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**Microbial pABA Enables Renewable PBA Whiskers with Enhanced Crystallinity,
Thermal Stability, and Surface Smoothness via a Biosynthetic Pathway**

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Abstract

The development of fully renewable high-performance aramids has been limited by the absence of biosourced aromatic monomers suitable for A–B type polymerization. Here, we report the synthesis of poly(p-benzamide) (PBA) whiskers derived entirely from microbially produced p-aminobenzoic acid (pABA), achieving 100% biogenic carbon content verified by radiocarbon analysis. The high chemical purity of the biosynthesized monomer enables PBA whisker formation via phase-transition-driven polymerization under conditions identical to those used for conventional petroleum-derived monomers. The resulting bio-based whiskers maintain the same orthogonally oriented single-crystal architecture as their petroleum-derived analogues, while exhibiting slightly higher crystallinity, marginally improved thermal stability, and smoother faceted surfaces. These subtle enhancements may originate from differences in monomer synthesis routes, particularly the reduced impurity levels inherent to microbial production processes. Although these structural refinements do not significantly alter dispersion behavior, they provide a cleaner crystalline morphology advantageous for probing fundamental structure–property relationships. By integrating microbial monomer production with established aramid crystallization pathways, this work demonstrates that complete renewable sourcing can be achieved without compromising material performance, while offering modest improvements linked to biosynthetic monomer origins.

Keywords: bio-derived aramid; microbial p-aminobenzoic acid (pABA); poly(p-benzamide) whiskers; phase-transition polymerization; crystal surface smoothness; sustainable high-performance materials

1. Introduction

Sustainable high-performance polymers are pivotal to decarbonizing materials-intensive sectors, yet aramid fibers—among the most widely used high-modulus polymers—still depend on fossil-derived monomers, thereby imposing life-cycle burdens through greenhouse-gas emissions and non-renewable resource consumption. A durable transition thus requires renewable feedstocks without sacrificing the hallmark thermal and mechanical performance of aramids [1,2]. Within this context, bio-based aramids have gained traction as a route to improved resource circularity, but most published efforts rely on AA–BB monomer pairs in which only the diacid component can be readily sourced from biomass (e.g., FDCA [3,4] or bio-derived terephthalic acid), while the aromatic diamine remains petrochemical due to biosynthetic bottlenecks [3–6,7,8]. As a result,

bio-based content typically plateaus at ~50–70%, limiting genuine life-cycle impact [5,7,8].

The core challenge originates from the scarcity of natural routes to positional-specific aromatic diamines (e.g., p-phenylenediamine and m-phenylenediamine), and from strict enzyme selectivity, narrow substrate scopes and intermediate toxicity in microbial pathways for multi-amino-substituted aromatics [6]. In contrast, A–B type monomers offer a conceptual bypass to the diamine bottleneck if the single-functionalized aromatic precursor can be produced renewably at meaningful scale.

Here we address this gap by establishing a materials platform for fully bio-derived aramids using poly(4-benzamide) (PBA) as an archetype. The A–B monomer, p-aminobenzoic acid (pABA), has been microbially produced in engineered *Escherichia coli* and can, in principle, enable complete renewable sourcing of the aramid backbone [9,10]. Historically, PBA exhibited excellent fiber properties and a well-defined crystalline structure [11,12], yet its potential as a fully bio-derived high-performance polymer and as a self-assembled single-crystal reinforcement has remained unexplored.

Building on our recent findings, we show that PBA undergoes phase-change-driven polymerization [13,14] into prismatic single-crystal whiskers [15] that reproduce the orthogonal chain orientation reported previously for PBA whiskers synthesized from conventional (petroleum-derived) monomers [16]. Under identical processing conditions, the bio-derived whiskers not only reproduce the crystallinity, thermal stability, and dispersion behavior of their petroleum-derived counterparts but also exhibit slightly higher crystallinity, marginally improved thermal stability, and smoother faceted surfaces—differences that may plausibly arise from variations in monomer synthesis routes, particularly reduced impurity levels associated with microbial production. These observations are supported throughout by the same characterization framework as in prior work [16] and by radiocarbon verification of renewable content in the microbial monomer [17].

In this bio-derived context, we frame practical guidance that integrates microbial A–B monomer production (pABA), radiocarbon verification of renewable content, and phase-transition polymerization windows applicable to PBA and potentially other A–B aramids. Additionally, the bio-derived PBA whiskers exhibit reduced residual impurities and smoother surfaces; while this did not measurably change dispersion performance under our conditions, it offers a cleaner platform for probing interfacial chemistry in composites.

This study therefore unifies two sustainability levers at the molecular and microstructural scales: (1) complete renewable sourcing via A–B monomers accessible

to microbial synthesis (pABA for PBA) [9,10], which circumvents the diamine bottleneck that constrains AA–BB systems [5–8]; and (2) demonstration that self-assembled single-crystal whiskers with the previously reported orthogonal architecture can be reproduced from fully bio-derived feedstocks, preserving functional parity with the recently-reported system [16].

2. Experimental

2.1 Material

Synthesis of pABA

Microbial synthesis of p-aminobenzoic acid (pABA)

pABA was produced via microbial fermentation following the procedure reported by Koma *et al.*[9]. The *aroG^{br}*, *pabA*, *pabB*, and *pabC* genes were assembled on plasmid vectors and transformed into *Escherichia coli*. The recombinant strain was cultivated in a 5-L bioreactor containing M9-based medium supplemented with 5 g L⁻¹ glucose, 5 g L⁻¹ yeast extract, and the appropriate antibiotics. Protein expression was induced with 0.5 mM IPTG. Additional feedings of glucose (10 g L⁻¹) and (NH₄)₂SO₄ (1 g L⁻¹) were supplied every 8 h. After 72 h of fermentation, the culture broth was collected, and pABA was purified by recrystallization from water.

Chemical purity analysis of pABA

The chemical purity of pABA was determined by high-performance liquid chromatography (HPLC). Analyses were performed using a Shimadzu LC-20AD system equipped with a reverse-phase C18 column. The mobile phase consisted of an aqueous solution containing sodium 1-octanesulfonate (5 mM), KH₂PO₄ (10 mM), and H₃PO₄ (0.2 wt%), mixed with methanol at a 40:60 (w/w) ratio. The flow rate was set to 1 mL min⁻¹, and detection was conducted at 203 nm. The purified pABA exhibited a chemical purity exceeding 95%.

Radiocarbon analysis for biogenic carbon content of pABA

The biomass-derived carbon content of pABA was assessed according to ASTM D6866. Samples were ground to a fine powder, dried at 105 °C for 24 h, and approximately 1 g of material was combusted in sealed quartz tubes under an oxygen atmosphere. The resulting CO₂ was purified and analyzed by accelerator mass spectrometry (AMS) to determine the ¹⁴C/¹²C ratio. The biogenic carbon percentage was calculated by comparison with the modern reference standard (100% biogenic carbon). The measured ¹⁴C content corresponded to 100% biogenic carbon, with an analytical uncertainty of ±0.5% based on duplicate measurements. In ASTM D6866, the biogenic carbon fraction is determined by comparing the sample's radiocarbon signature to a contemporary

“modern” reference (defined as 100% biogenic carbon), enabling direct quantification of biomass-derived content.

Synthesis of the 4-acetamidobenzoic acid (4-ABA)

A 200 mL two-neck round-bottom flask equipped with a magnetic stir bar and a three-way stopcock was charged with 4-aminobenzoic acid under a nitrogen atmosphere. Anhydrous acetic anhydride was added, and the resulting mixture was stirred at 70 °C (oil bath temperature) for 20 h. After completion, the reaction was cooled to room temperature and poured into 150 mL of purified water. The suspension was stirred for 120 min, and the precipitate was collected by filtration, washed with purified water (5×50 mL), and dried under reduced pressure at 60 °C using a rotary oil pump to give a brown solid (2.7 g).

Purification and Analysis of the 4-acetamidobenzoic acid (4-ABA)

The crude brown solid (2.7 g) was dissolved in glacial acetic acid (55 g) at 80 °C and allowed to stand at room temperature. The precipitate was collected by filtration, washed with acetic acid (5×25 mL), and dried under reduced pressure at 80 °C (oil bath; rotary oil pump) to yield the first crop of crystals (light brown solid; 1.1 g). The combined filtrate and washings were concentrated to dryness and dissolved in glacial acetic acid (35 g). After standing at room temperature, the precipitate was collected by filtration, washed with acetic acid (5×15 mL), and dried under reduced pressure at 80 °C to afford the second crop of crystals (light brown solid; 0.5 g). NMR analysis of both crops confirmed the formation of the desired product. Approximately 1% residual acetic acid from the recrystallization solvent was detected (Fig. S1).

Synthesis of poly(p-benzamide) (PBA) whiskers via phase-change-polymerization methods

Poly(p-benzamide) (PBA) whiskers were synthesized via a phase-change polymerization process using 4-acetamidobenzoic acid as the monomer [16]. A 500 mL three-neck flask equipped with a mechanically stirred mantle heater was charged with 4-acetamidobenzoic acid (2.0g) and dibenzyltoluene (200 mL). The mixture was stirred at 300 rpm and heated to 230 °C, where it was held for 10 min until complete dissolution of the monomer was visually confirmed. Stirring was then stopped, and the temperature was increased to 340 °C and maintained for 8 h to allow polymerization and simultaneous crystal growth, resulting in the formation of high-aspect-ratio whiskers.

After completion of the reaction, the solid product was collected by filtration and washed thoroughly with acetone (500 mL) to remove unreacted monomer and byproducts. The obtained whiskers were subsequently dried under vacuum at 200 °C for 10 h before further characterization.

2.2 Method

2.2.1 Morphological and Crystallinity Analysis

Polarized optical microscopy (POM) was performed using a Nikon Eclipse LV100POL microscope to observe birefringence and overall morphology. Particle size distribution was measured via laser diffraction using a HORIBA LA-960 system.

Phase information of the PBA whisker powder was further confirmed via PXRD using a Rigaku RINT-TTR3 diffractometer with Cu K α radiation, operated at 40 kV – 40 mA and room temperature. To correlate morphological features with crystallographic orientation, selected-area electron diffraction (SAED) patterns were collected using a JEOL JEM-2100F transmission electron microscope operated at 200 kV. Low-dose conditions were employed with a small beam size (spot size 3), the electron beam was fully spread to a diameter $\sim 10\text{ }\mu\text{m}$ to minimize the irradiation damage of the crystals during observation. The SAED patterns were taken with a selected-area aperture $\sim 5\text{ }\mu\text{m}$ in diameter, with exposure time 0.3s.

2.2.2 Thermal Analysis

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed using a Mettler Toledo DSC1 and a Netzsch STA449 F1 instrument, respectively. DSC scans were conducted under nitrogen atmosphere from room temperature to 400 °C at heating/cooling rate 5 °C min⁻¹, for the PBA whisker samples. TGA measurements were carried out under argon atmospheres from 25 °C up to 700 °C at heating/cooling rate 10 °C min⁻¹.

2.2.3 AFM Analysis of Surface Morphology of PBA Whiskers

Atomic force microscopy (AFM) was employed to characterize the surface morphology of poly(p-benzamide) (PBA) whiskers. Samples were prepared by dispersing the whiskers in IPA via mild sonication, followed by drop-casting onto cleaned ITO-coated glass substrates and drying under ambient conditions. AFM imaging was conducted in non-contact mode using a Hitachi AFM5100N system equipped with silicon cantilevers. The resulting images revealed prismatic whiskers with typical dimensions of approximately 17 μm in length, 1 μm in width, and 0.5 μm in thickness.

3. Results

3.1 Microbial synthesis of monomer precursor p-aminobenzoic acid (pABA)

Engineered *E. coli* overexpressing *aroG*^{br}, *pabA*, *pabB*, and *pabC* genes produced p-

aminobenzoic acid (pABA) via microbial fermentation (Fig. 1a) [9]. The isolated pABA exhibited >95% chemical purity after recrystallization (Fig. 1b). Radiocarbon analysis (ASTM D6866 [17]) confirmed that the pABA contained 100% biogenic carbon (Fig. 2).

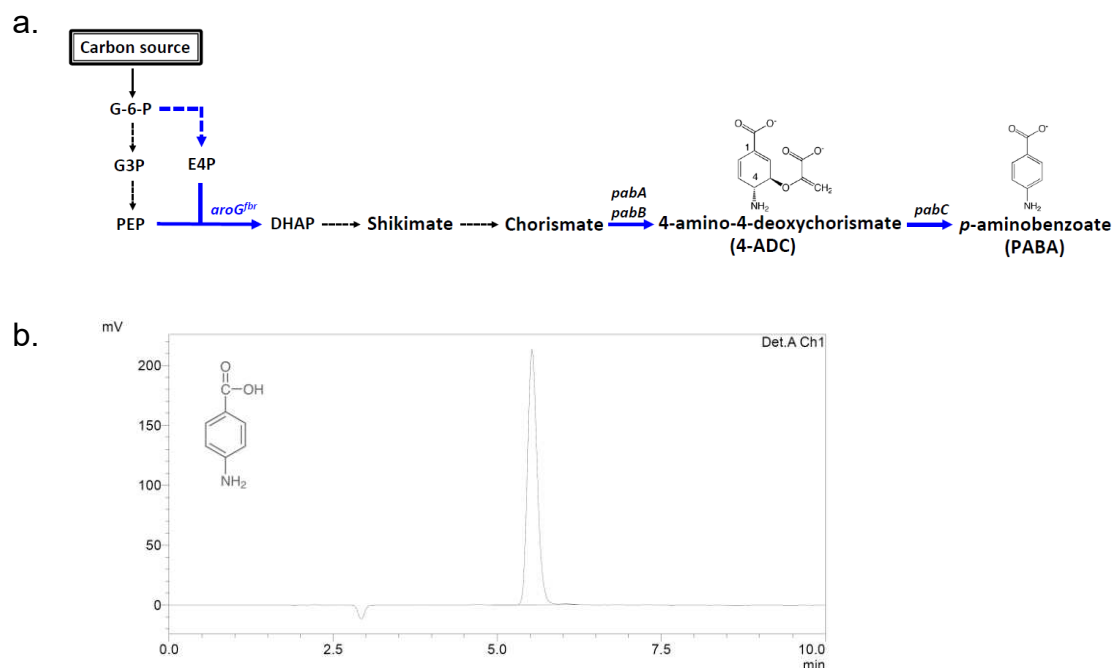


Fig. 1 a Microbial synthesis of p-aminobenzoic acid (pABA) by engineered *E. coli* b. Its chemical purity analysis

Result		100% Biobased Carbon Content (as a fraction of total organic carbon)
Laboratory Number	Beta-796913	
Percent modern carbon (pMC)	100.66 +/- 0.20 pMC	
Atmospheric adjustment factor (REF)	99.1; = pMC/0.991	



Fig. 2 Radiocarbon verification by ASTM D6866 [17] of renewable content in the microbial monomer

3.2 Monomer synthesis of 4-acetamidobenzoic acid (4-ABA)

Acetylation of pABA yielded crystalline 4-acetamidobenzoic acid in two crops (1.1 g and 0.5 g). NMR confirmed formation of the target compound, with ~1% residual acetic acid from the recrystallization solvent (Fig. S1) [18].

Synthesis of poly(p-benzamide) (PBA) whiskers via phase-change polymerization

4-Acetamidobenzoic acid underwent polymerization and crystallization at 340 °C for 8 h under controlled conditions to afford high-aspect-ratio PBA whiskers [16]. The whiskers were recovered by filtration, washed with acetone, and dried under vacuum at 200 °C for 10 h.

Morphology and crystallinity of bio-based PBA whiskers

POM imaging revealed that bio-based PBA whiskers exhibited high aspect ratios (Fig. 3).

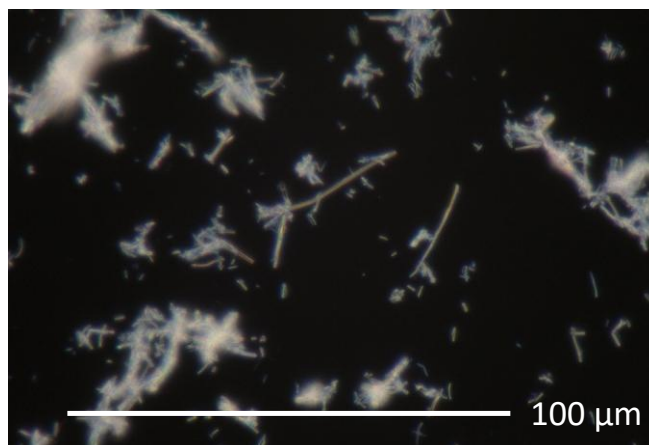


Fig. 3 Morphology of bio-based poly(p-benzamide) (PBA) whiskers observed by polarized optical microscopy (POM), showing high aspect ratios

Their aspect ratio was comparable to that of whiskers prepared from petroleum-derived monomers under identical conditions (Fig. S2) [16]. PXRD patterns showed sharp peaks assigned to the (110) and (200) planes, indicating high crystallinity (Fig. 4). When whiskers from petroleum-derived monomers were also plotted in Fig. 4, the bio-based whiskers exhibited even higher crystallinity under the same preparation conditions.

The crystal structure is identical to that of the petroleum-derived whiskers. Transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) further corroborate that the polymer chains are oriented perpendicular to the whisker long axis (Fig. S3) [16].

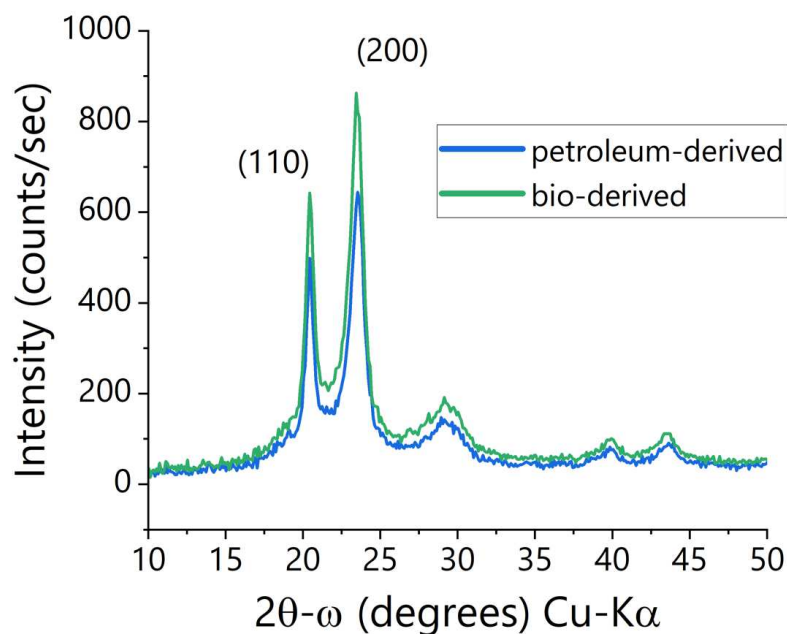


Fig. 4 Powder X-ray diffraction (PXRD) patterns of bio-based and petroleum-derived PBA whiskers. The bio-based whiskers exhibit sharper diffraction peaks corresponding to the (110) and (200) planes, demonstrating higher crystallinity compared with the petroleum-derived counterparts.

3.3 Thermal stability of bio-based PBA whiskers

DSC showed no glass transition or melting behavior up to 400 °C, indicating a stable crystalline phase (Fig. S4). This result was comparable to that of whiskers prepared from petroleum-derived monomers under identical conditions [16].

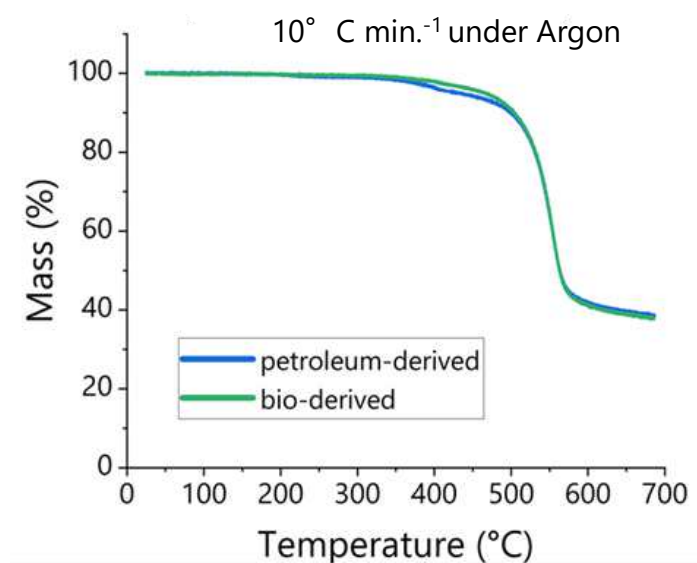


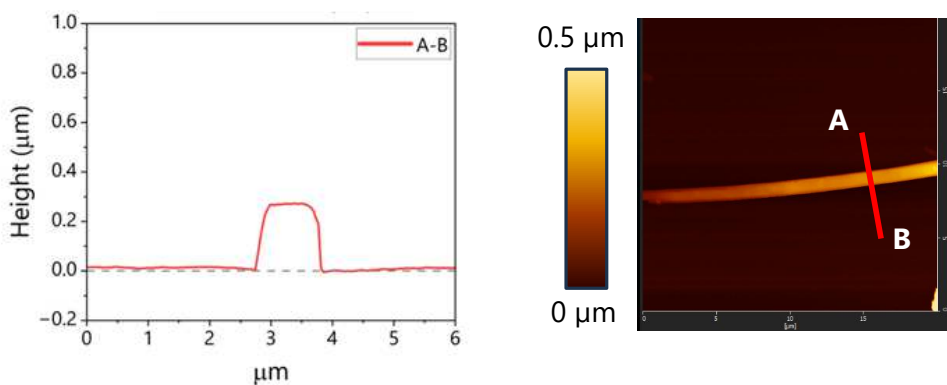
Fig. 5 Thermogravimetric analysis (TGA) profiles of bio-based and petroleum-derived PBA whiskers. The bio-based whiskers show no detectable decomposition before 400 °C and exhibit a slightly higher onset temperature than the petroleum-derived counterparts

TGA revealed decomposition onsets near 450 °C, with residual masses exceeding 60% under argon (Fig. 5). The bio-based whiskers exhibited a slightly higher onset temperature compared with those prepared from petroleum-derived monomers (Fig. S5), which is attributed to their higher crystallinity as shown in Fig. 4. Notably, the petroleum-derived whiskers show a small additional mass-loss feature around ~350 °C that is not observed for the biobased sample under identical conditions.

3.4 AFM analysis of surface morphology

AFM observations confirmed the presence of well-defined prismatic whiskers with characteristic faceted surfaces (Fig. 6a). Compared with whiskers prepared from petroleum-derived monomers under identical conditions, the surface was significantly smoother (Fig. 6b).

a.



b.

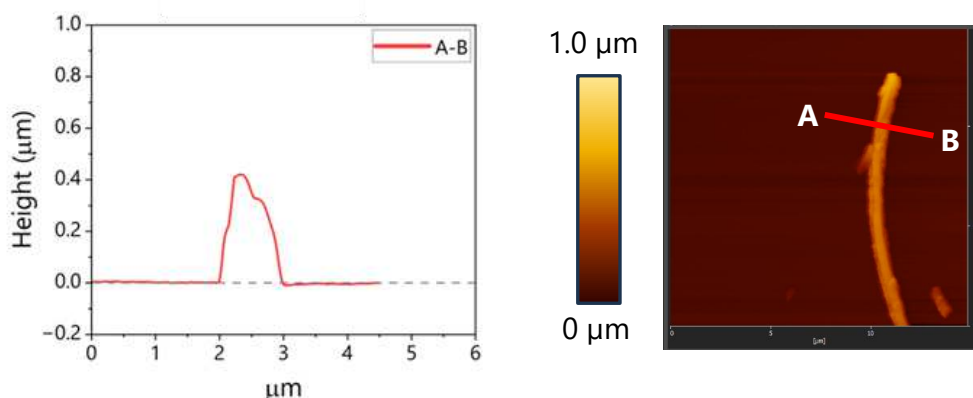


Fig. 6 Atomic force microscopy (AFM) images of PBA whiskers

a Bio-based whiskers exhibiting well-defined prismatic morphology with characteristic faceted surfaces
 b Comparison with whiskers prepared from petroleum-derived monomers under identical conditions, showing that the bio-based whiskers possess significantly smoother surfaces

4. Discussion

Although the crystalline lattice matches the previously reported PBA whiskers, the present study reveals previously unreported improvements in crystallinity, surface smoothness, and decomposition behavior, originating from the high chemical purity of biosynthesized pABA. The renewable production of pABA with >95% purity and 100% biogenic carbon confirms that microbial biosynthesis provides a fully renewable monomer supply. This demonstrates that bio-sourced pABA can serve as a practical feedstock for sustainable aramid production.

Trace impurities (<1% acetic acid) in 4-ABA indicate that the monomer purification process is sufficient for phase-change polymerization. The preservation of monomer purity ensures consistent polymer growth kinetics and minimizes defect formation during whisker crystallization. The successful formation of high-aspect-ratio whiskers indicates that A–B monomers (4-ABA) undergo polymerization-induced crystallization efficiently, consistent with prior observations for PBA whiskers [16]. These results confirm that renewable monomers integrate seamlessly into the established reaction-induced crystallization framework.

The near-identical PXRD profiles between bio-based and petroleum-derived PBA whiskers demonstrate that renewable monomers do not compromise crystalline packing or chain orientation. In fact, the bio-based whiskers exhibit slightly higher crystallinity, consistent with the marginally sharper diffraction peaks observed experimentally, while the preservation of anisotropic growth along the b axis further confirms that

crystallization thermodynamics are largely unaffected by monomer origin. These subtle enhancements may reflect differences in monomer synthesis routes, particularly the lower impurity levels associated with microbial production. A plausible materials-level explanation is that a narrower distribution of isomeric and nitrated byproducts suppresses defect-mediated nucleation events during polymerization-induced crystallization. Such trace species can act as chain-terminating or misfit units, locally perturbing hydrogen-bonding registry and introducing growth steps or kinks that broaden diffraction peaks. In contrast, the biosynthetic route is expected to deliver pABA with fewer structurally related impurities, enabling more uniform chain packing and smoother facet propagation, consistent with the sharper PXRD peaks and reduced AFM roughness observed here.

The absence of melting or glass transition below 400 °C, along with high char yields in TGA, indicates that renewable PBA whiskers possess thermal robustness comparable to traditional aramid materials. Notably, the bio-based whiskers display a slightly higher thermal decomposition onset than the petroleum-derived analogues, which is consistent with their marginally elevated crystallinity.

Petroleum-derived whiskers exhibit a minor mass-loss event around 350 °C, followed by the main degradation between 400–500 °C, whereas this initial weight-loss step is absent in the bio-based samples. This discrepancy suggests that the early-stage degradation is likely associated with trace impurities—such as m- or o-isomers, or nitro-containing byproducts—introduced during conventional petrochemical synthesis of pABA (Fig. 7). Because these impurities are thermally less stable than the para-isomer, they undergo decomposition at lower temperatures, giving rise to the characteristic two-step mass-loss profile. In contrast, the biosynthetic route yields pABA with a narrower isomer distribution and fewer such thermally labile species, resulting in a single, cleaner decomposition transition.

AFM observations revealed smooth faceted surfaces in whiskers synthesized from renewable monomers, suggesting a reduction in impurity-induced defects. The absence of early-decomposing species in the bio-based whiskers is fully consistent with this improved surface regularity: decomposition of trace isomers or byproducts during polymerization or early thermal exposure can locally disrupt crystal growth, generating nanoscale surface irregularities as reported previously [19, 20]. Thus, the lack of the 350 °C minor decomposition step not only reflects enhanced chemical purity but also explains the reduced surface roughness observed in the bio-based whiskers.

Overall, the improved surface uniformity, slightly higher crystallinity, and simplified thermal decomposition behavior underscore the advantage of biosynthetic monomer

supply, which inherently minimizes the presence of structurally related impurities that typically originate from multi-step petrochemical synthesis routes.

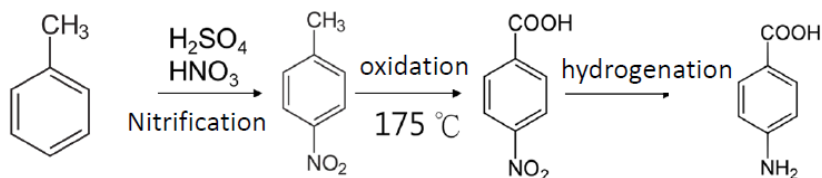


Fig. 7 Process flow for the chemical synthesis of p-aminobenzoic acid (pABA), illustrating key reaction steps and purification stages

Such surface regularity is expected to further enhance dispersibility in polymer matrices and strengthen interfacial interactions, offering practical advantages in composite processing.

The smoother facets and higher crystallinity of bio-derived PBA whiskers are expected to improve interfacial adhesion and dispersion uniformity in polymer matrices. These characteristics make them promising organic reinforcing fillers for lightweight, sustainable composite design.

5. Conclusion

This work demonstrates that fully bio-derived aramids can be realized by leveraging microbially accessible A–B monomers and reaction-induced crystallization to form orthogonally chain-aligned single-crystal whiskers of PBA. Comparative morphology and PXRD analyses confirm anisotropic growth along the b axis and slightly higher crystallinity in the bio-based whiskers, while maintaining the same crystal structure as their petroleum-derived counterparts. Thermal analyses reveal no glass transition or melting up to 400 °C and a decomposition onset near 450 °C, with the bio-based whiskers exhibiting a marginally higher onset temperature that is consistent with their enhanced crystallinity.

A key distinction emerges in the low-temperature decomposition behavior: petroleum-derived whiskers show a minor mass-loss event around 350 °C, whereas this step is entirely absent in the bio-based samples. This difference is attributed to trace m-/o-isomers and nitro-containing byproducts introduced during conventional petrochemical synthesis, which undergo early-stage degradation. The biosynthetic route, in contrast, minimizes such thermally labile impurities, leading to a single, cleaner decomposition profile.

AFM and optical microscopy further reveal smoother, well-faceted surfaces in the bio-based whiskers, consistent with the absence of early-decomposing impurities and the reduced defect density expected from a narrower isomer distribution. These surface characteristics—together with the slight increases in crystallinity and simplified thermal decomposition—underscore the intrinsic advantages of biosynthetic monomer purity and support improved dispersion behavior and interfacial compatibility in polymer matrices. These features motivate follow-up composite studies that quantify interfacial shear strength and mechanical reinforcement, where reduced surface defects and higher crystallinity are expected to translate into more reproducible processing–property relationships.

Collectively, these results show that complete renewable sourcing does not trade off performance; rather, it yields modest but meaningful improvements linked to the impurity-minimizing nature of microbial monomer production. The findings reinforce generalizable design rules rooted in chain planarity and directional hydrogen-bonding topology, while defining practical processing windows for phase-change polymerization. Beyond PBA, this approach provides a pathway to lightweight, dispersible organic reinforcements that avoid the density and interfacial penalties typical of inorganic fillers. Future efforts will quantify mechanical performance in composites, evaluate batch-to-batch reproducibility and scalability, and extend the framework to other bio-derived A–B aramids, including life-cycle and energy-use assessments for truly low-impact, high-performance materials.

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Statements and Declarations

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Competing Interests

S.O. is an inventor on a patent application related to the materials described in this work. All other authors declare no competing interests.

Author Contributions

S.O. and K.T. conceived and supervised the project. S.O., and J.L., designed the experiments and analyzed the data. P.C and K.L. synthesized bio-derived monomer. S.O. performed the other synthesis than bio-derived monomer and J.L., performed structural characterization of PBA whiskers. M.A. and D.H. conducted the micro-electron diffraction and crystallographic analysis. J.W. provided theoretical insights and contributed to the interpretation of the experimental data. S.O. wrote the manuscript with input from all authors. All authors discussed the results and contributed to the final version of the manuscript.

Data Availability

All data supporting the findings of this study are available within the article and its Supplementary Information files. Additional raw data are available from the corresponding author upon reasonable request.

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