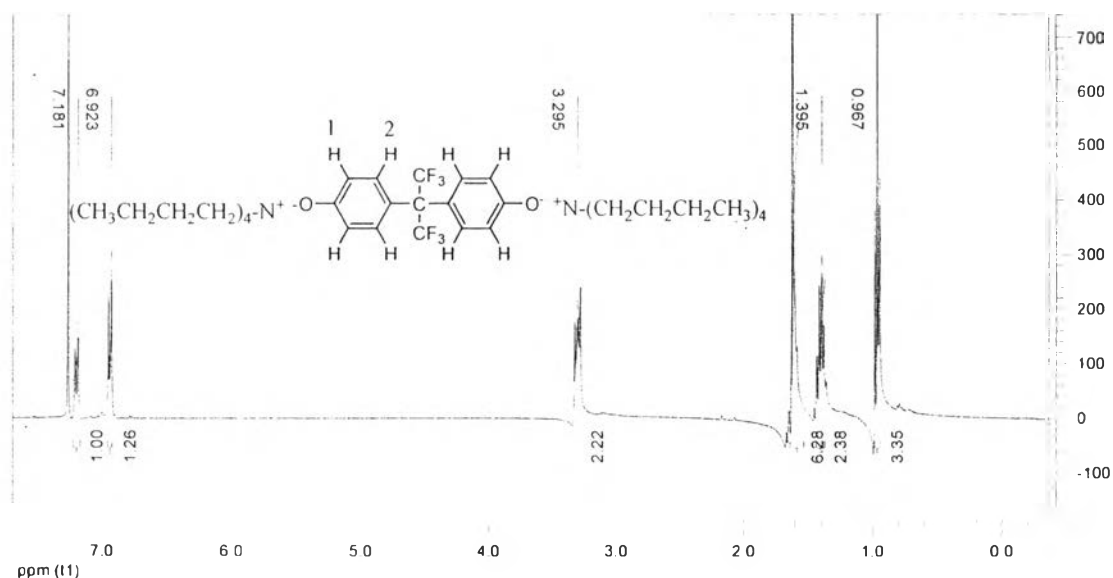
Figure 4.4 ^{1}H-NMR spectrum of ion pair between 6F-BPA and tetrabutylammonium.

Synthesis of PASE was achieved by using CaH$_2$ or Et$_3$N as a catalyst. The chemical structure of product was characterized by FT-IR. The molecular weight was determined by GPC using polystyrene standards and THF as the eluent. The results from GPC experiment show that both conditions have too less molecular weight of product; M$_w$ = 4056, M$_w$/M$_n$ = 1.194 and M$_w$ = 4699, M$_w$/M$_n$ = 1.280 for the CaH$_2$ and Et$_3$N catalyst reaction respectively. In addition, efficiency of reaction is not good because they still have residue monomers. FT-IR (KBr) spectra show the stretching vibration of the Si-O-C bonds at 1097 cm^{-1} and broad peak around wavenumber 3300 cm^{-1} which assigned to the O-H stretching.

Beside Et$_3$N, DMAP was used as an accelerating agent. PASE was achieved effectively. From FT-IR (KBr) spectrum (Fig. 4.5) , the peak of O-H stretching of monomer disappear , the strong peak at 1229-1296 cm^{-1} appeared which assigned to the C-O stretching vibration of ether bonds. Figure 4.6 shows the FT-IR spectra of PASE which achieved from different conditions ^{1}H-NMR (400 MHz, CDCl$_3$,TMS) spectrum (Fig. 4.7) shows the chemical shift at 5.6 and 6.0 ppm of doublet and 2.0 ppm of singlet belong to BHPFS molecule. The chemical shifts at around 6.6-7.6 ppm are aromatic proton characteristic. ^{13}C-NMR (400 MHz, CDCl$_3$,TMS) spectrum (Fig. 4.8) shows the chemical shift at around 100-140 ppm of aromatic carbons, 153.68 and 156.10 ppm of aromatic carbons with adjacent to the oxygen, 60.79 ppm of quaternary carbons. The chemical shifts at 114 ppm of =CH$_2$ groups, 12.8 ppm of primary carbons (-CH$_3$) are belong to BHPFS molecule. Molecular weights of products at 2:1 (PASE 1), 1:1(PASE 2), 1:1.25(PASE 3), 1:2 (PASE 4)and 1:3(PASE 5) monomer ratios are 811 (Mw/Mn = 1.116), 30,517(Mw/Mn = 1.537) (86.84% yeild), 37,443(Mw/Mn = 1.537) (86.65% yield), 17,659 (Mw/Mn = 3.872) (59.96% yield), 2,818 (Mw/Mn =2.544) respectively. Table 4.1 shows molecular weight of synthesized PASE. Figure 4.9 shows GPC distribution curve of PASE 3.

So the condition; Et$_3$N, DMAP, THF, room temperature at 1:1.25 monomer ratios having the highest molecular weight, was selected to synthesized PASE in order to produce cladding material.
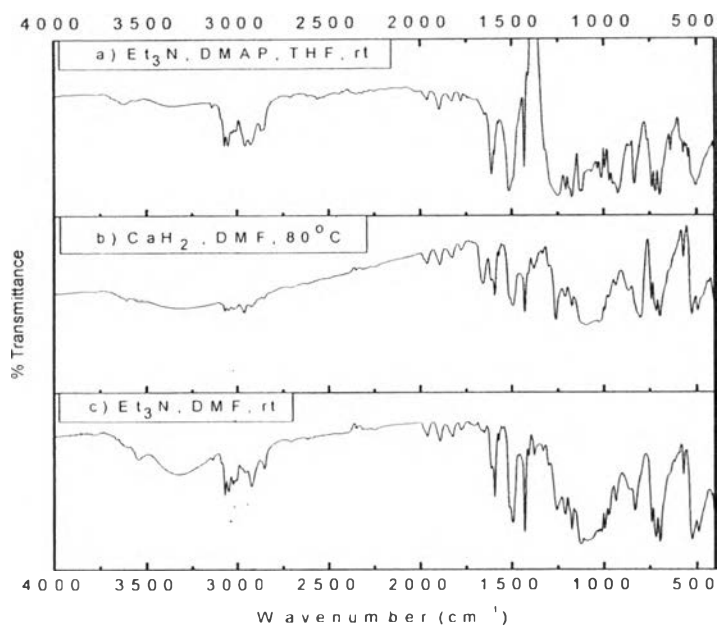
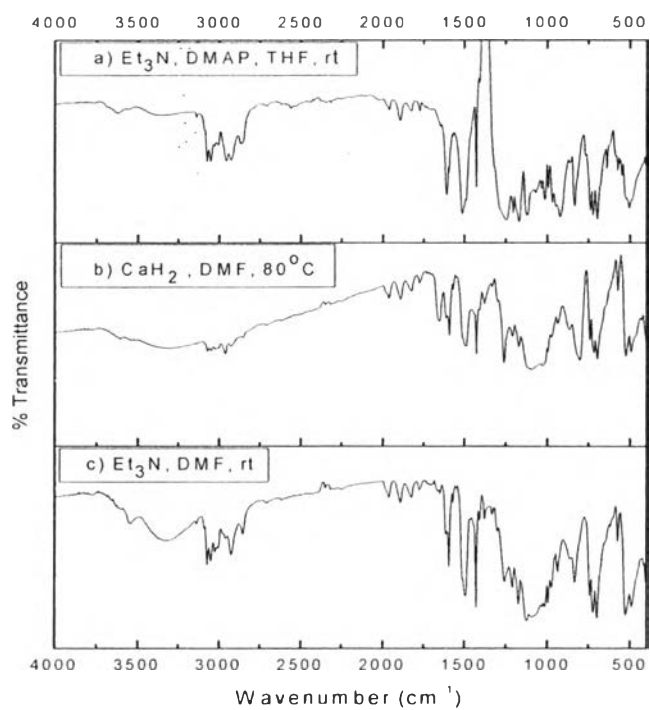**Figure 4.5** FT-IR spectra of PASE which achieved by Et₃N and DMAP catalysts and monomers.

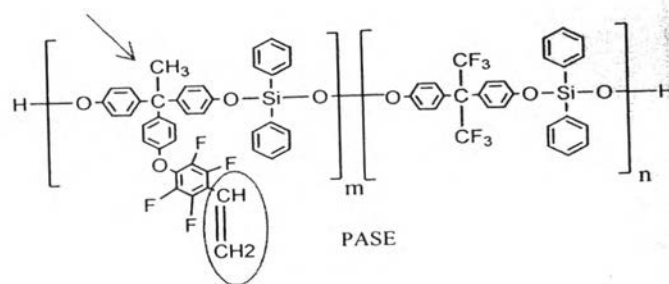**Figure 4.6** FT-IR spectra of PASE which achieved from different conditions.

PASE

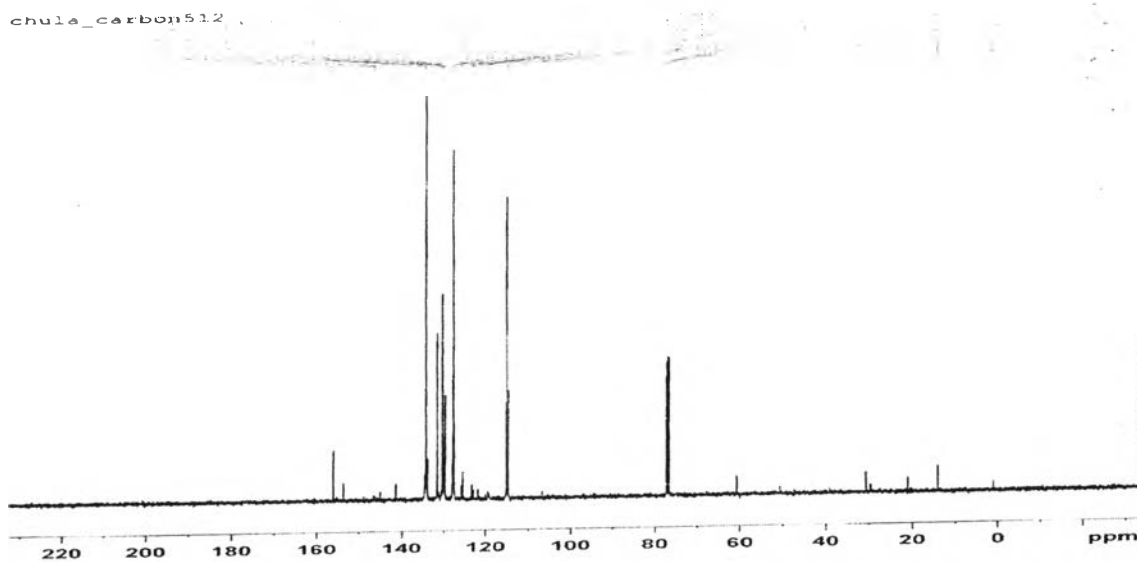**Figure 4.7** ¹H-NMR spectrum of PASE which achieved by Et₃N and DMAP catalysts.

Figure 4.8 ¹³C-NMR spectrum of PASE which achieved by Et₃N and DMAP catalysts.

Table 4.1 Molecular weight of synthesized PASE (The raw data is in the appendix
B.)

conditions	Mw	Mn	Mw/Mn
TBAB, toluene, rt, 48 h.			
	-	-	-
CaH2, DMF,80 ° C, 48 h.			
	4,056	3.397	1.191
Et3N, DMF, rt, 72 h.			
	4699	3670	1.280
Et3N, DMAP, THF, rt, 24 h.			
diphenol : silane			
2:1 (PASE 1)	811	727	1.116
1:1 (PASE 2)	30,517	19,851	1.537
1:1.25 (PASE 3)	37,443	22,037	1.699
1:2 (PASE 4)	17,659	4,561	3.872
1:3 (PASE 5)	2,818	1.108	2.544
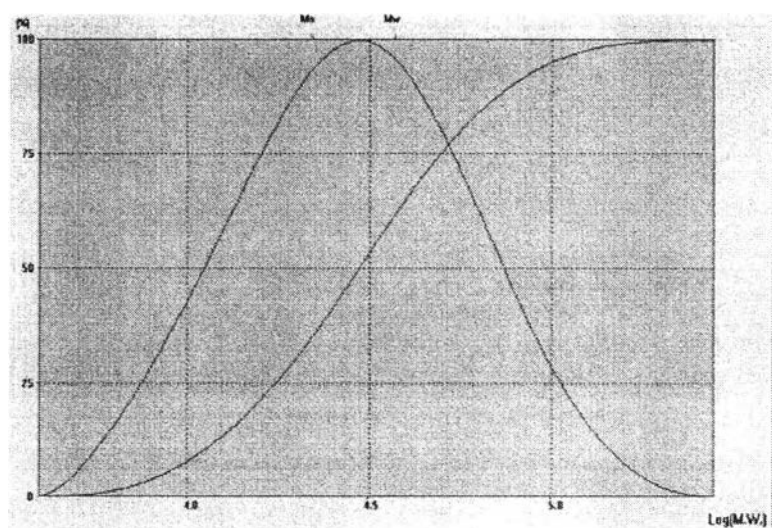
Figure 4.9 GPC distribution curve of PASE 3.
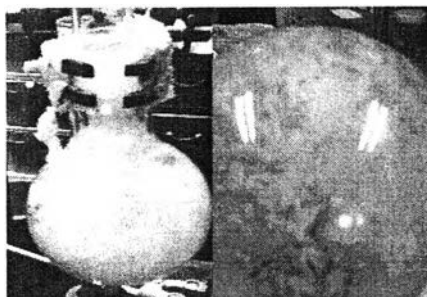
Figure 4.10 Pictures of PASE 3.

4.4.2 Thermal characterizations

The glass transition temperatures (T_g) of PASE 2, PASE 3 and PASE 4 from DSC are 39.66 $^\circ$ C, 47.61 $^\circ$ C and 35.44 $^\circ$ C respectively as shown in table 4.2 and figure 4.11. PASE 3 was selected to be a cladding in the further. TGA thermogram (Fig.4.12) shows the weight loss of PASE 3 occurring at about 218.7 $^\circ$ C, 391.0 $^\circ$ C, 477.5 $^\circ$ C and 538.4 $^\circ$ C with residue weight of 20% at 850 $^\circ$ C.

Since PASE has double bond from the side chain of BHPFS part, curing temperature was studied. DSC results (Fig. 4.13) show that BHPFS can cure by itself at 162-169 $^\circ$ C or by using dicumyl peroxide (DCP) as an initiator at 167.02 $^\circ$ C, DCP can cure the double bond in PASE at 175.53 $^\circ$ C. The endothermic peak at 42.88 $^\circ$ C comes from a melting of DCP. However, not only PASE cannot cure by itself but also PMMA/PASE blended can prevent the curing of PASE. Details of blending are in the next chapter.

Table 4.2 The glass transition temperature of PASE

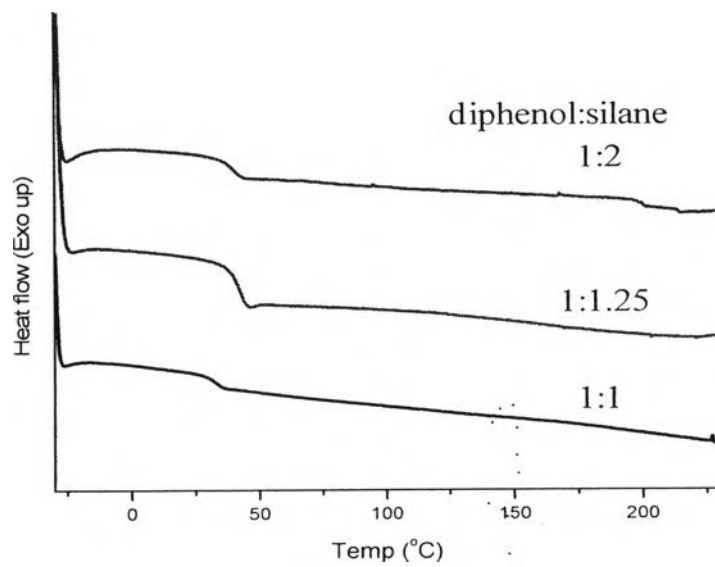| diphenol : silane	T_g ($^\circ$C)
1:1 (PASE 2)	39.66
1:1.25 (PASE 3)	47.61
1:2 (PASE 4)	35.44

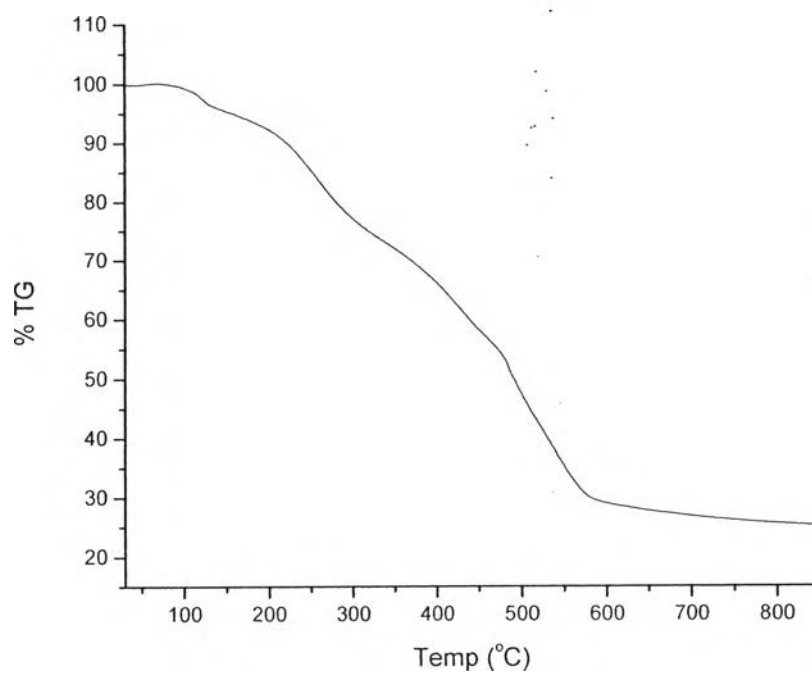**Figure 4.11** The DSC thermogram shows T$_g$ of PASE.

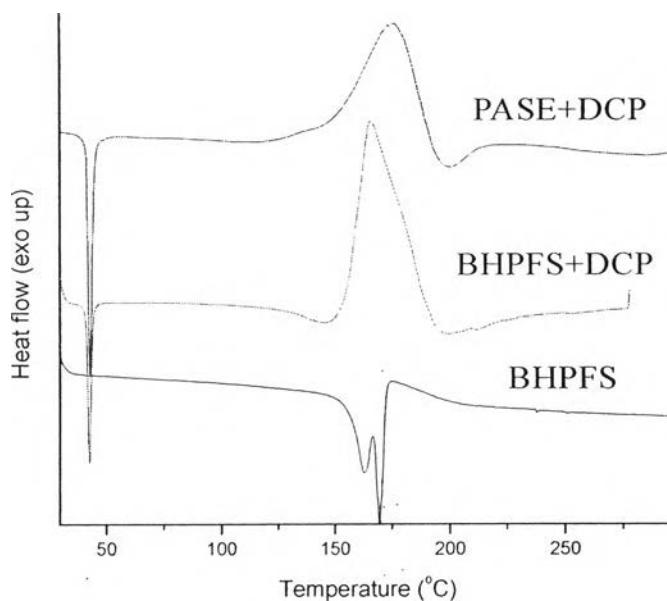**Figure 4.12** The TGA thermogram shows T$_d$ of PASE 3.

Figure 4.13 The DSC thermogram shows curing temperature.

4.5 Conclusions

Poly(arylene silyl ether)s (PASE) was successfully synthesized by using Et$_3$N as a catalyst and DMAP as a co-catalyst. The ratios of monomers are influence on the molecular weight of polymers. PASE which have M_w = 37,443 with M_n/M_w = 1.69 are achieved at ratio diphenol:silane equal to 1:1.25. Its T_g is 47.61 that is lower than PMMA (Tg = 103° C) so it can improve the flexibility of the cladding in a process.

4.6 Acknowledgement

4.7 References

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