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# Degradation

## Thermal Depolymerization Studies of New Poly(Dimethylenebenzoxazoles)

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### SUMMARY

Two polybenzoxazoles possessing $-CH_2CH_2-$ units in the backbone have been examined for their unusual thermal depolymerization behavior. In contrast to other polybenzoxazoles which displayed gradual TGA weight losses from 500-1000°, both the 2,5- and 2,6-dimethylene polymers displayed catastrophic degradation between 450° and 500° involving more than 50% weight loss over a 50° range (5 minutes of a 100 minute cycle). The pyrolysis-GC-MS data for the 2,5-isomer displayed numerous stable thermolysis products, several of which possessed parent m/z values of 289 consistant with dimers of the repeat unit. Thermal depolymerization in a sublimation apparatus gave "sublimed" polymer almost identical with the starting material. These results suggest that one of the major depolymerization pathways involves formation of a diradical intermediate similar to that observed for [2.2]-paracyclophane. Cyclodimerization (prior to GC separation) apparently competes with polymerization that is favored in the condensed phase region of the sublimation experiment.

### INTRODUCTION

Literature reports of heteroaromatic polymers that contain alkyl and alkenyl backbone moieties are rare with even fewer involving AB monomers. We recently reported a two-step procedure for conversion of several new AB monomers to alkyl and alkenyl polybenzoxazoles[1]. Description of the monomer syntheses and polymerization conditions[2] was followed by a detailed discussion of polymer characterization[3]. Figure 1 illustrates the polymerization process for 3-amino-4-hydroxyhydrocinnamic acid (1).

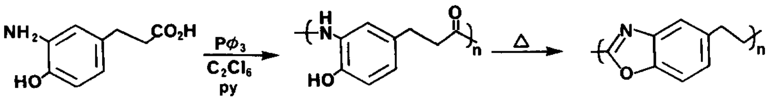

**Figure 1. Two-step synthesis of polybenzoxazoles.**

Somewhat to our surprise, the polybenzoxazoles exhibiting the best viscosity values were those obtained from monomer 1. The 2,5-dimethylene structure along with its 2,6-analog (2), also displayed unusual thermal behavior. This paper summarizes our observations on these two derivatives that support a major thermal depolymerization pathway involving formation of paracyclophane-like intermediates and dimers containing benzoxazole units.

## RESULTS AND DISCUSSION

The synthetic method employed for obtaining the intermediate hydroxy-substituted polymamides is mild but suffers from the major drawback that precipitation occurs before high viscosity polymers are obtained. Inherent viscosities of most of the polyamides studied were in the range 0.15-0.25[2]. However, thermal treatment to induce cyclization also increased the viscosities of the final polybenzoxazoles because of increased chain rigidity and further chain-end extension. Viscosity values of 2-3 were obtained for the polymer from 1 while that from 2 gave values of about 1[3].

TGA's of most polybenzoxazoles showed initial weight loss at 500-650°, continuing gradually up to 1000° with weight retention of 50-60%. Figure 2 gives the TGA traces for the two isomeric polymers containing $-CH_2CH_2-$ units. A catastrophic transition occuring between 450° and 500° resulted in significantly faster and greater weight loss. This suggested a degradation process facilitated by two adjacent methylene groups, especially since the monomethylene polymer behaved like the alkenyl- and all-aromatic polymers[3].

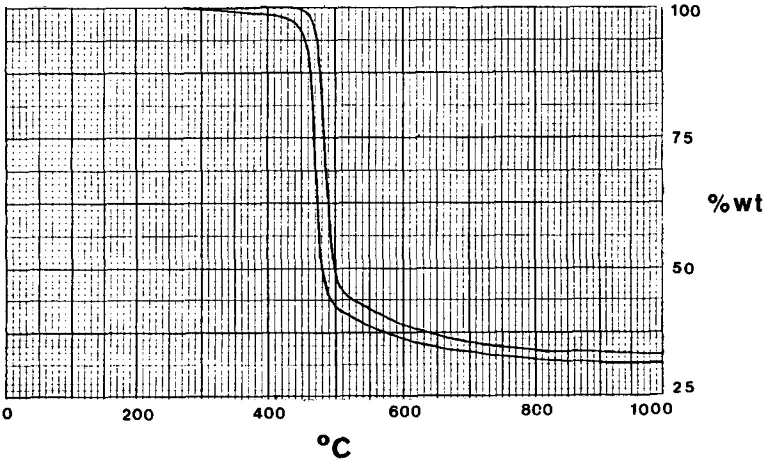

Figure 2. TGA plots of poly-2,5- (upper curve) and poly-2,6-dimethylenebenzoxazole (lower).

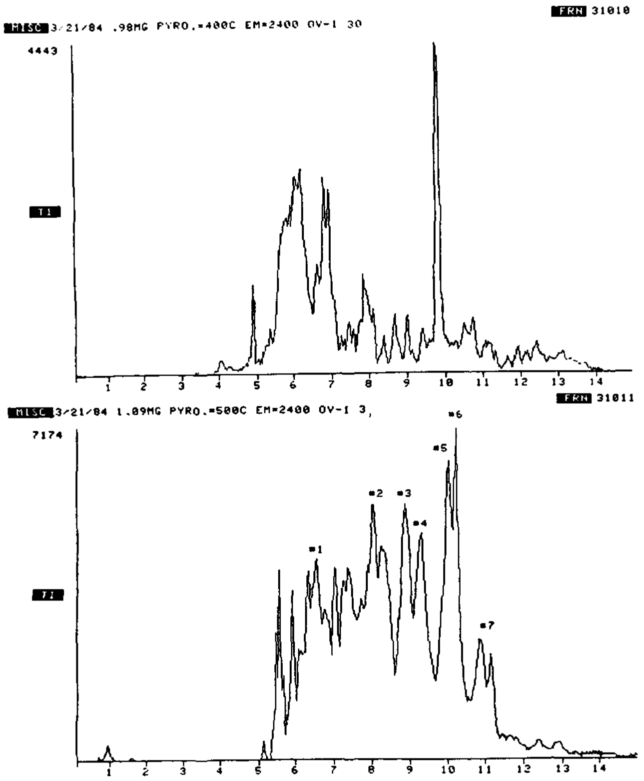

Figure 3. GC chromatograms of the products of poly-2,5-dimethylenebenzoxazole pyrolyzed at 400° (upper trace) and 500° (lower trace)

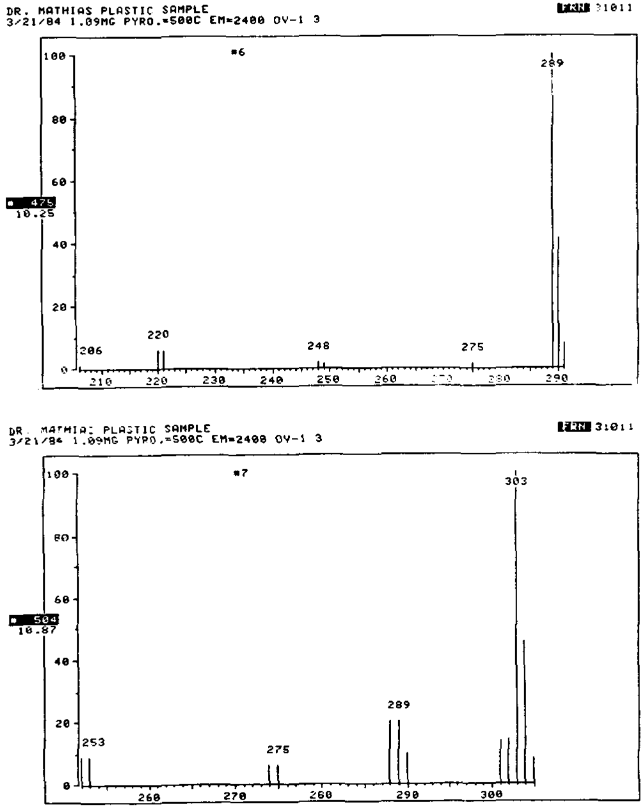

Figure 4. Mass spectra of peaks 6 (upper plot) and 7 (lower plot) from the pyrolysis of poly-2,5-dimethylenebenzoxazole at 500°.

The pyrolysis products of the polymer from monomer 1 were examined in more detail with GC/MS. Figure 3 gives the GC chromatograms obtained for two different pyrolysis temperatures. While significant changes were found on increasing the temperature from 400° to 500°, no further change was observed up to 900°. This behavior is consistent with a thermally activated, rapid backbone-cleavage reaction such as the free radical unzipping observed for many vinyl polymers and for polyparaxylylene (the phenyl analog of the two polymers described here)[4]. The complexity of the GC plot may indicate the existance of several competing degradation pathways.

Evidence for one of the major pathways is supplied by the mass spectra of several prominent GC peaks. Figure 4 gives representative spectra. The spectrum of peak 6 is essentially identical with those of peaks 3 and 5. The intense parent ion at 289 m/z corresponds to the M-1 peak of a compound whose molecular weight is exactly twice that of the repeat unit. These compounds may arise from thermal depolymerization of the polybenzoxazole to the resononce-stablized diradical shown in Figure 5. Cyclodimerization of this species would then give the symmetrical and unsymmetrical compounds. Alternatively, depolymerization might involve a more direct formation of one of the cyclodimers by chain cleavage and backbiting. The strongest GC peak in the 400° pyrolysis mixture (at 9.8 on the x-axis in Figure 3) also gave a parent ion of 289 m/z.

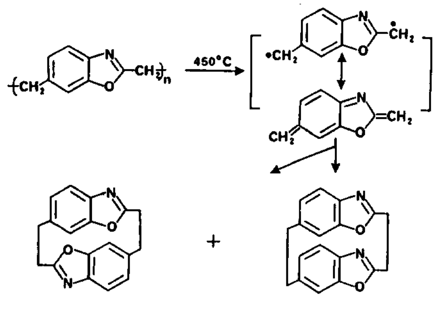

**Figure 5. Proposed depolymerization process leading to cyclodimers containing benzoxazole units.**

The mass spectra of GC peak 7 is also given in Figure 4 and displays a 303 parent ion. The parent ion of GC peak 4 (not shown) is at 275 m/z. The latter may correspond to a dimer minus one $-CH_2-$ group while the former is its complement, possessing an extra $-CH_2-$ unit. If these two compounds possess cyclic structures, they would contain [2.1] and [3.2] bridges.

A large number of cyclophanes have been described in the literature[4]. Included are several with monocyclic heteroaromatics such as pyridine and furan as well as condensed aromatic structures such as naphthalene and azulene. However, we are aware of no reports of [2.2]-cyclodimers of benzoxazoles or related compounds despite their structural and chemical similarity to those reported. More importantly, no stable [2.1] cyclophanes have yet been described. Both angle strain and interfacial repulsion caused by the single methylene bridge would be prohibitive. This argues strongly against the 275 species in peak 4 possessing a cyclophane structure, although cyclization is reasonable for major compounds displaying the 289 and 303 m/z values.

The polymer "sublimation" experiment was carried out on the high viscosity derivative of 4. A small round-bottom flask containing the polymer sample was heated under vacuum. Thermal degradation did not begin until just above 450°. Rapid polymer disappearance in the flask was followed by collection of the "sublimate" just above the heated zone of the reaction flask. The IR spectrum of this light yellow material was almost identical to that of the tan starting polymer (Figure 6). This suggests either oligomer sublimation or

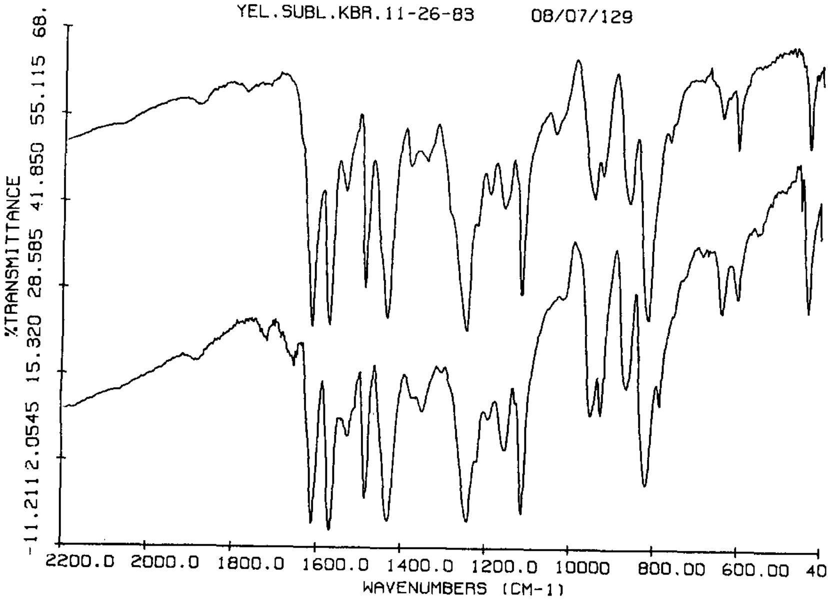

**Figure 6. Infrared spectra of poly-2,5-dimethylenebenzoxazole before sublimation (lower plot) and after (upper plot).**

depolymerization to a reactive species that subsequently repolymerized in the gas or condensed phase just above the heated zone. Formation of a diradical species like that found for xylylene[4] would entail more extended resononce for the benzoxazole (Figure 5) that would enhance stability.

With the reaction conditions used in the sublimation experiment, a relatively high concentration of the diradical "monomer" would exist in the region just above the heated zone. Condensation and rapid polymerization would readily occur. The presence of carrier gas plus the much lower total mass of polymer used in the pyrolysis-GC-MS experiments would favor dimer formation.

In summary, the results of these experiments indicate: unusual catastrophic thermal degradation of the two dimethylene polymers in the TGA; apparent thermal depolymerization and repolymerization in the sublimation apparatus; and the appearance of very stable dimer molecular ions of m/z 289 in the GC/MS spectra of the polymer pyrolysis products. These facts are consistent with rapid polymer unzipping to give intermediate "monomers" that can dimerize or polymerize depending on reaction conditions.

## EXPERIMENTAL

Polymers used in this study[1-3] were purified by repeated extraction with methanol and dried under vacuum. TGA data was collected on a Du Pont 990 analyzer while the pyrolysis-GC-MS studies were carried out on a Hewlett-Packard 5985.

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