

NOTES

New Comb-Like Aromatic Polyamides and Polyimides Containing 1,3,5-Triazine Rings in Their Side Chains

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It has been reported that polymers having long alkyl side chain so-called comb-like polymers can undergo side-chain crystallization.^{1,2} A lot of papers describe comb-like polymers having flexible backbone, which were obtained by polymerization of vinyl monomers having long alkyl groups.³⁻⁵ Comb-like polymers containing rigid main chain have attracted great interest because they have higher glass transition temperatures than those of vinyl comb-like polymers. There are very few studies on aromatic comb-like polymers. Takayanagi *et al.*^{6,7} reported that the poly(*N*-octadecylated *p*-phenylene terephthalamide) showed side-chain crystallization and liquid crystalline behavior of lyotropic type, but led to a decrease in thermal stability.

In previous papers of this series,⁸⁻¹¹ we reported the preparation and properties of novel aromatic polymers containing 1,3,5-

triazine and two long alkyl groups in their side chain using *m*-phenylene diamine derivatives, that is, 2,4-bis(*N*-octadecylanilino)-6-(3,5-diaminophenyl)-1,3,5-triazine (DA18) as a monomer.¹⁰ The introduction of long alkyl side chains in polymers led to obvious change in their solubilities. In addition, these polymers showed side-chain crystallization based on long alkyl groups.

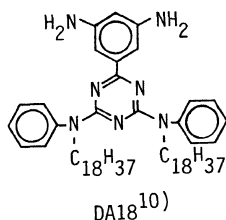
This paper describes the synthesis of novel aromatic polymers containing 1,3,5-triazine and one long alkyl group in their side chain using *m*-phenylene diamine derivatives, and the influence of increasing the number of methylene groups of an alkyl side chain on the thermal properties and solubilities.

EXPERIMENTAL

Preparation of Dinitro Compounds (*NnT*)

2-Amino-4-anilino-6-(3,5-dinitrophenyl)-1,3,5-triazine (NHT) was prepared by the reaction of phenylbiguanide¹² with 3,5-dinitrobenzoyl chloride and recrystallized from dimethylformamide (DMF)-water mixture. mp 299°C (lit.¹³ 297°C).

2-Amino-4-(*N*-methylanilino)-6-(3,5-dinitrophenyl)-1,3,5-triazine (NIT) was prepared



by the reaction of 48 g (0.25 mol) of 1-methyl-1-phenylbiguanide with 57.6 g (0.25 mol) of 3,5-dinitrobenzoyl chloride. A yellow powder of 77 g was obtained to give a yield of 42% with mp 214°C.

2-Amino-4-(*N*-hexylanilino)-6-(3,5-dinitrophenyl)-1,3,5-triazine (N6T) was prepared by the reaction of NHT (17.65 g, 0.05 mol) with hexyl bromide (8.25 g, 0.05 mol) after treating NHT with sodium hydride in DMF solution. A yellow powder of 17.28 g was obtained to give a yield of 79% with mp 122.5°C.

2-Amino-4-(*N*-octadecylanilino)-6-(3,5-dinitrophenyl)-1,3,5-triazine (N18T) was prepared by the reaction of NHT (17.65 g, 0.05 mol) with octadecyl bromide (16.65 g, 0.05 mol) in a similar method for N6T. Crude product was recrystallized from ethanol to give yellow crystal. mp 110°C.

Synthesis of Diamines (*AnT*)

2-Amino-4-anilino-6-(3,5-diaminophenyl)-1,3,5-triazine (AHT) was obtained by the reduction of NHT using SnCl₂ and hydrochloric acid by a described method,¹³ and then recrystallized from ethanol–water mixture. mp 125°C (lit.¹³ 126–127°C).

2-Amino-4-(*N*-methylanilino)-6-(3,5-diaminophenyl)-1,3,5-triazine (A1T) was prepared by the reduction of N1T (9.17 g, 0.025 mol) in a similar method for NHT, and then recrystallized from ethanol–water mixture. Yield 4.9 g (64%). mp 195°C. *Anal.* Found: C, 62.53%, H, 5.56%, N, 31.40%. Calcd for C₁₆H₁₇N₇: C, 62.54%, H, 5.53%, N, 31.92%. IR: 3200–3500, 2925, 1620, 1390, 820 cm⁻¹. ¹H NMR (DMSO-*d*₆) δ ppm: 3.5 (s, 3H, NCH₃), 4.77 (s, 4H, 2NH₂), 6.03 (t, 1H_p, Ar), 6.75 (s, 2H, NH₂), 6.8 (d, 2H_o, Ar), 7.2–7.6 (m, 5H, Ph).

2-Amino-4-(*N*-hexylanilino)-6-(3,5-diaminophenyl)-1,3,5-triazine (A6T) was prepared by the reduction of N6T (7.0 g, 0.016 mol) by a similar method for AHT, and then recrystallized from ethanol–water mixture. Yield 4.0 g (64%). mp 142°C. *Anal.* Found: C,

66.67%, H, 7.22%, N, 25.35%. Calcd for C₂₁H₂₇N₇: C, 66.84%, H, 7.16%, N, 25.99%. IR: 3200–3475, 2850–2900, 1640, 1400, 810 cm⁻¹. ¹H NMR (DMSO-*d*₆) δ ppm: 0.85 (t, 3H, CH₃), 1.27 (m, 8H, (CH₂)₄), 4.0 (t, 2H, NCH₂), 4.75 (s, 4H, 2NH₂), 6.05 (t, 1H_p, Ar), 6.7 (s, 2H, NH₂), 6.8 (d, 2H_o, Ar), 7.2–7.6 (m, 5H, Ph).

2-Amino-4-(*N*-octadecylanilino)-6-(3,5-diaminophenyl)-1,3,5-triazine (A18T) was prepared by the reduction of N18T (13.61 g, 0.022 mol) using 13 g of FeSO₄·7H₂O and 45 g of powder Fe in 250 ml of ethanol and 75 ml of water at reflux temperature for 3 h with stirring, and then recrystallized from ethanol. Yield 10.1 g (82%). mp 76°C, 96.5°C. *Anal.* Found: C, 72.82%, H, 9.45%, N, 18.01%. Calcd for C₃₃H₅₁N₇: C, 72.66%, H, 9.35%, N, 17.98%. IR: 3050–3450, 2850–2900, 1620, 1400, 810 cm⁻¹. ¹H NMR (DMSO-*d*₆) δ ppm: 0.83 (t, 3H, CH₃), 1.2 (m, 32H, (CH₂)₁₆), 3.45 (t, 2H, NCH₂), 4.0 (bs, 4H, 2NH₂), 6.05 (t, 1H_p, Ar), 6.63 (s, 2H, NH₂), 6.8 (d, 2H_o, Ar), 7.2–7.5 (m, 5H, Ph).

Polymerization

Polyamide. Terephthaloyl chloride (TC) (1.01 g, 0.05 mol) was added to a stirred solution of AHT (1.47 g, 0.05 mol) in 10 ml of hexamethylphosphoramide (HMPA)–*N*-methyl-2-pyrrolidone (NMP) (2:1 volume) at 0°C for 30 min and later at room temperature overnight under nitrogen atmosphere. The mixture was then poured into methanol. The isolated polyamide P(AHT-TC) was washed with hot ethanol and dried *in vacuo*. The yield was 2.01 g (95%). Other polyamides were prepared in a similar manner.

Polyamic Acid and Polyimide. Pyromellitic dianhydride (PA) (0.442 g, 2.03 mmol) was added to a stirred solution of AHT (0.595 g, 2.03 mmol) in DMAc (12 ml) at room temperature. After 24 h, the solution was poured into 300 ml of methanol. The resulting polyamic acid P(AHT-PA) was washed with methanol and dried. The yield was 1.03 g (100%).

Polyimide P(AHT-PI) was then prepared by heating the P(AHT-PA) at 200°C for 6 h *in vacuo*. Other polyimides were prepared in a similar manner.

RESULTS AND DISCUSSION

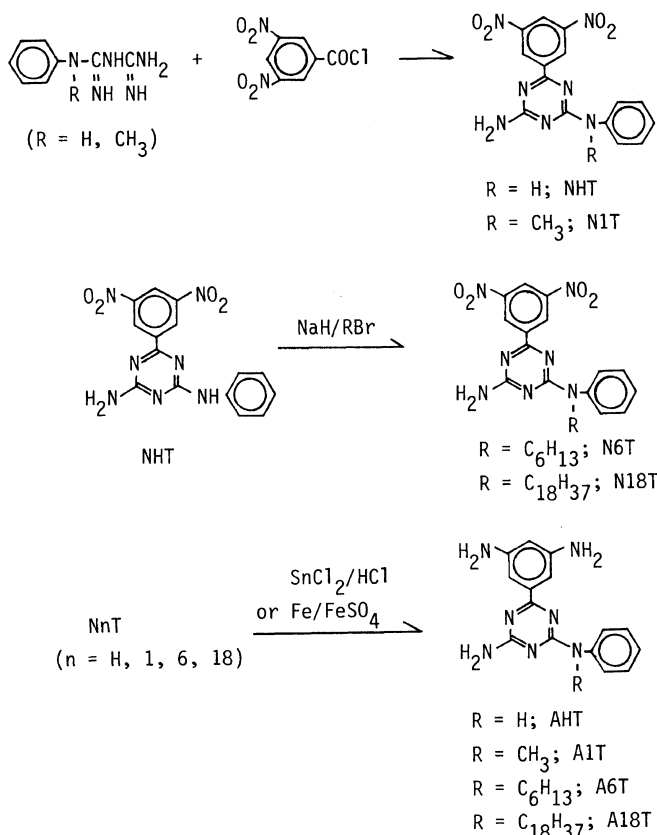
Synthesis of Diamines

2-Amino-4-anilino-6-(3,5-diaminophenyl)-1,3,5-triazine (AHT) and 2-amino-4-[*N*-methyl (A1T), hexyl (A6T) or octadecyl (A18T) anilino]-6-(3,5-diaminophenyl)-1,3,5-triazine were prepared according to Scheme 1. The structures of these diamines were confirmed by IR spectra, ¹H NMR spectra and elementary analysis. These data are presented in the Experimental section.

Preparation of Polymers

Scheme 2 shows the structures of the polymers. Polyamides were prepared by the polycondensation of diamines with terephthaloyl (TC) or isophthaloyl chloride (IC). The results of polyamides are listed in Table I. The structures of these polyamides were identified by elementary analysis and IR spectra. The results of the analysis agreed with the calculated values. IR spectra of polyamides showed the NH stretching band at 3300–3400 cm⁻¹, carbonyl stretching band at 1650 cm⁻¹, in addition to usual absorption bands of amino-1,3,5-triazine which appeared at 1500–1600, 1390, 815 cm⁻¹. Some polyamides also showed additional bands near 2900–2800 cm⁻¹ corresponding to the methylene groups.

Polyimides were prepared by a two-step

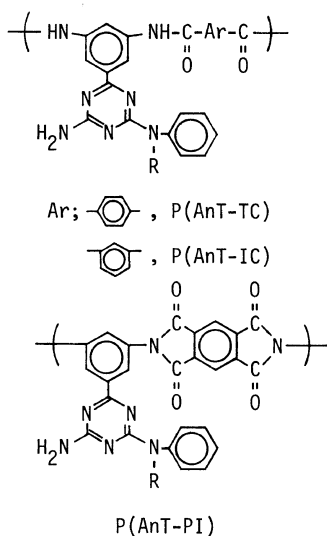


Scheme 1.

procedure. In the first step, polyamic acids P(AnT-PA) were synthesized by the ring-opening polyaddition of AnT with PA. In the second step, polyimides were prepared by the thermal cyclodehydration of the corresponding polyamic acids at 200°C for 6 h *in vacuo*. These results are listed in Table II and Table III. IR spectra of polyimides showed two absorption bands of imide ring at 1720 and 1775 cm⁻¹.

Thermal Properties

Glass transition temperatures (T_g) of poly-



Scheme 2.

amides except P(A6T-TC) and P(A18T-IC) were observed in DSC measurements (Table I). T_g s of polyamides decreased with increasing number of methylene groups of alkyl side chains. Polyimides did not show any glass transition temperature up to their decomposition temperatures.

Decomposition temperatures (T_d) of polymers were determined by TGA measurement. The TG curves for polyimides are shown in Fig. 1. The results are summarized in Tables I and III. T_d s of polyamides slightly decreased

Table I. Preparation of polyamides

Polyamides	Yield /%	η_{sp}/c^a dl g ⁻¹	Thermal properties	
			$T_g^b/^\circ\text{C}$	$T_d^c/^\circ\text{C}$
P(AHT-TC)	94	0.25	290	441
P(AHT-IC)	95	0.16	277	426
P(A1T-TC)	96	0.34	292	430
P(A1T-IC)	99	0.17	264	452
P(A6T-TC)	88	0.13	—	413
P(A6T-IC)	98	0.12	248	442
P(A18T-TC)	87	0.50	189	426
P(A18-IC)	86	0.23	—	436

^a $c=0.2\text{ g dl}^{-1}$ at 30°C in H₂SO₄ for P(AHT-TC)—P(A6T-IC) and in HMPA for P(A18T-IC) and P(A18AT-IC).

^b Glass transition temperature was measured by DSC.

^c Decomposition temperature was determined by TGA at a heating rate of 10°C min⁻¹.

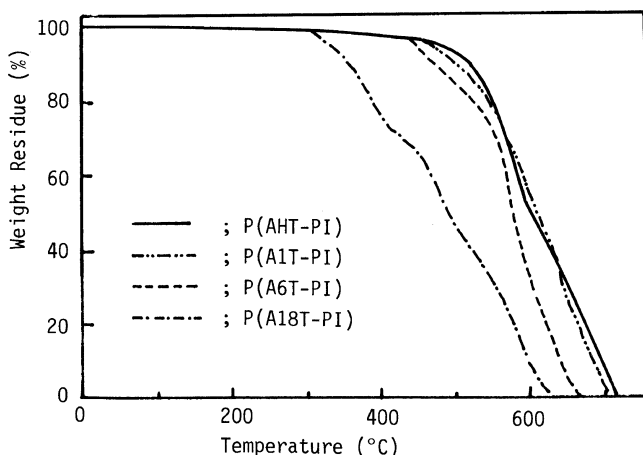


Figure 1. TG curves of polyimides as a heating rate of 10°C min⁻¹ in air.

with increasing number of methylene groups in their side chains. T_g s of polyimides were also determined (Table III). This suggests that the polyimides except P(A18AT-PI) have higher T_g s than the polyamides.

The side chain crystallization of the polyamides and polyimide with octadecyl side chain were investigated by low temperature DSC measurement. The polymer sample was precooled at -120°C , and heating and cooling experiments were then repeated at temperature range of -120°C to 120°C at a heating or cooling rate of $10^\circ\text{C min}^{-1}$. The polyamide P(A18T-TC) showed in the first heating run a broad endothermic peak at -51°C arising from the melting of side chain crystallites and its heat of fusion (ΔH_m) was small (0.15 cal g^{-1} , $0.10 \text{ kcal mol}^{-1}$). In the second cooling run a

broad and small exothermic peak was observed at -30°C arising from crystallization of alkyl side chain, and its heat of crystallization was 0.11 cal g^{-1} ($0.07 \text{ kcal mol}^{-1}$). In the second heating, an endothermic peak was also observed at -53°C and its heat of fusion was 0.12 cal g^{-1} ($0.08 \text{ kcal mol}^{-1}$). The values of polyamides having two long alkyl side chains in repeating unit were 1.18 – $1.80 \text{ kcal mol}^{-1}$.¹⁰ These results show the side chain crystallization of the aromatic polymers having one long alkyl side chain is very small compared with that of a polymer having two long alkyl side chains in the repeating unit.

Solubilities of Polymers

The solubilities of polyamides and polyimides are listed in Table IV. Polyamides

Table II. Preparation of polyamic acid P(AnT-PA)

Polyamic acids	Yield %	η_{sp}/c^a dl g ⁻¹	Water loss/% ^b	
			Found	Calcd
P(AHT-PA)	100	0.15	6.79	7.04
P(A1T-PA)	93	0.12	6.47	6.86
P(A6T-PA)	92	0.12	5.98	6.05
P(A18T-PA)	89	0.47	2.85	4.72

^a $c=0.2 \text{ g dl}^{-1}$ at 30°C in DMF for P(AHT-PA)—P(A6T-PA) and in HMPA for P(A18T-PA).

^b Water loss % by cyclization determined from TGA curves of polyamic acids at 180 – 240°C at a heating rate of $10^\circ\text{C min}^{-1}$.

Table III. Preparation of polyimides P(AnT-PI)

Polyimides	η_{sp}/c^a dl g ⁻¹	T_d^b °C
P(A1T-PI)	0.17	496
P(A6T-PI)	0.17	450
P(A18T-PI)	0.24	348

^a $c=0.2 \text{ g dl}^{-1}$ at 30°C in DMF.

^b Decomposition temperature were determined from TGA curves of polyimides at a heating rate of $10^\circ\text{C min}^{-1}$.

Table IV. Solubilities of polymers

Polymers	DMSO	DMF	NMR	<i>m</i> -Cresol	Pyridine	H ₂ SO ₄	HCOOH
Polyamides							
P(AHT-TC)	+	+	–	–	±	+	+
P(A1T-TC)	+	+	±	–	±	+	+
P(A6T-TC)	+	+	+	+	±	+	+
P(A18T-TC)	±	+	+	+	+	±	±
Polyimides							
P(AHT-PI)	+	+	+	–	±	+	+
P(A1T-PI)	+	+	+	–	±	+	+
P(A6T-PI)	±	+	+	–	±	+	+
P(A18T-PI)	–	+	+	–	±	±	–

+, soluble at room temperature; ±, swelling; –, insoluble.

having long alkyl chains are soluble in NMP, *m*-cresol and pyridine but insoluble in DMSO, sulfuric acid, and formic acid. All polyimide are soluble in DMF and NMP. Polyimide having long alkyl chains is soluble in pyridine but insoluble in DMSO, sulfuric acid and formic acid.

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