CHAPTER II

LITERATURE REVIEW

2.1 Graphene

According to the IUPAC definition from 1995, Graphene is a single carbon layer of graphite structure, describing its nature by analogy to a polycyclic aromatic hydrocarbon of quasi-infinite size (Fitzer *et al.*, 1995). Graphene is the subset of graphite, carbon nanotube and fullerene as shown in Figure 2.1. In this material, carbon atoms are arranged in a regular hexagonal pattern. It is a one-atom thick layer of the layered mineral graphite. This two-dimensional material constitutes a new carbon including layers of carbon atoms forming six-membered rings (Geim *et al.*, 2007). Its interaction with other materials and with light and its inherently two-dimensional nature produce unique properties. Graphene is distinctly different the unique properties which have fascinated the scientific community from from carbon nanotubes and fullerenes. Typically important properties of graphene are fractional quantum Hall effect at room temperature (Novoselov *et al.*, 2005, Zhang *et al.*, 2005, Novoselov *et al.*, 2007), an ambipolar electric field effect along with ballistic conduction of charge carriers (Novoselov *et al.*, 2004), tunable band gap (Han *et al.*, 2007) and high elasticity (Lee *et al.*, 2008). Although graphene is expected to be perfectly flat, ripples occur because of thermal fluctuations (Geim *et al.*, 2007).

Ideally graphene is a single-layer material, but graphene samples with two or more layers are being investigated with equal interest. Graphenes can be defined in to three different types: single-layer graphene, bi-layer graphene and few-layer graphene (number of layers $\leq$ 10). Although single-layer graphene and bi-layer graphene were first obtained by micromechanical cleavage (Novoselov *et al.*, 2004), since then, graphenes containing different numbers of layers have been prepared using diverse strategies (Park *et al.*, 2009, Rao *et al.*, 2009, Rao *et al.*, 2009). Graphene exhibits large specific surface area and unique electrical, mechanical and thermal properties (Novoselov *et al.*, 2004, Geim *et al.*, 2007, Geim, 2009, Rao *et al.*, 2009, Segal, 2009). It shows excellent physical and chemical properties, which makes it promising for variety of applications in the areas such as solar-cells (Wang

et al., 2007), energy storage (Stoller *et al.*, 2008), field effect transistors (Ponomarenko *et al.*, 2008), catalyst support (Si *et al.*, 2008), sensors (Schedin *et al.*, 2007), and nanocomposites (Stankovich *et al.*, 2006).

2.2 Methods for obtaining graphene

The ways for obtaining graphene have been reported in any experimental researcher. The methods can be getting graphene such as the exfoliating by mechanical and chemical, reduced graphene oxide, synthesis of graphene from molecular precursors, chemical vapour deposition using catalystic metal and nonmetal, epitaxial growth of graphene on SiC and transfer to arbitrary substrate.

Graphene

Fullerene   **Carbon nanotube**   **Graphite**
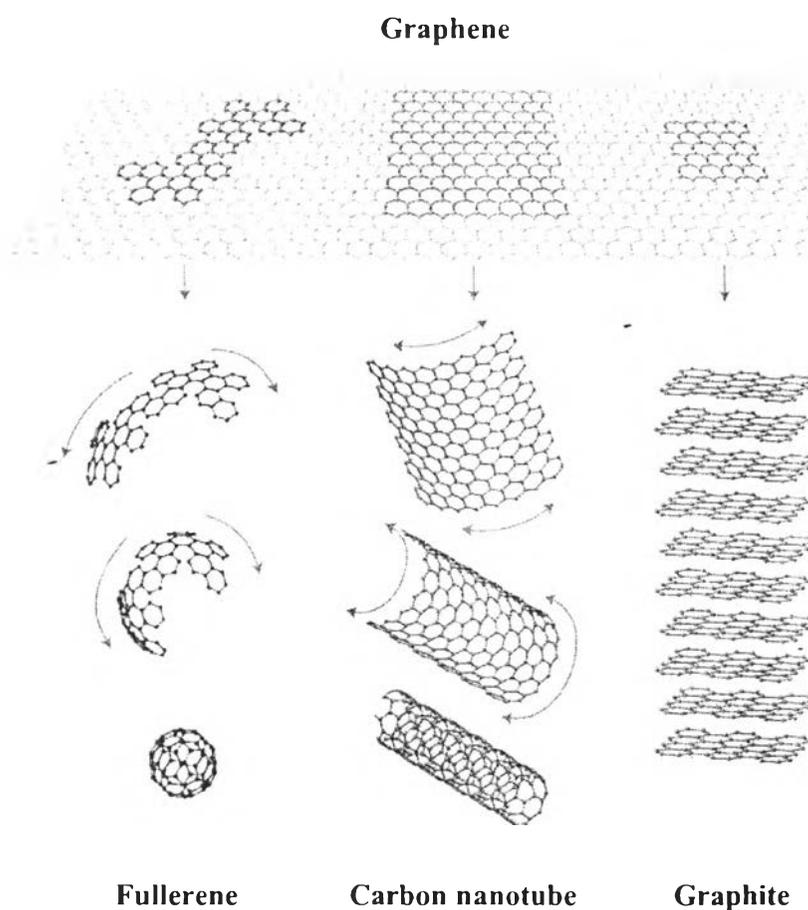
Figure 2.1 The Structure of fullerene, carbon nanotube, graphite and graphene: mother of all graphitic forms (Geim *et al.*, 2007).

In 2004, the first preparation of Single-layer graphene was reported by Novoselov and coworker. They have prepared by micromechanical cleavage from highly ordered pyrolyitc graphite. In this procedure, a layer is peeled off the highly ordered pyrolyitc graphite crystal by using scotch tape and then transferred on to a silicon substrate. After 2 years, the graphene milling was performed by Antisari and coworker (2006). They prepared carbon flakes with high respect ratios and reduced thickness to a limited number of graphene layer with micron sizes. One of the early studied on mechanical cleavage using an ultra-sharp diamond wedge combined with ultrasonic oscillation can produce few layer graphene with thickness 10 nm from highly ordered pyrolyitc graphite (Jayasena et al., 2011).

Chemical exfoliation is a great method for obtaining large amounts of micron sized graphene flakes in the various types of solvent. In 2007, Black and coworker reported the direct chemical exfoliation of graphite into graphene without a graphene oxide step. They placed graphite in dimethylformamide, sonicated and centrifuged to obtain monolayer and few layer graphene sheets. Another method was reported Li and coworker (2008). They prepared graphene nanoribbons in solution by sonicating commercial expandable graphite.

In 1985, the first preparation of graphite oxide was achieved by oxidative treatment of graphite by employing Hummers procedure (Hummers et al., 1958), Briefly, the process involved the treatment of cleaned graphite flakes of certain size (~300 μm) with sulphuric acid/nitric acid mixture to produce intercalatedgraphite. The intercalated graphite was given a thermal shock at 800 °C for about a minute that resulted in the exfoliation of graphite. After oxidation step using $KMnO_4$ and H_2O_2, the brown colored exfoliated graphene oxide was obtain. A chemical method to prepare single-layer graphene involves reduction of single-layer graphene oxide dispersion in dimethlyformamide with hydrazine hydrate was reported by Park and coworker (2009). Moreover, Choucair and coworker (2009) have prepared gram quantities of single-layer graphene by a solvothermal procedure using sodium and ethanol. At the same time, single-layer graphene have been exfoliated in N-methylpyrrolidone (Hernandez et al., 2008) or a surfactant/water solution using ultrasonication (Lotya et al., 2009).

Epitaxial growth of Single-layer graphene films are produced on the Si-terminated (0001) face of single crystal 6H-SiC by thermal desorption of Si. In this procedure, the substrates are subjected to electron bombardment in ultrahigh vacuum to 1000 °C to remove oxide contaminants and then heated to temperatures ranging from 1250 to 1450 °C for 1-20 min (Berger *et al.*, 2004, Rollings *et al.*, 2006, Emtsev *et al.*, 2009). Besides, chemical vapor deposition was used to prepare single-layer graphene by decomposing a variety of hydrocarbons on films or sheets such as methane, ethylene, acetylene and benzene, the number of layers varying with the hydrocarbon and reaction parameters of transition metal such as Ni, Cu, Co and Ru (Reina *et al.*, 2009).

The thermal exfoliation of graphitic oxide is an important method to prepare few-layer graphene at high temperatures (Schniepp *et al.*, 2006, Subrahmanyam *et al.*, 2008). In this method, is first prepared by the Staudenmaier method which is as follows. Graphite is added in the mixture of sulfuric acid, nitric acid and potassium chlorate. The samples were then preheated at 1050 °C. Another method of preparing few-layer graphene is by reacting single-layer graphene oxide in water with hydrazine hydrate at the refluxing temperature (Rao *et al.*, 2009) or by microwave treatment (Stankovich *et al.*, 2007). Graphene can be prepared by heating nanodiamond in an inert or a reducing atmosphere. The effect of heating nanodiamond at different temperatures has been studied by Enoki and coworker (1998, 2000). Annealing of nanodiamond at high temperatures in an inert atmosphere produces few-layer graphenes (Subrahmanyam et al., 2008, Andersson et al., 1998). The nanodiamond particles were soaked in concentrated HCl before use in ordered to avoid contamination with magnetic impurities and heated in a helium atmosphere at different temperatures (1650, 1850, 2050 and 2200°C) for 1 hr. they found that there is a slight increase in the number of layers and a decrease in lateral dimensions in the samples heated at 2200°C in comparison to 1650°C.

2.3 Polybenzoxazine

Polybenzoxazine as a novel developed class of thermosetting resins derived from phenolic resin. It possesses various good properties like high thermal stability, easy processability, very high char yield, fast development of mechanical properties as a function of conversion, glass transitions much higher than curing temperatures, good flame retardant and electronic properties. In addition, polybenzoxazines provide special properties such as low water absorption despite having many hydrophilic groups and also excellent dimensional stability due to the near zero shrinkage after processing, maintaining excellent mechanical properties. A method for preparing a desired benzoxazine compound comprises preparing a substantially homogeneous reaction mixture that includes a phenolic compound, a primary amine and an aldehyde. They have been synthesized from inexpensive raw materials and polymerized by a ring-opening addition reaction, yielding no reaction by-product (Ishida *et al.*, 1996, Ishida, 2011). The simply ring-opening polymerization reaction was shown in Scheme 2.1.
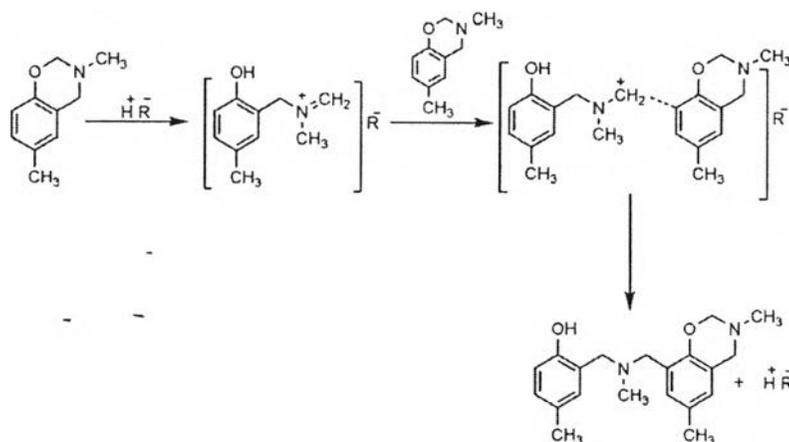
Scheme 2.1 Acid catalyst ring opening polymerization of 3,4-dihydro-2*H*-1,3-benzoxazines (Dunkers *et al.*, 1999).

Benzoxazine monomers are often synthesized using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either using solvent or non-

solvent methods. The solventless technique as very fast technique prepare with other. The different substitution groups of amines and phenols have been used to synthesize many types of benzoxazine monomer that polymerized to polybenzoxazine (Ghosh *et al.*, 2007). The ways of producing benzoxazine monomer based on the functional group of reactants. They are mono-functional, di-functional and multifunctional group.

2.4 Mono-Functional Group Benzoxazine Monomers

Mono-functional benzoxazines typically result to a linear or branched structure with a low molecular weight on the ordered of 500-2000 Da (Brunovska *et al.*, 1999). Thus, mono-functional benzoxazine monomers are precursors for polybenzoxazine show limited usefulness as structural materials. However, they might be useful as reactive diluents to facilitate the processing (Liu *et al.*, 2011). The first informing of the condensation reaction using primary amines with formaldehyde and substituted phenols for the synthesis of well defined benzoxazine monomers was reported by Holly and coworker (1944). According to the informed process, 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 a phenolic compound and forms a Mannich bridge. The synthetic procedure of the Mannich condensation for benzoxazine synthesis was found by Burke and colleague (1965). It was produced in a solvent proceeds by first addition of amine to formaldehyde at lower temperatures to form an 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 as in Scheme 2.2.
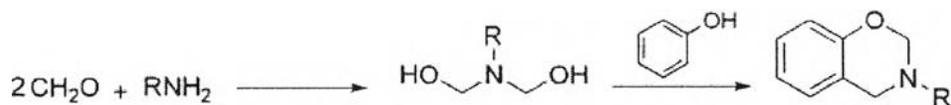
Scheme 2.2 Synthesis of 3,4-dihydro-2*H*-1,3-benzoxazines (Burke, 1949).

Burke and colleague (1964) were found a strongly basic amine and a less acidic phenol, more stable in the hot alcohols which used to synthesized benzoxazines. The stability of the benzoxzine ring depends on the substituent. Another aminoalkylation reaction results from the residence of more than one reactive ortho position in the initial product by McDonagh and colleague (1968). The Phenol having an ortho substituent gives the necessarily higher yield of benzoxazine. The synthesis with large amount of solvent results the slow reaction rate, in some cases, the principle disadvantages which are the poor solubility of the precursors participated with this process. The synthesis with large amount of solvent results the slow reaction rate, in some cases, the principle disadvantages which are the poor solubility of the precursors participated with this process. The increasing cost of the products and environmental problems cause from an organic solvent. The problems during processing of the benzoxazine resins also result from the solvent residue in the precursors. 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 a immense quantity of benzoxazine monomer.

2.5 Di- Functional and Multifunctional Group Benzoxazine Monomers

The thermally accelerated ring-opening polymerization of bifunctional benzoxazine monomers and their properties were firstly reported by Ning and coworker (1994). The benzoxazines were cured with mono-functional group and phenol resulted in low average molecular weight that is the formation of only oligomeric structures. Because the thermal dissociation of the monomer there is a race with chain propagation reaction resulted to no materail could be made from this method that wasn't obtained the high molecular weight linear structures. The polybenzoxazine can be enhanced the different performance in a wide range by using bifunctional benzoxazines in especially provide greater flexibility in molecular design than monofunctional monomers.

The classifications of bifunctional benzoxazine monomers, they are two types. The first type is bisphenol based bifunctional benzoxazine monomer which is

produced by the reaction of bisphenol with either aliphatic or aromatic monofunctional primary amine. Another type of bifunctional benzoxazines is diamine based bifunctional benzoxazine monomers, which can be synthesized by using aromatic or aliphatic diamines with a monofunctional phenolic structure of ortho-vacant position. All of these two types bifunctional benzoxazine monomers were reported by Ghosh and colleague (2007). The bifunctional benzoxazine monomers reaction was shown in Scheme 2.3.
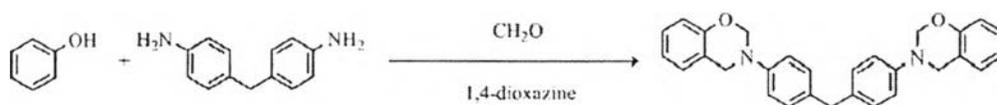
Scheme 2.3 Synthesis of DDM-based benzoxazine monomer (Ghosh *et al.*, 2007).

2.6 Preparation of High Molecular Weight Benzoxazine Precursors

Takeichi and colleague (2005) synthesized high molecular weight polybenzoxazine precursors from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde. Some-of the ring-opened structure was studied. On the other hand the ratio of the ring-closed benzoxazine structure was high. These crosslinked polybenzoxazines were achieved in the film processing, thermal stability, and mechanical property. The structure of a typical benzoxazine monomer prepared from bisphenol-A, aniline and formaldehyde along with the structure of its polybenzoxazine are shown in Scheme 2.4.

In 2010, they also reported the synthesis of high-molecular-weight polybenzoxazine prepolymers by using α,ω-bis(aminopropyl)polydimethylsiloxane and bisphenol-A with formaldehyde. These polybenzoxazine prepolymers were achieved in free standing films by casting. They had shown good mechanical and thermal properties. Agag and coworker (2007) studied novel high-molecular-weight polybenzoxazine precursors, namely AB-type benzoxazine precursors, were derived from tyramine, *p*-aminophenol including copolymer precursor from tyramine and *p*-aminophenol. They were synthesized from aminophenols and formaldehyde. They

showed the excellent thermomechanical properties as well as high thermal stability by increasing the crosslinking density. The example of cured polybenzoxazine precursors were shown in Scheme 2.5.
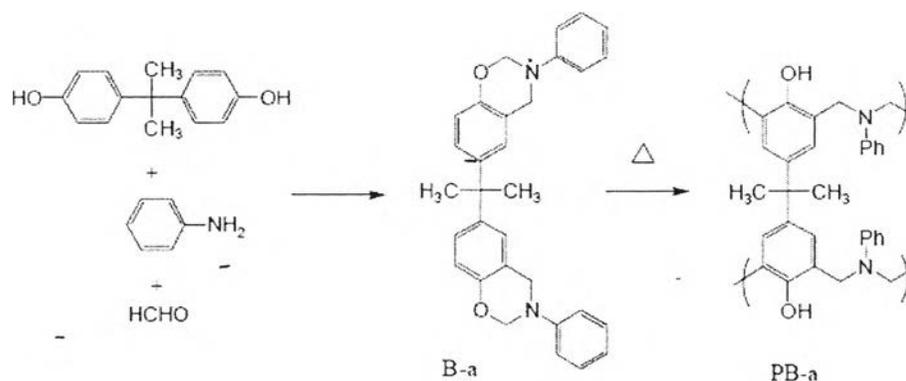
Scheme 2.4 The reaction of a typical benzoxazine monomer prepared from bisphenol-A, aniline and formaldehyde (Takeichi *et al.*, 2005).
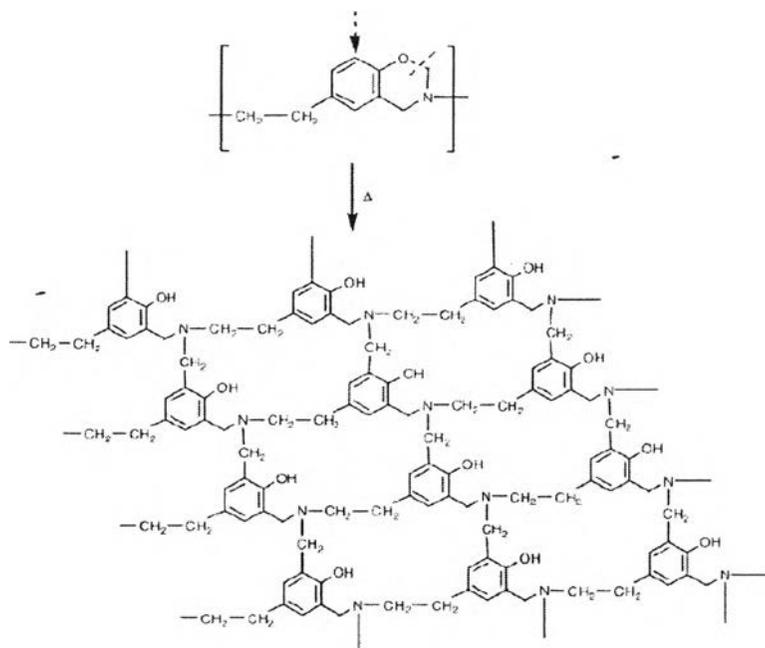
Scheme 2.5 The network structure of the cured polybenzoxazine precursors obtained from the thermal cure of the AB-type benzoxazine precursors (Agag *et al.*, 2007)

2.7 Two-Point Techniques for Measuring Resistivity

A number describing how much that material resists the flow of electricity is called the electrical resistivity of a material in units of ohm·centimeters (Ω·cm). The material has low resistivity due to electricity can flow easily through a material: In case of the electricity has great difficulty flowing through a material. It is called the material which is high resistivity. Electrical resistivity is represented by the Greek letter ρ, Electrical conductivity is represented by the Greek letter σ, and is defined as the inverse of the conductivity. This means a high resistivity is the same as a low conductivity, and a low resistivity is the same as a high conductivity. The relation of electrical resistivity and electrical conductivity was shown in equation 2.1 (Michael, 2003).

$$\rho \equiv \frac{1}{\sigma} \tag{2.1}$$

P. Drude and colleagues reported a simple microscopic model of electricity flowing through a material as shown in Figure 2.2. This model is an oversimplification and incorrect in several ways. It is still a very useful conceptual model for understanding resistivity and making rough estimates of some physical properties. A more correct understanding of the electrical resistivity of materials requires a thorough understanding of quantum mechanics was repoted by N. W. Ashcroft. On a microscopic level, electricity is simply the movement of electrons through a material. The smaller white circle in Figure 2.2 represents one electron flowing through the material. For ease of explanation, only one electron is shown. There are usually many electrons flowing through the material simultaneously. The electron tends to move from the left side of the material to the right side because an external force acts on it. The resistivity of a material can vary greatly at different temperatures. The resistivity of metals usually increases as temperature increases, while the resistivity of semiconductors usually decreases as temperature increases. The resistivity of a material can also depend on the applied magnetic field.
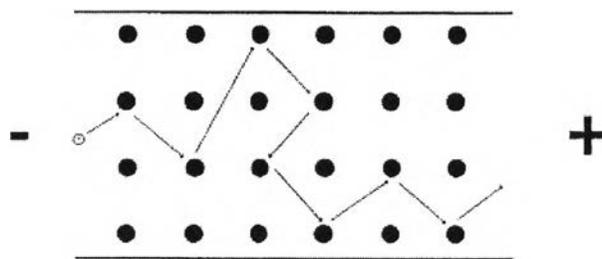
Figure 2.2 Simple model of electricity flowing through a material under an applied voltage. The white circle is an electron moving from left to right through the material. The black circles represent the stationary atoms of the material. Collisions between the electron and the atoms slow down the electron, causing electrical resistivity (Drude, 1900).
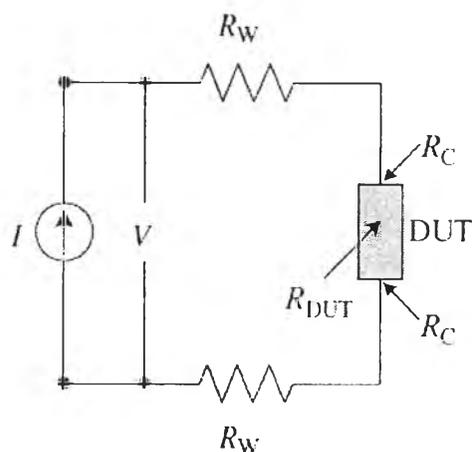
Figure 2.3 Two-terminal resistance measurement arrangement (Schroder, 2006).

Two-point probe methods would appear to be easier to implement, because only two probes need to be manipulated. But the interpretation of the measured data is more difficult. Consider the two-point probe or two-contact arrangement of Fig. 2.3. Each contact serves as a current and as a voltage probe. We wish to determine the resistance of the device under test (Schroder, 2006). The total resistance R_T is given by

$$R_T = \frac{V}{I} = 2R_W + 2R_C + R_{DUT} \qquad (2.2)$$

Where R_W = The wire or probe resistance

R_C = The contact resistance

R_{DUT} = The resistance of the device under test

The probe, contact, and spreading resistances of a two-point probe arrangement on a semiconductor are illustrated in Fig. 2.4.
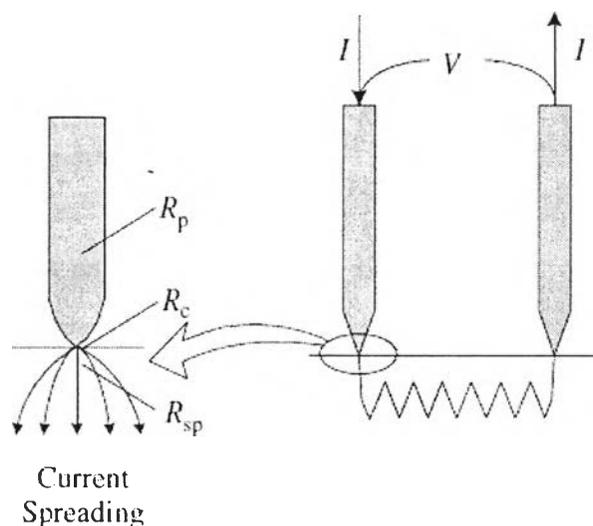
Figure 2.4   Two-point probe arrangement showing the probe resistance R_P, the contact resistance R_C, and the spreading resistance R_{SP} (Schroder, 2006).

The resistivity of a material can be obtained by measuring the resistance and physical dimensions of a material, as shown in Figure 2.5. In this case, the material was attached to both ends of the probs. This is called the two-point technique. A voltage source applies a voltage, causing a current to flow through the material. The amount of current that flows through the material is measured by the ammeter, which is connected in series with the material and voltage source. The resistance of the material is given by Equation 2.3.

$$R \equiv \frac{V}{I}$$
(2.3)

Where   R = Resistance in Ω

V = Voltage in V

I = Current in A
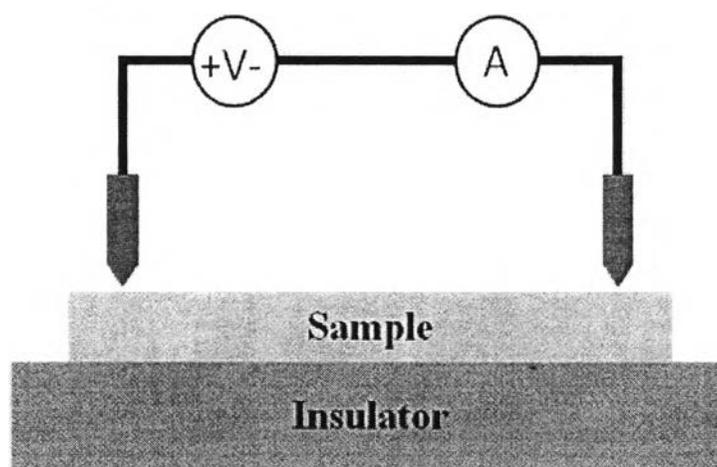
Figure 2.5 A two-point technique for measuring the resistivity of the sample. The voltage source applies a voltage across the sample thickness, and the ammeter measures the current flowing through the sample.

The resistance of material was obtained from slope of plot between voltage and current. The electrical conductivity values of the partially ordered carbons were calculated by Equation 2.4. The geometric correction factor was determined by calibrating the four-point probe with semi-conducting silicon sheets of known resistivity values and shown the relation in Equation 2.5. Applied dc currents were small to be in the linear Ohmic regime. The electrical conductivity of the partially ordered carbon was observed at room temperature by an electrometer with two-point probe (Densakulprasert et al., 2005).

$$\sigma \equiv \frac{1}{RtK} \qquad\qquad (2.4)$$

$$K \equiv \frac{w}{l} \qquad\qquad (2.5)$$

Where σ = Conductivity in S/cm

R = Resistance in Ω

t = Thickness of sample in cm

K = The geometric correction factor

w = The probe width

l = The probe length