CHAPTER I

INTRODUCTION

1.1 General

Aluminum is the most abundant metallic element in the earth's crust and always occurs in the combined state with other elements such as iron, oxygen, and silicon [Harte, L.D. and Lense, E., (1990)]. The hydrolysis chemistry of aluminum has been of interest for over a century because of its relationship to soil chemistry and because the most common mineral source of aluminum, bauxite, is composed largely of aluminum hydroxides and oxo-hydroxides. In the Bayer process [Bayer, (1888)], bauxite is reacted with hot sodium hydroxide to convert the aluminum in the ore to sodium aluminate according to the reaction (1.1)

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O \qquad (1.1).$$

After separation of the insoluble residue, consisting of mainly ferric oxide and silica, the aluminate solution is slowly cooled to 25°C to precipitate aluminum hydroxide $[Al(OH)_3]$ according to the reaction (1.2)

$$2NaAlO_2 + 2H_2O \longrightarrow Al(OH)_3 + NaOH \qquad (1.2).$$

The Al(OH)₃ is then thickened, washed, and calcined at 1100°C to produce aluminum oxide, Al₂O₃.

There are two forms of anhydrous Al₂O₃, namely *diaspore* [α-AlO (OH)] and *boahmite* [γ-AlO(OH)]. α- Al₂O₃ is stable at high temperatures and also indefinitely metastable at low temperatures. It occurs in nature as the mineral corundum and may be prepared by heating γ-Al₂O₃ or any hydrous oxide above 1000°C. γ -Al₂O₃ is obtained by dehydration of hydrous oxides at low temperatures (~450°C). α-Al₂O₃ is hard and resistant to hydration and to attack by acids. γ -Al₂O₃ readily absorbs water and dissolves in acids. The aluminas used for chromatography and conditioned to different reactivities are γ-Al₂O₃. Large quantities of α-Al₂O₃ are used in industry as a support material for heterogeneous catalysts.

Chemical (sol-gel and preceramic polymer) processing of glass and ceramic materials has become a major field of study in the past three decades because it provides access to novel ceramic and glass shapes (fibers, films/coatings, membranes, etc.) with novel microstructures (aerogels, zeolites, nanocomposites, etc.) and novel properties (gradient indices of refraction, superconductivity, superplasticity, abrasion resistance, etc.) [Laine, R.M., and Robinson, T.R., (1991)]. Chemical processing permits exceptional control of particle size and size distribution, phase and chemical purity, and microstructure.

One property of the sol gel process is the ability to control the process all the way, from the molecular precursor to the product. Sol-gel chemistry offers many advantages: a lower processing temperature allows the synthesis of metastable oxide phases and synthesis of new materials including both organic and inorganic components [Schmidt, H., and Scholze, H., (1984)]. The rheological properties of sols and gels allow the processing of fibers of films by techniques such as spin-drawing, dip-coating or screen - printing [Sanchez,

C. and Livage, J., (1990)]. Because of the remarkable uses of these compounds in the production of novel materials, such as ion conducting polymers [Chew et al, unpublished], liquid crystalline polymers [Ray et al, 1992], ceramic precursors [Zhang et al, 1991], and compounds exhibiting novel charge transfer neutral alkoxy silanes and alanes [Laine et al, unpublished]. These syntheses could provide new chemicals, polymers, and ceramics. in one or two steps directly from mineral sources.

1.2 Literature survey

Voronkov and Zelchan in 1965 proposed the term of metallatranes, or simply atranes which is an abbreviation used for aminotrialkoxy derivatives of different elements that contain a skeleton of general structure I,

I
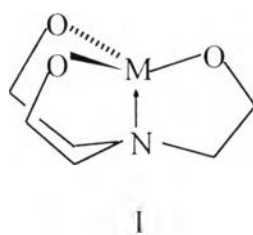
where M is an n-valent element having inorganic or organic substituents when n>3. For example, aminotrialkoxysilanes, aminotrialkoxyphosphoranes, and aminotrialkoxyboranes give silatranes, phosphatranes and boratranes, respectively. Atrane structures are generally characterized by the tricyclic model wherein a transannular M←N bond is assumed to be present.

In various literature reports [Bradley, Mehrota and Gaur, (1978); Voronkov and Baryshok, (1982); Mehrota and Rai, (1967)], the behavior of the alumatrane has been described as dimeric (depicted as I$_2$) in the gas phase; monomeric. hexameric, and octameric in solution; and tetremeric (by X-ray

crystallography) in the solid state. A mass spectroscopic (EI 70 eV) study clearly revealed the stability of the dimer [Lacey and McDonald, (1976)] and tetramer [Pinkas and Verkade, (1993)] in the gas phase. The tetramer contains one hexacoordinate and three pentacoordinate aluminums, depicted as I_4 [Pinkas and Verkade, (1993)]. There was also evidence indicating that the tetrameric structure of alumatrane was found in both the solution and solid state ^{27}Al-and ^{13}C-NMR [Pinkas and Verkade, (1993)].

I_2

I_4
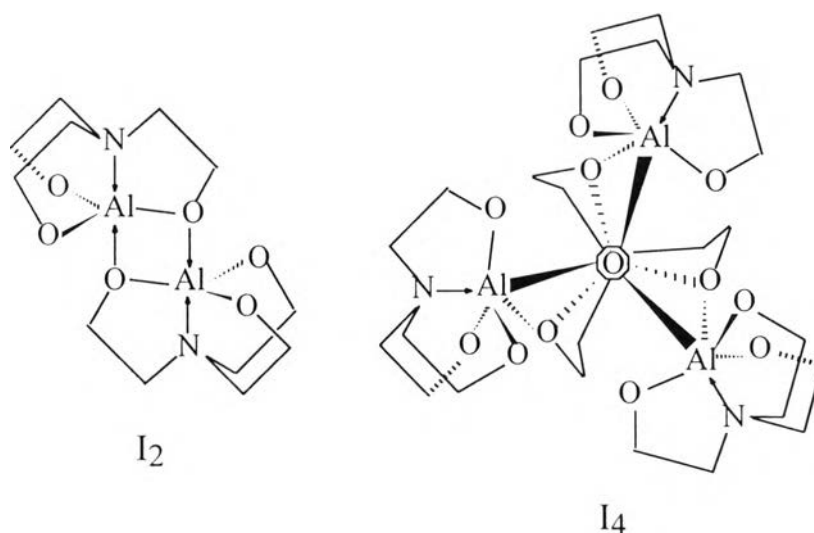
As for its applications, alumatranes are efficient catalysts for the transesterification of dicarboxylic acid esters [Thomas, Groszos and Day, (1961)], cocatalysts for removal of butadiene in the purification of the C4-fraction from the cracking and pyrolysis of oil [Braman, (1963)], and promoters for the formation of propylene glycol in the oxo-synthesis [Kaplan, Walker and O'Conner, (1979)]. They are also used to accelerate thermoreactive resin curin and as stabilizers in the storae of cured resins [Elbing and Finestone, (1964)], eta. [Icken and Jahren, (1964); Beekman and

Schmank. (1969); stanley. (1968); Furukawa and Kono, (1975); Rudner and Moores, (1961); Kugler and Prucek, (1970); March, (1968)].

There are several methods to prepare alumatranes. The simplest alumatrane was prepared in high yield 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); Elbing et al., (1964)] according to eq. 1.1

$$n\ Al(OR)_3\ +\ (HOCH_2CH_2)_3N \longrightarrow \left[\overline{Al(OCH_2CH_2)_3N}\right] \quad (1.1)$$
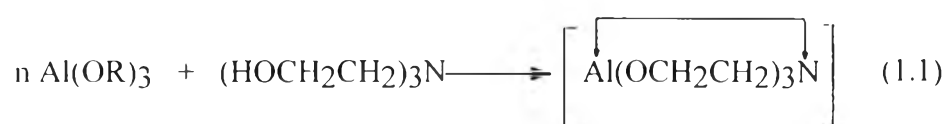
The starting materials to synthesize alumatrane complexes, aluminum alkoxides [Al(OR)$_3$] or aluminum alkyls [Al(R)$_3$], are expensive and the syntheses are multistep. Laine et al. have developed an inexpensive way to convert metal oxides, namely, alumina and silica, into novel materials ranging from ion conducting [Chew et al. Submitted for publication], liquid crystalline polymers [Ray et al., (1992)], to oligomeric and polymeric precursors.

Laine et al. found that higher boiling point amine bases (b.p.>200°C), such as triethanolamine (TEA) and triethylenetetramine (TETA) can be used either in catalytic or stoichiometric quantities to dissolve SiO_2. Moreover, they also found that approximately stoichiometric quantities of TEA will effectively dissolve $Al(OH)_3$. The "Oxide One Pot Synthesis Process (OOPS)" 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-Othemer, (1979); Cotton and Wilkinson, (1967)].

Synthesis of the Al-TEA alkoxyalane polymers from a very inexpensive and relatively abundant starting material, $Al(OH)_3$, offers significant potential to develop new types of aluminum chemistry. For example, new catalysts for the Meerwein - Ponndorf-Verley reduction /

Oppenauer oxidation [March, (1968)]. It also provides an explanation for the role TEA plays in stabilizing intermediate sols in sol-gel processing [Takahashi et al, (1988), Tohge et al, (1991)].

Petchsuk et al., (1995) synthesized alumatrane directly from $Al(OH)_3$ and TEA. and found pentamer, tetramer, trimer and the most stable species, dimer from mass spectroscopic data, ^1H-, ^{13}C-and ^{27}Al-NMR. Moreover when TETA. stronger base than TEA, was used, 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 first order wth respect to [TEA]. The activation energy for this reaction was obtained using the Arrhenius' equation and it was estimated to be 62 ± 5 KJ.mol^{-1}.

Recently, Opornsawad, Wongkasemjit, and Laine (1996) synthesized alumatrane directly from $Al(OH)_3$ and TIS, via the one step process, called "OOPS" process. Mass spectra revealed that products were oligomers. The main product was pentamer bonded with TIS that lost one H_2O molecule. The integral method is used to study the reaction kinetics. The reaction of $Al(OH)_3$ and TIS is second order overall, first order with respect to aluminum hydroxide and first order with respect to TIS. The dissolution rate increased when the reaction temperature increased. The activation energy of this reaction was about 24 ± 2 KJ.mol^{-1}.

Although, the synthesis of alumatrane complexes have been developed by many researchers but there are no published reports concerning with the physical properties such as viscous properties or the molecular weight of the synthesize products. Since the technique for determining the molecular weight such as GPC does not work for this kind of material, dynamic light scattering and viscometry are used to revel interesting properties of Al-TIS alkoxyalane polymers. These methods yield information about intrinsic viscosity ($[\eta]$), diffusion coefficient (D_f), and hydrodynamic volume (R_H). Combining the

information from two techniques, the molecular weight can be calculated by assumed the spherical particles.

The sol-gel transition can be studied by monitoring the change in viscoelastic behavior of the material . At the gel point, a power-law frequency dependence of the viscoelastic functions $G'(\omega)$, $G''(\omega)$ and $\eta^*(\omega)$ was observed. The relationship between the power-law exponent and the structure of the critical gel were discussed. Jamieson et al. (1993) studied the viscoelastic properties through the sol-to-gel transition of gelatin in the concentration range 4-14 % as a function of pH and ionic strength.

James C. Scanlan and H. Henning Winter studied the composition dependence of the viscoelastic of end-linked poly(dimethylsiloxane) at the gel point. Precursor composition is shown to have a considerable impact on the viscoelastic properties of a polymer at the gel point. End-linked poly-(dimethylsiloxane) polymers were prepared with various stoichiometry, chain length, and concentration.

Although rheological measurements characterize the bulk properties of a solution (for example, the viscosity or storage modulus), the dependence of rheological properties on concentration, molecular weight, or shear rate can be used to infer structure information on rather short length scales [Brinker, C.J. and Scherrer, G., (1989)]. Qualitative rheological investigations have been performed on numerous sol-gel silicate systems. For example, the gel point is often identified by examination to be the time at which the solution loses fluidity, i.e., no flow of the gel is observed when its container is tipped. Numerous quantitative viscosity measurements have also been performed during the course of the sol-to-gel transition. The gel point is often defined as the time at which the viscosity is observed to increase abruptly.

1.3 Objectives

Alumatrane complexes can be synthesized directly from reactions of aluminum hydroxide ($Al(OH)_3$) and triisopropanolamine (TIS). The products were characterized by TGA, FTIR, and ^{1}H-NMR. The viscosity measurement was used to study the effect of the concentration of triisopropanolamine, concentration of catalyst, TETA, reaction time, and reaction temperature on the viscous properties of the products. Moreover, the effect of triethylenetetramine (TETA) on the molecular weight of the products was studied by laser light scattering technique, as well.