

Chapter 2

Intra-molecular Hydrogen Bonding in Phenolic Resins

2.1 Background

As discussed in chapter 1, novolac and p-cresol formaldehyde (PCF) resins were synthesized by a similar procedure. By its nature, the PCF resin can polymerize only through the *ortho*- position to form a linear, unbranched structure. On the other hand, novolac, which can be linked at both *ortho*- and *para*-positions, has a highly branched structure. P-Cresol formaldehyde resin has an interesting property relative to phenol based polymers. This resin shows much stronger hydrogen bonding, compared to resol, novolac and other phenolic compounds. It has been proposed that an intra-molecular hydrogen bond exists in these small-molecule model compounds. In 1992, Fitzgerald et al.⁶ reported that the strength of hydrogen bonds is dependent on the degree of steric hindrance of the molecule. Fitzgerald compared the hydrogen bonded strength of two model compounds; "hindered" and "unhindered" all-*ortho*- linked phenolic oligomers, as illustrated in figures 2.1 and 2.2. The infrared spectroscopic results show a hydrogen bonded hydroxyl frequency at 3400 cm^{-1} and 3200 cm^{-1} for "hindered" and "unhindered" structures, respectively. This indicates that the absence of steric factors in the "unhindered" structure allows the molecule to rotate more freely to form a suitable conformation for stronger intra-molecular hydrogen bonding.

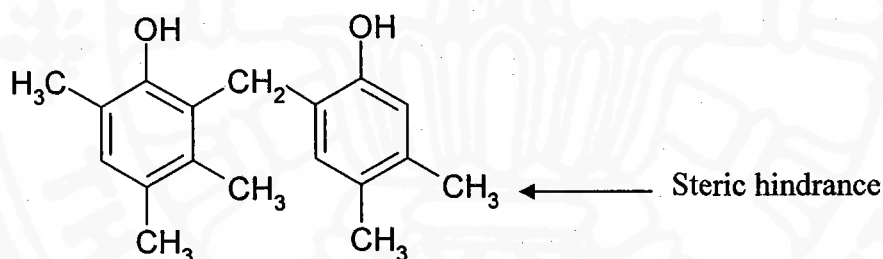


Figure 2.1 Structure of the "hindered" *ortho-ortho* bridged oligomer.

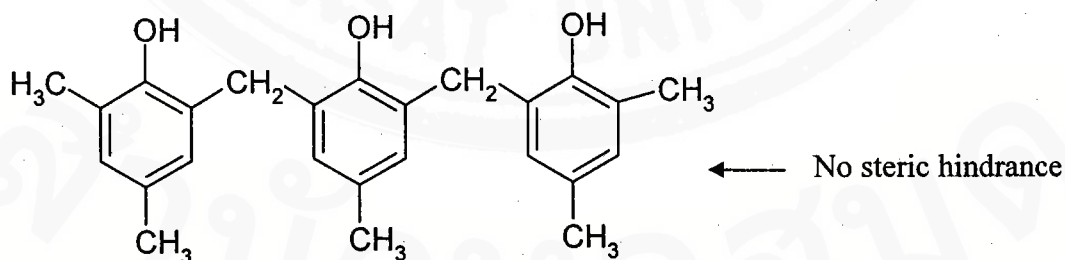


Figure 2.2 Structure of the "unhindered" *ortho-ortho* bridged oligomer.

We have found that p-cresol formaldehyde (PCF) resin, which presumably consists of a distribution of oligomers, also has a band characteristic of a remarkably strong hydrogen bond that is not observed in the spectra of novolac and other phenolic compounds. This could be the result of similar intra-molecular

hydrogen bonding, which stabilizes a cyclic structure similar to that found in calixarene compounds or semi-calixarenes (See figures 2.3 and 2.4) Furthermore, DSC experiments revealed that PCF shows an interesting thermal transition. The FTIR results also strongly support the existence of such structures in the PCF resin.

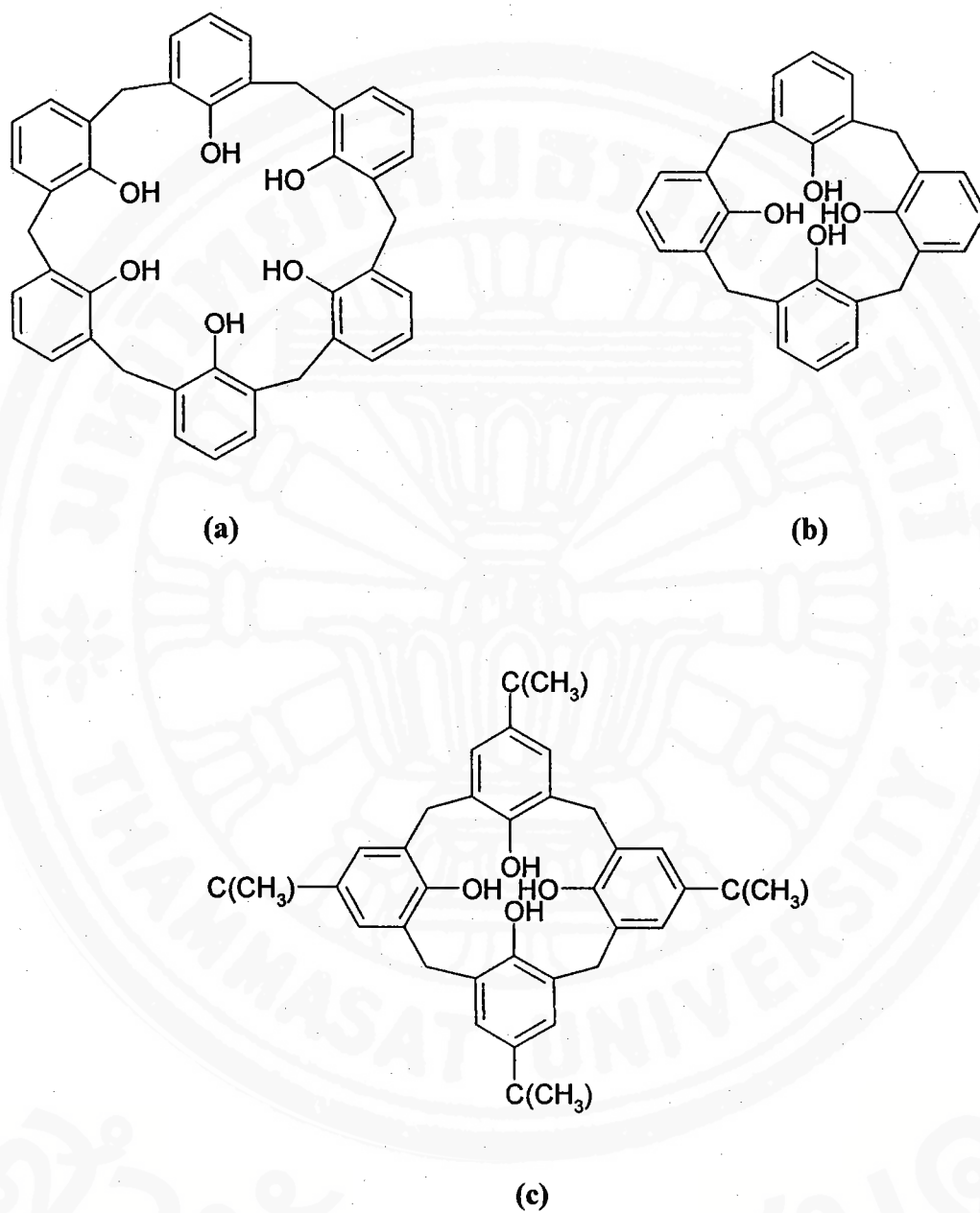


Figure 2.3 Structures of calix[6]arene (a), calix[4]arene (b), and *p*-*tert*-butylcalix[4]arene (c).

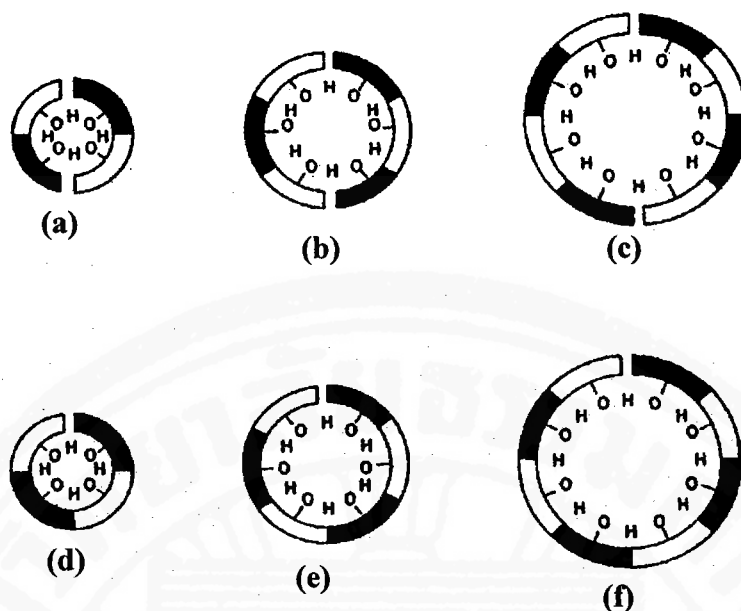


Figure 2.4 Structures of "hemi-calixarenes" and "pseudo-calixarenes": hemi-calix[4]arene (a), hemi-calix[6]arene (b), hemi-calix[8]arene (c), pseudo-calix[4]arene (d), pseudo-calix[6]arene (e), and pseudo-calix[8]arene (f).

(Source: C.D. Gustsche, "Calixarenes", The Royal Society of Chemistry, St. Louis, 1989)

2.2 FTIR Spectra

A comparison of structures and the infrared spectra of p-cresol formaldehyde (PCF) resin and other phenolic compounds are shown in figure 2.5 and 2.6. All materials show similar free hydroxyl bands near 3520 cm^{-1} , but the PCF resin has a hydrogen-bonded hydroxyl band at a much lower frequency around 3250 to 3200 cm^{-1} , compared to 3340 cm^{-1} for novolac, p-cresol, phenol and 2,4,6-trimethylphenol. This indicates that stronger hydrogen bonds exist in the PCF structure relative to other materials. By comparing the spectrum of the PCF resin to those of p-cresol and 2,4,6-trimethylphenol, we can say that this strong hydrogen bonding is not a result of the electron-donating methyl groups, but must result from the linear (unbranched) structure of the PCF resin itself. As described earlier, novolac polymerizes to give a branched structure, while PCF resin is in a linear form that allows the hydroxyl groups to form intra-molecular hydrogen bonding cyclic structure, as illustrated in figure 2.7.

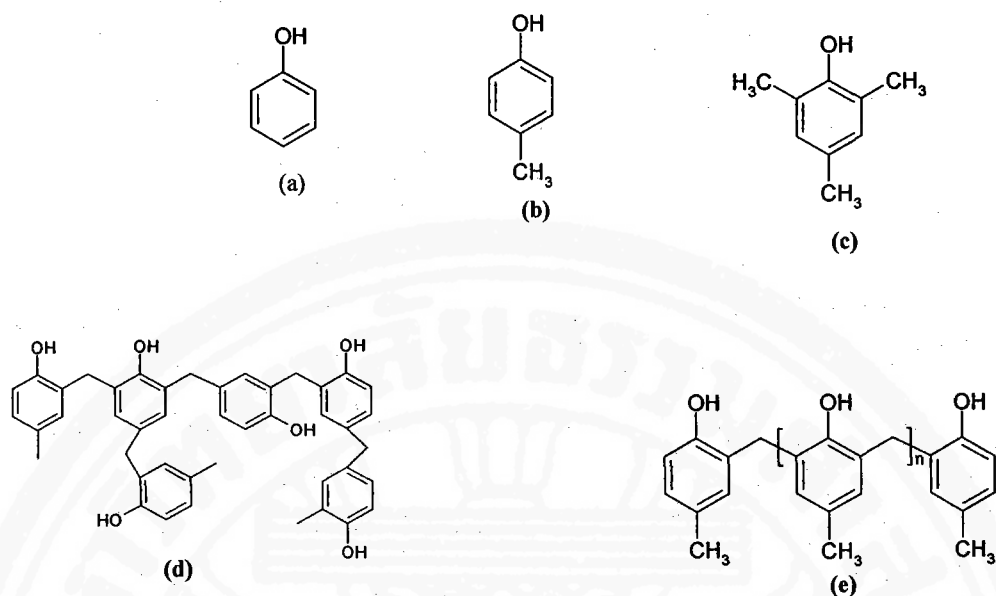


Figure 2.5 Molecular structures of phenol (a), p-cresol (b), 2,4,6-trimethylphenol (c), novolac (d), and p-cresol formaldehyde (PCF) resin (e).

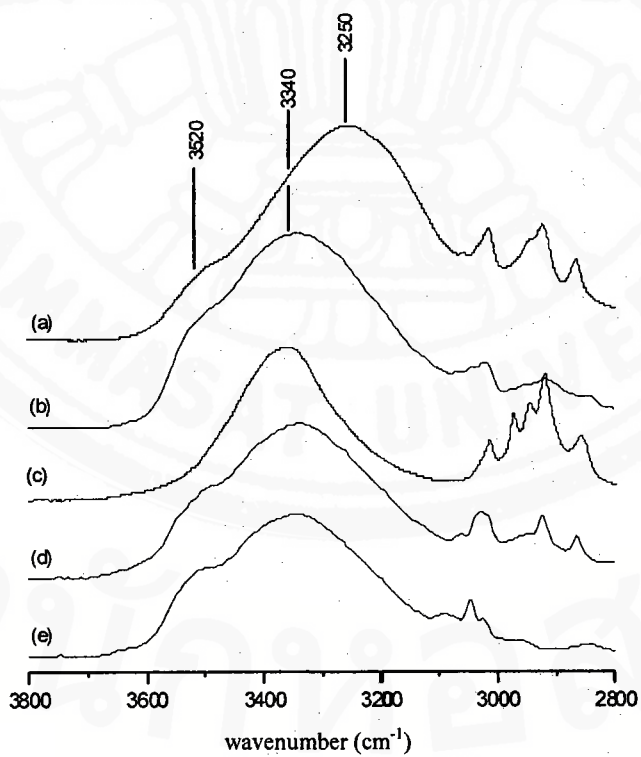


Figure 2.6 FTIR spectra of p-cresol formaldehyde (PCF) resin (a), novolac (b), 2,4,6-trimethylphenol (c), p-cresol (d), and phenol (e).

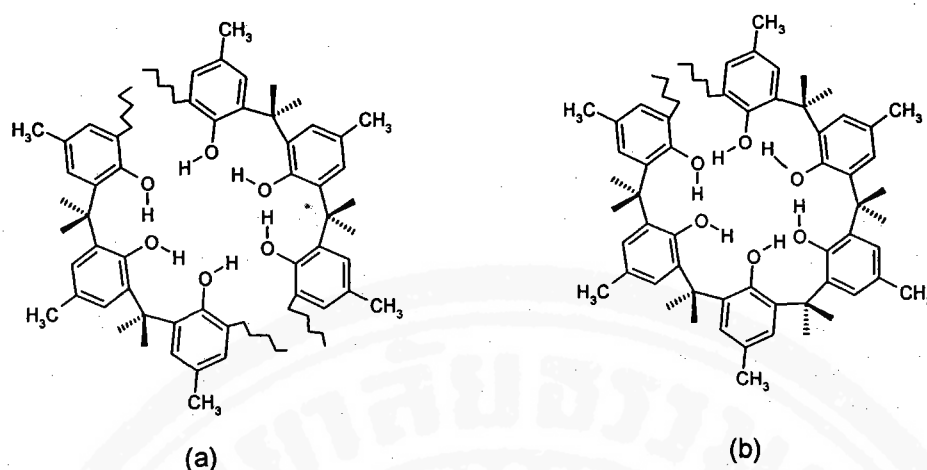


Figure 2.7 Cyclic structures of p-cresol formaldehyde (PCF) resin; "pseudo-calixarene" structure (a), and "hemi-calixarene" structure (b).

2.3 DSC Results

Intriguingly, results from DSC experiment showed a change in slope of the DSC curves at around 200 °C, which brings up a remarkable point. DSC thermograms from three sets of experiments; which are original resin (experiment 1), preheated sample (experiment 2), and annealed sample (experiment 3), all show the same T_g near 56 °C. (See figure 2.8) This suggests that heating to 200 °C does not affect the chemistry of the resin. However, in the experiment 1, we observed a change in slope of the DSC curve at temperatures around 175 to 200 °C, but no such transition can be seen in the experiments 2 and 3. This is probably due to a conformational transition in the PCF structure.

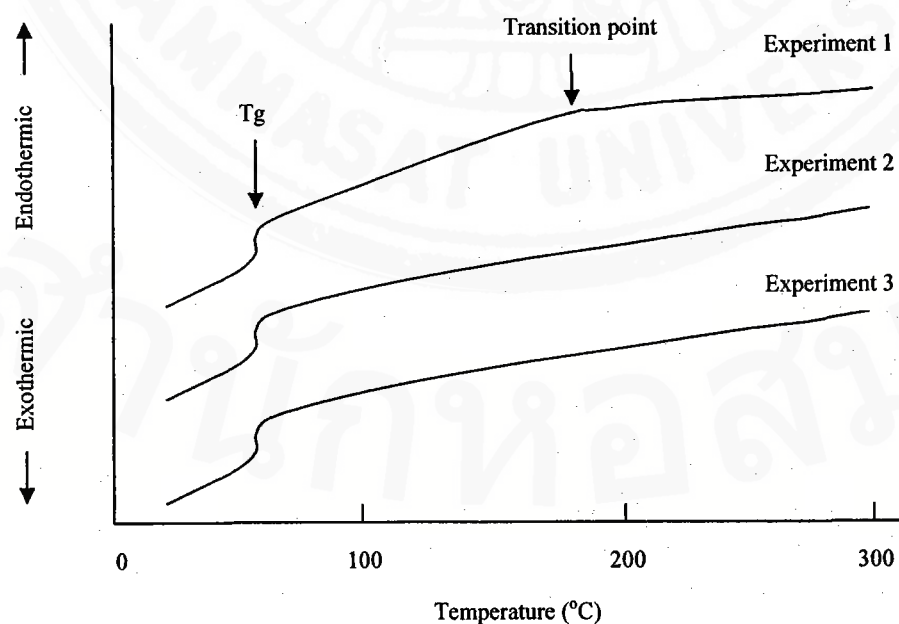


Figure 2.8 The DSC thermograms from experiments 1 to 3.

Results from FTIR spectroscopy and temperature study employing FTIR also show evidences of intra-molecular hydrogen bonding formation and a conformation transition, which are in good agreement with those observed from DSC experiments. However, it is useful to discuss the spectra of calixarenes before getting to the study on PCF resin, as this supports our band assignments. The name "calixarenes" was originally applied to the structure of a phenol-derived cyclic tetramer in which all four groups are connected in a ring system and oriented in the same direction. For other derivatives that have more than four aryl groups, a brackets number is inserted between calix and arene, for example, calix[6]arene. Various properties of calixarenes have been studied. The materials have unusually high melting points ranging from 250 to 450 °C, are soluble in water, but have a low solubility in most organic solvents. From the infrared spectrum, calixarenes show a remarkably low frequency OH stretching band, ranging from 3150 cm^{-1} for the calix[4]arene to 3300 cm^{-1} for the calix[6]arene. This is a consequence of strong intra-molecular hydrogen bonding, which varies with the size and geometry of the ring system and its flexibility.

The infrared spectra of calix[6]arene, calix[4]arene, and *p-tert*-butylcalix[4]arene are compared to that of the PCF resin in figure 2.9. It is well established that the strength of intra-molecular hydrogen bonding in these calixarenes increases with ring stiffness. Calix[6]arene, which is the most flexible system, has the weakest intra-molecular hydrogen bonding, with the highest frequency OH stretching mode at 3170 cm^{-1} and lowest frequency OH phenolic deformation mode at 1400 cm^{-1} . This implies that the weaker intra-molecular hydrogen bonding allows the hydroxyl group to (in-plane) deform more easily than in the other two compounds.

In calix[4]arene, the hydrogen bonding strength is increased along with the rigidity of the system, which is reflected in the lower frequency OH stretching mode at 3145 cm^{-1} and the increase of the OH phenolic deformation frequency to 1415 cm^{-1} . The strongest hydrogen bonding is found in *p-tert*-butylcalix[4]arene, which has *p-tert*-butyl substituted groups. These large, non-polar groups can repel each other, forcing the hydroxyl groups at the opposite site of the system into closer contact, which enhances the strength of intra-molecular hydrogen bonding in the system. This is reflected in the lowest OH stretching frequency at 3135 cm^{-1} and the highest OH phenolic in-plane deformation frequency at 1427 cm^{-1} . The spectrum of the PCF resin shows a band at 3250 cm^{-1} with a lower frequency shoulder near 3200 cm^{-1} . This is close to the mode observed in calix[6]arene, indicating that there are cyclic structures present in this system that have stronger hydrogen bonds than novolac, but somewhat weaker bonds than the calixarenes. This is at least in part due to the distribution of chain lengths found in the PCF resin, which would result in a distribution of hydrogen bonded structures.

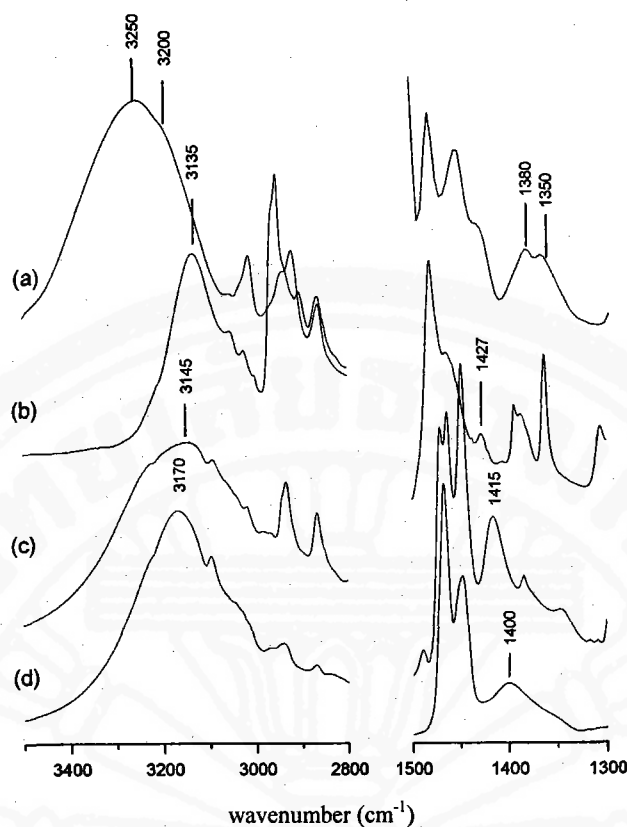


Figure 2.9 FTIR spectra of PCF resin (a), *p*-*tert*-butylcalix[4]arene (b), calix[4]arene (c), and calix[6]arene (d).

2.4 FTIR Temperature Study

In an attempt to understand the transition near 175°C observed in the PCF resin, the temperature-dependent properties of a solid-state calix[4]arene were studied by heating the compound to 175°C and recording the FTIR spectrum. The result is shown in figure 2.10. Upon increasing the temperature from 25°C to 175°C, the OH stretching frequency increases from 3170 to 3330 cm^{-1} , and the OH in-plane deformation frequency decreases from 1400 to 1368 cm^{-1} indicating that the hydrogen bonding strength decreases with temperature. This is a result of a conformational change in the calix[4]arene structure. As calix[4]arene has 4 conformations; cone, partial cone, 1,2-alternate and 1,3-alternate. The cone conformation is the structure that enables the compound to form the strongest intra-molecular hydrogen bonding, because ring stiffness forces hydroxyl groups to be in the closest orientation. At room temperature, the cone conformation is the most favorable state, so that the compound shows strong hydrogen bonding. However, when the temperature is increased, thermal energy allows the molecule to rotate and reduces the stiffness of the ring. Consequently, other conformations that have weaker intra-molecular hydrogen bonding are present.

As noted above, the FTIR spectrum of *p*-cresol formaldehyde resin shows unusually strong hydrogen bonds compared to other phenolic compounds. We have shown that this is a consequence of the structural conformation of the resin itself, and is not due to electron-donor-substituted groups or solvent-resin interactions. Considering that the hydrogen bonded OH frequency of this PCF resin (3250-3200 cm^{-1}) falls in

the same range of that of calixarenes and "calixarene-like" compounds, and the similarity of the molecular structure of all-*ortho* linked phenolic compounds, it is likely that a mixture of "pseudo-calixarene" and "hemi-calixarene" structures is responsible for this strong hydrogen bonding, despite the fact that the PCF resin must consist of a distribution of oligomers.

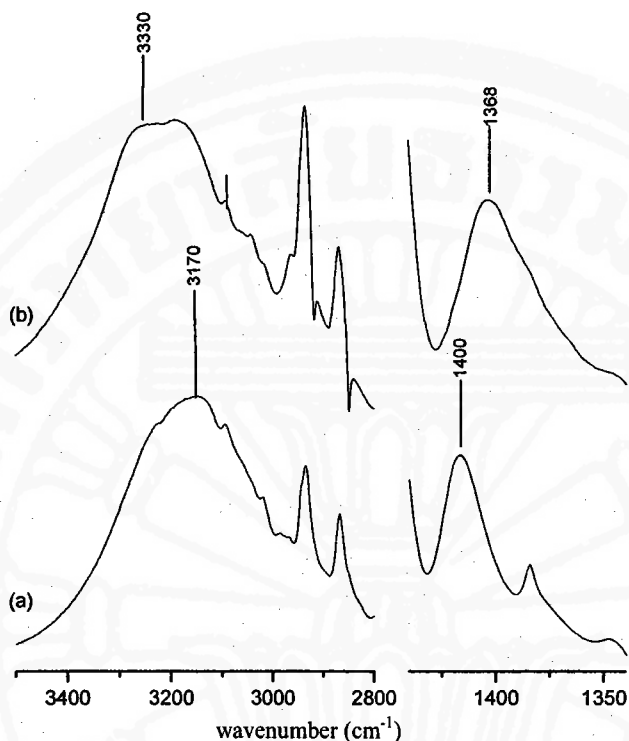


Figure 2.10 FTIR spectra of the temperature study of calix[4]arene; 25 °C (a), and 175 °C (b).

The effect of temperature on hydrogen bonding in PCF has been studied. Two sets of experiments have been performed by heating the sample to 175 °C and to 200 °C and recording the FTIR spectra. The result of the first experiment is shown in figure 2.11. Upon increasing the temperature up to 175 °C, the hydrogen bonded OH stretching band shifts from 3250 to 3370 cm⁻¹ and shift back to the same position at 3250 cm⁻¹ when the sample is cooled down to room temperature. Another major change is also observed in the band near 1300 cm⁻¹, which is assigned to the in-plane deformation of the phenolic hydroxyl group. At room temperature, the higher frequency mode at 1380 cm⁻¹ is the strongest. Upon heating, this band decreases in intensity and a band at lower frequency (1321 cm⁻¹) becomes the major peak at 175 °C. However, the higher frequency band recovers its intensity when the sample is cooled down. This indicates that intra-molecular hydrogen bonded cyclic structures are reformed upon cooling.

When the resin is heated to 200 °C, however, both the hydrogen bonded OH stretching and in-plane deformation bands are not recovered by simply cooling, as shown in figure 2.12. In the FTIR spectrum of the cooled sample, the hydrogen bonded OH stretching is at 3408 cm⁻¹ and the in-plane deformation is dominated by the lower frequency mode (1321 cm⁻¹). However, the strong hydrogen bonded structure can be recovered when the sample is dissolved and recast from solvent, indicating that there has been no

chemical change. Accordingly, at 200°C, which is high enough to overcome the stabilizing energy of the cyclic structure, most intra-molecular hydrogen bonding has been destroyed and limitations on the chain or conformational rotation, presumably enhanced by intermolecular hydrogen bonds, prevent their being reformed upon cooling. On the other hand, when the resin is re-dissolved in solvent, the breaking of those bonds and subsequent enhanced rotational freedom of the chains allows the reformation of the cyclic structure. In order to study the possibility of recovering the cyclic structure by annealing, the PCF sample was heated to 200°C and the annealed at 85°C (above the T_g of the PCF resin) for 1 hour. The FTIR spectrum of this sample is similar to the cooled sample (without annealing), indicating that the cyclic structure, once destroyed, cannot be recovered by simply cooling or annealing.

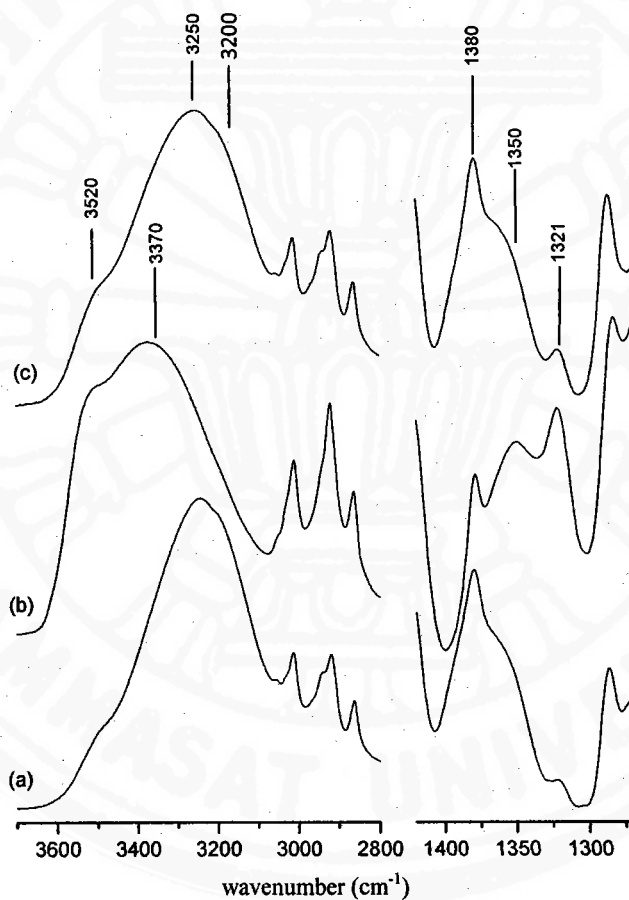


Figure 2.11 FTIR spectra of the temperature study of PCF (heating to 175 °C); 25 °C (a), 175 °C (b), and 25 °C cooled down (c).

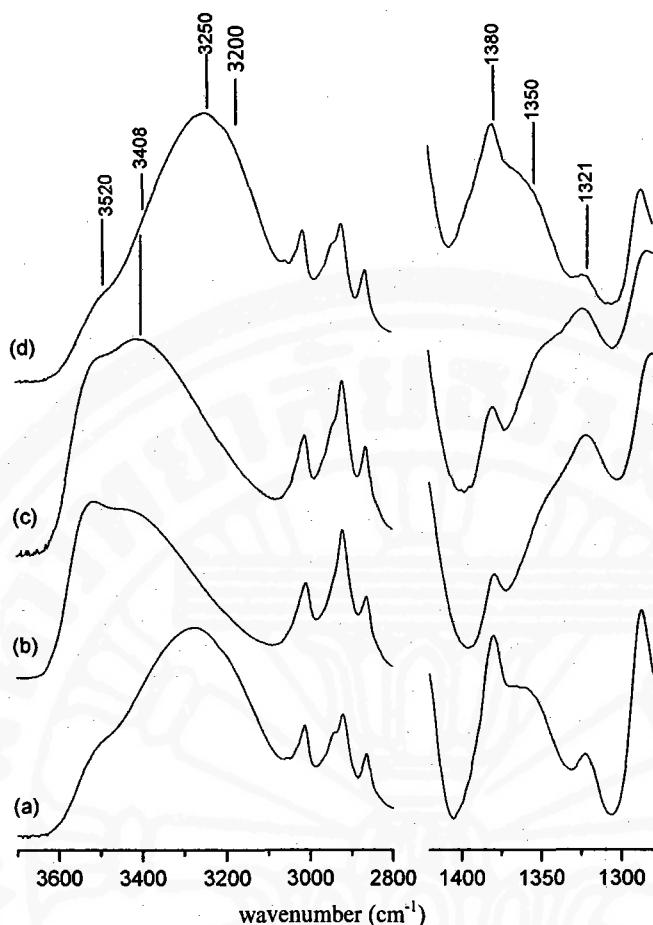


Figure 2.12 FTIR spectra of the temperature study of PCF (heating to 200°C); 25°C (a), 200°C (b), 25°C cooled down (c), and recast film (d).

The results of thermal analysis support the transition point of “calixarene-like” structures observed by FTIR spectroscopy. As described in the previous section, the DSC curve of original PCF shows a change of slope at around 175 to 200°C, which indicates a change of the PCF conformation. This agrees with the results from FTIR experiments, which also indicate a transition point in this temperature range. At room temperature, most of the PCF molecules exist in cyclic structures, stabilized by intra-molecular hydrogen bonding. Upon increasing the temperature to 200°C, the cyclic structure appeared to be completely destroyed and the molecules display bands characteristic of the type of intermolecular hydrogen bonding observed in other phenolics. These presumably prevent recovery of cyclic structures upon cooling, and this is reflected in the subsequently absence of a transition point in the DSC curve of experiment #2. (i.e. upon reheating)

The evidences as discussed earlier suggested that the all-*ortho* linkage molecules of PCF, which consists of a distribution of oligomer molecules, form a mixture of “pseudo-calixarene” and “hemi-calixarene” structures that leads to a highly stabilized structure at room temperature. These structures are stabilized by two factors; the close proximity of hydroxyl groups and the relative stiffness (i.e. hindered bond rotation) of methylene bridge linkages. Figure 2.13 summarizes this work on the conformational distribution of the PCF

resin. In the state obtained from solution, the PCF resin is mainly in "calixarene-like" structures, with a mixture of both "pseudo-calixarene" and "hemi-calixarene" structures. These structures are stabilized by two factors, as previously discussed. This results in stronger hydrogen bonds than those found in novolac and other phenolic compounds. However, when heated up to a transition point at around 175 to 200°C, the "calixarene-like" structure is destroyed and apparently largely replaced by intermolecular hydrogen bonding. Once destroyed, the cyclic structure cannot be recovered by simply cooling down or annealing, because the freedom of conformational rotation of the methylene linkage coupled with a new pattern of hydrogen bonding is presumably not enough to allow the molecule to do so. However, the recovery of the structure can be obtained by dissolving and recasting the sample from solution. This is presumably because the dissolution process breaks the barriers imposed by intermolecular hydrogen bonding and provides a high degree of freedom of conformational rotation of the methylene linkages.

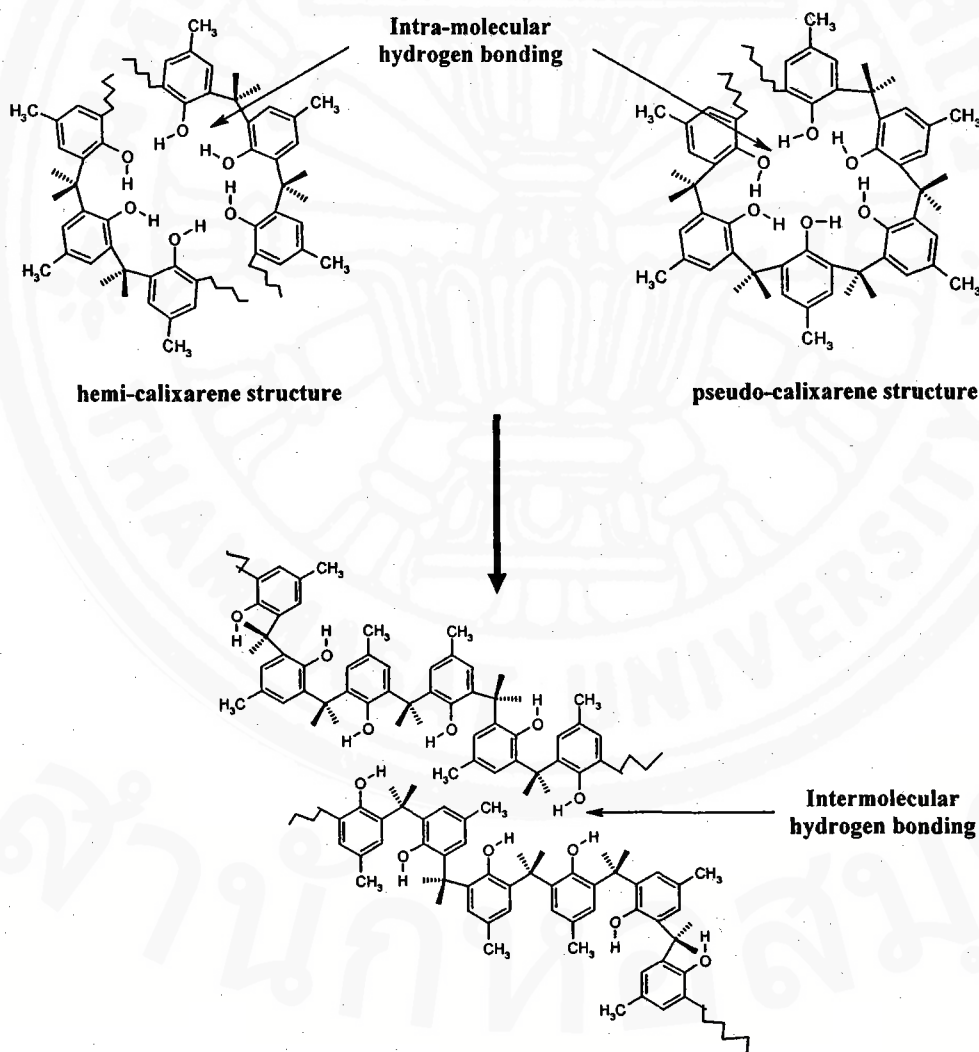


Figure 2.13 Summary of conformation distributions of PCF resin.