CHAPTER II
LITERATURE REVIEW

2.1 Porous Material

As defined by Ishizaki *et al.* (1998), porous materials are any solid materials containing pores, which generally have pore volume fraction in the range between 0.2-0.95. Porous materials have been used in a wide range of applications from daily utilizations, such as purifying drinking water, to aerospace applications, such as dust capturing in outer space. According to the IUPAC classification, porous materials have been regularly categorized into three groups based on predominant pore size, as follows.

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

Table 2.1 Definitions about porous solids

Nowadays, the term "nanoporous materials" is widely used for both micro and mesoporous materials. The pore presenting in the porous materials can also be classified into two types on a basis of pore morphology, which are opened and closed pores. The opened pore is the pore that connects to the outside of the materials. On the other hand, the closed pore is the pore isolated from the outside and may contain fluid inside the pore.

2.2 Carbon Xerogels

In the 1990s, Carbon aerogels were first by Pekala *et al.* in the resorcinol-formaldehyde (RF) aerogel through a sol-gel polycondensation of resorcinol and formaldehyde by using base (Na_2CO_3). Their various characteristics make them attractive as various applications such as electrode materials for supercapacitors, the deionization of ionic solutions, advanced catalyst supports, chromatographic packing and adsorbents. The physical, chemical and electrochemical characteristics of carbon aerogels depend strongly on the fabrication method; therefore, different synthesis and processing methods can be used to produce tailored gels for specific applications *(Sepehri et al., 2009).*

2.2.1 Preparation of Carbon xerogel

Li *et al.* (2006) Carbon xerogel was prepared by the polycondensation of resorcinol with formaldehyde, and sodium carbonate was added as a catalyst. Carbon xerogel was derived from pyrolysis of a resorcinol–formaldehyde (RF) gel. The molar ratio of formaldehyde to resorcinol was held at a constant value of 2. They were dissolved in distilled ion-exchanged water, the mass percentage of the reactants in solution was set at RF = 40%, and the molar ratio xerogels can be obtained through pyrolysis of organic xerogels, which can be obtained by ambient drying is an amorphous material with a pearly network structure, and can be regarded as partly graphitized carbon. They are generally supercritical dried prior to pyrolysis of the organic xerogels to preserve their pore texture.

In order to expand the source of raw materials and reduce the cost, many alternative materials were used to prepare carbon xerogels.

Li and Guo (2000) carried out some experiments for the preparation of low density carbon xerogels. In their work, a cresol mixture was first used to polycondensation with formaldehyde by using NaOH as a catalyst for the preparation organic xerogels. They concluded that a cresol mixture can be used as a raw material to prepare low density monolithic, crack-free xerogels and carbon xerogels. Density is an important index to judge the aerogel quality. The lower the carbon xerogel density, the lower the electrical resistivity, hence the preparation of the super-low-density aerogel is important in understanding the physical transport mechanism with in these

materials. Li *et al.* (2002) attempted to make lower cost xerogel by using cresol. A mixture of cresol (Cm), resorcinol and formaldehyde has been used as an alternative economic route to the classical resorcinol-formaldehyde systhesis. The porous structure of the mixed carbon xerogels (CmRF) was similar to that of RF carbon xerogels.

Fu *et al.* (2003) reported the polycondensation reaction of resorcinol and furfural for the synthesis of carbon xerogels. According to the reported procedure, this reaction was performed in isopropyl alcohol with HCl as a catalyst, and the resulted alcogels were then dried directly with supercritical isopropyl alcohol, which was followed by carbonization.

Wu and Fu (2005) also prepared organic and carbon xerogels by gelation of phenol-furfural using HCl as a catalyst and supercritical drying in ethanol. The experimental results showed that the gelation ability of the phenol–furfural system could be enhanced by increasing the phenol–furfural concentration, the mass ratio of HCl to phenol (HCl/P), the mole ratio of phenol to furfural (P/F) and the gelation temperature. Furthermore, organic and carbon xerogels could be obtained by directly drying phenol–furfural alcogels at ambient pressure under proper preparation conditions.

In addition, xerogels from other organic starting materials have been produced such as polyurethanes (Biesman *et al.*, 1998), polyureas (Je K. L., 2006) and melamine-formaldehyde (Zhang *et al.*, 2002).

2.2.2 Control of Porous Structure of Organic and Carbon Xerogels

Organic xerogels, prepared according to the method proposed by Pekala *et al.*, have been elucidated that resorcinol–formaldehyde (RF) xerogels are mesoporous materials with high surface areas and have few micropores (Tamon *et al.*, 1997).

Tamon *et al.* (1998) studied the mesoporous structure of organic and carbon xerogels by taking into account of the synthesis conditions of the RF aquagels. They concluded that the mesoporous radius of the RF xerogel can be controlled in the range of 2.5-9.2 nm by changing the mole ratio of resorcinol to sodium carbonate used as a catalyst and the ratio of resorcinol to distilled water used as a diluent. Shrinkage also plays a role in the control of the mesopore radius. The pyrolysis temperature is also significant, as it increases, the mesopore volume becomes small but the peak radius of pore distribution is maintained. It was also noticed that with

the increase in the pyrolysis temperature, ethane adsorption becomes larger than ethylene adsorption on the xerogels. The carbon xerogels prepared by pyrolysis at 1000°C have the same adsorption characteristics of ethane and ethylene as activated carbons do.

2.3 Polybenzoxazine

Polybenzoxazine is a newly developed type of addition cured phenolic resin that can overcomes the short-comings of traditional phenolic resins. Benzoxazine monomers were derived from the reaction between various aromatic/aliphatic amines, mono/diphenols, and formaldehyde. Then the monomers polymerize through ring opening of cyclic monomers by heat treatment process without catalyst and without generating any by-product (Figure 2.1). Since the benzoxazine monomers can synthesize by using a wide variations of raw materials, the molecular design flexibility of cyclic monomers were obtained. Polybenzoxazines provide good characteristics found in the traditional phenolic resins such as flame retardance and heat resistance; they also provide characteristics that are not found in the traditional phenolic resins such as excellent dimensional stability, low water absorption and good dielectric properties. Thus, polybenzoxazines are an attractive materials for wide applications including a matrix of polymer composites or materials used in electronic packaging (Pakkethati *et al.*, 2011). Nevertheless, polybenzoxazines have some short-comings such as the cured materials are brittle and a relatively high temperature is needed for the ring-opening polymerization and processing into thin films is due to their brittleness (Takeichi *et al.*, 2005).
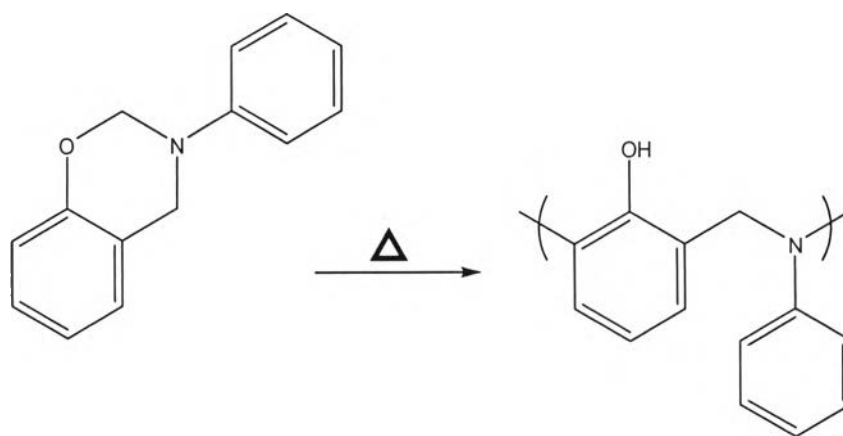

Figure 2.1 Curing reaction of benzoxazine monomer to polybenzoxazine.

Benzoxazines were first synthesized by Cope and Holy in 1940s (Sun *et al.*, 2008), after that the researchers have paid attention in these materials due to their lot of attractive properties such as near-zero volumetric change upon curing, low water absorption, some type of polybenzoxazines have glass transition temperature much higher than curing temperature, high char yield, no strong acid catalysts required for curing, and release of no toxic by-product during curing. The molecular structures of polybenzoxazines have high design flexibility, which allows the properties of the cured materials to be used in a wide range of applications (Ghosh *et al.*, 2007; Allen *et al.*, 2005).

2.3.1 Chemical Methodologies for Synthesis of Benzoxazine Monomers

Benzoxazine monomers are typically synthesized using phenol, formaldehyde, and amine (aliphatic or aromatic) as starting materials either by employing solution or solventless methods. Various types of benzoxazine monomer can be synthesized using various phenols and amines with different substitution groups attached (Ghosh et al., 2007).

2.3.1.1 Mono-Functional Benzoxazine Monomers

Holly and Cope (1944) first reported the polycondensation reaction of primary amine with formaldehyde and substituted phenols for the synthesis of well defined benzoxazine monomers. According to the reported procedure, this reaction was performed in a solvent in two steps. Later, Burke (1949) found that the benzoxazine ring reacted preferentially with free ortho positions of the phenolic compound and formed a Mannich bridge. The procedure of the Mannich condensation for benzoxazine synthesis in a solvent proceeded by first adding amine to formaldehyde at lower temperatures to form N,N-dihydroxymethylamine derivative, which then reacted with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the elevated temperature to form the oxazine ring (Burke *et al.* 1965).
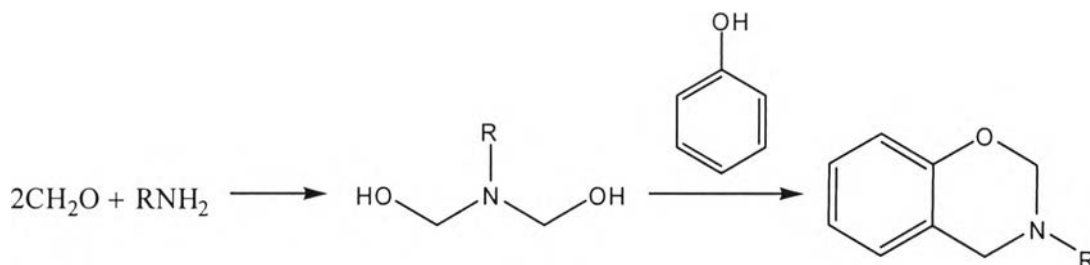
Figure 2.2 Synthesis of 3,4-dihydro-2H-1,3-benzoxazines (Ghosh et al., 2007).

The slow reaction rate, large amount of solvent required for the synthesis and, in some cases, the poor solubility of the precursors was the disadvantages of Mannich condensation process. The use of an organic solvent also increased the cast of products and created the environmental problems. Furthermore, the solvent residue in the precursors led to problems during processing of the benzoxazine resins (Brunovska et al., 1998). To overcome these shortcomings, Ishida et al. (1996) developed a solventless synthesis in a melt state. The reaction mechanism and kinetics of solventless synthesis were proposed by Liu (1995) in order to use this procedure to prepare a large quantity of benzoxazine monomers.

2.3.1.2 Di-Functional Benzoxazine Monomers

Ishida *et al.* (1994 and 2002) have developed a new class of difunctional and multifunctional benzoxazine monomers and their curing into phenolic materials with the ring opening reaction being initiated by dimers and higher oligomers in the resin composition. The precursor was synthesized using bisphenol-A, formaldehyde and methylamine in different solvents and referred to as B-m, as a reference to two of its original ingredients: bisphenol-A 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.
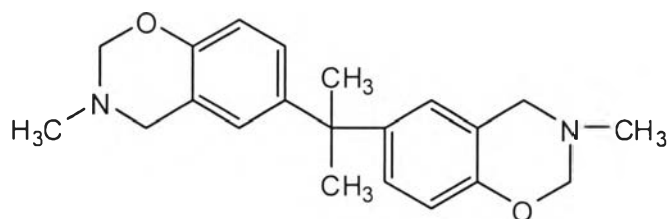
Figure 2.3 Chemical structure of benzoxazine (B-m) monomer (Ghosh et al., 2007).

2.4 Surfactant

Liu *et al.* (2007) Surfactant templating mesoporous carbon foam was preapared by method in Figure 2.4 Typically, phenol and formaldehyde were dissolved in ethanol. Surfactant sorbitan monooleate was added into the above solution under stirring to form a homogeneous solution. The molar composition of phenol/formaldehyde/ethanol/sorbitan monooleate is 1:2:60:0.38. NaOH was added into the mixed solution, and formaldehyde and resorcinol began to polymerize. Then NaOH in the polymerized phenolic resin was removed by immersing it in water (60°C) for several times. Finally the dried polymer precursor was carbonized at 1000 °C in a purified nitrogen flow with a heat rate of 1 °C/min to decompose the surfactant template and to obtain mesoporous carbon foams.
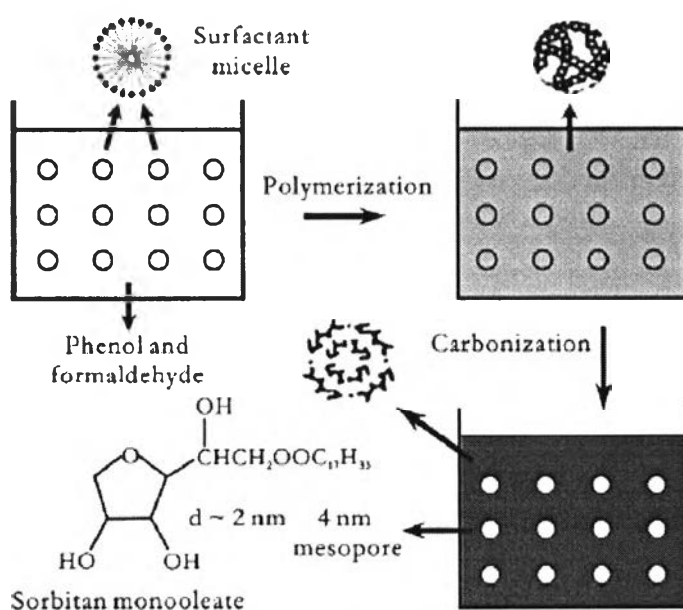

Figure 2.4 Preparation of mesoporous carbon foams by a surfactant templating approach.

Matos *et al.* (2006) studied effect of surfactants on the porosity of carbon xerogels. The addition of three different types of surfactants, nonionic, anionic and cationic, originates carbon xerogels with different porous properties. The surfactant concentration has an important role on pore size distribution and shape. Carbon xerogels prepared with the anionic surfactant exhibit mesopores of different shapes and larger sizes (2–180 nm) compared with those prepared with non-ionic and cationic ones. Carbon xerogels obtained by using cationic surfactants exhibit cylindrical pores with sizes in the range of 2–25 nm. The effect of non-ionic surfactants was not relevant in the textural modification of the original carbon xerogel.

Carbon xerogels prepared with anionic surfactants exhibit larger mesopores and macropores and a broader mesopores size distribution, compared with those prepared with cationic surfactants. With cationic surfactants the positive heads of the micelles interact electrostatically with the resorcinol anions, in such a way that the polymer chains are likely to be formed in the close vicinity of the surfactant rods (Figure 2.5A). On the other hand, as the anionic surfactant has negative heads, electrostatic repulsions between the micellar surface and the resorcinol anions may occur preventing the condensation reaction and therefore polymerisation, in the close vicinity of that micellar surface (Figure 2.5B).
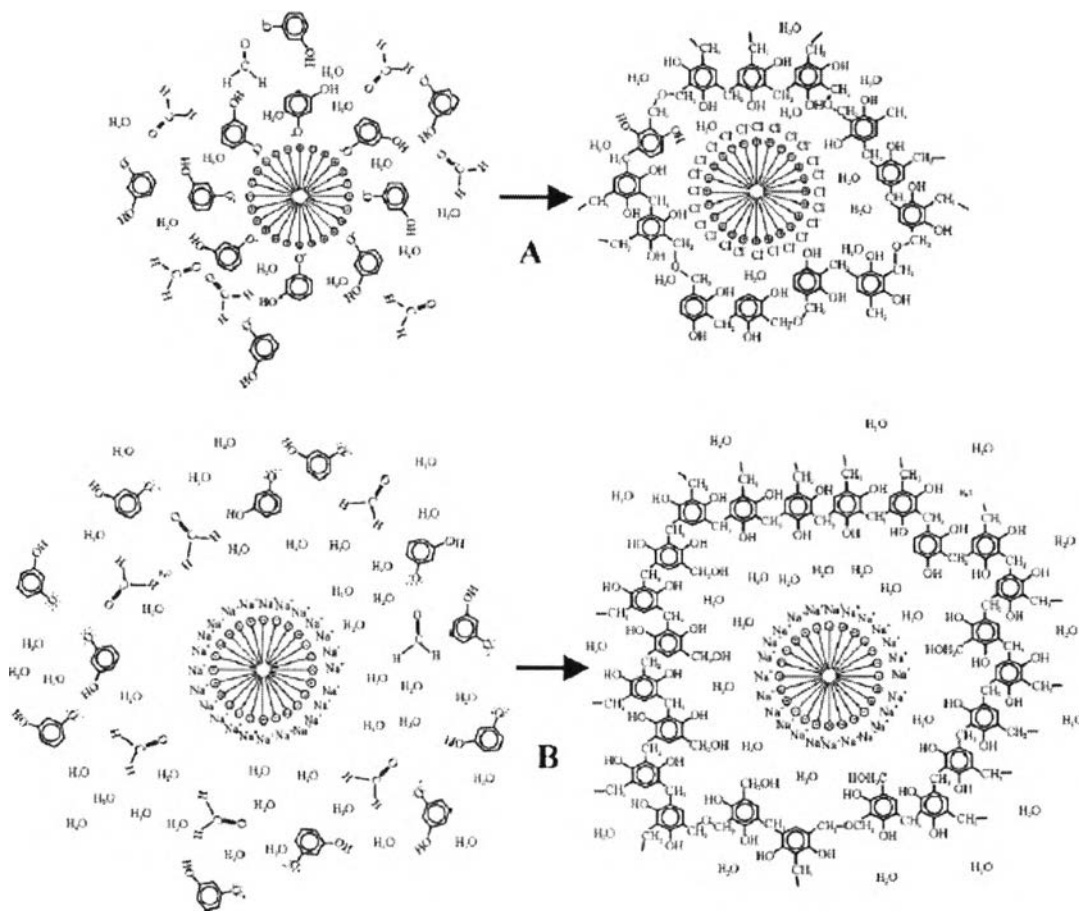
Figure 2.5 Effect of surfactants on the polymer pore size. (A) cationic surfactant; (B) anionic surfactant.

Thubsuang *et al.* (2013) carried out some experiments for the preparation of polybenzoxazine with surfactant and study the effect of non-ionic (Synperonic NP30) and cationic (CTAB) surfactants on porous structure of polybenzoxazine-based carbon xerogels. Inter-connected structure of mesoporous carbon xerogels with mesopore diameters in the range of 15.57-36.07 nm was obtained by using different concentrations of CTAB (Table 2.2). In addition, carbon xerogel nanospheres with the size of 50-200 nm were also obtained through the emulsion process. The mesopore diameters started to decrease when the carbon xerogel nanospheres were formed at the CTAB concentration of equal to or exceeding 0.030 M. By using Synperonic NP30 as a surfactant, the properties of the obtained carbon xerogels were shifted from mesoporous materials for the reference carbon xerogel (no surfactant added) to obviously microporous materials at higher concentrations of Synperonic NP30

(0.009 M - 0.180 M) (Table 2.3). The carbon xerogel microspheres with the diameter size of about 2.5 μ m were also obtained through the emulsion process when the concentration of Synperonic NP30 was reached at 0.180 M.

Table 2.2 Pore structure of PBZ-based carbon xerogels prepared from 10%w/w of benzoxazine precursor using different concentrations of CTAB

Sample	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{total} (cm^3/g)	APD_{micro} (nm)	APD_{meso} (nm)
CX	280	0.08	0.20	0.28	0.76	34.78
CX-CTAB-0.003	284	0.11	0.21	0.32	0.66	35.85
CX-CTAB-0.009	275	0.10	0.19	0.29	0.80	36.07
CX-CTAB-0.030	323	0.12	0.20	0.32	0.76	25.38
CX-CTAB-0.090	369	0.12	0.52	0.64	1.00	25.25
CX-CTAB-0.180	271	0.10	0.17	0.27	0.66	15.57

Notes : S_{BET}: BET surface area; S_{meso}: mesopore surface area; V_{micro}: micropore volume; V_{meso}: mesopore volume; V_{total}: total pore volume; APD_{micro}: average micropore diameter; APD_{meso}: average mesopore diameter; APD: average pore diameter

Table 2.3 Pore structure of PBZ-based carbon xerogels prepared from 10%w/w of benzoxazine precursor using different concentrations of Synperonic NP30

Sample	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	V_{total} (cm^3/g)	APD_{micro} (nm)	APD_{meso} (nm)
CX	280	0.08	0.20	0.28	0.76	34.78
CX-NP30-0.003	284	0.08	0.34	0.42	0.66	56.78
CX-NP30-0.009	276	0.13	0.08	0.21	0.70	6.20
CX-NP30-0.030	290	0.13	0.09	0.22	0.66	3.57
CX-NP30-0.090	292	0.13	0.08	0.21	0.76	3.57
CX-NP30-0.180	262	0.12	0.04	0.16	1.00	4.53

Notes : S_{BET}: BET surface area; S_{meso}: mesopore surface area; V_{micro}: micropore volume; V_{meso}: mesopore volume; V_{total}: total pore volume; APD_{micro}: average micropore diameter; APD_{meso}: average mesopore diameter; APD: average pore diameter

The mesopore size distribution of all samples, calculated by BJH method, was illustrated in Figure 2.6 CX and CX-NP30-0.003 show higher amount of mesopore volume and lager average mesopore size than those of other samples. An average mesopore size was also shifted to smaller mesopore diameter ranging from 3.57 nm to 6.20 nm, when increasing the concentration of Synperonic NP 30. Moreover, from Figure 2.7, amount of mesopore volume of carbon xerogels derived from Synperonic NP30 at concentration of 0.009-0.180 M, was clearly lower than those of CX and CX-NP30-0.003 as well.
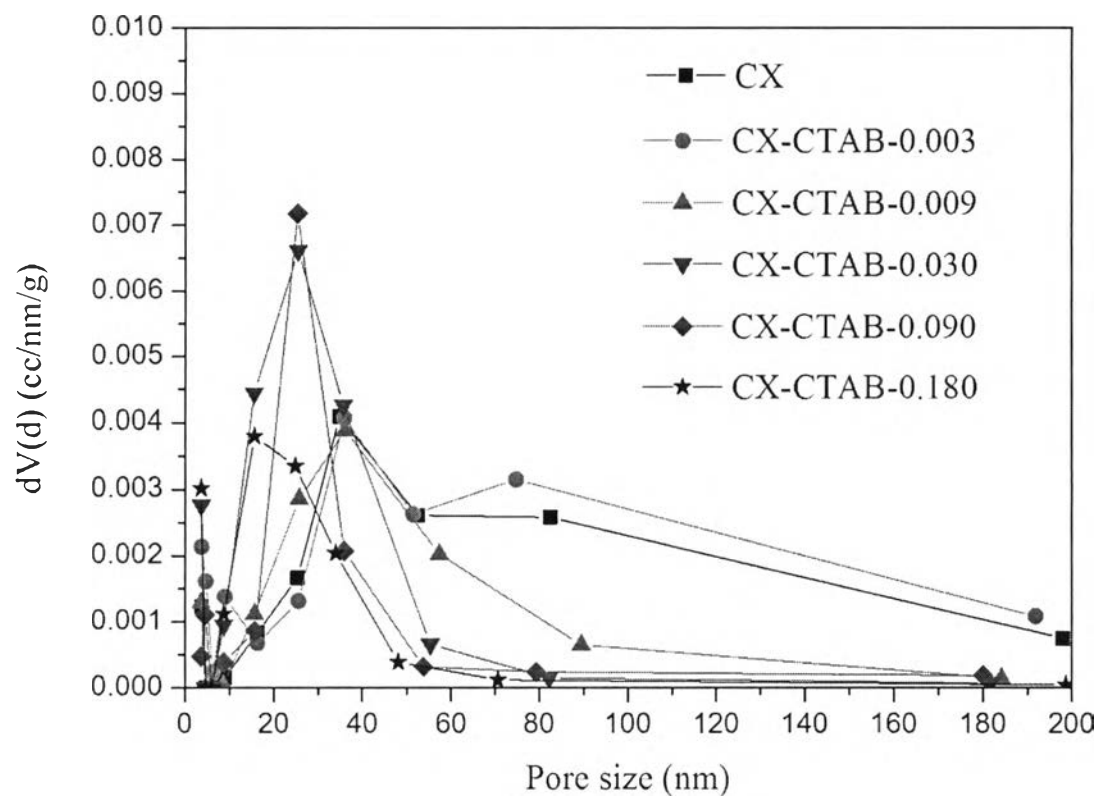
Figure 2.6 Mesopore size distributions of polybenzoxazine-based carbon xerogels using different concentrations of CTAB, determined by BJH method.
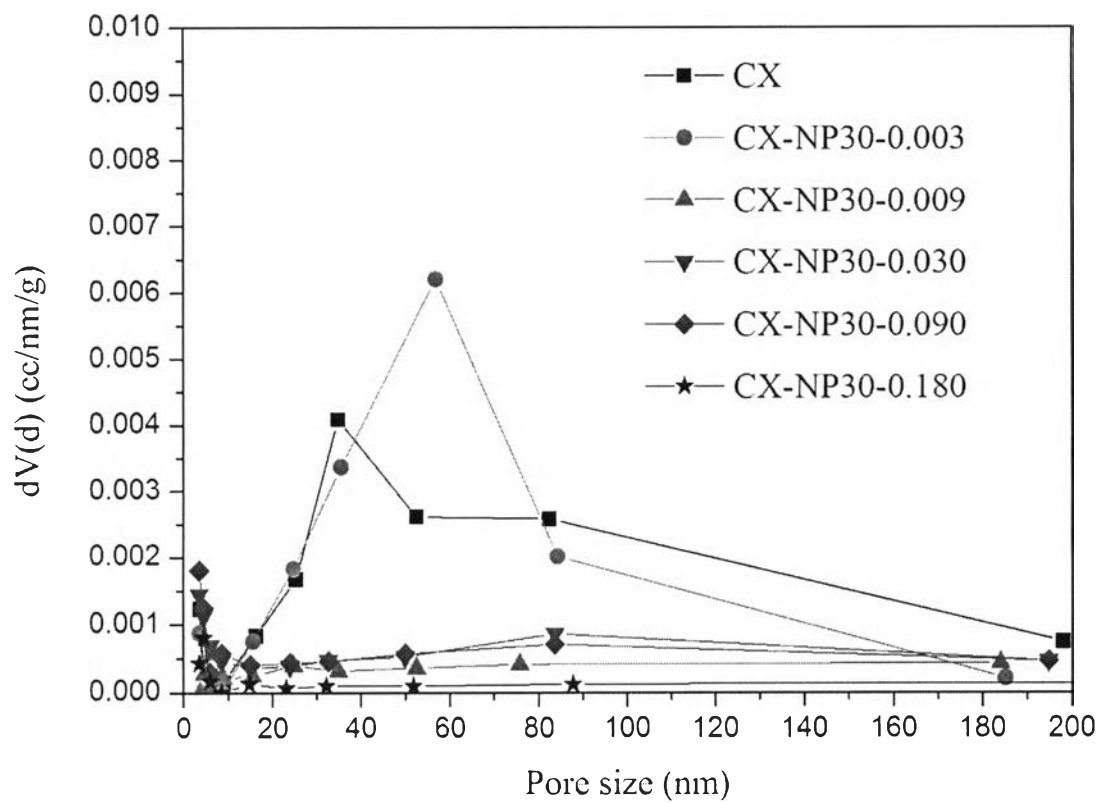
Figure 2.7 Mesopore size distributions of polybenzoxazine-based carbon xerogels using different concentrations of Synperonic NP30, determined by BJH method.