Thermal Degradation and Flame Resistivity of Tetrabrominated Epoxy Resin

Shigeo Nara[a]; Kentaro Matsuyama[a]

[a] Ibaraki Annex Electrical Communication Laboratory Tokai, Ibaraki, Japan

PLEASE SCROLL DOWN FOR ARTICLE

Thermal Degradation and Flame Resistivity of Tetrabrominated Epoxy Resin

SHIGEO NARA and KENTARO MATSUYAMA

Ibaraki Annex
Electrical Communication Laboratory
Tokai, Ibaraki, Japan

SUMMARY

The thermal degradation mechanism of tetrabrominated epoxy resin was investigated in order to explain its flame retardant mechanism. From the results obtained it was concluded that the flame retardant mechanisms are 1) a lowering of temperature through degradation and 2) the formation of hydrogen bromide and its role in catalysis in the condensation reaction of the resin.

These mechanisms were investigated by the pyrolysis behavior of the resin by gas chromatography, thermal gravimetric analysis, and differential thermal analysis studies.

INTRODUCTION

Flame resistant polymers have been worthy of investigation by material scientists dealing with electrical communication devices because organic insulators have been used under conditions of very high temperatures. Halogen and phosphorous compounds are quite commonly employed today in flame resistant polymers, but the flame resistant mechanism is not well understood. We have studied the mechanism of the flame resistivity of tetrabrominated epoxy resin by considering the pyrolysis behavior of the resin up to 600°C.

1205

The formula of tetrabrominated epoxy resin is:

$$CH_2 - CH - CH_2 - O - \overset{Br}{\underset{Br}{\bigcirc}} - \overset{CH_3}{\underset{CH_3}{C}} - \overset{Br}{\underset{Br}{\bigcirc}} - O - CH_2 - CH - CH_2$$
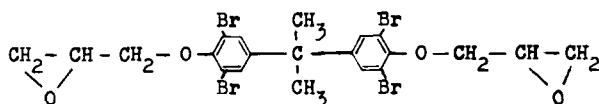
EXPERIMENTS

Materials

DER #542 (Dow Company Ltd.) was used as the tetrabrominated epoxy resin sample, and Epikote #1001 (Shell Company Ltd.) was used as the non-brominated epoxy resin. These materials did not react with the curing agent.

Gas Chromatography

The pyrolysis products were observed by gas chromatography (Shimadzu Co., GC-2C type). Samples of 10 mg were pyrolyzed in a carrier gas atmosphere (He gas) at 300~600°C for 10 sec. Just after the pyrolysis, the gases produced were introduced into the gas chromatography column (150°C), packed with dinonylphthalate, and with a flowing He carrier gas at 23 ml/min.

TGA and DTA

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out, and the thermograms of one sample were observed at the same time with a thermal analyzer Catalog Model No. 8002 CS of Rigaku Electric Co., Ltd.

DTA and TGA studies were made using a 10-mg sample which was heated at a constant rate (1°C/min~20°C/min) from room temperature to 600°C in an atmosphere of air or N_2 gas.

Infrared Spectroscopy

Pyrolyzed gas products and residual materials were observed by IR
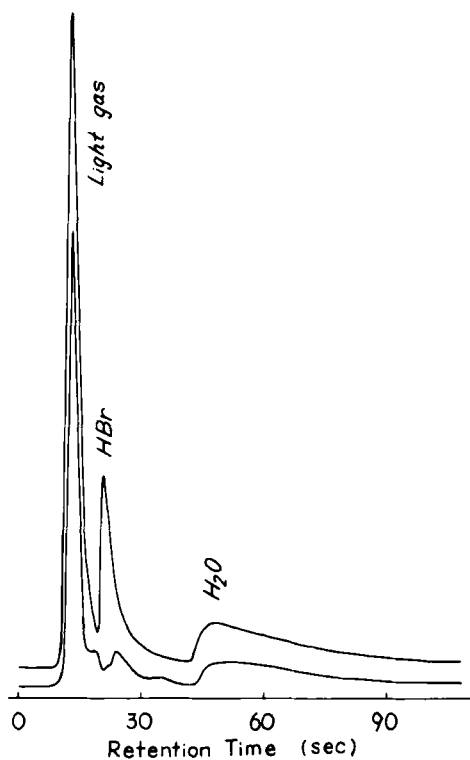
Fig. 1. Pyrogram of brominated and nonbrominated epoxy resin. Ten milligram sample, 500°C, for 10 sec in He.

spectroscopy. The gas products were captured in a gas cell made of KRS-5 crystal, and the charred materials were dissolved in acetone and dried on an NaCl plate. IR spectra of these samples were observed with a Hitachi EPI-S2 type IR spectrophotometer at room temperature.

Molecular Weight Measurements

   The molecular weights of tetrabrominated epoxy resin and its pyrolyzed

chars were measured by the osmotic pressure method with benzene at a concentration of $10^{-3} \sim 10^{-4}$ mole/liter, as solvent.

RESULTS

Pyrolysis Gas Chromatography

DER #542 and Epikote #1001 were pyrolyzed at $500°C$ for 10 sec in a He atmosphere. Their gas chromatograms are shown in Fig. 1.

Light gases and water were detected in brominated and nonbrominated epoxy resins, but it is worth noting that there was formation of hydrogen bromide gas in brominated epoxy resin only.

IR spectra of the pyrolyzed gases are shown in Fig. 2. From the spectra it was concluded that hydrogen bromide gas was really formed.
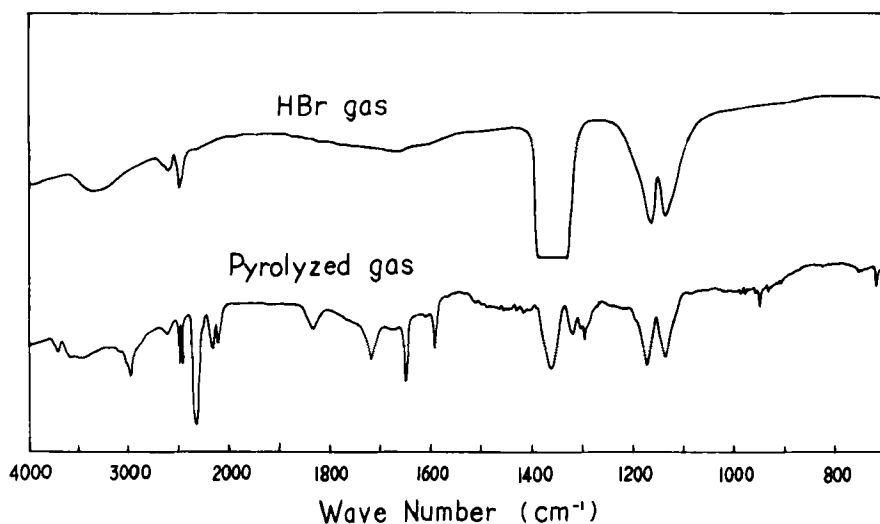
Fig. 2. IR spectra of HBr gas and pyrolyzed gas of the brominated epoxy resin.

Hydrogen bromide gas was generated by dropping hydrobromic acid into hot sulfonic acid. The gas generating was introduced and bubbled into sulfonic acid, and we staged it to the gas cell and the microsyringe for the measurements by IR and gas chromatography, respectively.
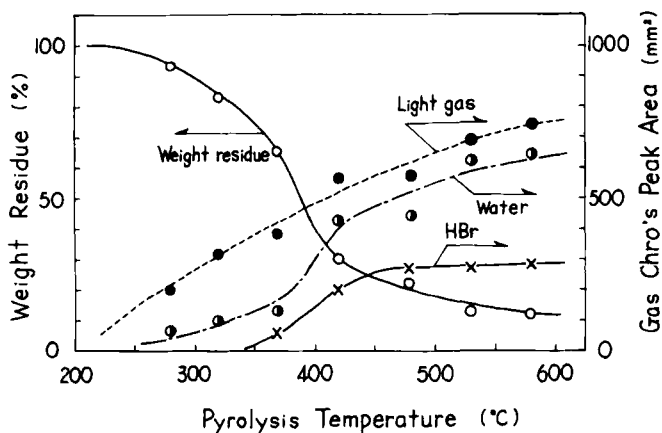
Fig. 3. Thermal degradation and formation of light gases, HBr, and water of brominated epoxy resin in He. Pyrolysis times are all 10 sec.

We will now discuss the thermal decomposition and the mechanism of flame resistivity of tetrabrominated epoxy resin by weight change and the generation of hydrogen bromide gas.

In Fig. 3, we show the relation of weight decrease of tetrabominated epoxy resin (4 mg) and the formation of light gases, hydrogen bromide, and water by pyrolysis at various temperatures for 10 sec in He atmosphere.

The sample residue decreased with increasing pyrolysis temperature while the light gases and water evolved increased. The production of hydrogen bromide accelerated near 400°C and it leveled off at about 500°C.

We carried out mild pyrolysis of the brominated resin by isothermal decomposition of the resin at 300°C in He atmosphere. The results are shown in Fig. 4, and the change in the molecular weight of the residued materials are also shown in this figure. The decomposition of the resin began after about 30 sec at 300°C, and the molecular weight fell from 750 (original weight) to 400 at about 40 sec but after this it increased abruptly as pyrolysis progressed and the resin finally condensed as a carbonized material.

Figures 5 and 6 show the gas chromatograms of the gases produced and the IR spectra of the residue produced by this pyrolysis, as shown in Fig. 4, respectively. From these results, the peaks of hydrogen bromide gas in gas chromatograms were observed from a pyrolysis time of 40 sec, and we also investigated the ⬡-Br band [i] at 720 cm^{-1} in IR spectra at the same time.
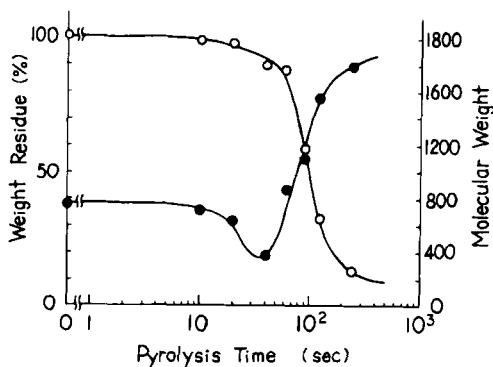
Fig. 4. Thermal degradation and molecular weight change of the brominated epoxy resin at 300°C.
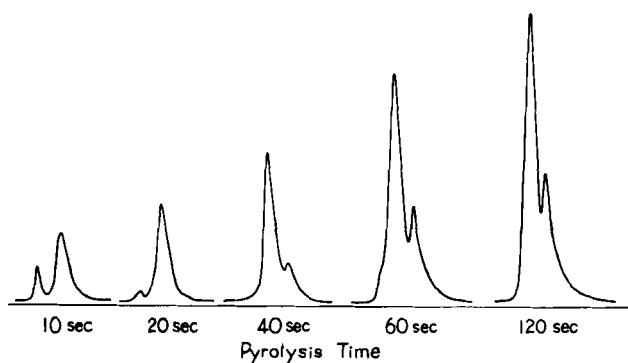
Fig. 5. Pyrogram of the brominated resin pyrolyzed at 300°C for various times in He.

More important results are shown in Fig. 6, that is, the epoxide groups disappear in comparison with the rate of decay of ⟨ ⟩—Br groups, and the disappearance of epoxide groups corresponds to the molecular weight decrease in Fig. 4.

TGA and DTA

In order to understand the detailed mechanism of the pyrolysis of tetra-brominated epoxy resin, we carried out DTA and TGA studies of the resin.

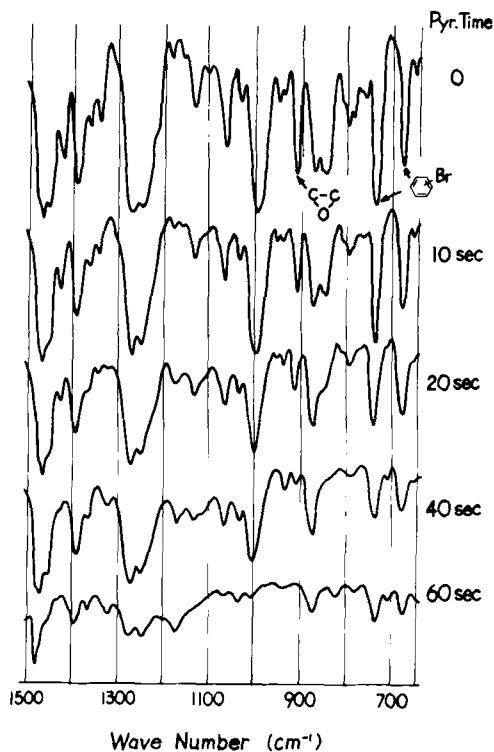**Fig. 6.** IR spectra of residue materials from thermal degradation of the brominated resin at 300°C for various times in He.

TGA results on brominated resin are shown in Fig. 7, which was obtained under various heating rates in an air atmosphere.

Brominated resin is obviously more unstable thermally than nonbrominated epoxy, and three temperature regions in which the weight decrease was very rapid were found. When TGA was performed at a very slow heating rate, we obtained the results of Fig. 8, and the isothermal decomposition of the resin at 300°C are shown in Fig. 9.

From the above-mentioned results, we concluded that thermal degradation of the resin occurred in three steps (the first, second and third drops), which hereafter will be identified as the A, B, and C regions, respectively.

We were interested in the results shown in Figs. 8 and 9, that is, the percent loss of weight in the A and B regions which correspond to the
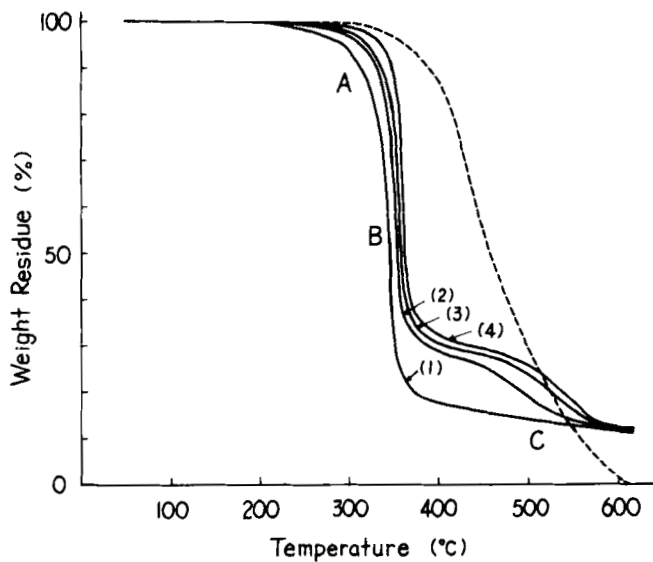
Fig. 7. TGA curves of the brominated resin in air. Heating rate; (1) 5,
(2) 10, (3) 15, and (4) 20°C/min. Dotted line is the nonbrominated resin
at 15°C/min.
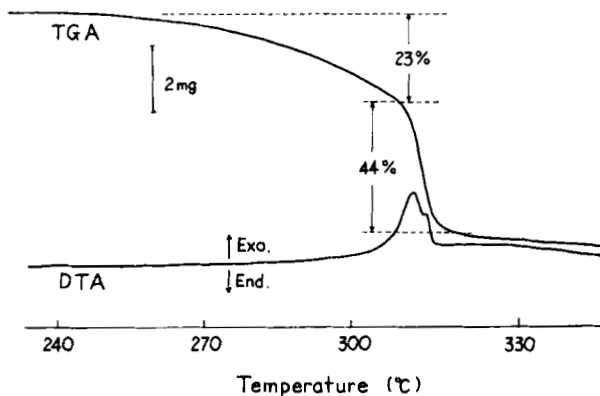
Fig. 8. TGA and DTA curve of the brominated resin at a heating rate of
1°C/min.

Fig. 9. Isothermal degradation of the brominated resin at 300°C.

molecular weight ratio of CH_2 –CH–CH_2 –O and the bromine parts of
$$\backslash \quad / $$
$$O$$
tetrabrominated epoxy resin, and this will be discussed later.

The activation energies of the pyrolysis of the brominated resin in the three decomposition regions were obtained by Ozawa's method [2]. These results are illustrated in Fig. 10, and the activation energies of regions A, B, and C are 25.3, 67.5, and 20.0 kcal/mole, respectively.
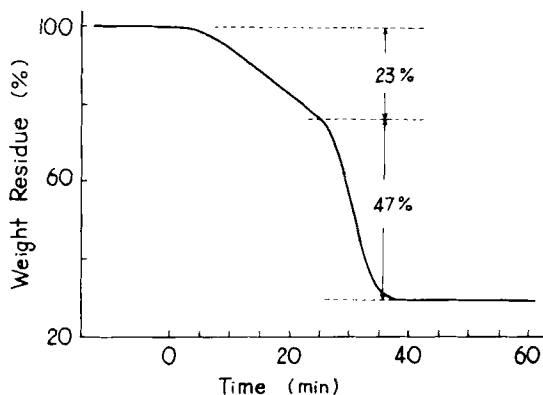
We show, in Fig. 11, DTA curves of the tetrabrominated epoxy resin. They were obtained at the same time as the measurements of TGA in Fig. 7, and the peak temperatures became higher under larger heating rates. The DTA thermograms of the resin showed two exotherms with peaks at about 360 and 550~600°C in air. In nitrogen, the new endotherm peaks appeared at 310 and 380°C, and the exotherm peak at about 600°C disappeared.

DISCUSSIONS

According to the results of pyrolysis gas chromatography, the brominated resin is not as thermally stable as the usual epoxy resin, and the carbonized residue of the brominated resin is greater than that of the nonbrominated resin. Furthermore, the formation of hydrogen bromide gas by thermal degradation should be mentioned. Hydrogen bromide is the catalyst for the condensation reaction, as is well known, and it may also act as the catalyst for the carbonized reaction of the resin.
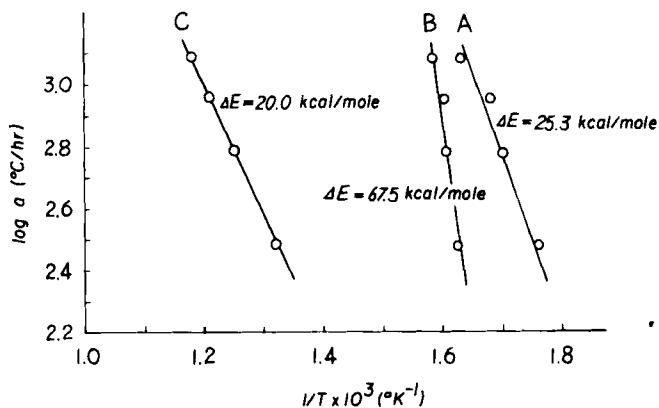
Fig. 10. Activation energies of the thermal degradation region of A, B, and C of the brominated resin by Ozawa's method.
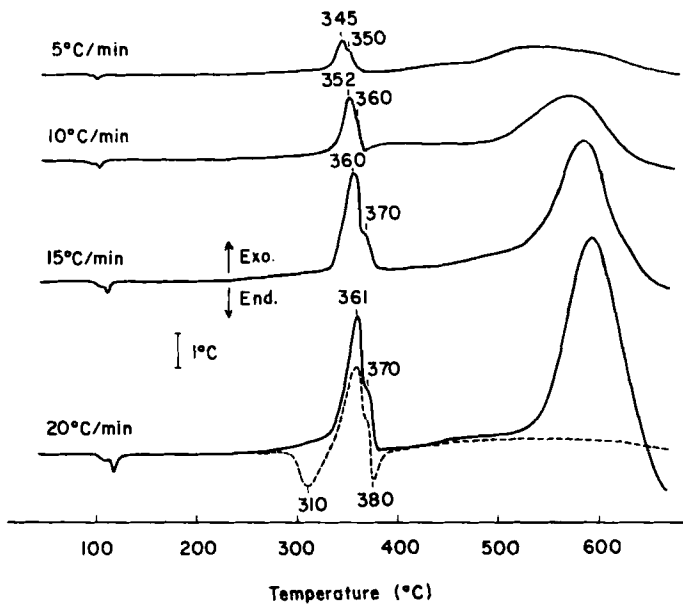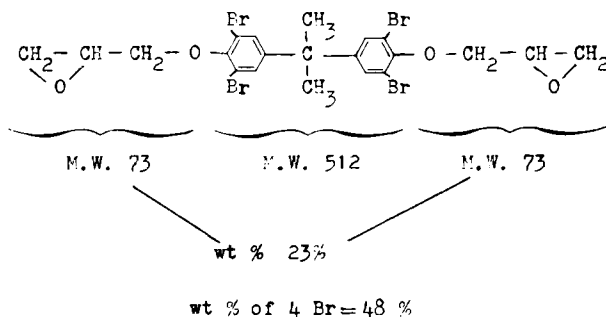

Fig. 11. DTA curves of the brominated resin in air. Dotted line is in N_2.

In addition, from the results of the measurement of the molecular weight change and IR spectroscopy of the decomposed materials, the weight loss percent of TGA curves in the decomposition Region B, we conclude the pyrolysis mechanism is as follows: In Region A the epichlorohydrin parts of the brominated epoxy resin are separated by the scission of ether bonding. Region B bromine is separated from the phenyl groups and forms hydrogen bromide gas. It is shown by the disappearance of epoxide groups,

but Br band is more stable than the epoxide groups in the IR

spectra of Fig. 6, and the decrease of molecular weight in Fig. 4. This is very clear from the illustration of the formula and molecular weights of tetrabrominated epoxy resin.

$$CH_2 - CH - CH_2 - O -\text{[}Br\text{]}- \underset{CH_3}{\overset{CH_3}{C}} -\text{[}Br\text{]}- O - CH_2 - CH - CH_2$$

M.W. 73   M.W. 512   M.W. 73

wt % 23%

wt % of 4 Br = 48 %

The weight decrease in Regions A and B corresponds to the weight percent of the epichlorohydrin parts and four bromines.

This mechanism is also explained by DTA results. The endotherm peaks at about 110°C correspond to the melting point of the resin. The first exothermic reaction occurs simultaneously with the major weight loss; this exothermic peak may be oxidization and the formation of light gases and hydrogen bromide. The second exothermic reaction is possibly due to the bond formation (condensation) and combustion of the resin. But in a nitrogen atmosphere, two endothermic reactions occur at about 310 and 380°C.

From the above discussions it is concluded that, in nitrogen atmosphere, the ether bonding is scissioned and hydrogen is formed at the first and second endothermic processes, respectively. Accordingly, the two endotherm peaks in air are apparently overshadowed by the large exothermic reaction which is attributed to the oxidized process.

The large exothermic reaction at about 600°C may be due to the combustion and condensation reactions.

The activation energy in Region B, obtained from Fig. 10, corresponds to the C—Br bond energy. However, the calculated values in Regions A and C are not presently understood.

Therefore, we illustrate the mechanism of thermal decomposition of tetrabrominated epoxy resin as shown on the following page.

Accordingly, the flame retardant mechanisms of tetrabrominated epoxy resin are due to 1) a lower temperature through decomposition, and 2) the generation of hydrogen bromide gas by thermal decomposition and its role in the catalysis of the carbonization reaction. The first mechanism can be
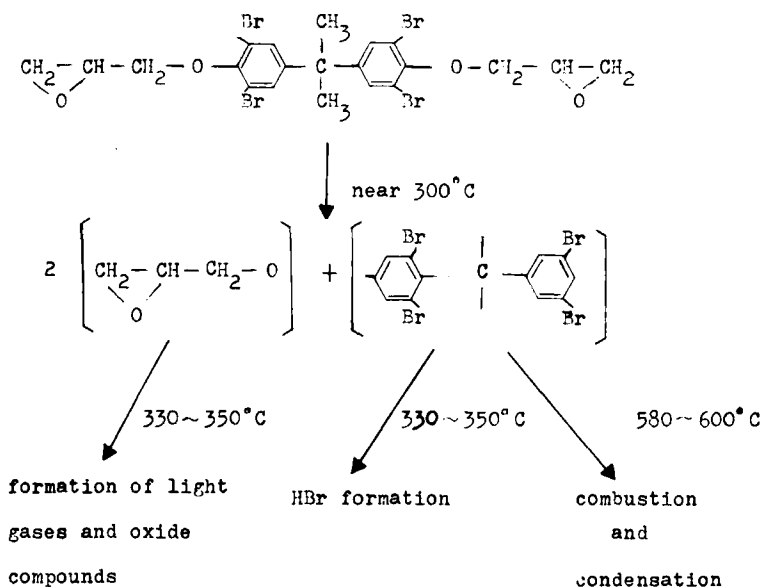
understood by Schmidt's rule [3], that is, the organic molecule having the following structure is easily scissioned by the resonance effect:
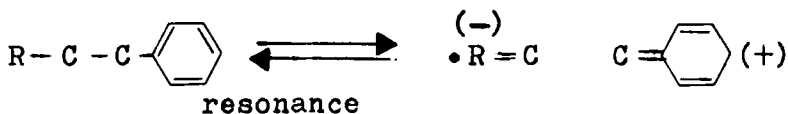
From the above effect by heat treatment, tetrabrominated epoxy resin,

having the electronegative bromine substituted on a conjugated system,
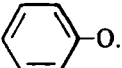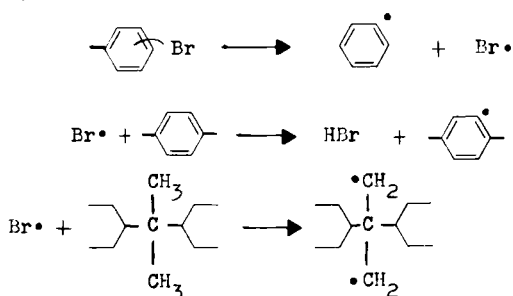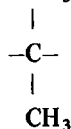
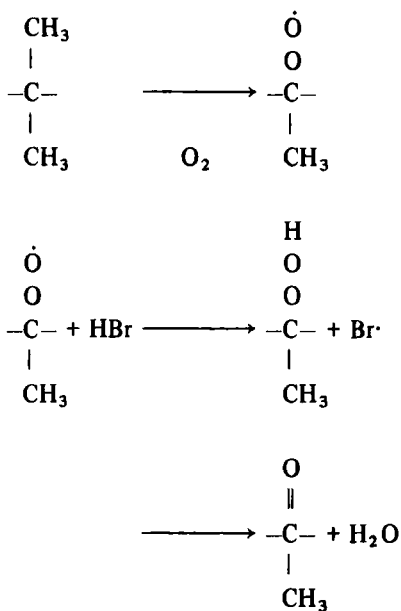is easily scissioned to the ether bonding 〈benzene ring〉-O.

Furthermore, the condensation reaction is assumed to be:

$$-\langle\text{ring}\rangle\text{Br} \longrightarrow \langle\text{ring}\rangle^{\bullet} + \text{Br}\bullet$$

$$\text{Br}\bullet + -\langle\text{ring}\rangle- \longrightarrow \text{HBr} + -\langle\text{ring}\rangle^{\bullet}-$$

$$\text{Br}\bullet + \quad \rangle-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\langle \longrightarrow \rangle-\overset{\displaystyle \bullet CH_2}{\underset{\displaystyle \bullet CH_2}{\overset{|}{\underset{|}{C}}}}-\langle$$

The carbonized reaction of the brominated resin may proceed by the above-
described processes, and the protection effect of CH_3 groups have been

$$-\overset{|}{\underset{|}{C}}-$$
$$CH_3$$

considered as follows;

$$\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{-C-}}}} \quad\xrightarrow{\quad O_2\quad}\quad \overset{\displaystyle \overset{\bullet}{O}}{\underset{\displaystyle CH_3}{\overset{\displaystyle O}{\underset{|}{\overset{|}{-C-}}}}}$$

$$\overset{\displaystyle \overset{\bullet}{O}}{\underset{\displaystyle CH_3}{\overset{\displaystyle O}{\underset{|}{\overset{|}{-C-}}}}} + \text{HBr} \longrightarrow \overset{\displaystyle H}{\underset{\displaystyle CH_3}{\overset{\displaystyle O}{\underset{|}{\overset{\displaystyle O}{\overset{|}{-C-}}}}}} + \text{Br}\bullet$$

$$\longrightarrow \overset{\displaystyle O}{\underset{\displaystyle CH_3}{\overset{\|}{\underset{|}{-C-}}}} + H_2O$$

REFERENCES

[1]   W. Herbert, M. Joseph, and T. Spalik, *Polym. Eng. Sci.,* **5**, 39 (1965).
[2]   T. Ozawa, *Bull. Chem. Soc. Jap.,* **38**, 1881 (1965).
[3]   Schmidt, *Z. Phys. Chem.,* **A159**, 337 (1932).