Polymeric Schiff Bases. VIII. The Synthesis and Evaluation of Polyketanils

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Summary

The condensation of aryldiketones, $Ar'(COCH_3)_2$, with aryldiamines, $Ar''(NH_2)_2$, in solution produces yellowish-brick-dust, insoluble polymers. Black tractable polymers are obtained by (1) melt condensation of the diketones with diamines alone, or (2) in the presence of the monomeric azomethines, $C_6H_5CH=NC_6H_5$ or

$$C_6H_5\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{C}=NC_6H_5,$$ or (3) in the presence of aniline and the carbonyl

compound, $C_6H_5\overset{\overset{\displaystyle R}{\displaystyle |}}{C}=O$, from which the monomeric azomethines were derived, or by (4) the amine-, (5) the keto-, or (6) the bis-exchange reactions. Continued condensation in nitrogen to 400, 600, and 1176°C yields insoluble, infusible, black polymers whose thermal stabilities closely approximate those of the polymeric Schiff bases.

In previous papers [1-5], the synthesis and the evaluation of the thermal stabilities of polymeric Schiff bases of the general structure ⧧HC—Ar'CH=NAr''N⧧ₙ (I), in which Ar' and Ar'' are aryl moieties, were described. The thermal stabilities of the polymeric Schiff bases were shown [1-5] to be relatively high and to be dependent to some degree on the extent and type of conjugation in the Ar' and Ar'' moieties. The fully conjugated Schiff base poly-

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*Abstracted in part from the B.S. Thesis of J. M. Hornback, NSF Undergraduate Research Participant 1964-1965.
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mers were found to possess the highest thermal stabilities, which were closely approximated by some of the pseudo-conjugated polymers. The nonconjugated polymers, in which Ar″ consisted of aliphatic linkages, $+CH_2+_n$, were lowest in the thermal stability scale. Meta- and para-position isomerism in the Ar′ and Ar″ structures was found to influence stability only to a minor degree. This was shown [3] in the evaluation of the thermal stabilities of the four isomeric, para-para- para-meta-, meta-para-, and meta-meta-xylylidenephenylenediamine polymers, $+HCC_6H_4CH=NC_6H_4N+_n$.

Since the presence of aliphatic groups in the Schiff base polymers, such as in $+HCC_6H_4CH=NC_6H_4(CH_2)_4C_6H_4N+_n$ and $+HCC_6H_4CH=N(CH_2)_4N+_n$, was shown [1] to produce polymers of much lower thermal stabilities than the reference polyxylylidenephenylenediamines, it was considered advisable to determine the effect on thermal stabilities of the polymers when an aliphatic hydrocarbon group is substituted for the hydrogens in the xylylidene moiety. Such a substitution would yield ketanil derivatives of the formula $+CAr'C=NAr''N+_n$ (with R substituents) (II), which obviously are closely related to the Schiff bases.

The published literature on the polyketanils is very meager. The synthesis of the simplest parent ketanil, $+C-C_6H_4C=NC_6H_4N+_n$ (with CH_3 substituents), does not appear to have been reported. During the course of our studies, the polycondensations of p-phenylenediamine with each of two substituted diketones, $CH_3CO-C_6H_4-CH_2-C_6H_4-OCCH_3$ and $CH_3CO-C_6H_4-O-C_6H_4-OCCH_3$, were reported [6] as yielding respectively a dark blue product melting at 96–100°C, and a brown product, melting point 98–100°C; the condensation products were of relatively low molecular weight of the order of about 1000, and soluble in dimethylacetamide, formic, acetic, and sulfuric acids. The details of synthesis, however, were not described [6]. By analogy to the polymeric Schiff bases, black, relatively highly thermally stable polymers should be expected when the conjugation in the polyketanils is sufficiently extensive. Our preliminary studies had shown that the condensation of p-diacetyl benzene with a number of arylenediamines by the continuous azeotrope method [7] in benzene yield infusible, intractable, brick-dust polymers ranging in color from yellow to brown. Since such polymers have little or no utility, tractable polyketanils would comprise a class of desirable polymers, if they possessed relatively high thermal stabilities. Accordingly, studies were undertaken to synthesize some black polyketanils, (II), and to compare their thermal stabilities with the Schiff base poly-

mers, (I). To minimize the probability of degradation in the aliphatic R groups, either by oxidation or pyrolysis, the methyl group was selected in this study as the R group in the polyketanils,

$$\left. = \!\!\!\begin{array}{c} CH_3 \\ | \\ C \end{array}\!\!\!-\!\!\!\left\langle \bigcirc \right\rangle\!\!\!-\!\!\!\begin{array}{c} CH_3 \\ | \\ C \end{array}\!\!\!=\!NAr''N\!=\!\!\!\right\}_n, (III).$$
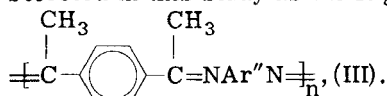
The syntheses of the polyketanils investigated parallel those used [1, 3, 4, 8] for the polymeric Schiff bases:

1. By the direct condensation of aryldiamines with aryldiketones as melts or in solution:

$$nCH_3COC_6H_4OCCH_3 + nH_2NAr''NH_2 \rightarrow$$

$$O\!=\!\!\!\begin{array}{cc} CH_3 & CH_3 \\ | & | \\ CC_6H_4C \end{array}\!\!\!=\!\!NAr''N\!=\!\!\!\Big\}_n H_2 + (n-1)H_2O \qquad (1)$$
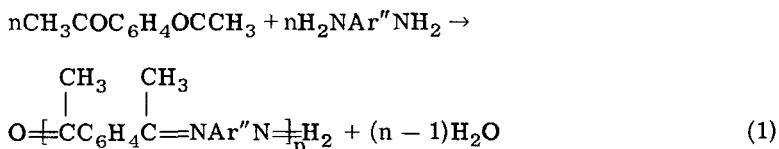
2. By the amine exchange [1, 8] reaction:

$$nH_5C_6N\!=\!\!\!\begin{array}{cc} CH_3 & CH_3 \\ | & | \\ C\!-\!C_6H_4C \end{array}\!\!\!=\!\!NC_6H_5 + nH_2NAr''NH_2 \rightarrow$$

$$H_5C_6N\!=\!\!\!\begin{array}{cc} CH_3 & CH_3 \\ | & | \\ C\!\!-\!\!-\!C_6H_4C \end{array}\!\!\!=\!\!NAr''N\!=\!\!\!\Big\}_n H_2 + (n-1)C_6H_5NH_2 \qquad (2)$$
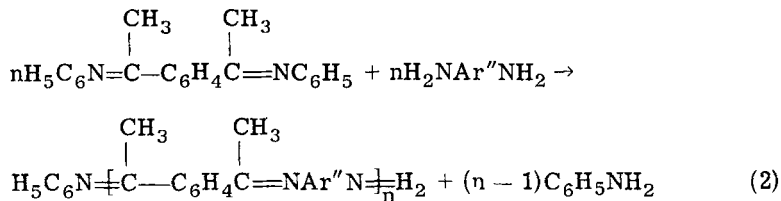
3. By the ketone exchange [1, 8] reaction:

$$nCH_3COC_6H_4OCCH_3 + nC_6H_5\!\!\!\begin{array}{c} CH_3 \\ | \\ C \end{array}\!\!\!=\!\!NAr''N\!=\!\!\!\begin{array}{c} CH_3 \\ | \\ C \end{array}\!\!\!-\!\!C_6H_5 \rightarrow$$

$$O\!=\!\!\!\begin{array}{ccc} CH_3 & CH_3 & CH_3 \\ | & | & | \\ C\!-\!\!-\!C_6H_4C & =\!\!NAr''N\!=\!\!\!\Big\}_n C & \!-\!\!-\!C_6H_5 \end{array} + (n-1)CH_3COC_6H_5 \qquad (3)$$
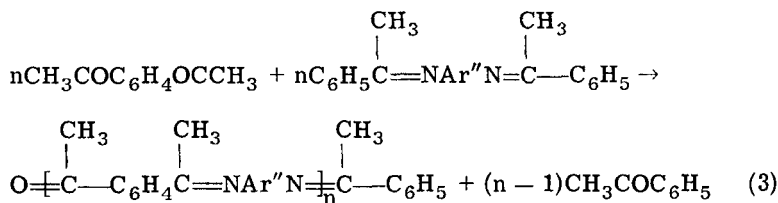
4. By the bis exchange [1, 8] reaction:

$$nH_5C_6N\!=\!\!\!\begin{array}{cc} CH_3 & CH_3 \\ | & | \\ C\!-\!\!-\!C_6H_4C \end{array}\!\!\!=\!\!NC_6H_5 + nC_6H_5\!\!\!\begin{array}{cc} CH_3 & CH_3 \\ | & | \\ C\!=\!\!NAr''N\!=\!C & \!-\!\!-\!C_6H_5 \end{array} \rightarrow$$

$$\underset{\substack{| \\ CH_3}}{C_6H_5N=\!\!\!\!\!\!\mid\!C}-C_6H_4\underset{\substack{| \\ CH_3}}{C}=NAr''N=\!\!\!\!\!\!\mid\!\!\!\underset{\substack{| \\ CH_3}}{\overset{n}{C}}-C_6H_5 \; +$$
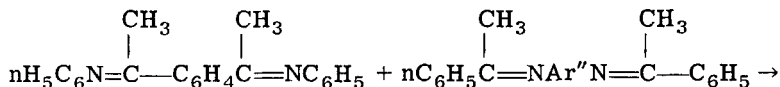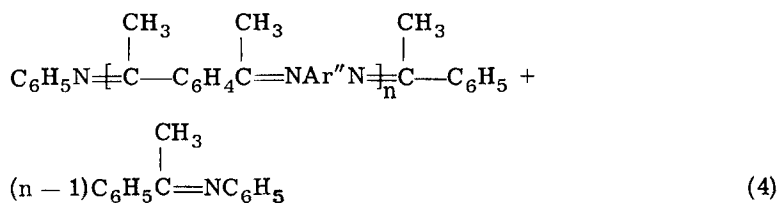
$$(n-1)C_6H_5\underset{\substack{| \\ CH_3}}{C}=NC_6H_5 \qquad\qquad (4)$$

5. By the direct synthesis from the diketone and the diamine in

a monomeric azomethine (4) $C_6H_5\underset{\substack{| \\ R}}{C}=NC_6H_5$ such as

$C_6H_5CH=NC_6H_5$ and $C_6H_5\underset{\substack{| \\ R}}{C}=NC_6H_5$ or in a mixture (4) of the

carbonyl compound, $C_6H_5\underset{\substack{| \\ R}}{C}=O$, and the amine, $C_6H_5NH_2$, from which
the monomeric azomethine was derived:

$$nCH_3COC_6H_4COCH_3 + nH_2NAr''NH_2 \xrightarrow{\begin{array}{c} C_6H_5\underset{\substack{| \\ R}}{C}=NC_6H_5 \text{ or} \\ \hline C_6H_5\underset{\substack{| \\ R}}{C}=O + C_6H_5NH_2 \end{array}}$$

$$\underset{\substack{| \\ CH_3}}{C_6H_5N=\!\!\!\!\!\!\mid\!C}-C_6H_4\underset{\substack{| \\ CH_3}}{C}=NAr''N=\!\!\!\!\!\!\mid\!\!\!\underset{\substack{| \\ R}}{\overset{n}{C}}C_6H_5 \qquad\qquad (5)$$
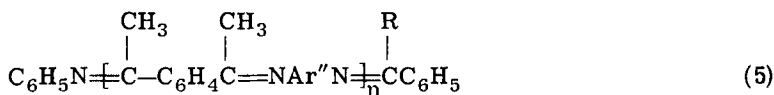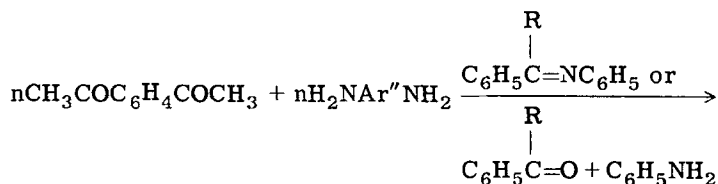
The use of di-Schiff bases [1, 8], $C_6H_5CH=NAr''N=HCC_6H_5$,

instead of the ketanils, $C_6H_5\underset{\substack{| \\ CH_3}}{C}=NAr''N=\underset{\substack{| \\ CH_3}}{C}-C_6H_5$, used in Eqs.
(3) and (4) was also evaluated, in which cases, an aldehyde [Eq. (6)]
and a mono-Schiff base [Eq. (7)], respectively, are produced as by-
products, instead of a ketone and a ketanil, respectively:

$$nCH_3COC_6H_4COCH_3 + nC_6H_5CH=NAr''N=HCC_6H_5 \rightarrow$$

$$O=\!\!\!\!\!\!\mid\!\!\!\underset{\substack{| \\ CH_3}}{C}-C_6H_4\underset{\substack{| \\ CH_3}}{C}=NAr''N=\!\!\!\!\!\!\mid\!\!\!\overset{n}{HC}C_6H_5 + (n-1)C_6H_5CHO \qquad (6)$$

$$nC_6H_5N=\underset{\underset{CH_3}{|}}{C}{-}C_6H_4\underset{\underset{CH_3}{|}}{C}=NC_6H_5 + nC_6H_5CH=NAr''N=HCC_6H_5 \rightarrow$$

$$H_5C_6N=\underset{\underset{CH_3}{|}}{C}{-}C_6H_4\underset{\underset{CH_3}{|}}{C}=NAr''N\underset{\overline{n}}{=}HCC_6H_5 + (n-1)C_6H_5CH=NC_6H_5$$

$$(7)$$
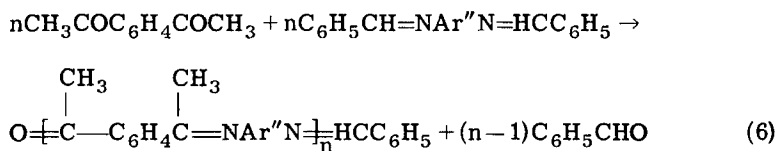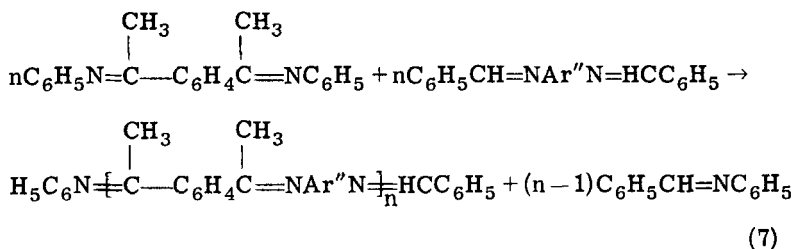
The application of the amine, carbonyl, and bis exchange reactions of ketanils for the synthesis of polymers does not appear to have been reported previously.
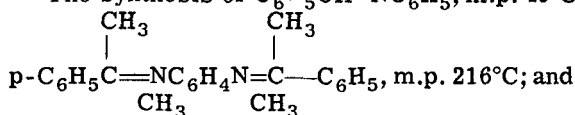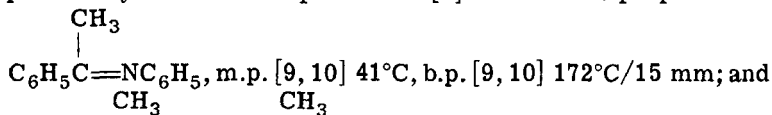
EXPERIMENTAL

Monomers

The synthesis of $C_6H_5CH=NC_6H_5$, m.p. 49°C;

$$p{-}C_6H_5\underset{\underset{CH_3}{|}}{C}=NC_6H_4N=\underset{\underset{CH_3}{|}}{C}{-}C_6H_5, \text{ m.p. } 216°C; \text{ and}$$

$$p{-}C_6H_5N=\underset{\underset{CH_3}{|}}{C}{-}C_6H_4\underset{\underset{CH_3}{|}}{C}=NC_6H_5, \text{ m.p. } 214°C, \text{ have been reported [7]}$$

previously. The azeotrope method [7] was used to prepare

$$C_6H_5\underset{\underset{CH_3}{|}}{C}=NC_6H_5, \text{ m.p. } [9,10]\ 41°C, \text{ b.p. } [9,10]\ 172°C/15 \text{ mm; and}$$

$$m{-}C_6H_5\underset{\underset{CH_3}{|}}{C}=NC_6H_4N=\underset{\underset{CH_3}{|}}{C}{-}C_6H_5, \text{ m.p. } 28°C.$$

Analysis: Calcd. for $C_{22}H_{20}N_2$: C, 84.62; H, 6.41; N, 8.97
Found: C, 84.55; H, 6.46; N, 8.92

p-Diacetylbenzene, m.p. 114–114.5°C, was purchased from Aldrich Chemical Company, Inc., and recrystallized from benzene–ethanol, p, p'-diacetyldiphenyl methane [11], m.p. 95.1°C, p, p'-diacetyldiphenyl oxide [12], m.p. 101.5°C, and p, p'-diacetyldiphenyl sulfide [13], m.p. 91.2°C, were prepared by published procedures [11–13].

The p, p'-diacetyl sulfone, m.p. 161–163°C, was prepared by oxidizing [14] the corresponding sulfide [13] with hydrogen peroxide in acetic acid.

Analysis: Calcd. for $C_{16}H_{14}O_4S$: C, 63.58; H, 4.64; S, 10.59
Found: C, 62.29; H, 4.67; S, 10.64

Typical infrared spectra of the monomers are illustrated in Fig. 1 for p-$CH_3COC_6H_4COCH_3$, in Fig. 2 for

$$p\text{-}C_6H_5 \overset{\overset{\displaystyle CH_3}{\displaystyle |}}{C}=NC_6H_4N=\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{C}-C_6H_5, \text{ and in Fig. 3 for}$$

$$C_6H_5N=\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{C}-C_6H_4-\overset{\overset{\displaystyle CH_3}{\displaystyle |}}{C}=NC_6H_5.$$
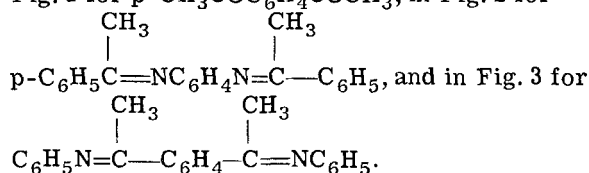
Polymerizations

Procedures similar to those previously published [1, 4, 5] for the synthesis of the polymeric Schiff bases were used. The following typical procedures are included to illustrate the differences found in the reactions of the aldehydes in the synthesis of the poly-Schiff bases and in the ketones in the preparation of the polyketanils.

Polymerization in Solution

Azeotrope Method [1] (a) The apparatus has been previously described [1]. A mixture of 1.62 g (0.01 mole) of p-diacetylbenzene, 1.08 g (0.01 mole) of m-phenylenediamine, and 170 ml of benzene was introduced into the reaction flask and the mixture heated under a nitrogen atmosphere to reflux temperature. After 2 hr of reaction, no water was collected in the Dean–Stark trap, and the reaction solution had acquired only a slightly yellow color. At this point, a catalytic amount of p-toluenesulfonic acid, 0.01 g, was added to the reaction mixture and the mixture heated at reflux for an additional 20 hr, and only a trace of water was collected in the Dean–Stark trap, although the yellow color of the reaction solution had deepened slightly. The reaction was terminated at this time.

(b) A mixture of 1.62 g (0.01 mole) of p-diacetylbenzene, 1.08 g (0.01 mole) of m-phenylenediamine, 0.01 g of p-toluenesulfonic acid, and 100 ml of benzene was reacted at reflux temperature for 24 hr. During the course of the reaction the color of the solution became intensely yellow and polymer product precipitated in the flask; 0.135 ml of water was collected in the trap. The mixture was allowed to cool to room temperature, the solid was isolated by filtration, washed with benzene, and dried in a vacuum oven at room temperature, yielding 1.79 g (71%) of a yellow brick-dust polymer. The polymer did not melt when exposed to the heat of a bunsen burner flame; it was insoluble in common organic solvents but soluble in formic acid and concentrated sulfuric acid. The infrared spectrum, Fig. 4, was recorded using the KBr disc technique.

(c) A mixture of 1.62 g (0.01 mole) of p-diacetyl benzene, 1.08 g (0.01 mole) of p-phenylenediamine, 0.01 g of p-toluenesulfonic acid, and 90 ml of benzene were reacted at reflux temperature
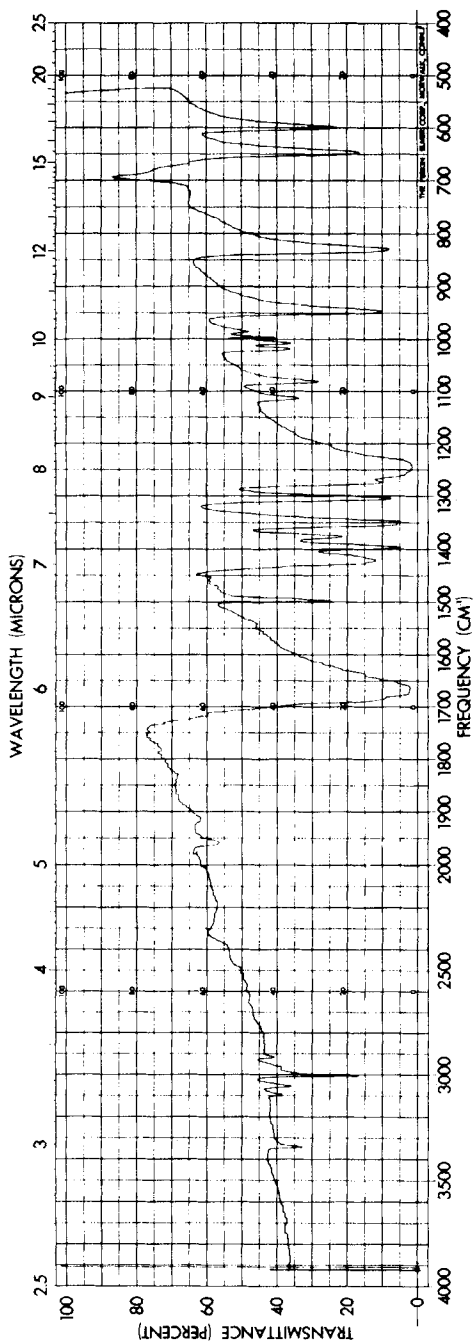
FIG. 1. Infrared spectra of p—CH$_3$COC$_6$H$_4$OCCH$_3$. KBr disc.
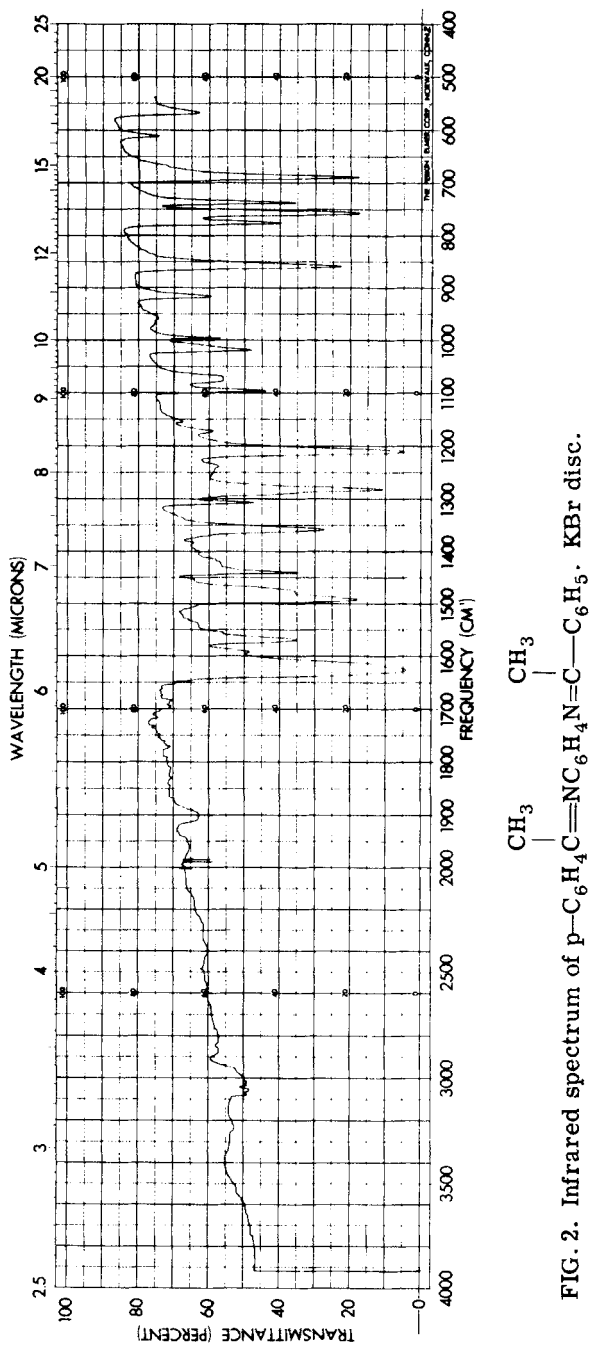
FIG. 2. Infrared spectrum of p—C_6H_4C=NC_6H_4N=C—C_6H_5. KBr disc.
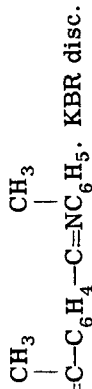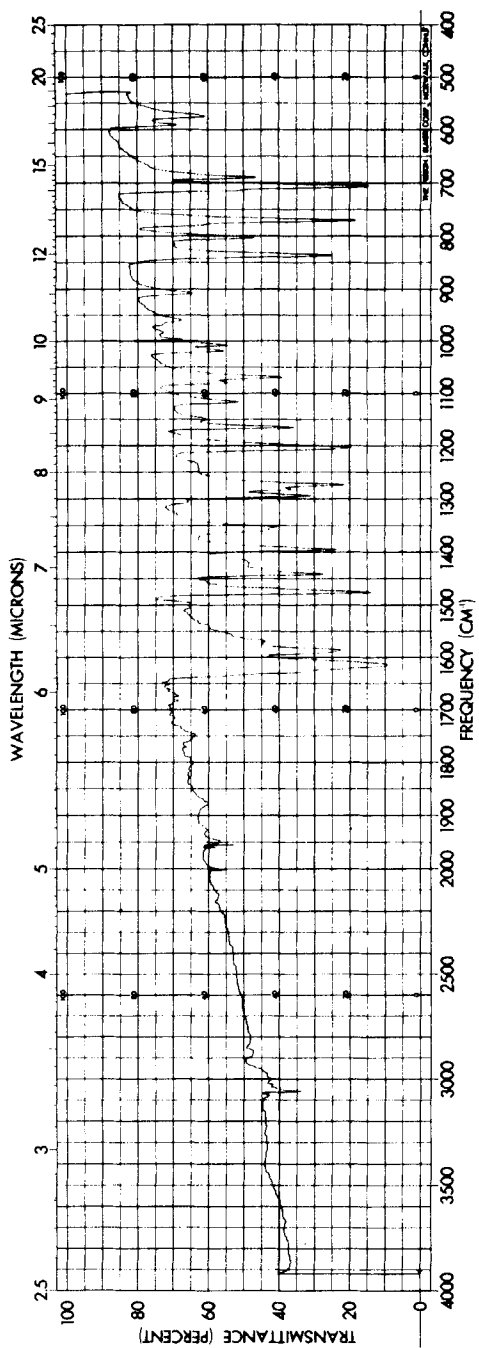
FIG. 3. Infrared spectrum of p-$C_6H_5N=C-C_6H_4-C=NC_6H_5$. KBR disc.

with CH$_3$ groups labeled above:

$$CH_3 \qquad CH_3$$
$$| \qquad\qquad |$$
$$\text{p-}C_6H_5N=C-C_6H_4-C=NC_6H_5$$
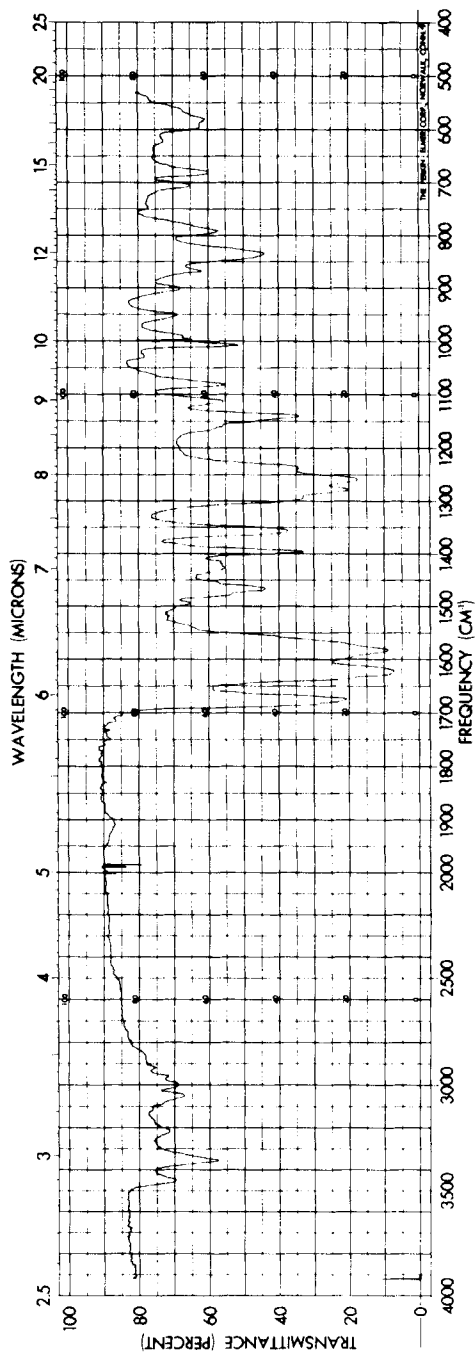
FIG. 4. Infrared spectrum of yellow polymer

$$O=C-C_6H_4-C(CH_3)=N-C_6H_4-N\!\!+\!\!_n.$$ KBr disc.
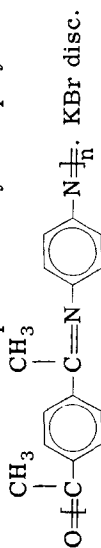
for 46 hr; 0. 96 ml of water was collected in the trap and the color of the solution, which contained a solid polymer, was bright orange. The solid polymer (a) was removed by filtration, washed with benzene and dried; it was a yellow-brown, brick-dust polymer (yield 1. 08 g, 42. 5%) which did not melt at 300°C and was insoluble in common organic solvents but soluble in formic acid and concentrated sulfuric acid. Its infrared spectrum is shown in Fig. 5.

The orange-colored benzene filtrate was concentrated at 15 mm Hg pressure at room temperature, yielding a yellow-orange solid (b), which was washed with carbon tetrachloride and dried; yield, 1. 16 g (46%). The yellow-orange solid, designated as polymer 2-Y-O, melted at about 90°C, was slightly soluble in chloroform, carbon tetrachloride, tetrachloroethane, dimethylformamide, dimethylacetamide, phenol, m-cresol, formic acid, and sulfuric acid. Its infrared spectrum is shown in Fig. 6.

(d) A mixture of 0. 01 mole of the appropriate diketone, 0. 01 mole of the corresponding diamine, 75 ml of dry benzene, and 0. 2 g of p-toluenesulfonic acid were reacted for about 48 hr in the azeotrope apparatus [1] until 0. 18 ml of water was collected in the trap. The polymers were collected by filtration, washed with benzene, and dried. The yields were approximately quantitative; the data is shown in Table 1.

The infrared spectra of these polymers showed the typical absorptions for C=O in the region of 1676 cm^{-1}, for NH_2 in the region of 3380 cm^{-1}, and for C=N in the region of 1620 cm^{-1}. The infrared spectra for polymers 1-Y and 2-Y were identical to those of the corresponding yellow polymers shown in Figs. 4 and 5, respectively.

In Active Solvents. (a) A mixture of 1. 62 g (0. 01 mole) of the p-diacetylbenzene, 1. 08 g (0. 01 mole) of m-phenylenediamine, and 50 ml of dimethylformamide were heated at 155°C under a nitrogen atmosphere for 8 hr, during which time the solution acquired a light-brown color. The reaction mixture was then transferred to a distillation equipment and the dimethylformamide removed by distillation at 15 mm Hg pressure while the flask temperature was maintained at 100°C, leaving 2. 10 g of a brown solid which was washed with benzene and dried, leaving 0. 81 g (32% yield) of a brown brick-dust polymer. Its infrared spectrum was similar to that of the yellow polymer shown in Fig. 4. The brown polmer was insoluble in the common organic solvents but slightly soluble in dimethylformamide and readily soluble in formic acid. This polymer did not melt below 300°C, but when held in the heat of a bunsen burner flame, it first melted, becoming dark red and eventually solidified to a black polymeric mass.

The water of reaction was isolated from the dimethylformamide distillate by azeotroping it with benzene, and 0. 15 g (calculated 0. 189 g) of water was isolated.
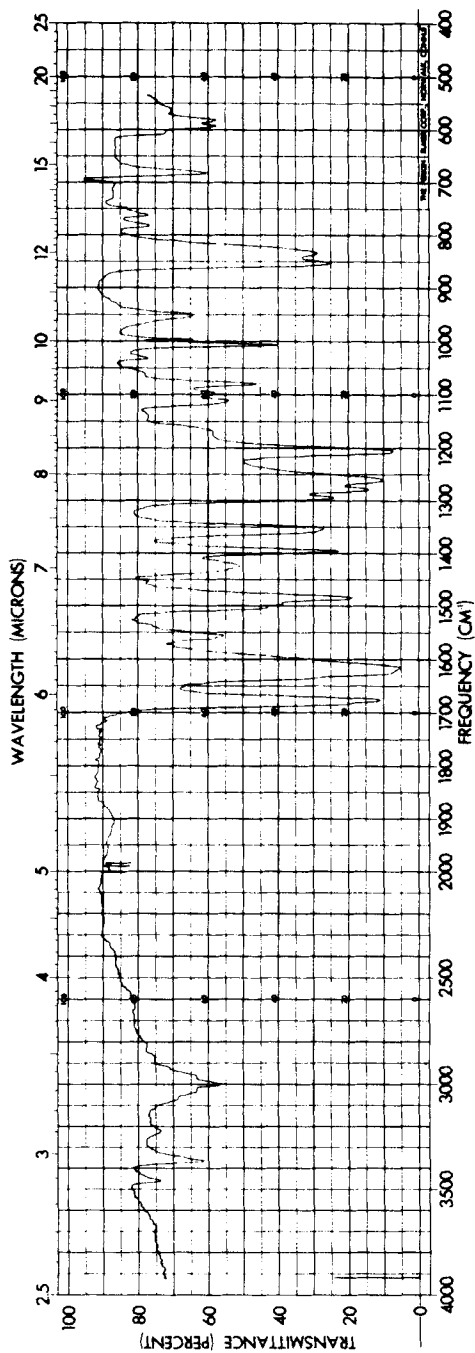
FIG. 5. Infrared spectrum of yellow-brown polymer,

$$O = \overset{CH_3}{\underset{}{\overset{|}{C}}} - \underset{}{\overset{}{\bigcirc}} - \overset{CH_3}{\underset{}{\overset{|}{C}}} = N - \underset{}{\overset{}{\bigcirc}} - N \underset{n}{=} H_2 . \quad KBr \ disc.$$
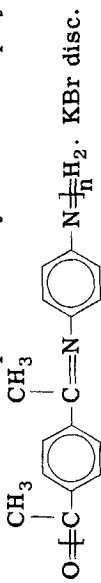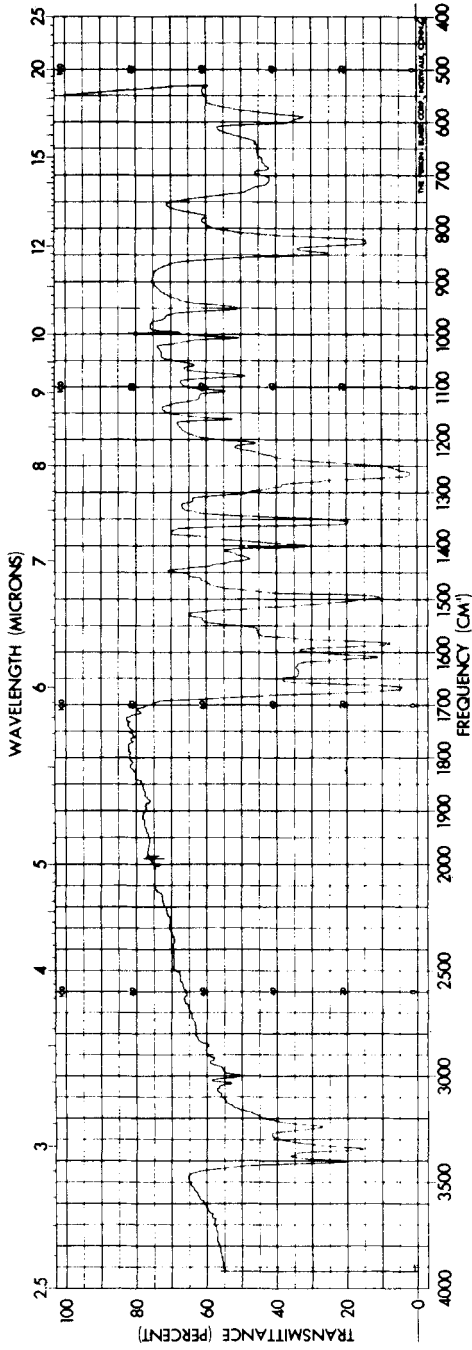
FIG. 6. Infrared spectrum of yellow-orange polymer, $2-Y-O$,
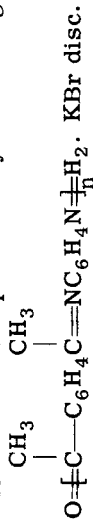
$$O = \left[C - C_6H_4C = NC_6H_4N \right]_n H_2.$$

with CH_3 groups. KBr disc.

$$O-\left[CC-Ar'-C=N-Ar''N\right]_n H_2$$

with CH_3, CH_3 substituents

TABLE 1. Data on $O-\left[\overset{CH_3}{\underset{}{C}}\overset{CH_3}{\underset{}{C}}-Ar'-C=N-Ar''N\right]_n H_2$ Polymers Prepared by the Azeotrope Method

| Polymer | Ar' | Ar'' | DPa approx. | Analysis | | | | | |
| | | | | % Calcd. | | | % Found | | |
				C	H	N	C	H	N
1-Y	$p\text{-}C_6H_4$	$m\text{-}C_6H_4$	3.2	80.28	5.71	11.69	80.31	5.76	11.74
2-Y	$p\text{-}C_6H_4$	$p\text{-}C_6H_4$	4.0	80.50	5.97	11.74	80.55	5.90	11.77
3-Y	$p\text{-}C_6H_4$	$p\text{-}C_6H_4CH_2C_6H_4$	5.0	83.09	6.51	9.10	82.96	6.58	9.14
4-Y	$p\text{-}C_6H_4$	$p\text{-}C_6H_4OC_6H_4$	5.0	78.81	5.81	9.03	78.44	5.76	9.08
5-Y	$p\text{-}C_6H_4OC_6H_4$	$p\text{-}C_6H_4OC_6H_4$	6.0	79.81	5.23	6.65	80.02	5.27	6.69

aEstimated from analytical data.

(b) Procedure (a) was repeated using, in addition, 0.028 g of zinc chloride as a catalyst and there was isolated 1.621 g (64%) of a dark brown brick-dust polymer whose characteristics were identical to the polymer prepared under (a).

Analysis: Calcd. for $O=\!\!\left[C\!\!-\!\!C_6H_4\overset{\overset{\displaystyle CH_3}{|}}{C}=\!\!NC_6H_4N\overset{\overset{\displaystyle CH_3}{|}}{}\right]_7\!\!H_2$

C, 81.02; H, 5.98; N, 11.79

Found: C, 80.91; H, 5.94; N, 11.70
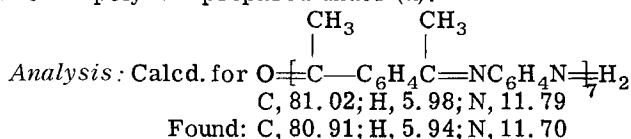
Melt Polymerizations

The melt procedure previously reported was used [1]. (a) Intimately mixed p-diacetylbenzene, 3.24 g (0.02 mole), and m-phenylenediamine, 2.16 g (0.02 mile), were reacted under a nitrogen atmosphere at 270°C. During the course of the reaction, the color of the mixture passed through various stages, changing progressively from yellow to orange to red to very dark brown. After approximately 4 hr of reaction at 270°C, the melt was extremely viscous, and, at the end of 5 hr, the viscous mass gave marked evidence of bubbling in the center of the mass. The mixture was allowed to cool, then ground and extracted with ethanol in a Sohxlet extractor for 12 hr and dried; yield, 3.23 g (68.9%) of a dark brown polymer which melted at about 275°C and was soluble in dimethylformamide, dimethylacetamide, formic acid, and concentrated sulfuric acid. Its infrared spectrum, shown in Fig. 7 as brown H270 polymer, is similar to the yellow polymer of Fig. 4.

Analysis: Calcd. for $\left[C\!\!-\!\!C_6H_4\overset{\overset{\displaystyle CH_3}{|}}{C}=\!\!NC_6H_4N\right]_{n=\infty}$

C, 82.05; H, 5.99; N, 11.96

Found: C, 81.68; H, 5.93; N, 11.84

(b) Procedure (a) was repeated and the reaction at 270°C was continued for 5 instead of 4 hr; then the pressure in the reaction system was reduced from atmospheric to 1.5 mm Hg for 1 hr, and an aliquot portion was withdrawn. This black polymer sample was soluble in concentrated sulfuric acid, slightly soluble in formic acid, but insoluble in dimethylacetamide. Its spectrum is shown as a black H270 polymer in Fig. 8. Then the temperature of the polymer in the reaction tube was raised over the period of 2 hr to 375°C at 1.5 mm Hg pressure and over the next hour to 400°C, at which temperature it was held for 72 hr. There was isolated 3.62 g (77.3%) of a shiny black polymer which was insoluble in sulfuric acid, formic acid, dimethylformamide, and dimethyl sulfoxide. Its infrared spectrum, given in Fig. 9 as a black insoluble H400 polymer, shows the absence of bands at 1676 cm^{-1} for C=O
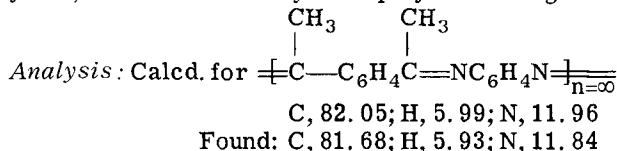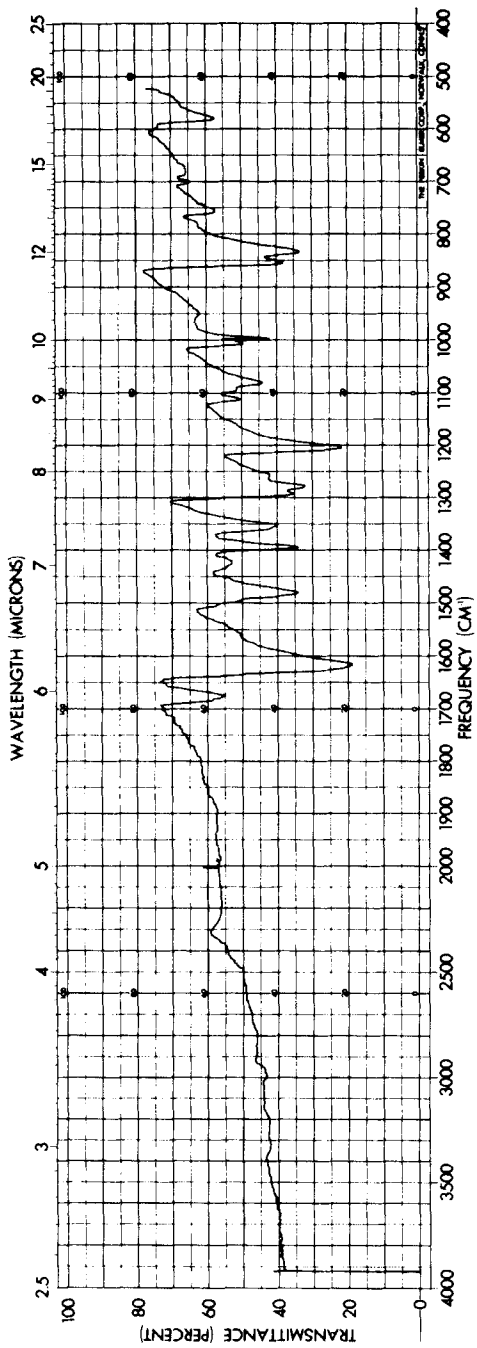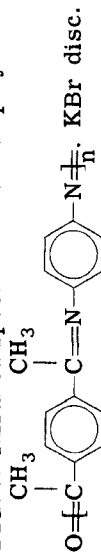
FIG. 7. Infrared spectrum of brown polymer H270,

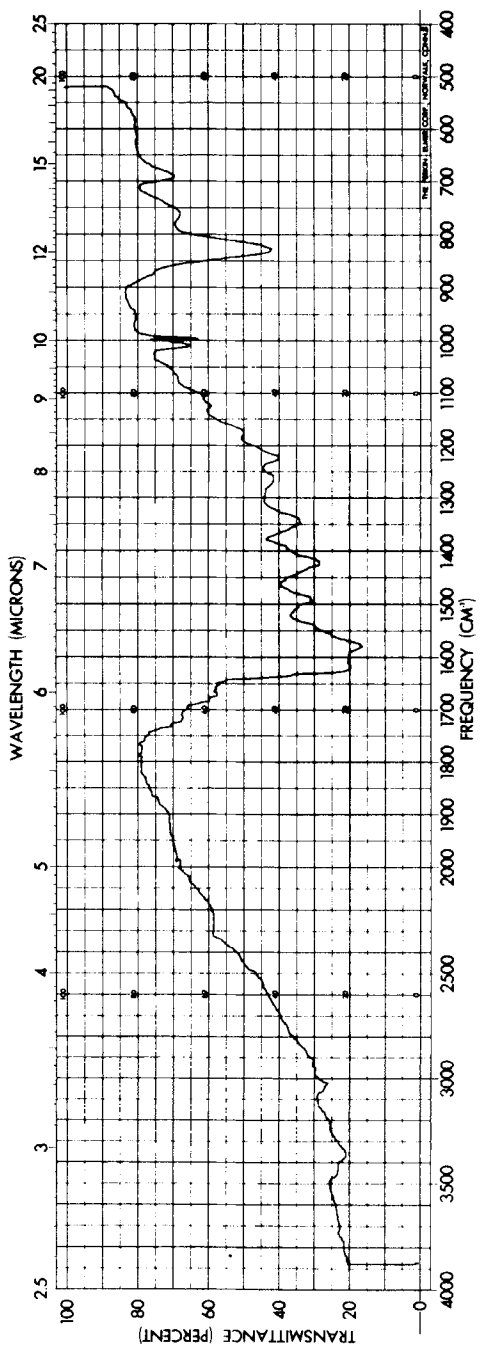KBr disc.

FIG. 8. Infrared spectrum of black, sulfuric acid soluble, H270 poly–

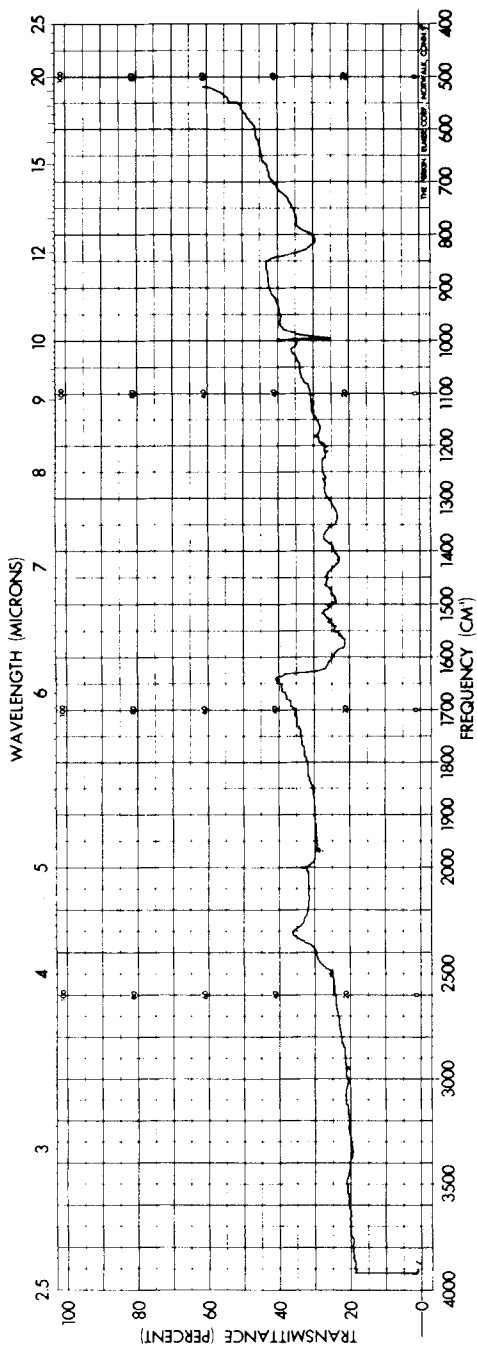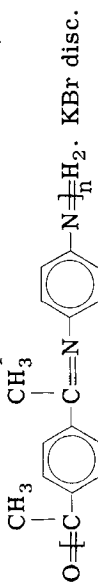mer, $O \leftarrow C \cdot \bigcirc \cdot C=N \cdot \bigcirc \cdot N \rightarrow_n H_2$. KBr disc.

FIG. 9. Infrared spectrum of black insoluble, H400 polymer, KBr disc.

and at 3380 cm^{-1} for NH$_2$, but in the 1600 cm^{-1} region, the band for C=N is found at 1685 cm^{-1}.

(c) A 0.5 g sample of the above black insoluble H400 polymer was added to 5.0 g of benzylideneaniline and the mixture heated, under nitrogen, at a reflux temperature of 310°C; within the first 2 hr of heating, the color of the benzylideneaniline changed from very light yellow to orange to dark red to dark brown, and most of the polymer became solubilized. However, at the end of 60 hr of reflux, approximately 0.1 g of polymer remained undissolved. When the experiment was repeated and a catalytic amount of zinc chloride was added to the reaction mixture, complete dissolution occurred within 24 hr. On cooling to room temperature, the mixture solidified to a brown solid, m.p. about 60°C; the brown solid was soluble in acetone. This brown solid was then subjected to distillation at 1.5 mm Hg pressure, with a flask temperature of 190°C to remove benzylideneaniline. The polymer was isolated as a solid black residue which was no longer soluble in acetone but soluble in concentrated sulfuric acid. Its infrared spectrum, polymer 1M-H400-BA, given in Fig. 10, shows absorptions at 760 cm^{-1} and 690 cm^{-1} typical of terminal —C$_6$H$_5$ groups.

(d) The following procedure was used to prepare the melt polymers shown in Table 2. A mixture of 0.02 mole of diketone, 0.02 mole of diamine, and 0.015 g of zinc chloride was reacted at 180°C for 60 min; then the temperature was raised to 270°C over the period of 1 hr and held at 270°C for 4 hr. Aliquot samples were withdrawn for the elemental analyses given in Table 2 and for infrared spectra measurements. The infrared spectra of these polymers showed marked absorptions for C=O in the 1676 cm^{-1}, for C=N in the 1620 cm^{-1}, and for NH$_2$ in the 3380 cm^{-1} regions, similar to those shown in Figs. 5, 6, and 7. The temperature of the remainder of the reaction mixture was then raised over a period of 2 hr to 400°C and held at that temperature for 48 hr. The infrared spectra of these 400°C polymers showed no absorptions for the C=O and NH$_2$ groups and a broadened band in the 1620 cm^{-1} region for C=N similar to that shown in Fig. 9.

Exchange Polymerizations

The exchange procedures which have been previously reported [1] were used. The following are typical procedures used in this study.

Amine Exchange. (a) Intimately mixed

$$p\text{-C}_6\text{H}_5\text{N}=\overset{\overset{\displaystyle \text{CH}_3}{\displaystyle |}}{\text{C}}\text{—C}_6\text{H}_4\overset{\overset{\displaystyle \text{CH}_3}{\displaystyle |}}{\text{C}}=\text{NC}_6\text{H}_5$$, 3.12 g (0.01 mole), and m-phenylenediamine, 1.08 g (0.01 mole), were reacted under nitrogen at 160°C for 10 hr, then the temperature was raised slowly over a period of
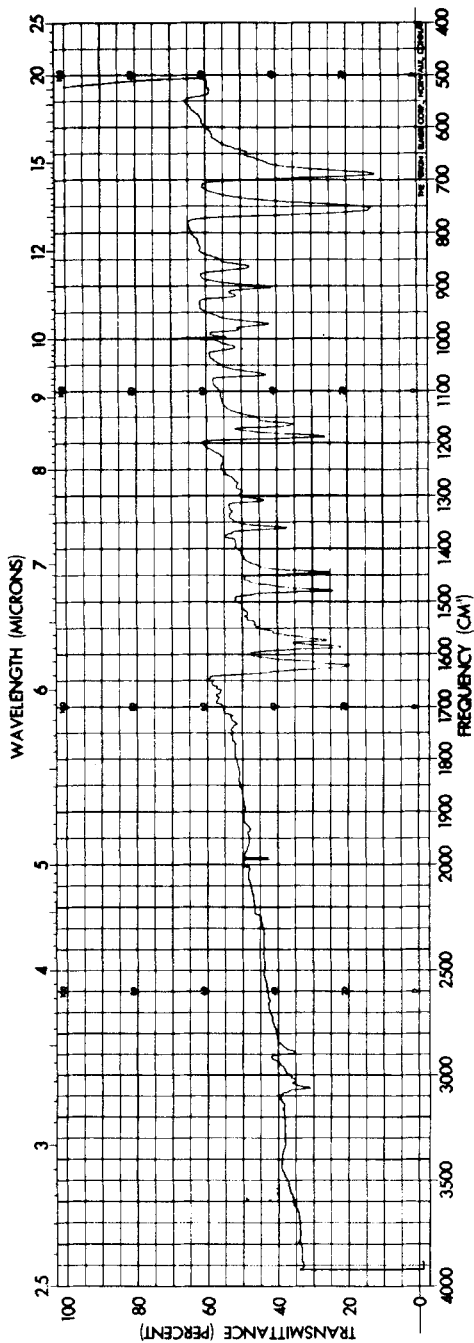
FIG. 10. Infrared spectrum of polymer 1M-H400-BA,

$$CH_3 \quad CH_3$$
$$C_6H_5N\!=\!C-\!\!\left\langle\bigcirc\right\rangle\!-C\!=\!N-\!\!\left\langle\bigcirc\right\rangle\!-N\!\!\left[=\!HCC_6H_5\right]_n, \text{ from reaction of}$$
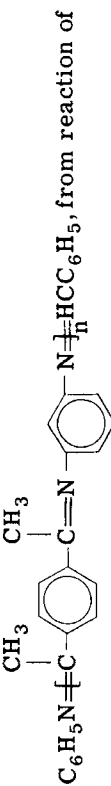
H400 polymer of Fig. 8 with benzylideneaniline. KBr disc.
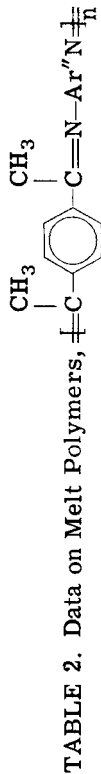
TABLE 2. Data on Melt Polymers, $\left[C-C_6H_4-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-C=N-Ar''N\right]_n$

Polymer	Ar″	Yield[a], % at 400°C	Analyses of H270 polymers					
			% Calcd.			% Found		
			C	H	N	C	H	N
1-M	m-C$_6$H$_4$	96.6	82.05	5.99	11.96	81.12	5.81	11.87
2-M	p-C$_6$H$_4$	94.3	82.50	5.99	11.96	81.41	5.90	11.84
3-M	p-C$_6$H$_4$CH$_2$C$_6$H$_4$	95.1	85.19	6.20	8.61	84.36	6.16	8.57
4-M	p-C$_6$H$_4$OC$_6$H$_4$	94.4	80.98	5.51	8.51	80.12	5.48	8.48
5-M	p-C$_6$H$_4$SO$_2$C$_6$H$_4$	97.5	70.59	4.81	7.49	70.02	4.89	7.41

[a]Based [1] on $\left[C-C_6H_4-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-C=N-Ar''N\right]_{n=\infty}$
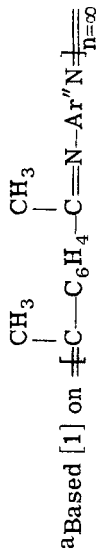
6 hr to 330°C; then the samples were withdrawn for analysis, following which the pressure was reduced to 1.5 mm Hg and the temperature increased to 400°C. The reaction was maintained at this temperature for 48 hr. Aniline in the distillate was identified as its benzylideneaniline derivative. There was isolated 1.99 g (78.3%) of an infusible, black shiny polymer which was insoluble in formic acid and sulfuric acid. Its infrared spectrum, given in Fig. 11, shows the absence of absorption bands for the NH_2 and $C=O$ groups but the presence of absorption bands for $C=N$ and terminal C_6H_5. The data on the amine exchange polymers are given in Table 3.

TABLE 3. Data on Amine Exchange Polymers,

$$C_6H_5N=\!\!\!\!\overset{\overset{\textstyle CH_3}{\textstyle |}}{C}-\!\!\!\bigcirc\!\!\!-\overset{\overset{\textstyle CH_3}{\textstyle |}}{C}=NAr''N\!\!\mid_{\overline{n}}\!\!H_2$$
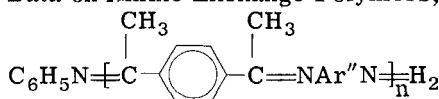
Polymer	Ar″	Yield[a] % at 400°C	Analysis of H330 polymers		
			% Found		
			C	H	N
1-A	m-C_6H_4	78.3	81.87	6.03	12.10
2-A	p-C_6H_4	86.4	81.64	6.11	11.96
3-A	p-$C_6H_4CH_2C_6H_4$	91.1	85.49	5.66	8.87
4-A	p-$C_6H_4OC_6H_4$	90.6	84.48	5.83	9.17

[a]Based on $=\!\!\!\overset{\overset{\textstyle CH_3}{\textstyle |}}{C}-C_6H_4\overset{\overset{\textstyle CH_3}{\textstyle |}}{C}=NAr''N\!\!\mid_{\overline{n=\infty}}$.
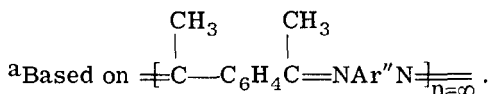
Ketone Exchange. (a) Intimately mixed p-diacetyl benzene, 1.62 g (0.01 mole), and m-$C_6H_5\overset{\overset{\textstyle CH_3}{\textstyle |}}{C}=NC_6H_4N=\overset{\overset{\textstyle CH_3}{\textstyle |}}{C}-C_6H_5$, 3.12 g (0.01 mole), and 0.01 g of zinc chloride were reacted under the same schedule of temperature and pressure used in the amine exchange. Acetophenone was identified in the distillate by its infrared spectrum. The polymers were shiny black, infusible, and insoluble in concentrated sulfuric acid. The data on the ketone exchange polymers is given in Table 4; the infrared spectrum of polymer 1-K is shown in Fig. 12.

FIG. 11. Infrared spectrum of amine exchange polymer, 1A-H400, $C_6H_5N \overset{CH_3}{\underset{CH_3}{=C}} \left[\text{—} \bigcirc \text{—} \overset{CH_3}{\underset{}{C}} = N \text{—} \bigcirc \text{—} N = \right]_n H_2$. KBr disc.
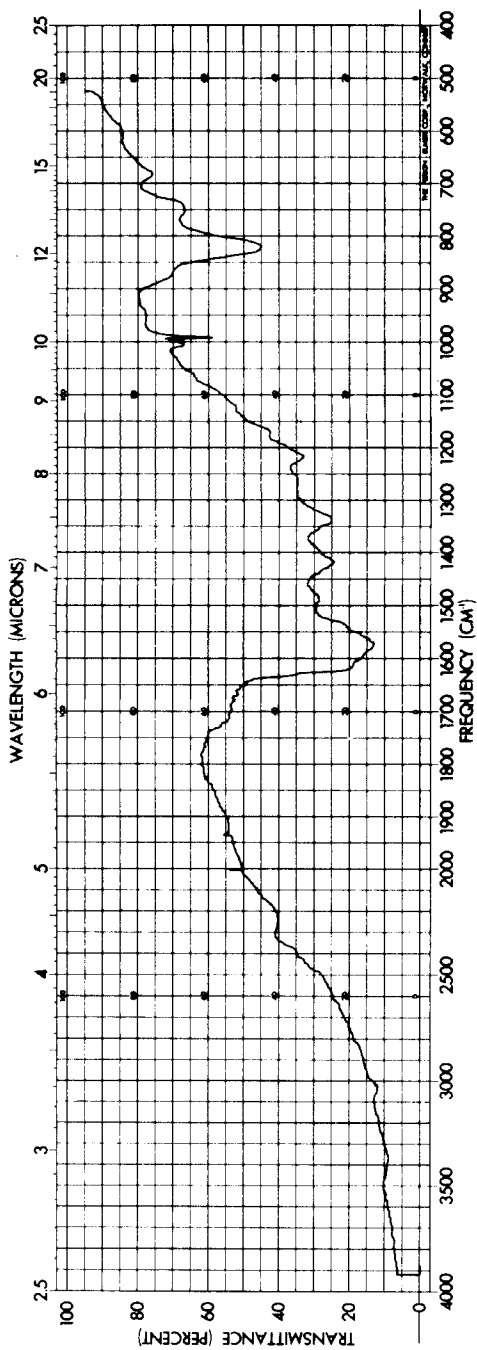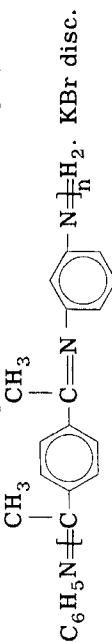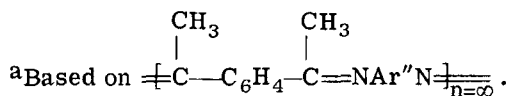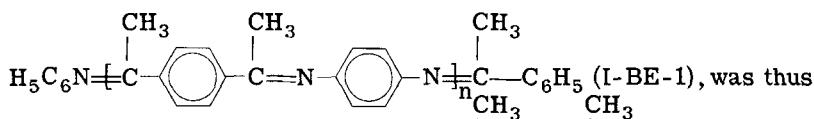
TABLE 4. Data on Ketone Exchange Polymers

$$O\!=\!\!\underset{\underset{n}{|}}{\overset{CH_3}{\underset{|}{C}}}\!\!-\!\!\bigcirc\!\!-\!\!\overset{CH_3}{\underset{|}{C}}\!=\!NAr''N\!\!=\!\!\overset{CH_3}{\underset{|}{C}}\!\!-\!\!C_6H_5$$

Polymer	Ar″	Yield[a] % at 400°C	Analyses of H330 polymers		
			C	H	N
1-K	$m\text{-}C_6H_4$	83.3	81.66	6.18	11.98
2-K	$p\text{-}C_6H_4$	86.9	81.57	6.09	12.07

[a]Based on $=\!\!\underset{|}{\overset{CH_3}{\underset{|}{C}}}\!\!-\!\!C_6H_4\!\!-\!\!\overset{CH_3}{\underset{|}{C}}\!=\!NAr''N\!\!=\!\!\Big|_{n=\infty}$.

Bis-Ketanil Exchange. (a) The experimental procedures used for these bis exchange reactions were similar to those previously described [1]. The conditions of time, temperature, and pressure used were similar to those used above in the amine exchange. The ketanil exchange reaction was found to be more sluggish than the bis-Schiff base exchange reaction [1] and, accordingly, zinc chloride was used as a catalyst in the amount of 0.001 mole per mole of the mixture of the two reactants. The bis exchange ketanil polymer,

$$H_5C_6N\!=\!\!\overset{CH_3}{\underset{|}{C}}\!\!-\!\!\bigcirc\!\!-\!\!\overset{CH_3}{\underset{|}{C}}\!=\!N\!\!-\!\!\bigcirc\!\!-\!\!N\!\!=\!\!\underset{n}{\overset{CH_3}{\underset{|}{C}}}\!\!-\!\!C_6H_5 \text{ (I-BE-1), was thus}$$

prepared in 91% yield from $p\text{-}C_6H_5N\!=\!\!\underset{|}{\overset{CH_3}{\underset{|}{C}}}\!\!-\!\!C_6H_4\overset{CH_3}{\underset{|}{C}}\!=\!NC_6H_5$ (3.12 g,

0.01 mole), $p\text{-}C_6H_5\overset{CH_3}{\underset{|}{C}}\!=\!NC_6H_4N\!=\!\!\overset{CH_3}{\underset{|}{C}}\!\!-\!\!C_6H_5$ (3.12 g, 0.01 mole) and and 0.006 g of zinc chloride. The polymer I-BE-1 was shiny black, infusible, and insoluble in concentrated sulfuric acid. Its infrared spectrum, given in Fig. 13, shows the presence of an absorption band for C=N at 1590 cm^{-1} and for C_6H_5 at 690 and 760 cm^{-1}. The infrared spectrum of the polymer I-BE-2, synthesized by using 2.84 g (0.01 mole) of $p\text{-}C_6H_5CH\!=\!NC_6H_4N\!=\!HCC_6H_5$ instead of the

$C_6H_5\overset{CH_3}{\underset{|}{C}}\!=\!NC_6H_4N\!=\!\overset{CH_3}{\underset{|}{C}}\!\!-\!\!C_6H_5$, was substantially identical to that shown in Fig. 13.
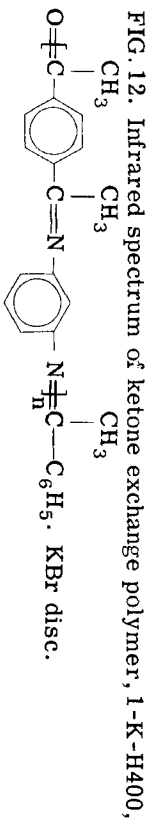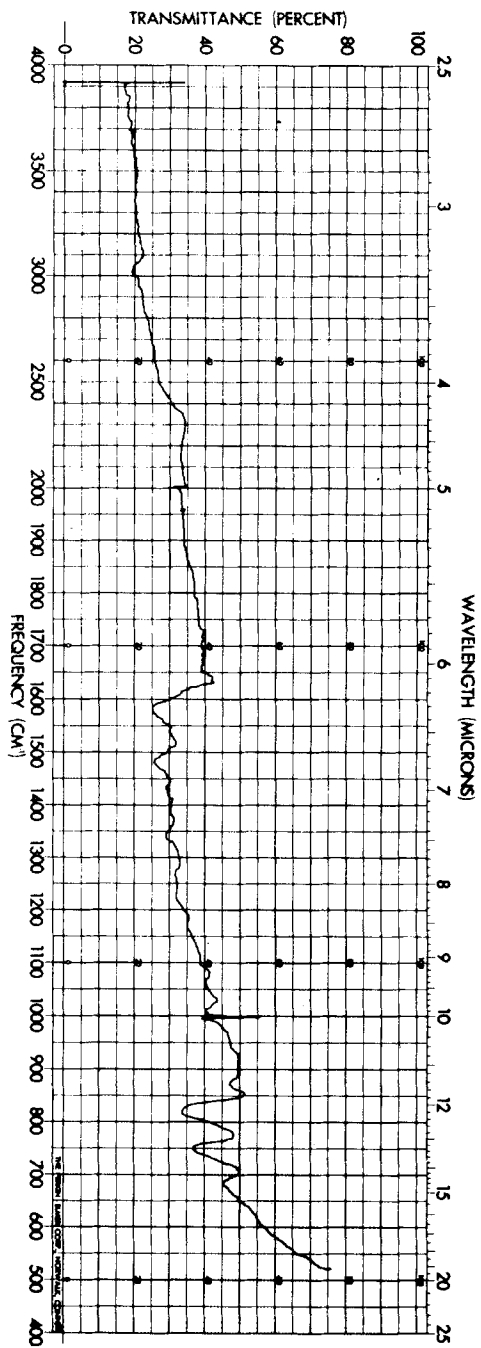
FIG. 12. Infrared spectrum of ketone exchange polymer, 1-K-H400,

$$O=C \overset{CH_3}{\underset{CH_3}{|}} \bigcirc C=N \overset{CH_3}{\underset{CH_3}{|}} \bigcirc N=C \overset{CH_3}{\underset{n}{|}} \text{—} C_6H_5. \text{ KBr disc.}$$
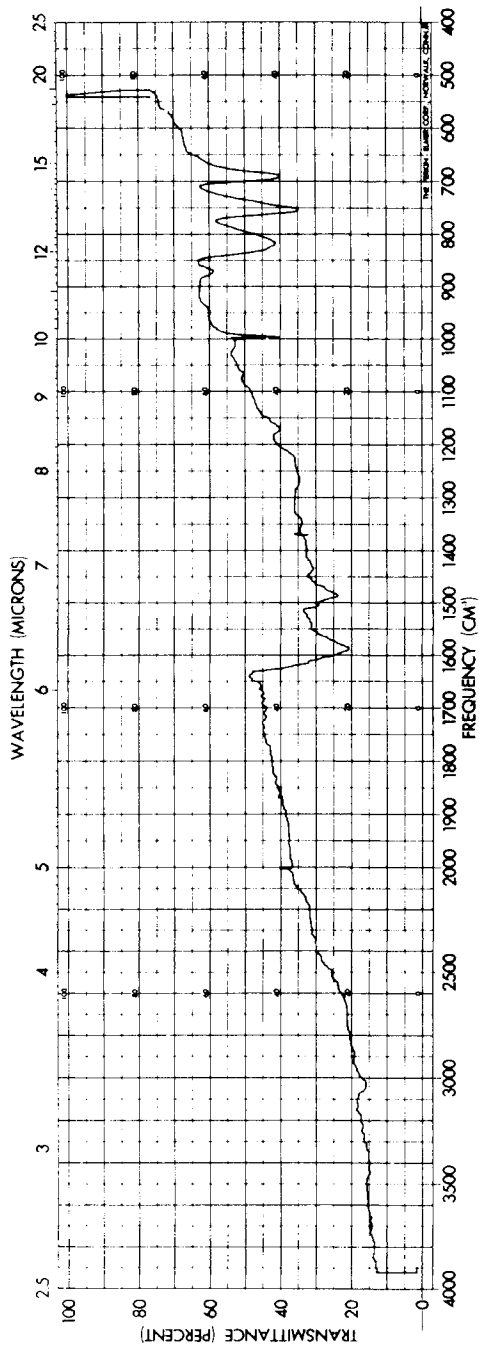
FIG. 13. Infrared spectrum of bis-ketanil exchange polymer,
I-BE-1-H400, $C_6H_5N{=\!\!\!=}C$
CH_3
KBr disc.

Direct Syntheses. Since the "direct synthesis" method is simpler and equivalent [1] to the bis exchange method, most of the polymers prepared in this study were synthesized by the direct method. The previously published procedure [4] for the direct synthesis from dicarbonyl compound and diamines in monomeric azomethines was used in these syntheses.

$$\overset{\displaystyle R}{\underset{\displaystyle |}{}}$$

Condensation in $C_6H_5C=NC_6H_5$. (a) A catalytic quantity of zinc chloride, 0.001 mole per mole of mixture of diamine and diketone, was used to accelerate the reaction. The condensations were carried to a temperature of 400°C and the polymers are designated

$$\overset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$$

as the D-H400 series. Both $C_6H_5C=NC_6H_5$ and $C_6H_5CH=NC_6H_5$ were evaluated as media for the reaction in a quantity of 0.2 mole

$$\overset{\displaystyle R}{\underset{\displaystyle |}{}}$$

of $C_6H_5C=NC_6H_5$ for the mixture of 1 mole of diketone and 1 mole of diamine. Samples were withdrawn at the end of the 300°C heating period and analyzed for nitrogen. The infrared spectra show bands in the region 1590–1600 cm^{-1} for C=N and bands in the region 690–700 cm^{-1} and 760–770 cm^{-1} for C_6H_5, similar to the bands shown in Figs. 10 and 13. Data relative to the direct condensation in monomeric azines are shown in Table 5.

$$\overset{\displaystyle R}{\underset{\displaystyle |}{}}$$

Condensation in Aniline and $C_6H_5C=O$. The procedure [4] previously published for the direct synthesis of polymeric Schiff bases from dialdehydes and diamines in an equimolar mixture of a monamine and a monocarbonyl compound was used in this study. (a) A catalytic quantity of zinc chloride, 0.001 mole per mole of mixture of diamine, dicarbonyl compound, monoamine, and monocarbonyl compound was used to accelerate the reaction. The mole ratio of the dicarbonyl, the diamine, the monocarbonyl, and the monoamine used were 1:1:0.2:0.2. Samples were withdrawn at the end of the 300°C heating period and analyzed for nitrogen; then the condensations were carried to 400°C. The infrared spectra of these polymers were substantially the same as those prepared in preformed

$$\overset{\displaystyle R}{\underset{\displaystyle |}{}}$$

$C_6H_5C=NC_6H_5$, and the data relative to these condensations are shown in Table 6.

Postheating of Polymers

Samples of polymers 1-A-H400, 1-K-H400, 1-BE-1-H400, and 2-BE-2-H400 were heated at 600 and to 1176°C by procedures

TABLE 5. Data on the Direct Syntheses of Polyketanils in $C_6H_5C=NC_6H_5$ (with R above C)

Polymer	Diketone	Diamine	R	Yield, %[a]	% N Calc.[a]	% N Found
1-D-H400	p-$CH_3COC_6H_4COCH_3$	m-$H_2NC_6H_4NH_2$	CH_3	96.2	11.96	11.77
2-D-H400	p-$CH_3COC_6H_4COCH_3$	p-$H_2NC_6H_4NH_2$	CH_3	96.6	11.96	11.83
3-D-H400	p-$CH_3COC_6H_4COCH_3$	p,p'-$(H_2NC_6H_4)_2$	CH_3	97.1	9.03	9.27
4-D-H400	p-$CH_3COC_6H_4COCH_3$	p,p'-$(H_2NC_6H_4)_2CH_2$	CH_3	96.7	8.61	8.86
5-D-H400	p-$CH_3COC_6H_4COCH_3$	p,p'-$(H_2NC_6H_4)_2O$	CH_3	95.3	8.51	8.79
6-D-H400	p-$CH_3COC_6H_4COCH_3$	p,p'-$(H_2NC_6H_4)_2S$	CH_3	93.8	8.18	8.39
7-D-H400	p-$CH_3COC_6H_4COCH_3$	p,p'-$(H_2NC_6H_4)_2SO_2$	CH_3	96.5	7.49	7.74
8-D-H400	p-$CH_3COC_6H_4COCH_3$	p-$H_2NC_6H_4NH_2$	H	94.7	11.96	11.79
9-D-H400	p-$CH_3COC_6H_4COCH_3$	m-$H_2NC_6H_4NH_2$	H	94.8	11.96	11.84
10-D-H400	p-$CH_3COC_6H_4COCH_3$	p,p'-$(H_2NC_6H_4)_2$	H	95.1	9.03	9.31
11-D-H400	p-$CH_3COC_6H_4COCH_3$	p,p'-$(H_2NC_6H_4)_2CH_2$	H	97.3	8.61	8.88
12-D-H400	p-$CH_3COC_6H_4COCH_3$	p-p'-$(H_2NC_6H_4)_2O$	H	98.0	8.51	8.78
13-D-H400	p-$CH_3COC_6H_4COCH_3$	p,p'-$(H_2NC_6H_4)_2SO_2$	H	94.9	7.49	7.72
14-D-H400	p,p'-$(CH_3COC_6H_4)_2CH_2$	m-$H_2NC_6H_4NH_2$	H	96.2	8.91	9.18
15-D-H400	p,p'-$(CH_3COC_6H_4)_2O$	m-$H_2NC_6H_4NH_2$	H	95.7	8.86	9.09
16-D-H400	p,p'-$(CH_3COC_6H_4)_2S$	m-$H_2NC_6H_4NH_2$	H	97.3	8.43	8.74
17-D-H400	p,p'-$(CH_3COC_6H_4)_2SO_2$	m-$H_2NC_6H_4NH_2$	H	97.4	7.69	7.95

[a]Based on $\left[\!\!\begin{array}{c} CH_3 \quad CH_3 \\ C-Ar'C=NAr''N \end{array}\!\!\right]_{n=\infty}$.
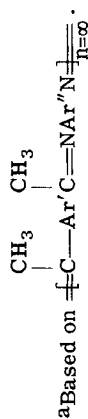
TABLE 6. Condensation of p-$CH_3COC_6H_4COCH_3$ and $H_2NC_6H_4NH_2$ in

$$\underset{\underset{Aniline\ and\ C_6H_5C=O}{|}}{R}$$
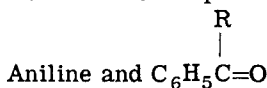
Polymer	Diamine	$\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C_6H_5C{=}O}}$	Yield,[a] % at 400°C	% N Calcd.[a]	Found
18-D-H400	p-$H_2NC_6H_4NH_2$	CH_3	96.6	11.96	11.78
19-D-H400	p-$H_2NC_6H_4NH_2$	H	95.9	11.96	11.80
20-D-H400	m-$H_2NC_6H_4NH_2$	CH_3	97.2	11.96	11.82
21-D-H400	m-$H_2NC_6H_4NH_2$	H	96.8	11.96	11.84

[a]Based on $\left[{=}\underset{\underset{CH_3}{|}}{C}{-}Ar'\underset{\underset{CH_3}{|}}{C}{=}NAr''N{=}\right]_{n=\infty}$
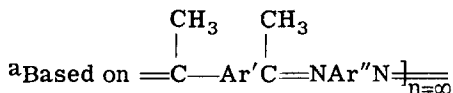
previously published [1] and, as previously [1], are indicated, res-
pectively, as H600 and H1176 polymers. The infrared spectra of
the 1-A-H400-600 and 1-BE-1-H400-600 polymers are typical
and are shown in Figs. 14 and 15, respectively.

Thermogravimetric Analyses

Thermogravimetric procedures previously published were
used [1] and performed on a du Pont 900 differential thermal ana-
lyzer in conjunction with a 950 thermogravimetric analyzer. To
compare the thermal stabilities of the polyketanils with those of
the poly-Schiff bases [1], similar conditions of tests were used in
the present studies. The sample size was 10 mg ground to a pow-
der of approximately 500 pieces; the rate of heating was 15°C min
in a dry nitrogen or air stream at a gas flow rate of 1 standard
liter/min to a recorded 1200°C temperature, which corresponds
to 1176°C when corrected for the nonlinearity of the chromel–
alumel thermocouple.

The data from the thermoanalysis in nitrogen of the Y series
of polymers prepared in solution are given in Table 7. The thermo-
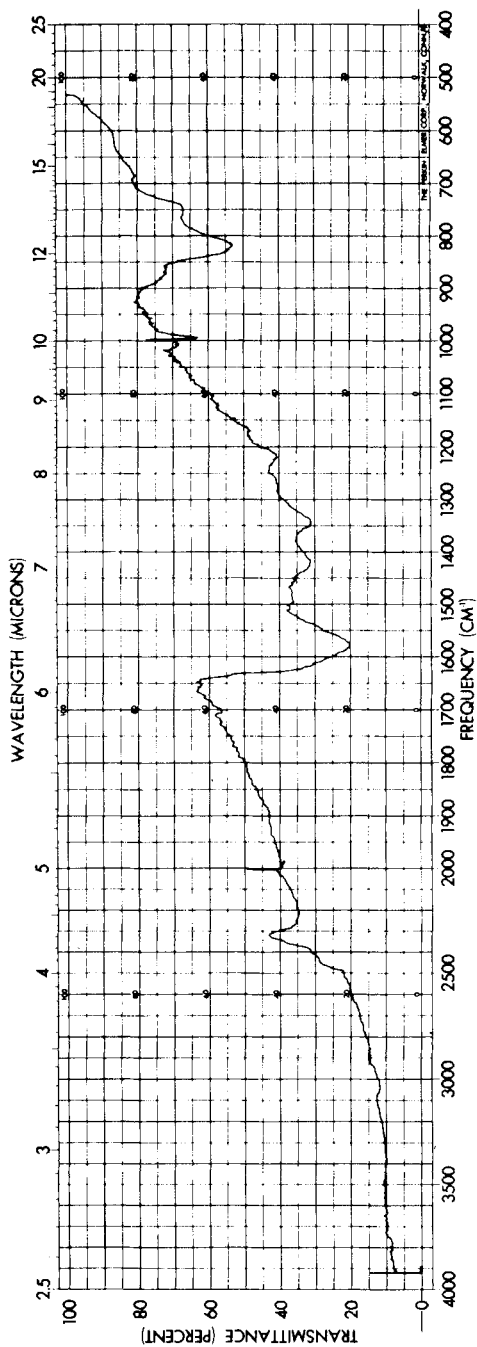
FIG. 14. Infrared spectrum of polymer 1-A-H400-600,

$$C_6H_5N = C - \underset{CH_3}{\overset{CH_3}{|}}{C} - \langle \bigcirc \rangle - C = N - \langle \bigcirc \rangle - N = H_2 \cdot \text{ KBr disc.}$$
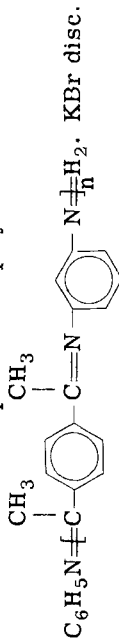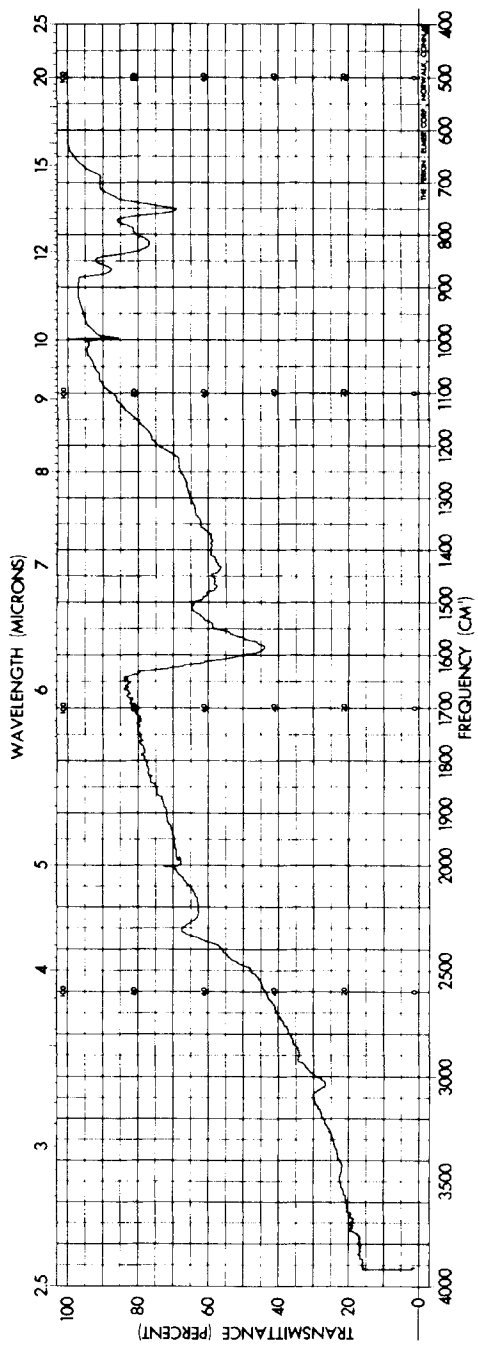
FIG. 15. Infrared spectrum of polymer 1-BE-1-H400-600,

$$C_6H_5N = C\cdot C_6H_4\cdot CH_3 \quad CH_3 \quad C = N\cdot C_6H_4\cdot N \cdot HCC_6H_5 \cdot \text{KBr disc.}$$

TABLE 7. Per Cent Weight Loss of Y Solution Series of Polymers at Various Temperatures While Being Heated in Nitrogen

Polymer	% Weight loss at °C									
	200	300	400	500	600	700	800	900	1000	1176
1-Y	4.0	8.1	19.0	23.2	38.1	45.0	49.1	51.1	52.4	52.8
2-Y	1.0	3.0	12.0	36.0	46.0	50.0	53.0	55.0	55.2	55.4
3-Y	2.1	4.1	13.2	37.0	47.1	51.2	53.3	54.3	55.3	55.5
4-Y	1.9	3.9	12.9	36.8	46.9	51.0	53.4	54.5	55.4	55.6
5-Y	1.7	3.7	12.7	36.8	46.8	51.4	53.5	54.5	55.5	55.7
2-Y-O	14.0	44.0	74.0	80.0	82.0	83.0	84.0	84.7	84.2	84.2

gram is shown in Fig. 16 for polymer 1-Y, and it is typical also for polymers 2-Y, 4-Y, and 5-Y and is compared to the thermogram of the yellow-orange polymer 2-Y-O.

The data for the thermoanalysis in nitrogen of the M series of polymers prepared as melts to a condensation temperature of 400°C are given in Table 8.
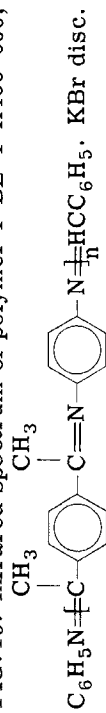
TABLE 8. Per Cent Weight Loss of M Melt Series of H400 Polymers at Various Temperatures While Being Heated in Nitrogen

Polymer	% Weight loss at °C									
	200	300	400	500	600	700	800	900	1000	1176
1-M-H400	0.0	0.0	0.0	0.0	3.0	9.1	12.1	14.0	15.1	18.2
2-M-H400	0.0	0.0	0.0	0.0	2.6	4.8	8.1	13.7	14.6	17.7
3-M-H400	0.0	0.0	0.0	0.0	3.2	9.4	12.3	14.3	15.3	18.5
4-M-H400	0.0	0.0	0.0	0.0	3.3	9.5	12.4	14.5	15.5	18.8
5-M-H400	0.0	0.0	0.0	0.0	3.0	9.6	12.5	14.6	15.5	18.7
1-B-RP-H400[a]	0.0	0.0	2.0	6.0	17.0	28.0	34.0	36.0	37.0	38.0
1-M-H400-BA[b]	2.0	5.0	14.0	30.0	40.0	46.0	48.0	49.0	49.5	50.1

[a]1-B-RP-H400 is the black polymer previously reported and prepared [1] by rapid heating under nitrogen of terephthaldehyde and p-phenylenediamine.

[b]1-M-H400-BA is the polymer of Fig. 10.
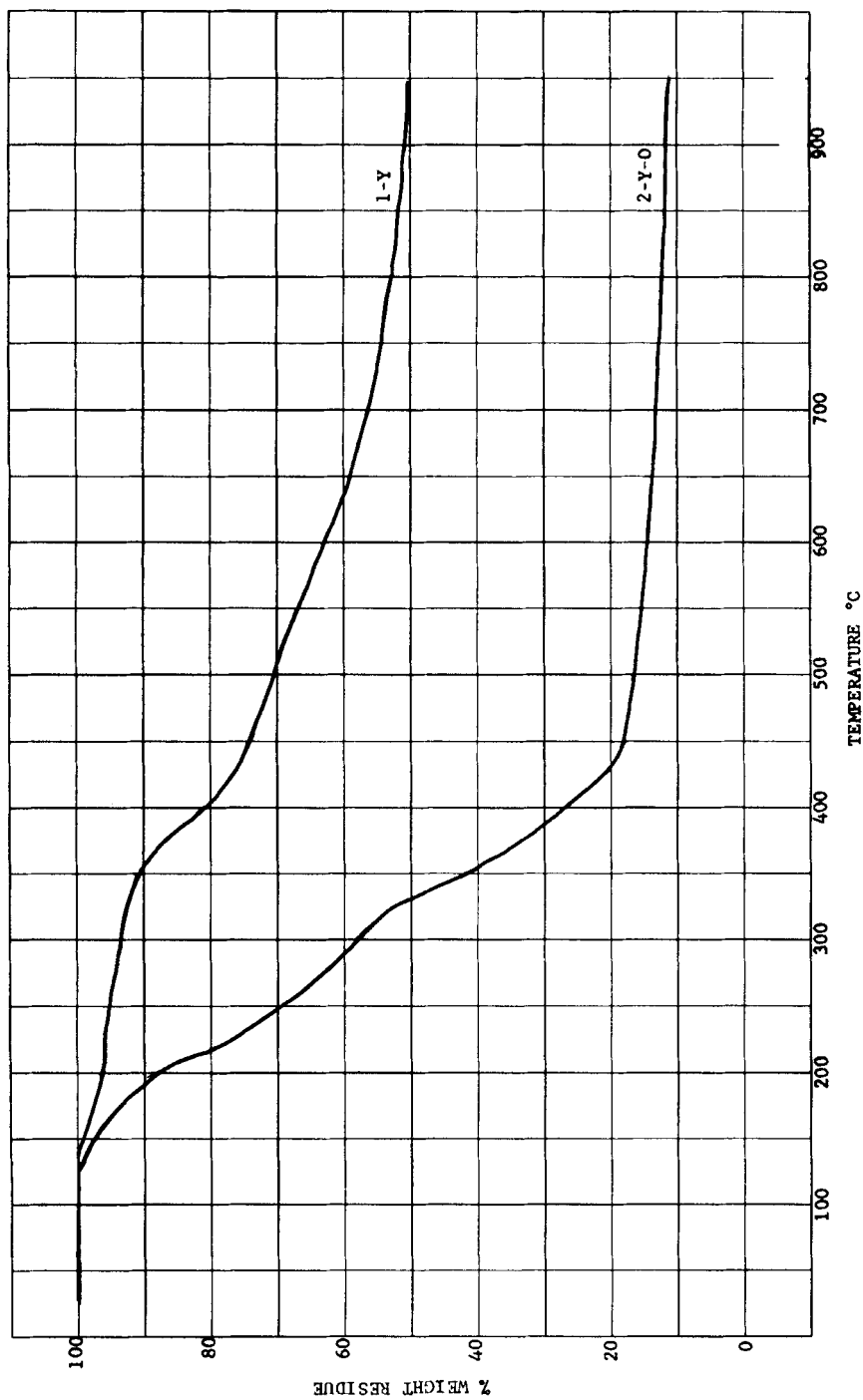
1-Y

2-Y-0

% WEIGHT RESIDUE

TEMPERATURE °C

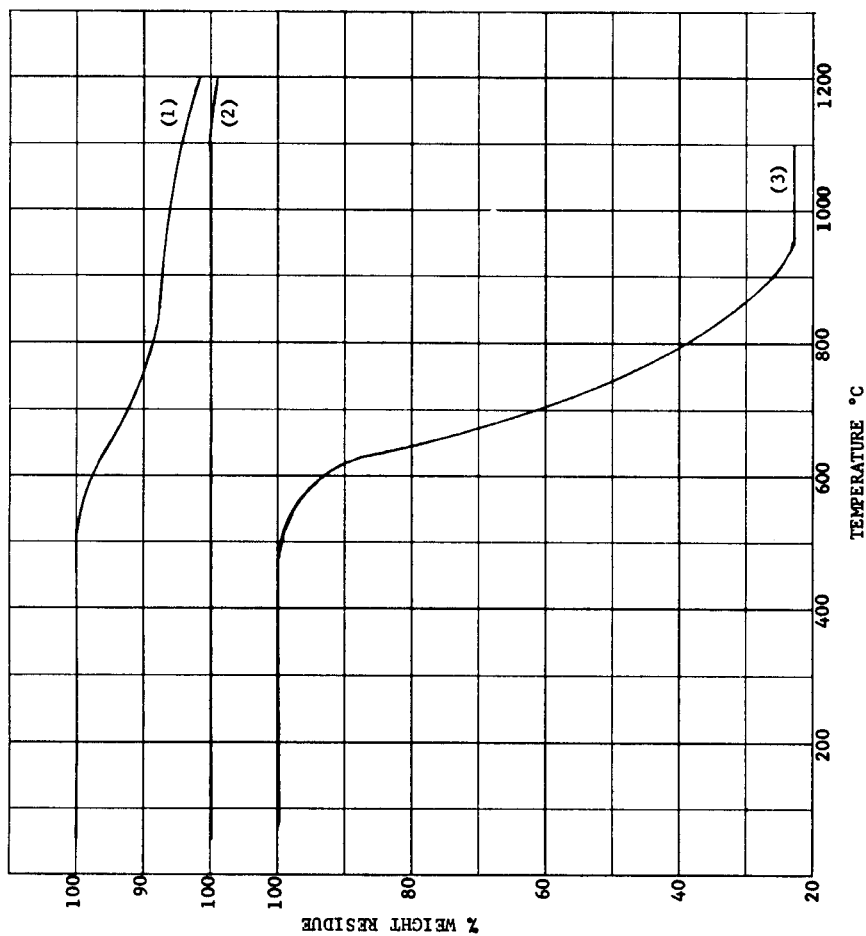FIG. 16. Thermograms of polymers 1-Y and 2-Y-O in nitrogen.

FIG. 17. Thermogram for melt polymers: curve (1) for polymer 1-M-H400 in nitrogen; curve (2) for polymer 1-M-H1176 in nitrogen; curve (3) for polymer 1-M-H1176 in air.

A typical thermogram in nitrogen for the M-H400 series of polymers is shown in curve 1 of Fig. 17 for the 1-M-H400 polymer.

The data for the thermoanalyses in nitrogen of the A series of polymers prepared by amine exchanges to a condensation temperature of 400°C are given in Table 9.

TABLE 9. Per Cent Weight Loss of Amine Exchange
H400 Polymers at Various Temperatures
While Being Heated in Nitrogen

Polymer	% Weight loss at °C						
	500	600	700	800	900	1000	1176
1-A-H400	0.0	4.0	11.1	16.0	20.2	22.1	27.0
2-A-H400	0.0	3.8	10.9	15.7	19.9	21.9	26.7
3-A-H400	0.0	5.2	12.2	17.2	21.4	23.5	27.9
4-A-H400	0.0	4.1	11.2	16.0	20.2	22.4	27.2

A typical thermogram for the amine exchange polymers is shown in curve 1 of Fig. 18 for the 1-A-H400 polymer.

The data for the thermoanalyses in nitrogen of the K series of polymers prepared by ketone exchanges to a condensation temperature of 400°C are given in Table 10. A typical thermogram in nitrogen for the ketone exchange polymers is shown in curve 1 of Fig. 19 for the 1-K-H400 polymer.

The data for the thermoanalyses in nitrogen of the BE series of polymers prepared by the bis exchange reaction to a condensation

TABLE 10. Per Cent Weight Loss of Ketone
Exchange H400 Polymers While
Being Heated in Nitrogen

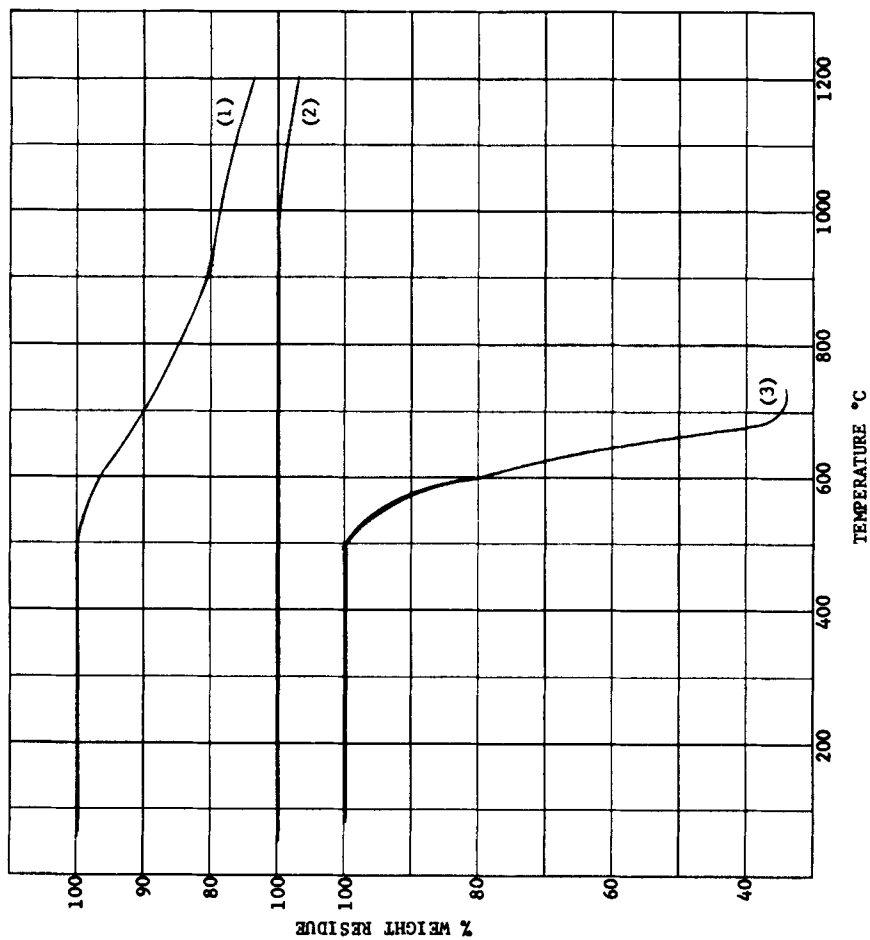| Polymer	% Weight loss at °C					
	600	700	800	900	1000	1176
1-K-H400	0.0	4.0	9.1	12.2	14.0	19.2
2-K-H400	0.0	3.8	8.9	12.0	13.6	18.8

FIG. 18. Thermogram for amine exchange polymer: curve (1) for 1-A-H400 in nitrogen; curve (2) for 1-A-H1176 in nitrogen; curve (3) for 1-A-H1176 in air.
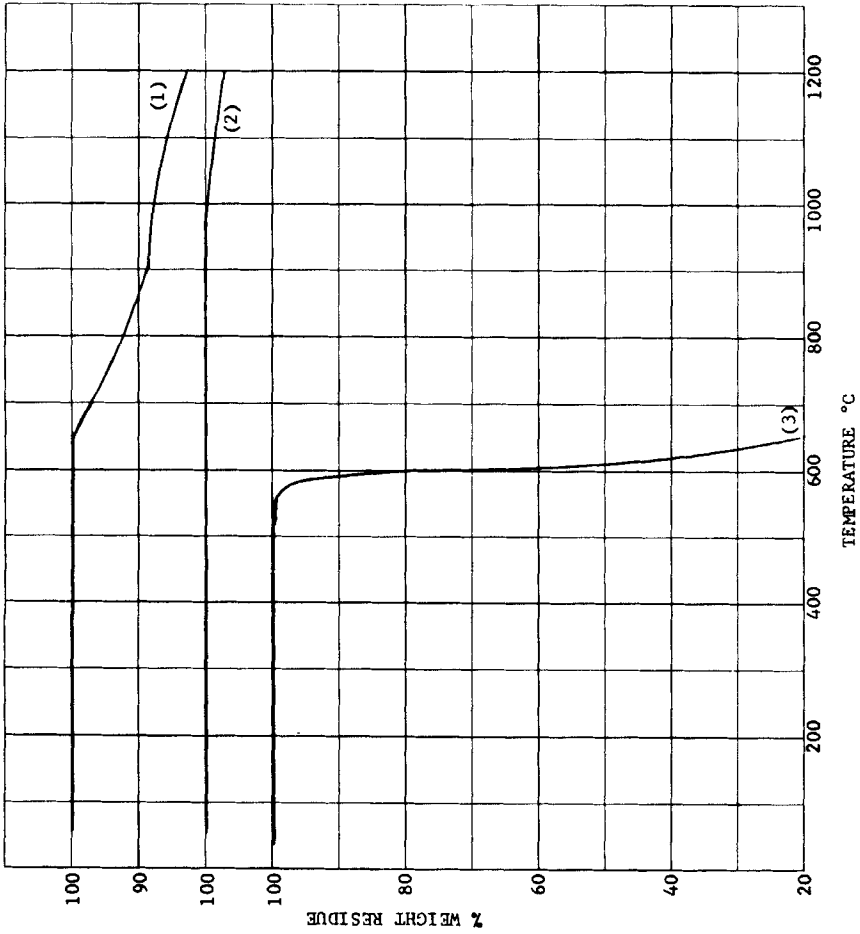
FIG. 19. Thermogram for ketone exchange polymers: curve (1) for 1-K-H400 in nitrogen; curve (2) for 1-K-H1176 in nitrogen; curve (3) for 1-K-H1176 in air.

TABLE 11. Per Cent Weight Loss of Bis Exchange H400
Polymers While Being Heated in Nitrogen

Polymer	% Weight loss at °C						
	500	600	700	800	900	1000	1176
1-BE-1-H400	0.0	4.0	14.0	18.0	19.1	20.2	23.3
1-BE-2-H400	0.0	0.0	3.7	8.8	11.6	13.1	19.2

TABLE 12. Per Cent Weight Loss of Some Poly-
ketanil H400 Polymers Prepared by
Direct Synthesis Method While Being
Heated in Nitrogen

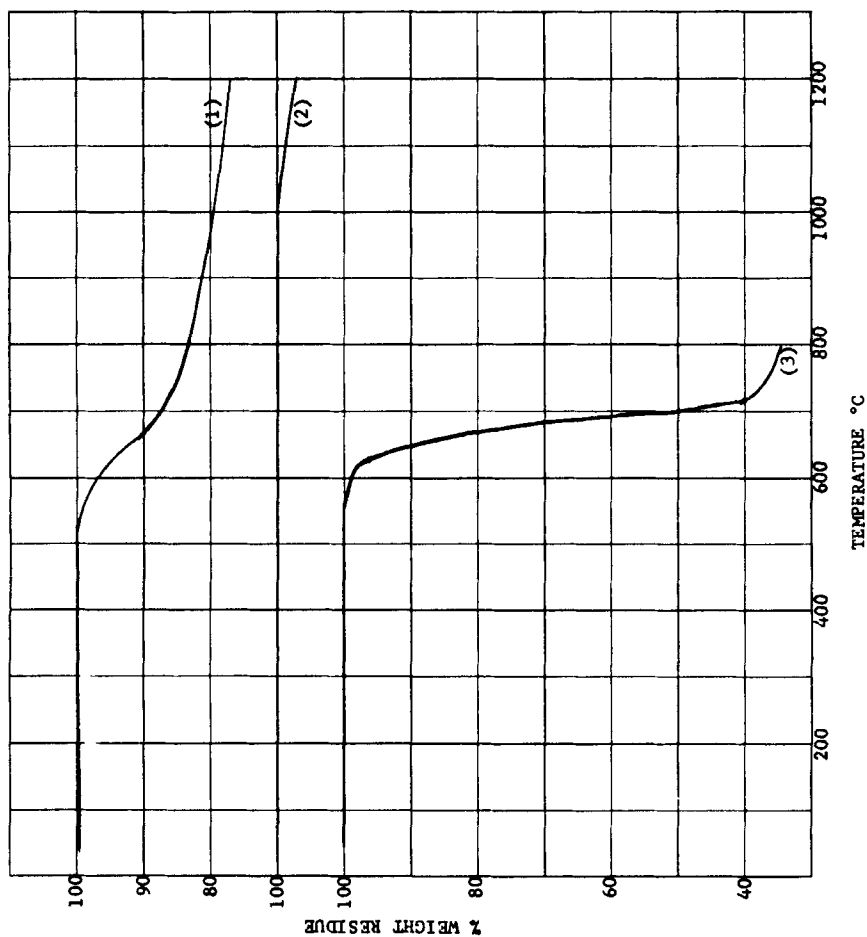| Polymer	% Weight loss at °C					
	600	700	800	900	1000	1176
1-D-H400	0.0	3.1	8.1	11.0	12.5	18.7
2-D-H400	0.0	2.8	7.8	10.6	11.9	18.1
5-D-H400	0.0	2.9	7.6	10.3	11.7	18.0
7-D-H400	0.0	3.0	7.5	10.6	11.8	18.3
8-D-H400	0.0	2.9	8.0	10.8	12.3	18.4
9-D-H400	0.0	2.6	7.6	10.4	11.7	17.9
12-D-H400	0.0	2.8	7.4	10.1	11.5	18.2
13-D-H400	0.0	3.1	7.5	10.4	11.7	18.4
14-D-H400	0.0	4.1	8.2	12.2	13.6	20.4
15-D-H400	0.0	3.8	8.0	11.9	13.7	21.2
16-D-H400	0.0	4.4	9.1	13.1	14.0	23.1
17-D-H400	0.0	4.2	8.6	11.7	13.6	21.4
18-D-H400	0.0	3.0	8.4	11.3	12.8	20.0
19-D-H400	0.0	2.8	8.0	11.0	12.5	19.7
20-D-H400	0.0	2.9	7.9	10.8	12.2	21.4
21-D-H400	0.0	2.8	7.9	10.9	12.4	19.9

FIG. 20. Thermogram for bis exchange polymers: curve (1) for 1-BE-1-H400 in nitrogen; curve (2) for 1-BE-1-H1176 in nitrogen; curve (3) for 1-BE-1-H1176 in air.

TABLE 13. Typical Per Cent Weight Loss of Some
Polyketanils While Being Heated in Air

Polymer	% Weight loss at °C					
	200	300	400	500	600	700
1-Y	1.6	4.2	6.8	80.0	100.0	—
2-Y	1.4	4.4	16.6	75.8	100.0	—
1-M-H400	0.0	0.0	0.0	8.9	100.0	—
2-M-H400	0.0	0.0	0.0	9.8	100.0	—
4-M-H400	0.0	0.0	0.0	6.2	100.0	—
1-A-H400	0.0	0.0	0.0	3.5	80.0	100.0
2-A-H400	0.0	0.0	0.0	3.3	81.1	100.0
4-A-H400	0.0	0.0	0.0	3.6	87.4	100.0
1-K-H400	0.0	0.0	0.0	3.0	82.1	100.0
2-K-H400	0.0	0.0	0.0	2.9	80.7	100.0
1-BE-1-H400	0.0	0.0	0.0	3.8	76.1	100.0
1-BE-2-H400	0.0	0.0	0.0	3.5	74.8	100.0
1-D-H400	0.0	0.0	0.0	5.0	70.0	100.0
2-D-H400	0.0	0.0	0.0	3.2	71.0	100.0
5-D-H400	0.0	0.0	0.0	5.1	70.6	100.0
7-D-H400	0.0	0.0	0.0	6.4	89.2	100.0
8-D-H400	0.0	0.0	0.0	3.3	72.6	100.0
19-D-H400	0.0	0.0	0.0	2.8	84.0	100.0
20-D-H400	0.0	0.0	0.0	2.2	68.8	100.0

temperature of 400°C are given in Table 11. The thermogram for a
typical exchange polymer is shown in curve 1 of Fig. 20 for the
1-BE-1-H400 polymer.

The data of the thermoanalyses in nitrogen of the D series of
polymers prepared by the direct condensation method to a condensa-
tion temperature of 400°C are given in Table 12. A typical thermo-
gram is very similar to that shown in curve 1 of Fig. 20.

The data of the thermoanalyses in air of typical ketanil polymers
prepared by solution, melt, exchange, and direct reaction methods are

TABLE 14. Typical Per Cent Weight Losses
of Some H600 Polyketanils
While Being Heated in Air

Polymer	% Weight loss at °C		Inflection point, °C
	500	600	
1-M-H400-H600	0.0	73.9	508
1-A-H400-H600	0.0	74.2	514
1-K-H400-H600	0.0	70.8	510
1-BE-H400-H600	0.0	68.6	530
2-BE-H400-H600	0.0	68.4	545

given in Table 13. Typical thermograms in air for the polyketanils
are shown in Fig. 21.

Table 14 summarizes the typical thermogravimetric data in air
of some of the polyketanils which have been condensed to 600°C.

Table 15 summarizes typical data of the thermoanalyses in nitro-
gen and in air of some polyketanils which have been condensed to a
temperature of 1176°C. Typical thermograms are shown in curves
2 and 3 of Fig. 18, 19, and 20.

TABLE 15. Typical Per Cent Weight Losses of Some H1176 Polyketanils
While Being Heated in Nitrogen and in Air

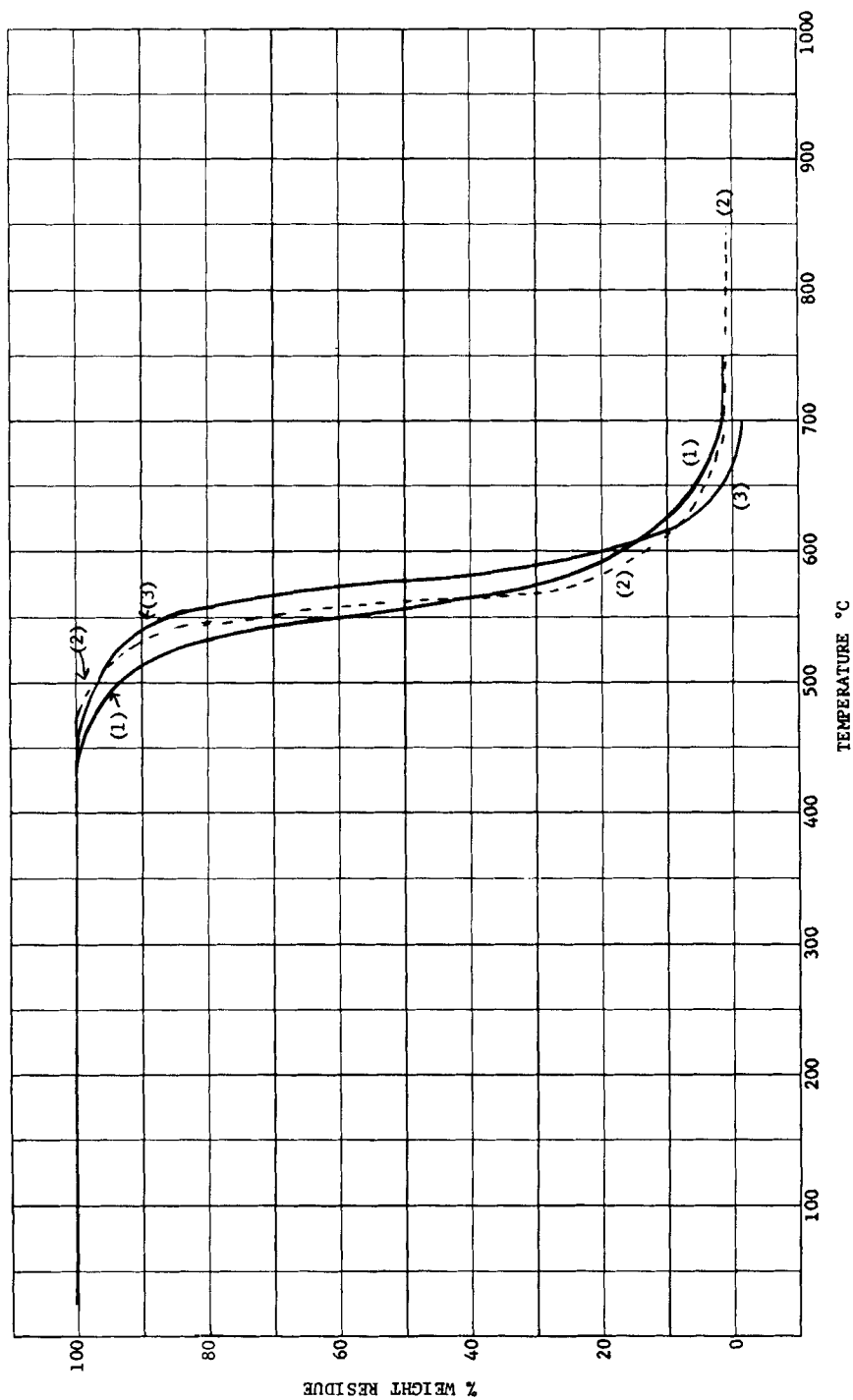| Polymer	Atmosphere	% Weight loss at °C						
		500	600	700	800	900	1000	1176
1-A-H400-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	3.6
	Air	0.0	28.0	100.0	—	—	—	—
1-K-H400-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	3.6
	Air	0.0	18.1	100.0	—	—	—	—
1-M-H400-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	2.9
	Air	0.0	9.2	100.0	—	—	—	—

FIG. 21. Thermogram for H400 ketanil polymers in air: curve (1)
for 1-A-H400; curve (2) for 1-K-H400; curve (3) for 1-BE-1-H400.

TABLE 16. Calorimetric Data on Some Polyketanils

Polymer	Atmosphere	Calorimetry peaks, °C	Heat of reaction, cal/g
1-Y	Air	390	4800–5500
1-M-H400	Air	525	3100–3600
1-M-H600	Air	550	2700–3400
1-K-H600	Air	535	2800–3500
1-D-H600	Air	540	2900–3400
1-A-H1176	Nitrogen	—	500–560
	Air	540	4800–5600
1-K-H1176	Nitrogen	—	400–450
	Air	535	4900–5400
1-M-H1176	Nitrogen	—	410–460
	Air	550	4700–5250
Graphite [5]	Nitrogen	—	—
	Air	680	520–550

Calorimetric Determinations. The procedure described in previous publications [5] was used to obtain calorimetric thermograms at a heating rate of 15°C/min from 4.5 g of polymers 1-Y, 1-M-H400 1-M-H600, 1-K-H600, 1-D-H600, 1-A-H1176, 1-K-H1176, and 1-M-H1176 for comparison with pyrolytic graphite [5]. The calorimetric thermograms were similar in character to those found for the Schiff base polymers. The data are summarized in Table 16.

The data in the table parallel those found for the poly-Schiff bases [5] in that the heat of reaction in air of 500–550 cal/g for graphite, is much less than the 4700–5600 cal/g found for the H1176 polymers, whose values are more closely related to the 4800–5500 cal/g for the 1-Y solution polymer and to 2700–3600 cal/g for the H400 and H600 polymers. This evidence indicates, as it did in the case of the Schiff base polymers [5], that when the polyketanils are heated to 1000°C under the conditions used, they have not been converted to graphitic-type polymers.
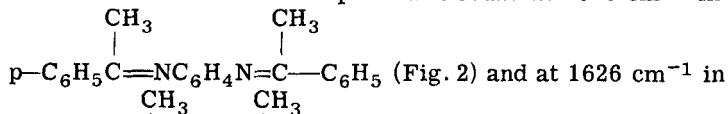
DISCUSSION

Polymerizations

The condensation by the azeotropic method [1] in benzene solution proceeded much more slowly for the reaction between the aryldike-

tones and the aryldiamines than it did for the reaction of aryldial-
dehydes with the same diamines [1]. The reaction with the dialde-
hydes proceeded uncatalyzed, whereas a Lewis acid catalyst was re-
quired when the diketones were used. A similar difference in reac-
tivity was found [7] in the reaction of aniline with benzaldehyde and
acetophenone, respectively. The condensation was also found to be
slow in dimethylacetamide unless catalyzed. The polymers prepared
in benzene were isolated in most cases as infusible brick-dust poly-
mers, and in this respect they resemble the poly-Schiff bases; but
they differ considerably from the ketanil polymers previously repor-
ted [6]. However, when the condensations were performed in an ac-
tive solvent, such as dimethylacetamide, the condensation products
were of low molecular weight and soluble in dimethylacetamide; thus
they did not precipitate from the reaction mixture. Infrared spectral
methods were used, as previously [1], to elucidate the structure of
these and the other polymers reported in this study.

The region of 1676 cm^{-1} was assigned to the keto group, C=O, on
the basis of the spectra of acetophenone and p-diacetylbenzene
(Fig. 1). This compares to the region of 1700 cm^{-1} for the aldehyde
function [1]. The region of 3380 cm^{-1} was previously assigned [1] to
the aromatic NH$_2$ group. The C=N— double bond stretching is usually
placed in the region of 1630 cm^{-1} for various azomethine compounds
[15].

The band for C=N absorption was found at 1616 cm^{-1} in

$$\text{p—C}_6\text{H}_5\underset{\overset{|}{\text{CH}_3}}{\text{C}}\text{=NC}_6\text{H}_4\text{N=}\underset{\overset{|}{\text{CH}_3}}{\text{C}}\text{—C}_6\text{H}_5 \quad \text{(Fig. 2) and at 1626 cm}^{-1}\text{ in}$$

$$\text{p—C}_6\text{H}_5\text{N=}\underset{\overset{|}{\text{CH}_3}}{\text{C}}\text{—C}_6\text{H}_4\underset{\overset{|}{\text{CH}_3}}{\text{C}}\text{=NC}_6\text{H}_5$$

p—C$_6$H$_5$N=C—C$_6$H$_4$C=NC$_6$H$_5$ (Fig. 3). The C$_6$H$_5$ absorptions were
found [1] in the Schiff bases in the regions 775 and 690 cm^{-1}; where-
as in the ketanils these absorptions were found at 690 and 760 cm^{-1}
(Fig. 2) and at 710 and 770 cm^{-1} (Fig. 3).

The infrared spectra of the polymers prepared in solution, shown
in Figs. 4, 5, and 6, show bands in the region 3380 cm^{-1} for NH$_2$, in
the region of 1676 cm^{-1} for C=O, and in the region 1620 cm^{-1} for
C=N. The sharp absorption peaks for NH$_2$, C=O, and C=N indicate
the low molecular weight nature of these condensation products; this
is indicated by their elemental analyses.

The melt polymerization of Ar'(COCH$_3$)$_2$ with Ar''(NH$_2$)$_2$ pro-
ceeded readily without added catalysts at temperatures of 270°C or
higher; the amine apparently catalyzed the reaction at these high
temperatures. Clear melts were obtained in all cases. In the vis-
cous stage, these melt polymers, 1—M to 5—M, were soluble in dime-
thylacetamide, and on first reaching the solid stage they became in-
soluble in dimethylacetamide but were soluble in sulfuric acid; on
further condensation they became insoluble in sulfuric acid.

In the early stages of the melt condensations, the infrared spectra (Fig. 7) showed marked absorption peaks characteristic of NH_2, C=O, and C=N, but as the reaction progressed, the intensity of the bands for NH_2, in the region 3380 cm^{-1}, for C=O in the region 1676 cm^{-1}, and for C=N in the region 1620 cm^{-1} decreased (Fig. 8). When further condensed, these bands at 3380 cm^{-1} for NH_2 and at 1676 cm^{-1} for C=O disappeared (Fig. 9), whereas the peak of the band in the region of 1620 cm^{-1} for C=N decreased and broadened in a fashion similar to that found in the poly-Schiff bases [1].

That these black melt polymers were not cross-linked was shown by dissolving them in benzylideneaniline, which was shown [1] to be a reactant as well as a solvent for the poly-Schiff bases. The presence, in Fig. 10, of C_6H_5 absorption bands at 690 and 760 cm^{-1} and the absence of bands at 3380 cm^{-1} for NH_2 and at 1676 cm^{-1} for C=O gave evidence that benzylideneaniline also reacted with, as well as solvated, the polyketanils.

The exchange polymerizations were found also to proceed readily. Aniline was eliminated in the amine exchange polymerization, and at an early stage of condensation the infrared spectra showed bands for NH_2 at 3380 cm^{-1}, for C=N at 1620 cm^{-1}, and for C_6H_5 in the 755 and 690 cm^{-1} regions. As the condensation proceeded, the bands (Fig. 10) for NH_2 and C_6H_5 decreased and the band at 1620 cm^{-1} broadened. Acetophenone was eliminated in the ketone exchange polymerization, and, at the early stage, the infrared spectra showed the bands for C=O at 1676 cm^{-1}, for C=N at 1620 cm^{-1}, and for C_6H_5 at 755 and 690 cm^{-1}, but, as the polymerization progressed, the bands at 1676, 755 and 690 cm^{-1} decreased while the band at 1620 cm^{-1} broadened.

The bis exchange polymerizations proceeded smoothly with the

$$\overset{\displaystyle R}{\underset{\displaystyle |}{}}$$

elimination of $C_6H_5C=NC_6H_5$, and the infrared spectra clearly showed the presence (Fig. 13) of end C_6H_5 groups in the 690 and 755 cm^{-1} regions, the intensity of which decreased with continued condensation, which also caused a broadening of the C=N absorption band.

As in the case of the poly-Schiff bases [4], the direct condensation of aryldiketone with aryldiamines, either in

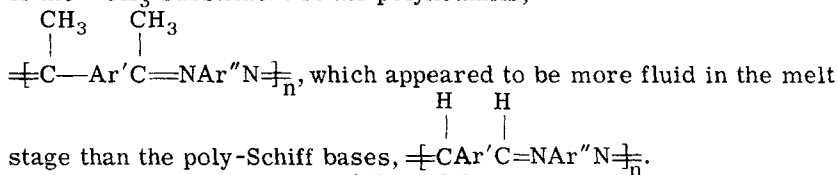$$\overset{\displaystyle CH_3}{\underset{\displaystyle |}{}}$$

$C_6H_5C=NC_6H_5$, $C_6H_5CH=NC_6H_5$, or in equimolar mixtures of aniline with C_6H_5CHO or $C_6H_5COCH_3$, respectively, yielded polymers substantially identical with those prepared by the bis exchange polymerizations. In all cases the infrared spectra of the polymers condensed to 400°C showed absence of absorption bands at 3380 cm^{-1} for NH_2, at 1676 cm^{-1} for C=O, but they showed bands in the region 690–710 and 755–770 cm^{-1} for C_6H_5, and a broadened band for C=N

in the 1620 cm^{-1} region. As the polymers were heated to higher temperatures, these bands broadened even further and were undistinguishable from background noises in polymers which had been heated at temperatures of 700°C or higher. It was noted also that in the more fully condensed polymers, the absorption band for C=N was found in the region of 1590 cm^{-1} and was observed even in polymers condensed to 700°C.

The thermogravimetric data in Tables 7 to 15 inclusive, and the thermograms of Fig. 16 to 20, inclusive, clearly indicated that the thermal stabilities of the polyketanils prepared in solution as brick-dust polymers were lower than those of the poly-Schiff bases similarly prepared. However, the thermal stabilities of the polyketanils prepared by condensation to temperatures of 300°C or higher are comparable to those of the Schiff base polymers [1–5] when evaluated in nitrogen and in air at a heating rate of 15°C/min and at a gas flow rate of 1 standard liter/min. The calorimetric studies also indicated that the polyketanils are similar to the poly-Schiff bases in that they were not converted to graphitic-type polymers when heated under the specified conditions to temperatures in the range of 1000°C.

CONCLUSION

The condensation of aryldiamines, $Ar''(NH_2)_2$, with aryldiketones, $Ar'(COCH_3)_2$, is much slower than with aryldialdehydes, $Ar''(CHO)_2$, but the rate can be accelerated highly by catalytic quantities of a Lewis acid. The polyketanils obtained by condensation in solution are brick-dust polymers similar in character to the poly-Schiff bases. The polyketanils are more readily prepared by melt reactions of the diketones with the diamines than are the corresponding poly-Schiff bases from dialdehydes and diamines. The synthesis of poly-ketanils by means of the amine, ketone, and bis exchange methods are more facile than the corresponding reaction used to synthesize the Schiff base polymers. This difference is attributed to the presence of the $-CH_3$ substituent in the polyketanils,

$$\begin{matrix} CH_3 & CH_3 \\ | & | \\ \end{matrix}$$
$=\!\!\!\!{-}C\!\!-\!\!Ar'C\!\!=\!\!NAr''N\!\!{-}\!\!\!\!=_{\overline{n}}$, which appeared to be more fluid in the melt

stage than the poly-Schiff bases, $\begin{matrix} H & H \\ | & | \\ =\!\!\!\!{-}CAr'C\!\!=\!\!NAr''N\!\!{-}\!\!\!\!=_{\overline{n}}. \end{matrix}$

The thermal properties of the polyketanils in nitrogen and in air closely approximate those of the poly-Schiff bases.

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Zusammenfassung

Durch Kondensation von Aryldiketonen, $Ar'(COCH_3)_2$, mit Aryldia-
minen, $Ar''(NH_2)_2$, in Lösung wurden gelbliche, unlösliche Polymere
erhalten. Schwarze bearbeitbare Polymere wurden erhalten durch
(1) Schmelzkondensation des Diketons mit dem Diamin allein, oder
(2) in Gegenwart von monomeren Azomethinen, $C_6H_5CH=NC_6H_5$
oder $C_6H_5C(CH_3)=NC_6H_5$, oder (3) in Gegenwart von Anilin und der
Carbonylverbindung C_6H_5COR, aus der sich die monomeren Azome-
thine ableiten, oder durch (4) Amino-, (5) Keto-, oder (6) Doppelaus-
tauschreaktionen. Weitere Kondensation in Stickstoff bei 400°C,
600°C, und 1176°C ergab unlösliche, unschmelzbare, schwarze Poly-
mere, deren thermische Stabilität jener der polymeren Schiff-Basen
gleichkam.

Résumé

La condensation en solution des aryldicétones, $Ar'(COCH_3)_2$, avec les aryldiamines, $Ar''(NH_2)_2$, produit des polymères insolubles, de couleur jaune-brique-poussiéreux. Les polymères traitables sont obtenus par (1) la condensation en fusion de dicétones avec les diamines seules, ou (2) en présence des azomethines monomères

$$C_6H_5CH{=}NC_6H_5 \text{ ou } C_6H_5\overset{\overset{\displaystyle CH_3}{|}}{C}{=\!=}NC_6H_5, \text{ ou (3) en présence d'aniline et}$$

d'un compose carbonyl $C_6H_5\overset{\overset{\displaystyle R}{|}}{C}{=}O$ dont ces azomethines monomères sont derivées, ou par (4) l'amino- (5) céto-ou (6) bis-échange réaction. Une condensation continue dans l'azote à 400°C, 600°C, et 1176°C donne des polymères insolubles, infusibles, noires, avec des stabilités thermiques très proches de celles de bases de Schiff polymères.