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Polymeric Schiff Bases. XVI. Alternative Syntheses for the Iminobenzylidene Polymers

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SUMMARY

Eight monomers, considered as suitable for the direct synthesis of iminobenzylidene polymers, $=\![NC_6H_4CH=]_n$, which pass through a tractable, fusible stage, have been synthesized. The polymerization of four of these monomers yielded insoluble, infusible brick-dust polymers. With the exception of p-$CH_3CONHC_6H_4CHO$ and p-$C_6H_5CH{=}NC_6H_5CH{=}NC_6H_5$, little advantage accrues to the use of these new monomers in the synthesis of the desired polymers, which appear to be best prepared by polymerizing the trimers of m- and p-aminobenzaldehyde in a solution of benzylideneaniline.

INTRODUCTION

Direct synthesis [Eq. (1)] of high molecular weight, black poly[o-iminibenzylidene], $H_2\![NC_6H_4CH=]_nO$, from o-aminobenzaldehyde was reported in a previous publication [1]:

$$n\ o\text{-}H_2NC_6H_4CHO \longrightarrow H_2\![NC_6H_4CH=]_nO + (n-1)H_2O \qquad (1)$$

Direct synthesis of the analogous meta and para polymers was not accomplished because the methods used [1] to synthesize monomeric m- and p-aminobenzaldehydes from nitrobenzaldehydes by catalytic

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or stannous chloride reductions yielded, instead, yellow brick-dust trimers. The formation of trimers is attributable to the acidic medium which catalyzed the self-condensation of the aminoaldehyde. Black meta and para polymers were prepared [1] by polycondensation in benzylideneaniline [Eq. (2)], which was shown to be equivalent to a bis-Schiff base exchange reaction [2, 3].

$$nH_2{\neq}NC_6H_4CH{\neq}_3O + nC_6H_5CH{=}NC_6H_5 \longrightarrow$$

$$nC_6H_5CH{\neq}NC_6H_4CH{\neq}_3NC_6H_5 \longrightarrow$$

$$C_6H_5CH{\neq}NC_6H_4CH{\neq}_{3n}NC_6H_5 + (n-1)C_6H_5CH{=}NC_6H_5 \qquad (2)$$

The synthesis of crude p-aminobenzaldehyde in an alkaline medium by the reaction of p-nitrotoluene with an aqueous mixture of sodium polysulfide, flowers of sulfur, and sodium hydroxide has been reported [4]. The yields are relatively low and the product may contain low molecular weight polymers as impurities. Attempts at recrystallization from many solvents, and even from water, lead to further polycondensation and a product with a broad melting-point range is obtained [4]. In an extension of the previous studies [1], we observed that the rapid heating of p-aminobenzaldehyde at 170-180°C in nitrogen yielded orange-colored, intractable brick-dust polymers. Accordingly, it appeared desirable to investigate other syntheses of the polyiminobenzylidenes from other reagents, some of which might be relatively more stable as monomers than the aminobenzaldehydes.

This paper reports some new monomers synthesized for this purpose, the results of the polymerization of these monomers, and a comparison of the properties of these polymers with those of the polymers previously prepared [1] from the trimers by Eq. (2).

The monomers selected for this study are A-B-type monomers [1], in which the chemical nature of the reactive groups corresponds to those previously studied [2] in the reactions of A-A with B-B monomers. Thus the polymerizations of these A-B monomers can be similarly classified [1] as amine exchange, bis exchange, etc., as shown in Eqs. (3)-(10):

Amine exchange [2]:

$$nH_2NC_6H_4CH{=}NC_6H_5 \longrightarrow H_2N{\neq}NC_6H_4CH{\neq}_nNC_6H_5 + (n-1)C_6H_5NH_2 \qquad (3)$$

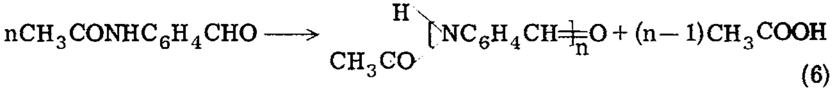
Aldehyde exchange [2]:

$$nC_6H_5CH{=}NC_6H_4CHO \longrightarrow C_6H_5CH{\neq}NC_6H_4CH{\neq}_nO + (n-1)C_6H_5CHO \qquad (4)$$

Bis exchange [2]:

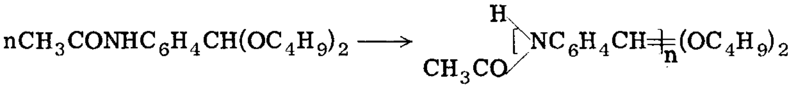
$$nC_6H_5CH{=}NC_6H_4CH{=}NC_6H_5 \longrightarrow C_6H_5CH{=}\left[NC_6H_4CH{=}\right]_n NC_6H_5 + (n-1)C_6H_5CH{=}NC_6H_5 \quad (5)$$

Aldehyde-amide exchange [5, 6]:



$$nCH_3CONHC_6H_4CHO \longrightarrow \overset{H}{\underset{CH_3CO}{\diagdown}}\left[NC_6H_4CH{=}\right]_n O + (n-1)CH_3COOH \quad (6)$$

Acetal-amide exchange [5, 6]:



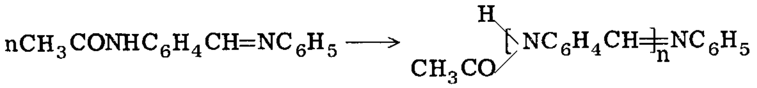
$$nCH_3CONHC_6H_4CH(OC_4H_9)_2 \longrightarrow \overset{H}{\underset{CH_3CO}{\diagdown}}\left[NC_6H_4CH{=}\right]_n(OC_4H_9)_2$$

$$+ (n-1)C_4H_9OH + (n-1)CH_3COOC_4H_9 \quad (7)$$

Acetal-Schiff base exchange [5, 6]:

$$nC_6H_5CH{=}NC_6H_4CH(OC_4H_9)_2 \longrightarrow C_6H_5{=}\left[NC_6H_4CH{=}\right]_n(OC_4H_9)_2 + (n-1)C_6H_5CH(OC_4H_9)_2 \quad (8)$$

Schiff base-amide exchange [5, 6]:



$$nCH_3CONHC_6H_4CH{=}NC_6H_5 \longrightarrow \overset{H}{\underset{CH_3CO}{\diagdown}}\left[NC_6H_4CH{=}\right]_n NC_6H_5$$

$$+ (n-1)CH_3CONHC_6H_5 \quad (9)$$

Amine-acetal exchange [5, 6]:

$$n\ p\text{-}H_2NC_6H_4CH(OC_4H_9)_2 \longrightarrow H_2\left[NC_6H_4CH{=}\right]_n(OC_4H_9)_2 + 2(n-1)C_4H_9OH \quad (10)$$

The polymerization reactions of Eqs. (3)-(10) would be contingent, of course, on the successful syntheses of the required monomers.

EXPERIMENTAL

Monomers

1. p-Aminobenzaldehyde (I), m.p. 69-71°C, was prepared in a 54% yield by the procedure published in *Organic Syntheses* [4].

2. p-Formylacetanilide, p-$CH_3CONHC_6H_4CHO$ (II), was purchased from Eastman Kodak Chemicals, recrystallized from absolute ethanol, and dried in a vacuum oven; m.p. 149-153°C. Its infrared spectrum is shown in Fig. 1.

3. p-Acetamidobenzylidenedibutyl ether, p-$CH_3CONHC_6H_4CH(OC_4H_9)_2$. Attempts to synthesize this monomer from (II) and butyl alcohol, using p-toluenesulfonic acid catalysis by the continuous benzene-azeotropic method previously reported [5, 6] for the synthesis of p-xylylidenetetrabutyl ether, yielded a brick-dust product, m.p. $>$ 300°C, which was insoluble in dimethylacetamide and whose infrared spectrum showed a low concentration of the acetal function. The elemental analysis for carbon, hydrogen, and nitrogen yielded values which indicated that the product was an oligomer.

Analysis:	Calcd. for $C_{17}H_{27}NO_3$:	C, 69.62; H, 9.22; N, 4.77
	Calcd. for $C_{38}H_{42}N_4O_3$:	C, 75.72; H, 7.02; N, 9.29
	Found:	C, 77.16; H, 8.04; N, 8.32

4. p-Acetamidobenzylideneaniline, p-$CH_3CONHC_6H_4CH{=}NC_6H_5$ (III), was prepared from (I) and aniline by the continuous azeotrope method previously reported [7]; m.p. 140-141°C. Its infrared spectrum is shown in Fig. 2.

Analysis:	Calcd. for $C_{15}H_{14}N_2O$:	C, 75.61; H, 5.92; N, 11.76
	Found:	C, 74.93; H, 5.87; N, 11.78

5. p-Nitrobenzylidenedibutyl ether, p-$O_2NC_6H_4CH(OC_4H_9)_2$, was prepared from p-nitrobenzaldehyde and butyl alcohol using p-toluene sulfonic acid catalysis by the continuous azeotropic method previously reported [5, 6]; b.p. 146°C/0.25 mm, $n_D^{25} = 1.4953$. Its infrared spectrum is given in Fig. 3.

Analysis:	Calcd. for $C_{15}H_{23}NO_4$:	C, 64.04; H, 8.24; N, 4.98
	Found:	C, 64.13; H, 8.19; N, 4.96

6. p-Aminobenzylidenedibutyl ether, p-$H_2NC_6H_4CH(OC_4H_9)_2$ (IV). Attempts to synthesize (IV) by the catalytic hydrogenation (5% palladium on charcoal) of p-nitrobenzylidenedibutyl ether in benzene or dioxane at room temperature by procedures reported previously for the reduction of nitroacetophenones [1], yielded 60% of the product as infusible polymer (m.p. $>$ 300°C) and 40% as an oily product, $n_D^{25} = 1.5235$, which was glassy when cooled to 0°C; its infrared spectrum is shown in Fig. 4, and its elemental analysis indicated that it was a mixture of monomer and dimer.

Analysis:	Calcd. for $C_{15}H_{25}NO_2$:	C, 71.67; H, 10.02; N, 5.57
	Found (for oil):	C, 72.55; H, 9.27; N, 6.89

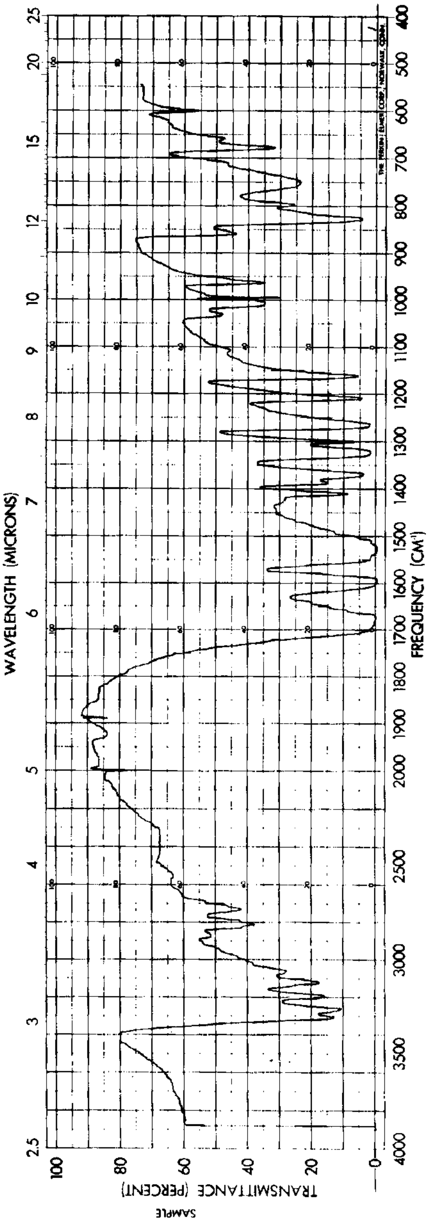


Fig. 1. Infrared spectrum of p-$CH_3CONHC_6H_4CHO$ (II), KBr disk.

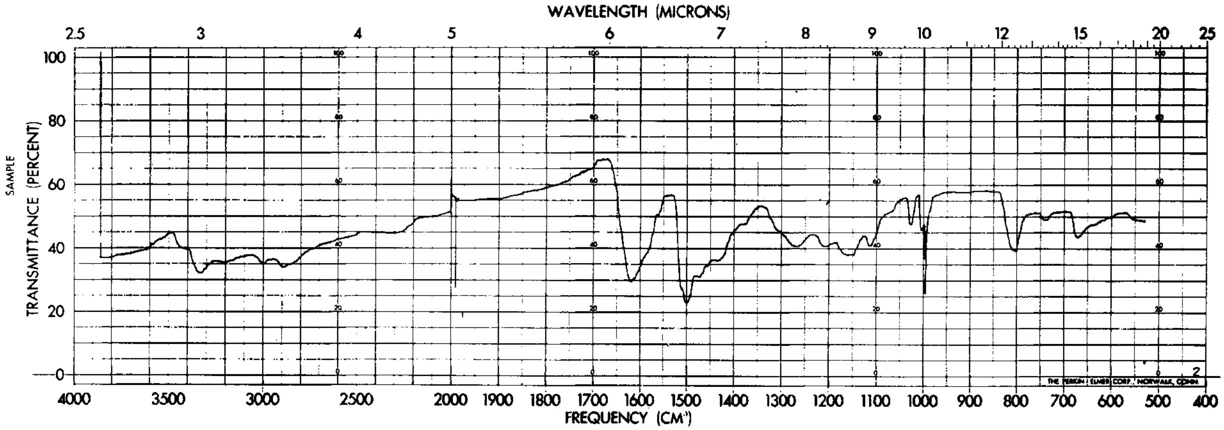


Fig. 2. Infrared spectrum of p-$CH_3CONHC_6H_4CH{=}NC_6H_5$ (III), KBr disk.

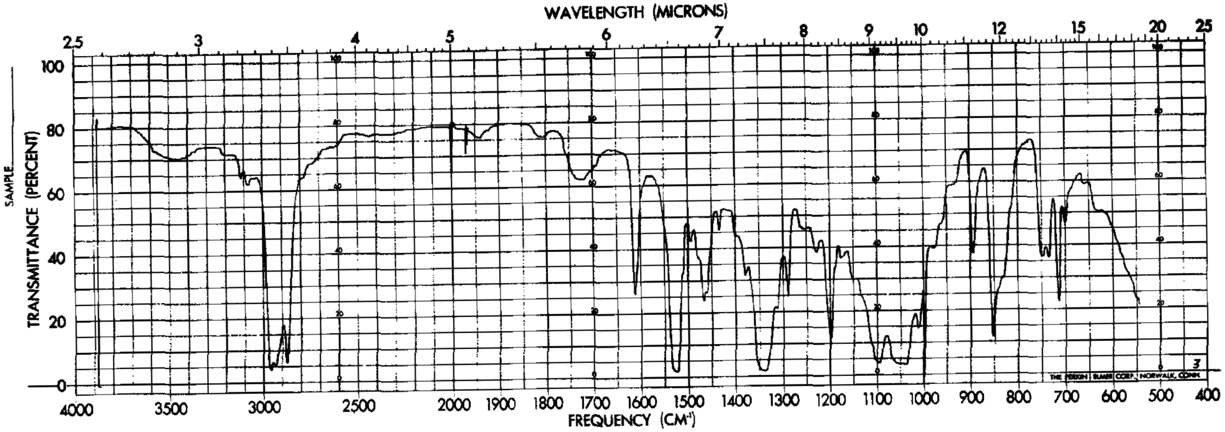


Fig. 3. Infrared spectrum of p-$O_2NC_6H_4CH(OC_4H_9)_2$, KBr disk.

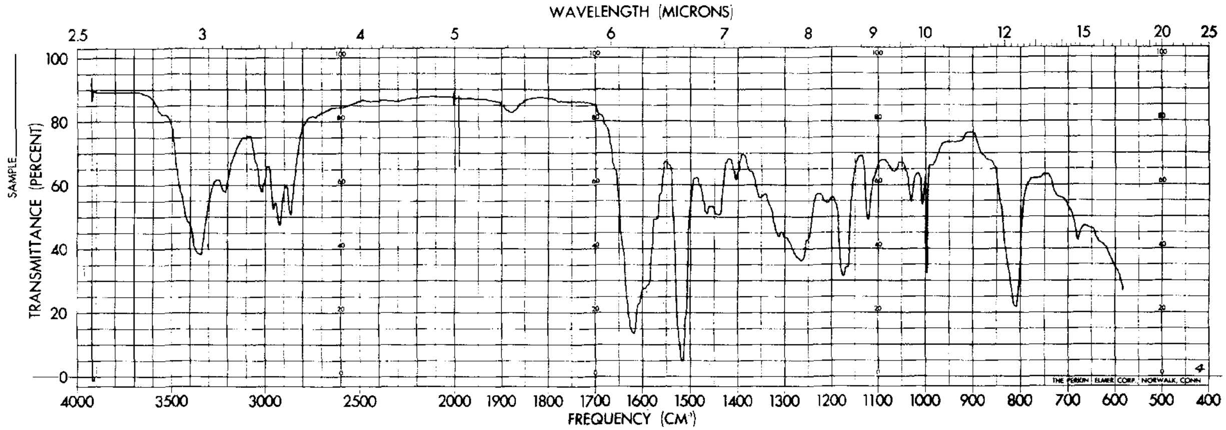


Fig. 4. Infrared spectrum of p-$H_2NC_6H_4CH(OC_4H_9)_2$ (IV), KBr disk.

7. p-Aminobenzylideneaniline, p-$H_2NC_6H_4CH{=}NC_6H_5$ (V), was prepared by the method given by Rossi [8], from aniline and freshly prepared p-aminobenzaldehyde (I), m.p. 110-115°C, accompanied by polymerization. Its infrared spectrum is given in Fig. 5.

Analysis: Calcd. for $C_{13}H_{12}N_2$: C, 79.56; H, 6.16; N, 14.27
Found: C, 79.77; H, 6.08; N, 14.11

8. p-Formylbenzylideneaniline, $C_6H_5CH{=}NC_6H_4CHO$ (VI), was prepared from freshly prepared p-aminobenzaldehyde [4] and freshly distilled benzaldehyde by the method given by Rossi [8] for (V); on heating it showed decomposition and melting in the range 100-120°C. Its infrared spectrum is shown in Fig. 6.

Analysis: Calcd. for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.69
Found: C, 80.28, H, 5.33; N, 6.72

9. p-Benzylideneiminobenzylidenedibutyl ether, p-$C_6H_5CH{=}NC_6H_4CH(OC_4H_9)_2$ (VII). The reaction of (IV) with benzaldehyde in benzene by the continuous azeotropic method [7] yielded a mixture of dimers and trimers which were fusible, having a broad softening range of 130-145°C, and whose infrared spectrum, shown in Fig. 7, is more representative of an oligomer than of a monomer, and in which the bands for the acetal moieties are absent.

Analysis: Calcd. for $C_{22}H_{29}NO_2$: C, 77.84; H, 8.61; N, 4.13
Found: C, 79.71; H, 7.15; N, 7.02

10. p-Benzylideneiminobenzylideneaniline, p-$C_6H_5CH{=}NC_6H_4CH{=}NC_6H_5$ (VIII), was prepared by the continuous azeotropic method [7] from (a) benzaldehyde with (V), and (b) from aniline with (VI). Its infrared spectrum is shown in Fig. 8, m.p. 85°C.

Analysis: Calcd. for $C_{20}H_{16}N_2$: C, 84.47; H, 5.67; N, 9.85
Found: C, 84.51; H, 5.67; N, 9.79

Polymerizations

The polymers were prepared by the melt polymerization technique under an inert atmosphere using procedures previously published [1, 2]. The polymerization cycle was as follows:

Temp., °C	Time, hr
180	1
225	2
325	8

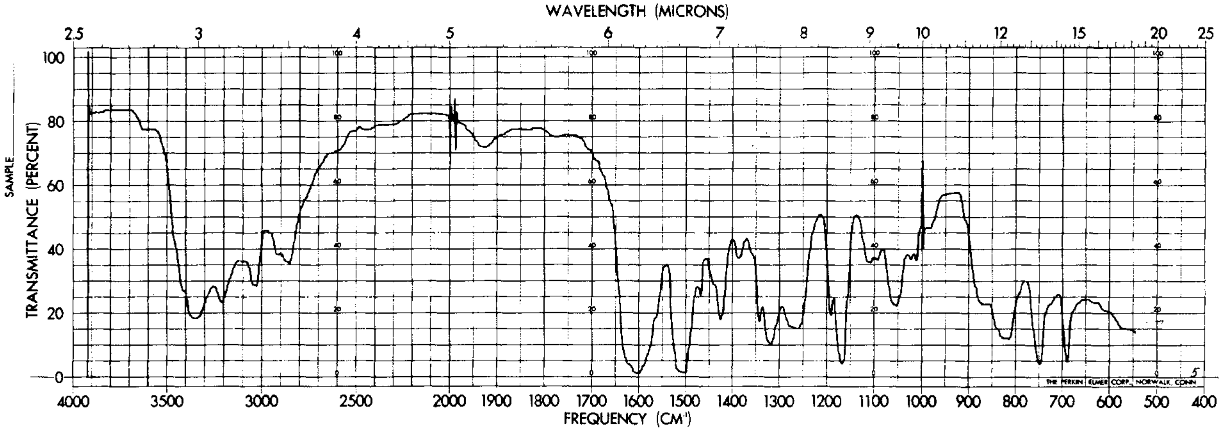


Fig. 5. Infrared spectrum of p-$H_2NC_6H_4CH{=}NC_6H_5$ (V), KBr disk.

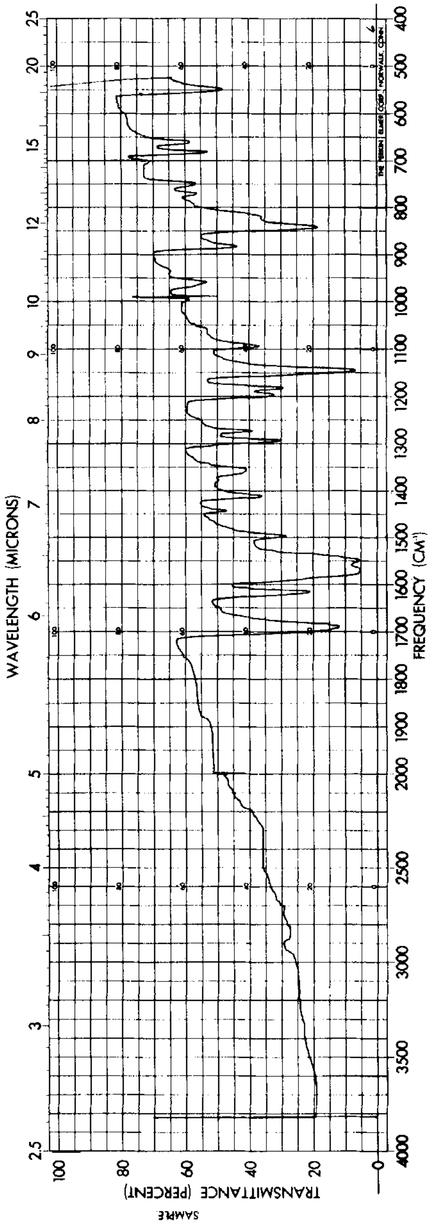


Fig. 6. Infrared spectrum of p-$C_6H_5CH{=}NC_6H_4CHO$ (VI), KBr disk.

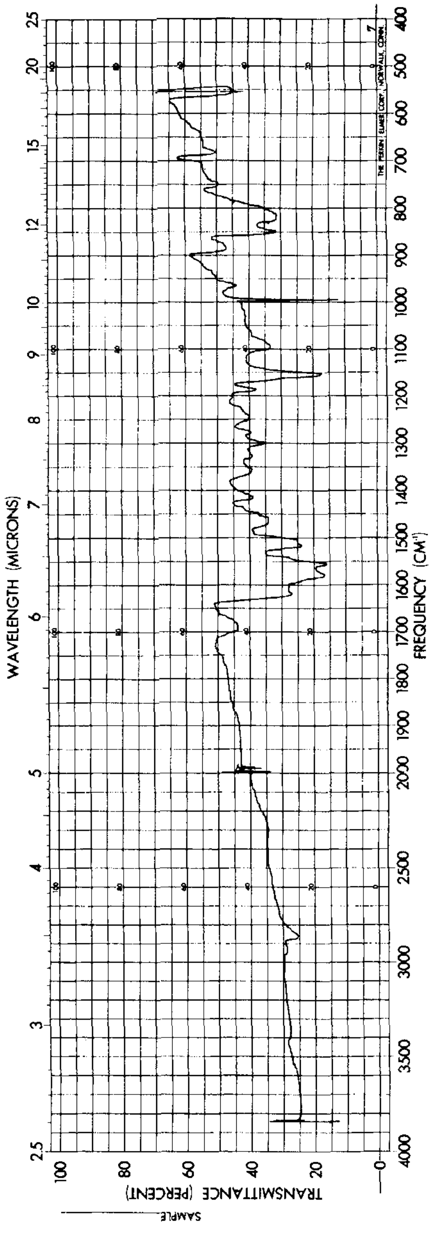


Fig. 7. Infrared spectrum of p-$C_6H_5CH{=}NC_6H_4CH(OC_4H_9)_2$ (VII), KBr disk.

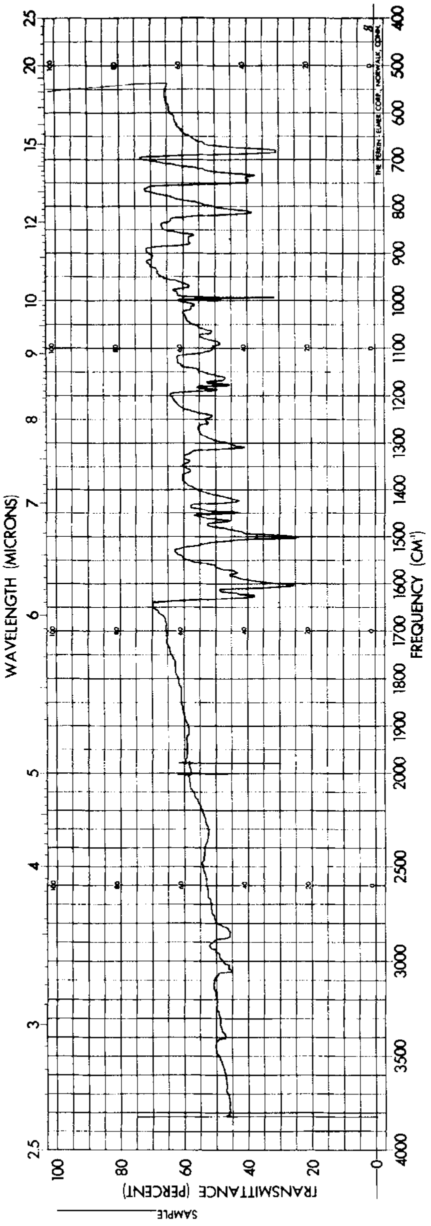


Fig. 8. Infrared spectrum of p-$C_6H_5CH{=}NC_6H_4CH{=}NC_6H_5$ (VIII), KBr disk.

Table 1. Some Relevant Data on the H325 and H400 Polymers

		$A{+}NC_6H_4CH{+}_nB$			%	Analysis per cent			H400 polymer
Monomer	$ZnCl_2$	A	B	Observations	Yield	C	H	N	% yield
I	No	H– H–	=O	No melt; yellow brick-dust polymer	99.0	77.16	5.17	12.81	—
II	No	H– CH_3CO–	=O	Fusible melt; dark brown, glassy button	73.1[a]	81.63	4.59	13.08	62.6
III	Yes	H– CH_3CO–	$=NC_6H_5$	Fusible melt, light brown, glassy button	82.6	81.74	4.52	13.21	73.4
IV[b]	No	H– H–	$-OC_4H_9$ $-OC_4H_9$	Dark orange, brick dust, infusible	102.0	—	—	—	—
V	No	H– H–	$=NC_6H_5$	Yellow, brick dust, infusible	101.7	—	—	—	—
VI	Yes	$C_6H_5CH=$	=O	Orange brown, brick dust, infusible	102.4	—	—	—	—
VII[c]	Yes	$C_6H_5CH=$	$-OC_4H_9$ $-OC_4H_9$	Fusible melt, dark brown, glassy button	97.2	81.88	4.51	12.12	88.6
VIII	No Yes	$C_6H_5CH=$	$=NC_6H_5$	Fusible melt, brown-black, glassy button	96.1 108.7	85.34 85.62	5.37 5.15	9.49 9.83	91.2 101.1

[a] Part of monomer sublimed during reaction.
[b] Fusible monomer-dimer mixture.
[c] Oligomeric and fusible.

The polymerizations were attempted first as uncatalyzed reactions; when polymerization did not occur readily under these conditions, the reactions were repeated using 0.5 wt.% of zinc chloride as the catalyst. The infrared spectra of the polymers were recorded as KBr disks [1]. In accordance with previous coding [1, 2], these products are designated as H325 polymers. The relevant data are given in Table 1.

Postheating of Polymers at 400°C

Portions of some of the H325°C polymers were postheated [2] under nitrogen at 400°C for 4 hr, and the yields are given in Table 1. In accordance with previous coding [1, 2], these products are designated as H400 polymers.

Thermogravimetric Analyses

The procedure previously published was used in the thermanalyses of the polymers [1, 2]. Only those polymers which passed through a fusible stage were evaluated; the brick-dust polymers were not tested. The thermogravimetric data for the H400 polymers are summarized in Table 2.

Table 2. Thermogravimetric Data in Nitrogen for the H400 Polymers

Polymer	Per cent weight loss at °C							
	400	500	600	700	800	900	1000	1176
II	0.0	0.0	2.7	5.0	8.2	13.1	14.8	15.8
III	0.0	0.0	2.8	5.2	8.4	14.0	15.1	18.1
VII	0.0	0.0	3.6	5.4	8.6	14.4	15.3	18.4
VIII	0.0	0.0	1.7	5.1	8.3	13.6	14.6	17.3

DISCUSSION AND CONCLUSIONS

Monomers

Since the polymerization tendency of the m- and p-aminobenzaldehydes, prepared by the reduction of the corresponding nitroaldehydes, were substantially identical [1], the present study was limited only to the para-substituted monomers. In this study, crude monomeric p-aminobenzaldehyde (I), m.p. 69-71°C, was prepared [4] in a 54% yield from p-nitrotoluene. The high tendency to self-condensation was evident when recrystallizations were attempted from numerous solvents, including benzene, ethanol, dioxane, and water. In solution, trimeric products formed readily, thereby increasing and broadening the melting-point range of the product. When refluxed in the solvent, infusible oligomeric products, m.p. > 300°C, were obtained. When held at its melting point of 69-71°C, (I) was converted to a yellow, oligomeric brick dust.

The polymerization tendency of (I) was reduced somewhat when its $-NH_2$ or $-CHO$ group or both groups were converted to appropriate derivatives. The p-formylacetanilide (II) was much more stable than (I) and it showed only a slight tendency to polymerize at its melting point. However, attempts to convert (II) to the dibutyl acetal by the acid-catalyzed reaction with butyl alcohol by the continuous benzene-azeotropic method found effective for other aromatic aldehydes yielded insoluble, infusible polymeric products by the elimination of acetic acid in the form of butyl acetate. However, the uncatalyzed reaction of (II) with aniline by the continuous azeotropic procedure yielded easily the corresponding benzylideneaniline derivative (III). Monomer (III) showed little tendency to polymerize at its melting point.

Numerous attempts to produce the dibutyl acetal (IV) directly from (I) were unsuccessful; partial success of the synthesis of (IV) was achieved by the catalytic reduction of p-nitrobenzylidenedibutyl ether, yielding a mixture of brick-dust oligomers and an oil whose analysis indicated that it was a mixture of monomer and dimer; this oil was used directly since attempts to isolate the monomer from the mixture yielded further amounts of polymer.

Monomer (V) was prepared by the method of Rossi [8] from freshly prepared (I) and a large excess of aniline (1:10 mole) by heating the mixture to the boiling point of aniline followed by cooling in an ice-water mixture, separating the precipitate, and washing it with a 50 : 50 mixture of hexane/diethyl ether. Prolonged heating of the reaction mixture at the boiling point of aniline precipitated brick-dust polymers. At its melting point (V) polymerized readily.

Monomer (VI) was prepared from (I) and benzaldehyde by the same procedure used to prepare (V); a nitrogen atmosphere was used to avoid oxidation of the benzaldehyde; on heating, (VI) polymerized in the range 100-120°C.

The uncatalyzed reaction of (IV) with benzaldehyde did not yield the monomeric benzylidene derivative (VII) but gave an oligomeric product which was fusible with a broad softening range of 130-145°C; when held at 145°C the oligomers polymerized further. Monomer (VIII) was the most stable of the monomers prepared, and it showed little or no tendency to polymerize at its melting point.

POLYMERIZATIONS

Monomers (IV), (V), and (VI) polymerized to infusible, low molecular weight brick dusts varying in color from yellow to orange and in this respect were similar to (I). However, monomers (I), (IV), (V), and (VI) and the resulting brick dust polymers, as well as the trimer of p-acetamidobenzylidenedibutyl ether, could be polymerized in solution in benzylideneaniline [1], but since the purpose of this study was to evaluate new monomers which would yield fusible, tractable, black polymers directly on polymerization, they were not investigated further.

The uncatalyzed polymerization of (II) yielded acetic acid as shown in Eq. (6), and during the course of its polymerization considerable amounts of monomer sublimed from the reaction mass, causing a reduction in the yield of polymer. However, since this is an A-B type of polymerization, the critical stoichiometry is not disturbed by the loss of A-B monomer. The polymerization was well moderated and the viscosity of the melt increased as the color changed progressively from light to dark brown to a hard, brown-black glassy button. The polymerization was highly accelerated by the addition of catalytic quantities of Lewis acid; the addition of 0.25 wt. % of zinc chloride to the monomer increased the yield to 94%. This polymerization of the A-B monomer (II) differs markedly with the comparable unsuccessful A-A plus B-B monomer reaction [6] of p-$CH_3CONHC_6H_4NHOCCH_3$ + p-$OHCC_6H_4CHO$, which yielded insoluble, intractable, infusible polymer products with little or no evidence for the presence of a C=N structure in the polymers, even though the monomeric prototype reactions yielded Schiff bases [6]. It is believed that the intractability of the condensation product prevented elimination of the acetic acid. In the case of the A-B monomer, the polymer, as it is formed, was soluble in unconverted (II), which maintained the mixture as a melt and allowed the reaction to proceed to completion. This belief was confirmed, to some measure, by dissolving p-aminobenzaldehyde trimer, $H_2{+}NC_6H_4CO{+}_3O$, in (II) and polymerizing the solution to a tractable, fusible polymer [9].

The uncatalyzed polymerization of (III), shown as Eq. (9), was very sluggish and, accordingly, zinc chloride was used as a catalyst. Its polymerization paralleled that of (II), eliminating acetanilide instead of acetic acid. In this polymerization the A-B monomer solubilized the polymer as it was formed and allowed the reaction to proceed to a higher degree of condensation; thus it also differs with the related unsuccessful A-A with B-B monomer type of polymerization [6] of p-$CH_3CONHC_6H_4NHOCCH_3$ with p-$C_6H_5CH{=}NC_6H_4N{=}HCC_6H_5$.

The polymerization of the fusible oligomers of (VII), used instead of the monomer shown in Eq. (8), was sluggish and required zinc chloride catalysis; it yielded a dark-brown polymer rather than a brownish-black product and in this respect is similar to the acetal-Schiff base exchange of the A-A plus B-B polymerization [6] of p-$C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5$ with p-$(BuO)_2HCC_6H_4CH(OBu)_2$, which proceeded best [6] in the presence of benzylideneaniline.

The polymerization of (VIII) by the Schiff base exchange reaction of Eq. (5) proceeded as a well-moderated uncatalyzed or catalyzed reaction to yield a product which was equivalent to the product obtained by the polymerization of the trimer of p-aminobenzaldehyde in benzylideneaniline [1]. The zinc chloride-catalyzed reaction produced a higher yield of polymer at 325 and 400°C than the uncatalyzed reaction; both the catalyzed and uncatalyzed reactions produced higher yields of polymer than the other reactions, which did not eliminate benzylideneaniline. This is in agreement with previous findings [10-12] which indicated not only that the benzylideneaniline is retained tenaciously by the polymer, but that it may also undergo reaction with the polymer.

The infrared spectra of all the brown or black H325 and H400 polymers of this study were substantially identical to those published [1] for aminobenzaldehyde trimers polymerized in benzylideneaniline. Similarly, the thermogravimetric data for the brown to black H325 and H400 polymers of this study were substantially identical to those published for the polymeric azomethines prepared from aminoarylcarbonyl monomers [1].

The present study indicated that, because of their instability, most of the new monomers synthesized, including p-aminobenzaldehyde, were not too suitable for the preparation of the polymers. The exceptions to this generalization were the formylacetanilide (II), its Schiff-base derivative (III), and the bis-Schiff base (VIII). Monomer (III), which eliminated acetanilide, offered little or no advantage over (II), which eliminated acetic acid, since acetic acid is eliminated more readily than acetanilide. In addition, (III) is synthesized from (II), adding an additional step to the process, for which no advantage is gained. Monomer (II) is derived by acetylation of (I); this additional step contributes an advantage in that a tractable, fusible intermediate polymer can be obtained from the direct polymerization of (II) and not of (I) without the expediency of adding benzylideneaniline as a solvent. The stability of monomer (VIII) is about the same as (II) and polymerizes readily to satisfactory polymers. However, the polymer product is identical to that obtained by the polymerization of aminobenzaldehyde polymers in benzylideneaniline, and the complications of the synthesis of (VIII) does not particularly warrant its preparation to achieve a result which can be obtained rather simply by the use of the trimer in benzylideneaniline.

Although a number of new syntheses for the iminobenzylidene polymers has been achieved, it may be concluded that the choice syntheses are those from (I) p-formylacetanilide (II), and (2) the aminobenzaldehyde trimers dissolved in benzylideneaniline.

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