ABSTRACT

Efforts towards developing biobased chemicals primarily focus on generating molecules chemically analogous to those derived from petroleum. However, the compositional uniqueness of biomass can also be leveraged to reinvigorate the chemical industry with novel multifunctional molecules. We demonstrate the value and potential of these new compounds in the case of Nylon-6,6, a commodity polyamide that suffers from poor flame resistance. The conventional route to inhibit flammability involves blending the polymer with additives, an approach that comes with significant trade-offs on the mechanical properties of the final product compared to the parent polyamide. Herein, we address this limitation through the synthesis of a novel multifunctional
comonomer derived from renewably sourced \textit{trans}-3-hexenedioic acid (t3HDA). t3HDA was subjected to a one-pot isomerization and functionalization strategy where the double bond migrates to render this molecule active for phospha-Michael-addition (MA) with 9,10-Dihydro-9-Oxa-10-Phosphaphenanthrene-10-Oxide (DOPO), a prominent halogen-free flame-retardant (FR). This monomer was introduced in the polyamide’s backbone through copolymerization and the obtained polymer was compared to physical mixtures containing proportionate amounts of DOPO and Nylon-6,6. Thermal and mechanical properties of the blends and the FR-grafted polymers were characterized through a suite of techniques that revealed superior crystallinity, thermal, and mechanical properties for the DOPO-tethered bio-advantaged polyamides relative to blends with comparable flame retardance. The synthesis strategy presented herein can be extended for a variety of functional groups for property-modified bio-advantaged polymers.

KEYWORDS: polyamide, flame-retardant, multifunctional chemical, biobased molecules, Michael addition
INTRODUCTION

Synthetic polymers are ubiquitous to society and serve as the basis of countless advances in the fields of medicine, manufacturing, automotive, and consumer products. Monomers for most commodity polymers are derived from fossil-based carbon feedstock. However, utilization of biomass as a renewable alternative has been gaining prominence due to environmental concerns and growing consumer awareness. Efforts towards utilizing biomass have so far focused on generating chemically analogous replacements for petrochemicals using a bio-feedstock.\textsuperscript{1–3} However, the unique composition of biomass, for instance, the high oxygen content of its building blocks and their distinct stereochemistry, offers opportunities to generate novel chemicals and materials previously unattainable through petroleum-based feedstock.\textsuperscript{4,5}

Biologically-derived platform intermediates that give access to both direct replacements and novel molecules were recently identified through reaction network analysis and generation.\textsuperscript{6–9} The versatility of these bioprivileged compounds allows for their utilization as a platform for the production of bio-derived commodity chemicals while derisking production of new performance-advantaged molecules. Fermentation-derived muconic acid has received increasing attention due to its bioprivileged nature.\textsuperscript{8,10} This platform molecule can be obtained from glucose and lignin derivatives using metabolically-engineered bacteria (\textit{E. coli} and \textit{P. putida} KT2440) or yeast (\textit{S. cerevisiae}).\textsuperscript{11–17} Previous work has demonstrated the diversification of muconic acid to commodity chemicals such as adipic acid,\textsuperscript{11,13,16,18–21} hexamethylene diamine,\textsuperscript{22} \textit{ε}-caprolactam,\textsuperscript{23,24} and terephthalic acid.\textsuperscript{25–27} Muconic acid-derivatives have additionally been gaining prominence for the production of performance advantaged fiber-reinforced polyesters\textsuperscript{28–30} and polyamides.\textsuperscript{26,6}

The present work is based on the hypothesis that novel monomers derived from muconic acid could be molecularly engineered to become multifunctional, offering more than one target
property with a single chemical. This approach could enable the chemical industry to overcome the drawbacks and tradeoffs usually associated with the utilization of additives in polymer manufacturing. For instance, flame retardant additives are typically blended with polymers to lower their flammability and, therefore, broaden the range of their applications while lowering the risks of personal and property damage in the case of a fire. While vital, these flame retardants act as plasticizers and lower the mechanical properties of the final product compared to the parent polymer. Here, we explored the potential of \textit{trans}-3-hexenedioic acid (t3HDA), a C6 monounsaturated diacid that is stereoselectively produced by electrochemical hydrogenation of muconic acid.\textsuperscript{31} We employed the carbon-carbon unsaturation in t3HDA as a tethering point to generate flame-inhibiting monomers that imparted improved mechanical properties in Nylon-6,6 (PA66). PA66 provided an attractive candidate due to its application as a versatile engineering thermoplastic. It has excellent mechanical properties and high thermal stability due to greater hydrogen bonding between adjacent chains.\textsuperscript{32,33} As a result, PA66 finds applications in a wide range of industries such as automotives, electronics, films and coatings. Despite its advantages, PA66 suffers from poor flame performance due to its hydrocarbon backbone, giving it an oxygen index value ranging from 21-23\% \textsuperscript{34} and UL 94 rating of V-2.\textsuperscript{32} The current approach for improving flame performance includes addition of glass and other chemical modifiers in these polyamides to achieve an improved V-0 rating.\textsuperscript{32,35–37} However, other polymer properties are considerably diminished due to the modifiers and there is potential leaching of chemical additives at high temperatures.

The flame retardant (FR) candidate that was chosen for this study is 9,10-Dihydro-9-Oxa-10-Phosphaphenanthrene-10-Oxide (DOPO), a phosphorus-based flame retardant that has been extensively studied for its superior flame-inhibiting characteristics. DOPO exhibits high thermal
stability and improved environmental compliance compared to traditionally used brominated FRs. For the synthesis of a DOPO tethered diacid, dimethyl-trans-3-hexenedioate (dm3HD) underwent a base-catalyzed one-pot isomerization and functionalization through Michael-addition (MA). The isomerization of dm3HD to dimethyl-trans-2-hexenedioate (dm2HD) rendered the molecule active towards MA, consequently allowing DOPO to form a Michael-adduct. The resulting monomer was incorporated into the standard PA66 backbone through copolymerization with adipic acid and hexamethylenediamine. To compare the use of the bio-derived monomer over commercially used FR-blends, a physical mixture between DOPO and PA66 was prepared and characterized. DOPO grafted to the polymer backbone showed a 20% improvement in crystallinity, an insignificant decrease in mechanical properties, and ~8% improvement in flame-inhibition with respect to FR-blended polymers. Overall, this study highlights the potential of using novel bio-derived monomers for performance-advantaged polymers.

EXPERIMENTAL SECTION

**Materials:** Dimethyl-trans-3-hexenedioate (dm3HD), 9,10-Dihydro-9-Oxa-10-Phosphaphenanthrene-10-Oxide (DOPO), and hexamethylene diamine (HMDA) were purchased from TCI America. Dimethyl formamide (DMF), ethyl acetate, methanol, and tetrahydrofuran (THF) were supplied by Fisher Scientific. Triethylamine (TEA), lithium hydroxide (LiOH), deuterium oxide (D2O), trifluoroacetic anhydride (TFAA), and adipic acid (AA) were procured from Sigma-Aldrich. Additionally, nitrogen gas was purchased from Airgas, deuterated chloroform (CDCl3) and dimethyl sulfoxide-d6 (DMSO-d6) from Cambridge isotopes, and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) from Oakwood Chemical.
**Monomer Synthesis and Purification:** A one-pot isomerization, Michael addition, and de-esterification was carried out to synthesize the biobased comonomer used in this study. $\text{dm}_3\text{HD}$ (15 ml) and 1.5 mol equivalent of DOPO (31.07 g) were added to a round bottom flask equipped with a condenser. 20 ml of TEA and 20 ml of DMF served the dual role of solvent and catalyst for isomerization of $\text{dm}_3\text{HD}$ to $\text{dm}_2\text{HD}$ and its subsequent Michael addition. The reaction was carried out at 85°C for 4 days (~96 h) under static nitrogen with a stirring rate of 350 rpm. The reaction mixture was analyzed daily by gas chromatography/mass spectrometry (GC/MS) until complete consumption of $\text{dm}_3\text{HD}$ was observed upon which the reaction was stopped.

At this point, the dimethyl ester groups were converted to the dicarboxylic acid through base-catalyzed hydrolysis. 4 molar eq. lithium hydroxide in a 5:1 (v/v) water:methanol mixture was added to the original reaction vessel and reacted for 24 h. Separation of the desired product (DOPO-HDA) was carried out by washing the aqueous layer multiple times with ethyl acetate to remove unreacted DOPO and organic solvents. Finally, DOPO-HDA was precipitated in the aqueous layer through the addition of 2 M HCl until the reaction mixture reached pH 1. DOPO-HDA was extracted using ethyl acetate and the solvent was evaporated to recover the final product. The overall yield after synthesis and purification was 79.9 % measured through $^1\text{HNMR}$.

**Polymerization:** Conventional Nylon-6,6 salt was prepared by dissolving equimolar amounts of AA and HMDA in methanol till complete dissolution. The two solutions were mixed and reacted for 1 h at 40 °C. The precipitated salt was recovered through filtration and was dried overnight in a fume hood. DOPO-functionalized Nylon-6,6 was obtained following a similar procedure. Due to the low solubility of DOPO-HDA in methanol, the salt for this diacid was prepared separately using THF as solvent. Prior to polymerization, the two salts were combined in desired ratios and mixed with 60 wt% DI water to improve mixing. Samples were polymerized in a pressurized
microreactor (Parr 4900) equipped with a heating jacket. The temperature was monitored through an external thermocouple. To ensure an inert environment during polymerization, the reactor was purged with nitrogen five times and finally pressurized to 150 psig. In the initial stage of the polymerization, the reactor was held at an external set point of 265 °C for 2 h. At the end of this stage, nitrogen and water were vented out. Subsequently, the temperature was increased to 300 °C and held there for 3 h. The mixture was stirred at 400 rpm during the entire polymerization process.

Monomer and Polymer Characterizations: $^1$H NMR, $^{13}$C NMR, and $^{31}$P NMR spectra were collected with either a Bruker AVIII600 or Bruker NEO 400 spectrometer. Results were analyzed with MestReNova software. About 30-50 mg of monomer and salt samples were dissolved in DMSO-d$_6$ and D$_2$O, respectively. For polyamides, approximately 50 mg of sample were dissolved in a 3:2 (v/v) mixture of CDCl$_3$ and TFAA. GC/MS was carried out on an Agilent Technologies Model 6890 equipped with a DB-1 column. 1 μL of sample solution was injected with a 3.5 min solvent delay. The temperature was held at 50 °C for 0.2 min, ramped at 12.5 °C/min to 250 °C, and finally ramped at 25 °C/min to 340 °C. Analysis of the MS results was done through AMDIS software (NIST).

Gel Permeation Chromatography: EcoSEC gel permeation chromatography (GPC) system was used to measure polymer molecular weight distributions. The GPC system was equipped with UV and refractive index detectors and consisted of a Tosoh TSKgel SuperH6000 column in series with two Agilent PL HFIP gel columns. Approximately 5 mg polyamide samples were dissolved in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and filtered through a 0.45 μm PTFE filter. Sample aggregation and ionic interactions were suppressed by the addition of sodium trifluoroacetate at a concentration of 0.02 mol/L HFIP (1.7 g/kg HFIP). A 10 μL sample volume was injected and
analyzed at 45 °C under a 0.3 mL/min flow rate. Mₙ and Mₘ of samples were measured using polymethyl methacrylate (PMMA) standards.

**Dynamic Scanning Calorimetry (DSC):** Thermal characterizations were conducted using a TA DSC Q2500 instrument. Specimens measuring under 5 mg were sealed in hermetic aluminum pans and were cycled thrice under nitrogen over a range of 30 °C to 300 °C with a ramp rate of 10 °C/min. Results were calculated using Trios software from the third cycle to minimize the influence of the polymer’s thermal history. ΔHₘ was calculated by integrating the melting peak, while Tₘ and Tₑ were calculated at the peak of the melting and crystallization events, respectively. The degree of crystallinity χₖ_DSC was determined using the following equation:

\[ \chi_{c,DSC} = \frac{\Delta H_m}{\Delta H_{f,crystal}} \times 100\% \]

Where \( \Delta H_{f,crystal} = 57.8 \text{ kJ/mol} \) and refers to the enthalpy of fusion of a single crystal of Nylon-6,6.

**Thermogravimetric Analysis (TGA):** TGA measurements were performed in triplicates on a Netzsch STA449 F1 instrument using Proteus software for data analysis. Specimens measuring 5-10 mg were placed in alumina pans. A 5-minute isothermal stage was followed by a 10 °C/min ramp to 800 °C under 20 ml/min nitrogen flow. The decomposition temperature, Tₐ₁₀, was calculated at 10 % mass loss and the residual char was measured at 500 °C. Differential thermogravimetric (DTG) curves were calculated using the first derivative of the TGA data and were plotted as the rate of mass loss versus temperature.

**Wide-Angle X-ray Scattering (WAXS):** WAXS patterns were collected for annealed samples using a XENOCS Xeuss 2.0 SWAXS system equipped with Dectris Pilatus3 R 1M detector.
calibrated using a silver behenate standard. The WAXS measurements were performed under vacuum with the samples fixed directly on the holder. Monochromatized light ($\lambda = 1.54 \text{ Å}$) from Cu Kα radiation was used over an acquisition period of 600 s. Results were analyzed with Foxtrot 3.3.4 (SOLEIL Synchrotron, France) for absolute intensity correction of the background signal. The degree of crystallinity ($\chi_{c,WAXS}$) was calculated through the following equation based on the ratio of the area of the crystalline fraction ($A_c$) to the total area ($A_a + A_c$) under the WAXS curve.

$$\chi_{c,WAXS} = \frac{A_c}{A_c + A_a} \times 100\%$$

Microscale Combustion Calorimetry (MCC): A micro-combustion calorimeter (MCC) was used to measure the heat of combustion of gases evolved during the controlled pyrolysis of the polyamides. The samples were analyzed under nitrogen using a 1 °C/s heating rate from 200 to 700 °C using method A of ASTM D7309 (pyrolysis under nitrogen). The measurements were performed in triplicate to evaluate their reproducibility. The MCC provided the heat release rate as a function of temperature, where total heat released (THR) was calculated as the area under the curve. Char yield was obtained by measuring the difference in sample mass before and after pyrolysis. Fire growth capacity (FGC) was calculated using ASTM D7309 to provide insights into the potential for the material to ignite and grow in fire intensity once ignited.

Dynamic Mechanical Analysis (DMA): Polyamide samples in the ISO527-2-1BB geometry were prepared by injection molding under an argon atmosphere using a HAAKE MiniJet Pro. Samples were subsequently annealed under inert conditions at 150 °C for 24 h. Torsional DMA was carried out for annealed samples using a TA Ares G2 instrument. Specimens were heated using a 5 °C/min ramp in the linear viscoelastic regime from 0 °C to 100 °C with an angular frequency of $\omega = 10$
Analysis was performed using Trios software. The storage (E') and loss (E'') moduli were measured at 0 °C. The tan (δ) curve was calculated as a ratio between E’ and E’’. T_g values are reported at the peak of the tan (δ).

**Tensile Tests:** Tensile properties were measured using an Instron Universal Testing Machine (3369 series) with a 10 mm/min extension rate. Triplicates were tested with ISO527-2-1BB geometry and averages were reported.

**RESULTS AND DISCUSSION**

**Synthesis of FR-grafted monomer:**

A one-pot base-catalyzed isomerization and Michael-addition (MA) was carried out to graft flame-retardant (DOPO) onto dm3HD (Scheme 1). Equal volumes of TEA and DMF were used to shift the double bond in dm3HD from the β-γ to α-β position, rendering it active for MA. Subsequently, DOPO underwent a nucleophilic 1,4 phospha-MA onto dm2HD. This synthesis was performed on the diester (dm3HD) over the diacid (t3HDA) as methyl groups prevented ring-closing and formation of lactone by-products under basic conditions. Additionally, t3HDA exhibited limited reactivity towards MA compared to dm3HD. The selective formation of the desired phospha-MA product was confirmed through GC/MS (Figure S1) and 1H NMR (Figure 1), which showed DOPO-HDA as the sole product. Peaks corresponding to DOPO were observed in the aromatic range of 7 - 8.5 ppm, whereas the alkene peak of dm3HD (5.6 ppm) disappeared completely. Recovery to the final product (DOPO-HDA) was achieved through base-catalyzed de-esterification (overall yield: 79.9 %) and characterized by 1H NMR (Figure 1). DOPO-HDA was further utilized for copolymerization and insertion in the Nylon-6,6 backbone.
Scheme 1. Base-catalyzed isomerization of dmt3HD to dmt2HD (Michael acceptor) and its subsequent Michael-addition with DOPO (Michael donor). The diester was hydrolyzed back to the final diacid (DOPO-HDA) prior to polymerization.

Figure 1. $^1$H NMR spectra of the starting diester (dmt3HD) (a), DOPO-grafted diester (b), and desired product (DOPO-HDA) in CDCl$_3$ (c)
Polymerization and characterization of monomer incorporation

Conventional Nylon-6,6 salt was prepared by precipitating HMDA and AA in MeOH. Next, DOPO-nylon blends were prepared by polymerizing the Nylon-6,6 salt in the presence of a desired quantity of DOPO (5 or 10 wt%). This range was selected recognizing the potential adverse impact of incorporating large quantities of a bulky pendant group on the resulting mechanical properties of the polymer. Post-polymerization, these FR-blended polyamides were referred to as PA66-5B and PA66-10B for the samples containing 5 and 10 wt% DOPO, respectively (Scheme 2).

Similarly, a zwitterionic salt was prepared by independently precipitating HMDA and DOPO-HDA in THF (Scheme 2, Figure S2). The novel FR-salt was then mixed with the standard Nylon-6,6 salt in the desired ratios to emulate the DOPO loading in the blends. The polyamides wherein DOPO was tethered to the backbone are referred to as PA66-5F and PA66-10F in this study.

Scheme 2. Polymerization of 5 and 10 wt% DOPO physically blended with PA66 (left) versus equivalent quantities of DOPO grafted onto the PA66 backbone (right).
Table 1 compares the theoretical and actual incorporation of DOPO in the polyamide as determined by $^1$H-NMR (Figure S3). Actual DOPO incorporation was calculated by integrating the aromatic peaks belonging to DOPO with respect to the HMDA peak at 3.7 ppm. The calculated values confirmed that the concentration of DOPO in the blends and functionalized samples closely followed the expected values (Table 1) and, therefore, the flame retardant properties of both sample series can be directly compared (vide infra). Additional confirmation for the survival of the grafted DOPO post polymerization was provided by $^{31}$P NMR (Figure S4) and the $^1$H-$^{31}$P heteronuclear multiple bond correlation (HMBC) spectra presented in Figure 2. PA66-10B exhibited one phosphorus peak showing cross-peaks only in the aromatic region, which substantiated that DOPO remains as a free molecule in the polymer matrix. In contrast, two phosphorus peaks were observed for PA66-10F (Figure 2b). The sharper peak (44 ppm) was associated with the tethered DOPO, established by cross-peaks appearing in both the aromatic and aliphatic regions. Ratio between the two phosphorus peak integrations showed that ~25% DOPO detached from the polymeric backbone and, therefore, is present as a free molecule such as with the blends. However, as a majority of the DOPO remained attached to the polyamide backbone, differences in properties between blended and functionalized samples are still driven by the tethered groups.
Molecular weights of polymer series

The GPC chromatograms for the polyamide series are shown in Figure S5. The corresponding molecular weights, calculated with respect to PMMA standards, are displayed in Table 1. Under similar polymerization conditions, neat Nylon-6,6 exhibited considerably higher molecular weights than all the DOPO polyamides. This demonstrates that both free and tethered DOPO had suppressive impacts on final MW of polymers. However, the extent of DOPO loading (5 wt% versus 10 wt%) had minimal influence on M_n as PA66-5B/10B showed comparable weights.

Achieving comparable molecular weights is highly relevant while commenting on the effect of DOPO (grafted/blended) on the thermal and mechanical performance of the polymers. Therefore, PA66 was polymerized for a shorter reaction time to achieve similar MW as the other samples in the study. This sample (PA66-low MW) is used hereafter for all base-case comparisons.
Table 1. Comparison of theoretical and actual DOPO incorporation into polyamide through 1H-NMR and molecular weights of polymer series.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Expected mol% incorporation (%)</th>
<th>Actual mol% incorporation (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Mn&lt;sup&gt;b&lt;/sup&gt; (kDa)</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA66-high MW</td>
<td>-</td>
<td>-</td>
<td>119.2</td>
<td>1.9</td>
</tr>
<tr>
<td>PA66-low MW</td>
<td>-</td>
<td>-</td>
<td>48.8</td>
<td>1.8</td>
</tr>
<tr>
<td>PA66-5B</td>
<td>4.8</td>
<td>4.9</td>
<td>51.8</td>
<td>2.5</td>
</tr>
<tr>
<td>PA66-5F</td>
<td>4.8</td>
<td>5.0</td>
<td>31.42</td>
<td>2.0</td>
</tr>
<tr>
<td>PA66-10B</td>
<td>9.6</td>
<td>8.7</td>
<td>52.8</td>
<td>2.7</td>
</tr>
<tr>
<td>PA66-10F</td>
<td>9.6</td>
<td>11.0</td>
<td>23.2</td>
<td>2.0</td>
</tr>
</tbody>
</table>

<sup>a</sup>Incorporation of DOPO was calculated through <sup>1</sup>H NMR analysis of the polymers  
<sup>b</sup>Mn: Number-average molecular weight of polymers were calculated with respect to PMMA standards

Thermal and crystal properties

The effect of blended and tethered DOPO on thermal properties and crystallinity was investigated through DSC, WAXS, and TGA (Figures 3-5, Table 2). PA66 exhibited the highest melting temperature ($T_m = 260.5 \degree C$) and degree of crystallinity ($\chi_{C,DSC} = 26 \%$) based on DSC (Figure 3a). DOPO incorporation, whether as a blend or a pendant group, inhibited crystal formation and led to a decrease in $T_m$ and $\chi_{C,DSC}$. While PA66-5B/5F exhibited similar $\Delta H_m$ and $T_m$, a prominent difference was observed with the higher DOPO loaded samples. PA66-10B showed the lowest $T_m$ ($239.7 \degree C$) and $\chi_{C,DSC}$ (15 %). In contrast, the tethering of DOPO to the PA66 backbone in the 10F sample showed superior crystallinity of over 18 %.
Table 2. Thermal properties of the polyamides with different loadings of DOPO as blends or tethered into the backbone.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tₘ (°C)</th>
<th>ΔHₘ (J/g)</th>
<th>χₖ_DSC (%)</th>
<th>Tₑ (°C)</th>
<th>χₖ_WAXS (%)</th>
<th>Char500°C (%)</th>
<th>Tₙ₁₀ (°C)</th>
<th>Peak 1(°C)</th>
<th>Peak 2(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA66</td>
<td>260.5</td>
<td>66.4</td>
<td>26.0</td>
<td>226.7</td>
<td>42.2</td>
<td>3.04 ± 1.4</td>
<td></td>
<td>487.2</td>
<td>448.4 ± 3.6</td>
</tr>
<tr>
<td>PA66-5B</td>
<td>248.8</td>
<td>50.8</td>
<td>19.9</td>
<td>208.8</td>
<td>35.0</td>
<td>4.05 ± 0.6</td>
<td>330.7</td>
<td>391.2 ± 4.0</td>
<td>466.2 ± 1.55</td>
</tr>
<tr>
<td>PA66-5F</td>
<td>247.9</td>
<td>49.5</td>
<td>19.4</td>
<td>211.2</td>
<td>38.8</td>
<td>4.04 ± 0.3</td>
<td>325.0</td>
<td>393.5 ± 3.5</td>
<td>462.3 ± 3.1</td>
</tr>
<tr>
<td>PA66-10B</td>
<td>239.7</td>
<td>38.2</td>
<td>15.0</td>
<td>193.3</td>
<td>31.8</td>
<td>3.96 ± 0.8</td>
<td>327.5</td>
<td>377.2 ± 5.2</td>
<td>458.3 ± 7.8</td>
</tr>
<tr>
<td>PA66-10F</td>
<td>242.9</td>
<td>46.8</td>
<td>18.3</td>
<td>211.0</td>
<td>38.2</td>
<td>4.57 ± 0.2</td>
<td>302.7</td>
<td>384.4 ± 2.31</td>
<td>463.5 ± 0.25</td>
</tr>
</tbody>
</table>

aTₘ: melting temperature; ΔHₘ: enthalpy of melting; Tₑ: crystallization temperature; χₖ_DSC: percent crystallinity (DSC). bχₖ_WAXS: percent crystallinity from WAXS (annealed). cChar500 °C: residual mass at 500 °C; Tₙ₁₀, decomposition temperature at 10% mass loss under N₂ from TGA. dDTG peaks: calculated from the derivative of TGA curves.

To evaluate the crystalline structure, room temperature WAXS was performed on polymer samples annealed for 24 h (Figure 3b). The semi-crystalline nature of these polyamides was established by the sharp peaks representing crystalline segments and the characteristic broad halo corresponding to the amorphous regions. The percent crystallinity (χₖ_WAXS) is reported as the ratio of the areas under the peaks normalized over the total area. PA66 exhibited two characteristic peaks at approximately 20° and 24°, corresponding to the (100) and (010)/(110) doublet of the α-phase. PA66 possesses a triclinic structure, in which the (100) peak represents intrasheet scattering caused by adjacent polymer chains in a sheet and the (010)/(110) peak corresponds to the intersheet scattering between polymer sheets. Following the results from DSC, it was expected that both
modes of DOPO incorporation would retard crystallization. While that effect was observed, the difference in %crystallinity between blends and functionalized samples was amplified post polymer annealing. In the case of the blended specimens at 5 and 10 wt% loadings (PA66-5/10B), the polymers showed a decrease in crystallinity of 31 % and 37 % respectively compared to the parent Nylon-6,6. In contrast, the functionalized samples PA66-5/10F showed less than a 25 % reduction in crystallinity for both loadings. In both cases, expulsion of free DOPO and functionalized DOPO segments to the amorphous phase was anticipated. However, annealing for sufficient time above the glass-transition temperature allowed PA66-5/10F to have higher thermodynamic preference for crystallization compared to the blends (Figure 4).

![Figure 3. DSC thermograms for the flame-retardant polyamide series with respect to PA66 showing (a) melting/crystallization event and (b) room temperature wide-angle X-ray scattering.](https://doi.org/10.26434/chemrxiv-2023-nnww9 ORCID: https://orcid.org/0000-0001-9035-634X Content not peer-reviewed by ChemRxiv. License: CC BY-NC-ND 4.0)
Figure 4. Crystal formation in the presence of free and tethered DOPO. Functionalized DOPO attached to the polymer backbone shows higher crystallinity than its blended counterpart.

Thermogravimetric analysis (TGA) was performed on PA66 and FR polyamides to investigate the influence of DOPO on thermal decomposition and flame inhibition (Figure 5a). The DTG curve (1st derivative of the TGA curve) shows thermal decomposition events more prominently (Figure 5b). PA66 showed one decomposition peak consistent with the literature, whereas polymers containing DOPO exhibited two decomposition events. The first stage corresponds to the evolution of DOPO out of the polymer matrix, which is corroborated by the boiling point of DOPO reported at ~380 °C. Tethering DOPO to the polymer backbone allowed it to evolve marginally later compared to the DOPO blended samples. This is demonstrated in Table 2 where PA66-10B showed its 1st decomposition peak 8 °C lower than its tethered counterpart (PA66-10F). From Figure 5a and Table 2, char yield for all samples containing DOPO increased compared to PA66. Phosphorus is known to promote char formation through phosphoric acid derivatives, which in turn may act as cross-linkers to decomposed polymeric byproducts. The char layer subsequently acts as a mass and heat transfer barrier to slow flame spread. Char yield was seen to be the highest for the 10F sample, which could be the result of tethering DOPO to the polyamide backbone and allowing it to interact with the solid phase. Therefore, tethering FR to
polymeric backbone reduced volatilization of the FR and enabled it to increase interaction with the condensed phase.

**Figure 5.** (a) TGA thermograms and (b) DTG curves showing a single step decomposition for PA66 and a two-stage decomposition of FR polyamides. Samples were run in triplicates under nitrogen with a 10 °C/min ramp rate.

**Flame-inhibition analysis**

MCC was used to measure the heat release rate (HRR) versus temperature to gauge flame performance for the polyamide series (Figure 6). Compared to the PA66 control sample, all DOPO-containing materials showed improvements in terms of heat release and char yield (Table S1, Figure S6). In contrast to PA66, the FR-samples showed two peaks of heat release, which indicates that DOPO chemistry is changing the thermal decomposition characteristics of the polyamides. Fire growth capacity (FGC) is a parameter calculated through ASTM D7309, which is dependent on chemical structure and gives insights into ignition and flame-growth once ignited.²⁹ The FGC of PA66 decreased from 500 J/g-K to 327.5 J/g-K for PA66-10B and 302.6 J/g-K for PA66-10F. Additionally, a large reduction in peak HRR was observed for the PA66-10B
and PA66-10F showing that higher loadings of DOPO enhance flame inhibition (Table S1). Overall, it can be seen that DOPO enhanced flame-retardance compared to neat PA66, however its mode of incorporation affected polymer performance minimally. A more drastic difference might be expected between blends and tethered FRs if lower boiling point modifying chemicals are used.

![Figure 6](Image)

**Figure 6.** Comparison of combustion characteristic of polymers in this study. (a) Total HR was shown to decrease with DOPO containing samples. PA66-F samples showed a lower FGC compared to PA66-B specimens. (b) HRR versus temperature for triplicates.

**Rheology and mechanical properties**

Torsional dynamic mechanical analysis (DMA) was conducted to understand the viscoelastic response of the annealed polyamides to a known deformation as a function of temperature (Figure 7). Values for the storage modulus (E’), loss modulus (E’’), and tan δ are summarized in Table 3. E’ and E’’ were reported at the glassy plateau of 0 °C. Tan δ is calculated through the ratio between E’ and E’’, where δ is the phase angle between the stress and the strain. In this study, the glass-transition temperature of the polymers (T_g) was located using the maxima
of tan δ. $T_g$ is a key polymer property and is characterized as the temperature at which long-range motion in the amorphous domains ceases as a polymer melt is cooled. Over this transition, dramatic changes in properties are observed as the polymer shifts from a rubbery to glassy state.

PA66 showed the lowest $E'$, followed by PA66-5B/F. A slight reduction in $E'$ was also observed for the 10F sample relative to 10B, potentially due to their reduced $M_n$. However, a significant increase in $T_g$ (~10 °C) was observed between PA66-10B and 10F. In the blends, free DOPO molecules act as plasticizers in the amorphous domains of the polymer. This enables chain mobility at lower temperatures, which is revealed by the suppressed $T_g$ exhibited by the blends. In contrast, when DOPO is tethered to the polyamide backbone, chain mobility and diffusivity are reduced due to the anchored pendant group. This effect is observed through the consistently increased $T_g$ in both functionalized samples (5F/10F) compared to their corresponding blends.

**Table 3.** Viscoelastic properties of polyamides measured through torsional DMA.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E'$ (MPa)</th>
<th>$E''$ (MPa)</th>
<th>$T_{g, DMA}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA66</td>
<td>1860.6</td>
<td>9.5</td>
<td>71.6</td>
</tr>
<tr>
<td>PA66-5B</td>
<td>1940.7</td>
<td>6.2</td>
<td>79.9</td>
</tr>
<tr>
<td>PA66-5F</td>
<td>1941.0</td>
<td>9.9</td>
<td>83.1</td>
</tr>
<tr>
<td>PA66-10B</td>
<td>2403.7</td>
<td>3.9</td>
<td>80.8</td>
</tr>
<tr>
<td>PA66-10F</td>
<td>2315.7</td>
<td>6.9</td>
<td>90.3</td>
</tr>
</tbody>
</table>
Mechanical properties of the samples were assessed using tensile tests that were run in triplicate (Table 4). Mechanical properties of polymers are related to the crystallinity and molecular weights of the samples. This is seen as the low MW PA66 was more brittle and demonstrated lower ultimate tensile stress (UTS) compared to its higher MW counterpart. At 5% loading, the functionalized sample (5F) showed a significantly higher UTS and Young’s modulus compared to both neat PA66 and PA66-5B. This can be explained due to the suppressed crystallization in the 5B sample compared to the 5F sample. This trend should have also been evident with the 10 wt% DOPO samples. However, the vastly different $M_n$, where 10B had over double the molecular weight of 10F, interfered with making a direct comparison. The 10F sample showed brittle failure before 10B along with suppressed values for Young’s modulus. Future work should focus on synthesizing a 10F sample through extended polymerization time to produce similar molecular weights as the 10B sample. Therefore, the reduced molecular weight of the 10F sample was expected to exhibit suppressed performance.

Figure 7. (a) Loss and (b) storage modulus of polyamide samples with different modes of DOPO incorporation.
Table 4. Mechanical properties of polymer specimens (triplicates) as determined through tensile testing

<table>
<thead>
<tr>
<th>Samples</th>
<th>UTS (MPa)</th>
<th>Toughness (MPa)</th>
<th>Young’s Modulus (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA66-high MW</td>
<td>113.52 ± 2.9</td>
<td>73.53±3.4</td>
<td>1.19E3±19</td>
<td>73.4±1.5</td>
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<tr>
<td>PA66-low MW</td>
<td>84.24 ±10.6</td>
<td>3.69±1.03</td>
<td>1.18E3±23</td>
<td>8.03±1.2</td>
</tr>
<tr>
<td>PA66-5B</td>
<td>88.95 ± 13.0</td>
<td>3.50±1.1</td>
<td>1.47E3±7</td>
<td>7.25±1.2</td>
</tr>
<tr>
<td>PA66-5F</td>
<td>128.66±6.4</td>
<td>9.97±3.9</td>
<td>1.47E3±58</td>
<td>12.7±2.8</td>
</tr>
<tr>
<td>PA66-10B</td>
<td>90.41 ± 4.5</td>
<td>3.39±0.42</td>
<td>1.56E3±45</td>
<td>7.02±0.5</td>
</tr>
<tr>
<td>PA66-10F</td>
<td>68.66 ± 24.9</td>
<td>2.15±1.17</td>
<td>1.46E3±222</td>
<td>5.5 ±1.3</td>
</tr>
</tbody>
</table>

CONCLUSION

Utilization of biobased molecules can be leveraged to give access to novel multifunctional monomers that are key towards producing performance-advantaged polymers. Demonstrated in this study is the potential of a multifunctional monomer produced using fermentation-derived t3HDA for flame-retardant applications. Currently, flame-retardance in polymers is primarily achieved through physical blending of prominent flame retardants with polymers. However, this approach can lead to leaching of the FRs that ultimately diminish flame-inhibiting performance but also detrimentally affect mechanical properties in the polymer caused by the disruption in crystal formation. To address these drawbacks, a novel diacid was prepared by tethering legacy FR molecule DOPO onto the unsaturation offered by t3HDA and copolymerized into a Nylon-6,6 backbone. For equivalent comparison, Nylon-6,6 was physically blended with DOPO and the impact of the two modes of DOPO incorporation on polymer properties was investigated. Tethering the FR group achieved improved flame retardance at higher loadings compared to FR blends. However, significant improvements in crystallinity were offered by DOPO-functionalized polyamides over the blends. $\chi_c$ was minimally affected compared to neat PA66 and its effect was observed through improved mechanical properties when molecular weights were comparable. As
the DOPO segments and free molecules were relegated to the amorphous regions, properties observed via DMA seemed to be affected compared to parent Nylon-6,6. $T_g$ and $E'$ were increased compared to the unmodified Nylon-6,6 due to the rigidity offered by the aromatic rings in DOPO. This study leverages bioadvantaged and bioprivileged concepts and uses t3HDA as a vehicle for inserting flame-retardance while minimally compromising on other key polymer properties. Extension of this chemistry would create new opportunities to investigate halogen-free nitrogen and phosphorus-based FRs that were previously not considered due their volatility as free molecules. Furthermore, the synthesis framework can be used to accelerate development of biopolymers by allowing selective alteration of polymer properties.

ACKNOWLEDGMENTS

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Figure S1. GC-MS for the one-pot isomerization and Michael-addition product after 96 hours of reaction time.
Figure S2. $^1$HNMR of salt in D$_2$O. The salt was prepared by precipitating the functionalized diacid with HMDA in THF.
**Figure S3.** $^1$HNMR of polymers shown in this study. Percent incorporation of DOPO was calculated through the integration of the aromatic region with respect to the HMDA peak at 3.7 ppm.
Figure S4. $^{31}$PNMR of polymers with 10 wt% DOPO incorporation.
Figure S5: GPC chromatograms for the polyamide series.
Figure S6. Char residues of the samples that underwent MCC. Images suggest that samples flowed before charring and flowed up to the edges of crucibles prior to being fully pyrolyzed.
Table S1. Heat release rate (HRR) and other MCC data for polyamides.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Char Yield (wt%)</th>
<th>FGC (J/g-k)</th>
<th>HRR Peak (s)</th>
<th>HRR Max Temp (°C)</th>
<th>Total HR (kJ/g)</th>
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<tbody>
<tr>
<td>PA66</td>
<td>1.45</td>
<td>487</td>
<td>560</td>
<td>478</td>
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<td>1.28</td>
<td>487</td>
<td>566</td>
<td>480</td>
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</tbody>
</table>

*aAn additional replicate was run for PA66-10B sample due to the scatter in heat release data*