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Exploring the Thermal Degradation Mechanisms of Some Polybenzoxazines Under Ballistic Heating Conditions in Helium and Air

Scott Thompson^{1,†}, Brendan J. Howlin¹, Corinne A. Stone², Ian Hamerton^{3*}

¹ Department of Chemistry, Faculty of Engineering and Physical Sciences, University of Surrey, Guildford, Surrey, GU2 7XH, UK

² Dstl, Porton Down, Salisbury, SP4 0JQ, UK

³ Bristol Composites Institute (ACCIS), Department of Aerospace Engineering, School of Civil, Aerospace, and Mechanical Engineering, Queen's Building, University of Bristol, University Walk, Bristol, BS8 1TR, UK

[†] Present address: Hexcel Composites Ltd., Duxford, Cambridge, CB22 4QD, UK

*Corresponding author ian.hamerton@bristol.ac.uk

ABSTRACT: The degradation behaviour of five polybenzoxazines (PBZs) is studied using pyrolysis-GC/MS. Upon heating to 800 °C in helium the PBZs generate a variety of similar pyrolysis products including aniline (the major product in all cases), substituted phenols, acridine, and 9-vinylcarbazole. During the initial stages of heating (200 to 300 °C) aniline is the dominant pyrolysis product; from 350 °C onwards substituted phenols are released, particularly 2-methylphenol and 2,6-dimethyl phenol. The same major species are produced on heating in air, but in addition isocyanatobenzene is observed which results from the oxidation of Mannich bridges, along with a number of sulphurous species from the monomer containing a thioether bridge. This suggests that sulphur is more likely to be retained in the

char in a helium atmosphere, but takes part in oxidative reactions to form pyrolysis fragments in air. During the ramped temperature cycles in both air and helium atmospheres the release of aniline was observed to rise, fall and then to rise again. This may be due a combination of the very high heating rate, poor thermal conduction of the polymer and the availability of the Mannich bridges to undergo breakdown.

Keywords: Polybenzoxazines, thermal stability, pyrolysis, degradation mechanisms.

INTRODUCTION

Polybenzoxazines (PBZs) form a comparatively new family of thermosetting resins that are being explored¹ as potential higher performance replacements for phenolic² or epoxy resins³ and, whilst they are not currently widely used in civil aviation, are being evaluated in this application. PBZs are formed through step growth ring-opening polyaddition from *bis*-benzoxazine monomers (Fig. 1), which are in turn the products of the Mannich reaction between a mono- or *bis*-phenol, formaldehyde, and a primary amine⁴. Unlike many other commercial thermosetting resins, which evolve condensation products such as water or ammonia, benzoxazine monomers react relatively cleanly to form a polymer with few reaction by-products⁵, although the exact mechanism of the polymerisation reaction to form a network has not been fully elucidated. Our group has examined the influence of additives on the nature of the polymerisation mechanism, the formation of the polymer network structure and the resulting final properties⁶.

Figure 1. Schematic showing polymerisation of bisbenzoxazines through ring opening and crosslinking.

The synthetic route employed (in which both polyphenol and amine might be varied) offers the potential to yield polymers with improved toughness over conventional phenolics.

Cured PBZs offer a combination of favourable thermal and mechanical performance (*e.g.* dry T_g values of 246 °C, hot/wet $T_g = 207$ °C are possible⁷, coupled with low moisture uptake) that gives an attractive property profile. Although requiring toughening for some engineering applications, PBZs can be combined with epoxy resins⁸ or inherently tough engineering thermoplastics (*e.g.* oligomeric polyethersulphone, $K_{IC} = 0.99 \text{ MPa m}^{1/2}$)⁹ to yield impressive enhancements.

The thermal degradation of the same series of PBZs was studied in air and nitrogen using thermogravimetric analysis (TGA) and reported in a previous publication^{Error! Bookmark not defined.}. The influence of particle size, and the structure of the bisphenyl unit, on the manner in which the crosslinked polymer undergoes degradation was examined. Although the method

indicated the degree of degradation and allowed distinction of degradation stages it did not yield direct mechanistic information about the chemical processes which are occurring during the thermal degradation. In contrast, a technique such as pyrolysis-GC/MS allows the products of thermal degradation to be identified and quantified *via* gas chromatography coupled with mass spectroscopy. The nature of the identified pyrolysis products can then be used to postulate the reactions which have given rise to these species. Pyrolysis uses high heating rates (in this work a heating rate of 20000 K s^{-1} is used) which reduces the likelihood of secondary reactions, resulting in pyrolysis fragments which should reflect the original structure of the sample more closely than those formed at slower heating rates.

EXPERIMENTAL

Materials. All monomers were supplied by Huntsman Advanced Materials (Basel), characterised fully, and used as supplied. The characterisation data are included as supplementary information (Table S1 and Figs. S1 – S5). The BF-a monomer (a mixture of isomers) is known to contain *ca.* 1 wt % of aniline, arising from the production process.

Cure conditions. All monomers (Fig. 2), except the monomer containing the phenolphthalein moiety (BP-a), were degassed at approximately $90\text{ }^{\circ}\text{C}$ for one hour using a vacuum oven to reduce void formation during the subsequent curing process. BP-a was found to be very difficult to control under degassing conditions (excessive void formation) and so was simply melted and held at $120\text{ }^{\circ}\text{C}$ over the same time period that the other samples were degassed. Following degassing, all samples were placed in an air circulating oven at $120\text{ }^{\circ}\text{C}$ and the following cure schedule was applied: heating 2 K min^{-1} to $180\text{ }^{\circ}\text{C}$ (isothermal two hours) followed by heating at 2 K min^{-1} to $200\text{ }^{\circ}\text{C}$ (isothermal two hours).

Figure 2. Structures of the monomers examined in this study.

Characterisation and Measurements. Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) was performed on samples prepared by shaving pieces from a cured puck using a micro-plane. Samples were weighed in a quartz pyrolysis boat before analysis and after the final pyrolysis event. Sample mass (100–600 μg) was chosen such that products could be identified without overloading the analytical system. Pyrolysis was carried out using a CDS 5200 pyrolyser (Analytix Ltd, Boldon, Tyne and Wear, UK) in trap mode with a Tenax TA^{TM} sorbent trap. The rest temperatures for the interface and trap were set at 50 °C and the trap desorb temperature was set to 280 °C for 2 minutes and the valve oven and transfer line held at 310 °C. The final temperature of the pyroprobe was held for 15 seconds with heating rate set to maximum (20000 K s⁻¹). The interface was held at the final temperature for 2 minutes for each method. The GC-MS analysis of the volatile organic components was performed on a PerkinElmer AutoSystem XL gas chromatograph coupled to a PerkinElmer Clarus 560S

mass spectrometer. Separation was performed on a Zebron ZB-1701 chromatographic column (dimensions 30 m x 0.25 mm ID x 0.25 μ m film thickness). The carrier gas was helium and constant pressure of 8 psi (0.8 MPa) was applied. Split mode was used with an injector temperature of 310 °C. The oven temperature program was 45 °C for 4.5 minutes, 10 K min⁻¹ to 130 °C, hold for 3 min, 10 K min⁻¹ to 280 °C, hold for 2 minutes; the total run time was 33 minutes. Mass spectrometric detection was performed with electron impact (EI) ionisation at 70 eV in full scan mode (m/z 34 to 450) with a solvent delay of 2 minutes. The source temperature was 230 °C with inlet line temperature of 280 °C. Analysis of the pyrolytic products was performed following pyrolysis. Data were compared against a series of standards: phenol, *o*-cresol, *p*-cresol, 2,4-dimethylphenol, 2,6-dimethylphenol, 2,4,6-trimethylphenol, *o*-xylene, *p*-xylene, 1,3,5-trimethylbenzene, aniline, *o*-toluidine, *p*-toluidine, formanilide, 9H-xanthene, phenanthrene, and acridine.

RESULTS AND DISCUSSION

Selection of Experimental Parameters. In our previous work, TGA was used over the range room temperature to 800 °C and so it is across this range that pyrolysis-GC/MS has been applied. Initially, a small sample of ground poly(BA-a) was heated to 800 °C under an atmosphere of helium which was subsequently repeated for each PBZ. The chromatograms produced for each of these analyses are presented in Fig. 3, from which it is immediately apparent that the various PBZs generate many of the same pyrolysis products but that there are also numerous peaks in the chromatograms which are unique to one sample.

Figure 3 - GC data produced from pyrolysis-GC/MS of various PBZs (RT to 800 °C).

The mass spectra of the peaks were obtained and compared with the NIST database¹⁰ for identification, as well as comparison with standards run under the same conditions. In particular these chromatograms all share many of the intense peaks: the major peak in all of the analyses represents aniline, with the peaks in the range 13-17 minutes representing substituted phenolic and aniline species. In all, twelve pyrolysis products were shared by all the PBZs (see Supplementary Fig. S6). The origins of many of these molecules are relatively straightforward to identify through bond scission within the PBZ structure. For instance, an aniline moiety is pendant from the Mannich bridge that connects the benzoxazine repeat units and cleavage of the two C-N bonds surrounding the nitrogen atom will result in release of aniline. This situation has already been postulated by Low and Ishida following work using TGA-FTIR¹¹. Similar scenarios can be suggested for the production of the remaining smaller molecules in Table 1, the production of indole, acridine, and 9-vinylcarbazole might arise from secondary reactions where smaller molecules have recombined or are released at high temperatures when carbonaceous char decomposes. The pyrolysis products reported in the present work also tend to share similar structural features, however there is no evidence of Mannich base or biphenyl compounds being produced by the PBZs. It is possible that these molecules had formed but broken down further or recombined and thus their production might have been masked.

The analysis carried out in this work is not strictly quantitative, but due to the overwhelming abundance of aniline in all of the chromatograms, presenting the integration values of the peaks relative to the value of their respective aniline peaks allows a useful interpretation of the data (Fig. 4) and this presentation of results underlines the dominance of phenol and aniline based species. This is to be expected as the three major stages of PBZ thermal degradation are: breakdown of Mannich bridges that are at the chain ends or side chains (this

structure is abundant in monomeric benzoxazine derived polymers), and breakdown of the Mannich bridges that are in the main chain discrete from the chain ends (this structure dominates polymers that are derived from the main-chain type precursor). The first degradation peak observed in the TGA around 300 °C nearly disappears in the main-chain type PBZs and thus this degradation process is attributed to the degradation of the chain ends. Both of these processes release aniline; they are followed by bisphenol linkage breakdown (releasing phenols) and finally char degradation¹².

It is perhaps surprising that aniline dominates the chromatograms, for in the data acquired under nitrogen using TGA^{Error! Bookmark not defined.} the bisphenol linkage breakdown stage is the major degradation process for many of these PBZs. The larger species, such as acridine, are produced at such a relatively low level, when it has been observed that by approximately 600 °C the polymer samples have become very blackened and carbonaceous in nature. It is possible that both of these anomalies can be explained by the speed of the pyrolysis. Mannich bridge breakdown is thought to occur at relatively low temperatures, therefore when heated quickly it may be that only this early stage of degradation has the opportunity to take place fully whereas there is less time for the latter stages (*e.g.* char breakdown) to proceed. The other major pyrolysis product, which is specific to only one of the PBZs, is butanol, which is added as a processing aid to at least one commercial formulation of the BP-a monomer.

Predictably, sulphurous molecules are observed in the pyrolysis products of poly(BT-a), but the amounts (of *meta*-methoxybenzenethiol and 1-methoxy-3-(methylthio)benzene) released are very low compared with the other products. Considering that the levels of phenolic type

pyrolysis products (which are assumed to be released upon bisphenol linkage breakdown) are not dissimilar for the other PBZs it is inferred that the sulphur in the PBZ structure remains in

Figure 4 - Pyrolysis products of PBZs under helium when heated to 800 °C (integrated values relative to aniline)

the char as the material is heated rather than being released. This may, in turn, contribute to the fact that the char yield of poly(BT-a) has been found to be one of the highest of this PBZ set. Alternatively, thiols may undergo reaction with some PBZs, particularly aliphatic polymers, the extremely high temperature might facilitate this although the authors have no evidence to support this possible pathway.

Examination of thermal degradation mechanism. To build a greater understanding of how the thermal degradation of PBZ proceeds with an increase in temperature a stepwise pyrolysis-GC/MS programme was applied. For this procedure the same experimental set up described in the previous section was used, but the sample was heated to 200 °C, then to 250 °C and subsequently incrementally to 300, 350, 400, 450, 500, and 600 °C. The upper temperature was selected from examination of the TGA data, which indicated that by that temperature the major degradation events had ceased. Figs 5a to 5f demonstrate how the concentrations of degradation products vary with PBZ backbone at various stages during the stepwise heating programme to 450 °C under helium.

(a)

!"#\$

(c)

Figure 5 - Pyrolysis-GC/MS products relative to aniline, under helium at (a) 200 °C, (b) 250 °C, (c) 300 °C, (d) 350 °C, (e) 400 °C, (f) 450 °C.

At lower temperatures (200 to 300 °C) the major pyrolysis product found in all the polymers tested is aniline, followed by aniline derivatives, whose release accompanies breakdown of the Mannich bridges. Although there are two types of cleavage site available along this Mannich bridge structure (one N-C and one aromatic C-C) the results presented here would suggest that cleavage of both C-N bonds is favourable to the cleavage of one, or both of the C-C bonds, presumably reflecting the polarity of the C-N bond supporting movement of the electrons to reside on the nitrogen. This is supported by the relative amounts of products: the yield of aniline vastly outweighs that of *n*-methylaniline; this is true throughout the entire

temperature cycle, not only at these lower temperatures. The reported bond energies (C-C, 348 kJ/mol.; C-N 293 kJ/mol) [13] are also consistent with this suggestion.

Low and Ishida¹¹ postulated from TGA-GC/MS data that a conjugated Schiff base would be produced in competition with *n*-methylaniline, particularly in the case of poly(BA-a), although the present work shows no sign of Schiff base throughout the analysis of any of the PBZs (see Supplementary Figs. S1 - S3). This may be a result of differing experimental parameters between the TGA-GC/MS and pyrolysis-GC/MS configurations, in particular a far more rapid heating rate is employed during pyrolysis (20000 K s⁻¹) compared to the TGA (10 K min⁻¹). *n*-Phenylformamide is also produced at these lower temperatures, although it is more difficult to identify the origin of this product (unless one assumes the degradation of an unreacted monomer unit, to form a new double bond resulting from the O-C cleavage). The hypothesis for this event is supported by DSC data, which have shown the PBZs in this work cure to approximately 90 %, leaving a significant quantity of unopened heterocyclic rings available to react in this way. The pyrolysis product plots confirm that this *n*-phenylformamide production is low compared to aniline at approximately 5-10 %, which agrees with the 90 % degree of cure values. It has also been postulated that monomer units can be liberated during thermal degradation of PBZs¹⁴ and so it is possible that this has occurred followed by further degradation.

The major difference at these temperatures between the PBZs is the production of butanol from poly(BP-a). Butanol production has previously been seen when raising the temperature directly and rapidly to 800 °C, where the principal release of the alcohol occurs between 200 and 250 °C and dominates the plot for poly(BP-a). Release at these relatively low temperatures supports the notion that this is free butanol remaining in the cured resin. With

only aniline being released for all of the other PBZs it is suggested that at these temperatures Mannich bridge breakdown is occurring, which should not be particularly influenced by the various bisphenol linkages in this set of materials. Therefore, as butanol is the only additional species apparent at this temperature, it is logical to assume that this merely results from evaporation rather than degradation of the PBZ structure.

As the temperature increases from 300 to 450 °C other species, such as phenols, begin to be released. Again, this is to be expected as this is the temperature range over which bisphenol linkage degradation occurs. The appearance of 2,6-dimethylphenol and 2-methylphenol supports the hypothesis that the second stage in PBZ degradation is bisphenol linkage breakdown. Thus, following aniline release, the cleavage between the bisphenol group and phenolic moiety to release both 2,6-dimethylphenol and 2-methylphenol can be envisaged. These two phenolic compounds are seen first in PBA-a followed by PBP-a, suggesting that the bisphenol linkages in these two structures are weaker than in the other PBZs. Furthermore, in this temperature range 2,6-dimethylphenol is more prevalent than 2-methylphenol, which again suggests that C-N cleavage is preferred to C-C cleavage, until higher temperatures are reached when the trend is reversed.

Of the PBZs studied, poly(BA-a) generates more complex molecules at a significantly earlier stage of the degradation process compared with the other materials. For instance, at 350 °C poly(BA-a) releases 2-methylquinoline, 4-(1,1-dimethylethyl)benzenemethanol, 2-(2-methyl-2-propenyl)phenol and hexamethylbenzene. It follows that if the backbone structure of poly(BA-a) has started breaking down before the other materials, that secondary reactions and recombinations would occur first for poly(BA-a). These four species may be split into two categories where 2-methylquinoline and hexamethylbenzene are products of secondary reactions, and 4-(1,1-dimethylethyl)benzenemethanol and 2-(2-methyl-2-propenyl)phenol are

generated from more simple cleavage of the primary structure. Following Mannich bridge breakdown, the generation of these two molecules from the poly(BA-a) structure by bisphenol linkage breakdown is a reasonable hypothesis. However, it is true that the production of 2-(2-methyl-2-propenyl)phenol might arise more logically through cleavage from the poly(BA-a) structure if the (2-methyl-2-propenyl) group was located in the 4-position on the phenolic ring rather than 2-position. As this molecule has been identified by comparison of mass spectra it is possible that isomers exist, which is suggested by the ^1H NMR spectrum⁶. These two molecules are only apparent for poly(BA-a) throughout the whole temperature cycle, which confirms that the nature of the monomer backbone influences the pyrolysis pathway. Later in the analysis, 2-methyl-5-(1-methylethyl)phenol is also found to be generated solely by poly(BA-a) and this again fits this structure well, particularly if the (1-methylethyl) group is attached at position 4 instead of 5.

By 450 °C the degradation products from the remaining four PBZs contain more complex molecules and by 600 °C, in most cases, aniline is no longer the biggest contributor to the pyrolysis products. At these higher temperatures there are subtle differences in the species generated where bisphenol linkage breakdown is expected to occur in all of the PBZs. If one considers just the simple phenolic species: 2,4-dimethylphenol dominates the degradation products of poly(BF-a) at 450 and 500 °C, as it arises from a simple cleavage of the methylene bridge; whereas it is not a major degradation product for the remaining PBZs.

Indeed, unlike poly(BF-a) and poly(BA-a), it is difficult to find any strong evidence of release of molecules containing the bisphenol linkage group for poly(BP-a), poly(BT-a), and poly(BD-a). This is most obvious for poly(BT-a), owing to an almost a complete lack of pyrolysis products containing sulphur (aside from the more complex 4-nitro-*N*-(2,6-xylylbenzene)sulfonamide that occurs at a low level, 0.3 %). When the analysis is run

directly to 800 °C (see previous section) two or three sulphur containing molecules are formed, albeit at relatively low magnitude (~10 %). These observations lead to two hypotheses: (a) stopping the pyrolysis procedure at various temperature intervals has an effect on the thermal degradation processes occurring in the sample; (b) sulphur is more likely to remain in the sample by contributing to char than to be released as a pyrolysis product (see the previous comments relating to thiol reactivity towards benzoxazine monomers). Similarly, for poly(BP-a) and poly(BD-a) there are no signs of phenolphthalein nor dicyclopentadienyl moieties being found in the respective pyrolysis products. This is not surprising as it is likely that these large groups would themselves undergo breakdown. It is likely that, in the case of the dicyclopentadiene group in poly(BD-a), this gives rise to a large range of more complex pyrolysis products (*e.g.* dicyclopentadiene is prone to undergo a retro Diels-Alder reaction to yield two equivalents of cyclopentadiene)¹⁵. For example, in the 500 °C plot (Fig. 6a) it is poly(BD-a) which dominates the central portion of the graph displaying a variety of indole- and indenone-related molecules.

(a)

Figure 6 Pyrolysis-GC/MS products relative to aniline, under helium at (a) 500 °C, (b) 600 °C.

The data for poly(BP-a) show that a number of phenolic species are produced upon pyrolysis, supporting the view that bisphenol linkage breakdown occurs, although at higher temperatures the species tend to occur for all of the PBZs studied and are no longer unique to poly(BP-a). For example, acridine is a large molecule which is common to all five PBZs, but poly(BP-a) generates 170 % relative to aniline, whereas the other four materials produce at most only 10 % at 600 °C. The presence of the phenolphthalein moiety in the original structure may allow the material to contribute an extra benzene ring to the reaction mixture, which then gives rise to an increase in the larger polyaromatic pyrolysis products. At 600 °C a variety of larger species, common to all the PBZs, are produced (Fig. 6b). Thus, the likes of acridine, quinolone, and vinylcarbazoles suggest that the final stage of thermal degradation involves degradation of char, which has formed from secondary reactions or recombinations. Ishida *et al.*¹⁶ observed large fragments, including both rings and bridging moieties such as $\text{C}_6\text{H}_4\text{NHCH}_2\text{C}_6\text{H}_4\text{NHCH}_2-$, from the thermal degradation of PBZ when using direct pyrolysis mass spectrometry (DP-MS). Interestingly, no such fragments have been found in any of the pyrolysis analyses carried out within this work. It may be that these fragments are being produced but, owing to the less direct nature of the pyrolysis-GC/MS, secondary reactions are taking place before they can be detected.

Fig. 7 depicts a plot of the integrated values of the pyrolysis products against the temperature of the analysis for poly(BA-a). Here a number of molecules arising from the pyrolysis have been selected and the trends for this material are also seen in the other PBZs. The most striking aspect of this plot is the bimodal trend for aniline production.

This graph shows that the amount of aniline being released by poly(BA-a) increases between 200 and 250 °C and, as expected as the Mannich base structures start to breakdown at these low temperatures, and then decrease from 250 to 350 °C. However, counter-intuitively, this trend is then reversed from 350 to 500 °C as aniline production increases once again. The breakdown of the bisphenol linkage to release phenolic species has been shown to occur in this temperature range and this is supported by this graph, which confirms that the release of 2-methylphenol and 2,6-dimethylphenol both increase over this range.

Figure 7- Selected pyrolysis products of poly(BA-a) tracked through a temperature cycle (helium).

TGA data¹⁵ show that the initial release of aniline should end at around 350 °C, which matches well with the first peak in this graph. At this stage, no definitive attribution can be made for the presence of the second peak centred around 500 °C. Consequently, this is

attributed to the experimental technique: the extremely high heating rates are likely to promote the growth of the first aniline peak representing degradation of the easily accessible Mannich bridges, while the second peak represents degradation of Mannich bridges within the bulk polymer, that become exposed following further degradation. Alternatively, this may reflect the relative stabilities of the Mannich bridges located at the chain ends or side chains and those present in the main chains. The same effect and trends in species are seen for all other PBZs using this analytical technique.

Pyrolysis under Air. The Pyrolysis-GC/MS analysis previously carried out under an atmosphere of helium was repeated in an atmosphere of air. All five PBZs were heated to 800 °C, before applying a temperature cycle. Fig. 8 shows a plot of all the pyrolysis products relative to their respective aniline peak, from which it can be seen that a wide variety of molecules are produced by the pyrolysis process. Furthermore, similar molecules are generally produced by each PBZ, particularly in the case of aniline and substituted phenols.

Figure 8 - Pyrolysis products of PBZs under air when heated to 800 °C (integrated values relative to aniline).

Some 15 molecules (substituted benzenes or polycyclics) are found to be pyrolysis products common to all of the PBZs studied in this work (see Supplementary Fig. S6). The origin of many of these species is easy to discern within the PBZ structure, *e.g.* 2-methylphenol is likely to be produced from cleavage of Mannich bridges and bisphenol linkages. The formation of many of these species has been discussed in detail when discussing pyrolysis under helium. There are also larger shared molecules, which suggests that the secondary reactions, recombinations and char formation in all of the PBZs are similar.

There are almost one hundred more molecules produced *via* pyrolysis under air than under helium, but many of these compounds are produced at a very low level. This is seen in Fig. 8 which, although it has a much longer x-axis, shows that the major pyrolysis products are very similar to those under helium. Once again, aniline dominates the plots with phenolic, aniline and benzene derivatives and acridine and 9-vinylcarbazole being the other major contributors. In common with the analysis performed in helium, although there are differences between the materials, these are generally more subtle than the molecules that predominate, suggesting that the PBZ backbone has a subtle effect on thermal degradation. Butanol production is again the obvious difference in the plots, apparent only in the pyrolysis of poly(BP-a). The other result of note is that poly(BT-a) produces a much higher level of acridine, which is consistently the most common of the more complex molecules with longer retention times, than the other materials. From an integration analysis, poly(BT-a) produces almost four times as much acridine as the next PBZ, poly(BP-a), which perhaps shows a greater ability of poly(BT-a) to produce char material.

Temperature Cycles under Air. The same experimental protocol was applied to the pyrolysis of the PBZs in air. Plots showing the integrated values of the products of pyrolysis

relative to aniline are presented in Figs 10a-10h. In general, the pyrolysis process seems to proceed in much the same way as under nitrogen (previously reported^{Error! Bookmark not defined.}) with aniline and aniline related molecules being produced at lower temperatures before the rise of phenolic species from 350 °C and subsequently larger aromatics like acridine are produced above 450 °C. This suggests that the thermal degradation pathways of PBZs are very similar in both nitrogen or air. Initially, Mannich bridge breakdown occurs, releasing aniline, which coincides with the start of bisphenol linkage breakdown, finally followed by products of secondary reactions or degradation of char. Under TGA conditions it has been found that there is generally an extra degradation stage from approximately 500 °C, which is believed to be breakdown of char with release of carbon dioxide.

Figure 10 - Pyrolysis-GC/MS products relative to aniline, under air at (a) 200 °C, (b) 250 °C, (c) 300 °C, (d) 350 °C, (e) 400 °C, (f) 450 °C (g) 500 °C, h 600 °C.

A similarity in degradation products under inert and oxidative atmospheres has been observed before¹¹, in fact the only difference was the production of a small amount of isocyanatobenzene (~1%) when heated in air. Isocyanatobenzene has also been found to be produced in this work, albeit at very low levels, which is believed to arise from the oxidation of Mannich base (Scheme 1).

Scheme 1- Oxidation of PBZ Mannich base in the presence of hydrogen bonding (redrawn from Low and Ishida¹¹).

The production of isocyanatobenzene is of a very low level compared with *n*-methylaniline and aniline, suggesting that thermal cleavage of the Mannich base in the absence of hydrogen bonding still predominates. When run in an atmosphere of helium only one pyrolysis product of poly(BT-a) was found to contain sulphur, although this was a particularly complex molecule and was present at approximately 0.3 %. However, in air three sulphurous molecules are produced: *n*-sulphinylbenzenamine, isocyanatobenzene and benzothiazole. The latter are present at a low level

(0.5-1.5 %), but are more prevalent than in helium. Furthermore, they appear more than once throughout the cycle, suggesting that under a reactive atmosphere the sulphur in the PBZ structure is more likely to react and form fragments than to become incorporated in the resulting char.

n-Sulphinylnbenzenamine, whose structure suggests that it is produced from a secondary reaction between aniline- and sulphur-containing fragments following oxidation, was first observed at 400 °C, at which point phenolic species are also detected, suggesting that this is facilitated by the breakdown of bisphenol linkages. Furthermore, there is no evidence of *n*-methylaniline following degradation of PBT-a throughout the temperature cycle, despite evidence for the same molecule arising from the remaining PBZs at multiple temperature stages. However, *n*-methylaniline is produced by poly(BT-a) under helium, which suggests that its production is replaced by *n*-sulphinylnbenzenamine under air, for which a more complex mechanism would evidently be involved.

The level of *n*-methylaniline produced by the other PBZs is much lower in air (maximum level is 8.5 %) than helium (maximum level is 33 %) and the competitive production of isocyanatobenzene (previously discussed) may contribute to this, although this seems to be present at too low a level to be the major contributor. Aside from isocyanatobenzene, there does not seem to be an obvious replacement for the *n*-methylaniline. For instance, at 350 °C poly(BF-a) produces aniline, *n*-methylaniline and *n*-phenylformamide in both air and helium with the addition of 1.8 % isocyanatobenzene in air and a very small amount of 4-dimethylbenzenamine in helium (Table 1). The lack of another major pyrolysis product in air suggests that at these temperatures the degradation processes in helium are more numerous than under air, which is perhaps counterintuitive, given the inert nature of the helium. Another possibility is that carbon dioxide is an additional degradation product following demethylation of *n*-methylaniline leading to a possible increase in the detection of aniline.

Table 1- Pyrolysis products of poly(BF-a) under varying atmospheres.

MS Library Match	% Relative to Aniline (Air)	% Relative to Aniline (Helium)
Isocyanatobenzene	1.78	-
Aniline	100	100
<i>N</i> -Methylaniline	2.59	14.47
4-Dimethylbenzenamine	-	0.34
<i>N</i> -Phenylformamide	3.04	1.32

In common with the experiment carried out in a helium atmosphere, as the temperature cycle moves from 300 to 450 °C (and following Mannich bridge breakdown) the concentrations of the phenolic molecules in the pyrolysis products increases as the bisphenol linkages in the PBZ backbone undergo cleavage. However, there are distinct differences when considering the degradation pathways of the different PBZs in this temperature regime. For instance, for poly(BT-a), at 450 °C 2-methylphenol is found at 25 % relative to aniline, while the next highest value is only 14 % for poly(BP-a). Thus, the intensity of phenolic production by poly(BT-a) in this temperature range may be linked to the sulphur-containing pyrolysis products mentioned earlier. The lack of aniline moieties in the pyrolysis products of poly(BT-a) suggests that more bisphenol linkages are being broken earlier in poly(BT-a) than for the other materials, it would then follow that more phenolic species would also be produced as a result. This contrasts with the trends that are seen under helium suggesting that poly(BT-a) is most affected by a change in atmosphere.

By 500 °C the production of phenolic species for the pyrolysis of the other PBZs reaches a similar level to that of poly(BT-a) and once again this is most marked for poly(BP-a), particularly in the production of 2-methylphenol which overtakes that of aniline by 600 °C and reaches 239 % in air *cf.* 527 % in helium. In common with the experiment carried out under helium, at 600 °C many larger species are produced (see Supplementary Figure S7) with acridine and 9-vinylcarbazole being the

major contributors. However, under air 9-methylacridine replaces iminostilbene as one of the chief pyrolysis products. These two species have similar structures and so it may be that the analysis has been unable to distinguish between the two mass spectra rather than a different mechanism being at work. In general, these pyrolysis products (towards the right-hand side of the plot) are lower in concentration in air than when produced in helium. This is not surprising if carbon dioxide is being produced as a pyrolysis product at these temperatures under air then there will be less carbonaceous char formed, in turn leading to the release of fewer large aromatic species. The central region of the 600 °C plot is again dominated by poly(BD-a) which once more shows a tendency to produce indenones.

The integrated values of a representative group of pyrolysis products have been plotted against temperature to visualize the progress of the degradation process in air, exemplified by poly(BA-a) (Fig. 11); this plot is very similar to that obtained in helium (Fig. 7). Aniline is once again observed to rise to 250 °C only for it to fall to 350 °C before once again reaching a maximum at 450 °C. This shows that under both oxidative and inert atmospheres there seems to be breakdown of surface Mannich bridges before further degradation results in more Mannich bridges becoming available. This is also similar to the profile of other aniline derivatives observed at lower temperatures under helium, followed by an increase in phenolic moieties and gradual increase of larger structures such as acridine occurring towards the end of the temperature cycle.

Figure 11 - Selected pyrolysis products of PBA-a tracked through a temperature cycle (air).

CONCLUSIONS

Upon heating to 800 °C under an inert atmosphere of helium the PBZs studied herein degrade to generate a variety of similar pyrolysis products, which range from simple molecules such as aniline (the major product in all cases), substituted phenols and larger structures like acridine and 9-vinylcarbazole. During the initial stages of heating (200 to 300 °C) aniline is the dominant pyrolysis product, which is released upon Mannich base breakdown. *n*-Methylaniline is also produced at a lower level and this suggests the existence of competitive processes, while release of *n*-phenylformamide in this temperature regime suggests that monomeric units are still present in the resins (supported by the observed degree of cure) which also break down. From 350 °C onwards

substituted phenols are released, particularly 2-methylphenol and 2,6-dimethyl phenol, which may be released following the Mannich bridge collapse and breakdown of the bisphenol linkage.

The variety of pyrolysis products is dependent on the bisphenol linkage, *e.g.* the dominant phenolic species in the degradation of poly(BF-a) is 2,4-dimethylphenol, which could arise from a simple cleavage in the bisphenol linkage in this structure. Surprisingly, only one sulphurous species is produced (at a very low level) throughout the whole pyrolysis procedure, which contributes the bisphenol linkage of poly(BT-a). This suggests that under helium sulphur remains in and contributes to the char of poly(BT-a), which may account for the high char yield produced by poly(BT-a) compared with many of the other polybenzoxazines studied in this work. At the higher temperature end of the analysis larger, more complex molecules are released (*e.g.* acridine and 9-vinylcarbazole), which must result from secondary recombination reactions as the char starts to degrade.

In air very similar results are seen, with aniline and phenolic structures dominating the pyrolysis products and acridine and 9-vinylcarbazole again being produced at higher temperatures. The results generated from applying a temperature cycle to the pyrolysis under air also shows that very similar degradation processes are occurring with Mannich bridge breakdown being followed by bisphenol linkage collapse and finally degradation of char to release larger molecules. Subtle differences between pyrolysis under the two atmospheres can be seen: production of isocyanatobenzene under air results from the oxidation of Mannich bridges, although Mannich bridge breakdown *via* the mechanism observed under helium still predominates. Unlike the analysis in helium, following pyrolysis in air a number of sulphurous species are released, which suggests that sulphur is more likely to take part in oxidative reactions to form fragments that can be removed from the degrading structure.

Throughout ramped temperature cycles in both air and helium atmospheres the release of aniline was observed to rise, fall and then to rise again. This is thought to be related to the availability of the Mannich bridges to undergo breakdown. The heating rate in these analyses is very high which may result in surface Mannich bridges (or those at chain ends) being broken initially, until further bridges within the bulk (or within main chains) become available following further degradation.

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