Synthesis, Thermal Properties, and Rheological Characteristics of Indole-Based Aromatic Polyesters

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Supporting Information

ABSTRACT: Currently, there is an intensive development of bio-based aromatic building blocks to replace fossil-based terephthalates used for poly(ethylene terephthalate) production. Indole is a ubiquitous aromatic unit in nature, which has great potential as a bio-based feedstock for polymers or plastics. In this study, we describe the synthesis and characterization of new indole-based dicarboxylate monomers with only aromatic ester bonds, which can improve the thermal stability and glass-transition temperature ($T_g$) of the resulting polyesters. The new dicarboxylate monomers were polymerized with five aliphatic diols to yield 10 new polyesters with tunable chemical structures and physical properties. Particularly, the $T_g$ values of the obtained polyesters can be as high as 113 °C, as indicated by differential scanning calorimetry and dynamic mechanical analysis. The polyesters showed decent thermal stability and distinct flow transitions as revealed by thermogravimetric analysis and rheology measurements.

INTRODUCTION

Today, the production of plastics (polymers) is facing major challenges, which include, for example, the deployment of fossil resources, the rise of petrochemical prices, and the environmental issues associated with the polymer production. Therefore, there is a strong motivation from the society and industry to switch to sustainable bio-based feedstocks for the production of plastics. To date, the most successful development of bio-based plastics is Coca-Cola’s partially bio-based poly(ethylene terephthalate) (PET) (PlantBottle), which constitutes approximately 75% of all of the bioplastics on the market. Unfortunately, this bio-PET only contains ~30% mass originated from bio-based production (i.e., bio-based ethylene glycol), while the remaining ~70% mass was still based on the use of fossil-based terephthalic acid (TPA) or dimethyl terephthalate (DMT). The production of TPA or DMT from renewable starting materials has been an active research area, which has achieved lab-scale success. Other benzenoid aromatic monomers (e.g., dicarboxylates or monohydroxyxycarboxylates) have also been synthesized and used for the production of aromatic polyesters as a potential substitution for PET, and their raw materials include, for example, lignin-derived molecules, vanillic acid, resorcinol, and cinnamic acid. In the meantime, alternative nonbenzenoid aromatic building blocks have also received growing attention, among which furan derivatives have been intensively explored.

Furan structures exist widely in nature and can be produced via different biosynthetic pathways. Particularly, furan-dicarboxylic acid (FDCA) has been a popular research topic recently, because its derived polyester (e.g., poly(ethylene furanoate) or PEF) has comparable mechanical and even better barrier properties compared with PET. Other furan-based dicarboxylates and polyesters have also been reported in the literature. Unfortunately, the thermal instability of furan derivatives (e.g., FDCA, or precursors like S-hydroxymethylfurural, or S-hydroxymethyl-2-furoic acid) has caused undesirable degradation and coloration during the production and processing at high temperatures (>200 °C), which hinders the further development of furan-based polyesters. Recently, a novel procedure to prepare bottle-grade PEF was reported, using a three-step synthesis including polycondensation, oligomerization, and ring-opening polymerization. However, this procedure is complicated and its feasibility for the plastic industry remains to be explored.

Considering these challenges, it is time to consider other bio-based aromatics as “Plan B” for polyester production. Recently, indole has attracted our attention because it is a large aromatic unit that exists widely in nature and urban wastes. Indole is also a major byproduct in coal mining, petroleum, tobacco, and livestock farming industries and is widely used in pharmaceuticals, agrochemicals, and material sciences. Several bioproduction methods for indole are available, including thermocatalytic conversion and ammonization of biomass-derived furfural and furan, microalgae pyrolysis, yeast and bacteria fermentation, reduction of indigo that is derived from plants and microbial production, and direct conversion from bio-based ethylene glycol and aniline.
Surprisingly, little attention has been paid to the development of indole-based polyesters. In the literature, the use of indole structures has been limited to conducting polymers and microporous materials,53–56 polymers with indole pendant groups, polyethersulfones, and poly(N-arylene diindolylmethane).57–63 There was only one report in the 1980s describing bis-indole-containing polyesters without the characterization of properties.64 Recently, a new series of fully bio-based polyesters were synthesized and reported by our group using a new indole-based dicarboxylate monomer and five different aliphatic ester bonds (i.e., esters derived from aliphatic carboxylic acids, structure a, Figure 1), which are not present in PET. Such aliphatic ester bonds are expected to lower the thermal stability of the resulting polyesters. To achieve better thermal properties, indole-based polyesters without labile aliphatic ester bonds are of great interest. Herein, we report our recent synthesis and characterization of two indole-based dicarboxylate monomers with only aromatic ester bonds (i.e., ester bonds derived from aromatic acids) and their polymerization with five bio-based aliphatic diols to yield in total 10 indole-based polyesters. The thermal, mechanical, and rheological properties of the resulting polyesters were reported. According to our result, the absence of weak aliphatic ester bonds in the new series of polyesters clearly enhanced the thermal stability.

**RESULTS AND DISCUSSION**

**Polymer Synthesis.** Methyl indole-3-carboxylate (1) was employed as the starting material for monomer synthesis, which can be conveniently synthesized from sustainable raw materials, e.g., by a base-mediated carboxylation of indole, followed by transesterification with methanol.65 A possible synthetic route for 1 from biosourced raw materials is depicted in Figure S1, Supporting Information.Dicarboxylate monomers (3a, b) were synthesized by a simple SN2 reaction of commercially available methyl indole-3-carboxylate 1 and two different 1,6-dibromoalkanes (2a, b), respectively (Scheme 1). Purification of the crude products 3a, b by straightforward recrystallization from toluene afforded white crystals of monomers with >80% yields. Afterward, monomers 3a, b were polymerized with five potentially bio-based aliphatic diols (4a–e), according to a conventional bulk polycondensation protocol using dibutyltin(IV) oxide (DBTO) catalyst (1 mol %).65,67,68 The polymerization was performed in two stages. In the first stage (transesterification), an excess of diol (3 equiv of OH groups for 4c–e and 4 equiv of OH groups for 4a, b) was reacted with dicarboxylates (3a, b) at 180 °C under a slow nitrogen flow to remove the condensed methanol. Once the transesterification was completed (ca 3 h, according to 1H NMR analysis), a second stage (polycondensation) was carried out at 220 °C with a stronger N2 gas flow to completely remove the condensed diols. In the literature, the removal of the condensed diols was usually achieved under high vacuum conditions.69 However, when the vacuum condition was applied for our polymerizations, the obtained polymers always showed an intense red color, while our new protocol under a N2 gas flow provided white or colorless polymers (see examples in the Supporting Information, Figure S4a,b). The purification of the polymers was achieved by simple precipitation in methanol from their solutions. We noticed that 5bc and 5bd were only soluble in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) or mixtures of HFIP and chloroform but insoluble in other commonly used organic solvents like chloroform, dimethyl sulfoxide, dimethylformamide (DMF), dimethylacetamide, and tetrahydrofuran. The other polymers were all soluble in chloroform. It was also noted that the indole-based polyester solution in chloroform slowly developed pink coloration at room temperature after 5 days. A thin film of 5ad is shown in Figure S4c, which was prepared using

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**Scheme 1. Synthesis of Monomers 3ab and Polymerization of 5xy Biopolymesters**

![Scheme 1](image-url)
the solution of 5ad in chloroform that was stored at room temperature for 5 days. Polymer films that were prepared directly after the synthesis of the polymers were colorless and stable when being stored at room temperature.

The chemical structures of the monomers and polyesters were confirmed by their $^1$H NMR spectra. Figure 2 shows the $^1$H NMR spectra of the polymer series 5ay ($y = a$–e).

**Table 1. Summary of Molecular Weight, Thermal and Thermomechanical Analyses, as well as WLF Parameter of Biopolymesters 5xy**

| sample | $M_n$ (g/mol) | $M_w$ (g/mol) | PDI | $T_g$ ($^\circ$C) | $T_{1\%}$ | $T_{5\%}$ | $T_{\delta}$ | $C_1$ (K) | $C_2$ (K) | $C'_1$ (K) | $C'_2$ (K) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 5aa | 21 300 | 30 000 | 1.89 | 113 | 125 | 347 | 376 | 410 | 9.95 | 308.3 | 15.23 | 201.3 |
| 5ab | 11 500 | 20 400 | 1.77 | 94 | 104 | 347 | 375 | 419 | 4.80 | 205.9 | 13.00 | 79.5 |
| 5ac | 35 000 | 59 800 | 1.71 | 90 | 104 | 347 | 375 | 419 | 4.80 | 205.9 | 13.00 | 79.5 |
| 5ad | 21 300 | 42 100 | 1.98 | 83 | 96 | 335 | 361 | 394 | 4.28 | 198.3 | 13.85 | 61.3 |
| 5ae | 23 700 | 41 700 | 1.76 | 71 | 83 | 330 | 360 | 403 | 3.41 | 151.8 | 16.26 | 31.8 |
| 5ba | 14 900 | 26 800 | 1.80 | 100 | 112 | 320 | 353 | 390 | 3.41 | 151.8 | 16.26 | 31.8 |
| 5bb | 6 700 | 12 000 | 1.80 | 85 | 97 | 327 | 337 | 384 | 4.53 | 205.9 | 13.00 | 79.5 |
| 5bc | 33 500 | 60 300 | 1.80 | 87 | 97 | 330 | 365 | 403 | 4.53 | 205.9 | 13.00 | 79.5 |
| 5bd | 29 500 | 57 300 | 2.00 | 80 | 91 | 358 | 374 | 405 | 4.39 | 183.1 | 14.83 | 43.1 |
| 5be | 17 500 | 27 800 | 1.60 | 65 | 76 | 331 | 356 | 390 | 3.41 | 151.8 | 16.26 | 31.8 |

*“DSC: second heat ramp; N$_2$, 10 ºC/min. $T_g$ determined as the inflection point of step transition. ”*DSC: second heat ramp; N$_2$, 10 ºC/min. $T_g$ determined as the inflection point of step transition. *“DMA: bending mode, 3 ºC/min, 1 Hz. $T_g$ determined as the peak maximum in tan $\delta$ curves. ”*DMA: bending mode, 3 ºC/min, 1 Hz. $T_g$ determined as the peak maximum in tan $\delta$ curves. *“TGA: N$_2$, 10 ºC/min. ”*TGA: N$_2$, 10 ºC/min. *“WLF parameters based on reference temperature $T_r = 220 ºC. ”*WLF parameters based on reference temperature $T_r = 220 ºC. *“WLF parameters based on $T_g. ”*WLF parameters based on $T_g.

For monomer 3a, the chemical shifts of CH$_2$ (a and b) appeared at 2.46 and 4.24 ppm, respectively. The chemical shift of the methyl carboxylate group (c) was found at 3.92 ppm, which was used to monitor the progress of polymerization during the first stage (transesterification). The chemical shifts for the indole units (e–h) were observed at 7.14–8.21 ppm. After the polymerization, all of the signals became broad (Figures 2 and S2). The signal b (CH$_2$ next to the nitrogen in 3a) for all of the polymers shifted upfield (from 4.10 to 3.90 ppm). Moreover, it was observed that when longer diols were used, the chemical shift of signal b moved closer to the chemical shift of the corresponding peak in the monomer. The same effect was also observed for signal a, which appeared at 2.46 ppm in the monomer spectrum, but moved to higher field for the polymers (2.29 ppm). The signals for the diol units (c–f) were also clearly observed in all of the polymer spectra. The peak corresponded to the CH$_2$ next to the ester bonds (signal c) was observed at 4.53–4.30 ppm with a downfield shift trend for the polymers with shorter diols. Between 2.20 and 1.40 ppm, the signals corresponded to the other methylene groups (d–f) were observed. According to the $^1$H NMR spectra, polymers 5ay ($y = a$–e) were formed.
The $^1$H NMR spectra of the other series 5by ($y = a−e$) were also unambiguously assigned (Supporting Information, Figure S3), which indicated the successful formation of the polymers.

The molecular weight of the obtained polyesters was determined by size exclusion chromatography (SEC, Table 1). Except for two polymers 5ab and 5bb, all of the other polyesters achieved relatively high molecular weights ($M_n \sim 15 000−35 000$ g/mol and $M_w \sim 27 000−60 000$ g/mol). For 5ab and 5bb, we have investigated reaction temperature and time, but the resulting polyesters 5ab and 5bb always showed considerably lower molecular weights compared with other polymers. This could be attributed to the lower thermal stability of 5ab and 5bb compared with the other polyesters according to thermogravimetric analysis (TGA) measurements (Table 1).

The thermal stability of the obtained polyesters was assessed by TGA (Figure 3). A single-step weight-loss profile was observed (maximum decomposition rate temperature $T_d > 380 ^\circ$C) for all of the polyesters, and the onset of weight loss ($T_{5\%}$, temperature for a 5% weight loss) was higher than $330 ^\circ$C. This showed good thermal stability of the resulting polyesters.

A closer examination of the thermograms in the initial stages of the thermal decomposition revealed that the $T_{1\%}$ values were all above $270 ^\circ$C, and there was a significant linear correlation between the $T_{1\%}$ values and the corresponding weight average molecular weight ($M_w$; see the inset of Figure 3). It is unclear whether the lower molecular weight was caused by the decreased thermal stability of the polyesters or the lower thermal stability was caused by the increased content of vulnerable chain ends for lower-molecular-weight polyesters.

**Thermal Characterization.** The thermal transition of the obtained indole-based polyesters was studied by differential scanning calorimetry (DSC) (Figure 4).

All of the obtained polyesters were completely amorphous without any melting endotherm on the heating curves. The glass transitions were clearly observed with $T_g$ values in the range of 71−113 °C for 5ay series and 65−100 °C for 5by series. As shown in Figure S, the $T_g$ values of the same series of polyesters (5ay and 5by) decreased with the decreased length of the diols used, which was expected because of the higher flexibility of the polymers with longer methylene "bridges". In addition, 5ay displayed higher $T_g$ values than the corresponding 5by (with the same diol used), due to their higher rigidity imparted by the shorter methylene bridges inside monomer 3a compared to that of monomer 3b. The $T_g$ values were also independently measured by dynamic mechanical analysis (DMA). As shown in Figure 6, the $T_g$ values of the polyesters were determined using peak maximum in the tan $\delta$.
Polyesters S\text{ab} and S\text{bb} could not be measured by DMA due to the insufficient physical integrity for the samples prepared for DMA measurements, which was possibly caused by their relatively low molecular weights. In fact, the effects of the relatively low molecular weights of S\text{ab} and S\text{bb} were also reflected in their lower $T_g$ values with respect to the expected values (Figure 5a). Expectedly, the $T_g$ values measured by DMA showed the same trend as those obtained from the DSC (Figure 5). The differences in the $T_g$ values according to DSC and DMA are typical, which arise from the different processes that were measured\textsuperscript{72}

In addition, DMA also provided valuable information regarding the mechanical characteristics of the obtained polyesters in the solid state. Figure 6 shows the storage modulus ($E'$) and the tan $\delta$ as a function of the temperature. All of the polyesters displayed typical temperature-unaffected glassy modulus below $T_g$. The observed $E'$ values at 30 °C were found between 1.8 and 2.7 GPa for S\text{ay} and 1.7 and 2.2 GPa for S\text{by}. Both series showed decreasing $E'$ values as longer diols were used.

**Rheological Analysis.** Polyesters having a $T_g$ superior to PET (76 °C), namely, S\text{aa}, S\text{ac}, S\text{ad}, S\text{ba}, S\text{bc}, and S\text{bd}, were studied by melt rheology.\textsuperscript{34} The time–temperature superposition was applied to the data obtained from the measurements in a frequency range between 500 and 0.1 rad/s at 10 °C intervals from 170 to 220 °C (S\text{aa} was studied between 180 and 230 °C). The thermorheological simplicity of these polyesters was confirmed as good overlap was attained by shifting moduli and viscosity into master curves. A reference temperature ($T_r \sim 220$ °C) was used for the comparison among all of the obtained polyesters in a frequency range of five decades up to $10^4$ rad/s. As a representative plot, Figure 7 shows the master curve of both storage ($G'$) and loss ($G''$) moduli of S\text{bd}, which depicts its typical linear viscoelastic behavior at the terminal zone and beyond the limit of the rubbery plateau region. At the crossover frequency $\omega_c$ (where $G' = G''$), a typical terminal relaxation time $\tau_c = 1/\omega_c$ was observed. This relaxation was consistent with the disentanglement relaxation time, which was observed in all of the measured polyesters (Figure S5). Furthermore, the storage modulus $G'$ (Figure 7) showed an additional relaxation time at low frequencies, which could be attributed to the observed bubbles in the samples after the rheology measurements.

The deformation of these bubbles during the oscillatory shear deformation can cause an additional elastic component that dominates at low frequencies.\textsuperscript{73,74} As a result, an increased $G'$ but unchanged $G''$ was observed by the slopes of 0.95–0.97, which was consistent with the expected slope of $G'' \approx 1$ for non-cross-linked polymer melts at low frequencies in the terminal region.

Figure 8 shows the complex viscosity $\eta^*$ master curves of polyesters S\text{aa}, S\text{ac}, S\text{ad}, S\text{ba}, S\text{bc}, and S\text{bd}. In the low-
frequency limit, the elastic component to $\eta^*$ disappears and
the viscosity becomes independent of the frequency as the
material behaves increasingly Newtonian. This frequency-
dependent viscosity is the zero-shear viscosity $\eta_0$, which is
approximately proportional to $M_w$ for most polymers.75
However, the soft increase in the complex viscosity observed
at low frequencies can be ascribed to the increase of $G'$ caused
by the existence of bubbles. At higher frequencies, a typical
shear-thinning behavior was observed as the polyesters became
non-Newtonian. All of the polyesters displayed comparable
w for most polymers.75

All of the six measured polyesters showed thermorheological
simplicity, which obeyed the Williams–Landel–Ferry (WLF)
equation

$$\log(a_T) = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)}$$

(1)

In the WLF equation, $a_T$ is the temperature shift factor
employed to generate the master curves, $T$ is the temperature,
$T_r$ is an arbitrary reference temperature ($220 \ ^\circ C$ in this study),
and $C_1$ and $C_2$ are the empirical constants obtained from curvefitting.75

As shown in Figure 9b, the WLF fits displayed a
typical behavior for $a_T$ against the temperature. The values of
$C_1$ and $C_2$ depended on $T_r$, and they can be transformed into
$C^f_1$ and $C^f_2$ values according to eqs 2 and 3 below that are
comparable with literature values.75

As shown in Table 1 and
Figure 9b, the $C^f_1$ and $C^f_2$ values for the obtained polyesters 5aa,
5ad, 5ba, 5bc, and 5bd were consistent with the literature
values for commercial polymers like PET, polylactic acid,
etc.75–77

Interestingly, the most rigid polyester that we
prepared (5aa) showed a significantly deviated $C^f_2$ value, for
which the exact reason still remained to be unraveled.

$$C^f_1 = \frac{C_1C_2}{C_2 + (T_g - T_r)}$$

(2)

$$C^f_2 = C_2 + (T_g - T_r)$$

(3)

### CONCLUSIONS

A series of indole-based polyesters were successfully synthe-
sized by the bulk polycondensation of indole-based dicarbox-
syrate monomers and five aliphatic bio-based diols. The
obtained polyesters contained only aromatic ester bonds,
which enhanced their thermal stability and structural rigidity.
Varied lengths of methylene bridges were contained in the new
indole-based polyesters, which resulted in tunable $T_g$ values
in the range of 65–113 °C. This indicated that these polymers
could be potentially used in a wide range of applications
replacing commercial polyesters like PET, poly(ethylene
terephthalate) glycol (PETG), Akestra, or Tritan. The new
indole-based polyesters were amorphous and optically trans-
parent, which could be conveniently prepared into nontactile
thin films. Melt rheology measurements of the new polyesters
showed a distinct relaxation associated with disentanglements.
In the future, investigations on the copolymerization of indole-
based dicarboxylate monomers with rigid bis-phenolic building
blocks (e.g., various “phytomonomers” derived from lignin)75–77
to produce whole aromatic polyesters may have the potential
to further improve the thermal and mechanical properties of
indole-based polyesters toward high-performance engineering
bioplastics.

### EXPERIMENTAL SECTION

**Materials.** 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP), 1,3-
dibromopropane (99%), 1,4-dibromobutane (99%), dibutyllin-
(IV) oxide DBTO (98%), methyl indole-3-carboxylate (99%),
1,3-propanediol (98%), 1,4-butanediol (>99%), 1,5-pentanediol (>97%),
1,6-hexanediol (>99%), 1,8-octanediol (98%), and sodium hydride (a 60% dispersion in mineral oil) were
purchased from Sigma-Aldrich. Toluene (analytical grade, ACS),
xylenes (analytical grade, ACS), and chloroform (analytical grade, stabilized with ethanol) were purchased
from Scharlau. Methanol was purchased from Honeywell.
Dimethylformamide (DMF) (ACS, Reag. Ph. Eur.) was
purified from VWR Chemical. All chemicals were used as
received with the exception of DMF, which was obtained from
a dry solvent dispenser.

**Synthesis of Monomers and Polymers.** Dimethyl 1,1′-
(propane-1,3-diy)bis(1H-indole-3-carboxylate) (Monomer
3a): General Method. To a 300 mL round-bottom flask
equipped with a magnetic stirrer, methyl indole-3-carboxylate
(20.14 g, 114.9 mmol, 2.10 equiv) and 200 mL dry DMF were
added and cooled in an ice bath. To the resulting solution,
sodium hydride (5.04 g of a 60% dispersion in mineral oil,
125.8 mmol) was added and cooled in an ice bath. The resulting
solution, sodium hydride (5.04 g of a 60% dispersion in mineral oil,
125.8 mmol, 2.10 equiv) was added and cooled in an ice bath. To the resulting solution,
sodium hydride (5.04 g of a 60% dispersion in mineral oil,
125.8 mmol, 2.10 equiv) was added and cooled in an ice bath. To the resulting solution,
sodium hydride (5.04 g of a 60% dispersion in mineral oil,
125.8 mmol, 2.10 equiv) was added and cooled in an ice bath. To the resulting solution,
sodium hydride (5.04 g of a 60% dispersion in mineral oil,
125.8 mmol, 2.10 equiv) was added and cooled in an ice bath. To the resulting solution,
sodium hydride (5.04 g of a 60% dispersion in mineral oil,
125.8 mmol, 2.10 equiv) was added and cooled in an ice bath. To the resulting solution,
White powder (99% yield). 1H NMR (400.13 MHz, CDCl3) δ, ppm: 8.21 (d, 2H, (Hh)), 7.74 (s, 2H, (Hg)), 7.29 (td, 2H, (He)), 7.25 (td, 2H, (Hf)), 7.17 (d, 2H, (Hd)), 4.12 (t, 4H, (He)), 3.92 (s, 6H, (Hb)), and 2.46 (q, 2H, (Ha)). 13C NMR (100.61 MHz, CDCl3). δ, ppm: 165.34, 136.33, 133.77, 126.86, 123.22, 122.27, 122.07, 109.79, 107.84, 51.16, 43.86, and 29.74. FT-IR ν (cm⁻¹): 3108, 3045, 2950, 1680, 1531, 1265, 1232, 1183, 1153, 1106, 1092, 1013, 775, 749, 728, and 557. HRMS (ESI+) exact mass calcd for C23H22N2O4 391.1685, found 391.1685, mp: 184 °C (DSC).

Dimethyl 1,1′-(butane-1,4-diyl)bis(1H-indole-3-carboxylate) (Monomer 3b). 1H NMR (400.13 MHz, CDCl3) δ, ppm: 8.18 (m, 2H, (Hh)), 7.73 (s, 2H, (Hg)), 7.30–7.27 (m, 3H, (Hd, He, Hf)), 4.10 (q, 4H, (He)), 3.9q (s, 6H, (Hb)), and 1.87 (q, 2H, (Hc)). 13C NMR (100.61 MHz, CDCl3). δ, ppm: 165.47, 136.42, 134.05, 126.84, 124.03, 126.13, 122.05, 119.87, 107.50, 51.14, 46.35, and 27.34. FT-IR ν (cm⁻¹): 3118, 2946, 1686, 1533, 1404, 1269, 1228, 1149, 1118, 1091, 1028, 775, and 739. HRMS (ESI+) exact mass calcd for C24H24N2O4 405.1819, found 405.1814. mp: 205 °C (DSC).

Synthesis of Polyesters. The procedure for the synthesis of Sad was described as a general protocol, and all of the other polyesters were prepared similarly. 1,6-Hexanediol (0.94 g, 10.09, 6.0 mol.) was added dropwise. The mixture was stirred for 2 h and allowed to reach room temperature overnight. The mixture was poured into a 1700 mL ice–water mixture and stirred for 2 h. The white solid was filtered and washed extensively with distilled water. Recrystallization from toluene (×2) afforded 17.86 g of white platelike crystals (yield: 83%). 1H NMR (400.13 MHz, CDCl3) δ, ppm: 8.21 (d, 2H, (Hh)), 7.74 (s, 2H, (Hg)), 7.29 (td, 2H, (He)), 7.25 (td, 2H, (Hf)), 7.17 (d, 2H, (Hd)), 4.12 (t, 4H, (He)), 3.92 (s, 6H, (Hb)), and 2.46 (q, 2H, (Ha)). 13C NMR (100.61 MHz, CDCl3). δ, ppm: 165.34, 136.33, 133.77, 126.86, 123.22, 122.27, 122.07, 109.79, 107.84, 51.16, 43.86, and 29.74. FT-IR ν (cm⁻¹): 3108, 3045, 2950, 1680, 1531, 1265, 1232, 1183, 1153, 1106, 1092, 1013, 775, 749, 728, and 557. HRMS (ESI+) exact mass calcd for C23H22N2O4 391.1685, found 391.1685, mp: 184 °C (DSC).

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64.02, 46.47, 29.32, 29.06, 27.41, and 26.19. FT-IR $\nu$ (cm$^{-1}$): 2927, 1683, 1531, 1223, 1198, 1089, 1013, 775, and 744.

**Analytical Methods.** Nuclear magnetic resonance (NMR) measurements were carried out on a Bruker DRX400 spectrometer at a proton frequency of 400.13 MHz and a carbon frequency of 100.61 MHz. Fourier transform infrared (FT-IR) spectra were measured with an attenuated total reflection setup using a Bruker Alpha FT-IR spectrometer. Twenty-four scans were coadded using a resolution of 4 cm$^{-1}$.

Size exclusion chromatography (SEC) was performed in chloroform at 35 °C with a flow rate of 1.0 mL/min. The SEC equipment used was a Viscotek 305 TDA, which included a guard column and two Malvern Panalytical general purpose mixed bed columns with an exclusion limit of 20 $\times$ 10$^6$ Da for polystyrene. Detection consisted of a conventional dual-cell refractive index detector, a four-capillary bridge viscometer, and a light scattering detector operating at 3 mW, at a wavelength of 670 nm, and measurement angles of 90 and 7°.

**Dynamic mechanical analysis (DMA)** was performed on a TA Instruments Q800 dynamic mechanical analyzer in an oscillatory bending mode at a frequency of 1 Hz, an oscillatory strain to determine the viscoelastic linear region.

**Author Information**

The authors declare no competing financial interest.

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