Chapter III

Result and discussion

3.1. Synthesis of organotin monomers.

Grignard reaction was used for the synthesis of organotin monomers in this studies. The reactants and the solvents must be absolutely dry and the moisture must be totally exduded from the reaction medium. This can be acchieved by using proper equipments and known procedures. The Grignard synthesis, consisting of many steps, required careful operation [18].

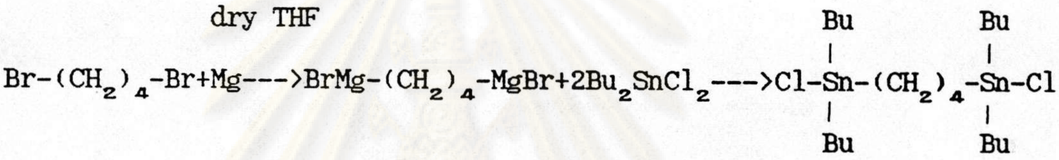
The di-Grignard synthesis was modified by replacing the solvent, tetrahydrofuran (THF), by benzene after the Grignard reagent had been synthesized and allowed the Grignard reagent to react with di-organotin chloride in benzene. This increased the yield of the product and prevented the formation of a magnesium bromide ether complex [17] which its IR spectrum is shown in the appendix. Then iodine and 1, 2 dibromoethane were added as initiater in order to improve the yield of di-Grignard reagents.

Several organotin monomers were prepared by various modification which could be described as follows.

3.1.1. Synthesis of organotin monomers by using iodine as initiator.

3.1.1.1. 1,4-Butylene-bis (dibutyltin chloride)

The reaction of di-Grignard reaction of dibromobutane and dibutyltin dichloride in refluxing dry benzene under carbon dioxide-free nitrogen gave the title compound



$$\mathrm{Br{-}(CH_2)_4{-}Br + Mg \xrightarrow{\text{dry THF}} BrMg{-}(CH_2)_4{-}MgBr + 2Bu_2SnCl_2 \longrightarrow Cl{-}\underset{Bu}{\overset{Bu}{Sn}}{-}(CH_2)_4{-}\underset{Bu}{\overset{Bu}{Sn}}{-}Cl}$$

where Bu = n butyl

as crystalline solid with melting point of 112-114°C. The elemental analysis was consistent well with the formular, 1,4 butylene-bis(dibutyltin chloride). IR spectrum was shown in Fig.4 and H^1 NMR and ^{13}C NMR spectra were shown in Fig.5 and Fig.6.

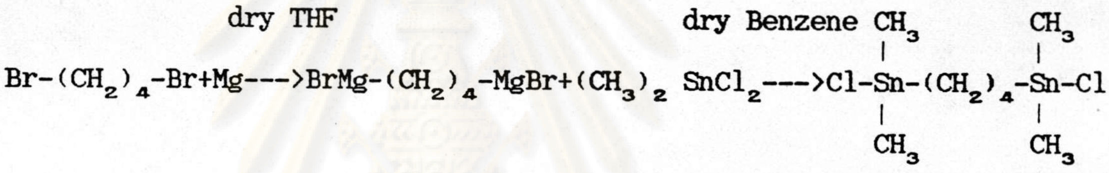
3.1.1.2. This product was synthesized from 1,4 dibromobenzen and dibutyltin dichloride by using iodine as initiator.

The IR spectrum was shown at Fig.7 and ^1H NMR and ^{13}C spectra shown in Fig.8 and Fig.9.

However, when iodine was used as initiater, another product was obtained as a white solid with melting point of 108-110°C. This product was presumably a compound with Sn-Sn bond [25, 26].

3.1.1.3. 1,4-butylene-bis (dimethyltin chloride)

The reaction of 1, 4 dibromobetane and dimethyltin dichloride gave the title compound as



$$Br-(CH_2)_4-Br+Mg \xrightarrow{\text{dry THF}} BrMg-(CH_2)_4-MgBr+(CH_3)_2\,SnCl_2 \xrightarrow{\text{dry Benzene}} Cl-\overset{CH_3}{\underset{CH_3}{Sn}}-(CH_2)_4-\overset{CH_3}{\underset{CH_3}{Sn}}-Cl$$

a colourless liquid with boiling point of 85-87°C at 4 mmHg.

This product had bad smell, and was soluble in chloroform, tetrahydrofuran, etc. Spectrum of IR and NMR showed in Fig.19, 20 and 21.

3.1.1.4. The Product obtained from the reaction of 1,4-dibromobutane and diphenyltin dichloride.

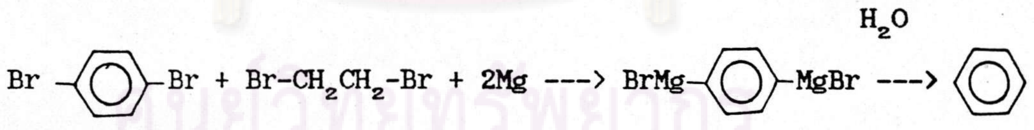
This product dissolved in chloroform and tetrahydrofurn., etc. IR and NMR spectra were shown in Fig.13 and 14, 15.

However, when iodine was used as initiater another product was obtained as a white solid with melting point of 192-193°C. This product was presumably a compound with Sn-Sn bond [25, 26].

3.1.2. Synthesis of organotin monomer by using di-Grignard reagent of 1, 2 dibromoethane

3.1.2.1. Synthesis of di-Grignard reagent.

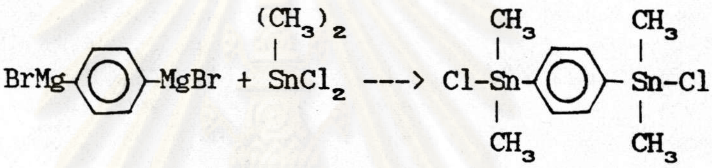
The direct preparation of di-Grignard reagent from organic dihalides using conventional conditions gave very poor yields. Dibromoethane was used as initiator which was called "entrainment" [14, 16, 18]. However, when dibromoethane was added as initiator in the so called "entrainment", the yield was improved significantly.



Gas chromatography was used to monitor the formation of di-Grignard reagent. It showed that benzene was obtained in (retention time : tetrahydrofuran 7.368 min, benzene 8.51 min) the reaction proceeded according to the above equation.

3.1.2.2. Synthesis of 1,4-phenylene-bis-(dimethyltin chloride)

The method of preparation 1,4-phenylene bis-(dimethyltin chloride) was similar to that of 3.1.1.3 except that 1,4-dibromolbenzene was used instead of 1, 4-dibromobutane. 1,4 phenylene bis-(dimethyltin chloride) is a solid with melting point of 162-163°C.



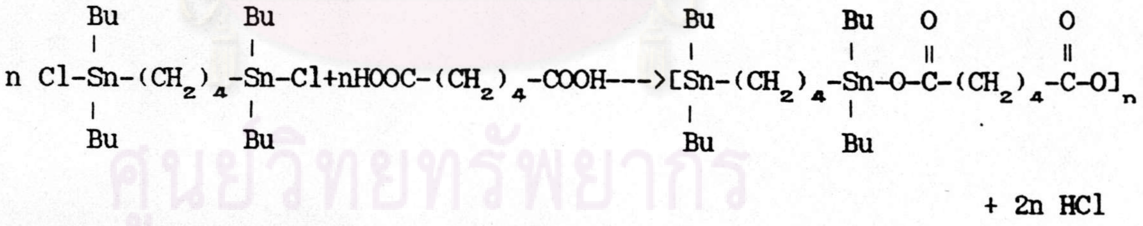
IR, NMR Spectrum were shown in Fig.22, 23 and 24. Result of elemental analysis was consistent well with the proposed structure.

3.2. Preparation of Condensation Polymerization [21]

3.2.1. Poly[1,4-butylene bis-(dibutlyltin) adipate], [Poly(1,4-BDDAA)]

Poly[1,4-butylene-bis-(dibutyltin) adipate] was obtained from the polymerization of 1,4-butylene-bis-(dibutyltin chloride) and adipic acid in o' dichlorobenzene.

o'-dichlorobenzene was used because of three reasons. Firstly, Poly(1,4-BDDAA) was a polyester that should dissolve in chlorinated solvent [11]. Secondly, in synthesizing polyester, polymersization temperature should be used between 150-200°C [1]. Finally when the polymerization was finished, Poly(1,4-BDDAA) was obtained in good yield.



$$n\ \mathrm{Cl{-}\overset{Bu}{\underset{Bu}{Sn}}{-}(CH_2)_4{-}\overset{Bu}{\underset{Bu}{Sn}}{-}Cl + nHOOC{-}(CH_2)_4{-}COOH \longrightarrow [\overset{Bu}{\underset{Bu}{Sn}}{-}(CH_2)_4{-}\overset{Bu}{\underset{Bu}{Sn}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}O]_n + 2n\ HCl}$$

Poly(1,4-BDDAA) was a white solid at room temperature, and was insoluble in most solvent except o'dichlorobenzene. Ethyl acetate was used to precipitate this polymer from o-dichlorobenzene solution because it gave the best yield and both reactants dissolved in this solvent.

IR Spectrum of Poly(1,4-BDDAA) was shown in Fig.25, 26 and 27.

Elemental analysis of poly(1,4-butylene-bis-(dibutyltin) adipate). The results were consistent with the molecular formular $C_{26}H_{52}O_4Sn_2$ of the propose polymer structure which has C 46.85% : H 7.89% : Sn 35.69% : 09.61%.

Poly(1,4-BDDAA) was prepared by a condensation polymerization which the byproduct regulated the yields or percent conversion. Therefore, if the byproduct is eliminated from the reaction during polymerization, conversion will increase [2]. The byproduct of this reaction was hydrogen chloride. Therefore the reaction was purged with nitrogen in order to eliminate hydrogen chloride or trapped with pyridine to form pyridine hydrochloride [6]. Therefore, polymerization in the presence of pyridine gave the best yields.

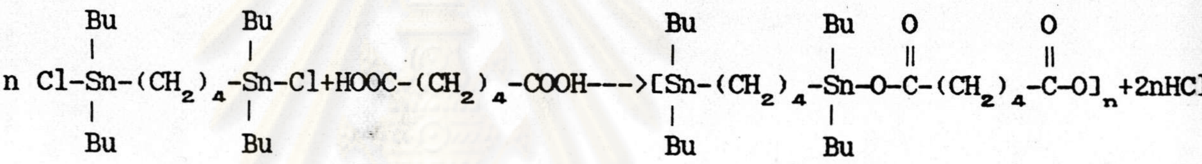
In condensation polymerization, conversion or yields depended on time [1]. From this study the longer the reaction time, the higher the percent conversion and the yield (Fig.32,43). The best yield was obtained when the mole ratio of 1,4-butylene bis-(dibutyltin chloride : adipic acid was 1 : 1.

Solubility of poly(1,4-BDDAA was shown in Table.13 Poly(1,4-BDDAA) dissolved only in o-dichlorobenzene. Molecular weight could not be determined because of solubility problem [12, 25].

Tg, Tc, Tm of polymers were shown in Table 12 and Fig.44, 52, [12, 13, 19].

3.2.2. Poly[1,4-butylene-bis-(dibutyltin) malonate]

Poly(1,4-BDDMA) was synthesized (sec 2.3.2) from the reaction of 1,4-butylene-bis-(dibutyltin chloride) and malonic acid at 150°C in o-dichlorobenzene for 20 hrs. Under oxygen-free nitrogen using pyridine as catalyst.



$$n\ Cl-\underset{Bu}{\overset{Bu}{Sn}}-(CH_2)_4-\underset{Bu}{\overset{Bu}{Sn}}-Cl+HOOC-(CH_2)_4-COOH\text{---}>[\underset{Bu}{\overset{Bu}{Sn}}-(CH_2)_4-\underset{Bu}{\overset{Bu}{Sn}}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O]_n+2nHC$$

where Bu = n-butyl

The (1,4-BDDMA) polymer was a white solid and its IR spectrum was shown in Fig.29 and 30. Solubility of polymers was shown in Table 13. Elemental analysis was crresponded to the propose formular.

Elemental analysis of Poly (1,4-BBDAA) $C_{23}H_{46}Sn_2O_4$

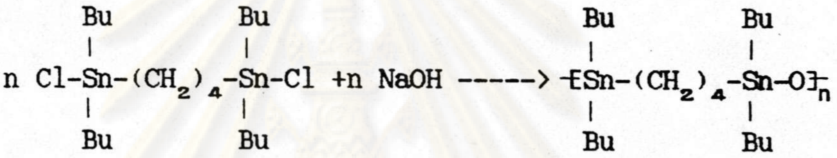
Poly (1,4 BDDAA)	C	H	Sn	O
Calculated	44.24	7.45	38.05	10.26
Found in prepared ODB	44.48	7.06	38.55	9.91
Found in prepared DMF	44.12	7.86	37.85	10.17

The polymer where prepared in o-dichlorobenzene, was odorless but the polymer prepared in DMF had bad smell. The Polymer prepared in DMF was easily soluble in o-dichlorobenzene.

3.3. Reaction between organotin monomer with sodium hydroxide.

3.3.1. Reaction between 1,4-butylene-bis-(dibutyltin chloride) and Sodium hydroxide.

The reaction between 1,4-butylene-bis-(dibutyltin chloride) and sodium hydroxide was carried out in aqueous tetrahydrofuran.



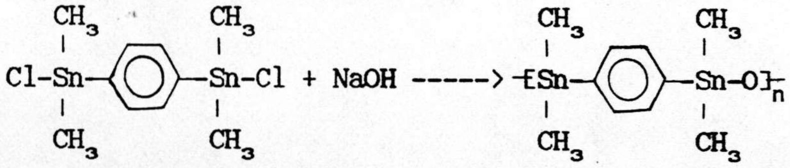
$$n\ Cl-\underset{Bu}{\overset{Bu}{Sn}}-(CH_2)_4-\underset{Bu}{\overset{Bu}{Sn}}-Cl + n\ NaOH \dashrightarrow -\!\!\left[Sn... \right]$$

where Bu = n-butyl.

This product is a white solid and insoluble in any solvents. IR spectrum was shown in Fig 31. From the IR spectrum, the 780-850 cm^{-1} peak was the characteristic peak of O-Sn group [3]. Result of elemental analysis was agreed with the propose formular. Solubility of this product was shown in Table 13.

3.3.2. Raction between 1,4-phenylene-bis-(dimethyltin chloride) and sodium hydroxide

Reaction (sec. 2.4 B) between 1,4-phenylene-bis-(dimethyltin chloride) and sodium hydroxide was carried out in aqueous tetrahydrofuran.



$$\mathrm{Cl{-}}\underset{CH_3}{\overset{CH_3}{\mathrm{Sn}}}\mathrm{{-}C_6H_4{-}}\underset{CH_3}{\overset{CH_3}{\mathrm{Sn}}}\mathrm{{-}Cl} + \mathrm{NaOH} \dashrightarrow \left[\underset{CH_3}{\overset{CH_3}{\mathrm{Sn}}}\mathrm{{-}C_6H_4{-}}\underset{CH_3}{\overset{CH_3}{\mathrm{Sn}}}\mathrm{{-}O}\right]_n$$

The product was a white solid at room temperature. Its IR spectrum was shown in Fig 53. This product was insoluble in any solvents.