

Synthesis of New Comb-Like Polymers from 2-Amino-4-(*m*-acylaminoanilino)-6-isopropenyl-1,3,5-triazines

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ABSTRACT: A series of new isopropenyl-1,3,5-triazines, that is, 2-amino-4-(*m*-acylaminoanilino)-6-isopropenyl-1,3,5-triazine (AnIT, where “*n*” means the number of carbon atoms in the acyl group) was synthesized from the reaction of 2-amino-4-(*m*-aminoanilino)-6-isopropenyl-1,3,5-triazine with various acyl chlorides, including acetyl to octadecanoyl. These monomers were polymerized and copolymerized with styrene or methyl methacrylate in dimethyl sulfoxide using AIBN as an initiator, and copolymerization parameters (r_1 , r_2 , Q , and e values) of these monomers (M_2) were determined. Glass transition temperatures of the homopolymers of A6IT through A18IT were around 182°C. The long acyl side-chains of poly(A16IT) and poly(A18IT) could crystallize and their melting temperatures were -21°C and 9°C , respectively. The crystallinity of the side-chains decreased with increasing content of styrene or methyl methacrylate in the copolymers.

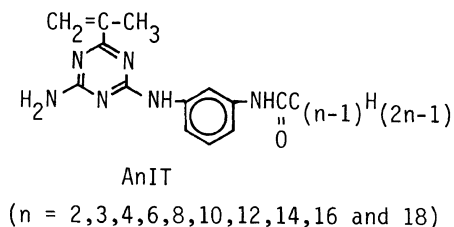
KEY WORDS Comb-Like Polymer / Isopropenyl-1,3,5-triazine / Long Alkyl Group / Side-Chain Crystallization / Copolymerization /

Polymers having long alkyl groups in their side chains can undergo side-chain crystallization.¹ These so called comb-like polymers have attracted much attention due to specific properties such as peculiar mechanical properties,¹ ability of liquid crystal formation,²⁻⁴ and formation of Langmuir-Blodgett film.⁵ The conventional comb-like polymers⁶ were prepared by the polymerization of vinyl monomers. These polymers contain at least four carbon atoms in the side chains and have flexible backbones.¹ In general, the glass transition temperatures (T_g) of these comb-like polymers are low and the melting points of their side chain crystallites are higher than their T_g s.^{7,8} Therefore, one of the major problems for the use of comb-like polymers is that they become rubbery after melting of their side chain crystallites. We reported that the polymers containing triazine rings have high T_g s.⁹ Comb-like polymers containing triazine rings

have attracted interest because they have higher T_g than the melting temperatures of side-chain crystallites.

This paper describes the synthesis and properties of new comb-like polymers obtained from 2-amino-4-(*m*-acylaminoanilino)-6-isopropenyl-1,3,5-triazine (AnIT, where “*n*” means the number of carbon atoms in acyl groups).

The structures and abbreviations of isopropenyl-1,3,5-triazines used in this study are shown in Scheme 1.



Scheme 1.

EXPERIMENTAL

Materials and Monomers

The starting material, 2-amino-4-(*m*-aminoanilino)-6-isopropenyl-1,3,5-triazine (AHIT) was prepared by the literature method.¹⁰ mp 217°C (lit.¹⁰ 214.5°C). All monomers were prepared from AHIT by acylation with acid chloride in the presence of triethylamine as a hydrochloride acceptor. A typical preparation is as follows.

Stearoyl chloride (37.5 g, 0.12 mol) was added dropwise to a stirred solution of AHIT (30 g, 0.12 mol) and triethylamine (12.5 g, 0.12 mol) in 300 ml of dimethylacetamide at 0–5°C. The reaction mixture was filtered after 3 h of stirring, and the filtrate was poured into water. The precipitate was separated and washed thoroughly with hot water. Recrystallization from methanol–acetone mixture gave 56.8 g (yield 89.3%) of 2-amino-4-[*m*-(octadecanoylamino)anilino]-6-isopropenyl-1,3,5-triazine (A18IT). mp 129°C. ¹H NMR (DMSO-*d*₆) δ (ppm): 0.88 (3H, t, CH₃), 1.27 (30H, m, (CH₂)₁₅), 2.09 (3H, s, CH₃), 2.32 (2H, t, CH₂), 5.50 (1H, s, =CH), 6.38 (1H, s, =CH), 6.89 (2H, s, NH₂), 7.2–8.0 (4H, m, Ar), 9.33 (1H, s, NH), and 9.73 (1H, s, NH).

Other monomers were prepared in a similar manner (Table I).

Polymerization

A DMSO solution of the prescribed amount of AnIT with AIBN as an initiator, and in the case of copolymerization a DMSO solution of St or MMA (M₁) with AIBN were placed in a polymerization tube. The monomers and AIBN concentrations were 0.3–0.4 mol l⁻¹ and around 1.4 mmol l⁻¹, respectively. This tube was degassed and the reaction was allowed to proceed for a prescribed time period at 60°C. The polymers were precipitated in excess methanol, filtered, dried *in vacuo*, and weighed. The conversion of the copolymers was kept below 15%. The compositions of the copoly-

mers were calculated by their analysis values of carbon (C%) and nitrogen (N%).

Differential Scanning Calorimetric Studies

Melting temperatures of monomers and *T*_gs of polymers were determined by differential scanning calorimetry (DSC) on a Rigaku-Denki DSC-8230 at a heating rate of 20°C min⁻¹. DSC at low temperature region was measured from –100°C to 110°C on a Rigaku-Denki Thermoflex with a low temperature unit (Rigaku-Denki DSC 8131BL) at the heating and cooling rates 10°C min⁻¹.

RESULTS AND DISCUSSION

Preparation of Monomers

A series of 2-amino-4-(*m*-acylaminoanilino)-6-isopropenyl-1,3,5-triazines (AnIT) was prepared in good yield by the acylation reaction of 2-amino-4-(*m*-aminoanilino)-6-isopropenyl-1,3,5-triazine (AHIT) with various acyl chlorides. The results are summarized in Table I. The elementary analysis agreed well with the calculated values. NMR data were analyzed according to the structural formula. IR spectra of monomers showed in all cases absorption at 1700 cm⁻¹ corresponding to the amide structure, absorption at 2800–2900 cm⁻¹ corresponding to the methylene group, absorption at 1550, 1410, and 820 cm⁻¹ corresponding to the aminotriazine ring, and absorption 920 cm⁻¹ corresponding to the isopropenyl group.

A4IT showed dimorphism characteristics like those reported previously for 2-amino-4-(*p*-anisidino,¹¹ *p*-chloroanilino,¹² *p*-actamidoanilino,¹³ or *p*-hydroxyanilino¹⁴)-6-isopropenyl-1,3,5-triazine as a result of the difference in crystallization conditions. A4IT recrystallized from methanol was named A4IT- α , and A4IT precipitated in water from methanol solution was named A4IT- β . Figure 1 shows the DSC thermogram. A4IT- α showed only one endothermic peak at 187°C, while A4IT- β showed two endothermic peaks at 137°C and

Table I. Preparation of monomers

Monomer	Yield	mp	Elemental analysis (Calcd)		
			C/%	H/%	N/%
<i>AnIT</i>	%	°C			
A2IT	51.5	184	59.06 (59.14)	6.03 5.67	29.15 29.56; C ₁₄ H ₁₆ N ₆ O
A3IT	85.7	166	60.08 (60.39)	6.12 6.08	27.75 28.17; C ₁₅ H ₁₈ N ₆ O
A4IT	61.4	187	61.25 (61.52)	6.49 6.45	26.73 26.90; C ₁₆ H ₂₀ N ₆ O
A6IT	70.3	114	63.20 (63.51)	7.21 7.11	24.39 24.69; C ₁₈ H ₂₄ N ₆ O
A8IT	84.4	113	64.77 (65.19)	7.83 7.66	22.46 22.81; C ₂₀ H ₂₈ N ₆ O
A10IT	91.3	121	66.84 (66.64)	8.50 8.13	21.27 21.19; C ₂₂ H ₃₂ N ₆ O
A12IT	84.2	121	67.49 (67.89)	9.00 8.55	19.52 19.79; C ₂₄ H ₃₆ N ₆ O
A14IT	87.9	104	68.75 (68.99)	9.27 8.91	18.23 18.57; C ₂₆ H ₄₀ N ₆ O
A16IT	84.0	130	69.70 (69.96)	9.41 9.23	17.11 17.48; C ₂₈ H ₄₄ N ₆ O
A18IT	89.3	129	70.54 (70.83)	10.50 9.51	16.13 16.52; C ₃₀ H ₄₈ N ₆ O

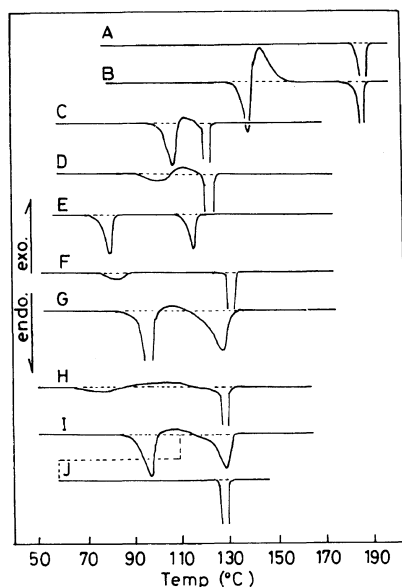


Figure 1. DSC curves for some monomers at a heating rate of 20°C min⁻¹. A, A4IT- α ; B, A4IT- β ; C, A10IT, D, A12IT; E, A14IT; F, A16IT recrystallized from methanol; G, A16IT recrystallized from methanol-water; H, A18IT recrystallized from methanol; I, A18IT recrystallized from methanol-water; J, A18IT annealed at 110°C.

186°C, and one exothermic peak. These A4IT- α and β are different in IR spectra and X-ray diagram in the solid state, but identical in NMR spectra and elementary analysis. A2IT, A3IT and A6IT showed only one endothermic peak, while the other monomers showed two endothermic peaks and one exothermic peak between these endothermic peaks (Figure 1). The samples of these monomers annealed at around 100°C showed only one endotherm. The vinyl compounds having long alkyl group are well-known to show polymorphism.¹⁵ In conclusion, the present results suggest that these *AnIT*s also have dimorphic forms.

Homopolymerization

The homopolymerizations of *AnIT*s were carried out using DMSO as a solvent and azobisisobutyronitrile (AIBN) as an initiator at 60°C. The results are shown in Table II. Each polymer was soluble in THF, DMF, DMA, pyridine, and *m*-cresol. Poly(A10IT) through poly(A18IT) were insoluble in DMSO

Table II. Homopolymerization of *AnIT*

Monomer	Conditions			Conv.	Homopolymers		
	[M] ₀ ^a	[AIBN]	Time		η_{sp}/c^b		T_g^c
	mol l ⁻¹	mmol l ⁻¹	min		in DMF	in THF	°C
A2IT	0.30	1.49	360	12.5	0.38	—	218
A3IT	0.30	1.41	360	42.9	0.38	—	210
A4IT	0.29	1.25	420	38.1	0.33	—	205
A6IT	0.30	1.58	360	35.4	0.44	—	183
A8IT	0.30	2.17	860	13.5	0.20	—	183
A10IT	0.30	1.67	640	2.4	0.20	—	183
A12IT	0.23	1.40	640	23.5	0.16	—	188
A14IT	0.28	1.53	1220	38.8	0.17	—	178
A16IT	0.30	1.50	1440	51.1	0.11	0.32	175
A18IT	0.30	1.54	1320	33.3	0.08	0.29	181

^a Polymerized at 60°C in DMSO.^b Measured at $c=0.2$ g dl⁻¹ at 30°C.^c Measured by DSC at a heating rate of 20°C min⁻¹.

after drying. The polymers up to poly(A8IT) were insoluble in cyclohexanone, but poly(A10IT) through poly(A18IT) were soluble in cyclohexanone.

Copolymerization

All *AnITs* (M_2) could be copolymerized with styrene (St) or methyl methacrylate (MMA), and white solid copolymers were obtained. The compositions of copolymers were calculated from elementary analysis and the monomer reactivity ratios r_1 and r_2 were determined by the Fineman–Ross method. Figure 2 shows the monomer–copolymer composition curves for the copolymerization of A18IT (M_2) with St and MMA. The plots fit the curves calculated from the monomer reactivity ratios. The Q and e values of *AnITs* were determined in terms of Alfrey–Price's equation assuming $Q=1.0$ and $e=-0.8$ for St, and $Q=0.74$ and $e=0.4$ for MMA. The results are listed in Table III. Significant effect of alkyl chain length on copolymerization parameters (r_1 , r_2 , Q , and e values) of *AnITs* could not be observed. Similar results for alkyl methacrylates have been reported by Otsu *et al.*¹⁶ and Ito *et al.*¹⁷ Because the alkyl group exists at a fairly distant

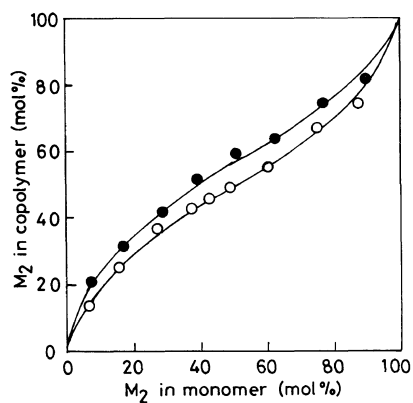


Figure 2. Monomer–copolymer composition curves for the copolymerization of A18IT (M_2) with styrene (●) and methyl methacrylate (○).

position from the active site in isopropenyl-triazines, the reactivity ratios would be independent of the alkyl chain length. The e values depend on comonomers, that is, positive for the copolymerization with St and negative for MMA. This is general behavior for the copolymerization of isopropenyl-1,3,5-triazines as described previously.⁹ The average values of these parameters are $r_1=0.40$, $r_2=0.58$, $Q=0.97$ and $e=0.42$ for St, and

Table III. Copolymerization parameters of AnIT.^a

M ₂	M ₁	r ₁	r ₂	Q ₂	e ₂	1/r ₁
A2IT	St	0.39	0.55	0.95	0.44	2.56
	MMA	0.47	0.45	0.96	-0.85	2.13
A3IT	St	0.46	0.69	0.92	0.27	2.17
	MMA	0.54	0.37	0.82	-0.87	1.85
A4IT	St	0.42	0.58	0.92	0.40	2.38
	MMA	0.55	0.26	0.77	-0.99	1.82
A6IT	St	0.44	0.60	0.90	0.35	2.27
	MMA	0.56	0.22	0.74	-1.05	1.79
A8IT	St	0.48	0.63	0.87	0.30	2.08
	MMA	0.52	0.25	0.80	-1.03	1.92
A10IT	St	0.43	0.63	0.93	0.34	2.33
	MMA	0.54	0.24	0.77	-1.08	1.85
A12IT	St	0.39	0.58	0.97	0.42	2.56
	MMA	0.55	0.25	0.71	-0.98	1.82
A14IT	St	0.33	0.53	1.05	0.52	3.03
	MMA	0.58	0.25	0.73	-0.99	1.72
A16IT	St	0.34	0.48	1.00	0.55	2.94
	MMA	0.48	0.38	0.92	-0.90	2.08
A18IT	St	0.28	0.55	1.19	0.57	3.57
	MMA	0.45	0.36	0.96	-0.95	2.22
AAIT ^a	St	0.39	0.78	1.07	0.29	2.56
	MMA	0.45	0.56	1.03	-0.77	2.22

^a 2-Amino-4-anilino-6-isopropenyl-1,3,5-triazine.

$r_1=0.52$, $r_2=0.30$, $Q=0.81$ and $e=-0.97$ for MMA, respectively. These values are also similar to that of 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine (AAIT) without acylamino group.

Glass Transition Temperatures of Polymers

The glass transition temperatures (T_g) were determined by DSC measurement. The T_g s of homopolymers are shown in Table II. The T_g s of poly(A6IT) through poly(A18IT) were similar, being about 180°C.

The effect of the alkyl group on the T_g of the copolymers was investigated. Figure 3 shows the relations between T_g and compositions for the copolymers of A3IT with St and MMA. T_g increases almost linearly with increasing content of isopropenyl triazines in the copolymers and reaches T_g of homopolymer in analogy with previous reports.^{9,18} Other copolymers showed a similar relation. This result would be due to the strong

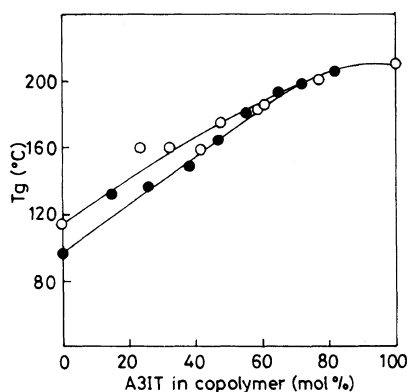


Figure 3. Glass transition temperatures (T_g) for copolymers of A3IT with styrene (●) and methyl methacrylate (○).

intermolecular interaction of the triazine unit such as hydrogen bonding of amino group and amido groups.

Crystallization of Acyl Side-Chains

The crystallization behavior of acyl side

chains for the resulting comb-like polymers was investigated by DSC measurement. The polymer samples were first heated from -100°C to 110°C (the first run), then cooled to -100°C (the second run), and again heated to 110°C (the third run), at a scanning rate of $10^{\circ}\text{C min}^{-1}$ in each case. No peaks were observed in this temperature range for polymers having an acyl side chain up to 14 carbon numbers. DSC curves of poly(A14IT), poly(A16IT) and poly(A18IT) are shown in Figure 4. Endothermic peaks ascribed to the melting of crystallites and exothermic peaks ascribed to the crystallization were observed in the range of about -40°C to $+20^{\circ}\text{C}$. Copolymers obtained from A16IT and A18IT exhibited the same tendency.

Poly(A18IT) showed two endothermic peaks on the first run. A endothermic peak at 40°C is probably due to the melting of crystallites formed on standing at room temperature after polymerization, whereas a endothermic peak

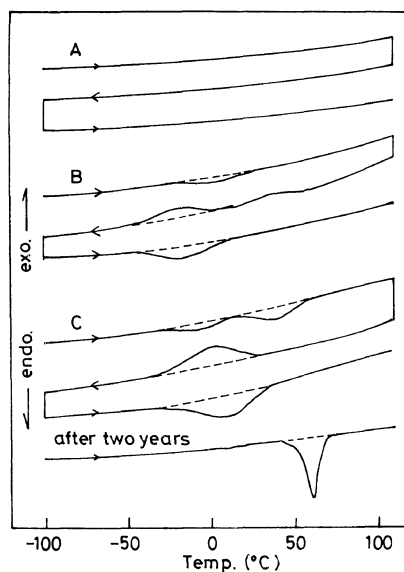


Figure 4. DSC curves for homopolymers of A14IT (A), A16IT (B), and A18IT (C). Heating and cooling rate of $10^{\circ}\text{C min}^{-1}$ from -100°C to 110°C .

Table IV. Side-chain crystallization of polymers obtained from A16IT and A18IT

Polymers	dM_2	T_m	ΔH_m	ΔS_m	N
$P(M_2\text{-}co\text{-}M_1)$	mol%	$^{\circ}\text{C}$	kcal mol^{-1}	$\text{cal deg}^{-1} \text{mol}^{-1}$	
Poly(A16IT)	100	-21	0.52	2.06	0.7
P(A16IT- <i>co</i> -MMA)	77.7	-28	0.64	2.61	0.9
	64.9	-30	0.43	1.77	0.6
	41.7	-38	0.18	0.77	0.2
P(A16IT- <i>co</i> -St)	83.9	-26	0.64	2.59	0.9
	72.6	-29	0.33	1.35	0.4
	41.7	-38	0.09	0.38	0.1
Poly(A18IT)	100	9	1.57	5.58	2.1
P(A18IT- <i>co</i> -MMA)	88.0	2	2.15	7.82	2.9
	71.7	-1	1.66	6.10	2.3
	55.3	-29	1.05	4.30	1.4
	48.3	-25	0.87	3.51	1.2
	46.0	-25	0.54	2.18	0.7
	41.4	-28	0.52	2.12	0.7
	35.6	-29	0.24	0.98	0.3
P(A18IT- <i>co</i> -St)	89.8	0	2.19	8.02	3.0
	74.0	0	1.32	4.84	1.8
	69.9	-5	1.41	5.26	1.9
	63.0	-7	0.96	3.61	1.3
	61.3	-14	1.18	4.56	1.6
	40.7	-27	0.39	1.59	0.5
	30.4	-31	0.21	0.87	0.3

at -4°C is attributed to the melting of the crystallites formed during cooling from room temperature to -100°C before the DSC measurement. In the case of the reported comb-like polymers the DSC curves on the first and third runs are similar.^{19,20} The difference for the DSC curves of poly(A18IT) on the first and third runs in this study is believed to be due that the glassy state of the main chain prevents side-chain crystallization. The poly(A18IT) standing for two years showed a clear endothermic peak at 60°C . Because of the same history of thermal treatment in DSC measurement, the third run was used for the evaluation and comparison of thermal properties of polymers. The melting temperatures (T_m) from the peak tops, and heat of fusion (ΔH_m), estimated from the DSC peak areas, were determined based on the third run. The entropy of fusion (ΔS_m) was also calculated from ΔH_m and T_m . The results are summarized in Table IV.

Figure 5 also shows the relationship of the compositions and thermal properties of copolymers of A16IT and A18IT, respectively. The T_g s of these copolymers are higher than T_m s. Thermal parameters of poly(A16IT) are smaller than those of poly(A18IT). T_m of copolymers decreased with decreasing the A16IT or A18IT (M_2) content and was independent of comonomers. ΔH_m and ΔS_m show maximum values at 90 mol% M_2 content, possibly due to the role of comonomer as a spacer.

The numbers of crystallizing CH_2 groups (N) in the side chains were calculated from ΔH_m on the basis of the heat of fusion per CH_2 of n -alkanes in the hexagonal packing ($735 \text{ cal mol}^{-1} \text{ CH}_2^{-1}$).²¹ The N numbers are shown in Table IV. N of poly(hexadecyl and octadecyl methacrylate) was 4.0 and 5.6, respectively.⁶ The resulting polymers in this work give smaller N than that of the conventional comb-like polymers. T_g s of the conventional comb-like polymers were lower than the melting points of the side-chain crystallites. For example, T_g

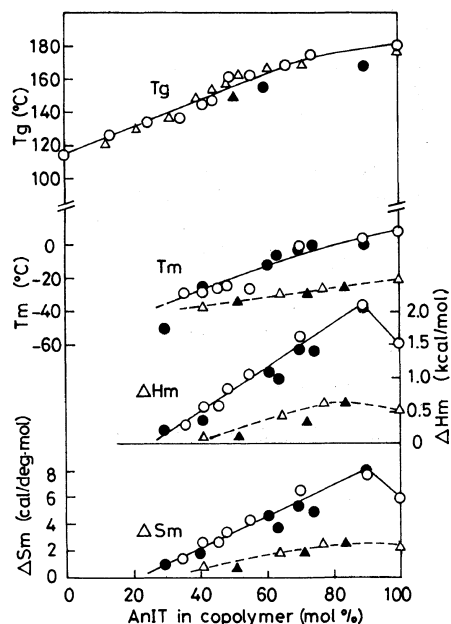


Figure 5. Relationship between glass transition temperatures (T_g), melting temperature (T_m), heat of fusion (ΔH_m), and entropy of fusion (ΔS_m) of alkyl side chains of copolymers and triazine content in copolymer of A16IT with styrene (\blacktriangle) and methyl methacrylate (\triangle) and A18IT with styrene (\bullet) and methyl methacrylate (\circ).

of poly(octadecyl methacrylate) was estimated in the vicinity of -100°C .^{7,8} Therefore, the main-chain of the conventional comb-like polymers would be flexible enough to allow side-chain packing. However, T_g s of the present polymers are higher than melting points of the side-chain crystallites, and the side-chains crystallized below T_g of the main-chain. Consequently, the less flexible main-chain of the present polymers would prevent side-chains crystallization and give smaller N numbers.

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