

Article

Eugenol and Chavicol-Based Polyamides from Synthesis to Degradation: Moving Towards Closing the Circle

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Abstract

A new series of polyamides (PAs) employing two phenolic natural compounds as starting materials, eugenol and chavicol, has been successfully prepared. The synthesis was carried out through a solvent-free protocol using the environmentally friendly organocatalyst 1,5,7-triazabicyclo[4.4.0]dec-3-ene (TBD). The obtained materials have been properly characterized. Moreover, the prepared materials, all of them amorphous, showed a wide range of transition temperatures (T_g s) depending on the structure of the diester counterpart used in the polymerization reaction. In addition, the influence of the methoxy group present in eugenol on the thermal properties of the resulting polyamides was studied. The synthesized polyamides demonstrated excellent thermal stability, high hydrophobicity, and great dimensional integrity. Furthermore, the obtained polymers could be depolymerized under alkaline hydrolysis conditions to yield, with good to excellent recovery ratios, the corresponding starting diamine monomer, which could eventually be used in the synthesis of new polymers. Closed-loop chemical recycling emerges as a sustainable alternative to conventional end-of-life management strategies for discarded polymers, while also constituting a promising pathway to mitigate the accumulation of polyamide (PA) waste.

Keywords: green polymerization; chemical closed-loop recycling; biobased monomers; high bio-content polyamides



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1. Introduction

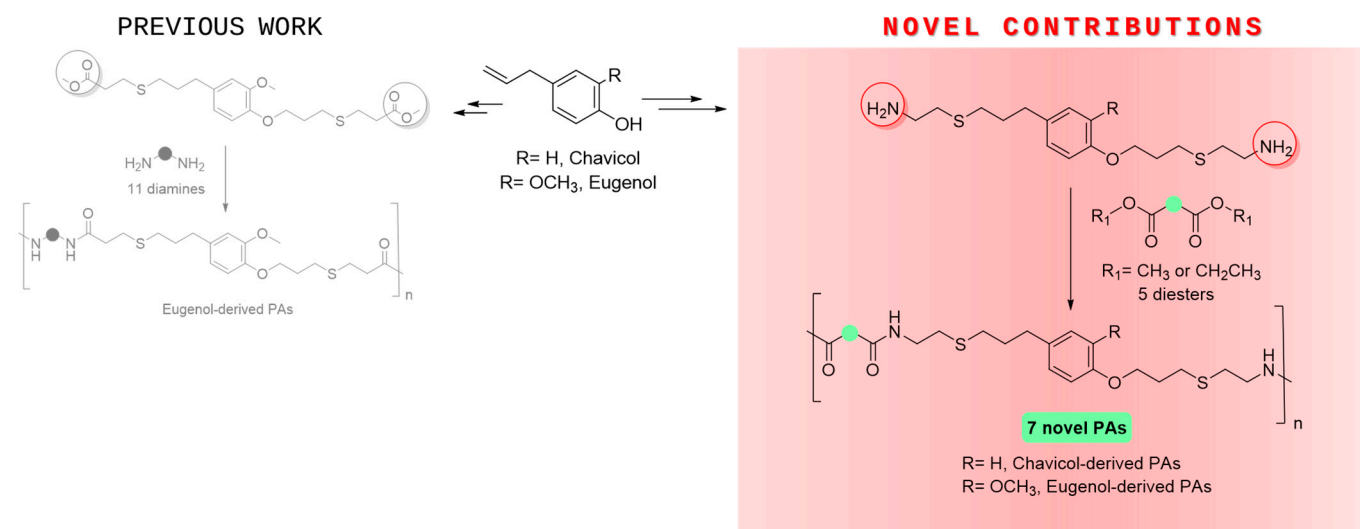
Polyamides (PAs), commercialized shortly after World War II, are a major class of semicrystalline thermoplastics traditionally produced from petroleum-derived feedstocks. Due to their high melting temperatures, robust mechanical performance, and favorable chemical resistance, they are widely classified as engineering plastics [1]. Additional attributes, including electrical insulation, biocompatibility, and excellent impact and tensile strength, have enabled their extensive use across automotive, biomedical, optical, and other advanced applications [2–4]. The strong intermolecular hydrogen bonding characteristic of PAs imparts remarkable thermal and chemical stability [5]. Nevertheless, this same durability severely limits their environmental degradability. As a result, PA residues can persist for centuries, contributing to long-term environmental pollution [6]. Addressing the issue associated with PA accumulation has therefore become an urgent and essential challenge [7].

In this context, the widespread use of PAs has raised both economic and environmental concerns once their service life ends, and to manage the end-of-life stage of these materials, either mechanical or chemical recycling techniques must be employed [8]. In addition, the inherent stability of PAs makes their complete degradation to the corresponding monomers a significant challenge [9].

Moreover, the production of conventional polymeric materials relies on fossil-based feedstocks, leading to major drawbacks such as resource depletion [10], price volatility, and contributions to climate change [11,12]. The increasing demand for environmentally friendly materials goes hand in hand with the growing focus on sustainable bio-based polymers and plastics in the decades ahead. Replacing conventional plastics with bio-derived alternatives is expected to play a key role in reducing global carbon footprints [5]. Bio-based PAs [13] have been known since the 1940s [8]; however, although some monomers derived from sugars [14] or terpenes [15–17] have been reported, most of the described bio-based PAs are long chain aliphatic polymers derived from vegetable oils [18–20]. Although useful, these materials often show low thermal and mechanical properties due to the lack of aromaticity [21]. Therefore, it is urgent to find bio-based PAs with a certain degree of aromaticity that ensures improved properties. Lignin [22–24], the second most abundant natural polymer after cellulose [25], represents an attractive aromatic feedstock, and its depolymerization products, such as eugenol, offer promising monomeric platforms [23]. The allylic and phenolic functionalities of eugenol enable efficient derivatization toward difunctional monomers required for polycondensation [11,26]. Recently, we reported a broad family of sulfur-containing PAs prepared from a eugenol-derived diester and various aliphatic and aromatic diamines, demonstrating the strong influence of the diamine structure on polymer properties [26]. All resulting materials were amorphous, consistent with the known impact of the eugenol methoxy group in disrupting backbone symmetry and crystallinity in related polyesters (PEs) [27].

Conversely, chavicol, another lignin-related phenolic compound present in several essential oils, lacks the methoxy group on the aromatic ring and may therefore provide improved structural symmetry. Although the difunctional character of this natural compound makes it an optimal precursor for various polymeric materials, its potential as a precursor for PAs remains unexplored, and no reports of chavicol-based PAs exist to date [28].

Taking this framework into account, and continuing our efforts toward the development of new bio-based materials [26], the main objective of this work was to design, synthesize and characterize a new series of PAs with high bio-content using eugenol (Scheme 1). To this end, several diester monomers were polycondensed with a diamine readily obtained from this natural phenolic compound. In addition, to evaluate the influence of the methoxy moiety on the structure–property relationship of the resulting polymers, a parallel series of chavicol-derived PAs was synthesized. We hypothesized that the absence of the methoxy group could lead to a more symmetrical polymer backbone, potentially promoting higher crystallinity and consequently modifying the thermal and physical properties of the materials. Finally, the degradability of the polymers was assessed to explore their potential within a circular economy framework. The results demonstrate that the original diamine monomer can be efficiently recovered, highlighting the feasibility of a closed-loop approach and reinforcing the sustainability potential of these newly developed bio-based polyamides [29–31].



Scheme 1. Comparative scheme: previous work [26] and novel contributions presented in this work.

2. Materials and Methods

2.1. Reagents and Solvents

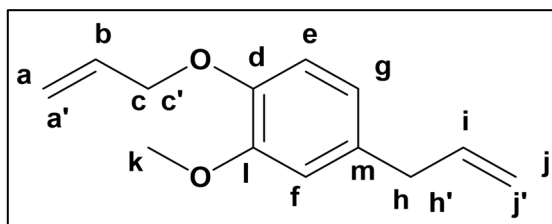
The necessary reagents for the synthesis of allyl eugenol and 1-allyl-4-allyloxybenzene (**3**) are: eugenol (99%, Sigma Aldrich, Darmstad, Germany), chavicol (Sigma Aldrich, Darmstad, Germany), potassium carbonate (K_2CO_3 , >99.0%, Sigma Aldrich, St. Louis, MO, USA) and allyl bromide (99%, Sigma Aldrich St. Louis, MO, USA). For the synthesis of allyl eugenol-derived diamine **2**, phenyl-*bis* (2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO, 97%, Sigma Aldrich, St. Louis, MO, USA) was employed as initiator, and cysteamine hydrochloride (>98%, Sigma Aldrich, St. Louis, MO, USA) as reagent. In addition to these reagents, other solvents and reagents were used, including ethyl acetate (EtOAc, 99.5%, Macron, Darmstad, Germany), ethanol (EtOH, 99.8%, Macron, Darmstad, Germany), *N,N*-dimethylformamide (DMF, Macron, Gliwice, Poland), dichloromethane (CH_2Cl_2 , Macron, Gliwice, Poland), sodium sulphate anhydrous (Na_2SO_4 , 99.5% Panreac, Darmstad, Germany) and brine solution. Additionally, 1,5,7-triazabicyclo[4.4.0]dec-3-ene (TBD, 98%, St. Louis, MO, USA) was purchased as catalyst for the synthesis of PAs, and dimethyl adipate (**5**, >99%, Sigma Aldrich, St. Louis, MO, USA), dimethyl terephthalate (**7**, >99%, Sigma Aldrich, Darmstad, Germany), diethyl oxalate (**6**, >99%, Sigma Aldrich, St. Louis, MO, USA), dimethyl isophthalate (**8**, 99%, Sigma Aldrich, St. Louis, MO, USA) and dimethyl phthalate (**9**, Sigma Aldrich, Darmstad, Germany) were used as monomers for the synthesis of PAs. Lastly, methanol (MeOH, Sigma Aldrich, St. Louis, MO, USA) was used for the cleaning of the obtained PAs. For the degradation of the biobased PAs, sodium hydroxide pellets (NaOH, Sigma Aldrich, St. Louis, MO, USA) and hydrochloric acid (HCl, 37%, Sigma Aldrich, St. Louis, MO, USA) were used.

2.2. Synthesis of Monomers

2.2.1. Synthesis of 1-Allyl-4-Allyloxy-3-Methoxybenzene (**1**)

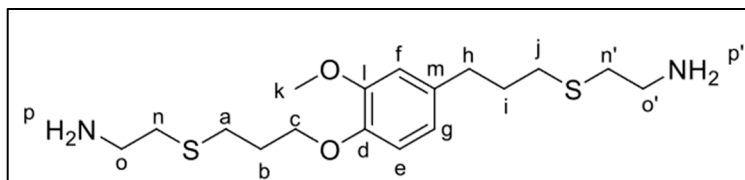
The synthesis of **1** was carried out following the procedure described by T. Modjinou et al. [32]. For that, a solution of eugenol (10.0 g, 0.061 mol) in DMF (100 mL) was treated with K_2CO_3 (17.5 g, 0.126 mol), and the resulting mixture was introduced on an ice-bath. Then, allyl bromide (12 mL, 0.134 mol) was added, and the reaction was allowed to react for 72 h. Once time passed, water (250 mL) was poured and the mixture was stirred for 30 min. Following that, the mixture was extracted with EtOAc (3 × 60 mL), and the organic layer was washed with Brine solution (2 × 60 mL) and dried over sodium sulphate anhydrous.

Finally, the solvent was evaporated under reduced pressure, concentrating the product and yielding **1** as a yellow liquid (11.4 g, 92%) for further utilization in subsequent reactions; $^1\text{H-NMR}$ (300 MHz, CDCl_3), δ (ppm): 6.82 (d, $J = 8.0$, 1H, He), 6.71 (dt, $J = 8.0$, 1.9 Hz, 2H, Hg, Hf), 6.18–5.87 (m, 2H Hb, Hi), 5.45–5.22 (m, 2H, Ha, a'), 5.14–5.02 (m, 2H, Hj, j'), 4.59 (dt, $J = 5.4$, 1.5 Hz, 2H, Hc, c'), 3.86 (s, 3H, Hk), 3.34 (d, $J = 6.7$ Hz, 2H, Hh, h'); $^{13}\text{C-NMR}$ (74.5 MHz, CDCl_3), δ (ppm): 149.6 ($\text{C}_{\text{arom-O}}$, Cl), 146.4 ($\text{C}_{\text{arom-O}}$, Cd), 137.8 ($\text{C}_{\text{sp}^2\text{-H}}$, Ci), 133.4 ($\text{C}_{\text{sp}^2\text{-H}}$, Cb), 133.2 ($\text{C}_{\text{arom-C}}$, Cm), 120.2 ($\text{C}_{\text{arom-H}}$, Cg), 117.9 ($\text{C}_{\text{sp}^2\text{-H}}$, Ca), 115.75 ($\text{C}_{\text{sp}^2\text{-H}}$, Cj), 113.82 ($\text{C}_{\text{arom-H}}$, Cf), 112.5 ($\text{C}_{\text{arom-H}}$, Ce), 69.7 ($\text{C}_{\text{sp}^3\text{-H}}$, Cc), 55.9 (OCH_3 , Ck), 39.9 ($\text{C}_{\text{sp}^3\text{-H}}$, Ch); FT-IR (KBr), ν (cm^{-1}): 3080 ($\text{C}_{\text{sp}^2\text{-H}}$), 2985–2829 ($\text{C}_{\text{sp}^3\text{-H}}$), 1640 ($\text{C}=\text{C}$).



2.2.2. Synthesis of Monomer 2. Thiol–Ene Photochemical Reaction of **1** with Cysteamine Hydrochloride

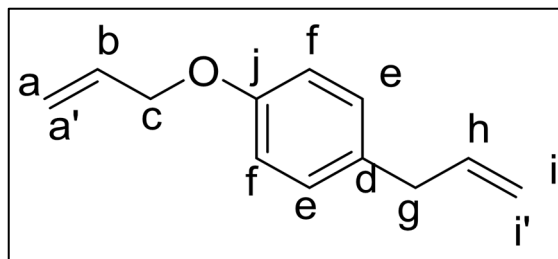
The synthesis of **2** was carried out by photochemical conditions described by Zhang et al. [33] in excellent yields [26]. Therefore, a solution of cysteamine hydrochloride (950 mg, 8.3 mmol) and BAPO photoinitiator (10% wt with respect to **1**) previously dissolved in ethanol (minimum amount) were added to **1** (1.0 g, 4.2 mmol). Afterwards, it was irradiated with UV light (365 nm) and allowed to stir for 80 min until a white-yellow solid was obtained. Subsequently, the solid was filtered off, and then K_2CO_3 solution (1 M) was added. Then, extraction was carried out with CH_2Cl_2 (3×60 mL). The organic phase of the extract was washed with brine solution (2×60 mL) and dried over anhydrous Na_2SO_4 . Finally, the solvent was evaporated under reduced pressure, yielding **2** as a yellow liquid (2.8 g, 80%), which was later used without any further purification for the synthesis of PAs. $^1\text{H-NMR}$ (300 MHz, CDCl_3), δ (ppm): 6.88–6.61 (m, 3H, He, f, g), 4.07 (t, $J = 6.2$ Hz, 2H, Hc), 3.83 (s, 3H, Hk), 2.85 (dd, $J = 12.3$, 6.2 Hz, 4H, Ho, o'), 2.75–2.54 (m, 8H, Hn, n', a, j), 2.49 (t, $J = 7.3$ Hz, 2H, Hh), 2.07 (m, 2H, Hb), 1.96–1.75 (m, 2H, Hi), 1.49 (s, 4H, Hp, p'); $^{13}\text{C-NMR}$ (300 MHz, CDCl_3), δ (ppm): 149.4 ($\text{C}_{\text{arom-O}}$, Cd), 146.5 ($\text{C}_{\text{arom-O}}$, Cl), 134.6 ($\text{C}_{\text{arom-C}}$, Cm), 120.4 ($\text{C}_{\text{arom-H}}$, Ce, f, g), 113.6 ($\text{C}_{\text{arom-H}}$, Ce, f, g), 112.4 ($\text{C}_{\text{arom-H}}$, Ce, f, g), 67.6 ($\text{OC}_{\text{sp}^3\text{-H}_2}$, Cc), 55.9 (OCH_3 , Ck), 41.1 ($\text{C}_{\text{sp}^3\text{-H}_2}$, Co, o'), 36.6 ($\text{C}_{\text{sp}^3\text{-H}_2}$, Ch), 34.3 ($\text{C}_{\text{sp}^3\text{-H}_2}$, Ci), 31.4 ($\text{C}_{\text{sp}^3\text{-H}_2}$, Cj), 31.1 ($\text{C}_{\text{sp}^3\text{-H}_2}$, Cn, n'), 29.4 ($\text{C}_{\text{sp}^3\text{-H}_2}$, Ca), 28.3 ($\text{C}_{\text{sp}^3\text{-H}_2}$, Cb); FT-IR (KBr), ν (cm^{-1}): 3429–3255 ($-\text{NH}_2$), 2907 ($\text{C}_{\text{sp}^2\text{-H}}$), 2840 ($\text{C}_{\text{sp}^3\text{-H}}$), 1594 ($\text{C}_{\text{sp}^2\text{-H}}$).



2.2.3. Synthesis of 1-Allyl-4-Allyloxybenzene (**3**)

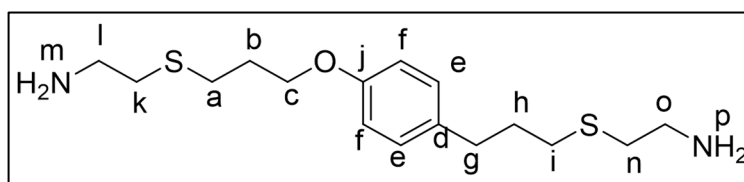
For the synthesis of **3**, a solution of chavicol (1.5 g, 0.011 mol) in DMF (15 mL) was treated with K_2CO_3 (3.1 g, 0.023 mol), and the resulting mixture was cooled to 0°C . Then, allyl bromide (2.1 mL, 0.0241 mol) was added, and the reaction was allowed to react for 24 h at room temperature. Once time passed, water (25 mL) was poured, and the mixture was stirred for 30 min. Following that, the mixture was extracted with EtOAc (3×10 mL), and the combined organic phases were washed with brine solution (2×10 mL) and dried

over anhydrous Na_2SO_4 . Finally, the solvent was evaporated under reduced pressure, yielding **3** as a yellow liquid (87%) which was employed in subsequent reactions without ulterior purification. $^1\text{H-NMR}$ (300 MHz, CDCl_3), δ (ppm): 7.01 (d, $J = 8.8$ Hz, 2H, He), 6.77 (d, $J = 8.8$, 2H, Hf), 6.08–5.75 (m, 2H, Hb/Hh), 5.32 (dt, $J = 17.3$, 1.6 Hz, 1H, Ha'), 5.19 (dt, $J = 10.5$, 1.6 Hz, 1H, Ha), 5.06–4.88 (m, 2H, Hi/Hi'), 4.43 (dt, $J = 5.3$, 1.6 Hz, 2H, Hc), 3.24 (dt, $J = 6.7$, 1.4 Hz, 2H, Hg); $^{13}\text{C-NMR}$ (74.5 MHz, CDCl_3), δ (ppm): 157.0 ($\text{C}_{\text{arom-O}}$, Cj), 137.9 ($\text{C}_{\text{arom-C}}$, Cd), 133.5, 132.3, 129.6, 129.5, 117.5, 115.5, 114.8 ($\text{C}_{\text{sp}^2\text{-H}}$), 68.9 ($\text{C}_{\text{sp}^3\text{-H}}$, Cc), 39.4 ($\text{C}_{\text{sp}^3\text{-H}}$, Cg); FT-IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3089 ($\text{C}_{\text{sp}^2\text{-H}}$), 2968–2854 ($\text{C}_{\text{sp}^3\text{-H}}$).



2.2.4. Thiol–Ene Photochemical Reaction of **3** with Cysteamine Hydrochloride. Synthesis of 2-((3-(4-((3-((2-Aminoethyl)thio)propoxy)phenyl)propyl)thio)ethan-1-Amine (**4**)

To complete the synthesis of **4**, a solution in EtOH (minimum amount) of cysteamine hydrochloride (1.3 g, 11.5 mmol) and a photoinitiator (10% wt of **3**) were added to **3** (1.0 g, 5.7 mmol). Afterwards, it was irradiated with UV light (365 nm) and allowed to stir for 80 min until a white-yellow solid was obtained. Subsequently, the solid was filtered off, and then K_2CO_3 solution (1 M) was added. After redissolving the solid with CH_2Cl_2 , the extraction of the solution was carried out with CH_2Cl_2 (3×20 mL). The organic phase of the extract was washed with brine solution (2×20 mL) and dried over anhydrous Na_2SO_4 . Finally, the solvent was evaporated under reduced pressure, yielding **4** (49%), which was later used without any further purification for the synthesis of **PA6** and **PA7**. $^1\text{H-NMR}$ (300 MHz, CDCl_3), δ (ppm): 7.07 (d, $J = 8.6$ Hz, 2H, He), 6.81 (d, $J = 8.6$ Hz, 2H, Hf), 4.03 (t, $J = 6.0$ Hz, 2H, Hc), 2.86 (m, 4H, Ho/Hl), 2.75–2.54 (m, 6H, Hk/Hn/Hg), 2.49 (m, 2H, Ha), 2.40–2.17 (m, 2H, Hi), 2.08–1.99 (m, 2H, Hb), 1.94–1.78 (m, 2H, Hh), 1.69 (s, 4H, Hm/Hp); ^{13}C NMR (300 MHz, CDCl_3), δ (ppm): 157.1 ($\text{C}_{\text{arom-O}}$, Cj), 133.6 ($\text{C}_{\text{arom-C}}$, Cd), 144.5, 128.9 ($\text{C}_{\text{arom-H}}$), 66.2 ($\text{C}_{\text{sp}^2\text{-H}}$, Cc), 41.4, 41.1, 37.9, 36.2, 33.9, 31.5, 31.1, 29.5, 28.3 ($\text{C}_{\text{sp}^3\text{-H}}$); FT-IR (KBr), $\tilde{\nu}$ (cm^{-1}): 3365 ($-\text{NH}_2$), 3017–2919 ($\text{C}_{\text{sp}^2\text{-H}}$), 2863 ($\text{C}_{\text{sp}^3\text{-H}}$).



2.3. Solvent Free Polymerization. Synthesis of Polyamides **PA1–PA7**

2, or alternatively **4**, (1 eq.) and the corresponding diester (5 eq.) were reacted using TBD (0.05 equiv. relative to amine groups) as a catalyst under a nitrogen atmosphere, and the reaction mixture was kept at 30 mbar and 180 °C for 24 h, the optimal reaction conditions as concluded in our previous work [26]. After the reaction time, the resulting polymers were cleaned using methanol and characterized by the techniques explained in the characterization techniques section.

2.4. Degradation of PAs

2.4.1. Acidic Hydrolysis

Biobased PAs were reacted with HCl (5 M, 25 mL) for 24 h and 110 °C [29]. Subsequently, the mixture was neutralized with NaOH (5 M) and then extracted with CH₂Cl₂ (3 × 10 mL). The combined organic phases were collected and cleaned with brine solution (2 × 8 mL). Then, the organic phase was dried with anhydrous Na₂SO₄, and the solvent was evaporated under reduced pressure, thereby recovering the corresponding diamine monomer **2** or **4**. The mass of recovered monomer relative to starting PA mass was around 10%.

2.4.2. Alkaline Hydrolysis

PAs (0.02 ~ 0.04 g) were reacted with an aqueous solution of NaOH (5 M, 25 mL) at 110 °C for 72 h. After reaching room temperature, the mixture was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic phases were washed with brine (2 × 8 mL). Then, the organic phase was dried with anhydrous Na₂SO₄, and the solvent was evaporated under reduced pressure, thereby recovering the spectroscopically pure corresponding diamine monomer **2** or **4**.

2.5. Characterization Techniques

Proton and carbon nuclear magnetic resonance (¹H- and ¹³C-NMR) spectra were obtained on a Bruker AC-300 and AC-500 spectrophotometer (Reinstetten, Germany) at 20–25 °C (300 and 500 MHz for ¹H-NMR and 75.4 and 125.8 MHz for ¹³C-NMR), using CDCl₃ and DMSO as solvents and tetramethylsilane (TMS) as the internal standard.

Fourier transform infrared (FTIR) spectra of the synthesized monomers, polymers and various reactants were recorded on a NICOLET Nexus 670 FT-IR spectrophotometer (Thermo Electron Corporation, Waltham, MA, USA). The conditions applied for each sample analysis were 32 scans, a wavelength range of 4000 cm^{−1} to 500 cm^{−1} and a resolution of 4 cm^{−1}.

The differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo 822^e calorimeter, (Mettler Toledo, Columbus, OH, USA). The thermal analysis of the samples (10 mg) involved three different scans. Firstly, the samples were heated from −100 °C to 200 °C at a heating rate of 20 °C·min^{−1} and then cooled from 200 °C to −100 °C. After the cooling scan, the second heating scan was performed from −100 °C to 200 °C to determine the glass transition temperature (T_g). The heating and cooling cycles were conducted under a nitrogen flow rate of 20 mL/min.

Thermogravimetric analysis (TGA) measurements were performed using an SDT Q600 (TA Instruments, DE, USA), and each 10–15 mg sample was scanned from 30 °C to 800 °C at a heating rate of 10 °C/min under nitrogen flow (100 mL/min) to prevent sample oxidation. The degradation temperature was calculated as the temperature at which the maximum rates of decomposition occurred, and the temperature at which 5% weight loss occurred was also calculated.

Molecular weight distributions and dispersities of the polyamides were determined by Gel Permeation Chromatography (GPC). The GPC analysis of PA was carried out in a Waters 2695 (Waters Corporation, Milford, MA, USA) with a light-scattering multiangle (MALS) Wyatt miniDAWN Treos detector and a refractive index detector (DRI) Wyatt Optilab TRex. Samples were eluted at 50 °C on a set of 500 Å and 1000 Å Phenogel columns (5 µm, 4.6 × 300 mm) connected in series using DMF (0.1% LiBr) at 0.25 mL/min as eluent.

The water absorption was measured by soaking in Sartorius SE2 microbalance (Göttingen, Germany) a known-mass of PA (~10 mg) in distilled-water for 10 days, and after this, the samples were dried with tissue paper. The water absorption percentages were

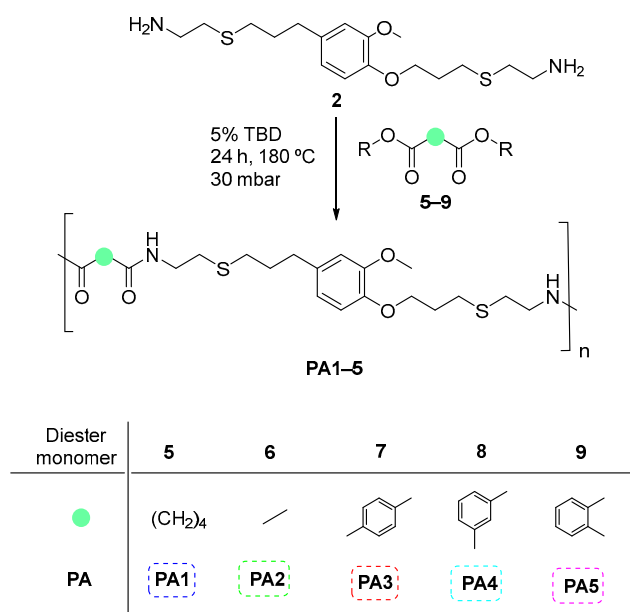
calculated by the ratios of dry and their wet samples. Three specimens were measured for each sample to calculate the mean and error.

Water Contact Angle (WCA) measurements were performed to evaluate the wettability of the synthesized polymers (OCA 15 EC, NEURTEK Instruments, Eibar, Spain). Milli-Q water was used as the probe liquid, and measurements were carried out at room temperature using the sessile drop method, with a drop volume of 2 μ L. The reported values correspond to the average of ten measurements for each composition.

3. Results and Discussion

3.1. Polycondensation Reaction of Diamine **2** with Diesters **5–9**. Synthesis of Eugenol-Derived Polyamides **PA1–PA5**

The diamine compound **2** was prepared from allyl eugenol (**1**) as described in our previous work [26]. Subsequently, this monomer was reacted with structurally different esters with the aim of extending the scope of the methodology and studying the influence of the structure of the diester component on the properties of the final polymer. So, to evaluate the impact of the length of the aliphatic chain, dimethyl adipate (**5**) and diethyl oxalate (**6**) were polycondensed with the monomer **2**. Regarding aromatic diester monomers, *para* (**7**), *meta* (**8**), and *ortho* (**9**) diester regioisomers were examined. In all cases, the polymerization reactions were carried out under the conditions optimized in our previous work [26]. That is, the environmentally friendly superbase TBD [34] was employed as the catalyst (5%), and the mixture was heated at 180 °C under *vacuum* in the absence of any solvent. Under these conditions, new PAs **PA1–5** were successfully obtained (Scheme 2).



Scheme 2. Solvent-free polymerization procedure to obtain PAs **PA1–5**, reacting the diamine monomer **2** and **5–9** diesters using TBD as catalyst.

The analysis of NMR and FT-IR spectra of the obtained PAs (see Figures 1 and 2) concluded that the polycondensation reactions had taken place successfully. Indeed, in the ¹H-NMR spectra, a new signal around 8 ppm appeared, corresponding to the NH proton of the amide (Figure 1). Moreover, all the synthesized materials presented a new signal at approximately 170 ppm in ¹³C-NMR, corresponding to the carbonyl carbon of the amide moiety (Supporting Material).

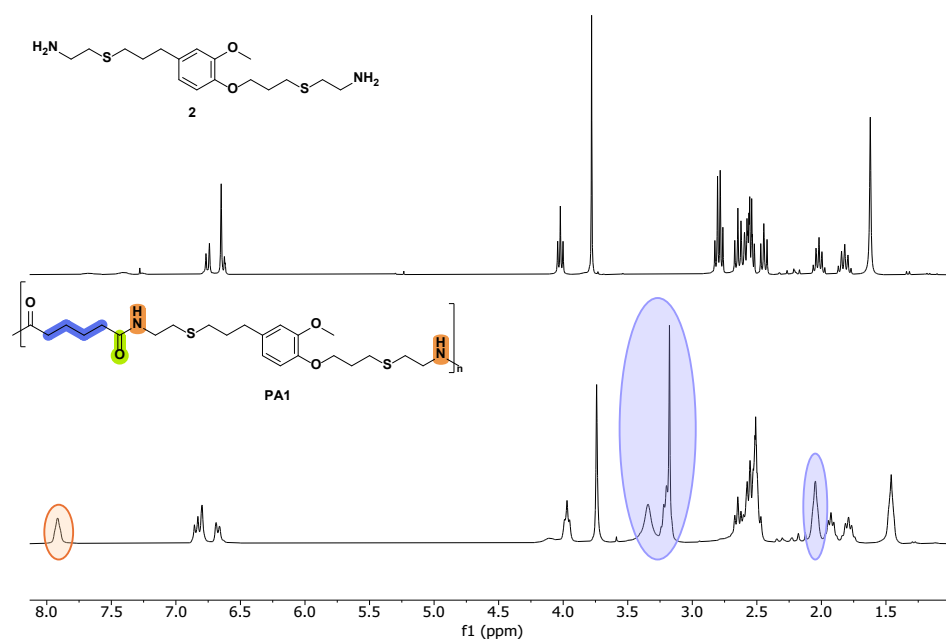


Figure 1. NMR analysis of the PA1 polymer compared with the starting monomer 2.

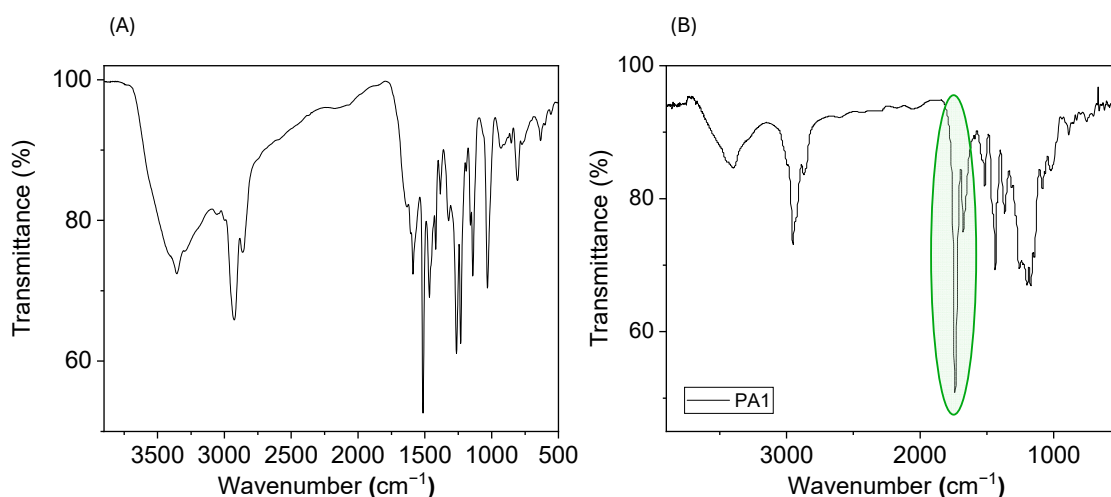


Figure 2. (A) FT-IR analysis of the diamine monomer 2, and (B) FT-IR analysis of the polymer PA1.

In addition to the most significant signals previously described, which corroborated the successful formation of the polyamide chains—as shown in Figure 1—the ^1H NMR spectra of PA1 displayed resonances ester in the aliphatic region attributable to the methylene groups derived from the adipate ester segment. Furthermore, as anticipated, in PA3 and PA4, signals appeared in the aromatic region (ca. 7.5–8.0 ppm), attributable to aromatic protons (see Supporting Material). Due to the reduced symmetry of the isophthaloyl moiety relative to the terephthaloyl analogue, the multiplicity pattern in this region manifested enhanced spectral complexity.

Regarding FT-IR spectra, a narrow and intense band was observed in the 1650–1750 cm^{-1} region, corresponding to the stretching vibration of the C=O bond of the amide groups (Figure 2).

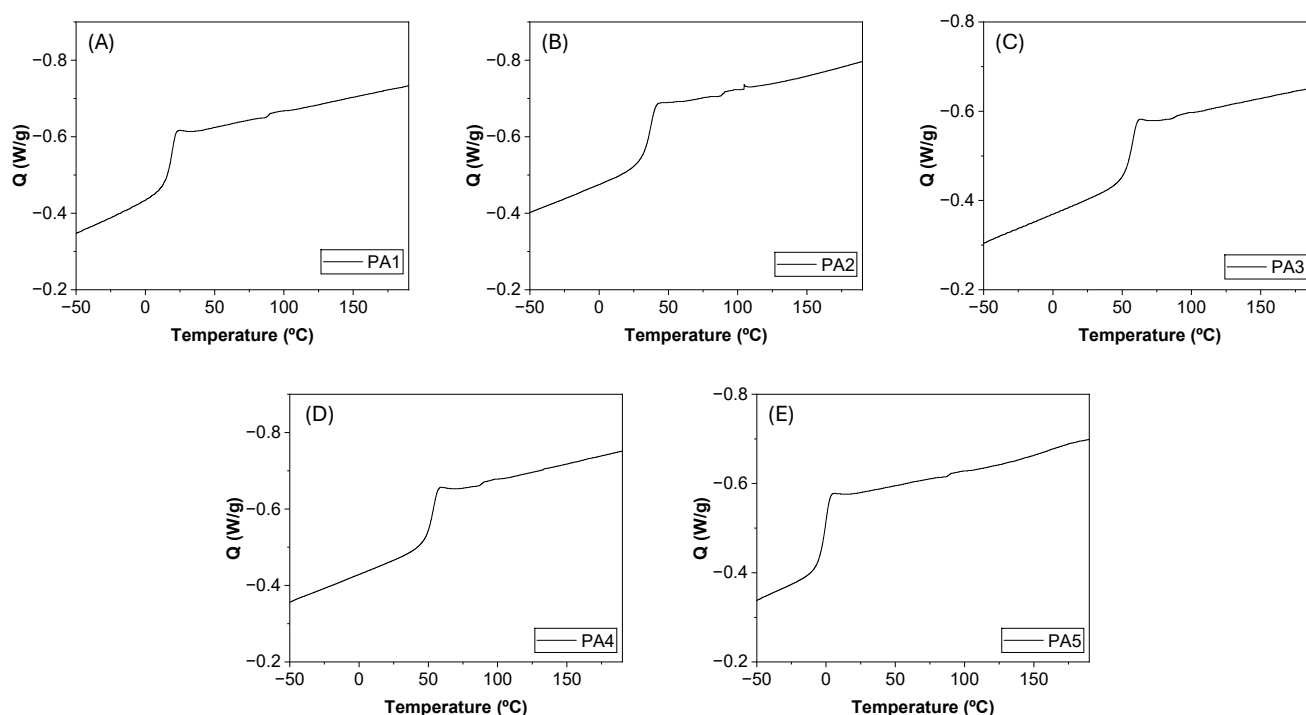
Once the structural characterization of the obtained materials was completed, confirming that the desired PAs had been successfully synthesized, the thermal properties were analyzed, and the molecular weights and distributions of these polymers were determined. As observed in Table 1, relatively high M_n values and low dispersities were obtained in most cases.

Table 1. Synthesis and properties of the obtained PA1–5.

Entry	Diester	M_n ^[a] (Da)	$\bar{D}$ ^[a]	T_g ^[b] (°C)	T_d^5 ^[c] (°C)	T_d^{max} ^[c] (°C)
PA1	5	44,400	1.22	18.0	299	372
PA2	6	-	-	36.3	309	373
PA3	7	71,600	1.18	56.2	313	380
PA4	8	93,000	1.14	38.2	296	381
PA5	9	485	1.75	−1.5	289	389

M_n : Number average molecular weight; $\bar{D}$: dispersity = M_w/M_n ; T_g : glass transition temperatures; T_d^5 : temperatures at which 5% weight loss occurred; T_d^{max} : temperatures at which the maximum rate of decomposition happened; ^[a] Analyzed with the DMF GPC system; ^[b] Analyzed with DSC at 20 °C/min, second scan; ^[c] Analyzed in TGA system.

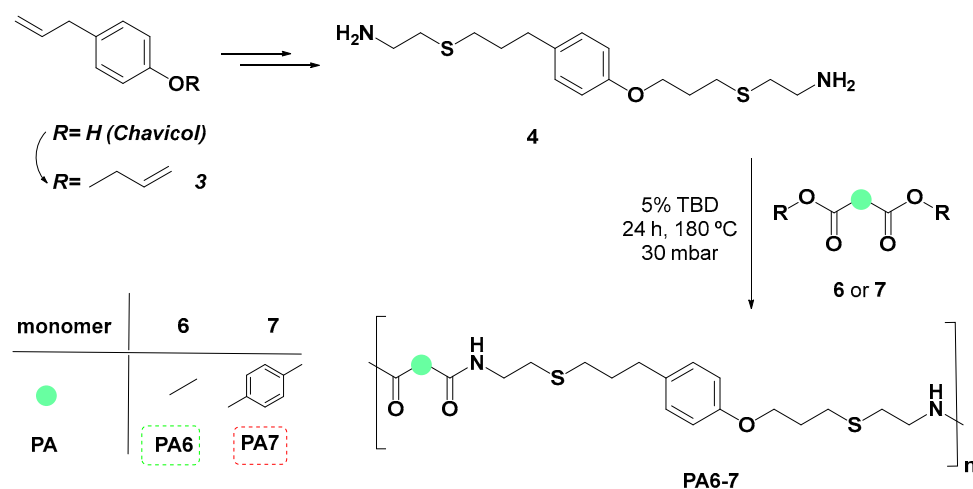
When the diamine monomer **2** was polymerized with dimethyl adipate (**5**), **PA1** was obtained, which presented a T_g close to 20 °C. In addition, when the diamine **2** was reacted with diethyl oxalate (**6**), as a consequence of the shorter length of the aliphatic chain, a more rigid polymer was obtained (Figure 3), which was reflected in a higher T_g of 36 °C. The possibility of forming double hydrogen bonds between adjacent chains due to the presence of oxalyl groups is probably also responsible for the increase in the rigidity of this material [35]. It is worth noting that the M_n value of this material could not be measured, as it was entirely insoluble in all solvents typically employed in GPC.

**Figure 3.** Second heating of DSC thermograms of PA1–5. (A) PA1; (B) PA2; (C) PA3; (D) PA4; (E) PA5.

Furthermore, when the polymerization reactions between monomer **2** and aromatic diesters (**7–9**) were carried out, several conclusions could be obtained. First, when the *para* regioisomer was employed, the obtained polymer turned out to be more rigid. This result is consistent with those obtained in our previous work [26] and with other reports in the literature, which describe that *para* bonding confers additional stiffness and, consequently, increases the T_g of the polymer [36,37]. On the other hand, due to the steric hindrance of the *ortho*-substituted monomer, dimethyl phthalate (**9**), only very short chain oligomers were obtained with, as expected, a considerably lower T_g [38].

Figure 3 shows the second heating of the DSC thermograms of the eugenol-based PAs synthesized in this work, which exhibit the previously described T_g values. Furthermore, the complete absence of endothermic melting peaks can be observed, indicating, therefore, that the synthesized materials were completely amorphous like those obtained in our previous work [26]. The large size of the biobased monomer [39], the relatively large atomic radius of the sulfur atom [36], and, probably, the methoxy group of the aromatic ring from eugenol prevent systematic and effective packing, resulted in the lack of crystallinity [27].

As mentioned before, chavicol is another natural phenolic compound very similar to eugenol; indeed, the only difference between them is the absence of the methoxy moiety in chavicol. Our next goal at this point was to employ chavicol as starting material to synthesize biobased PAs analogous to those obtained with eugenol. In this way, in addition to expanding the range of natural compounds as viable starting substrates for the synthesis of polymeric materials, we could examine the influence of the methoxy group on the properties of the materials. With this purpose, it was necessary to carry out the synthesis of chavicol-derived diamine monomer **4** following an analogous methodology to that used with eugenol derivatives. Therefore, 1-allyl-4-allyloxybenzene (**3**) was prepared by reacting chavicol with allyl bromide via Williamson synthesis. Subsequently, the so-obtained 1-allyl-4-allyloxybenzene (**3**) was reacted through the photochemical click reaction with cysteamine hydrochloride, obtaining the monomer **4**. Taking into account the results previously obtained with eugenol, diethyl oxalate (**6**) and dimethyl terephthalate (**7**) were chosen as diester counterparts. As expected, the corresponding PAs **PA6** and **PA7** were successfully obtained (Scheme 3).



Scheme 3. Synthesis of the chavicol-derived PAs (**PA6** and **PA7**), starting from **4** and diester monomers (**6** or **7**).

Likewise, the polyamides derived from chavicol exhibited a complete absence of endothermic transitions in their DSC thermograms (Figure 4) and therefore remained fully amorphous. These observations indicate that the methoxy group present in eugenol is not the determining factor responsible for the lack of crystallization nucleation sites. However, significant differences were observed in the T_g values. Specifically, the polyamides derived from chavicol exhibited higher T_g s than their eugenol-derived counterparts. This behavior is plausibly associated with the lack of a methoxy substituent on the aromatic ring, which promotes a more efficient packing of the polymer chains and, as a result, leads to increased glass transition temperatures (Table 2).

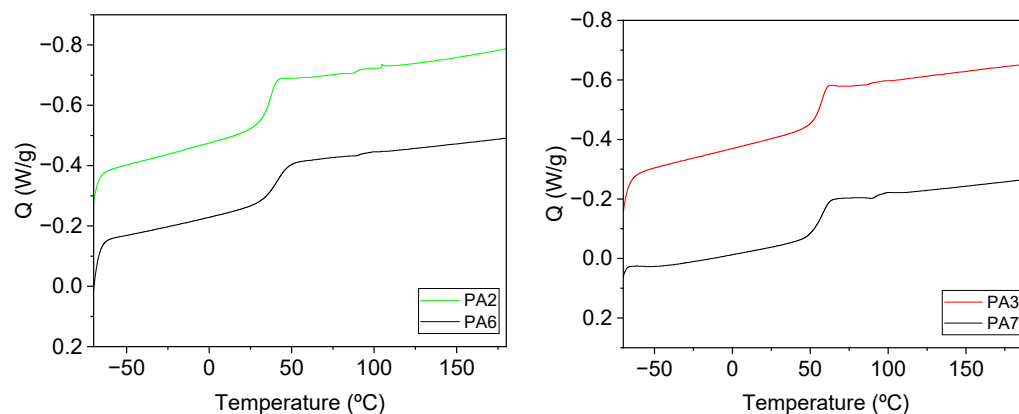


Figure 4. Comparison of DSC analysis of eugenol and chavicol-derived PAs.

Table 2. Properties of chavicol-derived semi-aromatic PAs.

Entry	Diester	M_n ^[a] (Da)	$\bar{D}$ ^[a]	T_g ^[b] (°C)	$T_d^{5\%}$ ^[c] (°C)	T_d^{max} ^[c] (°C)
PA6	6	-	-	41.4	278	357
PA7	7	156,000	3.50	56.3	295	392

M_n : Number average molecular weight; $\bar{D}$: dispersity = M_w/M_n ; T_g : glass transition temperatures; $T_d^{5\%}$: temperatures at which 5% weight loss occurred; T_d^{max} : temperatures at which the maximum rate of decomposition occurred; ^[a] Analyzed with the DMF GPC system; ^[b] Analyzed with DSC at 20 °C/min, second scan; ^[c] Analyzed in TGA system.

Continuing with the thermal properties, all the synthesized PAs, regardless the structure of the monomers, were thermally stable, having degradation temperatures of about 370 °C and with major losses of mass in the 250–450 °C range. In addition, it was observed that the degradation took place in a single step without any prior decomposition at lower temperatures (see Figure 5, the thermogram of PA1). Therefore, these materials presented a high thermal stability very similar to the semiaromatic PAs described in our previous work [26].

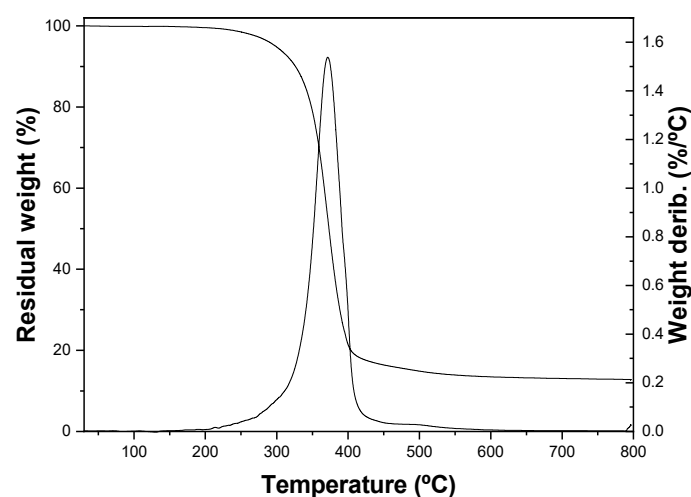


Figure 5. TGA analyses of PA1: Weight loss proportion by increasing the temperature; and derivative of the weight loss respect to the temperature when the temperature increases.

PAs are renowned for their ability to absorb water via hydrogen bonding with amide groups [40]. Indeed, the most commonly used Nylons, PA-6 and PA-66, can take in up to 10% moisture from humid air [7]. The absorbed water can act as a plasticizer and, in consequence, can influence negatively the mechanical and thermal properties of the material. In fact, it is generally accepted that the dimensional stability of PAs is poor due to this marked

hygroscopicity [9]. The water absorption rates of PAs are compiled in Table 3. In all cases, the relative amounts of absorbed water were less than 2%, and some values were even less than 1%. The presence of the bulkier sulfur atom and relatively hydrophobic sulfide linkages probably has a great impact on this reduced hygroscopicity [41,42]. Therefore, it can be concluded that the materials presented in this work exhibit high dimensional integrity in wet environments. In addition, all synthesized polyamides showed static water contact angles superior to 100°, indicating a pronounced hydrophobic surface character and aligning with the very low water absorption (<2%) measured for these materials. This correlation between increased contact angle and reduced hygroscopicity suggests that the overall polymer architecture effectively limits both surface wettability and bulk water uptake compared to conventional polyamides, which typically absorb more moisture [43].

Table 3. Water absorption measurements of the synthesized semi-aromatic PAs.

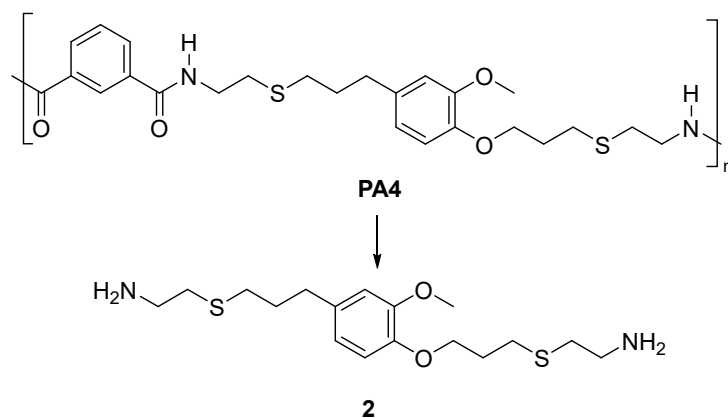
PA	Water Absorption (%) ^[a]	Water Contact Angle (°) ^[b]	
PA1	0.49 ± 0.39	103.7 ± 3.2	
PA2	1.91 ± 1.30	102.5 ± 6.9	
PA3	0.75 ± 0.29	107.6 ± 5.5	
PA4	1.65 ± 0.07	104.3 ± 3.7	
PA6	1.23 ± 0.49	106.6 ± 2.9	

^[a] Weighed on a microbalance; ^[b] Measured using a contact angle goniometer.

3.2. Chemical Degradation of Biobased PAs

As mentioned, figuratively speaking, the chemical structure of PAs has a double face. On the one hand, the amide group is responsible for the excellent properties of this type of materials [44]. However, on the other hand, the high chemical stability of this moiety makes degradation extremely difficult, which, considering the widespread use of these polymers, is a major environmental issue [7].

Thus, a study on the chemical degradability of the synthesized PAs was carried out. **PA4** was elected to perform the preliminary study because of the greater simplicity in NMR analysis (Scheme 4). **PA4** was subjected to different acidic and basic hydrolysis conditions (Figure 6). In all cases, at the beginning of the reaction, the PA remained completely insoluble in the aqueous phase, but it gradually dissolved. In fact, when NaOH 5 M was used and the reaction time was extended to 72 h, no insoluble polymeric residue remained. In these conditions, the percentage of recovered monomer was 66% relative to the initial PA mass. Considering that, in the case of **PA4**, the diamine counterpart in the repeating unit constituted 71% in mass, it could be concluded that, in these conditions, the **PA4** was almost completely (around 90%) hydrolyzed. The complete absence of other aromatic protons in the ¹H-NMR spectra, except those corresponding to the aromatic ring from eugenol, was decisive in concluding that all the amide bonds of the polymer had been hydrolyzed, thus recovering the diamine monomer (Figure 7). When a more diluted base was used or reaction times were shorter, the recovered monomer mass was considerably lower (Figure 7). Regarding acid hydrolysis, in addition to the lower amount of recovered mass, it is also important to note that NMR of the extract revealed the presence of other degradation products in addition to the monomer.



Scheme 4. Degradation reaction of **PA4** to obtain the monomer **2**.

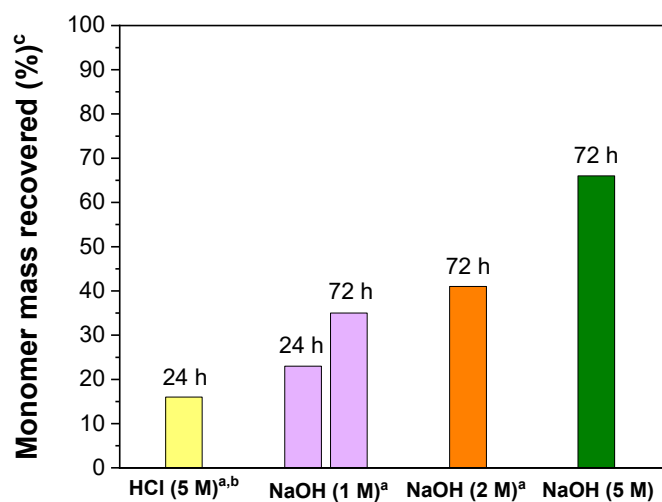


Figure 6. Bar chart comparison of the degraded weight of the **PA4** in different conditions. ^[a] The polymer did not totally dissolve; ^[b] The obtained monomer was considerably impure; ^[c] Recovered mass relative to the reacted PA.

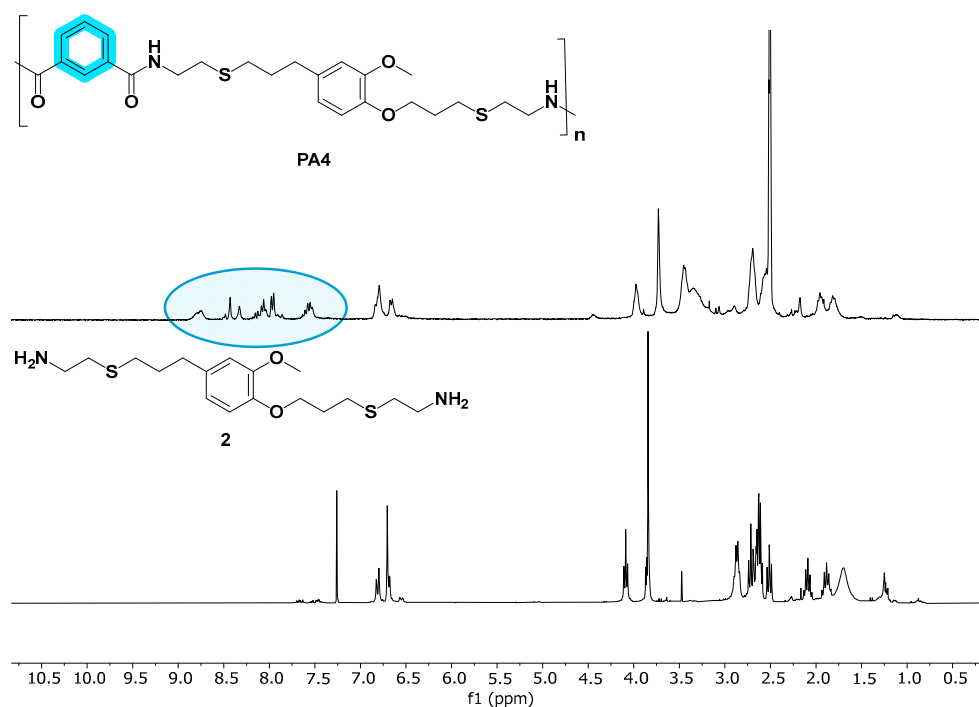


Figure 7. ¹H-NMR spectra of **PA4** and recovered monomer after chemical degradation.

Taking into account the excellent results obtained in the alkaline hydrolysis of **PA4**, the remaining synthesized PAs were then subjected to the same reaction conditions. Importantly, in all cases, the corresponding diamine monomer, **2** or **4**, was recovered. It is important to note that the effectiveness of the depolymerization reaction was dependent on the structure of the PA. Results are depicted in Figure 8.

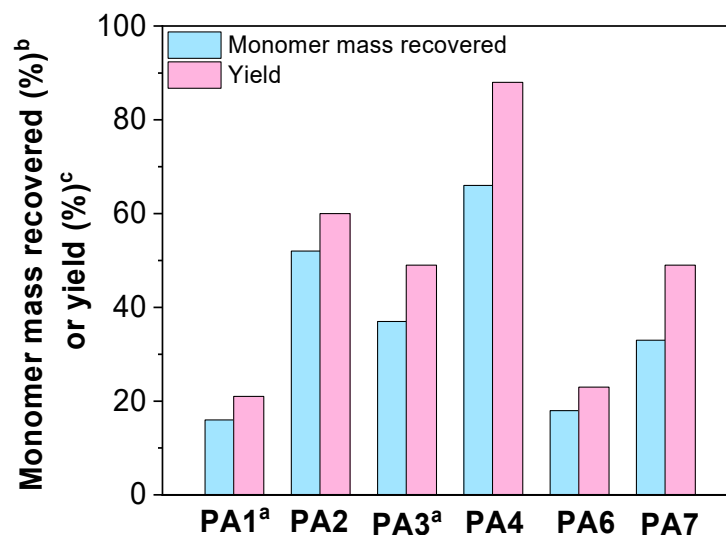


Figure 8. Bar chart comparison of the degradation of eugenol-derived PAs. ^[a] The polymer did not totally dissolve; ^[b] Recovered mass relative to the reacted PA mass; ^[c] Yield of the depolymerization reaction.

Regarding PAs derived from aliphatic diesters, the hydrolysis of the oxalate-derived PA (**PA2**) was more effective than the adipate-derived **PA1** hydrolysis. The electron-withdrawing effect of the adjacent carbonyl groups is probably responsible for the superior effectiveness of the basic hydrolysis reaction. Furthermore, greater entanglement of the polymer chains due to the longer aliphatic chain could hinder the access of water to the carbonyl moieties. Regarding aromatic-derived PAs, the following trend was observed: the higher the T_g , the lower the yield in the depolymerization reaction. That is, **PA3**, when compared with **PA4**, presented greater stiffness and higher T_g , revealing a lower yield in the alkaline hydrolysis reaction. Surely, the more orderly arrangement of the polymeric chains and, consequently, stronger interactions between them, triggered greater difficulties for water to carry out the nucleophilic attack over the carbonyl moieties of PAs. These results are also consistent with the water absorption data shown in Table 3.

In any case, alkaline hydrolysis has proven to be an effective method for the depolymerization of these bio-based PAs, thus aiding in their recyclability. In fact, in these conditions, the original monomer can be recovered with high to excellent yields, allowing its reuse for the synthesis of further PAs.

4. Conclusions

A new series of sulfur containing semi-aromatic PAs has been successfully synthesized starting from natural phenolic compounds eugenol and chavicol. The corresponding diamine monomer has been polycondensed with structurally different diesters, effectively yielding a new series of sulfur-containing biobased PAs. Concerning the properties of the so-obtained polyamides, all of them have been demonstrated to be amorphous materials with a wide range of T_g depending on the structure of the diester counterpart. All the synthesized materials have shown high hydrophobicity, excellent dimensional integrity, and thermal stability. It has been demonstrated that the bifunctional nature of chavicol—specifically, the presence of a phenolic hydroxyl group and the allyl substituent

on the aromatic ring—renders it a highly versatile molecular platform for the synthesis of monomers suitable for polycondensation processes. The comparative study revealed that the presence of the methoxy moiety in eugenol-derived monomers is not responsible for the complete absence of crystallinity in the resulting materials. However, it does exert a measurable influence on their thermal properties, indicating a subtle effect on chain packing and thermal transitions. From an environmental perspective, the biobased nature of the starting substrates, the solvent-free protocol, and the benign nature of the catalyst used in the polymerization are significant aspects. From a sustainability standpoint, it is acknowledged that certain reagents and solvents employed in the synthetic procedures are not fully aligned with green chemistry principles, and that some components still derive from fossil-based feedstocks. Nevertheless, it is important to emphasize that the overall bio-based content of the developed polyamides is relatively high, which contributes positively to their sustainability profile. The incorporation of renewable building blocks derived from natural phenolic compounds reduces reliance on petrochemical resources. Importantly, the demonstrated recoverability of the diamine monomer through controlled degradation constitutes a significant advantage, as it supports a circular materials approach and enhances resource efficiency.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/polym18050589/s1>. Figure S1: ^1H -NMR spectra of **3**; Figure S2: ^{13}C -NMR spectra of **3**; Figure S3: ^1H -NMR spectra of **4**; Figure S4: ^{13}C -NMR spectra of **4**; Figure S5: ^1H -NMR spectra of **PA1**; Figure S6: ^{13}C -NMR spectra of **PA1**; Figure S7: FT-IR spectra of **PA1**; Figure S8: FT-IR spectra of **PA2**; Figure S9: ^1H -NMR spectra of **PA3**; Figure S10: ^{13}C -NMR spectra of **PA3**; Figure S11: FT-IR spectra of **PA3**; Figure S12: ^1H -NMR spectra of **PA4**; Figure S13: ^{13}C -NMR spectra of **PA4**; Figure S14: FT-IR spectra of **PA4**; Figure S15: ^1H -NMR spectra of **PA5**; Figure S16: ^1H -NMR spectra of **PA5**; Figure S17: FT-IR spectra of **PA5**; Figure S18: FT-IR spectra of **PA6**; Figure S19: FT-IR spectra of **PA7**; Figure S20: TGA analysis of **PA1-5**; Figure S21: TGA analysis of **PA6** and **PA7**.

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Abbreviations

The following abbreviations are used in this manuscript:

BAPO	Phenyl- <i>bis</i> (2,4,6-trimethylbenzoyl)-phosphine oxide
DMF	<i>N,N</i> -dimethylformamide
DSC	Differential scanning calorimetry
EtOAc	Ethyl acetate
EtOH	Ethanol

FT-IR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
MeOH	Methanol
NMR	Nuclear magnetic resonance
PA	Polyamide
PE	Polyester
TBD	1,5,7-triazabicyclo[4.4.0]dec-3-ene
T _g	Glass transition temperature
TGA	Thermogravimetric analysis

References

- Winnacker, M.; Rieger, B. Bio-Based Polyamide 56: Recent Advances in Basic and Applied Research. *Macromol. Rapid Commun.* **2016**, *37*, 1391–1413. [\[CrossRef\]](#)
- Arai, K.; Tsutsuba, T.; Wasano, T.; Hirose, Y.; Tachibana, Y.; Kasuya, K.I. Synthesis of Biobased Polyamides Containing a Bifuran Moiety and Comparison of Their Properties with Those of Polyamides Based on a Single Furan Ring. *ACS Appl. Polym. Mater.* **2023**, *5*, 3866–3874. [\[CrossRef\]](#)
- Ali, M.A.; Kaneko, T. Syntheses of Aromatic/Heterocyclic Derived Bioplastics with High Thermal/Mechanical Performance. *Ind. Eng. Chem. Res.* **2019**, *58*, 15958–15974. [\[CrossRef\]](#)
- Porfyrus, A.; Vouyiouka, S.; Papaspyrides, C.; Rulkens, R.; Grolman, E.; Vanden Poel, G. Investigating Alternative Routes for Semi-Aromatic Polyamide Salt Preparation: The Case of Tetramethylenediammonium Terephthalate (4T Salt). *J. Appl. Polym. Sci.* **2016**, *133*, 42987. [\[CrossRef\]](#)
- Khedr, M.S.F. Bio-Based Polyamide. *Phys. Sci. Rev.* **2023**, *8*, 827–847. [\[CrossRef\]](#)
- Senthilkannan, S.; Miguel, M.; Gardetti, A. *Sustainable Textiles: Production, Processing, Manufacturing & Chemistry Sustainability in the Textile and Apparel Industries Sourcing Synthetic and Novel Alternative Raw Materials*; Springer: Berlin/Heidelberg, Germany, 2021.
- Ali, M.A.; Okajima, M.; Kanek, T. Recycling and Environmental Degradation of Polyamides. In *Composites: Modeling and Manufacturing*; CRC Press: Boca Raton, FL, USA, 2024; Volume 29, pp. 180–192. [\[CrossRef\]](#)
- Magnin, A.; Entzmann, L.; Bazin, A.; Pollet, E.; Avérous, L. Green Recycling Process for Polyurethane Foams by a Chem-Biotech Approach. *ChemSusChem* **2021**, *14*, 4234–4241. [\[CrossRef\]](#) [\[PubMed\]](#)
- Rist, M.; Greiner, A. Synthesis, Characterization, and the Potential for Closed Loop Recycling of Plant Oil-Based PA X.19 Polyamides. *ACS Sustain. Chem. Eng.* **2022**, *10*, 16793–16802. [\[CrossRef\]](#)
- Van Schoubroeck, S.; Van Dael, M.; Van Passel, S.; Malina, R. A Review of Sustainability Indicators for Biobased Chemicals. *Renew. Sustain. Energy Rev.* **2018**, *94*, 115–126. [\[CrossRef\]](#)
- Morales-Cerrada, R.; Molina-Gutierrez, S.; Lacroix-Desmazes, P.; Caillol, S. Eugenol, a Promising Building Block for Biobased Polymers with Cutting-Edge Properties. *Biomacromolecules* **2021**, *22*, 3625–3648. [\[CrossRef\]](#) [\[PubMed\]](#)
- Huang, W.; Zhai, J.; Zhang, C.; Hu, X.; Zhu, N.; Chen, K.; Guo, K. 100% Bio-Based Polyamide with Temperature/Ultrasound Dually Triggered Reversible Cross-Linking. *Ind. Eng. Chem. Res.* **2020**, *59*, 13588–13594. [\[CrossRef\]](#)
- Diaz-galbarriatu, M.; Sánchez-bodón, J.; Hernández-laviña, E.; Vilas-vilela, J.L.; Moreno-benítez, I. Biobased Polyamides: A Journey from the Biomass Towards Cutting Edge Materials. *Polymers* **2025**, *17*, 2599. [\[CrossRef\]](#)
- Wu, Y.; Enomoto, Y.; Masaki, H.; Iwata, T. Synthesis of Polyamides from Sugar Derived D-Glucaric Acid and Xylylenediamines. *J. Appl. Polym. Sci.* **2019**, *136*, 47255. [\[CrossRef\]](#)
- Louisy, E.; Khodyrieva, V.; Olivero, S.; Michelet, V.; Mija, A. Use of Limonene Epoxides and Derivatives as Promising Monomers for Biobased Polymers. *Chempluschem* **2022**, *87*, e202200190. [\[CrossRef\]](#)
- Kleybolte, M.M.; Zainer, L.; Liu, J.Y.; Stockmann, P.N.; Winnacker, M. (+)-Limonene-Lactam: Synthesis of a Sustainable Monomer for Ring-Opening Polymerization to Novel, Biobased Polyamides. *Macromol. Rapid Commun.* **2022**, *43*, e2200185. [\[CrossRef\]](#)
- Winnacker, M. Polyamides Derived from Terpenes: Advances in Their Synthesis, Characterization and Applications. *Eur. J. Lipid Sci. Technol.* **2023**, *125*, 2300014. [\[CrossRef\]](#)
- Gaddam, S.K.; Boddu, V.R.; Boga, K.; Bhatt, H.K.; Das, P.; Pinjari, S.D.; Qi, X.; Gaddam, R.R.; Arukula, R. Maleinized Vegetable Oil: A Green Approach for Sustainable Polyamide Composites. *Polym. Adv. Technol.* **2025**, *36*, 70069. [\[CrossRef\]](#)
- Park, M.; Hong, S.J.; Kim, N.K.; Shin, J.; Kim, Y.W. Vegetable Oil-Derived Polyamide Multiblock Copolymers toward Chemically Recyclable Pressure-Sensitive Adhesives. *ACS Sustain. Chem. Eng.* **2023**, *11*, 10095–10107. [\[CrossRef\]](#)
- Zhang, C.; Garrison, T.F.; Madbouly, S.A.; Kessler, M.R. Progress in Polymer Science Recent Advances in Vegetable Oil-Based Polymers and Their Composites. *Prog. Polym. Sci.* **2017**, *71*, 91–143. [\[CrossRef\]](#)

21. Ye, Z.; Liu, Y.; Chen, W.; Yu, Z.; Fang, Y.; Zhou, X.; He, Y.; Wang, Y.; Tang, Z. Bio-Based, Closed-Loop Chemical Recyclable Aromatic Polyamide from 2,5-Furandicarboxylic Acid: Synthesis, High Performances, and Degradation Mechanism. *Eur. Polym. J.* **2024**, *210*, 112935. [\[CrossRef\]](#)
22. Huang, J.; Fu, S.; Gan, L. Lignin-Modified Materials and Their Applications. In *Lignin Chemistry and Applications*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 181–210. ISBN 9780128139417.
23. Llevot, A.; Grau, E.; Carlotti, S.; Grelier, S.; Cramail, H. From Lignin-Derived Aromatic Compounds to Novel Biobased Polymers. *Macromol. Rapid Commun.* **2016**, *37*, 9–28. [\[CrossRef\]](#)
24. Yang, C.; Shen, T.; Tan, Z.; Zhuang, W.; Zhu, C.; Li, M.; Ying, H. Lignin Modification for In-Situ Cured Lignin-Maleyl Network in Semi-Crystalline Polyamide/Lignin Shape Memory Composites. *Ind. Crops Prod.* **2023**, *197*, 116665. [\[CrossRef\]](#)
25. Karunarathna, M.S.; Lauer, M.K.; Thiounn, T.; Smith, R.C.; Tennyson, A.G. Valorisation of Waste to Yield Recyclable Composites of Elemental Sulfur and Lignin. *J. Mater. Chem. A Mater.* **2019**, *7*, 15683–15690. [\[CrossRef\]](#)
26. Diaz-Galbarriatu, M.; Sánchez-Bodón, J.; Laza, J.M.; Moreno-Benítez, I.; Vilas-Vilela, L. Amorphous Sulfur Containing Biobased Polyamides through a Solvent-Free Protocol: Synthesis and Scope. *Eur. Polym. J.* **2025**, *229*, 113864. [\[CrossRef\]](#)
27. Hu, K.; Zhao, D.; Wu, G.; Ma, J. Synthesis and Properties of Polyesters Derived from Renewable Eugenol and α,ω -Diols via a Continuous Overheating Method. *R. Soc. Chem.* **2015**, *6*, 7138–7148. [\[CrossRef\]](#)
28. Dumas, L.; Bonnaud, L.; Olivier, M.; Poorteman, M.; Dubois, P. Chavicol Benzoxazine: Ultrahigh Tg Biobased Thermoset with Tunable Extended Network. *Eur. Polym. J.* **2016**, *81*, 337–346. [\[CrossRef\]](#)
29. Feng, Y.; Li, X.; Ma, T.; Li, Y.; Ji, D.; Qin, H.; Fang, Z.; He, W.; Guo, K. Preparation of Chemically Recyclable Bio-Based Semi-Aromatic Polyamides Using Continuous Flow Technology under Mild Conditions. *Green Chem.* **2024**, *26*, 5556–5563. [\[CrossRef\]](#)
30. Schilling, C.; Weiss, S. A Roadmap for Industry to Harness Biotechnology for a More Circular Economy. *N. Biotechnol.* **2021**, *60*, 9–11. [\[CrossRef\]](#)
31. Gómez Isa, F. Sustainable Development Goals (SDG): Towards a New Intra-and Inter-Generational Social Contract. *Estud. Deusto* **2015**, *70*, 191–224. [\[CrossRef\]](#)
32. Modjinou, T.; Versace, D.; Abbad-Andallousi, S.; Bousserhine, N.; Dubot, P.; Langlois, V.; Renard, E. Antibacterial and Antioxidant Bio-Based Networks Derived from Eugenol Using Photo-Activated Thiol-Ene Reaction. *React. Funct. Polym.* **2016**, *101*, 47–53. [\[CrossRef\]](#)
33. Zhang, Y.; Zhai, M.; Ma, F.; Li, Y.; Lyu, B.; Liu, T.; Gao, Z.; Wang, L.; Vincent, D.; Kessler, M.R. Fully Eugenol-Based Epoxy Thermosets: Synthesis, Curing, and Properties. *Macromol. Mater. Eng.* **2022**, *307*, 2100833. [\[CrossRef\]](#)
34. Kim, J.G.; Lee, G.S.; Lee, A. Triazabicyclodecene: A Versatile Catalyst for Polymer Synthesis. *J. Polym. Sci.* **2024**, *62*, 42–91. [\[CrossRef\]](#)
35. Chen, M.; Zhang, G.; Wang, R. Synthesis of Poly(Butylene Succinate) Catalyzed by Tetrabutyl Titanate and Supported by Activated Carbon. *Materials* **2025**, *18*, 1315. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Nguyen, P.H.; Spoljaric, S.; Seppälä, J. Renewable Polyamides via Thiol-Ene ‘Click’ Chemistry and Long-Chain Aliphatic Segments. *Polymer* **2018**, *153*, 183–192. [\[CrossRef\]](#)
37. Cureton, L.S.T.; Napadensky, E.; Annunziato, C.; La Scala, J.J. The Effect of Furan Molecular Units on the Glass Transition and Thermal Degradation Temperatures of Polyamides. *J. Appl. Polym. Sci.* **2017**, *134*, 45514. [\[CrossRef\]](#)
38. Tsuji, K.; Saito, M.; Tani, T. Ionization Potentials of Phenylenediamines and Steric Effect in the Ortho Isomer. *Denki Kagaku* **1973**, *41*, 688–692. [\[CrossRef\]](#)
39. Jasinska, L.; Villani, M.; Wu, J.; Van Es, D.; Klop, E.; Rastogi, S.; Koning, C.E. Novel, Fully Biobased Semicrystalline Polyamides. *Macromolecules* **2011**, *44*, 3458–3466. [\[CrossRef\]](#)
40. Van Velthoven, J.L.J.; Gootjes, L.; Noordover, B.A.J.; Meuldijk, J. Bio-Based, Amorphous Polyamides with Tunable Thermal Properties. *Eur. Polym. J.* **2015**, *66*, 57–66. [\[CrossRef\]](#)
41. El-Hibri, M.J. Polymers Containing Sulfur, Polysulfones. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley: Hoboken, NJ, USA, 2000; pp. 1023–1046.
42. Negi, Y.S.; Razdan, U.; Saran, V. Soluble Aromatic Polyamides and Copolyamides. *J. Macromol. Sci. Part C Polym. Rev.* **1999**, *39*, 391–403. [\[CrossRef\]](#)
43. Li, J.F.; Ku, X.L.; Li, Y.D.; Ran, Y.; Zeng, J.B. Biobased Polyamides with Polyethylene-like Properties through Catalyst-Free Polycondensation. *ACS Sustain. Chem. Eng.* **2025**, *13*, 13492–13500. [\[CrossRef\]](#)
44. Li, S.; Jiang, S.; Gong, S.; Ma, S.; Yang, H.; Pan, K.; Deng, J. Preparation Methods, Performance Improvement Strategies, and Typical Applications of Polyamide Foams. *Ind. Eng. Chem. Res.* **2021**, *60*, 17365–17378. [\[CrossRef\]](#)

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