Thermal decomposition of 4,4′-diaminodiphenylsulphone

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Abstract

The thermal decomposition of 4,4′-diaminodiphenylsulphone (DDS) was studied by thermogravimetry, differential scanning calorimetry and thermal volatilisation analysis. Solid residues, high-boiling and gaseous products of degradation were collected at each step of thermal decomposition and analysed by infrared spectroscopy and gas chromatography/mass spectrometry.

On programmed heating at normal pressure, DDS starts to evaporate at 250°C. Thermal decomposition, which probably proceeds through homolytic scission of the S–C bond is simultaneously observed. The resulting sulphonyl radicals provoke polymerisation and cross-linking of the solid residue which undergoes a limited degradation at 350°C with elimination of heteroatoms N and S as volatile moieties. Above 400°C, the residue undergoes a complex charring process leading to an aromatic char typical of carbonised aromatic polymers.

Keywords: Charring; Epoxy hardener; Thermal degradation

1. Introduction

4,4′-Diaminodiphenylsulphone (DDS)
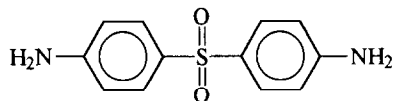
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is widely used as a hardener for high-performance epoxy resins in aerospace applications [1]. In addition to the required mechanical properties, these materials must show appropriate thermal and fire retardant performance. However, in spite of considerable practical interest, there is very little information in the literature concerning the thermal decomposition behaviour of epoxy resins cured by DDS [2].

We have carried out and reported here a mechanistic study of the thermal decomposition of DDS. These results make it easier to understand the mechanism of thermal degradation of DDS-cured epoxy resins, by isolating the thermal behaviour of DDS structures which are incorporated in the resin by curing.

2. Experimental

2.1. Materials

4,4'-Diaminodiphenylsulphone (DDS, HT 976) from Ciba-Geigy was used as received. The assignments of the major IR absorptions of DDS [3–5] (Fig. 1) are listed in Table 1. DDS shows four absorptions in the region of $\nu(NH_2)$ at 3500–3300 cm^{-1} which we attribute on the basis of an infrared spectrum of DDS carried out at the temperature of liquid nitrogen ($-196°C$). On cooling, the absorptions at 3397 and 3340 cm^{-1} increased their intensity and shifted to lower wavenumbers by 10–15 cm^{-1} which is typical of hydrogen-bonded amino groups [6]; the absorptions at 3454 and 3365 cm^{-1}, however, were little influenced by decreasing the temperature.

The absorptions at 1632 and 730 cm^{-1} shifted to higher wavenumbers on cooling, as expected for deformation of hydrogen-bonded groups [6], and were attributed to mixed $\nu(\Phi$, quadrant) and $\delta(NH_2)$, or to $\delta_{wag}(NH_2)$, respectively. As well as NH_2, the sulphone group is likely to participate in hydrogen bonding because the absorptions at 1143 and 1104 cm^{-1} attributed to SO_2 (Table 1) shifted to higher wavenumbers on cooling with liquid nitrogen [6].

2.2. Thermal analysis

The thermal decomposition of DDS was studied under nitrogen flow (60 cm^3 min^{-1}) by thermogravimetry and differential scanning calorimetry (DSC), using a Du Pont 2100 thermal analyser provided with a TGA 2950 high-resolution module. Thermogravimetric analyses were carried out either in normal mode (TG) or in high-resolution mode (HRTG, resolution factor $+5$) in which the resolution of overlapping processes is improved by decreasing the heating rate when the rate of weight loss, as monitored by derivative TG, tends to increase.

Thermal degradation under dynamic vacuum (10^{-3}–10^{-4} mm Hg) was carried out by thermal volatilisation analysis (TVA) [7]. In all cases the heating rate was 10°C min^{-1}.

Solid degradation products were collected during thermogravimetry at the end of each step of the thermal decomposition of DDS. High-boiling degradation products
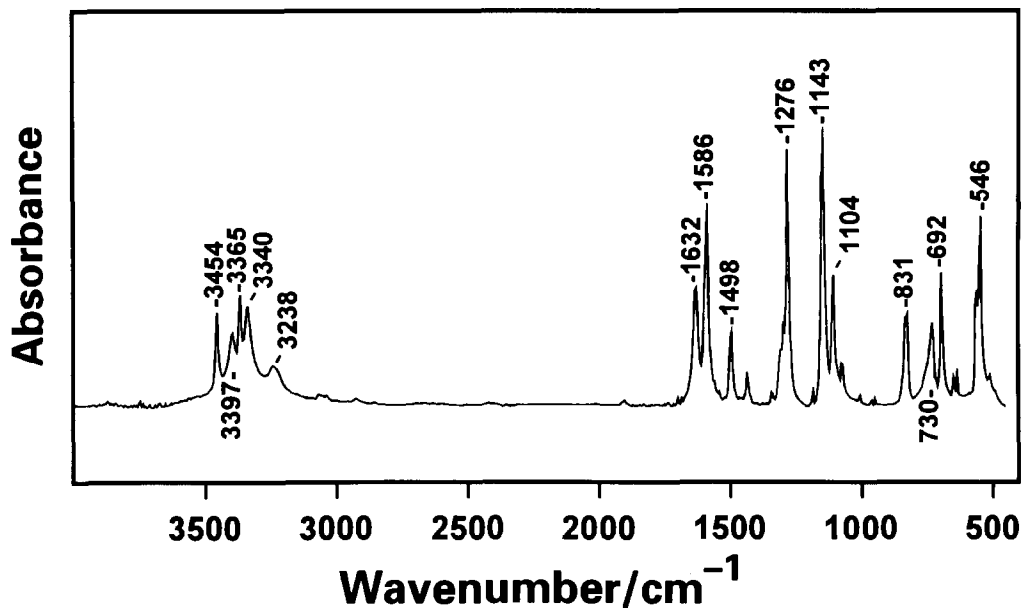
Fig. 1. FTIR spectrum of DDS. Pellet in KBr.

condensable at room temperature were collected either on the cold section of the glass envelope of the thermobalance emerging from the furnace or on the water-cooled upper part of the glass degradation tube in the TVA apparatus. Gases evolved on thermal decomposition were trapped by liquid nitrogen in the TVA apparatus. The identification of the degradation products was carried out either by infrared (Perkin-Elmer 2000 FT-IR) or by gas-chromatography/mass-spectrometry (Hewlett Packard 5970B).

3. Results

3.1. Thermogravimetry

The onset of weight loss of DDS in nitrogen occurs at 250°C (Fig. 2). Three steps of weight loss are observed in normal TG (Fig. 2, curve a): 55% of weight is lost at 250–340°C and 6% at 340–420°C. Above 420°C, the material loses weight at a low constant rate, reaching 4% weight loss at 600°C.

In high-resolution mode, the first main step of weight loss (which occurs in quasi-isothermal conditions) is larger (66%) and takes place in a narrower temperature interval (250–300°C, curve b) than in normal TG (curve a). The behaviour of DDS in the second and third steps of degradation is identical in terms of weight loss in TG (curve a) and HRTG (curve b), whereas the temperature of the second step is lower in

Table 1
Assignment of the infrared absorptions of DDS

Wavenumber/(cm^{-1})	Assignment	References
3454	$v_{as}(NH_2)$	This work
3397	$v_{as}(NH_2$, hydrogen bonded)	This work
3365	$v_s(NH_2)$	This work
3340	$v_s(NH_2$, hydrogen bonded)	This work
3238	$v(\Phi–H)$	[4]
1632	$v(\Phi$, quadrant) and $\delta(NH_2)$	[4, 6]
1586	$v(\Phi$, quadrant)	[3–6]
1498	$v(\Phi$, semicircle, para subst.)	[3–6]
1276	$v_{as}(S=O)$	[3, 4]
1143	$v_s(S=O)$	[3–5]
1104	$v(\Phi–S)$	[3]
831	$\delta_{wag}(\Phi–H$, para)	[3–6]
730	$\delta_{wag}(NH_2)$	[3, 4, 6]
692	$v_s(\Phi–S–\Phi)$	[3, 4]
546	$\delta_{scissors}(SO_2)$	[4]

HRTG (320–370°C). Thus, DDS leaves a 35% residue stable at 600°C in TG and 24% in HRTG.

3.2. Differential scanning calorimetry

Three endothermic effects with minima at 77, 177 and 355°C were detected on the DSC curve of DDS (Fig. 3, curve a). These effects were previously attributed to a solid-to-solid crystal transition, melting and thermal decomposition of DDS respectively [8]. An exothermic peak (maximum at 358°C, curves a and b) overlaps the endothermic peak at the highest temperature; this was not commented on in Ref. [8].

3.3. Products of degradation

3.3.1. Solid residue

Fig. 4 shows the infrared spectra of DDS (spectrum a) and of the solid residues at the end of each step of weight loss (spectra b–d). All the absorptions of DDS are present in the spectrum of the residue of the first step of degradation, although they are somewhat shifted and there is some change in intensity (Fig. 4, spectra a and b). For example, the absorptions due to NH bonds are strongly reduced in spectrum b; this is most clear in the stretching region (3500–3300 cm^{-1}). A slight decrease in the SO_2 absorptions (1143–1141, 1282–1276, 546 cm^{-1}) is observed as well, while new absorptions arise in spectrum b at 1450, 1302, 1224, 1186, 1030, 857 and 748 cm^{-1}.

The disappearance of the absorptions of the NH groups at 3460–3454, 3397, 3369–3365, 3340–3337, 1632–1624 and 730 cm^{-1} and of the absorptions of the SO_2
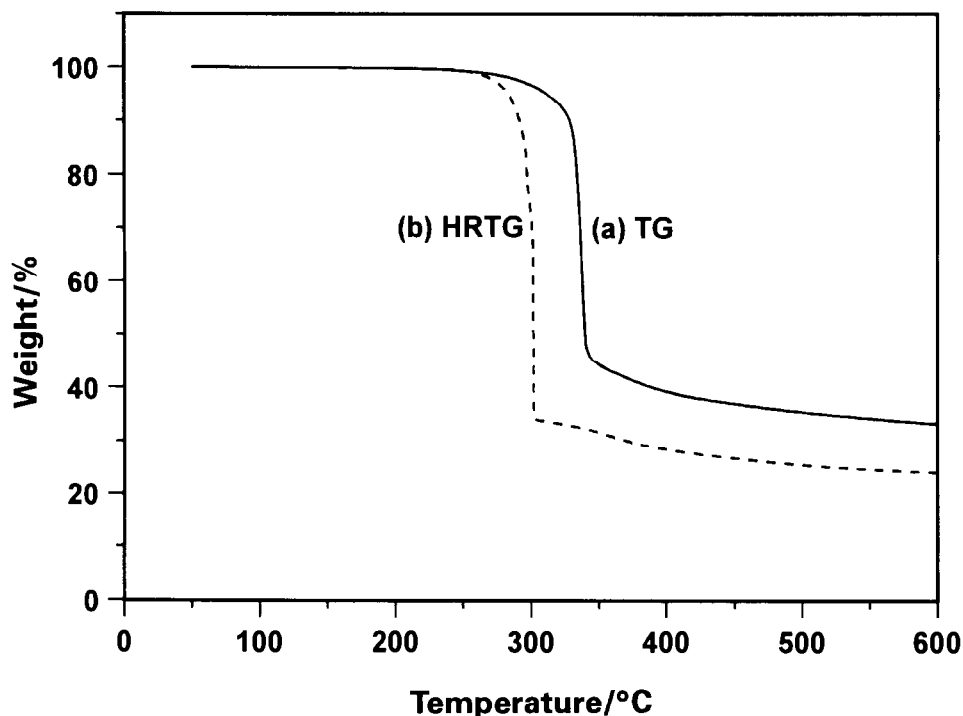
Fig. 2. Thermogravimetry curves of DDS: (a) TG (normal mode) and (b) HRTG (high-resolution mode, resolution factor $+5$). Heating rate, 10°C min^{-1}; nitrogen flow, 60 cm^3 min^{-1}.

groups, is the most evident feature in the infrared spectrum of the residue of the second step of degradation (spectrum c).

The residue obtained at 600°C shows the infrared absorption pattern typical of carbonised polymers with a high content of aromatics [9]. In particular, the absorption at 1109–1104 cm^{-1} of the spectra a–c, which is due to the Φ–S bond (Table 1), is absent from spectrum d.

3.3.2. Volatile products

High-boiling products evolving from DDS in the first step of weight loss are condensed in two separate rings on the glass envelope of the thermobalance. The major high-boiling product which was collected in the ring closer to the furnace is evaporated DDS, whereas the minor one is aniline. Under vacuum in TVA experiments, DDS evaporates completely without decomposition.

The volatile products of the further steps of degradation were studied by TVA of the residue obtained by heating DDS in nitrogen at 310°C to completion of the first step. The TVA curve of Fig. 5 shows evolution of gases in two overlapping steps with maxima at 362 and 490°C which correspond to the second and third step of degrada-
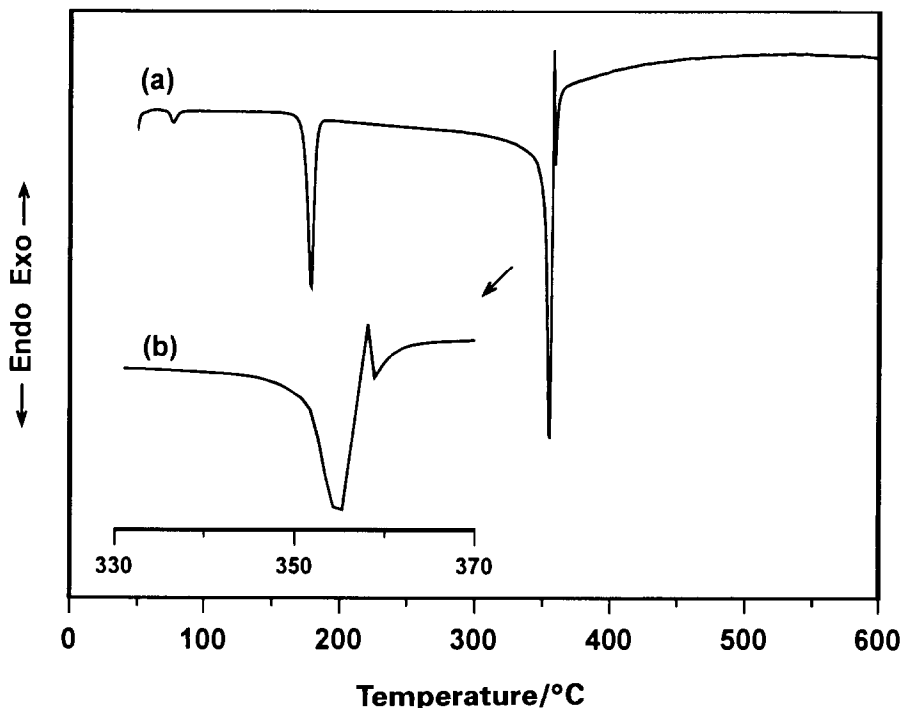
Fig. 3. DSC curve of DDS. Insert (b) has an enlarged temperature scale. Heating rate, $10°C$ min^{-1}; nitrogen flow, 60 cm^3 min^{-1}.

tion in thermogravimetry. The evolution of non-condensable gases at high temperature is negligible.

The degradation steps were separated by first heating the material in the TVA apparatus at $10°C$ min^{-1} to $340°C$ and keeping it at this temperature to the end of gas evolution. The procedure was repeated by heating the residue to $450°C$.

The high-boiling fraction is the major component of the volatiles evolved in the second step of degradation of DDS under vacuum. Its infrared spectrum (Fig. 4, spectrum e) shows typical absorptions associated with NH_4^+ (1400, 3128 cm^{-1}) and an absorption pattern at 1300–900 cm^{-1} together with an absorption at 675 cm^{-1} which are characteristic of sulphonic acid anions $(R–SO_3^-)$ [4]. The simultaneous presence of aromatic absorptions at 1606 and 1496 cm^{-1} suggests that an aromatic ammonium sulphonate is the major high-boiling product evolved in the second step of degradation of DDS. The absorption at 2576 cm^{-1} which can be attributed to strongly hydrogen-bonded acidic OH groups [4], could indicate that free sulphonic acid is present in the high-boiling fraction together with the ammonium salt.

Aniline, which is evolved in the first step of degradation, is also evolved throughout the second and third steps of the degradation of DDS in which benzene is also evolved. Moreover, in the third step, CS_2 is evolved together with traces of $(SCN)_2$, HCN, acetonitrile and unsaturated hydrocarbons.
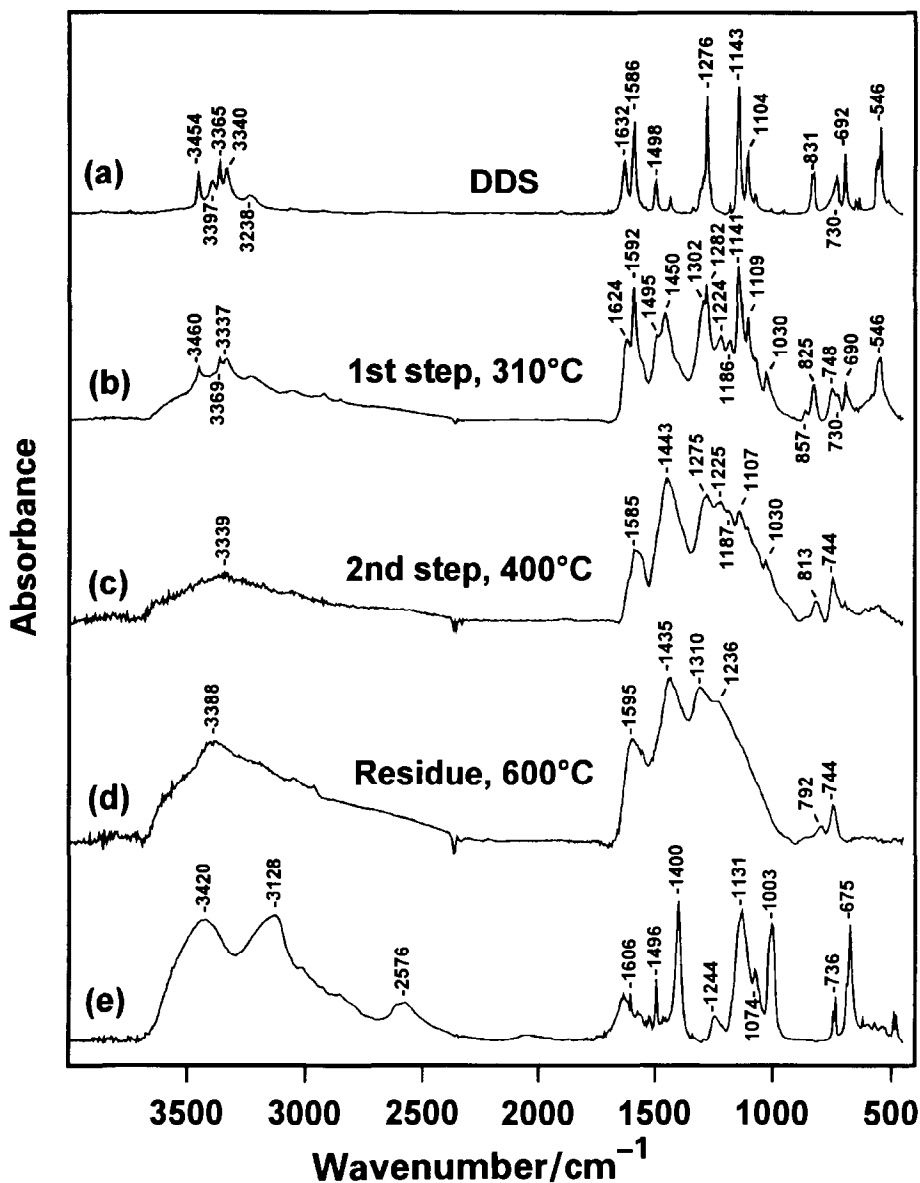
Fig. 4. FTIR spectra of: (a) DDS; and of residues collected in HRTG experiments at: (b) 310°C, 66% weight loss; (c) 400°C, 72% weight loss; (d) 600°C, 76% weight loss and (e) high-boiling products collected in TVA experiments at 400°C. Pellets in KBr.

4. Mechanism of degradation

These results show that on heating DDS, a competition takes place between evaporation and thermal degradation which gives volatile products and a relatively
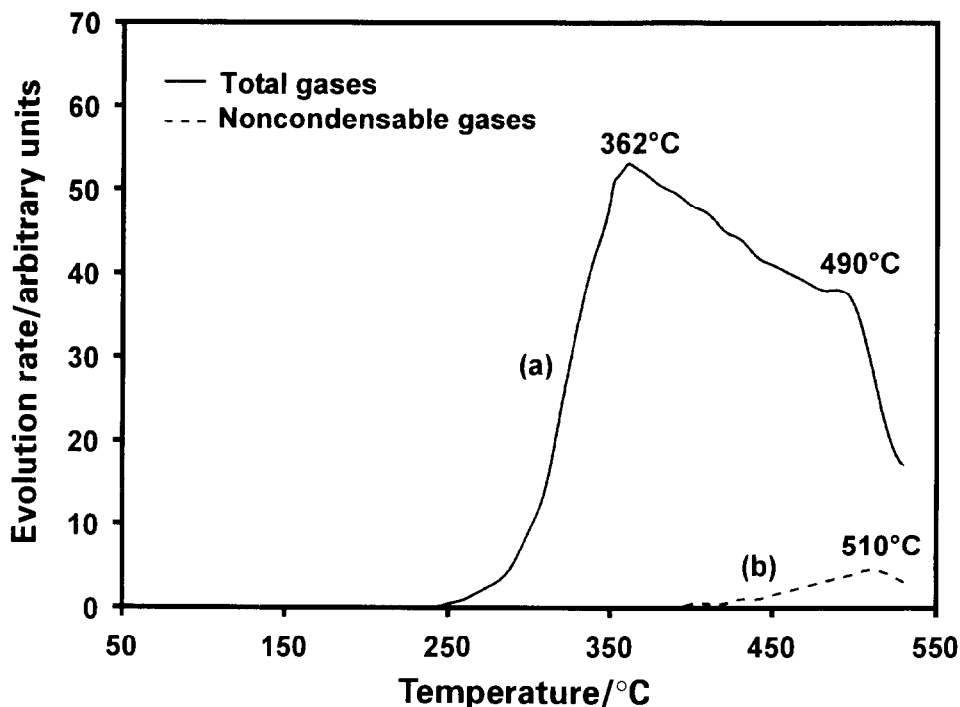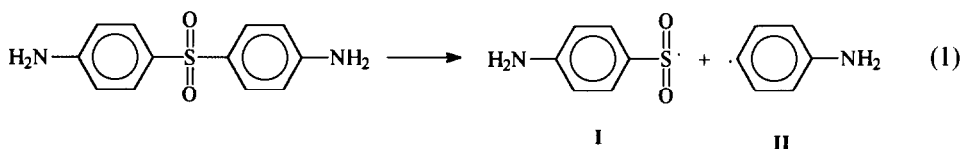
Fig. 5. TVA curves of solid residue prepared in HRTG at 310°C: (a) total gases and (b) gases non-condensable at −196°C. Heating rate, 10°C min^{-1}; dynamic vacuum 10^{-3}–10^{-4} mm Hg.

stable residue. Evaporation dominates under vacuum and occurs at a larger extent on quasi-isothermal conditions in HRTG as compared with TG (Fig. 2).

The Φ–S bond was shown to be the weakest bond in diphenylsulphone structures [10–14]. Reaction (1) should therefore take place in competition with evaporation when DDS is heated with programmed raising of temperature

$$H_2N-\bigcirc-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\bigcirc-NH_2 \longrightarrow H_2N-\bigcirc-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\cdot + \cdot\bigcirc-NH_2 \qquad (1)$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad I \qquad\qquad\qquad II$$

Literature data show that phenylsulphonyl radicals from thermal decomposition of polyarylsuphones [5, 10, 14, 15] or radiolytic decomposition of diarylsulphones [16] may completely eliminate SO_2. However, it was also found that thermal degradation [12] or photodegradation [13, 17] of polyarylsulphones may give sulphide moieties as well as SO_2. This led to the hypothesis that partial disproportionation of phenyl-sulphonyl radicals could take place, for which no mechanism, however, was proposed.

In our case there was no detectable elimination of SO_2 on thermal degradation of DDS. Therefore, we suggest that the following disproportionation reaction proposed in the literature for arylsulphonyl radicals resulting from interaction of benzyol peroxide with SO_2 [18] or from photolyses of diaryl disulphones [19] in solution, may take place in the thermal degradation of DDS
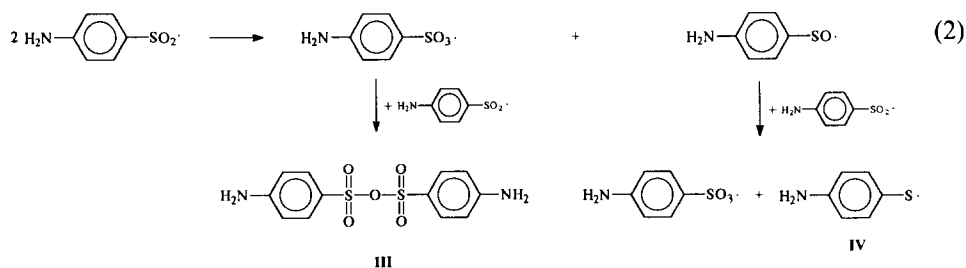

This mechanism could account for formation of the residue and of new absorptions in its infrared spectrum.

Indeed, p-aminophenylsulphonic anhydride (III) reacts very easily with amino groups [20] forming sulphamide (V) and sulphonate (VI)
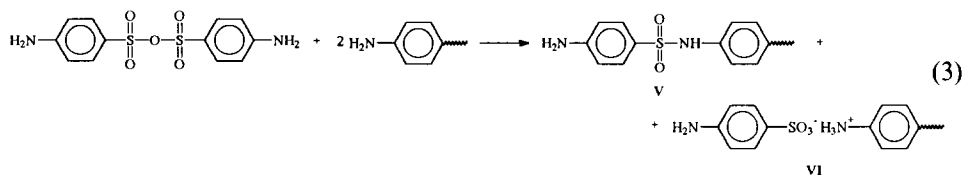
Reaction (3) leads to an increase in the molecular weight of DDS and its repetition would give rise to a polymer.

Furthermore, the sulphonyl radical (I) which is reported to be too stable to abstract hydrogen from aromatic rings [21] such as those of DDS or to do it very slowly [22], could give an addition reaction [23]
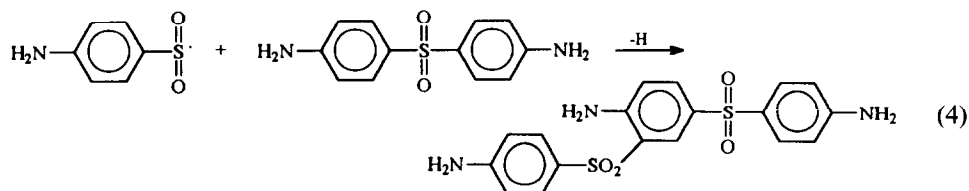
The repetition of this reaction gives a thermally stable substituted polysulphone. Furthermore, the thiyl radicals (IV) might also propagate polymerisation and cross-linking through addition to the aromatic ring with formation of a polysulphide network [5, 24]. Thus, polymerisation through reactions (2) and (4) and of radicals (IV)
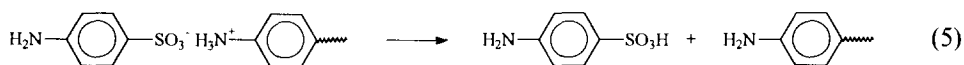
can explain the formation of the residue from the thermal degradation of DDS which competes with its evaporation on heating.

The exotherm overlapping the evaporation–decomposition endotherm in DSC (Fig. 3), could be due to the polymerisation processes. The structure of the poly-sulphone obtained in reaction (4) is in agreement with the fact that the major functional infrared absorptions of the residue of DDS degradation are those of DDS, with slight shifts (Fig. 4, spectrum b). The simultaneous occurrence of reactions (3), (4) and of thiyl radical polymerisation would lead to a copolymer containing sulphide, sulphamide and sulphonate groups as well as SO_2. Indeed, the new absorptions at 1186 and $1030\,cm^{-1}$, in the region of SO_2 stretching in the infrared spectrum of the residue at 310°C (Fig. 4, spectrum b), might be attributed to $NH–SO_2–$ of V and/or v_{as} and v_s of $–SO_3^-$ of VI, whereas the polysulphide structures cannot be detected by infrared because of overlapping with the absorptions of sulphone groups. The new absorptions found in the spectrum of the residue at 1450, 1224, 857 and $748\,cm^{-1}$ could be attributed to aromatic substitution in the polymeric residue which is different from DDS.
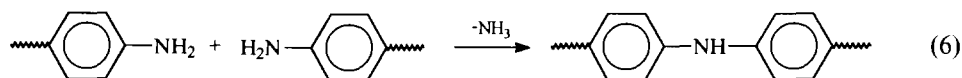
The aminophenyl radical formed in reaction (1) is likely to abstract hydrogen atoms to give aniline found in the first step of degradation of DDS. Elimination of aniline can account for the reduction in NH infrared absorptions in the infrared spectrum of the residue (Fig. 4, spectrum b).

The polymeric material formed in the first step of degradation of DDS (310°C) undergoes a limited further degradation on heating at higher temperatures. From 340°C (second step, weight loss 6%), the disappearance of NH_2 and SO_2 groups (Fig. 4, spectrum c) with evolution of aromatic sulphonic acid or ammonium salt (spectrum e) are the major effects of heating the polymeric residue.

This behaviour could be explained by assuming that the sulphone groups are further modified on heating giving, at least partially, volatile products. For example, sulphon-ate structures VI might decompose on heating, liberating sulphonic acid which volatilises

$$H_2N-\!\!\!\bigcirc\!\!\!-SO_3^-\ H_3N^+\!\!\!-\!\!\!\bigcirc\!\!\!-\!\!\!\text{\tiny www} \longrightarrow H_2N-\!\!\!\bigcirc\!\!\!-SO_3H\ +\ H_2N-\!\!\!\bigcirc\!\!\!-\!\!\!\text{\tiny www} \qquad (5)$$

Ammonium sulphonate could be formed if ammonia were evolved by condensation of NH_2 groups

$$\text{\tiny www}\!\!\!-\!\!\!\bigcirc\!\!\!-NH_2\ +\ H_2N-\!\!\!\bigcirc\!\!\!-\!\!\!\text{\tiny www} \xrightarrow{-NH_3} \text{\tiny www}\!\!\!-\!\!\!\bigcirc\!\!\!-NH-\!\!\!\bigcirc\!\!\!-\!\!\!\text{\tiny www} \qquad (6)$$

which reacted with evolving sulphonic acid. Reaction (6) could also take place at lower temperatures and contribute to the polymerisation of DDS, in agreement with the decrease of NH_2 absorptions in spectrum b of Fig. 4. However, our experi-

mental setup did not allow the detection of ammonia evolution in the first step of DDS degradation.

Aniline and benzene found in the second and third step of degradation of DDS derive from partial fragmentation of polymerised DDS to p-aminophenyl and phenyl radicals followed by hydrogen abstraction. Above 400°C (third step of degradation), the residue undergoes a complex charring process with elimination of residual heteroatoms S and N, to reach the typical aromatic structure of chars from pyrolised polymers [9].

5. Conclusions

On heating above 250°C, DDS undergoes competition between evaporation and homolytic scission of the carbon–sulphone bond into sulphonyl and p-aminophenyl radicals. The sulphonyl radical leads to a stable polymeric residue either through addition reactions or disproportionation followed by reactions of the resulting species. The p-aminophenyl radical abstracts hydrogen and volatilises as aniline.

The polymerised residue obtained from DDS decomposition partially degrades above 340°C with elimination of volatile species containing the heteroatoms S and N. Above 400°C, a charring process takes place with elimination of residual heteroatoms.

These results will be useful to predict the expected thermal behaviour of DDS structures in DDS-cured epoxy resins in which their evaporation is prevented by incorporation in the resin network. In particular, the contribution of DDS structures to the charring process, which is of paramount importance in fire retardance, can be speculated on the basis of this study and will be verified in a forthcoming paper.

Acknowledgement

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