CHAPTER I

INTRODUCTION

1.1 Background

The history of liquid crystalline (LC) polymers started in 1956 when Flory published a paper on concentrationed polymer solutions. Flory stated that rigid-rod chain polymers, at a critical concentration, became liquid crystalline [Flory, P.J.; 1956]. The LC phase has a degree of order in between that of a solid crystalline phase and that of the isotropic liquid phase. It possesses neither the full long-range order of the centers of mass as in a three dimensional lattice of a crystal nor the complete absence of long-range order as in an isotropic liquid having three translation degrees of freedom of the molecular centers. The common structural element for molecules having LC phases is an elongated configuration possessing anisotropic polarizability. [Jonhson, H.; Gedde, U.W. and Hult, A.; 1992]

Liquid crystallinity occurs when molecules become aligned in a crystalline array while still in the liquid state; in the other words, the liquid exhibits anisotropic behavior. The ordered regions in the liquid are called mesophases. To make polymers behave as liquid crystals it is necessary to introduce some structural rigidity. Liquid crystals exhibit certain properties not found in the liquid state or solid state. For example, their morphology may be influenced by external magnetic or electric fields, sometimes they change color with temperature, and some exhibit extremely high optical rotation. At the same time, they exhibit the fluidity of liquids and the opaqueness of crystalline solids.

Liquid crystals are classified into two major types based on the processing: *lyotropic* and *thermotropic*. Lyotropic liquid crystals form under the influence of solvent. Thermotropic liquid crystals form in the melt. These classifications are broken down further (nematic, smectic, chloresteric, etc.) according to how the molecules are oriented in the mesophases. [Stevens, M.P.; 1990]. In the nematic phase, the least ordered one, the centers of the molecules are completely random in their location just as in a normal liquid. No long-range positional order exists, just orientational, and the long axes of the molecules are oriented in a universal, selected direction. The smectic phase, has some degree of positional order in addition to orientational order. This positional order results in the formation of equidistant planes or layers which are free to move with respect to each other. The molecules are arranged inside the layers, e.g. parallel or tilted with respected to the normal to the layer, or in the degree of positional order present within the layer. A compound can possess one or more mesophases, smectic as well as nematic, with the degree of order decreasing with increasing temperature, ie. an ordered smectic phase always appears before a non-ordered phase which appears before a namatic. The mesophases are identified by polarized light microscopy or x-ray diffraction. [Demus, D.; Richter, L.; 1978 and Gray, G.W.; Goodby, J.W.; 1984]

Most liquid crystalline polymers are usually organic aromatic polyesters or polyamides. While organic liquid crystal technology has developed, attention was given to liquid crystals that contain some inorganic elements.

Compounds containing inorganic elements are of interest because organic polymers have some weaknesses; for example, many organic polymers degrade by reacting with oxygen or ozone over long periods of time. Most of them burn, often with the release of toxic smoke. Many organic polymers degrade on exposure to ultraviolet or gamma radiation, and sometimes soften at

unacceptably low temperatures, or they swell or dissolve in organic solvents, oils, or hydrodraulic fluids.

At the environmental level, few organic polymers degrade at an acceptable rate in the biosphere. Finally, the suspicion exists that the availability of many organic polymers may one day be limited by the anticipated scarcities of petroleum. It is generally accepted that polymers that contain inorganic elements in the molecular structure may avoid some or all of these problems.

Moreover, inorganic elements generate combinations of properties in polymers that are different from what is achieved with carbon. For one thing, the bonds formed between inorganic elements are often longer, stronger, and more resistant to free radical cleavage reactions than those formed by carbon. Thus, the incorporation of inorganic elements into the backbone of a polymer can change the bond angles and bond torsional mobility, and this can change the materials properties to a remarkable degree. Thus, the future development of polymer chemistry and polymer engineering may well depend on the inorganic aspects of the field for the introduction of new molecular structures, new combinations of properties, and new insights into the behavior of macromolecules in solution and in the solid state. Thus, inorganic polymers provide an opportunity for an expansion of fundamental knowledge and , at the same time, for the development of new materials that will advance the technology.

At the present time, most of the known inorganic polymer systems are based on relatively few elements that fall within the regions of the Periodic Table known as the "Main Group" series. These elements occupy groups III, IV, V and VI including silicon, germanium, tin, phosphorus and sulfur. Of these, polymers based on the elements silicon and phosphorus have received by far the most attention [Mark J.E. et al., 1992].

Organosilicon polymers, macromolecules that contain inorganic element silicon in the chain and organic moieties as pendant groups [Friedel, 1865], were first reported by Friedel and Crafts [1863]. The first systematic studies performed on organosilanes were carried out by Kipping et al. [1937].

Silicon is one of the most abundant elements (ca. 28% of the earth's crust) and occurs in a great variety of silicate minerals and as quartz, SiO_2. Pure SiO_2 occurs in two forms, quartz and cristobalite. Silicon is always tetrahedrally bound to four oxygen atoms but the bonds have considerable ionic character. In cristobalite, the silicon atoms are placed as the carbon atoms in diamond, with the oxygen atoms midway between each pair of silicon atoms. In quartz, there are helices so that enantiomorphic crystals occur, and these may be easily recognized and separated mechanically. Quartz and cristobalite can be interconverted when heated. These processes are slow because the breaking and reforming of bonds is required and the activation energy is high [Albert, C.F.; Geoferey, W.; Paul, L.G.; 19 [Albert, C.F.; Geoferey, W.; Paul, L.G.; 1987].

The industrial route to silicon-based feed-stock compounds starts with the carbothermal reduction of silica with coke to get elemental silicon which was then converted into tetrachlorosilane, per (1) and (2) [Rochow E.G., 1945; Stark et al., 1982; Hardman and Torkelson, 1987].

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

$$Si + 2Cl_2 \longrightarrow SiCl_4 \qquad (2)$$
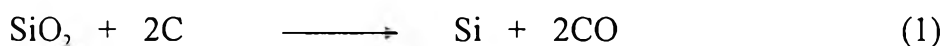
The ammonolysis of alkylchlorosilanes gives polysilanes [Boberski, W.G., 1951], polysilazanes [Stock, A.; 1921] and polysiloxanes, etc.

$$R_3SiCl + 2R'_2NH \longrightarrow R_3SiNR'_2 + R'_2NH_2^+Cl^- \qquad (3)$$

The primary problem with the use of silica, which is abundant in nature and low cost, as the feedstock chemical in the industrial process is that the Si-O bond in silica is one of the strongest in nature. Its bond energy is 128 kcal (535 kJ)/mole. The approach to overcome this problem is to use base catalysts in silica depolymerization through silicon-oxygen bond cleavage. Rosenheim et al. [1931] first reported the depolymerization of silica to monomeric silicate compounds. They found that silica converts to hexacoordinate complexes in water by the reaction with catechol and inorganic base and that catechol could be transformed by using a wide variety of metal oxides to catecholato complexes as in Scheme 1.
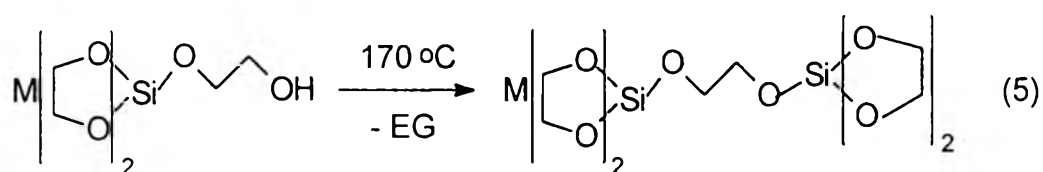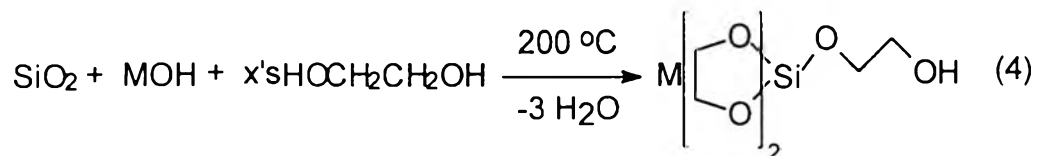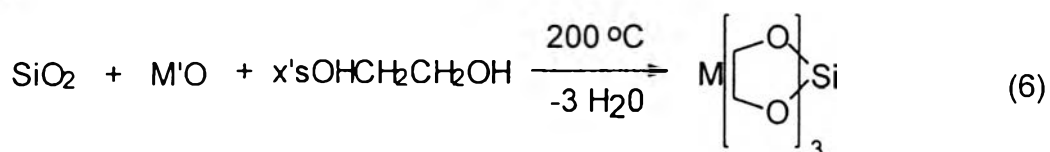

hexacoordinate silicate complex
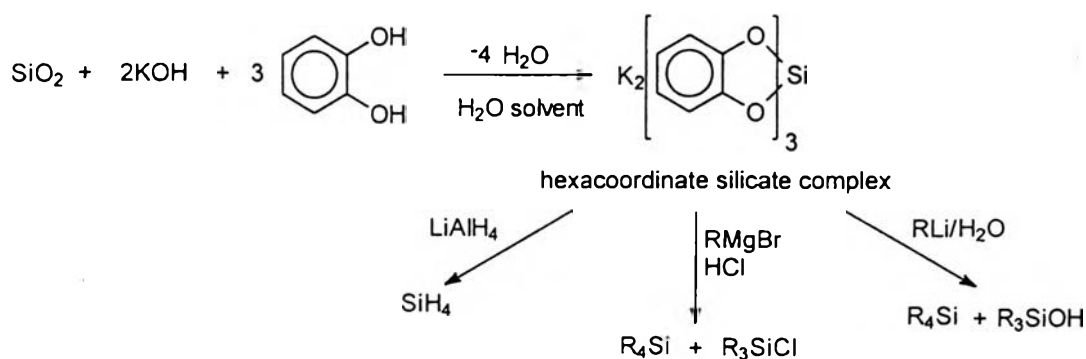
Scheme 1

This discovery suggested a route to form organosiloxane compounds from silica without converting it to elemental silicon. Corriu et al. [1983, 1988, 1990] found a new route to transform tricatecholatosilicates into a variety of novel organosilanes via reaction with strong nucleophiles, for example aryl or alkyl Grignard or lithium reagents as shown in Scheme 1.

Laine et al. [1991; 1993; 1994] reported that analogous pentacoordinate anionic and hexacoordinate dianionic silicate complexes could be synthesized directly in one step from silica, with equivalent amounts of group I

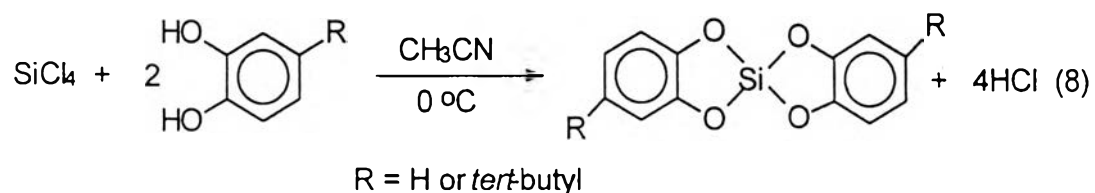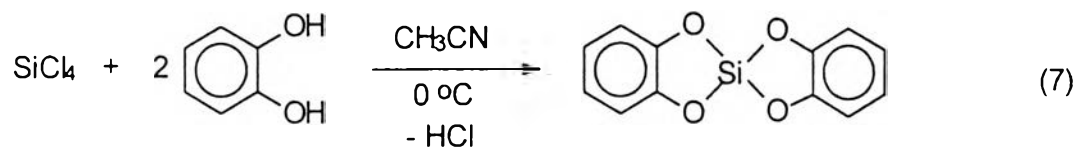hydroxide or group II oxide as base catalyst in ethylene glycol (EG) solvent, as shown in equation (4)-(6).

$$SiO_2 + MOH + x'sHOCH_2CH_2OH \xrightarrow[-3 \ H_2O]{200 \ ^oC} M\left[\begin{array}{c} O \\ O \end{array}Si^{O\diagdown\diagup OH}\right]_2 \quad (4)$$

$$M\left[\begin{array}{c} O \\ O \end{array}Si^{O\diagdown\diagup OH}\right]_2 \xrightarrow[- \ EG]{170 \ ^oC} M\left[\begin{array}{c} O \\ O \end{array}Si^{O\diagdown\diagup O}Si\begin{array}{c} O \\ O \end{array}\right]_2 \quad (5)$$

M = Li, Na, K, or Cs

$$SiO_2 + M'O + x'sOHCH_2CH_2OH \xrightarrow[-3 \ H_2O]{200 \ ^oC} M\left[\begin{array}{c} O \\ O \end{array}Si\right]_3 \quad (6)$$

M' = Ca, or Ba

Penta- and hexacoordinate silicon complexes are precursors which can be used to prepare phase pure ceramic powders, coatings or fibers. In addition, sol-gel processing of these materials provides access to high surface area ceramic powder with electrorheological properties [Laine et al., 1994].

Allcock [1972] first synthesized the tetracoordinate siloxanes, biscatecholsilane, by using carbothermally derived $SiCl_4$ with catechol as the starting materials, as shown in equation (7). Bis(4-*t*-butylcatechol) silane, analogue of biscatecholsilane, could also be synthesized [Robinson T.R., 1990], as shown in equation (8).

$$\text{SiCl}_4 + 2 \quad \text{catechol(OH, OH)} \xrightarrow[\substack{0\,^\circ\text{C} \\ -\text{HCl}}]{\text{CH}_3\text{CN}} \quad \text{biscatecholatosilicate} \qquad (7)$$

$$\text{SiCl}_4 + 2 \quad \text{HO, HO, R} \xrightarrow[0\,^\circ\text{C}]{\text{CH}_3\text{CN}} \quad \text{product} \quad + \text{ 4HCl} \qquad (8)$$

R = H or *tert*-butyl

The product from Allcock's method was amorphous white powder of bis(1,2-dioxyphenyl)silane or biscatecholatosilicate. Polymerization of this product gives rod-like oligomers with neutral, tetracoordinate silane. The crystal structure was determined by Honle et al. [1989] as shown in Figure 1.1.
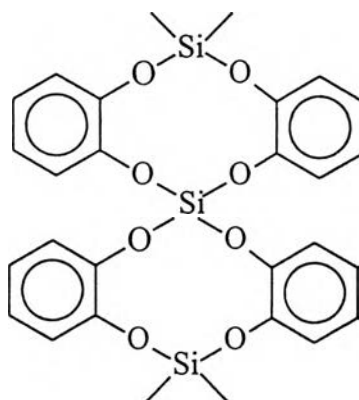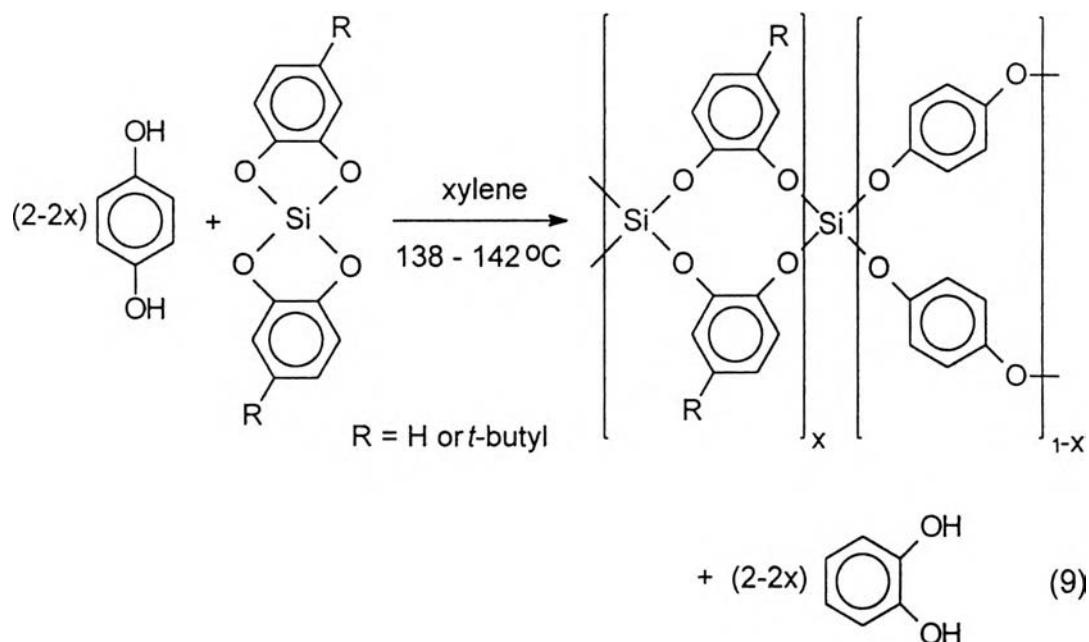

Figure 1.1 Bis(1,2-dioxyphenyl)silane

Ray et al. [1993] followed Allcock's method to synthesize biscatecholsilane and bis(4-*t*-butylcatechol)silane, and copolymerized them with and without hydroquinone as in reaction (9).

$$R = H \text{ or } t\text{-butyl} \qquad + \ (2\text{-}2x) \qquad \qquad (9)$$

The transmitted polarized light microscopy of the resulting copolymers showed the presence of nematic phases, and additionally lyotropic nematic phases in xylene. The conditions giving rise to liquid crystallinity varied with the ratio of monomers, the temperature at which the polymerization reaction occurred, and the reaction time.

Lately, Rangsitphol J. [1995] studied the one step synthesis, called OOPS (Oxide One Pot Synthesis) process, of bis(1,2-dioxyphenyl)silane directly from silica and catechol using triethylenetetramine (TETA) as a catalyst in ethylene glycol (EG) solvent, as shown in equation (10).

$$SiO_2 \ + \ 2 \qquad \xrightarrow[- \ 2 \ H_2O]{\underset{200 \ ^oC}{EG \ , \ TETA}} \qquad \qquad (11)$$
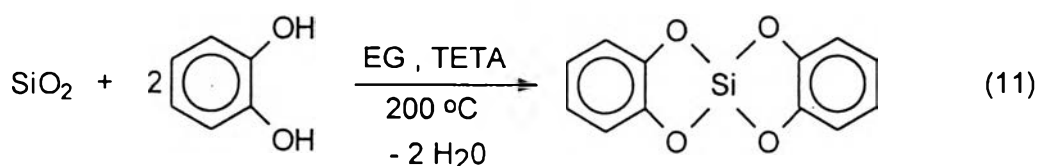
This product, the same as that from Allcock's method, is a precursor that can be copolymerized with hydroquinone to form high temperature copolymers.

It is interesting to prove that liquid crystalline copolymers can also be synthesized directly via a one step process wherein silica, catechol and *t*-butylcatechol are reacted, as shown in equation (11).

R = H or *t*-butyl
(11)
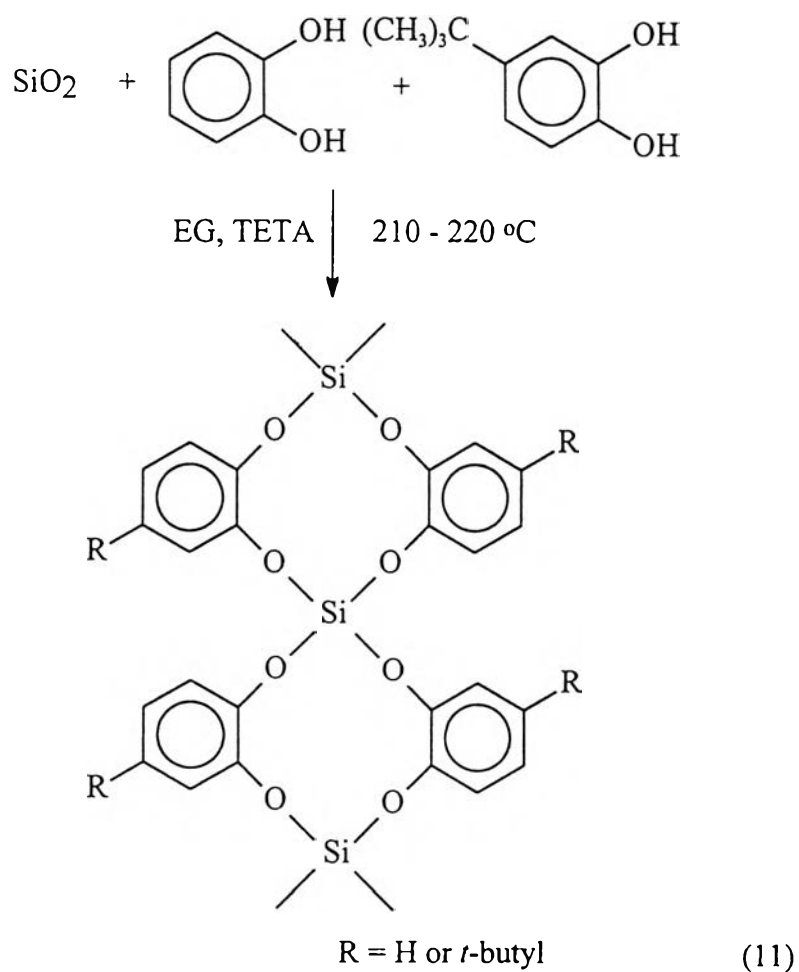
1.2 Objectives

This research has its goals to first synthesize an inorganic liquid crystalline copolymer by a one step process directly from silica, catechol and t-butylcatechol using TETA as catalyst, and then characterize the product by thermal analysis, FTIR, XRD, NMR and EI^+-MS. The optimal mole ratio of silica, catechol and t-butylcatechol; the appropriate reaction time, and the suitable mole% of TETA are also investigated.