

Chapter 4

Conclusions and Output

4.1 Conclusions

Phenolic resins were the first synthetic polymer produced commercially, which are widely used in adhesive industry. The adhesion properties of this class of materials are strictly related to hydrogen bonding formed by their hydroxyl groups. The resins contain phenol units linked by methylene bridges at their *ortho*- or *para*- positions. Depending upon synthesis reaction conditions and curing properties, phenolic resins are classified into two classes; resol and novolac. The former can be self-hardened to form a "cross-linked" network, while the latter needs an addition of curing agents. Substituted phenol-formaldehyde resins, for example, p-cresol/formaldehyde (PCF) - synthesized from a p-methyl substituted phenol - are also found useful and can be produced by a similar procedure.

It is observed that linear structured p-cresol/ formaldehyde (PCF) resins have much stronger hydrogen bonds than those found in ordinary branched-structured phenolic resins, i.e., resol and novolac. The former unbranched polymer exhibits an unusual thermal transition due to intra-molecular hydrogen bonding in the form of "calixarene-like" structures, which cannot be formed in the branched structures of the latter. When heated up to a transition temperature, the "calixarene-like" structure in PCF is destroyed and apparently largely replaced by intermolecular hydrogen bonding. Once destroyed, the cyclic structure cannot be recovered by simply cooling down or annealing. However, the original structure can be obtained by dissolving and recasting the sample from solution. This suggests that in these materials there is an interesting coupling of the conformational freedom of the chains with intra- and intermolecular interactions.

To obtain insight into this, the nature of hydrogen bonding formation in low molecular weight models are investigated. Two low molar mass phenolic analogues; bis-2-hydroxyphenylmethane (B2HPM), and bis-4-hydroxyphenyl methane (B4HPM) are employed to represent the linear and branched structures of phenolic resins, respectively. FTIR spectra of these two compounds in dilute solution of cyclohexane as a function of concentration is examined. The result shows single OH-stretching band in B4HPM, indicating almost purely "free" OH in this compound, compared to two patterns of hydrogen bonded OH characteristics observed in B2HPM, reflecting intra- and intermolecular hydrogen bonding, respectively. In addition, structural analysis is conducted to investigate rotational potential of the dihedral angle α of the two analogue models by applying ab initio calculations.

4.2 Output

A peer-reviewed proceeding of an international conference:

Opaprakasit P., Lawtrakul L., Intra-Molecular Hydrogen Bonding in Calixarene-Like Structures of Phenolic Resins: Phenolic Analogue Models, *Proceedings of Pure and Applied Chemistry International Conference 2008 (PACCON2008)*, 2007, Bangkok, Thailand, 675-680.