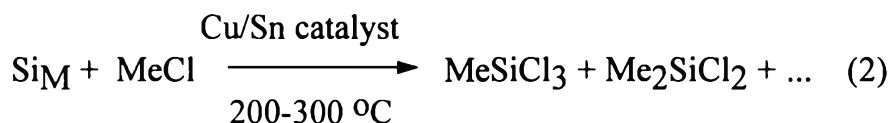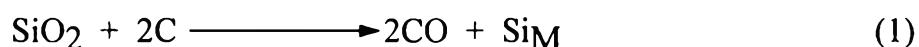# CHAPTER I

INTRODUCTION

1.1 Background

Polymers impinge on nearly every aspect of modern life, from electronic materials, to medicine, to the wide range of fiber, films, elastomers, and structural materials on which every one depends. Most of these polymer are organic based materials that derive either from petroleum, plants, animals or microoganisms. In spite of the widespread use of organic polymers, attention is being focused increasingly toward polymers that contain inorganic as well as organic components. The reasons for this fall into two categories. First, most of the known organic polymers represent a compromise in properties as compared with the ideal materials. For example, many organic polymers degrade on long term exposure to oxygen or ozone. Most organic polymers burn, often with the release of toxic smoke. A second set of reasons is connected with the anticipated differences between organic and inorganic components. For example, the bonds formed between inorganic elements are often longer, stronger, and more resistant to free radical cleavage reactions than C-C bonds [Mark, J.E., Allcock, H.R., and West, R., 1992].

The widespread utility of silicon and its compounds comes because it is one of the most abundant elements in the earth's crust and so versatile. Its chemical and physical properties are so unusual, and so varied that they just cry out for research into creative and ingenious uses. Moreover, silicon is

a friendly element, devoid of specific elemental toxicity unlike arsenic, lead or plutonium, and is to long associated with the insides and outsides of living systems [Rochow, E.G., 1987].

Organosilicon compounds are members of the broader class of *organoelement compounds,* the polymers of which can combine the thermal stability of inorganic materials with the elasticity and solubility of organic polymer [Akhmetor, N.S., 1983]. Organosilicon compounds do not occur naturally. They are synthesized from silicon dioxide, as shown in Eq. (1),(2) [Friedel, C. and Craft, J.M., 1865]. First, carbothermal reduction of SiO_2 to metallurgical grade silicon (Eq. 1) provides access to organosilicon compounds via oxidation of Si_M with alkyl or aryl chlorides in the presence of catalyst as following in Eq. 2

$$SiO_2 + 2C \longrightarrow 2CO + Si_M \qquad (1)$$

$$Si_M + MeCl \xrightarrow[\text{200-300 }^oC]{\text{Cu/Sn catalyst}} MeSiCl_3 + Me_2SiCl_2 + ... \qquad (2)$$

Silica provides an interesting array of structural types that show greater variety than usually encoutered for compounds of other elements and is also of great technical importance. The composition of silicate minerals used to be given in terms of mole ratios of oxides, for example forsterite, $2MgO{\cdot}SiO_2$, and orthoclase, $K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$ [Douglas, B.E., 1983]. Silica melts at a high temperature (1731 °C), is very hard and chemically stable. Only fluorine, liquid and gaseous hydofluoric acid, phosphoric acid and basic solutions will react with it under normal conditions. It is insoluble in water at 150 °C, but its solubility improves to 0.25 weight percent at 500 °C [Iler, R.K., 1979].

Specially analogies are frequently drawn between the chemistries of silicon and carbon since both are group IVA element [Cotton, F.A. and Wilkinson, G.F., 1992]. However, they do not have the same properties, for example, carbons readily form cyclopropane rings, whereas until relatively recently, similar compounds containing silicon were unknown [Seyferth, D., Annarelli, J., 1975]. Likewise, C-E (E = element) multiple bonds are common, but Si-E triple bonds remain a challenge [Colegrove, B.T., SchaeferIII, H.F., 1991]. However, organosilicon polymers with single Si-E bonds are commercially important to be creamic precursors [Kansal, P., 1994], and to be liquid crystalline precursor [Rangsitpol, J., 1994].
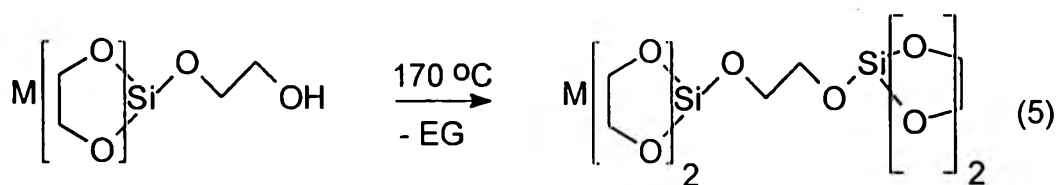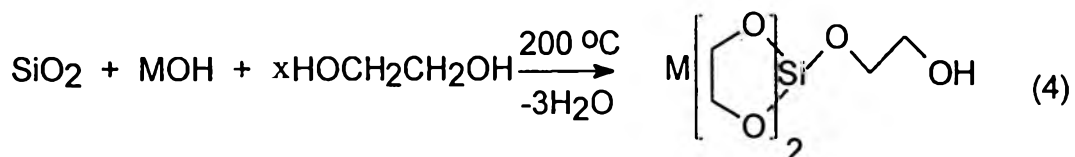
1.2 Historical Review

The depolymerization of silica to monomeric silicate compounds was first reported by Rosenheim [Rosenheim, A., Raibmann, B., Schendel, G.Z., 1931]. It was converted to hexacoordinated complexes in water by reaction with catechol and an inorganic base

$$SiO_2 + 2KOH + 3 \quad \xrightarrow[\text{H}_2\text{O}]{-4\text{H}_2\text{O}} \quad (3)$$

Solvent

hexacoordinated silicate
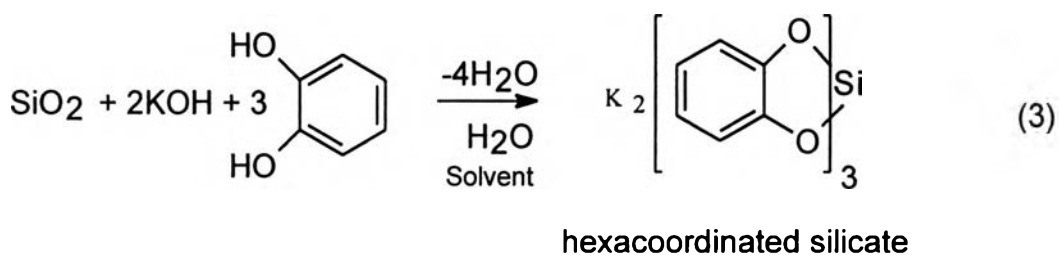
Laine et al. [Laine, R.M., Treadwell, D., Muiller, B.L., 1994] reported the synthesis of pentacoordinated anionic and hexacoordinated dianionic glycolato silicate complexes by direct reaction of silica gel, fused silica or sand
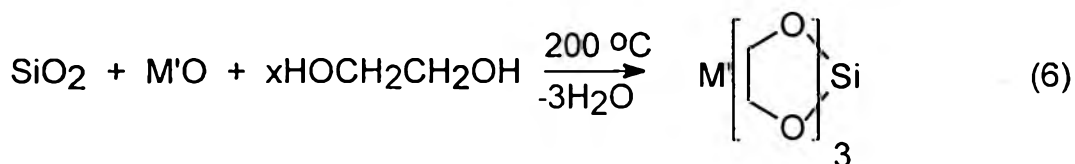
with equivalent amounts of group I/II metal hydroxide/oxide in excess ethylene glycol (EG), eqs. (4)-(6).

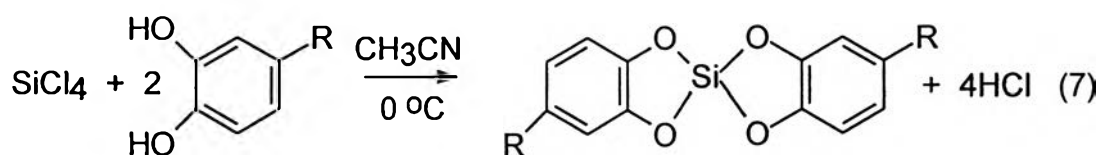**Pentacoordinated silicate complex anion**

$$SiO_2 + MOH + xHOCH_2CH_2OH \xrightarrow[-3H_2O]{200\ ^oC} M\left[\overset{O}{\underset{O}{\bigcirc}}Si\overset{O}{\diagdown}OH\right]_2 \quad (4)$$

$$M\left[\overset{O}{\underset{O}{\bigcirc}}Si\overset{O}{\diagdown}OH\right] \xrightarrow[-EG]{170\ ^oC} M\left[\overset{O}{\underset{O}{\bigcirc}}Si\overset{O}{\diagdown}O\cdot Si\overset{O}{\underset{O}{\bigcirc}}\right]_2 \quad (5)$$

M = Li, Na, K, Ca

Hexacoordinated silicate complex dianion

$$SiO_2 + M'O + xHOCH_2CH_2OH \xrightarrow[-3H_2O]{200\ ^oC} M'\left[\overset{O}{\underset{O}{\bigcirc}}Si\right]_3 \quad (6)$$

M' = Mg, Ca, Ba

Tetracoordinated siloxanes were first synthesized, from carbothermally derived SiCl4 by Allcock [Allcock, H.R., Nugent, T.A., Smeltz, L.A.,1972]. The synthesis of bis(4-t-butyl-catechol)silane is analogous [Robinson, T.R., 1990], as shown in reaction (7).

$$SiCl_4 + 2\ \overset{HO}{\underset{HO}{\diagup}}\!\!\!\!\!\!\!\bigcirc\!\!\!\!\!-R \xrightarrow[0\ ^oC]{CH_3CN} R\!-\!\bigcirc\!\!\!\overset{O}{\underset{O}{\diagup}}Si\overset{O}{\underset{O}{\diagdown}}\!\!\!\bigcirc\!-R + 4HCl \quad (7)$$

R = H or t-butyl

The Allcock method gives 56% yields of bis(1,2-dioxyphenyl)silane, an amorphous white powder. Bis(1,2-dioxyphenyl)silane polymerizes easily to rod-like oligomer, containing neutral, tetracoordinated silane. Honle et al. [Honle, V.W., 1989] determined the structure which is shown in Fig 1.1.
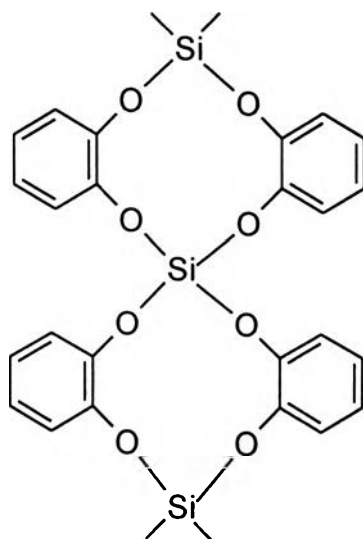

Figure 1.1 Bis(1,2-dioxyphenyl)silane polymer.

Ray et al. [Ray, D.J., Laine, R.M., Robinson, T.R., Viney, C., 1993] synthesized bis(1,2-dioxyphenyl)silane via Allcock's method and copolymerized it with hydroquinone. They found that liquid crstalline phases were not detected in homopolymer, or in copolymers prepared from mixed solutions of bis(1,2-dioxyphenyl)silane and hydroquinone but it show crystalline properties when mixed solutions of bis(1,2-dioxyphenyl)silane and 3-tert-butyl catechol. The method requires 2 steps via (8)-(9) as shown below.

(8)

(9)
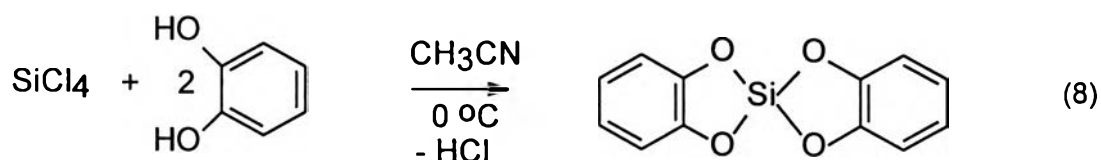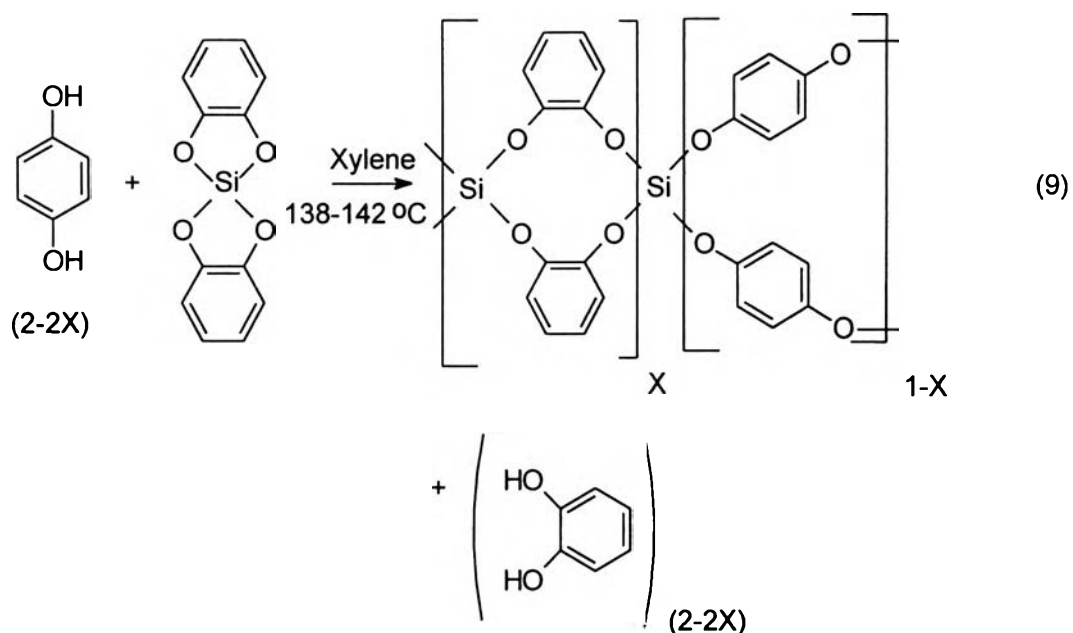
Recently, Rangsitphol J. [Rangsitphol J., 1995] synthesized bis(1,2-dioxyphenyl)silane, tetracoordinated silicate compound, via the oxide one pot synthesis process (OOPS process) directly from silica using triethylenetetramine (TETA) as a catalyst in ethylene glycol solvent, as illustrated in the reaction (10).

(10)
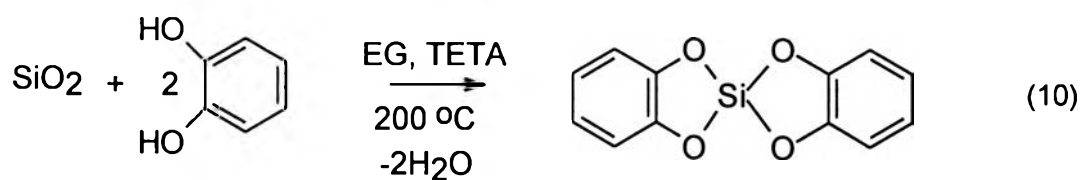
In organic liquid crystalline polymer, ortho-linked unit have been used with more frequency as comonomer in main-chain liquid crystalline copolymers [Navarro, F. and Serrano, J.L., 1992] while hydroquinone which is para-linked unit can be copolymerized forming copolyester which show liquid

crystalline thermoset behavior [Price, D.M. et al., 1994; Skrifvars, M. and Schmidt, H.W., 1995], as shown in Fig 1.2.
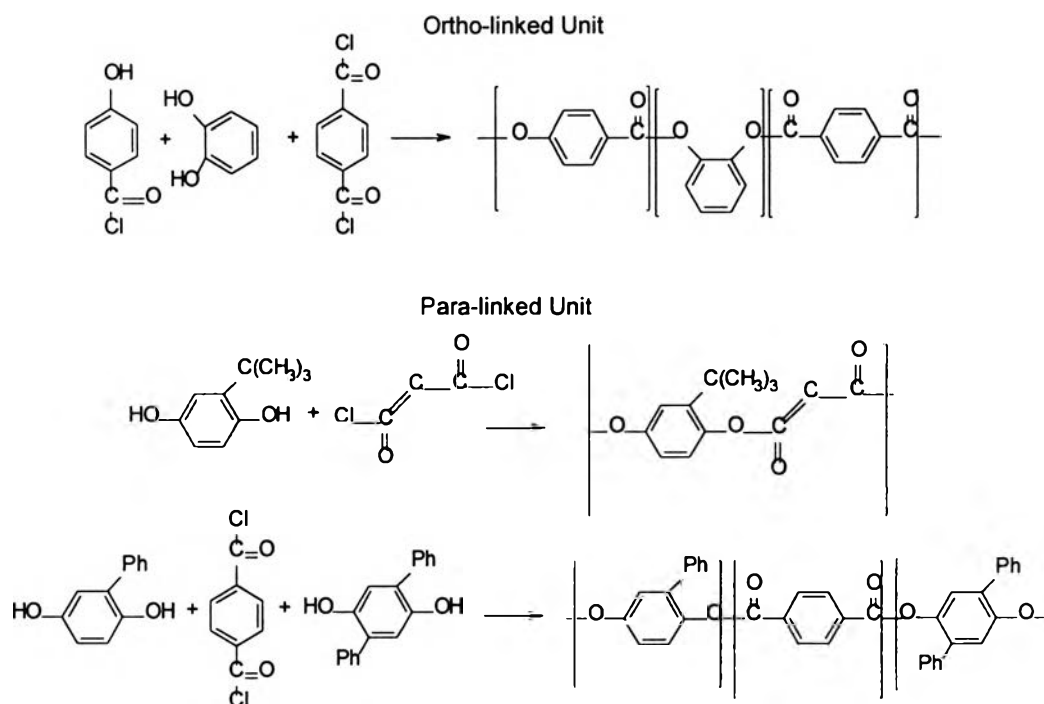

Figure 1.2 Ortho-/Para- linked units in liquid crystalline structure.

In addition, during the last few years, numerous papers on the synthesis and structure of ionic organosilicates have been published [Tandura, S.N. et al., 1986 ; Voronkov, M. G. et al., 1987 ; Corriu, R. J. P., 1990 ; Day, R.O. et al., 1991 ; Tamao, K. et al., 1992]. Most ionic organosilicate contain a pentacoordinate silicon atom. Because of the versatile properties of silica and the structure strength of aromatic, it is challenging for copolymerization of aromatic ortho-/para- unit with silicon atom to provide a novel copolymer.

1.3 Objectives

The purposes of this research are thus to synthesize and characterize inorganic/organic copolymers directly from a naturally abundant material, silica, catechol, and hydroquinone, using triethylenetetramine, an organic base, as a catalyst in ethylene glycol solvent. The optimal mole ratio of silica : catechol : hydroquinone, appropriate reaction time of this reaction, and mole% of triethylenetetramine are investigated, as well.