# CHAPTER 6

## Synthesis and Characterisation of Copolymers of L-lactide and ε-Caprolactone

One of the main interests in this work was to study the synthesis of polyesters. In this research, copolyesters of L-lactide (LL) and ε-caproactone (CL) with a composition ratio of LL:CL = 75:25 mol % was synthesised using novel tin(II) alkoxide initiators for absorbable surgical suture application.

### 6.1 Monomer Preparation and Purification

For potential use as suture, high molecular weight of the copolyester is necessary to obtain high strength fibre. The purity of the monomers used has an important influence on its subsequent polymerisability.

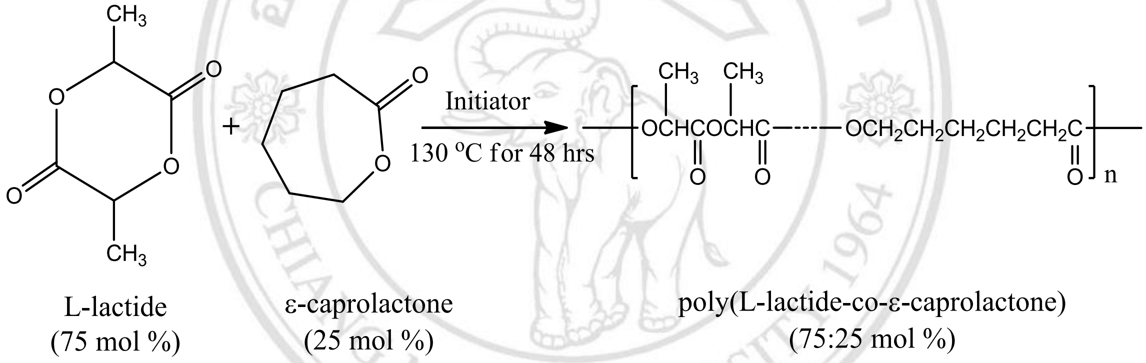
The cyclic ester monomer L-lactide was synthesised from its much cheaper precursor, L-lactic acid. It was then purified by recrystalisation from distilled ethyl acetate. The purified L-lactide was filtered through a sintered glass filter (porosity no.4) and washed with cold ethyl acetate. Its crystalline solid was dried to constant weight at 55°C in a vacuum oven. The purified L-lactide was obtained as a white needle-like crystalline solid. In order to determine the actual purity of the recrystallized L-lactide, the instrument's Purity Analysis Software Program by DSC was employed. The purity of L-lactide used was computed from its DSC thermogram in Figure 2.1 ($T_m$ peak = 97.82 $^{o}$C) to be 99.5 % as shown in Figure 2.2.

ε-Caprolactone was purified by fractional vacuum distillation before use as described previously in section 2.2.2.

## 6.2 Synthesis of Poly(L-lactide-co-ε-caprolactone), PLC, 75:25 mol %

The ring-opening bulk polymerisation procedure for L-lactide (LL) and ε-caprolactone (CL) monomers with a composition of LL:CL = 75:25 mol % using various novel initiators were carried out as described below.

The monomers (LL and CL) and initiators were accurately weighted and placed in a round-bottomed flask with a magnetic bar in a dry nitrogen atmosphere glove box at room temperature. The flask was then immersed in a silicone oil bath at 130°C for 48 hrs (Figure 6.1). PLC copolymer product obtained (as shown in the equation shown below) was then taken out from the silicone oil bath and left to cool to room temperature. PLC was cut into small pieces and dried in a vacuum oven at 55°C to constant weight.



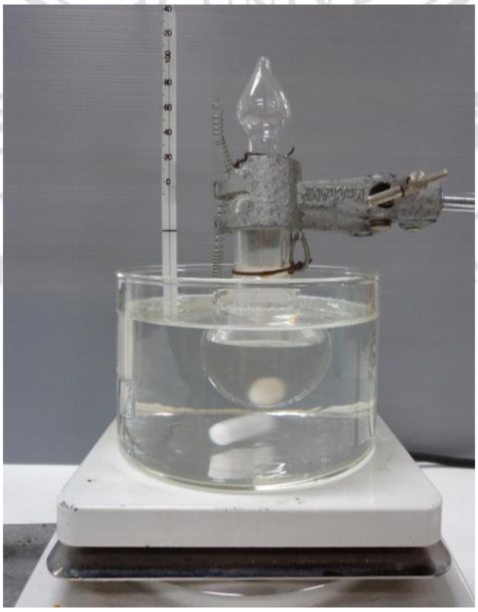


Figure 6.1 Apparatus used for copolymerisation.

## 6.3 Characterisation of PLC Copolymers

The copolymer products synthesised using different initiator systems were characterised by a combination of techniques: chemical structure analysis by FT-IR, chemical composition determination by $^1$H-NMR, chemical microstructure analysis by $^{13}$C-NMR, molecular weight determination by dilute-solution viscometry and GPC, thermal transition analysis by DSC and thermal stability by TGA.

### 6.3.1 Fourier-Transform Infrared Spectroscopy (FT-IR)

A Bruker FTIR TENSOR 27 Fourier Transform Infrared Spectrometer was used for the structural characterisation of the PLC copolymers. The samples were prepared in the form of thin films casting from solution in chloroform onto NaCl discs. FT-IR spectra recorded in the range 400 – 4000 cm$^{-1}$ for the PLC polymer products obtained using different initiator systems are shown in Figures 6.2-6.10.

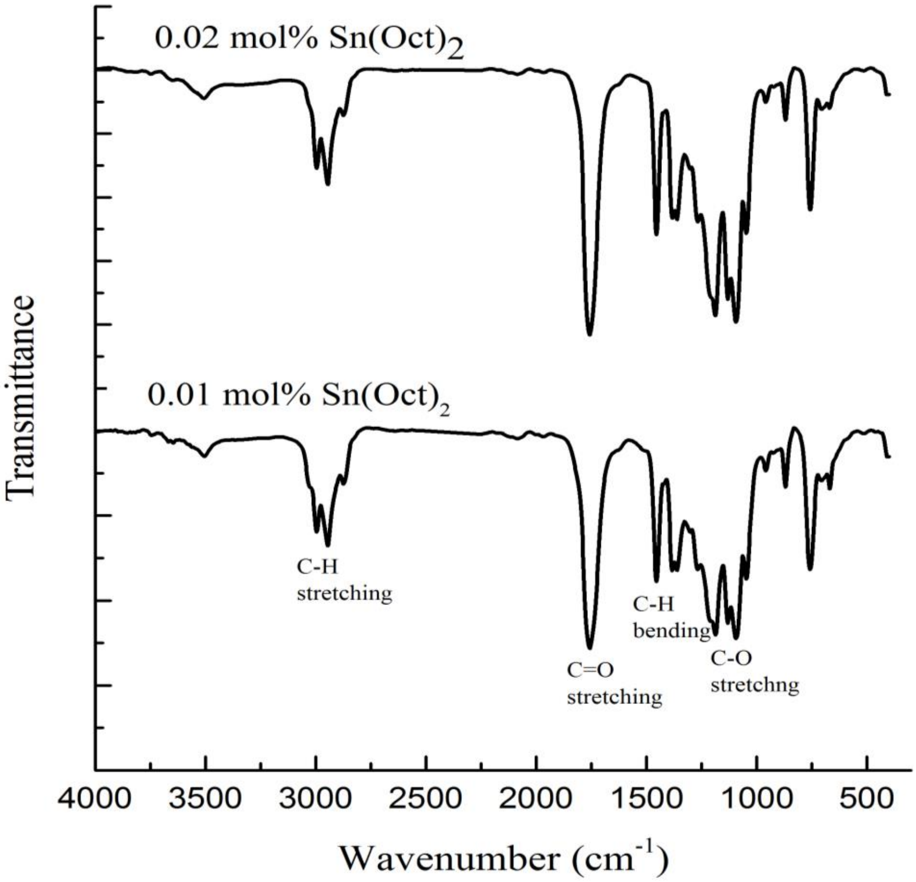


Figure 6.2 FT-IR spectra of PLC using Sn(Oct)$_2$ as initiator.

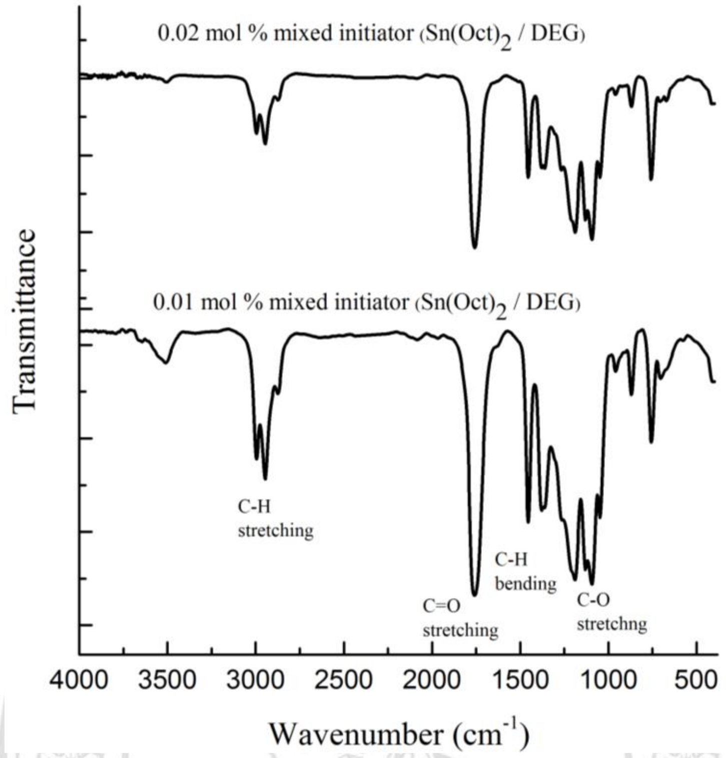


Figure 6.3 FT-IR spectra of PLC using mixed initiator ($Sn(Oct)_2$ / DEG).

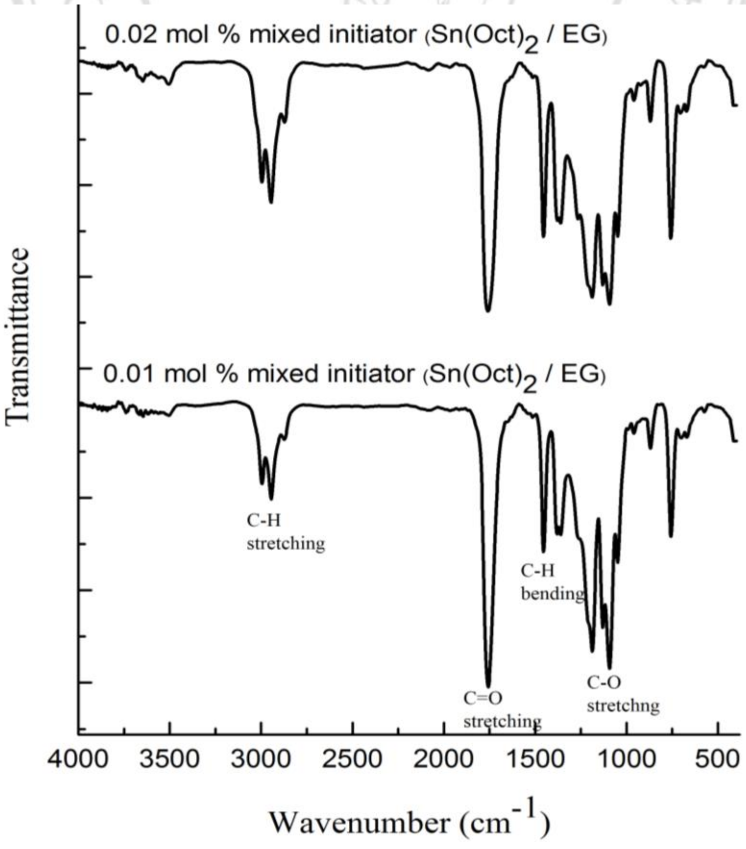


Figure 6.4 FT-IR spectra of PLC using mixed initiator ($Sn(Oct)_2$ / EG).

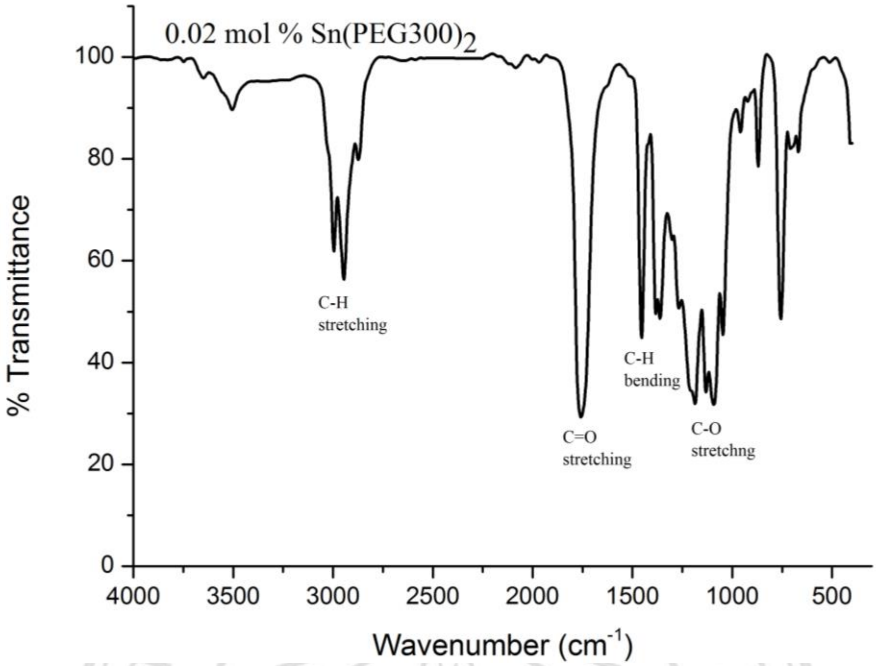


Figure 6.5 FT-IR spectrum of PLC using solid $Sn(PEG300)_2$ as initiator.

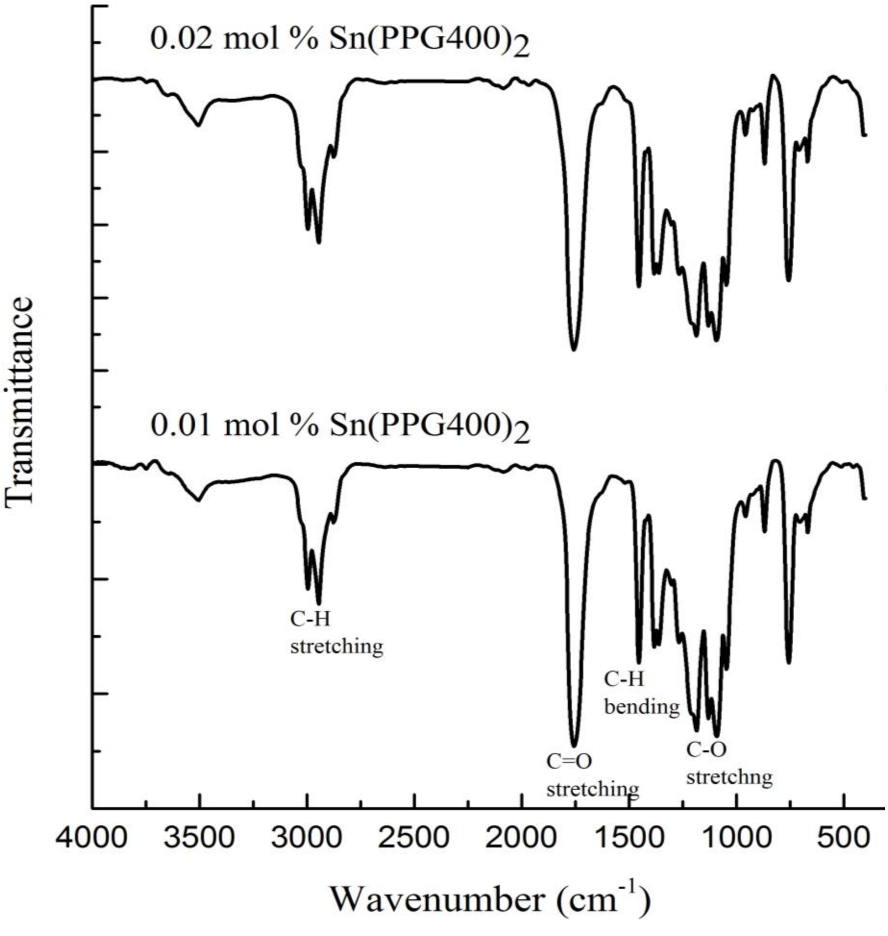


Figure 6.6 FT-IR spectrum of PLC using solid $Sn(PPG400)_2$ as initiator.

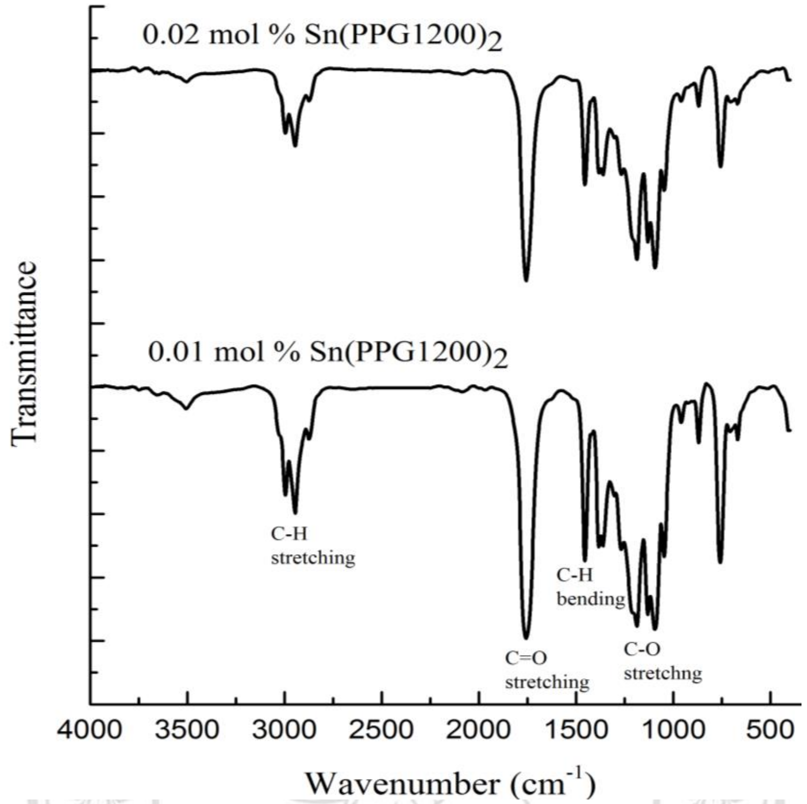


Figure 6.7 FT-IR spectrum of PLC using solid $Sn(PPG1200)_2$ as initiator.

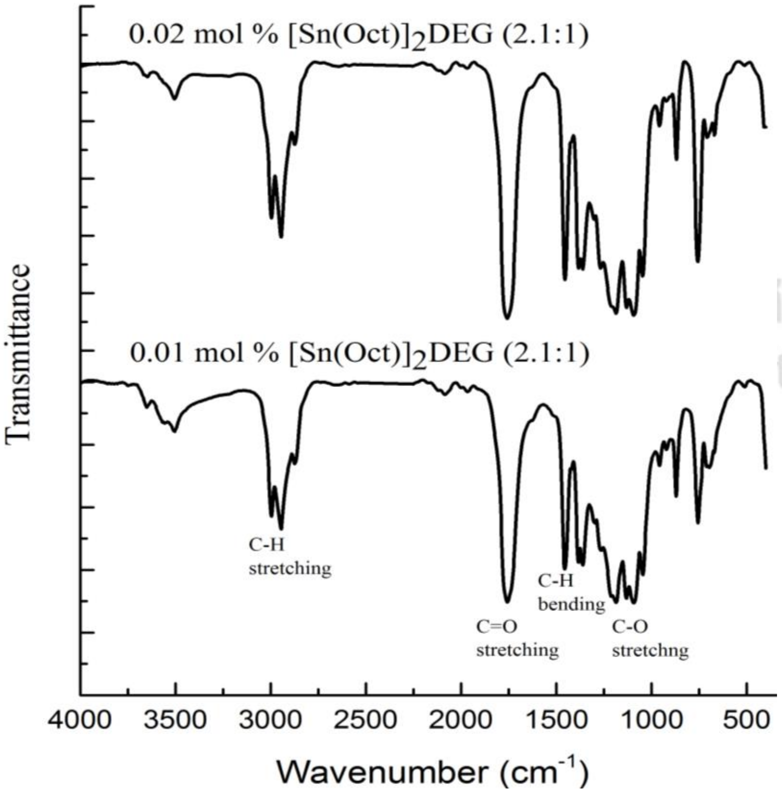


Figure 6.8 FT-IR spectra of PLC using liquid $[Sn(Oct)]_2DEG$ (2.1:1) as initiator.

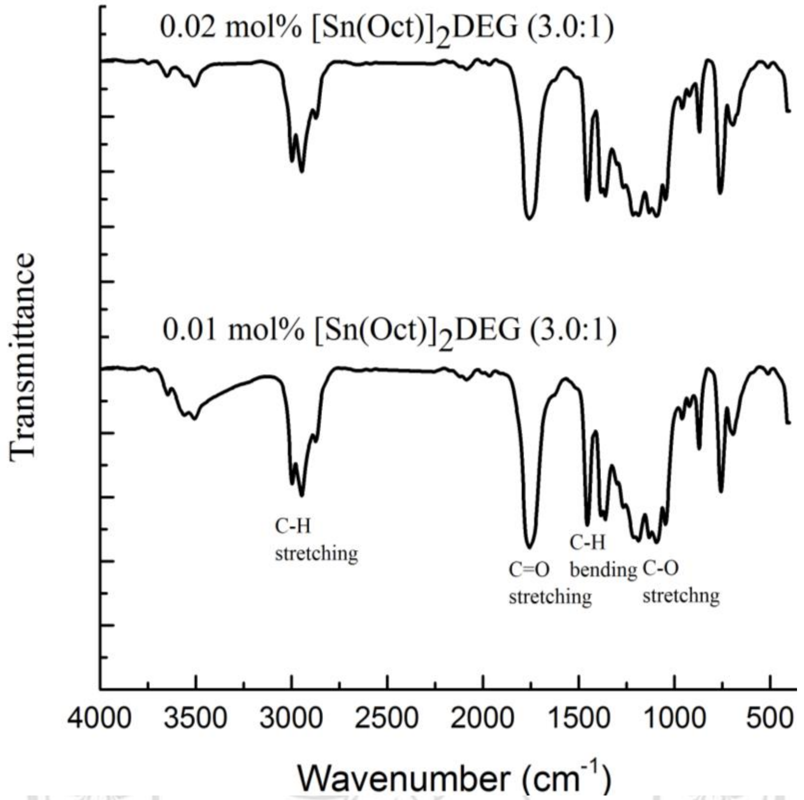


Figure 6.9 FT-IR spectra of PLC using liquid $[Sn(Oct)]_2DEG$ (3.0:1) as initiator.

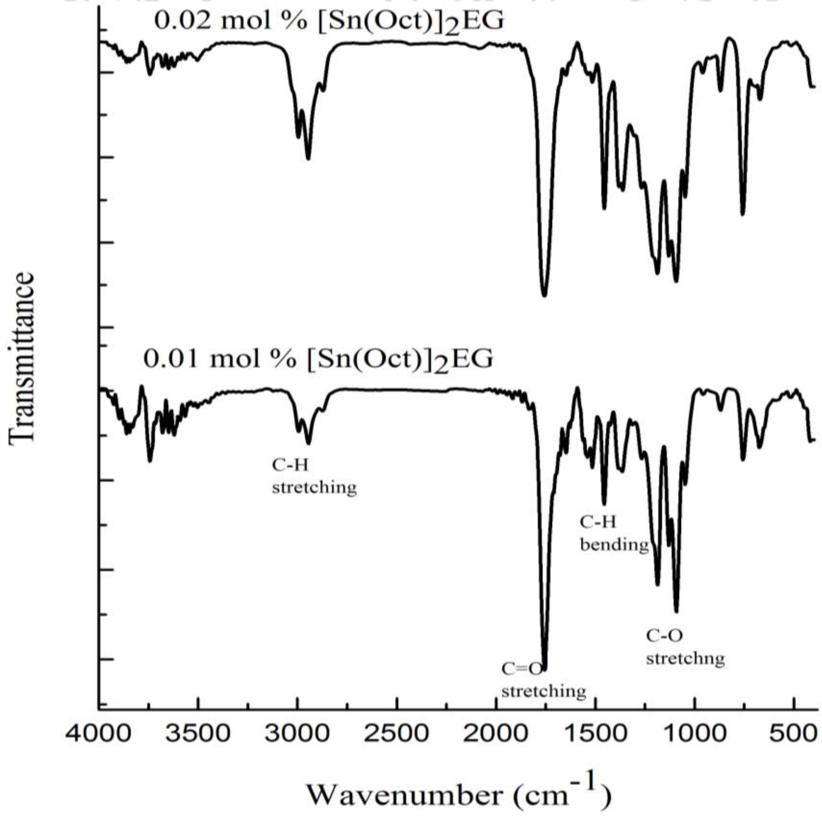


Figure 6.10 FT-IR spectrum of PLC using liquid $[Sn(Oct)]_2EG$ as initiator.

All of the FT-IR spectra are very similar in appearance, as would be expected. The main difference is in the size of the O-H peak in the region of 3400-3600 $cm^{-1}$ which is due to a combination of unreacted OH end-groups from the initiator and moisture impurity. Since both the LL and CL repeat units in the copolymer contain the same bond vibrations at the same frequencies, it is not possible to determine the copolymer composition from the IR spectrum. Instead, the copolymer composition is best determined from the $^1$H-NMR spectrum, as described in the following section.

### 6.3.2 Nuclear Magnetic Resonance (NMR) Spectrometry

Polymer compositions and monomer sequencing were characterised by a combination of 400 MHz $^1$H and 100 MHz $^{13}$C Nuclear Magnetic Resonance (NMR) Spectroscopy using a Bruker Model DPX 400. The samples were dissolved in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as internal standard for NMR analyses.

#### 6.3.2.1 Proton Nuclear Magnetic Resonance ($^1$H-NMR) Spectrometry

The $^1$H NMR spectra of all the samples are shown in Figures 6.11-6.12. The copolymer chemical compositions are calculated using the MestReNova data processing software for peak area integrations. The copolymer chemical compositions were calculated as described in the section below.

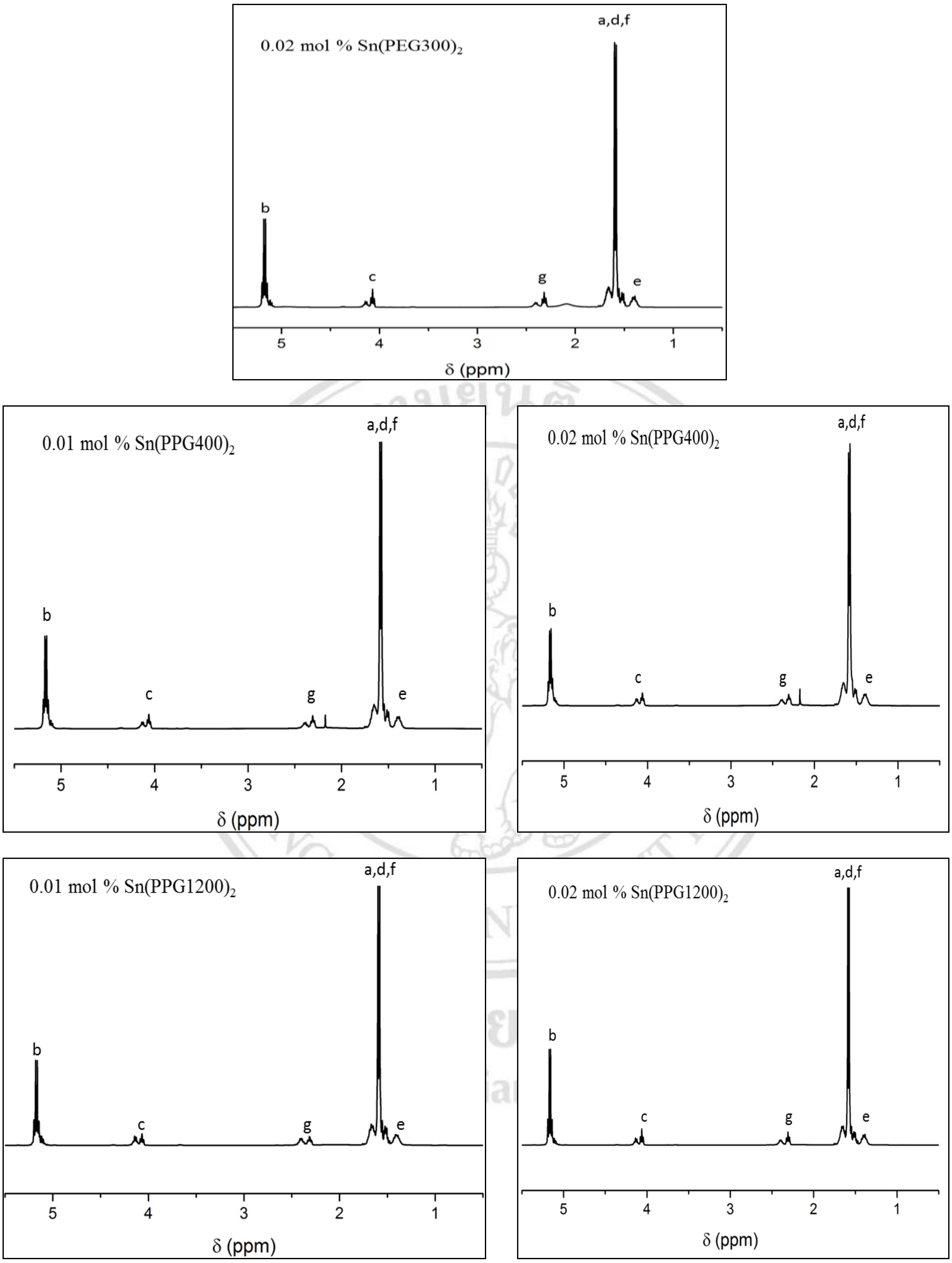


Figure 6.11 400 MHz $^1$H-NMR spectra of the PLC copolymers using: the solid tin(II) alkoxide initiators.

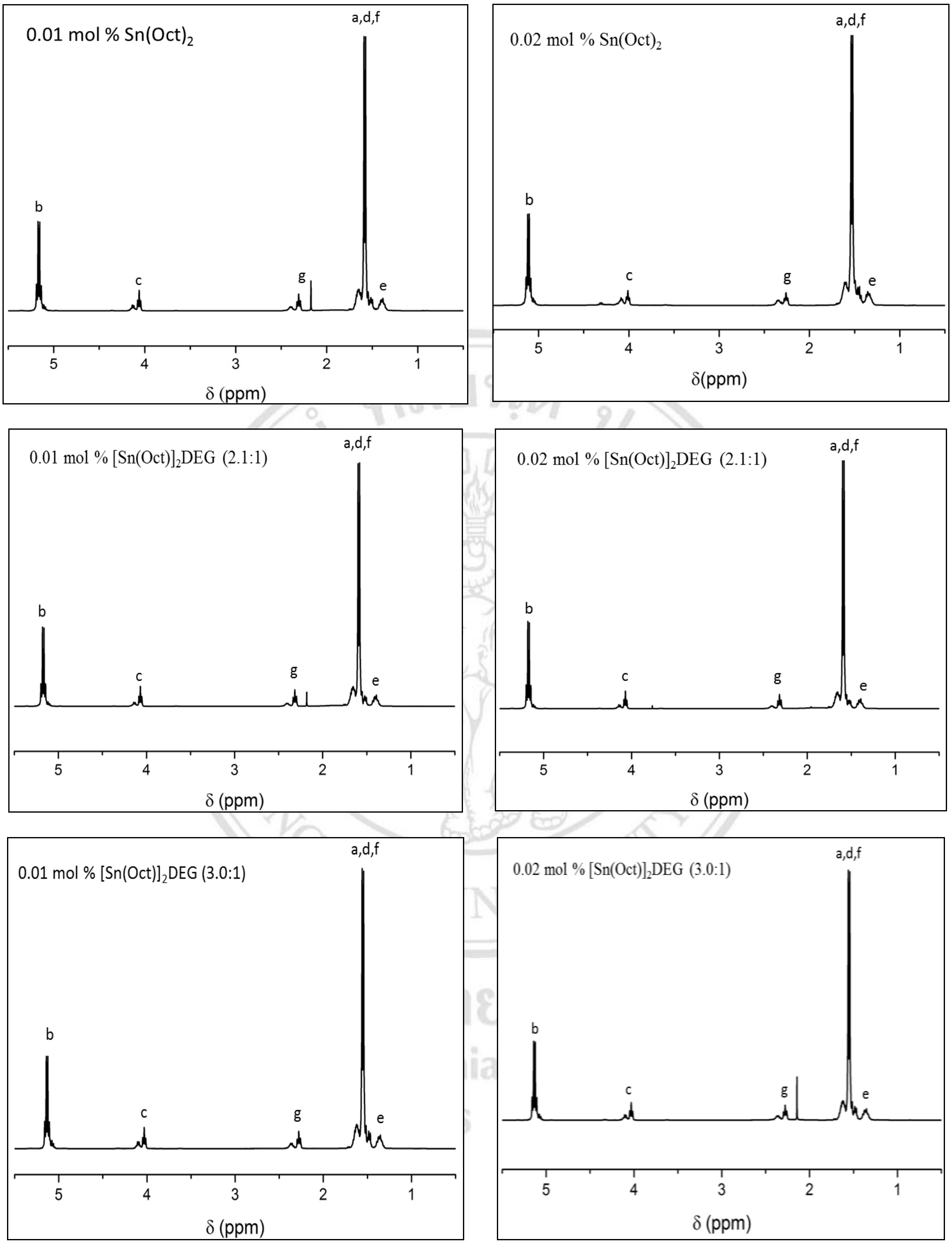


Figure 6.12 400 MHz $^1$H-NMR spectra of the PLC copolymers using the liquid tin(II) alkoxide initiators.

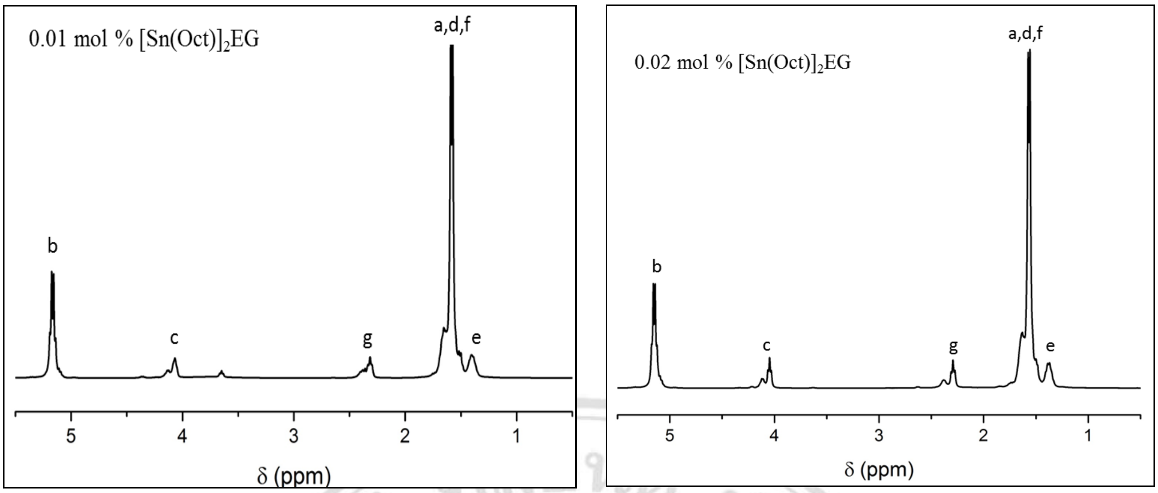


Figure 6.12 (continued).

**Compositional Analysis**

The $^1$H-NMR spectrum of PLC using 0.02 mol % $Sn(Oct)_2$ initiator is used as an example to calculate the copolymer composition. The molecular ratio of LL : CL for the PLC copolymer can be calculated from the $^1$H-NMR peak area integrations for the methine protons in LL (b) and the ε-methylene protons in CL (c), as shown below in Figure 6.13. The copolymer composition calculation is as follows:

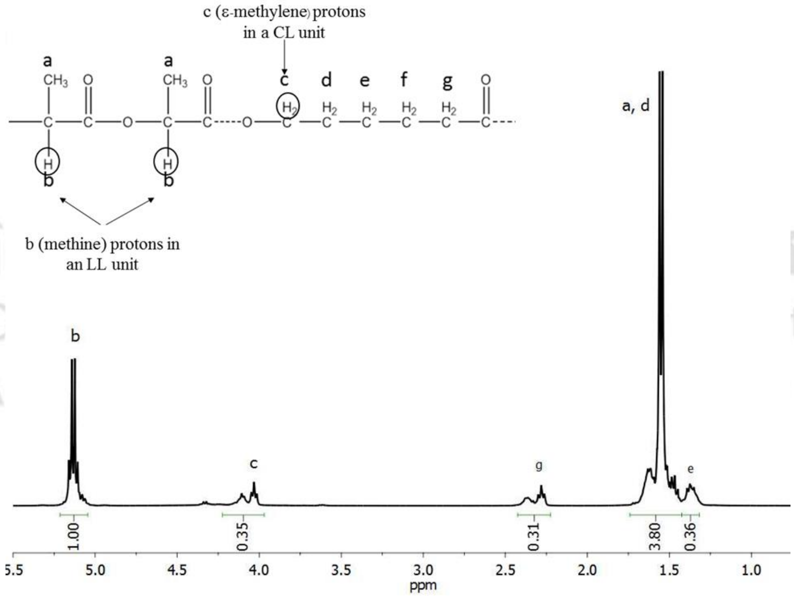


Figure 6.13 $^1$H-NMR spectrum of PLC using 0.02 mol % $Sn(Oct)_2$ initiator.

| peak integration of methine protons (2H/LL unit) | | peak integration of ε-methylene protons (2H/CL unit) |
|---|---|---|
| $\frac{1.00}{2}$ | : | $\frac{0.35}{2}$ |
| 0.50 | : | 0.18 |

Thus, the PLC copolymer composition is:

LL : CL = 0.50 : 0.18
= 73.53 : 26.47 mol %
≅ 74 : 26 mol %

The PLC copolymer compositions were calculated similarly from their NMR spectra and the results are shown in Table 6.1. The results show that the final polymer compositions are close to the initial monomer feeds (LL:CL = 75:25 mol %). It may be concluded that the synthesis reactions were taken to near completion so that almost all of the initial monomers went into forming the final polymer.

#### 6.3.2.2 Carbon-13 Nuclear Magnetic Resonance ($^{13}$C-NMR) Spectrometry

The main purpose of this $^{13}$C-NMR study is to investigate the chain microstructure (monomer sequencing) of the copolymers that $^{1}$H-NMR is insensitive to. This is made possible by the fact that, in $^{13}$C-NMR spectrum, the chemical shifts are spread over a wide range of over 200 ppm, as compared with the relatively narrow 10 ppm range in $^{1}$H-NMR. Therefore, much smaller differences in chemical environment can be distinguished in $^{13}$C-NMR making it a much more powerful technique than $^{1}$H-NMR for studying polymer microstructure, in particular monomer sequencing in copolymers.

Table 6.1 The calculated copolymer PLC compositions from $^1$H-NMR spectra.

| Initiating System | Initiator concentration (mol %) | Calculated copolymer Composition (LL:CL) (mol %) |
|---|---|---|
| $Sn(PEG300)_2$ | 0.02 | 75 : 25 |
| $Sn(PPG400)_2$ | 0.01 | 76 : 24 |
| | 0.02 | 78 : 22 |
| $Sn(PPG1200)_2$ | 0.01 | 75 : 25 |
| | 0.02 | 75 : 25 |
| $Sn(Oct)_2$ | 0.01 | 76 : 24 |
| | 0.02 | 74 : 26 |
| $[(Sn(Oct)]_2DEG$ (2.1:1) | 0.01 | 76 : 24 |
| | 0.02 | 76 : 24 |
| $[(Sn(Oct)]_2DEG$ (3.0:1) | 0.01 | 76 : 24 |
| | 0.02 | 75 : 25 |
| $[(Sn(Oct)]_2EG$ | 0.01 | 79 : 21 |
| | 0.02 | 77 : 23 |

In this research, 100 MHz $^{13}$C-NMR spectra of the copolymers were obtained using a Bruker Model DPX 400 Nuclear Magnetic Resonance Spectrometer. The PLC samples were run in deuterated chloroform solution at room temperature giving spectra as shown in Figure 6.14 as an example.

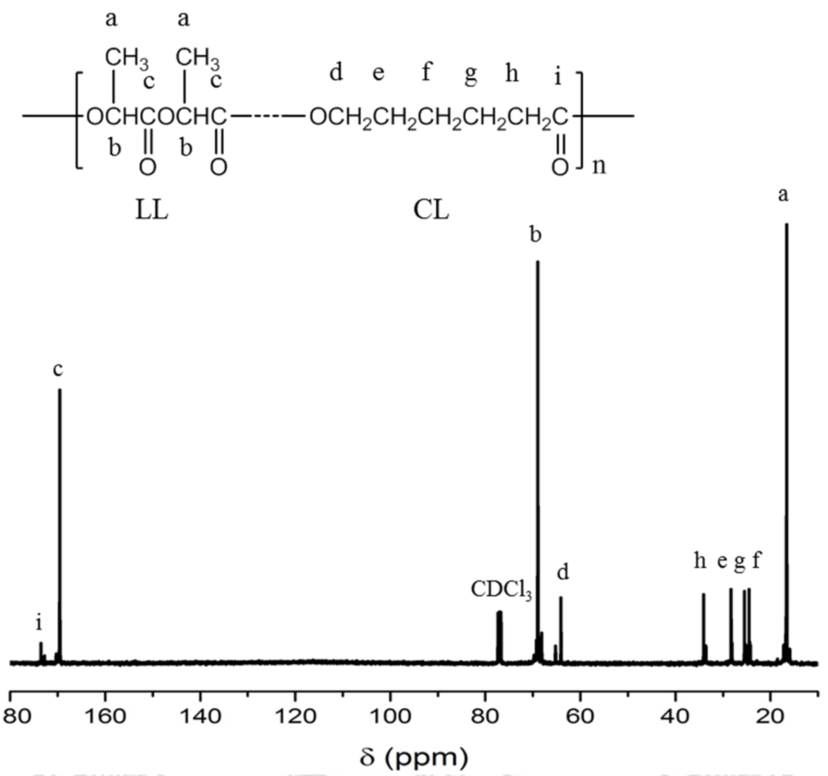
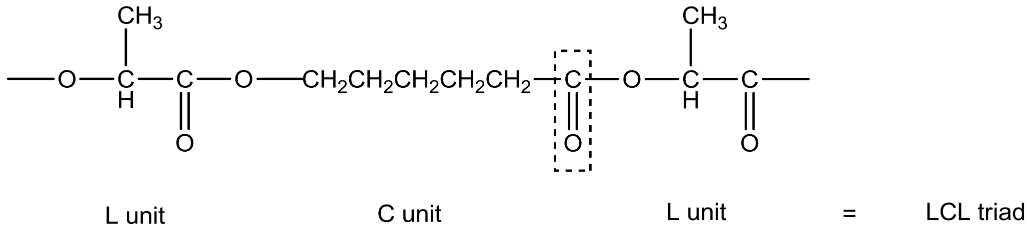


Figure 6.14 Typical $^{13}$C-NMR spectrum of a PLC copolymer.

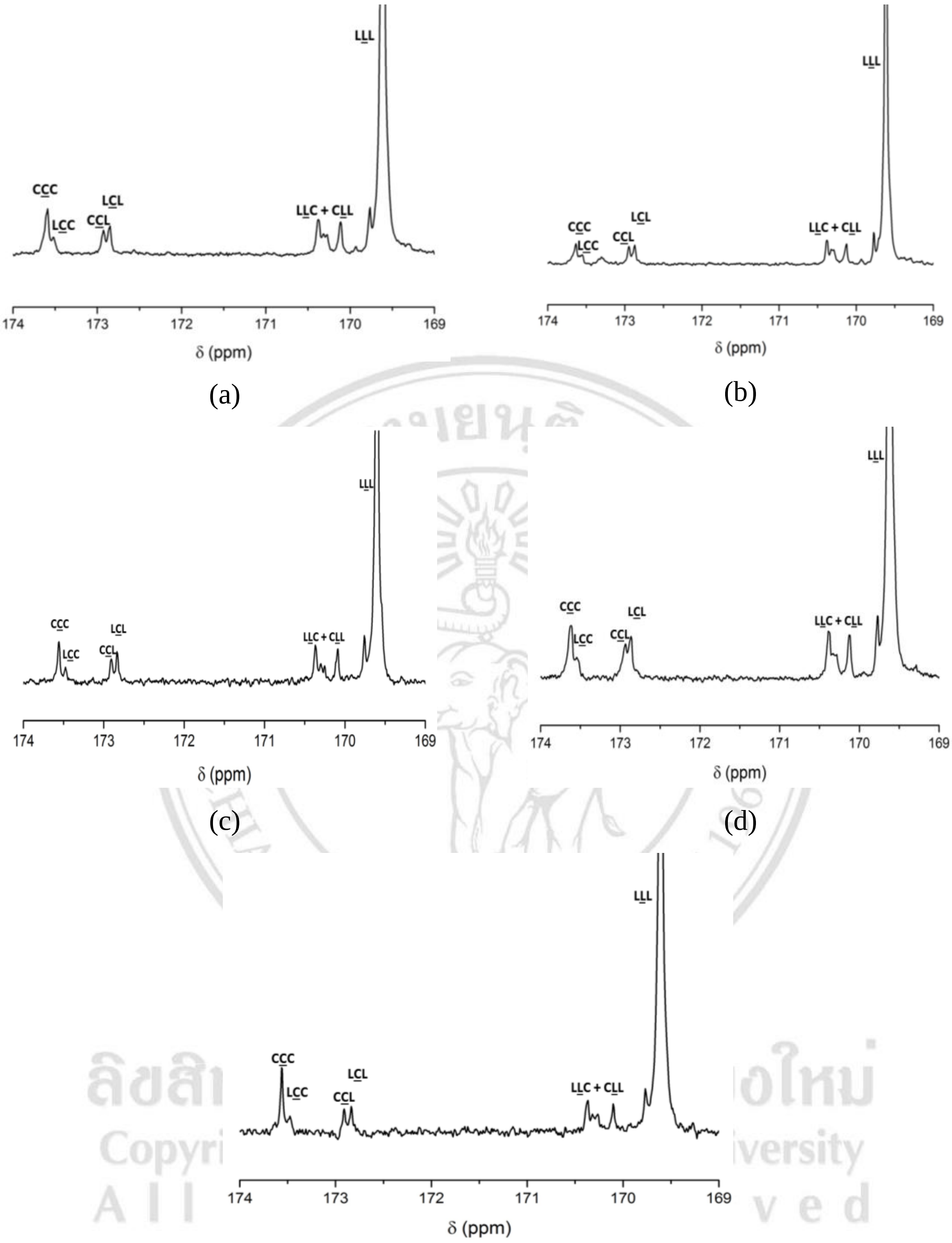
In the $^{13}$C-NMR polymer spectrum, carbonyl (C=O) carbon atoms have shown to be especially sensitive to sequencing variations, much more so than C-H carbons (methyl, methylene and methane). Therefore, it is the carbonyl region of the spectrum from δ = 168-175 ppm which provides the most information about the copolymer chain microstructure. When this carbonyl region is expanded, as shown in Figure 6.15, there appears additional small peaks between 169.5 and 173.5 ppm. This indicates the presence of adjoining L and C units which can be identified as those occurring in the various heterounit triad sequences CCC, LCC, CCL LCL, LLC, CLL and LLL. These various triad sequences can be identified with reference to the homopolymer spectra and related literature reports [98,114,115] confirming the random character of the PLC copolymers.

For example, the carbonyl carbon which is associated with the LCL peak is the carbonyl carbon of the central caprolactone (C) unit as shown below:



Since the area under each peak is proportional to its triad concentration, it follows that the more in number and the larger in size are the heterotriad peaks between the homotriad CCC and LLL peaks, the more randomized is the monomer sequencing. Thus it can be concluded from the $^{13}C$-NMR spectra in Figure 6.15 that, since the LLL and CCC peaks are the most prominent in terms of size, these PLC copolymers are best described as being tapered (i.e., partly blocky) rather than random copolymers. This in turn is a consequence of the differing reactivity ratios (LL>CL) of the LL and CL comonomers.

It should also be mentioned that, since the LL and CL monomer reactivities are much different, there will inevitably be a compositional distribution in the final copolymer. This is because, since the residual monomer concentrations are constantly changing throughout the copolymerisation, the instantaneous copolymer composition also changes. Thus, it should be understood that the $^{13}C$-NMR in Figure 6.15 and also the previous $^{1}H$-NMR spectra are of the final copolymers as a whole and so the data derived from then are in fact average values for the complete range of their compositional and microstructural distributions.



(a) (b)

(c) (d)

(e)

Figure 6.15 Expanded carbonyl regions of the $^{13}$C-NMR spectra of the PLC copolymers using the various initiators: (a) 0.01 mol % $Sn(Oct)_2$ (b) 0.02 mol % $Sn(Oct)_2$ (c) 0.01 mol % $[Sn(Oct)]_2DEG$ (3.0:1) (d) 0.02 mol % $[Sn(Oct)]_2DEG$ (3.0:1) and (e) 0.02 mol % $[Sn(Oct)]_2EG$.

### 6.3.3 Molecular Weight Determination

#### 6.3.3.1 Gel Permeation Chromatography (GPC)

The average molecular weights and polydispersity ($\overline{M}_w / \overline{M}_n$) indices of the PLC copolymers using the various initiator systems were determined by gel permeation chromatography (GPC) (flow rate 1 ml min$^{-1}$) through three PL gel 5 mm 300 x 7.5 mm mixed-C columns using a degassed THF eluent system containing 2% (v/v) TEA and 0.05% (w/v) BHT. The system, operating at 40 $^{o}$C, was calibrated with narrow polystyrene standards [116]. The molecular weights and polydispersities of the PLC copolymers were calculated from their GPC curves and the results compared in Table 6.2. It should be noted that these molecular weights determined by GPC are not absolute values due to the calibration of the GPC by polystyrene standards which only give a relative value of the polymer molecular weight. The GPC results are therefore used as a qualitative tool to compare the copolymer molecular weights across a series rather than give exact values.

From the results, the liquid initiators tended to give the higher molecular weights except for $Sn(Oct)_2$ alone. This was probably due to their complete solubility in the comonomers compared with the only partially soluble solid initiators. Generally, melt spinning of aliphatic polyesters requires a value of $\overline{M}_n \geq 30,000$ and so the $\overline{M}_n$ values in Table 6.2, with just one exception, are considered to be high enough for fibre production.

Table 6.2 Molecular weights of PLC copolymers from GPC.

| **Initiators** | **PLC** | |
|---|---|---|
| | $\overline{M}_n$ **(x 10$^{-4}$)** | **PD ($\overline{M}_w/\overline{M}_n$)** |
| **Solid Initiators** | | |
| 0.02 mol % Sn(PEG300)$_2$ | 3.66 | 1.864 |
| 0.01 mol % Sn(PPG400)$_2$ | 4.44 | 1.859 |
| 0.02 mol % Sn(PPG400)$_2$ | 3.05 | 1.731 |
| 0.01 mol % Sn(PPG1200)$_2$ | 5.20 | 2.240 |
| 0.02 mol % Sn(PPG1200)$_2$ | 4.31 | 2.021 |
| **Liquid Initiators** | | |
| 0.01 mol % Sn(Oct)$_2$ | 3.86 | 2.016 |
| 0.02 mol % Sn(Oct)$_2$ | 1.77 | 1.954 |
| 0.01 mol % [Sn(Oct)]$_2$DEG (2.1:1) | 6.70 | 1.659 |
| 0.02 mol % [Sn(Oct)]$_2$DEG (2.1:1) | 5.60 | 1.665 |
| 0.01 mol % [Sn(Oct)]$_2$DEG (3.0:1) | 6.48 | 1.873 |
| 0.02 mol % [Sn(Oct)]$_2$DEG (3.0:1) | 4.09 | 1.826 |
| 0.01 mol % [Sn(Oct)]$_2$EG | 4.04 | 1.779 |
| 0.02 mol % [Sn(Oct)]$_2$EG | 10.00 | 1.297 |

### 6.3.3.2 Dilute-Solution Viscometry

The intrinsic viscosities, [η], of the PLC products were determined from dilute solution viscometry. The viscosities were measured at concentration of 0.25-1.00 % (w/v) in $CHCl_3$ as solvent at 30.0 ± 0.1 $^oC$ with an Ostwald viscometer (Technico Size A). Each solution concentration was separately prepared in order to eliminate any dilution errors. The results were plotted between reduced and inherent viscosity versus concentration as shown in Figures 6.16-6.18 and the results summerized in Table 6.3.

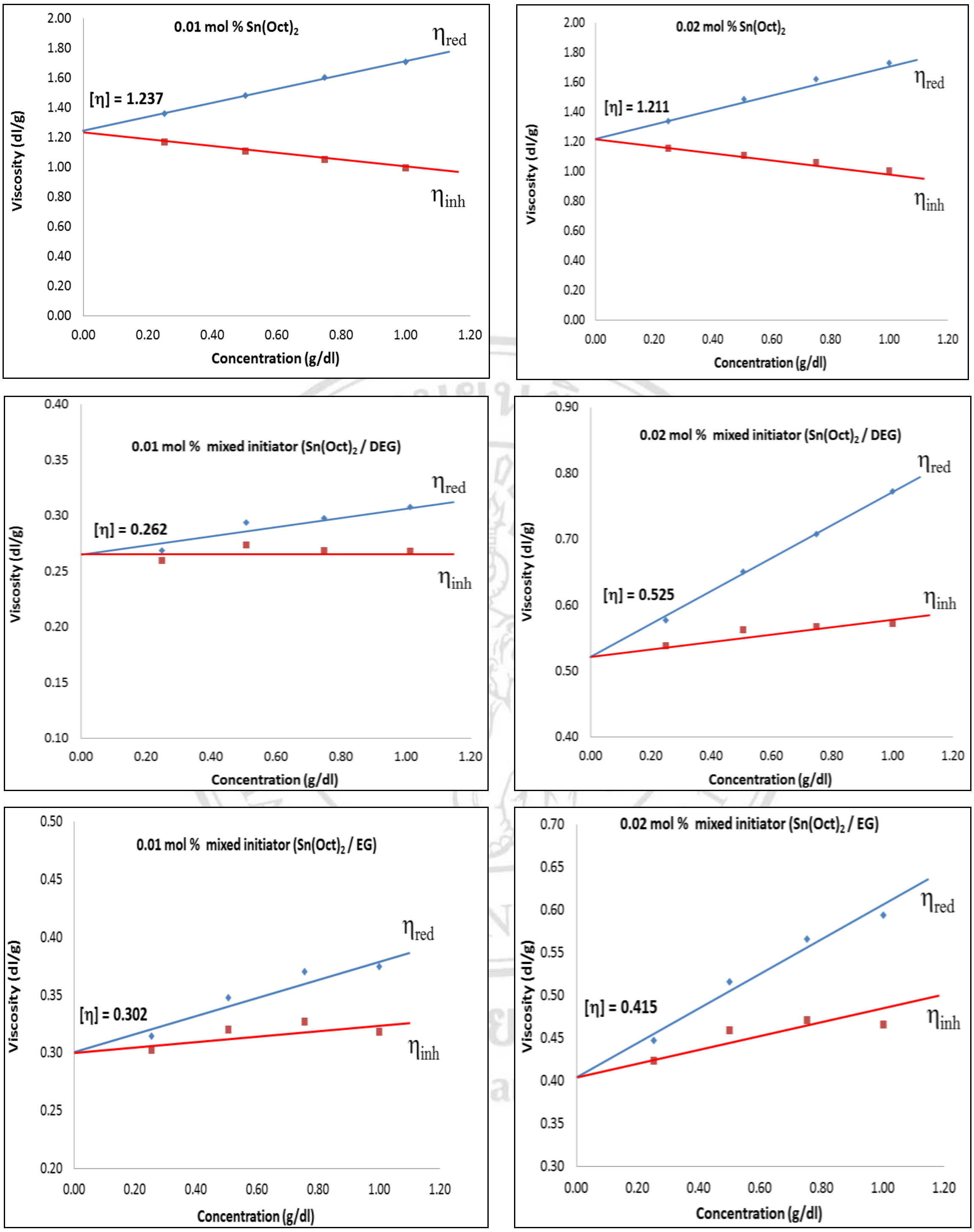


Figure 6.16 Plots of $\eta_{red}$ and $\eta_{inh}$ vs concentration of PLC synthesised using $Sn(Oct)_2$ and mixed initiators.

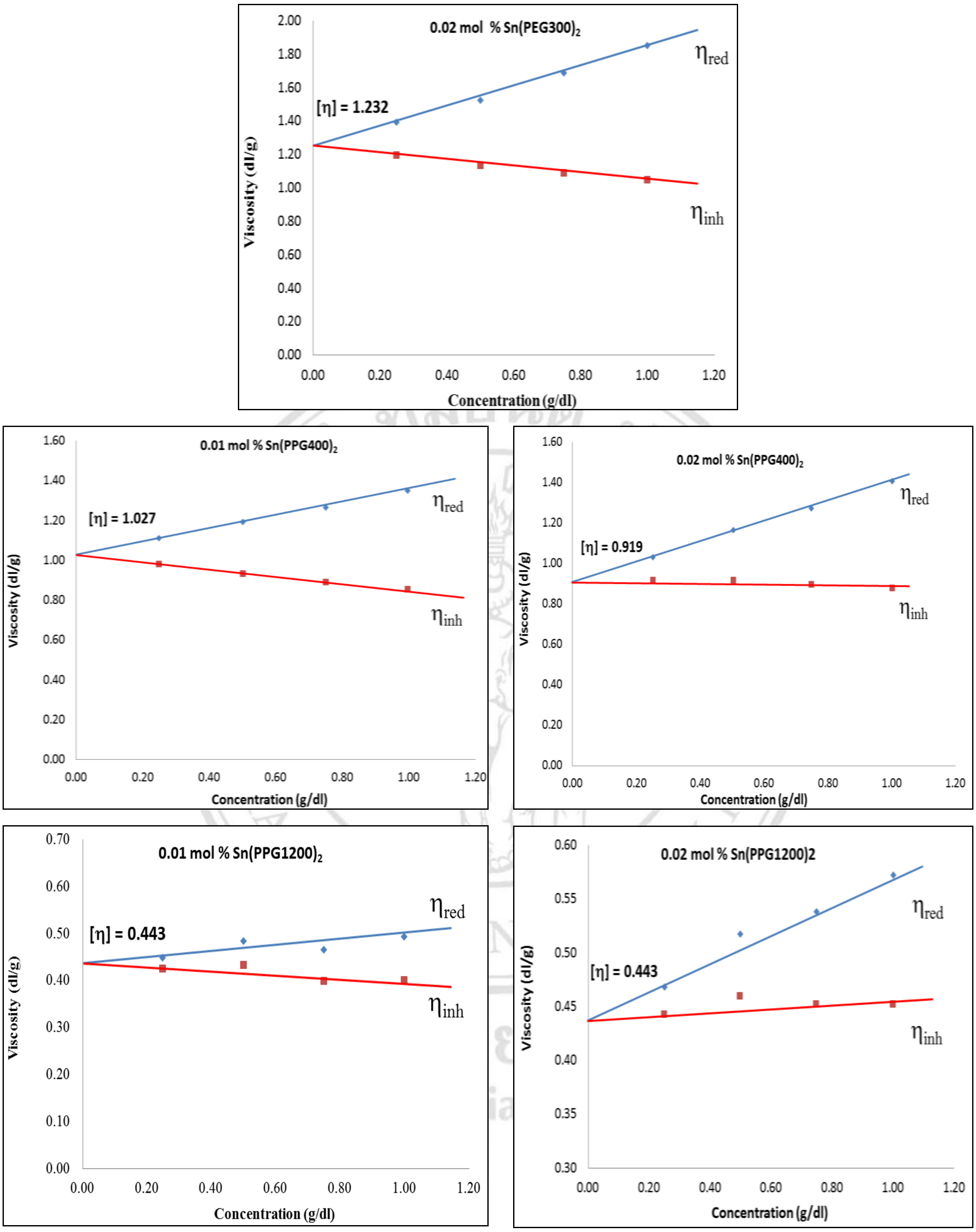


Figure 6.17 Plots of $\eta_{red}$ and $\eta_{inh}$ vs concentration of PLC synthesised using the solid initiators.

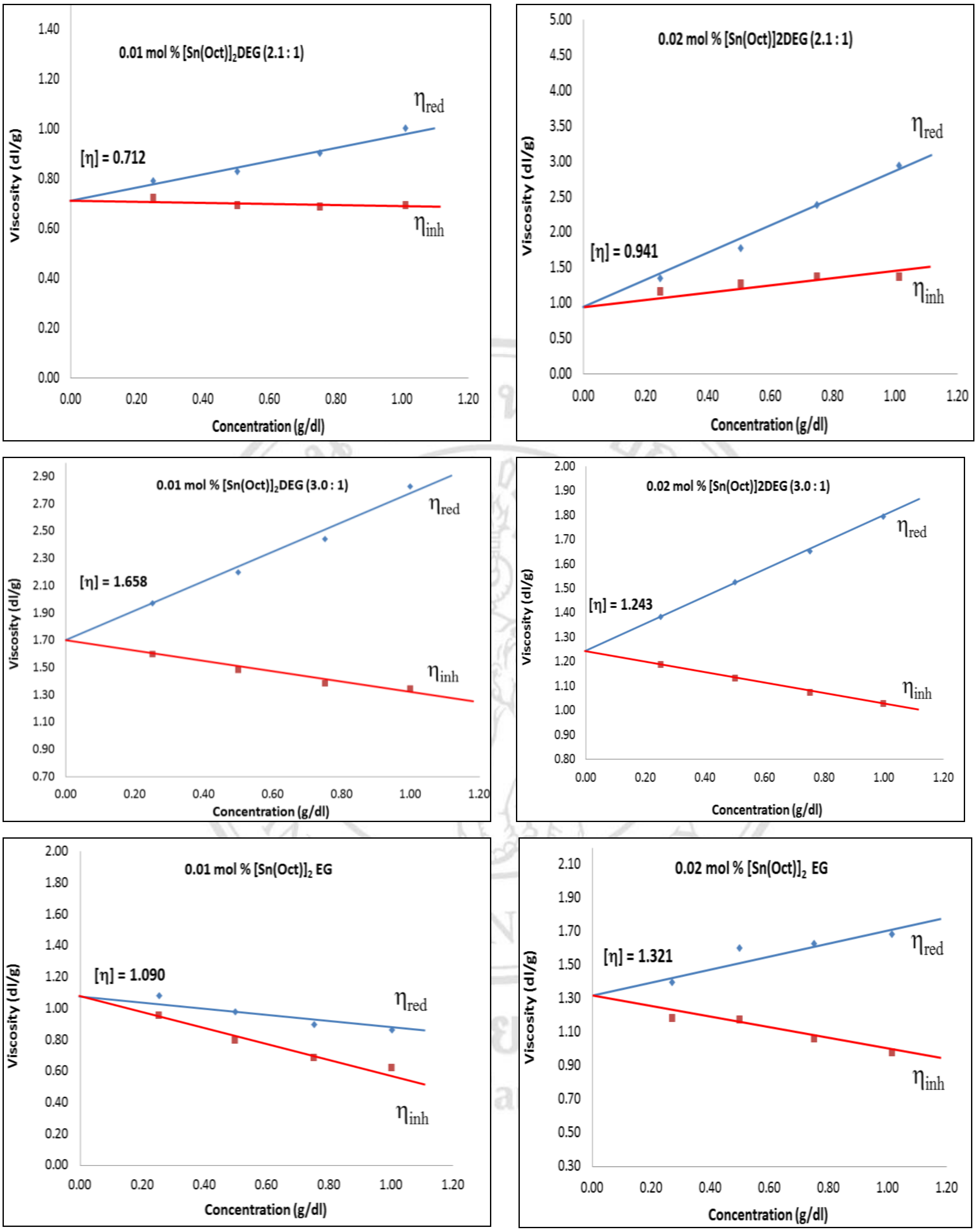


Figure 6.18 Plots of $\eta_{red}$ and $\eta_{inh}$ vs concentration of PLC synthesised using the liquid initiators.

Table 6.3 Intrinsic viscosities, [η], of PLC copolymers from dilute-solution viscometry.

| **Initiators** | **[η] (dl/g)** |
|---|---|
| **Mixed Initiators** | |
| 0.01 mol % $Sn(Oct)_2$ / DEG | 0.262 |
| 0.02 mol % $Sn(Oct)_2$ / DEG | 0.525 |
| 0.01 mol % $Sn(Oct)_2$ / EG | 0.302 |
| 0.02 mol % $Sn(Oct)_2$ / EG | 0.415 |
| **Solid Initiators** | |
| 0.02 mol % $Sn(PEG300)_2$ | 1.232 |
| 0.01 mol % $Sn(PPG400)_2$ | 1.027 |
| 0.02 mol % $Sn(PPG400)_2$ | 0.919 |
| 0.01 mol % $Sn(PPG1200)_2$ | 0.443 |
| 0.02 mol % $Sn(PPG1200)_2$ | 0.443 |
| **Liquid Initiators** | |
| 0.01 mol % $Sn(Oct)_2$ | 1.237 |
| 0.02 mol % $Sn(Oct)_2$ | 1.211 |
| 0.01 mol % $[Sn(Oct)]_2DEG$ (2.1:1) | 0.712 |
| 0.02 mol % $[Sn(Oct)]_2DEG$ (2.1:1) | 0.941 |
| 0.01 mol % $[Sn(Oct)]_2DEG$ (3.0:1) | 1.658 |
| 0.02 mol % $[Sn(Oct)]_2DEG$ (3.0:1) | 1.243 |
| 0.01 mol % $[Sn(Oct)]_2EG$ | 1.090 |
| 0.02 mol % $[Sn(Oct)]_2EG$ | 1.321 |

As shown in Table 6.3, the liquid initiators tended to give the highest [η] values which is consistent with the highest $\overline{M}_n$ values from GPC. It is also significant to note that the liquid initiators that were pre-prepared gave much higher [η] values than the corresponding mixed initiator combinations. This is strong evidence to support the view that using the true initiator directly in a known concentration gives less side-reactions (e.g., chain transfer) which can limit the molecular weight than generating the true initiator in situ. This is particularly relevant in applications where mechanical strength is an important property requirement such as in surgical sutures.

### 6.3.4 Thermal Analysis

#### 6.3.4.1 Differential Scanning Calorimetry (DSC)

The temperature transitions of the PLC copolymers were investigated by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC7 instrument with Pyris software. The thermal properties measurements were run from 0 to 200 $^{o}$C at a heating rate of 10 $^{o}$C min$^{-1}$. The samples with a typical mass of 3-5 mg were encapsulated in sealed aluminum pans and were heated and cooled under nitrogen atmosphere. The DSC thermograms are shown in Figures 6.19 - 6.21 and their data are listed in Table 6.4. These DSC thermograms were obtained from the 2nd run after quenching the samples back to 0 $^{o}$C in order to obtain clearer thermal transitions of $T_g$, $T_c$ and $T_m$ and also to ensure that the samples all had identical thermal histories so that they could be compared equally.

All of the DSC thermograms are similar in general appearance, as would be expected. The most noticeable difference is that the $T_c$ and $T_m$ peaks for the copolymers from the liquid initiators in Figure 6.21 are more clearly defined which could be a result of their generally higher molecular weights. With respect to their intended application as monofilament suture fibres, their $T_g$ values in Table 6.4, which are mainly in the range of 25-35 $^{o}$C, are suitable for ensuring that the fibres will have sufficient flexibility at room temperature. These experimental $T_g$ values can be compared with the calculated value of 25 $^{o}$C, as predicted by the Fox Equation below:

$$\frac{1}{T_{g\,PLC}} = \frac{W_L}{T_{g\,PL}} + \frac{W_C}{T_{g\,PC}}$$

where $W_L$ and $W_C$ are the respective weight fractions of L and C in the PLC (calculated from their 0.75 and 0.25 mol fractions) and $T_{g\,PL}$ and $T_{g\,PC}$ are the respective $T_g$ s ($T_{g\,PL}$ = 60 $^{o}$C = 333 $^{o}$K, $T_{g\,PC}$ = -60 $^{o}$C = 213 $^{o}$K) of PL and PC.

$$\frac{1}{T_{g\,PLC}} = \frac{0.79}{333} + \frac{0.21}{213} = 2.37 \times 10^{-3} + 0.99 \times 10^{-3}$$

$$T_{g\,PLC} = 298\ ^{o}K = 25\ ^{o}C$$

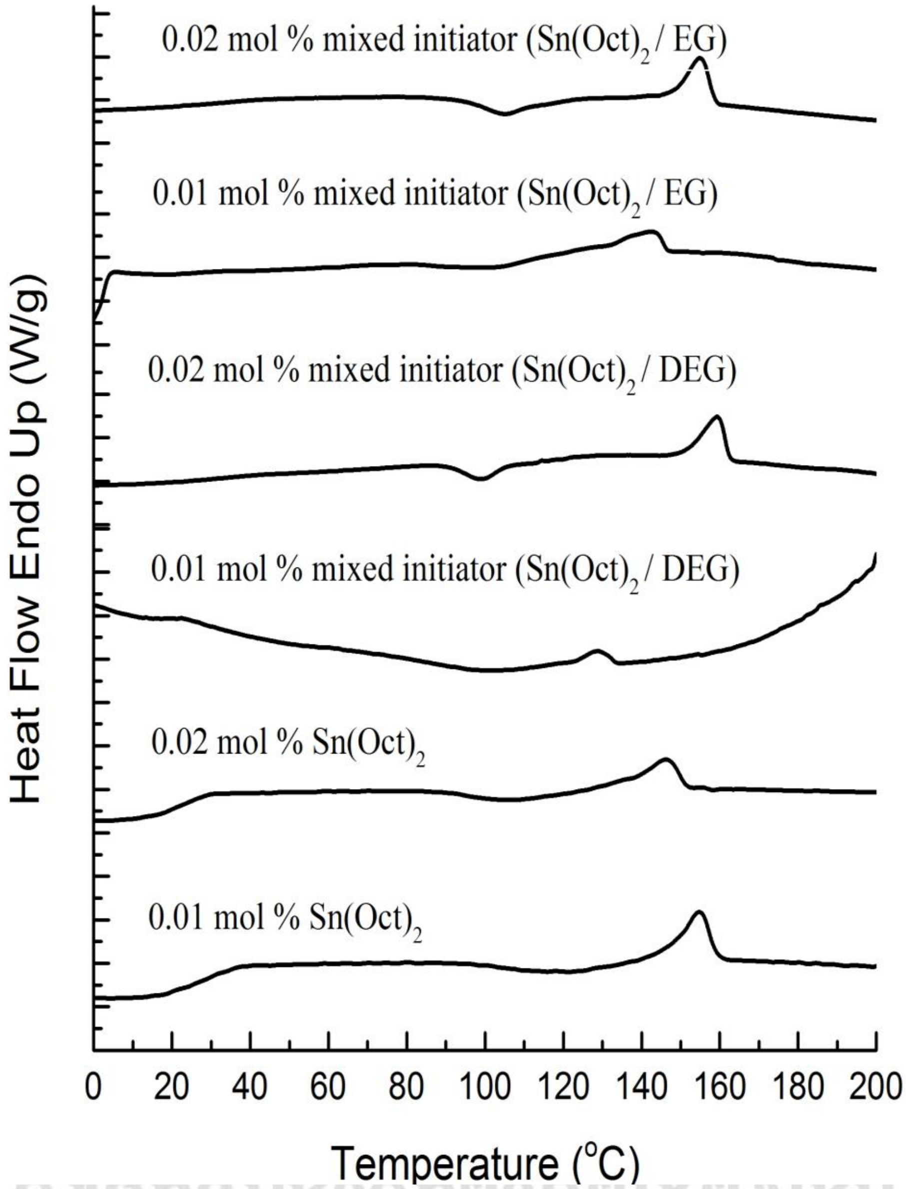


Figure 6.19 DSC thermograms of the synthesised the PLC copolymers using $Sn(Oct)_2$ and the mixed initiators.

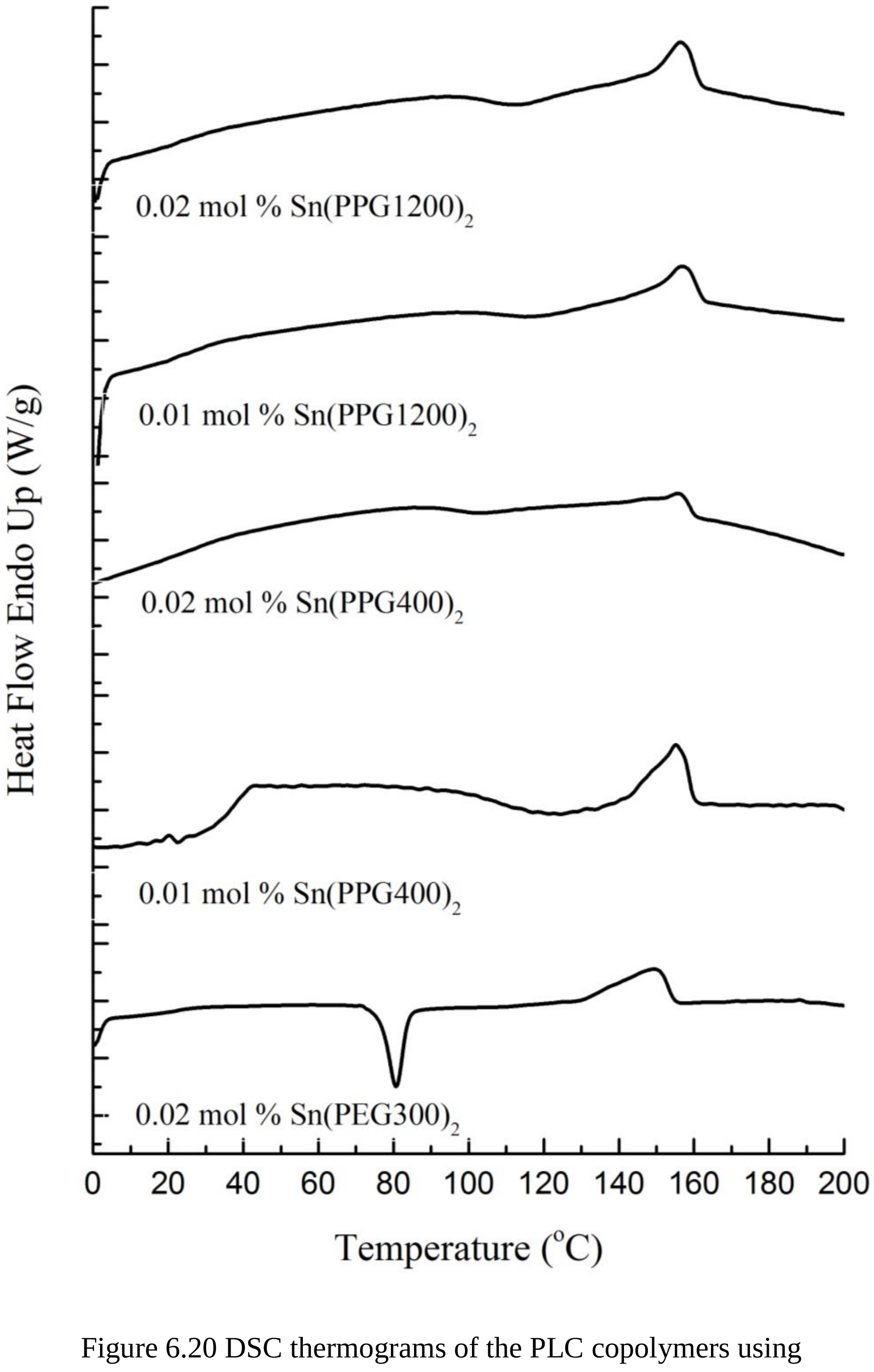


Figure 6.20 DSC thermograms of the PLC copolymers using 0.01 and 0.02 mol % of the various solid tin(II) alkoxide initiators.

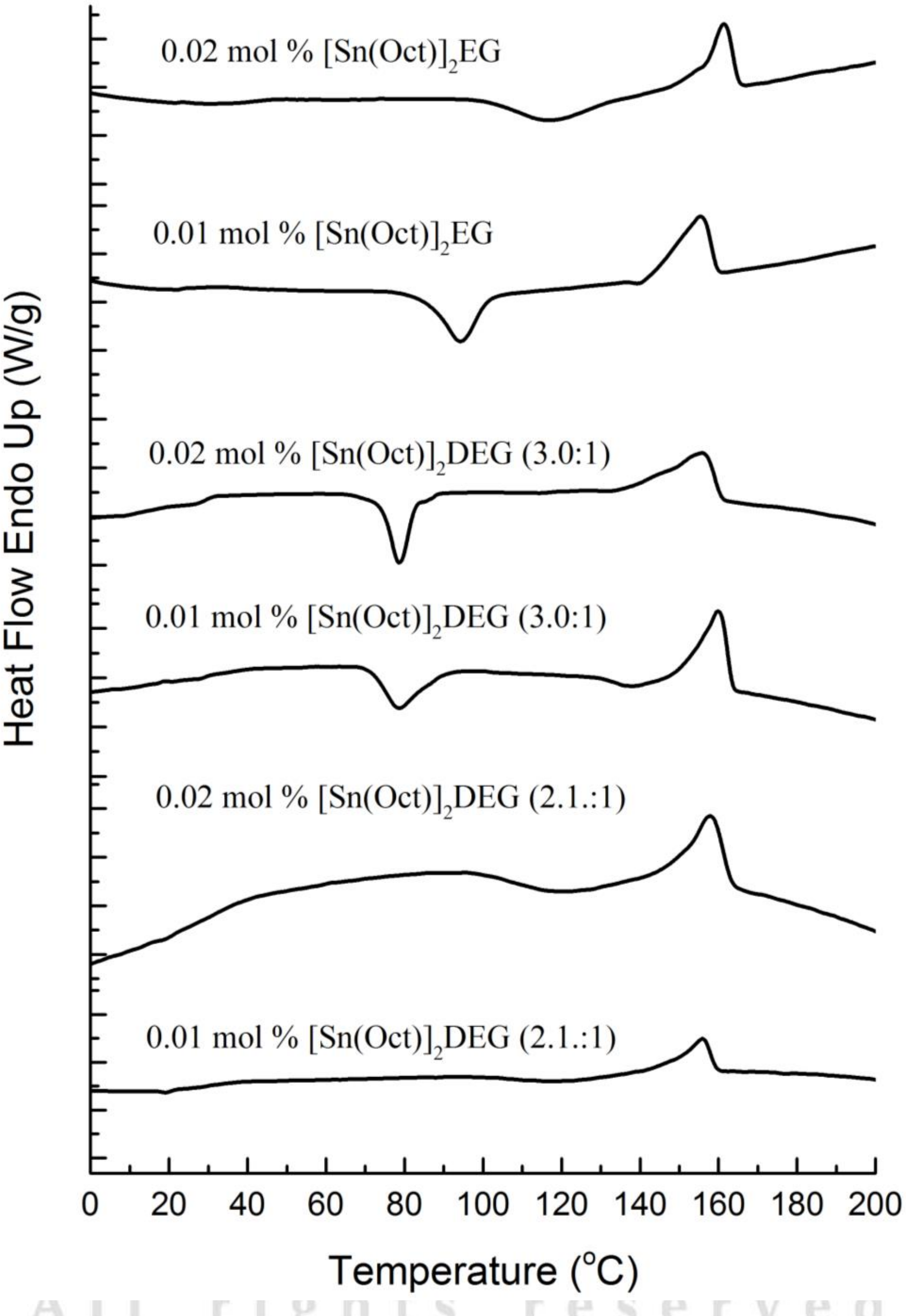


Figure 6.21 DSC thermogram of the PLC copolymers using 0.01 mol % of the various  the liquid tin(II) alkoxide initiators.

Table 6.4 DSC results of the PLC copolymers.

| **Initiators** | **$T_g$ ($^oC$)** | **$T_c$ ($^oC$)** | **$\Delta H_c$ (J/g)** | **$T_m$ ($^oC$)** | **$\Delta H_m$ (J/g)** |
|---|---|---|---|---|---|
| **Mixed Initiators** | | | | | |
| 0.01 mol % $Sn(Oct)_2$ / DEG | 18 | 99 | 5.9 | 129 | 2.0 |
| 0.02 mol % $Sn(Oct)_2$ / DEG | 31 | 99 | 16.8 | 159 | 23.4 |
| 0.01 mol % $Sn(Oct)_2$ / EG | 25 | 102 | 18.1 | 142 | 25.9 |
| 0.02 mol % $Sn(Oct)_2$ / EG | 32 | 105 | 23.1 | 155 | 29.0 |
| **Solid Initiators** | | | | | |
| 0.02 mol % $Sn(PEG300)_2$ | 21 | 81 | 20.0 | 149 | 24.5 |
| 0.01 mol % $Sn(PPG400)_2$ | 36 | 121 | 4.9 | 155 | 6.0 |
| 0.02 mol % $Sn(PPG400)_2$ | 29 | 104 | 5.7 | 156 | 24.1 |
| 0.01 mol % $Sn(PPG1200)_2$ | 28 | 119 | 6.9 | 157 | 17.4 |
| 0.02 mol % $Sn(PPG1200)_2$ | 26 | 115 | 15.8 | 157 | 23.2 |
| **Liquid Initiators** | | | | | |
| 0.01 mol % $Sn(Oct)_2$ | 25 | 122 | 3.7 | 155 | 6.0 |
| 0.02 mol % $Sn(Oct)_2$ | 21 | 105 | 5.0 | 146 | 7.0 |
| 0.01 mol % $[Sn(Oct)]_2DEG$ (2.1:1) | 29 | 119 | 6.5 | 156 | 10.5 |
| 0.02 mol % $[Sn(Oct)]_2DEG$ (2.1:1) | 31 | 120 | 8.7 | 158 | 13.7 |
| 0.01 mol % $[Sn(Oct)]_2DEG$ (3.0:1) | 32 | 77 | 19.5 | 160 | 33.6 |
| 0.02 mol % $[Sn(Oct)]_2DEG$ (3.0:1) | 26 | 79 | 23.3 | 156 | 31.0 |
| 0.01 mol % $[Sn(Oct)]_2EG$ | 25 | 94 | 24.1 | 155 | 26.3 |
| 0.02 mol % $[Sn(Oct)]_2EG$ | 39 | 117 | 23.3 | 161 | 24.2 |

#### 6.3.4.2 Thermogravimetry Analysis (TGA)

Thermogravimetry was used as a method for investigation of the thermal stability of the PLC copolymers. TGA was carried out on a Perkin-Elmer Pyris instrument with a TGA7 Model. The heating rate given to the sample was 20 $^oC$ $min^{-1}$ from 50 $^oC$ to 500 $^oC$ with initial sample weights in the range of 5-10 mg. Data were recorded as a thermogram of % weight loss versus temperature as shown in Figures 6.22 - 6.24. Nearly all ($T_d$) the results showed that PLC obtained using the various initiator systems started to degrade at around 250 $^oC$ except for the 0.01 mol % mixed initiators ($Sn(Oct)_2$/DEG), $Sn(Oct)_2$/EG)) and 0.01 mol % $[Sn(Oct)]_2EG$. However, their curves decreased only slightly (weight loss ~ 10 %) followed by a one-step weight loss. Together with the previous DSC data, this TGA data defines the melt processing range for fibre spinning as the range between $T_m$ and $T_d$. Since this range is about 90 $^oC$ wide (160 → 250 $^oC$), it means that the copolymers can be safely melt spun at a temperature slightly above $T_m$ without accompanying thermal degradation.

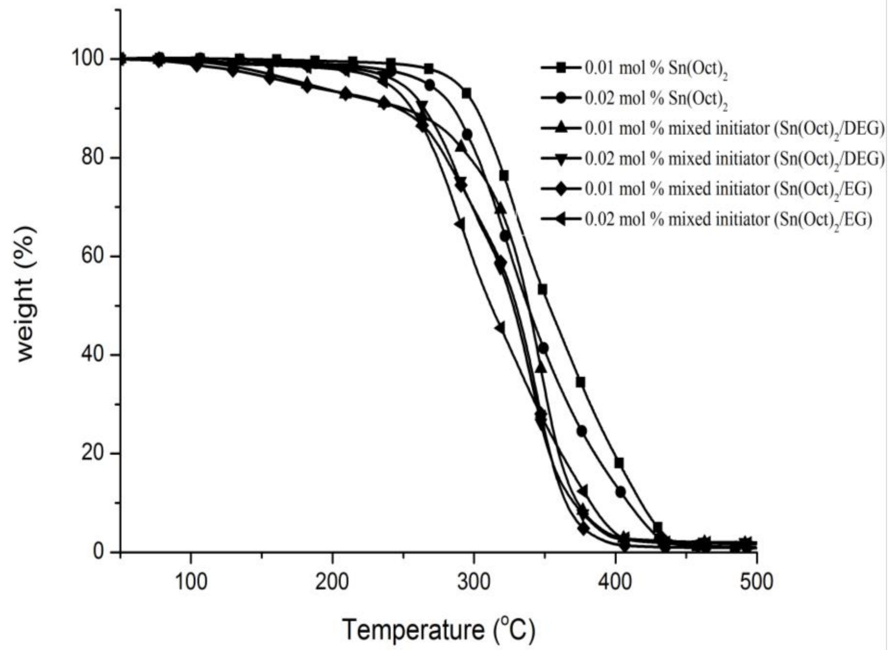


Figure 6.22 TG thermograms of the PLC copolymers using $Sn(Oct)_2$ and the mixed initiators.

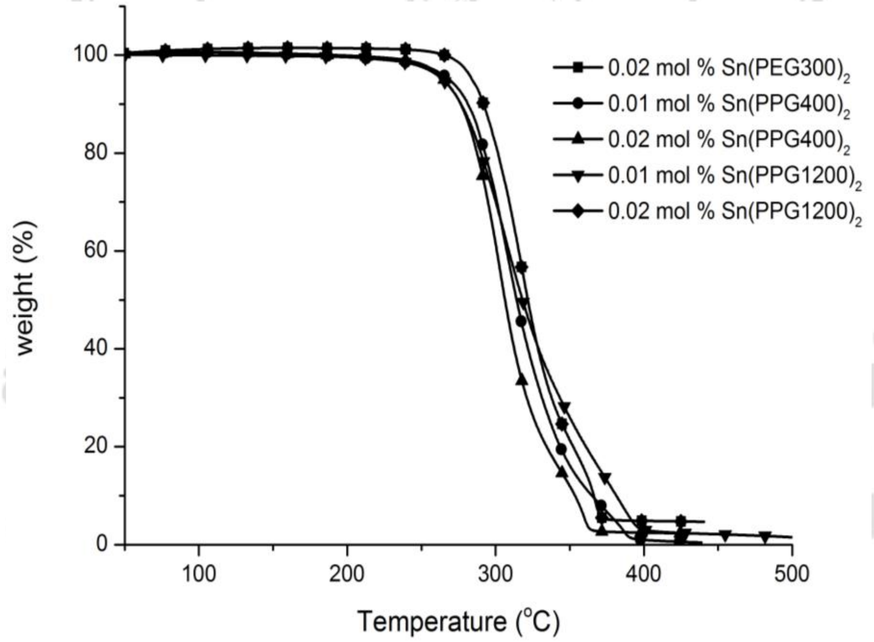


Figure 6.23 TG thermograms of the PLC copolymers using the solid tin(II) alkoxide initiators.

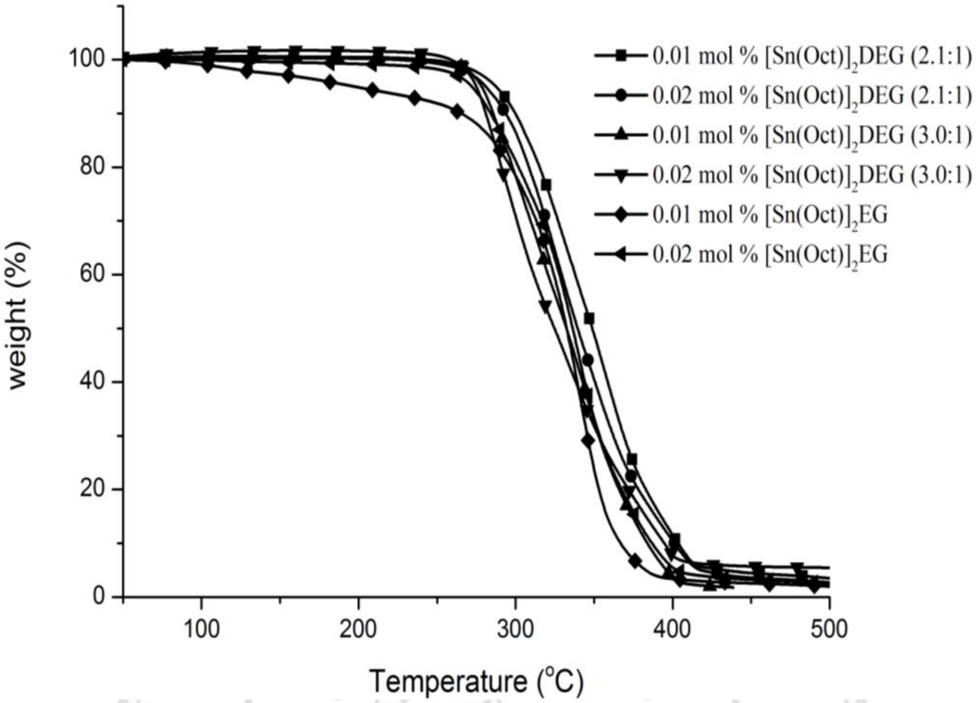


Figure 6.24 TG thermograms of the PLC copolymers using the liquid tin(II) alkoxide initiators.