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Summary

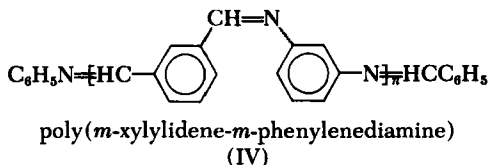
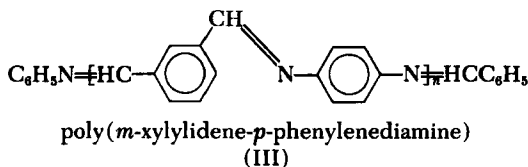
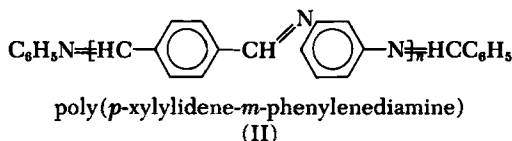
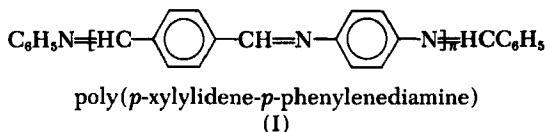
The four isomeric Schiff base polymers, poly(*p*-xylylidene-*p*-phenylenediamine), poly(*p*-xylylidene-*m*-phenylenediamine), poly(*m*-xylylidene-*p*-phenylenediamine), and poly(*m*-xylylidene-*m*-phenylenediamine) were synthesized by the bis-Schiff base exchange reaction from the appropriate pairs selected from the four monomers, *N,N'*-bisbenzylidene-*p*-phenylenediamine, *N,N'*-bisbenzylidene-*m*-phenylenediamine, *p*-xylylidenedianil, and *m*-xylylidenedianil. The differences in the thermal stabilities in nitrogen and in air of these four isomeric polymers prepared by condensation to temperatures of 400 and 600°C are minor.

The synthesis and evaluation of a series of black polymeric Schiff bases of the general formula $\text{=HCAr'CH=NAr''N}\frac{1}{n}$, in which Ar represents an arylene moiety, were described in a previous publication (1). To determine (1) the effect of changes in structure on the thermal stability of the polymers, the Ar' structure was maintained constant as paraphenylene, *p*-C₆H₄—, while changes were introduced in the Ar'' structures yielding thereby conjugated, homoconjugated, and pseudoconjugated polymers. The position substitution of the various Ar'' structures used (1), such as —C₆H₄—, —C₆H₄—C₆H₄—, —C₆H₄OC₆H₄—, —C₆H₄SO₂C₆H₄—, etc., was also maintained constant as para substitutions. Thus, *p*-xylylidene-*p*-phenylenediamine, $\text{=}\left[\text{—C}_6\text{H}_4\text{—CH=N—C}_6\text{H}_4\text{—N} \right]_n$, became the reference polymer for the $\text{=HC—C}_6\text{H}_4\text{—CH=NAr''N}\frac{1}{n}$ poly-

mers which had various degrees of conjugation in the Ar'' structures. However, modification of the degrees of conjugation can be obtained also by position substitution in the benzene ring (2).

Such a modification was observed (2) readily in the bathochromic shift in the ultraviolet spectra of the polyphenylenes, $H-[C_6H_4]_nH$. In the *p*-polyphenylenes, λ_{max} shifted asymptotically to a maximum from 251.5 $m\mu$ for $n = 2$ to 317 $m\mu$ for $n = 6$, whereas in the case of the *m*-polyphenylenes, λ_{max} shifted very slowly to 253 $m\mu$ for $n = 6$ to only 255 $m\mu$ for $n = 12$.

Similar bathochromic shifts should be expected in the Schiff base homologues and accordingly λ_{max} was evaluated for a number of monomeric Schiff bases. The λ_{max} for benzylideneaniline, $C_6H_5-CH=NC_6H_5$, was observed (1) previously at 263.0 $m\mu$; and when it was found that the λ_{max} for *p*- $C_6H_5CH=NC_6H_4N=HCC_6H_5$ and *p*- $C_6H_5N=HCC_6H_4CH=NC_6H_5$ were much higher than their meta analogues, *m*- $C_6H_5CH=NC_6H_4N=HCC_6H_5$ and *m*- $C_6H_5N=HCC_6H_4CH=NC_6H_5$, it was deemed advisable to evaluate the effect of position substitution on the thermal stabilities of the xylylidene-phenylenediamine polymers of (I). Para and meta substitutions in both Ar and Ar'' moieties yield the four isomeric polymers,



For purposes of brevity and convenience, the four polymers are referred to in this paper as the para-para polymer (I), the para-meta polymer (II), the meta-para polymer (III), and the meta-meta polymer (IV), with the position substitution of the xylidene moiety listed first in this nomenclature. This paper reports studies on the syntheses and thermal stabilities of these four isomeric xylidenediphenylenediamine polymers.

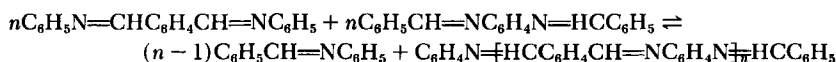
EXPERIMENTAL

Monomers

The four monomers (a) *N,N'*-bisbenzylidene-*p*-phenylenediamine, m.p. 140°C; (b) *N,N'*-bisbenzylidene-*m*-phenylenediamine, m.p. 106°C; (c) *p*-xylidenedianil, m.p. 166°C; and (d) *m*-xylidenedianil, m.p. 53°C, were prepared by procedures previously published (3); their infrared spectra, recorded on a Perkin-Elmer Model 421 grating spectrophotometer, are shown in Figs. 1 to 4. Their ultraviolet λ_{\max} values, determined on a Bausch and Lomb Spectronic Model 505 using dimethylacetamide solutions of the monomers, are given in Table 1.

Polymerizations

The polymers were prepared by means of the bis-Schiff base exchange reaction,



using 0.01 mole of the appropriate complimentary reactants by the procedure previously published (1), using the following modified

TABLE 1
 λ_{\max} Values for Some Monomeric Schiff Bases

Monomer	λ_{\max} , m μ
$\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_5$	263.0
<i>p</i> - $\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{N}=\text{HCC}_6\text{H}_5$	357.0
<i>m</i> - $\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{N}=\text{HCC}_6\text{H}_5$	267.4
<i>p</i> - $\text{C}_6\text{H}_5\text{N}=\text{HCC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5$	347.0
<i>m</i> - $\text{C}_6\text{H}_5\text{N}=\text{HCC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5$	266.0

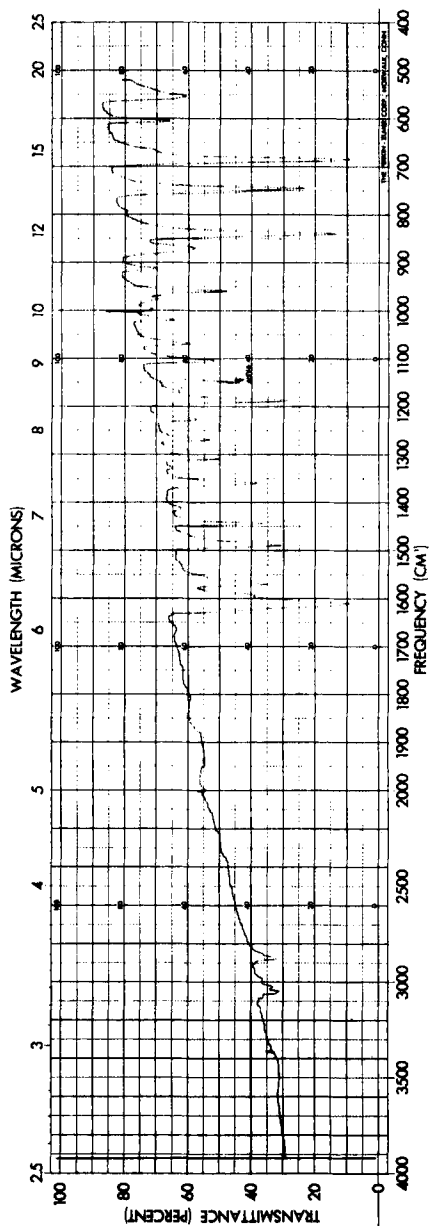


FIG. 1. *N,N'*-Bisbenzylidene-*p*-phenylenediamine. KBr disc.

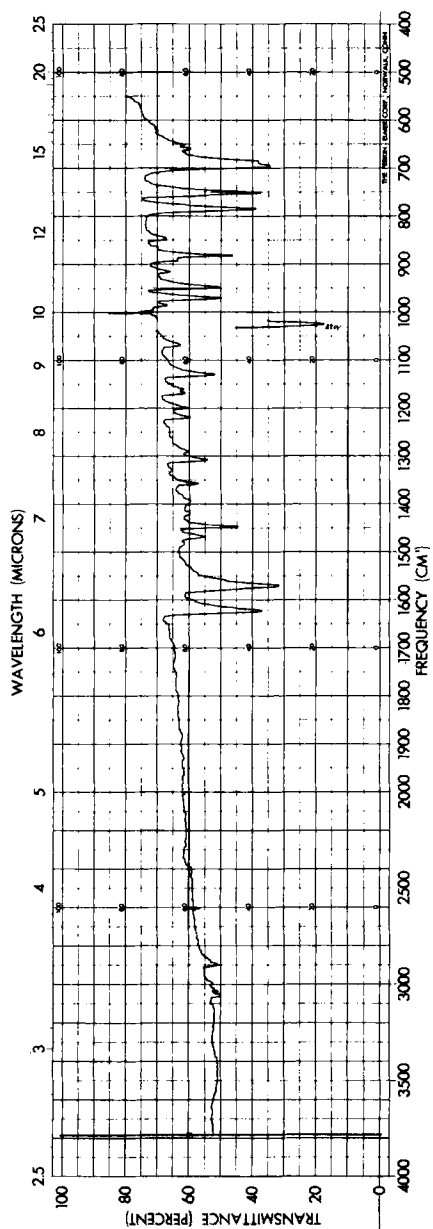


FIG. 2. N,N' -Bisbenzylidene-*m*-phenylenediamine, KBr disc.

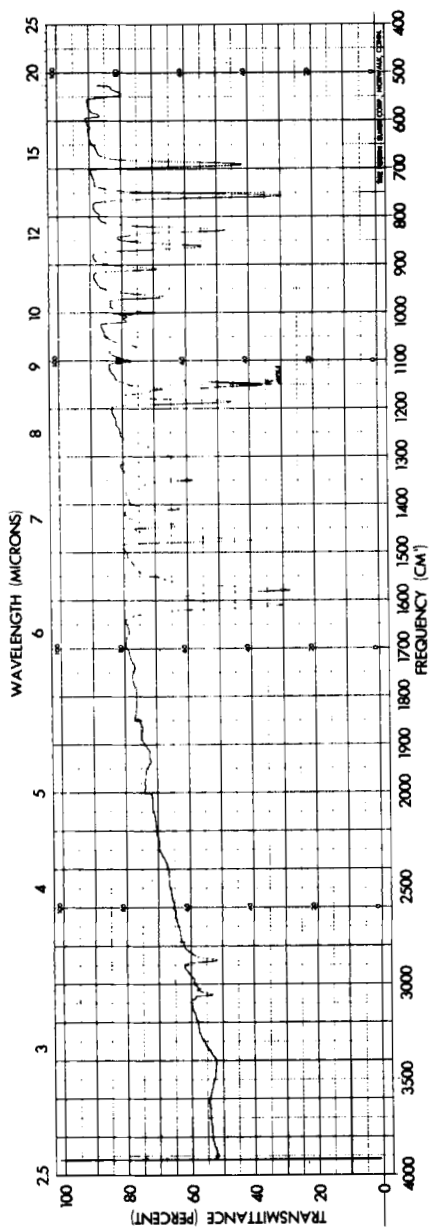


FIG. 3. *p*-Xylylidenedianil. KBr disc.

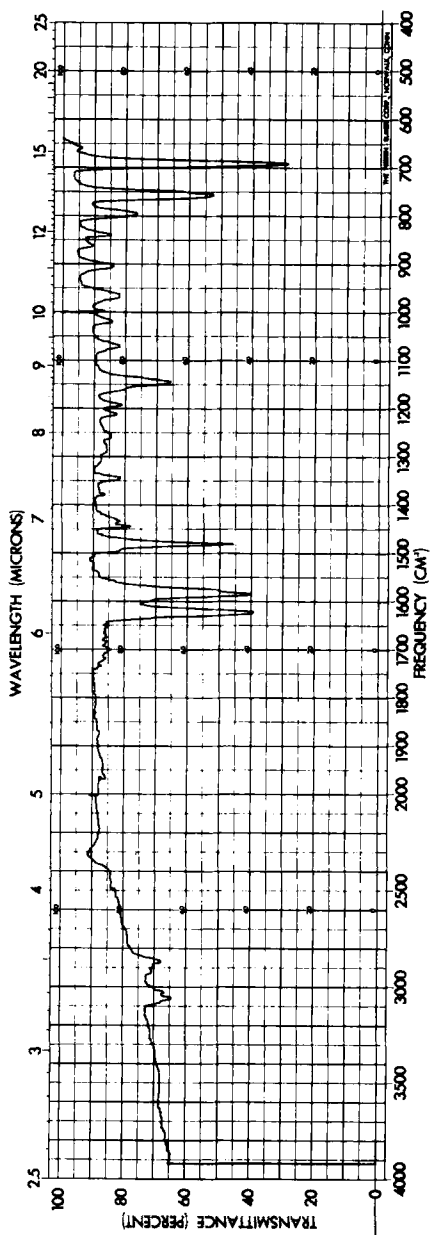
FIG. 4. *m*-Xylylidenedianil. KBr disc.

TABLE 2
Reaction Conditions

Time, hr	Temp., °C	Pressure, mm Hg
2	200	760
2	260	760
10	300	760
10	320	760
10	380	1.0
15	400	1.0

heating schedule given in Table 2. The polymers prepared under these conditions are designated H400 polymers to indicate, as was done previously (1), that the maximum temperature under which they were condensed was 400°C.

Portions of the H400 polymers were condensed to 600°C for 60 min by procedures previously reported (1) and are designated as H600. Additional amounts of benzylideneaniline were collected during the heating at 600°C. The yield data of these polymerizations are given in Table 3 and the infrared spectra of the H400 polymers are shown in Figs. 5 to 8. Figure 9 details the infrared spectra of the polymer H600, and Fig. 10 is the infrared spectrum (1) of the meta-meta (IV) H600 polymer. Figure 11 contrasts the infrared spectra of the meta-meta (IV) H600 and H700 polymers.

Postheating of the H600 Polymers

Portions of the H600 polymers were postheated to 700°C in a du Pont Model 950 thermogravimetric apparatus, by the technique

TABLE 3
Yield Data for the Isomeric Xylylidenephenylenediamine Polymers

Polymer		Reactant monomers	Per cent yield ^a at °C	
Number	Isomer		400	600
I	Para-para	(a) + (c)	138	112
II	Para-meta	(b) + (c)	124	110
III	Meta-para	(a) + (d)	129	111
IV	Meta-meta	(b) + (d)	114	108

^a Calculated (1) on the basis of $C_6H_5N=CHC_6H_4CH=NC_6H_4N=CHC_6H_5$.

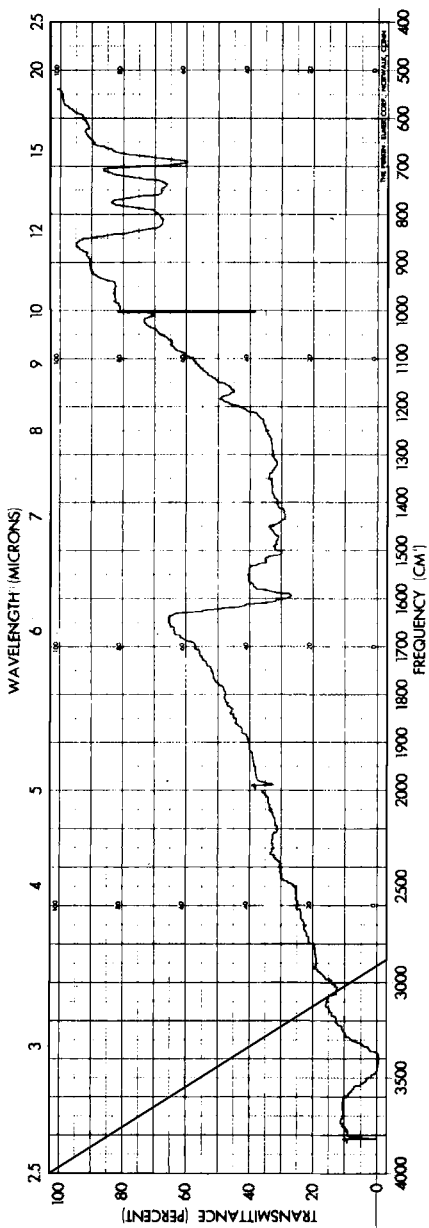


FIG. 5. *p*-Xylylidene-*p*-phenylenediamine polymer H400. KBr disc.

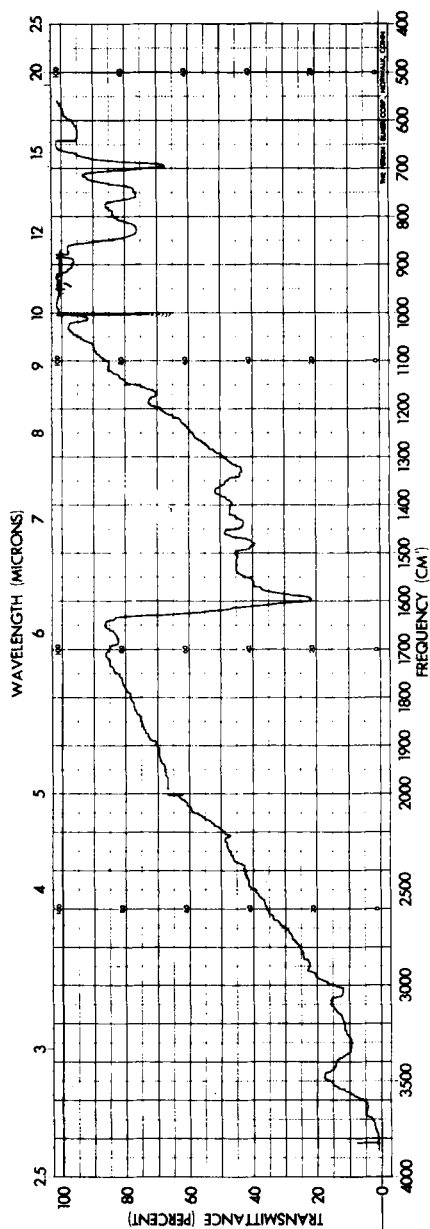


FIG. 6. *p*-Xylylidene-*m*-phenylenediamine polymer H400. KBr disc.

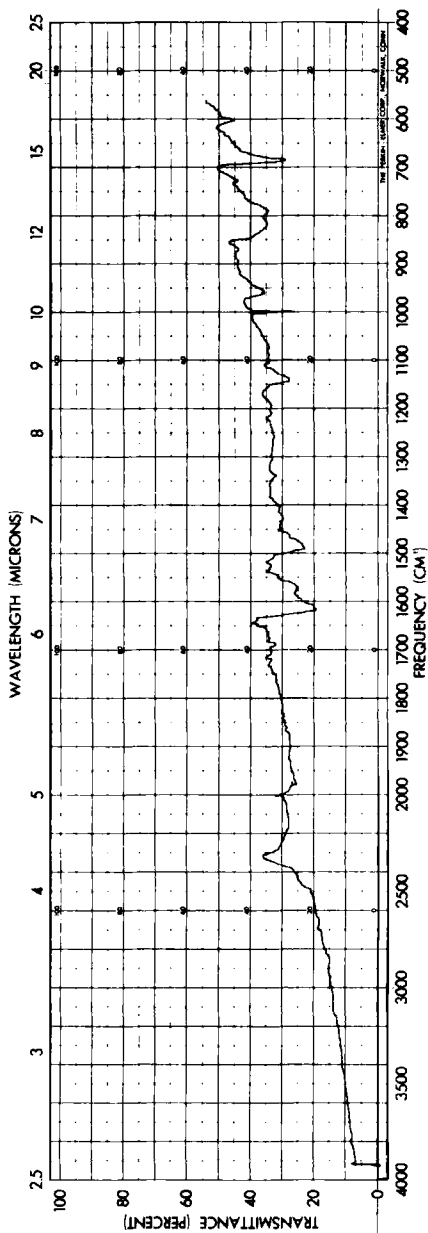


FIG. 7. *m*-Xylylidene-*p*-phenylenediamine polymer H400. KBr disc.

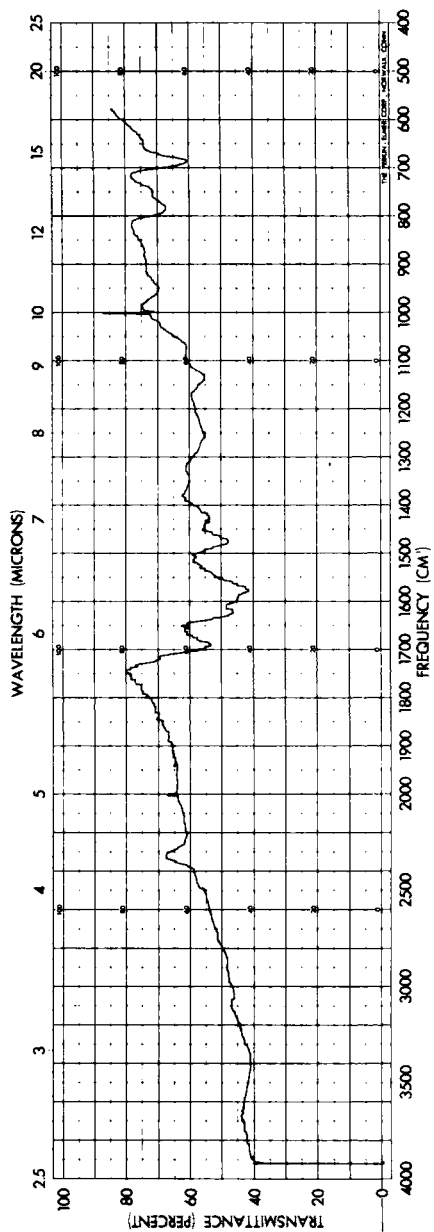


FIG. 8. *m*-Xylylidene-*m*-phenylenediamine polymer H400. KBr disc.

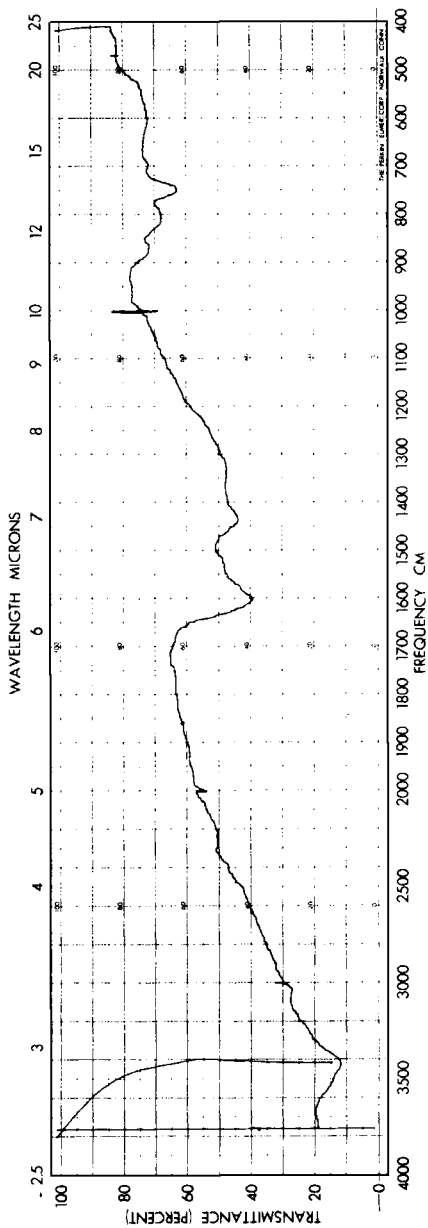


FIG. 9. *p*-Xylylidene-*p*-phenylenediamine polymer H600. KBr disc.

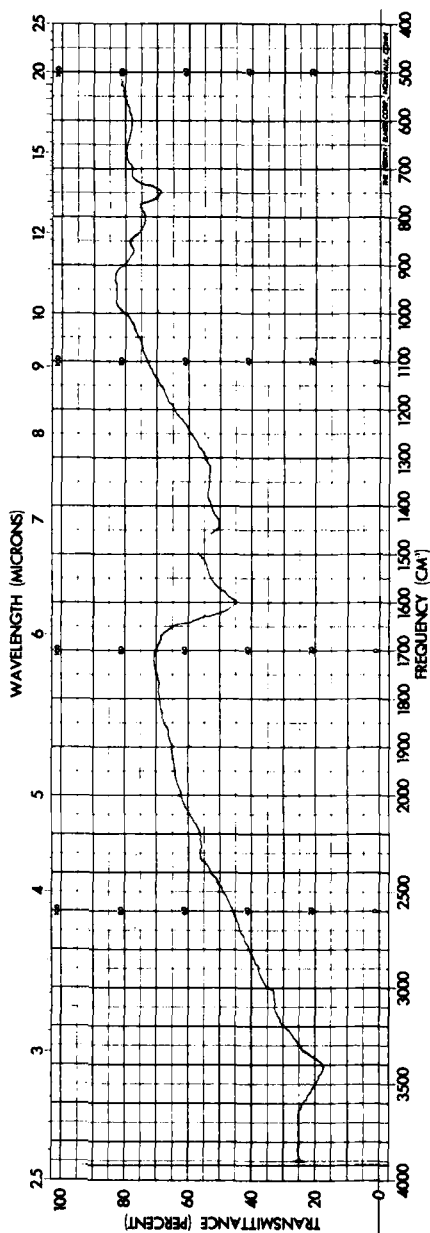


FIG. 10. *m*-Xylylidene-*m*-phenylenediamine polymer H600. KBr disc.

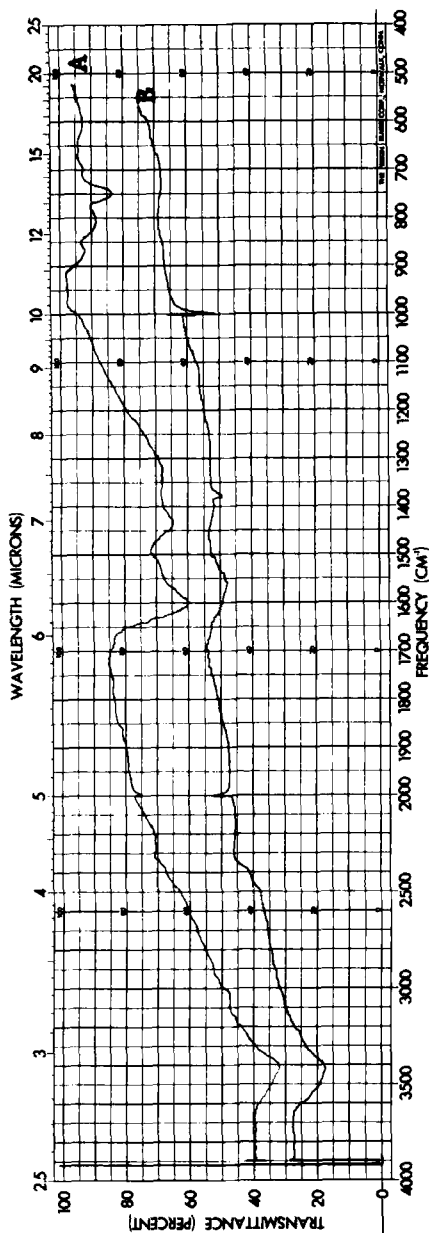


FIG. 11. *m*-Xylylidene-*m*-phenylenediamine polymer; A is H600 and B is H700. KBr disc.

previously reported (1), and held at this temperature for 30 min. Typical spectra of the H600 and H700 polymers are contrasted in Fig. 11. Using the procedure previously reported (1), portions of these polymers were also postheated to a recorded 1200°C in the thermogravimetric apparatus, which, when corrected for the non-linearity of the Chromel-Alumel thermocouple, is 1176°C.

Thermogravimetric Analyses

All thermogravimetric analyses were performed on a du Pont Model 900 differential thermal analyzer in conjunction with a du Pont Model 950 thermogravimetric analyzer using the technique and conditions previously reported (1). The sample weight of 10 mg was ground to a fine powder of about 50 pieces per milligram. The heating rate was 15°C/min in a stream of dry nitrogen or in air at a gas flow rate of 1 standard liter/min. The H600 and H1176 polymers were also thermogravimetrically analyzed in air. The thermogravimetric data in nitrogen are given in Table 4 and in air in Table 5, and the consolidated thermograms are given in Figs. 12 and 13.

TABLE 4

Thermogravimetric Data on Xylylidenephenylenediamine Polymers in Nitrogen

Polymer	Per cent weight loss at °C								Inflection point
	400	500	600	700	800	900	1000	1176	
<i>p-p</i> I: H400	0	2.0	9.4	16.0	18.8	21.8	22.9	29.8	475
<i>p-m</i> II: H400	0	2.0	6.9	12.5	13.8	15.9	17.6	23.7	480
<i>m-p</i> III: H400	0	3.0	7.1	12.7	14.7	16.6	18.7	24.6	476
<i>m-m</i> IV: H400	0	2.0	3.9	8.0	10.0	10.2	11.0	20.1	485
<i>p-p</i> I: H600	—	—	0	1.0	4.0	6.1	9.2	17.0	630
<i>p-m</i> II: H600	—	—	0	1.7	3.9	7.1	9.8	17.3	612
<i>m-p</i> III: H600	—	—	0	2.1	3.8	8.0	10.5	18.2	610
<i>m-m</i> VI: H600	—	—	0	1.2	4.0	6.2	10.1	19.2	600
<i>p-p</i> I: H1000	—	—	—	—	—	—	0	2.8	1050
<i>p-m</i> II: H1000	—	—	—	—	—	—	0	3.2	1035
<i>m-p</i> III: H1000	—	—	—	—	—	—	0	3.4	1030
<i>m-m</i> IV: H1000	—	—	—	—	—	—	0	3.7	1020

TABLE 5
 Thermogravimetric Data on Isomeric Xylylidenephenylenediamine
 Polymers in Air

Polymer	Per cent weight loss at °C				
	500	600	700	800	900
<i>p-p</i> I: H600	0	70.5	100.0	—	—
<i>p-m</i> II: H600	0	73.1	100.0	—	—
<i>m-p</i> III: H600	0	74.3	100.0	—	—
<i>m-m</i> IV: H600	0	76.2	100.0	—	—
<i>p-p</i> I: H1176	0	30.0	65.0	90.0	100.0
<i>p-m</i> II: H1176	0	32.0	63.0	91.0	100.0
<i>m-p</i> III: H1176	0	30.0	64.0	92.0	100.0
<i>m-m</i> IV: H1176	0	31.0	64.0	89.0	100.0

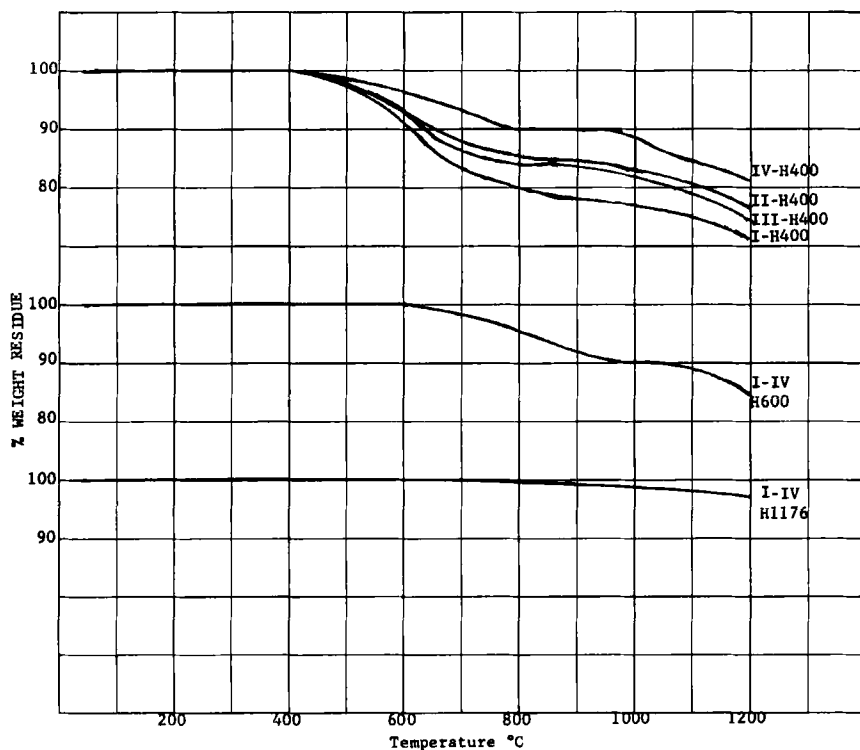


FIG. 12. Thermogravimetric data for polymers (I) to (IV) in nitrogen.

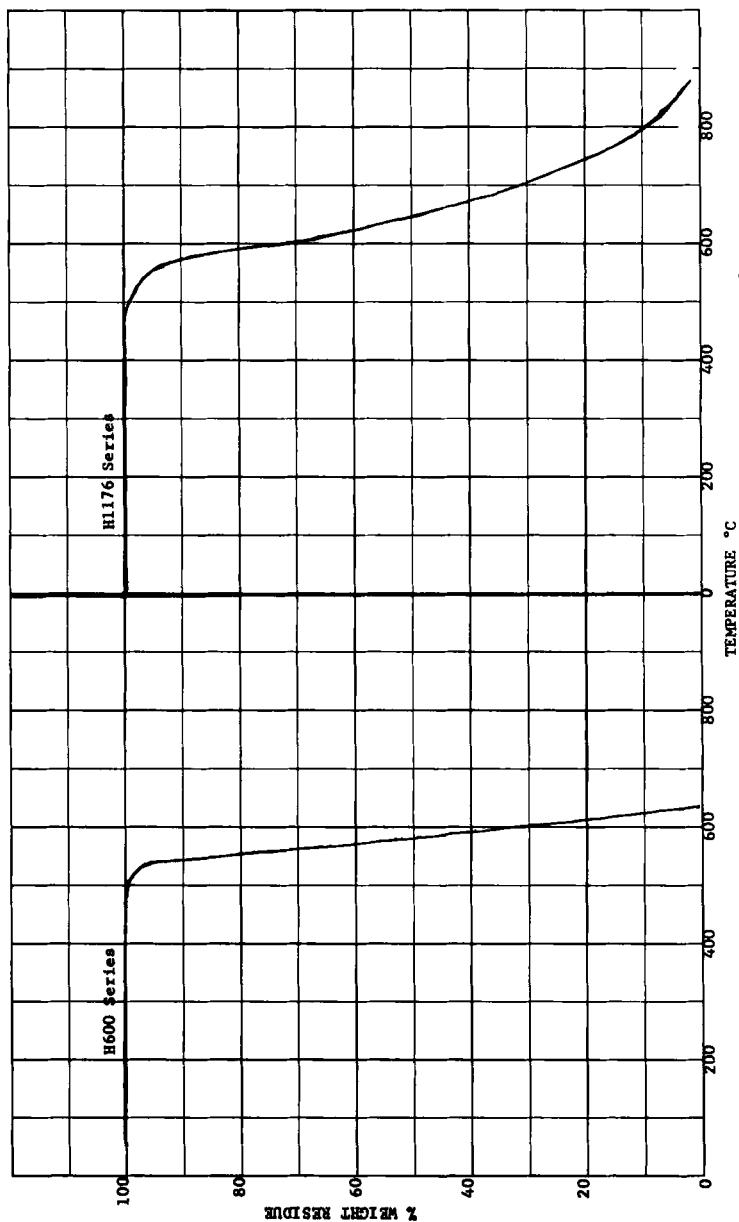


FIG. 13. Thermogravimetric data for the (I) to (IV) H600 and (I) to (IV) H1176 polymers in air.

DISCUSSION

The bis-Schiff base exchange reactions used for the syntheses of the four isomeric xylylidenephenylenediamine polymers were found to be well moderated and to proceed smoothly with the reaction mixtures changing successively in color from yellow to orange to red to brown to black with the continuous evolution of benzylideneaniline. Thus the preparation of the three related isomers was substantially identical in behavior, generally, to that previously reported (1) for the para-para (I) polymer. However, some specific differences were noted which could be attributed to isomeric structural differences. The meta-meta (IV) reaction mixture was, during the course of the reaction, up to until the solid stage was reached, much more fluid than the para-para (I) reaction mixture. The removal of by-product benzylideneaniline from the meta-meta (IV) reaction was more facile than from the para-para (I) reaction mixture, thereby allowing it to more closely approach the calculated yield. The yield at 400°C of the meta-meta (IV) polymer of 114% compares with 138% for the para-para polymer. The fluidities and the yields of the para-meta(II) and meta-para (III) reaction products were intermediate to those of the para-para (I) and meta-meta (IV) reaction mixtures. The different geometric structures of the isomers, however, did not influence the yields of the polymers to the same extent when the condensations were carried to 600°C; the yield of the meta-meta polymer was 108% of theory compared to 112% for the para-para polymer, while the 110% and the 111% yields of the para-meta and meta-para polymers, respectively, closely approximated the yield of the para-para polymer.

The expected differences, attributable to substitution isomerism, were found in the infrared spectra of the monomers. The carbon-nitrogen double-bond stretching is usually placed at 1630 cm^{-1} in various azomethine compounds (4). This bond was found to absorb at 1615 cm^{-1} in *N,N'*-bisbenzylidene-*p*-phenylenediamine and at 1614 cm^{-1} in *p*-xylylidenedianil but at 1620 cm^{-1} for the two monomers, *N,N'*-bisbenzylidene-*m*-phenylenediamine and *m*-xylylidenedianil.

The carbon-nitrogen double-bond stretching absorption was found to shift from the 1614–1615 cm^{-1} region for the para monomers to 1590 cm^{-1} for the para-para polymer (I), whereas in the case of the meta-meta polymer (IV) absorption occurred at 1620 cm^{-1} ,

which corresponds exactly to the wavelength of the two meta monomers from which it was derived. It had been anticipated that the carbon-nitrogen double-bond absorption for the para-meta (II) and the meta-para (III) polymers would fall between the two values of 1590 cm^{-1} for the para-para polymer and 1620 cm^{-1} for the meta-meta polymers. However, it was found that $\text{C}=\text{N}-$ absorption for the para-meta polymer (II) was found at 1590 cm^{-1} similarly to the para-para polymer (I), and for the meta-para (III) polymer the absorption was found at 1620 cm^{-1} similarly to the meta-meta polymer. Evidently, in both the monomers and polymers, the position of the absorption band is determined by the para or meta position substitution present in the xylylidene, $=\text{HCC}_6\text{H}_4\text{CH}=\text{}$, moiety.

When the polymers were heated from 400°C to progressively higher temperatures, the bands in the infrared spectra generally broadened and decreased in intensity. Noticeable broadening of the bands was also observed when the polymers were heated at 600°C in nitrogen for 10 min. The infrared spectrum for the para-para (I) H600 polymer is shown in Fig. 9, and the spectrum of the para-meta (II) H600 polymer is substantially identical to Fig. 9; the infrared spectrum for the meta-meta (IV) H600 polymer is given in Fig. 10, and the spectrum of the meta-para (III) H600 polymer is substantially identical to Fig. 10. When the H600 polymers were heated at 600°C for 20 or more min, substantial differences were found in the fingerprint region of the spectrum; the bands at 690 cm^{-1} and 1006 cm^{-1} decreased in intensity while the band at 825 cm^{-1} remained at about the same intensity and a new band appeared at 875 cm^{-1} . These changes in spectra have been shown (1) to be due, in addition to further chain-end coupling, to other structural changes in the polymer. After heating to 700°C or higher, the bands are only poorly distinguishable from background noises as shown in Fig. 11, which contrasts the H600 with the H700 polymers. As the polymers were heated to the higher temperatures, carbocyclic-heterocyclic phenanthroline structures were formed (1) from the para-para (I) polymer, and this behavior has now also been confirmed for the para-meta (II), meta-para (III), and meta-meta (IV) polymers.

The thermogravimetric data show that the thermal stabilities in nitrogen of the four isomeric H600 polymers were much higher than those of the H400 polymers, showing losses of only about 10% by weight at 1000°C in contrast with the H400 polymers, which lost

about 10% by weight in the region of 650°C. These results are in agreement with data previously obtained (I) on a series of other Schiff base polymers.

Some differences in the thermal stabilities of the H400 polymers were observed but the differences in magnitude are relatively low. The per cent weight loss for the para-para (I) H400 polymer at 1176°C was about 30%, while that of the meta-meta (IV) H400 polymer was about 20%. The weight losses for the para-meta (II) H400 and of the meta-para (III) H400 polymers of about 24% were intermediate to the values of 30 and 20%. The lower value for the meta-meta (IV) polymer was attributed to the higher degree of condensation due to the higher fluidity of the reaction mixture.

The differences found in the weight losses in nitrogen of the H400 polymers were not experienced in the H600 polymers; in the H600 polymers the differences in the thermal stabilities are minor. The weight loss for the para-para (I) H600 polymer at 1176°C was about 17% and for the meta-meta (IV) H600 polymer was about 19%. The weight losses of the para-meta (II) H600 and meta-para (III) H600 polymers were intermediate to these values and were 17.3 and 18.2%, respectively. These same minor differences were observed when the H600 polymers were thermoanalyzed in air; the four polymers have thermal stabilities in air in excess of 500°C and all of them lost about 70% by weight at 600°C.

That the differences in the four isomeric H600 polymers are minor was confirmed also by the phenanthroline-type polymers obtained by heating the H600 polymers to 1176°C in nitrogen; the four isomeric polymers showed thermal stabilities of about 550°C in air and all had lost about 30% by weight at 600°C.

Acknowledgments

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Zusammenfassung

Vier Polymere auf der Basis von isomeren Schiff'schen Basen, Poly(*p*-xylyliden-*p*-phenylendiamin), Poly(*p*-xylyliden-*m*-phenylendiamin), Poly(*m*-xylyliden-*p*-phenylendiamin), und Poly(*m*-xylyliden-*m*-phenylendiamin) wurden durch zweifache Schiff'sche Basenaustauschreaktion synthetisiert ausgehend von den entsprechenden Paaren der vier Monomeren: N,N'-Bisbenzyliden-*p*-phenylendiamin, N,N'-Bisbenzyliden-*m*-phenylendiamin, *p*-Xylylidendianil, und *m*-Xylylidendianil. Die Unterschiede in der thermischen Stabilität dieser vier isomeren durch Kondensation erhaltenen Polymeren sind in Stickstoff als auch Luft im Temperaturbereich von 400 bis 600° nur geringfügig.

Résumé

Synthèse des polymères isomères de quatre bases de Schiff, la poly(*p*-xylylidène-*p*-phénylènediamine), la poly(*p*-xylylidène-*m*-phénylènediamine), la poly(*m*-xylylidène-*p*-phénylènediamine), et la poly(*m*-xylylidène-*m*-phénylènediamine), par la réaction d'échange de bis-bases de Schiff avec des paires sélectionnés parmi quatre monomères, la N,N'-bisbenzylidène-*p*-phénylènediamine, la N,N'-bisbenzylidène-*m*-phénylènediamine, le *p*-xylylidenedianil, et le *m*-xylidenedianil. Les différences dans les stabilités thermiques en atmosphère d'azote et dans l'air de ces quatre polymères isomères, préparés par condensation aux températures de 400 et 600°C, sont très légères.

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