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Polymeric Schiff Bases. X. The Synthesis and Evaluation of Polymeric Azomethines from Aminoarylcarbonyl Monomers

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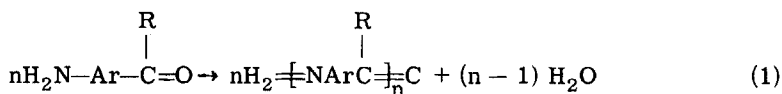
Summary

The syntheses of polymeric azomethines from aminoarylcarbonyl monomers, $H_2NArCOR$, are described and the thermal stabilities of the polymers found to be comparable to polymers prepared by the reaction of aryldicarbonyl compounds with aryldiamines.

In a number of previous papers [1-5], the syntheses of polymeric Schiff bases and polymeric ketanils were described as the reaction

products of aryldicarbonyl compounds, $Ar'(C=O)_2$, with aryldiamines $Ar''(NH_2)_2$, or of the appropriate derivatives of these two classes of reactants. These polymerizations [1-5] fall in the classification as the reactions of A-A plus B-B type monomers in which the related

functional $-C=O$ and $-NH_2$ groups are located in different molecules. The syntheses of polymeric azomethines from A-B type monomers do not appear to have been reported. Such polymerizations can be expressed by



wherein R is hydrogen or an hydrocarbon group such as methyl or

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phenyl. When R is hydrogen, the polymer is a poly-Schiff base and when R is methyl or phenyl, the product is a polyketanil.

In view of the differences in respective reactivities of the dialdehydes and diketones [5] with diamines, a similar difference should be expected in the self-condensations of $H_2NArCOCH_3$ and $H_2NArCHO$, respectively. This difference is evident in the syntheses of these two classes of monomers. The nitroaryl ketones, $O_2NArOCCH_3$, are readily reduced to the isolable aminoketones, $H_2NArCOR$, and are products of industry. In contrast, in most cases, the reduction of the nitroaldehydes, $O_2NArCHO$, leads to amino compounds which self-condense immediately to form low molecular weight condensation products, usually dimers, trimers, or tetramers of relatively high melting points. Thus the aminoaryl-aldehydes appear to be unsuitable as starting materials for the syntheses of polymers.

The purpose of this paper is to describe the syntheses of polymers by the self-condensation of aminoarylcarbonyl compounds, and to compare the thermal stabilities of these polymers with their poly-Schiff base [1-4] and polyketanil [5] counterparts obtained by the reactions of aryldicarbonyl compounds with aryldiamines.

EXPERIMENTAL

Reagents and Monomers. o-Nitro-benzaldehyde, m.p. 43-46°C; m-benzaldehyde, m.p. 55-57°C; p-nitrobenzaldehyde, m.p. 105-108°C; o-nitroacetophenone, b.p. 159°C/16 mm Hg; m-nitroacetophenone, m.p. 74-78°C; p-nitroacetophenone, m.p. 80-82°C; o-aminoacetophenone, m.p. 16-18°C; p-aminoacetophenone, m.p. 105-107°C; p-aminobenzophenone, m.p. 121-124°C; o-aminobenzaldehyde, m.p. 36-38°C, and m-aminobenzaldehyde (trimer), m.p. > 300°C, were purchased from the Aldrich Chemical Company, Inc. m-Aminoacetophenone, m.p. 92.4°C, was purchased from Distillation Products Industries, Inc., and p-aminobenzaldehyde (trimer), m.p. > 300°C, was purchased from Fluka, AG. The syntheses of benzylidene-



aniline [6], and the ketanil [5], $C_6H_5C=NC_6H_5$, were reported previously [5, 6].

Reduction of Nitroarylcarbonyl Compounds. The following is a typical procedure used to reduce the nitro compounds. Five grams of the nitroarylcarbonyl compound, 0.70 g of 5% palladium on charcoal, and 200 ml of absolute ethanol were placed in a Parr bottle mounted in the Parr apparatus. The bottle was flushed three times with hydrogen and then filled with hydrogen to 42 psig. The mixture was agitated at room temperature for 2 hr, the pressure in the bottle released, and the solution filtered. The insoluble reduction products in the case of the m- and p-aminobenzaldehydes were recovered at

this filtration. In the case of the soluble products, they were recovered from the filtrate by evaporation to dryness in vacuo, followed by recrystallization from ethanol and drying in a vacuum oven at room temperature.

The reduction of *m*-aminoacetophenone, *p*-aminoacetophenone, *p*-aminobenzophenone, and *o*-aminobenzaldehyde yielded compounds whose infrared spectra and melting points corresponded to the purchased compounds, and which showed no depression of melting point when mixed in equal weights with authentic samples. The reduction of *m*-aminobenzaldehyde and *p*-aminobenzaldehyde yielded infusible products, m.p. > 300°C, whose infrared spectra showed absorptions in the regions of 1620 cm⁻¹ for the C=N, at 3380 cm⁻¹ for the NH₂ and at 1685 cm⁻¹ for the C=O structures.

Analysis:

Cal'd. for H₂-NC₆H₄CH=O: C, 77.05; H, 5.19; N, 12.85

Found for *m*-H₂-NC₆H₄CH=O: C, 77.32; H, 5.14; N, 12.93

Found for *p*-H₂-NC₆H₄CH=O: C, 77.16; H, 5.16; N, 12.87

A number of the above nitro compounds were reduced by the stannous chloride-concentrated hydrochloric acid method [7]. This procedure was cumbersome and tedious, particularly in the cases of *m*-nitrobenzaldehyde and *p*-nitrobenzaldehyde, which yielded highly impure polymeric products in low yield and which required extensive purification from *N,N*-dimethylacetamide solutions.

Typical infrared spectra of the aminoarylcarbonyl compounds are shown in Figs. 1 to 6.

POLYMERIZATIONS

In Solution

Azeotrope Method [1, 2]. The following is a typical procedure of the method which has been reported previously [1, 2]. A mixture of 0.02 mole of the aminoarylcarbonyl monomer, 50 ml of benzene, and 0.02 g of *p*-toluenesulfuric acid, if used, were reacted at reflux for 24 to 36 hr. Then the reaction was filtered hot and allowed to cool, and, if precipitated products formed, they were removed by filtration and dried. Then the filtrate was concentrated by removal of the benzene at a reduced pressure of 15 mm Hg; the solid product was recovered and recrystallized by benzene. The starting monomers, *m*-aminoacetophenone, *p*-aminoacetophenone, *p*-aminobenzophenone, and *o*-aminobenzaldehyde, respectively, were recovered unchanged when reacted by the azeotropic method, either uncatalyzed or catalyzed by *p*-toluenesulfonic acid.

The infrared spectra and the mixed melting points with authentic samples of the products recovered from the uncatalyzed and catalyzed

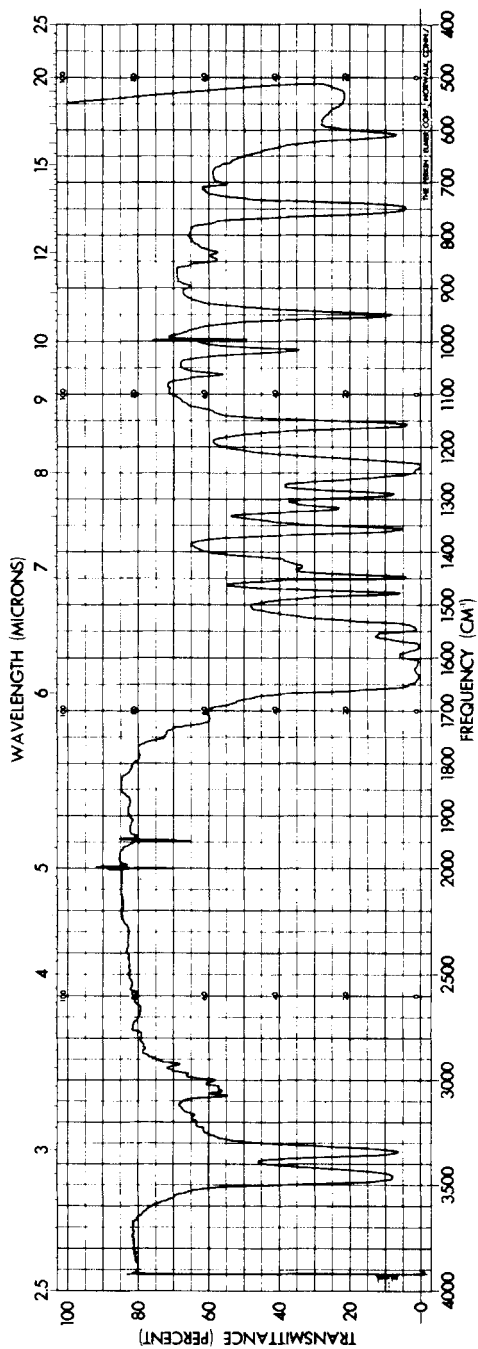


FIG. 1. Infrared spectrum of o-aminoacetophenone. KBr disc.

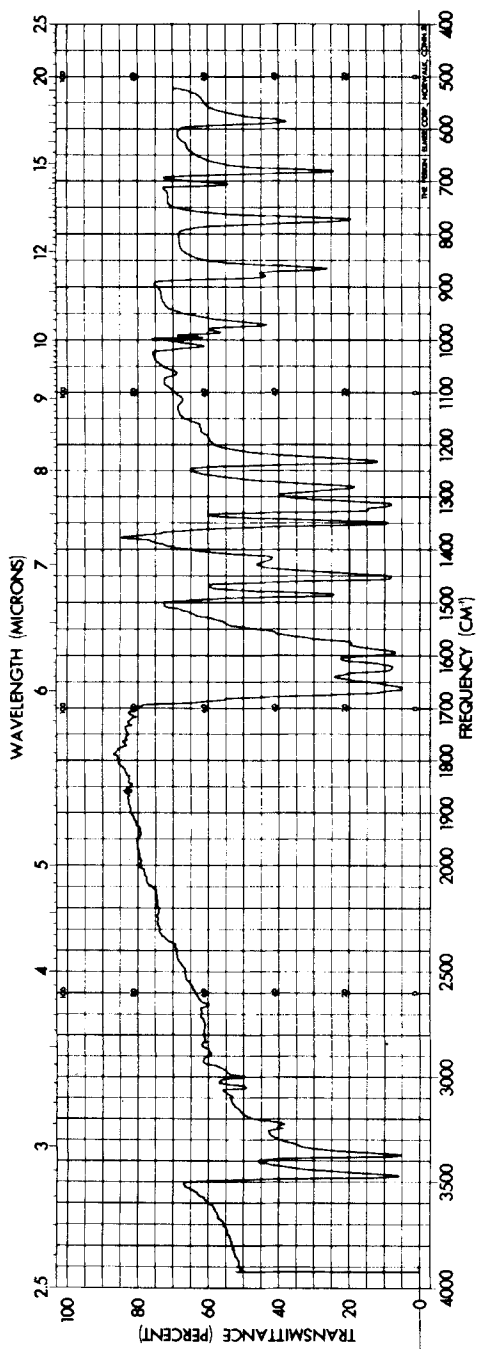


FIG. 2. Infrared spectrum of m-aminoacetophenone. KBr disc.

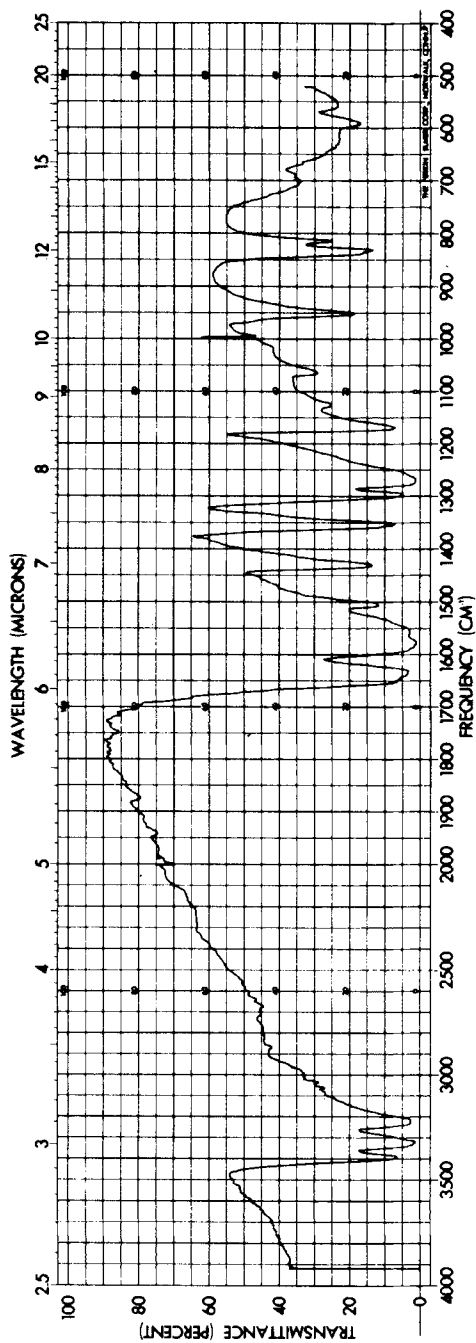


FIG. 3. Infrared spectrum of p-aminoacetophenone. KBr disc.

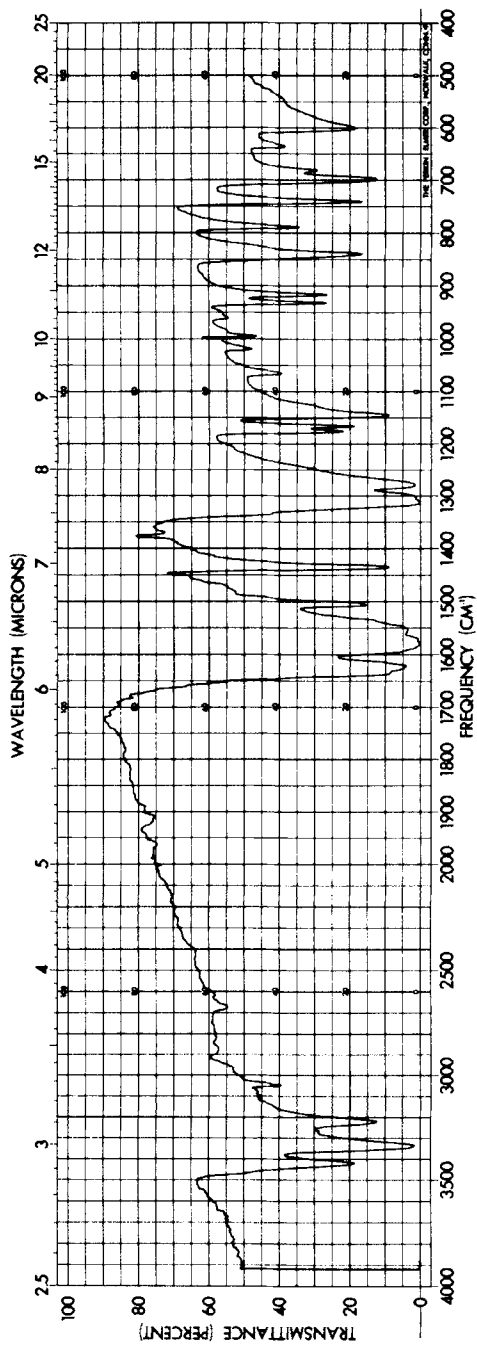


FIG. 4. Infrared spectrum of p-aminobenzophenone. KBr disc.

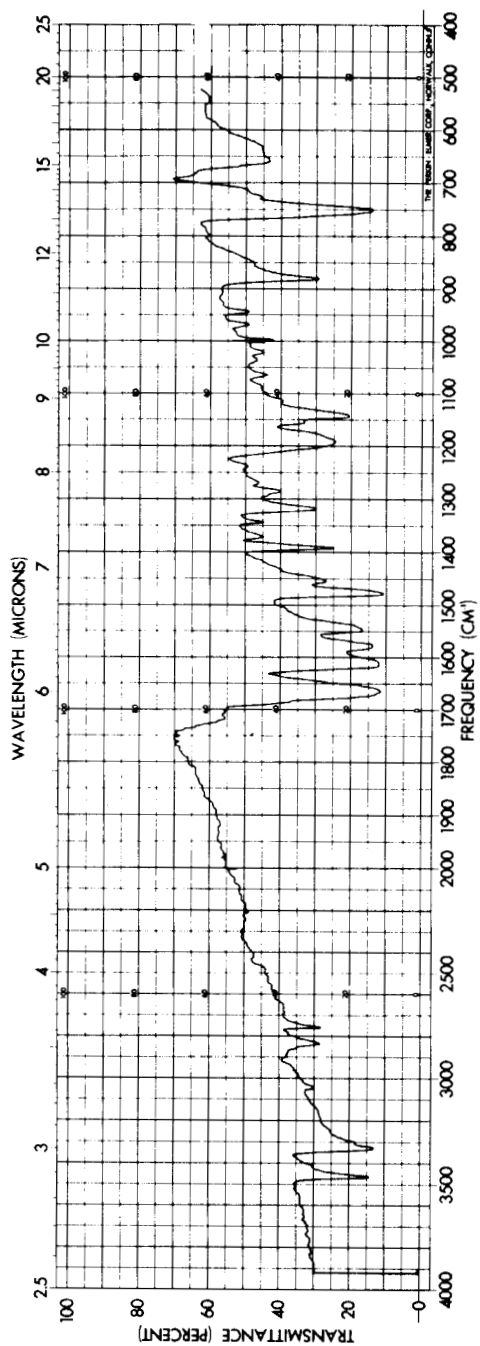


FIG. 5. Infrared spectrum of o-aminobenzaldehyde. KBr disc.

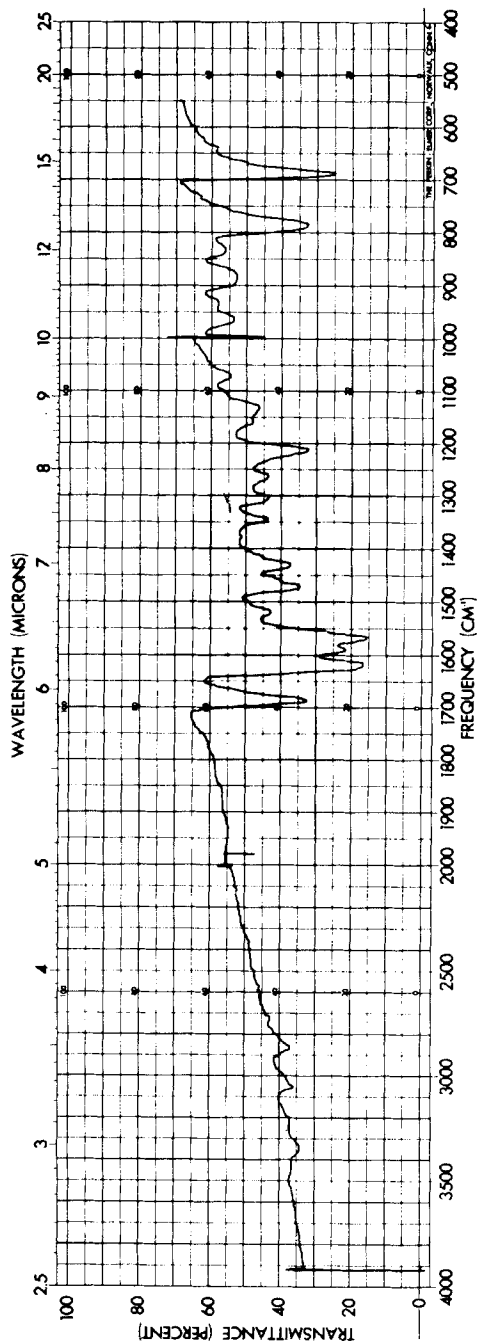


FIG. 6. Infrared spectrum of m-aminobenzaldehyde (trimer).
KBr disc.

zed condensation reactions of p-aminoacetophenone, m-aminoacetophenone, and p-aminobenzophenone were substantially identical to those of the starting monomers; this indicated that little or no reaction had occurred.

Melt Polymerizations. (a) The following is a typical procedure of the method which had been reported previously [2-4]. An intimately ground mixture of the monomer and 0.5% by weight of anhydrous zinc chloride were reacted in a nitrogen atmosphere for 2 hr at 300°C; then the viscous reaction product was allowed to cool and was isolated. The infrared spectra of the polymers isolated after melt condensation at 300°C are shown in Figs. 7-11 and other relevant data are summarized in Table 1.

(b) Portions of H300 polymers I to VII inclusive were heated [1] under nitrogen at 400°C for 4 hr and typical infrared spectra are shown in Figs. 12-16. Table 2 summarizes relevant data.

(c) An intimately ground mixture of 3.27 g (0.01 mole) of $\text{H}_2\text{C}=\text{NC}_6\text{H}_4\text{CH}=\text{O}$ and 1.77 g (0.01 mole) of benzylideneaniline was heated [1] in nitrogen at 220°C for 1 hr and at 300°C for 2 hr; then the sample was cooled in an aliquot portion was condensed at 400°C for 3 hr. The yield and other relevant data are given in Table 3.

The infrared spectra of the BA-H300 polymers show only minor



absorptions for C=O at 1676 cm^{-1} and the absence of a band for NH_2 at 3380 cm^{-1} , but do show the presence of C_6H_5 end groups at 690 and 750 cm^{-1} . The infrared spectra for the I-BA-H300 and I-BA-H400 polymers are shown in Figs. 17 and 18.

Thermogravimetric Analyses

The procedure previously published was used in the thermoanalyses of the polymers [1-5]. A du Pont 900 differential thermal analyzer in conjunction with a 950 thermogravimetric analyzer was used in these tests. To compare the thermal stabilities of these polymers with those of the polymeric azomethines previously reported [1-5], similar conditions of tests were used in these evaluations. The sample size was 10 mg ground to a powder of approximately 500 pieces, the rate of heating was 15°C/min in a dry nitrogen or air stream at a gas flow rate of 1 standard liter/min to a recorded temperature of 1200°C, which corresponds to 1176°C when corrected for the nonlinearity of the chromel-alumel thermocouple. The polymer samples evaluated were those which were condensed to a temperature of 400°C, and these are indicated, as previously [1], as H400 polymers. Portions of the H400 samples were heated to 600°C for 20 min by procedures previously reported [1] and these samples are designated as H600 polymers; other portions were condensed to 1176°C in the thermogravimetric analyzer using the technique pre-

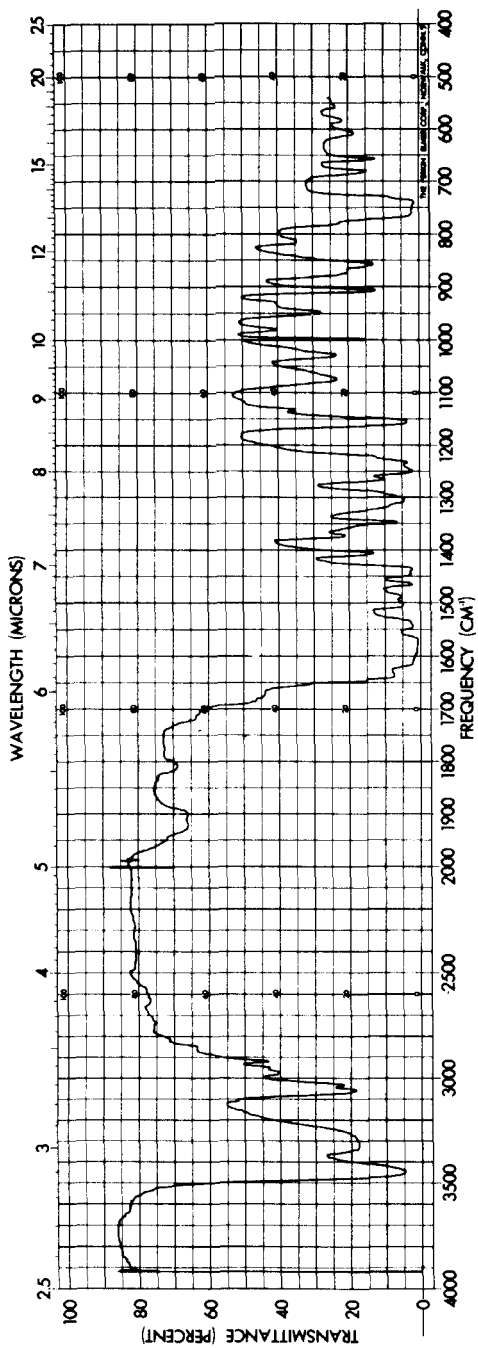
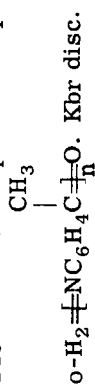


FIG. 7. Infrared spectrum of polymer I-H300,



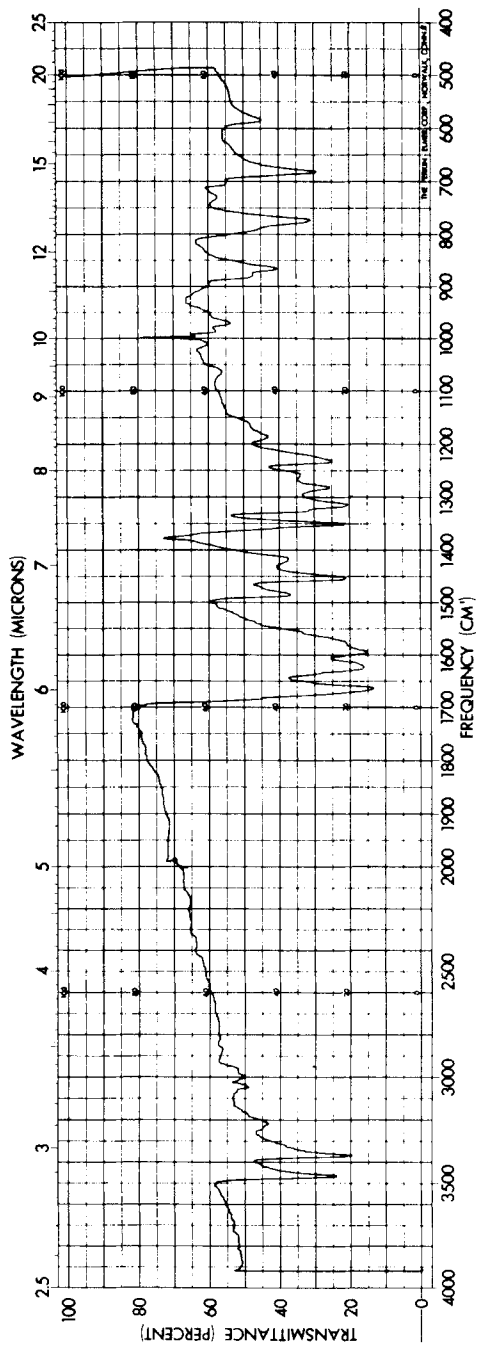
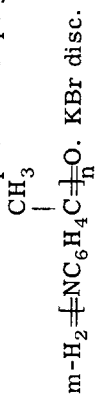


FIG. 8. Infrared spectrum of polymer II-H300,



KBr disc.

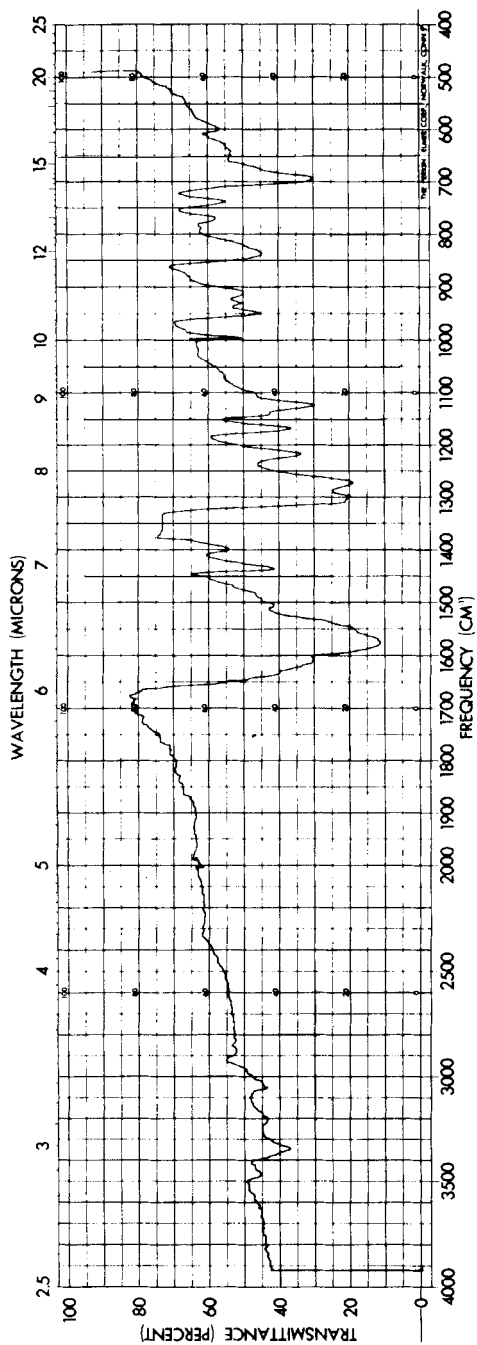
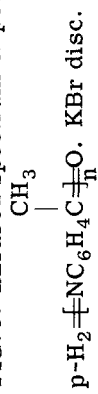


FIG. 9. Infrared spectrum of polymer III-H300,



KBr disc.

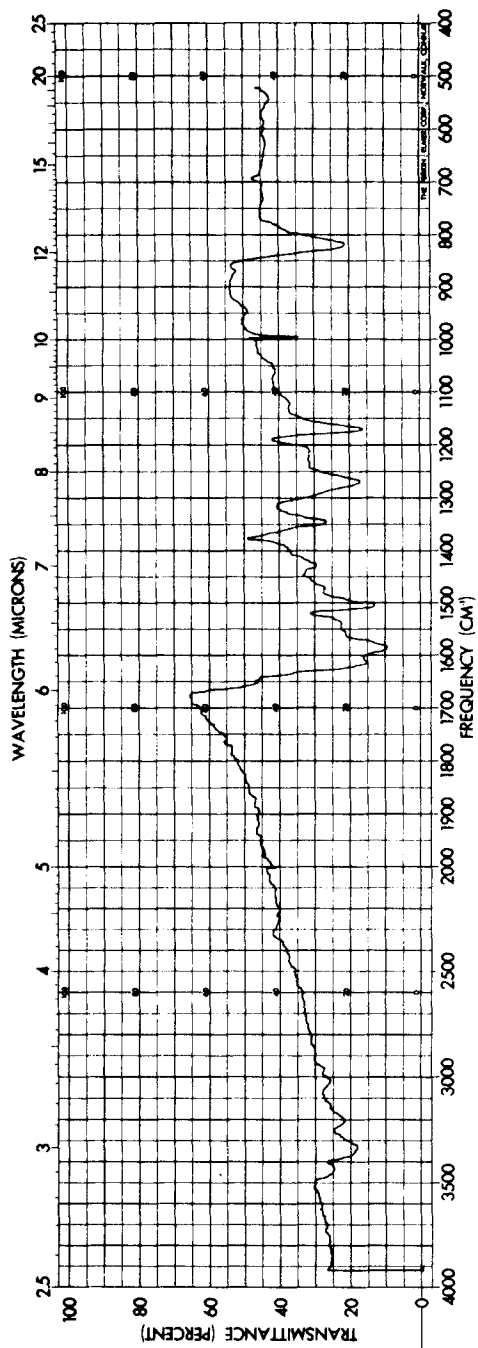
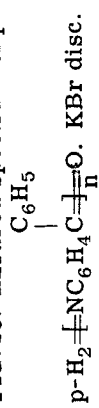


FIG. 10. Infrared spectrum of polymer IV-H300,



KBr disc.

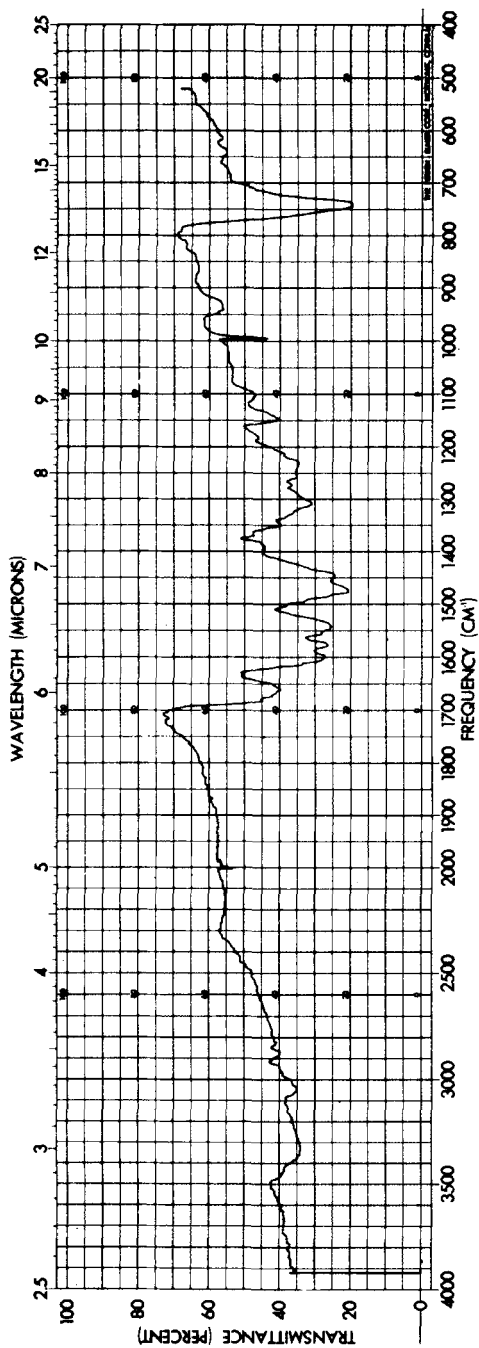


FIG. 11. Infrared spectrum of polymer V-H300,
 $\text{o-H}_2\text{-}\left[\text{NC}_6\text{H}_4\text{CH}=\text{O}\right]_n$. KBr disc.

TABLE 1. Data on the Syntheses of the H300 Polymers

Polymer	Monomer	Yield, ^a %	Color	Fluidity at 300°C	Softening point (°C)	Solubility in		Analyses, %		
						Acetone	DMAC ^c	C	H	N
I-H300	o-Aminoacetophenone	103.0	brown	Melt	70.2	Yes	Yes	81.01	6.09	11.78
II-H300	m-Aminoacetophenone	103.4	brown	Melt	97.8	Yes	Yes	80.84	6.10	11.83
III-H300	p-Aminoacetophenone	103.8	red-brown	Melt	106.8	Yes	Yes	80.50	6.07	11.74
IV-H300	p-Aminobenzophenone	103.6	greenish yellow	Melt	110.2	Slightly	Partial	85.59	5.12	7.71
V-H300	o-Aminobenzaldehyde	102.9	brown	Melt	158.1	Yes	Yes	80.18	4.99	13.40
VI-H300	m-Aminobenzaldehyde ^b	no re- action	dark- yellow	No melt	≥300°C	Very slightly	Yes	77.07	5.18	12.83
VII-H300	p-Aminobenzaldehyde ^b	no re- action	dark- yellow	No melt	≥300°C	Very slightly	Yes	77.01	5.16	12.79

^aCalculated on the basis of $\text{NArCR} \frac{\text{H}}{\text{H}=\infty}$.

^bThese products are trimers.

^cDMAC, N,N-dimethylacetamide.

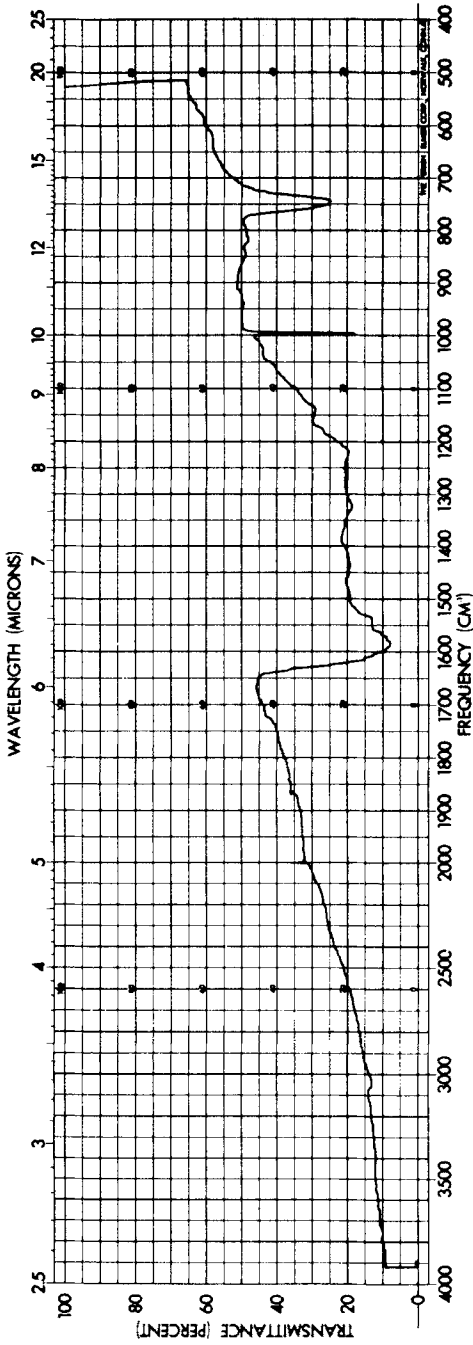
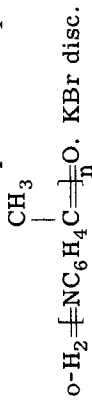


FIG. 12. Infrared spectrum of polymer I-H400,



KBr disc.

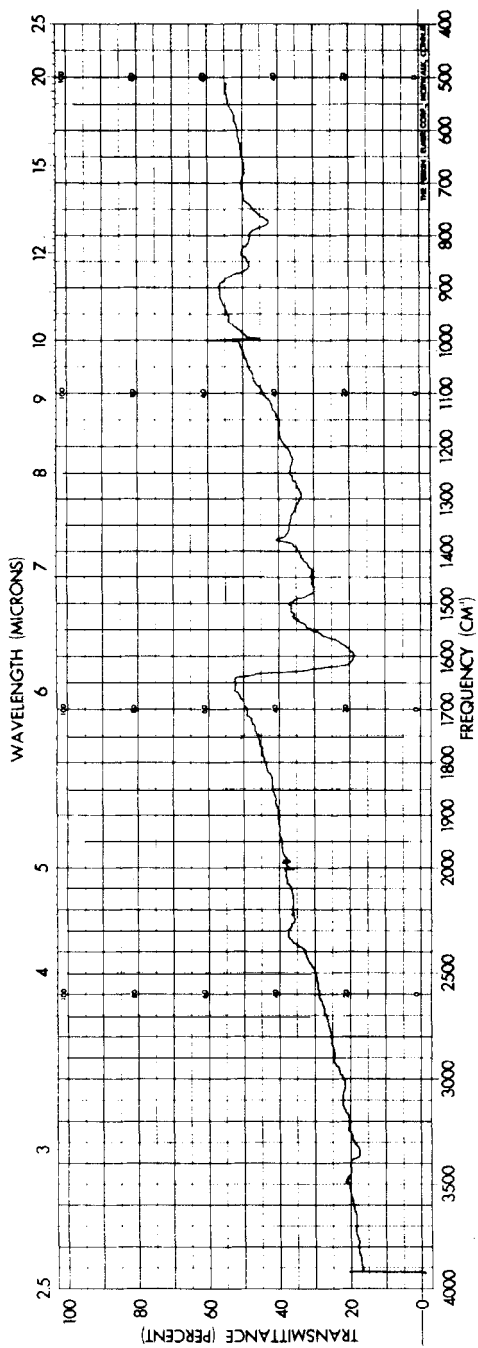
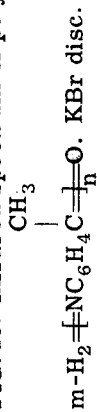


FIG. 13. Infrared spectrum of polymer II-H400,



KBr disc.

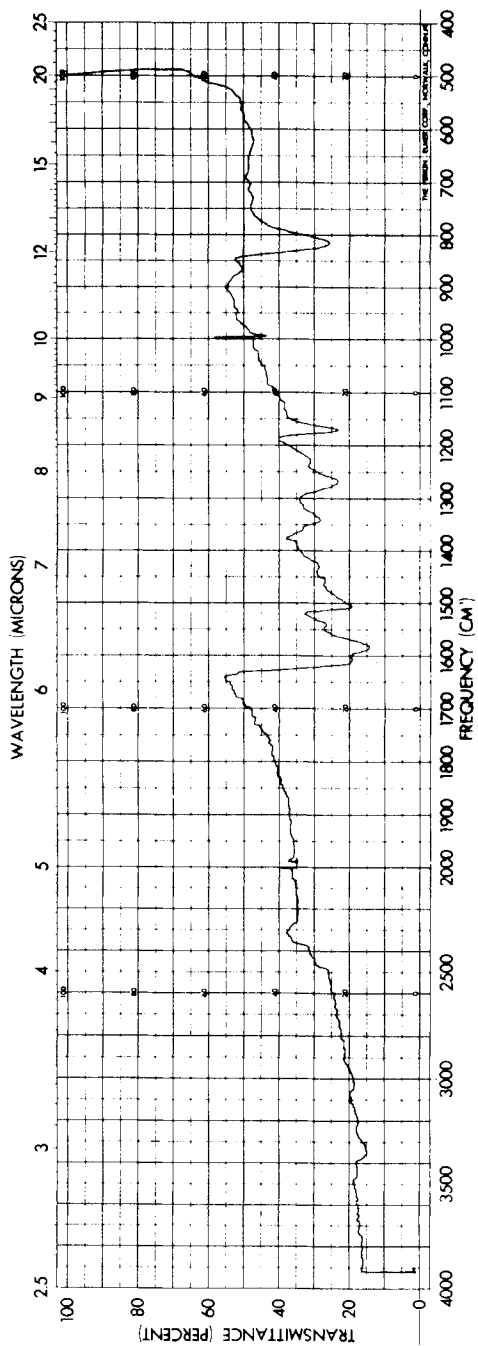
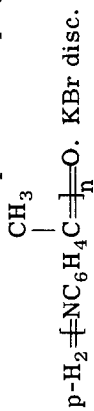


FIG. 14. Infrared spectrum of polymer III-H400,



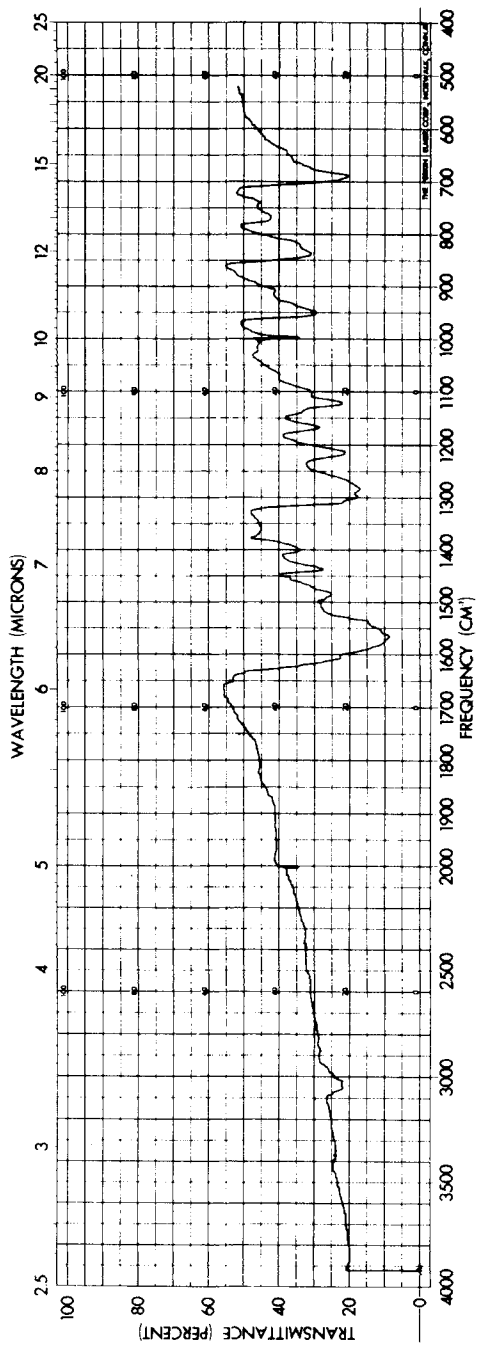
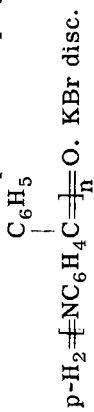


FIG. 15. Infrared spectrum of polymer IV-H400,



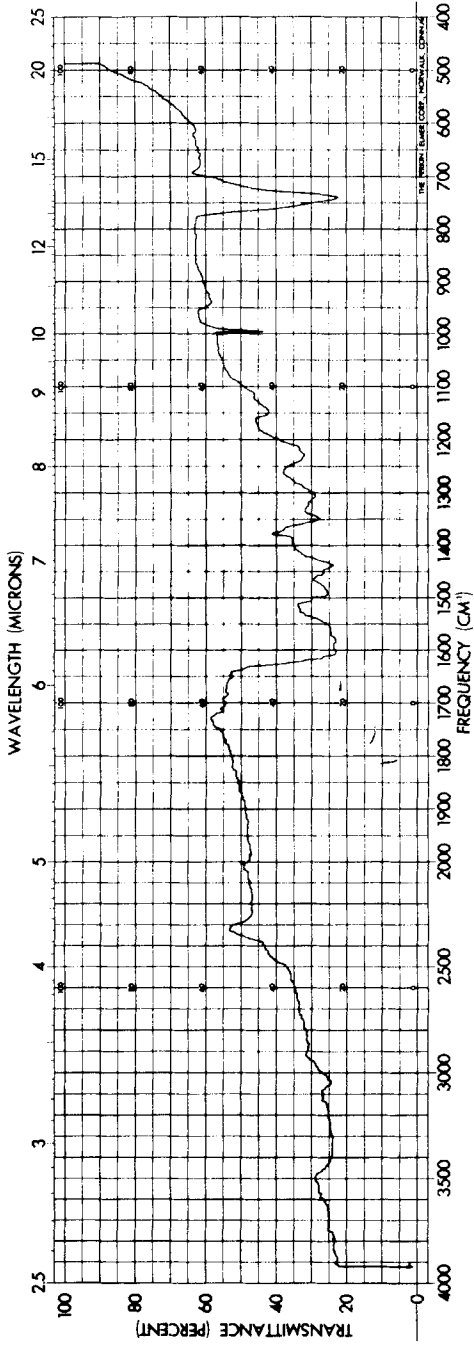


FIG. 16. Infrared spectrum of polymer V-H400,
 $o\text{-H}_2\text{=NC}_6\text{H}_4\text{CH=}$ $\left[\text{C}_6\text{H}_4 \right]_n$. KBr disc.

TABLE 2. Data on the Syntheses of the H400 Polymers

	Polymer	Color	% Yield ^a	Analysis, % N
I-H400	Ortho, $\text{-(NC}_6\text{H}_4\text{C(CH}_3\text{))}_n\text{-}$	Black	101.8	11.87
II-H400	Meta, $\text{-(NC}_6\text{H}_4\text{C(CH}_3\text{))}_n\text{-}$	Black	102.1	11.92
III-H400	Para, $\text{-(NC}_6\text{H}_4\text{C(CH}_3\text{))}_n\text{-}$	Black	102.6	11.83
IV-H400	Para, $\text{-(NC}_6\text{H}_4\text{C(C}_6\text{H}_5\text{))}_n\text{-}$	Black	101.7	7.79
V-H400	Ortho, $\text{-(NC}_6\text{H}_4\text{CH)}_n\text{-}$	Black	101.7	13.46
VI-H400	Meta, $\text{H}_2\text{-(NC}_6\text{H}_4\text{CH)}_n\text{-O}$	Light brown	93.6	12.89
VII-H400	Para, $\text{H}_2\text{-(NC}_6\text{H}_4\text{CH)}_n\text{-O}$	Light brown	93.1	12.81

^aBased on $\text{-(NArC)}_n\text{-}$.

viously described [1] and these samples are designated as H1176 polymers. The thermogravimetric data are summarized in Tables 4 to 8.

Calorimetric Determinations

The procedure described in a previous publication was used [4] obtain calorimetric data at a heating rate of 15°C/min at a gas flow rate of air of 1 standard liter/min, using 3.5 g samples of polymer. The calorimetric data are summarized in Table 9.

DISCUSSION

The aminoaryl ketones, $\text{H}_2\text{NC}_6\text{H}_4\text{COR}$, failed to condense to polymers when heated at reflux temperature in benzene solutions even when catalyzed by Lewis acid. In this respect, the nonreactivity of

TABLE 3. Data on the Polymerization of Aminobenzaldehyde Trimers in Benzylideneaniline

Polymer Trimer	Color	% Yield ^a at 300°C	Analysis	
			% N in polymer at 300°C	% N in polymer at 400°C
I-BA	m-H ₂ -[NC ₆ H ₄ CH=O] ₃	Black 103.2	12.69	100.7
II-BA	p-H ₂ -[NC ₆ H ₄ CH=O]	Black 104.6	12.64	101.2

^aBased on C₆H₅CH=NC₆H₄CH=NC₆H₅.

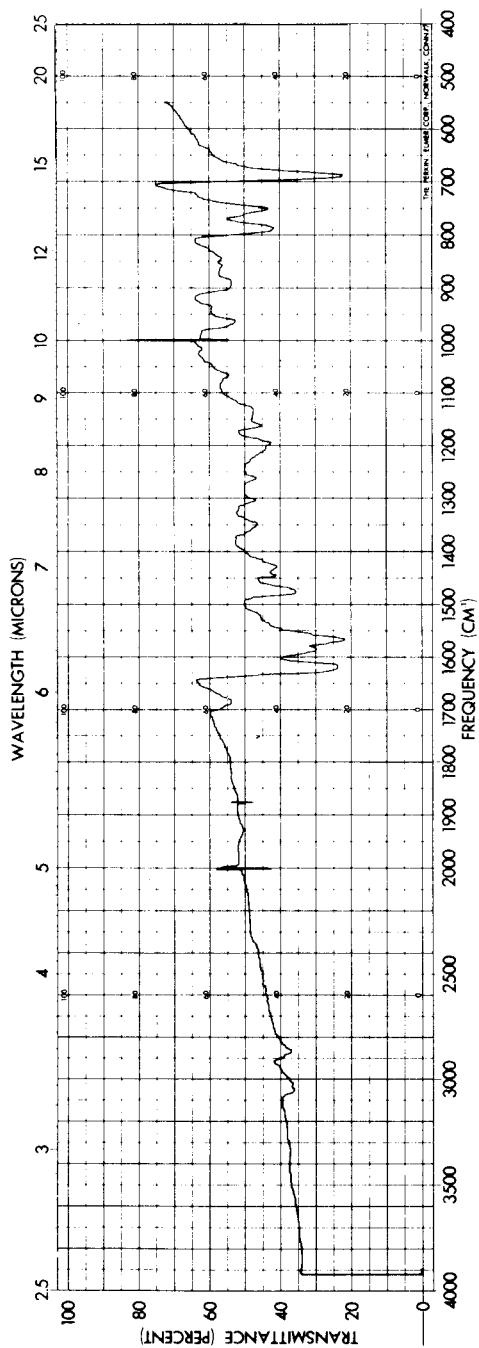


FIG. 17. Infrared spectrum of I-BA-H300 polymer, $m\text{-C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5$. KBr disc.

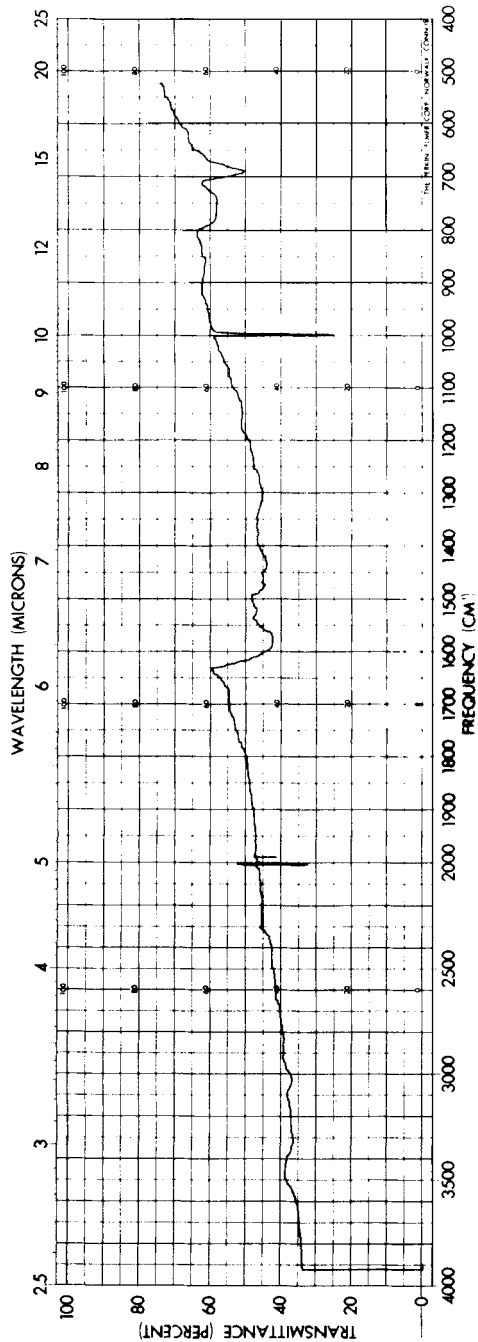


FIG. 18. Infrared spectrum of I-BA-H400 polymer,
 $m\text{-C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5$. KBr disc.

TABLE 4. Thermogravimetric Data in Nitrogen for the H400 Polymers

Polymer	% Weight loss at °C									
	300	400	500	600	700	800	900	1000	1176	
I-H400	0.0	0.0	0.0	3.2	9.6	12.5	14.6	15.6	18.8	
II-H400	0.0	0.0	0.0	2.7	4.9	8.3	13.9	14.9	18.0	
III-H400	0.0	0.0	0.0	3.0	9.7	12.7	14.9	15.9	21.2	
IV-H400	0.0	0.0	0.0	2.9	5.1	8.2	14.0	15.0	18.1	
V-H400	0.0	0.0	0.0	2.1	4.3	9.6	13.4	14.3	17.3	
I-BA-H400	0.0	0.0	0.0	2.3	4.5	9.8	13.6	14.6	17.6	
II-BA-H400	0.0	0.0	0.0	2.8	5.0	8.2	13.9	14.8	18.0	

TABLE 5. Thermogravimetric Data in Air for the H400 Polymers

Polymer	% Weight loss at °C			
	400	500	600	700
I-H400	0.0	3.5	81.0	100.0
II-H400	0.0	2.9	80.6	100.0
III-H400	0.0	3.2	71.1	100.0
IV-H400	0.0	3.3	72.5	100.0
V-H400	0.0	2.7	70.4	100.0
I-BA-H400	0.0	2.5	71.0	100.0
II-BA-H400	0.0	2.4	70.2	100.0

TABLE 6. Thermogravimetric Data in Nitrogen for the H600 Polymers

Polymer	% Weight loss at °C			
	600	800	1000	1176
I-H600	0.0	6.6	11.3	16.0
II-H600	0.0	5.8	10.7	15.2
III-H600	0.0	7.7	10.6	15.0
IV-H600	0.0	9.3	10.8	16.7
V-H600	0.0	7.6	11.1	15.0
I-BA-H600	0.0	7.5	10.7	15.0
II-BA-H600	0.0	7.1	10.4	14.8

TABLE 7. Thermogravimetric Data in Air for the H600 Polymers

Polymer	% Weight loss at °C		
	500	600	Inflection point
I-H600	0.0	71.2	507
II-H600	0.0	70.1	512
III-H600	0.0	67.9	514
IV-H600	0.0	68.8	526
V-H600	0.0	67.3	540
I-BA-H600	0.0	69.1	535
II-BA-H600	0.0	68.6	542

TABLE 8. Thermogravimetric Analyses in Nitrogen and in Air for the H1176 Polymers

Polymer	Gas	% Weight loss at °C						
		500	600	700	800	900	1000	1176
I-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Air	0.0	18.4	100.0	—	—	—	—
II-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Air	0.0	17.6	100.0	—	—	—	—
III-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Air	0.0	13.9	100.0	—	—	—	—
IV-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Air	0.0	11.6	100.0	—	—	—	—
V-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Air	0.0	10.1	100.0	—	—	—	—
I-BA-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Air	0.0	9.4	100.0	—	—	—	—
II-BA-H1176	Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Air	0.0	10.2	100.0	—	—	—	—

TABLE 9. Calorimetric Data in Air for Some Aminoarylcarbonyl Polymers

Polymer	Calorimetric peak, °C	Heat of reaction, cal./g
Graphite [4]	680	520-550
I-H600	527	3000-3200
II-H600	525	3100-3400
I-H1176	530	4800-5100
I-BA-H1176	535	4900-5400
I-H400	410	3500-3700

these A-B monomers differs markedly from the reactivity, previously reported [5], of the A-A with the B-B monomers, as exemplified by the reactions of the aryldiketones with the aryldiamines. This difference may be attributed to the fact that the NH_2 and RCO groups are attached to the same aromatic nucleus in the A-B monomers, whereas these functions reside in two different molecules in the reactions involving diketones with diamines. Surprisingly, *o*-aminobenzaldehyde did not condense to polymers in refluxing benzene even in the presence of catalytic amounts of *p*-toluenesulfonic acid. This unreactivity at this temperature can be attributed to steric factors resulting from hydrogen bonding of the amino hydrogen with the *o*-carbonyl. In contrast, as evidenced in the reduction of the *m*- and *p*-nitrobenzaldehydes, respectively, the resulting *m*- and *p*-aminobenzaldehydes condense immediately to precipitate as yellow, brick-dust polymers. In this respect, the reactivities of the *m*- and *p*-aminobenzaldehydes, as A-B monomers, are similar to reactivities found in the reactions of the A-A plus B-B monomers, as exemplified by the reaction of terephthalaldehyde with *p*-phenylenediamine. These condensations in solution do, however, point to a greater reactivity for the aminoarylaldehydes than for the aminoarylketones. This greater reactivity of the aminoarylaldehydes was noted in the melt polymerizations of these two classes of aminoarylcarbonyl monomers. The uncatalyzed polymerization of *o*-aminobenzaldehyde was much more rapid, as a melt, at 300°C than any of the aminoaryl ketones. However, the polymerization at 300°C in the presence of catalytic quantities of zinc chloride of the aminoarylcarbonyl monomers, as exemplified by the self-condensations of *o*-aminobenzaldehyde and of the aminoaryl ketones, was most facile; all of them yielded fluid melts whose viscosities increased with reaction time; the color of the reaction mixture changed from light yellow to brown within a heating period of 1 hr at 300°C. The polymerization of *p*-aminobenzophenone was the slowest of the monomers studied, reflecting the steric effect due to the bulky terminal phenyl group in the ketone structure. These polymers prepared by condensation at 300°C for 2 hr were brown in color and showed marked solubility in a number of solvents, such as in acetone and dimethylacetamide; this solubility and the elemental analyses indicated their molecular weights were not very high. However, when the condensation was continued at 400°C for an additional 3 hr, the polymers became hard and shiny black with the elimination of additional amounts of water; their solubility in common solvents and in formic and sulfuric acids became negligible. Also, their infrared spectra show the disappearance of the bands characteristic of the NH_2 and C=O groups and a broadening of the band for the C=N structure in the region of 1590 cm^{-1} . The yield of polymers obtained after condensation at 400°C approached the theoretical yield, and the elemental analyses for nitrogen indicated a measurable increase in the molecular

weight. Attempts were made to polymerize the trimers of *m*-aminobenzaldehyde by heating them at 300°C under similar conditions under which the other monomers were treated. These trimers did not melt under these conditions; the yellow color of the polymers darkened somewhat and no apparent reaction occurred, although traces of water collected on the surface of the reaction tube. Melting failed to occur also when the trimers were treated at 400°C, although their colors changed from dark yellow to brown and a weight loss of approximately 7% occurred as a result of the heating. However, the trimers were readily converted to black polymers by continuing the condensation in benzylideneaniline [1]. Elemental analyses and infrared spectral data indicated that benzylideneaniline not only solvated the polymer but telomerized the ends of the polymer chains. The polymerization of these trimers in benzylideneaniline paralleled that found [1] for the polymerization in benzylideneaniline of low molecular weight Schiff base polymers prepared from aryldialdehydes and aryldiamines. The yields of benzylideneaniline polymerized trimers at 400°C closely approximated the theoretical amount, and the elemental analyses and their infrared spectra indicated molecular weights of the order of magnitude found for the yellow dialdehydediamine Schiff base polymers similarly polymerized [1] in benzylideneaniline.

The thermogravimetric data in nitrogen and in air for the H400, H600, and H1176 polymers show that the thermal stabilities of the polymers prepared from aminoarylcarbonyl monomers are comparable to the polymers prepared [1-5] by the reaction of the dicarbonyl compounds, $\text{Ar}''(\text{COR})_2$, with the diamine compounds, $\text{Ar}''(\text{NH}_2)_2$.

The calorimetric data obtained for the aminoarylcarbonyl polymers of this study is similar to that found for the poly-Schiff bases [4] and for the polyketanils [5]; the data indicate that these polymers have not been converted to graphitic-type polymers when heated to 1176°C in nitrogen under the experimental conditions used.

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Zusammenfassung

Die Synthese von polymeren Azomethinen aus Aminoarylcarbonylmonomeren, $H_2NArCOR$, wird beschrieben und die thermische Stabilität dieser Polymerer wurde als vergleichbar mit solchen Produkten gefunden, die durch Reaktion von Aryldicarbonylverbindungen mit Aryldiaminen erhalten wurden.

Résumé

Description de la synthèse des azométhines polymériques à partir de monomères aminoarylcarbonylés, $H_2NArCOR$. On a trouvé que les stabilités thermiques de ces polymères sont comparables à celles des polymères, préparés par la réaction des composés aryl-dicarbonylés avec les diamines.