CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Nanoporous Material

Nanoporous carbon can be synthesized by various methods such as chemical activation, physical activation, carbonization of carbon precursor consist of thermosetting and thermal unstable etc. But, some method produced a broad pore-size distribution. So, we need to use method that can overcome this problem. There can be called template synthesis method which can be classified in to two types; hard-templating and soft-templating.

2.2 Template Synthesis Method

2.2.1 Hard Template Method

The template acts as a mold to form mesoporous carbon materials. Porous carbon can basically be prepared as follows (a) the preparation of a porous template with control porosity, (b) the impregnation of suitable carbon precursor by wet impregnation or chemical vapor deposition or a combination of both method, (c) polymerization and carbonization of carbon precursor to generate an organic/inorganic composite, (d) the inorganic template removal by using acid (HF) or base (NaOH) to obtain porous carbon.
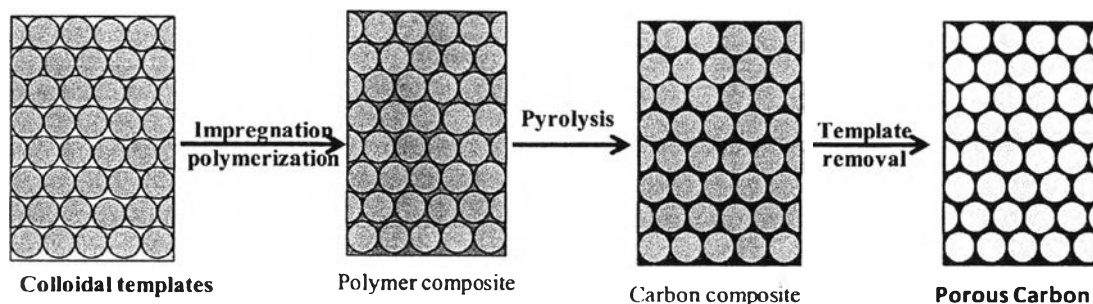

Colloidal templates   Polymer composite   Carbon composite   Porous Carbon

Figure 2.1 Preparation of porous carbon by using hard-templating method (Aled *et al.*, 2014).

In addition, mesoporous carbon spheres (MCS) have been synthesized by using chemical vapor deposition (CVD) and SiO_2 as a template. Hexadecyl trimethyl ammonium bromide (CTAB) was used to accelerate the deposition of carbon during CVD. After the CVD reaction, the composition was treated by hydrofluoric acid to remove the silica in order to obtain the final product. These mesoporous carbon spheres have high specific surface area of 666.8 m2/g and good electrochemical properties suitable for using as electrodes for supercapacitor. (Wilgosz *et al.*, 2012)

Xing *et al.* (2013) prepared mesoporous carbon nanofibers (MCNFs) by using colloidal silica incorporated porous anodic aluminum oxide (AAO) as a template by taking the advantage of commercially available materials and the templates can be removed in one step. The result showed that high surface area and nanostructure (21 nm) were obtained. The as-prepared MCNF electrode material has demonstrated a significantly higher hydrogen storage capacity than the other nanostructured carbon material (i.e., OMC) with a similar specific surface area reported for this application.
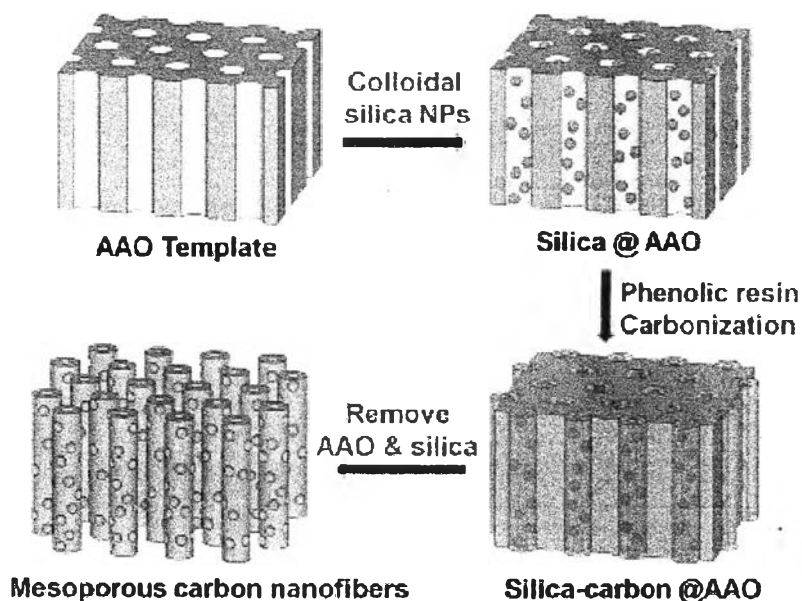

Figure 2.2 Schematic diagram for the synthesis of MCNF. AAO stands for anodic aluminum oxide and NPs for nanoparticles.

2.2.2 Soft Template Method

The soft-template method usually produces monolithic or spherical nanoporous by self-assembly of organic molecules. The obtained pore structure depends on the synthesis conditions such as solvent, types of surfactant, mixing ratios.
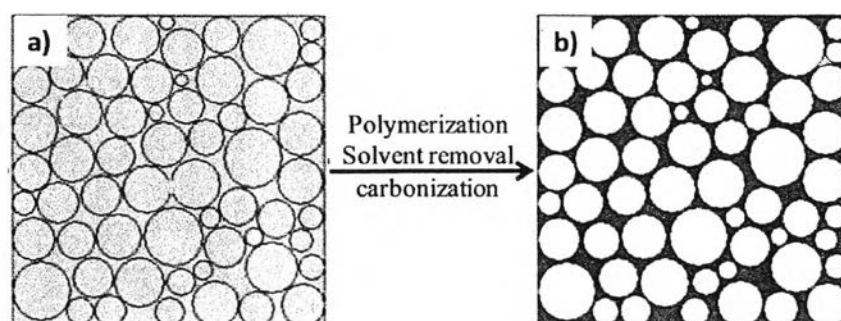

Figure 2.3 Preparation of porous carbon by using soft-templating method (Aled *et al.*, 2014).

Saha *et al.* 2012 introduced hexaphenol as an organic precursor for the synthesis of mesoporous carbon by self-assembly with triblock copolymer Pluronic P123 as an organic template. The resulting carbons can be used for several applications such as membrane separation, drug delivery, chemical sensor or selective sorption of large molecules.

Tao *et al.* (2013) prepared fabricate magnetic mesoporous silica (MMS) by using surfactant, $FcC_{11}PyBr$ (11-[(ferrocenyl carbonyloxyl-undecyl pyridinium bromide).The result showed that surfactant provided the best ability to produce mesopores with tetrathoxysilane at suitable molar ratio. Using $FcC_{11}PyBr$ as the structure –directing agent, it was also easy to control the morphology of MMS. After oxidation reaction at 573 K, the MMS material showed an obvious magnetic property with large surface area and pore volume.

2.3 Polybenzoxazine

Polybenzoxazines are a type of additional curing phenolic resin. They provides many advantages over conventional novolac and resole types of phenolic resin such as high heat resistance, flame retardance, near-zero shrinkage, good dielectric properties, etc.

Benzoxazine resin can be synthesized by combination of phenolic derivatives, formaldehyde and primary amine derivatives without using strong acid or catalysts. Polybenzoxazine will occur via thermally activated ring-opening mechanism. So, this reaction has no by-product. (Figure 2.4) (Ishida *et al*, 2011)
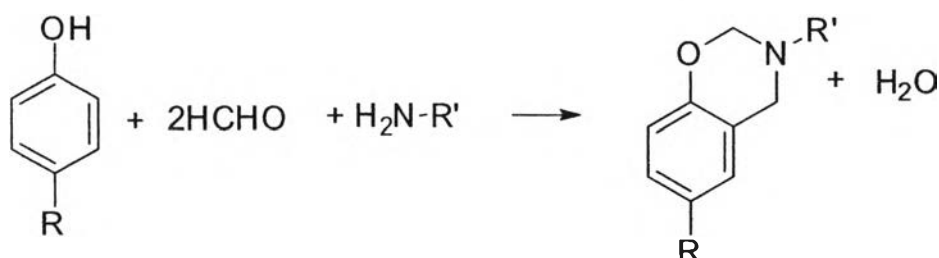

Figure 2.4 Synthesis of benzoxazine resin, where X and R are substituents.R' includes a group such as C_2H_5, CH_3, and benzene ring.

2.3.1 Chemical Methodologies for Synthesis Polybenzoxazine Monomer.

Phenol, formaldehyde and primary amine (aliphatic or aromatic) are using basically as starting materials for polybenzoxazine synthesis. Various types of benzoxazine monomer can be prepared by using various phenols and amines with different substituted group attached. (Ghosh *et al.*, 2007)

The synthesis of monofunctional benzoxazine monomer was firstly reported by Holly and co-worker in 1944. (Holly *et al.*, 1944) The condensation reaction of primary amines with formaldehyde and substituted phenol for the well-defined benzoxazine monomer. However, monofunctional benzoxazines as a precursor for polybenzoxazine show limited usefulness as structural materials. (Figure 2.5)
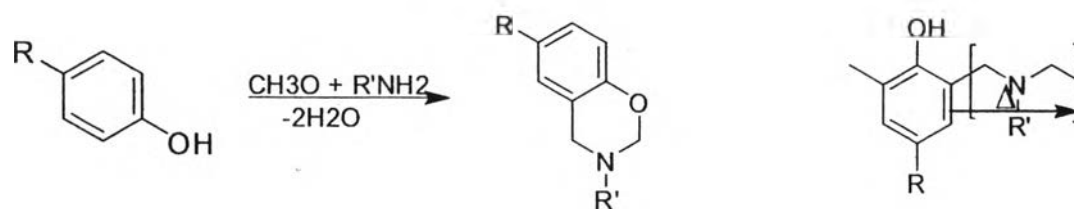
Figure 2.5 Synthesis of monofunctional benzoxazine.

Liu *et al.* 2011 studied the thermally accelerated ring-opening polymerization of bifunctional benzoxazine monomer and the properties of their crosslink polymer. The result showed that bifunctional benzoxazine offer more flexibility in molecular design and better performance than monofunctional benzoxazine monomer. The bifunctional is classified into two classes; the first one is bisphenol-based bifunctional benzoxazine monomer which is a reaction of bisphenol-A with monofunctional primary amine as shown in Figure 2.6
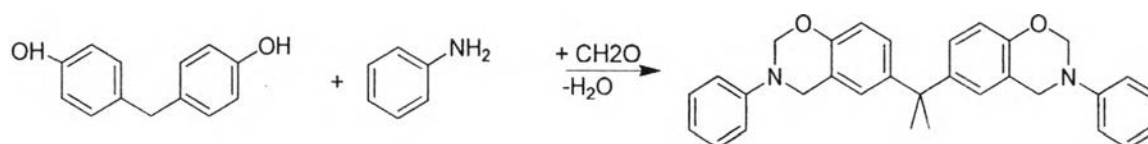

Figure 2.6 Synthesis of bisphenol A- and methylamine-based benzoxazine.

Another class is diamine-based bifunctional benzoxazine monomer, which is the reaction of monofunctional phenolic structure of ortho-vacant position as shown in Figure 2.7
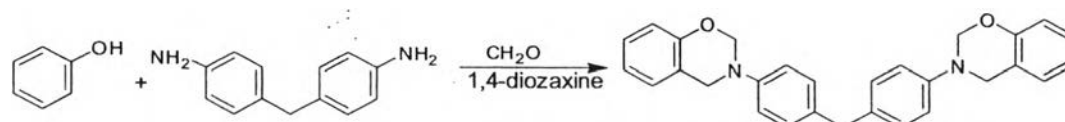

Figure 2.7 Synthesis of methylenedianiline (DDM)-based benzoxazine monomer (P-ddm).

Ishida *et al.* (1994 and 2002) have reported the development of novel type of difunction or multifunctional benzoxazine monomer. The precursor synthesized by using bisphenol-A and methyl amine in different solvents and refered to as B-m (Figure 2.8)
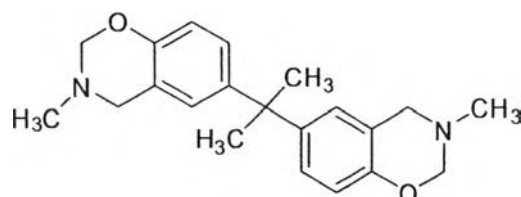

Figure 2.8 Chemical srtrucrure of benzoxazine (B-m) monomer.

2.4 Preparation of High Molecular Weight Benzoxazine Precursor

Takeichi *et al.* (2005) synthesized High molecular weight polybenzoxazine precursors from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde in Figure 2.9.

The precursor solution was cast on glass plate, giving transparent and self-standing precursor films, which was thermally cured up to 240 °C to give brown transparent polybenzoxazine films. The toughness of the crosslinked polybenzoxazine films from the high molecular weight precursors was greatly enhanced compared with the cured film from the typical low molecular weight monomer. Tensile measurement of the polybenzoxazine films showed that polybenzoxazine from aromatic diamine presented the highest strength and modulus and polybenzoxazine from longer aliphatic diamine had higher elongation at break.
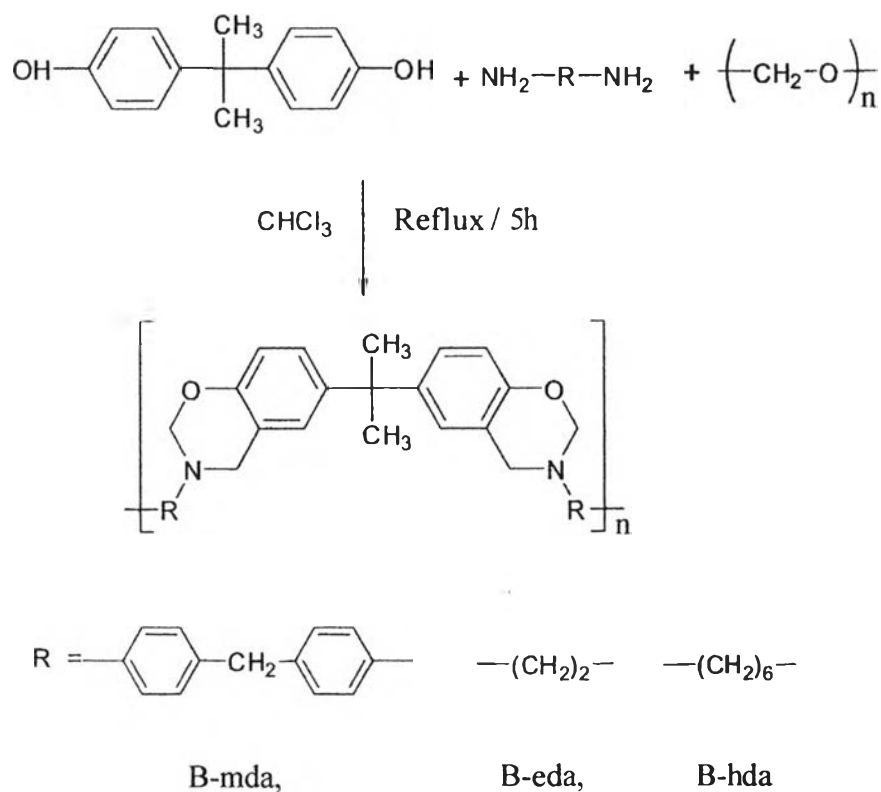
Figure 2.9 Preparation of polybenzoxazine precursors.

Benzoxazine can be polymerized through the ring-opening of the cyclic monomer only by heat treatment without the need of catalysts and no by-product or volatile and the excellent dimensional stability is obtained. The typical benzoxazine monomer (B-a) prepared from bisphenol-A, formaldehyde and aniline along with structure of its polybenzoxazine (PB-a) are shown in Figure 2.10. (Lorjai *et al.*, 2009)
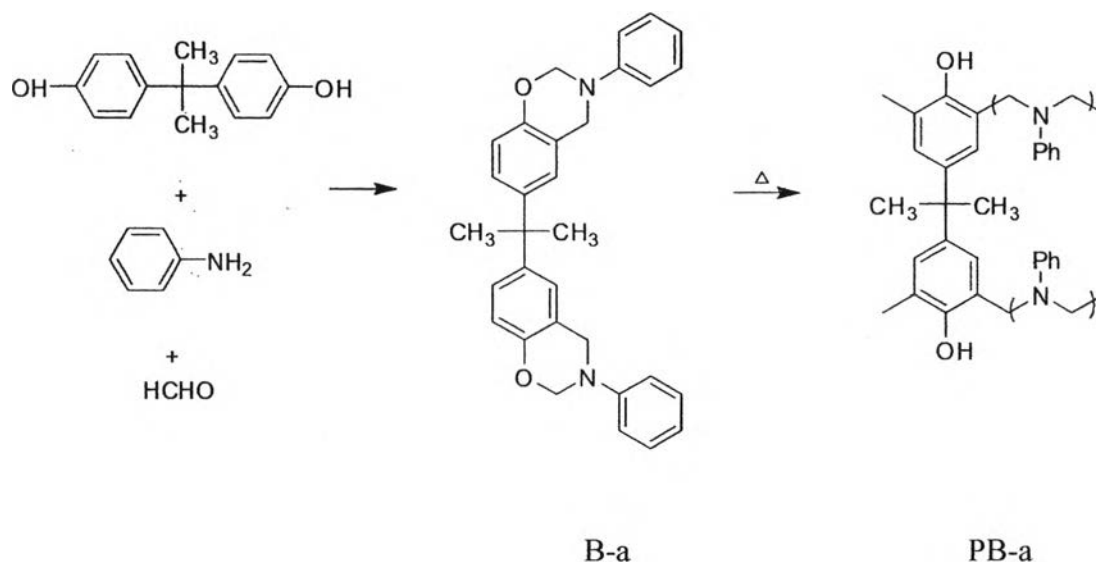
Figure 2.10 Structures of B-a and PB-a.

Katanyoota et al. (2010) prepared the carbon aerogel for using in supercapacitors from two types of polybenzoxazine. They use two difference amines; aniline (BA-a) and triethylenetetramine (BA-teta). The precursors were prepared from three main chemicals; bisphenol-A, formaldehyde and aniline or triethylenetetramine. The molar ratio of the reaction for BA-a is 1:4:2 bisphenol-A:formaldehyde:aniline and the molar ratio for BA-teta is 1:4:1 bisphenol-A:formaldehyde: triethylenetetramine. The result showed that BA-teta had a lower thermal stability than BA-a because of no presence of oxazine ring in figure 2.11 and figure 2.12
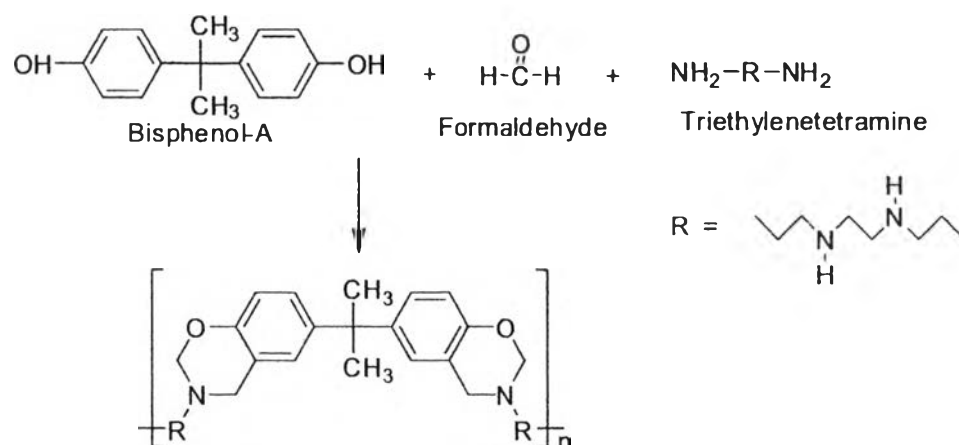
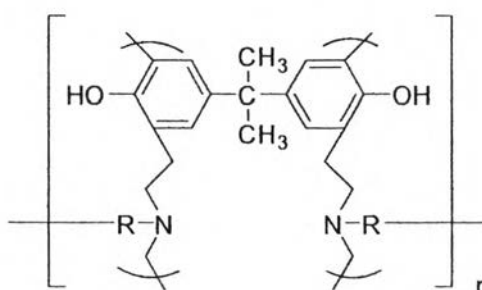**Figure 2.11** Preparation of poly BA-teta precursor.

Figure 2.12 the structure of poly BA-teta in the fully cured state.

However a char yield of BA-teta was higher because they had high crosslink density from the result of H-bonding of the secondary amine in the chain.

2.5 Application of Polybenzoxazine

Polybenzoxazine can be used in various application because of its high performance properties such as high heat resistance, low water absorption, frame retardance and good dielectric properties.

Su *et al.* (2005) studied the morphologies and dielectric constants of nanoporousmaterials derived from benzoxazine-terminated poly(3-caprolactone)/polybenzoxazine co-polymers. The result showed that the slight degree of hydrogen bonding between the two polymers effected micro-phase separation

without an excess degree of aggregation occurring that generated thin, transparent, and nanoporous film that has a very low dielectric constant.

So, we can design morphologies of porous carbon material from polybenzoxazine to be used in desirable applications.

2.6 Designing the Morphology of Porous Carbon

Jin *et al.* (2009) reported the synthesis of ordered mesoporous carbon by an organic-organic self-assembly method using resocinol(R) and formaldehyde (F) and two kinds of triblock copolymer (Pluronic F127 and P123) act as soft templates. The pore size and pore structure of the mesostructure polymer and carbon were effected by the composition of the triblock copolymer. The carbon prepraed from RF resin and Pluronic F127 block polymer possesed a chanel structure with hexagonol symetry (COU-1). The pore size of COU-1 was increase from 4.7 to 5.8 nm at high molar ratio of F127. The carbon with the warm-like structure was also obtained by using the Pluronic P123 triblock copolymer and when P123/F127 mixed triblock copolymer were used, the COU-1 structure was formed but the pore size of COU-1 was increased to 6.8 nm.

Li and Xue (2012) used soft template methode to synthesize high ordered mesoporous carbon nanoporous with well-controlled morphology from spherical to rod-like structure by using phenol-formaldehyde as carbon, yielding compound and triblock copolymer Pluronic F127 as soft template. They found that structure of orderd mesoporous carbon nanoparticles depend on concentration of F127. At low concentration of F127 (3 wt% and 6 wt%), spherical porous carbon nanoparticles with different patricle size were obtained. By increasing the F127 concentration to 9 wt%, warm-like structure was obtained. On the other hand, when the concentration was increased to 12 wt.% rod- shape nanoparticles were obtained.
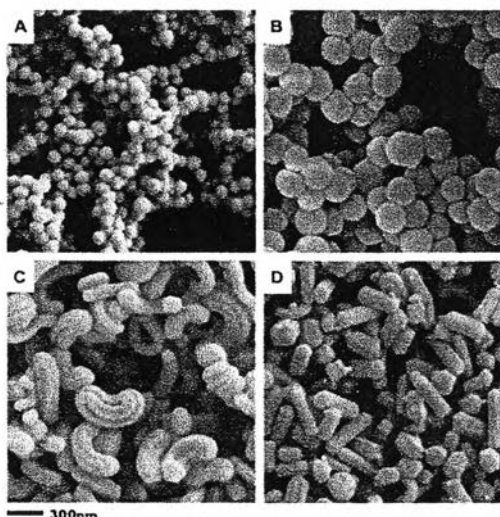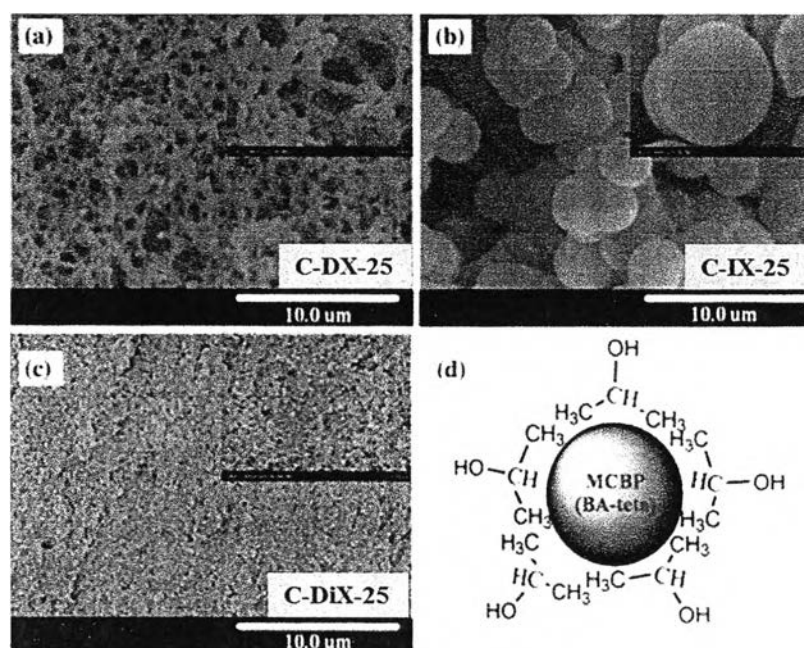
Figure 2.13 SEM images of the ordered porous carbon nanoparticles with different morphologies (A) 3wt.% (B) 6wt.% (C) 9wt.% (D) 12wt.% F127 (Li and Xue, 2012).

Thubsuang *et al.* (2014) study about effect of solvent and resin concentration on morphology of polybenzoxazine. They found that solubility parameter between Polybenzoxazine and solvent Thubsuang *et al.* (2014) has an influence on morphology of polybenzoxazine. In case of using dimethyformamide and dioxane as solvent. Focus on solubility parameter, DMF has large different solubility from Polybenzoxazine. So, phase separation occurs very fast that why the structure is looser. On the other hand dioxane has solubility close to polybenzoxazine, therefor phase separation occurs slower that lead to dense structure. However, in case of using isopropanol as solvent. Isopropanol behaves like surfactant so, spherical particle was obtained.

self-micelle-like formation mode

Figure 2.14 SEM images of the polybenzoxazine porous carbon nanoparticles with different morphologies a) C-DX-25: carbon from 25% polybenzoxazine in dimethyformamine (b) C-IX-25: carbon from 25% polybenzoxazine in isopropanol (c) C-DiX-25: carbon from 25% polybenzoxazine in dioxane (Thubsuang *et al.*, 2014).