



CHAPTER I INTRODUCTION

1.1 Nanoarchitecture and Nanomaterials

In recent years, the products with high technology have reached to the concept of compact size with a full operating function consuming little energy. The development of materials, thus, can no longer achieved by just reducing the size or compressing the component by the ways of well-packing. The advanced products such as flat luminescence displays, cellular phones, notebook computers are, thus, in the new material revolution era where the bottom-up research and development (Balzani, 2000) is an alternative approach to fulfil the needs.

The smallest compositions of matter, the molecules, have to be considered in various aspects for the complete bottom-up route of materials, under the term of nanoarchitecture. In the first stage, the molecular structure of either a single molecule or polymer chain has to be well clarified about the chain polarity, hydrophilic-hydrophobicity, and charge or ionic property. In the next stage, the consequence of molecular interaction, molecular alignment and the assembly including the induced specific structures and properties have to be clarified.

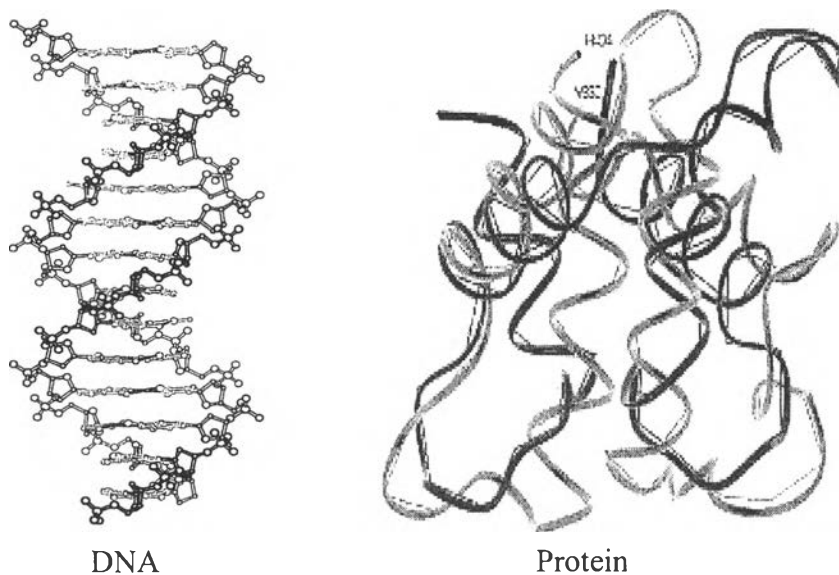
Through this approach, the materials can be controlled at 1-100 nm size range where the properties are obtained from the molecular level, so-called nanomaterials. In recent years there are many researches aiming for nanomaterials, for examples, Clay reinforced epoxy nanocomposites (Pinnavaia, 1996), DNA hybridization (Franzen, 2002), nanospheres (Hiwatari, 2001).

1.2 Supramolecular Chemistry for Nanomaterials

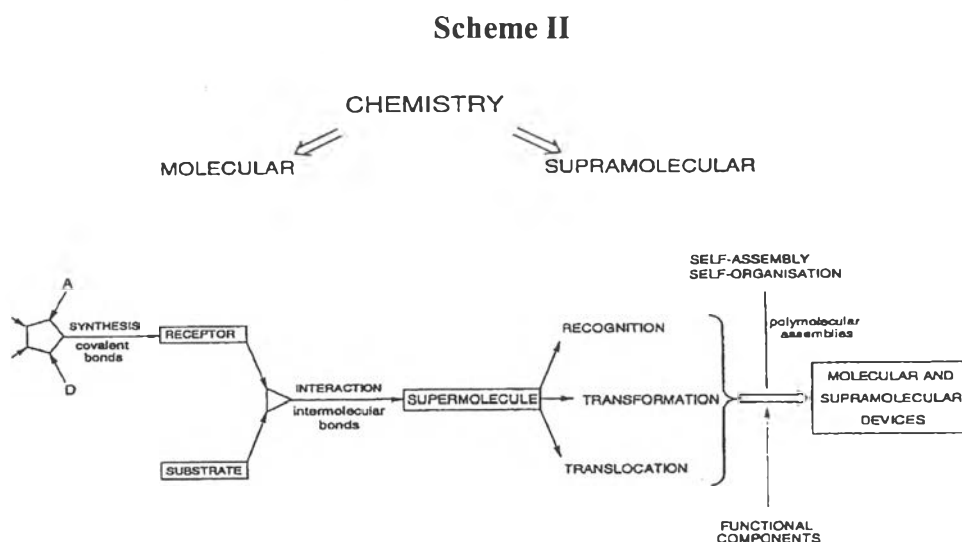
Although the chemistry of covalent bonded species are well clarified for polymeric materials with the specific properties of which the individual molecules have never achieved, it has to be noted that for all cases, those functions are induced from a group of molecules. Polyamide is a typical engineering polymer not because of the chain with amide group but because of each chain packing with a strong hydrogen bond through the amide group. Thus, in this century, the chemistry of non-covalent bonded assembly (Ciferri, 2000) is a challenge to be understood and

developed from the molecular level. In some cases, molecules or polymer chains aligned or packed to each other under a particular controlled structure with secondary forces, such as hydrogen bonding, polar-polar interaction, π - π interaction, stacking conformation, etc. At that stage the unique properties are induced incredibly, as seen in the cases of DNA, RNA, and protein, where supramolecular structures are formed (Scheme I).

Scheme I



Supramolecular structured molecules, thus, are considered to be a fundamental study to explore the nanomaterials. Lehn, (Lehn, 1978) the Nobel Laureate in 1987, defined the supramolecular chemistry as “There is a field of molecular chemistry based on the covalent bond, there is a field of supramolecular chemistry based on the molecular assemblies and the intermolecular bonds”. In other words, supramolecular chemistry can be defined as “Chemistry beyond the molecules, bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces” (Scheme II) (Lehn, 1978).



Two essential factors to consider supramolecular chemistry are, (i) the molecules, which can either be single individual molecules, macromolecules, or polymers, and (ii) the induced intermolecular bonds for molecular assembly such as, hydrogen bond, van der Waals, ionic interaction, hydrophobic or hydrophilic interaction, etc.

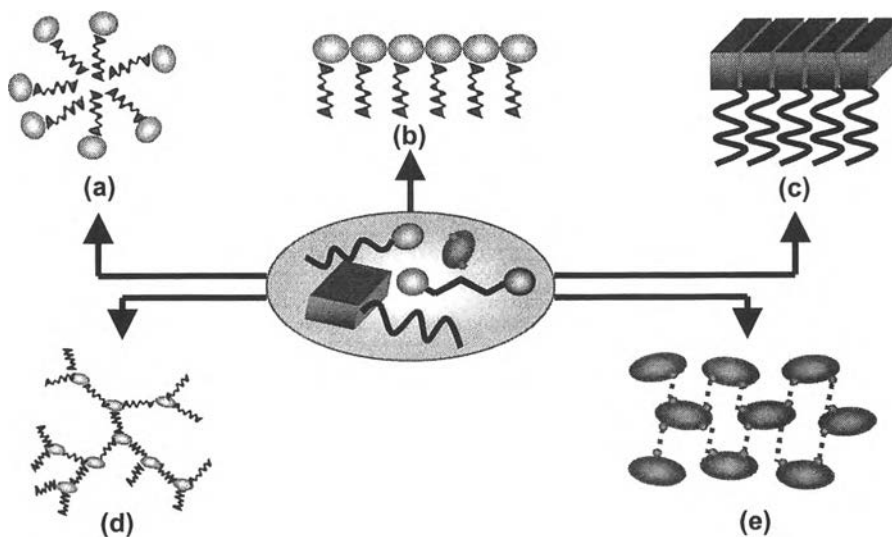


Figure 1. Individual molecules and the induced supramolecular structured assembly of: (a) micelle, (b) Langmuir-Blodgett membrane, (c) liquid crystal, (d) dendrimer, and (e) inclusion compound.

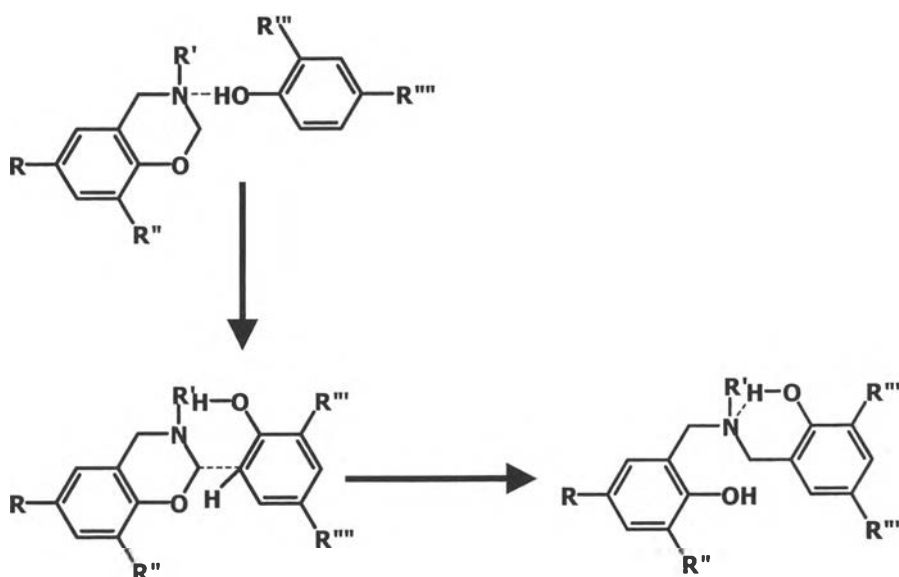
Figure 1 shows stages of supramolecules from the level of individual molecules to the assembly structured supramolecules which can be developed for micelle (Gin et al., 2001), LB membrane (Kyuwon, 2002), liquid crystal (Gray and Kelly, 1984), dendrimer (Shisawa et al., 2000), and inclusion compound (Miyata, 1993).

1.3 Aza-methylene-phenol: A Unique Structured Molecule

For the past few years, our group has focused on the ring opening reaction of benzoxazine derivatives. It is important to note that although the chemistry of ring opening has been well defined since 1950's (Burke et al., 1965), the development of polybenzoxazines are rarely reported (Reiss et al., 1985). Ishida et al. reported a novel phenolic resin by using bisphenol-based benzoxazines of which the ring opening polymerization is successful (Ishida et al., 1994).

Recently, we found that in the case of *p*-substituted phenol based benzoxazines, the ring opening polymerization is likely to terminate at dimer level to be aza-methylene phenol compounds (Laobuthee et al., 2001). The speculated mechanism for dimerization where the electron movement from nitrogen to hydroxyl group can be well explained for the termination at dimer level is shown in Scheme III.

Scheme III



The x-ray crystallography studies declared that the simultaneous intermolecular and intramolecular hydrogen bonds stabilize the aza-methylene phenol compounds (Figure 2) (Chirachanchai, 1999). The reaction on the aza-methylene phenol can give either asymmetric compounds or symmetric compounds by changing the reaction conditions (Laobuthee, 2002). In our related work, aza-methylene-phenol was clarified for inclusion properties to entrap alkali, alkaline earth, and transition metals (Laobuthee, 2002). Thus, it is our challenge to apply aza-methylene-phenol under the basis idea of supramolecular structured compound to develop the supramolecular structured materials.

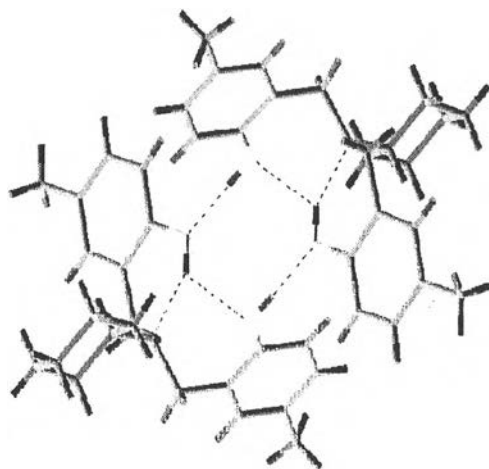


Figure 2. Crystal structure of N,N-bis(2-hydroxy-5-methylbenzyl)cyclohexylamine.

1.4 Development of Aza-methylene Phenols: From a Simple Backbone to Molecular Assembly

It is important to note that the aza-methylene phenol can be utilized as a backbone molecule owing to the variety of functional group possibly attached to the structure. For example, we clarified the synthesis pathway to obtain a series of esterified compounds in a high yield (over 85%) (Laobuthee, 2002). Considering each functional group on aza-methylene compound, the modifications of (i) esterification or etherification at OH group, (ii) the hydrophobic or hydrophilic enhancement at *para*-position at phenol ring and nitrogen atom by choosing phenol derivatives and types of amine in the reaction, are possible (Figure 3).

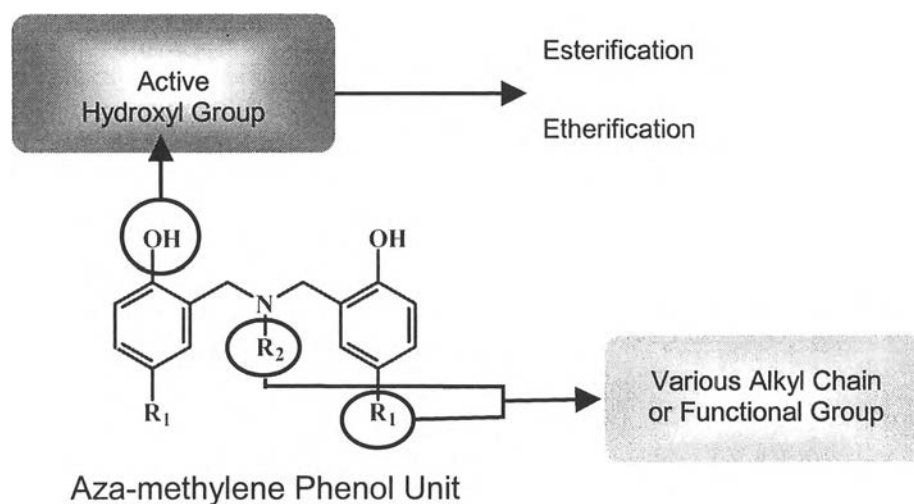


Figure 3. Unique molecular designs for azamethylene phenol compounds.

By those modifications, it can be expected that the molecules perform molecular assembly via secondary forces induced either from the hydrophobic-hydrophilicity of the chain or the hydrogen bonding between the molecules.

1.5 Scope of the Present Work

The present work is focused on the unique molecular designs and syntheses of aza-methylene phenol compounds and the induced molecular assembly. Two main molecular approaches (Scheme IV), which are, (i) hydrophobicity enhanced at aza group by introducing of alkyl chain (C₁-C₁₈) and (ii) hydrophilicity enhanced at OH group by conjugating with polyethylene glycol methyl ether. The studies also extend to the observation of the induced molecular alignment and the molecular assembly via thermal process.

Scheme IV

