CHAPTER 3

Synthesis and Characterisation of Tin(II) Alkoxides

In the synthesis of tin (II) alkoxides, there are some reagents used in which trace amounts of moisture/impurities could be present, they therefore required further purification. Moreover, tin(II) alkoxides are both moisture and air-sensitive and so their synthesis needs to be carried out in an inert atmosphere.

3.1 Purification of Reagents

3.1.1 Tin(II) Chloride

Anhydrous tin(II) chloride ($SnCl_2$), was used as supplied (Acros Organics, 98 %) without further purification. Due to its hygroscopic nature, it was stored in a tightly sealed container in a vacuum desiccator. On exposure to air, anhydrous $SnCl_2$ readily absorbs moisture and converts to the much less reactive dihydrate, $SnCl_2.2H_2O$.

3.1.2 Tin(II) Octoate

Commercial tin(II) octoate (stannous octoate, $Sn(Oct)_2$), was purified by vacuum distillation to remove 2-ethylhexanoic acid (octanoic acid) which could be present. Purified $Sn(Oct)_2$ remaining in the heating flask was obtained as a pale yellow viscous liquid and was stored over molecular sieves 4 Å before use.

3.1.3 Diols

Diols (HOROH), their chemical structures are shown below, used for the synthesis of tin(II) alkoxides were purified by heating at 130 ^oC with stirring and connected to a vacuum pump in order to evaporate any moisture impurities that might be present.

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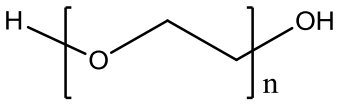
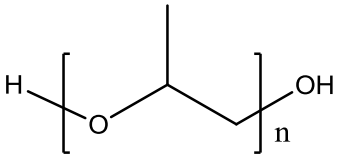
Polyethylene Glycol 300 (PEG300)



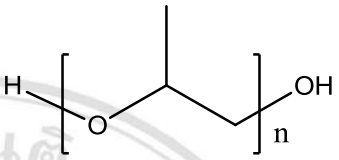
(n ≈ 6-7)

Polypropylene Glycol 400 (PPG400)



(n ≈ 6-7)

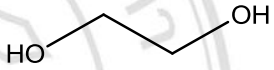
Polypropylene Glycol 1200 (PPG1200)



(n ≈ 20-21)

Diethylene Glycol (DEG)

Ethylene Glycol (EG)



3.1.4 Triethylamine

Triethylamine (Ajax, assay 99 %) was purified by fractional distillation at atmospheric pressure using a similar procedure and apparatus to that for the alcohols as shown in Figure 3.1. The constant boiling fraction at 86 ^{o}C / 730 mm Hg (cf. lit [100] 88.8 ^{o}C / 760 mm Hg) was collected and then stored in a vacuum desiccator until required for use in synthesis.

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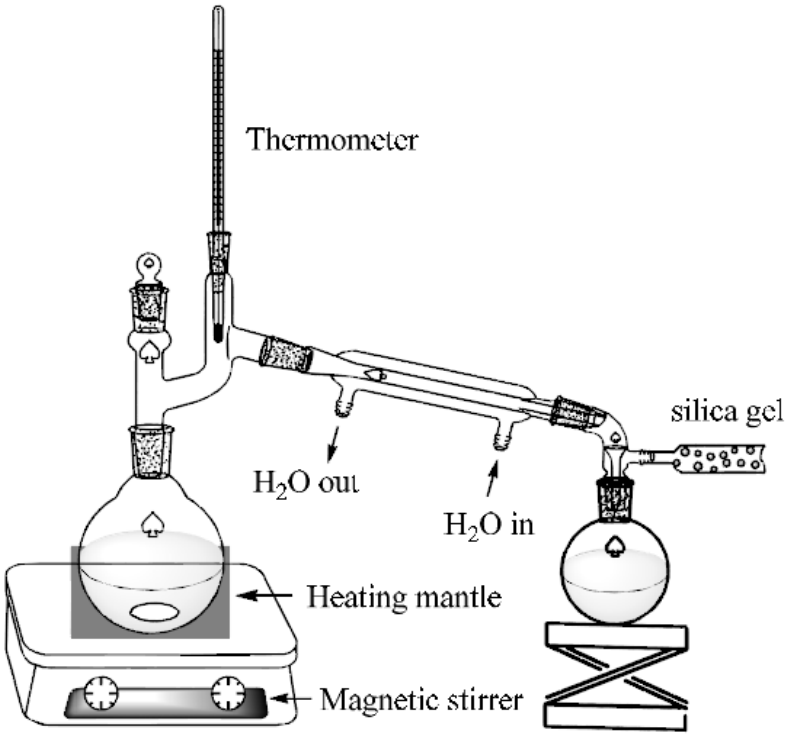

Figure 3.1 Simple distillation apparatus for purification of reagents.

3.2 Synthesis and Characterisation of Tin(II) Alkoxides

There are two methods used for the synthesis of novel initiator tin(II) alkoxides as described below.

3.2.1 Method 1:

A series of tin(II) alkoxides, $Sn(OR)_2$, in solid form were readily prepared from the reaction of anhydrous $SnCl_2$ with the corresponding excess dry diols in the presence of triethylamine, as described by Morrison and Haendler [101] (Equation 3.1).

$$SnCl_2 + 2\ HOROH + 2\ (C_2H_5)_3N \rightarrow Sn(OROH)_2 + 2\ (C_2H_5)_3N.HCl \quad (3.1)$$

(in an excess of HOROH)

In a typical experiment, $SnCl_2$ was dissolved in a large excess of alcohol in a 250 ml round bottomed flask under a dry nitrogen atmosphere at room temperature (Figure 3.2). Triethylamine was then added with magnetic stirring to cause a permanent precipitate and stirring continued for a further 3 hrs.

This solid product was a mixture of both the tin(II) alkoxide and the triethylamine hydrochloride by-product, according to the Equation 3.1. The

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$Sn(OROH)_2$ was separated from the triethylamine hydrochloride by-product by solvent extraction. The insoluble $Sn(OROH)_2$ was then filtered and dried to constant weight in a vacuum oven at 40 ^oC. Finally, due to their sensitivity towards oxygen and moisture, the $Sn(OROH)_2$ products were stored in tightly sealed containers in a vacuum desiccator until required for use.

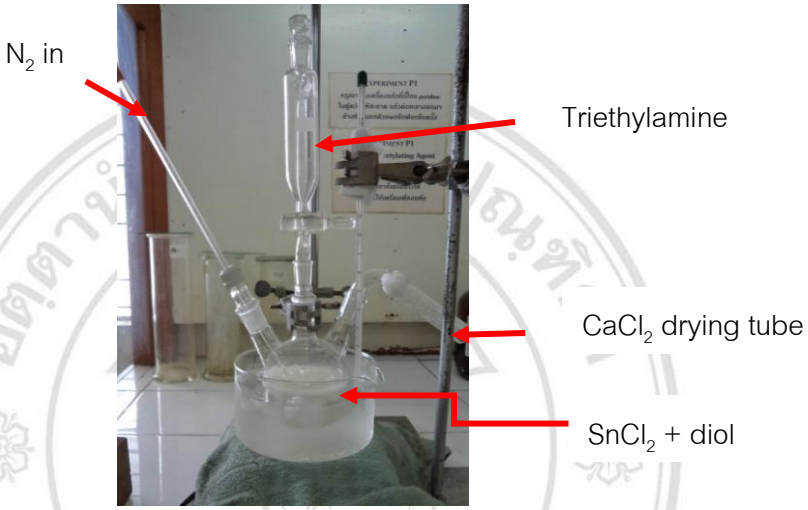

Figure 3.2 Apparatus used for the synthesis of the solid tin(II) alkoxides by Method 1.

Percentage yields of the synthesised initiators

Based on the assumption from Equation 3.1, the percentage yields (by mol) of the $Sn(OR)_2$ initiators could be calculated from the Equation 3.2:

$$\%Yield = \frac{\text{mol of } Sn(OR)_2 \text{ product obtained}}{\text{Initial mol of } SnCl_2 \text{ used}} \text{ x } 100\% \qquad (3.2)$$

The physical appearances and percentage yields of all of the purified $Sn(OR)_2$ products are given in Table 3.1.

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Table 3.1 Physical appearances and percentage yields of the purified $Sn(OROH)_2$ products.

Tin(II)Alkoxide	**Physical Appearance**	**% Yield**
Tin(II) polyethylene glycol 300 [$Sn(PEG300)_2$] $Sn[(OCH_2CH_2)_nOH]_2$	White solid powder	96.0
Tin(II) polypropylene glycol 400 [$Sn(PPG400)_2$] $Sn[(OCH(CH_3)CH_2)_nOH]_2$	White solid powder	92.6
Tin(II) polypropylene glycol 1200 [$Sn(PPG1200)_2$] $Sn[(OCH(CH_3)CH_2)_nOH]_2$	White solid powder	89.8
Tin(II) diethylene glycol [$Sn(DEG)_2$] $Sn(OCH_2CH_2OCH_2CH_2OH)_2$	White solid powder	95.5

Before polymerisations were carried out using the synthesised initiators of tin(II) alkoxide complexes, it is of significant interest to examine their structural features. The initiators were prepared as partial solutions in chloroform and characterised using FT-IR and NMR spectroscopy. The spectra were obtained from samples prepared in the form of a particle layer evaporated on NaCl. The FT-IR spectra of the solid tin(II) alkoxides are shown in Figure 3.3. Major peaks corresponding to their significant modes of vibration are interpreted and the results are given in Table 3.2. Four common peaks corresponding to bond stretching and bending within the initiator structure were found at wavenumbers of 3000-2800 (C-H stretching), 1470-1360 (C-H bending), 1300-1000 (C-O stretching) and 800-500 (Sn-O stretching) cm^{-1} (Table 3.2).

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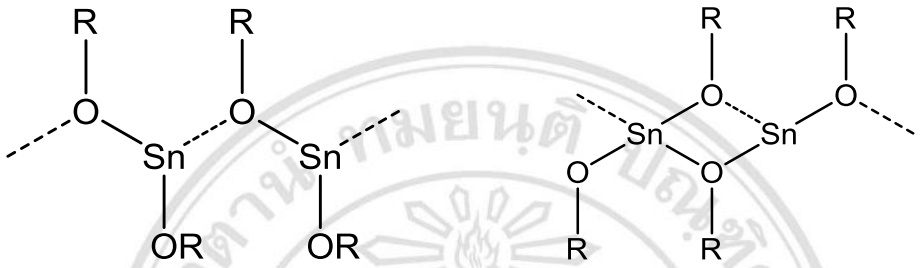
It is worth to mention here that all the solid tin(II) alkoxides synthesised were found to be only partially soluble. This is indicative of the presence of molecular aggregation in equilibrium as shown below [102].

$$\underset{\text{non-aggregated}}{n\ \text{Initiator}} \rightleftharpoons \underset{\text{aggregated}}{[\text{Initiator}]_n}$$



(a) Single bridge type (b) Double bridge type

Molecular aggregation in tin(II) alkoxides.

Molecular aggregation could appear in the form of "oligomeric" species by a single oxygen bridge (a) or "polymeric" species by a double oxygen bridge (b). This aggregation derives from the availability of empty valence "d" orbital on the tin atom. However, it was found that the solid tin(II) alkoxides are white when freshly prepared but rapidly turn pale yellow during storage and solubility in organic solvent also decrease. The colour change has also been associated with polymerisation of organic compounds [103, 104].

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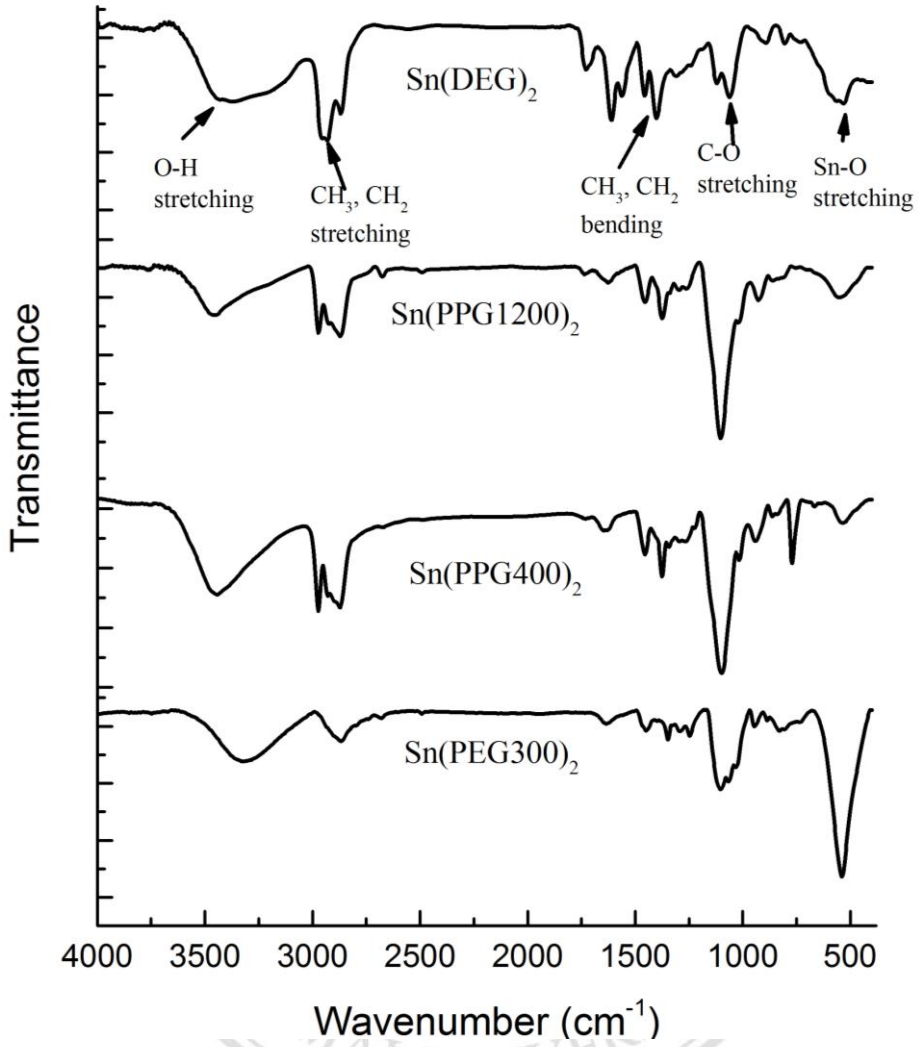

Figure 3.3 FT-IR spectra of the solid tin(II) alkoxides.

Table 3.2 FT-IR absorption band assignments for the solid tin(II) alkoxides.

Assignment	Wavenumber (cm^{-1})			
	$Sn(PEG300)_2$	$Sn(PPG400)_2$	$Sn(PPG1200)_2$	$Sn(DEG)_2$
O-H (stretch)	3318 (s)	3443 (s)	3450 (m)	3368 (m)
C-H in CH_3 (stretch)	-	2973 (m)	2972 (m)	-
C-H in CH_2 (stretch)	2866 (m)	2873 (m)	2870 (m)	2868 (m)
C-H in CH_3(bend)	-	1375 (w)	1374 (w)	-
C-H in CH_2(bend)	1450 (w)	1455 (w)	1454 (w)	1458 (m)
C-O (stretch)	1103 (m)	1098 (s)	1105 (s)	1121 (m)
Sn-O (stretch)	539 (s)	536 (w)	558 (w)	569 (m)

Notes: s = strong, m = medium, w = weak

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The proton nuclear magnetic resonance (^{1}H-NMR) spectra of the solid tin(II) alkoxide products are shown in Figure 3.4. The spectra were recorded at 400 MHz using d_6-DMSO as solvent. In the case of the solid tin(II) alkoxides, they were only partially soluble in the d_6-DMSO which meant that their ^{1}H-NMR signals were not as strong as those for the liquid products from the following Method 2.

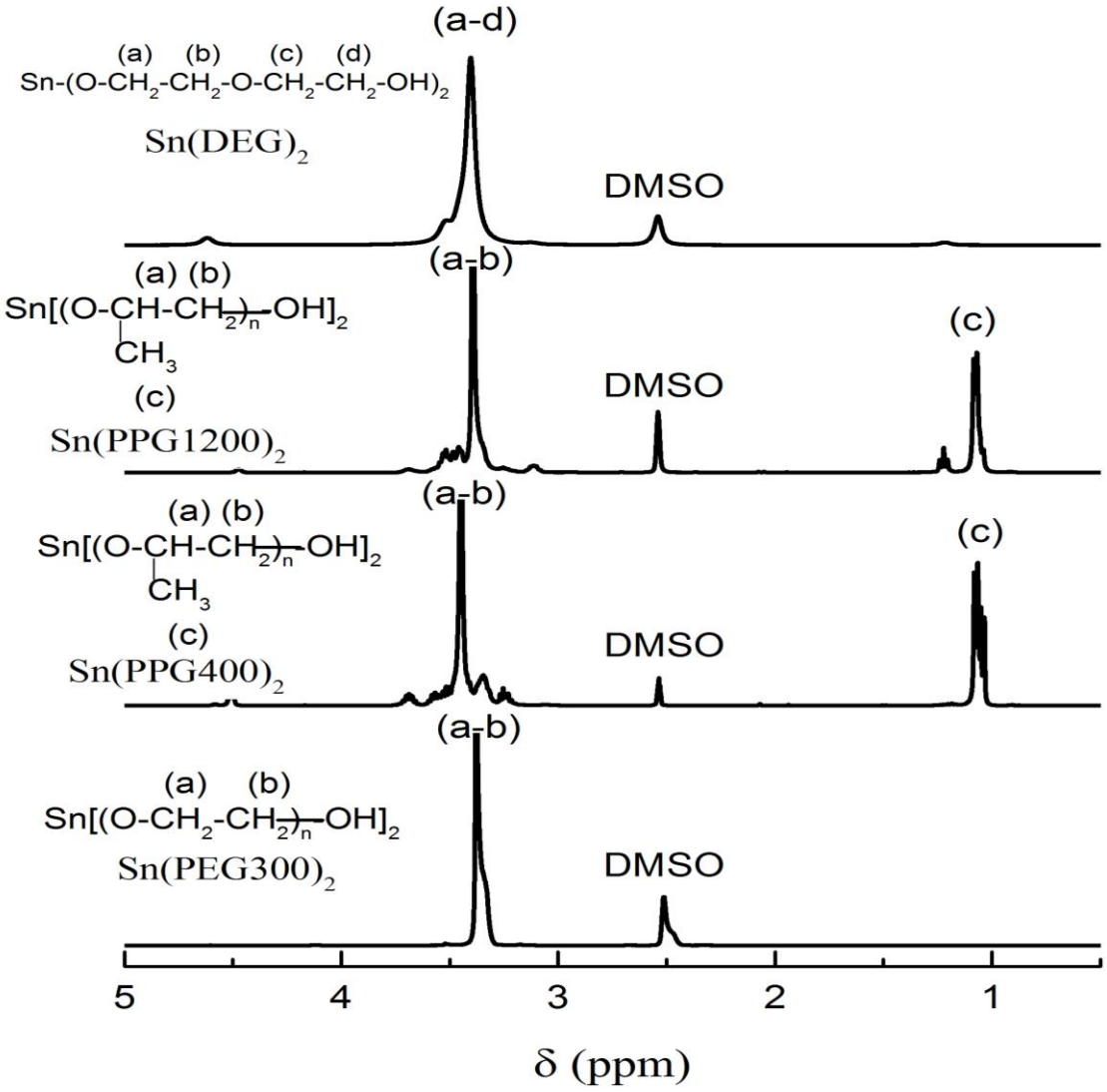

Figure 3.4 NMR spectra of the solid tin(II) alkoxides.

The structural differences of the alkoxide chain between initiators can be seen from the ^{1}H-NMR spectra (Figure 3.4). The peaks show to correspond well with the alkoxide chain.

Thermal characterisation of the tin(II) alkoxides were carried out via the following combination of analytical techniques:

1) Differential scanning calorimetry (DSC)
2) Thermogravimetric analysis (TGA)

Differential Scanning Calorimetry (DSC)

The thermal transitions of the tin(II) alkoxide products were determined by differential scanning calorimetry (DSC). The DSC analyses of the tin(II) alkoxides were conducted at a heating rate of 10 ^{o}C/min under a flowing nitrogen atmosphere. Sample weights were typically in the range of 3-5 mg. Their DSC thermograms showed no thermal transition peaks appeared from 0 to 250 ^{o}C (see Figure 3.5).

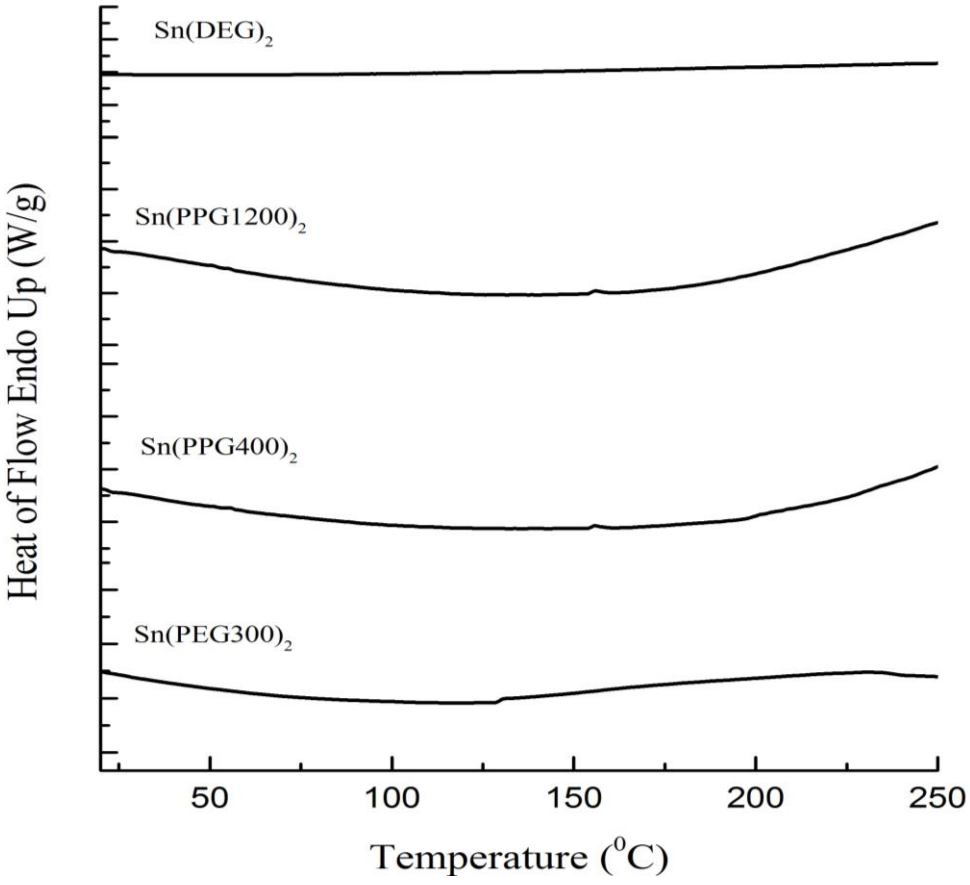

Figure 3.5 DSC Thermograms of the solid tin(II) alkoxides.

Thermogravimetric Analysis (TGA)

The main purpose of this TGA study was to define the upper temperature limits for the initiator which could be safely polymerised without accompanying degradation.

The dynamic (non-isothermal) TGA thermograms of the solid tin(II) alkoxides are shown in Figure 3.6 to compare and contrast the weight loss-temperature profiles of the synthesised tin(II) alkoxides. In each case, a heating rate of 20 ^{o}C min^{-1} was used over the temperature range 45-600 ^{o}C under an inert flowing nitrogen atmosphere.

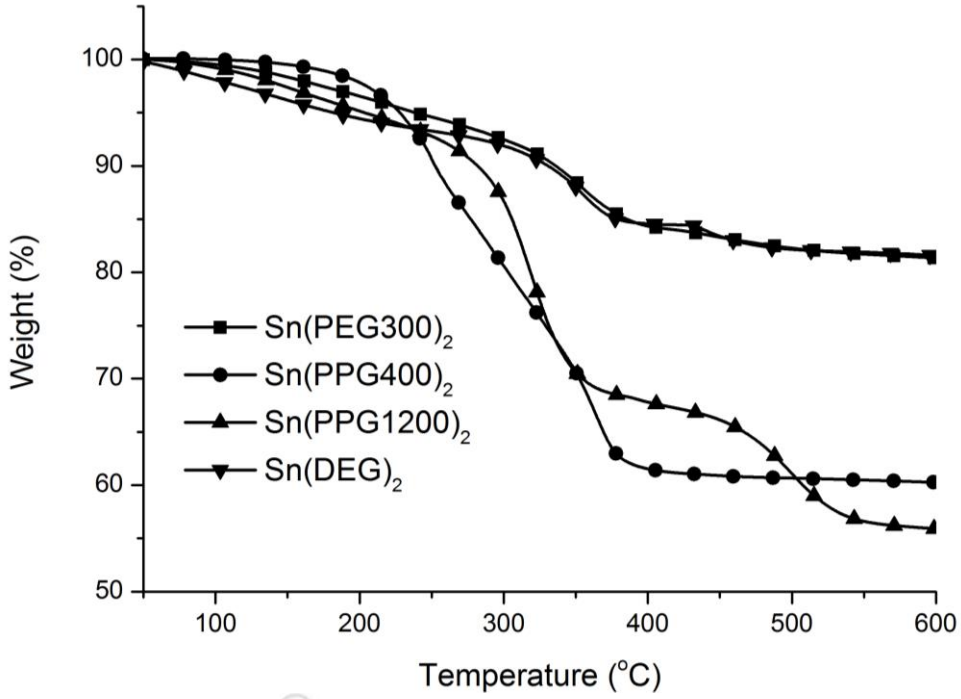

Figure 3.6 TGA thermograms for the solid tin(II) alkoxides.

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According to the TGA thermograms, it can be observed that the solid tin(II) alkoxides start to gradually decline to the lowest % weight loss not more than 50 %. These results correspond to their high molecular aggregation, then the more thermally stability relate to their polymeric structures that can be considered as double oxygen bridged form [43].

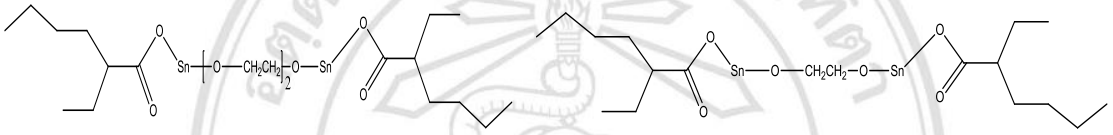
From the TGA thermograms in Figure 3.6, it can be seen that all initiators can be used for polymerisation at around 130 ^{o}C without thermal degradation being a problem.

3.2.2 Method 2:

A series of tin(II) alkoxides in liquid form were prepared from the reaction of stannous octoate ($Sn(Oct)_2$) with the corresponding alcohols as shown in Equation 3.3.

$$2Sn(Oct)_2 + HO\text{-}R\text{-}OH \rightleftharpoons (Oct)Sn\text{-}O\text{-}R\text{-}O\text{-}Sn(Oct) + 2OctH \qquad (3.3)$$

The alcohols used are diethylene glycol ($HOCH_2CH_2OCH_2CH_2OH$; DEG) and ethylene glycol ($HOCH_2CH_2OH$; EG). The chemical structures of the corresponding Tin(II) alkoxides obtained are shown below.



Bis(tin(II) octoate) diethylene glycol
$[Sn(Oct)]_2DEG$

Bis(tin(II) octoate) ethylene glycol
$[Sn(Oct)]_2EG$

In the experiment, $Sn(Oct)_2$ was dissolved in the alcohol in a round bottomed flask under vacuum at 130^{o}C for 3 hrs. to remove the octanoic acid by-product OctH (see Figure 3.7). All tin(II) alkoxide products were obtained as slightly viscous, pale yellow liquids.

Figure 3.7 Apparatus used for the synthesis of the liquid tin(II) alkoxides by Method 2.

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Tin(II) alkoxides obtained were then characterised using FT-IR and NMR spectroscopy. The FT-IR spectra of the liquid tin(II) alkoxide products are shown in Figure 3.8. Major peaks corresponding to their significant modes of vibration are interpreted and the results are given in Table 3.3. Four common peaks corresponding to bond stretching and bending within the initiator structure were found at wavenumbers of 3000-2800 (C-H stretching), 1470-1360 (C-H bending), 1300-1000 (C-O stretching) and 800-500 (Sn-O stretching) cm^{-1} (Table 3.3).

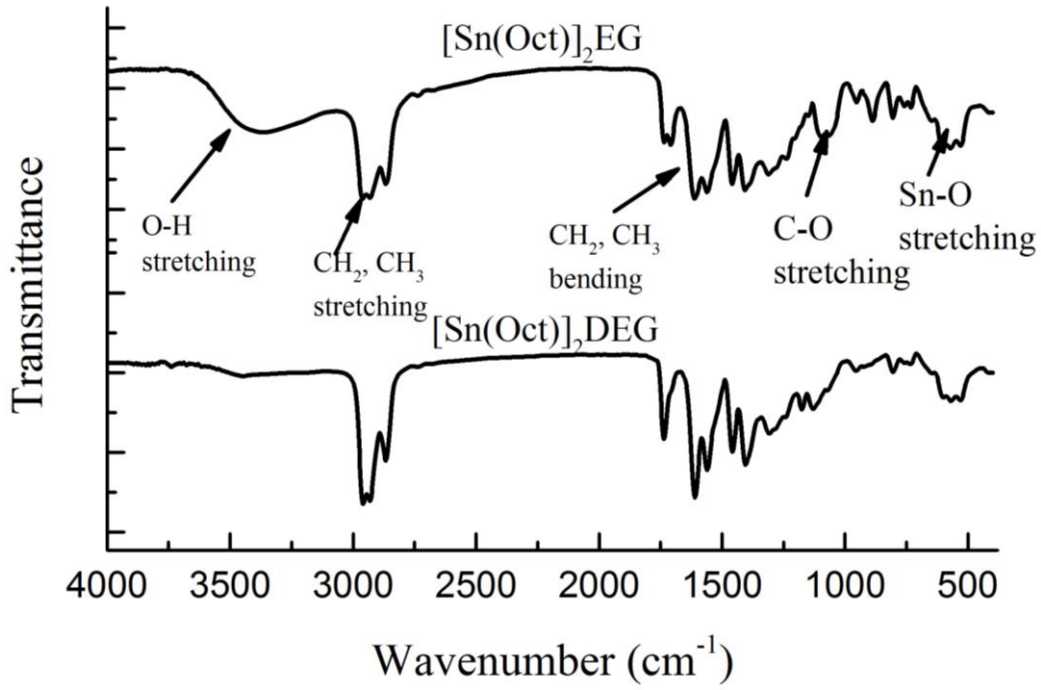

Figure 3.8 FT-IR spectra of the liquid tin(II) alkoxides.

Table 3.3 FT-IR absorption band assignments for the liquid tin(II) alkoxides.

Assignment	Wavenumber (cm^{-1})	
	$[Sn(Oct)]_2DEG$	$[Sn(Oct)]_2EG$
C-H in CH_3 (stretch)	2959 (s)	2960 (s)
C-H in CH_2 (stretch)	2867 (m)	2866 (s)
C-H in CH_3(bend)	1405 (m)	1407 (s)
C-H in CH_2(bend)	1458 (m)	1460 (s)
C-O (stretch)	1128 (w)	1095 (m)
Sn-O-Sn (stretch)	804 (w)	805 (w)
Sn-O (stretch)	569 (w)	571 (m)

Notes: s = strong, m = medium, w = weak

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For all the spectra, there occurs broad band peak at 3600-3200 cm^{-1} which is due either to the O-H bond stretching of residual alcohol and/or moisture impurities present in the sample. Further investigation to examine the residual alcohol was to vary the mole ratio of $Sn(Oct)_2$: DEG (2.1 : 1, 2.3 : 1, 2.5 : 1 and 3.0 : 1) for the synthesis of $[Sn(Oct)]_2$DEG and then characterised by FT-IR Spectroscopy. The FT-IR spectra of the products are shown in Figure 3.9.

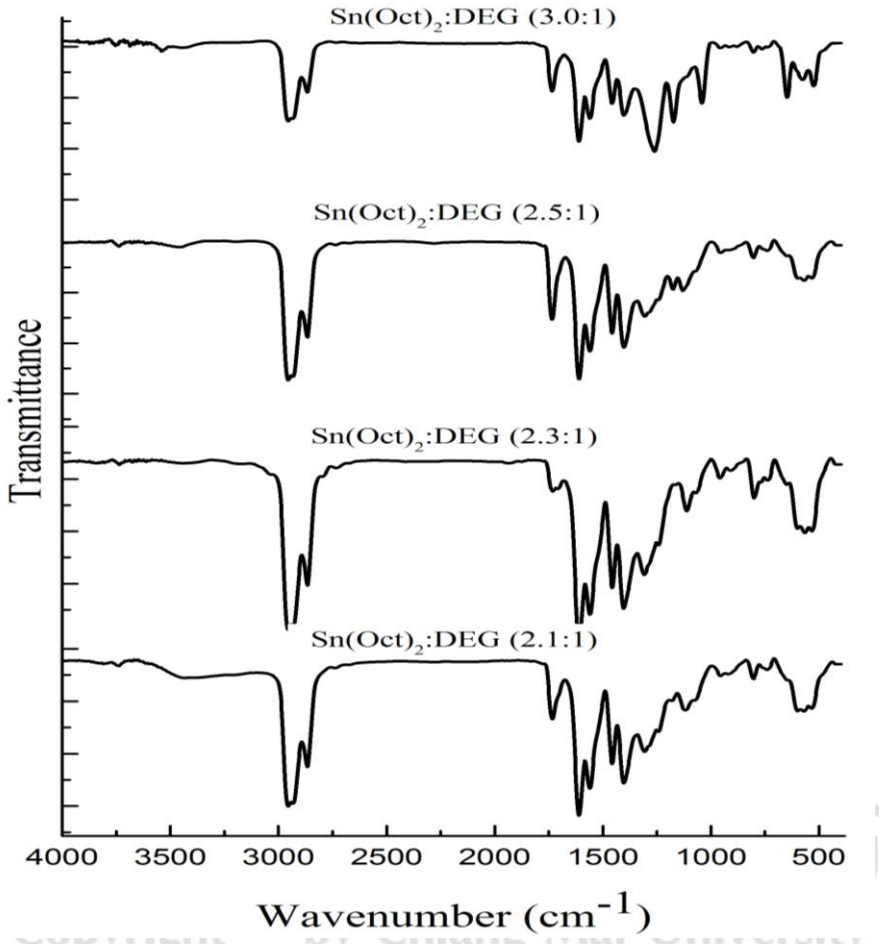

Figure 3.9 Comparison of FT-IR spectra of $[Sn(Oct)]_2$DEG initiators synthesised from difference mole ratios of $Sn(Oct)_2$: DEG.

The spectra in Figure 3.9 show that the broad band peak at 3600-3200 cm^{-1} disappears as the mole ratio of $Sn(Oct)_2$: DEG increases. This confirms that the OH groups of the DEG have completely reacted with the Oct groups of the $Sn(Oct)_2$. The spectra in Figure 3.9 suggest that a stoichiometric excess of the $Sn(Oct)_2$ of around 10% above the theoretical 2:1 ratio is sufficient to ensure complete reaction of the DEG.

The proton nuclear magnetic resonance (^{1}H-NMR) spectra of the liquid tin(II) alkoxide products are shown in Figures 3.10-3.11. The spectra were recorded at 400 MHz using $CDCl_3$ as solvent. The structural differences of the alkoxide chain between initiators can be seen from the ^{1}H-NMR spectra. The peaks show to correspond well with the alkoxide chain.

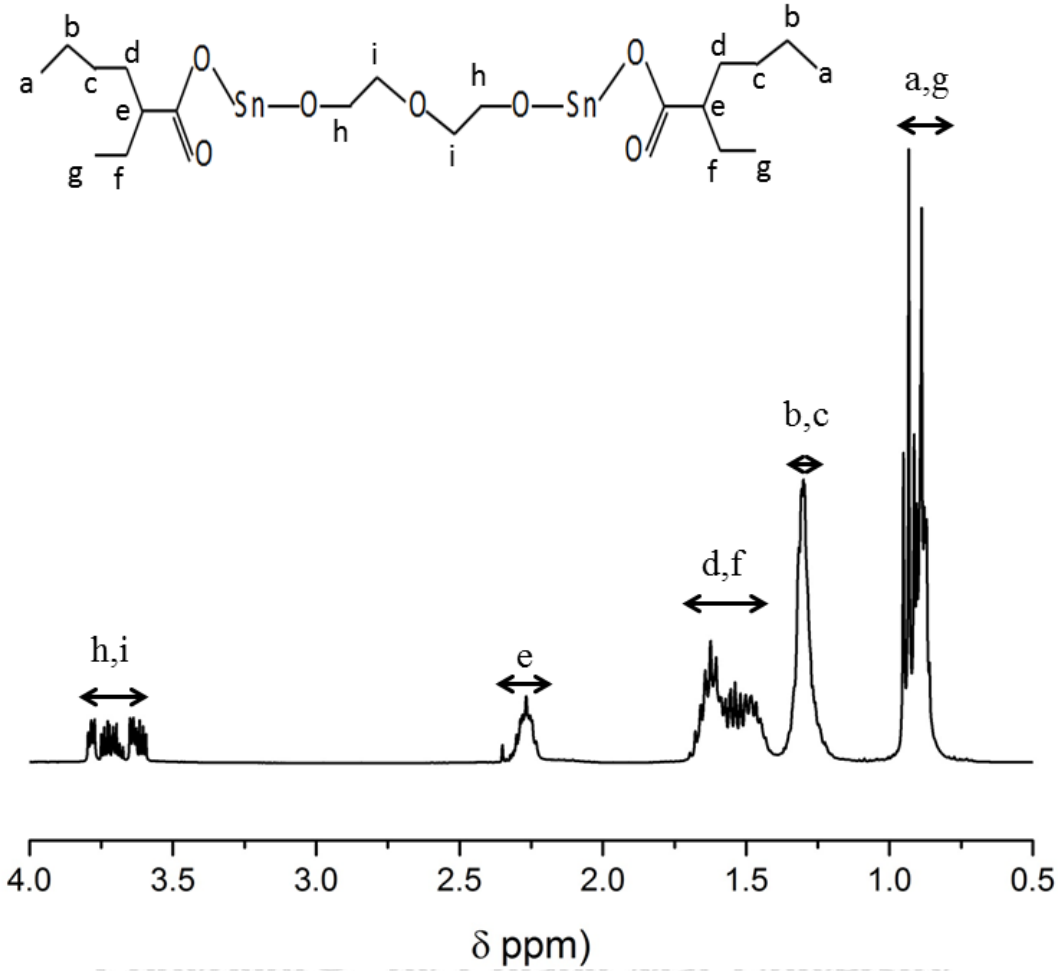

Figure 3.10 NMR spectrum of $[Sn(Oct)]_2$DEG.

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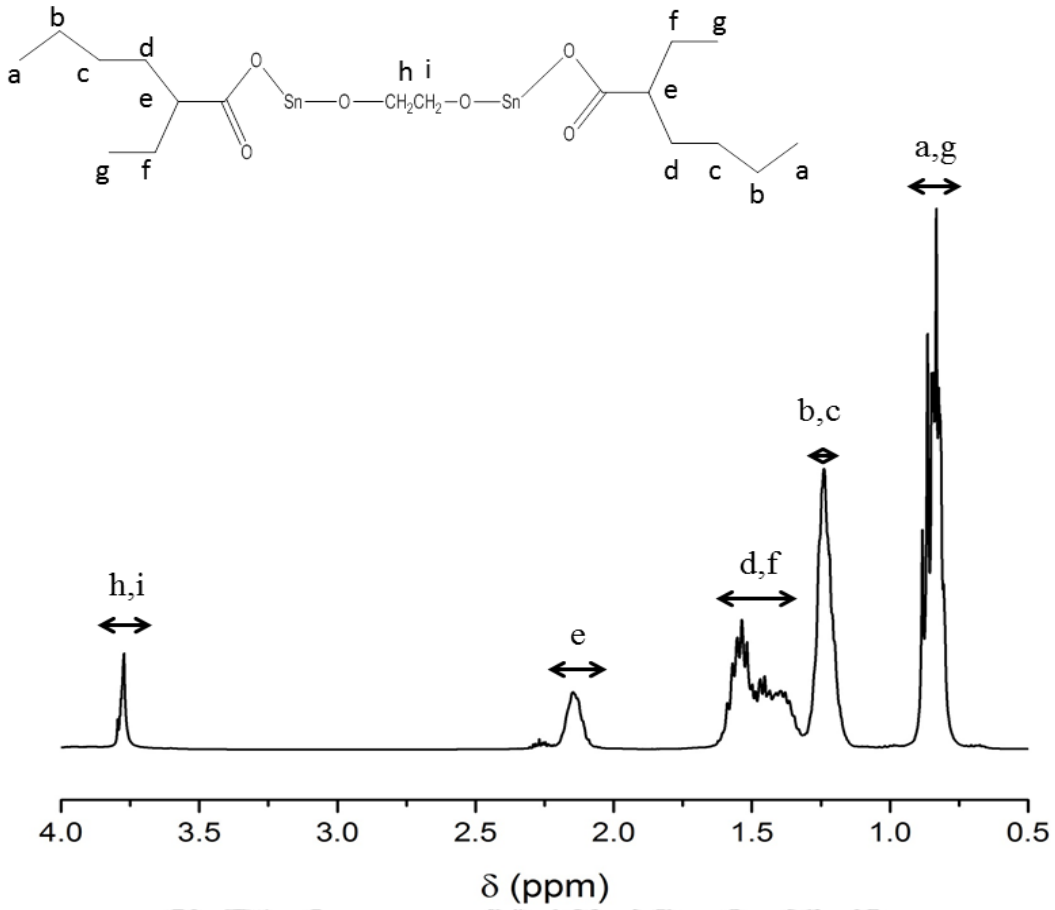

Figure 3.11 NMR spectrum of $[Sn(Oct)]_2EG$.

The $[Sn(Oct)]_2DEG$ and the reagents involving its synthesis, $Sn(Oct)_2$, DEG and OctH, were structurally characterised by Liquid Chromatography Mass Spectroscopy (LC-MS).

Mass spectroscopy (MS) is the one of useful techniques that can be used for structural characterisation. The LC-MS spectra of $Sn(Oct)_2$, DEG, OctH and $[Sn(Oct)]_2DEG$ are shown in Figures 3.12-3.15. There are many molecular ion peaks present in each spectrum. The major peaks in MS spectra of $Sn(Oct)_2$, DEG and OctH are at m/z 405, 106 and 144 respectively as indicated in the Figures. However, any molecular ion peaks of $[Sn(Oct)]_2DEG$ appeared are not corresponding to its molecular weight. This is probably due to that $[Sn(Oct)]_2DEG$ is very sensitive to oxygen, moisture and polar protic solvent, such as methanol, which is used as the mobile phase. Methanol can form a complex with tin(II) alkoxide, generating complicated fragments in the ionization system.

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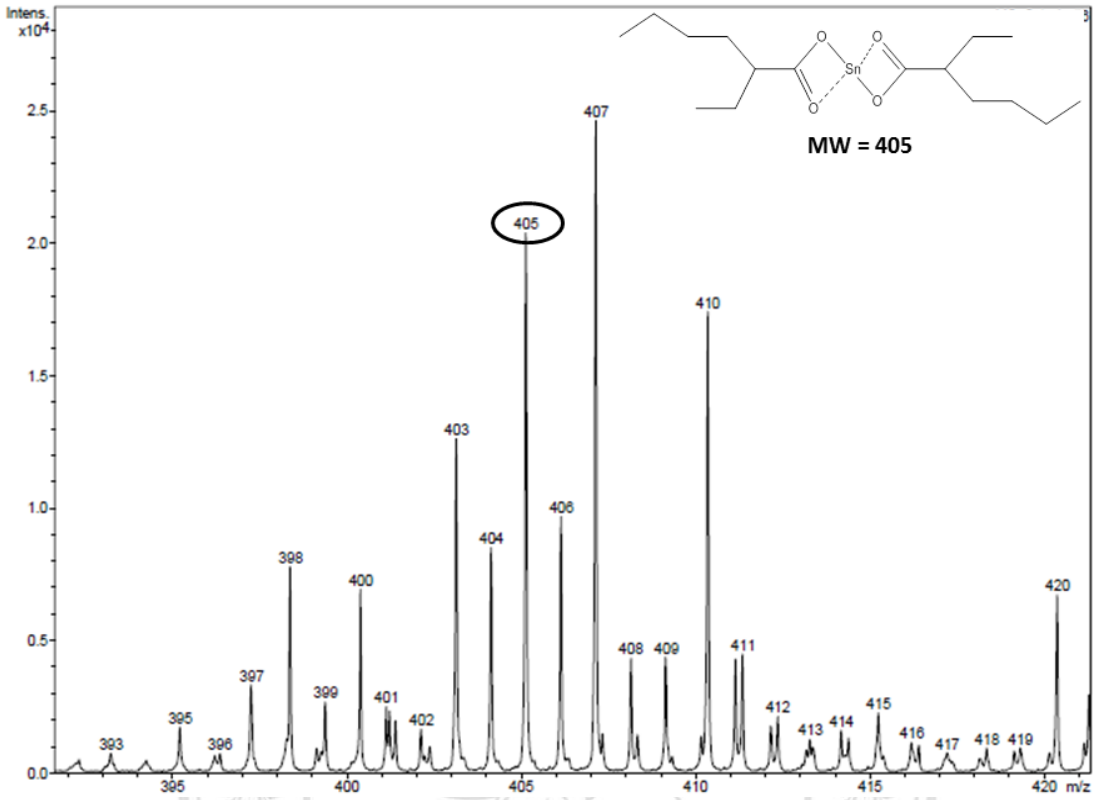

Figure 3.12 LC-MS spectra of stannous octoate ($Sn(Oct)_2$).

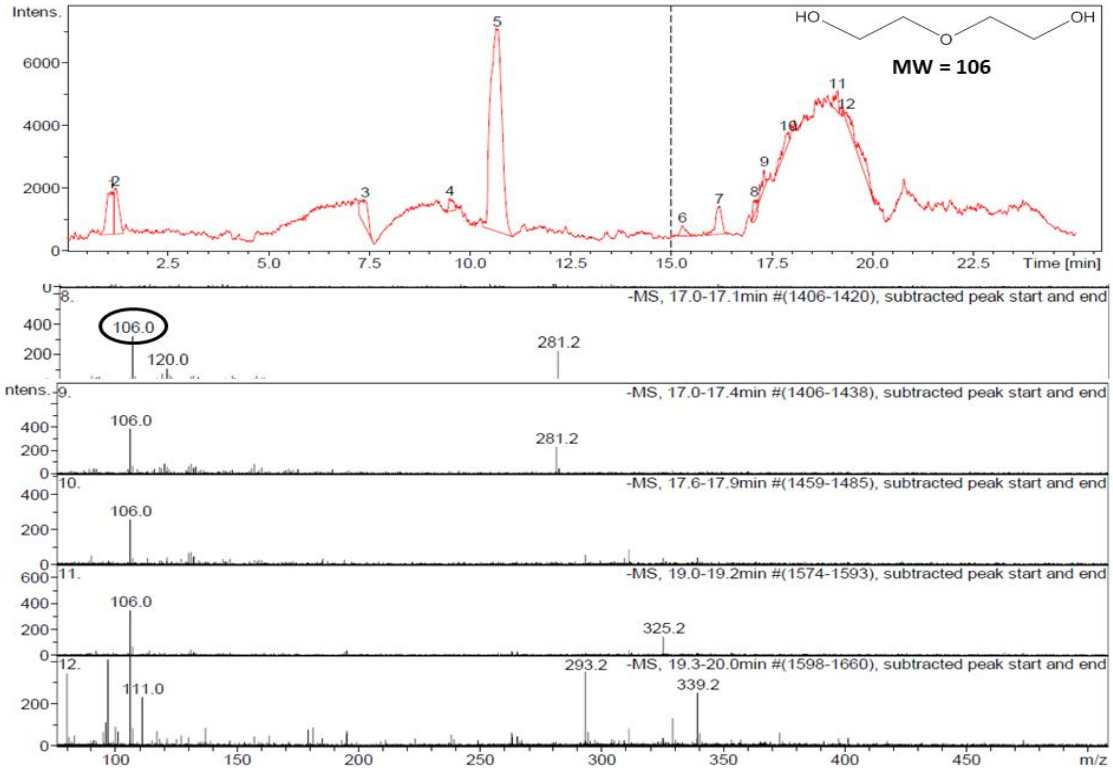

Figure 3.13 LC-MS spectra of diethylene glycol (DEG).

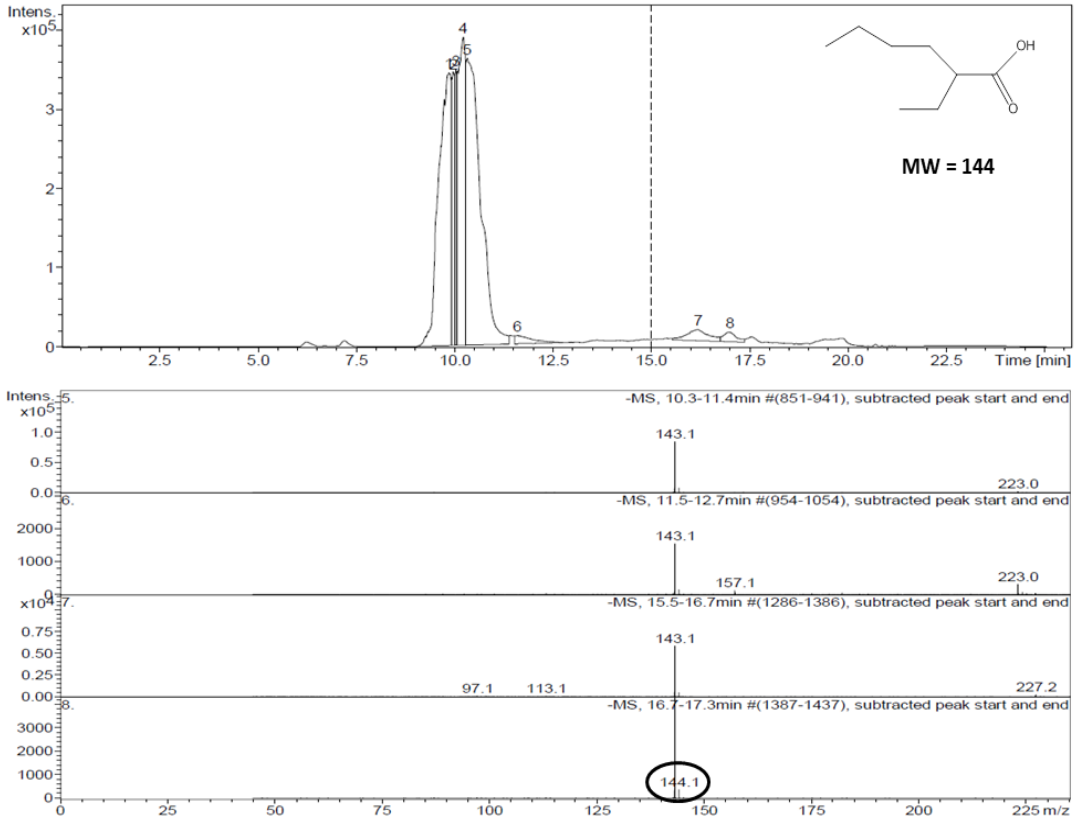

Figure 3.14 LC-MS spectra of octanoic acid (OctH).

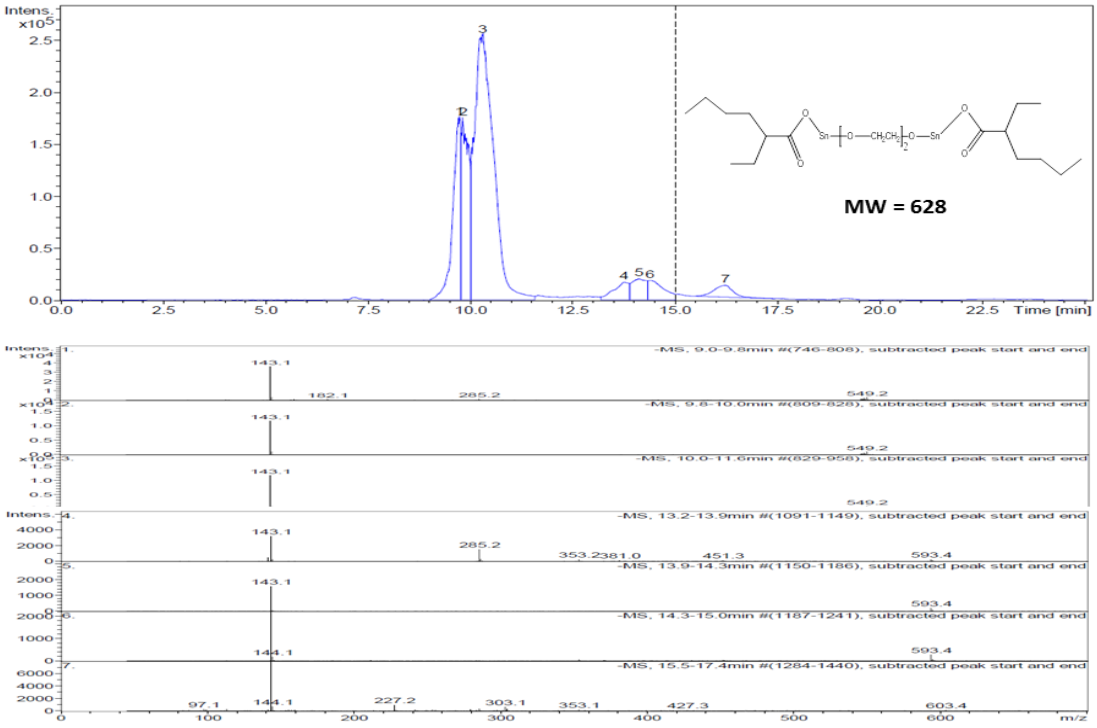

Figure 3.15 LC-MS spectra of $[Sn(Oct)]_2DEG$.

Thermogravimetric Analysis (TGA)

The TGA thermograms of the two liquid tin(II) alkoxides and $Sn(Oct)_2$ are shown in Figure 3.16. The most important point to note is that all three of the initiators exhibit good thermal stability up to 130 ^oC which is the polymerisation temperature at which they were used. Thereafter, thermal degradation sets in at around 150 ^oC and continues up to 250-300 ^oC in a single-step weight loss which finishes at between 70-90 % weight loss. These weight losses are significantly greater than those for the solid initiators previously due to these liquid initiators having much less molecular aggregation. The thermal stability of the initiator at the polymerisation temperature is essential for it to be able to perform its primary function efficiently. It was therefore important to establish that the initiators used in this work would not degrade before they could initiate.

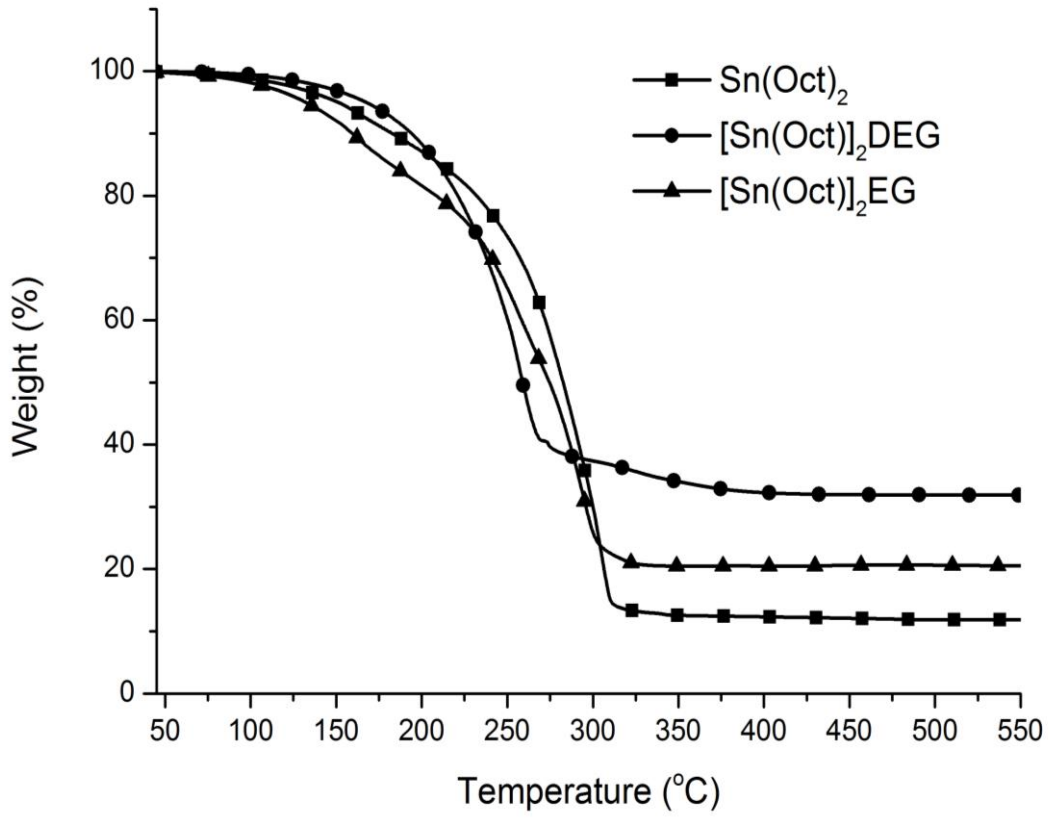

Figure 3.16 TGA thermograms of the liquid tin(II) alkoxides.