Syntheses of Soluble Biopolyimides Using 4-Aminophenylalanine

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Abstract 4-Aminophenylalanine (4APhe), an exotic amino acid which is obtained as a microorganism metabolite of glucose, is polycondensed with various tetracarboxylic dianhydrides as a diamine monomer to obtain poly(amic acid)s. Subsequent thermal imidization of poly(amic acid)s is made at 220 °C with stepwise heating from 100 °C. Some of the obtained polyimides (PIs) exhibited good solubility in organic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, and more. The progress of imidization was observed by proton nuclear magnetic resonance and infrared spectroscopy to confirm that the imidization ratio was up to 98%. Carboxylate group of the side-chains of PIs affected their solubilities despite the high imidization ratio, and the solubility was lost for any organic solvents by decarboxylation at 280 °C, confirmed from mass-loss of thermogravimetric analysis. Thus, a new series of PIs were obtained with abilities of solvent-molding in PI state and thermal resistivity enhancement by further heating after molding.

Keywords Bio-based polymers; Polyimides; Amino acids; 4-Aminophenylalanine; Soluble polyimides

INTRODUCTION

In order to build a sustainable society, the development of bio-based polymers, which are materials obtained from plants that fix atmospheric carbon dioxide in their body, is urgently required.\cite{1} Due to those enormous achievements, various bio-based polymers have been developed in the world.\cite{2−4} Poly(lactic acid)s are the representative bio-based polymers, and give various functions to expand the range of applications.\cite{5,6} However, there are only a small number of reports on the high-thermosistance bio-based polymers because almost conventional bio-based polymers are made from low durability, materials development independent of petroleum industry can be performed. In addition, such durable bio-derived materials can be expected to fix carbon dioxide from the atmosphere and store inside them for a long time.

The highly heat-resistant bio-based plastics with durability such as polybenzazoles,\cite{7−9} polyimides (PIs),\cite{10−13} polyamides,\cite{14,15} and polyureas\cite{16} have been developed by using microbial metabolites such as 3-hydroxy-4-aminobenzoic acid or 4-aminocinnamic acid. These bio-based plastics having excellent thermal and mechanical properties are expected to be a metal substitute requiring high stabilities. 4-Aminocinnamic acid monomers can be produced by microorganisms including skimate pathways through chorismate, 4-aminophenylpyruvic acid, and 4-aminophenylalanine (4APhe) as the intermediates.\cite{10} For instance, the polyimide soluble in an organic solvent can be obtained by using the dianhydrides having a bent structure, such as cycloalkanes or mellophanic dianhydride.\cite{12,13,17} In addition, bio-based polyimides using isoxeoxide and adenine have also been reported.\cite{18−20} These trends indicate that the production of bio-based high-performance plastics is one of the topics attracting attention in recent years. The obtained bio-based PIs, especially 4-amino- cinnamic acid-based PIs, showed low solubilities in organic solvents similarly to conventional PIs. In addition, the production of 4-aminocinnamic acid by microorganisms requires multistage biological production and the subsequent chemical modification such as photodimerization and esterification including purifications causes low yields and high energy.

Here we focus on 4APhe, the microorganism product used as a diamine having an aromatic ring, carboxylic acid, and methylene, which gives flexibility to impart bio-based PIs solubility. In addition, 4APhe utilization has an advantage in a sustainable society by omitting the step number of biological
and chemical production compared to that of 4-aminocinnamic acid-based PI (Fig. 1).

EXPERIMENTAL

Materials

4-Aminophenylalanine dihydrochloride was purchased from Watanabe Chemical Industries, LTD. Sodium hydroxide and ethanol were purchased from Kanto Chemical Co., INC. N-methyl-2-pyrrolidone (NMP, super dehydrate, water content < 10 ppm) and N,N-dimethylacetamide (DMAc) were purchased from FUJIFILM Wako Pure Chemical Co., 1,2,3,4-Cyclobutanetetracarboxylic dianhydride (CBDA), 3-(carboxymethyl)-1,2,4-cyclo-pentanetracarboxylic acid 1,4,2,3-dianhydride (TCAAH), cyclo-(2.2.2)oct-7-ene-2,3,5,6-tetraacryllic dianhydride (BTA), 4-(2,5-dioxoetrahydrofuran-3-yl)-1,2,3,4-tetraydrodronaphthalene-1,2-dicarboxylic anhydride (TDA), pyromellitic dianhydride (PM DMA), 4,4′-biphenyl anhydride (BPDA), 3,4′-biphenyl anhydride (aBPDA), 4,4′-oxydiphthalic anhydride (OPDA), 3,3′,4,4′-benzeno- phenonetetracarboxylic dianhydride (BTDA), 3,3′,4,4′-diphenyl- sulfonnetetracarboxylic dianhydride (DSDA), 4,4′-(hexafluoro-isopropylidene)diphthalic anhydride (6FDA), 1,4-phenylene bis(1,3-dioxy-1,3-dihiyrodsobenzofuran-5-carboxyate) (TAHQ), and 4,4′-(4,4′-isopropylene dinediphenoxy)diphthalic anhydride (BPADA) were purchased from Tokyo Chemical Industry Co., LTD.

Measurements

Proton nuclear magnetic resonance (1H-NMR) measurements were carried out using Bruker Bio-spin AG 400 MHz. Gel permeation chromatography (GPC) was performed on the Shodex column (SB 806 M × 2), column oven (GL Science, CO 631A, set at 40 °C), degassing unit (GL Science, GC 6608), pump (JASCO, PU-2080 Plus), refractive index detector (JASCO, 830-R), and ultraviolet detector (JASCO, UV-2075 Plus) using 0.01 mol·L−1 of lithium bromide (LiBr) solution of N,N-dimethylformamide (DMF) as an eluent (flow rate, 1.0 mL·min−1). Thermal gravimetric analysis (TGA) was carried out by using HITACHI STA 7200 under nitrogen flow (gas flow rate, 200 mL·min−1) from 25 °C to 800 °C with a heating rate of 5 °C·min−1 to determine the 5% and 10% mass loss temperature (TD5 and TD10). Differential scanning calorimetry (DSC) was performed by SEIKO X-DSC7000T to measure glass transition temperatures (Tg) which were measured from 25 °C to 300 °C at a heating rate of 10 °C·min−1 with 5 mg (approx.) of sample.

Synthesis of 4-Aminophenylalanine (4APhe)

4-Aminophenylalanine dihydrochloride (15.02 g, 59.34 mmol) was suspended in ethanol (250 mL) at room temperature. While stirring, 1.0 mol-L−1 of aqueous NaOH (108.5 mL, 108.5 mmol) was added to ethanol solution to adjust pH to 8.0. After stirred for 30 min, white product was observed and collected by filtration and dried in vacuum. After drying, 4-aminophenylalanine (4APhe) was obtained as white solid (Yield, 6.78 g (63.4%)).

Synthesis of 4APhe-based Polyimides (PIs)

An example of the experiment is shown below. 4APhe (1.0913 g, 6.0557 mmol) was suspended in NMP (6.0 mL) at room temperature and nitrogen atmosphere. PMDA (1.3210 g, 6.0563 mmol) was added to NMP solution in the heterogeneous state. When polymerization proceeded, the reaction mixture became homogeneous. After reacted for 24 h, the polymerization mixture was precipitated to acetone at room temperature to obtain the white fibril. The obtained fibril was collected by filtration and dried in vacuum to give poly(amic acid) as precursor of PI (Yield, 2.05 g (84.9%)). The obtained poly(amic acid) (750 mg) was dissolved into DMAC (1.50 mL) and casted on silicon wafer, then the film was dried at 80 °C for 3 h. After dried, thermal imidization was carried out at 100, 150, 200, and 220 °C with vacuuming for 1 h of each steps to get a PI with quantitative yield. For syntheses of the other PIs, the objective polyimides could be synthesized by using corresponding tetracarboxylic dianhydrides (DAs).

RESULTS AND DISCUSSION

Design of 4APhe-based Soluble PIs

In order to improve the solubility to the insoluble polymers such as PIs, flexibility was introduced into main chain using monomers with bending structures and solubility-inducing polar groups such as carboxylate or sulfonate groups. Thus, 4APhe is the most suitable candidate for obtaining the soluble bio-based PIs. 4APhe was synthesized by neutralization of 4-aminophenylalanine dihydrochloride using aqueous NaOH solution. The structure of white precipitates of 4APhe was confirmed by 1H-NMR measurement (Fig. S1 in the electronic supplementary information, ESI). PIs were prepared from 4APhe with various DAs; 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA), 3-(carboxymethyl)-1,2,4-cyclo-pentanetracarboxylic acid 1,4,2,3-dianhydride (TCAAH), cyclo-(2.2.2)oct-7-ene-2,3,5,6-tetraacrylic dianhydride (BTA), 4-(2,5-dioxo-tetrahydrofuran-3-yl)-1,2,3,4-tetraydrodronaphthalene-1,2-dicarboxylic anhydride (TDA), pyromellitic dianhydride (PM DMA), 4,4′-biphthalic anhydride (BPDA), 3,4′-biphthalic anhydride (aBPDA), 4,4′-oxydiphthalic anhydride (OPDA), 3,3′,4,4′-benzenonetetracarboxylic dianhydride (BTDA), 3,3′,4,4′-diphenylsulfonnetetracarboxylic dianhydride (DSDA), 4,4′-(hexafluoro-isopropylidene)diphthalic anhydride (6FDA), 1,4-phenylene bis(1,3-dioxy-1,3-dihiyrodsobenzofuran-5-carboxyate) (TAHQ), and 4,4′-(4,4′-isopropylene dinediphenoxy)diphthalic anhydride (BPADA) were purchased from Tokyo Chemical Industry Co., LTD.

![Fig. 1 4-Aminophenylalanine (4APhe) usage for preparation of soluble and cost-effective bio-based polymides (PIs).](https://doi.org/10.1007/s10118-020-2450-6)
tetracarboxylic dianhydride (DSDA), 4,4′-hexafluoroisopropylidene)dipthalic anhydride (6FDA), 1,4-phenylene bis(1,3-dioxo-1,3-dihydroisobenzofuran-5-carboxylate) (TAHQ), and 4,4′-(4,4′-isopropylidene-diphenoxy)dipthalic anhydride (BPADA), to obtain the corresponding poly(amic acids) and PI-1 to PI-13 (Scheme 1). As a result, all the poly(amic acids) were synthesized by mixing in NMP at room temperature. The structures of the obtained poly(amic acids) were confirmed by 1H-NMR spectra (Fig. S2 in ESI). From these spectra, the signals assigned to the aromatic rings were complicated. This is because the 4APhe was asymmetric in addition to taking a different ring-opening behavior when the amine group was added to DAs (details are described later). However, this structural irregularity also contributes to the addition of solubility, which was the key point of this work. Furthermore, PIs were obtained by stepwise heating (thermal imidization) using these poly(amic acids). The progress of imidization was confirmed by FTIR measurement (Fig. 2). For instance, absorption derived from C=O stretching vibration and C−N stretching vibration of polyimide obtained using PMDA (PI-5) were observed at 1710 and 1360 cm−1, respectively (other FTIR spectra of the polymers are shown in Fig. S3 in ESI).

Solubility of 4APhe-based Polyimides

As a result of a solubility test of the obtained PIs, it was found that some of the PIs exhibited good solubilities in organic solvents (Table 1). In fact, 6FDA, TAHQ, and BPADA are known as monomers for soluble-Pis, and it was expected that they exhibit excellent solubility. Each PI such as PI-11, PI-12, and PI-13 showed the property of dissolving in organic solvents such as N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), NMP, and DMAC. In addition, even PIs with high rigidity such as PI-5, for which PMDA was used as monomer, showed solubility in DMF, DMSO, NMP, and DMAC. This is one of the most important results of this study. Despite PMDA’s lack of flexible molecular structure and bulky side-chains, its solubility in the resulting PI strongly supports the significant effect of the carboxylate group in the side-chain of 4APhe unit. This solubility test revealed that PI-1, 3, 4, 5, 7, 8, 10, 11, 12, and 13 were dissolved in organic solvents.

The 1H-NMR spectra of the soluble PIs showed similar patterns. For instance, in the case of PI-5 with PMDA used as the monomer, the spectrum showed very complicated patterns in the state of poly(amic acid) (Fig. 3a). This was because 4APhe, which is a hetero-diamine, attaches to DA in the form of head-to-tail, head-to-head, tail-to-head, and tail-to-tail, respectively (Fig. 4). This irregularity can contribute to enhancement of the solubility of PIs. Furthermore, the imidization ratios of soluble polyimides were calculated to be up to 98% from integration value of amide proton in the 1H-NMR spectra (Fig. 5). In addition, GPC measurement using DMF-LiBr eluent confirmed that the poly(amic acid) showed enough high molecular weight and good polydispersity (Mw/Mn) (Table 2).
Then PI should be of high molecular weight though molecular weights of the PIs except for PI-10 were not directly obtained. In PI-10, the values of the weight-average molecular weight ($M_w$) of 3.19 × $10^4$, the number-average molecular weight ($M_n$) of 6.48 × $10^4$, and $M_w/M_n$ of 2.03 indicated that the solubility of PIs was obtained with no decrease in the molecular weight in thermal imidization process. From the above results, it is suggested that the PIs solubility was caused by the interaction of the side-chain carboxylic acid instead of the polymer being decomposed.

**Thermal Stability of 4APhe-based Polyimides**

Thermal stabilities of all the prepared PIs were analyzed by TGA at a heating rate of 5 °C·min$^{-1}$ under nitrogen atmosphere and the values of $T_d5$ and $T_d10$ (the temperatures for 5% and 10% weight losses) were measured (Table 3). TGA analysis was performed up to 800 °C. The $T_d10$ values of PIs ranged in a temperature of up to 350 °C and showed much higher values than conventional bioplastics such as poly(lactic acid) (PLA, 300 °C$^{[22]}$) and polyhydroxybutyrate (PHB, 260 °C$^{[3]}$). In addition, almost all the PIs showed no $T_g$. However, in PI-13 (4APhe and BPADA as monomers), $T_g$ was observed at 222 °C. BPADA is a DA used for Ultem$^\text{TM}$, polyetherimide as thermo plastics, and the corresponding polyimide PI-13 had comparable performances to Ultem$^\text{TM}$, presumably owing to hydrogen bonding between the side-chain carboxy groups of 4APhe-based PI. The obtained TGA curve showed a two-step mass decreasing, suggesting that the decomposition of PI was caused by heating (Fig. 6a). From that, the first weight loss of approximately 10% was observed between 250 and 300 °C.

In addition, after heat-treatment at 280 °C for 3 h, PI-5 showed less weight decreasing (Fig. 6b). These results indic-

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**Table 1**  Solubility test of biopolyimides prepared from polycondensation of 4-aminophenylalanine (4APhe). a

| Polymer (DA) | MeOH | THF | DMSO | DMF | NMP | DMAC | EtOAc | CH$_2$Cl$_2$ |
|-------------|------|-----|------|-----|-----|------|-------|------------|
| PI-1 (CBDA) | +    | +   | +    | +   | +   | +    | −     | −          |
| PI-2 (TCAAH) | −    | −   | ±    | −   | ±   | −    | −     | −          |
| PI-3 (BTA)  | −    | −   | +    | +   | +   | +    | +     | +          |
| PI-4 (TDA)  | −    | −   | +    | −   | −   | −    | −     | −          |
| PI-5 (PMDA) | −    | −   | +    | +   | +   | +    | +     | +          |
| PI-6 (BPDA) | −    | −   | +    | −   | −   | −    | −     | −          |
| PI-7 (aBPDA) | −    | −   | +    | −   | −   | −    | −     | −          |
| PI-8 (OPDA) | −    | −   | +    | +   | +   | +    | +     | +          |
| PI-9 (BTDA) | −    | −   | −    | −   | −   | −    | −     | −          |
| PI-10 (DSDA)| −    | −   | +    | −   | −   | −    | −     | −          |
| PI-11 (6FDA)| −    | −   | +    | +   | +   | +    | +     | ±          |
| PI-12 (TAHQ)| −    | −   | +    | +   | +   | +    | +     | ±          |
| PI-13 (BPADA) | −    | +   | +    | +   | +   | +    | ±     | ± ±       |

*Sample weight, 10 mg; Solvent volume, 1.0 mL; +, soluble at room temp (approx. 20 °C); ±, swellable (partially soluble); −, insoluble. Abbreviations $n$-P (r: 1–13) corresponds to structures shown in Scheme 1.*
Table 2 Molecular weight ($M_n$ and $M_w$), and polydispersity ($M_w/M_n$) of poly(amic acid)s prepared from 4APhe.

| Polymer (DA) | $M_n$ (g·mol$^{-1}$) | $M_w$ (g·mol$^{-1}$) | $M_w/M_n$ |
|--------------|----------------------|----------------------|-----------|
| PAA-1 (CBDA) | $6.23 \times 10^4$   | $1.16 \times 10^5$   | 1.86      |
| PAA-2 (TCAAH) | $4.73 \times 10^4$   | $9.23 \times 10^4$   | 1.95      |
| PAA-3 (BTA)  | $4.17 \times 10^4$   | $5.92 \times 10^4$   | 1.42      |
| PAA-4 (TDA)  | $3.20 \times 10^4$   | $6.44 \times 10^4$   | 2.01      |
| PAA-5 (PMDA) | $4.14 \times 10^4$   | $6.57 \times 10^4$   | 1.59      |
| PAA-6 (BPDA) | $2.50 \times 10^4$   | $5.82 \times 10^4$   | 2.32      |
| PAA-7 (aBPDA) | $2.55 \times 10^4$   | $3.38 \times 10^4$   | 1.33      |
| PAA-8 (OPDA) | $5.30 \times 10^4$   | $9.32 \times 10^4$   | 1.76      |
| PAA-9 (BTDA) | $3.80 \times 10^4$   | $8.33 \times 10^4$   | 2.14      |
| PAA-10 (DSDA) | $4.07 \times 10^4$   | $8.19 \times 10^4$   | 2.01      |
| PAA-11 (6FD) | $2.48 \times 10^4$   | $6.47 \times 10^4$   | 2.61      |
| PAA-12 (TAAH) | $2.15 \times 10^4$   | $4.97 \times 10^4$   | 2.31      |
| PAA-13 (BPADA) | $4.31 \times 10^4$   | $7.37 \times 10^4$   | 1.71      |

* Determined by GPC using DMF containing 0.01 mL·min$^{-1}$ of LiBr as eluent; flow rate 1.0 mL·min$^{-1}$; standards, polystyrene. PAA refers to poly(amic acid)s as polyimide precursors and $n$ (n: 1−13) corresponds to polyimides structures shown in Scheme 1.

Table 3 Thermal properties ($T_{d5}$, $T_{d10}$, and $T_g$) of polyimides prepared from 4APhe. *

| Polymer (DA) | $T_{d5}$ (°C) | $T_{d10}$ (°C) | $T_g$ (°C) | $T_{d5}$ (°C) | $T_{d10}$ (°C) |
|--------------|--------------|--------------|-----------|--------------|--------------|
| PI-1 (CBDA)  | 322          | 362          | n.d.      | 383          | 392          |
| PI-2 (TCAAH) | 303          | 347          | n.d.      | 376          | 392          |
| PI-3 (BTA)   | 393          | 406          | n.d.      | 398          | 413          |
| PI-4 (TDA)   | 342          | 373          | n.d.      | 366          | 378          |
| PI-5 (PMDA)  | 347          | 370          | n.d.      | 378          | 410          |
| PI-6 (BPDA)  | 401          | 427          | n.d.      | 399          | 428          |
| PI-7 (aBPDA) | 330          | 377          | n.d.      | 396          | 420          |
| PI-8 (OPDA)  | 361          | 393          | n.d.      | 386          | 398          |
| PI-9 (BTDA)  | 323          | 365          | n.d.      | 399          | 429          |
| PI-10 (DSDA)| 303          | 377          | n.d.      | 391          | 406          |
| PI-11 (6FD)  | 294          | 405          | n.d.      | 418          | 437          |
| PI-12 (TAAH)| 388          | 410          | n.d.      | 398          | 431          |
| PI-13 (BPADA)| 373          | 413          | 222       | 409          | 430          |

* $T_{d5}$ and $T_{d10}$ were determined by TGA at N$_2$ atmosphere, heating rate 5 °C·min$^{-1}$. $T_g$ was determined by DSC at a heating rate of 10 °C·min$^{-1}$. Samples were pre-heated at 280 °C for 3 h before measurements. $T_g$ was not detected under 300 °C. Abbreviations PI-n (n: 1−13) corresponds to structures shown in Scheme 1.
ated the decarboxylation occurred by heating in carboxylate group of 4APhe-unit. In Fig. 6(a), the percentage of mass loss was approximately 10%, which corresponded to decarboxylated unit molecular weight of PI-5, 12% (Fig. 6c). Thus, heat treatment caused this decarboxylation to afford de-
carboxylated PI which showed the higher $T_{d5}$ and $T_{d10}$ values as shown in Table 3. Furthermore, after the heat treatment, solubility in the organic solvents, DMF, DMSO, NMP, and DMAc, was lost, and then NMR measurement was not performed. Moreover, the IR spectra of the pristine PI-5 and the heat-treated one were compared, and a change in the peak shape around 1600 cm$^{-1}$ was observed (Fig. S4 in ESI). This is due to the C=O stretching in COOH, and it is considered that the peak shape changed by the decrease of side-chain. Decarboxylation from the polymer side-chains should result in a more rigid molecular structure. In addition, these results strongly indicated that decarboxylation of 4APhe-based PIs occurred while heating at 250–300 °C. Other soluble PI also showed the same manner (Figs. S5 and S6 in ESI, and Table 3). Therefore, it has been clarified that the heat resistance was improved by decarboxylation to obtain a more rigid structure, but the solubility was reduced. The property means that by applying more heat after applying it in a solution state, it can be converted to a substance with higher heat resistance, and it can be expected to be used as a material for new coating technology.

CONCLUSIONS

PIs were synthesized by polymerization of 4APhe, a functional α-amino acid, as a diamine monomer with various DAs. By thermal imidization at 220 °C, PIs soluble in organic solvents such as DMF, DMSO, NMP, and DMAc were obtained, and their heat resistance was comparable to that of conventional PIs. The imidization ratio of the obtained PIs, dissolved in the organic solvent, was calculated from $^1$H-NMR measurements to be up to 98% in each case, which means that the thermal imidization at 220 °C proceeded almost quantitatively. Although the thermal stabilities of the present PIs were as high as those of conventional PIs, it was found that heat resistivity was improved by the decarboxylation of side-chain of 4APhe-component around 250–300 °C. As a result, the molecular structure of the PIs became rigid by decarboxylation and the heat resistance was improved, but also the solubility in the organic solvent was limited. The unique function is considered to be applicable to coating technology and the like. The PIs are is soluble in organic solvents and can be chemically modifiable. By taking advantage of the function, it is possible to extend the researches to develop a series of functional PIs.

Electronic Supplementary Information

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REFERENCES

1 Sheldon, R. A. Green and sustainable manufacture of chemicals from biomass: state of the art. *Green Chem.* 2014, 16, 950–963.

2 Willibon, P. A.; Chu, F.-C.; Tang, C. Progress in renewable polymers from natural terpenes, terpenoids, and rosin. *Macromol. Rapid Commun.* 2013, 34, 8–37.

3 Isiggor, F. H.; Becer, R. Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. *Polym. Chem.* 2015, 6, 4497–4559.

4 Froidevaux, V.; Negrelli, C.; Caillol, S.; Pascualt, J. P.; Boutevin, B. Biobased amines: from synthesis to polymers present and future. *Chem. Rev.* 2016, 116, 14181–14224.

5 Rasal, R. M.; Janorkar, A. V.; Hirt, D. E. Poly(lactic acid) modifications. *Prog. Polym. Sci.* 2010, 35, 338–356.

6 Auras, R.; Harte, B.; Selke, S. An overview of polylactides as packaging materials. *Macromol. Biosci.* 2004, 4, 835–864.

7 Ali, M. A.; Shimosegawa, H.; Nag, A.; Takada, K.; Kaneko, T. Synthesis of thermotropic polybenzoxazole using 3-amino-4-hydroxybenzoic acid. *J. Polym. Res.* 2017, 24, 214.

8 Nag, A.; Ali, M. A.; Singh, A.; Vedarajan, R.; Matsumi, N.; Kaneko, T. N-boronated polybenzimidazole for composite electrolyte design of highly ion conductive pseudo solid-state ion gel electrolytes with high Li-transferance number. *J. Mater. Chem. A* 2019, 7, 4459–4468.

9 Nag, A.; Ali, M. A.; Watanabe, M.; Singh, M.; Amornwachirabodee, K.; Kato, S.; Mitsumura, T.; Takada, K.; Kaneko, T. High-performance poly(benzoxazole/benzimidazole) bio-based plastics with ultra-low dielectric constant from 3-amino-4-hydroxybenzoic acid. *Polyim. Degrad. Stab.* 2019, 162, 29–35.

10 Suvannasara, P.; Tateyama, S.; Miyasato, A.; Matsumura, K.; Shimoda, T.; Ito, T.; Yamagata, Y.; Fujita, T.; Takaya, N.; Kaneko, T. Polyimides from 4-aminocinnamic acid and disulfonic acid. *Macromolecules* 2014, 47, 1586–1593.

11 Kumar, A.; Tateyama, S.; Yasaki, K.; Ali, M. A.; Takaya, N.; Singh, R.; Kaneko, T. Ultrahigh performance bio-based polyimides from 4,4'-diaminostilbene. *Polym. Chem.* 2016, 83, 182–189.

12 Dwivedi, S.; Sakamoto, S.; Kato, S.; Mitsumura, T.; Kaneko, T. Effect of biopolyimide molecular design on their silica hybrids thermo-mechanical, optical and electrical properties. *RSC Adv.* 2018, 8, 14009.

13 Takada, K.; Karikome, S.; Dwivedi, S.; Kaneko, T. Fully bio-based aromatic polyimide using 4-aminocinnamic acid and mellophanic dihydrazide as bio-derived monomers. *ECS Transactions* 2018, 88, 99–105.

14 Tateyama, S.; Masuo, S.; Suvannasara, P.; Oka, Y.; Miyasato, A.; Yasaki, K.; Teerawatananond, T.; Muangsin, N.; Zhou, S.; Kawasaki, Y.; Zhu, L.; Zhou, Z.; Takaya, N.; Kaneko, T. Ultra-strong, transparent polyyctrauxilamides derived from microbial photodimers. *Macromolecules* 2016, 49, 3336–3342.

15 Takada, K.; Mae, Y.; Kaneko, T. Fluorinated and bio-based polyamides with high strength and low yellowness index. *Polymers* 2018, 10, 1311.

16 Jin, X.; Tateyama, S.; Kaneko, T. Salt-induced reinforcement of anionic bio-polyureas with high transparency. *Polym. J.* 2015, 47, 727–732.

17 Feng, X.; Yang, Z.; Zhang, S.; Gao, L.; Ding, M. Polymides derived from mellophanic dihydrazide. *Macromolecules* 2002, 35, 8708–8717.

18 Ji, X.; Wang, Z.; Yan, J.; Wang, Z. Partially bio-based polyimides from isohexide-derived diamines. *Polymers* 2015, 7, 38–45.

19 Hu, J.; Wang, Z.; Lu, Z.; Chen, C.; Shi, M.; Wang, J.; Zhao, E.; Zeng, K.; Yang, G. Bio-based adenine-contaoning high performance polyimide. *Polymers* 2017, 119, 59–65.

20 Hu, J.; Li, R.; Chen, C.; Lu, Z.; Zeng, K.; Yang, G. New insights into mechanism of negative in-plane CTE based on bio-based adenine-containing polyimide film. *Polymers* 2018, 146, 133–141.

21 Fang, J.; Guo, X.; Harada, S.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. Novel sulfonated polyimides as polyelectrolytes for fuel cell application. 1. Synthesis, proton conductivity, and water stability of polyimides from 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid. *Macromolecules* 2002, 35, 9022–9028.

22 Lee, S. H.; Kim, S. H.; Han, Y. K.; Kim, Y. H. Synthesis and degradation of end-group-functionalized polycarbonate. *J. Polym. Sci., Part A: Polym. Chem.* 2001, 39, 973–985.

23 Hong, S. G.; Gau, T. K.; Huang, S. C. Enhancement of the crystallization and thermal stability of polyhydroxybutyrate by polymeric additives. *J. Therm. Anal. Calorim.* 2011, 103, 967–975.