



## CHAPTER IV

### EFFECT OF MOLECULAR STRUCTURE ON DIELECTRIC PROPERTIES OF POLYBENZOXAZINE

#### 4.1 Abstract

The effect of molecular structure of polybenzoxazine on dielectric properties was studied. In this work, aniline based (BA-a) and fluorinate based (BA-f) benzoxazine monomer were synthesized by solventless method, and their structures were confirmed by FTIR,  $^1\text{H}$  NMR and  $^{19}\text{F}$  NMR. The curing temperatures of the monomers were investigated by DSC thermograms. Dielectric properties of the polymers were measured by Hewlett-Packard 4194A Impedance/Gain-Phase Analyzer as functions of frequency and temperature. It was showed that the dielectric constants of the polymers were nearly stable with frequency range of 1 kHz–10 MHz. At temperature around 25-160°C the dielectric properties of the polymers were stable upto the temperature of 160°C. At higher temperature, the dielectric constant and dielectric loss increased significantly because the segmental mobility of the polymers was improved. It also found that, dielectric constant of fluorinate based polybenzoxazine was lower than the aniline based polybenzoxazine due to small dipole and low polarizability of C–F bond comparing with C-H bond.

**Keywords:** Aniline based polybenzoxazine, Fluorinate based polybenzoxazine, Dielectric constant, Dielectric loss.

#### 4.2 Introduction

Polybenzoxazines are a new class of thermosetting phenolic resins. They have been developed to overcome several short comings of conventional phenolic resins by combining the thermal stability of phenolics and the mechanical performance and molecular design flexibility of advance epoxy systems. Thus polybenzoxazines are more interested as alternative materials applied in many fields such as the electronics and aerospace industries to the traditional phenolic, epoxy and polyimide resins in the recent year. Polybenzoxazines provide characteristics found in

the conventional phenolic resins such as high heat resistance and flame retardant properties. They also provide characteristics that are not found in the traditional ones such as excellent dimensional stability, low water absorption, high glass transition temperature, excellent electrical properties, wide molecular design flexibility and no need to use strong acids as catalysts and no releasing condensation by-products during for polymerization reaction [1].

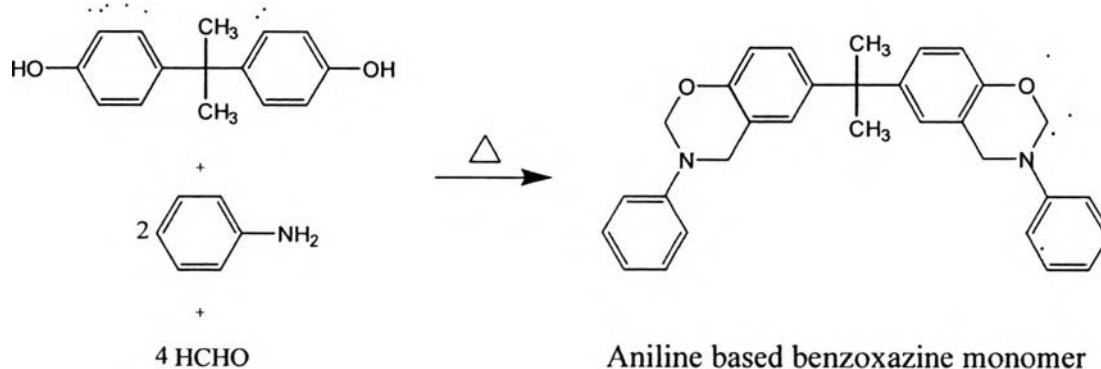
A series of polybenzoxazines is obtained by the ring-opening polymerization of cyclic benzoxazine monomers at high temperatures in the absence of a catalyst and without generating any by-products. Benzoxazine monomers are heterocyclic compounds that were first synthesized by Holly and Cope through the Mannich condensation of a phenol with formaldehyde and amine (aliphatic or aromatic) as starting materials [2]. Various types of benzoxazine monomer can be synthesized by using various phenols and amines with different substitution groups attached. The synthesis of benzoxazine monomers can be done either by employing solution or solventless methods [3]. In the case of the solution method, the use of an organic solvent also increases the cost of the products and causes environmental problems. Furthermore, the solvent residue in the precursors also leads to problems during processing of the benzoxazine resins. To overcome these shortcomings, a solventless synthesis in the melt state was developed. In a typical synthesis, the reactants are physically mixed together, heated to their melting temperature, and then maintained at a temperature sufficient to complete the interaction of the reactants to produce the desired benzoxazine. The main advantages of the solventless synthetic method are improvement of reaction times compared with the traditional synthetic route and formation of fewer unwanted intermediates and by-products [4].

Because there are several choices of phenols and amines for the synthesis of benzoxazine monomers. Hence, polybenzoxazines can be addressed in many fields, including in electronics applications. In order to address these applications, dielectric properties (such as dielectric constant or permittivity and dielectric loss) of the materials should be mainly concerned. So, the effect of different substitution groups of benzoxazine monomers on dielectric properties was studied in this research.

### 4.3 Experimental

#### 4.3.1 Aniline Based Benzoxazine Monomer Preparation

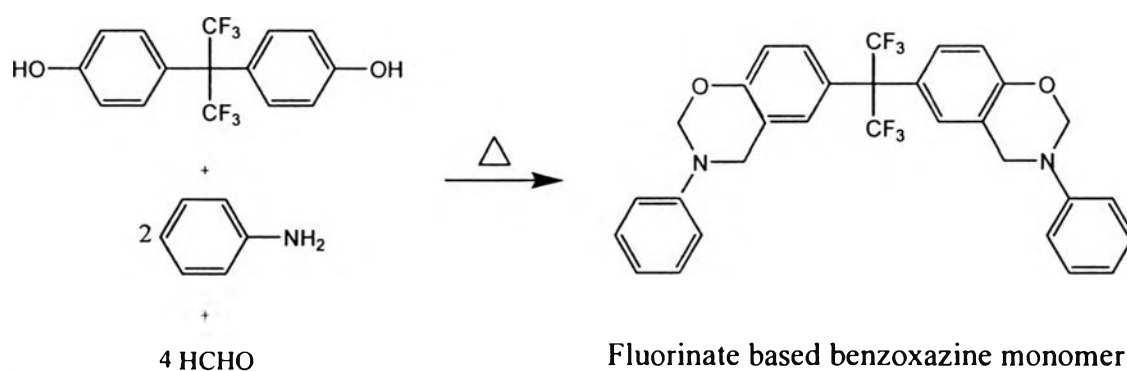
The synthesis of aniline based benzoxazine monomer is based on the reaction of bisphenol A, paraformaldehyde, and aniline at the molar ratio of 1:4:2 respectively, as shown in Figure 4.1. For this experiment, the monomer was prepared from solventless method; the starting materials were mixed together without solvent at temperature of 100°C for 30 min. Then the product with high yellow viscous liquid was obtained. This viscous product was dissolved in chloroform and washed sequentially with 0.1 N NaOH and water for three times to eliminate any unreacted formaldehyde and dried over Na<sub>2</sub>SO<sub>4</sub>. The chloroform was then removed with a rotary evaporator and the solid products were washed by cool methyl alcohol at least three times to obtain white powder benzoxazine monomer.



**Figure 4.1** Synthesis reaction of benzoxazine monomer based on bisphenol A, aniline and paraformaldehyde.

### 4.3.2 Fluorinate Based Benzoxazine Monomer Preparation

The fluorinate based benzoxazine monomer was prepared by the reaction of hexafluorobisphenol A, paraformaldehyde, and aniline at a molar ratio of 1:4:2, respectively, as shown in Figure 4.2, with the same procedure as aniline based monomer.



**Figure 4.2** Synthesis reaction of benzoxazine monomer based on hexafluorobisphenol A, aniline and paraformaldehyde.

### 4.3.3 Characterizations

The chemical structure of aniline based and fluorinate based benzoxazine monomers were confirmed by Proton and Fluorine Nuclear Magnetic Resonance Spectrometer ( $^1\text{H}$  NMR and  $^{19}\text{F}$  NMR). The  $^1\text{H}$  NMR spectra were recorded on Bruker Avance DPS-400. The solvent used in these techniques was deuterated chloroform. Functional groups of the benzoxazine monomers were measured by a fourier transformation infrared spectrophotometer (NEXUS 670 FTIR). All spectra were recorded with absorbance mode in the wave number range of  $4000\text{-}400\text{ cm}^{-1}$  and 32 scans per resolution. Differential scanning calorimeter 7, DSC 7 (Perkin Elmer) was performed to measure curing temperature of the benzoxazine monomers. The samples were heated from  $30\text{-}300^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  under  $\text{N}_2$  purge.

Dielectric measurement of polybenzoxazines was performed with Hewlett-Packard 4194A Impedance/Gain-Phase Analyzer in parallel capacitance ( $C_p$ ) mode as function of frequency (1 kHz-10 MHz) and temperature ( $25^\circ\text{C}$ - $200^\circ\text{C}$ ). The

dielectric constant ( $\epsilon$ ) of the composites was calculated from the measured thickness and capacitance by using the following equation:

$$\epsilon = \frac{Cd}{\epsilon_0 A}$$

where  $C$  is the capacitance (F),  $\epsilon_0$  is the free space dielectric constant value ( $8.85 \times 10^{-12}$  F/m),  $A$  is the capacitor area ( $m^2$ ), and  $d$  is the thickness of specimen (m).

## 4.4 Results and Discussion

### 4.4.1 Benzoxazine Monomers and Polymers Characterization

The functional groups of BA-a monomer and BA-f monomer synthesized from solventless method were investigated by FTIR Spectrometer and the FTIR spectra as shown in Figure 4.3 and 4.4, respectively. The tri-substituted benzene ring mode in the oxazine ring structure is observed at  $1496 \text{ cm}^{-1}$  for BA-a monomer and at  $1499 \text{ cm}^{-1}$  for BA-f monomer. The bands around  $1240\text{-}1020 \text{ cm}^{-1}$  and  $830\text{-}740 \text{ cm}^{-1}$  attributes to the antisymmetric and symmetric C-N-C stretching modes, respectively. The antisymmetric C-O-C stretching mode can be found in the region of  $1240\text{-}1210 \text{ cm}^{-1}$ , while the symmetric mode appears at  $1040\text{-}1020 \text{ cm}^{-1}$ . In addition, the characteristic modes of benzene with an attached oxazine ring are appeared at  $940\text{-}920 \text{ cm}^{-1}$  [6]. However the BA-f monomer shows the C-F characteristic absorption bands between  $1200$  and  $1100 \text{ cm}^{-1}$ . From FTIR spectra of BA-a monomer and BA-f monomer, the absence of the bands between  $3600$  and  $3200 \text{ cm}^{-1}$ , which is the characteristic peaks of intermolecular hydrogen bonded group, can ensure the purification of the synthesized monomers [7].

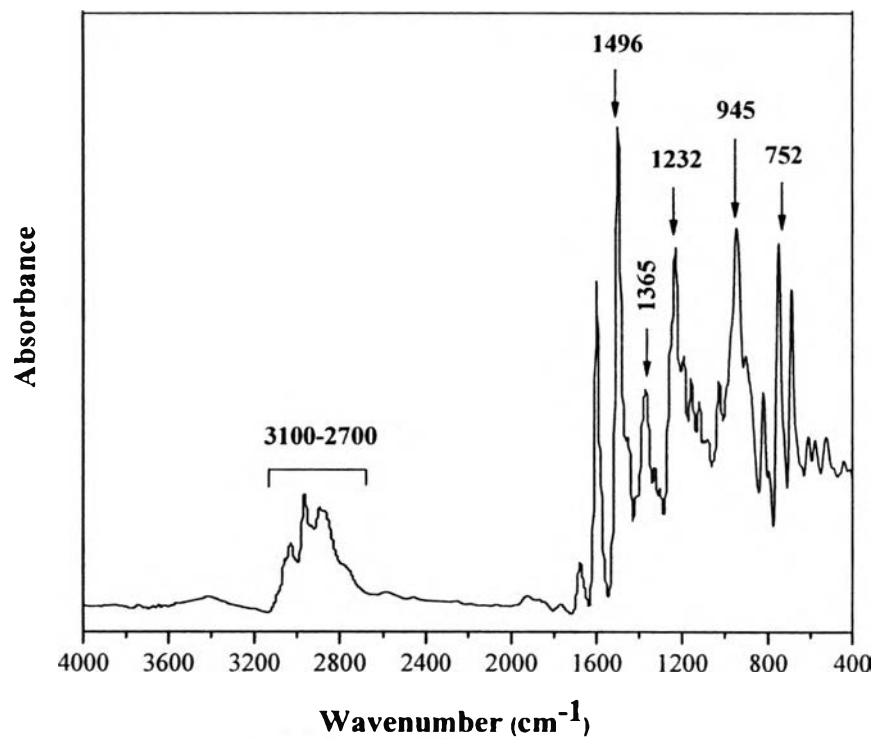


Figure 4.3 FTIR spectra of the aniline based benzoxazine (BA-a) monomer.

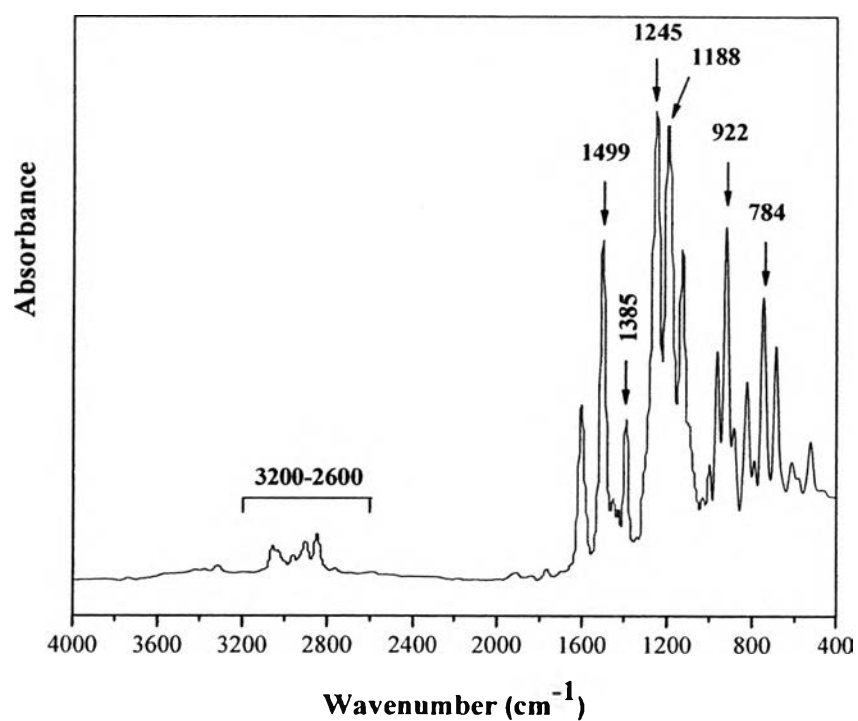
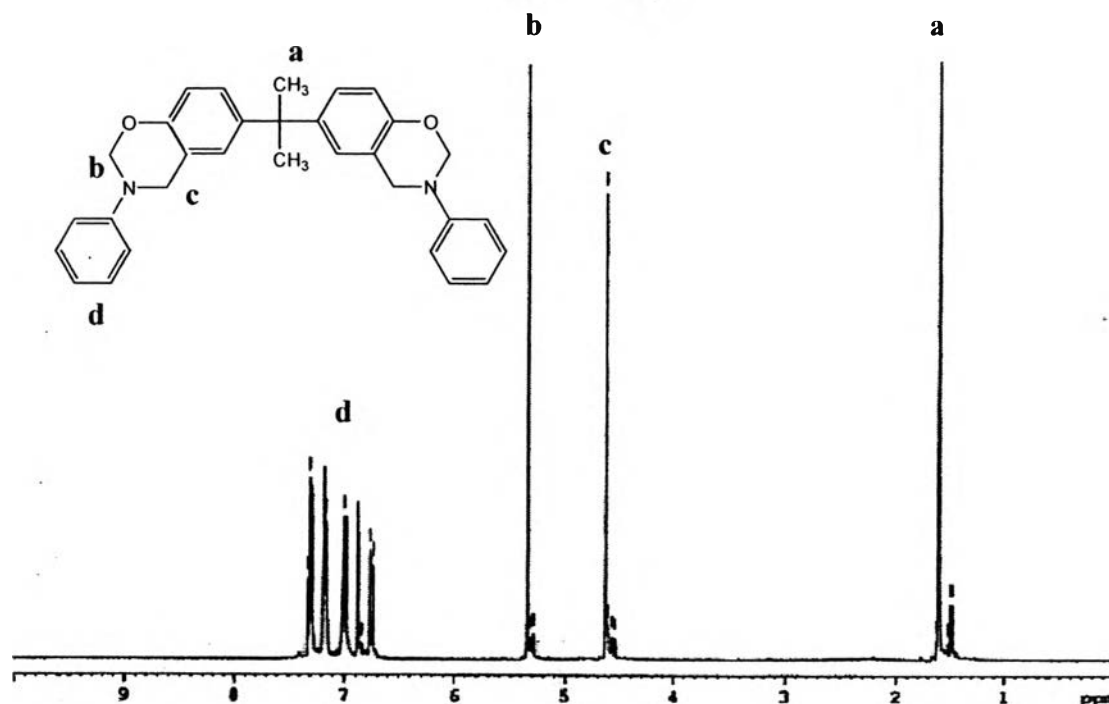


Figure 4.4 FTIR spectra of the fluorinate based benzoxazine (BA-f) monomer.

The chemical structure of the monomers can be also confirmed by NMR spectra and the  $^1\text{H}$  NMR spectra of BA-a monomer and BA-f monomer are shown in figure 4.5 and 4.6, respectively. For BA-a monomer, the characteristic peak assignable to methyl proton of bisphenol A ( $-\text{CH}_3$ ) was observed at 1.6 ppm. The methylene ( $\text{O}-\text{CH}_2-\text{N}$ ) and methylene ( $\text{Ar}-\text{CH}_2-\text{N}$ ) of oxazine ring showed peaks at 5.35 and 4.6, respectively. And the aromatic proton showed multiplets around 6.7-7.3 ppm. While the BA-f monomer displayed peaks at 5.4, 4.6 and 6.8-7.3 ppm for  $\text{O}-\text{CH}_2-\text{N}$ ,  $\text{Ar}-\text{CH}_2-\text{N}$  and aromatic proton, respectively [6]. From the  $^{19}\text{F}$  NMR spectra of BA-f monomer shown in Figure 4.7, the spectrum of  $\text{C}-\text{CF}_3$  at -64.9 to -65.05 ppm was observed. This slight chemical shift (within 1 ppm) indicates that the structure of the fluorinate benzoxazine ring was formed [8]. From  $^1\text{H}$  NMR spectra of both BA-a monomer and BA-f monomer there were no peaks appeared at around 3.10 and 3.60 ppm, assignable to the methylene groups from the oligomers produced by opening structures of oxazine ring which confirmed the purity of the monomer [9].



**Figure 4.5**  $^1\text{H}$  NMR spectra of the aniline based benzoxazine (BA-a) monomer.

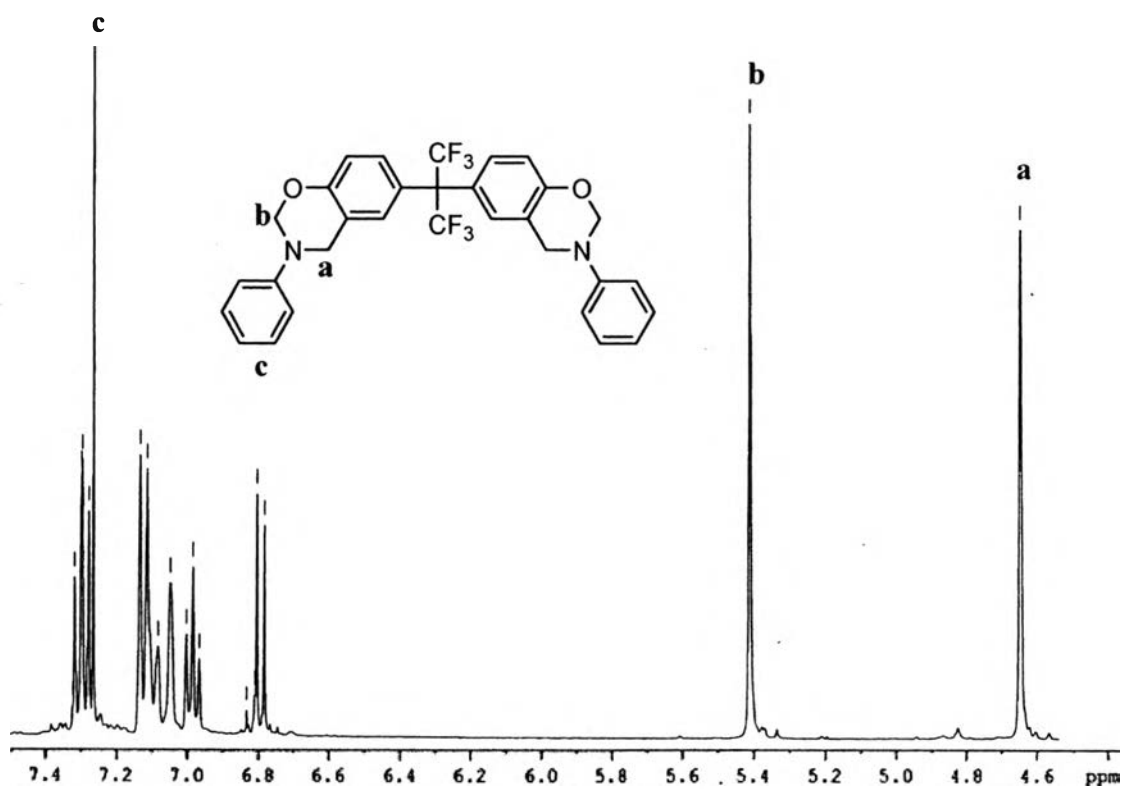


Figure 4.6  $^1\text{H}$  NMR spectra of the fluorinate based benzoxazine (BA-f) monomer.

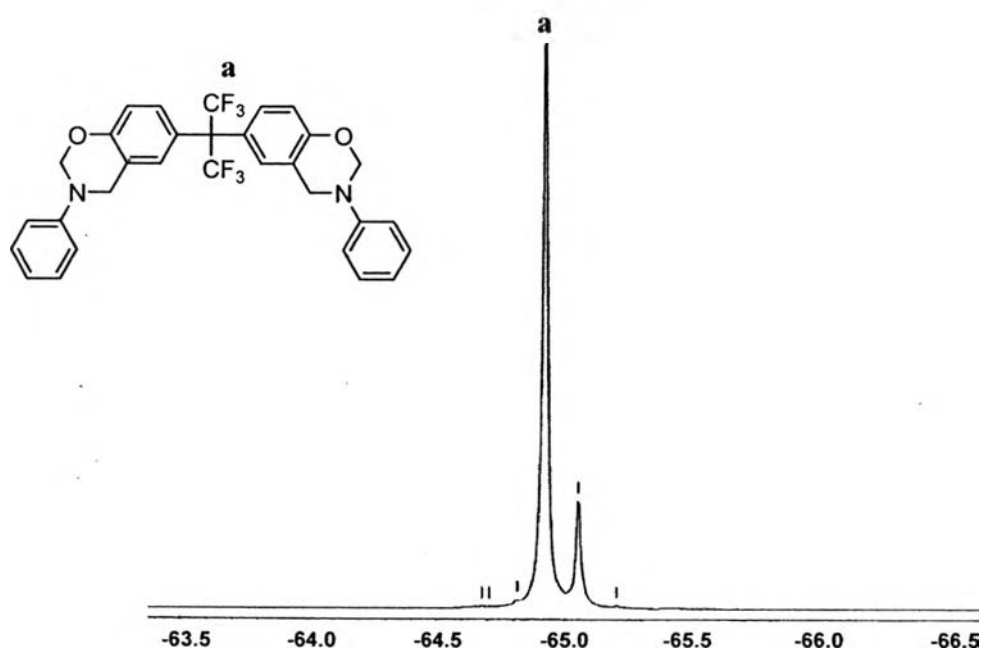
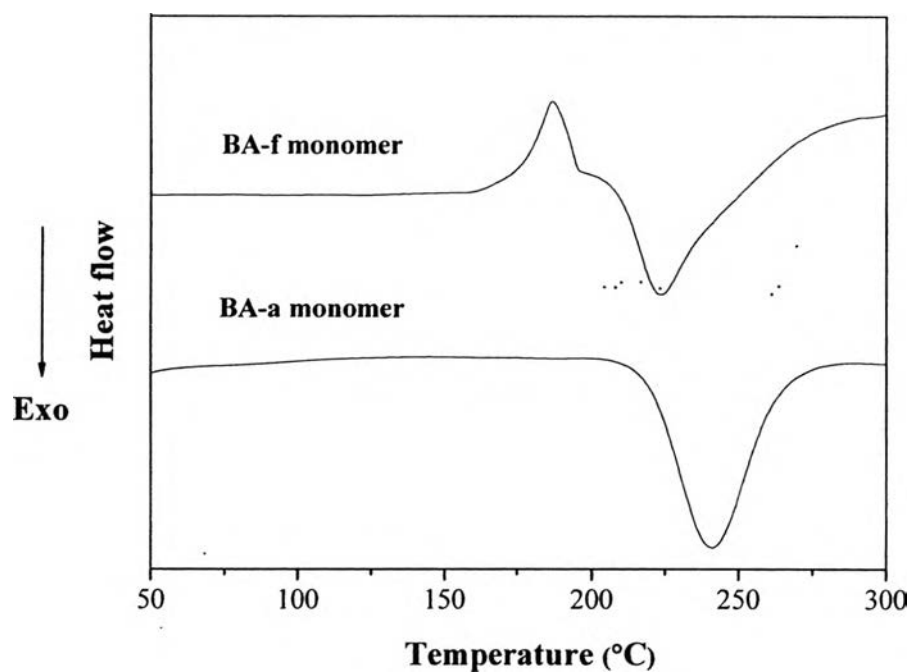


Figure 4.7  $^{19}\text{F}$  NMR spectra of the fluorinate based benzoxazine (BA-f) monomer.



The DSC thermogram of the benzoxazines polymerization reaction is shown in Figure 4.8. For BA-a monomer, the exotherm onset and the peak maximum were observed at 221.44°C and 240.83°C, respectively. This result indicates that the ring opening polymerization reaction of BA-a monomer is initiated by heat at temperature of 221.44°C. In the case of BA-f monomer, there is an appearance of melting endotherm peak at 186.83°C which close to the exotherm peak at 223.83°C (curing temperature) which indicates that the monomer starts to polymerize and crosslink immediately after melted.



**Figure 4.8** Differential scanning calorimetry (DSC) thermogram of BA-a and BA-f monomer.

## 4.4.2 Dielectric Properties of Polybenzoxazine

### 4.4.2.1 *Frequency Dependence*

Figure 4.10 shows the dependence of dielectric constant of polymers on frequency range 1 kHz-10 MHz. It was observed that the dielectric constant of the PBA-a and PBA-f slightly decreased with increasing frequency while the dielectric loss of the polymers showed no significant difference at various frequencies, as shown in Figure 4.11. The slightly decrease of dielectric constant was occurred by the decreasing in dipolar polarization in the polymers. When the frequency of applied electric field was above the relaxation frequency of the dipolar polarization mechanism, the contribution from this mechanism was dramatically reduced because this polarization was too slow to completely follow the oscillation of the applied electric field [10].

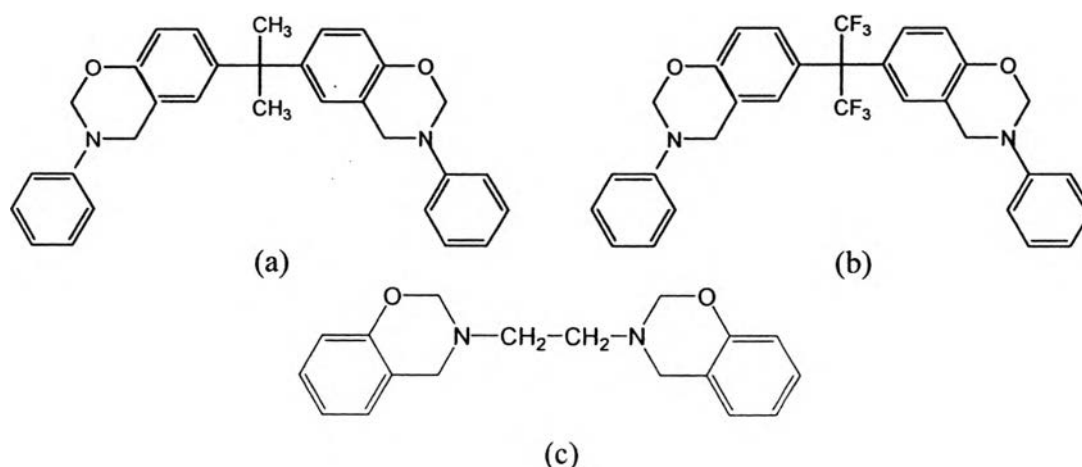
### 4.4.2.2 *Temperature Dependence*

The dielectric constant and dielectric loss of the polymers were measured as a function of temperature varying from 25°C-200°C at 1 MHz and the results are shown in Figure 4.12 and 4.13, respectively. From the dielectric constant of polymers at various temperatures shown in Figure 4.12, it was found that the dielectric constants of the polymers were stable at temperature range 25-160°C, however, the dielectric constants significantly increased at the temperature above 160°C. This result can be explained that the segmental mobility of polymers was improved at high temperature then the dipole orientation polarization was the dominant mode of polarization resulting in increasing of permittivity or dielectric constant of the polymers [11]. For the dielectric loss of polymers, it also had a similar behavior as shown in Figure 4.13. At high temperature, the dipole orientation polarization was the dominant mode. This type of the polarization mode is a relative slow process in comparison with electronic and atomic polarization which is more significant mode in the solid state of polymers at room temperature. When the electric field was applied, the orientation dipoles inevitably lagged behind the applied field, giving rise to energy dissipation so this phenomenon may give rise to the dielectric loss of the polymers [5].

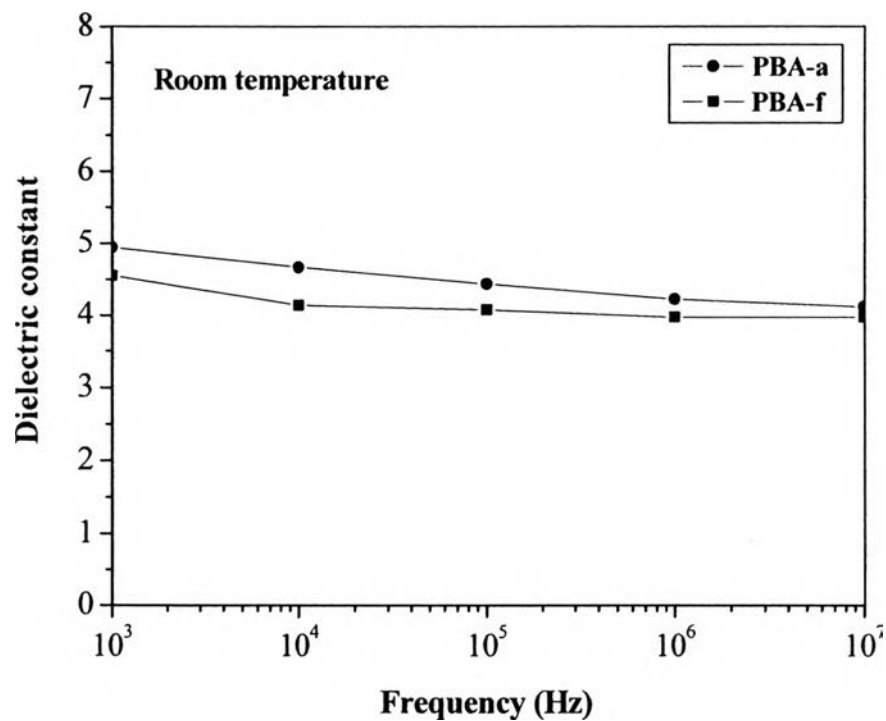
#### 4.4.2.3 Effect of Polymer Structure

From Figure 4.10, it can be seen that the dielectric constant of PBA-a (4.94 at 1 kHz) was greater than PBA-f (4.54 at 1 kHz). This result implies that the incorporation of fluorinated substitutes into polymer structure is able to lower its dielectric constant. There are three main reasons: (a) Substitution of hydrogen with  $-CF_3$  group decreases the electronic polarizability due to the lower polarizability of C-F bond compared with that of the C-H bond. (b) The lower polarizability of C-F bond can induce the hydrophobicity of polymer. Since the moisture has the very high dielectric constant so it strongly affects the dielectric constant of the polymer. (c) The bulky  $-CF_3$  group is able to reduce efficient molecular packing and increase the free volume thus more air can be trapped in the polymer chain resulting in lower dielectric constant due to the low dielectric constant value of the air [5].

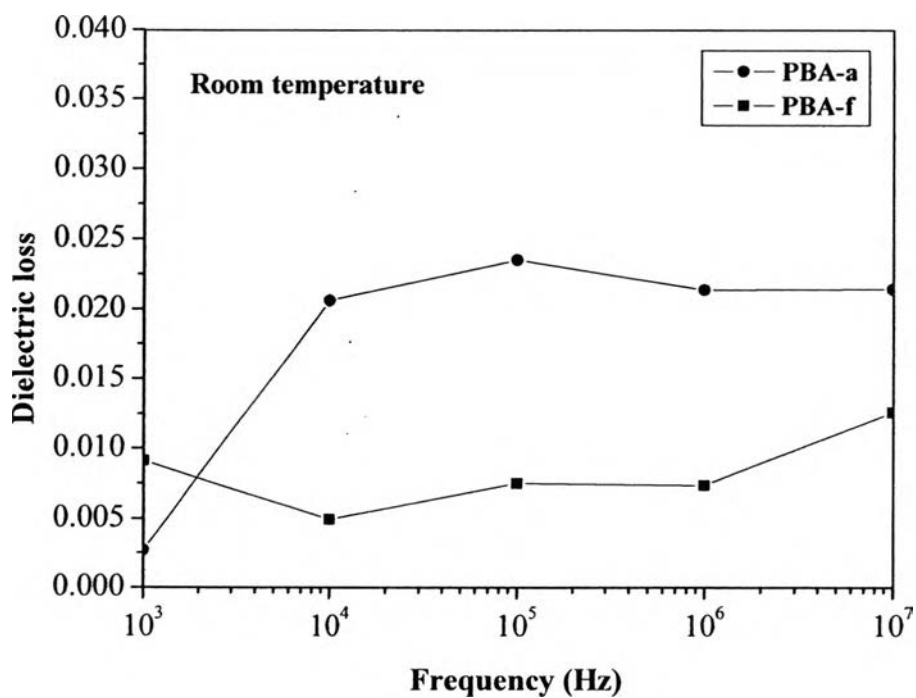
Considering from the previous research of Panomsuwan G. [12], the dielectric properties of diamine based polybenzoxazine was studied and the dielectric constant was reported as 3.81 at 1 kHz (while PBA-a and PBA-f gave 4.94 and 4.54, respectively). The lower in dielectric constant of the diamine based polybenzoxazine than the others is due to the lower number of aromatic rings, consequent in lower conjugated double bonds. Because the polymer which contains more C=C bonds, is expected to have higher relative permittivity or dielectric constant, since the bond polarizability of C=C bonds is much higher than those of C-H bonds and C-C bonds.



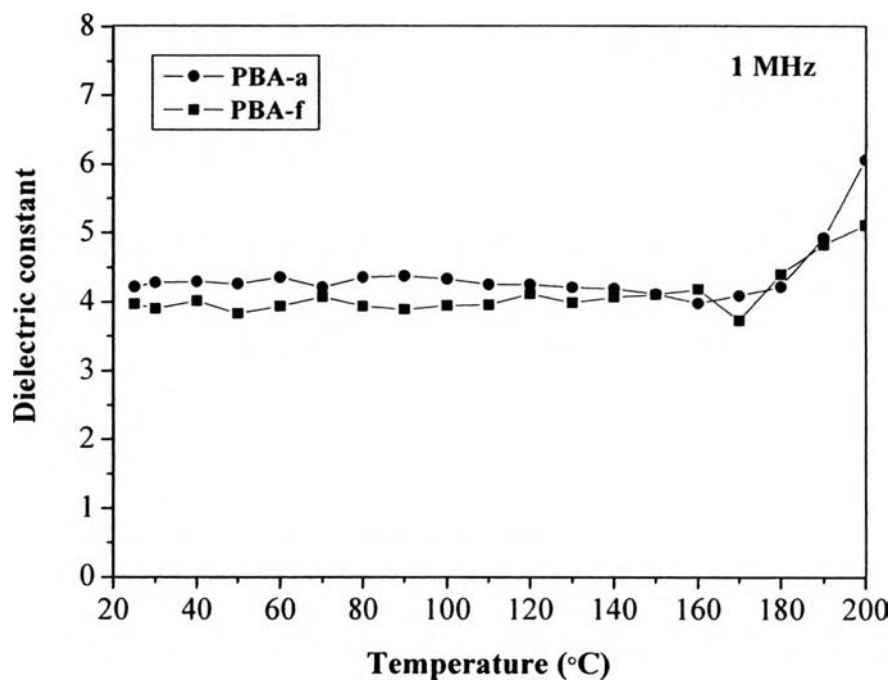
**Figure 4.9** The structure of (a) aniline based benzoxazine monomer, (b) fluorinate based benzoxazine monomer, and (c) diamine based benzoxazine monomer.



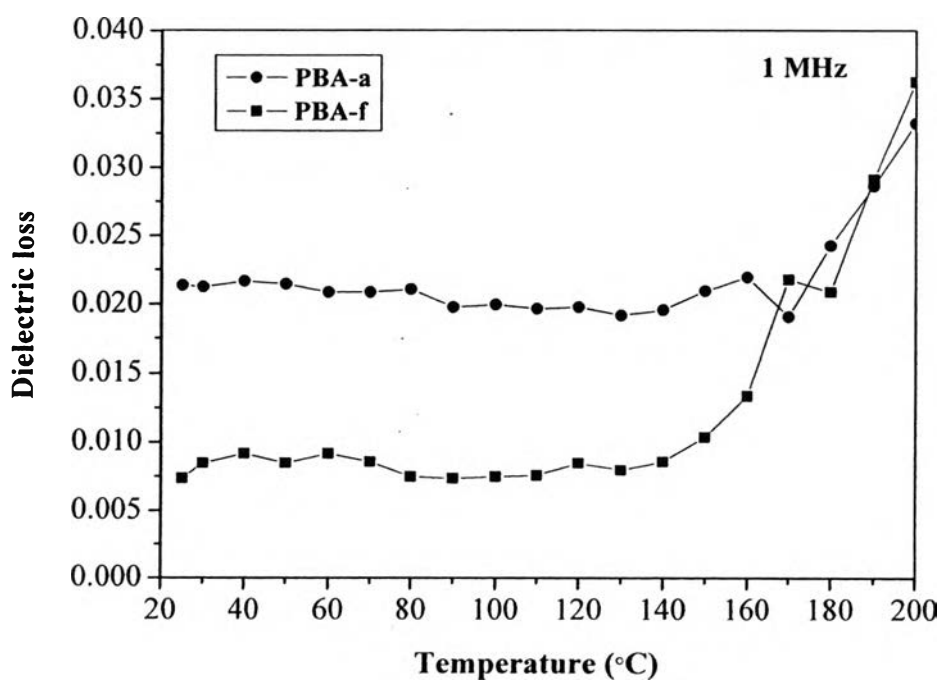
**Figure 4.10** The dielectric constant of aniline based and fluorinate based polymer as a function of frequency.



**Figure 4.11** The dielectric loss of aniline based and fluorinate based polymer as a function of frequency.



**Figure 4.12** The dielectric constant of aniline based and fluorinate based polymer as a function of temperature.



**Figure 4.13** The dielectric loss of aniline based and fluorinate based polymer as a function of temperature.

#### 4.5 Conclusions

The dielectric constant of PBA-a and PBA-f were 4.94 and 4.54 at 1 kHz, respectively. However the dielectric constants of the polymers showed nearly stable with the frequency range 1 kHz-10MHz. The positive temperature coefficient (PTC) of dielectric properties was nearly zero in the temperature range of 25-160°C, which indicated the low relaxation behavior. However, the dielectric properties of the polymers significantly increased at high temperature, it is because the segmental mobility of polymers was improved. The structure of polymers is another factor to effect on the dielectric properties. It was found that the incorporation of fluorinated substitutes into polybenzoxazine was able to reduce dielectric constant and dielectric loss because of small dipole and the low polarizability of C—F bond compared with that of the C-H bond. However, the fluorinated substitution does not effect on the dielectric constant as high as the incorporation of aromatic rings or conjugated bonds due to the much higher polarizability of the C=C bonds comparing with C-H bonds and C-F bonds.

#### 4.6 Acknowledgements

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#### 4.7 References

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