CHAPTER II
LITERATURE REVIEW

In daily life, there are many serious environmental problems due to discharge of many pollutants from the combustion of solid, liquid and gas fuels in various mobile/stationary energy systems, have been reported as major global problems involving not only pollutants such as NO_x, SO_x and soot, but also greenhouse gases like carbon dioxide. Carbon dioxide is considered crucial greenhouse gas that is produced by combustion of coal or hydrocarbons, the fermentation of sugars in beer and winemaking and by respiration of all living organisms. There are more concerns about global climate change and, therefore, an increased interest in reducing emissions of greenhouse gases, particularly CO_2 During the last decade, the development of new technologies and materials for CO_2 capture and storage has been gaining increasing attention.

To produce nanoporous carbon material as gas-separation technique to get high efficiency for CO_2 permselectivity, low weight and low maintenance. The possible processes for CO_2 separation include physical and chemical absorption, membrane separation, gas-solid absorption and cryogenic separation (Y. Ding et al., 2001).

2.1 Nanoporous Material

Nanoporous materials as a subset of nanostructured materials have been a focus of nanoscience and nanotechnology that possess unique surface area, pore structural, light weight and bulk properties. These materials have many uses in various fields such as gas separation, electrode, catalysis, ion exchange, purifications, sensor and biological molecular isolation. Nanoporous materials are also of scientific and technological importance because of their much efficiency to adsorb and interact with atoms, ions and molecules on their large interior surfaces and in the nanometer sized pore space. In the past, the terms of "micropore" and "macropore" have been applied in different ways by physi-chemisorption and some other scientist. With an attempt to explain this situation, the limits of size of the different divisions of pores

included in **Table 2.1** have been proposed by the International Union of Pure and Applied Chemistry (IUPAC) (Rouqueol et al.,1999).

Table 2.1 Definitions about porous solids

Term	Definition
Porous solid	Solid with cavities or channels which are deeper than they are wide
Micropore	Pore of internal width less than 2 nm
Mesopore	Pore of internal width between 2 and 50 nm
Macropore	Pore of internal width greater than 50 nm
Pore size	Pore width (diameter of cylindrical pore or distance between opposite walls of slit)
Pore volume	Volume of pores determined by stated method
Surface area	Extent of total surface area determined by given method under stated conditions

Normally, micropores and mesopores are especially important in the context of adsorption process. Moreover, micro- and mesoporous materials are generally called "nanoporous materials". Particularly, mesoporous materials are remarkably very suitable for catalysis applications, whereas the pores of microporous materials may become easily plugged during catalyst preparation is high loading is sought. If this material have both micropores and mesopores, it will be effective in absorption process.

An activated carbon is one of the nanoporous carbons that have excellence pore structure, high internal surface area and good mechanical characteristics, which provide it with many advantageous properties; it has been employed in a wide number of applications on an industrial scale, including technologies for the storage of gases. Guo et al., (2009) carbonized coconut shell at pyrolysis temperature of 600 °C by CO_2 activation to obtain activated carbon. Usually, carbonization temperature range between 400 and 850 °C, sometimes reaches 1000 °C, and

activation temperature range between 600 and 900 °C. The methods for preparing an activated carbon can be divided into two categories: physical activation and chemical activation. In this work, they selected the physical method using carbon dioxide (CO_2) gas as the activating agent and studied the effects of activation temperature, activation time and flow rate of CO_2 on the BET surface area, total volume, micropore volume and yield of activated carbon. It was indicated through the results that (i) when increase activation temperature resulting increase mesoporosity; (ii) increasing activation time to increasing of micropores and mesopores; but longer activation time would cause pores to collapse; (iii) an increase CO_2 flow rate would induce samples to burn off, and had no contributions to the formations of pores. For the best conditions in this work to obtain activated carbon that has maximum surface area 1700 m^2/g were 900 °C of activation temperature; 240 min of activation time; 800 cm^3/min of CO_2 flow rate.

Dobele et al., (2012) successfully provides highly porous carbons were obtained from solid wastes generated in the chemical processing of birch wood such as substandard kraft cellulose, hydrolysis lignin, chips and bark derived from the mechanical processing of birch wood as low-cost precursors of nanoporous carbons using the hydroxides of alkali metals (NaOH) as activating agents at 575-800 °C to suitable electrodes for supercapacitors and adsorbents CO_2 capture. The resulted in a large variety of highly nanoporous carbons with surface areas above 1100 m^2 g^{-1} and pores centered in the supermicropores range.

2.2 Carbon Dioxide Capture

Carbon dioxide (CO_2) is considered to be the primary greenhouse gas leading to the warming of the earth's atmosphere observed over the past 50 years. Over the last decade, the environmental problem and the warming of the earth's atmosphere brought by CO_2 emission has become a serious problem in the world. As we known, the increased CO_2 is mainly discharged by combustion of the large amount of fossil fuels. Accordingly, there are developable new technological and materials for cutting CO_2 emission to atmosphere: (1) improve the utilization efficiency of fossil fuels; (2) develop cleaner energy and increase the use of renewable energy such as wind

renewable energy such as wind energy, nuclear energy and solar energy; (3) capture CO_2 from flue gas with inexpensive adsorbents and then sequester it underground. Capture and storage of CO_2 offers several advantages in short term.   Chen   et al., (2012) recently, studied the CO_2 capture from flue gas and discussed the effect of a nitrogen-functionalized porous material was obtained through pyrolysis of a porous polymer prepared from terephthalaldehyde and melamine. This nitrogen-rich porous carbon exhibited the highest capacities among the carbon materials reported to date under these conditions. The hierarchical micro-mesopore structure is expected to be suitable for CO_2 capture. Whilst pyrolysis at 800 and 900 °C produced very resembling textural properties in the samples, pyrolysis at 700 °C led to a sample with lower surface area and smaller pore volume. For Comparison of textural properties and CO_2 capture capacities of various adsorbents measured at 25 °C, 1 atm. Shown in **table 2.2**

Table 2.2 Physical and chemical characteristic of samples

Samples	S_{BET} (m^2/g)	V_{total} (cm^3/g)	CO_2 uptake (mg/g)	Ref.
Nitrogen-rich porous polymer	441	0.73	59	Present work
Nitrogen-rich porous carbon	993	0.82	141	Present work
Darco G-60(-100 mesh powder)	889	0.65	99	Present work
Amine-grafted porous carbon	15	0.04	50	[26]
Nitrogen-enriched porous carbon	490	0.91	99	[27]
Nitrogen-doped carbon monolith	618	1.30	138	[29]
Zeolite 13X	893	0.34	231	[20]
Na-Zeolite β	508	0.52	120	[6]
ITQ-6/AP	103	0.12	53	[22]
MCM-41	1486	1.00	8.6	[18]
Mesoporous alumina	812	0.83	52	[20]
PEI-MCM-41	4	0.01	110[a]	[18]
Tri-PE-MCM-41	429	1.10	122	[21]
CuBTC	1333	0.66	220	[10]
K-Sod-ZMOF	363	0.16	60	[16]

[a] CO_2 capture capacity measured at 75 °C.

[a] V_{total} = total pore volume calculated from nitrogen adsorption at P/P_0 = 0.995.

[b] V_{micro} = micropore volume calculated from nitrogen adsorption at P/P_0 = 0.1.

[c] N contents were analyzed by Elemental Analysis.

[d] Darco G-60 (-100 mesh powder) was supplied by Sigma–Aldrich.

The polymer is made of a highly porous network with high nitrogen content, and pyrolysis of this polymer resulted in a carbon material with high surface area, and high nitrogen content.

Zhi-hong et al., (2013) prepared nanoporous carbons with a hierarchical pore structure from thermosetting phenolic resin containing silica nanoparticles, pyrolysis and KOH activation by hard-template method. In this work, the mixture with a mass ratio of SiO_2/ Thermosetting phenol resin (TPR) was labeled as 4:1, followed by heat-treatment in nitrogen at 800 $^{\circ}C$ for 1 h to obtain SiO_2/C nanocomposite. As-obtained sample was further activated by KOH at different mass ratios of KOH/ mesoporous carbon (MC) from 1:1 to 4:1. The results shown that BET surface area of mesoporous carbon was 681 m^2/g and BET surface areas increased after the templated carbon was activated by KOH. Because when the BET surface area increase should be attributed to the abundant micropores generated by KOH activation, which was further verified by the decrease of average pore diameter. The decrease of average pore diameter was attributed to the appearance of abundant micropores. The other result could show in **table 2.3**

Table 2.3 Porous parameters of as-prepared carbons

Sample MC : KOH	S_{BET} m^2/g	V_{total} cm^3/g	V_{micro} cm^3/g	D_{ave} nm
1 : 0	681	2.36	0.09	12.00
1 : 1	1,362	2.38	0.16	7.00
1 : 2	1 719	2.04	0.22	4.76
1 : 3	2,053	2.01	0.24	3.92
1 : 4	2 400	2.05	0.21	3.41

Wahby et al., (2012) recently, provides carbon molecular sieves (CMS) were obtained from different polymeric precursors, on their ability for CO_2 adsorption at different temperatures (273, 298 and 323 K). The CO_2 adsorption, separation and/or storage on carbon materials by means of physical/chemical adsorption or combination of both processes have created great expectations. At the three studied temperatures, samples with a high volume of narrow micropores exhibit higher amounts of CO_2 adsorbed. Additionally, the narrow micropores seem to be the key factor, leading to a maximum capacity of CO_2 adsorption.

2.3 Template Synthesis Method

2.3.1 Hard-template Synthesis Strategy for Nanoporous Carbon Material

The template acts as a mold to form nanoporous carbon material, and no chemical reaction between carbon precursors and templates. Preparation of porous carbon are shown in **Fig. 2.1**: (a) carbon precursor and the inorganic template were mixed together by wet impregnation, chemical vapor deposition or a combination of both methods; (b) polymerization and carbonization of carbon precursor; (c) the removal of inorganic templates by using strong acid or strong base to yield a porous carbon.
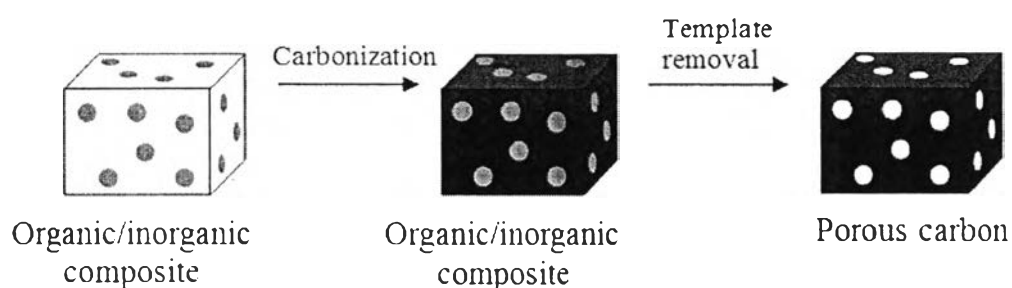

Figure 2.1 Preparation of porous carbon by using hard-templating method.

Goscianska et al., (2014) successfully sorption L-phenylalanine by ordered mesoporous carbon, CMK-3 and CMK-8 via hard template method with the use of

ordered silicas SBA-15, KIT-6 as solid state matrices and sucrose as carbon precursor. The highly ordered SBA-15 and KIT-6 was prepared using the triblock copolymer, $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, BASF) as template. The mesoporous carbons CMK-8 was prepared by using SBA-15 while CMK-8 material was prepared by the same method using KIT-6 instead of SBA-15. The results of ordered mesoporous carbons CMK-8 and CMK-3 show much higher adsorption capacities towards L-phenylalanine than the ordered silicas KIT-6 and SBA-15. The capture capacities of different mesoporous adsorbents decrease in the following order: CMK-8 (2446 μ mol/g) > CMK-3 (1654 μ mol/g) > KIT-6 (420 μ mol/g) > SBA-15 (389 μ mol/g) and the other textural properties of the materials obtained are collected in **Table 2.4**.

Table 2.4 Textural parameters of mesoporous materials

Sample	BET surface area [m^2/g]	Total pore volume [cm^3/g]	Average pore diameter [nm]
SBA-15	876	1.03	5.24
CMK-3	1115	1.12	3.52
KIT-6	893	1.08	5.83
CMK-8	1390	1.29	4.05

Wang et al., (2012) successfully synthesized a mesoporous carbon material replicated from TUD-1 using the conventional hard template method that involves the synthesis of silica hard template with controlled porosity, infiltration of carbon precursor into the porous template, carbonization of the precursor and removal of the hard template by chemical etching, following the steps A→B→C→F (liquid precursor) or A→D→F (gaseous precursor) as illustrated in **Fig. 2.2.**
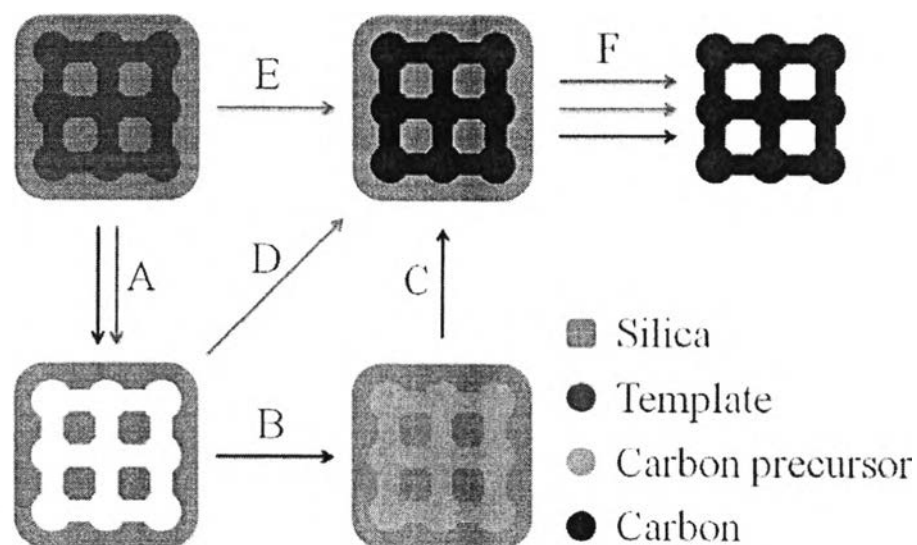
Figure 2.2 A schematic illustration of typical synthesis procedures to produce N-doped mesoporous carbon: (A) calcination to remove the templating agent, (B) infiltration of a liquid N-containing carbon precursor, (C) carbonization, (D) infiltration of a gaseous N-containing carbon precursor, (E) direct carbonization of the templating agent, and (F) removal of the silica hard template.

2.2.2 Soft-template Synthesis Strategy for Nanoporous Carbon Material

Produce nanostructures by self-assembly of organic molecules. Pore structures are determined by synthetic conditions such as mixing ratios, solvents, and temperature.
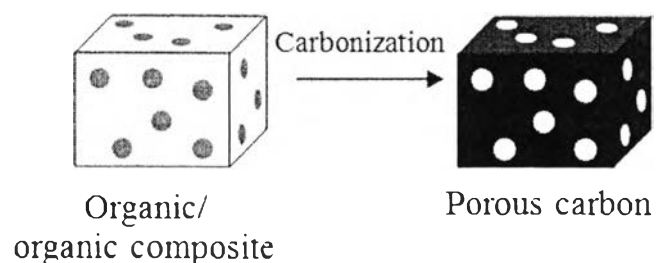
Figure 2.3 Preparation of porous carbon by using soft-templating method.

Recently, Cheng et al., (2013) have prepared mesoporous carbon nanospheres and hollow carbon nanofibers using coal tar pitch based amphiphilic carbonaceous materials (ACMs) as the precursor and amphiphilic triblock copolymer Plutonic P123 as the only soft template. The hydroxyl groups on ACM are hydrogen donors and the hydrophilic group on P123 is hydrogen bonding acceptor. The morphologies of the mesoporous carbon depending on the stacking of the micelles of P123 which can be controlled by vary the P123 concentration and the mass ratio of P123 to ACM. After carbonized at 800 °C, various mesoporous carbon materials were obtained. In a typical synthesis, P123 (2, 4 and 6 g; 13.3, 26.7 and 40 g/L in terms of the concentration of P123, cp) and ACM (the mass ratio of P123 to ACM is 2, 1.6, 1.2 and 0.8, respectively) The mechanism of the formation of sphere and cylinder containing ordered lyotropic liquid crystals is illustrated in **Fig. 2.4.**
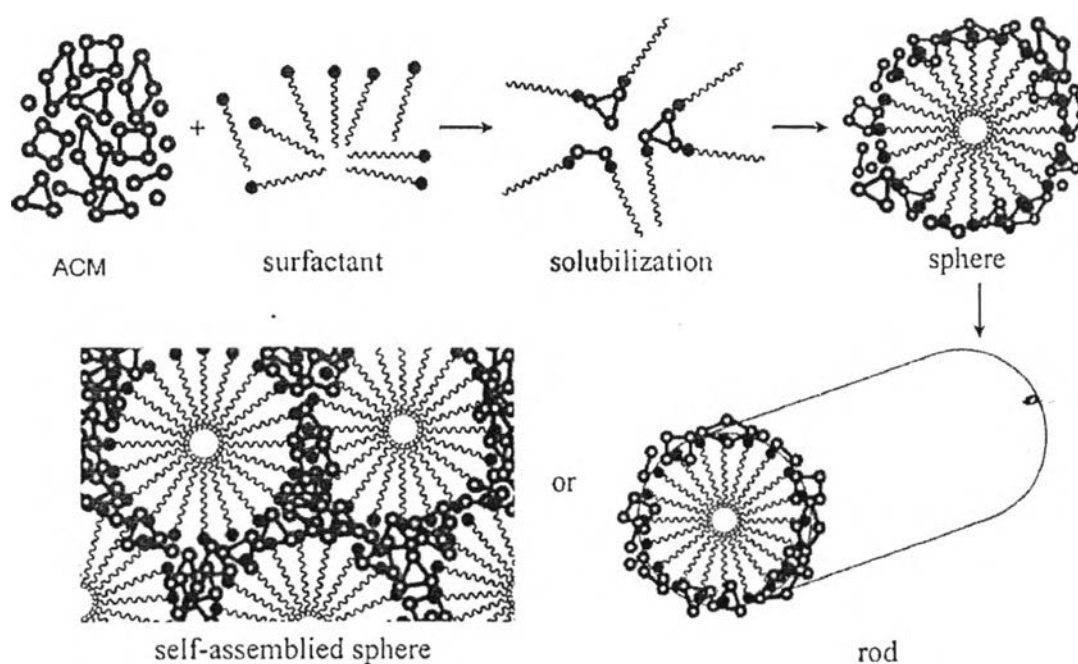

Figure 2.4 The formation of ordered lyotropic liquid crystal of P123/ACM.

The results shown the effect of the mass ratio between P123 and ACM that nanospheres with diameter of 30–150 nm were obtained when the mass ratio of P123 to ACM is 1.2 and the P123 concentration is 13.3 g/L, while hollow carbon nanofibers with diameter of 50–200 nm were obtained when the mass ratio is 2 and

the P123 concentration is 26.7 g/L. The morphologies of mesoporous carbon nanospheres and hollow carbon nanofibers proved in the SEM images in **Fig. 2.5 (a) and (b).**
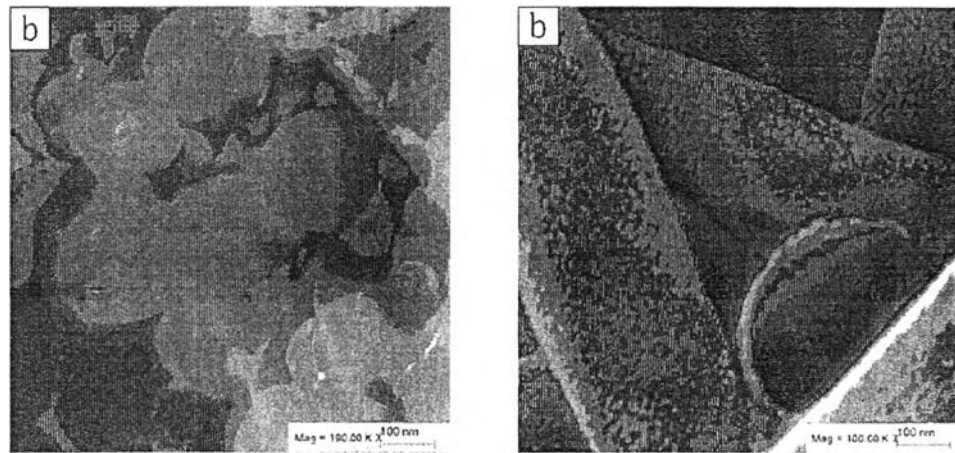

Figure 2.5 SEM images of carbonized samples: (a) Carbon nanospheres (P2-ACM1.2-800), (b) Hollow carbon nanofibers (P4-ACM2-800).

Martins et al., (2010) synthesized macro–mesoporous aluminas presenting hierarchical structure of pores through the conjugation of the sol–gel route based on a dual soft template technique that consists of dispersed oil droplets of decahydronaftalen (DHN) and micelles of Pluronic P123 (poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide)) block copolymer were used as soft template agents for the meso- and macropores structuring,. By using this strategy, a series of aluminas with hierarchical macro–mesopores and presenting controlled amount of macroporosity are readily obtained.
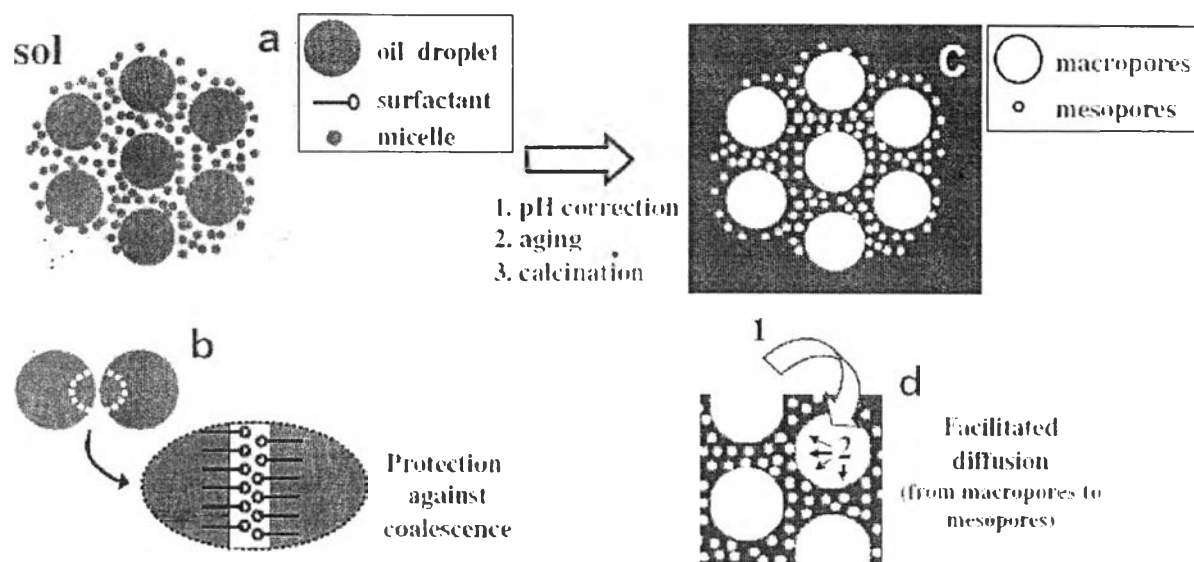
Figure 2.6 Dual soft templating method.

Dual soft templating method used to obtain solids presenting hierarchical macro–mesopores: (a) Oil droplets and surfactant micelles dispersed in aqueous sol, (b) surfactant at the droplets interface, (c) porous solid obtained after gelation, aging and calcination and (d) macro–mesoporous solid presenting facilitated diffusion from macropores to mesopores (from 1 to 2).

2.4 Polybenzoxazine

Polybenzoxazines are relatively novel classes of thermosetting phenolic resin that possess various advantageous characteristics such as excellent dimension stability, high thermal stability, frame retardant, high glass transition temperature, high char yield, easy processability and excellence electrical properties. Moreover, polybenzoxazines have the unique properties are low water absorption despite having many hydrophilic groups and near zero shrinkage after processing. Benzoxazine consist of a heterocyclic six-membered ring with oxygen and nitrogen atom and attached to a benzene ring. There are many Benzoxazine structures depending on the position of the heteroatoms as shown in Scheme 2.1. (Ishida, 2011)

(a) 1,3-Benzoxazine (b) 3,1-Benzoxazine (c) 1,4-Benzoxazine (d) 1, 3-Benzoxazine
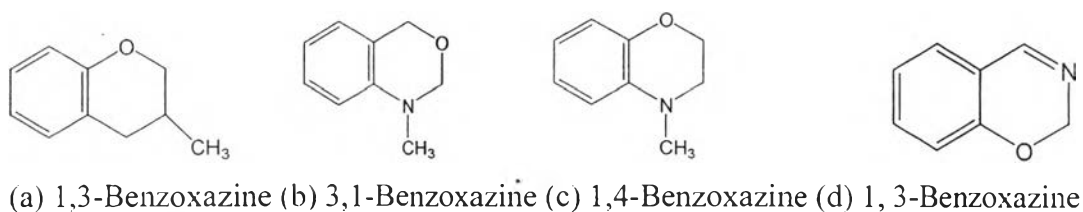
Scheme 2.1 Various structures of benzoxazine molecules. (a) 3-methyl-2H, 4H-benzo[e]1,3-oxazine; (b) 1-methyl-2H,4H-benzo[d]1,3-oxazine; (c) 4-methyl-2H,3H-benzo[e]1,4-oxazine; and (d) 2H-benzo[e]1,3-oxazine.

Benzoxazine precursor can be easily synthesized by a combination of phenolic derivative, formaldehyde, and a primary amine (aliphatic or aromatic) either using solvent or non-solvent methods. Various substitution types of amines and phenols have been used to synthesize new many types of benzoxazine precursor that polymerized to polybenzoxazine based on the functional group of reactants. (Ghosh et al., 2007). They are mono-functional, di-functional and multifunctional group.

For the mono-functional of benzoxazines representatively result to a linear or branched structure with a low molecular weight on the ordered of 500-2000 Da (Brunovska et al., 1999). Although, it is limited usefulness as structural material, they might be useful diluent reactive to facilitate the processing (Liu et al., 2011). The first reported the mono-functional of benzoxazines by Holly and coworker (1944) that synthesized via condensation reaction of primary amine with formaldehyde and substituted phenols as shown in Scheme 2.2.
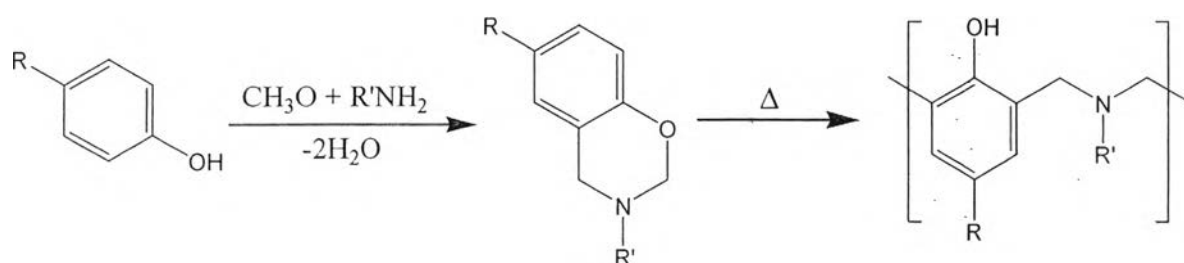
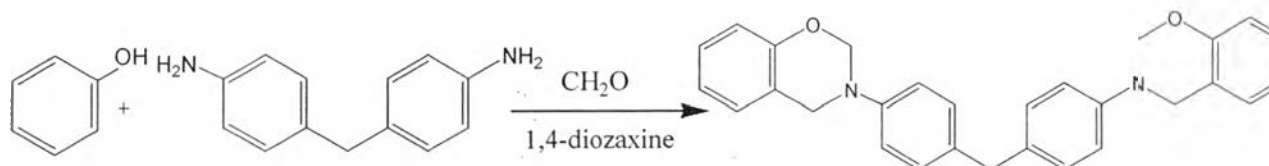**Scheme 2.2** Synthesis of monofunctional benzoxazine.

In some cases, the reaction with large amount of solvent results the slow reaction rate which are the poor solubility of the precursors participated with this process. As problems during processing of the benzoxazine resins also result from the solvent residue in the precursors and increasing cost of the products and environmental problems cause from an organic solvent. Ishida and coworker (1996) developed a solventless synthesis in the melt state to defeat these defects. Liu (1995) reported the reaction mechanism and kinetic of this solventless synthesis for using this precursors to prepare an immense quantity of benzoxazine monomer.

For the difunctional of benzoxazine monomers can be classified into two classes; the first class is bisphenol-based difunctional benzoxazine monomer which is produced by the reaction of bisphenol with either aliphatic or aromatic monofunctional primary amine as shown in Scheme 2.3.
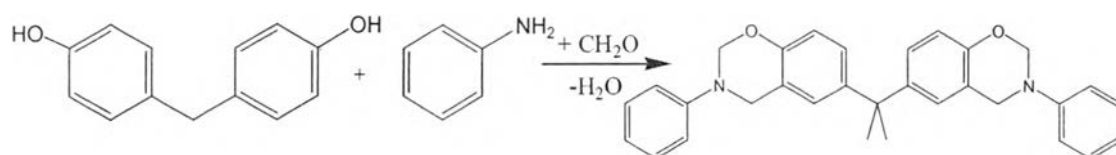
**Scheme 2.3** Synthesis of bisphenol A- and methylamine-based Benzoxazine.

Another class of difunctional benzoxazines is diaminebased bifunctional benzoxazine monomers, which can be synthesized by the reaction of aromatic or aliphatic diamines with a monofunctional phenolic structure of ortho-vacant position as shown in Scheme 2.4

Scheme 2.4 Synthesis of methylenedianiline (DDM)-based benzoxazine monomer (P-ddm)

Ishida and coworkers (1994 and 2002) have developed a new class of difunctional and multifunctional benzoxazine monomers via the ring opening reaction being initiated by dimers and higher oligomers. The precursor was synthesized using bisphenol-A, formaldehyde and methylamine. The main constituent of the resulting products was a monomer with difunctional benzoxazine ring structures at both ends of the bisphenol-A. The rest of the composition consisted of a mixture of dimmers and oligomers, with both benzoxazine rings and free phenol structures.

Moreover, recent researchers have developed a new class of difunctional or multifunctional benzoxazine monomers yielding the ring opening reactions during curing to produce phenolic materials which initiated by dimers and higher oligomers in the resin composition as shown in Scheme 2.5:
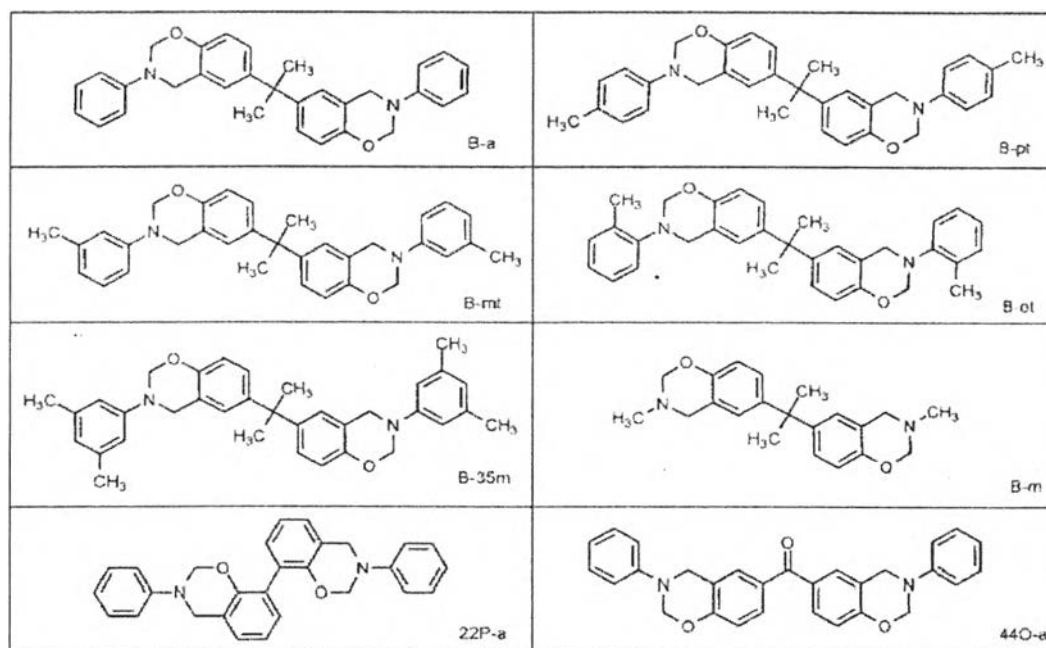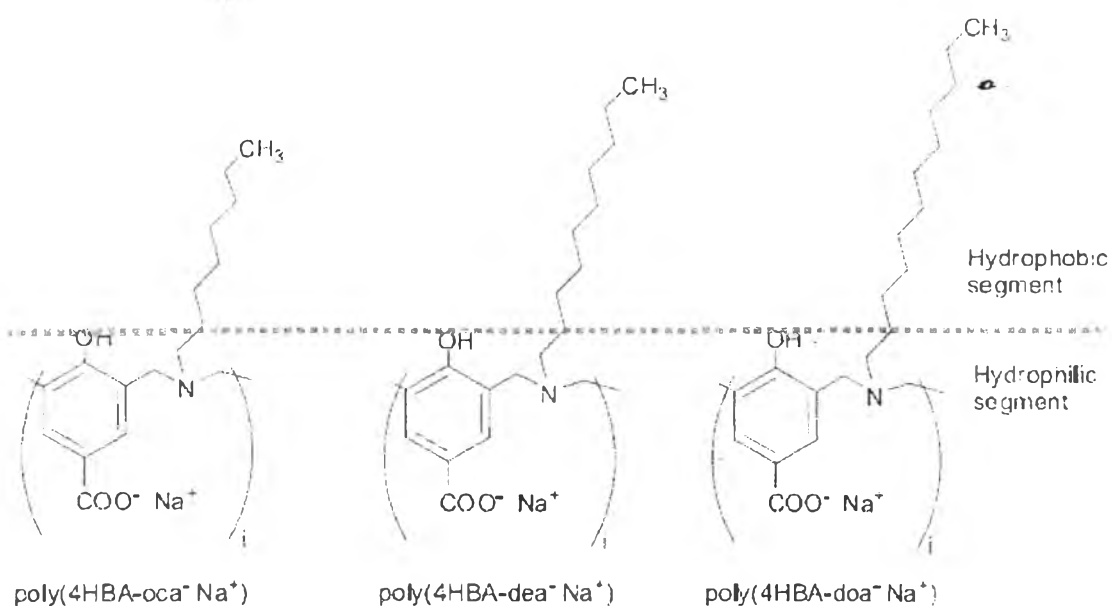

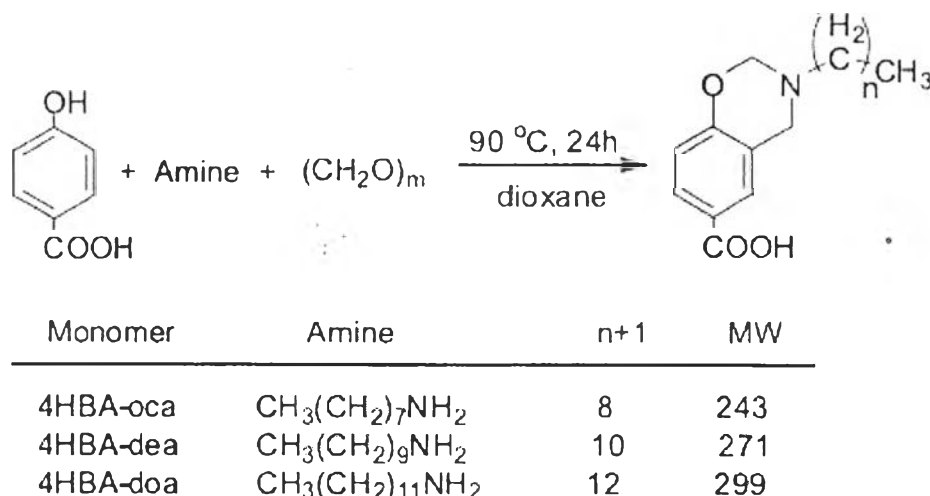**Scheme 2.5** Chemical structures of multifunctional benzoxazine monomers.

Some important characteristic properties of polybenzoxazines compiled by Roger et al. are revealed in **Table 2.5:**

Table 2.5 Characteristic properties of polybenzoxazines

Properties	Results
Visual appearance	Yellow chunks
Melting point, °C	80-85
Viscosity @ 125°C, cps	185
Volatile, %	~2
Curing cycle	2hr/180°C + 2hr/200°C
Compression properties dry at RT	**Results**
Modulus, ksi, MPa	508, 3505
Strength, ksi, MPa	33, 228
Elongation, %	8.3

Recently, Mahfud et al., (2013) synthesized novel anionic polymeric surfactants from benzoxazine monomers by vary several chain lengths (C_8, C_{10} and C_{12}) of aliphatic amine, with 4-hydroxybenzoic acid and paraformaldehyde to obtained poly(4HBA-ocaNa+), poly(4HBA-deaNa+), and poly(4-HBA-doaNa+), respectively. (Scheme 2.6)

Scheme 2.6 Representative structures of the three anionic polymeric surfactants.

| Monomer	Amine	n+1	MW
4HBA-oca	$CH_3(CH_2)_7NH_2$	8	243
4HBA-dea	$CH_3(CH_2)_9NH_2$	10	271
4HBA-doa	$CH_3(CH_2)_{11}NH_2$	12	299

Scheme 2.7 Synthesis of benzoxazine monomers 4HBA-oca, 4HBA-dea and 4HBAdoa. The chain length of the hydrophobic segment is (n+1).

Benzoxazines are typically hydrophobic materials and limited solubility in water. The polymerized benzoxazines contain alkyl chain as hydrophobic segment distributed throughout the whole polymer backbone in a comb-like polymer form. The anionic polymeric surfactants introduced have quite unusual properties in terms of high affinity for the air/water interface at low concentration, low critical micelle concentration (cmc) and high water-solubility. The hydrophobicity of the synthesized polymeric surfactants was varied by using three different chain lengths of the primary amine, C_8, C_{10}, and C_{12}. The three Benzoxazine monomers were synthesized following the same procedure.

Katanyoota et al. (2010) was prepared carbon aerogel based on polybenzoxazine to made an electrode for supercapacitors by derived from two types of difference amines; aniline (BA-a), and triethylenetetramine (BA-teta). The first method of benzoxazine precursors (BA-teta) was prepared by using a quasi-solventless method reported by Ishida et al., (1996). The molar ratio of bisphenol-A: formaldehyde: triethylenetetramine (TETA) were 1:4:1 dissolved in dioxane as a solvent. While another benzoxazine precursors (BA-a) was prepared by using a solventless method. The molar ratio of bisphenol-A: paraformaldehyde: aniline were 1:4:2. The BA-teta consisted of a partially cured state similar to the traditional

preparation of polybenzoxazine precursors by Takeichi et al. (2005), but had a lower thermal stability than BA-a due to no presence of aromatic group at (C) position after the fully cured stage. Nevertheless, a char yield of the BA-teta was higher because crosslinking density might be higher which result from H-bonding of the secondary amines in the chain.

Moreover, the obtained carbon aerogels found that the surface area of from both BA-a and BA-teta was 391 and 368m^2/g, respectively. The pore size of each carbon aerogel was in the range of 2–5 nm, which is a suitable pore size for use as electrodes in electrochemical applications.
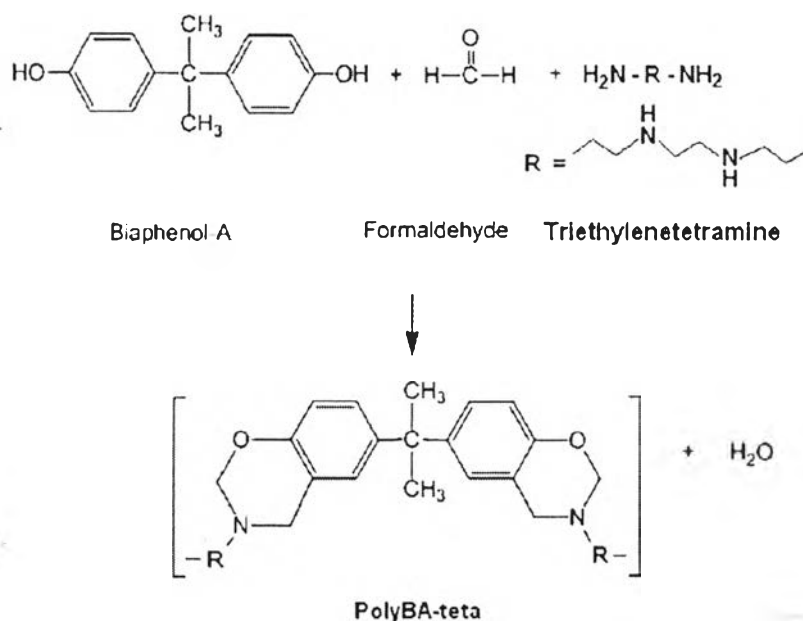
Scheme 2.8 Preparation of poly BA-teta precursor (Katanyoota et al., 2010).