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The Synthesis and Polymerization of Vinyl- and Isopropenyl-*s*-triazines

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Some new vinyl monomers with an amino-*s*-triazinyl group were synthesized. 2,4-Amino- and substituted amino-6-vinyl-*s*-triazines were synthesized by the reaction of the substituted biguanides with acrylyl chloride, while 2-amino-4-substituted amino-6-isopropenyl-*s*-triazines were prepared from the substituted biguanides with methyl methacrylate. It has been found that vinyl-*s*-triazines thermally polymerized immediately after melting and gave insoluble polymers. Polymers with amino-*s*-triazinyl groups in the side chain were obtained by the radical polymerization of some vinyl- and isopropenyl-*s*-triazines. The copolymerization of these monomers with styrene has been investigated in dimethyl sulfoxide using α,α'-azobisisobutyronitrile as an initiator. The monomer reactivity ratios were determined, and the *Q* and *e* values for these vinyl-*s*-triazines were calculated. Some discussions are presented.

A vinyl monomer with an amino-*s*-triazine ring is interesting as a reactive monomer. Overberger and Shapiro[1,2] have reported on the synthesis and polymerization of 2,4-diamino-6-vinyl-*s*-triazine and 2-amino-4-anilino-6-vinyl-*s*-triazine from the reaction of biguanide and phenylbiguanide respectively with acrylyl chloride. Thurston[3] has reported on the reaction of biguanide with methyl methacrylate to give 2,4-diamino-6-isopropenyl-*s*-triazine. We have repeated these synthesis and, in addition, synthesized various vinyl- and isopropenyl-*s*-triazines.

The polymerizations of 2,4-diamino-6-vinyl-*s*-triazine and 2-amino-4-*o*-toluidino-6-vinyl-*s*-triazine have previously been reported.[4,5] Continuing the studies of vinyl-*s*-triazines, the homopolymerization and copolymerization of several vinyl- and isopropenyl-*s*-triazines have now been investigated. In particular, the copolymerization with styrene was studied. The copolymerization of 2,4-diamino-6-vinyl-*s*-triazine hydrochloride with styrene will also be reported here.

Experimental

Materials. The aliphatic biguanides were prepared by the method of Kono and Odo.[6] The aromatic biguanides were prepared by the method of Cohn[7] from the reaction of dicyanodiamide with aromatic amines hydrochlorides in hot water. The styrene was purified by the usual method and was distilled again before use. The initiator, α,α'-azobisisobutyronitrile (AIBN), was a commercial material. The

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[1] C. G. Overberger and F. W. Michelotti, *J. Amer. Chem. Soc.*, **80**, 988 (1958).

[2] C. G. Overberger and S. L. Shapiro, *ibid.*, **76**, 1061 (1954).

[3] J. T. Thurston, U. S. 2461943 (1946); *Chem. Abstr.*, **43**, 3854 (1949).

[4] Y. Yuki, N. Hiramatsu, T. Kakurai and T. Noguchi, *Kobunshi Kagaku*, **26**, 134 (1969).

[5] Y. Yuki, T. Kakurai and T. Noguchi, *ibid.*, **26**, 141 (1969).

[6] K. Kono and K. Odo, *Yukigosei Kagaku Kyokaishi*, **20**, 649 (1962).

[7] G. Cohn, *J. Prakt. Chem.*, **84**, 394 (1911).

dimethyl sulfoxide (DMSO) was fractionally distilled under reduced pressure in the presence of nitrogen. All the other reagents were commercially available and were used after purification if necessary.

2-Amino-4-anilino-6-methyl-s-triazine. Phenylbiguanide (1.77 g, 0.01 mol) was dissolved in 4 m*l* of methanol, and then 3.7 g (0.05 mol) of methyl acetate were added. After the reaction mixture had then been allowed to stand for five days at room temperature, the methanol and excess methyl acetate were removed. The residue was washed with water to give 1.2 g (60%) of a product which melted at 173—175°C.

The other 2,4-disubstituted-6-methyl-*s*-triazines were prepared in a similar manner.

2-Amino-4-anilino-6-isopropenyl-s-triazine. To a solution of 17.7 g (0.1 mol) of phenylbiguanide in 50 m*l* of methanol, we added 15.0 g (0.15 mol) of methyl methacrylate. After the reaction mixture had been allowed to stand for six days at room temperature, the methanol was removed and water was added to give 7.1 g (34%) of a white product. The product was recrystallized from a methanol-water mixture, mp 174—175.5°C.

The other 2,4-disubstituted-6-isopropenyl-*s*-triazines were prepared in a similar manner.

2-Amino-4-anilino-6-vinyl-s-triazine. 2-Amino-4-anilino-6-vinyl-*s*-triazine and the other 2,4-disubstituted-6-vinyl-*s*-triazines were prepared in a manner similar to that previously described.[5]

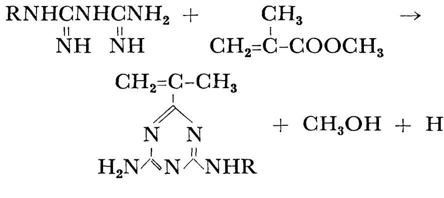
Procedure. All the polymerization experiments were carried out in a DMSO solution by AIBN at 60°C in a glass tube sealed under a vacuum. Methanol was used as a precipitant. The composition of the copolymer was calculated from the carbon and nitrogen contents.

Results and Discussion

Preparation of Monomers. The synthesis of 2,4-amino- or substituted amino-6-substituted-*s*-triazines was effected by the reaction of substituted biguanides with carboxylic acid derivatives (acid esters or acid chlorides).[8]

Methyl-*s*-triazines were synthesized for the model compounds of vinyl-*s*-triazines according to the directions of Overberger and Shapiro.[9] The results are shown in Table 1.

Isopropenyl-*s*-triazines were given by the reaction of substituted biguanides with methyl methacrylate in methanol,



The results are shown in Table 2.

Vinyl-*s*-triazines were prepared from the reaction of the substituted biguanides with acrylyl chloride in acetone at a low temperature, as has previously been reported in the case of 2-amino-4-*o*-toluidino-6-vinyl-*s*-triazine.[5] The results are shown in Table 3.

The UV absorption data of *s*-triazines determined in ethanol are given in Table 4. When 2- and 4-substituents are amino or alkyl amino groups, the vinyl- and isopropenyl-*s*-triazines show a bathochromic shift compared with methyl-*s*-triazines. This is probably due to the conjugation of the double bond with the triazine nucleus. On the other hand, when the 4-substituents are aryl amino groups, the vinyl- and isopropenyl-*s*-triazines show a hypsochromic shift. Overberger and Shapiro[11] found this same effect on 2-amino-4-anilino-6-vinyl-*s*-triazine. These results indicate little conjugation of 4-aryl amino groups.

The thermal behavior of vinyl- and isopropenyl-*s*-triazines was studied by the techniques of differential thermal analysis (DTA) and thermogravimetric analysis (TGA). 2,4-Diamino-6-vinyl-*s*-triazine was reported to be decomposed without melting at 300—310°C[1] Figure 1 shows the DTA and TGA curves of 2,4-diamino-6-vinyl-*s*-triazine. It was found that 2,4-diamino-6-vinyl-*s*-triazine was gradually sublimed above 170°C and was thermally polymerized at about 260°C without melting. This thermally-polymerized product was insoluble, but it swelled in formic acid. Its IR spectrum was identical with that of the polymer obtained by the solution polymerization using AIBN in DMSO.[4] All the other vinyl-*s*-triazines,

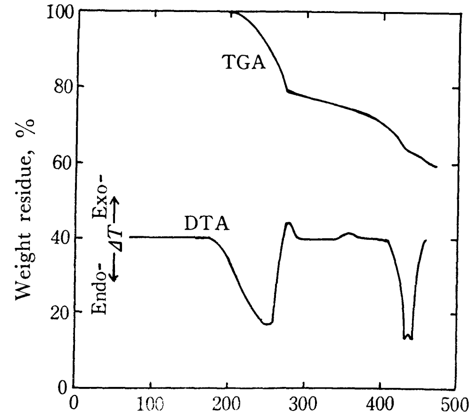


Fig. 1. Thermal analysis of 2,4-diamino-6-vinyl-*s*-triazine in air.
TGA (5°C/min), DTA (20°C/min)

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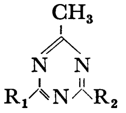
[8] E. M. Smolin and L. Rapoport, "*s*-Triazines and Derivatives" Interscience Publishers, New York (1959), p. 226.

[9] C. G. Overberger and S. L. Shapiro, *J. Amer, Chem. Soc.*, **76**, 93 (1954).

[10] S. L. Shapiro, E. S. Isaacs, V. A. Parrino and L. Freedman, *J. Org. Chem.*, **26**, 68 (1961).

[11] C. G. Overberger and S. L. Shapiro, *J. Amer. Chem. Soc.*, **76**, 1855 (1954).

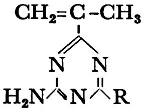
TABLE 1. 6-METHYL-*s*-TRIAZINE DERIVATIVES



R_1, R_2	Yield (%)	Mp[a] (lit.) (°C)	Found (Calcd.)		
			C (%)	H (%)	N (%)
R_1=NH_2					
R_2=NHC_6H_5	60	173—175 (176—177[6])			
$NHC_6H_4CH_3$(*p*)	67	204—205 (211—213[10])			
$NHC_6H_4OCH_3$(*p*)	65	213—214 (213—214[10])			
NHC_6H_4Cl(*p*)	27	195.5—196 (194—196[10])			
$NHC_6H_4NHCOCH_3$(*p*)	29	268—269	55.88 (55.81)	5.21 (5.43)	32.49 (32.56)
$NHC_6H_4COOC_2H_5$(*p*)	30	246—247	57.27 (57.14)	5.27 (5.49)	25.89 (25.64)
$NHC_6H_4CH_2CN$(*p*)	50	220—221	60.16 (60.01)	5.29 (5.00)	34.99 (34.96)
$NHC_6H_4NO_2$(*m*)	42	222—223	49.16 (48.76)	3.96 (4.09)	33.86 (34.13)
NHC_6H_4CN(*m*)	36	228—229	58.73 (58.40)	4.28 (4.46)	37.27 (37.15)
$N(CH_3)C_6H_4$	47	156—157	61.43 (61.68)	5.98 (6.07)	32.29 (32.71)
$N(C_6H_5)_2$	69	188.5—189.5	69.59 (69.31)	5.29 (5.42)	25.23 (25.27)
R_1=R_2=NHC_6H_5	35	233.5—235	68.75 (69.30)	5.39 (5.45)	25.31 (25.25)

a) Recrystallized from methanol-water or methyl cellosolve-water mixture.

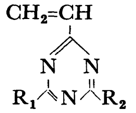
TABLE 2. 2-AMINO-4-SUBSTITUTED-6-ISOPROPENYL-*s*-TRIAZINES

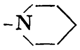


R	Yield (%)	Mp[a] (°C)	Found (Calcd.)		
			C (%)	H (%)	N (%)
NH_2	10	247—248[b]	48.31 (47.67)	5.93 (6.00)	45.93 (46.33)
$N(CH_3)_2$	19	191—192	53.89 (53.61)	7.37 (7.31)	38.85 (39.08)
NHC_6H_5	34	174—175.5	62.81 (63.42)	5.83 (5.77)	30.43 (30.81)
$NHC_6H_4CH_3$(*p*)	14	166.5—168	63.77 (64.70)	5.89 (6.27)	28.43 (29.03)
$NHC_6H_4NHCOCH_3$(*p*)	36	144.5—145	55.09 (55.26)	5.75 (5.30)	27.62 (27.62)
$NHC_6H_5CH_3$(*o*)	5	186.5—187.5			28.69 (29.03)
$N(CH_3)C_6H_5$	16	170.5—171	65.05 (64.70)	6.33 (6.27)	29.09 (29.03)
$N(C_6H_5)_2$	54	117—119	71.79 (71.27)	5.80 (5.65)	23.32 (23.09)

a) Recrystallized from methanol-water mixture.
b) Lit,[3] 246—247°C.

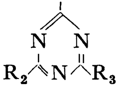
TABLE 3. 6-VINYL-*s*-TRIAZINE DERIVATIVES

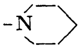


R_1, R_2	Yield (%)	Mp[a] (°C)	Found (Calcd.)		
			C (%)	H (%)	N (%)
$R_1=NH_2$					
$R_2=NHCH_3$	31	152—153	47.78 (47.67)	5.96 (6.00)	46.57 (46.33)
$N(CH_3)_2$	26	191—192	50.33 (50.89)	6.83 (6.71)	42.80 (42.39)
	poor	170—171	58.52 (58.52)	7.28 (7.37)	34.20 (34.12)
NHC_6H_5	15	174—175.5[b]	61.72 (61.96)	5.07 (5.20)	32.73 (32.84)
$NHC_6H_4CH_3(p)$	29	180—181	63.79 (63.42)	6.17 (5.77)	30.04 (30.81)
$NHC_6H_4OCH_3(p)$	25	190.5—191.5	58.56 (59.26)	5.65 (5.39)	27.49 (28.79)
$NHC_6H_4CN(p)$	10	181—183	60.81 (60.50)	4.37 (4.23)	35.40 (35.27)
$N(CH_3)C_6H_5$	26	141.5—143	63.75 (63.42)	5.84 (5.77)	30.41 (30.81)
$R_1=R_2=NHC_6H_5$	12	166—167	71.02 (70.57)	4.81 (5.23)	24.16 (24.20)

a) Recrystallized from methanol-water mixture.
b) Lit,[2] 180—181°C.

TABLE 4. ULTRAVIOLET ABSORPTION SPECTRA OF *s*-TRIAZINE



R_2, R_3	R_1 λ_{max}[a] (mμ) ($\varepsilon \times 10^{-3}$)		
	$CH=CH_2$	$C(CH_3)=CH_2$	CH_3
$R_2=NH_2$,			
$R_3=NH_2$	281 (3.2)	276 (3.8)	256 (4.0)[b]
$NHCH_3$	290 (3.5)		
$N(CH_3)_2$	296 (3.5)	292 (4.2)	264 (5.0)
	299 (3.9)		
NHC_6H_5	257 (19.4)[c]	256 (28.8)	270 (22.8)[d]
$NHC_6H_4CH_3(p)$	259 (25.7)	258 (33.7)	270 (21.0)
$NHC_6H_4OCH_3(p)$	262 (22.3)		273 (20.0)
$NHC_6H_4CN(p)$	297 (28.4)		
$NHC_6H_4NHCOCH_3(p)$		276 (32.7)	287 (28.3)
$NHC_6H_4CH_3(o)$	shoulder	shoulder	shoulder
$N(CH_3)C_6H_5$	shoulder	shoulder	shoulder
$N(C_6H_5)_2$		shoulder	255 (17.8)
$R_2=R_3=NHC_6H_5$	267 (41.1)		271 (42.8)

a) Measured in ethanol.
b—d) Ref. 11. b) 252—256 (3.2) in water, c) 255 (22.5) in methanol, d) 271 (20.38) in methanol.

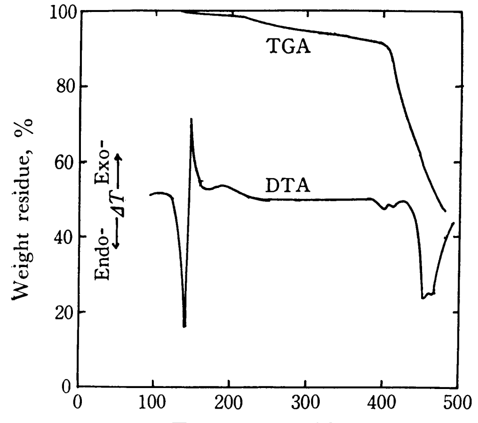


Fig. 2. Thermal analysis of 2-amino-4-*N*-methylanilino-6-vinyl-*s*-triazine in air.
TGA (5°C/min), DTA (20°C/min)

which gave a sharp melting point, were found, by a study of DTA and TGA curves, to polymerize immediately after melting. The curves of 2-amino-4-*N*-methylanilino-6-vinyl-*s*-triazine are shown in Fig. 2 as a typical example. After the exotherm, no double-bond absorption was observed in the IR spectra of the heated samples. This polymer was also insoluble. On the other hand, no thermal polymerization of isopropenyl-*s*-triazines was observed, even after its melting.

Polymerization. The results of the homopolymerization of some vinyl- and isopropenyl-*s*-triazines by AIBN in DMSO are presented in Tables 5 and 6 respectively. Poly-2-amino-4-methylamino-6-vinyl-*s*-triazine and poly-2,4-diamino-6-isopropenyl-*s*-triazine were insoluble in common organic solvents, but they were soluble in formic acid, acetic acid, and mineral acid. The polymerization of 2-amino-4-dimethylamino-6-vinyl-*s*-triazine proceeded homogeneously, but the polymer isolated was insoluble in DMSO. The polymers containing aryl amino groups were soluble in DMSO, DMF, DMA, and dioxane.

TABLE 5. POLYMERIZATION OF VINYL-*S*-TRIAZINES

Monomer 2-amino-4-substituted-6-vinyl-*s*-triazine	Conversion (%)	η_{sp}/C b) in	
		DMSO	formic acid
4-Methylamino	38	insoluble	1.34
4-Dimethylamino	75	insoluble	0.58
4-Anilino	56	0.23	0.59
4-*p*-Toluidino	51	0.30	
4-*p*-Anisidino	20a)	0.12	0.17
4-*N*-Methylanilino	86	0.10	0.21

Polymerization conditions; $[M]=0.20\ \mathrm{mol}/l$, $[\mathrm{AIBN}]=1.35\times10^{-3}\ \mathrm{mol}/l$, at 60°C, 5 hr.
a) 3 hr. b) $C=0.3\ \mathrm{g/d}l$, at 30°C.

TABLE 6. POLYMERIZATION OF ISOPROPENYL-*S*-TRIAZINES

Monomer 2-amino-4-substituted-6-isopropenyl-*s*-triazine	Conversion a) (%)	η_{sp}/C b) in	
		DMSO	formic acid
4-Amino	31	insoluble	12.2
4-Anilino	43	0.82	4.2
4-*N*-Methylanilino	62	0.67	3.4

a) Polymerization conditions: $[M]=0.40\ \mathrm{mol}/l$, $[\mathrm{AIBN}]=1.35\times10^{-3}\ \mathrm{mol}/l$, at 60°C, 5 hr.
b) $C=0.2\ \mathrm{g/d}l$, at 30°C.

Copolymerization. The copolymerization of vinyl- and isopropenyl-*s*-triazines with styrene were carried out at 60°C in DMSO. The polymerization conditions were as follows; $[M_1]+[M_2]=0.20\ \mathrm{mol}/l$ and $[\mathrm{AIBN}]=1.35\times10^{-3}\ \mathrm{mol}/l$. The polymerization proceeded homogeneously. The rates of copolymerization decreased as the styrene contents in the monomer mixtures increased. The relationship between the composition of the monomer feeds and that of the copolymers is summarized in Tables 7 and 8. The copolymerization of 2,4-dianilino-6-vinyl-*s*-triazine with styrene gave a colloidal solution when the reaction mixture was poured in methanol, and the copolymer was not isolated quantitatively.

The η_{sp}/C values of several copolymers were measured in DMSO and in formic acid. The η_{sp}/C values of the copolymers in formic acid increased as the *s*-triazine content in copolymers increased.

The copolymers of 2,4-diamino-6-vinyl-*s*-triazine hydrochloride with styrene were not precipitated in methanol, but they were isolated by the addition of aqueous ammonia. The results are shown in Table 7. On the basis of these data, the

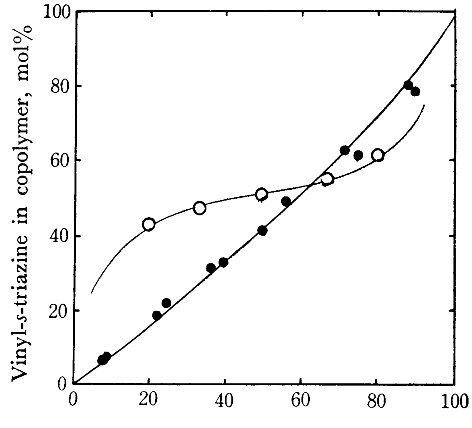


Fig. 3. Monomer-copolymer composition curves for styrene with 2,4-diamino-6-vinyl-*s*-triazine hydrochloride (○) and free base (●).[4] — calcd.

TABLE 7. COPOLYMERIZATION OF VINYL-*s*-TRIAZINES (M_2) WITH STYRENE (M_1)

M_2 in monomer (mol%)	Reaction time (hr)	Yield (%)	M_2 in polymer (mol%)	η_{sp}/C a) in	
				DMSO	formic acid
M_2: 2-Amino-4-*N*-methylanilino-6-vinyl-*s*-triazine					
79.54	3	17.3	74.09	0.45	2.02
66.03	3.66	11.2	63.23	0.56	2.47
49.29	3.66	16.8	51.12	0.48	2.32
32.70	4.5	14.6	38.09	0.44	1.39
19.55	6	13.4	27.11	0.37	0.79
M_2: 2-Amino-4-*p*-toluidino-6-vinyl-*s*-triazine					
79.54	3	12.0	63.80	0.52	1.55
66.03	3.17	11.2	53.57	0.52	1.61
49.29	3.5	9.3	40.66	0.54	1.61
32.70	4	1.8	30.27	—	—
19.55	5.5	8.8	20.60	0.40	0.33
M_2: 2-Amino-4-*p*-anisidino-6-vinyl-*s*-triazine					
79.83	3	10.5	64.05	0.40	1.33
66.43	3.25	10.8	53.09	0.40	1.27
49.73	4	2.5	41.67	—	—
33.10	4.5	8.5	29.56	0.34	0.86
19.83	6	9.3	20.72	0.27	0.30
M_2: 2-Amino-4-*p*-cyanoanilino-6-vinyl-*s*-triazine					
72.99	3	11.2	58.26	0.52	1.16
59.04	4	12.2	50.41	0.51	1.27
44.77	5.33	13.1	41.38	0.52	1.15
30.19	6.5	9.5	30.90	—	0.80
11.90	8	9.2	15.04	0.21	0.13
M_2: 2-Amino-4-dimethylamino-6-vinyl-*s*-triazine					
79.72	3	20.1	77.20	b)	2.46
66.28	3.33	14.4	66.26	b)	2.37
49.57	4	14.7	54.57	0.38	—
32.95	4.75	10.6	37.74	0.29	—
19.73	6	7.7	22.59	0.24	0.49
M_2: 2,4-Diamino-6-vinyl-*s*-triazine hydrochloride					
79.89	3	5.6	61.69	0.45	—
66.52	5.5	19.5	55.89	0.37	2.14
49.83	5.5	23.4	51.65	0.53	2.42
33.18	6.5	31.5	47.89	0.31	2.47
19.89	7	36.2	42.28	0.41	2.88

a) Measured $C=0.2$ g/d*l* at 30°C.
b) Insoluble.

monomer-copolymer composition curves are drawn in Fig. 3; they are shown in comparison with the free base previously reported on.4)

The monomer reactivity ratios were determined by the method of Fineman and Ross.[*2] The values obtained are given in Tables 9 and 10. Assuming $Q=1.0$ and $e=-0.8$ for styrene, the Q-e values for vinyl- and isopropenyl-*s*-triazines were calculated. These are summed up in Table 9 for vinyl-*s*-triazines and in Table 10 for isopropenyl-*s*-triazines.

In general, the *s*-triazinyl group acts as an electron-withdrawing group because of the electron-attracting character of nitrogen atoms. This is why 2,4-dimethyl-6-vinyl-*s*-triazine has a positive *e* value.12) However, the negative *e* values obtained for 2,4-amino and alkylamino derivatives may be due to the presence of two strong electron-donating groups attached to the triazine ring. The

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[*2] In the case of copolymerization of 2,4-diamino-6-vinyl-*s*-triazine hydrochloride with styrene, the integral method of Mayo and Lewis was used.

12) A. T. Coscia, R. L. Kugel and J. Pellon, *J. Polymer Sci.*, **55**, 303 (1961).

Table 8. Copolymerization of vinyl-*s*-triazines or isopropenyl-*s*-triazines (M_2) with styrene (M_1)

M_2 in monomer (mol %)	Reaction time (hr)	Yield (%)	M_2 in polymer (mol %)
M_2: 2-Amino-4-anilino-6-vinyl-*s*-triazine			
75.0	3.25	12.0	58.1
62.5	3.33	10.2	49.9
50.0	3	6.7	44.6
50.0	4	9.8	42.7
37.5	5	9.5	37.5
25.0	3.25	5.1	27.6
M_2: 2,4-Dianilino-6-vinyl-*s*-triazine			
75.6	3.5	—	64.7
63.1	4.5	—	56.9
50.6	3	—	48.9
50.6	5	—	43.5
38.1	5.5	—	49.4
25.5	6	—	30.9
M_2: 2,4-Diamino-6-isopropenyl-*s*-triazine			
74.27	3	8.3	72.60
65.81	3.66	10.0	68.25
49.04	5.66	10.6	53.54
32.48	6.33	6.8	39.25
19.39	7	7.3	24.35

M_2 in monomer (mol %)	Reaction time (hr)	Yield (%)	M_2 in polymer (mol %)
M_2: 2-Amino-4-dimethylamino-6-isopropenyl-*s*-triazine			
71.92	4	13.3	78.04
58.73	4	12.4	67.31
39.04	4.5	8.9	57.64
25.46	5	7.2	42.08
M_2: 2-Amino-4-anilino-6-isopropenyl-*s*-triazine			
74.95	3	12.5	77.38
66.61	3	10.3	68.37
49.94	3.17	7.7	55.77
33.28	3.66	6.6	44.38
19.96	4.25	6.3	30.68
M_2: 2-Amino-4-*N*-methylanilino-6-isopropenyl-*s*-triazine			
74.38	3	25.6	83.05
61.73	3	19.1	72.88
42.06	3.17	13.6	58.49
24.39	4	10.7	43.20
10.79	5	8.3	25.85

Table 9. The copolymerization parameters of vinyl-*s*-triazines (M_2)

6-Vinyl-*s*-triazine	r_1	r_2	Q	e
2,4-Diamino-[4]	1.30	0.65	0.55	−0.38
2-Amino-4-dimethylamino-	0.70	0.81	0.78	−0.05
2-Amino-4-*o*-toluidino-[5]	0.45	0.93	1.05	0.13
2-Amino-4-*N*-methylanilino-	0.50	0.58	0.82	0.31
2-Amino-4-*p*-toluidino-	0.80	0.30	0.48	0.40
2-Amino-4-*p*-anisidino-	0.78	0.29	0.48	0.42
2,4-Dianilino-	0.53	0.40	0.70	0.45
2-Amino-4-*p*-cyanoanilino-	0.64	0.31	0.57	0.47
2-Amino-4-anilino-	0.60	0.24	0.55	0.59
2,4-Dimethyl-[12]	0.12	0.92	2.54	0.68*
2,4-Diamino-, hydrochloride	0.09	0.14	2.08	1.29

* Coscia reported $Q=2.1$ and $e=0.92$.

Table 10. The copolymerization parameters of isopropenyl-*s*-triazines (M_2)

6-Isopropenyl-*s*-triazine	r_1	r_2	Q	e
2,4-Diamino-	0.66	0.97	0.89	−0.13
2-Amino-4-*N*-methylanilino-	0.29	1.39	1.80	0.01
2-Amino-4-dimethylamino-	0.32	1.17	1.45	0.16
2-Amino-4-anilino-	0.39	0.78	1.07	0.29

slight effect of the *p*-substituents of substituted anilino groups on the *e* values and the positive *e* values of these monomers show a weak conjugation of anilino groups with a double bond through the triazine nucleus; these results coincide with those of the UV spectra.

The positive *e* value of 2,4-diamino-6-vinyl-*s*-triazine hydrochloride shows that the *s*-triazinyl cation is a strong electron-withdrawing group. It is very interesting to be able to change the *Q*-*e* values easily by using the salt of the monomer.

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