Polymeric Schiff Bases. IX. The Syntheses of Polymeric Schiff Bases from Acetals and Amine Compounds

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Summary

Six new potential reactions for the syntheses of black polymeric Schiff bases were evaluated: the reaction of aryldiacetals with (1) aryldiamines, (2) aryldiamine salts, (3) dibenzylidenearylenediamines, and (4) N, N'-diacetylarylenediamines, respectively, (5) the reaction of aryldialdehydes with N, N'-diacetylarylenediamines, and (6) the reaction of bis-Schiff bases with N, N'-diacetylarylenediamines. Reactions (1) and (3) were found to be satisfactory and were applied to the syntheses of a number of polymers. The thermal stabilities of the polymers thus prepared were shown to be equivalent to those prepared by bis-Schiff base exchange reactions.

A number of syntheses for polymeric Schiff bases have been reported in previous publications.[1-3] These papers described [1-3] the syntheses by reaction of aryldialdehydes or appropriate derivatives with aryldiamines or appropriate derivatives. The direct reaction in solution of dialdehydes with diamines [1] was found usually to yield insoluble, infusible, brick-dust polymers, whereas the melt reaction of these reagents was difficult to control. However, the melt reaction could be moderated [1-3] by the addition of mono-
$$\overset{R}{\underset{|}{}}$$
meric azines, $C_6H_5C=NC_6H_5$. The use of acetals instead of alde-hydes was also considered [1], as a means of moderating the polymerization reaction. However, before utilizing the reaction of the aromatic diacetals with aromatic diamines or their derivatives it was necessary to confirm that these reactions would be substantially
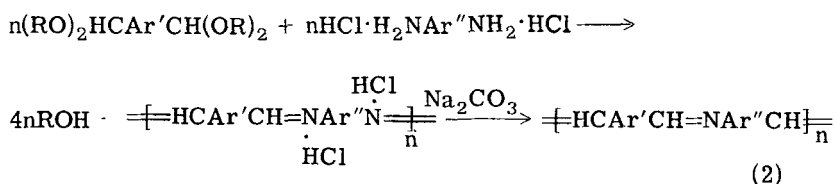
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free of side reactions which could lead to undesirable by-products and that the yields of desired products would be high. Accordingly, the reactions were studied in monomeric systems as prototypes for the polymer reactions [4, 5]. The confirmation [4] that the reactions of the acetals of aromatic aldehydes with aromatic amines or specific amine derivatives yielded monomeric Schiff bases led to considering applying these reactions to the syntheses of polymeric Schiff bases. Polymer synthesis requires that both reactants must be polyfunctional. To correlate the results of polymerization studies, the reactants were selected so that they would possess the same chemical nature as the reagents used in the prototype studies. The systems studied involved the reaction of aromatic diacetals, $(RO)_2HCAr'CH(OR)_2$, with (1) aromatic diamines, $H_2NAr''NH_2$; (2) salts of the diamines, $Ar''(NH_2 \cdot HCl)_2$; (3) bis-Schiff bases of the diamines, $Ar''(NH=CHC_6H_5)_2$; and (4) diacyl derivatives of the aryldiamines, $(CH_3CONH)_2Ar''$, respectively.

The polymerization reaction between a diacetal and a diamine can be generalized as follows:

$$n(RO)_2HCAr'CH(OR)_2 + nH_2NAr''NH_2 \longrightarrow$$

$$4nROH + \text{—}[HCAr'CH=NAr''N]_n\text{—} \tag{1}$$
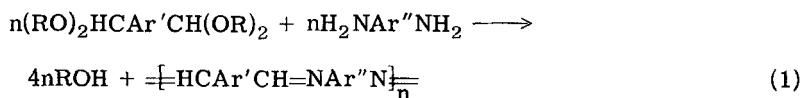
The reaction between a diacetal and a diamine salt can be written as

$$n(RO)_2HCAr'CH(OR)_2 + nHCl \cdot H_2NAr''NH_2 \cdot HCl \longrightarrow$$

$$4nROH \cdot \text{—}[HCAr'CH=NAr''N \overset{HCl}{\underset{HCl}{\cdot}}]_n\text{—} \xrightarrow{Na_2CO_3} \text{—}[HCAr'CH=NAr''CH]_n\text{—} \tag{2}$$

The polymerization reaction between a diacetal and a bis-Schiff base can be expressed as

$$n(RO)_2HCAr'CH(OR)_2 + nArCH=NAr''N=CHAr \longrightarrow$$

$$2nArCH(OR)_2 + \text{—}[HCAr'CH=NAr''N]_n\text{—} \tag{3}$$
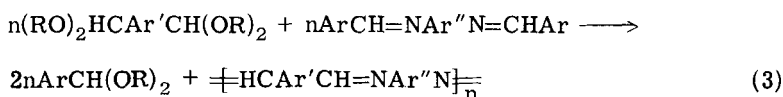
The reaction between a diacetal and a N, N'-diacetylarylenediamine can be given as

$$n(RO)_2HCAr'CH(OR)_2 + RCONHAr''NHOCR \longrightarrow$$

$$2nROH + 2nRCOOR + \text{—}[HCAr'CH=NAr''N]_n\text{—} \tag{4}$$
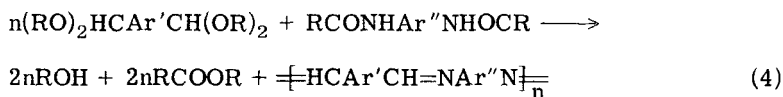
The use of aryldialdehydes, instead of the diacetals, in Eqs. (1)–(3 has been reported previously [1–5]. To complete the investigation and to compare the results with those obtained by the use of diacetals in Eq. (4), the reaction of aryldialdehydes with N, N'-diacetylarylenediamines was included in this investigation; this reaction can be written as

$$nOHCAr'CHO + nCH_3CONHAr''NHOCCH_3 \longrightarrow$$

$$2nCH_3COOH + {+}HCAr'CH{=}NAr''N{+}_n \qquad (5)$$
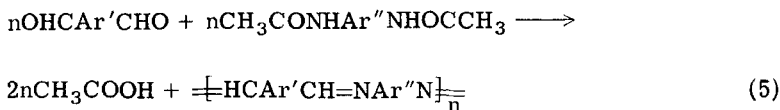
The following related reaction, that of a bis-Schiff base with a N, N'-diacetylarylenediamine, was also studied:

$$nC_6H_5N{=}HCC_6H_4CH{=}NC_6H_5 + nCH_3CONHC_6H_4NHOCCH_3 \longrightarrow$$

$$2nCH_3CONHC_6H_5 + {+}HCC_6H_4CH{=}NC_6H_4N{+}_n \qquad (6)$$
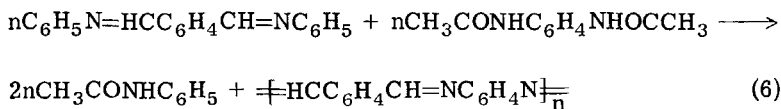
The paper reports studies on the syntheses of polymeric Schiff bases by the reactions given in Eqs. (1) to (6) inclusive. The study was divided into two parts. The first part of the study concerned itself with evaluating the reactions given by these equations and eliminating the less satisfactory reactions. Then the polymeric Schiff bases were synthesized by applying those reactions which yielded satisfactory polymers and the thermal stabilities of these polymers were evaluated.

EXPERIMENTAL

Monomers and Reagents

The syntheses of p-xylylidenetetraethyl ether [4], p-xylylidenetetrabutyl ether [4], the dibenzylidenearylenediamines [6], and benzylideneaniline [6] were reported previously. Acetic anhydride and p-phenylenediamine were reacted in acetic acid [7] to yield N, N'-diacetylphenylenediamine, m.p. 303–305°C, lit. [7] m.p. 295–303°C.

Analysis: Calcd. for $C_{10}H_{12}N_2O_2$: C, 62.49; H, 6.29; N, 14.40
　　　　　　　　　　　　　　Found: C, 62.28; H, 6.44; N, 14.87
The infrared spectra for p-$C_6H_4[CH(OC_2H_5)_2]_2$, p-$C_6H_4[CH(OC_4H_9)_2]_2$, and p-$C_6H_4(NHOCCH_3)_2$ are given in Figs. 1, 2, 3, respectively.
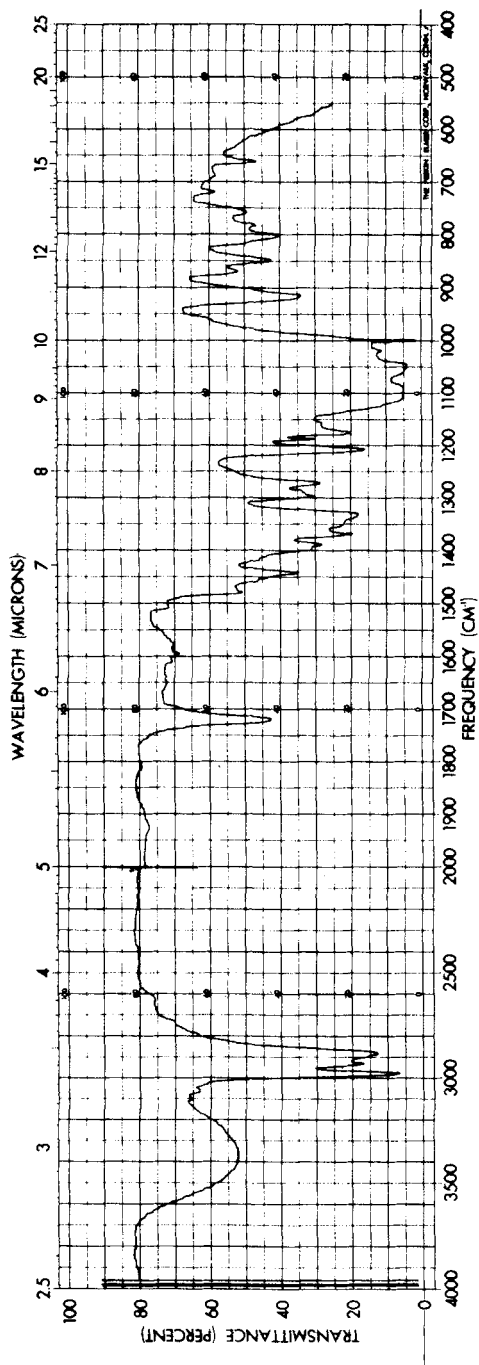
FIG. 1. Infrered spectrum of p-C_6H_4[CH(OC$_2$H$_5$)$_2$]$_2$. Neat, NaCl.
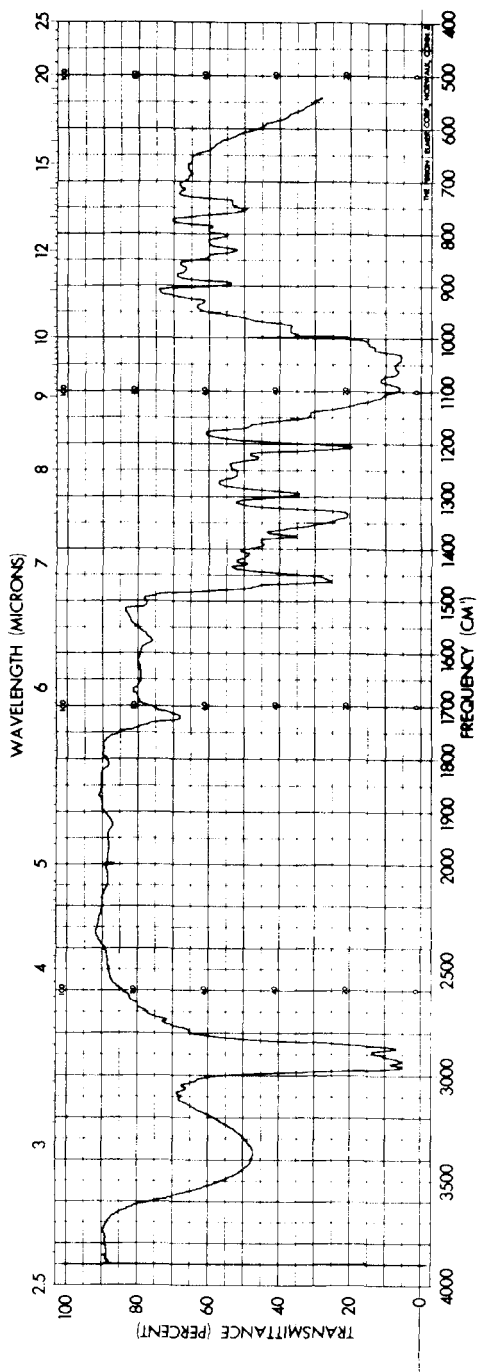
FIG. 2. Infrared spectrum of p-$C_6H_4[CH(OC_4H_9)_2]_2$. Neat, NaCl.
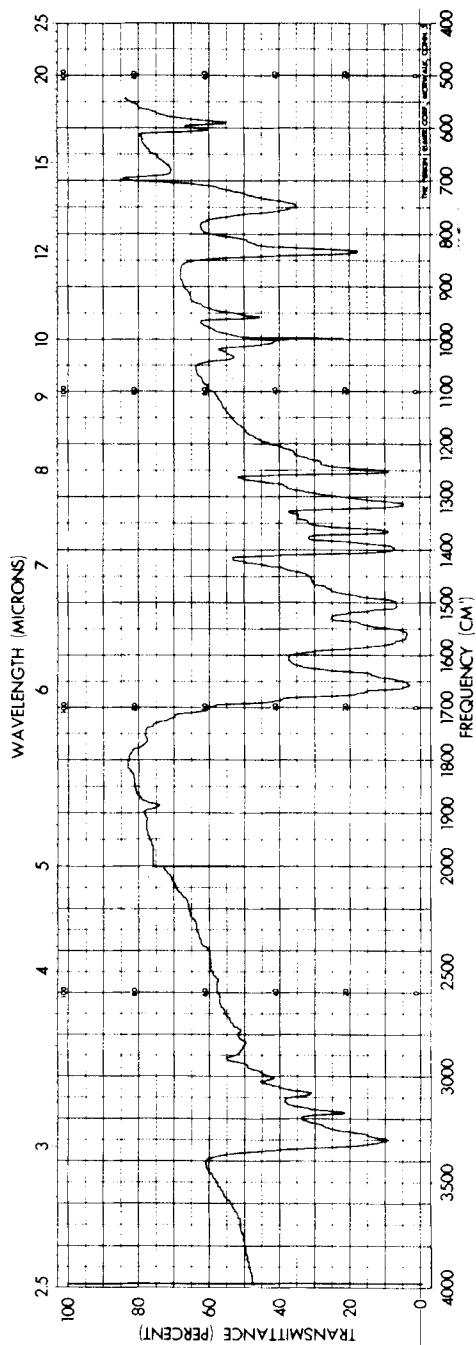
FIG. 3. Infrared spectrum of p-C$_6$H$_4$(NHOCCH$_3$)$_2$. KBr disc.

Polymerization. Part I

Xylylidenetetraalkyl Ethers with Diamines. The general procedure used has been previously described [1] and consisted in mixing the reactants in a reaction tube equipped with a distilling head, a condenser, a receiver, nitrogen gas inlet and outlet, an attachment to a vacuum pump, heating means, etc., and heating the mixture at atmospheric pressure to a temperature 10-50°C above the melt temperature of the mixture; then raising the temperature over a period of hours, while the pressure was reduced from 760 mm Hg to 0.5 mm Hg. In a number of reactions, benzylideneaniline, dimethylformamide, and dimethylacetamide were evaluated as solvents for the reaction. The results of these studies are shown in Table 1, in which the temperature given is the range over which the mixture was reacted for the number of hours specified as the pressure was reduced [1] within the first 4 hr to 0.5 mm Hg pressure.

Xylylidenetetraalkyl Ethers with Diamine Dihydrochlorides. Typical polymerization procedures are given in the following examples.

1. A mixture of 1.0 g of p-phenylenediamine dihydrochloride and 1.56 g of p-xylylidenetetraethyl ether were mixed in a microflask and reacted under an atmosphere of nitrogen. The mixture was heated over a period of 2 hr from room temperature to 220°C. A clear melt formed in the range 60-80°C. Then the temperature was raised slowly over a period of 24 hr to 280°C, after which the reaction mixture was allowed to cool to room temperature. The polymer was ground to a fine powder, transferred to 20 ml of water, neutralized with 8% aqueous sodium carbonate solution, and this mixture stirred constantly at room temperature for 8 hr; the polymer was isolated by filtration. Then the neutralized polymer was washed with distilled water, isolated by filtration, and dried in a vacuum oven at room temperature. There was obtained 1.8 g of a polymer which was mostly brown but contained portions which were colored yellow and blue. Analysis found: C, 80.18; H, 4.95; N, 12.37.

Its infrared spectrum was similar to the brown-yellow (first polymer, Table 1) polymer prepared directly from p-xylylidenetetraethyl ether and the p-phenylenediamine.

2. A mixture of 1.0 g of p-phenylenediamine dihydrochloride and 1.56 g of p-xylylidenetetraethyl ether were reacted in a nitrogen atmosphere in the presence of various solvents under the conditions given in Table 2. Following reaction for the specified time, the reaction mixtures were neutralized with aqueous sodium carbonate according to the procedure given above, isolated, and dried. The infrared spectra of the isolated polymers were similar to the polymers prepared from the acetals and the amines with the exception of the polymers prepared in N-methyl pyrrolidone, which gave marked evidence of incorporation of the pyrrolidone in the polymer.

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TABLE 1. Data on Reaction of p-Xylylidenetetraalkyl Ethers with Phenylenediamines

Acetal used, g	Diamine used, g	Solvent[a] used, g	Temp., °C	Time, hr	Yield,[b] %	Color	Analyses,[c] % C	H	N
Ethyl, 5.41	Para, 14.12	—	220–300	25	115	Brown-yellow	79.60	4.91	12.43
Ethyl, 3.92	Meta, 1.40	—	180–230	29	108	Brown-black	81.01	4.98	12.99
Ethyl, 8.10	Meta, 1.04	—	140–330	20	115	Black	81.37	4.96	13.10
Ethyl, 8.10	Para, 0.99	—	140–370	25	101	Brown	80.67	4.89	13.43
Butyl, 3.67	Para, 1.21	—	160–250	48	93	Brown	80.11	4.97	13.03
Butyl, 4.99	Para, 1.25	—	160–230	22	104	Yellow	79.98	5.07	12.27
Ethyl, 3.11	Meta, 1.11	BA, 5	180–230	36	254	Black	83.66	5.89	10.23
Ethyl, 3.24	Para, 1.19	BA, 5	100–230	53	150	Brown	82.24	5.30	12.14
Ethyl, 2.72	Meta, 1.01	BA, 5	100–300	42	200	Black	83.71	5.88	10.46
Ethyl, 3.92	Para, 1.45	BA, 5	240–400	47	156	Brown	82.62	5.77	10.65
Ethyl, 3.82	Meta, 1.42	BA, 5	240–440	47	173	Black	82.97	5.91	10.33
Butyl, 4.10	Para, 1.37	DMAC, 6	160–250	50	93	Brown	82.09	4.94	12.88
Butyl, 4.66	Para, 1.17	DMF, 10	160–230	23	111	Yellow	79.46	4.93	12.34
Butyl, 3.62	Para, 0.91	BA, 11	200–250	24	86	Yellow	79.66	5.10	12.38
Butyl, 4.50	Para, 1.13	BA, 5	220–310	89	94	Yellow	79.55	4.98	12.33

[a] BA, benzylideneaniline; DMA, dimethylacetamine; DMF, dimethylformamide.
[b] Calculated on the basis of $+HCC_6H_4CH=NC_6H_4N]_{n=\infty}$; analysis for $C_6H_5CH=NC_6H_5$: C, 88.16; H, 6.07; N, 7.73.
[c] Calculated for $+HCC_6H_4CH=NC_6H_4N]_{n=\infty}$: C, 81.53; H, 4.88; N, 13.58.

TABLE 2. Data on Reaction of p-Xylylidenetetraethyl Ether with p-Phenylenediamine Dihydrochloride in Solvents

Solvent, [a]	g	Temp., °C	Time, hr	Yield, g	Color	Analyses, %		
						C	H	N
C_2H_5OH,	35	78.5	24	1.0	Yellow	79.94	5.14	12.28
DMF,	40	100.0	24	1.5	Yellow	79.97	5.08	12.38
DMF,	40	150.0	24	1.8	Yellow Brown	79.66	4.92	12.23
N-MP,	40	100.0	24	1.5	Brown	76.38	4.81	12.79
N-MP,	40	200.0	4	1.1	Yellow	76.42	4.84	12.83
N-MP,	40	200.0	24	1.2	Brown	83.98	6.17	12.97
H_2O,	40	100.0	24	1.1	Yellow	79.45	4.93	12.34

[a]DMF, dimethylformamide; N-MP, N-methylpyrrolidone.

Xylylidenetetraalkyl Ethers with Dibenzylidenephenylenediamines. The apparatus consisted of a microflask equipped with a nitrogen inlet, a thermometer, a distilling head, a condenser, a receiver, a vacuum outlet, and a metal-alloy bath heated by an electric mantle. The general procedure [1] consisted in introducing the reagents into the flask, sweeping out the flask and its contents with deoxygenated nitrogen and then heating the reagents while a slow stream of nitrogen at a pressure of 400-500 mm Hg was passed through the mixture at the temperatures for the time indicated in Table 3, and collecting by-product benzylidenedialkyl ether. At the end of the reaction time, the residue in the reaction flask was allowed to cool to room temperature and isolated. The products were then extracted in a Soxhlet apparatus with hexane or 95% ethanol in which the polymers are insoluble, to separate the polymer from unconverted reagents. The yields given in Table 3 are for the hexane- or alcohol-insoluble fractions.

Products from Postheating. The procedure previously reported [1] was used. A mixture of 10.09 g of dibenzylidene-p-phenylene-diamine, 10 g of p-xylylidene-tetrabutyl ether, and 10 g of benzylideneaniline was reacted as follows:

1.0 hr at 220°C   at 760 mm Hg pressure
1.0 hr at 220-250°C at 140 mm Hg pressure
11.0 hr at 250-270°C at   1 mm Hg pressure
4.0 hr at 300-325°C at   1 mm Hg pressure

TABLE 3.   Data on Reaction of p-Xylylidenetetraalkyl Ether with Dibenzylidenephenylenediamines

Acetal used, g		$(C_6H_5CH{=}N)_2C_6H_4$ used, g		Catalyst, g	Solvent,[a] g	Temp., °C	Time, hr	Yield g	%[b]	Color	Infrared C=N band	Analyses, % C	H	N
XTEE,	2.000	Para,	2.018	—	—	170	90	0.30	1.5	Dark-yellow	Yes	78.62	6.83	12.02
				—	—	220	23	1.30	59.0	Brown	Yes	79.11	6.10	12.33
				—	—	265	6	1.90	87.0	Black	Yes	80.49	5.11	12.97
				TsOH, 0.12	—	170	24	2.50	113.0	Brown	Yes	78.88	6.17	12.27
				TsOH, 0.12	—	220	5	2.47	110.0	Brown	Yes	79.76	6.08	12.30
XTEE,	1.399	Meta,	1.399	—	—	180-270	10	1.10	107.0	Black	Yes	80.65	5.22	12.53
XTEE,	4.000	Para,	2.000	—	—	220-400	75	2.10	143.0	Black	Yes	—	—	12.91
		Meta,	2.000	—	—	270-400	75	2.40	163.0	Black	Yes	—	—	13.01
XTBE,	2.530	Para,	1.810	—	—	240	27	0.00	0.0	No reaction	—	—	—	—
XTBE,	1.860	Para,	1.250	—	BA, 5.0	240	20	0.00	0.0	No reaction	—	—	—	—
XTEE,	2.000	Para,	2.018	—	NNDM, 10.0	220	32	5.40	370.0	Yellow	No	Contains dimethyl-naphthylamine		
				—	NMP, 10.0	253	18	2.20	150.0	Black	Yes	Contains N-methyl-pyrrolidone		
XTEE,	1.000	Para,	1.000	—	PPA, 10.0	220-230	28	1.80	240.0	Black	Yes	High phosphorus content		
				—	BA, 7.0	220-260	24	1.60	220.0	Black	Yes	83.09	5.73	10.09
				—	BA, 1.4	220-370	19	0.70	110.0	Black	Yes	81.15	5.42	11.31
XTEE,	3.000	Para,	3.027	—	BA, 3.0	220-300	64	2.00	132.0	Black	Yes	81.62	5.50	10.22
XTEE,	10.090	Para,	10.090	—	BA, 10.0	220-320	20	3.60	185.0	Black	Yes	83.14	5.69	10.21
XTEE,	1.500	Meta,	1.500	—	BA, 5.0	180-270	60	1.66	155.0	Black	Yes	81.87	5.50	11.36
XTBE,	2.319	Para,	1.500	TsOH, 0.10	DMAC, 10.0	280	12	1.00	100.0	Black	Yes	81.55	5.16	12.84
XTBE	1.860	Para,	1.810	TsOH, 0.10	—	240	24	1.34	107.0	Black	Yes	80.41	5.43	12.67
		Meta,	1.840	TsOH, 0.10	—	240	24	1.42	113.0	Black	Yes	80.78	5.31	12.74

[a]XTEE, p-xylylidenetetraethyl ether; NNMD, N, N-dimethylnaphthylamine; PPA, polyphosphoric acid; XTBE, p-xylylidene-tetrabutyl ether; NMP, N-methylpyrrolidone; DMAC, N, N-dimethylacetamide.
[b]Based on $\text{+HCC}_6H_4CH{=}NC_6H_4N\overline{\overline{}}_{n\,=\,\infty}$.

and 13. 6 g (yield 185% of theory) of black polymer isolated. Then 2. 823 g of the polymer was ground to a very fine powder and reheated for 24 hr at 325–350°C at 1 mm Hg pressure; there was isolated 2. 543 g (166% yield). The distillate consisted primarily of benzylideneaniline. Heating, then, was continued at 350–420°C for 10 hr at 0. 5 mm Hg pressure, and the yield of polymer was 2. 11 g (140%); the distillate consisted mostly of benzylideneaniline and small quantities of dibenzylidene–p–phenylenediamine. Then the heating was continued at 420–450°C for 45 hr at 0. 2 mm Hg pressure and the yield of polymer was 1. 81 g (120%) with the distillate consisting of benzylideneaniline, and very small quantities of aniline, p-pheny-lenediamine, and a trace of benzaldehyde.

Xylylidenetetrallkyl Ether with N, N'-diacetylphenylenediamines. The general procedure [1] consisted in mixing the diacetals and the diamide in a microflask equipped with a nitrogen inlet, a condenser, a thermometer, a receiver, a nitrogen outlet, and a molten metal bath held at the desired temperature. A slow stream of deoxygenated nitrogen was passed through the apparatus during the reaction. The condensation products were extracted in a Soxhlet apparatus first with 95% ethanol, then with acetic acid to separate unconverted reactants from the polymers which are insoluble in these solvents. Two acetals, p-xylylidenetetraethyl ether (XTEE) and p-xylylidene-tetrabutyl ether (XTBE), respectively, were used in the reactions with N, N'-diacetyl-p-phenylenediamine, in the absence and in the presence of p-toluenesulfonic acid as a catalyst, and in the absence or presence of solvents. Typical data relative to the reactions in the absence of solvent are given in Table 4, and in the presence of solvents in Table 5. The yields given are for the solvent-extracted products.

Reaction of Aryldialdehydes and N, N'-Diacetylphenylenediamines. (a) A mixture of 1. 0 g of terephthaldehyde and 1. 4 g of N, N'-diace-tyl-p-phenylenediamine was heated in an atmosphere of nitrogen in a microflask at 220°C for 35 hr. During the reaction, trace quantities of terephthaldehyde sublimed from the reaction mixture. After heating, the mixture was allowed to cool to room temperature and there was isolated 2. 2 g of a brown, insoluble, infusible polymeric product. Its infrared spectrum did not show the absorption band characteristic of the C=N structure in the 1600-cm^{-1} region.

(b) Isophthaldehyde, 1. 0 g, was used instead of the terephthalde-hyde in (a) and reacted under similar conditions and 2. 25 g of a brown, insoluble, infusible polymer was obtained whose infrared spec-trum did not show the absorption band for C=N in the 1600-cm^{-1} region.

(c) Experiments (a) and (b) were repeated with the addition of 0. 1 g of p-toluenesulfonic acid as a catalyst and the yield in both cases was 2. 1 g of a brown insoluble, infusible polymer. The infra-

TABLE 4. Data on Reaction of p-Xylylidenetetraalkyl Ethers with N, N'-Diacetyl-p-Phenylenediamine

Acetal[a] used, g	Diamine, g	Catalyst, g	Temp., °C	Time, hr	Polymer yield g	%[b]	Color	Analyses, % C	H	N	Infrared C=N band
XTEE, 2.00	1.3630	None	170	90.0	0.000	0	—	—	—	—	—
	1.3630	None	220	23.0	0.900	61	Brown	75.28	5.28	10.59	Present
	1.3630	None	265	3.5	1.600	110	Brown	75.56	5.85	10.62	Present
XTEE, 1.65	1.0223	None	210	3.5	1.055	111	Brown	75.77	5.42	10.61	Present
XTEE, 2.10	1.0223	None	210	3.5	1.430	98	Dark brown	75.68	5.39	10.58	?
XTEE, 2.00	1.3630	TsOH, 0.12	170	28.0	0.900	64	Black	70.99	5.64	6.18	?
	1.3630	TsOH, 0.12	220	19.0	1.610	111	Black	71.07	5.45	5.97	?
XTBE, 3.02	1.1300	None	170	24.0	0.000	0	—	—	—	—	—
	1.1300	TsOH, 0.1	200	24.0	1.000	51	Brown	74.01	5.52	6.32	?

[a]XTEE, p-xylylidenetetraethyl ether; XTBE, p-xylylidenetetrabutyl ether.
[b]Based on $\vdash HCC_6H_4CH=NC_6H_4N\dashv_n$, $n = \infty$.

TABLE 5. Data on Reaction of p-Xylylidenetetraethyl Ethers with N,N'-Diacetyl-p-phenylenediamine in the Presence of Solvents

Acetal, g	Diamide, g	Catalyst, g	Solvent[a] used, g	Time, hr	Temp., °C	Polymer yield g	Polymer yield %[b]	Color	Analyses, % C	Analyses, % H	Analyses, % N
2.300	1.3630	None	BPC 6.0	26	220	1.15	68	Brown	—	—	—
1.000	0.6815	None	BA 6.0	5	185–320	1.1	150	Black	81.55	5.65	5.96
5.000	3.4070	None	BA 8.0	60	240–260	4.94	144	Black	83.77	5.48	7.35
2.000	1.3630	None	NNDM 8.0	24	170	0.0	0	—	—	—	—
	1.3630	None	NNDM 8.0	32	220	0.0	0	—	—	—	—
	1.3630	None	NMP 10.0	18	200	1.7	116	Black	76.41	4.82	12.80
	1.3630	None	NMP 10.0	8	250	2.2	150	Black	75.92	4.84	12.76
1.000	1.6850	—	PPA 10.0	20	170	1.7	230	Brown	Contains high P		
	1.6850	—	PPA 10.0	23	220	2.1	288	Brown	Contains high P		
2.000	1.3630	TsOH, 0.12	NMP 7.0	40	170–220	1.87	129	Black	73.21	5.10	11.66
1.000	0.6815	TsOH, 0.10	NMP 3.0	25	170–250	1.2	165	Black	72.84	4.87	12.01
1.200	0.6815	TsOH, 0.10	NMP 3.0	25	170–250	1.4	192	Black	71.06	4.93	11.87
2.045	3.000	TsOH, 0.20	BA 7.0	43	220–360	7.8	354	Black	83.11	5.43	8.11
3.020	1.1260	None	BA 5.0	31	220–240	0.0	0	—	—	—	—
4.778	1.8030	None	DMAC 10.0	31	220–240	0.0	0	—	—	—	—
3.100	1.1320	TsOH, 0.20	DMAC 10.0	41	200–280	1.03	106	Black	85.96	5.46	7.33

[a]BPC, benzylidene-p-chloroaniline; BA, benzylideneaniline; NNDM, N,N-dimethylnaphthylamine; NMP, N-methylpyrrolidone; PPA, polyphosphoric acid; DMAC, dimethylacetamide.
[b]Based on $\pm HCC_6H_4CH{=}NC_6H_4N\pm_n$ = ∞.

red spectra of these polymers did not show absorptions in the $1600\text{-}cm^{-1}$ region.

Reaction of Xylylidenedianils and N, N'-Diacetylphenylenediamines.
(a) A mixture of 2. 96 g of p-xylylidenedianil and 2. 0 g of N, N'-diacetyl-p-phenylenediamine was heated in an atmosphere of nitrogen in a microflask at 260°C for 24 hr at 20 mm Hg pressure. The reaction mixture was heterogeneous during most of the reaction period; the molten portion of the mixture did not become viscous. When cooled, the mixture was extracted with alcohol in a Soxhlet apparatus and all the reagents were recovered unchanged.

(b) N, N'-Diacetyl-m-phenylenediamine was substituted for the para derivative in (a) and the mixture reacted under the same conditions as in (a); the starting materials were recovered unchanged.

(c) Experiments (a) and (b) were repeated with the addition of 0. 1 g of p-toluenesulfonic acid. During the course of the reaction there was collected 0. 45 g of aniline as a distillate and 0. 35 g of N, N'-diacetyl-p-phenylenediamine as a sublimate. When cooled, there was obtained 4. 0 g of a yellow, brittle polymeric product whose infrared spectrum did not show the absorption band characteristic of the C=N structure in the $1600\text{-}cm^{-1}$ region.

Polymerization. Part II

Diacetals with Diamines. The procedure used has been reported previously [1]. The intimately mixed reagents were reacted under an atmosphere of deoxygenated nitrogen and the temperature of the reaction was controlled in a Model 1422-071 temperature controller from the Cole-Parmer Instrument and Equipment Company. For the sake of uniformity, the following reaction schedule was maintained for all polymerizations. For each of the periods of time indicated, the temperature was slowly raised over the period of time from the lower to the higher temperature:

>1. 5 hr at 100–130°C at 760 mm Hg
>1. 0 hr at 130–150°C at 760 mm Hg
>17. 0 hr at 150–230°C at 760 mm Hg
>23. 0 hr at 230–320°C at   1 mm Hg

The reactions between the diacetals and the diamines were uncatalyzed and were performed in the absence and in the presence of benzylideneaniline. The data on the reactions between p-xylylidene-tetrabutyl ether with p-phenylenediamine, m-phenylenediamine, and mixtures of m- and p-phenylenediamines, respectively, are given in Table 6 (see also Table 7). The designation H320 is placed at the end of the polymer number to indicate that the polymer has been condensed to a temperature of 320°C.

TABLE 6. Data on the Reaction of p-Xylylidenetetrabutyl Ether with Phenylenediamines

Polymer	Acetal, g	Diamine used, g		BA,[a] g	Yield g	Yield %	C	H	N
I-H320	3.3606	Para,	0.8840	None	1.80	103	80.76	5.33	12.89
II-H320	3.3079	Para,	0.8736	5.3649	2.51	145	81.21	5.44	11.09
III-H320	4.4250	Meta,	1.4100	None	2.33	106	80.98	5.18	13.13
IV-H320	4.5120	Meta,	1.4950	5.019	4.75	166	81.76	5.55	12.01
V-H320	3.2740	Meta	0.2158	None	1.73	101	80.57	5.39	12.78
		+							
		Para	0.6474						
VI-H320	5.5321	Meta	0.7266	None	2.97	103	80.81	5.24	12.96
		+							
		Para	0.7266						
VII-H320	3.2223	Meta	0.6310	None	1.70	102	80.74	5.29	12.83
		+							
		Para	0.2106						

The "Analyses, %" header spans columns C, H, N.

[a]BA, benzylideneaniline.

[b]Calculated on the basis of $\frac{}{}HCC_6H_4CH=NC_6H_4N\frac{}{}{}_{n=\infty}$.

Yellow Polymer Y-H320. A yellow Schiff base polymer was prepared as a reference polymer by reacting a mixture of 0.6721 g of p-xylylidenetetrabutyl ether with 0.1768 g of p-phenylenediamine under the following conditions:

Temp., °C/pressure, mm Hg	Time, hr
100−130/760	1.5
130−150/760	1.0
150−320/0.6	0.5

and the yield of polymer Y-H320 of dull, unfused yellow polymer was

TABLE 7.   Observations During Reactions of p-Xylylidenetetrabutyl Ether with Phenylenediamines

Polymer	1.5 hr at 100–130°C at 760 mm Hg	1.0 hr at 130–150°C at 760 mm Hg	17.0 hr at 150–230°C at 760 mm Hg	23.0 hr at 230–320°C at 1 mm Hg
I-H320	Brown liquid, no distillate	Some sublimation, 2.14 g of BuOH distillate	Yellow-brown solid, no distillate	Brown-black solid, 0.25 g of solid distillate
II-H320	Yellow paste, no distillate	Yellow liquid, some sublimation, 2.24 g of BuOH distillate	Dark-yellow liquid, no distillate	Brown solid, 3.37 g of solid distillate
III-H320	Two layers, no distillate	Red-brown liquid and solid, 3.60 g of BuOH distillate	Black liquid and solid, no distillate	Black solid, 0.32 g of solid distillate
IV-H320	Orange liquid, no distillate	Red-brown melt, 3.61 g of BuOH distillate	Black liquid and solid, no distillate	Black solid, 1.93 g of distillate
V-H320	Two layers, no distillate	Brown liquid, some sublimation, 2.20 g of BuOH distillate	Brown solid, no distillate	Brown-black solid, no distillate
VI-H320	Two layers, no distillate	Red-brown liquid and solid, 3.62 g of BuOH distillate	Orange solid, no distillate	Black solid, no distillate
VII-H320	Two layers, no distillate	Yellow-brown melt, 2.34 g of BuOH distillate	Brown solid, no distillate	Brown solid, 0.43 g of solid distillate

0. 385 g (110%) on the basis of DP = n = ∞, but only 81% on the basis of a mixture of dimer and trimer.

Analysis : Calcd. per cent for

n = 2, $C_{36}H_{40}N_4O_2$: C, 77. 14; H, 7. 14; N, 10. 00; O, 5. 71
n = 4, $C_{64}H_{60}N_8O_2$: C, 79. 01; H, 6. 17; N, 11. 52; O, 3. 29
n = ∞, $C_{14}H_{10}N_2$: C, 81. 53; H, 4. 88; N, 13. 59
                Found: C, 78. 06; H, 6. 65; N, 10. 77

p-Xylylidenetetrabutyl Ether with Dibenzylidenephenylenediamines. The procedure and heating schedules used for the reaction between the diacetals and the diamines was used for the reaction of the diacetals with the dibenzylidenephenylenediamines, except that in those reactions which contained benzylideneaniline as a solvent, the heating at 320°C/1 mm Hg was extended for an additional 24 hr. See Tables 8 and 9.

Postheating of the Polymers to 425, 600, and 1176°C. The experimental technique used was the same as that previously reported [1]. The postheatings of the polymer samples at 425 and 600°C were performed in quartz tubes under a nitrogen atmosphere. The postheating of the samples at 425°C was for a period of 40 hr; at 600°C for a period of 20 min.

Other portions of the polymer samples were postheated under nitrogen in the du Pont thermogravimetric analyzer by procedures previously reported [1], to a recorded temperature of 1200°C, which, when corrected for the nonlinearity of the chromel−alumel thermocouple, corresponds to 1176°C. The designations H320, H425, H600, and H1176 after the polymer number indicates the maximum temperature to which the polymer has been heated. The designation H320-425 means that the portion of the sample which was prepared at 320°C was postheated at 425°C; the designation H425-600 means that a portion of the polymer condensed to 425°C was postheated at 600°C. The designation H320-1176 means that a sample of the polymer condensed to 320°C was postheated to 1176°C, and H600-1176 means that the sample of the polymer condensed to 600°C was postheated to 1176°C. Table 10 summarizes the yields of the polymers obtained at the condensation temperatures of 320 and 425°C. The infrared spectra of typical H320, H425, and H600 Schiff base polymers are given in Figs. 4 to 16 inclusive.

Thermogravimetric Analyses. The du Pont 950 thermogravimetric analyzer was used to determine the thermal properties of the polymers under conditions identical to those used in previous studies [1]. The heating rate used was 15°C/min. A number of thermogravimetric measurements were made in nitrogen and in air at a flow rate of 1 standard liter/min. Sample weight was standardized at 10 mg. A temperature correction has been made for the nonlinearity of the chromel−alumel thermocouples. The thermogravimetric data are

TABLE 8.   Data on Reaction of p-Xylylidenetetrabutyl Ether with Dibenzylidene-phenylenediamines

Polymer	Acetal, g	DBPD[a] used, g	BA,[a] g	$ZnCl_2$, g	Yield g	Yield %[b]	Analyses, % C	H	N
VIII-H320	3.0807	Para, 2.2152	—	0.09	2.02	125	81.12	5.41	12.24
IX-H320	3.3170	Para, 2.4140	5.25	0.10	3.13	179	82.73	5.59	10.74
X-H320	2.8116	Meta, 2.0165	—	0.10	2.50	171	81.01	5.49	12.06
XI-H320	2.8116	Meta, 2.0170	4.60	0.10	3.25	223	83.10	5.74	10.11

[a]DBPD, dibenzylidenephenylenediamine; BA, benzylideneaniline.
[b]Calculated on the basis of $\text{—HCC}_6\text{H}_4\text{CH=NC}_6\text{H}_4\text{N—}_n$ $n = \infty$.

TABLE 9. Observations During Reaction of p-Xylylidenetetrabutyl Ether with Dibenzylidenephenylenediamines

Polymer	1.5 hr at 100–130°C/ 760 mm Hg	1.0 hr at 130–150°C/ 760 mm Hg	17 hr at 150–230°C/ 760 mm Hg	23 hr at 230–320°C/ 1 mm Hg	47 hr at 320°C/ 1 mm Hg
VIII	Brown liquid, some solid, no distillate	Brown solution, no distillate	Black solid, black liquid, 1.3 g of distillate	Black solid, 1.5 g of distillate	—
IX	Brown liquid, no distillate	Brown solution, no distillate	Black liquid; 0.99 g of distillate	Viscous black melt	Black solid, 6.0 g of distillate
X	Light-brown liquid, no distillate	Brown solution, no distillate	Black solid, black liquid, 1.14 g of distillate	Black solid, very little distillate	—
XI	Brown liquid, some solids	Brown solution	Black liquid, 1.39 g of distillate	Viscous, black melt	Black solid, 3.8 g of distillate

TABLE 10.   Effect of Postheating on Per Cent Yield and
Color of Polymer

Polymer	320°C		425°C	
	% Yield[a]	Color	% Yield[a]	Color
Y	110	Yellow	71	Brown
I	103	Brown-black	73	Dull black
II	145	Brown	86	Dull black
III	106	Black	103	Shiny black
IV	166	Black	134	Shiny black
V	101	Brown-black	76	Dull black
VI	103	Black	82	Dull black
VII	103	Brown	86	Shiny black
VIII	125	Black	49	Dull black
IX	179	Black	89	Dull black
X	171	Black	147	Dull black
XI	223	Black	91	Shiny black

[a]Calculated on the basis of $=\!\!\!\text{HCC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_4\text{N}\!\!\!=_{\overline{n\,=\,\infty}}$.

shown in Tables 11 and 12. Typical thermograms of the polymers in
nitrogen and in air are shown in Figs. 17 and 18, respectively.

DISCUSSION

Part I

   Diacetals and Diamines. The polymerization reaction between the
ethyl acetal, p-xylylidenetetraethyl ether, and the diamines was found
to proceed readily. When the mixture of the diamine and ethyl ace-
tal was heated, the liberation of ethyl alcohol was detected at 84°C,
at which temperature a partial melt of the reactants occurred, and a
homogeneous melt of the monomers was observed in the range
95–100°C.
   Usually within about 15 min at 100°C, a yellow brick-dust poly-
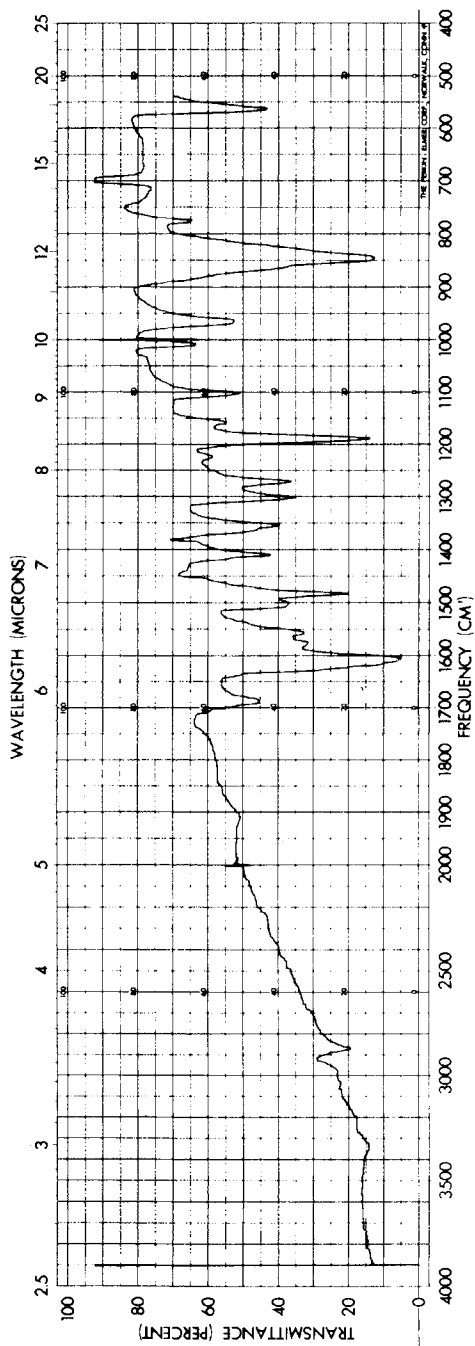mer precipitated, but on raising the temperature of the mixture to

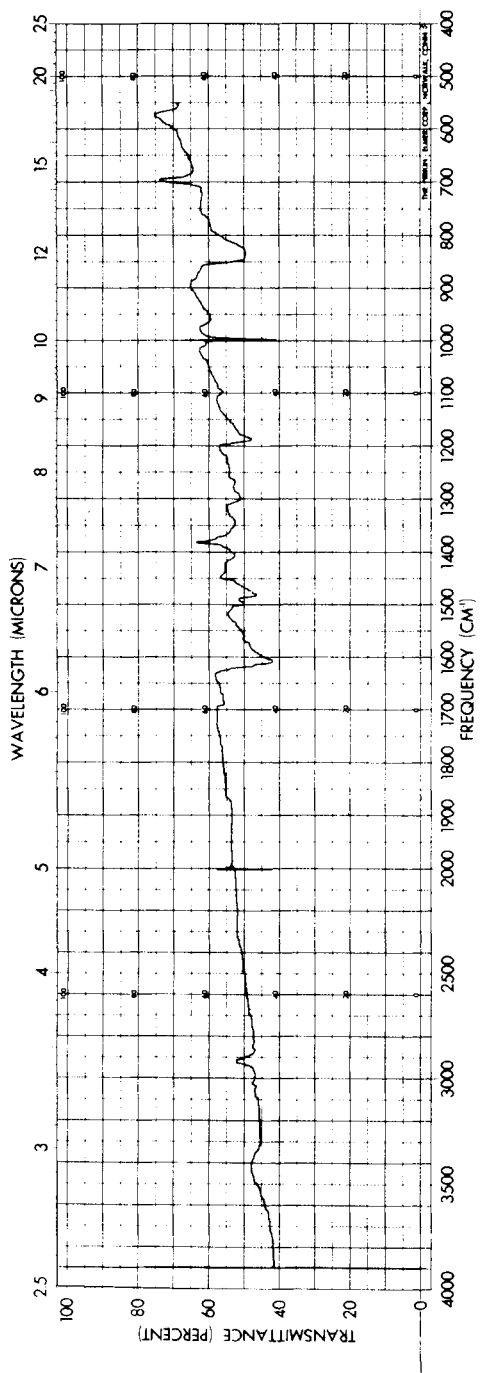FIG. 4. Infrared spectrum of yellow polymer Y. KBr disc.
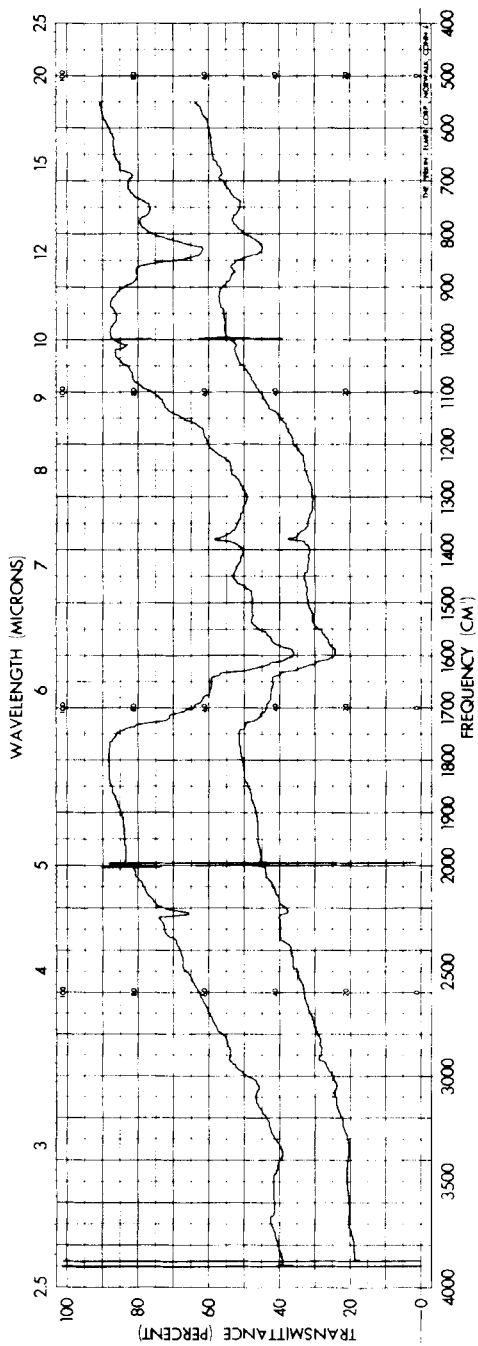
FIG. 5. Infrared spectrum of polymer I-H320. KBr disc.

FIG. 6. Infrared spectra of polymer I. KBr disc. Upper curve,
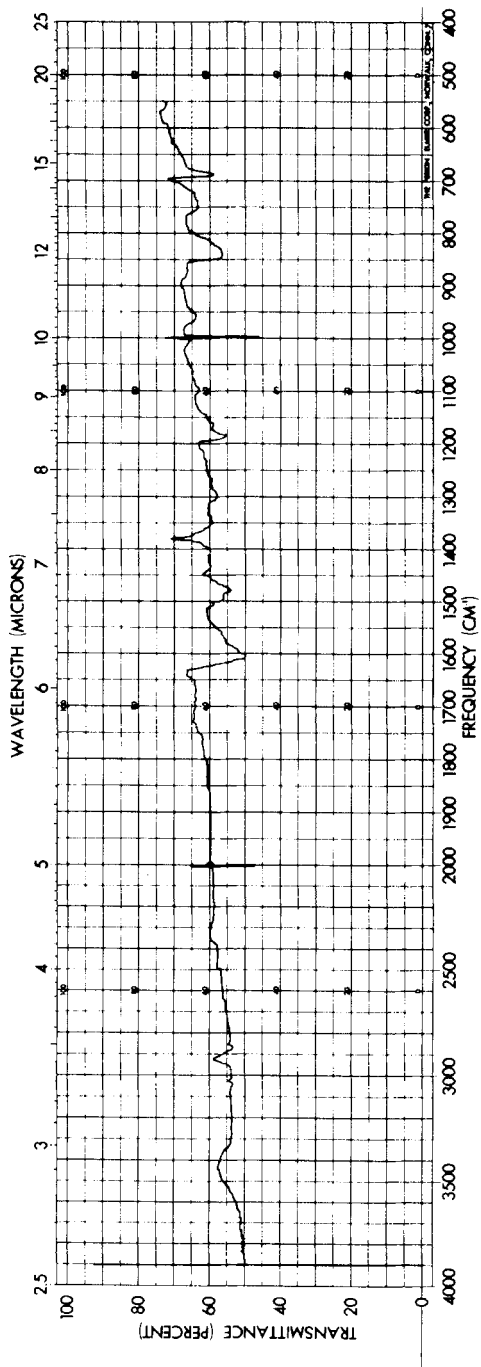H425; lower curve, H600.

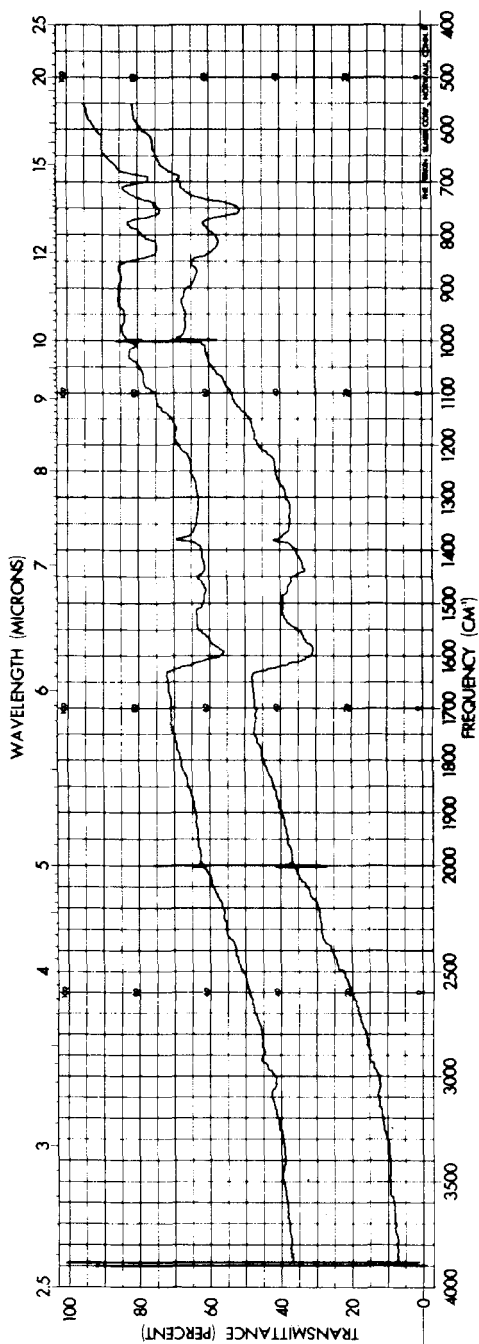FIG. 7. Infrared spectrum of polymer II-H320. KBr disc.

FIG. 8. Infrared spectra of polymer II. KBr disc. Upper curve, H425; lower curve, H600.
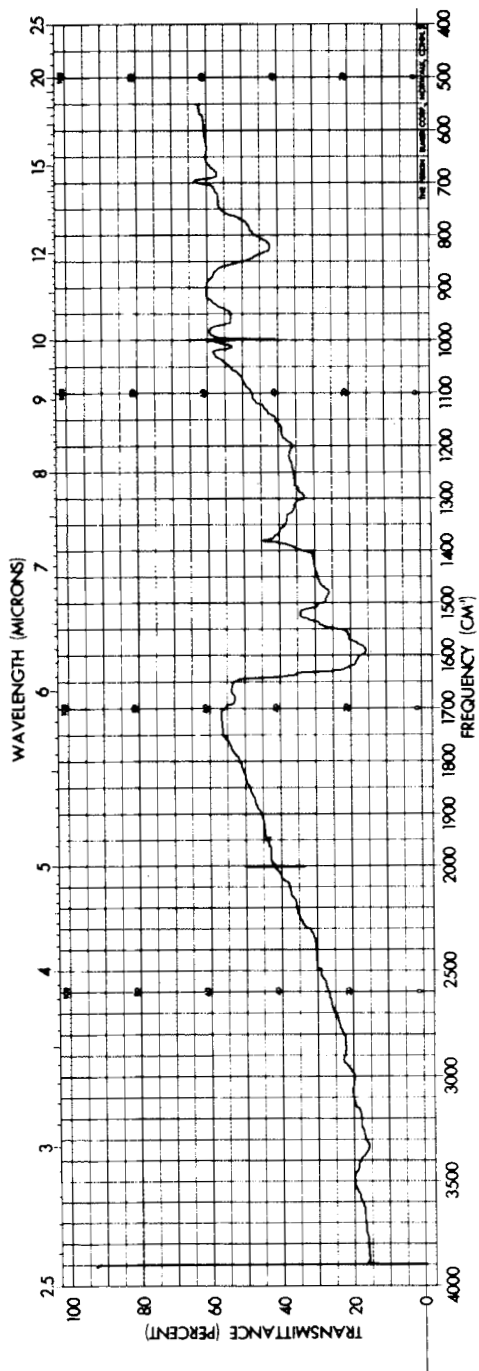
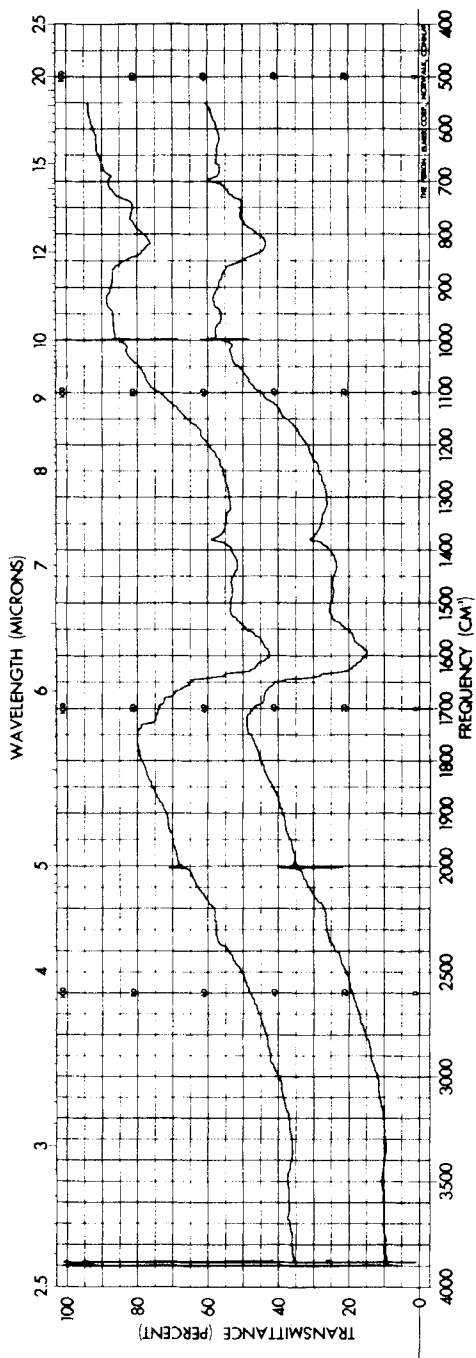FIG. 9. Infrared spectrum of polymer III, H320. KBr disc.

FIG. 10. Infrared spectra of polymer III. KBr disc. Upper curve, H425; lower curve, H600.
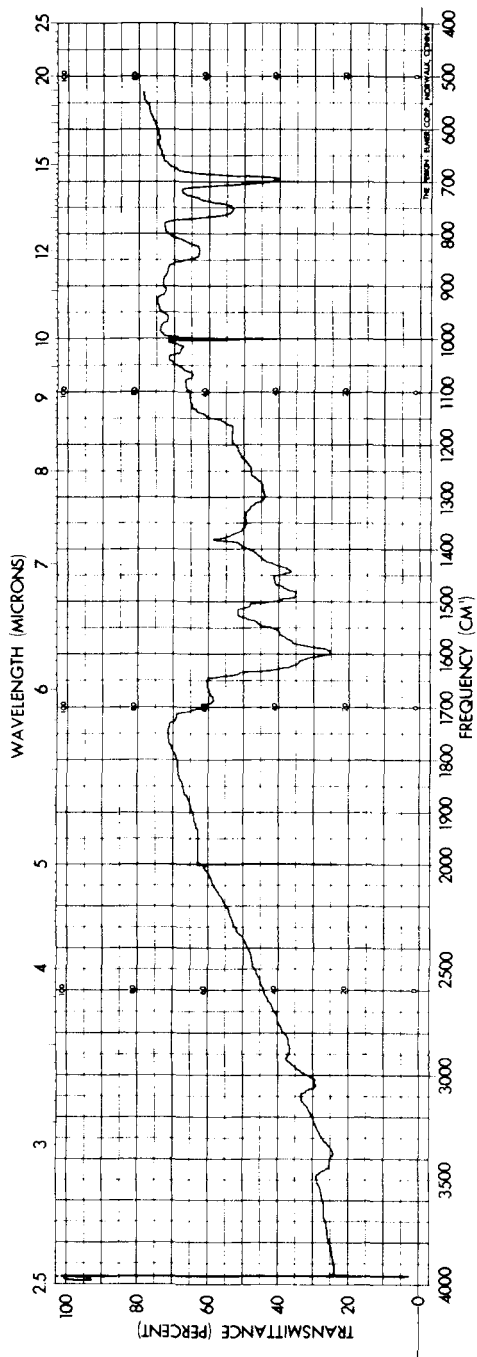
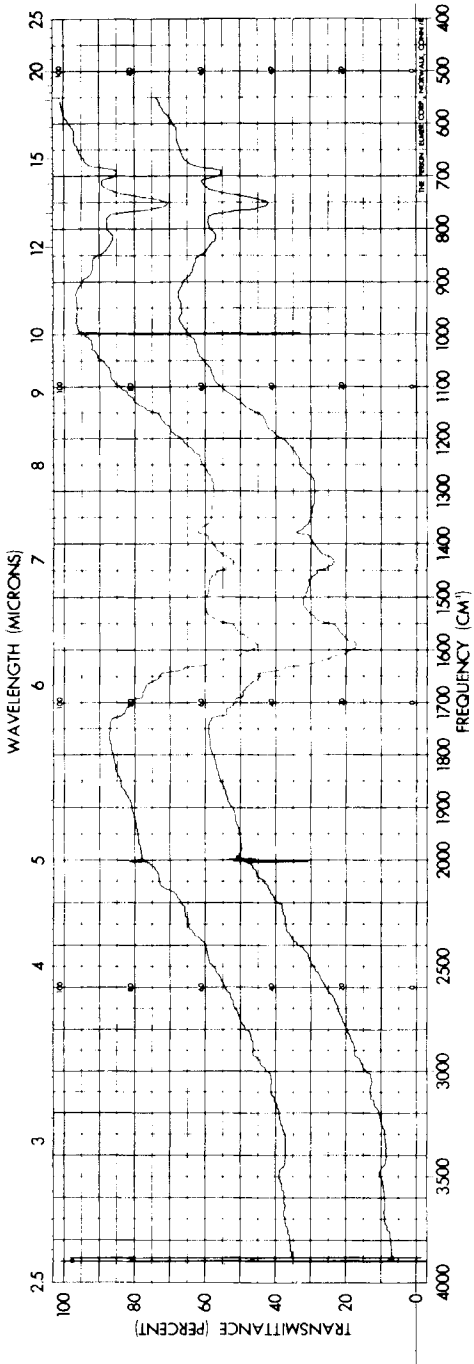FIG. 11. Infrared spectrum of polymer IV, H320. KBr disc.

FIG. 12. Infrared spectra of polymer IV. KBr disc. Upper curve, H425; lower curve, H600.

FIG. 13. Infrared spectra of polymer VIII. KBr disc. Upper curve, H320; lower curve, H425.

FIG. 14. Infrared spectra of polymer IX. KBr disc. Upper curve,
H320; lower curve, H425.

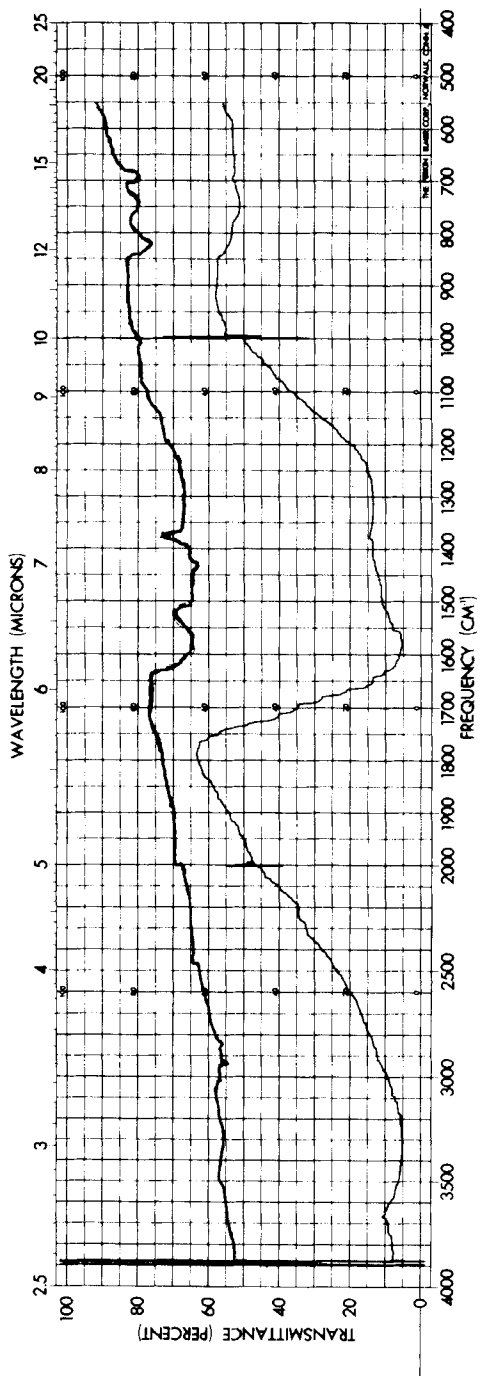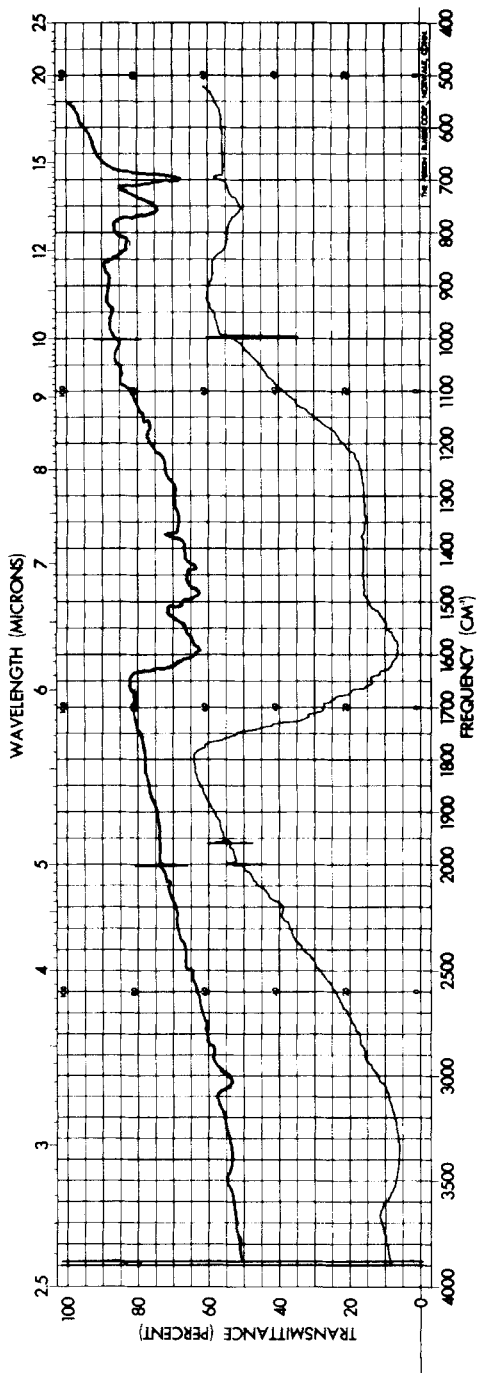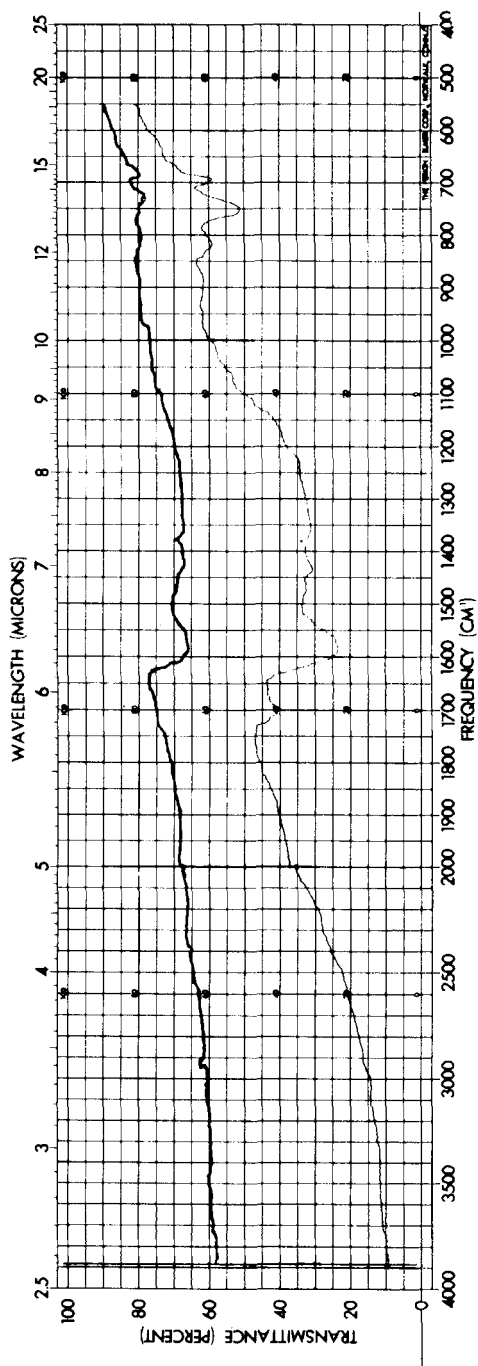FIG. 15. Infrared spectra of polymer X. KBr disc. Upper curve, H320; lower curve, H425.
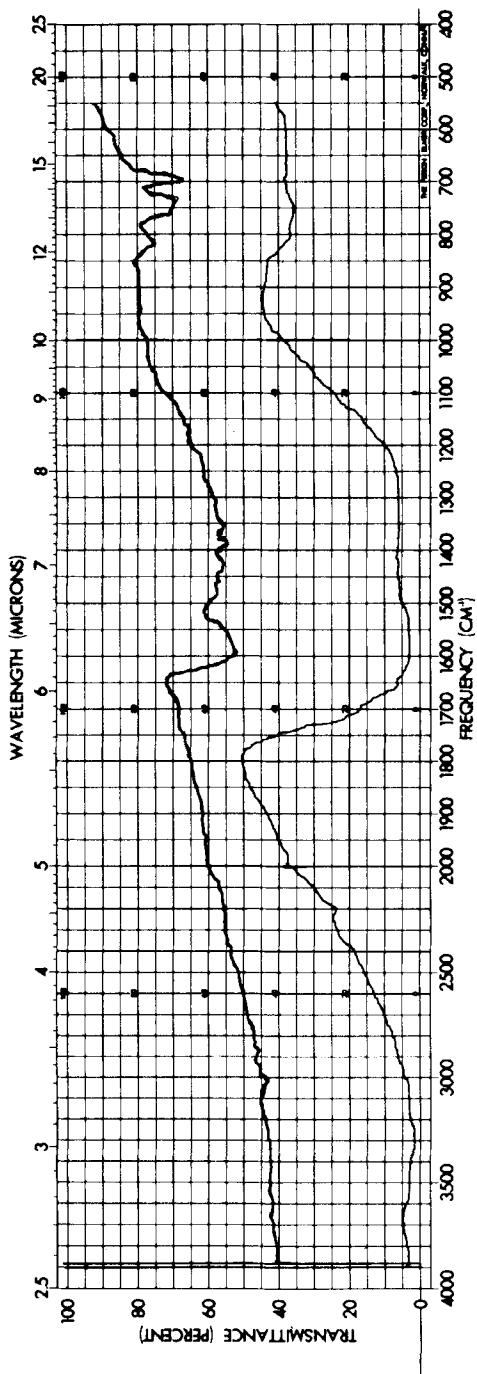
FIG. 16. Infrared spectra of polymer XI. KBr disc. Upper curve, H425.

TABLE 11. Per Cent Loss of Weight of Polymers at Various
Temperatures While Being Heated in Nitrogen

Polymer	% Weight Loss at °C					Temp. (°C) at which loss begins
	400	600	800	1000	1176	
I-H320	3.0	39.0	51.0	54.0	56.5	289
I-H320-425	0.0	2.0	18.0	23.0	27.0	575
I-H320-600	0.0	1.0	10.0	15.0	19.0	605
I-H320-1176	0.0	0.0	0.0	2.0	4.5	880
II-H320	14.0	43.0	52.0	53.0	56.0	220
II-H320-425	0.0	6.0	18.0	21.0	22.5	560
II-H320-600	0.0	1.0	7.5	11.0	15.0	610
II-H320-1176	0.0	0.0	0.0	1.5	2.3	960
III-H320	1.0	20.0	27.0	30.0	35.0	430
III-H320-425	0.0	2.0	4.5	16.0	22.0	575
III-H320-600	0.0	2.0	7.5	11.0	16.0	560
III-H320-1176	0.0	0.0	0.0	1.0	2.3	950
IV-H320	0.0	21.0	27.0	30.0	36.0	420
IV-H320-425	0.0	1.0	4.5	15.0	22.0	570
IV-H320-600	0.0	3.0	9.5	12.0	17.0	550
IV-H320-1176	0.0	0.0	0.0	0.0	2.3	100
V-H320-600	0.0	2.0	9.0	14.0	19.5	520
V-H320-1176	0.0	0.0	0.0	1.0	5.0	860
VI-H320-600	0.0	1.0	6.0	10.0	15.0	580
VI-H320-1176	0.0	0.0	0.0	2.0	2.3	910
VII-H320-600	0.0	2.0	7.0	10.0	15.6	595
VII-H320-1176	0.0	0.0	0.0	5.0	5.4	900
VIII-H320	4.0	10.0	25.0	36.0	45.0	200
VIII-H320-1176	0.0	0.0	0.0	3.0	5.6	880
IX-H320	0.0	4.6	20.0	25.0	36.5	500
IX-H320-1176	0.0	0.0	0.0	0.5	6.0	980
X-H320-425	0.0	3.0	11.0	14.0	19.0	545
X-H320-1176	0.0	0.0	0.0	0.0	2.5	1000
XI-H320-425	0.0	3.5	19.0	26.0	32.0	440
XI-H320-1176	0.0	0.0	0.0	0.0	1.4	1000
Y-H320	6.0	59.0	68.0	70.0	73.0	200

TABLE 12. Per Cent Weight Loss of Polymers at Various
Temperatures While Being Heated in Air

| | % Weight loss at °C | | | | Temp. (°C) at which | |
| | | | | | Weight loss begins | Sample disappears |
Polymer	400	500	600	700		
I-H320	7.0	73.0	100.0	—	380	600
I-H320-425	0.0	2.0	78.0	100.0	480	690
I-H320-600	0.0	52.0	93.0	100.0	400	640
I-H320-1176	0.0	0.0	4.0	50.0	525	800
II-H320	20.0	29.0	73.0	100.0	255	670
II-H320-425	0.0	2.0	48.0	99.0	440	720
II-H320-600	0.0	27.0	97.0	100.0	400	640
II-H320-1176	0.0	0.0	0.0	52.0	550	830
III-H320	4.0	38.0	88.0	100.0	350	650
III-H320-425	0.0	1.0	39.0	99.0	450	740
III-H320-600	0.0	0.0	21.0	97.0	480	742
III-H425-600	0.0	0.0	10.0	52.0	535	805
III-H320-1176	0.0	0.0	0.0	14.0	590	920
III-H320-600-1176	0.0	0.0	0.0	11.0	610	1000
IV-H320	2.5	20.0	86.0	100.0	320	670
IV-H320-425	0.0	1.0	32.0	94.0	470	790
IV-H320-600	0.0	1.0	28.0	97.0	460	725
IV-H425-600	0.0	0.0	16.0	94.0	525	870
IV-H320-1176	0.0	0.0	1.0	21.0	560	980
IV-H425-600-1176	0.0	0.0	0.0	16.0	605	1000
V-H320	4.0	31.0	92.0	100.0	340	660
V-H320-425	0.0	1.0	22.0	100.0	515	688
V-H320-1176	0.0	0.0	12.0	57.0	530	990
VI-H320	1.0	25.0	89.0	100.0	370	670
VI-H320-425	0.0	1.0	42.0	94.0	430	775
VI-H320-600	0.0	8.0	80.0	96.0	440	800
VI-H320-1176	0.0	0.0	5.0	30.0	560	920
VII-H320	1.0	18.0	62.0	100.0	380	710
VII-H320-425	0.0	12.0	52.0	97.0	395	735
VII-H320-600	0.0	6.0	88.0	100.0	400	670
VII-H320-1176	0.0	0.0	4.0	33.0	580	910
VIII-H320	5.0	56.0	90.0	100.0	340	650
VIII-H320-425	0.0	16.0	68.0	100.0	370	660
VIII-H320-600	0.0	0.0	8.0	36.0	545	895

TABLE 12. Per Cent Weight Loss of Polymers at Various
Temperatures While Being Heated in Air (cont.)

| | % Weight loss at °C | | | | Temp. (°C) at which | |
Polymer	400	500	600	700	Weight loss begins	Sample disappears
IX-H320	3.0	48.0	91.0	100.0	355	640
IX-H320-425	2.0	43.0	97.0	100.0	350	630
IX-H320-1176	0.0	0.0	14.0	100.0	520	860
X-H320	0.0	54.0	93.0	100.0	420	790
X-H320-425	0.0	9.0	68.0	100.0	400	720
X-H320-1176	0.0	0.0	31.0	87.0	505	960
XI-H320	0.0	9.0	68.0	100.0	420	700
XI-H320-425	0.0	11.0	38.0	97.0	400	721
XI-H320-1176	0.0	0.0	6.0	40.0	560	900
Y-H320	4.0	60.0	81.0	100.0	150	680

at least about 220°C, the color of the polymer changed to a brown
color. The color of these polymers was darker than the color of the
polymers obtained from the reaction in solution of the diamine and
the dialdehyde [1]. These brown polymers were found to be soluble
in benzylideneaniline and to be convertible to black polymers when
the benzylideneaniline solution was heated and further condensation
achieved. The difference in the behavior of m-phenylenediamine and
p-phenylenediamine in their reactions with p-xylylidenetetraethyl
ether was very marked. Consistently, the colors of the polymers
obtained with m-phenylenediamine were very dark brown or black,
compared with the yellow polymers obtained from p-phenylene-
diamine. The yields of polymers obtained from the m-phenylene-
diamine reactions more closely approximated the theoretical yield
than the reactions using p-phenylenediamine. This difference is due
to the fact that the systems based on m-phenylenediamine remained
a fluid melt for longer periods of time than the reactions using p-
phenylenediamine, thereby allowing propagation to occur to a higher
degree of polymerization. This observation confirmed similar re-
sults previously reported [2, 3] on the direct condensation of the di-
aldehydes and the diamines. However, when p-phenylenediamine was
condensed with p-xylylidenetetraethyl ether in excess of molar
quantities, the polymers obtained were dark brown in color and in
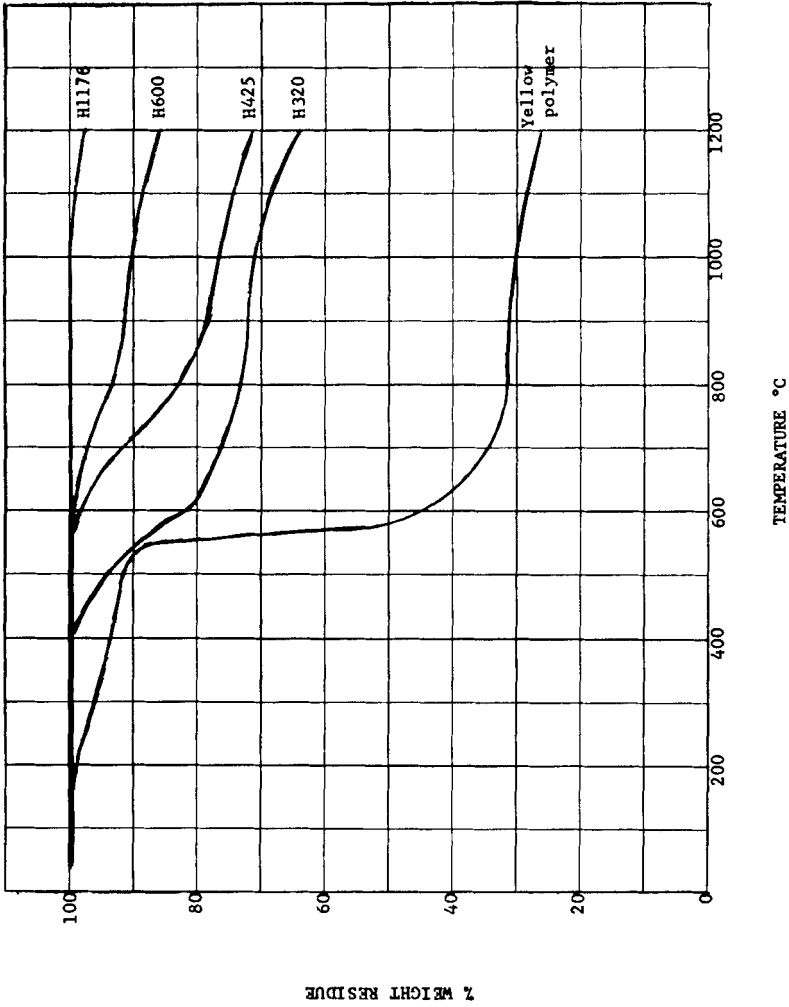approximately theoretical yield.

FIG. 17. Typical thermograms in nitrogen of black Schiff base polymers which were condensed to the temperatures indicated and compared to yellow Schiff base polymer, Y -H320.
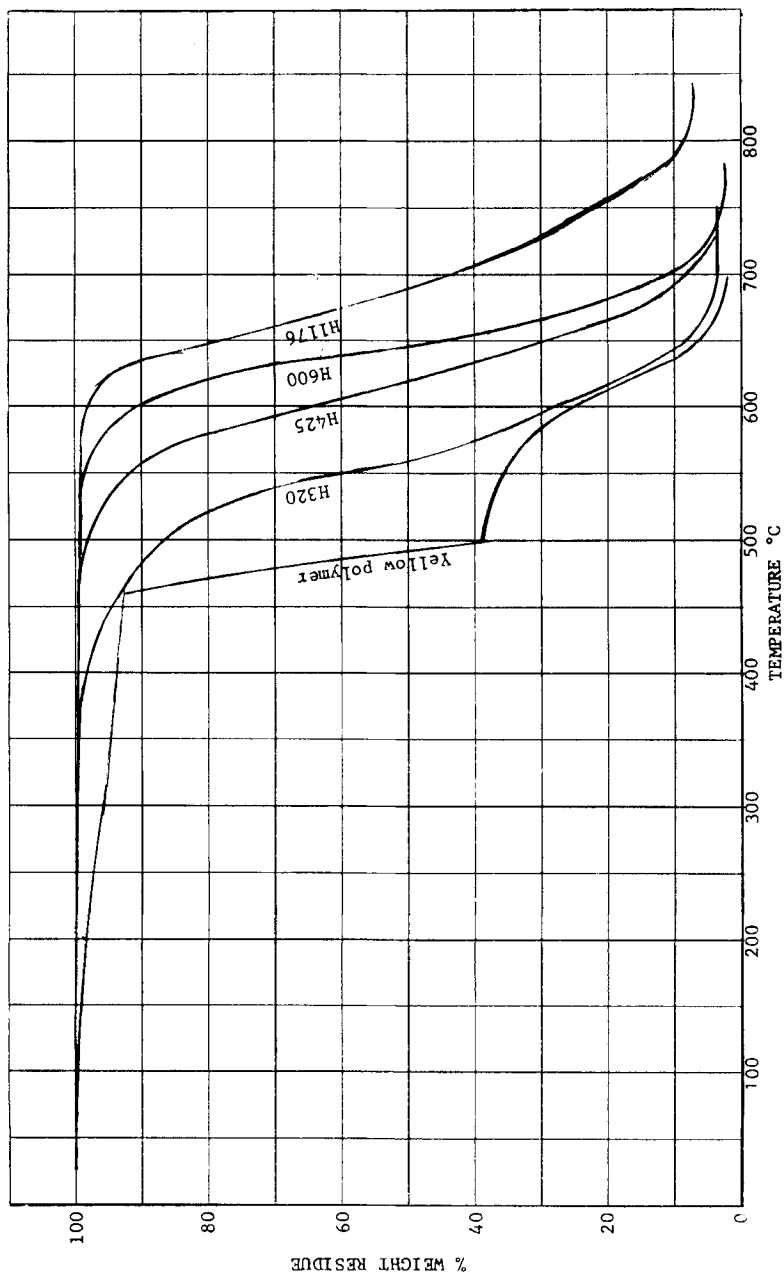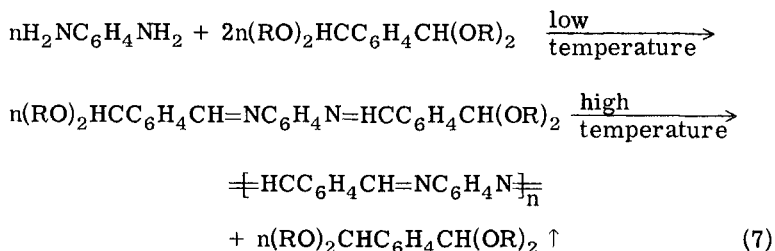
FIG. 18. Typical thermograms in air of black Schiff base poly-
mers which were condensed to the temperatures indicated and
compared to yellow Schiff base polymer.

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The infrared spectra of the polymers showed absorption bands in the region of 1600 cm^{-1}, characteristic of the C=N frequency of the Schiff base linkage; the bands characteristic of the acetal linkages in the region 1055 and 1100 cm^{-1} were markedly evident in the yellow polymers, but the intensity of these peaks dimished as the color of the polymer darkened from yellow to brown to black.

When p-xylylidenetetraethyl ether in excess of molar quantities was condensed with p-phenylenediamine, the polymers obtained were dark brown in color and the yields approximated the theoretical amount. The infrared spectra of these dark brown polymers showed bands characteristic of the C=N linkage in the region 1600 cm^{-1} as well as those for the acetal linkages at 1055 and 1100 cm ^{1} during the the early polymerization stages, the intensity of which diminished markedly with continued polymerization, as would be expected from the following reaction:

$$nH_2NC_6H_4NH_2 + 2n(RO)_2HCC_6H_4CH(OR)_2 \xrightarrow{\text{low temperature}}$$

$$n(RO)_2HCC_6H_4CH=NC_6H_4N=HCC_6H_4CH(OR)_2 \xrightarrow{\text{high temperature}}$$

$$\equiv\!\!\!\vdash HCC_6H_4CH=NC_6H_4N\vdash\!\!\!\equiv_n$$

$$+ n(RO)_2CHC_6H_4CH(OR)_2 \uparrow \qquad (7)$$

The reactivity of p-xylylidenetetra n-butyl ether with the phenylenediamines, in contrast to the ethyl derivative, was markedly low, and reaction did not occur below 150°C. However, reaction did occur at a temperature of about 160°C, and the yield of condensation product in all cases was approximately theoretical. This low reactivity of the butyl derivatives can be attributed to steric factors which contribute to moderating the reaction.

The synthesis of Schiff base polymers from the diacetals and diamines was similar in behavior in its kinetic aspects to the direct condensation of the dialdehydes and diamines. The elimination rate constant relationships, for the two-stage elimination of the alcohol, have been shown previously [5] to be $k_2 \simeq k_1$, or $k_2 > k_1$, and this relationship was also observed in these polymerizations, so that the isolation of a soluble intermediate, $\vdash HCC_6H_4CH\text{—}NC_6H_4N\vdash_n$, was

$$\qquad\qquad\qquad\qquad OR \quad OR\ H \quad\ \ H$$

not achieved. However, the reaction between the diacetals and the diamines was more moderated than the reaction between the dialdehydes and the diamines and, in general, produced darker-colored polymers, although the elemental analyses of the polymers indicated that they were oligomeric in character. Nonetheless, this reaction

appeared to be a suitable candidate for further evaluation. However, higher molecular weight black polymers were readily obtained when the polymerization was conducted in the presence of benzylideneaniline as a solvent, which also was shown to function as a reactant [1]. In these polymerizations, conversions to the black polymers was facilitated by the use of benzylideneaniline, but due to the incomplete elimination of benzylideneaniline as a result of telomerization and complex formation, a large increase in the yield above theory was observed [1]. This agrees with previous data [1] and the yields approximated the theoretical values only when the polymers were heated to temperatures in excess of 500°C. In contrast, when the polymerizations were conducted in such active solvents as dimethylformamide or dimethylacetamide, only yellow, insoluble, infusible brick-dust polymers were obtained. This behavior parallels that found for the condensation of the dialdehydes with diamines in the same solvents [1].

Acetals and Amine Hydrochlorides. The reaction between the diacetals and the diamine hydrochlorides was found to proceed readily in melt and in a number of solvents to form the polymer hydrochlorides from which the Schiff base polymers could be isolated by neutralization with sodium carbonate. These melt polymerizations yielded, on neutralization, higher molecular weight polymers than those obtained from the diacetals and diamines directly but they were heterogeneous in character, as evidenced by areas in the polymers containing yellow and other colored portions dispersed in a brown mass. This melt system involving the hydrochloride appeared to offer no advantage over that of the direct reaction between a diacetal and a diamine.

The reaction between the diacetals and the diaminehydrochlorides was studied with the expectation that the resulting polymer hydrochlorides would be sufficiently soluble in the medium to allow the condensations to proceed to higher molecular weights. The polymer hydrochlorides showed poor solubility in the solvents evaluated and only polymers of relatively low molecular weights were obtained. Their infrared spectra corresponded substantially to those prepared directly from the diacetal and the diamine except when N-methylpyrrolidone was used as a solvent; in this case the infrared spectrum showed bands which indicated the incorporation, through reaction, of the solvent in the polymer.

Acetals and Dibenzylidenephenylenediamines. The uncatalyzed melt polymerization between p-xylylidenetetraethyl ether and the di-Schiff base [Eq. (3)] was found to proceed very slowly at 170°C, moderately fast at 220°C to yield brown polymers, and very rapidly at 265°C to produce black polymers. Catalysis with Lewis acids such as p-toluenesulfonic acid or zinc chloride accelerated the reaction markedly even at 170°C. The distillate from the reaction was shown to be benzylidenediethyl ether, as expected from the mechanism of

the reaction. The infrared spectra of the polymers were found to be similar to the Schiff base polymers prepared [1] from the dialdehyde and the diamine. When the reactions were performed in N, N-dimethylnaphthylamine, N-methylpyrrolidone, or polyphosphoric acid, yields greatly in excess of theory were obtained, even after the polymer was subjected to extended periods of extraction with extractants in which the solvent was soluble. The infrared spectra of these extracted high-yield polymers showed bands characteristic of the polymerization solvent, indicating, as was found in the case of the reactions of the diacetals with the diamine hydrochlorides or the diacyldiamines, respectively, copolymerization of such solvents as N-methylpyrrolidone or complex formation with N, N-dimethylnaphthylamine. Yields lower than, or closer to, theoretical values were obtained when the reactions were performed in benzylideneaniline, but the tendency to higher than theoretical yields was increased by the addition of Lewis acid catalysts. The difference in the behavior of dibenzylidene-m-phenylenediamine and dibenzylidene-p-phenylenediamine in the reactions with p-xylylidenetetraethyl ether paralleled that found in the reactions of the m- and p-phenylenediamines with the diacetals. The greater fluidity and solubility of the systems using the meta derivatives allowed them to proceed more readily to the black polymer stage.

The reactivity of p-xylylidenetetrabutyl ether with the dibenzylidenephenylenediamines is much lower than that of the corresponding ethyl homologue and reaction did not occur even at 240°C, but reaction occurred readily at temperatures of 240°C or higher in the presence of p-toluenesulfonic acid to yield black polymers quantitatively or almost so, in the presence or the absence of benzylideneaniline. The reaction of the xylylidenetetraalkyl ethers with the dibenzylidenephenylenediamines, under appropriate conditions, appeared to be a suitable reaction for the preparation of black polymeric Schiff bases.

Diacetals and Diacylamides. The uncatalyzed reaction of the diacetals and the diacylamides was found to proceed very slowly or not at all at melt temperatures in the range 170–200°C, but the reaction did proceed readily in the range 210–265°C. The infrared spectra of these polymers showed many peaks typical of poly-Schiff bases. It was also found that the polymerization reaction proceeded in two steps in which the elimination of alcohol preceeded the elimination of the ester of the alcohol. Usually, the greater portion of the alcohol was eliminated within the first hour of the reaction and the ester within the next 2 to 4 hr. These results are in agreement with those obtained in the earlier prototype studies of this reaction [3, 5]. The reaction between the diacetals and the diacylamides is highly catalyzed by p-toluene sulfonic acid and the reaction occurs readily at 170°C. The spectra of the polymers prepared in the presence of p-toluenesulfonic acid possess many

features characteristic of Schiff base polymers, but the absorption bands in the 1600 cm^{-1} for C=N were broad and an unequivocal assignment to the C=N structure could not be made, since $-C_6H_4CH=HCC_6H_4-$ structures also absorb in this region [8]. Such structures can arise from the p-toluenesulfonic acid–catalyzed decomposition of the diacetal, preliminary evidence for which is found in the elemental analyses of the polymers prepared in the presence of catalyst and in which polymers the nitrogen values are very low.

The reaction of the diacetals with the diamides in solvent was also found to be sluggish at temperatures in the range of 170°C, but they did proceed at higher temperatures; however, they did proceed at 170°C when catalyzed by Lewis acids. From the high yields obtained, elemental analyses, and interpretations of their infrared spectra, the reactions performed in N-methylpyrrolidone and in polyphosphoric acid were shown to contain substantial quantities of these solvents which obviously could react to produce copolymerization products. Similar data on the polymers prepared in N, N-dimethylnaphthylamine also showed that substantial amounts of this naphthalene, even after prolonged extraction with solvents, were tenaciously held in the polymer. Since this naphthalene lacks chemically reactive groups, the assumption that complexes were formed with the polymer seems plausible. The yield of polymers was also high when the reaction was performed in benzylideneaniline, indicating that telomerization by exchange with the polymer has occurred [1], and that, in addition, benzylidene aniline could also be complexed with the polymer.

From the viewpoint of preparing fusible polymers which can be converted to infusible, black polymers, the uncatalyzed reaction between the diacetals and the diamides appears to be better suited than the catalyzed reaction. This uncatalyzed reaction can be performed more readily in the presence of benzylideneaniline. However, these reactions offer no advantages in the syntheses of the polymers over the more simple and attractive syntheses from the acetals with either the diamines or their dibenzylidenediamine derivatives, respectively.

Dialdehydes and Diamides. Since the reaction of the diacetals with the diacylamides yielded polymers which evidenced [5] Schiff base linkages, the use of the dialdehydes as alternatives to the diacetals in the reaction was evaluated.

This reaction, Eq. (5), was studied in uncatalyzed and catalyzed melt polymerizations. The uncatalyzed reaction between terephthaldehyde and the N, N'-diacetylphenylenediamines proceeded with reluctance even at 220°C but more readily when catalyzed with toluenesulfonic acid. Polymers were obtained in the catalyzed and uncatalyzed reaction, but the infrared spectra of the polymers were not typical of polymeric Schiff bases and lacked the absorption

bands in the 1600-cm^{-1} region characteristic of the Schiff base poly-
mers. It is apparent that the reaction does not proceed according to
that written for Eq. (5) and that this method is unsatisfactory for the
preparation of polymeric Schiff bases.

Dibenzylidenephenylenediamines and Diacylamides. Since the
reaction of the dialdehydes with the diacylamines did not yield poly-
meric Schiff base, whereas Schiff base polymers were obtained by
the reaction of diacetals with the same diacylamines, the bis-Schiff
bases of the dialdehydes were evaluated to determine whether or not
other derivatives of the dialdehydes could be used in the reaction.

This reaction, Eq. (6), was studied in uncatalyzed and catalyzed
melt polymerizations. Reaction failed to occur even at 260°C during
the course of 24 hr. However, a reaction was achieved at this tem-
perature when p-toluenesulfonic acid was used as a catalyst, and a
polymer product was obtained whose infrared spectrum was not
typical of a polymeric Schiff base and lacked the characteristic ab-
sorption band for C=N in the 1600-cm^{-1} region. Further, the high
yield of polymeric product, 140% in reference to the quantity of Schiff
base expected, indicates that the elimination reaction was far from
complete. These results confirmed those obtained in previous pro-
totype studies [4, 5].

Part II

The purpose of the studies of the reaction of the p-xylylidenetetra-
butyl ether with the diamines or their dibenzylidene derivatives was
to obtain polymers which, through thermogravimetric analyses,
would indicate the influence of varying the reactants and reaction
conditions on the thermal stabilities of the polymers. It was ex-
pected that these studies would provide a means for deciding be-
tween the phenylenediamines or their corresponding dibenzylidene
derivatives as the amine reactant, and also whether or not a solvent
would be required to prepare satisfactory polymers by these reac-
tions. Since earlier studies [1] had shown that benzylideneaniline
was a satisfactory medium in which to perform this type of polymeri-
zation, it was chosen as the solvent. It was observed, in the present
studies, that in the absence of solvent, m-phenylenediamine reacted
with p-xylylidenetetrabutyl ether more smoothly, producing homo-
geneous liquid melts and intermediate, fusible black polymers for
longer periods of time than p-phenylenediamine. The p-phenylene-
diamine reacted more rapidly than its meta analogue, resulting in
early precipitation of yellow or brown low molecular weight poly-
mers followed by sublimation of the reactants later in the process.
In addition, in those cases where p-phenylenediamine was used in
admixture with m-phenylenediamine, sublimation of reactants to the
upper portion of the reaction tube occurred early in the course of
the reaction. Also, the presence of p-phenylenediamine in ad-

mixtures with m-phenylenediamine in the range 75–25 to 25–75 mole% caused premature precipitation of polymers which appeared as solids and persisted for hours as dispersions in the liquid mixture. It was also observed that the by-products were removed more readily in the reactions involving m-phenylenediamine than in those in which p-phenylenediamine was used.

The yields of polymer obtained by the condensation to 320°C of the diamines with p-xylylidenetetrabutyl ether were in the vicinity of 100% of theory, varying from 101 to 106%, calculated on the basis of $\leftmoon HCC_6H_4CH=NC_6H_4N\rightmoon_{n=\infty}$. However, elemental analyses of the polymers indicated that the molecular weight of the polymers at this stage was not high and, as previously shown [1], the condensation was far from complete at this temperature and the yields should be higher than 100% of theory. Accordingly, these yields should have been higher and of the order of 110–115% of theory. The lower values found were the result of incomplete reaction and loss of the acetal and diamine under the reduced pressure used in the later stages of the reaction.

In those reactions in which benzylideneaniline was used as a solvent, the yield of polymer was much higher than in the polymerizations performed without solvent, confirming previous studies [1] that benzylideneaniline is a coreactant as well as a solvent.

Low yield values were also found when the yellow polymer, Y, was synthesized, for which the yield, on the basis of $\overline{DP} = \infty$, was 110% but on the basis of the dimer-trimer, $(C_4H_9O)_2\leftmoon HCC_6H_4CH= NC_6H_4N\rightmoon_3 H_2$, was of the order of 80%. The reaction between the acetals and the diamines was accelerated highly by Lewis acids, and we expect to perform such catalyzed studies in the near future.

The exchange polymerizations of p-xylylidenetetrabutyl ether with the dibenzylidenephenylenediamines were much slower than the corresponding reaction with the diamines, and, for this reason, zinc chloride was used as a Lewis acid catalyst to accelerate the reaction. Although the difference in the reactivities of p-dibenzylidenephenylenediamine and m-dibenzylidenephenylenediamine, respectively, with p-xylylidenetetrabutyl ether was not as marked as it was in the case of their parent diamines, there was a noticeable difference in the melt characteristics of their reaction products. The viscous melt of the polymer obtained from m-dibenzylidenephenylenediamine persisted for a longer period of time than that from the para derivative.

In the polymerizations in which benzylideneaniline was used as a solvent, the yields were much higher than in the systems from which it was omitted, indicating its coreactivity [1], as well as its solvent nature.

Postheating. The initial polymers, I to XI inclusive, were condensed to a temperature of 320°C, a temperature at which the condensation is incomplete [1]. Since a number of polymerizations des-

cribed in previous reports [1-3] were terminated at reaction tem-
peratures in the range 425-600°C, temperatures at which additional
amounts of by-products were eliminated without substantial changes
in the infrared spectra of the polymers, appropriate portions of
H320 polymers I to XI inclusive were postheated to 425 and 600°C,
to compare their thermal stabilities with those prepared previously
[1] by other reactions. The yield of polymers, on postheating, was
reduced as in the previous cases [1]. To determine the influence of
the thermal history on the stability of the polymers, a number of
samples of H425 polymers was also postheated at 600°C; these are
designated as H425-H600 polymers.

Also, the postheatings of the H320 polymers to 425°C were per-
formed to eliminate adduct components or retained unreacted re-
agents from the polymers. It was hoped that the nature of the chemi-
cal processes that occurred during postheating could be resolved by
identifying the distillates collected during the postheating period.
The composition of the distillates was determined by their infrared
spectra. As shown in previous studies [1], the compounds found in
the distillates collected during the postheating were originally pres-
ent in the system as a solvent or as a reaction product. The data
obtained in these studies are similar to those obtained in earlier
studies [1] and again indicate that scission of the polymer chain is
not significant either during polymerization or during postheating at
higher temperatures. This is indicated also by a comparison of the
infrared spectra of the H600 polymers with those of the H425 poly-
mers in Figs. 6, 8, 10, and 12.

Postheating to 1176°C. It had been previously shown [1] that it
was desirable to evaluate the thermal properties of polymers which
have been heated to temperatures in the region of 1000°C. According-
ly samples of the H325 polymers were heated in nitrogen to 1176°C
and their thermal stabilities evaluated in nitrogen and in air. A few
samples of H600 polymers were also postheated to 1176°C, and these
are designated as H600-1176.

Thermal Stability. The thermogravimetric data of Tables 11 and
12 indicate that the polycondensations carried to a temperature of
320°C are not complete. This was indicated by the losses in weight
when these polymers were heated in nitrogen compared to the much
lower losses when the polymers were condensed to temperatures of
425°C or higher. This confirmed results previously obtained [1-3]
for the polymeric Schiff bases prepared from other reactants. When
the H325 polymers were heated in nitrogen, the thermogravimetric
data suggested that the polycondensation, as well as other types of
condensations, continued up to a recorded temperature of 1176°C.
It was observed, in the thermograms, that little or no loss in weight
occurred when the samples were heated to higher temperatures un-
til some definite temperature was reached; at this temperature a
first distinct negative slope occurred until it reached a second high-

er temperature at which it tended to level out as a second but smaller negative slope became evident; this second slope then continued to the temperature limit of the apparatus. The first negative slope has been attributed [1] to losses of by-products due to continued condensation, and the temperature at which it originated depended on the previous history of the sample. For example, the first negative slope in the H325 polymers was found approximately in the 450–650°C region, in the H425 polymers in the 550–650°C region, in the H600 polymers in the 600–750°C region, and in the H1176 polymers in the 1000–1200°C region.

From the character of the thermograms, the second negative slope has been interpreted [1–3] as originating before the factors responsible for the first negative slope are completed and it may be estimated that, generally, it takes origin in the 750–850°C range. Although the losses in this region are attributed [1–3] in minor part to continued condensation, they are also due to inter- and intramolecular condensations which yield fused-ring structures by loss of hydrogen and other products. It was interesting to note the appearance of the polymers after they have been heated to 1176°C in nitrogen; the finely powdered 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. When heated to 1176°C, the yellow brick-dust polymer also became black, but the product was dull and retained its brick-dust character. The thermal stability, in nitrogen, of the yellow brick-dust polymer was noticeably much lower than any of the black polymers.

The thermal stabilities in air of the H320 polymers derived from the reaction of p-xylylidenetetrabutyl ether with the phenylenediamines and the dibenzylidenephenylenediamines were found to be in the vicinity of 400°C. When the H320 polymers were prepared in benzylideneaniline as a solvent, the benzylideneaniline retarded the polycondensation and lowered the thermal stabilities of the polymers. However, when the condensations to 320°C of p-xylylidenetetrabutyl ether with the dibenzylidenephenylenediamines were performed in benzylideneaniline in the presence of zinc chloride, the polycondensations proceeded more readily, and the thermal stabilities of the polymers fell again in the 400°C region. The thermal stabilities in air of the polymers condensed to 425°C were in the 500°C region, with most of them in the 500–550°C range and a few in the 480°C region. The four polymers III-H425, IV-H425, V-H425, and VI-H425 showed thermal stabilities in air of about 550°C; these are all derivatives of m-phenylenediamine. When benzylideneaniline was used as a solvent in the H425 polymers the thermal stabilities in air of the polymers were reduced to the region of 475–500°C. These lower values indicate that chain-end coupling in the benzylideneaniline-telomerized polymers was not completed at 425°C for the time interval used, and that all the benzylideneaniline by-product or solvent

had not diffused from the polymer. This conclusion was substantia-
ted in part by the higher weight losses found in these polymers over
comparable polymers prepared in the absence of benzylideneaniline;
the presence of released benzylideneaniline in the exit tube of the
thermogravimetric analyzer also tended to confirm this conclusion.

When the condensations were carried to a temperature of 600°C,
a number of effects were noted with regard to the thermal stabilities
of the polymers. In most cases, 20 min of heating time at 600°C of
the H325 polymer did not raise the thermal stability of the polymer
to as high a value as the same polymer postheated at 425°C for 40 hr.
The weight losses, in nitrogen, also indicated that the polyconden-
sations at 600°C for this short period of time were not complete.
Yet, under the specific conditions of these experiments, little or no
difference was found in the thermal stabilities in air of the polymers
derived from m-phenylenediamine or its dibenzylidene derivative
between the polymers condensed to 425°C and those condensed to
600°C; both showed stability values in air of 550°C. However, in the
case of the p-phenylenediamine–derived polymer, the polymers con-
densed at 600°C for 20 min were found to have a lower thermal
stability in air than those condensed at 425°C for 40 hr. This dif-
ference was also observed in polymers prepared from mixtures of
p- and m-phenylenediamines. However, when the H425 polymers
were postheated at 600°C for 20 min, the thermal stabilities of the
H425-H600 polymers were higher than either the H325-H425 or the
H325-H600 polymers. When the H320, H425, or H600 polymers were
condensed to 1176°C, little difference was found in the thermal stabi-
lities of the H1176 polymers in air; all showed thermal stabilities
in air in excess of 500°C with a spread in temperature range of
500–600°C. Four polymers, II-H320-1176, III-H320-1176, III-H320-
600-1176, and IV-H425-600-1176, showed stabilities of about 600°C in
air. This is interpreted to mean that, if the polycondensations are
substantially complete, as would be expected [1] at this high tempera-
ture, the polymers derived from the m- and p-phenylenediamines
and their benzylidene derivatives have substantially identical ther-
mal stabilities, and that when benzylideneaniline was used as a sol-
vent, it was substantially eliminated at these temperatures.

CONCLUSIONS

The yellow, brick-dust polymers have lower thermal stabilities
than the black polymers. Black polymeric Schiff bases, which pass
through a fusible stage, can be prepared from p-xylylidenetetrabutyl
ether and either m- or p-phenylenediamine or their dibenzylidene
derivatives in the absence or presence of benzylideneaniline as a
solvent. The syntheses of the polymers are smoother and more facile
with m-phenylenediamine or its dibenzylidene derivative than from

the p-phenylenediamine compounds. The thermal stabilities of the polymers prepared from m-phenylenediamine compounds are comparable to those prepared from the p-phenylene compounds. The thermal stabilities in nitrogen and in air of the polymers prepared from the reaction of p-xylylidenetetrabutyl ether with m-phenylenediamine or dibenzylidene-m-phenylenediamine are comparable to similar polymers previously [1] prepared by bis-Schiff base exchange reactions.

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Zusammenfassung

Sechs neue Reaktionen zur Synthese von scharzen, polymeren Schiff'schen Basen wurden untersucht. Es sind dies die Reaktion von Aryldiacetalen mit (1) Aryldiaminen, (2) Aryldiaminsalzen, (3) Dibenzylidenarylendiaminen, beziehungsweise mit (4) N, N'-Diacetylarylendiaminen, (5) die Reaktion von Aryldialdehyden mit N, N'-Diacetylarylendiaminen, und (6) die Reaktion von Di-Schiff'schen Basen mit N, N'-Diacetylarylendiaminen. Die Reaktionen (1) und (3) erwiesen sich als sehr zufriedenstellend und wurden deshalb zur Synthese einer Reihe von Polymerer herangezogen. Es ergab sich, dass die thermische Stabilität der so hergestellten Polymeren der Stabilität jener Produkte äquivalent war, die mittels der Di-Schiff'schen Basen-Austauschreaktion hergestellt waren.

Résumé

On a evalué six nouvelles réactions qu'on peut utiliser dans les

synthèses des bases de Schiff polymères noires, notamment, la réaction des aryldiacétals avec (1) les aryldiamines, (2) les sels des aryldiamines, (3) les dibenzylidène-arylènediamines, et (4) les N, N'-diacétylary-lènediamines resp., (5) la réaction des aryldialdéhydes avec les N, N'-diacétylarylènediamines, et (6) la réaction des bases de Schiff avec les N, N'-diacétylarylènediamines. On a trouvé que les réactions (1) et (3) sont satisfaisantes et on les a appliqué à la synthèse d'un nombre de polymères. On a montré que les stabilités thermiques des polymères ainsi preparés sont équivalentes à celles des polymères obtenus par la réaction d'échange de di-bases de Schiff.