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Polymeric Schiff Bases. XIII. The Direct Synthesis of Cross-Linked Polymeric Azomethines

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SUMMARY

A number of polymeric azomethines were synthesized to determined the influence on char yields by the deliberate introduction of cross links in their structures. The linear reference polymer was $\left[=C(CH_3){-}C_6H_4{-}C(CH_3){=}NC_6H_4N{=}\right]_n$, considered as having a cross-link density, ρ, of zero. Two series were prepared with ρ values between zero and 1, using 1, 3, 5-$C_6H_3(COCH_3)_3$ and 1, 3, 5-$C_6H_3(NH_2)_3$, respectively, 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. Within certain limitations, the yield of char is increased by the introduction of cross links.

INTRODUCTION

Polymers which yield a high amount of char residue at relatively high temperatures are of interest in aerospace technology as charring ablators [1-9]. Generally, the higher the thermal stability of the polymer, the higher the yield of char. The most widely used

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polymeric charring ablator is a phenol-formaldehyde polymer; its utility is attributed to its three-dimensional cross-linked structure [4, 10].

A number of high performance, thermally stable polymers have been synthesized in recent years which produce a high yield of char, such as the polyimides [11-13], polybenzimidazoles [14], polyoxadiazoles [15, 16], polybenzothiazoles [17, 18], polytriazoles [19], polypyrazoles [20], polybenzoxazoles [21, 22], polyquinoxalines [23, 24], polypyrrones [25], poly(bis-benzimidazobenzophenanthrolines) [26], N, N'-diphenylpolybenzimidazoles [27], and polyazomethines [28-35].

These polymers, as usually written, show the normally classical linear structure devoid of cross links, yet they produce char in higher yields [4] than the cross-linked phenolic resins [10]. High char yields would be expected if the linear chains were sufficiently stable so that scission of the backbone into smaller fragments would not occur at temperatures in the region 350-400°C; thus rings or cross links could be generated at these temperatures, thereby stabilizing the polymer to higher temperatures. The cross links [4, 28, 36] are thereby the incidental or accidental consequence of the thermal treatment of the polymer. The literature appears to be negligible on the influence of deliberately introduced cross links on the char yield of thermally stable, normally "linear" polymers.

Thermogravimetric analyses in an inert atmosphere are used to evaluate the thermal stability of a polymer and its char-forming properties [4]. The polymeric azomethines have been shown to have high thermal stability and to be char-forming to a high degree [28-34]. Accordingly, some of the polymeric Schiff bases and ketanils were selected as candidates to determine the changes that would result in the char yields by the deliberate introduction of cross links in their structures. These cross-linked polymers are also of interest in our semiconductor studies now in progress, the results of which will be published later.

The linear polymeric azomethines have been synthesized [28-34] from reactants whose functionality, f, was 2, as, for example, by the intercondensation of aryl dicarbonyl compounds, $Ar(COR)_2$, and aryl diamines, $Ar(NH_2)_2$ [28, 32], as well as by exchange reactions of their appropriate difunctional derivatives [28, 32].

Trifunctional aryl tricarbonyl compounds, $Ar(COR)_3$, and aryl triamino compounds, $Ar(NH_2)_3$, were used to introduce the cross links in the new polyazomethines. The average functionality, $\bar{f}$, of a system consisting of equivalent quantities of $Ar(NH_2)_3$ and $Ar(COR)_3$ is 3; in such a system every bond that forms would be a cross link and the polymer molecule can be considered as having a maximum cross-link density which, in this paper, is defined as 1. When one of the reactant molecules is bifunctional and the complimentary reactant is trifunctional, as in the reaction of $3Ar(NH_2)_2$ with $2Ar(COR)_3$,

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the average functionality, $\bar{f}$, of the system is 2.4; thus every other bond that forms would lead to a cross link and the polymer is considered as having a ρ value equal to 0.5. In the cases where each reactant is bifunctional, $\bar{f}$ is 2 and ρ is zero.

Polymers with cross-link densities between 0.0 and 1.0 were prepared by reacting appropriate molar quantities of the trifunctional reactants with bifunctional monomers. The relationship of the average functionality, $\bar{f}$, of the reactants to the theoretical cross-link density, ρ, on the assumption that all the functionalities were effective in the polycondensations, is given by the expression $\rho = 3 - (6/\bar{f})$.

This paper reports the studies on the cross-linked polymers obtained by the direct reaction [32] of aryl polycarbonyl compounds with aryl polyamine compounds. The polymers thus obtained were chosen as the reference for the related polymers synthesized by exchange reactions. The studies on the polymers synthesized by the carbonyl, amine, and bis exchange reactions are the subject of a subsequent publication [38].

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EXPERIMENTAL

Monomers

Monomers, 1,4-$C_6H_4(COCH_3)_2$ and 1,3-$C_6H_4(NH_2)_2$, were purified by recently described procedures [37]; 1,3,5-$C_6H_3(COCH_3)_3$ was purchased from Aldrich Chemical Company and recrystallized from 50 : 50 benzene-ethanol, m.p. 165°C. The method described by McLean et al. [39] was used to prepare 1,3,5-$C_6H_3(NH_2)_3$.

Polymerizations

The mixture of monomers was reacted under nitrogen using the apparatus and procedures previously described [28, 32] at the following time-temperature schedule: 2 hr at 180°C; 2 hr at 225°C; 17 hr at 325°C; and $2\frac{1}{2}$ 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. Two series of polymers were prepared. The first series (1A-1E) used varied equivalent quantities of 1,3,5-$C_6H_3(COCH_3)_3$ as the cross-linking agent for the pair 1,4-$C_6H_4(COCH_3)_2$ and 1,3-$C_6H_4(NH_2)_2$. In the second series (2A-2E), 1,3,5-$C_6H_3(NH_2)_3$ was used as the cross-linking reactant. The average yield data for both series in terms of molar concentrations of zinc chloride per total molar concentration of reactants is given in Table 1.

A concentration of 0.01 mole of zinc chloride per mole of reactants was selected for the preparation of the polymers to be evaluated. The required amount of catalyst was added volumetrically as a

Table 1. Average Per Cent Conversion at 400°C as Function of ρ and Molar Concentration of $ZnCl_2$

ρ of reactants	% Yield at molar concentration of $ZnCl_2$ 0	0.001	0.01
0.00	72.0	75.5	96.0
0.05	72.1	77.5	96.1
0.25	73.5	86.5	97.0
0.50	79.0	76.5	98.9
1.00	84.0	95.5	100.0

10% aqueous solution of zinc chloride and thoroughly mixed with the other reagents before reaction.

Tables 2 and 3 list the quantities of the various complimentary reactants used in the preparation of the two series of polymers, the average functionalities of the systems, the theoretical values of ρ for the polymers, and the yields calculated on the basis of $\overline{DP} = \infty$. The analytical data for these polymers are summarized in Tables 4 and 5.

Table 2. Data on the 1-Series of H400 Polymers

Reactants	Polymer designation 1A,[a] g	1B, g	1C, g	1D, g	1E,[a] g
$1,3,5\text{-}C_6H_3(COCH_3)_3$	0.000	0.041	0.204	0.408	0.408
$1,4\text{-}C_6H_4(COCH_3)_2$	0.486	0.437	0.243	0.000	0.000
$1,3\text{-}C_6H_4(NH_2)_2$	0.324	0.324	0.324	0.324	0.000
$1,3,5\text{-}C_6H_3(NH_2)_3$	0.000	0.000	0.000	0.000	0.246
$\bar{f}$	2.000	2.035	2.182	2.400	3.000
Per cent yield at 400°C	96.4	97.0	98.0	99.4	100.0
ρ	0.000	0.050	0.250	0.500	1.000

[a] 1A and 1E are the same as 2A and 2E, respectively.

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Table 3. Data on the 2-Series of H400 Polymers

	Polymer designation				
Reactants	2A,[a] g	2B, g	2C, g	2D, g	2E,[a] g
1,3,5-$C_6H_3(COCH_3)_3$	0.000	0.000	0.000	0.000	0.408
1,4-$C_6H_4(COCH_3)_2$	0.486	0.486	0.486	0.486	0.000
1,3-$C_6H_4(NH_2)_2$	0.324	0.291	0.162	0.000	0.000
1,3,5-$C_6H_3(NH_2)_3$	0.000	0.024	0.123	0.246	0.246
$\bar{f}$	2.000	2.035	2.182	2.400	3.000
Per cent yield at 400°C	96.4	96.5	97.3	98.6	100.0
ρ	0.000	0.050	0.250	0.500	1.000

[a] 2A and 2E are the same as 1A and 1E, respectively.

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

	Calculated, %			Found, %			% Yield[a]
Polymer	C	H	N	C	H	N	at 600°C
1A-H400	82.05	5.98	11.97	82.11	5.33	10.41	85.5
1B-H400	81.94	5.96	12.10	82.23	5.06	10.72	87.6
1C-H400	81.45	5.88	12.67	81.94	5.40	11.33	87.0
1D-H400	80.77	5.77	13.46	80.79	5.28	13.07	90.2
1E-H400	79.12	5.50	15.38	77.20	6.05	15.92	90.0

[a] Based on H400.

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Table 5. Analytical Data of H400 Polymers and Yields when Heated to 600°C

	Calculated, %			Found, %			% Yield[a] at 600°C
Polymer	C	H	N	C	H	N	
2A-H400	82.05	5.98	11.97	82.11	5.33	10.41	85.5
2B-H400	81.94	5.96	12.10	83.08	5.33	10.88	85.9
2C-H400	81.45	5.88	12.67	81.27	5.25	11.70	87.2
2D-H400	80.77	5.77	13.46	78.62	5.06	14.11	88.6
2E-H400	79.12	5.50	15.38	77.20	6.05	15.92	90.0

[a] Based on H400.

Table 6. 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	95.0	87.0	81.0	77.0	76.0	75.0	70.0
1B-H400	0.05	100.0	94.0	87.0	85.0	83.0	82.0	81.0	77.0
1C-H400	0.25	100.0	96.0	90.0	87.0	84.0	83.0	82.0	78.0
1D-H400	0.50	100.0	95.0	90.0	85.0	83.0	81.0	80.0	76.0
1E-H400	1.00	100.0	97.0	90.0	87.0	83.0	82.0	80.0	77.0

Table 7. 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	95.0	87.0	81.0	77.0	76.0	75.0	70.0
2B-H400	0.05	100.0	94.0	90.0	88.0	86.0	84.0	82.0	78.0
2C-H400	0.25	100.0	98.0	91.0	89.0	86.0	85.0	83.0	79.0
2D-H400	0.50	100.0	94.0	90.0	87.0	84.0	83.0	81.0	80.0
2E-H400	1.00	100.0	97.0	90.0	87.0	83.0	82.0	80.0	77.0

Table 8. 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	99.0	96.0	93.0	92.0	88.0
1B-H600	100.0	97.0	94.0	93.0	91.0	87.0
1C-H600	100.0	97.0	95.0	94.0	93.0	88.0
1D-H600	100.0	99.0	96.0	94.0	90.0	87.0
1E-H600	100.0	98.0	95.0	94.0	91.0	86.0

Table 9. 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	99.0	96.0	93.0	92.0	88.0
2B-H600	100.0	94.0	94.0	93.0	92.0	88.0
2C-H600	100.0	98.0	95.0	94.0	92.0	87.0
2D-H600	100.0	98.0	97.0	94.0	92.0	87.0
2E-H600	100.0	98.0	95.0	94.0	91.0	86.0

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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 [28, 37]. Tables 4 and 5 summarize the per cent yields of H600 polymers obtained from H400 polymers as the 100% basis.

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 one standard liter per minute in a du Pont thermal analyzer, by procedures previously published [31]. The thermogravimetric data are summarized in Tables 6 to 9.

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DISCUSSION

The direct condensations of the aryl polyketones and the aryl polyamines were facile and yielded tractable, fusible polymers at the intermediate condensation stages. 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 H400 polyketanils previously reported [32]. The particular heating schedule used in the preparation of these polymers was selected, after preliminary experimentation, so that it could be used also in the preparation of polymers by the exchange reactions [38], thereby permitting a reasonable comparison among the polymers.

The presence of the trifunctional reagents, $Ar(COCH_3)_3$ and $Ar(NH_2)_3$, 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 $\bar{f}$ was 2.4, 2.182, and 2.035. The polymers in which $\bar{f}$ was 2 were the last to convert to the solid condition. Qualitative studies indicated that the per cent conversion at the gellation stage was given approximately by the expression $2/\bar{f}$ [40].

Preliminary studies on the uncatalyzed condensation confirmed the previous observation [32] that the rates and yields were lower than for the catalyzed reactions. Since the polycondensations performed with 0.01 mole of zinc chloride per mole of total reactants gave satisfactory yields, the polymers thus prepared were evaluated. The elemental analyses of these H400 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 small differences between the calculated and the found values may be attributed, in part, to the oxygen of the terminal carbonyl, the concentration of which was sufficiently low that, in the infrared spectra of the polymers, the bands for C=O, as well as for terminal $-NH_2$, were absent. Also, part of the difference can be attributed to other inter- and intramolecular condensation reactions which can occur at 400°C [28], as are indicated by the insolubility of these polymers in concentrated sulfuric acid. The good agreement between the calculated and found elemental analysis would tend to indicate that these secondary reactions were minor. In the earlier stages of condensation, the infrared spectra showed marked bands characteristic of NH_2, C=O, and C=N at 3380, 1676, and 1620 cm^{-1} respectively, but when condensed further, the bands for NH_2 at 3380 cm^{-1} and C=O at 1676 cm^{-1} disappeared, whereas the peak at 1620 cm^{-1} for C=N broadened, as previously reported for related polymers [32]. Al-though the yields of polymers obtained at lower and zero catalyst concentrations were less than from the catalyzed reactions, the elemental analyses and thermal stabilities were in close agreement to the values found in the polymer prepared at higher catalytic concentrations. This would indicate that under the polymerization conditions used, equilibration was achieved by a Schiff-base exchange mechanism [28] similar to that found in polyesters [41, 42]. In the tables, polymer 1A of $\rho = 0$ is identical to 2A, and polymer 1E of $\rho = 1$ is identical to 2E.

A comparison of the data in Tables 6 and 7 shows that the introduction of cross links in the H400 polymers increases the amount of char obtained at 1176°C by about 10% in the first series cross-linked by $C_6H_3(COCH_3)_3$ and by about 12% in the second series cross-linked by $C_6H_3(NH_2)_3$. However, in both cases, additional cross linking above $\rho = 0.05$ does not appear to increase the amount of char. These results would tend to indicate that (1) even though some cross links may have formed in the polymers of $\rho = 0$, as a result of the heating at 400°C, additional cross links introduced at $\rho = 0.05$ did contribute some added stability to the polymer; and (2) no further increase in stability was obtained by an additional increase in cross-link density above about one cross link deliberately introduced for every 20 repeating units, because of the inherently stable nature of the backbone chain, which did not fragment catastrophically at 400°C. This is confirmed to some degree by the data on this 1-series of H600 polymers. Polymer 1A-H400 lost 14.5% of its weight when postheated to 600°C, whereas the remainder of the series, 1B-H400-1E-H400, lost as an average 12.3%. Polymers 1B-H400-1D-H400 lost as an average 11.7% by weight compared to 10% for 1E-H400 when they were postheated to 600°C. Similar results were obtained when the 2-series of H400 polymers were postheated to 600°C. In general, also, the agreement between the weight loss when the H400 polymers were heated to 600°C and the values obtained from the thermograms of the H400 polymer is good, as shown in columns B and C of Table 10.

The differences in char yields of the H600 polymers, shown in Table 8 and 9, and column E of Table 10, were minor within each series. The average char yields shown in column E of Table 10 for the 1-series of H600 polymers was 87.0%, and for the 2-series of H600 polymers it was 87.2%. The results within each series are in accord with previous results obtained on other H600 polyazomethine polymers [28] and are attributable to polynuclear formation.

The differences in char yields as a result of the deliberate introduction of cross links are insignificant in the H600 (column E, Table 10) compared to the differences for the H400 polymers (column D, Table 10). The overall yields calculated on such factors as (1) per cent yield at 400°C, (2) losses in post heating to 600°C, and (3) per cent char residue at 1176°C are also shown in Table 10.

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Table 10. Comparison of Per Cent Residues of the Various Polymers

	A	B	C	D	E	% Overall yield at 1176°C	
						H400	H600
Polymer	% Yield[a] of H400	% Yield of H600 on heating H400	% Char of H400 at 600°C TGA	% Char of H400 at 1176°C	% Char of H600 at 1176°C	AxD	AxBxE
1A	96.6	85.5	87.0	70.0	88.0	67.6	68.5
1B	97.7	87.6	87.0	77.0	87.0	75.2	74.4
1C	98.8	87.0	90.0	78.0	88.0	77.1	78.2
1D	99.4	90.2	90.0	76.0	87.0	75.5	77.8
1E	100.0	90.0	90.0	77.0	86.0	77.0	77.4
2A	96.6	85.5	87.0	70.0	88.0	67.6	68.5
2B	96.5	84.0	90.0	78.0	88.0	75.3	76.6
2C	97.3	83.9	91.0	79.0	87.0	76.9	77.0
2D	98.6	85.0	90.0	80.0	87.0	78.9	77.2
2E	100.0	90.0	90.0	77.0	86.0	77.0	77.4

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

Substantially no differences are found in the overall yields between the H400 and the H600 polymers at the given values of ρ. This would be the expected result in a relatively simple polycondensation system which is uncomplicated by side reactions, as are the exchange reactions [38]. The H600 polymers behave as if they were the products of interrupted H400 polymerizations. However, the yields of all polymers above $\rho = 0$ are higher than those of $\rho = 0$.

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