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Syntheses of Soluble Biopolyimides Using 4-Aminophenylalanine

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Electronic Supplementary Information

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

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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.^[1] Due to those enormous achievements, various bio-based polymers have been developed in the world.^[2–4] Poly(lactic acid)s are the representative bio-based polymers, and give various functions to expand the range of applications.^[5,6] However, there are only a small number of reports on the high-thermoreistance bio-based polymers because almost conventional bio-based polymers contained ester bonds in polymer backbones. Furthermore, if a biocompound such as an amino acid obtained by fermentation can be used as a starting material for polymers having high thermal stabilities and 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,^[7–9] polyimides (PIs),^[10–13] polyamides,^[14,15] and polyureas^[16] have been developed by using mi-

crobial 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 shikimate pathways through chorismate, 4-aminophenylpyruvic acid, and 4-aminophenylalanine (4APhe) as the intermediates.^[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.^[12,13,17] In addition, bio-based polyimides using isohexide and adenine have also been reported.^[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-aminocinnamic acid-based PIs, showed low solubilities in organic solvents similarly to other 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

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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-cyclopentanetricarboxylic acid 1,4:2,3-dianhydride (TCAAH), bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BTA), 4-(2,5-dioxotetrahydrofuran-3-yl)-1,2,3,4-tetrahydronaphthalene-1,2-dicarboxylic anhydride (TDA), pyromellitic dianhydride (PMDA), 4,4'-bipthalic anhydride (BPDA), 3,4'-bipthalic anhydride (aBPDA), 4,4'-oxydipthalic anhydride (OPDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA), 4,4'-(hexafluoro-isopropylidene)dipthalic anhydride (6FDA), 1,4-phenylene bis(1,3-dioxo-1,3-dihydroisobenzofuran-5-carboxylate) (TAHQ), and 4,4'-(4,4'-isopropylidenediphenoxy)dipthalic anhydride (BPADA) were purchased from Tokyo Chemical Industry Co., LTD.

Measurements

Proton nuclear magnetic resonance ($^1\text{H-NMR}$) measurements were carried out using Bruker Bio-spin AG 400 MHz. Gel permeation chromatography (GPC) was performed on the Shodex column (SB 806M $\times$ 2), column oven (GL Science, CO 631A, set as 40 $^\circ\text{C}$), degassing unit (GL Science, DG 660B), pump (JASCO, PU-2080 Plus), refractive index detector (JASCO, 830-RI), 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 flowing (gas flow rate, 200 mL-min $^{-1}$) from 25 $^\circ\text{C}$ to 800 $^\circ\text{C}$ with a heating rate of 5 $^\circ\text{C-min}^{-1}$ to determine the 5% and 10% mass loss temperature (T_{d5} and T_{d10}). Differential scanning calorimetry (DSC) was performed by SEIKO X-DSC7000T to measure glass transition temperatures (T_g) which were measured from 25 $^\circ\text{C}$ to 300 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C-min}^{-1}$ 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 $^\circ\text{C}$ for 3 h. After dried, thermal imidization was carried out at 100, 150, 200, and 220 $^\circ\text{C}$ 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^[13,17] and solubility-inducing polar groups such as carboxylate or sulfonate group.^[21] 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 $^1\text{H-NMR}$ 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-cyclopentanetricarboxylic acid 1,4:2,3-dianhydride (TCAAH), bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BTA), 4-(2,5-dioxotetrahydrofuran-3-yl)-1,2,3,4-tetrahydronaphthalene-1,2-dicarboxylic anhydride (TDA), pyromellitic dianhydride (PMDA), 4,4'-bipthalic anhydride (BPDA), 3,4'-bipthalic anhydride (aBPDA), 4,4'-oxydipthalic anhydride (OPDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride (DSDA), 4,4'-(hexafluoro-isopropylidene)dipthalic anhydride (6FDA), 1,4-phenylene bis(1,3-dioxo-1,3-dihydroisobenzofuran-5-carboxylate) (TAHQ), and 4,4'-(4,4'-isopropylidenediphenoxy)dipthalic anhydride (BPADA).

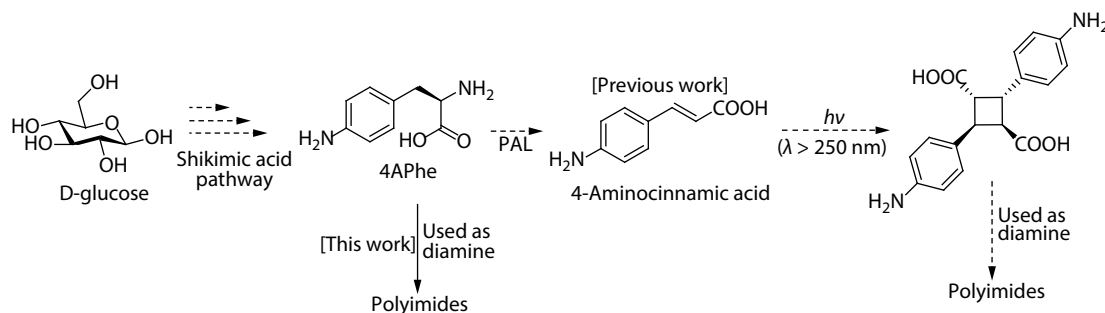


Fig. 1 4-Aminophenylalanine (4APhe) usage for preparation of soluble and cost-effective bio-based polyimides (PIs).

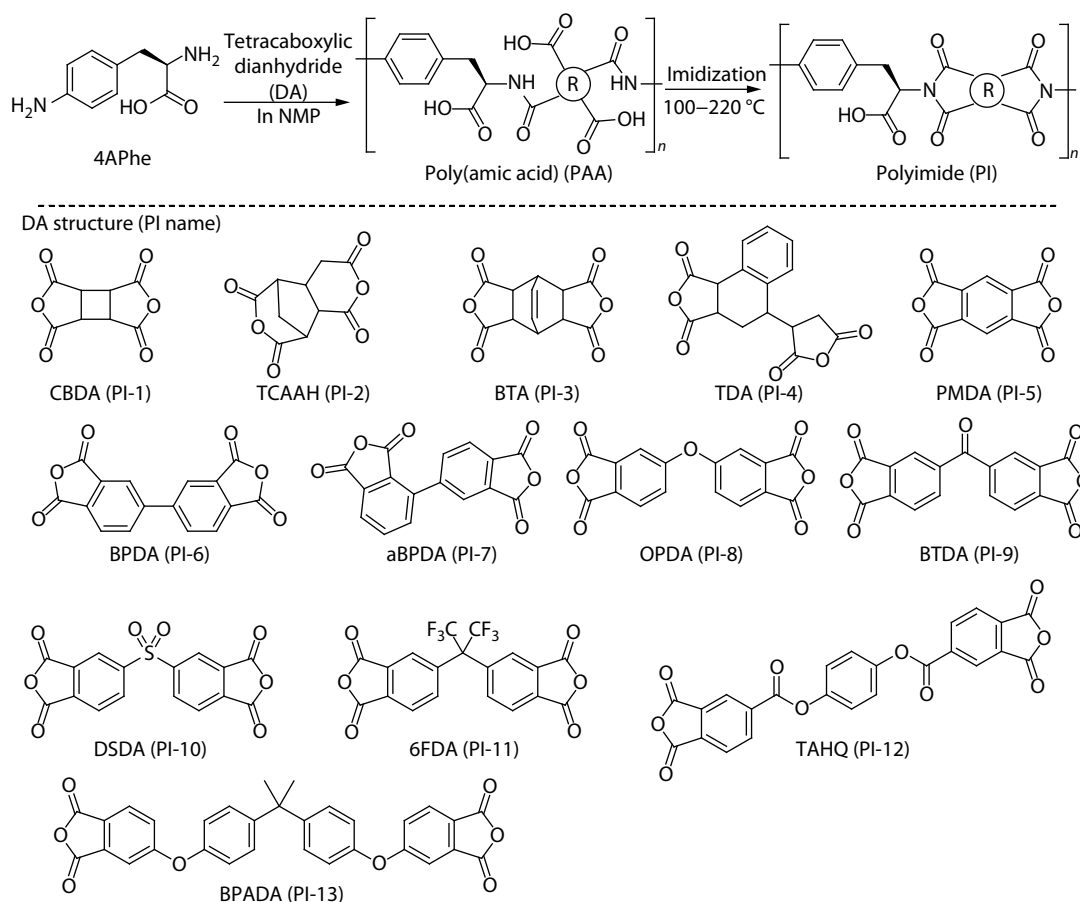
tetracarboxylic dianhydride (DSDA), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 1,4-phenylene bis(1,3-dioxo-1,3-dihydroisobenzofuran-5-carboxylate) (TAHQ), and 4,4'-(4,4'-isopropylidene-diphenoxy)diphthalic anhydride (BPADA), to obtain the corresponding poly(amic acid)s and PI-1 to PI-13 (Scheme 1). As a result, all the poly(amic acid)s were synthesized by mixing in NMP at room temperature. The structures of the obtained poly(amic acid)s were confirmed by $^1\text{H-NMR}$ 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 acid)s. 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 $^1\text{H-NMR}$ 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 $^1\text{H-NMR}$ 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 (M_w/M_n) (Table 2).



Scheme 1 Syntheses of 4-aminophenylalanine (4APhe)-based polyimides (PIs) using various tetracarboxylic dianhydride (DA).

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

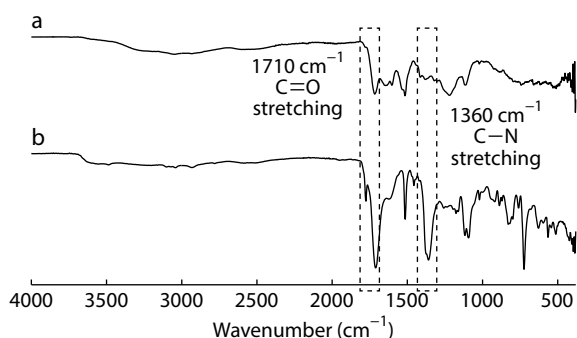


Fig. 2 FTIR spectra of the 4APhe/PMDA-based poly(amic acid) (a) and corresponding polyimide (PI-5) (b).

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)	–	+	+	+	+	+	±	±

^a Sample weight, 10 mg; Solvent volume, 1.0 mL; +, soluble at room temp (approx. 20 °C); ±, swellable (partially soluble); –, insoluble. Abbreviations PI-*n* (*n*: 1–13) corresponds to structures shown in Scheme 1.

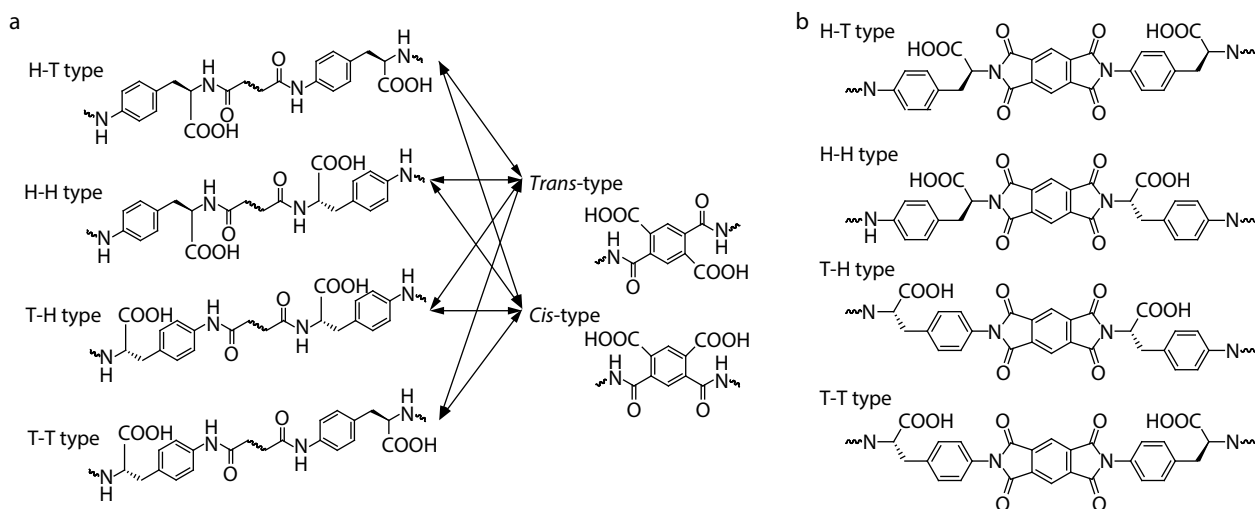


Fig. 4 Variation of stereoregularity of PAA (a) and PI (b) (in the case of PI-5, PMDA as a counter monomer).

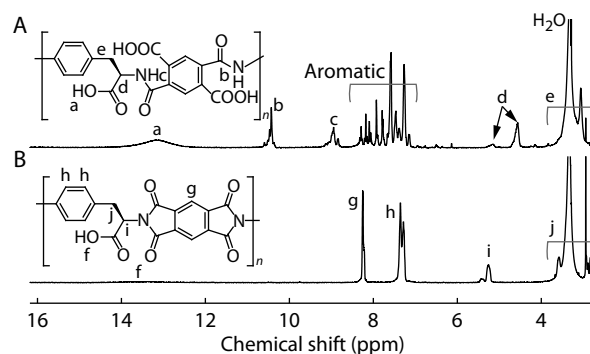


Fig. 3 ¹H-NMR spectra of poly(amic acid) (A) and PI-5 (B) (400 MHz, measured in DMSO-*d*₆).

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).^[23] 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 UltemTM, polyetherimide as thermo plastics, and the corresponding polyimide PI-13 had comparable performances to UltemTM, 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-

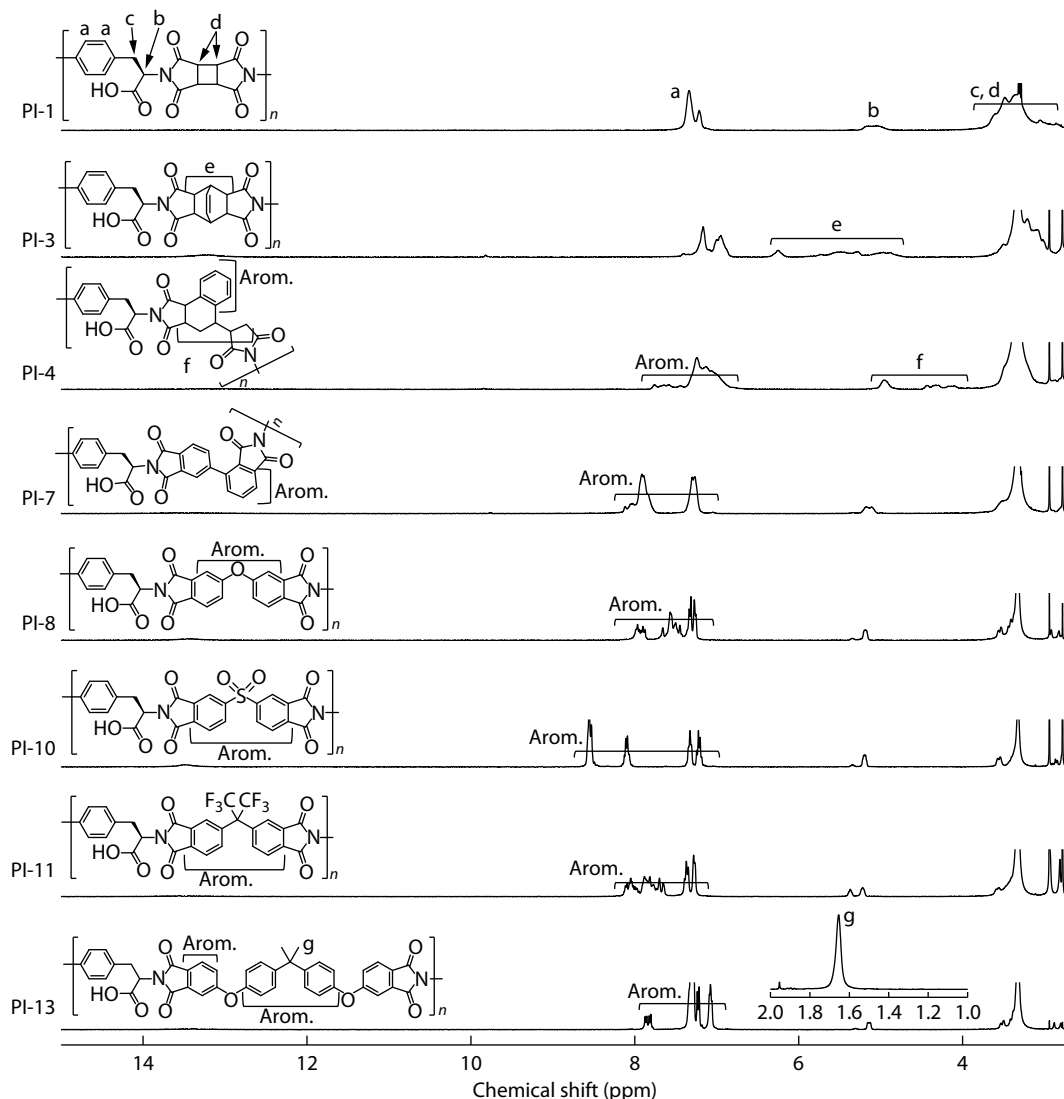


Fig. 5 ^1H -NMR spectra of soluble PIs, PI-1, PI-3, PI-4, PI-7, PI-8, PI-10, PI-11, and PI-13 (400 MHz, measured in DMSO-d_6). Inset: polyimide structures.

Table 2 Molecular weight (M_w and M_n), and polydispersity (M_w/M_n) of poly(amic acids) prepared from 4APhe.

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

^a Determined by GPC using DMF containing $0.01 \text{ mL}\cdot\text{min}^{-1}$ of LiBr as eluent; flow rate $1.0 \text{ mL}\cdot\text{min}^{-1}$; standards, polystyrene. PAA refers to poly(amic acids) 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. ^a

Polymer (DA)	T_{d5} ($^{\circ}\text{C}$)	T_{d10} ($^{\circ}\text{C}$)	T_g ($^{\circ}\text{C}$)	T_{d5}^b ($^{\circ}\text{C}$)	T_{d10}^b ($^{\circ}\text{C}$)
PI-1 (CBDA)	322	362	n.d. ^c	383	392
PI-2 (TCAAH)	303	347	n.d. ^c	376	392
PI-3 (BTA)	393	406	n.d. ^c	398	413
PI-4 (TDA)	342	373	n.d. ^c	366	378
PI-5 (PMDA)	347	380	n.d. ^c	378	410
PI-6 (BPDA)	401	427	n.d. ^c	399	428
PI-7 (aBPDA)	330	377	n.d. ^c	396	420
PI-8 (OPDA)	361	393	n.d. ^c	386	398
PI-9 (BTDA)	323	365	n.d. ^c	399	429
PI-10 (DSDA)	303	377	n.d. ^c	391	406
PI-11 (6FDA)	294	405	n.d. ^c	418	437
PI-12 (TAHQ)	388	410	n.d. ^c	398	413
PI-13 (BPADA)	373	413	222	409	430

^a T_{d5} and T_{d10} were determined by TGA at N_2 atmosphere, heating rate $5 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. T_g was determined by DSC at a heating rate of $10 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

^b Samples were pre-heated at $280 \text{ }^{\circ}\text{C}$ for 3 h before measurements. ^c T_g was not detected under $300 \text{ }^{\circ}\text{C}$. Abbreviations PI- n (n : 1–13) corresponds to structures shown in Scheme 1.

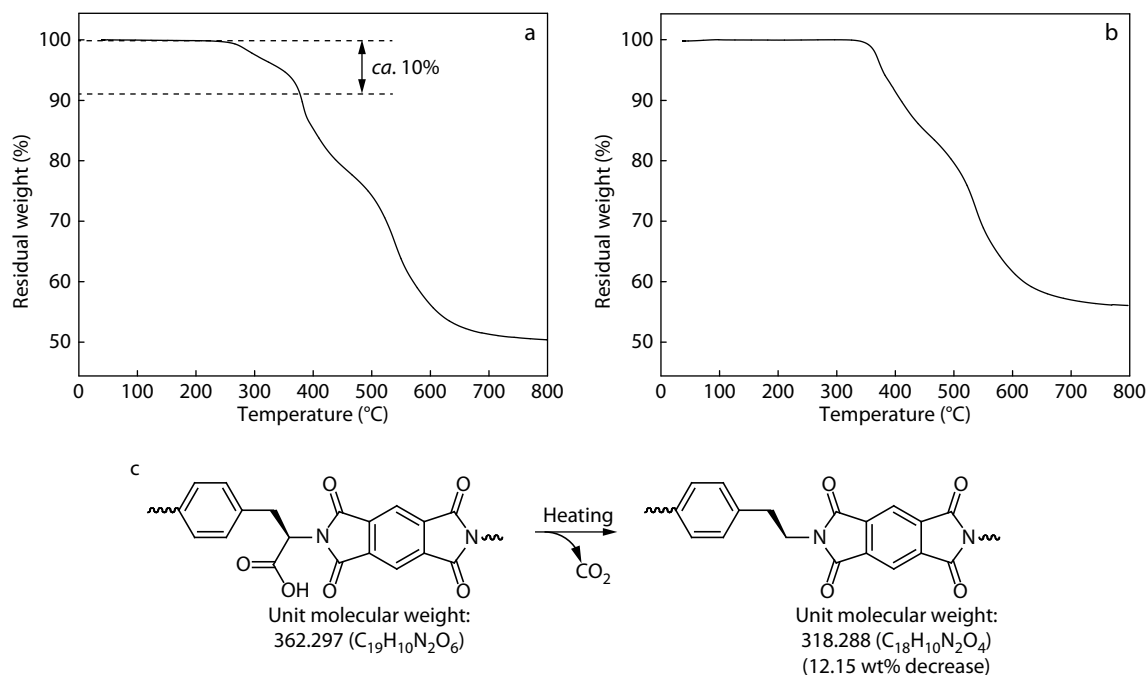


Fig. 6 TGA curves of the heat-decomposed PI-5 before heating (a) and after heating (b) at 280 °C for 3 h; mechanism of decarboxylation of 4APhe-based PI to improve the heat resistivity and insolubility (c).

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 decarboxylated 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 ^1H -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 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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