

THE DIRECT SYNTHESIS OF CROSSLINKED POLYMERIC AZOMETHINES.

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Polymers which yield a high amount of char residue at relatively high temperatures are of interest in aerospace technology as charring ablaters. Generally, the higher the thermal stability of the polymer, the higher the yield of char. A number of high performance, thermally stable polymers, such as the polyimides, polybenzimidazoles, polyimidazopyrrolones, polyazomethines and others, have been synthesized in recent years. These new polymers are usually written as having the normally classical linear structures, yet they produce higher yields of char than the crosslinked phenolic resins. High char yields would be expected if the linear chains were sufficiently stable in the region of 350 to 400°C so that rings or crosslinks could be generated by inter- or intramolecular reactions at these and higher temperatures, thereby stabilizing the polymers to higher temperatures. The thermal stability is the incidental consequence of the thermal treatment of the polymer. The literature appears to be negligible on the influence of deliberately introduced crosslinks on the char yield of thermally stable normally "linear" polymers.

Accordingly, a number of polymeric azomethines were selected as candidates to determine the changes that would result in char yields by the deliberate introduction of crosslinks in their structures. The linear refer-

ence polymer selected for this study was the polyketanil, $\left[\text{C} \begin{array}{c} \text{CH}_3 \\ | \\ \text{---} \end{array} \text{C}_6\text{H}_4 \text{C} \begin{array}{c} \text{CH}_3 \\ | \\ \text{---} \end{array} \text{NC}_6\text{H}_4\text{N} \right]_n$ prepared from 1,4- $\text{CH}_3\text{COC}_6\text{H}_4\text{COCH}_3$ and 1,3- $\text{H}_2\text{NC}_6\text{H}_4\text{NH}_2$, and was considered as having a crosslink density, ρ , of zero. In this paper, the ρ value polymers prepared from equivalent quantities of 1,3,5- $\text{C}_6\text{H}_3(\text{COCH}_3)_3$ and 1,3,5- $\text{C}_6\text{H}_3(\text{NH}_2)_3$ were considered as one, since every effective bond would lead to a crosslink. Two series of polymers with ρ value between zero and one were prepared. In the first series, 1,3,5- $\text{C}_6\text{H}_3(\text{COCH}_3)_3$ was used with the pair 1,4- $\text{CH}_3\text{COC}_6\text{H}_4\text{COCH}_3$ and 1,3- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ to introduce the crosslinks so that the ρ values were 0.00; 0.05; 0.25; 0.50 and 1.00.

In the second series, 1,3,5- $\text{C}_6\text{H}_3(\text{NH}_2)_3$, was used as the crosslinking agent to give ρ values corresponding to the polymers of the first series. All of the polymers were prepared by melt condensation under nitrogen at atmospheric pressure at the following time-temperature schedule: two hours at 180°C; two hours at 225°C; seventeen hours at 325°C and two and one-half hours at 400°C; these polymers are designated as H400 polymers. The elemental analyses of the H400 polymers were in good agreement with theory.

The yields of the H400 polymers obtained from the uncatalyzed reactions were found to increase with an increase in the amount of trifunctional crosslinking agent but these yields were lower than the yields obtained from the zinc chloride catalyzed reactions. The yields of the catalyzed reaction also increased with an increase in catalyst concentration. The yields catalyzed by 0.01 mole of zinc chloride per mole of total reactants increased from 96% for systems of $\rho = 0$ to 100% for $\rho = 1$.

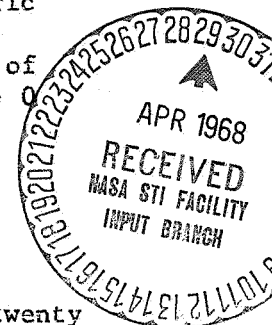
The char yields of the polymers were determined by thermogravimetric analyses on 10 mg samples ground to a fine powder of approximately 500 pieces at a heating rate of 10°C per minute in nitrogen at a flow rate of one standard liter per minute. The char yields of the polymers of $\rho > 0$ were higher than those of $\rho = 0$. Typical values were:

| ρ | Per Cent Char at °C | | | | |
|--------|---------------------|-----|-----|------|------|
| | 400 | 600 | 800 | 1000 | 1176 |
| 0.0 | 97 | 84 | 74 | 72 | 67 |
| 0.025 | 97 | 87 | 81 | 79 | 75 |

Portions of the H400 polymers were postheated under nitrogen for twenty minutes at 600°C; conditions which have been shown to yield polynuclear condensation products. These polymers are designated as H600 polymers. The weight loss under these conditions for polymers of $\rho = 0$ was about 14.5%, which was slightly higher than the 10% for the related polymers of $\rho > 0$.

Page - 2
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The char yields, determined thermogravimetrically, were substantially identical for all of the H600 polymers, ranging from 86 to 88% at 1176°C. A typical value for the H600 polymers is

| | Temperature °C | | | | |
|--------|----------------|-----|-----|------|------|
| | 500 | 700 | 900 | 1000 | 1176 |
| % Char | 100 | 98 | 93 | 92 | 88 |

In the H400 polymers, the deliberate introduction of crosslinks corresponding to $\rho = 0.05$ increased the amount of char remaining at 1176°C by about 12% above the char value found for polymers of $\rho = 0$; further increases in ρ above 0.05 did not increase the char yield. In contrast, no increase in char yield was found in the H600 polymers when ρ was increased from 0 to 1. However, when total yields were calculated on the basis of per cent conversion in the condensation polymerization stage to 400°C, losses in the postheating at 600°C, and the per cent char residue at 1176°C, an increase in the crosslink density from 0 to 1 yielded an increase in char of about 13% in the H400 polymers and about 7% in the H600 polymers.