High-resolution pyrolysis-gas chromatography for the study of epoxy resins cured with prepolymers of varying molecular weight

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Epoxy resins cured with prepolymers of varying molecular weight were studied by high-resolution pyrolysis-gas chromatography. Various phenols and the glycidylethers of bisphenol A characteristic of the prepolymer backbone were observed in the pyrograms of the prepolymers. In addition, pyrolysates characteristic of the curing agents were also observed in cured resin systems. In both cases, the peak intensities changed as a function of the molecular weight of the original prepolymers. The molecular weights of the original prepolymers were calculated from the peak intensities of the characteristic products for the uncured prepolymers and the cured resins.

(Keywords: high-resolution Py-g.c.; epoxy resin; bisphenol A-type prepolymer; number-average molecular weight; epoxide equivalent weight)

INTRODUCTION

Recently, polymeric materials such as epoxy resins, which are highly effective as electrical insulation, adhesives, coatings and reinforced plastics, have met with wide acceptance in industry because of their excellent physicochemical properties. The variety of their properties directly depends on their chemical structures, which can be changed by differing the chemical composition and the conditions of the cure reactions. The types and the molecular weight of the prepolymers are among the important factors which influence the chemical composition and the crosslinking density of the resulting resins.

The molecular weight and the types of the epoxy prepolymers are most extensively studied by liquid chromatography (l.c.), including size exclusion chromatography (s.e.c.). Eppert *et al.*[1] analysed bisphenol A-type epoxy prepolymers by high performance liquid chromatography (h.p.l.c.). In addition to the bisphenol A-type oligomers, by-products with glycolic, phenolic and chlorohydrinic terminal groups were separated. The same technique was also utilized to monitor variations in the composition of commercial epoxy resin prepreg materials[2]. S.e.c. has been shown to be a powerful technique for analysing the molecular weight distribution of epoxy prepolymers after suitable calibration[3,4]. More recently, Gorshkov *et al.*[5] have proposed a technique where l.c. operated near the polymer adsorption critical point was combined with s.e.c. to simultaneously analyse the functionality types and molecular weight distribution of the epoxy prepolymers. Rogers[6] showed that information obtained by ^{1}H n.m.r. and s.e.c. could be utilized for the analysis of bisphenol A-type prepolymers.

In contrast to the above-mentioned techniques, high-resolution pyrolysis-gas chromatography (Py-g.c.) has been shown to be a powerful technique for analysing both cured epoxy resins and the prepolymers[7,8]. In these studies, the identification of the epoxy prepolymers and the curing agents was carried out and the curing processes were studied by analysing the changes in the peak intensities of the characteristic pyrolysis products.

In this paper, epoxy prepolymers of varying molecular weight before and after curing with diamine, dicarboxylic acid anhydride or imidazole accelerator are studied by high-resolution Py-g.c. In the pyrograms of the prepolymers, various pyrolysates characteristic of the prepolymer backbone are observed in addition to the intact diglycidylether of bisphenol A (DGEBA). Various pyrolysates characteristic of the curing agents are also observed in the pyrograms of cured resin samples. The peak intensities of these characteristic products change with the molecular weight of the prepolymers. The epoxide equivalent weight (EEW) of the original prepolymers is estimated from the peak intensity of these characteristic products for the uncured prepolymers and the cured resins with dicarboxylic acid anhydride. The mechanisms of formation of certain pyrolysates are discussed in connection with the possible structural differences caused by varying the molecular weights of the prepolymers.

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EXPERIMENTAL

Conditions for Py-g.c.

A vertical microfurnace-type pyrolyser (Yanagimoto GP-1018) was directly coupled to a gas chromatograph (Shimadzu GC9A) with a flame ionization detector (f.i.d.) and a high-resolution fused silica capillary column (0.25 mm i.d. × 25 m long) coated with immobilized methylphenylsilicone (5% phenyl, 0.25 μm) supplied by Quadrex. The capillary column was temperature programmed from 50 to 300°C at a rate of 4°C min^{-1}. The optimum pyrolysis temperature was empirically fixed at 590°C to ensure sufficient recovery of the characteristic products[7].

Additionally, another Py-g.c. system (Shimadzu GC7A with the same pyrolyser) was used with a fused silica capillary column (0.25 mm i.d. × 60 m long) coated with immobilized cyanopropylphenylmethylsilicone (7% cyanopropyl and 7% phenyl, 0.25 μm) supplied by J & W. The column temperature was programmed from 10°C (4°C min^{-1}) to separate the lower boiling pyrolysates. In this case, a higher pyrolysis temperature of 640°C was adopted to enhance the yield of the lower pyrolysates. In both cases, the nitrogen carrier gas flow (50 ml min^{-1}) at the pyrolyser was reduced to 0.5 ml through a splitter. Weighed samples ($\sim 150\,\mu$g) were pyrolysed.

Materials

The bisphenol A-type epoxy prepolymers used are given in *Table 1* together with their number-average molecular weight ($\bar{M}_n$), molecular weight distribution ($\bar{M}_w/\bar{M}_n$) EEW and average degree of polymerization ($\bar{n}$). These prepolymers and cured resin samples were provided by Yuka Shell Epoxy Co. Ltd. The average molecular weights and the EEW of the prepolymers were determined by the supplier using s.e.c. and titration with perchloric acid, respectively. The $\bar{n}$ value was calculated according to the following relation:

$$\bar{n} = (\bar{M}_n - 340)/284 \qquad (1)$$

where 284 is the fractional molecular weight of the repeating unit contained in the prepolymer backbone shown in *Table 1* and 340 is that of the residual moiety related to the molecular terminals.

The compositions of the cured epoxy resin samples are listed in *Table 2* together with the associated prepolymers, curing agents and accelerators. The curing reaction of the epoxy resins with the curing agents and accelerators has been given previously[7].

Table 1 Bisphenol A-type[a] prepolymers used

Prepolymer	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	EEW	$\bar{n}$
E827	340	1.10	180–190	0.00
E1001	900	1.57	450–500	1.97
E1004	1600	1.74	875–975	4.44
E1007	2900	1.98	1750–2220	9.01

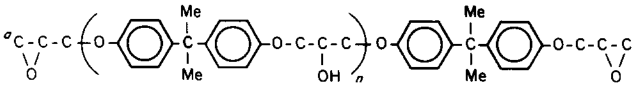


Table 2 Composition of the cured epoxy resin samples

Prepolymer	Curing agent[a]	Accelerator
1B2MZ-cured resin		
E827	—	1B2MZ (4)
E1001	—	1B2MZ (4)
E1004	—	1B2MZ (4)
E1007	—	1B2MZ (4)
DDM-cured resin		
E827	DDM (26.8)	—
E1001	DDM (10.5)	—
E1004	DDM (5.3)	–
E1007	DDM (2.6)	–
HHPA-cured resin		
E827	HHPA (70.7)	BDA[b] (0.5)
E1001	HHPA (27.8)	BDA (0.5)
E1004	HHPA (14.2)	BDA (0.5)
E1007	HHPA (6.2)	BDA (0.5)

[a] Weight per cent prepolymer

[b] Benzyldimethylamine

RESULT AND DISCUSSION

Prepolymers

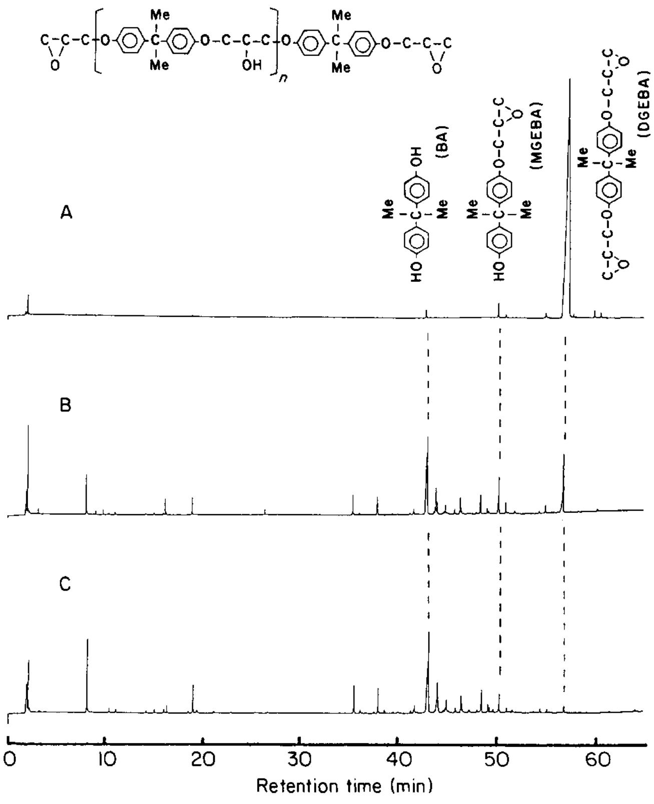
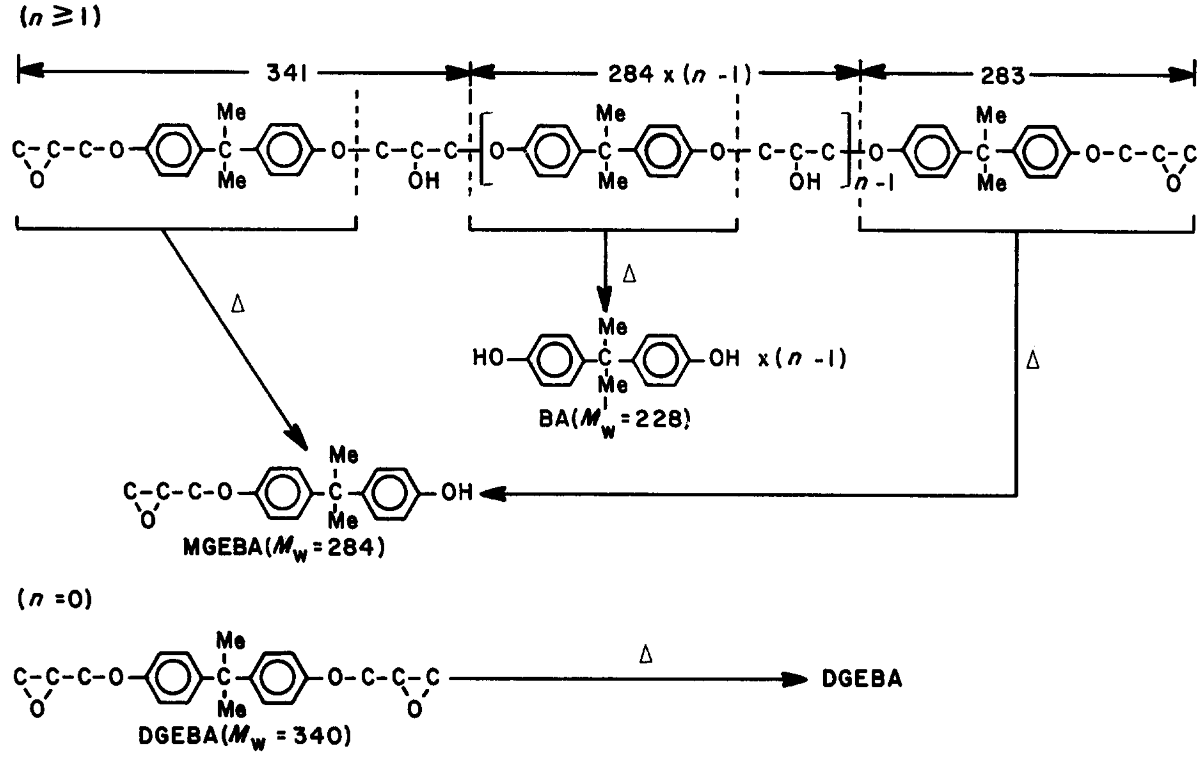


Figure 1 High-resolution pyrograms of prepolymers with various molecular weights at 590°C: (A) E827 ($\bar{n} = 0$); (B) E1001 ($\bar{n} = 1.97$); (C) E1004 ($\bar{n} = 4.44$)

Figure 1 shows pyrograms of typical prepolymers [E827 ($\bar{n} = 0$), E1001 ($\bar{n} = 1.97$) and E1004 ($\bar{n} = 4.44$)] at 590°C. An intense peak of the volatilized original monomer (DGEBA) is observed in the pyrogram of E827 together with minor peaks of the monoglycidylether of bisphenol A (MGEBA) and bisphenol A (BA), which are formed by the thermal degradation of DGEBA. On the other hand, relatively stronger peaks of low boiling pyrolysates and various phenols characteristic of the prepolymer skeleton are observed in the pyrograms of the prepolymers with higher molecular weights. The products with glycidyl functionalities decrease markedly with increase in molecular weight, while those of the characteristic phenols show the opposite tendency.

From these observations, the formation of DGEBA,



Scheme 1

MGEBA and BA from the prepolymers (*Scheme 1*) should be attributed mainly to the following processes, respectively:

1. Intact DGEBA contained in the sample is vaporized and recovered almost quantitatively as the associated peak in the pyrogram.
2. MGEBA is formed almost exclusively through the thermal degradation of the terminals of the prepolymers whose n is >1.
3. BA is mostly formed through the thermal degradation of the prepolymer backbone whose n is >2.

Here, when the numbers of BA, MGEBA and DGEBA molecules formed from a given prepolymer sample are n_b, n_m and n_d, respectively, the $\bar{M}_n$ for the sample is calculated from:

$$\begin{aligned}\bar{M}_n &= \Sigma n_i M_i / \Sigma n_i \\ &= [340 n_d + (341 + 283) n_m/2 + 284 n_b]/(n_d + n_m/2)\end{aligned} \qquad (2)$$

since the total number of sample molecules (Σn_i) is equal to $n_d + n_m/2$ and the total weight of sample molecules ($\Sigma n_i M_i$) is equal to $340n_d + (341 + 283)n_m/2 + 284n_b$, where 340, 341, 283 and 284 are the fractional molecular weight of the associated moiety. If peak intensities of BA(I_b), MGEBA (I_m) and DGEBA (I_d) in the pyrograms are observed for the prepolymer sample, the molecular numbers for the corresponding components are calculated as follows:

$$\begin{aligned} n_b &= kI_b/13.8 \\ n_m &= kI_m/15.4 \\ n_d &= kI_d/17.0 \end{aligned} \qquad (3)$$

where 13.8, 15.4 and 17.0 are the effective carbon numbers for BA, MGEBA and DGEBA to the f.i.d., respectively, and k is a common constant. Combining equations (2) and (3), $\bar{M}_n$ can be expressed as follows:

$$\bar{M}_n = (5240 I_d + 5300 I_m + 5391 I_b)/(15.4 I_d + 8.5 I_m) \qquad (4)$$

Table 3 Number-average molecular weight and epoxide equivalent weight of uncured prepolymers and HHPA-cured resins

Prepolymer	$\bar{M}_n$[a]	EEW[a]
Uncured prepolymers[b]		
E827	375 (340)	188 (180–190)
E1001	699 (900)	350 (450–500)
E1004	1820 (1600)	909 (875–975)
E1007	3670 (2900)	1830 (1750–2220)
HHPA-cured resins[c]		
E827	370[d]	185[d]
E1001	896	448
E1004	1690	844
E1007	3690	1840

[a] Values in parentheses were obtained by the supplier (see *Table 1*)
[b] Calculated from the peak intensities of BA, MGEBA and DGEBA
[c] Calculated from the relative peak intensity of HHPA
[d] Standard values for calculation

The $\bar{M}_n$ values estimated by equation (4) are listed in *Table 3* together with the EEW values which are simply calculated as $\bar{M}_n/2$. Generally, these observed values are in fairly good agreement with the corresponding values obtained by the manufacturer even though the recovery rate (%) of the original prepolymers as the pyrolysates in the pyrograms are relatively low for the prepolymers with higher molecular weights (the values for E1001, E1004 and E1007 relative to E827 are 59, 50 and 47, respectively). The smaller $\bar{M}_n$ value for E1007 by s.e.c. might be attributed to the inadequate column calibration of s.e.c. using polystyrene standards for epoxy prepolymers at higher molecular weight.

Typical pyrograms in the low boiling point region for the prepolymers are shown in *Figure 2*. Characteristic pyrolysates such as ethylene oxide, propylene, acetaldehyde, acrolein, acetone and allyl alcohol commonly observed in the pyrograms were also shown to change depending on the $\bar{n}$ values of the prepolymers. Relationships between the yields of these pyrolysates and the $\bar{n}$ values are shown in *Figure 3*. The yield is calculated as the observed peak intensity for the corresponding components normalized by the weight (μg) of epoxy prepolymer utilized. Among these, ethylene oxide and acrolein, which are presumably formed from the epoxide terminals as shown in *Scheme 2*, decrease markedly with increase in $\bar{n}$.

On the other hand, acetone and acetaldehyde show a tendency to increase slightly with increase in $\bar{n}$. Consequently, these pyrolysates are considered to be formed mainly from the 2-hydroxypropyl moieties of the prepolymer backbone as shown in *Scheme 3*. These results indicate that changes in the yields of the low boiling pyrolysates formed from epoxide terminals and 2-hydroxypropyl moieties in the prepolymer backbone also provide good information on the molecular weight of the prepolymers.

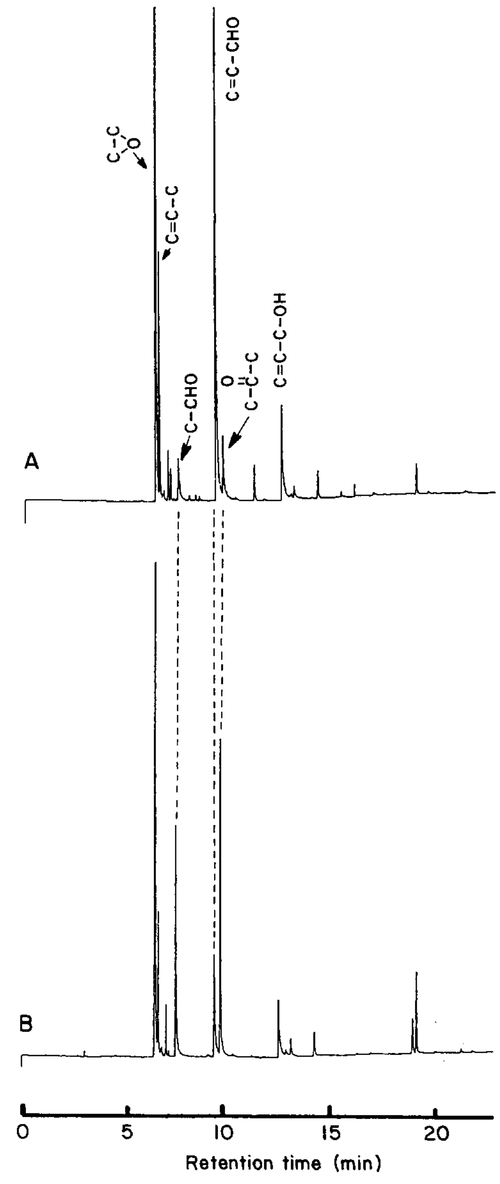


Figure 2 Pyrograms in the low boiling point region for prepolymers at 640°C: (A) E829 ($\bar{n}=0$); (B) E1007 ($\bar{n}=9.01$)

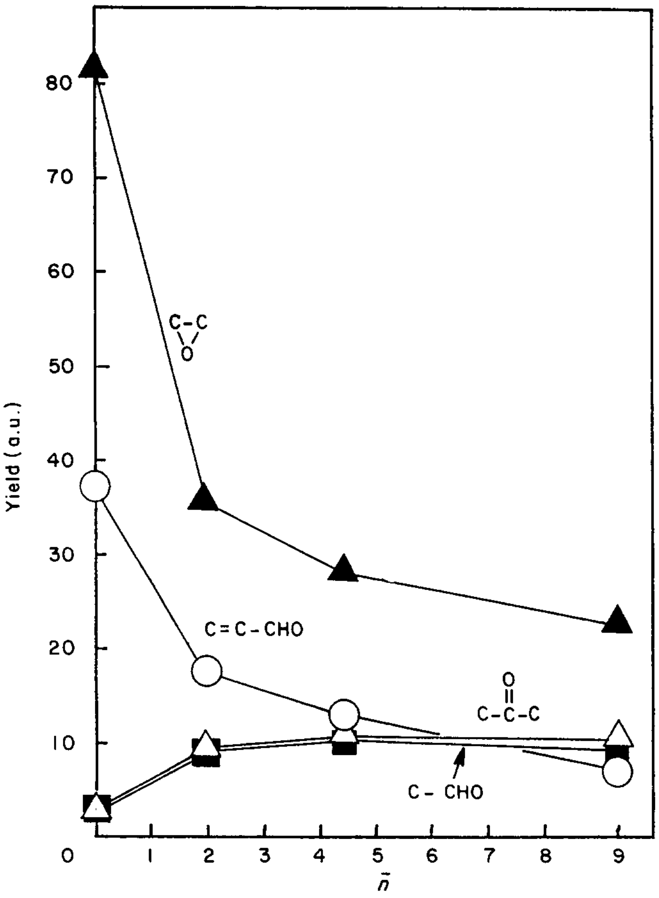
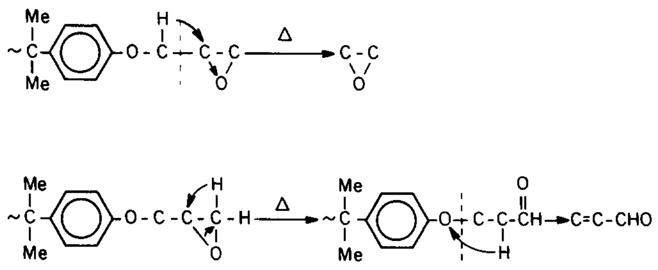
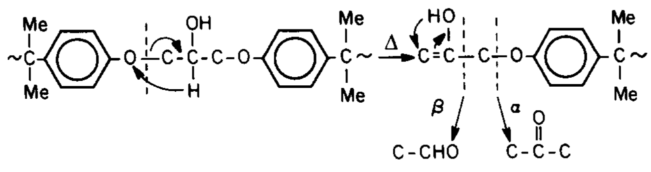


Figure 3 Relationship between the yield of low boiling pyrolysates and $\bar{n}$ for uncured prepolymers



Scheme 2



Scheme 3

Cured resin samples

Figure 4 shows typical pyrograms of the resin samples cured with hexahydrophthalic anhydride (HHPA). In addition to BA and various phenols characteristic of the prepolymer backbone, HHPA is observed in the pyrograms[7,8]. On the other hand, products with glycidyl terminals are scarcely observed even in the case of E827, showing that epoxide groups are almost quantitatively consumed through the curing reaction. As expected from the composition of the resins, the peak intensities of the phenols commonly increase with the molecular weight of the prepolymers used, whilst that of HHPA shows the opposite tendency. The peak intensity of HHPA should correspond to the weight of HHPA in the resin sample, provided that the reacted HHPA is quantitatively recovered in the pyrogram through pyrolysis. When a prepolymer with EEW of epoxide (E) is cured with HHPA ($\bar{M}_w = 154$), the HPPA content (W_h, wt%) of the resulting resin is expressed as:

$$\begin{aligned} W_h &= 100 \times 0.85 \times 154/(0.85 \times 154 + \mathrm{E}) \\ &= 1.31 \times 10^4/(1.31 \times 10^2 + \mathrm{E}) \qquad (5) \end{aligned}$$

since 0.85 mole of HHPA was added per mole of the epoxide group to obtain a resin with the least thermal deformation at elevated temperatures. Consequently, the relationships between the relative peak intensity (I') of HHPA and E for a given sample could be expressed as follows (since I' is directly proportional to W_h):

$$I' = 1.31 \times 10^4 k'/(1.31 \times 10^2 + \mathrm{E}) \qquad (6)$$

where k' is a constant. Here, the relative peak intensity (I') is calculated as the peak intensity normalized by the sum of peak intensities observed in the pyrogram. When k' is obtained from a given resin sample prepared from E827 (EEW = 185) for which I' is regarded to be 100, equation (6) could be reduced to:

$$\begin{aligned} E &= 1.31 \times 10^4 k'/(I' - 131) \\ &= 3.16 \times 10^4/(I' - 131) \qquad (7) \end{aligned}$$

By equation (7), the EEW for the prepolymer used for the resin cured with HHPA is estimated by using the I' value of HHPA in the resulting pyrogram. The estimated EEW values are listed in *Table 3* together with $\bar{M}_n$ values. Generally, these values correspond well with the values provided by the manufacturer and those obtained from the uncured prepolymers by Py-g.c.

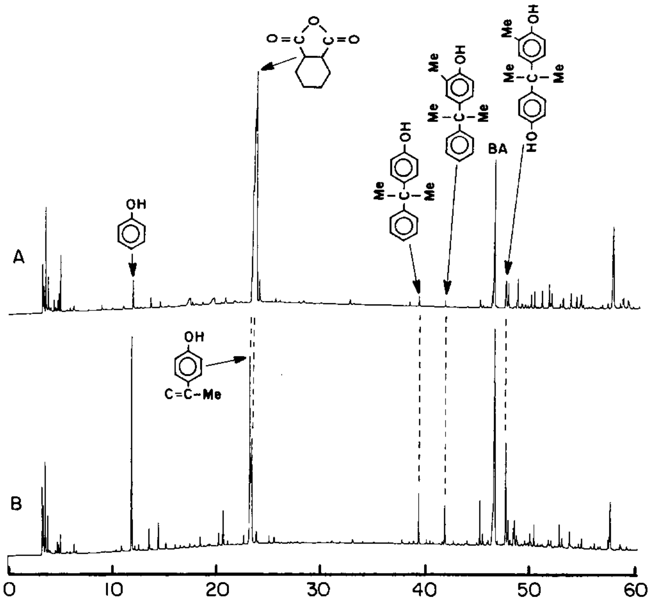


Figure 4 High-resolution pyrograms at 590°C for resin samples cured with HHPA: (A) E827 ($\bar{n} = 0$); (B) E1004 ($\bar{n} = 4.44$)

The pyrograms of the resin samples cured with an imidazole accelerator (1-benzyl-2-methylimidazole, 1B2MZ) were basically the same as those reported previously, in which very strong BA and characteristic phenols are commonly observed[7,8]. However, differences between the pyrograms for the cured resins for which the original prepolymer had different $\bar{M}_n$s were much less than those for the corresponding prepolymers. This phenomenon suggests that the glycidyl groups react to form networks through ether linkages behaving similarly to the 2-hydroxypropyl moiety in the prepolymer backbone during pyrolysis.

The pyrograms of the resin samples cured with diaminodiphenylmethane (DDM) were similar to those reported previously in which the additional peaks of N-methylated DDMs characteristic of the reacted curing agent were observed[7]. As in the case of HHPA-cured resins, the peak intensities of N-methylated DDMs increased with increase in DDM content of the resins, which in turn provides information on the molecular weight of the prepolymer.

When comparing the pyrograms for the cured resins in detail, the yields of some phenols are found to increase with the molecular weight of the prepolymers used in every case as shown in *Figure 5*. Here, the yield is defined as the observed peak area normalized by the amount (μg) of prepolymer contained in the sample. The formation of α-methylated BA and its homologue is associated with thermal rearrangements during pyrolysis[9]. The fact that these products are formed more abundantly from the cured resins prepared from the

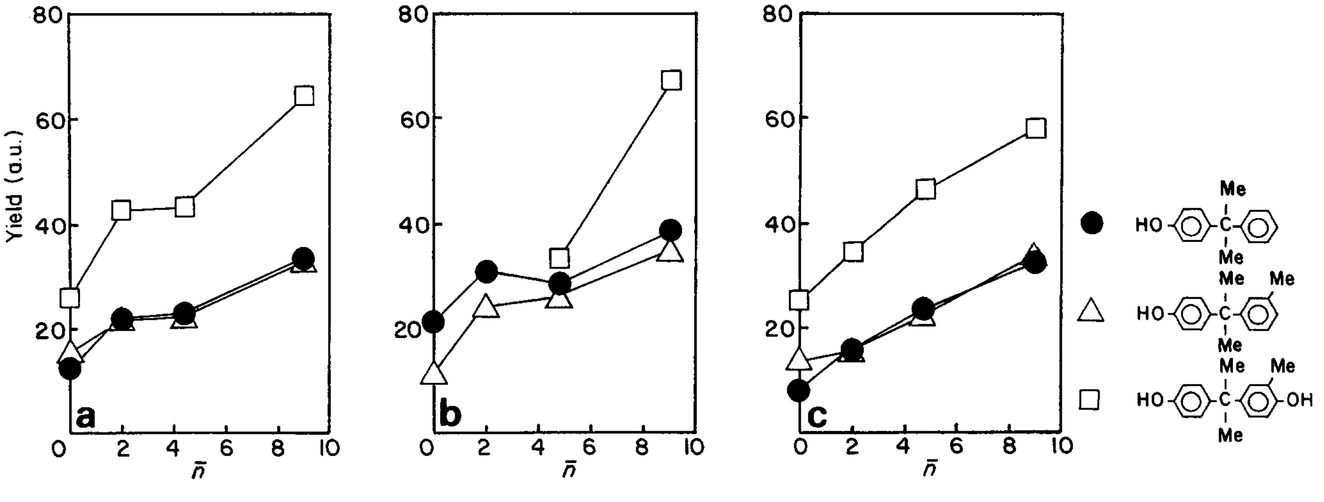


Figure 5 Relationship between the yield of characteristic phenols and $\bar{n}$ for the resin samples cured with (a) 1B2MZ, (b) DDM and (c) HHPA

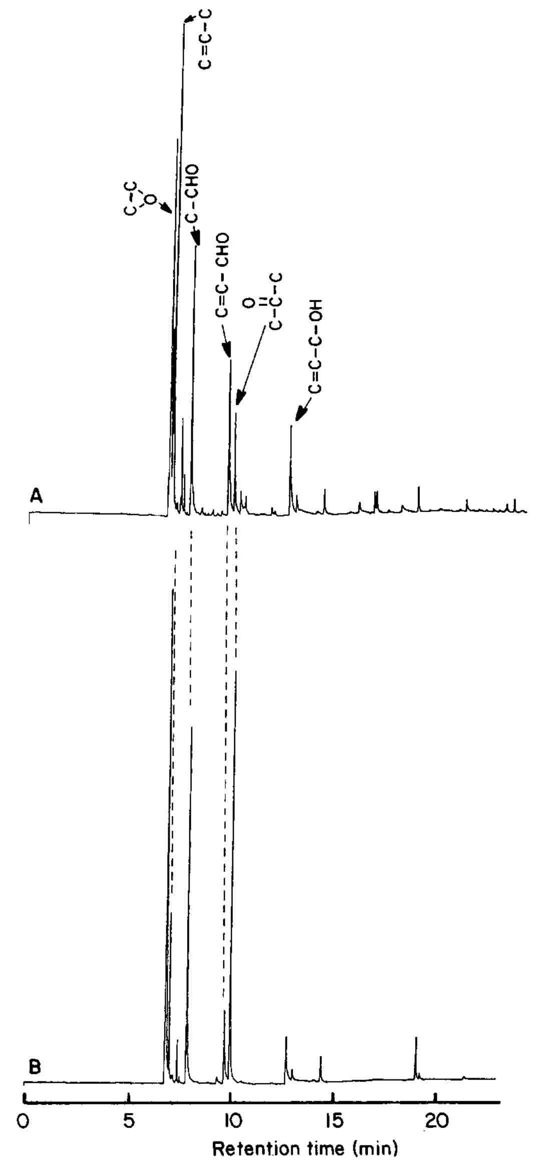


Figure 6 Pyrograms in the low boiling point region at 640°C for resin samples cured with 1B2MZ: (A) E827 ($\bar{n} = 0$); (B) E1007 ($\bar{n} = 9.01$)

prepolymers with higher $\bar{n}$ suggests that the formation of these products should be associated mainly with the benzene ring adjacent to the 2-hydroxypropyl moiety in the prepolymer backbone, rather than that attached to the reacted glycidyl moiety.

Typical expanded pyrograms at 640°C for the low boiling point region for the resin systems cured in the presence of imidazole accelerator are shown in *Figure 6*. These pyrograms consist of the common degradation products such as ethylene oxide, propylene, acetaldehyde, acrolein, acetone and allyl alcohol which are also observed for the uncured prepolymers (*Figure 2*). Furthermore, basically the same pyrolysates were also observed for the other resin systems curing in the presence of either DDM or HHPA. Relationships between the yields of the major pyrolysates and $\bar{n}$ of the prepolymers used for the cured resins are shown in *Figure 7*. Here it is interesting to note that the yield of ethylene oxide is almost constant in the case of 1B2MZ- and DDM-cured resins regardless of the change in $\bar{n}$, while it decreased markedly with increase in $\bar{n}$ for the uncured prepolymers (*Figure 3*). These results suggest that the residual amount of epoxide groups after curing becomes almost constant regardless of the molecular weight of the original prepolymers. A slight decrease in the yield of ethylene oxide with increase in $\bar{n}$ for the HHPA-cured resins might be related to the fact that 15% of the original epoxide group is left unreacted even after the cure is completed since 0.85 mole of HHPA is added per mole of epoxide group.

In general, pyrolysates whose yields increase with the increase in $\bar{n}$ should be mainly formed from the 2-hydroxypropyl moiety in the prepolymer backbone similar to the uncured prepolymers. On the other hand, formation of pyrolysates whose yields decrease with increase in $\bar{n}$ are closely associated with the reacted epoxide groups to form network structures. For example, pyrolysates such as propylene and acrolein might be formed mainly from the reacted epoxide moiety to form either linkage as shown in *Scheme 4* in the case of 1B2MZ-cured samples.

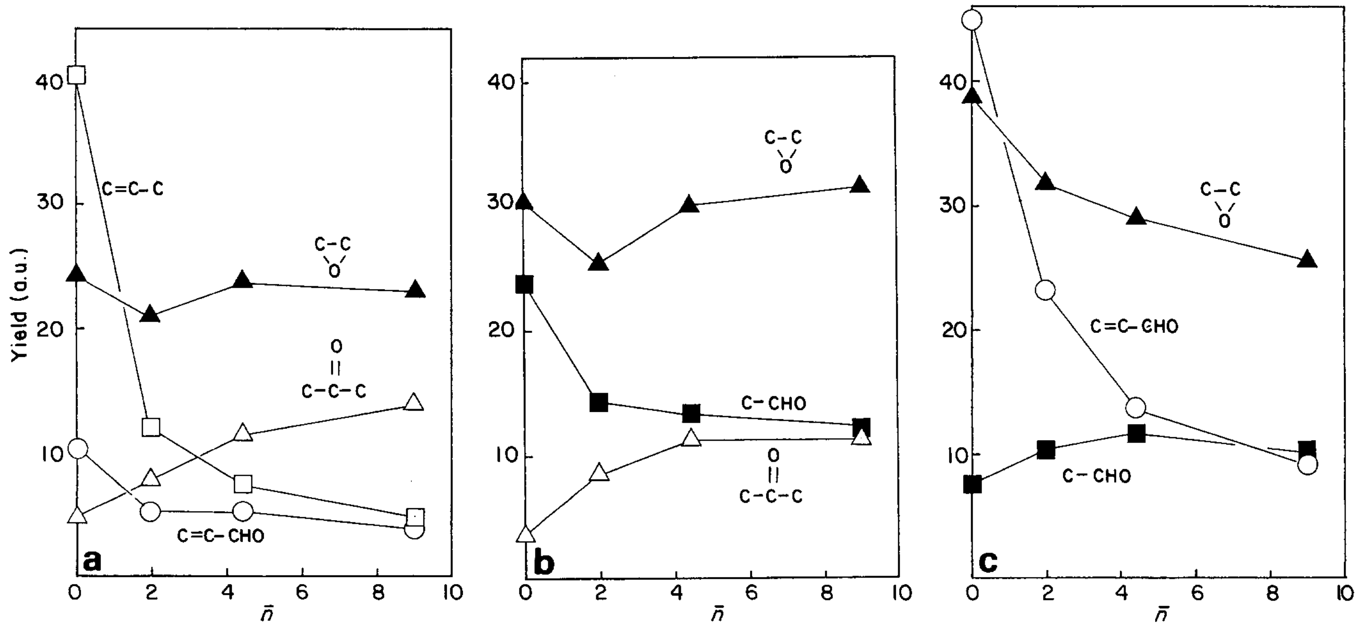
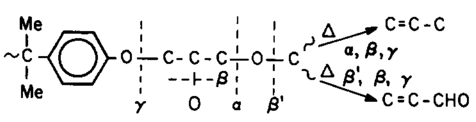
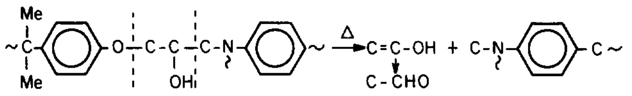


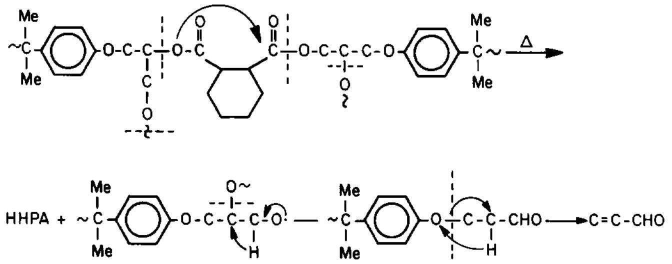
Figure 7 Relationship between the yield of low boiling pyrolysates and $\bar{n}$ for the resin samples cured with (a) 1B2MZ, (b) DDM and (c) HHPA



Scheme 4



Scheme 5



Scheme 6

Similarly, acetaldehyde formation from DDM-cured samples might be related to the reacted epoxide groups with DDM as shown in *Scheme 5*. The reaction in *Scheme 5* is also supported by the fact that the major pyrolysates from the reacted DDM moiety are N-methylated DDMs, while intact DDM is scarcely observed[7].

The acrolein formation from HHPA-cured samples might also be mainly attributed to the mechanism shown in *Scheme 6*, which involves the reaction of the epoxide group with HHPA[8]:

In conclusion, Py-g.c. proved to be a unique technique for characterizing epoxy resins cured with prepolymers of varying molecular weights. Various pyrolysates characteristic of the prepolymers and curing agents were identified in the resulting pyrograms. As long as the pyrolysis conditions are carefully controlled, the molecular weights of the original prepolymers could be accurately estimated not only for the uncured prepolymers but also for the cured resins with HHPA; this was difficult to carry out using other techniques.

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