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Polyamides and Polyureas Containing *s*-Triazine Rings

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Several new aromatic diamines containing *s*-triazine rings were prepared by the reaction of the related dinitro-compounds prepared from biguanide derivatives and carboxylic acid chlorides. Polyamides and polyureas containing amino-*s*-triazine were synthesized by the polycondensation of these diamines with dicarboxylic acid chlorides and diisocyanates respectively. Their preparations and physical properties are described.

Among many studies for preparing thermally-stable organic polymers, the syntheses of polyamides containing heterocyclic rings from dicarboxylic acid chlorides and diamines with heterocyclic rings have been reported recently.[1)]

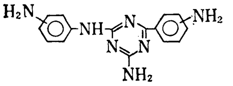
$$NH_2R(Het)R'NH_2 + ClCOR''COCl \longrightarrow$$

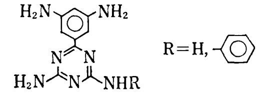
$$\text{-(-}NHR(Het)R'NHCOR''CO\text{-)-} + 2HCl$$

where Het is a heterocyclic ring.

This paper will describe the preparation of several new aromatic diamines, polyamides, and polyureas containing *s*-triazine rings.

Diamines of two types were prepared, that is, 2-amino-4-aminoanilino-6-aminophenyl-*s*-triazine and 2-amino-4-amino- or anilino-6-(3,5-diaminophenyl)-*s*-triazine. The former gave the polymers containing *s*-triazine in a main chain, while the latter gave the polymers containing it in a side chain.

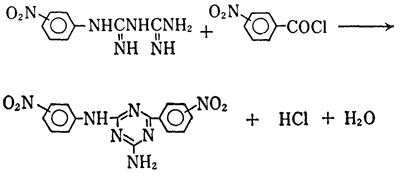




An amino group on *s*-triazine has a character like that of an amino group in the amide group because of the electron-attraction of the *s*-triazine ring, and it does not react with carboxylic acid chloride at low temperatures.[2)] In this study, an amino group on *s*-triazine was found not to be subject to a reaction with carboxylic acid chloride or isocyanate.

Results and Discussion

Preparation of Diamines. It is well known that 2-amino-4-substituted amino-6-substituted-*s*-triazines can be prepared by the reaction of substituted biguanides with carboxylic acid chlorides. The dinitro-compounds containing *s*-triazine rings were thus synthesized. 2-Amino-4-nitroanilino-6-nitrophenyl-*s*-triazine was prepared in a good yield by the reaction of nitrophenylbiguanide with nitrobenzoyl chloride. The reaction can be written as follows;



2-Amino-4-amino- or anilino-6-(3,5-dinitrophenyl)-*s*-triazine was prepared from biguanide or phenylbiguanide and 3,5-dinitrobenzoyl chloride.

These dinitro-compounds were then reduced to give diamines with tin and hydrochloric acid in ethanol. Some physical and analytical data of the reduced products are shown in Table 1. The yields were almost quantitative except in the case of 2,4-diamino-6-(3,5-diaminophenyl)-*s*-triazine (17%). Thurston[3)] has reported the synthesis of 2-amino-4-*p*-aminoanilino-6-*p*-aminophenyl-*s*-triazine dihydrochlorides.

A comparison of the UV spectra of these diamines and of 2-amino-4-anilino-6-phenyl-*s*-triazine ($\lambda_{max} = 260\ m\mu$, $\varepsilon = 43.4 \times 10^3$ in ethanol[4)]) indicated the bathochromic effect of the *p*-aminophenyl group attached directly to the triazine ring.

Preparation of Polyamides. The low-temperature-solution polycondensation using organic

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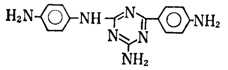
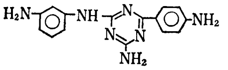
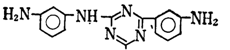
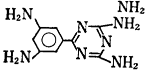
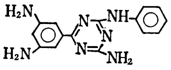
1) a) J. Preston and W. B. Black, *J. Polym. Sci., Part C*, **19**, 17 (1967). b) Y. Iwakura, K. Uno, Y. Imai and M. Fukui, *Makromol. Chem.*, **77**, 41 (1964).

2) E. M. Smolin and L. Rapoport, "*s*-Triazines and Derivatives," Interscience Publishers, New York (1959), p. 333.

3) J. T. Thurston, U. S. 2447440 (1948); *Chem. Abstr.*, **42**, 9196c (1948).

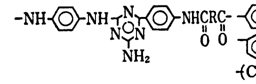
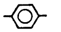
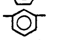
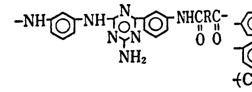
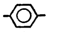
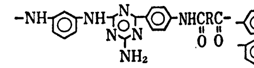
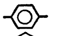
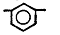
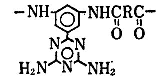
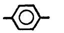
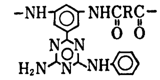
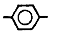
4) Y. Yuki, T. Kakurai and T. Noguchi, *Yuki Gosei Kagaku Kyokai Shi*, **26**, 1119 (1968).

TABLE 1. DIAMINES CONTAINING *s*-TRIAZINE RINGS

Diamine	No.	Mp (°C)	Found (Calcd.) C(%)	H(%)	N(%)	UV spectra c) λ_{max} (mμ) ($\varepsilon\times10^{-3}$)
	I	231—231.5	61.50 (61.42)	5.12 (5.15)	32.89 (33.43)	316(39.7)
	II	211.5—212	61.29 (61.42)	4.98 (5.15)	32.75 (33.43)	320(39.7)
	III	158.5—159	60.90 (61.42)	4.89 (5.15)	32.98 (33.43)	237 (53.9) 256^s(35.4) 306 (10.7)
	IV	258—259.5	47.36 (47.78)	5.33 (5.35)	42.54 (43.34)a)	254^s(16.4) 284 (8.2)
	V	126—127	58.45 (58.05)	5.12 (5.20)	31.57 (31.59)b)	256 (30.1) 294 (15.2)

a) Calcd. for $C_9H_{11}N_7\cdot\frac{1}{2}H_2O$
b) Calcd. for $C_{15}H_{15}N_7\cdot H_2O$
c) Measured in methyl cellosolve

TABLE 2. POLYAMINDES CONTAINING *s*-TRIAZINE RINGS

Polymer	R	No.	η_{sp}/C a)	Elementaly analysis b) C(%)	H(%)	N(%)
		1	0.41	60.31	3.77	21.79
		2	0.38	59.93	3.76	20.81
	$-(CH_2)_4-$	3	0.29	58.11	5.43	21.82
		4	0.17	60.52	3.54	21.22
		5	0.26	60.13	3.59	20.67
	$-(CH_2)_4-$	6	0.17	58.62	5.51	21.69
		7	0.18	60.56	4.24	21.96
		8	0.52	61.50	4.17	21.18
	$-(CH_2)_4-$	9	0.22	59.23	5.36	23.79
		10	0.14	48.37	4.84	21.90
		11	0.33	49.73	4.78	23.81
		12	0.12	58.91	4.60	20.86
		13	0.19	58.58	4.38	20.27

a) Measured in DMSO at 30°C, $C=0.3$ g/d*l*.
b) Calcd for $C_{23}H_{17}N_7O_2\cdot2H_2O$: C, 60.12; H, 4.61; N, 21.34; about No. 1, 2, 4, 5, 7, and 8
for $C_{21}H_{21}N_7O_2\cdot2H_2O$: C, 57.40; H, 5.69; N, 22.32; about No. 3, 6, and 9
for $C_{17}H_{13}N_7O_2\cdot3H_2O$: C, 50.83; H, 3.99; N, 24.44; about No. 10 and 11
for $C_{23}H_{17}N_7O_2\cdot3H_2O$: C, 57.86; H, 4.82; N, 20.55; about No. 12 and 13

polar solvents is well known to be effective in preparing high-molecular-weight polyamides from aromatic diamines and dicarboxylic acid chlorides. This procedure was used here. The diamines used are described in Table 1; the carboxylic acid chlorides used were terephthaloyl chloride, isophthaloyl chloride, and adipoyl chloride.

The results of the preparation of polyamides by the solution polycondensation using dimethylacetamide (DMA) as a solvent are shown in Table 2. The polyamides were obtained almost quantitatively and were all a white powder except the No. 1 (yellow) and 2 (yellow) polymers. Poly-*m*-phenylene isophthalamide was prepared for the purpose of comparison.

Properties of Polyamides. Figure 1 shows the IR spectra of several polyamides. The spectra of the model compound, 2-amino-4-anilino-6-*p*-benzamidophenyl-*s*-triazine, and 2-amino-4-*p*-aminoanilino-6-*p*-aminophenyl-*s*-triazine are also shown. The bands at 815, 1390, and 1500—1600 cm^{-1} are characteristic of the amino-*s*-triazine ring. In polyamides and the model compound, the bands of amide I and amide II are masked by

Table 3. Solubilities of polyamides

Solvent	Polymer												
	1	2	3	4	5	6	7	8	9	10	11	12	13
DMF	++[a]	++	++	++	++	++	++	++	++	+	+	++	++
DMA	++	++	++	++	++	++	++	++	++	++	++	++	++
DMSO	++	++	++	++	++	++	++	++	++	++	++	++	++
Methyl cellosolve	+	++	++	++	++	++	+	++	+	−	−	+	+
Formic acid	+	+	+	+	+	++	+	+	++	++	++	++	++
Acetic acid	−	+	+	+	−	+		+		−	−	+	+
Sulfuric acid	++	++	++	++	++	++	++	++	++	++	++	++	++

a) ++; soluble. +; partially soluble or swelling. −; insoluble.

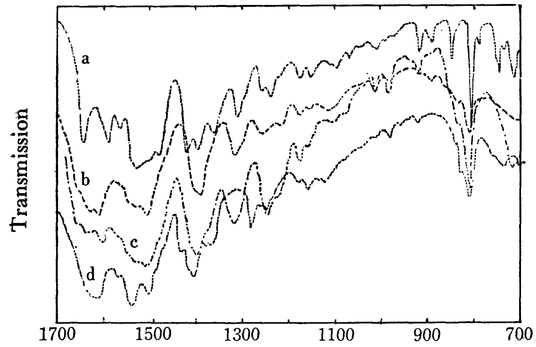


Fig. 1. IR spectra (KBr).

a : the model compound (2-amino-4-anilino-6-*p*-benzamidophenyl-*s*-triazine)
b : polyamide No. 1, c : polyamide No. 2,
d : 2-amino-4-*p*-aminoanilino-6-*p*-aminophenyl-*s*-triazine

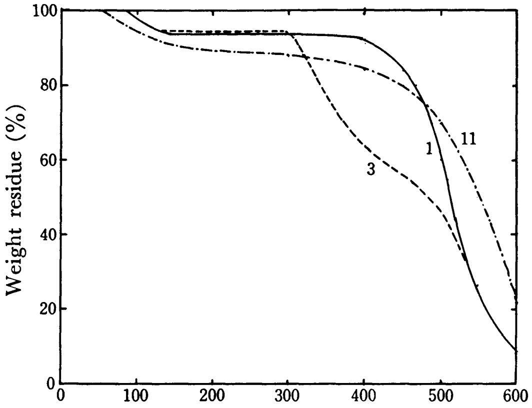


Fig. 2. TGA of some polyamide.

ΔT=5°C/min, in air, No. of polymer are shown in Table 2.

the broad bands of amino-*s*-triazine, but the band of amide III at 1320 cm^{-1} is present.

The solubilities of the polyamides are shown in Table 3. These polyamides were soluble in DMF, DMSO, DMA, and sulfuric acid, but were insoluble in the usual organic solvents. These results show that these polymers are linear and that the amino group on *s*-triazine is free.

The thermal stabilities of these polyamides were determined by thermogravimetric analysis (TGA) and by differential thermal analysis (DTA). The TGA curves of some typical polymers are shown in Fig. 2. The TGA curves of the Nos. 2, 4, 5, 7, and 8 polymers are like of No. 1, those of Nos. 6 and 9 were like that of No. 3, and those of Nos. 10, 12, and 13 were like that of No. 11. The aromatic polyamides containing *s*-triazines in the main chain showed a good thermal stability and began to decompose above 450°C. On the other hand, those containing *s*-triazines in the side chain gradually decomposed above 300°C, like poly-*m*-phenylene isophthalamide. The data of the thermal analysis of polyamides are summed up in Table 4.

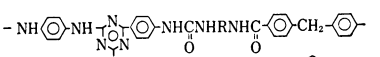
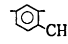
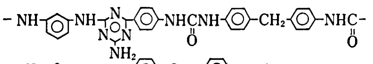
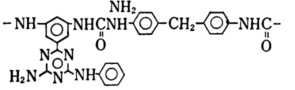
Table 4. Thermal properties of polyamides

Polymer	DTA (°C)		Decomp.[a]	TGA (°C) 5% weight loss
No.	Tg.	Mp		
1	325	410	470	445
2	315	425	455	440
3	215	320	330	320
4	300	430	460	—
5	280	435	465	480
6	215	325	420	365
7	265	438	475	430
8	295	—	465	435
9	200	340	385	360
10	325	—	420[b]	380
11	350	—	400[b]	410
12	240	450	500	420
13	280	445	475	440

a) A top of exothermic peak
b) Arising point of exothermic peak

Preparation of Polyureas. The polyureas were prepared by the polyaddition of diamines containing *s*-triazine with diisocyanates in DMA. The results are shown in Table 5. The polymers

Table 5. Polyureas containing *s*-triazines

Polymer	R	No.	Condition (°C/hr)	η_{sp}/C[a]	Found (calcd) C(%)	H(%)	N(%)
		14	0/5	0.17	63.50 (62.18)	5.22 (5.01)	21.15 (21.76)[b]
		15	0/7	0.14	57.79 (57.26)	5.80 (4.97)	23.74 (25.05)[c]
	$-(CH_2)_6-$	16	0/7	0.31	56.91 (55.53)	6.45 (6.24)	25.62 (25.05)[d]
		17	15/8	0.16	62.28 (62.18)	5.20 (5.01)	21.50 (21.76)[b]
		18	15/8	0.16	58.41 (58.53)	5.71 (5.40)	19.57 (20.47)[e]

a) Measured in DMSO at 30°C, $C=0.3$ g/d*l*.
b) Calcd for $C_{30}H_{25}N_9O_2 \cdot 2H_2O$
c) Calcd for $C_{24}H_{21}N_9O_2 \cdot 2H_2O$
d) Calcd for $C_{23}H_{27}N_9O_2 \cdot 2H_2O$
e) Calcd for $C_{30}H_{25}N_9O_2 \cdot 4H_2O$

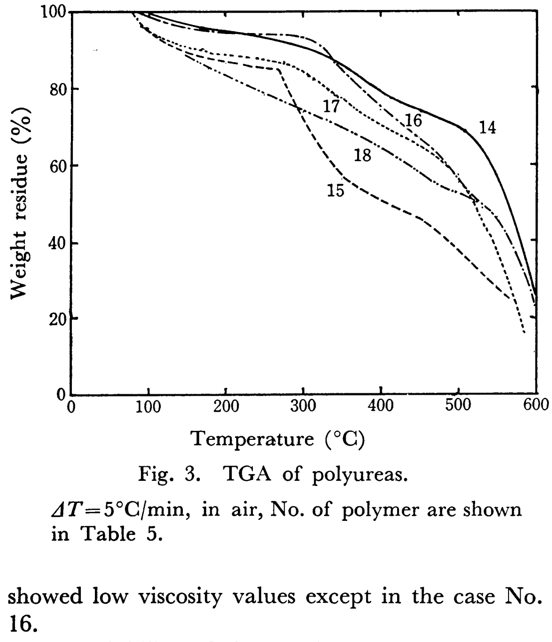


Fig. 3. TGA of polyureas.

$\Delta T = 5$°C/min, in air, No. of polymer are shown in Table 5.

showed low viscosity values except in the case No. 16.

The solubility of these polyureas was like that of the above polyamide, and they were soluble in DMSO, DMA, DMF, formic acid, acetic acid, and mineral acid.

The TGA curves of these polyureas are shown in Fig. 3. The thermal stability of polyureas was inferior to that of polyamides.

Experimental

Materials. The arylbiguanides were prepared by the reaction of dicyanodiamide with related arylamine hydrochlorides following the method of Cohn.[5] The biguanide was prepared by the method of Odo.[6] All the other reagents were commercially available and were used after purification if necessary.

2-Amino-4-p-nitroanilino-6-p-nitrophenyl-s-triazine. A suspension of 33 g (0.15 mol) of *p*-nitrophenylbiguanide in 300 m*l* of acetone was treated with 25 g (0.135 mol) of *p*-nitrobenzoyl chloride, and then 7.5 g (0.135 mol) of potassium hydroxide in water were added. Stirring and cooling at 0—5°C were continued during the reaction. After the acetone had then been removed, the yellow precipitate was separated and washed with hot water. The product was given almost quantitatively; 47.5 g, mp 300°C. (Found: N, 27.95%; Calcd.: N, 27.75%)

The other dinitro-compounds were prepared in a similar manner.

2-Amino-4-p-aminoanilino-6-p-aminophenyl-s-triazine. By stirring and refluxing, to a suspension of 11.5 g (0.033 mol) of the above dinitro-compound and 17.5 g (0.15 mol) tin in 100 m*l* of ethanol we added, drop by drop over 1-hr period, 100 m*l* of 12 N hydrochloric acid. The reaction mixture became clear and then formed a precipitate. When the precipitate was separated, dissolved in water, and treated with strong alkali, a white precipitate was also given. The product was separated; 9.0 g (93%), mp 231—231.5°C

The reduction of the other dinitro-compounds was carried out in a similar manner.

Preparation of Polyamides. In a 100-m*l*, three-necked flask equipped with a stirrer and a nitrogen inlet, we placed 7 m*l* of DMA, 0.300 g of 2-amino-4-*p*-aminoanilino-6-*p*-aminophenyl-*s*-triazine, and 0.15 g of lithium chloride; then 0.216 g of terephthaloyl chloride was gradually added at 25°C. After 8 hr, the reaction mixture was poured into methanol. The polymer was isolated, washed with water, dipped in a dilute alkali solution, repeatedly washed again with water and methanol, and dried. The polymer obtained amounted to 0.429 g.

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

[6] K. Kono and K. Odo, *Yuki Gosei Kagaku Kyokai Shi*, **20**, 649 (1962).

The other polyamides and polyureas were treated in a similar manner.

Preparation of the Model Compound. 2-Amino-4-anilino-6-*p*-nitrophenyl-*s*-triazine was prepared by the reaction of phenylbiguanide with *p*-nitrobenzoyl chloride; yellow powder, mp 206.5—208°C.

Found: C, 58.25; H, 4.13; N, 27.43%. Calcd for $C_{15}H_{12}N_6O_2$: C, 58.04; H, 3.89; N, 27.27%.

2-Amino-4-anilino-6-*p*-aminophenyl-*s*-triazine was given by the reaction of the nitro-compound with tin and hydrochloric acid in ethanol; mp 200.5—201.5°C.

The model compound, 2-amino-4-anilino-6-*p*-benzamidophenyl-*s*-triazine, was prepared by the reaction of the above amine with benzoyl chloride by a method of preparation similar to that used for the polyamides; mp 222—222.5°C, 69%. The results of elementary analysis agreed with the value calculated for semihydrate.

Found: C, 67.63; H, 4.70; N, 21.19%. Calcd for $C_{22}H_{18}N_6O\cdot\frac{1}{2}H_2O$: C, 67.51; H, 4.89; N, 21.47%.

The authors wish to thank Mr. T. Saito of Tokyo Institute of Technology for his elementary analysis.