CHAPTER I
INTRODUCTION

1.1 Background

Directionally dependent anisotropic properties are observed independent of the state of aggregation only for substances having a regular arrangement of constituent molecules. If the degree of order is 3-dimensional in nature then the substance is a crystalline solid, while 2- or 1-dimensional order is characteristic of liquid crystals [Steinsträsser R. and Pohl L.,1973].

The ordered regions in the liquid crystalline are called mesophases, which exhibit properties not found in the liquid or solid state. Most liquid crystalline polymers are usually organic aromatic polyesters or polyamides. Recently, liquid crystalline polymers that contain some inorganic elements have become an interesting research [D. Jean Ray et al., 1993].

Polymer compounds containing inorganic elements are interesting because inorganic elements generate combinations of properties in polymers that are different from those achieved with carbon [Gray, G.W.; Goodby, J.W.; 1984]. For example, the bonds formed are often stronger, longer (facilitating conformational changes), more resistant to free radical cleavage reactions than those formed by carbon since many organic polymers degrade by reacting with oxygen or ozone or on exposure to radiation, and also burn, often with the release of toxic smoke. If the introduction of inorganic elements into the backbone of a polymer can change the bond angles and bond torsional mobility, the material may exhibit novel properties.

Thus, the development of inorganic materials that provide new chemical and physical properties, and new combinations of properties in macromolecules in solution and in the solid state, will advance technology.
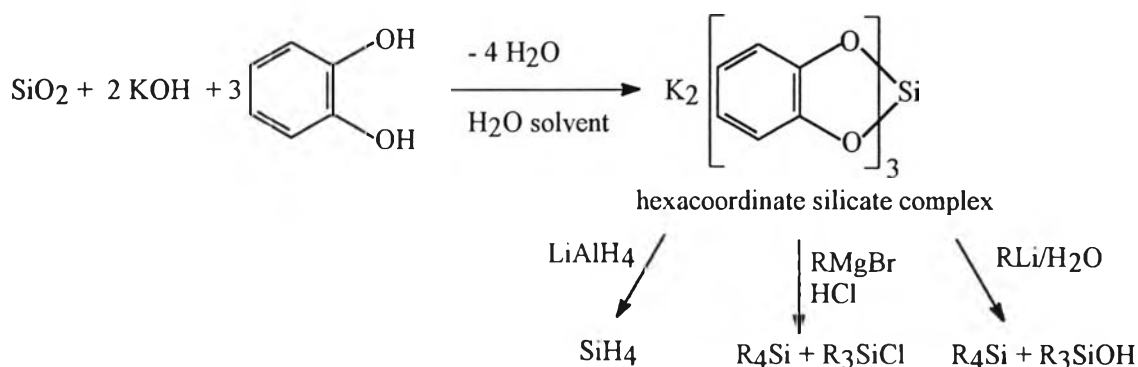
Silicon is one of the most abundant element (ca. 28% of the earth's crust), devoid of specific elemental toxicity unlike arsenic, lead, plutonium, and is to long associated with the insides and outsides of living systems[Rochow, E.G., 1987]. The widespread availability of SiO_2 and its extremely low cost make it an excellent material for use as a silicon feedstock chemical. However the primary problem with SiO_2 is high chemical bond strength, and high melting temperature which makes it a stable material that is difficult to manipulate chemically.

Organosilicon polymers can combine the thermal stability of inorganic materials with the elasticity and solubility of organic polymers [Akhmetor, N.S., 1983]. The silicon atom has more electrons ($[Ne]3s^23p^2$]) than carbon, and a partially occupied d-orbital, which tend to force formation of single bonds. Si-E (E = element) multiple bonds are unstable, thus Si-E double bonds have only been prepared rather recently [D. H. Pae et al., 1991]. thus Si-E triple bonds remain a challenge [Colegove, B T., Schacfor III, H. F., 1991]. However, organosilicon polymers with single Si-E bonds are commercially important to ceramic precursors [Kansal, P., 1994], and to liquid crystalline precursor [Rangsitphol, J., 1995].
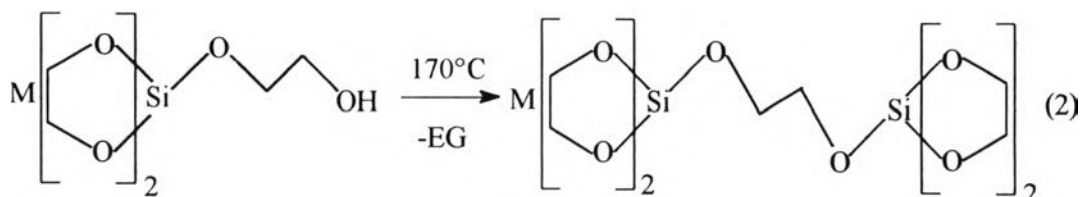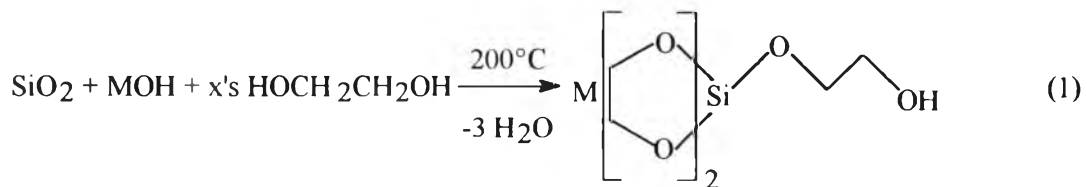
1.2 Historical Review

1.2.1 Synthesis

The silicon-oxygen bond can only be cleaved during silica depolymerization using base catalyst since the Si-O bond is quite stable. The depolymerization of silica to monomer silicate compounds was first reported by Rosenheim et al. [1931]. They found that silica converts to hexacoordinate complexes in water by reaction with inorganic base and catechol, which can be used to transform a wide variety of metal oxides into catecholato complexes. Corriu et al. [1983, 1988, 1990] found new synthetic routes to transform tricatecholatosilicate into a wide variety of silicon containing compound, see Scheme I.
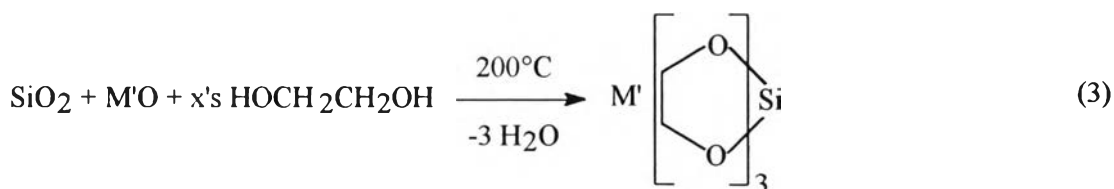

$$SiO_2 + 2\,KOH + 3 \quad \text{(catechol)} \quad \xrightarrow[\text{H}_2\text{O solvent}]{-4\,H_2O} \quad \text{(hexacoordinate silicate complex)}$$

hexacoordinate silicate complex

$$LiAlH_4 \quad\quad RMgBr/HCl \quad\quad RLi/H_2O$$

$$SiH_4 \quad\quad R_4Si + R_3SiCl \quad\quad R_4Si + R_3SiOH$$

Scheme I

Laine et al. [1994] reported the synthesis of pentacoordinate anionic and hexacoordinate dianionic glycolato silicate complexes by direct reaction of silica, with equivalent amounts of groupI/II metal hydroxides/oxide in excess ethylene glycol solvent (as shown in equations 1-3). These complexes are precusors to phase pure ceramic powders, coatings or fibers. Futhermore, sol-gel processing of these materials provides access to high surface area ceramic powders with electrorheological properties [Laine et al., 1994].
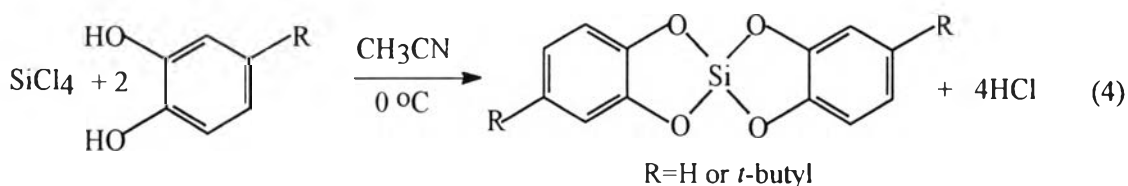
$$SiO_2 + MOH + x's\ HOCH_2CH_2OH \xrightarrow[-3\ H_2O]{200°C} M\left[\underset{O}{\overset{O}{\diagdown}}Si\diagup O \diagdown\diagup OH\right]_2 \tag{1}$$

$$M\left[\underset{O}{\overset{O}{\diagdown}}Si\diagup O\diagdown OH\right]_2 \xrightarrow[-EG]{170°C} M\left[\underset{O}{\overset{O}{\diagdown}}Si\diagup O\diagdown\diagup O Si\overset{O}{\underset{O}{\diagup\diagdown}}\right]_2 \tag{2}$$

M = Li, Na, K, or Cs

$$SiO_2 + M'O + x's\ HOCH_2CH_2OH \xrightarrow[-3\ H_2O]{200°C} M'\left[\underset{O}{\overset{O}{\diagdown}}Si\right]_3 \tag{3}$$

M' = Ca, or Ba

Bis(catecholato)silicate, a tetracoorinated siloxane, was synthesized from $SiCl_4$ and catechol in acetronitrile solvent by Allcock [Allcock H.R., Nugent T.A., Smeltz L.A., 1972]. This spirosilane polymerizes easily to a rod-like oligomer. The structure was determined by Hönle et al. [1989]. The synthesis of bis(4-tert-butyl-catecholato)silicate is analogous [Robinson, T.R., 1990], as shown in equation 4.

$$SiCl_4 + 2\ \begin{array}{c}HO\\HO\end{array}\diagdown\bigcirc\diagup R \xrightarrow[0\ °C]{CH_3CN} R\diagdown\bigcirc\underset{O}{\overset{O}{\diagup\diagdown}}Si\underset{O}{\overset{O}{\diagdown\diagup}}\bigcirc\diagup R\ +\ 4HCl \tag{4}$$

R=H or *t*-butyl

Ray et al. [1993] prepared copolymers bis(catecholato)silane, bis(4-tert-butyl-catecholato)silane; by following Allcock's route, with hydroquinone as a comonomer in xylene solvent, as shown in equation 5. The lyotropic nematic phases in xylene of various copolymers showed liquid crystalline

properties that varied with the ratio of monomer, reaction temperature, and reaction time.


(5)
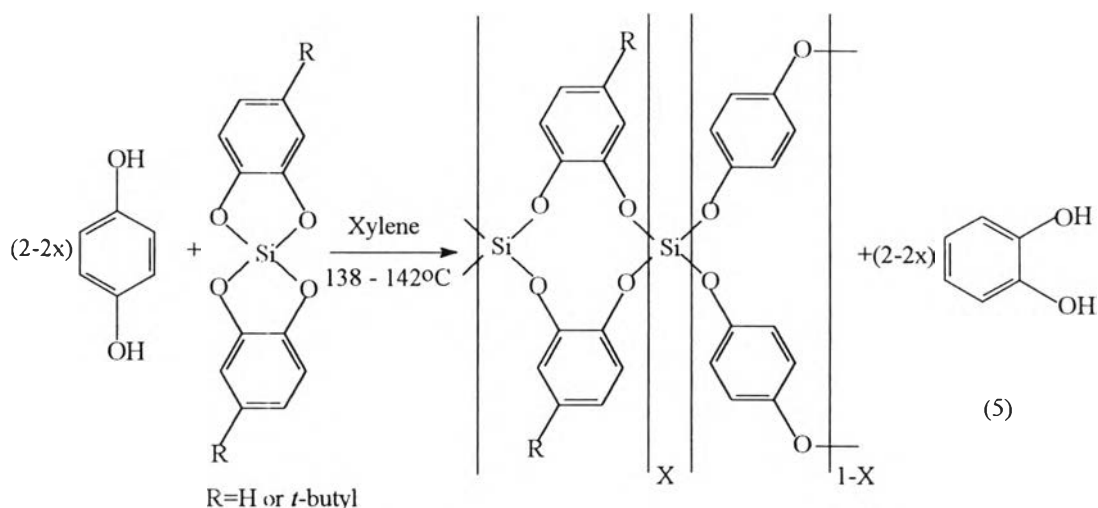
Lately, Rangsitphol J. [1995] used the "OOPS" (oxide one pot synthesis) process to synthesize bis (1,2-dioxyphenyl)silane from SiO_2, catechol, triethylenetetramine (TETA) as catalyst in highly boiling point of ethylene glycol solvent (equation 6).


(6)
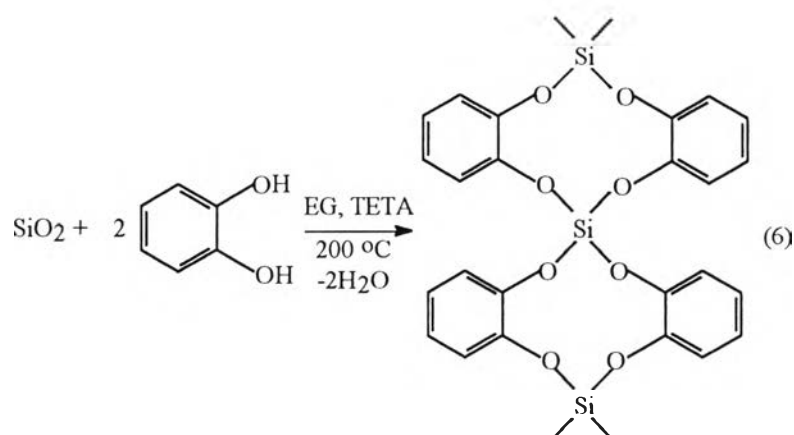
Recently, Phongpisitsakun N. [1997] (equation 7) and Silpa-Archa M. [1997] synthesized organosilicon copolymers using the OOPS process from SiO_2, and catechol with different comonomers to obstruct the formation of ladder structure, namely, 4-tert-butylcatechol which is an ortho-linked that

tert-butyl groups as a side group and hydroquinone having a para-linked, respectively. Both products show different properties.

$$R = H \text{ or } t\text{-butyl}$$
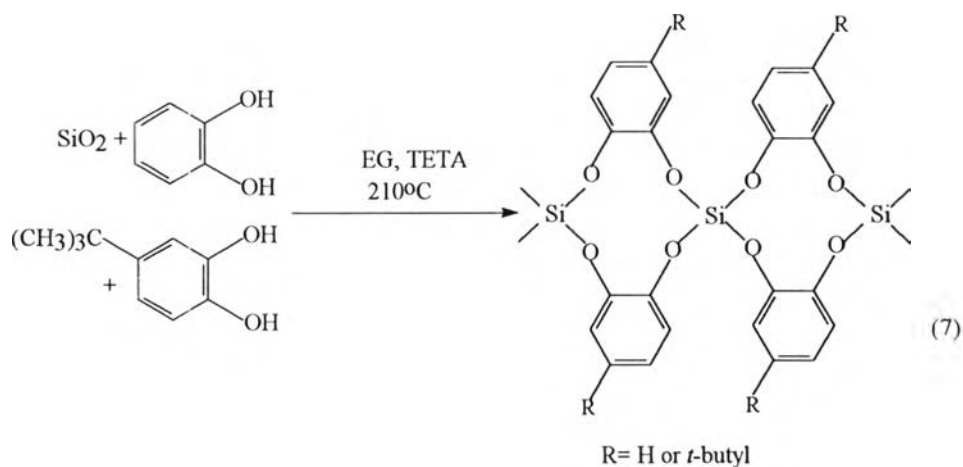
This research thesis focuses on the synthesis of Si containing species directly via the OOPS process from SiO_2, catechol, hydroquinone, and 4-tert-butylcatechol in ethylene glycol solvent while having triethylenetetramine as a catalyst or stoichiometric quantities to dissolve SiO_2, as shown in equation 8.

if R =H, then R'=H or t-butyl and,
if R'=H, then R =H or t-butyl also
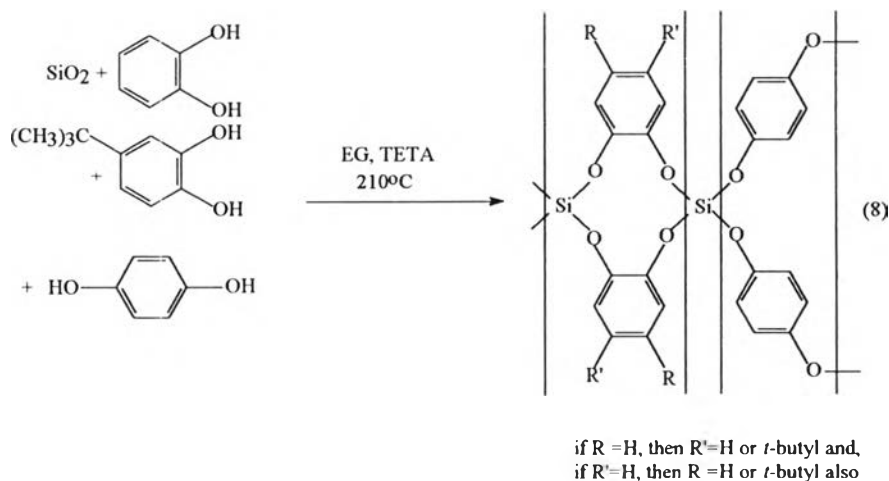
1.2.2 Kinetics

Chemical kinetics, also called reaction kinetics, is the study of the rates and mechanisms of chemical reactions. To measure the reaction rate, r, one must follow the concentration of a reactant or product as a function of time.

In the chemical method, one places several reactions with identical initial compositions in a constant-temperature bath. At intervals, one withdraws samples from the bath, slows down or stops the reaction, and rapidly analyzes the mixture chemically. Methods for slowing the reaction include cooling the sample, removing a catalyst, greatly diluting the reaction mixture, and adding a species that quickly combines with one of the reactants. However, physical methods are usually more accurate and less tedious than chemical methods. Thus, one prefers measuring a physical property of the reacting system as a function of time.

For the determination of the rate, r, experiment data give species concentration at various times during the reaction. That is, $r = f([A],[B],...)$, or

$$r = k[A]^{\alpha}[B]^{\beta}...[L]^{\lambda}$$

It is usually best to find the orders α, β,..., λ and then find the rate constant k. Four methods for finding the orders are as follows:

1. Half-life method

2. Powell-plot method

3. Isolation method (Reduction concentration method)

4. Initial-rate method

The rate law of the reaction which is studied is;

$$r = k[SiO_2]^{\alpha}[catechol]^{\beta}[hydroquinone]^{\gamma}[4\text{-tert-butylcatechol}]^{\lambda}$$

The methods 1-2 will be applied when the reaction has the rate law in the form of $r = k[A]^n$. As for the method 3, it is more difficult than the last method since we must make the initial concentration of reactant A much less

than the concentration of all other species (more than 10^{-2} times) and use raw material concentrations more than the method 4.

For the initial rate method, one must measure the initial rate, r_0, for several runs, varying the initial concentration of one reactant at a time. Suppose we measure r_0 for the two different initial A concentrations $[A]_{0,1}$ and $[A]_{0,2}$ while keeping $[B]_0$, $[C]_0$,... fixed. With only $[A]_0$ changed and with the rate law assumed to have the form: $r = k[A]^{\alpha}[B]^{\beta}...[L]^{\lambda}$, the ratio of initial rates for runs 1 and 2 is:

$$r_{0,2}/r_{0,1} = ([A]_{0,2}/[A]_{0,1})^{\alpha},$$

from which α is readily found (we found r_0 by the plotting $[A]$ versus time and the tangent line at $t = 0$). The order β,γ, ..., λ are also found similarly. For this work, unreacted catechol, hydroquinone, and 4-tert-butylcatechol are difficult to measure when the reactions are stopped because these reactants are air-sensitive compounds. We can only follow unreacted SiO_2.

Rate constants depend strongly on temperature, typically increasing rapidly with increasing T. In 1889 Arrhenius noted that the $k(T)$ data for many reactions fit the equation $k = Ae^{-E_a/RT}$ where A (pre-facter) and E_a are constants, and R is the gas constant. The units of A are the same as those of k. The units of E_a are the same as those of RT.

Taking logs of Arrhenius equation, we get

$$\ln k = \ln A - (E_a /RT) \quad \text{or} \quad \log_{10} k = \log_{10} A - (E_a/2.303RT)$$

$$d \ln k/dT = E_a/RT^2$$

$$r = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}[D]^{\lambda} \quad \text{----------}> \quad r = J[A]^{\alpha} \; ; J = k[B]^{\beta}[C]^{\gamma}[D]^{\lambda}$$

Then, we can use J values instead of k values to plot $\ln J$ versus $1/T$ to determine E_a from the slope (E_a/R; $R=8.314$ J $K^{-1}mol^{-1}$or 1.987 cal $mol^{-1}K^{-1}$)

1.3 Objectives

This research has its aims to synthesize and characterize a novel copolymer by the OOPS process directly from silica, catechol, hydroquinone, and 4-tert-butylcatechol, using triethylenetetramine (trien or TETA) as a catalyst to dissolve SiO_2 in ethylene glycol solvent. The products were characterized using FTIR, TGA, DSC, XRD, NMR, EI^+-MS. The suitable mole ratio of hydroquinone and 4-tert-butylcatechol, as comonomers, and kinetic studies of the dissolution process were also studied, as well.