

# Evaluation of DGEBA

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## SYNOPSIS

Analytical studies using chemical, spectral, and chromatographic methods have been carried out for four commercial diglycidyl ether of bisphenol A (DGEBA) resins (AER, EER, DER, and NER) in order to evaluate the essential parameters of DGEBA for synthesizing 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)]phenyl propane (BIS-GMA), an important precursor for dental composites. Parameters such as epoxy equivalent weight, hydroxyl value, and hydrolyzable chlorine content have been estimated. The role of these parameters in determining the final purity of BIS-GMA has also been discussed.

## INTRODUCTION

BIS-GMA, a resin synthesized from bisphenol A and glycidyl methacrylate (GMA), has been used as the matrix for commonly used dental composite materials in anterior and posterior restorations.<sup>1,2</sup> It has also been reported<sup>3</sup> to be synthesized by another method which involves a two-step process:

- i. Reaction between bisphenol A and epichlorohydrin to produce the intermediate DGEBA
- ii. Reaction between DGEBA and methacrylic acid to produce BIS-GMA resin

DGEBA forms an important intermediate in this synthesis and is easily available commercially. Hence, the second step, i.e., DGEBA to BIS-GMA can be carried out using commercially available DGEBA. However, commercial DGEBA resins are available in several molecular weight ranges and some may be composed of a mixture of more than one type of epoxy resin, and may contain modifiers and diluents.<sup>4</sup> In the field of restorative dentistry, purity of the methacrylate resin, BIS-GMA, which forms the matrix in several formulations, is an important factor for clinical reasons. Successful performance of methacrylate resins in various end applications also depends on the purity of DGEBA to

a great extent. The setting characteristics and curing nature of the final dental composite is also determined by the nature of the resin used as matrix.

The specifications or the required parameters to select DGEBA as a precursor for the synthesis of medical grade BIS-GMA are not available. The present study therefore aims at the evaluation of DGEBA by chemical, spectroscopic, and chromatographic methods and to understand the relevance and impact of these parameters on the purity of BIS-GMA synthesized from DGEBA.

## EXPERIMENTAL

### Materials

Four commercial DGEBA resins (AER, EER, DER, and NER) from Ciba-Geigy, Dr. Beck, SIP Resins, and Namaste Polymers were used. Pyridine (AR, E. Merck), acetic anhydride (AR, Glaxo), potassium hydroxide (AR, Ranbaxy), and ethyl acetate and dichloro methane (HPLC grade, BDH) were used as such without further purification. Methanol (AR, E. Merck), benzene (AR, S.D's), acetone (AR, E. Merck), and toluene (AR, E. Merck) were used after distillation. Methacrylic acid (AR, E. Merck) and *N,N*-dimethyl-*p*-toluidine (DMPT) were purified by distillation under reduced pressure.

## CHEMICAL METHODS

1. Epoxy equivalent weight: It may be defined as weight of the resin in grams which contain

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1 g eq of the epoxy group. The procedure, described elsewhere,<sup>5</sup> was determined by the pyridinium chloride–pyridine method. The epoxy resin in pyridinium chloride solution was refluxed and the excess acid present was estimated using standard alkali.

- Hydroxyl value<sup>6</sup>: This refers to the weight of the resin containing 1 eq of the hydroxyl group. It may be expressed as eq/100 g. It was determined by acetylation with acetic anhydride in pyridine solution. The excess anhydride was decomposed with water and the resulting acetic acid formed both in the hydrolysis and in the acetylation process was titrated with standard alkali solution.
- Hydrolyzable chlorine content<sup>5</sup>: It was determined by heating the resin solution with alcoholic KOH and titrating it against standard HCl.

## SPECTRAL METHODS

IR spectra of the commercial DGEBA samples were recorded in a Perkin-Elmer 597 double beam IR spectrophotometer. A thin film of the resin between sodium chloride cells was used for all the samples. <sup>1</sup>H-NMR spectra of the DGEBA samples were recorded in a Varian EM-360 60 MHz NMR spectrometer in CDCl<sub>3</sub>, using tetramethyl silane (TMS) as an internal indicator. Refractive indices of the DGEBA samples were measured at 25°C using an Atago Abbe refractometer, Type 2T.

High performance liquid chromatograms (HPLC) of the DGEBA samples were recorded using a Model 6000 A solvent delivery system (Waters Associates) with a Model 440 absorbance detector. Porosil column (0.39 × 30 cm) was used with mixture of solvent (methylene chloride : ethyl acetate, 80 : 20 v/v) as a mobile phase (flow rate 2 mL/min) using a UV (254 nm) detector.

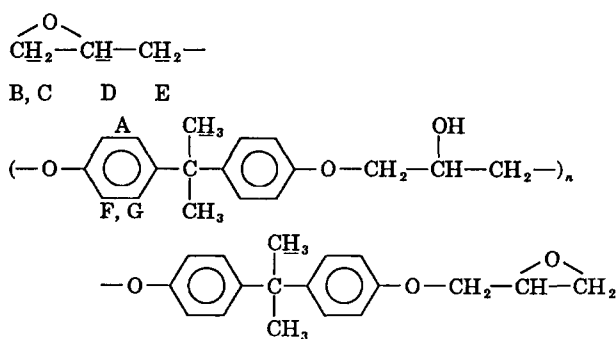
## Synthesis and Characterization of BIS-GMA

BIS-GMA was synthesized using all the four DGEBA samples by reacting them with methacrylic acid as per the reported procedure.<sup>7</sup> Refractive indices and IR spectra of all the synthesized samples were recorded as mentioned before. Gel permeation chromatograms of the synthesized samples were recorded on a Model 6000A solvent delivery system (Waters Associates) with a Model 440 absorbance detector. Microstyrigel columns were used with tetrahydrofuran (THF) as the mobile phase (flow rate 1 mL/min) using a UV detector.

## RESULTS AND DISCUSSION

### Structural Analysis

DGEBA resins are highly viscous liquids and are pale yellow in color. Structural analysis of these resins were done by IR and NMR spectroscopy. The IR spectra of all the DGEBA resins (Fig. 1) showed the characteristic absorption frequency of the terminal epoxy group at 917 cm<sup>-1</sup>, the aliphatic ether group at 1020–1040 cm<sup>-1</sup>, the aromatic ether group at 1220–1240 cm<sup>-1</sup>, and the hydroxyl group at 3400–3450 cm<sup>-1</sup>. The NMR spectra of all the DGEBA samples were identical (Fig. 2). The characteristic groups, the number of protons, and their integration values are presented in Table I. The characteristic peaks for DGEBA are singlet at  $\delta = 1.6$  ppm corresponding to methyl protons (A, -CH<sub>3</sub>), a multiplet at  $\delta = 2.6$  ppm due to methylene protons (B and C) in the terminal epoxy group, and the two multiplets D and E at  $\delta = 3.1$ – $3.3$  3.8–4.2 ppm, respectively, corresponding to the methine protons in the terminal epoxy group and -Ar-O-CH<sub>2</sub> methylene protons. The two different aromatic protons F and G are observed as a quartet at  $\delta = 6.5$ –7.2 ppm. From the integration data, the structure of the DGEBA resins was confirmed for all the commercial samples and is given below:



Diglycidyl ether of bisphenol A,  $n = 0$

### Chemical Analysis

The epoxy equivalent weight, the hydroxyl value, and the hydrolyzable chlorine content were determined using chemical methods (Table II). The epoxy equivalent weights of all the four commercial epoxy resins were found to lie in the range of 179–186. Spectral examination showed a linear diepoxide structure for all the analyzed DGEBA samples. The epoxy equivalent weight for a linear diepoxide is one-half of its molecular weight.<sup>5</sup> Hence, the molecular weights of the four commercial resins are expected

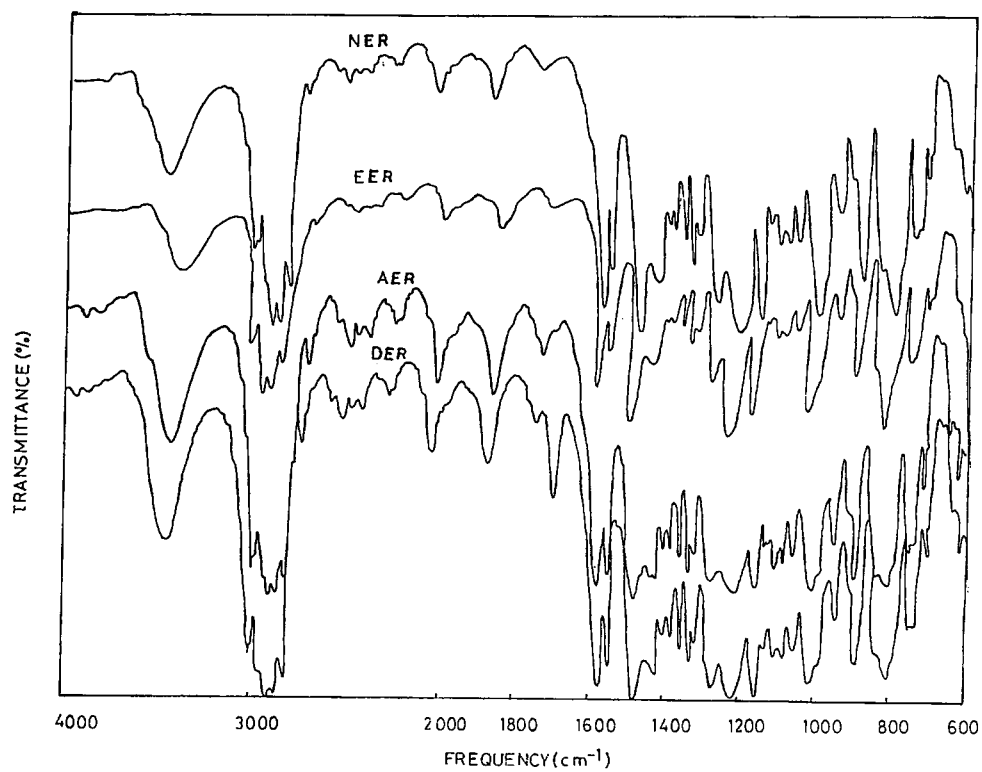


Figure 1 IR spectra of four commercial DGEBA.

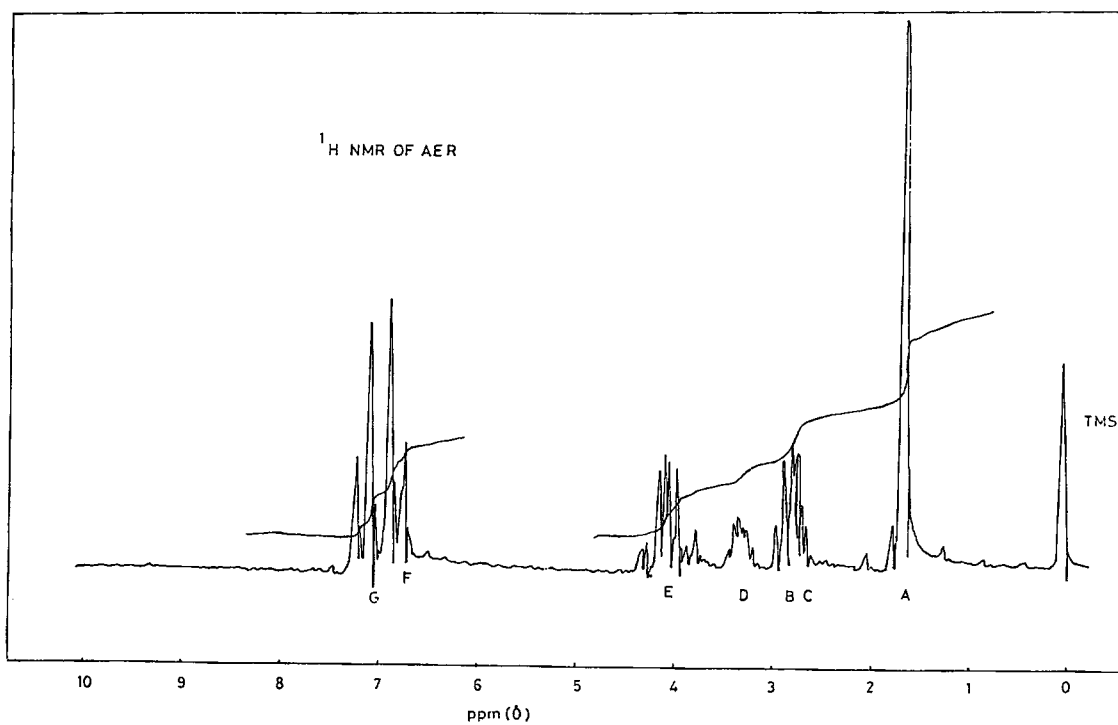


Figure 2 NMR spectrum of AER.

**Table I** The Proton NMR Identification Data of the Commercial DGEBA Samples

Group and Number of Protons	Chemical Shift (ppm)	Integration (cm)			
		NER	AER	DER	EER
A-methyl 6	1.6 (s)	2.05	2.2	2.0	2.4
B-methylene (cis) 2	2.6 (s)	0.65	0.75	0.65	0.75
C-methylene (trans) 2	2.8 (d)	0.75	0.75	0.65	0.75
D-methine 2	3.1–3.3 (m)	0.70	0.70	0.70	0.80
E-methylene 4	3.8–4.2 (m)	1.4	1.5	1.4	1.6
F-aromatic 4	6.5–6.9 (d)	1.35	1.4	1.3	1.6
G-aromatic 4	6.9–7.2 (d)	1.35	1.4	1.3	1.6

to lie in the range of 358–372 with an average  $n$  value between 0 and 0.1.

The hydroxyl value of the four commercial resins were found to be in the range 0.14–0.22 eq/100 g (Table II). Among the four resins, AER showed the lowest hydroxyl value of 0.1474 eq/100 g.

Generally, the presence of hydrolyzable chlorine content is reported to be due to many side reactions,<sup>8</sup> such as incomplete dehydrohalogenation, abnormal addition of epichlorohydrin, and formation of bound chlorine, which occur during the synthesis of the DGEBA resin. The presence of chlorine affects the properties of the end products prepared from the DGEBA resin. Chlorine content can be reduced by modifying the synthesis conditions of DGEBA. The percentage of chlorine content was high for NER and DER resins (Table II) when compared with the reported value of pure DGEBA.<sup>5</sup> EER resin showed a moderate value whereas AER revealed a very low value (i.e., 0.2810%), which is less than the reported value<sup>5</sup> (i.e., 0.52%).

The refractive indices of all the four resins are also presented in Table II. The values varied from 1.5700 to 1.5722 for the four samples studied, which corresponds with the reported values.

### Chromatographic Analysis

The purity of the resins were determined by analytical high performance liquid chromatography

(HPLC). HPLC is highly sensitive to compound type, but it is low sensitive to different molecular weight solute species. HPLC of all the four resins are identical with respect to their retention times (Fig. 3). The figures showed two peaks. The very poor resolution between these two peaks may be attributed to the presence of two different molecular weight species of the DGEBA molecule. Out of these two, the percentage of one component was very low compared to that of the other. It was found difficult to correlate the HPLC data of DER and NER to their higher chlorine content and hydroxyl value.

### Purity of BIS-GMA

The final product, BIS-GMA, was synthesized from all four commercial DGEBA resins by reacting them with methacrylic acid as per the reported procedure.<sup>7</sup> The four BIS-GMA resins, AKM, EKM, DKM, and NKM, were then characterized by IR, refractive index, and GPC. BIS-GMA formation was confirmed by the disappearance of the characteristic absorption peak at 918  $\text{cm}^{-1}$  due to the terminal epoxide group (Fig. 4). Refractive index value of AKM is almost equal to that of EKM (Table III). In GPC data, AKM showed a single component BIS-GMA (Fig. 5) with trace of higher molecular weight species of BIS-GMA present. This was found to be similar to the HPLC of AER resin. This trace of higher mo-

**Table II** Analysis Report of Commercial DGEBA Resins

Sample Code	Refractive Index (25°C)	Chlorine Content (%)	Epoxy Eq. wt. (eq/100 g)	Hydroxyl Value (eq/100 g)
AER	1.5714	0.2810	179	0.1474
DER	1.5700	0.6890	178	0.1926
EER	1.5716	0.5092	186	0.1626
NER	1.5722	0.8790	180	0.2168

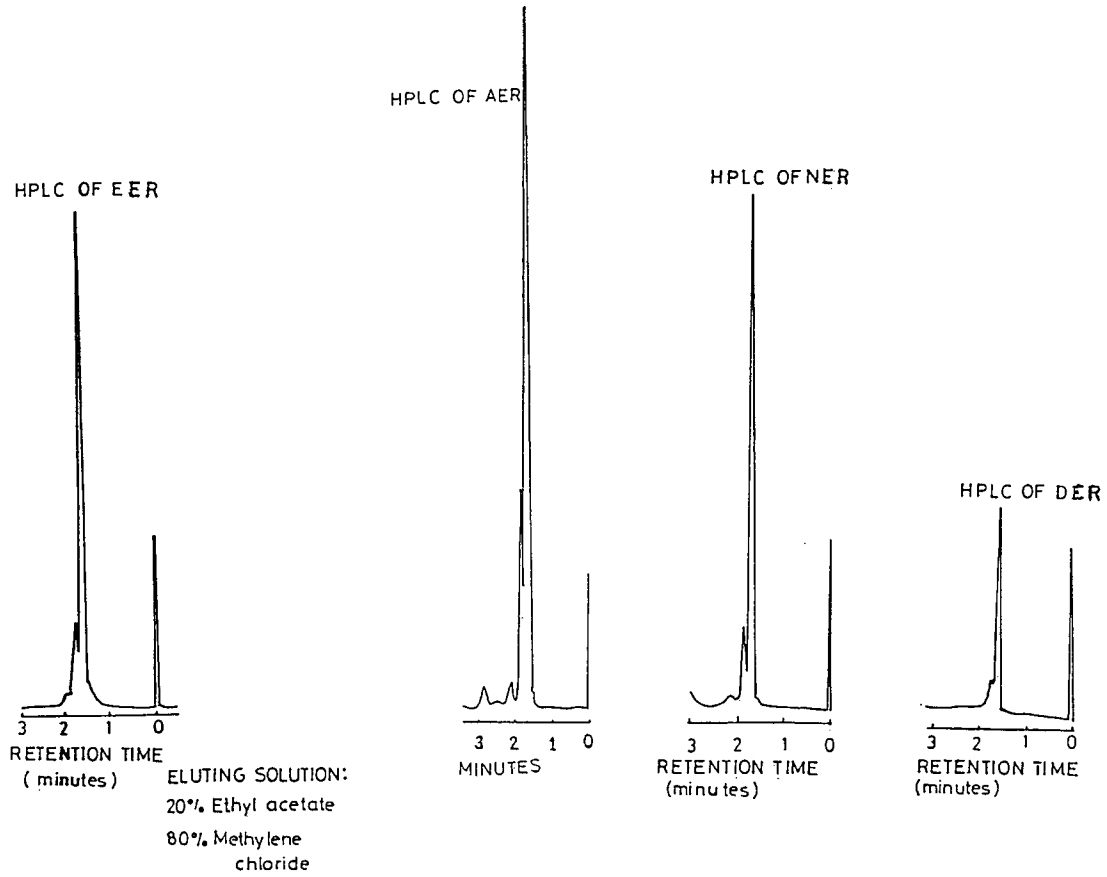


Figure 3 HPLC of the four commercial DGEBA.

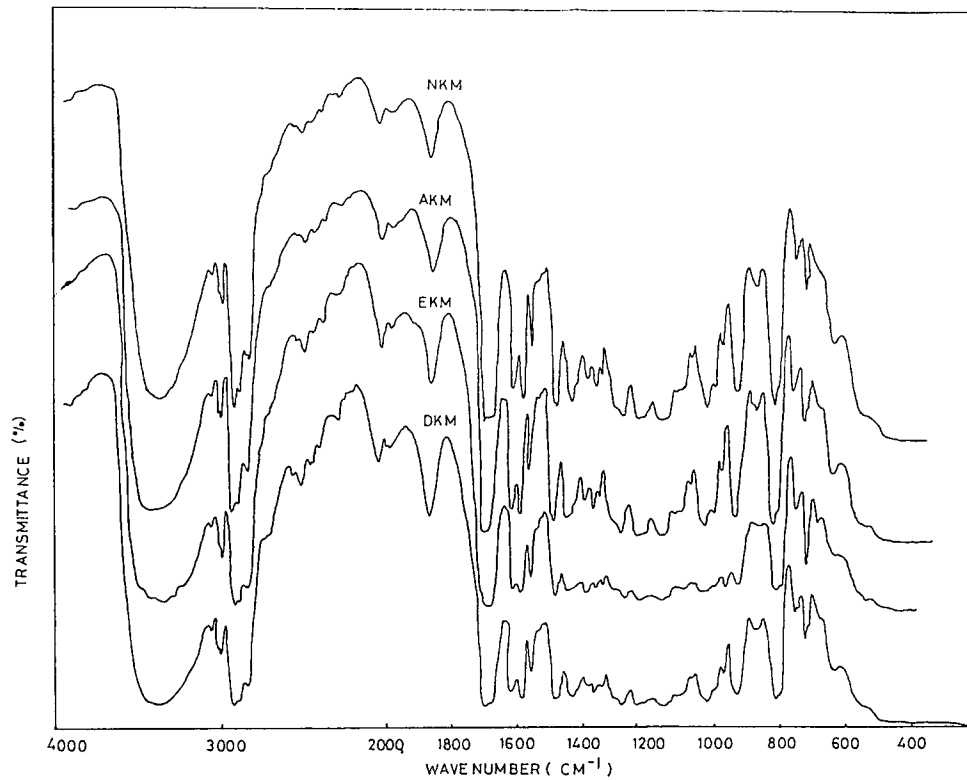
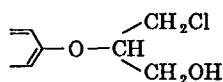


Figure 4 IR spectra of the four synthesized BIS-GMA resins.

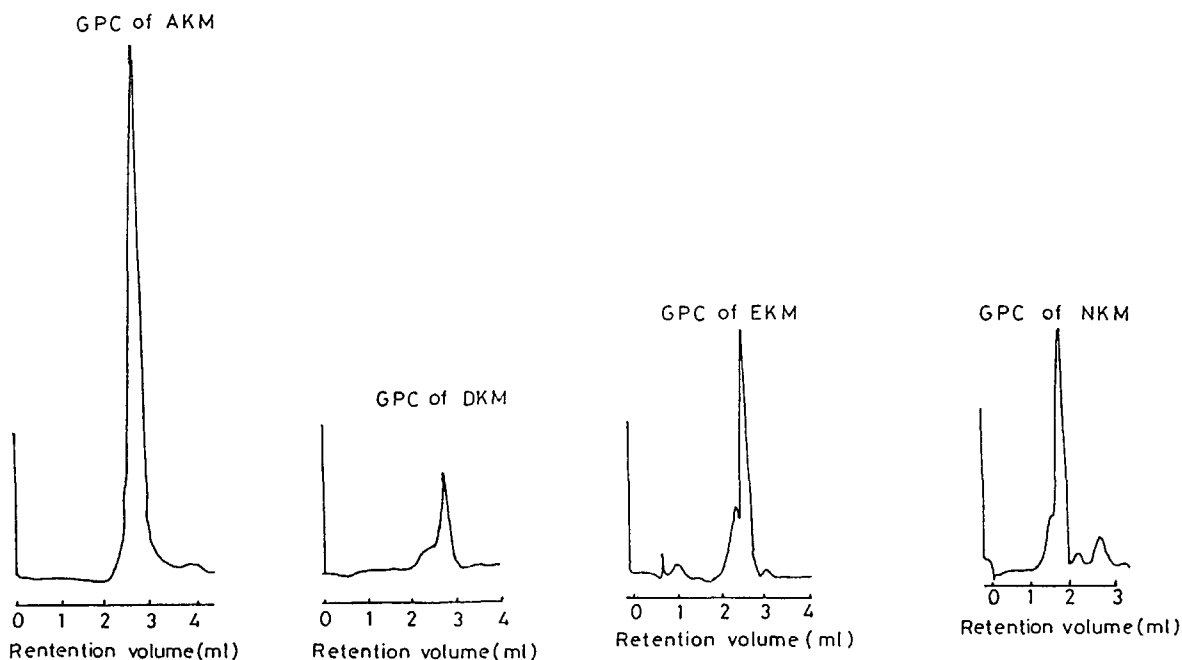
**Table III BIS-GMA Characterization**

Sample Code		Refractive Index	Color
DGEBA	BIS-GMA		
AER	AKM	1.5490	Pale yellow
EER	EKM	1.5492	Pale yellow
DER	DKM	1.5452	Pale yellow
NER	NKM	1.5480	Pale pink

lecular weight species of BIS-GMA was more in the products EKM and DKM obtained from EER and DER resins. In addition to this, two more peaks of lower molecular weight compounds were obtained in the GPC data of NKM (Fig. 5). Actually, NER resin has higher values of hydroxyl value and hydrolyzable chlorine content. It may be accounted that NER may contain a species<sup>8</sup> having chlorine in the CH<sub>2</sub>Cl group that is not adjacent to the -OH group, in small amounts:



This type of products present in the NER accounts for the low molecular weight components in NKM. The color of this product was darker than the other BIS-GMA resins due to high moisture absorption. The value of chlorine content and hydroxyl value played a major role in the purity of BIS-GMA.

**Figure 5** GPC of the four synthesized BIS-GMA resins.**Table IV Comparative Analysis of Commercial DGEBA Resins<sup>a</sup>**

Analysis	AER	DER	EER	NER
Spectral				
IR	S	S	S	S
NMR	S	S	S	S
Chemical				
Epoxy eq. wt	S	S	S	S
Hydroxyl value	MS	NS	MS	NS
% Chlorine	S	NS	S	NS
HPLC	S	S	S	S
R I	S	S	S	S

<sup>a</sup> S = suitable, MS = moderately suitable, and NS = non-suitable.

### Comparative Analysis and Conclusion

Finally, Table IV gives a comparative analysis of all the four commercial DGEBA samples with respect to their being considered suitable/moderately suitable/not suitable for further reaction of DGEBA to give BIS-GMA. Suitability of the samples with respect to IR and NMR data is considered in comparison with the spectra of pure DGEBA reported.<sup>5</sup> Resins with epoxide equivalent in the range 170–200 are suitable for BIS-GMA synthesis. Regarding the results of chemical analysis, it is established that

higher chlorine content and hydroxyl value of DGEBA affect the purity of BIS-GMA. The hydroxyl value should be very low (0.14–0.16 eq/100 g) so as to reduce the moisture absorbance to a minimum.<sup>5</sup> The percentage of hydrolyzable chlorine content should also be on the lower side (< 0.51%) so that its interference in further reaction of the resin with Lewis base catalysts can be minimized.<sup>5</sup>

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