

# CHAPTER I

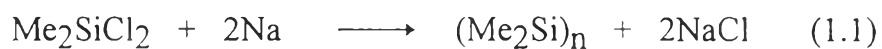
## INTRODUCTION



### 1.1 Background

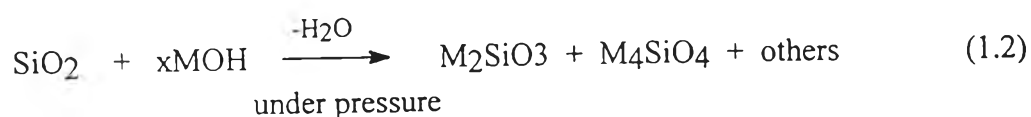
Organosilicon polymers are macromolecules containing silicon in the backbone with organic moieties as pendant groups. The polymers combine the thermal stability of inorganic materials with the elasticity and solubility of organic polymers (Akhmetov, 1983). The entire area of organosilicon chemistry has flourished since Kipping's preparation by the more convenient Grignard process (Kipping, 1937).

The first clear example of a polysilane polymer appears in a classic paper by C.A. Burkhard (Burkhard, 1949) in equation 1.1. The polymer is a highly crystalline material, that rearranges above 250°C without melting and is essentially insoluble in all organic solvents.



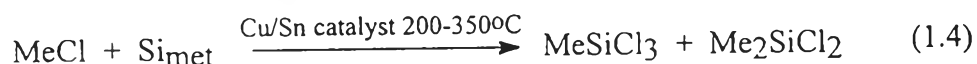
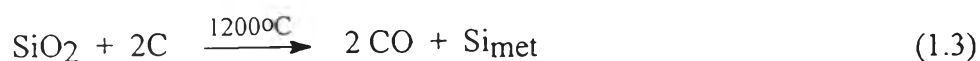
Silicon, in the form of silica ( $\text{SiO}_2$ ), accounts for 28% by weight of the Earth's crust. The synthetic routes to organosilicon polymers stemming from the use of silica would be extremely attractive because of the modest cost of the pure starting material. Although both silicon and carbon are Group IVA elements (Cotton and Wilkinson, 1992), they do not have the same properties. Silicon with its electronic configuration of  $1s^2 2s^2 2p^6 3s^2 3p^2$  is similar to carbon in forming predominantly tetravalent compounds.

All silicon-based feedstock compounds do not occur naturally. They have to be synthesized from silicon dioxide by two relatively mature processes. The first, the dissolution of SiO<sub>2</sub> in strong base, provides access to various kinds of inorganic silicates, as illustrated in equation 1.2 (Iler, R.K., 1979).

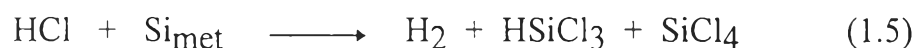


M = alkali metal

(Si<sub>met</sub>) in reaction 1.3, provides access to high organosilicon compounds via reaction of Si<sub>met</sub> with alkyl or aryl chlorides (most typically MeCl) in the presence of a catalyst :



Alternately, Si<sub>met</sub> is reacted with a variety of oxidants to prepare related products. For example, reaction with HCl provides :



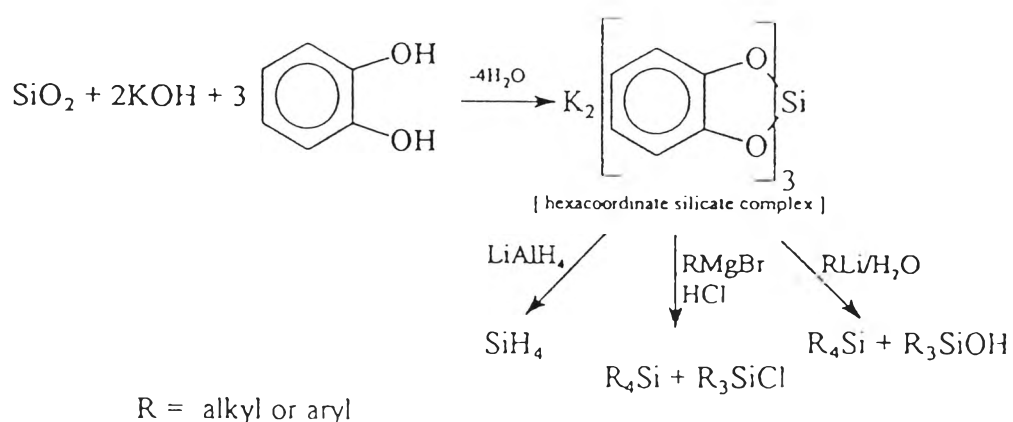
SiCl<sub>4</sub> is a feedstock for the preparation of Si(OEt)<sub>4</sub>. HSiCl<sub>3</sub> is disproportionated according to reaction 1.6 to form silane, the primary source of electronics grade Si metal.



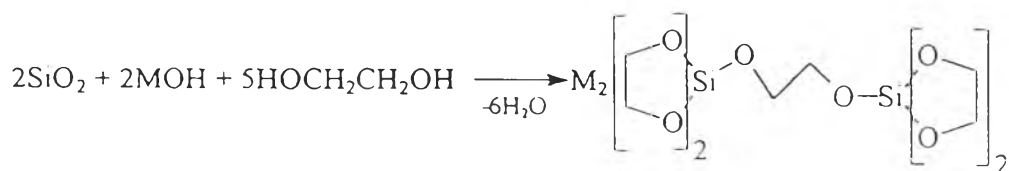
The widespread availability of  $\text{SiO}_2$  and its relatively low cost, continue to make it the most ideal starting material for any new route(s) to silicon feedstock chemicals. However, the primary problem with developing any large scale industrial process based on  $\text{SiO}_2$  is that the Si-O bonds in  $\text{SiO}_2$  are some of the strongest in nature [128 kcal (535 kJ/mol)]. This problem has been solved by Laine et al. (1993) who have explored ways to activate the high bond strength and polymerize  $\text{SiO}_2$ .

## 1.2 Literature Survey

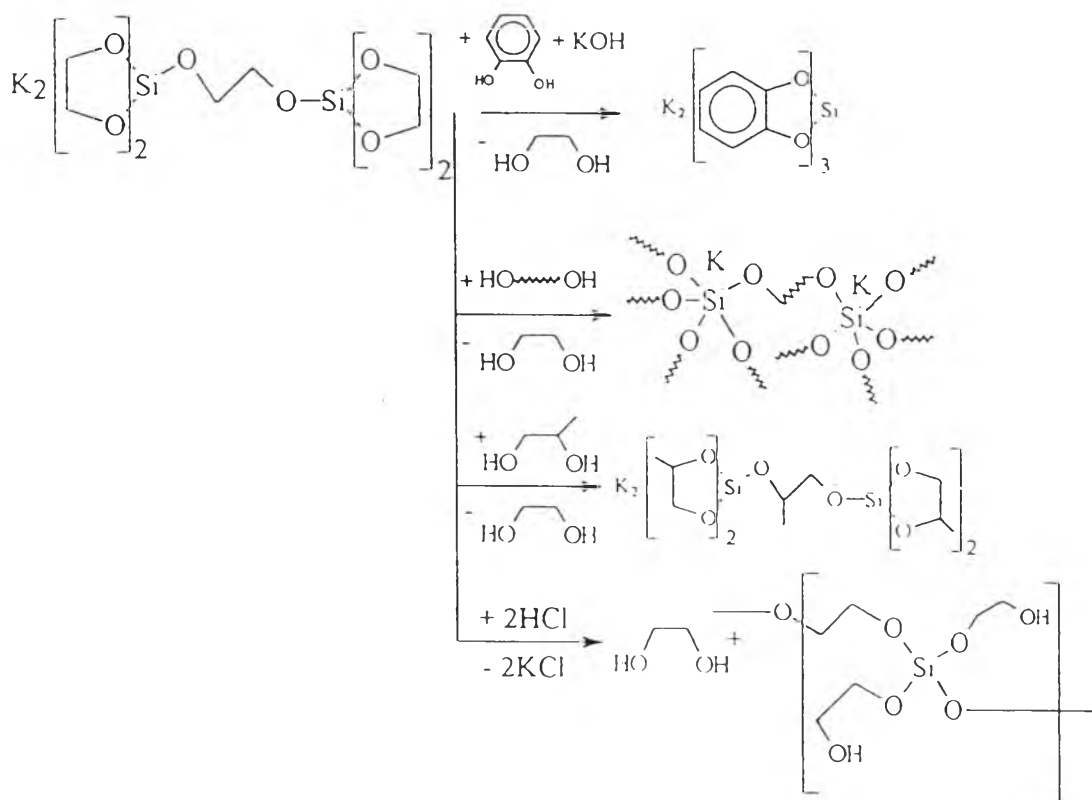
Rosenheim and coworkers (1931) were the first groups to describe the direct reaction of silica with a coordinating ligand. They found that catechol could be used to transform a wide variety of metal oxides into catecholato complexes, as illustrated in Scheme I :



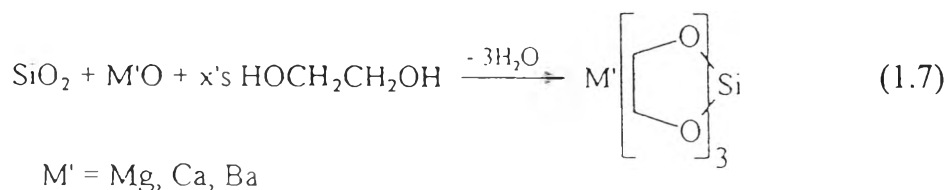
**Scheme I : Transformation of catechol to catecholato complexes.**



M = Li, Na, K or Cs



**Scheme II : Synthesis of pentacoordinate anionic and hexacoordinate dianionic glycolato silicate complexes.**

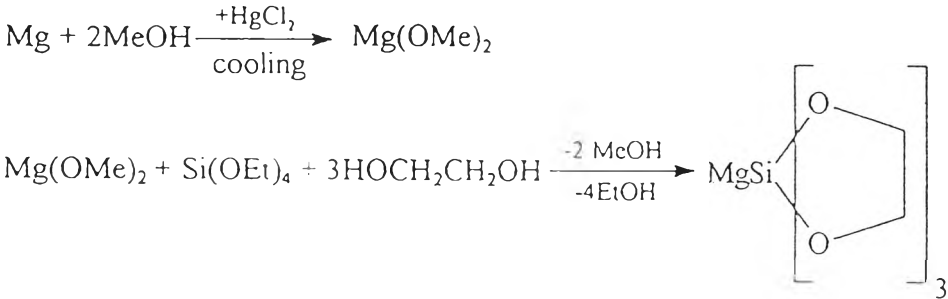


Corriu et al.(1983; 1986; 1988; 1990), in pursuit of new synthetic routes to silicon containing compounds, explored methods of transforming the resulting triscatecholato silicate into a wide variety of silicon containing compounds by reaction with strong nucleophiles, such as aryl or alkyl Grignard or lithium reagents, as shown in Scheme I.

Thus, Corriu et al. elegantly proved that it is possible to prepare organosilanes from SiO<sub>2</sub> without intermediate carbothermal reduction. Unfortunately, triscatecholato silicate is very stable and reacts only under forcing conditions with strong nucleophiles. Consequently, it is only possible (except with very sterically hindered alkyl groups) to generate tri- or tetrafunctionalized silicon species. Difunctional species would be most useful because they offer the opportunity to form polymers.

Laine et al. (1991; 1993) recently described the synthesis of pentacoordinate anionic and hexacoordinate dianionic glycolato silicate complexes by reaction SiO<sub>2</sub> with equivalent amounts of Group I/II metal hydroxides/oxides in excess ethylene glycol, as illustrated in Scheme II and reaction 1.7. The resulting glycolato silicates are very reactive, inexpensive and offer unique opportunity to develop new routes to silicon-containing glasses, ceramics and zeolites.

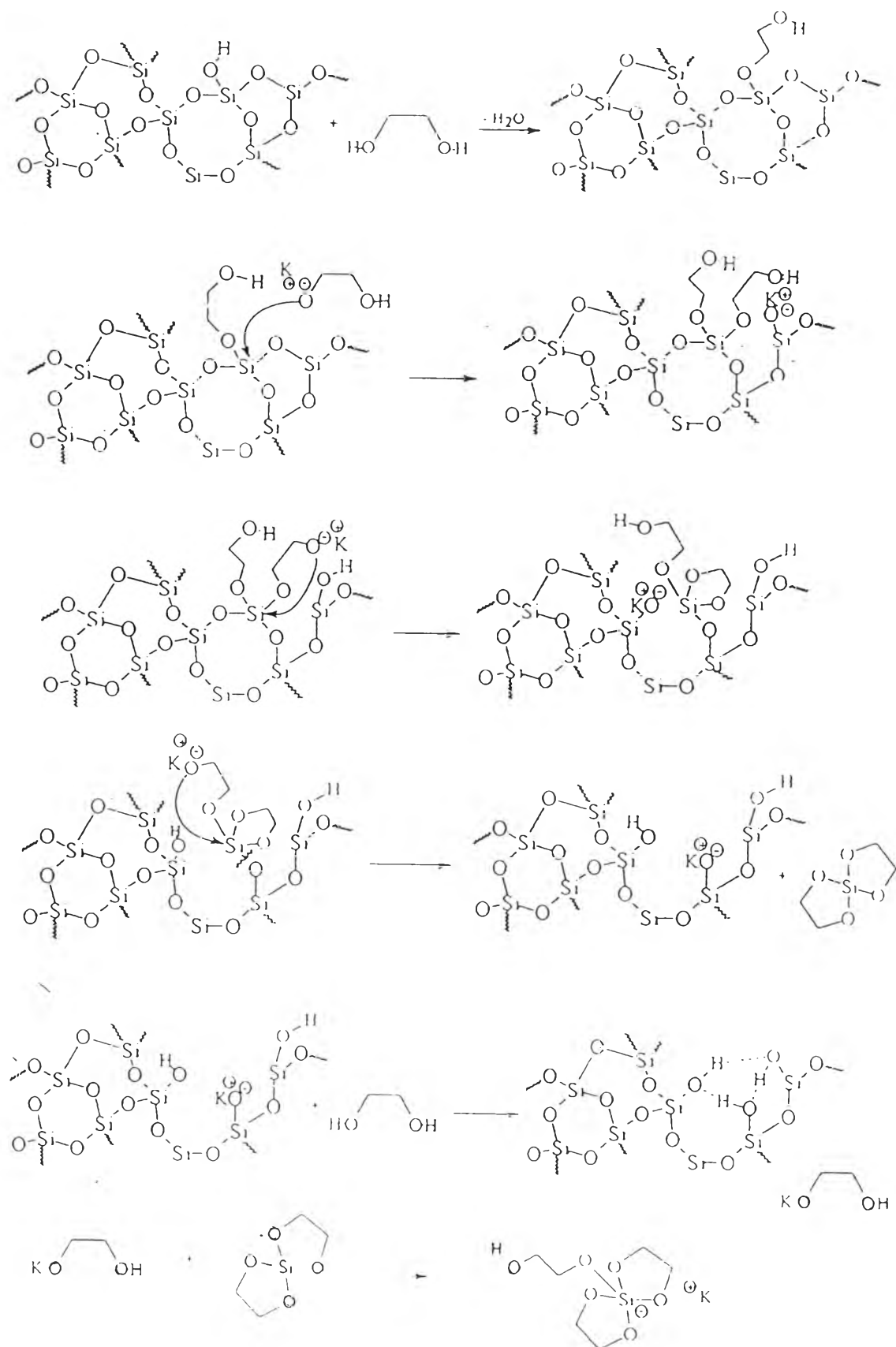
However, when MgO was used in reaction 1.7, the yields were very low. As a result, an alternative synthesis was developed (Scheme III) :



**Scheme III : Synthesis of silicon-containing compound using MgO as a base.**

Furthermore, Blohowiak et al.(1994) found that pentacoordinate alkali glycolato silicates can be synthesized directly from  $\text{SiO}_2$  by either using amorphous silica gel or fused silica. However, the reaction is slower when crystalline  $\text{SiO}_2$  of comparable surface areas is used in place of the amorphous materials. The rate of dissolution of  $\text{SiO}_2$  during the synthesis of pentacoordinate silicon complexes (Scheme II) was linearly dependent on the surface and initial base concentration. The apparent activation energy for dissolution was  $14 \pm 2$  Kcal/mol. The enthalpy ( $\Delta H$ ) and the entropy ( $\Delta S$ ) values confirmed that the slow step in this reaction was associative rather than dissociative. The amount of silica that dissolves in the absence of base is much smaller than in the presence of base. EG may initially interact with the  $\text{SiO}_2$  surface to form pendant  $\text{Si-OCH}_2\text{CH}_2\text{OH}$  groups. However, it was proven that these interactions did not exist on the exposure to KOH/EG at normal reaction temperature. The potassium glykoxide species are simply reacting with Si-OH moieties to form ionic molecules, as illustrated in Scheme IV. Either by direct reaction or by nucleophilic attack of  $\text{KOCH}_2\text{CH}_2\text{OH}$  on a Si center, pendant  $\text{Si-OCH}_2\text{CH}_2\text{OH}$  species are formed on the  $\text{SiO}_2$  surface. By hydrogen bonding between the pendant  $\text{Si-OCH}_2\text{CH}_2\text{OH}$  group and the potassium glykoxide, glykoxide nucleophilic attack at the same Si atom could be induced while the Si-O-Si linkage is broken spontaneously.

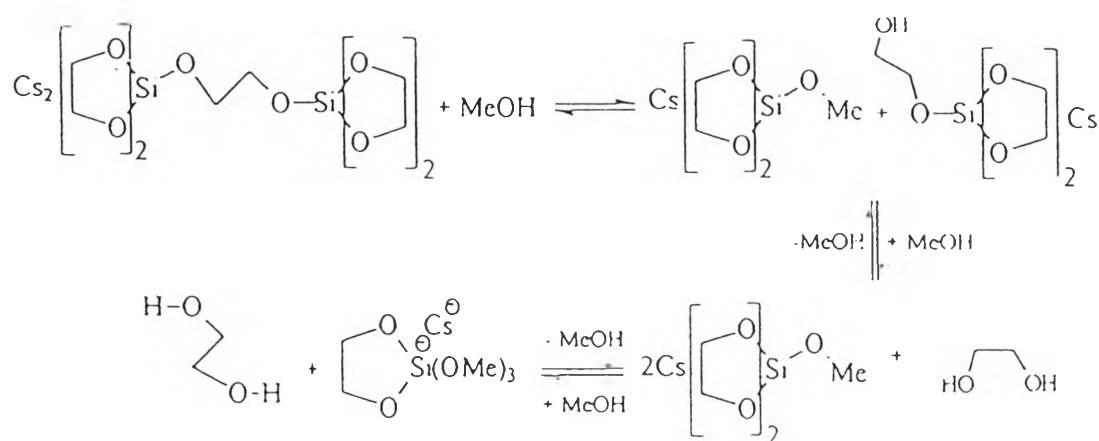
Generally, the alkali glycolato silicates are not extremely moisture sensitive and can be handled in air for minutes; however, they will eventually hydrolyze. In some cases, typically when excess base is used, the potassium salt turns pink or red. This discoloration is readily washed away with ethanol.



**Scheme IV : Reaction between the potassium glycooxide species and Si-OH moieties.**

Penta- and hexacoordinate silicon complexes play a major role in sol-gel processing of silicate glasses in organic synthesis and polymerization, and as precursors to organosilicon compounds. Actually, any stoichiometric combination of  $\text{SiO}_2$  and Group I metal hydroxides or Group II metal oxides can be dissolved to form a precursor. These precursors can be used to prepare phase pure ceramic powders, coating, or fibers. Moreover, sol-gel processing of these materials provides access to high surface area ceramic powder that offers electrorheological properties (Laine et al., 1994).

The Cs glycolato pentacoordinate silicate is an exceptional case since its solubility properties are quite different from other complexes. It is soluble in MeOH to give hydrolyzed products, as illustrated in Scheme V.

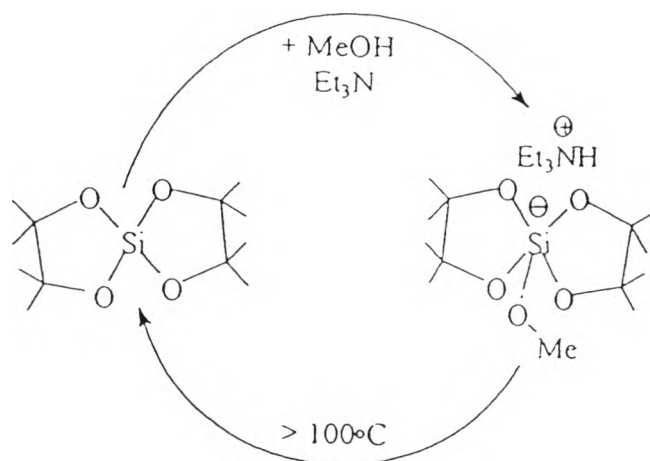


**Scheme V : Cs glycolato pentacoordinate silicate in MeOH.**

In related work, Frye (1970; 1971) discovered that spirosilicates react in MeOH at ambient temperature with amine base, e.g. triethylamine ( $\text{Et}_3\text{N}$ ), to form pentacoordinate anionic silicate with ammonium counterions, and these species were not stable above  $\approx 100^\circ\text{C}$ , at



which temperature the reverse reaction occurs to form tetracoordinate spirosilicate, as shown in Scheme VI.



**Scheme VI : Synthesis of pentacoordinate anionic silicate from reaction of spirosilicate and amine base .**

Frye's observation led us to explore the use of high boiling point (bp.> 200°C) amine base in place of Group I hydroxides or Group II oxides, e.g. triethylenetetramine (bp.~266°C, TETA) and triethanolamine [N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub>, bp. 250°C (at 25 torr), TEA]. Both amines can be used either in catalytic or stoichiometric quantities to dissolve SiO<sub>2</sub> as discovered by Laine et al. (unpublished work).

All of the above information show that Si-O bonds cleavage occur at the same time as new, chemically equivalent Si-O bonds form. This phenomenon has been investigated as the possible crosslinking reaction whereby glycolato silicates react with the crosslinking agent glycerol.

### 1.3 Research Objectives

The objectives of this work are to synthesize glycolato siloxanes and crosslink with glycerol ( $\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ ). Preliminary studies on the physical properties of crosslinked products were carried out. In addition, the mechanical properties measurement is studied by the changing of the modulus.