Design and characterisation of novel blends of poly(lactic acid)

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CHAPTER 3

CHARACTERISATION OF
POLY(α-ESTER) HOMOLOGUES
Chapter 3  
Characterisation of poly(α-ester) homologues

The materials characterised in this chapter are all homologues of poly(lactic acid). They share the poly(α-ester) repeat unit:

\[
\begin{array}{c}
\text{R}_1 \\
\text{O} - \text{C} - \text{CO} \\
\text{R}_2 \\
\end{array}
\]

in which \( R_1 = H \) and \( R_2 = \text{CH}_3 \) for PLA itself. These materials were all synthesised in these laboratories, as described in Chapter 2. The synthetic routes are summarised briefly in Figure 3.1.

![Synthetic routes for poly(α-ester) homologues.](image)

**Figure 3.1** The synthetic routes for poly(α-ester) homologues.

Poly(lactic acid) and its homologues are poly(α-esters), which contain the ester functional group and substituent, aliphatic and aromatic groups, on the position of the \( \alpha \)-carbon in their main chains. These poly(α-esters) possess different characteristic chain structures consisting of the different multiple repeat units that are related to a particular trend of miscibility in polymer blends based on PLLA. Therefore, \(^{13}\text{C}\) and \(^1\text{H}\) nuclear magnetic resonance spectroscopy (NMR), differential scanning calorimetry (DSC) and hot-stage microscope are used to characterise novel polyesters, particularly poly(α-esters) to notify the effect of substituent groups on the compatibility of polymers. All poly(α-ester) homologues used in this work are shown in Table 3.1.
### Table 3.1  Pre-synthesised poly(α-esters).

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Poly(α-esters)</th>
<th>Pendent groups</th>
<th>Molecular Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic α-polyesters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PGA (synthesised)</td>
<td>Poly(2-hydroxy ethanoic acid) or Poly(glycolic acid)</td>
<td>-H, -H</td>
<td><img src="image1" alt="Molecular Structure" /></td>
</tr>
<tr>
<td>α1(dimethyl)</td>
<td>Poly(2-hydroxy-2-methyl-propanoic acid)</td>
<td>-CH₃, -CH₃</td>
<td><img src="image2" alt="Molecular Structure" /></td>
</tr>
<tr>
<td>α2(diethyl)</td>
<td>Poly(2-hydroxy-2-ethyl-butanoic acid)</td>
<td>-C₂H₅, -C₂H₅</td>
<td><img src="image3" alt="Molecular Structure" /></td>
</tr>
<tr>
<td>α3(cyclopentyl)</td>
<td>Poly(2-hydroxy-2-cyclopentyl-ethanoic acid)</td>
<td></td>
<td><img src="image4" alt="Molecular Structure" /></td>
</tr>
<tr>
<td>α4(cyclohexyl)</td>
<td>Poly(2-hydroxy-2-cyclohexyl-ethanoic acid)</td>
<td></td>
<td><img src="image5" alt="Molecular Structure" /></td>
</tr>
<tr>
<td>α5(cycloheptyl)</td>
<td>Poly(2-hydroxy-2-cycloheptyl-ethanoic acid)</td>
<td></td>
<td><img src="image6" alt="Molecular Structure" /></td>
</tr>
<tr>
<td>α6(chloromethyl-methyl)</td>
<td>Poly(2-hydroxy-2-chloromethyl-propanoic acid)</td>
<td>-CH₃, -CH₂Cl</td>
<td><img src="image7" alt="Molecular Structure" /></td>
</tr>
</tbody>
</table>
Table 3.1 Pre-synthesised poly(α-esters). (Continued)

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Poly(α-esters)</th>
<th>Pendent groups</th>
<th>Molecular Structures</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aromatic α-polyesters</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ArS1 (pentafluoro phenyl-methyl)</td>
<td>Poly PFAAC: Poly(2-hydroxy-2-pentafluorophenyl propanoic acid)</td>
<td>-CH₃, <img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>ArS2 (phenyl-methyl)</td>
<td>Poly AAAC: Poly(2-hydroxy-2-phenyl propanoic acid)</td>
<td>-CH₃, <img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>ArS3 (phenyl)</td>
<td>Poly MAAC: Poly(2-hydroxy-2-phenyl ethanoic acid)</td>
<td>-H, <img src="image" alt="Structure" /></td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Copolymer of ArS1 and ArS3</td>
<td>Copolymer of poly(2-hydroxy-2-pentafluoro phenyl propanoic acid) and poly(2-hydroxy-2-phenyl ethanoic acid)</td>
<td>Pendent of ArS1 and ArS3</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Copolymer of ArS1 and PGA (synthesised)</td>
<td>Copolymer of poly(2-hydroxy-2-pentafluoro phenyl propanoic acid) and poly(glycolic acid)</td>
<td>Pendent of ArS1 and PGA (synthesised)</td>
<td><img src="image" alt="Structure" /></td>
</tr>
</tbody>
</table>
Pre-synthesised poly(α-esters) were analysed to determine their number average molecular weights ($M_n$) and approximate average degree of polymerisation (DP) by gel permeation chromatography (GPC) \cite{5, 6}. The $M_n$ and some general properties of these poly(α-esters) are given in Table 3.2.

**Table 3.2** Number average molecular weight ($M_n$), degree of polymerisation (DP), crystallinity, and solubility in chloroform of pre-synthesised poly(α-esters).

<table>
<thead>
<tr>
<th>Pre-synthesised poly(α-esters)</th>
<th>$M_n$</th>
<th>DP</th>
<th>Crystallinity</th>
<th>Solubility (in chloroform)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aliphatic α-polyesters:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\alpha_1$(dimethyl)</td>
<td>6000</td>
<td>70</td>
<td>Crystalline</td>
<td>Yes</td>
</tr>
<tr>
<td>$\alpha_2$(diethyl)</td>
<td>19000</td>
<td>165</td>
<td>Crystalline</td>
<td>No *1</td>
</tr>
<tr>
<td>$\alpha_3$(cyclopentyl)</td>
<td>9260</td>
<td>83</td>
<td>Amorphous</td>
<td>Yes</td>
</tr>
<tr>
<td>$\alpha_4$(cyclohexyl)</td>
<td>12240</td>
<td>97</td>
<td>Amorphous</td>
<td>Yes</td>
</tr>
<tr>
<td>$\alpha_5$(cycloheptyl)</td>
<td>1760</td>
<td>12</td>
<td>Amorphous</td>
<td>Yes</td>
</tr>
<tr>
<td>$\alpha_6$(chloromethyl-methyl)</td>
<td>12000</td>
<td>149</td>
<td>Amorphous</td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Aromatic α-polyesters:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ArS1 (pentfluorophenyl-methyl)</td>
<td>2900</td>
<td>-</td>
<td>Amorphous</td>
<td>Yes</td>
</tr>
<tr>
<td>ArS2(phenyl-methyl)</td>
<td>1774</td>
<td>-</td>
<td>Amorphous</td>
<td>Yes *2</td>
</tr>
<tr>
<td>ArS3(phenyl)</td>
<td>2972</td>
<td>-</td>
<td>Amorphous</td>
<td>Yes</td>
</tr>
<tr>
<td>Copolymer of ArS1 and ArS3</td>
<td>801</td>
<td>-</td>
<td>Amorphous</td>
<td>Yes</td>
</tr>
<tr>
<td>Copolymer of ArS1 and PGA(synthesised)</td>
<td>696</td>
<td>-</td>
<td>Amorphous</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Note: *1 $\alpha_2$(diethyl) required addition of hexafluoropropanol to aid dissolution. *2 difficult to dissolve.
3.1 NMR analysis of the molecular structures of poly(α-esters)

$^1$H NMR and $^{13}$C NMR were carried out to study the molecular structures of these polymers. The assignment of the chemical shifts, as shown by letters (a, b, c etc.), are shown along with the corresponding polymer structures.

3.1.1 α1(dimethyl):

α1(dimethyl) is effectively the first systematic homologue of PLA, having two symmetrical methyl pendant groups at the α-carbon in the backbone. It was dissolved in deuterated chloroform (CDCl$_3$) for the NMR analysis. Figures 3.2(A) and (B), respectively, display the $^1$H NMR and $^{13}$C NMR spectra of α1(dimethyl).

It is clear from the proton spectrum, Figure 3.2(A), that peak a at a chemical shift of 1.6 ppm corresponds to the constituent protons of the two-methyl groups. The methyl protons in α1(dimethyl) are shown as a single peak because they do not cause splitting among themselves.

From the carbon spectrum, Figure 3.2(B), peaks at positions a, b and c at chemical shifts of 23.9, 78.8 and 170.7 ppm are assigned to -CH$_3$, -C=, and C=0, respectively. Both of the proton and carbon spectra show aromatic hydrocarbon contaminant peaks (probably from nitrobenzene used as a solvent in polymerisations) at a chemical shift of 7.6-8.4 and 123-135 ppm, respectively. $^1$H and $^{13}$C NMR peaks of CDCl$_3$ are also shown in the figure.
Figure 3.2 $^1$H NMR (A) and $^{13}$C NMR (B) spectra of α1(dimethyl) recorded in CDCl$_3$. 
3.1.2 α2(dieyl):

\[ \begin{align*}
\text{C}_2\text{H}_5 & \quad \text{OH} \\
\text{C} & \quad \text{O} \\
\text{H} & \quad \text{n}
\end{align*} \]

α2(dieyl) is effectively the second poly(α-ester) homologue after α1(dimethyl) studied in this research. It contains two ethyl groups at the α-carbon in the backbone, which gives α2(dieyl) a symmetrical structure. The chemical structure of α2(dieyl) was also studied by NMR. α2(dieyl) was dissolved in CDCl3 and a few drops of hexafluoroisopropanol (HFIP) were added to aid dissolution. Figures 3.3(A) and (B), respectively, display the \(^1\)H NMR and \(^{13}\)C NMR spectra of α2(dieyl).

It can be seen from the proton spectrum, Figure 3.3(A), that peak \(a\) represents protons from –CH\(_3\) groups at a chemical shift of 0.9 ppm and peak \(b\) protons from –CH\(_2\) which appear at a chemical shift of 2.0 ppm. Proton peaks from CDCl\(_3\) occur at a chemical shift of 7.3 ppm and HFIP at a chemical shift of 4.4 ppm. The peak at a chemical shift of 3.2 ppm is that of hydroxyl protons (-OH). These hydroxyl protons are expected because protons from water or residual hydroxy acid starting material may be presented.

From the carbon spectrum, Figure 3.3(B): peak \(a\) at a chemical shift of 7.0 ppm represents carbon atoms from –CH\(_3\) groups; peak \(b\) at a chemical shift of 27.0 ppm corresponds to carbon atoms from –CH\(_2\) groups; peak \(c\) at a chemical shift of 86.0 ppm corresponds to α-carbons in the backbone; peak \(d\) at a chemical shift of 170.0 ppm corresponds to carbonyl carbons from –C=O groups. Two peaks of the carbon atoms from –CH and –CF in HFIP and one peak of the carbon atom from CDCl\(_3\) are also shown in this figure.

It can be observed that the methyl groups of α1(dimethyl) resonate at lower field strengths increasing the chemical shift values compared to that of α2(dieyl). The NMR spectra of α2(dieyl) shows a number of changes when compared with α1(dimethyl).
Figure 3.3 $^1$H NMR (A) and $^{13}$C NMR (B) spectra of α2(diethyl) recorded in HFIP and CDCl$_3$. 
3.1.3 \( \alpha_3(\text{cyclopentyl}) \):

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{C} \\
\text{OH}
\end{array}
\]

\( \alpha_3(\text{cyclopentyl}) \) is one of the poly(\( \alpha \)-ester) homologues having cycloalkyl groups, in this case cyclopentyl linked to the backbone with a carbon atom shared between the backbone and cyclic substituent. It is dissolved in deuterated water (D\( _2 \)O) and deuterium chloride (DCl) for NMR analysis. The \( ^1 \text{H} \) NMR and \( ^{13} \text{C} \) NMR spectra of \( \alpha_3(\text{cyclopentyl}) \) with the detailed assignment of the different peaks are shown in Figures 3.4(A) and (B), respectively.

A typical proton spectrum, Figure 3.4(A), shows three different proton peaks corresponding to three different positions of methylene hydrogens in cyclopentyl rings, in addition to peak \( a \) at a chemical shift of 1.6 ppm, \( b \) at 1.7 ppm and \( c \) at 2.0 ppm. Proton peaks of water and hydrochloric acid show at a chemical shift of 8.6 ppm.

From the carbon spectrum, Figure 3.4(B), two carbon peaks located at the positions \( a \) and \( b \) are methylene protons at the symbol \( a \) and \( b \) in cyclopentyl ring, which appear at chemical shifts of 21.5 ppm and 38.0 ppm, respectively. Peak \( c \) at a chemical shift of 79.6 ppm represents quaternary carbons in cyclopentyl ring at the position \( c \) in the structure. The \( ^{13} \text{C} \) NMR peak of carbonyl carbons (C=O) shows a very weak signal at a chemical shift of around 170 ppm.

However, both NMR spectra confirm the particular structure of \( \alpha_3(\text{cyclopentyl}) \) and show no other contaminating substances in this sample.
Figure 3.4 $^1$H NMR (A) and $^{13}$C NMR (B) spectra of α3(cyclopentyl) recorded in D$_2$O and DCI.
3.1.4 $\alpha 4$(cyclohexyl):

$\alpha 4$(cyclohexyl) has a six-membered ring of cyclohexyl at the $\alpha$-position of the backbone instead of a five-member ring of cyclopentyl as seen in $\alpha 3$(cyclopentyl). The cyclohexyl ring in $\alpha 4$(cyclohexyl) contains four different methylene protons, which have dissimilar neighbours and would be expected to show four different proton peaks in NMR spectra.

Figure 3.5(A), shows the $^1$H NMR spectrum of $\alpha 4$(cyclohexyl) with annotated assignments. The four different methylene proton peaks of $\alpha 4$(cyclohexyl) at the positions a, b, c and d appear at chemical shifts of 1.4 ppm, 1.7 ppm, 1.9 ppm and 2.2 ppm, respectively. The peak at the chemical shift of 7.3 ppm is of chloroform protons, which is seen at the same position in the spectrum of $\alpha 1$(dimethyl) and $\alpha 2$(diethyl). The protons from contaminating aromatic hydrocarbon (likely to be from nitrobenzene used as a solvent in the polymerisation) are also shown at chemical shifts between 7.6 and 8.4 ppm, corresponding to those seen in the spectrum of $\alpha 1$(dimethyl).

The $^{13}$C NMR spectrum of $\alpha 4$(cyclohexyl) is shown in Figure 3.5(B) with the detailed structure assignments. Peaks at the positions a, b and c, at chemical shifts of 21.2 ppm, 25.1 ppm and 32.1 ppm, are assigned to methylene carbons contained in the cyclohexyl ring at the symbols a, b and c as shown in the chemical structure. Peak d is assigned to the quaternary carbon, appearing at a chemical shift of 80.8 ppm. Peak e corresponds to carbonyl carbons $\alpha 4$(cyclohexyl), and can be observed at a chemical shift of 170.6 ppm. The carbon peak from CDCl$_3$ is seen at the chemical shift of 78.0 ppm.
Figure 3.5 $^1$H NMR (A) and $^{13}$C NMR (B) spectra of α4(cyclohexyl) recorded in CDCl$_3$. 

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Characterisation of poly(α-ester) homologues
3.1.5 $\alpha_5($cycloheptyl$)$:

$a_5($cycloheptyl$)$ is a poly($\alpha$-ester) containing the cycloheptyl group in the backbone. Its molecular structure was studied by NMR after first dissolving in CDCl$_3$. Figures 3.6(A) and (B), respectively, display the $^1$H NMR and $^{13}$C NMR of $a_5($cycloheptyl$)$ with molecular assignment.

Peaks at the positions $a$, $b$ and $c$, at chemical shifts of 1.6, 2.1 and 2.3 ppm in the proton spectrum (Figure 3.6(A)), are assigned to the three different regions of the methylene protons shown with the symbols $a$, $b$ and $c$ in the chemical structure. The peak at the chemical shift of 7.3 ppm corresponds to chloroform protons, which is seen at the same position in the spectrum of $a_1($dimethyl$)$, $a_2($diethyl$)$, and $a_4($cyclohexyl$)$.

The carbon spectrum, Figure 3.6(B), shows three single peaks of $a$, $b$ and $c$, approximately the same height of the equal amount of methylene carbons at the symbols $a$, $b$, and $c$ in the chemical structure. Peak $d$, at a chemical shift of 85.0 ppm, is that of the quaternary carbon in cycloheptyl. Peak $e$ corresponds to carbonyl carbons certainly observed at the chemical shift of 170.0 ppm. The carbon peak from CDCl$_3$ is seen at the chemical shift of 78.0 ppm.

The relative assignment of all peaks in compounds confirmed that the $a_5($cycloheptyl$)$ sample contains a comparatively small quantity of contaminants.
Figure 3.6 $^1$H NMR (A) and $^{13}$C NMR (B) spectra of \( \alpha \)5(cycloheptyl) recorded in CDCl$_3$. 
Chapter 3  

**Characterisation of poly(α-ester) homologues**

### 3.1.6 α6(chloromethyl-methyl):

![Chemical structure](attachment:structure.png)

α6(chloromethyl-methyl) is an unsymmetrically substituted poly(α-ester) containing a methyl group and chloromethyl group at the α-carbon in the backbone. Its molecular structure was studied by NMR after first dissolving in CDCl$_3$. Figures 3.7(A) and (B), respectively, display the $^1$H NMR and $^{13}$C NMR of α6(chloromethyl-methyl) with molecular assignment.

From the proton spectrum, Figure 3.7(A), peak $a$ corresponds to the methyl protons shown at a chemical shift of 1.6 ppm. Peaks $b_1$ and $b_2$ at chemical shifts of 3.8 and 4.1 ppm are slightly different. This poly(α-ester) has an asymmetric carbon atom (like PLA). It will thus have effectively D and L sequences in the backbone. Such a chemical shift is characteristic with the difference between DD or LL and D-L. It is the strong polarisation of the CH$_2$Cl that causes the shift. The peak at a chemical shift of 7.3 ppm corresponds to chloroform protons.

From the carbon spectrum, Figure 3.7(B); peaks $a_1$ and $a_2$ at chemical shifts of 18.0 and 19.0 ppm correspond to the methyl carbons: peaks $b_1$ and $b_2$ at chemical shifts of 46.0 and 47.0 correspond to the methylene carbons: peaks $c_1$ and $c_2$ at chemical shifts of 82.0 and 83.0 correspond to the quaternary carbons: peaks $d_1$ and $d_2$ at chemical shifts of 168.0 and 168.5 correspond to the hydroxyl carbons. It can be seen the slightly difference of carbon peaks between $a_1$ and $a_2$ for instant, which is caused by the difference between DD or LL and D-L sequences in the α6(chloromethyl-methyl) backbone. It is the strong polarisation of the CH$_2$Cl that causes the shift. The carbon peak from CDCl$_3$ is seen at the chemical shift of 78.0 ppm.
Figure 3.7 $^1$H NMR (A) and $^{13}$C NMR (B) spectra of α6(chloromethyl-methyl) recorded in CDCl$_3$. 
3.1.7 ArS1(pentafluorophenyl-methyl):

ArS1(pentafluorophenyl-methyl) or poly(2-hydroxy-2-pentafluorophenyl propanoic acid) is a novel poly(α-ester) substituted with pentafluorophenyl and methyl groups at the α-carbon in the backbone. $^1$H and $^{13}$C NMR were used to monitor the chemical structure of ArS1(pentafluorophenyl-methyl), shown in Figure 3.8(A) and (B), respectively. It was dissolved in deuterated chloroform (CDCl$_3$) for the NMR analysis.

In the proton spectrum, Figure 3.8(A), peak $a$, at a chemical shift approximately at 2.1 ppm, corresponds to the methyl protons. The peak at the chemical shift of 7.3 ppm corresponds to protons from the solvent. Peaks at approximately 8, 8.5 and 8.9 ppm correspond to the protons from pyridine, which was used as an initiator for polymerisation. The upfield peaks from peak $a$ are expected to correspond to the proton peaks of pentafluoro acrylactic acid which has pentafluoro phenyl and methyl groups as substituted groups. The broad peak at approximately 3 ppm corresponds to the hydroxyl protons.

In the carbon spectrum, Figure 3.8(B), two peaks of $a$ in the region of 22 ppm and 26 ppm correspond to the methyl carbons of ArS1(pentafluorophenyl-methyl). One is of the methyl carbon, the coupling peak of carbon coupled long range to $^{19}$F. Four peaks of $b$ around 136 ppm, 139 ppm, 143 ppm and 147 ppm correspond to pentafluorophenyl carbons. The upfield peaks around peak $a$ are expected to be the carbon peaks of methyl from the parent acid and that of peak $b$ the carbon peaks of pyridine. However, the peak of the alpha-carbon cannot be observed. Because of the electron-withdrawing power of the –Cl group and C$_6$F$_5$ groups it seems that the α-carbon lies under the CDCl$_3$ solvent. The peak at a chemical shift of 78 ppm corresponds to the carbon from solvent.
Figure 3.8 $^1$H NMR (A) and $^{13}$C NMR (B) spectra of ArS1(pentafluorophenyl-methyl) recorded in CDCl$_3$. 
3.1.8 ArS2(phenyl-methyl):

\[ \text{ArS2(phenyl-methyl)} \]

ArS2(phenyl-methyl) or poly(2-hydroxy-2-phenyl propanoic acid) is a novel poly(α-ester) substituted with phenyl and methyl groups at the α-carbon in the backbone. It was dissolved in deuterated chloroform (CDCl₃) and deuterated dimethyl sulfoxide (d₆-DMSO) for NMR analysis. ¹H NMR and ¹³C NMR spectra of ArS2(phenyl-methyl) are shown in Figure 3.9 (A) and (B), respectively.

In the proton spectrum, Figure 3.9 (A), two peaks of \( a \) at approximately 2.0 and 2.5 ppm correspond to the methyl protons and \( b \) to the phenyl protons. The peak at a chemical shift of around 1.1 ppm and broad peak at approximately 6.5 ppm are, respectively, expected to be the methyl protons and the hydroxyl protons from the parent acid. Three peaks at chemical shifts of 7.4, 7.6 and 8.0 ppm correspond to the phenyl protons from pyridine, the initiator for polymerisation. The proton peaks of d₆-DMSO and CHCl₃ are shown at chemical shifts approximately at 3.6 and 7.3 ppm, respectively.

In the carbon spectrum, Figure 3.9 (B), peaks \( a \) at chemical shifts approximately at 130 ppm correspond to phenyl carbons. Peaks of methyl, quaternary, and carbonyl carbons could not be observed. The carbon peaks of d₆-DMSO and CDCl₃ are shown at chemical shifts of 40 and 78 ppm, respectively. The rest of the peaks are expected to be the carbon peaks of pyridine and the parent acid.
Figure 3.9 $^1$H NMR (A) and $^{13}$C NMR (B) spectra of ArS$_2$(phenyl-methyl) recorded in CDCl$_3$ and d$_6$-DMSO.
3.1.9 ArS3(phenyl):

ArS3(phenyl) or poly (2-hydroxy-2-phenyl ethanoic acid) is a novel poly(α-ester) substituted with hydrogen and phenyl groups at the α-carbon in the backbone. It was dissolved in deuterated chloroform (CDCl₃) for NMR analysis. ¹H NMR and ¹³C NMR spectra of ArS3(phenyl) are shown in Figures 3.10(A) and (B), respectively.

In the proton spectrum, Figure 3.10(A), peak a at a chemical shift of approximately 4.3 ppm corresponds to the protons at alpha-carbon and peak b at a chemical shift of approximately 7.2 ppm to the phenyl protons. At the phenyl proton region, the proton peak of chloroform is observed at a chemical shift of 7.3 ppm. The rest of the peaks are expected to be the proton peaks of the parent acid and pyridine.

In the carbon spectrum, Figure 3.10(B), peak a at a chemical shift of 75 ppm corresponds to alpha-carbon. Peak b at a chemical shift of 126 ppm corresponds to the five carbons of the phenyl ring (at the position b in the chemical structure). Peak c at a chemical shift of 132 ppm corresponds to the quaternary carbon in the phenyl ring. Peak d at a chemical shift of 166.5 ppm corresponds to the carbonyl carbon. The carbon peak of CDCl₃ is shown at a chemical shift of 78 ppm. The rest of the peaks are expected to be the carbon peaks of the parent acid and pyridine.
Figure 3.10 $^1$H NMR (a) and $^{13}$C NMR (b) spectra of ArS3(phenyl) recorded in CDCl$_3$. 
3.1.10 PGA(synthesised):

\[
\begin{array}{c}
\text{H} \\
\text{O} \quad \text{C} \\
\text{H} \quad \text{C} \\
\text{O} \quad \text{OH}
\end{array}
\]

This sample of PGA was synthesised via the anhydrosulphite route. Poly(glycolic acid) or poly(2-hydroxy ethanoic acid) is the simplest structure of the poly(α-esters), which is substituted with two hydrogen atoms at the α-carbon in the backbone. It was dissolved in deuterated dimethyl sulfoxide (d<sub>6</sub>-DMSO) for NMR analysis. <sup>1</sup>H and <sup>13</sup>C NMR spectra of PGA(synthesised) are shown in Figure 3.11(A) and (B), respectively.

In the proton spectrum, Figure 3.11(A), peak a at a chemical shift of 4.9 ppm corresponds to the two protons at the α-carbon. The proton peak of DMSO is observed at a chemical shift of 2.5 ppm. The broad peak observed at a chemical shift of approximately 3.4 ppm corresponds to the hydroxyl proton, which is expected to be from water. This is because poly(glycolic acid) is very susceptible to moisture. The proton peak of d<sub>6</sub>-DMSO is observed at a chemical shift of 2.5 ppm. The rest of the peaks are expected to be the proton peaks of the parent acid and pyridine.

In the carbon spectrum, Figure 3.11 (B), peak a at a chemical shift of 61 ppm corresponds to the methylene carbons. Peak b at a chemical shift of 167 ppm corresponds to the carbonyl carbons. It can be observed that the carbonyl carbon peak of PGA (synthesised) is a remarkable peak compared with other poly α-esters. The carbon peak of d<sub>6</sub>-DMSO is shown at a chemical shift of 40 ppm. The rest of the peaks are expected to be the carbon peaks of the parent acid and pyridine.

This is unlikely to be high molecular weight polymer since glycolic anhydrosulfide is one of the most difficult anhydrosulfide to purify and polymerise. The reasons are because; poly(glycolic acid) is very susceptible to moisture and the parent acid is very hydroscopic.
Figure 3.11 ¹H NMR (A) and ¹³C NMR (B) spectra of PGA(synthesised) recorded in d₆-DMSO.
3.1.11 Copolymer of 
ArS1(pentafluorophenyl-methyl) 
and ArS3(phenyl):

The copolymer of ArS1(pentafluorophenyl-methyl) and ArS3(phenyl) is expected to be a copolymer of poly(2-hydroxy-2-pentafluorophenyl propanoic acid and poly(2-hydroxy-2-phenyl ethanoic acid). It was dissolved in deuterated chloroform (CDCl$_3$) for NMR analysis. $^1$H and $^{13}$C NMR spectra of the copolymer are shown in Figure 3.12(A) and (B), respectively.

In the proton spectrum, Figure 3.12(A), peak a corresponds to the methyl protons in ArS1(pentafluorophenyl-methyl). It is shown at a chemical shift of 2.1 ppm similar to ArS1(pentafluorophenyl-methyl) itself. Peak b at a chemical shift of 6.0 ppm corresponds to the proton peaks at the alpha-carbon of ArS3(phenyl), which shifts from ArS3(pentafluorophenyl-methyl) itself (shown at 4.28-4.30 ppm). Peak c at a chemical shift of approximately 7.3 ppm corresponds to the phenyl protons of ArS3(pentafluorophenyl-methyl). The proton of chloroform is observed at a chemical shift of 7.3 ppm. Peaks at approximately 1.2 and 1.3 ppm are expected to be the methyl proton peaks of parent acid. The broad peak at 3.5 ppm corresponds to the hydroxyl protons. Peaks at approximately 7.9, 8.5, and 8.9 ppm correspond to the pyridine protons.

In the carbon spectrum, Figure 3.12(B), peak a at chemical shifts of 22 and 26 ppm corresponds to the methyl carbons of ArS1(pentafluorophenyl-methyl). Peak b at a chemical shift of 78 ppm corresponds to the proton at the alpha-carbon of ArS3(phenyl). Peak c at a chemical shifts of approximately 130 ppm corresponds to the phenyl carbons of ArS3(phenyl). Peak d at 136, 140, 144 and 147 ppm corresponds to the pentafluorophenyl carbons of ArS3(phenyl). Peak e at 170 ppm corresponds to the carbonyl carbon of both ArS1(pentafluorophenyl-methyl) and ArS3(phenyl). The carbon of chloroform is observed at 78 ppm. The rest of the peaks are expected to be the carbon peak of parent acid and pyridine.
Figure 3.12 $^1$H NMR (A) and $^{13}$C NMR (B) spectra of copolymer of ArS1(pentafluoro phenyl-methyl) and ArS3(phenyl) recorded in CDCl$_3$. 
3.1.12 Copolymer of

ArS1(pentafluorophenyl-methyl)
and PGA(synthesised):

This copolymer is expected to be a copolymer of poly(2-hydroxy-2-pentafluorophenyl propanoic acid) and poly(glycolic acid). It was dissolved in deuterated chloroform (CDCl$_3$) for NMR analysis. $^1$H and $^{13}$C NMR spectra of the copolymer are shown in Figure 3.13(A) and (B), respectively.

In proton spectrum, Figure 3.13(A), peak $a$ at a chemical shift of approximately 22 ppm corresponds to the methyl protons of ArS1(pentafluorophenyl-methyl). Peak $b$ at a chemical shift of approximately 4.8 ppm corresponds to the protons at the $\alpha$-carbon of PGA(synthesised). The proton of chloroform is observed at a chemical shift of 7.3 ppm. The proton peaks at very low chemical shifts (less than 1.0 ppm) are expected to be the proton peaks of grease and silicone used in the process. The rest of the peaks are expected to be the proton peaks of parent acid and pyridine.

In carbon spectrum, Figure 3.13(B), peak $a$ at chemical shifts of 22 and 26 ppm corresponds to the mehyl carbons of ArS1(pentafluorophenyl-methyl). Peak $b$ at a chemical shift of 29.5 ppm corresponds to the $\alpha$-carbon of PGA(synthesised). Peak $c$ at 136, 139, 144 and 147 ppm corresponds to the pentafluorophenyl carbons of ArS1(pentafluorophenyl-methyl). The carbon of chloroform is observed at 78 ppm. The rest of the peaks are expected to be the carbon peak of parent acid and pyridine.
Figure 3.13 ¹H NMR (a) and ¹³C NMR (b) spectra of copolymer of ArS₁(pentafluoro phenyl-methyl) and PGA(synthesised) recorded in CDCl₃.
3.2 Thermal analysis by differential scanning calorimetry (DSC)

The considerable thermal properties, such as the glass transition temperature ($T_g$), the melting temperature ($T_m$), and the melting enthalpy ($\Delta H_m$), of the pre-synthesised poly($\alpha$-ester) homologues including poly(lactic acid) (PLA), poly($\varepsilon$-caprolactone) (PCL), and cellulose acetate butyrate (CAB), were observed by DSC analysis. The DSC traces plotted between heat flow endothermic up and temperature (°C) - of PLLA1 ($M_w = 28000$) and PLLA2 ($M_w = 94800$) for instance are shown in Figure 3.14.

![DSC traces of PLLA1 and PLLA2](image)

**Figure 3.14** DSC traces of PLLA1 and PLLA2: heated from 25°C to 220 °C at 20°C/min.

The $T_g$, $T_m$, and $\Delta H_m$ of PLA, the pre-synthesised poly($\alpha$-ester) homologues, and other polymers used for blending are shown in Table 3.3.
Table 3.3 The $T_g$, $T_m$, and $\Delta H_m$ of the pre-synthesised poly($\alpha$-ester) homologues.

<table>
<thead>
<tr>
<th>Poly $\alpha$-esters</th>
<th>$T_g$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA1 ($M_n = 18,700$)</td>
<td>53</td>
<td>52.02</td>
<td>162</td>
</tr>
<tr>
<td>PLLA2 ($M_n = 63,500$)</td>
<td>61</td>
<td>42.06</td>
<td>172</td>
</tr>
<tr>
<td>PDLLA</td>
<td>59</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Aliphatic Substitutions:**

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGA(synthesised)</td>
<td>-</td>
<td>62.11</td>
<td>120</td>
</tr>
<tr>
<td>$\alpha_1$(dimethyl)</td>
<td>-</td>
<td>51.60</td>
<td>175</td>
</tr>
<tr>
<td>$\alpha_2$(diethyl)</td>
<td>-</td>
<td>52.02</td>
<td>185</td>
</tr>
<tr>
<td>$\alpha_4$(cyclohexyl)</td>
<td>-</td>
<td>24.90</td>
<td>82</td>
</tr>
<tr>
<td>$\alpha_5$(cycloheptyl)</td>
<td>-</td>
<td>42.34</td>
<td>148</td>
</tr>
<tr>
<td>$\alpha_6$(chloromethyl-methyl)</td>
<td>60</td>
<td>8.33</td>
<td>134</td>
</tr>
<tr>
<td>$\alpha_2$(diethyl)-high MW</td>
<td>74</td>
<td>3.14$^2$</td>
<td>192</td>
</tr>
</tbody>
</table>

**Aromatic Substitutions:**

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ArS1(pentafluorophenyl-methyl)</td>
<td>72</td>
<td>0.01</td>
<td>103</td>
</tr>
<tr>
<td>ArS3(phenyl)</td>
<td>71</td>
<td>0.20</td>
<td>115</td>
</tr>
<tr>
<td>Copolymer of ArS1 and ArS3</td>
<td>80</td>
<td>1.94</td>
<td>158-195$^*1$</td>
</tr>
<tr>
<td>Copolymer of ArS1 and</td>
<td>77</td>
<td>17.6</td>
<td>115-185$^*1$</td>
</tr>
<tr>
<td>PGA(synthesised)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL1 ($M_n = 7,500$)</td>
<td>-</td>
<td>69.23</td>
<td>53</td>
</tr>
<tr>
<td>PCL2 ($M_n = 57,800$)</td>
<td>-</td>
<td>53.47</td>
<td>58</td>
</tr>
<tr>
<td>CAB</td>
<td>114</td>
<td>14.32$^2$</td>
<td>151</td>
</tr>
<tr>
<td>PGA</td>
<td>38</td>
<td>55.4</td>
<td>218</td>
</tr>
<tr>
<td>TPU</td>
<td>63</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

**Note:** $^*1$ the $T_m$ peaks were very broad. $^*2$ some of these values are unusual, however, the $\Delta H_m$ value depends on the sample and applied experimental conditions, i.e. sample size, sample’s thermal history, molecular weight, heating and cooling rates which were similar in each case.
From Table 3.3, it can be seen that the $T_m$ of high molecular weight polymer (e.g. PLLA2, PCL2) is higher than low molecular weight (e.g. PLLA1, PCL1) whereas the $\Delta H_m$ in contrast is slightly lower. In the case of amorphous polymers-PDLLA—which cannot crystallise, there can be no $T_m$. The $T_g$ of the aliphatic poly(α-ester) homologues are not generally observed, excluding α6(chloromethyl-methyl) and α2(diethyl)-high MW, whereas the $T_g$ of aromatic poly(α-ester) homologues can be observed. PLLA, α1(dimethyl), and α2(diethyl) show higher $T_m$ and $\Delta H_m$ than other aliphatic poly(α-ester) homologues. The $T_m$ of the copolymer of aromatic poly(α-ester) homologues are very broad, which might be caused by the molar mass dispersity of the samples.

The percent crystallinity of PLLA1, PLLA2, PCL1, and PCL2 is calculated using the following equation: [51]

$$
\%\text{Crystallinity} = \frac{\Delta H_m}{\Delta H_{m\text{ideal}}} \times 100\%
$$

where $\Delta H_m$ is the measured melting enthalpy and $\Delta H_{m\text{ideal}}$ is the melting enthalpy of a 100% crystalline polymer. Table 3.4 shows $\Delta H_m$, $\Delta H_{m\text{ideal}}$, and percent crystallinity (after crystallisation has already taken place) of PLLA and PCL.

**Table 3.4** $\Delta H_m$, $\Delta H_{m\text{ideal}}$, and percent crystallinity of PLLA and PCL.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$\Delta H_{m\text{ideal}}$ (J/g) [76]</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA1</td>
<td>52.02</td>
<td>135.7</td>
<td>38</td>
</tr>
<tr>
<td>PLLA2</td>
<td>42.06</td>
<td></td>
<td>31</td>
</tr>
<tr>
<td>PCL1</td>
<td>69.23</td>
<td>93.7</td>
<td>74</td>
</tr>
<tr>
<td>PCL2</td>
<td>53.47</td>
<td></td>
<td>57</td>
</tr>
</tbody>
</table>
3.3 Crystallite imaging by hot-stage microscopy (HMS)

Hot-stage microscopy analysis can be used to observe the crystal form, however, the usefulness of the technique depends on the temperature and the heating and/or cooling rate used during the process. It was used to be a guide-line to observe the crystallinity of all poly(α-ester) homologues and polymers used in this work, e.g. PCL, CAB. The light intensity obtained from HSM images is an alternative value to describe the changes occurring at the surface of the polymer. It diminishes the crystallinity of polymers. The HSM images were observed at the same magnification. A few HSM images were shown in this section to demonstrate whether the polymers were crystalline or amorphous.

Figure 3.15 shows HSM images of PLLA1 ($M_n = 18,700$) and PLLA2 ($M_n = 63,500$) films. The crystalline spherulites of both PLLA1 and PLLA2, which are semi-crystalline polymers can be clearly seen. The HSM images of PCL1 ($M_n = 7,500$) and PCL2 ($M_n = 57,800$) films also show crystalline spherulites. However, PLLA1 and PCL1 cast films are opaque whereas PLLA2 and PCL2 cast films are clear although the reason for this marked difference is not entirely obvious. The HSM image of cellulose acetate butyrate (CAB) does not show crystalline spherulites because CAB is an amorphous polymer.

![HSM images of PLLA1 and PLLA2 films](image1.png)

**Figure 3.15** The HSM images of PLLA1 ($M_n = 18,700$) and PLLA2 ($M_n = 63,500$) films.
Figure 3.16 shows the HSM image of PGA(synthesised) at the initial stage of crystallisation (left) and during continuing growth (right). It shows good crystalline spherulites even though this PGA(synthesised) is not of high molecular weight. PGA from commercial sources has a very high degree of crystallinity and small spherulites sizes compared to PGA(synthesised).

![Image of PGA(synthesised).](image-1)

**Figure 3.16** The HSM images of PGA(synthesised).

Figure 3.17 shows the HSM images of \( \alpha_2(\text{diethyl}) \) and \( \alpha_6(\text{chloromethyl-methyl}) \). The crystalline spherulite can be observed in \( \alpha_2(\text{diethyl}) \) which is a crystalline polymer, whereas it can not be observed in \( \alpha_6(\text{chloromethyl-methyl}) \) which is an amorphous polymer. The HSM image of \( \alpha_1(\text{dimethyl}) \), a semi-crystalline polymer also shows crystalline spherulites similar to \( \alpha_2(\text{diethyl}) \). However, the degree of crystallinity of both \( \alpha_1(\text{diethyl}) \) and \( \alpha_2(\text{diethyl}) \) are less than PLLA1 and PLLA2 as observed from their HSM images. The HSM images of other aliphatic poly(\( \alpha \)-esters), all aromatic poly(\( \alpha \)-esters), and the copolymer of ArS1 and ArS3 are similar to the HSM image of \( \alpha_6(\text{chloromethyl-methyl}) \). However, the HSM image of the copolymer of ArS1 and PGA(synthesised) shows some crystalline spherulites.
Chapter 3  
Characterisation of poly(α-ester) homologues

3.4 SUMMARY OF THE CHAPTER

Hot-stage microscopy analysis showed that $\alpha_1$(dimethyl) and $\alpha_2$(diethyl) are crystalline polymers, while other pre-synthesised poly(α-ester) homologues are amorphous polymers. In addition, the DSC analysis showed that $\alpha_1$(dimethyl) and $\alpha_2$(diethyl) have high $T_m$ compared to the others. This is because of the small and the symmetrical substituted side groups (less than ca. 5 Å). The solubility of $\alpha_2$(diethyl) is effected by the high degree of crystallinity, for example, $\alpha_2$(diethyl) will not dissolve in chloroform. It can be seen at the different thermal analysis that $T_g$, $T_m$, and crystallinity of poly(α-ester) homologues are different.

In summary, the characterisation worked here confirmed these are polymers. They have appropriate structure NMR. They are novel poly(α-esters) which could not find in the commercial sources. These characterisation results will help to understand the miscibility of the blends in the next chapter.