Synthesis and polymerization of isopropenyl-1,3,5-triazines with a branched alkyl group

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2-Amino-4-(*N*-alkylanilino)-6-isopropenyl-1,3,5-triazines were synthesized by the reaction of 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine with alkyl bromides in the presence of sodium hydride in dimethyl sulphoxide. The alkyl groups of the monomers were isopropyl, isobutyl, sec-butyl, pentyl, isopentyl, 1-methylbutyl and benzyl. Solution homopolymerization of these monomers and their copolymerization with styrene, methyl methacrylate and methyl acrylate was carried out using azobisisobutyronitrile as an initiator. Copolymerization parameters were determined for these monomers. The glass transition temperature of the resulting polymers depended on the length and the shape of the alkyl side-chain. A polymerization exothermic peak was observed in differential scanning calorimetry curves above the melting point for the monomers. The ceiling temperature (T_c) and heat of polymerization (ΔH_p) were determined from the exothermic peaks. The influence of branched alkyl groups on T_c and ΔH_p is discussed.

(Keywords: glass transition; isopropenyltriazines; ceiling temperature)

INTRODUCTION

Monomers containing a branched alkyl group are of interest in the specific polymerization behaviour and properties of the resulting polymers. Ito *et al.*[1] found that tert-butyl isopropenyl ketone does not undergo radical homopolymerization under standard conditions due to its low ceiling temperature (T_c) in contrast to the polymerizability of n-alkyl isopropenyl ketones. Yamada *et al.*[2,3] reported that the introduction of a branched alkyl group such as isopropyl, sec-butyl and tert-butyl groups in the *o*-position of phenyl methacrylate results in a remarkable lowering of the overall rate of polymerization, monomer reactivity and T_c as a result of steric hindrance. In addition, it has been reported that the glass transition temperature (T_g) of poly(alkyl acrylates), poly(alkyl methacrylates), poly(*p*-alkylstyrenes) and poly(*N*-alkylacrylamides) having a branched alkyl group on their side-chain is remarkably higher than those having an n-alkyl side-chain[4].

Recently, we showed the synthesis[5], homopolymerization[5], copolymerization[6] and thermodynamics of polymerization[7] of 2-amino-4-(*N*-n-alkylanilino)-6-isopropenyl-1,3,5-triazines. The polymerization rate and copolymerization parameters were independent of the alkyl chain length, whereas the thermodynamic parameters of polymerization, such as ceiling temperature, heat of polymerization and entropy of polymerization decreased with increasing length of the alkyl group. The T_g of the resulting polymers also decreased with increasing alkyl chain length.

In order to explore the effects of a branched alkyl group on the polymerization behaviour and the properties of the polymer, this paper deals with the synthesis, homopolymerization, copolymerization, thermodynamics of polymerization and T_g of the polymers for isopropenyl-1,3,5-triazines with a branched alkyl group.

EXPERIMENTAL

Materials

2-Amino-4-anilino-6-isopropenyl-1,3,5-triazine (AAIT) was prepared from 1-phenylbiguanide with methacryloyl chloride as described in the previous paper[8]. Dimethyl sulphoxide (DMSO) was distilled over calcium hydride under reduced pressure and an atmosphere of nitrogen. Sodium hydride as a suspension in paraffin and alkyl bromides were commercially available and used without further purification. Commercially available styrene (St), methyl methacrylate (MMA) and methyl acrylate (MA) were purified by the usual procedures.

Monomers

*2-Amino-4-(*N*-isopropylanilino)-6-isopropenyl-1,3,5-triazine (N3i).* AAIT (22.7 g, 0.1 mol) was added to DMSO (300 ml) in the presence of sodium hydride (60% suspension in paraffin) (4.4 g, 0.11 mol) with stirring, and the solution was further stirred at 30°C for 2 h. Then isopropyl bromide (12.3 g, 0.1 mol) was added dropwise at 30°C and stirred for 24 h. The reaction mixture was poured into a large excess of water to precipitate a solid. The solid was filtered, and washed with water. A crude product was recrystallized four times from a mixed solvent of acetone and n-hexane (1:3, v/v). Elemental

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analysis. Calcd for $C_{15}H_{19}N_5$: C, 66.89%; H, 7.11%; N, 26.00%. Found: C, 66.68%; H, 7.16%; N, 25.99%. ^{1}H n.m.r. (DMSO-d_6), δ 1.11 (d, 6H, CH_3), 1.95 (s, 3H, CH_3), 5.20 (m, 1H, N–CH), 5.40 (br s, 1H, =CH), 6.20 (s, 2H, NH_2), 7.05–7.70 ppm (m, 5H, C_6H_5).

*2-Amino-4-(*N*-isobutylanilino)-6-isopropenyl-1,3,5-triazine (N4i).* N4i was synthesized by the reaction of AAIT with isobutyl bromide similarly to the synthesis of N3i. The crude product was recrystallized three times from a mixed solvent of acetone and n-hexane (1:5, v/v). Elemental analysis. Calcd for $C_{16}H_{21}N_5$: C, 67.82%; H, 7.47%; N, 24.71%. Found: C, 67.99%; H, 7.30%; N, 24.81%. ^{1}H n.m.r. (DMSO-d_6), δ 0.85 (d, 6H, CH_3), 1.80 (m, 1H, CH), 1.98 (s, 3H, CH_3), 3.86 (d, 2H, N–CH_2), 5.45 (br s, 1H, =CH), 6.26 (br s, 1H, =CH), 6.75 (s, 2H, NH_2), 7.37 ppm (s, 5H, C_6H_5).

*2-Amino-4-(*N*-sec-butylanilino)-6-isopropenyl-1,3,5-triazine (N4s).* N4s was synthesized by the reaction of AAIT with sec-butyl bromide similarly to the synthesis of N3i. The crude product was recrystallized from a mixed solvent of acetone and n-hexane (1:5, v/v), and further recrystallized four times from n-hexane. Elemental analysis. Calcd for $C_{16}H_{21}N_5$: C, 67.82%; H, 7.47%; N, 24.71%. Found: C, 67.84%; H, 7.43%; N, 24.67%. ^{1}H n.m.r. (DMSO-d_6), δ 0.91 (t, 3H, CH_3), 1.05 (d, 3H, CH_3), 1.41 (m, 2H, CH_2), 1.95 (s, 3H, CH_3), 4.98 (m, 1H, N–CH), 5.40 (br s, 1H, =CH), 6.23 (br s, 1H, =CH), 6.68 (s, 2H, NH_2), 7.05–7.70 ppm (m, 5H, C_6H_5).

*2-Amino-4-(*N*-pentylanilino)-6-isopropenyl-1,3,5-triazine (N5).* N5 was synthesized by the reaction of AAIT with pentyl bromide similarly to the synthesis of N3i. The crude product was recrystallized from n-hexane, and further recrystallized three times from methanol. Elemental analysis. Calcd for $C_{17}H_{23}N_5$: C, 68.66%; H, 7.79%; N, 23.55%. Found: C, 68.87%; H, 7.52%; N, 23.58%. ^{1}H n.m.r. (DMSO-d_6), δ 0.82 (t, 3H, CH_3), 1.04–1.85 (m, 6H, C_3H_6), 1.98 (s, 3H, CH_3), 3.98 (t, 2H, N–CH_2), 5.41 (br s, 1H, =CH), 6.25 (br s, 1H, =CH), 6.70 (s, 2H, NH_2), 7.29 ppm (s, 5H, C_6H_5).

*2-Amino-4-(*N*-isopentylanilino)-6-isopropenyl-1,3,5-triazine (N5i).* N5i was synthesized by the reaction of AAIT with isopentyl bromide similarly to the synthesis of N3i. The crude product was recrystallized in a similar manner as N5. Elemental analysis. Calcd for $C_{17}H_{23}N_5$: C, 68.66%; H, 7.79%; N, 23.55%. Found: C, 68.59%; H, 7.72%; N, 23.42%. ^{1}H n.m.r. (DMSO-d_6), δ 0.84 (d, 6H, CH_3), 1.18–1.78 (m, 3H, CH_2 + CH), 1.99 (s, 3H, CH_3), 4.00 (t, 2H, N–CH_2), 5.43 (br s, 1H, =CH), 6.26 (br s, 1H, =CH), 6.70 (s, 2H, NH_2), 7.29 ppm (s, 5H, C_6H_5).

*2-Amino-4-[*N*-(1-methylbutyl)anilino]-6-isopropenyl-1,3,5-triazine (N5s).* N5s was synthesized by the reaction of AAIT with 2-bromopentane similarly to the synthesis of N3i. The crude product was recrystallized in a similar manner as N5. Elemental analysis. Calcd for $C_{17}H_{23}N_5$: C, 68.66%; H, 7.79%; N, 23.55%. Found: C, 68.65%; H, 7.74%; N, 23.54%. ^{1}H n.m.r. (DMSO-d_6), δ 0.90 (t, 3H, CH_3), 1.06 (d, 3H, CH_3), 1.20–1.70 (m, 4H, C_2H_4), 1.95 (s, 3H, CH_3), 5.12 (m, 1H, N–CH), 5.40 (br s, 1H, =CH), 6.20 (br s, 1H, =CH), 6.66 (s, 2H, NH_2), 7.05–7.70 ppm (m, 5H, C_6H_5).

*2-Amino-4-(*N*-benzylanilino)-6-isopropenyl-1,3,5-triazine (NBz).* NBz was synthesized by the reaction of AAIT with benzyl bromide similarly to the synthesis of N3i. The crude product was recrystallized three times from ethanol. Elemental analysis. Calcd for $C_{19}H_{19}N_5$: C, 71.90%; H, 6.03%; N, 22.06%. Found: C, 71.98%; H, 5.94%; N, 21.95%. ^{1}H n.m.r. (DMSO-d_6), δ 1.98 (s, 3H, CH_3), 5.27 (s, 2H, N–CH_2), 5.42 (br s, 1H, =CH), 6.30 (br s, 1H, =CH), 6.90 (s, 2H, NH_2), 7.30 ppm (s, 10H, C_6H_5).

The yields, m.p., and ultra-violet spectral data of the synthesized monomers are shown in *Table 1*.

Measurements

^{1}H n.m.r. spectra were recorded on a Hitachi R-600 spectrometer operated at 60 MHz in DMSO-d_6, and the chemical shifts are given as δ values in ppm from TMS as an internal standard. Ultra-violet (u.v.) spectra were measured by a Hitachi EPS-3T type spectrophotometer. Molecular weights of polymers were determined by gel permeation chromatography (g.p.c.) on a TOSOH HLC-803D with G2000H, G3000H and G5000H TSK gel columns and a differential refractometric detector in THF. The columns were calibrated with a set of monodisperse polystyrene standards. T_gs of polymers were determined by differential scanning calorimetry (d.s.c.) on a Rigaku-Denki DSC-8230 at a heating rate of 20°C min^{-1}.

Table 1 Synthesis of 2-amino-4-(*N*-alkylanilino)-6-isopropenyl-1,3,5-triazines

Monomer	Alkyl group	Yield[a] (%)	M.p. (°C)	UV[b]
				λ_{max} ($\varepsilon \times 10^{-4}$) (nm)
N3i	$CH(CH_3)_2$	65	138	216 (3.39), 232^s (2.75), 285 (0.35)
N4i	$CH_2CH(CH_3)_2$	78	117	217 (3.24), 235^s (2.26), 295^s (0.40)
N4s	$CH(CH_3)CH_2CH_3$	51	107	216 (3.33), 232^s (2.80), 287 (0.40)
N4t	$C(CH_3)_3$	7		
N5	$CH_2(CH_2)_3CH_3$	87	99	217 (3.31), 235^s (2.34), 293^s (0.44)
N5i	$CH_2CH_2CH(CH_3)_2$	81	114	217 (3.25), 235^s (2.34), 293^s (0.44)
N5s	$CH(CH_3)CH_2CH_2CH_3$	51	86	216 (3.50), 232^s (2.84), 290 (0.37)
NBz	$CH_2C_6H_5$	89	129	213 (3.86), 235^s (2.60), 290^s (0.51)

[a] Determined by ^{1}H n.m.r. spectroscopy
[b] Measured in ethanol

Solution polymerization

Homopolymerization of isopropenyltriazines and their copolymerizations with St, MMA and MA was carried out using azobisisobutyronitrile (AIBN) as an initiator in DMSO at 60°C. The monomer and AIBN concentrations were $0.4\,\mathrm{mol\,l^{-1}}$ and $1.4\,\mathrm{mmol\,l^{-1}}$, respectively. The required volumes of monomer and AIBN solutions were charged into polymerization tubes and degassed by three alternate freeze–pump–thaw cycles. After being sealed, the tubes were placed in a constant temperature bath for specified times. The polymers were precipitated in excess methanol, filtered, dried *in vacuo* and weighed. The composition of the copolymer was calculated by elemental analysis of the carbon and nitrogen contents.

Thermal polymerization

The course of thermal polymerization of these monomers was followed by d.s.c. measurement. A 1–4 mg monomer was accurately weighed and placed in an aluminium pan covered with a lid. The heating rate was varied from 1.25 to $20^\circ\mathrm{C\,min^{-1}}$. The heat of fusion and the apparent heat of polymerization were calculated from the areas of the d.s.c. curves. Indium (m.p. 156.4°C, ΔH_m $28.41\,\mathrm{J\,g^{-1}}$) was used as the standard for the calibration of the temperature and heat energy. After thermal polymerization, the residual monomer content was determined by u.v. spectrometry on the absorbance at 216–217 nm for the extracted monomer in ethanol. The conversion of the thermal polymerization was calculated from the residual monomer content. The calculation was based on the assumption that weight loss of the sample was due to vaporization of monomer and occurred at high temperature. The weight loss was not more than 1% for all polymerizations.

The entropy change of polymerization (ΔS_p°) was obtained by equation (2), which is derived from the thermodynamic equation of polymerization (1)[9].

$$T_c = \frac{\Delta H_p}{\Delta S_p^\circ + R\ln[M]_e} \qquad (1)$$

$$\Delta S_p^\circ = \frac{\Delta H_p}{T_c} - R\ln\frac{1000}{M_w} + R\ln s \qquad (2)$$

where $[M]_e$, R, M_w and s denote the equilibrium monomer concentration ($\mathrm{mol\,l^{-1}}$), the gas constant, the molecular weight of monomer and the specific gravity of the monomer in a molten state, respectively. ΔS_p° can be calculated when s is assumed to be 1.

RESULTS AND DISCUSSION

Synthesis of monomers

We have reported the synthesis of 2-amino-4-(*N*-n-alkylanilino)-6-isopropenyl-1,3,5-triazines by the reaction of 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine (AAIT) with n-alkyl halides in the presence of sodium hydride in DMSO[5]. The reaction proceeded selectively through the anilide anion of AAIT, which could be followed by the measurement of n.m.r.

By application of the above information, reactions of AAIT with eight alkyl bromides were carried out in order to introduce a branched alkyl group (*Figure 1*). The alkyl groups were isopropyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, 1-methylbutyl and benzyl groups. The results of monomer synthesis are shown in *Table 1*. The yield of the monomers was estimated from the peak intensity ratio of methyl protons in isopropenyl groups between AAIT and the product in the ^{1}H n.m.r. spectrum of the reaction mixture. The reactions of AAIT with secondary alkyl bromides such as isopropyl bromide, sec-butyl bromide and 2-bromopentane showed the yield to be lower than those with primary alkyl bromides such as isobutyl bromide, pentyl bromide and isopentyl bromide. This would be due to steric hindrance on substitution and concurrence of elimination on the secondary alkyl bromides. The substitution scarcely proceeded for the reaction with tert-butyl bromide, which would be due to the preferential elimination. The desired monomers could be isolated by recrystallization of reaction mixtures except for N5t. The monomers were characterized by i.r., ^{1}H n.m.r. and elemental analysis. *Figure 2* shows typical ^{1}H n.m.r. spectra for N5, N5i and N5s. The structure of the monomers could be confirmed by the spectra.

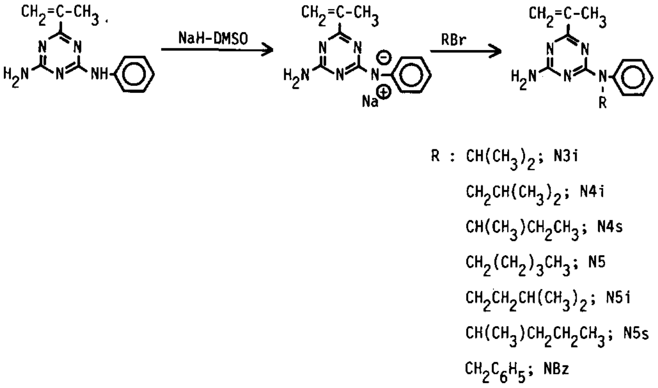

Figure 1 Synthesis of isopropenyl-1,3,5-triazines

Homopolymerization

Results of solution homopolymerizations of the isopropenyltriazines are shown in *Table 2*. These monomers readily underwent radical homopolymerization and gave colourless solid polymers. No significant difference in polymerization yield was observed. In a previous paper[5], we reported that yields were also around 50% for polymerization of 2-amino-4-(*N*-n-alkylanilino)-6-isopropenyl-1,3,5-triazines with alkyl groups ranging from propyl to dodecyl in DMSO for 5 h. Molecular weights of poly(N4i), poly(N4s) and poly(N5s), determined by g.p.c. in THF, were lower than those of the other polymers. However, the reduced viscosities of these polymers, measured in DMSO, were almost the same as those of the others. These polymers would shrink in THF, which is a poor solvent for these polymers. Therefore, g.p.c. measurement of these polymers would underestimate their molecular weight. In view of the viscosity values, the true molecular weight for the present polymers seems to show no significant difference.

Glass transition temperatures (T_g) of the polymers were determined by d.s.c. measurements. The T_g is plotted in *Figure 3* against the carbon numbers of alkyl groups for the polymers. *Figure 3* includes the previous data for poly(2-amino-4-(*N*-n-alkylanilino)-6-isopropenyl-1,3,5-triazines) whose alkyl groups are ethyl (N2)[10], propyl (N3)[5], butyl (N4)[10], hexyl (N6)[5] and

Table 2 Solution homopolymerization of isopropenyl-1,3,5-triazines[a]

Monomer	Yield (%)	η_{sp}/c[b] (dl g^{-1})	G.p.c. $\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	T_g[c] (°C)
N3i	51.2	0.54				231
N4i	56.3	0.51	0.5	1.6	3.2	220
N4s	49.4	0.47	0.3	0.9	3.0	232
N5	57.9	0.52	7.1	10.4	1.5	179
N5i	53.0	0.45	6.1	9.2	1.5	198
N5s	41.3	0.39	0.2	0.3	1.5	208
NBz	61.1	0.64	9.1	21.0	2.3	195

[a] Polymerization condition: $[M]_0 = 0.4$ mol l^{-1}, [AIBN] = 1.4 mmol l^{-1} at 60°C in DMSO for 5 h
[b] $c = 0.2$ g dl^{-1} at 30°C in DMSO
[c] Measured by d.s.c. at a heating rate of 20°C min^{-1}

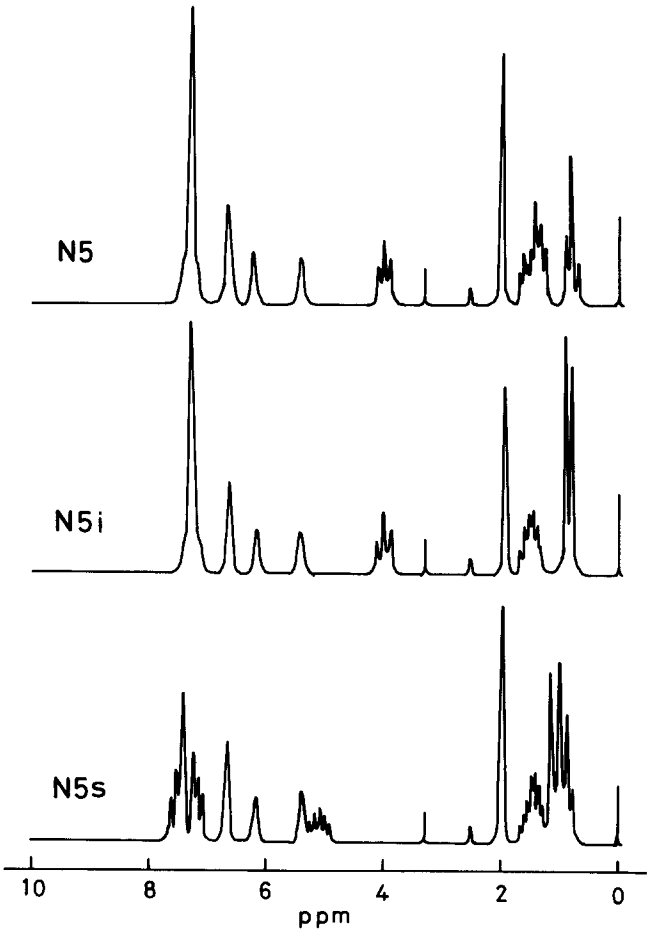

Figure 2 ^{1}H n.m.r. spectra of N5, N5i and N5s in DMSO-d_6

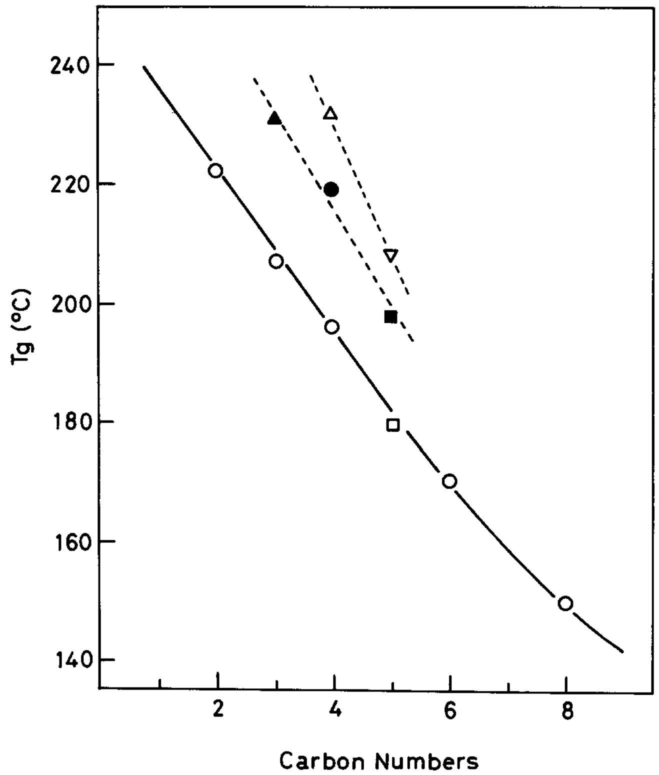

Figure 3 Relationship between T_g of homopolymer and carbon numbers of the alkyl group: (▲) N3i; (●) N4i; (△) N4s; (□) N5; (■) N5i; (▽) N5s; (○) previous data

octyl (N8)[5]. The T_g of poly(N5) is on the line of previous data. T_gs of the polymers containing branched alkyl groups are higher than those of polymers containing n-alkyl groups. A similar tendency was observed for poly(4-alkylstyrenes) and poly(alkyl methacrylates). The T_g of poly(4-sec-butylstyrene) (86°C) and poly(sec-butyl methacrylate) (60°C) were higher than that of poly(4-n-butylstyrene) (6°C) and poly(n-butyl methacrylate) (20°C), respectively[4]. This would indicate that the branched alkyl group prevents the segmental motion of the polymer backbone. Furthermore, the T_g of the polymers containing secondary alkyl groups such as poly(N4s) and poly(N5s) is higher than that of the polymers containing isoalkyl groups such as poly(N4i) and poly(N5i). This would be due to the increase in the preventive effect of the secondary alkyl group compared to the isoalkyl group.

Copolymerization

Copolymerizations of these isopropenyltriazines (M_2) with St, MMA, or MA (M_1) were carried out in DMSO using azobisisobutyronitrile as an initiator. All the monomers could be copolymerized to give colourless solid copolymers. In all cases the polymer conversion was kept below 15%. The copolymer composition was calculated from the carbon–nitrogen ratio in the elemental analysis. The monomer reactivity ratios were determined by the method of Kelen and Tüdös[11]. *Figure 4* shows the monomer–copolymer composition curves for the copolymerization of N5, N5i and N5s (M_2) with

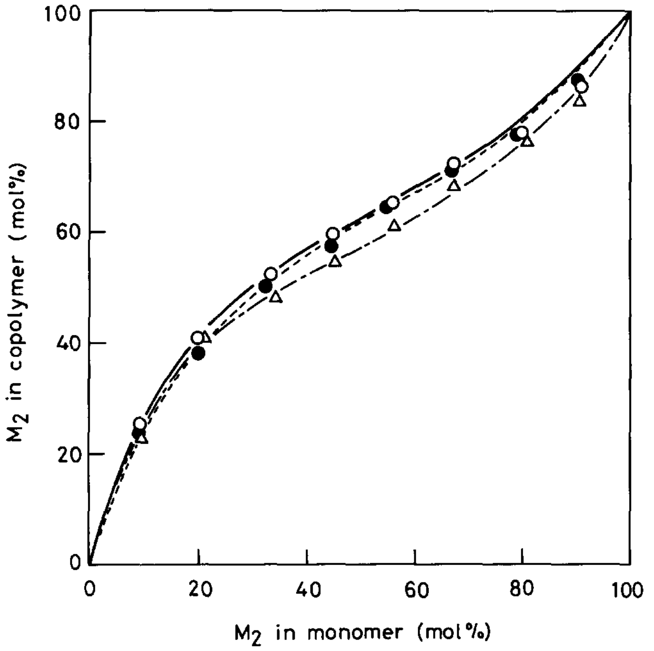

Figure 4 Monomer–copolymer composition curves for the copolymerization of: (○) N5; (●) N5i and (△) N5s (M_2) with styrene (M_1) at 60°C in DMSO

styrene. As can be seen in *Figure 4*, the plots fit the curves calculated from the reactivity ratios. The values of r_1, r_2 and $1/r_1$ are listed in *Table 3* together with the previous values for the monomers such as N3[6] and N4[9]. The values of $1/r_1$, which indicates monomer reactivity, were not varied significantly by changes in length and shape of the alkyl group.

Alfrey-Price Q and e values for these monomers calculated from the monomer reactivity ratios are listed in *Table 3*. The e values depend on comonomers, that is, positive for the copolymerization with St and negative for MMA and MA. This is a type of behaviour general for the copolymerization of isopropenyltriazines as described previously[6,12,13]. The reason for this behaviour is not clear at the present stage. The copolymerization might include a steric effect, because the present monomers have bulky substituents. Furthermore, the possibility of a charge transfer complex of isopropenyltriazines with St and/or MMA might be present in these copolymerizations, although evidence for the formation of such a complex could not be found in the spectral measurements such as absorption spectra and ^{1}H n.m.r. spectra.

Figure 5 shows the relationships between T_g and composition for the copolymers of N5, N5i and N5s (M_2) with MMA. The T_g increases with the M_2 content and reaches the T_g of the homopolymers. This would be due to the strong intermolecular interactions of isopropenyltriazine units such as hydrogen bonding of the amino group. The T_g of copolymers was in the following order: N5s > N5i > N5 over the whole composition region. The order is the same as that of homopolymers. A similar tendency was observed for N3i and N3, and for N4s, N4i and N4, respectively.

Thermodynamics of polymerization by d.s.c.

We reported that thermodynamic parameters such as ceiling temperature (T_c) and heat of polymerization (ΔH_p) can be determined from the d.s.c. curve of thermal polymerization in previous papers[7,13–18]. By application of this method, thermodynamic parameters of polymerization for the present monomers were obtained by means of d.s.c.

Thermal polymerization using d.s.c. was carried out at various heating rates. *Figure 6* shows typical d.s.c. curves at the heating rate of 5°C min^{-1}. A polymerization

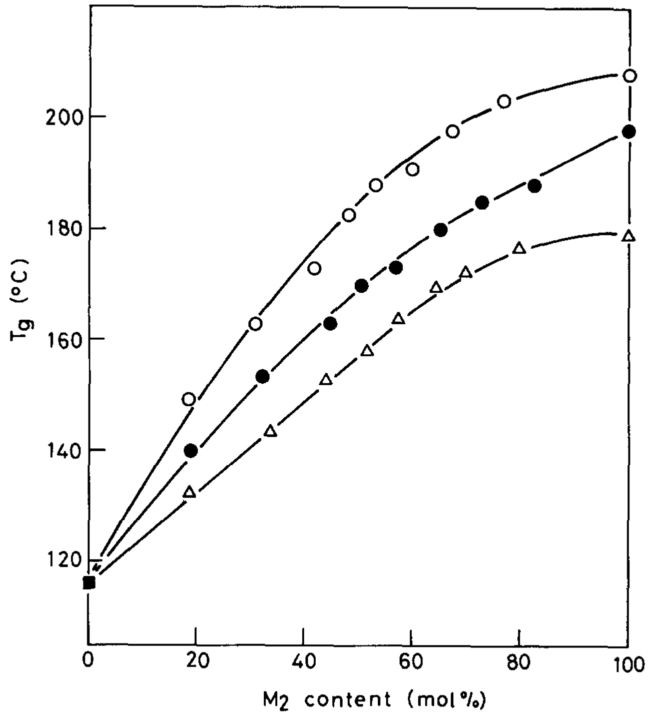

Figure 5 Relationship between T_g and M_2 content in copolymers of: (△) N5; (●) N5i and (○) N5s (M_2) with methyl methacrylate (M_1)

Table 3 Copolymerization parameters of isopropenyl-1,3,5-triazines

M_2	M_1	r_1	r_2	$1/r_1$	Q_2	e_2
N3i	St	0.27	0.77	3.7	1.36	0.45
	MMA	0.29	0.39	3.5	1.41	−1.08
	MA	0.10	0.73	10.0	1.59	−1.02
N4i	St	0.22	0.89	4.6	1.64	0.48
	MMA	0.30	0.44	3.3	1.40	−1.02
	MA	0.11	0.93	9.1	1.54	−0.91
N4s	St	0.24	0.63	4.2	1.39	0.57
	MMA	0.34	0.43	2.9	1.25	−0.99
	MA	0.12	1.16	8.3	1.51	−0.80
N5	St	0.18	0.93	5.6	1.91	0.54
	MMA	0.30	0.57	3.3	1.45	−0.93
	MA	0.08	1.12	12.5	2.07	−0.95
N5i	St	0.25	0.94	4.0	1.53	0.40
	MMA	0.33	0.62	3.0	1.35	−0.86
	MA	0.09	0.94	11.1	1.82	−0.97
N5s	St	0.20	0.58	5.0	1.55	0.67
	MMA	0.32	0.37	3.1	1.29	−1.06
	MA	0.16	1.11	6.3	1.19	−0.71
NBz	St	0.21	0.83	4.8	1.65	0.52
	MMA	0.35	0.34	2.9	1.18	−1.06
	MA	0.13	0.92	7.7	1.35	−0.86
N3[a]	St	0.23	0.85	4.4	1.56	0.48
	MMA	0.32	0.56	3.1	1.37	−0.91
	MA	0.12	0.89	8.3	1.43	−0.90
N4[b]	St	0.25	0.76	4.0	1.43	0.49
	MMA	0.33	0.45	3.0	1.29	−0.98
	MA	0.10	1.25	10.2	1.77	−0.84

[a] 2-Amino-4-(*N*-propylanilino)-6-isopropenyl-1,3,5-triazine
[b] 2-Amino-4-(*N*-butylanilino)-6-isopropenyl-1,3,5-triazine

exothermic peak was observed in the d.s.c. curves above the melting endothermic peak for all monomers. The apparent heat of fusion ($\Delta H'_m$) and apparent heat of polymerization ($\Delta H''_p$) can be obtained from the peak areas. These values at the various heating rates are shown in *Table 4*. The $\Delta H'_m$ values are almost constant regardless of the heating rate for N3i, N4s, N5 and N5s. This indicates that the melting endotherm and polymerization exotherm do not compensate each other. On the other hand, the $\Delta H'_m$ values of N4i, N5i and NBz depend on the heating rate and the values decrease at the lower heating rate. This is caused by the compensation of both peaks. It is necessary to determine true heat of fusion (ΔH_m) to correct the $\Delta H''_p$ values. Because the $\Delta H'_m$ values at the heating rates of 2.5–20°C min^{-1} for N4i and at 5–20°C min^{-1} for NBz show almost constant values, the mean of these values should be ΔH_m. Although there was no constant $\Delta H'_m$ value for N5i, we assumed the value at 20°C min^{-1} to be ΔH_m from the d.s.c. curve which did not seem to incur the compensation. The compensated $\Delta H''_p$ values were corrected by use of the ΔH_m, and they are shown in *Table 4* as $\Delta H'_p$.

After the thermal polymerization, conversion was obtained from residual monomer content determined by u.v. spectrometry. Both the $\Delta H''_p$ or $\Delta H'_p$ and the conversion decrease with increasing heating rate. The heat of polymerization (ΔH_p) can be calculated from $\Delta H''_p$ or $\Delta H'_p$ and the conversion. The ΔH_p values are almost constant regardless of the heating rate in each monomer, as shown in *Table 4*.

The final temperature of the polymerization exothermic peaks (T_f) is shown in *Table 4*. Although the monomer still remains abundant, the thermal polymerization is

Table 4 Thermal polymerization of isopropenyl-1,3,5-triazines by means of d.s.c.

Monomer	Heating rate (°C min^{-1})	M.p. (°C)	$\Delta H'_m$[a] (kJ mol^{-1})	T_f[b] (°C)	$-\Delta H''_p$[c] (kJ mol^{-1})	$-\Delta H'_p$[d] (kJ mol^{-1})	Conversion (%)	$-\Delta H_p$ (kJ mol^{-1})
N3i	1.25	137	30.59	147	8.54		19.6	43.6
	2.5	137	30.25	149	4.48		10.3	43.5
	5.0	137	30.33	151	1.92		4.4	43.6
	10.0	138	30.12					
	20.0	138	30.12					
N4i	1.25	116	15.98	135	25.40	28.68	65.5	43.8
	2.5	116	19.20	138	21.09		47.2	44.7
	5.0	116	19.33	144	18.50		41.6	44.5
	10.0	117	19.12	152	11.63		25.9	44.9
	20.0	117	19.37	154	5.62		13.0	43.2
N4s	1.25	107	22.05	138	17.87		41.7	42.9
	2.5	107	22.26	143	14.14		33.3	42.5
	5.0	107	22.26	144	6.43		15.3	42.0
	10.0	107	22.13	146	4.44		10.6	41.9
	20.0	107	22.01	148	1.00		2.3	43.5
N5	1.25	99	33.85	130	23.77		52.6	45.2
	2.5	99	33.85	142	19.25		43.6	44.2
	5.0	99	34.18	143	16.23		36.6	44.3
	10.0	99	33.93	145	9.41		22.1	42.6
	20.0	99	33.89	150	4.35		10.1	43.1
N5i	1.25	114	17.41	127	20.00	27.07	61.8	43.8
	2.5	114	20.46	133	21.42	25.44	58.6	43.4
	5.0	114	21.42	139	20.13	23.19	53.0	43.8
	10.0	114	22.72	144	16.36	18.12	42.2	42.9
	20.0	114	24.48	151	14.52		33.2	43.7
N5s	1.25	85	23.77	128	23.77		55.6	42.8
	2.5	85	24.39	130	23.06		54.5	42.3
	5.0	85	24.43	137	16.78		39.2	42.8
	10.0	86	24.73	143	12.25		29.2	42.0
	20.0	86	24.23	146	5.65		13.5	41.9
NBz	1.25	129	18.58	141	22.55	31.49	70.4	44.7
	2.5	129	24.06	144	25.82	29.28	65.8	44.5
	5.0	129	27.45	149	22.34		50.0	44.7
	10.0	129	27.32	153	12.30		27.8	44.2
	20.0	129	27.78	157	4.77		10.8	44.2

[a] Apparent heat of fusion obtained from endothermic peak

[b] Final temperature of exothermic peak

[c] Apparent heat of polymerization obtained from endothermic peak

[d] Values corrected by considering the compensation using postulated heat of fusion ΔH_m. $-\Delta H'_p = -\Delta H''_p + (\Delta H_m - \Delta H'_m)$

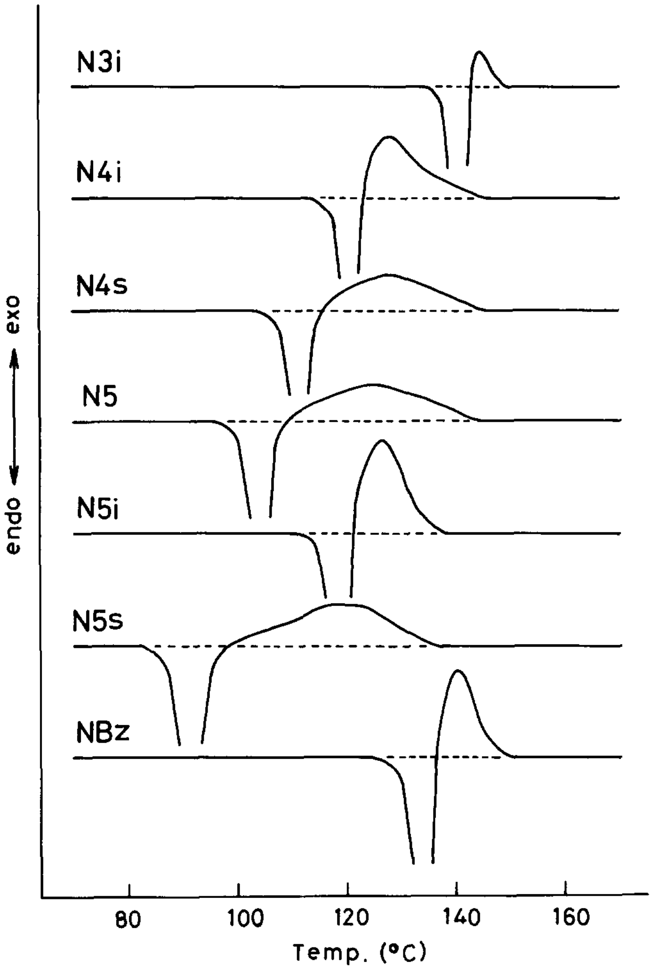

Figure 6 D.s.c. curves of isopropenyl-1,3,5-triazines at a heating rate of 5°C min^{-1}

terminated at T_f. This is due to the limitation of polymerization by the ceiling temperature (T_c). In previous papers[7,13–18], we found that the final temperature of polymerization exothermic peak in the d.s.c. curve for isopropenyltriazines could be approximated to T_c when the polymerization terminated at low conversion. The T_c of the present monomers was also determined according to the above information. The T_f at the lowest conversion, that is, the T_f at a heating rate of 20°C min^{-1}, except for N3i which is at 5°C min^{-1}, approximated to T_c in bulk. The conversion of N5i at 20°C min^{-1}, which was 33.2%, might be too high to estimate T_c. A heating rate faster than 20°C min^{-1} might give a better estimation. However, because the faster rate leads to a large error in the heat energy and temperature, d.s.c. measurement was carried out at a heating rate of below 20°C min^{-1} in this study.

The thermodynamic parameters of polymerization (T_c, ΔH_p and ΔS_p°) are summarized in *Table 5* together with the values of previous monomers. The ΔH_p is the mean of the values in *Table 4*. The T_c and ΔH_p in *Table 5* are plotted in *Figure 7* against the number of carbon atoms in the alkyl group of the monomers. Previously, we reported that the thermodynamic parameters of polymerization for 2-amino-4-(*N*-n-alkylanilino)-6-isopropenyl-1,3,5-triazines decrease with increasing length of the alkyl chain as a result of steric hindrance[7]. As can be seen in *Figure 7*, the values of N4i, N5 and N5i are near the line of the previous data. This indicates that the effect of isobutyl and isopentyl groups on the thermodynamics of polymerization is similar to that of the corresponding n-alkyl groups. On the other hand, the values of N3i, N4s and N5s are lower than those of the other monomers.

Signals of phenyl protons for N5s showed multiplet absorption in contrast to a singlet for N5 and N5i in the

Table 5 Thermodynamic parameters of fusion and polymerization for isopropenyl-1,3,5-triazines

Monomer	M.p. (°C)	ΔH_m (kJ mol^{-1})	ΔS_m (J K^{-1} mol^{-1})	T_c (°C)	$-\Delta H_p$ (kJ mol^{-1})	$-\Delta S_p^\circ$ (J K^{-1} mol^{-1})
N3i	137	30.3	73.9	151	43.6	113.7
N4i	116	19.3	49.6	154	44.2	114.0
N4s	107	22.1	58.1	148	42.6	111.6
N5	99	33.9	91.1	150	43.9	113.8
N5i	114	24.5	63.3	151	43.5	112.6
N5s	85	24.3	67.8	146	42.4	111.2
NBz	129	27.5	68.4	157	44.5	113.0
N1[a]	118	31.4	80.3	166	50.2	126.1
N2[b]	107	27.6	72.6	163	46.9	118.9
N3[c]	107	31.5	82.9	157	45.8	117.4
N4[d]	78	31.8	90.6	155	42.7	110.2
N6[e]	68	24.1	70.6	149	43.2	112.0
N8[f]	61	24.6	73.6	143	42.1	110.1
N10[g]	67	32.2	94.7	140	41.4	108.5

[a] 2-Amino-4-(*N*-methylanilino)-6-isopropenyl-1,3,5-triazine[10]
[b] 2-Amino-4-(*N*-ethylanilino)-6-isopropenyl-1,3,5-triazine[10]
[c] 2-Amino-4-(*N*-propylanilino)-6-isopropenyl-1,3,5-triazine[7]
[d] 2-Amino-4-(*N*-butylanilino)-6-isopropenyl-1,3,5-triazine[10]
[e] 2-Amino-4-(*N*-hexylanilino)6-isopropenyl-1,3,5-triazine[7]
[f] 2-Amino-4-(*N*-octylanilino)-6-isopropenyl-1,3,5-triazine[7]
[g] 2-Amino-4-(*N*-decylanilino)-6-isopropenyl-1,3,5-triazine[7]

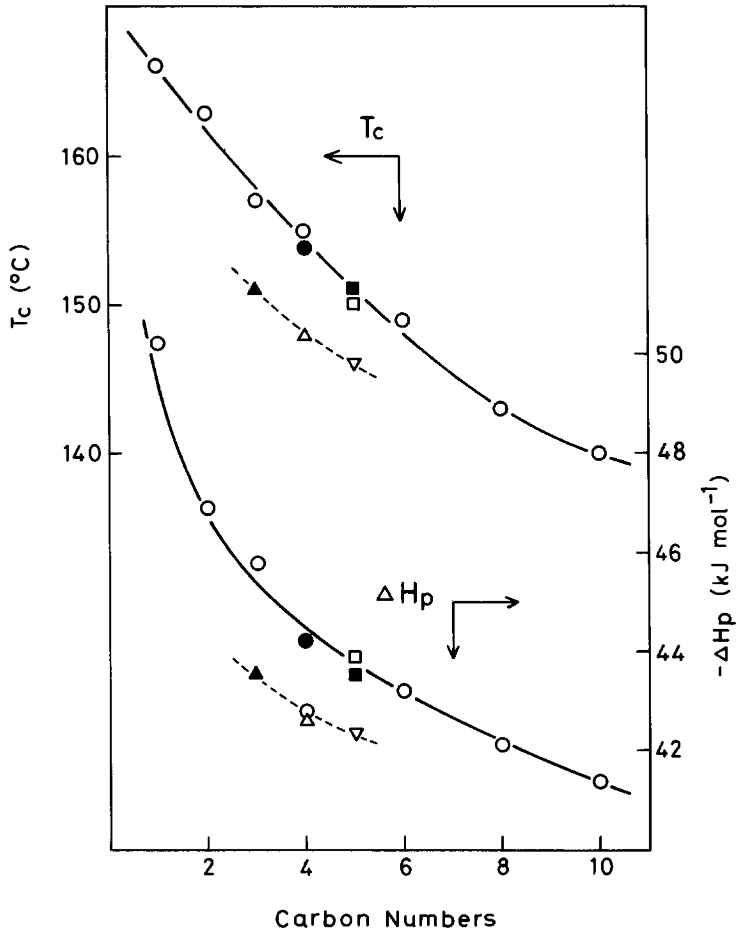

Figure 7 Relationship between thermodynamic parameters of polymerization (T_c and ΔH_p) and carbon numbers of the alkyl group: (▲) N3i; (●) N4i; (△) N4s; (□) N5; (■) N5i; (▽) N5s; (○) previous data

^{1}H n.m.r. spectrum as shown in *Figure 2*. A similar signal was observed for N3i and N4s. In addition, u.v. spectra of N3i, N4s and N5s showed different absorption from those of N4i, N5 and N5i. These results suggest a different conformation of the benzene ring in the monomers containing a secondary alkyl group from those containing a primary alkyl group. The singlet peak in the ^{1}H n.m.r. of the monomers containing a primary alkyl group indicates free rotation around the anilino nitrogen and carbon in the benzene ring. On the other hand, the phenyl group in the monomers containing a secondary alkyl group would be fixed in a twisted conformation to the plane involving the triazine ring and the anilino nitrogen. The phenyl group in the polymers containing primary alkyl groups would be given a relatively stable conformation by the rotation in order to avoid the steric repulsion, whereas the polymers containing a secondary alkyl group would not be given a stable conformation due to the steric demands of the secondary alkyl group. Consequently, the lowering of the thermodynamic parameters of polymerization seems to result from a less stable state in the polymer side caused by the steric crowding of phenyl groups between adjacent monomer units along the main chain.

The thermodynamic parameters of polymerization for NBz were close to those for N3 or N4. The steric effect of the benzyl group on the thermodynamics of polymerization seems to be similar in extent to that of n-propyl or n-butyl groups.

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