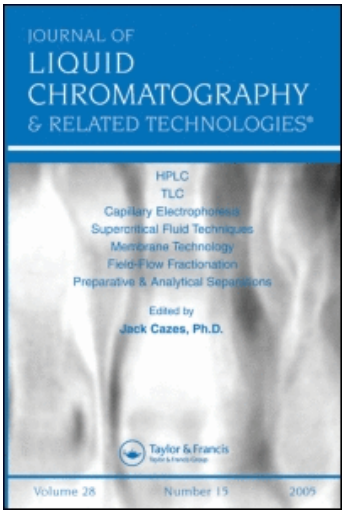

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Characterization of Methoxymethylmelamine Resins by Liquid Chromatography and Mass Spectrometry

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CHARACTERIZATION OF METHOXYMETHYLMELAMINE RESINS BY LIQUID CHROMATOGRAPHY AND MASS SPECTROMETRY

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ABSTRACT

High performance size exclusion (HPSEC) and high resolution reversed phase liquid chromatographic (HPLC) methods are described for the analysis of methylated melamine-formaldehyde resins. Monomer, oligomer and polymer components of a resin were isolated by HPSEC. The molecular weights of components within each HPSEC fraction were determined by fast atom bombardment/mass spectrometry (FAB/MS). The HPSEC fractions were also analyzed by HPLC and their chromatograms compared to the whole resin HPLC chromatogram. Based on the elution time of the major component, hexakis(methoxymethyl)melamine, and on comparison with a different resin having a lower degree of methylation, it is possible to assign tentative structures to all major HPLC peaks.

INTRODUCTION

Methylated melamine-formaldehyde resins are an established group of compounds used in various industries

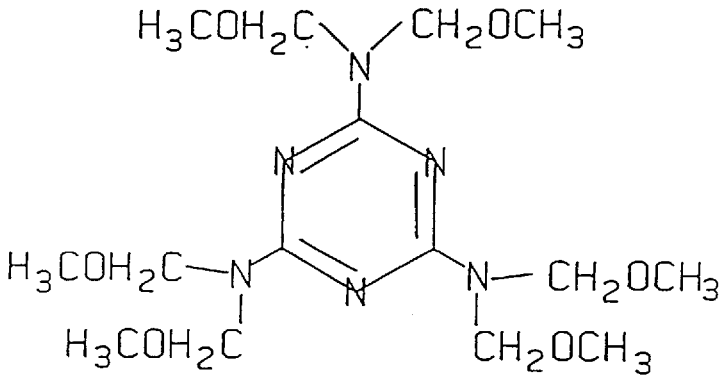

Figure 1. Hexakis(methoxymethyl)melamine - MF_6Me_6.

as binder components and cross-linkers. The cross-linking reaction mechanisms have been investigated by Koral(1) and coworkers and also by Blank(2). The resin synthesis involves two major steps: melamine is first reacted with formaldehyde to produce a hydroxymethylated melamine, then the hydroxymethyl groups are methylated to produce methoxymethyl groups. The structure of the fully methoxymethylated compound, hexakis(methoxymethyl)-melamine, is shown in Figure 1. HPLC and HPSEC analyses (3-5) have shown that methylated melamine-formaldehyde resins contain a multitude of species. These species presumably have varying degrees of substitution on the melamine ring and varying degrees of methylation on the hydroxymethyl groups.

The fully methoxymethylated monomeric species can be represented by the formula MF_6Me_6 where M represents the number of melamine rings, F the number of formaldehyde units on the three primary amino groups and Me the number of methyl groups replacing the active hydrogen of the

hydroxymethyl group. Other compounds having various numbers of F and Me groups can be represented by the general formula MF_xMe_y where x and y need not be equal but y must be equal to or less than x. In addition, the resin may also contain oligomeric or polymeric species in which two or more of any of the monomers have condensed.

During our investigations, we developed an HPLC method which achieves baseline resolution of a large number of monomeric components having various degrees of substitution and thus different polarities. Oligomers are also separated but are superimposed chromatographically because of the large range of molecular sizes and their polarity. This degree of HPLC resolution has not been reported previously in the analysis of these types of resins.

The objectives of our study were as follows:

i. to determine where the monomeric species elute and whether the oligomeric species observed by HPSEC analysis elute in the HPLC separation;

ii. to determine the extent of self-condensation by analysis of the different HPSEC fractions by mass spectrometry;

iii. to determine the extent of substitution on the monomeric and oligomeric compounds represented by peaks in the HPLC chromatogram.

To achieve these goals, we have undertaken the HPLC and FAB/MS analyses of five fractions collected from the HPSEC separation of a methoxymethylmelamine resin CYREZ® 963 brand resin.

MATERIALS

A methylated melamine-formaldehyde resin supplied by American Cyanamid Company, CYREZ® 963 Resin, was used for the major portion of this study. A second resin, CYREZ® 350, was analyzed by HPLC to aid the identification process. For the HPLC analysis, "OMNISOLV®" HPLC grade methanol and water (EM Science, Gibbstown, NJ) were used. For the HPSEC analysis, Burdick and Jackson "B & J Brand™" (distilled in glass) HPLC grade methylene chloride was used.

EXPERIMENTAL

HPSEC Analysis

For the preparative scale isolation, the CYREZ® 963 Resin was dissolved in HPLC grade methylene chloride at about 3.0% (w/v). This relatively high concentration did not affect the resolution adversely compared with a 0.2% concentration routinely used for analytical assay. A modular system for HPSEC consisting of a Waters Associates (Milford, MA) M6000A pump, a Waters Model R401 differential refractometer, and a Waters Model 710B automatic injector was used. Mobile phase flow rate was set at 1.0 mL/min. All sample solutions and solvents were filtered through 0.2 micron silver filters (Osmonics, Inc., Minnetonka MN) and glass microfibre filters (Grade GF/F, Whatman Inc., Clifton, NJ). The HPSEC columns (30 cm x 8.0 mm) used were four PLgel® - polystyrenedivinylbenzene packing - (Polymer Labs, Inc., Amherst, MA) having a 5 micron particle size. For the separation (as well as the re-injections to determine the

purity), the porosities of the PLgel® columns were two each of 100A and 500A. (When necessary to monitor flow rate, elemental sulfur(6) at 0.03% (w/v) was added to the injected solutions as an internal marker). The fraction collection was performed with a Model 210 Gilson Fraction Collector used in the Time Programming Mode. Over fifty repeat injections of 300 microliters were made with minor periodic program adjustments to correct for flow rate changes.

FAB/MS Analysis

A Kratos MS50 mass spectrometer equipped with an M-Scan FAB source was used for mass spectrometric analyses. The FAB matrix was thioglycerol with sodium chloride. Methylated melamine-formaldehyde species produce very weak protonated molecular ions. However, in the presence of sodium chloride, they generate intense sodium-adduct ions with little fragmentation.

HPLC Analysis

CYREZ® 963 Resin samples were dissolved in methanol at a concentration of 0.05% (w/v). The fractions isolated by HPSEC in CH_2Cl_2 were diluted 1:10 with methanol before injection. Injection volumes of 10 microliters were sufficient for both the resin solution and the fractions. An Uptight pre-column (Upchurch Scientific, Inc., Oak Harbor, WA) packed with Perkin Elmer Pellicular C18 was used with a Waters Associates, Inc. NOVAPAK® C_{18} column (15 cm x 3.9 mm). The Waters column was found to give the most reproducible chromatography and the highest resolution. Most of the analyses were conducted at 25°C without a pre-column. This gave a

TABLE 1

HPLC Mobile Phase Conditions

Time (min)	% Water	% Methanol
0	75	25
25	0	100
35	0	100
40	75	25
45	75	25

shorter elution time but equivalent resolution to runs analyzed with a pre-column.

A Hewlett Packard 1090L Liquid Chromatograph with a ternary DR5 solvent delivery system and UV diode array detector (225 nm) was used for the HPLC analysis. This instrument was found to give the most reproducible gradient and has the lowest dead volume among commercially available instruments that we have evaluated for this analysis. The conditions of the methanol/water linear gradient used to elute the resin components at a flow rate of 1.2 mL/min are listed in Table 1. The mobile phase components were continuously sparged with helium.

Data from both chromatography systems were collected and processed on a Hewlett Packard (HP) Laboratory Automation System (LAS-3357) with series 1000 software.

RESULTS AND DISCUSSION

HPSEC Analysis

The HPSEC chromatogram of a typical CYREZ® 963 Resin is shown in Figure 2. The peaks from 38 to about 41

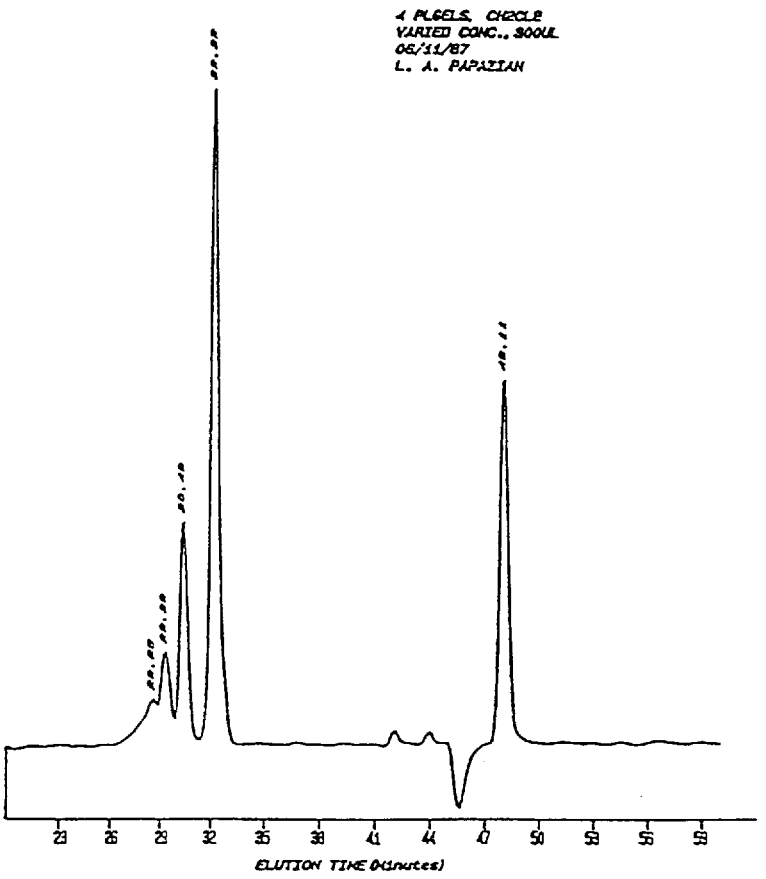

Figure 2. HPSEC chromatogram of CYREZ® 963.

minutes in this figure are solvent related. The sulfur marker peak elutes at about 48 minutes. Five fractions were isolated according to the collection windows illustrated in Figure 3. Methylene chloride solutions of the fractions were reinjected "as is" to determine their purity as shown in Figure 4. The wavy baseline in fraction A is merely baseline noise, while fractions D and E have some minor overlap with adjacent peaks.

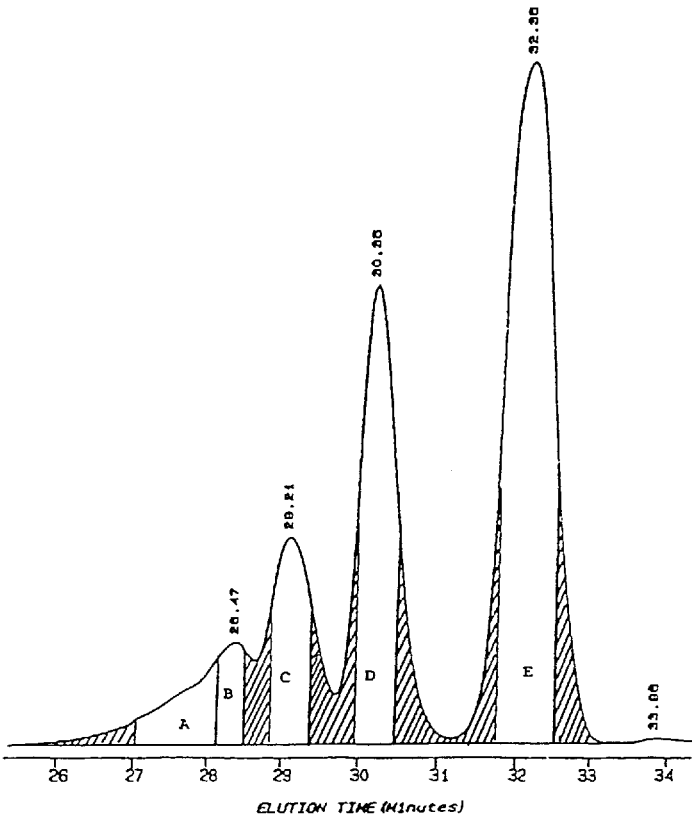

Figure 3. Collection windows for five fractions collected from the HPSEC chromatogram of CYREZ® 963.

FAB/MS Analysis

FAB/MS analyses of HPSEC fractions B-E confirm that fraction E is the monomeric fraction, D the dimeric fraction, and C the trimeric fraction. Fractions B and A represent successively higher molecular weight oligomer mixtures. The mass spectra also confirm that every HPSEC fraction is a complex mixture of species of similar

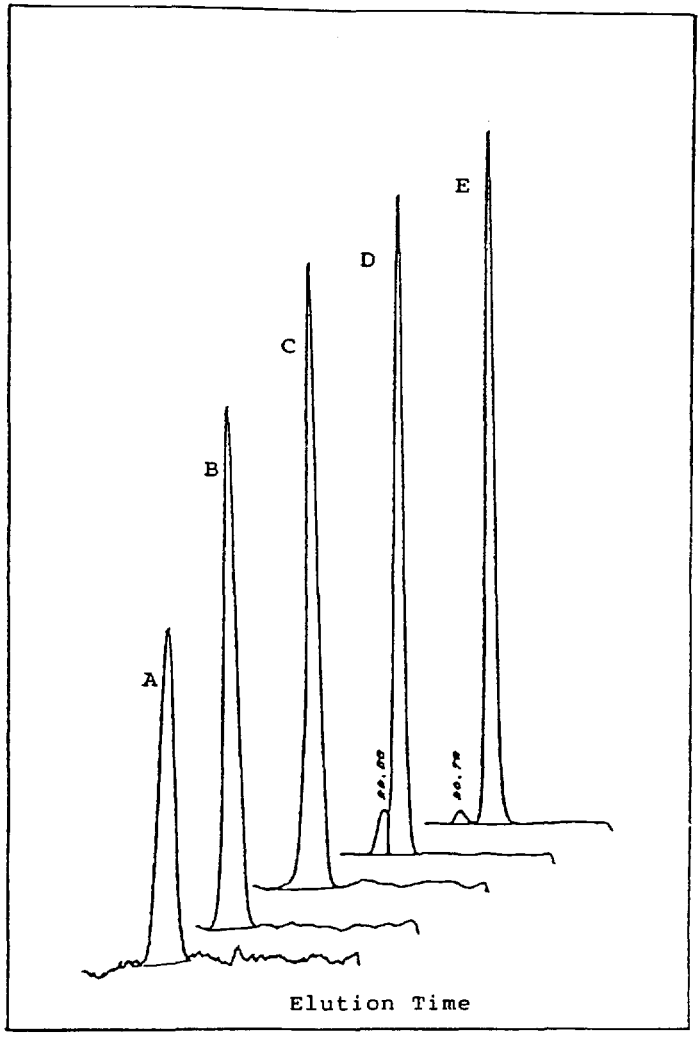

Figure 4. HPSEC chromatogram of fractions A-E. The scale of each peak is not equivalent. Chromatogram portions are shown to demonstrate purity of each fraction.

molecular size, i.e., same number of rings. This is especially evident in the mass spectra of the higher oligomer fractions.

Using thioglycerol as the FAB matrix, CYREZ® 963 Resin produced a FAB spectrum consisting mostly of fragment ions with very weak protonated molecular ions. However, the presence of alkali salts in the FAB matrix enhanced the molecular ions by forming alkali adduct ions.

The mass spectrum of fraction E (Figure 5) represents the monomeric fraction. It appears that the natriation is not complete under the employed FAB matrix conditions. The spectrum shows the presence of both sodium adduct molecular ions and fragment ions and fragment ions from the protonated molecular ions. In Figure 6, the predominant ion at m/z 413 is the sodium adduct ion of MF_6Me_6. A less intense ion at m/z 443 is the sodium adduct ion of MF_7Me_6. The intense mass ions below m/z 360 are mostly fragment ions from the protonated (non-natriated) molecular ions. For instance, m/z 359, 347 and 313 correspond to $[(MF_6Me_6)H^+ - CH3OH]$, $[(MF_6Me_6)H^+ - (CH_3OH + C_2H_4O)]$ and $[(MF_6Me_6)H^+ - C_2H_6O]$, respectively. The presence of the MF_7Me_6 compound was suspected (2), but had not been previously confirmed. This fraction also contains several other minor components which could correspond to various monomeric MF_xMe_y compounds. Since the main objective of this analysis was to confirm the monomeric nature of this fraction, a detailed mass spectral assignment of the minor components was not pursued.

The spectra of fractions D, C and B show molecular ions ranging from m/z 600-800 with a general formula of

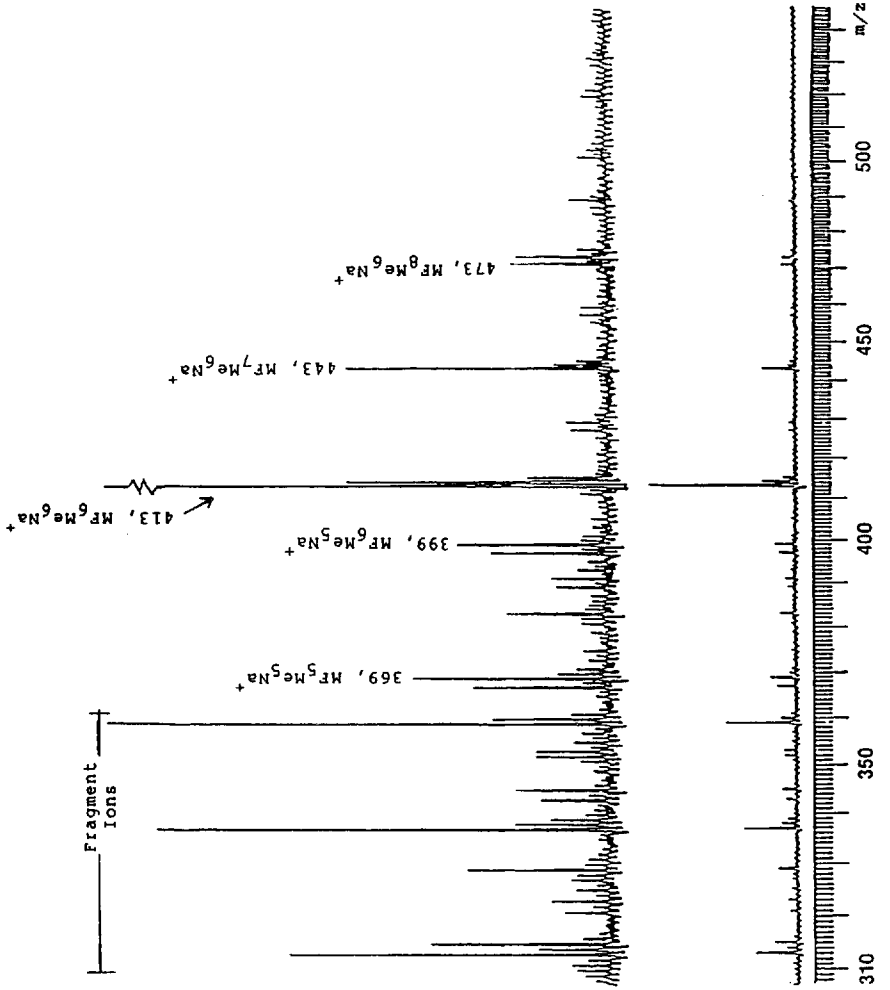

Figure 5. FAB-MS analysis of HPSEC fraction E - monomeric fraction.

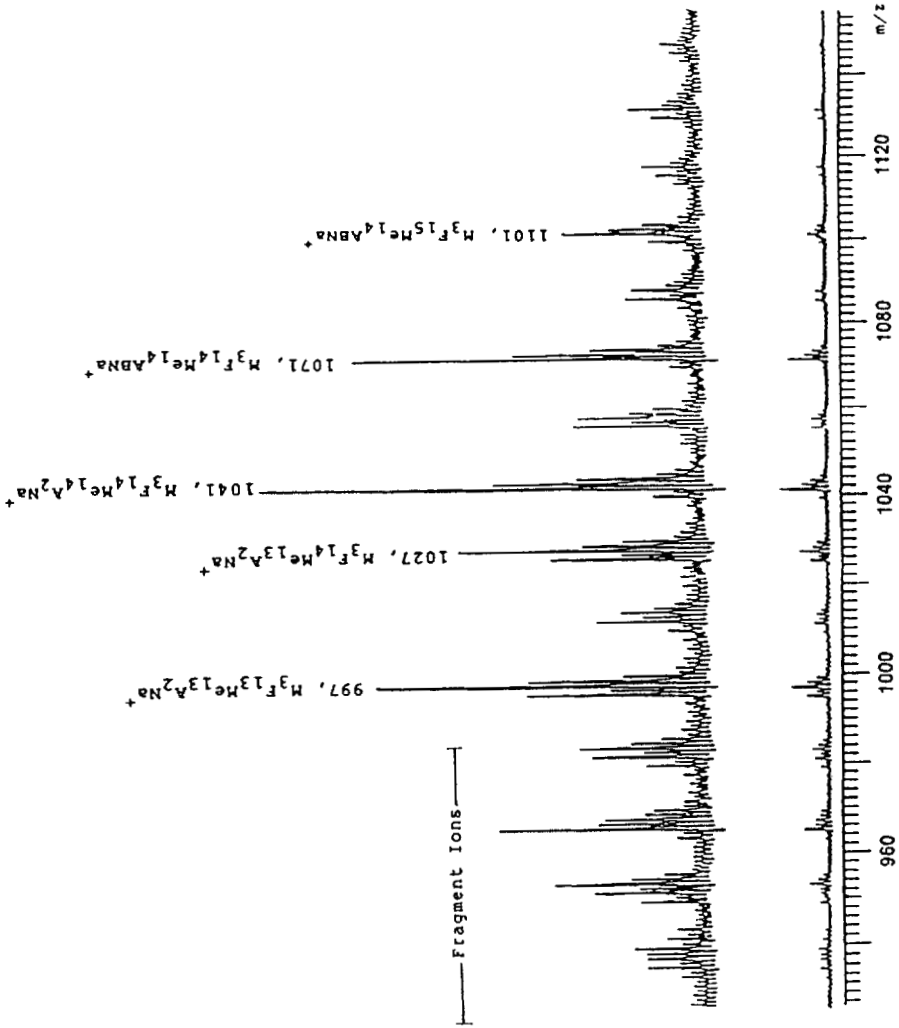

Figure 6. FAB-MS analysis of HPSEC fraction C - trimeric fraction.

$M_2F_xMe_y$, m/z 900-1100 with a general formula of $M_3F_xMe_y$ and m/z 1200-1400 with a general formula of $M_4F_xMe_y$, confirming that they are the dimeric, trimeric and tetrameric fractions respectively. The complexity of the mixture increases with the degree of oligomerization. For instance, the trimeric fraction (fraction C shown in Fig. 6) does not have a single predominant component as is the case of the monomeric fraction (fraction E shown in Fig. 5). Instead, the spectrum is comprised of several major molecular ions. The m/z 997, 1027, 1041, 1057 and 1071 are sodium adduct ions of $M_3F_{13}Me_{13}A_2$, $M_3F_{14}Me_{13}A_2$, $M_3F_{14}Me_{14}A_2$, $M_3F_{14}Me_{13}AB$ and $M_3F_{14}Me_{14}AB$, respectively, where A represents a $-CH_2-$ linkage between two monomers and B represents a $-CH_2OCH_2-$ linkage between two monomer units. The presence of methylene and methylene ether bridges between monomer units has previously been detected by ^{13}C-NMR(8).

HPLC Analysis

The HPLC chromatogram of CYREZ® 963 Resin is shown in Figure 7. The 10x expansion of this chromatogram in Figure 8 clearly demonstrates the multitude of components found in these types of resins. These chromatograms were obtained with a precolumn so that the major component elutes at about 11.2 minutes. The HPLC chromatograms of fractions A-E are shown in Figure 9. The major component of fraction E elutes at about 9.2 minutes. This species has been identified as MF_6Me_6, the hexakis(methoxymethyl)melamine by HPLC analysis of an authentic sample of this monomer. FAB-MS results have also confirmed this fraction as the monomeric portion of the resin. Since the HPSEC chromatogram of fraction E shows that it contains a small amount of dimer, it is reasonable to

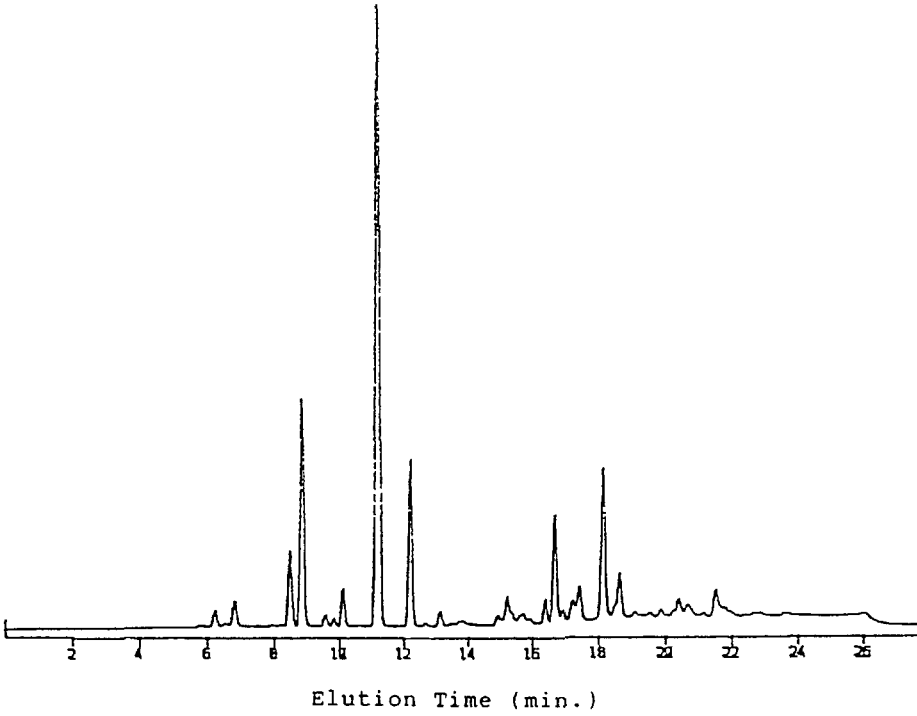

Figure 7. HPLC chromatogram of CYREZ® 963 resin.

match the peaks found in both the HPLC chromatograms of fractions D and E and attribute these to the dimer fraction. The monomer portion of the resin elutes from about 2 to 11 minutes. as shown in the fraction E chromatogram.

The HPLC column and gradient conditions are such that the resin components elute according to decreasing polarity. Thus, it is highly likely that the resin species elute according to the number of hydroxymethyl and methoxymethyl groups on the melamine moiety. Since the peak at 9.2 minutes represents the fully

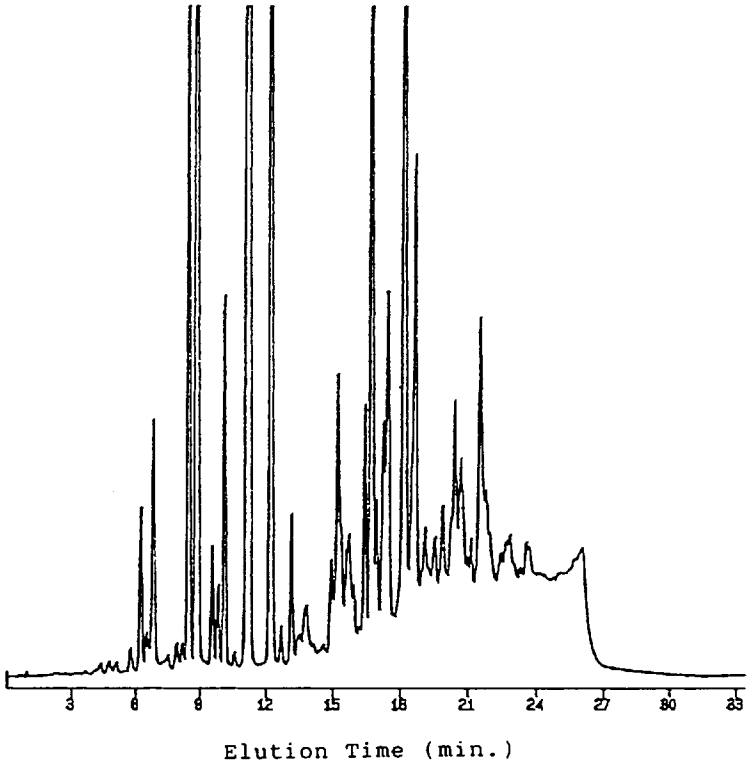

Figure 8. Ten times expansion of HPLC chromatogram of CYREZ® 963 resin.

methoxymethylated species, then the compounds eluting earlier must have either hydrogens or hydroxymethyl groups instead of methoxymethyl groups. The less substituted the primary amino nitrogens, the more polar the species. Chromatography of a resin with a lower degree of methylation shows an interesting pattern of groups of peaks between the retention times of 3 to 11 minutes. The HPLC chromatogram of such a resin, CYREZ® 350, is shown in Figure 10. (This sample was analyzed

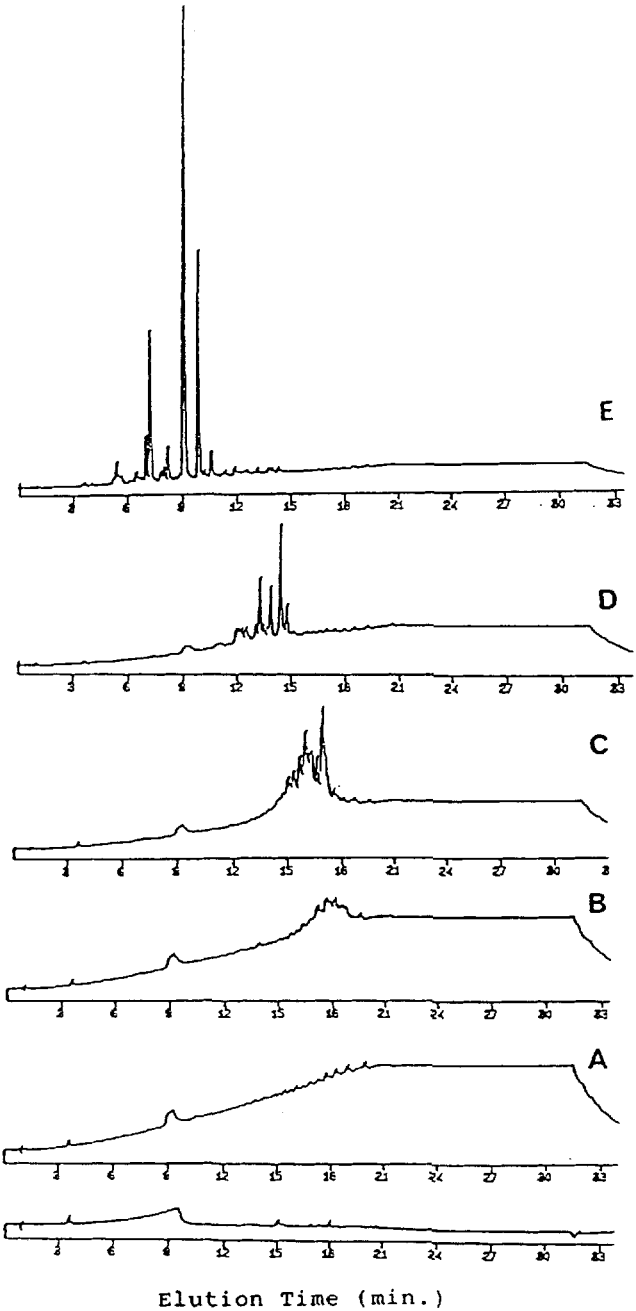

Figure 9. HPLC chromatograms of HPSEC fractions A-E and methylene chloride. (Chromatographic expansion decreases from A-E.)

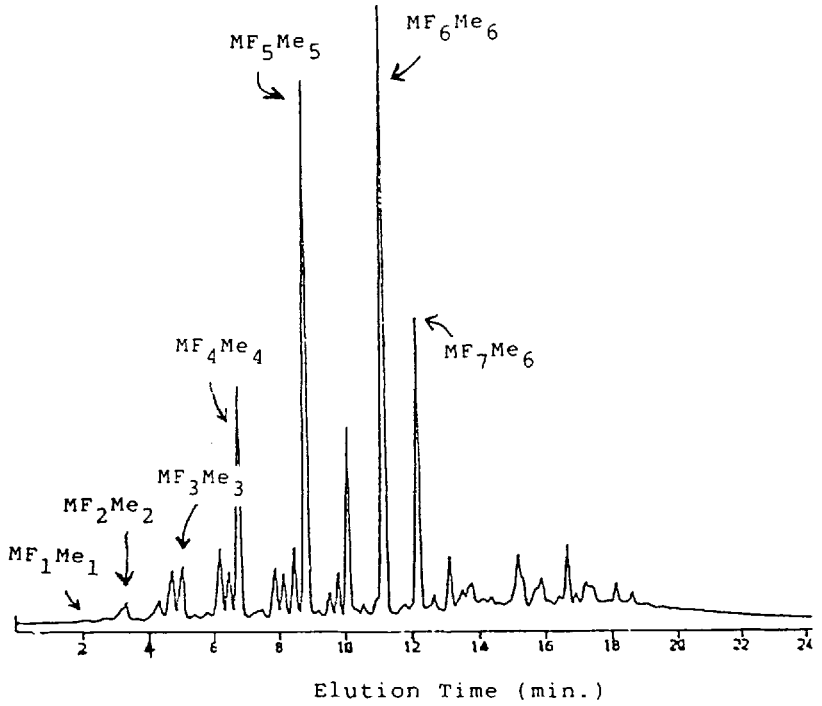

Figure 10. HPLC chromatogram of CYMEL® 350 resin.

under the same HPLC conditions as those of the sample shown in Figures 7 and 8). The main peak, hexakis(methoxymethyl)melamine or MF_6Me_6, elutes at about 11.2 minutes. The next major peak elutes at about 9 minutes, and is tentatively attributed to MF_5Me_5. The peak at about 7 minutes is possibly the MF_4Me_4, the peak at about 5 minutes may be the MF_3Me_3 and the peak at about 3.2 minutes may be the MF_2Me_2 species. The peaks systematically interspersed among these peaks arise from species that are more polar than each of the species where x and y are equal, i.e., those containing methylol groups on the primary amino nitrogens. A similar HPLC

method for the separation of methylolmelamines published by Ebdon et. al.(9) shows that the retention time of a methylolmelamine species increases with the degree of substitution.

The dimer portion, fraction D, elutes from 11 to 15.5 minutes (see Figure 9). Some trimer peaks are present in the chromatogram of fraction D (see also HPSEC chromatogram of Fraction D). The trimer portion elutes from about 13 to 20 minutes with the major portion of the species eluting between 15 and 17 min. The tetramer portion also elutes from about 13 to 20 min with the major portion of discrete peaks eluting between 17 and 18 min. The higher oligomer portion elutes between 11 and 21 minutes with some very small peaks eluting along the gradient slope. The fact that these various oligomeric species extend through a large elution range is an indication that the molecules have a wide range of polarities and are composed of oligomers with varying degrees of methylation and methylolation.

The small peak eluting at about 9.2 minutes in the chromatograms of Figure 9 is largely due to some impurity found in the water, methanol(10) and methylene chloride. The chromatogram of a methylene chloride blank injection is also shown in Figure 9.

The HPLC analysis presented in this work can resolve the large number of monomeric species. Area percent calculations for each monomer species are easily accomplished. These results, however, cannot be converted directly to weight percent since Ebdon et. al.(9) have shown that hydroxymethylmelamines have different UV absorptivities depending on the number of hydroxymethyl groups on the primary amino nitrogens.

This is probably also true for methoxymethyl groups. If one could synthesize the various pure monomers, individual response factors could be obtained and the weight percent of each species be determined.

CONCLUSIONS

Isolation of different molecular size fractions by HPSEC has elucidated the complex elution pattern observed in the HPLC chromatogram of methoxymethylmelamine resin CYREZ® 963. In addition, the mass spectral analysis of these fractions has shown the complexity and identity of these fractions. The results of this study permit the following conclusions:

1. Methylated melamine-formaldehyde resins contain monomeric, oligomeric and polymeric components as determined by HPSEC analysis and confirmed by mass spectral analyses of the HPSEC fractions. Mass spectral results show the following:

a) Each HPSEC fraction is a complex mixture of species having the same number of rings and therefore similar molecular size.

b) Within the monomer fraction, the presence of a species containing seven $-CH_2O-$ groups has been confirmed by FAB/MS.

c) Oligomeric species can comprise more than four self-condensed methylated melamine-formaldehyde units.

d) The melamine units of some oligomeric species are connected by methylene and dimethylene ether linkages.

2. The HPLC analysis presented here provides a high resolution chromatogram of monomeric and oligomeric components found in methylated melamine-formaldehyde resins. The elution pattern is relatively simple for the first 12 minutes during the elution of the monomer species. For the most part, these are baseline resolved so that the HPLC method permits both the relative and absolute quantitation of monomeric resin species. The elution pattern becomes increasingly complex at longer retention times because of the increasing overlap of oligomeric species. These reversed phase HPLC conditions cause resin components to elute in order of decreasing polarity. Therefore, even though the molecular weight of an oligomeric species is high, the substitution pattern on the primary amino nitrogens may make it relatively polar so that it elutes rather early in the HPLC chromatogram.

3. Although individual monomer species cannot be easily synthesized and isolated as pure components, it is possible to infer their identity from this HPLC separation based on polarity differences. Confirmation of the tentative structure of monomer species by LC/MS analysis is in progress and will be the subject of another publication.

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