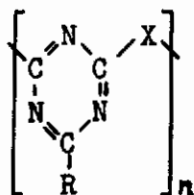


SYNTHESIS, STRUCTURE AND THERMAL STABILITY OF
NITROGEN AND SULFUR-BRIDGED-S-TRIAZINE OLIGOMERS

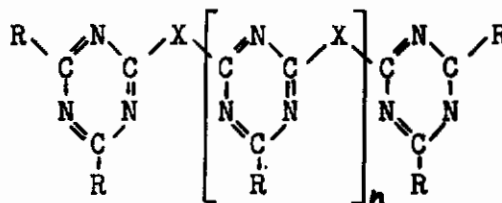
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I. INTRODUCTION

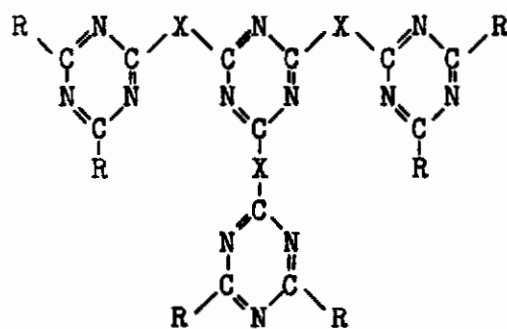
The purpose of this work is to synthesize model compounds and polymers containing the s-triazine ring system in the "backbone" of the polymeric chain, to evaluate their thermal stability, and if possible to compare them with other aromatic systems. Properties, such as radiation stability, fibre forming ability, film strength and flexibility are also of interest. In general the model compounds and polymers discussed in this report consist of structures in which alkyl or aryl substituted s-triazine molecules are linked with each other through nitrogen or sulfur bridges. Their general structures can be formulated as follows:



I



II



III

where R is alkyl, or phenyl, X is -N-H; -N-CH₃; -N-C₆H₅; or S, and n is an integer.

A. Synthesis of N-Bridged S-Triazines

1. Model Reactions

As a guide for the estimation of optimal conditions for the formation of condensation polymers from the reaction of -A-A- and -B-B- type monomers, and for later self condensation of -A-B type monomers, certain model melt reactions and solution reactions in diphenylether were run at 150° to 400°C in a stream of nitrogen or under vacuum between a number of halogen and amino-substituted

-s-triazines. The per cent conversion was determined by titrating the HCl evolved with N/10NaOH.

The model reactions were run between such halogen substituted -s-triazines as cyanuric chloride, I, 2-methyl-4,6 dichloro-s-triazine, II, 2-phenyl-4,6 dichloro-s-triazine, III, and 2,4 diphenyl-6-chloro-s-triazine, IV, and such amino substituted -s-triazines as 2,4 diphenyl-6-N-methylamino-s-triazine, V, 2-phenyl-4,6-bis-(N-phenylamino)-s-triazine, VI, 2,4 diphenyl-6-(N-phenylamino)-s-triazine, VII, and 2-phenyl-4,6-bis-(N-methylamino)-s-triazine, VIII.

The reactions were conducted either as melt reactions or in solution in diphenylether (DPE). The sample was placed in a 1" x 5" reaction tube and heated in an aluminum block by a heating mantle. The temperature was controlled by a thermocap relay with an accuracy of better than $\pm 1^{\circ}\text{C}$. N_2 was swept through the apparatus from a tube fitted to the adaptor attached above the reaction tube. The evolved HCl was absorbed in water and titrated at short intervals with N/10NaOH. When vacuum was used, a trap (containing NaCl) was cooled in a dry ice-acetone bath followed by a drying tower packed with Drierite.

Reactions went to completion more rapidly under vacuum than under N_2 at the same temperature, presumably due to a high loss of starting material by sublimation. Conversion generally was higher under N_2 than vacuum. Cyanuric chloride, I, 2-methyl-4,6 dichloro-s-triazine, II, and 2-phenyl-4,6 dichloro-s-triazine, III, all exhibit a high degree of sublimation at the temperatures used. The degree of sublimation varied from two to sixteen per cent under nitrogen, and up to 50% under vacuum, in the temperature range of $200^{\circ} - 250^{\circ}\text{C}$. Hence, calculation of the per cent conversion involved corrections for the amount of sublimation. Reactions conducted at 150°C usually were incomplete, while at 400°C the reaction products appeared to be partially degraded although conversion was 100%. Reaction under nitrogen at $200^{\circ} - 250^{\circ}$ for from 12 to 30 hours appear to give optimum results.

After reaction was complete the crude products were crystallized from a suitable solvent such as benzene, toluene, dioxane, or THF. The pure products were high melting white crystalline compounds and have not been described previously in the literature. They can be considered as low molecular weight nitrogen linked triazine oligomers which can be expected to possess some of the properties of higher molecular weight nitrogen linked -s-triazine polymers. The new compounds have been defined as:

1. 2,2'-(N-phenyl)-bis-(4,6 diphenyl-s-triazine), IX.
2. Bis-[N-phenyl-N-(4',6'-diphenyl-s-triazinyl-27)] -2,4-diamino-6-methyl s-triazine, X.
3. Bis-[N-phenyl-N-(4',6'-diphenyl-s-triazinyl-2)] -2,4 diamino-6-phenyl-s-triazine, XI.
4. Tris-[N-phenyl-N-(4',6' diphenyl-s-triazinyl-2')] -2,4,6-triamino-s-triazine, XII.
5. Tris-[N-methyl-N-(4',6'-diphenyl-s-triazinyl-2')] -2,4,6-triamino-s-triazine, XIII.

Their reaction schemes are given in Figure 1 and their properties are shown in Table I.

Figure 1
Preparation of N-Linked-S-Triazinylene Oligomers

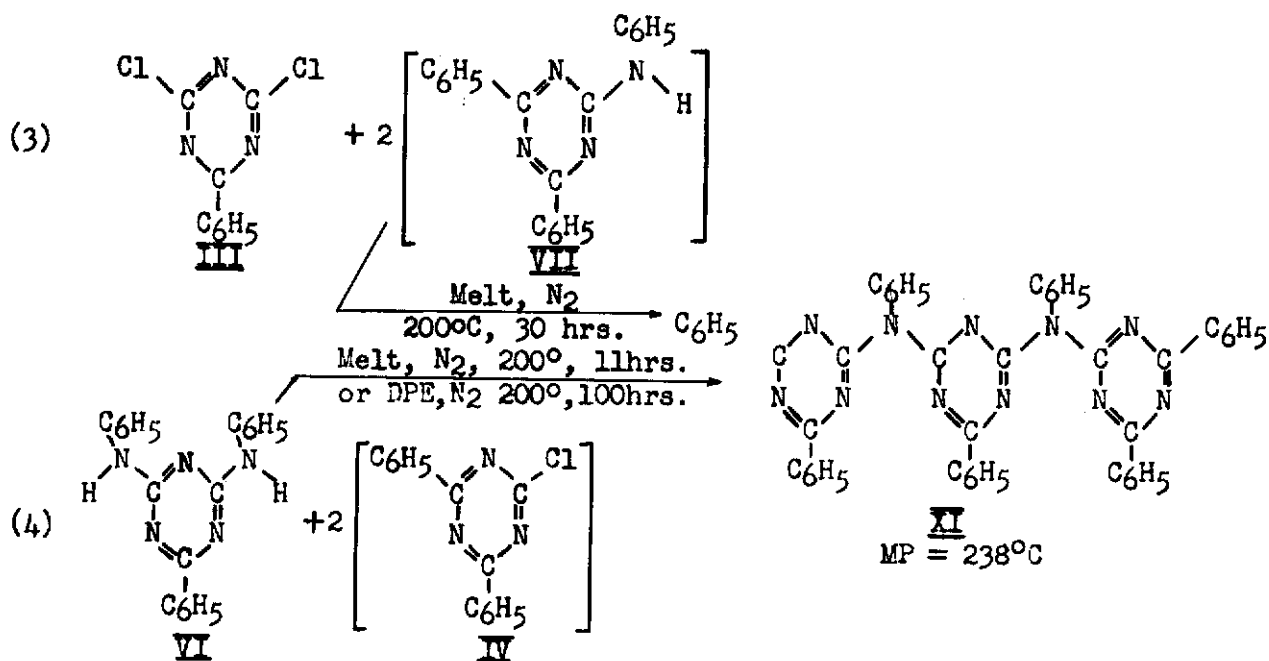
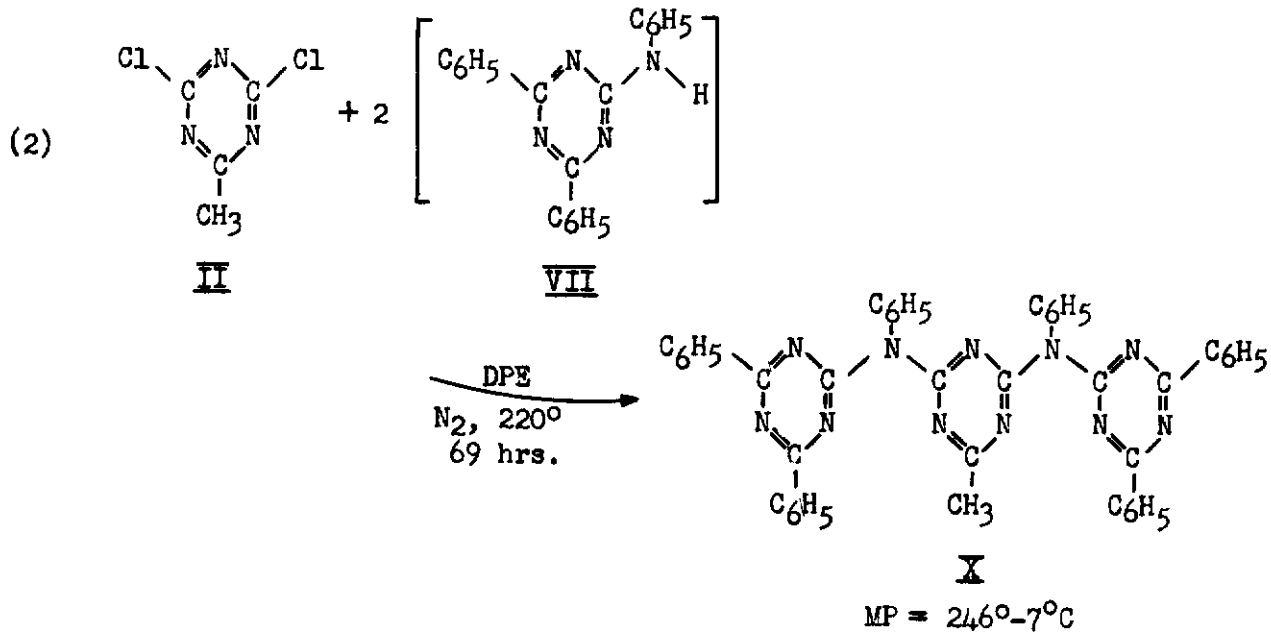
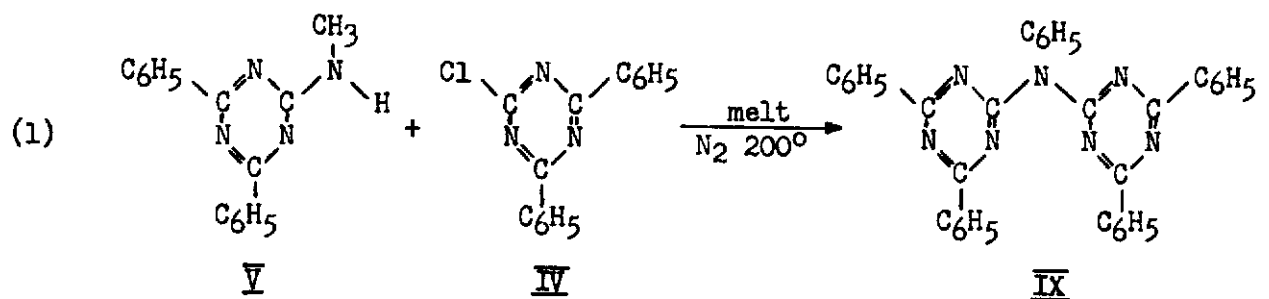


Figure 1 (Cont'd.)

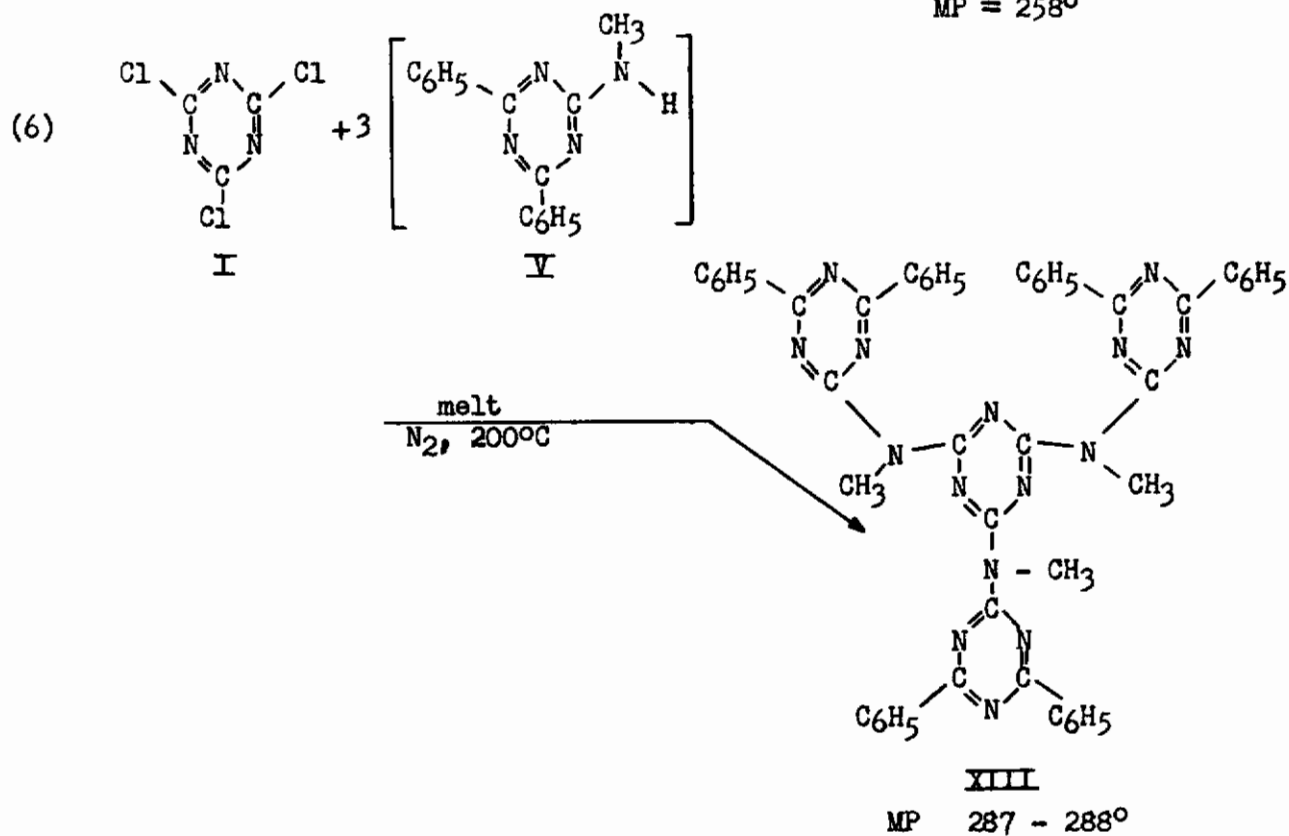
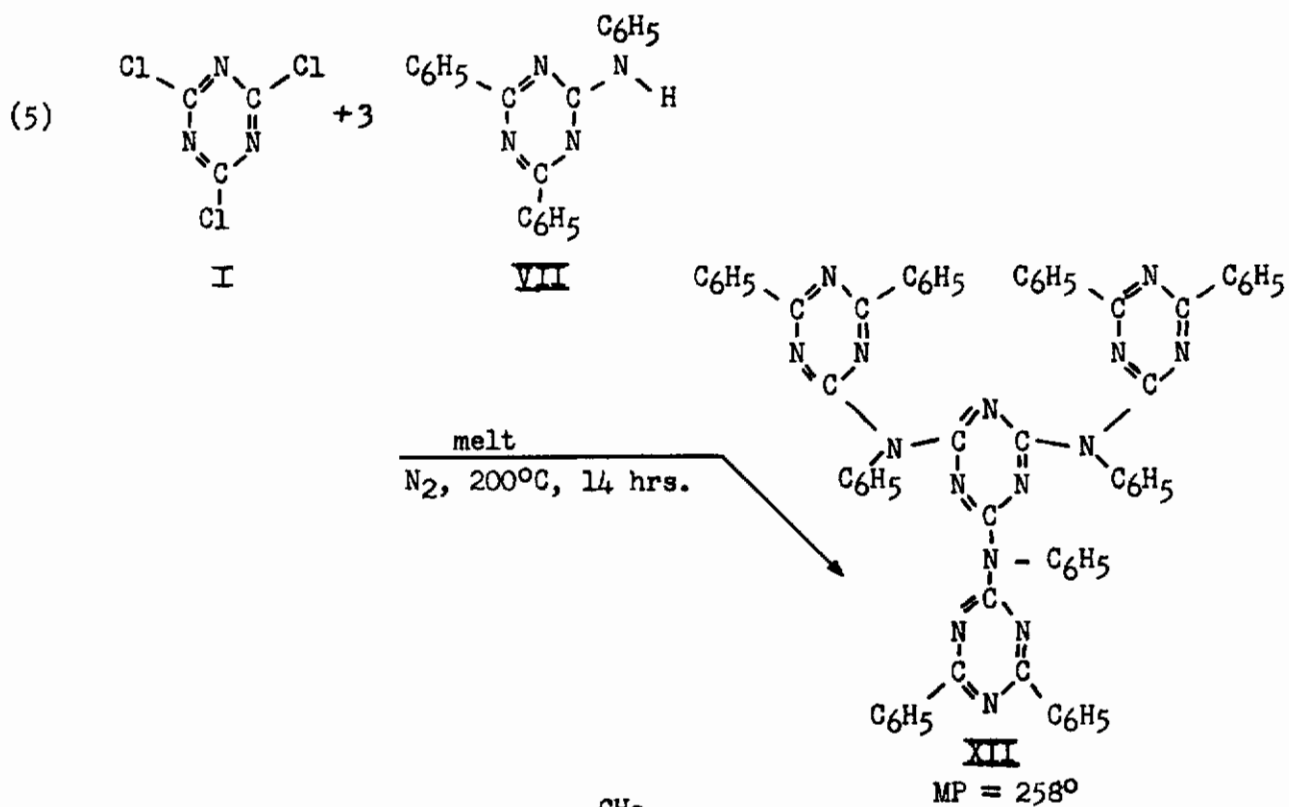


TABLE I

MODEL REACTION BETWEEN CHLORO-S-TRIAZINES AND ANILINO-S-TRIAZINES

Trial No.	Reactants	Solvent	Temp. °C	Reaction Time (hrs)	% Conversion	M.P. of Residue in °C
1	I + VII	None	150	34	68.7	204-215
2	I + VII	"	200	13	95.0	237-238.5
3	I + VII	"	200	8	85.8	193-196
4	I + VII	"	250	5	88.0	120-133
5	I + VII	"	150	311	83.5	208-220
6	I + VII	"	200	27	93.6	230-235
7	I + VII	"	200	29½	91.5	210-229
8	I + VII	"	250	6½	93.7	233-242
9	I + VII	"	200-400*	54	100.0	200
10	III + VII	"	200	30	97.3	126-130
11	III + VII	"	200	46	96.1	125-132
12	IV + VI	DPE	200-220	112	96.4	---

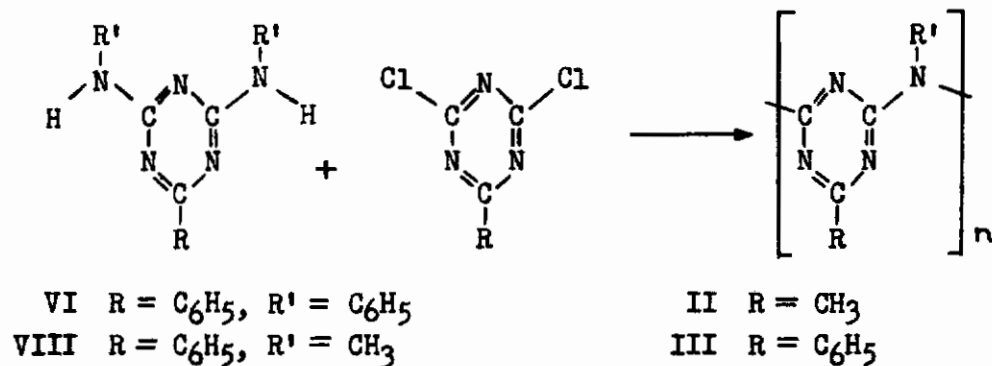
* 47 hrs. at 200°C; 2 hrs. at 300°C; 5 hrs. at 400°C.

- A I Cyanuric Chloride
- B III 2-phenyl-4,6 dichloro-s-triazine
- C IV 2,4 diphenyl-6-chloro-s-triazine
- D VI 2-phenyl-4,6 dianilino-s-triazine
- E VII 2,4 diphenyl-6-anilino-s-triazine

After a study of the model reactions, and the experimental techniques, essentially two basic methods were used for the synthesis of -N-bridged s-triazine polymers, both of them involving melt condensations, reactions in solution, and interfacial condensation.

2. Condensation of -A-A With -B-B Type Monomers.

The first method involves the condensation reaction of two difunctional monomers, -A-A, and B-B with each other, as represented by reaction between equimolar quantities of a 2-alkyl or aryl substituted -4,6-bis-(N-alkylamino or N-arylamino)-s-triazine, VI or VIII, and a 2-alkyl or aryl substituted -4,6-dichloro-s-triazine, II or III.



Melt condensation of equimolar quantities of 2-phenyl-4,6-dianilino-s-triazine, VI, and 2-phenyl-4,6 dichloro-s-triazine, III, as described previously, gave low molecular weight products with inherent viscosities in the order of 0.01 to 0.07. When an "interfacial" condensation was attempted between a suspension of VI in a solution of III in CCl_4 , no reaction occurred. However, a melt condensation between equimolar quantities of III and 2-phenyl-4,6-bis-(N-methyl-amino)-s-triazine, VIII, at 200° for 160 hours under N_2 gave poly-6-phenyl-N-methyl-2,4 triazinylene imine, XV, $\text{MP} = 432^\circ$. The polymer had a relative viscosity of 0.35, and this represents a significant increase in molecular weight. The same reaction in phenol at 170° for 96 hours lowered the inherent viscosity to 0.035 while no reaction occurred in DPE at 200°C over 24 hours. The improvement in molecular weight by substitution of an N-methyl group in place of the N-phenyl group led to an investigation of the effect of substitution of alkyl groups for phenyl groups both on the triazine ring and attached to the nitrogen bridge. In general, increase in viscosities were noted although not as great as expected. Presumably, this may be due not only to difficulty in the stoichiometry of -A-A- plus -B-B-type condensation reactions, but also to sublimation and other experimental factors. The results are shown in Table II.

TABLE II
CONDENSATION OF -A-A-PLUS-B-B-TYPE MONOMERS

Reactants	Solvent	Temp. $^\circ\text{C}$	Time Hrs.	$[\eta]$	M.P. $^\circ\text{C}$	Structure
B + C	None	200	160	0.35	432	
B + C	DPE	200	24	no	reaction	
B + C	Phenol	170	96	0.035	230-70 $^\circ$	
B + D	None	200	41	0.07	365-400	
A + E	None	200	49	0.18	400	
A + F	None	200	42	insol.	400	

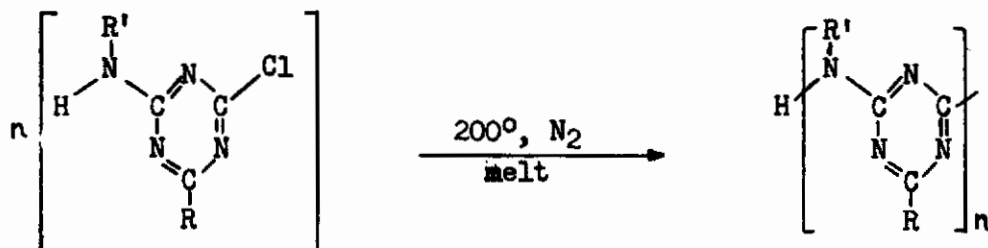
TABLE II (Cont'd.)

Reactants	Solvent	Temp. °C	Time Hrs.	$[\eta]$	M.P. °C	Structure
B + E	None	200	49	0.06	400	

- A: 2-Methyl-4,6-dichloro-s-triazine.
 B: 2-phenyl-4,6-dichloro-s-triazine.
 C: 2-phenyl-4,6-bis-(N-methylamino)-s-triazine.
 D: 2-phenyl-4,6-bis-(N-ethylamino)-s-triazine.
 E: 2-methyl-4,6-bis-(N-methylamino)-s-triazine.
 F: 2-methyl-4,6-bis-(N-ethylamino)-s-triazine.

3. Self Condensation of -A-B Type Monomers

The second method involves the self condensation of -A-B-type monomers as represented by 2-alkyl or aryl substituted -4-chloro -6-alkylamino or arylamino-s-triazines.



A number of melt polycondensations were carried out with 2-phenyl-4-chloro-6-anilino-s-triazine, XIV, alone or in the presence of a catalytic amounts of acidic and alkaline materials, and peroxide under nitrogen. The reaction product, poly-6-phenyl-N-phenyl-2,4-triazinylene imine, XVI, was washed with water for several hours where water soluble additives had been used. All the crude products were extracted with ether to remove starting materials, and then melting points, chlorine content, inherent viscosity were determined and I.R spectra were obtained. No improved products were obtained and the best products had an estimated D.P. between 2 and 10 based on inherent viscosities of up to $n = 0.07$. D.P.'s calculated on the basis of chlorine and end group analyses were low and unreliable. The results of these runs are listed in Table III.

When an attempt was made to condense 2-phenyl-4-chloro-6-anilino-s-triazine, XIV, in con. H_2SO_4 at $105^\circ C$ partial decomposition occurred, and the inherent viscosity was found to be lower than products from the melt reaction.

Replacement of the N-phenyl group with N-methyl resulted in a substantial increase in molecular weight. The resulting polymer, poly-2 phenyl-N-methyl-4,6 triazinylene imine, XV, had a M.P. of $395^\circ C$ and an inherent viscosity

TABLE III

SELF-CONDENSATION REACTIONS OF 2-PHENYL-4-CHLORO-6-ANILINO-S-TRIAZINE

Trial No.	Atmosphere	Temp. °C	Time (hrs)	Additives (Catalysts)	M.P. (°C)	[η]	% Cl	D.P. Viscosity	From Cl Content
1	N ₂	200	67	None	222-7	0.07-0.09	0	5-16	Infinite or cyclic!
2	N ₂	200	56	0.05g of FeCl ₃	246-52	0.07	0.74	5-9	20
3	N ₂	200	24	0.05g of BF ₃ -400	210-225	0.02	0.17	1-2	80
4	N ₂	200	21	0.05g of cu par.	215-240	0.05	1.95	3-6	8
5	N ₂	200	23	2g of H ₃ PO ₄	310	—	—	—	—
6	N ₂	200	—	—	—	—	—	—	—
7	N ₂	190	48	—	138-260	—	0	—	Infinite or cyclic!
8	N ₂	200	48	—	204-260	0.04	2.50	2-5	6
9	N ₂	200	42	—	273-305	0.08	0.35	6-16	40
10	N ₂	115	70	—	230-265	0.03	—	2	—

of 0.30, corresponding quite closely to the properties of the same polymer obtained from the -A-A- plus -B-B- reaction. Further increases in molecular weight can be expected in runs now being conducted by prolonged heating at higher temperatures. The results of the self-condensation of A-B-type monomers are listed in Tables III and IV.

B. Synthesis of Sulfur Bridged S-Triazinylene Oligomers and Polymers

1. Model Compounds

The synthesis of a limited number of pure low molecular weight sulfur bridged 2-phenyl substituted-s-triazine oligomers was begun in order to determine their structure and physical properties, and to obtain thermal stability data which may be useful for predicting the thermal stability characteristics of higher molecular weight polymers of the triazinylene sulfide structure.

(a) Linear straight and branched oligomers.

Dimeric, trimeric, and tetrameric -2-phenyl s-triazinylene 2,4 monosulfides were prepared in solution (usually dioxane) by reaction of 2,4 diphenyl-6-chloro-s-triazine, IV, with the appropriate thiol derivative, XXII, XXIII, or XXIV (see Figure 3), or by reaction of 2,4 diphenyl-6-mercapto-s-triazine, XXII, with the appropriate dichloro derivative, II, III, or XXV in the presence of an acid acceptor such as pyridine, sodium hydroxide, or sodium ethylate. In some cases the sodium salts of the thiol derivatives, XXII, XXIII,

TABLE IV

SELF CONDENSATION OF 2-ALKYL-OR-ARYL-4-CHLORO-6-(N-ALKYL OR ARYL)-S-TRIAZINES

Monomer	Solvent	Temp. °C	Time Hrs.	[n]	M.P.	Structure
G	None	200	67	0.076	222-7	
G	Con H ₂ SO ₄	105	24	0.04	350	
H	None	220	10	0.30	395	
H	DPE	200	48	Insufficient Product	275	
I	None	230	10	Insol	463	

G: 2-phenyl-4-chloro-6-(N-phenylamino)-s-triazine.
H: 2-phenyl-4-chloro-6-(N-methylamino)-s-triazine.
I: 2-phenyl-4-chloro-6-amino-s-triazine.

or XXIV, were prepared in situ and reacted with the chloro derivatives. The new compounds were obtained in relatively high yields, 70 to 90% or better and were purified by crystallization from dioxane, benzene or chlorobenzene. The pure monosulfide oligomers are all white crystalline high melting compounds as is the dimeric disulfide, 2,2' dithiobis-(4,6 diphenyl-s-triazine), XXX, which was prepared by nitrous acid oxidation of 2,4 diphenyl-s-triazine-6-thiol. These oligomers are new compounds and have not yet been described previously in the literature. The new compounds have been defined as:

1. 2,2' thiobis-(4,6 diphenyl-s-triazine) XXVI.
2. 2,4 bis-(2'-thio-4',6'-diphenyl-s-triazinyl)-6-phenyl-s-triazine, XXVII.
3. 2,2' diphenyl-4,4' bis-(2"-thio-4",6" diphenyl-s-triazinyl)-6,6'-s-triazinyl sulfide, XXVIII.
4. Tris-(2'-thio-4',6'-diphenyl-s-triazinyl)-s-triazine, XXIX.
5. 2,2' dithiobis-(4,6 diphenyl-s-triazine), XXX.

Their reaction schemes are given in Figure 2 and their properties are summarized in Table V.

Figure 2
Synthesis of Linear S-Triazine Sulfide Oligomers

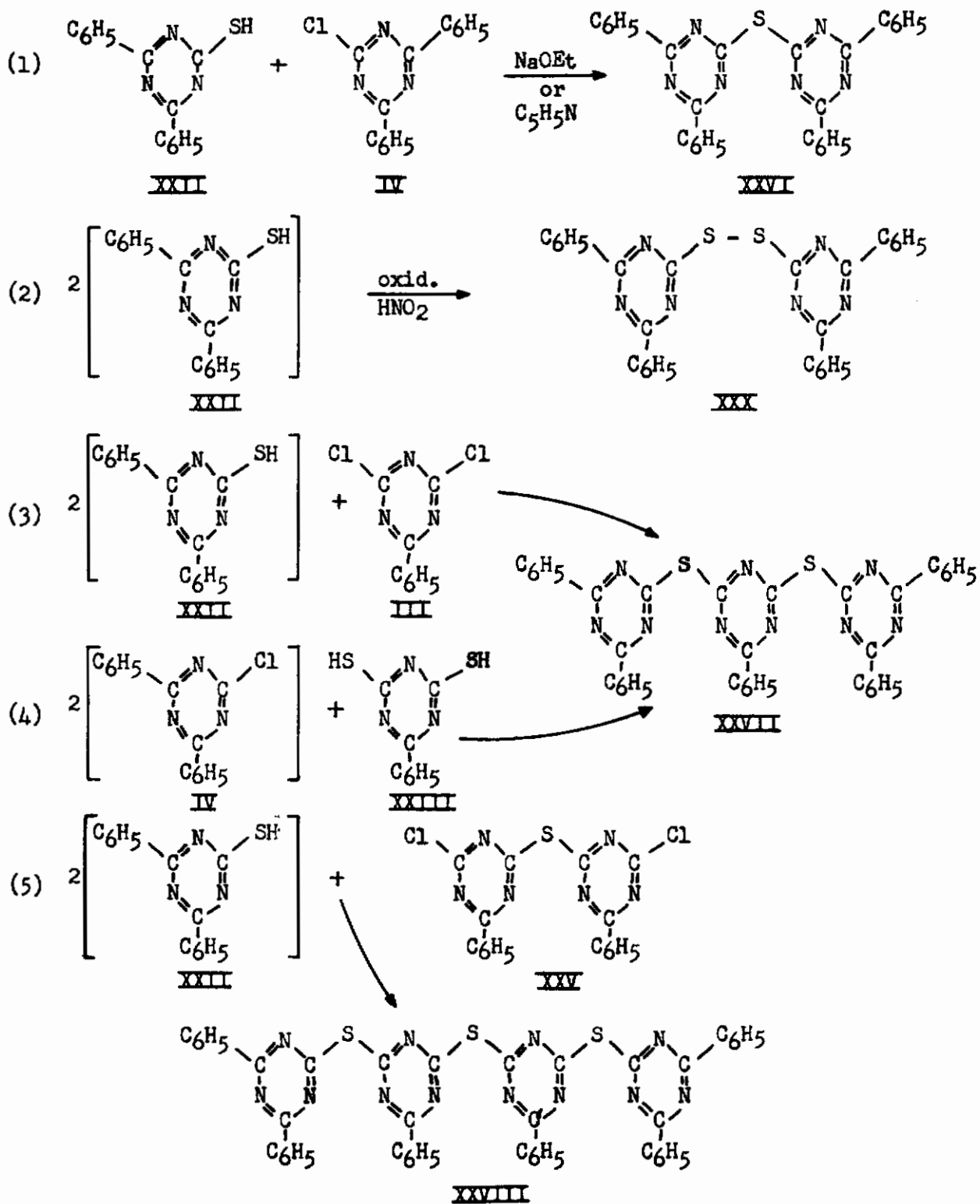


Figure 2 (Cont'd.)

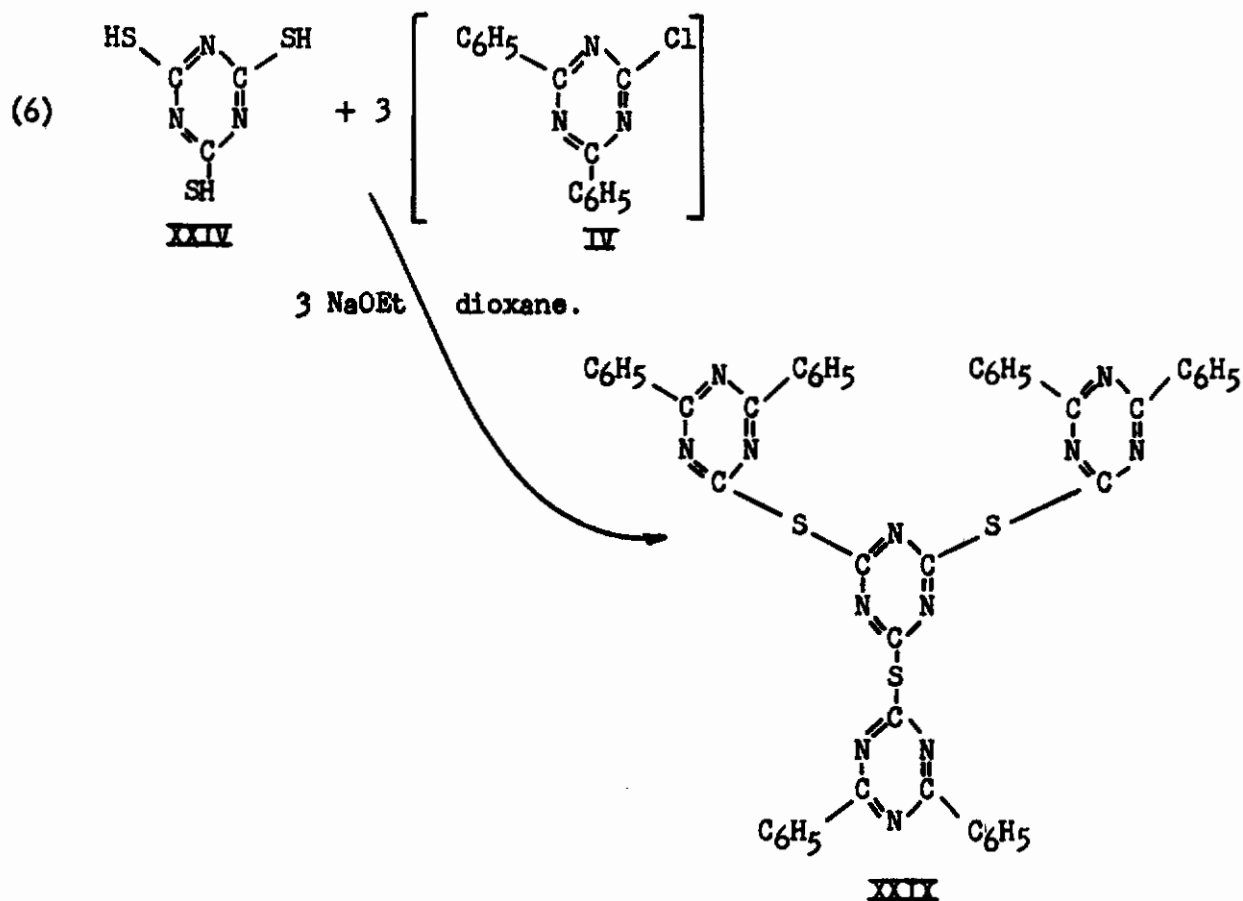


TABLE V

PROPERTIES OF LINEAR S-TRIAZINYLENE SULFIDE OLIGOMERS

Compound	Empirical Formula	% Yield	M.P. (°C)	Molecular Weight*	
				Calc'd.	Obs.
1. (XXVI)	C ₃₀ H ₂₀ N ₆ S	95	223-4°	496	528 454
2. (XXX)	C ₃₀ H ₂₀ N ₆ S ₂	99	275-6°	528.6	566 540 528
3. (XXVII)	C ₃₉ H ₂₅ N ₉ S ₂	90	249-52°	684	732
4. (XXVIII)	C ₄₈ H ₃₀ N ₁₂ S ₃	90	251-3°	871	602 638
5. (XXIX)	C ₄₈ H ₃₀ N ₁₂ S ₃	86	230-5°	871	630

* ebullioscopic, benzene

(b) Cyclic Oligomers

Dropwise addition of aqueous sodium sulfide to an equimolar quantity of 2-phenyl-4,6 dichloro-s-triazine, III, in dioxane at room temperature or at 100°C gave a white fibrous material, XXXI, $C_9H_5N_3S$, MP = 265-7°C. Its molecular weight (ebulloscopic, benzene) was 531 indicating that the compound is a poly-2-phenyl-s-triazinylene 4,6 monosulfide, XXXI with a degree of polymerization of 2.84. Absence of Cl end groups suggests that the product has a cyclic structure, containing three triazinylene units. Similarly, addition of aqueous NaSH to a dioxane solution of 2-methyl-4,6 dichloro-s-triazine, II gave a white granular solid, $C_4H_3N_3S$, M.P. = 212-15°C. Its molecular weight was 361, indicating a degree of polymerization of about 2.9. This compound was identified as cyclotrimeric 2-methyl-s-triazinylene 4,6-monosulfide, XXXII.

Oxidation of 2-phenyl-4,6 dimercapto-s-triazine, XXIII, with nitrous acid at 90°C gave a white crystalline product, $C_9H_5N_3S_2$, M.P. = 282-3°C. The compound had a molecular weight of 791, indicating a degree of polymerization of 3.6. Absence of end groups suggest that this product also has a cyclic structure, XXXIII, corresponding to cyclotrimeric or tetrameric 2-phenyl-s-triazinylene-4,6-disulfide.

Attempts to prepare the corresponding 2-methyl derivative under the same conditions were unsuccessful due to ring scission.

When 2-phenyl-4,6 dichloro-s-triazine, III, was added to a solution of 2-phenyl-4,6 dimercapto-s-triazine, XXIII, and sodium ethylate in alcohol at 70°-80°C, a white crystalline product, XXXIV, M.P. 265-7°C was formed. Infrared spectra indicates that this product is identical with that of the previously prepared cyclotrimeric 2-phenyl-s-triazine-4,6-monosulfide.

The properties of the cyclic poly-triazinylene sulfides and disulfides are compared in Table VI, reaction schemes are given in Figure 3.

TABLE VI
PROPERTIES OF CYCLIC POLYTRIAZINYLENE SULFIDES

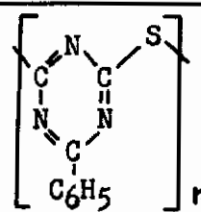
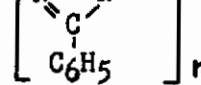
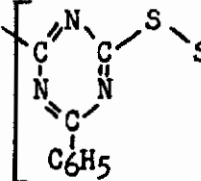
Reactants	Polymer	Yield (%)	M.P. (°C)	MW	D.P.
III + Na ₂ S		96	265-7	638 ^a	3.4
III + Na ₂ S		92	266-7	530 ^b	2.9
III + XXIII 2NaOEt		--	265-7	--	--
III + XXIII 2NaOEt		--	243-8	--	--
III + XXIII NaOH oxid.		99	267-9	791 ^b	3.6
XXIII + HNO ₂		96	282-3	774 ^b	3.5
XXIII + HNO ₂		--	265-7	--	--

TABLE VI (CONT'D.)

Reactants	Polymer	Yield (%)	M.P. (°C)	MW	D.P.
II NaSH } II NaSH }	$\left[\begin{array}{c} \text{N} \quad \text{S} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{N} \quad \text{N} \\ \\ \text{C} \\ \\ \text{CH}_3 \end{array} \right]_h$	69	d	385 ^b	3.1
		71	d	360 ^b	2.9

a Neumayer Method (osmotic pressure) in chloroform.

b Ebullioscopic in benzene.

Figure 3

Preparation of 2-Alkyl or Aryl-s-Triazinylene-4,6-Mono and Disulfide Cyclopolymers

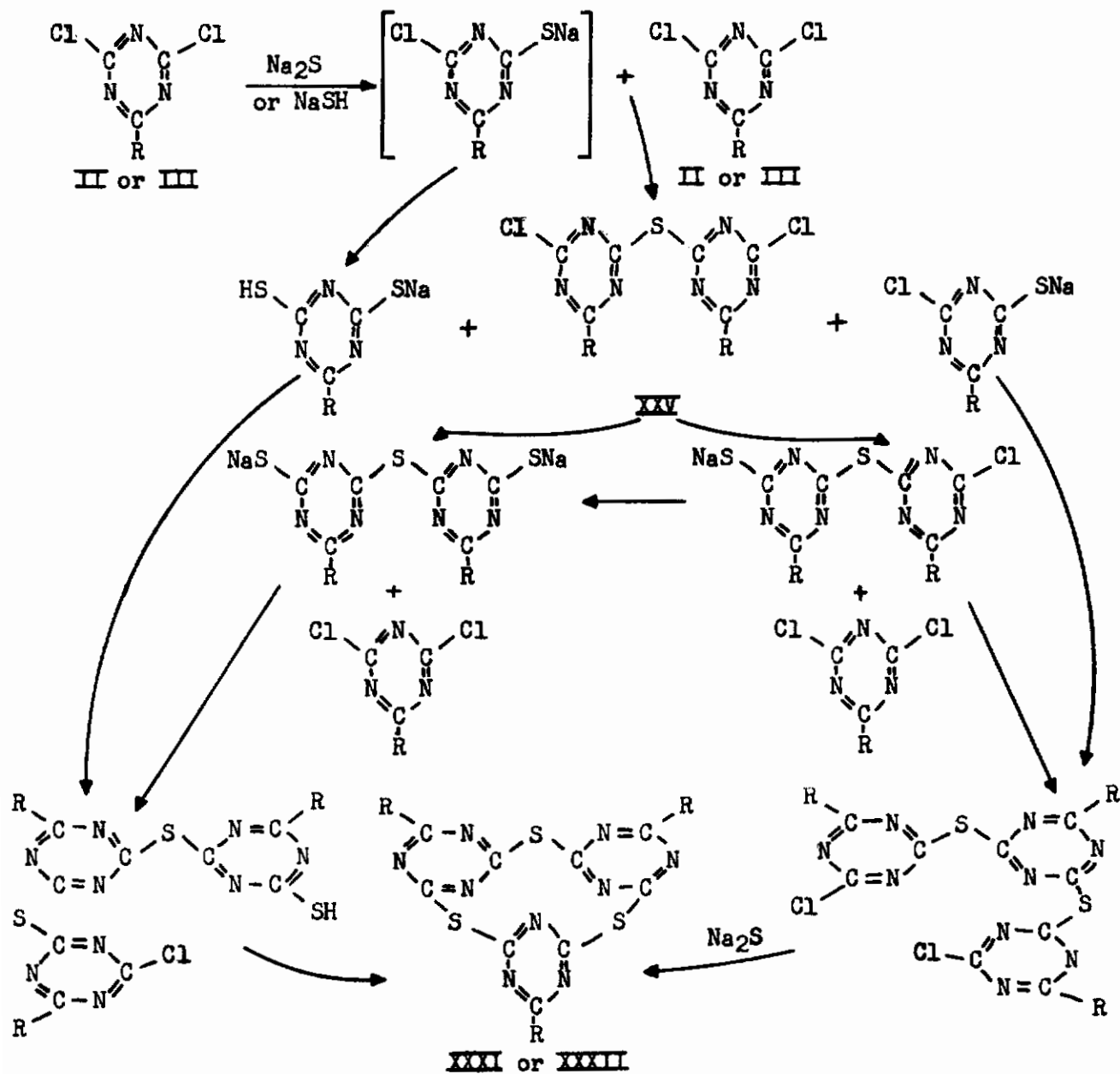
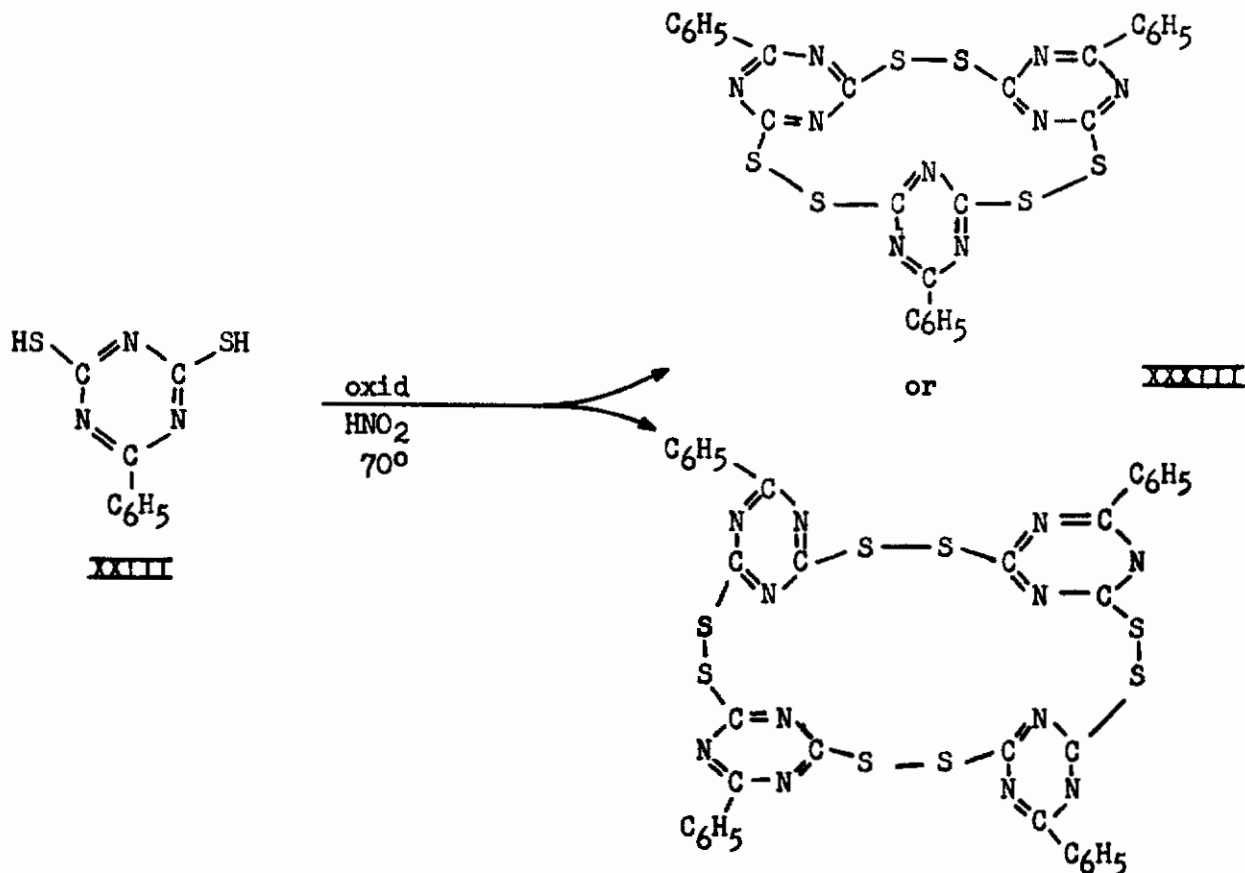


Figure 3 (Cont'd)



2. Melt Condensations of -A-A- and -B-B-Type Monomers

A number of A-A plus B-B melt condensations were carried out. For these condensations highly purified recrystallized samples of 2-phenyl-4,6 dichloro-s-triazine, III, and 2-phenyl-4,6 dimercapto-s-triazine, XXIII, were used in equimolar amounts, at temperatures ranging from 200° to 300°C under nitrogen. The conversions as measured by HCl evolution varied from 97.5 to 97.8%. Several difficulties were encountered during the reaction. The most serious problem was sublimation of 2-phenyl-4,6 dichloro-s-triazine, III. From time to time, the reaction mixture was cooled and the sublimed material was "scraped" back into the reaction mixture which then had to be broken up and "pulverized" as well as possible. It was difficult to maintain a homogeneity throughout the reactions. In all cases the reaction products consisted of two components: (1) about 47% of a hard brittle dioxane insoluble resin, possibly of high molecular weight, and (2) about 53% of a low melting dioxane soluble polymer with a relative viscosity of 0.042 to 0.045. This suggests a low polymer with a possible molecular weight range of 700 to 1400, or a degree of polymerization between 3.7 and 7.5. Prolonged heating did not improve the molecular weight of the dioxane-soluble material.

Investigation of the properties of the dioxane-insoluble polymer has not been completed. It appears to be partially soluble to a low degree in

hot diphenylether, which suggests that viscosity measurements may be feasible in this solvent with a sample of the fractionated material. It is difficult at this stage to conclude whether the melt viscosity technique will be helpful, because the product which is a hard resin at 200°C and which softens gradually with increasing temperature did not appear to melt to a flowable liquid before decomposition began at about 400°C. It therefore will be necessary to find a method to fractionate and purify this resinous product before further evaluation can be made.

Another melt condensation was carried out in a sealed tube under nitrogen at 200°C for 16 hours with equimolar quantities of 2-phenyl-4,6 dichloro-s-triazine, III, and the disodium salt of 2-phenyl-4,6 dimercapto-s-triazine, XXIII. The salt was prepared by reaction of 2-phenyl-4,6 dimercapto-s-triazine, XXIII, with the sodium-naphthalene complex in dry THF. The reaction product as before consisted 46% of a dioxane-soluble fraction with an inherent viscosity of 0.038 and the remaining component was insoluble in dioxane. The properties of the polymers are given in Table V. As before, the chief difficulties encountered were sublimation and lack of homogeneity.

TABLE VII

MELT CONDENSATION OF 2-PHENYL-4,6 DICHLORO-S-TRIAZINE, III, AND 2-PHENYL-4,6 DIMERCAPTO-S-TRIAZINE XXIII

Reactants	Reaction Time	Temp. (°C)	Conversion %	Products		[η]
				Soluble	Insoluble	
HS-C ₆ H ₅ N ₃ -SH	148	200°	98.5	47	53	0.045
+ Cl-C ₆ H ₅ N ₃ -Cl	18 4½	200° to 300°	98.0	46	54	0.042
NaS-C ₆ H ₅ N ₃ -SNa	16	200°	—	45	55	0.038
+ Cl-C ₆ H ₅ N ₃ -Cl						

D. Thermogravimetric Analysis

Thermogravimetric analyses were run on the "high" molecular weight sample of linear poly-2-phenyl-N-methyl-4,6-triazinylene imine, XV, of an inherent viscosity of 0.30, and on samples of the branched oligomers X, XI, XII, and XXIX, under nitrogen on a modified Chevenard thermal balance. The heating rate was set at 150°C per hour.

The T.G.A. curve for poly-2-phenyl-N-methyl-4,6-triazinylene imine XV, as shown in Figure 4, exhibits initial breakdown in the 350° to 420°C region with a loss of about 10%, followed by rapid decomposition to the extent of about 55% up to 460°C. Subsequently, the rate of decomposition begins to show down at 900°C, only about 10% residue remains. This appears to indicate that the polymer would be servicable for only a short period of time in the 400 to 450°C range.

The T.G.A. curves for the branched oligomers are plotted together in Figure 5. The nitrogen branched oligomers gave similar curves with decreasing

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stability in the order, X, XII, and XI, with corresponding initial breakdown temperatures at about 475°C, 450°C, and 390°C. With all these materials rapid breakdown occurs in the 400° to 500°C range with losses of 70 to 90%. The sulfur branched oligomer exhibited earlier breakdown beginning at about 340°C losing up to 50% of its weight at 440°C, and up to about 87% to 480°C. Since, sublimation is observed when XXIX is heated at 350 to 400°C in a tube under nitrogen it can be inferred that the early weight loss between 340°C and 440°C may be partially due to sublimation, because the remainder of the weight loss curve appears in the same region as those of the nitrogen branched oligomers, and the polymer XV.

While all of these compounds appear to show different degrees of stability, these differences actually are minor, and the overall stability of the nitrogen or sulfur-branched oligomers and polymers is limited to the 400°C to 500°C range where complete breakdown occurs. It is also of some significance that the relative thermal stability of a polymer system can be estimated from thermogravimetric data obtained from low molecular weight oligomers thus eliminating the necessity for a major research effort to synthesize high molecular weight polymers for testing.

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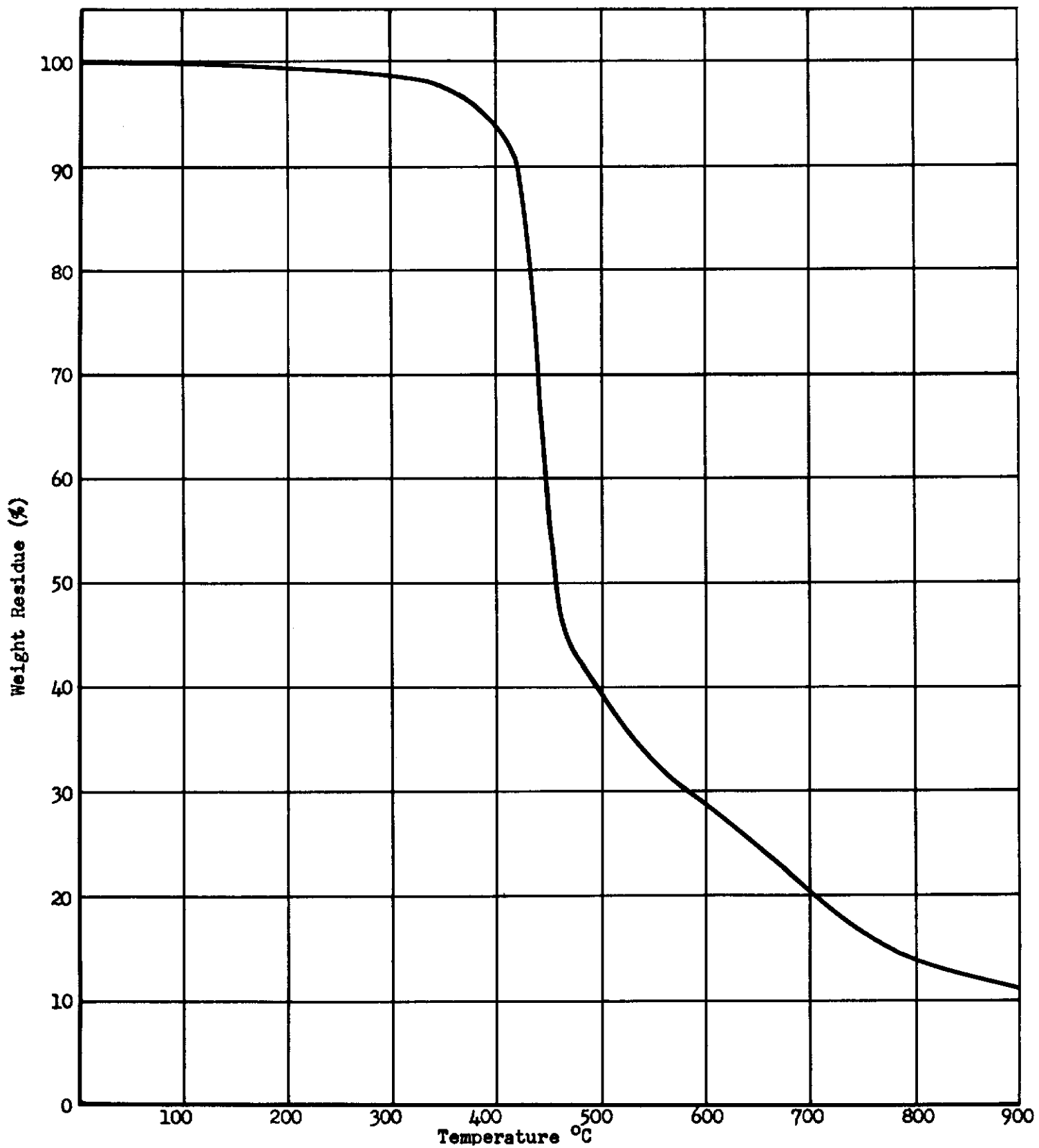


Figure 4. T.G.A. Curve Poly-2-phenyl-N-methyl-4,6 Triazinylene Imine..

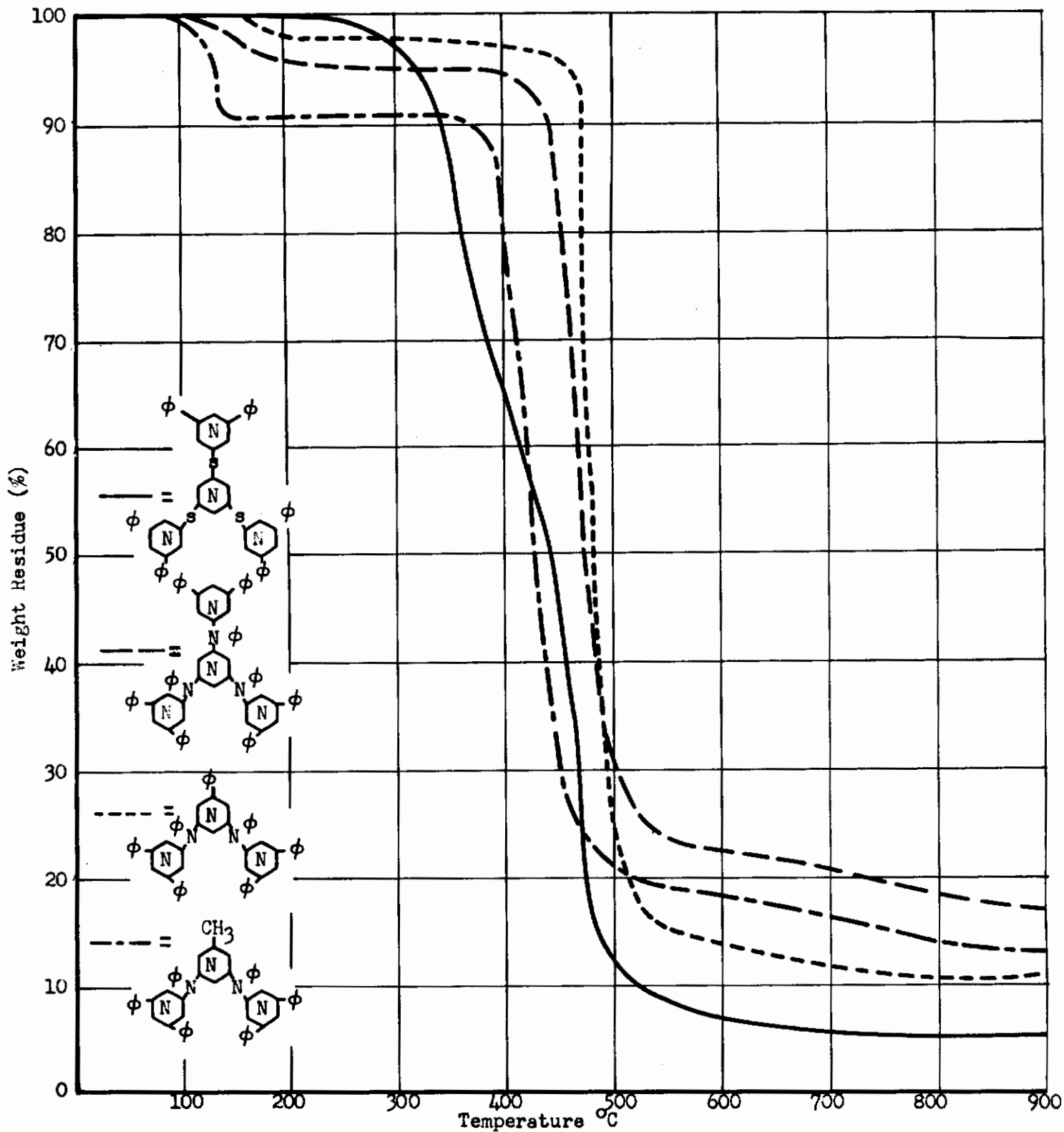


Figure 5. T.G.A. Curves. Branched Nitrogen and Sulfur Linked Triazine Oligomers.