

ORIGINAL ARTICLE

Direct condensation polymerization of *N*-alkylated *p*-aminobenzoic acid and packing of rigid-rod main chains with flexible side chains

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Direct condensation polymerization of *N*-alkylated *p*-aminobenzoic acid, in which methyl, propyl, butyl, pentyl, heptyl, octyl and heptadecyl substituents were used as the alkyl group, was performed using hexachloroethane, triphenylphosphine and pyridine as condensation reagents. Pale-yellow *N*-alkylated poly(*p*-benzamide) (PABA_{*n*}) polymers, where *n* is the number of carbon atoms of the alkyl side chain, were obtained in 46–87% yields with an inherent viscosity of 0.06–0.65 per 100 ml g^{−1} (conc. H₂SO₄, 30 °C). The structures of PABA_{*n*} were identified using infrared, nuclear magnetic resonance and elemental analysis. PABA_{*n*} with long alkyl side chains (*n* > 3) showed good solubility in chloroform, as well as conc. H₂SO₄ and *m*-cresol. The glass transition temperature (*T*_g) of PABA_{*n*} measured by differential scanning calorimetry gradually decreased with an increase in the length of the alkyl group. The endothermic peak corresponding to melting was observed for PABA_{*n*} with *n* = 3, 4, 5 and 17 on DSC profiles. The wide-angle powder X-ray scattering of the polymer samples indicated that PABA_{*n*} polymers with *n* = 0, 1, 3, 4, 5 and 17 were crystalline polymers. X-ray scattering profiles showed PABA_{*n*} with *n* = 3, 4 and 5 crystallized in an orthorhombic lattice, whereas PABA₁ crystallized in a monoclinic lattice. PABA₁₇ crystallized in hexagonal packing at the long side chain with an interplanar spacing of 4.2 Å.

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Keywords: comb polymer; crystalline polymer; direct condensation polymerization; *N*-substituted *p*-aminobenzoic acid; PABA_{*n*}

INTRODUCTION

Comb polymers are useful materials because of the different solid-state natures of main chains and side chains, which generally afford long-range phase-segregated structures.^{1,2} Crystalline main chain with amorphous side chain^{3–11} comb polymers and amorphous main chain with crystalline side chain^{12–18} ones have been studied extensively and reviewed in terms of their chemistry^{19,20} and physical properties.²¹ The movement of crystalline segments is variably inhibited by the amorphous portion; thus, formation of various segregated structures is often observed from similar materials. The ‘crystalline–crystalline’ comb polymers,^{22–25} especially those with aromatic main chain polymers,^{26–29} are of interest because packing of the bulky aromatic polymer main chain can be changed by varying the crystallinity of side chains. As the first example, Kevlar, poly(*p*-phenylene terephthalamide), was functionalized with linear hydrocarbons of 3, 4, 7, 12 and 18 carbon atoms through metalation of poly(*p*-phenylene terephthalamide) using sodium hydride (degree of substitution (DS) was 86–99%, inherent viscosity (η_{inh}) 0.06–0.14), and the packing mode was investigated for the resulting comb polymers, which were all

amorphous except for the polymer with C₁₈H₃₇ side chains.³⁰ Poly (3-*n*-alkyl-4-oxybenzoate)s (PAOBA)s with alkyl side chains varying from 1 to 18 carbon atoms were prepared and their phase properties fully investigated.³¹ The structure and thermal transition from crystalline to mesophase of PAOBA with short alkyl chains, such as propyl groups, was controlled by the rigid-rod main chain, whereas those of PAOBA having longer alkyl chains were controlled by the nature of side chains. *N*-Alkylated poly(*p*-benzamide) (PABA_{*n*}, DS > 96%) (from 10 to 18 carbon atoms) was also prepared by the metalation method, and their packing structure was investigated.³² In contrast to the high crystallinity of PAOBA, all PABA_{*n*} polymers, except for the one with the 18-carbon alkyl chain, were amorphous because of bulky aromatic rings and relatively sparse semicrystalline alkyl chains. We expected that well-defined PABA_{*n*} should pack easily in a different form on polymerization of a completely alkylated monomer with a side chain containing a number of carbon atoms ranging from 1 to 17. Therefore, this study focused on the preparation of high-molecular-weight PABA_{*n*} from *N*-alkylated *p*-aminobenzoic acid and investigation of the packing that occurred on varying the length of alkyl side chains.

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EXPERIMENTAL PROCEDURE

Measurements

Fourier transform infrared (IR) spectra were measured with a Jasco IR-5500 (Jasco, Tokyo, Japan) by transmittance absorption spectroscopy (KBr tablet method). The molecular mass of polyamides (weight average (M_w)) was determined using a Viscotek T60A gel permeation chromatograph (Viscotek, Houston, TX, USA) equipped with a three detector system: refractive index, light scattering detector and viscometer detector. The scattering angles, dn/dc (refractive index increment) and sample concentrations were set to be 90.0, 0.185 and 1.0 mg ml^{-1} , respectively. Separation was carried out with Tosoh HLC-8120 GPC (Tosoh, Tokyo, Japan) using a consecutive polystyrene gel column (TSK-GEL GMHHR-M and GMHHR-N) at 40°C and eluted with tetrahydrofuran (THF) at a flow rate of 1.0 ml min^{-1} . Nuclear magnetic resonance (NMR) was performed on a Bruker AC-400P spectrometer (Bruker BioSpin K.K., Yokohama, Japan) at 400 MHz for ^1H and at 100 MHz for ^{13}C measurements. Deuterated chloroform (CDCl_3) was used as a solvent with tetramethylsilane as an internal reference. Thermal analyses were carried out on a Seiko thermal analyzer (Seiko Instruments Inc., Chiba, Japan) (SCC 5200 system) at a heating rate of $10^\circ\text{C min}^{-1}$ for thermogravimetric analysis (by TG/DTA 320) under air or nitrogen. Differential scanning calorimetry (DSC) was performed on a Shimadzu DSC-60 (Shimadzu Corporation, Kyoto, Japan) at a heating rate of $20^\circ\text{C min}^{-1}$ under nitrogen. The packing modes of several polymers in the crystalline phase were examined by wide-angle X-ray powder diffraction (WAXD) measurements using a Rigaku R-axis Rapid diffractometer (Rigaku Corporation, Tokyo, Japan) equipped with a graphite monochromator, with $\text{CuK}\alpha$ radiation at 45 kV and 200 mA. The layer structure of comb polymers was characterized with a small-angle X-ray scattering (SAXS) instrument (M18XHF, MAC Science, Bruker AXS K.K., Yokohama, Japan) consisting of an 18-kW rotating-anode X-ray generator with a Cu target (wavelength, $\lambda=0.154 \text{ nm}$) operated at 50 kV and 300 mA. This instrument contained a pyrographite monochromator, pinhole collimation system ($\phi=0.3, 0.3, 1.1 \text{ mm}$), vacuum chamber for the scattered beam path and a two-dimensional imaging plate detector (DIP-220). The sample-to-detector distance was adjusted to 710 mm. The exposure time for each sample was 30 min. For SAXS measurements, a sample of $\sim 1\text{-mm}$ thickness was placed in the sample holder so that its position remained unchanged.

Reagents

p-Aminobenzoic acid ethyl ester and *p*-(*N*-methylamino)benzoic acid were purchased from Wako Pure Chemical Industries (Osaka, Japan) and TCI Chemical Industry (Tokyo, Japan), respectively, and used as received. Dry pyridine was purchased from Kanto Chemical (Tokyo, Japan) and used under nitrogen. Hexamethylphosphorous triamide was dried over calcium hydride and distilled under reduced pressure. The other reagents and solvents were used as received.

Synthesis of *p*-(*N*-propylamino)benzoic acid

Into a three-necked flask equipped with a reflux condenser, a thermometer and a three-way stopcock was added *p*-aminobenzoic acid ethyl ester (79.3 g, 0.480 mol) under nitrogen. Hexamethylphosphorous triamide (222 ml) was then added and the mixture was stirred until the solid was completely dissolved at 20°C . 1-Iodopropane (42.9 g, 0.252 mol) was then added to this solution, and the mixture was stirred at 130°C for 4 h. The resultant mixture was poured into water (1 l), and the precipitate was washed with methanol/water (1:5 v/v)-mixed solvent to remove the residual solvent and salt. The solid was collected by filtration, purified by recrystallization from methanol and dried *in vacuo* at 80°C for 12 h to give *p*-(*N*-propylamino)benzoic acid ethyl ester as yellow needles. Yield: 46.5 g (88.9%); m.p.: $70\text{--}73^\circ\text{C}$; IR (KBr): ν 3373 (N-H), 3063 (aromatic C-H), 2964 (aliphatic C-H), 1676 (ester C=O), 1343 (Ar-N), 1173 (C-O) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ 1.00 (t, 3H, CH_3), 1.36 (t, 3H, CH_3), 1.65 (m, 2H, CH_2), 3.13 (t, 2H, CH_2), 4.11 (s, 1H, NH), 4.31 (q, 2H, CH_2), 6.53 (d, 2H, ArH), 7.86 (d, 2H, ArH) p.p.m.; ^{13}C NMR (CDCl_3 , 100 MHz): δ 11.6, 14.5, 22.5, 45.2, 60.1, 111.3, 118.4, 131.5, 152.1, 166.9 p.p.m. The resulting *p*-(*N*-propylamino)benzoic acid ethyl ester (38.3 g, 0.185 mol) was placed in a 500-ml two-necked flask equipped with a reflux condenser. Potassium hydroxide (56.8 g, 0.923 mol) and ethanol (450 ml) were added to this flask and heated to 90°C . After 7 h, the reaction mixture was

poured into water, and the pH of the solution was adjusted to be around 4 with hydrochloric acid. The precipitate was collected, washed with water, recrystallized with methanol and dried *in vacuo* at 80°C for 12 h to give the title compound as yellow needles. Yield: 21.2 g (64.1%); m.p.: $164\text{--}169^\circ\text{C}$; IR (KBr): ν 3377 (N-H), 3058 (aromatic C-H), 2961 (aliphatic C-H), 1663 (C=O), 1313 (Ar-N), 1171 (C-O) cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ 1.01 (t, 3H, CH_3), 1.66 (q, 2H, CH_2), 3.15 (t, 2H, CH_2), 6.55 (d, 2H, ArH), 7.91 (d, 2H, ArH); ^{13}C NMR (CDCl_3 , 100 MHz): δ 11.5, 22.5, 45.1, 111.3, 117.0, 132.3, 152.7, 172.2 p.p.m.; anal. calcd for $\text{C}_{10}\text{H}_{13}\text{NO}_2$: C, 67.02; H, 7.31; N, 7.82%; found: C, 66.92; H, 7.26; N, 7.88%.

Synthesis of *p*-(*N*-butylamino)benzoic acid

The title compound was prepared in a manner similar to that described above. The solid was collected by filtration, purified by recrystallization from methanol and dried *in vacuo* at 80°C for 12 h to give pale-yellow needles. Yield: 1.36 g (74.0%); m.p.: $149\text{--}155^\circ\text{C}$.

Synthesis of *p*-(*N*-pentylamino)benzoic acid

The title compound was prepared in a manner similar to that described above. The solid was collected by filtration, purified by recrystallization from methanol and dried *in vacuo* at 80°C for 12 h to give colorless needles. Yield: 18.6 g (68.0%). m.p.: $132\text{--}133^\circ\text{C}$.

Synthesis of *p*-(*N*-heptylamino)benzoic acid

The title compound was prepared in a manner similar to that described above. The solid was collected by filtration, purified by recrystallization from methanol and dried *in vacuo* at 80°C for 12 h to give colorless needles. Yield: 11.3 g (75.0%). m.p.: $107\text{--}122^\circ\text{C}$.

Synthesis of *p*-(*N*-octylamino)benzoic acid

The title compound was prepared in a manner similar to that described above. The solid was collected by filtration, purified by recrystallization from methanol and dried *in vacuo* at 80°C for 12 h to result in yellow needles. Yield: 13.6 g (84.0%); m.p.: $117\text{--}125^\circ\text{C}$.

Synthesis of *p*-(*N*-heptadecylamino)benzoic acid

The title compound was prepared in a manner similar to that described above. The solid was collected by filtration, purified by recrystallization from methanol and dried *in vacuo* at 80°C for 12 h to result in white needles. Yield: 9.60 g (64.0%); m.p.: $126\text{--}127^\circ\text{C}$.

Synthesis of poly(*p*-benzamide) (PABA₀)

Into a three-necked flask equipped with a reflux condenser, a three-way stopcock and a thermometer were added lithium chloride (10.5 g, 0.247 mol, 4 wt% to the solution), *N*-methyl-2-pyrrolidone (200 ml) and pyridine (50 ml). The mixture was stirred until the solid was dissolved. *p*-Aminobenzoic acid (13.7 g, 0.100 mol) was then added to the flask, followed by triphenylphosphine oxide (31.3 g, 0.100 mol) in one portion. The flask was heated to 100°C , and the mixture was stirred for another 6 h. The resulting heterogeneous solution was poured into methanol (1 l) and stirred for 5 h. The precipitate was collected, washed with hot water and dried *in vacuo* at 220°C for 24 h to give the title compound. Yield: 11.4 g (95.0%); $\eta_{\text{inh}}=1.18$ per 100 ml g^{-1} (0.5 g per 100 ml in conc. H_2SO_4 , 30°C); IR (KBr): ν 3446 (N-H), 1669 (C=O), 1315 (Ar-N), 1177 (amide C-N) cm^{-1} ; anal. calcd for $(\text{C}_7\text{H}_5\text{NO})_n$: C, 70.58; H, 4.23; N, 11.76%; found: C, 69.33; H, 4.75; N, 10.96%.

Typical procedure of the direct polymerization of *N*-alkylated monomers: synthesis of *N*-methylated poly(*p*-benzamide) (PABA₁)

Into a three-necked flask equipped with a reflux condenser, a three-way stopcock and a thermometer, were added *p*-(*N*-methylamino)benzoic acid (4.55 g, 30.1 mol), triphenylphosphine (9.44 g, 36.0 mmol) and pyridine (30 ml). The mixture was stirred until the solid was dissolved. Hexachloroethane (8.52 g, 36.0 mmol) was then added to this solution and the mixture was refluxed for 24 h. After the solution was cooled to room temperature, it was poured into methanol/hydrochloric acid and stirred for 5 h. The precipitates

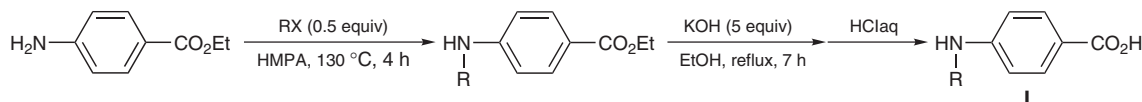
were collected, stirred in hot methanol for 12 h and dried at 220 °C for 24 h to give the title compound. Yield: 2.22 g (55.6%); η_{inh} = 0.61 per 100 ml g⁻¹ (0.5 g per 100 ml in H₂SO₄, 30 °C); IR (KBr): ν 3051 (N-H), 2923 (aliphatic C-H), 1645 (C=O), 1368 (Ar-N), 1175 (amide C-N) cm⁻¹; anal. calcd for (C₈H₇NO)_n: C, 72.16; H, 5.30; N, 10.52%; found: C, 71.49; H, 5.29; N, 10.39%.

RESULTS AND DISCUSSION

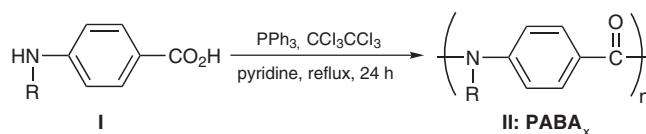
Monomer synthesis and polymerization

The crystalline structure of comb polymers can be formed by the interaction between polymer main chains or polymer side chains. To carefully evaluate the crystalline phase of PABA_n, we selected the carbon number of alkyl side chain to be 0, 1, 3, 4, 5, 7, 8 and 17. The crystalline structure of PABA_n, where *n* is 0, 1, 3, 4, 5, 7 and 8, would have arisen from the influence of the polymer main chain, and that of PABA₁₇ could have been from the polymer side chain. *p*-(*N*-Alkyl-amino)benzoic acids (alkyl groups: propyl, butyl, pentyl, heptyl, octyl and heptadecyl) were prepared from *p*-aminobenzoic acid ethyl ester according to a previously published method³³ (Scheme 1). The monomers were characterized by IR, NMR and elemental analyses. The polycondensation of *p*-aminobenzoic acid was performed using the method of Yamazaki *et al.*,³⁴ involving a triphenyl phosphine oxide/pyridine/lithium chloride condensation agent system, to give the corresponding polymer (PABA₀) with an inherent viscosity of 1.18 per 100 ml g⁻¹ (0.5 g per 100 ml in conc. H₂SO₄, 30 °C). However, this condensation system was not effective for the polycondensation of *p*-(*N*-alkylamino)benzoic acid monomers, probably because of the very low nucleophilicity of secondary amine moieties that are further deactivated by the inductive effect of a *p*-carbonyl group.³⁵ A hexachloroethane/triphenylphosphine

condensation agent system was developed for the preparation of peptides,³⁶ polyesters³⁷ and polyamides.³⁸ Heitz and his coworker³⁹ applied this system for the polycondensation of *p*-(*N*-methylamino)-benzoic acid to give the corresponding PABA₁ in 47% yield with an inherent viscosity of 0.37 per 100 ml g⁻¹ (0.5 g per 100 ml in conc. H₂SO₄, 30 °C) (M_w = 27 300). Thus, we applied this method for the preparation of PABA_n (Scheme 2). Table 1 summarizes the results of polycondensation of *p*-(*N*-alkylamino)benzoic acids. The inherent viscosity of the polymer decreased from 0.65 to 0.06 per 100 ml g⁻¹ (0.5 g per 100 ml in conc. H₂SO₄, 30 °C) with the length of the alkyl side chain. PABA_n (*n* ≥ 7) is soluble in THF; therefore the weight-average molecular weight (M_w) of the polymer was determined by the light scattering method in THF. The M_w values of PABA₇, PABA₈ and PABA₁₇ were 47 800, 20 600 and 93 400, respectively. In general, introduction of bulky substituents into the reactive functional group or its neighbors reduces reactivity, resulting in lower-molecular-weight polymers. Introduction of a sufficiently long alkyl group also hampers the reaction, but increases the solubility of the resulting polyamide, resulting in a relatively high-molecular-weight product as seen for PABA₁₇. Because all polymers have a molecular weight distribution around 2.0, the degree of polymerization was calculated to be 45 for PABA₈ and > 100 for other PABA_n polymers. These molecular weights were high enough to evaluate the differences in packing based on the characteristics of the polymer main chain and polymer side chain. Table 2 shows the solubility of PABA_n in typical organic solvents. PABA₀ is soluble only in conc. H₂SO₄, but PABA₁ is soluble in *m*-cresol on heating. An increase in the length of the PABA_n alkyl chain resulted in an improvement in the solubility of the polymer in solvents such as *N*-methyl-2-pyrrolidone, chloroform and THF. This



Scheme 1 Monomer synthesis.



Scheme 2 Direct polycondensation of monomer I.

Table 1 Analyzed data for the polymerization products of direct polycondensation of II

R	Yield (%)	η_{inh} (100 ml g ⁻¹)	M_{wLS}	Formula	Elemental analysis of III					
					Calculated (%)			Found (%)		
					C	H	N	C	H	N
H	95	1.18 ^a	—	(C ₇ H ₅ NO) _n	70.58	4.23	11.76	69.33	4.75	10.96
Methyl	56	0.61 ^a	—	(C ₈ H ₇ NO) _n	72.16	5.30	10.52	71.49	5.29	10.39
Propyl	46	0.65 ^a	—	(C ₁₀ H ₁₁ NO) _n	74.51	6.88	8.69	74.31	6.84	8.73
Butyl	52	0.42 ^a	—	(C ₁₁ H ₁₃ NO) _n	75.40	7.48	7.99	75.31	7.44	8.25
Pentyl	64	0.29 ^a	—	(C ₁₂ H ₁₅ NO) _n	76.16	7.99	7.40	76.03	7.90	7.71
Heptyl	62	0.15 ^a	47 800	(C ₁₄ H ₁₉ NO) _n	77.38	8.81	6.45	77.31	8.81	6.78
Octyl	51	0.06 ^a	20 600	(C ₁₅ H ₂₁ NO) _n	76.16	7.99	7.40	77.88	9.04	6.17
Stearyl	87	0.34 ^b	93 400	(C ₂₄ H ₃₉ NO) _n	80.61	10.99	3.92	80.67	11.12	4.08

Abbreviations: M_{wLS} , weight-average molecular weight determined by light scattering method; R, alkyl group.

^aDetermined in conc. H₂SO₄ (0.5 g per 100 ml, 30 °C).

^bDetermined in chloroform (0.5 g per 100 ml, 30 °C).

Table 2 Solubility of polymers

Polymer	Solubility										
	NMP	DMAc	DMSO	CHCl ₃	THF	H ₂ SO ₄	C ₆ H ₅ Cl	C ₆ H ₄ Cl ₂	C ₆ H ₅ NO ₂	m-Cresol	Py
PABA ₀	—	—	—	—	—	+	—	—	—	—	—
PABA ₁	—	—	—	—	—	+	—	—	±	+	±
PABA ₃	±	—	—	— ^a	—	+	— ^b	—	— ^a	±	±
PABA ₄	+	—	—	++	—	++	+	+	+	++	±
PABA ₅	±	—	—	++	—	++	+	—	—	++	±
PABA ₇	++	++	—	++	++	++	++	++	++	++	++
PABA ₈	++	++	—	++	++	++	++	++	++	++	++
PABA ₁₇	+	—	—	++	++	+	++	++	++	++	++

Abbreviations: C₆H₄Cl₂, 1,2-dichlorobenzene; DMAc, *N,N*-dimethylacetamide; DMSO, dimethyl sulfoxide; NMP, *N*-methyl-2-pyrrolidone; Py, pyridine; THF, tetrahydrofuran.

Determined using 1 mg of the polymer sample in 1 ml of solvent. ++: soluble at room temperature; +: soluble on heating; ±: partially soluble; —: insoluble even on heating.

^aSwollen at room temperature.

^bSwollen on heating.

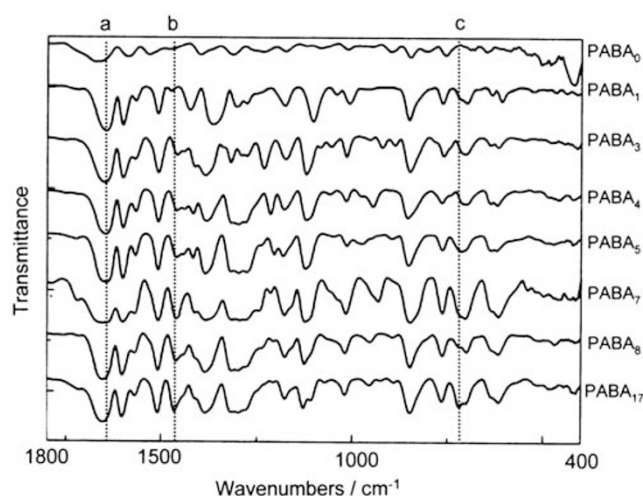


Figure 1 Infrared spectra of *N*-alkylated poly(*p*-benzamide) (PABA_{*n*}) (*n*=0, 1, 3, 4, 5, 7, 8, 17). The dotted lines *a*, *b* and *c* indicate wavenumbers at 1640, 1464 and 720 cm^{−1}, respectively.

indicates that the dipolar–dipolar interaction between polymer chains is effectively weakened by bulky hydrocarbon substituents. The IR of PABA_{*n*} spectra supports this assumption (Figure 1 and Supplementary Figure 1); the amide carbonyl absorption of PABA_{*n*} with *n*=1, 3, 4 or 5 was 1640 cm^{−1}, whereas those of PABA_{*n*} with *n*=7, 8 and 17 shifted to longer wavenumbers. Thus, the amide groups of PABA_{*n*} with *n*=7, 8 or 17 are isolated by bulky hydrocarbon substituents, whereas those of PABA_{*n*} with *n*=1, 3, 4 and 5 can interact with each other, which also prevents the intrusion of organic solvents.

Thermal properties of PABAs

To determine the thermal transition and thermostability of PABA_{*n*}, DSC and thermogravimetric analyses were carried out under air and nitrogen (Table 3). Figure 2 depicts the thermogravimetric analysis profiles of PABA₀, PABA₁ and PABA₁₇ under N₂. These three polymers showed a similar 10% weight loss near 440 °C under nitrogen; however, PABA₁₇ rapidly decomposed and lost 95% of its weight by 500 °C thereafter. In the presence of oxygen, PABA₁₇ had the lowest decomposition temperature compared with other polymers, probably because of the presence of the alkyl side chain (Figure 2b). This is a general characteristic of comb polymers.³⁰ Figure 3 shows the second

heating DSC curves of PABA_{*n*}. PABA₀ shows no transition or endothermic peak of melting, whereas PABA₁ shows a glass transition temperature (*T*_g) at 197 °C. Increasing the length of the alkyl side chain causes the *T*_g of polymers to gradually decrease and eventually become constant (Figure 4), because of the independence of the relaxation of the polymer main chain when the alkyl chain length is regarded as infinity. PABA₃, PABA₄ and PABA₅ show exothermic and endothermic peaks after *T*_g, which were attributed to the crystallization (*T*_c) and melting temperatures (*T*_m), respectively. A further increase in the alkyl side chain length (*n* ≥ 7) diminishes the crystalline nature of the polymer, until PABA₁₇, which possesses crystallinity (Figure 3). This phenomenon suggests that the packing mode of PABA_{*n*} with *n*=3, 4 and 5 is determined by the polymer main chain, and that of PABA₁₇ is determined by the polymer side chain. PABA_{*n*} polymers with *n*=3, 4 and 5, which form the packing mode between main chains, also rearranged in the crystallization temperature of the heating process because this type of polymer has a relatively slow crystallization rate. On the other hand, the octadecyl side chain itself in PABA₁₇ has high crystallization ability. Note that the reported *T*_m of PABA₁₇ (with a 97% degree of substituents), prepared by alkylation of poly(*p*-benzamide) with sodium hydride, was 3 °C, which was unexpectedly lower than that of *n*-hexadecane (*T*_m=22 °C).⁴⁰ The authors attributed this reason to the difficult packing of PABA₁₇ because of the bulky phenylene groups. However, in our case, PABA₁₇ (with a 100% degree of substituents) melts at 31 °C, which indicates that only a 3% deficit in the introduction of alkyl side chains significantly decreases side-chain crystallinity for PABA₁₇. The heat of fusion per monomeric unit of PABA₁₇ determined by DSC was −36.8 J g^{−1}, which is comparable with the reported value of comb polyamides.^{40,41}

X-ray scattering study of PABAs

The packing mode of PABA_{*n*} was investigated using WAXD measurements. Figure 5 depicts the WAXD patterns and profiles with a reciprocal lattice of PABA_{*n*} polymers. High-resolution WAXD profiles can be found in Supplementary Figures 2–9 in the Supplementary material. All polymers, except PABA₇ and PABA₈, produced several sharp diffraction peaks, indicating crystalline structures. Several studies have reported a crystalline structure for PABA₀, in which polymers are tightly packed through hydrogen bonding of the amide group (*trans* conformation) to form orthorhombic systems with order parameters of *a*=7.74, *b*=5.27 and *c*=12.82 Å.^{42,43} However, the polymer we prepared shows only two peaks at 20.3 and 23.3° in 2θ (4.4 and 3.8 Å, respectively), indicating that the polymer is loosely

Table 3 Thermal properties and the crystallinity of polymers

Polymer	T_g (°C) ^a	T_c (°C) ^a	T_m (°C) ^a	T_{d5} (air) (°C) ^b	T_{d10} (air) (°C) ^b	T_{d5} (N ₂) (°C) ^b	T_{d10} (N ₂) (°C) ^b	ΔH (J g ⁻¹) ^c	ΔH (kJ mol ⁻¹) ^c
PABA ₀	—	—	—	412	444	412	450	—	—
PABA ₁	197	—	—	394	425	408	432	—	—
PABA ₃	136	227	319	404	421	426	437	-18.0	-2.9
PABA ₄	124	189	281	399	412	424	435	-28.2	-4.9
PABA ₅	83.5	135	291	399	417	428	437	-58.7	-11.1
PABA ₇	45.9	—	—	386	403	419	433	—	—
PABA ₈	30.0	—	—	382	400	417	430	—	—
PABA ₁₇	—	—	30.9	325	350	432	444	-36.8	-13.2

Abbreviations: T_g , glass transition temperature; T_c , crystallized temperature at the highest peak; T_m , melting temperature; T_{d5} , 5% weight-loss temperature; T_{d10} , 10% weight-loss temperature.

^a T_g , T_c and T_m were measured by differential scanning calorimetry (DSC) (20 °C min⁻¹, N₂).

^bDetermined by thermogravimetric analysis (10 °C min⁻¹).

^cHeat of fusion determined by DSC (20 °C min⁻¹, N₂).

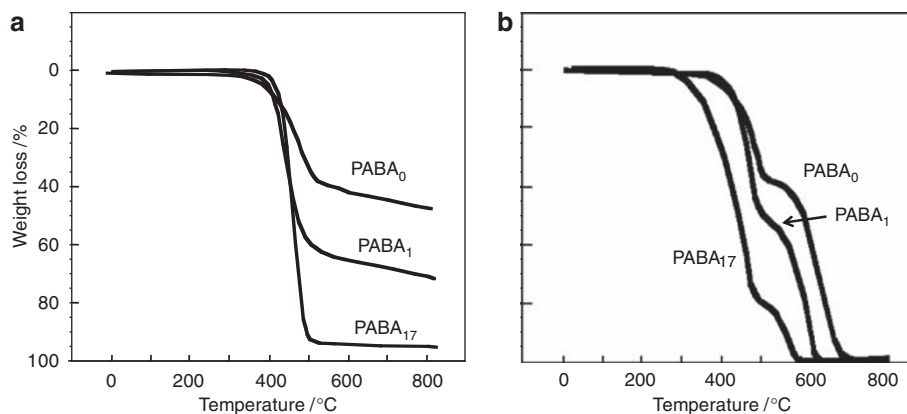


Figure 2 Thermogravimetric analysis profiles of *N*-alkylated poly(*p*-benzamide) (PABA_{*n*}) (*n*=0, 1, 17) at a heating rate of 10 °C min⁻¹ under (a) nitrogen and (b) air.

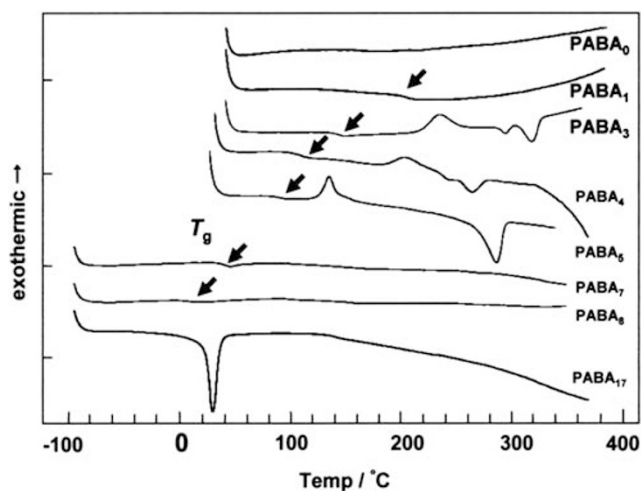


Figure 3 Differential scanning calorimetry profiles of *N*-alkylated poly(*p*-benzamide) (PABA_{*n*}) (*n*=0, 1, 3, 4, 5, 7, 8, 17) at a heating rate of 20 °C min⁻¹ under nitrogen.

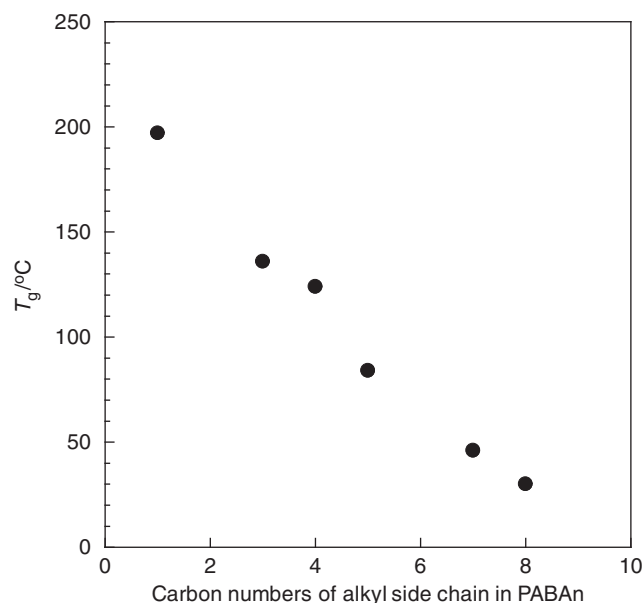


Figure 4 Relationship between the alkyl chain length and T_g of *N*-alkylated poly(*p*-benzamide) (PABA_{*n*}).

packed and contained some crystalline structure. Generally, the crystallization degree of crystalline polymers remarkably depended on how to crystallize. The crystallization degree of PABA₀ reported in literature⁴² is relatively high. However, we merely discuss the crystal

structure at polymerization crystallization. Essentially, aromatic polyamides having a rigid main chain are hard to crystallize with a high degree. From our experimental findings, it is found that the PABA₀

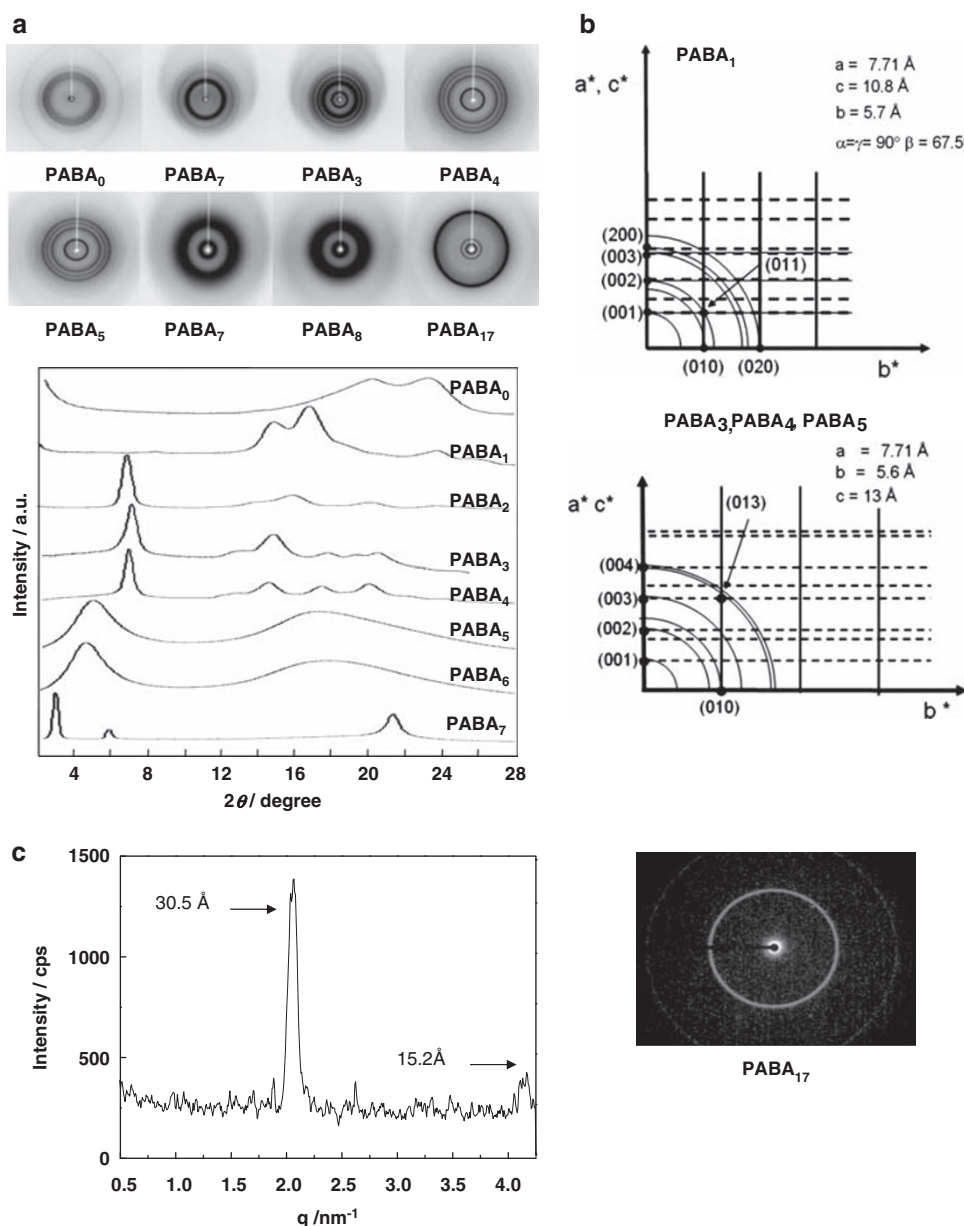


Figure 5 (a) Two-dimensional X-ray patterns and X-ray intensity with diffraction angle θ for *N*-alkylated poly(*p*-benzamide) (PABA_{*n*}) (*n*=0, 1, 3, 4, 5, 7, 8, 17). (b) Analysis of wide-angle X-ray powder diffraction (WAXD) peaks on the reciprocal lattice of PABA₁ and PABA_{*n*} (*n*=3, 4 and 5). *a*^{*}, *b*^{*}, and *c*^{*} in a coordinate axis mean a vector of reciprocal lattice. (c) Small-angle X-ray scattering pattern and profile of PABA₁₇.

crystal formed by polymerization crystallization shows low crystallinity. Interestingly, the X-ray diffraction pattern of PABA₁ shows two clear peaks at 14.9 and 16.8°, along with smaller ones at 8.4, 23.8, 25.8 and 29.2° in 2θ . From the results of analysis for the reciprocal lattice to diffraction peak and previously reported crystal system of similar polymers, it is found that PABA₁ are packed into a monoclinic lattice with order parameters of $\alpha=\gamma=90^\circ$, $\beta=67.5^\circ$, $a=7.7\text{ \AA}$, $b=5.7\text{ \AA}$ and $c=10.8\text{ \AA}$ (Figure 5b). The reported crystal systems of similar polymers in literature, such as poly(*p*-phenylene terephthalamide)³⁰ and poly(*p*-benzamide),³² are monoclinic ($a=7.8\text{ \AA}$, $b=5.19\text{ \AA}$, $c=12.9\text{ \AA}$, $\gamma=90^\circ$) and orthorhombic ($a=7.71\text{ \AA}$, $b=5.14\text{ \AA}$, $c=12.8\text{ \AA}$) systems, respectively. In contrast, PABA_{*n*} polymers with $n=1, 3, 4$ or 5 are packed into an orthorhombic lattice with $\alpha=\beta=\gamma=90^\circ$, $a=7.7\text{ \AA}$, $b=5.6\text{ \AA}$ and $c=13.0\text{ \AA}$, because all WAXD

peaks of these polyamides can be located on the reciprocal lattice of an orthorhombic system (Figure 5b).

Figure 6 shows the molecular arrangement and packing models of PABA₁ and PABA_{*n*} ($n=3, 4$ and 5). The small methyl moiety of PABA₁ could distort the crystal lattice to afford a type of packing different from that of others. In addition, the periodic structure of 10.8 Å for PABA₁ and 13.0 Å for PABA_{*n*} at $n=3, 4$ and 5 is the pitch of the helix induced by the structural propensities of the *cis* conformation of *N*-alkylated amide bonds and *syn* arrangement of the benzene ring.³⁷ Orthorhombic packing has an extremely high symmetry, similar to that of crystalline polymers. The polyethylene also packs the orthorhombic system. The polymer chains of PABA₃, PABA₄ and PABA₅ are orderly packed in crystal lattice without the interference of side chains. In addition, the development of length along the *c*-axis is characteristic

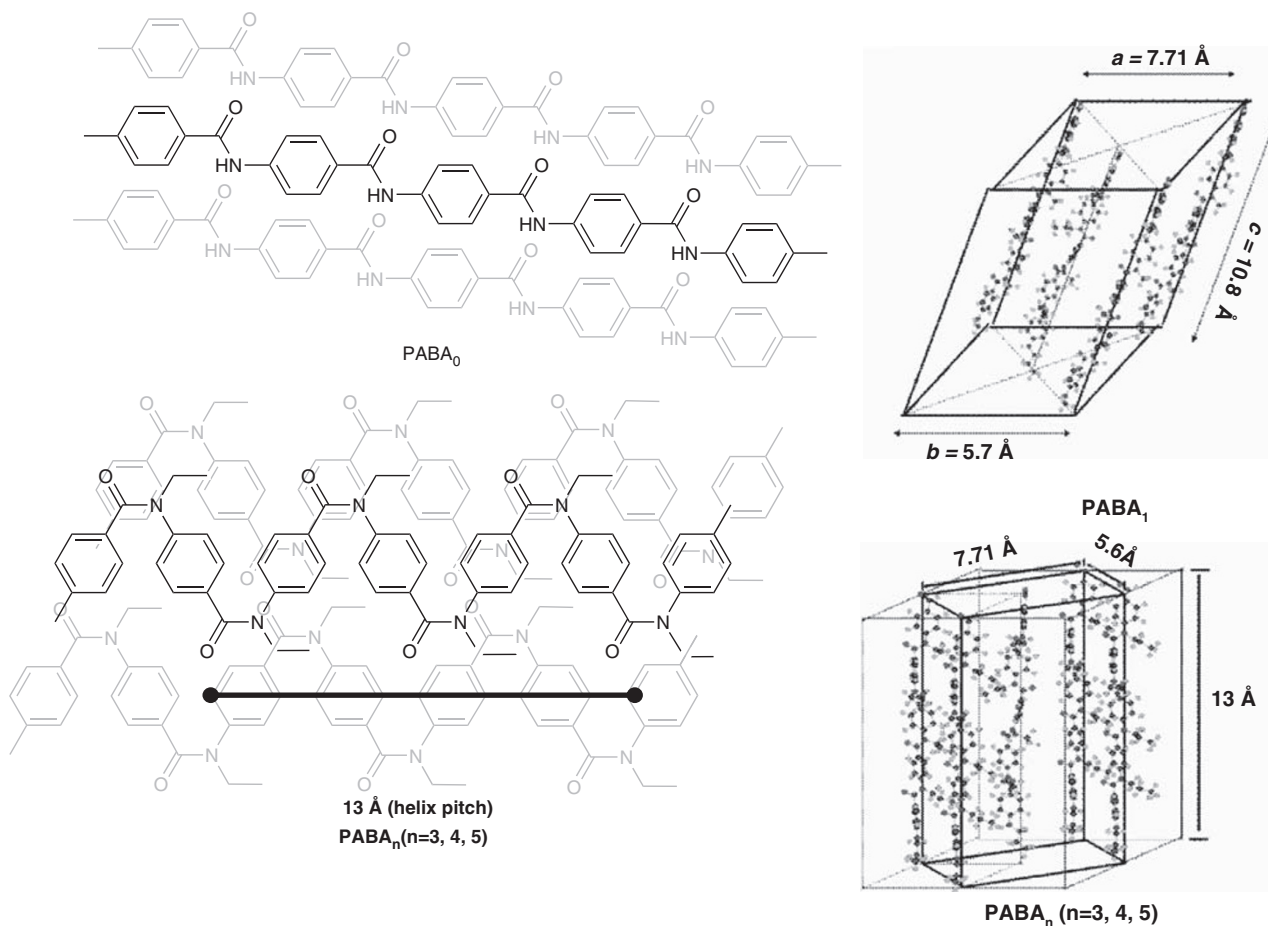


Figure 6 Proposed arrangement of main and side chains in *N*-alkylated poly(*p*-benzamide) (PABA_{*n*}) (*n*=0, 1, 3, 4, 5).

of crystalline polymers with a helical conformation (for example, PTFE, PLLA, PMMA and so on). A subtle distortion of the lattice of the PABA₁ crystal exhibits the contribution of side chains to lattice formation; that is, this is a contribution for the enhancement of van der Waals interaction between neighboring chains to lattice formation and symmetry. PABA₇ and PABA₈ showed disordered structures from WAXD profiles, which support the DSC results. It seems that existence of too long side chain disturbs the lattice formation because of steric hindrance.

In the case of PABA₁₇, we can see the typical WAXD profile of 'side-chain crystalline' polymers. PABA₁₇, which contains a longer alkyl chain, shows sharp peaks at 2.9°, 5.8° and 21.3° in 2θ (d_{001} =30.5, d_{002} =15.2, and d_{100} =4.2 Å),⁴⁴ which indicates that the side-chain crystalline structure of PABA₁₇ is in hexagonal packing form, similar to that observed in a comb polymer. The typical *trans* conformation of the CH₂ group appeared at 1466 cm⁻¹ in the IR spectrum, and in our case, PABA₁₇ also shows a strong and clear absorption at 1464 cm⁻¹, which supports the hexagonal packing structure as suggested by WAXD measurements. According to the extended structure of polyethylene, an increase in CH₂ resulted in a spacing increase of 1.25 Å.³⁸ Thus, the double-layered space of side-chain crystal domains is calculated to be 1.25 Å × 2 × 17 = 42.5 Å and that estimated on the basis of the WAXD of PABA₁₇ was 30.5 Å, which is much smaller than the calculated value. These results are also supported by SAXS measurements as shown in Figure 5c and Supplementary

Figure 10. In the low-angle region below $2\theta=2^\circ$, further scattering peaks and a highly ordered structure could not be confirmed. Side chain crystal is hard to form in the only single layer by van der Waals interaction because of a distance between each side chain based on the existence of a rigid aromatic ring in the main-chain. Formation of an interdigitated structure in the double-layer structure shortens both long spacing along the *c*-axis and the distance between side chains along the main-chain direction. Therefore, it seems that formation of an interdigitated arrangement in the layer structure is suitable. Therefore, the packing structure of the PABA₁₇ side chain could be interdigitated as shown in Figure 7, and the formation of a solid-state structure for *N*-alkylated polyamides depends on side chain length, systematically. PABA₁₋₅ polymers crystallize under the control of rigid-rod main chains. Specifically, PABA₃₋₅ polymers pack orthorhombically, whereas PABA₁ forms a distorted monoclinic system. In contrast, PABA₇₋₈ polymers cannot form a crystalline structure and remain amorphous. The steric hindrance of longer alkyl side chains must obstruct the formation of a crystalline structure. PABA₁₇, owing to its long side chains, no longer packs on the basis of rigid main chains. Instead, this polymer packs hexagonally by van der Waals interactions between heptadecyl side-chain substituents. These experimental findings indicate that control of the first-order structure during polymer synthesis is directly related to the structural control of crystalline morphology (third-order structure) in this system.

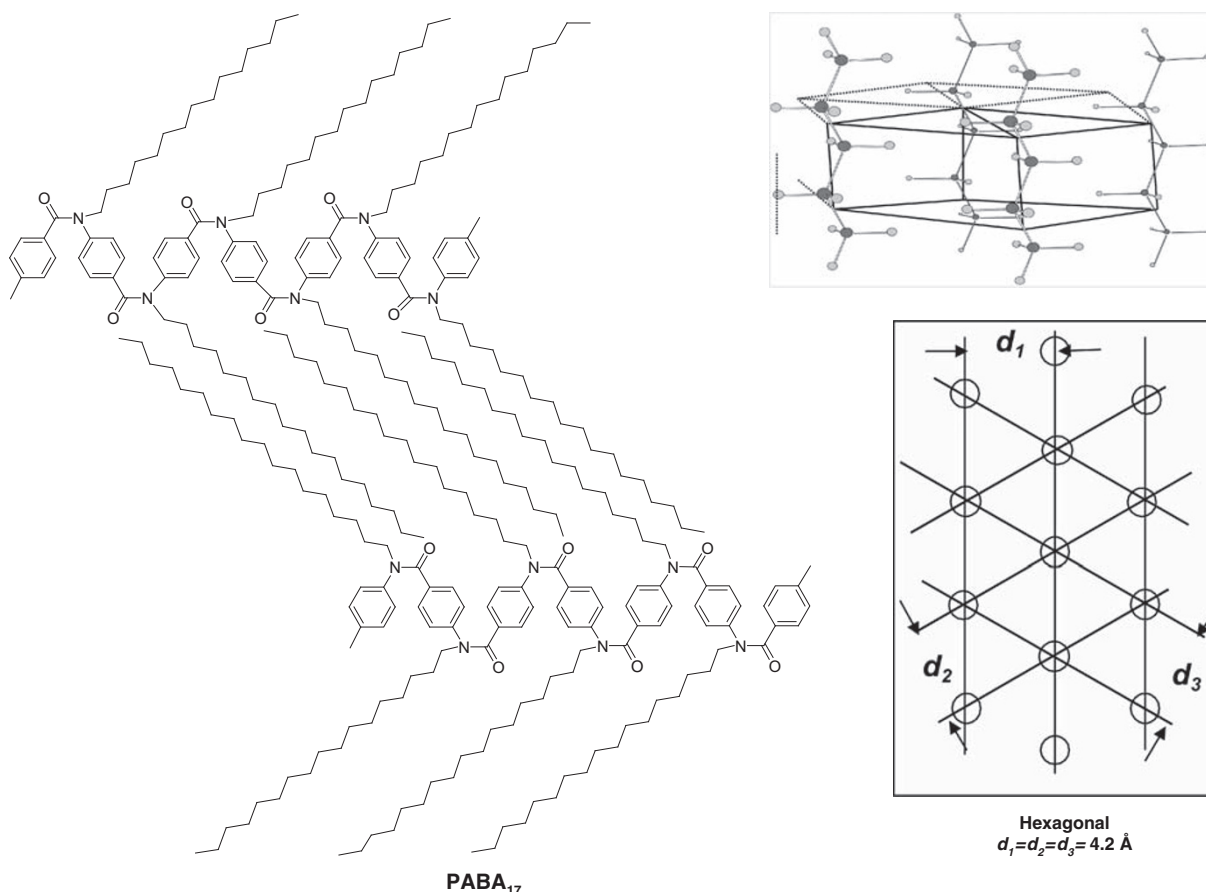


Figure 7 Proposed arrangement of main and side chains in PABA₁₇.

Summary

A route for the direct condensation polymerization of *p*-(*N*-alkyl-amino)benzoic acids was demonstrated using hexachloroethane, triphenylphosphine and pyridine as condensation reagents, and using methyl, propyl, butyl, pentyl, heptyl, octyl and heptadecyl substituents as alkyl side groups. Pale-yellow PABA_{*n*} polymers were obtained in 46–87% yields with inherent viscosity values of 0.06–0.65 per 100 ml g^{−1} (conc. H₂SO₄, 30 °C). The structures and packing of PABA_{*n*} polymers were elucidated using IR spectroscopy, elemental analysis, DSC, WAXD and SAXS, which showed that PABA₁, PABA_{*n*}, where *n*=3, 4 and 5, and PABA₁₇ possess crystalline structures in monoclinic, orthorhombic and hexagonal packing lattices, respectively. The variable packing modes of comb polymers with aromatic main chains will be useful for the development of materials that require thermal and mechanical stability in engineering applications.

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