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ON

THE

FUNDAMENTAL STUDIES ON THE SYNTHESIS OF HEAT-RESISTANT POLYMERS

TO

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

WASHINGTON, D.C.

PERFORMED

UNDER

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DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NOTRE DAME

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PROGRESS REPORT NUMBER 4

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by

G. F. D'Alelio

PRINCIPAL INVESTIGATOR

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NOTRE DAME

NOTRE DAME, INDIANA

September 15, 1964

FOREWORD

This report is a summary report of the researches performed under NASA Grant NsG339 for the period 1 February 1963 to 1 June 1964 on the synthesis of heat-resistant polymers. To assure completeness of the technical aspects of this report, the researches performed during the period 17 April 1962 to 20 June 1962, prior to the receipt of the grant, have been included. The technical aspect of this grant is administered by Mr. Bernard Achhammer, Office of Advanced Research and Technology, NASA Headquarters, Washington, D. C.

The research under this grant is being conducted in the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana under the technical direction of Professor G. F. D'Alelio, principal investigator.

This report covers studies performed by G. F. D'Alelio, L. Mallavarapu, T. Huemmer, T. Kurosaki, W. Fessler, and J. Crivello.

Date September 15, 1964

Signed G. F. D'Alelio

G. F. D'Alelio
Principal Investigator

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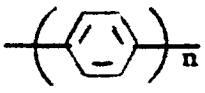
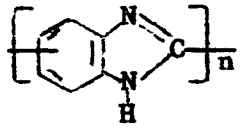
INTRODUCTION

Organic polymers which can withstand temperatures in excess of 400°C for sustained periods of time without significant degradation or phase changes may be considered as heat resistant.[1] High heat-resistant polymers have been of general interest for many years and until recently only limited success was achieved in their synthesis. The material requirements of space technology has stimulated new interest in heat-resistant polymers and has led to the formulation of certain general principles[2] which must be met by an organic polymer to be stable, namely,

1) only the strongest chemical bond should be used in the polymer structure
2) the structure must allow no easy pathways for molecular rearrangement
3) there must be a maximum use of resonance stabilization
4) all ring structures in the polymer should have normal bond angles
5) the polybinding principle should be used as much as possible.

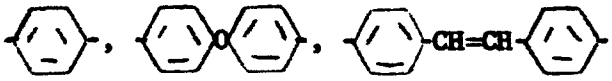
It is not surprising, therefore, in light of these principles that the most promising heat-resistant organic polymers are the poly-conjugated and the poly-aromatic type. Marvel, in particular, has shown[3] that the polyphenyls  and the polybenzenimidazoles,  show remarkable heat stability. Analogous to these polymers, one might expect that a conjugated system linked together by -C=N- in an aromatic system, -ArC=N-Ar-, might show this remarkable heat stability. The simplest compounds possessing this structure are the non-polymeric Schiff bases, $C_6H_5CH{=}NC_6H_5$, $C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5$ and $C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5$, which are sufficiently stable that they can be distilled at atmospheric pressure without decomposition.

Consideration, therefore, was then given[4] to the synthesis of polymers containing these structures.

Specifically, the conjugated polymeric Schiff bases have been selected, under this research, as candidates for synthesis and for evaluation as Heat Resistant Polymers. These polymers have the generic structure

$$\{N\text{-}ArN{=}CHArCH\}_n$$

wherein Ar represents an arylene-type moiety such as



It has been shown in our previous reports[5-7] that the classical method of preparing Schiff bases is not completely satisfactory when applied to polymer syntheses by using a dialdehyde and a diamine in solution:

$$n\ OHCArCHO + n\ H_2NArNH_2 \xrightarrow[CH_3COOH]{H_2O\ or} n\ H_2O + \{NArN{=}CHArCH\}_n \qquad \text{(eq. 1)}$$

Syntheses in solution yield insoluble, infusible, non-fabricable "brick-dust polymers" of low molecular weight ranging in color from yellow to orange. Black polymers should be expected if the molecular weight is sufficiently high so that conjugation is extensive. Preliminary experiments demonstrated[5,6] that these dialdehyde and diamino compounds could be reacted in a melt to produce as intermediates highly conjugated black, soluble, fusible polymers. However, because of the melt temperatures required, the polymerization is difficult to control but fabricable, soluble, fusible polymers could be obtained by interrupting the reaction at early degrees of polymerization.

The deficiencies of the solution and melt processes indicated that a decrease in the reactivity of the (a) aldehyde function or (b) the amine function, or (c) both functions, might be beneficial to the polymerization reaction by slowing down the polycondensation reaction as well as by preventing oxidation and degradation during the polymerization reaction.

The decrease in reactivity of the reagents was to be achieved by converting the aldehyde function, -CHO (1) to other suitable derivatives such as the aldimine function -CH=NR (2), and to the acetal function $-CH-(OR)_2$ (3), and to convert the amine function $-NH_2$ (4) to suitable derivatives such as an anil function -N=CHR (5), and to the amide function -NHOCR (6), and the retardation of the reaction was to be achieved by using these derivatives in place of the aldehydes and amines respectively, as shown in Table 1 for the syntheses of typical Schiff bases.

Table 1

Reagents for Possible Syntheses of Schiff Bases

Aldehyde or Derivative	plus	Amine or Derivatives
(1) -CHO		(4) $-NH_2$
(2) -CH=NR		(5) -N=CHR
(3) $-CH(OR)_2$		(6) -NHOCR

From the reagents in Table 1, nine reactions, (1) + (4); (1) + (5); (1) + (6); (2) + (4); (2) + (5); (2) + (6); (3) + (4); (3) + (5); and (3) + (6) are possible for the syntheses of Schiff bases. These are summarized in Table 2. Simple non-polymeric Schiff bases are to be expected in a reaction when both reagents are monofunctional, whereas the production of polymers would require that both reagents have a functionality of at least two. The synthesis of non-polymeric Schiff bases from aldehydes and amines, (1) + (4), have been known for some time,[8] and the application of this reaction by using dialdehyde and diamines to the synthesis of polymers is relatively recent.[11-13] The literature on the synthesis of non-polymeric Schiff bases by an amine exchange reaction (2) + (4) is meager[9,10] and has not been applied to polymeric reactions. None of the other reactions listed in Table 2 appears to be reported in the

Table 2

Reactants for Non-Polymeric and Polymeric Schiff Bases

Reaction Pairs	Functional Groups		Literature (ref.)	
			Non-Polymers	Polymers
(1) + (4)	-CHO	+ $-NH_2$	ref. 8	ref. 11-13
(1) + (5)	-CHO	+ -N=CHR	unreported	unreported
(1) + (6)	-CHO	+ -NHOCR	unreported	unreported
(2) + (4)	-CH=NR	+ $-NH_2$	ref. 9,10	unreported
(2) + (5)	-CH=NR	+ -N=CHR	unreported	unreported
(2) + (6)	-CH=NR	+ -NHOCR	unreported	unreported
(3) + (4)	$-CH(OR)_2$	+ $-NH_2$	unreported	unreported
(3) + (5)	$-CH(OR)_2$	+ -N=CHR	unreported	unreported
(3) + (6)	$-CH(OR)_2$	+ -NHOCR	unreported	unreported

literature. Accordingly, it was necessary to establish the validity of these reactions in prototype syntheses of non-polymeric Schiff bases and to apply these reactions to the syntheses of polymers, if they were found to be operative. Preliminary tests[4-7] showed that most of the reactions of Table 2 are applicable broadly to the syntheses of non-polymeric and polymeric Schiff bases, and further experimental data have confirmed the earlier conclusions.[4-7] Accordingly, the investigations were divided into two sections: (I), the syntheses of non-polymeric Schiff bases and related compounds, and (II) polymeric Schiff bases and related structures.

I. Syntheses of Non-Polymeric Schiff Bases and Other Azo-Methines.

A number of non-polymeric Schiff bases and related azo-methines were selected for synthesis on the basis of structures which were related to the desired polymers. The reactions by which they were synthesized were considered as prototype reactions on which the syntheses of the polymers would be based, if the postulated reactions were successful. In general, these syntheses were predicated on the usual reactions of carbonyl compounds or suitable derivatives thereof with amino compounds or their suitable derivatives. Since there are pairs of amino and carbonyl compounds which do not react as expected, other syntheses which would yield the desired derivative were also considered. One such synthesis is included in the reaction of an arylamine and a carbonyl compound, even though the reaction is not a condensation reaction but actually is an oxidation-reduction reaction.

A. From Carbonyl Compounds and Amines.

1. From Aromatic Aldehydes and Aromatic Amines.

Historically, the term "Schiff Base" has referred to benzylidene aniline, $C_6H_5CH{=}NC_6H_5$, its homologues and derivatives.

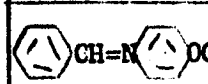
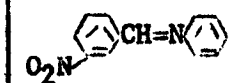
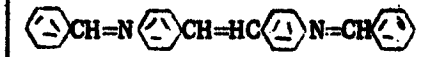
Non-polymeric Schiff bases are usually prepared[8] by reacting the amine and the aldehyde compound directly or in a solvent such as ethyl alcohol or water in the presence of a Lewis acid to give an equilibrium yield of the Schiff base, thus

$$ArNH_2 + ArCHO \underset{\text{HCl}}{\rightleftharpoons} ArN{=}CHAr + H_2O \qquad \text{(eq. 2)}$$

Since the non-polymeric Schiff bases were required in this research both as intermediates and as monomers, an improved method for their synthesis was developed.[5] This new improved method, which uses[5] an azeotroping media such as benzene or toluene in a Dean-Stark apparatus, consists in refluxing the mixture of amine, aldehyde and the azeotroping agent until the theoretical amount of water of reaction is obtained to yield an almost quantitative yield of the

Table 3

Syntheses of Non-Polymeric Schiff Bases

Schiff Base	M.P. °C	Ref	Types of Syntheses: Equilibrium Exper. No.	Equilibrium Crude Yield %	Azeotropic Exper. No.	Azeotropic Crude Yield %	Analyses: Found C ; H ; N	Calculated C ; H ; N
	49	14	DA-24-40	84-87	DA-29-1	100	-----;----;-----	-----;----;-----
	72	15	DA-29-142	86.5	DA-29-73	100	-----;----;-----	-----;----;-----
	93	16	DA-29-143	93.3	DA-29-88	100	-----;----;-----	-----;----;-----
	66	17	DA-29-144	91.6	DA-29-75	100	-----;----;-----	-----;----;-----
	140	18	DA-24-43	84	DA-29-33	100	-----;----; 9.77	-----;----; 9.86
	104-106	19	DA-24-44	63.9-74	DA-29-13	100	-----;----; 9.85	-----;----; 9.86
	164-166	--	DA-24-42	78	DA-29-2	100	-----;----; 9.86	84.5 ;5.63;9.86
	230-231	--	--------	-------	DA-29-9	98.3	86.13;5.79; 8.18	86.67;5.66; 7.78
	204	--	--------	-------	DA-29-21	97.2	75.9 ;5.33;18.82	75.52;4.89;19.58
	268-270	--	DA-24-80	58	--------	----	87.08;5.97; 6.38	87.05;5.70; 7.25

crude Schiff base. The recrystallized compounds prepared by this method were compared with compounds prepared by the normal equilibrium method, or with compounds known in the literature and found to be identical. The syntheses of a number of Schiff bases by the solution and azeotropic methods is summarized in Table 3.

2. Azo-Methines from Other Carbonyl Compounds and Amines.

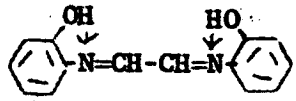
By common usage, the term Schiff base has been applied to compounds other than the benzylidene-anilines, and such compounds as the ket-anils, $R_2C{=}NAr$; the quinone-anils, $C_6H_5N{=}C\langle^{CH=CH}_{CH=CH}\rangle C{=}NC_6H_5$ and the azines $C_6H_5CH{=}N{-}N{=}CHC_6H_5$, etc., have been termed "Schiff bases." The historical Schiff base and these compounds belong properly to the class of azo-methines whose basic structure comprises the $-N{=}C\langle$ moiety. In this research preliminary studies were undertaken to determine whether any of the azo-methines, related structurally to the benzylidene-anil type Schiff base had possible uses as intermediates in the preparation of polymers.

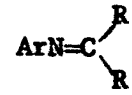
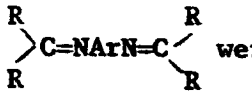
Usually, the Schiff bases are the reaction product of an aromatic aldehyde, such as benzaldehyde and an aromatic primary amine such as aniline, RCHO, and an aromatic amine, $ArNH_2$, would be of interest as possible intermediates in preparation of Schiff base polymers by exchange reactions. In most cases, however, the reaction product is not the expected compound, but an alkylene derivative, $RCH(NHAr)_2$ or aniline-type resin.[20] In this research all attempts to produce $C_6H_5N{=}CHCH{=}NC_6H_5$ from glyoxal and aniline produced aniline-aldehyde type resins instead of the desired derivative. However, by using ortho-aminophenol, it was possible to obtain a derivative of the parent substance, according to the reaction[21]

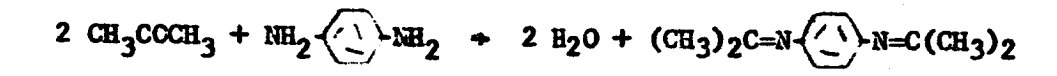
$$OHCCHO + 2\ o\text{-}H_2NC_6H_4OH \rightarrow \text{(OH-C}_6\text{H}_4\text{-N=CH-CH=N-C}_6\text{H}_4\text{-OH)} + 2\ H_2O \qquad \text{(eq. 3)}$$

which could possibly be used as an intermediate in polymerization reactions.

The absence of resin formation in this derivative is attributed to stabilization due to chelation involving the hydrogen of the phenolic hydroxyl with the nitrogen atoms, thus

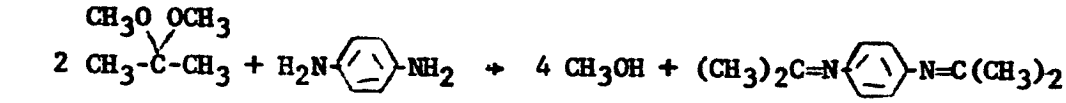


Since, in this research, it was necessary to establish the breadth and depth of exchange reactions and to establish that a terminal aryl group is not essential in the exchange reactions, the syntheses of bases having the azo-methine structures,  , were considered. Compounds of the general structure  were considered as possible candidates and their synthesis from ketones and arylene diamines undertaken.[6] The reaction of acetone and p-phenylene diamine,



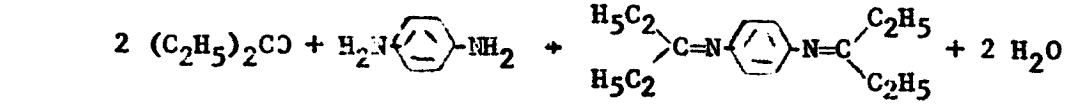
(eq. 4)

was tried[22] without success. Modifications of equation 4 were attempted using 2,2'-dimethoxy propane[23] according to equation

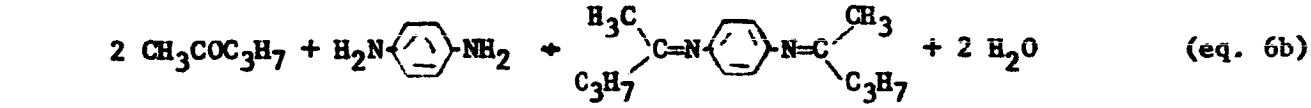


(eq. 5)

were also unsuccessful as were the related procedures[24-25] using acetone, the amine and potassium cyanide in the presence of acetic acid. However, this class of compounds was successfully synthesized by using higher boiling aliphatic ketones of low water solubility, such as diethyl ketone and 2-pentanone, which are capable of azeotroping water, and refluxing the reaction mixture in a Dean-Stark apparatus until the theoretical amount of water is eliminated by the reaction:

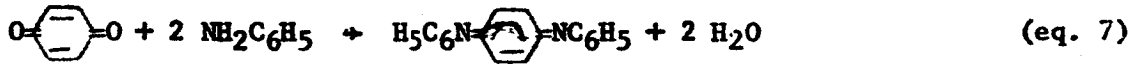


(eq. 6a)



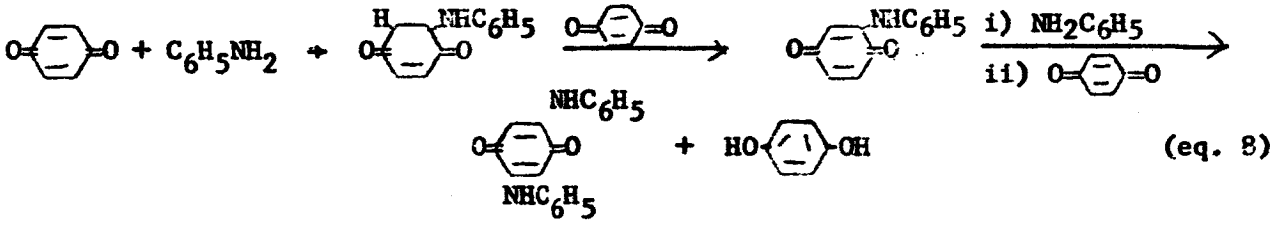
(eq. 6b)

The quinone-dianils are related structurally to the aliphatic azo-methines and are also of interest as intermediates for polymer synthesis. Their syntheses would be expected[5] from the reaction of a quinone and an aniline according to the equation



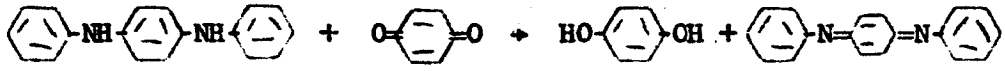
(eq. 7)

The synthesis according to this reaction was not successful since the first reaction is an addition of aniline to the quinone ring, followed by oxidation by unreacted quinone[26] thus:



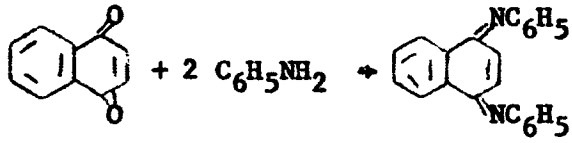
(eq. 8)

The desired quinone dianil was synthesized by the mild oxidation[27,28] of triphenylene imine by quinone according to the equation



(eq. 9)

Attempts to prepare naphthaquinone dianil by the reaction of naphthaquinone and aniline,

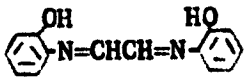
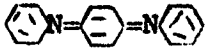
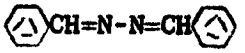


(eq. 10)

failed to produce the expected product even when its synthesis was attempted by the azeotropic method. The product melting at 189-192°C previously reported[6] as the desired product gave elemental analyses which showed that it was a mixture of substituted naphthaquinones, probably formed by a mechanism similar to that found in the reaction of the parent quinone and aniline. In contrast to quinone and naphthaquinone, anthraquinone failed to react with

Table 4

Syntheses of Other Azo-Methines Related to Schiff Bases

Reagents		Exper. No.	Ref.	Product	M.P.°C or B.P.°C	Yield %	Analyses			
								C	H	N
OHCCHO	2 $C_6H_5NH_2$	DA-24-94	--	resin						
OHCCHO	2 o-$NH_2C_6H_4OH$	DA-24-106	21		M.P. 204°C	62	Found:	70.31	5.12	11.48
							Calc.:	70.0	5.0	11.67
$2(C_2H_5)_2CO$	p-$H_2NC_6H_4NH_2$	DA-29-99	--		B.P. 147-148°C / 0.8 mm	95-98	Found:	77.25	9.69	10.23
							Calc.:	78.6	9.84	10.48
$2CH_3COC_3H_7$	p-$H_2NC_6H_4NH_2$	DA-29-105	--		B.P. 182°C / 1.2 mm	95	Found:	79.04	9.96	9.36
							Calc.:	78.6	9.84	11.48
		DA-24-110	27 28		M.P. 180-181°C	70.8	Found:	83.83	5.47	10.72
							Calc.:	83.72	5.43	10.85
2 C_6H_5CHO	H_2NNH_2	DA-24-79	29		M.P. 93°C	95				

aniline under a variety of conditions including $ZnCl_2$ catalysis.

Another azo-methine of possible interest as an intermediate in polymer synthesis is the azine, benzalazine, $C_6H_5CH=N-N=CHC_6H_5$, which is readily prepared[29] from benzaldehyde and aqueous hydrazine.

The syntheses of these azo-methine compounds of interest in this project and which are related to the Schiff bases, are summarized in Table 4.

3. Experimental.

a. From Carbonyl Compounds and Amines.

i) The Equilibrium Method.

The procedure given in Organic Syntheses[14] was used when the carbonyl compound or the amine or both were liquids; this procedure was also found to be applicable when a 64% aqueous hydrazine solution was reacted with benzaldehyde in the preparation of benzylidene azine and when 30% aqueous glyoxal was reacted with o-aminophenol.

ii) Azeotropic Method.[6]

Into a ground-glass jointed round-bottom flask is placed 1000 ml of azeotroping agent such as benzene or toluene per each mole of expected product, the carbonyl compound and the amine in proper molar proportions, and the flask attached to a Dean-Stark trap equipped with reflux condenser and required accessories. The trap is filled with the azeotroping agent and then the mixture heated at reflux until the theoretical amount of water is collected in the trap. The reaction mixture is then cooled, allowed to crystallize and the reaction product removed from the mother liquor by filtration. By concentrating the mother liquor to 10-20% of its original volume under water aspirator pressures at room temperature, additional product can be obtained. Due to mechanical losses the isolated yield of crude product in small batches may be reduced to 95-97%. Two or three recrystallizations from 95% or absolute alcohol

yield final products of high purity. Best results are obtained when freshly purified reagents are used in the syntheses.

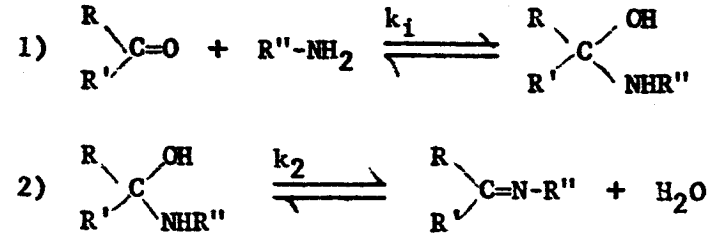
In the reaction of p-phenylene diamine with diethyl ketone and 2-pentanone respectively to prepare the corresponding ketanils, the ketone was used as the azeotroping agent in the absence of benzene or toluene, and the reaction continued until the theoretical amount of water was obtained. Since the final products are oily liquids, they were isolated by distillation to narrow boiling fractions. The final yields of products triple-distilled in the range of 0.8 to 1.2 mm pressure were from 35-45%.

b. By Oxidation of Aryl Amines.

The procedure[27] of Ciusa, Brüll, and G. Ottolino was uzed to oxidize triphenyleneimine by quinone to produce quinone-dianil. 2.48 g. of Triphenylene imine, 1.08 g. of benzoquinone and 30 ml of 95% ethyl alcohol were mixed in a ground-glass jointed flask attached to a reflux condenser and the mixture heated to reflux for fifteen minutes; a heavy dense precipitate formed. The mixture was then cooled to 0°C and the precipitate removed by filtration. Melting point of the crude product was 165-180°C. Recrystallization from alcohols, and then from benzene gave a product of m.p. 180-181°C (literature[27] m.p. 180°C).

4. The Mechanism for Amines and Carbonyl Compounds.

The simple condensation of a primary amine and an aldehyde or ketone to produce a Schiff base has been shown to occur in two distinct steps.[30-32]



where: R = Alkyl or aryl
R' = H, Alkyl or aryl
R" = Alkyl or aryl.

The first step consists of an addition of an amine to the polarized carbonyl with the production of an aldehyde-ammonia type compound. Isolation of these intermediates has been achieved only in certain cases.[33-34] It can be predicted that an aldehyde in which the carbonyl moiety is polarized by electron-withdrawing groups on the alpha carbon should stabilize the intermediate. This has been found to be true, as in the case of chloral.[35,36]

The second step in the mechanism consists of an elimination of water, thus producing an imine-type compound in a manner similar to the crotonization step in the aldol condensation. Since it has been observed that this condensation is normally exothermic, it can be implied that the overall position of the equilibrium lies to the right.

B. By Schiff Base Exchange Reactions.

By a Schiff base exchange reaction is meant[7] the displacement of the amino or the carbonyl fragment in a Schiff base and its substitution by another amino or another carbonyl fragment. This exchange reaction can be illustrated by the following reactions:

$$C_6H_5CH{=}NC_6H_5 + H_2NC_6H_4X \rightarrow C_6H_5CH{=}NC_6H_4X + C_6H_5NH_2 \qquad \text{(eq. 11)}$$

$$C_6H_5CH{=}NC_6H_4 + OHCC_6H_4X \rightarrow XC_6H_4CH{=}NC_6H_5 + C_6H_5CHO \qquad \text{(eq. 12)}$$

These reactions may be considered as related to transesterification and transamidation reactions. As an extension of the simple type of Schiff base exchange represented by equations 11 and 12, a bis-exchange reaction could be considered as feasible and is represented by the equation

$$XC_6H_4CH{=}NC_6H_5 + C_6H_5CH{=}NC_6H_4Y \rightarrow C_6H_5CH{=}NC_6H_5 + XC_6H_4CH{=}NC_6H_4Y \qquad \text{(eq. 13)}$$

The literature on the types of reactions represented by equations 11, 12, and 13 is very meager and the broad aspects of Schiff base exchange reaction, as such, are not described. However, in 1921 Reddelien described[9] the displacement of amine residues in the anils, $R_2C{=}NC_6H_5$ by aryl amines:

$$C_6H_5\underset{CH_3}{C}{=}NC_6H_5 + C_{10}H_7NH_2 \rightarrow C_6H_5\underset{CH_3}{C}{=}NC_{10}H_7 + C_6H_5NH_2 \qquad \text{(eq. 14)}$$

to be followed in 1953 by Koshits and his co-workers[10] who described amine displacements in some substituted benzylidene anilines:

$$C_6H_5CH{=}NC_6H_4NO_2 + H_2NC_6H_4OCH_3 \rightarrow C_6H_5CH{=}NC_6H_4OCH_3 + O_2NC_6H_4NH_2 \qquad \text{(eq. 15)}$$

The carbonyl exchange reaction represented by equation 12 and the bis-exchange reaction represented by equation 13 do not appear to be described in the literature. Also, apparently absent are exchange reactions involving multifunctional Schiff bases with monofunctional aldehydes or monofunctional amines, such as

$$C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5 + 2\ XC_6H_4CHO \rightarrow XC_6H_4CH{=}NC_6H_4N{=}CHC_6H_4X + 2\ C_6H_5CHO \qquad \text{(eq. 16)}$$

$$C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5 + 2\ XC_6H_4NH_2 \rightarrow XC_6H_4N{=}CHC_6H_4CH{=}NC_6H_4X + 2\ C_6H_5NH_2 \qquad \text{(eq. 17)}$$

or multifunctional aldehyde or multifunctional amines, with monofunctional Schiff bases such as

$$NH_2C_6H_4NH_2 + 2\ C_6H_5CH{=}NC_6H_5 \rightarrow C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5 + 2\ C_6H_5NH_2 \qquad \text{(eq. 18)}$$

$$OHCC_6H_4CHO + 2\ C_6H_5CH{=}NC_6H_5 \rightarrow C_6H_4N{=}CHC_6H_4CH{=}NC_6H_5 + 2\ C_6H_5CHO \qquad \text{(eq. 19)}$$

Since these Schiff base exchange reactions, and particularly those involving polyfunctional molecules might be applicable to the synthesis of polymers, they were investigated as methods of synthesis for non-polymeric Schiff bases as prototypes to the polymeric systems. The Schiff base exchange study is divided into three sections:

1. The Amine Exchange
2. The Carbonyl Exchange
3. The Bis Exchange

1. The Amine Exchange.

The amine exchange reaction has now been shown to be applicable to the reaction of monofunctional and polyfunctional amines with mono-Schiff bases

Table 5

Syntheses of Some Schiff Bases by Amine Exchange

Reagents	Exper. No.	% crude yield	Product	M.P. °C		Catalyst
				Found	Lit.	
$p\text{-}CH_3OC_6H_4NH_2 + C_6H_5CH{=}NC_6H_5$	DA-29-77	100	$C_6H_5CH{=}NC_6H_4OCH_3$	72	72	none
$p\text{-}H_2NC_6H_4NH_2 + 2C_6H_5CH{=}NC_6H_5$	DA-29-33 DA-29-47	100	$C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5$	140	140	$ZnCl_2$
$m\text{-}CH_3OC_6H_4NH_2 + C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5$	DA-29-79	100	$CH_3OC_6H_4N{=}CHC_6H_4CH{=}NC_6H_4OCH_3$	219	220	none

or poly-Schiff bases, as illustrated by equations 11, 17, and 18.

These exchange reactions are readily performed by heating the reagents usually at least to the melting point of the mixture and removing the displaced amine by distillation, using reduced pressures if necessary. The exchange reaction will proceed readily in the absence of a catalyst, though catalytic quantities of a Lewis acid such as $ZnCl_2$ may be used. The relative boiling points of the reagents and of the products appear to be the main factors in this reaction. Therefore, the desired product should have a higher boiling point than the starting reagents. Reaction occurs usually at the melting point of the reagent mixture and by distilling out the by-product, the equilibrium of the reaction is shifted to completion. The crude yields are substantially quantitative. The syntheses are summarized in Table 5.

a. Experimental.

The reactions were performed by placing the reagent in a round-bottomed ground glass jointed flask equipped with a distilling head, condenser, receiver, a nitrogen gas inlet, etc. The reaction vessel was heated by a molten metal bath and all reactions were performed under a nitrogen atmosphere to avoid oxidation at the temperatures used. The reaction was continued until the theoretical amount of eliminated amine was collected. The product was then recrystallized from 95% or absolute ethanol.

i) Preparation of Benzylidene-p-methoxyaniline (DA-29-77).

1.23 g. (0.01 mole) p-Anisidine and 1.81 g. (0.01 mole) benzylidene-aniline were placed together without catalyst in a 50 cc round-bottom micro flask fitted with a distilling head, condenser, and nitrogen inlet, etc. The reaction mixture was heated by immersing the reaction flask into a metal bath at 200°C while a slow-stream of nitrogen was passed through the reaction mixture. Then the pressure was reduced to about 100 mm. The reaction was

continued in this manner for one and one-half hours, after which no more aniline was collected in the receiver. The 72°C melting point of the recrystallized product and its infrared spectra corresponded to that of an authentic sample.

ii) Preparation of Dibenzylidine-p-phenylenediamine (DA-29-33).

1.858 g. (0.0125 mole) p-Phenylenediamine and 4.53 g. (0.025 mole) benzylidene-aniline with 10 mg of $ZnCl_2$ catalyst were reacted by the procedure given in DA-29-77 at 110°C, at which point aniline distilled from the reaction mixture. After about fifteen minutes, the evolution of aniline ceased, then the temperature was raised for about five minutes to 150°C and the reaction terminated. The yield of crude product before recrystallization was 100%. Recrystallization from ethanol gave a product which melted at 140°C, and is identical to that of an authentic sample.

iii) Preparation of p-Xylylidene-di-p-methoxyaniline (DA-29-79).

2.46 g. (0.02 mole) p-Anisidine and 2.84 g. (0.01 mole) terephthaldianil without catalyst were subjected to the procedure of DA-29-33, except that a temperature of 200°C for two hours was used. The yield of the crude product was quantitative and its melting point 219°C; its infrared spectrum was identical to that of an authentic sample.

2. The Carbonyl Exchange.

Since it was shown that the amino fragment in a Schiff base could be replaced, the possibility of exchanging the carbonyl fragment, as represented generally by equation 12, was also considered, and then evaluated. This research has confirmed the carbonyl exchange reaction.

The procedure considered is similar to that used in the amine exchange reaction. The reagents were heated to temperatures at least above the melting point of the mixture and removing the displaced aldehyde by distillation, using reduced pressures, if necessary. The carbonyl exchange reaction was found to

Table 6

Syntheses of Some Schiff Bases by Carbonyl Exchange

Reagents	Exper. No.	Product	% Yield Crude	M.P. °C		Catalyst
				Found	Lit.	
$p\text{-}O_2NC_6H_4CHO + C_6H_5CH{=}NC_6H_5$	DA-29-51	$p\text{-}O_2NC_6H_4CH{=}NC_6H_5$	100	91	93	none
$p\text{-}OHCC_6H_4CHO + 2C_6H_5CH{=}NC_6H_5$	DA-29-31 DA-24-46	$C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5$	100	159	159	$ZnCl_2$
$p\text{-}O_2NC_6H_4CHO + C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5$	DA-29-81	$O_2NC_6H_4CH{=}NC_6H_4N{=}HCC_6H_4NO_2$	100	245	249	none

proceed in the absence of catalyst but can be accelerated by Lewis acids such as zinc chloride. As in the case of amine exchange, the initial exchange is an equilibrium reaction, and since the equilibrium is displaced by removing the product of reaction, the relative boiling points of the reagents and products is the main factor in the reaction.

The carbonyl exchange reaction was found to be applicable to the reaction of monofunctional and polyfunctional aldehydes, with monofunctional and polyfunctional Schiff bases, as illustrated by equation 12, and by equations 16 and 19. The experimental data is summarized in Table 6.

a. Experimental.

i) Preparation of p-Nitrobenzylidene-aniline (DA-29-51).

Using the same equipment and procedure as described for the amine exchange reaction, 1.51 g. (0.01 mole) p-nitrobenzaldehyde and 1.81 g. (0.01 mole) benzylidene-aniline were heated without catalyst under a nitrogen atmosphere at 200°C at about 50 mm Hg for one hour. The collected distillate was quantitative and shown to be benzaldehyde. One recrystallization from 95% ethanol gave the product which melted at 91°C; literature melting point, 93°C.

ii) Preparation of p-Xylylidene-di-aniline (DA-29-31).

In the presence of about 10 mg of $ZnCl_2$, 4.53 g. (0.025 mole) benzylideneaniline and 1.7 g. (0.0125 mole) terephthaldehyde were reacted at 200°C as in DA-29-51. The reaction time was completed in one-half hour, and the yield of the crude product was quantitative. Recrystallization from EtOH gave a yield of 86.5% pure product, melting point 166°C.

iii) Preparation of di-m-Nitrobenzylidine-p-phenylenediamine (DA-29-81).

Following the procedure of DA-29-51, 3.02 g. (0.02 mole) m-Nitrobenzaldehyde and 2.84 g. (0.01 mole) dibenzylidine-p-phenylenediamine were reacted together without catalyst for five hours at 130°C at about 50 mm pressure.

The yield of crude product was quantitative. One recrystallization from acetone gave a product which melted at 245°C, and corresponds to an authentic sample.

3. The Bis-Exchange.

The amine exchange and the carbonyl exchange reactions in Schiff bases led to the consideration of the possibility of a bis-Schiff base exchange reaction.[5] This would involve reacting two Schiff bases and exchanging the groups within the bases. This bis-exchange can be generalized by equation 20:

$$RCH{=}NR' + R''CH{=}NR''' \rightleftharpoons RCH{=}NR''' + R''CH{=}NR' \qquad \text{(eq. 20)}$$

Confirmation of this bis-reaction was left[5] originally to be tested in the preparation of polymers. The reaction of the two Schiff bases, if it proceeds, produces four bases when equilibrium is established. This was verified to a limited extent by paper chromatography but quantitative data was difficult to obtain because of problems of analysis. Accordingly, systems were selected in which one of the reaction products, either RCH=NR''' or R''CH=NR' could be removed selectively or almost so by distillation so as to force the equilibrium to completion. In this manner, the bis-Schiff base exchange reaction was verified and shown to be applicable to mono-Schiff bases and poly-Schiff bases, as shown in equations 21 and 22. The experimental data are summarized in Table 7.

$$p\text{-}O_2NC_6H_4CH{=}NC_6H_5 + C_6H_5CH{=}NC_6H_4OCH_3 \longrightarrow C_6H_5CH{=}NC_6H_5\uparrow + O_2NC_6H_4CH{=}NC_6H_4OCH_3 \qquad \text{(eq. 21)}$$

$$C_6H_5CH{=}NC_6H_4Cl + C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5 \longrightarrow C_6H_5CH{=}NC_6H_5\uparrow + ClC_6H_4N{=}CHC_6H_4CH{=}NC_6H_4Cl \qquad \text{(eq. 22)}$$

Table 7

Syntheses of Some Schiff Bases by Bis-Exchange Reactions

Exper. No.	Product	% Yield Recrys.	Catalyst	M.P. °C		Ref.
				Found	Lit.	
DA-29-89	$p\text{-}O_2NC_6H_4CH{=}NC_6H_4OCH_3$	78.9	None	135	139	37
DA-26-188	$p\text{-}ClC_6H_4N{=}CHC_6H_4CH{=}NC_6H_4Cl\text{-}p$	70.0	$ZnCl_2$	180	---	--

a. Experimental.

The same apparatus and general procedures used for the amines and carbonyl exchange was applied to the bis-exchange reactions. The yields reported are of recrystallized products obtained from initial experiments and no effort has been made to improve them. Since the bis-exchange reactions appear to occur with about the same ease as the amine and carbonyl exchange, it is anticipated that with a few minor adjustments in technique, that quantitative yields should be obtainable.

i) Preparation of p-Nitrobenzylidine-p-methoxyaniline (DA-29-89).

2.11 g. (0.01 mole) p-Nitrobenzylidineaniline and 2.26 g. (0.01 mole) p-benzylidine-p-anisidine were mixed with five milligrams of $ZnCl_2$ in a 50 ml flask and heated to 200°C under nitrogen at 5 mm Hg pressure for eighteen hours in the exchange apparatus described above, and benzylidene-aniline collected as the distillate. Then the contents of the flask were isolated and after one recrystallization from ethanol, there was obtained 2.02 g. (78.9%) of the desired product, m.p. 135°C; lit.[30] m.p. 139°C.

ii) Preparation of p-Xylylidine-di-p-chloroaniline (DA-26-188).

The same equipment and general procedure as used above was employed in this reaction. 10 g. Benzylidine-p-chloroaniline and 2 g. terephthaldianil were heated at 220°C for sixty-four hours, then the pressure was reduced to 20 mm and

heating continued for one hour, following which the pressure was reduced to 3 mm to distill off excess benzylidine-p-chloroaniline. There remained 2.1 g. of crude product which was recrystallized from benzene and a 70% yield of terephthal-bis-p-chloroaniline was obtained. The infrared spectrum of the product was identical to an authentic sample, m.p. 180°C, prepared directly from $p\text{-}ClC_6H_4NH_2$ and $OHCC_6H_4CHO$.

iii) Attempted Chromatographic Separations (DA-29-69).

Equimolar quantities of the two bis-Schiff bases,

 and 

were melted together and heated at 200°C under a nitrogen atmosphere in a suitable glass apparatus and maintained at this temperature for one-half hour. As a result of an exchange reaction the resulting mixture contains in addition to the starting compounds, the new Schiff base,  , and could represent a maximum of 50 molar per cent of the total mixture. Then, the reaction was cooled, and separation was attempted using three chromatographic techniques:

(a) Column Chromatography.

A 50 cm chromatographic column packed with alumina was utilized for this attempted separation. After placing the Schiff base mixture on the column from an ethanol solution, the following sequences of eluants were passed through the column:

Eluant	Ratio
1) petroleum ether	---
2) petroleum ether - benzene	3:1
3) petroleum ether - benzene	2:1
4) petroleum ether - benzene	1:1
5) benzene	---
6) benzene - ethanol	3:1
7) benzene - ethanol	2:1
8) benzene - ethanol	1:1
9) ethanol	---

Upon evaporation and evaluation of the fractions taken at a 30 ml volume, no effective separation appeared to have taken place.

(b) Paper Chromatography.

Whatman #1 chromatographic paper was spotted respectively with an alcoholic solution of the Schiff base mixture and with also authentic samples of the three components present in the mixture. The samples were then chromatographed in one and two dimensions using the following systems:

Solvent System	Ratio
1) phenol - water	3:1
2) pyridine - water	2:1
3) n-butanol - water- acetic acid	3:1:2

Then, aqueous $CuCl_2$ was used as a developing agent. Some separation was evident but none of these systems, however, showed good separation. It was concluded, therefore, that the Rf values were too close in these compounds.

(c) Thin Layer Chromatography.

The solution of Schiff base mixture along with the reference samples were spotted as before on a silica-gel coated glass plate. Elution was accomplished using the system methanol - ethylacetate (1:1 ratio). The chromatogram was developed using concentrated H_2SO_4. Very little separation was observed and thus no conclusions could be drawn from this experiment.

4. The Mechanisms of the Exchange Reactions.

When considering proposals for the mechanisms of the Schiff base exchange reactions, it is necessary first to determine which reactions are characteristic of compounds possessing the $\rangle C{=}N-$ linkage. This bond being analogous to the carbonyl bond, undergoes many reactions similar to the $\rangle C{=}O$ bond. Addition reactions are especially characteristic of these compounds. Mercaptans, active hydrogen ccmpounds, and sodium bisulfite all add to the $\rangle C{=}N-$ bond, as for example:[38-42]

$$R\text{-}CH{=}N\text{-}R' + NaHSO_3 \rightarrow R\text{-}\underset{\underset{SO_3Na}{|}}{CH}\text{-}NHR' \qquad \text{(eq. 23)}$$

and

$$R\text{-}CH{=}N\text{-}R' + CH_2\text{-}(COOEt)_2 \rightarrow R\text{-}\underset{\displaystyle CH(COOEt)_2}{\overset{\displaystyle |}{CH}}\text{-}NHR' \qquad \text{(eq. 24)}$$

These reactions indicate therefore that this C=N bond is quite polar, possessing considerable reactivity. It is possible, thus, to propose mechanisms for the Schiff base exchange reactions assuming that an initial addition of the amine, aldehyde, or Schiff base to the $\rangle C{=}N\text{-}$ bond takes place.

Another factor which must be noted prior to considering a mechanism for the exchange reactions, is that a mixture of all possible products is obtained by a simple heating of the reaction mixture. One product can be obtained exclusively only when one of the exchange products is removed from the reaction system; and thus it appears that these reactions are in equilibrium.

a. Of the Amine Exchange.

The following mechanism is proposed for the amine exchange reaction:

$$R\text{-}CH{=}N\text{-}R' + R''\text{-}NH_2 \underset{}{\overset{k_1}{\rightleftharpoons}} R\text{-}\underset{\displaystyle NH\text{-}R''}{\overset{\displaystyle |}{CH}}\text{-}NHR' \qquad \text{(eq. 25)}$$

$$R\text{-}\underset{\displaystyle R''\text{-}N\text{---}H}{\overset{\displaystyle |}{CH}}\text{---}NH\text{-}R' \overset{k_2}{\rightleftharpoons} R\text{-}CH{=}NR'' + R'NH_2 \qquad \text{(eq. 26)}$$

The first step involves an addition of the amine to the Schiff base, thus forming a diamino adduct. The adduct is unstable under the conditions of the reaction and proceeds to break down reversibly yielding the displaced amine and the new Schiff base. As the displaced amine is removed from the reaction by distillation, the equilibrium is shifted and the new Schiff base is obtained exclusively.[43]

The literature gives some basis for this mechanism. It is well known that when acetaldehyde reacts with two moles of aniline a diamine is obtained.[44]

$$CH_3\text{-}CHO + 2\ C_6H_5\text{-}NH_2 \rightarrow CH_3\text{-}\underset{\displaystyle NHC_6H_5}{\overset{\displaystyle NHC_6H_5}{CH}} + H_2O \qquad \text{(eq. 27)}$$

In this reaction, it is assumed that the Schiff base is first formed, and then the second mole of aniline adds across the carbon nitrogen double bond.

In order to demonstrate the existence of the diamino intermediate in the amine exchange reaction the following experiment was performed (DA-29-57). An equimolar mixture of N,N-dimethyl-p-phenylenediamine and benzylidene-aniline was heated in a nitrogen atmosphere from 108-121°C in forty-five minutes. Samples were taken at various intervals and dissolved in chloroform, and the infrared spectrum of the sample taken. The data obtained from the infrared spectra are recorded in the following Table 8.

Table 8

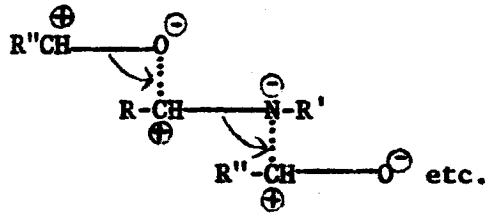
Infrared Spectral Data of a Bis-Exchange Reaction (DA-29-57)

Reaction time minutes	Presence of $-NH_2$	Trans. NH_2 / Trans. C-N	Presence of -C=N-	Trans. -C=N- / Trans. -C-N-
0	yes	-----	yes	-----
5	yes	0.338	yes	$\frac{1}{0.81} = 1.235$
10	yes	0.284	yes	$\frac{1}{1.34} = 0.746$
15	yes	0.200	yes	$\frac{1}{1.45} = 0.690$
15	yes	0.260	yes	-----

The data indicate that as the reaction proceeds, the amine and carbon nitrogen double bond absorption decreases indicating the formation of an intermediate complex. Towards the end of the reaction the absorption of these two bonds again increases as exchange occurs, and the chromophores reappear. Isolation of this intermediate does not appear to be feasible since it apparently has only a short lifetime and is present only in small amounts.

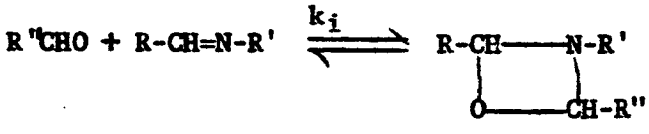
b. Of the Carbonyl-Exchange.

Two mechanisms are possible to explain the carbonyl exchange reaction. The first mechanism is of the concerted type in which an intermediate of the following type may be written:



In this mechanism, the dipoles of the polarized aldehyde and Schiff base are aligned in such a manner that exchange can occur by a simple shift of electrons.

The second mechanism proposed for the carbonyl exchange reaction is considered as occurring in two steps:



(eq. 23)

(eq. 29)

In the first step, the carbonyl moiety itself adds across the carbon nitrogen double bond giving a four-membered ring intermediate. This intermediate then may break down reversibly in either of two ways: one giving back the starting materials and the other giving rise to the exchange products. Determination of the presence of the four-membered ring has been attempted in the following experiment, (DA-29-52).

An equimolar mixture of p-nitrobenzaldehyde and benzylidene-aniline were heated together at 110°C in a reaction flask under a nitrogen atmosphere. Samples were taken at five-minute intervals, dissolved in chloroform and infrared spectra taken. The infrared data obtained in this experiment are summarized in Table 9.

Table 9

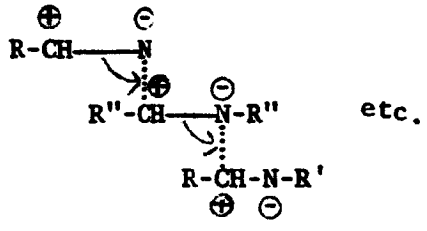
Infrared Data of a Bis-Exchange Reaction (DA-29-52)

time minutes	Presence of -CHO	Trans. Ar-H / Trans. -CHO	Presence of -CH=N-	Trans. -CH=N- / Trans. Ar-H
0	yes	0.754	yes	1.033
5	yes	0.754	yes	1.150
5	yes	0.740	yes	1.000
10	yes	0.756	yes	0.855
10	yes	0.794	yes	0.956

As was noted in the amine exchange reaction, the carbonyl and carbon-nitrogen double bond absorption decreases to a minimum during the course of the reaction. The concentration of the intermediate appears to be low in this case also, then rises again near the end of the reaction. This evidence serves to lend some weight to the existence of the four-membered ring intermediate which has been proposed, particularly in view of the fact that no noticeable increase in viscosity during the reaction was observed, which should be expected if a concerted mechanism was in operation, resulting in an "ionic type" polymer.

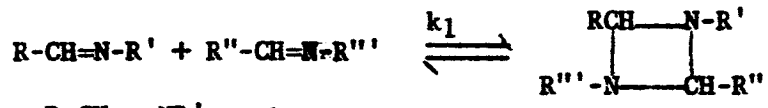
c. Of the Bis-Exchange.

Mechanisms analogous to the carbonyl exchange reaction may be proposed for the bis Schiff base exchange reaction. A concerted mechanism of the type:

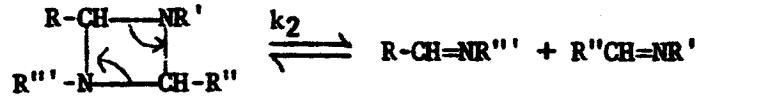


may be proposed utilizing the polar character of the Schiff base linkage. By a shift of pairs of electrons exchange can occur in chain-type reaction.

The reaction may also occur through a four-membered transition state in which both Schiff bases participate,



(eq. 30)



(eq. 31)

and in which destruction of the intermediate accounts for the products which are formed.

As of the present time, none of the experiments conducted using U.V. or I.R. has offered convincing proof of the four-membered ring intermediate due to overlap of spectral bands, etc. However, the absence of any noticeable increase in viscosity during the reaction tends to eliminate the concerted mechanism which would produce an "ionic type" polymer.

C. From Aromatic Acetals and Amine Compounds.

The synthesis of Schiff bases using aromatic acetals was considered[5] as a means of moderating the reaction of the aldehyde with the amine. The confirmation of this reaction led to the consideration of other reactions involving aromatic acetals for Schiff base synthesis. The ease of the Schiff base exchange reactions suggested that derivatives of the amines should also be considered for reaction with the acetals. Two classes of amine derivatives were selected for investigation, namely, the Schiff base, ØCH=NØ, and an acyl derivative, RCONHØ. The postulated reactions for aromatic acetals with the amine, Schiff base and acyl amides are generalized in equations 32, 33 and 34 respectively.

$$X\text{-}ØCH(OR)_2 + ØNH_2 \rightarrow X\text{-}ØCH{=}NØ' + 2\ ROH \qquad \text{(eq. 32)}$$

$$X\text{-}ØCH(OR)_2 + Y\text{-}ØCH{=}NØ' \rightarrow X\text{-}ØCH{=}NØ' + Y\text{-}ØCH(OR)_2 \qquad \text{(eq. 33)}$$

$$X\text{-}ØCH(OR)_2 + R'CONHØ' \rightarrow X\text{-}ØCH{=}NØ' + ROH + R'COOR \qquad \text{(eq. 34)}$$

Accordingly, the investigation was divided into three sections:

Syntheses from Aromatic Acetals with Aryl Amines;

Syntheses from Aromatic Acetals with Schiff Bases;

Syntheses from Aromatic Acetals with N-Acyl-arylamines;

and each will be considered separately.

1. From Aromatic Acetals and Amines.

The syntheses of Schiff bases by reaction of aromatic acetals with aromatic amines given in equation 32 do not appear to be in the literature. This reaction was found to proceed readily[5,6] with or without a catalyst over a wide range of temperatures and in the presence or absence of solvents. The reaction is performed simply by heating the reagents in a suitable apparatus, removing the alcohol, and isolating the product. Table 10 summarizes the synthesis of benzylidene-aniline from the acetal and the amine according to the equation

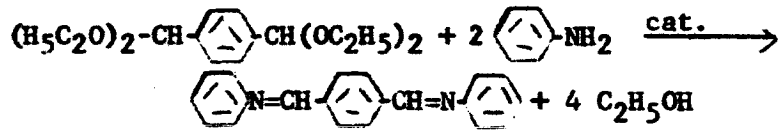
$$C_6H_5CH(OC_2H_5)_2 + C_6H_5NH_2 \rightarrow C_6H_5CH{=}NC_6H_5 + 2\ C_2H_5OH \qquad \text{(eq. 35)}$$

Table 10

Syntheses of $C_6H_5CH{=}NC_6H_5$ from $C_6H_5NH_2$ and $C_6H_5CH(OC_2H_5)_2$

Exper. No.	Catalyst	Solvent	Reaction Temp.	Reaction time (hour)	Yield % Crystallized Product
DA-26-16	$CH_3C_6H_4SO_3H$	Benzene	Reflux	2	71
DA-26-18	$ZnCl_2$	Benzene	Reflux	3	70
DA-26-15	$CH_3C_6H_4SO_3H$	None	55°C	1	90
DA-26-19	None	None	100°C	0.17	90

The difunctional acetals were also shown to react with aniline similarly to the monoacetals to produce di-Schiff bases. In particular the following reaction (DA-26-24) was studied

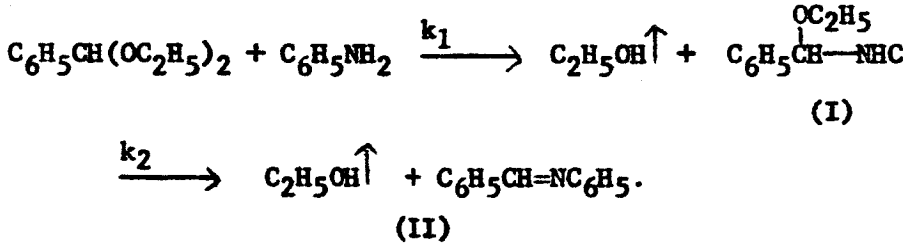


(eq. 36)

and an 80% yield of recrystallized Schiff base was obtained. The product of the reaction was identified by comparison of its infrared spectrum and melting point with an authentic sample.

a. The Mechanism of Reaction.

The reaction of the acetal and the amine produces the Schiff base by a double elimination for which the postulated reaction is given as:



(eq. 37)

This reaction was studied in detail with the hope that it could be stopped at the intermediate (I), $C_6H_5\overset{OC_2H_5}{\overset{|}{C}}H\text{-}NHC_6H_5$. If this were possible, the reaction could be utilized to keep the intermediate polymer soluble to a high molecular weight stage and thereafter the reaction continued to produce the polymeric Schiff base by elimination of the second molecule of alcohol. The reaction was studied with and without catalysts, and at various temperatures and times in attempts to isolate the intermediate as a physical entity; these studies were not successful. Studies were then undertaken to confirm the existence of the intermediate by physical methods. Two physical methods were investigated, namely, (1) the decay in specific absorption bands in the infrared spectrum and (2) the kinetics of the reaction.

i) Infrared Studies.

A series of reactions were performed between $C_6H_5CH(OC_2H_5)_2$ and $C_6H_5NH_2$ with and without catalysts and at various temperatures and the reaction mixture sampled at various times and the infrared spectrum of the reaction

Table 11

Absorption Bands in the Spectra of the Reaction of $C_6H_5CH(OC_2H_5)_2$ and $C_6H_5NH_2$

Materials Examined	Reaction time hours	Ratio of 3480 cm^{-1} to 3395 cm^{-1}	1100 cm^{-1}	1050 cm^{-1}	1630 cm^{-1}	3400 cm^{-1} wide
$C_6H_5NH_2$	-----	0.80	No	No	No	No
$C_6H_5CH(OC_2H_5)_2$	-----	----	Yes	Yes	No	No
Unreacted mixture of $C_6H_5NH_2$ and $C_6H_5CH(OC_2H_5)_2$	-----	0.70	Yes	Yes	No	No
Exper. DA-26-13	0.5	0.70	Yes	Yes	No	No
Reaction at 55°C	2.5	0.75	Yes	Yes	No	No
No catalyst	23.5	----	No	Yes	Yes	Yes
Exper. DA-26-15	1.0	----	No	Yes	Yes	Yes
Reaction at 55°C with	2.5	----	No	Yes	Yes	Yes
$CH_3C_6H_4SO_3H$ cat.	23.0	----	No	Yes	Yes	Yes
Exper. DA-26-19						
Reaction at 100°C	0.33	----	No	Yes	Yes	Yes
No catalyst						
	0.25	----	Yes	Yes	No	No
Exper. DA-26-21	1.25	0.75	Yes	Yes	No	No
at 20°C with	4.5	0.70	Yes	Yes	No	No
$H_3CC_6H_4SO_3H$ cat.	6.0	0.74	Yes	Yes	No	No
	46.5	0.80	Yes	Yes	No	No

products compared for specific wavelengths to the spectra of the individual starting reagents and mixtures of the reagents. The spectral data of these experiments is summarized in Table 11.

The data in Table 11 fail to offer conclusive proof for the existence of a stable isolable intermediate.

The bands at 3480 cm^{-1} and 3395 cm^{-1} are characteristic of $-NH_2$ structures and a decrease in the ratio of 3480 cm^{-1} to 3395 cm^{-1} would show a disappearance of the primary amine $-NH_2$, and only indirectly the formation of a secondary amine in the reaction process, by the disappearance of the 3395 cm^{-1}. However, as the reaction proceeds alcohol is liberated even in the first stage and its presence is observed at 3400 cm^{-1} in the form of a wide band which masks the area and prevents interpretation of the changes in the 3480 cm^{-1} to 3395 cm^{-1} ratio. The peaks at 1100 cm^{-1} and 1050 cm^{-1} are characteristic of the acetal linkage and at least one of them should disappear when compound (I) or (II) is formed. When reaction occurs, the peak at 1100 cm^{-1} was found to disappear but that at 1050 cm^{-1} persisted and shown to be attributable to the $-CH_2O-$ structure of the liberated ethyl alcohol. The peak at 1630 cm^{-1} is one of the -C=N- absorption bands and the wide band at 3400 cm^{-1} is characteristic of ethyl alcohol. From these results, the actual existence of intermediate compound (I) cannot be confirmed especially because of the overlap of the 3480 cm^{-1} and the wide 3400 cm^{-1} bands, and of the closeness of the 1630 cm^{-1} band with an -N-H stretching band in aniline at 1600 cm^{-1}. In these experiments, it was observed that when the temperature is low, such as at 20°C, the reaction is sluggish even in the presence of a catalyst and no reaction occurs (DA-26-21) in forty-six and one-half hours.

At 55°C, the reaction is sluggish in the absence of a catalyst (DA-26-13) and no reaction was observed for two and one-half hours whereas in the presence of a catalyst at 55°C (DA-26-15) the reaction is rapid. At 100°C the

reaction (DA-26-19) is rapid even in the absence of a catalyst. In those cases where reaction occurs, the reaction in this system appears to proceed through the two stages at rates whose specific rate relationships are such that the intermediate compound (I) cannot be confirmed by spectral means.

ii) Kinetic Studies.

An attempt was made to establish the existence of the intermediate (I), $C_6H_5\overset{OC_2H_5}{\underset{|}{C}}HNHC_6H_5$, from observations on the rates of elimination of alcohol in the reaction as shown in equation 37. When k_1 is much larger than k_2, the overall rate of elimination of alcohol should be different before and after the generation of (I); and when $k_1 = k_2$ or $k_1 < k_2$ no change of the overall rate of the elimination should be expected. The reaction of the acetal, $C_6H_5CH(OC_2H_5)_2$ and aniline, $C_6H_5NH_2$ was performed at reflux in benzene with toluene sulfonic acid as the catalyst. During the reaction, heating was so controlled that the azeotropic mixture of benzene and the alcohol formed in the reaction, distilled off at a fairly constant rate of 1 cc. a minute, while recording the vapor temperature during the distillation. Under these restrictions, if $k_1 > k_2$, the vapor temperature would tend to increase after the formation of (I) to the boiling point of benzene because of the shortage of alcohol required to maintain the normal azeotrope. If, however, $k_1 = k_2$ or $k_1 < k_2$ no change in vapor temperature should occur.

The experimental data (DA-26-22) is illustrated in Figure 1 in which the relationship between vapor temperature and volume of distillate is shown.

It will be noted in Figure 1 that there is no marked change in the rate of alcohol elimination before or after the point corresponding to the calculated amount of alcohol at which the intermediate (I) is formed. Rather, the data indicate that $k_2 = k_1$ or $k_2 > k_1$ and that isolation of the intermediate should be difficult indeed.

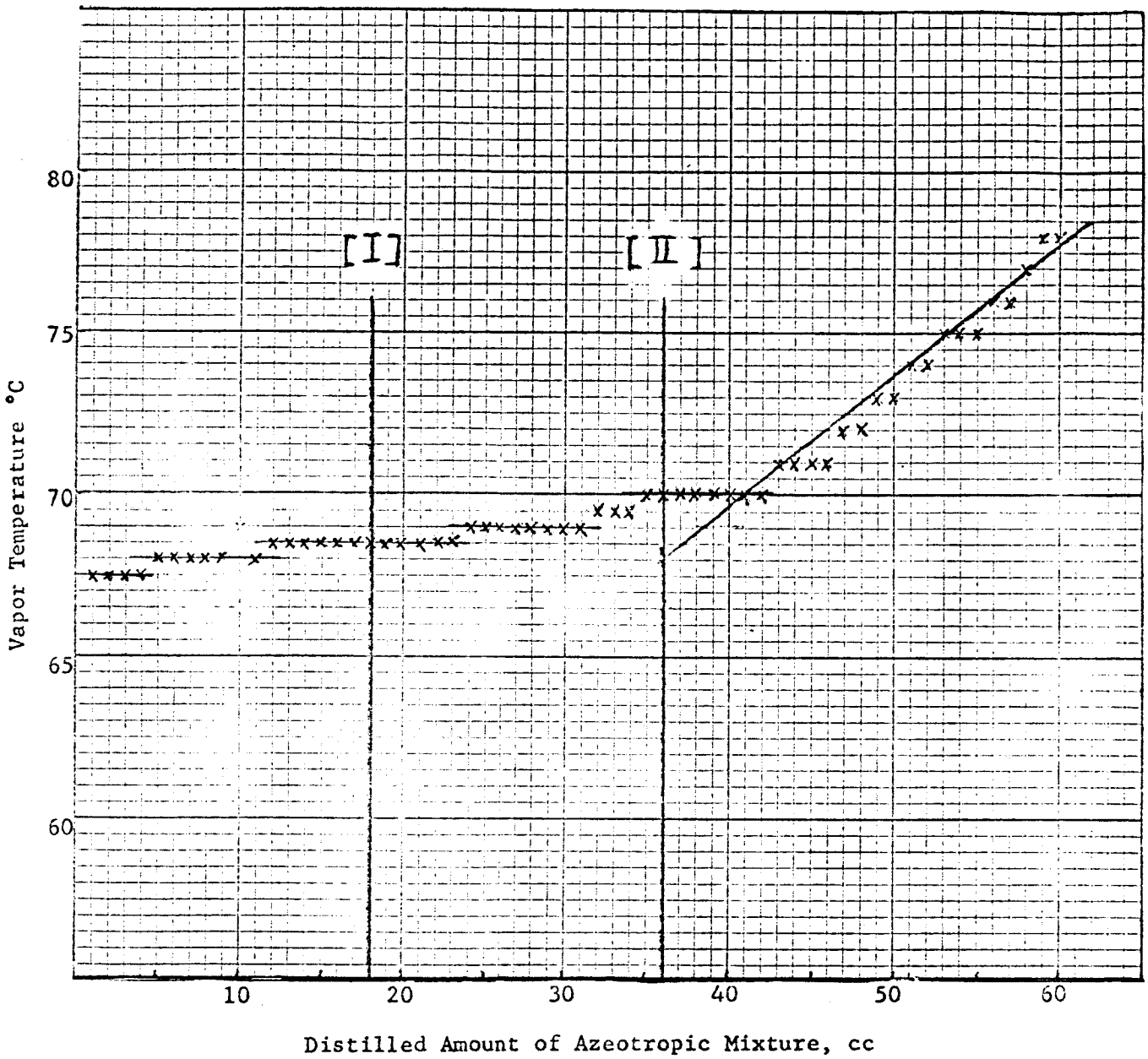


Figure 1. Relationship between vapor temperature and volume of distillate in acetal-amine reaction (DA-26-22).

b. Experimental.

i. (DA-26-9). Syntheses of Benzylidenediethyl Ether, $C_6H_5CH(OC_2H_5)_2$.

A modified procedure of Post[45] was used for this preparation. A mixture of 53 g. benzaldehyde, 80 g. ethyl orthoformate and 3 g. p-toluene sulfonic acid were mixed in a 250 ml round-bottomed flask and attached to a Dean-Stark trap fitted with a reflux condenser, etc. The mixture was heated at its boiling point for two hours and the theoretical amount of ethyl formate collected in the trap. Solid Na_2CO_3 was then added to the cooled mixture and allowed to stand overnight. It was then filtered and the filtrate distilled to yield $C_6H_5CH(OC_2H_5)_2$, yield 75%, b.p. 223°C/760 mm; 108°C/20 mm, and 93°C/10 mm; lit.[45] b.p. 222°C/760 mm.

ii) Synthesis of p-Xylidenetetraethyl Ether, $(C_2H_5O)_2CHC_6H_4CH(OC_2H_5)_2$.

The same procedure was used in this preparation as in the synthesis of benzylidene diethyl ether by reacting a mixture of 116 g. terephthaldehyde, 330 g. ethyl orthoformate and 3 g. p-toluene sulfonic acid for six hours and collecting 150 cc. ethyl formate (theoretical 156 g.). The neutralized and filtered reaction product was distilled, 75%, b.p. 146-148°C/3.2 mm; 143.5-145°C/3 mm, $n_{20}^{D} = 1.4742$; purity as determined by gas chromatography in F & M Model 609 Flame Ionization Gas Chromatograph with a column 10 ft. carbowax 1500 at 150°C was greater than 99.9%. The infrared spectrum was recorded, and by comparing the absorption peaks at 5.85 and 3.35μ, the amount of $p\text{-}C_6H_4(CHO)_2$ as impurity in the acetal can be readily estimated as shown in Fig.2.

Elemental Analysis calc. for: C, 68.05; H, 9.31

Found: C, 68.02; H, 9.30.

iii) Reactions of $C_6H_5CH(OC_2H_5)_2$ and $C_6H_5NH_2$ Under Various Conditions.

(a) DA-26-16.

A mixture of 60 g. $C_6H_5CH(OC_2H_5)_2$, 32 g. aniline, 120 ml benzene and 0.25 g. TsOH were refluxed two hours, then 50 cc. alcohol-benzene was distilled

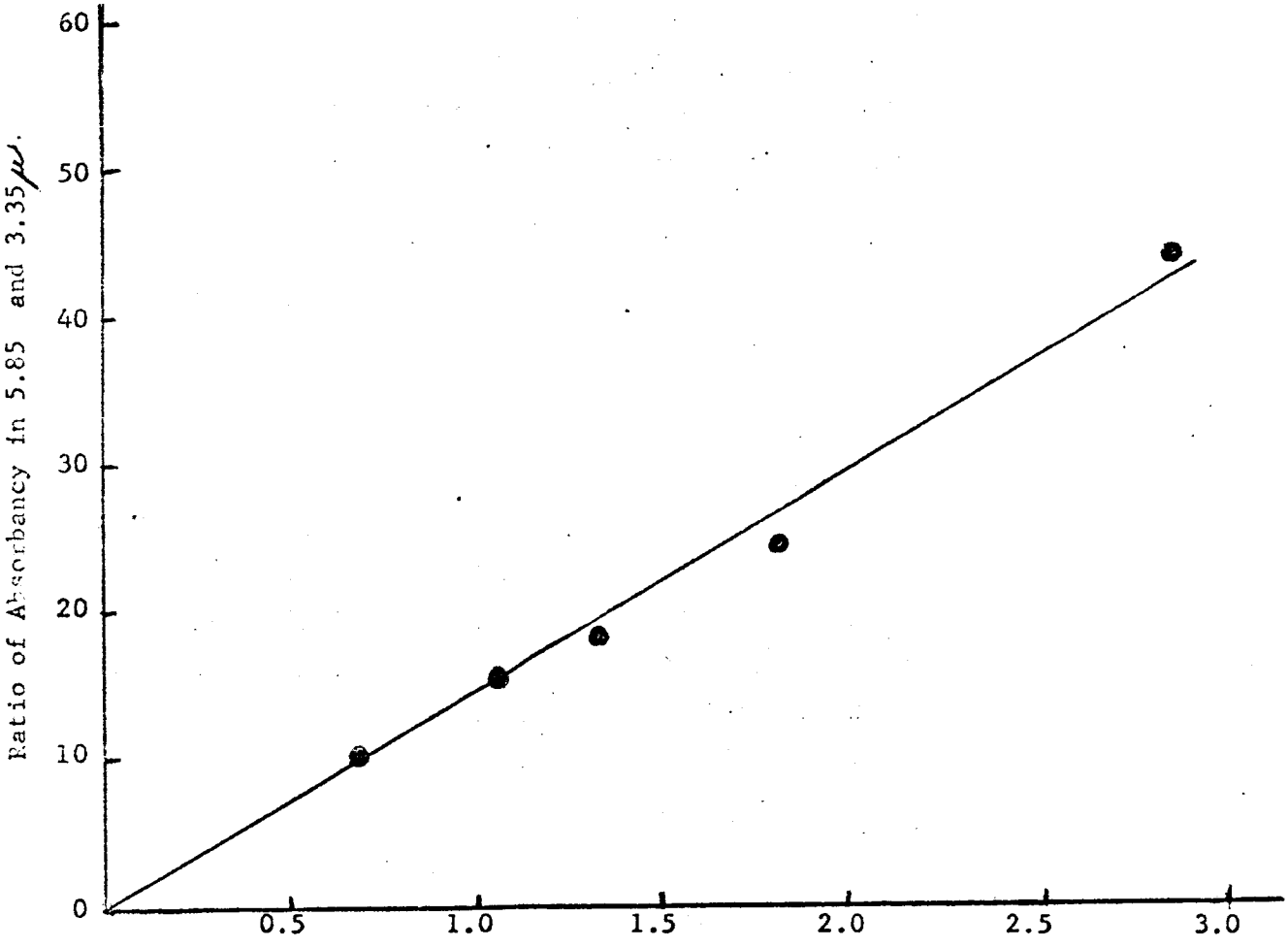


Figure 2. Per cent concentration (g/cc) of $C_6H_4(CHO)_2$ (g) in $(C_2H_5O)_2CHC_6H_4CH(OC_2H_5)_2$ (cc)

from the mixture and the mixture allowed to cool and crystallization to occur. The product, $C_6H_5CH=NC_6H_5$ was removed by filtration and recrystallized from 95% alcohol and characterized by I.R., M.P. and by mixed melting point with an authentic sample. Yield recrystallized product, 71%.

(b) DA-26-18.

A mixture of 30 g. $C_6H_5CH(OC_2H_5)_2$, 16 g. aniline, 0.1 g. $ZnCl_2$ and 58 ml benzene were reacted for three hours by the procedure of DA-26-16 and a recrystallized yield of 22 g. $C_6H_5CH=NC_6H_5$ (71%) was obtained.

(c) DA-26-15.

A mixture of 1 g. $C_6H_5CH(OC_2H_5)_2$, 0.51 g. $C_6H_5NH_2$ and 0.1 g. TsOH were heated in a micro-flask at 55°C by means of a mineral-oil bath maintained at 55°C. Samples of the reaction product were withdrawn at the intervals of one, two and one-half, and twenty-three hours and I.R. spectra of the samples recorded.

(d) DA-26-19.

A mixture of 9.0 g. $C_6H_5CH(OC_2H_5)_2$ and 4.65 g. of aniline were placed in a 20 ml reaction flask attached to a Dean-Stark trap and condenser. The mixture was then heated to 100°C and the elimination of alcohol assured by the 76°C temperature of the distillate vapor. Samples of the reaction mixture were withdrawn at the intervals of ten, twenty, one hundred forty-three, and three hundred fifty-three minutes, and I.R. spectra recorded. This reaction showed the definite presence of the Schiff base at the seventy-minute reaction period. On the completion of the reaction, there was isolated and characterized 8 g. (90% yield) of recrystallized $C_6H_5CH=NC_6H_5$.

(e) DA-26-13.

A mixture of 1 g. $C_6H_5CH(OC_2H_5)_2$ and 0.51 g. aniline were reacted at 55°C in a micro-flask heated by means of a mineral oil bath. Samples of the reaction product were withdrawn at the intervals of one-half, two and one-half

and twenty-three hours and I.R. spectra of the samples recorded.

(f) DA-26-21.

A mixture of 9.0 g. $C_6H_5CH(OC_2H_5)_2$, 4.65 g. aniline and 0.05 g. TsOH were maintained at 20°C in a reaction flask; samples were withdrawn at the intervals of 0.25, 1.25, 4.5, 6.0, and 46.5 hours, and the spectra of the samples recorded. No changes in the spectra were observed in any of the samples.

iv. DA-26-22. Measurements of the Elimination Rate of Ethyl Alcohol.

A mixture of 18 g. of $C_6H_5CH(OC_2H_5)_2$, 9.3 g. aniline, 1 g. TsOH, and 200 cc. benzene were placed in a 200 ml flask attached to a cendenser and calibrated receiver. The reaction mixture was heated by means of an electric mantle heater with a variac control so that approximately one ml of liquid was distilled per minute while recording the vapor temperature of the distillate as a function of the amount of distillate. The data is given in Table 12, and from this data, the data of Figure 1 was derived.

2. From Aromatic Acetals and Aryl Amine Hydrochlorides.

The reaction of benzylidenediethyl ether and aniline hydrochlorides instead of the free base was also studied in attempts to isolate the intermediate (I), $C_6H_5\overset{OH}{\underset{|}{C}}H\text{-}NHC_6H_5$. In the reaction of some aldehydes with some amines, the intermediate has been isolated when the hydrochloride, rather than the free amine, was used. Erlenmeyer[46] actually isolated the reaction product of benzaldehyde and certain aromatic amines as adducts, namely,

$$C_6H_5\overset{OH\ H}{\underset{|\ \ |}{C}}H\text{-}N\text{-}C_6H_4Cl(p) \quad \text{and} \quad C_6H_5\overset{OH\ H}{\underset{|\ \ |}{C}}H\text{-}N\text{-}C_6H_4Br(p)$$

by reacting benzaldehyde with the amine hydrochlorides, $p\text{-}ClC_6H_4NH_2.HCl$ and $p\text{-}BrC_6H_4NH_2.HCl$ respectively in a mixture of benzene and water, and then neutralizing the reaction product with sodium carbonate.

Dimroth and Zoeppritz also reported[47] the isolation of $C_6H_5\overset{OH}{\underset{HCl}{\underset{|}{\underset{|}{C}}}}HNHC_6H_5$

Table 12

Rate Data on the Elimination of Alcohol (DA-26-22)

Reaction time minutes	Volume of Azeotropic mixture, cc	Temperature of Azeotropic mixture (°C)	Reaction time minutes	Volume of Azeotropic mixture, cc	Temperature of Azeotropic mixture (°C)
5.0	1	67.0	30.5	31	69.0
6.5	2	67.0	31.5	32	69.5
7.5	3	67.5	32.0	33	69.5
8.0	4	67.5	32.5	34	69.5
8.5	5	68.0	33.5	35	70.0
9.0	6	68.0	34.5	36	70.0
9.5	7	68.0	35.0	37	70.0
10.0	8	68.0	36.0	38	70.0
10.5	9	68.0	36.5	39	70.0
11.0	10	69.0	37.5	40	70.0
12.5	11	68.0	38.5	41	70.0
13.0	12	68.5	39.0	42	70.0
15.0	13	68.5	39.5	43	71.0
16.0	14	68.5	40.5	44	71.0
17.0	15	68.5	41.5	45	71.0
18.0	16	68.5	42.5	46	71.0
18.5	17	68.5	43.5	47	71.0
19.0	18	68.5	44.5	48	72.0
20.0	19	68.5	47.0	49	73.0
21.0	20	68.5	47.5	50	73.0
21.5	21	68.5	48.5	51	74.0
22.5	22	68.5	50.0	52	74.0
23.0	23	68.5	52.0	53	75.0
23.5	24	69.0	53.0	54	75.0
25.0	25	69.0	54.0	55	75.0
26.5	26	69.0	55.0	56	76.0
27.0	27	69.0	55.5	57	76.0
27.5	28	69.0	56.0	58	77.0
28.0	29	69.0	57.0	59	77.5
29.5	30	69.0	57.5	60	77.5

from the reaction of benzaldehyde and aniline; however, when the product was neutralized, it decomposed to benzaldehyde and aniline,

$$C_6H_5CHO + C_6H_5NH_2{\cdot}HCl \rightarrow C_6H_5CHOHNHC_6H_5{\cdot}HCl \rightarrow$$

$$\xrightarrow{1/2\ Na_2CO_3} C_6H_5CHO + C_6H_5NH_2 + NaCl + H_2O + CO_2 \qquad \text{(eq. 38)}$$

This was in contrast[42] to the isolation of $C_6H_5\overset{OH}{C}H\text{-}NHC_6H_4NO_2(p)$, $p\text{-}HOC_6H_4\overset{OH}{C}HNHC_6H_5$ and $m\text{-}HOC_6H_4\overset{OH}{C}HNHC_6H_5$ which were obtained as neutralization products of the corresponding hydrochloride. Later, in 1921, Lowy isolated[48] adducts of 2,4,6-trinitrobenzaldehyde and several aromatic amines.

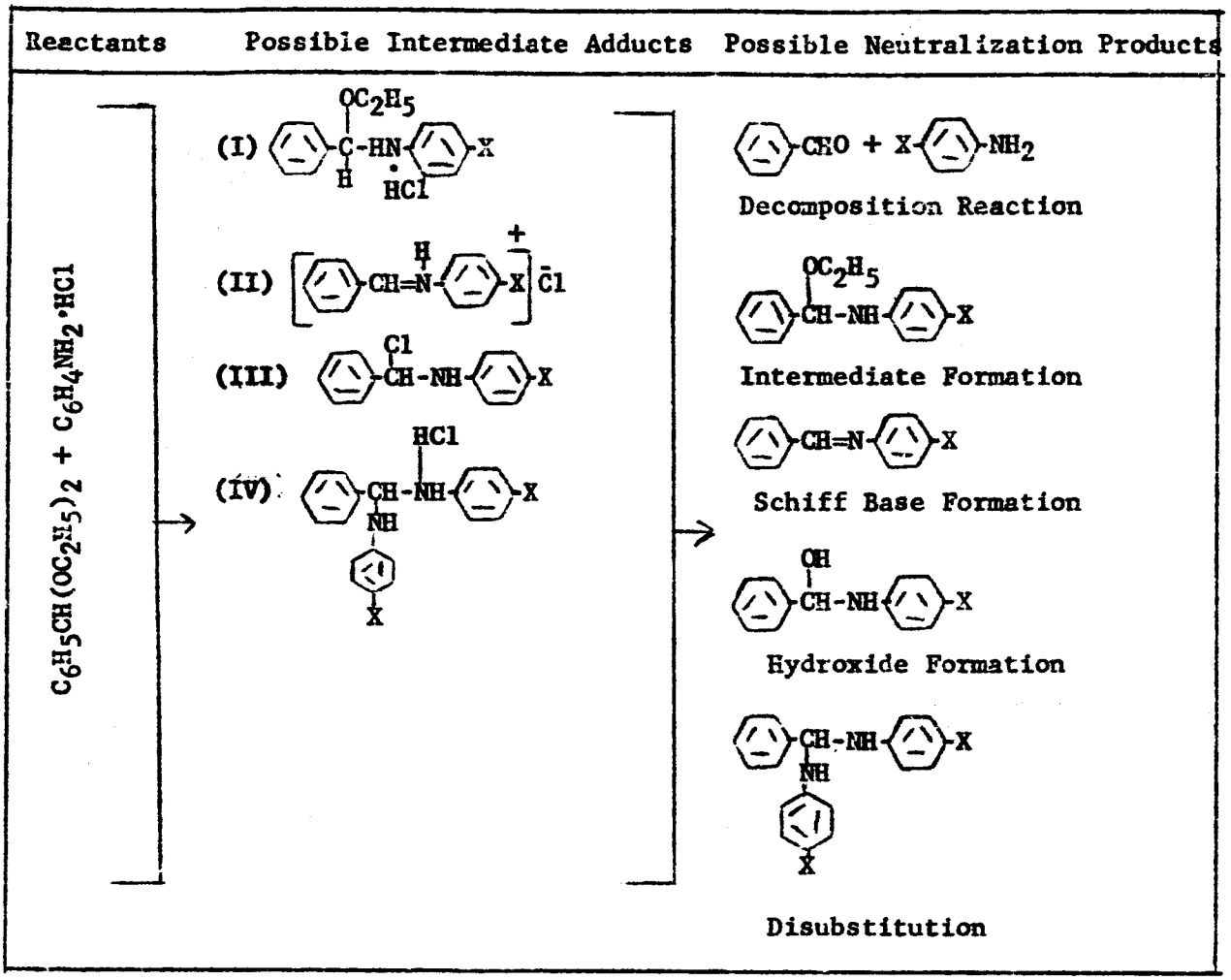
a. The Mechanism of Reaction.

Accordingly, studies were made of the reactions of the acetals and the aromatic amine hydrochlorides in bulk and in aqueous and non-aqueous organic solvents in attempts to isolate non-Schiff base type intermediates. The reaction of $C_6H_5CH(OC_2H_5)_2$ and $XC_6H_4NH_2{\cdot}HCl$ can lead to a number of postulated chlorine-containing adducts, which, in turn, can, when treated with a base yield a number of neutralization products, as shown in Table 13, all of which can, by further reaction and elimination, lead to a Schiff base.

A number of adducts were prepared by reacting the acetal with aniline and some substituted anilines, and the adducts isolated. Since the molecular weights of proposed adducts (II) and (III) are identical and lower than the molecular weights of adducts (I) and (II), molecular weight determinations were considered as being useful in assigning the adducts to one of these groups.

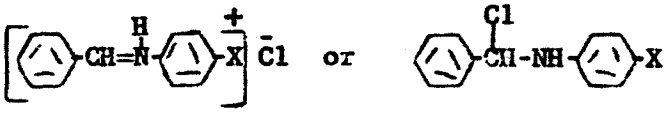
Table 13

Possible Compounds from Reaction of $C_6H_5CH(OC_2H_5)_2$ and $C_5H_5NH_2 \cdot HCl$



The molecular weight data obtained for a number of adducts prepared at various temperatures and in various solvents is shown in Table 14.

The data of Table 14 show that the adducts are of either type (II) or (III):



and not types (I) or (IV). The deviations found when X = H are attributable to the instability of the neutralized adduct similar to that reported[43] by Dimroth in the neutralization of $C_6H_5\overset{OH}{\underset{|}{C}}HNHC_6H_5 \cdot HCl$. The minor deviations in calculated and found molecular weights noted in a few of the other adducts is due to the fact that in all cases, the unpurified crude adduct had to be used

since all attempts to purification by crystallization resulted in some decomposition of the adduct. The deviations found are on the low side of the calculated value; this would indicate further the absence of type (I) and type (IV) adduct, since their presence would augment the values rather than decrease them.

Table 14

Molecular Weights of Adducts of $C_6H_5CH(OC_2H_5)_2$ and $X\text{-}C_6H_4NH_2 \cdot HCl$

Exper. No.	Substituent X	Reaction Medium	Reaction Temperature	Molecular Weight	
				Found	Calculated for Adduct (II) or (III)
DA-26-27	H	water	ice	188	218
DA-26-29	H	alcohol	ice	200	218
DA-26-30	H	dioxane	room	201	218
DA-26-31	p-NO_2	water	ice	262	262
DA-26-32	p-NO_2	alcohol	room	248	262
DA-26-33-1	p-Cl	none added	room	252	252
DA-26-33-2	p-Cl	water	room	246	252
DA-26-33-3	p-Cl	toluene	room	250	252
DA-26-33-4	p-Cl	alcohol	room	238	252
DA-26-33-5	p-Cl	dioxane	room	252	252
DA-26-35	p-Cl	dimethyl formamide	room	248	252

The reaction of the amine hydrochlorides was also evaluated with the difunctional acetal, xylidenetetraethyl ether and the data is summarized in Table 15.

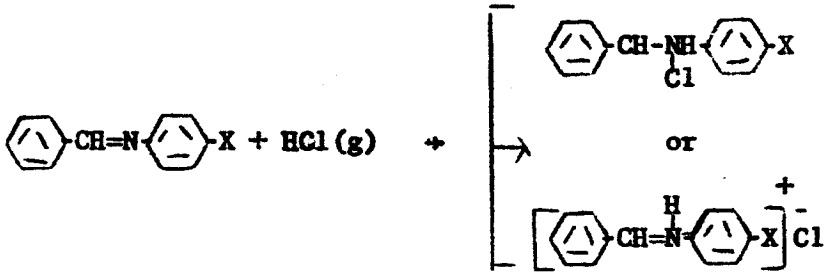
Table 15

Adducts of $(C_2H_5O)_2CHC_6H_4CH(OC_2H_5)_2$ and $X\text{-}C_6H_4NH_2$

Exper. No.	Substituent X	Solvent	Reaction Temperature	Molecular Weight	
				Found	Calculated as Adduct (II) and (III)
DA-26-36	-H	none	60°C	344	356
DA-26-37	p-Cl	none	60°C	408	424

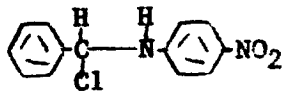
Again, the data in Table 15 indicates that the adduct formed is of either the (II) or (III) type.

This conclusion was confirmed by comparing the I.R. spectra of the adducts with products obtained by the addition of hydrogen chloride to pre-formed substituted Schiff bases, according to the equation:

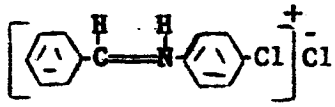


(eq. 39)

The infrared spectra of the adduct of $C_6H_5CH(OC_2H_5)_2$ with p-nitroaniline hydrochloride was completely identical to the reaction product (DA-26-44) of $C_6H_5CH{=}NC_6H_4NO_2(p)$ with HCl(g); and the infrared spectra of the adduct of $C_6H_5CH(OC_2H_5)_2$ with p-chloroaniline hydrochloride was also found to be completely identical with the reaction product (DA-26-45) of $C_6H_5CH{=}NC_6H_5Cl(p)$ with HCl(g). An interpretation of absorption bands of these spectra seems to indicate that the nitroaniline adduct has the structure



and the chloroaniline adduct has the structure



The study of the adducts included an evaluation of the products obtained from the adducts on neutralization with aqueous sodium carbonate. The constitutions of the products were determined from their infrared spectra, and the data are summarized in Tables 16 and 17.

The products of neutralization shown in Table 16 confirm the structures assigned to the nitro- and chloro adducts. Also, the formation of benzaldehyde and aniline on the neutralization of the adduct when X is H, confirms the

instability of the adduct obtained with the unsubstituted aromatic compounds compared to those more stable adducts which contain electron-withdrawing substituents. This same observation can be made from the data shown in Table 17. In view of the data of Table 16 on the unsubstituted aniline hydrochloride adduct, one would be led to assume that neutralization of the aniline hydrochloride adduct with $(C_2H_5O)_2CHC_6H_4CH(OC_2H_5)_2$ would lead to the regeneration of $OHCC_6H_4CHO$ and aniline; however, the =HC-  -CH= moiety in the adduct behaves as a substituted X-  -CH= with an electron-withdrawing capacity in its para substitution.

Table 16

Products from Neutralization of Adducts of $C_6H_5CH(OC_2H_5)_2$ with $XC_6H_4NH_2 \cdot HCl$

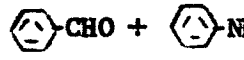
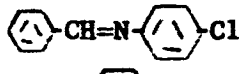
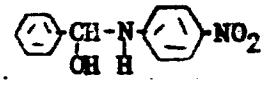
Exper. No.	Substituent X	Product of Neutralization
DA-26-38	-H	
DA-26-39	p-Cl	
DA-26-40	p-NO_2	

Table 17

Products from Neutralization of Adducts of $(C_2H_5O)_2CHC_6H_4CH(OC_2H_5)_2 + H_2NC_6H_4X \cdot HCl$

Exper. No.	Substituent X	Product of Neutralization
Da-26-41	-H	
DA-26-42	p-Cl	

The data obtained by reacting the acetal with an aniline hydrochloride leads to the same conclusion obtained in the reaction of the acetal with the free base, namely, that it is improbable that the monoethoxy intermediate,

$C_6H_5\overset{H}{\underset{OC_2H_5}{C}}-NHC_6H_4X$ can be isolated readily; however, these reactions are well suited to the preparation of Schiff bases.

b. Experimental.

1. Preparation of Adducts of $C_6H_5CH(OC_2H_5)_2$ and $X-C_6H_4NH_2HCl$ under Various Conditions.

(a) DA-26-27.

A mixture of 5 g. $C_6H_5CH(OC_2H_5)_2$ and 1 g. of water in a reaction flask was cooled in an ice-water bath and to the cooled mixture were added 2 g. of $C_6H_5NH_2 \cdot HCl$ slowly and with vigorous stirring. A clear solution first resulted, then a precipitate formed. After one hour at the ice-water temperature, the solid was removed by filtration, washed with absolute alcohol and dried in a vacuum dessicator. Yield of adduct 1.1 g.

(b) DA-26-29.

A mixture of 7.0 g. $C_6H_5CH(OC_2H_5)_2$ and 10 g. ethyl alcohol in a flask were cooled in an ice-water bath; then 2.5 g. $C_6H_5NH_2 \cdot HCl$ were slowly added with vigorous stirring. A clear solution formed and after ten minutes precipitation began. After one hour at ice-water temperature, the precipitate is removed by filtration and dried in a vacuum dessicator. Yield of adduct, 3 g.

(c) DA-26-30.

To mixture, at room temperature, of 5 g. $C_6H_5CH(OC_2H_5)_2$ and 5 g. dioxane in a flask is added slowly with vigorous stirring 1 g. $C_6H_5NH_2 \cdot HCl$, and the reaction allowed to proceed at room temperature. The mixture did not become homogeneous. After two hours, the solid was removed by filtration and dried in a vacuum dessicator. Yield of adduct, 1.6 g.

(d) DA-26-31.

The reaction of 10 g. $C_6H_5CH(OC_2H_5)_2$, 1 g. H_2O and 5 g. $p\text{-}O_2NC_6H_4NH_2 \cdot HCl$ were reacted for two hours using the procedure of DA-26-27. Yield of adduct 5 g. yellow solid.

(e) DA-26-32.

The reaction of 5 g. $C_6H_5CH(OC_2H_5)_2$, 20 ml. of ethyl alcohol and $p\text{-}O_2NC_6H_4NH_2 \cdot HCl$ were reacted at room temperature for two hours using the procedure of DA-26-29. Yield of Adduct, 3 g. yellow solid.

(f) DA-26-33.

The reaction of 2 g. $C_6H_5CH(OC_2H_5)_2$ in 2 ml. of various solvents with 0.5 g. $p\text{-}ClC_6H_4NH_2 \cdot HCl$ were performed for two hours at room temperature and the adduct isolated and dried. The solvent and yields of adducts were:

Exper. No.	Solvent	Yield of Adduct, g.
DA-26-33-1	none	0.7
DA-26-33-2	water	0.7
DA-26-33-3	toluene	0.8
DA-26-33-4	alcohol	0.6
DA-26-33-5	dioxane	0.7

(g) DA-26-35.

A mixture of 5 g. of $C_6H_5CH(OC_2H_5)_2$, 5 g. of dimethyl formamide and 1 g. $p\text{-}ClC_6H_4NH_2 \cdot HCl$ were reacted at room temperature for two hours. The precipitate was removed by filtration, washed with alcohol, and dried. Yield of adduct, 1.2 g.

(h) DA-26-36.

A mixture of 5 g. xylidenetetraethyl ether, $(H_5C_2O)_2CHC_6H_4CH(OC_2H_5)_2$ and $C_6H_5NH_2 \cdot HCl$ were reacted without solvent at 60°C for two hours. The solid was washed with alcohol and dried. Yield of adduct, 1.9 g.

(i) DA-26-37.

A mixture of 5 g. $(H_5C_2O)_2CHC_6H_4CH(OC_2H_5)_2$ and 1 g. $p\text{-}ClC_6H_4NH_2$ were reacted at 60°C by the procedure of DA-26-36. Yield of adduct 1.5 g.

ii) Neutralization Reactions of the Adducts from Acetals and Aniline Hydrochlorides.

The molecular weights of the adducts were determined by alkalimetry using 0.1 N NaOH as the titrant.

(a) DA-26-36 to DA-26-42 inclusive.

The general procedure consisted in preparing a solution of 1 g. Na_2CO_3 in 10 g. H_2O and cooling the solution to between 0°C and 10°C. Then 1 g. of adduct is added to the sodium carbonate solution with vigorous stirring and cooling continued for twenty minutes, after which the solution is filtered to remove the precipitate, which is allowed to dry in air at room temperature. Yield of products, 0.7∼0.9 g.

(b) DA-26-44.

Addition of HCl to $C_6H_5CH{=}NC_6H_4NO_2(p)$. Gaseous HCl (dried by passing it through conc. H_2SO_4) is passed into a solution of 5 g. $C_6H_5CH{=}NC_6H_4NO_2(p)$ in 100 ml. dry benzene maintained at 0-5°C until no more HCl is absorbed. The solid is removed by filtration, washed with ether and dried in a vacuum dessicator. Yield of product, 4.2 g.

(c) DA-26-45.

Addition of HCl to $C_6H_5CH{=}NC_6H_4Cl(p)$. A solution of 5 g. of $C_6H_5CH{=}NC_6H_4Cl(p)$ in 100 ml. dry benzene is treated with dry HCl by the procedure of DA-26-44. Yield of product, 3.5 g.

3. From Aromatic Acetals and N-Acyl Arylamines.

The synthesis of Schiff bases by the reaction of the aromatic acetals with the aniline hydrochlorides led to the consideration of other aniline derivatives such as the N-substituted anilines. The substituent group should be

a group that could be displaced or eliminated in a chemical reaction with the acetal. The N-acyl derivatives appeared to meet these requirements and the acetyl group was selected as the substituent for study.

The overall reaction for the proposed reaction may be written as

$$CH_3CONHC_6H_5 + C_6H_5CH(OC_2H_5)_2 \rightarrow C_2H_5OH + CH_3COOC_2H_5 + C_6H_5CH{=}NHC_6H_5 \qquad \text{(eq. 40)}$$

The reaction between the acetanilide and the acetal to obtain the Schiff base was found to be sluggish at temperatures below 150°C and to proceed readily in the range of 150-220°C. At the start of the reaction, the distillate from the reaction was essentially ethyl alcohol. As the reaction proceeded, the quantity of alcohol in the distillate progressively decreased and the amount of ethyl acetate progressively increased.

a. Experimental.

i. DA-26-52. Reaction of Acetanilide and Benzylidenediethyl Ether.

A mixture of 6 g. acetanilide and 8 g. of $C_6H_5CH(OC_2H_5)_2$ were heated in a distillation flask at 180°C to 222°C, and the distillate collected into several fractions, and their I.R. spectra taken to determine their composition. At the end of three hours 2 ml. of distillate were collected and the composition of the fractions were as follows:

Fraction Number	Volume (cc) of distillate	Composition
1	first drop	alcohol
2	0.5	alcohol
3	0.5	alcohol and ethyl acetate
4	0.5	alcohol and ethyl acetate
5	0.5	alcohol and ethyl acetate

with the concentration of ethyl acetate increasing progressively in fractions 3, 4, and 5. Hexane was added to the cooled reaction mixture in the flask to

isolate an hexane soluble and an hexane insoluble fraction. From the hexane soluble fraction there was isolated 4.2 g. (53% yield of $C_6H_5CH{=}NC_6H_5$. From the hexane insoluble fraction there is isolated 0.8 g. of a white solid which appears, on preliminary examination, to be impure $C_6H_5CH(OC_2H_5)NHC_6H_5(OCCH_3)$ or $C_6H_5CH(N(C_6H_5)OCCH_3)_2$

b. Proposed Mechanism of Reaction.

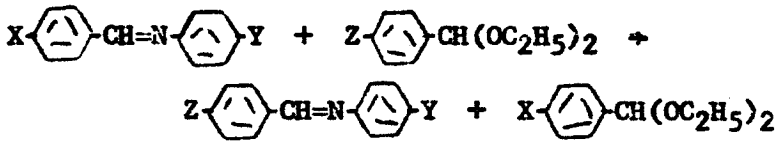
This reaction, obviously, involves a double elimination first of alcohol and then of ethyl acetate, from which the following mechanism can be proposed:

$$CH_3CONHC_6H_5 + C_6H_5CH(OC_2H_5)_2 \xrightarrow{k_1} C_2H_5OH + C_6H_5NH\text{-}CH(OC_2H_5)\text{-}C_6H_5 \text{ (C=O, } CH_3\text{)} \xrightarrow{k_2} C_6H_5CH{=}NC_6H_5 + CH_3COOC_2H_5 \quad \text{(eq. 41)}$$

The appearance of alcohol exclusively in the early stages of the reaction and of ethyl acetate later in the reaction leads to the conclusion that $k_1 > k_2$ and since this is so, the production of a soluble and/or fusible intermediate in the polymerization reaction of such polyfunction reagents as $CH_3CONHC_6H_4NHOCCH_3$ with $(H_5C_2O)_2CHC_6H_4CH(OC_2H_5)_2$ may be possible.

4. From Aromatic Acetal and Schiff Base.

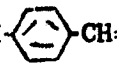
The reaction proposed for this synthesis can be written generally as:



(eq. 42)

This reaction was found to proceed readily in the presence of catalysts at temperatures above 150°C; whereas in the absence of a catalyst, reaction failed to occur except in the case where X was $-NO_2$. The reaction was also evaluated using the polyacetal $p\text{-}(H_5C_2O)_2CHC_6H_4CH(OC_2H_5)_2$, for which the experimental data is presented in Tables 18 and 19.

Table 18

Acetal Exchange Between X-  -CH=N-  -Y + Z-  -$CH(OC_2H_5)_2$

Exper. No.	Substituents			Catalyst	Temperature °C	Pressure mm Hg	Distillate	Product
	X	Y	Z					
DA-26-73	H	H	p-NO_2	None	150-250	760	$C_6H_5CH(OEt)_2$ and $C_6H_5CH=NHC_6H_5$	Black ?
DA-26-74	H	H	p-NO_2	None	170-195	15	$C_6H_5CH=NCC_6H_5$	None
DA-26-75	H	H	p-NO_2	TsOH	160-165	30-50	$C_6H_5CH(OC_2H_5)_2$ 30%	$O_2NC_6H_4N=CHC_6H_5$ 30%
DA-26-77	H	p-NO_2	p-NO_2	TsOH	170-180	760 → 1.5	$C_6H_5CH(OC_2H_5)_2$ 40%	$O_2NC_6H_4N=CHC_6H_4NO_2$ 25%
DA-26-78	H	p-NO_2	p-NO_2	TsOH	180	25	$C_6H_5CH(OC_2H_5)_2$ 20%	$O_2NC_6H_4N=C_6H_4NO_2$ 43%
DA-26-87	H	H	p-Cl	TsOH	170	10-40	$C_6H_5CH(OC_2H_5)_2$ 87%	$ClC_6H_4CH=NC_6H_5$

Table 19

Acetal Exchange Between X-  -CH=N-  -Y and $(C_2H_5O)_2CH$-  -$CH(OC_2H_5)_2$

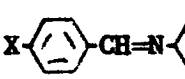
Exper. No.	Substituents		Catalyst	Temperature °C	Pressure mm Hg	Distillate	Product
	H	Y					
DA-26-56	H	H	TsOH	200-220	760	$C_6H_5CH(OC_2H_5)_2$ 52%	$C_6H_5N=CHC_6H_4CH=NC_6H_5$ 60% crude
DA-26-84	H	H	None	150	15	----------	No reaction
DA-26-85	H	H	TsOH	170	15-35	$C_6H_5CH(OC_2H_5)_2$ 52%	$C_6H_5N=CHC_6H_4CH=NC_6H_5$ 50%
DA-26-86	H	H	TsOH	170	22	$C_6H_5CH(OC_2H_5)_2$ 53%	$C_6H_5N=CHC_6H_4CH=NC_6H_5$ 85%
DA-26-79	H	p-NO_2	None	150-300	760	$C_6H_5CH(OC_2H_5)_2$ 60%	Black
DA-26-81	H	p-NO_2	TsOH	170	15-30	$C_6H_5CH(OC_2H_5)_2$ 30%	$O_2NC_6H_4N=CHC_6H_4CH=NC_6H_4NO_2$ 20%
DA-26-82	H	p-NO_2	TsOH	170	20	$C_6H_5CH(OC_2H_5)_2$ 35%	$O_2NC_6H_4N=CHC_6H_4CH=NC_6H_4NO_2$ 30%
DA-26-89	H	p-Cl	TsOH	170-180	17-27	$C_6H_5CH(OC_2H_5)_2$ 38%	$ClC_6H_4N=CHC_6H_4CH=NC_6H_4Cl$ 20%
DA-26-90	H	p-Cl	TsOH	170-200	15	$C_6H_5CH(OC_2H_5)_2$ 80%	$ClC_6H_4N=CHC_6H_4CH=NC_6H_4Cl$ 42%
DA-26-91	p-Cl	H	TsOH	175	15	$ClC_6H_4(OC_2H_5)_2$ 75%	$C_6H_5N=CHC_6H_4CH=NC_6H_5$ 35%

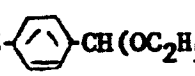
The data in Tables 18 and 19 indicate that the synthesis of a Schiff base by acetal exchange is possible, at least in the presence of a catalyst. In those reactions in which a nitro group was present as a substituent there was evidence of some side reaction which led to discoloration and to the formation of by-products.

a. The Mechanism of Reaction.

To confirm the need of a catalyst in the reaction and to propose a mechanism for the reaction another series of experiments were performed at temperatures varying from room temperature to 220°C, without catalysts and with catalysts, with H, -Cl, and -NO_2 as substituents in the reagents. The course of the reaction was followed by recording changes in the I.R. spectra of the reaction mixtures. The data for the uncatalyzed reactions are summarized in Table 20, and for the catalyzed reactions, in Table 21.

Table 20

Uncatalyzed Reaction Between X-  -Y

and Z- 

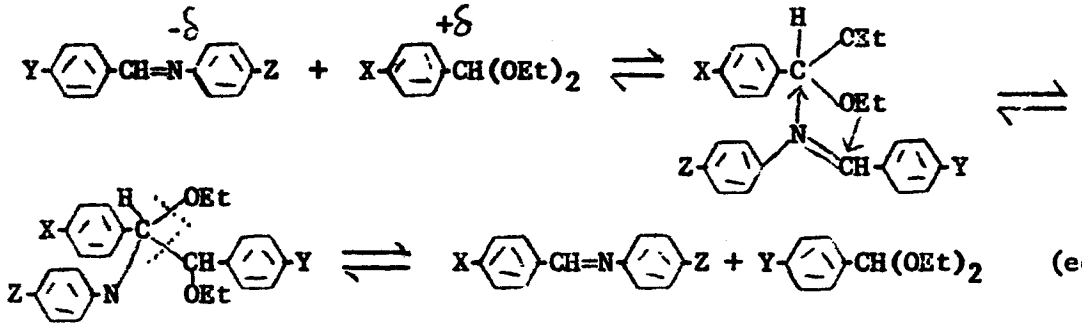
Exper. No.	Substituent			Reaction Temperature, °C	Reaction Time, hours	Evidence from I.R. Spectra
	X	Y	Z			
DA-26-61	H	H	H	room	72.0	no reaction
	H	H	H	40	2.0	no reaction
	H	H	H	130	18.0	no reaction
	H	H	H	160	6.0	no reaction
	H	H	H	180	16.0	no reaction
Da-26-62	Cl	H	H	88	4.0	no reaction
	Cl	H	H	150	28.0	no reaction
	Cl	H	H	220	3.5	no reaction
DA-26-63	NO_2	H	H	150	1.5	no reaction
	NO_2	H	H	150	7.0	no reaction
	NO_2	H	H	150	24.0	reaction
	NO_2	H	H	150	30.0	reaction
DA-26-64	H	H	Cl	120	45.0	no reaction
	H	H	Cl	180	2.0	no reaction

Table 21

Catalyzed Reaction Between X-C$_6$H$_4$-CH=N-C$_6$H$_4$-Y and Z-C$_6$H$_4$-CH(OC$_2$H$_5$)$_2$ Under Various Conditions

Exper. No.	Substituent X	Y	Z	Reaction Temperature °C	Reaction time, hours	Evidence from I.R. Spectra
DA-26-65-1	H	H	H	140	0.25	no reaction
	H	H	H	140	7.0	reaction
DA-26-65-2	Cl	H	H	140	0.25	no reaction
	Cl	H	H	140	7.0	reaction
DA-26-65-3	NO_2	H	H	140	0.25	no reaction
	NO_2	H	H	140	7.0	reaction

The following mechanism is proposed for the acetal exchange reactions on the basis of I.R. spectra and the data of Tables 18 to 21 inclusive.

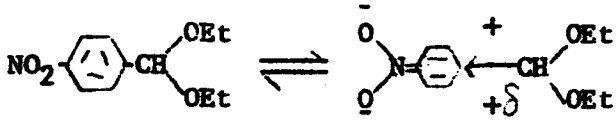


(eq. 43)

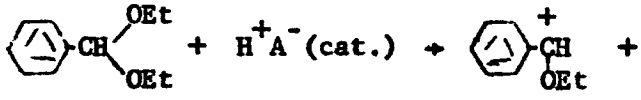
The principal absorption band at 1625 cm^{-1} for -C=N-, and at 1055 cm^{-1} and 1100 cm^{-1} for the acetal are seen in the original reaction mixture and as the reaction proceeds, these peaks with the exception of the 1100 cm^{-1} band, decrease substantially. The 1100 cm^{-1} band is characteristic of an ether linkage.

Furthermore, the absorption at 1600 cm^{-1} attributed to ring stretching in C$_6$H$_4$-N-, and at 1330 cm^{-1} attributed to -C-N stretching in C$_6$H$_4$-C-N-, increased with the reaction time, indicating the formation of the intermediate type compound in equation 42. These decays in I.R. spectra offer good evidence for the proposed mechanism and were found in the uncatalyzed experiment,

DA-26-63, in which reaction occurred, and in all the catalyzed reactions, DA-26-65-1, -2, -3. In the reaction mechanism described above, if substituent "X" is highly electron-withdrawing, the positive character of the attacking carbon of the acetal is enhanced, thus

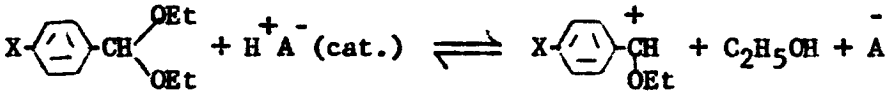


making easier its attachment to the negative nitrogen of the Schiff base to form the intermediate-type compound. In this case, a catalyst is not always required to cause reaction. Without a highly-electron-withdrawing substituent on the aromatic ring of the acetal, a catalyst is needed to promote the reaction, thus:



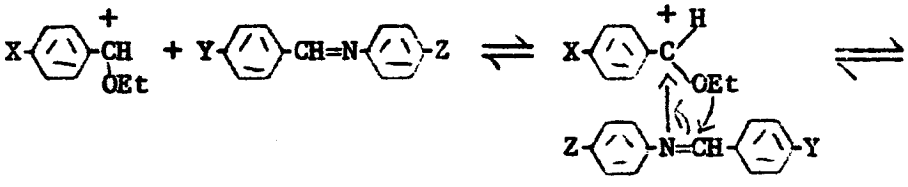
(eq. 44)

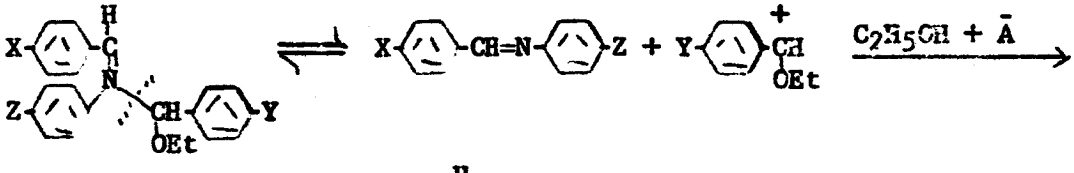
Then, the electropositive species formed by protonation by the catalyst attacks the unpaired electrons of the nitrogen of the Schiff base, thereby becoming the intermediate, thus:

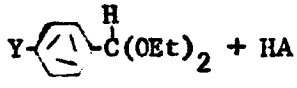


(eq. 45)

then







(eq. 46)

b. Experimental.

i. DA-26-60-1. Synthesis of p-$ClC_6H_4CH(OC_2H_5)_2$.

This compound was prepared from $ClC_6H_4CHO + HC(OC_2H_5)_3$ by the same modified procedure of Post[41] used in DA-26-9: B.P. 128-130°C/15 mm Hg. Yield, 83%.

ii. DA-26-60-2. Synthesis of p-$O_2NC_6H_4CH(OC_2H_5)_2$.

This compound was prepared from p-$O_2NC_6H_4CHO$ and $HC(OC_2H_5)_3$ by the same modified procedure of Post[41] used in DA-26-9 : B.P. 137-138°C/3 mm Hg. Yield 86%.

iii. DA-26-73. Reaction of Benzylidene-aniline and p-Nitrobenzylidene-diethyl Ether Without Catalyst.

A micro-distillation flask containing a mixture of 1.55 g. $C_6H_5CH=NC_6H_5$ and 2 g. p-$O_2NC_6H_4CH(OC_2H_5)_2$ maintained under a slow-stream of nitrogen gas was immersed in a molten-metal bath heated to 150°C, and then the temperature slowly raised until reflux began at 250°C. The distillate was shown to be a mixture of $C_6H_5CH(OC_2H_5)_2$ and $C_6H_5CH=NC_6H_5$. The heating was continued at 250°C for two hours and the reaction terminated, since the contents of the flask had become a black viscous liquid when hot, and which solidified at room temperature to a resin-like solid.

iv. DA-26-74.

Experiment DA-26-73 was repeated at 175-195°C at 15 mm Hg. At this temperature and pressure, $C_6H_5CH=NC_6H_5$ distilled from the mixture without the occurrence of a reaction.

v. DA-26-75. Reaction of Benzylidene-aniline and p-Nitrobenzylidene-diethyl Ether in the Presence of a Catalyst.

A mixture of 4 g. $C_6H_5CH=NC_6H_5$, 3.1 g. of p-$O_2NC_6H_4CH(OC_2H_5)_2$ and 0.1 g. TsOH were reacted at 160-165°C in a distillation flask under a nitrogen atmosphere at a reduced pressure of 50 mm Hg for ten minutes, then at 30 mm for twenty minutes, and at 10 mm for five minutes. The distillate contained 1.3 g.

$C_6H_5CH(OC_2H_5)_2$, 30% yield. Two (2) g. of a solid product was obtained which was recrystallized from alcohol to yield 1.5 g. $C_6H_5CH{=}NC_6H_5$ which was characterized by melting point and I.R. spectrum.

vi. DA-26-77. Reaction of Benzylidene-p-nitroaniline and p-Nitrobenzylidenediethyl Ether.

A mixture of 2.0 g. $C_6H_5CH{=}NC_6H_4NO_2(p)$, 2.0 g. $p\text{-}O_2NC_6H_4CH(OC_2H_5)_2$, and 0.1 g. TsOH were reacted in a distillation flask at 760 mm Hg pressure in a nitrogen atmosphere for two and one-half hours at 170°C, then for one and one-half hours at 170-180°C at 1.5 mm Hg. The distillate consisted of 0.6 g. $C_6H_5CH(OC_2H_5)_2$, 40% yield. The residue in the distillation flask was recrystallized from benzene and there was obtained 0.6 g. $p\text{-}O_2NC_6H_4CH{=}NC_6H_4NO_2(p)$, m.p. 199-200°C, yield 25%.

vii. DA-26-78. Reaction of Benzylidene-p-nitroaniline and p-Nitrobenzylidenediethyl Ether.

A mixture of 2.0 g. $C_6H_5CH{=}NC_6H_4NO_2(p)$, 2.0 g. $p\text{-}O_2NC_6H_4CH(OC_2H_5)_2$ and 0.1 g. TsOH in a distillation flask was heated under an atmosphere of N_2 at a reduced pressure of 25 mm Hg at 180°C for forty minutes. The distillate consisted of 0.3 g. $C_6H_5CH(OC_2H_5)_2$; 20% yield.

The residue in the distillation was recrystallized from benzene and there was obtained 1.0 g. $p\text{-}O_2NC_6H_5CH{=}NC_6H_4NO_2(p)$, m.p. 200°C; yield 43%. The filtrate from the recrystallization yielded 0.4 g. of yellow crystalline material, m.p. 124-140°C.

viii. DA-26-87. Reaction of Benzylidene-aniline and p-Chlorobenzylidenediethyl Ether.

A mixture of 1.7 g. $C_6H_5CH{=}NC_6H_5$, 2.0 g. $p\text{-}ClC_6H_4CH(OC_2H_5)_2$ and 0.1 g. TsOH in a distillation flask in a nitrogen atmosphere was heated at 170°C for sixty minutes at 40 mm Hg pressure and for ten minutes at 10 mm Hg. The distillate consisted of 1.4 g. $C_6H_5CH(OC_2H_5)_2$; yield 87%. An infrared spec-

trum of a hexane solution of the reaction residue in the flask showed that the major portion of the reaction produced is p-$ClC_6H_4CH{=}NC_6H_5$, m.p. 61°C.

ix. DA-26-56. Reaction of Benzylidene-aniline and Xylidenetetraethyl Ether with Catalyst.

A mixture of 6.5 g. $C_6H_5CH{=}NC_6H_5$, 5.0 g. p-$(C_2H_5O)_2CHC_6H_4CH(OC_2H_5)_2$ and 0.1 g. TsOH were reacted in a distillation flask at ~ 760 mm for four hours at 200-220°C and there was collected as a distillate 3.4 g. of $C_6H_5CH(OC_2H_5)_2$ 52% yield. Crystallization from alcohol of the reaction product in the flask yielded 5.4 g. of impure $C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5$, m.p. 156-160°C, yield 60%.

x. DA-26-84. Reaction of Benzylidene-aniline and Xylidenetetraethyl Ether Without Catalyst.

A mixture of 3.0 g. $C_6H_5CH{=}NC_6H_5$ and 2.34 g. p-$(C_2H_5O)_2CHC_6H_4CH(OC_2H_5)_2$ were heated at 150°C for twelve hours under a nitrogen atmosphere at 15 mm Hg pressure. No evidence of reaction could be noted.

xi. DA-26-85. Reaction of Benzylidene-aniline and Xylidenetetraethyl Ether With Catalyst.

A mixture of 3.0 g. $C_6H_5CH{=}NC_6H_5$, 2.34 g. p-$(C_2H_5O)_2CHC_6H_4CH(OC_2H_5)_2$ and 0.1 g. TsOH were reacted in a distillation flask under a nitrogen atmosphere at 170°C for thirty minutes at 35 mm Hg pressure, and then for ten minutes at 15 mm Hg pressure. There was collected 1.6 g. $C_6H_5CH(OC_2H_5)_2$ as distillate, 52% yield. The residue in the flask was crystallized from ethyl alcohol, yielding 1.2 g. $C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5$, m.p. 153-155°C, 50% yield.

xii. Reaction of Benzylidene-aniline and Xylidenetetraethyl Ether With Catalyst.

The reagents of DA-26-85 were reacted for one and one-half hours at 170°C under nitrogen at 22 mm Hg pressure. The distillate was 1.7 g. $C_6H_5CH(O_2C_5H_2)$ 53% yield. The residue in the flask was washed with ethyl alcohol, dried, and weighed, 2.0 g., yield 83%. It was identified as $C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5$.

xiii. DA-26-79. Reaction of Benzylidene-p-nitroaniline and Xylidene-tetramethyl Ether with Catalyst.

A mixture of 3.2 g. $C_6H_5CH{=}NC_6H_4NO_2$(p) and 2.0 g. p-$(C_2H_5O)_2CHC_6H_4CH(OC_2H_5)_2$ were heated slowly at 760 mm Hg without a catalyst under a N_2 atmosphere in a distilling flask, by immersion in a molten metal bath maintained at 150°C. The temperature was gradually raised to 300°C and maintained at 300°C for two hours. The distillate consisted of 1.5 g. $C_6H_5CH(OC_2H_5)_2$, 63% yield. The residue in the distillation flask was a dark, brittle solid.

xiv. DA-26-81. Reaction of Benzylidene-p-nitroaniline and Xylidene-tetraethyl Ether with Catalyst.

A mixture of 3.2 g. $C_6H_5CH{=}NC_6H_4NO_2$(p), 2.5 g. $(C_2H_5O)_2CHC_6H_4CH(OC_2H_5)_2$ and 0.1 g. TsOH were reacted in a distillation flask at 170°C for fifteen minutes at 30 mm Hg pressure, then for fifteen minutes at 15 mm Hg pressure. The distillate consisted of 1.4 g. $C_6H_5CH(OC_2H_5)_2$, 30% yield. Recrystallization from benzene of the residue in the reaction flask yielded 1.1 g. p-$O_2NC_6H_4N{=}CHC_6H_4CH{=}NC_6H_4NO_2$, m.p. 277-279°C, yield 20%.

xv. DA-26-82.

Experiment DA-26-81 was repeated except that the reaction conditions were 170°C, 20 mm Hg pressure for one hour. Yield of distillate was 1.6 g. $C_6H_5CH(OC_2H_5)_2$, 35% yield; and 1.4 g. p-$O_2NC_6H_4N{=}CHC_6H_4CH{=}NC_6H_4NO_2$(p), 30%.

xvi. DA-26-89. Reaction of Benzylidene-p-chloroaniline and Xylidenetetraethyl Ether.

A mixture of 6.0 g. $C_6H_5CH{=}NC_6H_4Cl$(p), 4.0 g. $(C_2H_5O)_2CHC_6H_4CH(OC_2H_5)_2$ and 0.1 g. TsOH were reacted under a N_2 atmosphere in a distillation flask at 170°C for ten minutes at 27 mm Hg pressure, then at 180°C for thirty minutes at 17 mm Hg pressure. The distillate consisted of 1.8 g. $C_6H_5CH(OC_2H_5)$, 38% yield. Recrystallization of the residue from benzene yielded 1.0 g. of p-$ClC_6H_4N{=}CHC_6H_4CH{=}NC_6H_4Cl$-p, m.p. 179°C, yield 20%.

xvii. DA-26-90. Reaction of Benzylidene-p-chloroaniline and Xylidenetetraethyl Ether.

A mixture of 3.0 g. $C_6H_5CH{=}NC_6H_4Cl$, 2.0 g. $(C_2H_5O)_2CHC_6H_4CH(OC_2H_5)_2$ and 0.1 g. TsOH were reacted in a distillation flask at 170-200°C for thirty minutes at 15 mm Hg pressure. Weight of distillate, $C_6H_5CH(OC_2H_5)_2$, 1.9 g; 80% yield. Weight of p-$ClC_6H_4N{=}CHC_6H_4CH{=}NC_6H_4Cl$-p, m.p. 178-179°C, 1.1 g.; 42% yield.

xviii. DA-26-91. Reaction of p-Chlorobenzylidene-aniline and Xylidenetetraethyl Ether.

A mixture of 3.0 g. $ClC_6H_4CH{=}NC_6H_5$, 2.0 g. $(C_2H_5O)_2CHC_6H_4CH(OC_2H_5)_2$ and 0.1 g. TsOH were reacted in a distillation flask under a nitrogen atmosphere for sixty minutes at 175°C at 15 mm Hg pressure. Amount of distillate, $ClC_6H_5CH(OC_2H_5)_2$, 1.7 g. 75% yield. Yield of recrystallized $C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5$, 1.7 g., 35% yield.

D. From Aromatic Aldehydes and N-Acyl Aryl Amines.

The formation of a Schiff base from the reaction of an acetal and an N-acyl aromatic amine led to the consideration of using the free aldehyde instead of the acetal.

1. The Mechanism of Reaction.

The mechanism proposed for this reaction was originally considered as that of a simple addition to produce an aldol-type compound which eliminates acetic acid to yield the Schiff base. This reaction can be written as

$$C_6H_5CHO + CH_3CONHC_6H_5 \rightarrow C_6H_5\underset{OH}{CH}\!\!-\!\!\underset{OCCH_3}{NC_6H_5} \rightarrow CH_3COOH + C_6H_5CH{=}NC_6H_5 \qquad \text{(eq. 47)}$$

This system was studied even though little hope was held that it would succeed. The reaction was evaluated using benzaldehyde and acetanilide, both without a catalyst and with toluene sulfonic acid as a catalyst. Only a small amount of acetic acid was obtained in the uncatalyzed and catalyzed reactions performed at 180 ~ 220°C, indicating a reluctance of the reaction as postu-

lated in equation 48 to proceed readily, although in the uncatalyzed reaction a small amount of the Schiff base, $C_6H_5CH{=}NC_6H_5$ was obtained. The postulated reaction appears to be complicated under the conditions specified by side reactions such as the reaction of one mole of aldehyde with two moles of amide:

$$C_6H_5CHO + 2\ CH_3CONHC_6H_5 \rightarrow H_2O + C_6H_5CH(\underset{\underset{OCCH_3}{|}}{NC_6H_5})_2 \qquad \text{(eq. 48)}$$

as well as by other side reactions. For these reasons these reactions were not explored further, at this time. There is, however, the possibility of controlling the reaction conditions to assure the formation of the intermediate $C_6H_5CHOH\underset{\underset{OCCH_3}{|}}{NC_6H_5}$ shown in equation 49 by performing the original condensation first under basic catalytic conditions:

$$C_6H_5CHO + CH_3CONHC_6H_5 \xrightarrow{\text{base}} C_6H_5CHOH\underset{\underset{OCCH_3}{|}}{NC_6H_5} \qquad \text{(eq. 49)}$$

and then causing the elimination of acetic acid to occur under neutral or acid conditions:

$$C_6H_5CHOH\underset{\underset{OCCH_3}{|}}{NC_6H_5} \xrightarrow{\text{acid}} CH_3COOH + C_6H_5CH{=}NC_6H_5 \qquad \text{(eq. 50)}$$

2. Experimental.

a. DA-26-58. Reaction of Benzaldehyde and Acetanilide Without Catalyst.

A mixture of 14.0 g. $CH_3CONHC_6H_5$ and 10.0 g. C_6H_5CHO were heated for forty-eight hours in a distillation flask at 180 ~ 220°C, in the presence of a slow stream of dry nitrogen gas, and about 0.5 g. of acetic acid collected in the distillation receiver. The residue in the distillation flask was extracted with water in a Soxhlet apparatus and there was recovered 9.6 g. (70%) of unreacted acetanilide. The water-extracted residue was recrystallized from alcohol and 2.0 g. of the Schiff base, $C_6H_5CH{=}NC_6H_5$, which was identified by its M.P. and I.R. spectrum, was recovered.

b. DA-26-69. Reaction of Benzaldehyde and Acetanilide with Catalyst.

A mixture of 2.5 g. benzaldehyde, 3.5 g. of acetanilide and 0.25 g. of

TsOH were reacted at 180~220°C in a distillation flask as in DA-26-58. The contents were heated at 180°C for fifteen minutes and then 210-220°C for two and one-half hours and the distillate (1.0 g.) collected and contained CH_3COOH and C_6H_5CHO. Then heating was continued for four hours at 220°C after which the reaction product was cooled and neutralized with aqueous $NaHCO_3$. Water extraction of the residue in a Soxhlet apparatus yielded 1.5 g. of unreacted $CH_3CONHC_6H_5$. From the water insoluble portion of the reaction residue, there was isolated by crystallization from alcohol 0.8 g. of a yellow solid, m.p. 137°C, which, as determined from its I.R. spectrum, is not the Schiff base nor the compound $C_6H_5CHOHN(C{=}O)CH_3$-C_6H_5.

E. From N-Acyl Arylamine and Schiff Bases.

The formation of Schiff bases by the reaction of acetals and N-acyl arylamines suggested that another type of aldehyde derivative be evaluated in the reaction; the Schiff bases as addehyde derivatives, were selected for this evaluation. The overall equation for this reaction could be written as

$$XC_6H_4CH{=}NC_6H_4Y + CH_3CONHC_6H_4Z \rightleftharpoons XC_6H_4CH{=}NC_6H_4Z + CH_3CONHC_6H_4Y \qquad \text{(eq. 51)}$$

The postulated reaction was evaluated with and without catalysts, as shown in Table 22.

Table 22

Some Reactions of Schiff Bases and N-Acyl Arylamines

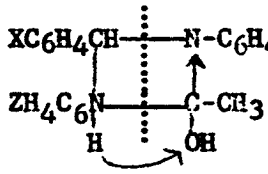
Exper. No.	Reagents	Catalyst	Reaction Conditions	Product
DA-26-245	p-$CH_3CONHC_6H_4OCH_3$ and $C_6H_5CH{=}NC_6H_5$	none	240°C, 15 hrs/760mm and 260°C, 10 hrs/20mm	no reaction
DA-26-247	p-$CH_3CONHC_6H_4OCH_3$ and $C_6H_5CH{=}NC_6H_5$	TsOH	240°C, 15 hrs/760mm and 260°C, 10 hrs/20mm	yes, but not the expected Schiff base

1. The Mechanism of the Reaction.

For the reaction to occur a four-membered ring complex or compound would have to be considered as an intermediate in the reaction. As shown in Table 22, no reaction was observed in the absence of a catalyst, and therefore a mechanism was not considered for an uncatalyzed system. In the case of the catalyzed system, the following mechanism is considered:

$$CH_3CONHC_6H_4Z + HA\ (cat.) \rightleftharpoons CH_3\overset{+}{C}(OH)\text{-}NC_6H_4Z + A^- \qquad \text{(eq. 52)}$$

then $XC_6H_4CH{=}\overset{-}{N}C_6H_4Y + CH_3\overset{+}{C}(OH)\text{-}NHC_6H_4 \rightleftharpoons$



$$XC_6H_4CH{=}NC_6H_4Z + HA + CH_3C(OH){=}NC_6H_4Y \rightleftharpoons CH_3CONHC_6H_4Y \qquad \text{(eq. 53)}$$

2. Experimental.

a) DA-26-245. Reaction of Benzylidene-aniline and N-Acyl-p-methoxy Aniline.

A mixture of 6.0 g. $C_6H_5CH{=}NC_6H_5$ and 4.0 g. p-$CH_3CONHC_6H_4OCH_3$ were reacted in a glass flask under an atmosphere of nitrogen for fifteen hours at 240°C at 760 mm pressure, then at 260°C for ten hours at 20 mm Hg pressure. There was no color change during the reaction and substantially all of the $CH_3CONHC_6H_4OCH_3$ was recovered unreacted.

b. DA-26-247. Reaction of Benzylidene-aniline and N-Acyl-p-methoxy Aniline in Presence of Catalyst.

A mixture of 4.0 g. $C_6H_5CH{=}NC_6H_5$, 3.0 g. p-$CH_3CONHC_6H_4OCH_3$ and 0.1g. TsOH were reacted under conditions identical to DA-26-245, yielding a dark-red reaction product. The reaction product was extracted with hexane to yield 2.2 g. of unreacted $CH_3CONHC_6H_4OCH_3$ and a reddish-brown resinous material which was neither $C_6H_5CH{=}NC_6H_5$, $CH_3CONHC_6H_5$ nor $C_6H_5CH{=}NC_6H_4OCH_3$. Its deep color suggests that it may be some derivative of a Schiff base.

From the experimental data, it is concluded that the reaction between an N-acyl aryl amine and a Schiff base, in the absence of a catalyst, is difficult to achieve in contrast to the aromatic acetals. Even in the presence of an acid catalyst, reaction occurs with difficulty and the Schiff base is not obtained as suggested in a possible mechanism for such a reaction.

F. Summary and Conclusions.

Nine possible reactions, Table 1, involving reagent pairs of aldehyde or selected derivatives of aldehydes and primary amines or selected derivatives of amines were investigated in the syntheses of non-polymeric Schiff bases and related azo-methines. Of these nine reactions, only one, namely, the reaction of a carbonyl compound and an amine, was well-known and has been applied to the syntheses of non-polymeric and polymeric Schiff base compounds. A second reaction, that of the reaction of a Schiff base with an amine to produce a derived Schiff base was also known, but the technical literature on this reaction is meager. None of the other seven possible reactions appeared to be in the literature. Accordingly, before these reactions could be applied to the synthesis of polymers, the syntheses of non-polymeric Schiff bases was undertaken with them, as prototype reactions, to determine their probable applicability as polymerization reactions. All of the nine reactant pairs underwent reaction to some extent; eight of the pairs yielded Schiff bases and one failed to do so. The data is summarized in Table 23.

The polymerization reaction of arylene diamines and arylene dicarbonyl compounds has been shown[5-7] to yield as a precipitate the insoluble, infusible brick-dust polymers directly. Accordingly, it was considered that if the reaction conditions could be controlled or modified, so that stable, or relatively stable, "aldol" types intermediate compounds could be isolated or shown to be present in the reaction, the syntheses of higher molecular weight polymers should be feasible with the added possibility that they could be

Table 23

Possible Reaction Pairs for Synthesis of Non-Polymeric Schiff Bases

Reaction Pairs	Functional Groups		Reaction	Schiff Base
(1) + (4)	-CHO	+ $-NH_2$	Yes - good	yes
(1) + (5)	-CHO	+ -N=CHR	Yes - good	yes
(1) + (6)	-CHO	+ -NHOCR	Yes - poor	yes
(2) + (4)	-CH=NR	+ $-NH_2$	Yes - good	yes
(2) + (5)	-CH=NR	+ -N=CHR	Yes - good	yes
(2) + (6)	-CH=NR	+ -NHOCR	Yes - fair	no
(3) + (4)	$-CH(OR)_2$	+ $-NH_2$	Yes - good	yes
(3) + (5)	$-CH(OR)_2$	+ -N=CHR	Yes - good	yes
(3) + (6)	$-CH(OR)_2$	+ -NHOCR	Yes - good	yes

obtained in a soluble or fusible state, at least at some stage of the reaction. To acquire this type of basic information, the studies involving the syntheses of the prototype non-polymeric Schiff bases included efforts to isolate such intermediates, or to establish that they exist and to propose a mechanism for the generation of the intermediates and for the final products of the reaction.

In the course of these studies, a new, azeotropic method was developed for the syntheses of Schiff bases and other azo-methines in which the yield of crude product is substantially quantitative.

As a result of these studies, six new chemical reactions for the syntheses of Schiff bases have been established and one obscure method involving the displacement of the amine fragment in a Schiff base by another amine has been confirmed and extended. This displacement has been classified[5-7] as the species of "Amine-Exchange" within the broader concept of Schiff Base Exchange Reactions. These investigations have established also that the carbonyl fragment in a Schiff base can be displaced by another carbonyl compound,

and this is classified[5-7] as a "Carbonyl-Exchange." These exchange studies were extended further and have shown that a "Bis-Exchange" between two Schiff bases resulting in the generation of two new Schiff bases occurs as readily as the amine- or carbonyl-exchange.

The acetals were shown to be very similar in behavior to the aldehydes in their reactions with amines and with Schiff bases; and thus the acetals may offer advantages over the aldehydes in polymerization reactions because of their greater thermal stability and greater resistence to oxidation. In the reactions of acetals with amine derivatives, the acetals appear to be superior to the aldehydes undergoing, for example, an "acetal" exchange with Schiff bases; and in the reaction with acyl anilides, a two-step elimination of alcohol and ethyl acetate was shown to proceed readily. In contrast the reaction of the aldehyde with an acetanilide proceeds with difficulty.

In all of the reactions studied the specific rate constants were shown by direct and indirect methods to be unfavorable for the actual isolation of postulated intermediates with the possible exception of the reaction between acetals and acetanilides in which part of the alcohol is eliminated before ethyl acetate appears. In a number of cases, however, the existence of an intermediate was shown by changes in the infrared spectrum of the reaction mixture as a function of reaction time. By the use of the aniline hydrochlorides instead of the anilines in a number of reactions, a number of intermediates in the form of their hydrochlorides were isolated and structures assigned to the intermediates. Neutralization of the hydrochlorides yielded products whose structure depended on the electro-negative character of the substituent on the benzene rings of the Schiff bases. Unsubstituted benzylidine-aniline hydrochloride on neutralization yields the reagents benzaldehyde and aniline. p-Xylylidene-di-aniline hydrochloride on neutralization yields the Schiff base and not terephthaldehyde and aniline as might be

expected on the basis of the benzylidine-aniline hydrochloride. The formation of the Schiff base was shown to conform to the effect of electro-negative substitution since both the terephthaldehyde and its dianil are actually electro-negatively substituted aryl compounds, $=HC-C_6H_4CH=$.

In anticipation of requiring polyfunctional reagents or monomers for the polymerization reactions, many of the above reactions were studied with polyfunctional molecules in non-polymeric reactions; for example, the amine-, the carbonyl-, and the acetal-Schiff base exchange reactions were evaluated with polyfunctional molecules and they were shown to be applicable to polyfunctional systems as well as to monofunctional molecules.

The evaluation of the reactions listed in Table 23 in the synthesis of polymers will be given in Part II of this report.

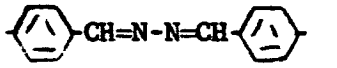
II. Syntheses of Polymeric Azo-Methines.

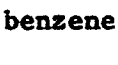
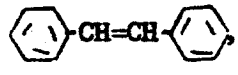
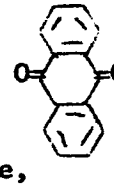
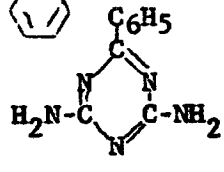
This section deals with the applicability of the non-polymeric reactions summarized in Part I to the syntheses of polymers. The approach to the problem consisted in performing a sufficient number of preliminary experiments on which to base the selection of the best systems for the more detailed research. In Part I, the average functionality, $\bar{f}$, of the reactant pairs in all cases was at least one and always less than two. For polymer formation to occur the average functionality of all the reagents involved in the reaction must be at least two. Thus, in the reaction of the reactant pairs, -CHO + NH_2, each reagent must have at least two functional groups, such as OHC-Ar-CHO and H_2N-Ar-NH_2. In these studies, the reaction pair of aldehyde and amine will be used as a reference point for the other reactions evaluated. All of the reaction pairs given in Table 23 were evaluated in these preliminary studies, including minor experimentation with the unpromising reaction pairs:

OHC-Ar-CHO + RCONHArNHOCR and RN=HCArCH=NR + RCONHArNHOCR.

The greatest part of the polymerization studies was devoted to the synthesis of conjugated Schiff base, that is, compounds that have a benzene ring attached to both sides of the -C=N- structure. Generically, these polymers are polymeric azo-methines. Accordingly, the reactions of Part I were evaluated in the syntheses of other poly-azo-methines such as those containing the azine linkage, =N-N=; the glyoxalidene linkage, -CH=N-N=CH-; and the quinonidine linkage, -N=  =N-; with co-reagents that were expected to produce conjugated polymers.

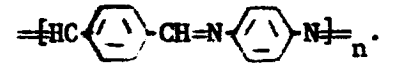
Since it would be expected that the thermal stabilities and other physical properties of the poly-azo-methines would depend on a number of factors, some of which are: molecular weight, the resonance energy of the substituents in the chain, the bond-stability of the linkages in the chain and steric factors, some preliminary experiments were performed to yield a qualitative evaluation

of these factors, thereby narrowing the types of structures to be investigated. After preliminary tests, the thermal instability of the  and  structures, eliminated the polymeric azines and poly-azo-methines with aliphatic linkages from further consideration, leaving the "aromatic type" poly-azo-methines for investigation. These aromatic-type azo-methine polymers can be described generally as $=\{HCArCH=NArN\}=_n$. The influence of the resonance energy factor of the Ar group also was evaluated qualitatively in these studies.

The simplest Ar group is the benzene ring,  , which in the polymer would exist as a meta- or para-phenylene moiety,  . An increase in the resonance factor of the benzene ring can be brought about by increasing its conjugation; this, in turn, increases its size, which in turn can be expected to influence reactivity during reaction and stability of the resulting polymer after the reaction. However, if the increase is achieved by an increase in its linear dimension, such as by substituting  or  , the steric factors can be expected to be at a minimum while at the same time demonstrating the influence of increased conjugation. For example, the substitution of p,p'-diaminostilbene for p,p'-diaminobenzene in a reaction with p-terephthaldehyde should not influence reactivity in the reaction, but the yellow color in the polymer, $=\{HCC_6H_4CH=NC_6H_4N\}=_n$ would be expected to be shifted to a darker color. The substitution of quinone for terephthaldehyde would also be expected to produce a similar color effect. In contrast, when the conjugation is increased by using an Ar group of higher conjugation because of lateral increase in size, such as by using anthraquinone,  , instead of terephthaldehyde with phenylene diamine, or benzoguanamine,  , instead of

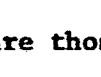
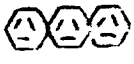
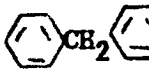
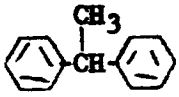
p-phenylenediamine with terephthaldehyde steric factors would be expected to influence reactivity during reaction and the stability of the resulting polymer.

These effects which were observed in preliminary experiments led to the judgment that the major efforts should be devoted to the syntheses of polymers whose Ar groups were aromatic in character and therefore resonance stabilized, and that the Ar group should be small in volume and devoid of lateral bulk. The benzene ring is the simplest aromatic structure which appears to meet this requirement, and the simplest polymer therefore would have the structure



This polymer has been reported,[5-7] when prepared by classical methods to be infusible, insoluble and of yellow color. The structure of the polymer, as written, shows uninterrupted conjugation. The color of any specific conjugated structure, and particularly of a polymer, should depend on the extent of conjugation; and if the conjugation is sufficiently extensive, the color of the polymer would be expected to be black. The reported yellow color of the polymer indicates lack of sufficient conjugation which means that its molecular weight is not sufficiently high to meet the requirements necessary for the darker colors to be in evidence. The prior syntheses of this polymer have produced it as an insoluble, infusible powder, commonly known as a "brick dust" polymer, and of limited utility since its infusibility precludes fabrication into useful products. Therefore, another purpose of this research was to evaluate syntheses which would produce poly-[xylylidene-phenylenediamine] as black polymers by means of a reaction which would allow interruption of the polymerization at a soluble or fusible stage; and thereafter permit conversion to higher molecular weight by post-reactions.

If such a reaction system could be developed, then it could be applied to the syntheses of polymers which would contain Ar groups other than the benzene

ring. These other Ar groups would be chosen to be free of "lateral bulk", among which are those such as the pyridyl  ; the diphenyl  ; the terephenyl  ; the diphenyl ethylene ; the diphenylacetylene, groups, etc., and their corresponding perfluoro-derivatives, as well as the perfluoro-benzene ring. All of these Ar groups contain uninterrupted conjugation. At some later stage of the investigation, these structures could be contrasted to -Ar- rings whose Ar conjugation was interrupted, such as in diphenyl oxide  ; the diphenyl alkylenes,  ,  ,  ; etc.

Studies with trifunctional amine or carbonyl compounds or their derivatives were also contemplated in these researches. Since the high functionality of these compounds would yield three dimensional polymers of complex structure, they would complicate the current investigations which already produce linear infusible, insoluble polymers from reagents whose average functionality is two. Accordingly, polymerization reactions with reagents of functionality greater than two have been postponed for study at a future time.

In these studies, the yields of polymer were recorded as percentages of the theoretical 100% yield obtained when n, the degree of polymerization, is infinity, $n = \infty$, thus: $=\{HCArCH=NArN\}=_{n=\infty}$.

Since these polymers are condensation polymers which eliminate a by-product in their preparation, a degree of condensation less than complete gives an amount of polymer larger than theoretical and therefore, relatively greater than 100%. Values in excess of 100% may also be due to reasons other than the degree of polymerization, particularly in cases where the reaction is performed in a medium or solvents which can participate in the reaction by copolymerization or by adduct formation or by other chemical reactions.

A. Syntheses from Bifunctional Amines and Carbonyl Compounds.

The general polymerization reaction for the polycondensation of a dicarbonyl compound and a diamine may be illustrated by the diamine H_2NArNH_2, and the dicarbonyl-type compounds, OHCArCHO, thus:

$$n\ OHCArCHO + n\ H_2NArNH_2 \rightarrow n\ H_2O + =[CHArCH=NArN]=_n \qquad \text{(eq. 54)}$$

The mechanism postulated for the reaction is similar to that proposed in the monomeric synthesis which involves the formation of an aldol intermediate followed by the elimination of water

$$OHCArCHO + H_2NArNH_2 \rightarrow \sim\sim Ar\text{-}\underset{\underset{:OH\ H:}{\vdots\vdots}}{CH}\text{-}N\text{-}Ar\text{-}N\text{-}\underset{\underset{:H\ OH:}{\vdots\vdots}}{CH}\text{-}Ar\sim\sim \rightarrow$$

$$\sim\sim ArCH=N\text{-}Ar\text{-}N=CH\text{-}Ar\sim\sim + H_2O \qquad \text{(eq. 55)}$$

The general reaction of equation 54 was evaluated in the syntheses of polymeric Schiff bases as well as other polymeric azo-methines with selected amines and carbonyl compounds under various polymerization conditions and methods.

1. Polymerization Methods.

The polymerizations were performed in systems classified as Solution, Melt, and Melt-Solution Polymerizations.

The amines used in the studies were p-phenylenediamine, hydrazine, benzoguanamine, and melamine; and the carbonyl compounds used were terephthaldehyde, glyoxal, benzophenone and anthraquinone.

a. Solution Polymerization.

The reactions were first evaluated by standard techniques using solvents to dissolve insoluble reagents such as ethyl alcohol, dimethyl aniline, benzene, acetic anhydride, xylene, etc.; other reactions were performed with water as the medium. The continuous azeotropic technique was also used. These reactions are classified as "solvent polymerizations" even though the polymer as formed was precipitated in the medium.

In cases where reaction failed to occur, zinc chloride was used as a catalyst in attempts to force the reaction.

b. Melt Polymerization.

These solution polymerizations were then compared to reactions in which the reagents were heated to a molten condition. These have been classified as "melt polymerizations" and were performed in the absence of any other media.

c. Melt-Solution Polymerizations.

A number of reactions were performed with benzylidene-aniline as possible solvent. Since it and the reagents are solid, the mixture was heated and the reaction performed at melt temperatures. These reactions are classified as "melt-solution" polymerizations.

2. Post-Treatment of Polymers.

A number of polymers were subjected to post-treatments for various reasons. Some were heated alone, others were heated with benzylidene-aniline, with and without catalyst.

a. Heat Treatment.

i) In efforts to increase the molecular weight of non-black polymers and convert them to black polymers, they were heat-treated in the absence of additives and also in the presence of benzylidene-aniline.

ii) In some studies directed to lowering yields which were in excess of 100% of theory, the polymers were post-heated to effect lost of solvent or to extend the condensation reaction.

iii) Insoluble, infusible black polymers were heated in benzylidene-aniline with and without catalysts in attempts to effect solution.

3. Experimental.

a. Solution Polymerizations.

i) DA-24-24a. Reaction of Terephthaldehyde and p-Phenylenediamine in Ethyl Alcohol.

A mixture of 0.7 g. terephthaldehyde, 0.51 g. p-phenylenediamine, 0.05 g. acetic acid, and 15 ml of ethyl alcohol in a round-bottom flask were refluxed for four hours under a nitrogen atmosphere. A bright-yellow precipitate formed, which was removed by filtration and dried. Yield 1.12 g. = 102%. The polymer does not melt at temperatures in excess of 300°C.

ii) DA-24-24b. Reaction of Terephthaldehyde and Phenylenediamine in Dimethyl Aniline.

A mixture of 0.7 g. terephthaldehyde, 0.51 g. p-phenylenediamine, 0.05 g. acetic acid and 15 ml of dimethyl aniline in a round-bottom flask were refluxed for eight hours without the formation of a precipitate. Then 0.15 g. conc. HCl was added and reaction continued forming a light-yellowish brown precipitate whose color did not change after eight hours of continued reflux. The polymer was removed by filtration and dried. Yield ~100% of a yellowish-brown precipitate which does not melt.

iii) DA-24-24c. Reaction of Terephthaldehyde and 4,4'-Diaminostilbene.

A mixture of 0.7 g. of terephthaldehyde, 1.05 g. of 4,4'-diaminostilbene, 0.05 g. of acetic acid and 15 ml of ethyl alcohol were reacted by the procedure of DA-24-24a and there was obtained 1.74 g. (101%) of orange polymer.

iv) DA-24-25. Reaction of Terephthaldehyde and p-Phenylenediamine in Water.

A mixture of 1.0 g. terephthaldehyde, 1.0 g. p-phenylenediamine, 10 ml water, and 0.05 g. acetic acid in a round-bottom flask were refluxed under a nitrogen atmosphere for twenty-five minutes, forming a yellow precipitate. In an attempt to force the reaction, 0.15 g. of conc. HCl was added and reflux continued for two hours. The mixture was neutralized with 5% aqueous NaOH solution, filtered, and the precipitate washed with water and dried. Yield

~100% of a yellow-orange polymer which does not melt.

v) DA-24-31. Reaction of Terephthaldehyde and Hydrazine in Water.

A mixture of 0.7 g. terephthaldehyde, 0.3 g. of hydrazine in the form of a 64% aqueous solution and 10 ml of water in a flask were refluxed under a stream of nitrogen for three hours, yielding a very bright-yellow precipitate which was removed by filtration, washed with water, and dried, yielding 100% of a very bright-yellow polymer which does not melt up to 300°C, but shows evidence of decomposition with liberation of nitrogen and other gases.

vi) DA-24-33. Reaction of Glyoxal with p-Phenylenediamine in Water.

To a solution of 1.7 g. of glyoxal (5.8 g. of a 30% aqueous solution) in 20 ml of water in a reaction flask was added 3.2 g. of p-phenylenediamine with the immediate formation of a yellow precipitate; and on heating to reflux, the color changed rapidly to orange, and finally to dark-red. No further color change occurred after twenty minutes of reaction. The precipitate was removed by filtration, washed with water, and dried. Yield of polymer, ~100%, which was infusible but which decomposed on heating at temperatures above 250°C.

vii) DA-29-84. Azeotropic Method for Reaction of Terephthaldehyde and p-Phenylenediamine.

The reaction of Davidov[12] was modified and adapted to the continuous azeotropic method.[6,7] A mixture of 1.44 g. phenylenediamine, 1.34 g. of terephthaldehyde, and 350 ml of benzene in a 500 ml round-bottom flask attached to a Dean-Stark trap and reflux condensers were reacted at reflux. The reaction appeared to be complete at the end of one hour, but it was continued for twenty hours. The color of the precipitate was bright yellow, and it did not change in color as the reaction was continued. Yield of polymer, 2.13 g.; 103.4%.

viii) DA-24-26a. Reaction of Terephthaldehyde and Benzoguanamine in Acetic Anhydride.

A mixture of 1.34 g. of terephthaldehyde and 1.87 g. of benzoguanamine in 10 ml of acetic anhydride in a 50 ml round-bottom flask were refluxed in a nitrogen atmosphere for three hours. No color change occurred during this time. The reaction was terminated and the reagents recovered by precipitation in water and recrystallization from ethyl alcohol. A repeat reaction was attempted with the addition of $ZnCl_2$ as a catalyst, and reaction failed to occur.

ix) DA-24-36. Reaction of Terephthaldehyde and Melamine in Xylene.

A mixture of 1.2 g. melamine, 2.0 g. terephthaldehyde and 100 ml of xylene in a round-bottom flask attached to a Dean-Stark trap, reflux condenser etc., were heated to reflux under a nitrogen atmosphere for six hours; there was no evidence of any reaction, since no water of reaction was found in the trap and no color changes were noted. A repeat reaction was attempted with the addition of $ZnCl_2$ as a catalyst, and reaction failed to occur.

x) DA-24-26c. Reaction of Anthraquinone and p-Phenylenediamine.

A mixture of 2.0 g. of anthraquinone, 1.0 g. of p-phenylenediamine and 10 ml of ethanol in a round-bottomed flask were refluxed for six hours under a nitrogen atmosphere. Removal of the alcohol by evaporation at 15 mm Hg pressure left a mixture of unreacted amine, quinone, and a trace of black condensation, which melted $\sim$120°C.

xi) Reaction of Benzoquinone with p-Phenylenediamine in Ethyl Alcohol.

A solution of 1.1 g. of benzoquinone in 10 ml of 95% alcohol was added with vigorous stirring to a flask containing a solution of 1.1 g. of p-phenylenediamine in 10 ml of 95% alcohol. A brown finely divided precipitate formed immediately which was filtered and dried; yield 1.5 g. product which decomposes $\sim$285°C, and apparently not a Schiff base. The filtrate was a black

solution containing low molecular weight condensation products.

xii) DA-24-32. Reaction of Benzoquinone with p-Phenylenediamine in Xylene.

A mixture of 4.0 g. benzoquinone, 4.0 g. of p-phenylenediamine and 200 ml of xylene in a reaction flask attached to a Dean-Stark trap, reflux condenser, etc., were refluxed under nitrogen for four hours, and only a trace of water collected in the trap, indicating that an addition rather than a condensation reaction had occurred. During reflux, the reaction mixture became quite dark, forming a precipitate. The precipitate was removed by filtration, washed with boiling ethanol and dried. The xylene filtrate was a black solution containing dissolved product. Yield of precipitate $\sim$ 5.0 g. of insoluble, infusible black powder, similar to the solid product of DA-24-23.

xiii) DA-24-30. Reaction of Benzoquinone with Hydrazine in Water.

To 0.5 g. benzoquinone in 10 ml of water in a flask equipped with a reflux condenser, etc., there was added slowly 0.3 ml of 64% aqueous hydrazine. Reaction occurs immediately on addition with the formation of a black solution; the mixture was refluxed for three hours under a nitrogen atmosphere, with little or no increase in viscosity. Then the water was removed by distillation at atmospheric pressure, leaving 0.45 g. of a sticky resinous mass which with decomposition became infusible, on continued heating for thirty minutes at 180°C.

b. Melt Polymerizations.

i) DA-24-35b. Melt-Reaction of Terephthaldehyde and p-Phenylenediamine.

A mixture of 1.08 g. p-phenylenediamine and 1.34 g. terephthaldehyde were mixed thoroughly by grinding in a mortar and pestle and then introduced into 10 ml microflask and blanketed with a slow stream of nitrogen. The mixture was heated gently by means of a flame of a micro bunsen burner until the mixture became a fluid melt and held as a melt at about 150-160°C for approximately two minutes. The melt became increasingly viscous, changing in color

from light yellow to orange to brown to black. Then the contents of the flask was heated by means of an electric mantle for one hour at 180°C and one hour at 260°C, to yield a black infusible polymer. Yield 2.0 g., 97%.

ii) DA-24-27. Melt-Reaction of Terephthaldehyde and Benzoguanamine.

A mixture of 2.7 g. terephthaldehyde and 3.8 g. of benzoguanamine were mixed in a microflask and blanketed with a slow stream of nitrogen and the mixture heated slowly by means of an electric mantle. The terephthaldehyde melted first, with slight sublimation, causing the benzoguanamine to dissolve and melt. When the mixture was substantially completely melted, the viscosity increased and the color of the melt became a brownish-black. Heating was continued at 235°C for five hours, the flask cooled and the product, which was a very brownish-black polymer, isolated and found to be infusible. During the reaction water and some benzonitrile were eliminated. Yield $\sim$ 97%.

iii) DA-24-28. Melt-Reaction of Terephthaldehyde and Benzoguanamine.

A mixture of 3.8 g. of benzoguanamine, 2.7 g. of terephthaldehyde and 40 ml of dimethylaniline were refluxed for four hours to yield a dark solution which contained no precipitate. The dimethyl aniline was then removed by distillation, leaving a black melt which, on continued heating at 250°C, eliminated water, produced a black, infusible polymer; yield $\sim$ 96%. Some benzonitrile was eliminated during the reaction.

iv) DA-24-29. Melt-Reaction of Benzoquinone and p-Phenylenediamine.

A mixture of 3.0 g. of benzoquinone and 3.0 g. of p-phenylenediamine were reacted by the procedure of DA-24-27 and there was obtained a shiny-black infusible polymer; yield $\sim$ 60%. Some sublimation occurred during the reaction and the infusible polymer was obtained almost immediately on melting.

v) DA-24-34. Melt-Reaction of Anthraquinone and p-Phenylenediamine.

A mixture of 4.1 g. of anthraquinone and 2.1 g. of p-phenylenediamine were reacted by the procedure of DA-24-27 for six hours and there was obtained

a shiny deep-black very brittle, infusible polymer. During the reaction some of the anthraquinone sublimed. Yield of product ~ 90%.

c. Melt-Solution Polymerizations.

i) DA-24-36. Reaction of Terephthaldehyde and p-Phenylenediamine in Presence of Benzylidene-aniline.

A mixture of 1.08 g. of p-phenylenediamine, 1.34 g. of terephthaldehyde and 1.0 g. of benzylidene-aniline were reacted by the procedure of DA-24-35b and then at 325°C for four hours. The viscosity of the melt was lower than that of DA-24-35b and did not increase noticeably until the benzylidene-aniline was eliminated by heating at 325°C. The reaction appeared to be very homogeneous and more controllable than the comparable experiment in the absence of benzylidene-aniline. The polymer was shiny black; yield 2.16 g., 120%.

ii) DA-29-129. Melt Reaction of Terephthaldehyde with a Solution of p-Phenylenediamine in Benzylidene-aniline.

A mixture of 1.0 g. of p-phenylenediamine and 10 g. of benzylidene-aniline in a flask equipped with a distillation head, etc., were melted together at 120°C under an atmosphere of nitrogen and to this melt was added 1.34 g. of terephthaldehyde, then the reaction was carried out under a slow stream of nitrogen under the following conditions:

Time hours	Temperature °C	Pressure Hg
2	120-220	atm.
5	200	atm.
10	260	atm.
10	290	atm.
10	290	140 mm

The polymer obtained was dark-brownish black, and infusible. Yield 2.24 g., 107.8%.

d. Post-Treatment of Polymers.

i) DA-29-90. Heat Treatment of Yellow Polymer DA-29-84.

(a) A sample of 0.5 g. of yellow polymer DA-29-84 was heated in a micro-distillation apparatus at 200°C for one-half hour in a nitrogen atmosphere and small trace amount of H_2O were collected on the surface of the distillation head. Then the sample was cooled, isolated, and analyzed; its color was light yellow and its infrared spectrum recorded.

Analysis %	C	H	N
original	80.55	5.25	13.58
after heating	79.94	5.21	12.82

(b) The yellow polymer sample, DA-29-84, was heat-treated in the same apparatus as in DA-29-90a for three hours at 250°C during which time a few clear crystals collected in the distillation head. These were shown to be p-phenylenediamine, m.p. 139°C. The polymer was cooled, isolated, and analyzed; its color was dull yellow and its infrared spectrum was recorded.

Analysis %	C	H	N
after heating	79.96	4.98	13.14

ii) DA-29-109. Post Heat-Treatment of Yellow Polymer DA-29-84 in Benzylidene-Aniline.

A mixture of 4.0 g. of benzylidene-aniline and 1.0 g. of yellow polymer DA-29-84 were mixed together in a distillation flask equipped with a nitrogen inlet, condenser, etc., and heated in the presence of a slow stream of nitrogen under the following conditions:

Time hours	Temperature °C	Pressure Hg
4.5	140	atmospheric
0.5	310	atmospheric
12.0	280	140 mm
24.0	280	7 mm

and then allowed to cool to room temperature, and there was obtained a very black shiny polymer. In the course of the heating black polymer formation was first observed after solution at about 140°C.

iii) DA-29-151. Heat-Treatment of Black Polymer DA-29-129.

One g. of polymer of DA-29-129 is finely ground and placed in a micro-flask which is degassed with nitrogen and the polymer heated at 400°C for thirty-six hours at 1.5 mm Hg pressure, and 480°C for fourteen hours at 1.5 mg. $C_6H_5N{=}CHC_6H_5$ is obtained as a distillate, leaving 0.64 g. of very black polymer. With this correction factor the yield of DA-29-129 is 92%.

iv) DA-29-148.

One gram of the insoluble polymer of DA-29-129 is finely ground and mixed with 10.0 g. of benzylidene-aniline in a micro-reflux flask and heated to reflux under a nitrogen atmosphere for forty-eight hours. The polymer remained undissolved. Then, 0.05 g. of zinc chloride was added and the mixture refluxed for forty-eight hours and a black homogeneous solution was obtained, which solidified on cooling to room temperature. The solid was treated with alcohol in a Soxhlet extractor for five days, the polymer isolated and dried. There remained 6.2 g. of black polymer. The alcohol extract contained low molecular weight black condensation products.

4. Discussion.

a. Solution System.

A number of qualified conclusions can be made concerning solution polymerizations by reference to the direct reaction between the bifunctional amines and carbonyl compounds using terephthaldehyde and p-phenylenediamine as a reference point. These two reagents react readily when placed in solution or in water to yield an almost quantitative yield of a yellow, insoluble, infusible polymer. When prepared in a high boiling medium such as dimethyl-aniline, the color of the polymer is darkened slightly to a yellowish brown

polymer, and this can be considered as a temperature effect. Further, polymer growth is evidently retarded by the rapidity of the reaction and the insolubility of the polymer in the solvents studied. Post-heating of the isolated yellow polymer up to temperatures of 250-260°C gives evidence of a minor increase in condensation by the elimination of water, but the infusibility as well as the insolubility in each other of the polymer chains of various degrees of polymerization which constitute the polymer mass do not allow black polymers to be formed at these post-heating temperatures.

In these preliminary studies, the importance of the nature or type of azo-methine linkage in the polymer structures also became evident in the ready decomposition of the polymers prepared from glyoxal and phenylenediamine,

$$n\ NH_2C_6H_4NH_2 + n\ OHCCHO \rightarrow =[NC_6H_4N=CH-CH]=_n + n\ H_2O \qquad \text{(eq. 56)}$$

This polymer contains aliphatic linkage in the =CH-CH= moiety in a conjugated structure; the polymers derived from the terephthaldehyde and hydrazine,

$$n\ OHCC_6H_4CHO + n\ NH_2NH_2 \rightarrow =[HCC_6H_4CH=N-N]=_n + H_2O \qquad \text{(eq. 57)}$$

also decomposed when heated.

The decomposition products appear to be mostly nitrogen contaminated with some basic gaseous substance, and the final product of decomposition appears to be a stable polystilbene. In fact, this sequence of reactions offers promise for the preparation of a stable polystilbene, thus

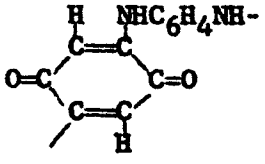
$$=HC[C_6H_4CH=N-N=CHC_6H_4]_nCH=N-N- \rightarrow N_2 + =HC[C_6H_4CH=CHC_6H_4]_nCH=N-N= \qquad \text{(eq. 58)}$$

by a mechanism which eliminates nitrogen capable of foaming the polymer during the melt and leaving an infusible char-like polystilbene polymer or copolymer. Such a product and mechanism has deep implications in ablation systems.

The steric factor also was evident in these solution polymerization studies. In solution, anthraquinone failed to react with p-phenylenediamine at temperatures at which terephthaldehyde reacts even when catalyzed with a Lewis acid. 2,4,4-Triamino-1,3,5-triazine (melamine) also failed to react

with terephthaldehyde even at the reflux temperature of xylene in the presence of zinc chloride. Another triazine derivative, 2,4-diamino-6-phenyl-1,3,5-triazine also failed to react in the presence of zinc chloride in a refluxing acetic anhydride solvent which is capable of functioning also as a dehydrating agent.

In the solution polymerizations, a number of observations were made concerning the resonance energies of the system. The polymer of the reaction of terephthaldehyde with p,p'-diaminostilbene was of definite orange color compared to the yellow color obtained with p-diaminobenzene. Further, the resonance effect on the color of the polymer was shown dramatically by the ready reactions in solution of benzoquinone with phenylenediamine and hydrazine respectively. The evidence indicated that the polymers were not "clean" polymers and that the quinone reacted with the phenylenediamine in a fashion similar to its reaction with aniline, which was discussed in Part I. This reaction consisted in the addition of the amine to the double bond adjacent to the C=O structure and its re-oxidation to the substituted anilidoquinone by quinone. The less than theoretical polymer yield indicates a similar reaction for the reaction of benzoquinone and p-phenylenediamine, and the polymer contains the probable structures:



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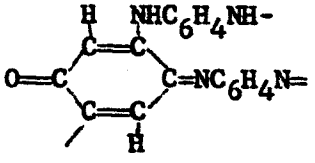

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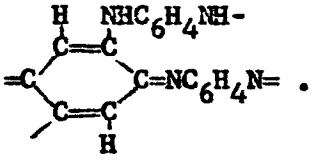
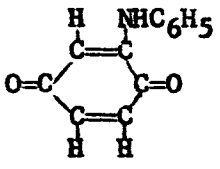


.

Any or all of these segments would be expected to be black since the products[26] prepared from benzoquinone and aniline,



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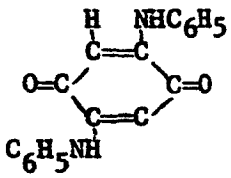

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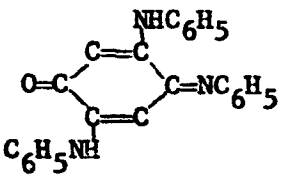
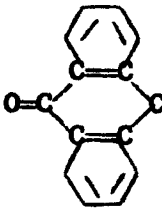


are black.

However, the polymer showed signs of decomposition at 285°C which possibly reflects the influence of bulk factors in the condensation reaction and on the stability of the polymer. In contrast, the failure of p-phenylenediamine to react in solution with anthraquinone, in which all the carbon atoms adjacent to the -C=O groups are blocked by substitution as part of a fused ring,



, lends support, that the primary reaction of quinone with the diamine is by an addition and not by a condensation mechanism.

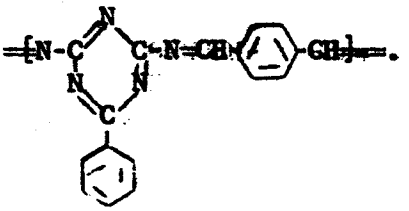
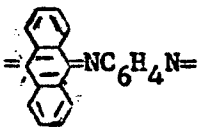
The reaction of hydrazine with quinone in water apparently follows an addition mechanism similar to that of p-phenylenediamine to produce a low-molecular weight water-soluble black condensation product, which can be converted to an insoluble, infusible mass by continued heating at 180°C, during which time decomposition is very marked.

As a result of these solution studies and a preliminary qualitative evaluation of the polymers, further intermediate studies on polymers derivable from glyoxal with diamines, or from hydrazines with dicarbonyl compounds were postponed to a later date.

b. Melt Systems.

Solution polymerization failed to yield black polymers from terephthaldehyde and phenylenediamine either directly or when the isolated polymer was post-heated for extended periods of time at 250-260°C. In contrast, when the same reagents were melted together and heated as a melt at about 150-160°C, the melt became increasingly viscous, changing in a few minutes from a colorless melt to yellow to orange to brown to black. At the initiation of the black stage the polymer is fusible. The reaction at 150-160°C is sufficiently rapid that in a few minutes it becomes infusible, appearing as a brittle, glassy, resinous mass. Continued heating of the infusible polymer at

increasing higher temperatures produces a less brittle polymer, indicating that continued polymerization in the solid state can occur when the polymer mass is of the "glassy" rather than of the "brick-dust" type.

The reaction of terephthaldehyde and benzoguanamine failed to occur in solution. This failure could be attributed to steric factors which would be more evident at low temperatures than at high temperatures. An increase in temperature, by using a higher boiling medium such as N,N-dimethylaniline was insufficient to produce reaction, but when the dimethylaniline was removed by distillation and the mixture of reagents heated to melt, reaction occurred readily, producing a black melt which, on continued heating at 235-250°C, became infusible. However, during the reaction, some decomposition was evident by the elimination of benzonitrile, C_6H_5CN; this reflects the bulk factor in the polymer, the triazine ring, introduced by the pendant phenyl group in  . Anthraquinone differs from quinone in that it does not undergo aniline-type addition; it was found to be unreactive with p-phenylenediamine in solution systems, probably because of steric factors. However, when anthraquinone and phenylenediamine were made to react in a melt system, the condensation product at a most early stage of reaction was black due to the increased resonance energies in the Ar group in the repeating unit,  . The black polymer was infusible, very brittle and friable, apparently reflecting a low molecular weight as a result of bulk and steric factors. Similarly, to anthraquinone, benzoquinone reacted on melting with p-phenylenediamine to produce a black product but it became infusible very rapidly, indicating a crosslinking reaction due to a functionality higher than two in the system. This can be attributed to the addition

of the amine to the carbon atoms adjacent to the carbonyl groups resulting in a functionality of three or four for the quinone reagent. As a result of these melt studies and a preliminary qualitative evaluation of the polymers prepared by the melt technique, studies on azo-methine polymers derivable from quinone, naphthaquinone, anthraquinone, or benzoguanamine were limited to a few experiments, and further studies have been postponed for a later time.

c. Melt-Solutions.

The melt polymerization of terephthaldehyde and phenylenediamine proceeds sufficiently rapidly with a corresponding increase in viscosity that isolation of the polymers at a predetermined viscosity is difficult. When the same reaction was performed in a melt of benzylidene-aniline, the reagents were observed to dissolve completely with the formation of a clear, viscous solution which changed slowly in color to a black solution. On further heating, the viscosity of the solution increased to a maximum beyond which it did not progress until the benzylidene-aniline was removed by distillation at higher temperature. As the benzylidene-aniline was removed, the viscosity increased and the polymer finally became insoluble and infusible. The behavior indicates that benzylidene-aniline performs a dual function. It functions first as a solvent. Its second function appears to be that of a moderator of the reaction by means of a bis-Schiff exchange reaction to telomerize the polymer with $C_6H_5CH=$ and $C_6H_5N=$ groups in an equilibrium system. Then, as the benzylidene-aniline was removed by distillation, the equilibrium was disturbed, condensation of the chains which are soluble in each other occurred through terminal groups to produce more benzylidene-aniline.

Condensation can also occur between one chain both ends of which are terminated by $C_6H_5CH=$ and another chain both ends of which are terminated by $C_6H_5N=$ groups. It is also conceivable that benzylaniline may form an adduct

or complex with the polymer and thereby moderate the reaction. If the benzal-aniline functions as a moderator by either mechanism, then the yield of polymer should be greater than the theoretical 100% yield expected from the condensation with the simple elimination of water; such is the actual experience when the reaction is performed at temperatures as high as 325°C at atmospheric pressure, or at 290°C at 140 mm pressure.

d. Post-Treatment of Polymers.

The post-heating of the yellow polymer (DA-29-84), previously obtained in the solution polymerization of terephthaldehyde and p-phenylenediamine, for extended periods of time at temperatures at which black polymers are obtained by the melt process, failed to convert the yellow polymer to a black polymer. In fact, very little change was found even in the C, H, and N elemental analyses.

The yellow polymer is considered as infusible and insoluble, showing limited solubility in formic and concentrated sulfuric acid. This yellow polymer was found to be soluble in molten benzylidene-aniline to form a clear solution, and when this solution was heated, further polymerization occurred; a black polymer resulted, reaching a maximum viscosity until the benzylidene-aniline was removed by distillation, and thereafter increased until a black insoluble, infusible polymer resulted. In contrast to the yellow polymer, the higher molecular weight, infusible, insoluble black polymer of DA-29-129 is not soluble in benzylidene-aniline even when refluxed at atmospheric pressure for forty-eight hours or more. However, when a catalytic quantity of zinc chloride was added to the refluxing mixture of the polymer and benzylidene-aniline, a black homogeneous solution of polymer was obtained lending some credence to an exchange mechanism which results in shorter end-terminated chains. Isolation of the polymer from solution yielded black alcohol-insoluble polymers, and some brown alcohol-soluble condensation

products. The yield of alcohol-insoluble polymer is greatly increased. Depending on the amount of benzylidene-aniline used as a solvent, black polymers which are soluble, partially soluble or insoluble in HCOOH or H_2SO_4 can be obtained.

Whether the benzylidene-aniline is held in the polymer as a complex or adduct, or as a monofunctional reactant cap at the end of the chain in a medium of high (solid) viscosity, its removal at condensation temperatures used would be expected to be difficult unless the reaction was continued for extreme periods of time. The alternate method to effect its removal would be to use high temperature to induce total elimination. A sample of the black polymer DA-29-129 obtained in yield of 107.8% of theory, was heated at 1.5 mm pressure at 400°C and at 480°C. $C_6H_5CH{=}NC_6H_5$ was obtained as a distillate within the first two hours at 400°C and its quantity was not increased by the end of thirty-six hours but was increased by further heating at 480°C for fifteen hours.

B. By Schiff Base Exchange Reactions.[4-7]

The three exchange reactions:

(1) The Amine Exchange

(2) The Carbonyl Exchange

(3) The Bis-Exchange

were evaluated in the syntheses of polymers.

1. The Amine Exchange.

The reaction for the amine exchange can be written as

$$n\ H_2NArNH_2 + n\ ArN{=}CHArCH{=}NAr \rightarrow 2n\ ArNH_2 + {=}[NArN{=}CHArCH]{=}_n \qquad \text{(eq. 59)}$$

and was studied specifically in a melt system with p-phenylenediamine and p-xylylidenedianiline:

$$H_2NC_6H_4NH_2 + C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5 \rightarrow 2\ C_6H_5NH_2 + [NC_6H_4N{=}CHC_6H_4CH]_n \qquad \text{(eq. 6C)}$$

To determine whether other amino compounds, in which the amino groups are much less basic than in phenylenediamine, can undergo a Schiff base exchange, the reaction was evaluated with benzoguanamine and terephthaldehyde as reactants. The reaction of phenylenediamine and p-xylylidenediamine was also evaluated in a melt-solution system with benzylidene-aniline as the solvent.

a. Experimental.

i) DA-24-51. Reaction of p-Phenylenediamine and p-Xylylidenedianiline at Atmospheric Pressure.

A mixture of 2.84 g. of p-xylylidenedianiline and 1.08 g. of phenylenediamine were mixed in a 50 ml reaction flask equipped with thermometer, distillation head, condenser, receiver, vacuum take-off and an electric mantle, and heating begun. The temperature of the mixture increased in ten minutes to 128-132°C, at which it melted, reacting immediately to form an orange solution which resolidified in about five minutes. Then the temperature was raised to 189-190°C for forty-five minutes, and 190-195°C for forty-five minutes, the polymer becoming orange-brown. The system was then heated for four and one-half hours at ~300°C at 1-20 mm pressure, and allowed to cool to room temperature. The distillate, 1.5 g., consisted mostly of aniline, and the polymer was dark-brown, insoluble, infusible and heterogeneous in color; yield ~2.0 g.

ii) DA-24-57. Repeat of DA-24-51 Under Reduced Pressure.

The reagents were mixed in the reaction apparatus of DA-24-51 and degassed at 1 mm after which N_2 was bled into the apparatus. The degassing was repeated twice, then the system evacuated to 2 mm Hg pressure and heating begun. The mixture melted at 130-132°C, the temperature rising to 185°C in ten minutes to produce a solid yellow-orange mass which sintered but did not melt. Heating was continued and aniline began to distill at 189°C, the mass becoming orange in color. Then the temperature was raised to 275-290°C for

one hour and allowed to cool to room temperature. The polymer, 2.1 g., was dark-orange, insoluble and infusible.

iii) DA-29-40. Reaction of p-Phenylenediamine and p-Xylylidenedianiline with a Sweep Gas.

A mixture of 1.08 g. p-phenylenediamine and 2.84 g. of p-xylylidenedianiline were heated together for three hours at 300°C in a 50 ml microflask equipped with a nitrogen inlet, distillation head, condenser, receiver, etc. The reaction was performed under a constant slow flow of nitrogen; and aniline collected in the receiver. Then the temperature was raised to 310°C and the pressure reduced to 0.1 mm Hg. Yield of insoluble brown polymer was $\sim$ 100%.

iv) DA-24-75. Reaction of Benzoguanamine and p-Xylylidenedianiline.

A mixture of 2.84 g. xylylidenedianiline and 1.87 g. benzoguanamine were reacted in an apparatus similar to that used in DA-29-40. On heating at atmospheric pressure, a complete yellow melt was obtained at about 100°C, and the reaction continued at 270-275°C for ninety minutes with the color changing from orange to dark red. Then the pressure was reduced to 1 mm Hg; the temperature was raised to 310°C for three and one-half hours. The reaction melt became black, while distilling off aniline and some unreacted xylylidenedianiline, leaving 2.64 g. (93%) of a black, infusible polymer.

v) DA-29-42. Reaction of Benzoguanamine and p-Xylylidenedianiline.

In the reaction apparatus of DA-29-40, a mixture of 1.87 g. of benzoguanamine and 2.84 g. p-xylylidenedianiline were melted together and heated at 300°C for one hour, then reaction mixture was distilled at 1 mm and aniline collected as a distillate. Heating was then continued for one hour at 1 mm pressure. There was obtained a reddish-black porous polymer mass, yield $\sim$ 100%.

vi) DA-24-58. Reaction of p-Phenylenediamine, p-Xylylidenedianiline Benzylidene-aniline in 1:1:1 Molar Ratio.

The reaction was performed in an apparatus similar to that used in DA-29-40. A mixture of 1.08 g. p-phenylenediamine, 2.84 g. p-xylylidenedianiline and 1.81 g. benzylidene-aniline were ground thoroughly in a mortar and pestle and introduced into the reaction flask and degassed at 1 mm; nitrogen was bled into the flask to atmospheric pressure, and the mixture heated Most of the mixture had melted at 195°C and it was held at 195-197°C for forty-five minutes during which aniline was observed to reflux. The temperature was raised to 210°C for ten minutes and aniline collected. The temperature was then raised to 300°C to remove excess benzylidene-aniline and the reaction flask allowed to cool to room temperature. The polymer was a dark-brown infusible solid, yield 107%.

vii) DA-24-60. Reaction of p-Phenylenediamine, p-Xylylidenedianiline and Benzylidene-aniline in 1:1:2 Molar Ratio.

The reaction between 1.08 g. p-phenylenediamine, 2.84 g. p-xylylidenedianiline and 3.62 g. of benzylidene-aniline were reacted in the apparatus of DA-24-58. On heating slowly over a period of two hours, initial melting began at about 100°C and a complete homogeneous brown solution was obtained by the time the temperature reached 160°C; distillation began at about 210°C continuing to 330°C yielding aniline and benzylidene-aniline. The pressure was then reduced to 0.4 mm and distillation continued for one hour at 330-350°C. The reaction flask was allowed to cool and the isolated polymer was black and infusible. Yield 2.14 g., 104%.

viii) DA-29-65. Reaction of Xylylidenedianiline with p-Phenylenediamine in Benzylidene-aniline.

The apparatus and process of DA-29-40 was used. A mixture of 1.18 g. p-phenylenediamine and 10 .0 g. benzylidene-aniline were melted together in

the microflask at about 130°C. To this melt there was added 2.8 g. of p-xylylidenedianiline, the temperature was raised to 270°C over a period of two hours, then held at 270°C for five hours during which time excess benzylidene-aniline was removed by distillation. The temperature was then raised quickly to 330°C and maintained at this temperature for twelve hours. The flask was allowed to cool to room temperature, and the yield of isolated polymer was 48.5%, and it was black in color.

b. Discussion.

The amine exchange using p-phenylenediamine and p-xylylidenedianiline as a means of preparing polymeric azo-methines was found to proceed readily in the melt process producing polymers darker in color than the diamine and terephthaldehyde in the solution process. This melt reaction, however, appears to be faster than the melt reaction of the diamine and the dialdehyde resulting in a brown rather than black polymer; the aniline liberated in the reaction appearing to act as a catalyst. Benzoguanamine was also found to react by amine exchange. As in the case of the melt reaction of terephthaldehyde and p-phenylenediamine, the amine exchange reaction was found to be moderated and controlled by benzylidene-aniline and probably for the same reason since the degree of moderation increased with an increase in the amount of benzylidene-aniline.

2. The Carbonyl Exchange.

The polymerization reaction for the carbonyl exchange can be expressed as

$$n\ RCOArCOR + n\ ArCH{=}NArN{=}CHAr \rightarrow 2n\ ArCHO + \left\{\begin{matrix} R & R \\ | & | \\ C\text{-}Ar\text{-}C{=}NArN \end{matrix}\right\}_n \qquad \text{(eq. 61)}$$

and the specific reaction between terephthaldehyde and di-benzylidene-p-phenylenediamine is written as

$$n\ OHCC_6H_4CHO + n\ C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5 \rightarrow$$
$$2n\ C_6H_5CHO + \{HCC_6H_4CH{=}NC_6H_4N\}_n \qquad \text{(eq. 62)}$$

The reaction of equation 62 was evaluated using a melt process with and without a catalyst, at various ratios of reagents and in the presence of benzylidene-aniline. A number of other experiments were also performed to try to establish the broader range of equation 61. Benzoquinone, chloranil and dibenzylidene hydrazine were evaluated to determine if they could undergo the carbonyl exchange reaction.

a. Experimental.

i) DA-24-49. Reaction of Terephthaldehyde and Dibenzylidene-p-phenylenediamine.

A mixture of 1.34 g. of terephthaldehyde and 2.84 g. of dibenzylidene-p-phenylenediamine were mixed in a 50 ml microflask equipped with thermometer, distilling head, condenser, receiver, vacuum take-off, and electric heating mantle. The apparatus was degassed to 1 mm pressure and N_2 was bled into the apparatus to atmospheric pressure and heating begun; a yellow melt formed at 95°C. The reaction conditions were as follows:

Time, Minutes	Temperature, °C	Pressure mm Hg.	Observation
0	95	760	yellow melt
5	150	760	light orange melt
8	180	760	orange melt
15	220	760	deep orange melt
25	230	760	orange-red melt
60	240	760	dark-orange melt
67	240	760	orange-red melt
120	280	760	cherry-red melt
130	310	760	cherry-red melt, benzylidene-aniline begins to distill
140	310	3.8	viscous dark-red resin
150	310	0.7	dark-red solid
270	310	0.7	reddish-black solid

and the heating terminated. The product was allowed to cool to room temperature. The distillate, 1.2 g., was identified as aniline; the reaction product, 2.26 g., was reddish-black and infusible.

ii) DA-24-62 - DA-24-72 . Reactions of Terephthaldehyde and Dibenzylidene-p-phenylenediamine at Various Mole Ratios.

A series of related experiments were performed in which the mole ratio of terephthaldehyde to dibenzylidene-p-phenylenediamine was varied from 2:1 to 1:2 in 0.01 to 0.03 molar quantities and compared to a 1:1 molar reaction product. The experiments were performed in an apparatus similar to that used in DA-24-49. The mixture of reagents was introduced into the reaction flask, the apparatus degassed at 0.4 mm and nitrogen bled into the apparatus. The mixture was heated. In all cases, melting of the mixture occurred below or at 100°C. Then the temperature was raised to 190-220°C and reaction continued for five to six hours and benzaldehyde collected as a distillate. The reaction product was allowed to cool to room temperature and recovered. These experiments are summarized as follows:

Mole Ratio of A = $C_6H_4(CHO)_2$ to B = $C_6H_4(N{=}CHC_6H_5)_2$	Exper. No.	Observations
2:1	DA-24-62	Brown-red polymer; excess A sublimes out
3:2	DA-24-66	Yellow-red solid, m.p. crude, range 180-280°C
4:3	DA-24-67	Orange solid, m.p. range 130-160°C
6:5	DA-24-72	Red solid, m.p. range 180-190°C
5:6	DA-24-71	Orange-red solid, m.p. range 190-200°C
3:4	DA-24-65 DA-24-70	Yellow-orange solid, m.p. (crude) 128°C
2:3	DA-24-69	Yellow-orange solid, m.p. range 145-220°C
1:2	DA-24-64 DA-24-68	Some red polymer, and orange solid, m.p. (crude) 140-141°C
1:1	DA-24-49	Insoluble, infusible, black polymer

iii) DA-29-39a. Reaction of Terephthaldehyde and Benzylidene-p-phenylenediamine.

A mixture of 1.34 g. of terephthaldehyde and 2.84 g. of dibenzylidene-p-phenylenediamine in a suitable reaction flask heated to reflux for one hour at 185°C then raised to 200°C and the pressure lowered to 15 mm to remove benzaldehyde. Unreacted terephthaldehyde sublimed from the reaction during the distillation and a multicolored red-yellow-brown-black polymer was obtained.

iv) DA-29-39b.

DA-29-39a was repeated using 1.45 g. of terephthaldehyde instead of 1.34 g.; and after reflux the temperature was raised from 185°C to 200°C over a period of six hours, then distillation performed at 15 mm. The polymer was also multicolored but less so than the polymer of DA-29-39a.

v) DA-29-37. Reaction of Terephthaldehyde and Benzylidene-p-phenylenediamine with $ZnCl_2$.

A mixture of 1.34 g. of terephthaldehyde, 2.84 g. of dibenzylidene-p-phenylenediamine and 0.1 g. $ZnCl_2$ were reacted in a micro-distillation flask at 200°C at atmospheric pressure for three hours during which time benzaldehyde distilled from the reaction mass, leaving an unhomogeneous red and brown two-color polymer.

vi) DA-29-61. Reaction of Terephthaldehyde and Benzylidene-p-phenylenediamine in Tetralin.

A mixture of 1.36 g. terephthaldehyde and 2.84 g. dibenzylidene-p-phenylenediamine in 10 ml of tetralin were refluxed at 207°C under a nitrogen atmosphere for two hours without a color change or formation of polymer.

vii) DA-29-62. Reaction of Terephthaldehyde, Benzylidene-p-phenylenediamine and Benzylidene-aniline.

A mixture of 1.34 g. terephthaldehyde, 2.84 g. benzylidene-p-phenyldi-

amine and 2.0 g. of benzylidene-aniline were reacted in an apparatus similar to that used in DA-24-49. The mixture was slowly heated from room temperature to 300°C over a period of twelve hours at 150 mm pressure, then the temperature was raised to 330°C and there remained in the reaction flask 0.61 g. of very black polymer.

viii) DA-24-73. Reaction of Dibenzylidene-p-Phenylene-diamine and Benzoquinone.

A mixture of 2.84 g. of dibenzylidene-p-phenylenediamine and 1.00 g. of benzoquinone were reacted in an apparatus similar to that used in DA-24-29, except that it was also equipped with a nitrogen inlet to sweep other gases out of the system. The reaction mixture was heated and a clear yellow melt was obtained at 100°C and a rapid reaction took place. The reaction conditions were as follows:

Time minutes	Temperature °C	Pressure mm Hg	Observations
0	100	760	Yellow melt
10	165	760	Color changes to light red to dark red to black
15	248	760	Black melt
30	290	760	Black viscous melt
47	286	760	Very viscous melt
50	286	15	C_6H_5CHO distills off
60	286	15	Solid black polymer

The reaction product was allowed to cool to room temperature and there was isolated 2.01 g. of black, brittle, porous, infusible polymer.

ix) DA-29-44. Reaction of Dibenzylidene-p-phenylenediamine and Benzoquinone.

A mixture of 2.84 g. of dibenzylidene-p-phenylenediamine and 1.08 g. of benzoquinone were mixed in a reaction flask and heated; a complete melt was obtained at 180°C, then the reaction was refluxed for two hours, following which the pressure was reduced to 15 mm to remove benzaldehyde, leaving

a shiny-black infusible polymer, yield 2.0 g.

x) DA-24-77. Reaction of Dibenzylidene-p-phenylenediamine and Chloranil.

A mixture of 2.84 g. of dibenzylidene-p-phenylenediamine and 2.46 g. of chloranil were reacted in the apparatus of DA-24-73 at atmospheric pressure. The mixture melted at 67°C and was completely black at 100°C. Extensive decomposition resulting in the liberation of HCl was noted, and the experiment terminated at the end of three hours. The reaction conditions were:

Time Minutes	Temperature °C	Observations
0	room	Solid mixture
0	67	Yellow melt
3	110	Black melt; some sublimation of chloranil
8	200	Black melt; HCl present
28	252	Black melt; HCl present
43	295	Black solid; HCl present
188	265	Black solid; HCl present

The polymer, 1.8 g., was black, hard and brittle.

xi) DA-24-81. Reaction of Terephthaldehyde and Dibenzylidenehydrazine.

A mixture of 2.68 g. of terephthaldehyde and 4.16 g. of dibenzylidenehydrazine were reacted in the apparatus of DA-24-73. The mixture was heated and melting of the mixture occurred in the range of 50-95°C with the color changing from yellow to orange to red. The mixture was reacted at 250-300°C for sixty minutes and the pressure was then reduced to 15 mm at 300°C, and 1.5 g. of benzaldehyde collected as a distillate. The polymer, 2.8 g., was dark-red, insoluble, and infusible.

xii) DA-29-46. Reaction of Terephthaldehyde and Dibenzylidenehydrazine.

A mixture of 1.34 g. of terephthaldehyde and 2.08 g. of dibenzylidenehydrazine in the reaction apparatus of DA-24-73 were melted at 100°C, the mixture changing in color from yellow to red; then the mixture was heated to 290-300°C for three hours and the pressure reduced to 15 mm to eliminate

benzaldehyde and there was obtained a hard, brittle, red polymer. During the reaction decomposition of the polymer with the liberation of gas, probably nitrogen, was noted during the reaction at the higher temperatures.

xiii) DA-24-82. Reaction of Dibenzylidenehydrazine and Benzoquinone.

A mixture of 4.16 g. of dibenzylidenehydrazine and 2.26 g. of benzoquinone were reacted in the apparatus of DA-24-73. The reaction mixture was heated and melting occurred at 90-100°C with the formation of a dark solution and some sublimation of the quinone. Reaction was performed at 250-260°C for twenty hours distilling off benzaldehyde and leaving a foamed glassy, black polymer, 1.1 g. in the reaction flask. Upon heating to the flame temperature of a bunsen burner, a sample of the polymer melted and on continued heating, foamed to an infusible, foamed mass.

b. Discussion.

The carbonyl exchange reaction, as a polymerization reaction, was found in the melt system to proceed readily and more moderately than the corresponding amine exchange; thereby producing darker polymers than the amine exchange reaction. The carbonyl reaction was greatly accelerated by zinc chloride catalysis. The blackest polymers were obtained in a 1:1 mole ratio of terephthaldehyde to benzylidene-para-phenylenediamine. Little or no reaction occurred when these reagents were reacted at 200°C in tetralin, but reacted readily in a melt-solution system with benzylidene-aniline to produce black polymers.

Dibenzylidene-p-phenylenediamine was found to undergo carbonyl exchange with benzoquinone to produce a black polymer; reaction also occurred with chloranil but decomposition with the liberation of HCl was extensive. Dibenzylidene-hydrazine was also found to undergo carbonyl exchange with terephthaldehyde and with benzophenone to produce polymers which decomposed when heated to 300°C or higher.

3. Bis-Exchange.

The bis-exchange polymerization reaction can be expressed generally as

$$n\ ArCH{=}NArN{=}CHAr + n\ ArN{=}CHArCH{=}NAr \rightleftharpoons 2\ ArCH{=}NAr + \{NArN{=}CHArCH\}_n \qquad \text{(eq. 63)}$$

The specific reaction between dibenzylidene-p-phenylenediamine and xylylidene-di-aniline is written as:

$$n\ C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5 + n\ C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5 \rightleftharpoons 2n\ C_6H_5CH{=}NC_6H_5 + \{NC_6H_4N{=}CHC_6H_4CH\}_n \qquad \text{(eq. 64)}$$

The reaction of equation 64 was evaluated using the melt-process, with and without catalyst and over a broad range of conditions. It was also evaluated in the melt-solution system with benzylidene-aniline as the solvent. Two bis-exchange reactions were tried with dibenzylidene-hydrazine as one of the reagents.

a. Experimental.

i) DA-24-53. Reaction of p-Xylylidene-di-aniline and Dibenzylidene-p-phenylenediamine.

A mixture of 2.84 g. of p-$C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5$ and 2.84 g. of p-$C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5$ were ground together in a mortar and pestle and then placed in a 50 ml microflask equipped with a thermometer, distillation head, condenser, receiver, and vacuum take-off. The apparatus was degassed of air, nitrogen bled into the system and heat applied by means of an electric mantle. The mixture was melted completely in the range of 80-85°C. The initial reaction conditions were as follows:

Time Minutes	Temperature °C	Observations
0	80	Yellow melt
5	130	Yellow melt
15	170	Yellow melt
20	245	Light-red melt
25	265	Benzylidene-aniline begins to reflux
30	285	Very red melt
52	298	Reddish-brown viscous melt
80	305	Dark-red-brown very viscous melt
150	332	Reddish-black very viscous melt
240	334	Dark reddish-black melt

Then the pressure was reduced slowly to about 50 mm and most of the benzylidene-aniline collected, with the formation in the flask of a black polymer. The pressure was reduced further to 1.5-2.0 mm for eight additional hours while the temperature was maintained at 320-350°C, and the reaction terminated and allowed to cool to room temperature. There was isolated 2.40 g. of very black, shiny, porous, tough polymer which was infusible and did not melt at red heat.

(ii) DA-24-55. Repeat of DA-24-53 Under Different Temperature and Pressure Conditions.

Melting started at 60°C and was completed at 80°C. The reaction conditions were as follows:

Time Minutes	Temperature °C	Pressure mm Hg.	Observations
0	80	760	Yellow melt
5	185	760	Yellow-orange melt
30	293	760	Red melt
67	297	760	Dark-brown melt
120	308	760	Dark-brown melt
265	325	760	Very dark-brown viscous melt
270	320	95	$C_6H_5CH=NC_6H_5$ begins to distill
360	313	95	Black polymer
510	308	95	Black polymer
700	290	90	Black polymer
765	300	90	Black polymer
1005	307	70	Black polymer
1035	340	50	Black polymer
1108	348	30	Black polymer
1175	314	0.8	Black polymer
1220	314	0.8	Black polymer
1265	316	0.6	Black polymer
1585	316	0.6	Black polymer

Then the reaction mixture was allowed to cool to room temperature and there was obtained 2.65 g. of black, infusible, insoluble polymer.

iii) DA-24-90. Repeat of DA-24-53 Under Different Conditions.

A mixture of 5.165 g. of p-$C_6H_5N=CHC_6H_4CH=NC_6H_5$ and 5.165 g. of p-$C_6H_5CH=NC_6H_4N=CHC_6H_5$ were placed in the reaction flask and the apparatus degassed and nitrogen bled into the apparatus. The reaction flask was immersed into a molten Woods-metal bath heated to $\sim$300°C; the reaction mixture became a clear yellow melt at 135°C, which remained homogeneous throughout the polymerization. The temperature of the reaction mixture was allowed to rise to 300°C and then raised to 350°C and held there for five hours. At 350°C, benzylidene-aniline began to reflux. As the reaction proceeded the color of the melt changed from yellow to light orange, to brilliant orange, to orange-red, to red, to brilliant red, to very dark red, and to black.

At the end of five hours, the pressure on the system was reduced as follows:

Time, hours	Pressure, mm Hg.
5.0	150
6.5	125
6.75	100
7.0	75
7.5	12
8.0	7
21.0	3.5

Then the reaction was allowed to cool to room temperature. A hard, shiny black polymer, 4.38 g., was isolated from the bottom of the flask and 4.5 g. of benzylidene-aniline collected in the receiver.

iv) DA-29-41. Repeat of DA-24-53 Under Different Conditions.

A mixture of 2.84 g. of p-$C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5$ and 2.84 g. of p-$C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5$ were melted together at 200°C at atmospheric pressure, then the temperature raised slowly to 300°C over the course of one hour. The pressure was then reduced to $\sim$ 150 mm Hg and the reaction continued for four hours to remove benzylidene-aniline, leaving 2.4 g. of hard, black polymer.

v) DA-29-72. Repeat of DA-29-41 Under Different Conditions.

The reagents were heated at 290°C for six hours at atmospheric pressure, then eight hours at 560 mm Hg. Then the temperature was raised to 350°C and the pressure lowered to 10 mm Hg and maintained under these conditions for twenty-four hours. There was obtained 2.62 g. (92.3%) of tough, black polymer.

vi) DA-29-74. Repeat of DA-29-41 Under Different Conditions.

In this reaction 5.68 g. of each reagent instead of 2.84 g. were used. The reagents were heated together after melting at 270°C at atmospheric pressure for twenty-four hours, then at 300°C for twenty-four hours. The pressure was then reduced to 640 mm for twenty-four hours, and 540 mm for forty-eight hours. The yield of polymer was 6.17 g. (149.8%), brown in color, and its texture resembled clay.

vii) DA-29-54. Reaction of Dibenzylidene-m-phenylenediamine and p-Xylylidene-bis-disnil.

The procedure and apparatus was similar to that used in DA-29-41 except that the meta derivative, dibenzylidene-m-phenylenediamine instead of the para derivative was used and the reaction conditions were slightly modified. The reagents were melted together at 160°C, then the temperature raised to 300°C and the pressure reduced slowly ovor a period of thirty-five hours to 2 mm pressure and held there for five hours. The polymer, 1.83 g. (88.9%), was dark-brown in color and contained unreacted reagents.

viii) DA-29-56. Repeat of DA-29-54 with $ZnCl_2$ Catalyst.

To the reagent mixture was added 0.1 g. $ZnCl_2$, and the mixture refluxed at atmospheric pressure for two hours at 300°C. Then the pressure was reduced to 2 mm and benzylidene-aniline removed by distillation, leaving a porous red-black polymer, 1.50 g. (72.8%).

ix) DA-29-149. Repeat of DA-29-41 Under Different Conditions.

The reagents were heated at reflux temperature of 320°C, and at atmospheric pressure, for twelve hours; then eleven hours at 320°C at 20 mm Hg pressure; six hours at 320°C at 1.5 mm Hg pressure; forty-five hours at 420°C at 1.5 mm Hg pressure. There was obtained 109% yield of a very black polymer.

x) DA-24-92. Reaction of p-Xylylidene-di-aniline and Di-benzylidene hydrazine.

A mixture of 5.78 g. of $p\text{-}C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5$ and 4.16 g. of $C_6H_5CH{=}N\text{-}N{=}CHC_6H_5$ were reacted in the apparatus of DA-24-90 and heated by means of a molten metal bath. A clear yellow homogeneous melt was formed at 150°C, and refluxing was observed at 220°C. At 300-325°C, the mixture was boiling vigorously with some evidence of decomposition and elimination of non-condensible gases. The mixture was maintained at 325°C for eighteen hours, then the pressure was reduced to 1.5 mm and held there for six hours,

following which it was allowed to cool to room temperature. The distillate amounted to 2.1 g. of $C_6H_5CH{=}NC_6H_5$; and 2.35 g. of black, glossy, spongy polymer was isolated from the flask.

xi) DA-29-50. Reaction of Di-benzylidene-p-phenylenediamine and p-Xylylidene-di-α-aminopyridine.

A mixture of 2.86 g. of di-benzylidene-p-phenylenediamine and 2.84 g. of p-xylylidene-di-α-aminopyridine were reacted by the procedure of DA-29-54. After melting and as the temperature increased the color of the melt changed from yellow to red to brown. The distillate consisted of benzylidene-α-aminopyridine, and 2.49 g. of a dark-brown infusible polymer was obtained.

xii) DA-29-43. Reaction of Dibenzylidene-hydrazine and Glyoxalidine-di-p-methoxyaniline.

A mixture of 2.08 g. of $C_6H_5CH{=}N{-}N{=}HCC_6H_5$ and 2.68 g. of $CH_3OC_6H_4N{=}CH{-}CH{=}NC_6H_4OCH_3$ were melted together and reacted at 280°C at atmospheric pressure for two hours. During the reaction non-condensing gases, which were basic to wet litmus paper and of an ammoniacal order, were liberated. Then the pressure was reduced to 150 mm Hg pressure and benzylidene-p-methoxyaniline collected as the distillate. A black resinous-tarry substance remained as the residue in the reaction flask.

xiii) DA-29-64. Reaction of p-Xylylidene-di-aniline and Dibenzylidene-p-phenylenediamine in the Presence of Benzylidene-aniline.

A mixture of 2.84 g. of $p\text{-}C_6H_5N{=}CHC_6H_4N{=}C_6H_5$, 2.84 g. of $p\text{-}C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5$ and 2.0 g. of $C_6H_5CH{=}NC_6H_5$ were melted together at 200°C at atmospheric pressure and the temperature raised over a period of one hour to 300°C, the color of the reaction melt changing from yellow to orange with no further color change occurring over the next three-hour period, then the pressure was reduced to 150 mm and benzylidene-aniline removed by distillation during a period of four hours. As the benzylidene-aniline was removed the

color of the reaction mixture changed from orange to brown to black. The black polymer, 1.38 g., was shiny and infusible.

b. Discussion.

The bis-exchange polymerization reaction was found to be the best moderated and the best controlled reaction among those tried to this point. It proceeds without added catalysts and is accelerated by Lewis acid-type catalysts. The reactions given by equation 63 and 64 are equilibrium reactions.

Further control is achieved in the solution-melt system by the addition of benzylidene-aniline which, in equation 64, is shown as the by-product of the reaction. The reaction, as given in equation 64, was shown to be an equilibrium reaction, since in the presence of excess benzylidene-aniline, the reaction proceeded to a yellow-condensation product and remained there even at 300°C, until the benzylidene-aniline was removed by distillation. Once the polymer was formed, continued heating in the solid state converted a brittle polymer to a tough polymer by continued polymerization in the solid state.

Dibenzylidene-hydrazine was found to undergo bis-exchange with p-xylylidene-dianiline to yield, with signs of decomposition, a black spongy polymer similar to that obtained from hydrazine and terephthaldehyde. Dibenzylidene-hydrazine also gave evidence of undergoing the bis-exchange reaction with glyoxalidine-di-p-methoxyaniline, by the formation of p-methoxybenzylidene-aniline. The polymer which should have the structure $\{CH\text{-}CH{=}N\text{-}\}_n$ and reported[7] as a yellow product underwent decomposition in the process to yield a black tar-like resin.

C. From Acetals and Amine Compounds.[5-7]

Difunctional acetals instead of the dialdehydes were used in the preparation of polymers and were evaluated in four reactions:

(1) Acetals with Amines
(2) Acetals with Amine Hydrochlorides
(3) Acetals with N-Acylamines
(4) Acetals with Schiff Bases.

1. From Acetals and Amines.

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

$$n\ (RO)_2HCArCH(OR)_2 + n\ H_2NArNH_2 \rightarrow 4n\ C_2H_5OH + \text{=[HCArCH=NArN]=}_n \qquad \text{(eq. 65)}$$

and the specific reaction between p-phenylenediamine and p-xylylidenetetraethyl ether, is written as

$$n\ (H_5C_2O)_2HCC_6H_4CH(OC_2H_5O)_2 + n\ H_2NC_6H_4NH_2 \rightarrow 4n\ C_2H_5CH + \text{=[HCC}_6\text{H}_4\text{CH=NC}_6\text{H}_4\text{N]=}_n \qquad \text{(eq. 66)}$$

The reaction of equation 66 was evaluated without solvent and without catalyst.

a. Experimental.

i) DA-26-25. Reaction of p-Phenylenediamine and p-Xylylidene-tetraethyl Ether.

A mixture of 2.0 g. of p-phenylenediamine and 0.766 g. of xylylidene-tetraethyl ether were mixed in a reaction flask equipped with distilling head, condenser, receiver, and a nitrogen inlet. The mixture was heated under a slow continuous flow of nitrogen to 280°C, held at that temperature for thirty hours; then the reaction mixture was cooled. There was obtained as a reaction product, 1.2 g. (83%) of an infusible, insoluble yellowish-brown polymer. An infrared spectrum of this polymer was recorded. This polymer is insoluble in molten benzylidene-aniline and is converted to a black polymer by further reaction.

Analyses	% C	% H	% N
Calculated	81.55	4.85	13.59
Found	79.98 79.66 79.60 79.46	5.08 5.10 4.81 4.93	12.28 12.38 12.23 12.34

ii) DA-26-198. Reaction of p-Phenylenediamine and Xylylidene-tetraethyl Ether.

A mixture of 14.12 g. of p-phenylenediamine and 5.407 g. of p-xylylidene-tetraethyl ether were reacted in the apparatus of DA-26-25. The reaction time was twenty-five hours at 220-300°C. During the reaction 8.7 g. of ethyl alcohol was collected, leaving 10.5 g. (105% yield) of an infusible yellow-brown polymer. An infrared spectrum of the polymer was recorded. This polymer was also found to dissolve in molten benzylidene-aniline.

b. Discussion.

The polymerization reaction between the diacetal and the diamine was found to proceed easily. When the mixture of the diamine and diacetal was heated, the liberation of alcohol was detected at 84°C at which temperature a partial melt of the reactants occurred, and a complete melt of the monomers observed at 95-100°C. Within fifteen minutes at 100°C a dark-yellow precipitate was formed. On raising the temperature to 280°C and continued heating, a dark-brown polymer was obtained. The polymer obtained in this reaction is darker in color than the polymer obtained by the reaction in solution of the diamine and terephthaldehyde which has been post-heated to the same temperature. The brown polymers of the acetal were also found to be soluble in benzylidene-aniline and to be convertible to black polymers when this solution is heated and further condensation achieved.

This synthesis from the acetal and the amine is similar in behavior in its kinetic aspects to the direct condensation of the dialdehyde and diamine. The elimination rate constant relationships, for the two-stage elimination of alcohol have been shown in Part I of this report to be $k_2 \cong k_1$ or $k_2 > k_1$ and have been verified in these polymerization reactions, so that the isolation of a soluble and/or fusible intermediate is not achieved.

The I.R. spectra of the polymers showed absence of the 690 cm^{-1} and 760 cm^{-1} bands attributed to δ-C-H of the monosubstituted phenyl ring and the presence of marked absorption in the 850 cm^{-1} due to the δ-C-H of the 1,4-substituted phenylene ring. The spectra also showed absorption of 1600 cm^{-1} characteristic of the -C=N- frequency of the Schiff base linkage and a complete absence of acetal linkages. The elemental analyses for C, H, and N compared to the calculated for n = ∞, indicated that the molecular weight of the brown polymer was not high.

2. From Acetals and Amine Hydrochlorides.

The polymerization between the acetal and the amine hydrochlorides can be generalized as

$$n\ HCl\cdot NH_2ArNH_2\cdot HCl + n\ (RO)_2CHArCH(OR)_2 \rightarrow$$

$$4n\ ROH + \left[\begin{matrix}HCl\\ \dot{N}ArN{=}CHArCH\\ \dot{H}Cl\end{matrix}\right]_n \xrightarrow{Na_2CO_3} \left[NArN{=}CHArCH\right]_n \qquad \text{(eq. 67)}$$

and the specific reaction between p-phenylenediamine hydrochloride and p-xylylidenetetraethyl ether is written as

$$n\ HCl\cdot NH_2C_6H_4NH_2\cdot HCl + n\ (H_5C_2O)_2CHC_6H_4CH(OC_2H_5)_2 \rightarrow$$

$$4n\ C_2H_5OH + \left[\begin{matrix}N\text{-}C_6H_4N{=}CHC_6H_4CH\\ \dot{H}Cl\quad\quad \dot{H}Cl\end{matrix}\right]_n \xrightarrow{Na_2CO_3} \left[N\text{-}C_6H_4N{=}CHC_6H_4CH\right]_n \qquad \text{(eq. 68)}$$

The reaction of equation 68 was evaluated in solution and in a melt system. The hydrochlorides from the melt, and the hydrochlorides from the solution after isolation by filtration for the solvent, were dispersed in water (1.0 g. in 10 ml H_2O) and neutralized with 8% aqueous Na_2CO_3. The neutralized polymers were then isolated by filtration and dried in a vacuum dessicator to constant weight.

a. Experimental.

i) DA-26-48-2. The melt-Reaction of p-Phenylenediamine Dihydro-

chloride and p-Xylylidenetetraethyl Ether.

A mixture of 1.0 g. of phenylenediamine hydrochloride and 1.56 g. of p-xylylidenetetraethyl ether were mixed in a microflask equipped with a reflux condenser and a nitrogen inlet. The mixture was heated slowly under a slow stream of nitrogen from room temperature to 220°C, forming a clear melt at 60-80°C. Heating was continued for twenty-four hours, slowly increasing the temperature from 220-280°C and the reaction terminated. The polymer was transferred to ~ 20 cc H_2O, neutralized with 8% aqueous Na_2CO_3 and allowed to stand for four to eight hours. The neutralized polymer was removed by filtration, dried in a vacuum dessicator. The polymer was mostly black with areas of yellow and blue; yield 1.0 g. An I.R. spectrum was recorded.

ii) DA-26-48-1. The Reaction of p-Phenylenediamine Di-hydrochloride and p-Xylylidenetetraethyl Ether in Alcohol.

A solution of 1.0 g. of p-phenylenediamine hydrochloride and 1.56 g. of p-xylylidenetetraethyl ether in 40 ml of ethyl alcohol in a 100 ml flask were heated, under a slow steady stream of nitrogen, to reflux for twenty-four hours. A precipitate formed almost immediately on reflux, and persisted throughout the reaction. After cooling to room temperature the precipitate was removed by filtration, added to ~ 20 cc H_2O, and neutralized with 8% aqueous Na_2CO_3 and allowed to stand for four to eight hours. The neutralized polymer was then removed by filtration, dried in a vacuum dessicator. Yield of yellow polymer ~ 1.0 g.

iii) DA-26-50-1. The Reaction of p-Phenylenediamine Dihydrochloride with p-Xylylidenetetraethyl Ether in N-Methylpyrrolidone at 100°C.

A mixture of 1.0 g. p-phenylenediamine hydrochloride and 1.56 g. of p-xylylidenetetraethyl ether in 40 ml of N-methyl pyrrolidone were reacted by the procedure of DA-26-49-1 for twenty-four hours at 100°C. A precipitate also formed in this reaction; it was isolated, neutralized and dried. Yield

of brown polymer, 1.5 g.

iv) DA-26-50-2. Repeat of DA-26-50-1 at 180-220°C.

The reaction time in this experiment was four hours. A precipitate was also formed in this reaction; it was isolated, neutralized, and dried. Yield, yellow polymer, 1.1 g.

v) DA-26-50-3. Repeat of DA-26-50-2 for Twenty-four Hours.

This reaction was performed at 180-220°C for twenty-four hours. A precipitate was also formed, which was isolated, neutralized, and dried. Yield of brown polymer, 1.2 g. An I.R. spectrum was recorded.

vi) DA-26-49-1. Reaction of p-Phenylenediamine Dihydrochloride with p-Xylylidenetetraethyl Ether in Dimethyl Formamide at 150°C.

The quantities and procedure used in DA-26-48-1 were repeated using 40 ml of dimethyl formamide as the reaction medium instead of ethyl alcohol. The temperature of reaction was 150°C for twenty-four hours, yielding an insoluble precipitate which was isolated, neutralized, and dried. Yield of yellow polymer, 1.5 g.

vii) DA-26-49-2. Repeat of DA-26-49-1 at 100°C.

A precipitate also formed in this reaction; it was isolated, neutralized, and dried. Yield of brown polymer, 1.85 g.

b. Discussion.

The reaction between the diamine hydrochloride and the acetal was found to proceed readily in bulk and in solvents to form the polymer hydrochlorides. The solvents used were alcohol, dimethyl formamide and N-methyl pyrrolidone with the expectation that the polymer hydrochlorides would be sufficiently soluble in them to allow condensations to high molecular weights. The polymer hydrochloride showed poor solubility in the solvents tried in the polymerizations. Further tests with the isolated hydrochlorides in a number of solvents indicated very poor solubility. Judging from the color of the solvent, a

qualitative estimate of the solubilizing ability of some of the solvents was obtained: Dimethyl formamide $\gtrsim$ N-methylpyrrolidone $>$ alcohol $>$ dioxane $\gtrsim$ benzene, toluene, ether, and n-hexane. A greater portion of the neutralized polymer obtained from the melt-reaction was black in color but it was heterogeneous, containing yellow and blue areas. Its I.R. psectrum was similar to the spectrum of the polymer prepared from the acetal and free amine, whereas the I.R. spectra of polymers prepared in N-methyl pyrrolidone gave evidence of incorporation of the pyrrolidone into the polymer.

3. From Acetals and N-Acylamines.

The polymerization reaction of acetals and acylamines can be generalized as

$$n\ RCONRArNHOCR + n\ (RO)_2HCArCH(OR)_2 \rightarrow 2n\ ROH + 2n\ RCOOR + \text{=}\{\text{N-ArN=HCArCH}\}\text{=}_n \qquad \text{(eq. 69)}$$

and the specific reaction between N,N'-diacetyl-p-phenylenediamine and p-xylylidenetetraethyl ether is written as

$$n\ CH_3CONHC_6H_4NHOCCH_3 + n\ (H_5C_2O)_2HCC_6H_4CH(OC_2H_5)_2 \rightarrow 2n\ C_2H_5OH + 2n\ CH_3COOC_2H_5 + \{NC_6H_4N=CHC_6H_4CH\}_n \qquad \text{(eq. 70)}$$

The reaction of equation 70 was evaluated under various conditions and the reaction was performed in a melt system at various temperatures and pressures without and with catalysts as well as in the presence of N,N-dimethylnaphthalamine, N-methylpyrrolidone and polyphosphoric acid. It was also evaluated in melt-solution systems with benzylidene-aniline as the solvent. A modification of the melt-solvent system was also tried which included partially polymerizing the reagents prior to the addition of benzylidene-aniline. Most of the polymers which were prepared were analyzed for C, H, and N, and their infrared spectra recorded and interpreted.

a. Experimental.

i) DA-26-125. The Reaction of p-Xylylidenetetraethyl Ether and N,N'-Diacetyl-p-phenylenediamine.

A mixture of 2.0 g. of the ether and 1.363 g. of the diacylamine were reacted in a microflask equipped with a nitrogen inlet, condenser, receiver, etc., at 170°C for ninety hours under a continuous slow stream of nitrogen. Part of the amide remained undissolved during the reaction. The yellow-white reaction product was allowed to cool and extracted with hexane to remove acetal leaving a product, 1.47 g., m.p. 303-306°C which was washed with alcohol to yield a white product, 1.24 g., m.p. 303-306°C, which was identified by m.p. and I.R. as unconverted amide. No polymer was formed in this reaction.

ii) DA-26-127. Repeat of DA-26-125 at 220°C.

The reaction conditions for this experiment were 220°C for twenty-three hours under a continuous slow stream of nitrogen. The reaction mixture was also heterogeneous as in DA-26-125. Toward the end of the reaction time, the mixture had increased slightly in viscosity and contained insoluble particles. The reaction mixture was treated in a Soxhlet extractor with CH_3COCH and EtOH to yield 1.9 g. of wet, crude pale-white solid which was repurified and shown by m.p. (303-306°C) and I.R. spectrum to be p-$CH_3CONHC_6H_4NHOCCH_3$. The insoluble fraction from the extraction amounted to 0.9 g. (61% of theoretical) of brown polymer which was shown by I.R. spectrum to contain -C=N- structures.

iii) DA-26-129. Repeat of DA-26-125 at 265°C.

The reaction conditions for this experiment were 265°C for three and one-half hours under a continuous slow stream of N_2. The reaction mixture at the early stages was heterogeneous becoming very viscous and almost homogeneous toward the end of the reaction period, yielding a dark-brown polymer mass. The product was extracted with alcohol and its I.R. spectrum was identical to the spectra of polymers obtained by other polymerization methods, such as by p-$C_6H_4(CHO)_2$ and p-$C_6H_4(NH_2)_2$. Yield, 110% of theory.

iv) DA-26-158. Reaction of 10% Excess p-Xylylidenetetraethyl Ether with N,N'-Diacetyl-p-phenylenediamine.

A mixture of 1.65 g. of the acetal and 1.0223 g. of the diacylamide were reacted under nitrogen in the apparatus of DA-26-125 at 175°C for two hours at 100 mm Hg, and then at 210°C at 100 mm Hg for one and one-half hours. Alcohol and ethyl acetate were eliminated during the reaction, which was heterogeneous throughout and not completely liquid. The residue in the flask was a reddish-brown solid which was extracted with acetic acid in a Soxhlet apparatus for eighty-two hours. Yield, 1.055 g. (72%) of insoluble, infusible, dark-brown polymer.

v) DA-26-159. Reaction of 20% Excess of p-Xylylidenetetraethyl Ether with N,N'-Diacetyl-p-phenylenediamines.

The procedure of DA-26-158 was used to react 2.1 g. of the acetal with 1.0223 g. of the diacylamine. The residue in the flask amounted to 1.83 g. and after extraction with acetic acid yielded 1.43 g. (98%) of brownish-black, insoluble, infusible polymer.

vi) DA-26-141. Reaction of p-Xylylidenetetraethyl Ether and N,N'-Diacyl-p-phenylenediamine with Toluene Sulfonic Acid Catalyst at 170°C

A mixture of 2.0 g. of the acetal and 1.363 g. of the diacylamine and 0.12 g. toluene sulfonic acid were reacted in the apparatus of DA-26-125 under nitrogen at 170°C for twenty-eight hours. The reaction mixture became viscous as heating continued, becoming a solid black mass, 1.4 g., toward the end of the reaction. The mass was extracted with alcohol leaving 0.9 g. (64% yield) of black polymer.

vii) DA-26-143. Repeat DA-26-141 at 220°C.

The reaction conditions were 220°C for nineteen hours. Reaction mixture was homogeneous throughout the reaction, and the viscosity increased with

reaction time; the color of the mass changing from yellow to black in the course of the reaction. Yield of black polymer after extraction with CH_3COOH, 1.61 g. (111%).

viii) DA-26-184. Reaction of p-Xylylidenetetraethyl Ether and N,N'-Diacetyl-p-phenylenediamine in Benzylidene-p-chlorcaniline.

A mixture of 2.0 g. of the acetal and 1.363 g. of the diamide in 6.0 g. benzylidene-p-chloroaniline were reacted in a microflask equipped with a N_2 inlet, condenser, receiver, vacuum outlet, etc., for one hour at 220°C at atmospheric pressure, and 0.5 ml of ethyl alcohol collected. Then, during the next two and one-half hours, the pressure was reduced to 100 mm Hg, and there was collected 0.4 ml of a mixture of ethyl alcohol and ethyl acetate. The residue in the flask consisted of 1.15 g. (77%) brownish-black polymer.

ix) DA-26-166. Reaction of p-Xylylidenetetraethyl Ether and N,N'-Diacetyl-p-phenylenediamine in Excess of Benzylidene-aniline.

A mixture of 1.0 g. of the acetal, 0.6815 g. of the diacylamine and 6.0 g. of benzylidene-aniline were reacted in the apparatus of DA-26-125, under a nitrogen atmosphere. The reaction conditions were 185°C for one and one-half hours at atmospheric pressure; 220°C for five hours at atmospheric pressure; 260°C for two hours at 100-200 mm Hg pressure, and 320°C for one and one-half hours at 20 mm Hg pressure. The reaction mixture was homogeneous throughout the period of the reaction with an increase in viscosity as the reaction proceeded, with no further increase until the excess benzylidene-aniline was removed at 20 mm pressure at 320°C, whereat it became very viscous, and finally a black solid. Yield of black polymer, after extraction with alcohol, 1.1 g. (150% of theory). The polymer was soluble in HCOOH and H_2SO_4 but insoluble in $HCON(CH_3)_2$.

x) DA-26-197. Reaction of Xylylidenetetraethyl Ether and N,N'-Diacetyl-p-phenylenediamine in Presence of Benzylidene-aniline.

A mixture of 5.0 g. of the acetal, 3.407 g. of the diamide and 8.000 g. of benzylidene-aniline were reacted in the apparatus of DA-26-184 at 240°C. At the end of sixty minutes 0.75 ml of ethyl alcohol was collected; and at the end of three hundred minutes an additional 2.25 cc of distillate was collected, which was a mixture of ethyl alcohol and ethyl acetate. The distillate amounted, at this stage, to 70% of theoretical. Heating was then continued at 260°C for sixty hours. During the course of the reaction the color of the reaction mixture changed from yellow to brown to black, becoming more viscous as the reaction proceeded, and finally becoming a black solid. Final yield, 135%. During the reaction samples were withdrawn at 100 (DA-26-197), 140 (DA-26-197-2), and 300 (DA-26-197-3) minutes, and I.R. spectra of the reaction products taken.

xi) DA-26-133. Reaction of p-Xylylidenetetraethyl ether and N,N'-Diacetyl-p-phenylenediamine in N,N'-Dimethylnaphthalamine at 170°C.

A mixture of 2.0 g. of the acetal, 1.363 g. of the diacylamine and 8 ml of N,N'-dimethylnaphthylamine were reacted in the apparatus of DA-26-125 in an atmosphere of N_2. The reaction conditions were 170°C for twenty-four hours at atmospheric pressure and forty-two hours at 100 → 70 mm Hg. The reaction mixture was homogeneous, darkening in color and increasing in viscosity as the reaction proceeded. When terminated, the product was a dark-brown viscous liquid even at room temperature. After washing with hexane there remained 6.3 g. of a hexane-insoluble oily product. This product was dissolved in acetone leaving 0.8 g. of acetone-insoluble brown-yellow material. From the acetone solution there was recovered by precipitation with alcohol 1.8 g. of crude solid which was recrystallized from alcohol and identified as unreacted N,N'-diacetyl-p-phenylene-diamine.

xii) DA-26-135. Repeat of DA-26-133 at 220°C.

The reaction conditions were 220°C for thirty-two and one-half hours at atmospheric pressure under N_2. The reaction product was extracted as before, and the white, acetone-insoluble product amounted to 1.4 g., and the creamy-colored acetone-soluble product, to 3.1 g.

xiii) DA-26-137. Reaction of p-Xylylidenetetraethyl Ether and N,N'-Diacetyl-p-phenylenediamine in N-Methylpyrrolidone at 200°C.

A mixture of 2.0 g. of the acetal, 1.363 g. of the diacylamine and 10.0 g. of N-methylpyrrolidone were reacted in the apparatus of DA-26-125 at 200°C for seventeen and one-half hours under a slow stream of nitrogen. The mixture became homogeneous within five minutes after the start of the reaction with the formation of a yellow color changing to dark-brown at the end of the reaction period. The product of the reaction was a dark, viscous liquid which was dissolved in ethyl alcohol, leaving 1.7 g. (116%) of a brown polymer product.

xiv) DA-26-139. Repeat of DA-26-137 at 253°C.

The reaction conditions were 253°C for eight hours. The color of the homogeneous solution was brownish-yellow which became a black solid at the end of eight hours of reaction, from which there was isolated 2.2 g. (150% yield) of black, infusible polymer.

xv) DA-26-149. Reaction of p-Xylylidenetetraethyl Ether and N,N'-Diacetyl-p-phenylenediamine in Polyphosphoric Acid.

A mixture of 1.0 g. of the acetal and 0.6815 g. of the diacylamine in 10.0 g. of polyphosphoric acid were reacted in the apparatus of DA-26-125 at 170°C for twenty hours under a slow stream of N_2. The solution became viscous and dark-brown during the reaction and did not solidify on cooling. The reaction mixture was poured into 200 ml of ethanol; the solid separated by filtration and treated in a Soxhlet extractor with ethanol. The yield of

reddish-brown polymer was 1.7 g. (230%).

xvi) DA-26-151. Repeat of DA-26-149 at 220-260°C.

The reaction conditions were 220°C for twenty-three and one-half hours and 260°C for five hours. The changes in color, viscosity and the final product were similar to that obtained in DA-26-149. The yield of brownish-black polymer after extraction with alcohol was 2.1 g. (288%).

xvii) DA-26-145. Reaction of p-Xylylidenetetraethyl Ether, N,N'-Diacetyl-p-phenylenediamine with Toluene Sulfonic Acid in N-Methylpyrrolidone.

A mixture of 2.0 g. of the acetal, 1.363 g. of the diamide, 7.0 g. of N-methylpyrrolidone and 0.12 g. of toluene sulfonic acid were reacted in the apparatus of DA-26-125. The reaction conditions were 170°C for twenty-two hours at atmospheric pressure and eighteen hours at 220°C at 200 mm Hg pressure. The reaction mixture was dark-brown and very viscous. After extraction of the reaction product with CH_3COOH and C_2H_5OH there remained 1.87 g. (129%) of black polymer.

xviii) DA-26-152. Repeat of DA-26-145 Under Modified Conditions.

A mixture of 1.0 g. of the acetal, 0.6815 g. of the diamide, 3.0 g. of N-methylpyrrolidone and 0.1 g. of toluene sulfonic acid were reacted under a nitrogen atmosphere at 170°C at atmospheric pressure for three hours; at 215°C for fifteen and one-half hours; and then at 250°C for six and one-half hours at 200 mm Hg pressure, to yield a black solid mass which, after extraction with alcohol, yielded 1.2 g. (165%) of black polymer.

xix) DA-26-153. Repeat of DA-26-152 with Excess Acetal.

A mixture of 1.2 g. of acetal, 0.6815 g. of the diamide, 3.0 g. of N-methylpyrrolidone and 0.1 g. of toluene sulfonic acid were reacted under conditions identical to DA-26-152 and there was isolated 1.4 g. (192%) of black polymer.

xx) DA-26-154. Partial Reaction of p-Xylylidenetetraethyl Ether, N,N'-Diacetyl-p-phenylenediamine and N-Methylpyrrolidone Before Addition of Toluene Sulfonic Acid.

A mixture of 2.0 g. of acetal, 1.363 g. of the diamide and 3.0 g. of N-methylpyrrolidone were reacted under nitrogen in the apparatus of DA-26-125 at 210°C for three hours at atmospheric pressure, then 0.1 g. of toluene sulfonic acid added and the reaction continued at 240°C for twelve hours; at 265°C for four hours at 100 mm Hg pressure. A yellow color developed with the first ten minutes of reaction, which was heterogeneous, becoming homogeneous after fifteen minutes reaction time. The viscosity increased continuously and was noticeably viscous at the end of sixty minutes. When the reaction was terminated, it was a black solid. After extraction with acetic acid, there was obtained 2.6 g. (185%) of a black polymer.

xxi) DA-26-155. Repeat of DA-26-154 With Excess Acetal.

The reagents and procedure were identical to that of DA-26-154, except that 2.4 g. of acetal instead of 2.0 g. was used. The yield of black, insoluble, infusible polymer after extraction was 2.7 g. (185%).

xxii) DA-26-178. Reaction of p-Xylylidenetetraethyl Ether, N,N'-Diacetyl-p-phenylenediamine with Toluene Sulfonic Acid in Benzylidene-aniline.

A mixture of 2.045 g. of the acetal, 3.0 g. of the diamide and 0.2 g. of toluene sulfonic acid and 7.0 g. of benzylidene-aniline were reacted under nitrogen in the apparatus of DA-26-125 at 220°C for two and one-half hours at atmospheric pressure; at 250°C for twenty-one hours at 150 mm Hg; and at 360°C for twenty hours at 3 mm Hg pressure to yield a viscous solution which solidified on cooling. The product was extracted in a Soxhlet extractor with ethyl alcohol for five days to give 7.8 g. (354%) of black insoluble polymer.

xxiii) DA-26-167. Partial Reaction of p-Xylylidenetetraethyl Ether and N,N'-Diacetyl-p-phenylenediamine Before Addition of Benzylidene-aniline.

A mixture of 1.0 g. of the acetal, and 0.6815 g. of the diamide were reacted in the apparatus of DA-26-125 under a nitrogen atmosphere at atmospheric pressure for six and one-half hours at 220°C, with the formation of a brown solid polymer. Then to the mixture was added 6.0 g. of benzylidene-aniline, and on addition, dissolution of the solid occurred. The reaction was continued for twelve additional hours at 220°C; then at 200 mm Hg pressure at 260°C for two hours, and at 20 mm at 320°C for four hours. The viscosity of the reaction mixture increased as a function of time, and the product was a black solid at the end of the reaction time. The product was extracted with ethyl alcohol in a Soxhlet apparatus for ten hours and there was obtained 0.8 g. (109%) of a black polymer which was soluble in HCOOH and H_2SO_4.

xxiv) DA-26-169. Modified Repeat of DA-26-167.

A mixture of 2.0 g. of acetal and 1.363 g. of diamide were reacted in a nitrogen atmosphere at 130°C for thirty-one hours producing a completely solid brown polymer mass; then there was added 4.0 g. of benzylidene-aniline and dissolution of the solid occurred and the reaction temperature raised to 320°C for three and one-half hours. As the reaction progressed the viscosity increased markedly and the color changed to black. The reaction product was extracted with alcohol for eighty-two hours in a Soxhlet apparatus and there was obtained 1.4 g. (100% of theory) of a black polymer which was soluble in HCOOH and H_2SO_4.

xxv) DA-26-179. Catalyzed Partial-Reaction of p-Xylylidenetetraethyl Ether with N,N'-Diacetyl-p-phenylenediamine Before Addition of Benzylidene-aniline.

A mixture of 3.0 g. of the acetal, 2.045 g. of the diamide and 0.2 g.

of toluene sulfonic acid were reacted under a nitrogen atmosphere in the apparatus of DA-26-125 at 220°C at atmospheric pressure for two and one-half hours; then 6.0 g. of benzylidene-aniline were added and the reaction continued at 250°C at 150 mm Hg pressure for twenty-one hours; and at 360°C at 3 mm Hg pressure for twenty hours. The reaction product was isolated and extracted with ethyl alcohol in a Soxhlet apparatus to yield 6.5 g. (300%) of a black insoluble polymer.

xxvi) DA-26-168. Partial Reaction Product of Xylylidenetetraethyl Ether and N,N'-Diacetyl-p-phenylenediamine in Nitrobenzene Before Addition of Benzylidene-aniline.

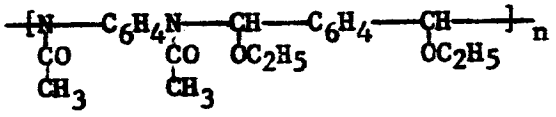
A mixture of 2.0 g of the acetal, 1.63 g. of the diamide and 10.0 g. of nitrobenzene were reacted in the apparatus of DA-26-125 under a nitrogen atmosphere at 180°C for fifty-two hours at atmospheric pressure. The mixture was homogeneous with the formation of light-brown color with little or no change in viscosity. Then 3.0 g. of benzylidene-aniline were added and the temperature raised to 240°C for twelve hours during which time the solvent distilled from the mixture and the reaction mass darkened to a black solid. The solid was extracted with ethyl alcohol in a Soxhlet apparatus and there was obtained 1.8 g. (124% yield) of black polymer, speckled with small amounts of yellow solid. The polymer was soluble in HCOOH and H_2SO_4.

b. Discussion.

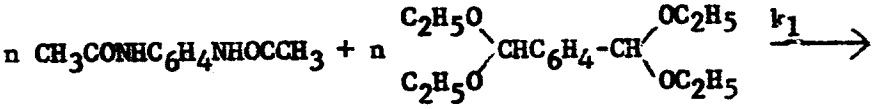
The uncatalyzed reaction of the acetal and the acylamid ewas found to proceed very slowly or not at all at melt temperarures, but it did proceed at temperatures of ~ 265°C or higher. However, the reaction was readily catalyzed by toluene sulfonic acid so that it proceeded at a temperature of about 170°C.

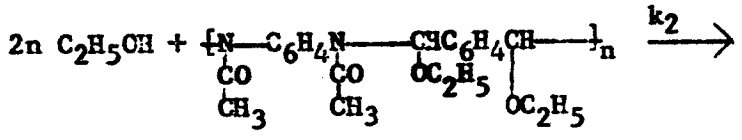
The I.R. spectra of the polymer products were those of a typical poly-Schiff base. It was also determined that the polymerization reaction pro-

ceeded in two steps with elimination of alcohol preceeding the elimination of ethyl acetate. This was clearly shown in DA-26-184 in which 0.5 ml of ethyl alcohol was collected in the first hour of reaction, and 0.4 cc of a mixture of ethyl alcohol and ethyl acetate were collected in the next two and one-half hours. A similar observation was made in DA-26-197 in which 0.75 ml of alcohol were collected in the first hour of reaction and 2.25 ml of an alcohol-ethyl acetate mixture collected during the next four hours, establishing the existence of the intermediate polymer:

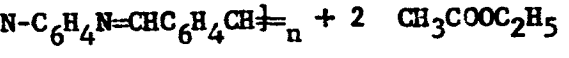


This intermediate arises from the reaction





soluble



insoluble

(eq. 71)

The soluble intermediate eliminates $CH_3COOC_2H_5$ at a rate k_2 which is smaller than the k_1 for the elimination of ethyl alcohol. These results are in accord with the mechanism proposed in Part I of this report for the equivalent non-polymeric reactions.

From the high yields obtained and from the I.R. spectra, the reactions performed in N-methyl pyrrolidone and polyphosphoric acid were shown to contain substantial quantities of these solvents which obviously could co-react in the system to produce copolymerization products. The yield data and the spectra of polymers prepared in N,N-dimethylnaphthylamine also showed

that substantial amounts, after extraction with solvents for the N,N-dimethylnaphthylamine, were tenaciously held in the polymer; and since it seems to lack reactive groups, the assumption that complexes or adducts are formed with the polymers, appears plausible.

The yields of polymers were also high when the reactions were performed in benzylidene-aniline, indicating that telomerization by exchange with the polymer occurs in the melt-solution system; and that, in addition, benzylidene-aniline could also be complexed with the polymer. The larger yields, that is, those exceeding 100% of theory appear to be favored by the presence of catalysts, a condition observed earlier in this report as favoring exchange reactions.

In general, it was found that the uncatalyzed reactions were best from the viewpoint of preparing soluble polymers and that these could be converted to insoluble, infusible black polymers. This conversion was simplified, however, by the addition of benzylidene-aniline to the partially reacted system. However, from the viewpoint of preparing fusible polymers, soluble in HCOOH or H_2SO_4, which varied in color from dark-brown to black, the uncatalyzed reaction in benzylidene-aniline appears to be the best method.

4. From Acetals and Schiff Bases.

The polymerization reaction of acetals and Schiff bases can be generalized as

$$n\ (RO)_2CHArCH(OR)_2 + n\ ArCH{=}NArN{=}CHAr \rightarrow 2n\ ArCH(OR)_2 + {=}\left[NArN{=}CH\text{-}ArCH\right]_n{=} \qquad \text{(eq. 72)}$$

and the specific reaction between p-xylylidenetetraethyl ether and dibenzylidene-phenylenediamine as

$$n\ (C_2H_5O)_2CHC_6H_4CH(OC_2H_5)_2 + n\ C_6H_5CH{=}NC_6H_4N{=}HCC_6H_5 \rightarrow 2n\ C_6H_5CH(OC_2H_5)_2 + {=}\left[NC_6H_4N{=}CHC_6H_4CH\right]_n{=} \qquad \text{(eq. 73)}$$

The reaction of equation 73 was evaluated under the various conditions of

time, temperature, catalyst, and in melt, solution, and melt-solution systems similar to the studies performed for the reaction of the acetals with the acylamines. The solvents investigated in this case were also N,N-dimethyl-naphthylamine, N-methylpyrrolidone, polyphosphoric acid, and benzylidene-aniline. In the catalyzed system, toluene sulfonic acid was used as the catalyst.

Most of the polymers which were prepared were analyzed for C, H, and N and their I.R. spectra recorded and interpreted.

a. Experimental.

In the following reactions, the apparatus consisted of a microflask equipped with a nitrogen inlet, thermometer, distilling head, condenser, receiver, vacuum outlet and a metal-alloy bath heated by an electric mantle. The general procedure consisted in introducing the reagents into the flask, sweeping out the air with N_2 and then heating the reagents while a slow stream of nitrogen is passed through the mixture, at the temperatures and pressures for the indicated times while collecting by-product benzylidene-diethyl ether, at the end of the reaction time the residue in the flask allowed to cool. In some cases this was the final product; in other cases, where indicated, the product was fractionated or extracted to separate polymer and other products.

i) DA-26-124. Reaction of p-Xylylidenetetraethyl Ether and Di-Benzylidene-p-phenylenediamine at 190°C.

A mixture of 2.0 g. of the acetal and 2.018 g. of the Schiff base were heated for ninety hours at 170°C at 500 mm Hg pressure. At the end of the reaction the mixture was then a liquid at 170°C but solid at room temperature, and was dark-brown in color. Benzylidenediethyl ether was collected as a distillate. By washing and extracting the solid with alcohol and hexane,

six fractions were isolated, five of which showed low melting points in the range of 105-190°C, totalling 3.55 g. One fraction, 0.3 g., was golden yellow and polymeric and its I.R. spectrum showed presence of -C=N- structures.

ii) DA-26-126. Repeat of DA-26-124 at 220°C.

The reaction time was twenty-three hours. The viscosity of the mixture increased noticeably as the reaction proceeded with a color change from yellow to dark brown at the end of the reaction; the product was very viscous when hot and it solidified in cooling. The product was separated into three fractions by means of hexane; two of which showed low melting points in the range of 105-107°C, 2.5 g. One fraction (1.3 g.) was yellowish-brown and polymeric; its I.R. spectrum showed presence of -C=N- bonds.

iii) DA-26-128. Repeat of DA-26-124 at 265°C.

The reaction time was six hours. The viscosity of the mixture increased rapidly during the reaction with a corresponding color change to black. The product was solid when hot at the end of the reaction. It was treated in a Soxhlet extractor with acetic acid for thirty-two hours and with ethyl alcohol, leaving 1.9 g. of black, solid, infusible polymer.

iv) DA-26-132. Reaction of p-Xylylidenetetraethyl Ether and Dibenzylidene-p-phenylenediamine in N,N-Dimethylnaphthylamine at 170°C.

A mixture of 2.0 g. of the acetal, 2.018 g. of the Schiff base and 10 ml of N,N-dimethylnaphthylamine were reacted at 170°C for twenty-four hours at 170 mm Hg and for twenty-two hours at 100 mm. At the end of the reaction, the hot mixture was of low viscosity and light-brown in color; it did not solidify on cooling. A yellow precipitate was obtained by the addition of 25 ml of hexane to the reaction mixture. The precipitate was removed by filtration, and recrystallized from acetone; yield of yellow product, 2.9 g. (198%), m.p. 185-195°C.

v) DA-26-134. Repeat of DA-26-132 at 220°C.

The reaction time was thirty-two and one-half hours at 170 mm Hg pressure. The final reaction product was brown and of low viscosity and became a sticky viscous mass on cooling to room temperature. It was dissolved in acetone and reprecipitated by the addition of ethyl alcohol; yield, yellow polymer, 5.4 g. (370%),m.p. 155-160°C. Its infrared spectrum showed no -C=N- peaks.

vi) DA-26-136. Reaction of p-Xylylidenetetraethyl Ether and Dibenzylidene-p-phenylenediamine in N-Methylpyrrolidone at 200°C.

A mixture of 2.0 g. of the acetal, 2.0189 g. of the Schiff base in 10.0 g. N-methylpyrrolidone were reacted at 200°C for seventeen and one-half hours at 700 mm Hg pressure. In the course of the reaction the mixture changed from light-yellow to a dark-brown color with a marked increase in viscosity, becoming a solid at the end of the reaction. It was dissolved in acetone and reprecipitated by the addition of ethanol. Yield 1.4 g. (95%) of dark-brown polymer. Its infrared spectra showed the presence of small amounts of -C=N- structures.

vii) DA-26-138. Repeat of DA-26-136 at 253°C.

The reaction proceeded very rapidly at this temperature and the final reaction product was a black solid which was dissolved in acetone and reprecipitated by the addition of ethanol. Yield, 2.2 g. (150%) dark-brown polymer.

viii) DA-26-148. Reaction of p-Xylylidenetetraethyl Ether and Dibenzylidene-p-phenylenediamine in Polyphosphoric Acid at 170°C.

A mixture of 1.0 g. of the acetal, 1.0 g. of the Schiff base in 10.0 g. of polyphosphoric acid were reacted at 760 mm at 170°C for twenty hours. No distillate was collected from this reaction which, at the end of the reaction time, was a dark-brown viscous liquid. The product was poured into ethyl alcohol and there was isolated as a precipitate 1.7 g. (230%) of a yellow-

brown fusible polymer which contains combined phosphorous.

ix) DA-26-150. Repeat of DA-26-148 at Higher Temperatures.

The reaction conditions were 220°C for twenty-three and one-half hours and 260°C for five hours at atmospheric pressure. The reaction product was a black viscous solution which was poured into alcohol and there was obtained 1.8 g. (240%) of a dark-brown polymer which contains combined phosphorous.

x) DA-26-164. Reaction of p-Xylylidenetetraethyl Ether and Dibenzylidene-p-phenylenediamine in Benzylidene-aniline.

A mixture of 1.0 g. of the acetal, 1.0 g. of the Schiff base and 7.0 g. of benzylidene-aniline were reacted at 220°C for seven and one-half hours at 100 mm; 260°C for twenty-one and one-half hours at 50 mm; and 260°C for two hours at 2 mm Hg pressure. On heating, the color of the solution became black and the mixture showed noticeable increase in viscosity after seven and one-half hours of reaction but was not converted to a solid by the end of the reaction time. However, it became a black solid on cooling to room temperature. When the product was extracted with acetic acid, no insoluble products were obtained, indicating that the black polymer was of low molecular weight and soluble in acetic acid.

xi) DA-26-170. Reaction of p-Xylylidenetetraethyl Ether and Benzylidene-p-phenylenediamine in a Reduced Amount of Benzylidene-aniline.

A mixture of 0.8043 g. of the acetal, 0.8043 g. of the Schiff base and 1.5 g. of benzylidene-aniline were reacted at 220°C for four hours at 100 mm; 240°C for twelve hours at 180 mm; and 320°C for three and one-half hours at 20 mm Hg pressure. The reaction mixture became black and viscous at 220°C and solidified within one hour at 320°C. The product, after extraction with alcohol, was a black solid polymer, 0.7 g. (110%) which was soluble in conc. H_2SO_4 and partially soluble in HCOOH.

xii) DA-26-173. Repeat of DA-26-170 Under Different Conditions.

The amounts used were four times the quantity of DA-26-173 and the reaction conditions were 220°C for twenty-five hours at 100 mm; 330°C for three hours at 100 mm, at which a sample (1) was withdrawn; and 300°C for five hours at 150 mm Hg pressure. When sample (1) was removed it was a sticky dark-brown solid at this temperature, but solidified at room temperature; it was soluble in HCOOH and H_2SO_4 and partially soluble in dimethylformamide. The final reaction product was black and insoluble in the solvents. Yield of black polymer, 2.8 g. (110%).

xiii) DA-26-165. Addition of Benzylidene-aniline to Partial-Reaction Product of p-Xylylidenetetraethyl Ether and Dibenzylidene-p-phenylenediamine.

The quantities and reaction conditions were the same as DA-26-164 except that the benzylidene-aniline was added to the reaction flask seven and one-half hours after the acetal and Schiff base had reacted. Within the first seven and one-half hours of reaction, the mixture had become a dark-brown solid and on the addition of benzylidene-aniline a clear viscous solution was formed which remained viscous to the end of the reaction but solidified on cooling. After extraction with ethyl alcohol there remained 1.7 g. (233%) of brown polymer soluble in HCOOH and H_2SO_4.

xiv) DA-26-171. Modification of DA-26-165.

In this modification there was used 2.0 g. of the acetal, 2.01 g. of the Schiff base and 3.0 g. of benzylidene-aniline which was added after four hours of reaction. The reaction conditions were: four hours at 220°C at 100 mm; twelve hours at 245°C at 70 mm; and thirty-five hours at 320°C at 20 mm Hg pressure. The addition of the benzylidene-aniline caused dissolution of the brown polymer formed in the first four hours, and the solution remained as a viscous liquid which solidified in the first hour at

320°C. After extraction of the solid with ethyl alcohol there remained 1.9 g. (130%) of black polymer soluble in HCOOH and H_2SO_4.

xv) DA-26-174. Modification of DA-26-171.

In this modification, the ratio of benzylidene-aniline to reactants was increased using 4.0 g. of the acetal, 4.036 g. of the Schiff base and 12.0 g. of benzylidene-aniline, which was added after twenty-five hours of reaction. The reaction conditions were: twenty-five hours at 220°C at 100 mm Hg; five hours at 270°C at 150 mm Hg; three hours at 330°C at 100 mm Hg (sample (1) withdrawn); five hours at 330°C at 150 mm Hg. After extraction of the solid reaction product with ethyl alcohol there remained 4.35 g. (113%) of black polymer, insoluble in HCOOH and H_2SO_4, whereas sample (1) was found to be soluble in HCOOH and H_2SO_4.

xvi) DA-26-140. Reaction of p-Xylylidenetetraethyl Ether and p-Benzylidene-p-phenylenediamine with a Catalyst at 170°C.

A mixture of 2.0 g. of the acetal, 2.018 g. of the Schiff base and 0.120 g. of toluene sulfonic acid were reacted at 170°C for twenty-nine hours at 40 mm Hg pressure. On initial heating the mixture became homogeneous, slowly solidifying and at the end of one hour the mass was completely solid. In the course of the reaction the color of the solid product changed from yellow to brown. The product was treated with acetic acid in a Soxhlet extractor leaving 2.5 g. (113%) brownish-yellow infusible polymer.

xvii) DA-26-142. Repeat of DA-26-140 at 220°C.

The reaction conditions were 220°C for nineteen hours at 100 mm Hg pressure. After extraction with ethyl alcohol for five hours followed by acetic acid for three hours, there remained 2.47 g. (168%) of a reddish-brown infusible polymer.

xviii) DA-26-146. Reaction of p-Xylylidenetetraethyl Ether and Dibenzylidene-p-phenylenediamine in N-Methylpyrrolidone with a

Catalyst.

A mixture of 2.0 g. of the acetal, 2.018 g. of the Schiff base, 6.0 g. of N-methylpyrrolidone and 0.12 g. of toluene sulfonic acid were reacted at 170°C for three hours at 200°C; for three hours at 500 mm Hg pressure; then at 250°C for four hours at 20 mm. At the beginning of the reaction the solution became clear; then a small amount of precipitate formed which re-dissolved; and in three hours the reaction product became dark and viscous, becoming converted to a black solid mass at the end of the reaction. After extraction of the solid with acetone, alcohol and acetic acid, there remained 2.9 g. (200%) of black polymer. Its infrared spectrum showed the presence of N-methylpyrrolidone units in the polymer.

xix) DA-26-147. Repeat of DA-26-146 with Acetal in Excess.

A mixture of 1.7 g. of acetal, 1.085 g. of Schiff base, 5.0 g. of N-methylpyrrolidone and 0.1 g. of p-toluene sulfonic acid were reacted under conditions identical to DA-26-146. The yield of black polymer, after extraction was 1.9 g. (240%), and its infrared spectrum showed the presence of N-methylpyrrolidone in the polymer.

xx) DA-26-176. Reaction of p-Xylylidenetetraethyl Ether, Dibenzylidene-p-phenylenediamine in Benzylidene-aniline and Catalyst.

A mixture of 3.000 g. of the acetal, 3.027 g. of the Schiff base, 8.0 g. of benzylidene-aniline and 0.5 g. of toluene sulfonic acid were reacted at 100 mm for four hours at 220°C and sixteen hours at 240°C; four hours at 265°C at 20 mm; two hours at 300°C at 2 mm; and twenty-one hours at 250°C at 2 mm Hg pressure. The reaction product remained viscous throughout the entire period and never became solid even when cooled to room temperature. After extraction of the reaction product with alcohol there remained 8.8 g. of black polymer which was soluble in H_2SO_4 and partially soluble in HCOOH.

xxi) DA-26-179. Addition of Benzylidene-aniline to the Catalyzed Partial Reaction of Dibenzylidene-p-pheuylenediamine, p-Xylylidenetetraethyl Ether and Toluene Sulfonic Acid.

A mixture of 3.000 g. of the acetal, 3.027 g. of the Schiff base and 0.50 g. of toluene sulfonic acid were reacted at 220°C for four hours at 100 mm; then at 240°C for sixteen hours at 100 mm Hg pressure, yielding a dark-brown solid. At this point, 8.0 g. of benzylidene-aniline was added, causing complete dissolution of the mass. The reaction was continued at 265°C for four hours at 20 mm; at 300°C for two hours at 2 mm; and at 350°C for twenty-one hours at 2 mm Hg pressure to produce a viscous black reaction mass which did not become solid at the reaction temperatures but which solidified on cooling. After extraction of the solid with ethyl alcohol there remained 6.2 g. (205%) of black polymer which was soluble in HCOOH and H_2SO_4.

b. Discussion.

The uncatalyzed melt reaction between the acetal and the Schiff base to produce a polymer was found to proceed very slowly at 170°C; moderately fast at 220°C to produce a brown polymer, and rapidly at 265°C to give a black polymer. Catalysis with toluene sulfonic acid accelerated the reaction markedly even at 170°C. The I.R. spectra of the polymers showed them to be similar to the Schiff base type polymers prepared from the aldehyde and amine. The distillate from the reaction was shown to be benzylidenediethyl ether as expected from the mechanism of the reaction.

When the reactions were performed in N,N-dimethylnaphthylamine, or N-methylpyrrolidone or in polyphosphoric acid, yields greatly in excess of the 100% theoretical were obtained, even after the polymer was subjected to extended periods of extraction with extractants in which the solvent was soluble. The I.R. spectra of these extracted high-yield polymers showed bands characteristic of the polymerization solvent, indicating, as was shown in

the reactions of the acetals with the acylamines, copolymerization of such solvents as N-methylpyrrolidone or complex formation with N,N-dimethylnaphthylamine.

Higher than theoretical yields were also obtained in the melt-solution systems with benzylidene-aniline; this can be attributed in part to the existence of a Schiff-exchange reaction. In all cases the tendency to higher than theoretical yield was increased by the presence of catalysts.

However, yields close to theoretical were obtained in the polymerizations performed in bulk and in solution-melt in benzylidene-aniline. From the viewpoint of preparing fusible and soluble black polymers, the uncatalyzed reaction of the acetal and Schiff base in benzylidene-aniline, or a modification of this reaction which consists in adding benzylidene-aniline to a partially condensed system of acetal and Schiff base, appear to be satisfactory.

D. From Aldehydes and N-Acylamines.

The polymerization reaction of aldehydes and acylamines can be generalized as

$$n\ OHCArCHO + n\ RCONHArNHOCR \rightarrow 2n\ RCOOH + \frac{1}{2}HCArCH{=}NArN{=}\frac{1}{2}_n \qquad \text{(eq. 74)}$$

and the specific reaction between terephthaldehyde and N,N'-diacetyl-p-phenylenediamine is written as

$$n\ OHCC_6H_4CHO + n\ CH_3CONHC_6H_4NHOCCH_3 \rightarrow 2\ CH_3COOH + \frac{1}{2}HCC_6H_4CH{=}NC_6H_4N{=}\frac{1}{2}_n \qquad \text{(eq. 75)}$$

This type of reaction was found in Part I to be unpromising. However, the reaction of equation 75 was evaluated to determine whether or not polymer formation occurs and if any -C=N- structures appear in the polymer if a polymer is formed. The reaction was studied in uncatalyzed and catalyzed melt systems.

1. Experimental.

a. DA-26-59. Reaction of Terephthaldehyde and N,N'-Diacetyl-p-phenylenediamine Without Catalyst.

A mixture of 1.0 g. of terephthaldehyde and 1.4 g. of N,N'-diacetyl-p-phenylenediamine was heated in a microflask for thirty-five hours at 220°C in an atmosphere of nitrogen. During the reaction, trace amounts of terephthaldehyde sublimed from the reaction. The mixture was cooled and there was isolated 2.2 g. of a brown polymeric, infusible solid. The infrared spectrum was taken and no -C=N- linkage could be identified in the spectrum.

b. DA-26-70. Reaction of Terephthaldehyde and N,N'-Diacetyl-p-phenylenediamine With Catalyst.

The procedure of DA-26-59 was used and a mixture of 1.0 g. of terephthaldehyde, 1.39 g. of N,N'-diacetyl-p-phenylenediamine, and 0.1 g. of toluene sulfonic acid were reacted for thirty-five hours at 220°C. There was obtained 2.1 g. of a dark-brown infusible polymer whose I.R. spectrum showed the absence of -C=N- structures.

2. Discussion.

The uncatalyzed reaction between terephthaldehyde and N,N'-diacetyl-p-phenylenediamine proceeded with reluctance even at 220°C, but more readily in the presence of toluene sulfonic acid. Polymer products were obtained in both cases whose I.R. spectra showed the absence of -C=N- peaks even though the polymers were brown. This reaction evidently does not proceed according to the reaction given in equation 75, and is considered as unsatisfactory for the preparation of polymeric azo-methines.

E. From Schiff Bases and N-Acylamines.

The polymerization reaction of Schiff bases and N-acylamines can be generalized as

$$n\ ArN{=}CHArCH{=}NAr + n\ RCONHArNHOCR \rightarrow 2n\ RCONHAr + \{CHArCH{=}NArN\}_n \qquad \text{(eq. 75)}$$

and the specific reaction between p-xylylidene-dianiline and N,N'-diacetyl-p-phenylenediamine as

$$n\ C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5 + n\ CH_3CONHC_6H_4NHOCCH_3 \rightarrow$$
$$2n\ CH_3CONHC_6H_5 + \left[HCC_6H_4CH{=}NC_6H_4N\right]_n \qquad \text{(eq. 77)}$$

This type of reaction was found in Part I not to be very promising for the syntheses of Schiff bases. However, the reaction of equation 77 was evaluated to determine whether or not polymer formation occurs; and if a polymer is obtained, to determine whether or not it possesses -C=N- structures.

1. Experimental.

a. DA-26-246. Reaction of N,N'-Diacetyl-p-phenylenediamine and p-Xylylidene-dianiline Without Catalyst.

A mixture of 2.0 g. of N,N'-diacetyl-p-phenylenediamine and 2.96 g. of p-xylylidene-dianiline was heated in a reaction flask equipped with condenser, etc., at 260°C for twenty-four hours at 20 mm Hg pressure. The reaction mixture was heterogeneous containing small amounts of unmelted reagents during most of the reaction period. After twenty-four hours at 260°C the mixture was cooled and examined. The product was not polymeric. By extraction with alcohol and recrystallization of the alcohol-soluble and insoluble portions substantially all of the reagents were recovered unchanged.

b. DA-26-248. Reaction of N,N'-Diacetyl-p-phenylenediamine and p-Xylylidene-dianiline with Catalyst.

A mixture of 2.9 g. of N,N'-diacetyl-p-phenylenediamine, 2.96 g. of p-xylylidene-dianiline and 0.1 g. of toluene sulfonic acid were reacted in the apparatus of DA-26-246 at 260°C for twenty-four hours at 20 mm Hg pressure. During the course of the reaction there was collected 0.45 g. of aniline as distillate and 0.35 g. of N,N'-diacetyl-p-phenylenediamine as a sublimate. After twenty-four hours reaction time, the product was cooled;

it was a yellow, brittle polymeric solid. The yield was 140% in reference to the expected Schiff base, indicating that the elimination reaction was far from complete. The infrared spectra of the polymer did not show the presence of -C=N- structures.

2. Discussion.

The uncatalyzed reaction between N,N'-diacetyl-p-phenylenediamine failed to react at 260°C within twenty-four hours. Reaction, however, was achieved at this temperature when toluene sulfonic acid was used as a catalyst. The yield of the polymeric product was much higher than expected if a Schiff base had formed. The I.R. spectrum of the polymer showed the absence of -C=N- linkages. This reaction evidently does not proceed according to that given in equation 77, and is considered as not applicable to the syntheses of polymeric azo-methines.

F. The Problems in Molecular Weight Determination.

Preliminary studies on these polymers indicated that major difficulties would be encountered in the determinations of their molecular weights. In these considerations the polymers of complex composition or structures which were prepared in polyphosphoric acid, N-methyl pyrrolidone, dimethylnaphthaline, etc., were discarded.

The molecular weights of polymers are usually derived from suitable physical measurements of dilute polymer solutions. The most commonly used methods derive a molecular weight average from measurement of osmotic pressure, solution viscosity or light scattering to yield a number average, a viscosity average or a weight average, respectively.

1. The Problem Involving Solutions.

It is known[49] that polyconjugated polymers become insoluble and infusible at low degrees of polymerization, and solution methods cannot be used to determine their molecular weights. The poly-Schiff bases of this inves-

tigation are polyconjugated; they fall within this insolubility pattern and become insoluble at relatively low degrees of polymerization.

By interrupting the polymerization at low degrees of conversion, it may be possible to determine the molecular weights of these interrupted polymers by solution methods. Since they are condensation-type polymers, they can be expected to follow the weight-average and number-average distribution shown by Flory.[50] At low conversions the number of monomer molecules is more plentiful than polymer species and that the molecular weight of the most prevalent polymer is indeed low; and its molecular weight will shift to higher values with conversion. Information of this type is useful in determining the conversion at which initial insolubility occurs, but is of little or no value in correlating physical properties with molecular weight in the insolubility range.

The terms "solubility" and "solution" when applied to the poly-Schiff bases require clarification. Most of the reaction pairs used in the polymer preparations in these studies are soluble in many of the common organic solvents such as alcohol, acetone, benzene, toluene, etc., and these solvents have been used in these studies to extract unconverted reagents from their derived polymers. The yellow, orange, red, brown, and black polymers are insoluble in these types of solvents. Yet the yellow, red, brown, and some black polymers were found to be soluble in 98+% formic acid, acetic acid, and acetic anhydride, concentrated sulfuric acid and in a saturated solution of sodium bisulfite. However, these solutions are not true solutions of the polymers but solutions of derivatives of these polymers, as evidenced by a number of changes in the polymer itself. When a yellow polymer is dissolved in a bisulfite solution, the brilliant yellow color disappears; the solution becomes colorless, and the solution remains colorless even after acidification with H_2SO_4. Obviously, conjugation was either lost

or sufficiently decreased or interrupted in the polymer, thereby destroying its color.

The addition reaction of bisulfite to non-polymeric Schiff bases is reported in the literature,[35,51-56] to yield a sulfonic derivative, thus

$$ArCH{=}NAr + NaHSO_3 \rightarrow ArCH(SO_3Na)-NHAr \qquad \text{(eq. 78)}$$

This same addition reaction undoubtedly also occurred with the yellow polymer since its I.R. spectra showed the disappearance of a conjugated structure. The solubility of the polymers in the other solvents must also be attributed to derivative formation, particularly since these polymers even at the yellow stage are insoluble in dimethyl formamide, diethyl acetamide and dimethyl sulfoxide, which are considered as very active solvents for most polymers.

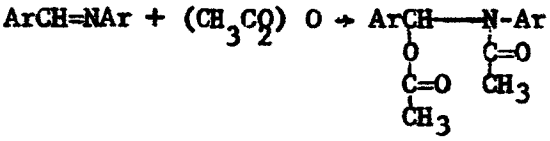
The reactions of non-polymeric Schiff bases with some organic compounds which are often used also as solvents have been reported. In the Wallach reaction[57] of an aldehyde and an amine in formic acid, a Schiff base is obtained[58] as an intermediate, which reacts with formic acid with reduction to yield[59,60] an amine:

$$ArCH{=}NAr + HCOOH \rightarrow ArCH(O{-}C{=}O{-}H)NHAr \rightarrow ArCH_2{-}NHAr + CO_2 \qquad \text{(eq. 79)}$$

Ammonium formate and formamides may be substituted[59,60] for formic acid in this reaction.

When the yellow poly-Schiff base is dissolved in formic acid, the yellow color of the polymer also disappears, indicating that a similar reaction has occurred. Since acetic acid is not a reducing acid, reduction to the amine cannot occur; it was found to be a poorer solvent for the yellow polymer than formic acid, causing only a slight reduction in color, indicating incomplete acylation.

Solubilization of the polymeric Schiff bases in acetic anhydride must also be attributed to a chemical reaction since it has been shown[61,62] that non-polymeric Schiff bases react with it, thus:



(eq. 80)

The yellow polymer was found to be only slightly soluble in acetic anhydride even at reflux temperatures, and little or no color change occurred.

The solution of yellow polymer in H_2SO_4 produces a yellow solution usually darker than the color of the starting material; this indicates that addition to the -C=N- structure, if it occurs, is not complete and that solution may be due in part to salt formations which are more stable than the free base,[63] and it is this salt that is soluble in excess sulfuric acid.

Addition reactions to the -C=N- linkage in Schiff bases is not limited to the solvent reagents of the type mentioned above, since others are known. The addition to non-polymeric Schiff bases of HCN,[64-67] alkyl halides,[68] bromine,[69] Grignard reagents,[70-72] and active α-hydrogen compounds[73,74] such as methylethyl ketone, malonic esters, etc., are known.

When some of these reagents were evaluated as solvents for the yellow polymer, they were found to be much poorer than acetic acid.

If the molecular weights of these polymers are to be obtained from their derivatives, then the reaction by which the derivative is prepared should be quantitative. Indications that this is not so was evident in the failure of some of the derivates to become colorless, as would be expected if addition occurred at substantially all of the -C=N- bonds. Attempts to prepare 1% solutions of selected black polymers in formic acid at room temperature, and at short periods of reflux, failed to yield solution and much

of the polymer remained undissolved. Removal of the formic acid from these solutions, and by filtration, precipitation of the polymer by the addition of water to the filtrate, yielded black polymers. Even extended periods of reflux of 0.002 g. of the polymer in 10 ml in formic acid yielded a light-brown solution and not a colorless solution; while some of the polymer still remained undissolved after twenty hours of reflux. These experiments indicate that formic acid is extracting only the lower-molecular weight black or dark-brown polymers. Similar difficulties were experienced in attempts to prepare solution of black polymers in acetic anhydride, sulfuric acid, and saturated aqueous sodium bisulfite, in that solution was only partial or that the color of the solution was very dark.

Finally, may other black polymers, which were assumed to be of higher molecular weight as a result of longer reaction times, etc., were found to be insoluble or only very slightly soluble, in formic and sulfuric acids. That these polymers were not crosslinked was shown by "dissolving" them in benzylidene-aniline.

Practically all of the polymers, whether yellow or brown or black, can be dissolved in benzylidene-aniline by simply heating the mixture as a melt in the case of the lower molecular weight polymers, or in the presence of catalytic quantities of zinc chloride in a melt in the case of the higher molecular weight polymer. Solution of these polymers is also due to a reaction by a bis-Schiff base exchange mechanism which "reduces" the average molecular weight of the polymer by changing its distribution and therefore, is of little value in determining the molecular weight of the initial polymer.

Conceivably, it may be possible by determining the molecular weight distribution of the mixtures after reaction with benzylidene-aniline in various concentrations of aniline, to derive, by statistical methods, the

probable distribution of the original polymer. This is an approach which is far beyond the scope of this project.

2. Difficulties in Elemental Analyses.

Preliminary studies were made to determine if elemental analyses could be used to give an estimate of molecular weight of the polymer. Consideration was given to those polymers prepared by bis-exchange or in the presence of benzylidene-aniline, and to those prepared from the dialdehydes and the diamines. In all of these polymers, the nitrogen content of the polymer should increase with the degree of polymerization, that is, with molecular weight.

The polymers prepared by bis-exchange, or in the presence of benzylidene-aniline are considered as having the structure

$$C_6H_5N\!=\!CHC_6H_4CH\!=\!NC_6H_4N\!=\!_nCHC_6H_5$$

and when n is ∞, the calculated values for the elemental compositions are % C = 81.55, % H = 4.85, and % N = 13.59.

By selecting any or all of the elements, the values should change with the value of n, as is shown by the nitrogen contents; then

Value of N	% Nitrogen
1	10.85
2	11.80
6	12.80
10	13.10
30	13.40
∞	13.59

A similar relationship is found in the polymers prepared from the dialdehyde and the diamine and considered to have the structure

$$O\!=\!CHC_6H_4CH\!=\!NC_6H_4N\!=\!_nH_2.$$

When n = ∞, the per cent values are % C = 81.53, % H = 4.88, % N = 13.59, and O = zero. These values also change with the values of n, thus

Values of n	Per Cent			
	C	H	N	O
1	75.00	5.36	12.50	7.14
2	78.14	5.12	13.02	3.72
6	80.38	4.94	13.39	1.28
10	80.85	4.90	13.48	0.77
30	81.32	4.87	13.55	0.26
∞	81.53	4.88	13.59	0.0

The yellow polymer of terephthaldehyde and p-phenylenediamine, DA-29-S, as prepared and vacuum-dried to constant weight was analyzed for C, H, and N. Then it was heated in a nitrogen atmosphere (a) for one-half hour at 200°C and another sample (b) was heated at 250°C for three hours. The original and post-heated samples were soluble in formic acid. Analyses of these samples for C, H, and N yielded the following values which were compared to other published[12] values, sample c.

	Per Cent		
	C	H	N
Original sample	80.55	5.25	13.58
Sample a	79.74	5.21	12.82
Sample b	79.96	4.98	13.14
Sample c	78.56	5.15	12.47

By comparison of these data, no absolute conclusion can be made for the n values of the polymer, since, if a value of n is assigned on the basis of the value of carbon, it does not agree well with the n value assignable from hydrogen or nitrogen analyses, etc. The solubility of these polymers in formic acid and their color indicates that their molecular weights are are low, yet the carbon analysis of the original samples indicates $n \sim 8$, the nitrogen value indicates $n = \infty$ and the hydrogen value indicates n as between 1 and 2. Evidently, the elemental analyses are not sufficiently precise to make the decision required. The analyses on these and other polymers were performed by two well-qualified analytical laboratories,

Schwarzkopf Microanalytical Laboratories, New York, New York, and Midwest Microlab, Indianapolis, Indiana; and the nitrogen values were determined in many cases both by the Dumas and Kheldahl methods.

The problem became more severe when black polymers were analyzed, and the deviations from calculated values increased with the molecular weight of the polymers. One of the first problems encountered in the elemental analyses of the black polymer was that of achieving total combustion of the polymer. A Dumas analysis of the bis-exchange polymer, DA-29-41, gave the following results: % C, 75.20; % H, 4.74; and % N, 6.80, and ash was reported as present; $\leq$ elements = 86.74%. A separate and total combustion in a crucible over a meeker burner at red-heat showed that the polymer was ash-free. Upon reanalysis with extended combustion time at higher temperatures, the values obtained were: % C, 81.55; % H, 4.66; and % N, 9.49; $\leq$ elements = 95.9%, and no ash.

These values correspond to a $n = \infty$ on the basis of C, with a hydrogen value which is less than the value required for $n = \infty$, and the nitrogen value of only about 70% of that required for $n = \infty$. The difference in the total elemental values, 100-95.9 = 4.1% cannot be attributed to oxygen since the polymer was prepared in the absence of oxygen and because the value of 81.55% C corresponds to $n = \infty$ for the polymer of $C_6H_4(CHO)_2$ with $C_6H_4(NH_2)_2$, while its hydrogen value is less than the 5.11% H for the aldehyde-amine polymer. Further, an oxygen content of 4.9%, even if it were prepared solely from the dialdehyde and diamine, is that of a polymer whose value is between $n = 1$ and $n = 2$.

The first analyses of balck polymer, DA-29-67, prepared from terephthaldehyde and p-phenylenediamine were reported as : % C = 83.25; % H = 5.47; % N = 6.08. A repeat analysis at higher temperatures and longer compustion times yielded the values: % C = 85.59; % H, 5.17; and % N, 9.76; $\leq$ = 100.52%. In both analyses of DA-29-67, the value for carbon is high while the % N is lower

than the value of N in any formula that can be written. However, it is interesting to note that the $\lesssim$ of % C and % N = 85.59 + 9.76 = 95.34, which is almost identical to an $n = \infty$ value of C = 81.55 + N = 13.59 = 95.14%. It is very probable that the oxides of nitrogen produced in combustion are not being completely reduced to N_2 and are incorporated in the values obtained from carbon as CO_2.

The study of the results of the elemental analyses of a number of other polymers were also made; some of them were:

DA-26-25: from diacetal and diamine;

DA-26 129: from diacetal and diamide;

DA-26-143: from diacetal and diamide with toluene sulfonic acid;

DA-26-169: from diacetal and diamide in benzylidene-aniline;

DA-26-128: from diacetal and di-Schiff base;

DA-26-146: from diacetal and di-Schiff base with toluene sulfonic acid;

DA-26-170: from diacetal and di-Schiff base with benzylidene-aniline;

DA-26-174-1: from diacetal and di-Schiff base with benzylidene-aniline.

Then, a number of correlations were sought for in such relationships as % N versus % yield; % N as a function of the polymerization conditions, and % N versus % C. No correlation could be established, since the sum of all the elements did not total 100% in all analyses.

Some of these discrepancies could be attributed to incomplete combustion which was reported as ash. In those cases where no ash remained, there is the possibility that other side reactions or incomplete reduction of nitrogen oxides, etc., were responsible for the discrepancies. Another possibility is that the polymer structure is not as represented and that decomposition could have occurred during its synthesis with loss of nitrogen in one form or another.

A still further possibility is that some side reaction, such as an adduct formation with benzylidene-aniline could have occurred which would have reduced the nitrogen content of the structure. Both of these possibilities were examined.

a. Possible Loss of Nitrogen.

It is conceivable that during the course of polymerization, decomposition of the polymer could occur lowering the nitrogen content of the polymer. The course of decomposition is at this time unknown, since the polymers appear to be stable to temperatures of at least 400 $\sim$ 450°C. Nonetheless, if the assumption is made that decomposition can occur, the loss could be explained if the products were gaseous and removed from the reaction mixture thus:

$$C_6H_5N{=}CHC_6H_4CH{=}NC_6H_4N{=}CHC_6H_5$$

$$\downarrow \text{Decomposition}$$

$$C_6H_5NH_2,\ N_2,\ (C{\equiv}N)_2,\ H_2,\ HCN,\ C_6H_4(NH_2)_2,\ \text{etc.}$$

Accordingly, a polymer was synthesized in benzylidene-aniline and a study made to determine if gaseous decomposition products were formed.

In another case, a brown polymer, DA-26-98 was prepared from p-xylylidene-tetraethyl ether and p-phenylenediamine, and added to various quantities of benzylidene-aniline and the reaction studied for possible decomposition products. The reagents in both cases were placed in ampoules, then evacuated to remove air, moisture and volatiles, and sealed. Then the mixture was heated for extended periods of time and cooled. The gases were then collected and analyzed by means of a mass spectrograph. The polymers were also isolated and extracted with solvent to remove any excess benzylidene-aniline and the I.R. spectra of the polymer recorded.

The stability of p-xylylidenetetraethyl ether and benzylidenediethyl ether were also evaluated to assure that they were not decomposing in the course of the reaction.

i) Experimental.

(a) DA-26-198. Repeat of DA-26-25 for use in Mass Spectra Studies.

A mixture of 14.119 g. of p-xylylidenetetraethyl ether and 5.40 g. of p-phenylenediamine were reacted at atmospheric pressure by gradually heating the mixture from room temperature to 220°C during the course of twelve hours, and then by slowly raising the temperature to 300°C during the next twenty-four hours. The yield of yellow-brown polymer was 10.5 g. (105%).

(b) DA-26-200.

A mixture of 1.5 g. of the polymer DA-26-198 and 3.0 g. of benzylidene-aniline were placed in an ampoule and evacuated for five hours at 0.03×10^{-3} mm to remove air, moisture and volatiles and sealed. The ampoule was then heated at 250-260°C for six hours. During the reaction the mixture became homogeneous, and viscous and black. At the end of the reaction time, the product was extremely viscous and not solid at 260°C, but it solidified on cooling to room temperature. The product was isolated and treated with alcohol in a Soxhlet extractor for twenty-four hours and there was obtained 3.4 g. (225%) of a dark-brown polymer and an I.R. spectrum recorded.

(c) DA-26-201.

A mixture of 1.5 g. of polymer DA-26-198 and 4.0 g. of benzylidene-aniline were sealed and heated in an evacuated ampoule (0.03×10^{-3} mm) equipped with a break-seal, stopcocks, etc., for sixty hours at 220°C and ten hours at 270-290°C, and the dark-brown mixture cooled. After reaction and cooling, the pressure in the 100 cc ampoules was 0.855 mm Hg; the gases were free of N_2, H_2, $(C{\equiv}N)_2$, $C_6H_5NH_2$ and $C_6H_4(NH_2)_2$. The m/e in the mass spectrograph showed a value of 91-92. The polymer was isolated and treated with alcohol in a Soxhlet extractor for twenty-two hours, leaving 3.1 g. (20%) of a brown polymer.

(d) DA-26-202.

A mixture of 1.009 g. of dibenzylidene-p-phenylenediamine, 1.0 g. of p-xylylidenetetraethyl ether and 2.0 g. of benzylidene-aniline were sealed and heated in an evacuated ampoule (pressure 0.03 x 10^{-3} mm) as in DA-26-201 for forty-eight hours at 220°C and ten hours at 260°C. The pressure in the cooled 150 cc ampoule at the end of the reaction was 0.435 mm Hg, and the m/e of 46 showed it to be ethyl alcohol. The isolated polymer was dark-brown, 1.00 g. (130%).

(e) DA-26-205. Thermal Stability of p-Xylylidenetetraethyl Ether.

10 g. of p-Xylylidenetetraethyl ether were heated in a flask equipped with condenser, receiver, etc., under a slow stream of nitrogen over the range of 220-260°C and samples withdrawn at the following time intervals and the I.R. spectrum of the sample taken:

Temperature °C	Time, hours	I.R. Designation
Room		26-105
220	1.0	26-105-1
220	4.5	26-105-2
220	20.5	26-105-3
260	43.5	26-105-4
260	53.5	26-105-5

No distillate or other products were collected or condensed during the reaction period, and there were no changes in the I.R. spectra of the samples as a function of heating time with the exception of a small increase in $\rangle C{=}O$ absorption band, which was so small as not to be considered important.

(f) DA-26-206. Thermal Stability of Benzylidenediethyl Ether.

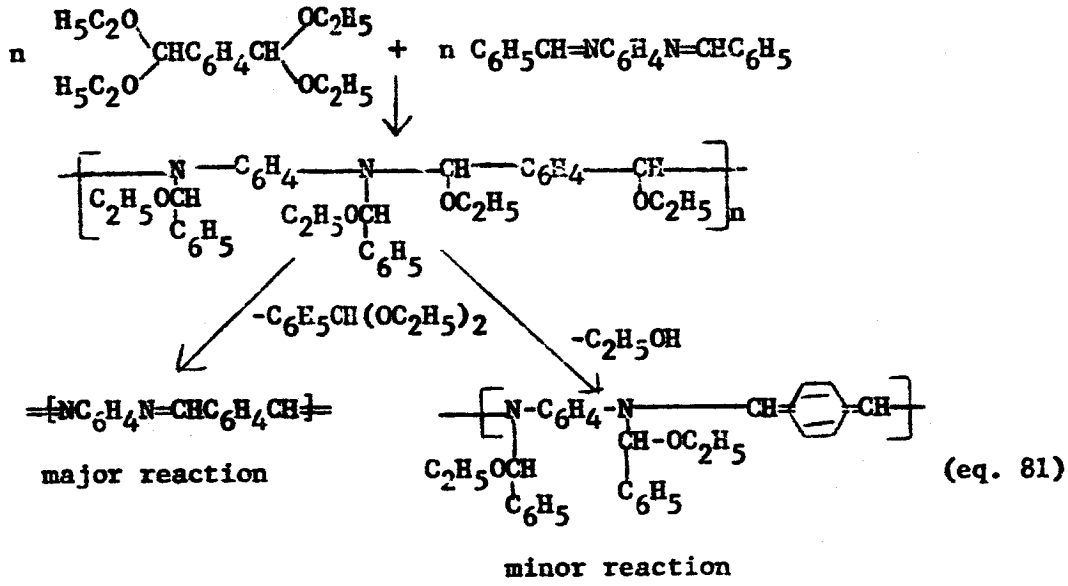
The procedure of DA-26-205 was repeated using benzylidene-diethyl ether instead of the p-xylylidene compound and it too was shown to be exceptionally stable in the temperature range in which it was evaluated.

ii) Discussion.

Little or no gaseous decomposition products were found in these reactions.

The very small amount of m/e = ~92 in DA-26-201 was not identified, but the very small amount of gaseous products in DA-26-202 was shown to be traces of ethyl alcohol. It may be concluded that decomposition does not occur during polymerization and that nitrogen is not lost during the reaction to account for the low values of nitrogen encountered in polymer analyses.

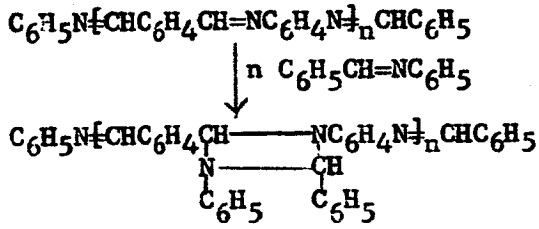
The presence of traces of alcohol indicates that a minor side reaction occurs in the polymerization reaction which can be postulated as follows:



(eq. 81)

b. Adduct Formation or Reaction With Benzylidene-aniline.

The existence of adduct formation, or some complex reaction was considered as possible explanation for low analytical nitrogen values. One such possibility can be expressed as the reaction of the polymer with benzylidene-aniline, thus



(eq. 82)

or a π-complex of such compounds.

This type of reaction or adduct could also contribute to an overall yield in excess of 100% of theory.

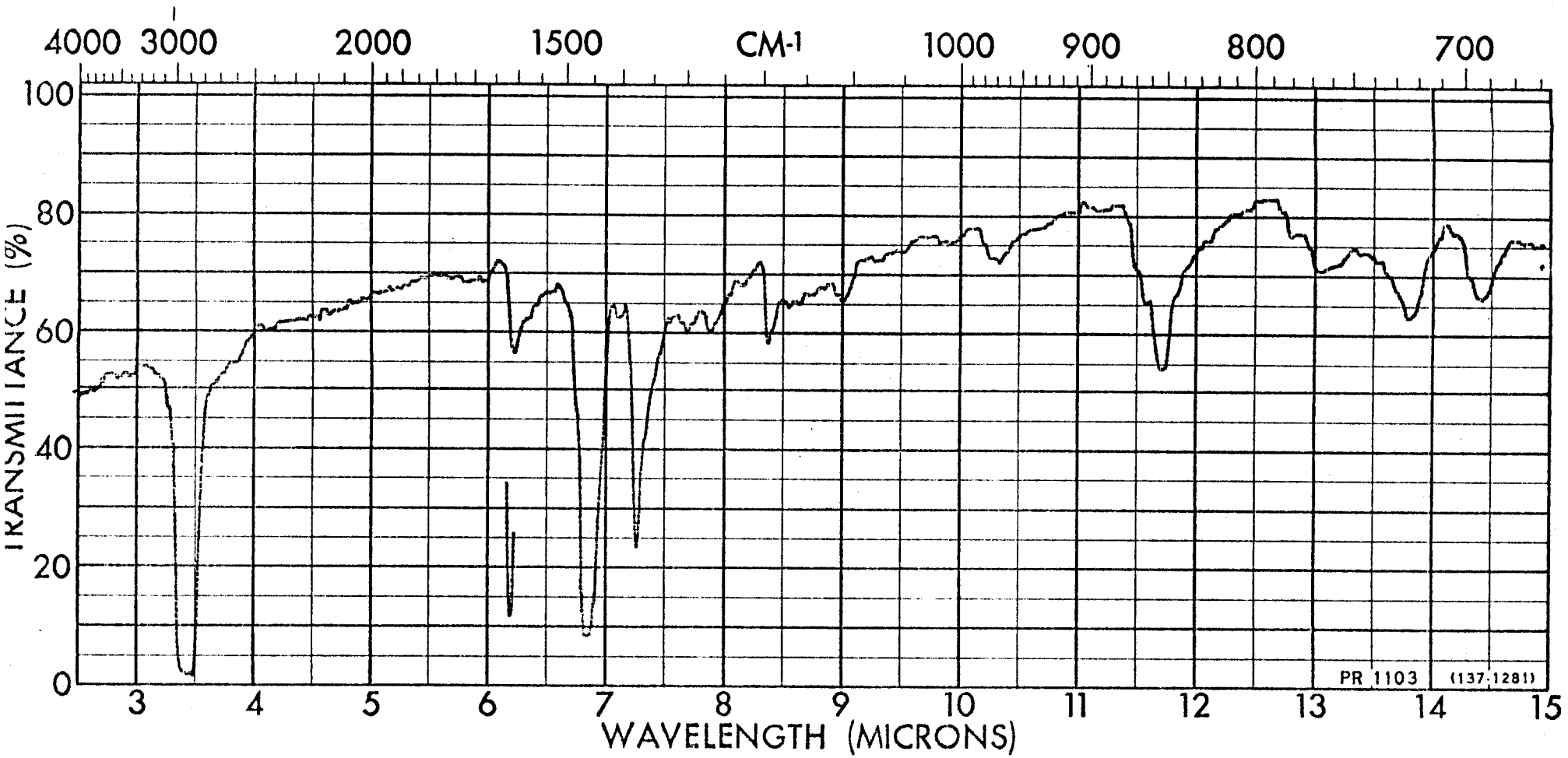


Figure 3. A Typical Infrared Spectrum of the Polymer $\{HCC_6H_4CH=NC_6H_4N\}_n$ (DA-29-125)

To resolve if such types of complex reaction or formation occur, the I.R. spectra of a number of polymers were examined, among which were:DA-26-67, prepared from terephthaldehyde and p-phenylene-diamine; DA-29-41, prepared from a bis-Schiff base exchange; DA-26-25 (or DA-26-198) from diacetal and diamine; DA-26-124, -126, -128, -165, -171, -174, and -177, prepared from diacetal and di-Schiff base; DA-26-127, -129, -166, -167, and -169, prepared from diacetals and diacyl amines; and DA-26-200, -201 prepared by heating the polymer of DA-26-198 in benzylaniline. The syntheses of these polymers are given in earlier experimental sections of this report. Also investigated were polymers DA-26-186, -196 prepared from diacetals and di-Schiff bases, DA-26-187, -197 prepared from di-acetals and diacylamines, whose synthesis is given in the adjacent experimental section.

The dialdehyde-diamine polymer, DA-27-67; and the diacetal-diamine polymers, DA-26-25 and DA-26-198 were used as reference points for comparison of the spectra. A typical spectra of $\{HCC_6H_4CH=NC_6H_4N\}_n$ is shown in Figure 3.

i) Experimental.

(a) DA-26-186. Reaction of p-Xylylidenetetraethyl Ether, Dibenzyledene--p-phenylenediamine and Benzylidene-p-chloroaniline.

A mixture of 4.000 g. of the acetal, 4.036 g. of the bis-Schiff base and 12.0 g. of the mono-Schiff base were reacted under the following conditions and samples taken at the indicated times. The samples were treated with ethyl alcohol in a Soxhlet extractor, dried, weighed, and their I.R. spectra recorded.

Sample. No.	Total time, hours	Temperature °C	Pressure, mm Hg	Weight of Extracted Sample for I.R.
---	12	220	145	-----
---	14	260	145	-----
DA-26-186-1	16	310	100	0.35 g.
DA-26-186-2	19	315	10	0.59 g.
DA-26-186-3	26	315	5	0.25 g.
DA-26-186-4	40	350	5	1.0 g.
DA-26-186-5	45	500	5	0.6 g.

Total yield of precipitated polymer, 2.7 g. (93%).

(b) DA-26-196. Reaction of p-Xylylidenetetraethyl Ether, Dibenzylidene-p-phenylenediamine and Benzylidene-aniline.

A mixture of 5.0 g. of the acetal, 5.045 g. of the Schiff base, and 10.0 g. of benzylidene-aniline were reacted similarly to DA-26-186 but under the following conditions.

Sample No.	Total time, hours	Temperature °C	Pressure mm Hg	Weight of Extracted Sample for I.R.
DA-26-296-1	6	240	atmosphere	0.21
DA-26-296-2	12	240	atmosphere	0.30
----------	33	260	atmosphere	----
DA-26-296-3	58	260	15	0.30
DA-26-296-4	97	260	2	1.33
DA-26-296-5	133	260	2	0.76
DA-26-296-6	206	260	2	0.84
DA-26-296-7	281	260	2	3.00

Total weight of extracted products, 5.74 g., (154%).

(c) DA-26-187. Reaction of p-Xylylidenetetraethyl Ether, N,N'-Diacetyl-p-phenylenediamine and Benzylidene-p-chloroaniline.

A mixture of 4.0 g. of the acetal, 4.036 g. of the diamide and 12.0 g. of the Schiff base were reacted according to the temperature, pressure, and time schedule of DA-26-186, and samples of DA-26-187-1 to DA-26-187-5 inclusive, taken; extracted with ethyl alcohol and the I.R. spectra taken. Total weight of balck polymer 3.05 g. (105%).

(d) DA-26-197. Reaction of p-Xylylidenetetraethyl Ether, N,N-Diacetyl-p-phenylenediamine and Benzylidene-aniline.

A mixture of 5.0 g. of the acetal, 3.407 g. of the diamine and 8.0 g. of benzylidene-aniline were reacted according to the temperature, pressure and time schedule of DA-26-196 and the infrared spectra of samples DA-26-197-1 to DA-26-197-7 inclusive taken after extraction with ethyl alcohol. Total dark-

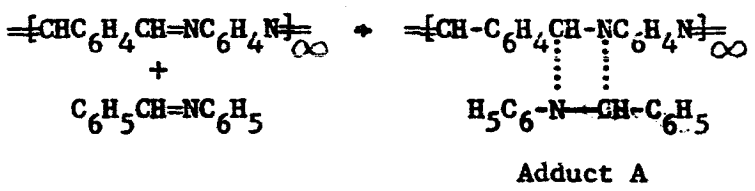
brown polymer 4.94 g. (135%).

ii) Discussion.

A comparison of the I.R. charts with reference charts of DA-29-67, and DA-26-25, -198 having typical poly-Schiff base absorption bands, with those polymers prepared in benzylidene-aniline showed changes in the I.R. spectra. First, it was difficult to determine if there was a decrease in the concentration of the -C=N- in the products (1600 cm^{-1}) because the newly added phenyl ring has an absorption band in the 1600 cm^{-1} region. The I.R. spectra of those products which were soluble were made on products which were reprecipitated from formic acid solutions into alcohol and were considered free of excess benzylidene-aniline. In the case of the insoluble products, the I.R. spectra were taken on Soxhlet-extracted samples. All of these products showed absorptions in the region of 690 cm^{-1} and 760 cm^{-1} attributable to C_6H_5- greater than was found in DA-26-25. Many of the polymers that showed higher absorption in the 690 and 760 cm^{-1} regions were lustrous black and of higher molecular weight than the yellow polymer of DA-26-25, whose conjugation is less extensive. On this basis, one would expect that the black polymers would contain less C_6H_5- groups. Even in the case of polymers DA-26-200, -201 which are the products obtained by heating. DA-26-25 in benzylidene-aniline, the I.R. spectra showed an increase in the number of C_6H_5- ends. These results indicate incorporation of some kind of the $C_6H_5CH{=}NC_6H_5$ into the polymer. This could be the result of either complex-adduct formation or bis-exchange reaction. Some interesting observations were made in the changes of the spectra in the reactions of DA-25-186, -187 as a function of time. In the early stages of the reaction, the typical spectrum of poly-Schiff base was observed, which then was followed in time by an increase in the concentration of C_6H_5- structures.

First, if adduct formation is considered and one benzylaniline molecule

complexes with each segment in a polymer of n = ∞, thus



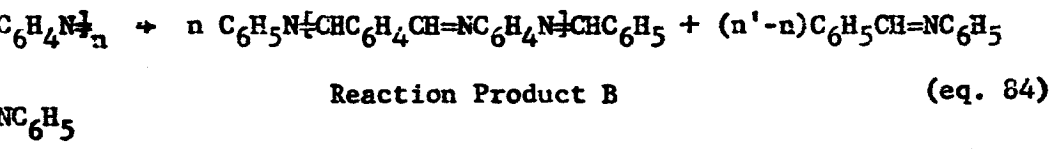
(eq. 83)

Adduct A

the yield and elemental analysis will also change

Yield	Original Polymer	Adduct A
	100%	187%
% C; H; N	81.50; 4.85; 13.59	83.72; 5.42; 10.85

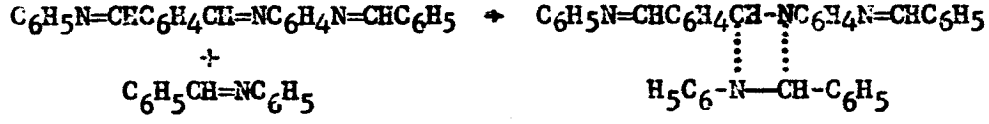
If a complete bis-exchange reaction occurs, then a low molecular weight non-polymeric product should be obtained as the final product:



Reaction Product B (eq. 84)

and the yield and elemental analysis will correspond exactly to the values found in Adduct A.

As an extreme case, the oligomer where n = 1 (reaction product B) can also be considered as complexing with more benzylaniline, thus



(eq. 85)

Adduct C

The calculated elemental values for adduct C are: % C, 84.68; % H, 5.46; and % N, 9.68. The yield relative to reaction product B is 146%; and the yield relative to adduct A is 275%.

All the products, adduct A, reaction product B, and adduct C reflect an increase in C_6H_5- bonds, so they cannot be distinguished on that basis. The reaction product B of n = 1 and adduct C (n = 1) are expected to be very soluble; a characteristic that is not found in these polymers. There remains, then, as possible range for the polymer products, as one extreme, an A-type

adduct with 0 to ∞ molar amounts of benzylidene-aniline complexed with the polymer, to the other limit, a B-type reaction product with various values of n higher than one, which can also form complexes with benzylidene aniline. The limits of elemental analysis, therefore, are

% C : 81.50 to 84.68

% H : 4.85 to 5.46

% C : 12.59 to 9.68.

Some of the polymers fall within this range; in others, one or more elements may fall within the range and the remainder out of range. In terms of analysis and yields, the polymers under study appear to be B-type reaction polymers, $C_6H_5CH\frac{1}{2}NC_6H_4N=CHC_6H_4CH\frac{1}{2}_nNC_6H_5$ with n' moles of $C_6H_5CH=NC_6H_5$ complexed with it.

Non-polymeric, four-membered ring compounds, Ar-C-N-Ar / Ar-N-C-Ar, have been prepared[75] and found to be very unstable, regenerating the Schiff bases easily. Rings of this type should also form with a Schiff base polymer, but as in most polymer reaction, not all of the Schiff linkages in the polymer can be expected to react. Also once the complexes formed, removal of the benzylidene-aniline will be made more difficult by a polymeric medium of high viscosity as compared to the unhindered decomposition of a non-polymeric four-membered ring compound. Nonetheless, the removal of complexed benzylidene-aniline should be more facile than the generation of benzylidene-aniline resulting from the reaction of the termini of the polymer chains, thus

$$\sim\!\!\sim\!\!=NC_6H_4N=CHC_6H_5 \;+\; C_6H_5N=CHC_6H_4CH=\sim\!\!\sim \;\rightarrow\; \sim\!\!\sim\!\!=NC_6H_5=CH-C_6H_5CH=\sim\!\!\sim \;+\; C_6H_5CH=NC_6H_5 \qquad \text{(eq. 86)}$$

In those preparations, in which benzylidene-aniline is involved in the preparation either as a by-product in the Schiff-base exchange, or where it is used as a solvent for the reaction, or where a low molecular weight polymer is post-reacted in it, or when an insoluble, infusible polymer is reacted with it

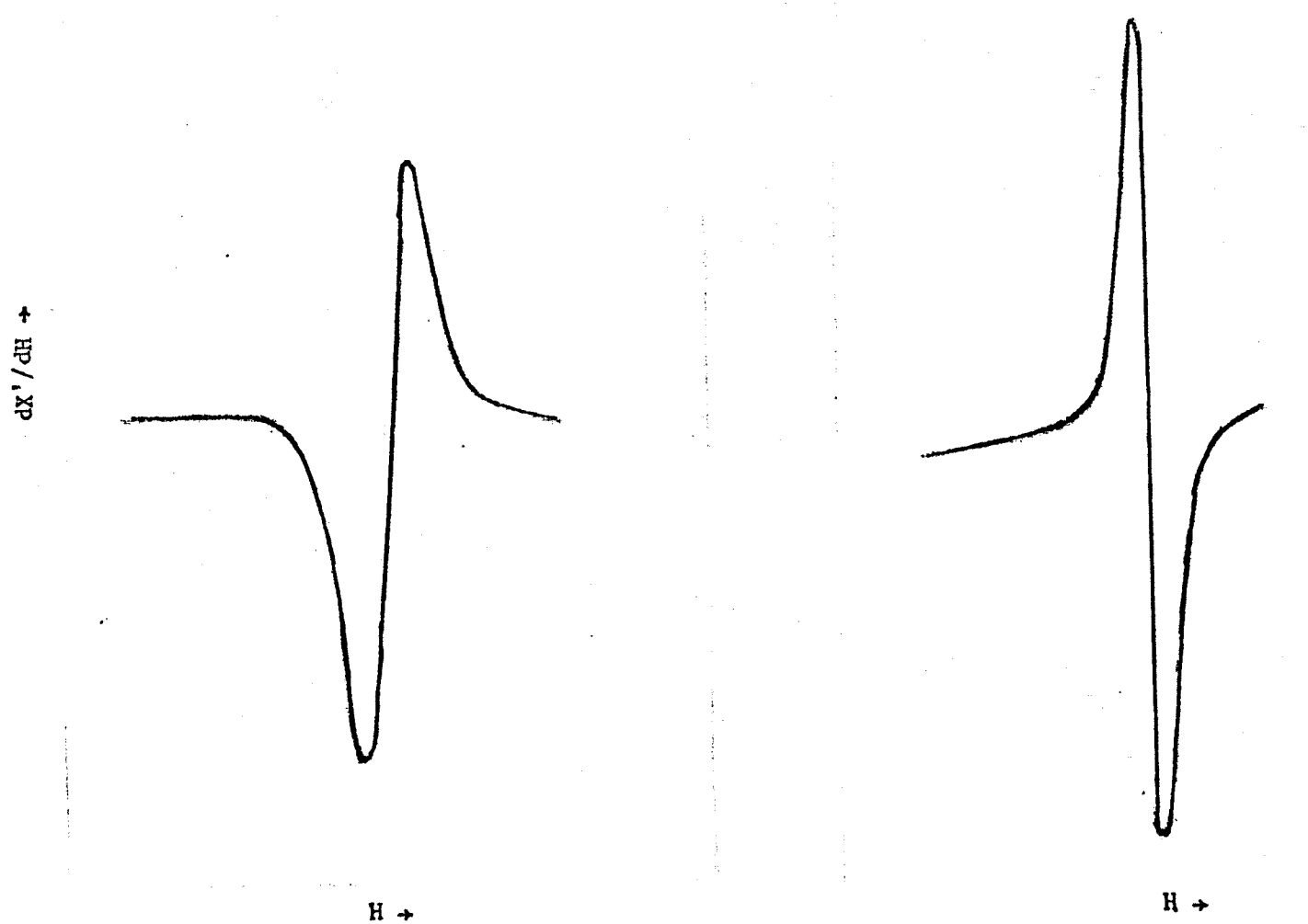
in $ZnCl_2$, the yield of polymer recovered was always higher than 100% at reaction temperatures up to 330°C even when heated at 1.5 mm Hg pressure. However, when they are heated to ~400°C some benzylidene-aniline is eliminated rapidly, and this probably is complexed benzylidene-aniline. After this, more benzylidene-aniline is eliminated at much slower rate, such as would be expected from the kinetics due to a decreasing concentration of functional groups, and eventually a theoretical yield is approached. Even then, the analytical values for C, H, and N are not sufficiently precise to yield an estimate of molecular weight.

3. Molecular Weight from Spectral Methods.

a) From EPR Spectra.

Preliminary measurements were made on some of the polymers to determine whether or not signal intensity could be correlated to molecular weights. An increase in the degree of conjugation in a conjugated system tends to decrease the binding energies of the π-electrons in the systems. This decrease in the binding energy is due to resonance within the system.[76] Thus, from purely theoretical consideration, one may expect that the π-electrons in long conjugated chains would be held rather weakly so that low excitation energies will cause electrons to flow along the chain. Molecules possessing high degrees of conjugation should show conductivity. This phenomenon has been observed in certain condensed aromatic systems[77] such as phthalocyanine and anthracene which were shown to possess semi-conductor properties and to obey Ohms' law.[77] These properties are due to the existence of trapped radical or unpaired electrons or to both in the chemical structure and these substances give intense bands in the ESR spectrum.[78,79] The areas under the peaks are proportional to the number of unpaired electrons in this structure.

In the poly-Schiff bases, the signal is attributed to the unpaired electrons in the -C=N- structure. A number of polymers were evaluated and among these were the polymers of DA-29-8, DA-29-41, DA-26-25, DA-26-129, DA-26-168,



POLYMER DA-26-129

POLYMER DA-29-41

Figure 4. Typical EPR Spectra of $\{HCC_6H_4CH=NC_6H_4N\}_n$ Polymers.

DA-26-169, DA-26-170, and DA-26-172. All showed high signal response. Some typical EPR signals are shown in Figure 4.

In the relationships of $\delta X'/\delta H$ and H in Figure 4, the narrow signal without a superfine structure confirms the existence of unpaired electrons on the polymer. An effort was made to correlate dX'/dH vs H to molecular weight by evaluating samples of polymer withdrawn from a reaction as a function of increasing time, and therefore to molecular weight with increasing conjugation. The preliminary efforts to correlate signal intensity or areas under the peaks with probable sizes of the polymer were not initially successful.

b. From I.R. Spectra.

As molecular weight increases, a shift occurs in the conjugation bands in the I.R. spectra. A preliminary investigation of these regions have indicated this technique is not satisfactory as a tool for determining molecular weights.

4. Some Conclusions Regarding Molecular Weight Determination.

The preliminary attempts to establish a method of determining molecular weights of the polymers of this research already indicate that it is an extremely difficult task. It is believed that the solution to this problem is a major research project in itself. The problem of determining the molecular weights of the so-termed infusible, insoluble polymers is not peculiar to the Schiff-base polymers alone. It is common to the poly-aromatics, poly-benzimidazoles and a number of others. It is also believed that further progress in this research will suffer if too much effort is diverted to studies concerned with establishing a method for molecular weight determination. As methodology research, it should be considered as part of the broader problem involving other "insoluble" polymers. It appears that in this project, we will have to rely on other types of physical measurements, such as TGA, DTA, and modulus of elasticity in flexure, etc., as tools to evaluate the polymers

G. Summary and Conclusions

In these studies it was shown that

1. Aromatic, conjugated, polymeric Schiff bases could be prepared from the nine reaction pairs:
   (a) aromatic dialdehydes and aromatic diamines;
   (b) aromatic dialdehydes and aromatic diamine hydrochlorides;
   (c) aromatic diamines and aromatic di-Schiff bases;
   (d) aromatic aldehydes and aromatic di-Schiff bases;
   (e) an aromatic di-carbonyl Schiff base and another aromatic diamine Schiff base;
   (f) aromatic diacetals and aromatic diamines;
   (g) aromatic diacetals and aromatic diamine hydrochloride;
   (h) aromatic diacetals and N,N-acylyl aromatic diamines;
   (i) aromatic diacetals and aromatic di-Schiff bases;
   of which all but the reaction (a) of dialdehydes and diamines are new reactions.
2. The two reaction pairs:
   (j) aromatic dialdehyde and N,N'-diacylaryldiamines;
   (k) aromatic di-Schiff bases and N,N'-diacylaryldiamines
   reacted with difficulty and failed to produce polymeric Schiff bases.
3. A number of polymeric azo-methines, besides Schiff bases, were also prepared by some of these reactions to demonstrate their applicability to the synthesis of other polymers. Some of them may be useful as carbonizing ablators.
4. Solution polymerization of the reaction pairs in media such as alcohol water, toluene, benzene, tetralin, etc., do not yield black polymers but lower molecular weight, yellow to orange, "brick-dust" polymers. A number of reaction pairs failed to react in such media.

5. The melt-polymerization of the reaction pairs, including the dialdehydes and diamines, yield higher molecular weight polymers, usually blacker in color than obtained by solution polymerization, and that many reaction pairs react in a melt-polymerization which do not react in a solution polymerization.

6. Solution polymerizations performed in certain high-boiling media such as N,N-dimethylnaphthylamine, N-methylpyrrolidone and polyphosphoric acid yield polymers in which the solvent is bound either by copolymerization as in the case of the pyrrolidone, by co-reaction as in the case of polyphosphoric acid or by some form of complexing as in the case of the dimethylnaphthalene and should be avoided.

7. Molten benzylidene-aniline was found to be an excellent solvent for the polymerization reactions and that it functioned as a moderator by participating in the reaction either by an exchange mechanism or by adduct formation or by both mechanisms.

8. Yellow or orange, fusible poly-Schiff bases dissolve readily in benzylidene-aniline and can be converted to black polymers by continued reaction.

9. Black, soluble, fusible poly-Schiff bases can be prepared by interrupting some of the reactions before complete converaion.

10. That polymerization of infusible, insoluble brittle black polymer can be continued in the solid state to much less brittle product.

11. That black polymers can be prepared which are infusible, and insoluble in boiling benzylidene-aniline for extended periods of time. However, the presence of catalytic quantities of a Lewis acid will cause solution to occur probably by an exchange mechanism. Resolution lends some support to the belief that the polymer is substantially linear and not crosslinked, and that the infusibility and insolubility is due to

resonance stabilization, polarization between chains, etc.

12. The black polymers can be prepared which are completely soluble, partially soluble or insoluble in formic acid.

13. The determination of molecular weights of the polymers will be most difficult.

14. That the solution of low molecular weight polymer in such solvents as formic acid, acetic acid, acetic anhydride, and aqueous sodium bisulfite is only apparent and that solution occurs by derivative formation; whereas solutions in concentrated sulfuric acid appears to be solutions of the sulfate salt in excess acid.

15. That the higher molecular weight polymers are only slightly soluble in the above solvents due to incomplete derivative formation.

16. Low molecular weight polymers dissolve in benzylidene-aniline and that solution of higher molecular weight polymers in benzylidene-aniline does not occur unless zinc chloride is present, in which case, a bis-exchange reaction occurs causing a redistribution of the polymer chains to lower molecular weights and that this solution is of no value in determining the molecular weight of the original polymer.

17. That the higher molecular weight polymers are refractory and present problems in the elemental analyses for C, H, and N.

18. That polymers prepared in the presence of benzylidene-aniline, or synthesized by a Schiff base exchange which generates it, contain the benzylidene-aniline as the terminal ends of the polymer as wellas in the form of adducts or complexes with the polymer; that both factors appear to explain many cases of higher than theoretical yields and that benzylidene-aniline can be eliminated at high temperatures.

19. That low analytical values for nitrogen are not due to the loss of nitrogen or nitrogen compounds during synthesis.

20. That the values of % C or % N obtained from elemental analyses cannot be used to estimate molecular weight.

21. EPR and I.R. methods are not satisfactory for estimating molecular weights.

22. That the polymers show an intense EPR signal; that they contain unpaired electrons in the -C=N- linkage and that they have the extended conjugation required for good organic semi-conductors.

23. Sufficient data has been acquired on which to select the better polymerization systems for detailed research.

H. Polymer Systems Selected for Further and Detailed Studies.

One of the major purposes of the studies undertaken in this report was to develop data on which to select the most promising systems among those studied for continued and detailed research. The systems chosen are:

1. p-$C_6H_4(CHO)_2$ with m- or p-$C_6H_4(NH_2)_2$ in $C_6H_4CH{=}NC_6H_5$.

2. Prepolymer of p-$C_6H_4(CHO)_2$ with m- or p-$C_6H_4(NH_2)_2$ in $C_6H_5CH{=}NC_6H_5$.

3. a. Bis-exchange of

   m- or p-$C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5$ with p-$C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5$

   b. the bis-exchange of 3a in $C_6H_5CH{=}NC_6H_5$.

4. The carbonyl exchange

   a. of p-$C_6H_4(CHO)_2$ with the ketanil, m- or p-  .

   b. the bis-exchange of 4a in $C_6H_5CH{=}NC_6H_5$.

5. Acetal exchange with Schiff base

   a. $C_6H_4[CH(OR)_2]_2$ with $C_6H_4(N{=}CHC_6H_5)_2$

   b. the exchange of 5a in $C_6H_5CH{=}NC_6H_5$.

6. Acetal reaction with N-acyl amines

   a. $C_6H_4[CH(OR)_2]_2 + C_6H_4(NHOCCH_2)_2$

   b. acetal reaction of 6a in $C_6H_5CH{=}NC_6H_5$.

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