



Syntheses of carboxylated poly(arylene ether ketone)s with hyperbranched and linear architectures through the self-condensations of aromatic dicarboxylic anhydrides

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Received: 24 May 2018 / Revised: 20 June 2018 / Accepted: 23 June 2018 / Published online: 1 August 2018
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Abstract

Carboxylated poly(arylene ether ketone)s with hyperbranched and linear architectures were synthesized by the self-condensations of aromatic dicarboxylic anhydrides. A linear poly(arylene ether ketone) was obtained from an AB monomer, 4-phenoxyphthalic anhydride, whereas a hyperbranched poly(arylene ether ketone) was obtained using an AB₂ monomer, 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride. The method for the synthesis of the hyperbranched poly(arylene ether ketone) is notable, because it provides a high ion-exchange capacity, above 7 mmol g⁻¹, through a one-pot polycondensation. These functional polymers are soluble in several organic solvents and aqueous NaOH, in contrast to typical poly(ether ketone)s, while they retain the high thermal stabilities of their backbones.

Introduction

Poly(arylene ether ketone)s (PAEKs) are recognized as being high-performance engineering thermoplastics due to their high thermal and chemical stabilities along with their mechanical strengths; consequently, they are used in a variety of applications. PAEKs are typically obtained in two ways, namely, through nucleophilic aromatic substitution reactions that form ether bonds or by Friedel–Crafts electrophilic substitutions that form ketone bonds [1–5]. A variety of functional units, such as sulfonyl [6–10], carboxyl [11–15], hydroxyl [13], methyl [13], azobenzene [16], and phthalocyanine [17] groups, have been introduced in order to control the properties of PAEKs and expand their applications. These functionalized PAEKs are prepared through the co-polymerization of monomers bearing the

desired functional groups or through the post functionalization of pre-prepared PAEKs.

The synthesis of a hyperbranched polymer is a facile method for producing a functionalized PAEK, as it can contain numerous functional groups on its termini and can easily be prepared through the self-polycondensation of AB_x-type monomers or through A₂ + B₃ approaches [18]. These approaches have been used to synthesize other aromatic polymers, such as poly(arylene ether sulfone)s [19], polyamides [20, 21], and polyimides [22, 23]; these polymers have been proposed for catalytic applications [24–26]. In the case of PAEKs, Shu and Leu [15] reported the synthesis of a hyperbranched PAEK with carboxylic acid termini through the polycondensation of 5-phenoxyisophthalic acid, an AB₂-type monomer. A polymer with the same design has been used to modify carbon nanotubes [27]. Wang et al. [17] reported the synthesis of a hyperbranched PAEK functionalized with nickel phthalocyanine through an A₂ + B₃ approach. More recently, our research group reported the synthesis of a hyperbranched PAEK with a 2.8 mmol g⁻¹ carboxylic-acid-group content through the polycondensation of 4,4'-(*m*-phenylenedioxy)bis(benzenecarboxylic acid), which resulted in a high molecular weight [28]. This polymer was proposed to be a weakly acidic catalyst for the hydrolysis of cellulose. Moreover, this polymer acted as an oxidation catalyst for alcohols after modification of the terminal carboxylic groups with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) moieties [29, 30].

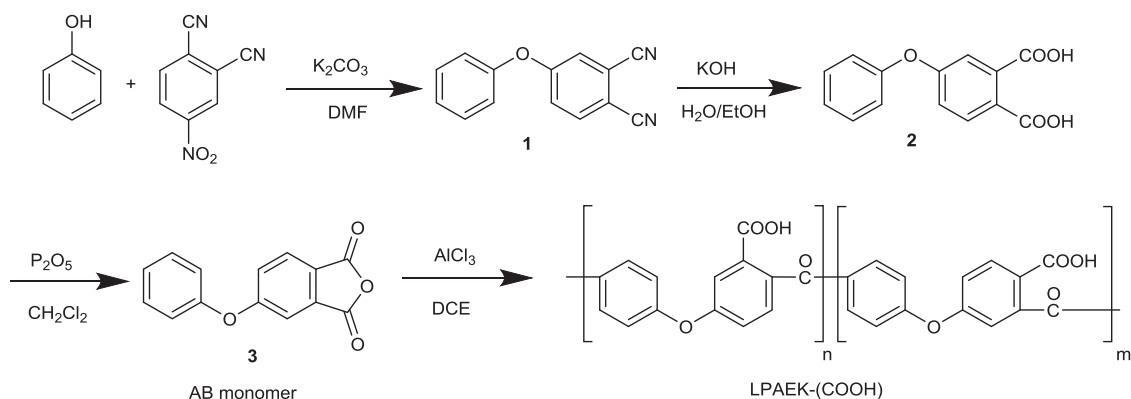
Electronic supplementary material The online version of this article (<https://doi.org/10.1038/s41428-018-0106-y>) contains supplementary material, which is available to authorized users.

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In this context, we have focused our interests on the self-polycondensations of aromatic dicarboxylic anhydrides as a more facile approach to producing carboxylated PAEKs. Friedel–Crafts electrophilic substitutions of aromatic rings with dicarboxylic anhydrides form ketone bonds and a free carboxylic acid group, and this process does not require any post functionalization. Moreover, this polycondensation process is clearly advantageous because it does not produce any byproducts, whereas the typical synthesis routes mentioned above produce halogen-containing byproducts. This polycondensation chemistry has been used in a very limited number of $A_2 + B_2$ examples [14, 31], but no self-polycondensation employing the Friedel–Crafts reaction has been reported for the preparation of functionalized PAEKs. In addition, we have a particular interest in the hyperbranched polymers obtained from the self-polycondensations of aromatic dicarboxylic anhydrides, because they provide phthalic acid units on their terminals, which might result in a new class of catalytic materials for the hydrolysis of cellulose [32].

The objective of this study is to establish a facile approach to obtain carboxylated PAEKs with hyperbranched and linear structures through the self-condensations of aromatic dicarboxylic anhydrides. We hereby demonstrate the self-polycondensation of 4-phenoxyphthalic anhydride (Scheme 1) to obtain a linear PAEK loaded with 4.16 mmol g^{-1} carboxylic acid groups (LPAEK-(COOH)) and that of 4,4'-(*m*-phenylenedioxy)bis(phthalic anhydride) (Scheme 2) to obtain a hyperbranched PAEK with 7.14 mmol g^{-1} carboxylic acid groups (HBPAEK-(COOH)₃). The hyperbranched PAEKs exhibited a very high ion-exchange capacity (IEC) compared with well-known ion-exchange resins such as Amberlyst-15® (4.7 mmol g^{-1}) and Nafion® ($1.0\text{--}1.1 \text{ mmol g}^{-1}$), and are soluble in several organic solvents and aqueous NaOH, in contrast to typical poly(ether ketone)s, while they retain the high thermal stabilities of their backbones.



Scheme 1 Synthesis route to the linear PAEK

Materials and methods

Materials

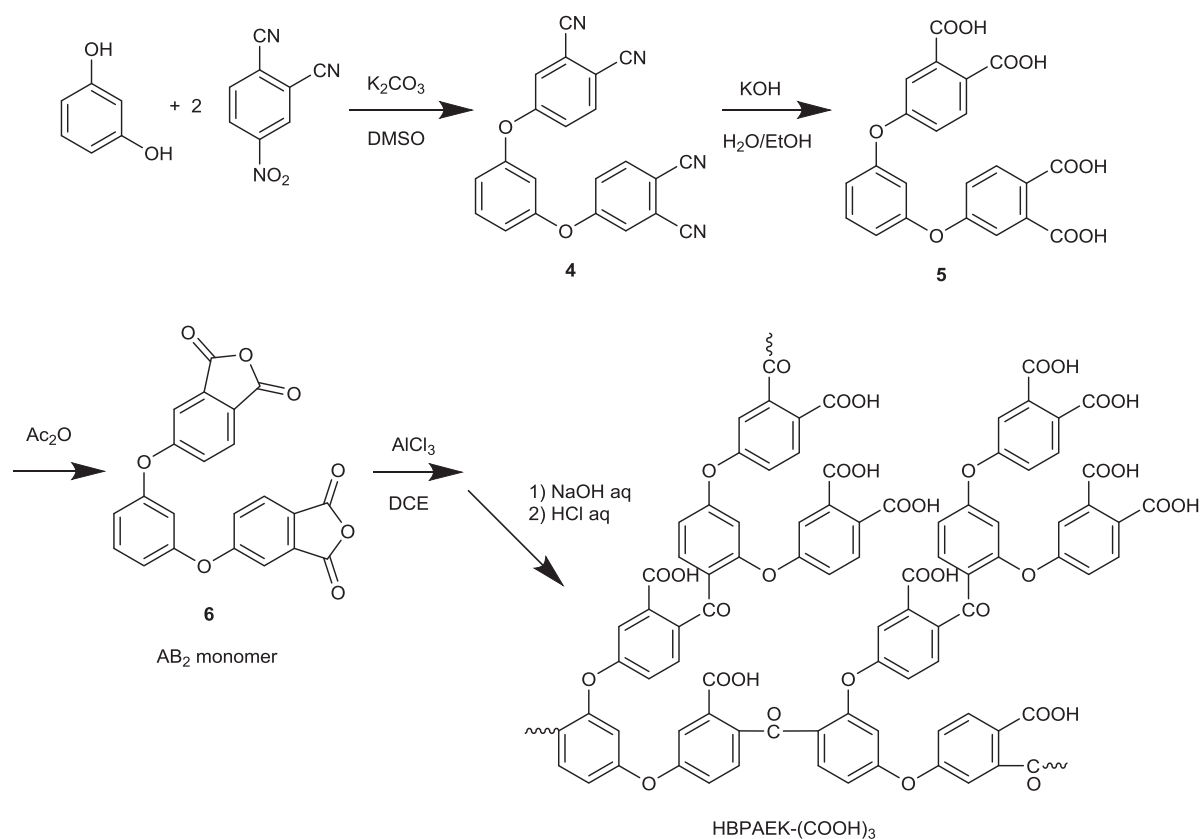
All materials were of reagent grade, purchased from Wako Chemical (Osaka), Tokyo Chemical Industry (Tokyo), or Sigma-Aldrich (Tokyo), and used without further purification.

Syntheses of 4-phenoxyphthalonitrile (1)

Phenol (2.39 mL, 29.5 mmol) and 4-nitrophenalonitrile (4.72 g, 27.2 mmol) were dissolved in *N,N*-dimethylformamide (DMF, 60 mL) in a 500 mL flask equipped with a condenser, after which K_2CO_3 (7.39 g, 53.5 mmol) was added. The mixture was stirred at 80°C for 3 h and then poured into water (1.5 L). The precipitate was collected by filtration, washed with water, and dried under vacuum at 70°C to obtain a whitish powder (4.97 g, 91%). Proton nuclear magnetic resonance ($^1\text{H-NMR}$) (400 MHz, $DMSO-d_6$, δ): 8.09 (d, 1 H), 7.77 (s, 1 H), 7.50 (t, 2 H), 7.37–7.34 (dd, 1 H), 7.32 (t, 1 H), 7.19 (d, 2 H). Infrared spectrum (IR) (KBr, cm^{-1}): 2233 (nitrile stretch).

Syntheses of 4-phenoxyphthalic acid (2)

4-Phenoxyphthalonitrile (1) (5.79 g, 26.3 mmol) and KOH (85%, 8.20 g, 125 mmol) were dissolved in 1:1 (v/v) water/ethanol (120 mL) in a 500 mL flask equipped with a condenser and refluxed for 24 h. Another portion of KOH (85%, 8.20 g, 125 mmol) was added and the mixture was refluxed for a further 24 h, after which it was poured into water (1.5 L). After adjusting the pH to 1 with 1 M aqueous HCl, the precipitate was collected by filtration, washed with dilute HCl and water, and then dried under vacuum at 70°C to obtain a whitish powder (5.11 g, 82%). $^1\text{H-NMR}$ ($DMSO-d_6$, δ): 12.89 (s, 2 H), 7.96 (d, 4 H), 7.51 (t, 1 H), 7.11 (d, 4 H), 6.97–6.95 (dd, 2 H), 6.89 (s, 1 H). IR (KBr, cm^{-1}): 3000–2500 (O-H, broad), 1672 (C = O stretch).



Scheme 2 Synthesis route to the hyperbranched PAEK

Synthesis of 4-phenoxyphthalic anhydride (3)

4-Phenoxyphthalic acid (**2**) (2.56 g, 9.92 mmol) was dissolved in dichloromethane (100 mL) in a 200 mL flask equipped with a condenser. Phosphorous pentoxide (P_2O_5 , 6.8 g) was added and the mixture was refluxed for 3 h. After filtration, the solvent was removed by evaporation, and the 4-phenoxyphthalic anhydride (**3**) residue was purified by sublimation under vacuum at 120 °C to obtain a whitish powder (0.857 g, 36%). 1H -NMR (DMSO- d_6 , δ): 8.08 (d, 1 H), 7.54 (d, 2 H), 7.51 (d, 1 H), 7.42 (s, 1 H), 7.35 (t, 1 H), 7.22 (d, 2 H). IR (KBr, cm^{-1}): 3100–3000 (C–H stretch), 1851 (C=O stretch).

Synthesis of 1,3-bis(3,4-dicyanophenoxy)benzene (4)

Resorcinol (3.3 g, 30 mmol) and 4-nitrophthalonitrile (10.4 g, 60 mmol) were dissolved in dimethyl sulfoxide (DMSO) (60 mL) in a 100 mL flask fitted with a N_2 balloon and stirred at room temperature for 24 h. The mixture was poured into 1:1 (v/v) water/methanol (1.2 L) and filtered. The precipitate was washed with water and dried under vacuum at 60 °C to obtain a whitish powder (10.8 g, 99%). 1H -NMR (DMSO- d_6 , δ): 8.13 (d, 2 H), 7.93 (d, 2 H), 7.61

(m, 1 H), 7.56 (dd, 2 H), 7.15 (s, 1 H), 7.14 (dd, 2 H). IR (KBr, cm^{-1}): 2231 (nitrile stretch), 1246 (C–O stretch).

Synthesis of 1,3-bis(3,4-dicarboxyphenoxy)benzene (5)

1,3-Bis(3,4-dicyanophenoxy)benzene (**4**) (10.8 g, 30 mmol) and KOH (85%, 20 g, 300 mol) were dissolved in 1:1 (v/v) water/ethanol (200 mL) in a 500 mL flask equipped with a condenser and stirred at 95 °C for 64 h. After hot filtration, dilute HCl was added to the filtrate, and the precipitate was collected by filtration and dried under vacuum at 60 °C to obtain a whitish powder (12.5 g, 98%). 1H -NMR (DMSO- d_6 , δ): 13.24 (s, 4 H), 7.78 (d, 2 H), 7.52 (t, 1 H), 7.17 (m, 4 H), 6.99 (m, 3 H). IR (KBr, cm^{-1}): 1708 (C=O stretching).

Synthesis of 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride (6)

1,3-Bis(3,4-dicarboxyphenoxy)benzene (**5**) (12.5 g, 28.5 mmol) and acetic anhydride (120 mL) were added to a 300 mL flask fitted with a condenser and stirred at 120 °C for 5 h. After cooling in an ice bath, the precipitate was collected by filtration, washed with toluene, and dried under vacuum at 80 °C. The crude powder was recrystallized from acetic

anhydride to obtain a whitish powder (8.5 g, 74%). ^1H -NMR (DMSO- d_6 , δ): 8.10 (d, 2H), 7.64–7.62 (m, 5H), 7.14–7.12 (m, 3H). Carbon-13 (^{13}C) NMR (DMSO- d_6 , δ): 163.3, 162.5, 156.0, 134.1, 132.3, 127.9, 125.3, 125.1, 117.1, 113.5, 112.5. IR (KBr, cm^{-1}): 1850 (C=O stretch), 1246 (C–O stretch).

Synthesis of LPAEK-(COOH)

AlCl_3 (1.67 g, 12.5 mmol) was dispersed in 1,2-dichloroethane (DCE, 12 mL) in a 100 mL flask equipped with a condenser and stirred under N_2 at room temperature for 30 min. In a separate vial, 4-phenoxyphthalic anhydride (**3**) 1.20 g (5.0 mmol) was dissolved in DCE (12 mL) and this solution was transferred to the flask by syringe. After stirring at 50 °C for the prescribed reaction time, the mixture was poured into 1 M aqueous HCl (500 mL), and the precipitate was collected by filtration. The collected powder was washed three times with dilute HCl and dried under vacuum at 70 °C. This crude powder was dissolved in a small amount of DMSO and reprecipitated in acetone, collected, washed with water, and then dried under vacuum; at 80 °C to obtain LPAEK-(COOH) as a whitish powder.

Synthesis of HBPAEK-(COOH)₃

AlCl_3 (1.67 g, 12.5 mmol) was dispersed in DCE (2 mL) in a 100 mL flask equipped with a condenser and stirred under N_2 at –20 °C for 20 min. In a separate vial, 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride (**6**) (0.95 g, 2.36 mmol) was dissolved in DCE (26 mL), and this solution was transferred to the flask by syringe. After stirring at 50 °C for the prescribed time, the mixture was poured into water (250 mL), and the precipitate was collected by filtration. The collected powder was washed with 5 M aqueous HCl (100 mL) and then stirred in 6 M aqueous NaOH (10 mL) at 80 °C for 2 h. After filtration, dilute HCl was added to the filtrate, and the precipitate was collected by filtration, washed with dichloromethane and water, and then dried under vacuum at 35 °C to obtain HBPAEK-(COOH)₃ as a brownish powder.

Polymer esterification

To perform size exclusion chromatography (SEC) on the prepared polymers, their carboxylic acid termini were converted into ethyl esters in the following manner. The carboxylic acid-terminated polymer (0.11 g) and K_2CO_3 (0.26 g, 18.8 mmol) were dissolved in DMSO (0.5 mL) in a 5 mL reactor and stirred at 50 °C for 1 h. Iodoethane (603 μL , 7.5 mmol) was then added and the mixture was stirred for another 24 h. The polymer was partitioned between

water (10 mL) and ethyl acetate (10 mL) in a separating funnel, and the collected organic phase was washed twice with saturated brine. After drying over MgSO_4 and evaporation, the residue was dried under vacuum at 60 °C to obtain a polymer with ethyl ester termini, namely, LPAEK-(COOEt) and HBPAEK-(COOEt)₃.

Characterization

^1H and ^{13}C NMR spectra were recorded on a JEOL ECS400 (400 MHz) spectrometer. ^{13}C NMR spectra were recorded using distortionless enhancement of polarization transfer with a flip angle of 90° (DEPT-90) and a pulse delay of 5 s. IR spectra were recorded on a JASCO 4100 spectrometer using the KBr pellet method. Thermogravimetric analysis (TGA) was performed with an SII TGA 7300 system at a heating rate of 10 °C min^{-1} . SEC was performed in DMF containing 0.05 M LiBr as the eluent on a Viscotek GPC-1000 system equipped with a TDA 302 triple detector and a TSK-GEL α -M column. The weight-averaged molecular weight (M_w) was calculated from light-scattering data. Inherent viscosity was measured using a 0.5 g dL^{-1} polymer solution in concentrated H_2SO_4 using an Ostwald viscometer in a thermostatic bath at 30 °C. The IEC was determined by reverse titration as follows: 30 mg of polymer was stirred overnight in 3 mL of 0.1 M aqueous NaOH and then diluted to 10 mL with Millipore water prior to titration with a 0.05 M HCl standard solution.

Results and Discussion

Polymer synthesis

LPAEK-(COOH) was prepared by the polymerization of the AB monomer, 4-phenoxyphthalic anhydride (**3**), for times ranging from 3 to 48 h; the results are summarized in Table 1. Polymerization for 3 h resulted in a 61% yield of a polymer with a M_w of 13,000. The M_w was observed to increase with increasing reaction time to give an insoluble precipitate after 48 h. The decrease in yield with increasing reaction time is mainly ascribable to the difficulties associated with collecting the polymer due to high viscosity.

HBPAEK-(COOH)₃ was prepared by the polymerization of the AB₂ monomer, 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride (**6**), for times ranging from 1 to 24 h. Polymerization for 1 h resulted in a 38% yield of a polymer with a M_w of 12,000. The M_w increased with increasing reaction time to reach 224,000 after 24 h. The higher molecular weight of HBPAEK-(COOH) compared with LPAEK-(COOH)₃ is probably due to its solubility during polymerization, which is improved by the hyperbranched architecture.

Polymer structure

The detailed structures of the synthesized polymers were characterized by NMR spectroscopy. Figure 1 displays the $^1\text{H-NMR}$ spectra of LPAEK-(COOH) and its monomers in their dehydrated and hydrolyzed forms. The spectra of the monomers correspond to those reported elsewhere [33]. For LPAEK-(COOH), the dicarboxylic anhydride has two available positions for the Friedel–Crafts acylation reaction; consequently, the NMR spectra of the polymers are slightly complicated. To obtain further details, including

Table 1 Characterization data for polymers produced over different reaction times

	Reaction time [h]	Yield [%]	$M_w^a / 10^3$	m/n	IEC [mmol/g]	η_{inh}^b [dL/g]
LPAEK-(COOH)	3	61	13	0.48	4.4	0.22
	8	58	25	0.37	4.3	0.26
	24	41	37	0.47	4.2	0.35
	48	32	- ^c	- ^c	- ^c	- ^c
HBPAEK-(COOH) ₃	1	38	12	0.47	7.2	0.08
	3	46	29	0.51	7.3	0.12
	8	63	68	0.34	6.6	- ^c
	12	56	150	0.54	6.4	- ^c
	24	53	224	0.56	7.4	- ^c

^aDetermined by SEC in DMF containing 0.05 M LiBr using a light-scattering detector, after converting the polymers to LPAEK-(COOEt) and HBPAEK-(COOEt)₃.

^bMeasured for a 0.5 g dL⁻¹ polymer solution in conc. H₂SO₄ at 30 °C

^cThe polymer did not dissolve

DMF, *N,N*-dimethylformamide; IEC, ion-exchange capacity; SEC, size exclusion chromatography

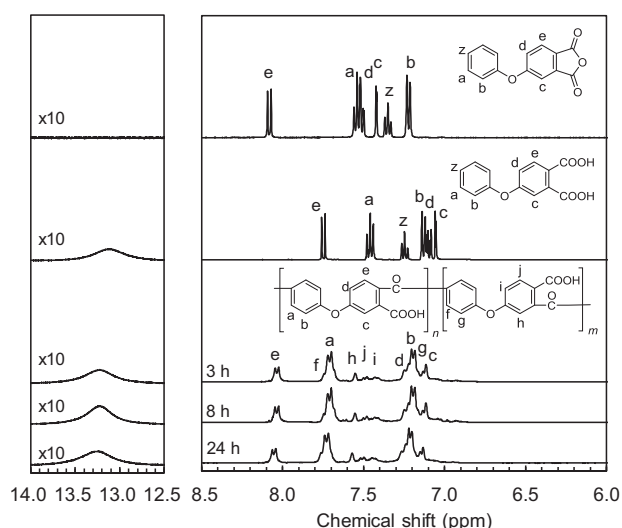


Fig. 1 $^1\text{H-NMR}$ spectra of LPAEK-(COOH) produced over different reaction times and its monomers

regioselectivity information, the $^{13}\text{C-DEPT-90}$ spectra of LPAEK-(COOH) (M_w : 25,000) and its monomers were also recorded (Fig. 2a). The DEPT sequence was used, because it provides a high signal/noise ratio on the basis of $^1J_{\text{CH}}$ coupling, rather than simple peak assignment. Peaks were assigned based on the two-dimensional spectra recorded with the heteronuclear multiple quantum correlation (HMQC) sequence (Figure S1) and by comparisons with the spectra of the monomers. As all peaks were reasonably assigned, the polymerization illustrated in Scheme 1 appears to have been successful. As the $^1J_{\text{CH}}$ coupling constants for all C–H bonds in this polymer are similar and this $^{13}\text{C-DEPT-90}$ spectrum was recorded with a sufficiently long pulse delay, this spectrum provides quantitative information [34]. Therefore, the regioselectivity was determined by comparing the areas of peaks e and j in the $^{13}\text{C-DEPT-90}$ spectrum, which gave m/n values of 0.37–0.48 (Table 1), suggesting that this condensation slightly favors the para-position of the aromatic ring of the dicarboxylic anhydride.

$^1\text{H-NMR}$ and $^{13}\text{C-DEPT-90}$ spectra for HBPAEK-(COOH)₃ (M_w : 29000) and its monomers are shown in Figs. 3 and 2b, respectively. The spectra of the monomers correspond to those reported elsewhere [35, 36]. The NMR spectra of HBPAEK-(COOH)₃ could be more complicated than those of LPAEK-(COOH) because of its hyperbranched structure that contains linear, dendritic, and

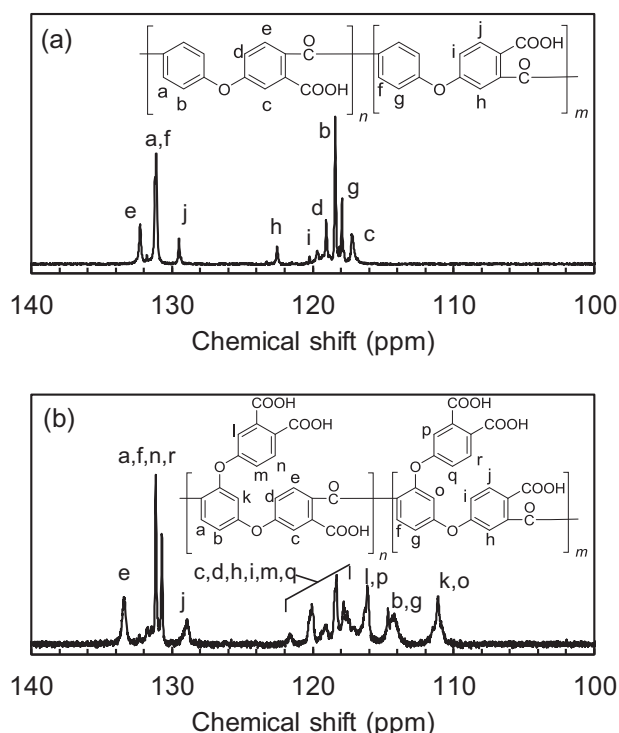


Fig. 2 DEPT-90 spectra of **a** LPAEK-(COOH) (M_w : 25,000) and **b** HBPAEK-(COOH)₃ (M_w : 29,000)

terminal units, as illustrated in Fig. 4; the regioselectivity of HBPAEK-(COOH)₃ was determined in the same manner as that of LPAEK-(COOH). We attempted to distinguish the linear, dendritic, and terminal units in the NMR spectra to determine the degree of branching but found that the differences in the chemical shifts among these units were too small. In Fig. 3, for instance, the (k, o) and (b, g) peaks of HBPAEK-(COOH)₃ were slightly broader than those of LPAEK-(COOH), which probably reflects small changes derived from the linear, dendritic, and terminal units; however, the peaks are not well enough resolved. Therefore, peak assignments were determined based on the linear units. All ¹H-NMR (Fig. 3), ¹³C-DEPT-90 (Fig. 2b), and HMQC (Figure S2) spectra were reasonably assigned, suggesting

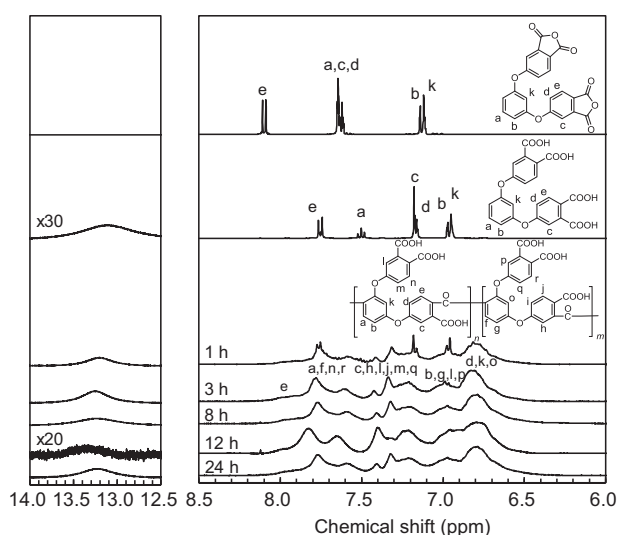


Fig. 3 ¹H-NMR spectra of linear HBPAEK-(COOH)₃ produced over different reaction times and its monomers

that HBPAEK-(COOH)₃ had been successfully formed. The regioselectivity was determined by comparing the areas of peaks e and j in the ¹³C-DEPT-90 spectra, which gave *m/n* values of 0.34–0.56, suggesting that the para-position of the aromatic ring of the dicarboxylic anhydride is slightly favored during condensation.

Physicochemical properties

The IECs of LPAEK-(COOH) and HBPAEK-(COOH)₃ were investigated by reverse titration, the results of which are summarized in Table 1. All tested LPAEK samples exhibited reasonable IEC values close to the theoretical value (4.16 mmol g⁻¹), whereas the HBPAEK-(COOH)₃ samples exhibited even higher IEC values, 6.4–7.3 mmol g⁻¹, due to the presence of phthalic acid units. It should be noted that the IEC values for HBPAEK-(COOH)₃ are much higher than those of typical ion-exchange resins and polymers with such high IECs were obtained through a one-pot polycondensation followed by a simple purification procedure.

The inherent viscosities of LPAEK-(COOH) and HBPAEK-(COOH)₃ were investigated using an Ostwald viscometer and are summarized in Table 1. Some of the polymer samples were not able to be measured in this viscosity study, because they did not dissolve in H₂SO₄. The inherent viscosity of HBPAEK-(COOH)₃, 0.08–0.12 dL g⁻¹, is smaller than that of LPAEK-(COOH), 0.22–0.35 dL g⁻¹, which probably reflects the low entanglements of these hyperbranched polymers.

The solubilities of LPAEK-(COOH) (*M*_w: 25,000) and HBPAEK-(COOH)₃ (*M*_w: 29,000) in a variety of solvents were investigated, the results of which are summarized in Table 2. These polymers are soluble in *N*-methyl-2-pyrrolidone, *N,N*-dimethylacetamide, DMSO, DMF, THF,

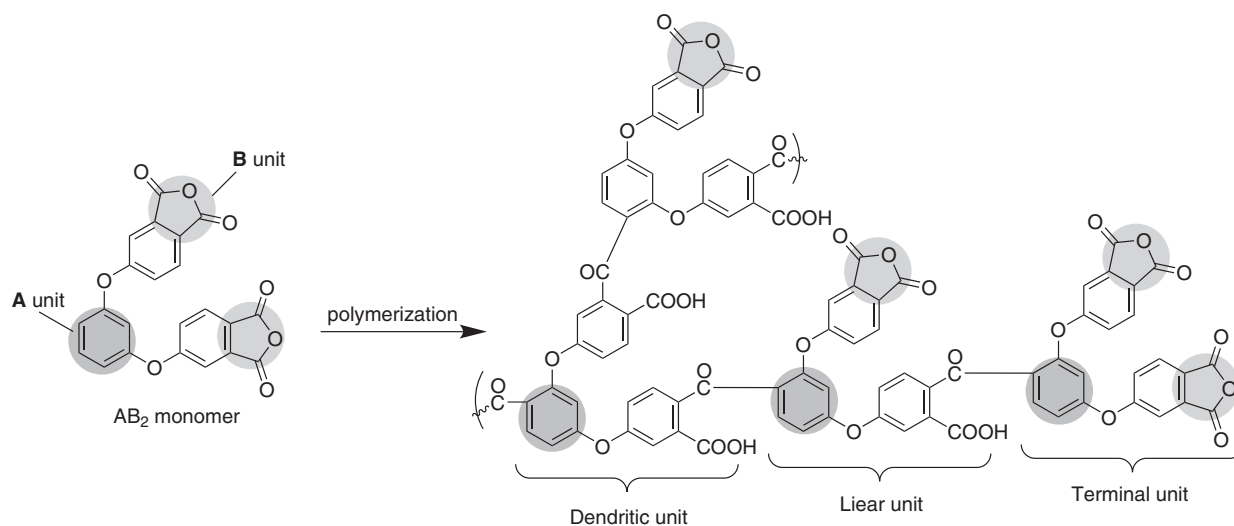


Fig. 4 The polymerization of the AB₂ monomer to afford HBPAEK

Table 2 Solubilities of HBPAEK-(COOH)₃ and LPAEK-COOH in various solvents^a

	NMP	DMAc	DMSO	DMF	THF
HBPAEK ^b	+	+	+	+	+
LPAEK ^c	+	+	+	+	+
	Acetone	DCM	Chloroform	Hexane	Ethyl acetate
HBPAEK ^b	+	-	-	-	-
LPAEK ^c	±	-	-	-	-
	Toluene	MeOH	EtOH	Deionized water	0.1 M NaOH aq
HBPAEK ^b	-	-	-	-	+
LPAEK ^c	-	-	-	-	+

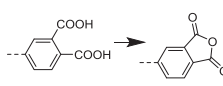
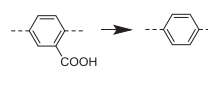
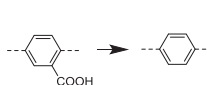
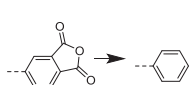
^aThe polymer (50 mg) was dissolved in 1.5 mL of solvent. + soluble at room temperature, ± partially soluble, - insoluble at room temperature

^b M_w : 29,000

^c M_w : 25,000

DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; NMP, *N*-methyl-2-pyrrolidone

Table 3 Weight losses at the various stages during the thermal decompositions of HBPAEK-(COOH)₃ and LPAEK-COOH

Stage	LPAEK-(COOH)	HBPAEK-(COOH) ₃
I	Moisture	Moisture
II	Unknown	
III		
IV	Carbonization	
V	Carbonization	Carbonization

poly(ether ketone)s are known to be generally insoluble in solvents.

The thermal stabilities of the LPAEK-(COOH) (M_w : 25,000) and HBPAEK-(COOH)₃ (M_w : 29,000) were studied by TGA, as summarized in Fig. 5 and Table 3. The derivative thermogravimetric (DTG) trace for LPAEK-(COOH) exhibits five peaks followed by gradual weight loss due to carbonization. Stage I, below 100 °C, corresponds to moisture evaporation. Stage II is difficult to assign but might involve some crosslinking reactions related to the carboxylic acid groups, while Stage III is possibly ascribable to the decomposition of the carboxylic acid groups, followed by gradual carbonization. Although the DTG trace for HBPAEK-(COOH)₃ exhibited the same trend and was similar to that obtained for LPAEK-(COOH)₃, different behavior was also observed due to its phthalic acid groups. Although Stages I and II correspond to the loss of water, Stage II is probably associated with a ring-closure reaction that forms phthalic anhydride units at the termini of the hyperbranched polymers. Carbonyl-group decompositions are also distributed across Stages III and IV, corresponding to the decompositions of single carboxylic acid groups and those of phthalic anhydride units. These results suggest that the main backbones of LPAEK and HBPAEK are thermally stable up to approximately 400 °C, whereas the carboxylic acid groups decompose near 300 °C.

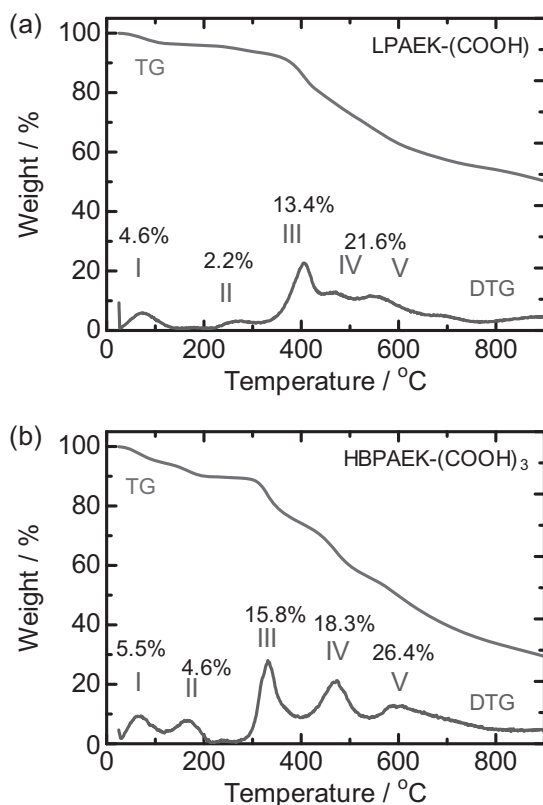


Fig. 5 TG and DTG traces for **a** LPAEK-(COOH) (M_w : 25,000) and **b** HBPAEK-(COOH)₃ (M_w : 29,000). The numbers indicate the weight loss at each stage

acetone, and 0.1 M aqueous NaOH. These solubilities are ascribable to the carboxylic acid groups, whereas typical

Conclusions

Carboxylated PAEKs with hyperbranched and linear architectures were successfully synthesized by the self-

condensations of aromatic dicarboxylic anhydrides. The synthesis of the hyperbranched PAEK from 1, 3-bis(3, 4-dicarboxyphenoxy)benzene dianhydride, as an AB₂ monomer, is especially notable because of its high IEC (over 7 mmol g⁻¹), and it was obtained through a one-pot polycondensation. These functional polymers are soluble in several organic solvents and aqueous NaOH, in contrast to typical poly(ether ketone)s, and retain the high thermal stabilities of their main backbones. Further studies of the applications of these polymers in various fields, such as catalysis and ionic materials, will form part of the future work.

Acknowledgements This study was supported by JSPS KAKENHI (17K17709). We thank Dr Shigeki Kuroki for valuable discussions regarding the NMR study.

Compliance with ethical standards

Conflict of interest The authors have no conflict of interest to declare.

References

- Mullins MJ, Woo EP. The synthesis and properties of poly(aromatic ketones). *J Macromol Sci Part C Polym Rev*. 1987;27:313–41.
- Shukla D, Negi YS, Uppadhya JS, Kumar V. Synthesis and modification of poly(ether ether ketone) and their properties: a review. *Polym Rev*. 2012;52:189–228.
- Kanetaka Y, Yamazaki S, Kimura K. Preparation of poly(ether ketone)s derived from 2,5-furandicarboxylic acid via nucleophilic aromatic substitution polymerization. *J Polym Sci Part A Polym Chem*. 2016;54:3094–101.
- Kanetaka Y, Yamazaki S, Kimura K. Preparation of poly(ether ketone)s derived from 2,5-furandicarboxylic acid by polymerization in ionic liquid. *Macromolecules*. 2016;49:1252–8.
- Kanetaka Y, Yamazaki S, Kimura K. Synthesis of poly(ether ketone)s from 2,5-thiophenedicarboxylic acid. *J Photopolym Sci Technol*. 2016;29:243–6.
- Bauer B, Jones DJ, Rozière J, Tchicaya L, Alberti G, Casciola M, et al. Electrochemical characterisation of sulfonated polyetherketone membranes. *J New Mater Electrochem Syst*. 2000;3:93–98.
- Alberti G, Casciola M, Massinelli L, Bauer B. Polymeric proton conducting membranes for medium temperature fuel cells (110–60°C). *J Memb Sci*. 2001;185:73–81.
- Xing P, Robertson GP, Guiver MD, Mikhailenko SD, Wang K, Kaliaguine S. Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes. *J Memb Sci*. 2004;229:95–106.
- Miyake J, Miyatake K. Fluorine-free sulfonated aromatic polymers as proton exchange membranes. *Polym J*. 2017;49:487–95.
- Sivasubramanian G, Hariharasubramanian K, Deivanayagam P, Ramaswamy J. High-performance SPEEK/SWCNT/fly ash polymer electrolyte nanocomposite membranes for fuel cell applications. *Polym J*. 2017;49:703–9.
- Guo M, Liu B, Guan S, Liu C, Qin H, Jiang Z. Novel poly(arylene ether ketone)s containing sulfonic/carboxylic groups: synthesis and properties. *J Memb Sci*. 2010;362:38–46.
- Zhao X, Zhang G, Jia Q, Zhao C, Zhou W, Li W. Adsorption of Cu(II), Pb(II), Co(II), Ni(II), and Cd(II) from aqueous solution by poly(aryl ether ketone) containing pendant carboxyl groups (PEK-L): equilibrium, kinetics, and thermodynamics. *Chem Eng J*. 2011;171:152–8.
- Donetskii KI, Ryabev AN, Shaposhnikova VV, Salazkin SN, Komarova LI, Afonicheva OV. Synthesis and properties of copoly(arylene ether ketones) with side reactive groups. *Polym Sci Ser A*. 2008;50:25–30.
- Zolotukhin MG, Colquhoun HM, Sestiaa LG, Rueda DR, Flot D. One-pot synthesis and characterization of soluble poly(aryl ether ketone)s having pendant carboxyl groups. *Macromolecules*. 2003;36:4766–71.
- Shu C, Leu C. Hyperbranched poly(ether ketone) with carboxylic acid terminal groups: synthesis, characterization, and derivatization. *Macromolecules*. 1999;32:100–5.
- Zhang J, Zhang H, Chen X, Zhang Y, Li X, Chen Q, et al. Synthesis and characterization of novel photoactive poly(arylene ether ketone) with azobenzene pendants. *Mater Lett*. 2010;64:337–40.
- Wang D, Zhang S, Zhang Y, Wang H, Mu J, Wang G, et al. Preparation and nonlinear optical characterization of a novel hyperbranched poly(aryl ether ketone) end-functionalized with nickel phthalocyanine. *Dye Pigment*. 2008;79:217–23.
- Jikei M, Kakimoto M. Hyperbranched polymers: a promising new class of materials. *Prog Polym Sci*. 2001;26:1233–85.
- Matsumoto K, Ueda M. Synthesis of hyperbranched aromatic poly(ether sulfone) with sulfonyl chloride terminal groups. *Chem Lett*. 2006;35:1196–7.
- Jikei M, Chon S-H, Kakimoto M, Kawauchi S, Imase T, Watanebe J. Synthesis of hyperbranched aromatic polyamide from aromatic diamines and trimesic acid. *Macromolecules*. 1999;32:2061–4.
- Yang G, Jikei M, Kakimoto M. Synthesis and properties of hyperbranched aromatic polyamide. *Macromolecules*. 1999;32:2215–20.
- Yamanaka K, Jikei M, Kakimoto MA. Preparation of hyperbranched aromatic polyimide without linear units by end-capping reaction. *Macromolecules*. 2001;34:3910–5.
- Hao J, Jikei M, Kakimoto MA. Hyperbranched polyimides prepared by ideal A₂ + B₃ polymerization, non-ideal A₂ + B₃ polymerization and AB₂ self-polymerization. *Macromol Symp*. 2003;199:233–41.
- Nabae Y, Liang J, Huang X, Hayakawa T, Kakimoto M. Sulfonic acid functionalized hyperbranched poly(ether sulfone) as a solid acid catalyst. *Green Chem*. 2014;16:3596–602.
- Nabae Y, Tomita M, Taniguchi T, Liang J, Yamamoto K, Hayakawa T, et al. Hyperbranched vs. linear polymers in the catalysis by sulfonic acid functionalized poly(ether sulfone). *Polym J*. 2018;137:324–329.
- Nabae Y, Mikuni M, Takusari N, Hayakawa T, Kakimoto M. Aerobic oxidation of benzyl alcohol over TEMPO-functionalized polyimide as a heterogeneous catalyst. *High Perform Polym*. 2017;29:646–50.
- Wang DH, Mirau P, Li B, Li CY, Baek J-B, Tan L-S. Solubilization of carbon nanofibers with a covalently attached hyperbranched poly(ether ketone). *Chem Mater*. 2008;20:1502–15.
- Shi Y, Nabae Y, Hayakawa T, Kobayashi H, Yabushita M, Fukuoka A, et al. Synthesis and characterization of hyperbranched aromatic poly(ether ketone)s functionalized with carboxylic acid terminal groups. *Polym J*. 2014;46:722–7.
- Shi Y, Nabae Y, Hayakawa T, Kakimoto M. Modification of graphene with hyperbranched poly(ether ketone) for heterogeneous catalyst. *J Photopolym Sci Technol*. 2015;28:187–90.
- Shi Y, Nabae Y, Hayakawa T, Kakimoto M. Hyperbranched aromatic poly(ether ketone) functionalized with TEMPO as a heterogeneous catalyst for aerobic oxidation of alcohols. *RSC Adv*. 2015;5:1923–8.

31. Hunter RA, Turner PD, Rimmer S, Li H, Gardner SL, Davies RM, et al. Suspension cross-linking of poly(aryl ether ketone)s containing carboxylic acid functionality. *J Mater Chem.* 2001;11:736–40.
32. Kobayashi H, Yabushita M, Hasegawa J, Fukuoka A. Synergy of vicinal oxygenated groups of catalysts for hydrolysis of cellulosic molecules. *J Phys Chem C.* 2015;119:20993–9.
33. Petroselli M, Melone L, Cametti M, Punta C. Lipophilic *N*-hydroxyphthalimide catalysts for the aerobic oxidation of cumene: towards solvent-free conditions and back. *Chem - A Eur J.* 2017;23:10616–25.
34. Jiang B, Xiao N, Liu H, Zhou Z, Mao XA, Liu M. Optimized quantitative DEPT and quantitative POMMIE experiments for ¹³C NMR. *Anal Chem.* 2008;80:8293–8.
35. Yang C-P, Su Y-Y, Wen S-J, Hsiao S-H. Highly optically transparent/low color polyimide films prepared from hydroquinone- or resorcinol-based bis(ether anhydride) and trifluoromethyl-containing bis(ether amine)s. *Polym (Guildf).* 2006;47:7021–33.
36. Liu C, Wang J, Lin E, Zong L, Jian X. Synthesis and properties of phthalonitrile-terminated oligomeric poly(ether imide)s containing phthalazinone moiety. *Polym Degrad Stab.* 2012;97:460–8.