# CHAPTER II

## LITERATURE REVIEW

Silica nanostructures, such as nanowires and nanofibres have attracted considerable attention because of their unique properties and promise for application in mesoscopic research, nanodevices, optoelectronics devices, and chromatographic supports with high absorption capacities. To date, these materials have been successfully prepared in different ways such as by excimer laser ablation, chemical vapour deposition, stress-limited oxidation, thermal evaporation, carbothermal reduction synthesis, vapour-liquid-solid mathod, and finally electrospinning process. Due to the ease of the technique, electrospinning process will be focused on this work. There are several publications on the electrospinning process due to the various aspects of the process and its application. The formation of fibre in the electrospinning process can be divided into two parts which are the initiation of the jet and the continuous flow of the jet. For the initiation of the jet, the following equation is satisfied:

$$V_{*} = (4\pi r\gamma)^{1/2}$$

where $V_{*}$ is the critical potential, r is the droplet radius, and $\gamma$ is the surface tension of the solution.

Taylor (Taylor, 1969) analysed a droplet of water deformed by an electric field and showed that a viscous fluid exists in equilibrium in an electric field when it has the form of a cone with a semivertical angle of 49.3°.

Several publications reported investigation on the effects of various parameters on the morphology of electrospun polymeric nanofibres.

Deitzel and coworkers (Deitzel *et al*, 2001) studied the effects of spinning voltage and solution concentration on the morphology of the electrospun polyethylene oxide fibres. They found that spinning voltage was strongly correlated with the formation of bead in the fibres. Changes in solution concentration contributed most to the size of the fibres, with the fibre diameters increasing with increasing solution concentration according to a power law relationship. In addition, electrospinning from solutions of high concentration was found to produce fibres having a bimodal size distribution.

The effects of viscosity of solution, charge density carried by the jet, and surface tension of the solutions on the formation of beads on the fibres were investigated by Fong and coworkers (Fong *et al*, 1999). Beads and beaded fibres were less likely to be formed in highly viscous solutions and in jets with high net charge density. Increasing net charge density favored the formation of small fibres. Decreasing the surface tension coefficient of the solution favors the formation of larger fibres.

Bioabsorbable nanofibrous membranes were electrospun by Zong and coworkers (Zong *et al*, 2002). The effects of solution properties and processing parameters on the structure and morphology of the electrospun membranes were investigated. Results demonstrated that the morphology of electrospun films depended on the strength of the electric field, the solution viscosity (e.g. concentration), the charge density of the solution (by salt addition), and the solution feed rate. It was shown that the higher the concentration and the charge density of solution, the more the formation of uniform nanofibres without beads. The diameters of the nanofibres increased with electrospinning voltage as well as feeding rate of the solution, whereas they decreased with the addition of salts.

This work focuses on preparation and characterisation of silica fibres using the electrospinning technique. There are several reports on successful preparation of silica fibres based on the electrospinning technique.

Shao *et al* (2000) prepared electrospun polyvinylalcohol/silica thin fibres by using a sol-gel technique to incorporate silica compounds in the fibres. After calcination of fibres, amorphous silica nanofibres with diameters of 200-300 nm could be prepared. They suggested that this route open a new door for making inorganic nanofibres. Only a year later, Shao *et al* (2003) claimed that fibre mats of polyvinylalcohol/silica fibres with different silica content were successfully prepared. Madhugiri *et al* (2003) have demonstrated that an electrospinning process can produce a non-woven mesh of mesoporous molecular sieve fibres from DAM-1 and SBA-15 gels. Moreover, they found that by using a dual electrospinning technique one can prepare a non-woven mesh of polymer and molecular sieve fibres that can be handled like tissue paper. Choi *et al* (2003) stated that they could prepare the silica fibres using the sol-gel method and electrospinning techniques. They also claimed that the TEOS (tetraethylsilicate) used in this study does not contain any gelator or binder to help spinnability.

Despite all of these reports, there has been no report on preparation of electrospun silica fibres from silatrane precursor with the electrospinning technique. Therefore, it is challenging to prepare silica fibres from this precursor. In terms of advantages, electrospinning is a unique process which can produce polymer fibres with diameter ranging from micrometres down to nanometres. Owing to the smallness of their diameters, electrospun fibres posses unusually large surface-to-volume ratios and are expected to display morphologies and properties very different from those of the conventional fibres. In addition, electrospun fibres in the form of non-woven fabrics offer unique capabilities to control pore size.

Electrospinning is a fast processing technique in which the operation time is much shorter than that of the conventional technique. The required equipment for electrospinning is also simple, and only small quantity of polymer is needed to obtain nanofibres. From several advantages of electrospun fibres which posses large surface area/mass ratios and small diameters , the fibres can be suitable for a number of applications:

1. They can be used as reinforcing materials in composites such as transparent nanocomposite of electrospun nylon-4,6 fibers with epoxy resin (Bergshoef and Vancso , 1999), nylon 6-montmorillonite nanocomposite (Fong *et al*, 2002).

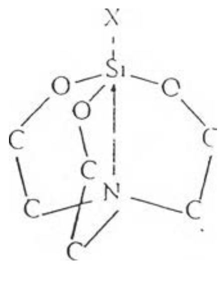
2. They can be used as filters with very fine pore sizes. Applications of filter are removing nanometre scale particles and droplets; for example, air conditioning for buildings and vehicles, clean-room technology for semi-conductor industry, and filtration of liquids for the fabrication of semiconductor chip circuit.

3. Nanofibres can also be used as supports for catalysts or enzymes.

4. Biomedical applications from nanofibres can be used as drug delivery system (Zong *et al*, 2002), scaffolds for tissue engineering, wound dressing materials, etc.

5. The production of protective textiles from electrospun nanofibres (Gibson *et al*, 2002) has been developed. It has been applied to fabrics as a protective membrane layer which provides a protection from extreme weather conditions, enhances fabric breathability, and improves chemical resistance of clothing to toxic chemical exposure. These protective fabrics can be made into seamless garments that would reduce a soldier's risk of chemical exposure.

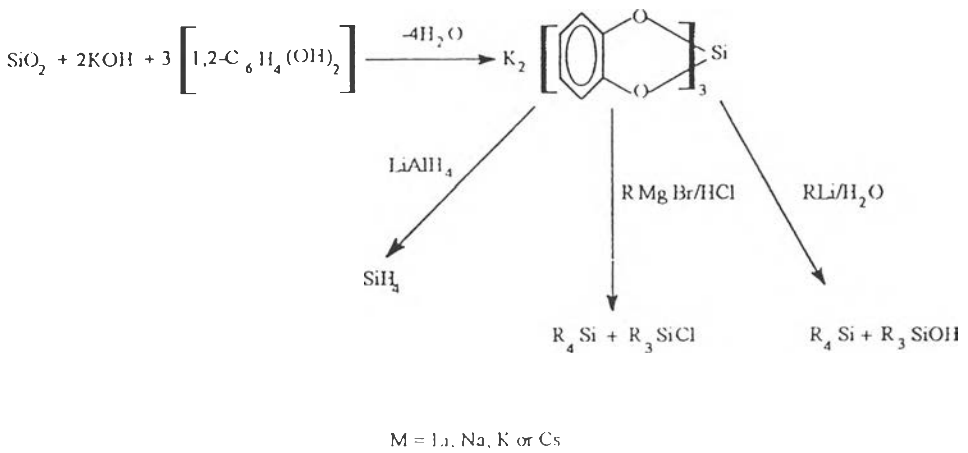
In the synthesis of silatrane compounds, there are several publications emphasizing on this topic, the first silatrane complexes, as shown in scheme 2.1 (with X = $C_6H_5$ and $C_2H_5O$), were patented by Finestone in 1960 who suggested the existence of the Si -> N transannular dative bond in the synthesised silatrane molecule. In 1961, Frye, Vogel, and Hall reported a number of new, 1-substituted silatrane, scheme 2.1 [X = H, $CH_3$, n-$C_{18}H_{37}$, $C_6H_5(CH_3)CH$ and etc.].



**Scheme 2.1**

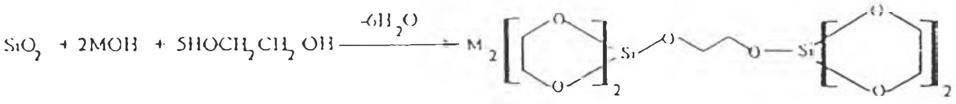
They described the 1-ethoxy and 1-phenylsilatranes (melting points = 100-102 °C and 208-209 °C, respectively) and reported some data in support of intramolecular transannular dative bonds in silatrane complexes.

In 1931, Rosenheim *et al* reported that silica, sand, and quartz powder could also be employed to react with alkali catecholates to give hexacoordinate silicate complexes. However, Courrie's group (Corriu R. J. P., 1988) demonstrated that these catechol silicate complexes were quite unstable. They could only be modified by reacting with strong nucleophile to obtain tri- and tetrasubstituted products, which were necessary in the industry primarily for polymer synthesis, as shown in scheme 2.2.



**Scheme 2.2**

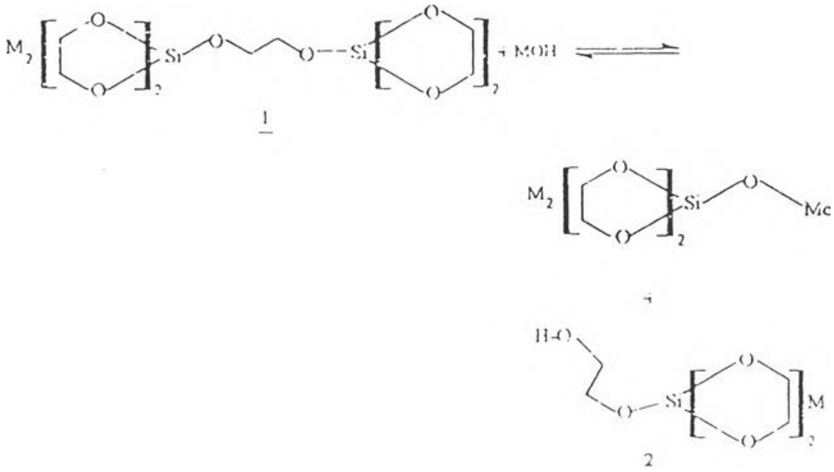
R.M. Laine and coworkers (Laine *et al*, 1991) discovered new synthetic routes to organosilicon compounds. By reacting $SiO_2$ with ethylene glycol in the presence of an alkali base, highly reactive pentacoordinate silicates are obtained, as shown in scheme 2.3.



M = Li, Na, K or Cs

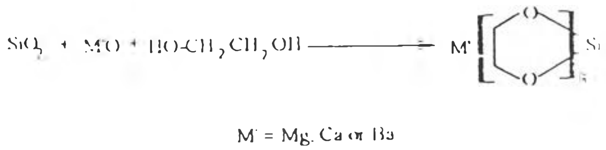
Scheme 2.3

The elemental analysis of the above products showed that if M was Li, Na, or K, the product was dimeric pentacoordinate species, labeled 1 in the scheme 2.4. However, if Cs was used, the product acted as monomeric species, labeled 2. These results were confirmed by FTIR peak found for $\nu_{O\text{-}H}$ at 3,300 cm$^{-1}$.



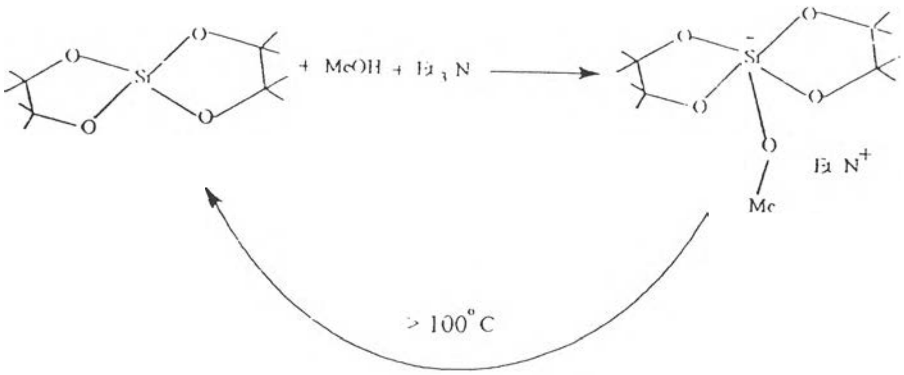
Scheme 2.4

Furthermore, hexacoordinate silicate complexes were obtained when reacting $SiO_2$ with group II oxide in ethylene glycol, as shown in 2.5.



Scheme 2.5

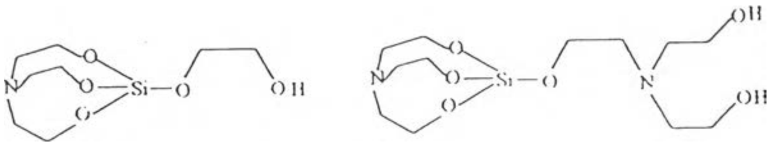
Frye's observation (Frye C.L., 1970:1971) indicated that spirosilicates could react with MeOH and amine base (e.g. $Et_3N$) to form pentacoordinate, anionic silicate with ammonium counterion at ambient temperature. These species were not stable above 100 °C, reverting to the tetracoordinate spirosilicate, as shown in scheme 2.6.



Scheme 2.6

This observation prompted Laine's group to try (boiling point > 200°C) amine bases with high boiling points in place of group I or II hydroxides or oxides. Triethylenetetramine (boiling point 266°C, TETA) and triethanolamine [TEA] were used as either catalyst or reactant, respectively. They found that TETA did not promote the formation of stable ammonium pentacoordinate silicates, an evidence from $^{29}$Si

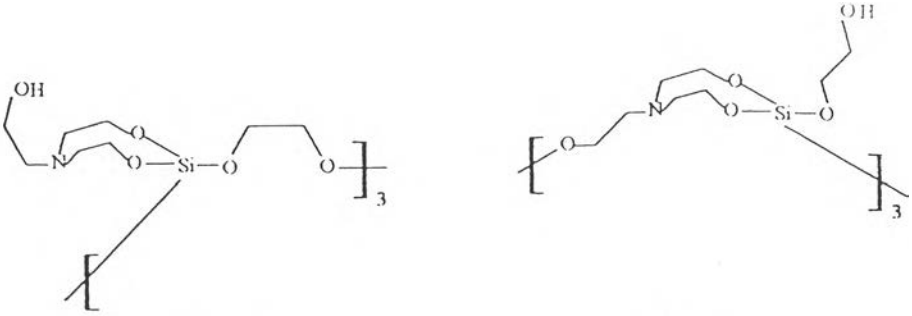
NMR peaks of the product at –78, -79, -80 and –82 ppm. If TEA was used in place of TETA, similar product was obtained, depending on the amount of TEA. With up to two equivalents of TEA, the product had two silatrane species suggested by FAB$^+$-MS, as shown in scheme 2.7.



m/e = 235 m/e = 322

Scheme 2.7

If one equivalent of TEA or less was employed, the primary product was the ethylene glycoloxysilatrane. $^{29}$Si-NMR of this complex gave a single peak at –96.2 ppm, which is typical of Si in silatrane (vs. TMS). TGA data gave % ceramic yield of 25.6. When the product was further dried under vacuum, higher M.W. oligomers were obtained, characterised by FAB$^+$-MS, see scheme 2.8.



m/e = 706 m/e = 706

Scheme 2.8

In 1995, Punchaipetch synthesised organosilicon complexes by reacting $SiO_2$ with TEA in ethylene glycol in the presence and absence of TETA. The $FAB^+$-MS results indicated that the product was oligomeric with a repeating unit equal to 235 Da, see scheme 2.7. She also studied the kinetics of formation of silatrane complexes by using the integral method to determine the reaction order. She found that the overall reaction was pseudo second order. The activation energy from Arrhenius's equation was equal to 64 ± 8 KJ/mol or 15 ± 2 kcal /mol. etc (Punchaipetch, 1995).