

Epoxy Resins Based on Trimethylolpropane.

I. Determination of Chemical Structures

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SYNOPSIS

The chemical structure of an aliphatic epoxy resin was studied by using gel permeation chromatography (GPC), Fourier transform infrared (FTIR), FTIR-TGA (thermogravimetric analysis), mass spectrometry in fast atom bombardment (FAB) mode, and wet analysis. We found that when trimethylolpropane is used as starting monomer, only two OH groups are epoxidized. The resin and its different fractions have a functionality of two. Under the conditions of synthesis used by the supplier, three main products were found with masses of 246, 339, and 430. No trifunctional product was detected. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The epoxy resins based on aliphatic polyols are interesting because they impart flexibility to the final product, and the glass-transition temperature, T_g , is lower than aromatic epoxy resins which can be an important feature when the cure is close to room temperature. Our aim in the first part of this study was to determine the chemical structures, to identify the products, and to characterize them by using various analytical techniques.

The aliphatic resins should be useful products in civil engineering where cure at room temperature is necessary. The typical aromatic resins (mainly based on bisphenol A) need (for the full cure) two important kinds of additives: diluents (and/or solvents) to reduce the viscosity, and to plasticize, flexibilize, or dilute to lower $T_{g\infty}$. The connection between T_g , α , and the cure temperature, T_c , is well known. The epoxy systems cured with amines, without modification, have $T_{g\infty}$ values above 80°C and even well above 150°C when aromatic amines are used as curing agents. These systems cannot be used properly for curing at room temperature because the α value

obtained is low, and the reaction practically stops when $T_{gc} = T_c$ if $T_{gc} < T_{g\infty}$ (vitrification).

The additives tend to degrade the mechanical, chemical, and thermal properties and can be dangerous to health. On the other hand these products can affect the film formation adversely from an esthetic point of view (in the case of paint and levelling compounds). Even though the reactivity of aromatic epoxy resins is higher than aliphatic resins,¹ if we introduce OH groups in the resin the reactivity greatly increases, which is an important feature in many applications at room temperature.

EXPERIMENTAL

Materials

The aliphatic resin used was a glycidyl ether of trimethylolpropane (TMP), TRIEPOX GA (supplied by Gairesa, Spain). The resin was studied under purified and supplier form.

Purification of Resin

The best method found was water used as a solvent. We previously washed the resin with pentane in order to separate the chlorhydrins of low molecular weight. This previous separation was followed by

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gas chromatography (GC)-mass (we used a Perkin-Elmer GC Autosystem connected to a mass spectrometer, mod Q Mass 910 also Perkin-Elmer through a heating transfer line). We considered the resin ready for further purification when after several washings with pentane no more peaks appeared in further GC-mass spectra. These peaks were identified as chlorhydrins of low molecular weight.

The pentane-washed resin was treated with water to which we added sodium bisulfite to prevent emulsification (58 g resin, 500 mL water, and 0.3 bisulfite). After that we added 500 mL of chloroform to separate the resin from the water solution and it was distilled *in vacuo*. A residue that was not chloroform soluble was identified by Fourier transform infrared (FTIR) as TMP basically. The fractions obtained were: soluble in water, 39%; insoluble in water, 61%; TMP (no reaction), 5% (calculated on total resin).

TECHNIQUES

Gel Permeation Chromatography (GPC)

In order to separate the different species present in the resin, GPC was used. GPC study was carried out by using Spectra physics equipment with an isocratic pump (SP 100), universal injector system 50 μ L loop (Rheodyne 7125 SN), refraction index detector

(Shodex RI-71), integrator Spectra-physics (Data jet-CH2) and software package (Spectra-physics, winner/386).

We used a column (30 cm \times 7.8 mm i.d.) packet with 5 μ m spherical particles, with a exclusion limit of 4×10^3 \AA (Polymer Laboratories, ref. 1110-6520) and a column (30 cm \times 7.8 mm i.d.) packed with 5 μ m spherical particles and 1×10^3 \AA exclusion limit (Phenogel, ref. 00H-0442-KO). This was used to collect the GPC fractions. For calibration and sample analysis only the first column was used. Both columns were used to collect the fractions (carrier: THF at 1 mL/m). The column was calibrated by means of polystyrene standards ($M_w = 162, 680, 980, 1700, \text{ and } 2950$) and diglycidyl ether of bisphenol A (BADGE, $M_w = 340$).

Mass Spectrometry

Mass spectrometry tests were performed in a Kratos MS9/50 TC. The samples collected in the GPC column were injected directly into the spectrometer after being dissolved in glycerol (about 20–30%).

FTIR

We used an FTIR Md 1720 Perkin-Elmer equipped with IRDM software (also from Perkin-Elmer). The spectra were recorded at room temperature using CINA windows.

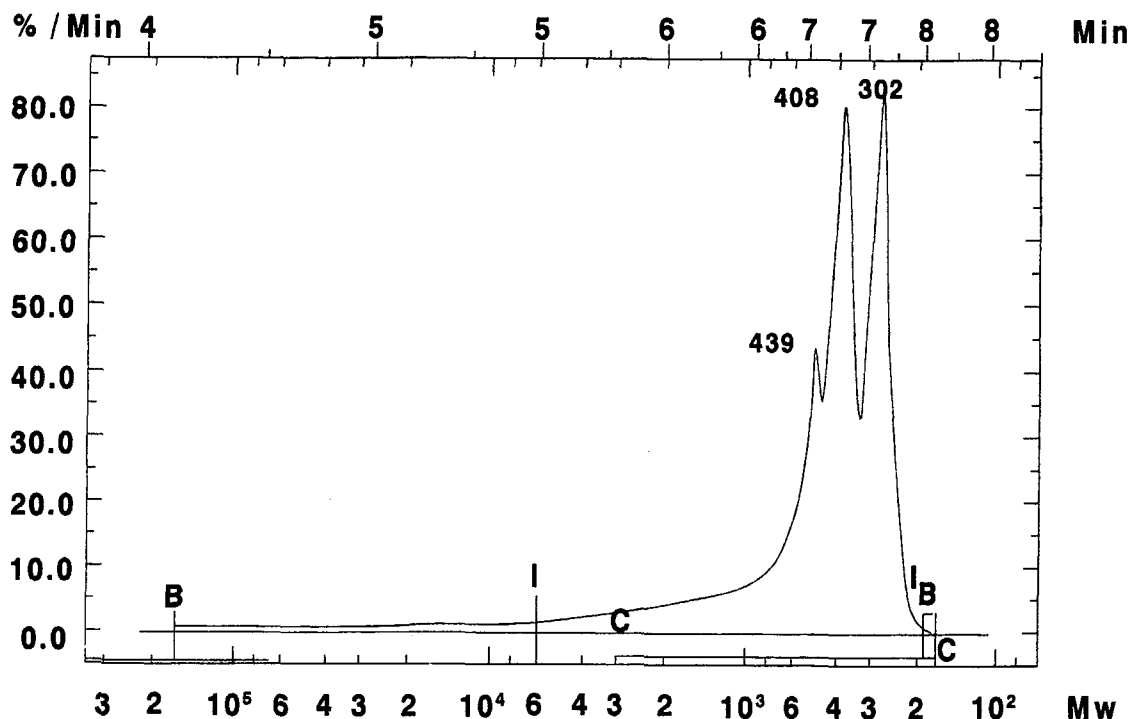


Figure 1 GPC resin as supplier.

FTIR-TGA

By combination of both techniques, FTIR analysis and thermogravimetry, we obtained IR gas spectra under N_2 atmosphere. We used a Perkin-Elmer TGA 7 and 1720 FTIR connected through a heating transfer line. More details about the procedure can be found elsewhere.²

RESULTS AND DISCUSSION

GPC and Mass Results

Figure 1 shows the GPC chromatogram, where we can see three peaks at 439, 408, and 302. On the other hand (Figs. 2, 3) the mass spectra correspond to two fractions (Fig. 2 peaks at 408 and 302, and Fig. 3 at 1^o GPC fraction, peak at 439). The protonated masses that we found in the first fraction were mainly 283, 339, and 430, the last one being the major intensity peak. The second GPC peaks at 408 and 302 have protonated masses mainly of 247, 339, 395, and 431. Figure 4 shows the chromatogram of purified resin (water soluble fraction) with two narrow peaks at 408 and 302.

The differences between both analytical techniques are probably for two reasons. One peak represents more than one mass and although the cali-

bration was tested with our DGEBA standard,³ it was done with polystyrene standards. However if there were trifunctional species in these resins it would imply that at least the mass 302 and other superior masses (reaction between TMP and 302 mass and later epoxidation) should exist, which is not so. The epoxidation of TMP is not complete and one of the OH groups does not react with the epichlorohydrin.

FTIR and FTIR-TGA Results

Figure 5 shows the IR spectrum for the resin without purification where the most representative bands are:

Frequency (cm^{-1})	Group
3475	O—H stretching vibration
3056	CH ₂ stretching vibration of terminal epoxide
1254	Symmetrical-ring breathing mode (epoxy)
1099	C—O—C asymmetric stretching vibration
911	Asymmetric ring bending mode (epoxy)
840	C—H vibration (epoxy)

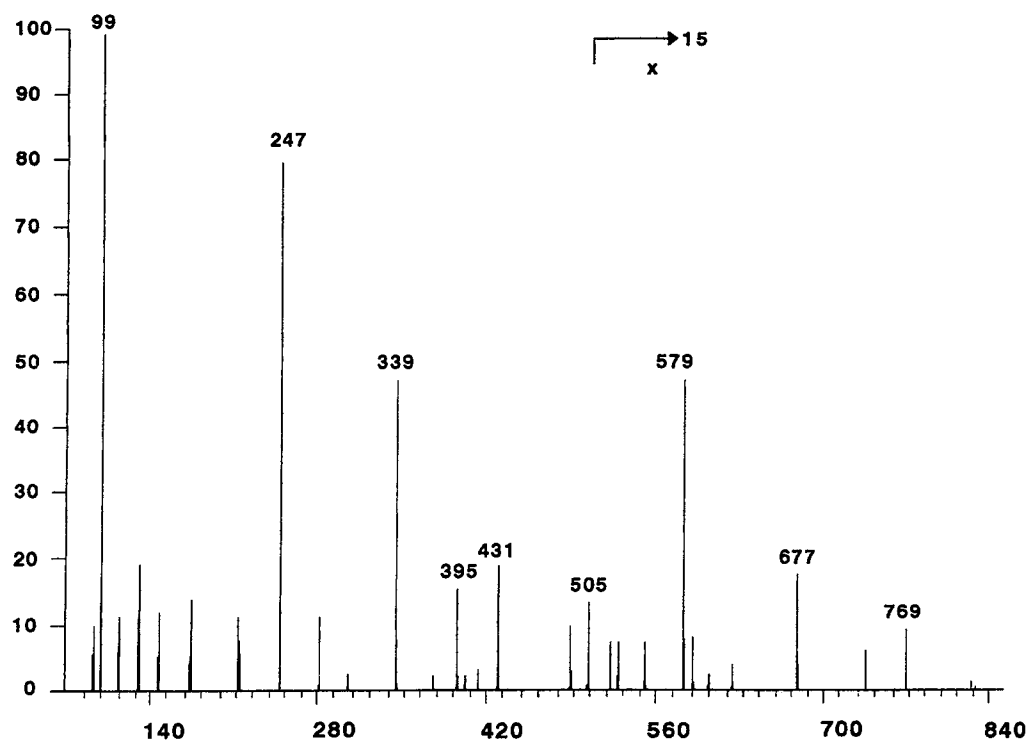


Figure 2 Mass spectrum (FAB) GPC fractions at 408 and 302.

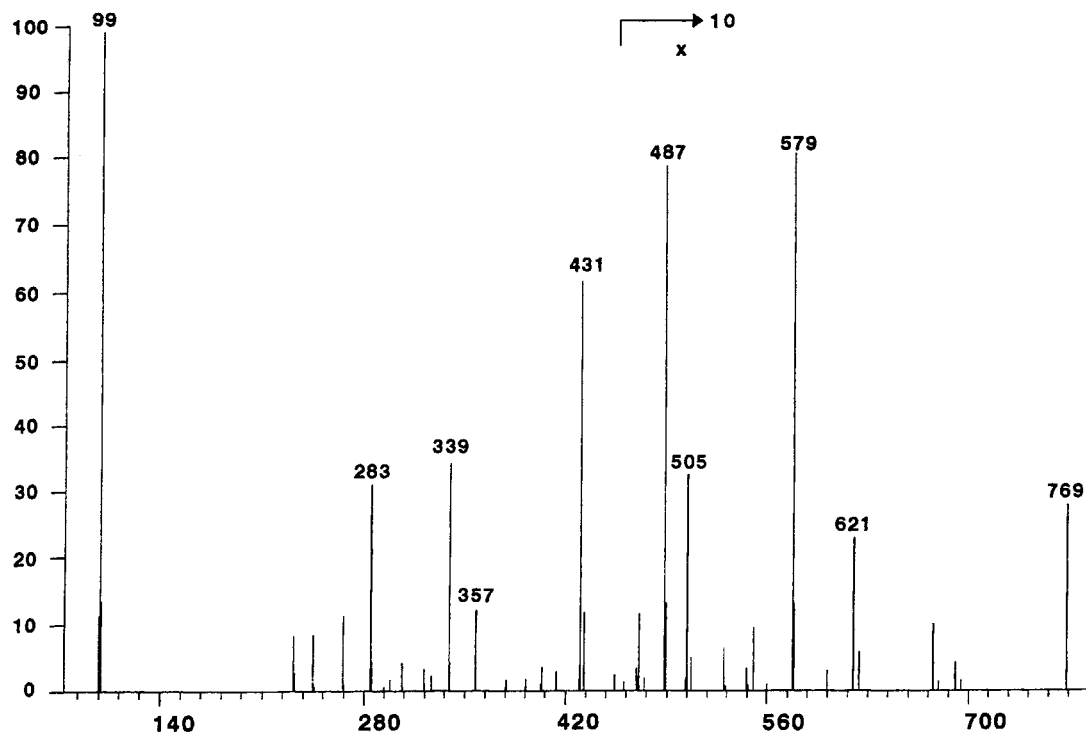


Figure 3 Mass spectrum (FAB) GPC fraction at 439.

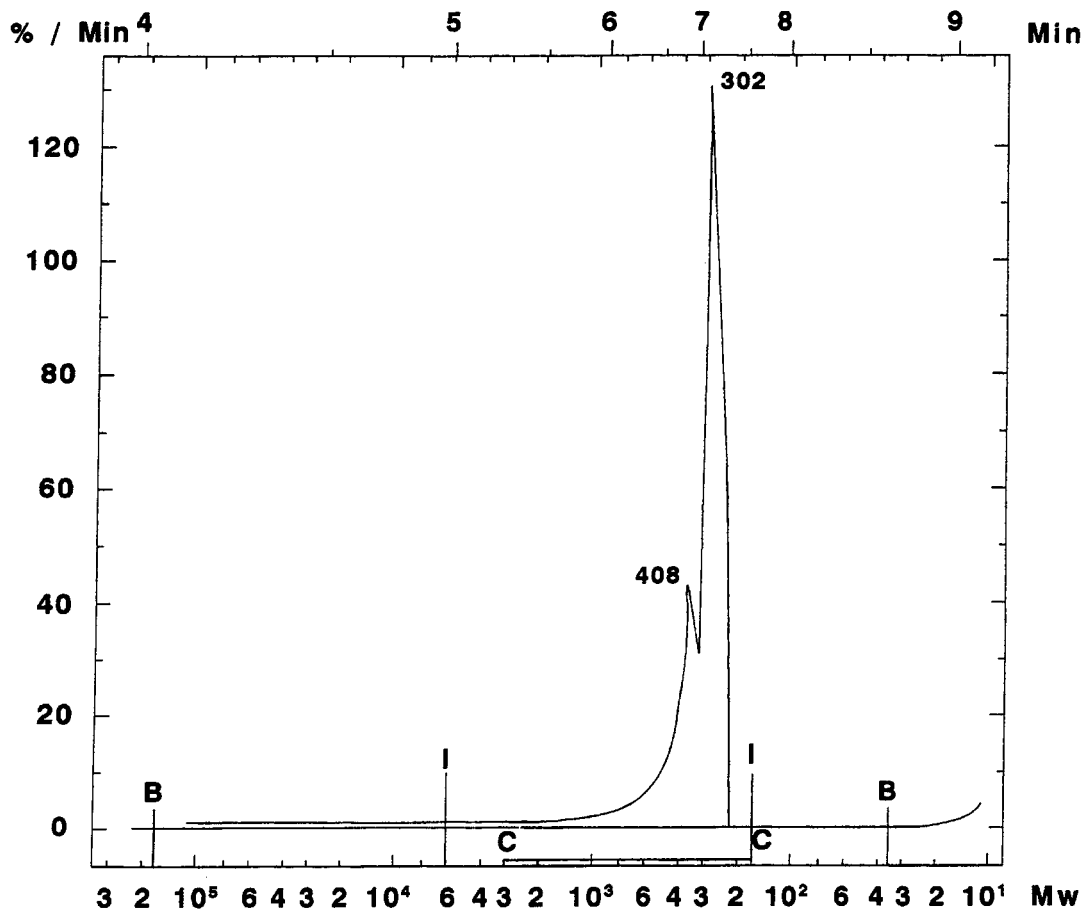


Figure 4 GPC soluble fraction.

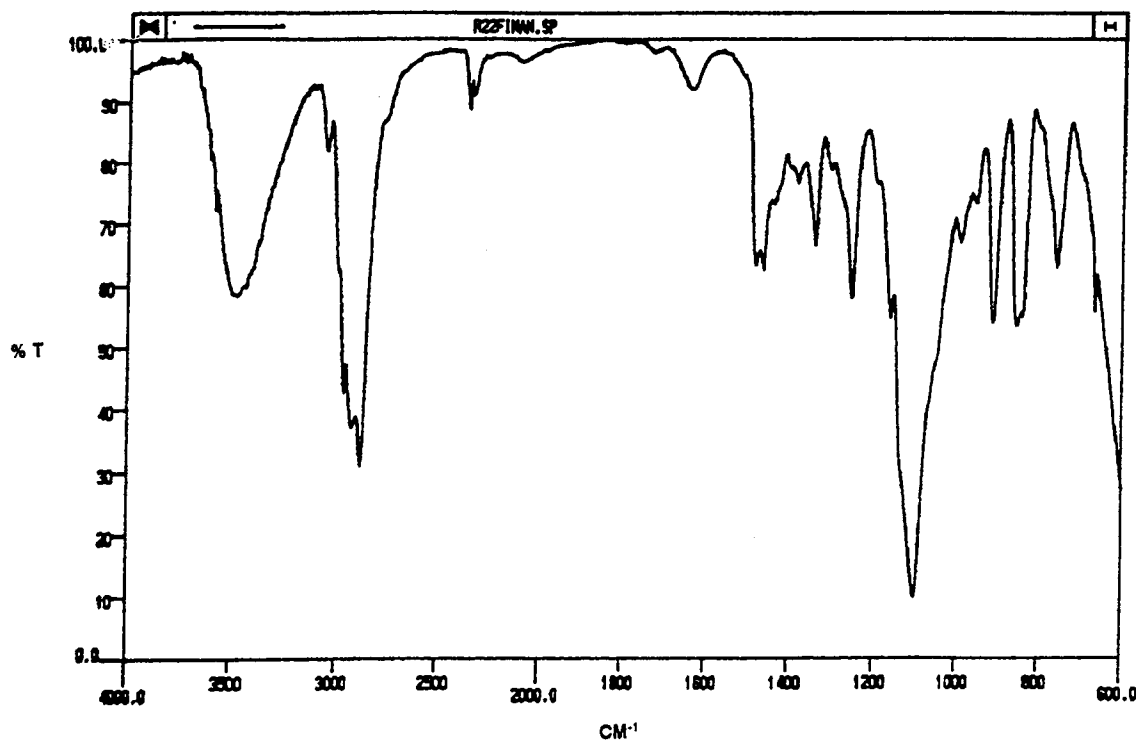
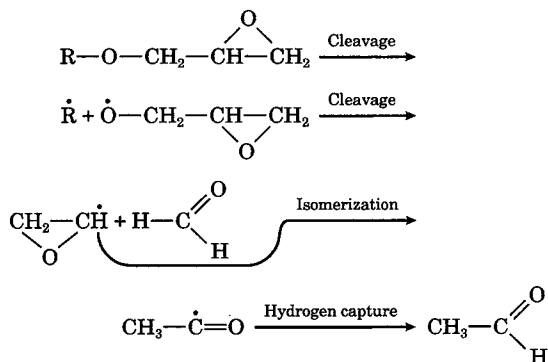


Figure 5 IR spectrum resin as supplier.

Figures 6 and 7 show the FTIR-TGA spectra for both resins, in supplier form (Fig. 6) and purified resin (Fig. 7):

Frequency (cm ⁻¹)	Group
2963	CH ₂ stretching asymmetric
2885	CH ₂ stretching symmetric
2325	Antisymmetric stretch of CO ₂
1732	C=O stretching aldehydes

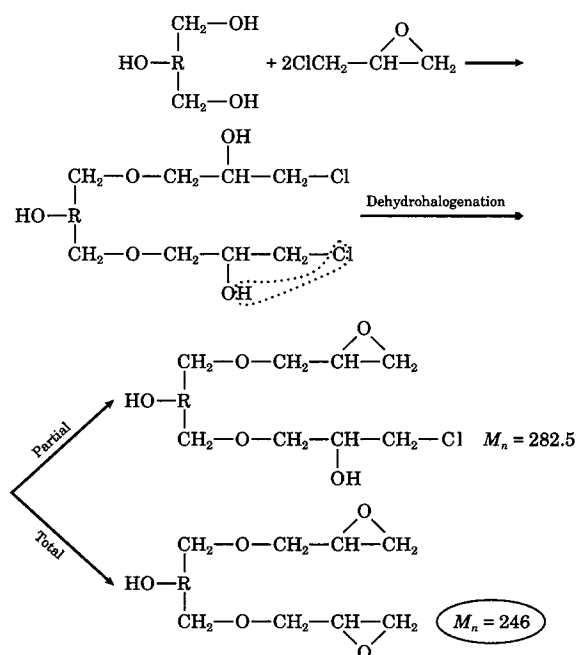
Of the few interesting differences between both products found in the FTIR-TGA experiment, two should be especially mentioned: negative absorption (with reference to the background) of CO₂ (soluble fraction resin) and the band at 704 cm⁻¹, C—Cl (resin as supplier form). The carbonyl group probably originates from an epoxy group.^{4,5}

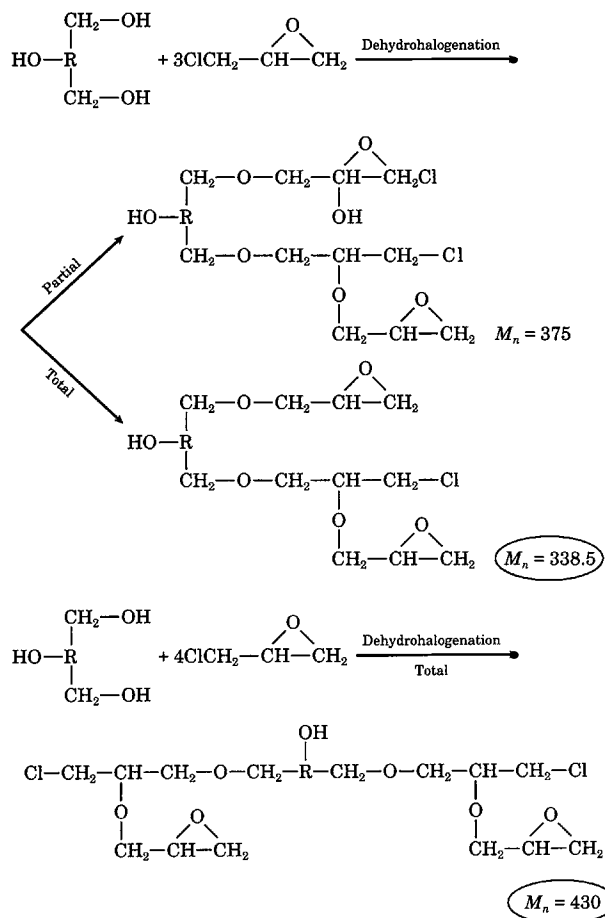


Structures, Molecular Weights, and Functionalities

Table I shows the experimental and theoretical results. The epoxy content, (OH) content, and chlorine content were determined by wet analysis.⁶

According to mass spectra (Figs. 2, 3) the most significant protonated masses in this resin are 247, 339, and 430 and their structures are as follows:





If we take into account the GPC quantitative results (24, 36, and 40% for peaks at 439, 408, and 302, respectively), and if we suppose that each peak corresponds basically with each structure determined in the mass spectra (430, 338.5, and 246, respectively) we can calculate the values for epoxy content, OH content, and Cl content. By applying mixing rules, the theoretical epoxy value is 154 g eq⁻¹ against 150 g eq⁻¹ found experimentally. Also the results for OH and Cl contents (directly estimated from structures) were 5.3 and 7.7% (6.1 and 6.8% experimental results). On the other hand, the water soluble fraction had close agreement between theoretical prediction and experimental results, especially with reference to epoxy content (134 g eq⁻¹ 136). The differences of OH and Cl contents between theoretical prediction and experimental results probably resulted from the fact that other products present in the compositions and also from experimental variability were not taken into account. However, we have basically three masses and we can evaluate both molecular weight average and functionality average.

As previously, taking the GPC quantitative values, we obtained M_n for both resins: $M_{n,\text{supplier form}} = 323$ (40% of 246, 36% of 338.5, and 24% of 430), $M_{n,\text{soluble fraction}} = 274$ (70% of 246, and 36% of 338.5), and the functionalities average ($f = M_n/\text{epoxy exp. Eq.}$), $f_{\text{supplier form}} = 2.15$ and $f_{\text{soluble fraction}} = 2.01$.

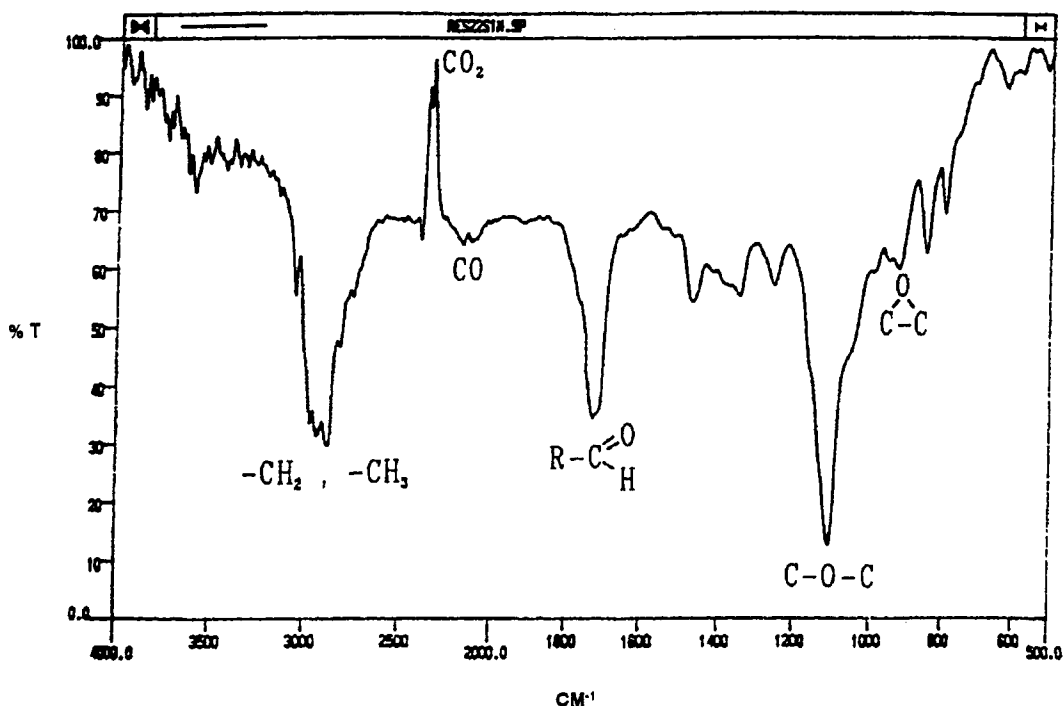


Figure 6 FTIR-TGA spectrum resin as supplier.

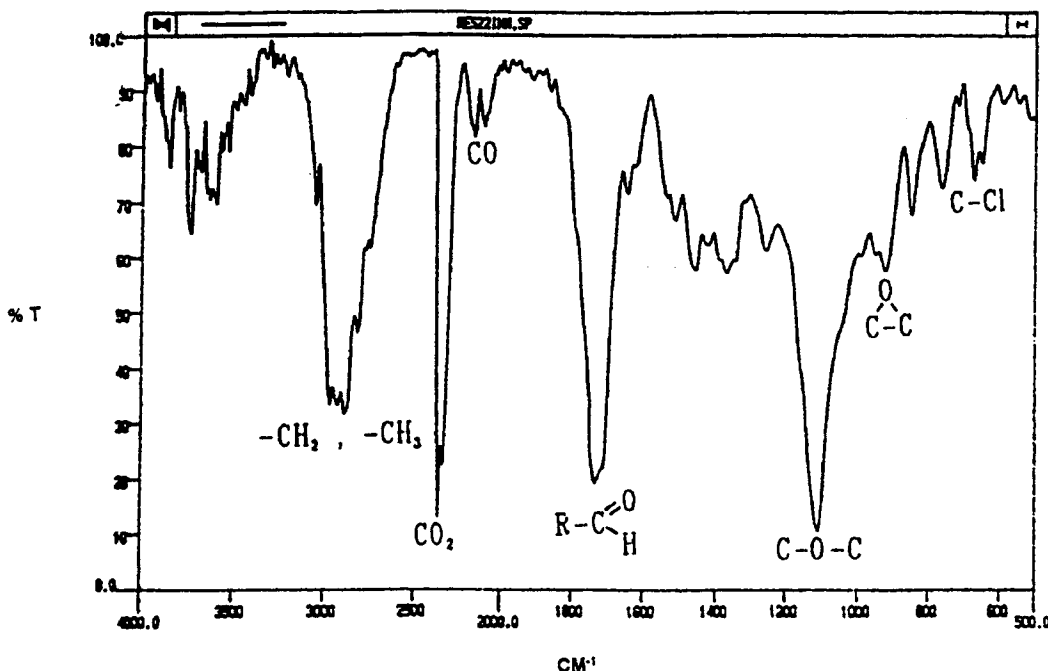


Figure 7 FTIR-TGA spectrum soluble fraction.

A value of $f > 2$ implies that species with functionality $f = 3$ exist of which we have no experimental evidence, so probably the value of M_n is not quite correct. But we assumed as a first approximation that no other mass exists apart from those already stated, which is not exact. However the fact that the soluble fraction "purified resin" has a value close to 2 indicates that the hypothesis is essentially correct. The functionality is practically equal to 2. Other products present in the full resin tend to increase the molecular weight. In part II we will compare these results with those from the kinetic study.

CONCLUSION

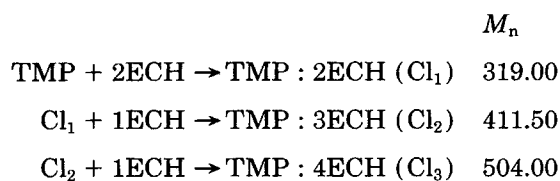
In agreement with our results, it seems that in the resin there are no trifunctional species, and the resin

must be basically bifunctional. It means that at least under the synthesis conditions one OH group, probably the adjacent group to a quaternary carbon, is not epoxidable, otherwise we would have found molecular masses of 302 and other condensation products between the triglycidyl ether of TMP (302 as stated) and TMP followed by posterior epoxidation which does not happen. So the "true" functionality of TMP, with respect to epoxidation seems to be 2. The supplier informed us that they studied the epoxidation reaction under different synthesis conditions; ECH, TMP molar ratios (from 10/1 to 2/1), temperature, catalyst concentration, and the kind and concentration of dehydrohalogenant. This resin has the highest epoxy content and lowest viscosity found, and it is made with a molar excess of ECH taking into account the TMP functionality to be 2, so the OH groups generated during the epox-

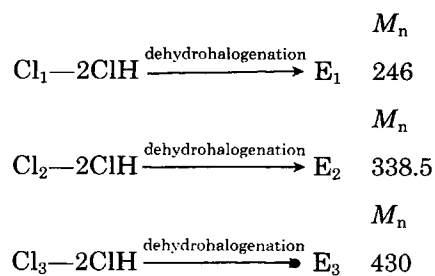
Table I Elemental Chemical Analysis

Resin	Parameter	Value	
		Theoretical	Experimental
As supplier	Weight per epoxy equivalent (g/Eq)	154	150
	OH content (%)	5.3	6.1
	Cl content (%)	7.7	6.8
Purified	Weight per epoxy equivalent (g/Eq)	134	136
	OH content (%)	6.2	5.9
	Cl content (%)	3.1	2.9

idation reaction must be more reactive than the OH group initially present in the TMP (OH over quaternary carbon). And the reaction follows a consecutive reaction dominated by chlorhydrins formation:



The chlorhydrins (Cl₁, Cl₂, Cl₃) react with the dehydrohalogenant to give



The dehydrohalogenation in alkaline medium leads to the formation of the epoxy resins E₁, E₂, and E₃, whose structures we have determined.

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