

CHAPTER II

LITERATURE SURVEY

2.1 Literature Survey

The sol gel process offers new syntheses of oxide materials [*Laine, R. M. (1989)*]. Starting from molecular precursors, such as metal alkoxides, an oxide network is obtained via inorganic polymerization reaction. Initiation is performed by the hydroxylation of metal alkoxides which occurs upon the hydrolysis of alkoxy group as follows:



As soon as hydroxy groups are generated, propagation occurs through a polycondensation process. Depending on experimental conditions, two competitive mechanisms have to be considered. They can be described as follow:

- i) Olation: formation of hydroxo bridges through the elimination of solvent molecules

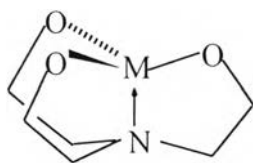


ii) Oxolation: formation of oxygen bridges through the elimination of H_2O or ROH .



These three reactions (hydrolysis, oxolation, olation) can be involved in the transformation of a metal alkoxide precursor into an oxide network. The structure and the morphology of the resulting network strongly depend on the relative contribution of each of them. These reactions can be described as nucleophilic substitutions which depend on the nucleophilic group (H_2O , OH^- , HO-M), the leaving group (ROH , H_2O) and the metal atom (Si , Ti , Zr , $\text{Al} \dots$).

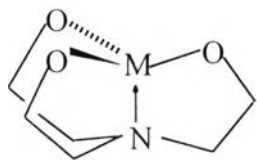
Voronkov and Zelchan (1965) proposed term metallatrane, simply atranes that are intramolecular complex cyclic ester or alkoxides of tris(2-hydroxyalkyl)amines. They have a skeleton of general structure I, used for aminotrialkoxy derivatives of different element.



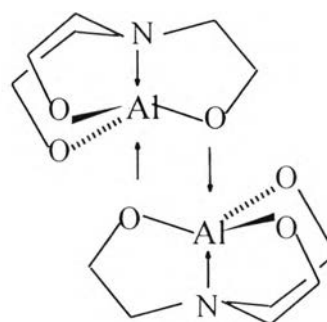
I

Where M is an n -valent element having inorganic or organic substituents when $n > 3$. Altrane structures are generally characterized by the tricyclic model wherein a transannular $\text{M} \leftarrow \text{N}$ bond is assumed to be present.

The properties of alumatrane monomer I and its oligomers have been reported in many works [Hein and Albert (1952); Mehrotra (1962); Shiklover et al. (1984); Bradley et al. (1978); Voronkov and Baryshok (1982); Mehrotra and Rai (1991)]. Cryoscopy [Hein and Albert (1952)] and ebullioscopy [Mehrotra (1962)] are indicated the degree of association to be octameric and hexameric, respectively. A mass spectroscopic (EI 70 eV) study [Mehrotra (1962)] revealed the stability of dimer II in gas phase.

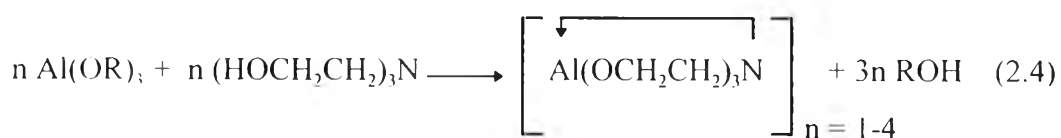


Monomer I

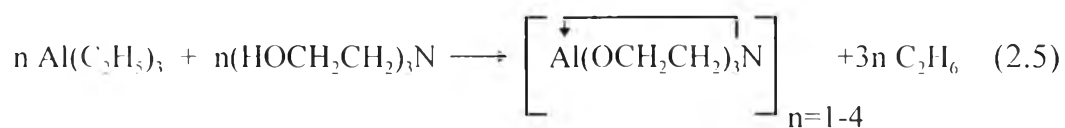


Dimer II

Alumatranes can be synthesized via several methods. The simplest alumatrane was prepared by the reaction of aluminum alkoxide with triethanolamine in an aromatic solvent (benzene [Mehrotra (1962)], toluene [Thomas et al., (1961)]) or with no solvent [Hein et al., (1952); Icken et al., (1964); Stanley (1968); Elebing et al., (1964)], as shown in equation 2.4

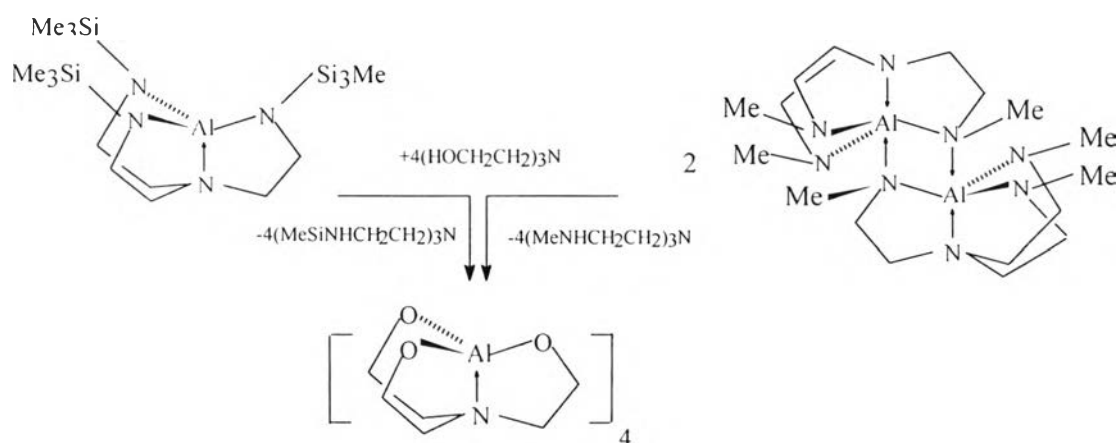
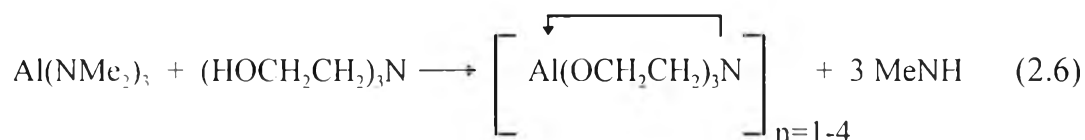


Triethylaluminum also reacts with triethanolamine in toluene or hexane at -78°C to form alumatrane [Higashi et al., (1968)] (eq 2.5).



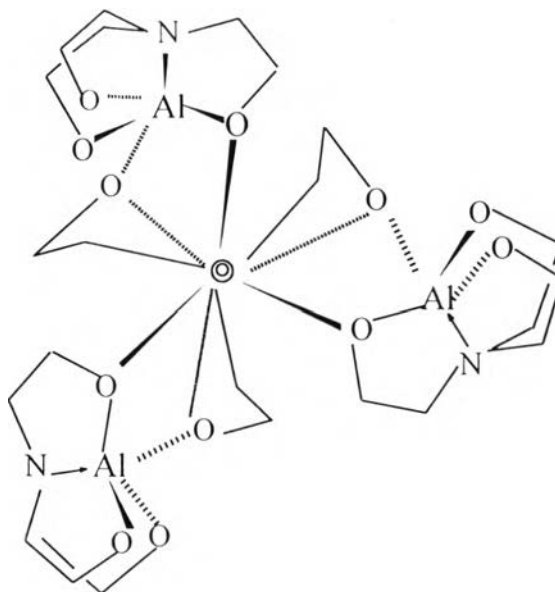
R = *i*-Pr, *i*-Bu

Verkade et al., (1993) synthesized alumatrane by alcoholysis of tris(dimethylamido)aluminum with triethanolamine (eq 2.6) and transligation of monomeric and dimeric alumatranes with triethanolamine (Scheme 2.1).



Scheme 2.1 Transligation of Monomeric and Dimeric Alumatranes with Triethanolamine, Source: adapted from *Verkade (1993)*.

Verkade et al., (1993) also found tetramers in solution and mass spectra also suggested the stable tetramer ion in the gas phase (Scheme 2.2).



Scheme 2.2 Newman Projection Down the Al-N Bond from an X-ray Crystallographic Determination of Tetrameric Alumatrane, Source : Adapted from *Verkade (1993)*.

The starting materials of all synthesized alumatrane complexes involved either aluminum alkoxide $[Al_2(OR)_3]$ or aluminium alkyls $[Al(R)_3]$ which are expensive and multistep syntheses. *Laine et al.* have developed an inexpensive method of converting metal oxides, namely aluminum and silica, into novel materials ranging from ion conducting (*Chew et al. Submitted for publication*), liquid crystalline polymers (*Ray et al.*, (1992) to oligomeric and polymeric precursors.

Laine et al. (1992), found that by employing higher boiling point amine base (b.p. >200°C), such as triethanolamine (TEA, b.p. 270°C at 15 torr) and triethylenetetramine (TETA, b.p. 266°C), in place of group I or II hydroxides or oxides, they can be used either in catalytic or stoichiometric quantities to dissolve SiO₂. Moreover, they also found that approximately stoichiometric quantities of TEA will effectively dissolve Al(OH)₃. The “oxide one pot synthesis (OOPS) process” for alkoxyalanes was developed after it was discovered that stoichiometric amounts of TEA would dissolve aluminum hydroxide, the source material for most pure alumina [*Kirk-Othmer (1979)*; *Cotton and Wilkison (1987)*].

Petchsuk A., Wongkasemjit S., and Laine(1994) synthesized alumatrane directly from Al(OH)₃ and TEA, and found pentamer, tetramer, trimer and most stable species, dimer, from mass spectroscopic, ¹H-, ¹³C- and ²⁷Al-NMR data. When using TETA in the reaction, mass spectroscopic data indicated the same mixture of oligomers. The integral method is used to study the reaction kinetics. The reaction of Al(OH)₃ and TEA is second order overall, first order with respect to Al(OH)₃ and first order with respect to TEA. The activation energy of this reaction was obtained using the Arrhenius’s equation and it was estimated to be 62 ± 5 kJ.mol⁻¹.

Recently, *Laine et al., (1996)* reported that the most important observations are automatically-mixed materials providing ready access to phase pure ceramics in MgO, SiO₂, Al₂O₃ system. In addition, they are very easily prepared even in large quantities (kg scale) from inexpensive starting materials, and readily processed into a variety of shapes. While atomic-mixing is seen for the spinel precursor, the cordierite and mullite precursors because the precursors are highly homogeneous rather than molecular, bi- and trimetallic alkoxydes.

Masaoki and coworkers, (1994) studied on dynamic viscoelasticity through gelation process of a linear polymer having functional groups at both ends. The gelation proceeds by irreversible end-linking reaction and the molecular weight between crosslinks is almost constant. Critical exponents for viscosity, compliance, and equilibrium shear modulus are obtained.

Akihiro et. al, (1994) reported about dynamic viscoelasticity of α,ω -dimethyl silyl poly(propylene oxide) solutions through the gelation process with end-linking. The gel point was determined as the reaction time, $t = t_c$, at which the storage and the loss shear moduli, $G'(\omega)$ and $G''(\omega)$, respectively, both became proportional to ω^n over the whole ω range measured. Effect of polymer molecular weight, M , and concentration, c , on the steady-state viscosity η before the gel point and the equilibrium modulus G_{eq} after the gel point were examined in terms of critical exponents, k and z , defined by power laws. The presence of entanglement coupling in the prepolymer solutions made the critical behaviour of η and G_{eq} obscure and affected the exponent values.

De Groot A.W. et.al, (1991) reported the using of quasielastic light scattering to determine the diffusion coefficients of cellulose in the ammonia/ammonium thiocyanate ($\text{NH}_3/\text{NH}_4\text{SCN}$) solvent system and the effective hydrodynamic radius of the dissolved molecules. Additionally, they used light microscopy to determine the minimum critical volume fraction or liquid crystal formation.

Jamieson A.M. et.al., (1992) used the dynamic light scattering to study nematic monodomains which contain side-chain and main-chain liquid crystal polymers dissolved in a low molar mass nematogen, 4'-n-pentyl-4-cyanobiphenyl (5CB). Addition of both side-chain and main-chain polymers results in substantial decreases in the relaxation rates of the splay, twist and bend director distortions. However, for the side-chain polymers, the relative decrease in the relaxation rate of bend mode is larger than twist and splay

modes and is strongly dependent on backbone flexibility and space length. In contrast, for main chain polymers, the relative decrease in relaxation rate is large for splay and twist and small for the bend mode.

2.2 Objectives

The aim of this research are to synthesize and characterize alumatrane complexes that produced by the oxide one pot synthesis, OOPS, process directly from aluminum hydroxide ($\text{Al}(\text{OH})_3$) and triethanolamine. Products were characterized by TGA, FTIR, viscosity measurement and light scattering measurement. Viscosity measurement was used for investigate the effect of concentration variation of TEA, reaction temperature, reaction time and TETA concentration on the properties of alumatrane complexes. Dynamic light scattering measurement was utilized for study of diffusivity of alumatrane complex chains in solutions to confirm the characteristic appearance of alumatrane complexes behavior observed by viscosity measurements.