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. I. The Synthesis and Evaluation of Polymeric Schiff Bases Prepared by Schiff Base Exchange Reactions

G. F. D'alelio[a]; J. V. Crivello[a]; R. K. Schoenig[a]; T. F. Huemmer[a]
[a] DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA

To cite this Article D'alelio, G. F. , Crivello, J. V. , Schoenig, R. K. and Huemmer, T. F.(1967) 'Polymeric Schiff Bases. I. The Synthesis and Evaluation of Polymeric Schiff Bases Prepared by Schiff Base Exchange Reactions', Journal of Macromolecular Science, Part A, 1: 7, 1161 — 1249

To link to this Article: DOI: 10.1080/10601326708053766

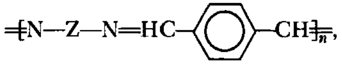
URL: http://dx.doi.org/10.1080/10601326708053766

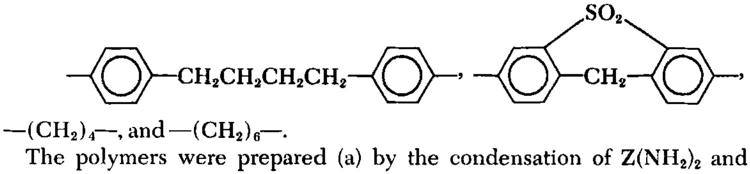
J. MACROMOL. SCI.—CHEM., A1(7), pp. 1161–1249, Nov., 1967

Polymeric Schiff Bases.
I. The Synthesis and Evaluation of Polymeric Schiff Bases Prepared by Schiff Base Exchange Reactions

G. F. D'ALELIO, J. V. CRIVELLO, R. K. SCHOENIG, and T. F. HUEMMER
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA

Summary

This paper compares the syntheses and the thermal stabilities of twelve related conjugated, pseudoconjugated, and nonconjugated Schiff base polymers of the general formula, , in which Z represents



—$(CH_2)_4$—, and —$(CH_2)_6$—.

The polymers were prepared (a) by the condensation of $Z(NH_2)_2$ and p—$C_6H_4(CHO)_2$ in (1) solution and (2) as melts, and (b) by three new Schiff base exchange reactions: (1) the aldehyde exchange,

$$n\mathrm{OHCC_6H_4CHO} + n\mathrm{C_6H_5CH{=}N{-}Z{-}N{=}HCC_6H_5} \rightleftharpoons$$
$$(2n-1)\mathrm{C_6H_5CHO} + \mathrm{C_6H_5CH}\!\left[\mathrm{N{-}Z{-}N{=}HCC_6H_4CH}\right]_n\!\mathrm{O}$$

(2) the amine exchange.

$$nH_2N{-}Z{-}NH_2 + nC_6H_5N{=}HCC_6H_4CH{=}NC_6H_5 \rightleftharpoons (2n-1)C_6H_5NH_2 + H_2{=}\!\left[N{-}Z{-}N{=}HCC_6H_4CH\right]_{n}\!{=}NC_6H_5$$

and (3) the bis exchange,

$$nC_6H_5N{=}HCC_6H_4CH{=}NC_6H_5 + nC_6H_5CH{=}N{-}Z{-}N{=}HCC_6H_5 \rightleftharpoons (2-1)C_6H_5CH{=}NC_6H_5 + C_6H_5CH{=}\!\left[N{-}Z{-}N{=}HCC_6H_4CH\right]_{n}\!{=}NC_6H_5$$

The nonconjugated polymers were prepared conveniently in solution by the reaction of the aliphatic diamines, $H_2N(CH_2)_nNH_2$, with terephthaldehyde as well as by the bis exchange method; they were white or cream in color and had thermal stabilities of about 300°C in nitrogen and 250°C in air.

The condensations in solution of the conjugated and pseudoconjugated diamines with terephthaldehyde yielded yellow, low molecular weight, intractable, infusible, brick-dust polymers, whereas melt polymerizations yielded, after passing through a fusible, tractable stage, highly conjugated black polymers of relatively high thermal stabilities. These melt polymerizations were difficult to control. However, the polymers were prepared most readily by the Schiff base exchange reactions, of which the bis exchange was the most highly moderated and best controlled.

The bis exchange polymerization method produced fusible, tractable polymers which underwent color changes progressively from yellow to orange to red to brown to black; on continued heating the black polymers became infusible. The thermal stabilities of the polymers depended on the maximum temperature at which the condensations had been performed. The polycondensation was shown to be incomplete at temperatures up to 400°C, yet the thermal stabilities of polymers thus prepared were in the range 500–550°C in nitrogen and 430–480°C in air. When condensed to 600°C, the polymers showed a weight loss in nitrogen of less than 5% at 700°C and of less than 18% at 1176°C; the thermal stabilities in air were in the range 510–550°C. When the condensation was carried to temperatures of about 700°C or higher, hydrogen was eliminated, most probably, as the result of the intramolecular formation of carbocyclic-heterocyclic phenanthridine structures. When condensed to 1176°C, the polymers showed thermal stabilities in nitrogen in excess of 1100°C, and in air in the range 440–600°C; the highest thermal stability was shown by the fully conjugated poly(*p*-xylylidene-*p*-phenylenediamine).

The relationship of the thermal stability of a polymer to its chemical structure has been discussed in several papers (*1–4*). Maximum thermal stability in polymers is usually obtained when (1) thermally unreactive ring structures constitute a major portion of the polymer composition, (2) maximum use is made of resonance stabilization, (3) high bond energy exists between the atoms in the chain, (4) the ring structures have normal bond angles, and (5) the structure offers no easy pathway for rearrangement.

High-resonance-energy structures can be obtained by use of appropriate aromatic or heterocyclic groups; their thermal unreactivity can be estimated from the thermal reactivity data of Lewis (*5*). Most of the available bond-energy values have been determined from studies of small molecules in the gaseous or liquid state. Although these values can be used in the design of polymer molecules, interactions in polymers can exert a considerable effect on the stability of a given bond under a specific set of conditions (*1*), and thus the bonds in polymers often behave as if they were stronger than in simple monomeric molecules. It is not surprising, therefore, in the light of these principles, that the more promising heat-resistant, thermally stable polymers are the polyconjugated aromatic types, such as the polybenzimides (*6–9*), the polybenzimidazoles (*6,10–13*), the polybenzoxazoles (*13*), the polyoxadiazoles (*13*), the polyparaphenylenes (*14,15*), and other polymers of related structures (*7,13*).

In an analogy to these polymers, one might expect that a conjugated system, linked together by a simple $\mathrm{—\overset{|}{C}{=}N—}$ bridge in an aromatic system, $\mathrm{—Ar'\overset{|}{C}{=}N—Ar'—}$, might show remarkable thermal stability. The simplest compounds possessing this structure are the monomeric Schiff bases, $C_6H_5CH{=}NC_6H_5$, $C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5$, and $C_6H_5N{=}HCC_6H_4CH{=}NC_6H_5$; they are sufficiently stable so that they can be distilled at atmospheric pressure without decomposition. Accordingly, the conjugated polymeric Schiff bases were selected (*16*) as candidates for synthesis and evaluation as thermally stable polymers. These polymers have the general structure

$$=\!\!\left[\mathrm{N—Ar'—N{=}HCAr''CH}\right]_{n}\!\!=$$

(I)

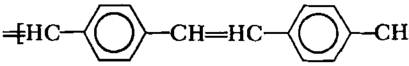
in which Ar′ and Ar″ represent arylene moieties.

The application of the principles which yield thermally stable polymers usually produce insoluble, infusible, intractable brick-dust polymers. Polymers which possess desirable physical properties at high temperature, but which pass through a tractable stage which permits them to be fabricated into an ultimate product, have been a long-standing, challenging goal to the polymer scientist. In recent years, this objective has been met by a number of polymers, such as the polypyromellitimides (*6–9*), the polybenzimidazoles (*6,10–13*), and others (*14,15*), by isolating the condensation products in the "prepolymer" or "hemipolymer" stage, a stage in which they are soluble and tractable before ring closure occurs in the linkages between the arylene groups. The "hemipolymer" approach, which would require the isolation of an intermediate, has not been successful in the synthesis of the polymeric Schiff bases. Marvel (*17–19*) appears to be the first to have prepared a substituted polymeric Schiff base, from the reaction of 5,5'-methylene-bissalicylaldehyde and *o*-phenylenediamine in tetrahydrofuran or acetic acid solvents. The polymer was isolated in an 87.5% yield as a yellow-orange precipitate whose inherent viscosity (1% in dimethylformamide) was 0.05. Numerous attempts were made (*19*) to increase the molecular weight of the polymers by variations in solvent systems, catalysts, temperature, use of dehydrating agents, and azeotropic removal of water, but none of these modifications resulted in significant improvement in molecular weight. The zinc chelates of these polymers showed thermal stability up to 250°C.

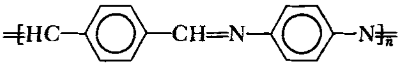
During the course of our work, some data appeared which indicated that even low molecular weight Schiff base polymers possess significant thermal stability. Akitt and his co-workers reported (*20*) that the substituted yellow Schiff base polymer, derived from the condensation in dimethyl sulfoxide of terephthaldehyde and 2,4-diaminophenol, did not melt or decompose below 300°C. Topchiev and his co-workers reported (*21*) a decomposition temperature of 350°C in air for the yellow brick-dust polymer obtained by the condensation in benzene of terephthaldehyde and *p*-phenylenediamine. Stivala et al. (*22*) found that when the yellow, low molecular weight polymer, resulting from the reaction of terephthaldehyde and *m*-phenylenediamine in dimethylformamide, was subsequently heated in nitrogen to 250°C, it was stable to about 400°C at a pressure of 0.1 mm Hg.

The Schiff base polymers described above were prepared by the usual solution procedure used (*23*) in the synthesis of monomeric Schiff bases. Our preliminary studies had shown also that syntheses performed in solution, using a large variety of solvents for a diverse number of aryl diamines and aryl dicarbonyl compounds, yielded insoluble, infusible, nontractable brick-dust polymers of low molecular weight, ranging in color from yellow to orange. In such solution polymerizations, the low molecular weight has been attributed

(*24*) to the insolubility of the growing polymer chains in the medium resulting in precipitation which thereby prevents the attainment of higher molecular weights. We also observed that when these precipitated polymeric Schiff bases were heated at 250°C in the solid state, they changed in color from yellow to orange and in some cases to brown, indicating that some chain extension might have occurred. Black polymers should be expected if the chain length of the conjugated polymer is sufficiently long, as is evidenced in the case of polystilbene (II) to which the poly-Schiff base, poly(*p*-xylylidene-*p*-phenylenediamine) (III), is structurally related:



(II)



(III)

Thermal stabilities (*25*) comparable to those found in the polystilbenes should be found also in the poly-Schiff bases, whereas only lower stabilities have been reported (*17–22*).

Exploratory experiments demonstrated (*16,26,27*) that when aromatic dialdehyde and aromatic diamines were reacted rapidly in a molten condition, black, highly conjugated polymeric Schiff bases were obtained. However, because of the high melt temperatures required, and of the high reactivity of the reactants, the polymerization was extremely difficult to control even though tractable, black polymers could be obtained by interrupting the reaction at the early stages of polymerization, usually after a few minutes of reaction (*16,26,27*).

The deficiencies of these solutions and melt processes indicated that a decrease in the reactivity of the aldehyde function or of the amine function, or of both functions, which would slow down the polycondensation, might be beneficial to the polymerization reaction.

The decrease in reactivity could be achieved by converting the aldehyde function, —CHO (1), to other suitable derivatives, such as to an aldimine function, —CH=NR (2), or to an acetal function, —CH—$(OR)_2$ (3), and by converting the amine function, —NH_2 (4), to other suitable derivatives, such as to an anil function, —N═CHR (5), or to an amide function, —NHOCR (6). Then the retardation of the reaction was to be achieved by using the corresponding derivatives in place of the aldehydes and amines, respectively. The polymers prepared from these derivatives would contain the corresponding end groups, which, conceivably, could contribute to homogeneity in the reaction mixture. In addition, since the derivatives are more stable to oxidation than the parent compounds, degradative oxidation during and after synthesis might also be reduced. The nine reactions possible between the three aldehyde-type reagents, (1), (2), and (3), with the three amine-type reagents, (4), (5), and (6), are shown in Table 1.

Simple monomeric, that is nonpolymeric, Schiff bases are to be expected in a reaction when both reagents are monofunctional, whereas the production of polymers would require that both reagents be at least bifunctional. The synthesis of monomeric Schiff bases from aromatic aldehydes and aromatic amines (reaction A), has been known for some time, (23), and the application of this reaction, using dialdehydes and diamines for the synthesis of polymers is relatively recent (*11–15*). The literature on the synthesis of monomeric Schiff bases by an aldehyde exchange (reaction B), which we defined (*16*) as the displacement of the aldehyde function in a Schiff base and its replacement by another aldehyde, is meager (*28*) and has not been applied to the synthesis of polymers.

TABLE 1

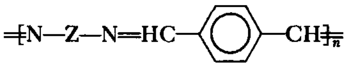
Reactants for Synthesis of Monomeric and Polymeric Schiff Bases

Reaction	Functional groups in reaction pairs	Literature refs.	
		Monomers	Polymers
A	—CHO (1) + —NH$_2$ (4)	23	11–15
B	—CHO (1) + —N═CHR (5)	28	Unreported
C	—CHO (1) + —NHOCR (6)	Unreported	Unreported
D	—CH═NR (2) + —NH$_2$ (4)	Unreported	Unreported
E	—CH═NR (2) + —N═CHR (5)	Unreported	Unreported
F	—CH═NR (2) + —NHOCR (6)	Unreported	Unreported
G	—CH(OR)$_2$ (3) + —NH$_2$ (4)	Unreported	Unreported
H	—CH(OR)$_2$ (3) + —N═CHR (5)	Unreported	Unreported
I	—CH(OR)$_2$ (3) + —NHOCR (6)	Unreported	Unreported

Although the amine exchange, reaction D, which consists in the displacement of the amine function in a Schiff base and its replacement by another amine, is not described, the related amine exchange with ketanil monomers is disclosed (*29,30*).

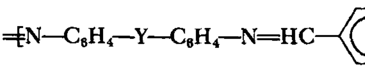
None of the remaining reactions given in Table 1 appears to have been described in the literature. However, before applying any of these reactions to polymer systems, it was necessary to establish their validity in prototype syntheses of monomeric Schiff bases to assure that the yields, at least, were very high, if not quantitative, and that the reactions were substantially free of detrimental side reactions. The results of these prototype studies, which are reported in other publications (*31,32*) show that seven of the reactions, A, B, D, E, G, H, and I of Table 1, are applicable broadly to the synthesis of monomeric Schiff bases. Some Schiff bases were obtained also from reactions C and F, in which an acylanilide is a reactant, but the yields were less than quantitative and the reactions were complicated somewhat by the presence of by-products resulting from side reactions. These seven reactions were evaluated in polymerization systems. They were also found to be applicable to the same degree found for the monomer systems and were applied to the synthesis of simple, black, Schiff base polymers which pass through a tractable stage. Since the thermal stability as well as other physical properties of heat-resistant polymers have been attributed to uninterrupted conjugation in their chain structures, it was considered important to determine how the stability of Schiff base polymers would be influenced by decreasing or interrupting the conjugation by inserting appropriate groups or structures in the backbone of the polymers. For the study of this specific phase, it was decided to maintain Ar″ in the arylidene moiety in (I) constant as *p*-phenylene,

and to introduce the changes in conjugation in Ar′ of the diamine moiety, to yield polymers of the general formula,

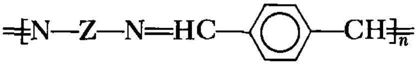


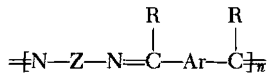
(IV)

thus Z represents the bivalent structure, Ar′, in which changes in conjugation were introduced. Polymers in which Z is the *p*-phenylene moiety, *p*—C_6H_4—, were selected as the reference points for the evaluation of changes in properties with changes in the nature or the extent of conjugation. Modification of the degree of conjugation can be accomplished by changes in position substitution on the benzene ring as by the use of the *m*-phenylene group, *m*—C_6H_4—, instead of *p*—C_6H_4—, or extending the conjugation by the use of two phenylene structures as in the diphenyl group, —C_6H_4—C_6H_4—. A relatively simple method of changing the character and extent of conjugation in aromatic compounds is to introduce changes in the diphenylene group by the insertion of other atoms or groups of atoms, such as —O—, —S—, —SO_2—, —CH_2—, —NH—, etc., between the benzene rings, thus —C_6H_4—Y—C_6H_4—, thereby yielding polymers of the general structure



Since a number of Y groups, such as —O— and —NH—, are bridges containing unshared pairs of electrons, they can make some contribution to the resonance structure; and polymers containing such structures cannot be considered as completely nonconjugated; rather, because of this character, they can be considered pseudoconjugated polymers and more closely related to polymers in which Z is —C_6H_4— and —C_6H_4—C_6H_4— than to those in which Z is aliphatic in nature, such as $-(CH_2)_4-$ and $-(CH_2)_6-$. Even when Y is —CH_2—, homoconjungation has been shown (33) to exist, since overlap can occur between orbitals of the two benzene rings which are so situated that the orbitals are close to one another. Orbital overlap of this kind exists also when Y is —O—, —S— and —NH—, but it is greatly reduced when Y is —$CH_2CH_2CH_2CH_2$—.

When the Z group in  is phenylene, the polymer is the poly(*p*-xylylidene-*p*-phenylenediamine), (III), and may be termed the para-para polymer. The syntheses and the comparison of the thermal properties of the three isomeric para-meta, meta-para, and meta-meta polymers with the para-para polymer is the subject of another publication (34). Substitution of the carbonyl hydrogens by R groups in =HCC_6H_4CH= yields the polyketanils,



$$=\!\left[N{-}Z{-}N{=}\overset{\displaystyle R}{\overset{|}{C}}{-}Ar{-}\overset{\displaystyle R}{\overset{|}{C}}\right]_{n}$$

these also have been prepared and will be reported (*35*) separately. Accordingly, to minimize the number of variables in the study of the influence of conjugation on the thermal stability of the polymer, appropriate para-para polymers of structure (IV) were prepared which contained the Z structures shown in Table 2.

Three new polymerization reactions, which we have termed "Schiff base exchange" reactions (*16,26,27*), (1) the amine exchange, (2) the aldehyde exchange, and (3) the bis exchange, were used to prepare the polymers of Table 2.

The aldehyde exchange polymerization (reaction B, Table 1) can be written as

$$\begin{aligned}&n\mathrm{OHC{-}C_6H_4{-}CHO} + n\mathrm{C_6H_5CH{=}N{-}Z{-}N{=}HCC_6H_5} \rightleftharpoons\\&\qquad (2n-1)\mathrm{C_6H_5CHO} + \mathrm{C_6H_5CH}{=}\!\left[\mathrm{N{-}Z{-}N{=}HC{-}C_6H_4{-}CH}\right]_{n}\!{=}\mathrm{O}\qquad (1)\end{aligned}$$

and the amine exchange polymerization (reaction D, Table 1) as

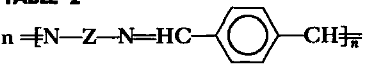
$$\begin{aligned}&n\mathrm{H_2N{-}Z{-}NH_2} + n\mathrm{C_6H_5N{=}HC{-}C_6H_4{-}CH{=}NC_6H_5} \rightleftharpoons\\&\qquad (2n-1)\mathrm{C_6H_5NH_2} + \mathrm{H_2}{=}\!\left[\mathrm{N{-}Z{-}N{=}HC{-}C_6H_4{-}CH}\right]_{n}\!{=}\mathrm{NC_6H_5}\qquad (2)\end{aligned}$$

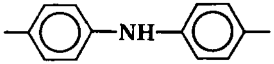
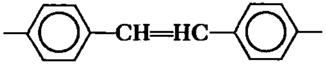
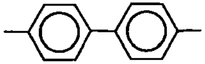
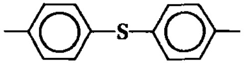
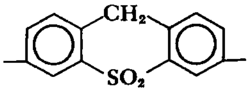
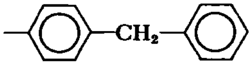
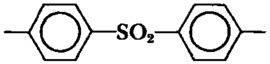
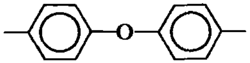
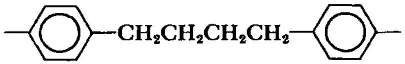
and the bis exchange, which involves the mutual replacement of the aldehyde and amine functions in two distinct Schiff bases to produce two new Schiff bases (reaction E, Table 1), as

$$\begin{aligned}&n\mathrm{C_6H_5N{=}HC{-}C_6H_4{-}CH{=}NC_6H_5} + n\mathrm{C_6H_5CH{=}N{-}Z{-}N{=}HCC_6H_5} \rightleftharpoons\\&(2n-1)\mathrm{C_6H_5CH{=}NC_6H_5} + \mathrm{C_6H_5CH}{=}\!\left[\mathrm{N{-}Z{-}N{=}HC{-}C_6H_4{-}CH}\right]_{n}\!{=}\mathrm{NC_6H_5}\qquad (3)\end{aligned}$$

The general procedure consisted in melting the mixture of reagents in a suitable apparatus in an inert atmosphere until equilibrium was established and thereafter removing the lower molecular weight by-products by distillation to shift the equilibrium to the polymer product. The bis exchange reaction differs from the amine and the aldehyde exchanges in that benzylideneaniline, which is a Schiff base, is eliminated as the by-product in this reaction, whereas aniline and benzaldehyde, respectively, are eliminated in the other exchange reactions. Since benzylideneaniline is a monomeric Schiff base, which is physically and chemically related to the resulting polymer, it could be presumed to be acting as a solvent in the reaction. To establish the validity of this assumption, the amine-

TABLE 2

Types of Z Groups Used in 

1.		5.		9.	
2.		6.		10.	
3.		7.		11.	$-CH_2CH_2CH_2CH_2-$
4.		8.		12.	$-CH_2CH_2CH_2CH_2CH_2CH_2-$

and the aldehyde-exchange polymerizations were conducted also in the presence of benzylideneaniline.

This paper compares the syntheses and thermal stabilities of selected Schiff base polymers prepared by (a) the condensation, in solution, of diamines and dialdehydes; (b) the melt polymerization of diamines and dialdehydes; and (c) the solution and melt polymerizations involving (1) amine exchange, (2) aldehyde exchange, and (3) bis exchange reactions.

EXPERIMENTAL

Monomers

The Schiff base monomers used in these studies were prepared, characterized, and purified by procedures reported elsewhere (*36*). The amines and aldehydes used for the syntheses of these monomers and for other reactions were obtained from commercial sources and were purified by distillation or crystallization before use (*36*).

Polymerizations

Equilibrium Solution Polymerizations of Dialdehydes and Diamines. A typical procedure is illustrated by the following example: A mixture of equimolar portions of 0.54 g (0.005 mole) of *p*-phenylenediamine and 0.67 g (0.005 mole) of terephthaldehyde, 15 ml of ethyl alcohol and 0.05 g of acetic acid in a 50-ml round-bottom, three-neck flask equipped with a reflux condenser, gas inlet tube, gas outlet tube, and an electric heating mantle was refluxed under a nitrogen atmosphere for 4 hr. The bright-yellow precipitate which formed was removed by filtration and dried to constant weight, 1.12 g, in a vacuum oven at room temperature. The product did not melt when heated to temperatures up to 300°C. It was insoluble in common organic solvents as well as in dimethylformamide, dimethylacetamide, dimethyl sulfoxide, and butyrolactone, but was soluble in 98% formic acid, glacial acetic acid, acetic anhydride, and saturated aqueous sodium bisulfite. The infrared spectra showed adsorption bands for the NH_2 group in the region of 3380 cm^{-1} and for the —CHO group in the region of 1700 cm^{-1}.

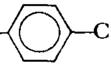
Analysis: Found: C, 78.49%; H, 5.09%; N, 12.96%
Calcd. for $O{=}\!\left[HCC_6H_4CH{=}NC_6H_4N\right]_{2.5}{=}H_2$: C, 78.69%; H, 5.07%; N, 13.07%

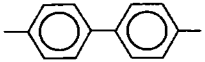
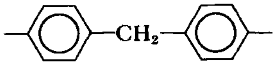
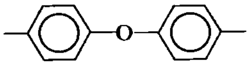
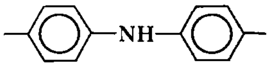
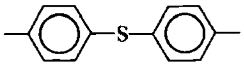
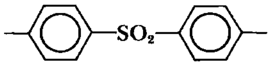
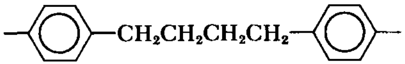
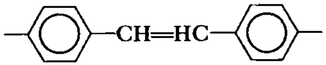
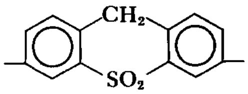
In subsequent experiments, water, benzene, toluene, xylene, acetic anhydride, dimethylformamide, dimethylacetamide, dimethylaniline, and tetrahydrofuran were substituted for the ethyl alcohol; and hydrochloric acid, sulfuric acid and *p*-toluenesulfonic acid were substituted for the acetic acid; in all cases, similar condensation products were obtained in yields varying from 93.6 to 96.2%, and their infrared spectra showed the presence of NH_2 and CHO functions.

Continuous Azeotropic Solution Condensation of Dialdehydes and Diamines. A typical procedure is illustrated by the following example: into a 250-ml three-neck, round-bottom flask equipped with a reflux condenser, a gas inlet and outlet tube, a Dean-Stark trap, a magnetic stirrer, and an electric heating mantle were placed 100 ml of freshly distilled benzene and 0.01 mole of the appropriate diamine. A slow stream of deoxygenated nitrogen was passed through the apparatus and the mixture heated, with stirring, until the diamine was dissolved; then 0.01 mole of terephthaldehyde dissolved in 100 ml of benzene was added to the solution, the mixture refluxed, and the azeotroped water collected in the Dean-Stark trap. The reaction appeared to be completed at the end of 2 hr, but to assure completeness it was continued for 20 hr, and the reaction mixture cooled to room temperature. In all cases the conjugated and pseudoconjugated polymers precipitated during reaction from the solution as fine, intractable, brick-dust type powders; they were recovered by filtration and dried to constant weight in a vacuum oven at 25°C at 5 mm Hg pressure. The colors of these polymers varied from light yellow to greenish yellow and orange-yellow, and they did not melt when heated to temperatures up to 400°C. The infrared spectra of the polymers showed the presence of NH_2 function at 3380 cm^{-1} and —CHO function at 1700 cm^{-1}. The two polymers containing aliphatic bridges, $=N-(CH_2)_4-N=$ and $=N-(CH_2)_6-N=$, which were prepared by reacting 1,4-diaminobutane and 1,6-diaminohexane, respectively, with terephthaldehyde, remained in solution during the reaction and precipitated on cooling. Their white color was in marked contrast with the yellow color of their aromatic counterparts. Table 3 summarizes the yields, colors, nitrogen analyses, and average $\overline{DP}$, calculated from the nitrogen analyses of the polymers prepared in solution.

The nitrogen analyses indicated that the polymers were of relatively low molecular weight. Analyses for carbon and hydrogen

TABLE 3

Data on $\mathord{=}\!\!\!\!\![N—Z—N{=}HC$  $CH]_{\overline{n}}$ Polymers Prepared by Solution Method

Polymer designation	Z group	Color	Yield, %	Yield, % N	Approx. $\overline{DP}$
1-Y		Yellow	98.4	13.28	4.0
2-Y		Yellow	97.1	9.38	3.6
3-Y		Yellow	92.3	9.30	4.2
4-Y		Yellow	92.6	9.27	5.0
5-Y		Orange-yellow	93.4	9.21	3.4
6-Y		Yellow	91.4	9.35	3.9
7-Y		Yellow	95.9	8.06	3.7
8-Y		Cream-yellow	95.8	8.16	4.1
9-Y		Orange-yellow	96.3	8.29	3.8
10-Y		Greenish yellow	95.8	7.68	3.1
11-Y	$—(CH_2)_4—$	White	86.5	14.84	7.1
12-Y	$—(CH_2)_6—$	White	81.0	12.94	8.0

also yielded values which characterized them as low molecular weight products. A typical analysis is illustrated by that for polymer 1-Y.

Analysis: Found: C, 79.55%; H, 5.15%; N, 13.28%
Calcd. for: (1) $C_{22}H_{11}N_2O_2$: $OHCC_6H_4CH{=}NC_6H_4N{=}HCC_6H_4CHO$: C, 77.60%; H, 4.70%; N, 8.23%
(2) $C_{20}H_{21}N_4$: $H_2NC_6H_4N{=}HCC_6H_4CH{=}NC_6H_4NH_2$: C, 75.70%; H, 6.64%; N, 17.65%
(3) $O[C_{14}H_{10}N_2]_nH_2$: $O{=}\!\!\left[CHC_6H_4CH{=}NC_6H_4N\right]_{n}\!H_2$:
$n = 1$: C, 75.00%; H, 5.36%; N, 12.50%; O, 7.15%
$n = 3$: C, 79.25%; H, 5.03%; N, 13.12%; O, 2.50%
$n = 5$: C, 80.15%; H, 4.96%; N, 13.36%; O, 1.52%
$n = 10$: C, 80.94%; H, 4.90%; N, 13.48%; O, 0.77%
$n = \infty$: C, 81.53%; H, 4.88%; N, 13.59%

The analytical data indicate that polymer 1-Y was, as an average, a tetramer. A sample, 0.5 g, of polymer 1-Y was heated in a microdistillation apparatus in a slow stream of nitrogen (a) for ½ hr at 200°C, and another sample, (b), for 3 hr at 250°C. Trace amounts of water and *p*-phenylenediamine, m.p. 139°C, collected on the surface of the distilling head. The polymer samples were then cooled, isolated, and analyzed. The yield of 1-Y-a was 0.495 g, and its yellow color was unchanged from that of the original, and the yield of 1-Y-b was 0.493 g, and its color was a light-orange yellow. The infrared spectra of the original and postheated polymers showed the presence of $—NH_2$ and —CHO functions. The samples, before and after heating, were soluble in formic, acetic, and sulfuric acids, and saturated aqueous sodium bisulfite. They were also soluble, at 140°C, in benzylideneaniline. The intrinsic viscosities of polymers 1-Y, 1-Y-a, and 1-Y-b at 25°C in 95.3% sulfuric acid were 0.051, 0.053, and 0.055, respectively. Analyses of these samples for C, H, and N yielded the following values, which were compared to values published (37) for the polymer 1-Y-c prepared in solution and which was considered to be a dimer.

Analysis: Found: 1-Y: C, 79.55%; H, 5.15%; N, 13.28%
1-Y-a: C, 79.74%; H, 5.11%; N, 12.82%
1-Y-b: C, 79.76%; H, 4.98%; N, 13.14%
1-Y-c (37): C, 78.56%; H, 5.15%; N, 12.47%

Condensation in Sulfuric Acid. To 27.6 g of 95.3% sulfuric acid, cooled to 5°C, there was added slowly, with stirring, 0.54 g (0.005 mole) of *p*-phenylenediamine; then the temperature was raised slowly to 20°C and a clear solution resulted. The solution was again cooled to 0–5°C and 0.67 g of terephthaldehyde added slowly in portions over a period of about 10 min; then the temperature of the mixture was allowed to rise to 25°C, and a clear yellow solution resulted. When an aliquot part of about 1 ml of the solution was poured onto 20 g of crushed ice, a yellow precipitate formed immediately, which on standing after the ice had melted, disappeared in about 10 min by dissolution in the acidified water. When, however, the polymer solution was dripped slowly into a 5% sodium hydroxide solution cooled to 0–5°C, the yellow precipitate remained and was removed by filtration, washed several times in boiling water, until the water was neutral, isolated, and dried to constant weight. The infrared spectrum of the yellow product showed the presence of NH_2 and CHO functions as well as the band for —C=N—; intrinsic viscosity in sulfuric acid at 25°C, 0.06. The intrinsic viscosities in sulfuric acid at 25°C of the brown and dark-brown polymers which were isolated as precipitates after the sulfuric acid solution had stood at room temperature for 5 and 8 days, were 0.36 and 0.41, respectively.

Melt Polymerization of *p*-Phenylenediamine and Terephthaldehyde. *By Rapid Heating.* In a nitrogen atmosphere in a dry box, 1.08 g (0.01 mole) of freshly purified *p*-phenylenediamine and 1.34 g (0.01 mole) of terephthaldehyde were thoroughly mixed and ground by means of a mortar and pestle, and transferred to a 10-ml micro distilling flask equipped with a thermometer, nitrogen gas inlet, condenser, receiver, and gas outlet. The mixture was heated rapidly under a slow stream of nitrogen by means of a blue flame of a micro Bunsen burner until the mixture became fluid at about 160°C, as indicated by the thermometer whose bulb was immersed in the mixture. In about 2 min, the melt became increasingly viscous, changing progressively in color from a yellow to orange to brown and to a black solid. Then the contents of the flask were heated by means of an electric mantle for 1 hr at 180°C and 1 hr at 260°C. The yield of this polymer, 1-B-RP-260, was 2.03 g (98.5%); it was insoluble in formic acid and in molten benzylideneaniline, and only slightly soluble in sulfuric acid. The infrared spectrum showed the absence of $-NH_2$ functions but the presence of a low concentration of $-CHO$ groups.

Analysis: Found: First analysis: C, 83.25%; H, 5.47%; N, 6.08%; $\Sigma = 94.80\%$
Second analysis: C, 85.59%; H, 5.17%; N, 9.79%; $\Sigma = 100.5\%$
Third analysis: C, ---; H, ---; N, 13.48%

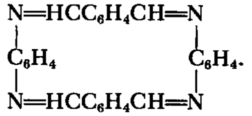
When polymer 1-B-RP-260 was reheated in nitrogen to 400°C for 1 hr, the resulting polymer, 1-B-RB-H400, became completely insoluble in sulfuric acid and its infrared spectra showed the absence of NH_2 and CHO functions.

One gram of the heated, insoluble polymer 1-B-RP-H400 was finely ground and mixed with 10.0 g of benzylideneaniline and 0.05 g of zinc chloride in a microflask equipped with a gas inlet and steam-heated reflux condenser; the mixture was then heated under a nitrogen atmosphere to reflux at 310°C for 48 hr. The solution became dark-colored when reflux temperature was reached, and a homogeneous black solution resulted in about 18 hr. On cooling to room temperature, the mixture solidified to a black polymeric solid, 1-B-RP-H400-S, which was soluble in sulfuric acid. Distillation of the mixture to 330°C at 15 mm Hg pressure eliminated much of the benzylidene rapidly, at which time a sample was withdrawn and found to be soluble in concentrated sulfuric acid. Then the heating was continued to 600°C, and 1.09 g of a solid black polymer, insoluble in sulfuric acid, was obtained.

By Slow Heating. A mixture of 0.01 mole each of *p*-phenylenediamine and terephthaldehyde was mixed under nitrogen in a dry box by the procedure given above and placed in a 1-in.-diameter 50-ml Pyrex glass reaction tube equipped with a nitrogen capillary inlet, supported by a Teflon adapter, a side arm to which was attached a condenser with an adapter for evacuation, and a receiver which was submerged in an acetone–solid carbon dioxide trap. All joints were ground glass and of standard taper. After the oxygen in the system was displaced with deoxygenated nitrogen, the tube assembly was inserted into a metal heat sink, preheated to 300°C, which consisted of a cube of aluminum, 3 in. long, on an edge. A hole, 1 in. in diameter, was drilled in the center of one face of the cube to house the reaction tube, and a probe hole was located within ½ in. of the inserted reaction tube. The metal cube was heated by a special Glas-Col square mantle, custom-made for the cube. The temperature was maintained at 300°C by a Model 1422-071 ProportioNull electronic controller (Cole-Parmer Instrument and Equipment Co.), whose upper limit of control is 400°C. For heating above 400°C, as required in other experiments, a quartz reaction tube and a heat sink of copper were used and the temperature controlled by a variable transformer and determined by means of a thermocouple. The maximum temperature of the apparatus equipped with a quartz reaction tube is 600°C. When the tube was inserted into the block at 300°C, the reactants softened to a paste but did not pass through a clear melt stage, but a small amount of water refluxed within the tube and a small amount of sublimed material collected in the uppermost part of the reaction tube. Heating was continued at atmospheric pressure for 4 hr. Then the pressure was reduced to 1 mm Hg and the heating continued at 300°C for an additional 2 hr. The polymer mass, 1.766 g (86% yield), was porous throughout; its color was light brown on the top and dark brown on the bottom and in the interior of the mass. The polymer was soluble in formic acid, glacial acetic acid, and sulfuric acid and its infrared spectrum showed the presence of $—NH_2$ and —CHO functions. Its intrinsic viscosity in 95.3% sulfuric acid at 25°C was 0.16.

Analysis: Found: C, 80.64%; H, 4.92%; N, 13.46%; which corresponded approximately to the calculated values for a heptamer

Schiff Base Exchange Polymerizations. *Amine Exchange. In Solution.* A mixture of 2.84 g (0.01 mole) of *p*-xylylidenedianiline and 1.08 g (0.01 mole) of *p*-phenylenediamine was dissolved in 200 ml of benzene and the mixture refluxed under a nitrogen atmosphere for 1 hr, and no reaction occurred. Then 0.002 g of *p*-toluenesulfonic acid was added to the mixture and a yellow flocculent precipitate appeared within a few minutes. The reaction was continued at reflux for 4 hr, the mixture cooled to room temperature, the yellow condensation product removed by filtration, washed with benzene, and dried in a vacuum oven at 25°C to constant weight; yield 2.13 g. The product was soluble in formic acid, glacial acetic acid, and sulfuric acid. Its infrared spectrum showed the presence of bands for $—NH_2$ at 3380 cm^{-1}, for $—C{=}N$ at 1612 cm^{-1}, and for $N—C_6H_5$ at 750 and 690 cm^{-1}. The yellow filtrate was refluxed for 12 hr and, on cooling the solution, two distinct products precipitated. The first fraction, 0.311 g, was a greenish-yellow powder whose infrared spectrum showed strong peaks at 3380 cm^{-1} for $—NH_2$ and at 1615 cm^{-1} for $C{=}N—$. This and its elemental analysis, C: 75.26; H: 6.52; N: 17.86, indicated that it was impure $H_2NC_6H_4N{=}HCC_6H_4CH{=}NC_6H_4NH_2$. The second fraction, 0.478 g, was a well-defined orange-colored crystalline material. Its infrared spectrum showed strong peaks in the $—C{=}N—$ region at 1614 cm^{-1} and in the phenylene regions at 1006 and 812 cm^{-1}. Peaks attributable to monosubstituted phenyl groups at 750 and 690 cm^{-1} were absent. Based on these spectral data and on its elemental analysis: C, 81.53; H, 4.88; N, 13.59, the compound appears to be the cyclic derivative



$$\begin{array}{lcr} N{=}HCC_6H_4CH{=}N & & \\ | & & | \\ C_6H_4 & & C_6H_4. \\ | & & | \\ N{=}HCC_6H_4CH{=}N & & \end{array}$$

Neither of these compounds melted when heated to 300°C, but when heated they changed color, becoming orange at about 130°C.

In a subsequent experiment, in which the toluene sulfonic acid was omitted the mixture was refluxed for 12 hr, and a yield of 1.9 g of yellow condensation product was obtained.

Other experiments in which ethyl alcohol, xylene, and tetralin, respectively, were used as solvents and hydrochloric acid and sulfuric acid, respectively, as catalysts yielded similar yellow condensation products.

In Melt. By Rapid Heating. A mixture of *p*-xylylidenedianiline 2.84 g (0.01 mole) and *p*-phenylenediamine 1.08 g (0.01 mole) were ground together with a mortor and a pestle in a dry box under nitrogen, transferred to a 10-ml micro distilling flask suitably equipped and the mixture heated rapidly under nitrogen by means of a blue flame of a micro Bunsen burner, as previously described above. The mixture melted at about 132°C, rising rapidly to about 200°C, eliminating aniline. In a few minutes the melt became increasingly viscous, changing progressively in color from yellow to orange to brown to black. The contents of the flask were then heated for 1 hr at 250°C; yields of aniline recovered, 1.67 g, and of polymer, 2.04 g. The polymer was somewhat soluble in sulfuric acid. Its infrared spectrum showed a peak in the region of 1598 cm^{-1} for C=N, a weak peak at 3380 cm^{-1} for NH_2, and peaks at 750 and 690 cm^{-1} for $—C_6H_5$. Then, when this polymer was postheated at 380°C for 1 hr, it became insoluble in sulfuric acid and its infrared spectrum showed the absence of NH_2 functions.

By Slow Heating. A mixture of 2.84 g (0.01 mole) of *p*-xylylidenedianiline and 1.08 g (0.01 mole) of *p*-phenylenediamine was thoroughly mixed by grinding under an inert atmosphere by the procedure given above and placed in the glass reaction tube. The mixture was then degassed at 1 mm Hg pressure, after which nitrogen was bled into the apparatus. The degassing procedure was repeated two additional times, the tube inserted in the aluminum heat sink previously described, and heating of the mixture started. The temperature of the mixture increased in 10 min to 132°C, at which temperature it melted, reacting immediately to form an orange solution which then solidified in about 5 min. Then the temperature was raised to 190°C for 45 min, then to 195°C for 45 min, and the color of the polymer became orange-brown. The mixture was then heated at 300°C for 1½ hr at 20 mm Hg pressure, and for 3 hr at 1 mm Hg pressure, then allowed to cool to room temperature. There was collected as a distillate 1.5 g of aniline, and 2.0 g of polymer which was dark-brown and only slightly soluble in sulfuric acid. Its infrared spectrum showed the presence of NH_2 functions at 3380 cm^{-1} as well as peaks for the —C=N— and $—C_6H_5—$ functions.

Aldehyde Exchange. In Solution. A mixture of 1.34 g (0.01 mole) of terephthaldehyde and 2.84 g (0.01 mole) of dibenzylidene-*p*-phenylenediamine and 25 ml of toluene (b.p. 110.8°C) was refluxed under a nitrogen atmosphere for 4 hr, without the formation of polymer or a change in color of the solution. Polymer formation did not occur, also, when tetralin (b.p. 207.2°C) was substituted for the toluene. However, when 0.010 g of zinc chloride was added to the mixture of reactants, 2.41 g of yellow polymer and 2.29 g of orange polymer, respectively, were obtained when toluene and tetralin, respectively, were used as solvents. Both polymers were soluble in sulfuric acid, and their infrared spectra, which were typical of the low molecular weight polymeric Schiff bases, also showed bands for the presence of —CHO at 1700 cm^{-1} and of —C_6H_5— at 750 and 695 cm^{-1}. The analysis for the yellow polymer (found: C, 81.17%; H, 4.92%; N, 11.30%), indicated that, as an average, it was a trimer, while the analysis for the orange polymer (found: C, 81.36%; H, 4.94%; N, 12.37%) indicated that it was, on the average, a pentamer.

In Melt. A mixture of 1.34 g (0.01 mole) of terephthaldehyde and 2.84 g (0.01 mole) of dibenzylidene-*p*-phenylenediamine was allowed to react under nitrogen in a 50-ml reaction tube by the procedure given above. The reaction was initiated by immersing the reaction tube in a metal sink previously heated to 310°C. A clear yellow melt formed at 95°C. The reaction conditions and observations were as shown in Table 4. The distillate, 1.2 g, was identified as benzaldehyde by its infrared spectrum and by the preparation of benzylideneaniline as a derivative. The reddish-brown polymer, 2.26 g, was insoluble in dimethylformamide but soluble in formic and concentrated sulfuric acids. Its infrared spectrum showed bands for the presence of —CHO at 1700 cm^{-1} and for —C_6H_5 at 750 and 795 cm^{-1}.

Analysis: Found: C, 81.38%; H, 4.91%; N, 13.49%

TABLE 4

Reaction Conditions

Time, min	Temp., °C	Pressure, mm Hg	Observation
0	95	760	Yellow melt
5	150	760	Light-orange melt
8	180	760	Orange melt
15	220	760	Deep-orange melt
25	230	760	Red-orange melt
60	240	760	Red-orange melt
67	260	760	Orange-red melt
120	280	760	Cherry-red melt
130[a]	310	760	Cherry-red melt
140	310	3.8	Viscous dark-red resin
150	310	0.7	Dark-red solid
270	310	0.7	Brown-red solid

[a] Liquid began to collect as a distillate at this time.

A series of related experiments were performed in which the mole ratio of terephthaldehyde to dibenzylidene-*p*-phenylenediamine was varied from 1:2 to 2:1 for comparison of the color of the reaction product with that of the 1:1 molar reaction mixture described above. The experiments were performed in the apparatus as described above. The mixture of reagents was introduced into the reaction flask, the apparatus degassed at 0.4 mm, and a slow stream of nitrogen introduced into the apparatus. The mixture was then heated, and to avoid forcing conditions which would favor polymer formation, the temperature was not allowed to rise above 220°C. In all cases, melting of the mixtures occurred below or at about 100°C. The temperature was maintained at 220°C for 6 hr at atmospheric pressure, and benzaldehyde collected as a distillate. The reaction product was then allowed to cool to room temperature. The observations listed in Table 5 were made during the course of the reaction.

Bis Exchange. In Solution. A mixture of 2.84 g (0.01 mole) of *p*-xylylidenedianil and 2.84 g (0.01 mole) of N,N′-bisbenzylidene-*p*-phenylenediamine and 25 ml of toluene 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 to the mixture of reactants, 2.32 g of yellow polymer was obtained. When tetralin was used as the solvent, 2.41 g of an orange polymer was obtained. Both polymers were soluble in sulfuric acid and their infrared spectra showed bands for the presence of terminal C_6H_5— groups at 750 and 695 cm^{-1}.

In Melt. The two Schiff bases were thoroughly mixed and reacted under nitrogen in the quartz reaction tube inserted in the metal heat sink by the procedure described above. A number of exploratory polymerizations were performed in this apparatus in which the time, temperature, and pressure conditions were varied over a wide range. An evaluation of these polymerizations was made with respect to ease of control, minimum loss of monomers, yield, and color of polymer. To standardize the syntheses, all the polymers, with the exception of those derived from the aliphatic diamines, were prepared under identical conditions of time, temperature, and pressure. These selected standardized conditions are given in Table 6. Under these selected conditions, the polymerizations were found to proceed smoothly with the reaction mixture changing successively in color from yellow to orange to red to brown to black

TABLE 5

Reactions of Terephthaldehyde and Dibenzylidene-*p*-phenylenediamine at Various Mole Ratios

Mole ratio $C_6H_4(CHO)_2$/ $C_6H_4(N{=}HCC_6H_5)_2$	Most probable structure[a] of the product observations[b]
1:1	$O{=}[HCC_6H_4CH{=}NC_6H_4N]_n{=}HCC_6H_5$ black polymer
1:2	$H_5C_6CH{=}NC_6H_4N{=}[HCC_6H_4CH{=}NC_6H_4N]_1{=}HCC_6H_5$ yellow solid; m.p. 140–141°C; mixed with some orange-red polymer
2:3	$H_5C_6CH{=}NC_6H_4N{=}[HCC_6H_4CH{=}NCC_6H_4N]_2{=}HCC_6H_5$ orange-yellow solid; m.p. 145–220°C
3:4	$H_5C_6CH{=}NC_6H_4N{=}[HCC_6H_4CH{=}NC_6H_4N]_3{=}HCC_6H_5$ yellow-orange solid; m.p. 128–178°C
5:6	$H_5C_6CH{=}NC_6H_4N{=}[HCC_6H_4CH{=}NC_6H_4N]_5{=}HCC_6H_5$ orange-red solid; m.p. 190–200°C
2:1	$OHCC_6H_4CH{=}[NC_6H_4N{=}HCC_6H_4CH]_1{=}O$ some $C_6H_4(CHO)_2$ sublimed, resulting in brown-red polymer; infrared spectrum shows —CHO
3:2	$OHCC_6H_4CH{=}[NC_6H_4N{=}HCC_6H_4CH]_2{=}O$ orange-yellow solid; m.p. 180–280°C; infrared spectrum shows —CHO
4:3	$OHCC_6H_4CH{=}[NC_6H_4N{=}HCC_6H_4CH]_3{=}O$ orange solid; m.p. 130–160°C; infrared spectrum shows —CHO
6:5	$OHCC_6H_4CH{=}[NC_6H_4N{=}HCC_6H_4CH]_5{=}O$ orange-red solid; m.p. 180–190°C; infrared spectrum shows —CHO

[a] Value of *n* in formulas is assumed from ratios of reactants used; even with this assumption the value must be considered as an average of higher and lower values.

[b] Melting points were measured on a calibrated Fisher-Johns melting point apparatus.

TABLE 6

Reaction Conditions

Time, hr	Temp., °C	Pressure, mm Hg
2	200	760
2	260	760
10	320	760
20	380	1
20	400	1

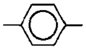
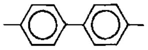
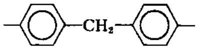
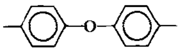
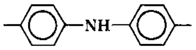
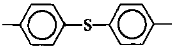
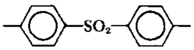
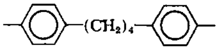
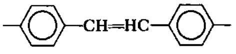
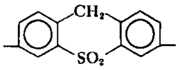
with the continuous evolution of benzylideneaniline. When the pressure was reduced in the final stages of the polymerization, it was necessary to exercise care to avoid loss of reactants due to "bumping." It was found necessary to reduce the pressure slowly from 760 mm to 1 mm over the course of $\frac{1}{2}$ to 1 hr.

1. The following is a typical polymerization: a mixture of 2.84 g (0.01 mole) of *p*-xylylidenedianil and 2.84 g (0.01 mole) of N,N'bis-benzylidene-*p*-phenylenediamine was ground in a mortar and pestle and placed in the reactor tube. The system was degassed to 1 mm Hg pressure, then refilled with dry deoxygenated nitrogen; the degassing was repeated two additional times and the apparatus repressured with nitrogen to atmospheric pressure. The tube was then placed in the metal heat sink preheated to 200°C. The mixture melted completely in the temperature range 80 to 85°C, at which time it was thoroughly shaken to assure homogeneity, and the reaction continued under the selected standardized conditions of time, temperature, and pressure. As the reaction proceeded, the reaction mixture changed (38) from a yellow fluid melt to a light-orange fluid melt, to a brilliant-orange fluid melt, to a red thick melt, to a brown viscous melt, then to a dark brown very viscous melt as benzylideneaniline began to reflux from the mixture at 320°C. As benzylideneaniline was distilled from the mixture, a black, very viscous melt was obtained, becoming a very shiny, hard, black mass. The benzylideneaniline collected, 2.92 g, was identified by its melting point (54°C) and its infrared spectra. At the end of the reaction, the apparatus was allowed to cool to room temperature and the polymer isolated as a solid button. It weighed 2.26 g, yield 109.7%.

The 109.7% yield was calculated by comparing the 2.26 g of polymer yield with a weight of 2.06 g as the reference point for a 100% yield. The reference point selected was based on a yield in which $n = \infty$ in the polymer, $\mathrm{=\!\![HCC_6H_4CH{=}NC_6H_4N]\!\!=_{\infty}}$, in which case end groups would make only a very minor contribution to yield weight. When the end groups are included in calculations involving finite values of n, $\mathrm{C_6H_5N{=}\![HCC_6H_4CH{=}NC_6H_4N]\!=_{n}HCC_6H_5}$, the calculated yield varies with the value of n. In this case, the 2.26 g yield of polymer, when the end groups are included in the structure, would represent a 109.6% yield if $n = 1000$; 109.3% if $n = 100$ and 108.5% if $n = 50$ and 102.4% if $n = 10$. These calculations assumed that all the benzylideneaniline produced in the reaction has been eliminated from the mass. Table 7 lists the polymers prepared by the bis-exchange method, in which the Z linkage was varied.

TABLE 7

$\lbrack N{-}Z{-}N{=}HCC_6H_4CH \rbrack_n$ Polymers Prepared by Bis Exchange

Polymer no.	Z group	Yield, %[a]	Color	Solubility in H_2SO_4	N, % Calcd.	N, % Found
1-B-H400		109.7	Black	Insoluble	13.59	13.46
2-B-H400		106.4	Black	Insoluble	9.93	9.80
3-B-H400		105.4	Black	Insoluble	9.45	9.31
4-B-H400		110.0	Black	Insoluble	9.40	9.26
5-B-H400		107.4	Black	Insoluble	9.42	9.29
6-B-H400		106.2	Black	Insoluble	8.92	8.82
7-B-H400		104.9	Black	Insoluble	8.09	7.97
8-B-H400		106.3	Black	Insoluble	8.26	8.14
9-B-H400		107.1	Black	Insoluble	9.09	8.91
10-B-H400		105.0	Black	Insoluble	8.06	7.93
11-B-H250	$-(CH_2)_4-$	79.8	Orange	Soluble	15.05	15.00
12-B-H250	$-(CH_2)_6-$	102.2	Orange	Soluble	13.08	13.02

[a] Calculated on the basis of $\lbrack N{-}Z{-}N{=}HCC_6H_4CH \rbrack_n$ as 100%.

The suffix H400 after the polymer number indicates that the maximum temperature used in their preparation was 400°C. All the conjugated and pseudoconjugated polymers were insoluble in concentrated sulfuric acid but could be solubilized in benzylideneaniline by heating at 310°C in the presence of catalytic quantities of zinc chloride or sulfuric acid.

2. Preliminary experiments showed that the conditions used for the preparation of the conjugated and pseudoconjugated polymers were unsuited for the preparation of the aliphatic bridged polymers 11 and 12, $\lbrack N(CH_2)_nN{=}HCC_6H_4CH \rbrack_n$, because of their instability at the temperatures used. The selected, modified conditions

under which these aliphatic type polymers were prepared are listed in Table 8.

3. A mixture of 2.84 g (0.01 mole) *p*-xylylidenedianil and 2.84 g (0.01 mole) of N,N′-bisbenzylidene-*p*-phenylenediamine were reacted under the selected standardized conditions followed by 10 hr at 450°C, and there was recovered 3.2 g of distillate, identified by infrared spectrum as benzylideneaniline, and 2.4 g of black, tough polymer 1-B-H450. The total weight of product isolated was 5.6 g, 98.62%.

Analysis: Calcd.: First analysis: C, 75.20%; H, 4.74%; N, 6.80%; Σ of elements, 86.94%
Second analysis: C, 81.55%; H, 4.66%; N, 9.49%; Σ of elements, 95.80%
Third analysis: C, ---; H, ---; N, 13.51%
Calcd. for $\mathrm{=\!\!\{NC_6H_4N{=}CHC_6H_4CH\}\!\!=}$: C, 81.53%; H, 4.88%; N, 13.59%

4. A mixture of 2.84 g (0.01 mole) of *p*-xylylidenedianil and 2.84 g (0.01 mole) of N,N′-bisbenzylidene-*p*-phenylenediamine were mixed in the reactor tube equipped with a nitrogen capillary inlet supported by a Teflon adapter and evacuated to 0.1 mm and repressured to atmospheric pressure with dry-deoxygenated nitrogen. The degassing was repeated two additional times; a 500-ml balloon filled with nitrogen was attached to the nitrogen inlet tube and the reactor tube inserted into the metal heat sink previously heated to 325°C. When the mixture melted, it was shaken vigorously and a clear homogeneous mixture resulted. The reaction was then allowed to continue under a static head of nitrogen at atmospheric pressure, during which time benzylideneaniline refluxed from the mixture and a black viscous solution formed. At the end of 2 hr, a

TABLE 8

Reaction Conditions

Time, hr	Temp., °C	Pressure, mm Hg
2	150	760
10	200	760
10	250	1

distillation adapter with side arm, etc., was attached to the reactor and a slow stream of nitrogen allowed to flow over the melt slowly, distilling out the benzylideneaniline. As the benzylideneaniline was removed, the viscosity of the melt increased. When the melt appeared to be very viscous but still exhibited flow, sample 1-B-H325-A was withdrawn; then the reaction was continued until the melt appeared to lose its flow and become solid, and sample 1-B-H325-B was taken, at which time 2.59 g of benzylideneaniline had been collected. Samples A and B were soluble in concentrated sulfuric acid. The intrinsic viscosities at 25°C in 96.1% sulfuric acid were 0.511 for sample A and 0.824 for sample B.

5. Six separate mixtures of 1.00 g of N,N'-bis(4-chlorobenzylidene)-*p*-phenylenediamine and 1.00 g of *p*-xylylidene-di-4-chloroanil were reacted at 300°C under nitrogen by procedures given above under the following condition and the by-product *p*-chlorobenzylidene-*p*-chloroaniline and the polymers collected:

Polymer 14C-1: 3 min at 760 mm Hg pressure
14C-2: 120 min at 760 mm Hg pressure
14C-3: 180 min at 760 mm Hg pressure
14C-4: 360 min at 760 mm Hg pressure
14C-5: 300 min at 760 mm Hg pressure
180 min at 1.5 mm Hg pressure
14C-6: 180 min at 760 mm Hg pressure
1440 min at 1.5 mm Hg pressure

Elemental analyses were performed on the polymers and the ultraviolet spectra recorded of those samples which were soluble in dimethylacetamide.

A finely ground sample, 0.1189 g of polymer 14C-5, was added to 10 ml (18.4 g) of concentrated sulfuric acid and the mixture maintained at 25°C for 70 hr. Then the polymer was removed by filtration, washed with water until neutral, and dried to constant weight; the weight loss was 0.0207 g (17.4%). When the extraction was repeated at 60°C for 24 hr, the weight loss was 0.02604 g (21.9%). The filtrate possessed the greenish-yellow color similar to that of a reference solution of *p*-chlorobenzylidene-*p*-chloroaniline in concentrated sulfuric acid. When the dried sample was reextracted with concentrated sulfuric acid at 120°C, an additional 0.0417 g (35.1%) was extracted.

By Exchange Reactions in Benzylideneaniline. 1. A mixture of 2.84 g (0.01 mole) of *p*-xylylidenedianil, 1.08 g (0.01 mole) of *p*-phenylenediamine, and 3.62 g (0.02 mole) of benzylideneaniline was mixed and reacted under nitrogen in a 10-ml microflask. The reaction mixture was heated slowly; initial melting of the mixture was observed at about 100°C and a completely homogeneous brown solution was obtained at 160°C. The reaction was maintained at 160°C for 2 hr before slowly raising the temperature over a period of 2 hr to 330°C. Distillation of aniline began at about 210°C and continued to 330°C to yield aniline and benzylideneaniline. The pressure of the system was then reduced to 0.4 mm Hg and distillation continued for 1 hr while heating the mass at 350°C. As distillation proceeded, the viscosity of the mixture increased and the color of the reaction product changed from brown to black. The yield of black infusible polymer, insoluble in sulfuric acid, was 2.14 g.

2. A mixture of 1.34 g (0.01 mole) of terephthaldehyde, 2.84 g (0.01 mole) of N,N'bis-benzylidene-*p*-phenylenediamine, and 3.62 g (0.02 mole) of benzylideneaniline were reacted as in the preceding experiment except that the mixture was maintained at 180°C for 3 hr before slowly raising the temperature of the reaction mass to 330°C. Benzaldehyde began to distill from the reaction mass at a temperature of about 195°C. The yield of black, infusible polymer, insoluble in sulfuric acid, was 1.96 g.

3. A mixture of 2.84 g (0.01 mole) of *p*-xylylidenedianil, 2.84 g (0.01 mole) of N,N'-bis-benzylidene-*p*-phenylenediamine, and 1.95 g (0.0125 mole) of benzylideneaniline was placed in a 10-ml microflask and refluxed at 300°C under a nitrogen atmosphere. The color of the melt changed rapidly from a light yellow to a darker yellow; no further color change occurred when the heating was extended to 2 hr. Then the benzylideneaniline was removed slowly by distillation at 150 mm Hg pressure over a period of 4 hr. As the benzylideneaniline was removed, the color of the reaction mixture changed to orange to red to brown to black. The yield of black polymer 1-BA-H300 was 1.38 g; it was slightly soluble in concentrated sulfuric acid. Samples of the various colored polymers were withdrawn at various times of reaction, from a duplicate experiment, and the ultraviolet spectra recorded of those samples soluble in dimethylacetamide.

One gram of polymer 1-BA-H300 was ground in a mortar and pestle and reintroduced into the reaction tube, and the system degassed at 1 mm Hg pressure and repressured with nitrogen. The degassing was repeated twice. Then the polymer was heated for 1 hr at 480°C under a slow stream of nitrogen and allowed to cool to room temperature. There was recovered 0.960 g of black polymer, 1-BA-H480, and, as a distillate, 0.026 g of benzylideneaniline which was identified by its infrared spectrum.

Mass Spectral Analyses. Forty milligrams (0.040 g) of polymer 1-B was placed in a special ignition–mass spectral tube and degassed at 1×10^{-6} mm for 4 hr. The tube, made of quartz, was 20 cm long and 2 cm in diameter and fitted with a vacuum stopcock to which was attached a male standard-taper 12/30 ground-glass joint. After degassing, the cock was sealed and the tube was inserted into the copper block which had been preheated to 700°C, and the contents heated at this temperature for 1 hr, then allowed to cool to room temperature. The tube was then attached directly to the spectrometer. The spectrum was recorded and the major peaks were located at $M/e = 2$, 78, 92, and 93. A small amount of yellow oil which collected in the cooler portion of the ignition–mass spectral tube was examined and determined by infrared spectroscopy to be primarily benzylideneaniline containing a smaller quantity of aniline. The weight of the polymer after heating was 0.036 g.

Postheating of Polymers. *At 600°C.* The H400 polymers (0.5 g) were first ground to a fine powder in a mortar and pestle and then placed in a quartz reaction tube similar to the reaction tubes used in the melt polymerizations. The reaction tube was degassed at 0.5 mm, then flushed with deoxygenated nitrogen; the degassing procedure was repeated three times. Then the reaction tube was inserted into the metal block, which had been preheated to 600°C, and the polymers postheated in a deoxygenated nitrogen atmosphere at 600°C for 20 min. Volatile products were collected in the receiver cooled by an acetone–dry ice mixture. The suffix H600 after the polymer number indicates that the polymer had been postheated to 600°C.

To 1176°C. The H400 polymers were first ground to a fine powder in a stainless-steel grinding capsule, and the 10-mg samples were placed in the cell of the Model 950 thermogravimetric analyzer. The samples were heated at a rate of 15°/min under a stream of deoxygenated nitrogen gas at a flow rate of 1 standard liter/min, from room temperature to a recorded 1200°C temperature which, when corrected for the nonlinearity of the Chromel-Alumel thermocouple, was 1176°C. The suffix H1176 after the polymer designation indicates that the polymer has been postheated to 1176°C. When both H600 and H1176 are used as suffixes, it indicates that the polymer was first heated at 600°C. then at 1176°C.

Spectral Analyses. 1. The infrared spectra were recorded on a Perkin-Elmer Model 137 infrared spectrophotometer using standard solution and mull techniques. A Perkin-Elmer Model 421 grating spectrophotometer was used to examine those samples prepared as potassium bromide discs.

2. The ultraviolet spectra were recorded on a Bausch and Lomb Spectronic Model 505, using solutions of the polymers in dimethylacetamide.

3. Mass spectral analyses were performed on a Consolidated Engineering Corporation Model 21-103A mass spectrophotometer.

4. Electron paramagnetic resonance spectra were obtained through the use of a Varian Model V-4500 electron paramagnetic resonance spectrometer.

Thermogravimetric Analyses. All thermogravimetric determinations and differential thermal analyses were performed on a du Pont Model 900 differential thermal analyzer in conjunction with a du Pont Model 950 thermogravimetric analyzer. The polymers were first ground in a stainless-steel vibrating grinding capsule to a fine powder whose particle size averaged about 50 pieces per milligram. Then a 10-mg sample of the ground polymer was placed in the cell of the Model 950 thermogravimetric analyzer. The samples were heated at a rate of 15°C/min in a dry nitrogen stream or in air at a gas flow rate of 1 standard liter/min, to a recorded 1200°C temperature, which, when corrected for the nonlinearity of the Chromel-Alumel thermocouple, was 1176°C.

Elemental Analyses. Elemental analyses on the monomers and polymers were performed by the Midwest Microlab, Indianapolis, Indiana; Schwarzkopf Microanalytical Laboratory, Woodside, New York; and by Micro-Analysis, Inc., Wilmington, Delaware.

DISCUSSION AND RESULTS

Solution Polymerizations

The reactions of the various diamines $Z(NH_2)_2$, with $C_6H_4(CHO)_2$, in the usual organic solvents, yielded products with varying backbone structures; the colors of these condensation products depended on the degree of conjugation and on the extent of condensation. The colors of the conjugated and pseudoconjugated products, 1-Y to 10-Y, were yellow or near yellow, such as orange-yellow or greenish yellow; this indicated their oligomeric, low molecular weight character. In contrast, the nonconjugated products, 11-Y and 12-Y, in which Z is aliphatic $-(CH_2)_{\overline{n}}$, were white in color, while the color of product 9-Y, in which Z is $-C_6H_4(CH_2)_4C_6H_4-$, was cream-yellow, indicating a close relationship to the aliphatic-type polymers while still retaining considerable aromatic character. The degree of polymerization, *n*, for polymers 11-Y and 12-Y was approximately twice that of polymers 1-Y to 10-Y; this is explained on the basis that the condensation reactions in 11-Y and 12-Y proceed under conditions of a homogeneous solution, while in the case of 1-Y to 10-Y, the growing chains were insoluble in the medium and precipitated at an early stage of reaction, thereby retarding further chain growth. Further support for this assumption was found in the observation that extended heating of the isolated dry 1-Y to 10-Y polymers at 250°C did not result in noticeable increases in chain length.

The continuous azeotropic method appeared, when the reaction time was extended for periods as long as 20 hr, to yield oligomeric products of slightly higher molecular weight, $\bar{n} = 4$, than the regular solution method, which yielded oligomers in which $\bar{n} = 2$. These oligomers, although insoluble in such common solvents as ethyl alcohol, benzene, toluene, dimethylformamide, dimethylacetamide, etc., were soluble in formic acid, acetic acid, acetic anhydride, saturated aqueous sodium bisulfite, and sulfuric acid. However, these solutions were not true solutions of the polymers but solutions of derivatives, as was evidenced by a number of changes in the polymers. When a yellow oligomer was dissolved in the bisulfite solution, the brilliant yellow color disappeared; the solution became colorless and remained colorless even after acidification with sulfuric acid. Obviously, conjugation was either lost or sufficiently decreased or interrupted, thereby destroying the chromophores. The addition of bisulfite to monomeric Schiff bases has been reported (*39–45*) to yield sulfonic derivatives,

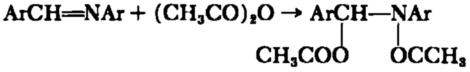
$$ArCH{=}NAr + NaHSO_3 \rightarrow \underset{\displaystyle SO_3Na}{ArCH}{-}NHAr \qquad (4)$$

The infrared spectrum of the bisulfite addition product of the polymer, 1-Y, showed the loss of the —C=N— band at 1612 cm^{-1}. The solubility of the yellow polymers in formic acid, acetic anhydride, and sulfuric acid can also be attributed to derivative formation.

In the Wallach reaction (*46*) of an aldehyde with an amine in formic acid, a Schiff base is obtained (*47*) as an intermediate, which then is reduced by formic acid, to yield (*48,49*) a substituted amine:

$$\mathrm{ArCH{=}NAr + HCOOH \rightarrow \underset{\underset{\displaystyle HCOO}{|}}{ArCH}NHAr \rightarrow ArCH_2NHAr + CO_2} \qquad (5)$$

When the yellow polymer was dissolved in formic acid, the yellow color and the infrared adsorption band at 1612 cm^{-1} disappeared, indicating that a similar reaction had occurred. Acetic acid is not a reducing agent and reduction to the substituted amine did not occur; it was a poorer solvent than formic acid, and in the absence of sulfuric acid causes only a slight reduction in color as the consequence of incomplete acylation. Solubilization in acetic anhydride can also be attributed to derivative formation, since monomeric Schiff bases react with it (*50,51*):



$$\mathrm{ArCH{=}NAr + (CH_3CO)_2O \rightarrow \underset{\underset{\displaystyle CH_3COO}{|}}{ArCH}{-}\underset{\underset{\displaystyle OCCH_3}{|}}{NAr}} \qquad (6)$$

The dissolution of the yellow polymer in sulfuric acid is attributed to salt formation which is more stable than the free base (52):

$$\mathrm{ArCH{=}NAr + \tfrac{1}{2}H_2SO_4 \rightarrow ArCH{=}NAr{\cdot}\tfrac{1}{2}H_2SO_4} \qquad (7)$$

The intrinsic viscosities of the yellow polymers were readily measured in concentrated sulfuric acid. The solutions of the polymers in sulfuric acid were yellow at first, and on standing gradually became darker in color. This was due to the continued intermolecular condensation between terminal —NH_2 and —CHO groups of the oligomers. The intrinsic viscosity at 25°C for 1-Y in 95.3% sulfuric acid, when measured within 10 min after it was placed in solution, was approximately 0.05, dl/g at 25°C, and on standing for 48 hr it became 0.16. This same behavior was observed when *p*-phenylenediamine and terephthaldehyde were condensed directly in concentrated sulfuric acid. When these reactants were added to 95.3% sulfuric acid, a yellow solution of the polymer, of intrinsic viscosity 0.06, was obtained. During the course of 5 days the color of the sulfuric acid solution, which was allowed to stand at room temperature, changed gradually and progressively to dark yellow to yellow-brown to dark brown. The intrinsic viscosity of the polymer at the soluble dark-brown stage was 0.36. After 8 days of standing at room temperature, some dark-brown polymer precipitated from the reaction mixture; it was isolated and found to be soluble in 95.3% sulfuric acid and had an intrinsic viscosity of 0.41 at 25°C.

The failure of the diamine-dialdehyde condensations in solution to produce black polymers led to investigating alternative syntheses using exchange reactions. The aldehyde exchange reaction of Eq. (1), the amine exchange reaction of Eq. (2) and the bis exchange reaction of Eq. (3) were first evaluated in common organic solvents such as benzene, toluene, tetralin, dimethylacetamide, etc., and the expected reactions failed to occur. However, when the reaction was catalyzed by *p*-toluenesulfonic acid or zinc chloride, yellow polymers were obtained from those systems containing the lower boiling solvents, such as benzene (b.p. 80.1°C) and orange polymers in those systems containing the higher boiling solvents, such as in tetralin (b.p. 207.2°C). These results appear to lend some substance to the conclusion that solubility seems to be a factor that exerts at least some control on the molecular weight of the polymer in solution polymerizations to the extent that chain extension is effectively restricted by the insolubility of the polymer in the solvent-polymer system. This appears to explain why black polymers were not obtained in exchange reactions even when higher boiling solvents were used. Thus, since the low molecular weight polymer is only slightly soluble in boiling tetralin, only a minor, not a major, increase in molecular weight was obtained when the higher boiling tetralin was used instead of benzene or toluene as the reaction medium.

The oligomers obtained by bis-Schiff base exchange reactions in solution differed significantly, however, from the low molecular weight polymers produced from the diamines and dialdehydes in solution. When these polymers were heated to 250–300°C, they melted first, then underwent changes in color and could be converted to dark, higher molecular weight products by continued heating at higher temperatures. In contrast, the yellow oligomers prepared from the diamine and dialdehydes in solution, such as 1-Y to 10-Y, did not melt or react significantly when heated to

300°C, and the heated products were not black but retained their yellow color.

The bis-Schiff base exchange polymerizations were shown to occur even at low temperatures when catalyzed by zinc chloride or toluenesulfonic acid. The facility with which this reaction proceeds is surprising, as is the property of the resulting oligomers of being capable of being polymerized further to black polymers. Bis-Schiff base exchange solution polymers, then, yielded low molecular weight polymers with reactive end groups derived from the reactants, which could end-couple, when melted, to yield higher molecular weight products.

In general, it may be concluded that the ordinary solution methods are not suited for the direct preparation of high molecular weight polymeric Schiff bases either from aromatic diamines and dialdehydes or from their appropriate derivatives amenable to exchange reactions.

Melt Polymerizations

To ascertain whether or not the syntheses of black polymeric Schiff bases could ever be achieved by any method, an equimolar mixture of *p*-phenylenediamine and terephthaldehyde was heated in the absence of solvent. When heated slowly, the mixture became pasty and did not form a clear melt. Continued condensation at 300°C produced a brown, porous polymer which was soluble in formic acid and had an intrinsic viscosity of 0.16 in sulfuric acid at 25°C. In contrast, when the mixture of these reagents was heated very rapidly, it formed a fluid melt at about 160°C, changing in color within a few minutes from yellow to orange to brown to black. Continued heating at 260°C for 1 hr produced a black, spongy polymer which was insoluble in benzylideneaniline and in formic and sulfuric acids; it did not melt in a nitrogen atmosphere at temperatures up to 1000°C. However, when the polymer was heated for extended periods of time in refluxing benzylideneaniline (b.p. 310°C), a homogeneous black solution was obtained.

Similar behaviors were observed when the amine exchange polymerizations were conducted as melt reactions. Black polymers were obtained only when the mixture was heated rapidly, and in this regard the amine exchange appears to be almost as rapid as the diamine-dialdehyde melt reaction. These reactions appear to be accelerated at the temperatures used by the presence of amine structures. This assumption is based on the fact that the aldehyde exchange reaction was much more moderated than the amine exchange reaction, producing the more extended, highly conjugated red-brown polymers, which were also soluble in formic and sulfuric acids. The aldehyde exchange reaction was highly accelerated, also, by the addition of catalytic amounts of zinc chloride.

The bis exchange polymerization reaction was found to be the most highly moderated and best controlled reaction among those reported in this study. It proceeded in the absence of additives but was accelerated by Lewis acid–type catalysts.

The bis-Schiff base exchange reaction differed from the amine and aldehyde exchanges in that benzylideneaniline was eliminated as the by-product of the reaction, whereas aniline and benzaldehyde, respectively, were eliminated in the first two reactions. Since benzylideneaniline is a monomeric Schiff base, which is physically and chemically related to the resulting polymer, it could be presumed that it was acting as a solvent in the reaction. The function of the benzylideneaniline appeared to be that of a solvent, which, by solvating the growing polymer chains, retained the growing chains in solution, thereby enabling them to propagate to higher molecular weights. This assumption, in addition to the fact that all the solution polymers, as well as the melt fusion polymer I-RP, could be dissolved in benzylideneaniline, led to its evaluation as a solvent for the amine and the aldehyde exchange reactions. It was also recognized that the effect of benzylideneaniline might not be due solely or entirely to its solvent properties. In systems containing free —NH_2 or —CHO moieties, benzylideneaniline could, at the temperature used, function as a reactant (*31*) as well as a solvent.

The amine and aldehyde exchange reactions were found to be well moderated and controlled when performed in benzylideneaniline; these reactions yielded black polymers free of terminal amine and aldehyde structures but they did contain terminal $C_6H_5N=$ and $C_6H_5CH=$ groups, respectively, as a result of exchange reactions with the benzylideneaniline. Thus these reactions in benzylideneaniline became equivalent or identical to a bis-Schiff base exchange reaction. That such exchange reactions did occur was established in the following way. When the low molecular weight solution polymers, such as 1-Y, or the melt amine exchange or aldehyde exchange polymers were dissolved and heated

(53) in $p\text{-}\mathrm{ClC_6H_4N{=}CHC_6H_4Cl}\text{-}p$ or $\mathrm{FC_6H_4N{=}CHC_6H_4F}$, terminal end groups, $\mathrm{XC_6H_4}$—, were found in polymers isolated from the reaction. The observations made on the reactions, in which benzylideneaniline was involved, led to alternative methods of syntheses which are the subject of a separate communication (54). Accordingly, the bis exchange reaction was selected as the preferred method of synthesis, and the polymers so prepared were compared with comparable polymers made by solution techniques.

The bis exchange reaction of Eq. (3) was shown to be an equilibrium reaction. When equivalent quantities of two complementary Schiff bases were reacted and the by-product, benzylideneaniline, retained in the reaction mixture, the color of the mixture changed gradually from an initial yellow to a very dark brown or black, and the mixture remained fluid at the reaction temperature until the by-product, benzylideneaniline, was removed. When the same polymerization was performed in the presence of benzylideneaniline, initially added to the mixture, the reaction advanced to the yellow-colored condensation stage and the color remained unchanged on extended reaction, even at 300°C, until the benzylideneaniline was removed by distillation. As the benzylideneaniline was removed, the color of the reaction product darkened eventually, leaving a solid black polymer. A similar behavior was observed for the polymers prepared by the amine and the aldehyde exchanges performed in benzylideneaniline. After the solid black polymer was reached, further heating converted the brittle polymer to a tough polymer by continued polymerization in the solid state. Throughout the course of these polymerizations, the reaction mixture remained homogeneous; the end groups on the polymer appeared to play some role in maintaining this homogeneity. This was evident when the complementary monomer pairs used (53) contained halogen substitution in their terminal structure:

$$\begin{aligned}&n\,p\text{-}\mathrm{ClC_6H_4N{=}HCC_6H_4CH{=}NC_6H_4Cl}\text{-}p\\&\quad+n\,p\text{-}\mathrm{ClC_6H_4CH{=}NC_6H_4N{=}HCC_6H_4Cl}\text{-}p\rightarrow\\&\qquad p\text{-}\mathrm{ClH_4C_6N{=}\!\left[HCC_6H_4CH{=}NC_6H_4N\right]_{n}\!{=}HCC_6H_4Cl}\text{-}p\\&\qquad\qquad+n\,p\text{-}\mathrm{ClC_6H_4{=}NC_6H_4Cl}\text{-}p\end{aligned}\tag{8}$$

$$\begin{aligned}&n\,p\text{-}\mathrm{FC_6H_4N{=}HCC_6H_4CH{=}NC_6H_4F}\text{-}p+n\,p\text{-}\mathrm{FC_6H_4CH{=}NC_6H_4N{=}HCC_6H_4F}\text{-}p\rightarrow\\&p\text{-}\mathrm{FC_6H_4N{=}\!\left[HCC_6H_4CH{=}NC_6H_4N\right]_{n}\!{=}HCC_6H_4F}\text{-}p+n\,p\text{-}\mathrm{FC_6H_4CH{=}NC_6H_4F}\text{-}p\end{aligned}\tag{9}$$

$$\begin{aligned}&n\mathrm{F_5C_6N{=}HCC_6H_4CH{=}NC_6H_5}+n\mathrm{F_5C_6CH{=}NC_6H_4N{=}HCC_6H_5}\rightarrow\\&\qquad\mathrm{F_5C_6N{=}\!\left[HCC_6H_4CH{=}NC_6H_4N\right]_{n}\!{=}HCC_6H_5}+n\mathrm{F_5C_6CH{=}NC_6F_5}\end{aligned}\tag{10}$$

The p-Cl and p-F terminally substituted polymers were much more soluble in $XC_6H_4CH{=}NC_6H_4X$ than their unsubstituted counterparts were in $C_6H_5CH{=}NC_6H_5$; and the pentafluoro terminally substituted polymers were even more soluble in $F_5C_6CH{=}NC_6F_5$ than the corresponding monofluoro-substituted polymers were in $FC_6H_4CH{=}NC_6H_4F$.

Infrared Spectral Studies

Infrared absorption spectroscopy was used to elucidate the structure of the polymers. Prominent bands were assigned by studying the spectra of model compounds and of the low molecular weight polymers. The region of 3380 cm^{-1} was assigned to the aromatic $—NH_2$ group on the basis of the spectra of aniline, *p*-phenylenediamine, *m*-phenylenediamine, and *p,p'*-diaminodiphenyl oxide. The band at 1700 cm^{-1} was assigned to the —CHO function from the spectra of benzaldehyde, terephthaldehyde, and *p*-methoxybenzaldehyde.

The carbon-nitrogen double-bond stretching absorption is usually placed at about 1630 cm^{-1} in various azomethine compounds (55). This bond was found to absorb at 1628 cm^{-1} in benzylideneaniline (Fig. 1), shifting to 1615 cm^{-1}, in N,N'-bisbenzylidene-*p*-phenylenediamine (Fig. 2), to 1614 cm^{-1} in *p*-xylylidenedianil (Fig. 3), and to 1612 cm^{-1} in the yellow solution polymer, 1-Y (Fig. 4), and to 1597 cm^{-1} in the black bis exchange polymer, 1-B (Fig. 5).

In the fingerprint region, two bands corresponding to 1,4 aromatic disubstitution were found at 1006 cm^{-1} and 825 cm^{-1}. Monosubstituted aromatic absorptions occur at 755 cm^{-1} and 690 cm^{-1} and are observed in Fig. 5 but not in Fig. 4. This difference is attributed to phenyl end groups of $C_6H_5—$ in the polymer which exist as a result of the bis exchange reaction. The characteristic bands in the two regions of 1500 cm^{-1} to 1600 cm^{-1} and in the fingerprint region of 1000 cm^{-1} to 600 cm^{-1} were particularly useful in characterizing the polymers and were observed in all the conjugated and pseudoconjugated polymers prepared.

Postheating

The Schiff base polymers, synthesized under the selected standardized polymerization conditions, were condensed to a maximum temperature of 400°C. Preliminary thermogravimetric analyses in nitrogen of 1-B which had been condensed to 400°C indicated that

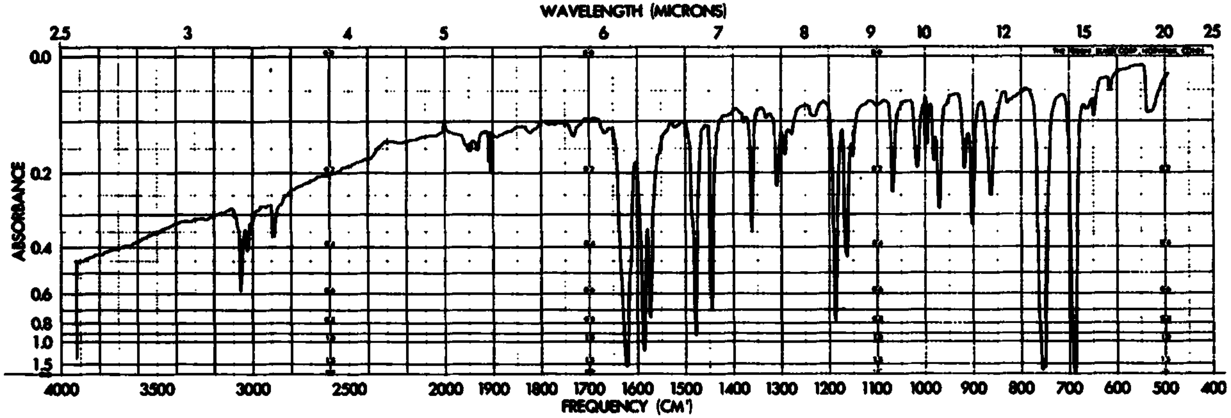


FIG. 1. Benzylideneaniline. KBr disc.

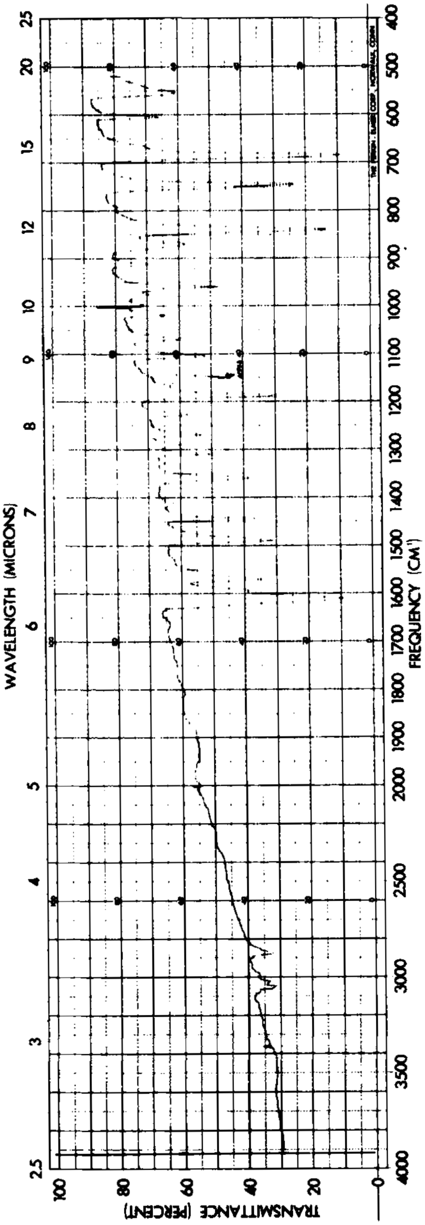


FIG. 2. N,N'-bisbenzylidene-*p*-phenylenediamine. KBr disc.

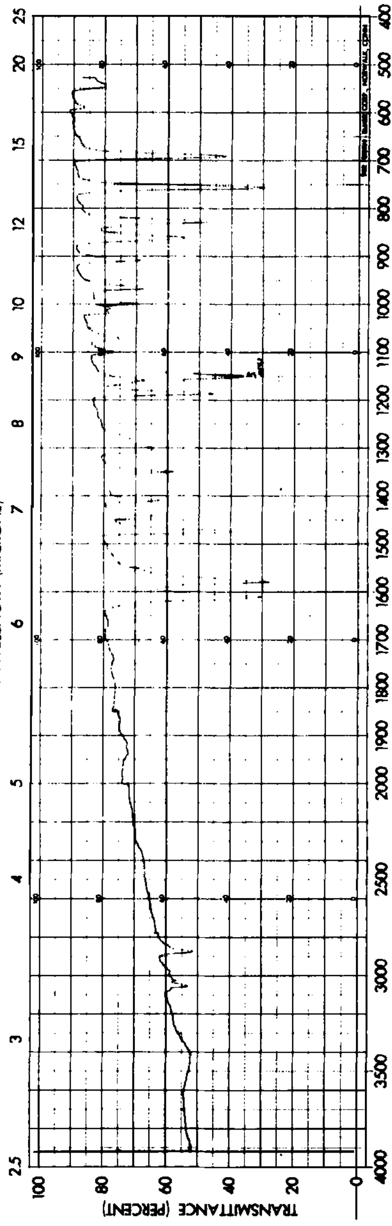


FIG. 3. *p*-Xylylidenedianil. KBr disc.

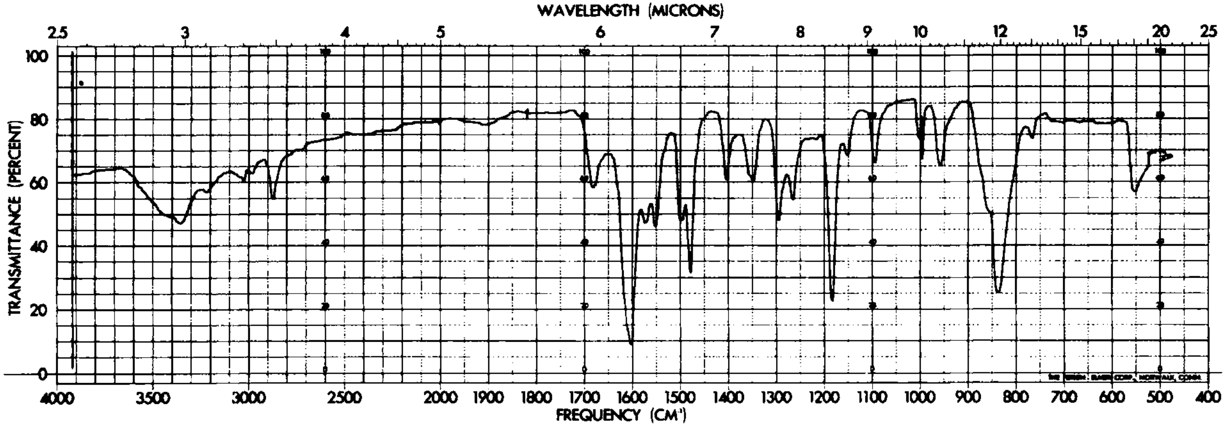
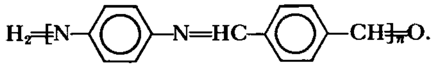


FIG. 4. Yellow solution polymer 1-Y,



. KBr disc.

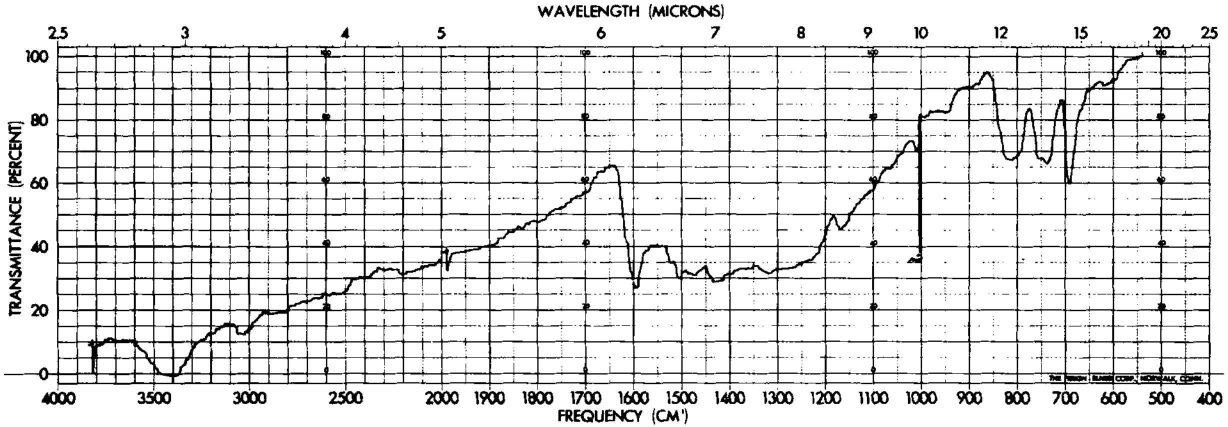
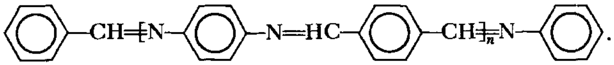


FIG. 5. Black bis-Schiff base exchange polymer 1-B-400,



KBr disc.

although the polymer exhibited good thermal stability, the thermogram showed a definite weight loss, which began at about 600°C and leveled off at about 800°C. Since benzylidene was identified as the elimination product, the weight loss was attributed to continued polycondensation. The incompleteness of the precondensation was verified by collecting a larger amount of benzylideneaniline when 1-B was resynthesized and condensed directly to a temperature of 480°C instead of 400°C. The thermogram of this 480°C polymer also showed a weight loss which began at about 600°C, which also leveled off at about 800°C, but the weight loss was much less than found for the polymer prepared at 400°C. The infrared spectra of both of these polymers were substantially identical, except that the bands decreased in intensity and broadened, as would be expected if chain-end coupling had occurred and led to an extension of chain length. These observations suggested that an evaluation should be made of polymers which had been prepared to condensation temperatures in the region of 600°C as well as to some temperature in excess of 800°C, preferably in the region 1000 to 1200°C. These were designated H400, H600, and H1200 polymers.

To minimize the introduction, on the synthesis, of unpredictable variables, such as result from differences in stoichiometry that can occur in weighing, control of inert atmosphere, heating rates, etc., if the H400, H600, and H1200 polymers were performed in three separate syntheses, the H400 polymers were synthesized first; then aliquot parts of this polymer were subjected to postheating to the desired temperature. The postheatings to 600°C were performed for 20 min in quartz reactor tubes similar in design, dimensions, and accessories to those used in the 400°C polymerization. Additional quantities of benzylideneaniline were collected during the 600°C heating. The apparatus used for postheating the polymers to 600°C was not suitable for postheating the polymers to higher temperatures. The du Pont Model 950 thermogravimetric apparatus was used for this purpose by placing the polymer sample on the platinum pan of the thermogravimetric analysis cell at room temperature, and heating the polymer under a slow stream of deoxygenated nitrogen to the desired temperature. The furnace and the sample were allowed to cool to room temperature in the nitrogen atmosphere before the sample was removed.

The infrared spectra of a series of polymer samples, 1-B-H400, postheated to 600, 700, 800, 1000, and 1200°C show that the bands generally broadened and decreased in intensity as the polymers were subjected to increasingly higher temperatures. After heating to 800°C, the bands are only poorly distinguishable from instrument background noise. The infrared spectra of polymers 1-B-H600 and 1-B-H700 are shown in Figs. 6 and 7, respectively. The spectrum of the 1-B-H700 polymer showed no shift in the positions of the carbon-nitrogen double-bond absorption. Substantial differences, however, were found in the fingerprint region of the spectrum of the 1-B-H700 polymer; the bands at 690 cm^{-1} and 1006 cm^{-1} decreased in intensity, the band at 750 cm^{-1} increased in intensity, the band at 825 cm^{-1} remained at about the same intensity, and a new band appeared at 875 cm^{-1}.

That some structural changes, in addition to further chain-end coupling, occurred as the polymer was heated to higher temperatures was evidenced by these changes in spectra. The decrease in the intensity of the 690 cm^{-1} band, assigned to monosubstituted aromatic absorption, was interpreted as showing a decrease in the concentration of end groups due to continuing chain-end coupling. Bands in the 750 cm^{-1} region have been assigned also to absorptions other than monosubstituted aromatic-type absorption. Bands in this region have also been observed for substituted benzanthrenes and other polynuclear compounds having 1,2,4-type aromatic substitution and for aromatic compounds having ortho 1,2-type aromatic substitution (56). Also, the bands absorbing in the region of 825 cm^{-1}, assigned to 1,4-type aromatic substitution, have also been assigned to a 1,2,4- or to a 1,2,3,4-type aromatic substitution and are generally ascribed to polynuclear-type compounds (57,58).

The spectral data gave evidence, then, that the black H400 polymers underwent further condensation and chain propagation when heated at higher temperatures, and that these polymers retained their Schiff base structure as written, for example, $=\!\![N{-}Z{-}N{=}HC{-}C_6H_4{-}CH]\!\!=_n$, up to about 600°C, while at a temperature of about 700°C other processes began to occur. The bands in the spectra obtained of the polymers postheated to 800°C or higher temperature were broadened and uninterpretable; it was most probable that not only has the molecular weight increased further as a result of end-chain coupling, but that the changes in the Schiff base structure, which were initiated at the lower temperature, were also

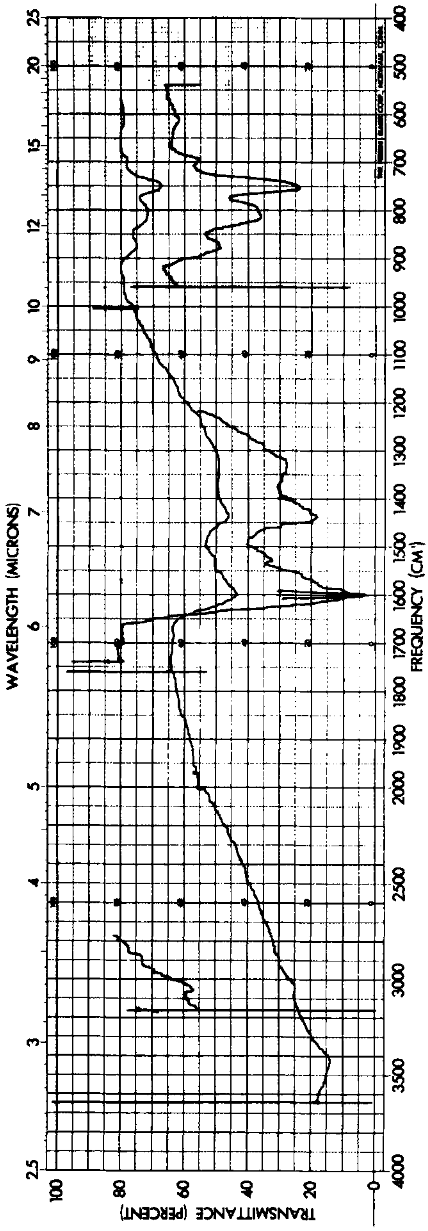


FIG. 6. Bis-Schiff base exchange polymer 1-B-H400, postheated to 600°C. KBr disc.

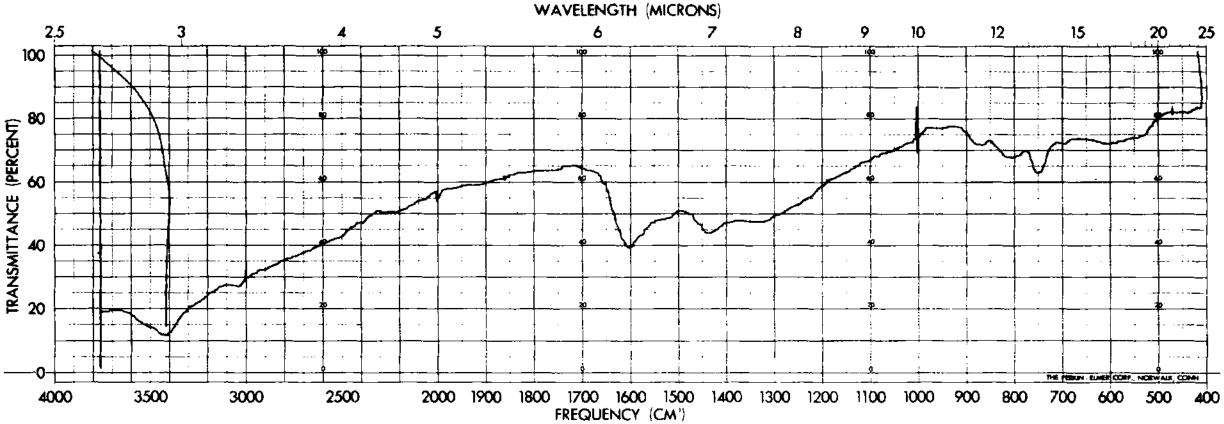
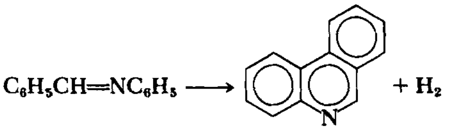


FIG. 7. Bis-Schiff base exchange polymer 1-B, postheated to 700°C. KBr disc.

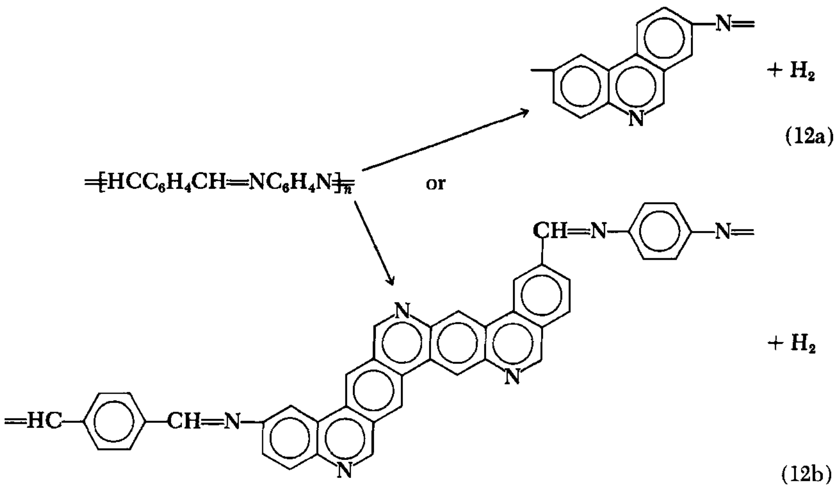
intensified. In an attempt to identify these structural changes, a mass spectral analysis was made of the products obtained after heating polymer 1-B-H400 to 700°C for 1 hr. Small amounts of benzylideneaniline and aniline were identified as sublimates in the reaction tube. Mass spectral analysis of the gases showed major peaks at $M/e = 2$, 92, and 93 corresponding to H_2, $C_6H_5CH_3$, and $C_6H_5NH_2$. Pyl had shown (59) that when benzylideneaniline was heated in an iron tube at 800°C, phenanthridine and hydrogen were obtained:



(11)

It had been reported (*60*) also that benzylideneaniline in solution was converted by ultraviolet light to phenanthridine, and, in addition, part of the benzylideneaniline was reduced to benzylaniline, $C_6H_5CH_2NHC_6H_5$. The *M/e* of 2 found in our spectrum of the products is readily explained by these reactions, as are toluene and aniline, which result from the reductive hydrogenation of benzylideneaniline by hydrogen. Values corresponding to *M/e* of 171 for benzylideneaniline, 183 for benzylaniline, and 178 for phenanthridine were not detected in the spectrum, but at higher ionization potentials, the fragments, of toluene—benzene, $M/e = 78$ and benzyl, $M/e = 91$—were observed in the spectra. These data and infrared evidence indicated that chain scission was not significant either during polymerization or postheating at relatively high temperatures, but that changes did occur, yielding new structures containing, most probably, 1,2,4- and 1,2,3,4-type substitutions.

It was considered that the changes in the spectra may have been due to the retention by the polymer of phenanthridine generated from the liberated benzylideneaniline, but at temperatures of higher than 600°C and at high rates of flow of the sweep gas over the finely divided polymer, the amount retained would be expected to be small indeed. Accordingly, by an analogy to the conversion of benzylideneaniline to phenanthridine, segments of the Schiff base polymer apparently condensed to produce some aromatic carbocyclic-heterocyclic structures in the polymer which are either phenanthridines [Eq. (12a)] or derived phenanthrolines [Eq. (12b)]:

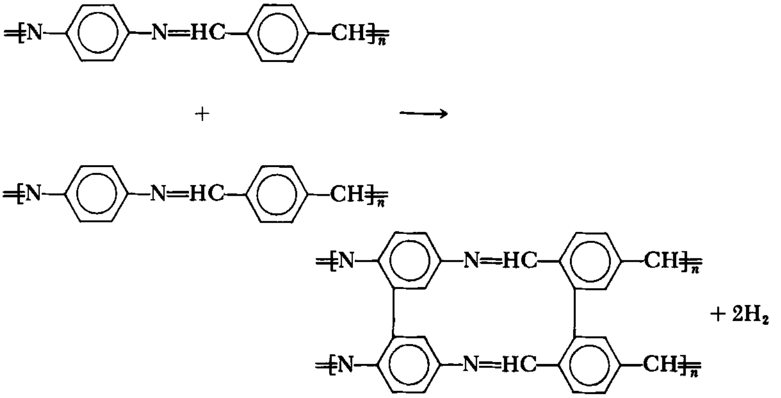


(12a)

(12b)

It seemed reasonable to assume that if carbocyclic-heterocyclic structures were formed at 700°C, greater portions of the polymer segments would also condense to a ladder-type structure as the temperature was increased to even higher temperatures. The process is an intramolecular one and Bruck (*61*) observed this type of intramolecular rearrangement during the vacuum pyrolysis of aromatic polypyromellitimides. The presence of hydrogen in the mass spectrum led to the consideration of other processes which could produce hydrogen.

The presence of hydrogen could be explained as arising from processes, such as by the formation of cross-links by interaction between chains, for example:



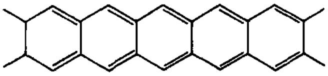
(13)

In addition, the phenanthradine-type structures could have been the products of an intermolecular process involving Schiff base segments of the polymer and a quantity of retained or liberated benzylideneaniline, which, in the H600 polymers, is small indeed. Intra- and interreactions of this kind which show carbocyclic-heterocyclic structures either as part of the linear chain or as branches appended to the linear chain or as cross-links between chains can all be written as alternative structures; but such interpretations would be unprecise, because an unequivocal selection could not be made from the broadened bands present in their infrared spectra. The insolubility of these polymers, even in benzylideneaniline–$ZnCl_2$ mixtures, precluded depolymerizing them and investigating the depolymerized polymers. The intermolecular coupling of AA-type chain ends would also be considered as another source of hydrogen, involving the formation of a biphenyl linkage by analogy to the synthesis of biphenyl from benzene:

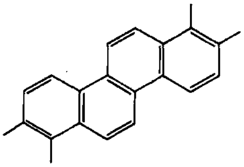
$$2C_6H_5CH{=}\!\!\left[NC_6H_4N{=}HCC_6H_4CH\right]_{n}\!\!{=}NC_6H_5 \rightarrow$$
$$C_6H_5CH{=}\!\!\left[NC_6H_4N{=}HCC_6H_4CH\right]_{n}\!\!{=}NC_6H_4C_6H_4N{=}\!\!\left[HCC_6H_4CH{=}NC_6H_4N\right]_{n}\!\!{=}H_5C_6 + H_2 \qquad (14)$$

If this reaction were the *sole* reaction, the resulting polymer would be capable of being "redissolved" in benzylideneaniline–$ZnCl_2$ systems by a depolymerization mechanism. The fact that all these polymers are "insoluble" in $ZnCl_2$–benzylideneaniline tends to eliminate biphenyl formation as the dominating reaction and lends some substance to the conclusion that the major mechanism was an intramolecular formation of carbocyclic-heterocyclic structures. The thermal stability of the resulting polymers lent additional support to this conclusion.

The thermal stabilities of the linearly fused aromatic carbocyclics, the polyacenes,



and the laterally fused carbocyclics, the polyphenes,



are higher (62) than the linear, unfused carbocyclics. The same thermal stability relationship exists (*63*) in their heterocyclic nitrogen analogues. It has been predicted (63) that the thermal stability of the high molecular weight polyacenes, polyphenes, and their nitrogen analogues would appraoch the thermal stability of graphitic structures. The very marked difference in the thermal stabilities in nitrogen and in air of the H400, H600, and H1000 Schiff base polymers offers indirect evidence that the final structures in these polymers, when heated above 600°C, are those of polyphene analogues.

Thermogravimetric Analyses

The du Pont Model 950 thermogravimetric analyzer, in conjunction with a du Pont Model 900 differential thermal analyzer, was used to determine the thermal stabilities of the polymers. All measurements were standardized at a heating rate of 15°C/min in nitrogen and in air at a gas flow rate of 1 standard liter/min. A temperature correction was made in the measurements for the nonlinearity of the thermocouples. A sample weight of 10 mg which had been ground to about 50 particles per milligram was used for the measurements. A separate thermoanalytical study, in which particle size, heating rate, gas flow rate, the nature of the gas, and other parameters were evaluated, will be reported separately (*64*).

The studies reported here consisted in performing thermoanalyses in nitrogen and in air on a sufficient number of polymer samples so that their thermal stabilities could be related to the following experimental parameters:

1. The degree of polymerization as evidenced by the yellow color of the Y series of solution polymers and by the black color of the B-H400 series of Schiff base polymers synthesized by the bis exchange method.

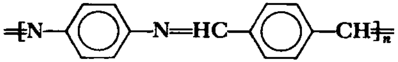
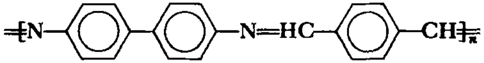
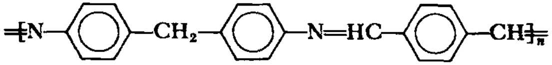
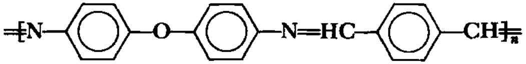
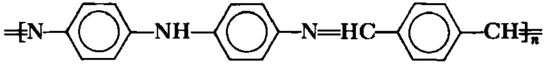
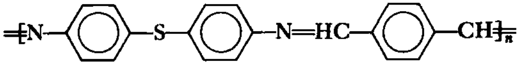
2. The nature and extent of conjugation by comparing the polymers containing the aliphatic Z groups, $-(CH_2)_{n}-$, with those containing the various conjugated and pseudoconjugated aromatic Z groups.

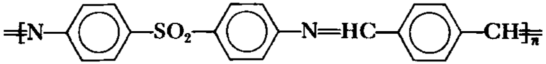
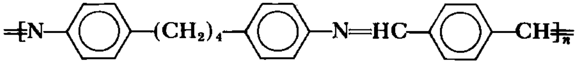
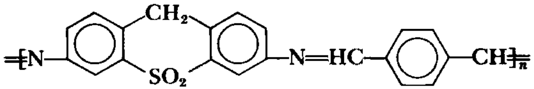
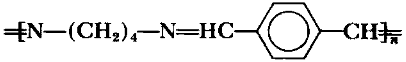
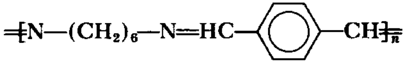
3. The maximum final temperature of condensation by comparing the black polymers of the B-H400 series polymers with those of the B-H600 series and the B-H1176 series.

Table 9 summarizes the thermogravimetric data obtained when the polymers 1-Y to 10-Y and the black 1-B-H400 to 10-B-H400 poly-

TABLE 9

Per Cent Weight Loss of the B-H400 and the Y Series of Polymers at Various Temperatures While Being Heated in Nitrogen

Polymer designation	Per cent weight loss at °C											Inflection point, °C
	200	300	400	500	600	700	800	900	1000	1100	1176	
												
1-B-H400	0.0	0.0	0.2	0.8	3.6	8.0	12.0	13.6	14.4	16.4	20.4	550
1-Y	2.4	5.4	7.4	24.4	61.4	66.8	66.8	70.6	72.0[a]	—	—	450
												
2-B-H400	0.0	0.0	0.4	2.4	44.8	50.6	53.0	54.4	55.0	—	—	530
2-Y	0.0	54.0	68.0	69.9	88.0	89.2	90.0	—	—	—	—	245
												
3-B-H400	0.0	0.4	4.2	7.0	24.6	32.0	35.2	36.6	37.6[a]	—	—	503
3-Y	0.0	0.0	0.4	41.0	64.6	67.6	68.4	70.6	71.6[a]	—	—	460
												
4-B-H400	0.0	0.2	0.5	2.0	15.4	24.0	25.4	27.4	28.6	31.6	34.4	525
4-Y	0.0	4.6	39.0	65.0	73.0	—	—	—	—	—	—	400
												
5-B-H400	0.0	0.8	1.2	3.2	16.4	23.0	25.6	27.0	28.8	32.0	35.4	520
5-Y	2.0	6.4	8.0	45.8	63.0	69.4	—	—	—	—	—	460
												
6-B-H400	0.0	0.0	0.6	2.4	12.6	22.2	26.4	28.4	30.0	32.4	35.0	522
6-Y	0.0	0.6	1.4	9.0	48.0	54.8	58.0	59.6	61.0[a]	—	—	590

												
7-B-H400	0.0	0.0	0.2	2.2	11.6	17.6	21.2	22.6	24.6[a]	—	—	525
7-Y	0.6	6.6	9.0	25.0	61.0	65.0	66.4	67.2	69.6[a]	—	—	
												
8-B-H400	0.0	0.0	4.0	11.3	42.1	47.0	54.8	57.6	61.6	—	—	420
8-Y	0.0	46.8	67.4	71.0	85.5	88.3	89.4	91.0	—	—	—	328
												
9-B-H400	0.0	0.0	0.3	1.1	6.9	23.5	32.2	34.7	36.8	—	—	535
9-Y	0.0	0.0	0.0	2.1	44.2	69.8	70.2	71.6	73.8	74.2	—	450
												
10-B-H400	0.0	0.6	0.8	1.4	13.5	15.0	19.2	22.4	28.6[a]	—	—	500
10-Y	0.8	2.0	6.0	17.2	37.0	44.4	50.0	52.0	52.4[a]	—	—	400
												
11-B-H250	0.6	2.0	18.0	60.0	71.0	84.0	85.4	—	—	—	—	320
11-Y	0.8	19.0	31.0	49.0	56.6	59.6	61.2	—	—	—	—	235
												
12-B-H250	0.6	2.4	16.0	51.6	68.4	71.0	72.6	73.0	—	—	—	300
12-Y	0.8	8.0	20.4	62.0	72.8	74.2	74.8	—	—	—	—	275

---

[a] When the measurement was made on a scale of 100°C/in., the maximum temperature recorded was 1000°C.

mers were heated in nitrogen to the limit of the apparatus, 1176°C. It also contrasts the behavior of the aliphatic polymers, 11-Y and 12-Y, prepared in solution, with the corresponding 11-B and 12-B polymers prepared by bis exchange reactions. The data obtained from these numerous thermograms have been consolidated and are shown in Figs. 8 to 10. Figure 8 shows the range of thermal stabilities in nitrogen found for polymers 1-B-H400 to 10-B-H400; the dotted line in the figure is the value found for the black polymer 1-B-RP-H400 prepared by the rapid heating of *p*-phenylenediamine and terephthaldehyde. The comparable consolidated thermogram for the polymers 1-Y to 10-Y inclusive is given in Fig. 9 and for polymers 11-B, 12-B, 11-Y, and 12-Y is given in Fig. 10.

Table 10 summarizes the thermogravimetric data when polymers 1-B-H400 to 10-B-H400, 11-B, 12-B, and 1-Y to 12-Y are thermoanalyzed in air instead of in nitrogen, and the consolidated thermograms are given in Figs. 11 and 12. Since there was no substantial difference in behavior of polymers 11-Y and 12-Y when heated in nitrogen or in air, the thermograms for their thermoanalysis in air have not been included and are identical to those shown for nitrogen in Fig. 10.

Table 11 summarizes the thermogravimetric data of three B-H600 polymers when heated in nitrogen and in air, respectively, and their related thermograms are shown in Fig. 13.

Tables 12 and 13 summarize the data obtained when the B-H1176 polymers were heated in nitrogen and in air, respectively, for which the consolidated thermograms are given in Fig. 14.

Figure 15 compares the behavior of 1-B-H1176 in nitrogen and in air with that of pyrolytic graphite. The determination of whether or not these polymers which have been postheated to 1176°C are identical to graphite is treated in another communication (*64*).

A number of conclusions can be drawn from the thermogravimetric data given above. The data are best interpreted by (1) contrasting the data obtained from the Y series of polymers prepared in solution with those obtained from the Y series synthesized by the bisexchange technique and (2) comparing the data obtained from the B-H400, B-H600, and B-H1176 series of polymers.

Contrast of the Thermal Properties of the Polymers 1-B-H400 to 10-B-H400 and 11-B-H250 to 12-B-H250 with the Polymers 1-Y to 12-Y Series.

1. The data showed definitely that the condensations in the 1-B-H400 to 10-B-H400 polymers were not completed when they were

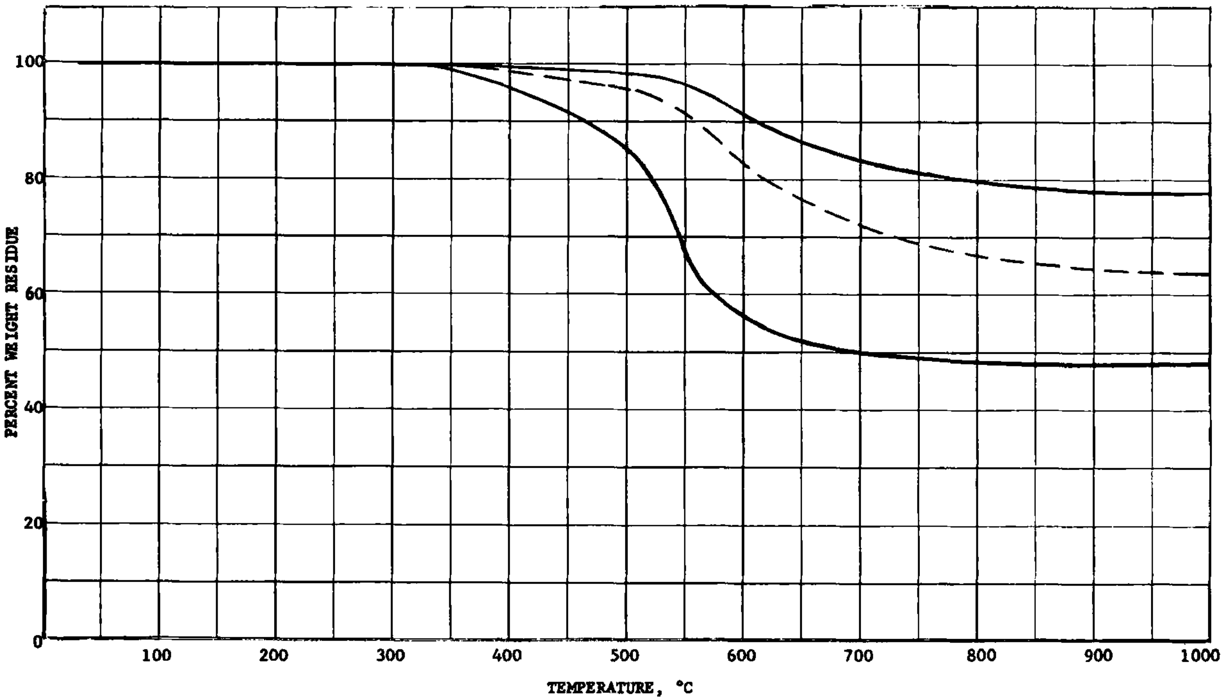


FIG. 8. Range of thermal stabilities in nitrogen for polymers 1-B-H400 to 10-B-H400 inclusive. Broken line is for polymer 1-B-RP-400.

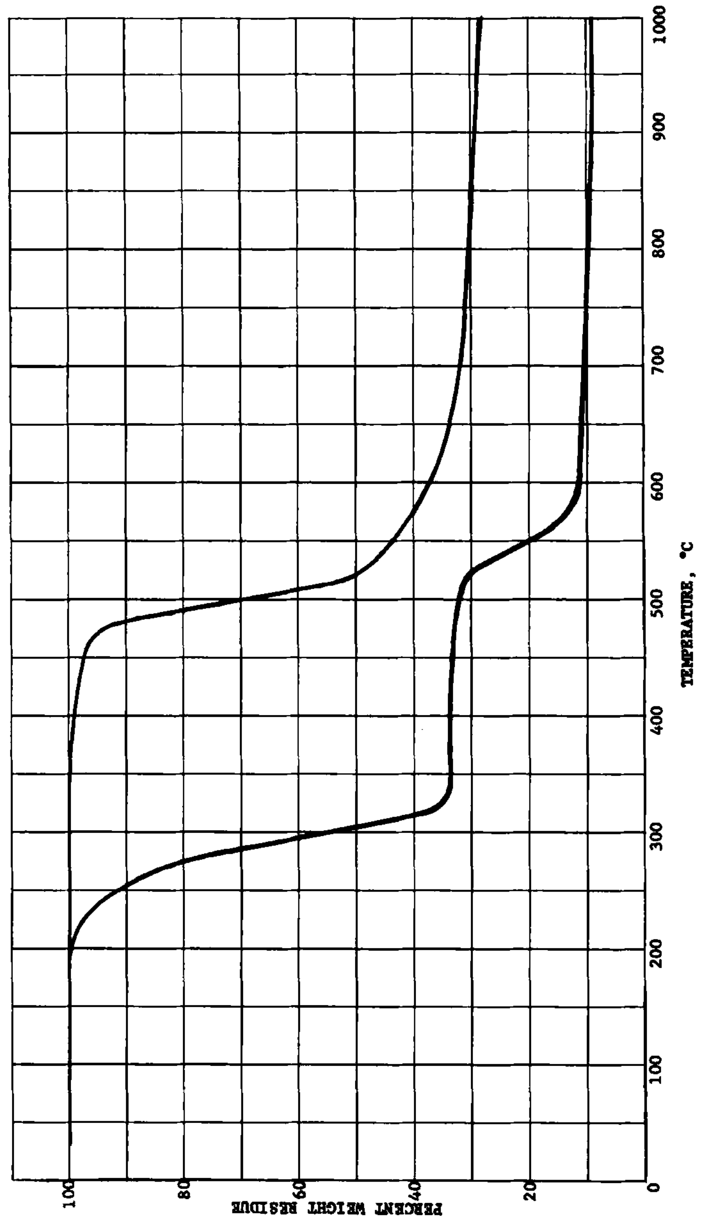


FIG. 9. Range of thermal stabilities in nitrogen for polymers 1-Y to 10-Y inclusive.

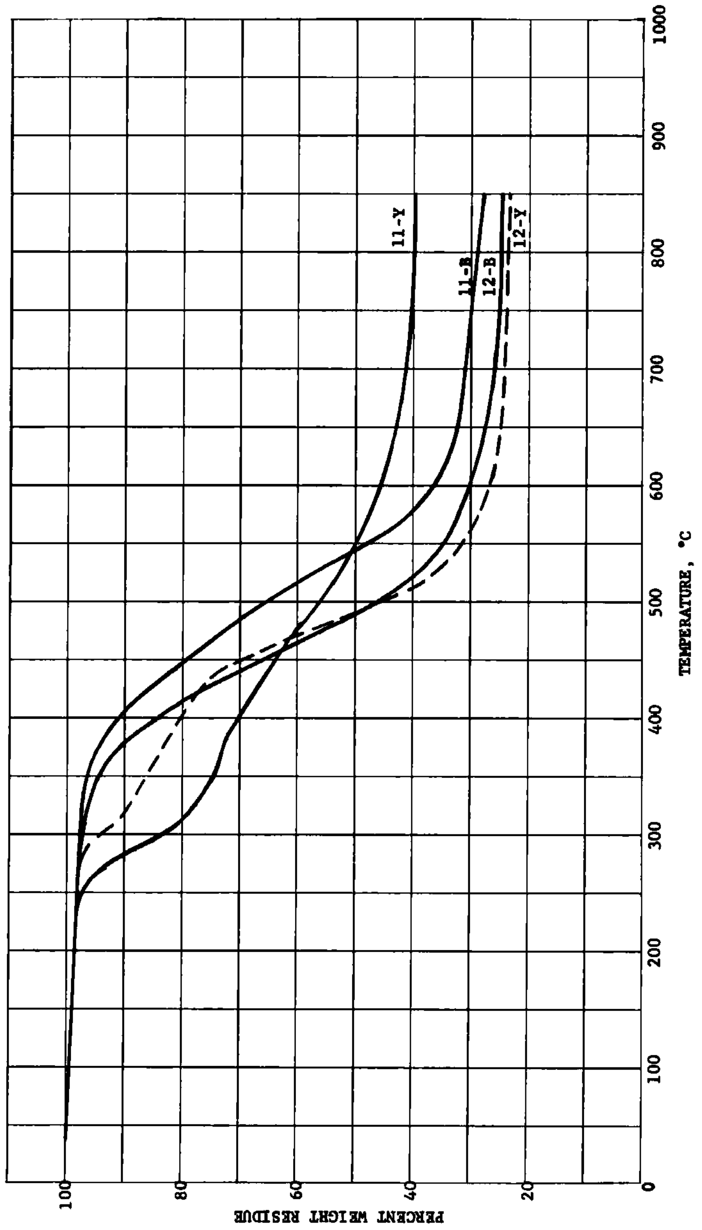
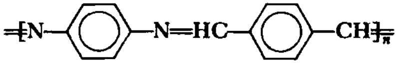
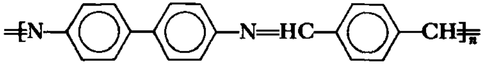
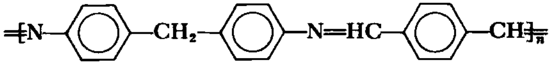
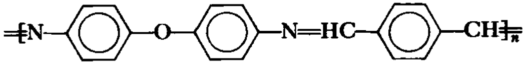
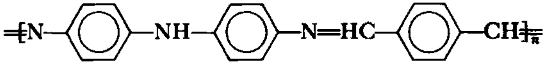
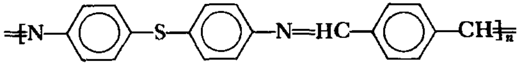
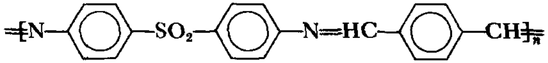
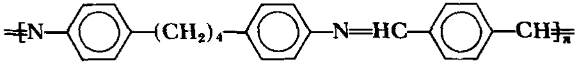
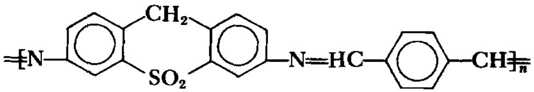
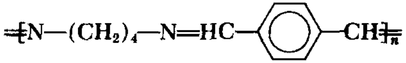
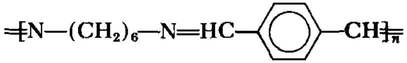


FIG. 10. Thermogravimetric analyses in nitrogen of polymers 11-B, 12-B, 11-Y, and 12-Y.

TABLE 10

Per Cent Weight Loss of B-H400 and Y Series of Polymers at Various Temperatures While Being Heated in Air

Polymer designation	Per cent weight loss at °C						Inflection point, °C
	200	300	400	500	600	700	
							
1-B-H400	0.0	0.0	0.0	3.2	69.0	100.0	480
1-Y	1.6	4.0	6.0	75.6	100.0	—	420
							
2-B-H400	0.0	0.0	0.6	16.6	96.8	100.0	440
2-Y	1.6	58.4	59.0	95.0	100.0	—	232
							
3-B-H400	0.0	0.0	0.0	12.6	94.0	100.0	450
3-Y	0.0	0.0	28.4	82.0	99.0	100.0	318
							
4-B-H400	0.0	0.0	0.0	5.0	70.0	100.0	475
4-Y	0.0	0.6	60.0	97.0	100.0	—	375
							
5-B-H400	1.4	1.8	2.6	54.0	100.0	—	430
5-Y	2.8	7.0	32.0	69.0	91.0	100.0	375

							
6-B-H400	0.0	0.0	0.0	6.0	83.0	100.0	475
6-Y	0.6	1.0	1.6	31.0	88.0	100.0	428
							
7-B-H400	0.0	0.0	6.4	90.4	100.0	—	475
7-Y	1.2	3.6	10.0	77.2	97.6	100.0	280
							
8-B-H400	0.0	0.0	6.8	52.7	100.0	—	350
8-Y	0.5	3.6	36.3	71.4	100.0	—	275
							
9-B-H400	0.0	0.0	0.0	6.2	86.6	100.0	435
9-Y	0.0	0.0	20.0	76.0	94.1	100.0	380
							
10-B-H400	1.2	1.2	0.8	4.6	87.0	100.0	475
10-Y	0.0	0.6	2.0	18.0	90.0	100.0	400
							
11-B-H250	2.0	6.6	22.0	34.0	92.6	100.0	250
11-Y	0.6	4.0	16.4	31.0	94.0	100.0	225
							
12-B-H250	0.4	1.6	10.0	62.6	89.6	100.0	250
12-Y	1.2	9.0	18.8	50.0	98.6	100.0	240

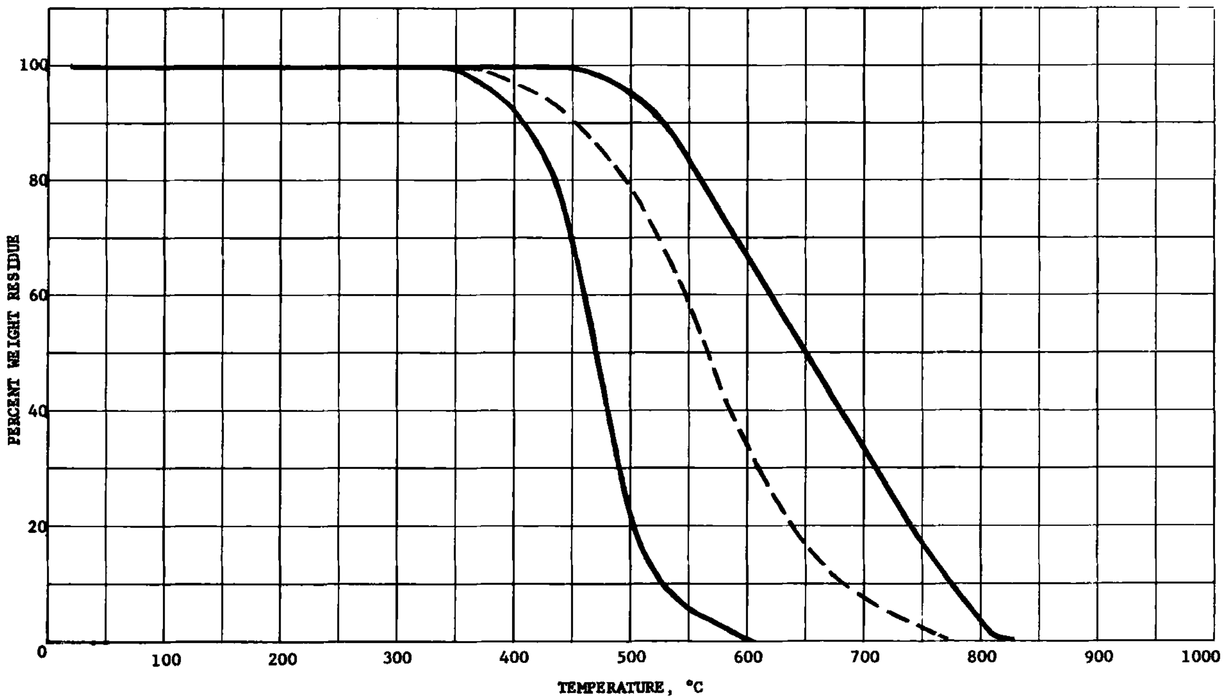


FIG. 11. Range of thermal stabilities in air for polymers 1-B-H400 to 10-B-H400 inclusive. Broken line is for polymer 1-B-RP-400.

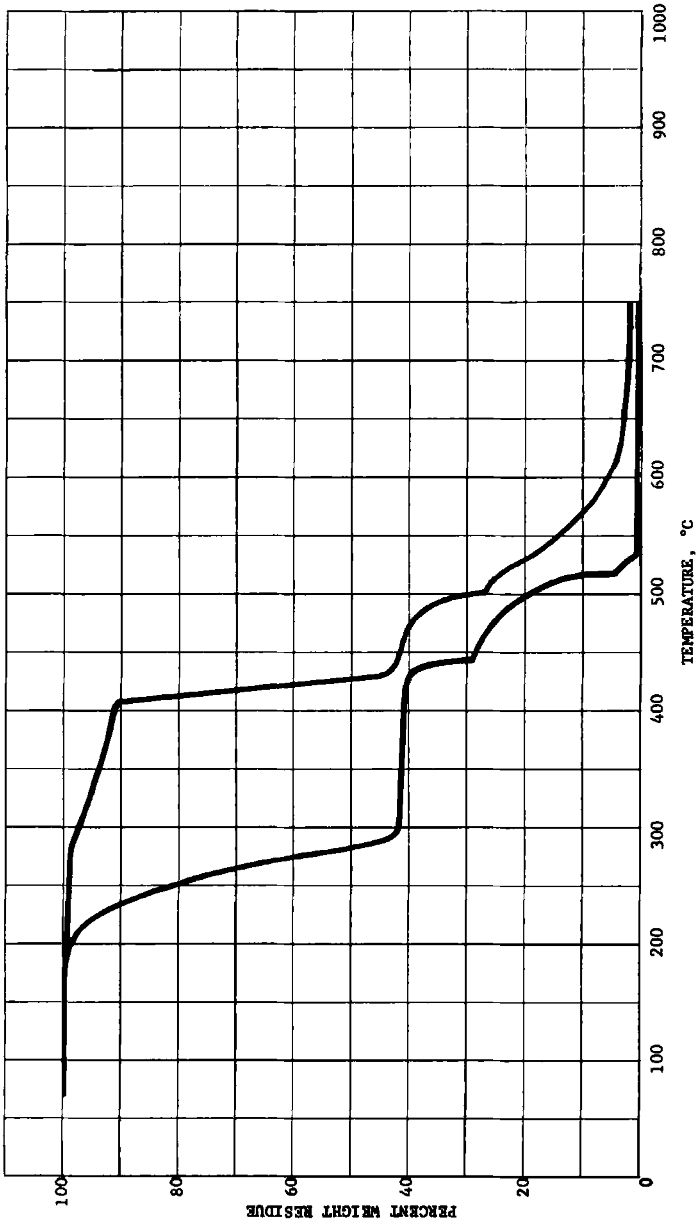
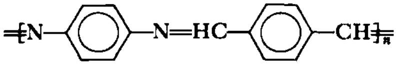
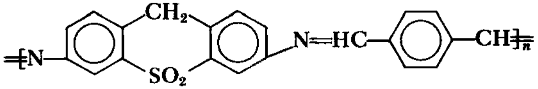


FIG. 12. Range of thermal stabilities in air for polymers 1-Y to 10-Y inclusive.

TABLE 11

Per Cent Weight Losses of the H600 Polymers While Being Heated in Nitrogen and in Air

Polymer designation	Gas	Per cent weight loss at °C 500	600	700	800	900	1000	1100	1176	Inflection point, °C
 1-B-H600	N_2	0.0	1.0	4.0	7.2	8.8	10.0	12.2	14.4	630
	Air	0.0	70.5	98.0	—	—	—	—	—	550
 9-B-H600	N_2	0.0	1.0	4.2	7.0	8.9	11.1	12.5	15.6	600
	Air	0.8	68.0	100.0	—	—	—	—	—	515
 10-B-H600	N_2	0.0	2.2	4.8	9.4	12.2	13.4	14.6	18.0	560
	Air	0.0	68.8	100.0	—	—	—	—	—	510

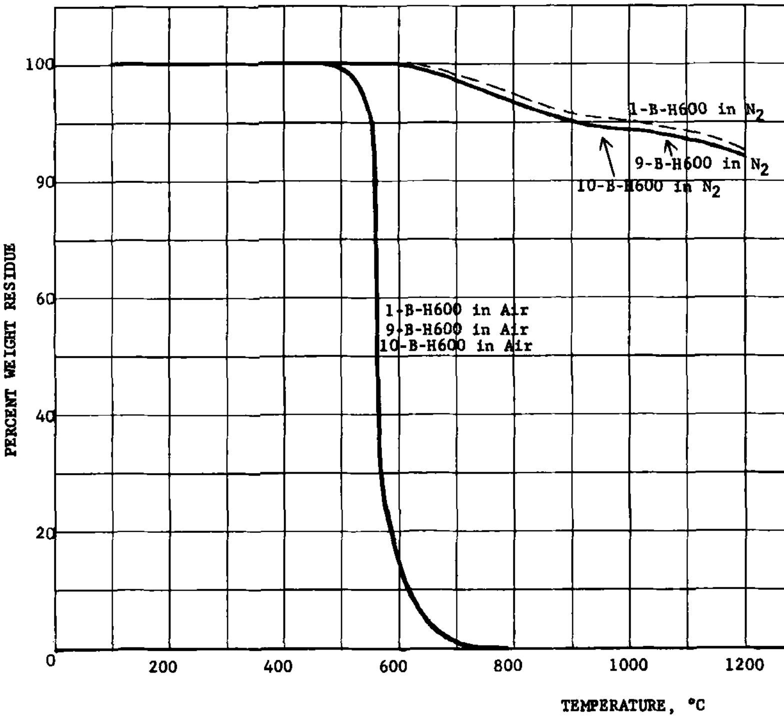


FIG. 13. Thermogravimetric analyses in nitrogen and in air of the B-H600 polymers.

performed to a maximum temperature of 400°C. When heated in nitrogen, their by-product losses were much higher than those which had been condensed to 600°C or higher.

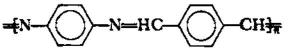
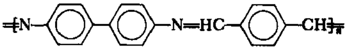
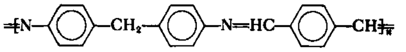
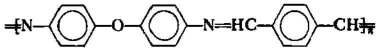
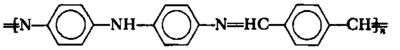
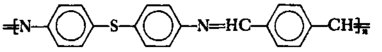
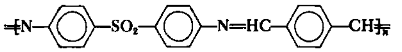
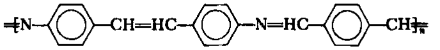
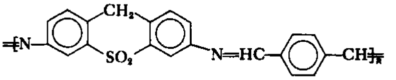
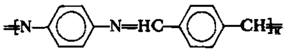
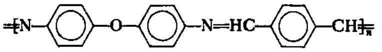
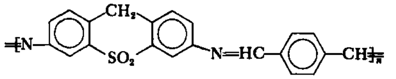
2. The thermal stabilities in nitrogen and in air of the 1-B-H400 to 10-B-H400 polymers prepared by the melt bis exchange reaction were much higher than the stabilities of the corresponding yellow brick-dust, 1-Y to 10-Y, polymers prepared in solution.

3. The thermal stabilities in nitrogen and in air of the aliphatic-type nonconjugated Schiff base polymers prepared either by the melt bis exchange reaction (11-B and 12-B) or in solution (11-Y and 12-Y) were much lower than the conjugated and pseudoconjugated polymeric Schiff bases.

4. The differences in the thermal stabilities of the aliphatic-type Schiff base polymers prepared by melt Schiff base exchange (11-B and 12-B) and by solution methods (11-Y and 12-Y) were small.

TABLE 12

Per Cent Weight Losses of H-1176°C Polymers Heated in Nitrogen

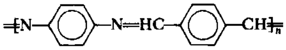
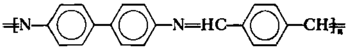
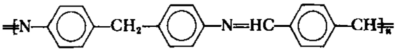
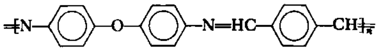
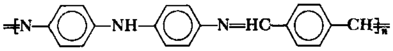
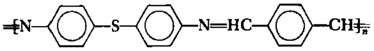
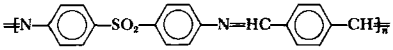
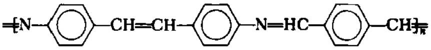
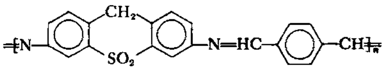
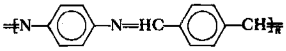
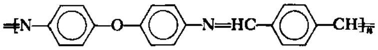
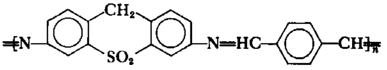
Polymer	Polymer designation	Per cent loss at 1176°C
	1-B-H1176	2.8
	2-B-H1176	2.6
	3-B-H1176	2.4
	4-B-H1176	3.0
	5-B-H1176	2.8
	6-B-H1176	4.0
	7-B-H1176	4.4
	9-B-H1176	2.5
	10-B-H1176	2.8
	1-B-H600 H1176	2.4
	4-B-H600 H1176	2.5
	10-B-H600 H1176	2.8

This contrasts with the data on the conjugated and pseudoconjugated Schiff base polymers and the difference was attributed to the fact that the polymerization condensations of the aliphatic-type polymers were homogeneous in both melt and solution systems, whereas in the preparation of the conjugated and pseudoconjugated polymers the condensations were homogeneous in the melt bis exchange system and heterogeneous in the solution system.

5. The thermal stabilities of the aliphatic-type Schiff base polymers, $\mathrm{=\!\![N{-}(CH_2)_4{-}N{=}HC{-}C_6H_4{-}CH]\!\!=_{\overline{n}}}$ and $\mathrm{=\!\![N{-}(CH_2)_6{-}N{=}HC{-}C_6H_4{-}CH]\!\!=_{\overline{n}}}$, were surprisingly good: of the order of about 300°C in nitrogen and 250°C in air.

TABLE 13

Temperatures at Which Weight Loss Begins, Has Occurred to 20%, and Is Complete When B-H1176 Polymers Are Heated in Air

Polymer designation	Sample begins to lose weight at °C	20% weight loss at °C	Sample disappears at °C
 1-B-H1176	510	565	800
 2-B-H1176	520	650	800
 3-B-H1176	450	590	660
 4-B-H1176	520	620	860
 5-B-H1176	550	660	900
 6-B-H1176	443	530	740
 7-B-H1176	480	620	900
 9-B-H1176	530	630	820
 10-B-H1176	475	620	720
 1-B-H600-H1176	600	660	1000
 4-B-H600-H1176	545	642	935
 10-B-H600-H1176	500	630	860

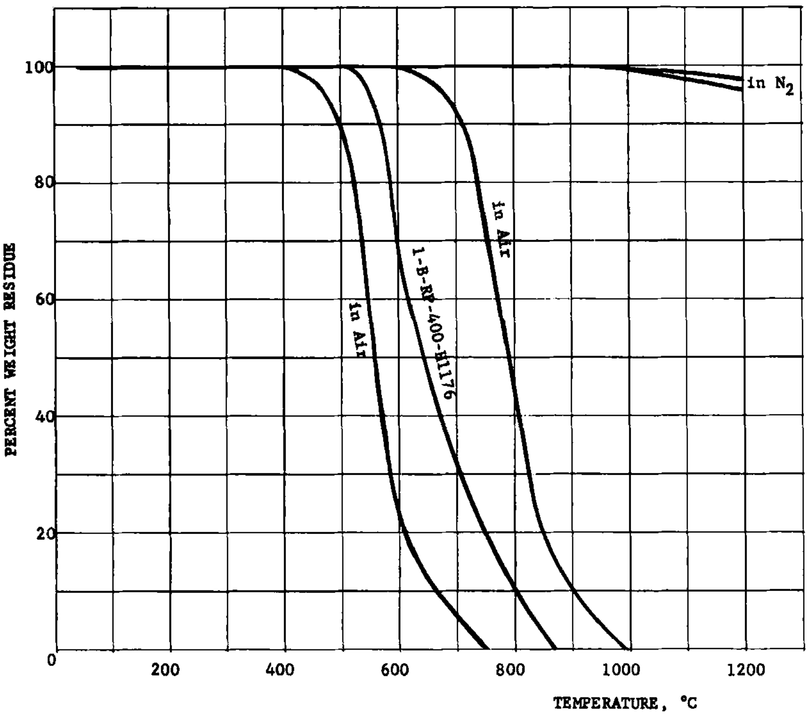


FIG. 14. Range of thermal stabilities for H1176 polymers in nitrogen and in air compared to that of polymer 1-B-RP-400-H1176.

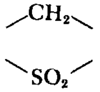
6. The thermal stabilities of the 1-B-H400 to 10-B-H400 polymers in nitrogen below the inflection point were very good and within the range 500–550°C.

7. The completely conjugated polymers, 1-B, 2-B, and 9-B, showed the best overall thermal stability in nitrogen when judged from the inflection point and total weight loss at 1000 and 1176°C. At high temperatures the polymer containing the diphenyl moiety, 2-B-H400, showed less stability than would be expected. The anomaly cannot be explained at this time.

8. The effect of thermal stability in nitrogen of the polymers resulting from changes in conjugation of the polymers was not as great as was expected, particularly in those polymers which were pseudoconjugated, that is, in polymers of the structure, $\mathrm{+N{-}Ar{-}X{-}Ar{-}N{=}HC{-}Ar{-}CH+_{\mathit{n}}}$, in which the conjugation was not com-

pletely inhibited by the X bridge between the two benzene rings.

The pseudoconjugated polymers, in which the bridges were —CH_2—, —$(CH_2)_4$—, —O—, —NH—, —S—, —SO_2—, and



had thermogravimetric inflection points in nitrogen of the order of 25–60°C lower than those of the conjugated polymers; and their weight losses in the range 600–1000°C were about 0–50% higher than those of the conjugated polymers. The greatest loss at 1000°C was shown by the polymer containing the —CH_2— bridges between two benzene rings. The weight losses in nitrogen of the pseudoconjugated polymer in increasing order of stability at 1000°C

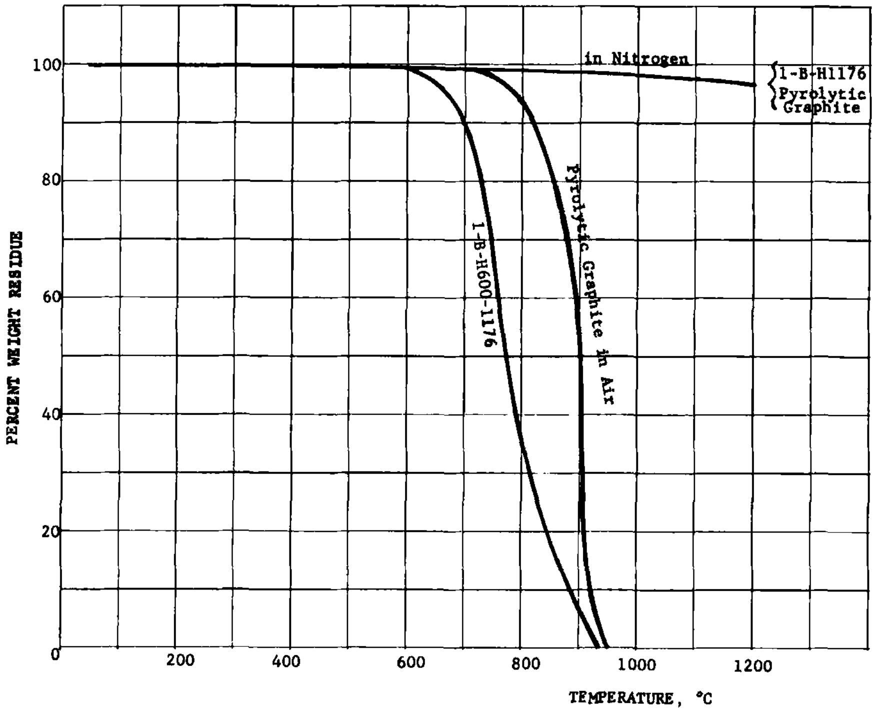
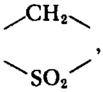


FIG. 15. Thermogravimetric analyses of polymer 1-B-H600-1176 and pyrolytic graphite in nitrogen and in air.

for the various X bridges between the two benzene rings were $-(\mathrm{CH_2})_4-$, 61.6%; $-\mathrm{CH_2}-$, 37.6%; —S—, 30.0%; —NH—, 28.8%;



$\mathrm{CH_2}$ / $\mathrm{SO_2}$, 28.6%

and $-\mathrm{SO_2}$, 24.6%.

9. The thermogravimetric analytical data obtained on the pseudoconjugated polymers, which had been prepared under arbitrarily selected polymerization conditions, indicated a good possibility that the thermal stabilities of these polymers in nitrogen could be improved by modifying the polymerization conditions, and thereby approximate those of the conjugated polymers.

10. When the conjugated and pseudoconjugated, polymers, 1-B to 10-B, were condensed to a maximum temperature of 400°C, the thermal stabilities of the polymers in air were found to be in the range 430–480°C. The highest stability of 480°C in air was shown by conjugated, 1-B-H400 polymer, $=\!\![\mathrm{N{-}C_6H_4{-}N{=}HC{-}C_6H_4{-}CH}]_{n}\!\!=$. Of the pseudoconjugated polymers, polymer 4-B-H400, $=\!\![\mathrm{C_6H_4{-}O{-}C_6H_4{-}N{=}HC{-}C_6H_4{-}CH}]_{n}\!\!=$, showed the highest thermal stability in air with an inflection temperature of 475°C. In fact, its weight loss in air at 600°C of 70% compared favorably with the values of 64% for the 1-B-H400 conjugated polymer.

11. The indication that the condensation polymerization was not completed at 400°C was observed in the differences in the thermoanalyses of the 1-B-H400 and the 1-B-H450 polymers. The per cent weight loss in air at 600°C for the former was 69%, and for the latter it was 39.2%. This also indicated the possibility of achieving greater thermal stability in the Schiff base polymers by continuing the condensation to temperatures higher than 400°C.

Thermal Stabilities of the B-H600 Polymers

1. The thermograms of polymers 1-B-H600, 9-B-H600, and 10-B-H600 clearly showed that their stabilities in nitrogen were higher than the corresponding polymers which had been condensed to 400°C. The three H600 polymers showed weight losses of less than 5% at 700°C and less than 18% at 1176°C.

2. The thermograms of the three H600 polymers show that little or no loss in weight occurred when the samples were heated in nitrogen to higher temperatures until some definite temperature was reached; then a first distinct negative slope occurred until it

reached a second higher temperature, when it tended to level out as a second but smaller negative slope became evident, which then continued to the temperature limit of the apparatus, 1176°C. The first negative slope was attributed to losses of by-products due to continued condensation polymerization, and the temperature at which it originated depended, as would be expected, on the previous thermal history of the sample. For example, in the B-H400 polymers the first negative slope was found in the 500–600°C region; whereas in the B-H600 polymer it was found in the region near 700°C.

The second negative slope could be interpreted from the nature of the plots as originating before the factors responsible for the first negative slope were completed and it was approximated that, generally, the second slope took origin in the 800–850°C region. Although the losses in this region could be attributed in part to continued condensation, which would be expected to be minor, they also could be due to intramolecular and intermolecular condensations to yield fused ring structures by loss of hydrogen or other by-products.

In any case, the thermograms performed in nitrogen indicated that condensation polymerization should be continued for a sufficient time to some temperature above 600°C, probably to a temperature in the region 800°C or higher.

It was interesting to note the appearance of the H600 polymers after being heated in nitrogen to 1176°C; the finely powdered, heat-treated samples had the appearance of relatively shiny, very black particles of the original shape, and not of dusty, powdery products characteristic usually of carbonized polymers. The thermal-stability values in air of the B-H600 polymers were higher than the values found for the B-H400 polymers. The highest thermal stability in air, when based on inflection points, was found to be 550°C for polymer 1-B-H600; this compared to 515°C for polymer 9-B-H600 and 510°C for polymer 10-B-H600.

Thermal Stabilities of the H1176 Polymers. When the H1176 polymers were heated in nitrogen, the thermograms gave no evidence of further condensations; this was indicated by the substantially horizontal linear plots of weight versus temperatures in each curve. The weight losses varied in the range of only 2.4–4.4%, but this loss was found only at temperatures above 1000°C, in the twelve polymers evaluated. These data indicated that by condensing the polymers in an inert atmosphere to temperatures in excess of 800°C, for example, in the region of 1000°C, a polymer could be obtained which showed high thermal stability in a nitrogen atmosphere to a temperature in excess of 1100°C. Since these low loss values could be attributed to a gain in weight by reaction of the polymer with nitrogen-counterbalancing pyrolysis losses, other studies (64) in which helium and argon were substituted for the nitrogen yielded substantially the same loss values.

All the H1176 polymers showed thermal stabilities in air in excess of 440°C, with a spread in temperature range of 440–600°C. The highest value of 600°C was shown by polymer 1-B-H600-H1176, which had been condensed at 600°C for 20 min before being postheated to 1176°C. This improvement would indicate that a condensation performed at a very slow heating rate progressively from 400 to 600°C before heating to 1176°C would be beneficial toward improving the thermal stabilities of these polymers.

Difficulties of Elemental Analyses

Difficulties in elemental analyses followed as a consequence of synthesizing the black, thermally stable Schiff base polymer. Analyses of the yellow and brown low molecular weight polymers, as well as higher molecular weight black polymers, were performed by three well-qualified analytical laboratories; the nitrogen values were determined in many cases by both the Dumas and the Kjeldahl methods. Elemental analyses of the low molecular weight, yellow and orange, easily combustible, Schiff base polymers gave values in good to fair agreement with the calculated values; this was shown in the analyses of the solution polymerizations of dialdehyde and diamines as well as in a number of oligomers prepared by the exchange reactions in solution. The deviations from the calculated values increased as the color of the polymers darkened. The problem became more severe when the black polymers were analyzed and the deviations from calculated values increased with the molecular weight of the polymers. The calculated value for the *p*-xylylidene-*p*-phenylenediamine polymer, $\left[\mathrm{N{-}C_6H_4{-}N{=}HC{-}C_6H_4{-}CH}\right]_n$, is C, 81.53; H, 4.88; N, 13.59; yet a Dumas analysis of polymer 1-B-RP-H260 gave the per cent values C, 83.25; H, 5.47; N, 6.08; with a sum of elements as 94.80%; and ash was reported as present. A repeat analysis, in which the combustion was conducted at higher temperatures (1200°C) for longer periods of time, yielded the per cent value C, 85.59; H, 5.17; N, 9.76; with the sum of elements as 100.52%.

In both analyses, the per cent values for carbon is higher while that for nitrogen is lower than any formula that can be written for a polymer which was obtained in 98.5% yield and which had not been heated to temperatures in excess of 260°C, a temperature which is a very much lower temperature than the 600–800°C temperatures at which structural changes in the polymer appear. However, it was interesting to note that in the repeat analysis the sum of the per cent values for carbon and nitrogen (85.59 + 9.75) was 95.34%, which is almost identical to the calculated sum of (81.53 + 13.59) 95.12%. It appears to be probable that the oxides of nitrogen produced at the high combustion temperatures were not being reduced completely to nitrogen and these nitrogen values were incorporated as CO_2 in the values for carbon.

The analyses of the bis exchange polymer, 1-B-H450, $=\!\!\left[N{-}C_6H_4{-}N{=}HC{-}C_6H_4{-}CH\right]_{n}\!\!=$, gave the per cent values C, 75.20; H, 4.74; N, 6.80; with ash reported as being present; the sum of the elements was 86.74%. A separate and total combustion in a crucible over a Meeker burner at red heat showed that the polymer was ash-free. Upon reanalysis with extended combustion time at higher temperatures, the new per cent values obtained were C, 81.55; H, 4.66; N, 9.49; the sum of the elements was 95.7%. These values correspond to a $n = \infty$ on the basis of carbon; the hydrogen value is less than the value required for $n = \infty$ and the nitrogen value of only about 70% that required for $n = \infty$. The difference in the total elemental values, $100.0 - 95.7 = 4.3\%$, cannot be attributed to oxygen, since the polymer was prepared in the absence of oxygen from monomers containing no oxygen atoms by the same techniques used in preparing polymer 1-B-RP, which also showed the absence of detectable oxygen. If the value of n in this polymer sample was a value in the range 10–30, and if it had been prepared solely from the dialdehyde and diamine directly, its oxygen content would be between 0.26 and 0.77%; thus an oxygen content of 4.3% would correspond to that of an oligomer whose value is between $n = 1$ and $n = 2$, a fact which was belied by its color and its thermal stability.

The nitrogen values determined by the Dumas method and the usual macro Kjeldahl method did not agree. The Kjeldahl analyses for nitrogen were also low, although usually they averaged 2–4% higher than the values obtained by the Dumas method. This can be explained to some degree by the observations made on heating samples of the polymers 1-B-RP and 1-B-H450 in concentrated sulfuric acid. To 10 ml (1.84 g) of concentrated sulfuric acid in a micro Kjeldahl digestion flask there was added 0.5 g of polymer 1-B-H400 and the mixture heated in the digestion rack over the direct flame of a Bunsen burner to the refluxing temperature (about 300°C) of the acid. The dissolution of the polymer did not occur until it had been heated for 16 hr; the color lightened to dark brown in 24 hr and the solution did not become colorless at the end of 96 hr, at which time the experiment was terminated.

When 100 mg of $HgSO_4$ and 100 mg of $CuSO_4$ were added to a second mixture of 0.5 g of polymer and 10 ml of sulfuric acid and the mixture heated, dissolution occurred in about 6 hr, but the brown color did not disappear at the end of 72 hr, at which time the experiment was terminated. Then a mixture of 80 mg of polymer, 100 mg, of $HgSO_4$, 100 mg of $CuSO_4$, and 10 ml of sulfuric acid was heated as in the previous experiments, and a clear, greenish-yellow solution was obtained in 5½ hr. This digestion was repeated a number of times and extended for longer periods of time with the results given in Table 14. This resistance to digestion was also evident in the hydrolytic stability of these black polymers. Finely ground 0.100-g samples of the polymers 1-B-RP-260 and 1-B-450, respectively, were refluxed in 100 ml of 5 and 10% sulfuric acid solutions, respectively, and were recovered quantitatively after 96 hr at reflux temperatures.

Other experiments (65–69) report similar difficulties in elemental analyses of insoluble, infusible, highly thermally stable polymers.

TABLE 14

Effect of Digestion Time on % N Found in Polymers

Digestion time, hr	% N found in polymer	
	1-B-RP-H260[a]	1-B-H450[a]
5.5	8.53	8.81
12.0	9.63	10.15
24.0	11.78	12.61
72.0	13.48	13.41

[a] Theoretical, N = 13.59 at $n = \infty$.

Bell and Pezdirtz (*67*) report that exceptional thermal stability of some of their nitrogen-containing polymers was also apparent in their elemental analyses, and that the discrepancies indicated the inadequacy of combustion analytical methods to degrade thermally stable polymers to an extent where accurate results can be obtained. In fact, they show that identical analytical procedures give carbon values 5% below theory for pyrolytic graphite (100% C). It has also been reported (*70*) that when the Kjeldahl method was applied to some of these polyimidazole-type polymers, digestion had to be continued for extended periods of time of the order of 48 hr or more in concentrated sulfuric acid, to give nitrogen values which approach the calculated values.

An alternative satisfactory method of obtaining Kjeldahl nitrogen values consisted in "solubilizing" the polymer in benzylideneaniline with zinc chloride catalysis, performing the analysis on an aliquot part of the mixture, and correcting the nitrogen value for the amount contributed by the benzylideneaniline. Such an analysis was obtained by first dissolving 1.0 g of 1-B-RP-H400 in 10.0 g of benzylideneaniline, then digesting an aliquot part for 18 hr in sulfuric acid to yield the per cent value N, 8.17; theoretical, 8.26. If the nitrogen values obtained by such tedious procedures were used to correct the sum of nitrogen and the carbon values obtained by the Dumas method, the per cent analytical values for 1-B-RP were C, 81.48; H, 5.17; N, 13.49; and for 1-B-H450: C, 81.55, H, 4.66; N, 13.51, which are in fair agreement with the calculated values: C, 81.53; H, 4.88; N, 13.59.

Problems in Molecular Weight Determinations

By Elemental Analyses of the Polymers. In poly-*p*-xylylidene-*p*-phenylenediamine, $H_2{=}\!\!\left[NC_6H_4N{=}HCC_6H_4CH\right]_n\!\!{=}O$, the elemental analyses change with the value of *n*; as *n* increases from 1 to ∞, the per cent values of C increase from 75.00 to 81.53 and of nitrogen from 12.50 to 13.59, while the per cent values of H decrease from 5.36 to 4.88 and of oxygen from 7.14 to 0.0. A similar relationship is found in the corresponding bisexchange polymer, $C_6H_5CH{=}\!\!\left[NC_6H_4N{=}HCC_6H_4CH\right]_n\!\!{=}NC_6H_5$. Elemental analyses can be used to assign average values to the relatively lower molecular weight polymers in which *n* is about 10 or less, but the minor differences calculated for the values of C, H, and N in polymers in the range of

$\bar{n} > 10$ to $n = \infty$ fall within the limits of error of the available analytical methods. This, in addition to the fact that the carbon analyses obtained by combustion must be corrected on the basis of a Kjeldahl nitrogen value, precludes the use of carbon or other values for assigning molecular weight values to the polymers.

By Measurements of Solutions of the Polymers. The molecular weights of polymers are usually derived from suitable physical measurements of dilute polymer solutions such as measurements involving viscosity, osmotic pressure, and light scattering. It is known (*71*) that many polyconjugated polymers become insoluble and infusible at low degrees of polymerization. The dark-colored polyconjugated Schiff bases of this investigation fall within this insolubility pattern. Most of the low molecular weight yellow, orange, and brown-colored Schiff base polymers can be dissolved in concentrated sulfuric acid and their intrinsic viscosities in concentrated sulfuric acid measured. By interrupting the bis exchange polymerizations at low degrees of conversion, it is possible to isolate black polymers on the borderline of solubility in sulfuric acid, although such polymers still contain retained benzylideneaniline. The highest intrinsic viscosity measured in these studies of such "interrupted" polymers, 1-B-H325-B, was 0.824. By reference to the intrinsic viscosities of 0.3 to 1.4 reported (*72*) for the benzimidazo-benzophenanthroline polymers, these Schiff base polymers can be considered as possessing a reasonably high molecular weight at this stage of condensation.

Since they are condensation-type polymers, they can be expected to follow the weight-average and number-average distribution shown by Flory (*73*). At low conversions, the number of monomer molecules is more plentiful than polymer species and the molecular weight of the most prevalent polymer is indeed low; and its molecular weight will shift to higher values with conversion. Information of this type is useful in determining the conversion at which initial insolubility occurs but is of little or no value in correlating physical properties with molecular weight in the insolubility range.

The terms "insolubility" and "solution" when applied to the poly-Schiff bases are confusing. Most of the reaction pairs used in the polymer preparations in these studies were soluble in many of the common organic solvents, such as alcohol, acetone, benzene, and toluene, and these solvents were used in these studies to extract unconverted reagents from their derived polymers. The yellow, orange, red, brown, and black polymers were insoluble in these types of solvents. Yet most of the yellow, red, and brown polymers were found to be soluble in formic acid, acetic acid, acetic anhydride, concentrated sulfuric acid, and in a saturated solution of sodium bisulfite. However, these solutions were not true solutions of the polymers but solutions of derivatives of these polymers. Acetic acid was found to be a poorer solvent for the yellow polymers than was formic acid, causing only a slight reduction in color, indicating incomplete acylation.

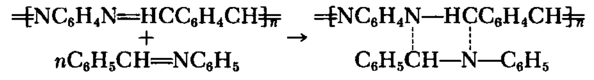
Addition reactions to the —C=N— linkage in Schiff bases is not limited to the solvent reagents of the type mentioned above, since others are known. The addition to monomeric Schiff bases of HCN (*74–77*), alkyl halides (*78*), bromide (*79*), Grignard reagents (*80–82*), and active α-hydrogen compounds (*83,84*) such as methyl ethyl ketone and malonic esters are also known. When some of these reagents were evaluated as solvents for the yellow polymers, they were found to be much poorer than acetic acid.

If the molecular weights of these polymers are to be obtained from their derivatives, then the reaction by which the derivatives are prepared should be quantitative or nearly so. That this was not so was evident in the failure to obtain colorless derivates, as would be expected if addition occurred at substantially all the —C=N— bonds. Attempts to prepare 1% solutions of some selected, very finely divided black polymers in formic acid at room temperature, and at reflux temperatures for short periods of time, failed to yield solutions and most of the polymer remained undissolved. Even an extended reflux for 7 days of 0.002 g of the polymer in 10 ml of formic acid yielded only a slight brown solution and not a colorless solution, leaving most of the polymer undissolved. The addition of the filtered formic acid solution to 100 ml of water precipitated only trace quantities of a brown polymer, which indicated that formic acid was reacting incompletely with the polymer and extracting only the lower molecular weight products. Similar difficulties were experienced in attempts to prepare solutions of some hard black polymers in acetic anhydride, saturated aqueous sodium bisulfite, and sulfuric acid.

Finally, many other black polymers, which were assumed to be of higher molecular weight as a result of longer reaction time, etc., were found to be completely insoluble in formic and sulfuric acids.

That these polymers were not cross-linked was shown by "dissolving" them in benzylideneaniline.

Practically all the polymers, except those heated to 600°C or higher, whether yellow or brown or black, could be dissolved in benzylideneaniline simply by heating the mixture alone as a melt in the case of the lower molecular weight polymers, or in the presence of added catalytic quantities of zinc chloride added to the melt mixture in the case of the higher molecular weight polymers. Solution of these polymers was due to a reaction by a bis-Schiff base exchange reaction between polymers and benzylideneaniline which "reduced" the average molecular weight of the polymer by changing its distribution and therefore was of little value in determining the molecular weight of the initial polymer. The "solubilization" of the polymers in benzylideneaniline was considered as offering a possible solution to this problem. This solution might be found by relating the molecular weight distribution of the thus equilibrated, solubilized mixture, to the various concentrations of benzylideneaniline used in the reaction, and from the data derive the probable distribution of the original polymer by the extrapolation to a zero concentration of benzylideneaniline; such data probably can be obtained from light scattering or intrinsic viscosity measurements. Such an approach would be the inverse or reverse of that used by Flory (85) to derive the distribution data for condensation polymers. Such an approach would have to assume the absence of adduct or π-complex formation between the dissolved "equilibrated" polymer and benzylideneaniline:



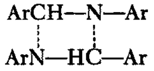
$$\begin{array}{c} =\!\!\left[\mathrm{NC_6H_4N{=}HCC_6H_4CH}\right]\!\!=_{n} \\ + \\ n\mathrm{C_6H_5CH{=}NC_6H_5} \end{array} \rightarrow \begin{array}{c} =\!\!\left[\mathrm{NC_6H_4N{-}HCC_6H_4CH}\right]\!\!=_{n} \\ \vdots \quad \vdots \\ \mathrm{C_6H_5CH{-}N{-}C_6H_5} \end{array} \qquad (15)$$

In attempts to resolve whether or not such complexes were formed, the infrared spectra of a number of polymers, in which benzylideneaniline was involved either (a) as a by-product of the reaction, or (b) as the solvent for the yellow polymer, 1-Y, or (c) as a solvent for the depolymerizing of an insoluble bis-Schiff base exchange polymer, 1-B-RP-H400, or (d) as the reaction medium for the bis-Schiff base exchange reaction, were examined. The reference spectra were those of 1-Y and 1-B-RP, which were synthesized in the complete absence of benzylideneaniline.

A comparison of the infrared spectra of these "equilibrated" polymers showed that changes, indeed, do occur. However, it was difficult to determine whether or not there was a decrease in the concentration of —C═N— groups in the product because the newly added phenyl group also has an absorption band in the 1600 cm^{-1} region. However, all the products showed absorptions in the 690 cm^{-1} and 760 cm^{-1} regions, attributable to the terminal C_6H_5— groups; such bands were originally absent in the 1-Y and 1-B-RP polymers. A number of interesting observations were made of the changes in spectra as 1-Y was heated in benzylideneaniline. At the early stages of reaction, the typical spectrum of the original poly-Schiff base was observed, which then was followed with increase in reaction time, by an increase in the concentration of the absorption bands for the C_6H_5— structures, which indicated some kind of incorporation of the benzylideneaniline. This incorporation could be the result of an exchange reaction or of complex-adduct formation or of both. The first stages were shown to involve exchange and would account for the presence of C_6H_5— structures; but as the viscosity of the melt, and therefore chain length, increased, the relative amount of terminal C_6H_5— groups should have decreased, instead of increasing, as a result of chain-end coupling and benzylideneaniline elimination. This increase would indicate retention of benzylideneaniline.

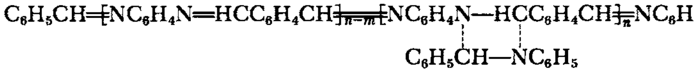
In all the preparations in which benzylideneaniline was involved either as a by-product in an exchange reaction, or where it was used as a solvent for the reaction, or where a low molecular weight polymer was propagated in it, or when an insoluble, infusible polymer was "solubilized" in it, the yield of polymer recovered by distillation was always higher than 100%, even when the polymer was heated to 330°C at 1.5 mm Hg pressure (benzylideneaniline, b.p. 310°C/760 mm). However, when these high-yield polymers were heated further to 400°C, additional benzylideneaniline was eliminated rapidly; most probably this was the result of decomplexing and not of chain-end coupling, which would be expected at this stage of condensation to be relatively slow. At temperatures above 400°C, benzylideneaniline was eliminated at a much slower rate, as would be expected from the kinetics for chain-end coupling in a system of decreasing concentration of functional end groups. Eventually a theoretical 100% yield was approached as the temperature was increased to about 600°C. When this point was reached, the system could be considered as relatively free of complexed benzylideneaniline, as was evidenced also in the thermograms, but the product at this stage was insoluble in all solvents evaluated, and therefore was useless for the molecular weight determinations.

Monomeric four-membered ring adducts,



$$\begin{array}{l} \mathrm{ArCH{-}N{-}Ar} \\ \quad \vdots \quad\ \vdots \\ \mathrm{ArN{-}HC{-}Ar} \end{array}$$

have been reported (*31,86*) and found to be very unstable, regenerating the Schiff bases readily. Rings of this kind should be expected to be formed by reaction between benzylideneaniline and the Schiff linkages in the polymer, but not all linkages can be expected to react (*87*). Also, if such four-membered ring complexes were formed, removal of the benzylideneaniline should be expected to be more difficult because of the polymeric medium of high viscosity from which it must diffuse, when compared to the unhindered decomposition of a monomeric four-membered ring compound. Equation (15) also shows that the calculated elemental per cent values should change from C, 81.53; H, 4.88; N, 13.59 for the uncomplexed 1-B-RP polymer to C, 83.72; H, 5.42; N, 10.85 for the 1:1 complex. The values obtained on a limited number of samples which were withdrawn as the benzylideneaniline was removed from the solubilized polymer gave values which fell within this range, with the values for the unsolvated polymer being approached after the polymer was heated to 550°C. Analytical values of this kind were not sufficiently precise or reproducible to specify values for the amount of complexed or solvated benzylideneaniline, but in terms of infrared spectra, elemental analyses, yields, and thermal behavior the polymers appeared to be solvated by or complexed with benzylideneaniline; thus



$$\mathrm{C_6H_5CH{=}\!\!\left[NC_6H_4N{=}HCC_6H_4CH\right]_{n-m}\!\!{=}\!\left[NC_6H_4\underset{\substack{\vdots \\ C_6H_5CH}}{N}{-}\underset{\substack{\vdots \\ NC_6H_5}}{H C}C_6H_4CH\right]_{m}\!\!{=}NC_6H_5}$$

This benzylideneaniline could be removed only by heating at temperatures well above the boiling point of benzylideneaniline.

Related evidence of a similar kind was obtained also when *p*-chlorobenzylidene-*p*-chloroaniline was used as the solvent reactant instead of benzylideneaniline. A number of attempts were made to extract these bound benzylideneanilines from the finely ground polymers with dimethylacetamide; the results are discussed under the section dealing with molecular weight determinations based on end-group analyses.

Molecular Weights from End-Group Analyses

An attempt was made to establish at least an order of magnitude of the molecular weights of the polymers by relying on the elemental analyses of polymers containing atoms other than carbon, hydrogen, or nitrogen. Since polymers containing halogen end groups appeared to offer some promise, a number of such Schiff base polymers were prepared. The pertinent data obtained from the syntheses and analyses of the chlorine-tagged polymers, 14-Cl-1 to 14-Cl-6, inclusive, are given in Table 15.

The halogen contents of polymers 14-Cl-1 and 14-Cl-2 were in fair agreement with the values for $n \sim 2$ and $n \sim 3$, respectively, and the colors of these polymers confirm these approximations. The dark-brown color of the polymer 14-Cl-3 and the lower yield, 84%, of the polymer obtained gave indications that its chain length was higher than that of the brown-orange polymer, 14-Cl-2, 90% yield, yet the halogen analysis of 18.28% chlorine corresponds to an n value of less than 1. Similarly, the black color and the viscosity of the melt of polymer 14-Cl-4 gave evidence of a molecular weight higher than that of polymer 14-Cl-3, yet its chlorine values placed the value of n at slightly higher than 1. Similar conflicting conclusions could be made from the chlorine values found for polymers 14-Cl-5 and 14-Cl-6, even though progressively larger quantities of *p*-chlorobenzylidene-*p*-chloroaniline had been collected as the reaction times were increased and as the pressures in the systems were lowered. These high chlorine values could be explained by the fact that by-product *p*-chlorobenzylidine-*p*-chloroaniline was being retained more tenaciously, probably as an adduct, by the higher molecular weight viscous polymers than by the oligomeric dimers and trimers. Since the by-product contains 28.1% chlorine, retention of significant amounts could produce a large shift in elemental analysis. The quantity of retained by-product, if any, could be calculated from the elemental analysis values for C, N, and Cl. For polymer 14-Cl-5 the amount of retained by-products was calculated from the nitrogen values to be 61.0%, and 60.0% from the carbon values, and for polymer 14-Cl-6 the amount of

TABLE 15

Pertinent Data on the Chlorine-Tagged Schiff Base Polymers

Polymer	Time, min	Pressure, mm Hg	Weight of polymer obtained	% of original reactants	Color of polymer	Analyses[a]				λ_{max}, mμ
						% C	% H	% N	% Cl	
14Cl-1	3	760	1.8791	94	Yellow	75.29	4.41	10.32	10.81	320
14Cl-2	120	760	1.8036	90	Brown-orange	73.84	4.67	10.04	10.54	350
14Cl-3	180	760	1.6733	84	Very dark brown	70.84	3.68	5.93	18.28	335
14Cl-4	360	760	1.4423	72	Black	72.26	3.65	6.94	15.81	330
14Cl-5	300 + 180	760 + 1.5	1.3602	68	Solid Shiny black	72.64	3.56	6.49	15.40	330
14Cl-6	180 + 1440	760 + 1.5	1.300	65	Solid Shiny black	74.33	3.62	6.73	14.60	—

[a] Calcd. for monomers ($ClC_6H_4CH{=}NC_6H_4N{=}HCC_6H_4Cl$ and $ClC_6H_4N{=}HCC_6H_4CH{=}NC_6H_4Cl$)$C_{20}H_{14}N_2Cl_2$: % Cl = 20.1; for by-product ($ClC_6H_4CH{=}NC_6H_4Cl$)$C_{13}H_9NCl_2$: % Cl = 28.1; for $ClC_6H_4CH{=}[NC_6H_4N{=}HCC_6H_4CH]_n{=}NC_6H_4Cl$: % Cl when $n = 1$, 16.22; $n = 2$, 11.29; $n = 10$, 3.08; $n = 20$, 1.63; $n = 30$, 1.10; $n = 40$, 0.84; $n = 50$, 0.67; $n = 100$, 0.34; $n = 150$, 1.23; $n = 200$, 0.18; $n = \infty$, 0.0.

retained by-products was calculated to be 53.0% from the nitrogen values and 50.0% from the carbon values. Since *p*-chlorobenzylidene-*p*-chloroaniline is soluble in 95% alcohol, these polymers were ground and extracted in a Soxhlet apparatus, continuously for 24 hr, until the condensate in the thimble chamber gave a negative test for chlorine by the Beilstein copper wire method. Only 25 and 7.5% of the weight of polymers 14-Cl-5 and 14-Cl-6, respectively, were extracted instead of the much higher values expected. The chlorine contents of the extracted materials for polymers 14-Cl-5 and 14-Cl-6 were 27.61 and 27.7%, respectively, corresponding well to the calculated value for *p*-chlorobenzylidene-*p*-chloroaniline. The alcohol-extracted polymers were then subjected to a second Soxhlet extraction with dimethylacetamide and the extracted polymers dried to constant weight in a vacuum oven at 60°C at 1.5 mm for 16 hr. Additional amounts of *p*-chlorobenzylidene-*p*-chloroaniline and other low molecular weight products were recovered from the dimethylacetamide by distillation and combined with by-products recovered by the alcohol extraction. The total amount of by-products extracted from polymer 14-Cl-5 was 63.3% and from polymer 14-Cl-6 was 52.8% of the original weight of the polymers.

In both cases, the weight of the remaining polymer, after the dimethylacetamide extraction, exceeded greatly the weight of the original sample placed in the extractor. Since retention of dimethylacetamide was suspected, the polymer was extracted for a third time with acetone for 16 hr, and only about 50% of the retained dimethylacetamide was recovered. The remaining amount of the retained dimethylacetamide was recovered by heating the polymers to 300°C and collecting it in an acetone–dry ice trap. The final weights of the dried extracted polymers were 35.2 and 46.1%, respectively, for polymers 14-Cl-5 and 14-Cl-6.

Elemental analyses for chlorine of the extracted polymers gave values of 0.37% for polymer 14-Cl-5 and 0.21% for polymer 14-Cl-6. These values are in fair agreement with the values calculated from the chlorine contents of the extracts. On this not too satisfactory basis, since in this range of chlorine content small errors in chlorine values introduce large errors in the calculations for molecular weight, the molecular weight of the residual dimethylacetamide insoluble polymer, 14-Cl-5, was about 21,000 and of polymer 14-Cl-6 it was about 32,000.

The presence of retained *p*-chloroxylylidene-*p*-chloraniline in 14-Cl-5 polymer was confirmed by extracting it from the polymer with sulfuric acid. The quantity extracted in a static system at 60°C by 95.3% sulfuric acid amounted to 21.9%, compared to the value of 25% removed by alcohol in a continuous extraction in a Soxhlet apparatus, while at 120°C the amount extracted by sulfuric acid was 39.69% compared to 38.3% extracted by dimethylacetamide in a continuous process.

Comparable studies were also made on the polymers synthesized from using fluorine-substituted monomers without achieving any greater degree of accuracy.

Molecular Weights from Spectral Methods

From Infrared Spectra. As the molecular weight increases in a homologous series of conjugated polymers, a shift occurs in the conjugation bands in their infrared spectra. This shift was observed by comparing the bands in benzylideneaniline, N,N′-dibenzylidene-*p*-phenylenediamine and *p*-xylylidenedianil with those in the yellow and black polymers. A preliminary investigation of these regions have indicated that this was not a satisfactory method for even approximating the molecular weight of the black polymer, because once the "early" black polymer stage had been reached, the magnitude of further spectral shifts with continued condensation was either too small or undetectable to be useful.

From Ultraviolet Spectra. It is well known (88,89) that the ultraviolet spectrum of a conjugated chromophore will have the maximum intensity absorption band, λ_{max}, shift to longer wavelengths as the extent of conjugation is increased. It was believed that, since such bathochromic shifts are approximately cumulative, they would give some indication of the relative extent of conjugation and therefore of a relative value of the polymer molecular weights. In the *p*-polyphenyls (*90*), λ_{max} for diphenyl is found at 251 mμ, shifting to 280 mμ for $H{-}(C_6H_4)_3{-}H$, to 300 mμ for $H{-}(C_6H_4)_4{-}H$, 310 mμ for $H{-}(C_6H_4)_5{-}H$, and 317 mμ for $H{-}(C_6H_4)_6{-}H$.

The para monomers, $C_6H_5CH{=}NC_6H_4N{=}HCC_6H_5$ and $C_6H_5N{=}HCC_6H_4CH{=}NC_6H_5$, showed relatively sharp λ_{max} at 357 mμ and 347 mμ, respectively, while the λ_{max} for the by-product $C_6H_5CH{=}NC_6H_5$ was found at 263 mμ. When these monomers were reacted to a relatively low degree of condensation, the λ_{max} of the mixture, which included the liberated by-product, was found, for the various yellow-colored polymers, in the region 290–305 mμ and for the various orange and orange-brown colored polymers in the region 350–360 mμ. But at the brown and dark-brown colored polymer stages, a reversal to lower λ_{max}, 310–330 mμ, was observed as the concentration of the by-product $C_6H_5CH{=}NC_6H_5$ (λ_{max} at 263) increased as a result of continued polycondensation. When the benzylideneaniline was removed by distillation, the λ_{max} shifted again to the higher wavelengths to the region 355–365 mμ until the polymer became insoluble in dimethylacetamide, which precluded further comparative measurements.

Similar results were obtained with the chlorine-tagged polymers of the 14-Cl series. The λ_{max} of the para monomers, $ClC_6H_4CH{=}NC_6H_4N{=}HCC_6H_4Cl$ and $ClC_6H_4N{=}HCC_6H_4CH{=}NC_6H_4Cl$ were 362 mμ and 350 mμ, respectively, and λ_{max} of the by-product, $ClC_6H_4CH{=}NC_6H_4Cl$, was 315 mμ. The λ_{max} values shown in Table 15 were obtained on the polymers as prepared and which still contained, as was shown, considerable amounts of the by-product, $ClC_6H_4CH{=}NC_6H_4Cl$. In this case also, a shift first to higher λ_{max} was observed, and this was followed by a reversal to lower λ_{max} as the concentration of by-product increased. When this by-product was removed by distillation, λ_{max} also shifted again to higher wavelengths in the 350–365 mμ region, the region found for the unsubstituted Schiff base, indicating that the influence of the terminal halogens on λ_{max} is minor when the value of *n* in these polymers is still relatively low, and estimated to be about 5 to 6.

In their behavior, these Schiff base polymers parallel the polyphenyls; the amount of shift to higher λ_{max} decreases rapidly and asymptotically with increases in the value of *n* at low values of *n*, and thus ultraviolet spectroscopy is no more a satisfactory technique for estimating the molecular weights of the higher polymers than is infrared spectroscopy.

From Electron Spin Resonance Spectra. A number of electron spin resonance spectra were recorded of a number of polymers to determine whether or not signal intensity could be correlated to molecular weights. An increase in the extent of conjugation in a conjugated system tends to decrease the binding energies of the π electrons in the systems. This decrease in the binding energy is attributed to resonance within the system (*91*). Thus, from a purely theoretical consideration, one may expect that the π electrons in long conjugated chains would be held rather weakly, so that low excitation energies will cause electrons to flow along the chain. Molecules possessing high degrees of conjugation should show conductivity. This phenomenon has been observed in certain condensed aromatic systems (92) such as phthalocyanine and anthracene, which were shown to possess semiconductor properties and to obey Ohms' law (*91*). These properties are due to the existence of trapped radical or unpaired electrons or to both in the chemical structure, and these substances give intense bands in the electron spin resonance spectrum (*93,94*). The areas under the peaks are proportional to the number of unpaired electrons in this structure.

In the poly-Schiff bases, the signal is attributed to the unpaired electrons in the $-C{=}\ddot{N}-$ structure, and all the yellow to brown polymers showed good signal response. All the black polymers showed high signal response. Figure 16 illustrates some typical electron spin resonance spectra: curve (a) for the 1-B-H260 polymer and curve (b) for the 1-B-H300 polymer.

In the relationships of $\delta X'/\delta H$ and H in Fig. 16, the narrow signal

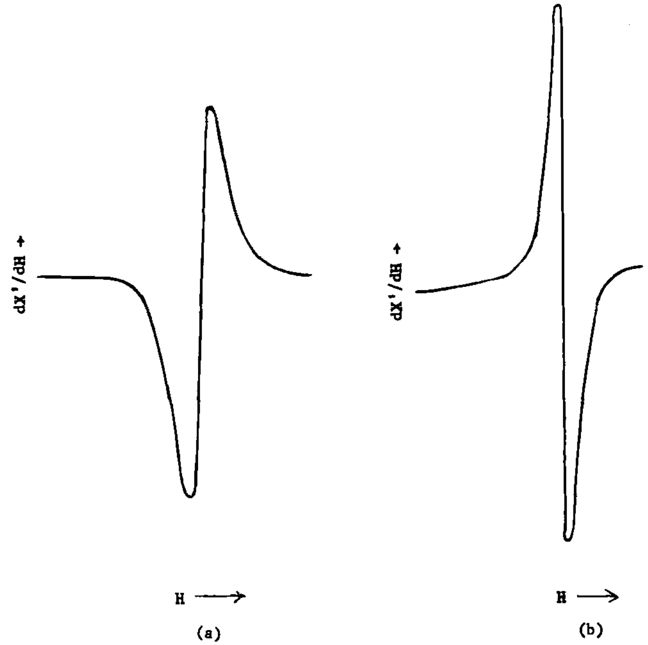


FIG. 16. Typical EPR spectra of $-\!\![HCC_6H_4CH{=}NC_6H_4N]\!\!-_{\overline{n}}$ polymers.

without a superfine structure confirms the existence of unpaired electrons in the polymer. An effort was made to correlate $\delta X'/\delta H$ versus H to molecular weight by evaluating samples of polymer withdrawn from a reaction as a function of increasing viscosity with time, and therefore to molecular weight with increasing conjugation. The preliminary efforts to correlate signal intensity or areas under the peaks with probable sizes of the polymer were not initially successful.

Further studies on the comparison of the electrical and photoconductive properties of the yellow with the black poly-Schiff bases have been initiated.

Our initial attempts to establish a method for determining the molecular weight of the solid black, infusible, poly-Schiff bases indicated that it was a difficult task indeed, and the problem was not resolved. The problem of determining the molecular weights of the so-termed "infusible," "insoluble," thermally stable polymers is not peculiar to the Schiff base polymers alone; it is common to many polyaromatics, such as the polyphenylenes and polystilbenes, the polybenzimidazoles, the pyrrones, and numerous others. It is believed that the solution to this specific problem, identified peculiarly with highly thermally stable polymers, is itself the subject of a major research undertaking.

Acknowledgments

This work was supported by Grant NsG339 of the National Aeronautics and Space Administration. Abstracted in part from a portion of the Ph.D. dissertation of James V. Crivello, University of Notre Dame, February 1966.

REFERENCES

1. B. G. Achhammer, M. Tryon, and G. M. Kline, *Modern Plastics,* **36,** 131 (1959).
2. E. Strebel, *SPE Tech. Papers,* **7**(3), 4 (1961).
3. I. B. Johns and H. R. Dipietro, *Proceedings of the Conference on High Temperature Polymer and Fluid Research, Polymer Branch, USAF ASD-TRD-62-372,* 77 (1962).
4. G. de Gaudemaris and B. Sillion, *Rev. Inst. Franc. Petrole Ann. Combust. Liquides,* **20,** 690 (1965).
5. I. C. Lewis and T. Edstron, *J. Org. Chem.,* **28,** 2050 (1963).
6. R. Phillips and W. Wright, *J. Polymer Sci.,* **B2,** 47 (1964).

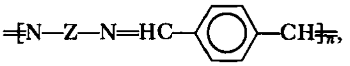
7. *Chem. Week*, **95**, 46 (1961).
8. J. I. Jones, F. W. Ochynski, and F. A. Rackley, *Chem. Ind. (London)*, **1962**, 1686.
9. C. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Ber, W. M. Edwards, and K. L. Olivier, *J. Polymer Sci.*, **A3**, 1373 (1965).
10. K. C. Brinker and I. M. Robinson, U.S. Pat. 2,895,984 (July 1959).
11. H. Vogel and C. S. Marvel, *J. Polymer Sci.*, **50**, 511 (1961).
12. H. Vogel and C. S. Marvel, *J. Polymer Sci.*, **A1**, 1531 (1963).
13. M. M. Koton, *Russ. Chem. Rev.* **31**, 81 (1962).
14. C. S. Marvel and G. E. Hartzell, *J. Am. Chem. Soc.*, **81**, 488 (1959).
15. P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.*, **85**, 454 (1963).
16. G. F. D'Alelio, L. Mallavarapu, T. F. Huemmer, T. Kurosaki, W. Fessler, and J. V. Crivello, *NASA Rept. N65-33776* (1964).
17. C. S. Marvel and N. Tarköy, *J. Am. Chem. Soc.*, **79**, 6000 (1957).
18. C. S. Marvel and N. Tarköy, *J. Am. Chem. Soc.*, **80**, 832 (1958).
19. C. S. Marvel and P. V. Bonsignore, *J. Am. Chem. Soc.*, **81**, 2668 (1959).
20. J. W. Akitt, F. W. Kayem, B. E. Lee, and A. M. North, *Makromol. Chem.*, **56**, 195 (1962).
21. A. V. Topchiev, U. V. Korshak, V. A. Popov, and L. D. Rosenstein, *J. Polymer Sci.*, **C1**, 305 (1963).
22. S. S. Stivala, G. R. Sacco, and L. Reich, *Polymer Letters*, **2**, 943 (1964).
23. A. I. Vogel, *A Textbook of Practical Organic Chemistry*, Longmans, Green, London, 1954, p. 923.
24. R. McDonald and T. Campbell, *J. Organic Chem.*, **24**, 1246 (1959).
25. R. McDonald and T. Campbell, *J. Am. Chem. Soc.*, **82**, 4669 (1960).
26. G. F. D'Alelio, *Fundamental Studies on Heat-Resistant Polymers, Status Rept. 1, NASA Grant NsG339* (1963).
27. G. F. D'Alelio, *Fundamental Studies on Heat-Resistant Polymers, Status Rept. 2, NASA Grant NsG339* (1963).
28. C. K. Ingold, *J. Chem. Soc.*, **127**, 1141 (1925).
29. G. Reddelien, *Ber.*, **54B**, 3121 (1921).
30. B. A. Porai Korshits and A. L. Remizov, *Sb. Statei Obshch. Khim.*, **2**, 1570 (1953).
31. G. F. D'Alelio, J. V. Crivello, T. Kurosaki, and R. K. Schoenig, *J. Macromol. Sci.*, **A1**(7), 1259 (1967).
32. G. F. D'Alelio, T. Kurosaki, and R. K. Schoenig, *J. Macromol. Sci.*, **A1**(7), 1279 (1967).
33. R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).
34. G. F. D'Alelio, R. K. Schoenig, T. F. Huemmer, and A. Raghunath, *J. Macromol. Sci.*, **A1**(7), 1299 (1967).
35. G. F. D'Alelio and J. M. Hornback, *J. Macromol. Sci.*, **A2** (1968), in press.
36. G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.*, **A1**(7), 1251 (1967).
37. B. E. Davidov, B. A. Krentsel, V. A. Popov, and W. V. Prokofieva, *Vysokomolekul. Soedin.*, **5**(3), 321 (1963).
38. These color changes have been documented in NASA Educational Film,

HQ143, *The Poetry of Polymers: An Adventure in Research,* available on request from Educational Division, Headquarters, National Aeronautics and Space Administration, Washington, D.C.

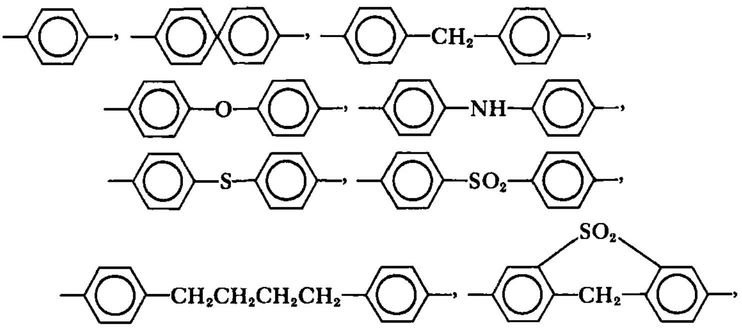
39. A. Lowy and T. B. Downey, *J. Am. Chem. Soc.,* **43,** 346 (1921).
40. E. Abderhalden, *Fermentforsch.,* **15,** 522 (1938).
41. H. Bucherer and A. Schwalbe, *Ber.,* **39,** 2796 (1906).
42. G. Goldschmidt, *Chem. Ztg.,* **27,** 395 (1903).
43. L. Henry, *Compt. Rend.,* **23,** 401 (1904).
44. E. Knoevenagel, *Ber.,* **38,** 213 (1905).
45. R. Lepetit, *Atti Real. Accad. Lincei,* **26**(5), 126, 172 (1917).
46. O. Wallach, *Ann.,* **343,** 54 (1905).
47. E. Staple and E. C. Wagner, *J. Org. Chem.,* **14,** 559 (1949).
48. R. Leuckart, *Ber.,* **18,** 2341 (1885).
49. K. Loeffler, *Ber.,* **43,** 2035 (1910).
50. J. B. Edeley, M. C. Swisher, and C. C. Johnson, *Gazz. Chem. Ital.,* **62,** 81 (1932).
51. H. R. Snyder, R. H. Levin, and P. F. Wiley, *J. Am. Chem. Soc.,* **60,** 2025 (1938).
52. O. Dimroth and R. Zoepritz, *Ber.,* **35,** 984 (1902).
53. G. F. D'Alelio, T. F. Huemmer and R. K. Schoenig, unpublished results.
54. G. F. D'Alelio, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.,* **A1**(7), 1321 (1967).
55. L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules,* Wiley, New York, 1962, p. 267.
56. L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules,* Wiley, New York, 1962, p. 270.
57. S. D. F. Orr and H. W. Thompson, *J. Chem. Soc.,* **1950,** 218.
58. *Infrared Spectrograms 15224-15226,* Sadtler Standard Spectra, Midget Edition, Sadtler Research Laboratories, Philadelphia, 1959.
59. G. Pyl, *Ber.,* **60,** 287 (1927).
60. G. M. Badger, C. P. Joshua, and G. E. Lewis, *Tetrahedron Letters,* **1964,** 3711.
61. S. D. Bruck, *Polymer,* **6**(6), 319 (1965).
62. E. Clar, *Aromatische Kohlenswasserstoffe,* 2nd, ed., Springer, Berlin, 1952.
63. F. T. Wallenberger, *Angew Chem. Intern. Ed.,* **3,** 461 (1964).
64. G. F. D'Alelio, J. V. Crivello, and T. R. Dehner, *J. Macromol. Sci.,* **A1,** 1331 (1967).
65. P. J. Flory, *Principles of Polymer Chemistry,* Cornell Univ. Press, Ithaca, N.Y., 1953, p. 337.
66. G. F. Pezdirtz and V. L. Bell, *NASA Tech. Notes, NASA-TN-D-3148* (1965).
67. V. L. Bell and G. F. Pezdirtz, *J. Polymer Sci.,* **B6**(2), 742 (1965).
68. W. Fessler, thesis, University of Notre Dame, Notre Dame, Ind., 1966.
69. G. F. D'Alelio and R. K. Schoenig, *The Synthesis of Polymeric Azines,* to be published.
70. G. F. Pezdirtz, private communication.
71. L. Bonnot and G. Lefebvre, *Rev. Inst. Franc. Petrole Ann. Combust. Liquides,* **17,** 1508 (1962).
72. R. L. Van Deusen, *Polymer Letters,* **4,** 211 (1966).
73. P. J. Flory, *J. Am. Chem. Soc.,* **58,** 1877 (1936).
74. L. Henry, *Rec. Trav. Chem.,* **23,** 401 (1904).

75. W. von Miller and J. Plochl, *Ber.*, **25**, 2020 (1892).
76. K. Tiemanor and K. Prest, *Ber.*, **15**, 2028 (1882).
77. R. Tiollais, *Bull. Soc. Chim. France*, **1947**, 959.
78. H. Deker and P. Becker, *Ann.*, **395**, 362 (1913).
79. R. M. Herbst and L. L. Engel, *J. Biol. Chem.*, **107**, 505 (1934).
80. M. Busch, *Ber.*, **37**, 2691 (1904).
81. H. Gilman and R. H. Kirby, *J. Am. Chem. Soc.*, **55**, 1265 (1933).
82. R. B. Moffet and W. H. Hoehn, *J. Am. Chem. Soc.*, **69**, 1792 (1947).
83. C. Mayer, *Bull. Soc. Chim. France*, **33**(2), 157 (1905).
84. H. Snyder, H. A. Kornberg, and J. R. Romig, *J. Am. Chem. Soc.*, **61**, 3556 (1939).
85. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N.Y., 1953, p. 317.
86. C. K. Ingold and H. A. Piggot, *J. Chem. Soc.*, **2**, 2793 (1922).
87. E. M. Fettes, (ed.), *Chemical Reactions of Polymers*, Wiley (Interscience), New York, 1964.
88. G. W. Wheland, *Resonance in Organic Chemistry*, Wiley, New York, 1966, p. 257.
89. A. Weissberger, *Techniques of Organic Chemistry*, Vol. 9, Wiley (Interscience), New York, 1956, p. 654.
90. A. E. Gillam and D. H. Hey, *J. Chem. Soc.*, **1939**, 1170.
91. M. Becker, *Polymers as Conductors and Semiconductors*, Polytechnic Institute of Brooklyn, 1961.
92. W. B. Hannay, *Semiconductors, American Chemical Society Monograph*, Reinhold, New York, 1959.
93. E. J. Lawton, J. S. Balivit, and R. S. Powell, *J. Chem. Phys.*, **33**, 405 (1960).
94. F. H. Winslow, W. O. Baker, and W. A. Wager, *J. Am. Chem. Soc.*, **77**, 4751 (1955).

Zusammenfassung

Diese Arbeit vergleicht die Synthesen und die thermischen Stabilitäten von zwölf verwandten, konjugierten, pseudokonjugierten und nicht-konjugierten polymeren Schiff'schen Basen von der allgemeinen Formel: 

, wobei Z die folgenden Gruppen darstellt:



$—(CH_2)_4—$, und $—(CH_2)_6—$.

Die Polymeren wurden folgendermassen dargestellt: (a) durch Kondensation von $Z(NH_2)_2$ mit p-$C_6H_4(CHO)_2$ in (1) Lösung und (b) in der Schmelze, und (b) mittels dreier neuer Schiff'Basenaustauschreaktionen: (1) durch Aldehydaustausch:

$$nOHCC_6H_4CHO + nC_6H_5CH{=}N{-}Z{-}N{=}NCC_6H_5 \rightleftharpoons$$
$$(2n-1)C_6H_5CHO + C_6H_5CH{=}[N{-}Z{-}N{=}HCC_6H_4CH]_n{=}O$$

(2) durch Aminaustausch:

$$nH_2N{-}Z{-}NH_2 + nC_6H_5N{=}HCC_6H_4CH{=}NC_6H_5 \rightleftharpoons$$
$$(2n-1)C_6H_5NH_2 + H_2{=}[N{-}Z{-}N{=}HCC_6H_4CH]_n{=}NC_6H_5$$

und (3) durch zweifachen Austausch:

$$nC_6H_5N{=}HCC_6H_4CH{=}NC_6H_5 + nC_6H_5CH{=}N{-}Z{-}N{=}HCC_6H_5 \rightleftharpoons$$
$$(2n-1)C_6H_5CH{=}NC_6H_5 + C_6H_5CH{=}[N{-}Z{-}N{=}HCC_6H_4CH]_n{=}NC_6H_5$$

Die nichtkonjugierten Polymeren wurden in bequemer Weise in Lösung durch Reaktion der aliphatischen Diamine, $H_2N(CH_2)_nNH_2$, mit Terephtalaldehyd als auch mittels der zweifachen Austauschreaktion dargestellt. Die erhaltenen Produkte waren weiss bis cremefarben und hatten thermische Stabilitäten von ca. 300°C in Stickstoff und 250°C in Luft.

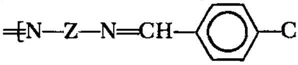
Die in Lösung durchgeführten Kondensationen von konjugierten und pseudokonjugierten Diaminen mit Terephtalaldehyd ergaben gelbe, niedermolekulare, spröde, unschmelzbare Polymere von Ziegelstaubartiger Beschaffenheit. Hingegen ergab die Polymerisation in der Schmelze nach Durchgang eines schmelzbaren, duktilen Zustandes hochkonjugierte, schwarze Polymere von relativ hoher thermischer Stabilität. Diese in der Schmelze durchgeführten Polymerisationen waren schwer zu handhaben. Die Polymeren wurden jedoch sehr leicht nach der Schiff'Basenaustauschreaktion hergestellt, wobei der zweifache Austausch der Prozess war, der am leichtesten gehandhabt werden konnte.

Die Methode des zweifachen Austausches ergab schmelzbare, duktile Polymere, die sukzessive Farbänderungen von gelb nach orange über rot nach braun und schwarz durchliefen; bei fortgesetztem Erhitzen wurden die Polymeren unschmelzbar. Die thermischen Stabilitäten dieser Polymeren hängen von der Maximaltemperatur ab, bei welcher die Kondensationen durchgeführt wurden. Es ergab sich, dass die Polykondensation bei Temperaturen bis zu 400° unvollständig ist, obwohl die thermischen Stabilitäten der auf diese Weise dargestellen Stoffe im Bereich von 500 bis 550°C in Stickstoff und 430 bis 480°C in Luft lagen. Wenn die Kondensation bei 600° durchgeführt wurde, ergaben die Polymeren bei 700° in Stickstoff einen Gewichtsverlust von weniger als 5% und bei 1176° von weniger als 18%; die thermischen Stabilitäten in Luft lagen im Bereich von 510 bis 550°C. Wenn die Kondensation bis zu Temperaturen von 700° durchgeführt wurde, oder bei höherer Temperatur, entwickelte sich Wasserstoff, was wahrscheinlich auf die intramolekulare Bildung von carbocyklischen, heterocyklischen Phenantridinstrukturen zurückgeführt werden dürfte. Wenn die Kondensation bis zu 1176°C durchgeführt wurde, zeigten die

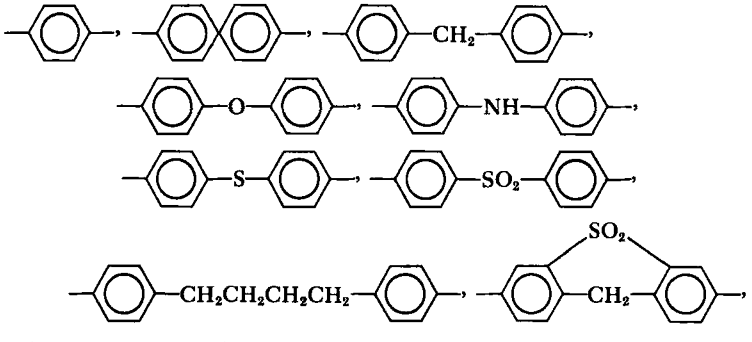
Produkte in Stickstoff thermische Stabilitäten von über 110°C und in Luft im Bereich von 440 bis 600°C. Die höchste thermische Stabilität hatte ein vollständig konjugiertes Poly(*p*-xylyliden-*p*-phenylendiamin).

Résumé

Dans cette note on compare les synthèses et les stabilités thermiques de douze polymères similaires de bases de Schiff, conjugués, pseudo-conjugués, et non-conjugués, d'une formule générale



$=\!\![N{-}Z{-}N{=}CH{-}C_6H_4{-}CH]_n\!\!=$, dans laquele Z représente



—$(CH_2)_4$—, et —$(CH_2)_6$—.

On a preparé les polymères par (a) la condensation de $Z(NH_2)_2$ et p-$C_6H_4(CHO)_2$ en (1) solution et (2) en fusion, et (b) par trois réactions d'échange nouvelles des bases de Schiff: (1) l'échange d'aldéhyde:

$$nOHCC_6H_4CHO + nC_6H_5CH{=}N{-}Z{-}N{=}HCC_6H_5 \rightleftharpoons (2n-1)C_6H_5CHO + C_6H_5CH{=}[N{-}Z{-}N{=}HCC_6H_4CH]_n{=}O$$

(2) échange d'amine:

$$nH_2N{-}Z{-}NH_2 + nC_6H_5N{=}HCC_6H_4CH{=}NC_6H_5 \rightleftharpoons (2n-1)C_6H_5NH_2 + H_2{=}[N{-}Z{-}N{=}HCC_6H_4CH]_n{=}NC_6H_5$$

et (3) l'échange bis:

$$nC_6H_5N{=}HCC_6H_4CH{=}NC_6H_5 + nC_6H_5CH{=}N{-}Z{-}N{=}HCC_6H_5 \rightleftharpoons (2n-1)C_6H_5CH{=}NC_6H_5 + C_6H_5CH{=}[N{-}Z{-}N{=}HCC_6H_4CH]_n{=}NC_6H_5$$

Les polymères non-conjugués sont preparés facilement en solution par la réaction des diamines aliphatiques $H_2N(CH_2)_nNH_2$ avec l'aldéhyde terephthalique et aussi par le methode d'échange bis; ce sont des corps de couleur blanche ou ivoire, et de stabilités thermiques d'environ 300°C dans l'azote et 250°C dans l'air. La condensation en solution des diamines conjugués et pseudo-conjugués avec l'aldéhyde terephthalique donne des polymères jaunes, à bas point de fusion, intraitables, infusibles, poussiéreux. La polymerisation en fusion donne, apres passage par un stade fusible, traitable, des polymères noirs, très conjugués, avec des stabilités thermiques relativement élevées. Ces polymérisations en fusion étaient difficiles à controller. Cependant, on a preparé ces polymeres très facilement par les réaction d'échange des bases de Schiff. Parmi celles l'échange bis est le plus moderé et le plus facile à controller.

La polymerisation d'échange bis donne des polymères fusibles, traitables, dont la couleur change progrèssivement de jaune en orange en rouge et brun jusqu'au noir. Par chauffage continue le polymères noirs deviennent infusibles. Les stabilités thermiques de ces polymères dépendent de la température maxima de la condensation. On a montré que la polycondensation est incomplete jusqu'à 400°C, mais les stabilités thermiques des polymères étaient dans l'intervale de 500 à 550°C dans l'azote, et 430 à 480°C dans l'air. Condensés à 600°C les polymeres montrent une perte de poids de moins de 5% dans l'azote à 700°C et de moins de 18% à 1176°C; les stabilités thermiques dans l'air étaient dans l'intervale de 510 à 550°C. Lorsque la condensation est effectuée aux températures excedant 700°C ou plus elevées, l'hydrogène s'élimine, très probablement comme résultat de la formation intamoléculaire des structures carbocycliques-hétèrocycliques de phenanthridine. Condensés à 1176°C les polymères montrent des stabilités thermiques dans l'azote excedant 1100°C, et dans l'air un intervale de 440 à 600°C. La stabilité thermique la plus elevée appartient à la poly(*p*-xylylidène-*p*-phénylènediamine) completement conjuguée.

Received by editor April 5, 1967
Submitted for publication August 22, 1967