CHAPTER II
LITERATURE REVIEW

2.1 Electrochemical Supercapacitors

Electrochemical supercapacitors are the energy–storage devices that offer much higher power density than conventional energy–storage devices such as batteries, capacitors, and fuel cells. The ability of high dynamic of charge propagation (short-term pulse) is a main advantage of this storage device to be useful in the hybrid power sources for electrical vehicles, digital telecommunication systems, UPS (uninterruptible power supply) for computers, and pulse laser technique. Another advantage of electrochemical capacitor system is a possibility of fully discharge, and a short circuit between the two electrodes is also not harmful (Frackowiak and Béguin, 2001).

Electrochemical supercapacitors from carbon can be divided into two types depending on the kinds of accumulate energy; the electrical double layer capacitors (EDLCs) and pseudocapacitors (Conway 1991).

2.1.1 Electrical Double-layer Capacitors (EDLCs)

EDLCs can store energy by charge separation at the electrode/electrolyte interface (Fig. 2.1). The capacitance of EDLCs is strongly dependent on the surface area of the electrode materials. Among many carbon materials, carbon aerogels are promising materials as electrodes for EDLCs due to their high performance and the ability to control morphology of carbon based on different synthesis paprameters (Pekala *et.al.*, 1992).
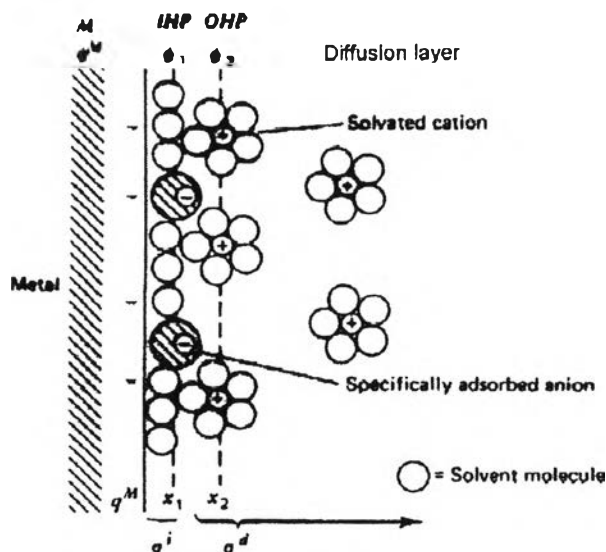
Figure 2.1 Scheme of the electrical double-layer capacitors (EDLCs).

2.1.2 Pseudocapacitors

Pseudocapacitors store energy via faradaic redox reactions on the interface of the electroactive materials and the electrolyte. The high capacitance of this capacitor is created by electrode material that can be reversibly oxidized and reduced over wide potential range. Thus, metal oxides and conductive polymers with various oxidation states are considered as promising materials for pseudocapacitors (Prasad and Miura, 2004). Furthermore, a combination of pseudocapacitive materials and carbonaceous materials suitable for EDLCs has been conducted to improve the electrochemical performance.

In general, the enhancement of specific capacitance for the carbon materials by quick faradaic reactions can be realized by the following modifications (Frackowiak and Béguin, 2001):

(1) The special oxidation of carbon for increasing the surface functionality through chemical treatment (Jurewicz and Frackowiak, 2000), electrochemical polarization (Momma *et al.*, 1996), and plasma treatment (Ishikawa *et al.*, 1996)

(2) The evolution of carbon/conductive polymer composites by electropolymerization of a suitable monomer (aniline, pyrrole) on the car-

bon surface (Ingram *et al.*, 1998) or using a chemical method for po-
lymerization

(3) The insertion of electroactive species of metals oxides such as RuO_2,
ZnO, NiO, MnO_2, SnO_2, etc. into the carbon material.

2.2 Metal Oxides

Metal oxides as the electroactive species in pseudocapacitors were in-
serted on the electrode surface to accelerate the faradaic redox reactions. Many stu-
dies have been continuously developed to increase the capacitance for supercapacitor
applications by applying various metal oxides. For example, RuO_2 has been widely
used in electrochemical capacitors due to its high specific capacitance and prominent
electrochemical properties (Zheng *et al.*, 1975), but it is too expensive to be used in
commercialization. Therefore, other inexpensive metal oxides which exhibit capaci-
tive behavior similar to RuO_2 have been explored instead for supercapacitors, for ex-
ample, ZnO (Kalpana *et al.*, 2006), SnO_2 (Hwang and Hyun, 2007), Fe_3O_4 (Du *et al.*,2009), etc. In addition, the preparation process of metal oxide nanoparticles, such
as γ-Fe_2O_3 (Lee *et al.*, 2004), Fe_3O_4 (Liu *et al.*, 2006), and (Du *et al.*, 2009), etc., was
also introduced in some researches with various methods.

2.2.1 Preparation of Metal-doped Carbon Aerogel Electrodes

Lee *et al.* (2010) prepared the metal-doped carbon aerogel for a super-
capacitor electrode by an impregnation method (Fig. 2.2) with a variation of cobalt
contents from 1 to 15 wt%. They found that 7wt% Co-doped carbon aerogel exhi-
bited the highest capacitance and stable cyclability due to the faradic redox reactions
of cobalt oxide. As a result, other metal-doped carbon aerogels were obtained
through the use of 7 wt% metal content for the preparation of as the electrodes with
the same method. Among these electrodes, Mn-doped carbon aerogel displayed the
highest capacitance while the most stable cyclability was obtained from Cu- and Fe-
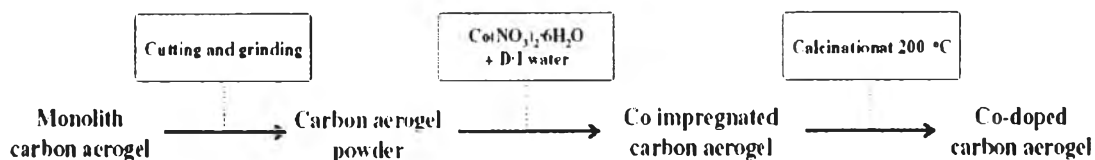doped carbon aerogels.

Figure 2.2 Impregnation method for preparation procedure of the Co-doped carbon aerogel (Lee *et al.*, 2010).

From Fig. 2.2, the Co-doped carbon aerogel was fabricated as an electrode by using ketjen black and polyvinylidene fluoride (PVDF) as a conductive additive and a binder, respectively. A weight ratio of Co-doped carbon aerogel, conductive additive, and binder was 75:15:10. These materials were dispersed in 2-propanol and they were then pressed onto stainless steel mesh to obtain an electrode (Lee *et al.*, 2010).

2.2.2 <u>Properties and Electrochemical Applications of Pseudocapacitors</u>

Du *et al.* (2009) prepared and investigated the electrochemical performance of activated carbon (AC)-Fe_3O_4 nanoparticles asymmetric supercapacitor cells in 6M KOH aqueous electrolyte. They reported that the system showed good electrochemical capacitance performance within potential range from 0 to 1.2 V with a specific capacitance of 37.9 F/g at a current density of 0.5 mA/cm^2. This pseudocapacitance was much greater than the value of 27 F/(g-Fe_3O_4) in mild aqueous electrolyte with an operation voltage range of 1.2 V which was reported by Wu *et al.* (2003). Furthermore, AC-Fe_3O_4 hybrid supercapacitor could retain 82% of initial capacity over 500 cycles.

2.3 Carbon aerogels

Carbon aerogels as a novel nanometer size porous amorphous carbon material have been developed for about 20 years. At first, the time-consuming preparation and supercritical drying condition affected the large-scale production (Pekala *et al.*, 1989). To solve these problems, the ambient drying was recommended by Wu *et al.* (2006). It was a simpler and cheaper method and thus could improve the

chances for large-scale applications such as electrode materials for supercapacitors, the deionization of ionic solutions, advanced catalyst supports, chromatographic packing, and adsorbents. However, various characteristics of carbon aerogels depend strongly on fabrication methods, so different synthesis and processing methods have been used to produce different morphologies for specific applications (Sepehri *et al.*, 2009).

2.3.1 Preparation of Carbon Aerogels

Carbon aerogels can be obtained by the polycondensation reaction of resocinal with formaldehyde as shown in Fig. 2.3. Normally, the preparation of carbon aerogels has four steps as follows: sol-gel formation, solvent exchange, a supercritical drying, and pyrolysis. These steps result in the porosity of carbon aerogels (Li *et al.*, 2008).
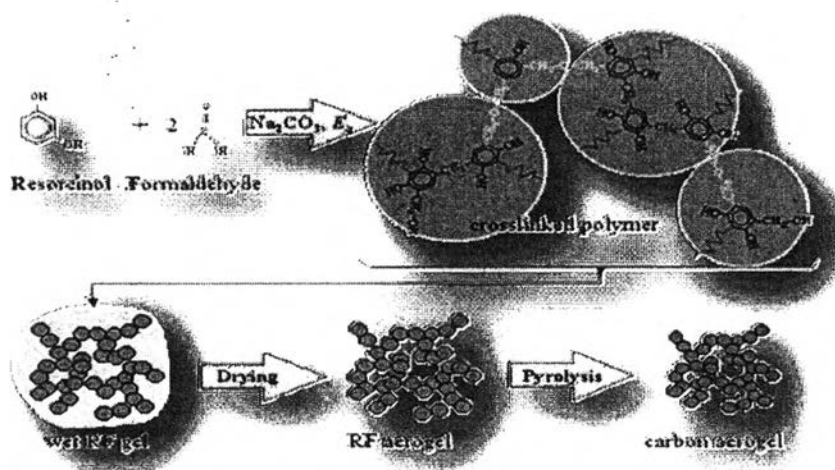

Figure 2.3 Schematic diagram of the reaction of resorcinol with formaldehyde (Berthon-Fabry and Achard, 2003).

Up to now, many alternative raw materials have been developed to satisfy the needs of applications and cost reductions for the carbon aerogel preparation.

Li *et al.* (2000) prepared low density carbon aerogels from a mixture of cresol and formaldehyde by using NaOH as a catalyst. They concluded that the

physical transport mechanism within the materials was an important parameter to design the morphology of carbon aerogels.

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

Wu *et al.* (2005) synthesized organic and carbon aerogels via the 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. Nevertheless, organic and carbon aerogels could still be prepared from directly drying phenol–furfural alcogels at ambient pressure under proper preparation conditions.

Moreover, researchers have also tried to produce aerogels from other organic starting materials such as polyurethanes (Biesman *et al.*, 1998), polyureas (Je Kyun Lee, US Pat. 2006), and melamine–formaldehyde (Zhang *et al.*, 2002).

2.3.2 Control of Mesoporous Structure of Organic and Carbon Aerogels

Tamon *et al.* (1997) prepared organic aerogels through the polymerization of a resorcinol–formaldehyde (RF) mixture that RF aerogels are obtained as mesoporous materials with high surface areas and have few micropores.

The effect of synthesis conditions of the RF aquagels on the mesoporous structure of organic and carbon aerogels were also studied by Tamon *et al.* (1998). They concluded that the mesoporous radius of the RF aerogel could be controlled in the range of 2.5-9.2 nm by changing the mole ratio of resocinal and sodium carbonate, using as a catalyst. Furthermore, they found that the ratio of resorcinol to distilled water used as a diluent also played a role in the control of the mesopore radius. In addition, the pyrolysis temperature was a significant factor, as it increased, the mesopore volume became smaller but the peak radius of pore distribution was maintained.

2.3.3 Properties and Electrochemical Applications of Carbon Aerogels

Carbon aerogels—having a monolithic three-dimensional mesoporous network structure consisting of carbon nanoparticles—exhibit high porosity (80-98%), low electrical resistivity, controllable pore structure, high surface area (up to 1100 m^2/g), good electrical conductivity (25-100 S cm^{-1}) (Pekala et al., 1992), and thermal and mechanical properties. These attractive properties make carbon aerogels very suitable as electrode materials for supercapacitors

Wang et al. (2001) studied the morphological effects on the electrical and electrochemical properties of carbon aerogels. The possibility of using carbon aerogel for supercapacitor was explored by Fisher et al. (1997), Saliger et al. (1998), and Pekala et al. (1998)

Meng et al. (2004), Frackowiak E. (2007) and Azaïs P. et al. (2007) studied the factors affecting the electrochemical performance of supercapacitors, including their specific surface area, pore volume, pore size distribution, as well as the surface functional groups of the electrode materials.

Meng et al. (2004) reported that both surface area and pore volume of carbon aerogels determined their specific capacitance. High pore volume and wide pore distribution contributed to the increase of the capacitance. Frackowiak (2007) concluded that micropore played an essential adsorption role in the formation of the electrical double layer, and the presence of mesopore was necessary for the efficient charge propagation into the bulk of the electrode material, allowing the so-called frequency response to be fulfilled. Azaïs et al. (2007) indicated that the concentration of surface functional groups and their nature were found to have an important influence on the performance degradation of supercapacitors.

Li et al. (2008) tried to investigate the structure and electrochemical properties of carbon aerogels, which were synthesized at ambient temperature. They concluded that the performance and the structure of carbon aerogels for supercapacitor applications depended strongly on the mole ratio of resorcinol to sodium carbonate used as catalyst (R/C). The carbon aerogels were porous materials with pearl-like network structure and when the particle size increased with the increase of R/C ratio. The total surface areas were in range of 600-1000 m^2/g. The conclusions were

also indicated that carbon aerogels electrodes had good electrochemical performance, high reversibility and high specific capacitance. The higher capacitance of 183.6 F/g was obtained with R/C ratio 1500. Apart from this, carbon aerogels with R/C ratio 1500 had low resistance and small leakage current and good electrical conductivity.

Katanyoota *et al.* (2010) studied the electrochemical properties of electrodes prepared from the benzoxazine derived carbon aerogels. The results can be concluded that the surface area of carbon aerogels from BA-a and BA-tetra was 391 and 368 m^2/g, respectively. The carbon aerogels consisted of a suitable pore size, 2 – 5 nm, for using as electrodes in electrochemical applications. However, the carbon aerogels derived from BA-tetra showed higher specific capacitance than that derived from BA-a because of having more mesopores; hence, BA-tetra aerogels provided better ions transport throughout the pores of the carbon aerogel layer.

2.4 Polybenzoxazines

Polybenzoxazines, as a new high performance phenolic resin, offer many advantages in comparison with the traditional phenolic resins. Benzoxazine monomers can be easily prepared from inexpensive raw materials, and polymerized without using strong acid or basic catalysts. Since the polymerization takes place via thermally activated ring-opening mechanism; as a result, no by-product is generated. Moreover, polybenzoxazines provide unique characteristics like low water absorption and high dimensional stability because of the near-zero shrinkage upon curing (Ishida *et al.*, 1996). Consequently, they have been applied in many fields such as materials for airplane interiors, protective coatings for circuits in television studios and computer chips, curing agents for other synthetic resins, and varnishes which form films with a good resistance to water, alkali and solvents. In case of the typical polybenzoxazines, they had some major problems about their brittleness and a high temperature needed for the polymerization. As a result, several studies relating to the improving performance of polybenzoxazines have been conducted in an effort to gain the enhanced performance for various applications—electronic materials, matrix resin for fiber-reinforced plastics, and adhesives—are expected.

2.4.1 Chemical Methodologies for Synthesis of Benzoxazine Monomers

Ghosh *et al.*, (2007) indicated the typical way of synthesis to obtain benzoxazine monomers by using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either by employing solution or solventless methods. Various types of benzoxazine monomers can be synthesized via using various phenols and amines with different substitution groups attached.

Mono-functional benzoxazine monomers

The polycondensation reaction of primary amine with formaldehyde and substituted phenols for the synthesis of well-defined benzoxazine monomers was first reported by Holly and Cope (1944). According to the reported procedure, this reaction was performed in a solvent in two steps. Later, Burke (1949) found that the benzoxazine ring reacts preferentially with the free ortho positions of the phenolic compound and forms a Mannich bridge. The procedure of the Mannich condensation for benzoxazine synthesis in a solvent proceeds by first adding amine to formaldehyde at lower temperatures to form N,N-dihydroxymethylamine derivative, which then reacts with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the elevated temperature to form the oxazine ring (Fig.2.4). For example, 3,4-dihydro-3-cyclohexyl-6-t-butyl-1,3,2H-benzoxazine was prepared by Burke *et al.* (1965).
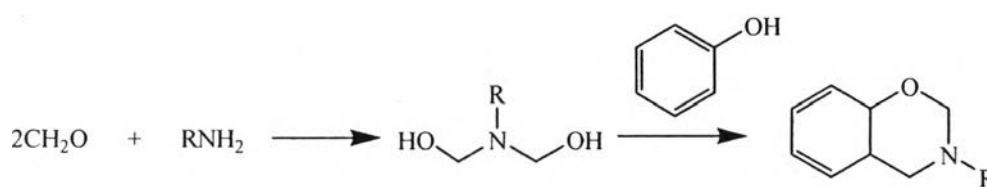

Figure 2.4 Synthesis of 3,4-dihydro-2H-1,3-benzoxazines (Ghosh *et al.*, 2007).

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 this procedure. The use of an organic solvent also increased the cost of products and created the environmental problems. In addition, the solvent residue in the precursors lead to problems during processing of the benzoxazine resins (Brunovska *et*

al., 1998). To overcome these shortcomings, Ishida *et al.* (1996) developed a solvent-less synthesis in a melt state.

Liu *et al.* (1995) proposed the reaction mechanism and kinetics of the solventless synthesis for using this procedure to prepare a large quantity of benzoxazine monomers. In this typical synthesis, the reactants, i.e., aldehyde, amine and phenolic precursors were physically mixed together, heated to their melting tempera-ture, and thereafter maintained at a temperature sufficient to complete the interaction of the reactants to produce the desired benzoxazine. It should be pointed out that formaldehyde was not typically used as it evaporates easily and causes stoichiometric imbalance. Instead, paraformaldehyde was used. The choice for phenols and amines provided the flexibility in designing monomer structure for tailoring the properties of the resulting polybenzoxazine polymer. The main advantages of the solventless syn-thetic method were the improving of reaction times compared with the traditional synthetic route and formation of fewer unwanted intermediates and by-products.

Di-functional and multifunctional benzoxazine monomers

A new class of di-functional/multifunctional benzoxazine monomers and their curing into phenolic materials with the ring opening reaction being initiated via dimers and higher oligomers in the resin composition were developed by Ishida and coworkers (1994 and 2002). The precursor synthesized from using bisphenol-A, formaldehyde and methylamine in different solvents and referred to as B-m (Fig. 1.4), 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 benzox-azine 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.
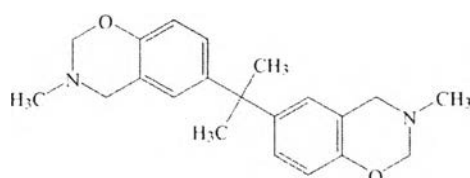

Figure 2.5 Chemical structure of benzoxazine (B-m) monomer (Ghosh *et al.*, 2007).

2.4.2 Preparation of High Molecular Weight Benzoxazine Precursors

High molecular weight polybenzoxazine precursors containing cyclic benzoxazine groups in the backbone were synthesized from bisphenol-A, aromatic or aliphatic diamines, and paraformaldehyde (Fig. 2.6). Partially, the ring-opened structure was observed, but the ratio of the ring-closed structure in the precursor was high enough to be used as benzoxazine precursors. This study also found the curing of benzoxazine groups from the high-molecular weight precursors greatly enhanced the film toughness and showed excellent thermal stability compared with the cured film from the typical low molecular weight monomer. (Takeichi *et al.*, 2005).
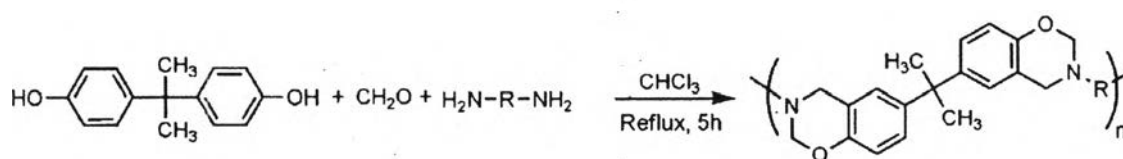

Figure 2.6 Synthesis of polybenzoxazine precursors (Takeichi *et al.*, 2005).

Agag *et al.* (2006) prepared polybenzoxazine matrix through high molecular weight polybenzoxazine precursors (Fig. 2.7). The AB-type aminophenol was used instead of amine and phenol separately and found that the precursors gave self-standing thin films when their solutions were cast in dioxane over glass plates and dried, and upon a gradual thermal curing up to 250°C, they afforded polybenzoxazine films. Both viscoelastic analyses and TGA indicated that the thermosets derived from these novel AB precursors showed excellent thermomechanical properties as well as high thermal stability. In particular, the enhancement of the thermal properties was attributed to increase the crosslinking density, thereby suggesting that the AB precursors were an effective approach in order to obtain the excellent thermomechanical properties for a novel polybenzoxazine matrix.
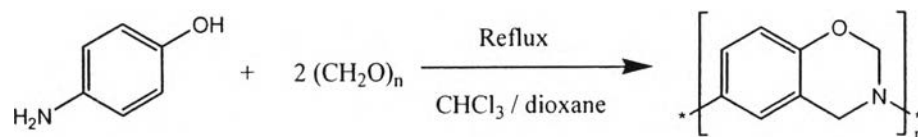
Figure 2.7 Preparation of AB-*p*-aminophenol (AB-PAP) as a benzoxazine prepolymer (Agag and Takeishi, 2006).

Katanyoota *et al.* (2010) synthesized two types of polybenzoxazine precursors using two different amines—aniline and triethylenetetramine—as the reactants and denoted them as BA-a and BA-tetra, respectively. These precursors were prepared from the main chemicals shown in Table 2.1 The BA-tetra precursor (Fig. 2.8) 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 groups at (c) position after the fully cured stage in Fig. 2.9 However, a char yield of the BA-tetra was higher because the crosslink density might be higher which resulted from H-bonding of the secondary amines in the chain.

Table 2.1 The molar ratio of bisphenol-A (BA), aldehydes, and amines in each precursor (Aniline is abbreviated as a and triethylenetetramine is abbreviated as teta (Katanyoota *et al.*, 2010))

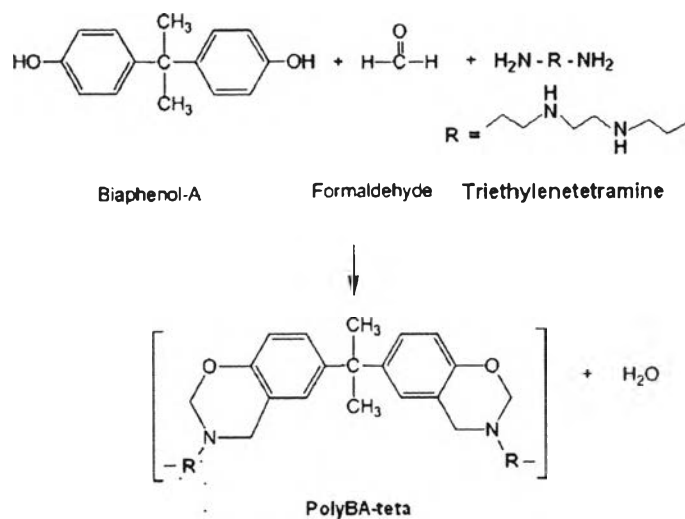| Precursors	The ratio of molar mass				
	Bisphenol-A	Aldehydes		Amines	
		Paraformaldehyde	Formaldehyde	Aniline	TETA
BA-a	1	4	–	2	–
BA-teta	1	–	4	–	1

Figure 2.8 Preparation of polyBA-teta precursor (Katanyoota *et al.*, 2010).
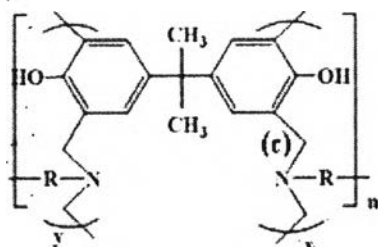

Figure 2.9 The structure of poly BA-tetra in the fully cured stage (Katanyoota *et al.*, 2010).