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Polymeric Schiff Bases. XV. The Synthesis of Cross-Linked Polymeric Azomethines from Amino Aryl Ketones

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SUMMARY

A number of polymeric azomethines were synthesized to determine the influence on char yields by the deliberate introduction of cross links in their structures. The linear reference polymer, $=\!\!\!\!\!+ NC_6H_4C(CH_3) =\!\!\!\!\!+_n$, was synthesized from $H_2NC_6H_4COCH_3$ and was considered as having a cross-link density, ρ, of zero. Two series were prepared with ρ values between zero and 1, using an equimolar mixture of 1,3,5-$C_6H_3(COCH_3)_3$ and 1,3,5-$C_6H_3(NH_2)_3$, or their respective Schiff bases, as the cross-linking agents.

Char yields were determined on polymers condensed initially to 400°C and on these same polymers postheated to 600°C, and compared to related polymers prepared by the reaction of aryl diamines with aryl diketones.

INTRODUCTION

The effect of deliberately introduced cross links on the char yields of polymeric azomethines derived from the reaction of AA with BB types of monomers have been reported recently [1,2]. The AA-BB type of polymer was prepared by the direct condensation method [1] as well as by the exchange methods [2,3].

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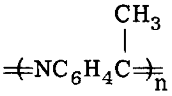
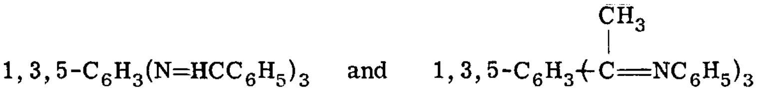
It became of interest to determine what effect cross linking would have on the char yield of azomethine polymers prepared from AB-type monomers. The reference polymer selected for this study was



$$\left(=NC_6H_4\overset{\overset{CH_3}{|}}{C}=\right)_n$$

prepared by the self-condensation of 3-aminoacetophenone [4]. One series of polymers was prepared in which equimolar quantities of $1,3,5\text{-}C_6H_3(NH_2)_3$ and $1,3,5\text{-}C_6H_3(COCH_3)_3$ were used as the cross linking means; in this series water would be the by-product of the reaction. In the second series, cross linking was achieved by the use of equimolar quantities of the trifunctional Schiff bases,



$$1,3,5\text{-}C_6H_3(N{=}HCC_6H_5)_3 \quad \text{and} \quad 1,3,5\text{-}C_6H_3(\overset{\overset{CH_3}{|}}{C}{=}NC_6H_5)_3$$

and in this case, benzylideneaniline would be the by-product. Polymers with cross-link densities, ρ, of 0.00, 0.05, 0.25, 0.50 and 1.00 were prepared as previously [1, 2] by the use of appropriate quantities of trifunctional and bifunctional reactants.

EXPERIMENTAL

Monomers

The purification or synthesis of the monomers have been described in recent publications [1-4].

Polymerizations

The mixture of monomers was reacted under nitrogen using the apparatus and procedures previously described [1-4], at the following time-temperature schedule; 2 hr at 180°C; 2 hr at 225°C; 17 hr at 325°C, and 2½ hr at 400°C. In accordance with previous coding, these polymers are designated by the suffix H400 to indicate the maximum temperature used in their preparation.

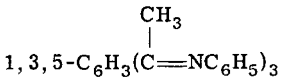
Tables 1 and 2 list the quantities of the various complimentary reactants used in the preparation of the two series of polymers, the theoretical values of ρ for the polymers and the yields calculated on basis of $\overline{DP} = \infty$. The analytical data for these polymers are summarized in Tables 3 and 4.

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

	Polymer designation				
Reactants	1A,[a] g	1B, g	1C, g	1D, g	1E, g
1,3,5-$C_6H_3(COCH_3)_3$	0.000	0.204	0.204	0.204	0.408
1,3-$H_2NC_6H_4COCH_3$	0.804	4.020	0.804	0.402	0.000
1,3,5-$C_6H_3(NH_2)_3$	0.000	0.123	0.123	0.123	0.246
Per cent yield at 400°C	95.0	96.1	98.0	99.9	100.0
ρ	0.00	0.05	0.25	0.50	1.00

[a] 1A is the same as 2A.

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

	Polymer designation				
Reactants	2A,[a] g	2B, g	2C, g	2D, g	2E, g
 1,3,5-$C_6H_3(\overset{\overset{CH_3}{\mid}}{C}{=}NC_6H_5)_3$	0.000	0.429	0.429	0.429	0.429
1,3-$H_2NC_6H_4COCH_3$	0.804	4.020	0.804	0.402	0.000
1,3,5-$C_6H_3(N{=}HCC_6H_5)_3$	0.000	0.387	0.387	0.387	0.387
Per cent yeild at 400°C	95.0	101.1	112.75	131.2	167.0
ρ	0.00	0.05	0.25	0.50	1.00

[a] 2A is the same as 1A.

Postheating of the H400 Polymers

Portions of the H400 polymers were postheated under a slow stream of nitrogen for 20 min at 600°C using procedures previously published [1,2]. Tables 3 and 4 summarize the per cent yields of H600 polymers obtained from H400 polymers as the 100% basis.

Table 3. Analytical Data of H400 Polymers and Yields when Heated to 600°C

	Calculated, %			Found, %			%Yield[a] at
Polymer	C	H	N	C	H	N	600°C
1A-H400	82.05	5.98	11.97	80.84	6.10	11.78	85.5
1B-H400	81.94	5.96	12.10	81.78	5.25	11.92	86.6
1C-H400	81.45	5.88	12.67	81.63	5.38	12.34	87.4
1D-H400	80.77	5.77	13.46	80.69	5.47	13.09	90.1
1E-H400	79.12	5.50	15.38	77.20	6.05	15.92	91.0

[a] Based on H400.

Table 4. Analytical Data of H400 Polymers and Yields when Heated to 600°C

	Calculated, %			Found, %			% Yield[a] at
Polymer	C	H	N	C	H	N	600°C
2A-H400	82.05	5.98	11.97	80.84	6.10	11.76	85.5
2B-H400	81.94	5.96	12.10	82.46	5.30	11.53	85.9
2C-H400	81.45	5.88	12.67	81.59	5.35	10.65	86.8
2D-H400	80.77	5.77	13.46	83.88	5.16	8.78	87.9
2E-H400	79.12	5.50	15.38	84.64	4.84	8.64	88.1

[a] Based on H400.

Thermogravimetric Analyses

The measurements were performed on 10-mg samples ground to about 500 pieces at a heating rate of 10°C/min in nitrogen at a flow rate of 1 standard liter per minute in a du Pont thermal analyzer, by procedures previously published [1, 2]. The thermogravimetric data are summarized in Tables 5 to 8. A comparison of the residues of the various polymers, based on $\overline{DP} = \infty$ as the 100% basis, is given in Table 9 and graphically represented in Figs. 1 and 2.

Table 5. Thermogravimetric Data for the 1-Series of H400 Polymers

		Per cent char residue at temperature (°C)							
Polymer	ρ	400	500	600	700	800	900	1000	1176
1A-H400	0.00	100.0	100.0	97.0	91.3	87.3	85.1	83.1	82.8
1B-H400	0.05	100.0	99.8	97.6	94.1	84.0	83.0	82.9	82.6
1C-H400	0.25	100.0	99.9	94.5	92.1	83.9	82.9	82.6	82.0
1D-H400	0.50	100.0	100.0	93.9	91.9	85.6	84.4	83.3	82.8
1E-H400	1.00	100.0	100.0	94.3	90.3	86.1	84.7	82.8	82.1

Table 6. Thermogravimetric Data for the 2-Series of H400 Polymers

		Per cent char residue at temperature (°C)							
Polymer	ρ	400	500	600	700	800	900	1000	1176
2A-H400	0.00	100.0	100.0	97.0	91.3	87.3	85.1	83.1	82.8
2B-H400	0.05	100.0	97.6	91.0	88.1	86.2	84.1	82.1	78.1
2C-H400	0.25	100.0	98.1	90.8	88.8	86.6	85.2	83.2	78.9
2D-H400	0.50	100.0	95.9	90.6	88.2	84.7	81.9	81.1	80.2
2E-H400	1.00	100.0	91.0	88.0	87.0	85.0	85.0	84.0	81.0

Table 7. Thermogravimetric Data for the 1-Series of H600 Polymers

	Per cent char residue at temperature °C					
Polymer	600	700	800	900	1000	1176
1A-H600	100.0	99.2	95.9	93.1	92.0	88.1
1B-H600	100.0	97.8	94.6	93.4	91.2	87.6
1C-H600	100.0	97.8	95.4	93.9	92.8	88.0
1D-H600	100.0	99.0	96.0	94.0	90.2	87.4
1E-H600	100.0	98.0	95.0	94.0	91.0	86.0

Table 8. Thermogravimetric Data for the 2-Series of H600 Polymers

	Per cent char residue at temperature °C					
Polymer	600	700	800	900	1000	1176
2A-H600	100.0	99.2	95.9	93.1	92.0	88.1
2B-H600	100.0	94.6	94.0	93.0	92.1	87.7
2C-H600	100.0	97.8	95.2	94.0	92.4	87.1
2D-H600	100.0	97.9	96.8	94.3	92.1	87.2
2E-H600	100.0	98.0	95.0	93.0	92.0	87.0

Table 9. Comparison of the Per Cent Residues of the Various Polymers

Polymer	% Yield of H400	% Yield of H600	TGA and residue of H400 at 600°C	Char residue at 1176°C of	
				H400	H600
1A	95.0	81.2	92.2	78.7	71.5
1B	96.0	83.1	93.7	78.5	72.8
1C	98.0	85.7	92.6	80.4	74.9
1D	99.9	90.0	90.0	82.0	78.7
1E	100.0	91.0	94.3	82.1	78.3
2A	95.0	81.2	92.2	78.7	71.5
2B	101.0	87.8	91.9	78.9	77.0
2C	112.8	97.9	102.4	89.0	85.3
2D	131.2	115.3	118.9	105.2	100.5
2E	167.0	147.1	146.9	135.2	128.0

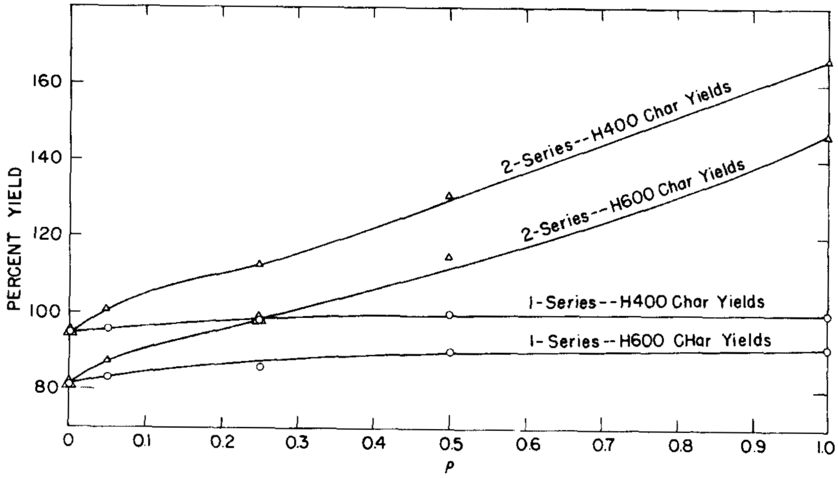


Fig. 1. Per cent yields on the 1- and 2-sëries of polymers at 400 and 600°C

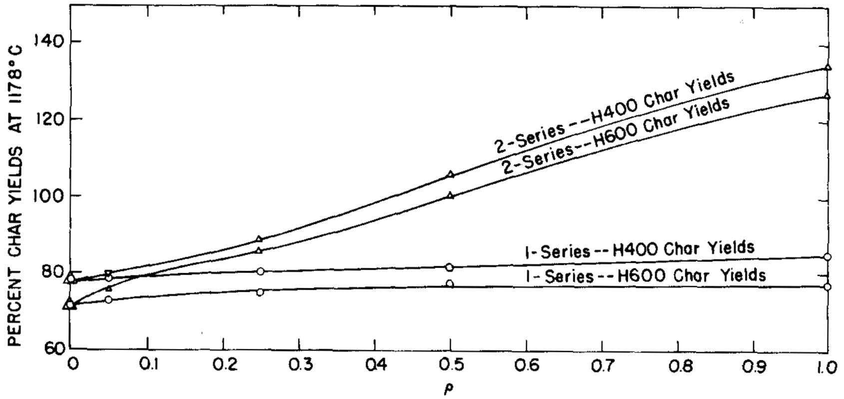


Fig. 2. Per cent char yields at 1176°C of the 1- and 2-series of the H400 and H600 polymers.

DISCUSSION

Both the 1- and 2-series of polycondensations were facile and yielded tractable, fusible polymers at the intermediate condensation stages. As in the previous series of polymers [1-4], the viscosities of the melts increased with reaction time while the color of the mixtures changed progressively from yellow to brown to black. All the polymers 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 so that the properties of the polymers could be compared to the related polymers, previously reported [1-4].

The presence of the trifunctional reagents in the reaction mixture produced effects which were easily observed. Gellation occurred first in those systems in which $\bar{f}$ was 3; this was followed, in the expected order, by the systems in which $\bar{f}$ decreased from 2.4 to 2.0. The polymers in which $\bar{f}$ was 2 were the last to convert to the solid condition.

In the 1-series the by-product of the condensation was water at all values of ρ, and the elemental analyses of these polymers were in good agreement with the theoretical values calculated on the basis that the $\overline{DP}$ was equal to ∞ and the polymers were free of end groups. The yields at 400°C were found to increase slowly as ρ increased from zero to 1. When these H400 polymers were postheated at 600°C, the weight lost, on the basis of the H400 polymers, decreased progressively from 14.5% for the polymer (1A-H400) of $\rho = 0$ to 9.0% for the polymer (1E-H400) of $\rho = 1$. Thus the overall yield at 600°C for the 1-series increased from 81.2% for $\rho = 0$ to 91.0% for $\rho = 1$. Yields of the H600 postheated polymers were in fair agreement with the per cent residue at 600°C of the H400 polymers determined by TGA at $\rho = 0, 0.05$, and 0.25 but in better agreement at the higher cross-link densities of 0.5 and 1.0. The char yields of the H400 and H600 polymers at 1176°C increased slowly from $\rho = 0$ to about $\rho = 0.25$ and then leveled off to $\rho = 1$. The behavior of the 1-series of the AB-ketanil polymers parallelled that of the series of the AA-BB-ketanil polymers [1] as cross-links are introduced in their structures. In this 1-series, this would be the expected result [1] in a relatively simple polycondensation system compared to the more complicated system involving exchange reactions [1, 2].

In the 2-series, polymer 2A is identical to 1A and was used as the common reference point in both series for $\rho = 0$. All the remaining members of the 2-series involve exchange reactions in which benzylideneaniline is a by-product to some extent. The theoretical by-product ratio of water to benzylideneaniline in the 2-series is as follows: at $\rho = 0$, 1 : 0; at $\rho = 0.05$, 10 : 1; at $\rho = 0.25$, 2 : 1; at $\rho = 0.50$, 1 : 1; at $\rho = 1.00$, 0 : 1. Previous studies have shown

[2] that an increase in polymer yield as well as char yield can be expected in those polyazomethines in which benzylideneaniline is a by-product. The data in Table 9 confirm the previous observation [1]; the yields at 400 and 600°C, and the char yields of the H400 and H600 polymers of the 2-series above $\rho = 0$, are higher at all values ρ than the values in the 1-series. This is attributed, as previously, to the retention of the by-product benzylideneaniline even at temperatures in excess of 1000°C, most probably in the form of a polymer product in a tight cross-linked polymeric cage. Further evidence that some mechanism responsible for this phenomenon is in operation in this case also was the identification of aniline [2] along with benzylideneaniline in the by-products of the reactions leading to polymers 2B, 2C, 2D and 2E, and the deviations in the elemental analyses, particularly in the values for nitrogen. Detailed studies now in progress on some novel reactions will be published in the near future [5].

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