Synthesis and Characterization of Thermally Stable Fully Bio-based Poly(ester amide)s from Sustainable Feedstock

By

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Lignin-derived precursors were used in the synthesis of bio-based high-performance polymers. The project consisted of synthesizing a series of poly(ester amide)s (PEAs) from lignin building blocks and natural amino acids. In particular, the amino acid moieties were incorporated into the PEAs’ architecture to explore the effect of the side-chain size on the thermal properties and the crystallinity of the resulting materials. The polymers, which were prepared by melt polycondensation, all possessed high thermal stability in nitrogen and air with onsets of thermal degradation (T_d onset) exceeding 330 °C and glass transition temperatures (T_g) ranging from 136 °C – 238 °C. It is worth noting that the T_g greatly depended on the size of the pendant R-group on the amino acid. Remarkably, the thermal stability was mostly maintained even after subjecting the polymers to various pH media (pH 1, 4 and 8) for 1 week at 50 °C. Furthermore, wide-angle X-ray scattering experiments revealed semi-crystalline polymers with identical diffraction patterns and percent crystallinity ranging from 21 – 37%. To probe the impact of chirality on the thermal properties, a meso polymer of DL-alanine was prepared and compared to the chiral version. A slight drop in the T_d onset and T_g of the DL-alanine-containing polymer relative to the L-alanine counterpart occurred, signifying moderate thermal stability.
resulting from the chiral group. Overall, these characteristics make these bio-based PEAs potential candidates for further investigation as alternatives to petrochemical-derived thermoplastics for high-performance materials.
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CHAPTER I
INTRODUCTION

1.1 Background on sustainable high-performance polymers.

High-performance materials possess outstanding properties, such as excellent thermal stability, mechanical strength, low specific density, high conductivity, high thermal, electrical, sound insulation properties, and superior flame resistance. These properties allow them to have applications in many fields, including the electronics and aerospace industry. [1] Polymers that are considered to possess most of these properties include polyesters, which are known for their moderate melting points and pliability, and polyamides, which possess high modulus, high tensile strength, abrasion and heat resistant properties. Presently, most high-performance commercial products are derived from petroleum-based compounds (petrochemicals).

Petrochemicals have dominated the commercial market for many decades; however, in recent years, there has been a push to replace them with functionally equivalent products derived from sustainable feedstocks, due to the unsustainability and cost volatility of petroleum. [2-6] In this regard, researchers and industrial companies have been working to develop ways to manufacture thermoplastics from sustainable feedstock such as lignocellulose (lignin). [7-10] Lignin is a complex structure comprised of a rich source of aromatic building blocks, making it an attractive resource for valuable aromatic synthetic precursors. In fact, lignin can be converted into appreciable amounts of aromatic aldehydes; hydroxybenzaldehyde, vanillin and syringaldehyde, which can reach a total of 14.6 wt %. [11-15]
Historically, bio-based polyesters such as polylactic acid and poly(ε-caprolactone) have been the main polymers employed in applications for biomedical and commodity materials. [16-19] In spite of their non-toxicity and biodegradability, other factors, including poor thermal and mechanical properties, have warranted a need for new biomaterials that can overcome these deficiencies. [20] To this end, poly(ester amide)s (PEAs) have been explored as an alternative to polyesters, since they not only consist of hydrolyzable ester linkages, but also amide functional groups that impart enhanced mechanical strength and thermal resistance due to the extensive networks of hydrogen bonding in the polymer matrix. [21] Moreover, the desired properties can be achieved even at much lower molecular weights for many PEAs, which is not the case for polyesters. [20] As such, they are being widely explored as materials for biodegradable plastics, drug delivery systems, tissue engineering, smart materials, and hydrogels. [21, 22]

1.2 Vegetable oils and α-amino acids as feedstock for “green” PEAs

Several PEAs have been prepared from bio-based feedstocks such as carbon dioxide, lignocellulose, vegetable oils and terpenes. [23] For example, PEAs prepared from α-amino acids, [24] and aliphatic alcohols and acids derived from vegetable oils, have been used as biodegradable materials due to the benign nature of their degradation products. [24-27] Rodriguez-Galan and coworkers prepared a semi-crystalline PEA from L-alanine, 1,12-dodecanedioic acid, and 1,12-dodecane diol and showed that it exhibited intrinsic viscosity of 0.73 dl/g with an onset of thermal degradation around 340 °C, and melting temperature below 100 °C (76 °C and 97.5 °C). [28] Furthermore, FTIR and 1H NMR studies indicated that the polymer readily degrades hydrolytically in pH 7.4 phosphate buffer solution, as well as proteinase k and papain proteolytic enzymes solutions. Karimi et al. explored other natural amino acids, such as L-phenylalanine and L-methionine as building blocks for PEAs with
sebacoyl chloride and a number of aliphatic diols. [29] PEAs with high molecular weights, narrow polydispersity ($M_n$ of up to 45,000 g/mol and PDI < 1.56), and good film forming properties were obtained. Hydrolytic and enzymatic degradation experiments illustrated the dependency of the rate of degradation on the amino acid hydrophilic/hydrophobic properties and the degradation medium. Even though most PEAs are being explored as biodegradable materials, our interest in PEAs is to manufacture high performance materials that are not readily degradable. Thus, while aliphatic PEAs are known for their degradability, aromatic PEAs are much less susceptible to degradation.

1.3 A case for high-performance PEAs derived from lignocellulose feedstock

Aromatic poly(ester amide)s (PEA) have been gaining prominence as high performance materials for adhesives and composites. [30, 31] Fully aromatic poly(ester amide)s were prepared by the Higashi group who synthesized several random copoly(ester amide)s between $p$-aminobenzoic acid ($p$-ABA) (40–70 mol %) and both $p$-hydroxybenzoic acid ($p$-HBA) and $m$-hydroxybenzoic acid ($m$-HBA) using a mix ratio of the two monomers and sometimes a third monomer. [32-34] The copoly($p$ABA-co-$m$HBA)s displayed thermotropic liquid crystalline properties with nematic mesophase within the range of 240–360 °C. The Löhden group also prepared both random and alternating amorphous copoly(ester amide)s between vanillic acid (VA) and $p$-ABA with a decomposition temperature around 300 °C; significantly lower than a polyamide, but higher than most polyesters. [35] The synthetic procedure used by the Löhden group was a melt polycondensation of the silylated carboxyl groups with acetylated phenol groups; however, since the polymers decomposed at the reaction temperature (300 – 350 °C), very low yields of the polymers were obtained ($\leq 55\%$). Many other research groups have demonstrated the potential of lignin-derived products in the preparation of “green”
thermoplastics. [11] Upton et al. synthesized a family of aromatic-aliphatic copoly(ester amide)s based on vanillin, syringic aldehyde, and p-HBA by interfacial polymerization with a series of aliphatic/aromatic diamines. [36] The resulted PEAs had T_g ranging from 64.7 °C - 138.2 °C and number average molecular weights up to 18,770 g/mol. They were shown to have moderate degradation depending on the aliphatic portion.

1.4 A summary on the poly(ester amide)s investigated in this work

In this thesis, we report the synthesis of a series of fully bio-based PEAs containing p-HBA or VA with three sterically distinct amino acids (glycine, L-alanine, and L-isoleucine) to explore the effects of steric factors on the thermal properties and solubility of these PEAs (Figure 1.1). A racemic version containing DL-alanine and p-HBA was also prepared to evaluate the effect of chirality on the thermal properties of the polymer. The polymers were prepared by melt polycondensation and characterized by 1H NMR and FTIR to determine their structural information. The thermal properties were investigated by TGA and DSC analysis, while the morphology was studied by WAXS. Intrinsic viscosity was measured to determine the size of the polymers relative to each other. The polymers were mostly stable after being treated to various pH conditions after 6 d at 50 °C as indicated by the TGA experiments. Predictably, the trend in the stability under degradation conditions correlates with that observed in thermal properties behavior. Ultimately, this illustrate the impact of the polymers’ packing ability on the bulk properties of the resulting materials.
Figure 1.1  \( p \)-HBA and VA-derived polymers studied in this project
CHAPTER II
RESULTS/DISCUSSIONS & EXPERIMENTAL

2.1 Results and discussions

2.1.1 Monomer synthesis

In our synthetic approach towards the PEAs, the amide bonds were first constructed to form AB-type monomers, since amide bonds are known to withstand melt polycondensation more readily than ester linkages. The AB monomers were subjected to melt polyesterification to produce the polymers. Seven monomers were synthesized from a combination of \( p \)-HBA or VA with glycine, L-alanine, L-isoleucine and DL-alanine amino acids. Following the synthetic route outlined in Scheme 2.1, compound 5 was initially synthesized via carbodiimide-assisted amidation of TBS-protected \( p \)-HBA (and/or VA) with the amino acid methyl esters. [39]

However, with this pathway, longer reaction times and poor yields became the major limitations. Moreover, the TBS-protection [40] of the substrates 1 and 2 results in two distinct products: the \(^1\)H NMR spectrum of the crude revealed that not only the phenol group could be silylated, but also the carboxylic acid group in a 2:1 ratio for protected \( p \)-HBA and 1:1 ratio for VA (Figures 2.2 and 2.1). Consequently, additional purification steps to isolate the monosilylated fraction were required, further reducing the overall yield of the synthesis. Alternatively, the crude silylated compounds could be converted to the acid chlorides using oxalyl chloride with catalytic DMF, which were then converted to the amides by reacting with the corresponding amino acid methyl esters (5a –5f). The silylated phenolic groups were deprotected with tetra-\( n \)-
butylammonium fluoride (TBAF) solution in THF to produce the AB monomers (6a – 6f) in good to moderate yields.

Scheme 2.1 Synthesis of monomers
Figure 2.1  Crude $^1$H NMR of compound 1 silylation in CDCl$_3$ showing the 2:1 mono to double silylation ratio

Figure 2.2  Crude $^1$H NMR of compound 2 silylation in CDCl$_3$ showing the 1:1 mono to double silylation ratio
2.1.2 Polymer synthesis

2.1.2.1 Melt polymerization ($p$-TsOH, Sb$_2$O$_3$)

Melt polycondensation was carried out on the monomers with 8 mol % $p$-toluenesulfonic acid ($p$-TsOH) as the catalyst (Scheme 2.2). The melt polycondensation is preferred over solution polycondensation because it requires no organic solvent, which makes the process green, sustainable, and convenient for industrial applications. [41, 42] Nevertheless, potential side reactions are a major limitation for this method, as high temperatures and long reaction times, which are vital to produce high molecular weights polymers, can degrade the monomers or form side products. [43-45] Therefore, care must be taken in the rate of heating, and the length of the heating process for the reaction. As such, the monomers were slowly heated to 5 – 10 ºC above their melting temperatures, and allowed to react until the melt becomes a viscous liquid and hardens (~ 2-8 h). The reaction mixtures were then ramped to higher temperatures (200 – 220 ºC) at which point they were subjected to vacuum at 100 mmHg for 3 h. The polymerization was not heated above 220 ºC due to the potential decomposition of the catalyst, Figure 2.3. However, being a strong Lewis acid, $p$-TsOH is expected to catalyze the polymerization reaction at lower temperatures relative to other polycondensation catalyst such as Sb$_2$O$_3$. In fact, polymers were prepared with Sb$_2$O$_3$ (1 mol %) as the catalyst at polymerization temperatures up to 250 ºC; however, those polymers were insoluble in all solvents and only thermal analysis were conducted, Table 2.1. Following the polymerization with $p$-TsOH, the polymers were purified before analysis. The yields of the polymerizations were low and is believed to be a result of inefficient heating and stirring during the polymerization reaction.
Scheme 2.2  Synthesis of the polymers

Table 2.1  Thermal properties and intrinsic viscosities of P1 – P6

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Sb$_3$O$_5$N$_2$ $T_d$ onset (°C)</th>
<th>$p$TsOH $N_2$ $T_d$ onset (°C)</th>
<th>$p$TsOH air $T_d$ onset [char yield]/$T_d$ 50% (°C)</th>
<th>Sb$_3$O$_5$N$_2$ $T_d$ 800 °C char yield (%)</th>
<th>$p$TsOH $N_2$ $T_d$ 800 °C char yield (%)</th>
<th>$T_d$ (°C)</th>
<th>$\eta$ $p$TsOH (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>353</td>
<td>340</td>
<td>333 [572]</td>
<td>58</td>
<td>48</td>
<td>238</td>
<td>0.32</td>
</tr>
<tr>
<td>P2</td>
<td>319</td>
<td>357</td>
<td>370 [552]</td>
<td>61</td>
<td>55</td>
<td>196</td>
<td>0.32</td>
</tr>
<tr>
<td>P3</td>
<td>326</td>
<td>344</td>
<td>371 [586]</td>
<td>57</td>
<td>48</td>
<td>150</td>
<td>0.35</td>
</tr>
<tr>
<td>P4</td>
<td>321</td>
<td>346</td>
<td>347 [570]</td>
<td>65</td>
<td>49</td>
<td>150</td>
<td>0.30</td>
</tr>
<tr>
<td>P5</td>
<td>321</td>
<td>344</td>
<td>374 [564]</td>
<td>60</td>
<td>40</td>
<td>159</td>
<td>0.56</td>
</tr>
<tr>
<td>P6</td>
<td>322</td>
<td>337</td>
<td>356 [528]</td>
<td>60</td>
<td>47</td>
<td>136</td>
<td>0.48</td>
</tr>
</tbody>
</table>
Figure 2.3 Thermal decomposition of the catalyst under nitrogen. The weight loss around 107 °C corresponds to the removal of water.

2.1.2.2 Solution polymerization (DCC/DMAP and diphenyl chlorophosphate (DCPC))

Solution polycondensation was explored to circumvent the drawbacks of melt polymerization. Attributes including higher polymer yields and molecular weights make this technique desirable. [42] Toward this end, the bulk polymerization monomers (6a and 6f) were subjected to base-catalyzed ester hydrolysis to afford the corresponding carboxylic acids in quantitative yields (Scheme 2.3). Proton NMRs of the reaction products confirm the successful transformation, Figure 2.4 and 2.5. There are several reports in the literature on the preparation of polyesters [46] and poly(phospho ester)s [47] using carbodiimide reagents. Apart from the strategy described above, DCPC is another promising chloro phosphate that has proved effective.
in the synthesis of high molecular weight polyesters when alkali metal salts are used as additives.

[48] This prompted us to explore the two conditions for the poly(ester amide)s synthesis.

Scheme 2.3  Synthesis of the AB monomers for solution polycondensation

Figure 2.4  Compound 7a ¹H NMR in DMSO-d₆
In the case of DCC/DMAP, the polymerization was performed in DMF for up to 2 d at room temperature. After work-up, the $^1$H NMR revealed that at best only some dimers had formed in the reaction (Figure 2.6). Further attempts to drive the polymerization forward by increasing the temperature (60 °C) failed. The observation of small oligomers is also supported by the thermal analysis data in Figure 2.7.
After the unsuccessful attempt with carbodiimides, the bifunctional monomers were subjected to the DPCP/LiCl condition. To probe the viability of the method, \( p \)-hydroxybenzoic acid was initially investigated in pyridine. The latter does not only play the role of a solvent, but also of a base that can accept a proton from the phenolic substrate. For \( p \)-HBA, the esterification proceeds rapidly at 120 °C and is indicated by the precipitation of the highly crystalline poly(\( p \)-hydroxybenzoic acid) only 10 min into the reaction. Any attempts to obtain some spectroscopic analysis of the crystalline polymer failed as the polyester proved to be very insoluble even in trifluoroacetic acid. For this reason, only thermal gravimetric data is reported, Figure 2.8.
Figure 2.8  Thermal decomposition thermograms of p-HBA and its polyester.

The promising results with p-HBA prompted us to explore the chloro phosphate condition with compound 7f. However, no precipitate was observed even after 2 d of the reaction. In fact, the ¹H NMR (Figure 2.10) and TGA (Figure 2.9) data affirm that only small oligomers were generated. Evidently, the DPCP/LiCl strategy seemed to work only in cases where the carboxylic acid is directly substituted on the phenyl ring. [48] A possible explanation of the phenomenon is that such substrates are more electrophilic at the carbonyl group relative to their aliphatic counterparts.
Figure 2.9  Thermal decomposition thermograms 7f and its oligomer

Figure 2.10  $^1$H NMR of the compound 7f polymerization in DMSO-d$_6$
2.1.3 Structural characterization of $p$-TsOH polymers

The $^1$H NMR spectra were recorded for each monomer and polymer. The $^1$H NMR spectra for the monomers (6a – 6g) are reported in the experimental while those of the polymers (P3 – P6) are shown in Figure 2.11. The region representing the aromatic protons (6.5 ppm – 7.0 ppm) reveals a broad peak, which is attributed to the proton resonance of the benzene ring that shifted up-field in going from the phenol to the ester. The two very sharp peaks in the aromatic region and the sharp peak around 2.25 ppm represent the $p$TsOH catalyst that remained in the sample, despite many washing cycles. This is especially prominent in P5. In the aliphatic region of the spectra, the methoxy group of the VA and the methine proton reside between 3.5 and 4 ppm. As is expected, the broad peak in this area is much smaller for P3 and P5 as they do not contain a methoxy group in the product. Further up-field in the spectra (0.5 ppm – 1.5 ppm) resonate the protons from the R group on alanine and isoleucine. The peaks are higher for P5 and P6 that contain the sec-butyl group. Unfortunately, no spectrum was recorded for P1 or P2 due to their insolubility in the solvent mixture (1:1 methylene chloride (CD$_2$Cl$_2$): trifluoroacetic acid (CF$_3$CO$_2$D). $^1$H NMR spectra were obtained for P1 and P2 in DMSO-d6; however, the concentration of the polymers in this solvent was also very low, and only trace amount of the polymers could be detected in the NMR spectra (Figure 2.12 and 2.13). The $^1$H NMR spectra did not reveal any end groups in the polymers, which suggest a high conversion for the reaction despite the low yields and intrinsic viscosities obtained.
Figure 2.11 $^1$H NMR spectra for P3 – P6 in CD$_2$Cl$_2$:TFA-d as solvent

Figure 2.12 P1 $^1$H NMR in CD$_2$Cl$_2$:TFA-d
Further structural evidence for the formation of the polymers can be seen in the solid state (powder) FTIR spectra shown in Figure 2.14. In region I of Figure 2.14, the frequency of the amide N-H stretching vibration appears as a broad peak centered at 3220 cm\(^{-1}\); it is difficult to ascertain from this area if there are H-bonding occurring although the broadness of the peak suggests that this could be the case. The aromatic C-H stretch is buried beneath the N-H stretch and is not identifiable; however the aliphatic C-H stretches are found around 2950 cm\(^{-1}\), and are more visible for P3 – P6 that contain the methyl and sec-butyl groups. Region II contains the carbonyl stretching frequencies for the amide I band. They can be found between 1600 cm\(^{-1}\) and 1700 cm\(^{-1}\) with lower than normal frequencies due to conjugation with the aromatic group and also H-bonding. The amide II band is observed around 1500 cm\(^{-1}\), while the C-O stretching vibration appears around 1200 cm\(^{-1}\). The FTIR spectra for the polymers were different than those

Figure 2.13 **P2** \(^1\)H NMR in CD\(_2\)Cl\(_2\):TFA-d
of the monomers (Figure 2.15), particularly in region 1 where pronounced peaks representing the phenolic O-H stretch is present in the FTIR spectra of the monomers and absent in the polymers.

Figure 2.14  Infrared spectra of the polymers P1 – P6

Figure 2.15  Stacked FTIR of the monomers M1 – M6
2.1.4 Thermal Characterization of \( p \)-TsOH polymers

The thermal decomposition of the polymers was analyzed by thermogravimetric analysis (TGA). The samples were simply ramped from room temperature to 1000 °C under both \( N_2 \) and air atmosphere. The polymers’ thermograms all possess excellent thermal stabilities (Figure 2.16). The onsets of thermal decomposition of the polymers in \( N_2 \) varied from 320 °C to 360 °C with no clear trend in the dependence of \( R \)-groups on the amino acids, or the catalyst used in the polymerization; however, the rates of thermal decomposition were slower for the \( Sb_2O_3 \) catalyzed polymers compared to that of the \( p \)-TsOH catalyzed polymers, Figure 2.16.

Interestingly, the temperatures at which 50% of the polymers decomposed (\( T_d \) 50%) ranged from 650 °C to > 800 °C in \( N_2 \) (Figure 2.16 and Table 2.1), resulting in the formation of char. For the \( Sb_2O_3 \) catalyzed polymers, the percent of the polymers that decomposed at 500 °C was very similar (~ 21% - 26%) for all the polymers; however, for the \( p \)-TsOH catalyzed polymers, \( P5 \) and \( P6 \) had the highest percent decomposed at 500 °C (43% and 47% respectively), and \( P1 \) and \( P2 \) had the lowest (29% and 34% respectively), suggesting that the small increase in size of the amino acid side chains led to a small increase in the rate of thermal degradation. Nonetheless, at 800 °C, there was no significant difference in the percent of char remaining for all the polymers (Table 2.1). Similar to the results in \( N_2 \), the PEAs exhibit great thermal stability in air with the onset of decompositions temperature slightly higher than the \( N_2 \) condition for most of the polymers (330 °C – 370 °C); however, unlike the \( N_2 \) results, the polymers fully decomposed in air, with the decomposition temperatures (\( T_d \) 50%) ranging from 526 °C – 585 °C (Table 2.1 and Figure 2.17). The VA-based polymers had a lower decomposition temperature by (16% – 30%) compared to the \( p \)-HBA-based polymers. These results affirm a small trend in the thermal instability for polymers with bulky \( R \)-group substituents on the amino acid and the benzene ring.
The more bulky isoleucine-based polymers were slightly less thermally stable than the alanine and the glycine-based polymers. Notwithstanding, the polymers all demonstrated good thermal stability, especially in air, and therefore have potential applications as high performance materials.

Figure 2.16  Thermal decomposition curves of M1 – M6 and P1 – P6
The effect of temperature on the polymers’ stiffness and chain mobility was investigated using a differential scanning calorimeter (DSC). In this experiment, a few milligrams of the powder were placed in a DSC pan and sealed. A separate empty pan was prepared to monitor the power differential between the loaded pan and the reference. To erase the polymers’ thermal history, the samples were first ramped to 150 °C at a rate of 10 °C/min and held for three min.
before cooling. Hereafter, two more heating and cooling cycles were recorded at 10 °C/min scanning rate. We made sure to not heat the powders past their degradation temperatures (TGA) as this would have introduced unwanted thermal transitions in the study. The thermograms shown in Figure 2.18 represent the 2nd heating cycle for all polymers. Unfortunately, the only transition observable in the temperature window of interest is the Tg in all cases. As expected, the glycine-based PEAs featured the highest Tg due superior packing that results from the less bulky substituents at the amino acid’s α-carbon. The noted trend held in the case of vanillic acid series as the size of the pendant group increases on the amino acid (Table 2.1). However, in the case of p-HBA polymers, P6 featured a higher Tg compared to L-ala-based P3. The discrepancy might be accounted for by the difference in the intrinsic viscosity values, which seem to indicate that P6 attained exceptionally higher molecular weight.

The melting endotherm was another transition that was expected in this study since the PEAs are semicrystalline. One can speculate that such peaks might occur past the decomposition temperature of the polymers and therefore are not detectable using the standard DSC instrument. For this kind of materials, an ultra-fast DSC scanner (hyper-DSC) is more appropriate because it heats the sample through a wide temperature window very rapidly. As such, the samples are not allowed enough residence time under the operational temperature for any significant thermal decomposition to take place. However, as it is expensive and only available in a few research institution, we were unable to run these experiments.
2.1.5 **Molecular weight characterization**

The molecular weight analysis was conducted in hexafluoroisopropanol (HFIP) at 40 °C with polystyrene as the standard. The samples were allowed to dissolve in HFIP overnight and then filtered. The HFIP soluble portions were then analyzed. The recorded molecular weights greatly depended on the residence time under the polymerization conditions and the solubility in the elution solvent. For instance, in the case of P1 and P2 (which are both glycine-based) the soluble portion in HFIP appears to be the very low molecular weight oligomers; Table 2.2 shows their number average molecular weight ($M_n$) at 910 and 928 g/mol respectively. This can be understood by the lack of bulky substituents on the α-C carbon in the vicinity of the reactive sites making it relatively easier for the polymer chains to densely pack, hence the poor solubility in
the GPC solvent. As a result, high molecular weight fractions become impervious to solvents and are filtered out before injection. On the other hand, L-Ala and L-Ile based polymers feature alkyl group substituents and for that reason their polymer networks are readily soluble and, in fact, show moderate molecular weights and average degree of polymerization (Table 2.2). The apparent low molecular weight in the case of P5 was unexpected. However, taking into account of the recorded polydispersity in Table 2.2 (4.99), it can be argued that a considerable amount of its oligomers did not combine in the final stage of the polycondensation. Presumably, this may be a result of insufficient allocated reaction time or the oligomers’ untimely hardening which prematurely stopped the stirring.

Some factors that could potentially have hampered further increase in molecular weight besides the catalyst degradation under the polymerization conditions, include the N-methylation [49], and the drawbacks associated with a transesterification via a phenolic hydroxyl group. [50] Generally, the N-methylation side reaction occurs at high temperatures when synthesizing polyamides from methyl esters and is therefore a serious molecular weight limiting factor. Secondly, it has been reported that the formation of ester linkages by a reaction of bisphenols/phenols, aliphatic diols and esters (transesterification) under melt polymerization conditions can be quite arduous, as the tetrahedral intermediate involved falls apart to liberate the better leaving group phenoxide and not the methoxide. Ultimately, this inhibits the generation of high molecular weight polymers via such polycondensation.
Table 2.2  Molecular weight properties by Gel Permeation Chromatography: the data represents only the soluble fraction of the polymers as they were only partially soluble in hexafluoroisopropanol

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Substrate</th>
<th>R Group</th>
<th>$\bar{M}_w$ (kDa)</th>
<th>$M_n$ (kDa)</th>
<th>$\bar{M}_w/M_n$</th>
<th>DP$_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>H</td>
<td></td>
<td>2.65</td>
<td>0.91</td>
<td>2.92</td>
<td>4.35</td>
</tr>
<tr>
<td>P2</td>
<td>H</td>
<td></td>
<td>3.62</td>
<td>0.93</td>
<td>3.90</td>
<td>3.89</td>
</tr>
<tr>
<td>P3</td>
<td>L-Me</td>
<td>L-Me</td>
<td>15.78</td>
<td>7.52</td>
<td>2.10</td>
<td>33.69</td>
</tr>
<tr>
<td>P4</td>
<td>L-Me</td>
<td>L-Me</td>
<td>11.07</td>
<td>6.33</td>
<td>1.75</td>
<td>25.00</td>
</tr>
<tr>
<td>P5</td>
<td>L-sec-butyl</td>
<td>L-sec-butyl</td>
<td>6.70</td>
<td>1.34</td>
<td>4.99</td>
<td>25.25</td>
</tr>
<tr>
<td>P6</td>
<td>L-sec-butyl</td>
<td></td>
<td>7.82</td>
<td>5.81</td>
<td>1.34</td>
<td>19.67</td>
</tr>
</tbody>
</table>

2.1.6  Viscosity measurements

Intrinsic viscosity measurements were performed in N-methylpyrrolidone (NMP) at 30 °C (Table 2.3). The polymers’ viscosity ranged from 0.30 dL/g to 0.60 dL/g. Correlating the viscometry data and GPC results, it is evident that there is a significant disparity. The intrinsic viscosity data suggest that the polymers’ $M_n$ were higher than the data obtained by GPC. One potential explanation for this discrepancy is the improved solubility of the polymer powders in NMP vs HFIP. Whenever possible, the molecular weight properties of these type of polymers should be studied in polar solvent at elevated temperatures for accurate results.
Table 2.3  Intrinsic viscosity study in NMP at 30 ºC

<table>
<thead>
<tr>
<th>Polymer entry</th>
<th>Average flow time (solvent) /s</th>
<th>Concentration g/dL</th>
<th>Average flow Time /s</th>
<th>Average intrinsic Viscosity /dLg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>140.18</td>
<td>0.30</td>
<td>154.34</td>
<td>0.32</td>
</tr>
<tr>
<td>P2</td>
<td>140.18</td>
<td>0.29</td>
<td>153.89</td>
<td>0.32</td>
</tr>
<tr>
<td>P3</td>
<td>140.18</td>
<td>0.27</td>
<td>154.05</td>
<td>0.35</td>
</tr>
<tr>
<td>P4</td>
<td>140.18</td>
<td>0.31</td>
<td>153.84</td>
<td>0.30</td>
</tr>
<tr>
<td>P5</td>
<td>140.18</td>
<td>0.22</td>
<td>158.24</td>
<td>0.56</td>
</tr>
<tr>
<td>P6</td>
<td>140.18</td>
<td>0.24</td>
<td>157.07</td>
<td>0.48</td>
</tr>
<tr>
<td>P7</td>
<td>144.82</td>
<td>0.10</td>
<td>150.22</td>
<td>0.37</td>
</tr>
</tbody>
</table>

2.1.7  Degradation studies of p-TsOH polymers

The vanillate-derived polymers (P2, P4 and P6) were subjected to three different pH solutions (pH 1, 4 and 8) to determine their stability. To speed up the degradation process, the polymers were stirred in the pH solutions at 50 ºC in air for 6 d. Citrate, sodium phosphate and potassium chloride/ hydrochloric acid buffers were prepared in order to investigate the degradation at the mentioned pH conditions. P2 demonstrated the most thermal stability after being subjected to the various pH media as the TGA curves for the treated polymers did not change much from the original polymer (Figure 2.19A). Although the TGA curves for P4 and P6 show some thermal instability compared to the original polymers, particularly after 6 d at various pHs, they were still relatively thermally stable. The 10% decomposition that occurred for P6 at pH 4 after 6 d (Figure 2.19C) is due to the loss of volatiles that were trapped in the polymer. Since all of the polymers were insoluble in the pH media, we conclude that P2 is slightly more
resistant to pH than P4 and P6; although all of the polymers show overall resistance to the various pH media. A similar trend is expected to occur for the p-HBA-based polymers.

Figure 2.19 Degradation studies of P2, P4 and P6 in various pH solutions

2.1.8 Polymers’ crystallinity

Finally, we evaluated the extent of crystallinity in the polymers using WAXS analysis (Figure 2.20). For this experiment, the polymers were first crushed to a very fine powder and run on a Xeuss 3.0 instrument (more details on the instrument are included in the appendix). The polymers all showed crystalline and amorphous regions. They all had three peaks with 2θ between 5° – 14°. There was no real trend in the crystallinity of the polymers, although there were some slight differences amongst some of the polymers. For example, the 2θ peak for P3 at 18.3° is more intense than the other polymers, and there is a shoulder in P5 with a 2θ peak at 4° that is not seen in any of the other polymers. The lack of a trend in the diffraction patterns of the polymers suggests that the differences in the R-groups on the amino acid were not sufficiently large to drastically affect the packing in the polymer chains that could be seen by WAXS analysis. These results are consistent with the thermal decomposition properties and highlights
the sensitivity of the glass transition temperature to the molecular structures. The small 2θ peak values suggest large crystalline lattice, which is not unusual for these kinds of semi-crystalline polymers.

Figure 2.20  WAXS analysis of P1 – P6

2.1.9  Racemic amino acids in PEA

To investigate the effect of chirality on the thermal properties of the PEAs, monomer 6g (DL-alanine derivative) was prepared and subjected to the same polymerization conditions and heating process as 6c. The FTIR and \(^1\)H NMR (Figure 2.21 and 2.22) analysis confirmed that the desired PEA was successfully prepared as the expected vibration frequencies and proton resonances overlaid very well with P3. The thermal properties of the DL-polymer (P7), although excellent, turned out to be slightly lower than that of its pure L-alanine counterpart (P3) in spite of their similar intrinsic viscosities (0.36 dL/g and 0.30 dL/g respectively). For example, the thermal degradation of P7 in air has an onset at 351 °C and \(T_d\) (50%) at 578°C, which is slightly lower than the \(T_d\) (onset) at 371 °C and \(T_d\) (50%) at 586 °C for P3 (Table 2.4). In addition, the \(T_g\)
for P7 was 10 °C lower than P3 (140 °C vs 150 °C respectively). These initial results indicate that there are some thermal stability resulting from the unidirectional arrangement of the methyl substituent in the case of P3 versus P7. We performed WAXS measurements for P7, which also showed a similar diffraction pattern as P3 (Figure 2.23). The peaks were broader than those in P3, except for the 2θ peak at 18.7°, suggesting a slightly lesser order in the P7. The reason for the sharper, more intense peak in P7 at 18.7° is currently unknown. Research is currently underway to determine the full effect of the chiral center on the thermal and mechanical properties of PEAs. Nonetheless, this experiment proves that racemic amino acids could also be utilized in the production of highly thermally stable PEAs.

Figure 2.21  Stacked FTIR spectra of P3 and P7
Table 2.4  Comparison of the properties of DL-PEA (P7) with L-PEA (P3)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>T_d onset N_2 °C</th>
<th>T_d onset air °C</th>
<th>T_d 50% air °C</th>
<th>T_g °C</th>
<th>[η] pTsOH (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 3</td>
<td>344</td>
<td>371</td>
<td>586</td>
<td>150</td>
<td>0.30</td>
</tr>
<tr>
<td>P 7</td>
<td>336</td>
<td>351</td>
<td>578</td>
<td>140</td>
<td>0.37</td>
</tr>
</tbody>
</table>

Viscosity measurements were conducted in NMP at 30 °C
2.2 Experimental

2.2.1 Materials

Vanillic acid (97% purity; Sigma-Aldrich), 4-hydroxybenzoic acid (99% purity; Sigma-Aldrich), tert-butyldimethylsilyl chloride (97%; Sigma-Aldrich), antimony (III) oxide (99.6% purity; Alfa Aesar), glycine (99%; Sigma-Aldrich), L-alanine (98%; Sigma-Aldrich), L-isoleucine (98%; Sigma-Aldrich), and tetrabutylammonium fluoride solution (1.0 M in THF; Sigma-Aldrich) were purchased and used without further purification. All solvents were reagent grade and used as such unless otherwise mentioned. Dry and degassed THF and CH$_2$Cl$_2$ were obtained from a VAC solvent purification system.

2.2.2 General synthesis

2.2.2.1 Amino acid methyl esters

Anhydrous methanol (1.0 M) was charged in an oven dried round bottom flask and chilled in an ice-bath for 10 min under inert atmosphere. Thionyl chloride (166.5 mmol) was added dropwise to the chilled methanol solvent and stirred for 1 h. The corresponding amino acids (66.6 mmol) were then added and stirred for another hour at 0 ºC. The reaction was then allowed to come to room temperature and stirred overnight. The reaction was concentrated under reduced pressure and the white solid was washed with cold acetone (3 X 50 mL) to remove any residual thionyl chloride. The corresponding amino acid methyl esters were used without further purification.

**Methyl 2-aminoacetate:** [37] conversion 99.5%, $^1$H NMR (500 MHz, D$_2$O) $\delta$ 3.86 (s, 2H), 3.76 (s, 3H).

**Methyl 2-aminopropanoate:** [37] conversion 99.7%, $^1$H NMR (500 MHz, D$_2$O) $\delta$ 4.13 (q, $J = 7.3$ Hz, 1H), 3.77 (s, 3H), 1.49 (d, $J = 7.3$ Hz, 2H).
Methyl 2-amino-3-methylbutanoate: [38] conversion 99.7%, $^1$H NMR (500 MHz, D$_2$O) $\delta$ 4.04 (d, $J = 4.1$ Hz, 1H), 3.77 (s, 3H), 2.00 (s, 1H), 1.44 – 1.37 (m, 1H), 1.29 – 1.22 (m, 1H), 0.93 (d, $J = 7.0$ Hz, 3H), 0.86 (t, $J = 7.4$ Hz, 3H).

Figure 2.24 $^1$H NMR of glycine methyl ester in D$_2$O
Figure 2.25  $^1$H NMR of L-alanine methyl ester in D$_2$O

Figure 2.26  $^1$H NMR of L-isoleucine methyl ester in D$_2$O
2.2.2.2 General synthesis of compound 5a – 5f

An oven-dried round bottom flask was charged with compound 1 or 2 (1 equiv.) and dissolved in anhydrous dichloromethane (0.42 M) under inert atmosphere. Anhydrous triethylamine (6 equiv.) was added at room temperature and the reaction flask was cooled in an ice bath. A solution of tert-butyldimethylsilyl chloride (TBSCI, 2.5 equiv.) was slowly added to the flask and the reaction was stirred at 0 °C for 3 h, then allowed to come to room temperature and stirred for 15 h. The solution was diluted with dichloromethane (100 mL) and washed with brine (3 X 200 mL). The organic layer was dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure to give a clear oily residue. The product was used in the next step without further purification.

The crude silylated product was taken up in anhydrous dichloromethane (0.5 M) to which 5 drops of anhydrous DMF was added, then the reaction mixture was cooled in an ice-bath. Oxalyl chloride (3 equiv.) was slowly added to the flask, and the reaction was stirred for 3 h at 0 °C, followed by 20 h at room temperature. The crude mixture (3 or 4) was concentrated under reduced pressure and used without further purification.

To the crude mixture of 3 or 4 (1 equiv.) in dry THF (0.18 M) was added the corresponding amino acid methyl ester hydrochloride (1.5 equiv.), followed by the dropwise addition of i-Pr₂NEt (4 equiv.). The reaction was stirred at 60 °C for 5 h. After completion, the reaction mixture was poured into ice water (100 mL) and extracted with ether (3 X 100 mL). The combined organic layers was dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure to give a highly viscous oil. The crude products were purified by flash column chromatography on silica gel with eluent ethyl acetate: hexane (35:65) to give the products as yellow powders.
Methyl 2-[[4-[[dimethyl(propan-2-yl)silyl]oxy]-3-methoxyphenyl]formamido]acetate (5a): Yield 62.0%. $^1$H NMR (500 MHz, DMSO) $\delta$ 8.85 (t, $J = 5.8$ Hz, 1H), 7.84 (d, $J = 8.6$ Hz, 2H), 6.94 (d, $J = 8.5$ Hz, 2H), 4.01 (d, $J = 5.8$ Hz, 2H), 3.66 (s, 3H), 0.95 (s, 9H), 0.21 (s, 6H). $^{13}$C $^1$H NMR (126 MHz, DMSO) $\delta$ 170.97, 166.6, 158.5, 129.7, 127.3, 120.0, 52.1, 41.6, 25.9, 18.4, -4.2. ESIHRMS calculated for C$_{16}$H$_{25}$NO$_4$Si (M+H) 324.1626; found 324.1626.

Methyl 2-[[4-[[dimethyl(propan-2-yl)silyl]oxy]phenyl]formamido]acetate (5b): Yield 64.9%. $^1$H NMR (500 MHz, DMSO) $\delta$ 8.84 (t, $J = 5.7$ Hz, 1H), 7.50 (d, $J = 1.6$ Hz, 1H), 7.42 (dd, $J = 8.2, 1.8$ Hz, 1H), 6.92 (d, $J = 8.2$ Hz, 1H), 4.00 (d, $J = 5.8$ Hz, 2H), 3.82 (s, 3H), 3.66 (s, 3H), 0.97 (s, 9H), 0.15 (s, 6H). $^{13}$C $^1$H NMR (126 MHz, DMSO) $\delta$ 170.99, 166.6, 150.6, 147.7, 127.8, 121.0, 120.5, 111.9, 55.9, 52.2, 41.7, 25.98, 18.6, -4.3. ESIHRMS calculated for C$_{17}$H$_{27}$NO$_5$Si (M+H) 354.1731; found 354.1731.

Methyl (2R)-2-[[4-[[dimethyl(propan-2-yl)silyl]oxy]phenyl]formamido]propanoate (5c): Yield 66.0%. $^1$H NMR (500 MHz, DMSO) $\delta$ 8.68 (d, $J = 6.9$ Hz, 1H), 7.84 (d, $J = 8.6$ Hz, 2H), 6.93 (d, $J = 8.6$ Hz, 2H), 4.47 (d, $J = 7.2$ Hz, 1H), 3.64 (s, 3H), 1.40 (d, $J = 7.3$ Hz, 3H), 0.95 (s, 9H), 0.21 (s, 6H). $^{13}$C $^1$H NMR (500 MHz, DMSO) $\delta$ 173.77, 166.17, 158.44, 129.91, 127.36, 119.94, 52.28, 48.67, 25.95, 18.43, 17.22, -4.13. ESIHRMS calculated for C$_{17}$H$_{27}$NO$_4$Si (M+H) 338.1782; found 338.1782.

Methyl (2R)-2-[[4-[[dimethyl(propan-2-yl)silyl]oxy]-3-methoxyphenyl]formamido]propanoate (5d): Yield 72.4%. $^1$H NMR (500 MHz, DMSO) $\delta$ 8.66 (d, $J = 6.9$ Hz, 1H), 7.50 (d, $J = 1.9$ Hz, 1H), 7.44 (dd, $J = 8.2, 2.0$ Hz, 1H), 6.91 (d, $J = 8.2$ Hz, 1H), 4.47 (p, $J = 7.2$ Hz, 1H), 3.83 (s, 3H), 3.65 (s, 3H), 1.41 (d, $J = 7.3$ Hz, 3H), 0.97 (s, 9H), 0.15 (s, 6H). $^{13}$C $^1$H NMR (126 MHz, DMSO) $\delta$ 173.8, 166.2, 150.6, 147.7, 127.8, 121.2, 120.4, 112.0, 55.95, 52.3, 48.7, 25.99, 18.6, 17.3, -4.2. ESIHRMS calculated for C$_{18}$H$_{29}$NO$_5$Si (M+Na) 390.1707; found 390.1707.
Methyl (2R)-2-[(4-[[dimethyl(propan-2-yl)silyl]oxy]phenyl)formamido]-3-methyl-butanoate (5e): Yield 74.3%. \( ^1 \)H NMR (500 MHz, DMSO) \( \delta \) 8.50 (d, \( J = 7.7 \) Hz, 1H), 7.84 (d, \( J = 8.6 \) Hz, 2H), 6.92 (d, \( J = 8.6 \) Hz, 2H), 4.32 (t, \( J = 7.7 \) Hz, 1H), 3.64 (s, 3H), 2.06 – 1.88 (m, 1H), 1.59 – 1.44 (m, 1H), 1.34 – 1.19 (m, 1H), 0.95 (s, 9H), 0.89 (d, \( J = 6.8 \) Hz, 3H), 0.86 (t, \( J = 7.4 \) Hz, 3H), 0.21 (s, 6H). \( ^{13} \)C{1H} NMR (126 MHz, DMSO) \( \delta \) 172.9, 166.8, 158.4, 130.1, 127.5, 119.9, 57.8, 51.99, 36.0, 25.96, 25.7, 18.4, 15.97, 11.3, -4.1. ESIHRMS calculated for \( \text{C}_{20}\text{H}_{33}\text{NO}_{4}\text{Si} \) (M+Na) 402.2071; found 402.2071.

Methyl (2R)-2-[(4-[[dimethyl(propan-2-yl)silyl]oxy]-3-methoxyphenyl)formamido]-3-methyl-butanoate (5f): Yield 67.2%. \( ^1 \)H NMR (500 MHz, DMSO) \( \delta \) 8.48 (d, \( J = 7.6 \) Hz, 1H), 7.48 (s, 1H), 7.46 (d, \( J = 8.3 \) Hz, 1H), 6.90 (d, \( J = 8.1 \) Hz, 1H), 4.35 (t, \( J = 7.7 \) Hz, 1H), 3.82 (s, 3H), 3.65 (s, 3H), 2.04 – 1.91 (m, 1H), 1.58 – 1.46 (m, 1H), 1.34 – 1.21 (m, 1H), 0.97 (s, 9H), 0.90 (d, \( J = 6.8 \) Hz, 3H), 0.87 (t, \( J = 7.4 \) Hz, 3H), 0.15 (s, 6H). \( ^{13} \)C{1H} NMR (126 MHz, DMSO) \( \delta \) 172.9, 166.7, 150.6, 147.7, 127.95, 121.4, 120.3, 112.3, 57.8, 55.95, 52.0, 36.0, 25.99, 25.7, 18.6, 15.99, 11.3, -4.2. ESIHRMS calculated for \( \text{C}_{21}\text{H}_{35}\text{NO}_{5}\text{Si} \) (M+H) 410.2357; found 410.2357.
Figure 2.27  Compound 3 $^1$H NMR in CDCl$_3$

Figure 2.28  Compound 4 $^1$H NMR in CDCl$_3$
Figure 2.29  Compound 5a $^1$H NMR in DMSO-d$_6$

Figure 2.30  Compound 5a $^{13}$C NMR in DMSO-d$_6$
Figure 2.31  Compound 5b \(^1\)H NMR in DMSO-d\(_6\)

Figure 2.32  Compound 5b \(^13\)C NMR in DMSO-d\(_6\)

41
Figure 2.33  Compound 5c $^1$H NMR in DMSO-d$_6$

Figure 2.34  Compound 5c $^{13}$C NMR in DMSO-d$_6$
Figure 2.35  Compound 5d $^1$H NMR in DMSO-d$_6$

Figure 2.36  Compound 5d $^{13}$C NMR in DMSO-d$_6$
Figure 2.37  Compound 5e $^1$H NMR in DMSO-d$_6$

Figure 2.38  Compound 5e $^{13}$C NMR in DMSO-d$_6$
Figure 2.39  Compound 5f $^1$H NMR in DMSO-d$_6$

Figure 2.40  Compound 5f $^{13}$C NMR in DMSO-d$_6$
2.2.2.3 General synthesis of monomer 6a–6g

An oven dried round bottom flask was charged with compound 5 (1 equiv.) and dissolved in anhydrous THF (0.062 M) under inert atmosphere. The reaction flask was cooled in an ice bath after which TBAF (1M solution in THF, 2 equiv.) was slowly added. The reaction was allowed to come to room temperature and stirred overnight. The reaction mixture was poured into brine solution (150 mL), and the pH was adjusted with HCl to pH 2. The crude mixture was extracted with ether (3 X 70 mL) and the combined organic layers was dried with anhydrous sodium sulfate, filtered and concentrated under reduced pressure to give a crude yellow powder. The crude product was purified by flash column chromatography on silica gel with eluent ethyl acetate: hexane (45:55) to give a yellow powder.

**Methyl 2-[(4-hydroxyphenyl)formamido]acetate (6a):** was obtained as a yellow powder in 62% yield, m.p. 209 °C – 212 °C. ¹H NMR (500 MHz, DMSO) δ 10.04 (s, 1H), 8.68 (t, J = 5.7 Hz, 1H), 7.74 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 3.97 (d, J = 5.8 Hz, 2H), 3.65 (s, 3H). ¹³C{¹H} NMR (126 MHz, DMSO) δ 171.1, 166.8, 160.9, 129.7, 124.8, 115.4, 52.1, 41.6. ESIHRMS calculated for C₁₀H₁₁NO₄ (M + H) 210.0761; found 210.0761.

**Methyl 2-[(4-hydroxy-3-methoxyphenyl)formamido]acetate (6b) was obtained as a yellow powder in 63% yield, m.p. 119 °C – 121 °C. ¹H NMR (500 MHz, DMSO) δ 9.62 (s, 1H), 8.73 (t, J = 5.6 Hz, 1H), 7.45 (d, J = 1.2 Hz, 1H), 7.38 (dd, J = 8.2, 1.6 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 3.98 (d, J = 5.8 Hz, 2H), 3.82 (s, 3H), 3.65 (s, 3H). ¹³C{¹H} NMR (126 MHz, DMSO) δ 171.1, 166.7, 150.2, 147.6, 125.0, 121.4, 115.3, 111.8, 56.1, 52.1, 41.7. ESIHRMS calculated for C₁₁H₁₃NO₅ (M + Na) 262.0686; found 262.0685.

**Methyl (2R)-2-[(4-hydroxyphenyl)formamido]propanoate (6c) was obtained as a brown powder in 63% yield, m.p. 172 °C – 174 °C. ¹H NMR (300 MHz, DMSO) δ 10.03 (s, 1H), 8.51 (d, J = 6.2 Hz, 1H), 7.76 (d, J = 8.2 Hz, 2H), 6.81 (d, J = 8.2 Hz, 2H), 4.52 – 4.37 (m, 1H), 3.63
(s, 3H), 1.38 (d, J = 7.1 Hz, 3H). $^{13}$C{1H} NMR (126 MHz, DMSO) $\delta$ 173.9, 166.4, 160.8, 129.9, 124.8, 115.2, 52.3, 48.6, 17.3. ESIHRMS calculated for C$_{11}$H$_{13}$NO$_4$ (M + Na) 246.0737; found 246.0737.

Methyl (2R)-2-[(4-hydroxy-3-methoxyphenyl)formamido]propanoate (6d) was obtained as a yellow powder in 87%, m.p. 121 °C – 124 °C. $^1$H NMR (500 MHz, DMSO) $\delta$ 9.60 (s, 1H), 8.54 (d, J = 6.8 Hz, 1H), 7.46 (s, 1H), 7.41 (d, J = 8.2 Hz, 1H), 6.82 (d, J = 8.2 Hz, 1H), 4.45 (p, J = 7.2 Hz, 1H), 3.82 (s, 3H), 3.64 (s, 3H), 1.40 (d, J = 7.3 Hz, 3H). $^{13}$C{1H} NMR (126 MHz, DMSO) $\delta$ 173.9, 166.3, 150.2, 147.6, 125.0, 121.6, 115.2, 111.9, 56.2, 52.3, 48.7, 17.3. ESIHRMS calculated for C$_{12}$H$_{15}$NO$_5$ (M + Na) 276.0842; found 276.0842.

Methyl (2R)-2-[(4-hydroxyphenyl)formamido]-3-methylbutanoate (6e) was obtained as a brown powder in 73% yield; m.p. 130 °C – 132 °C. $^1$H NMR (300 MHz, DMSO) $\delta$ 10.01 (s, 1H), 8.31 (d, J = 7.5 Hz, 1H), 7.77 (d, J = 7.0 Hz, 2H), 6.80 (d, J = 7.0 Hz, 2H), 4.31 (t, J = 7.5 Hz, 1H), 3.64 (s, 3H), 2.03 – 1.87 (m, 1H), 1.58 – 1.44 (m, 1H), 1.33 – 1.19 (m, 1H), 0.92 – 0.82 (m, 6H). $^{13}$C{1H} NMR (126 MHz, DMSO) $\delta$ 173.0, 166.9, 160.8, 130.1, 124.9, 115.2, 57.7, 51.98, 36.0, 25.7, 15.99, 11.3. ESIHRMS calculated for C$_{14}$H$_{19}$NO$_4$ (M + H) 266.1387; found 266.1387.

Methyl (2R)-2-[(4-hydroxy-3-methoxyphenyl)formamido]-3-methylbutanoate (6f): was obtained as a brown powder in 82%, m.p. 120 °C – 123 °C. $^1$H NMR (500 MHz, DMSO) $\delta$ 9.59 (s, 1H), 8.35 (d, J = 7.7 Hz, 1H), 7.45 (s, 1H), 7.43 (d, J = 8.2 Hz, 1H), 6.82 (d, J = 8.2 Hz, 1H), 4.33 (t, J = 7.8 Hz, 1H), 3.82 (s, 3H), 3.65 (s, 3H), 2.01 – 1.91 (m, 1H), 1.56 – 1.47 (m, 1H), 1.31 – 1.20 (m, 1H), 0.89 (d, J = 6.8 Hz, 3H), 0.86 (t, J = 7.5 Hz, 3H). $^{13}$C{1H} NMR (126 MHz, DMSO) $\delta$ 173.0, 166.8, 150.5, 147.6, 125.2, 121.8, 115.2, 112.2, 57.7, 56.2, 51.98, 36.0, 25.7, 15.99, 11.2. ESIHRMS calculated for C$_{15}$H$_{21}$NO$_5$ (M + H) 296.1492; found 296.1492.
Methyl (2R/S)-2-[(4-hydroxyphenyl)formamido]propanoate (6g) was obtained as a brown powder in 58% yield, m.p. 139 °C – 142 °C. \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 10.05 (s, 1H), 8.54 (d, \(J = 6.9\) Hz, 1H), 7.76 (d, \(J = 8.7\) Hz, 2H), 6.81 (d, \(J = 8.7\) Hz, 2H), 4.44 (p, \(J = 7.2\) Hz, 1H), 3.63 (s, 3H), 1.38 (d, \(J = 7.3\) Hz, 3H). \(^{13}\)C\{\(^1\)H\} NMR (126 MHz, DMSO) \(\delta\) 173.9, 166.4, 160.8, 129.9, 124.8, 115.2, 52.3, 48.6, 17.3.

Figure 2.41  M1 \(^1\)H NMR in DMSO-d\(_6\)
Figure 2.42  M2 $^1$H NMR in DMSO-$d_6$

Figure 2.43  M3 $^1$H NMR in DMSO-$d_6$
Figure 2.44  \textbf{M4} $^1$H NMR in DMSO-d$_6$

Figure 2.45  \textbf{M5} $^1$H NMR in DMSO-d$_6$
2.2.2.4  General synthesis of P1–P6 with antimony catalyst

The monomers (100 mg) and the catalyst (1 mol%) were charged in an oven dried round bottom flask and slowly ramped to 200 °C (215 °C for P1) at a rate of 1 °C /min under inert atmosphere and held at that temperature until a highly viscous oil formed (times specified below). The temperature was then ramped to 240 °C before applying a vacuum at 100 torr for 3 h. After the reaction, the polymers were stirred in hot methanol (3 X 20 mL) at 40 °C for 1 h to remove the catalyst and any unreacted monomers, followed by drying in a vacuum oven at 150 °C overnight. **P1**: The temperature was ramped to 215 °C and held for 3 h before ramping to 240 °C and applying vacuum at 100 torr. The polymer was obtained in 30% yield.
**P2:** The temperature was ramped to 200 °C and held for 5.5 h before ramping to 240 °C and applying vacuum at 100 torr. The polymer was obtained in 30.2% yield.

**P3:** The temperature was ramped to 200 °C and held for 6 h before ramping to 240 °C and applying vacuum at 100 torr. The polymer was obtained in 33.3% yield.

**P4:** The temperature was ramped to 200 °C and held for 6 h before ramping to 240 °C and applying vacuum at 100 torr. The polymer was obtained in 37.6% yield.

**P5:** The temperature was ramped to 200 °C and held for 7 h before ramping to 240 °C and applying vacuum at 100 torr. The polymer was obtained in 40.7% yield.

**P6:** The temperature was ramped to 200 °C and held for 8 h before ramping to 240 °C and applying vacuum at 100 torr. The polymer was obtained in 42.2% yield.

### 2.2.2.5 General synthesis of the polymers P1–P6 with p-TsOH catalyst

The monomers (300 mg) and the p-TsOH catalyst (8 mol%) were charged in an oven dried round bottom flask and slowly heated at a rate of 1 °C/min under inert atmosphere until a highly viscous oil is formed according to the reported temperatures below. After the specified heating times, the reaction was stirred at 220 °C at 100 mmHg for 3 h before stopping the reaction. After the reaction, the crude product was stirred overnight at 80 °C in a solution of saturated sodium carbonate (3 X 20 mL), then deionized water (3 X 20 mL) for 3 h to remove the acid catalyst. The polymers were then dissolved in 1:1 TFA: DCM and reprecipitated from ether. The precipitates were collected and the re-precipitation process was repeated two more times. The polymers were dried in vacuum overnight before NMR analysis. **Poly**(pHBA-co-Gly) (P1) was ramped to 220 °C and held at that temperature for 2 h before applying vacuum for 3 h. The polymer was obtained in 43% yield.
Poly(VA-co-Gly) (P2) was ramped to 200 ºC and held at that temperature for 2 h before applying vacuum for 3 h. The polymer was obtained in 49% yield.

Poly(pHBA-co-l-Ala) (P3) was ramped to 200 ºC and held at that temperature for 2 h, then ramped to 220 ºC and held at that temperature for 7.2 h before applying vacuum for 3 h. The polymer was obtained in 38% yield.

Poly(VA-co-l-Ala) (P4) was ramped to 200 ºC and held at that temperature for 2 h, then ramped to 220 ºC and held at that temperature for 7 h before applying vacuum for 3 h. The polymer was obtained in 38% yield.

Poly(pHBA-co-l-Ile) (P5) was ramped to 200 ºC and held at that temperature for 2 h, then ramped to 220 ºC and held at that temperature for 8 h before applying vacuum for 3 h. The polymer was obtained in 44% yield.

Poly(VA-co-l-Ile) (P6) was ramped to 200 ºC and held at that temperature for 2 h, then ramped to 220 ºC and held at that temperature for 8 h before applying vacuum for 3 h. The polymer was obtained in 35% yield.

Poly(pHBA-co-dL-Ala) (P7) was ramped to 200 ºC and held at that temperature for 2 h, then ramped to 220 ºC and held at that temperature for 8 h before applying vacuum for 3 h. The polymer was obtained in 44.9 % yield.

2.2.3 Intrinsic viscosity study

The polymer solutions for intrinsic viscosity measurements were prepared according to the following protocol:
50 mg of each polymer were weighed and dissolved in 11 ml of N-Methyl-2-pyrrolidone (NMP) with stirring. The solution was filtered over cotton, and the residue was dried and weighed to determine the real concentration of the polymers that are reported in Table 2.3.

The experiment was conducted with an Ubbelohde viscometer placed in a water bath at 30 °C. Firstly, the solvent, itself, was flowed through the apparatus and the average flow time was determined. It should be noted that the apparent discrepancy in the solvent’s average flow time is due to running the studies at different times. On the other hand, the polymer solutions were run six times for each polymer and the time of flow for each step was recorded (Table 2.3 shows the average of the six data points). The average intrinsic viscosity values were obtained by applying Billmeyer’s equation (Equation 2.1)

\[
\eta = 0.25/C \times ((V_{rel} - 1) + (3 \times \text{log}_e V_{rel}))
\]  

Equation 2.1: Billmeyer’s equation for intrinsic viscosity; where \( \eta \) is the intrinsic viscosity, \( C \) the polymer’s concentration in g/dL, and \( V_{rel} \) the relative viscosity. The latter is simply computed by taking the quotient of the polymer’s flow time over that of plain solvent.

### 2.2.4 Degradation studies

The degradation experiments were conducted according to the following protocol:

45 mg of each polymer were stirred in 3 ml of the buffer for 6 d at 50 °C. After each 2 d, 1 ml aliquots were isolated and centrifuged at 8000 rpm. To remove any residual buffer salts, 5 ml of water were added to the residue and the mixture was stirred on a hotplate for 10 min and then centrifuged. This was repeated two more times before drying the polymer powders in the oven at 120 °C.
CHAPTER III
CONCLUDING REMARKS AND OUTLOOK

This study explored the thermal properties of fully bio-based poly(ester amide)s comprised of lignin derivatives (p-hydroxybenzoic acid and vanillic acid) and L-amino acids (Gly, L-Ala, L-Ile). The synthesized polymers exhibit glass transition temperatures between 130 ºC and 230 ºC and thermal decomposition temperatures over 500 ºC in O₂ atmosphere, which are desirable for high performance polymers. Although the polymers had poor solubility in most organic solvents, they were partially soluble in DMSO and NMP, which allowed us to perform viscosity measurements. Besides L-amino acids, polymers made with DL-alanine featured comparable thermal stability in air and inert atmosphere as the L-counterpart. The combined results indicated that the size of the R-groups on the amino acids were not sufficiently different to produce large differences in the thermal properties of the polymers. pH degradation studies indicate that the polymers were stable in various pH media up to 6 d at 50 ºC. To this effect, research is currently ongoing in our group using amino acids with larger R-groups to prepare PEAs with p-HBA and VA in order to determine the effect of the side chain size on the thermal properties of the polymers. In addition, racemic polymers are also being prepared to demonstrate a true effect of the chirality on the thermal properties of the polymers. Ultimately, we have prepared thermally stable PEAs from amino acids and lignin-derived precursors that could find potential applications in high performance materials.
REFERENCES


[40] M. J. M. Ko, Myeong Seon; Jung, Jae Ho; Kang, Dae Ho; Kim, Yun Bong; Choi, Beom Gyu; Lee, Gi Yeol, "Production of Optically Anisotropic Compound, Resin Composition Containing it, and Optical Element," Korea Patent KR 2010071871, 2010.


APPENDIX A

INSTRUMENTATION AND WAXS ANALYSIS
A.1 Instrumentation

A Barnstead International 1201D MeL-Temp Capillary MP Apparatus was used to determine the melting points. $^1$H NMR (500 MHz) and $^{13}$C NMR (500 MHz) spectra were recorded in deuterated solvents on a Bruker ADVANCE 500 NMR Spectrometer. $J$ values are expressed in Hz and quoted chemical shifts are in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvents as an internal standard. The signals have been designated as follows: s (singlet), d (doublet), t (triplet), m (multiplets). High resolution mass spectra (HRMS) were determined on Bruker-micrOTOF-Q II Mass Spectrometer. TGA analysis were carried out using a TA Instrument) Q50 and DSC runs were carried out on a TA Instrument Q200. ATR-FTIR was recorded on a Cary 630 (Agilent technologies) fitted with a Diamond Attenuated Total Reflectance (ATR). Powdered sample was used without modification. WAXS measurements were performed on a Xenocs, Xeuss 3.0 (GI-)SAXS/WAXS/USAXS beamline at the School of Polymer Science and Engineering at the University of Southern Mississippi with the following parameters:

Exposure Time = 7200 sec; Beamstop center: Center_1 = 521.53565 pixel; Center_2 = 687.61855 pixel; PSize_1 = 172 um; PSize_2 = 172 um; Sample Distance = 169.047 mm; Wavelength (Å) = 1.54 Å
A.2 WAXS analysis

Figure A.1 Polymers P1 to P6: WAXS analysis [1,2]

\[ q = \left( \frac{4\pi}{\lambda} \right) \sin \theta \]

\[ q = q_B = \frac{2\pi}{d_{hkl}} \]
Figure A.2  **P1** 2D plot

Table A.1  **P1** peak results

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Figure A.3  **P2** 2D plot

Table A.2  **P2** peak results

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Figure A.4  P3 2D plot

Table A.3  P3 peak results

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Figure A.5  P4 2D plot

Table A.4  P4 peak results

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Figure A.6  P5 2D plot

Table A.5  P5 peak results

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Figure A.7  P6 2D plot

Table A.6  P6 peak results

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Figure A.8  P7 2D plot

Table A.7  P7 peak results

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</table>
A.3 References:
