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Syntheses and Properties of Copolymers of Isopropenyl-1,3,5-triazines and Methacrylic Esters

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Copolymerizations of 2-amino-4-(substituted amino)-6-isopropenyl-1,3,5-triazines (methacryloguanamine) with alkyl methacrylates using redox initiator gave polymers with high molecular weights in satisfactory yields. The monomer reactivity ratios and *Q*-*e* values were also determined. Softening and glass transition temperatures rose and specific gravity increased with the increase in the content of triazine units. The copolymers were slightly soluble in nonpolar solvents and readily soluble in polar solvents with a solubility parameter (δ) = 11—13. This polymer with aminotriazine groups showed high viscosity in acid solution and can be utillized as polyelectrolyte.

Polymers containing amino-1,3,5-triazine groups have been investigated as industrial materials and heat-stable polymers. Furthermore, the polymers with aminotriazine groups in the side or main chain are expected to have a variety of other properties, such as rigidity, intermolecular interaction, thermal stability and basicity.[1–3]

The polymerization of several vinyl- and isopropenyl-1,3,5-triazines and the copolymerization with styrene,[4] acrylic or methacrylic acid[1] have been studied previously. Recently isopropenyl-1,3,5-triazines were readily prepared in high yields from methacrylic active esters and biguanides.[5]

This paper describes the determination of copolymerization parameters of 2-amino-4-(substituted amino)-6-isopropenyl-1,3,5-triazines with methacrylic esters and a survey for synthetic conditions to obtain the desired polymers with high molecular weights. Physical and thermal properties of the polymers, *e.g.*, softening and glass transition temperature, specific gravity, solubilities and solution viscosities are also reported.

Experimental

Materials. The mono- and disubstituted biguanides were prepared by the method of Kono and Odo[6] or Cohn[7] from dicyanodiamide and the corresponding amines. Methacrylic esters and *N*,*N*-dimethylaniline were purified by the usual methods.

The initiator, α,α′-azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO) was a commercial material.

Dioxane was purified by drying with anhydrous magnesium sulfate, refluxing with sodium, and fractionally distilling. Dimethyl sulfoxide (DMSO) was fractionally distilled under reduced pressure in the presence of nitrogen after drying with calcium hydride.

All the other reagents were commercially available and were used after purification, if necessary.

2,4-Diamino-6-isopropenyl-1,3,5-triazine (AIPT): 9.2 g (0.165 mol) of potassium hydroxide dissolved in 90 ml of methanol was added dropwise to the solution of 22.7 g (0.165 mol) biguanide hydrochloride dissolved in 200 ml of methanol at 5—10 °C under stirring. The resulting potassium chloride was filtered off, then the filtrate was concentrated using vacuum evaporator at 30—40 °C. To the concentrate, dissolved in 120 ml of DMSO, was added phenyl methacrylate 24.3 g (0.15 mol). After the temperature was kept at 30 °C for 3 d, the reaction mixture was poured into 2 l of water. The crude product obtained was recrystallyzed from methanol–Methyl Cellosolve to afford colorless crystals, mp 247—248 °C (lit, 247—248 °C)[4] in 81.6% yield.

Other 2,4-substituted amino-6-isopropenyl-1,3,5-triazines were prepared by the procedure described before.[5]

2-Amino-4-anilino-6-isopropenyl-1,3,5-triazine (AAIPT) was recrystallyzed from methanol, mp 174—175 °C (lit, 174—175.5 °C).[4]

2-Amino-4-(*N*-methylanilino)-6-isopropenyl-1,3,5-triazine (NMeAIPT) was recrystallyzed from benzene, mp 117—118 °C (lit, 118—119 °C).[4]

2-Amino-4-dimethylamino-6-isopropenyl-1,3,5-triazine (DMAIPT) was recrystallyzed from methanol, mp 191—192 °C (lit, 191—192 °C).[4]

Procedure. All the polymerization experiments were carried out in a glass tube sealed under a vacuum. Methanol was used as a precipitant. The composition of the polymer was calculated from the carbon and nitrogen contents.

Measurement. Reduced and intrinsic viscosities were determined using an Ostwald and an Ubbelode viscometer, respectively. Number average molecular weights (Mn) were measured by osmometry in a benzene or toluene solution (high speed membrane osmometer Mechrolab 501). Gel permeation chromatography (GPC) was done on a Toyo Soda Model HLC 801A with tetrahydrofuran as the solvent. Ultraviolet absorption spectra were obtained with a Hitachi Model 139 spectrometer.

The softening temperature was measured with a Shimadzu Type MM-2 micro softening point determination apparatus. The glass transition temperature was determined by the same heat-expansion measurement as was reported before.[8] The specific gravity of a polymer film was measured by the suspension method in concentrated sodium chloride or sucrose solution.

Results and Discussion

Homopolymerization. As shown in Table 1, 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine (AAIPT), whose ceiling temperature was about 170 °C,[9] gave only polymers with reduced viscosities of 0.3—0.4 dl/g when polymerized at 60 °C using AIBN. However, poly(AAIPT) with high molecular weight (reduced viscosities of 2—3 dl/g) formed during a short reaction time in satisfactory yields when the polymerizations were attained at 30 °C using redox initiator.

Homopolymers of 2,4-diamino-6-isopropenyl-1,3,5-triazine (AIPT) precipitated from a solution, and their viscosities, obtained using both redox initiator

Table 1. Polymerization of isopropenyl-1,3,5-triazines

Monomer	Condition				Yield/%	η_{sp} c)
	Initiator	T/°C	t/h	Solvent		
2-Amino-4-anilino-6-isopropenyl-1,3,5-triazine	AIBN a)	60	4	DMSO	24.0	0.36
	AIBN a)	60	18	DMSO	39.0	0.27
	AIBN a)	60	12	Dioxane	31.5	0.29
	Redox b)	30	1/2	Dioxane	38.9	1.93
	Redox b)	30	2	Dioxane	47.1	2.75
2,4-Diamino-6-isopropenyl-1,3,5-triazine	AIBN a)	60	5	Dioxane	32.5	11.9 d)
	Redox b)	30	72	Dioxane	34.9	10.5 d)

a) Polymerization conditions: $[M]=0.20$ mol dm^{-3}, $[AIBN]=1.35\times10^{-3}$ mol dm^{-3}. b) Polymerization condition: $[M]=0.20$ mol dm^{-3}, [N,N-dimethylaniline] = [BPO] = 2.70×10^{-3} mol dm^{-3}. c) $c=0.30$ g/dl, in DMSO at 30 °C. d) $c=0.30$ g/dl, in formic acid at 30 °C.

Taable 2. Copolymerization of 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine(M_2) with methacrylic esters(M_1)

M_2 in monomer (mol%)	Reaction time a) h	Yield %	M_2 in copolymer (mol%)	η_{sp} c) in	
				Dioxane	Formic acid
M_1: Butyl methacrylate					
20.01	3 b)	25.4	25.62	0.40	—
5.31	65	37.5	9.08	1.20	—
7.72	65	40.3	13.20	1.32	12.0
20.81	65	68.0	26.43	1.30	15.1
28.83	72	71.7	35.40	0.88	13.4
48.30	72	57.8	55.31	0.72	15.6
58.40	48	30.5	65.10	0.63 d)	—
M_1: Ethyl methacrylate					
5.04	48	32.3	7.27	1.67	—
8.01	48	40.5	10.92	2.08	—
11.02	48	52.4	13.40	1.03	—
12.10	48	25.6	15.60	1.02	—
17.14	48	20.4	20.31	1.40	—
M_1: Methyl methacrylate					
5.02	65	15.7	13.24	0.57	—
10.40	65	21.3	24.52	0.50	—
15.71	65	29.0	27.70	0.57	—
25.03	65	22.5	49.41	0.44 d)	—
40.00	65	20.6	54.33	—	—
50.04	65	19.8	68.14	—	—

a) Polymerization conditions: $[M_1]+[M_2]=0.20$—0.80 mol dm^{-3}, [N,N-dimethylaniline] = [BPO] = $(1.35$—$4.00)\times10^{-3}$ mol dm^{-3}, in dioxane at 30 °C. b) Polymerization conditions: $[M_1]+[M_2]=0.20$ mol dm^{-3}, $[AIBN]=1.35\times10^{-3}$ mol dm^{-3}, in DMSO at 60 °C. c) $c=0.30$ g/dl, at 30 °C. d) $c=0.30$ g/dl, in DMSO at 30 °C.

and AIBN, were nearly equal.

Redox polymerizations of other 2-amino-4-(substituted amino) derivatives gave high polymers in 70—90% yields in 1—2 h polymerization period.

Copolymerization. Copolymerizations of AAIPT or AIPT with methacrylic esters such as methyl, ethyl, or butyl methacrylate (MMA, EMA, or BMA) were carried out as shown in Tables 2 and 3 respectively.

Copolymerizations of AAIPT with alkyl methacrylates using redox initiator gave polymers with high molecular weights (viscosities of 0.5—1.7 dl/g), whereas the viscosity of the polymer prepared using AIBN was 0.4 dl/g. Similarly, the redox polymerizations of AIPT with alkyl methacrylates gave high polymers with viscosities of 0.9—1.5 dl/g.

Next, the monomer reactivity ratios were determined by the method of Finemann and Ross or Mayo and Lewis; Q-e values are summarized in Table 4.

The r_1r_2 values for copolymerization of AIPT or AAIPT with methacrylic esters are larger than those with styrene. This suggests that copolymerizations of isopropenyl-1,3,5-triazines with methacrylic esters give a lower alternating tendency than that with styrene. Q values were 0.9—1.2. The negative e values for AIPT and the positive e values for AAIPT may be due to the presence of a strong electron-donating effect of two amino groups and a weaker conjugation of anilino group with double bond.[4]

Table 3. Copolymerization of 2,4-diamino-6-isopropenyl-1,3,5-triazine(M_2) with methacrylic esters(M_1)

M_2 in monomer (mol%)	Reaction time[a] h	Yield %	M_2 in copolymer (mol%)	η_{sp}[c] in Dioxane	Formic acid
M_1: Butyl methacrylate					
20.01	4[b]	20.6	26.10	0.41	—
5.30	72	35.4	7.53	1.28	—
7.71	96	59.8	10.03	1.49	14.2
9.56	72	30.7	13.90	1.63	—
13.55	96	48.1	20.72	1.01	20.9
20.03	96	67.2	29.14	0.92	—
29.52	96	64.3	38.10	0.43[d]	8.4
38.50	96	49.6	48.30	0.67[e]	—
M_1: Ethyl methacrylate					
4.87	72	50.1	7.75	0.94	—
9.10	72	49.4	14.20	1.05	—
11.12	72	45.6	18.71	0.72	—
14.14	72	47.6	23.14	0.75[d]	—
19.80	72	64.0	28.81	0.94	—
M_1: Methyl methacrylate					
5.30	68	15.7	10.17	0.93	9.2
7.75	68	22.4	15.13	0.57	—
18.91	68	48.1	26.70	1.21[e]	15.2
41.30	68	61.3	43.21	0.28[e]	—
58.33	68	43.0	52.60	—	—

a) Polymerization conditions: $[M_1]+[M_2]=0.20$—1.00 mol dm^{-3}, [*N*,*N*-dimethylaniline] = [BPO] = (1.35—4.00) × 10^{-3} mol dm^{-3}, in dioxane at 30 °C. b) Polymerization conditions: $[M_1]+[M_2]=0.20$ mol dm^{-3}, [AIBN] = 1.35 × 10^{-3} mol dm^{-3}, in DMSO at 60 °C. c) $c=0.30$ g/dl, at 30 °C. d) $c=0.30$ g/dl, in Methyl Cellosolve at 30 °C. e) $c=0.30$ g/dl, in DMSO at 30 °C.

Table 4. The copolymerization parameters of isopropenyl-1,3,5-triazine (M_2)

M_1[a]	r_1	r_2	r_1r_2	Q	e
M_2 = 2,4-Diamino-6-isopropenyl-1,3,5-triazine (AIPT)					
St	0.66	0.97	0.64	0.89	−0.13
BMA	0.51	1.42	0.72	1.07	−0.13
EMA	0.68	1.10	0.75	0.88	−0.15
MMA	0.47	1.50	0.71	1.24	−0.19
M_2 = 2-Amino-4-anilino-6-isopropenyl-1,3,5-triazine (AAIPT)					
St	0.39	0.78	0.30	1.07	0.29
BMA	0.68	1.25	0.85	1.15	0.05
EMA	0.63	1.39	0.88	1.02	0.03
MMA	0.42	2.10	0.86	1.50	0.02

a) St: Styrene ($Q_1=1.0$, $e_1=-0.8$), BMA: butyl methacrylate ($Q_1=0.74$, $e_1=0.39$), EMA: ethyl methacrylate ($Q_1=0.70$, $e_1=0.44$), MMA: methyl methacrylate ($Q_1=0.74$, $e_1=0.40$).

As shown in Table 5, viscosities in dioxane are different from those in benzene, and hence the affinities of triazine rings for solvent seem to influence to some extent the conformation of copolymers. $\overline{\text{M}}$n of copolymers with viscosities of 1.6—1.7 dl/g and 0.6—1.0 dl/g were (65—90) × 10^4 and (10—40) × 10^4 respectively. The peak count number in GPC decreased with increasing $\overline{\text{M}}$n, as recognized generally.

In the UV spectra of copolymers given in Table 6, λ_{max} was assigned to triazine rings in analogy with the model compound; ε values decreased with increasing triazine content, which may show the presence of an interaction between aminotriazine groups.

The other absorption at about 259 nm for AAIPT–BMA copolymers probably indicates the existence of steric hindrance between triazine rings and butyl ester groups in side chain. This may be substantiated by the fact that λ_{max} of *o*-toluidino derivative shifted to a much lower wavelength compared with that of anilino derivative.

Properties. The previous reports[1,2] showed that various polymers containing vinyl-1,3,5-triazines (acryloguanamine) were prepared by the reaction of cyano groups in polymer side chain with dicyanodiamide and/or from polymers containing active ester groups as a pendant and biguanides; then their several properties were investigated. In this paper the thermal and physical properties of polymers containing isopropenyl-1,3,5-triazines (methacryloguanamine) were studied in detail.

As shown in Figs. 1—4, the glass transition temperature (T_g) of polymers was generally about 2/3—3/4 times the softening temperature (T_s). Ts of AIPT–BMA copolymers rose linearly with AIPT content and became above 300 °C at 60 mol% of triazine rings. Ts of AAIPT–BMA copolymers rose in proportion to AAIPT content, but became much lower

Table 5. The intrinsic viscosities and the number average molecular weights of copolymers of isopropenyl-1,3,5-triazines with methacrylic esters

Polymer[a]	Content of isopropenyl-1,3,5-triazine	$[\eta]$ in Dioxane or (benzene) at 30 °C	$\overline{\mathrm{M}}\mathrm{n}\times10^{-4}$	Peak count number in GPC
Poly(BMA)	—	0.45 (0.50)	9.58	25.8
AIPT-BMA copolymer	12.9	1.07 (0.50)	47.5	23.5
AAIPT-BMA copolymer	11.0	0.55 (0.46)	15.9	25.6
NMeAIPT-BMA copolymer	19.0	0.99	37.5	
DMAIPT-BMA copolymer	20.5	0.55	24.3	
Poly(EMA)	—	1.61 (1.76)	87.9	23.0
AAIPT-EMA copolymer	7.3	1.67 (0.86)	65.0	23.1

a) BMA: Butyl methacrylate, EMA: ethyl methacrylate, AIPT: 2,4-diamino-6-isopropenyl-1,3,5-triazine, AAIPT: 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine, NMeAIPT: 2-amino-4-(*N*-methylanilino)-6-isopropenyl-1,3,5-triazine, DMAIPT: 2-amino-4-dimethylamino-6-isopropenyl-1,3,5-triazine.

Table 6. The UV spectra of copolymers of 2,4-diamino-6-isopropenyl-1,3,5-triazine (AIPT) or 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine (AAIPT) with butyl methacrylate

AIPT in AIPT-BMA copolymer (mol%)	λ_{max}/nm[a] ($\varepsilon\times10^{-3}$)	AAIPT in AAIPT-BMA copolymer (mol%)	λ_{max}/nm[a] ($\varepsilon\times10^{-3}$)	
7.53	258 (3.96)	26.43	259 (18.8)	274 (17.7)
13.90	258 (3.46)	35.40	259 (17.8)	274 (16.8)
29.14	258 (3.32)	55.31	259 (16.8)	274 (16.0)
38.10	258 (2.84)	65.10	259 (10.6)	274 (10.2)
2,4-Diamino-6-methyl-1,3,5-triazine	256 (4·00)[b]	2-Amino-4-anilino-6-ethyl-1,3,5-triazine		272 (18.7)[b]
2,4-Diamino-6-ethyl-1,3,5-triazine	254 (3.00)	2-Amino-4-(*o*-toluidino)-6-isopropenyl-1,3,5-triazine		261 (12.8)[b]

a) Measured in Methyl Cellosolve. b) Measured in ethanol.

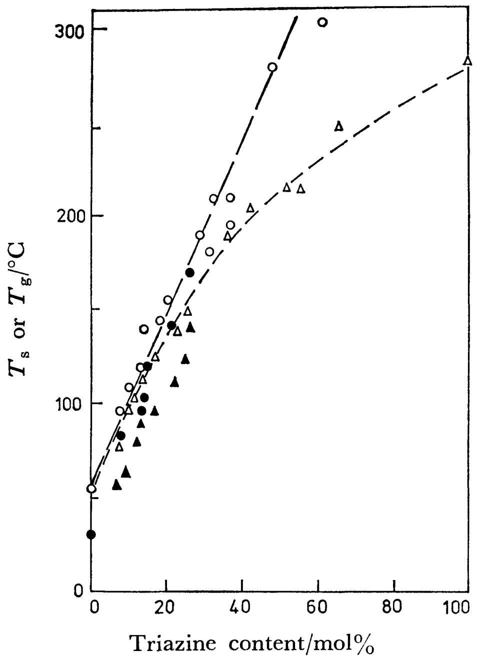

Fig. 1. The relationship between softening temperature (T_s) or glass transition temperature (T_g) and the composition of copolymer of 2,4-diamino-6-isopropenyl-1,3,5-triazine (AIPT) or 2-amino-4-anilino derivative (AAIPT) and butyl methacrylate (BMA). T_s: ○; P(AIPT-BMA), △; P(AAIPT-BMA), T_g: ●; P(AIPT-BMA), ▲; P(AAIPT-BMA).

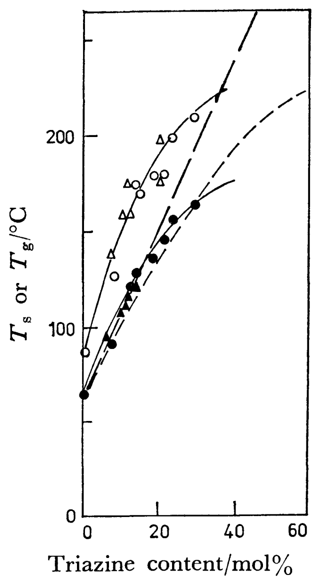

Fig. 2. The relationship between softening temperature (T_s) or glass transition temperature (T_g) and the composition of copolymer of 2,4-diamino-6-isopropenyl-1,3,5-triazine (AIPT) or 2-amino-4-anilino derivative (AAIPT) and ethyl methacrylate (EMA). T_s: ○; P(AIPT-EMA), △; P(AAIPT-EMA), T_g: ●; P(AIPT-EMA), ▲: P(AAIPT-EMA), ——: T_s of P(AIPT-BMA), - - -: T_s of P(AAIPT-BMA).

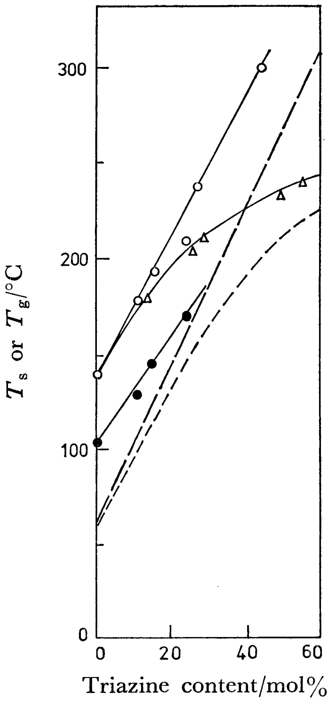

Fig. 3. The relationship between softening temperature (T_s) or glass transition temperature (T_g) and the composition of copolymer of 2,4-diamino-6-isopropenyl-1,3,5-triazine (AIPT) or 2-amino-4-anilino derivative (AAIPT) and methyl methacrylate (MMA).
T_s: ○; P(AIPT–MMA), △; P(AAIPT–MMA), T_g: ●; P(AIPT–MMA), ——: T_s of P(AIPT–BMA), - - -; T_s of P(AAIPT–BMA).

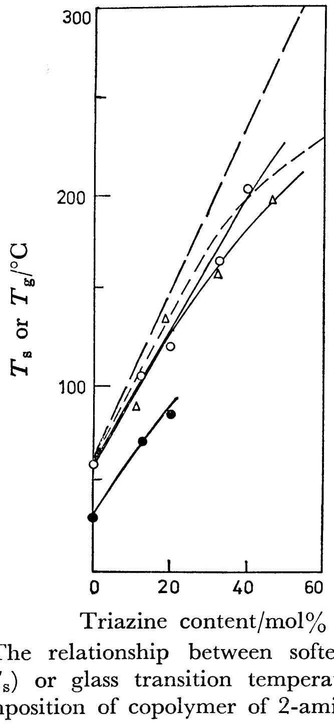

Fig. 4. The relationship between softening temperature (T_s) or glass transition temperature (T_g) and the composition of copolymer of 2-amino-4-dimethylamino-6-isopropenyl-1,3,5-triazine (DMAIPT) or 2-amino-4-(*N*-methylanilino) derivative (NMcAIPT) and butyl methacrylate (BMA).
T_s: ○; P(DMAIPT–BMA), △; P(NMeAIPT–BMA), T_g: ●; P(DMAIPT–BMA), ——; T_s of P(AIPT–BMA), - - -; T_s of P(AAIPT–BMA).

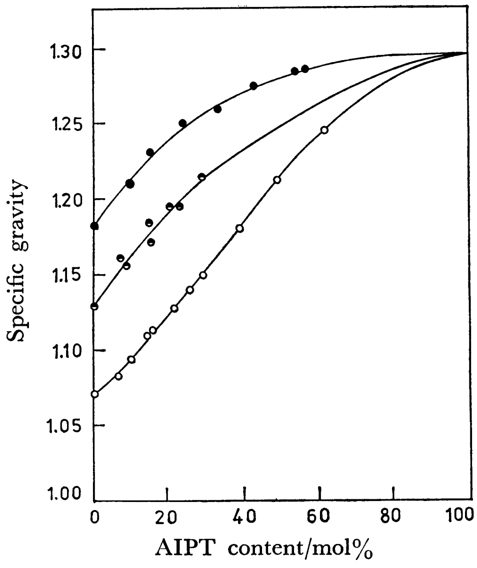

Fig. 5. The relationship between specific gravity and the composition of copolymer of 2,4-diamino-6-isopropenyl-1,3,5-triazine (AIPT) and methacrylic ester.
○: P(AIPT–BMA), ◓: P(AIPT–EMA), ●: P(AIPT–MMA).

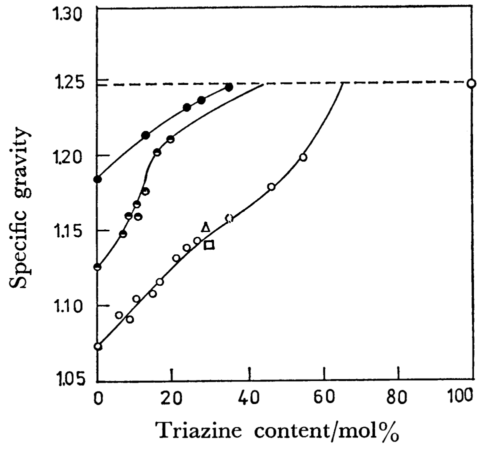

Fig. 6. The relationship between specific gravity and the composition of copolymer of 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine (AAIPT) and methacrylic ester.
○: P(AAIPT–BMA), ◓: P(AAIPT–EMA), ●: P(AAIPT–MMA), □: P(DMAIPT–BMA), △: P(NMeAIPT–BMA).

than that of polymers containing AIPT beyond 40 mol% of triazine rings.

For copolymers of isopropenyl-1,3,5-triazines and EMA, the content of AIPT or AAIPT influenced significantly on T_s or T_g. In the introduction of AIPT to poly(methyl methacrylate), T_s or T_g rose more remarkably than that of AAIPT. The effect of DMAIPT or NMeAIPT on T_s or T_g was approximately equal to that of AAIPT, as given in Fig. 4.

As a result, the introduction of triazine rings to a polymer as a pendant decreased the flexibility of the polymer chain. Specifically, the softening and glass transition points rose considerably with the increase in the content of triazine units. And interac-

TABLE 7. SOLUBILITIES OF COPOLYMERS OF 2,4-DIAMINO-6-ISOPROPENYL-1,3,5-TRIAZINE (AIPT) AND METHACRYLIC OR ACRYLIC ESTERS

Methacrylic or acrylic ester in copolymer	AIPT content in copolymer	Solubilities$^{a)}$								
		δ, 9.0 →			10.0 →		12.0 →		13.0	
	mol%	IPA	Bz	MEK	DOX	MCS	DMF	Ac.A	F.A	DMSO
Butyl methacrylate	7.53	+	++	++	++	++	++	+	−	−
	10.03	±	±	++	++	++	++	+	+	−
	20.72	−	−	−	++	++	++	+	+	+
	29.14	−	−	−	−	++	++	+	+	+
	38.10	−	−	−	−	+	−	+	+	+
Ethyl methacrylate	7.75	±	+	++	++	++	++	++	+	+
	14.20	±	−	+	++	++	++	++	+	+
	28.81	−	−	−	±	++	++	+	+	+
Methyl methacrylate	10.17	−	−	−	+	+	+	+	+	+
	26.70	−	−	−	−	±	±	++	++	+
	43.21	−	−	−	−	−	−	++	++	+
Methyl acrylate	2.27	−	±	+	±	++	+	++	++	+
	35.60	−	±	−	−	++	+	++	±	++
	57.84	−	−	−	−	±	−	++	+	+
Poly(AIPT)	100	−	−	−	−	−	−	±	+	−

a) ++: Readily soluble, +: soluble, ±: soluble on heating, −: insoluble, IPA: isopropyl alcohol, Bz: benzene, MEK: ethyl methyl ketone, DOX: dioxane, MCS: Methyl Cellosolve, DMF: *N,N*-dimethylformamide, Ac.A: acetic acid. F.A: formic acid, DMSO: dimethyl sulfoxide, δ: solubility parameter.

TABLE 8. SOLUBILITIES OF COPOLYMERS OF 2-AMINO-4-ANILINO-6-ISOPROPENYL-1,3,5-TRIAZINE (AAIPT) AND METHACRYLIC ESTERS

Methacrylic ester in copolymer	AAIPT content in copolymer	Solubilities$^{a)}$							
		δ, 9.0 →			10.0 →		12.0 →		13.0
	mol%	IPA	Bz	MEK	DOX	MCS	DMF	Ac.A	F.A
Butyl methacrylate	9.08	±	++	+	++	++	++	+	−
	13.20	±	++	+	++	++	++	+	+
	26.43	−	−	+	++	++	++	+	+
	55.31	−	−	−	+	+	+	+	+
	65.10	−	−	−	−	−	+	+	+
Ethyl methacrylate	7.27	±	+	++	++	+	+	++	−
	13.40	±	−	++	++	+	+	++	+
	20.31	−	−	±	++	+	+	++	+
Methyl methacrylate	13.24	−	+	+	+	+	++	+	+
	24.52	−	−	−	+	+	++	+	+
	49.41	−	−	−	+	+	+	+	+
Poly(AAIPT)	100	−	−	−	±	±	+	±	±

a) ++: Readily soluble, +: soluble, ±: soluble on heating, −: insoluble, δ: solubility parameter.

tions between triazine rings with two amino groups were stronger than those between triazine rings with one amino or anilino group, and phenyl groups attached to the triazine rings may act as the external plasticizer.

Further, 40—60 °C rises in Ts occurred for each 10 mol% of introduction of methacryloguanamines to poly(methyl methacrylate), whereas about 100 °C rise occurred for that of acryloguanamines.[2] This suggests that the α-methyl group weakens the interaction between aminotriazine groups.

Next, as shown in Figs. 5 and 6, specific gravities of poly(AIPT) and poly(AAIPT) were 1.296 and 1.245 respectively, which were close to that of poly(vinyl alcohol)(1.2—1.3) and poly(vinyl chloride) (1.3—1.4).

The specific gravities of copolymers of AIPT and alkyl methacrylate increased from 1.07 to 1.30 with increasing AIPT content. Moreover, specific gravities of polymers containing AAIPT increased considerably with AAIPT content and came into agreement with that of poly(AAIPT) at 40—60 mol% of triazine rings. A similar relation may hold for the copolymer containing NMeAIPT or DMAIPT.

In addition, the polymer with less than 25 mol% of triazine rings formed a very transparent flexible hard film.

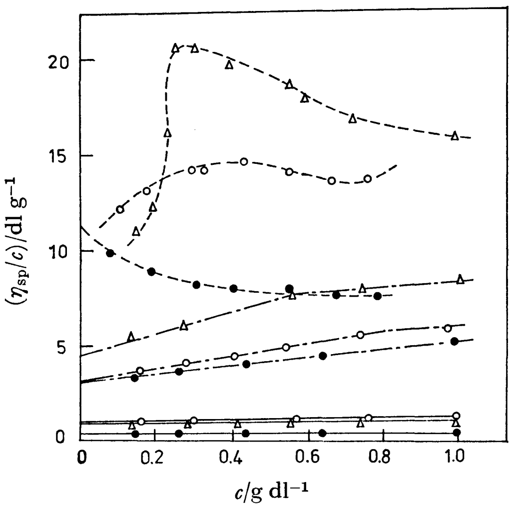

Fig. 7. The relationship between reduced viscosity and the concentration of copolymer of 2,4-diamino-6-isopropenyl-1,3,5-triazine (AIPT) and butyl methacrylate in various solvents.
Mole precent of AIPT in copolymer; ○: 7.53, △: 20.72, ●: 38.10, ——: in Methyl Cellosolve, —·—: in HCOOH+0.01 mol dm^{-3} HCOONa, – – –: in HCOOH.

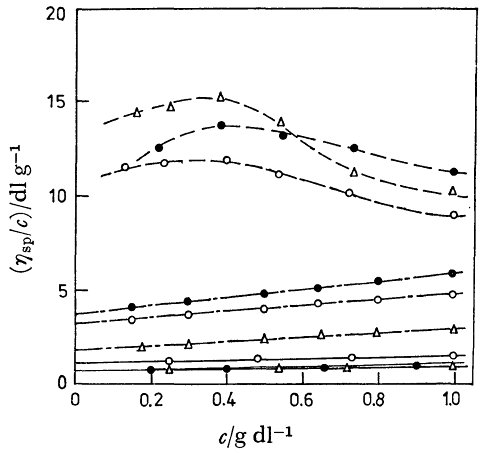

Fig. 8. The relationship between reduced viscosity and the concentration of copolymer of 2-amino-4-anilino-6-isopropenyl-1,3,5-triazine (AAIPT) and butyl methacrylate in various solvents.
Mole percent of AAIPT in copolymer; ○: 13.20, △: 26.43, ●: 35.40, ——: in dioxane, —·—: in HCOOH+0.1 mol dm^{-3} HCOONa, – – –: in HCOOH.

Since specific gravity is closely associated with index of refraction and dielectric constant, an introduction of aminotriazine rings to various polymers can be expected to improve their properties and produce materials useful industrially.

As given in Tables 7 and 8, the solubilities of copolymers of isopropenyl-1,3,5-triazines and alkyl methacrylates increased with increasing the number of carbon atoms of alkyl group.

Polymers containing below 20 mol% of AIPT were soluble in 2-propanol and polar solvents, but became insoluble in dioxane or DMF and soluble in only DMSO or organic acid at AIPT content of over 40 mol%. And even the introduction of 3 mol% of AIPT to poly(methyl acrylate) greatly decreased the solubilities, allowing effective interaction between aminotriazine groups in a very flexible polymer chain.

Further, polymers containing AAIPT were more readily soluble in organic solvents, with solubility parameter $(\delta)=10$—13. Namely, polymers containing 40—50 mol% of AAIPT were soluble in dioxane and Methyl Cellosolve. Other polymers containing 4-(substituted amino) derivatives also exhibited similar solubilities as described above.

It was noteworthy that even copolymers with 10 mol% of triazine rings were soluble in organic acids. As shown in Figs. 7 and 8, the viscosities in formic acid were 10—20 times that in dioxane or Methyl Cellosolve; these increased with dilution and had a maximum value at a certain concentration. However, the viscosities decreased linearly in formic acid–sodium formate solution.

This result indicates that the basic aminotriazine rings have affinities for acid, and hence the protonation at the nitrogen atom of the triazine ring increased the intra- and intermolecular excluded volume effects in polymer solution. Thus, polymers having triazine rings as a pendant can be utilized as polyelectrolytes.1)

In conclusion, the above-mentioned thermal and physical properties were markedly affected by the species and the number of substituted groups of triazine ring and the structure or composition of the polymer. Moreover, these effects were found to be based upon the rigidity of the basicity of triazine rings and their intra- and intermolecular interactions.

The knowledge obtained in this investigation can be available for the molecular design of polymer-containing heterocyclic rings with many nitrogen atoms.

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