

Polymers Containing the *s*-Triazine Ring. II. Synthesis of Poly(*s*-triazinylenehydrazones)

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Synopsis

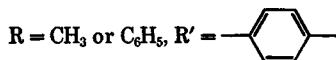
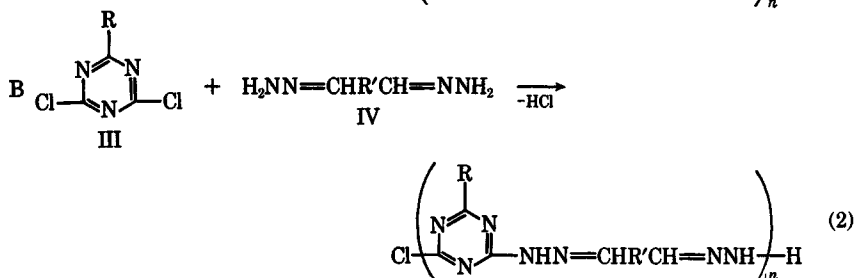
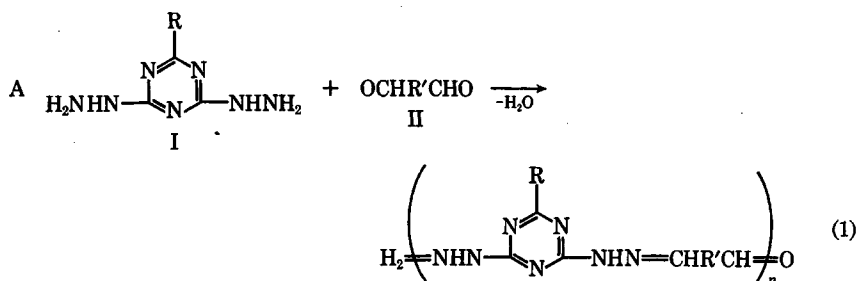
Poly(2-methyl- or 2-phenyl-*s*-triazinylenehydrazones) were prepared both by dehydration of dihydrazino-*s*-triazines with terephthalaldehyde and by dehydrochlorination of dichloro-*s*-triazines with terephthalaldehyde dihydrazone. The structure of the polymers was confirmed by infrared spectrometry and elemental analyses in comparison with those of a model compound. Dehydration yielded soluble polymers, while the dehydrochlorination yielded insoluble polymers. Most of the polymers degraded at about 350°C, and the polymers of higher molecular weight showed better thermal stability. The thermal behavior of the polymers indicated that the phenyl-substituted polymers obtained by dehydrochlorination and the methyl-substituted polymers obtained by dehydration had a degree of polymerization similar to that of the phenyl-substituted polymers obtained by dehydration. The soluble polymers could form chelate polymers, these took two accelerated decomposition phases. The lower phase suggested a decomposition accelerated by a metal. The higher phase, in which the chelate polymers decomposed more rapidly at a higher temperature (above 400°C) than their ligand polymer, was related to the atomic number and the electro-negativity of the metals. The formation of decomposition products, guanamines and nitrile compounds, in all cases indicate the preferential scission of nitrogen-nitrogen bonds.

INTRODUCTION

As useful starting materials for plastics containing an *s*-triazine ring, melamine and guanamines (2-substituted 4,6-diamino-*s*-triazine) have been widely used, yielding a commercially available thermosetting resin by addition reaction with formaldehyde. Other addition reactions involve those with diisocyanates, giving polyureas, as reported in our previous paper.¹ Similar reactions have also been reported.² The basicity of the amino group attached directly to the *s*-triazine ring, however, is weakened by the electron-withdrawing property of the ring, so that substitution reactions are usually difficult and require a high temperature, of about 300°C.³ For example, dehydration with carbonyl compounds in the heterogeneous phase at 225°–240°C has been reported, although analyses are not necessarily in accordance with the expected results.⁴ One of the methods to facilitate the substitution reactions is the interposition of an electron-donating element such as oxygen or nitrogen between the ring and the amino group. Exam-

ples are dihydrazino-*s*-triazines, which can also be regarded as *N,N'*-diaminoguanamines.

In the present study, an attempt was made to prepare dihydrazino-*s*-triazines and their polymers. Although the dehydration of 2-phenyl-4,6-dihydrazino-*s*-triazine with dialdehydes has been attempted,⁵ the dehydrochlorination of dichlorotriazines with diamines can also bring about the polymer of the same repeating unit. Thus, the following two procedures are available for obtaining the same structure with a difference in endgroups only:



These two procedures were compared with respect to polycondensation reaction and thermal behavior of the polymers and their metal chelate polymers.

EXPERIMENTAL

Materials

Dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), hexamethyl phosphoramide (HMPA), and benzaldehyde were used after distillation of the commercially available reagent of extra pure grade under reduced pressure (DMF was distilled at ordinary pressure). Polyphosphoric acid was prepared from phosphorus pentoxide and phosphoric acid.⁶ Hydrazine hydrate of extra pure grade was used without further purification. Cyanuric chloride was sublimed prior to use. Metal acetates of guaranteed grade were used for the formation of chelate polymers.

Preparation of *s*-Triazines and Other Monomer Compounds

Benzoguanamine was prepared from benzonitrile and dicyandiamide,⁷ yield 80%, mp 220°–1°C.

2-Phenyl-4,6-dichloro-*s*-triazine (PDCT; compound III, R = C₆H₅) has previously been prepared by the Grignard method.^{8,9} In the present study, however, it was prepared by hydrolysis of benzoguanamine with sulfuric acid,¹⁰ followed by chlorination of the dihydroxyl compound with thionyl chloride,¹¹ yield 60% (based on benzoguanamine), mp 119°C; Cl found 31.92%, calcd. 31.42%.

2-Methyl-4,6-dichloro-*s*-triazine (MDCT; compound III, R = CH₃) was prepared from cyanuric chloride with methylmagnesium bromide,⁸ yield 61%, mp 98.0–98.5°C; Cl found 42.60%, calcd. 43.25%.

2-Phenyl-4,6-dihydrazino-*s*-triazine (PDHT; compound I, R = C₆H₅) was prepared from PDCT with hydrazine hydrate,¹² yield 69%, mp 183°–184°C; found: C, 48.81%; H, 5.00%; N, 44.33%; calcd. for C₉H₁₁N₇: 49.77%; H, 5.07%; N, 45.16%.

2-Methyl-4,6-dihydrazino-*s*-triazine (MDHT; compound I, R = CH₃) was prepared in a similar manner as the 2-phenyl derivative. It was recrystallized from water and dried in vacuo. The yield was 50%, mp 228°C; found: C, 30.05%; H, 5.70%; N, 62.93%; calcd. for C₄H₉N₇: C, 30.97%; H, 5.81%; N, 63.23%.

Terephthalaldehyde (TPA; compound II) was prepared by oxidation of *p*-xylene,¹³ yield 44%, mp 115–116°C.

Terephthalaldehyde dihydrazone (TPDH; compound IV) was prepared from TPA and hydrazine hydrate,¹⁴ yield 77%, mp 161°–163°C; N found 32.24%, calcd. 34.57%.

2-Phenyl-4,6-dibenzylidenedihydrazino-*s*-triazine (PDBT) was prepared as follows: In 5 ml DMSO was dissolved 2.00 g (9.22 mmoles) PHDT, and 2.15 g (20.3 mmoles) benzaldehyde was added with stirring. The stirring was continued for 4 hr, and the solution was poured into 1:1 ethanol-water to precipitate the product. It was collected by filtration and recrystallized from ethanol. The yield was 2.47 g (68.1%); corrected mp 142°–143°C (sintering); found: C, 69.38%; H, 5.22%; N, 24.70%; calcd. for C₂₃H₁₉N₇: C, 70.23%; H, 4.83%; N, 24.94%.

All melting points, except for the last one, are uncorrected.

Polycondensation

Dehydration, Reaction (1). Run AP1 in Table I is given as a typical procedure: Into a 100-ml four-necked flask equipped with a stirrer, a thermometer, a nitrogen inlet, and an air-cooled condenser with a bubbler at the end, a solution of 1.519 g (7.00 mmoles) PDHT in 15 ml DMSO was placed, and a solution of 0.938 g (7.00 mmoles) TPA in 9 ml DMSO was added under nitrogen stream. The mixture was stirred at 50°C for 24 hr. The precipitate was collected by filtration, washed with a small amount of DMSO and methanol, and dried in vacuo (0.053 g, 2.4%, AP1b).

TABLE I
 Results of Polycondensations and Thermogravimetry

R	Product no.	Solvent ^a	Temp., °C	Time, hr	Yield, ^b %	$[\eta]^c$	Decomp. Temp., °C	Temp. at 10% loss, °C
C ₆ H ₅	AP1a	S	50	24	88	0.45	345	346
	AP1b	S	50	24	2	0.04		
	AP7a	S	100	3	98	0.37	330	332
	AP7b	S	100	3	12	0.14	200	215
	AP3b	S	100	12	106	0.12		
	AP4a	H	50	24	75	0.25		
	AP4b	H	50	24	25	0.14		
	AP5a	H	100	3	102	0.37	335	332
	PDBT						315	325
	AM2a	H	190	2	91		344	354
CH ₃	AM4a	H	150	1	33		339	352
	AM3a	P	100	1	100		339	341
				Reaction (2)				
C ₆ H ₅	BP1a	F	50	2	22			
	BP1b	F	50	2	31		330	340
	BM1b	F	50	2	78			
CH ₃	BM3b	F	50	0.5	75			
	BM2a	F	100	0.5	25		332	322
	BM2b	F	100	0.5	57			

^a S = DMSO; H = HMPA (hexamethylphosphoramide); P = polyphosphoric acid; F = DMF.

^b Based on the repeating unit of the polymer.

^c At 30°C in HMPA.

TABLE II
Elemental Analyses of Products

Product no.	C, %	H, %	N, %
AP1a	57.86	5.00	27.84
AP1b	57.73	5.20	25.41
AP3b	57.72	5.39	24.72
AP4a			26.19
AP4b			27.07
AP5a			26.84
BP1b	66.75	4.52	24.70
Calcd. ^a	58.11	4.88	27.90
AP1a ^b	64.13	4.34	30.83
Calcd. ^c	64.75	4.16	31.09

^a For $C_{17}H_{13}N_7 \cdot 2H_2O$.

^b Corrected values after drying at 50°C in vacuo.

^c For $C_{17}H_{13}N_7$, repeating unit of the polymer in the reactions (1) and (2).

The filtrate and DMSO washings were combined and poured into methanol to precipitate yellow to orange polymers which were then reprecipitated, washed with methanol, and dried in vacuo at room temperature (1.927 g, 87.4%, AP1a; see Table II for analysis). This operation should be enough to remove unreacted PDHT, because PDHT dissolved in DMSO at the same scale did not give any precipitate in methanol. Since MDHT is less soluble than PDHT, the polycondensation was carried out in a more dilute solution (3%-5%) at a higher temperature (100°-190°C). No precipitation occurred during the reaction period in the case of MDHT. When polyphosphoric acid was used, the reaction mixture was poured into water. The red-brown precipitate was washed with a 0.05*N* sodium carbonate solution.

Dehydrochlorination, Reaction (2). As a typical procedure, run BP1 is given as follows: In the same apparatus as for the dehydration, a solution of 0.648 g (4.00 mmoles) TADH in 12 ml DMF was placed and kept at 50°C under nitrogen. To this solution a solution of 0.904 g (4.00 mmoles) PDCT in 18 ml DMF was added. The reaction took place immediately, yielding an orange-yellow precipitate. After 2 hr, the precipitate was filtered, washed with alkaline DMF (containing KOH), water, and methanol successively, and dried in vacuo (0.396 g, 31.4%, BP1b). The filtrate and DMF washings were combined and poured into methanol to obtain further precipitates (0.280 g, 22.2%, BP1a). In some cases of MDCT, no precipitation occurred in methanol.

The interfacial condensation technique could be applied with ligroin as a solvent for the dichlorides and DMF for TADH. A yellow to orange solid was formed at the interface and precipitated.

Metal Chelate Polymers

To a 4% DMF solution of the polymer, a 4% DMF solution of a metal acetate containing $1/2$ mole of the acetate per repeating unit of the polymer

was added. The colored precipitate was formed immediately upon mixing the two reactants. The mixture was refluxed for 1.5 hr. The solid was filtered, extracted with DMF for 20–40 hr and then with ethanol for 5 hr, and dried in vacuo at 50°C overnight. The metal content was determined from the ash (divalent metal oxide) content after combustion.

Thermogravimetric Analysis

After the polymers had been dried at 50°C (100°C for chelate polymers) for 1 hr, about 50 mg of the dry polymer was weighed accurately in a quartz crucible and submitted to thermogravimetric analysis in air by using a thermobalance Model SE-52 of Tokyo Koki Seizosho. Temperature was raised at a rate of $2.5 \pm 0.5^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Formation of Polymers

The yields in the polycondensation reactions (1) and (2) are summarized in Table I, elemental analyses for some of the products are listed in Table II,

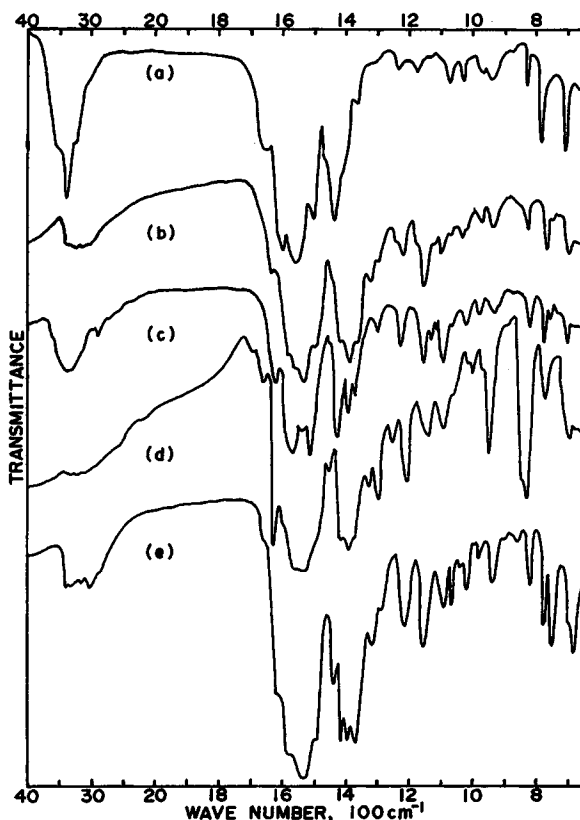


Fig. 1. Infrared spectra obtained by KBr pellet method of (a) PDHT, (b) AP1a, (c) AP1b (d) BP1b, (e) PDBT.

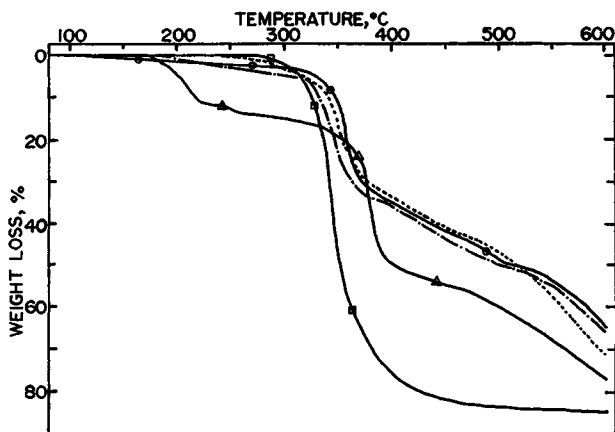


Fig. 2. Thermograms for (—○—) AP1a; (---) AP7a; (—△—) AP7b; (-----) BPlb; (—□—) PDBT.

and the infrared spectra are shown in Figure 1. The elemental analyses of the AP-products agree with the calculated values when water is present. Further drying of the products in vacuo at an elevated temperature of 50°C could remove the water. The corrected values for the found results of AP1a, for example, on the basis of the weight decrease after drying, agree well with the calculated values for the repeating unit of the polymer. In Figure 1, the strong absorptions at 3200–3400 cm^{-1} due to the NH_2 group were greatly reduced in relative intensity in AP1a, AP1b, and BPlb. The spectra of AP1a and BPlb show patterns similar to that of PDBT, which is the model compound. AM3a prepared in polyphosphoric acid also had a similar pattern, although the absorptions were broadened. These facts indicate that both dehydration and dehydrochlorination could yield the polymers. The relatively strong absorption at 830 cm^{-1} in BPlb can be attributed to a C—Cl stretching vibration as well as out-of-plane deformation of *s*-triazine rings.

The dehydration products marked "b" in Table I which precipitated during the reaction generally had a lower yield and smaller intrinsic viscosity than those marked "a" and showed a lesser relative intensity of the absorption at 1540 cm^{-1} assigned to the *s*-triazine ring, as is seen in Figure 1b and c. In addition, AP7b, one of the "b" products, started to decompose at a lower temperature than did AP1a and AP7a in Figure 2. These facts suggest that the "b" precipitates in the dehydration have a lower molecular weight and possibly such groups as $-\text{CH}(\text{OH})\text{NHNH}-$ or a hydrated triazine which may cause "b" products to be less soluble in the solvent. In the dehydrochlorination, however, "b" products were obtained as the main product in a higher yield and were regarded as the expected polymer with a higher molecular weight than "a" products; BP1a, for example, showed relatively intense NH_2 absorption, as compared with BP1b, at 3350 cm^{-1} due to the presence of the unreacted hydrazino group.

Solubility Characteristics of the Polymers

All AP-products were soluble in HMPA. AP4b was dissolved in HMPA for viscosity measurement when warmed to 70°–80°C and did not precipitate after being cooled to 30°C, probably because of low concentration. At a temperature of 100°C, HMPA in general could dissolve the products to a larger extent than did DMSO. This is shown by the yields of AP5 and AP7 in Table I. At a temperature of 50°C, AP4 gave a bigger proportion of "b" precipitate than did AP1, but the precipitate AP4b had a higher molecular weight than the precipitate AP1b. This fact indicates that HMPA, in comparison with DMSO, is capable of dissolving a product of a higher molecular weight. On the other hand, the products of the AM, BP, and BM groups were insoluble in the reaction solvents. Even the methanol-precipitated products such as BP1a and AM4a could not be dissolved after being dried. The lower solubility of the methyl-substituted compounds can probably be ascribed to the essential difference in the affinity to the solvent between the methyl and the phenyl group. In the dehydrochlorination products, a subsequent secondary reaction of the dichloro-*s*-triazine with imino groups —NH— cannot completely be avoided, possibly giving rise to branching which leads to the insoluble polymers.

Thermal Behavior of the Polymers

The thermogravimetric results for some of the polymers are shown in Figure 2 and 3. The decomposition temperature was defined in the present study as the intersection of the two lines drawn on the curve before and after the major change in slope. On the basis of the decomposition temperature of the polymers listed in Table I, it can be stated that the temperature at which the accelerated weight loss occurred was higher with increase in intrinsic viscosity or molecular weight. The similarity of BP1b with AP1a and AP7a in the thermogram shown in Figure 2 indicates that BP1b may have a molecular weight as large as that of AP7a, although the viscosity of

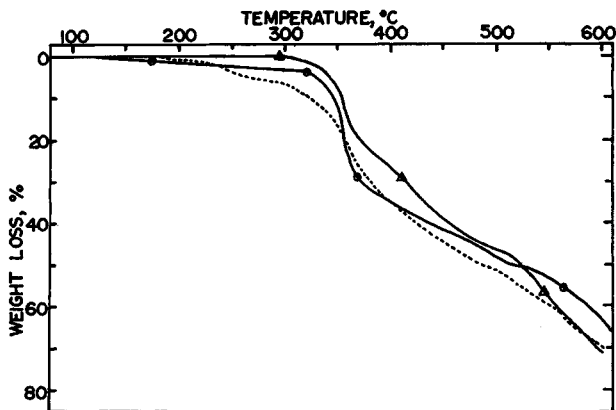
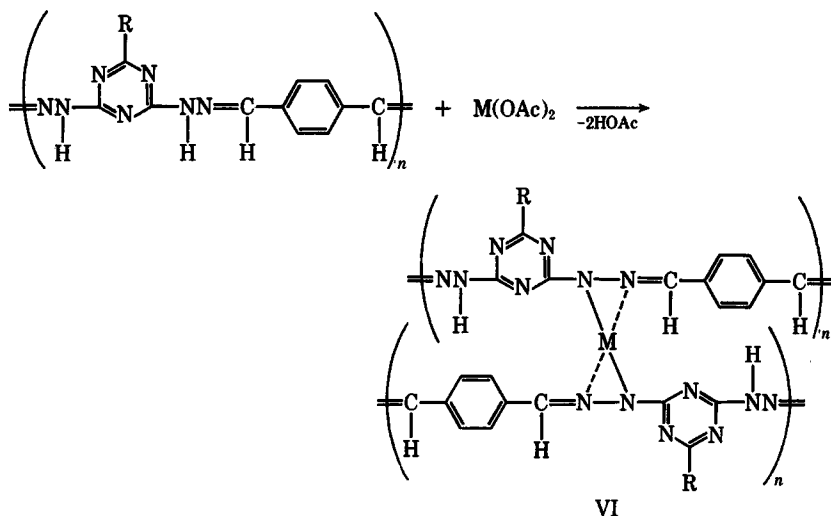


Fig. 3. Thermograms for (—○—) AP1a; (---△---) AM2a; (-----) BM3b.

from benzoguanamine, benzalazine ($C_6H_5CH=NN=CHC_6H_5$), and TADH, all of which have no imino groups. These facts support the formation of a chelate compound such as VI,



but not a coordination product between the metal and the triazine ring. As tabulated in Table III, half of the equivalent weight of the metal acetates was used in order to complete the reaction of the added acetates, although two metals can be stoichiometrically incorporated in the two repeating units of the polymer. A general feature in the thermal behavior of the chelate polymers shown in Figure 4 is the existence of two accelerated decomposition phases in all polymers; their temperatures are listed in Table IV. The

TABLE III
Preparation of Metal-Chelate Polymers (Refluxed at 150°C for 1.5 hr)

Acetate, g ^a	AP1a, g	DMF, ml	Yield, g	Color of precipitate	Metal per repeat- ing unit, g-atom
Mn(OAc) ₂ ·4H ₂ O, 0.098	0.252	2.0	0.051 ^b	yellow brown	0.28
Co(OAc) ₂ ·4H ₂ O, 0.100	0.252	8.8	0.229	dark brown	0.41
Ni(OAc) ₂ ·4H ₂ O, 0.068	0.200	7.0	0.199	dark yellow	0.44
Cu(OAc) ₂ ·H ₂ O, 0.060	0.189	6.3	0.168	dark brown	0.65
Zn(OAc) ₂ ·2H ₂ O, 0.066	0.189	6.3	0.151	yellow orange	0.61
Zn(OAc) ₂ ·2H ₂ O, 0.110	0.393 ^c	2.5	0.123 ^d	yellow	0.70

^a 0.5 g-atom of metal per repeating unit of polymer.

^b Extracted with ethanol for 10 hr but not extracted with DMF, owing to good solubility of product.

^c PDBT.

^d Extracted with methanol for 2 hr but not extracted with DMF, owing to good solubility of product.

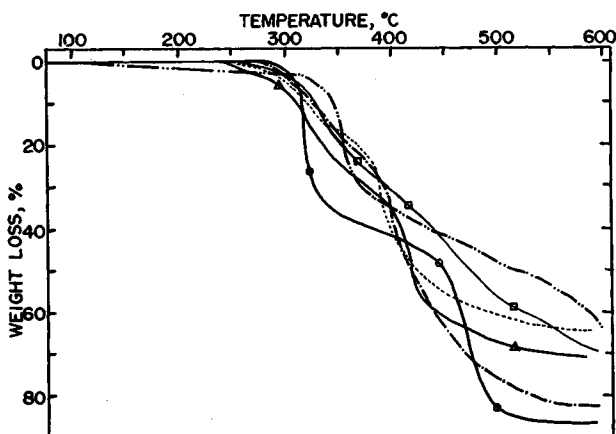


Fig. 4. Thermograms for (---) APla; and the chelate polymers (-O-) Mn, (-Δ-) Co, (· · · · ·) Ni, (- · - · - · -) Cu and (-□-) Zn.

first stage may be accounted for by some extent of N—N scission forming some volatile fractions, and also possibly by the incorporation of a small quantity of solvent which has reacted with the polymer in the presence of a metal compound and by the existence of the unreacted acetate group undetectable by infrared analysis. The greater weight loss of the Mn polymer at 315°C can be ascribed to the incapability of the extraction with DMF and the presence of the acetate residue whose decomposition temperature was exactly 315°C. The Zn-PDBT product showed a similar behavior, probably for the same reason. At the second stage, the thermal stability of the chelates based on the decomposition temperatures listed in Table IV could be related to the atomic number of the metals and their electronegativity in the order of $Mn > Co > Ni > Cu < Zn$. This order coincides with the results of the metal coordination polymer of 5,5'-[*p*-phenylenebis(methylidynenitrilo)] di-8-quinolinol.¹⁶ It is considered that the difficulty in the preparation of the Mn polymer, as represented by a low yield in Table III and the highest decomposition temperature at the second stage, is associated with the very stable energy state of Mn(II).

TABLE IV
Decomposition Temperature and Weight Loss

Metal	Atomic no.	Electro-negativity	1st Stage		2nd Stage	
			Decomp. temp., °C	Wt. loss, %	Decomp. temp., °C	Wt. loss, %
Mn	25	1.5	315	8	450	50
Co	27	1.7	300	7	405	40
Ni	28	1.8	294	2	396	32
Cu	29	1.9	302	5	386	26
Zn	30	1.6	310	5	420	35

The preferential scission of N—N bonds irrespective of the presence of the metals was confirmed by infrared analysis of the white decomposition product which sublimed and condensed on the tube wall, as shown in Figure 5. The spectrum (b) of the sublimate nearest to the furnace was in nearly complete agreement with that of benzoguanamine (c). The spectrum (a) of the sublimate most distant from the furnace stands for a nitrile compound, since a sharp and intense absorption at 2240 cm^{-1} can be assigned to the $\text{C}\equiv\text{N}$ group which is most likely attached to the benzene ring.

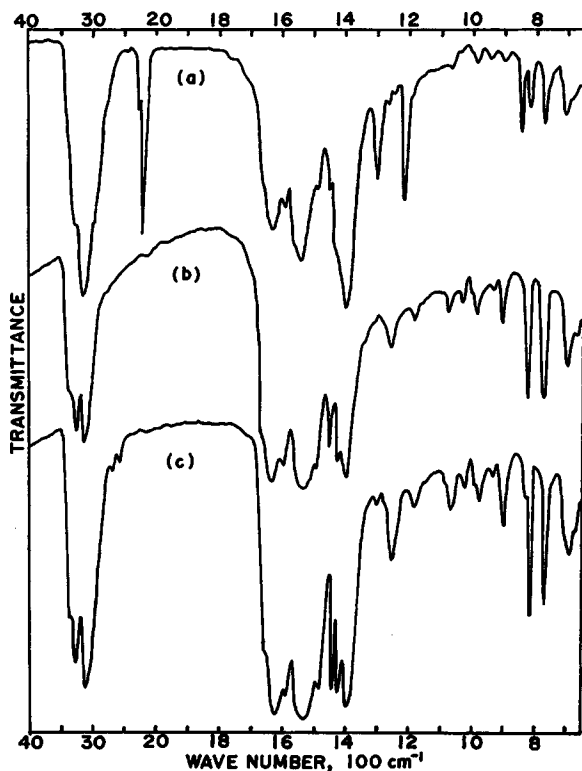


Fig. 5. Infrared spectra obtained by KBr-pellet method, of decomposition sublimes most distant from the furnace (a) and nearest to the furnace (b), and benzoguanamine (c).

In Figure 4, the chelate polymers at the second decomposition stage decomposed more rapidly than AP1a in the same temperature range, but the decomposition temperature was increased (Tables I and IV). The decomposition of the chelate polymers in two phases suggests that although the metals are prone to accelerate the scission of the N—N bonds to some extent at the first stage, the metal—ligand bonds and/or the rearranged organic part of the chelates at the second stage may be thermally rather stable and start to decompose at 400°C or over, along with the extensive N—N scission.

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