Polymerisation and degradation of an aromatic amine-based naphthoxazine

Tamer Uyar a, Zeynep Koyuncu b, Hatsuo Ishida a, Jale Hacaloglu b, * 

a Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106-7202, USA  
b Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

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Pyrolysis mass spectrometry (MS) analysis of aromatic amine-based naphthoxazine monomer (15-Na) and Poly15-Na has been carried out. Evaporation and degradation of the monomer are detected during the curing process while the polymerisation proceeded. The polymerisation and degradation mechanisms are proposed for 15-Na and Poly15-Na, respectively. The proposed polymerisation mechanism for naphthoxazine monomer was through the aniline units either by coupling of the radicals generated by cleavage of the side rings or by substitution to the benzene ring of aniline. It has been determined that polymerisation followed opposing paths yielding some thermally less stable linkages through which thermally crosslinked polynaphthoxazine (Poly15-Na) suffers from low thermal stability. It has been shown that pyrolysis MS is a very useful technique to investigate the polymerisation and degradation mechanisms and degradation products of these materials.

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1. Introduction

Various polybenzoxazines can be obtained by the ring-opening polymerisation of cyclic monomers, benzoxazines, which have been developed as a novel type of phenolic resin [1–3]. The monomers are easily prepared from phenols, primary amines and formaldehyde. The wide variations of raw materials, phenolic and primary amine compounds, allow considerable molecular design flexibility for the cyclic monomers. Polymerisation proceeds through the ring opening of the cyclic monomers by heat treatment only, without the need of catalyst and without generating by-products or volatiles. As a result of near-zero shrinkage during the polymerisation, excellent dimensional stability is obtained.

The typical exotherms for benzoxazines, due to thermally activated cationic ring opening polymerisation, are above 200 °C yielding crosslinked materials; polybenzoxazines. Typically, polybenzoxazines have initial weight loss starting around 275 °C and the main degradation occurs between 300 and 450 °C depending on the molecular structure [4–8]. In order to improve thermal properties of benzoxazines, additional polymerisable side functional groups were incorporated in the structure such as acetylene, nitrile, etc. [9,10]. Additionally, naphthoxazines were synthesized by using hydroxynaphthalenes as phenolic precursor to increase the thermal stability and char yield of the resulting thermosets, polynaphthoxazines [11,12]. Moreover, naphthazine terminated polymers of poly(propylene oxide)s and poly(3-caprolactone) (PCL) have also been reported to give curable polymers [13,14]. However, unlike benzoxazines, some naphthoxazines suffer from low thermal stability and require autoclave processing, since evaporation of the monomer cannot be avoided during curing. In a previous study among the four different polyfunctional naphthoxazines obtained, only one was successfully cured in an autoclave with a maximum pressure of 1.33 MPa to give a void-free resin [11]. Recently, allyl-functional naphthoxazines were synthesized to obtain high temperature stable polynaphthoxazine with extended network via the polymerisation of allyl functionalities [12]. Yet, thermal degradation/evaporation of monomers below 200 °C during thermal treatment of monomers was also recorded.

In this study, we investigated the degradation and the polymerisation mechanisms of naphthoxazines during curing. We synthesized naphthoxazine by the reaction of 1,5-dihydroxynaphthalene, aniline and formaldehyde (15-Na) and the thermal characterization of the material was carried out in detail by using direct pyrolysis mass spectrometry. This technique allows us not only to analyze the processes taking place during the curing of 15-Na but also to investigate the thermal decomposition and further reactions at high temperatures that affect the char formation of 15-Na.

Among the techniques used for investigation of thermal characteristics of polymers TGA–FTIR, TGA–MS, pyrolysis FTIR, pyrolysis GC–MS and direct pyrolysis MS can give information not only on thermal stability but also on the degradation products. Among these, direct pyrolysis mass spectrometry offers several advantages; secondary reactions and condensation reactions are avoided, detection of high mass pyrolyzates and unstable thermal degradation...
products is possible. Thus, thermal stability, degradation products and decomposition mechanism, which in turn can be used for structural characteristics of the compound under investigation, can be determined [15–20]. However, pyrolysis mass spectra of polymers are usually very complex, as thermal degradation products further dissociate in the mass spectrometer during ionization. Furthermore, all fragments with the same mass to charge ratio make contributions to the intensity of the same peak in the mass spectrum. Thus, in the case of direct pyrolysis MS analysis not only the detection of a peak, but also the variation of its intensity as a function of temperature, i.e. its evolution profile, is important. The trends in evolution profiles can be used to determine the source of the product and the mechanism of thermal degradation.

2. Experimental

2.1. Materials

Formaldehyde (37% in water), aniline (≥99.5%), pentafluoroaniline (98%), 1,5-dihydroxynaphthalene (97%) and 1,4-dioxane (≥99%) were purchased from Aldrich and were used without further purification.

2.2. Monomer synthesis and sample preparation

The naphthoxazine monomer, bis(4,5-dihydro-5-phenyl-oxazinyl) naphthalene (15-Na), was prepared as follows: 0.01 mol of aniline in 3 mL of dioxane was added dropwise to a solution containing 0.02 mol of formaldehyde (37% in water) in 3 mL of dioxane in an ice-bath (temperature below 5 °C). The mixture was stirred for 45 min in the ice-bath. After dropwise addition of 0.005 mol of 1,5-dihydroxynaphthalene in 20 mL of dioxane to formaldehyde–aniline solution, the temperature was raised to 100 °C and reflux maintained for 4 h. The precipitated product from the reacting solution was washed with ethanol several times and brownish powder was obtained.

The characteristics of the 15-Na are as follows: m.p. (194–195 °C). 1H NMR spectrum (CDCl3), ppm: δ = 4.70 (s, –CH2–, oxazine ring), 5.50 (s, –CH2–, oxazine ring), 6.90–7.65 (m, aromatic protons) and 3.7 (–CH2–, open ring of oxazine). IR spectrum (KBr, cm–1): 942–966 (C–H out-of-plane deformation of di-substituted naphthalene ring), 1029–1039 (sym. str. of C–O–C), 1232 (asym. str. of Ar–O–C) and 1368 (CH2 wag. oxazine).

Curing of 15-Na was performed on a high-pressure DSC 2910 (TA Instruments) for 2 h at 210 °C under pressure of 2.75 MPa using nitrogen purge. The high-pressure cell was used to minimize the evaporation of monomer during curing since 15-Na polymerises at high temperatures (above 200 °C). A dark brown crosslinked material, polynaphthoxazine (Poly15-Na), was obtained after curing.

3. Characterization

Proton nuclear magnetic resonance (NMR) spectrum was taken on a Varian Inova NMR spectrometer at a proton frequency of 600 MHz with averaging from 128 transients. Deuterated chloroform was used as a solvent and tetramethylsilane was added as an internal standard.

Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA 2950 under nitrogen atmosphere at a flow rate of 90 mL/min and a heating rate of 20 °C/min.

Differential scanning calorimetry (DSC) was performed to study the curing parameters of naphthoxazine on a TA Instruments DSC 2920. The temperature scanning was from room temperature to 275 °C with a heating rate of 10 °C/min under nitrogen purge (60 mL/min).

Fourier transform infrared (FTIR) measurements were performed to study the structural changes occurring during the curing of naphthoxazine monomer (15-Na). The FTIR spectrometer, Bomem Michelson MB 100, was used to record the spectra with a resolution 2 cm–1 at a co-added scans of 16 under dry air purge. 15-Na was cast from its chloroform solution onto a KBr disc and placed in a temperature controlled hot cell (Connecticut Instruments). The sample was heated at a rate of approximately 30 °C/min and held constant at target temperatures and the FTIR spectrum was recorded. The waiting time at constant temperature was about 2 min during FTIR data acquisition and the sample was heated again to the next target temperature.

5973 HP quadrupole mass spectrometry system coupled to a JHP SIS direct insertion probe was used for direct pyrolysis experiments. Samples (0.01 mg) were pyrolyzed in flared glass sample vials. 70 eV El mass spectra were recorded at a scan rate of 2 scans/s during the pyrolysis. In order to investigate the mechanisms of curing, pyrolysis mass spectrometry analyses of 15-Na were carried out at the high vacuum conditions of the MS by recording mass spectra while the same heating profiles used for curing process were applied (held at 210 °C). For pyrolysis analysis of Poly15-Na the temperature was increased from room temperature at a heating rate of 20 °C/min until the maximum attainable temperature of 450 °C was reached. The temperature was kept at this value for ten more minutes. All pyrolysis experiments were performed at least twice to confirm reproducibility.

4. Results and discussion

4.1. Naphthoxazine monomer (15-Na)

4.1.1. Chemical characterization and curing

The chemical structure of the naphthoxazine monomer (15-Na) and its thermal curing are shown in Scheme 1. The cure behaviour of 15-Na was studied by non-isothermal differential scanning calorimetry (DSC) in order to determine the curing step. A DSC thermogram shows that 15-Na has a melting point at around 195 °C and exhibits an exotherm peak with a maximum at 215 °C right after the melting (Fig. 1). The exotherm is possibly due to ring opening of naphthoxazine, yet, it is also possible that the evaporation/degradation of the monomer occurs at this temperature. Agag has observed evaporation of naphthoxazine monomers at low temperatures during curing [12]. In addition to this, Shen and Ishida reported that among the four different polyfunctional naphthoxazines synthesized, only 15-Na could be cured successfully when it was processed in an autoclave with a maximum pressure of 1.33 MPa [11]. Here, in order to have a clear understanding of the exotherm peak observed in the DSC thermogram,
we studied the naphthoxazine monomer with thermogravimetric analysis (TGA) as well (Fig. 2). We observed that the weight loss of naphthoxazine monomer starts as low as 170°C and continues gradually as the temperature increases. This finding showed that naphthoxazine monomer suffers from evaporation/degradation at low temperatures and explains the difficulty of curing reported earlier [11]. Thus, DSC and TGA data confirmed that naphthoxazine monomer (15-Na) is subject to both evaporation/degradation and polymerisation at the same time during curing. It is also worth saying that thermally crosslinked polynaphthoxazine (Poly15-Na) has high char yield (>60%) [11] even though it suffers from low thermal stability during curing.

Fourier transform infrared (FTIR) measurements were performed to study the structural changes occurring during the curing of naphthoxazine monomer (15-Na). Fig. 3 shows the FTIR spectra of 15-Na recorded at different curing temperatures. It was observed that the intensity of the characteristic benzene ring absorption band at 942 cm⁻¹, which is attributed to benzene ring to which an oxazine ring is attached, started to decrease at 200°C. The gradual decrease in peak intensity continued as the temperature reached 240°C. This is an indication of the polymerisation reaction due to ring opening of the naphthoxazine monomer. Additionally, a new absorption band at around 1670 cm⁻¹ observed above 200°C was assigned to the C\(\equiv\)N stretching from the Schiff base. No band that can be assigned to 1,2,4-trisubstituted naphthalene was detected.

4.1.2. Pyrolysis of naphthoxazine (15-Na)

The total ion current (TIC) curve and the pyrolysis mass spectra at the peak maxima present in the TIC curve recorded during the heating of 15-Na are shown in Fig. 4. The TIC curve shows a broad band with a maximum at 4.1 min corresponding to 110°C and a relatively sharp and intense peak that splits into two showing maxima at 8.5 (at 200°C) and 9.0 min (at 210°C). Yet, the pyrolysis mass spectra recorded in this region were almost identical. The molecular ion peak at \(m/z = 394\) Da was quite prominent as expected for a naphthoxazine molecule indicating continuous evolution of the monomer during the heating up to the curing temperature 210°C. However, continuous heating at around 210°C caused significant increase in the relative intensity of the peak at 93 Da indicating evolution of aniline (Fig. 4d).

For the naphthoxazine monomer under study, the base peak at 105 Da and the other intense peaks at 104 and 77 Da can readily be assigned to \(\text{CH}_2\text{NC}_6\text{H}_5\) ion and to products due to the elimination of hydrogen and HCN from \(\text{CH}_2\text{NC}_6\text{H}_5\), respectively. Intense peaks at \(m/z = 289\) and 184 Da due to the loss of one or two \(\text{CH}_2\text{NC}_6\text{H}_5\) groups, respectively (\([\text{M} - \text{CH}_2\text{NC}_6\text{H}_5]\) and \([\text{M} - 2\text{CH}_2\text{NC}_6\text{H}_5]\)) and peaks due to fragments generated by further losses of CO from these products (\([\text{M} - \text{CH}_2\text{NC}_6\text{H}_5\text{CO}]\) at \(m/z = 261\) Da, \([\text{M} - 2\text{CH}_2\text{NC}_6\text{H}_5\text{CO}]\) at \(m/z = 156\) Da and \([\text{M} - 2\text{CH}_2\text{NC}_6\text{H}_5\text{CO}]\) at \(m/z = 128\) Da) were quite intense. Peaks due to loss of one or two \(\text{O} = \text{CHNC}_6\text{H}_5\) groups from the monomer at 274, and 154 Da and due to loss of one or two \(\text{O} = \text{CHN(\text{CH}_2\text{C}_6\text{H}_5)}\) groups at 260, and 126 Da were also detectable, yet, were significantly weak. Thus, it can be concluded that the main fragmentation pathways during EI ionization of the 15-Na are the generation of \(\text{CH}_2\text{NC}_6\text{H}_5\) ion that further eliminates HCN and the loss of \(\text{CH}_2\text{NC}_6\text{H}_5\) yielding a resonance stabilised hydroxytropylium ion that further eliminates CO group. Consequently, the mass spectra are dominated by intense peaks due to aromatic products involving aromatic units and are quite distinctive.

Thus, the mass spectra pointed out the evaporation of the monomer at low temperature which is well below curing temperature before decomposition. Yet, similar fragments might have also been generated if the decomposition of the monomer occurred during the curing. In general, the similarity between the single ion
evolution profiles of the fragment ions with that of the molecular ion confirms evaporation before decomposition. Thus, in order to investigate all the possible processes taking place during curing, single ion evolution profiles of each product detected in the pyrolysis mass spectra were analyzed and compared with each other and with those of the molecular ion. In Fig. 5 single ion evolution products of some characteristic products detected during the curing process of 15-Na are shown.

In general, product evolutions were detected in two regions around 100 °C and 210 °C. The high temperature peak, at around 210 °C, present in the profiles of the characteristic products splits into two showing maxima at around 199 °C and 208 °C and variations in their relative intensities. Thus, it can be concluded that upon thermal excitation, the fragmentation patterns changed slightly and become competitive. Yet, it is clear that up to 210 °C, the main evolved product was the monomer. The maximum yield for the fragments due to the loss of CH2N(CH2)C6H5 from the monomer was detected 0.45 min after the curing temperature of 210 °C was reached. The yield of all products decreased almost exponentially shortly after the curing temperature. However, evolution of aniline and the characteristic fragments due to dissociative ionization of aniline increased drastically in this period. The maximum yield for these products was detected 0.9 min after the curing temperature. Aniline evolution diminished steadily, yet, continued throughout the curing. Above the curing temperature no peak was detected, except for the aniline and related peaks. Thus, it is clear that the dissociation of the monomer occurred around the curing temperature at least to a certain extent. Under the experimental conditions secondary reactions were almost completely eliminated. Therefore, abstraction of H to generate aniline was only possible within the thermally excited naphthoxazine monomer. Lack of any peak in the pyrolysis mass spectra that can be attributed to fragments involving naphthalene units indicates that the evolution of aniline had taken place upon ring opening and the polymerisation of the monomer.
4.2. Polynaphthoxazine

The TIC curve of the cured 15-Na showed two peaks (Fig. 6). The first one at around 100 °C corresponds to evaporation of unreacted monomer and/or lower oligomers. The second peak showed a shoulder at around 270 °C and a maximum at 410 °C. The pyrolysis mass spectra recorded at the peak maxima were dominated with diagnostic peaks of aniline (93, 66, and 49 Da peaks) (Fig. 6). Weak peaks that can readily be attributed to fragments involving N-substituted anilines were detected in the pyrolysis mass spectra recorded at low (250 °C) and moderate temperatures (below 400 °C) (Fig. 6c).

The peaks detected in the pyrolysis mass spectra were either due to the thermal decomposition products generated during pyrolysis or due to the products produced by the dissociative ionization of these thermal decomposition products during the EI ionization in the ion source. In general, it is assumed that the products with identical evolution profiles were generated through the same thermal decomposition routes or by dissociative ionization of a high molecular weight thermal degradation product. Among all the products having similar evolution profiles the one with the highest m/z value can be assumed to be generated during the pyrolysis. On the other hand, the products having smaller m/z values may be produced during the heating and/or by dissociative ionization of the parent fragment. The structural information that can be obtained from the pyrolysis mass spectral data is thus limited. Yet, the assignments for group of products with similar evolution profiles can be made taking into account the classical fragmentation patterns for EI ionization.

Thus, in order to obtain a better understanding, the fragments showing almost identical evolution profiles were grouped and then analyzed. Inspection of single ion evolution profiles of products revealed that although the main decomposition product was aniline, fragments containing N-substituted anilines and naphthoxazines were also generated over a broad temperature range. In Fig. 7, the single ion evolution profiles of fragments involving N-substituted anilines evolved mainly at initial stages of pyrolysis are shown. It is known that the mass spectrum of aliphatic amines is dominated by peaks due to the fragments generated by the α-cleavage reaction which give rise to the loss of the largest radical. The resulting fragments further break down by loss of ethene and transfer of a β-H to the positive nitrogen. In the case of N-alkyl anilines α-cleavage is again favoured and similar processes are expected. The assignments made for the low temperature (<400 °C) thermal decomposition products by analyzing pyrolysis mass spectra and the similarities in the single ion pyrograms are summarized in Table 1. In the table only the

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**Fig. 6.** The TIC curve and the pyrolysis mass spectra recorded at the peak maximum and shoulder present in the TIC curve recorded during the heating process of the cured monomer, Poly15-Na.

**Fig. 7.** The single ion evolution profiles of fragments involving N-substituted anilines. (Note: the intensities are normalized by a number factor as shown in the figure.)
ortho substituted N-alkyl anilines are shown. Actually generation of the para substituted analogues have equal probability. The fragments with \( m/z = 182, 105 \) and 77 Da showing identical trends were detected at initial stages of pyrolysis and were assigned to N-benzyl aniline radical. Thus, it may be thought that it was mainly generated by the loss of end groups or decomposition of thermally less stable linkages.

In a previous study, the increase in the room temperature density of 15-Na polynaphthoxazine was attributed to the increase of crosslink density. The minimum post-cure temperature to obtain fully cured 15-Na polynaphthoxazine was determined to be 260 °C or above [11]. Present results showed loss of weak linkages and/or end groups below 270 °C. Loss of these fragments would produce radicals that can readily couple to form a highly crosslinked structure and/or high molecular weight chains with higher thermal stability.

<table>
<thead>
<tr>
<th>( m/z ) (Da)</th>
<th>Assignment</th>
<th>Peak maxima (temp, °C)</th>
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<tr>
<td>182</td>
<td>N-CH₂-</td>
<td>250, 450</td>
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<tr>
<td>105</td>
<td>N=CH₂-</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td>C₆H₅N=CH=</td>
<td></td>
</tr>
<tr>
<td>119</td>
<td>or CH₂NH₂</td>
<td>390</td>
</tr>
<tr>
<td>121</td>
<td>N(CH₂)₂</td>
<td>290</td>
</tr>
<tr>
<td>29</td>
<td>CH₂=NH</td>
<td></td>
</tr>
<tr>
<td>93</td>
<td>NH₂</td>
<td>290, 400</td>
</tr>
<tr>
<td>66</td>
<td>C₆H₅N=CH=</td>
<td></td>
</tr>
<tr>
<td>195</td>
<td>N=CH=</td>
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<tr>
<td>207</td>
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</tr>
<tr>
<td>208</td>
<td>N=CH₂-</td>
<td>350, 450</td>
</tr>
</tbody>
</table>

II.1.

Scheme 2. (1) The linkages formed during the polymerisation of 15-Na. (2) Generation of aniline and unsaturated linkages by thermal degradation of Poly15-Na.

**Fig. 8.** The evolution profiles of some of the products involving naphthoxazine units or N-alkyne anilines. (Note: the intensities are normalized by a number factor as shown in the figure.)
The evolution of the major degradation product, aniline, occurred in a broad temperature range. The two maxima present in the single ion pyrograms of aniline and 66 Da fragment were at around 290 °C and at 400 °C. The low temperature evolutions of aniline can be associated with dissociative ionization of fragments involving aniline units such as loss of CH₂NH group from 121 Da fragment. Yet, the trends observed in the evolution profiles of aniline and other diagnostic fragment ions in the high temperature ranges were unique, and showed no resemblance to any other single ion evolution profile. These observations indicated that the main thermal decomposition process around 400 °C was the loss of aniline.

The very high yield of aniline throughout the pyrolysis indicates that recombination of –NCH₂ radicals has taken place yielding thermally less stable linkages involving β Hs as shown in Scheme 2(1). Loss of aniline then would yield naphthoxazines with unsaturated linkages that can further form a crosslinked structure with higher thermal stability as shown in Scheme 2(2). Aniline was also detected as the major decomposition product during the thermal degradation of polybenzoxazines [21].

However, if the polymerisation occurred only by recombination of N–CH₂ radicals generation of some fragments detected during the pyrolysis would not be likely. Evolution of 91 and 221 Da fragments following the same trends were detected over a broad temperature range but maximized at 450 °C. In general, presence of 91 Da fragment in the mass spectrum confirms alkyl substituted benzene ring (Fig. 8, Table 2). As decomposition of naphthalene ring was energetically unfavourable, the detection of 91 Da peak over a wide temperature range can be taken as a strong evidence for alkyl substitution to benzene ring of aniline. In fact, the bifunctional naphthoxazine monomer does not have a free ortho position as in the case of monofunctional benzoxazines. On the other hand, both of the para positions should be deactivated due to the presence of the other OH groups. Thus, polymerisation by the attack of –NCH₂ radicals directly to the naphthoxazine ring may be thought to be less likely compared to benzoxazines. The para and ortho positions of the benzene ring in aniline are also potentially reactive though to a lower extent compared to benzene ring of the phenols. Detection of ortho (or para) substituted anilines confirmed that the polymerisation took place by attack of –NCH₂ radicals to the benzene ring attached to the nitrogen (Scheme 3). In a recent GC–MS study on thermal and thermo-oxidative degradation of aromatic amine-based polybenzoxazines, besides the major degradation product, aniline, generation of p-aminotoluene (may be also o-aminotoluene, having almost identical mass spectrum) was detected [21]. In GC–MS, as thermal decomposition occurs in a close container outside the MS, secondary reactions cannot be avoided and only stable thermal decomposition products can be detected. Thus, detection of primary decomposition products such as alkyl or amine substituted aniline radicals was impossible. On the other hand, for the present study, the dissociative ionization of 221 Da fragment would also generate other low molecular weight fragments (such as the ones with 105 and 29 Da m/z value) involving aniline ring at low and/or moderate temperatures. Thus, the trends observed in their single ion pyrograms were in accordance with the assignments made. Furthermore, the absorption band emerged at around 1670 cm⁻¹ associated with C=NC stretching for the Schiff base at 200 °C was consistent with the mass spectral assignments (Fig. 3).

The evolution profiles of some of the products with m/z = 106, 221, 245, 259, 273, and 230 that can directly be attributed to

<table>
<thead>
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<th>m/z</th>
<th>Assignments</th>
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<tr>
<td>18</td>
<td>H₂O</td>
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<td>221</td>
<td>N=CH₂</td>
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<tr>
<td>91</td>
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<td>106</td>
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<td>273</td>
<td></td>
</tr>
<tr>
<td>330</td>
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</table>

Scheme 3. The linkages formed during the polymerisation of aromatic amine-based bifunctional naphthoxazines.

Table 2
Peaks present in the high temperature pyrolysis mass spectra and the proposed structures.
products involving naphthoxazine units or N-alkyne anilines are also included in Fig. 8 and related assignments are collected in Table 2. All products involving naphthoxazine units were undetectable in the temperature range 100–360 °C. Their presence below 100 °C was attributed to evolution of unreacted monomer and low molecular weight oligomers. The high temperature evolutions, maximizing at 450 °C, confirmed decomposition of a polymeric structure. Evolution of H2O also detected in this region confirming ortho substituted phenolic structure. Aniline evolution was decreased significantly in this region. However, N-alkyne anilines and methyl substituted N-alkyl anilines also showed a peak with a maximum at 450 °C indicating the higher stability of these linkages. Actually, if the benzene attached to the nitrogen reacted during polymerisation amount of dangling groups in polynaphthoxazines will be reduced which in turn may improve the thermal stability of the polymer.

In order to obtain a better understanding, pyrolysis mass spectrometry of cured (at 240 °C) naphthoxazine monomer prepared by using pentafluoroaniline instead of aniline was also studied. For this sample, pentafluoroaniline, the aniline analogue was the main degradation product. Single ion pyrograms of some characteristic products such as \( \text{C}_9\text{F}_3\text{N}(\text{CH}_2)_2 \) (\( m/z = 209 \text{ Da} \)), \( \text{C}_9\text{F}_3\text{NH}_2 \) (\( m/z = 183 \text{ Da} \)), \( \text{CF} = \text{CH} \) (\( m/z = 44 \text{ Da} \)), \( \text{C}_{10}\text{H}_4\text{OH}_2\text{CH} = \text{NH}_2 \) (\( m/z = 186 \text{ Da} \)), \( \text{HF} (m/z = 20 \text{ Da}) \), and \( \text{H}_2\text{O} (m/z = 18 \text{ Da}) \) are shown in Fig. 9. No peak that can be attributed to products due to attack of \( \text{CH}_2 \) radicals to benzene ring was detected in accordance with our expectations, as the presence of \( \text{F} \) atoms deactivates substitution to the benzene ring. The pyrolysis mass spectra mainly dominated with peaks due to the characteristic dissociative ionization pattern of pentafluoroaniline. HF and \( \text{H}_2\text{O} \) evolutions and presence of weak peaks characteristic to naphthoxazine units in the final stages of pyrolysis indicated presence of chains involving ortho substituted hydroxy naphthalene ring and pentafluoroaniline. Very high yield of pentafluoroaniline may be associated with polymerisation by coupling of \( \text{N}–\text{CH}_2 \) radicals generated by opening of the side chains. Evolution of products was detected in a narrower temperature range.

Thus, it can be concluded that pyrolysis mass spectrometry analyses of cured naphthoxazine samples showed strong evidence for polymerisation through the aniline units, either by coupling of the radicals generated by cleavage of the side rings or by substitution to benzene ring of aniline. Yet, although no indication for three-substituted naphthoxazine was detected, it is not possible totally to eliminate polymerisation by substitution to naphthalene ring.

5. Conclusion

In this study, we investigated the polymerisation and degradation mechanisms of an aromatic amine-based naphthoxazine monomer (15-Na) during curing by using direct pyrolysis mass spectrometry. It was observed that the weight loss of 15-Na starts below curing temperature and continues gradually as the temperature increases indicating that the monomer is subjected to both evaporation/degradation and polymerisation at the same time during curing process. Based on the pyrolysis mass spectrometry findings, polymerisation of 15-Na through the aniline units, either by coupling of the radicals generated by cleavage of the side rings or by substitution to benzene ring of aniline was proposed. It is also worth concluding that thermally crosslinked poly(naphthoxazine) (Poly15-Na) suffers from low thermal stability despite its high char yield (>60%), signifying that Poly15-Na may not be regarded as a very good candidate to be used as resins for composite preparation for the replacement of polybenzoxazines.

References