

Comb-Like Polymers from Acylated 2-Amino-4-anilino-6-isopropenyl-1,3,5-triazines

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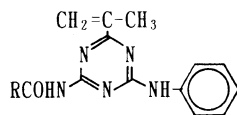
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ABSTRACT: Acylated isopropenyl-1,3,5-triazines, that is, 2-acylamino-4-anilino-6-isopropenyl-1,3,5-triazines (2*Cn*IT, where “*n*” means the number of carbon atoms in acyl group up to 18) and 2-amino-4-(*N*-acylanilino)-6-isopropenyl-1,3,5-triazines (4*Cn*IT) were polymerized and copolymerized with styrene or methyl methacrylate in dimethylacetamide using AIBN as an initiator. The copolymerization parameters (r_1 , r_2 , Q , and e values) of these monomers (M_2) were determined. The glass transition temperature was above 200°C for poly(2*Cn*IT) and 120–134°C for poly(4*Cn*IT). The long acyl side-chains of homo- and copolymers of 4C16IT and 4C18IT crystallized and melting temperatures of side-chain crystallites were –29°C and –13°C for poly(4C16IT) and poly(4C18IT), respectively, while the long acyl side-chains of poly(2*Cn*IT) did not crystallize.

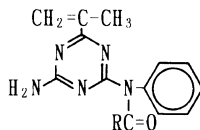
KEY WORDS Comb-Like Polymer / Isopropenyl-1,3,5-triazine / Long Alkyl Group / Side-Chain Crystallization / Copolymerization /

Polymers having long alkyl groups in their side chains called comb-like polymers can undergo side-chain crystallization.¹ The comb-like polymers containing triazine rings in the repeating unit have attracted much attention since they show higher glass transition temperatures (T_g) than the melting temperatures of side-chain crystallites.^{2–9}

In the preceding paper,¹⁰ we reported the



2*Cn*IT



4*Cn*IT

R = C₇H₁₅ ($n=8$), C₉H₁₉ ($n=10$), C₁₁H₂₃ ($n=12$),
C₁₃H₂₇ ($n=14$), C₁₅H₃₁ ($n=16$), C₁₇H₃₅ ($n=18$),
and Ph ($n=Ph$)

Scheme 1.

preparation and thermodynamics of polymerization of 2-acylamino-4-anilino-6-isopropenyl-1,3,5-triazines (2*Cn*IT, where “*n*” means the number of carbon atoms in acyl group) including octanoyl to octadecanoyl group and 2-amino-4-(*N*-acylanilino)-6-isopropenyl-1,3,5-triazine (4*Cn*IT) including tetradecanoyl to octadecanoyl group.

This paper describes the solution polymerization and copolymerization of 2*Cn*IT and 4*Cn*IT including the benzoyl group with styrene (St) and methyl methacrylate (MMA) for the synthesis of new comb-like polymers showing high T_g .

The structure and abbreviation of isopropenyl-1,3,5-triazines used in this work are shown in Scheme 1.

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EXPERIMENTAL

Polymerization

A dimethylacetamide (DMA) solution of the prescribed amount of monomer with azobisisobutyronitrile (AIBN) as an initiator, and in the case of copolymerization a DMA solution of St or MMA (M_1) with AIBN were placed in a polymerization tube. The monomers and AIBN concentrations were 0.13–0.4 mol l⁻¹ and around 1.4 mmol l⁻¹, respectively. This tube was degassed and polymerization was allowed to proceed for a prescribed time period at 60°C. The polymers were precipitated in tetrahydrofuran(THF)–methanol (1:10, v/v) mixture for 2CnIT or in excess methanol for 4CnIT, then filtered, dried *in vacuo*, and weighed. The conversion of the copolymer was kept below 15%. The composition of the copolymers was calculated by their analysis values of carbon (C%) and nitrogen (N%). Molecular weights of polymers were determined by gel permeation chromatography (GPC) on a TOSOH HLC-803D with G2000H, G3000H, and GMH TSK gel-columns and a differential refractometric

detector in THF. The columns were calibrated with a set of monodisperse polystyrene standards.

Differential Scanning Calorimetry

Glass transition temperatures (T_g) 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 100°C on a Rigaku-Denki Thermoflex with a low temperature unit (Rigaku-Denki DSC 8131BL) at the heating and cooling rates of 10°C min⁻¹.

RESULTS AND DISCUSSION

Homopolymerization

The homopolymerization of monomers was carried out using DMA as a solvent and AIBN as an initiator at 60°C. The results are shown in Table I. 2CnIT was fed at lower monomer concentration because of poor solubilities for organic solvents. Each monomer polymerized to give a white powder, even at the low monomer concentration of 0.10 mol l⁻¹ for 2C16IT

Table I. Homopolymerization of 2CnIT and 4CnIT

Monomer	Conditions			Conv. %	Homopolymers			T_g^d °C
	[M] ₀ ^a	[AIBN]	Time		η_{sp}/c^b	$M_w/10^4$	M_w/M_n^c	
	mol l ⁻¹	mmol l ⁻¹	min		dl g ⁻¹			
2C10IT	0.20	1.38	300	48.5	—	—	—	222
2C12IT	0.20	1.40	480	67.1	—	—	—	215
2C14IT	0.12	1.48	480	30.1	—	—	—	209
2C16IT	0.10	1.44	480	18.5	0.11	2.73	1.88	203
2C18IT	0.10	1.43	560	11.7	—	—	—	202
2CPhIT	0.16	1.40	490	15.2	0.24	4.57	1.41	190
4C14IT	0.25	1.41	482	20.2	0.10	3.89	1.35	121
4C16IT	0.30	1.44	360	14.8	0.09	1.83	1.40	126
4C18IT	0.30	1.52	535	21.2	0.11	3.34	1.65	134
4CPhIT	0.40	1.40	365	3.4	0.08	—	—	195

^a Polymerized at 60°C in DMA.

^b Measured at $c=0.2$ g dl⁻¹ at 30°C in THF.

^c Measured by GPC at 40°C in THF.

^d Measured by DSC at a heating rate of 10°C min⁻¹.

and 2C18IT. The equilibrium monomer concentration of 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine (AAIT) was 0.12 mol l^{-1} at 60°C ,¹¹ while that of 2-acetylamino-4-(*N*-methylanilino)-6-isopropenyl-1,3,5-triazine was 0.035 mol l^{-1} at 60°C .¹² The equilibrium monomer concentration of 2C*n*IT became lower than that of AAIT by the introduction of electron withdrawing acyl group, as previously reported.^{12,13}

Poly(2C16IT), poly(2CPhIT), and poly(4C*n*IT) were soluble in THF, and their reduced viscosities and molecular weights were not so high.

Copolymerization

All 2C*n*IT and 4C*n*IT (M_2) copolymerized with St and MMA to give white solid copolymers. The monomer reactivity ratios r_1 and r_2 were determined by the Fineman–Ross method. Figure 1 shows the monomer–copolymer composition curves for the copolymerization

of 2C12IT (M_2) with St and MMA. The plots fit the curves calculated from the monomer reactivity ratios. The Q and e values of 2C*n*IT and 4C*n*IT were determined by 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

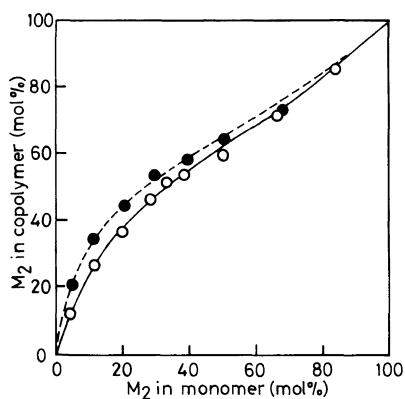


Figure 1. Monomer–copolymer composition curves for the copolymerization of 2C12IT (M_2) with styrene (●) and methyl methacrylate (○).

Table II. Copolymerization parameters of 2C*n*IT and 4C*n*IT

M_2	M_1	r_1	r_2	Q_2	e_2	$1/r_1$
2C10IT	St	0.11	1.22	2.93	0.62	9.1
	MMA	0.24	1.28	1.99	-0.69	4.2
2C12IT	St	0.15	1.14	2.30	0.53	6.7
	MMA	0.27	1.12	1.77	-0.69	3.7
2C14IT	St	0.13	1.40	2.92	0.51	7.7
	MMA	0.27	1.20	1.79	-0.66	3.7
2C16IT	St	0.14	1.00	2.33	0.60	7.1
	MMA	0.27	1.10	1.77	-0.70	3.7
2C18IT	St	0.16	1.56	2.44	0.38	6.3
	MMA	0.23	1.60	2.16	-0.60	4.3
2CPhIT	St	0.05	0.77	4.74	1.00	20
	MMA	0.45	0.90	1.12	-0.55	2.2
4C14IT	St	0.10	1.00	2.19	0.72	10.0
	MMA	0.31	1.19	1.60	-0.60	3.2
4C16IT	St	0.14	1.06	2.37	0.58	7.1
	MMA	0.37	1.20	1.40	-0.50	2.7
4C18IT	St	0.08	1.11	3.60	0.76	12.5
	MMA	0.22	1.20	2.12	-0.75	4.5
4CPhIT	St	0.18	1.08	2.00	0.48	5.6
	MMA	0.35	1.10	1.43	-0.58	2.9
AAIT ^a	St	0.39	0.78	1.07	0.29	2.6
	MMA	0.45	0.56	1.03	-0.77	2.2

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

results are listed in Table II. Significant effect of alkyl chain length on copolymerization parameters (r_1 , r_2 , Q , and e values) could not be observed. Similar results have been reported for 2-amino-4-(*N*-alkylanilino)⁴ or (*m*-acylaminoanilino)⁵-6-isopropenyl-1,3,5-triazines. Because the alkyl group exists at a fairly distant position from the active site in isopropenyltriazines, the monomer reactivity ratios were independent of the alkyl chain length as in other cases.^{14,15}

r_1 values were smaller and r_2 larger than unity, that is, $k_{11} < k_{12}$ and $k_{22} > k_{21}$ for both of 2*Cn*IT and 4*Cn*IT independent on comonomers. Compared with AAIT, the Q value became large and e value became more positive. These results show that the reactivity of acyl monomers became larger than that of AAIT because the electron density of isopropenyl group became smaller by the introduction of electron withdrawing acyl group. In other words, the degree of resonance between the isopropenyl group and electron withdrawing triazine ring would increase as a result of reduced resonance between the electron donating anilino group and the triazine ring due to introduction of the acyl group.

The e values depend on comonomers, that is, positive for the copolymerization with St and negative for MMA. This is general behavior found for the copolymerization of isopropenyl-1,3,5-triazines as described previously.¹⁶

Glass Transition Temperatures

The glass transition temperature (T_g) was determined by DSC measurement. T_g of the homopolymer is shown in Table I and Figure 2. T_g of poly(2*Cn*IT) up to $n=8$ was almost similar at 235–245°C and then slightly decreased with increasing n number. On the other hand, T_g of poly(4*Cn*IT) was below that of poly(2*Cn*IT) and slightly increased with increasing n number. These results show that the intermolecular interactions such as hydro-

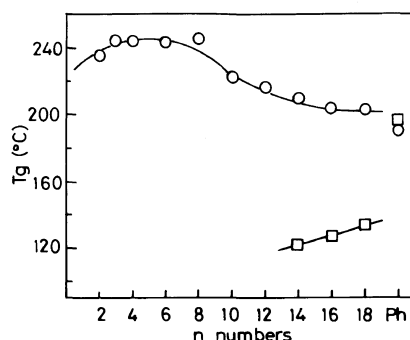


Figure 2. Relationship between glass transition temperature (T_g) of poly(2*Cn*IT) (○) and poly(4*Cn*IT) (□), and the carbon number of acyl side chain (n).

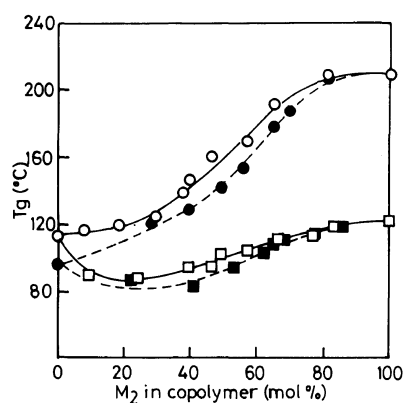


Figure 3. Glass transition temperature (T_g) for copolymers of 2C14IT (M_2) with styrene (●) and methyl methacrylate (○), and 4C14IT (M_2) with styrene (■) and methyl methacrylate (□).

gen bonding between the triazine unit and the amide group of poly(2*Cn*IT) are stronger than those between the triazine unit and amino group of poly(4*Cn*IT).

The effect of the acyl group on the T_g of the copolymers was also investigated. Figure 3 shows the relation between T_g and compositions for the copolymers of 2C14IT and 4C14IT with St and MMA. The curves of T_g with composition show "S" shape, and those for 4C14IT have minima at 20 mol% M_2 composition, because of internal plasticization caused by the introduction of a small amount of long acyl chain in monomer unit. Other

copolymers in this work showed a similar relation.

Crystallization of Acyl Side-Chains

The crystallization behavior of acyl side chains for the resulting comb-like polymers was investigated by DSC measurement. The sample was first quenched from room temperature to -100°C and heated to 100°C (the first run), then cooled to -100°C (the second

run), and again heated to 100°C (the third run), at a scanning rate of $10^{\circ}\text{C min}^{-1}$ in each case. DSC curves of poly(2C18IT), poly(4C16IT), and poly(4C18IT) are shown in Figure 4 as typical examples. No peak was observed in this temperature range for the polymer of a series of 2C*n*IT, and for a series

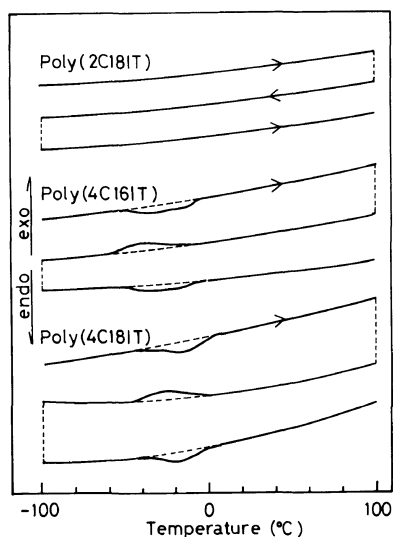


Figure 4. DSC curves for homopolymers of 2C18IT, 4C16IT, and 4C18IT, at heating and cooling rates of $10^{\circ}\text{C min}^{-1}$ from -100°C to 100°C .

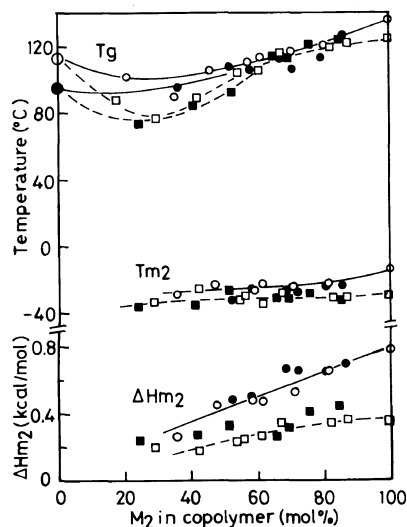


Figure 5. Relationship between the glass transition temperature (T_g), the melting temperature (T_{m2}) and the heat of fusion (ΔH_{m2}) of acyl side chain crystallites of copolymers, and the triazine content in copolymer of 4C16IT with styrene (■) and methyl methacrylate (□), and 4C18IT with styrene (●) and methyl methacrylate (○).

Table III. Side-chain crystallization of polymers obtained from 4C16IT and 4C18IT (M_2)

Polymers	dM_2	T_g	T_{m1}	T_{cr}	T_{m2}	ΔH_{m1}	$-\Delta H_{cr}$	ΔH_{m2}	N^a
$P(M_2-co-M_1)$	mol%	$^{\circ}\text{C}$				kcal mol^{-1}			
Poly(4C16IT)	100	126	-28	-44	-29	0.40	0.41	0.37	0.48
Poly(4C18IT)	100	134	-14	-25	-13	0.90	0.83	0.78	1.06
P(4C16IT-co-MMA)	87.8	121	-36	-45	-30	0.45	0.39	0.36	0.50
	54.4	107	-28	-45	-28	0.28	0.26	0.24	0.33
P(4C16IT-co-St)	85.3	123	-31	-47	-32	0.48	0.61	0.46	0.63
	52.7	92	-35	-41	-26	0.38	0.36	0.35	0.48
P(4C18IT-co-MMA)	80.7	118	-22	-32	-23	0.85	0.66	0.61	0.83
	57.8	109	-24	-35	-29	0.75	0.44	0.47	0.64
P(4C18IT-co-St)	79.8	111	-26	-33	-23	0.64	0.66	0.65	0.88
	58.8	104	-27	-37	-25	0.42	0.47	0.50	0.68

^a Number of crystallizing CH_2 groups in the side-chain.

of 4C*n*IT having an acyl side chain up to 14 carbon numbers. The strong intermolecular interactions described above for poly(2C16IT) and poly(2C18IT) would prevent side-chains crystallization. A small and broad endothermic peak ascribed to the melting of crystallites in the heating process and an exothermic peak ascribed to the crystallization in the cooling process were observed in the range of about -50°C to 0°C for poly(4C16IT) and poly(4C18IT). Copolymers obtained from 4C16IT and 4C18IT exhibited the same tendency.

The melting temperature (T_{m1}) from the peak top, the heat of fusion (ΔH_{m1}) estimated from the DSC peak area based on the first run, the crystallization temperature (T_{cr}) and the heat of crystallization (ΔH_{cr}) based on the second run, and the melting temperature (T_{m2}) and the heat of fusion (ΔH_{m2}) based on the third run, were determined for evaluation and comparison of thermal properties of polymers. The results of some polymers are shown in Table III with their T_g s. Figure 5 shows the relation between the thermal properties (T_g , T_{m2} , and ΔH_{m2}) and compositions of copolymers of 4C16IT and 4C18IT, respectively. T_g s of these copolymers are higher than their T_{ms} . ΔH_{m2} s of homo- and copolymers of 4C16IT are smaller than those for 4C18IT. T_{m2} and ΔH_{m2} of copolymers slightly decreased with decreasing the triazine (M_2) content and were independent of comonomers.

The numbers of crystallizing CH_2 groups (N) in the side chains were calculated from ΔH_{m2} on the basis of the heat of fusion per CH_2 of n -alkanes in the hexagonal packing ($735 \text{ cal mol}^{-1} \text{CH}_2^{-1}$).¹⁷ The N numbers are shown in Table III. The N of poly(hexadecyl and octadecyl methacrylate) was 4.0 and 5.6, respectively.¹⁸ The polymers in this work give very smaller N than that of the conventional comb-like polymers. T_g of poly(octadecyl methacrylate) was estimated to be in the vicinity of -100°C .¹⁹ Therefore, the main-chain of the conventional comb-like polymers would be flexible enough to allow side-chain

Table IV. N number of comb-like polymers showing high T_g

Polymers	T_g	N^a
	$^{\circ}\text{C}$	
Hexadecyl group		
Poly(mC16IT) ^b	163	1.9
Poly(pC16IT) ^c	194	2.1
Poly(A16IT) ^d	175	0.7
Poly(N16) ^e	136	0.8
Poly(4C16IT)	126	0.5
Poly(2C16IT)	203	None
Octadecyl group		
Poly(mC18IT) ^f	163	2.7
Poly(pC18IT) ^g	192	3.8
Poly(A18IT) ^h	181	2.1
Poly(N18) ⁱ	132	2.0
Poly(4C18IT)	134	1.1
Poly(2C18IT)	202	None

^a Number of crystallizing CH_2 groups in the side-chain.

^b 2-Amino-4-(*m*-hexadecyloxyanilino)-6-isopropenyl-1,3,5-triazine.⁸

^c 2-Amino-4-(*p*-hexadecyloxyanilino)-6-isopropenyl-1,3,5-triazine.²

^d 2-Amino-4-{*m*-(hexadecanoylamino)anilino}-6-isopropenyl-1,3,5-triazine.⁵

^e 2-Amino-4-(*N*-hexadecylanilino)-6-isopropenyl-1,3,5-triazine.³

^f 2-Amino-4-(*m*-octadecyloxyanilino)-6-isopropenyl-1,3,5-triazine.⁹

^g 2-Amino-4-(*p*-octadecyloxyanilino)-6-isopropenyl-1,3,5-triazine.²

^h 2-Amino-4-{*m*-(octadecanoylamino)anilino}-6-isopropenyl-1,3,5-triazine.⁵

ⁱ 2-Amino-4-(*N*-octadecylanilino)-6-isopropenyl-1,3,5-triazine.³

packing.

N numbers of comb-like polymers containing triazine ring are summed up in Table IV with their T_g s. In general, T_g s of the comb-like polymers containing triazine ring were higher than the melting point of the side-chain crystallites because the less flexible main-chain of the polymers would prevent side-chain crystallization. Another effect on the side-chain crystallization is the position of entry of the long alkyl (acyl) group. Poly(mC18IT), poly(pC18IT), and poly(A18IT) have long

alkyl chains near by benzene ring, while poly(N18) and present poly(4C18IT) have the chains on the nitrogen atom of the anilino group, and the ordering of side-chains was prevented by both triazine ring and benzene ring. In the case of poly(2C18IT), no crystallization of side-chain occurred because of the strong intermolecular interactions.

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