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REVIEW

NATURE-DERIVED ULTRAHIGH-PERFORMANCE AROMATIC BIOPLASTICS

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Abstract. Biomass, a renewable carbon source which can be processed using biorefinery system as a substitute of conventional fossil-based refineries. Aromatic precursor molecule synthesis involves chemical synthesis of fossil-fuel-based starting materials, such as benzene and xylene. These energy-intensive processes usually produce many by-products along with the desired molecule. If aromatic molecules can be extracted from natural resources involving minimum chemical conversions, that can be advantageous. Most of the reported approaches are expensive in nature and give the outcomes with lower yield. Microbial fermentation of the lignocellulosic derivatives is a solution to establish a sustainable society. In this paper, we will focus on the aromatic building block preparations starting from nonedible feedstock such as kraft pulp. Aromatic aminobenzoic acid (3-amino-4-hydroxybenzoic acid) preparation from renewable resources and its application in high-performance polymer synthesis will be discussed here.

Keywords: bioplastics, 3-amino-4-hydroxybenzoic acid, polybenzoxazole, polybenzimidazole

Classification numbers: 1.1.5, 2.3.1, 2.9.3

1. INTRODUCTION

Plant components such as wood biomass including starch, cellulose, plant oil, which are produced by photosynthesis of carbon dioxide and thus can be considered as one of the most abundant renewable resources [1]. Wood is basically xylem tissue, coming from the inner bark (cambium) of trees and they consist of lignocellulosic materials such as: cellulose (40 - 50 %), hemicellulose (25 - 35 %), lignin (18 - 35 %) and their extracts [2]. Commercial biofuels have already been produced from edible feedstocks, such as bioethanol (corn, sugarcane) and biodiesel (canola, beans, etc.), therefore the possibility of depleting food resources reduces their applicability in establishing sustainable society [3, 4]. Non-edible resources such as lignocellulosic feedstocks can be utilized to produce second or third generation of biofuels with better sustainability [5]. Lignocellulosic biomass consists of three major components, namely cellulose, lignin and xylene (hemicellulose). After cellulose, lignin is the most abundant renewable carbon source that is readily available, with substitution potential that may be an alternative source of many products currently sourced from petrochemical substances [6, 7]. Lignin is a natural branched and crosslinked network polymer that lends itself to use in materials. Among these, lignin is only made of aromatics, which represents 30 % of non-fossil resource of carbon on the earth and it has natural abundance of around 300 billion tons which increases at a rate of 20 billion tons per year [8]. Lignins are three-dimensional phenolic polymers composed of propyl phenyl units and generally the main component of support tissue in plants which provides mechanical strength and rigidity [9]. According to classifications, softwoods contain highest lignin content following hard wood and grass [10]. Lignin is isolated from lignocellulosic biomass by converting crude lignin to technical grade lignin using biomass treatment [8].

Developing high performance bio-based and renewable materials is the key to establish sustainable growth of the bio-based industry. Increased productivity of bioplastics, proper recycling, functionalization, capital supply, advanced technologies and effective policies create demand and opportunities which in turn are responsible for the success of bioplastic industries and circular economy [3, 4]. In the bioplastic industry aromatic building blocks obtained from natural resources can play a vital role to introduce functionality (heat resistance, strength, flexibility, etc.) and can substitute engineering and super-engineering grade plastics obtained only from fossil fuel resources so far [11, 12]. To reduce the negative environmental impact of using fossil fuels, their dwindling supplies, and their expensive processing, bioplastics are inevitable to switch over. However, the commercial production of bioplastics relies on the raw materials extracted from agricultural food crops, further exacerbating the global hunger problem [13]. On the contrary, producing biomonomers using inedible renewable feedstocks derived from genetically modified microbes may be the best choice considering the current scarcity of food resources [11, 14]. Sugarcane waste, maize, kraft pulp, etc. are a few examples of cellulosic precursors from which polymer building blocks such as lactic acid and succinic acid have been prepared to obtain respective bioplastics [13]. The purpose of the present review is to discuss the research advancements in the development of bioplastics using forestry resources.

Biobased polyester polyethylene terephthalate (PET) has already been prepared from biobased resources to contribute to a sustainable society. Renowned polymer manufacturer DuPont™ produces semi biobased polymers such as Sorona®EP and Hytrel®RS, using non-edible raw materials [15]. Two of the most abundant resources, carbohydrates and lignin for aromatic biomonomers, such as furandicarboxylic acid (FDCA), were an alternative to commercial polyesters [16 - 18]. Biologically derived FDCA can be further transformed to different monomers which result in various thermoplastic polyesters [19 - 22]. Another naturally derived precursor vanillin while reacts with acetic anhydride another biomonomer can be obtained, acetyldihydroferulic acid, which is the building block for poly(dihydroferulic acid) and withstands higher heat-resistance than commercial PET [22]. A series of polyesters with high thermostability is obtained using lignin-based precursors such as: vanillin, syringaldehyde, 4-hydroxybenzaldehyde [23]. Another renewable compound, ferulic acid, with natural abundance is a phenolic compound obtained from plant sources that competes with food resources, e.g. rice, peanut, cereal and other lignin based sources [24]. Ferulic acid chemically resembles bioderived cinnamic acids such as coumaric and caffeic acid [25]. These skeletons are used to prepare various bio-based polyesters and polyamides which are good alternatives to PET [26]. Another bio-based monomer caffeic acid, which can be converted to vinyl catechols by decarboxylation and protection, is ideal to be used for radical polymerization as well as for living anionic polymerization [27]. Similarly, bio-derived ferulic acid which was converted to various vinyl phenolicmoietiesusing decarboxylation, one example is 4-vinylguaiacol (4VG), which are the building blocks for poly(vinylguaiacol) and poly(vinylcatechol) and corresponding copolymers [28] α-pinene derived Pinocarvone, can be radically polymerized to obtain optically active polymers [29].

Another bio-based polyester poly[(*R*)-3-hydroxybutyrate] (P-3HB) can be derived from naturally obtained building blocks resembling thermal stability topolypropylene [30]. Copolymers consisting of 3HB, and stereoisomericlactates were prepared to include a variety of elastomers, and they confer a wide range of mechanical properties. Phenyl lactic acid (PhLA) with its natural abundance, acts as bio-based polymer precursor to be polymerized to poly-PhLA, which exhibits higher UV absorptivity and thermo-mechanical stability as compared to PLA [31]. Through the shikimate pathway, phenylalanine was produced during the metabolism of phenylalanine using glucose [32]. Lower concentrations of fermentation blockers cause a higher yield in PhLA bioproduction from cellulosic feedstock [24, 25] *Para*-coumaric acid (4HCA) has a high bioavailability; during the bioconversion of lignin to cinnamate, 4HCA is generated by phenylalanine ammonia-lyase and Cyt P450 [33], similarly it was found in photosynthetic bacteria as a protein component [34, 35]. Homopolymers and copolymers including 4-HCA along with various naturally obtained monomers have been produced, exhibiting exceptional thermo-mechanical stability and liquid crystalline behavior among degradable bioplastics [36 - 38].

Various bio-derived monomers made by genetic engineering are being utilized as building blocks to create a bio-based plastic economy, hence reducing the dependency on conventional plastics. To attain identical performance and application requirements in terms of thermo-mechanical stability to petroleum-based plastics, it is important to consider the aromatic ring building blocks to resemble those in regular super-engineering polymers, keeping in mind the economical aspects. Both the manufacture of ferulic acid-based biopolymers, which are components of gramineous plants, and the production of thermoplastic copolymer [39] employing the phenolic phytomonomers, *p*-coumaric acid and caffeic acid, are energy-intensive with poor yield. Microbial fermentation methods, on the other hand, are fairly energy-efficient along with better yield to obtain bio-based building blocks. Aromatic biopolyamides with superior strength comparable with glass and steel were created using recombinant E. coli strains from 4-aminophenylalanine and 4ACA, a biomonomer generated from glucose [40]. While interacting with various dianhydrides, diamine can be prepared through dimerization of 4ACA to obtain high-performance bio-based polyimides [41].

Several semi-bio-based polymers with a mix of bio- and petroleum-based monomers were produced in another category. Bio monomer succinic acid and petroleum-based butanediol can both be used to make poly(butylenesuccinate) (PBS) [42]. According to Wang *et al*. (2014), butanediol was prepared using succinic acid which makes PBS a totally bio-based plastic [43].

Combining bio-derived 1,3-propanediol with commercial terephthalic acid yields semi-bio-based poly(trimethylene terephthalate) (PTT), which is the substitute to PET. Nylon 6, 10 is a partly bio-based plastic with mechanical strength comparable to commercial nylon-6 and nylon-6, 6. It is obtained using bio-based sebacic acid and commercially available hexamethylenediamine [44, 45].

2. FERMENTATION OF 3-AMINO-4-HYDROXYBENZOIC ACID

Suzuki *et al*. discovered 3-amino-4-hydroxybenzoic acid (3, 4-AHBA) as an intermediate, derived from the shikimate route during the production of grixazone in 2008 [46]. Two main metabolites, C3 and C4, and two enzymes, GriI and GriH, are involved in the production of 3, 4-AHBA from *Streptomyces griseus* in two steps. The starting components for the biosynthesis of 3, 4-AHBA are dihydroxyacetone phosphate (DHAP) and aspartate semialdehyde (ASA). A C7 chemical, 3-acetylamino-4-hydroxybenzoic acid (3,4-AcAHBA), is produced in the first step, followed by deacetylation, yielding the end product, 3,4-AHBA involving two enzymes GriI and GriH [47].

By restricting 3,4-AcAHBA production while lowering the activity of the N-hydroxyarylamine O-acetyltransferase gene (nhoA), Shozui *et al.* (2017) developed an affordable approach for 3,4-AHBA production using *E. coli* [48].

The precursors of such bio-based building blocks are mostly obtained from food resources, putting a strain on the world's already scarce food supply. As a result, the development of bioplastics using inedible resources is prerequisite [49]. Even when following the sophisticated shikimate pathway, the use of lignocellulosic feedstock in the fermentation was restricted due to extremely poor yield and multiple by-products formed other than the intended phenolic biomonomers [50]. Separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), and consolidated bioprocessing (CBP) are three bioprocessing technologies used mostly to manufacture bio-based aliphatic compounds using polysaccharides. The most economically feasible CBP approach is acceptable over SHF and SSF; however, to overcome the limited productivity and feedstock availability for CBP-based approaches, continuous technical advancements to enhance cellulolytic activities and reaction productivities, as well as reduce fermentation inhibition, are required [51].

3. POLYMERIZATION OF 3, 4-AHBA

3,4-AHBA, an aromatic π-electron-rich bi-derived monomer, is derived from *S. griseus*, a renewable precursor. Intrinsically conductive polymers (ICPs), such as polyaniline (PANI), are useful in microelectronics, light-emitting diodes (LEDs), etc. [52, 53]. Despite receiving significant attention for conducting research on liquid crystalline polymers due to their thermomechanical stability, their applications are limited due to their further processability. To overcome this issue, the introduction of polar terminal groups has proven to be effective [54]. For the same reason, bio-derived 3,4-AHBA monomer (containing -OH and -COOH groups) was considered to be electropolymerized to form PANI polymers (Figure 1), and they were found to be active solvatochromism while soluble in polar solvents [55].

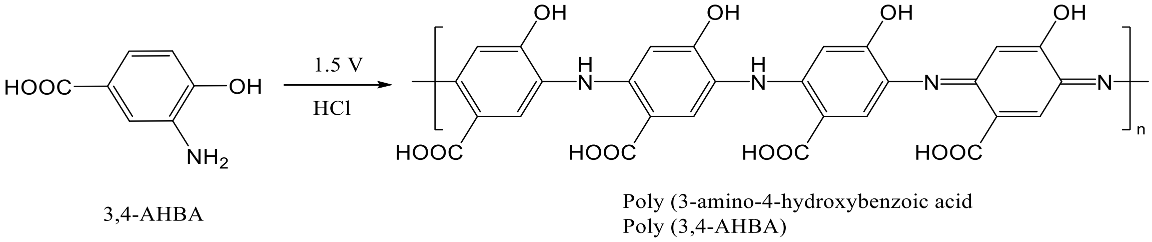

Figure 1. Polyaniline formation using electrochemical polymerization of 3,4-AHBA.

4. BIOBASED POLYESTERS USING 3, 4-AHBA

Liquid crystalline polymers (LCPs) are thermotropic in nature with superior thermo-mechanical strength and suitable for various lightweight applications due to their low density [56 - 59]. Aromatic polyester fibers, such as LCPs (Xyder®) are comparable to Kevlar™ and

Zylon™ in terms of their mechanical strength, due to their highly oriented structures [60, 61]. Aromatic polyesters, typically LCP, with high heat stability, durability and dimensional stability are ideal for commodity plastics such as PET (potentially reaching 25 million tonnes by 2023). However, due to processability concerns associated with their high melting temperature and limited chain flexibility, fully aromatic rigid-rod LCPs are not commonly used, especially in the case of homopolymers. Non-linear comonomers and alkyl side chains have been used to reduce the LCP rigidity [62 - 64].

Polymers exhibiting photoluminescence characteristics, on the other hand, are desirable for photolithography and metal ion sensors. Photosensitive polymers must have photoactive chromophores to be cleaved under UV irradiation [65 - 67]. Aromatic rigid-chain polymers are appropriate candidates for such structures; nevertheless, the lower solubility and processability restrict applicability.

Bioderived 3, 4-AHBA monomer was first converted into 3-benzylidene amino-4-hydroxybenzoic acid (3, 4-BAHBA) combined with naturally obtained benzaldehyde followed by copolymerization with another bio-derived building block *trans*-coumaric acid (4-HCA). Homopolymer of 4-HCA reported with thermotropic LC behavior was introduced into the copolymer poly(3, 4-BAHBA-*co*-4HCA) prepared (Figure 2). The thermal stability of such thermotropic copolymers was found to be dominating over most of the conventional bio-based plastics with a glass transition temperature (T_g) of 135 °C, and the 10 % degradation temperature (T_{d10}) was found to be 350 °C [68]. Due to their mesogenic activity, the 4-HCA unit copolymers cause a nematic LC phase to form; additionally, their flexibility increases the copolymers' processability, allowing them to overcome solubility flaws. The copolymers exhibit photoluminescence activity while soluble in NMP (0.1 %), with 4-HCA incorporation dominating over 75 % and polarized light emission under both parallel and crossing polarizers.

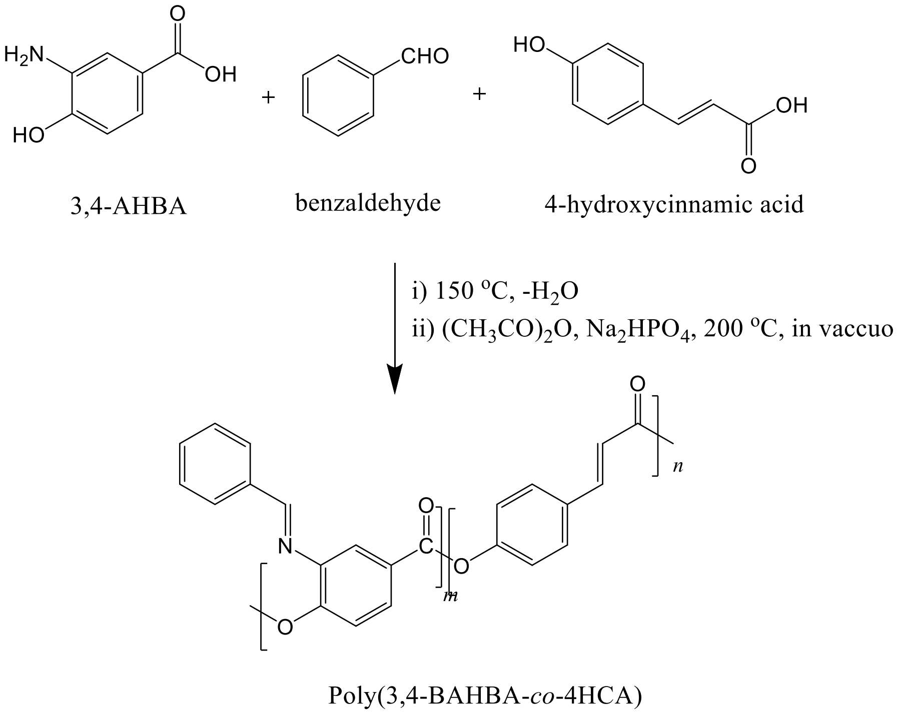

Figure 2. Synthetic scheme of biobased copolyester formation between 3,4-AHBA and 4-HCA.

5. PREPARATION OF BIO-BASED POLYBENZOXAZOLE

Polybenzoxazoles (PBOs) have piqued researchers' interest since their inception due to their extreme thermo-mechanical and chemical, as well as environmental stability. Furthermore, PBOs have a wide range of applications due to their low relative permittivity, which is justified by their low polarizable structures. They can be used as heat-stable insulating materials in high-performance motor coils, as well as in the electronics industry for integrated circuits or multichip production. Polycondensation using dicarboxylic acid or dialdehyde derivatives and bisphenol A is the most prevalent method for making PBOs (o-aminophenol). The initial step is to make poly(o-hydroxyamide)s, which are then cyclodehydrated to make PBOs [66,69–71]. The homopolymer of 3,4-AHBA and its isomer 4-amino-3-hydroxybenzoic acid (4, 3-AHBA) are high molecular weight PBOs such as poly(2, 5-benzoxazole) (ABPBO), and poly(2, 6-benzoxazole), respectively [72].

Bio-derived 3,4-AHBA monomer was homopolymerized to produce polybenzoxazole (PBO) and a patent was published [55]. Although PBO possesses similar physicochemical stability with commercial Zylon, it faces processability issues due to its rigid rod skeleton and aromatic chain [73].

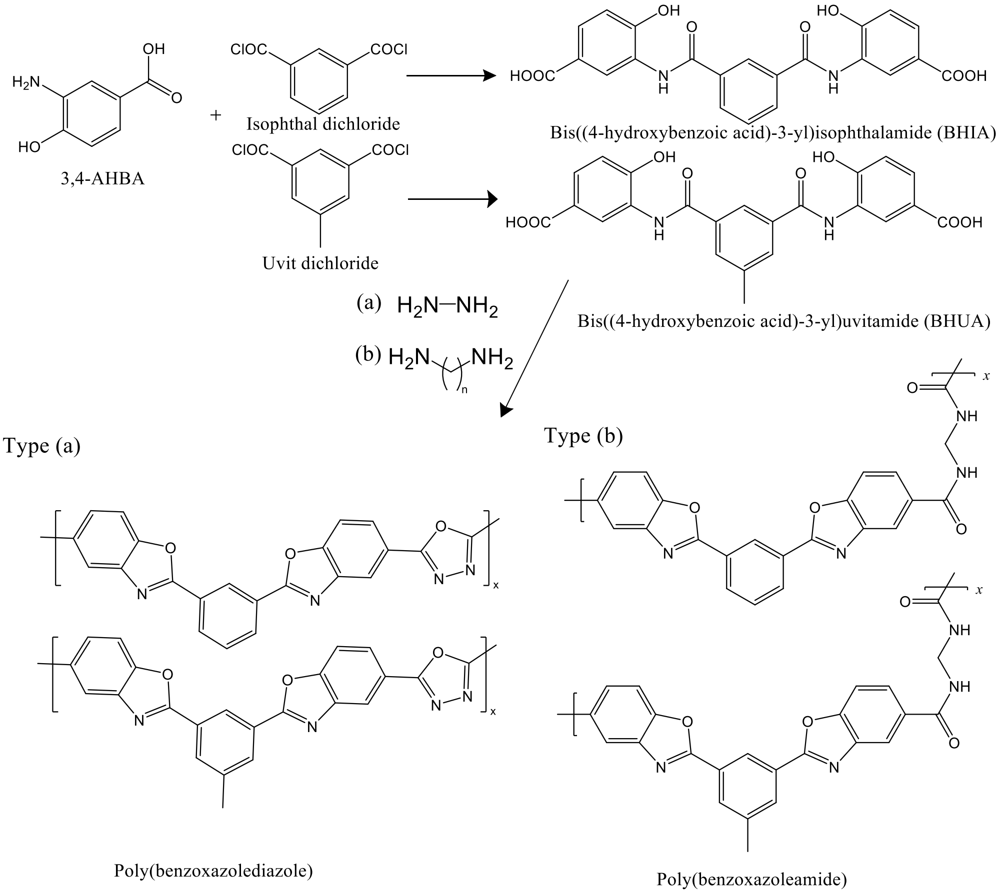

Figure 3. Synthetic scheme for polybenzoxazoles preparation using 3,4-AHBA.

Another biomonomers (e.g., *ort.ho*-hydroxyamide) which were obtained using isophthalic acid chloride and uvitic acid chloride were combined with 3,4-AHBA and polycondensed with diamines to introduce flexibility. Poly(benzoxazolediazole) is a combination of various *ortho-hydroxyamides* and hydrazine, whereas various poly(benzoxazoleamide)s can be synthesized by introducing various alkyl moieties with different *ortho*-hydroxyamides (Figure 3) [74]. Alkylation of PBO backbones produces better solubility and processability than Zylon while maintaining comparable thermomechanical stability. Such PBOs show liquid crystalline behavior above their T_g. Nematic phase LC behavior was confirmed, exhibiting schlieren chain texture using crossed-Nicol polarizer microscope of such PBO moieties.

6. APPLICATIONS OF POLYBENZOXAZOLES

Commercial PBOs are being used as ultra-strong fibers and photosensitive systems; however, PBOs combining flexible alkyl chains enhance the solubility [75 - 77]. The application of PBO membrane as flexible electronic displays are not properly investigated including T_g, high modulus strength, low processability, etc. [78].

Aromatic PBOs have recently attracted a lot of research attention because of their optical transparency and low relative permittivity, both are highly potential for their usage as photoresistors and electrical insulators. Relative permittivity (k) has been reduced by adding fluorinated side chains or alicyclic side chains to PBO backbone to lower molecule polarizability [79]. Commercial low-k polymers polyethylene and polypropylene have limitations due to their low thermo-mechanical stability, which highlights the scarcity of low-k materials with super-engineering strength [80, 81]. Various approaches have been already reported to reduce the k value such as introducing porosity, and SiO_2 moieties into the organic polymer structure, etc., resulting in the reduced mechanical strength [82]. On the contrary, organic dielectric polymers with ultralow-k are always appealing due to their attractive physico-chemical stability and improved processability such as polyimides (PIs); they can be applied as insulating coating materials on metal substrates [83].

PIs are not suitable to be used as ideal low-k or ultra-low k ($k < 2$) materials because of their moisture content and high k values [84,85]. Considering such issues PBOs are one of the best candidates for low-k materials due to the presence of polar carbonyl groups and exhibit higher chemical resistance, better metal surface adhesion, and lower coefficient of thermal expansion (CTE) as compared to the PIs. Zylon® is found to be one of the super-engineering plastics commercially available, considering mechanical performance and very low thermal expansion coefficient; however, its applications are limited in the low-k field due to extremely poor processability. Fukumaru *et al*. developed porous PBO structure by introducing tert-butoxycarbonyl (*t*-Boc)precursor into Zylon and later removed it to cyclize the PBO structure [86]. Moreover, they are useful for photolithography using photoacid generator, since *t*-Boc is sensitive to acid and soluble in alkaline developers [87]. To prepare high-performance low-k polymers, aromatic hyperbranched PBOs (HBPBO) were prepared and inserted into linear fluorinated polymer chains [88]. Alicyclic PBOs contains adamantyl groups with lesser conjugation and the resulting polymers show high transparency and low k, furthermore adamantyl groups reduce the molecular density in polymer chains, which makes them ideal candidates for use in optoelectronics and interlayer dielectric materials [89].

After carefully investigating the reported low-k PBOs with super-engineering properties and good processability, it can be summarized that a combination conjugated non-polar ring moieties will be the ideal candidate with the desired properties. 3,4-AHBA, a bio-derived monomer, can be utilized as an ABPBO precursor. Such PBO structures are crucial for producing low-k materials with super-engineering strength; additionally, controlling structural polarizability is vital for balancing between thermo-mechanical stability and dielectric properties [90]. Nag *et al.* reported the preparation of ABPBO homopolymer with an ultra-low k value of 1.9 at 1 MHz, while still possessing high thermo-mechanical stability [14].

7. BIO-BASED POLYBENZIMIDAZOLE

In high-temperature proton exchange membrane fuel cells (PEMFCs), polybenzimidazoles are well-established proton exchange membranes. Because of their ability of high temperature proton conduction, oxidative as well as chemical stability, low gas permeability, mechanical stability, and high acid uptake ability for proton conductivity, poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (m-PBI, Celazole®) and ABPBI have gained researchers' attention [91–95]. Compared to the commercial Celazole®, ABPBI offers a number of advantages. ABPBI's ability to form films improves processability. In addition, compared to Celazole®, ABPBI requires single monomer 3, 4-DABA, and improved stability is attained with acidic solvent doping [96]. 3,4-diaminobenzoic acid (3,4-DABA), a simple chemical conversion from 3,4-AHBA was employed as a building block of ABPBI (Figure 4) [13]. The Smiles rearrangement, an intramolecular nucleophilic aromatic substitution method, was found to be useful for the 3,4-AHBA to 3,4-DABA conversion.

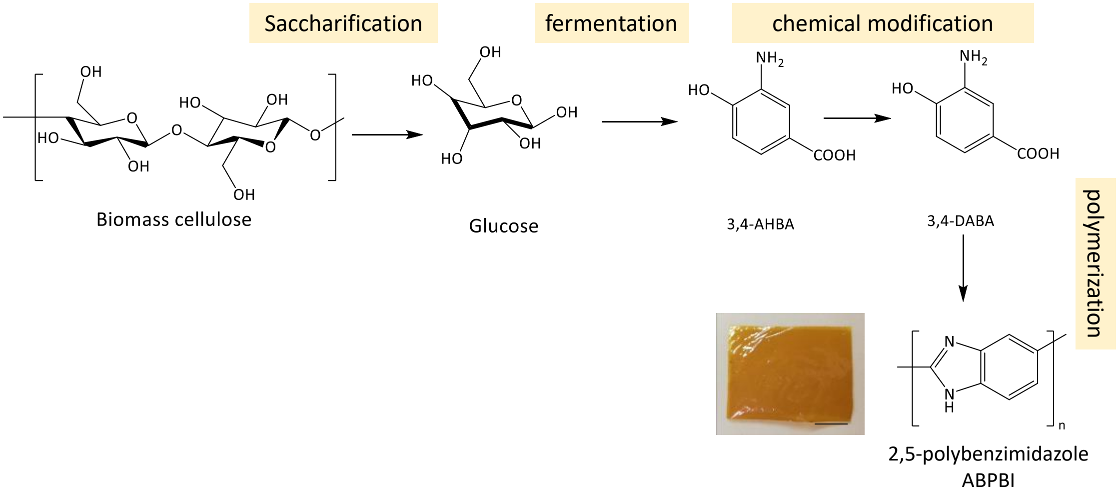

Figure 4. Schematic route for biobased ABPBI synthesis starting from nonedible cellulosic feedstocks.

Bio-based building block 3, 4-DABA was combined with another bioderived monomer 3, 4-AHBA to obtain the copolymers (PBO-*co*-PBI) (Figure 5), exhibiting better stability than the homopolymer ABPBO, while their dielectric properties are comparable with Kapton® [14]. In case of ABPBI, i.e. benzimidazole units, the -NH- group takes the place of the -O- group in ABPBO units, which results in an increase in polarity; consequently, the processability is improved, which helps the membrane casting process. Such low-*k* copolymers are advantageous over porous materials or fluorinated polymers in terms of processability and robustness. Such ultra-low-*k* copolymer films with super-engineering material properties can be useful for various applications such as interconnection technology to minimize crosstalk and interlayer dielectric polymers; and they are evidently better candidate than fluorinated or SiO_2 hybrid low-*k* polymers [97, 98].

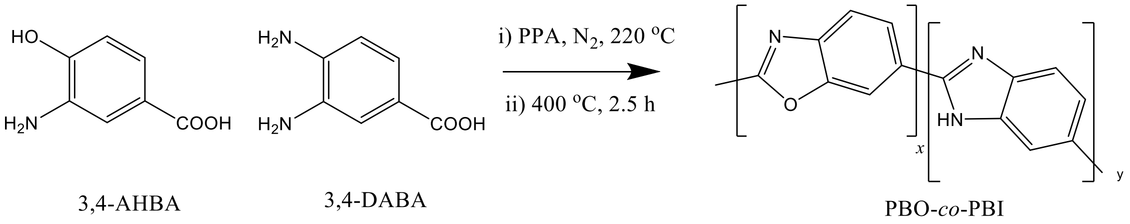

Figure 5. Synthetic scheme for the copolymer preparation using two bio-based monomers 3,4-AHBA and 3,4-DABA.

8. CONCLUSION

High-performance bio-based polymers made from natural resources are a prerequisite for establishing a sustainable society. Biomass other than food resources are preferable to manage depleting food stocks; alternatives such as wood, roots, pulps, and other recycle resources would be better candidates for establishing a sustainable society. Aromatic bioplastics produced from microbial conversion of biomass into phenolic monomers have various advantages over aliphatic bioplastics in terms of excellent thermo-mechanical stability and multifunctionality. Polybenzazoles are used as super-engineering plastic, because of their ultra-high performance, chemical stability, oxidative stability, and abundant scope of functionalization. However, bio-based precursor materials for polybenzazoles are difficult to obtain because they require aromatic building blocks that are difficult to obtain from natural sources. Bio-based polybenzoxazoles of various structures are the ideal choice for the preparation of advanced materials such as ultra-low-*k* devices and flexible LCDs, whereas bio-based polybenzimidazole (ABPBI) has ultrahigh thermostability and can also be used as a solid polymer electrolyte in LIBs.

CRediT authorship contribution statement. Aniruddha Nag: conceptualization, methodology, data analysis, and writing; Tatsuo Kaneko: conceptualization, formal analysis, writing, review and editing.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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