Synthesis and Characterization of New Comb-Like Aromatic Polymers Based on 2,4-Bis(amino-*N*-octadecylanilino)-6-Substituted-1,3,5-Triazines

Jui-Kun LIN, Yasuo YUKI,* Hideo KUNISADA,
Masashi KONDO, and Shuji KONDO

*Department of Materials Science and Engineering,
Nagoya Institute of Technology, Gokiso-cho,
Showa-ku, Nagoya 466, Japan*

(Received July 5, 1989)

ABSTRACT: A series of new comb-like poly(amide-guanamine)s, poly(urea-guanamine)s and poly(imide-guanamine)s containing two long alkyl side-chains for each unit, were prepared by reactions of 2,4-bis(*p*- or *m*-amino-*N*-octadecylanilino)-6-(unsubstituted, methyl and phenyl)-1,3,5-triazines with aromatic or aliphatic diacid chlorides, diisocyanates and pyromellitic dianhydride, respectively. These polymers except polyimides were soluble in tetrahydrofuran, chloroform and toluene, but insoluble in dimethyl sulfoxide and *N,N*-dimethylformamide. The polymers have good thermal stability though they contain the long alkyl side-chains. Differential scanning calorimetry showed these polymers to be characterized by side-chain crystallinity. The polymers having aliphatic moieties in the main chain gave higher degrees of side-chain crystallinity.

KEY WORDS Comb-Like Polymer / 1,3,5-Triazine / Polyamide / Polyurea / Polyimide / Long Alkyl Group / Side-Chain Crystallization /

The relations between the structure and the properties of so-called comb-like polymers having long alkyl side chains at regular intervals have been extensively studied.¹⁻⁴ Recently, Magagnini *et al.*⁵ reported the side-chain crystallization of a series of aromatic comb-like polyesters prepared from eicosane-diol-1,2 and isomeric three phthalic acids. The polyester obtained from terephthalic acid showed the lowest degree of side-chain crystallinity. Yokota *et al.*^{6,7} investigated the influence of the spaces between teeth on side-chain crystallization for several aliphatic comb-like polyesters, and concluded that the side chains are still able to crystallize even if bonded to every 26th⁷ atom of the flexible main chain.

In the previous paper,⁸ we described the synthesis and characterization of several aromatic comb-like polyamides, polyimides and

polyureas prepared from *m*-phenylenediamine containing 1,3,5-triazine ring with two long alkyl groups and aromatic comonomers. The long side chains of the polymers have been observed to crystallize by means of differential scanning calorimetry. It was found that the side-chain crystallization depends on the main-chain structure; the polyureas showed higher degrees of side-chain crystallinity than those of polyamides and polyimides.

In the present paper, we investigated the influence of the main chain structure and of the spacing between side chains on side-chain crystallization. Six new diamines with two long alkyl groups, 2,4-bis(amino-*N*-octadecylanilino)-6-substituted-1,3,5-triazines, were synthesized and polymerized with aromatic or aliphatic diacid chlorides, diisocyanates and pyromellitic dianhydride to give a series of new type comb-like polyamides, polyureas and

polyimides. The solubilities and thermal stabilities of the polymers are also discussed.

EXPERIMENTAL

Materials and Monomers

Terephthaloyl chloride (TC), isophthaloyl chloride (IC), sebacoyl chloride (SC), pyromellitic dianhydride (PA), 4,4'-diphenylmethane diisocyanate (MI), toluene 2,4-diisocyanate (TI) and hexamethylene diisocyanate (HI) were commercially available. The solvents used for reactions such as dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP) and tetrahydrofuran (THF) were purified by distillation. 2,4-Bis(*p*- or *m*-aminoanilino)-6-(unsubstituted, methyl and phenyl)-1,3,5-triazines were prepared by the literature method.^{9,10}

2,4-Bis(*p*-amino-*N*-octadecylanilino)-1,3,5-triazine [1]. 2,4-Bis(*p*-aminoanilino)-1,3,5-triazine (15 g, 0.051 mol) was added to a stirred solution of sodium hydride (4.48 g, 0.112 mol; 60% oil suspension) in 300 ml of DMSO at 40°C. After 1 h, *n*-octadecyl bromide (34.0 g, 0.102 mol) was added to this solution. The mixture was stirred at 40°C for 6 h and at room temperature for one night. The precipitated product was separated and washed by water. Recrystallization from benzene-hexane gave 28.62 g (70.3%) of [1] with mp 126, 133, 140°C. *Anal.* Found: C, 76.51%; H, 11.34%; N, 12.04%. Calcd for C₅₁H₈₇N₇: C, 76.74%; H, 10.98%; N, 12.28%. ¹H NMR (CDCl₃) δ (ppm): 0.88 (t, 6H, 2CH₃), 1.08—1.50 (m, 64H, 32CH₂), 3.68 (br s, 4H, 2NH₂), 3.88 (br s, 4H, 2NCH₂), 6.72 (d, 4H, 2Ar), 7.01 (d, 4H, 2Ar), 8.13 (br s, 1H, H-triazine).

Other monomers [2]—[6] were prepared by the above-mentioned method.

2-(*p*-Amino-*N*-octadecylanilino)-4-(*m*-amino-*N*-octadecylanilino)-1,3,5-triazine [2]. Yield 63.0%, mp 112°C. *Anal.* Found: C, 76.82%; H, 11.09%; N, 12.11%. Calcd for C₅₁H₈₇N₇: C, 76.74%; H, 10.98%; N, 12.28%. ¹H NMR (CDCl₃) δ (ppm): 0.91 (t, 6H, 2CH₃), 1.12—

1.70 (m, 64H, 32CH₂), 3.36—4.20 (m, 8H, 2NH₂ and 2NCH₂), 6.60 (m, 3H, *m*-Ar), 6.68 (d, 2H, *p*-Ar), 7.03 (d, 2H, *p*-Ar), 7.20 (br s, 1H, *m*-Ar), 8.18 (br s, 1H, H-triazine).

2,4-Bis(*p*-amino-*N*-octadecylanilino)-6-methyl-1,3,5-triazine [3]. Yield 62.5%, mp 135°C. *Anal.* Found: C, 76.78%; H, 11.27%; N, 11.88%. Calcd for C₅₂H₈₉N₇: C, 76.89%; H, 11.04%; N, 12.07%. ¹H NMR (CDCl₃) δ (ppm): 0.88 (t, 6H, 2CH₃), 1.00—1.55 (m, 64H, 32CH₂), 2.16 (s, 3H, CH₃-triazine), 3.64 (br s, 4H, 2NH₂), 3.86 (br s, 4H, 2NCH₂), 6.67 (d, 4H, 2Ar), 7.00 (d, 4H, 2Ar).

2-(*p*-Amino-*N*-octadecylanilino)-4-(*m*-amino-*N*-octadecylanilino)-6-methyl-1,3,5-triazine [4]. Yield 87.8%, mp 100, 116°C. *Anal.* Found: C, 76.56%; H, 11.07%; N, 11.86%. Calcd for C₅₂H₈₉N₇: C, 76.89%; H, 11.04%; N, 12.07%. ¹H NMR (CDCl₃) δ (ppm): 0.91 (t, 6H, 2CH₃), 1.10—1.68 (m, 64H, 32CH₂), 2.20 (s, 3H, CH₃-triazine), 3.30—4.10 (m, 8H, 2NH₂ and 2NCH₂), 6.55 (m, 3H, *m*-Ar), 6.65 (d, 2H, *p*-Ar), 7.05 (d, 2H, *p*-Ar), 7.30 (br s, 1H, *m*-Ar).

2,4-Bis(*p*-amino-*N*-octadecylanilino)-6-phenyl-1,3,5-triazine [5]. Yield 55.5%, mp 122°C. *Anal.* Found: C, 78.46%; H, 10.55%; N, 11.05%. Calcd for C₅₇H₉₁N₇: C, 78.30%; H, 10.49%; N, 11.21%. ¹H NMR (CDCl₃) δ (ppm): 0.88 (t, 6H, 2CH₃), 1.02—1.56 (m, 64H, 32CH₂), 3.66 (br s, 4H, 2NH₂), 4.04 (br s, 4H, 2NCH₂), 6.72 (d, 4H, 2Ar), 7.07 (d, 4H, 2Ar), 7.38 (m, 3H, Ph-triazine), 8.26 (m, 2H, Ph-triazine).

2-(*p*-Amino-*N*-octadecylanilino)-4-(*m*-amino-*N*-octadecylanilino)-6-phenyl-1,3,5-triazine [6]. Yield 75.5%, mp 86°C. *Anal.* Found: C, 78.18%; H, 10.82%; N, 11.09%. Calcd for C₅₇H₉₁N₇: C, 78.30%; H, 10.49%; N, 11.21%. ¹H NMR (CDCl₃) δ (ppm): 0.93 (t, 6H, 2CH₃), 1.12—1.65 (m, 64H, 32CH₂), 3.41 (br s, 4H, 2NH₂), 3.93 (br s, 4H, 2NCH₂), 6.62 (m, 3H, *m*-Ar), 6.75 (d, 2H, *p*-Ar), 7.11 (d, 2H, *p*-Ar), 7.20 (br s, 1H, *m*-Ar), 7.39 (m, 3H, Ph-triazine), 8.20 (m, 2H, Ph-triazine).

Polymerization

Poly(amide-guanamine)s Prepared from [1]–TC through [6]–SC. For example, [1]–TC: 0.798 g (1.0 mmol) of [1] was dissolved in 10 ml of THF–NMP (2:1 volume) with stirring. 0.203 g (1.0 mmol) of TC was added to this solution at room temperature. After 24 h, the solution was poured into 300 ml of methanol. The precipitated polymer was separated, washed thoroughly with methanol and dried *in vacuo*. The yield was 0.876 g (94%). [1]–TC was purified by reprecipitation from THF into acetone. *Anal.* Found: C, 76.66%; H, 10.15%; N, 10.92%. Calcd for $(C_{59}H_{89}N_7O_2)_n$: C, 76.33%; H, 9.66%; N, 10.56%.

Poly(urea-guanamine)s Prepared from [1]–MI through [6]–HI. For example, [1]–MI: MI (0.250 g, 1.0 mmol) was added to a stirred solution of [1] (0.798 g, 1.0 mmol) in 10 ml of THF–NMP (2:1 volume) at room temperature. This solution was stirred at room temperature for 6 h and 60°C for 2 h, and poured into 300 ml of methanol. The precipitated polymer was separated, washed thoroughly with methanol and dried *in vacuo*. The yield was 0.997 g (95%). [1]–MI was purified by reprecipitation from THF into acetone. *Anal.* Found: C, 75.50%; H, 9.37%; N, 11.66%. Calcd for $(C_{66}H_{97}N_9O_2)_n$: C, 75.60%; H, 9.32%; N, 12.02%.

Poly(imide-guanamine)s Prepared from [1]–PI through [6]–PI. For example, [1]–PI: A solution of [1] (0.798 g, 1.0 mmol) and PA (0.218 g, 1.0 mmol) in 10 ml of THF–NMP (2:1 volume) was stirred at room temperature for 24 h. The solution was poured into 300 ml

of methanol to give the polyamic acid [1]–PA. The yield was 0.975 g (96%). [1]–PA was reprecipitated from THF into acetone. *Anal.* Found: C, 71.04%; H, 9.08%; N, 9.41%. Calcd for $(C_{61}H_{89}N_7O_6)_n$: C, 72.08%; H, 8.82%; N, 9.64%. Polyimide [1]–PI was then prepared by heating the [1]–PA at 200°C for 6 h *in vacuo*. *Anal.* Found: C, 74.76%; H, 8.76%; N, 9.88%. Calcd for $(C_{61}H_{85}N_7O_4)_n$: C, 74.73%; H, 8.74%; N, 10.00%.

Other poly(amide-guanamine)s, poly(urea-guanamine)s, and poly(imide-guanamine)s were prepared in a similar manner.

Measurements

IR and 1H NMR spectra were recorded on a Hitachi 285 spectrophotometer and a Hitachi R600 FTNMR (60 MHz) spectrometer, respectively. Thermogravimetry and differential thermal analysis were performed with a Rigaku TG-DTA 812BH thermal analysis system. A Rigaku DSC 8131BL differential scanning calorimeter was used to study the side chain crystallization of polymers. Reduced viscosities were measured using an Ostwald viscometer.

RESULTS AND DISCUSSION**Synthesis of Diamines with Long Alkyl Groups**

2,4-Bis(*p*- or *m*-amino-*N*-octadecylanilino)-6-substituted-1,3,5-triazines [1]–[6] were synthesized by the alkylation of 2,4-bis(*p*- or *m*-aminoanilino)-6-substituted-1,3,5-triazines with *n*-octadecyl bromide in the presence of sodium hydride (Scheme 1). The structures of

Scheme 1

these diamines were confirmed by IR, ^1H NMR spectra and elemental analysis.

Preparation of Polymers

Our previous papers⁸ on the synthesis of aromatic comb-like polymers demonstrated that a mixed solvent of THF–NMP was the most suitable for preparing the polymer with the highest reduced viscosity.

Poly(amide-guanamine)s [1]–TC–[6]–SC were prepared by the solution polycondensation of diamines [1]–[6] with diacid chlorides TC, IC, and SC according to Scheme 2, and the results are listed in Table I.

Poly(urea-guanamine)s [1]–MI–[6]–HI were prepared by the polyaddition of [1]–[6] with diisocyanates MI, TI, and HI (Scheme 3). The results are listed in Table II.

Scheme 2

Scheme 3

Scheme 4

Table I. Preparation of comb-like poly(amide-guanamine)s

Polymer	R	Yield	η_{sp}/c^a	T_d^b
		%	dl g ⁻¹	°C
[1]-TC	H	86	0.27	425
[1]-IC	H	98	0.34	412
[1]-SC	H	76	0.33	420
[2]-TC	H	94	0.31	410
[2]-IC	H	92	0.24	397
[2]-SC	H	77	0.31	408
[3]-TC	CH ₃	96	0.29	412
[3]-IC	CH ₃	87	0.32	398
[3]-SC	CH ₃	79	0.49	407
[4]-TC	CH ₃	92	0.35	420
[4]-IC	CH ₃	94	0.45	408
[4]-SC	CH ₃	74	0.38	417
[5]-TC	C ₆ H ₅	87	0.33	415
[5]-IC	C ₆ H ₅	93	0.25	410
[5]-SC	C ₆ H ₅	86	0.29	407
[6]-TC	C ₆ H ₅	94	0.33	428
[6]-IC	C ₆ H ₅	98	0.34	425
[6]-SC	C ₆ H ₅	77	0.36	420

^a Measured in THF-NMP (3:1) at 30°C, $c=0.2$ g dl⁻¹.^b Decomposition temperature at which 5% weight loss was recorded by TG at a heating rate of 10°C min⁻¹ in air.**Table II.** Preparation of comb-like poly(urea-guanamine)s

Polymer	R	Yield	η_{sp}/c^a	T_d^b
		%	dl g ⁻¹	°C
[1]-MI	H	99	0.43	317
[1]-TI	H	98	0.30	293
[1]-HI	H	99	0.28	330
[2]-MI	H	95	0.22	328
[2]-TI	H	97	0.23	300
[2]-HI	H	96	0.25	323
[3]-MI	CH ₃	99	0.46	314
[3]-TI	CH ₃	98	0.35	302
[3]-HI	CH ₃	99	0.38	332
[4]-MI	CH ₃	98	0.30	317
[4]-TI	CH ₃	94	0.25	285
[4]-HI	CH ₃	92	0.25	320
[5]-MI	C ₆ H ₅	99	0.32	309
[5]-TI	C ₆ H ₅	98	0.36	281
[5]-HI	C ₆ H ₅	97	0.29	327
[6]-MI	C ₆ H ₅	94	0.42	325
[6]-TI	C ₆ H ₅	98	0.38	292
[6]-HI	C ₆ H ₅	98	0.22	325

^a Measured in THF-NMP (3:1) at 30°C, $c=0.2$ g dl⁻¹.^b Decomposition temperature at which 5% weight loss was recorded by TG at a heating rate of 10°C min⁻¹ in air.

Poly(imide-guanamine)s [1]-PI-[6]-PI were prepared by a two-step method (Scheme 4). In the first step, the polyamic acids [1]-PA-[6]-PA were prepared by reactions of [1]-[6] with pyromellitic dianhydride PA. In the second step, the polyimides, [1]-PI-[6]-PI, were obtained by the cyclodehydration of the corresponding polyamic acids at 200°C *in vacuo*. The results are listed in Table III.

The IR spectra of the poly(amide-guanamine)s showed typical absorptions of amides at 3450—3250, 1650, and 1310 cm⁻¹. Poly(urea-guanamine)s also showed absorption bands at these spectral regions due to ureylene groups. Polyamic acids showed absorption bands at 3450—3250, 1720, and 1650 cm⁻¹. These bands disappeared after cyclodehydration and new absorptions of imide ring were observed at 1780, 1730 and 1360 cm⁻¹.^{10,11} Further, all polymers showed ab-

Table III. Preparation of comb-like polyamic acids and poly(imide-guanamine)s

Polymer	R	Yield	η_{sp}/c^a	T_d^b
		%	dl g ⁻¹	°C
[1]-PA	H	99	0.55	
[1]-PI	H	90	0.40	453
[2]-PA	H	95	0.31	
[2]-PI	H	97	insol.	456
[3]-PA	CH ₃	99	0.58	
[3]-PI	CH ₃	91	insol.	450
[4]-PA	CH ₃	96	0.34	
[4]-PI	CH ₃	97	insol.	460
[5]-PA	C ₆ H ₅	98	0.36	
[5]-PI	C ₆ H ₅	97	0.31	451
[6]-PA	C ₆ H ₅	99	0.38	
[6]-PI	C ₆ H ₅	97	0.33	455

^a Measured in THF-NMP (3:1) at 30°C, $c=0.2$ g dl⁻¹.^b Decomposition temperature at which 5% weight loss was recorded by TG at a heating rate of 10°C min⁻¹ in air.

Table IV. Solubility of comb-like polymers^a

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

^a (++) , soluble at room temperature; (+) , soluble at 60°C; (±) , partially soluble or swelling; (—) , insoluble.

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

sorption bands of the triazine rings at 1410 and 820 cm⁻¹, and the octadecyl groups at 2920, 2850, and 720 cm⁻¹. The elemental analysis values of these polymers agreed with those calculated for the proposed structures.

Characterization of Polymers

The typical solubility behavior of the comb-like polymers obtained from [1] and [2] is listed in Table IV. These polymers except polyimides were soluble in THF and chloroform, but insoluble in polar aprotic solvents such as dimethylformamide, dimethylacetamide, NMP and DMSO. In addition, the polymers derived from aliphatic SC or HI were also soluble in benzene and toluene. Similar results were also observed in the methyl or phenyl substituted polymers. In contrast, the corresponding polymers without long side-chains were soluble in the above polar aprotic solvents, but insoluble in THF, chloroform and toluene.^{9,10} The solubilities of these polymers showed notable change under the influence of

Figure 1. TG and DTA curves of polymers at a heating rate of 10°C min⁻¹ in air: (A) polyamide [1]-TC; (B) polyamide [1]-SC.

long alkyl side-chains. This change is favorable for processability. Transparent and brittle films of the SC- and HI-polymers could be cast from the chloroform solutions.

The thermal properties of the polymers were

investigated by TG, DTA, and DSC. Typical TG and DTA curves of polyamides [1]-TC and [1]-SC are shown in Figure 1. The polymer [1]-SC with aliphatic moieties in the main chain showed the same degree of thermal stability as the wholly aromatic polymer [1]-TC. The other methyl or phenyl substituted polymers also showed similar results. The decomposition temperature (T_d) shown in Tables I, II, and III, were around 410°C for poly(amide-guanamine)s, 300°C for poly(urea-guanamine)s, and 450°C for poly(imide-guanamine)s. These T_d s values are close to those of the corresponding polymers without long side chains,^{9,10} and indicate that the introduction of long side chains has almost no effect on thermal stability. On the other hand, the DTA curve of [1]-SC showed an endothermic peak at 75°C. This should be attributed to the melting of crystals formed by long alkyl side-chains.

Figure 2 shows typical DSC curves of [1]-TC, [1]-SC, and [6]-SC. The polymer samples were pre-cooled at -120°C, and heating and cooling were then repeated at a scanning rate of 10°C min⁻¹. The polymers derived from TC or IC showed endo- and exothermic peaks at below room temperature during heating and cooling, respectively. This indicates that the

long alkyl groups of TC- and IC-polyamides are almost disordered at room temperature, and crystallization may occur in lower temperature ranges. The SC-polyamides and all polyureas showed major peaks at 50–80°C with broad peaks below room temperature in the first heating run. Temperature ranges of the broad peaks were similar to those of TC- and IC-polyamides. The explanation for this may be that the major peaks at 50–80°C are due to the melting of crystals formed at room temperature and the broad peaks below room temperature are due to the other long alkyl groups crystallized during the pre-cooling. The typical curves of X-ray diffraction of the powdered polymers at room temperature are shown in Figure 3. The TC- and IC-polymers were found to be almost amorphous such as curve (A) of Figure 3. The polymer [6]-SC which had a sharp endothermic peak in the first DSC heating run, showed strong reflection at $2\theta = 20.7^\circ$ (a spacing of 4.29 Å). This reflection corresponds to the spacing of the hexagonal crystalline packing reported for the common comb-like polymers.^{4,12} The hexagonal packing of the alkyl side groups was also proved by a single

Figure 2. DSC curves of polymers: (A) polyamide [1]-TC; (B) polyamide [1]-SC; (C) polyamide [6]-SC.

Figure 3. X-Ray diffraction patterns of polymers: (A) polyamide [1]-TC; (B) polyurea [1]-TI; (C) polyamide [1]-SC; (D) polyamide [6]-SC.

Table V. Side-chain crystallinity of comb-like polymers^a

Polymer	Melting or crystallization temperature			Enthalpy of fusion or crystallization			Number of crystallizing CH ₂ groups		
	°C			kcal mol ⁻¹					
	<i>T</i> _{m1}	<i>T</i> _{cr}	<i>T</i> _{m2}	ΔH_1	$-\Delta H_{cr}$	ΔH_2	<i>n</i> ₁	<i>n</i> _{cr}	<i>n</i> ₂
[1]-TC	7	-1	5	0.63	1.40	1.38	0.43	0.95	0.94
[1]-IC	-14	-20	-13	1.79	2.33	2.32	1.22	1.59	1.58
[1]-SC	76	16	26	1.94	3.16	2.92	2.01	2.15	2.00
[1]-PA	-3	-5	4	1.74	2.28	2.38	1.18	1.55	1.62
[1]-PI	43	-12	3	3.27	2.63	2.87	2.22	1.79	1.94
[1]-MI	66	-19	-11	1.97	1.77	1.73	1.34	1.20	1.18
[1]-TI	69	-22	-19	2.23	1.38	1.34	1.52	0.94	0.91
[1]-HI	76	-13	6	3.79	2.42	2.60	2.58	1.65	1.77
[2]-TC	-11	-21	-9	1.33	1.55	1.54	0.90	1.05	1.05
[2]-IC	-18	-23	-18	1.53	1.70	1.62	1.04	1.15	1.10
[2]-SC	68	-25	8	2.88	2.45	2.42	1.96	1.66	1.65
[2]-PA	-16	-25	-14	1.60	1.82	1.91	1.09	1.24	1.30
[2]-PI	11	-5	5	1.38	1.55	1.53	0.94	1.05	1.04
[2]-MI	65	-22	-14	2.32	1.79	1.84	1.58	1.22	1.25
[2]-TI	71	-24	-10	3.52	1.88	1.85	2.39	1.28	1.26
[2]-HI	76	-18	7	5.90	2.63	2.70	4.01	1.79	1.84
[6]-TC	-20	-28	-14	1.33	1.55	1.54	0.90	1.05	1.05
[6]-SC	77	-25	6	7.02	2.45	2.53	4.77	1.67	1.72

^a Measured by DSC on repeated runs from -120 to 120°C at a heating rate of 10°C min⁻¹. "1" means on first heating run, "cr" on cooling run, and "2" on second heating run.

absorption band at 720 cm⁻¹ in the IR spectrum.^{4,13} The other polymers also showed broad peaks at about $2\theta = 20.5^\circ$ (as curve (B) and (C) of Figure 3), and whose intensity was dependent on the sharpness of the DSC peak(s). As mentioned above, the long alkyl groups of these polymers are considered to crystallize in hexagonal form. However, it is possible that polymers having melting peaks below room temperature might also peak in another crystal form. Crystalline structures of long alkyl groups packed at low temperature should be studied further.

The crystallinity of the side chains of the polymers was evaluated by the heats of transition from DSC scanning. Typical data for DSC measurement are listed in Table V. Melting and crystallization temperatures (*T*_{m1}, *T*_{cr}, and *T*_{m2}) were determined by the tops of the DSC peaks. The enthalpies of fusion and

crystallization (ΔH_1 , ΔH_{cr} , and ΔH_2) were calculated from DSC peak areas. As mentioned above, both two endothermic peaks in the first heating run were considered to be the melting of crystals from the long alkyl groups in different thermal history. Therefore, ΔH_1 was calculated from total areas when the DSC curves contained two peaks. We assumed that all the polymers crystallized in hexagonal form, the average numbers of crystallizing CH₂ groups in the side chains (*n*₁, *n*_{cr}, and *n*₂) were calculated from their enthalpies (ΔH_1 , ΔH_{cr} , and ΔH_2) using 735 cal mol⁻¹ CH₂⁻¹, the reported value for hexagonal-packed *n*-alkanes.¹⁴ The values of *n*₁ were noted to be small in these polymers. However, the crystallization of side chains can be detected by means of DSC and X-ray analysis. It is thought that only some of the long alkyl groups can crystallize and most of the long

alkyl groups are disordered because of the rigid main chain. The results on polymers derived from aromatic TC, IC, PA, MI, and TI are similar to those of previous polymers derived from *m*-phenylenediamine derivative, 2,4-bis(*N*-octadecylanilino)-6-(3,5-diaminophenyl)-1,3,5-triazine.⁸ The polymers derived from aliphatic SC or HI showed higher both melting points and numbers of crystallizing CH₂ groups. This is because the SC- and HI-polymers contain relatively flexible moieties in the main chain, and allow their side chains to approach each other to give crystallinity. This indicates that the flexibility of the main chain has an important effect on the side-chain crystallization of comb-like polymer.

REFERENCES

1. C. G. Overberger, L. H. Arond, R. H. Wiley, and R. R. Garrett, *J. Polym. Sci.*, **7**, 431 (1951).
2. S. A. Greenberg and T. Alfrey, *J. Am. Chem. Soc.*, **76**, 6280 (1954).
3. E. F. Jordan, Jr., D. W. Feldeison, and A. N. Wrigley, *J. Polym. Sci., A-1*, **9**, 1835 (1971).
4. N. A. Platé and V. P. Shibaev, *J. Polym. Sci., Macromol. Rev.*, **8**, 117 (1974).
5. F. Andruzzi, C. Barone, D. Lupinacci, and P. L. Magagnini, *Makromol. Chem., Rapid Commun*, **5**, 603 (1984).
6. K. Yokota and T. Hirabayashi, *Polym. J.*, **18**, 177 (1986).
7. T. Hirabayashi, K. Kasabou, and K. Yokota, *Polym. J.*, **20**, 911 (1988).
8. J.-K. Lin, Y. Yuki, H. Kunisada, C. Miyagawa, and S. Kondo, *Polym. J.*, **21**, 709 (1989).
9. Y. Yuki and Y. Osaka, *Kobunshi Kagaku*, **30**, 720 (1973).
10. Y. Yuki and M. Kinoshita, *Nippon Kagaku Kaishi*, **4**, 549 (1977).
11. R. Takatsuka, T. Unishi, I. Honda, and T. Kakurai, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 1785 (1977).
12. B. Espenschied and R. C. Schulz, *Makromol. Chem., Rapid Commun.*, **4**, 633 (1983).
13. D. Chapman, *J. Chem. Soc.*, 4489 (1957).
14. M. G. Broadhurst, *J. Res. Nat. Bur. Stand.*, **66A**, 241 (1962).