

Synthesis and Characterization of New Aromatic Polymers Containing Long Alkyl Side Chains and 1,3,5-Triazine Rings

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Synopsis

A series of new aromatic polyamides, polyimides, and polyureas containing 1,3,5-triazine rings in the main chain and two flexible long side chains for each unit, were prepared by the reaction of 2-(*N*-phenyl-*N*-octadecylamino)-4-(*N*-aminophenyl-*N*-octadecylamino)-6-aminophenyl-1,3,5-triazines with aromatic diacid chlorides, pyromellitic dianhydride, and diisocyanates, respectively. These polymers were soluble in tetrahydrofuran, chloroform, and benzene, but had poor solubility in polar aprotic solvents such as dimethyl sulfoxide and *N,N*-dimethylformamide. These polymers were stable up to 410°C for polyamides, 430°C for polyimides, and 290°C for polyureas in air. The differential scanning calorimetric studies of the polymers indicated that the degree of side-chain crystallinity based side chain was 6–10%.

INTRODUCTION

It has been reported that polymers containing side chains of long alkyl groups can form side-chain crystallization.^{1,2} Many authors have investigated the relation between the structures and the properties of these so-called comblike polymers which have flexible backbone such as that obtaining by the polymerization of vinyl compounds.^{3–5} However, there are only few studies on concerning the aromatic condensation polymers having long alkyl side chains.

It is interesting that the polymer containing rigid backbone and flexible side chains, because the long alkyl groups as side chains bring about significant changes in properties of the polymer. Recently, Takayanagi et al.^{6,7} reported that *N*-octadecylated poly(*p*-phenylene terephthalamide) (PPTA) exhibited side-chain crystallization. In addition, the introduction of the long alkyl groups into amide groups of PPTA enhanced their solubilities but depressed their thermal stabilities. In a previous article⁸ we described the synthesis and characterization of several aromatic polymers having long alkyl side chains which were prepared from 2-amino-4-(*N*-aminophenyl-*N*-octadecylamino)-6-aminophenyl-1,3,5-triazines. Similar phenomena are observed on the solubility and thermal stability to those case of PPTA. However, the side-chain crystallization of these polymers was very slight.

In this work, four new diamines having two *N*-octadecyl groups, 2-(*N*-phenyl-*N*-octadecylamino)-4-(*N*-aminophenyl-*N*-octadecylamino)-6-aminophenyl-

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1,3,5-triazines, were synthesized and carried out the polymerization to obtain a series of aromatic polymers with long alkyl side chains. The effects of long alkyl side chains on thermal properties and solubilities of polymers will be discussed.

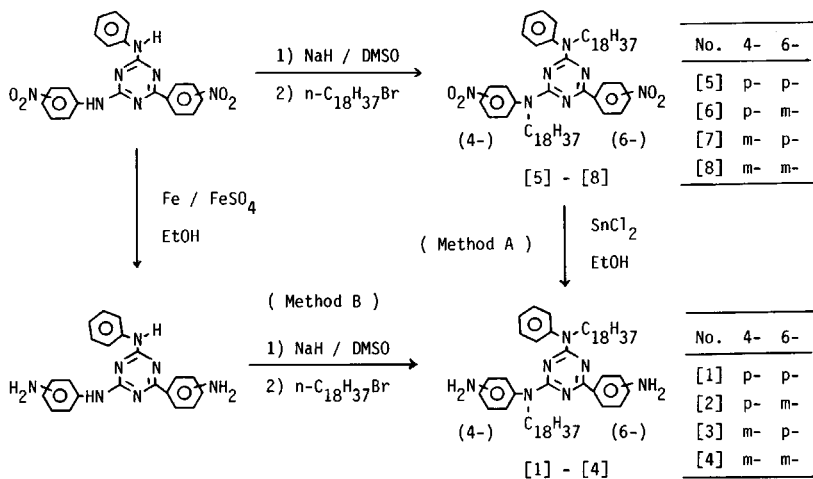
EXPERIMENTAL

Materials

2-Anilino-4-nitroanilino-6-nitrophenyl-1,3,5-triazines were prepared by the reaction of 1-phenyl-5-nitrophenylbiguanide with nitrobenzoyl chlorides following the method reported elsewhere.⁹ 2-Anilino-4-aminoanilino-6-amino-phenyl-1,3,5-triazines were obtained by the reduction of the above dinitro-compounds using the reducing agent of ferrous sulfate and iron powder in ethanol and water.⁸ Solvents used for the reactions such as dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP) and tetrahydrofuran (THF) were purified by distillation and drying. Terephthaloyl chloride (TC), isophthaloyl chloride (IC), pyromellitic dianhydride (PA), 4,4'-diphenylmethane diisocyanate (MI), and toluene 2,4-diisocyanate (TI) were used as received. Scheme 1 provides details on the individual components.

Preparation of 2-(*N*-phenyl-*N*-octadecylamino)-4-(*N*-*p*-nitrophenyl-*N*-octadecylamino)-6-(*p*-nitrophenyl)-1,3,5-triazine [5]: 21.5 g (0.05 mol) of 2-anilino-4-(*p*-nitroanilino)-6-(*p*-nitrophenyl)-1,3,5-triazine was added to a solution of 4.4 g (0.11 mol) of sodium hydride (60% oil suspension) in 300 mL of DMSO with stirring at 50°C. After 30 min, 33.34 g (0.10 mol) of *n*-octadecyl bromide was added into this solution and the mixture was stirred at 50°C for 8 h. The precipitated product was separated and washed with water. Recrystallization from acetone gave a yellow crystals. Yield: 39 g (85%), mp 62°C.

ANAL. Found: C, 73.19%; H, 9.34%; N, 10.35%. Calcd for C₅₇H₈₇N₇O₄: C, 73.27%; H, 9.38%; N, 10.49%.



Scheme 1

Other dinitro-compounds containing octadecyl groups; [6], [7], and [8] were prepared using the similar method above. 2-(*N*-phenyl-*N*-octadecylamino)-4-(*N*-*p*-nitrophenyl-*N*-octadecylamino)-6-(*m*-nitrophenyl)-1,3,5-triazine [6]: Yield 81%, mp 56°C.

ANAL. Found: C, 73.43%; H, 9.67%; N, 10.01%.

2-(*N*-phenyl-*N*-octadecylamino)-4-(*N*-*m*-nitrophenyl-*N*-octadecylamino)-6-(*p*-nitrophenyl)-1,3,5-triazine [7]: Yield 83%, mp 76°C.

ANAL. Found: C, 73.21%; H, 9.62%; N, 10.17%.

2-(*N*-phenyl-*N*-octadecylamino)-4-(*N*-*m*-nitrophenyl-*N*-octadecylamino)-6-(*m*-nitrophenyl)-1,3,5-triazine [8]: Yield 86%, mp 82°C.

ANAL. Found: C, 73.42%; H, 9.72%; N, 10.12%.

Preparation of Diamines

2-(*N*-phenyl-*N*-octadecylamino)-4-(*N*-*p*-aminophenyl-*N*-octadecylamino)-6-(*p*-aminophenyl)-1,3,5-triazine [1]: Method A: 60 mL of 12 *N* hydrochloric acid was added dropwise to a suspension of 15 g (0.016 mol) of [5] and 20 g (0.105 mol) of stannous chloride in 300 mL of ethanol. After one hour of stirring and refluxing, the suspension became a homogenous solution. The reaction then continued for 4 h and the solution was poured into an excess aqueous solution of sodium hydroxide at 0–5°C. The precipitated product was separated and washed thoroughly with water. Recrystallization from THF/methanol gave light yellow crystals. Yield: 11.6 g (83%), mp 72, 117°C.

ANAL. Found: C, 78.24%; H, 10.33%; N, 11.28%. Calcd for C₆₇H₉₁N₇: C, 78.29%; H, 10.49%; N, 11.21%.

¹H-NMR spectrum (CDCl₃): 3.50–4.10 ppm (m, 8H, 2× N-CH₂- and -NH₂); 1.25 ppm (m, 64H, 2× -(CH₂)₁₆-); 0.88 ppm (t, 6H, 2× -CH₃); 6.50–8.10 ppm (m, 13H, aromatic protons).

Method B: Alkylation was carried out with 2-anilino-4-(*p*-aminoanilino)-6-(*p*-aminophenyl)-1,3,5-triazine and *n*-octadecyl bromide in DMSO in the presence of sodium hydrides. The yield was 85%.

ANAL. Found: C, 78.30%; H, 10.54%; N, 10.93%.

¹H-NMR spectrum and mp data were in accordance with those in method A. The other diamines [2], [3], and [4] could also be prepared by both of methods A and B.

2-(*N*-phenyl-*N*-octadecylamino)-4-(*N*-*p*-aminophenyl-*N*-octadecylamino)-6-(*m*-aminophenyl)-1,3,5-triazine [2]: By method A: Yield was 82%, mp 81°C.

ANAL. Found: C, 78.27%; H, 10.61%; N, 10.89%.

¹H-NMR spectrum (CDCl₃): 3.48–3.90 ppm (m, 8H, 2× N-CH₂- and -NH₂); 1.25 ppm (m, 64H, 2× -(CH₂)₁₆-); 0.88 ppm (t, 6H, 2× -CH₃); 6.60–7.75 ppm (m, 13H, aromatic protons). By method B; yield was 86%. (Found: C, 78.07%; H, 10.52%; N, 11.00%).

2-(*N*-phenyl-*N*-octadecylamino)-4-(*N*-*m*-aminophenyl-*N*-octadecylamino)-6-(*p*-aminophenyl)-1,3,5-triazine [3]: By method A; Yield was 80%, mp 71°C.

ANAL. Found: C, 78.12%; H, 10.53%; N, 11.06%.

¹H-NMR spectrum (CDCl₃): 3.50–3.95 ppm (m, 8H, 2× N-CH₂- and -NH₂); 1.25 ppm (m, 64H, 2× -(CH₂)₁₆-); 0.88 ppm (t, 6H, 2× -CH₃); 6.48–8.15 ppm

(m, 13H, aromatic protons). By the method B; yield was 83%. (Found: C, 78.66%; H, 10.71%; N, 10.95%).

2-(*N*-phenyl-*N*-octadecylamino)-4-(*N*-*m*-aminophenyl-*N*-octadecylamino)-6-(*m*-aminophenyl)-1,3,5-triazine [4]: By method A; Yield was 81%, mp 82°C.

ANAL. Found: C, 77.95%; H, 10.74%; N, 10.91%.

¹H-NMR spectrum (CDCl₃): 3.45–4.15 ppm (m, 8H, 2× N-CH₂- and -NH₂); 1.25 ppm (m, 64H, 2× -(CH₂)₁₆-); 0.88 ppm (t, 6H, 2× -CH₃); 6.50–7.80 ppm (m, 13H, aromatic protons). By the method B; yield was 83%. (Found: C, 78.27%; H, 10.68%; N, 10.92%).

Preparation of Polymers

Polyamides prepared from [1]-TC through [4]-IC

For example, [1]-TC: Equal moles (1.0 mmol) of [1] and TC were polymerized in the mixed solvent (THF 6 mL and NMP 4 mL) by stirring under a nitrogen atmosphere at room temperature for 24 h. The solution was poured into 300 mL of methanol, and the resulting polyamide was filtered, washed with acetone, and dried at 50°C *in vacuo*. Yield was 99%. The other polyamides were prepared in a similar manner. Polymers were purified by the reprecipitation from THF or THF/NMP into methanol.

Polyimides prepared from [1]-PI through [4]-II

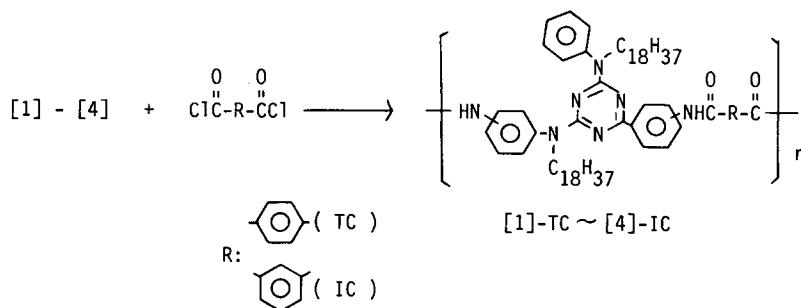
For example, [1]-PI: Equal moles (1.0 mmol) of [1] and PA were polymerized in THF 6 mL and NMP 4 mL at room temperature for 6 h and 60°C for 2 h. The resulting polyamic acid [1]-PA was obtained in 96% yield. Then, [1]-PI was prepared by the heating cyclodehydration of [1]-PA at 200°C for 6 h *in vacuo*. The other polyamic acids and polyimides were prepared in a similar manner.

Polyureas prepared from [1]-MI through [4]-TI

For example, [1]-MI: Equal moles (1.0 mmol) of [1] and MI were polymerized in THF 6 mL and NMP 4 mL at room temperature for 6 h and 60°C for 2 h under nitrogen atmosphere. The solution was poured into 300 mL of methanol. The resulting polyurea was filtered, washed with acetone, and dried at 50°C *in vacuo*. Yield was 97%. Purification was performed by the reprecipitation from THF into methanol. The other polyureas were prepared in a similar manner.

Measurements

IR spectra were recorded on a Hitachi 285 spectrometer by KBr tablets. ¹H-NMR spectra were performed using a Hitachi R600 FTNMR (60 MHz) spectrometer. Differential thermal analysis (DTA), thermogravimetry (TG) were performed with Rigaku TG-DTA 812BH system. A Rigaku DSC-8131 BL differential scanning calorimeter (DSC) was employed to study the side-chain crystallization of polymers. The reduced viscosities of polymers were determined for solution of 0.2 g/dL in THF/NMP (3/1 volume) at 30°C using a Ostwald viscometer.



Scheme 2

RESULTS AND DISCUSSION

Preparation of Diamines

2-(*N*-phenyl-*N*-octadecylamino)-4-(*N*-aminophenyl-*N*-octadecylamino)-6-aminophenyl-1,3,5-triazines [1]–[4] could be prepared by two possible methods in good yields according to Scheme 1. Triazines [1]–[4] were prepared by the alkylation of 2-anilino-4-nitroanilino-6-nitrophenyl-1,3,5-triazines with octadecyl bromide, followed by the reduction with stannous chloride (method A), and could also be prepared selectively by the alkylation of 2-anilino-4-aminoanilino-6-aminophenyl-1,3,5-triazines (method B). The results demonstrated that the nitrogen anion of anilino groups are more stable than those of amino groups due to the anilino groups combined directly with the electron-withdrawing triazine ring. The formations of [1]–[4] were confirmed from IR, ¹H-NMR spectra and elemental analysis. The results of elemental analysis were in good agreement with the calculated values. IR spectra of [1]–[4] showed absorption bands of triazine ring at 1410 and 820 cm⁻¹, ^{8–10} NH₂ groups at

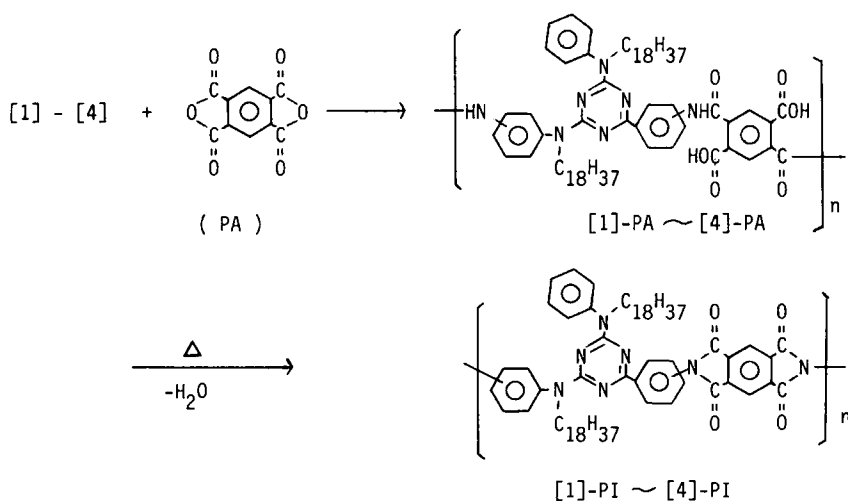
TABLE I
Preparation of Polyamides^a

Polymer no.	Yield (%)	η sp/C ^b (dL/g)	Elemental analysis ^c		
			C %	H %	N %
[1]-TC	99	0.34	76.82	9.53	9.64
[2]-TC	98	0.40	76.59	9.38	9.49
[3]-TC	99	0.45	76.72	9.30	9.67
[4]-TC	95	0.41	77.30	9.54	9.71
[1]-IC	99	0.34	76.03	9.51	9.54
[2]-IC	98	0.39	76.74	9.55	9.52
[3]-IC	98	0.43	76.97	9.61	9.67
[4]-IC	97	0.37	76.68	9.55	9.59

^a Polymerization was carried out with 1.0 mmol of the monomers in 6 mL of THF and 4 mL of NMP at room temperature for 24 h.

^b In C = 0.2 g/dL of NMP/THF ($\frac{1}{3}$ volume) at 30°C.

^c Calcd for C₆₅H₉₃N₇O₂: C, 77.72%; H, 9.33%; N, 9.76%.



Scheme 3

3250–3500 cm^{-1} and octadecyl groups at 2860 and 2920 cm^{-1} .^{7,8} The structures of these diamine compounds were characterized from these data.

Preparation of Polymers

Polyamides containing octadecyl groups in the side chains were prepared from [1]–[4] with TC or IC by the solution polycondensation in the mixed solvent of THF/NMP (6/4 volume) at room temperature (Scheme 2). These polymerizations proceeded homogeneously and the results are listed in Table I. All polymers were obtained in yields over 95% and showed reduced viscosities in the range of 0.34–0.45 dL/g in THF/NMP (3/1 volume) at 30°C. The IR

TABLE II
Preparation of Polyamic Acids and Polyimides^a

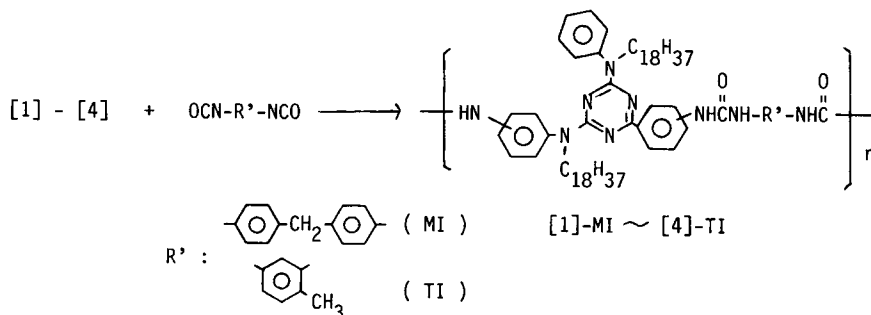
Polymer no.	Yield (%)	η sp/C ^b (dL/g)	Elemental analysis		
			C %	H %	N %
[1]-PA	96	0.23	72.91	9.03	9.15 ^c
[2]-PA	97	0.20	72.43	8.96	9.03 ^c
[3]-PA	96	0.27	72.46	9.11	9.15 ^c
[4]-PA	96	0.23	72.24	9.06	9.25 ^c
[1]-PI	93	0.26	75.74	8.76	9.45 ^d
[2]-PI	94	0.24	76.48	8.87	9.40 ^d
[3]-PI	93	0.30	76.18	9.03	9.50 ^d
[4]-PI	95	0.25	76.79	9.15	9.58 ^d

^a Polyamic acids were prepared from 1.0 mmol of the monomers in 6 mL of THF and 4 mL of NMP at room temperature for 24 h, polyimides were obtained at 200°C for 8 h *in vacuo*.

^b In C = 0.2 g/dL of NMP/THF ($\frac{1}{3}$ volume) at 30°C.

^c Calcd for $\text{C}_{67}\text{H}_{93}\text{N}_7\text{O}_6 \cdot \text{H}_2\text{O}$: C, 72.46%; H, 8.62%; N, 8.83%.

^d Calcd for $\text{C}_{67}\text{H}_{89}\text{N}_7\text{O}_4$: C, 76.17%; H, 9.15%; N, 9.58%.



Scheme 4

spectra of the polyamides showed typical absorptions of amides at 3450–3200, 1660, and 1320 cm^{-1} .

Polyimides (PI) were prepared from PA and [1]–[4] by the two-step procedure (Scheme 3). In the first step, polyamic acids were synthesized by the solution polymerization in the above solvents at room temperature. And then, PI's were prepared by the cyclodehydration of the corresponding polyamic acids at 200°C for 6 h *in vacuo*. Polyamic acids were found to be fluid over 170°C during the cyclodehydration process, indicating that the glass transition at this temperature occurs. The reduced viscosities and elemental analysis data of polyamic acids and PI's are listed in Table II. Polyamic acids exhibited absorption bands around 3650–3050, 1720, and 1660 cm^{-1} . These bands disappeared after cyclodehydration and new absorptions at 3450–3250, 1780, 1730, and 1330 cm^{-1} associated with the imide structure were observed.

Polyureas were prepared by the polyaddition of [1]–[4] with MI and TI in THF/NMP (6/4 volume) at room temperature for 6 h and 60°C for 2 h (Scheme 4). The results of preparation of polyureas are listed in Table III.

TABLE III
Preparation of Polyureas^a

Polymer no.	Yield (%)	η sp/C ^b (dL/g)	Elemental analysis		
			C %	H %	N %
[1]-MI	92	0.17	76.81	9.37	11.19 ^c
[2]-MI	95	0.18	76.45	9.32	11.06 ^c
[3]-MI	97	0.21	76.65	9.29	11.14 ^c
[4]-MI	96	0.20	76.54	9.45	11.03 ^c
[1]-TI	91	0.17	75.15	9.64	11.60 ^d
[2]-TI	94	0.18	75.22	9.47	11.74 ^d
[3]-TI	94	0.18	75.13	9.67	11.96 ^d
[4]-TI	93	0.20	75.27	9.61	11.88 ^d

^a Polymerization was carried out with 1.0 mmol of the monomers in 6 mL of THF and 4 mL of NMP at room temperature for 6 h and 60°C for 2 h.

^b In C = 0.2 g/dL of NMP/THF ($\frac{1}{3}$ volume) at 30°C.

^c Calcd for $\text{C}_{72}\text{H}_{101}\text{N}_9\text{O}_2$: C, 76.89%; H, 9.05%; N, 11.21%.

^d Calcd for $\text{C}_{66}\text{H}_{97}\text{N}_9\text{O}_2$: C, 75.60%; H, 9.32%; N, 12.02%.

TABLE IV
 Solubility of Polymers^a

Polymer	Solvent ^b							
	DMF	DMAc	NMP	DMSO	THF	Benzene	Chloroform	H ₂ SO ₄
[1]-TC	-	±	±	- (+)	±	±	± (-)	-
[2]-TC	±	±	±	- (+)	±	±	± (-)	±
[3]-TC	±	±	±	- (+)	+	+	+	±
[4]-TC	±	±	±	- (+)	+	+	± (-)	±
[1]-IC	-	±	±	- (+)	±	±	± (-)	±
[2]-IC	±	±	±	- (+)	+	+	± (-)	±
[3]-IC	±	±	±	- (+)	+	+	± (-)	±
[4]-IC	±	±	±	- (+)	+	+	± (-)	±
[1]-PA	±	±	±	± (+)	+	+	± (-)	±
[1]-PI	-	±	±	- (+)	+	+	± (-)	-
[1]-MI	±	±	±	- (+)	+	+	± (-)	±
[1]-TI	±	±	±	- (+)	+	+	± (-)	±

^a Solubility: +, soluble; ±, partially soluble; -, insoluble. Symbol in parentheses shows the solubility of the corresponding polymers with no alkyl side chains (see Ref. 11).

^b DMF: *N,N*-dimethylformamide; DMAc: *N,N*-dimethylacetamide; NMP: *N*-methyl-2-pyrrolidone; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

The absorptions of ureylene groups of polyureas were similar to the spectrum regions of polyamides.

Polyamides had higher reduced viscosities than those of polyimides and polyureas in THF/NMP (3/1 volume) at 30°C. All polymers showed absorption bands at 1410 and 820 cm⁻¹ due to the triazine rings and at 2920 and 2850 cm⁻¹ caused by the octadecyl groups.

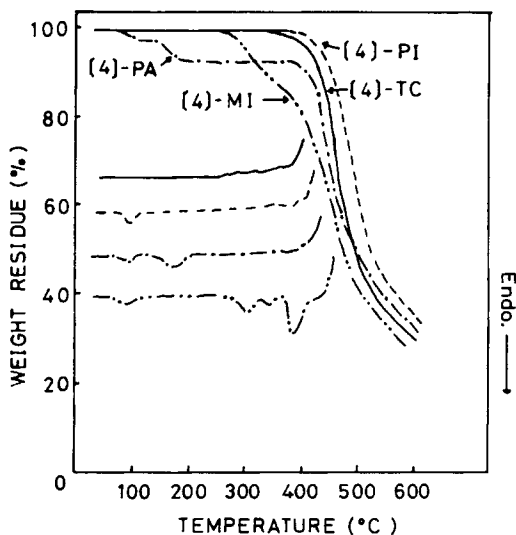


Fig. 1. TG and DTA curves of polyamide [4]-TC, polyamic acid [4]-PA, polyimide [4]-PI, and polyurea [4]-MI at a heating rate of 10°C/min in air.

TABLE V
 Thermal Behaviors of Long Side Chain Polymers^a

Polymer no.	T_d^b (°C)	T_m and T_{cr} of side chains (°C)			ΔH^c (Kcal/mole)			$n_{cryst.}^d$		
		T_{m_1}	T_{cr}	T_{m_2}	ΔH_1	$-\Delta H_{cr}$	ΔH_2	n_1	n_{cr}	n_2
[1]-TC	425	-17	-25	-18	1.26	0.82	0.84	0.84	0.56	0.57
[2]-TC	418	-8	-21	-7	1.77	1.57	1.58	1.20	1.07	1.07
[3]-TC	422	-7	-26	-5	2.07	2.03	2.06	1.41	1.38	1.40
[4]-TC	425	-12	-28	-8	2.18	1.89	1.92	1.48	1.28	1.31
[1]-IC	415	-9	-28	-10	1.28	1.25	1.27	0.86	0.85	0.86
[2]-IC	425	-10	-25	-12	2.10	1.88	2.08	1.42	1.28	1.41
[3]-IC	420	-11	-23	-15	2.24	2.10	2.17	1.52	1.43	1.47
[4]-IC	429	-15	-26	-15	2.01	1.92	1.98	1.36	1.31	1.35
[1]-PA	440	3, 74	-20	-1	2.65	2.58	2.51	1.80	1.75	1.71
[2]-PA	429	-7, 75	-24	-4	2.84	2.64	2.65	1.93	1.80	1.80
[3]-PA	432	6, 72	-20	2	2.91	2.70	2.95	1.98	1.84	2.00
[4]-PA	434	1, 77	-18	-2	2.71	2.63	2.66	1.75	1.65	1.81
[1]-PI	447	-16, 85	-28	-11	2.91	1.82	1.93	1.98	1.23	1.31
[2]-PI	437	-10, 90	-21	-6	2.98	1.85	1.90	2.03	1.26	1.29
[3]-PI	435	-19, 83	-30	-15	2.80	1.71	1.95	1.90	1.16	1.32
[4]-PI	437	-17, 81	-25	-15	2.85	2.02	1.99	1.94	1.37	1.35
[1]-MI	320	-5, 85	-28	-8	2.75	2.34	2.56	1.87	1.59	1.74
[2]-MI	316	-7, 81	-24	-7	2.79	2.30	2.57	1.90	1.56	1.75
[3]-MI	318	-10, 76	-30	-9	2.62	2.22	2.37	1.78	1.51	1.61
[4]-MI	325	-10, 84	-25	-12	2.72	2.33	2.42	1.85	1.58	1.65
[1]-TI	290	-3, 94	-22	-9	2.16	1.88	1.91	1.46	1.27	1.30
[2]-TI	295	-7, 96	-28	-10	2.28	1.94	1.95	1.55	1.32	1.32
[3]-TI	293	-8, 93	-28	-10	2.60	2.33	2.38	1.77	1.58	1.62
[4]-TI	300	-10, 94	-30	-11	2.26	2.19	2.20	1.60	1.49	1.50

^a Sample was repeated at a rate of 10°C/min. "1" is measured on initial heating, "cr" on cooling, and "2" on reheating.

^b Decomposition temperature at which 5% weight loss was recorded by TG in air.

^c Enthalpies of fusion and crystallization.

^d Number of crystallizing CH₂ groups in the side chain.

Characterization of Polymers

The typical solubilities of polymers are listed in Table IV. These aromatic polymers containing long alkyl side chains had good solubilities in THF, chloroform, and benzene. In addition, all polymers were easily soluble in the mixed solvents of THF/NMP, DMF or DMAc, but with poor solubilities in polar aprotic solvents such as DMF, DMAc, DMSO, and NMP. On the other hand, the corresponding polymers¹¹ without long alkyl side chains were soluble in those of polar aprotic solvents and concentrated sulfuric acid. Solubilities of these polymers showed a notable variation under the influence of long alkyl side chains. This change of solubility is advantageous in the processability of polymer, for instance the brittle films of [3]-TC, [4]-TC and [3]-IC could be cast conveniently from the THF solution.

Thermal properties of the polymers were investigated by TG, DTA, and DSC. Typical TG-DTA curves for these polymers are shown in Figure 1. It can

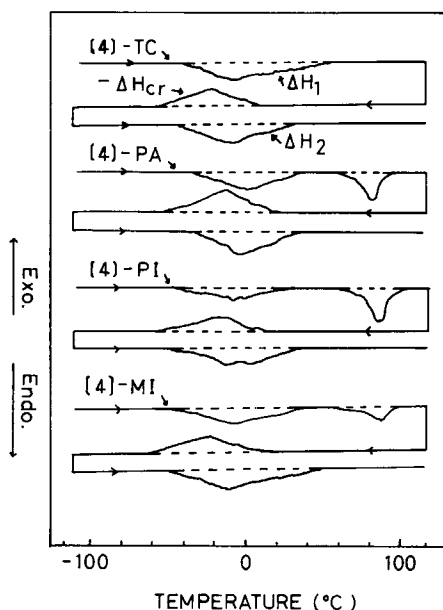


Fig. 2. DSC curves of polyamide [4]-TC, polyamic acid [4]-PA, polyimide [4]-PI, and polyurea [4]-MI at a heating rate of 10°C/min.

be seen that polyamides and polyimides show good thermal stabilities even though they contain the bulky long side chains. The decomposition temperature (T_d) was determined by TG curve at the temperature of 5% weight loss. T_d were above 410°C for polyamides, 430°C for polyimides and 290°C for polyureas in air (Table V), respectively. The T_d 's indicate that thermal stabilities of these polymers were only 5–50°C lower than those of corresponding polymers¹¹ without long side chains. DTA curves of polyamic acids, polyimides, and polyureas showed a small endotherm peak at 60–95°C, which is thought to be the melting of the crystals formed by the long alkyl groups. Therefore, the side chain crystallization of polymers was further examined by DSC in the lower temperature region.

Typical DSC curves of the polymers are shown in Figure 2. The polymer samples were pre-cooled at -120°C , then heating and cooling were repeated at a rate of 10°C/min. All polymers show a broad endotherm and exotherm at -65 – 50°C in the heating and cooling process, respectively. In addition, on the first heating run the other endotherm was found except for polyamides at 60–95°C, which are also observed in the above DTA curves. The endotherm peak in high temperature side is presumed that the crystalline structure is formed on standing at room temperature after polymerization.

The melting and crystallizing temperatures of side chains (Tm_1 , Tcr , and Tm_2) were determined by the tops of these peaks. The results of DSC studies are summarized in Table V. It has been reported that the alkyl side chains of comblike polymers crystallize in hexagonal form.⁵ In order to estimate the numbers (n_{cryst}) of crystallizing CH_2 groups in the side chains of these polymers, we assumed that the long side chains of polymers crystallize in hexagonal packing in this work. n_{cryst} was evaluated from the enthalpy of fusion and crystal-

lization (ΔH_1 , ΔH_{cr} , and ΔH_2) by the use of an enthalpy of transition value (735 cal/mole-CH₂) of hexagonal packing for *n*-alkane.⁵ The degree of crystallinity calculated from the value of n_2 , which having the same thermal histories, was found to be 6–10% on the basis of side chains in these polymers. The results in this work are lower than those of the general vinyl comblike polymer ones, such as 41% for poly(*n*-octadecyl acrylate)⁵ and 25% for poly(*N*-*n*-octadecyl acrylamide),⁵ but are close to a value of 9% for *N*-octadecylated poly(*p*-phenylene terephthalamide),⁷ which has a typical rigid backbone. This might be considered that the rigid structure in the main chain depresses the side-chain crystallization, which results in a low degree of crystallinity.

In conclusion, the reactivity of these diamines was almost not influenced by the substitution position of diamino groups. The solubility of polymers including polyimides had a desirable improvement by the introduction of long alkyl groups. These polymers kept a high degree on the thermal stability even if they contained the bulky long side chains. The degree of side chain crystallinity of these polymers was estimated by DSC to be 6–10%.

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