CHAPTER 3

TIN(II) ALKOXIDES

3.1 Previous Experimental Observations on Tin(II) Alkoxides

An alkoxide is the conjugate base of an alcohol and therefore has an organic group R bonded to a negatively charged oxygen atom, usually written as RO^-. Alkoxides are both strong bases and good nucleophiles (unless R is very bulky, creating steric hindrance). Alkoxides, through generally not stable in protic solvents such as water, are found as intermediaries in various reactions including the Williamson synthesis reaction for ether formation [53].

Interest in the chemistry of alkoxides is due to their widespread application in both materials science and organic synthesis. Metal alkoxides have been applied successfully in particular to promote several organic reactions as catalysts/initiators in the polymerisation of olefins and lactones. Strong Lewis bases, such as alkoxides of alkali metals, aluminum and lanthanides, have been shown to be highly active in the polymerisation of such monomers as lactones, lactams and epoxides [54].

The most widely used alkoxide initiators for the ROP of cyclic esters are various tin and aluminum alkoxides. Their predominance is due to their ability to produce stereoregular polymer of narrow molecular weight distribution and controllable molecular weight, with well-defined end-groups [55]. A major difference between tin- and aluminum-based initiators is that tin initiators are good transesterification catalysts whereas aluminum initiators are not. On the other hand, tin initiators have the advantage of being more hydrolytically stable than their

aluminum counterparts and are therefore easier to handle and to use in polymerisations. Furthermore, the large difference in reactivity between tin(II) dialkoxides and aluminum trialkoxides (10^2 times in favour of tin(II)) comes mostly from the difference in ionic radii of the metal atoms resulting in a stronger polarisation of the tin-oxygen bond [56]. Also, the higher reactivity of tin(II) compounds in comparison with their tin(IV) counterparts may be explained by the better steric accessibility of the tin atom in the divalent derivative as well as its more pronounced ability to coordinate the approaching monomer molecule. The positive induction effect of the alkyl groups on tin(IV) additionally decreases its reactivity toward nucleophilic agents. Thus, after several years of research on tin(II) alkoxides, controlled polymerisations are now possible. Under mild reaction conditions, undesirable transesterification reactions are less pronounced.

The synthesis of tin(II) alkoxides was first reported about 40 years ago by Morrison and Haendler [57]. It involves the reaction between anhydrous tin(II) chloride, various alcohols ROH and triethylamine as HCl scavenger, as shown in equation (3.1) below.

$$SnCl_2 + 2\,ROH + 2\,(C_2H_5)_3N \longrightarrow Sn(OR)_2 + 2\,(C_2H_5)_3N.HCl \quad (3.1)$$

This was followed by Gsell and Zeldin [58] who reported spectroscopic (mass, IR, ^{1}H-NMR and Mossbauer) data for $Sn(OCH_3)_2$, $Sn(OC_2H_5)_2$ and $Sn(OC_4H_9)_2$. Apart from these two papers [57, 58], little else seems to have been reported on the synthesis of tin alkoxides, $Sn(OR)_2$, with R > C_4H_9. It has to be concluded therefore that tin(II) alkoxides are a relatively unexplored class of compound which merit further study.

Gsell and Zeldin [58] demonstrated that tin(II) alkoxides are white solids which exhibit an increase in solubility in organic solvents as the length of the alkoxy chain increases. The low solubility of $Sn(OCH_3)_2$ is well known and reactions involving the compound are carried out heterogeneously [59]. Although $Sn(OC_2H_5)_2$ is slightly soluble in polar solvents (CH_3CN, CH_2Cl_2), the butoxide, $Sn(OC_4H_9)_2$, was reported to be readily soluble in all organic solvents and could be purified by recrystallisation from toluene.

Surprisingly, the chemistry of these tin(II) alkoxides has not been fully explored and there have been very few reports of its reactions. The slow development of this field may well be linked to the paucity of property and structure information on these compounds as well as their low solubilities in organic solvents and sensitivity to oxygen and moisture. Thus, in this present study, four tin(II) alkoxides (R = *n*-C_3H_7, *i*-C_3H_7, *n*-C_4H_9 and *t*-C_4H_9) have been prepared and characterized by a combination of spectroscopy (IR, Raman, ^{1}H-NMR) and thermal analysis (DSC, TGA).

3.2 Synthesis of Tin(II) Alkoxides: Tin(II) *n*-Propoxide, Tin(II) *iso*-Propoxide, Tin(II) *n*-Butoxide and Tin(II) *tert*-Butoxide

3.2.1 Purification of Reagents

Anhydrous tin(II) chloride ($SnCl_2$) was stored in vacuo and used without further purification. Triethylamine was purified by simple distillation over calcium hydride. All alcohols (methanol, *n*-propanol, *iso*-propanol, *n*-butanol and *tert*-butanol) were purified by fractional distillation over sodium before use. The boiling point ranges are given in Table 3.1 alongside the corresponding reference values.

Table 3.1 Comparison of the observed boiling points/ranges of the reagents used in this work with the corresponding reference values.

Reagent	Boiling Point/Range (°C)	
	Observed*	Reference**
Triethylamine	86.0-88.0	88.8
n-Propanol	96.0-98.0	97.0
iso-Propanol	83.0	82.0
n-Butanol	119.0	116.0-118.0
tert-Butanol	83.0-85.0	83.0
Methanol	65.0	64.7
Dichloromethane	40.0	39.8-40.0

* as measured at 730 mm Hg (atmospheric pressure)

** as measured at 760 mm Hg (taken from Aldrich Chemical Cataloque)

3.2.2 Synthesis Procedure

Each tin(II) alkoxide was prepared from the reaction between anhydrous $SnCl_2$ and the corresponding excess dry alcohol in the presence of triethylamine as HCl scavenger, as described by Morrison and Haendler [57]. In a typical synthesis, approximately 5 g $SnCl_2$ were dissolved in 100-150 ml of the dry alcohol in a 250 ml round-bottomed flask under a dry N_2 atmosphere at room temperature (Figure 3.1). Enough triethylamine was added to cause a permanent precipitate. The precipitate was filtered and then washed with methanol and dry dichloromethane to remove the triethylamine hydrochloride by-product. The tin(II) alkoxide was dried in a vacuum oven at 40 °C and stored in a vacuum desiccator to avoid contact with atmospheric oxygen or moisture.

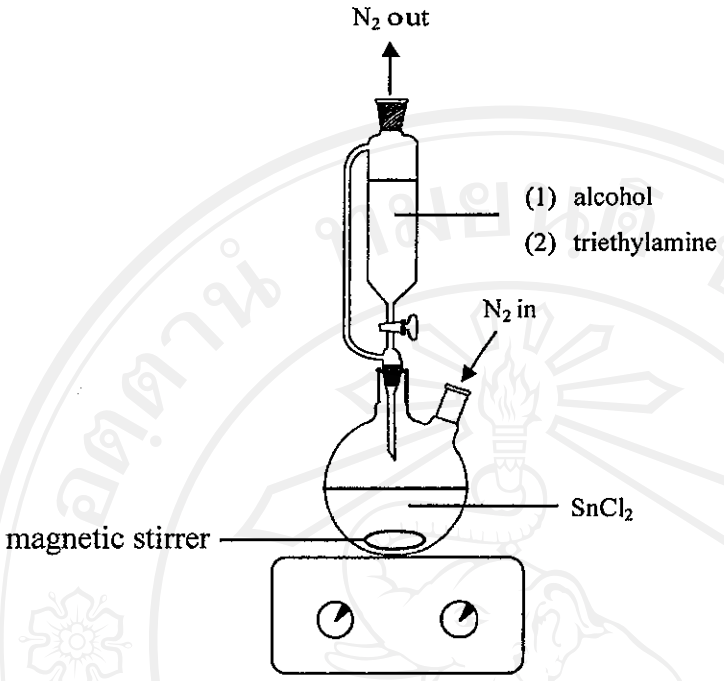


Figure 3.1 Apparatus used for the synthesis of the tin(II) alkoxides.

3.3 %Yields

Based on the assumption from equation (3.1) previously that

$$1 \text{ mol } SnCl_2 \longrightarrow 1 \text{ mol } Sn(OR)_2$$

the % yields (by mol) of the $Sn(OR)_2$ products were calculated from the equation:

$$\%\ Yield = \frac{mol\ of\ Sn(OR)_2\ product\ obtained}{initial\ mol\ of\ SnCl_2\ used} \times 100\%$$

The results are given in Table 3.2.

Sample Calculation of % Yield:

For the first sample (tin(II) *n*-propoxide) in Table 3.2

$$\% \text{ yield (by mol)} = \left(\frac{3.07\ g/236.81\ g/mol}{5.03\ g/189.62\ g/mol}\right) \times 100\%$$

$$= \frac{0.0130\ (mol)}{0.0265\ (mol)} \times 100\%$$

$$= 49\ \%$$

Table 3.2 Physical appearances and % yields of tin(II) alkoxides after purification.

Tin(II) Alkoxide	$SnCl_2$ (mol)	$Sn(OR)_2$ (mol)	Physical Appearance of Product at Room Temperature	% Yield (by mol)
Sn(*n*-OPr)$_2$	0.0265	0.0130	light yellow powder	49
Sn(*iso*-OPr)$_2$	0.0261	0.0133	light yellow powder	51
Sn(*n*-OBu)$_2$	0.0264	0.0157	light yellow powder	60
Sn(*tert*-OBu)$_2$	0.0261	0.0159	light yellow powder	61

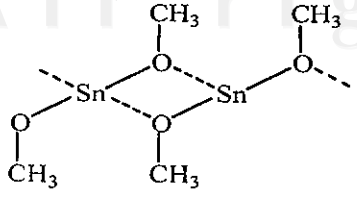
3.4 Characterisation of Tin(II) Alkoxides

3.4.1 Infrared Spectroscopy (IR)

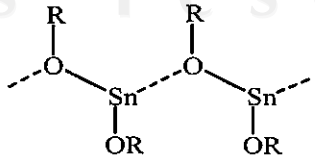
The infrared (IR) spectra of the purified tin(II) alkoxides products are shown in Figures 3.2-3.5. The spectra, which were obtained from samples prepared in the form of KBr discs, compare very closely with that of commercial tin(II) methoxide in Figure 3.6. The major vibrational peak assignments are listed in Table 3.2.

Even though the IR spectra of the synthesized products in Figures 3.2-3.5 are quite weak in terms of peak resolution, they are consistent with the chemical structures of tin(II) alkoxides by comparison with the spectrum of the commercial $Sn(OMe)_2$ in Figure 3.6. It is also significant to note that the product spectra do not contain peaks which are characteristic of triethylamine hydrochloride, $(C_2H_5)_3N.HCl$, the by-product which is formed as a co-precipitate with the alkoxides in the synthesis reactions. The spectrum of commercial triethylamine hydrochloride, as shown in Figure 3.7, contains many peaks which are quite distinct from those in the alkoxide spectra. This confirms that the hydrochloride by-product was completely removed from the alkoxides during their purification by solvent extraction with methanol.

By far the most prominent peak in the product spectra is that at around 550 cm^{-1} due to Sn-O bond stretching. This peak is highly characteristic of tin(II) alkoxides. Compared to this, the other bond vibrations (C-O, C-H) associated with the alkoxide groups are relatively weak. The broad O-H peak at 3700-3000 cm^{-1} in all of the spectra is due to moisture (H_2O) in the KBr used. These various bond vibrations are assigned in detail in Table 3.3. In the context of Table 3.3, it should be mentioned here that it has been suggested that $Sn(OCH_3)_2$ in the solid state exists in the polymeric form shown below on the left whereas higher alkoxides exist in the form on the right [58].



$Sn(OCH_3)_2$



$Sn(OR)_2$ $(R>CH_3)$

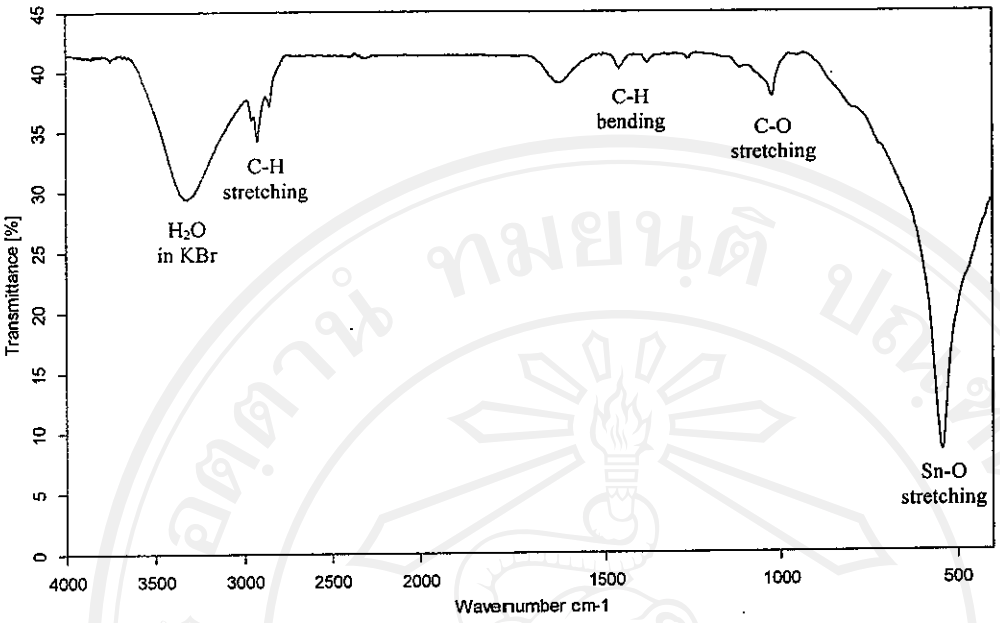


Figure 3.2 Infrared spectrum of the synthesized tin(II) *n*-propoxide, Sn(*n*-OPr)$_2$.

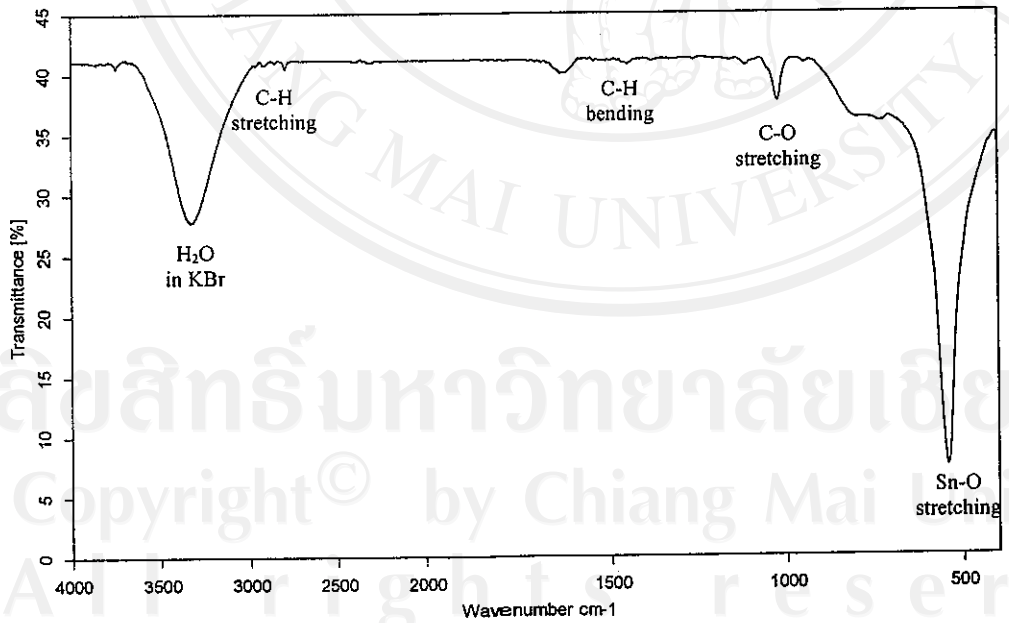


Figure 3.3 Infrared spectrum of the synthesized tin(II) *iso*-propoxide, Sn(*iso*-OPr)$_2$.

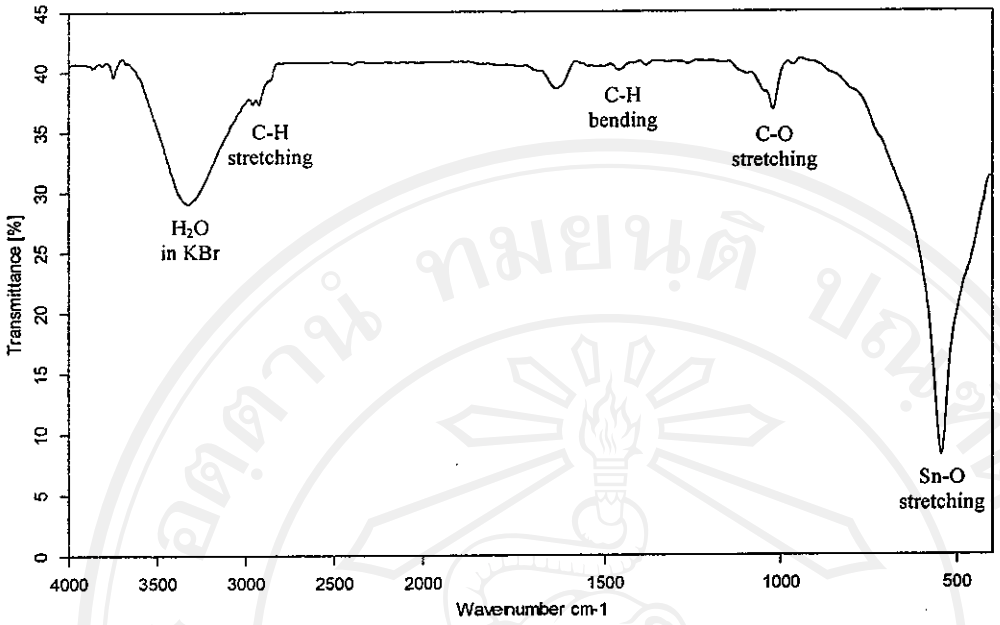


Figure 3.4 Infrared spectrum of the synthesized tin(II) *n*-butoxide, Sn(*n*-OBu)$_2$.

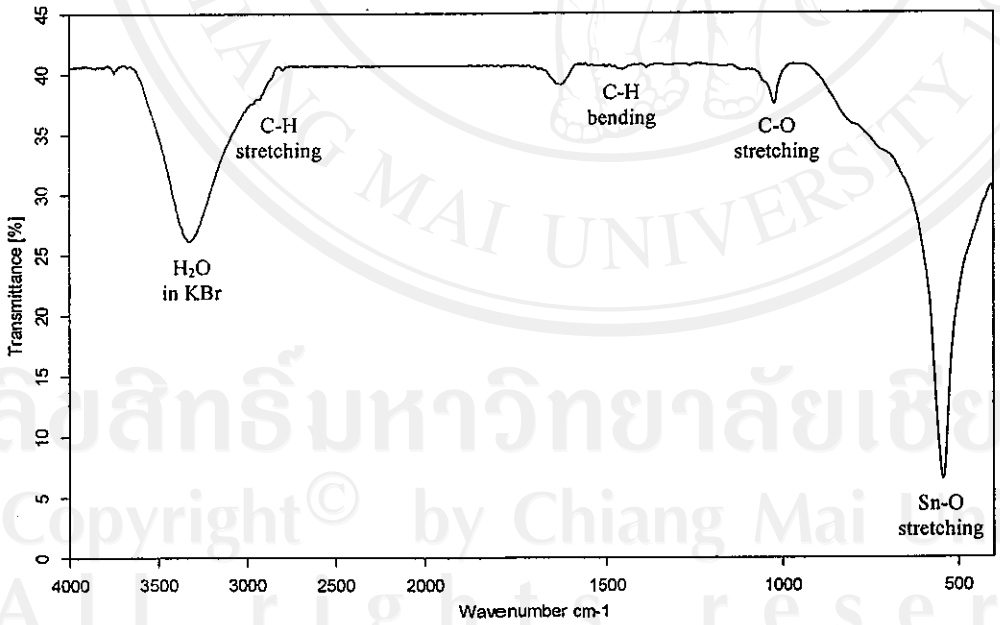


Figure 3.5 Infrared spectrum of the synthesized tin(II) *tert*-butoxide, Sn(*tert*-OBu)$_2$.

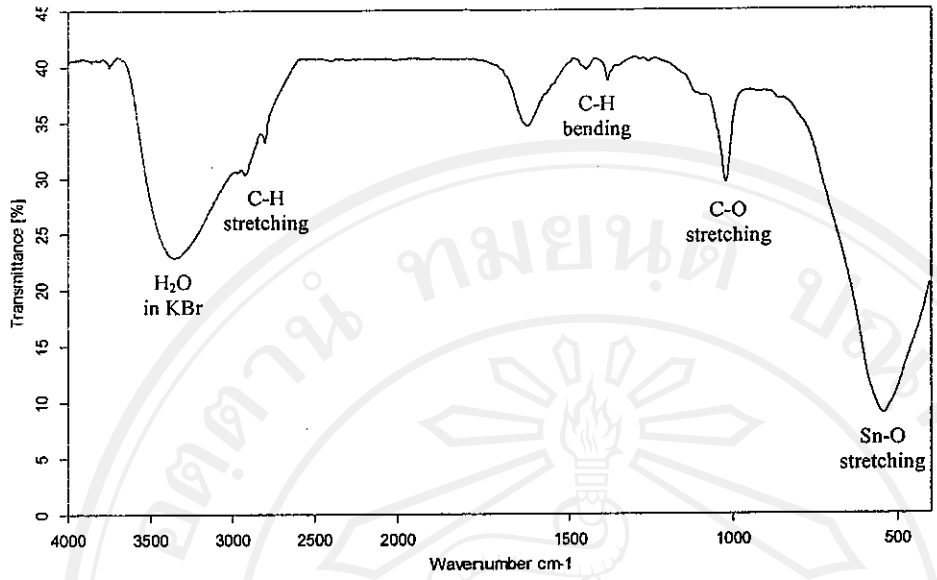


Figure 3.6 Infrared spectrum of commercial tin(II) methoxide, $Sn(OCH_3)_2$.

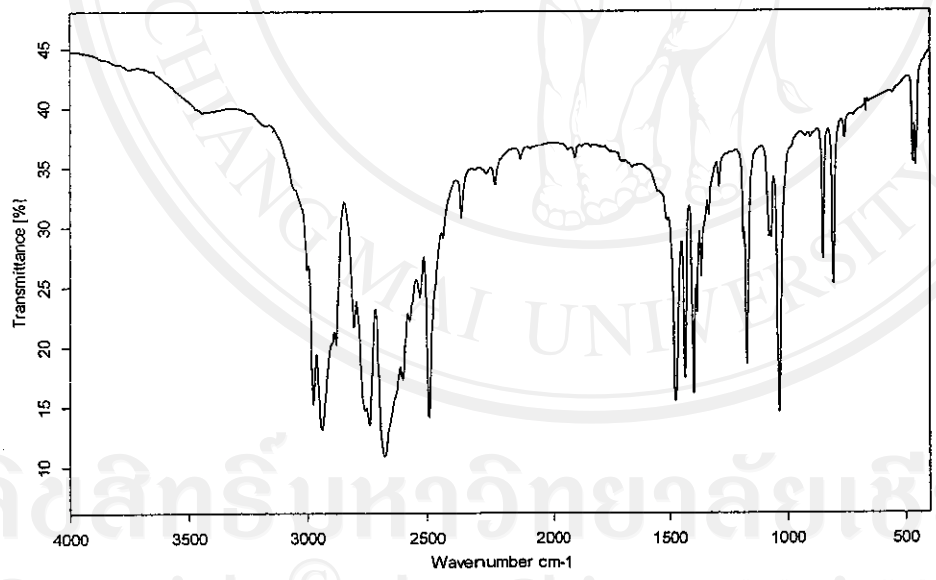


Figure 3.7 Infrared spectrum of commercial triethylamine hydrochloride.

Table 3.3 Infrared absorption band assignments for the tin(II) alkoxides, $Sn(OR)_2$.

Vibrational Assignment	Wavenumber (cm^{-1})				
	$Sn(OMe)_2$	$Sn(n\text{-}OPr)_2$	$Sn(iso\text{-}OPr)_2$	$Sn(n\text{-}OBu)_2$	$Sn(tert\text{-}OBu)_2$
C-H asym, CH_3	2900 (2926)	2950	2918	2966 [2955]	2926
C-H sym, CH_3	2798 (2806)	2854	-	2862 [2850]	2798
C-H asym, CH_2	-	2926	2798	2926 [2918]	-
C-H sym, CH_2	-	-	-	[2850]	-
C-H deformation, CH_3	1433 (1453)	1457	-	1465 [1457]	1461
C-H deformation, CH_2	-	1377	-	1385 [1374]	-
C-O stretching	1025 (1026)	1026	1026	1050 [1070]	1053
	-	-	-	1026 [1040]	1026
SnO_2Sn strecthing	-	-	735	738 [740]	730
Sn-O stretching	567 (547)	554	543	547 [573]	547
Sn-O-Sn stretching	(353)	-	-	[312]	-
O-H stretching*	3700-3000	3700-3000	3700-3000	3700-3000	3700-3000

( ) data from commercial product

[ ] data from reference [8]

* from moisture in the KBr used

3.4.2 Raman Spectroscopy

The Raman spectra of the synthesized tin(II) alkoxide products are shown in Figures 3.8-3.11. The spectra were obtained from pure solid samples contained in microscope slides with an optically flat base and positioned vertically in the laser beam and were recorded at room temperature. The Raman spectrum of the commercial tin(II) methoxide is also shown in Figure 3.12 for comparison.

The most obvious feature of the Raman spectra is the sharp peak at 230 cm^{-1} which is most likely due to Sn-O-Sn stretching. This is in sharp contrast to the broad, diffuse peak centred at 550-600 cm^{-1} due to Sn-O stretching. However, in general, the Raman spectra are much less informative than the IR spectra. This could be at least partly due to the sample preparation and the conditions under which the Raman spectra were recorded. Further studies need to be carried out in order to improve the quality of these Raman spectra. If this can be achieved, it would be very useful because the Raman technique provides information below 400 cm^{-1}, outside the range of the previous IR spectra. Some Sn-O bond vibrations occur in the range 200-400 cm^{-1}, the exact frequencies of which are sensitive to the nature of the alkoxy group.

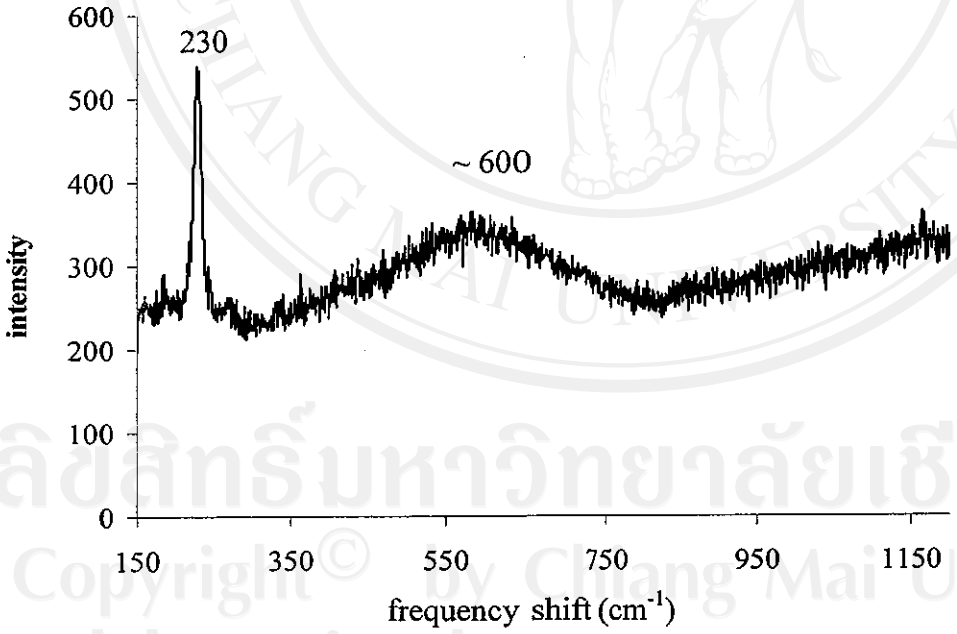


Figure 3.8 Raman spectrum of the synthesized Sn(*n*-OPr)$_2$.

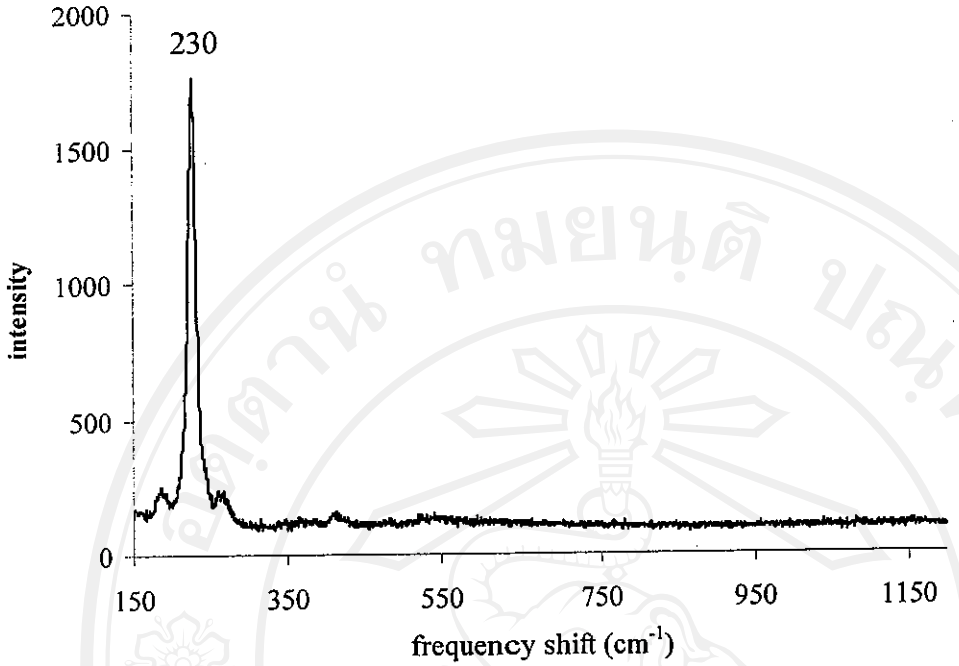


Figure 3.9 Raman spectrum of the synthesized Sn(*iso*-OPr)$_2$.

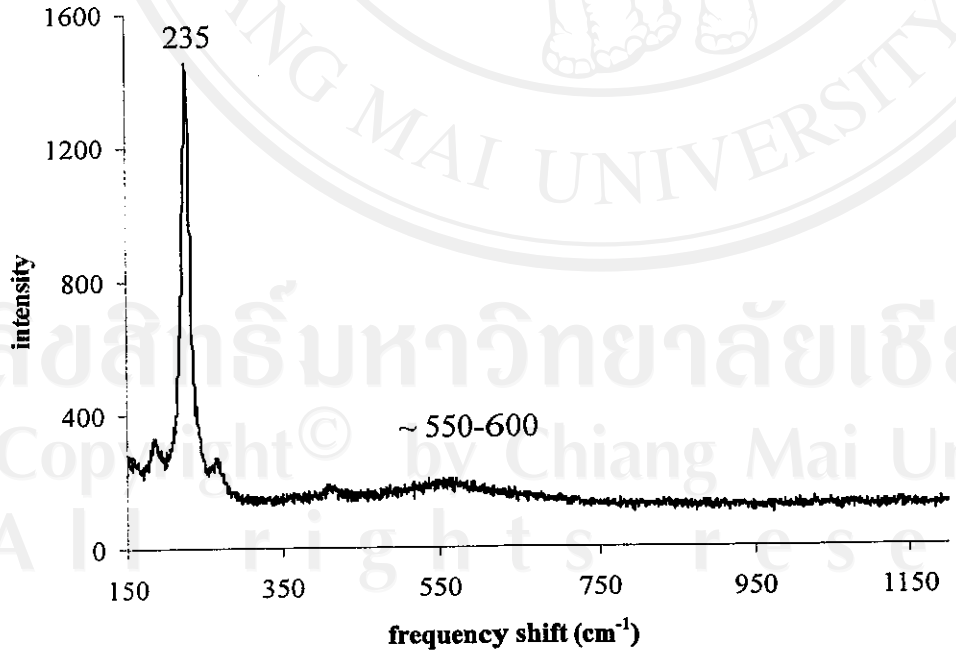


Figure 3.10 Raman spectrum of the synthesized Sn(*n*-OBu)$_2$.

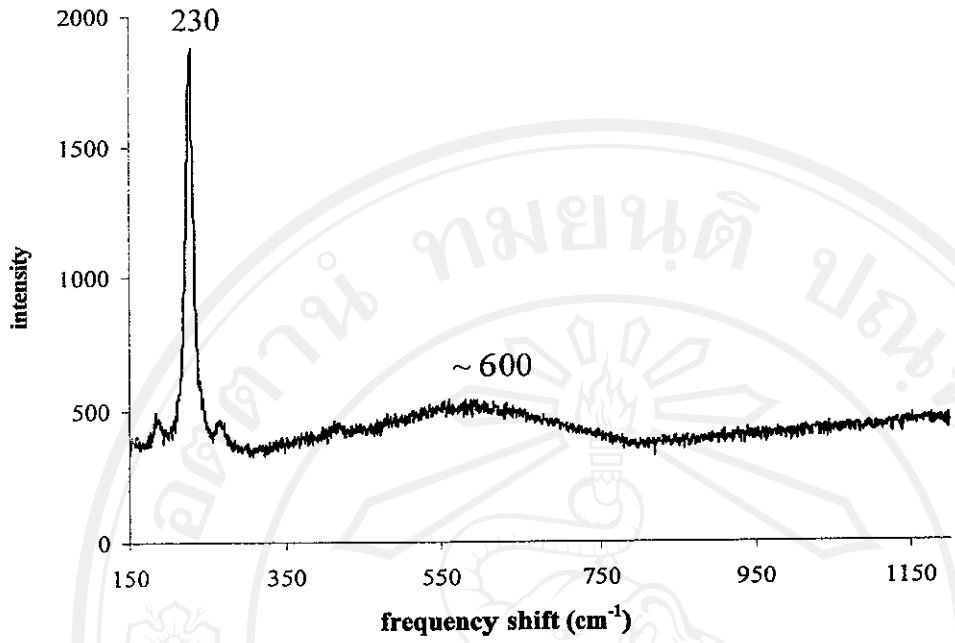


Figure 3.11 Raman spectrum of the synthesized Sn(*tert*-OBu)$_2$.

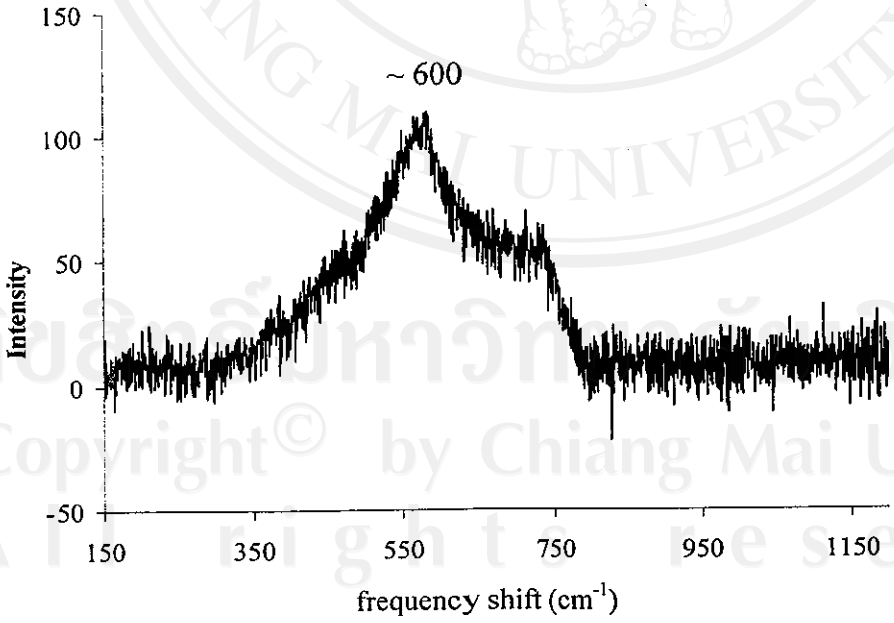


Figure 3.12 Raman spectrum of the commercial Sn(OMe)$_2$.

3.4.3 Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR)

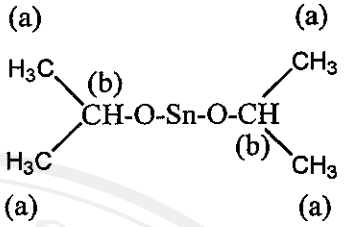
The proton nuclear magnetic resonance (^{1}H-NMR) spectra of the tin(II) alkoxide products are shown in Figures 3.13-3.16. The chemical shifts of the various peaks in the spectra are listed in Table 3.4 and the peaks assigned to the corresponding protons. The spectra were recorded at 400 MHz using deuterated chloroform ($CDCl_3$) as solvent at room temperature. The main problem was that the tin(II) alkoxides were only very sparingly soluble in the $CDCl_3$ which meant that their ^{1}H-NMR signals were very weak. However, after scale expansion, two of the four samples, the Sn(*n*-OPr)$_2$ and Sn(*n*-OBu)$_2$, yielded spectra of sufficient resolution for qualitative interpretation, as shown in Figures 3.13 and 3.15.

When the literature [8] data in Table 3.4 for Sn(*n*-OBu)$_2$ is compared with the experimental data for the Sn(*n*-OBu)$_2$ sample synthesized in this work, there is seen to be close agreement in the chemical shifts of the various protons. This is strong evidence in support of its chemical structure. Likewise, the NMR spectrum of the synthesized Sn(*n*-OPr)$_2$ also shows peaks which are consistent with its chemical structure. This NMR data in combination with the previous IR and Raman data is considered to be conclusive enough evidence that the synthesized products are indeed the tin(II) alkoxides. However, their polymeric nature in the solid state, which is responsible for their difficult solubility, remains a problem as far as their structural characterisation is concerned. This is an obvious area for further work to focus its attention on.

(a) (b) (c) (c) (b) (a)

CH_3-CH_2-CH_2-O-Sn-O-CH_2-CH_2-CH_3

tin(II) *n*-propoxide

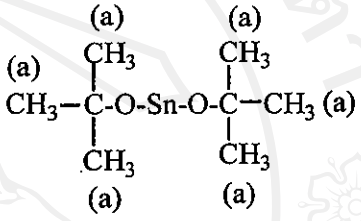


tin(II) *iso*-propoxide

(a) (b) (c) (d) (d) (c) (b) (a)

CH_3-CH_2-CH_2-CH_2-O-Sn-O-CH_2-CH_2-CH_2-CH_3

tin(II) *n*-butoxide



tin(II) *tert*-butoxide

Table 3.4 400 MHz ^{1}H-NMR chemical shifts and proton assignments for the tin(II) alkoxides.

Proton Assignment	Chemical Shift, δ (ppm)				
	Sn(*n*-OBu)$_2$*	Sn(*n*-OPr)$_2$	Sn(*iso*-OPr)$_2$	Sn(*n*-OBu)$_2$	Sn(*tert*-OBu)$_2$
a	0.85	1.03	0.89	0.85	1.25
b	1.30	1.65**	-	1.5-1.65**	-
c	1.65	3.70	-		-
d	3.80	-	-	3.70	-

* literature data taken from reference [8]

** overlapping with H_2O peak in $CDCl_3$

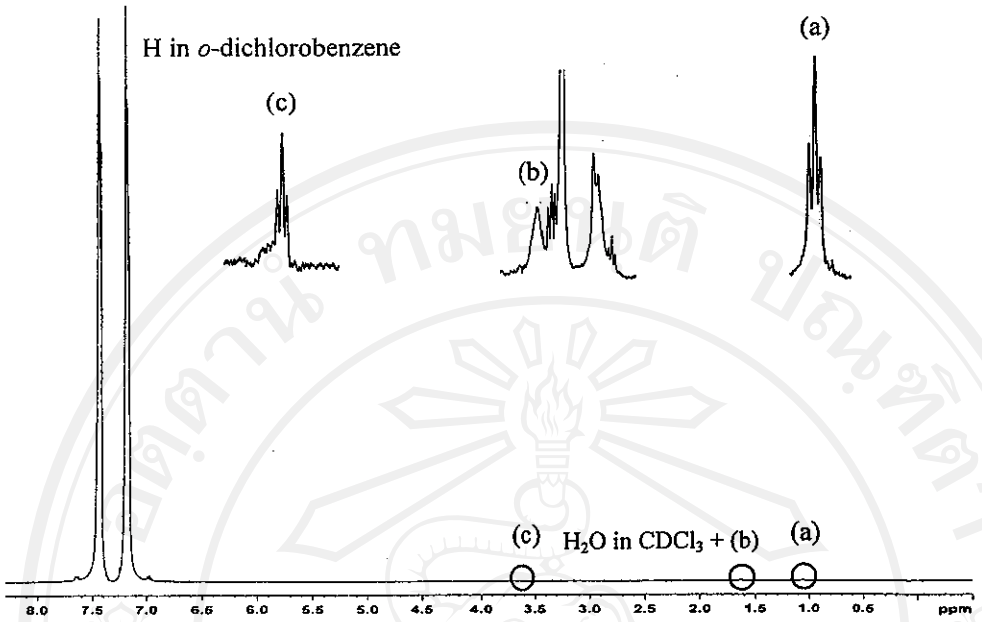


Figure 3.13 400 MHz ^{1}H-NMR spectrum of the synthesized Sn(*n*-OPr)$_2$ in *o*-dichlorobenzene at room temperature.

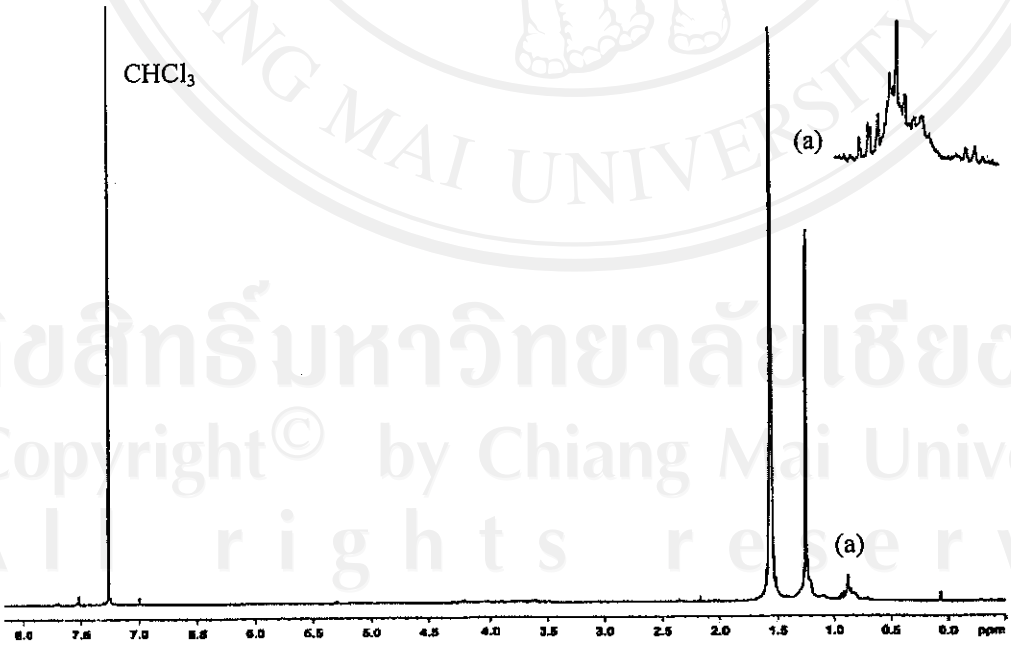


Figure 3.14 400 MHz ^{1}H-NMR spectrum of the synthesized Sn(*iso*-OPr)$_2$ in $CDCl_3$ at room temperature.

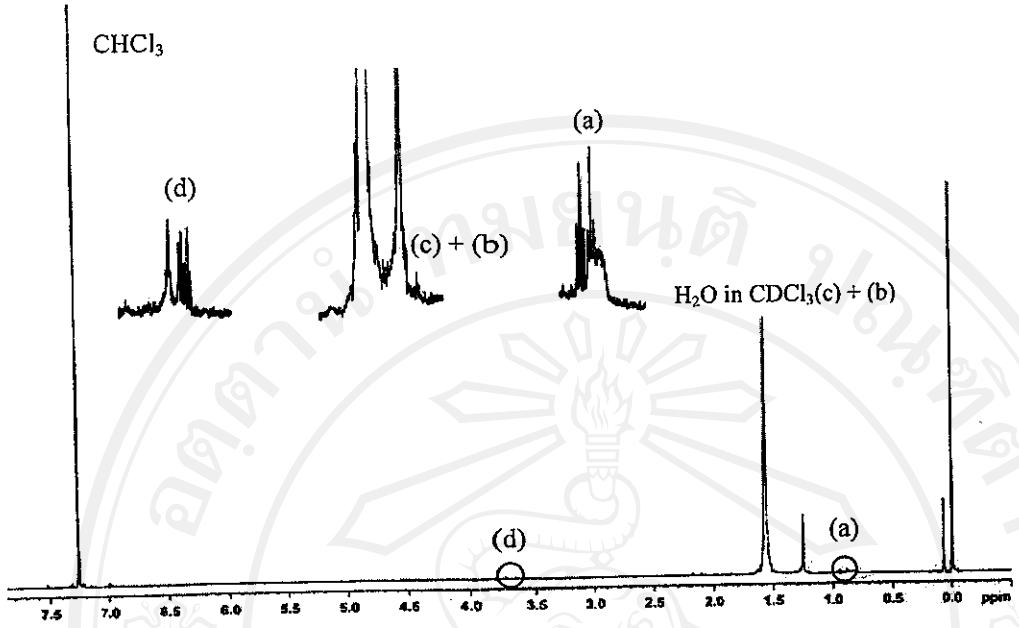


Figure 3.15 400 MHz ^{1}H-NMR spectrum of the synthesized Sn(*n*-OBu)$_2$ in $CDCl_3$ at room temperature.

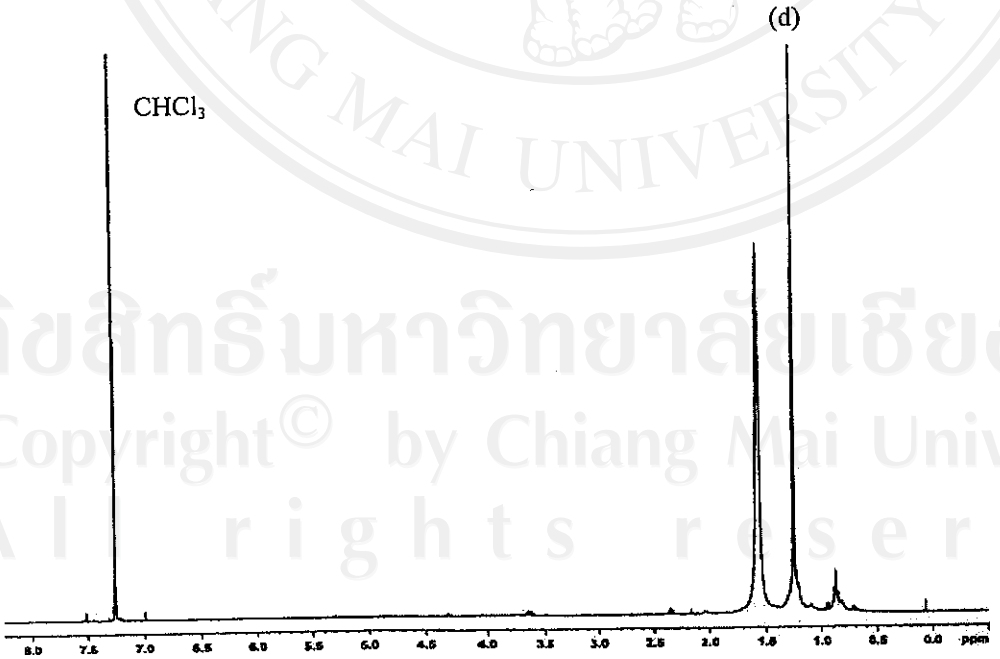


Figure 3.16 400 MHz ^{1}H-NMR spectrum of the synthesized Sn(*tert*-OBu)$_2$ in $CDCl_3$ at room temperature.

3.4.4 Differential Scanning Calorimetry

The thermal transitions of the tin(II) alkoxide products were determined by differential scanning calorimetry (DSC). The DSC thermograms of the synthesized products are shown in Figures 3.17-3.20 and can be compared with the commercial $Sn(OCH_3)_2$ in Figure 3.21. In each case, a heating rate of 10 °C/min was used under a nitrogen atmosphere with a sample size of 3-5 mg.

The DSC thermograms in Figure 3.17-3.21 all show melting endotherms over temperature ranges as wide as 50 °C. These broad melting ranges are indicative of the polymeric nature of the alkoxides as a result of their molecular aggregation in the solid state. The melting peak temperatures (T_m) and heats of melting (ΔH_m) are compared in Table 3.5. There are no clear correlations between these T_m and ΔH_m values and the nature of the alkoxide (OR) group. This is presumably because the alkoxides exist in varying degrees of molecular aggregation which also effects their melting characteristics.

Table 3.5 DSC melting parameters for the tin(II) alkoxides.

Tin(II) alkoxide	T_m (°C)	ΔH_m (J/g)
$Sn(OMe)_2$	255.0	59.4
$Sn(n\text{-}OPr)_2$	255.0	34.9
$Sn(iso\text{-}OPr)_2$	229.5	21.7
$Sn(n\text{-}OBu)_2$	236.7	44.7
$Sn(tert\text{-}OBu)_2$	234.2	19.7
Triethylamine hydrochloride	63.4	732.5

Data obtained from Figures 3.17-3.21.

T_m = melting peak temperature

ΔH_m = heat of melting $\propto$ melting peak area

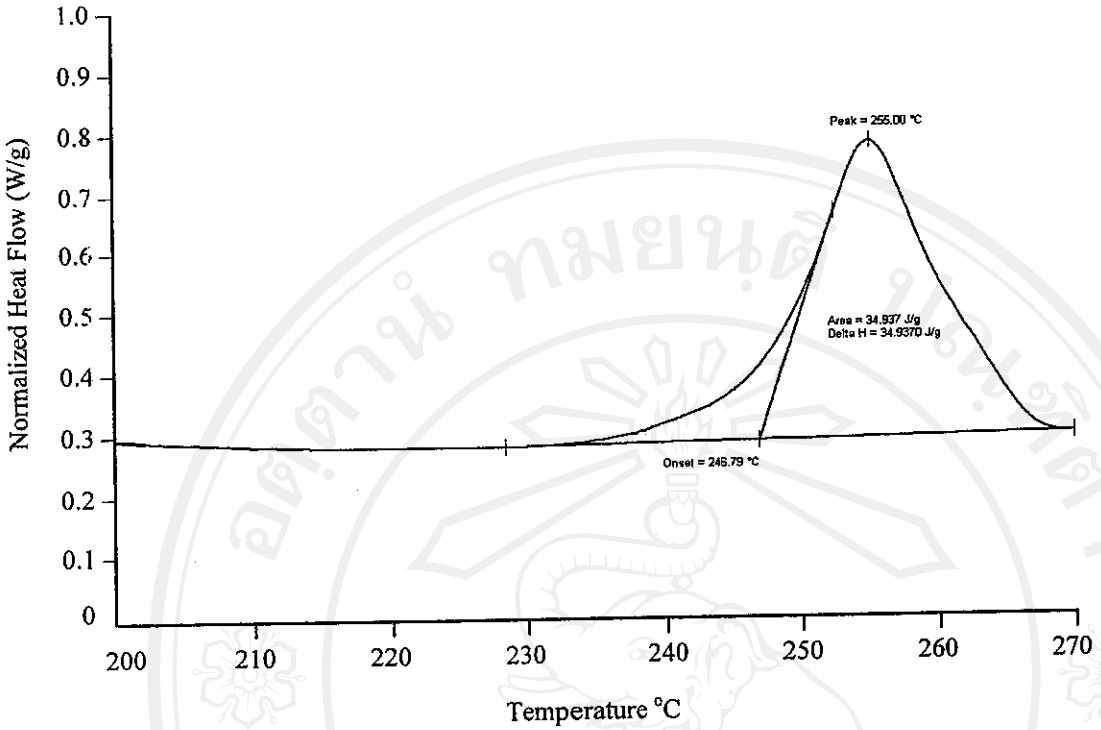


Figure 3.17 DSC thermogram of the synthesized Sn(*n*-OPr)$_2$.

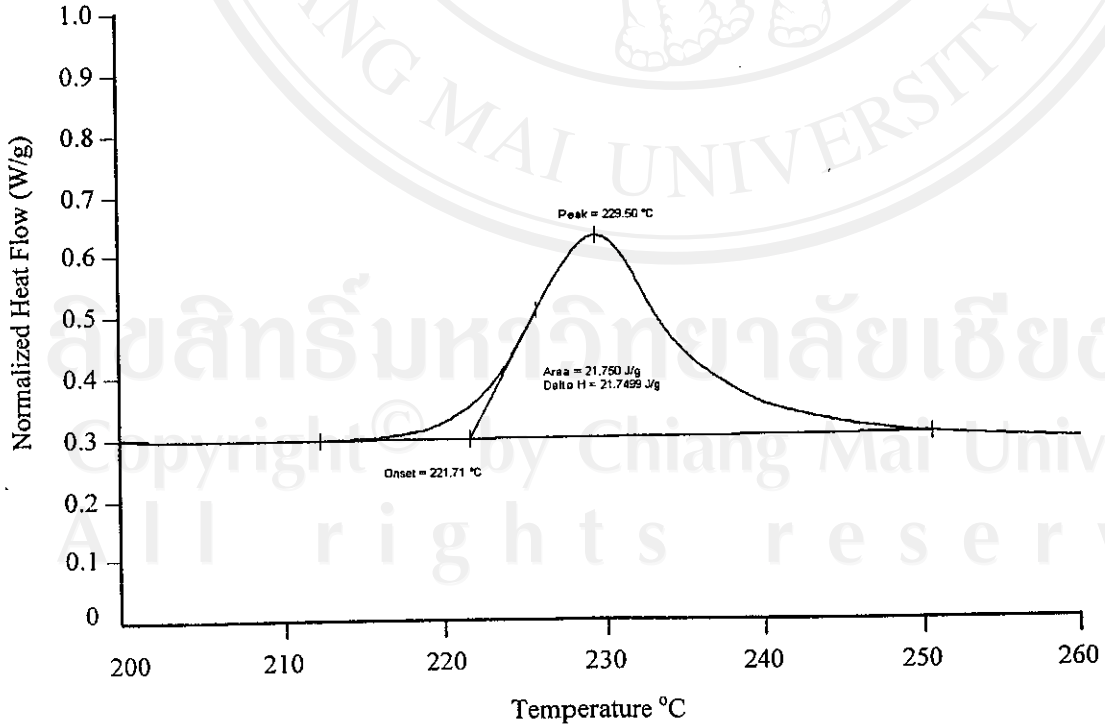


Figure 3.18 DSC thermogram of the synthesized Sn(*iso*-OPr)$_2$.

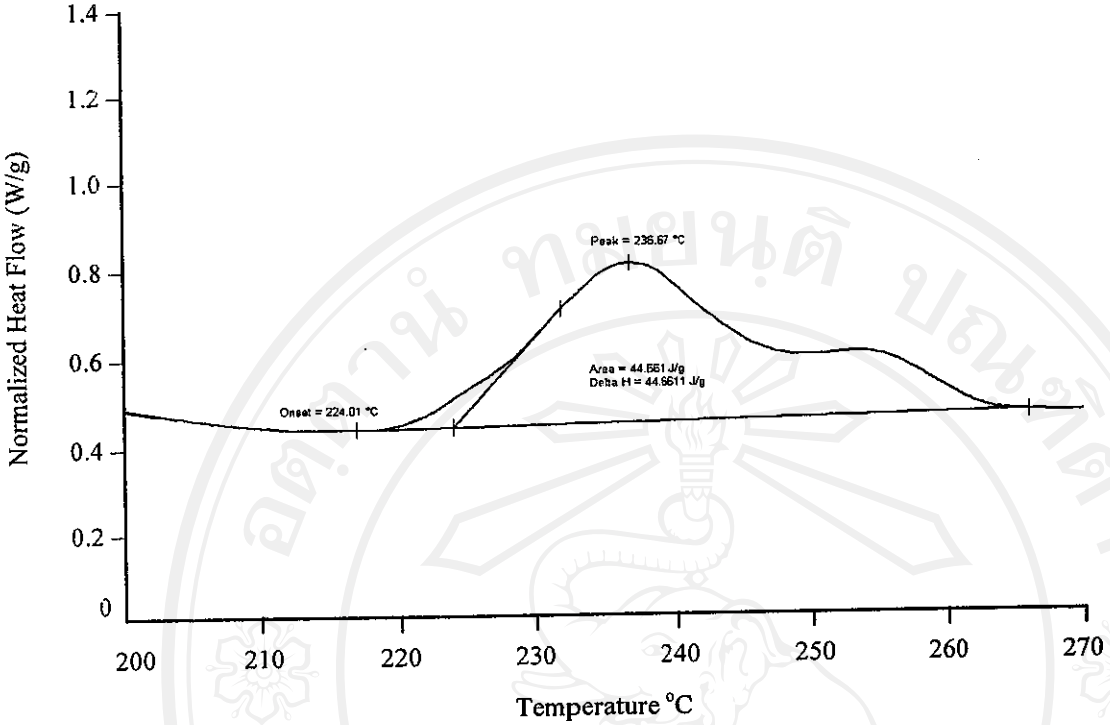


Figure 3.19 DSC thermogram of the synthesized Sn(*n*-OBu)$_2$.

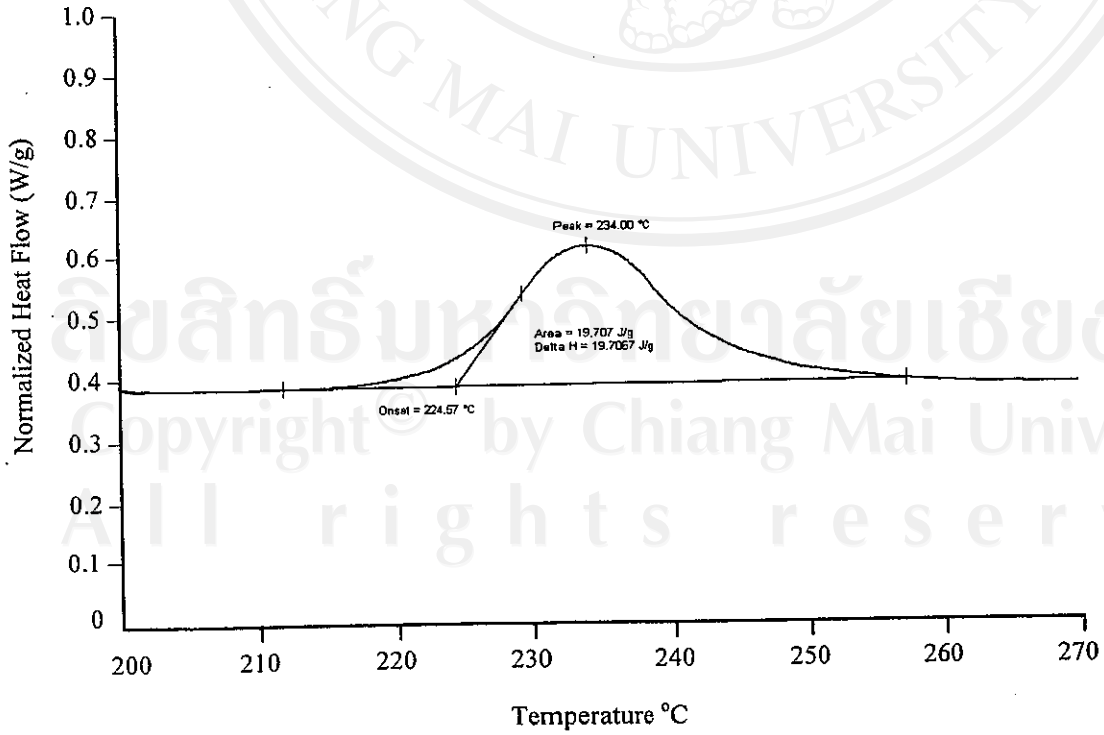


Figure 3.20 DSC thermogram of the synthesized Sn(*tert*-OBu)$_2$.

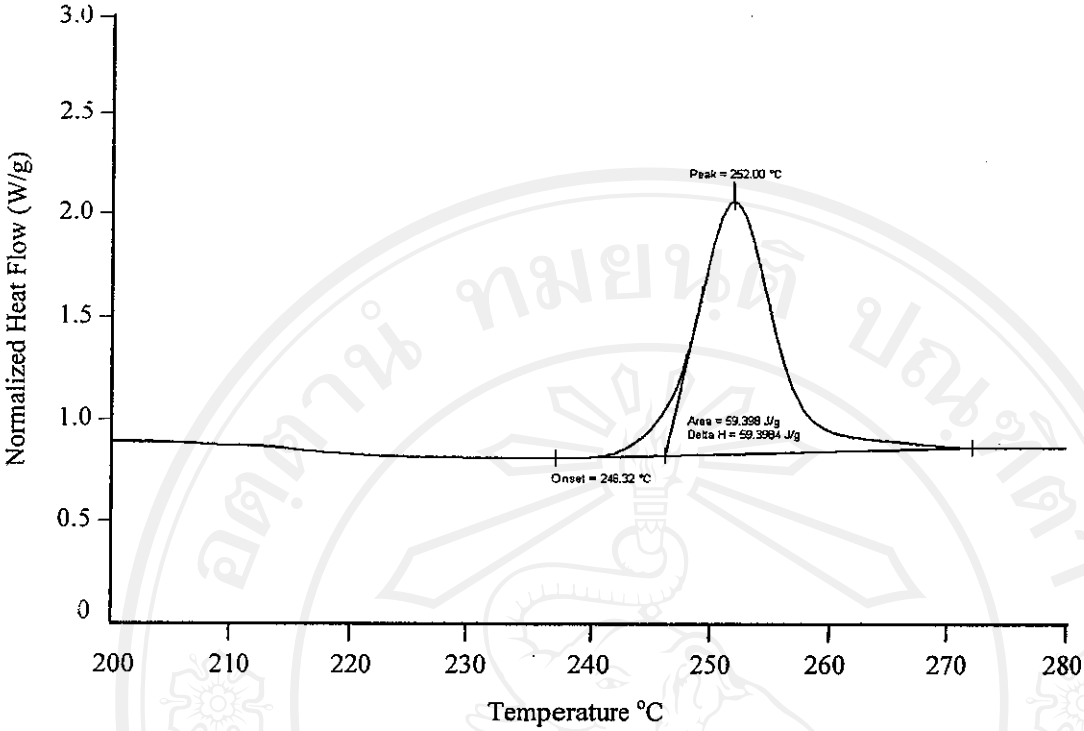


Figure 3.21 DSC thermogram of the commercial $Sn(OCH_3)_2$.

3.4.5 Thermogravimetric Analysis

The dynamic (non-isothermal) TGA thermograms in Figures 3.22-3.26 compare and contrast the weight loss-temperature profiles of the synthesized tin(II) alkoxides and the commercial tin(II) methoxide. In each case, a heating rate of 20 °C min^{-1} was used over the temperature range 50-600 °C under an inert flowing nitrogen atmosphere. The temperature ranges over which the weight losses occurred are compared in Table 3.6.

For each of the synthesized alkoxides, the weight losses up to 600 °C were less than 10%. It is likely that at least some of this weight loss was due to absorbed moisture since tin(II) alkoxides are known to be hygroscopic in nature. Apart from this, other volatiles at the higher temperatures are likely to come from thermal decomposition of the alkoxide groups, although the fact that the weight losses are so

small indicates that the alkoxides are thermally stable compounds in a non-oxidising atmosphere. This, in turn, indicates that thermal decomposition of the alkoxides when used as initiators in ring-opening polymerisation is not likely to be a problem at the relatively low (100-150 °C) bulk polymerisation temperatures which are normally used.

Table 3.6 TGA weight loss ranges for the tin(II) alkoxides.

Tin(II) alkoxide	Thermal Degradation Range (°C)
$Sn(OMe)_2$ (commercial)	62 – 400
$Sn(n\text{-}OPr)_2$	80 – 270, 400 – 500
$Sn(iso\text{-}OPr)_2$	130 – 320
$Sn(n\text{-}OBu)_2$	77 – 288, 422 – 507
$Sn(tert\text{-}OBu)_2$	60 – 600

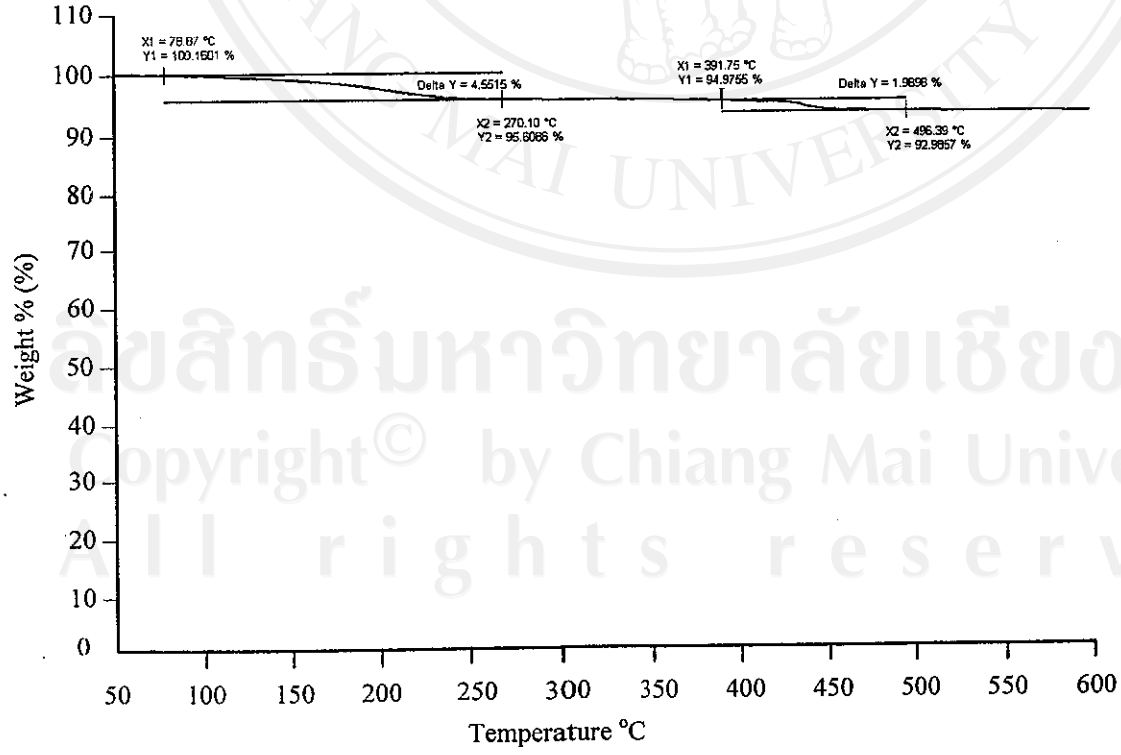


Figure 3.22 TGA curve for the synthesized $Sn(n\text{-}OPr)_2$.

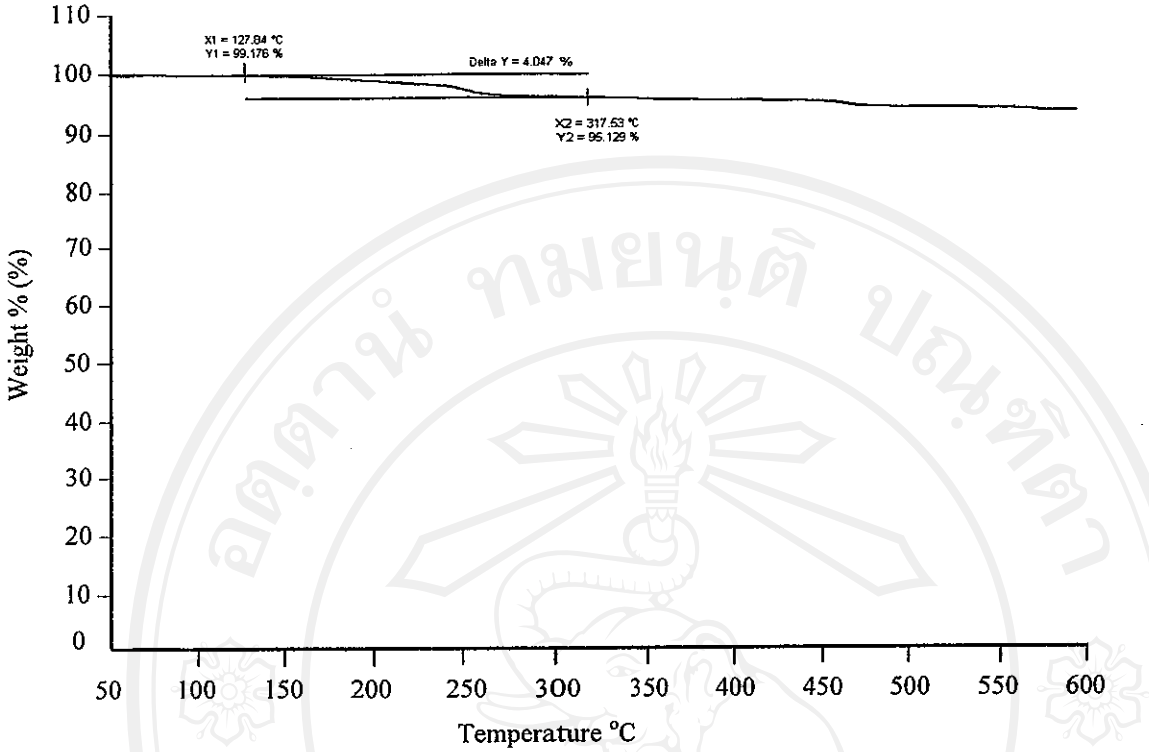


Figure 3.23 TGA curve for the synthesized Sn(*iso*-OPr)$_2$.

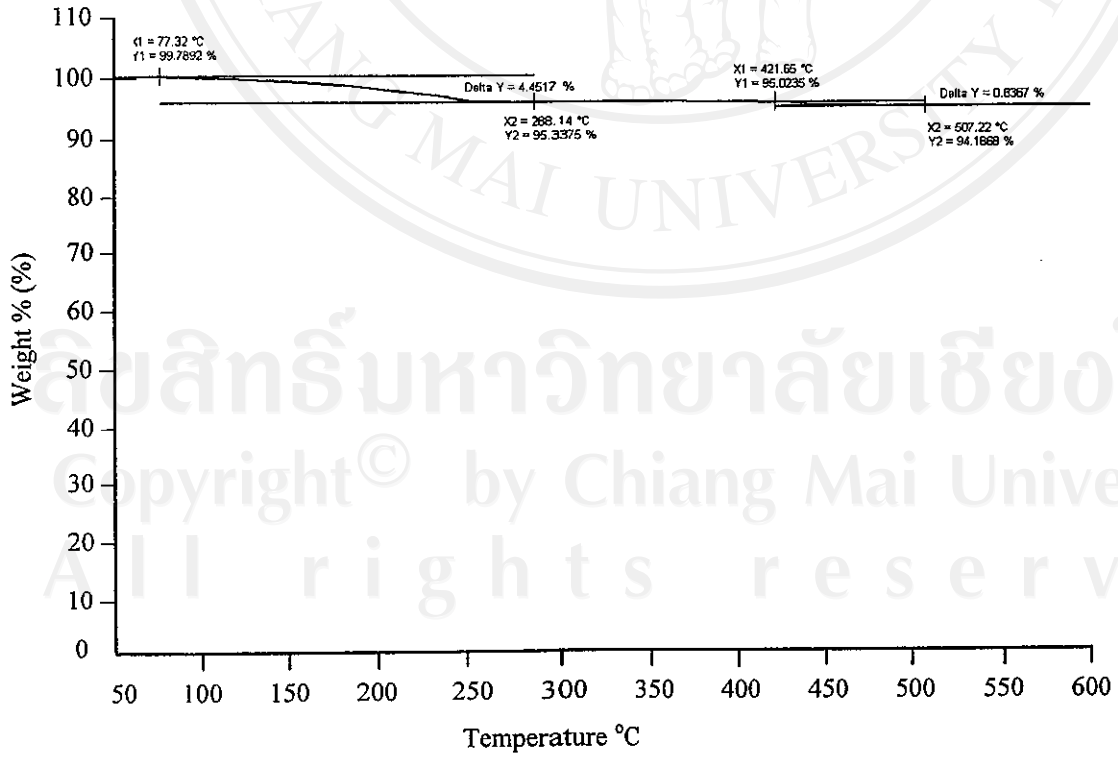


Figure 3.24 TGA curve for the synthesized Sn(*n*-OBu)$_2$.

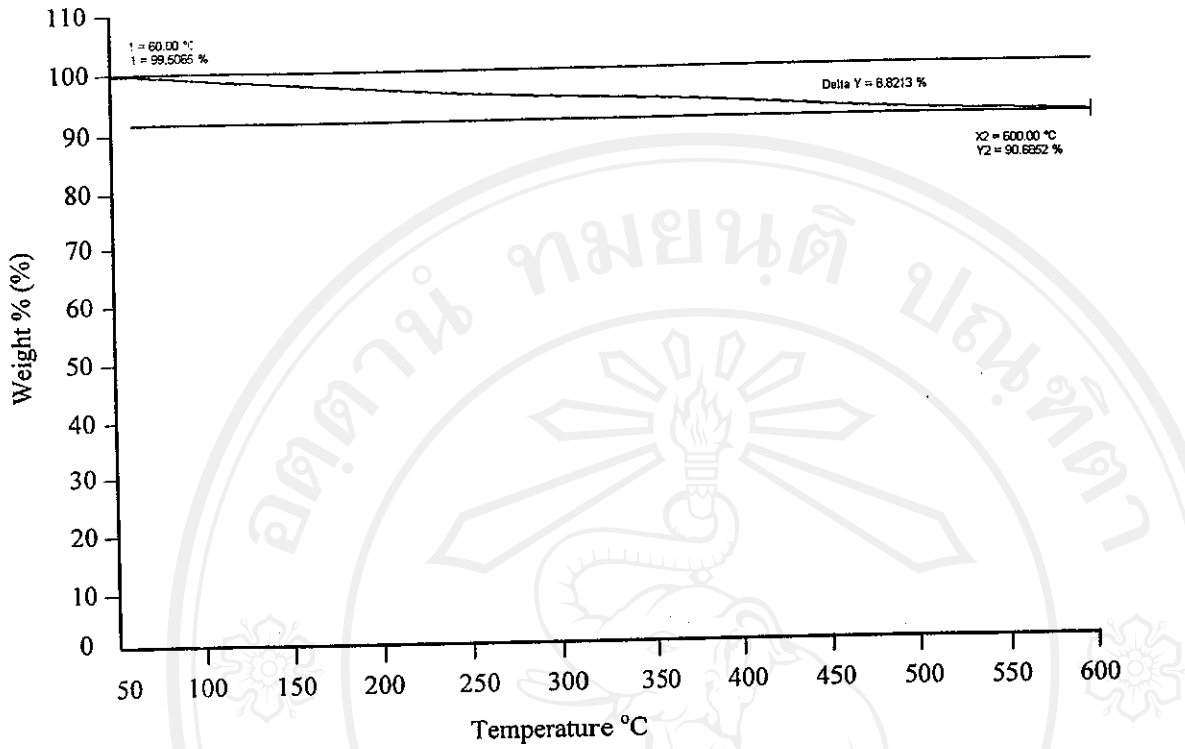


Figure 3.25 TGA curve for the synthesized Sn(*tert*-OBu)$_2$.

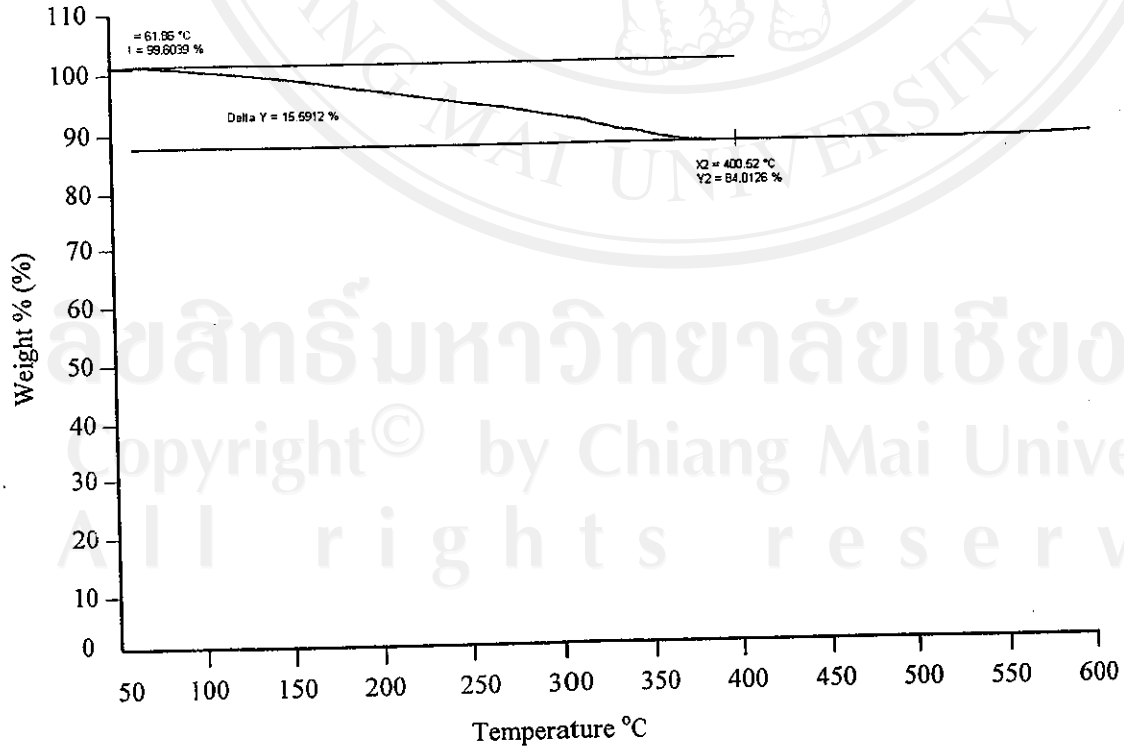


Figure 3.26 TGA curve for the commercial Sn(OCH$_3$)$_2$.