A Semicrystalline Furanic Polyamide Made from Renewable Feedstocks

Cristian P. Woroch, India W. Cox, and Matthew W. Kanan*

ABSTRACT: Semi-aromatic polyamides (SAPs) synthesized from petrochemical diacids and diamines are high-performance polymers that often derive their desirable properties from a high degree of crystallinity. Attempts to develop partially renewable SAPs by replacing petrochemical diacids with biobased furan-2,5-dicarboxylic acid (FDCA) have resulted in amorphous materials or polymers with low melting temperatures. Herein, we report the development of poly(5-aminomethyl-2-furoic acid) (PAMF), a semicrystalline SAP synthesized by the polycondensation of CO$_2$ and lignocellulose-derived monomer 5-aminomethyl-2-furoic acid (AMF). PAMF has glass-transition and melting temperatures comparable to that of commercial materials and higher than that of any previous furanic SAP. Additionally, PAMF can be copolymerized with conventional nylon 6 and is chemically recyclable. Molecular dynamics (MD) simulations suggest that differences in intramolecular hydrogen bonding explain why PAMF is semicrystalline but many FDCA-based SAPs are not.

INTRODUCTION

At present, nearly all synthetic polymers are derived from a small collection of petrochemical feedstocks. Petrochemical plastics are becoming increasingly unattractive because of concerns about sustainability: by 2050, plastics are projected to consume 20% of global petroleum production and 15% of the global carbon budget.\(^1\) Biomass is an attractive alternative feedstock for polymer production because it is abundant, renewable, and inexpensive.\(^2\)–\(^4\) However, biobased polymers do not comprise a sizeable portion of commercially available synthetic polymers because they lack the required properties for many applications and often have higher production costs.

Semi-aromatic polyamides (SAPs) are high-performance polymers primarily used in the automotive and electronic industries for their exceptional strength and thermomechanical stability.\(^5\)–\(^7\) Traditionally, these materials are made via polymerization of monomers such as hexamethylene diamine and terephthalic acid (Figure 1a). SAPs are often selected in applications where properties such as high crystallinity, high thermal stability, low moisture absorption, and manageable processing temperatures are needed.\(^7\) Previous efforts toward constructing renewable SAPs have primarily focused on replacing petroleum-based diacids with furan-2,5-dicarboxylic acid (FDCA) (Figure 1b).\(^8\)–\(^28\) While FDCA-based polyesters have improved physical properties compared to petrochemical polyesters,\(^29\),\(^30\) most FDCA-based polyamides are either amorphous or have low melting temperatures (<200 °C) and lack the thermomechanical properties required for many SAP applications.

Prior studies on FDCA-based polyamides suggest that the two amide protons form internal hydrogen bonds to the furan oxygen\(^31\),\(^32\) that may hinder the formation of semicrystalline domains. We hypothesized that a furanic polyamide with only one amide bond per furan is more likely to be semicrystalline as there are equal number of furan and amide moieties. Recent work in our group has demonstrated the synthesis of 5-aminomethyl-2-furoic acid (AMF) from CO$_2$ and furfuryl amine, which is produced from lignocellulose-derived furfural (Figure 1d).\(^33\) Herein, we report the first direct polymerization of AMF to poly(5-aminomethyl-2-furoic acid) (PAMF) and characterize some of its material properties (Figure 1c). PAMF was first reported via acid-catalyzed polymerization of N-(hydroxymethyl)furan-2-carboxamide, but IR was the only characterization provided.\(^34\) Gandini and colleagues improved on the original synthesis and demonstrated a similar polymerization with furanamide and formaldehyde, but the analysis of the reported thermal properties suggests that these polymers had very low molecular weights.\(^35\),\(^36\) In addition, two patents claim PAMF but provide no experimental details or characterization of the polymer.\(^37\),\(^38\) In this work, we demonstrate how PAMF is a promising renewable alternative to traditional SAPs.
RESULTS AND DISCUSSION

We identified two methods for the polycondensation of AMF. Organic phosphite polymerization (OPP) uses organic phosphites such as triphenyl or diphenyl phosphite as coupling agents in polar aprotic solvents at elevated temperatures. While this method is remarkably successful for polymerizing aromatic amino acids such as \( p \)-aminobenzoic acid, its use to polymerize semi-aromatic amino acids has proven to be more challenging. Starting from a reported method for the polymerization of \( p \)-aminobenzoic acid, we optimized an OPP method for PAMF on a small scale (Table S1). The reaction afforded the best results when conducted with stoichiometric amounts of triphenyl phosphite in a mixture of \( N \)-methyl pyrrolidone and pyridine with lithium chloride to improve solubility. The optimal conditions for OPP of PAMF were replicated at a 250 mg scale, resulting in 72% yield of an off-white polymer solid (Figures S1, 2a).

The OPP method requires organic solvents and stoichiometric amounts of triphenyl phosphite. Solvent-free polymerization methods can eliminate the waste associated with solvent and reagent use. Melt polymerization is frequently used but requires that the monomer forms a stable melt. As AMF does not melt before its decomposition temperature (Figures S8, S9), direct solid-state polymerization (SSP) was investigated. SSP does not require organic solvents or stoichiometric coupling agents and is performed industrially for the chain extension of polyesters, polycarbonates, and polyamides. However, there are only a few reports describing the use of SSP to synthesize SAPs from semi-aromatic amino acids. Preliminary experiments with various additives revealed that hypophosphite (\( H_2PO_2^- \)) facilitated the SSP of AMF (Table S2). Specifically, sodium hypophosphite (\( NaH_2PO_2 \)) was identified as an effective promoter of SSP that caused the least amount of discoloration in the polymer product (Figure S10). SSP was subsequently optimized on a small scale. The optimal conditions of SSP were replicated on a
250 mg scale, resulting in 84% yield of a tan polymer solid, with $M_n$ of 30.6 kDa and $M_w$ of 53.8 kDa (Figures 2a, S10).

NMR and MALDI measurements were used to compare PAMF produced by SSP to PAMF produced by OPP (Figures 2b and S11−S15). Notably, the $^1$H NMR spectra of SSP-generated PAMF had small additional peaks adjacent to the identified polymer peaks. Two-dimensional NMR was used to assign these additional peaks as corresponding to a furan at the C-termini of polymer chains. The fragment molecular weights measured by MALDI were also consistent with a C-terminal furan. A subsequent experiment in which furfurylamine was introduced to quench the C-terminus further supported the proposed assignment (Figure S16). Furoic acid derivatives are known to decarboxylate at elevated temperatures. De-carboxylation is often a substantial impediment toward the synthesis of high-molecular-weight furanic polymers. However, PAMF polymerized by SSP was found to have a high absolute molecular weight by GPC ($M_n = 30.6$ kDa and $M_w = 53.8$ kDa). We hypothesize that short decarboxylated PAMF chains are more soluble and thus show up prominently by NMR and MALDI but comprise a small proportion of the total polymer sample.

To better understand how SSP of PAMF can lead to high-molecular-weight polymers, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to examine the thermal properties of the reaction mixture (Figure S17). When heated together, AMF and NaH$_2$PO$_2$ undergo an endothermic event at approximately 225 °C, observed by DSC, which corresponds to a 13% mass loss by TGA. This endothermic event is not observed in the same AMF−NaH$_2$PO$_2$ sample upon second heating nor is it observed when PAMF and NaH$_2$PO$_2$ are mixed. Observations of the polymerization made by $^1$H and $^{31}$P NMR suggest that PAMF is the only major product, and the chemical shift of NaH$_2$PO$_2$ does not substantially change in either $^1$H or $^{31}$P NMR during polymerization, though the amount of NaH$_2$PO$_2$ does appear to decrease over the course of the reaction (Figure S18). As NaH$_2$PO$_2$ is not consumed stoichiometrically, we postulate that NaH$_2$PO$_2$ initiates polymerization through the formation of a molten component and then slowly thermally decomposes; after initiating the formation of short chains, PAMF polymerization is expected to proceed via a classic SSP mechanism.

SSP methods are most often used to increase the molecular weight of shorter polymers. We therefore investigated whether OPP could be combined with SSP to synthesize polymers with even higher molecular weights. First, PAMF with $M_n \sim 10$ kDa was synthesized via optimized OPP. After purification, the synthesized polymer was subjected to the optimized SSP conditions. The resulting polymer was isolated in 68% yield.

<table>
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<th>Entry</th>
<th>Polymer</th>
<th>$M_n$ GPC (kDa)</th>
<th>$M_w$ GPC (kDa)</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_{5%}$ (°C)</th>
<th>Semi-crystalline?</th>
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<td>145</td>
<td>315</td>
<td>331</td>
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<tr>
<td>2</td>
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<td>11.0</td>
<td>139</td>
<td>340</td>
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<td>Yes</td>
</tr>
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<td>3</td>
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<td>11.0</td>
<td>19.7</td>
<td>–</td>
<td>–</td>
<td>375</td>
<td>No</td>
</tr>
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Figure 3. Comparison of PAMF and related analogues. (a) Chemical structures of PAMF, PAMB, and PA2F and summary of the polymer properties. (b) PXRD; (c) TGA; (d) first DSC cycles; and (e) second DSC cycles.
and had greater molecular weight and dispersity ($M_n = 59.5$ kDa, $M_w = 147.1$ kDa, and $D = 2.47$) than the polymer synthesized by either of the two methods alone (Figure 2). Notably, the C-terminal furan arising from decarboxylation is not observed in this sample by $^1$H NMR or MALDI (Figures 2, S19). This result suggests that decarboxylation occurs during the early stages of SSP and can lead to the formation of short decarboxylated oligomers, but once a polymer is formed, decarboxylation is negligible.

Understanding the structure–property relationships of polymer materials is critical for determining their potential applications. To understand how the structure of PAMF impacts its thermal properties and crystallinity, we synthesized and characterized two analogous SAPs: poly(3-aminomethylbenzoic acid) (PAMB) and poly(ethylene-2,5-furanamide) (PA2F) (Figure 3a). PAMB is a phenyl analogue to PAMF and was synthesized to probe the effect of the furan ring on the polymer properties. PA2F is an FDCA-based analogue to PAMF and was synthesized to probe the effect of a bisfuranamide versus monofuranamide moiety. PAMB and PA2F were synthesized by OPP and interfacial polymerization, respectively, and subsequently characterized by NMR and MALDI to confirm their structure (Figures S20–S31). PAMF, PAMB, and PA2F were then compared by powder X-ray diffraction (PXRD), TGA, and DSC (Figure 3). PXRD suggests that both PAMF and PAMB are semicrystalline, whereas PA2F is amorphous, which agrees well with the previous characterizations of FDCA-based polyamides. TGA reveals that both PAMB and PA2F have onset decomposition temperatures ($T_{\text{d}}$) greater than that of PAMF. These results can be explained by the greater aromaticity and the consequent thermal stability of a phenyl ring compared to a furan (PAMB vs PAMF) and the apparent greater stability of a bisfuranamide compared to a monofuranamide (PA2F vs PAMF). In practice, additives and reinforcements are used to increase the thermal stability of SAPs. Future efforts will investigate which additives and reinforcements could be used to improve the thermal stability of monofuranamide-containing polymers.

Thermal phase behavior is similarly critical for determining the utility of a polyamide and was thus measured with DSC. On the first cycle of a DSC measurement, both PAMF and PAMB displayed a sharp endothermic event characteristic of a semicrystalline melting temperature ($T_m$), with enthalpies of 52.3 J/g and 86.5 J/g, respectively. On subsequent cycles, neither PAMF nor PAMB displayed strong melt transitions but did exhibit strong second-order transitions characteristic of the glass-transition temperature ($T_g$) at 145 °C and 139 °C, respectively. No thermal phase transitions were observed for PA2F by DSC. These data are consistent with the assertion that PA2F is amorphous, whereas both PAMF and PAMB are semicrystalline but do not rapidly crystallize from the melt. Notably, DSC reveals that PAMF has the highest $T_g$ and $T_m$ values for a furan-based polyamide. Previous attempts to make furan-derived SAPs have struggled to make materials with thermal properties comparable to that of petroleum-derived polymers. PAMF, however, has a $T_m$ in the range of many commercial SAPs ($T_m \sim 300$ °C) and a higher glass-transition temperature than some traditional petroleum-derived SAPs including poly(hexamethylene terephthalamide) ($T_g = 125$ °C) and poly(hexamethylene isophthalamide) ($T_g = 123$ °C).

FDCA-based polyamides are rarely semicrystalline; most reports describing FDCA-based polyamides do not report $T_m$ (Table S3). Therefore, we sought to investigate why PAMF is semicrystalline, whereas PA2F and other FDCA-based polyamides are amorphous. Previous studies have used model compounds and computational methods to understand the effect of the furanamide unit on the polymer properties. In particular, several studies have focused on the hydrogen-bonding interactions within furan-containing polymers. Previous molecular dynamics (MD) simulations of FDCA-based polyamides indicated fewer intramolecular hydrogen bonds and shorter intramolecular hydrogen-bond lifetimes compared to traditional nylons, which may hinder crystallization. NMR and FTIR characterization of an FDCA-based model compound indicated the presence of intramolecular hydrogen bonds between the furan oxygen and the amide protons, which may compete with the intramolecular hydrogen bonds required for crystallization in FDCA-based polyamides. Another study of an FDCA-based model compound by NOESY also reported the existence of a weak intramolecular hydrogen bond within the bisfuranamide unit that can coexist with the intramolecular hydrogen bonds between molecules.

To better understand the hydrogen-bonding interactions for PAMF, a model compound containing the polymer repeat unit was synthesized and characterized by X-ray crystallography (Figure 4). Two hydrogen-bonding interactions were observed in the crystal structure: an intermolecular hydrogen bond with a O–H distance of 1.99 Å and a weaker intramolecular hydrogen bond with a O–H distance of 2.35 Å. While the intramolecular hydrogen bond is stronger, the intramolecular hydrogen bond may play a significant role in defining the molecular orientation, particularly around the amide bond.

Computational modeling was used to further study how hydrogen bonding within PAMF may impact its properties relative to FDCA-based or phenyl-based polyamides. In particular, we monitored the dihedral angle of the bond linking the amide to the aromatic ring (O–C–C–O for PAMF and PA2F; C–C–C–O for PAMB) to understand how intramolecular hydrogen bonds might impact the polymer structure. Each polymer was modeled by a small-molecule analogue using density functional theory (DFT) and an amorphous polymer cell using MD simulations (Figure S32). The energy of the small-molecule analogue was computed as a function of the amide–aromatic dihedral angle. The amorphous polymer cell was equilibrated at 300 K before the dihedral angles were extracted and analyzed to determine the relative likelihood of different chain conformations. To test
the accuracy of our MD model, simulated \( T_g \) experiments were conducted. The predicted \( T_g \) values agreed well with those observed by experiment (Figures S33−S35). The DFT and MD analyses were combined to yield insights into the polymer chain geometry.

PAMF and PAMB have only one amide bond per repeat unit; thus, a single dihedral was examined (\( \alpha_1 \)), whereas PA2F has two amide bonds per repeat unit (\( \alpha_1 \) and \( \alpha_2 \)). For all three polymers, the DFT and MD models agree that the lowest energy states, and thus most populated states, are centered around either 0° or ±180°. The 0° or ±180° configurations, referred to as “bent” and “linear”, respectively, are equally likely for PAMB as there is no opportunity for an intramolecular hydrogen bond (Figure 5b). For PAMF, however, the bent configuration is favored: the bent configuration is approximately 3 kcal/mol more stable in the model DFT compound, and 69% of the dihedral angles in MD simulation are between −90 and 90° (Figure 5a). The energetic stabilization of the bent configuration is presumed to be the result of an intramolecular hydrogen bond between the amide proton and the furan oxygen. While only two configurations are prevalent for PAMF and PAMB, three types of configurations are common in PA2F due to two possible intramolecular hydrogen bonds: both dihedral angles equal to 180° (“linear”), both dihedral angles equal to 0° (“double bent”), and one angle equal to 180° and the other equal to 0° (“single bent”) (Figure 5c). To aid visualization, a representative 1D slice of the dihedral analysis for PA2F was extracted and plotted as Figure 5c (see Figures S36 and S37 for 2D contour plots). Like PAMF, the linear configuration in PA2F is disfavored compared to the bent configurations. DFT analysis of a PA2F model compound suggests that the double bent state is approximately 2 kcal/mol more stable than the single bent state, which agrees well with a previously reported calculation. However, the populations of single bent and double bent states in the MD simulation are 58% and 26%, respectively, suggesting that each single bent state is more favorable when a full polymer chain is considered. The interplay of the two intramolecular hydrogen bonds in PA2F may explain why it is amorphous: the three energetically comparable states may limit the likelihood that one configuration can dominate and establish a regular crystalline order. We observe that studies on other furan-based polyamides not based on FDCA are more likely to report a \( T_m \) if the repeat unit contains an equal number of amide protons and furan oxygens (Table S4).

Figure 5. Computational analysis of amide−aromatic dihedral angles. Plots show DFT-computed energies of model compounds and MD-computed probabilities vs indicated dihedral angles for (a) PAMF; (b) PAMB; and (c) PA2F. For PA2F, the plots represent 1D slices of the 2D dihedral analysis. See text and Supporting Information for additional details.
SAPs are often produced as copolymers between semi-aromatic polyamides and aliphatic polyamides so that the thermal and mechanical properties of the material can be tuned for optimal performance. AMF was therefore copolymerized via SSP with aminocaproic acid (A6) to produce copolymers of PAMF and nylon 6 (PAMF/PA6). One-dimensional and 2D NMR characterizations of the resulting materials are consistent with the formation of statistical copolymers (Figures S38, S39). The \( T_g \) and \( T_m \) values determined by DSC were compared to commercial SAPs, FDCA-based SAPs, and SAPs based on other furanic monomers (Figure 6). Copolymerization of PAMF with up to 50% PA6 allows for the tuning of \( T_g \) and \( T_m \) between 113–145 °C and 266–315 °C, respectively, which well matched with the properties of existing materials (Figure S40). Of the 134 commercial SAP datasheets collected for this study, only 2 reported a melting temperature below 250 °C (Table S5). A few studies have reported semicrystalline FDCA-based SAPs and SAPs based on other furan monomers, but to the best of our knowledge, PAMF is the only furanic SAP with a \( T_m \) value within the range of most commercial SAPs (Figure 6b).

High-performance polyamides are promising candidates for recycling as they are of high value and are only used in specialized products. Mechanical recycling is the most common and economical method of recycling to date; however, mechanical recycling can degrade the thermal and mechanical performance of materials over the course of recycling. Chemical recycling allows for the depolymerization of a polymer into monomer building blocks that can subsequently be re polymerized to a polymer of equal caliber. Polyamides are known to be chemically recyclable by numerous methods. After investigating several hydrolysis-based depolymerization methods, base-catalyzed hydrolysis was selected as a promising method for chemical recycling of PAMF (Table S6). In minimal amounts of 1 M NaOH at elevated temperatures, PAMF can be depolymerized back to AMF monomers, with yields up to 85% as determined by NMR (Figure 7). At the isoelectric point (\( pH = 5.7 \)), AMF slowly precipitates out of solution, which provides an opportunity for chemical recycling without solution-based separation methods. After the hydrolysis of PAMF on a 100 mg scale, the reaction mixture was titrated to the isoelectric point and allowed to stand for 24 h, at which point pure AMF precipitated and was collected with an isolated yield of 62%. The recycled AMF was found to have purity comparable to that of virgin AMF by NMR.

## CONCLUSIONS

To advance a more sustainable polymer economy, novel materials derived from renewable sources need to have properties comparable or superior to that of existing materials. Biobased polymers have not reached substantial adoption because of property deficiencies and high cost. This report describes the synthesis and characterization of a novel polyamide PAMF that is synthesized from inexpensive, renewable feedstocks (e.g., lignocellulose and CO\(_2\)), has thermal phase properties comparable to that of commercial materials (\( T_g = 145 \) °C, \( T_m = 315 \) °C), and can be chemically...
recycled. PAMF is one example of how exploring underutilized chemical structures from biomass feedstocks can lead to polymers with exceptional properties.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c11806.

Experimental procedures, instrumentation details, additional structural characterization (13C NMR, COSY NMR, HSQC NMR, HMBC NMR, and MALDI), thermal analysis (DSC and TGA), GPC traces, reaction optimization data, simulation details, force field parameters, and miscellaneous data (PDF)

**Accession Codes**
CCDC 2217815 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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**Notes**
The authors declare no competing financial interest.

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