Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polymeric Schiff Bases. XII. The Syntheses and Thermal Stabilities of Polyazines and Derived Polystilbenes

G. F. d'Alelio[a]; R. K. Schoenig[a]
[a] Department of Chemistry, University of Notre Dame, Notre Dante, Indiana

To cite this Article d'Alelio, G. F. and Schoenig, R. K.(1968) 'Polymeric Schiff Bases. XII. The Syntheses and Thermal Stabilities of Polyazines and Derived Polystilbenes', Journal of Macromolecular Science, Part A, 2: 5, 979 — 1043
To link to this Article: DOI: 10.1080/10601326808051454
URL: http://dx.doi.org/10.1080/10601326808051454

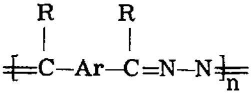
J. MACROMOL. SCI.—CHEM.. A2(5), pp. 979-1043, August, 1968

Polymeric Schiff Bases. XII. The Syntheses and Thermal Stabilities of Polyazines and Derived Polystilbenes

G. F. D'ALELIO and R. K. SCHOENIG*

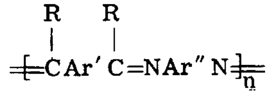
Department of Chemistry
University of Notre Dame
Notre Dame, Indiana

SUMMARY

The synthesis, thermal stability, and the nature of the pyrolytic decomposition of polymeric azines,  $\left[\overset{R}{\overset{|}{C}}-Ar-\overset{R}{\overset{|}{C}}=N-N \right]_n$, in which R is H and CH_3, are reported. These polymers were synthesized by the continuous azeotropic method to yield yellow, insoluble, infusible brick-dust polymers, and by exchange reactions in melts to obtain dark-colored, tractable, fusible polymeric azines which, on heating, became insoluble and infusible and were converted to polystilbene-type polymers. The azine polymers were not very thermally stable; they decomposed thermally at approximately 300°C to yield substantial quantities of nitrogen with the concomitant formation of stilbene segmers in the polymer chains. The derived polymers were thermally stable and their physical characteristics paralleled those of the poly-Schiff bases. Calorimetric and kinetic data on the decomposition reaction of the polyazines are discussed.

INTRODUCTION

Previous studies [1-7] have shown that the polymeric azomethines

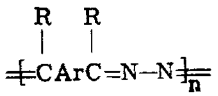


$$\left[\overset{R}{\overset{|}{C}}Ar'\overset{R}{\overset{|}{C}}=NAr''N \right]_n \qquad (I)$$

---

*Taken in part from the Ph.D. dissertation research of R. K. Schoenig.

in which Ar represents an arylene moiety and R is hydrogen or methyl, possess good thermal stabilities. Uninterrupted conjugation would exist also in the polymeric azines,



$$=\!\!\left[\overset{R}{\overset{|}{C}}Ar\overset{R}{\overset{|}{C}}=N-N\right]_n\!\!= \qquad \text{(II)}$$

and they, also, would be expected to exhibit a degree of thermal stability. Accordingly, as an extension of the previous work [1-7], some polymeric azines, (II), were synthesized to compare their thermal properties with those of the polymeric azomethines, (I), and to compare the contributions of the =NArN= and =N—N= moieties to the thermal stabilities of their respective polymers, (I) and (II). Marvel and Hill [8] appear to be the first to have prepared the polymeric aldazines by reaction in solvents of hydrazine with aromatic dialdehydes:

$$nH_2NNH_2 + nOHCArCHO \rightarrow O\!=\!\!\left[HCArCH=N-N\right]_n\!\!=H_2 + 2(n-1)H_2O \qquad (1)$$

The products were isolated [8] as yellow, insoluble, infusible brick-dust condensation products of relatively low molecular weight in the range 500 to 1000; these values were determined by end-group analyses. The low molecular weights were attributed to the insolubility of the condensation products, which caused them to separate from the reaction mixture too rapidly to allow the reaction to proceed further. More recently, a number of low molecular weight polymeric azines were synthesized [9-12] in solution by the reaction of hydrazine with glyoxal, biacetyl, and four aromatic diketones, respectively. These low molecular weight polymers decomposed [8, 9, 12] in the region of 250°C; this behavior would appear to eliminate their consideration for use as thermally stable polymers. However, the nature of the decomposition products was not defined.

The thermal stability of the yellow, low molecular weight, brick-dust, Schiff-base polymers, (I), also was relatively low [1], but this stability was noticeably higher than that of these polyazines, (II). The thermal stabilities of the black polymeric Schiff bases were very much higher than their yellow counterparts. Accordingly, one would expect that if the conjugation in the polyazines was extended by increasing their chain length, the color of the polyazines would also be black, and some improvement in their thermal stabilities should result. Yet the marked difference in the stability of the yellow polyazines and the yellow poly-Schiff base must also be due to differences in the =N—N= and =NArN= moieties. The monomeric Schiff bases [13] such as benzylideneaniline, the dibenzylidenephenylenediamines, the xylylidenedianils, and numerous others demonstrate remarkable thermal stabilities and can be distilled at atmospheric pressure without decomposition.

In contrast, the monomeric azines are relatively unstable. In 1889, Curtius first reported [14] that monomeric dibenzylideneazine decomposed to nitrogen and stilbene:

$$C_6H_5CH{=}N{-}N{=}HCC_6H_5 \rightarrow C_6H_5CH{=}CHC_6H_5 + N_2 \qquad (2)$$

Our preliminary experiments showed that when the yellow poly-(p-xylylidenehydrazine) of Marvel [8], $O{=}\left[{=}HCC_6H_4CH{=}N{-}N{=}\right]_n H_2$, was heated in nitrogen, approximately 3.0% water was eliminated in the temperature range 200 to 300°C, and approximately 30% decomposition products were obtained in the region 300 to 450°C. The decomposition products comprised nitrogen as the molecular species in greatest abundance. Formulated according to the Curtius decomposition [14] for monomeric azines, this would indicate that at least some segments of this azine polymer had decomposed to produce polystilbene segmers:

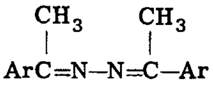
$$\left[{=}HCC_6H_4CH{=}N{-}N{=}\right]_n \rightarrow \left[{=}HCC_6H_4CH{=}\right]_n + N_2 \qquad (3)$$

Interest in this type of polymer is stimulated by the fact that the very act of decomposition liberates an inert nitrogen atmosphere while resynthesizing thermally stable polystilbene [15-17]. Such a polymeric system may well serve as a carbonizing ablator system in aerospace devices.

Before undertaking the synthesis and evaluation of the polyazines, some prototype studies with azine monomers were undertaken to establish the nature and conditions of decomposition as well as alternative methods of syntheses for the monomeric azines on which to base the syntheses of the polymers. The prototype studies on the arylaldazines,

$$ArCH{=}N{-}N{=}HCAr \qquad (III)$$

are the subject of a previous publication [18]. Since the decompositions of

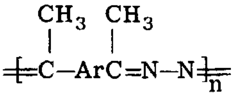


$$Ar\overset{\displaystyle CH_3}{\overset{|}{C}}{=}N{-}N{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}Ar \qquad (IV)$$

might differ substantially with (III), prototype studies were undertaken and are reported in this paper. Also reported are studies on the syntheses of the polyaldazines

$$\left[{=}HCArCH{=}N{-}N{=}\right]_n \qquad (V)$$

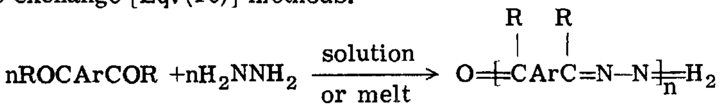
the polyketazines,



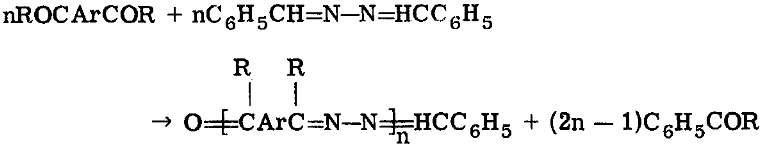
$$=\!\left[\overset{CH_3}{\overset{|}{C}}-Ar\overset{CH_3}{\overset{|}{C}}=N-N\right]_n\!= \qquad \text{(VI)}$$

an .evaluation of their thermal stabilities and some of the properties of their polymeric decomposition products.

Based on the prototype data, studies on the syntheses of the polyazines followed analogously those of the Schiff-base polymers [1-7]. The direct condensation [Eq. (4)] of the arylenedicarbonyl compounds with hydrazine was evaluated in solution and as a melt condensation and compared with the carbonyl-exchange [Eq. (5)]; the amine-exchange [Eq. (6)]; the bis-exchange [Eq. (7)]; the direct-reaction [Eq. (8)]; the acetal-amine [Eq. (9)]; and the acetal-Schiff-base exchange [Eq. (10)] methods.

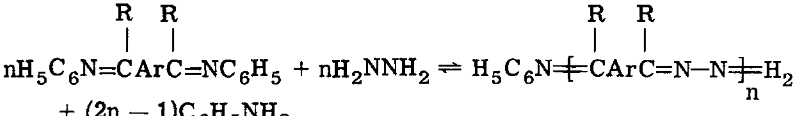


$$nROCArCOR + nH_2NNH_2 \xrightarrow[\text{or melt}]{\text{solution}} O=\!\left[\overset{R}{\overset{|}{C}}Ar\overset{R}{\overset{|}{C}}=N-N\right]_n\!=H_2 \qquad (4)$$



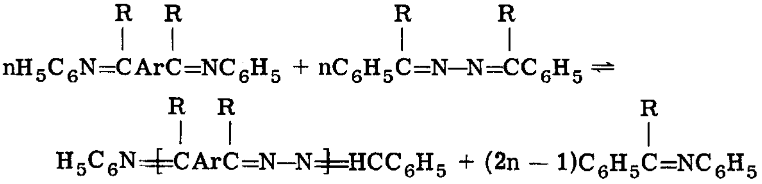
$$nROCArCOR + nC_6H_5CH=N-N=HCC_6H_5$$

$$\rightarrow O=\!\left[\overset{R}{\overset{|}{C}}Ar\overset{R}{\overset{|}{C}}=N-N\right]_n\!=HCC_6H_5 + (2n-1)C_6H_5COR \qquad (5)$$



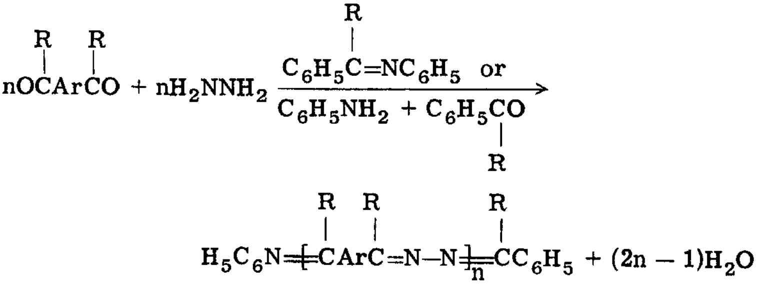
$$nH_5C_6N=\overset{R}{\overset{|}{C}}Ar\overset{R}{\overset{|}{C}}=NC_6H_5 + nH_2NNH_2 \rightleftharpoons H_5C_6N=\!\left[\overset{R}{\overset{|}{C}}Ar\overset{R}{\overset{|}{C}}=N-N\right]_n\!=H_2$$

$$+ (2n-1)C_6H_5NH_2 \qquad (6)$$



$$nH_5C_6N=\overset{R}{\overset{|}{C}}Ar\overset{R}{\overset{|}{C}}=NC_6H_5 + nC_6H_5\overset{R}{\overset{|}{C}}=N-N=\overset{R}{\overset{|}{C}}C_6H_5 \rightleftharpoons$$

$$H_5C_6N=\!\left[\overset{R}{\overset{|}{C}}Ar\overset{R}{\overset{|}{C}}=N-N\right]\!=HCC_6H_5 + (2n-1)C_6H_5\overset{R}{\overset{|}{C}}=NC_6H_5 \qquad (7)$$



$$n\overset{R}{\overset{|}{O}}CAr\overset{R}{\overset{|}{C}}O + nH_2NNH_2 \xrightarrow[C_6H_5NH_2\ +\ C_6H_5\underset{R}{\underset{|}{C}}O]{C_6H_5\overset{R}{\overset{|}{C}}=NC_6H_5\ \text{or}}$$

$$H_5C_6N=\!\left[\overset{R}{\overset{|}{C}}Ar\overset{R}{\overset{|}{C}}=N-N\right]_n\!=\overset{R}{\overset{|}{C}}C_6H_5 + (2n-1)H_2O \qquad (8)$$

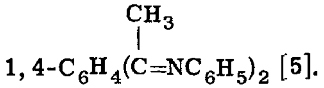
$$\mathrm{n(RO)_2HCArCH(OR)_2 + nH_2NNH_2 \rightarrow (RO)_2{-}\!\!\left[HCArCH{=}N{-}N{=}\right]_n\!\!H_2 + (2n-1)ROH} \qquad (9)$$

$$\mathrm{n(RO)_2HCArCH(OR)_2 + nC_6H_5CH{=}N{-}N{=}HCC_6H_5 \rightarrow}$$
$$\mathrm{(RO)_2{=}\!\!\left[HCArCH{=}N{-}N{=}\right]_n\!\!HCC_6H_5 + (2n-1)C_6H_5CH(OR)_2} \qquad (10)$$

EXPERIMENTAL

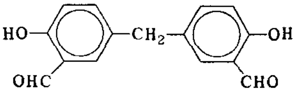
Monomers and Reagents

The following commercially available compounds, 1, 4-$C_6H_4(CHO)_2$ [13], 1, 3-$C_6H_4(CHO)_2$ [13], and 1, 4-$CH_3COC_6H_4OCCH_3$ [5] were purified by crystallization or distillation. Analytical-grade salicyclaldehyde was used as received. Recently published procedures were used to prepare the following monomers: 1, 4-$C_6H_4(CH{=}NC_6H_5)_2$ [13], $[C_6H_5CH{=}N\text{-}]_2$ [13], 1, 4-$C_6H_4[CH(OC_4H_9)_2]_2$ [6, 19], and



$1,4\text{-}C_6H_4(\overset{CH_3}{\overset{|}{C}}{=}NC_6H_5)_2$ [5].

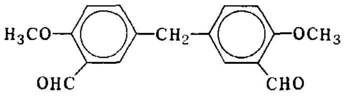
Bis(3-formyl-4-hydroxyphenyl)methane,



(VII)

was prepared by the following modification of Smith's procedure [20]. Salicylaldehyde, 122. 0 g (1. 00 mole); acetic acid, 250 ml; and 37. 1% aqueous formaldehyde, 40. 43 g (0. 50 mole) were mixed in a 1000-ml flask equipped with a stirrer and immersed in an ice-water bath. Over the period of about 1 hr there was added dropwise 500 ml of concentrated (97. 3%) sulfuric acid. The temperature of the reaction mixture was then allowed to rise to room temperature; the color of the mixture changed from yellow to cherry red, after which a solid precipitated from the mixture, which was isolated by filtration to yield 60. 0 g of crude product. No effort was made to recover additional product from the filtrate. The crude solid was recrystallized from xylene to give a cream-colored crystalline solid, m.p. 141 to 142°C; lit. [20, 21], 140°C.

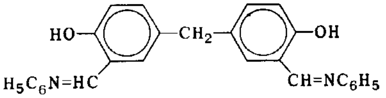
Bis(3-formyl-4-methoxyphenyl)methane,



(VIII)

was prepared by the following procedure: 20.28 g (0.078 mole) of (VII) was added to 100 ml of water in a flask equipped with stirrer, reflux condenser, etc., and the temperature of the mixture raised to 100°C. To the boiling solution was added 110 ml of 20% aqueous NaOH solution to generate the disodium salt in situ. This was followed by addition of 44.50 g (0.353 mole) of dimethyl sulfate over a ½-hr period. The boiling solution was then made alkaline again by addition of 26.4 ml of the aqueous 20% NaOH solution. This was followed by a last addition of 18.60 g (0.148 mole) of dimethyl sulfate added over 1.5 hr. A final addition of 22 ml of the 20% NaOH was then made. At this point a yellow precipitate formed which was removed by filtration, washed several times with distilled water, and then recrystallized from 95% ethanol. The yield was 22.1 g (100%), m.p. 130 to 131°C; lit. [22], 131 to 132°C.

Bis(3-formanilide-4-hydroxyphenyl)methane,

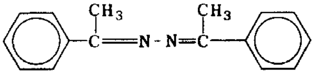


Aniline, 14.51 g (0.156 mole), was reacted with (VII), 20.00 g (0.077 mole), in 200 ml of benzene by the continuous azeotropic method previously published [13]. The yield of crude orange-yellow product was 31.26 g (100%); m.p., recrystallized from 95% ethanol, 145 to 146°C.

Analysis: Calc. for $C_{27}H_{22}N_2O_2$: C, 79.78; H, 5.46; N, 6.89
Found: C, 79.57; H, 5.52; N. 6.97.

Its NMR and infrared spectra are given in Figs. 1 and 2, respectively.

Acetophenoneketazine,



Anhydrous hydrazine was prepared from aqueous 85% hydrazine by the method given by Mellor [23]. Acetophenone, 10.32 g (0.0860 mole), and 1.37 g (0.043 mole) of anhydrous hydrazine were condensed in the presence of 55 ml of benzene and 0.10 g of p-toluenesulfonic acid by the azeotropic method published previously [13]. The yield of crude product (10.1 g) was quantitative; recrystallized from 95% ethanol; m.p. 123 to 124°C; lit. [24], 121 to 122°C. Its infrared spectrum is shown in Fig. 3.

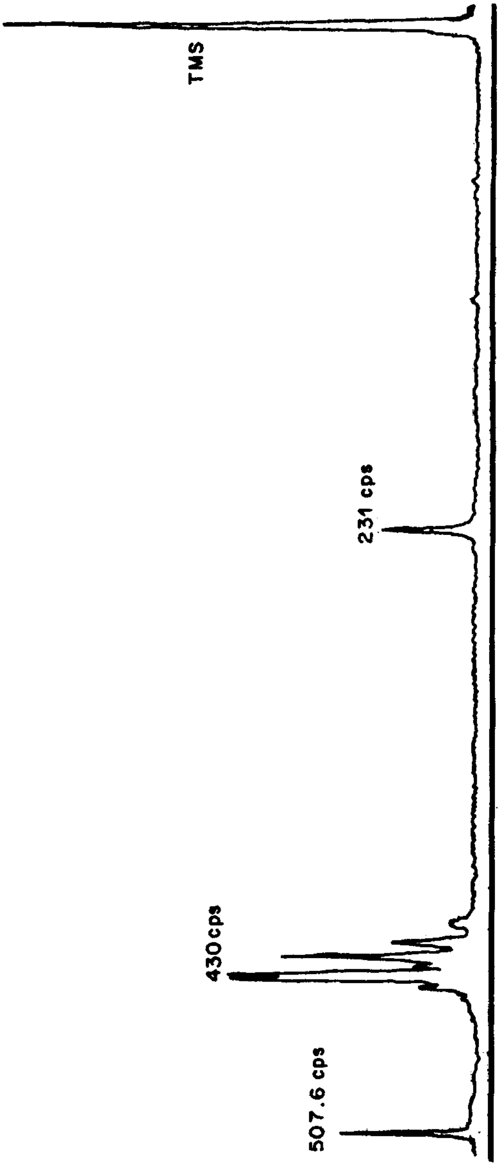


Fig. 1. NMR spectrum of bis(3-formanilide-4-hydroxyphenyl)methane.

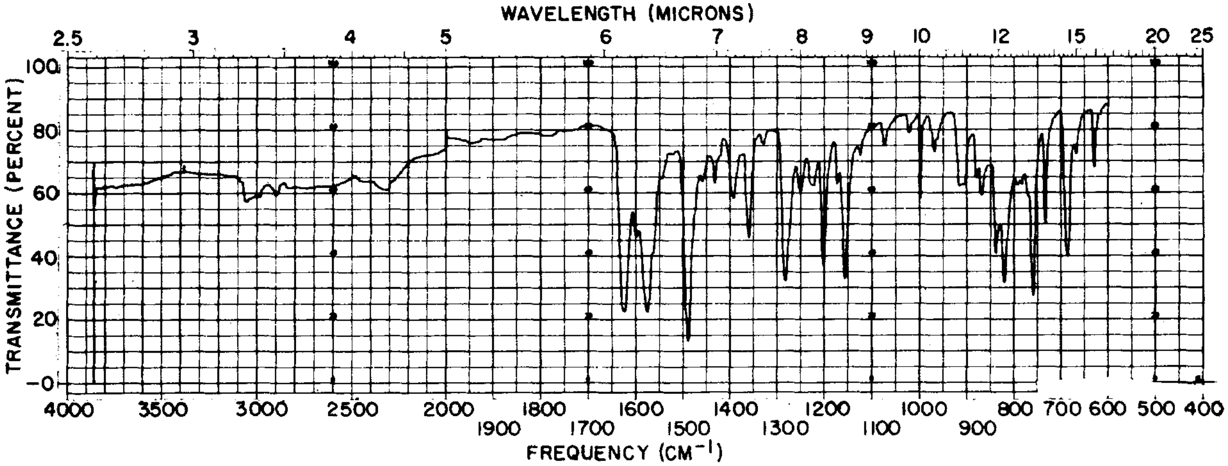


Fig. 2. Infrared spectrum of bis(3-formanilide-4-hydroxyphenyl)methane.

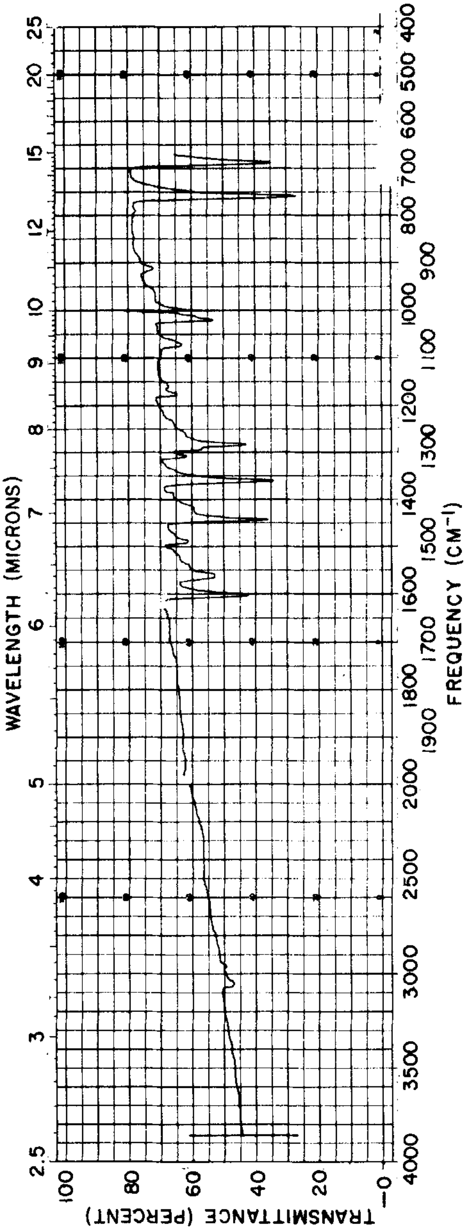
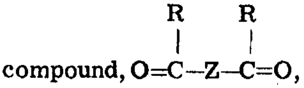


Fig. 3. Infrared spectrum of acetophenoneketazine.

POLYMERIZATIONS

In Solution

Direct Reaction. 1. The procedures previously published were used [1]. The ordinary solution method is illustrated by the following example. The dicarbonyl compound (0.005 mole) and anhydrous hydrazine (0.005 mole) were dissolved in 50 ml of absolute ethanol, water, or acetic acid, respectively, and heated in a nitrogen atmosphere at reflux temperatures for 12 hr. In each case, a yellow, low molecular weight, brick-dust polymer, which was infusible and insoluble in common solvents, was obtained. The infrared spectra of the polymers were similar to those obtained by the azeotropic method.

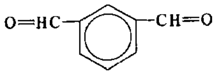
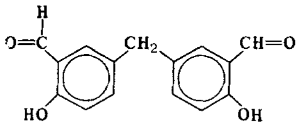
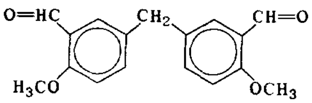
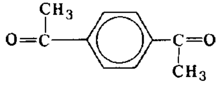
2. The azeotropic method is illustrated by the following example. One mole of dicarbonyl compound,  $O{=}\overset{R}{\overset{|}{C}}{-}Z{-}\overset{R}{\overset{|}{C}}{=}O$, and 1 mole of anhydrous hydrazine [23] were condensed by the previously published procedure [1] in a Dean-Stark apparatus using benzene as the azeotroping agent. The yields and other data are summarized in Table 1. The infrared spectra of these low molecular weight polymers show the presence of NH_2 in the region of 3400 cm^{-1}, C=O in the region of 1700 cm^{-1}, and C=N in the region of 1620 cm^{-1}. The polymers prepared by this method are designated by the suffix Y. The aldazine polymers are indicated by the letters AZ and the ketazine polymers by KZ.

Acetal Reaction. A mixture of p-xylylidenetetrabutyl ether, 1.8088 g (0.00458 mole), and anhydrous hydrazine, 0.1471 g (0.00458 mole), was dissolved in 50 ml of absolute ethanol in a suitable apparatus and the mixture refluxed, under a nitrogen atmosphere, for 2 hr. The solution remained clear and colorless. Then, 0.05 g of $ZnCl_2$ was added and the refluxing (~ 78°C) continued. The solution clouded immediately with the formation of a precipitate. At the end of 6 hr, the reaction was terminated; the precipitate was removed by filtration, washed with distilled water, and dried. There was obtained 0.0450 g (67% yield) of a yellow, insoluble, infusible brick-dust polymer.

However, when an equivalent amount of p-xylylidenetetraethyl ether was used instead of the tetrabutyl ether, a yellow, insoluble, infusible polymer was obtained without the use of a catalyst.

Amine Exchange. A mixture of p-xylylidenedianil, 1.009 g (0.00352 mole), and anhydrous hydrazine, 0.1127 g (0.00352 mole), was dissolved in 10 ml of absolute ethanol in a microflask and the mixture stirred at room temperature for 24 hr. The precipitate which formed was recovered by filtration, washed with ethanol, and dried. There was recovered 0.40 g (87% yield) of a yellow, insoluble, infusible, brick-dust polymer.

Table 1. Y series of $O{=}\!\!\left[\overset{R}{\overset{|}{C}}{-}Z{-}\overset{R}{\overset{|}{C}}{=}N{-}N\right]_{n}\!{=}H_2$ Polymers Prepared by the Azeotropic Method

Polymer	$O{=}\overset{R}{\overset{|}{C}}{-}Z{-}\overset{R}{\overset{|}{C}}{=}O$ used	Yield,[a] %	m.p.	Color	$\bar{n}$[b]	Analyses C	Analyses H	Analyses N	Infrared spectrum Fig. No.
1-AZ-Y		92	Infusible	Yellow	3	69.76	5.08	23.11	4
2-AZ-Y		99	Infusible	Yellow	3	70.07	4.93	20.66	5
3-AZ-Y		93	Infusible	Yellow	6	70.56	4.69	12.03	6
4-AZ-Y		91	Infusible	Yellow	3	70.94	5.98	10.74	7
1-KZ-Y		93	Infusible	Yellow	3	72.85	6.83	15.18	8

---

[a] Based on $\bar{n}$

[b] Estimated on the basis of elemental analysis.

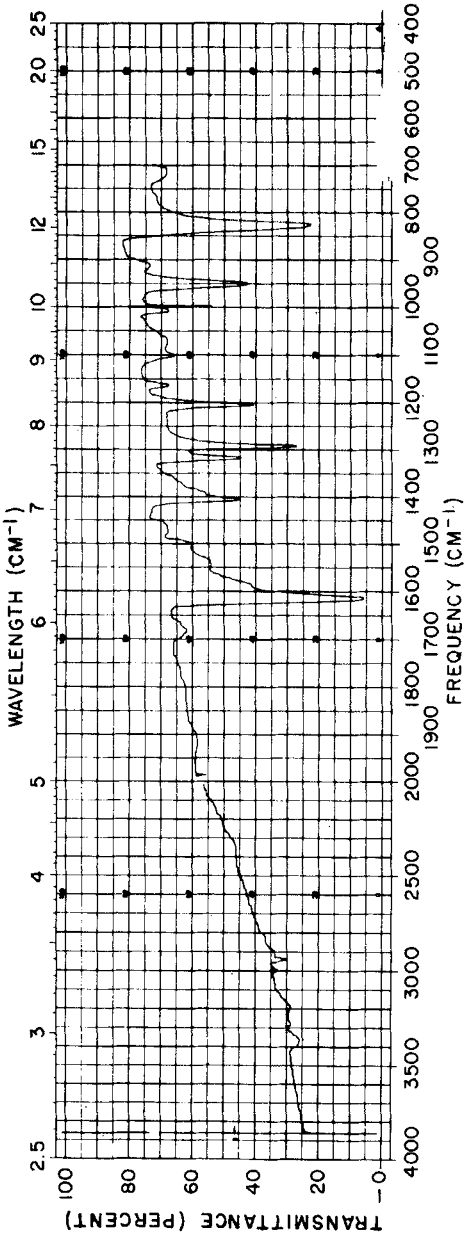


Fig. 4. Infrared spectrum of polymer 1-AZ-Y.

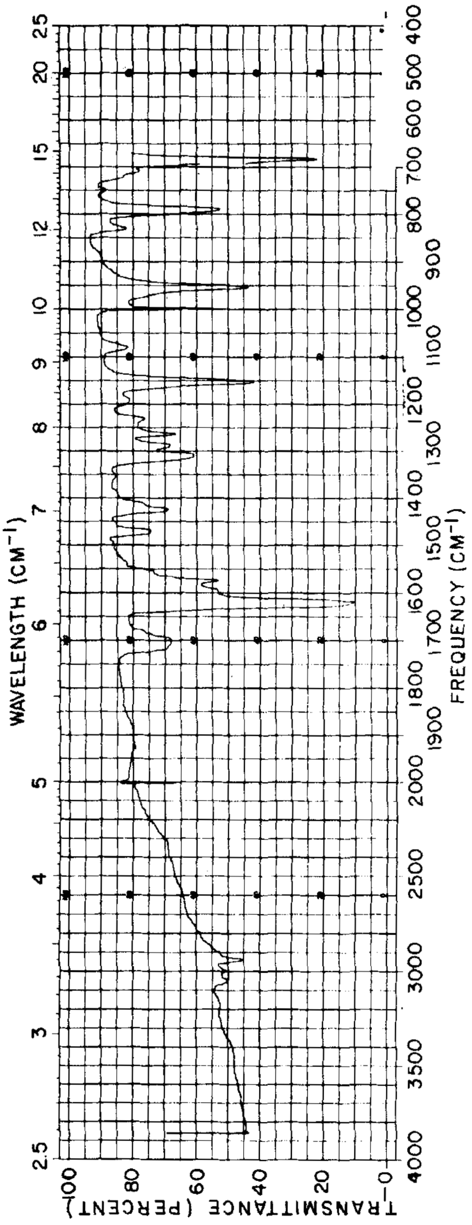


Fig. 5. Infrared spectrum of polymer 2-AZ-Y.

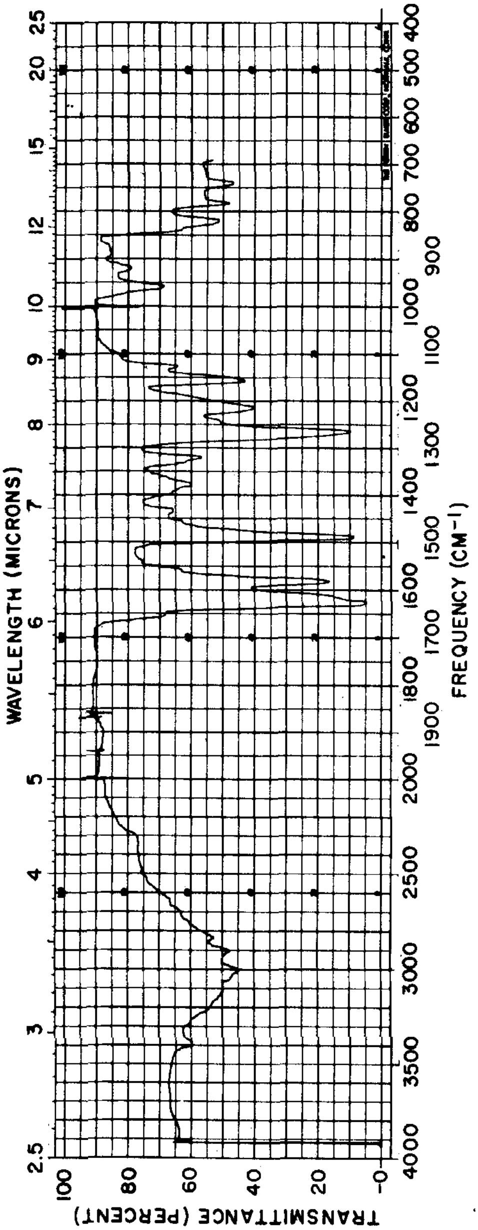


Fig. 6. Infrared spectrum of polymer 3-AZ-Y.

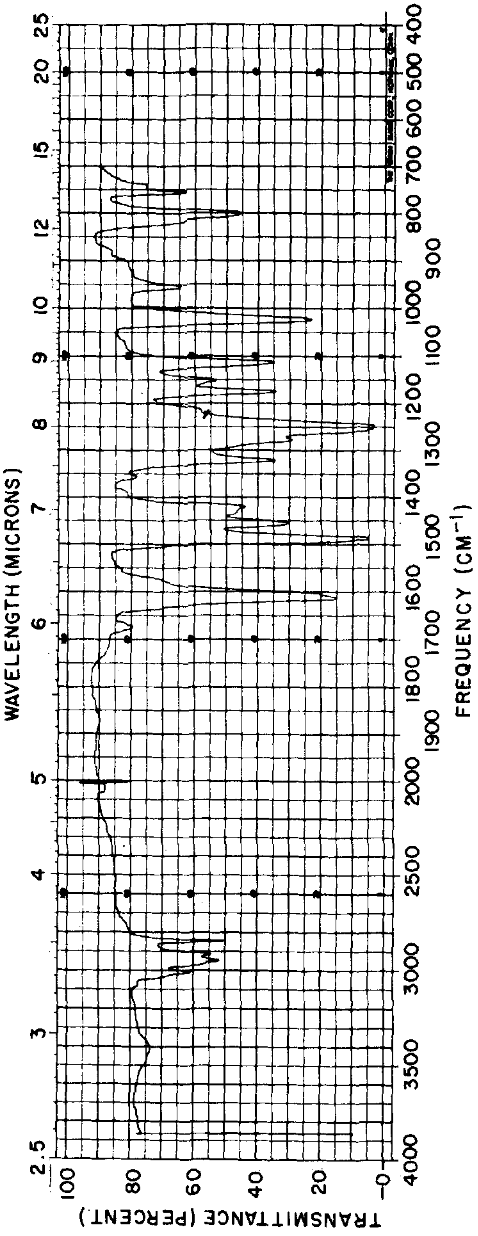


Fig. 7. Infrared spectrum of polymer 4-AZ-Y.

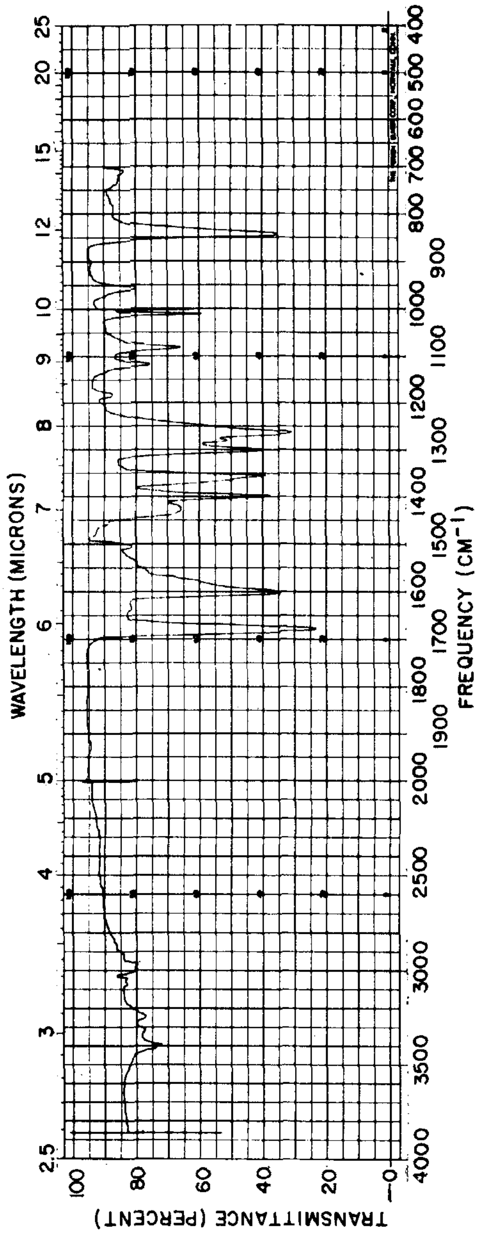
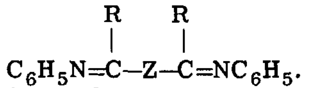


Fig. 8. Infrared spectrum of polymer 1-KZ-Y.

Carbonyl Exchange. A mixture of terephthaldehyde, 0. 5417 g (0. 002 mole); dibenzylideneazine, 0. 4172 g (0. 002 mole); and 50 ml of absolute ethanol was refluxed under a nitrogen atmosphere for 2 hr. The solution remained clear and colorless until 0. 05 g of $ZnCl_2$ was added to the reaction mixture, at which time it became clouded. At the end of 5 hr of reflux, there was isolated by filtration 0. 532 g (95% yield) of an insoluble, infusible, brick-dust polymer

Bis Exchange. A mixture of p-xylylidenedianil, 2. 84 g (0. 01 mole); dibenzylideneazine, 2. 801 g (0. 01 mole); and 25 ml of benzene was refluxed for 6 hr under a nitrogen atmosphere without a change in the color of the solution. However, when 0. 010 g of zinc chloride was added initially to the reaction mixture, a precipitate formed which was recovered by filtration and dried. There was isolated 2. 28 g of a yellow-orange polymer whose infrared spectrum showed bands for the presence of terminal C_6H_5 groups at 750 and 695 cm^{-1}.

Melt Reactions

Bis Exchange. The apparatus and procedure previously described [1] were used to condense 1 mole of $[C_6H_5CH{=}N\!-]_2$ with 1 mole of  $C_6H_5N{=}\overset{R}{\overset{|}{C}}-Z-\overset{R}{\overset{|}{C}}{=}NC_6H_5$. The maximum temperature, °C, used in the condensation reaction is indicated [1] by the suffix H followed by the numerical value of the temperature; the polymers prepared by the bis-exchange method are designated by the letter B following AZ for the polyaldazines and KZ for the polyketazines. Samples of the polymers were withdrawn at 225°C for elemental analyses. The reactions for the polyaldazines were terminated at 275°C. Since the polyketazine, 1-KZ-B-H275, was still very fluid and of low molecular weight, the condensation was continued at progressively higher temperatures to 350°C until a dark-colored, solid polymer was obtained. The schedule of Table 2 was used to prepare the polymers listed in Table 3.
During the course of the reactions, the color of the reaction mixtures changed from yellow, to orange, to red, to light brown, and then to dark brown.

The bis-exchange AZ-B-H225 and KZ-B-H350 polymers were infusible, brown in color, and insoluble in all common organic solvents but soluble in concentrated sulfuric acid; however, the B-H275 polymers were also infusible, black, glossy materials which were insoluble in all solvents tried.

Data on the B series of polymers prepared by the melt bis-exchange method are shown in Table 3.

Table 2. Schedule for Table 3.

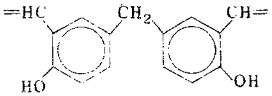
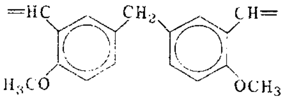
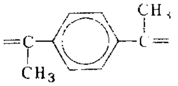
Polymer	Temp., °C	Time, hr	Pressure, mm Hg
B-H225	225	2	760.0
	225	1	150.0
	225	18	1.5
B-H275	220	2	760.0
	225	2	760.0
	250	2	760.0
	275	2	760.0
	275	2	1.5
B-H350	200	2	760.0
	225	2	760.0
	250	2	760.0
	275	4	1.5
	300	2	1.5
	325	2	1.5
	350	2	1.5

Direct Method. The following is a typical example of the direct method of synthesis. A mixture of 1, 4-$C_6H_4(CHO)_2$, 0.6326 g (0.0047 mole) anhydrous H_2NNH_2, 0.1509 g (0.0047 mole); and $C_6H_5CH{=}NC_6H_5$, 0.8536 g (0.0047 mole), or equivalent amounts of C_6H_5CHO and $C_6H_5NH_2$ were condensed in an apparatus [1, 3] using procedures previously described [3] and the following temperature, time, and pressure schedule:

Temp., °C	Time, hr	Pressure, mm Hg
200	2	Atm.
225	2	Atm.
250	2	Atm.
275	2	Atm.
275	2	1.5

The polymerization proceeded similarly to the bis-exchange methods. The color changes were similar, and a black glassy, infusible, insoluble polymer was obtained in 121% yield. The infrared

Table 3. B series of Polymers, $\overset{R}{\overset{|}{+\!\!\!=\!C}}-Z-\overset{R}{\overset{|}{C}}=N-N\!\!+\!\!\!=_{n}$, Prepared by Bis Exchange

Polymer	$\overset{R}{\overset{|}{=C}}-Z-\overset{R}{\overset{|}{C}}=$ structure	Yield[a] at 225°C, %	m.p. of H225, °C	Poly-mer	Analyses C	Analyses H	Analyses N	Infrared spectrum Fig. No.
1-AZ-B		132	Infusible	H225	74.80	5.28	20.04	—
				H275	86.59	5.20	7.19	9
2-AZ-B		126	Infusible	H225	73.70	4.56	11.18	—
				H275	83.62	5.11	5.73	10
3-AZ-B		115	Infusible	H225	73.96	6.00	9.02	—
				H275	79.87	5.83	3.53	11
1-KZ-B		119	Infusible	H225	75.70	6.68	15.90	—
				H350	87.90	5.00	5.20	12

[a] Based on $\overset{R}{\overset{|}{+\!\!\!=\!C}}-Z-\overset{R}{\overset{|}{C}}=N-N\!\!+\!\!\!=_{n=\infty}$.

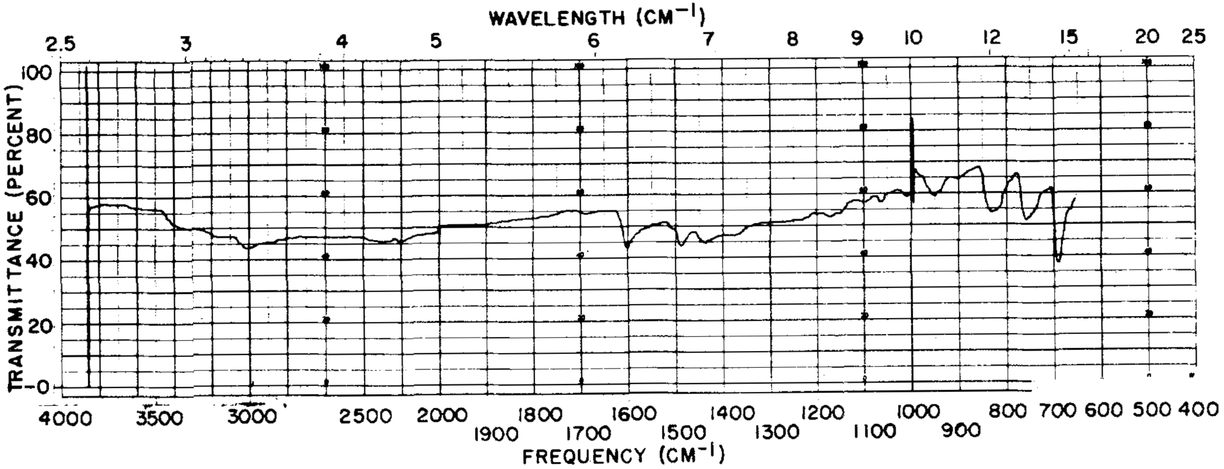


Fig. 9. Infrared spectrum of polymer 1-AZ-B-H275.

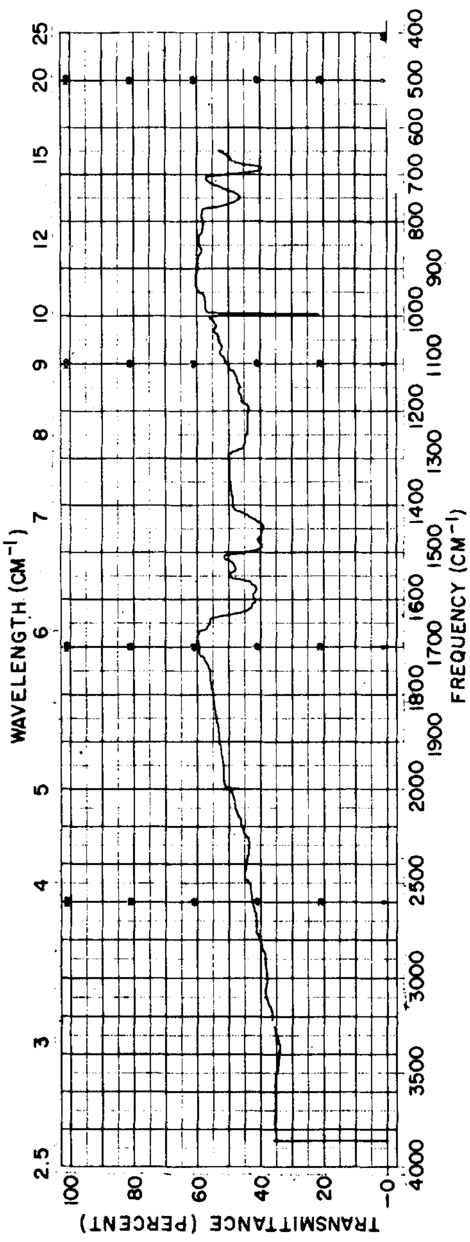


Fig. 10. Infrared spectrum of polymer 2-AZ-B-H275.

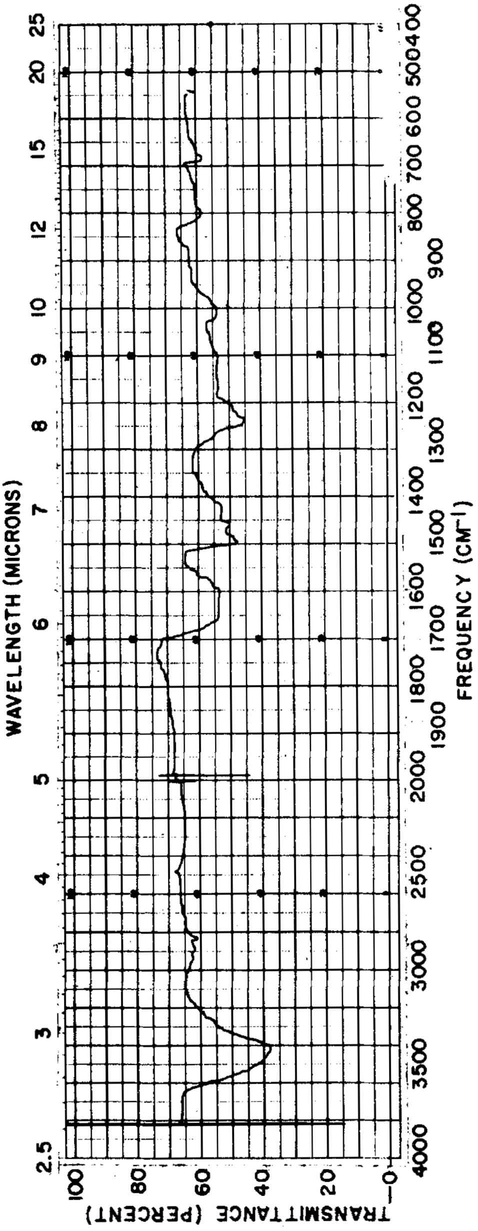


Fig. 11. Infrared spectrum of polymer 3-AZ-B-H275.

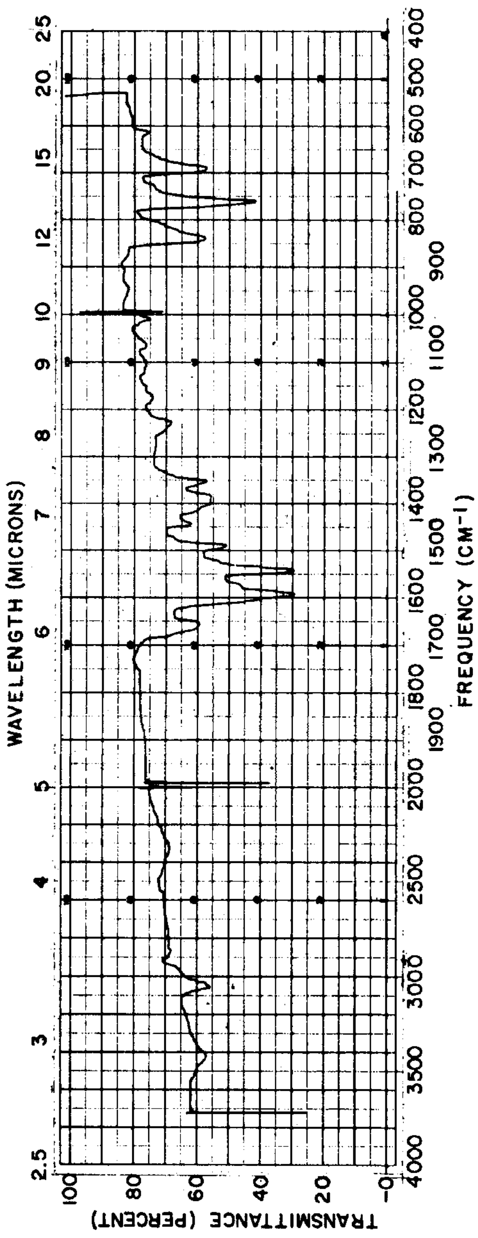


Fig. 12. Infrared spectrum of polymer 1-KZ-B-H350.

spectra and thermal characteristics of polymers prepared by this direct method were identical to the polymers prepared by the melt bis-exchange method.

Carbonyl Exchange. A mixture of terephthaldehyde, 0.5417 g (0.00404 mole), and benzylideneazine, 0.8403 g (0.00404 mole), was reacted under nitrogen by the procedure given [1] above by the bis-exchange method for the B-H225 polymers. Benzaldehyde was collected and identified in the distillate. There was recovered 0.6 g (116% of theory) of a brown, infusible polymer, whose infrared spectra showed the presence of bands for the CHO at 1700 cm^{-1} and for the monosubstituted benzene ring at 760 and 690 cm^{-1}. On further heating at 250 to 300°C for 60 min, an additional amount of benzaldehyde was collected with the simultaneous liberation of noncondensable gases; yield of final polymer, 0.475 g (86%).

Amine Exchange. A mixture of p-xylylidenedianil, 1.0003 g (0.00352 mole), and anhydrous hydrazine, 0.1119 g (0.00352 mole), was reacted in a nitrogen atmosphere in the apparatus previously described [1] with the metal sink previously heated to 225°C. A clear melt formed, hydrazine distilled from the reaction mixture, and at the end of 5 hr the mixture was allowed to cool to room temperature. There was obtained a heterogeneous mass which showed a very broad melting range and on recrystallization from alcohol was shown, by infrared spectra and mixed melting point with an authentic sample, to be mostly p-xylylidenedianil. A small portion, about 11% of theory, of low molecular weight, infusible polymer was isolated.

Acetal Exchange. A mixture of 1.0001 g (0.002537 mole) of p-xylylidenetetrabutyl ether and 0.5281 g (0.002537 mole) of dibenzylideneazine was reacted under nitrogen in the apparatus and procedure [1] given above for the B-H225 polymers. Benzaldehydedibutyl ether and traces of benzaldehyde were isolated as distillates together with 0.3410 g (110% yield) of brown, infusible, brick-dust polymer. The infrared spectrum of the polymer showed the presence of the acetal moiety at 1100 and 1055 cm^{-1}. Continued heating at 275°C and 25 mm Hg lowered the yield to 0.2728 g (79%).

Acetal Reaction. A mixture of p-xylylidenetetrabutyl ether, 1.1158 g (0.0028 mole), and hydrazine, 0.00896 g (0.0028 mole), was reacted under nitrogen in a microflask at 130°C for 45 min, during which time the mixture melted to a yellow solution, which then solidified to a yellow product. There was isolated 0.25 g of a yellow brick-dust polymer which did not melt at 300°C.

The melt polymerizations involving the bis, carbonyl, amine, and acetal exchanges and the direct method proceeded in a similar fashion. The original clear golden-colored melts gradually darkened in color and became more viscous as the polymerization proceeded. The liberation of noncondensable gases was also noted during the course of the polymerizations performed at temperatures in excess of 250°C.

THERMOGRAVIMETRIC ANALYSES

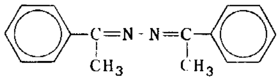
The thermal stabilities of some polymeric azomethines have been reported previously [1-7]. Since a comparison of the thermal stabilities of the polymeric azines, $\left[\overset{R}{\overset{|}{C}}Ar'\overset{R}{\overset{|}{C}}{=}N{-}N\right]_n$, with those of $\left[\overset{R}{\overset{|}{C}}Ar'\overset{R}{\overset{|}{C}}{=}NAr''N\right]_n$ was desired, the same procedures and apparatus [1-7] were used in the present evaluations. A du Pont Model 900 differential thermal analyzer in conjunction with a Model 950 thermogravimetric analyzer was used. The sample size was 10 mg ground to approximately 500 pieces; the rate of heating was 15°C/min in a stream of dry nitrogen or air at a flow rate of 1 standard liter per minute to a recorded temperature of 1200°C, which corresponds to 1176°C when corrected for the nonlinearity of the chromel-alumel thermocouple. Portions of the polymers were condensed to 1176°C in the thermogravimetric analyzer using the technique previously described [1] and the derived products are designated as H1176 polymers.

The thermogravimetric data are shown in Figs. 13 to 16 and are summarized in Tables 4 to 7. The thermogravimetric data for the B-H225 series of polymers were essentially the same as for the Y series and therefore have not been presented separately.

DECOMPOSITION STUDIES

Monomers

The decomposition of acetophenoneketazine,



,was studied using procedures previously published [18] for the various aldazines, $XC_6H_4CH{=}N{-}N{=}HCC_6H_4X$. The decomposition temperature of the ketazine was determined in the du Pont calorimeter cell. This bomb apparatus is a plug-in module for the du Pont Model 900 differential thermal analyzer console and quantitatively plots endo-or exothermic curves resulting from chemical or physical changes occurring in the sample. The results are expressed as ΔH in calories per gram. The test was

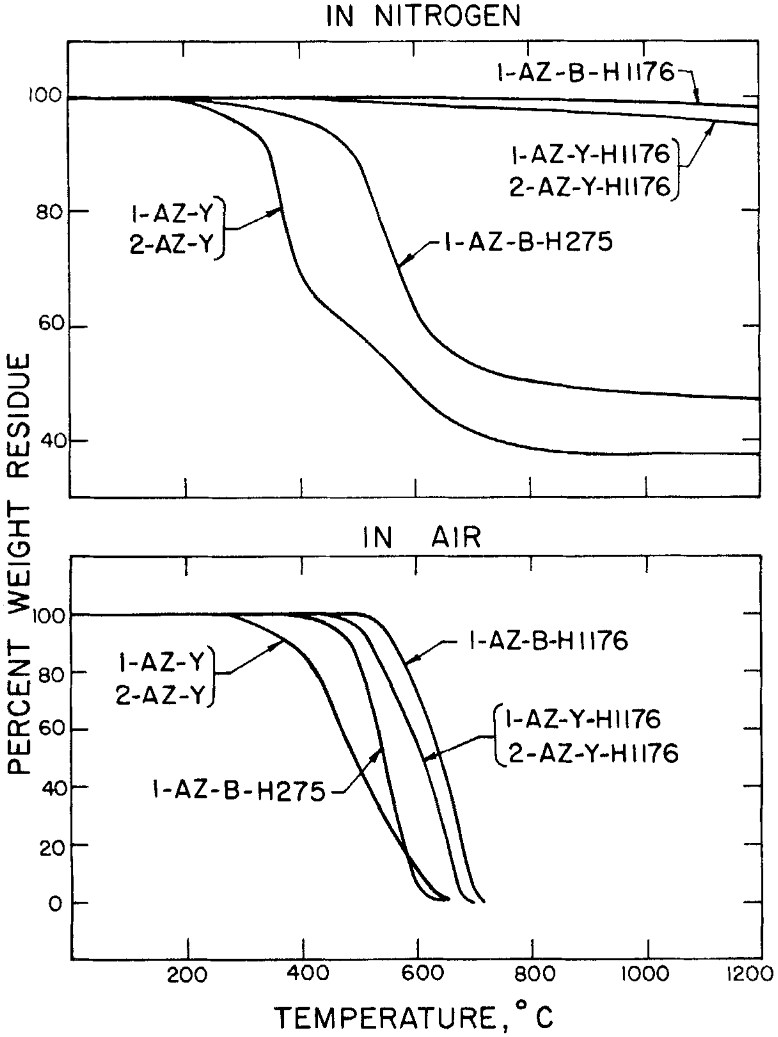


Fig. 13. Thermograms in nitrogen and air of 1-AZ-Y, 2-AZ-Y, 1-AZ-Y-H1176, 2-AZ-Y-H1176, 1-AZ-B-H275, and 1-AZ-B-H1176.

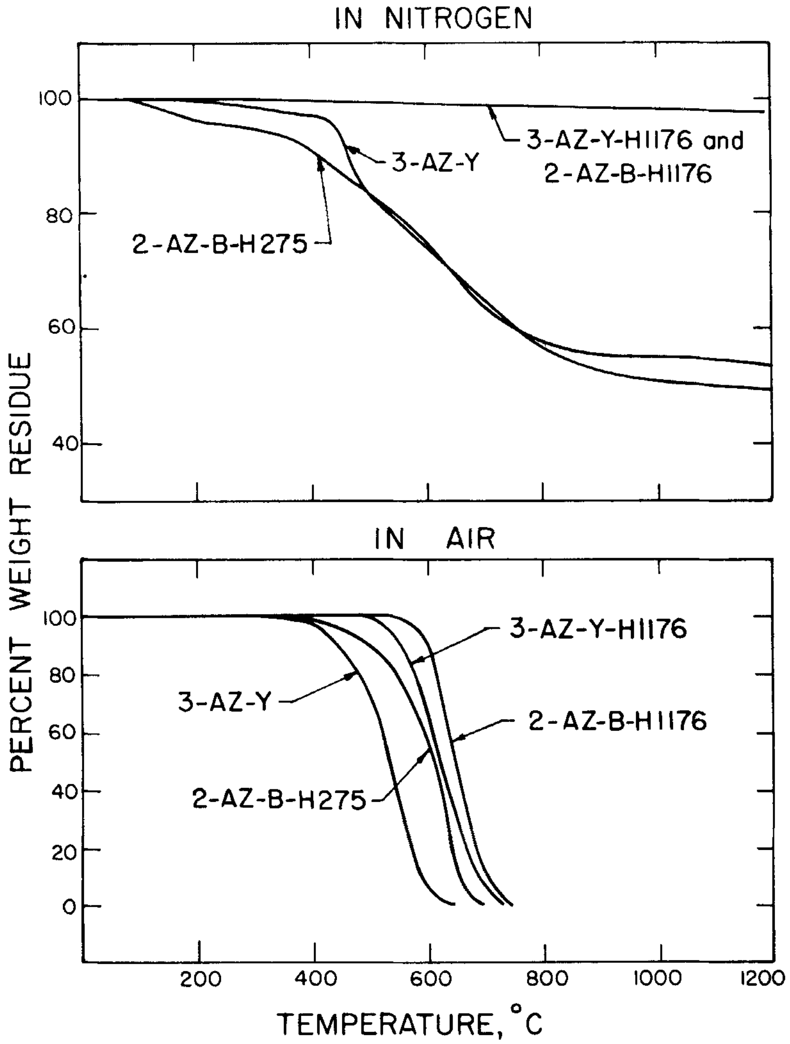


Fig. 14. Thermograms in nitrogen and air of 3-AZ-Y, 3-AZ-Y-H1176, 2-AZ-B-H275, and 2-AZ-B-H1176.

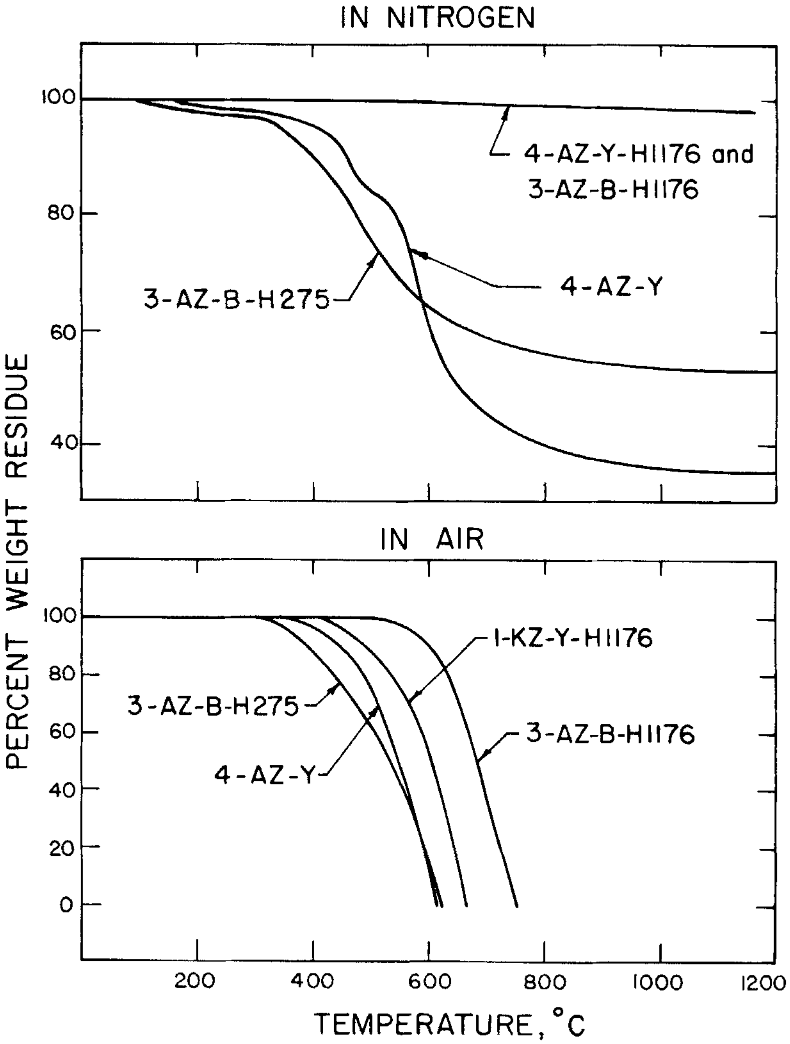


Fig. 15. Thermograms in nitrogen and air of 4-AZ-Y, 4-AZ-Y-H1176, 3-AZ-B-H275, and 3-AZ-B-H1176.

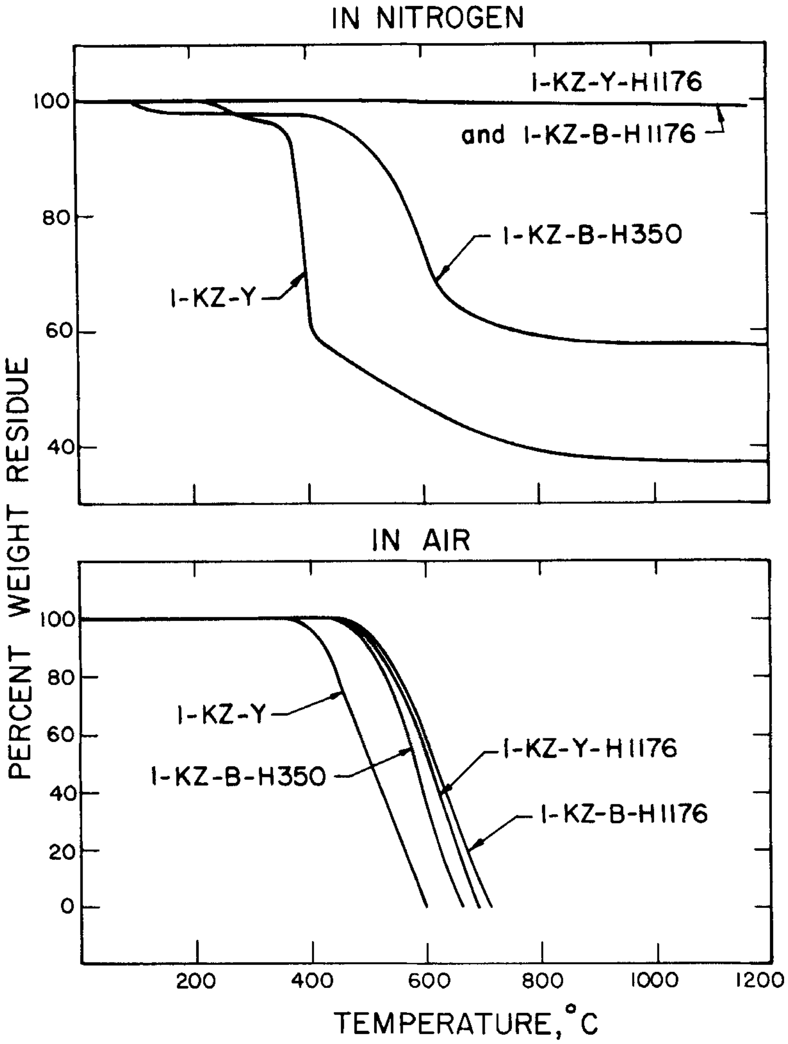


Fig. 16. Thermograms in nitrogen and air of 1-KZ-Y, 1-KZ-Y-H1176, 1-KZ-B-H350, and 1-KZ-B-H1176.

Table 4. Thermogravimetric Analyses in Nitrogen and Air of the Y Series of Polyazines

Polymer	Gas	Heating rate, °C/min	Weight loss at °C, %									
			200	300	400	500	600	700	800	900	1000	1176
1-AZ-Y	N_2	15	0.8	5.0	31.0	40.0	51.0	58.0	61.0	61.0	61.0	62.0
	Air	15	0.0	2.5	12.8	55.0	90.0	100.0	—	—	—	—
2-AZ-Y	N_2	15	0.0	4.7	29.8	37.1	47.4	55.2	58.6	59.2	60.1	62.3
	Air	15	0.0	2.5	14.0	56.2	90.5	100.0	—	—	—	—
3-AZ-Y	N_2	15	0.0	2.0	3.0	14.4	24.1	35.9	44.0	45.0	47.0	50.7
	Air	15	0.0	2.0	3.0	28.0	94.0	100.0	—	—	—	—
4-AZ-Y	N_2	15	0.5	1.5	4.0	16.0	38.0	54.0	60.0	62.0	63.0	64.5
	Air	15	0.0	2.0	12.0	26.0	85.0	100.0	—	—	—	—
1-KZ-Y	N_2	15	0.0	3.0	32.0	47.0	54.0	58.0	60.0	62.0	63.0	64.0
	Air	15	0.0	5.0	36.0	50.0	100.0	—	—	—	—	—

Table 5. Thermogravimetric Analyses in Nitrogen and Air of Polystilbene Types AZ-Y-H1176 and KZ-Y-H1176

Polymer	Gas	Weight loss at °C, %									
		200	300	400	500	600	700	800	900	1000	1176
1-AZ-Y-H1176	N_2	0.0	0.0	0.0	0.0	2.5	2.5	2.5	2.5	2.5	5.0
	Air	0.0	0.0	0.0	3.0	47.0	100.0	—	—	—	—
2-AZ-Y-H1176	N_2	0.0	0.0	0.0	0.0	2.4	2.4	2.4	2.4	2.4	4.8
	Air	0.0	0.0	0.0	5.3	44.2	100.0	—	—	—	—
3-AZ-Y-H1176	N_2	0.0	0.0	0.0	0.0	0.0	1.0	1.5	2.0	2.0	2.5
	Air	0.0	0.0	0.0	1.0	35.0	100.0	—	—	—	—
4-AZ-Y-H1176	N_2	0.0	0.0	0.0	0.0	0.0	0.5	1.0	1.5	1.5	2.0
	Air	0.0	0.0	0.0	4.1	9.0	50.0	100.0	—	—	—
1-KZ-Y-H1176	N_2	0.0	0.0	0.0	0.0	0.5	0.5	1.0	1.0	1.0	1.5
	Air	0.0	0.0	0.0	0.0	45.0	100.0	—	—	—	—

Table 6. Thermogravimetric Analyses in Nitrogen and Air of the AZ-B-H275 and KZ-B-H350 Series of Polyazines

		Heating rate,	Weight loss at °C, %									
Polymer	Gas	°C/min	200	300	400	500	600	700	800	900	1000	1176
1-AZ-B-H275	N_2	15	0.0	1.0	4.0	10.0	35.4	45.5	48.0	49.5	50.5	52.8
	Air	15	0.0	0.0	1.5	16.3	94.3	100.0	—	—	—	—
2-AZ-B-H275	N_2	15	4.0	5.0	9.0	17.2	25.0	35.0	42.0	44.0	44.0	45.0
	Air	15	0.0	0.0	2.0	9.0	43.0	100.0	—	—	—	—
3-AZ-B-H275	N_2	15	2.0	3.0	8.0	23.0	36.0	41.0	43.0	44.0	45.0	46.0
	Air	15	0.0	0.0	8.7	35.0	98.0	100.0	—	—	—	—
1-KZ-B-H350	N_2	15	2.0	2.0	2.0	7.0	25.0	38.0	40.0	41.0	42.0	42.0
	Air	15	0.0	0.0	0.0	8.0	60.0	100.0	—	—	—	—

Table 7. Thermogravimetric Analyses in Nitrogen and Air of the AZ-B-H1176 and KZ-B-H1176 Polymers

		Weight loss at °C, %									
Polymer	Gas	200	300	400	500	600	700	800	900	1000	1176
1-AZ-B-H1176	N_2	0.0	0.0	0.0	1.0	1.0	0.0	1.0	1.0	2.0	2.0
	Air	0.0	0.0	0.0	0.0	25.0	100.0	—	—	—	—
2-AZ-B-H1176	N_2	0.0	0.0	0.0	0.0	0.0	0.0	2.0	2.0	2.0	2.0
	Air	0.0	0.0	0.0	0.0	9.6	89.0	100.0	—	—	—
3-AZ-B-H1176	N_2	0.0	0.0	0.0	0.0	0.0	0.0	1.0	1.0	1.0	1.0
	Air	0.0	0.0	0.0	0.0	6.0	58.0	100.0	—	—	—
1-KZ-B-H1176	N_2	0.0	0.0	0.0	0.0	0.5	0.5	0.8	1.0	1.0	1.3
	Air	0.0	0.0	0.0	0.0	40.0	100.0	—	—	—	—

performed in a nitrogen atmosphere at a heating rate of 10°C/min and the derived thermogram is shown in Fig. 17, in which the onset of decomposition is shown at 325°C with the maximum at 339°C.

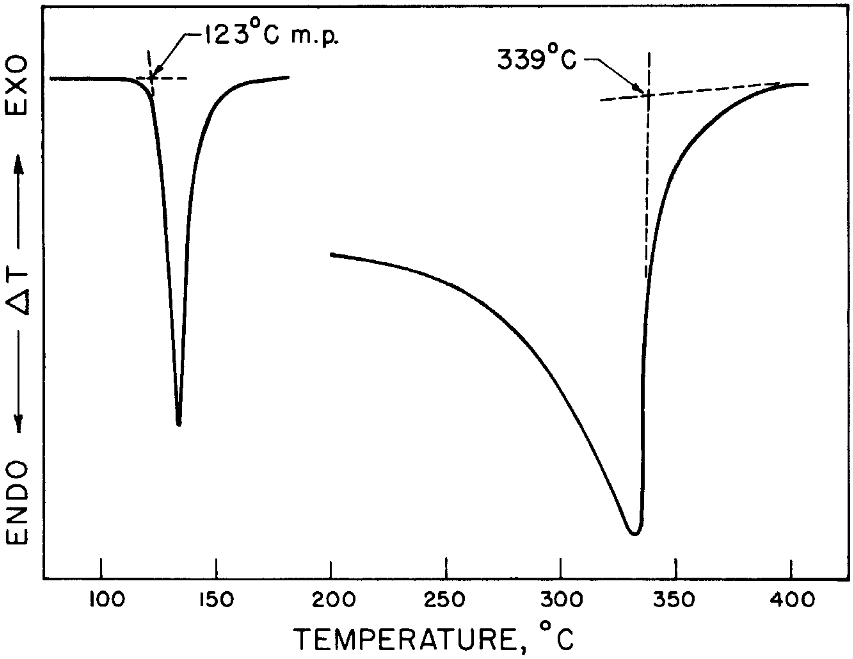


Fig. 17. Calorimetric thermogram of acetophenoneketazine in nitrogen.

Three isothermal decomposition temperatures were selected at which reaction rates were determined as indicated previously [18]. The Arrhenius temperature dependence of these rates yielded an activation energy of 36 kcal/mole with a reaction order essentially unity. The graphs on which these calculations were based are given in Figs. 18 to 21. The total mole per cent nitrogen collected for the acetophenoneketazine was 39%.

Isothermal Decomposition. A modification of the method previously published [18] was used. In these studies samples of the polymer were ground to a fine powder and weighed into a Pyrex reaction tube 12 cm in length and 2.5 cm in diameter. The tube was equipped with a 24/40 ground-glass joint which was connected to a gas buret calibrated in units of 0.1 ml. The tube and its contents were swept out

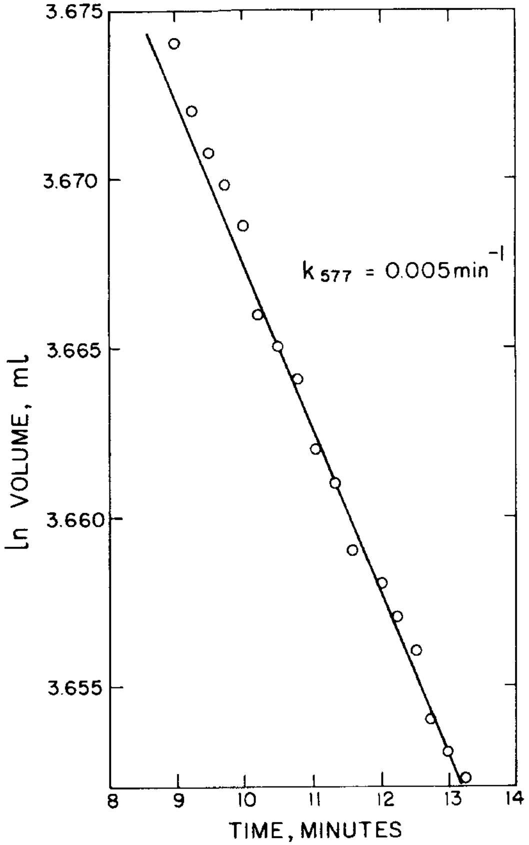


Fig. 18. Plot of ln C (volume N_2) as a function of time for the decomposition of acetophenoneketazine at 577°K.

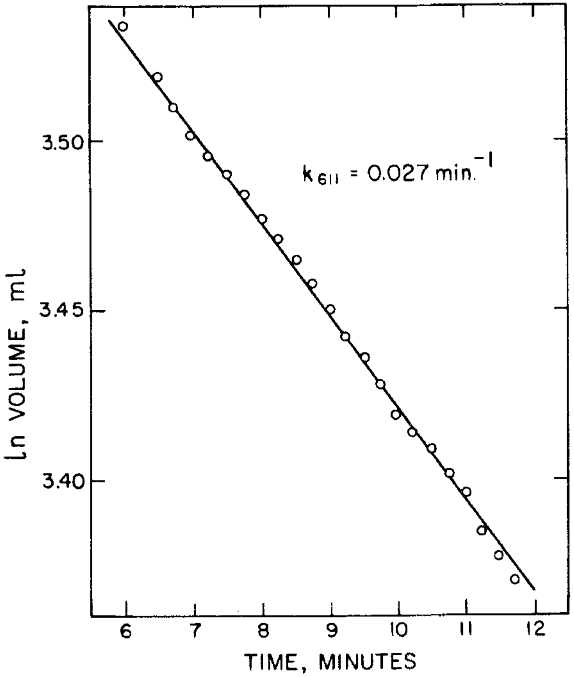


Fig. 19. Plot of ln C (volume N_2) as a function of time for the decomposition of acetophenoneketazine at 611°K.

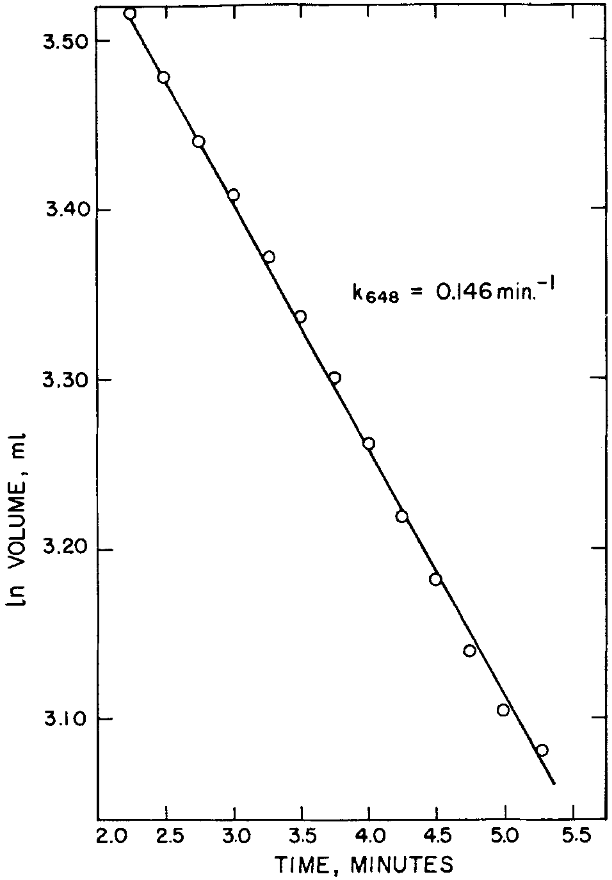


Fig. 20. Plot of ln C (volume N_2) as a function of time for the decomposition of acetophenoneketazine at 648°K.

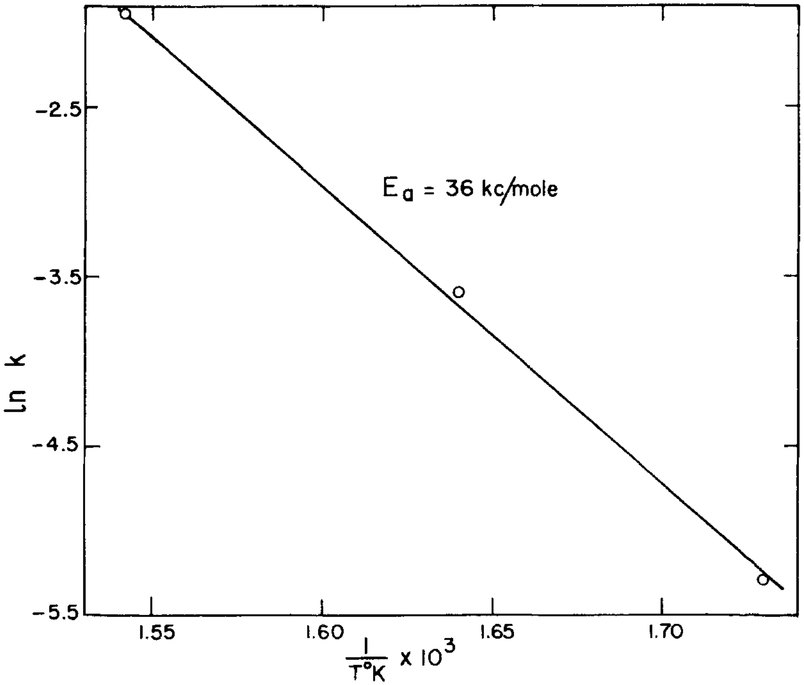


Fig. 21. Plot of ln k (reaction rate constant, min^{-1}) as a function of 1/T, °K × 10^3 for acetophenoneketazine.

thoroughly with deoxygenated nitrogen and then placed into a preheated aluminium block, the temperature of which was automatically maintained at 450 ± 1°C by a Proportionull Model 1300 precision temperature controller. The effluent, noncondensable water-insoluble gases, were collected and the volume measured in the gas buret, which was corrected to standard conditions. Elemental analyses and an infrared spectra were obtained on the residues after they had been extracted for 24 hr with 95% ethanol. The results are incorporated in Table 8 and the infrared spectra are shown in Figs. 22 to 26.

Table 8. Data on Thermal Decomposition of Polyazines at 450°C[a]

						Analysis of extracted H450 residues		
Polymer	W	a	b	c	d	C	H	N
1-AZ-Y	23.11	63.6	6.0	57.6	66.0	83.00	4.96	8.42
2-AZ-Y	20.66	62.0	9.0	53.0	65.0	84.06	4.88	7.80
3-AZ-Y	12.03	56.0	31.0	35.0	35.0	76.45	4.14	5.29
4-AZ-Y	10.74	74.0	12.0	62.0	105.0	81.30	5.09	2.78
1-KZ-Y	15.18	50.0	29.0	21.0	77.0	82.49	5.83	7.55
1-AZ-B-H275	7.19	—	Trace	—	Trace	—	—	—
2-AZ-B-H275	5.73	—	Trace	—	Trace	—	—	—
3-AZ-B-H275	3.53	—	Trace	—	Trace	—	—	—
1-KZ-B-H275	5.20	—	Trace	—	Trace	—	—	—

[a] W, % of N_2 is orginal polymer; a, % of W lost as determined by elemental analysis; b, % of W lost as NH_3; c, a — b; d, noncondensable gas collected in gas buret in terms of % of W.

Nonisothermal Decomposition and NH_3 Determination. These studies were made by the following procedure. The du Pont Model 950 thermogravimetric analyzer was used. An approximate 20-mg sample of the polymer was weighed into the platinum boat located in the TGA. A deoxygenated nitrogen atmosphere was established in the heating chamber at a flow rate of 1 standard liter per minute. The effluent gas then passed through a trap cooled by Dry Ice-acetone and then bubbled into a solution of approximately 0.8% aqueous boric acid. The temperature of the sample was raised at a rate of

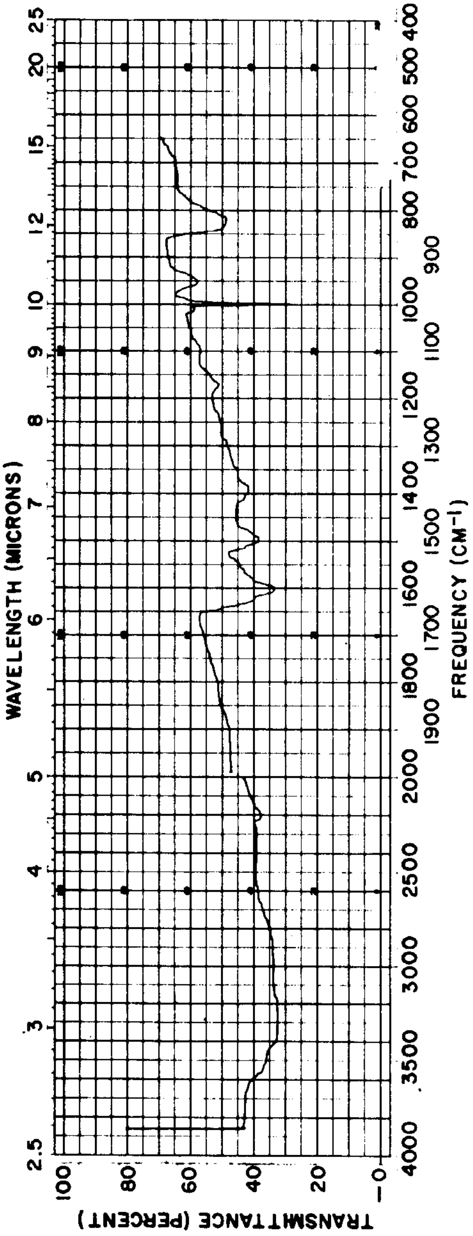


Fig. 22. Infrared spectrum of polymer 1-AZ-Y-H450.

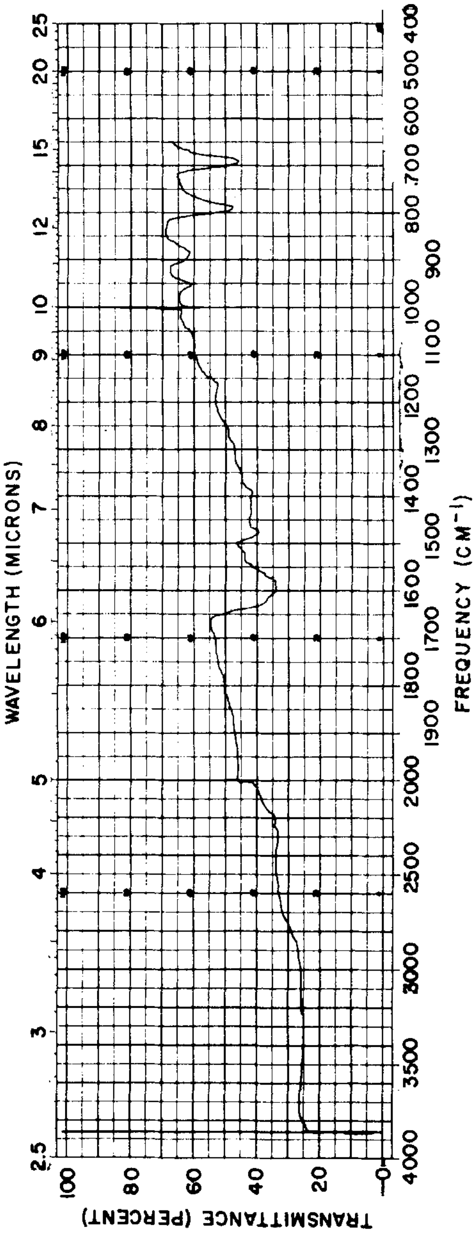


Fig. 23. Infrared spectrum of polymer 2-AZ-Y-H450.

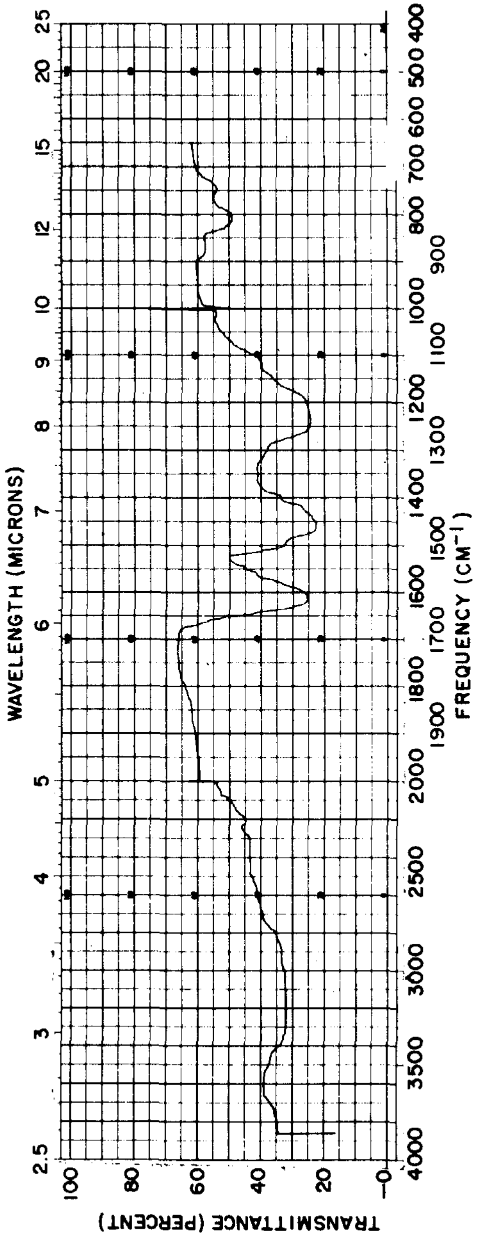


Fig. 24. Infrared spectrum of polymer 3-AZ-Y-H450.

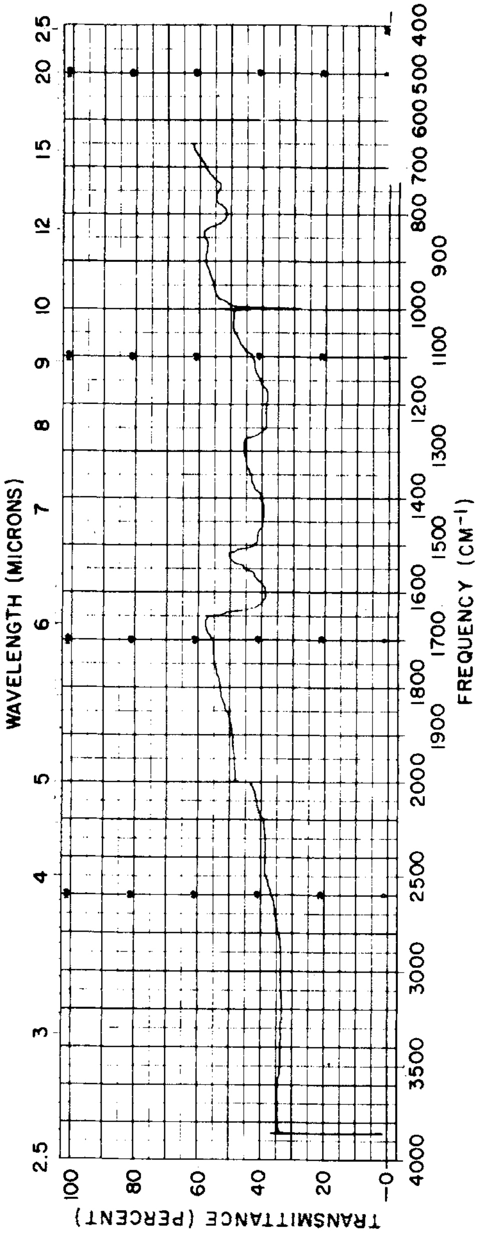


Fig. 25. Infrared spectrum of polymer 4-AZ-Y-H450.

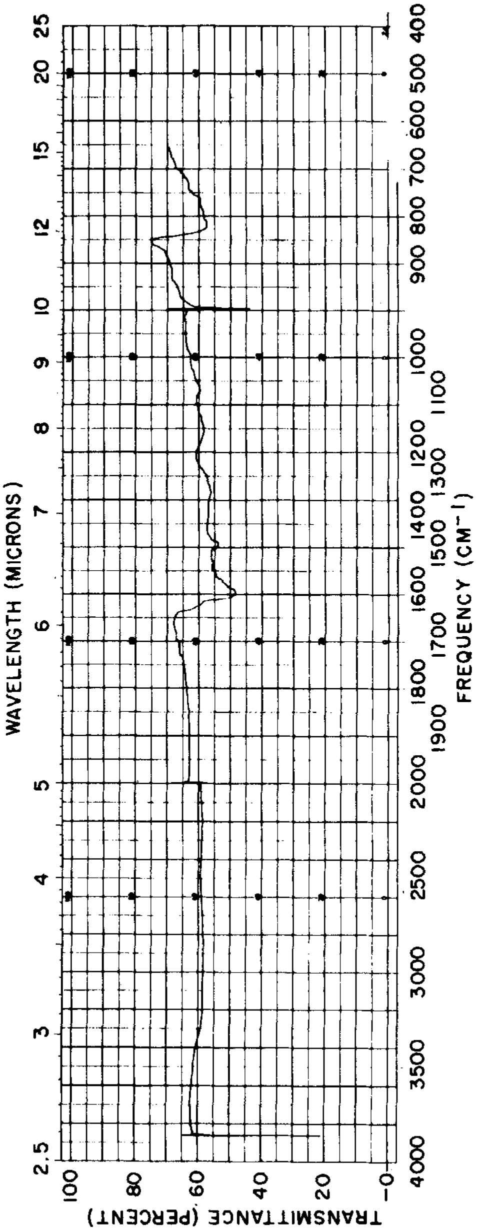


Fig. 26. Infrared spectrum of polymer 1-KZ-Y-H450.

15°C/min. When the temperature reached 475°C it was maintained there until no further weight loss was noted and no basic gases given off, as determined by passing the effluent gases over moist litmus paper. An aliquot of the boric acid solution was then titrated with standard hydrochloric acid and the equivalent amounts of ammonia from the pyrolysis calculated. The polymer sample was recovered after the apparatus had cooled to room temperature. It was extracted with 95% ethanol, its infrared spectrum recorded, and elemental analyses performed. The infrared spectra and elemental analyses of the various polymers were identical to those obtained from the residues of the isothermal decompositions. The results of the NH_3 determinations are incorporated in Table 8.

Calorimetric Studies. The du Pont calorimetric cell described previously [18] was used to determine ΔH values of the decomposing azine polymers. The Y series of polymers as prepared and post-heated to 1176°C by reported procedures [1] were evaluated. Atmospheres of nitrogen and of air were employed with heating rates of 10°C/min. The calorimetric thermograms are shown in Figs. 27 to 32 and the resultant values of ΔH for the polymers in Tables 9, 10, and 11.

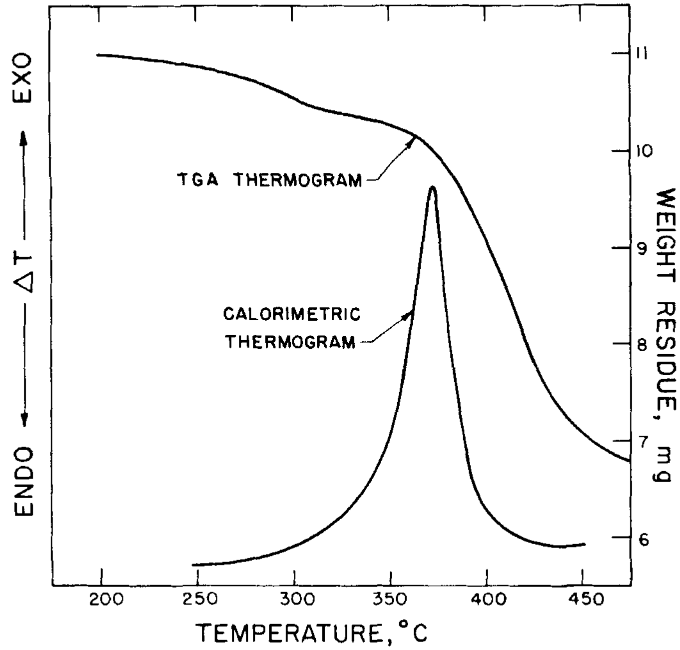
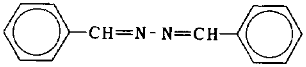
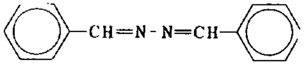
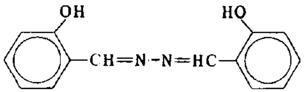
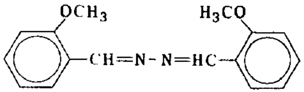
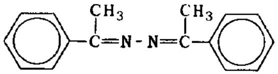


Fig. 27. TGA thermogram and calorimetric thermogram of 1-AZ-Y in nitrogen.

Table 9. ΔH and E_a in Nitrogen for Y Polymers and Related Monomers

Polymer	Nature of peaks	Maximum temp. of peaks, °C	ΔH, cal/g	Order of reaction	E_a kcal/mole	Monomer		Order of reaction
						Structure	E_a	
1-AZ-Y	Sharp	365	253	1	52		40	1
2-AZ-Y	Sharp	357	248	1	50		40	1
3-AZ-Y	Sharp Sharp	285 388	26 93	1	58		44	1
4-AZ-Y	Sharp Sharp	330 436	196 50	1	48		26	1
1-KZ-Y	Sharp	375	133	1	61		36	1

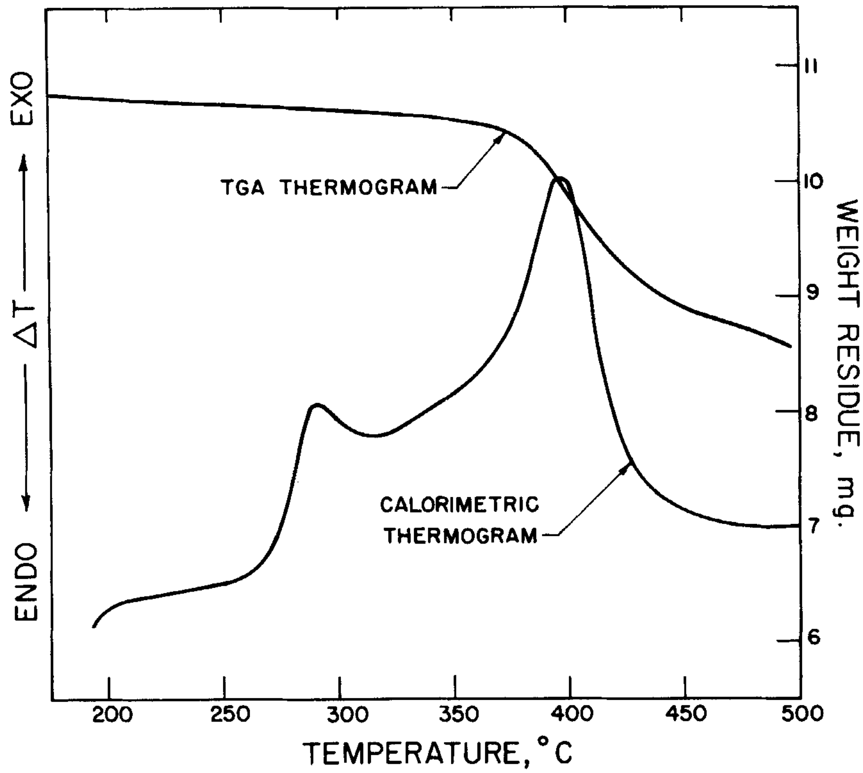


Fig. 28. TGA thermogram and calorimetric thermogram of 2-AZ-Y in nitrogen.

Table 10. ΔH in Air for AZ-Y-H1176 and KZ-Y-H1176 Polymers

Polymer	Nature of peak	Maximum temp. peak at °C	ΔH, cal/g	Nitrogen in H1176 polymer, %
1-AZ-Y-H1176	Sharp	477	1190	0.75
2-AZ-Y-H1176	Sharp	481	1200	0.73
3-AZ-Y-H1176	Sharp	509	1350	1.92
4-AZ-Y-H1176	Sharp	490	2380	1.00
1-KZ-Y-H1176	Sharp	494	3550	1.62
Pyrolytic graphite	Sharp	680	550	—

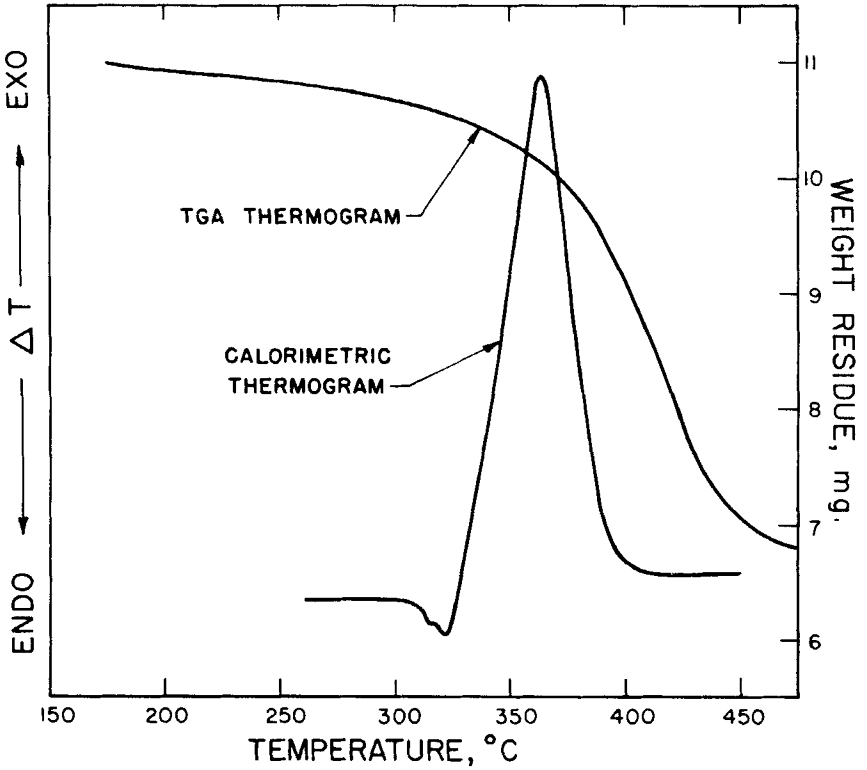


Fig. 29. TGA thermogram and calorimetric thermogram of 3-AZ-Y in nitrogen.

Table 11. ΔH in Air for AZ-B-H1176 and KZ-B-H1176 Polymers

Polymer	Nature of peaks	Maximum temp. peak at °C	ΔH, cal/g	Nitrogen in H1176 polymer, %
1-AZ-B-H1176	Sharp	640	2150	2.20
2-AZ-B-H1176	Sharp	627	2410	1.91
3-AZ-B-H1176	Sharp	638	2250	1.87
1-KZ-B-H1176	Sharp	645	2000	1.79
Pyrolytic graphite	Sharp	680	550	—

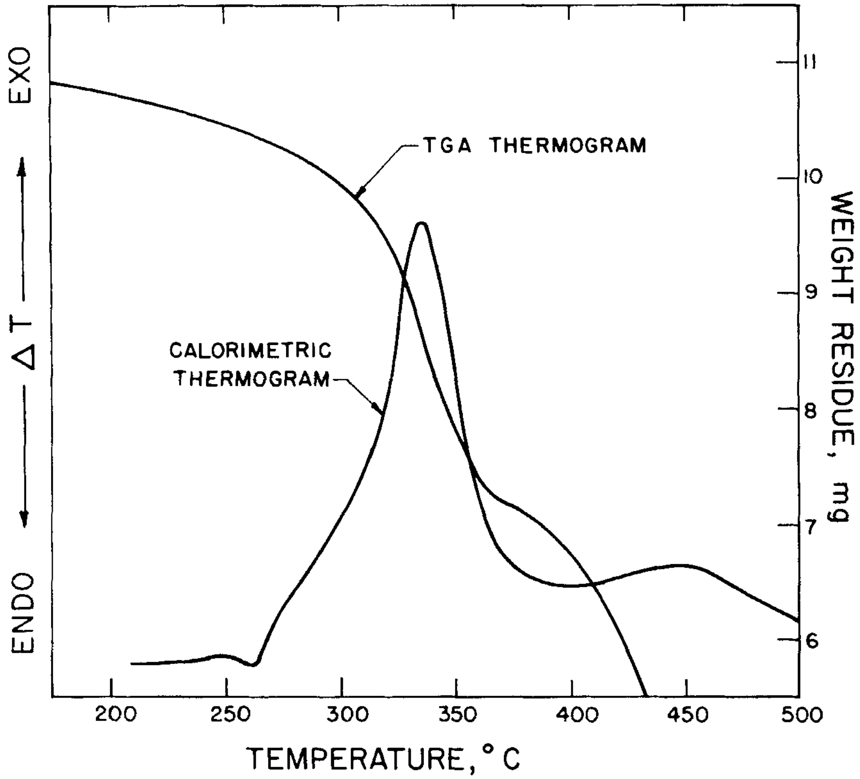


Fig. 30. TGA thermogram and calorimetric thermogram of 4-AZ-Y in nitrogen.

Kinetic Parameters of Decomposition. The thermogravimetric method of Horowitz and Metzger [27] was used to monitor the decomposition of the polyazines. The method uses data obtained from the TGA thermograms to plot the double logarithm of the reciprocal of the weight fraction of the reactant vs. the temperature. If this plot is a straight line, an activation energy and a preexponential factor may be calculated. The results are summarized in Table 9 and in Figures 27 to 31 and 33 to 37.

DISCUSSION

The condensation in solution of the aryldicarbonyl compounds with hydrazine yielded only low molecular weight yellow brick-dust polymers, which were infusible and insoluble in most common orga-

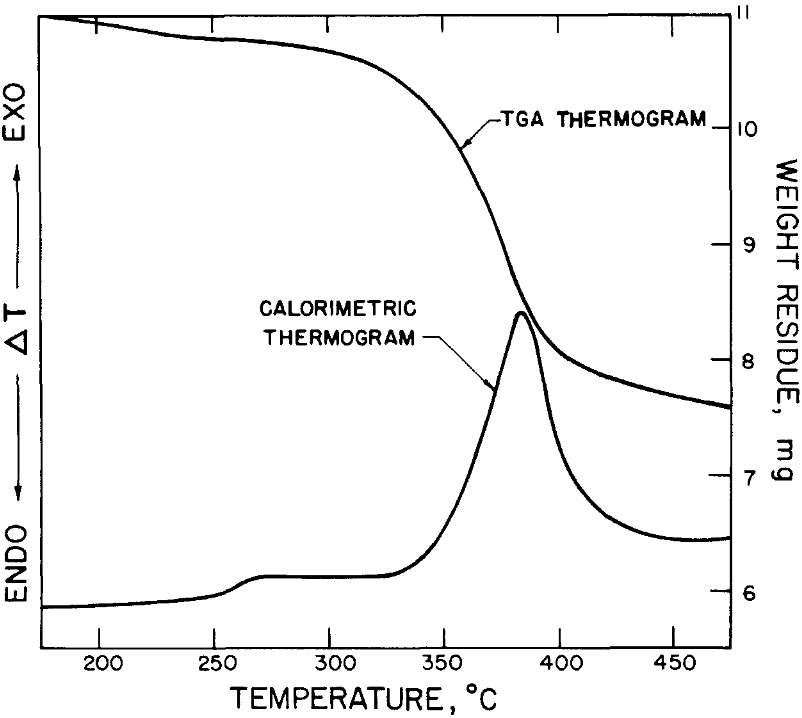


Fig. 31. TGA thermogram and calorimetric thermogram of 1-KZ-Y in nitrogen.

nic solvents. They were, however, soluble in concentrated sulfuric acid. Such solution polymerizations apparently proceeded until a $\overline{DP}$ of approximately 3 was reached, whereupon the polymer precipitated from the solvent, preventing further condensation. This behavior parallels that found for syntheses of the Schiff-base polymers [1-7]. The failure of p-xylylidenetetrabutyl ether to condense with hydrazine in low-boiling solvents, except in the presence of a Lewis acid, can be attributed to steric factors resulting from four bulky butyl groups, since the corresponding ethyl acetal condensed readily with hydrazine. Similarly, the acetal and bis exchanges failed to produce polymers in the absence of catalysts, and in this respect they are similar to the related Schiff-base exchange reactions [1]. The uncatalyzed amine-exchange reaction [Eq. (10)], however, proceeded readily, and thus it differed with the related reaction of the Schiff base [1]; this difference is attributed to the differences in the basicities of H_2NNH_2 and H_2NArNH_2.

In the solution method, the use of high-boiling solvents was avoided to minimize the risk of decomposition of the resulting poly-

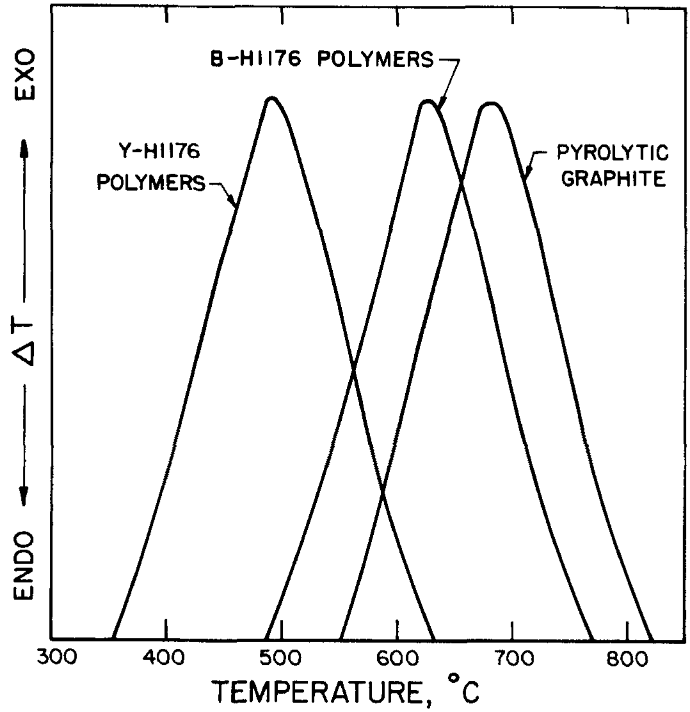


Fig. 32. Calorimetric thermograms of H-1176 polymers and pyrolytic graphite in air.

mers [18]. In those cases where Lewis acid catalysts were used, low-boiling solvents were chosen to maintain the temperature of the reaction mixture below the decomposition temperatures [18]. Since the azeotropic method was found to be the most practical and convenient of the solution methods evaluated, the Y series of polymers evaluated were prepared by this azeotropic method.

The B series of polymers was prepared from the reactants as melts. The most satisfactory method was found to be the bis exchange [Eq. (7)], and the polymers used for the evaluations were prepared by this method. On the basis of preliminary experiments, 225°C was chosen as the maximum temperature to be used in the preparation of these polymers since the condensations at 250°C or higher produced polymers whose nitrogen values were lower than the theoretical values for the polymeric azines, indicating a loss of nitrogen or nitrogenous compounds during condensation at 250°C. Lewis acids, such as zinc chloride and p-toluenesulfonic acid, could not be used to accelerate the reactions, since even at 225°C they in-

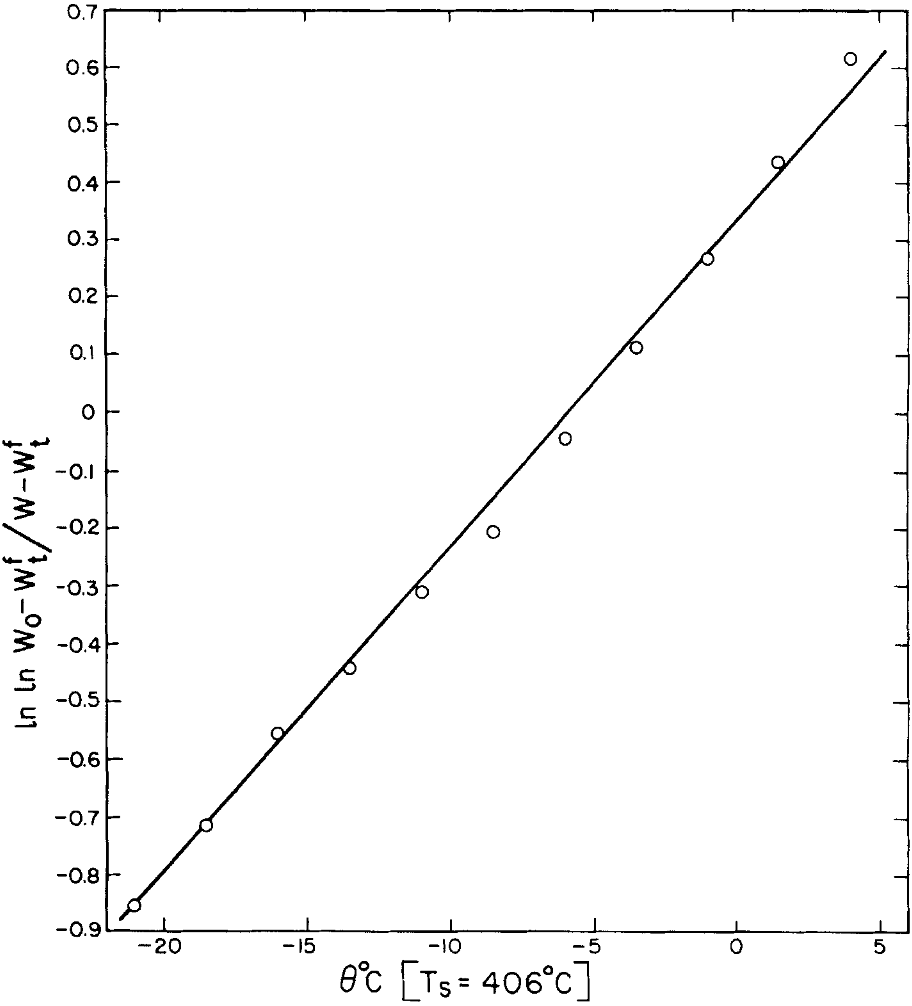


Fig. 33. Plot of ln ln $W_0 - W_t^f/W - W_t^f$ as a function of Θ, °C, for 1-AZ-Y. W_0, initial weight; W_t^f, final weight; W, weight at given temperature; T_S, temperature at maximum slope of weight-loss thermogram; Θ, T − T_S.

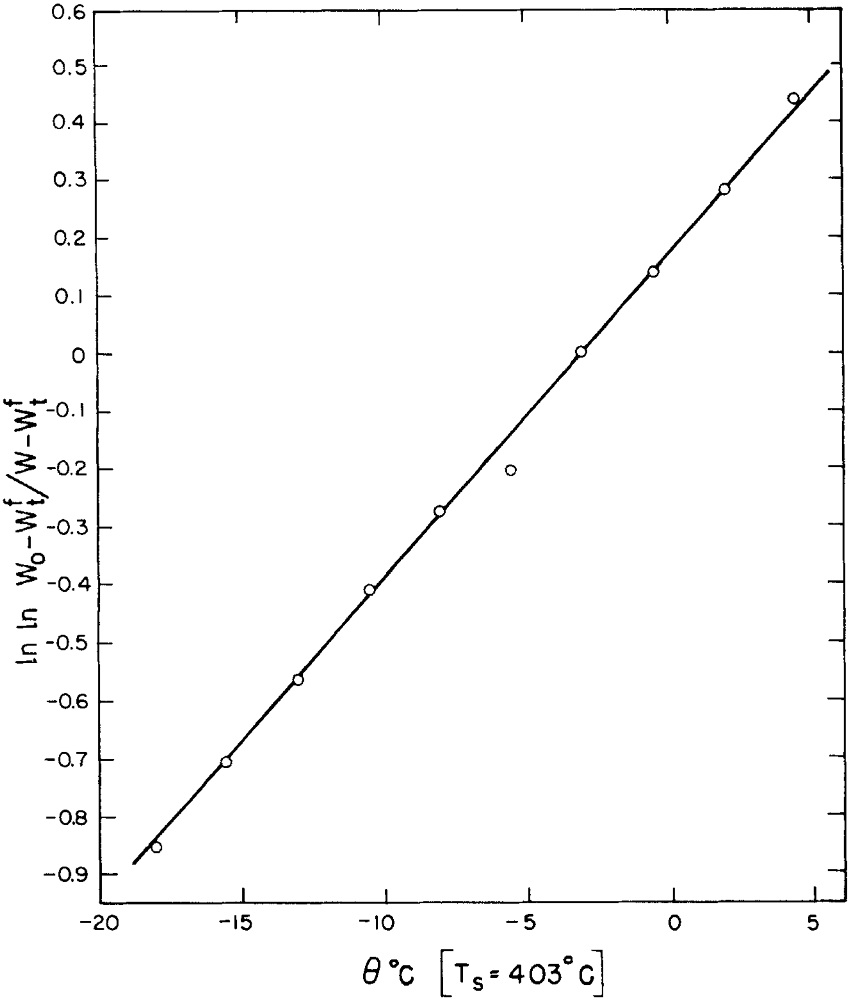


Fig. 34. Plot of ln ln $W_0 - W_t^f/W - W_t^f$ as a function of Θ, °C, for 2-AZ-Y. See Fig. 33 for key to symbols.

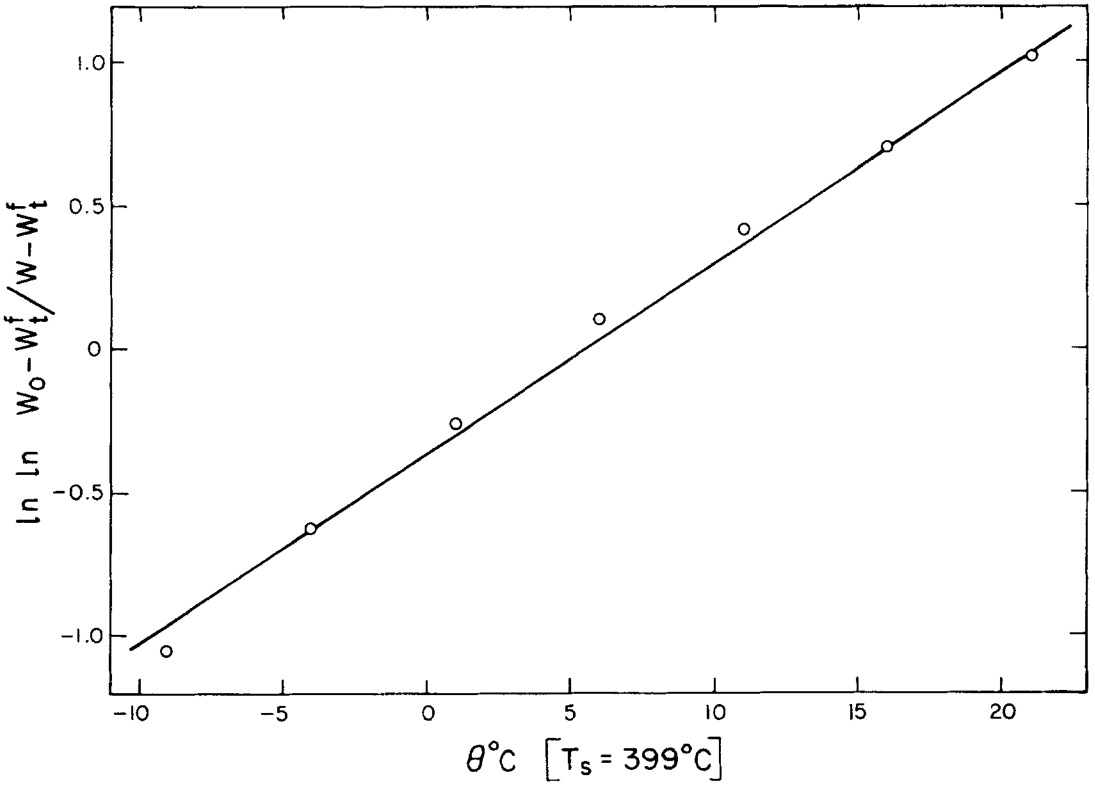


Fig. 35. Plot of $\ln \ln W_0 - W_t^f/W - W_t^f$ as a function of Θ, °C, for 3-AZ-Y. See Fig. 33 for key to symbols.

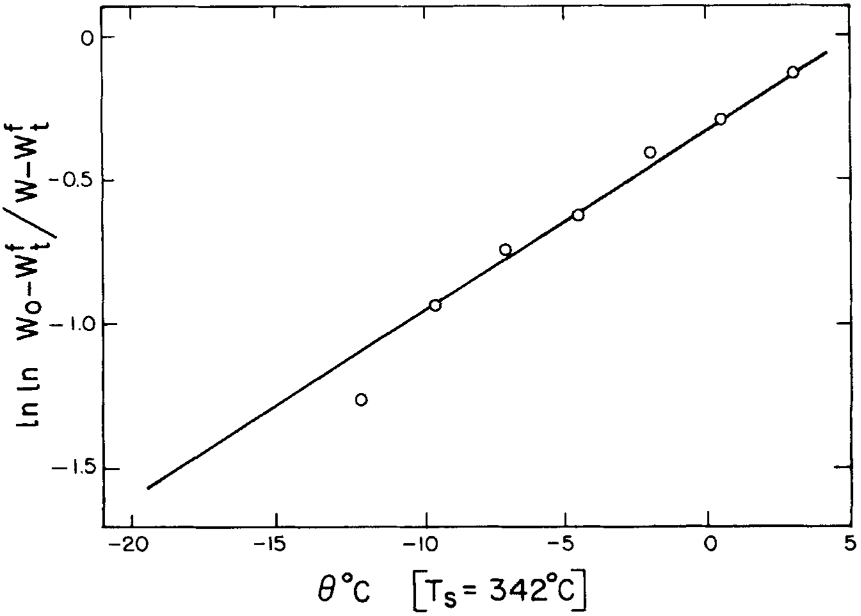


Fig. 36. Plot of ln ln $W_0 - W_t^f/W - W_t^f$ as a function of Θ, °C, for 4-AZ-Y. See Fig. 33 for key to symbols.

duced decomposition of the polymers and the loss of nitrogen.

The major difference between the Y and B series of polymers is that all of the Y series were intractable brick-dusts, whereas all of the B series passed through a tractable, fusible, homogeneous stage before reaching the insoluble, infusible state.

The infrared spectra and solubility characteristics of the B-H225 polyazines were similar to those found in the corresponding Y polyazines except for the bands at 760 and 690 cm^{-1}, characteristic of monosubstitution in a benzene ring, which accounted for the presence of the two exchanged end groups, $C_6H_5N=$ and $C_6H_5CH=$. Based on elemental analysis, the B-H225 polyazines appeared to have a $\overline{DP}$ of approximately 10 compared to approximately 3 for the yellow solution polymers.

In contrast to the results found in the Schiff-base polymers [1], the amine-exchange reaction in melt was not found to be practical for the synthesis of polyazines because the boiling point of hydrazine, 113.5°C, is much lower than that of the other reactants in the equilibrium reaction [Eq. (6)] (aniline, b.p. 184.3°C) and, on distillation, is eliminated first to reverse the reaction to the starting ingredients.

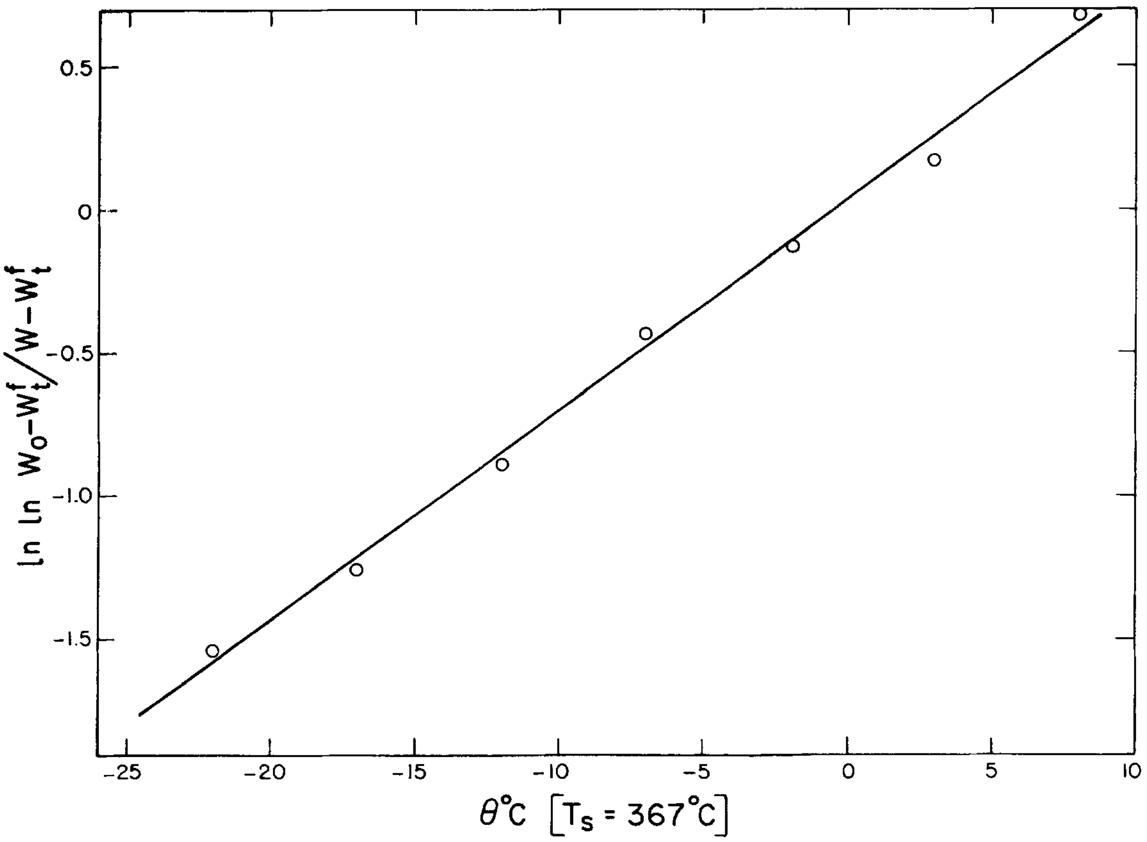
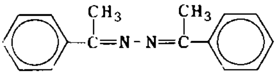
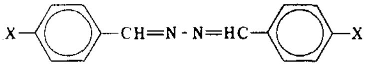
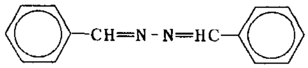


Fig. 37. Plot of ln ln $W_0 - W_t^f/W - W_t^f$ as a function of Θ, °C, for 1-KZ-Y. See Fig. 33 for key to symbols.

Heating the B-H225 polymers to 275°C caused a loss of nitrogen and a loss of solubility in concentrated sulfuric acid for the aldazine-B-AZ polymers. A marked difference was found between the aldazine and ketazine B polymers on heating above 225°C, in that a temperature of 350°C was required to convert 1-KZ-H225 to a dark-brown, hard solid compared to 275°C for the B aldazines.

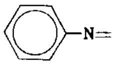
Portions of the Y and B series of polymers were postheated to 1176°C to compare the thermal properties of the derived abstracted polymers with polymeric Schiff bases similarly treated [1].

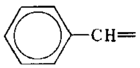
The decomposition of the ketazine  was studied to compare its behavior with the aldazines,  , reported previously [18]. The onset of the ketazine decomposition in nitrogen was found to be 325°C, which was approximately 19 degrees higher than the corresponding aldazine,  ; and the maximum was 339°C, which was approximately 10 degrees higher than the aldazine. The energy of activation of decomposition, E_a, for the ketazine was found to be 36,000 cal/mole; this is the same order of magnitude of 40,000 cal/mole found [18] for the aldazine and was derived from the values of $k_{577^\circ K} = 0.005\ \mathrm{min}^{-1}$, $k_{611^\circ K} = 0.027\ \mathrm{min}^{-1}$, and $k_{648^\circ K} = 0.146\ \mathrm{min}^{-1}$. The reaction order in both cases was essentially unity, with $k_{590^\circ K} = 0.01\ \mathrm{min}^{-1}$ for the ketazine and $k_{590^\circ K} = 0.039\ \mathrm{min}^{-1}$ for the aldazine [18]. The amount of nitrogen collected from the isothermal decomposition of the ketazine amounted to 39% of theory, whereas the corresponding aldazine [18] yielded 76% nitrogen; thus the decomposition of the ketazine is more similar to the decomposition of $(C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2$ reported by Hirsch [26] than to the unsubstituted aldazines [18].

A comparison of the thermogravimetric data for the Y series of polyazines (Table 4) with the comparable Y series of Schiff bases [1] indicated definitely that azomethine polymers containing the =N—N= moiety decomposed more readily at elevated temperatures than those containing the =NAr″N= structures. In view of the studies on prototype compounds [18], this behavior was not unexpected; it was also proposed [18] that a thermally stable polymer might result from such a decomposition, particularly if segmers of polystilbene, $\left[ArCH{=}CH\right]_n$, were formed in the process. The thermal stability of the polyketazine, 1-KZ-Y, was comparable to those of the aldazine, AZ-Y; which is in accord with previous data which showed [28, 29] that the thermal stabilities of the polyketanils were comparable to those of the poly-Schiff bases.

The thermal stabilities of the B-H225 polyazines were only slightly superior, or almost identical, to those of the Y series of polymers; these values indicated their relatively low molecular weights, which were increased by continuing the condensation at temperatures of 275°C or higher.

The thermal stabilities in nitrogen and in air of the B-H275 polymers were higher than the Y and B-H225 series and were of the same order of magnitude of the B-H400 Schiff-base polymers [1]. These results were not completely unexpected because actually the B-H275 polymers are not azine polymers but the end result of concomitant synthesis and decomposition of intermediate azine polymers. That they are not azine polymers is clearly evidenced by the following facts. Noncondensable, water-insoluble gases were collected during the polymerization reaction, their elemental analyses showed substantially lower nitrogen content than found in azine polymers, no salient calorimetric decomposition exotherm was found at temperatures where the yellow and B-H225 polymers decomposed, and only traces of N_2 and NH_3 were obtained when these polymers were heated to 450 to 475°C.

The infrared spectra shown in Figs. 9 to 12 of these B-H275 polymers are very similar to the Y-H450 polymers, Figs. 22 to 26, except for the additional bands at 690 and 760 cm^{-1} due to monosubstitution in a benzene ring due to 

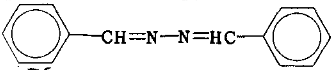
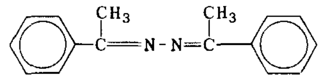
and 

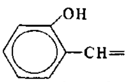
exchanged end groups or to benzylideneaniline entrapped within the polymer. The tenacious retention of the exchange by-product, benzylideneaniline, was also found in the case of the azomethines [1-7]. The principal C=N absorption at approximately 1,620 cm^{-1} was shifted in the B-H275 polymers to approximately 1,600 cm^{-1}; this shift, particularly since nitrogen had been lost, can be attributed to CH=CH linkages. Also, as in the Y-H450 polyazines, the infrared spectra of the B-H275 polymers appeared to confirm that polysubstitutions in the benzene rings had not occurred to a great extent, as would be expected if cross-linking occurred, although insolubility in concentrated sulfuric acid would seem to indicate some measure of cross-linking.

The data in Table 8 offer indirect evidence that some polystilbene segmers were formed in the decomposition of the polyazines.

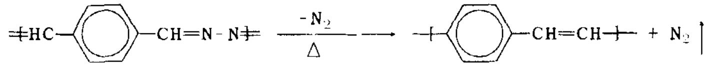
Column W summarizes the per cent of nitrogen found in the original undecomposed polymers. Column a tabulates the percentage of W lost when the polymers were heated to 450°C; these values were determined by analyses of the polymeric residues after heating. The data in column b represent the per cent of W which was lost as ammonia at 450°C. By subtracting the figures in column b from those in column a, the data in column c were obtained, assuming that all nitrogen from the polymer is lost either in the form of NH_3 or N_2. Column d represents the actual percentage of noncondensable gases, in terms of moles of W, which was collected in the gas buret during decomposition at 450°C. The values in column d are higher than those expected by column c; this can be explained by assuming an additional loss of H_2 in 1-AZ-Y, 2-AZ-Y, and 3-AZ-Y and by the loss of CH_4 or C_2H_6 to account for the much larger differences for 4-AZ-Y and 1-KZ-Y. The latter two polymers contain methyl moieties which are expected to be labile at 450°C. The bands in the infrared spectra of the resultant polymers, 4-AZ-Y-H450 and 1-KZ-Y-H450, shown in Figs. 30 and 31, respectively, are quite broad; these do not show bands characteristic of $-CH_3$ moieties.

The data in Table 8 also show that nitrogen is eliminated in substantial quantities by 1-AZ-Y, 2-AZ-Y, and 4-AZ-Y polymers and in smaller amounts by 3-AZ-Y and 1-KZ-Y. These data are in good agreement with the values reported previously for the corresponding azine prototype [18] monomers and in this work for the ketazine prototype.

The previous studies [18] established that the path of decomposition most favored for the azine monomers depended also largely on the steric factors surrounding the =N—N= linkage. Where these factors are minimal, the "normal" decomposition to yield stilbene and nitrogen involving the ionic chain carrying the species aryldiazomethane [25], $Ar{-}\overset{\ominus}{C}H{=}\overset{\oplus}{N}{\equiv}N$, predominated. When these steric factors are more aggravated, for example, by the introduction of a benzene ring on the methine carbon, Hirsch has shown [26] that decomposition proceeds almost exclusively by rupture of the N—N bond. This postulate is supported not only by the fact that dibenzylideneazine,  , yielded 76% nitrogen [18] compared to acetophenoneketazine,  (which in this study yielded 39% nitrogen under the same pyrolytic conditions) but also by the fact that the polymers have such structures.

The presence of the  moiety, α, to the azine linkage in the monomers also caused a decrease in nitrogen evolution [18]. The o-OH substituent seemed to favor the rupture of the N—N bond, probably because of hydrogen-bonding effects [18]. Also, after decomposition of the monomer, polymerization appeared to occur through the OH substituent to yield a polymer containing polyether linkages [18]. The lowered yield of nitrogen from the polymer is in good accord with the values found for the prototype monomer. The high insolubility and the high thermal stability of the polymeric residue obtained from the decomposition of the 2-AZ-B-H275 polymer indicated that some additional polymerization was obtained through the formation of polyether linkages.

Although the amount of nitrogen liberated as N_2 gas varied for the different polymeric azines, the amount of N_2 liberated was substantial in all cases. By analogy to the prototype monomers [18], the decomposition of the polyazines should lead to the abundant formation of polystilbene segmers as illustrated by

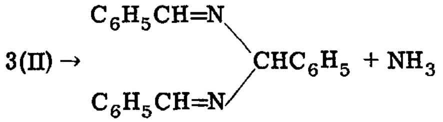


(11)

Such a reaction should enhance the practical thermal properties of the polymer by the introduction of the ablative effect accompanying the liberation of inert nitrogen gas with the simultaneous synthesis of a more stable polymer decomposition product.

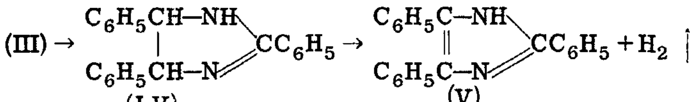
A definitive mechanism for the formation of ammonia from the polymer decomposition is not known at this time. However, the presence of ammonia in the monomeric azine decomposition was shown [18, 24] to result from the following sequence of reactions:

$$\underset{(I)}{C_6H_5CH{=}N{-}N{=}HCC_6H_5} \rightarrow [C_6H_5CH{=}N\cdot\cdot N{=}HCC_6H_5] \rightarrow C_6H_5C{\equiv}N + \underset{(II)}{HC{=}HCC_6H_5} \qquad (12)$$



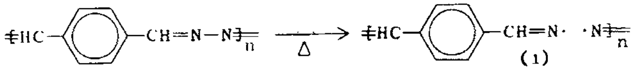
$$3(II) \rightarrow (C_6H_5CH{=}N)_2CHC_6H_5 + NH_3 \qquad (13)$$

(III)

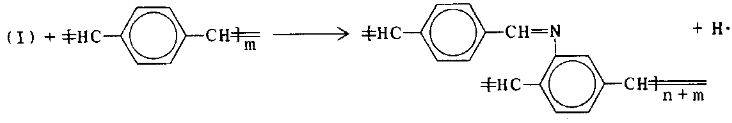


(IV) (V) (14)

The same type of mechanism involving end-group azine linkages in the polymer may account for ammonia liberation from the polymers. For both the monomers and the polymers, it was found that when the quantity of N_2 liberated was high, the amount of ammonia collected was low, and vice versa. This would indicate that at least two mechanisms were operative in the polymer decomposition as they were in the monomers [18]. The rupture of the N–N bond shown in Eq. (12) could account also for the presence in the H450 and H1176 polymers of nonazine nitrogen while explaining the insolubility of the polymers as due to cross-links; the formation of cross-links is illustrated by:



(15)



(16)

Reactions of this type would cause a concomitant increase in molecular weight; and undoubtedly they or similar reactions do occur, since polymers with $\overline{DP}$ of 3 to 10 would not exhibit the high thermal stability shown by the polymeric residues resulting from decomposition.

The infrared spectra (Figs. 22 to 26) of the resultant Y-H450 polyazines seem to substantiate the formation of polystilbene segmers. The spectra are rather broad and diffuse, as would be expected of high molecular weight polymers. They show that the band attributable to the C=N stretching frequency in the region 1615-1620^{-1} in the yellow polymers has disappeared while a band appeared at 1600 cm^{-1}, which is most probably due to the skeletal vibrations of the aromatic rings and the C=C stretch of the ethylene moiety. This is analogous to dibenzylideneazine, $C_6H_5CH{=}N{-}N{=}HCC_6H_5$, which shows a strong band at 1621 cm^{-1}, attributable to the C=N stretching vibration (Fig. 38), while trans-stilbene, $C_6H_5CH{=}HCC_6H_5$ shows only a strong band at 1595 cm^{-1}, attributable to the skeletal vibrations of the aromatic rings and the C=C stretch of the ethylene group (Fig. 39). The infrared spectra of the Y-H450 polymers also show a strong band in the region of 825 cm^{-1} which can be assigned to 1, 4 disubstitution in a benzene ring. Although there are no strong indications in the infrared spectra of bands which might be interpreted as being due to cross-links, the fact that these polymers are no longer soluble even in concentrated sulfuric acid would seem to indicate that at least some cross-linking has occurred.

Table 9 compares some kinetic and thermodynamic data on the pyrolytic decomposition of the azine polymers and their corresponding prototype monomers. The decompositions of the monomers and

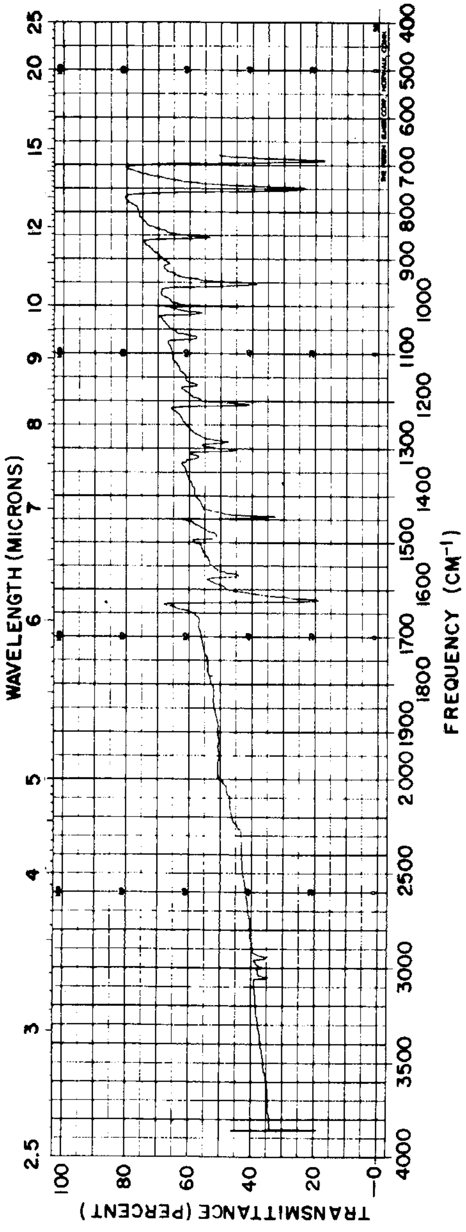


Fig. 38. Infrared spectrum of dibenzylideneazine.

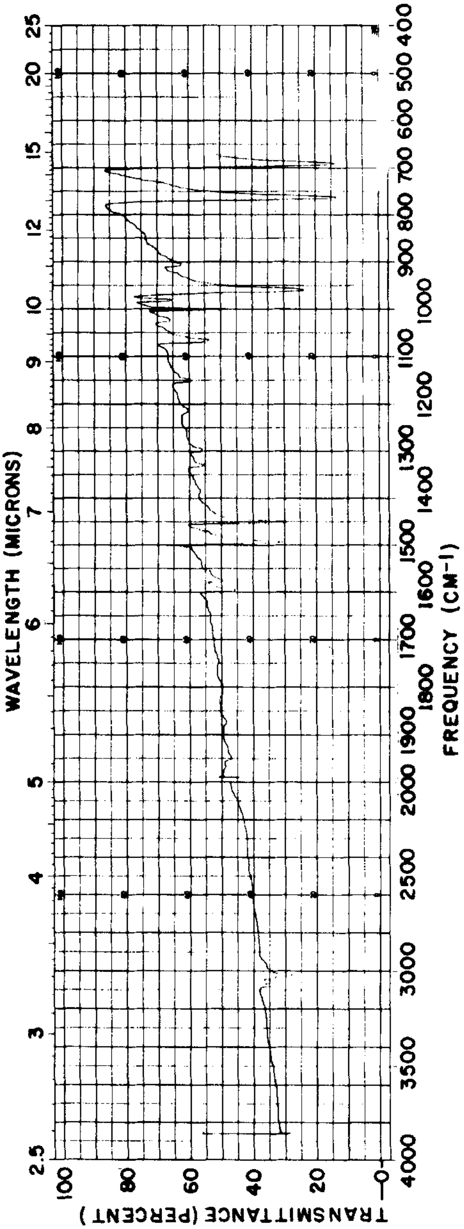
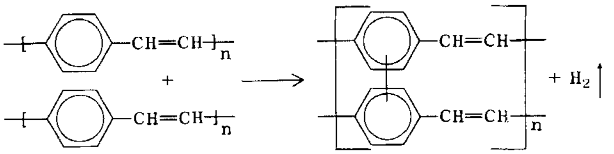


Fig. 39. Infrared spectrum of trans-stilbene.

polymers are essentially first order. The activation energies E_a, of the polymers are all higher than of the monomers, as might be expected, since the decomposition of the polymers occurs in a solid-state medium. The E_a values for the various carbon-nitrogen and nitrogen-nitrogen bonds are reported as 52 to 57 kcal/mole for C—N, 147 for C=N, and 32 for N—N [30]. The E_a values for the monomers and polymers appear to reflect a combination of E_a values corresponding to the rupture of C—N, C=N, and N—N bonds [18].

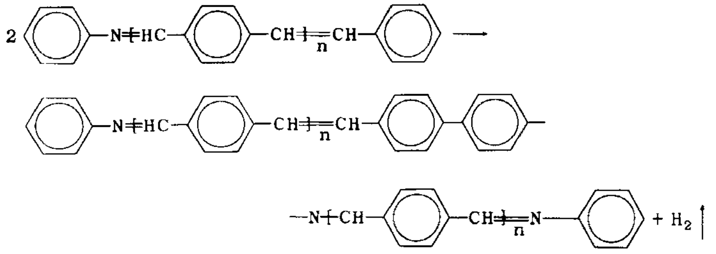
The temperature of the exotherms in the ΔH thermograms (Figs. 27 to 32) corresponded to the temperature at which steep weight losses occurred in the TGA thermograms. This coincidence indicated the exothermicity of the overall decompositions. The ΔH values ranged from 119 kcal/g for the 3-AZ-Y polymer to about 250 cal/g for the 1-AZ-Y and 2-AZ-Y polymers. The three polymers, 1-AZ-Y, 2-AZ-Y, and 4-AZ-Y, which suffered decomposition with the more abundant evolution of N_2 also had the highest ΔH values; whereas the 3-AZ and 1-KZ polymers, which liberated less N_2, had substantially lower values. These differences further indicate different reaction pathways.

The thermogravimetric data in Table 7 and in Figs. 13 to 16 show that the H1176 polymers possess high thermal stabilities, losing in nitrogen about 2% by weight upon heating to 1176°C; their thermal stabilities in air ranged between 600 and 650°C. The H-1176 polymers contained about 2% nitrogen in their composition. The ΔH values (Tables 10 and 11) for the combustion of the H1176 polymers and pyrolytic graphite indicate that the H275 polymers had not been converted to graphitic-type polymers when heated to 1176°C in nitrogen under the experimental conditions used. The B-H1176 polymers, undoubtedly, are neither azine- nor stilbene-type polymers. At temperatures above 500 or 600°C, reactions other than the normal bis-Schiff-base exchange reaction can also occur. The polymers can undergo additional cross-linking with the elimination of hydrogen to yield network polymers:



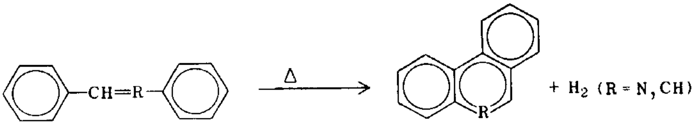
(17)

Also at higher temperatures, chain ends may couple with the elimination of hydrogen and the formation of a diphenyl group, thus increasing the molecular weight:

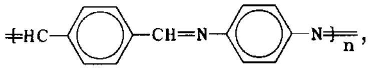


(18)

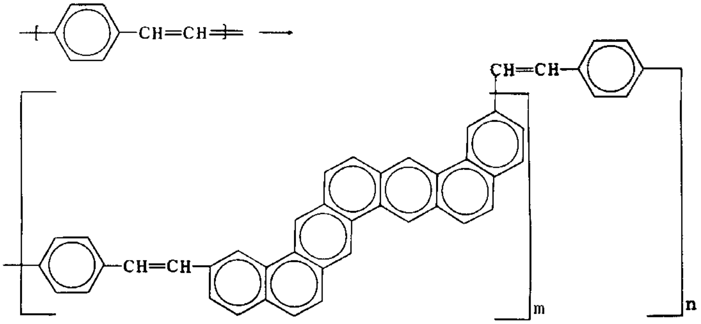
The ability of aromatic Schiff base compounds and stilbenes to undergo intermolecular cyclization by pyrolysis and photolysis [Eq. (19)] to form phenanthradines and phenanthrenes, respectively, has been well documented [32-34].



(19)

It has also been reported [1] that when the poly-Schiff base,  was heated to 700°C, a moderate amount of hydrogen in the gaseous by-products was detected by mass spectral analysis.

A partial step-ladder polymer, composed of polynuclear segmers, would be formed if a similar reaction occurred [Eq. (20)] in the heating of B-H275 polymers.



(20)

As the temperature is increased, greater portions of the polymer chain can condense to a ladder-type structure, with the overall result that this polymer would become more thermally stable. Bruck [34] has observed this type of intermolecular rearrangement during vacuum pyrolysis of aromatic polypyromellitimides.

ACKNOWLEDGMENT

This work was supported by Grant NsG-339 of the National Aeronautics and Space Administration.

REFERENCES

[1] G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.*, **A1**, 1161 (1967).
[2] G. F. D'Alelio, R. K. Schoenig, and J. V. Crivello, *J. Macromol. Sci.*, **A1**, 1299 (1967)
[3] G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.*, **A1**, 1321 (1967).
[4] G. F. D'Alelio, J. V. Crivello, T. R. Dehner, and R. K. Schoenig, *J. Macromol. Sci.*, **A1**, 1331 (1967).
[5] G. F. D'Alelio, J. M. Hornback, W. F. Strazik, and T. R. Dehner, *J. Macromol. Sci.*, **A2**, 237 (1968).
[6] G. F. D'Alelio, T. Kurosaki, and T. Ostdick, *J. Macromol. Sci.*, **A2**, 285 (1968).
[7] G. F. D'Alelio, W. F. Strazik, and T. F. Huemmer, *J. Macromol. Sci.*, **A2**, 335 (1968).
[8] C. S. Marvel and H. W. Hill, *J. Am. Chem. Soc.*, **72**, 4819 (1950).
[9] V. A. Kargin, A. V. Topchiev, B. A. Kreutsel, L. S. Polak, and B. E. Davidov, *Zh. Vses. Khim. Obsch.*, **5**, 507 (1960).
[10] A. A. Berlin, *Khim. Technol. Polimer*, **1960** (7-8), 139.
[11] A. V. Topchiev, V. V. Korshak, U. A. Popov, and L. D. Rosenstein, *Dokl. Acad. Nauk SSSR*, **147**, 645 (1962).
[12] A. V. Topchiev, V. V. Korshak, U. A. Popov, and L. D. Rosenstein, *J. Polymer Sci.*, C4, 1305 (1964).
[13] G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.*, A1, 1251 (1967).
[14] T. Curtius and R. Jay, *J. Prakt. Chem.*, **39**, 45 (1889).
[15] D. F. Hoeg, D. I. Lusk, and E. P. Goldberg, *J. Polymer Sci.*, **B2**, 697 (1964).
[16] R. McDonald and T. Campbell, *J. Am. Chem. Soc.*, **82**, 4669 (1960).
[17] R. McDonald and T. Campbell, *J. Org. Chem.*, **24**, 1246 (1959).
[18] G. F. D'Alelio and R. K. Schoenig, *J. Macromol. Sci.*, **A2**, 367 (1968).

[19] G. F. D'Alelio, T. Kurosaki, and R. K. Schoenig, *J. Macromol. Sci.*, **A1**, 1279 (1967).
[20] W. H. Smith, E. E. Sager, and I. J. Siewers, *Anal. Chem.*, **21**, 133 (1949).
[21] R. Auwers, *Ann.*, **356**, 137 (1907).
[22] T. Takada, *J. Pharm. Soc. Japan*, **71**, 1254 (1951).
[23] J. W. Mellor, *Inorganic and Theoretical Chemistry, Vol. VIII*, Longmans, London, 1937, p. 318.
[24] L. B. Howard and G. Hilbert, *J. Am. Chem. Soc.*, **54**, 3639 (1932).
[25] H. Zimmerman and S. Somasekhara, *J. Am. Chem. Soc.*, **82**, 5865 (1960).
[26] S. Hirsch, *J. Org. Chem.*, **32**, 2433 (1967).
[27] H. Horowitz and G. Metzger, *Anal. Chem.*, **35**, 1464 (1963).
[28] G. F. D'Alelio, J. M. Hornback, W. F. Strazik, and T. R. Dehner, *J. Macromol. Sci.*, **A2**, 273 (1968).
[29] G. F. D'Alelio, W. F. Strazik, and T. F. Huemmer, *J. Macromol. Sci.*, **A2**, 335 (1968).
[30] T. L. Cottrell, *The Strengths of Chemical Bonds*, Butterworth, London, 2nd ed., 1958, p. 207.
[31] G. Graebe, *Ann.*, **167**, 158 (1873).
[32] R. Buckles, *J. Am. Chem. Soc.*, **77**, 1040 (1955).
[33] G. Pyl, *Ber.*, **B60**, 287 (1927).
[34] S. D. Bruck, *Polymer*, **6** (6), 319 (1965).

Accepted by editor April 17, 1968
Received for publication May 8, 1968