

# Thermal decomposition of fire retardant brominated epoxy resins

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## Abstract

Brominated epoxy resin (BER) containing 20% Br has been prepared by curing a mixture of diglycidylethers of bisphenol A (DGBBA)/tetrabromobisphenol A (DGEBTBA) and 4,4'-diaminodiphenylsulphone (DDS). Its thermal stability has been studied by high resolution thermogravimetry and IR spectroscopy. Programmed heating condition using inert atmosphere has been applied to collect gaseous and high boiling product, which have been identified by means of gas chromatography–mass spectrometry (GC–MS). The mechanism of the thermal decomposition of the resin is discussed. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Thermal decomposition; Brominated epoxy resin (BER); Gas chromatography–mass spectrometry (GC–MS)

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## 1. Introduction

Diglycidylether of bisphenol A (DGEBA, (I)) is an epoxy monomer widely used for preparation of resins for advanced technologies. The fire risk of the epoxy resins obtained by copolymerization with traditional curing agent 4,4'-diaminodiphenyl sulfone (DDS, (II)) is a major drawback of these materials.

In the early 1980s halogenated fire retardants were applied to decrease the flammability of polymeric materials. As far as epoxy resins concern, diglycidylether

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of bis(3,3',5,5'-tetrabromophenol) A (DGEBTBA, (III)) was used as comonomer with DGEBA to obtain fire retardant materials. Indeed, aromatic brominated structures turned out to be very effective fire retardants and epoxies based on DGEBA and DGEBTBA were widely used in manufacturing printed circuit boards.

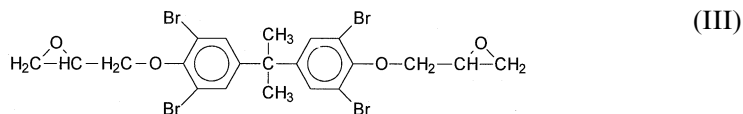
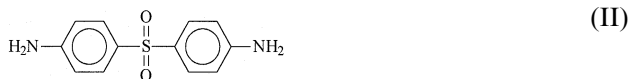
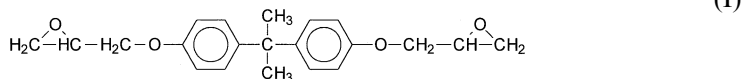
Later on it was recognized that bromine (as well as chlorine) containing structures could produce corrosive and obscuring smoke and might give supertoxic halogenated dibenzodioxines and dibenzofurans when burned. In this respect, environmentally friendly fire retardant systems are currently being developed to substitute halogen based systems.

Today many polymer wastes including epoxy resins containing brominated aromatics are collected. Thermal treatment of these wastes is one of the approaches of recycling. In this respect, a detailed knowledge of the mechanism of thermal degradation of polymer materials fire retarded by polybrominated aromatics, which is a main goal of this paper, is of great importance. Reportedly [1,2] DGEBTBA and brominated epoxy resin (BER, (IV)) are less stable at high temperatures than the non-brominated. Yan and Paczkowsky [2] studied the thermolysis of brominated epoxy FR-4 laminates cured by dicyandiamide. By means of FT-IR analysis of evolved gases they showed that in air, between 300 and 340 °C, CO<sub>2</sub>, H<sub>2</sub>O, HBr and several brominated and unbrominated phenols were released. Nakao et al. [3] investigated degradation of BER in air using gas chromatography–mass spectrometry (GC–MS). The main gaseous thermolysis products were found to be methyl bromide and other Br-complexes, acetaldehyde and other aldehydes, methanol and other alcohols, methyl formate and esters. Amines, silicones [3], copper oxides [4] were found significantly to accelerate the thermal decomposition of BER. Creasy [5] applied pyrolysis Fourier transform mass spectrometry to identify BER decomposition products.

## 2. Experimental

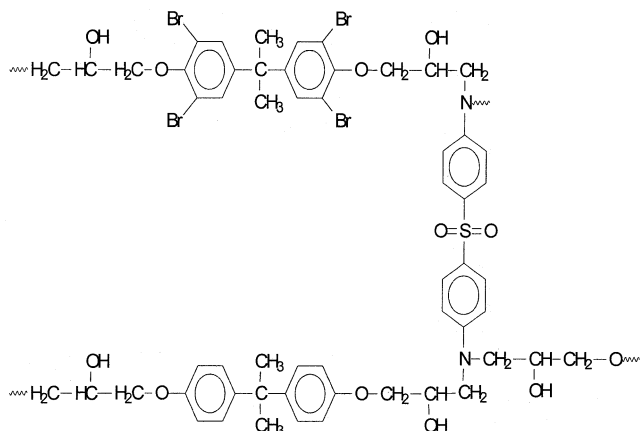
### 2.1. Materials

Commercial DGEBA ((I), Epicote 828EL, Shell Chemie) and DGEBTBA ((III), Shell Chemie) were used as received as epoxy monomers.



The mixture DGEBA/DGEBTBA was cured with 85% of stoichiometric amount of DDS ((II), HT 976, Ciba Geigy) under air in an oven heated for 1 h at 160 °C and for 1 h at 180 °C. The obtained epoxy resin (BER) contained 20% of bromine. Because of the deficient stoichiometry, mainly tertiary amine groups are present in the final network:

(IV)



## 2.2. Techniques

The thermal decomposition was studied at a heating rate of 10 °C min<sup>-1</sup> under nitrogen flow by thermogravimetry using the TGA 2950 Du Pont system either in the normal mode (TG) or in the high resolution mode (HRTG; resolution factor + 5).

Solid residues were collected at different steps of thermal decomposition in HRTG experiments and analyzed by FTIR (Perkin Elmer 2000).

To collect high boiling degradation products (HBP), degradation was carried out in inert atmosphere in a tube vertically placed in the oven. The bottom part of the tube was heated up at 10 °C min<sup>-1</sup> to 300 °C and held at this temperature for 15 min, whereas the upper part was cooled by running water. The gas flow from the tube was directed into a cell where volatile products were trapped at liquid nitrogen temperature and analyzed successively by GC–MS (HP5890/5970). HBP products collected on the tube wall were analyzed by IR. Their extract from acetone was analyzed by GC–MS using HP-5 30-m column and the following heating program: 70 °C (2 min), 10 °C min<sup>-1</sup> to 280 °C, 280 °C (10–20 min). MS identification was carried out using Wiley and NBS libraries. When very high score values (> 90) were obtained, identification was considered to be correct.

However, most of the brominated compounds were not included in the libraries. In this case they were identified on the basis of both the molecular ion *m/e* value and of the ion decomposition pattern constructed for the best fit with the mass spectrum [6]. In few cases, where standard were available, identification was

confirmed by retention time of GC chromatogram. However, the retention time of the compounds for which standard were not available, were plausible with the physical properties of the proposed structures.

### 3. Results

#### 3.1. Thermal analysis

Fig. 1 shows HRTG data obtained for the decomposition of BER under nitrogen. The epoxy resin starts to decompose at 295 °C in two major steps with maximum rate at 297 and 336 °C followed by a slow weight loss in the temperature region 360–600 °C. In the first step, which takes place in a very narrow range of temperature, BER loses 32% of its weight. In the second step, BER undergoes about 30% of weight loss. At 600 °C, 25% of solid residue is left.

Only two steps of weight loss are recognisable in the normal TG of the sample (Fig. 2). Owing to the lower resolution ability of this heating program the first two steps of HRTG are here overlapped.

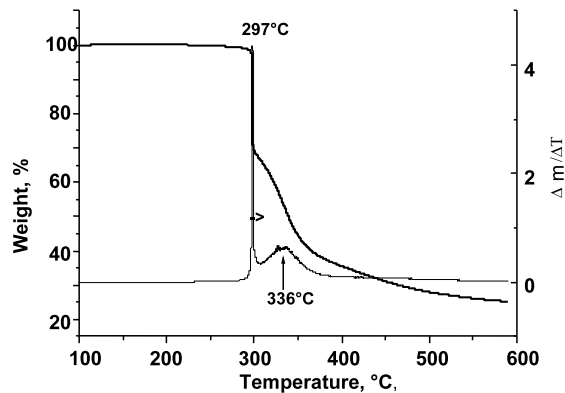


Fig. 1. HRTG analysis of the brominated epoxy resin (BER) in inert gas flow.

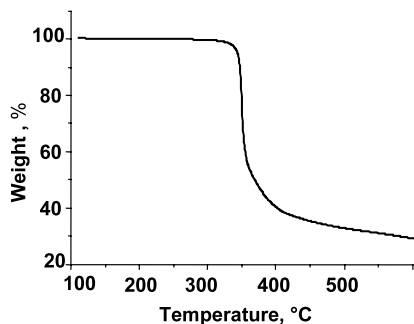


Fig. 2. TG analysis of BER in inert gas flow. Heating rate, 10 °C min<sup>-1</sup>.

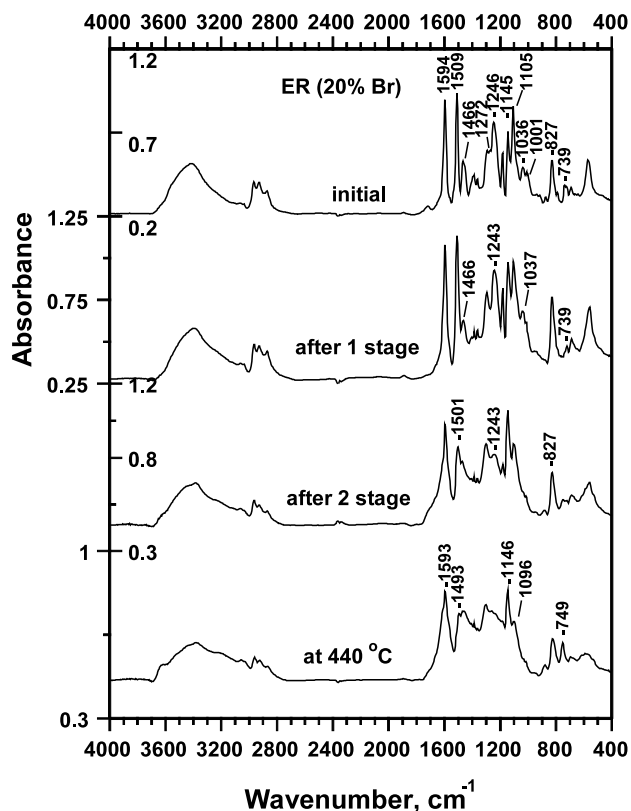


Fig. 3. Infrared spectra of the BER and solid residues obtained on heating to different temperatures in HRTG under nitrogen. Pellets in KBr.

### 3.2. Products of thermal degradation

Assignments of the IR spectrum of the initial epoxy resin (Fig. 3) reported in Table 1 are based on literature and on IR of individual components.

The intense bands at 1594, 1145, 1105 and 739  $\text{cm}^{-1}$  belong to the hardener DDS; those at 1509, 1246, 1036 and 827  $\text{cm}^{-1}$  are due to the unbrominated epoxy resin, whereas bands at 1466, 1272, 1001 and 739  $\text{cm}^{-1}$  are associated with the BER. The absorption of secondary alcohol formed when the epoxy ring is opened by the amine falls in the same range of C(phenyl)–S absorption of DDS (1105–1070  $\text{cm}^{-1}$ ) and can only be revealed by a careful comparison of the relative intensity of 1145 and 1105  $\text{cm}^{-1}$  bands in BER and in pure DDS [7]. The weak absorption of the C(phenyl)–Br bond in the region 1100–1000  $\text{cm}^{-1}$  is covered by strong absorption of DDS and of secondary alcohols.

As infrared shows (Fig. 3), after the first stage of decomposition (32% of weight loss), bands at 1466, 1272, 1001, 739  $\text{cm}^{-1}$  decrease. This indicates decomposition of BER, namely the splitting of the O–CH<sub>2</sub> bonds and changes concerning the

brominated aromatic ring. The decrease of the 1105 and 3500  $\text{cm}^{-1}$  bands also occurs, which is due to dehydration of secondary alcohols.

Further heating, up to the end of the second step of weight loss (360 °C), decreases the intensity of bands at 1509, 1243, 1037, 827  $\text{cm}^{-1}$ . This means that the decomposition of the unbrominated epoxy resin occurs. The spectrum also shows further decrease of intensity of OH and of  $\text{CH}_2\text{-O}$  stretching (at 3500–3400 and 1105–1070  $\text{cm}^{-1}$ , respectively) and the appearance of a shoulder at 1640–1660  $\text{cm}^{-1}$  due to absorption of  $\text{C}=\text{C}$  double bonds.

At 440 °C, the hardener DDS is still detected on absorption at 1594, 1276 and 1146  $\text{cm}^{-1}$ . New absorption at 749  $\text{cm}^{-1}$  could be attributed to NH bonds created as a result of the  $\text{C-N}$  bond scission followed by H abstraction.

Acetone soluble fraction of high boiling products (HBP) evolved in the degradation process of BER consists of many compounds as shown by the gas chromatogram of Fig. 4. MS identification of the main peaks is presented in Table 2.

The major products from the thermal decomposition of the brominated part of the epoxy resin are mono- and di-brominated phenols (products 3, 11, 15, 20, 26 and 30 in Table 2) and aromatic/aliphatic ethers containing one or two bromine atoms on the aliphatic chain (products 18 and 25 in Table 2). This indicates that the cleavage of both the  $\text{C}(\text{phenyl})\text{-Br}$ ,  $\text{C}(\text{phenyl})\text{-C}$ ,  $\text{N-CH}_2$  and  $\text{O-CH}_2$  bonds takes place. This last fact, in particular, is in agreement with IR spectroscopic finding on solid residue (Fig. 3, first stage residue).

Table 1  
Assignments and attribution of IR spectra of BER

Absorption ( $\text{cm}^{-1}$ )	Assignment	Origin
3500–3400	$\nu$ O–H	Opening of epoxy ring
1594	$\nu$ Aromatic ring	DDS
1509	$\nu$ Aromatic ring	DGEBA
1466	$\nu$ Aromatic ring	DGEBTBA
{ 1276 1272	$\nu_s$ S=O	DDS
	$\nu$ $\Phi$ -O	DGEBTBA
1246	$\nu$ $\Phi$ -O	DGEBA
1145	$\nu_{as}$ S=O	DDS
{ 1105 1070 1066 (w)	$\nu$ $\Phi$ -S	DDS
	$\nu$ $\text{CC-O}$	Opening of epoxy ring
	$\nu$ $\Phi$ -Br	DGEBTBA
1036	$\nu$ $\Phi\text{O-C}$	DGEBA
1001	$\nu$ $\Phi\text{O-C}$	DGEBTBA
835–825	$\delta$ $\Phi$ -H <i>p</i> -substitution	DGEBA, DDS
739	$\delta$ $\Phi$ -H	DGEBTBA

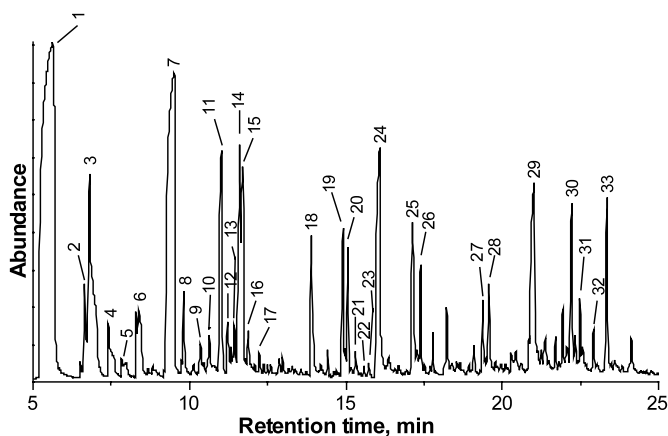


Fig. 4. Gas chromatogram of HBP products of the thermal decomposition of BER obtained on heating at  $10\text{ }^{\circ}\text{C min}^{-1}$  to  $300\text{ }^{\circ}\text{C}$  in inert atmosphere. Assignments of numbered peaks in Table 2.

The main products of the thermal decomposition of the unbrominated parts of the epoxy resin are substituted phenols and aromatic/aliphatic ethers (products 1, 4, 7, 24 and 29 in Table 2) indicating a favored splitting of the O–CH<sub>2</sub>, C(phenyl)–C, C–N bonds.

Sulphur (S<sub>8</sub>) was also found as a condensable product of decomposition in the tube for collecting gases, which implies that a reduction reaction takes place.

The MS identification of HBP reveals no N-containing products, possibly because their concentration was under detection level or because they accumulate in the solid residue.

The gas chromatogram of the gases of the thermal decomposition of BER is shown in Fig. 5 (see also Table 3). While only trace amount of HBr was found, the main products containing bromine are methyl, ethyl and propyl bromides and propilenyl bromide. The main non-brominated products are acetone, propene and water, in agreement with our previously published data [8].

## 4. Discussion

### 4.1. Mechanism of degradation

According to the experimental evidence and literature [9], the first degradation process concerns evolution of water and formation of unsaturated structures V, VI. These structures are unstable at the temperature at which they are formed and, therefore, degradation proceeds by scission of the weak allylic bonds in (V)(VI) ( $208\text{ kJ mol}^{-1}$ ) [10].

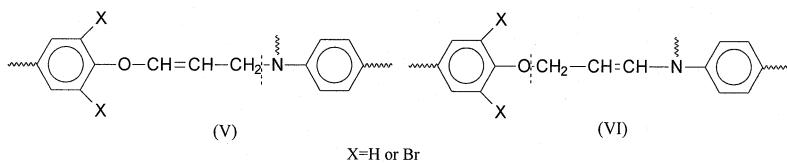


Table 2  
HBP of thermolysis of BER (20% Br)

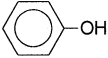
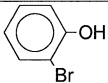
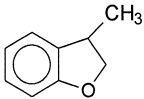
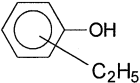
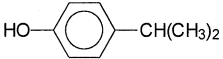
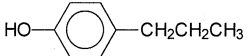
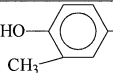
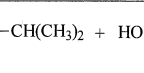
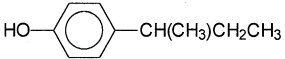
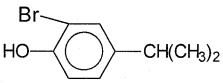
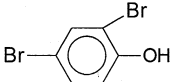
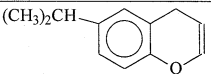
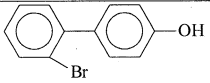
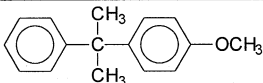
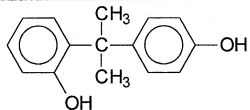
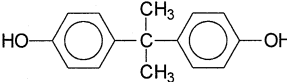
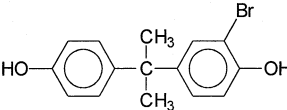
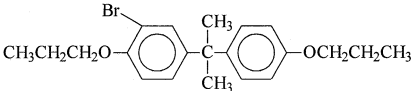
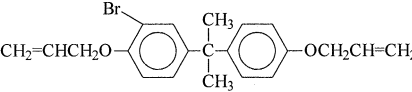
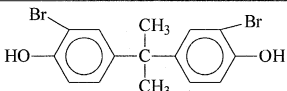
Peak n°	Relative amount	R <sub>t</sub> , min	Compound	Molecular mass
1 <sup>*)</sup>	XXX	5.24		94
2 <sup>*)</sup>	XX	6.66	Br CH <sub>2</sub> -CH(OH)CH <sub>2</sub> Br	218
3 <sup>*)</sup>	XXX	6.81		173
4 <sup>*)</sup>	XX	7.41		132
5 <sup>*)</sup>	X	7.84		122
6 <sup>*)</sup>	XX	8.30		
7 <sup>*)</sup>	XXX	9.29		136
8 <sup>*)</sup>	XX	9.82		136
9 <sup>*)</sup>	X	10.36	 + 	150, 173
10 <sup>*)</sup>	X	10.64		150
11	XXX	11.00		215
12 <sup>*)</sup>	X	11.21		252
13	X	11.44		174



Table 2 (Continued)

14 <sup>a)</sup>	XX	11.62		150
15 <sup>a)</sup>	XX	11.71		252
16	X	11.88		164
17	traces	12.23		213
18	XXX	13.91		231
19	XXX	14.91		192
20	XXX	15.06		294
21	traces	15.31		253
22	traces	15.86		255
23	traces	15.72		292
24 <sup>a)</sup>	XXX	16.06		170
25	XXX	17.12		273

Table 2 (Continued)

26	XXX	17.40		249
27	XX	19.37		226
28 <sup>*)</sup>	XX	19.57		228
29 <sup>*)</sup>	XXX	21.01		228
30	XXX	22.22		307
31	XX	22.49		349
32	X	22.92		345
33	XXX	23.34		386

<sup>1</sup> \* ) Identification by Wiley or NBS electronic libraries.

Further H abstraction leads to secondary amines and vinyl ethers (from (V)) or phenols and enamines (from (VI)). Bisphenol A (29/Table 2) and brominated bisphenol A are formed when this sequence of reactions takes place on both sides of the same monomeric structure. Mechanism of propene (2/Table 3) formation is

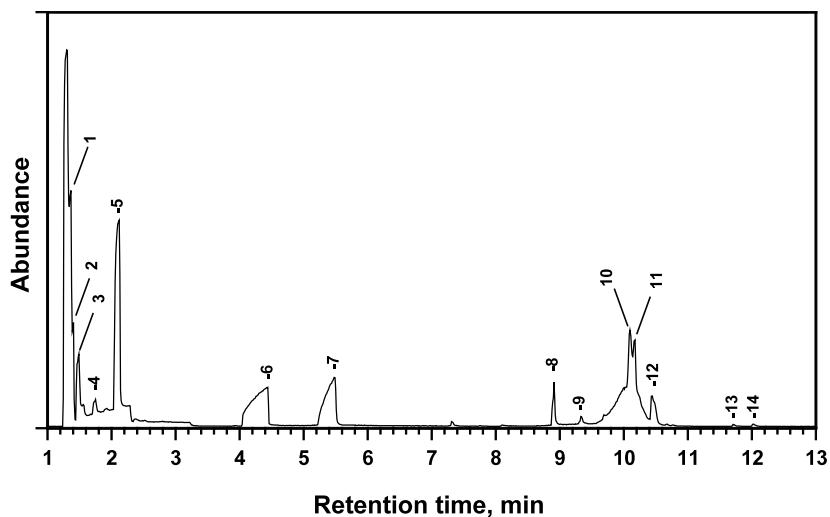


Fig. 5. Gas chromatogram of volatile products of the thermal decomposition of BER obtained on heating at  $10\text{ }^{\circ}\text{C min}^{-1}$  to  $300\text{ }^{\circ}\text{C}$  in inert atmosphere. Assignments of numbered peaks in Table 3.

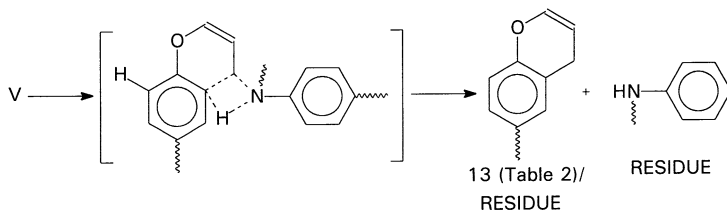
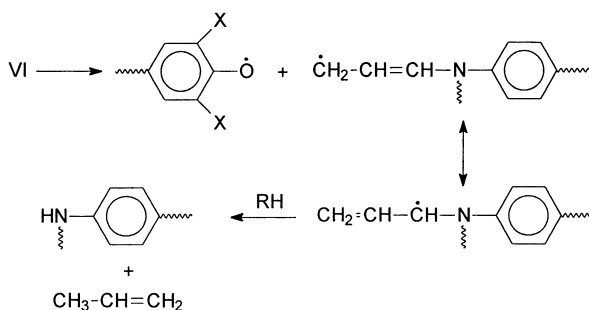
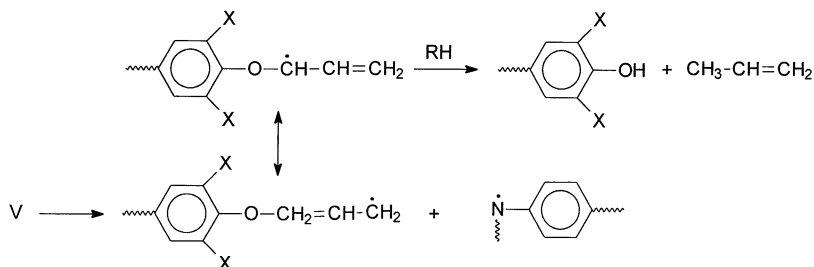
Table 3  
Gases of thermolysis of BER (20% Br)

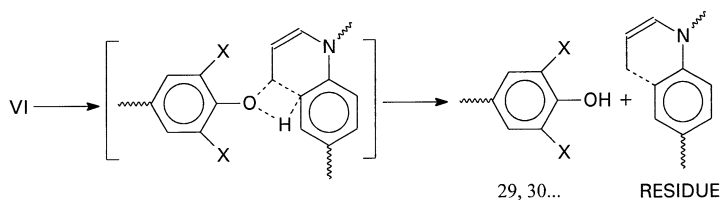
Peak number	Relative amount	Compound	Molecular mass
1	XX	$\text{H}_2\text{S}$	34
2	XX	$\text{CH}_3\text{CH}=\text{CH}_2$	42
3	XX	$\text{SO}_2$	64
4	X	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_3$	56
5	XXX	$\text{CH}_3\text{Br}$	95
6	XX	$\text{CH}_3(\text{C}=\text{O})\text{CH}_3$	58
7	XX	$\text{CH}_3\text{CH}_2\text{Br}$	109
8	X	$\text{CH}_3\text{CH}(\text{Br})\text{CH}_3$	123
9	X	$\text{Br}(\text{cyclopropane})$	123
10	XX, XXX	$\text{BrCH}_2\text{CH}=\text{CH}_2, \text{H}_2\text{O}$	121, 18
11	XX	$\text{CH}_3\text{C}(\text{Br})=\text{CH}_2$	121
12	X	$\text{CH}_3\text{CH}(\text{Br})\text{CH}_3$	123
13	tr	Benzene	78
14	tr	Toluene	92

All compounds identified by Wiley or NBS electronic libraries.

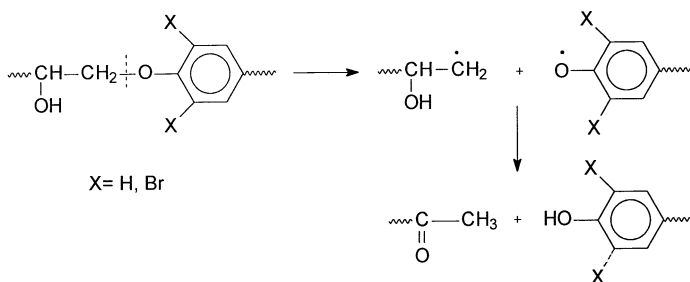
proposed in Schemes 1 and 2. Owing to the high crosslinking degree, amino groups concentrate in the residue.

Cyclic products either in the residue or in the volatile fraction are also possible through a concerted mechanism illustrated in Schemes 3 and 4. It can be emphasized that the initial degradative phenomenon encourages both residue as well as volatile production.

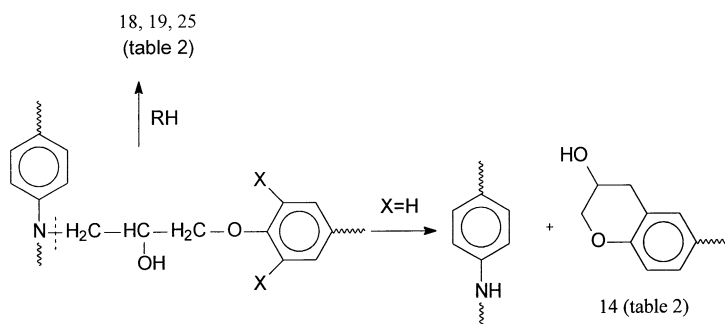




Scheme 4.



Scheme 5.



Scheme 6.

Splitting of the glycidil backbone cannot be excluded as a relevant process of thermolysis of BER when water elimination does not occur. This possible degradation path is depicted in Schemes 5 and 6.

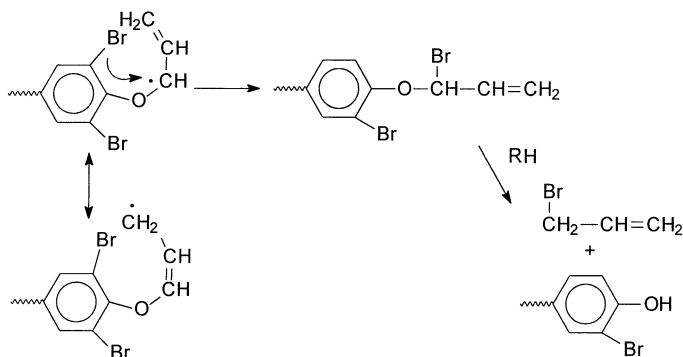
This is a pathway for acetone formation (Scheme 5). Product 14 (Scheme 6) is formed through a concerted mechanism whereas 19 by H abstraction.

The strength of the  $\text{CH}_2\text{-OPh}$  and  $\text{CH}_2\text{-NPh}$  bonds is 263 and 298  $\text{kJ mol}^{-1}$  [10], respectively. It is commonly estimated that a difference in 20  $\text{kJ mol}^{-1}$  in bond energy lowers the kinetic constant of their scission by two orders of magnitude at the same temperature [11]. It means that the rate of the processes of Schemes 5 and 6 in the first, quasi-isothermal, HRTG step of degradation is negligible in comparison to those of Schemes 1–4.

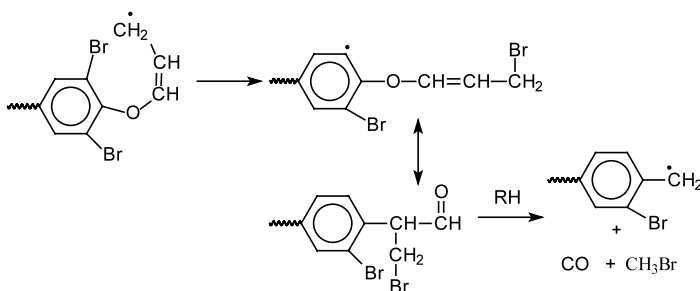
However, as shown by IR, the essential features of the first step of degradation is the breakdown of brominated part of BER. The strength of the Br–C<sub>6</sub>H<sub>5</sub> is 336.8 kJ mol<sup>-1</sup> [10], thus its scission should occur at a very slow rate at the temperature of the first HRTG step unless it is assisted by radicals present in the system as in Schemes 7 and 8.

Rearrangement such as vinyl ether to aldehyde has been proposed similar to what occur to vinyl esters [12]. In this way methyl and propenyl bromides, which have been detected as main volatile products (products 5, 10 and 11 in Table 3) are formed at a temperature lower than expected on the basis of Ph–Br bond strength. The phenyl radical of Scheme 8 can account for the formation of partially debrominated phenols with less number of bromine, i.e. compounds 3, 11, 18, 25, 26, 30, 31 and 33 in Table 2.

As previously stated, formation of tetrabromobisphenol A (TBBPA) can occur. This compound is less volatile than dibrominated phenols and will accumulate in the condensed phase. Therefore, it is possible that, as the residue is subjected at higher temperature to prolonged heating, evolution of HBr occurs. Indeed, a small quantity of HBr has been found in the gaseous products of degradation of BER up at 330 °C, together with a larger amount of mono-phenols, which come from



Scheme 7.



Scheme 8.

extensive degradation of the residue. In fact, scission of the isopropyl–phenyl bond occurs at a relevant rate only at higher temperature, because its bond energy is 369 kJ mol<sup>-1</sup>. Its homolysis has been proposed by Montaudo [13] and in the present case would lead to the formation of the unbrominated, and brominated phenols 1, 3, 15, 7, 11 and 20 and ethers 19, 23 and 25 of Table 2. The unsaturations accumulated in the residue contribute further to its charring process.

## 5. Conclusions

The thermal degradation of the brominated epoxy resin has been investigated in inert atmosphere using TG, HRTG, IR, and GC–MS of gases and HBP. The knowledge of this process could be of relevance in a pyrolytic approach to the recycling of thermosetting resins. Thermolysis occurs in three steps: decomposition of brominated part of BER, decomposition of non-brominated part of BER, char formation. The first two steps are partially overlapped in continuous heating condition whereas they can be separated operating in quasi-isothermal condition. Brominated aliphatics, mono- and dibrominated phenols are released in the first stage. Non-brominated part of BER decomposes with evolution of non-substituted and alkylsubstituted phenols, bisphenol A, alkoxyaromatics. The possible ways of the product formation are predominantly based on homolytic processes. The nitrogen-containing group accumulate in the residue due to the high level of crosslinking whereas unsaturated cycles contribute to the charring of the residue.

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