

Degradation of Epoxy Polymers: 3—Photo-degradation of Bisphenol-A Diglycidyl Ether

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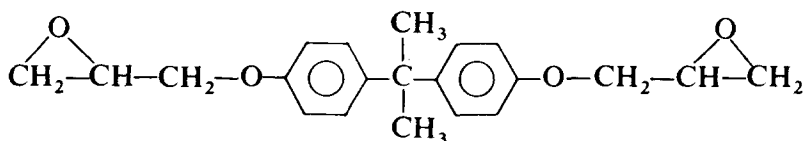
ABSTRACT

The principal characteristics and products of photo-degradation of a commercial epoxy resin, bisphenol-A diglycidyl ether, have been studied. Comparison with the results of thermal degradation shows that many of the products are identical, especially the phenols and derivatives of phenol. The principal differences are the appearance of hydrogen in the photo, but not in the thermal, reaction and a series of aromatic hydrocarbons, including xylenes and/or ethyl benzene, styrene, isopropyl benzene and isopropenyl benzene, which are completely absent from the products of thermal degradation. Mechanisms are outlined.

INTRODUCTION

Epoxy polymers are normally prepared from a low molecular weight epoxy resin and a curing agent which cross-links the resin to form a rigid

polymer. The considerable current interest in the thermal and photo-degradation of these polymers was discussed in the introduction to the first paper¹ of this series but these reactions are complicated by reason of the complex structure of the cross-linked resin. For this reason, the first two papers^{1,2} of this series were devoted to a description and discussion of the principal products, characteristics and mechanisms of thermal degradation of the common commercial resin, bisphenol-A diglycidyl ether:



In the present paper, the products, characteristics and mechanism of photo-degradation of this material will be described and discussed. It will become clear that there are many similarities in the products and methods of analysis of thermal and photo-degradation. Thus, to save repetition, and where appropriate, only differences will be emphasised.

Subsequent work will be devoted to comparable studies of the cross-linked resin.

EXPERIMENTAL

Purification of resin

The source of the resin and its purification were described previously.¹

Sources of irradiation

The Hanovia Chromatolite low-pressure mercury vapour lamp is practically monochromatic at 254 nm. The Hanovia medium-pressure mercury arc lamp emits over a wider range with 25% of its energy at 254 nm and below. Photo-degradation was extremely slow using the former so the latter was used predominantly in this work.

Degradation and analysis procedures

A fairly thick film of resin was prepared on a 2.5 cm diameter sodium chloride disc which was placed in a vacuum chamber with a silica top

through which the resin was irradiated. Since the medium-pressure lamp generates a great deal of heat, it was positioned 20 cm from the sample. Non-condensable products were collected in apparatus closely similar to the 'closed system' described in a previous paper. Other volatile products were collected in a continuously evacuated system based on TVA equipment.¹ The non-condensable products were analysed using a Micromass QX200 mass spectrometer. Other volatile products were analysed as described previously.¹ Bisphenol-A was irradiated in a closed system and the products analysed similarly.

RESULTS

Identification of volatile products

Evolution of volatile products was extremely slow using the Hanovia 254 nm Chromatolite lamp and even after prolonged periods of irradiation only acrolein and water could be positively identified. Rates were much higher using the Hanovia medium-pressure mercury lamp and the SATVA trace for the volatile products which had accumulated after 48 hours' irradiation is shown in Fig. 1. Comparison with the SATVA trace for the products of thermal degradation (*cf.* Fig. 2, Paper 1) reveals that the products are identical, although the relative quantities vary somewhat. The non-condensable gases, methane and carbon monoxide, are also found as in the thermal degradation but hydrogen, detected by mass spectrometry, was an additional product of photo-degradation.

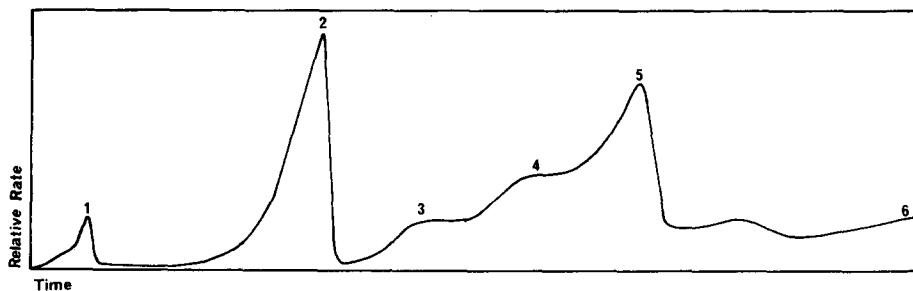


Fig. 1. SATVA trace of volatile products of photo-degradation of epoxy resin (48 h irradiation with medium-pressure mercury arc lamp). 1, CO₂ and propylene; 2, acrolein; 3, acetone; 4, allyl alcohol; 5, water; 6, low volatile fraction.

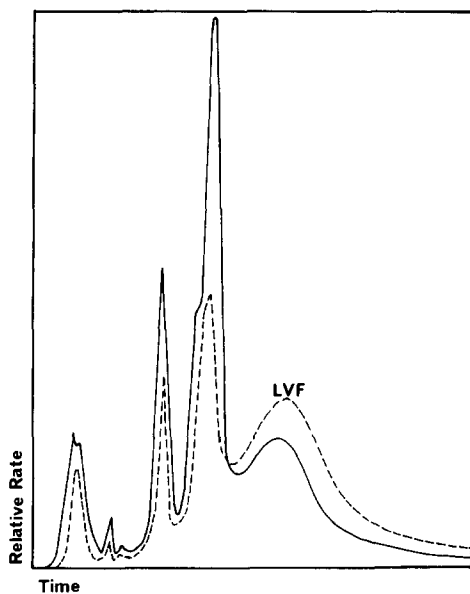


Fig. 2. SATVA traces of the volatile products of photo-degradation of epoxy resin during initial (—) and subsequent (-----) 5 h periods of irradiation.

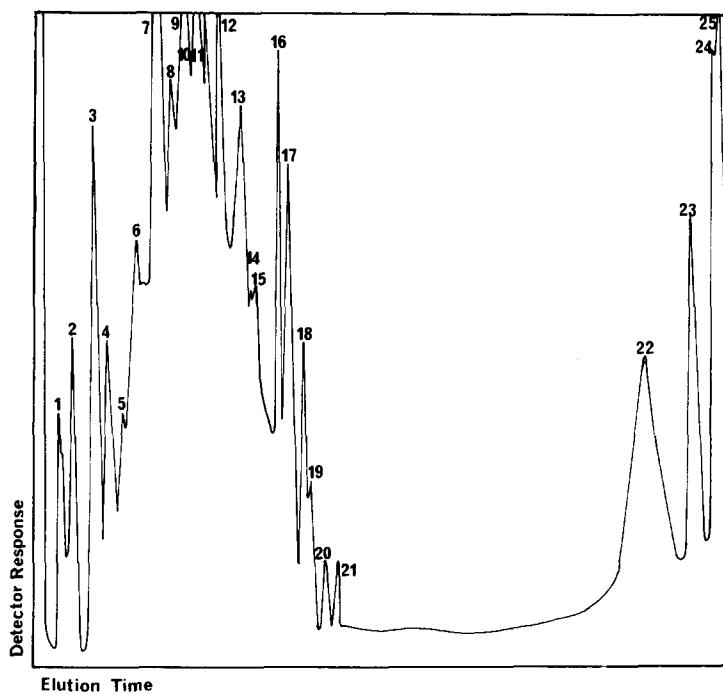


Fig. 3. Gas chromatogram of the low volatile fraction from photo-degradation of epoxy resin (48 h irradiation with medium-pressure mercury arc lamp).

The separation and examination of the products in the low volatile fraction (LVF) will be described in the following section. It is of interest to record at this point, however, that the amount of LVF increases relative to the more volatile products as the period of irradiation is increased. This is illustrated in Fig. 2. Thus, it would appear that the glycidyl moiety in the resin, from which the majority of the more volatile products are derived, decomposes preferentially during the initial stages of irradiation. Some of the epoxy groups must also undergo cross-linking as in the thermal reaction, since an insoluble skin is formed over the surface of the resin after as little as 1 hour's irradiation. After 4 h the skin assumes a white opaque appearance and, on removal, appears yellow on the underside. Attempts to analyse the yellow coloration were unsuccessful.

Analysis of low volatile products

The gas chromatograph of the LVF is shown in Fig. 3 but a detailed GC/MS analysis was not carried out as for the products of thermal degradation.^{1,2} Certain of the lower molecular weight products were identified by direct comparison with reference compounds and assignments of the first thirteen peaks are given in Table 1. Some of the later peaks were tentatively identified with peaks with similar retention times as products of thermal degradation.^{1,2} Others were not identified but

TABLE I
Analysis of the Low Volatile Fraction

<i>Peak number</i>	<i>Product</i>
1	<i>m</i> - and/or <i>p</i> -xylene and/or ethyl benzene
2	styrene and/or isopropyl benzene
3	unidentified
4	isopropenyl benzene
5	phenol
6	unidentified
7	<i>o</i> -cresol
8	<i>m</i> - and <i>p</i> -cresol
9	unidentified
10	a xlenol or ethyl phenol
11	unidentified
12	3,4-xlenol
13	2-isopropyl phenol

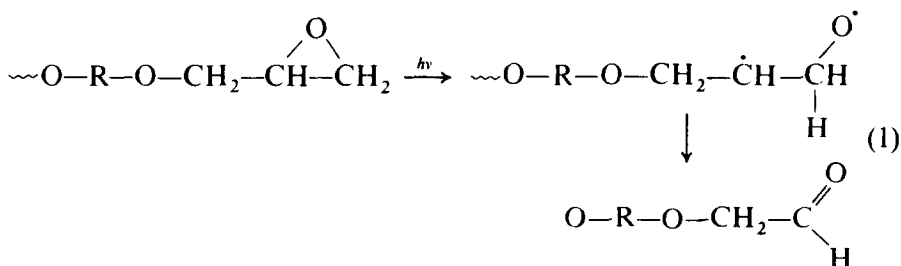
preliminary GC/MS data suggested that some of them might be derivatives of benzene rather than phenols. Thus, it is clear from the data in Fig. 3 and Table 1 that, in addition to the phenolic compounds which comprise the majority of the products of thermal degradation, very significant quantities of benzene derivatives are formed in the photo reaction. The xylenes, ethyl benzene, styrene, isopropyl benzene and isopropenyl benzene, for example, which are responsible for peaks 1, 2 and 4 in Fig. 3, are entirely absent from the products of thermal degradation, thereby suggesting that phenyl-oxygen scission plays a very much larger part than alkyl-oxygen scission in photo-degradation compared with the thermal reaction.

Photo-degradation of bisphenol-A

Further confirmation of the predominance of phenyl-oxygen scission over alkyl-oxygen scission in the photo-degradation of the resin was sought by a comparison of the products of thermal and photo-degradation of the parent compound, bisphenol-A. Apart from small amounts of methane and propylene, the principal products of thermal degradation were reported previously to be entirely phenolic; namely, phenol, 4-isopropyl phenol and 4-isopropenyl phenol. In the photo-reaction, on the other hand, they are revealed as *m*- and *p*-xylene, ethyl benzene and styrene, with only a trace of phenol.

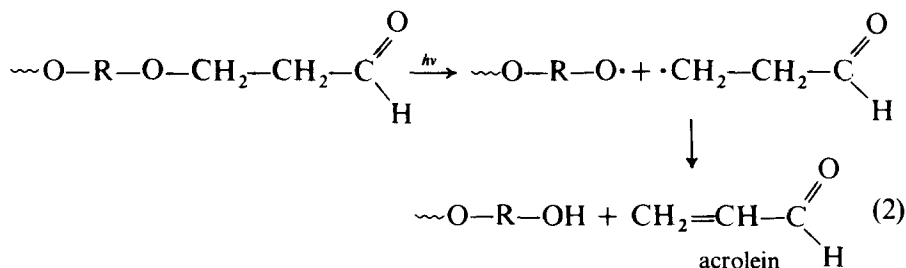
Mechanism of photo-degradation of bisphenol-A diglycidyl ether

It is suggested that excitation of the epoxy group, coupled with strain in the three-membered ring, causes bond scission followed by rearrangement to form a carbonyl group:

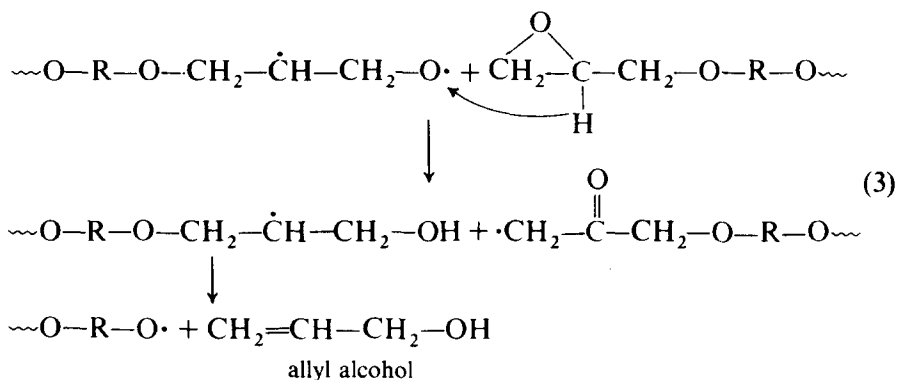


Although this carbonyl group is a potential chromophore, more energy will be required to break the adjacent carbon-carbon bond than to break the glycidyl ether bond near the chromophoric bisphenol-A residue.

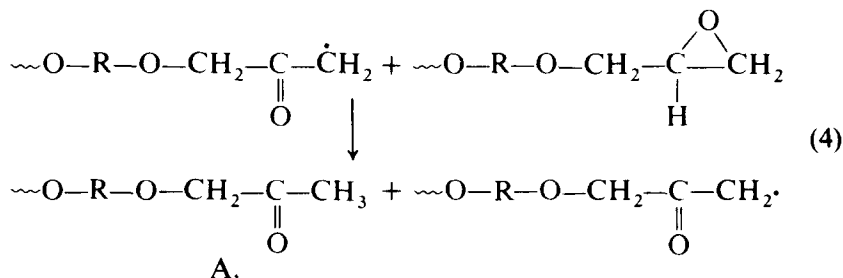
Thus, scission is likely to occur preferentially at the glycidyl ether followed by disproportionation to form acrolein, the major volatile product.



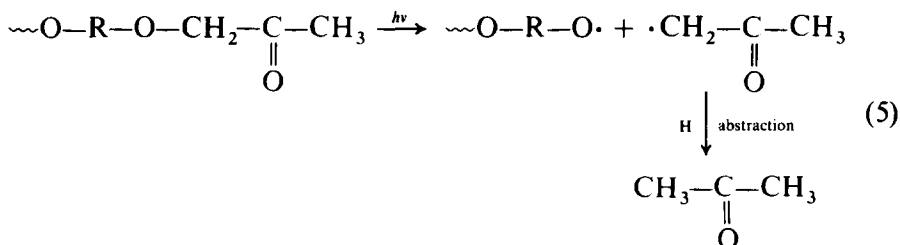
Allyl alcohol appears to be formed mainly during the initial stages of photo-degradation since its peak on the SATVA trace (Fig. 1) becomes less prominent after successive periods of irradiation of the same film. It is suggested that, as in the thermal reaction,^{1,2} the oxygen radical abstracts a reactive tertiary hydrogen atom from a neighbouring epoxy group with simultaneous or subsequent chain scission to form allyl alcohol:



The acetylonyl radical formed in eqn (3) may be stabilised by abstraction of a tertiary hydrogen atom from another epoxy group and thus a chain reaction could be initiated:

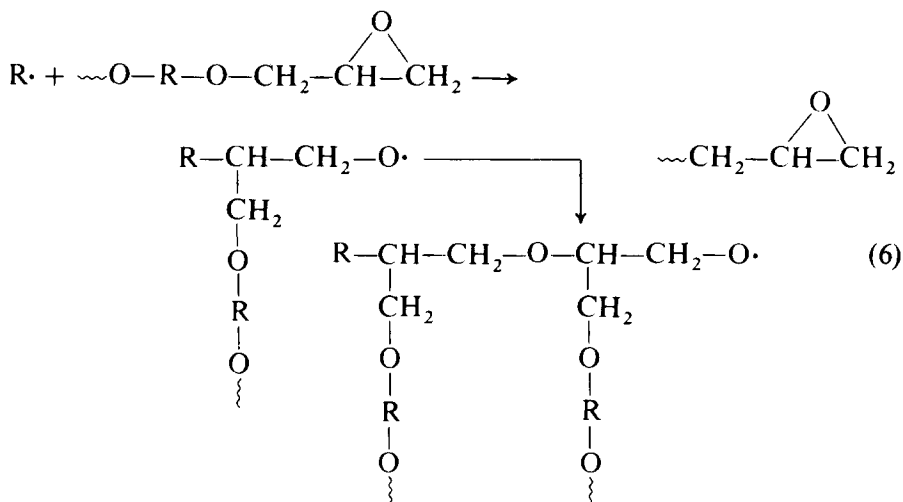


This chain reaction would lead to the accumulation of chain terminal structures of type A which, as in the thermal reaction, would be the precursor of acetone:



This chain reaction would also account for the fact that acetone is formed in greater amounts than allyl alcohol during photo-degradation of the resin.

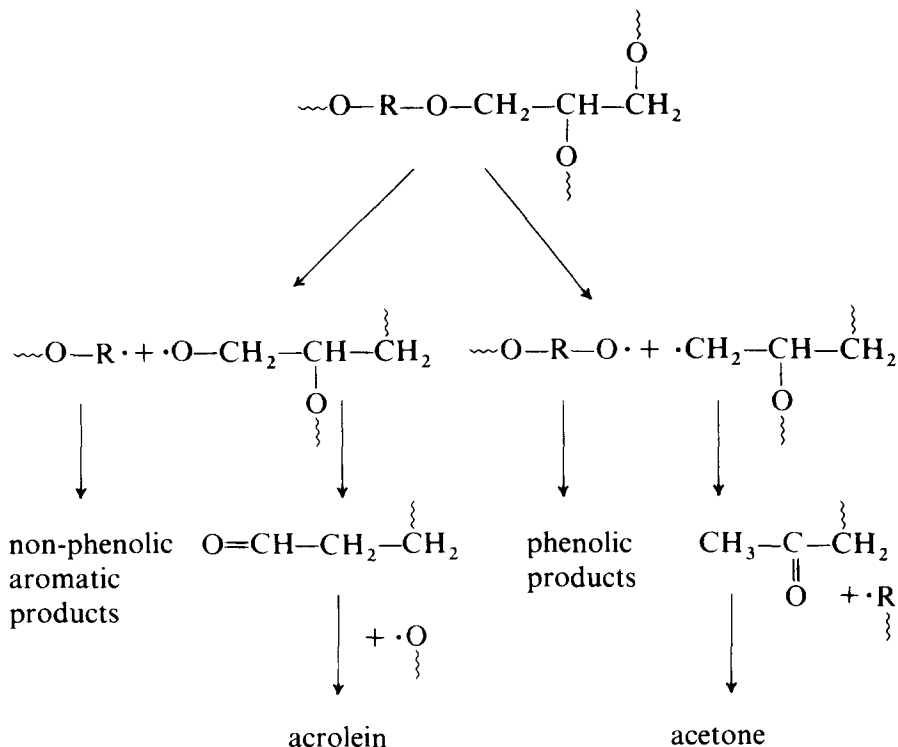
The skin which is formed on the surface of the resin within the first 5–10 h of irradiation is evidence of cross-linking by the polymerisation of epoxy groups as in the thermal degradation.² In that case it was represented as the linking up of diradicals but it may equally be represented as a conventional radical chain reaction:



As photo-degradation progresses, the concentration of epoxy groups in the residual resin will be rapidly depleted due to the reactions described above. However, the aromatic rings are powerful chromophores so that degradation processes initiated by absorption of radiation at these sites will become of increasing relative importance. This accounts for the rapid

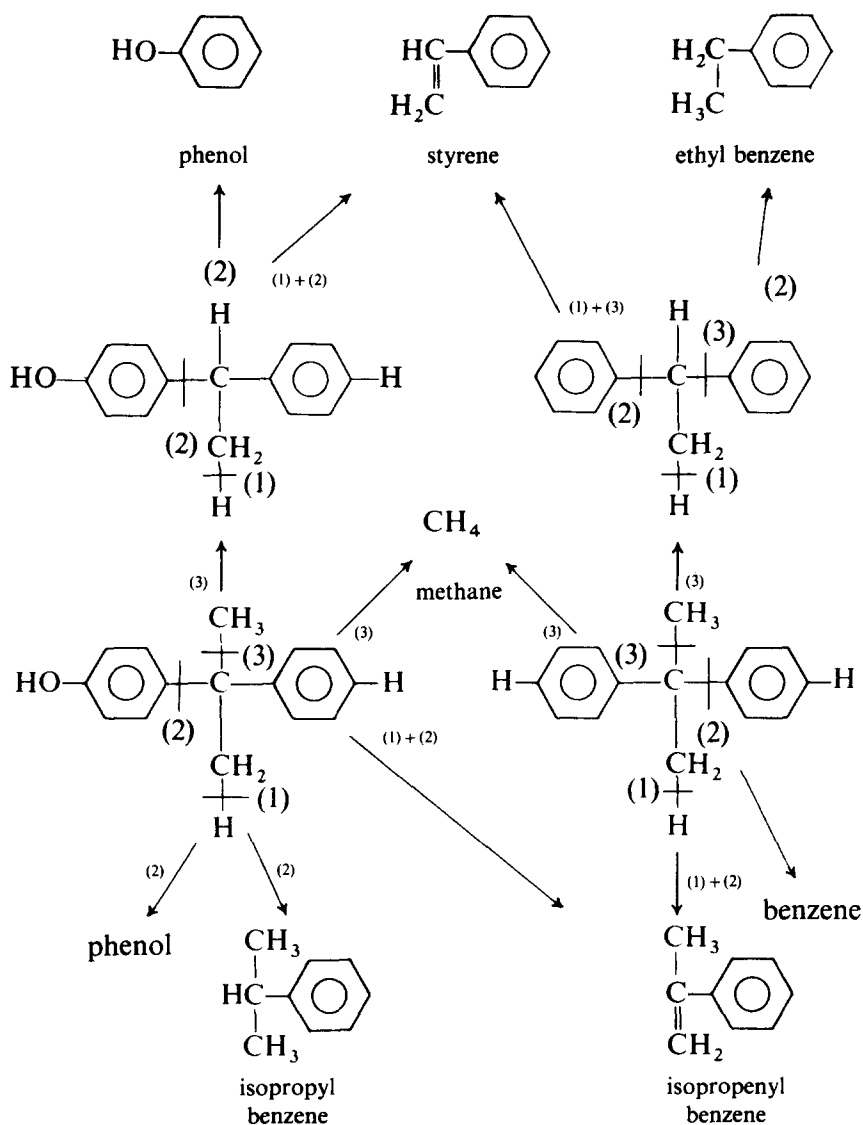
relative increase in the proportion of low volatile products compared with more volatile products as irradiation proceeds.

In the thermal reaction, scission in the vicinity of aromatic groups tended to occur at the alkyl ether bond. In photo-degradation, phenyl ether scission also becomes possible.

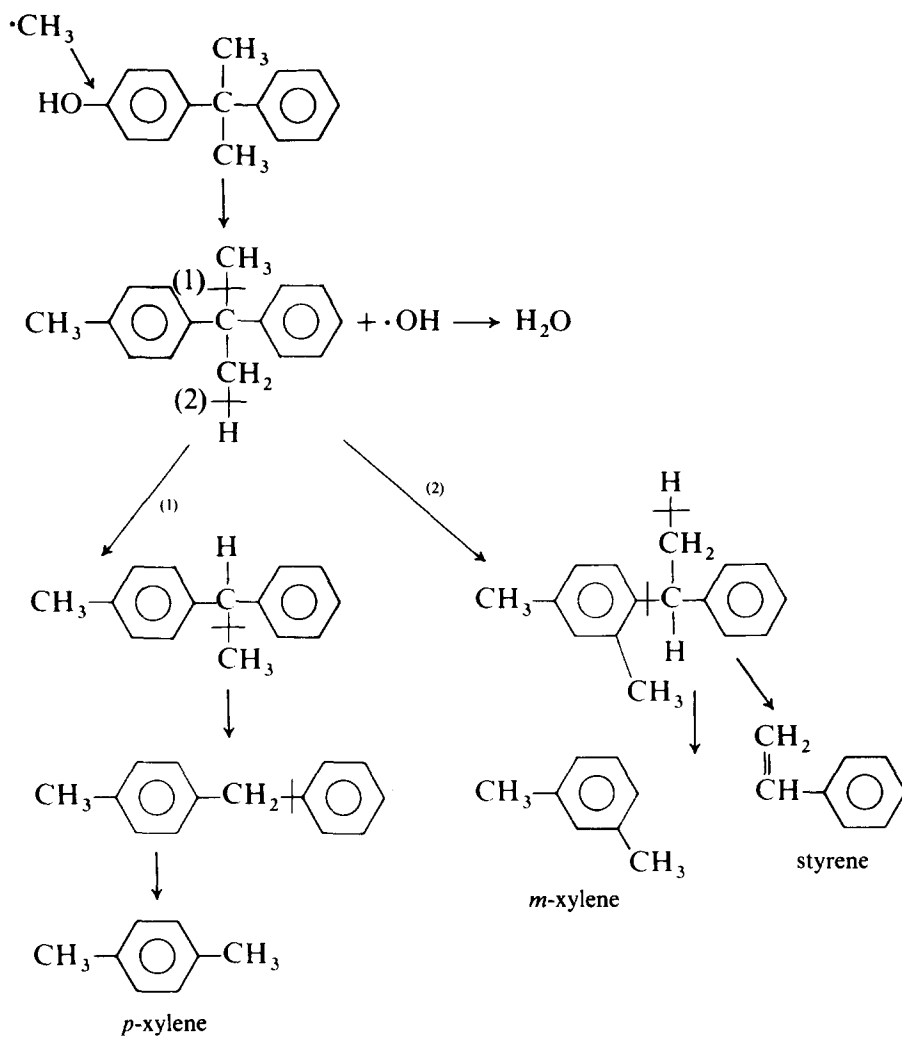


In this way both phenolic and non-phenolic aromatic structures become incorporated into the residual polymer, some of them ultimately appearing in volatile products. The volatile phenolic products will be formed in reactions analogous to those suggested for the thermal reaction. The non-phenolic products, which are entirely absent in the thermal reaction, are a dominant feature of the photo-degradation reaction and the mechanism of their formation may be represented as in Scheme 1, bisphenol-A or the corresponding monohydroxy compound being assumed to be the precursor.

The first product in Table 1 was presented as *m*- and/or *p*-xylene and/or ethyl benzene. These compounds have similar chromatographic retention



times and mass spectrometric fragmentation patterns so that absolute individual identification was not possible. The formation of ethyl benzene is much more easily explained, as in Scheme 1, than that of the xylenes. However, possible mechanisms for the production of *m*- and *p*-xylene are outlined in Scheme 2.



Scheme 2

REFERENCES

1. N. Grassie, M. I. Guy and N. H. Tennent, *Polym. Deg. and Stab.*, **12**, 65 (1985).
2. N. Grassie, M. I. Guy and N. H. Tennent, *Polym. Deg. and Stab.*, **13**, 21 (1985).