Polymer Degradation and Stability **14** (1986) 125–137

Degradation of Epoxy Polymers: Part 4—Thermal Degradation of Bisphenol-A Diglycidyl Ether Cured with Ethylene Diamine

Norman Grassie, Marilyn I. Guy

Department of Chemistry, University of Glasgow,
Glasgow G12 8QQ, Scotland, Great Britain

&

Norman H. Tennent

Glasgow Museums and Art Galleries,
Kelvingrove, Glasgow G3 8AG, Scotland, Great Britain

(Received: 11 July, 1985)

ABSTRACT

*The principal characteristics and products of thermal degradation of a commercial epoxy resin prepared by reaction of 2,2-bis-(4′-hydroxyl phenyl)propane (bisphenol-A) with 1-chloro-2,3-epoxy propane (epichlorhydrin) and cross-linked (cured) with ethylene diamine have been studied. The principal products are small amounts of hydrogen and methane, ethane, propene, ammonia, methylamine with a trace of trimethylamine, water, phenol, cresols, 4-isopropyl phenol, 4-isopropenyl phenol, bisphenol-A, 2-(benzo-fur-5-yl)-2-(*p*-hydroxy phenyl)-propane and 2-(benzo-pyran-6-yl)-2-(*p*-hydroxy phenyl)propane. These products appear from about 300°C and mechanisms for their formation are proposed.*

INTRODUCTION

In previous papers,[1–3] the products and mechanisms of the thermal and photo-degradation of the epoxy resin, bisphenol-A diglycidyl ether, have

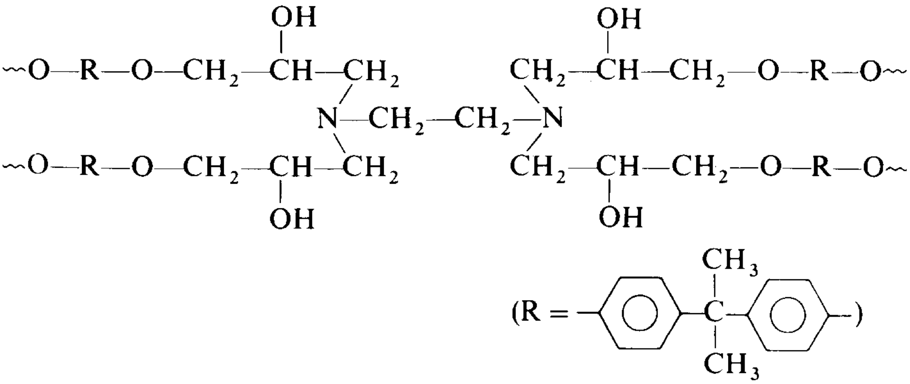
Polymer Degradation and Stability 0141-3910/86/$03·50

been described and discussed. That work has been extended to the highly cross-linked polymer which is formed when the resin is reacted (cured) with ethylene diamine. This paper is concerned with the thermal reaction. The photo-reaction will be reported upon subsequently.

EXPERIMENTAL

Preparation of cured resin

Ablebond 342-1 resin, manufactured by Ablestik Laboratories, USA, and supplied by Dage Intersen Ltd, Great Britain, was purified as described previously.[1] Synchemia grade ethylene diamine (Hopkin and Williams) was redistilled and used as curing agent. To obtain optimum cure the resin and curing agent were mixed in the stoichiometric proportions of one epoxide group per amine hydrogen atom of the curing agent. After thorough mixing by stirring, the mixture was pressed between sheets of polythene and allowed to cure at ambient temperature for 48 h. The degree of cure was estimated by measurement of the residual epoxy groups from measurements of the intensity of the infra-red epoxy band at 910 cm^{-1}. Degrees of cure of 97% were consistently obtained. Thus the cured resin had predominantly the following structure:



although a small proportion of residual amino hydrogen atoms and epoxy groups are also present.

Degradation procedures and analysis of products

The degradation procedures and thermal analysis and spectroscopic techniques were exactly as described previously.[1]

RESULTS

Identification of volatile products

The Subambient Thermal Volatilisation Analysis (SATVA) trace of the volatile products obtained on heating the polymer from ambient temperature to 500 °C at 10° min^{-1} is illustrated in Fig. 1. The products in the various peaks were identified by ir and mass spectrometry as follows: 1, ethane; 2, propene; 3, ammonia; 4, methylamine with a trace of trimethylamine; 5, water. A low volatile fraction (LVF) was evolved in the later stages of the SATVA experiment and will be discussed below with the cold ring fraction (CRF). Small amounts of hydrogen and methane were also detected when the reaction was carried out in a closed system.

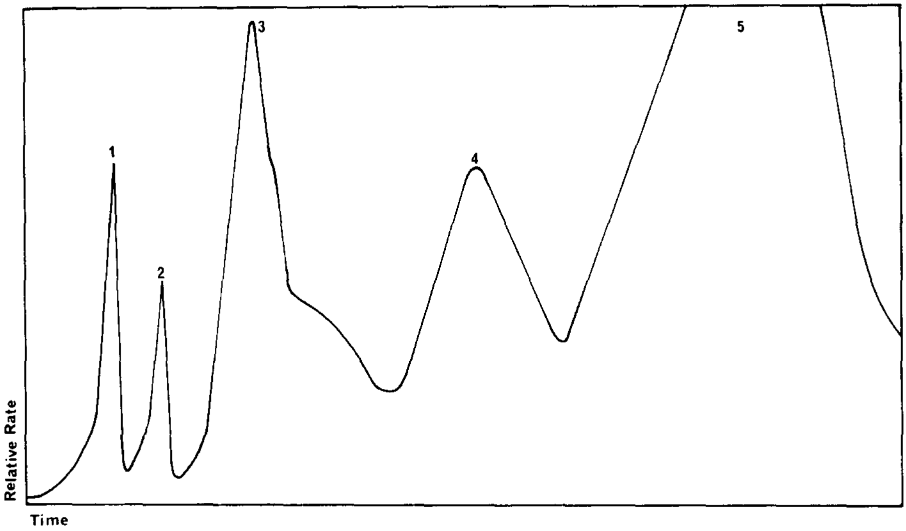


Fig. 1. SATVA trace of volatile products from cured resin heated from ambient to 500 °C at 10 °C min^{-1}.

Analysis of low volatile fraction and cold ring fraction

Gas liquid chromatograms of the LVF and CRF obtained from the cured resin after heating from ambient temperature to 500 °C at 10° min^{-1} are illustrated in Fig. 2. The products were identified by ir and mass spectrometric analysis as follows: 1, phenol; 2, *o*-cresol; 3, *n*- and *p*-cresol; 4, 4-isopropyl phenol; 5, 4-isopropenyl phenol; 6, bisphenol-A; 7,

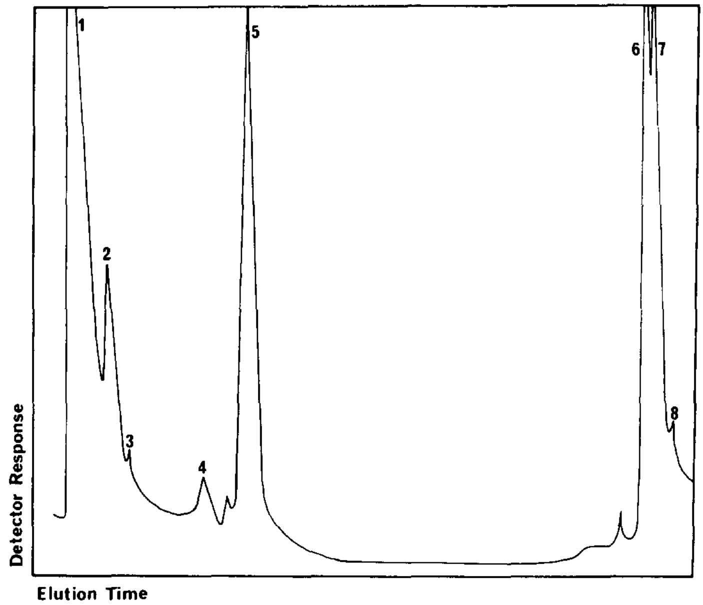
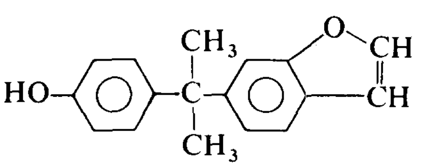
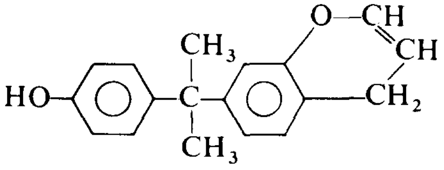


Fig. 2. Gas–liquid chromatogram of low volatile fraction (peaks 1–3) and cold ring fraction (peaks 4–8) from cured resin heated from ambient to 500 °C at 10 °C min^{-1}.

2-(benzo-fur-5-yl)-2-(*p*-hydroxy phenyl)propane (I); 8, 2-(benzo-pyran-6-yl)-2-(*p*-hydroxy phenyl)propane (II).


I


II

Thermal analysis

TVA

The TVA curves in Fig. 3 show that volatile products are formed from approximately 330 °C and that these products have a wide range of volatilities.

TG

A TG curve is presented in Fig. 4. About 3 % of the weight of the sample is lost between ambient temperature and 75 °C and a further 2 % between

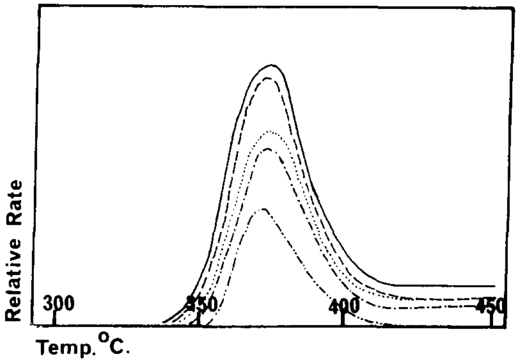


Fig. 3. TVA trace for cured resin.

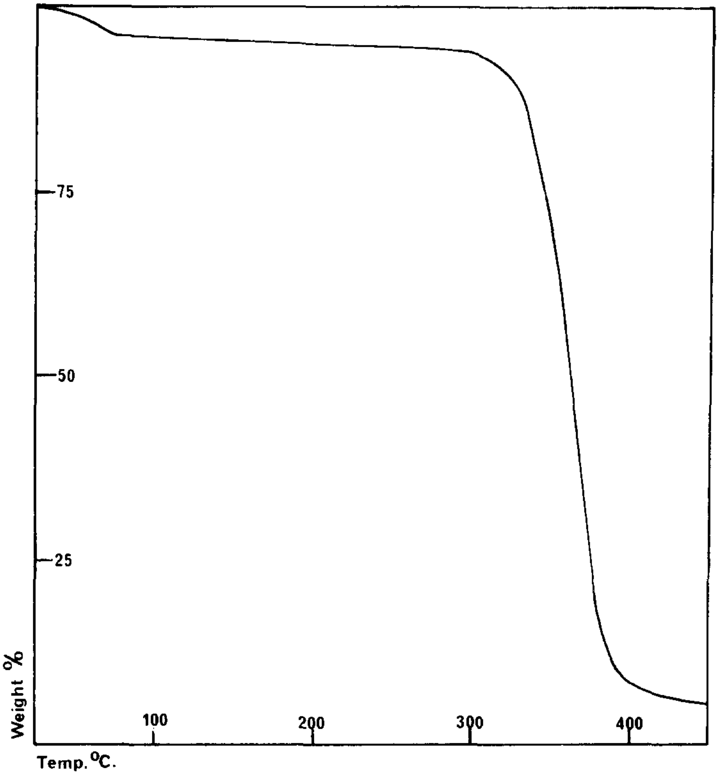


Fig. 4. TG curve for cured resin.

75° and 300°C. These weight changes are most probably due, respectively, to loss of residual solvents and absorbed moisture. Above 300°C the rate of weight loss increases steadily to a maximum in the same region as demonstrated by TVA. Further slow-weight loss occurs above 400°C.

DSC

A DSC scan, shown in Fig. 5, generally confirms the evidence of TG, demonstrating an endothermic process between ambient temperature and 80°C, which corresponds to loss of solvents and moisture, and the large exotherm centred near 360°C which corresponds to degradation.

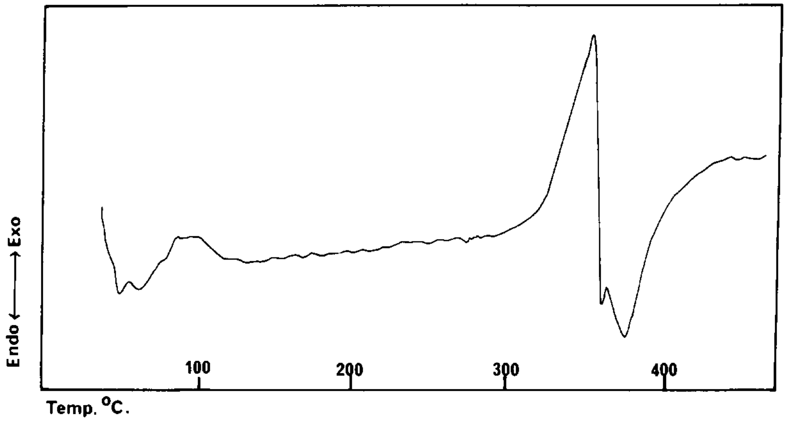


Fig. 5. DSC curve for cured resin.

The small exotherm which appears between 80° and 120°C is most probably due to reaction of residual epoxy and amino groups in the resin network. On the other hand, the endotherm in the region 360°–425°C, which immediately follows the degradation exotherm, may be explained by volatilisation of high molecular weight residual products such as I and II. This endotherm may correspond to the gradual weight loss which is demonstrated by TG to occur in the region 380°-500°C.

Isothermal degradation

To gain information about the site of degradation, samples were degraded isothermally at 300°, 310°, 320° and 340°C for 1 h. The volatile products were separated by the SATVA procedure and the results are

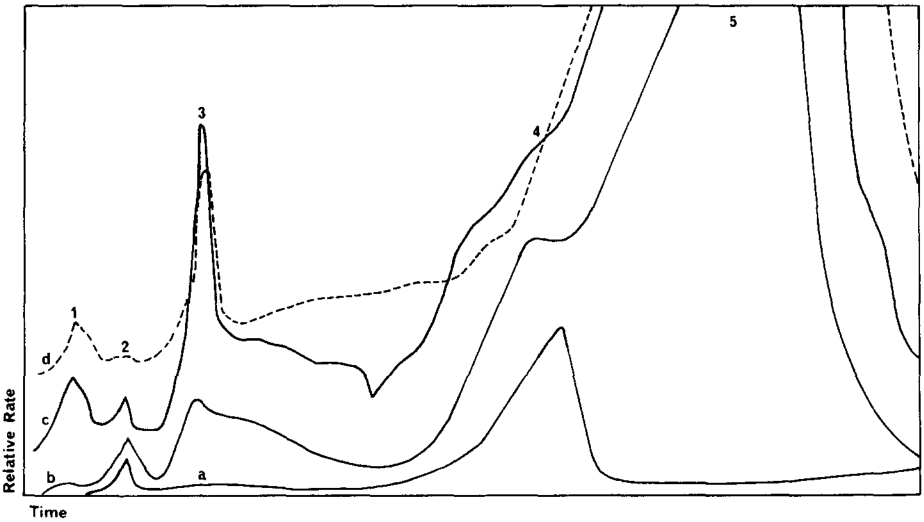


Fig. 6. SATVA traces for products of degradation of cured resin heated for 1 h at various temperatures: a, 300 °C; b, 310 °C; c, 320 °C; d, 340 °C. Products: 1, ethane; 2, propylene; 3, ammonia; 4, amines; 5, water.

illustrated in Fig. 6. At 300 °C, small amounts of propene, ammonia, water and low volatile products are formed. At 310 °C, a small amount of ethane was detected, ammonia was formed in more substantial amounts and the amine fraction was also in evidence as a shoulder on the water peak. At 320° and 340 °C, the amounts of water, amines and ammonia were increased substantially, ethane was increased somewhat although it and propylene were still minor products. A small amount of methane was also confirmed by mass spectral analysis and an ion peak at *m/e* 28 could have been due to carbon monoxide, although nitrogen was considered to be at least as probable a product of degradation of the cured resin.

Phenol was the only constituent of the low volatile fraction after isothermal degradation.

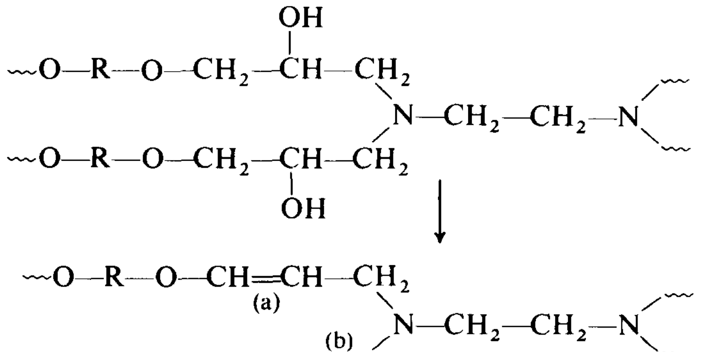
Gas-liquid chromatographic analysis of the cold ring fraction obtained at 300 °C showed that the main product was I, followed by bisphenol-A and a small amount of 4-isopropenyl phenol. At 310 °C, I and bisphenol-A were formed in comparable amounts with a small proportion of II. All these products were also formed at 320° and 340 °C as well as a small amount of isopropyl phenol.

Infra-red spectra of residual polymer after isothermal degradation for 1 h at temperatures from 300° to 380 °C showed that the most significant changes occurred in the range 300°–310 °C, at which temperatures the polymer had assumed a yellow colour. Between 300° and 305 °C there is a noticeable reduction in hydroxyl absorption at 3400 and 1300 cm^{-1}, aromatic absorption at 1600–1580 cm^{-1}, ether absorption at 1250 cm^{-1} and C—N absorption at 1020 cm^{-1}. A shoulder appears in the 1640–1680 cm^{-1} region which may be assigned to the formation of NH and NH_2 groups. This would account for the absence of ammonia and amines among the volatile products in the initial stages of degradation. Enamine structures may also be formed, absorbing at 1650–1690 cm^{-1}. After degradation at 310 °C the C—N absorption band at 1020 cm^{-1} and the shoulder at 1640 and 1680 cm^{-1} had virtually disappeared and this may be correlated with the formation of ammonia and amines among the volatile products.

Mechanism of thermal degradation of cured resin

In terms of bond energies, the weakest points in the cross-linked resin network should be C—N and O—CH_2 bonds. However, the high concentration of hydroxyl bonds in the cured resin favours localised intramolecular hydrogen bonding which would promote dehydration. The formation of water as the major product in the earliest stages of degradation confirms that this is the most facile reaction. The continuing development of unsaturation would account for the yellow coloration of the degraded polymer. Unsaturation would also induce stiffness into the polymer chains, thus accounting for the gradual embrittlement of the film.

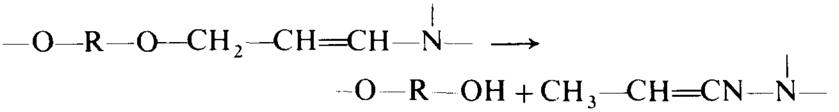
Of the two unsaturated structures depicted in (1), (a) is probably the more favoured. Oxygen has a greater negative inductive effect than



(1)

nitrogen so a hydrogen atom would be more easily withdrawn from the CH_2 group adjacent to the oxygen atom. However, absorption in the region 1650–1690 cm^{-1} suggests that the enamine structure (b) is also formed to some extent. In structure (a) the high electron density at the C═C bond will be delocalised in the vicinity of the aromatic ring. The opposing, but weaker, negative inductive effect of nitrogen would, in this case, make the C—N bond relatively stronger than the CH—CH_2 bond. Scission at the CH—CH_2 bond followed by cyclisation to the aromatic ring would account for the formation of 2-(benzo-fur-5-yl)-2-(*p*-hydroxy phenyl)propane (I) as a major initial product of degradation.

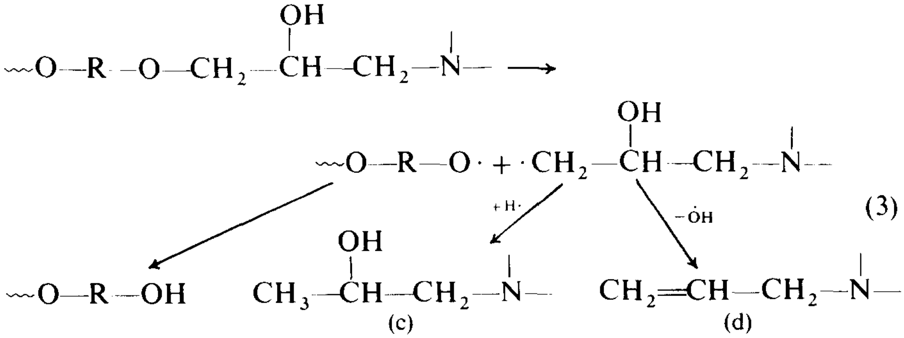
However, scission must also occur at the O—CH_2 bond in order to account for the formation of the phenolic hydroxyl groups in I and in bisphenol-A which are the main products in the cold ring fraction. The unsaturated structure (b) and the parent hydroxylated structure (eqn (1)) would both favour scission at the O—CH_2 bond. The radicals formed from the unsaturated structure would both be stabilised by hydrogen abstraction:



$$\text{—O—R—O—CH}_2\text{—CH=CH—}\overset{|}{\text{N}}\text{—} \longrightarrow \text{—O—R—OH} + \text{CH}_3\text{—CH=CN—}\overset{|}{\text{N}}\text{—} \quad (2)$$

However, the increased electron density at the nitrogen atom due to the unsaturation should strengthen the C—N bond so that formation of propylene, which must also be explained as an early product of degradation, would be less likely.

Formation of phenolic hydroxyl groups by scission of the O—CH_2 bond of the parent hydroxylated structure seems more likely. Stabilisation of the alkyl radical could occur either by hydrogen abstraction or loss of a hydroxyl radical:



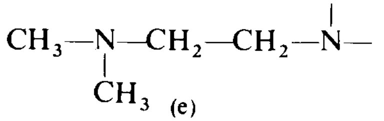
$$\text{∼O—R—O—CH}_2\text{—}\overset{\text{OH}}{\overset{|}{\text{CH}}}\text{—CH}_2\text{—}\overset{|}{\text{N}}\text{—} \longrightarrow \text{∼O—R—O}\cdot + \cdot\text{CH}_2\text{—}\overset{\text{OH}}{\overset{|}{\text{CH}}}\text{—CH}_2\text{—}\overset{|}{\text{N}}\text{—} \quad (3)$$

$$\text{∼O—R—OH} \qquad \text{CH}_3\text{—}\overset{\text{OH}}{\overset{|}{\text{CH}}}\text{—CH}_2\text{—}\overset{|}{\text{N}}\text{—}\ \text{(c)} \qquad \text{CH}_2\text{=CH—CH}_2\text{—}\overset{|}{\text{N}}\text{—}\ \text{(d)}$$

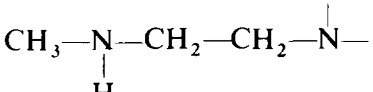
Since the energy of the $\overset{\diagdown}{\underset{/}{HC}}-H$ bond (≏ 102 kcal) is less than that of the $\sim CH_2-H$ bond (≏ 110 kcal), dehydration of structure (c) would most probably lead to $CH_3-CH{=}CH-\overset{|}{N}-$, which was suggested above to be an unlikely structure. Alternatively, scission at the CH_2-N or the tertiary hydrogen bond would be expected to lead ultimately to isopropanol and acetone, neither of which were detected among the degradation products.

The formation of structure (d) in eqn (3) seems the more likely since scission at the C—N bond followed by hydrogen abstraction would produce propylene and —NH structures, which is consistent with the experimental data. Although propylene is a relatively minor product, this may be rationalised by the assumption that degradation followed by chain scission and ring closure leading to I, as outlined above, is the predominating mode of decomposition of the parent hydroxylated structure.

Thus, while degradation and the elimination of bisphenol-A, propylene and the benzofuranyl derivative of bisphenol-A (I) are occurring during the early stages of degradation, amino, and possibly enamine, structures are accumulating in the polymer network. As the temperature is increased, these structures in turn break down. Four types of amino structures ((e) to (h)) may be formed:

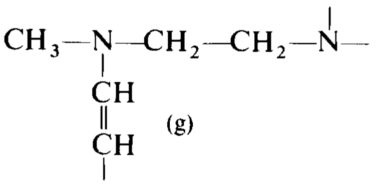


$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_2-CH_2-\overset{|}{N}-$$

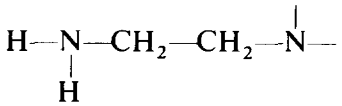


(f)

$$CH_3-\underset{\displaystyle H}{\underset{|}{N}}-CH_2-CH_2-\overset{|}{N}-$$



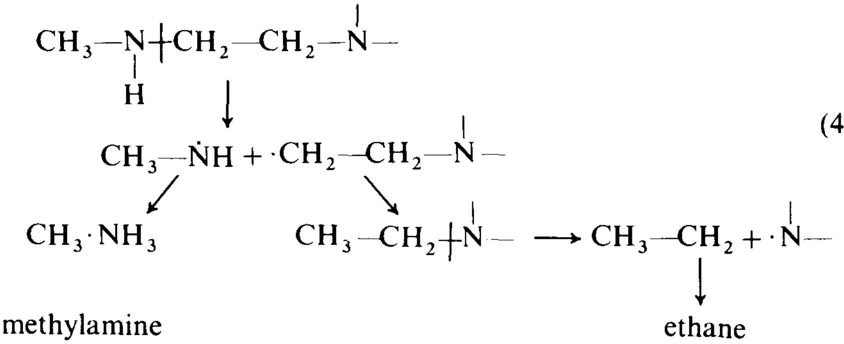
$$CH_3-\underset{\underset{\displaystyle \overset{\|}{CH}}{|}}{\underset{\displaystyle CH}{\underset{|}{N}}}-CH_2-CH_2-\overset{|}{N}-$$



(h)

$$H-\underset{\displaystyle H}{\underset{|}{N}}-CH_2-CH_2-\overset{|}{N}-$$

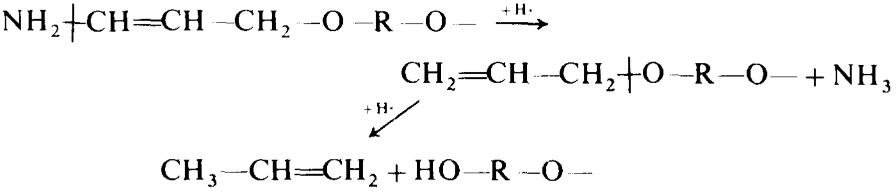
In (e), the electron repelling effect of the two methyl groups would strengthen the N—CH₂ bond, making C—C bond scission and the ultimate formation of trimethylamine more favourable. In structure (f), the electron repelling effect of the single methyl group will be less, so that the C—N bond is relatively weakened and scission now occurs predominantly there, which accounts for the relatively large yield of methylamine and the absence of dimethylamine among the degradation products. Structure (f) may also be the source of the small amount of ethane which is produced in the later stages of reaction:



$$CH_3-\underset{H}{N}\!\mid\!CH_2-CH_2-\overset{|}{N}- \;\rightarrow\; CH_3-\dot{N}H + \cdot CH_2-CH_2-\overset{|}{N}- \quad (4)$$

$$CH_3-\dot{N}H \rightarrow \underset{\text{methylamine}}{CH_3\cdot NH_3} \qquad \cdot CH_2-CH_2-\overset{|}{N}- \rightarrow CH_3-CH_2\!\mid\!\overset{|}{N}- \longrightarrow CH_3-CH_2 + \cdot\overset{|}{N}-, \quad CH_3-CH_2 \rightarrow \text{ethane}$$

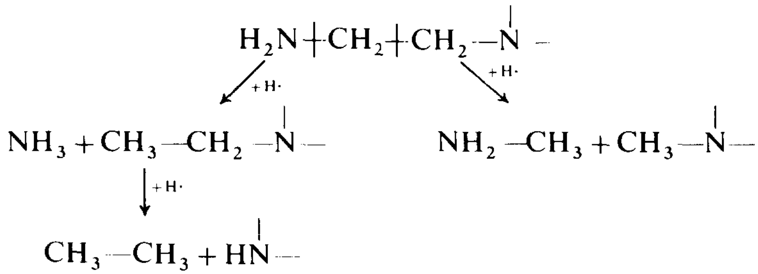
In structure (g), the double bond and the electron repelling methyl group would be expected to increase the electron density over the N—C═C and N—CH_2 bonds so that CH_3—N bond scission would probably be favoured. This would account for the small amount of methane among the products and the sequence of reactions of the resultant structure may account for the formation of ammonia, ethane and 2-(benzopyran-6yl)-2-(*p*-hydroxy phenyl)propane(II). (See eqn (5) on p. 136.) In the event of stabilisation by hydrogen abstraction of the ·CH═CH— radical formed in the last stage of this sequence, further production of propylene is possible:



$$NH_2\!\mid\!CH{=}CH-CH_2-O-R-O- \xrightarrow{+H\cdot} CH_2{=}CH-CH_2\!\mid\!O-R-O- + NH_3$$

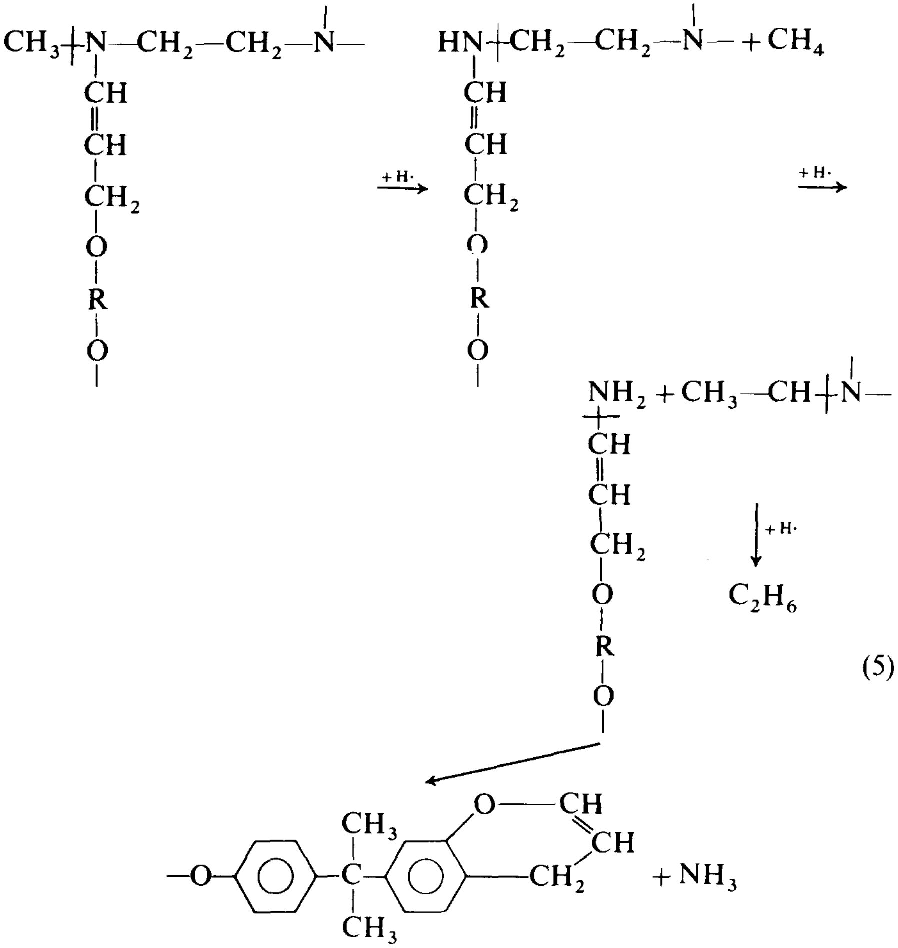
$$CH_2{=}CH-CH_2\!\mid\!O-R-O- \xrightarrow{+H\cdot} CH_3-CH{=}CH_2 + HO-R-O-$$

Ammonia and ethane are the most probable products from structure (h). However, scission may also occur at the C—C bond since some methylamine is produced on thermal degradation of ethylene diamine curing agent:



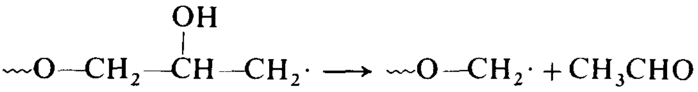
$$H_2N\!\mid\!CH_2\!\mid\!CH_2-\overset{|}{N}- \xrightarrow{+H\cdot} NH_3 + CH_3-CH_2-\overset{|}{N}- \xrightarrow{+H\cdot} CH_3-CH_3 + H\overset{|}{N}-$$

$$H_2N\!\mid\!CH_2\!\mid\!CH_2-\overset{|}{N}- \xrightarrow{+H\cdot} NH_2-CH_3 + CH_3-\overset{|}{N}-$$



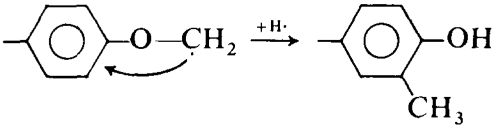
(5)

It has been suggested by Patterson-Jones[4] that a radical formed by scission at the C—N bond in the parent polymer undergoes rearrangement followed by elimination to form small amounts of acetaldehyde:

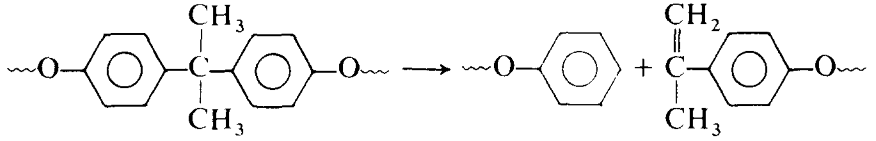


$$\sim O-CH_2-\underset{}{\overset{OH}{\overset{|}{C}}}H-CH_2\cdot \longrightarrow \sim O-CH_2\cdot + CH_3CHO$$

Acetaldehyde was not detected among the degradation products but such a reaction could explain the formation of small amounts of *o*-cresol:



During thermal degradation of the cured resin there is very little decomposition of the bisphenol-A moiety. That which does occur appears to depend upon scission at the C—ϕ bond followed by disproprotionation since 4-isopropenyl phenol and phenol are the main low molecular weight phenolic products:



Isopropyl phenol would be formed if the phenyl substituted isopropyl radical escaped from the cage and abstracted hydrogen elsewhere in the system. The formation of the other minor phenolic products, *m*- and *p*-cresol, has been discussed previously.[2]

REFERENCES

1. N. Grassie, M. I. Guy and N. H. Tennent, *Poly. Deg. and Stab.*, **12**, 65 (1985).
2. N. Grassie, M. I. Guy and N. H. Tennent, *Poly. Deg. and Stab.*, **13**, 11 (1985).
3. N. Grassie, M. I. Guy and N. H. Tennent, *Poly. Deg. and Stab.*, **13**, 249 (1985).
4. J. C. Patterson-Jones, PhD Thesis, Cape Town University (1969).