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Polymeric Schiff Bases. XIV. The Synthesis of Cross-Linked Polymeric Azomethines by Exchange Reactions

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Polymeric Schiff Bases. XIV. The Synthesis of Cross-Linked Polymeric Azomethines by Exchange Reactions

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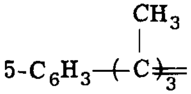
SUMMARY

Cross-linked polymeric azomethines were prepared by carbonyl, amine, and bis exchange reactions with cross-link density values of 0.00, 0.05, 0.25, 0.50, and 1.00, in which the cross-link moieties were  $1,3,5\text{-}C_6H_3\!-\!\!(\overset{CH_3}{\overset{|}{C}}\!=)_3$ and $1,3,5\text{-}C_6H_3\!-\!\!(N\!=)_3$. The yields at 400, 600, and 1176°C were determined as a function of the cross-link density and compared with the previously reported related polymers prepared by direct reactions. A tentative explanation is offered for the higher yields obtained by some of the exchange reactions.

INTRODUCTION

A previous publication [1] reported the influence of deliberately introduced cross links on the char yields of polyketanils produced by the direct reaction of aryl polyketones and aryl polyamines. This

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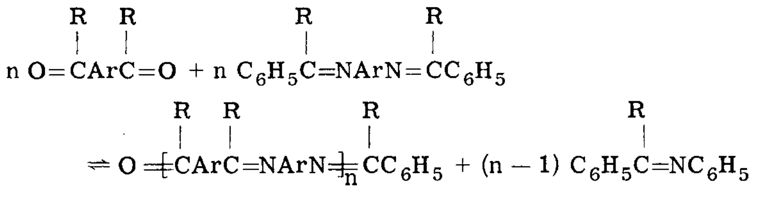
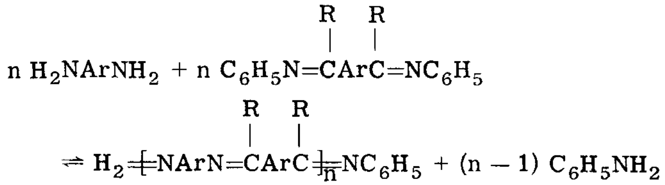
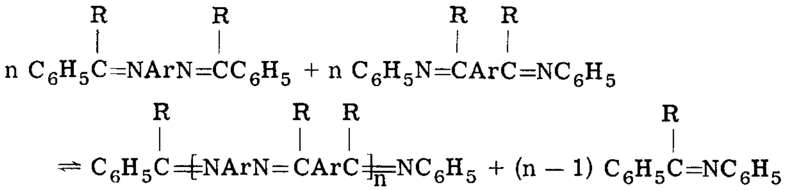
paper reports the extension of the study to polymeric azomethines produced by the carbonyl, amine, and bis exchange reactions [2-4], shown in Eqs. (1), (2), and (3), respectively:



$$\mathrm{n\ O{=}\overset{R}{C}Ar\overset{R}{C}{=}O + n\ C_6H_5\overset{R}{C}{=}NArN{=}\overset{R}{C}C_6H_5 \rightleftharpoons O{=}\!\left[\overset{R}{C}Ar\overset{R}{C}{=}NArN\right]_n{=}\overset{R}{C}C_6H_5 + (n-1)\ C_6H_5\overset{R}{C}{=}NC_6H_5} \quad (1)$$



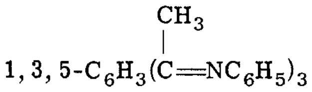
$$\mathrm{n\ H_2NArNH_2 + n\ C_6H_5N{=}\overset{R}{C}Ar\overset{R}{C}{=}NC_6H_5 \rightleftharpoons H_2\!\left[NArN{=}\overset{R}{C}Ar\overset{R}{C}\right]_n\!{=}NC_6H_5 + (n-1)\ C_6H_5NH_2} \quad (2)$$



$$\mathrm{n\ C_6H_5\overset{R}{C}{=}NArN{=}\overset{R}{C}C_6H_5 + n\ C_6H_5N{=}\overset{R}{C}Ar\overset{R}{C}{=}NC_6H_5 \rightleftharpoons C_6H_5\overset{R}{C}{=}\!\left[NArN{=}\overset{R}{C}Ar\overset{R}{C}\right]_n\!{=}NC_6H_5 + (n-1)\ C_6H_5\overset{R}{C}{=}NC_6H_5} \quad (3)$$

The exchange reactions given in Eqs. (1), (2), and (3), in which both reactants are bifunctional, yield polymers usually written as having the normally classical linear structure devoid of deliberately introduced cross links. The polymers prepared from monomers whose functionality, f, equals 2 are considered as having a cross-link density, ρ, of zero [1].

The trifunctional monomers, 1, 3, 5-triacetyl benzene, 1, 3, 5-$C_6H_3(COCH_3)_3$, or its tris-ketanil,



$$\mathrm{1,3,5\text{-}C_6H_3(\overset{CH_3}{C}{=}NC_6H_5)_3}$$

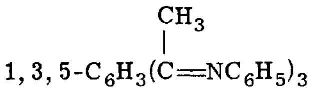
and 1, 3, 5-triaminobenzene, 1, 3, 5-$C_6H_3(NH_2)_3$, or its tris-Schiff base, 1, 3, 5-$C_6H_3(N{=}HCC_6H_5)_3$, were used to introduce the cross links in the polymers of this study. Polymers of cross-link densities between 0.0 and 1.0 were prepared by reacting appropriate molar quantities of the trifunctional reactants with bifunctional monomers [1]. Polymers in which $\rho = 1$ were prepared from molar quantities of complimentary monomers of f = 3 [1]. The relationship of ρ to $\bar{f}$ was given previously [1] as $\rho = 3 - (6/\bar{f})$.

EXPERIMENTAL

Monomers

Previous publications have described the synthesis or purification of the following monomers used in this study:
1, 4-$C_6H_4(COCH_3)_2$ [2], 1, 4-$C_6H_4(CHO)_2$ [3], 1, 3-$C_6H_4(NH_2)_2$ [3],
1, 3, 5-$C_6H_3(COCH_3)_3$ [1], 1, 3, 5-$C_6H_3(NH_2)_3$ [1],
1, 4-$C_6H_4(CH{=}NC_6H_5)_2$ [3], 1, 4-$C_6H_4(N{=}HCC_6H_5)_2$ [3], and
1, 3-$C_6H_4(N{=}HCC_6H_5)_2$ [3].

The monomer



$$1,3,5\text{-}C_6H_3(\overset{\overset{\displaystyle CH_3}{|}}{C}{=}NC_6H_5)_3$$

was prepared by reacting 1, 3, 5-$C_6H_3(COCH_3)_3$ and $C_6H_5NH_2$ in benzene under a nitrogen atmosphere by the continuous azeotropic method previously described [5] using 1 wt.% zinc chloride as the catalyst. Its infrared spectra showed strong bands for C=N at 1620 cm^{-1} and the absence of the band for C=O at 1676 cm^{-1}. The product was a resinous substance which was difficult to crystallize; it had a softening range of 85-90°C.

Analysis:

Calculated for $C_{30}H_{27}N_3$: C, 83.88; H, 6.34; N, 9.78.
Found: C, 83.96; H, 6.38; N, 9.59.

The monomer $C_6H_3(N{=}HCC_6H_5)_3$, m.p. 251-253°C, was prepared by reacting 1, 3, 5-$C_6H_3(NH_2)_3$ with C_6H_5CHO in benzene under a nitrogen atmosphere by the continuous azeotropic method [5]. The infrared spectrum of the product showed strong bands for C=N at 1620 cm^{-1} and the absence of the band for NH_2 at 3380 cm^{-1}.

Analysis

Calculated for $C_{27}H_{21}N_3$: C, 83.69; H, 5.46; N, 10.84.
Found: C, 84.01; H, 5.56; N, 10.30.

Polymerizations

The procedure and heating schedule used was identical to that used for the direct reaction of arylpolycarbonyl compounds with the arylpolyamines [1]. Tables 1 to 6 list the quantities of various complimentary reactants used in the preparation of the polymers, the average functionalities, $\bar{f}$, of the systems, the theoretical values of ρ for the polymers, and the yields of the H400 polymers calculated on the basis of $\overline{DP} = \infty$. The analytical data for the H400 polymers are summarized in Table 7 to 12.

Table 1. Data on the 3-H400 Series of Polymers

	Polymer designation				
Reactants	3A-H400, g	3B-H400, g	3C-H400, g	3D-H400, g	3E-H400, g
1, 3, 5-$C_6H_3(COCH_3)_3$	0.000	0.041	0.204	0.408	0.408
1, 4-$C_6H_4(COCH_3)_2$	0.486	0.437	0.243	0.000	0.000
1, 4-$C_6H_4(N{=}HCC_6H_5)_2$	0.852	0.852	0.852	0.852	0.000
1, 3, 5-$C_6H_3(N{=}HCC_6H_5)_3$	0.000	0.000	0.000	0.000	0.774
$\bar{f}$	2.000	2.035	2.182	2.400	3.000
Per cent yield at 400°C[a]	112.0	116.0	134.0	149.0	154.0
ρ	0.000	0.050	0.250	0.500	1.000

[a] Based on $\overline{DP} = \infty$.

Table 2. Data on the 4-H400 Series of Polymers

Reactants	Polymer designation 4A-H400, g	4B-H400, g	4C-H400, g	4D-H400, g
1,3,5-$C_6H_3(N{=}HCC_6H_5)_3$	0.000	0.0774	0.387	0.774
1,3-$C_6H_4(N{=}HCC_6H_5)_2$	0.586	0.7668	0.426	0.000
1,4-$C_6H_4(CHO)_2$	0.268	0.4020	0.402	0.402
$\bar{f}$	2.000	2.0350	2.182	2.400
Per cent yield at 400°C[a]	102.0	107.0	120.0	131.0
ρ	0.000	0.050	0.250	0.500

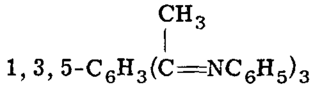
[a] Based on $\overline{DP} = \infty$.

Table 3. Data on the 5-H400 Series of Polymers

Reactants	Polymer designation				
	5A-H400, g	5B-H400, g	5C-H400, g	5D-H400, g	5E-H400, g
$1,3,5\text{-}C_6H_3(NH_2)_3$	0.000	0.024	0.123	0.246	0.246
$1,3\text{-}C_6H_4(NH_2)_2$	0.324	0.291	0.162	0.000	0.000
$1,4\text{-}C_6H_4(CH{=}NC_6H_5)_2$	0.852	0.852	0.852	0.852	0.000
$1,3,5\text{-}C_6H_3(\overset{\overset{CH_3}{\vert}}{C}{=}NC_6H_5)_3$	0.000	0.000	0.000	0.000	0.858
$\bar{f}$	2.000	2.035	2.182	2.400	3.000
Per cent yield at 400°C[a]	78.3	80.0	94.1	111.0	132.0
ρ	0.000	0.050	0.250	0.500	1.000

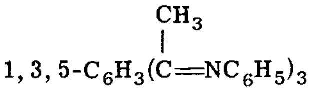
[a] Based on $\overline{DP} = \infty$.

Table 4. Data on the 6-H400 Series of Polymers

Reactants	Polymer designation				
	6A-H400,[a] g	6B-H400, g	6C-H400, g	6D-H400, g	6E-H400,[b] g
 $1,3,5\text{-}C_6H_3(\overset{CH_3}{\overset{\vert}{C}}{=}NC_6H_5)_3$	0.000	0.086	0.429	0.858	0.858
$1,4\text{-}C_6H_4(CH{=}NC_6H_5)_2$	0.852	0.767	0.426	0.000	0.000
$1,4\text{-}C_6H_4(N{=}HCC_6H_5)_2$	0.852	0.852	0.852	0.852	0.000
$1,3,5\text{-}C_6H_3(N{=}HCC_6H_5)_3$	0.000	0.000	0.000	0.000	0.774
$\bar{f}$	2.000	2.035	2.182	2.400	3.000
Per cent yield at 400°C[c]	138.0	140.0	145.0	162.0	167.0
ρ	0.000	0.050	0.250	0.500	1.000

[a] 6A is identical to 7A and 8A.
[b] 6E is identical to 7E.
[c] Based on $\overline{DP} = \infty$.

Table 5. Data on the 7-H400 Series of Polymers

Reactants	Polymer designation				
	7A-H400,[a] g	7B-H400, g	7C-H400, g	7D-H400, g	7E-H400,[b] g
1, 3, 5-$C_6H_3(N{=}HCC_6H_5)_3$	0.000	0.0774	0.387	0.774	0.774
1, 4-$C_6H_4(N{=}HCC_6H_5)_2$	0.852	0.7670	0.426	0.000	0.000
1, 4-$C_6H_4(CH{=}NC_6H_5)_2$	0.852	0.8520	0.852	0.852	0.000
 1, 3, 5-$C_6H_3(\overset{\overset{CH_3}{\vert}}{C}{=}NC_6H_5)_3$	0.000	0.0000	0.000	0.000	0.858
$\bar{f}$	2.000	2.0350	2.182	2.400	3.000
Per cent yield at 400°C[c]	138.0	150.0	162.0	190.0	167.0
ρ	0.000	0.0500	0.250	0.500	1.000

[a] 7A is identical to 6A and 8A.
[b] 7E is identical to 6E.
[c] Based on $\overline{DP} = \infty$.

Table 6. Data on the 8-H400 Series of Polymers

Reactants	Polymer designation				
	8a-H400,[a] g	8B-H400, g	8C-H400, g	8D-H400, g	8E-H400, g
1, 3, 5-$C_6H_3(COCH_3)_3$	0.000	0.041	0.204	0.408	0.408
1, 4-$C_6H_4(CH{=}NC_6H_5)_2$	0.852	0.767	0.426	0.000	0.000
1, 4-$C_6H_4(N{=}HCC_6H_5)_2$	0.852	0.852	0.852	0.852	0.000
1, 3, 5-$C_6H_3(N{=}HCC_6H_5)_3$	0.000	0.000	0.000	0.000	0.774
$\bar{f}$	2.000	2.035	2.182	2.400	3.000
Per cent yield at 400°C[b]	138.0	144.0	151.0	149.0	154.0
ρ	0.000	0.050	0.250	0.500	1.000

[a] 8A identical to 6A and 7A.
[b] Based on $\overline{DP} = \infty$.

Table 7. Analytical Data of H400 Polymers and Yields when Heated to 600°C

	Calculated, %			Found, %			% Yield at 600°C[a]
Polymer	C	H	N	C	H	N	
3A	82.02	6.02	11.96	85.32	5.11	9.16	86.0
3B	81.94	5.96	12.10	85.91	5.04	9.01	88.8
3C	81.42	5.92	12.66	86.17	5.19	8.63	89.6
3D	80.74	5.81	13.45	87.83	4.99	7.05	91.0
3E	79.10	5.53	15.37	85.33	5.24	8.57	91.9

[a] Based on H400 polymers.

Table 8. Analytical Data of H400 Polymers and Yields when Heated to 600°C

	Calculated, %			Found, %			% Yield at 600°C[a]
Polymer	C	H	N	C	H	N	
4A	81.53	4.88	13.59	81.36	4.94	12.87	58.6
4B	81.42	4.82	13.76	82.89	4.85	12.48	60.9
4C	80.83	4.66	14.51	83.96	4.68	10.92	70.7
4D	79.98	4.47	15.54	84.44	4.65	10.43	78.0

[a] Based on H400 polymers.

Table 9. Analytical Data of H400 Polymers and Yields when Heated to 600°C

	Calculated, %			Found, %			% Yield at 600°C[a]
Polymer	C	H	N	C	H	N	
5A	82.05	5.99	11.96	81.87	6.00	12.10	82.6
5B	81.42	4.82	13.76	80.97	4.89	13.98	83.3
5C	80.83	4.66	14.51	80.02	4.79	14.96	84.0
5D	80.00	4.44	15.56	78.83	4.23	13.70	86.7
5E	79.10	5.53	15.37	78.43	5.30	16.27	89.3

[a] Based on H400 polymers.

Table 10. Analytical Data of H400 Polymers and Yields when Heated to 600°C

	Calculated, %			Found, %			% Yield at 600°C[a]
Polymer	C	H	N	C	H	N	
6A[b]	81.53	4.89	13.58	83.25	5.47	9.95	81.2
6B	81.47	4.95	13.58	86.43	4.61	8.47	86.7
6C	81.16	5.13	13.53	87.56	4.77	7.72	91.3
6D	80.77	5.77	13.46	88.03	5.26	7.20	84.6
6E[c]	79.10	5.53	15.37	84.64	4.84	8.64	88.1

[a] Based on H400 polymer.
[b] 6A is identical to 7A and 8A.
[c] 6E is identical to 7E.

Table 11. Analytical Data of H400 Polymers and Yields when Heated to 600°C

	Calculated, %			Found, %			% Yield at 600°C[a]
Polymer	C	H	N	C	H	N	
7A[b]	81.53	4.89	13.58	83.25	5.47	9.95	81.2
7B	81.42	4.82	13.76	85.99	4.99	8.70	78.7
7C	80.83	4.66	14.51	85.33	4.90	9.87	87.0
7D	80.00	4.44	15.56	84.81	4.54	8.77	84.7
7E[c]	79.10	5.53	15.37	84.64	4.84	8.64	88.1

[a] Based on H400 polymers.
[b] 7A is identical to 6A and 8A.
[c] 7E is identical to 6E.

Table 12. Analytical Data of H400 Polymers and Yields when Heated to 600°C

	Calculated, %			Found, %			% Yield at 600°C[a]
Polymer	C	H	N	C	H	N	
8A[b]	81.53	4.89	13.58	83.25	5.47	9.95	81.2
8B	81.47	4.95	13.58	86.43	4.64	8.82	79.0
8C	81.16	5.31	13.53	87.99	5.05	5.98	84.4
8D	80.74	5.81	13.45	87.83	4.99	7.05	91.0
8E	79.10	5.53	15.37	85.33	5.24	8.57	91.9

[a] Based on H400 polymers.
[b] 8A is identical to 6A and 7A.

Postheating of the H400 Polymers

Portions of the H400 polymers were postheated under a slow stream of nitrogen for 20 min at 600°C, similarly to the polyketanils previously reported [1]. Tables 7 and 12 summarize the yields of H600 polymers obtained from the H400 polymers as the 100% base.

Thermogravimetric Analyses

The measurements were performed in the same apparatus following the identical procedures used for the polyketanils previously reported [1]. The thermogravimetric data are summarized in Tables 13 and 14.

DISCUSSION

The cross-linked polymeric azomethines synthesized in this report were prepared using a heating schedule identical to that used in the direct condensation of polycarbonyl compounds and polyamines [1], so that a direct comparison could be made between the various polymers. For this reason also, the concentrations of bifunctional and trifunctional monomers were selected to give the same crosslink densities of 0.00, 0.05, 0.25, 0.50, and 1.00. In all cases the viscosities of the melts increased as before [1] with reaction time while the color of the reaction mixtures changed progressively from yellow to brown to black. Gellation occurred first as previously [1] in those systems in which the average functionality, $\bar{f}$, was 3, followed, in the expected order, by those systems in which $\bar{f}$ progressively decreased from 2.4 to 2.0. All the polymers prepared by the exchange methods were hard and glassy, with a shiny black appearance during or at the end of the 325°C condensation stage. The condensation, however, was continued to 400°C; the H600 polymers were obtained by postheating portions of the H400 polymers to 600°C, so that both these new H400 and H600 polymers could be compared to the related direct-condensation polymers of the 1- and 2-series [1].

In the 1- and 2-series of polymers the by-product of the reaction was water, b.p. 100°C. The present exchange-reaction polymers differed essentially with the 1- and 2-series in the nature of the by-products. In the studies reported here, the by-products, shown in Table 15, had higher boiling points than water, such as benzaldehyde, b.p. 179.5°C, in the 3-series; aniline, b.p. 184.4°C in the 5-series; benzylideneaniline, b.p. 310°C in the 6- and 7-series; and a mixture of benzaldehyde and benzylideneaniline in some of the 4- and 8-series. Elimination of these by-products would be expected to be more difficult than the elimination of water (1), thereby increasing the apparent yields of the polymers.

Table 13. Thermogravimetric Data for the H400 Polymers

		Per cent char residue at temperature (°C)							
Polymer	ρ	400	500	600	700	800	900	1000	1176
3A	0.00	100	93	87.0	86	81	76	72	67
3B	0.05	100	95	90.0	89	84	78	73	68
3C	0.25	100	97	92.0	83	81	77	73	69
3D	0.50	100	98	93.0	84	82	76	74	70
3E	1.00	100	99	94.0	85	80	78	77	72
4A	0.00	100	88	72.0	70	66	65	64	62
4B	0.05	100	89	73.0	69	67	66	65	63
4C	0.25	100	87	75.0	72	69	68	68	64
4D	0.50	100	91	80.0	74	72	69	68	66
5A	0.00	100	89	83.0	81	79	77	75	73
5B	0.05	100	90	83.8	82	80	78	76	74
5C	0.25	100	91	84.5	83	81	78	77	74
5D	0.50	100	92	87.0	85	83	80	77	75
5E	1.00	100	95	91.1	87	85	83	80	77
6A	0.00	100	98	92.0	84	81	78	77	70
6B	0.05	100	87	80.0	78	77	77	76	73
6C	0.25	100	98	88.0	84	81	80	79	77
6D	0.50	100	94	84.0	78	77	76	75	73
6E	1.00	100	91	88.0	87	85	85	84	81
7A	0.00	100	98	92.0	84	81	78	77	70
7B	0.05	100	90	78.0	75	72	72	70	67
7C	0.25	100	93	86.0	81	79	78	77	75
7D	0.50	100	92	87.0	85	83	77	76	75
7E	1.00	100	91	88.0	87	85	79	78	74
8A	0.00	100	98	92.0	84	81	78	77	70
8B	0.05	100	97	92.0	89	86	84	83	79
8C	0.25	100	96	82.0	80	79	78	78	76
8D	0.50	100	98	93.0	84	82	76	74	70
8E	1.00	100	99	94.0	85	80	78	77	72

Table 14. Thermogravimetric Data for the H600 Polymers

		Per cent char residue at temperature (°C)						
Polymer	ρ	500	600	700	800	900	1000	1176
3A	0.00	100	99	96	93	90	88	84
3B	0.05	100	99	97	94	90	89	83
3C	0.25	100	100	98	94	91	91	85
3D	0.50	100	98	97	95	91	90	84
3E	1.00	100	100	98	94	91	90	86
4A	0.00	100	99	93	90	88	87	83
4B	0.05	100	99	94	90	89	88	84
4C	0.25	100	99	96	93	91	90	86
4D	0.50	100	100	97	94	93	91	87
5A	0.00	100	99	95	91	90	89	84
5B	0.05	100	98	93	90	89	87	84
5C	0.25	100	100	96	93	90	88	83
5D	0.50	100	99	95	92	90	88	82
5E	1.00	100	99	97	94	93	89	86
6A	0.00	100	100	99	96	94	91	86
6B	0.05	100	97	95	95	94	94	90
6C	0.25	100	99	97	94	92	91	87
6D	0.50	100	99	96	93	92	91	88
6E	1.00	100	96	94	93	93	92	87
7A	0.00	100	100	99	96	94	91	86
7B	0.05	100	98	97	96	95	91	87
7C	0.25	100	99	97	94	93	92	89
7D	0.50	100	98	95	94	94	93	88
7E	1.00	100	96	94	93	93	92	87
8A	0.00	100	100	99	96	94	91	86
8B	0.05	100	99	98	95	93	92	88
8C	0.25	100	99	96	93	92	91	89
8D	0.50	100	98	97	95	91	90	83
8E	1.00	100	100	98	94	91	90	86

Table 15. Composition per Mole of By-products of the Exchange Polymerizations

Polymer series	ρ				
	0.00	0.05	0.25	0.50	1.00
3	C_6H_5CHO	C_6H_5CHO	C_6H_5CHO	C_6H_5CHO	C_6H_5CHO
4	C_6H_5CHO	(0.9) C_6H_5CHO	(0.5) C_6H_5CHO	C_6H_5CHO	—
	—	(0.1) $C_6H_5CH{=}NC_6H_5$	(0.5) $C_6H_5CH{=}NC_6H_5$	—	—
5	$C_6H_5NH_2$	$C_6H_5NH_2$	$C_6H_5NH_2$	$C_6H_5NH_2$	$C_6H_5NH_2$
6	$C_6H_5CH{=}NC_6H_5$	$C_6H_5CH{=}NC_6H_5$	$C_6H_5CH{=}NC_6H_5$	$C_6H_5CH{=}NC_6H_5$	$C_6H_5CH{=}NC_6H_5$
7	$C_6H_5CH{=}NC_6H_5$	$C_6H_5CH{=}NC_6H_5$	$C_6H_5CH{=}NC_6H_5$	$C_6H_5CH{=}NC_6H_5$	$C_6H_5CH{=}NC_6H_5$
8	$C_6H_5CH{=}NC_6H_5$	(0.9) $C_6H_5CH{=}NC_6H_5$	(0.5) $C_6H_5CH{=}NC_6H_5$	—	—
	—	(0.1) C_6H_5CHO	(0.5) C_6H_5CHO	C_6H_5CHO	C_6H_5CHO

Benzylideneaniline, which has the highest boiling point of these by-products, and which had been shown to be retained physically or chemically by the Schiff-base polymers [2], should be expected to produce the largest deviation as an increase in yield over that calculated for $\overline{DP} = \infty$ [1].

The per cent yields of the H400 and H600 polymers, and the per cent of char residue for these polymers based on the yield for $\overline{DP} \doteq \infty$ as 100%, are summarized in Table 16 and graphically presented in Figs. 1 to 6.

There is another important difference between the polymers of the 3-8 series and the 1-2 series previously reported [1]. At least one monomeric bis-Schiff base was a reactant in the 3-8 series; in the 6-8 series both reactants were monomeric Schiff bases which yielded a monomeric Schiff base as a reaction by-product. In these cases, unconverted monomer, as well as by-product monomer, can be retained and also cause a deviation in yield.

In all cases in the 3-8 series, the yields and stabilities increased with the introduction of the first cross links at $\rho = 0.05$ and continued to rise with the introduction of more cross links; this increase was evident to some degree in the char yields at all temperatures up to 1176°C.

The per cent yields and per cent char residues of the polymers in the 6-8 series, in which benzylideneaniline was a by-product, were noticeably higher than in the 3-5 series. This can be explained, in part, at least below 400 and 600°C, by the lower volatility of benzylideneaniline compared to benzaldehyde and aniline; this lower volatility would be responsible for increased retention [2]. At temperatures higher than 600°C, the complete elimination of benzylideneaniline should be expected [2] and all the yields based on per cent of the theoretical should be identical or nearly so, as in the case of the direct condensations [1] unless other processes, heretofore not recognized, are in operation. This postulate concerning other processes will be discussed later.

The yields at 400, 600, and 1176°C for the 5-series of polymers, in which aniline was the by-product, increased with an increase in the degree of cross linking, ρ. The amine exchange is the most facile of the exchange reactions [2], but the low yield obtained at $\rho = 0$, under the preselected polymerization conditions, obviously left unconverted amounts of the monomeric Schiff bases retained chemically or physically in the polymer [2]. Most probably these bis-Schiff-base monomers were not eliminated at 400°C and probably only partly at 600°C, since temperatures of 600°C or higher were required to eliminate benzylideneaniline [2]. Owing to their higher volatilities, some aniline and unconverted phenylenediamine were also eliminated in the 400-600°C range and probably rather completely in the 700-800°C range. The aniline and phenylenediamine were identified by thin-layer chromatography. A higher temperature would be ex-

Table 16. Comparison of the Residues of the Various Polymers

Polymer designation	% Yield of H400	% Yield of H600	TGA % Residue of H400 at 600°C	Char residue at 1176°C of	
				H400	H600
3A	112.0	96.3	97.4	75.0	80.9
3B	116.0	103.0	104.4	78.9	85.5
3C	134.0	120.0	121.9	92.5	102.0
3D	149.0	135.6	138.6	104.3	116.6
3E	154.0	141.5	144.8	110.9	123.1
4A	102.0	59.8	73.4	63.2	49.6
4B	107.0	65.2	78.1	67.4	54.8
4C	120.0	84.8	90.0	76.8	72.9
4D	131.0	102.2	104.8	86.5	88.9
5A	78.3	64.7	65.0	57.2	54.3
5B	80.0	66.7	67.0	59.2	55.4
5C	94.1	79.0	79.5	69.6	65.6
5D	111.0	97.3	96.6	83.3	79.8
5E	132.0	117.4	120.9	101.6	101.0
6A	138.0	112.0	126.7	96.6	96.3
6B	140.0	121.3	112.0	102.2	109.1
6C	145.0	132.4	127.6	111.0	115.2
6D	162.0	137.1	136.1	118.3	120.6
6E	167.0	147.1	147.0	135.3	128.0
7A	138.0	112.0	127.0	96.6	96.3
7B	150.0	118.0	117.0	100.5	102.7
7C	162.0	140.9	139.3	121.5	125.4
7D	165.0	140.8	143.5	123.7	123.9
7E	167.0	147.1	147.0	135.3	128.0
8A	138.0	112.0	127.0	96.6	96.3
8B	144.0	113.9	125.5	113.8	99.4
8C	151.0	127.4	123.8	114.8	113.4
8D	149.0	135.6	138.6	104.3	112.5
8E	154.0	141.5	144.8	110.9	123.1

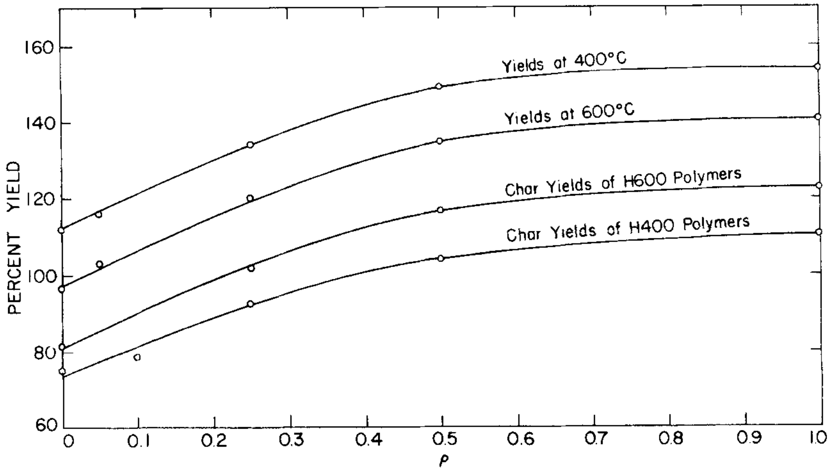


Fig. 1. Per cent yields for the 3-series of polymers.

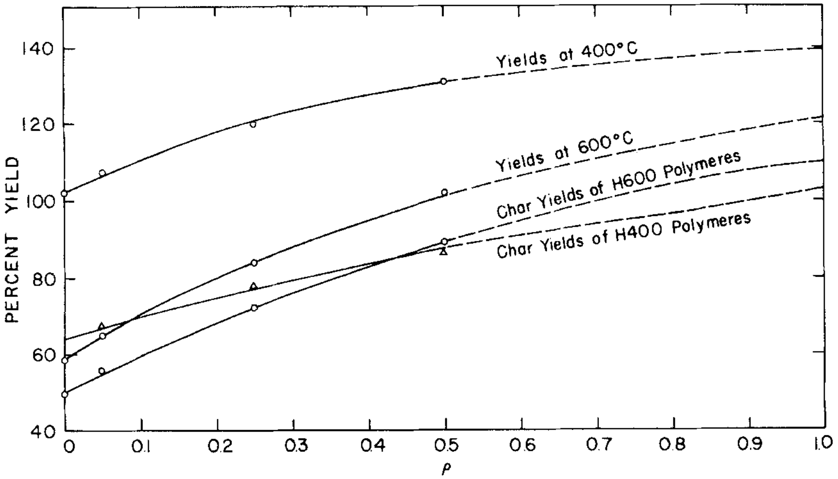


Fig. 2. Per cent yields for the 4-series of polymers.

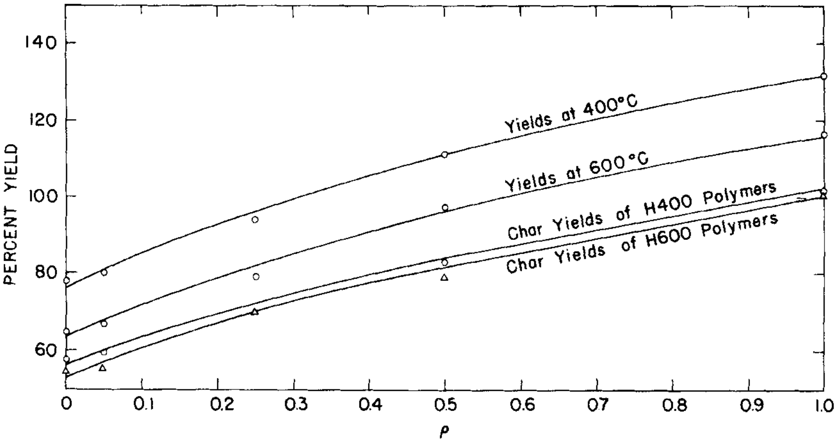


Fig. 3. Per cent yields for the 5-series of polymers.

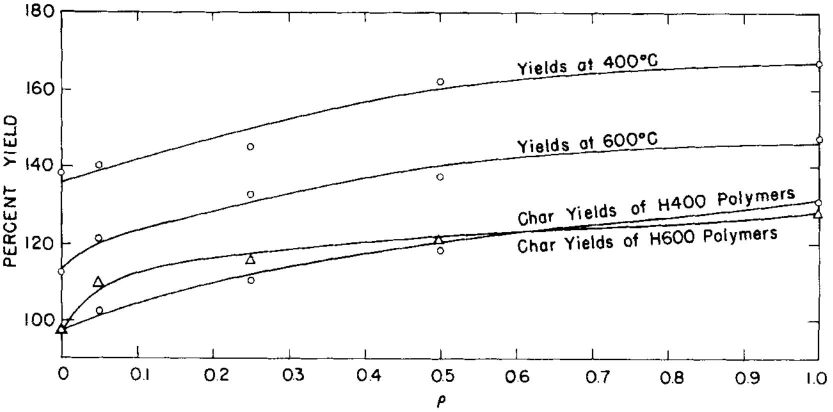


Fig. 4. Per cent yields for the 6-series of polymers.

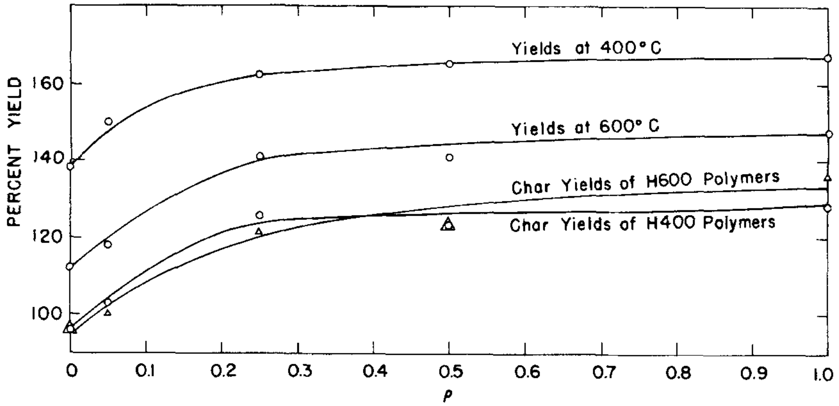


Fig. 5. Per cent yields for the 7-series of polymers.

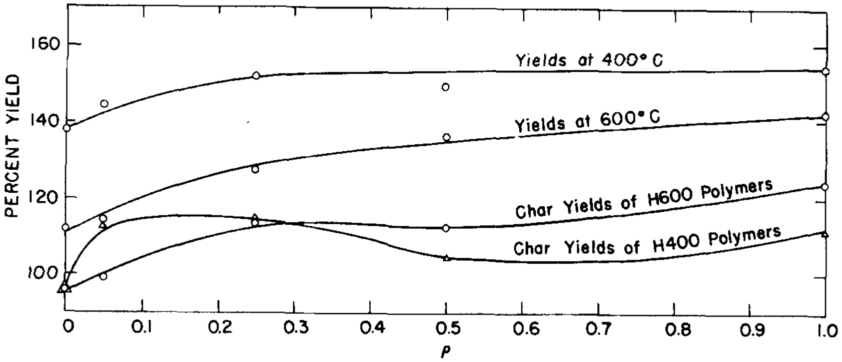


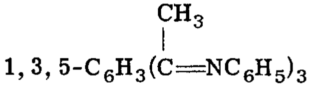
Fig. 6. Per cent yields for the 8-series of polymers.

pected to be required for the elimination of unreacted triaminobenzene, and at least part of it was probably retained in the polymer up to these temperatures. Also, the tendency for the formation of complexes of arylamines with Schiff bases is high, and this tendency would also favor their retention. As ρ is increased, the progressive increase in yields over the 100% of theory can be explained by the cage effect of three-dimensional structures, which more tenaciously retain unconverted monomers as well as by-products, so much so that for the H600 polymer of $\rho = 1$, the yield was 117.4% of theory. Since both the H400 and H600 polymers yielded a char value of about 101%, this may be taken as an indication that part of the retained unconverted monomers was converted to polymeric structures while being held within the polymeric cage. Further evidence for this postulate will be presented in the discussion of the 5-8 series.

The carbonyl exchange is less facile than the amine exchange [2]. Of the carbonyl exchange reactions, the aldehyde exchange proceeds more readily than the ketone exchange [2, 4]. The differences in behavior are evident in the contrast of the 3- with the 4-series of polymers and of the 3- and 4-series with the 5-series. The yields of the 4-series of polymers at 400°C were higher than those of the 5-series at the same temperature but lower at 600°C than those of the 5-series. This is indicative of low conversion at 400°C and a higher extent of elimination at 600°C of benzaldehyde and terephthaldehyde, which sublimes readily. Both of these products were identified by thin-layer chromatography in the by-products of the H400 polymers. Also identified was aniline in 4A, 4B, 4C, and 4D, even though this was an aldehyde exchange reaction and aniline was not expected to be present. Some benzulideneaniline was identified from 4B and 4C. The polymer of $\rho = 1$ in this series was not synthesized because of the unavailability of 1, 3, 5-$C_6H_3(CHO)_3$. In Fig. 2 the curves for $\rho = 1$, have been extrapolated to the yields that could be expected; the char yields of the H400 and H600 would be of the order of 100% at $\rho = 1$.

The yields of the 3-series of polymers, which are the results of a ketone exchange in which benzaldehyde is the by-product, were higher at all stages, as shown in Table 16, than for the 4- and 5-series. This is probably the result of lower conversion at the 400°C stage, since the ketone exchange of this series is less facile than the aldehyde exchange of the 4-series. Benzaldehyde and 1, 4-diacetylbenzene were identified in the by-products. The retention of unconverted monomeric Schiff base would account for the high yields, which, however, would be expected to be eliminated in the region of 700 to 1000°C. Yet, the char yield of 3C-H400, 3D-H400, 3C-H600, 3D-H600, and 3E-H600 were in excess of 100% of theory. This, again, would tend to indicate that the retained monomeric Schiff bases were converted to polymeric structures while being held within a polymeric cage; and that the tighter the cage, as follows from an increase in ρ, the firmer the retention and the higher the conversion of the retained monomeric Schiff bases to polymers. If this postulate is even partially correct, then the same observation would be made in those polymers prepared by bis exchange reactions, in which all reactants and the by-products are Schiff bases. The yields at 400 and 600°C and the char yield at 1176°C should then be higher at all values of ρ, and, as ρ increases, the yields should be substantially higher than 100% of theory.

The reference points for $\rho = 0$ and $\rho = 1$ are the same in the 6- and 7-series of polymers. The polymers with intermediate values of ρ were prepared in the 6-series with



$$1,3,5\text{-}C_6H_3(\overset{\displaystyle CH_3}{\overset{|}{C}}{=}NC_6H_5)_3$$

and in the 7-series with $1,3,5\text{-}C_6H_3(N{=}HCC_6H_5)_3$ as the cross-linking agents, respectively. The very high yields in both of these series at 400 and at 600°C showed that benzylideneaniline is being tenaciously held even at $\rho = 0$ [2], and that, as tighter cages were formed, the retention became higher and the retained by-products were not eliminated at 600°C or even at 1176°C. Some benzylideneaniline was found in the by-products at 400°C for all the polymers of the 6- and 7-series, but the amount of benzylideneaniline decreased while the amount of aniline increased with an increase in ρ. At 600°C, both aniline and benzylideneaniline were isolated in the by-products, but the ratios of aniline to benzylideneaniline were much higher than those obtained at 400°C. The formation of aniline had been attributed [2] to the formation of phenanthradine by ring closure of benzylideneaniline. If phenanthridine, b.p. 360°C, was formed in these reactions, it would have been eliminated from the polymer, certainly at temperatures in excess of 600°C. Evidently, some other mechanism accounts for the generation of aniline and for the high yields.

Some evidence for an alternative mechanism appears to be evident in the elemental analyses of the H400 polymers. The elemental analyses of polymers of the 1- and 2-series, resulting from the direct reactions of carbonyl moieties with amine moieties and water as the by-product [1, 4], were in good agreement with the calculated values of the polymers. In contrast, the agreement between the found and the calculated values for C, H, and N in the 6- and 7-series was poor, particularly with reference to the nitrogen content; the loss of nitrogen corresponded to a partial loss in the form of aniline, thereby increasing the carbon content. This same discrepancy was found in the 3- and 5-series but not in the 4-series, in which benzaldehyde was easily eliminated. This would indicate that the Schiff bases can undergo reactions other than those previously described [2]. Shannon et al. [6] have shown that Schiff bases can be photocyclized to 5, 6-benzoquinolines. The photocyclization of a Schiff base yielded [7] a trans-azobenzene and cis-stilbene through a 1, 2-diazetidine intermediate. More recently the photochemical formation of 1, 3-diazetidines has been described [8].

Data on the thermal conversion of Schiff bases to other products are, however, meager. The results obtained in this study would indicate that the Schiff bases themselves polymerize with the elimination of aniline among other products. Preliminary uncatalyzed and catalyzed studies at 325°C and at higher temperatures currently underway with a number of monomeric mono- and di-Schiff bases have confirmed indeed that aniline and polymer is formed in many of these reactions. The details of this study will be published in the near future [9].

On the basis of the above preliminary experiments, the 8-series was designed to yield a decreasing amount of benzylideneaniline and an increasing amount of benzaldehyde as by-product as ρ was increased from zero to 1. This series combined the simultaneous influence of the presence or absence of benzylideneaniline and cross-links. Thus, the yields, as a percentage of theory, should decrease with a decreasing amount of benzylideneaniline, and this decrease should be compensated to some extent by an increase in ρ. The amount of aniline found in the by-products was highest in the polymer of $\rho = 0$ and lowest in the polymer of $\rho = 1$. The plots for the yields of the H400 and H600 polymers and their yields of char at 1176°C, shown in Fig. 6, definitely show effects of the kind expected by contrasting the data for polymers 8A, 8B, and 8C with the data for polymers 8D and 8E. The yields increased progressively from 8A to 8C, followed by deflection at 8D. Since 8D and 8E both yield only benzaldehyde as a by-product, the yield of 8E should be higher than 8D as a result of the increase of ρ from 0.5 to 1.0, and such was found to be the case. The char yields at 1176°C of 8D-H400 and 8E-H400 were 104.3 and 110.9%, respectively; but, if the by-product had been benzylideneaniline instead of benzaldehyde, the yields would be 118.3 and 135.3%, respectively, as shown for 7D-H400 and 7E-H400. Similarly, the char yields for 8D-H600 and 8E-H600 were 112.5 and 123.1%, respectively, and, if benzylideneaniline had been the by-product, the yields would have been 120.6 and 128.0%, respectively, as shown for 7D-H600 and 7E-H600.

A related study, confirming some of the results reported in this paper on the synthesis of cross-linked polymeric azomethines, based on amino aryl ketones is the next article in this journal.

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